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ABSTRACTS

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PLENARY LECTURES

CATALYSTS ON CARBON MATERIALS BASIS: TECHNOLOGICAL ASPECTS AND TENDENCIES

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Catalysts on carbon carriers find wide application in petrochemical and organic synthesis processes. The most of them contains supported solid phases of different chemical compounds (acids, for example polyphosporic acid; salts, for example zinc acetate, metal chlorides, for example mercury, palladium, platinum, etc.). Despite on carbon carrier inertness to reaction mediums (catalytic reactions reagents) its physical-chemical properties influence essentially on supported component catalytic properties. Therefore both determination of the nature of this influence and revealing of roads to achieve necessary state of active compounds are actual direction of investigations in the field of scientific base of preparation of carbon-based catalysts.

The data of physical-chemical and catalytic investigations of mechanisms of formation of catalysts containing the following substances as supported component:

a. phosphoric acid (catalysts for olefins oligomerization);
b. metallic palladium (hydrogenation catalysts)

are presented in this report.

The forming stages of active centers of these catalysts from supported precursor have been studied using the wide set of physical-chemical analysis methods (XPS, NMR, HREM, XRD). On this basis we have concluded: chemical composition (functional cover) of carbon surface and carbon crystallite nanotexture (type of crystallite planes, exposed on the surface of carbon material particle) influence on the characteristics of these stages.

The obtained data have been used for improvement of silicophosphate-based propylene oligomerization catalysts. The parameters of synthesis of entered active phase in carbon matrix have been established. These parameters provide the achievement of catalyst high activity, selectivity and stability. Revealed regularities have been underlay in the basis of technology of synthesis of improved catalysts for propylene oligomerization and alpha-methylstyrol dimerization.

PL-1

In the case of “palladium on carbon” system physical-chemical investigations data have permitted to optimize methods of preparation of metallic palladium particles precursors for concrete hydrogenation process. During these catalysts synthesis it is necessary to achieve optimal for this process dispersity and width of metal particles size distribution which can be regulated by nature of their location places on carbon carrier surface which in their turn are determined by the supported precursors nature and by the condition of carrier treatment. The influence of these factors on activity is demonstrated by examples connected with the development of catalysts for the processes of nitroaromatic compounds hydrogenation, rosin disproportionation and monomers hydropurification.

PREPARATION OF CARBON FILMS ON CERAMIC SUPPORTS

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Introduction

Polymer derived nanoporous carbons offer many advantages over carbons based on naturally occurring carbon as catalyst supports. These include precisely controlled pore structure[1,2], greatly enhanced reproducibility, high purity and the ability to precisely control the surface chemistry[3]. In some cases the possibility also exists to produce the materials in a wide range of physical forms to suit different applications. MAST has spent several years, through a variety of collaborative projects[4,5] and in house research, developing a family of phenolic resin derived that can be produced in physical forms from extrudates and beads, through complex monolithic structures to asymmetric membranes. In the latter case these membranes can either be pure carbon systems or carbon coated ceramics. One of the major benefits of the phenolic system is that all of these physical forms exhibit a common pore and surface structure and therefore similar characteristics when used as catalyst supports. This presentation will therefore first review the pore, surface chemistry and catalyst characteristics of the phenolic resin derived carbons and subsequently the production, structure and performance the carbon-ceramic composite membrane devices based on phenolic resin.

Phenolic Resin Derived Carbons

The pore structure of the phenolic based carbons derives directly from the underlying polymer structure and is similar for all phenolic precursors. The production of the crosslinked resin from the novolak or resol precursors gives rise to a phase separation process within the polymer matrix during crosslinking that leads to the formation of microdomains of highly crosslinked resin a matrix of less cured resin. Pyrolysis then leads to the loss of the less crosslinked material leaving a matrix of interlinked, high density nanobeads of 5-10nm diameter where the resulting pore structure comprises the voids between these beads. It is this process that give the phenolic derived carbons their unique structure. This phase separation process also underpins the production of the mesoporous carbons via a secondary phase separation process.

The surface of these nanoporous carbons, produced by pyrolysis in either nitrogen or carbon dioxide, has almost no surface functionality as measured by Boehm titration, TGMS or surface spectroscopic techniques. This can then be readily enhanced by a variety of techniques including gas and liquid phase oxidation although some modifications can also be introduced by modifying the resin precursors. Some preparative conditions can lead to carbons that function as effective oxidation catalysts in the absence of any added metals[3]. The resulting functionality also has a major influence on the dispersion and distribution of any added metals.

The catalytic performance of the carbons and the metal/carbon systems have been evaluated for use in gas phase reactions (Ruthenium catalysed ammonia synthesis) and multiphase oxidation and hydrogenation reactions using slurry phase, trickle bed and monolithic (Taylor flow) reactor geometries. These studies have provided the foundation for the recent evaluation of the resin derived systems in membrane reactors.

Membrane Systems

The two main driving forces for the development of catalytic membrane reactors have been either safety, where in oxidation reactors the oxygen and hydrocarbon feeds can be separated, or equilibrium shifting, where typically one of the products of the reaction is selectively removed. The earlier studies tended to concentrate on gas phase dehydrogenation reactions whilst recently there has been greater interest in oxidation and in particular multiphase oxidation reactions. In the latter case the oxygen is generally in the gas phase on one side of the membrane whilst the reagent to be oxidised is in the liquid phase on the other side, with the gas/liquid interface located within the membrane and local to the active catalyst species. A key requirement in all cases, but most critically in the gas phase applications, has been the presence of a highly selective surface layer. There has been a significant interest in for instance dense oxide layers to give very high selectivity for high temperature oxygen permeation and dense palladium layers for high temperature hydrogen although the majority of the work has focussed on nanoporous membrane layers which have higher permeabilities and do not require high temperatures for effective operation. These nanoporous ceramic systems include zeolites, amorphous oxides and carbon.

To achieve acceptable permeabilities the separating layer must be very thin, typically less than a few microns and preferably <1micron. Whilst attempts have been made to achieve this using hollow fibre ceramic membrane systems, similar in geometry to the hollow fibre polymer gas separation membranes, these have so far been largely unsuccessful due to the mechanical properties of the hollow fibres and the problems of achieving very low levels of defects. The nearest approaches have been hollow carbon fibres produced by the carbonisation of hollow polymer fibres, first evaluated Koresh et al[6] and more recently by Koros er al[7], Linkhov et al[8], Tanihara et al[9], Barbosa-Coutinho et al[10]. and Sznejer at al[11]. The membranes commonly used have in nearly all cases been asymmetric with a thin nanoporous separating layer supported on a multilayer tubular support. The majority of this work has been targeted at the zeolite systems largely because of the extent to which the pore size can in theory be controlled but also due to the enhanced stability of the pore structure compared to the nanoporous amorphous oxide membranes that are usually prepared by sol gel type processes. Both systems are however complex and expensive to produce and the reliable production of defect free systems is still difficult to achieve on an industrials scale.

The manufacturing problems, costs and instability of the oxide membranes nanopore structures prompted the investigations into carbon membranes that commenced with the work of Koresh et al in 1983. Whilst these involved the studies into hollow fibres mentioned above they have largely been based on supported films and have encompassed a wide range of supports and polymer precursors. The critical limitation in the production of these carbon-ceramic composites is the shrinkage that the polymer undergoes during carbonisation which is typically in excess of 50% volume. This can lead to severe stress cracking during the pyrolysis process that becomes more severe as the film thickness increases. In the earlier studies into this preparation route by Rao et al[12] this could only be overcome by the deposition of multiple thin coats of the polymer precursor with a pyrolysis step between each deposition. In these studies the thickness of the carbon film required to approach a defect free membrane was also quite thick due to the pore structure of the ceramic support. Most of the recent studies now utilise the graded ceramic supports that are used to prepare the zeolite and amorphous oxide membranes. Whilst this leads to significant increases in cost it allows the production of much thinner carbon films which then permits the use of a single coat-pyrolyse preparation. The group of Fuertes has been responsible for much of the published work in this area and, whilst earlier papers covered a wide range of precursors, the more recent papers have concentrated exclusively on phenolic resins derived carbons[13], and on the optimisation of the properties of these films through thermal and oxidative treatments[14,15]. Whilst the preparative approach adopted by Fuertes et al is different to that used in MAST the resulting membranes have similar properties. These studies have shown that phenolic resin is uniquely versatile in the production of coated ceramic membranes and that the properties of the membranes can be tailored over wide ranges to suite various applications. The preparation and properties, of these membranes will be discussed in detail. This will cover both the gas separation properties[16] and the use of the MAST membranes in the catalytic conversion of water to hydrogen peroxide[17, 18]

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CHARACTERIZATION OF POROUS STRUCTURE OF CARBONACEOUS MATERIALS BY MEANS OF DENSITY FUNCTIONAL THEORY

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It has long been recognized that adsorption isotherms provide quite reliable information on structure of different porous materials and complements the data obtained with other tools of the pore structure analysis such as high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and small angle X-ray scattering. The topology of activated carbons is known to be highly complex and is far from being completely understood. Nevertheless, simulation technique and molecular theories developed for the latest decades allow determination basic structural properties of porous solids like the pore size distribution (PSD), surface area and energetic heterogeneity. One of the most effective tools for the PSD analysis is the nonlocal density functional theory (NLDFT), which is widely used in the software for the pore structure analysis with nitrogen and argon low temperature adsorption isotherms. Results of the PSD analysis are strongly dependent on a reference nonporous solid. In the case of carbonaceous materials the graphitized carbon black is mainly used as the reference system to adjust solid–fluid interaction parameters in the framework of the Lennard–Jones (LJ) potential. Given those parameters, the NLDFT is used for generating the set of local nitrogen or argon adsorption isotherms for slit pore model over the wide range of pore width accounting for the enhancement of the potential due to the overlapping potentials exerted by the opposite pore walls. The final stage of the technique is the inverse task to determine the pore size distribution function with the Tikhonov regularization procedure.

Despite the technique described above is commonly used, there are still unresolved problems mainly associated with poor correlation of adsorption isotherms. A source of such discrepancies could arise from inadequate model of the pore wall surface and the pore shape. To overcome this shortcoming we developed a refined NLDFT version as applied to amorphous solids assuming that the nongraphitized carbon black is a better choice for the reference system. To this end, a series of different samples of nongraphitized carbon black having specific surface area from 30 to 1500 m^2/g was thoroughly investigated using the developed NLDFT model, which allowed us to determine the solid–fluid potential as a function of the distance from the surface. It turned out that the adsorption in the first molecular layer is localized and controlled by short-range forces, with the surface being highly heterogeneous. Beyond the first molecular layer the solid–fluid potential obeys the power law and decays inversely the third power of the distance. Interestingly enough that the absolute value of the potential outside the first molecular layer is several times smaller than it is predicted by the LJ pair potential. This means that the individuality of a nonporous material is mainly restricted by the first molecular layer (more exact estimation is 1.3 of monolayer capacity) and partly explains the universality of adsorption isotherms at relative pressures above approximately 0.1, which is reflected in so-called t-curve. Some additional information we have obtained by the comparison of the behavior of nitrogen adsorbed on nongraphitized carbon black and nonporous silica. In the latter case the solid–fluid potential decays inversely the fourth power of the distance, meaning that, as opposed to carbon blacks, the potential is exerted by surface (oxygen) atoms. Analysis of N_2 adsorption in highly ordered MCM-41 silica samples has shown a startling result that the effect of the surface curvature on the solid–fluid potential is nearly absent, which indirectly confirms the conclusion that the adsorption potential of amorphous solids in contact layer is short-range.

Application of the developed NLDFT to activated carbons has convincingly shown that the use of nongraphitized carbon black as a reference system leads to much more reliable PSD functions and excellent fitting of experimental adsorption isotherms. For example, the PSD functions have become smoother and do not show any artificial peaks and gaps. Thus, the pore structure of carbonaceous materials, the surface area and its distribution over the pore size can now be reliably disclosed with the developed approach. Additionally, this technique provides the prediction of differential heat of adsorption and adsorption deformation (adsorption-induced contraction and swelling). The latter is important for the problem of methane and hydrogen storage. At present we carry out further investigations to develop a NLDFT-based tool to determine the surface chemistry of nonporous and porous carbonaceous materials. In particular, it will allow us to identify different functional surface groups, crystalline defects, relation of basal, prismatic, and defect surfaces, which is important for the application of those materials in catalysis. To summarize, one can state that the analysis of adsorption isotherms with NLDFT is a promising tool for determination of porous materials structure and further efforts are needed.

ROLE OF CARBON POROSITY AND FUNCTIONALITY IN ADSORPTION AND CATALYTIC PROCESSES

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Porous carbons, especially activated carbon, are very important from the points of view of adsorption and catalysis and both the porous texture and the chemical nature of the surface are of extraordinary importance for industrial processes such as adsorption and catalysis. Thus, an accessible and large surface area coupled with the right pore size distribution is a necessary but not sufficient condition for the preparation of adequate adsorbents and catalysts since the role of the chemical nature of the carbon surface is also very important.

Activated carbon is an excellent and versatile adsorbent [1] because of its immense capacity for adsorption from gas and liquid phases, this capacity being due to a highly developed porosity, which ranges from micropores (< 2 nm entrance dimensions) to mesopores (2-50 nm) and macropores (>50 nm). The adsorptive properties of activated carbon are a simultaneous function of the porosity and the chemical nature of the carbon surface, although there are some applications (for instance the adsorption of non-polar species) which can be directly related to the porosity, without significant contribution from the chemical nature. In these cases, the uniqueness of the microporous structure of activated carbon, with slit-shaped pores, is the key to important adsorption processes such as gas separation and gas storage. In these applications the shape of the micropores can distinguish between molecules as a function of molecular dimension and shape and, at the same time, the slit-shaped micropores are responsible for the larger packing density of adsorbed molecules as compared with cylindrical pores of identical dimensions.

In the case of adsorption of molecules with some polarity the chemical nature of the carbons surface is tremendously important, as shown when comparing the adsorption isotherms of this type of molecules in carbons subjected to treatments able to modify the functionality of the surface. For instance, the adsorption of polar molecules is generally favoured if the carbon is slightly oxidised to introduce oxygen surface groups, but one has also to considerer that in the case of gas phase applications oxygen groups will also increase the adsorption of humidity. It is also to be noted that the chemical nature of the carbon surface can condition the adsorption phenols and other molecules with aromatic rings, since in this case the interaction of the ring with the carbon surface is mainly through the π electron on the graphene layers of the structure; their amount decreases with the increase in oxygen surface groups, because of the high electronegativity of oxygen.

Carbon materials constitute a very flexible set of supports for heterogeneous catalysts and, additionally, some of them can act also as catalysts by themselves. Their physical (surface area and porous texture) and chemical surface properties (presence of surface heteroatom functionalities, mainly oxygen groups) can be tailored to develop a large surface area to disperse the active phase, the adequate pore size distribution to facilitate the diffusion of reactants and products to and from the surface, and the hydrophobic/hydrophilic and acid/base character needed to obtain the best performance.

Many types of carbon materials have been used as catalysts and catalyst supports: graphite, carbon blacks, activated carbons, activated carbon fibres and cloths, nanotubes, etc.; among them, the most important are, by far, activated carbons and carbon blacks. Nowadays, the most important reactions carried out using carbon supported catalysts include hydrogenations (mainly in fine chemistry processes), oxidation (CO), combustion (VOCs) and electro-oxidation reactions in fuel cells. For these applications, the intrinsic properties of carbonaceous materials play a major role in the catalytic properties. Thus, the absence of surface oxygen functionalities gives the carbon an hydrophobic character that is very important when it is going to be used as support for VOCs combustion catalyst, as these compounds are generally going to be treated in the presence of humidity. On the other hand, the presence of these oxygen functionalities is very important in the catalyst preparation stage, where they can be used to control the dispersion of the active metal. Furthermore, oxygen groups and surface sites generated on the carbon surface when they are removed under activation or reaction conditions, can be used to direct catalytic selectivity towards desired products in fine chemical selective hydrogenations. It is also worth to mention that in these processes (and in many others) bimetallic catalysts are used, and the intrinsic inertia of carbon supports can be used to facilitate the interaction between both metals. Finally, the easy control of the porous texture of carbonaceous materials makes it easy to design the appropriate pore size distribution to the size of the reactant molecules, allowing for the treatment of both large molecules in the liquid phase and small compounds in the gas phase. On the other hand, carbon-supported Pt or Pt-based alloys are the best electro-catalysts for the anodic and cathodic reactions in fuel cells. Here, together with the carbon properties described above, conductivity of carbon materials plays a major role.

KEYNOTE LECTURES

IS IT POSSIBLE TO SOLVE THE HYDROGEN STORAGE PROBLEM WITH ACTIVATED CARBONS?

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One of the key problems in the development of hydrogen-fueled vehicles is connected with the hydrogen storage. The complexity of the hydrogen storage is due to its “simple” molecular structure. The hydrogen molecule has only two electrons, which is the reason of an extremely weak intermolecular interaction. As a consequence, it has low melting point (14.01 K), low boiling point (20.3 K), low critical temperature (33.2 K), and low densities of all phases etc. Those complications have led to a search for solutions of the storage of hydrogen as a non-traditional fuel. At the present time there are several ways of solution of the problem, which are based on the following approaches: ***A***) deriving hydrogen directly at the vehicle by a catalytic reforming of hydrocarbons; ***B***) hydrogen storage in regenerated chemical adsorbents on the basis of metal hydrides of boron, lithium, aluminates, etc.; ***C***) physical adsorption in fine-porous adsorbents; ***D***) the use of compressed GH_2 at 35-70 MPa, and ***E***) cryogenic LH_2.

Each of the above methods has its principal drawback. The method ***A***) does not solve the problem of the carbon dioxide emission. Application of the method ***B***) with solid regenerated chemical adsorbents is complicated by their phase and volume changes during adsorption and desorption of hydrogen. The method ***D***) is dangerous because of a possibility of instantaneous release of mechanical energy of the compressed gas during an emergency. The method ***E***), much as it is seemed a bit exotic (the storage of H_2 at ~20 K, slush hydrogen at ~14 K, or compressed hydrogen at 30-50 K) has been tested in rocket and space technology long ago. Modern Dewar containers with multi-layer vacuum thermal insulation virtually allow keeping LH_2 for several weeks without any losses. The principal drawback of this method is associated not with the problem of storage in itself, but with power inputs required to refrigerate H_2 up to the temperature of liquefaction.

Minimal power inputs **L** required for obtaining the unit of cooling **Q** in the process of cooling of hydrogen from the initial temperature $\mathbf{T_0}$ down to the final temperature **T** is governed by the equation of the ideal reverse Carnot cycle: $\mathbf{L/Q = (T_0 - T)/T = (T_0/T)} - 1$. Estimations followed from this equation show that the hyperbolic type of this dependence with the sharp increase of $\mathbf{L/Q}$ appears only in the region $T < 70$ K, whilst at $T > 70$ K the required energy is virtually proportional to the temperature difference ΔT. Correspondingly, theoretical power inputs for obtaining one unit of cooling at the temperature decrease from 298 K down to ~20 K at the process of hydrogen liquefaction are five times of those required for cooling to “nitrogen” temperature, which is about 77 K (actual power inputs are even one order larger than the theoretical estimation). On the other hand, the cooling down to “nitrogen” temperature creates the possibility of the use of the method based on physical adsorption (***C***).

Physical condensation of H_2 is impossible at room temperatures, as the kinetic energy (that can be estimated as RT ~ 2.5 kJ/mol) is higher than the heat of condensation (~0.9 kJ/mol). However, the heat of adsorption of H_2 at the best carbonaceous nanostructural adsorbents (CNA’s) of type AX-21*[1] approaches 6.0-6.5 kJ/mol, which leads to sufficiently large amounts adsorbed at additional decrease of the RT contribution. We have developed a number of CNA’s having characteristics exceeding those of AX-21 (the formal specific surface area $\mathbf{A_{BET}}$ is greater than 3000 m^2/g, the micropore volume $\mathbf{V_\mu}$ is larger than 1.5 cm^3/g) that are able to reversibly adsorb hydrogen with a resulting capacity of more than 5wt% at 77 K and the pressure below 2-3 MPa. Estimated gravimetric density $\mathbf{W_f}$ of the adsorber with our CNA’s meets requirements of DOE[2] for 2007 ($\mathbf{W_f} \geq 4.5$ wt %). We hope, the optimization of the internal structure of our CNA’s will allow us to meet the requirements of DOE on volumetric density ($\mathbf{V_f} \geq 36$ kg H_2/м^2) and to increase specific amounts of H_2 adsorption per unit of mass. Our aim in the near future is to meet the requirements of DOE for 2010 ($\mathbf{W_f} \geq 6.0$wt % and $\mathbf{V_f} \geq 60$ kg H_2/м^2).

Our optimism rests on the observation that the heat of H_2 adsorption in single-walled carbon nanotubes (SWNT’s) approaches (from different sources) 12-20 kJ/mol, which leads to a higher density of the adsorbed phase. Consequently, those SWNT’s have more optimal pore sizes, but their total volume and surface are lower than CNA’s. For this reason adsorption characteristics of SWNT’s are lower than those of CNA’s.

Manufacturing of SWNT’s is principally more complex and more expensive compared to CNA’s. CNA’s can be obtained with the use of wide assortment of precursors, with all

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*[1] manufactured by Anderson Develop. Co (USA); the same is Maxsorb-1 Kansai Coke and Chemical Co Ltd (Japan)

*[2] DOE – US Department of Energy, generally accepted fashion legislator in the modern hydrogen technology.

technological operations for their synthesis being carried out at the temperatures less than 1000˚C. Mechanisms of the development of CNA's structure allow a possibility of increasing of values $\mathbf{A_{BET}}$ and $\mathbf{V_{\mu}}$. In our presentation we discuss a specific variant of adjustment of their structure that is based on the use of natural or artificial mineral templates.

The first stage of application of hydrogen power engineering will apparently start from the use of natural gas as a source of H_2 at vehicles with fuel cells. At the same time, CNA's are also effective adsorbents for methane storage at T~298K and P ~ 3.0-5.0 Mpa. Their application for CH_4 at such conditions will substantially simplify the process compared to the cryogenic hydrogen storage, of which the main shortcoming is associated with the necessity of the special infrastructure with cooling of hydrogen at refuelling stations.

Hence, for initial stages of the development of hydrogen power engineering the problem of fuel storage for vehicles with fuel cells could be solved with already developed carbon nanostructural adsorbents (CNA's)

KL-2

NITROGEN DOPED CARBON NANOFIBERS AND AMORPHOUS CARBONS FOR PEMFC CATHODE CATALYST PREPARATION

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The oxygen reduction activity of cobalt and iron cations on the surface of carbon supports can be considerably improved by bounding to nitrogen atoms doped to carbon material. This type of electrocatalysts is considered to be promising for partial or complete replacement of platinum in conventional cathode catalysts.

In this lecture we will report results of research comprising following main goals:

(1) development and characterization of N-containing carbon support materials of two types: N-doped carbon nanofibers (NCNF) and N-containing amorphous carbons (NAC);

(2) development of preparation procedures and characterization of electrocatalysts obtained by deposition of Co on the surface of these supports.

For the preparation of NCNF, the method of decomposition of C_2H_4-NH_3 mixture on metal catalysts Ni-Cu-Al_2O_3, Fe-Cu-Al_2O_3 etc. at temperatures 550-675 °C was used. NCNF belong to a family of mesoporous graphitic materials as was confirmed by XRD, XPS, TEM and adsorption methods. Depending on preparation conditions nanofibers with an average pore diameter 5–19 nm and S_{BET} 30 – 350 m^2/g can be produced. TEM studies showed that NCNF have a fishbone type structure with a fiber diameter of 60-100 nm. The fibers are twisted into spirals. The dependencies of NCNF yields on the nature of the catalyst and temperature were studied. The highest NCNF yields were observed at a low temperature 550°C on the catalyst Ni-Cu-Al_2O_3 (up to 70 $g/g_{cat.}$ after 20 h). The dependencies of N content on the catalyst nature, reaction time and temperature were studied. Lower temperature and short time on stream are favorable for formation of NCNF with a higher N content - up to 7 wt. %.

NAC materials were prepared by chemical and subsequent thermal treatment of various N-containing organic precursors, or their mixtures: o-nitroaniline, 8-oxyquinoline, benzotriazole, etc. The obtained products have N content in the range of 0.5-8 wt.%. The samples have a very high specific surface area (1000-3100 m^2/g) and a large fraction of micropores - over 70%. The effect of the nature of the precursor and the preparation conditions on nitrogen content and NAC properties were studied. It was shown that the BET area and pore volume generally decrease and the N content increases with lowering of the temperature.

The state of nitrogen species in N-doped carbon supports was studied by XPS. The results showed that two types of N are predominant in both types of supports: with binding energies of 398.5 eV and 400.8 eV. According to literature, these signals correspond to pyridine-like N and bridgehead-type N incorporated into graphitic network, respectively. The predominance of the former favors the coordination of Co ions and formation of the active sites for oxygen reduction. In addition a weak signal at 400.0 eV was observed in NAC samples, which may be assigned to amino or -C≡N groups.

Cobalt catalysts were prepared by treatment of suspension of NCNF or NAC in water with cobalt acetate taken in quantity to provide 1.5% Co content in the catalyst, followed by water evaporation, drying and subsequent heat treatment in different atmospheres (Ar or NH_3+H_2+Ar) at temperatures 600 and 900°C.

TEM study revealed the presence of metal cobalt particles in the initial catalysts. There are two groups of particles: with a size of 10-50 nm and with a size about 300 nm. After catalyst washing with sulfuric acid, the larger particles are removed and only small cobalt particles encapsulated into the support structure remain on the surface.

The study of the states of surface nitrogen atoms in the catalysts supported on NAC showed that there are three types of nitrogen atoms: pyridinic-type nitrogen atoms (398.6 eV to bridgehead-type N incorporated into graphitic network (400.9 eV) and nitrogen atoms in the composition of amino or -C≡N groups (400.0 eV). The XPS study in the Co 2p region showed the presence of signals belonging to Co^{2+} cations bound to nitrogen and to cobalt cations in surface cobalt oxides on metal cobalt particles.

The catalyst activity of the prepared samples with different nitrogen and cobalt contents was studied by the method of rotating disk. It was shown that oxygen reduction activities of the catalysts depend mostly on the N-bound cobalt content, and enhance with its increase.

Thus, the developed N-doped materials can be considered as prospective materials for preparation of non-Pt PEFC catalysts because they contain pyridinic type N atoms capable of binding Co^{2+} and forming active sites for oxygen reduction.

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KL-3

CARBON BASED STRUCTURED CATALYSTS FOR PROCESS INTENSIFICATION: OPPORTUNITIES AND LIMITS

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Intensification of heterogeneous catalytic processes involve besides of innovative engineering of reactors, the proper design of the catalyst. Moreover, the new paradigm requires the simultaneous development of the catalyst and the reactor. The catalyst design should be closely integrated with the reactor design taking into consideration the reaction mechanism, mass-/heat transfer and the energy supply addressing high selectivity/yield of the target product.

Structured catalysts and reactors are powerful tools for process intensification. Examples of this are structured reactors packed by honeycombs, foams, static mixers, gauzes, membranes, fiber arrays and cloths. They present multiple advantages as compared to conventional packed-bed reactors, like the higher ratio of surface/volume (up to 5-10 times), much higher catalyst efficiency due to short diffusion paths for the reactants, and a very low pressure drop during the flow passage (gas, or gas-liquid), through the catalytic bed.

Carbon materials (e.g. soot, charcoal, graphite …) are used since prehistoric time. Activated carbon is one of the most widely used adsorbents and catalytic support. Since the 1960s various novel carbon materials have been developed. Carbon fibers derived from polyacrylonitrile (PAN), pyrolytic carbons produced by chemical vapor deposition of hydrocarbons and active carbon fibers were introduced to the market. These materials have structures and textures that differ from the conventional carbon materials and have demonstrated already advantages when used as adsorbents and catalysts. More recently, fullerenes and carbon nanotubes were discovered opening completely different perspectives and undergoing a rapid development.

Some aspects of the design of novel carbon based catalysts and of the structure control over multiple scales will be discussed:

- Nano: for active sites and their environment;
- Micro: for spatial distribution of active sites and surface micro-composition;
- Meso: for pore structure and surface morphology;
- Macro: for catalyst form and geometry.

SYNTHESIS AND PROPERTIES OF CARBON SUPPORTS AND PALLADIUM-CARBON CATALYSTS FROM NATURAL ORGANIC RAW MATERIALS

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The rather high cost of synthetic carbon supports limits the scale of their application in the industrial catalysis.

Some results of the study of structure and properties of carbon supports and palladium-carbon catalysts produced with the use of natural graphites, anthracites and plant polymers are presented in this lecture.

Mesoporous carbons from plant biomass

The influence of wood nature (larch, aspen, beech) pyrolysis and activation conditions on the yield and the structure characteristics of produced chars and active carbons was established. The nature of lignocellulosic material and pyrolysis conditions define the distribution of solid, liquid and gaseous pyrolysis products, the porosity and reactive ability of obtained chars. The larch wood gives the highest yield of char and active carbon as compared with the other types of wood. The highest reaction ability in gasification processes was found for the aspen charcoal.

The influence of copper and zinc ions introduced to lignocellulosic materials and cellulose on the process of their carbonization and on the texture of obtained porous materials was investigated. The increase of pyrolysis temperature up to 500-700 °C results in the destruction of C-O-C bonds and generation of polycondensed aromatic systems.

Thermogravimetric analysis indicates a decrease of the start of thermal decomposition process on 50 °C for metal-containing samples in the comparison with non-modified cellulose. For original and Cu-modified samples of aspen wood and nutshell this difference was only 15-20 °C. SEM-data indicate that the carbonaceous products keep a fibre structure of the original cellulose. According to BET study the surface area of some metal-containing porous carbons can reach 600 m^2/g.

KL-4

The strong mesoporous carbons were produced by pyrolysis and activation of cedar nutshells at the selected conditions. The optimal process parameters of wood wastes (hydrolytic lignin, bark, sawdust) integrated carbonization-activation in a catalytic fluidized bed were selected in order to produce the powdery active carbons.

Microporous and mesoporous carbons from natural graphites and anthracites

The low reactivity of natural graphites and anthracites limits their use for porous carbons production.

The influence of chemical modification of de-ashing natural graphites and anthracites of different deposits on the formation of their microporosity at the further steps of thermal treatments was investigated. Data about structural and textural characteristics of intercalated and thermally exfoliated samples of Zavalevsky and Kyshtymsky graphites were obtained with the use of powder X-ray diffraction, SEM and HREM methods and from isotherms of nitrogen and carbon dioxide adsorption.

It was found that the applied method of intercalation makes the significant influence on the nano-textural characteristics of exfoliated graphite. Depending on the intercalation conditions the BET surface area of the thermally expanded graphites varies from 12 up to 70 m^2/g an the pore volume from 0,08 to 0,55 cm^3g.

Carbon supports from Donetsky anthracite (Progress mine) were prepared by consecutive steps of demineralization, chemical modification by $HClO_4$ and final activation by CO_2 or water-steam at temperature 1123°C. Depending on conditions of modification and activation the porosity of carbon products ranges from microporous to mesoporous types and their specific surface area varies from 400 to 1000 m^2/g.

Palladium catalysts on carbon supports from plant polymers, natural graphites and anthracites

Palladium catalysts were prepared by an impregnation of the carbon supports with a water-alcohol solution of H_2PdCl_4.

The size and shape of the supported palladium particles and their distribution over the carbon surface were found to depend on the method of the carbon support preparation.

The narrow distribution of the pores width in the fiber carbon support from carbonized cellulose promotes the formation of homogeneous distribution of palladium particles with size 4-5 nm on the carbon surface.

The most regular distribution of supported palladium particles with an average size of about 2 nm was observed for the supports prepared from the chemically modified natural graphites and anthracites. It was established that the activity of such catalysts in the reactions of cyclohexene and hexane-1 hydrogenation varies in wide limits depending on the size, structure and surface distribution of palladium particles and on carbon support texture.

KL-5

NANOSTRUCTURED CARBONS FOR THE DEVELOPMENT OF ADVANCED ELECTROCATALYSTS

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Proton-exchange membrane fuel cells (PEMFC), due to the low weight, fast start-up and high power density to volume ratio, are receiving large attention in recent years especially for distributed applications, but their commercialization requires further improving of their efficiency and energy density. PEMFC are typically prepared by supporting the catalyst (Pt) in the form of small particles on carbon-black and then depositing this electrocatalyst over a macro-structured support (carbon cloths) which is then hot-assembled with the proton-exchange membrane (such as Nafion®) eventually by adding also a porous hydrophobic layer (such as Teflon®). While it is known that all these components determine the fuel cell performances, the specific role of the nanostructure of the carbon was less investigated. The requirements of carbon materials for their application as a support for Pt-based electrocatalysts are the following: a high surface area for a high dispersion of the nanosized catalyst, excellent crystallinity or low electrical resistance to facilitate electron transport during the electrochemical reaction, a pore structure suitable for maximum fuel contact and byproduct release, and good interaction between the catalyst nanoparticles and the carbon support.

The recent growing possibilities for preparation also in large quantities and low cost of a number of different types of nanostructured carbon (carbon nanotubes, nanofibers, nano- and meso-porous materials, nanocoil and nanohorns, etc.) has open new possibilities. There is a growing research interest on the subject: NEC has recently developed a tiny fuel cell for mobile terminals claiming that the use of "carbon nanohorn" as support allows an improvement of one order of magnitude in the energy capacity compared with a lithium battery.

Still, most of authors consider the use of these advanced nanostructured carbons with respect to conventional carbon-black (Vulcan XC-72, for example) only for the possibility of improving metal dispersion and/or for the improvement of Pt utilization. However, these nanostructured carbons offer several additional aspects which make them highly interesting to develop advanced electrocatalysts: (i) the unique electrical properties of these materials which limit the charge of the supported metal particles, (ii) the improved mass-transfer and three-phase boundary due to the presence of an ordered structure, (iii) the possibility of preferential crystallographic orientation of the supported metal nanoparticles, (iv) the confinement effect inside nanotubes, (v) the possibility of oxide/carbon combination to improve the performances and/or reduce sensitivity to poisoning, and (vi) the possibility to develop hierarchically-organized structures (on a nano-meso-micro scale).

This lecture will discuss initially these general aspects with a short overview of the research trends in this attractive area. Then, the discussion will be focused on two specific cases:

1. the performances of nanostructured carbon in H_2 PEM fuel cells, where the role of three-phase boundary and charging effect on the metal particles will be discussed in particular;
2. the behavior of nanostructured-based electrocatalysts for the conversion of CO_2 to Fischer-Tropsch hydrocarbons at room temperature and pressure, where the role of the combination between confinement and three-phase boundary will be discussed. This anode is part of a photoelectrocatalytic (PEC) device aimed, in a longer term perspective, to realize the conversion of CO_2 to fuel using solar energy.

The final part of the lecture will discuss some of the perspectives for research in this area, and also the relevance for the development of novel catalysts based on nanostructured carbon.

KL-6

THEORY OF MECHANICAL BEHAVIOR OF MICROPOROUS CARBON CATALYSTS

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Researchers dealing with microporous carbon sorbents observed the sorption-striction phenomenon (a change in the sorbent volume), which can take different forms depending on the external conditions. When a sorbate enters a sorbent, the latter can expand at a high temperature, but also can contract at a sufficiently low temperature and a low amount of the sorbate with subsequent transition to expansion at higher sorbate amounts. Naturally, the phenomenon is determined by molecular interactions of the sorbate matter with the micropore walls. A special case is chemisorption that is typical for catalysis.

The theory of mechanical behavior of microporous carbon bodies reported in this presentation includes three parts. The first part contains the calculation of the pressure tensor inside a micropore where there cannot be the sorbate bulk phase, and the pressure tensor structure is determined by the micropore shape. Calculations have been carried out for spherical cavities, cylindrical pores, and flat (slit-like) pores. Since carbon interacts with dispersion forces, all calculations were made on the basis of the pair potential

$$\varnothing_{ij}(r) = -A_{ij}^{(\lambda)} r^{-\lambda} \qquad (1)$$

where r is the distance between molecules of sorts i and j, $A_{ij}^{(\lambda)}$ is a constant of interaction, $\lambda = 6$ for the ordinary van der Waals forces (at $r < 12$ nm) and $\lambda = 7$ for the van der Waals forces with electromagnetic retardation (at $r > 50$ nm). As Equation (1) itself, the whole computational scheme is based on the asymptotic theory of dispersion interactions (presuming the pore diameter to be considerably larger than the molecular size). The calculation yields a negative value for the normal (to the pore walls) pressure (leading to the self-contraction of a porous body) in vacuum and establishes conditions when the interaction with the first portion of a sorbate provokes an additional contraction (the most probable in the case of chemisorption). This additional contraction is shown to be attained easier the smaller is the pore size and is best realizable for nanoporous solids.

The second part is estimating the role of the surface tension of the pore walls. The difficulty of such estimation originates from the difference of the mechanical and thermodynamic definitions of surface tension for solids (in particular, the mechanical surface tension does not coincide with surface free energy). It is shown that the mechanical surface tension contributes to the initial contraction of a microporous catalyst in vacuum, but cannot cause an additional contraction with a sorbate since physical adsorption leads to a decrease of surface tension, while chemisorption does not influence surface tension at all. The introduction of the internal pressure tensor in a pore and of the surface tension of the pore walls determines a force applied to the bulk phase of a porous body. The resulting normal stress E_{N} in the solid phase is

$$E_{\mathrm{N}}(c) = 2\gamma c - p_{\mathrm{N}}(c)\,, \tag{2}$$

where c is the mean curvature of the pore wall, γ is the mechanical surface tension, and p_{N} is the normal (radial) component of the pressure tensor inside the pore. The knowledge of stress E_{N} permits passing to the calculation of strain. The third part of theory presented is devoted to such calculations within the frames of the theory of elasticity. The latter is quite applicable to this case because the mechanical effects under consideration are sufficiently small to assume the elastic behavior of a solid. Ready solutions were taken from the theory of elasticity to apply the problems of strain of a hollow tube and of a hollow ball to the cases of a cylindrical pore and a spherical pore, respectively. The result is expressed as the relative change in the volume and linear dimensions of a porous body. Examples of numerical estimations are given for microporous bodies in vacuum.

The work has been done under the financial support of the program “Leading Scientific Schools of Russian Federation”.

KL-7

MOLECULAR STRUCTURE EFFECT OF CARBONS ON THEIR CATALYTIC ACTIVITY IN THE ELECTRON AND PROTON TRANSFER REACTIONS

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Molecular structure of carbons depends on a number of factors, namely, precursor’s type, pyrolysis conditions, presence of heteroatoms in the lattice, etc. In turn, the molecular structure (the chemical nature of matrix) is influences on catalytic activity of carbons in various types reactions, all other things being equal.

In this presentation the attempt has been done to propose the phenomenological concept for explaining the mechanism of the influence of N- and O- heteroatoms on the catalytic activity of carbons in the electron and proton transfer reactions. We start from the state that N- and O- heteroatoms influence on the energetic parameters of π-conjugation in graphene-like system.

For the evaluation of individual and combine influence of N- and O-heteroatoms on carbons catalytic activity in the reactions of electron transfer, the energetic parameters (the energies of HOMO and LUMO and the value of forbidden zone) of clusters modeling the active carbons with various amount of N- and O-heteroatoms in different positions have been calculated using semi-empirical quantum-chemical method AM 1. π –conjugated systems containing 37 condensed rings have been computed. We consider that clusters with minimal values of work function (E HOMO) and gap (ΔE) correspond to carbons with maximal catalytic activity in the electron transfer reactions. That is N- and O-heteroatoms improve electron-donor function of carbons and reduce value of E HOMO as well as increase the mobility of carries and reduce value of ΔE.

In accordance with the prognostic data of quantum-chemical calculations we synthesized N- and O-containing carbons and studied their catalytic activity in the reactions of peroxides decomposition and H2S oxidation.

Thus active carbons are known as catalysts of oxidation for not only H_2S but several other organic (alcohols, amine acids, aldehydes) and inorganic (SO_2, $Fe^{2+,}$ Mn^{2+}, cyanides etc.) compounds, we conclude that less values of electron work function in the case of N- and

O- containing carbons provides more effective formation of $O_2^{\bullet-}$ superoxide-anions - reactive intermediate species of oxidation process in surface layer.

To confirm this approach we studied the process of oxygen reduction in the original electrochemical cell with separate electrode spaces [1]. It was found that carbons containing 1,5-2,5% of N- and 4-6% of O- in position pyrrolic and furanic type really have highest reductive ability (highest current of O_2 reduction).

It is well known that oxidized carbons contain the surface functional groups of carboxyl and phenol types with mobile proton.

Having applied the potentiometric to determine the acidity of surface groups in carboxylic cationites and oxidized carbons of various types we have shown that the acidity of such groups in carbons, produced from fruit shells far exceeds (pK~ 2) the acidity of carboxylic cationites (pK 2.5). It is likely due to the fact that π -electrons of oxygen atoms, forming the surface groups in carbon, are very much delocated by the π -conjugated system of the graphite-like planes. It reduced the effective negative charge on oxygen and, as a result, the mobility of proton increases and, therefore, -OH and -COOH groups become more acidic. It is worth to be noted that in the case of synthetic oxidized carbons, which possess much more perfect (almost without defects) structure of π -conjugation in the system of graphitic planes, the acidity of surface group even more (pK~1) as far as in this case the delocalization of electrons (π -electrons of oxygen) is mostly expressed.

To understand the general principles of catalysis by oxidized carbons in reactions of esterification we studied in details kinetics and mechanism of synthesis of buthyl acetate in gaseous phase in the wide range of temperatures (150-450 ^{o}C) using the H^+ modifications of oxidized carbons, as well as reaction of hydrolysis for some ethers and lipids.

Thus, introduction of N- and O- heteroatoms into carbon matrix essentially influences on their catalytic activity in the electron transfer reactions. On the other hand, π-conjugation in oxidized carbons provides the increase of proton mobility with the raise of oxidation degree. The last factor yields the growth of catalytic activity in the proton transfer reactions.

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Presentation of FGUP “ENPO Neorganica”

NEW RUSSIAN HIGH QUALITY CARBON SUPPORTS FOR Pt , Pd AND OTHER CATALYSTS

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The creation of large tonnage carbon industry in Russia became especially important in connection with the fast development of the catalysis processes in organic chemistry.

FGUP “ENPO “Neorganica” is the leading scientific center in the Russian Federation working at the development of active carbon technologies for different applications. This report presents the last achievements of the scientific center in the development of carbon absorbents and carbon supports for different catalysts including cleaning the air from hazardous toxic agents and hydrodechlorination of benzole chloride.

Special attention will be paid to new active carbons, mainly to carbon “FAC”, which possesses a unique mechanical strength, which significantly exceeds the “Sibunit” ones (up to 7000 kg/cm^2), and minimal ashes content (less than 0.5% of mass).

ORAL PRESENTATION

SECTION I NOVEL CARBON BASED CATALYSTS AND SUPPORTS: SYNTHESIS, CHARACTERIZATION, APPLICATION

SECTION II NEW TRENDS IN CARBON TECHNOLOGIES FOR ADSORPTION AND CATALYSIS

COBALT ON CARBON NANOFIBER CATALYSTS – STUDY OF PARTICLE SIZE AND PROMOTER EFFECTS IN FISCHER TROPSCH CATALYSIS

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Carbon nanofibers hold great potential as catalyst support material [1,2]. Supported cobalt catalysts are used to convert synthesis gas (H_2/CO) to higher alkanes and alkenes in the so-called Fischer Tropsch (FT) process. As synthesis gas can be produced from a variety of feedstocks including natural gas, heavy oil, coal and biomass and the products of FT can be used as high-quality transportation fuels the research on cobalt catalysts is increasing. The use of chemically inert carbon nanofibers as support material might limit the extent of interaction with cobalt and possible promoters used in the final catalyst. In this contribution we report on a study of (i) the effects of the cobalt particle size and (ii) the effects on manganese oxide promotion on cobalt.

Carbon nanofibers (CNF) were produced from H_2/CO over a Ni/SiO_2 catalyst as reported before [3]. The raw material was purified by washing with caustic solution followed by reflux in concentrated nitric acid. The latter treatment not only removed nickel but also gave rise to surface oxidation that facilitated catalyst preparation [4]. The deposition of cobalt onto CNF was carried out using several preparation techniques, viz. ion-adsorption, impregnation and drying and deposition precipitation. The cobalt loading was varied between 1-22 wt%. The catalysts were reduced at 350 °C prior to catalysis. Following reduction and passivation a 10%wt Co/CNF was impregnated with Mn(II) nitrate aqueous solution to arrive at loadings ranging from 0.02-1 %wt Mn. Characterization of the catalysts involved hydrogen chemisorption, XPS, (S)TEM, XRD and XANES/EXAFS. FT experiments were carried out at H_2/CO = 2 v/v, either at 1 bar and 220 °C or at 35 bar and 210 °C.

Co/CNF with cobalt particle size ranging from 2.7 to 24 nm with relatively narrow particle sizes were obtained. A representative TEM of Co/CNF with an average particle size of 13 nm is displayed together with the specific activity based on the amount of cobalt (CTY) for the series of catalyst.

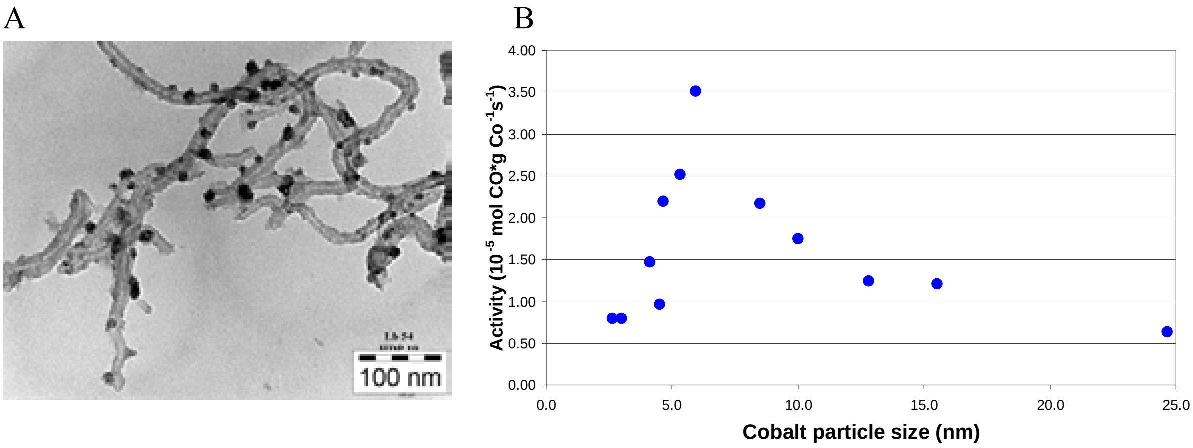

Figure 1: (A) TEM of Co/CNF and (B) CTY at 1 bar versus cobalt particle size.

The drop of activity with particle size beyond 6 nm is in line with a constant TOF of about 0.01 s^{-1}. The strong drop of activity below 6 nm points to a particle size effect. Using *in situ* XANES and EXAFS (Co K-edge), i.e. at 1 bar synthesis gas and 220 °C we could exclude formation of cobalt oxide and of cobalt carbide as possible causes of the particle size effect. EXAFS showed a drop of the coordination number upon exposure of Co/CNF (4 nm Co particles) to synthesis gas pointing to a reconstruction of the cobalt particles possibly due to a transformation of hemi-spherical to flat particles. Extensive reconstruction is in line with observations on single crystal cobalt surfaces [5].

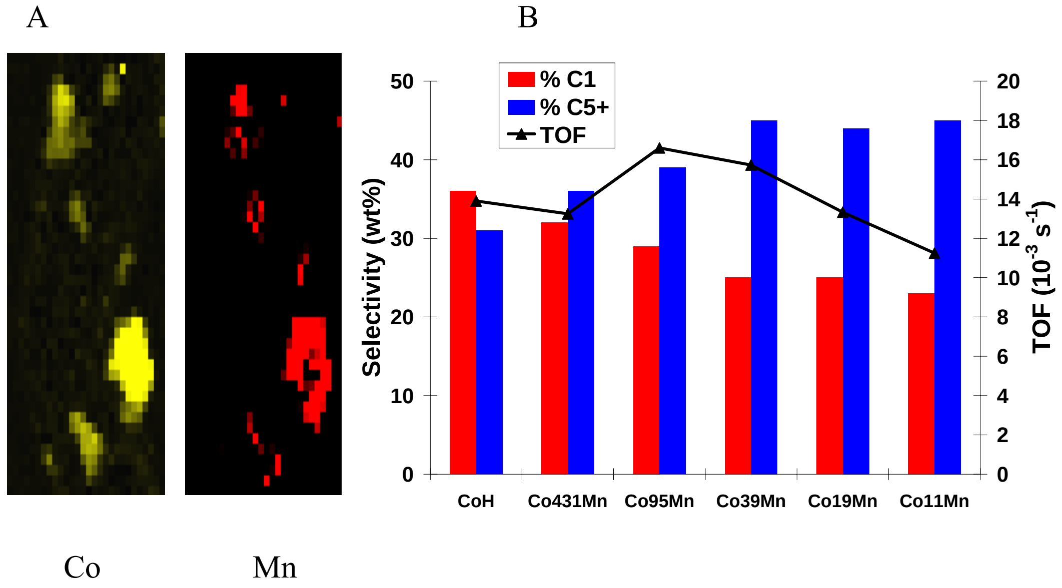

Figure 2: (A) Cobalt and manganese map from STEM-EELS and (B) Catalysis data for FT at 1 bar and 220 °C, CoxxMn with xx= Co/Mn atomic ratio.

The structure and effects of manganese oxide promotion on FT at 1 bar are shown in Figure 2. From STEM-EELS experiments [6] we have found that MnO was always associated with Co on the carbon nanofibers (Fig. 2A). The methane selectivity as found to decrease from 41 to 23 %, while the C5+ selectivity increased from 28 to 45 % (Fig. 2B). Although MnO covered up some of the Co surface the activity increased at low loadings but dropped at more elevated (> 0.1 %wt Mn) loadings. The very low loading of promoter to be effective in FT is a consequence of the nature of the carbon nanofiber support material.

In sum, carbon nanofiber supports are useful for fundamental studies in catalysis, in this case metal partice size and promoter effects in the Fischer Tropsch synthesis.

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OP-I-2

PREPARATION OF CNF SUPPORTED COBALT CATALYSTS WITH HIGH METAL LOADING BY DEPOSITION-PRECIPITATION

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Carbon nanofibers (CNFs) have been found to be an interesting support for a number of catalytic reactions. Particularly, Bezemer *et al.* [1] have demonstrated that CNFs are promising supports for Fischer-Tropsch (F-T) synthesis. F-T synthesis turnover rates on cobalt catalysts are believed to be independent of cobalt dispersion and support. Therefore, catalysts with high reaction rates require the synthesis of supported cobalt with high cobalt concentrations and small particle sizes. Homogeneous deposition-precipitation (DP) has been developed as a method for preparing highly loaded, highly dispersed metal/oxide catalysts, but it has been scarcely used for the deposition of metal precursors on CNFs [2]. This has been ascribed to the absence of a strong interaction between the support and metal precursor, which is assumed indispensable for DP.

In this study, a series of 12, 20, 40 wt.% Co catalysts supported on oxidized CNFs have been prepared by DP. Hydrolysis of urea at 363 K has been used to slowly increase the pH to control the precipitation of cobalt nitrate precursors. The catalysts were calcined at 573 K in flowing nitrogen, and characterized by TGA, XRD, TPR, BET, hydrogen chemisorption, TEM, etc.

TGA analysis shows that the actual loadings of cobalt are lower than, but very close to the nominal values, as shown in Table 1. Therefore, DP is suitable for the preparation of high loading Co/CNF catalysts even though the interaction between the support and metal is low. The difference between the nominal loading and the actual loading can be explained by the formation of soluble Co-amine complexes at the deposition pH of around 7. Cobalt probably nucleates as cobalt hydroxide and is anchored to the oxygen-containing groups of the CNFs. After calcination, the XRD study shows that for all the catalysts, there are two cobalt containing phases, CoO and Co_3O_4. The particle sizes calculated from the Scherrer equation shows that all the catalysts have small particle sizes around 9 nm, even at the highest cobalt loading. It is also interesting to observe that the particle sizes only increase very slightly with the metal loading.

TEM characterization demonstrates that all the cobalt is deposited on the fibres, free of any bulk precipitation. A representative TEM image of the 40 wt.% Co/CNF catalyst is shown in Fig. 1. The cobalt oxide particles are homogeneously distributed with a very narrow size distribution, and seem to cover the fibre uniformly at the 40 wt.% loading. The average particle size calculated from 120 particles is 8.3 nm, in good agreement with the XRD study.

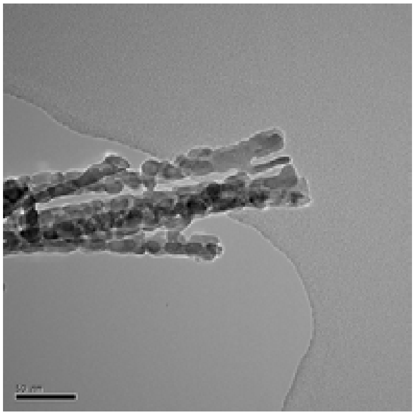
TPR study shows that all the catalysts are reduced through two main steps, from Co_3O_4 to CoO, and from CoO to Co. The first peak is relatively narrow and the second peak is quite broad. This also suggests the coexistence of Co_3O_4 and CoO. Compared with the reduction of Co/Al_2O_3, Co/CNF is reduced at a lower temperature. This is because for Co/Al_2O_3, cobalt will form a surface compound with alumina, which is difficult to be reduced. Hence, TPR study clearly shows the weak interaction of metal and CNF. This will also be an advantage of using CNF as support for F-T catalysts because high reduction temperatures are required for cobalt on strongly interaction supports, and they lead to the sintering of cobalt particles.

In conclusion, DP has been used to prepare highly loaded, highly dispersed cobalt on CNF catalysts. The precipitation has been controlled by slowly increase the pH of the solution. The Co/CNF catalysts have a small particle size and narrow particle size distribution. Combined with their easy-to-reduce property, these catalysts could be promising for F-T synthesis applications.

Table 1. Metal loading and particle sizes from catalyst. XRD and TEM of different catalysts.

Catalyst	Actual loading (wt.%)	Particle size (nm, XRD)	Particle size (nm, TEM)
12 wt.%	10.1	8.4	6.5
20 wt.%	17.1	9.5	-
40 wt.%	38.6	9.4	8.3

Fig. 1. TEM image of the 40 wt.%



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OP-I-3

BI-METALLIC CATALYSIS ON CARBON NANOTUBES FOR THE SELECTIVE HYDROGENATION OF CINNAMALDEHYDE

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Nanostructured carbon materials have already been successfully used in heterogeneous catalysis, but, unfortunately, a lack of systematic comparison with traditional activated carbon supported catalysts has to be noted. [1,2]. Additionally, there is very scarce studies dealing with the comparison of catalysts prepared on the different types of fibrous carbon, namely, multi-walled carbon nanotubes (MWNT), single-walled carbon nanotubes (SWNT) and graphite nanofibers (GNF).

Carbon nanotubes (MWNT, GNF, SWNT) based catalysts (Pt, Ru and Pt-Ru) were developed and compared to their counterparts on activated carbon for the selective reduction of cinnamaldehyde to its unsaturated alcohol. Prior to metals impregnation, the carbon supports were oxidised, in order to develop oxygen containing surface groups to act as anchoring sites for the precursors. Platinum and ruthenium were deposited on the different carbon supports by means of a surface organometallic approach, using $[Pt(CH_3)_2(\eta^4\text{-}C_8H_{12})]$ and $[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]$ as precursors. The use of mesoporous nanostructured support that decreases the mass transfer limitations allows significantly better activity than microporous activated carbon. As far as selectivity is concerned, activated carbon systems are more selective towards cinnamyl alcohol formation. The use of a platinum ruthenium bimetallic system (Fig. 1) permits to reach higher selectivities than with the monometallic systems. Finally, we demonstrate that, in the case of MWNT supported systems, high temperatures catalyst activation does promote significantly the selectivity towards cinnamyl alcohol (Fig. 2). The role of this high temperature treatments, which may affect the electrical conductivity of the support, the mean particle size, the cinnamaldehyde equilibrium adsorption and the electron transfer from the MWNT to the metal will be discussed.

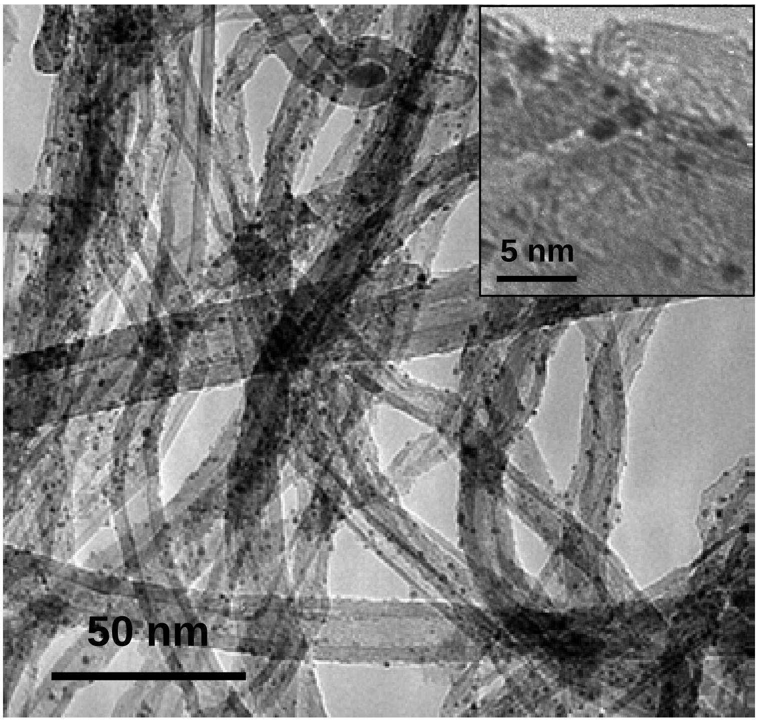

Figure 1: PtRu/MWNT catalyst

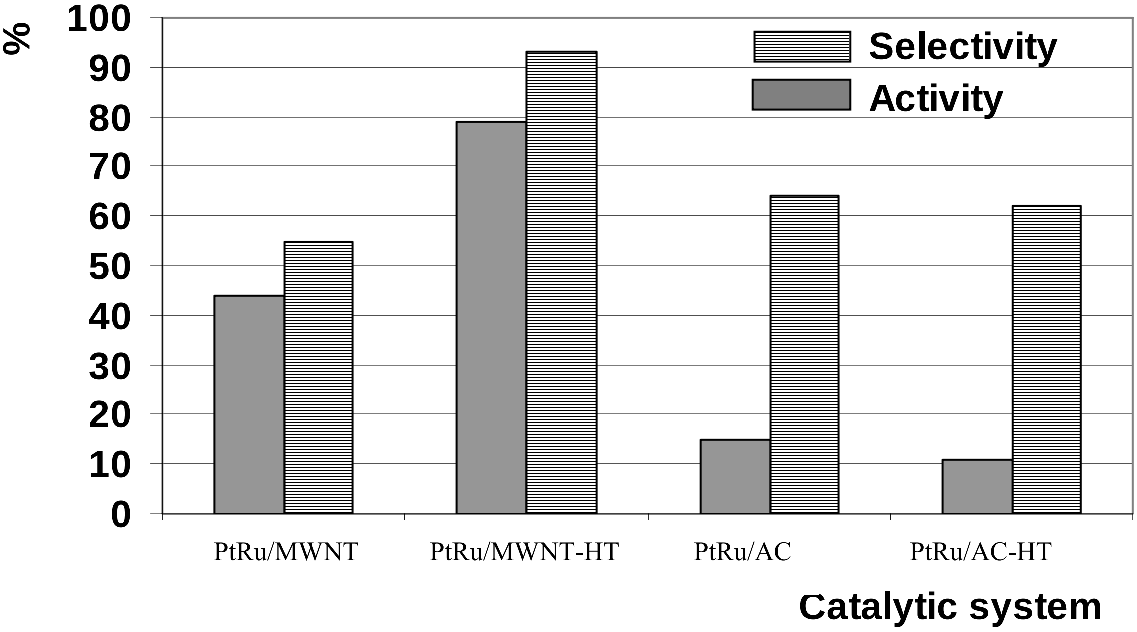

Figure 2: Performances of bimetallic systems on MWNT and activated carbon (AC) supports before and after (HT) high temperature treatment

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OP-I-4

PREPARATION AND CHARACTERISATION OF DISPERSED PALLADIUM CATALYSTS SUPPORTED ON CARBON PREVIOUSLY TREATED WITH DIFFERENT STRONG OXIDANTS

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It is well known that carbon is a useful support to obtain dispersed palladium catalysts. The interaction of palladium precursors with the carbon surface is mainly given by the oxygenated groups existing on the surface such as: lactones, carboxylic, carbonilic and phenolic groups. These oxygenated groups can strongly be increased by oxidation [1, 2] with oxygen but also by contacting the carbon surface with a solution of strong oxidant such as: permanganate, hydrogen peroxide or nitric acid [3]. It is possible, by using titration methods [1] to evaluate the distribution of the different sites on the surface.

Different catalysts have been prepared by supporting palladium acetate on carbon treated with four different oxidants dissolved in water, that is: potassium permanganate 0.1 M and 1 M, nitric acid 0.1 M, sodium hypochlorite 8% by weight, hydrogen peroxide 12 and 120 volumes. Prepared supports have been characterised, first of all, for what concerns the determination of the concentration (mmols/g) of respectively the carboxylic and of the hydroxyls group on the surface. The obtained values have then been compared with the initial concentrations for the untreated carbon. The obtained results are reported in Tab. 1.

Carbon support pretreatments	Conc. of -COOH groups	Conc. of -OH groups	Dispersion % for 1% Pd catalysts	Reaction rate (ml/h g of Pd)
Untreated carbon	0.16	0.05	56	12.24
Carbon + $KMnO_4$ (0.1 M)	0.83	0.39	56	19.24
Carbon + $KMnO_4$ (1.0 M)	1.21	0.88	54 (3% Pd)	13.71
Carbon + HNO_3 (0.1 M)	0.27	0.15	69	19.24
Carbon + NaClO (8% b.w.)	0.16	0.05	60	15.75
Carbon + H_2O_2 (12 vol.)	0.16	0.05	72	20.12
Carbon + H_2O_2 (120 vol.)	0.27	0.26	48	5.90

As it can be seen, potassium permanganate gives place to the greatest increase in both the concentrations.

All the supports of Tab. 1 have then been contacted with a palladium acetate solution dissolved in benzene (2 g of supports with 50 ml of a benzene solution of palladium acetate) for 2-3 hours. In the mentioned range of time all the palladium is adsorbed from the solution. The prepared catalysts contained about 1% by weight of palladium with the exception of the support prepared by oxidation with 1 M potassium permanganate that have been prepared with 3% by weight of palladium. An increase of -COOH and -OH would favour palladium dispersion as a consequence of the surface reaction:

$$\text{---- COOH} + \text{Pd(OOCCH}_3)_2 \longrightarrow \text{---- COOPd(OOCCH}_3) + \text{CH}_3\text{COOH}$$

The dispersion of all the prepared catalysts has been determined by measuring hydrogen chemisorption with a pulse method [4] and the obtained results are always summarized in Tab. 1. As it can be seen, all the catalysts resulted well dispersed and the effect of the oxidating treatment in some cases is significant even if not very strong. In particular there is not a direct correlation between the increase of –COOH and –OH concentrations and dispersion. This will be discussed and justified.

All the prepared catalysts have been submitted to an activity test consisting in the measurement in a batch reactor of the reaction rate of the cyclo-octene hydrogenation. The obtained results are always reported in Tab. 1. As it can be seen drastic treatments are detrimental while the oxidation in mild condition gives place to an improvement of the performances.

The properties and catalytic performances of the prepare Pd-carbon catalysts have also been compared with catalysts containing roughly the same amount of palladium but prepared by using other different supports, such as: alumina, silica and silica alumina and other palladium precursors. A discussion on the method more suitable for obtaining very high dispersed catalysts will conclude the work.

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OP-I-5

Ru-CeO_2/SIBUNIT CATALYSTS FOR CATALYTIC WET AIR OXIDATION

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The Catalytic Wet Air Oxidation (CWAO) process with oxygen at high temperatures and pressures is suitable for the elimination of both organic and inorganic substances in various industrial wastewaters. The main problem for this process is the design of a catalytic system stable in aggressive oxidizing wet process conditions. Noble metal (Ru, Pt, Pd) supported on carriers resistant to leaching such as ZrO_2, TiO_2, CeO_2 and carbon were shown to be stable and active catalysts for CWAO [1-3]. However there is very strong requirement for the economy of these processes to decrease the cost of catalysts and consequently the amount of noble metals.

We have shown earlier that the level of activity of Ru/carbon catalysts in the oxidation of various substances can be increased by using carrier based on graphite-like porous materials of Sibunit family promoted with CeO_2. It was also possible simultaneously to improve the stability of the catalyst and to reduce the amount of Ru from 5 to 0.5% [4,5].

In this work different Ru/CeO_2/Sibunit catalysts were tested under mild reaction conditions (T=160 – 200^{o}C and P_{O2} =1.0 MPa) for the complete oxidation of widespread contaminants of industrial wastewater such as phenol compounds. The optimal composition of catalyst was found to be 0.5-0.6%Ru/4-6%CeO_2/Sibunit-4.

Catalyst 0.6%Ru-5%CeO_2/Sibunit was also used in a well stirred autoclave to study the oxidation kinetics of phenol at 140-180°C. A rate law was established by carrying experiments as a function of reaction parameters (temperature, concentration). The following simplified mechanism of an initial stage of catalytic oxidation of phenol was suggested:

$Ph+[\ ] \Leftrightarrow [Ph]$ (1)

$O_2(gas) \Leftrightarrow O_2(sol)$ (2)

$O_2(sol)+2[\ ] \Leftrightarrow 2[O]$ (3)

$[Ph]+[O] \Leftrightarrow [A]+[\ ]$ (4)

$$[A] \Leftrightarrow A+[\ ] \qquad (5)$$

Kinetic analysis based on this mechanism gave the following rate equation for phenol conversion:

$$-\frac{dC_{Ph}}{dt} = \frac{K_1 C_{kat} C_{Ph} \sqrt{P_{Ox}}}{\left(1 + K_{Ph} C_{Ph} + \sqrt{K_{Ox} \frac{P_{Ox}}{H_c}}\right)} \qquad (6)$$

The kinetic modeling with equation (6) is in good agreement with the experimental data points. The constants of equation (6) allowing the best fitting the experimental data were calculated.

The importance of oxygen diffusion in the liquid phase on oxidation activity was established experimentally and theoretically. Modification of the autoclave reactor design to assure better oxygen diffusion to liquid increased significantly the oxidation rate.

Comparative TEM and XRD study of catalysts 5%Ru/Sibunit, 1%Ru/5%CeO_2/Sibunit and 0.6%Ru/4% CeO_2/Sibunit aimed to understand influence of CeO_2 promoter has been carried out. Ru-particles with average diameter 5 nm were found for 5%Ru/Sibunit sample. TEM have shown that in case of 0.6%Ru/4%CeO_2/Sibunit sample 1nm-large Ru-particles are flattened on 5 nm-large CeO_2 particles supported on the carbon surface. 1%Ru/5%CeO_2/Sibunit contains 1-5 nm CeO_2 particles. Ru particles were not detected on the surface of this catalyst but Ru was found closely associated to 5-nm large CeO_2 particles supported on carbon. This association is probably very beneficial to the activity of the catalyst.

The financial support of this study by INTAS grants Nr. 00-129 and Nr. 05-1000007-420 is gratefully acknowledged.

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OP-I-6

CARBON SUPPORTED PLATINUM CATALYSTS: INFLUENCE OF ACTIVATION TREATMENT OF A SYNTHETIC CARBON SUPPORT AND OF METAL DEPOSITION IN THE SELECTIVE LIQUID PHASE OXIDATION OF ALCOHOLS

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Oxidations of alcohols into carbonyl functionalities are key reactions in the synthesis of fine chemicals. The need to substitute stoichiometric oxidations (using mineral oxidants) with "green" oxidations using benign oxidizing agents like molecular oxygen or hydrogen peroxide has been often emphasized [1]. Supported noble metal catalysts, e.g. Pd/C or Pt/C are known to catalyse the oxidation of alcohols in the presence of molecular oxygen.

It was previously reported that benzylalcohol (Bzol) can be very selectively oxidized to benzylalcohol (Bzal) in dioxane, while the use of a 50/50 mixture of dioxane and alkaline aqueous solution yielded benzoic acid (Bzoic) by further oxidation of Bzal [2]. In this work, we examined the effect of the activation treatment of the synthetic carbon and of the method of deposition of the metal on the characteristics of the supported metallic catalyst and its activity in thi reaction.

Experimental

Synthetic carbon samples were activated carbons with controlled pore size. They were prepared by carbonisation at 800°C of a porous polymeric resin precursor prepared from Novolac resin and hexamethylenetetramine in polyethyleneglycol. The carbon particles thus produced were spherical particles (50-90 μm). Then, they were activated by a "burn off" technique using either CO_2 at 850°C (carbon noted xC) or air at 450°C (carbon noted xA), with x = burn-off percentage (MAST). In some cases, the carbons activated under CO_2 were oxidized with NaOCl before the cationic exchange (carbon note xC_{ox}).

Platinum deposition (nominal 3 wt. %) was performed by liquid phase impregnation using H_2PtCl_6 and in situ formaldehyde reduction in basic medium (noted *imp*) or by cationic exchange with $Pt(NH_3)_4Cl_2$ (noted *ex*) and reduction under hydrogen at 300°C.

Carbons were characterized by standard BET method, Boehm titration, TPD-MS. Catalysts were characterized by Transmission Electron Microscopy (TEM) and by CO chemisorption at 35°C. The catalytic activity of prepared catalysts was estimated using oxidation of benzylalcohol to benzaldehyde or benzoic acid with air in a 250 ml batch reactor.

Results and discussion

The Table summarizes the effect of the activation treatment of the carbon on the catalytic properties of Pt catalysts prepared by both methods

Both catalysts prepared by impregnation with the same dispersion behave similarly in dioxane, with comparable initial reaction rate, total conversion within 6-7 h and a very good selectivity to Bzal. In dioxane/alkaline aqueous solution, conversion of Bzol to Bzal was very rapid, but while Bzal was totally converted to the acid in the presence of 2%Pt$_{imp}$/C35C, only 46% of Bzoic were produced over 3%Pt$_{imp}$/C44A. These results are attributed to the polar groups on C44A which make the catalyst hydrophilic and retains a water film on the metallic surface.

The catalysts prepared by cationic exchange were surprisingly very poorly dispersed (5 and 20%). Dispersion of Pt in 3%Pt$_{ex}$/C35C$_{ox}$ and consequently the catalytic activity in dioxane/alkaline aqueous solution could be improved, by heating C39C$_{ox}$ under Ar at 500°C (noted C$_{ox\ cal)}$ to selectively eliminate carboxylic groups and preserve phenolic groups. Further improvement could be obtained by decomposition of the catalyst precursor under air, before the reduction step (noted C$_{ox\ cal}$ and C$_{ox/Ar\ cal}$). However the performances were lower than those of 2%Pt$_{imp}$/C35C.

Table: Oxidation of Bzol (100 mmol l^{-1}, 100 ml solvent, 1 g catalyst, 100°C, 10 bar air).

	Dispersion	In dioxane			In dioxane/alkaline water	
	(%)	Initial rate mol h^{-1}mol$_{Pt}^{-1}$	Bzol conv (%)/h	Bzal yield (%)/h	Bzol conv (%)/h	Bzoic yield (%)/h
2%Pt$_{imp}$/C44A	44	51	100/6	95/6	100/2	46/23
2%Pt$_{imp}$/C35C	35	63	99/7	98/7	99/2	98/23
2.7%Pt$_{ex}$/C39A	20	7	94/23	86/23	100/4	39/23
3%Pt$_{ex}$/C39C$_{ox}$	5	7	91/23	85/23	100/4	20/23
3%Pt$_{ex}$/C39C$_{ox/Ar}$	15				100/3	66/23
3%Pt$_{ex}$/C39C$_{ox\ calc}$	19				100/3	95/23
3%Pt$_{ex}$/C39C$_{ox/Ar\ cac}$	24				100/2	95/23

In conclusion, the activation treatment of this synthetic carbon and the mose of deposition of Pt are of prime importance for activity of the resulting supported platinum catalyst in selective oxidation of benzylalcohol.

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OP-I-7

CARBON SUPPORTED NOBLE METAL CATALYSTS PREPARED BY PHOTOCHEMICAL DEPOSITION

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Photochemical deposition of noble metals in different supports is gaining importance because of its simplicity and advantages. Its main advantage is the ability of spreading very effectively the metal throughout the support, thus leading to very high dispersions, resulting in higher molecular control, with a positive effect on both activity and selectivity. This type of catalysts is important for industrial preparation of fine chemicals. A common synthetic route in these processes is the selective catalytic hydrogenation of organic substrates containing unsaturated functional groups, like steroids or α,β-unsaturated aldehydes.

In the present study, hydrogenation catalysts prepared by photochemical deposition [1] are compared against the usual incipient wetness catalysts and other commercial available catalysts. Different supports were tested (carbon nanotubes, fullarenes, carbon fibers and titania) in order to establish potential metal to support interactions. Catalyst loads are also varied in order to achieve the desired conversion and selectivity.

The prepared catalysts were used in hydrogenation reactions to test their activity and selectivity. In the case of the model reaction of cinnamaldehyde selective hydrogenation, we tested a series of multi walled carbon nanotubes (MWNT) supported Pt catalysts with different thermal treatments, leading to different oxidation states of the metal .The reaction mixture contained heptane (solvent), cinnamaldehyde, decane (as an internal standard for gas chromatography) and the catalyst. The reaction temperature was 363K and the reaction started by feeding the reactor with hydrogen to a 10 bar pressure. Small aliquots of the reaction mixture were taken throughout the reaction to perform quantitative analysis (conversion and product selectivity). The analysis was performed in a GC DANI 1000, equipped with a WCOT Fused Silica column.

As example, we present the hydrogenation of cinnamaldehyde using a 1% Pt/MWNT, in mild conditions of 363 K and 10 bar of hydrogen pressure. A good selectivity for the cinnamyl alcohol is obtained after one hour of reaction.

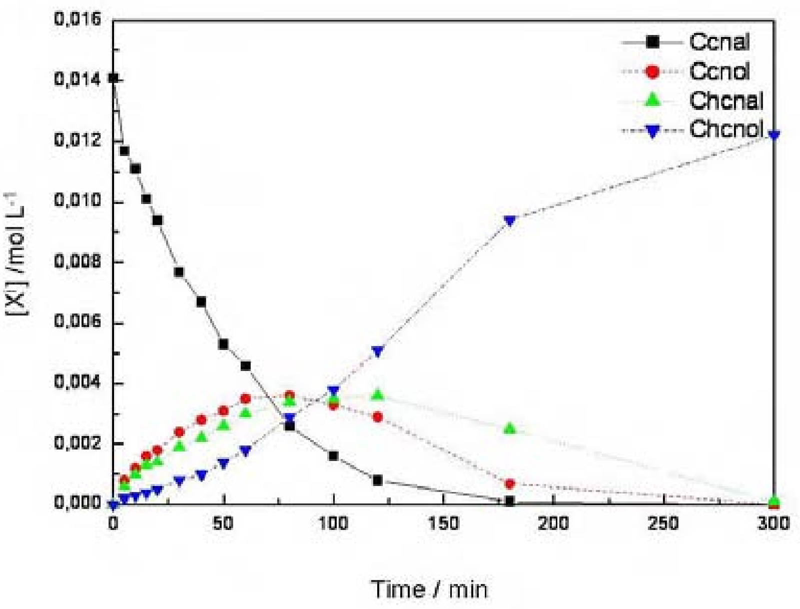

Figure 1 – Concentration of reactants and products as function of time. Ccnal: cinnamaldehyde; Ccnol: cinnamyl alcohol; Chcnal; hydrocinnamaldehyde; Chcnol hydrocinnamyl alcohol.

The photodeposition method is able to produce active and selective catalytic materials for selective hydrogenation of cinnamaldehyde.

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OP-I-8

PREPARATION OF Pd/C CATALYST BY ION EXCHANGE FOR HYDROGENATION REACTIONS

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Introduction

Noble metal catalysts supported on carbon are widely used in the fine chemical industry. Thermal treatments of the support, prior to noble metal loading, shape the catalytic properties of the materials. Oxidizing treatments can be used to functionalise the carbon surface through the formation of surface oxides (e. g. carboxylic groups, phenolic groups...) [1]. Some of these functions can be used as adsorption sites for metal cations [2], which can be in their turn exchanged by noble metal cations. Therefore this work will deal more particularly of the deposition of palladium on oxidized AC by this method of preparation.

In the first part of this study, the choice of the oxidizing treatment, the Pd exchange capacity and, the characterisation of the support and the final catalysts have been treated. In the second part, the activity of Pd/AC prepared by ion exchange will be compared to catalysts prepared by co-precipitation in selective hydrogenation of cinnamaldehyde.

Experimental part:

A commercial starting activated carbon with a specific area of 1000 $m^2.g^{-1}$ is treated with different oxidant reagents (NaOCl, HNO_3, H_2O_2). The amount of oxygen containing groups is determined by temperature programmed desorption (TPD) through the quantity of CO and CO_2 produced. The overall surface charge is evaluated by measuring the Zêta potential.

The adsorption kinetics was first studied in order to assess the time required to reach equilibrium. Adsorption of palladium ($Pd(NH3)_4^{2+}$solution) on Na-ion exchange carbon was studied and the amount of released Na^+ and adsorbed Pd^{2+} were monitored by atomic absorption spectrophotometer. After filtration, washing and drying, a back titration in HCl solution was performed on the resulting Pd exchange carbon.

After introduction of the metal, the catalyst is reduced in liquid media or hydrogen flow and characterised by temperature reduction programmed (TPR), X-ray diffraction and transmission electronic microscopy (TEM). The catalytic study of cinnamaldehyde hydrogenation was carried out at 60°C in a 100-mL steel autoclave under pressure.

Results

The carboxylic acid functions while dissociating into carboxylate and compensating cations allows the exchange. By measuring the back exchange, less than 10% of palladium initially deposited is retained through specific interactions like carbon surface structure defects. To reach great exchange capacities in palladium in order to obtain catalysts with strong palladium content (e.g. > 2% wt), the oxidizing pretreatment of the carbonaceous support by bleach is adapted because most surface oxygenated functions which it produces are primarily of carboxylic type. Moreover, this moderate treatment does not significantly change the textural properties of the support.

Compared to catalysts prepared by coprecipitation, which are reduced by hydrogen flow at 250°C reduction in liquid phase is preferable for ion-exchanged catalysts. With this kind of treatment, decomposition of oxygen functions but also sintering are avoided. Thus, high dispersion of palladium and homogeneous distribution of the particle size are achieved.

Selective hydrogenation of cinnamaldehyde has been used to evaluate the mode of preparation and reduction. Experimental parameters are optimised to reach good yield in hydrocinnamaldehyde.

In conclusion preparation of Pd/AC by ion exchange followed by liquid phase reduction is a simple preparation which leads to dispersed and efficient catalysts for hydrogenation reactions.

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OP-I-9

FABRICS OF ACTIVE CARBON FIBERS WITH Pd-NANOPARTICLES OF CONTROLLED DISPERSION FOR SELECTIVE 1-HEXYNE HYDROGENATION

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Catalytic hydrogenation is one of the key processes for manufacturing pharmaceuticals, vitamins and fine chemicals. The performance of the hydrogenation process and product distribution is strongly influenced by the catalyst activity and selectivity, the interaction of chemical kinetics and mass transfer, as well as the reactor design. Process intensification and integrated environmental protection can be improved by multiple catalyst reuses. To avoid internal and external mass transfer limitations and to attain high product selectivity catalyst particles of small diameter are required. In technical applications the minimal size, however, is limited due to the catalyst filtration after the reaction.

One novel approach to overcome these problems is the use of filamentous catalytic materials like woven cloths for the deposition of active components. The diameters of the filaments are in the order of several micrometers and correspond to the diameter of the traditional suspension catalysts. Therefore, the influence of internal mass transfer on overall kinetics could be suppressed.

Another problem of the catalyst design is related to the size control of the active metal nanoparticles and the size distribution. Traditional preparation by impregnation/ion-exchange gives broad distribution affecting activity/selectivity in the structure-sensitive reactions. The aim of this work was the development of Pd catalyst with monodispersed metal nanoparticles (~8 nm) deposited on active carbon fiber (ACF) fabrics efficient in selective liquid-phase alkyne hydrogenation.

Experimental

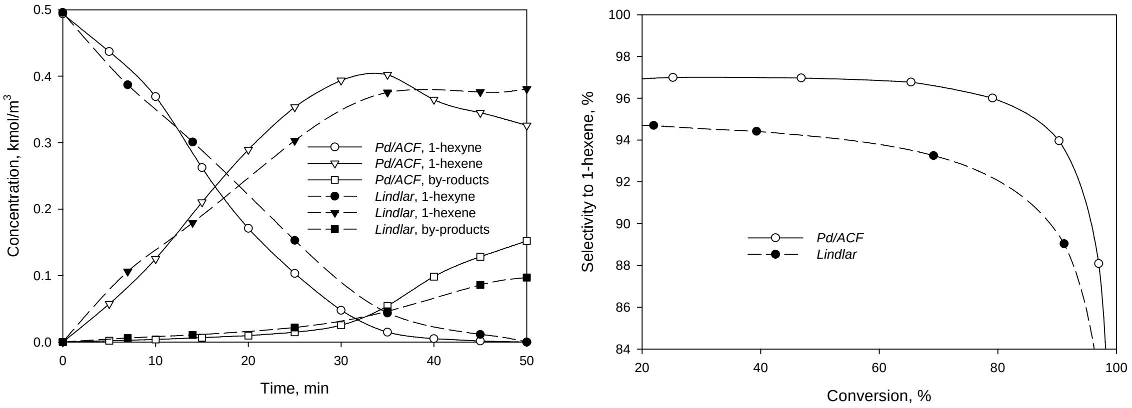
The catalyst preparation consists of a formation of Pd-nanoparticles of the controlled size in a reverse microemulsion, evaporation of liquid phases, surfactant removal by dissolution in methanol, ultrasound-assisted redispersion of flocculated nanoparticles in water and ACF impregnation. This method allows obtaining catalysts with high metal loading, retaining the nanoparticles monodispersity by avoiding calcination steps and recovering liquid phases of microemulsion and a part of a surfactant.

Hydrogenations were carried out in a batch stainless steel reactor equipped with a heating jacket and a hydrogen supply system at temperatures of 293-323K and hydrogen pressures between 0.4-1.7 MPa. The structured Pd/ACF catalyst was placed between two metal grids. As the reaction products, 1-hexene, n-hexane, 2-trans-hexene and 2-cis-hexene were found by GC. n-Heptane was used as a solvent.

Results and discussion

Catalysts with different Pd loading (0.4 wt.%, 0.6 wt.%, 1.2 wt.%) and the same dispersion showed an identical initial activity of 0.140 ±0.004 kmolH$_2$·kgPd^{-1}·s^{-1} (at 303 K, 1.3 MPa), indicating the absence of mass transfer limitations. Selectivity to 1-hexene was 97±0.4% up to 80% conversion, and 96±0.4% at 90% conversion was obtained.

The catalyst activity and selectivity were observed to be stable from the second run and no Pd leaching occurred during repeated catalyst reuse. The catalyst does not require any conditioning between runs. Both fresh and used Pd/ACF catalysts showed better catalytic performance than fresh conventional Lindlar catalyst (Figs. 1 and 2).



Figs.1 and 2: "Concentration – time" and "selectivity-conversion" profiles during 1-hexyne hydrogenation over the used 0.4 wt.% Pd/ACF catalyst (6th run) and fresh Lindlar catalyst (0.5 kmol/m^3 1-hexyne in n-heptane, 303K, H$_2$ pressure of 1.3 MPa, 1500 rpm, substrate/Pd=23,000 mol/mol).

Hydrogenation kinetics over Pd/ACF catalyst was studied and kinetic modelling was performed using Langmuir-Hinshelwood mechanism assuming weak hydrogen adsorption. The activation energy was found to be in the order of 50 kJ·mol^{-1}.

The improved catalytic performance of the new material in comparison with Lindlar catalyst was also demonstrated in solvent-free reactions. Higher maximum yield of 1-hexene was achieved (92% vs. 90% for Lindlar catalyst) for 1.2-fold lower reaction time.

OP-I-10

NOVEL CARBON BASED CATALYST FOR THE REDUCTION OF NO WITH COKE PETROLEUM ASHES AS ACTIVE PHASE: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

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Selective catalytic reduction (SCR) in the presence of ammonia has become lately one of the most outstanding technologies for the removal of nitrogen oxides. This process has been widely studied, commercialised and successfully applied [1]. However, in the high temperature range (300-500ºC) where commercial catalysts operate, SO_2 and particle poisoning of commercial TiO_2 based catalysts are very serious drawbacks. To circumvent these problems in NO_x stationary sources, an attractive option is to place the SCR unit downstream of the desulfuration device and particle removal equipment where both SO_2 and ashes have been removed [2]. Since the temperature at this point is typically below 200ºC, it is necessary to develop novel low-temperature SCR catalysts to avoid reheating of the flue gas and thus decreasing the cost of the process.

With this objective in mind, a wide range of low-temperature SCR catalysts under different forms and compositions have been prepared like powder catalysts (0.2-0.5mm), briquettes (10.5x13.5 mm) and carbon-coated monoliths (10x50 mm). All these catalysts are based on carbonaceous materials which are widely recognised as effective support precursors under suitable operating conditions. The use of carbon as a support precursor presents advantages over other catalysts like the simplicity of the preparation process, potentially low cost, easy availability of coal, possibility of obtaining samples with proper geometry, good mechanical resistance and finally an efficient performance at low temperature in the NO reduction.

For the preparation of the powder catalysts and the briquettes, a ground sieved Spanish low-rank coal was used as carbon support precursor. In both cases, the coal was pyrolyzed and subsequently activated with CO_2 or steam in a batch-mode fluidized bed reactor. The monoliths were prepared by coating cordierite monoliths with a blend of two polymers, viz. furan resin and polyethylene glycol (PEG). The coated monoliths were pyrolyzed and activated with CO_2. In all cases, coke petroleum was used for the production of petroleum coke ashes (PCA), by combustion under air at a temperature up to 650ºC. The PCA contains 23% (w/w) of V, 3.5% of Fe and 3% of Ni among other transition metals. The impregnation was carried out by equilibrium adsorption of the vanadium contained in PCA. Supports were immersed in a PCA suspension, stirred for several hours and carefully washed up afterwards.

Carbon supports as well as prepared catalysts were mechanical, physical and chemically characterised by means of different techniques like isotherm adsorption, temperature programmed desorption, chemisorption, X-ray, etc. Most of these materials show important specific surface areas, a good mechanical strength and a proper surface chemistry.

Catalysts were tested in an experimental device used to carry out the NO reaction which consists of a fixed bed reactor coupled to a mass spectrometer (Blazers) to analyse the gasses. All kind of catalysts have demonstrated their activity in the reduction of NO at low temperatures. Generally speaking, the NO reduction efficiency decreases initially with increasing temperature up to a point where it increases markedly reaching around 80% of conversion at 200ºC. The presence of SO_2 in the fed flow gasses seems to have a positive effect on the activity. This would imply an important advantage with respect to commercial TiO_2-based catalysts. On the other hand, a depletion of the activity is observed when water vapour is added to the reactant mixture. This effect becomes less important with increasing temperatures.

Finally, a kinetic study on the powder catalyst as well as the mechanical strength for the briquettes and monolith catalysts were tested. The kinetic studies revealed that the most suitable mechanism is a Mars van Krevelen one, what indicates that the limiting step may be the redox process which takes place on the catalyst surface. In the cases of briquettes and monoliths the mechanical properties were tested by means of impact, water and compressible tests. These forms seem to have enough resistant to be suitable for their application in medium-small scale stationary sources like waste incinerators or nitric acid production plants.

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OP-I-11

DENITROGENATION ACTIVITY OF Cu-Mn CATALYSTS SUPPORTED ON MINERAL, CARBON AND MINERAL CARBON MATERIALS

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Three groups of catalytic techniques, known as deNO$_x$ processes, can be applied for the removal of nitrogen oxides: no-selective reduction, selective catalytic reduction and decomposition. All of them eliminate nitrogen oxides by converting them to nitrogen, with water, carbon dioxide and/or oxygen appearing as nontoxic byproducts.

Four different supports were used in preparation of DeNOx catalysts: natural silicaalumina, active coke (grains), mineral carbon (monoliths) and cordierite monoliths coated with active carbon. On the base of our earlier studies we have found that the optimal active phase composition for carbon containing catalysts is 3 wt % Mn and 1.75 wt % Cu. Catalysts were prepared by dry impregnation metals using salt solutions of Cu and Mn and the concentration of the used salt solutions allowed obtaining the optimal metals content in the final catalysts. The base physicochemical properties, mechanical strength, porous structure and specific surface area of the catalysts were determined.

The activity studies were realized in laboratory flow equipment composed of model gas feeding system and dosage system, reactor and analyzer for determining the content of nitric oxide in the gas. The conditions of the process were: temperature range from 100 ^{o}C to 200 ^{o}C, for carbon containing catalysts and 100-450 ^{o}C for mineral catalyst, GHSV=5 000 h^{-1}. Model gas contained 6 vol. % O_2, NO content was changed in the range 400- 600 ppm, ratio NH_3/NO was equal to 1, and water vapor content in the model gas was ~ 1 %. Composition of model gas and reaction mixture was analyzed using the MSI 2500 Analyzer.

Active coke, grain form, was from commercial delivery (Hajnówka, Poland), and its basic properties were as follows, iodine number 200 mg I_2/g., C/H/N/S composition: 96/0.9/09/0.5 wt %, respectively. The prepared mineral-carbon monoliths contained 30 wt % of natural clay (as a binder). They were also characterized by dimensions, 1000x100x100 mm, wall thickness 2.7 mm and 121 (cells) longitudal channels (11x11). Pore volume attained value 0.69 cm^3/g and specific surface area ca 415 m^2/g, mainly micropores. Natural clay , from Jaroszów deposit, Lower Silesia Poland, used in preparation of monoliths was composed mainly from kaolinite (72 wt%), illite (23 wt %) and quartz (3 wt%).

Cordierite monoliths, from Corning Company, were coated with active carbon by carbonization of different gaseous hydrocarbons (propane-butane, styrene and toluene) at temperature 800 °C for 15-30 min. Total porosity of the prepared mineral carbon monoliths attained value ca 0.1 cm^3/g and specific surface area ca 500 m^2/g. The selected results of the activity studies are presented in Fig. 1.

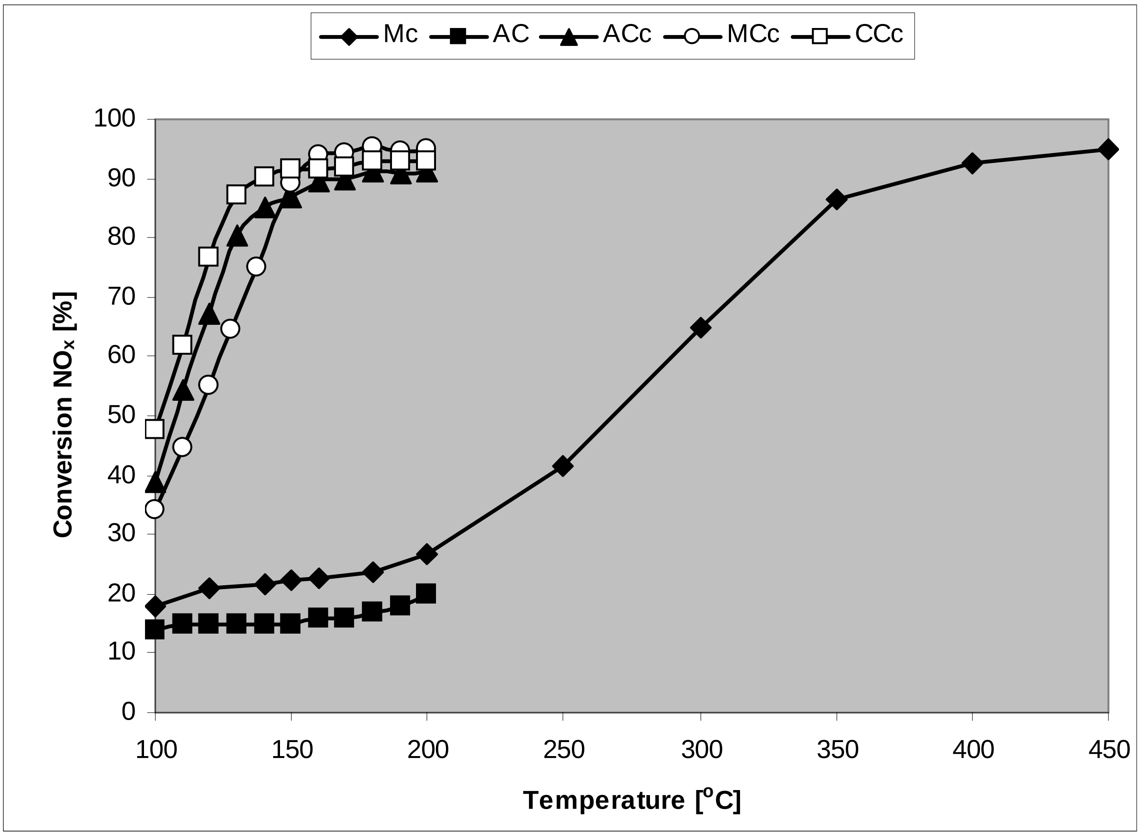

Fig. 1. Comparison of activity of the prepared MnCu catalysts in selective catalytic reduction (SCR) of NO by ammonia: Mc-natural clay catalyst, AC-active coke, ACc- active coke catalyst, MCc-mineral-carbon catalyst, CCc – cordierite – carbon catalyst.

The highest activity in SCR reaction was obtained using CCc catalyst. It was a result of the well developed surface of carbon coating at the cordierite support. However, similar activity was presented by mineral-carbon based catalyst although carbon phase was mixed and formed with mineral binder. It is seen in Fig. 1. that application of carbon containing SCR catalysts make it possible to lower process temperature to 150-200 °C from 400 -450 °C for mineral based catalyst.

OP-I-12

INFLUENCE OF THE SUPPORT HYDROFOBICITY ON THE PERFORMANCE OF COMBUSTION Pt –CATALYSTS

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The catalytic combustion of volatile organic compounds from dilute stream is one of the most interesting technological solutions to avoid air pollution. Noble metals, mainly Pt catalysts, are the most active and selective, and both organic and inorganic materials have been used as supports. Because the catalytic combustion must be developed at low temperature as possible, saving energy and avoiding the by-products formation, hydrophilic inorganic supports can adsorb the water generated by combustion blocking the catalyst active sites. Thus, we have previously shown that hydrophobic Pt/C catalysts totally mineralize toluene and xylenes at reaction temperatures sensibly lower than Pt/inorganic supports (1). However, increasing reaction temperature this effect decreases, and carbonaceous supports become unstable in air flow.

Therefore it is important to clarify the influence of support hydrophobicity on the catalysts activity, which permits the development of the most adequate supports. The use of organic-inorganic composite materials prepared by sol – gel method can offer the advantages of large porosity and surface areas but mainly guarantee the purity of the support, avoiding the interferences of inorganic matter present in classical activated carbons. In this work we have prepared, by impregnation, a series of Pt catalysts supported on carbon aerogel and on carbon-TiO_2, Al_2O_3 composites. The combination of Pt (the most active catalysts) with the different types of supports will permit to optimize the catalyst characteristics. Supported catalysts were physically and chemically characterized, taking special attention to their porous, acidic and hydrophilic character. They were used in the toluene combustion reaction and the results related with the physical properties of the supports.

Carbon aerogel was mainly mesoporous, while composite aerogels were macroporous (Table 1). The surface area of composite aerogels decreased about 50% regarding carbon aerogel, indicating the low surface area of inorganic phase.

The carbon matrix avoids the formation of large Al_2O_3 or TiO_2 crystallite in the composite, as shown by XRD. XPS show that both organic and inorganic phases were nearly independent, no significant interactions between them were observed. The carbon matrix, as well Al_2O_3 or TiO_2 oxides present similar XPS patterns than their pure phases. Their acidity, determined by isopropanol decomposition depended on the nature of the metal oxide present ($TiO_2 \geq Al_2O_3$) while the organic fraction was not active.

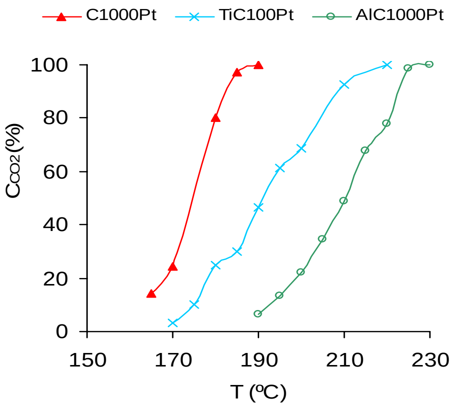
Regarding to the hydrophilic character of the samples, two types of active sites were determined by water adsorption at room temperature. The strong primary centres correspond to the micropore filling or water adsorption on acidic centres and weak secondary centres correspond to adsorption on hydrophilic (C=O) groups (2). Primary centres were more abundant and stronger on composites than in carbon aerogels according with their more acid character and smaller microporosity.

The activity order in toluene combustion was C1000Pt > TiC1000Pt > AlC1000Pt (Figure 1). In previous works (1) we found that catalyst activity increase with Pt-particle size, thus combustion is a structure sensitive reaction. In this sense, Al/C-Pt catalyst must be the most active of this series. The large concentration and strength of primary water adsorption sites on composite surface could be related with their smaller combustion activity.

Table 1. Textural characteristics and dispersion.

Sample	Oxide % wt	S_{CO_2} $m^2\ g^{-1}$	V_2 $cm^3\ g^{-1}$	V_3	d_{H2} nm
C-Pt	0	857	0.62	0.00	5.7
AlC-Pt	47	421	0.27	0.80	13.1
TiC-Pt	41	415	0.31	0.40	1.9

Figure 1. Catalysts activity



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OP-I-13

THE SYNTHESIS AND CATALYTIC PROPERTIES OF RHODIUM CHALCOGEN HALIDES OVER CARBON SUPPORTS IN THE METHANE OXIDATIVE CARBONYLATION

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Direct conversion of methane into useful chemicals or liquid fuels has a great advantage comparing to multi-stage technologies based on the synthesis gas. We have studied the gas phase carbonylation of methane in the presence of molecular oxygen over pure carbon carriers and carbon supported rhodium chalcogen halides.

Four different carbon supports were investigated in the reaction and used for catalyst preparation: activated carbon powder, spherical carbon, and two fractions of fullerene black obtained by pyrolysis of styrene and divinylbenzene copolymer. Rhodium selenochlorides were synthesized in Se_2Cl_2 used as reagent and non-aqueous media (molar ration $RhCl_3 : Se_2Cl_2 = 1:10$). The mixture was heated at 100°C during 120 h in an open reactor and then during 80 h in a closed reactor. Product was washed by CCl_4 and dried in vacuum. The product of the reaction is $Rh_4Se_{19}Cl_{11}$ according to the following reaction:

$$4RhCl_3{\cdot}4H_2O + 14Se_2Cl_2 \rightarrow Rh_4Se_{19}Cl_{11} + 4H_2SeO_3 + 5Se + 16HCl + 13/2Cl_2 + 4\,H_2O$$

Thermal destruction of rhodium chalcogen halides was carried out at 320°C during 40 h. It produces Rh_3Se_5Cl according to the following reaction

$$6Rh_4Se_{19}Cl_{11} \rightarrow 8Rh_3Se_5Cl + 33Se_2Cl_2 + 8Se_2$$

The volatile product Se_2Cl_2 precipitates on the cold part of the reactor.

Rh-containing catalysts over carbon carriers have been prepared by the following three different methods:

- thermal destruction of the rhodium chalcogen halide followed by mixing of the obtained solid with carbon carrier (method #1);

- thermal destruction of the mixture of the rhodium chalcogen halide and carbon carrier (method #2);
- synthesis of the rhodium chalcogen halide over the carbon surface followed by thermal destruction (method #3).

XPS and IR-spectroscopy data shows a formation of rhodium chalcogen halides in these solids prepared by different methods.

We have found that productivity of acetic acid by carbon supported rhodium chalcogen halides depends significantly on the carbon carrier and the method of the catalyst preparation. Namely, the catalyst with highest productivity of the acetic acid is prepared by synthesizing the rhodium chalcogen halide over the carbon support followed by thermal destruction. We have also found that rhodium chalcogen halides over activated carbons are more active comparing to fullerene supported catalysts.

OP-I-14

HYBRID CATALYSTS OF Rh COMPLEXES ON CARBON MATERIALS

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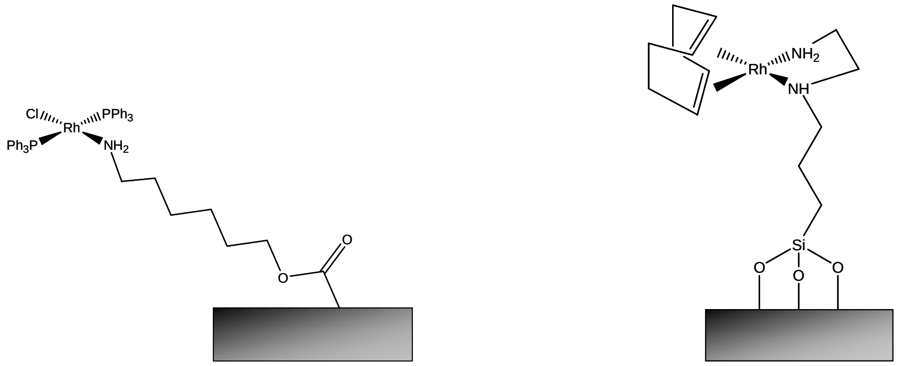
Introduction

Hybrid catalysts, consisting of a metal complex immobilized on a solid support, are regarded as a novel system able to combine the advantages and to overcome the drawbacks of heterogeneous and homogeneous catalysts. Carbon materials, with outstanding properties as catalyst support (high versatility in textural properties and surface chemistry, chemical stability in many conditions and easiness of active metal phase recovery), are also considered to be suitable for this application. The present work reports the results obtained on the immobilization of two rhodium complexes on carbon materials. The anchorage has been carried out by the creation of a covalent bond between a ligand and the oxygen groups of the carbon surface. Several carbon materials have been used as support: one granular and one pelletized activated carbon, an activated carbon cloth and multiwalled carbon nanotubes. These materials have been submitted to oxidation treatments in order to create specific oxygen functionalities on the surface. The two hybrid catalysts prepared are schematically shown in Figure 1.



Catalyst type A Catalyst type B

Figure 1.- Model of the anchorage through ester and siloxane bonds

Experimental

Catalysts type A: The carbon supports were oxidized with ammonium persulfate (saturated solution of $(NH_4)_2S_2O_8$ in H_2SO_4 1M 10mL/g carbon) and then treated with $SOCl_2$ (5mL in 5mL of toluene, 24h reflux) to create acyl chloride groups. The molecule 6-amino-1-

hexanol (AA) was anchored to the support by means of the creation of an ester bond between the –OH functionality and the acyl chloride groups on the carbon surface. The Wilkinson complex $[RhCl(PPh_3)_3]$ was introduced by substitution of one of its ligands by the anchored AA molecule.

Catalysts type B: The carbon materials were submitted to a heat treatment in synthetic air flow (40mL/min, 3h) at 623K or 773K. The metal complex $[RhNH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3(COD)]^+BF_4^-$, (abbreviated as Rh(NN)Si) was synthesized from complex $[RhCl(COD)]_2$ by treatment with $AgBF_4$ to form the $[Rh(COD)^+BF_4^-]$ species, followed by reaction with a solution of the ligand $NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$ in CH_2Cl_2. The anchorage of this complex was achieved via creation of a siloxane bond between the –$Si(OCH_3)_3$ groups and –OH functionalities on the carbon surface.

Characterization of the original and oxidized carbon materials was carried out by temperature programmed desorption (TPD), physical gas adsorption (N_2 (77K) and CO_2 (273K)), and X-ray photoelectronic spectroscopy (XPS). The hybrid catalysts were also characterized by XPS and inductive coupled plasma spectroscopy (ICP). The catalytic activity of the hybrid catalysts was tested in the hydrogenation of cyclohexene (5%v/v in toluene or methanol, 60-80ºC, 10bar H_2).

Results

The hybrid catalysts characterization shows that in both preparation methods the desired anchorage was achieved. The hybrid catalysts type A were active in the hydrogenation of cyclohexene, but less than the homogeneous Wilkinson complex. The catalytic activity decreases in consecutive runs. However, leaching of the complex was not detected by the analytical methods. XPS results show that the electronic environment of the Rh complex has not change after the reaction. This behaviour was observed for all the carbon materials used as support, however, differences in activity were observed, the highest activity was obtained with the catalysts prepared with support ROX-0.8.

The hybrid catalysts type B showed a high activity in the hydrogenation reaction, in all cases higher than that of the homogeneous [Rh(NN)Si] and Wilkinson complexes. These catalysts were tested in 5 consecutive runs, being the catalytic activity higher in the second and following runs. XPS results also show that the electronic environment of the Rh catalysts has not change during the reaction. It is noticeably high the catalytic activity observed for the catalyst prepared with the carbon nanotubes, which can be related to the particular structure of this type of support.

OP-I-15

PREPARATION OF CATALYSTS BY ANCHORING METAL COMPLEXES ONTO MESOPOROUS CARBONS

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Carbon materials are good catalyst supports especially for liquid phase reactions, since they present some advantages over conventional supports, such as higher stability in acid and basic media. In addition, both their porous texture and surface chemistry can be modified by appropriate methodologies. We have been using different strategies for the immobilization of metal complexes with *salen* ligands onto activated carbons, and the resulting catalysts proved to be efficient and reusable in various reactions [1-8]. However, they were found to be, in general, less active than the corresponding homogeneous catalysts, as a result of the slow diffusion of reactants in the micropores of activated carbon supports. This limitation can be overcome by using mesoporous materials instead, such as carbon xerogels.

Carbon xerogels (CX) were synthesized by the conventional sol-gel approach using formaldehyde and resorcinol [9]. The wet gel was dried by two different procedures followed by carbonization, leading to carbon xerogels with different textural properties: Direct drying (sample 01CX-UA with pores in the range 30-100 nm) and drying after solvent exchange (sample 02CX-UA with pores in the range 15-30 nm). A subsequent oxidation treatment introduces functional groups on the surface [10,11], which can be used as sites to anchor the metal complexes. These samples are designated as 01CX-y and 02CX-y, where y indicates the degree of burn-off (%). Textural characterization of these supports was based on the analysis of nitrogen adsorption isotherms by the t-plot, while the surface groups were determined by TPD-MS [11].

The *salen* ligands and their manganese (III) complexes were synthesized according to the procedures already described [4,5,8]. Mn (III) complexes were directly immobilized onto the supports by refluxing with *N*,*N*'-dimetilformamide solutions of the complexes [4,5,8]. After removing the physically adsorbed complex, the materials were dried at 120°C. Similar procedures were used to anchor a chiral Mn (III) complex.

These catalysts were tested in the epoxidation of alkenes at room temperature.

Table 1 summarizes the properties of the materials prepared. The results suggest that Mn(III) salen complexes with hydroxyl functionalised ligands are immobilised onto the oxidised carbon xerogels through reaction of the hydroxyl group with some of the oxygen functional groups on the surface, such as phenols, anhydrides and carbonyls.

Table 1 – Catalyst and Support Characterization

SAMPLES	**S_{BET} (m2/g)**	**S_{meso} (m2/g)**	**V_{micro} (cm3/g)**	**CO (μmol/g)**	**CO_2 (μmol/g)**	**Mn (μmol/g)**	**η%**
01CX-UA	645	216	0.094	234	98	-	-
Mn@01CX-UA	-	-	-	-	-	21.8	11.8
01CX-03	736	215	0.140	4714	478	-	-
Mn@01CX-03	603	218	0.080	-	-	98.3	53.1
02CX-UA	598	406	0.076	282	65	-	-
Mn@02CX-UA	-	-	-	-	-	12.0	6.5
02CX-10	786	425	0.151	2556	180	-	-
Mn@02CX-10	598	382	0.075	-	-	80.1	43.3

η%= quantity of Mn immobilised x 100 / initial quantity of Mn in solution

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OP-I-16

CATALYSIS OF METHANE DISSOCIATION BY CARBON MATERIALS

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Catalytic dissociation (or decomposition, pyrolysis) of methane has been researched as an environmentally attractive approach to production of hydrogen from natural gas [1,2]. The process produces hydrogen without CO/CO_2 byproducts, which eliminates the need for water gas shift and CO_2 removal stages required by conventional hydrogen production processes (e.g. steam methane reforming, SMR). Much research on methane decomposition over transition metal catalysts (e.g. Ni, Fe, Co, etc.) has been reported in the literature (e.g. [3]). These studies point to a catalyst deactivation problem associated with the carbon lay down on the catalyst surface.

The use of carbon-based catalysts offers certain advantages over metal catalysts: (i) high temperature resistance, (ii) tolerance to sulfur and other potentially harmful impurities in the feedstock, (iii) production of a marketable byproduct carbon (that could substantially reduce the net cost of hydrogen production), and (iv) effect to mitigate overall CO_2 emissions from the process. Earlier, we reported on the catalytic activity of a number of carbon materials of different origin and structure for methane decomposition reaction [4]. Disordered (amorphous) forms of carbon (e.g., carbon black, activated carbon) were found to be more catalytically active in methane dissociation than ordered (e.g., graphite) and turbostratic carbons. The objective of this work is to gain further understanding of the nature of the catalytic action of carbons during methane decomposition reaction and the correlation between the structural and surface properties of carbon materials and their catalytic activity.

The role of metal (Fe, Ni) impurities and oxygenated surface groups in carbon-catalyzed methane dissociation was discussed in [5]. It was demonstrated that although metals and surface groups somewhat affect the activity of carbons (particularly, at the early stage), there may be other major factors contributing to the catalytic activity of carbon materials.

On the surface of amorphous carbons, the regular array of carbon bonds is disrupted, forming “free” valences, discontinuities (i.e., the edges and corners of crystallites) and other energetic abnormalities that could be generalized as high-energy sites (HES). Evidently, the surface concentration of HES increases with the decrease in carbon crystallite size, and, vice versa, decreases as carbon becomes more ordered (e.g., during graphitization). This may point to the direct correlation between the surface concentration of HES and catalytic activity in methane decomposition reaction. The driving force for the catalytic action of carbon is that carbon atoms in HES tend to react with approaching methane molecules in order to satisfy their valency requirements and energetically stabilize.

It would be worthwhile to give some more consideration to how carbon structure affects its catalytic activity. The interlayer spacing in amorphous carbons (about 3.6 Å) is considerably larger than that in graphite (3.354 Å) [5]. XRD studies demonstrated that in the original carbon black sample (BP2000) the plates are not stacked in a columnar arrangement, but, instead, are randomly oriented with respect to each other. However, after exposure to hydrocarbons the ordering in the "columnar" or stacking direction has evolved. The distance between layers (d-spacing) was found to be d =3.4948 Å, which lies between the d-spacing for amorphous carbon and pure graphite. Thus, carbons produced by decomposition of methane and propane feature more ordered structure compared to amorphous carbons, but they are less structurally ordered than graphite (which is characteristic of turbostratic carbon). This clearly correlates with the order of catalytic activity of carbons toward methane decomposition (amorphous>turbostratic> graphite).

Based on the above considerations, it can be said that HES constitute the predominant fraction of active sites on the surface of carbons. Methane molecules dissociate via interaction with the chemically reactive edges of carbon crystallites (or other energetic abnormalities and/or active surface radicals). During this process, C - H bonds in methane molecule break and new C - C bonds in a hexagon layer of carbon form. The mechanism of the overall process at the molecular level is very complex and yet to be fully understood.

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OP-I-17

NOVEL NANOPOROUS CARBON MATERIALS FOR STYRENE CATALYSIS

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Production of styrene by dehydrogenation of ethylbenzene (EB) is an important process in chemical industry [1]. The technical catalyst for this process is iron oxide, but experiments indicate that the surface gets covered by a layer of carbon materials under reaction conditions [2]. This has led to the suggestion that carbon materials could be used as catalysts' for this reaction [3-7]. Subsequent experiments have also shown that different carbon materials such as carbon nanofilaments [4], onion-like carbon [5], carbon nanotubes [6] or nanoporous carbon molecular sieves [7] are indeed efficient catalysts for oxidative dehydrogenation (ODH) of ethylbenzene, but the origin of the catalytic activity remains unclear. This is in particular the case for the nanoporous carbon materials (NPC) since their structure is not well characterized. Such nanoporous carbon (NPC) constitutes an intermediate class of materials which are less ordered than graphite due to defects and voids, but still not completely amorphous. However, the defect concentration appears to be crucial, since Raman measurements of active carbon materials show that these materials contain a significant amount of defects [5]. In addition, XPS-experiments indicate that the presence of functional oxygen groups is vital to obtain a chemically active material [4,5].

We have therefore carried out an extensive study of NPC and how oxygen can assist ODH of ethylbenzene by density-functional calculations (DFT). The building blocks of NPC were first identified by a systematic study of defects in graphene and nanotubes: the ``motifs" [8]. These motifs were embedded in a graphene sheet in a supercell containing up to 112 atoms. Our DFT calculations revealed that the atomic relaxation transforms defects into combinations of non-hexagonal rings. These motifs lead to strain and local buckling of the structure. They also induce defect states close to the Fermi level, leading to that some of them being charged, which may facilitate molecule dissociation. Curvature modifies the properties of the motifs by lowering their formation energy in nanotubes and mixing the defect states with the π-band, such that the defect states lose their localized character. These motifs can then be combined to build a model of a NPC material with a certain concentration of non-hexagonal rings in the structure. This model indicates that NPC materials with up to 1 % motifs appear to have a comparable heat of formation to single wall nanotubes.

Our analysis of the chemical activity of the structural building blocks is supported by subsequent calculations, which show that the motifs are able to dissociate oxygen. This leads to the formation of functional C-O groups in agreement with the XPS-measurements of active OLC-materials [5]. The carbonyl group (indicated by C=O in Fig. 1) appears among these C-O groups to be the most promising candidate as an active site for ODH of ethylbenzene.

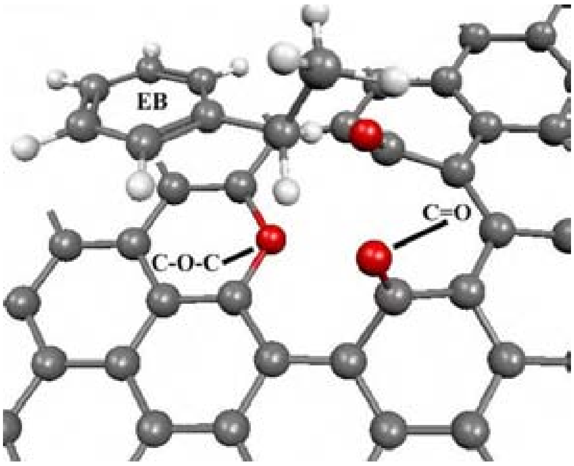

FIG. 1. The approach of an ethylbenzene molecule (EB) towards functional groups at an oxidized motif. The ether group is indicated by C-O-C and the carbonyl group by C=O.

We finally propose a reaction mechanism, where the dehydrogenation proceeds by transferring the hydrogen atoms from the ethylbenzene to the carbonyl groups at oxidized motifs as indicated in Fig. 1. The heat of reaction for the dehydrogenation step at the carbonyl groups is found to be slightly endothermic in agreement with the elevated temperatures needed to run the reaction [1].

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OP-I-18

HIGHLY ORDERED MESOPOROUS CARBON MATERIALS FOR OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE

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Synthesis of ordered mesoporous carbon materials with various structures (for instance CMK-1-5) has achievd great progress. Such carbon materials are usually synthesized by carbonization of sucrose, furfuryl alcohol or other suitable carbon sources inside silica or aluminosilicate mesopores that are interconnected into three-dimensional networks. The extremely high surface areas and controllable pore sizes of the ordered mesoporous carbons with large pore volumes make it to a promising candidate for applications in many fields of science and technology, such as storage of hydrogen and methane, super capacitor. The ordered carbon meosmaterials with three-dimensionaly (3-D) pore arrangements, or preferably, with 3-D interconnected pores and atomic orders similar to those in zeolites can be candidate as high performance catalyst for gas phase reaction. Here we report on the catalytic performance of highly ordered carbon materials in oxidative dehydrogenation (ODH) of ethy benzene to styrene with very promising results.

Sucrose was used as carbon source and SBA-15 as template for the synthesis. Figure 1A shows X-ray diffraction (XRD) patterns of mesoporous carbon. The well-resolved peaks at 1.01° and two week peaks at 1.75° and 2.0° indicte the highly ordered hexagonal mesoporous symmetry of the sample replicated from SBA 15 template. The nitrogen adsorption-desorption isotherm in figure 1B reveals that the sample exhibits typical IV isotherms with hysteresis loops, and the isotherm shows capillary condensation at medium relative pressures, indicating the existence of mesopores. Figure 2 displays the catalytic propertied of the investigated carbon materials with time on steam *t*. The ordered mesoporous carbon is highly active as catalyst in this reaction. After a short induction time a selectivity of EB to SB of 70 % is achieved at a convention rate of 68%. The high activity at the beginning of the reaction is accompanied by slight lower slectivity, but both tend to stable after 5 hours running. The TEM reveals that the ordered mesoporous structure remains unchanged during the catalytic reaction.

Acknowledgments:

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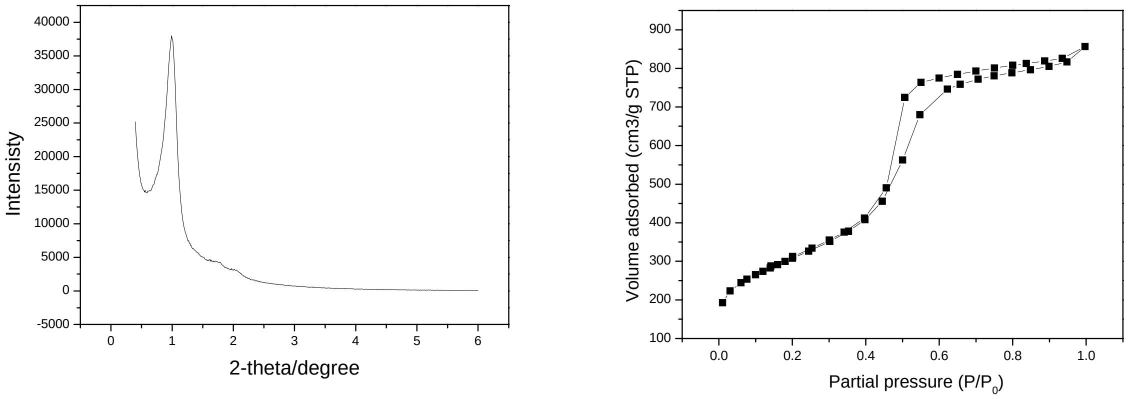

A

B

Fig.1 A) Small-angle XRD pattern of highly ordered carbon; B) N_2 Adsorption-desorption isotherms of highly ordered carbons.

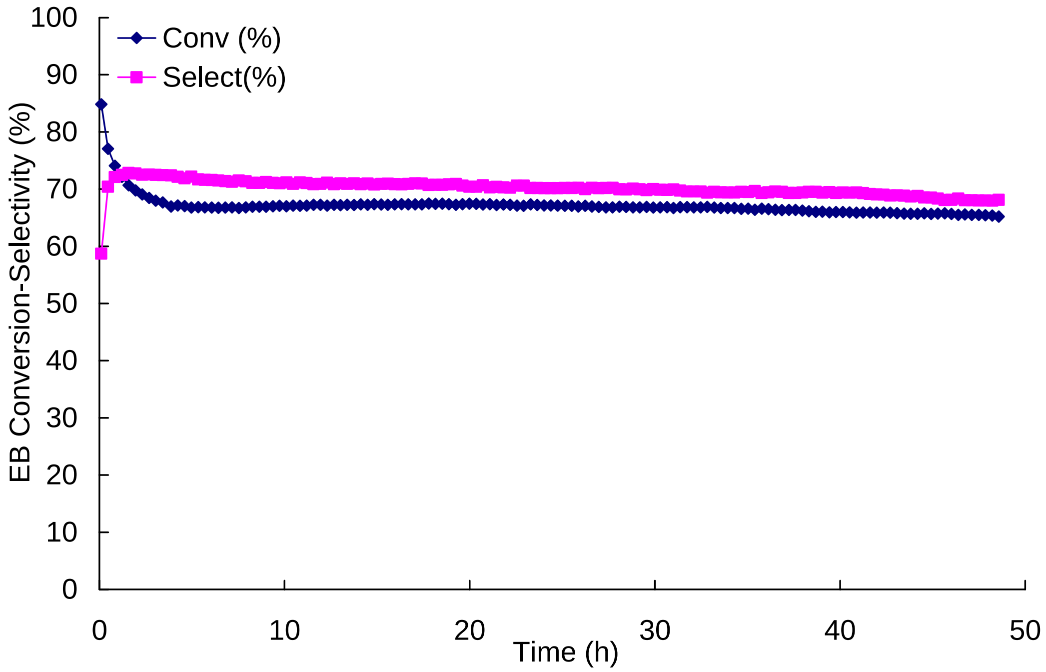

Figure 2. Conversion and selectivity of ethyl benzene to styrene over highly ordered carbons.

OP-I-19

TEMPERATURE-PROGRAMMED ANALYSIS OF CATALYTIC OXIDATIVE DEHYDROGENATION OF PROPANE OVER CARBON NANOFIBERS

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Introduction

Investigations on the catalytic oxidative dehydrogenation of propane (ODP) have been undertaken since this route is expected to lead lower costs of propylene production and has some virtues compared with direct dehydrogenation process. Vanadium and molybdenum oxides usually are the main elements present in catalysts used for ODP.

As a new kind of carbon materials, carbon nanofilament (tubes and fibers) has been testified to be a new catalysis material with unique characteristics. Previous, we reported that carbon nanofibers (CNF) after purification and surface modification could be the effective catalyst for ODP, whose catalytic performance is close to that of V-Mg-O catalyst. In this paper, mainly using temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR), the role of CNF surface oxygen complexes on catalytic performances, i.e. activity, selectivity and stability, is explored.

Experimental

Catalysts Preparation The CNF sample was produced by decomposition of CO over a γ-Al_2O_3 supported 20 wt% Ni-Fe alloy catalyst. To remove the metal inclusions, the sample was repeated washed in 4 M NaOH and 4 M HCl or was treated at 1700 °C for 3 or12 h under protection of argon to reduce the ash content to less than 0.1wt%. Then the samples were surface modified by different oxidation methods.

Catalysts Characterization Structures of the CNFs were characterized by SEM, TEM, N_2 adsorption-desorption isotherms, Raman, and XRD.

TPD was used to determine categories and amounts of surface oxygen complexes on CNF and Multi-Gaussian function was used to fit for the results. The TPD results were also testified by FT-IR and XPS characterization. TPSR of propane/propene was performed to explore the role of CNF surface oxygen complexes in catalyzing ODP. TPD and TPSR runs were carried out on Autochem II 2920 (Micromeritics, USA) and the outgoing gas was diverted to a quadrupole mass spectrometer (Questor, ABB Extrel, USA) to be analyzed.

Results and discussion

HRTEM images show that CNF used in this work is a fish-bone CNF. Except for the samples being severely oxidized in air, the physical properties of all the samples are close.

Only CO, CO_2 and C_3H_6 are detected as TPSR products. It's found that the amount of TPSR products increases along with the amount of carbonyl-like groups. Especially, when the surface oxygen complexes are totally removed by H_2 treatment at 900 ^{o}C or TPD up to 1000 ^{o}C, no product was detected, which implies that carbonyl-like groups could be the active sites for catalyzing ODP. Desorption of some surface oxygen complexes from samples without heat treatment at 1700 ^{o}C could be ascertained by material balance, which indicates that optimizing the surface oxygen complexes by heat treatment is necessary from the point of view of structure stability. The propene selectivity in TPSR runs decreases when increasing of the surface oxygen complexes. So, optimizing the surface oxygen complexes could restrain the direct over-oxidation of propane, which is testified by the fact that the initial propene selectivity in catalytic test decreases along with increase of the surface oxygen complexes.

The propene TPSR results show that carbonyl-like groups could also be active sites for propene combustion. The propene turnover frequency is lower over the sample experienced liquid phase oxidation than that of air oxidation sample. The possible reasons are that trace amount of Ni or Fe ion are removed or other heteroatom groups are introduced. The results of a propene TPSR run successively after TPD run show that free active sites on CNF produced by surface oxygen complexes desorption could lead propene cracking. But these sites are not responsible for propane conversion.

The sample without heat treatment has lower structure stability when tested as catalyst for ODP. One reason is that surface oxygen groups are facile to desorb, which has been mentioned above. The other one could be that CNF gasification is initialized by coking produced through CO disproportionation catalyzed by CNF itself. CO disproportation is suppressed after CNF being heat treated at 1700 ^{o}C.

OP-I-20

STRUCTURE ACTIVITY RELATION IN NITROGEN CONTAINING CARBON NANOTUBES FOR BASE CATALYSIS

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Introduction

Catalytic processes based on solid acids outnumber those based on solid bases[1]. New solid base materials are desired for the development of efficient and environmentally benign processes. A number of prerequisites have to be fulfilled for a material to be a suitable solid base catalyst, a.o., the catalyst must have the potential to be prepared in large quantities in a reproducible manner; the materials have to be chemically stable and mechanically strong. Modified carbon nanofibers/tubes (CNF/CNT) potentially possess these properties. When N atoms are incorporated in the graphene layers of CNT [2, 3], basic sites might be formed. The aim of the research is to investigate whether N incorporation in the CNT structure indeed introduces basic sites. As a point in case we used a Knoevenagel condensation as a test reaction. In addition the nature of the catalytically active sites in NCNT will be investigated.

Results and Discussion

NCNT were grown at temperatures between 773 and 1123K over Ni/SiO_2 or Co/SiO_2 catalysts using pyridine or acetonitrile as precursors. The type of nitrogen-carbon bonds in the graphitic framework of the N-CNT as well as the N-to-C ratio was determined with XPS. Results show that there are mainly two types of nitrogen-carbon bonds. One is of the pyridinic type (binding energy: 398.6 eV) located at the tube’s edges or at defects in the graphene layer. The other is of the quatenary type (binding energy: 401.4 eV) located in the graphene layers. The N-to-C ratio is dependent of the growth temperature and varies between 0.03 and 0.10. The number of active nitrogen sites at the surface was determined with acid-base titration (Fig. 1). Since all titration curves start at a pH around 9 it is clear that the NCNT are basic. From the evolution of the titration curves information can be obtained about the strength and number of basic sites. Clearly the materials displayed in Figure 1 show different responses to

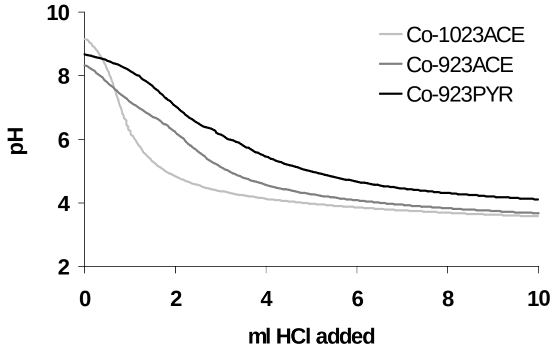

Figure 1: Titration curves of NCNT synthesized over Co/SiO_2 at different temperatures from acetonitrile (ACE) or pyridine (PYR)

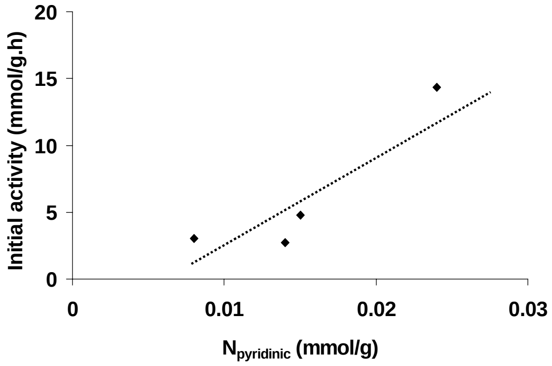

Figure 2: activity of NCNT as function of amount of pyridinic nitrogen.

addition of the titrant (HCl) thus indicating different basicities for the materials. Curve fitting and comparison with titrations of reference compounds, a study which is currently carried out, are expected to give insight in the nature of the different basic sites.

The activity of the NCNT was tested in a Knoevenagel condensation of benzaldehyde and ethylcyanoacetate. The formation of the product, ethyl-alfa-cyanocinnamate was monitored over time. The initial activity of different NCNT materials relates to the amount of pyridinic nitrogen incoporated in the NCNT structure (Figure 2).

Concluding remarks

The work is a significant step forward in broadening the scope of solid base catalysts. Pyridinic nitrogen incorporated whithin the graphene sheets of CNT showed base properties. A more detailed study on further tuning of the base properties of NCNT and their characterization is currently carried out.

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OP-I-21

CARBON AEROGELS AS CATALYST SUPPORTS

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Aerogels are highly porous materials, made using sol-gel process to form solvent-containing gels which are supercritical dried for purpose to prevent shrink or collapse the weak structure of the solid matrix. Organic and carbon aerogels were prepared for the first time by Penkala et al at, 1987. These aerogels consist of cross-linked organic polymer and they must be carbonized in an inert atmosphere to form carbon aerogels. The carbon aerogels prepared in the form of monoliths, powders or microspheres are characterized by high specific surface area and porosity, low thermal conductivity and electrical resistance and high capacitance. Taking into account their unique properties carbon aerogels are promising materials for numerous practical applications such as isolation materials, electrodes and specially as adsorbents and catalyst supports.

Organic RF aerogels are the most frequently prepared in multistage process which include aqueous polycondensation of resorcinol with formaldehyde at temperature 70-95 ^{o}C in the presence of Na_2CO_3 as a catalyst, exchanging of water from gel structure to acetone, exchanging of acetone to CO_2 before drying of the obtained gel and carbon dioxide supercritical drying of gels. The classic method of organic aerogel synthesis is time-consuming and including gel drying lasts about two weeks while two last steps take four days.

RF aerogels are the precursors of carbon aerogels and the porous structure of carbon aerogels depends on the porous properties of RF aerogels. Therefore, it is interesting to exploit a low-cost and time-saving preparation method of RF organic aerogels.

In this paper the results of studies on the influence of the catalyst type and molar ratio resorcinol to catalyst (R/C), concentration of resorcinol in water and curing time on porous structure of monolith and spherical RF aerogels type prepared by supercritical acetone and carbon dioxide drying and carbon aerogels derived from RF aerogels are presented.

RF hydrogels were synthesized by aqueous polycondensation of resorcinol (R) with formaldehyde (F) in a molar ratio of 1:2. Sodium hydroxide, potassium hydroxide and sodium carbonate were used as catalysts (C). The followed process parameters were studied:

resorcinol to catalyst molar ratio (R/C) from 100 to 200, and resorcinol concentration in water from 10 30 wt %, and curing time from 18 to 120 hours. Spherical aerogels were synthesized using emulsion polymerization processing of resorcinol and formaldehyde in surface active agent containing organic solutions.

The gels were dried at supercritical conditions (temperature 60 and 250 ^{o}C, pressure 12 MPa). The dried RF aerogels were carbonized in gravimetric apparatus at 400, 600 and 800 ^{o}C in argon atmosphere with heating rate 5 ^{o}C/min.

The porous structure of RF organic and carbon aerogels were determined by N_2 adsorption method at 77 K using an adsorption apparatus Quantachrome Autosorb 1-C. Samples were evacuated at 50 ^{o}C in case of the RF organic aerogels or at 150 ^{o}C in case of the carbon aerogels before the adsorption measurements. The Brunauer-Emmett-Teller surface area (S_{BET}), micropore volume (V_{mic}) and mesopore volume (V_{mes}) of the samples were analyzed by Brunauer-Emmett-Teller theory, t-plot theory and BJH theory, respectively.

It was stated on the base of the obtained results that potassium hydroxide can be effective catalyst of resorcinol-formaldehyde polycondensation in water medium. The obtained RF and their carbonization products at 600 ^{o}C are characterized by large specific surface area (400 – 800 m^2/g), mesopores volume (0.2 – 1.4 cm^3/g) pore diameter in the range 2-20 nm. Physicochemical properties of the final products depend on resorcinol concentration in water, resorcinol to catalyst (R/C) molar ratio and method of alcogels drying. In case of spherical carbon aerogels their porous structure and spheres diameter additionally depends on sol viscosity, stirring speed during the emulsion polymerization processing.

OP-I-22

RADIOISOTOPIC INVESTIGATION INTO THE ACTIVE SITE DYNAMICS OF Co(Ni)Mo SULPHIDE CATALYSTS SUPPORTED ON Al_2O_3 AND ACTIVATED CARBON AND MODIFIED BY P AND F ADDITIVES

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The nature of the support has big effect on the formation and acting of sulphide catalyst active sites (AS). Twoquestions are under consideration in the study:

1. The difference between support effects of Al_2O_3 and activated carbon on the formation and acting of the active phase of sulphide Co(Ni)Mo catalysts;
2. How support modification by P- and F-additives affects the AS acting.

Comparing Al_2O_3 and activated carbon support effects

Hydrotreating catalysts prepared by loading of activated carbon with an active phase (C-supported catalysts) are more active than conventional systems based on Al_2O_3. However, there are some reasons that limited C-supported catalysts industrial application. In order to understand the principles of functioning of the active phase on different supports, it is necessary to study the transformations of organosulphur compounds on the surface of this phase and to evaluate dynamic properties of the catalyst AS.

A tracer method enabled us to determine the number of surface SH groups, the number and reactivity of AS, and correlate these data with the composition of the active phase of the sulphide catalyst. The influence of the support (Al_2O_3 and activated carbon) on the activity of Mo, NiMo, and CoMo catalysts in thiophene hydrogenolysis is studied using ^{35}S as a tracer. The carbon-supported catalysts have more AS than their Al_2O_3-supported counterparts, while the turnover frequencies of these sites are similar. The turnover frequency of the AS depends on the promoter content of the active phase and is support-independent. The active phase in the C-supported catalysts is reduced to a greater extent than that in the Al_2O_3-supported catalysts. Raising the Mo content increases the reduction of the active phase in both the Al_2O_3- and C-supported catalysts. Thiophene desulphurization and hydrogenation of the resulting C_4 olefins take place at the same Mo sites. Tracer tests have demonstrated that the

AS in the catalysts examined are identical and that the support has an effect only on their concentration.

Comparing of Al_2O_3 modification by P- and F-addtives

The investigation of Al_2O_3 modification by P- and F-additives has shown that the introduction of the additives leads to the formation of new reduced sites (so-called “empty sites” - ES). The correlation between the growth of the support acidity and the number of the ES has been established. Modification effects by P and F are different: P-modification of Al_2O_3-support does not change the AS productivities of the AS related to Mo- and Co-sites but changes their ratio. F-modification leads to AS productivity decrease. F-adding results in decrease of both the number of the AS in CoMoS phase and their productivities. F affects the sites belonging to Co to a greater extent than the sites belonging to Mo.

Modifying of the Al_2O_3 by P or F results in changes of the nature of the active sites responsible for hydrodesulfurization and in the formation of new “empty sites” (ES) facilitating hydrogenation of aromatics.

Conclusions

1. The C-supported catalysts contain more mobile sulfur than the Al_2O_3-supported catalysts because of the smaller particle size of the active phase.
2. The nature of the support and the amount of active phase do not affect the reactivity of the active sites but affect their number. The dynamic properties of the active sites in the NiMo and CoMo catalyst are similar.
4. The hydrogenation of butenes that have resulted from thiophene hydrogenolysis takes place on sites that are associated with Mo and responsible for desulfurization.
5. Replacement of Al_2O_3 by activated carbon in supported catalysts leads to enlarging of the number of the active sites without any changes in their nature whereas modifying of Al_2O_3 by P- or F-additives may result in changes of the nature of the active sites and in formation of new sites.

OP-I-23

CHEMICAL MODIFICATION OF DIAMOND SURFACE

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Chemical modification of solids surfaces permits us to controllably vary their physicochemical properties. So, grafting of various functional groups to the surface of carbon materials gives a chance to regulate adsorptive and adhesive features of such materials, change their dispersity, and thus expanding the field of their application.

Diamond is the most suitable material for modification among carbon allotropes because all it's surface atoms (18 nm^{-2}) can be linked with functional groups, and in case of graphite functional groups can be only on the surface of prismatic faces.

Nanodiamond (ND) is generated at detonation of explosives with the negative oxygen balance in nonoxidizing ambient. ND manufacturing represents a science intensive technology of ammunition utilization and enable to recover money spent on their creation. Judging from the crystallite size (4-6 nm) and the fraction of surface carbon atoms C_{surf} in the total number of carbon atoms C_{total} in a particle ($15\cdot10^{-2} \div 1\cdot10^{-3}$), nanodiamonds are between organic molecules and diamond's crystals, i.e. they are colloidal diamonds. Each nanodiamond particle is a submolecule. It consists of nucleus of diamond lattice origin, which is formed by sp^3- hybridized carbon atoms and are surrounded by strained carbon shell and surface linked different atoms, groups of atoms and molecules. ND posses highly developed specific surface (200-300 m^2/g) that's why they represent a particular sort of diamond material with properties mainly depended upon its surface chemical state. Combination of mechanical, thermal, radiation and chemical stability of diamond with lability of surface functional cover is the main peculiarity of this material.

Various oxygen- and hydrogen-containing groups are often found after different treatment conditions: $\mathbf{\equiv C{-}OH}$, $\mathbf{-CHO}$, $\mathbf{>CO}$, $\mathbf{-COOH}$, $\mathbf{-C(O)O(O)C-}$, $\mathbf{\equiv C{-}O{-}C\equiv}$ et al. Providing treatment is carried out with the assistance of hydrogen, halogens, methane, ammonia and other reagents such groups as: $\mathbf{\equiv CH}$, $\mathbf{=CH_2}$, $\mathbf{-CH_3}$, : $\mathbf{\equiv CHal}$, $\mathbf{=CHal_2}$, $\mathbf{-CHal_3}$, $\mathbf{\equiv C{-}CH_3}$, $\mathbf{-CHHal_2}$, $\mathbf{\equiv C{-}NH_2}$ can be obtained.

Wide cycle of works on modification of diamond surface, investigation of functional groups formation and destruction conditions was performed by V.B.Aleskovskii's school. Conditions of chemical modification of diamond by various reagents to obtain mono- and polyfunctional surface cover were found. It was established, that carrying out chemical reactions on the diamond surface permit us to grow carbon atoms monolayers, for instance via reactions: **$\equiv C{-}H + CCl_4 \rightarrow \equiv C{-}CH_2Cl + HCl$, $\equiv C{-}CH_2Cl + CH_4 \rightarrow \equiv C{-}CH_2CH_3 + HCl$**

By treatment of diamond powders with volatile halogenides (**$TiCl_4$, VCl_5, $CrCl_3$**) surface metal-containing groups are formed that give us opportunities to perform surface synthesis for further chemical modification.

Covalent grafting, i.e. surface interaction with various substances-modificators, is of main interest in diamond surface chemical modification. This modification provides a basis for fundamentally new spatial structures creation on its base. Native cover polyfunctionality of ND prohibit from selective surface modification. As a result preliminary surface monofunctionalization is needed. One of the most effective procedures of ND functional cover unification consists in hydrogen stream treatment at 800 ^{o}C 5 hours. As a result of this hydride group's layer is formed on the diamond powder surface. This layer formation causes the reduction of diamond surface reaction capacity. For its activation and electrophile center creation it is subjected to halogenation. Photo- and thermochemical halogenation is inconvenient because of free halogens and high temperatures utilization. Liquid phase chlorination with SO_2Cl_2 in benzene and chlorine in carbon tetrachloride in argon ambient is more attractive. In the first case azobisisobutironitrile was used for initialization and in the second – light irradiation. Both variants of chlorination yielded in completely full surface hydrogen atoms substitution. However, hydrolytic instability of chlorinated diamond surface should be considered. Interaction of chlorinated ND powder with butyllithium, octadecyllithium and others resulted in alkyl groups grafting onto the diamond surface. Phenyl groups were grafted to the surface via reaction with phenyllithium. Reaction of chlorinated ND with sodium cyanide yielded in surface cyanide groups grafting.

Various physicochemical methods were used to characterize modified ND: IR- and Auger-spectroscopy, XPS, EELS, NMR-H1, ESR, electron microscopy etc.

Method development and conditions discovering for monofunctional cover creation on ND surface, on the one hand, can result in their more efficiently utilization, because ND application is restrained by nonreproductivity and instability of their physicochemical characteristics. On the other hand this may lead to creation of fundamentally new materials for biomedical application (nanoparticles for directional drug carry in vivo, chromatographic sorbents for HPLC etc.). In latter case sorbents based on modified porous ND cakes with highly developed specific surface together with thin size distributed nanoporoues are promising.

OP-I-24

SORPTION AND CATALYTICAL PROPERTIES OF THE NANOGRAPHITE MATERIAL

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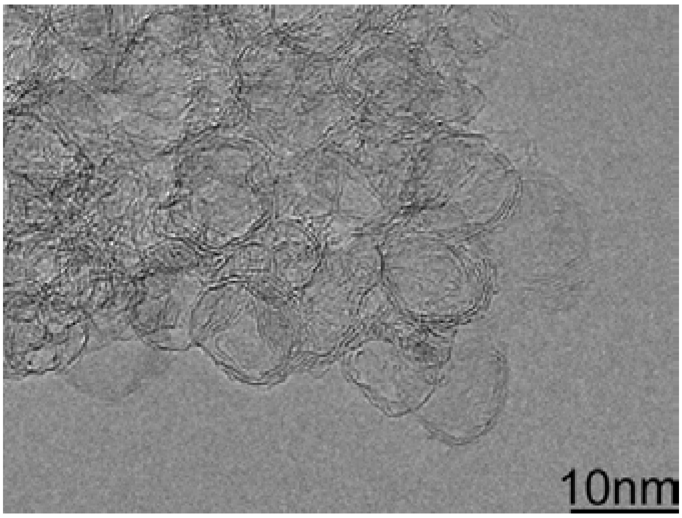
In the last some years a lot of researches of so-called carbon xerogels which are formed at carbonization of xerogels of phenol-, resorcinol-, cresol-formaldehyde and some other resins are carried out. Carbon xerogels possess a high specific surface 600-700 m^2/g [1, 2]. Activation by oxygen, water steam or carbon dioxide allows to increase a surface up to 1000-1500 m^2/g [1].

In Federal Nuclear Centre (Sarov) the technology of production of carbon nanosize and nanoporous materials (CNNM) by carbonization of porous phenol-formaldehyde resin (but not xerogel) is developed. The studying of these materials by a method of high-resolution electronic microscopy allows to attribute them to a class of nanographite. Materials are presented by globules with the size 5-10 microns and the last consist of chaotically located microblocks with the thickness in 3-4 graphene layers. The materials possess the advanced system of micropores with the size 1,5-2 nanometers. The specific surface of samples is 550-700 m^2/g. Varying conditions of preparation of resins and the subsequent carbonization it is possible to change over a wide range a ratio macro-, meso- and micropores. The materials possess the high mechanical strength. On the data of XRD the materials represents strongly disordered graphite with unique big interlayer distances - 0,375-0,39 nanometers.

The properties of CNNM in the relation to chemical adsorption gases, to absorption of hydrogen and catalytical properties of the metals supported on the these materials were investigated. In relation to chemical adsorption of light hydrocarbons CNNM shows properties more similar to the properties of silica and alumina, than carbon materials. Comparison of absorption of hydrogen with other carbon materials shows, that CNNM absorbs a little bit more hydrogen, than materials with comparable or even the greater specific surface.

The nickel supported on CNNM shows unique low catalytical activity in reactions of hydrogenation and decomposition of methane in comparison with other carbon supports such as sibunite and nanofibrous carbon. Deposition of palladium on the CNNM allows to prepare the catalyst with the low contents of palladium, which show high selectivity in hydrogenation of acethylenes and dienes hydrocarbons to alkenes. It shows high efficiency in clearing of ethylene from acetylene by hydrogenation.

The technology of production of CNNM allows to introduce various metals at a stage of preparation of porous phenoplasts. Studying of the sample containing nickel allowed to find out the new morphological form of carbon. It represents hollow spherical particles about 10 nanometers in size with thickness of walls 3-4 carbon layers (fig. 1). We designate this form caviare-like carbon. Except for the described spheres at the sample there present carbon nanofibers and spherical particles of metal nickel.



Carbon xerogels with introduced at a stage of preparation metals possess catalytical properties [3]. We also shown that a sample CNNM containing nickel, shows high catalytical activity in reactions of full hydrogenation of unsaturated hydrocarbons. However it does not show catalytical activity in hydrogenation of benzene and decomposition of methane.

Work is executed at financial support of RFBR, grant Leader Scientific Scools-2120.2003.3.

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OP-I-25

ON THE PORE SIZE DISTRIBUTIONS OF CARBONACEOUS CATALYSTS AND ADSORBENTS

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The carbonaceous materials (CM) are of great common interest for clearing, storage and transportation of gases, separation of liquid and gas mixtures, and also for some catalytic processes. Their properties in such applications in many respects depend on the pore size distributions (PSD). At an estimation of PSD by adsorption methods porous space CM usually represent as ensemble of slit-like pores with parallel graphite-like walls, infinite in lateral directions. However, even the experimental researches of the structures of graphitized carbon blacks show that they appear to be made up of graphitic blocks, packed together in a chaotic manner [1]. This assumes, that the real CM contain "corners" where the carbon planes meet and, probably, the interpretation based on the ideal slit-shaped pores, can result in errors. In 1998 GCMC comparisons of an adsorption of Ar at 80K [2] and methane at 308K [3] for the first time were carried out in slit-like, square-shaped, and rectangular-shaped pores, and the essential distinction in their adsorption behaviour was established.

In this work the modeling of a low temperature nitrogen adsorption in graphite mesopores with rectangular sections having the aspect ratio of the side lengths more than 7:1 has been executed by using the grand canonical Monte Carlo (GCMC) method. The adsorption branches of GCMC isotherms received were processed by methods of the non-local density functional theory (NLDFT) and Derjaguin - Broekhoff - de Boer (D-BDB) with the purpose of calculation of the formal PSD.

It is shown (table and fig.1) that the NLDFT underestimates the sizes (as “true” and “effective”) of the studied rectangular mesopores, though gives good estimations of total volume and surface area of pores.

It is shown also (table and fig.1), that the D-BDB-method very strong underestimates a specific surface area and overestimates total volume of pores. Both specified D-BdB distributions have a very wide distributive interval of apparent size and brightly expressed bimodal form (fig.1). Such completely wrong information about the size of investigated pores is a consequence of the macroscopic assumption of the D-BdB theory about a constancy of density of a capillary condensate in pores at various pressures.

Table 1. Initial and calculated summary characteristics of two model porous solids.

	$10\sigma_{ff}$ isotherm				$12\sigma_{ff}$ isotherm			
Method	S_Σ (m^2/g)	V_Σ (cc/g)	H_{tr} (nm)	H_{ef} (nm)	S_Σ (m^2/g)	V_Σ (cc/g)	H_{tr} (nm)	H_{ef} (nm)
GCMC (initial)	500.0	0.71	3.945	3.377	500.0	0.85	4.734	4.166
NLDFT	504.9	0.70	2.752	-	497.7	0.79	3.163	-
D-BdB	299.9	1.10	-	3.670	218.9	1.04	-	4.764

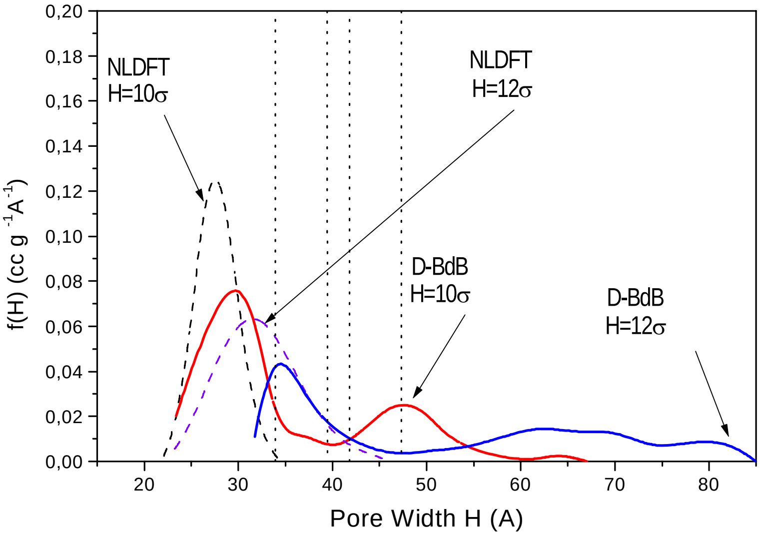

Fig. 1. The apparent volume PSDs calculated for the H_{tr}=10 and H_{tr}=12 adsorption branches by D-BDB and NLDFT techniques: dashed unimodal lines- NLDFT; solid bimodal lines- D-BdB.

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OP-I-26

FEATURES OF ELECTRON STRUCTURE AND CHARACTERISTICS OF LOW-DIMENSIONAL DEFECTS OF PYROLITIC GRAPHITE

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New regular method is developed for constructing exactly solvable models which describe the variations of electron spectra of low-dimensional 1D-, 2D- crystals and carbon tubulen type of one-dimensional structures at the formation of different structural defects (vacancies, substitutional impurities, interstitial atoms, and adsorbed particles) or the switching of various interactions (exchange interactions between isolated atoms involving in different system or the interparticle interactions linking electrons with quasi-particles (phonons and excitons)). These variations can not be reproduced by the perturbation theory.

The analytical expressions are obtained to determine the conditions in spectra of carbon nanotubes for formation of

- discrete levels of stationary and quasi- stationary states localized close to the monoatomic and polyatomic vacancies;
- discrete levels of stationary and quasi- stationary states localized close to the sites of dot exchange coupling;
- 1D zones of stationary and quasi-stationary states localized along the line of contacts of carbon nanotubes (CNT) with current-carrying substrates which are used in studies of CNT electron structure by the scanning tunneling spectroscopy (STS) methods;
- zones of forbidden states in spectra of CNT’s with superlattices of dot perturbations (defects and weak exchange coupling).

The obtained results determines the optimal conditions that the CNT phonon spectra can be studied by the scanning tunneling spectroscopy methods.

By the STM-STS methods, the atomic and electron structure of zero-dimensional defects of pyrolitic graphite (surface monoatomic and polyatomic carbon vacancies) are studied. It is observed the spectroscopic effects caused by the formation of near Fermi resonances (for monoatomic vacancies) and near Fermi energy zones without dispersion.

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THE CARBON FILMS ON Pt(111) SURFACE OBTAINED BY HYDROCARBON DECOMPOSITION AT HIGH TEMPERATURES. XPS, UPS, AND RAM STUDIES

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The formation of carbon deposits on the surface of active components of metallic supported catalysts plays an essential role in the catalytic processes resulting in the deactivation of catalysts. The investigation of carbon deposition on the surface of model surfaces, like planes of single crystals of metals, is one of successful ways to understand the mechanism of the catalysts deactivation. Earlier we revealed that carbon adsorbed on the Pt(111) surface have the structures that are quite different from the ones of planar graphite [1]. Their spectroscopic and subsequently electronic features are different also. It means that inert graphite planes can be modified to obtain ones the capability of chemical bond formation with various adsorbed atoms. Such adsorbed carbon layers, having good stability, can be used as a new model substrates with a possibility to study the dispersed metallic particle such as gold palladium etc.

In this work we discuss the application of structural and spectroscopic methods to study the chemical state and morphology of carbon films deposited by hydrocarbon cracking on the surface of Pt(111) plane. We report here about growth and electronic properties of the carbon films formed on the Pt(111) single crystal surface after their pretreatment in different hydrocarbons (methane, ethylene, propane) atmosphere at high temperature under the specific reaction conditions.

It occurred very striking and intriguing that depending on conditions and temperature the spectroscopic features of the films, obtained from ethylene, change essentially. For example, the XPS C1s spectra have the maximum position in the range 284.3-284.8 eV, characterizing different ratio of carbon atoms with sp^2 or sp^3 hybridization. UPS and AES spectra have new features and the binding (kinetic) energy shifts are clearly observed. As the spectroscopic characteristics of carbon films are quite different, so the structure of the carbon layers must be different too. The most significant spectroscopic features were observed using propane as the reagent gas. In this case the coverage achieves more than tenths of carbon layers. The special spectroscopic feature of C1s spectra -" shake-up satellite", which indicates sp^2-hybridization, is expressed with unusually high intensity.

When methane is used as the reagent under the same conditions such a behavior is not observed. We did not obtain any significant changes in C1s position of the spectra as well as changes in the shape of the Auger spectra in this case, although the experiments were carried out in the range of temperatures and pressure being even wider than those for ethylene.

The "high energetic films" (we refer it to the films where C1s have the position more than 284.6 eV) being different from planar graphite films are similar in the characteristics to nanotubes or fullerenes layers. Applying RAM we have found that these films consist of hills and pits with diameters about hundreds of nanometers.

The carbon films obtained by hydrocarbon interaction are stable enough, but less than planar graphite. We present systematic data concerning carbon burning by interaction with O_2. We have shown that the kinetic curves of the burning are very different and strongly depend on the structure of carbon adsorbed layers. The fullerite like adsorbed layers (E_b(C1s) > 284.7 eV) are characterized by constant reaction rate in the high coverage range, while the carbon adsorbed layers consisted of graphite islands layers (E_b(C1s) < 284.4 eV) are characterized by well known "S"-shape curve of carbon burning with high efficiency of this process. It is noteworthy that the graphite uniform layer was inert to the O_2 under the all studied conditions.

Under the high pressure action (> 10 Pa) of some hydrocarbons (ethylene and propane) at temperature above 850^0C the continuous growth of carbon films has been revealed. It was established that in the process of the thick carbon films formation their XPS futures are permanently altered. The obtained carbon films grown on the surface of Pt(111) can be used as different carbon substrates for investigation of the model supported catalysts.

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LASER RAMAN MICRO-SPECTROSCOPY AS AN EFFECTIVE NON-DESTRUCTIVE METHOD OF IDENTIFICATION AND INVESTIGATION OF VARIOUS sp^2-CARBON MODIFICATIONS

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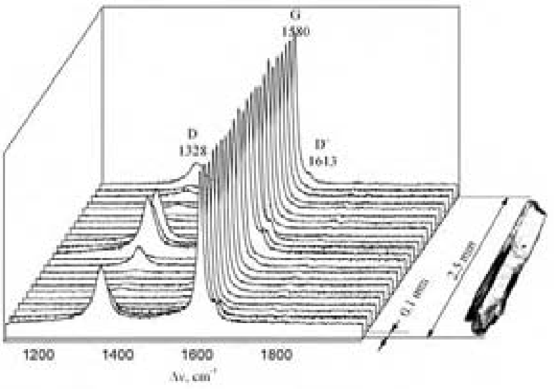
Graphite and various carbonaceous compounds are widely used in industry as modern high-technology constructural materials. These comprise graphene layers forming bundles and crystallites, whose size and packing are of great importance for macroscopic properties. That is why structural methods allowing determination of crystallite size and their ordering are of major interest.

Modern laser Raman spectrometers of the last generation (T64000, LabRAM Horiba-Jobin Yvon) equipped by high-sensitive CCD detectors and microscopes allow one to identify various carbon modifications, because each of the latter exhibits its own specific Raman spectrum, characterized by a given number of Raman lines with their particular parameters (frequency, intensity, half-width, contour). Besides, this non-destructive method gives a unique possibility of Raman micro-mapping of the samples, that is, obtaining information about sample heterogeneity. This method was applied in this study to many samples of sp^2-carbon including various graphites of natural and technical origin, as well as other carbonaceous materials, such as glassy carbon, diamond-like carbon, shungites etc. The results of Raman micro-mapping of a particle of Cylon graphite, demonstrating its heterogeneity, is given below as an example (fig. 1)

Fig. 1



OP-I-28

In 1970 Koenig *et al* have established a relationship between the ratio of intensities of G (1580 cm^{-1}) and D (1350 cm^{-1}) lines in the Raman spectra of various disordered sp^2 carbons and the size of micro-crystallites in the basal plane L_a [1]. The latter was measured by the WAXD method. Applicability of this relationship has been investigated by us, using the results of linear and planar Raman micro-mapping carried out for many samples of graphite of different origin and for other sp^2-carbon modifications. The typical spectra of less-ordered sp^2 carbon materials presented in Fig. 2 and 3 demonstrate their difference from the graphite spectrum.

Fig.2 Raman spectrum of glassy carbon

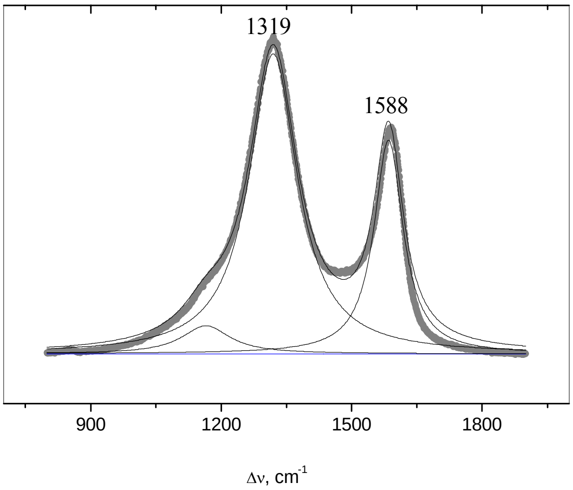
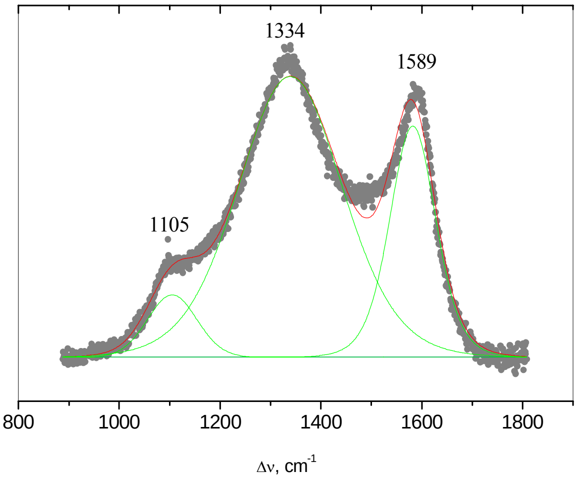


Fig.3 Raman spectra of smoke-black



The data obtained show that Koenig's correlation is not applicable to the crystallite size estimation. Spectral criteria have been elaborated for identification of various sp^2 carbon materials, based on the position, widths and contour of the D and G bands as well as I_D/I_G intensity ratio.

Acknowledgements

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OP-I-29

ELECTROCATALYTIC PROPERTIES OF PLATINUM DISPERSED IN PORES OF CARBON SKT-6A

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Development of electrochemical gas sensors and hydrogen-oxygen fuel cells requires producing electrode materials which has long been operated. Electrode material must possess good electronic and ionic electroconductivity, high catalytically active surface and porosity nesessary for reagents feed and reaction products removal. Finely dispersed platinum may be supported on the surface of electrolyte or carbon carrier with developed specific surface (activated carbon) with chemical, electrochemical or other methods. Nanocarbon materials or carbon materials with developed specific surface are usually used for the fixing of finely dispersed platinum on the carbon particle surface or inside of carbon particles. We chose carbon SKT-6A (specific surface $S \cong 1000\ m^2/g$) as a carbon carrier for finely dispersed platinum. Method of synthesis and fixing of finely dispersed platinum in carbon pores was developed. A procedure for the synthesis of a platinum catalyst using SKT-6A carbon as a support was developed, which involves the impregnation with polyacrylonitrile (PAN) and H_2PtCl_6 dissolved in dimethylformamide (DMFA) followed by the IR pyrolysis in a special IR-annealing chamber of a photonic pulse annealing set-up. The intensity of IR radiation was controlled by the temperature of the film sample, measured by a chromel-coppel thermocouple in quartz tube placed directly under the sample. Controlling unit provided the changes in intensity of IR radiation at a given computer program. Temperature of the sample was maintained within 0.25 ºC. IR annealing was performed in two stages: preliminary annealing (in air at 150 ºC for 15 minutes, then at 200 ºC also for 15 minutes) and main intensive annealing (in argon at 450^oC during 30 min). Efficient reduction of metal takes place in the course of IR pyrolysis of composite-precursor (DMFA solution of PAN and H_2PtCl_6) with participation of hydrogen, which is released in dehydrogenation of main polymeric chain of PAN.

Analysis of distribution of platinum nanoparticles on the SKT-6A carbon surface was done with X-ray microanalysis method. Specific surface of SKT-6A/Pt (10% mas) is equaled to 745 m^2/g.

Catalytic properties of platinum fixed in SKT-6A carbon pores were studied in the following reactions:

$$(A)\ H_2 - 2e = 2\ H^+ \quad \text{and} \quad (B)\ 1/2O_2 + 2\ H^+ + 2e = H_2O$$

The experimental data showed high activity of the Pt - SKT-6A - PAN electrode in reaction (A) and low activity in reaction (B). The current value is close to 40 mA/cm^2 in reaction (A) at 20 ^oC at platinum content equaled to 0,8-1,0 mg/cm^2.

The proton exchange with outer surface of Pt - SKT-6A - PAN is performed owing to contact with particles of solid protonic membrane and sulfuric acid solution. Proton exchange inside of Pt - SKT-6A - PAN is performed owing to contact with sulfuric acid within carbon particle.

The calculations show that at room-temperature reaction (A) could be enhanced up to 100-300 mA/cm^2 as a result of optimized reaction conditions, and, consequently, such a catalyst is promising for hydrogen gas sensors and hydrogen-oxygen fuel cells.

The work was supported with Program of basic research of RAS “Hydrogen Energetics”, project 2.4 and Foundation for Assistance to Small Innovative Enterprises (FASIE), project 5809.

SYNTHESIS OF MULTI-WALLED CARBON NANOTUBES WITH CONTROLLED MACROSCOPIC SHAPES

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Carbon nanotubes have recently received increasing interest due to their exceptional physical and chemical properties [1,2]. During their growth, MWNTs are highly entangled and interconnected, forming a dense and elastic network generally on a microscopic scale which render their direct use complicated because of their fluffy character. Thus, a post-synthesis treatment is needed to obtain a macroscopic shape. Such a post-treatment generally requires to mix the as-synthesized carbon nanotubes with a polymer or a chemical agent before processing the macroscopic shape. Processing carbon nanotubes with macroscopic shapes to obtain materials with practical use is nowadays a major challenge in the field of advanced materials. In the present work, we report the synthesis of pure MWNTs self-supported in a macroscopic shape, i.e., cylinder, disk, cube, etc…, at several centimeter scale using a CVD synthesis under macroscopic constraint without any need of foreign agent addition during the process [3]. The synthesis method allows the complete control of the macroscopic shapes of the carbon nanotubes by controlling the constraint shape of the macroscopic reactor in which the carbon nanotubes were grown. The synthesis method was extremely simple, based on a conventional CVD method which allows easy scaling-up with minimum cost investment. The as-synthesized self-supported MWNTs were subsequently used as a reversible adsorber for the removal of organic pollutants from water [4] or as catatlyst support.

The raw material, i.e. MWNTs, was obtained by a CVD method using a mixture of ethane and hydrogen and an iron-based catalyst (20 to 50 wt.%). The self-organized MWNTs with a macroscopic shape were made by placing the powder catalyst inside a quartz cylinder (inner diameter, 30 mm, length, 50 mm) with both ends closed by a gas-permeable disk of carbon felt made of an entangled network of micrometers carbon filaments purchased from

Carbone Lorraine Ltd. The catalyst ($Fe(NO_3)_3{,}6H_2O$) was deposited onto alumina so that the iron weight% is 20%, then it is calcinated at 350°C, and last reduced *in situ* under hydrogen flow at 400°C. The constraint synthesis allows a significant increase of the apparent density without any need of post-treatment or foreign agent addition as usually reported in the literature. This apparent density after synthesis under constraint is typically close to 200 kg/m^3. The shaped carbon nanotube pieces display a mechanical resistance high enough tobe handled without any breakage or significant fine formation.

The as-synthesized self-supported MWNTs were used as a selective and reversible adsorber for the removal of organic pollutants from water. The experiment was carried out with a mixture of water containing 10 vol.% of benzene. In contact with the solution, the carbon material totally ad- or absorbed the benzene. The pollutant can be released by plunging the MWNTs into an acetone (or ethanol) bath. The most surprising is the fact that if this piece is plunged again in a solution of water with benzene at its surface, the benzene is ad – or -absorbed again with a removal of acetone. Similar “depollution” phenomena were observed with other water pollutants than benzene like gas-oil.

Figure 1: A. Picture of the self-supported MWNTs, B. SEM picture of self-supported MWNTs after HNO_3 and NaOH washing.

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SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CARBON NANOFIBERS ON THE SURFACE AND IN THE PORES OF MODIFIED ACTIVATED CARBON

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Carbon nanotubes or nanofibers (CNTs or CNFs) have attracted the interest of many researchers because of their extraordinary properties, in particular in chemistry, physics, and nanotechnology. Applications of CNTs and CNFs are expected in broad areas, including field effect transistors, one-dimensional quantum wires, hydrogen storage materials, and so on. Loose CNTs or CNFs are unsuitable for applications in catalysis and environmental science because they are difficult for handling and cannot be controlled in the suprastructured properties. Immobilizing CNTs or CNFs on a substrate is highly desirable. However, it is mandatory to use the same element for the immobilization and to avoid combination of nanocarbon with any non-carbon support. Activated carbon (AC) is widely used as catalyst supports and adsorbents due to their high specific surface areas and well-developed porosities.

Hierarchically structured carbon with carbon nanofibers nested inside or immobilized onto modified activated carbon has been successfully synthesized by means of chemical vapour decomposition of ethylene [1]. The activated carbon is obtained from bio-waste of palm oil production, followed by a mild oxidation, the impregnation and reduction of iron supported on activated carbon catalyst. The morphology and yield of the CNFs/AC composites can be controlled by changing iron precursors, C_2H_4/H_2 ratios, reaction temperatures, and reaction time. The nano-architectured carbon composite has a great potential in the environmental application: abundance of the adsorbed heteropolymolybdate $[PMo_{12}O_{40}]^{3-}$ increases a factor of 27 after the growing of CNFs on the surface and inside the activated carbon. Detailed results will be presented at the conference.

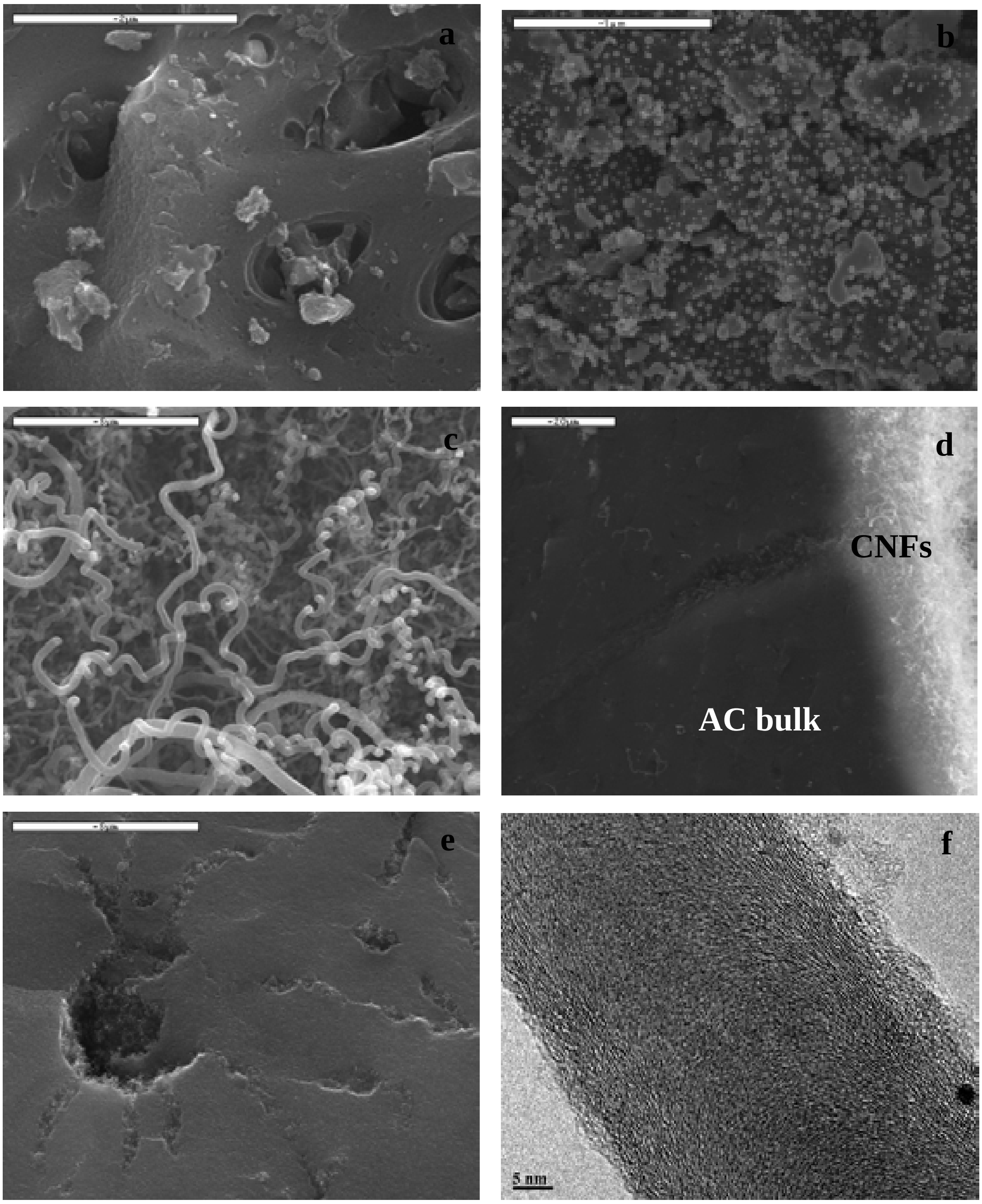

Figure 1 SEM images of (a) activated carbon, (b) 1 wt% Fe/AC catalyst, (c) Surface of CNFs/AC composite, (d) and (e) cross-section of CNFs/AC composite, (f) high resolution transmission electron microscopy image of a carbon nanofiber.

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TOWARDS LARGE SCALE PRODUCTION OF CNF FOR CATALYTIC APPLICATIONS

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Carbon nanofibres (CNF) have recently gained much interest for a series of applications due to their unique properties [1]. In particular, the inertness, the presence of stabilizing surface groups, and the conductivity and mesoporous character are thought to be interesting in terms of heterogeneous catalysis and electrocatalysis. The commercialization and use of CNFs relies on improving the synthesis process aiming at reducing the production costs and controlling the quality. Two main issues for the CNF production by catalytic chemical vapor deposition are addressed in this work. One is the effect of the residence time on CNF productivity and carbon structure relating to scale up of CNF-production and the other one is to directly use CNF to replace ceramics as supports for CNF-synthesis, in order to significantly reduce the requirement of CNF purification [2]. This possibility is being tested by synthesizing CNF from Ni/CNF catalysts. The challenges are addressed and some ideas for overcoming the obstacles are proposed.

The Tapered Element Oscillating Microbalance (TEOM) has been shown to be a powerful tool to study the kinetics of CNF synthesis, and was used to identify the most important parameters for scaling up Fishbone-CNF production. The effect of temperature and partial pressure of H_2 on CNF growth were studied on a hydrotalcite derived Ni catalyst. The results indicate that the optimal temperature is around 580 ºC, and that hydrogen partial pressure has a significant effect on the growth rate, as shown in Fig. 1. There exists an optimum partial pressure for CNF production, and the growth rate is significantly lower at higher partial pressures of hydrogen. The results suggest that the residence time of methane in the reactor will have a significant effect on the growth rate, since hydrogen is the product of methane decomposition. A series of large scale experiments has been performed in a fixed bed reactor with a production capacity of about 1kg of CNF per batch, as a benchmark for process scaling. Synthesis was performed in a ceramic reactor at 580 ºC with space velocities of methane ranging from 4.6 to 410 l/gcat h, corresponding to different conversions and thus different partial pressures of hydrogen. Fig. 2 clearly shows a higher coking rate at higher space velocities. The obtained coking rates are in good agreement with the values obtained from the TEOM reactor, as shown in Fig. 1. In addition, the quality of the CNF (structure, diameter and crystallinity) was found to be relatively independent of production scale. The scale of the CNF production reactor is typically about 200-300 grams per batch in the fixed bed, while it is about ten milligrams in the TEOM reactor. Thus, the present work has demonstrated a successful up-scaling by a factor in the range 10000. In principle, a CNF yield of 50 g/gcat can be obtained during a reaction time of 20 min at optimal conditions.

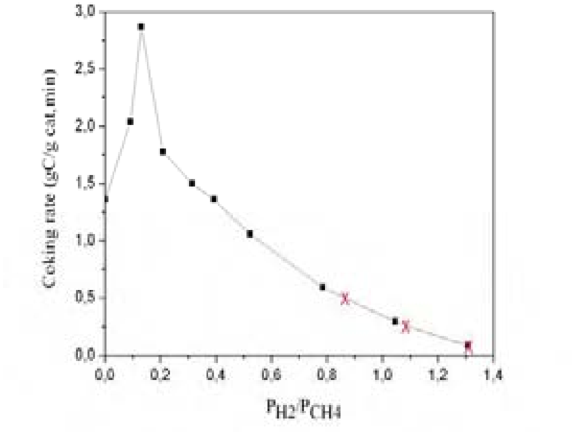

Figure 1. Coking rate as a function of H_2/CH_4 ratio at 580 ºC in TEOM (●) and fixed bed reactor (×)

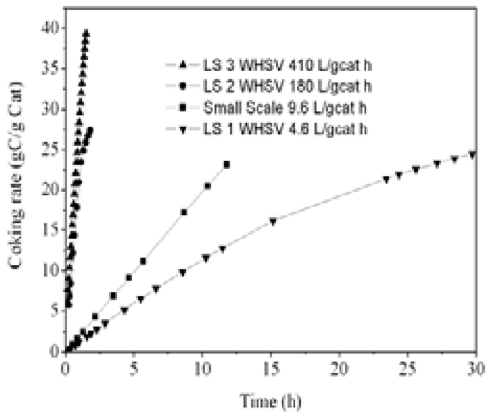

Figure 2: Coking rate as a function of time at different space velocities in the fixed bed reactor

The carbon nanofibre support used for CNF-synthesis was purified and oxidized in nitric acid to introduce surface groups. Ni particles corresponding to 10-20% loading were deposited on the carbon supports by employing both homogeneous deposition-precipitation (HDP) and impregnation (incipient wetness). The catalysts are characterized by TPO, TPR and XRD. Incipient wetness impregnation results in larger particles than HDP. The preparation by homogeneous deposition-precipitation resulted in homogeneously distributed Ni-particles. A mean particle size of 7 nm was found from XRD of the calcined catalyst. Reduction is followed by synthesis in a fixed bed reactor at 650ºC using ethane or methane as the carbon source. TEOM will be used to further reveal the kinetics of the carbon growth. The difficulty in removing the ceramic support in the purification process has been avoided.

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CO-CARBONIZATION OF POLYMERS - NEW CONCEPT OF CARBON COMPOSITES' PREPARATION

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The principles of thermochemical interaction of polymers based both on homo- and heterophase compatibility in solid phase, and in solution are considered. The temperature and kinetic parameters of maximum thermoreactivity of a number of carbo- and heterochain polymers are determined. The possibilities of intermolecular interaction of thermodynamically compatible macromolecular compounds depending on the chemical structure of initial composition components as well as concentration and temperature-time parameters are shown. It was established that favorable conditions for co-carbonization of polymers are both a close coincidence of temperature intervals of their thermostability and realization of interaction of initial components in diffusion area as well. The experimental information received for a number of nitrogen containing polymers (polyacrylonitrile, polyimide, polybenzimidazole, polyquinoline, chitin, chitosan etc.) shows forming of the products of carbonization with high thermal characteristics and coke number that are different from initial polymers. These products are perspective as catalysts for destructive treatment of polymeric waste.

OP-II-5

CARBON NANOFIBRES UNIFORMLY GROWN ON ALUMINA WASHCOATED CORDIERITE MONOLITHS

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1. Introduction

Carbon nanofibres as catalyst supports have shown promising advantages compared to activated carbon, such as: (i) the high purity of the material for avoiding self-poisoning, (ii) the mesoporous nature of these supports can be of interest for liquid-phase reactions, and (iii) specific metal-support interactions exists that can affect catalytic activity and selectivity [1].

However, carbon nanofibres in powder form have some drawbacks for slurry phase operation since the presence of fines may lead to agglomeration and difficulty of filtration. In order to optimise the hydrodynamic properties and to allow effective contact with the reactants it is therefore necessary to implement the CNFs into larger objects. This is the reason why considerable research efforts are dedicated to the immobilisation of CNFs on macroscopic supports. Carbon nanofibres have been immobilised on different substrates such as activated carbon [2], graphite felt [3], metallic filters [4] and foams [5] and ceramic monoliths [6].

In the present work, a uniform layer of CNFs has been grown on cordierite monoliths by thermal decomposition of C_2H_6:H_2 or CH_4:H_2 gas mixtures. As a result, a novel CNF-monolith composite has been synthesised that hold good promises as catalyst support for liquid phase reactions.

2. Experimental

Cordierite monoliths (from Corning, 1 cm diameter, 5 cm length, 400 cpsi) were washcoated with alumina. Nickel was deposited on the washcoat by adsorption from a pH-neutral nickel nitrate solution. The as-prepared catalyst was used as substrate to grow CNFs. The resulting CNF-monolith composites were characterised by SEM, N_2 physisorption (BET) and temperature programmed oxidation (TPO).

3. Results and discussion

A novel type of honeycomb monolith has been synthesised coated with an even layer of mesoporous carbon nanofibres (CNFs) with relatively small diameter as shown in figure 1. The CNF layer completely covers the surface of the monolith walls with a uniform thickness.

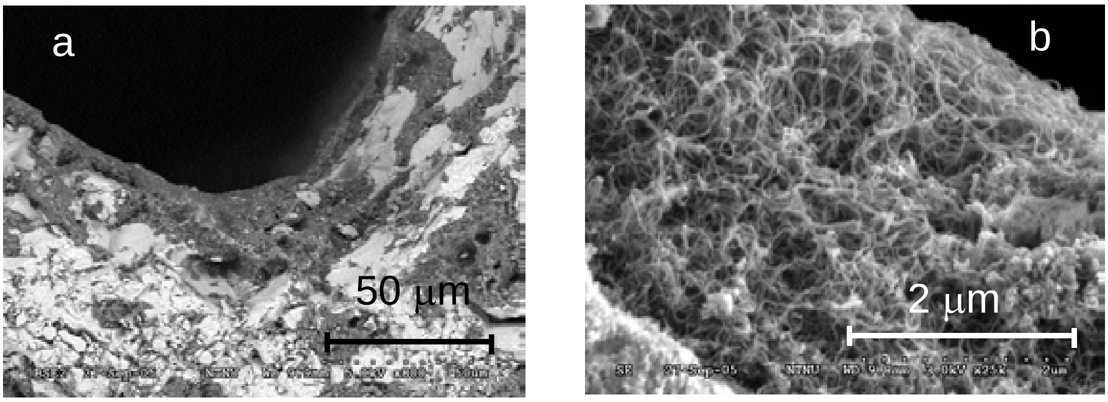

Figure1. SEM images of CNF layer grown with ethane:H_2 mixture at 873 K. a) corner detail, b) layer detail

It was found that the thickness of the CNF layer and the growth rate of the fibres have significant effects on the properties of the CNF-monolith composite. The preferred conditions are a mixture of C_2H_6 : H_2 as the carbon source and temperatures around 873-923 K. The CNF layer exhibits a relatively strong adhesion as tested by ultrasonic treatment. The porosity in the composite lies in the mesoporous range centered at approximately 17 nm pore size. This fact together with the absence of microporosity is advantageous for the diffusion of reactants in liquid phase reactions and improves the properties of previously reported CNF-monolith composites [6].

The CNF layer thickness and the CNF diameter can be tuned by the reaction temperature. For the same growing times, temperatures of 873 K and 923 K resulted in CNF layer thickness of 2 and 4 µm, respectively. CNFs with diameters of 5-10 nm with a narrow distribution are attained at 873 K. Larger diameters (10-30 nm) are found at 923 K and higher temperatures. The thin alumina coating (0.1 µm) prevents CNFs to be trapped inside the alumina and most of the CNFs are present as a uniform coating at the outermost surface of the monolith walls.

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OP-II-6

AVOIDING MASS TRANSFER LIMITATIONS IN CARBON SUPPORTED CATALYSIS BY USING CARBON XEROGEL TYPE SUPPORTS

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Porous carbon xerogel with tailored texture can be obtained by evaporative drying and pyrolysis of resorcinol-formaldehyde aqueous gels [1-2]. The pore texture is controllable by varying the pH of the precursors solution in a narrow range: depending on the pH, micro-macroporous, micro-mesoporous, microporous or non porous carbons are obtained. Solvent removal can be performed by the convective air drying process, which is commonly used in industry and very suitable to large-scale applications [3-4]. The pore texture is not influenced by the drying conditions. Due to their pore texture flexibility and mechanical resistance, these materials are suitable for many applications, among which catalyst supports. Moreover, the synthesis method is very simple and relatively cheap: industrial production can be envisaged.

The ability to control at will the pore size in carbon xerogels is a great advantage compared to classical active charcoals, whose textural parameters are mainly fixed by the origin of the raw material. Indeed, the pore texture of active charcoals obtained after thermal treatment strongly depends on the nature of the precursor. Moreover, these supports are mainly microporous, with low meso- or macropore volume. Even if the metal is well dispersed in micropores, mass transfer limitations decrease the performances of the catalyst. On the contrary, the presence of large amounts of meso- or macropores should minimize diffusional limitations inside carbon supports synthesized by sol-gel process, and these supports could be designed according to the considered reaction.

In this study, mass transfer inside carbon xerogels was analysed during a well known chemical reaction. The aim of this work is to show that it is possible to completely eliminate diffusional limitations inside the catalyst pellets provided that the carbon xerogel texture is adequately adjusted through an appropriate choice of synthesis variables values. Three carbon xerogels with various pore size were selected: one micro-mesoporous sample with small mesopores (maximum pore size = 10 nm), one micro-mesoporous sample with large mesopores (maximum pore size = 40 nm) and one micro-macroporous sample (maximum pore size = 80 nm). A commercial active charcoal was used as comparative. Pd-Ag catalysts were prepared by wet impregnation with aqueous solutions containing metal nitrates and nitric acid. After drying and reduction, each catalyst was crushed and sieved in order to prepare four samples with various pellet size (from 250 μm to 1250 μm). The presence or absence of mass transfer limitations was highlighted by testing the samples in selective hydrodechlorination of 1,2-dichloroethane into ethylene between 200 and 350°C.

Results show that diffusional limitations are completely avoided by adjusting correctly the pore size of the support. Indeed, a support with small mesopores (10 nm) leads to diffusional limitations, whatever the temperature, when the pellet size is larger than 250 μm: conversion and ethylene selectivity decrease when the pellet size increases. On the contrary, in the case of a macroporous support (80 nm), the 1,2-dichloroethane conversion, ethylene selectivity and reaction rate are completely independent from the pellet size. In the case of the active charcoal support, diffusional limitations are detected at any temperature and pellet size.

Mass transfer limitations were analysed via the estimation of the Weisz modulus, Φ, which compares the diffusion rate to the observed reaction rate. Since carbon xerogels are composed of interconnected microporous nodules (10 to 100 nm in diameter depending on the support), they were modelled as a hierarchical structure composed of two distinct length scales: a first one corresponding to the pellet itself, and a second one corresponding to the microporous carbon nodules. The Weisz modulus evaluation at both levels is in good agreement with experimental results. In each carbon xerogel support, $\Phi \ll 1$ at the nodule level, which confirms that no diffusional limitations occur in the micropores due to the short distance between the nodule surface and the metal particles. At the pellet level, Φ is close to or larger than unity, whatever the pellet size, in the case of the sample containing small mesopores: the diffusion rate has an effect on the global reaction rate. In order to avoid diffusional limitations, the pellets must be smaller than 250 μm in diameter. On the contrary, in the case of macroporous supports, $\Phi \ll 1$ for pellets up to about 4 mm (350°C) and 7 mm (300°C). Should the considered reaction be faster, the pore size could be enlarged by decreasing the initial pH of the precursors solution.

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IMPROVED ANODE PERFORMANCES IN PEM FUEL CELLS USING CARBON NANO-ENGINEERING[1]

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Introduction

Carbon nanotubes (CNT) and carbon nanofibers (CNF) have been intensively studied for a range of applications: H_2 storage, electronic and field emission devices, advanced sensors, polymer reinforcement, and catalysts support. However, surprising little attention has been dedicated to their application in the preparation of advanced electrocatalysts, although the interest is rapidly increasing parallelely to the increasing attention to the development of improved PEM (proton exchange membrane) fuel cells.

While usually research has been focused on the role of the metal particles and cell engineering, we have recently reported that the nanostructure of carbon, and not only its conductive characteristics, has a significant influence on the performances of PEM fuel cells [1]. In fact, the nano-architecture of carbon and the type of metal-carbon interaction, which in turns is also influenced from carbon nano-architecture, determine the possibility to have an efficient formation of the three phase boundary (gas-electrode-electrolyte) and an improved interaction between metal particles and the conductive carbon substrate. Both contribute in improving the efficiency in the chemical to electrical conversion, an important target towards the development of PEM fuel cells especially for light applications, but literature data on these aspects are still limited. Therefore, a better understanding of the role of carbon nano-architecture on the performances of PEM fuel cells is of key relevance for their improvement.

We will discuss here the electrocatalytic activity in hydrogen oxidation of novel nano-engineered anodes based on a hierachically organized structure: Pt nanoparticles are deposited on carbon nanotubes (CNT) or carbon nanofibers (CNF), which are grown directly on carbon cloth (carbon macro-fibers). Their performances are compared with those of a reference commercial Pt/carbon black electrode from E-TEK. The analysis of their performances and

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[1] In the frame of the activities of the Network of Excellence IDECAT (Integrated Design of Catalytic Materials for a Sustainable Production).

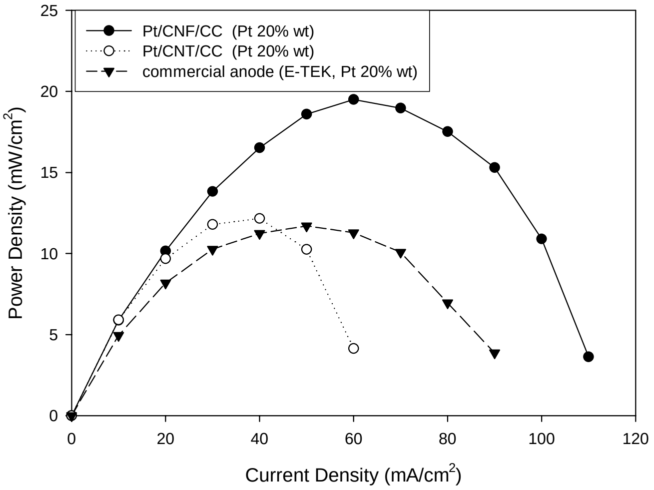
their advanced characterization by TEM, SEM and other physico-chemical techniques allow to derive some relevant indications on the role of carbon nano-architectures in PEM anodes.

Experimental

CNF or CNT were grown on carbon cloth (CC) by chemical vapor deposition (CVD) of ethane or propane, respectively. On the CC were first deposited Ni particles by incipient wetness impregnation (for CNF), or FeCoSBA-15 particles by dip-coating (CNT) [2]. Pt (20% wt) was finally deposited on these nano-engineered carbon anodes by incipient wetness impregnation of a C_2H_5OH/H_2O solution (1:1 v/v) with H_2PtCl_6.

The PEM fuel cells were then prepared by hot-pressing tecnique with Nafion® 112, used as proton exchange membrane, and with a commercial Pt/carbon black (20% wt) electrode from E-TEK, used as cathode. Electrocatalytic activity in hydrogen oxidation was measured in a PEM fuel cell (geometric area 1 cm^2) working at r.t. and atmospheric pressure.

Results and Discussion



The electrocatalytic activity of the nano-engineered anodes with hierachically organized structure (Pt/CNF/CC and Pt/CNT/CC) is higher than that of the commercial Pt/carbon black anode. With respect to the commercial anode, both novel anodes show improved power density up to a current density of about 40 mA/cm^2 (see Figure 1), but the Pt/CNT/CC deviates from this trend at higher current densities. The Pt/CNF/CC anode allows to obtain a maximum power density about twice as that of the commercial anode, with a consequent large increase in the efficiency in the chemical to electrical conversion efficiency. The physico-chemical characterization of the samples, in particular by TEM and SEM, indicates that the effect should be attributed to the more efficient formation of the three-phase boundary. The loss of efficiency in the Pt/CNT/CC anode at high current density is instead related to mass trasport losses, related mainly to the length of the carbon nanotubes. These losses could be reduced by reducing the length of CNT using a more optimized synthesis procedure.

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OP-II-8

THE ELECTROCATALYTIC ACTIVITY OF SILVER NANOPARTICLES DEPOSITED ON GLASSY CARBON

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The electrochemical reductive cleavage of carbon-halogen bonds in organic compounds has been the object of numerous studies and several reviews are available [1]. In particular, the electrochemistry of benzyl halides has attracted a considerable interest both from mechanistic and synthetic view points [2]. Most of the early studies were carried out using Hg or other active metals as electrode materials. Thus the processes were often found to be complicated by the intermediate formation of organometallic compounds. The mechanism at inert electrodes such as glassy carbon is well understood. It involves two successive electron transfers according to the following reaction sequence:

$$\mathrm{RX} + e^- \rightleftharpoons \mathrm{RX}^{\bullet -} \tag{1}$$

$$\mathrm{RX}^{\bullet -} \longrightarrow \mathrm{R}^\bullet + \mathrm{X}^- \tag{2}$$

$$\mathrm{RX} + e^- \longrightarrow \mathrm{R}^\bullet + \mathrm{X}^- \tag{3}$$

$$\mathrm{R}^\bullet + e^- \rightleftharpoons \mathrm{R} \tag{4}$$

The reduction process involves both radical and carbanion intermediates. The reduction potential of the radical $\mathrm{R}^\bullet$ is often more positive than that of the starting halide RX, especially with chlorides and bromides, so that it is rapidly reduced to the corresponding carbanion. Thus most alkyl halides exhibit a single $2e^-$ reduction wave. However, several exceptions to this general rule have been reported, especially with iodides.

The electrochemical reduction of organic halides at Ag cathodes has been intensively investigated in the past few years [3]. It has been shown that such an electrode material exhibits extraordinary electrocatalytic activities towards the reduction process, especially in the case of bromides and iodides. The electrocatalytic properties of Ag towards the reduction of RX have been exploited in a few cases for electrosynthetic purposes [4].

Recently some papers on the electrochemical deposition of silver nanocrystallites, as well as on the electrodeposition of mesoscale metal particles on graphite have appeared [5]. In effect, electrochemistry provides a means by which virtually any metal can be deposited at a precisely known coverage onto a conductive surface from ionic solution.

We investigated the electrocatalytic activity of nano and mesoscale silver particles deposited onto Glassy Carbon (GC) towards the electrochemical reduction of a model organic halide, namely benzyl chloride.

The working electrodes were built from a 6 mm diameter GC rod (Tokai GC-20) and were polished to a mirror finish with emery paper of decreasing grain size followed by diamond paste (3, 1 and 0.25 μm particle size). They were then cleaned in ethanol in an ultrasonic bath for about 5 minutes.

The electrodeposition of Ag was achieved by carrying out a chronoamperometry in a solution of 1 mM $AgClO_4$ in CH_3CN + 0.1 M $LiClO_4$ for different time intervals (typically 20-80 s) at a diffusion limit potential (– 0.4 V *vs* Ag^+/Ag). In this way we obtained a regular deposit of Ag nanoparticles 100-200 nm in size.

Reduction of $PhCH_2Cl$ on such a modified surface takes place practically at the same potential as at bulk Ag, which is ca. 500 mV less negative than the reduction potential at GC. Preparative-scale electrolyses of 10 mM solution of $PhCH_2Cl$ in CH_3CN + 0.1 M TEAP carried out at a modified GC plates, gave a two electrons reduction process in good agreement with results obtained at bulk Ag [4].

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OP-II-9

INFLUENCE OF THE CARBON SUPPORT ON THE PREPARATION OF HIGHLY ACTIVE RUTHENIUM-SELENIUM CATALYST FOR THE ELECTROREDUCTION OF OXYGEN

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Presently, metallic platinum nano-particles (about 2-5 nm), which are deposited on suitable carbon supports, are exclusively employed as catalysts in Polymer Electrolyte Membrane (PEM) fuel cells. For a long time the carbon support was only considered as a chemical inert and electrical conductive matrix, which enables the formation of porous gas diffusion electrodes with a high dispersion of the expensive noble metal catalyst. However, in the last years international research activities have been revealed that the morphology and the surface chemistry of the carbon support influences significantly the formation and the characteristic of the deposited catalytic nano-particles as well as the catalytic activity of the finally composed gas diffusion electrode. Therefore, in order to enhance the electrochemical efficiency of platinum catalysts in PEM-FCs investigations have been focused on the development of more suitable carbon supports and its selective surface modification.

However, the application of platinum as a cathode catalyst for the electroreduction of oxygen in PEM-FCs exhibits some significant drawbacks. An increasing demand of platinum causing increasing metal prizes could impede the widespread use of PEM FCs as mass product. Other disadvantages are the high overvoltage of the cathode reaction, migration and aggregation of platinum particles and the missing selectivity, which leads to effects of toxification and of depolarization by methanol in Direct Methanol Fuel Cells DMFC. Therefore, alternative catalysts are required for the further development of PEM fuel cell technology.

This contribution presents our results on the preparation and characterisation of a ruthenium-selenium-based material onto different carbon supports, which shows high and stable activity towards oxygen reduction in acidic media. Thermal decomposition of $Ru_3(CO)_{12}$ in organic solvents, chemical reduction of various ruthenium salts and colloidal techniques were tested in order to prepare carbon supported ruthenium-particles in the nanometer scale. It has been shown that the growth of ruthenium particles and its electronic coupling to the carbon support is influenced by the surface chemistry and the pore size distribution of the applied carbon.

Therefore, different commercial carbon supports have been applied for the preparation. Additionally, specific surface characteristics were tailored by partial oxidation or reduction of the carbon support and were characterised by XPS and gas sorption measurements. A subsequent modification of the ruthenium nano-particle surface by selenium leads to the final catalytic material. This surface modification increases the electrochemical activity by a factor of 10 and protects the ruthenium particle against oxidation. In order to evaluate the electrochemical activity of the final Ru-Se/C catalyst towards the electroreduction of oxygen, rotating disc electrode measurements were performed in diluted sulphuric acid.

These investigations reveal that a partial oxidation of the carbon surface by a heat treatment in a CO_2-atmosphere is beneficial for the forming of highly dispersive ruthenium nano-particles. Obviously, this effect is caused by oxygen containing surface groups which can act as anchoring centers for the metal precursor. By optimisation of the preparation conditions, metal loadings up to 40% could be achieved, a necessary preconditionfor high efficiencies in fuel cells. Analysis of the pore size distribution of the carbon supported catalyst gave evidence to a strong dependence of the activity on the amount of meso-pores whereas no correlation with the quantity of micro-pores could be found. This indicates that a well defined adjustment of the pore size distribution is necessary to obtain highly active catalysts.

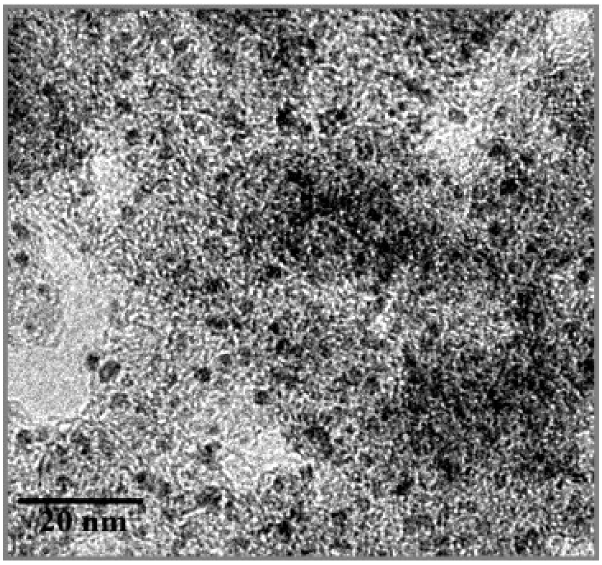

Fig 1: Ruthenium nano-particles, deposited onto CO_2-activated BlackPearls. The particles were formed by the reduction of adsorbed ruthenium chloride in a hydrogen atmosphere

OP-II-10

HYDROGEN STORAGE BY DECALIN DEHYDROGENATION/NAPHTHALENE HYDROGENATION PAIR OVER PLATINUM CATALYSTS SUPPORTED ON ACTIVATED CARBON

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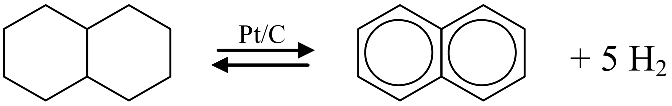
Introduction

Several kinds of hydrogen storage media have been proposed for proton exchange membrane fuel-cell (PEM-FC) vehicles. Liquid hydrogen consumes a huge amount of liquefaction energy, compressed hydrogen requires special vessels and hydrogen absorption alloys have a low hydrogen capacity (below 3% wt). An attractive idea is to use the couple of decalin dehydrogenation/naphthalene hydrogenation as a liquid organic hydride for hydrogen storage, which can afford sufficient hydrogen capacity (7.23 %wt, 63.7 kg-H_2/m^3).

Some advantages that this system offers are a high volumetric hydrogen content, which allows about 400 km for PEM-FC vehicles with 50 l of decalin, no evaporation loss during storage due to the high boiling points: 189ºC (trans-decalin), 191ºC (cis-decalin) and 217ºC (naphthalene). Besides they are socially accepted as safe chemicals (solvents and insect killers).

This work focuses on the catalytic dehydrogenation of decalin under mild conditions over Pt catalyst supported on activated carbon [1].



Experimental

Carbon-supported platinum catalysts were prepared by a conventional impregnation method followed by H_2 reduction. Granular powders of a commercial activated carbon (Engelhard) were stirred with the required amount of H_2PtCl_6 in aqueous solution at room temperature for 2 hours. The resulting samples were first dried in open air at room temperature for 24 h and then at 373 K for 1 h. Reduction took place in a tubular reactor charged with about 1 g of the sample. The total flow rate was 100 ml/min STP, which composition was 50% H_2 and 50% Ar. It was heated to 623 K with a heating rate of 3 K/min and then held at 623 K for 1,5 h. After cooling with Ar during 30 min, the sample was passivated with a 50 ml/min STP flow containing 1% O_2 overnight [2].

The dehydrogenation reaction of decalin was tested monitoring the hydrogen evolution volumetrically in a batch reactor at atmospheric pressure, under nitrogen atmosphere, heating over the boiling point of the reactant and refluxing. The tested factors were the percentage of Pt in the catalyst (1%, 3%), the temperature (513K, 533K) and the decalin/catalyst ratio (2, 2.7, 3.3 and 4 ml/g).

Results and discussion

The conversion of decalin after 2.5h and the initial hydrogen evolution rate were calculated from the measured hydrogen volumes. They are shown as a function of the decalin/catalyst ratio (Figures 1 and 2).

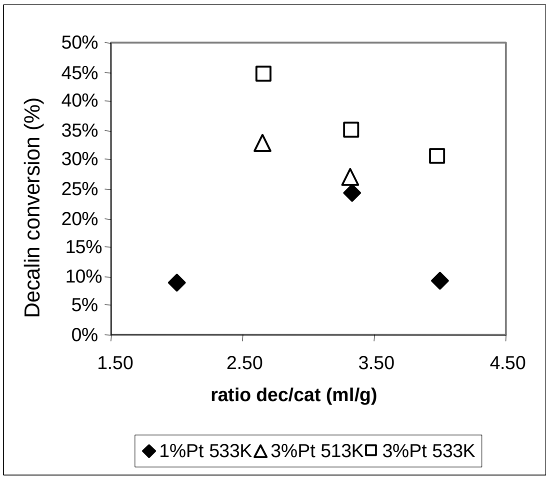


Fig 1. Relationship between conversion of decalin and decalin/catalyst ratios. Two catalysts (1% Pt and 3% Pt) and two temperatures (513 K and 533K)

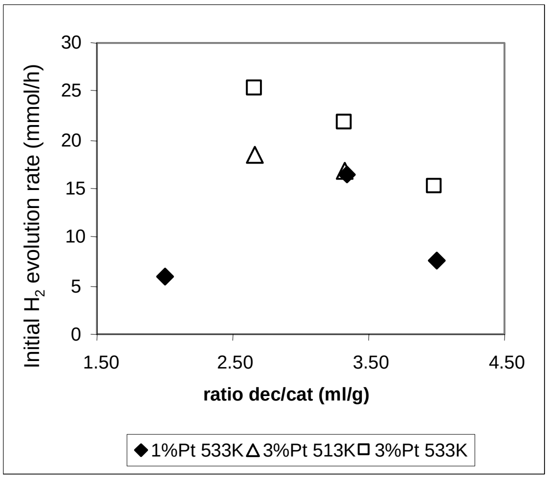


Fig 2. Relationship between initial rate and decalin/catalyst ratios. Two catalysts (1% Pt and 3% Pt) and two temperatures (513 K and 533K)

The highest conversion and the highest rate were attained at the highest temperature (533K) and the highest platinum content. Concerning the decalin/catalyst ratio, there is an optimum value that maximizes conversion and rate. This is because a special state designated as "liquid-film state" [1] is formed when the amount of decalin is not as low to become dry and as high to make the catalyst in a suspended state. This optimal decalin/catalyst ratio is between 2 and 3.3 ml/g.

The ongoing research is focusing on determining exactly the optimal conditions and characterizing the catalyst.

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OP-II-11

ACTIVATED CARBON-TUNGSTOPHOSPHORIC ACID CATALYSTS FOR THE SYNTHESIS OF TERT-AMYL ETHYL ETHER

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Due to the water pollution problems created by MTBE, ethanol based oxygenates atracted the attention of number of researchers and fuel producers as octane improving gasoline additives [1]. Such gasoline blending oxygenates also cause significant reduction in the exhaust emmissions of CO and unburned hydrocarbons.Tert-amyl ethyl ether (TAEE), which can be synthesized by the reaction of ethanol with isoamylenes, 2M2B (2-methyl-2 butene) or 2M1B (2-metyl-1 butene), over acidic catalysts is one of these oxygenates [2,3]. C_5 reactive iso-olefins (2M2B and 2M1B), which are available in light gasoline, may be reacted with bio-ethanol in fixed bed reactors or in a reactive distillation column to produce TAEE [4,5].

Heteropolyacid catalysts are excellent candidates to be used in the synthesis of TAEE. Originally these catalysts have rather low surface area values, being in the order of magnitude of a few m^2/g. The catalysts prepared by loading the heteropolyacid catalysts on the pore surfaces of high surface area activated carbons are expected to show higher activity and stability than pure heteropolyacid catalysts. In the present study, activated carbon-tungstophosphoric acid (TPA) ($H_3PW_{12}O_{40}.xH_2O$) catalysts were prepared and tested in the TAEE synthesis reaction. The effects of reaction temperature and the loading level of tungstophosphoric acid on the activity of these catalysts were investigated in the etherification reaction.

The loading of TPA into the activated carbon was achieved following an impregnation procedure by using the solutions of TPA in water and in ethanol. Before the impregnation step, the activated carbon (with an average particle size of 0.036 cm) was washed by acidic solutions. The impregnated particles were then dried and calcined at either 120°C or 180°C. These temperatures were decided from the TGA analysis of the catalysts, which indicated two peaks of weight losses before 120°C and at 170°C, due to the removal of water. A third wide peak of weight loss together with sintering of the catalyst was observed over 230 °C. The surface area of the acid treated activated carbon was decreased from 884 m^2/g to 501 m^2/g, as a result of loading of 31 wt% TPA into the activated carbon. The average pore size was about 1.4 nm.

The synthesis of TAEE was achieved in a gas phase tubular flow reactor in a temperature range between 80-97^{o}C, with a feed stream containing a molar ratio of 2M2B/Ethanol as 3/7. This mixture was diluted by helium and desired compositions were achieved. Comparison of the activities of the catalysts with TPA loadings of 25 wt % and 31 wt % indicated that activity increase was small after a TPA loading of 25 %. However, the calcination temperature of the catalyst was shown to be an important parameter. The fractional conversion of 2M2B to TAEE was increased from about 0.15 to 0.19 (in an experiment with 0.2 g TPA in the reactor) at 80 ^{o}C, by increasing the calcination temperature of the activated carbon-TPA catalyst from 120^{o}C to 180^{o}C. However, pure TPA catalyst (0.2 g) gave a lower conversion value of about 0.12 at the same conditions. These results clearly showed the significant enhancement of the catalytic activity of the catalyst by loading TPA into the activated carbon. Another important result was that by the increase of reaction temperature from 80^{o}C to 97^{o}C, fractional conversion of 2M2B decreased from about 0.19 to 0.07. Thermodynamic limitations and the decrease of the combined observed rate constant, due to the decrease of the surface coverage with an increase in temperature, are some of the possible reasons for this behaviour. Comparison of these results with the results obtained using a more conventional catalyst, namely Amberlyst-15, showed higher activity of the TPA containing catalysts.

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POSTER PRESENTATION

SECTION I	NOVEL CARBON BASED CATALYSTS AND SUPPORTS: SYNTHESIS, CHARACTERIZATION, APPLICATION
SECTION II	NEW TRENDS IN CARBON TECHNOLOGIES FOR ADSORPTION AND CATALYSIS

INVESTIGATION OF THE ELECTROCHEMICAL ACTIVITY OF α-C/NOBLE METAL THIN FILM CATALYSTS

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The sensitivity and selectivity of electrochemical gas sensors depends on several parameters, such as the type of catalyst used, the working temperature, and the applied electrical potential.

The traditional technology to produce gas permeable electrodes on porous substrates is based on a mixture of C and powder catalysts, where the carbon role is to prevent the noble metal grains from growing [1]. A disadvantage of this technology is the thickness of the active catalytic layer (several tens of micrometers), which results in a high noble metal consumption.

Amorphous carbon (α-C) thin films represent an alternative and perspective technology to produce catalytic layers for electrodes to be used in electrochemical gas sensors. In this case, the catalytic agent (for example, Pt nanoparticles) is co-deposited with C. Its relative concentration in the film can be easily changed to increase it above the percolation concentration, whereas the film thickness doesn't typically exceed 2-4 nm [2]. This ensures the required electrical conductivity and catalytic activity of the a-C/noble metal composite [3]. At the same time, the noble metal consumption is kept to a minimum.

In this work, plasma deposition is considered to produce thin catalyst films for electrochemical gas sensors. The films are based on nano-composite carbon layers doped with noble metals (Pt and Au). They were deposited — on silicon wafers and porous Teflon membranes — by magnetron sputtering (MS) of graphite-Pt (Au) targets in Ar [4]. The thickness of the layers ranged between 0.1 and 1 µm.

The performance of electrodes produced in this way was compared to that of traditional electrodes, referred to as “pasted electrodes” here, because they are prepared by depositing a mixture of platinum black (Au) powder and a Teflon suspension on a porous Teflon membrane, followed by thermal annealing.

We tested the sensitivity, in the amperometric regime, to H_2S and HCl of electrochemical sensors employing either type of electrodes. We measured their sensitivity to selected gases, their selectivity, background current, dynamic characteristics, long-term stability, and we compared the results with those obtained using gas sensors produced by leading companies in the field.

The MS deposited electrode resulted to be less sensitive than the pasted one, but it is nonetheless promising in view of the much lower amount of noble metal involved, better reproducibility, and better temperature stability. The results obtained are explained in terms of structural differences between the two electrodes, as derived from their morphological (Scanning Electron Microscopy, SEM), compositional (X-Ray Photoelectron Spectroscopy, XPS) and structural (X-Ray Reflectivity, XRR) characterization.

Preliminary measurements were also performed to investigate possible compositional and structural changes of electrodes that had worked a few weeks within the electrochemical gas sensor.

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SURFACE ELECTROCHEMISTRY OF CARBON IN IONIC MELTS

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Various carbon materials serve as anodes and cathodes during electrometallurgical process in melts for production of nonferrous metals.

The present study deals with electrochemical reactions taking place on the surface of glassy-carbon anodes in oxygen-containing melts.

In the NaCl-KCl-Li_2O [1] oxide ions discharge in stages (reactions 1 and 2):

$$O^{2-} + xC - 2\bar{e} = C_xO_{ads}, \qquad (1)$$

$$O^{2-} + C_xO_{ads} - 2\bar{e} = CO_2 + (1 - x)C. \qquad (2)$$

The reaction (1) is the reaction of electrochemical adsorption and the reaction (2) is the reaction of electrochemical desorption. Kinetic parameters of the reactions were determined in Ref. [1].

The following reactions take place on the electrodes in the NaCl–KCl–Na_2CO_3 melt [2, 3]:

$$CO_3^{2-} + CO - 2\bar{e} = 2CO_2, \qquad (3)$$

$$CO_3^{2-} + (x/2 + 2y)C - 2\bar{e} = 3/2xCO_2 + 3yCO, \qquad (4)$$

$$CO_3^{2-} + 1/2C - 2\bar{e} = 3/2CO_2, \qquad (5)$$

$$CO_3^{2-} + 2C - 2\bar{e} = 3CO. \qquad (6)$$

The reaction (4) is a combination of the reactions (5) and (6) with partial coefficients x and y. The coefficients x and y are related as $x = 2\alpha/(1 + 2\alpha)$ and $y = 1/(1+2\alpha)$ to the ratio of partial pressures in the gaseous phase $P(CO_2)/P(CO) = \alpha$. The contribution of the reactions (5) and (6) depends on the composition of the gaseous phase and, to some extent, the type of the carbon material of the electrode.

The ionic reaction

$$4OH^- + C = CO_3^{2-} + O^{2-} + 4H_{ads} \qquad (7)$$

takes place on glassy carbon in the NaOH-KOH melt [4].

The anodic polarization is accompanied by the electrochemical reaction

$$6OH^{-} + C - 4\bar{e} = CO_3^{2-} + 3H_2O \tag{8}$$

and the reaction

$$3O^{2-} + C - 4\bar{e} = CO_3^{2-}, \tag{9}$$

which involves oxide ions formed by the reaction (3).

In the Na_2CO_3-K_2CO_3 melt carbonate ions discharge in stages:

$$CO_3^{2-} + C - 2\bar{e} = CO_{ads} + CO_2, \tag{10}$$

$$CO_3^{2-} + CO_{ads} - 2\bar{e} = 2CO_2. \tag{11}$$

The reactions (10) and (11) represent reactions of electrochemical adsorption and desorption respectively.

The study revealed that the processes taking place on glassy-carbon anodes in ionic melts are irreversible. The anodes fail as a result of electrochemical oxidation.

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TEMPLATED SYNTHESIS OF NOBLE METAL CONTAINING CARBONS

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Introduction

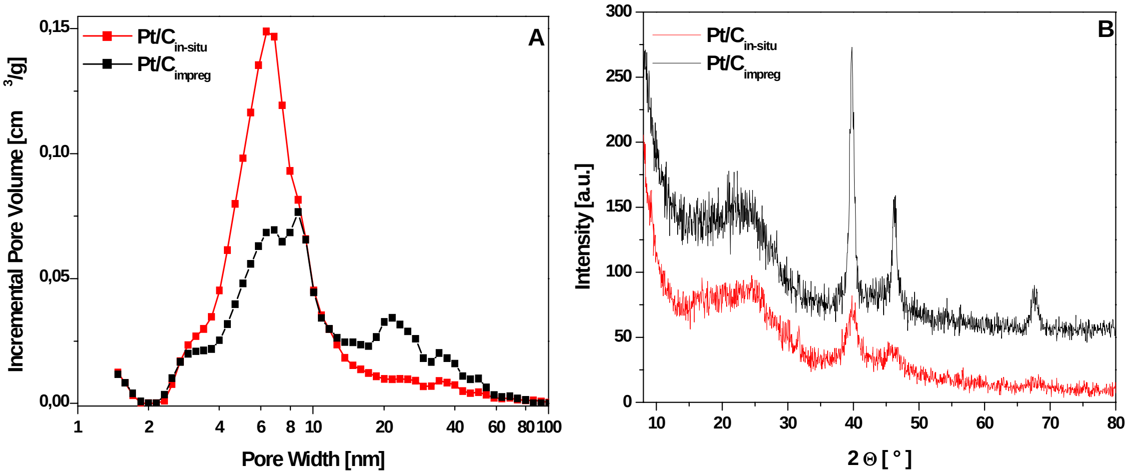
Activated carbons are widely used as noble metal supports for reactions such as liquid phase hydrogenation, dehydrogenation or oxidation. Since they have been originally prepared by carbonisation of natural precursors like wood or coal, their chemical and textural properties are often not well defined. Therefore, many efforts have been taken to develop carbon materials with improved properties. In the last seven years novel synthesis methods by using solid templates have been described [1]. The synthesis includes filling of an inorganic porous material (i.e. the template) with carbon precursor followed by carbonization and calcination steps. After removal of the inorganic material a carbon replica can be obtained. The aim of the present study was to advance this method by introduction of a metal compound. The use of a carbon precursor solution containing the metal compound results in a carbon material which possesses (partly) embedded metal particles in the pore walls. In such a way, the dispersity and the stability of the metal particles should be improved.

Experimental

All carbon materials were prepared by templated synthesis whereas two different ways of metal incorporation were applied. First, the carbon was synthesized following a procedure described elsewhere [2] and then loaded with the noble metal (5 wt. %) by impregnation. The alternative route combines the carbon synthesis and the modification with the metal compound in one step (*in-situ*): The template was impregnated using a solution of sucrose, hexachloroplatinic acid and water. After carbonization and calcination the obtained Pt/C/Si composite was reduced for 3 h at 400°C in hydrogen and then treated with HF solution. The prepared samples were characterized by N_2-adsorption, XRD-measurements, CO chemisorption, thermo analysis, elemental analysis, and catalytic test reaction (glucose oxidation).

PP-I-3

Results and Discussion



As shown as an example in Fig. 1 (A) platinum modified carbons are mainly mesoporous. For both materials, the BET surface area ranges between 960 and 1300 m²g^{-1} and the total pore volume between 1,6 and 2,0 cm³g^{-1}. The differences in the textural properties can be due to the action of the metal compound during the synthesis process.

The particle size of the platinum particles obtained from the XRD reflex at 40° 2Θ (*Scherrer* equation) ranges between 10 nm for the *in-situ* modified and 25 nm for the impregnated carbon, respectively (Fig. 1 (B)).

The development of pore structure depending on kind of metal precursor and the effect on catalytic activity in glucose oxidation will be discussed in detail.

Acknowledgment

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PROPERTIES AND STRUCTURE OF SORBENTS OBTAINED FROM MISCANTHUS USING WATER VAPOUR AS ACTIVATION AGENT

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The most crop effective grasses and the most frequently cultivated plants are grasses named *Miscanthus* such as miscanthus giant - *Miscanthus sinensis giganteus* and sugar miscanthus - *Miscanthus chariflorus*. The natural habitat of miscanthus grasses is located in central and South-East Asia. The miscanthus grasses grow to the high from 1 to 4 meters. They do not require very good soils and can to grow on soils of V and VI class, waste lands, as well as on soils contaminated with heavy metals. Miscanthus are perennial plants, their plantations can grow 15-20 years. Their cultivation is very cheap and the high crop of biomass can be harvested. In Poland the sugar miscanthus is mainly growed. Their crop are usually in the range of 5 - 30 tones of dry mass per hectare and depends on the type of soil and fertilization. The main components of miscanthus are: cellulose - 44 % and hemicellulose - 24 %, lignin - 17 % and other components 15 %.

Miscanthus was considered as a raw material for obtaining of active carbon useful for purification of aqueous solutions. Miscanthus is cheap, easy accessible, homogeneous and renewable material. In the literature there was rather quite few information about the investigations of sorbents from this material.

In the process of activation of char prepared from miscanthus using CO_2 as activation agent at temperatures of 750, 800 and 850 ^{o}C (activation times were from 15 to 90 min) the active carbon were obtained with efficiency from 92 to 56 %, respectively. Active carbons prepared from miscanthus, using CO_2 as gasifying agent, exhibited higher iodine number (140 - 930 mg I_2/ g) and methylene numbers (0 - 6 cm^3) in relation to char (13 and 0, respectively).

The char obtained from miscanthus shown the high efficiency in removal of toluene from aqueous solutions. Active carbons obtained using of CO_2 as gasifying agent very effectively cleaned the concentrated solutions of toluene, p-chlorophenol, methylene blue and Congo red.

Not large number of publication regarding the adsorbents prepared from miscanthus grass became the reason of our investigations on possibility of preparation of sorbents from this raw material in one step activation process, using water vapour as a gasifying agent.

The properties and structure of active carbons obtained from miscanthus grass were determined. Moreover, the applicability of these sorbents for purification of aqueous solutions contaminated with toluene, p-chlorophenol, methylene blue and Congo red was examined.

The raw material (miscanthus grass) was used in the form of briquettes.

One-step carbonization and activation process was performed in the horizontal pipe rotating reactor introduced in the electrical furnace. Preliminary (carbonization step) the sample was heated in the nitrogen atmosphere with the heating rate 10 deg/min up to the final temperatures: 700, 750 and 800 ^{o}C. The residence time at these temperatures was 15 min. Subsequently, the gasifying agent (steam) was introduced and activation step was conducted at a proper final temperature. The activation time was changed from 15 to 60 min.

During the investigations the following determinations were performed: microstrength, iodine number, methylene number and technical analysis of the raw material, char and selected active carbon. Additionally the purification tests for water contaminated by toluene, p-chlorophenol, methylene blue and Congo red were conducted.

It was stated that miscanthus grasses are the suitable raw material for obtaining of granular active carbons of high microstrength. The properties and structure of active carbons prepared from miscanthus grasses change with the temperature and the activation time.

The chars prepared from miscanthus grass exhibit relatively high microstrength. In their structure the ultramicropores are dominating. This is the reason for low iodine and methylene numbers observed. The chars were non-effective in water purification tests – only toluene was removed from the water solution by this chars.

The process of activation of char from miscanthus caused the growth of iodine and methylene numbers as well as the development of pore system in the range of wider micropores and mesopores.

The efficiency of decontamination of water solution from toluene, p-chlorophenol, methylene blue and Congo red by active carbons prepared from miscanthus grass is high and grows with temperature and activation time.

Toluene was observed to be the most easily removed contaminant using all active carbons prepared from miscanthus grass biomass. Congo red was the most troublesome contaminant for purification with examined sorbents.

CATALYSIS DURING SULPHUR COALS PROCESSING

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Sulphur coals could to be an interesting material for scientific investigations and industrial application because of their unique properties (high coking ability, ability to self-ignition and other). Thereby, it is necessary to understand the genetic nature of the organic and inorganic sulphur and its influence on the pyrolysis way.

The catalytic activities of the natural microelements, sulfates, metal sulfide in the coal liquefaction and gasification were estimated earlier.

The aim of this study was to investigate the catalytic activities of different sulphur forms in coal on their behaviour during semi-coking, coking ability and desulphurization processes.

The experiments were carried out with the special coal collection. The pairs of low- and high-sulphur coals of the same rank (C^{daf} = 65.4-93.7 %) and petrographically homogeneous (> 80% vitrinite) were investigated. Coals formed under less reductive conditions (LRC) are distinguished by a lower content of the total and pyrite sulphur and hydrogen contents as compared to the RC regardless of their rank.

The results of various pyrolysis experiments were compared for LRC and RC (with and without catalysts). The thermal behavior of coals was studied by differential thermal analyses, classical Fisher and Sapozhnikov methods, and pyrolysis in the water vapour stream. Analysis of semi-coking solid, gas and liquid products by the chemical methods, liquid chromatography, high resolution gas chromatography and others were applied for study the coal composition and thermal conversion**.**

Roles of pyrite in catalytic pyrolysis were to accelerate the tar removal, to hold the active species in the reaction zone under the catalytic pyrolysis of high sulphur coals (RC). Therefore the semi-coking of RC leads to a considerable increase in the yield of liquid products, volatile yield and sulfur emission in comparison with low- sulphur coals (LRC).

The reaction rate increases with increase of amount of FeS_2. As is seen from the Fig.1, the values of maximal rate of the coal decomposition and content of H_2 in the semi-coking gas changes considerably with the change of coal genetic type, i.e. from 9-12 mg/g·min for LRC to 17-24 mg/g·min for RC.

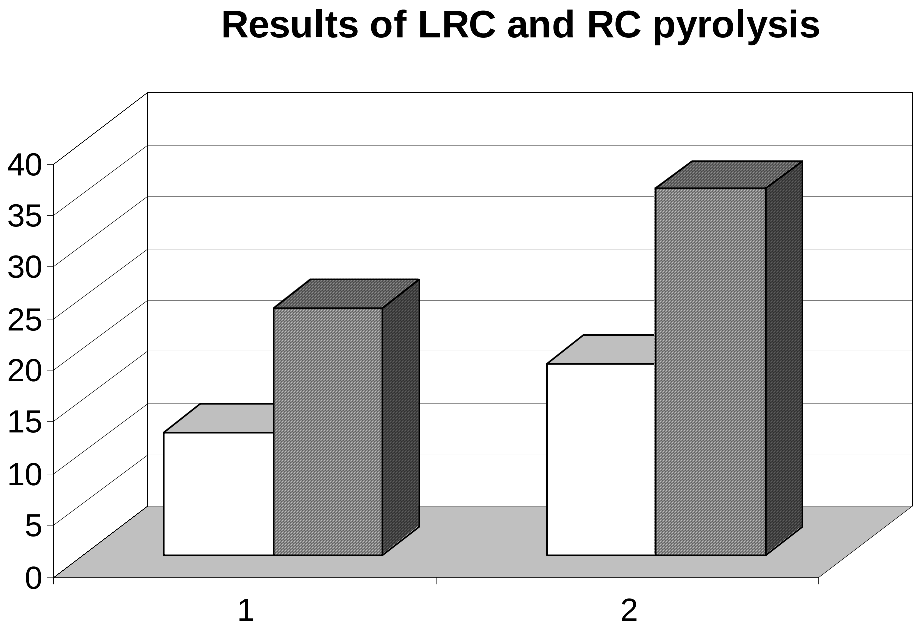

Fig. 1
1 – Maximal rate of the coal decomposition, mg/g·min;
2 – The content of H_2 in the semi-coking gas

The semi-coking gas of the catalytic conversion of RC is drastically reduced with higher content of H_2 + H_2S (47±13%) in comparison with thermal conversion. LRC under the same conditions more completely converted to CH_4 which is the main gaseous products (47.5±5%). Thus, pyrite is suitable for the production of H_2- rich gas from sulphur coals.

The results demonstrate that many -O-, -S- type bridges in real coals have an extremely reactivity and their condensation reactions lead to the formation of heavy products. RC creates fritted strong enough semi-cokes and cokes even from low rank coals under investigation.

Chemical pre-treatment by the radical polymerization initiator and adsorber oil increases the semi-coke yield, decreases the sulphur contents.

The results obtained are examined on the basis of the reaction path ways available for the catalytic and non-catalytic decomposition of coals.

ORDERED MESOPOROUS CARBONS SYNTHESIZED WITH SBA-15 SILICA TEMPLATE AS CATALYST SUPPORT FOR DIRECT METHANOL FUEL CELLS

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Introduction

Direct methanol fuel cells (DMFC) are attracting much more attention due to their potential as clean and mobile power sources in the future. However, a serious problem for polymer electrolyte fuel cells is the low reaction rate of oxygen reduction reaction in the cathode. One potentially effective solution is to use a novel carbon material as electrocatalyst support that improves mass activity of the catalyst. In this sense, novel carbon materials are very promising materials [1].

Porous carbons with high surface areas and controlled porosity in the mesopore range of 2-50 nm have recently received great attention because of their potential use as catalytic supports in fuel cell electrodes. There are numerous techniques for preparing mesoporous carbons, however only a few of these permit an accurate control of mesoporosity. The templating method, one of the most common synthesis techniques used to produce ordered mesoporous carbon, is based on the infiltration of carbon precursors into the pores of inorganic frameworks. Among the templates used, mesoporous silica is the most cited due to its controllable pore size structure [2]. However, the hydrophobic nature of porous carbons can be unfavourable for some applications. Therefore, their surface often needs to be modified to create surface functional groups which increase the hydrophilic properties and facilitate the interaction with guest species. The most frequently used method to generate surface oxygen groups is oxidation treatment.

In this work ordered mesoporous carbons have been prepared using SBA-15 silica as template. The texture and surface chemistry have been modified conveniently by means of different oxidation treatments to optimise their ability of dispersing active metal particles. Structure as well as textural and surface chemistry properties of SBA-15 and mesoporous carbons have been characterized by analytical techniques.

Experimental

Mesoporous silica SBA-15 was prepared from a triblock $EO_{20}PO_{70}EO_{20}$ copolymer (Aldrich) and TEOS (Aldrich) as silica source. For the synthesis of SBA-15, polymer was added to an aqueous solution of 1.7 M hydrochloric acid and stirred for 2 hours at 40 ºC. Next, TEOS was added dropwise and the mixture was stirred for 2 h. The synthesised gels were kept at 108 ºC for 24 h under static conditions. The final products were filtered, washed with water and dried at 108 ºC for 24 h. The synthesised samples were calcined under N_2 atmosphere at 500 ºC.

For preparing ordered mesoporous carbons, SBA-15 was impregnated with a mixture of furan resin (Huttenes Albertus) and acetone in different ratios, and nitric acid was used as catalyst. Then, it was cured at 120 ºC for 1 day. The impregnated SBA-15 samples were carbonised at 700 ºC and washed with HF to remove SBA-15. Finally, the texture and surface chemistry of ordered mesoporous carbons were modified by means of different oxidative treatments to optimise their ability of dispersing active metal particles.

Textural and surface chemistry properties of ordered mesoporous carbons were characterized by adsorption isotherms of N_2 and temperature programmed desorption (TPD), respectively. For the structural characterization the transmission electronic microscopy (TEM) and X-ray diffraction (XRD) were used.

Results and discussion

Small-angle XRD patterns of mesostrutured silica and carbon samples clearly show distinguishable reflections, what correspond to the hexagonal symmetry, indicating that the samples present an ordered porous structure.

This structure was confirmed with TEM images. They show that SBA-15 consists of the hexagonal arrangement of cylindrical mesoporous tubes, and the carbon nanostructure is exactly an inverse replica of SBA-15.

Pore size distribution of the SBA-15 and the mesoporous carbon structure was analyzed by N_2 adsorption-desorption isotherms. Both materials have a high surface area and a narrow mesopore size distribution.

Results obtained in the TPD experiments show that surface oxygen groups were created during the oxidative treatment, but sometimes the carbon structure could be destroyed.

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INFLUENCE OF FUNCTIONALIZATION ON THE PREPARATION OF CARBON NANOFIBER – SUPPORTED PLATINUM CATALYST FOR PEMFC

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Introduction

The proton exchange membrane fuel cell (PEMFC) is a highly attractive power source for mobile and stationary applications due to its high power density at lower temperatures (55-95ºC) and its compact design. The cost effective use of PEMFC is possible if the content of Pt in fuel cell, primarily in cathode, is substantially reduced maintaining or increasing the catalyst activity. To achieve uniform and highly dispersed Pt loadings, novel non-conventional materials are proposed as supports for platinum.

Recently, carbon nanofibers have attracted interest as electrocatalyst support because of their good mechanical and electrical properties [1]. They are grown from decomposition of carbon containing gases, like methane, on small metal particles. They have unique textural properties and contain neither micropores nor impurities. But their hydrophobic and inert nature can be unfavourable for some applications. Nevertheless, the texture and surface chemistry of the carbon nanofibers can be modified conveniently by means of different oxidation treatments to optimise their ability of dispersing active metal particles [2].

In this work, carbon nanofibers–supported platinum catalysts were prepared by an ion exchange technique. The influence of the number and the type of oxygen groups on the dispersion of platinum was studied. Textural and surface chemistry properties of the supports and the catalysts were characterised by different analytical techniques.

Experimental

Carbon nanofibers (CNF) were synthesised by thermocatalytic decomposition of methane. A Ni:Cu:Al catalyst was used. Prior to the carbon nanofibers growth, the catalyst was reduced at 823 K for 3 hours in a hydrogen flow. Next, the carbon nanofibers were grown at 973 K in a methane flow.

After growth carbon nanofibers were refluxed in HNO_3 2N, concentrated HNO_3 or in a mixture of HNO_3-H_2SO_4 at different temperatures and times in order to create surface oxygen groups and remove the catalyst. Textural and surface chemistry properties of carbon nanofibers were characterised by adsorption isotherms of N_2, scanning electronic microscopy (SEM) and temperature programmed desorption (TPD).

Pt was deposited on the CNFs after the different oxidative treatments. An aqueous solution of $Pt(NH_3)_4Cl_2$ (Alfa Aesar) was mixed with the CNFs and stirred overnight. Under these conditions, Pt is exchanged with the protons of the functional groups of the CNFs. Subsequently, the catalyst was reduced with H_2. The as-prepared catalysts have been characterized by ICP-OES, TEM and CO chemisorption to study the impact of the surface chemistry on the Pt loading and dispersion.

Results and discussion

The textural properties of carbon nanofibers were analyzed by means of N_2-physisorption and SEM. Furthermore, the carbon burn-off percentage after acid treatments was measured. Oxidation treatment of the carbon nanofibers resulted in a weight loss of about 6–10%, whereas oxidized carbon nanofibers in HNO_3-H_2SO_4 showed a considerable weight loss of 23%.

BET surface area of carbon nanofibers was over 100 m^2/g and increased up to 150 m^2/g after oxidation treatments. The micropore volume was negligible in all samples. Therefore, carbon nanofibers were mesoporous materials with a bimodal distribution of pore sizes.

The SEM images of oxidized samples were very similar to the SEM image of non-oxidized one, hence the carbon nanofibers maintain their structure after the oxidation treatment. However, the weight loss as well as the SEM images after the treatment in 1:1 HNO_3-H_2SO_4 indicate a partial destruction of the carbon nanofibers.

TPD experiments were used to determine the number of surface oxygen groups created during the oxidation treatments. These experiments demonstrated that an increase in oxidation severity results in an increase in the number of surface oxygen groups. The ongoing research is focusing on the characterization of the Pt catalyst.

Acknowledgements

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AROMATIZATION OF 5-PHENYL-PIRROLINE USING ACTIVATED CARBON

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In previous works of our group we have synthesised 5-aryl-2-iminopyrrole derivatives to be used as ligands for metal complexes syntheses (Figure 1) [1]. A suitable starting reagent for that type of products would be 2-aryl-pyrrole, which could easily be formylated or acetylated in position 5, using Vilsmeier-Haak conditions. A method recently developed by Sezen *et al.* [2] for the synthesis of 2-phenyl-pyrrole revealed to be very efficient, although very expensive, due to a Pd-catalysed arylation of the pyrrole ring.

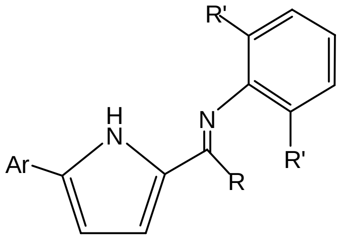
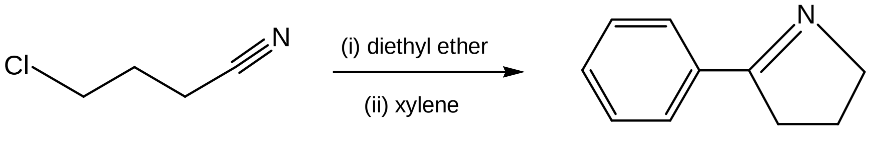


Figure 1 – Ligand precursor 5-aryl-2-iminopyrrole (Ar= phenyl, nafthalenyl, etc.; R= H, CH_3; R'= H, alkyl).

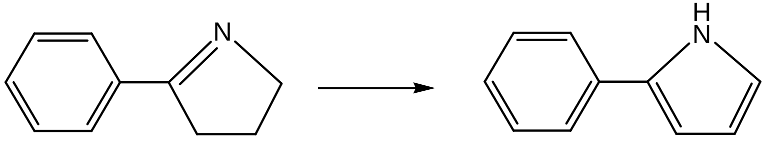
In order to find a cheaper route, we have devised an alternative method (Figure 2) based on the synthesis of 5-phenyl-pyrroline (5-phenyl-3,4-dihydro-2*H*-pyrrole), developed by Craig *et al.* [3]. This compound was further dehydrogenated, using activated carbon, generating the target molecule, 2-phenyl-1 *H*-pyrrole (Figure 3).



4-chlorobutyronitrile

5-phenyl-3,4-dihydro-2*H*-pyrrole
(5-phenyl-pyrroline)

Figure 2 - Synthesis of 5-phenyl-pyrroline by Craig *et al.* [3].



5-phenyl-3,4-dihydro-2*H*-pyrrole
(5-phenyl-pyrroline)

2-phenyl-1*H*-pyrrole

Figure 3 – Dehydrogenation of 5-phenyl-pyrroline.

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Reactions of aromatisation of 5-phenyl-pyrroline using activated carbon (well know as being effective in dehydrogenation reactions [4]) were carried out using both hexane and toluene, at reflux. These studies showed that the best results were obtained for activated carbon in toluene, and only 30 minutes were sufficient for the dehydrogenation to occur. Tests done in both inert and air atmosphere revealed no significant differences.

Studies were performed using commercial Activated Carbon Merck (powder), washed with distilled water, filtered and dried in oven at 120ºC for at least two months. Conversion values were determined by NMR, analysing a small portion of the solution, filtered through cotton wool placed in a Pasteur pipette, evaporated to drieness and redissolved in $CDCl_3$.

Maximum conversion values were obtained at *ca.* 98%, corresponding to yields of 2-phenyl-pyrrole of ca. 45% (as it is shown in Figure 4). The final product, after recrystallisation from ethanol, showed high purity, as determined by NMR analysis.

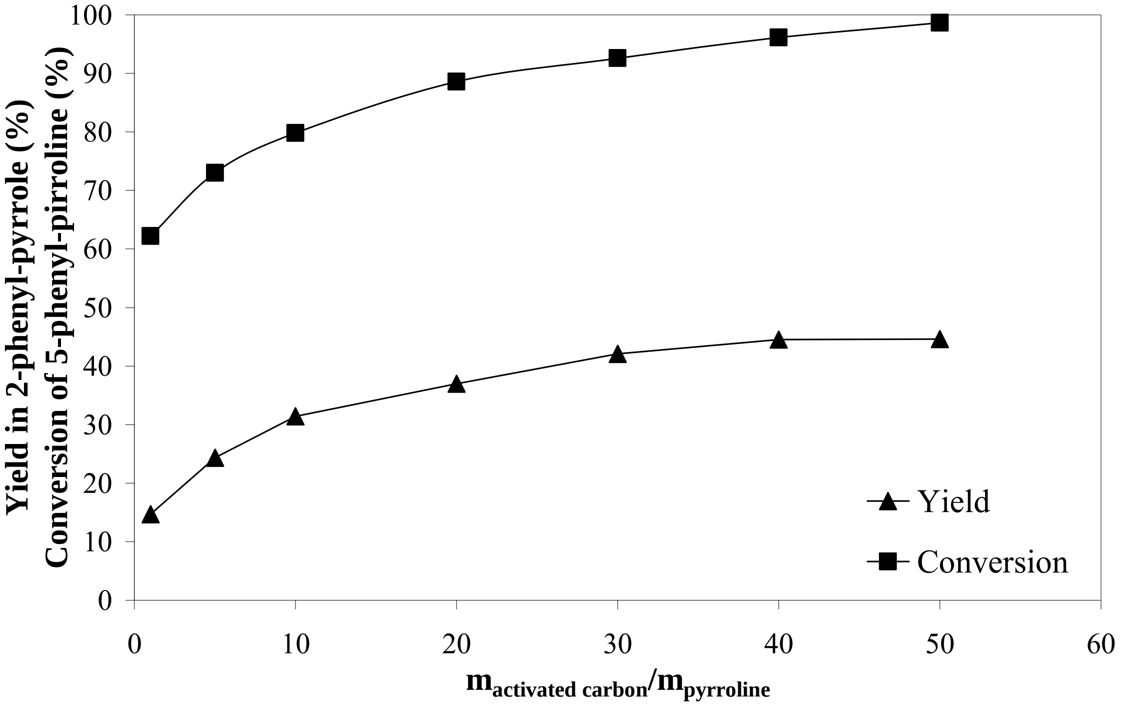

Figure 4 – Yield in 2-phenyl-pyrrole and conversion of 5-phenyl-pyrroline using activated carbon as dehydrogenation catalyst as a function of the mass ratio of activated carbon and 5-phenyl-pyrroline.

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PP-I-9

N_2O CONVERSION USING BINARY MIXTURES OF IRON SUPPORTED ON ACTIVATED CARBON

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Although N_2O is a pollutant gas that has an extremely long lifetime (about 150 years) and plays a significant role in the depletion of the ozone layer, its harmful effects have been virtually ignored in comparison with the attention given to NO. Relatively few studies exist of the reaction of N_2O with activated carbon [1-9].

In the present work the kinetics of N_2O conversion reaction with activated carbon impregnated with binary mixtures of 4%Fe with 4% of Co, Cu, Mg, Ni, Pb and V (4% in metal weight for each precursors salts) was studied in the temperature range between 300ºC to 800ºC using a microbalance. Good synergetic effects were found. For the Fe+Mg and Fe+Pb mixtures, the reaction rate at 350ºC increases, respectively, 3 and 6 times more than the sum of the rates obtained for the individual components. At 600ºC, the reaction rate increases 2 times. For other mixtures, the effects were less notorious.

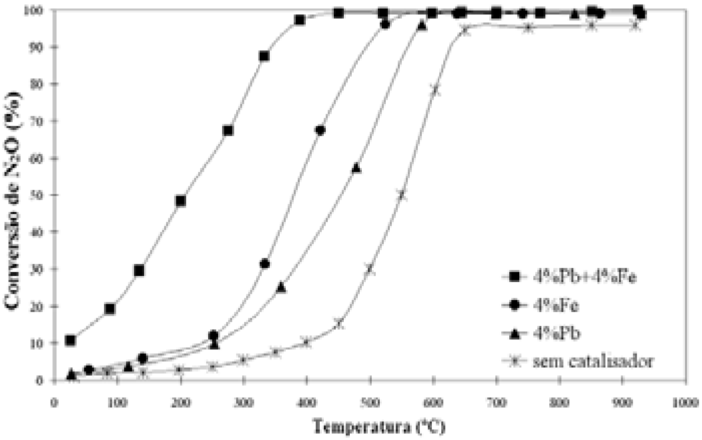

Figure 1 - N_2O conversion (TPR) for carbon parent sample and samples doped with with Pb, Fe and Pb+Fe binary mixture.

N_2O conversion was also followed using a differential reactor connected to a GC/MS apparatus (Figure 1). The reaction products were N_2 and CO_2, in agreement with literature [1,4-7]. Also some CO was detected at higher temperatures at higher temperatures as shown before [1,6,7].

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In situ XRD was carried out to identify the phases present during reactions. Precursor salts are decomposed and reduced to lower oxidation states such as Fe_2O_3, Fe_3O_4; MgO, $MgCO_3$; PbO, Pb_3O_4, as shown in Figure 2.

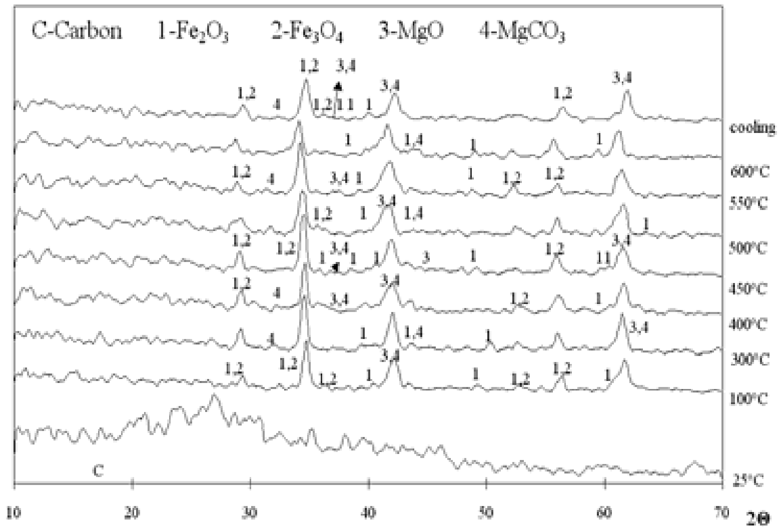

Figure 2 - *In situ* XRD data obtained in N_2O on heating sample doped with Fe at several temperatures.

No evidence of a new phase responsible for the synergetic effect was observed as the same active phases were present in the XRD spectra of the monometallic and bimetallic catalysts XRD spectra. However, apparently a reduced catalyst surface is required for N_2O conversion.

As temperature increases, some peaks become less intense (Figure 2). This behaviour suggests that the catalyst is melting and thus is spreading to form an amorphous thin film on the carbon surface. For the mixtures, this melted phase is formed at a lower temperature than that for the individual catalysts. The ability of the iron oxides to melt and spread on the carbon surface and chemisorb the gases going through redox transference of oxygen to the carbon reactive sites seems to explain catalytic reactivity. Similar behaviour has been reported by several authors in various atmospheres [4,6,7,11-17].

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PP-I-10

SIEVING PROPERTIES OF CARBON RECEIVED BY CARBONIZATION OF POLYMER SYNTHESIZED IN INTERLAYER SPACE OF ALUMINOSILICATE MATRIX

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The development of new methods of microporous materials design is the result of increasing interest to generation of effective techniques for separation and accumulation of fine-molecule size gases. The intercalation of organic molecules in interlayer space of layered 10-14Å-wide aluminum silicate with the following carbonization of received organo-mineral composite is one of the advanced directions of synthesis of the new materials with molecular-sieving properties.

The results of the texture analysis of carbon-mineral composites (CMC) and carbon obtained from CMC after mineral matrix dissolving are presented in this report. The natural aluminosilicate – montmorillonite (MMT) – has been used as mineral matrix. The monomers (acrylamide and styrene) were intercalated in MMT interlayer space and their polymerization was fulfilled at 80^{o}C during 17-24 hours. Modified MMT was purified from polymer formed on the external surface of particles, dried in air at 100^{o}C (stage 1) and calcined in argon atmosphere at 350-590^{o}C (stage 2).

Interlayer spacing d_{001} determined by X-ray diffraction analysis method, specific surface A_{BET} and micropores specific surface (measured by CO_2 sorption at 273 K) of obtained CMC are presented in the Table 1.

Table 1. Texture characteristics of carbon-mineral composites obtained after stage 1 and stage 2.

Monomer	d_{001}, Stage 1	Stage 2			
		t^0, ^{o}C	d_{001} Å	A_{BET}, m^2/g	A_{CO2}, m^2/g
Acrylamide	16.7	350	14.0	<1	–
		450	13.4	5	87.6
		590	12.7	5	113.6
Styrene	21.0	350	13.8	23	102.2
		450	12.7	85	120

The Table 1 demonstrates that interlayer spacing MMT (d_{001}=14.4 Å for basic MMT) increases up to 16.7 and 21 Å after stage 1. Calcination in argon atmosphere at the temperature above 450^{o}C reduces interlayer spacing up to 12.7 Å independently of polymer nature interstitial in interlayer galleries (stage 2). Specific surface A_{BET} of carbon-mineral sorbents received after tempering in argon atmosphere has a value of 5–85 m^2/g. Determined by CO_2 sorption surface (micropores surface) has the value more than 100 m^2/g, that fact confirms the presence of molecular-sieving properties of received carbon-mineral composites.

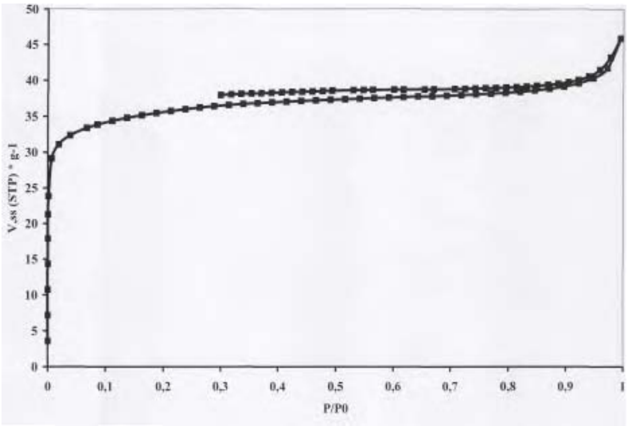

Fig. 1. Nitrogen adsorption-desorption isotherm at 77 K.

Mineral part of CMC received by acrylamide application was dissolved in HF, HCl and H_2SO_4 consequently. For residual carbon the structure analysis by XRD- adsorption methods were carried out. X-ray diffraction analysis showed that the received carbon has graphite-like structure (d_{002}=3.42Å) and its particles were 15 ± 3 Å in size.

Nitrogen adsorption-desorption isotherm at 77 K of the carbon pattern is demonstrated by the Figure 1. The form of adsorption and desorption isotherm curves, long-term equilibrium reaching at the initial stage of isotherm (about 4 hours at every point) and impediment nitrogen desorption indicate on the presence of ultramicropores in the pattern (received from distribution curve by Norvath-Kawazoe method average size of micropores was in the range of 4.9Å). CO_2 adsorption method at 273 K was applied for the complementary diagnostics of the ultramicropores presence. Comparison data of nitrogen adsorption (77.4 K) and carbon dioxide (273 K) are presented by the Table 2.

Table 2. Characteristics of patterns microporous structure by TVFM method (Dubinin-Radushkevich equation).

Adsorptive	Micropore volume, W_o,cc/g	Surface area, S_{micro}, m^2/g	Characteristic energy, E_0, kJ/mol
N_2	0.055±0.01	156	20.6
CO_2	0.091±0.015	240	15.6

From data obtained it is possible to conclude that received at CO_2 adsorption higher (in comparison with N_2 adsorption) values of volume pores and micropores also confirm the presence of ultramicropores in carbon obtained under procedure mentioned above.

PP-I-11

THE FORMATION AND PHYSICAL-CHEMICAL PROPERTIES OF CONDENSATION PRODUCTS – THE SELECTIVE CATALYSTS OF OXIDATIVE DEHYDROGENATION OF LIGHTS ALKANES

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It is known, that the carbon materials could exhibited high catalytic activity and selectivity in the oxidative reactions of various hydrocarbons. Oxidative condensation products (OCP), which are formed and accumulated in the course of reaction on acid catalysts, were identified as an active component in the ammoxidation of toluene [1] and in the oxidative dehydrogenation of alkylbenzenes [2]. The polycyclic compounds containing O, S, or N atoms with a developed system of conjugated bonds and a high concentration of paramagnetic centers are catalytically active OCP.

It was found that the OCP exhibited high catalytic activity in the oxidative dehydrogenation of propane by SO_2. The carbonization of silica (surface area 40 m^2/g) from 0 to ~40 wt % in course of the reaction was accompanied by an increase of propylene yield from 3.4 to 46 mol % (640^{O}C; C_3H_8:SO_2:He = 10:10:80 vol %) [3]. The formation and nature of active and deactivated condensation products on some Al-Si oxides was studied by DRIFTS, UV-VIS, EPR, XPS, thermal and chemical analysis, and electron microscopy.

The initial stage of formation of a carbon coating was accompanied by a the relatively sharp decrease in the concentrations of basic and strong acid sites of oxides. The further carbonization of the catalyst causes the complete blocking of the oxides surface. We observed transformation of OCP during its formation: the weakly condensed aromatic (probably, polyphenyl) compounds with branched alkyl substituents → the condensed polycyclic aromatic structures → the polyaromatic rings of highly condensed coke (Fig. 1).

It was found that catalytic activity of OCP in oxidation dehydrogenation of propane by sulfur dioxide depends on the C/H ratio of the coke. Structural changes of OCP in the course of their accumulation or high temperature pretreatment were detected in rising of coke condensation. The OCP with a maximum exothermic effect of coke burning (T_{max}) at 823-853 K were highest selective catalysts. The accumulation of highly condensed OCP with T_{max} at 908-993 K decreased selectivity to propylene. The carbon-like coke (with T_{max} at 993 K) close to sibunit are nonselective catalysts.

We suppose that the active OCP are the three-dimensional polymer presented by graphitized and condensed aromatic structures cross-linked by alkyl or sulfur bridges. The quinone, C=S, lactone, carboxyl, and alkyl groups in oxidative condensation products were detected by DRIFTS. There are probably the terminal substituents of polynuclear structures. The sulfate groups were found at the surface of carbonized alunima.

The catalytic properties of OCP depends on the oxygen functional surface groups composition. It is not revealed lactone groups in deactivated coke.

The coke morphology on the surface of silica is significantly different from one on alumina or Si - Al oxides. Aggregated clusters of OCP were formed on silica, but total coverage of coke was formed on alumina surface.

It was found that the acidity of oxide catalysts influence on the accumulating coke condensation. The OCP having a lower degree of condensation and less C/H ratio (1:0,6 for OCP/γ-Al_2O_3) was formed at the week acidic sites. At the strong acidic sites of Al-Si catalysts was formed the coke with more C/H ratio (1:0,3). It was found that the maximum exothermic effect of coke burning increases with increasing the strength of Lewis acidic centers for Al-Si-O catalysts (Fig. 2). The OCP/silica samples are the most selective catalysts. The highest selectivity to propene and selectivity to alkenes (propene and ethene) are 74,5% and 85% at the propane conversion of 35% in the oxidative dehydrogenation of propane by SO_2.

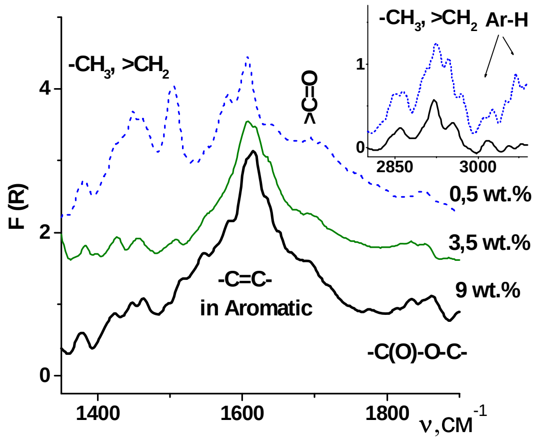

Fig.1. The coke transformation in course of carbonization of silica.

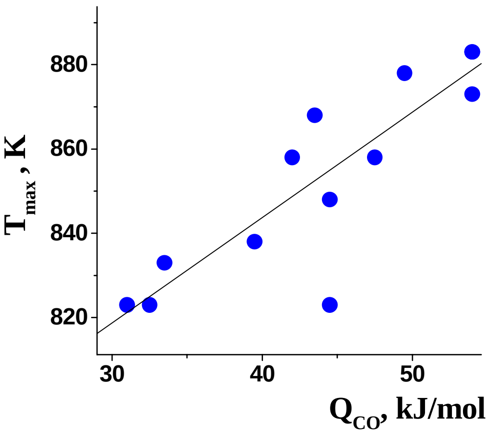

Fig. 2. The dependence of the T_{max} of OCP on oxides Lewis acidic centers strength.

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PP-I-12

PORE SIZE ANALYSIS OF SORBENTS FROM MANCHURIAN NUTSHELLS AND HYDROLYTIC LIGNIN

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Plant biomass serves as a conventional raw material for the preparation of microporous activated carbons (AC) and carbon molecular sieves (CMS). The well known precursors for synthesis of CMS are fruit-stones and nutshells, especially coconut shells [1-3].

In the Siberian region of Russia there are resources of cedar and manchurian nutshells suitable for preparation of carbon porous materials [4]. The other available in Russia raw material of plant biomass origin is hydrolytic lignin – side product of biochemical plants. Hydrolytic lignin is formed by chemical transformation of native lignin at elevated temperature (150-190 ^{o}C) and pressure (0.8-1.0 MPa) in the acidic medium [4].

The textural characteristics of produced carbon sorbents are depended on the following main groups of factors: precursor nature and conditions of raw material carbonization, activation and chemical modification.

The pore size distribution (PSD) is a key element in the characterization of porous carbons and a number of classical methods (TVFM-equations and methods which are based on the Kelvin equation) and of new calculation models based on non-local density functional theory (NLDFT-method) were developed for the PSD analysis [5].

The present work aims first to evaluate the pore size distribution of sorbents from manchurian nutshells and hydrolytic lignin using the NLDFT-method and show the comparison with the conventional procedures.

The micro- and meso- pore size distributions of a series of lignin-based and nut-based activated carbon samples has been determined from nitrogen adsorption isotherms at 77K with the nonlocal density functional theory (NLDFT), the Dubinin-Radushkevitch-Stoeckli (TVFM) method, the Dollimor-Hill (DH) and Broekhoff- de Boer (BDB) methods. The NLDFT approach provides better information about PSD at wide pore-width range of 7-50 Å.

The results (tables 1, 2) obtained from different methods indicate that sorbents have micropore volumes of 0.16-0.32 cc/g with an average width of micropores of 9-12 Å.

Activation with steam promotes the formation of mesopores with an average diameter of 20-40 Å but their volume smaller than of 0.15-0.20 cc/g at 35-37% burn off.

Table 1. Microporous characteristics of the sorbents produced by manchurian nutshells obtained from NLDFT and TVFM interpretation of N_2 adsorption data (77K)

Burn off* (%)	V_{micro}, cc/g		S_{micro}, m^2/g		H, Å	
	NLDFT	TVFM	NLDFT	TVFM	NLDFT	TVFM
5.2	0.1612	0.1648	270	259	8.7	12.7
13.5	0.2867	0.2465	493	513	11.4	9.6
37.0	0.3316	0.3104	576	621	10.5	10.0

*- nutshell was carbonized at 700 °C and then treated by steam at 800 °C

Table 2. Mesoporous characteristics of the sorbents produced by manchurian nutshells as determined from a number of calculation methods:
NLDFT-method; DH-method (Dollimor-Hill); BDB-method (Broekhoff - de Boer)

Burn off (%)	V_{meso}, cc/g,			$D_{мезо}$, Å		
	DH	BDB	NLDFT	DH	BDB	NLDFT
5.2	0.066	0.071	0.060	23	37	32
13.5	0.065	0.069	0.070	24	35	22
37.0	0.125	0.168	0.133	29	45	23

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PP-I-13

SYNTHESIS AND ELECTROCHEMICAL STUDY OF SINGLE-WALLED NANOTUBE-POLYACETYLENE COMPOSITE

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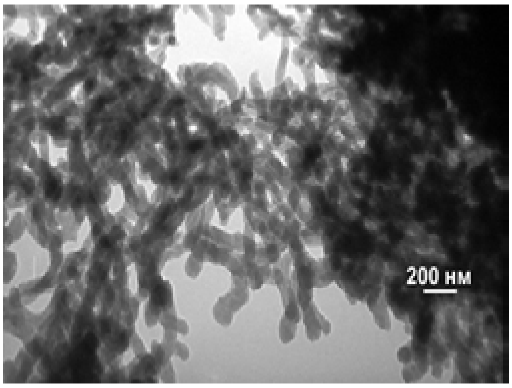
The work is aimed at the preparation of composite materials comprising single-walled nanotubes (SWNT) (2.4 w/w. %) covered with polyacetylene (PA) using the method of polymerization filling [1], and the study of electrochemical intercalation-deintercalation of lithium in these composites. We showed [2] that the insertion of electroconducting filler, namely, graphite, SWNT and multi-walled nanotubes (MWNT) into starting PA by mechanical blending sharply enhances conductivity. A percolation threshold for PA-SWNT composites [2] is close to 3 v/v.% and is somewhat lower that for composites filled with graphite. This effect was called "physical" doping in [2, 3]. The increase of conductivity from 10^{-1} to 10^{0} $S \cdot cm^{-1}$ was interpreted by the authors to be due to the injection of electrons to PA from filler particles. According to [4], the calculation shows that there is a portion of increased charge density between a PA chain and a wall of SWNT.

In the present work we synthesized PA directly on SWNT in the presence of a Ziegler catalyst, $Al(i\text{-}C_4H_9)_3$ and $Ti(OBu)_4$, in toluene ([Al]/[Ti]= 4/1, [Ti] = $3{\cdot}10^{-3}$ mole/l). SWNT were prepared by an arc discharge method and purified from by-products (catalyst, soot particles, and amorphous carbon) to yield a material with mass content of nanotubes equal to 80-90%.

Composite morphology was characterized using a JEM- 100 CX transmission electron microscope. The composite was found to consist of SWNT covered by a polyacetylene shell. An average diameter of structural units of the composite was determined to be ≈ 80 nm. No free polyacetylene was observed between the tubes covered by PA. This indicates that polymerization occurs only on SWNT possibly due to the adsorption of catalytic centers on an outer surface of SWNT. Such adsorption can be accompanied by



separation of bundles formed by SWNT to single nanotubes. Obviously, the composite volumes are 2-2.5 times higher than that of PA of the same mass due to loose packing of composite particles. The presence of SWNT in a catalytic mixture does not affect high yield of polymer (96%). However, the polymerization time increases by two times. Possibly, a catalyst forms a less catalytically active complex with nanotubes. According to the data of IR and Raman spectroscopy, PA bound to SWNT is a defectless long-chain polymer comprising extended enough both *trans*- and *cis*-rings (80% of *trans*- and 20% of *cis*-isomers).

Electrochemical behavior of the electrodes pressed from a PA-SWNT composite was studied using cyclic voltammetry (CVA) in 1 M $LiPF_6$ dissolved in ethylene carbonate – diethyl carbonate – dimethyl carbonate (1:1:1) mixture. At 1 mV/s scan rate, the currents of Li^+ intercalation are 50 times higher as compared to starting PA that is evidence of changes in the structure of PA chains on the outer surface of SWNT. The absence of a cathodic peak at 1.95-1.80 V (vs. Li/Li^+ reference electrode) indicates a full transition of PA to a *trans*-form. One could assume that the composite appears as an infinite cluster of large surface area formed by SWNT, which are covered by a PA layer possessing enhanced conductivity that results in higher electrochemical activity.

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PP-I-14

NOVEL NANOSTRUCTURED Pt-Ru/CARBON ANODIC CATALYST FOR DIRECT METHANOL OXIDATION

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The noble metals (Pt, Ru, Pd etc.) are known as the catalysts of electrooxidation of methanol. However the problem of catalyst poisoning by intermediate products of reaction (e.g., CO_{ad}) should be solved for successful application in fuel cells. This goal may be achieved by modification of a content and dispersion of catalytically active particles.

The aim of this work is the demonstration of principal possibility of preparation of electrocatalyst based on IR-pyrolyzed polyacrylonitrile (PAN) with immobilized nanosized particles of catalytically active metals of platinum group for direct methanol electrooxidation.

Composite precursor film was prepared directly on the electrode surface by spin-coating technique from DMFA solution of PAN and Pt and Ru salts (Pt:Ru=9:1). Then three component PAN/H_2PtCl_6-$RuCl_3$ composite films were exposed to IR radiation in a special IR-annealing chamber of a photonic pulse annealing set-up. The intensity of IR radiation was controlled by the temperature of the film sample, measured by a chromel-coppel thermocouple in a quartz tube placed directly under the sample. Controlling unit provided the changes in intensity of IR radiation by a given computer program. Temperature of the sample was maintained within 0.25 ºC.

IR annealing was performed in two stages: preliminary annealing (in air at 150 ºC for 15 minutes, then at 200 ºC also for 15 minutes) and main intensive annealing (in argon at 700^{o}C). Chemical and structural transformation occurring in PAN under noncoherent IR-radiation was shown to form ordered graphite-like structure. It is amorphous due to the irregular shift of graphene layers in the plane *ab* and small size of domains where the crystallite scattering is coherent.

Carbon materials obtained are the porous hydrophobic conductive films and powders with controlled level of conductivity up to the extent of metallic one. They are characterized by high stability at increased temperatures (temperature of testing should not exceed the temperature at which the material is produced, though), as well as high resistance to humid and aggressive (acidic and alkaline) media and under hyperbaric conditions.

The nanosized bimetalic particles were introduced into the structure of carbon matrix directly in the course of IR pyrolysis of composite-precursor on the basis of PAN and mentioned above Pt and Ru compounds. Efficient reduction of metal takes place in the course of IR pyrolysis of composite-precursor with participation of hydrogen, which is released in dehydrogenation of main polymeric chain of PAN.

According to X-ray diffraction data, bimetallic nanosized particles are alloys with simple cubic lattice (a=3.888 Å). The decrease of the lattice parameter to this value from a=3.923 Å for Pt attests to formation of solid solutions of substitution. It is shown by transmission electron microscopy method that bimetallic nanoparticles of diameter from 2 to 9 nm are finely dispersed in carbon matrix, the ~90% Pt-Ru nanoparticles being 4-7 nm in size.

Nanocomposites IRPAN/Pt-Ru supported on carbon glassy were tested as catalysts in reaction of direct electrochemical oxidation of methanol. The oxidation current was 2 mA/mg. Not very high value of current obtained is connected with quite low value of catalytic surface. Carbon-carbon nanocomposite based on IRPAN and multiwalled carbon nanotubes (10% mas.) was applied as a carrier in order to increase catalytic activity.

Thus, developed method allows the inclusion of catalytically active metals in the structure of carbon matrix in the course of the formation latter in the conditions of IR-pyrolysis, providing an uniform distribution of Pt-Ru bimetallic nanosized particles.

PP-I-15

GOLD BASED CATALYSTS ON STRUCTURED CARBON NANOFIBRES

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Carbon felt (CF) and carbon nanofibres (CNF) are known to have high thermal conductivity. This property makes it possible to utilize the material as an electric conductor between two electrodes. Introduction of a current in this system will cause thermal heating, which can be used for direct heating of chemical reactors. The obtained temperature depends on the resistance in the material.

Small catalyst particles may be a concern in catalytic reactors since diffusion limitations may arise. The problem can be avoided by anchoring nanoparticles onto a macroscopic substrate. This can be achieved by growing CNF on macroscopic structures such as CF or monoliths and use the CNF as a support material for catalysts. The size and morphology of CNF provides a high surface area while maintaining macroscopic pore sizes and hence good flow properties and absence of diffusion limitations [1].

Highly dispersed gold nanoparticles in association with a partially reducible oxide have been shown to exhibit high catalytic activity in oxidation reactions such as CO oxidation [2]. High catalytic activity is achieved by keeping the particle size of both Au and TiO_2 under 10 nm. The structure and morphology of the support seem to be very important for the catalytic activity [3].

This work reports the synthesis of a carbon-carbon composite consisting of CNF grown onto a CF and the preparation of Au/TiO_2 catalysts and activity measurement for the CO oxidation. The CNF/CF composite has two functions; as a support for the Au-based catalyst and as a direct heating source for the micro reactor.

The CF (Carbon Lorraine Company) has a low surface area (approx. 1 m^2/g). The CF was cut to pieces and refluxed in concentrated nitric acid for 1 hour, washed and dried before subsequent impregnation (incipient wetness) with a nickel nitrate solution and drying. Both pure ethanol and pure water have been used as solvents for the impregnation and two different drying conditions have been tested. The nickel catalyst was loaded in a reactor and reduced in situ. Ethane and hydrogen were used for the synthesis of the CNF at 650 ºC for 5 hours and the composition of the outlet gases were continuously analysed. The synthesis has been performed with different space velocities. The preparation of the catalysts has been performed in two steps:

Titania was prepared by hydrolysis of $TiCl_4$ solution using polyethylene imine (PEI) when deposited onto the CNF/CF [4]. Gold colloids were prepared from a $HAuCl_4$ solution and added dropwise to the suspended TiO_2/CNF/CF to produce the catalyst [5,6]. The catalysts are being characterised by several methods such as BET, XRD, TPO, SEM and TEM.

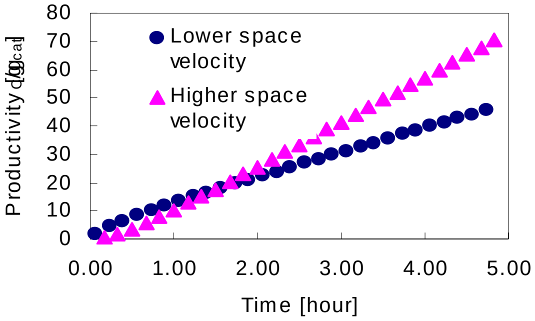

Figure 1: The obtained amount of CNF from the growing process

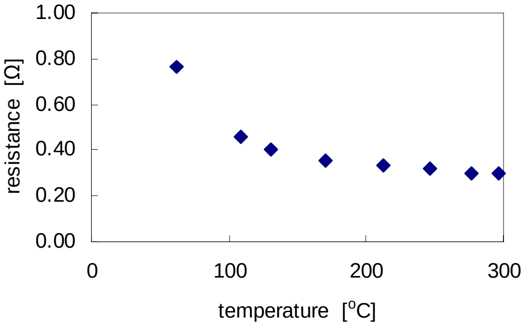

Figure 2: Logarithmic plot of the resistance in the carbon composite as a function of temperature

The results show that the homogeneity of the nickel dispersion on the CF/CNF composite depends on the preparation conditions. The composite pieces were weighted before and after the growth of CNF. Larger weight differences are seen for the pieces grown at low space velocity and also the calculated amount of CNF per gram Ni was lower as shown in figure 1. The surface area of the carbon composite was measured to be around 100 m^2/g. The total surface area did not change after deposition of the titania but an increase in the amount of mesopores is observed. Earlier results have shown that the oxide on CNF have different surface properties than the unsupported oxide particles that contribute to improved catalytic stability [6]. This indicates that the CNF are capable of stabilising the mesoporous structure of titania at elevated temperatures. Results from XRD show that titania is predominantly present as anatase and that the CNF are highly crystalline. The Au particle size obtained with deposition of Au-sol is from 2 to 7 nm. Temperature testing by application of power in the CF gave a lower temperature increase compared to the carbon composite. The resistance in the CNF/CF decreases with increasing temperatures as shown in figure 2. The system gives a stable temperature and rapid temperature responses are obtained. The catalysts are currently being tested for CO oxidation activity.

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PP-I-16

METALS SUPPORTED ON CARBON-BASED HONEYCOMB MONOLITHS: INFLUENCE OF THE PREPARATION METHOD ON THE TEXTURAL AND STRUCTURAL PROPERTIES

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In this work different catalysts constituted by copper and manganese supported on carbon-based honeycomb monoliths obtained at lab scale have been prepared with a further intention of using them for Selective Catalytic Reduction of nitrogen oxides. The main scope at this stage was to study the influence of the metal phase incorporation procedure on the final textural and structural properties of the catalysts. For this purpose the following preparative variables were investigated: 1) the way of introducing the metal, either by impregnation of the monoliths with a precursor solution or through its integration in the paste before the extrusion or even by homogeneous deposition-precipitation from urea decomposition; 2) the concentration of the precursor solution in those catalysts prepared via impregnation technique (1M or 2M); 3) the time of contact between the monoliths and such solution (ranging from 30 to 90 minutes); 4) the use or not of a support pre-treatment with HNO_3 and/or NaOH, and 5) the drying method (conventional or using microwaves) (see Figure 1).

X-Ray Fluorescence, Inductively Coupled Plasma Spectroscopy (ICP-AES) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (EDS) have been used as complementary techniques to analyze the metal loading of the catalysts. In addition, isotherms of N_2 adsorption at 77 K have shown significant differences both in the specific surface area and the porosity of the samples. Finally, X-Ray diffraction has allowed to identify the metal phases present in each catalyst and to obtain data of the metal dispersion.

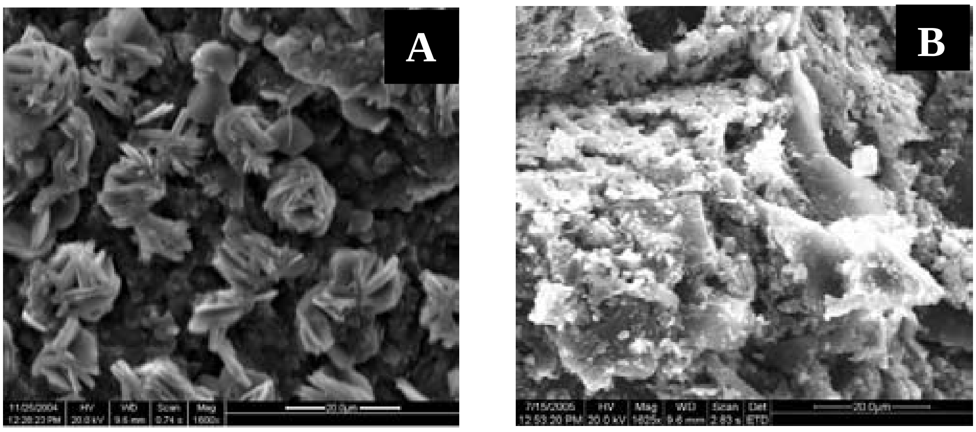

Figure 1. SEM images corresponding to two supported Cu catalysts prepared following the same technique (impregnation), from equal precursors (1M nitrate solution), after same contact time with the monolith (30 min), both without support pre-treatment, and just differing in the final drying method: A) in air at 80 ºC overnight; B) using microwaves (1 min). After being dried, both catalysts were treated in Ar at 250ºC.

PP-I-17

INFLUENCE OF MOLECULAR CARBON STRUCTURE AND MORPHOLOGY ON THE ELECTROCATALYTIC ACTIVITY OF PYROLYSED CoTMPP IN OXYGEN REDUCTION

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Currently, carbon-supported platinum catalysts are established as state of the art cathode material in polymer electrolyte membrane fuel cells (PEM-FC). Although they reveal high activity and stability in the oxygen reduction in acid media, their meaningful disadvantages, i.e. increasing price due to an increasing demand, easy inhibition, unsuitable material for the direct methanol fuel cell as well as migration and aggregation of the platinum nano particles on carbon surface, require the development of noble metal free catalysts. In the last decades, N_4 macrocycles (porphyrines and phthalocyanines) have drawn attention as alternative as a cheap and highly active cathode material in the PEM-FC.

The activity and stability are significantly improved when organometallic complexes are heat treated in an inert atmosphere. Thereby, the molecules are disintegrated forming a conductive carbon matrix in which the catalytic centres are molecularly embedded. The catalytic centres have been characterised as MeN_x moieties by EXAFS, XANES and Mößbauer spectroscopy [1, 2]. However, the constitution of the in-situ formed carbon matrix has been neglected in the past research, although its morphology and molecular structure play a key role in the catalytic process.

In the work presented, based on cobalt-tetramethoxyphenylporphyrin (CoTMPP) the pyrolysis process and the molecular structure of the formed carbon matrix are characterised by thermogravimetric measurements, Raman spectroscopy and X-Ray diffractometry (XRD) and correlated to the electrochemical activity (Rotating-Disc-Electrode and cyclovoltametry). Thus, fundamental characteristics of the carbon matrix have been found which provide a basis for the development of new preparation strategies. Higher electrochemical activities could be achieved when the catalyst consists of extended graphen layers with restored CoN_X centres.

The high catalytic potential of the chelate-based eletrocatalysts could be elaborated by the preparation with structure forming agents (metal oxalates) [3, 4]. Thereby, meso-porous catalysts particles (up to 800 m^2/g) have been produced, which show kinetic current density like commercial platinum catalysts (10 % Pt/C). Related to the low metal loading (< 1 wt-% Co and < 2 wt-% Fe) in the CoTMPP-based electrocatalyst, the activity of the chelate-based centres is three times higher than the one of the platinum catalyst. The molecular structure of the carbon matrix has been characterised by X-Ray photoelectron spectroscopy (XPS), Raman spectroscopy and XRD. It reveals that graphen bends with extended planar sections benefits the electrochemical activity at the centres. Obviously, the electronic surrounding of catalytic centres presents a crucial point for the electron transfer in the oxygen reduction.

In morphological investigations by gas sorption of prepared CoTMPP-based electrocatalysts with different pore structures, a super proportional relation between activity and accessible electrochemical surface has been found [4]. This shows that beside the molecular constitution the pore structure and fractal dimension of the surface influence the performance.

Due to morphological drawbacks of the catalytic material prepared by pyrolysis, more suitable preparation methods are required. Therefore, for the first time low temperature plasma technique has been employed successfully as suited method to carbonise CoTMPP to a catalytic active material [5, 6]. Operation parameters (power, duration of treatment, type of plasma) have been varied. Optimised conditions have been found in Argon plasma at high plasma power (400 W, 10 min). Plasma treated catalytic material reveals equal electrochemical activity than its thermal reference. However, particle size measurement using light scattering has been demonstrated that the particle size is reduced from 870 (thermal treatment) to 60 nm (plasma technique). Due to the limited heat input in the low temperature plasma treatment, the negative effect of sintering can be circumvented.

UV-Vis, Raman and IR, as well mass spectroscopy were applied in order to analyse the development of product's structure. It has been found that during catalyst formation an catalyticly active cobalt containing poly-pyrrole intermediate occurs, which is finally carbonised to form graphen layers with embedded CoN_X centres.

This innovative preparation strategy affords the application of sputter technology which could be successfully applied on CoTMPP. This sputter technology could initiate an automatised production of platinum-free gas diffusion electrodes. Furthermore a controlled particle growth in the sputter process enables fundamental research to find structure-activity correlation parameters.

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PP-I-18

THE WAY OXIDATIVELY MODIFIED CARBON SORBENTS INFLUENCE THE PROPERTIES OF SUPPORTED SALT CATALYSTS

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As has been stated earlier, salt adsorption process ($HgCl_2$, $Zn(OAc)_2$) and catalytic activity of salt catalysts during hydrochlorination [1] and hydroacetylation of C_2H_2 [2] are highly dependent on surface oxidation with strong oxidizing agents (HNO_3 and H_2O_2).

Depending on the mode of carrier modification [3] the form of kinetic equations changes as well. We report here on the outcome of the process of producing of $Zn(OAc)_2$ catalyst supported on activated AGN-2 carbon oxidated with hydrogen peroxide.

It was shown that specific surface of AGN-2 activated carbon increased by 44 $m^2 \cdot g^{-1}$ ($S_{sp.}$=914 $m^2 \cdot g^{-1}$) when treated with the oxidizing agents, part of mesopores also increases up to ~ 25 % (fig.1).

The amount of available adsorption sites of both polar (H_2O, CH_3COOH) and nonpolar substances like benzene, as well as adsorption capacity (*a*) increased by 25-30%. However, as for benzene, when surface was entirely filled (P/P_s=0,8), (*a*) for benzene increased by 14%, while that for H_2O by 36%, the number of sites changing as well. Thus water heat $\Delta H_{ad.}$ increased by 58 kJ/mole while benzene heat increased by 7 kJ/mole only.

The relatively more evident growth of surface polarity (hydrophylity) agrees with the increase of adsorption capacity according to methylene blue (2,5 times). Such changes of surface characteristics (together with the increase of mesopores volume) are true of increase of adsorption capacity as to $Zn(OAc)_2$ (fig.2) as well.

Adsorption capacity (on oxidized with H_2O_2 surface of AGN-2) as to AcOH rises sharply as is shown on fig.3.

Catalyst activity in the process of vinyl acetate synthesis (VA) demonstrates an evident rise as compared with nonoxidized AGN-2.

Thus productivity according to VA of samples with ≈22% of salt ($S_{sp.}$=198 $m^2 \cdot g^{-1}$) at 175, 205 and 230°C, is as much as 42,5; 198 and 342 $g_{VA} \cdot l^{-1}{}_{ca} \cdot h^{-1}$ respectively (volume rate of mixture C_2H_2, AcOH and N_2 being 765±5 h^{-1} at proportion 6,2:1).

The mode of catalyst drying proved to be of importance.

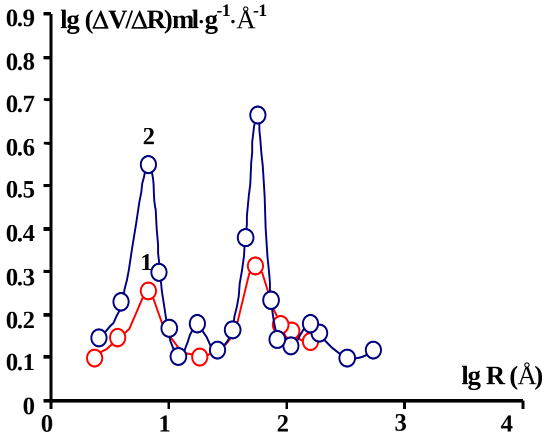

Fig. 1. Differential curves of pore size distribution of AC modified with H_2O_2 (2) and initial AGN-2 (1) as to the benzene vapour adsorption isotherms AGN-2K.

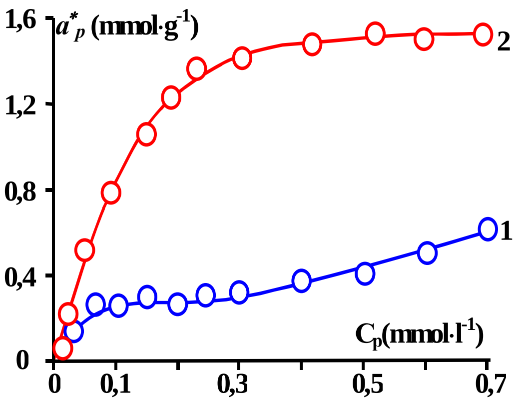

Fig. 2. Adsorption isotherms of $Zn(OAc)_2$ on AC AGN-2K, modified with H_2O_2 (2) and initial AGN-2 (1), at T=25°C.

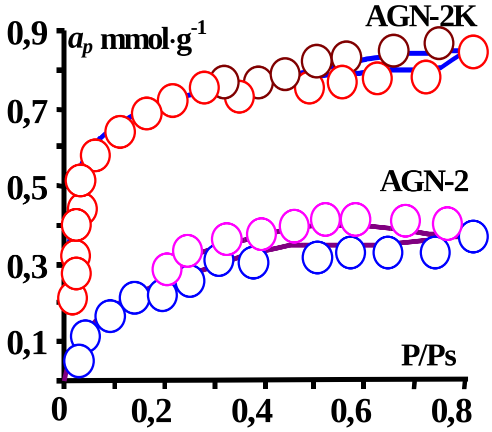

Fig.3. Adsorption isotherms of the vapours AcOH on AC AGN-2K, modified with H_2O_2 and initial AGN-2, at T=25°C.

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PP-I-19

SOME REGULARITIES OF THE PREPARATION OF N-CONTAINING CATALYTIC FILAMENTOUS CARBON BY PYRIDINE DECOMPOSITION

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Nitrogen containing catalytic filamentous carbons (N-CFCs) is a new type of carbon materials. N-CFCs have great importance, primarily, as promising catalyst supports. The synthesis of these carbons with the predetermined properties is complex process because of variety of reactions occurring in the gas phase, on the catalyst surface and on the newborn N-CFC filament itself. In this work we revealed some factors defining the yield, texture and chemical composition of the N-CFCs prepared by deposition of gaseous mixtures of pyridine (C_5H_5N, Py) with H_2 or Ar over $NiCu/Al_2O_3$ catalyst (Ni - 64 wt %, Cu – 4 wt %) at 550-800^{o}C [1, 2].

Table data show the Py decomposition in the presence of H_2 at 750^{o}C provides the maximum N-CFC yield (sample № 4). In case of Py/Ar the yield of carbon decreases more than by an order (sample № 6).

№	Reaction conditions 1)			N-CFC		Oligomers
	T, ^{o}C	mixture 2)	Time, h	yield, g/g (Ni+Cu)	composition 3)	
1	550	Py/H_2	4,50	33	$NC_{104}H_{13}$	-
2	650		4,50	42	$NC_{56}H_6$	-
3	700		4,50	50	$NC_{46}H_5$	-
4	750		4,50	73	$NC_{(32-38)}H_3$	+
5	800		2,25	26	$NC_{33}H_{0,7}$	++
6	750	Py/Ar	4,50	5	$NC_{18}H_{1,4}$	-

1) 0.05 g of the catalyst, atmospheric pressure and flow rate of mixture ~ 6 l/h; 2) [Py] = 10 %, mol; 3) elemental analysis data.

We have concluded that the stage of Py hydrodenitrification (HDN) catalyzed by Ni precedes the N-CFC formation in Py/H_2 mixture. The carbon fragments are formed by decomposition of HDN products, supposedly of C_5-hydrocarbons. As a consequence, such carbons have a lower content of nitrogen in comparison with N-CFC, prepared of Py/Ar mixtures. High catalyst activity in N-CFC formation is explained by lower binding energies in the molecules of C_5-hydrocarbons in comparison with the ones in molecule of pyridine itself.

Electron-microscopic studies testify that the filaments of different morphological types were formed from Py/H_2 and Py/Ar mixtures [2]. The filaments have a diameter from 30 to 180 nm (Fig. 1). Intertwining in chaotic way, the thinner filaments form fascicles of thicker fibers. In the samples prepared from Py/H_2 the diameter of such fibers reaches 0,5 μm.

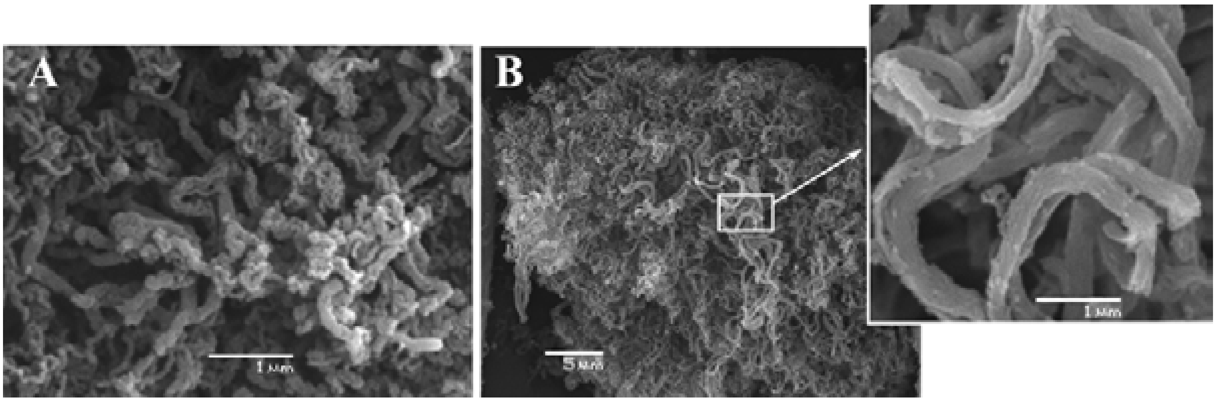

Fig.1. REM-pictures of the samples prepared from Py/Ar (A) and Py/H_2 (B) mixtures at 750°C.

One should note, oligomers were formed as products of uncatalyzed reactions at high-temperature decomposition of pyridine in the presence of H_2 (Table). Their pyrolysis leads to formation of disordered carbon. This material accumulates in the structure of the growing fibers and decreases the values both V_Σ and A_{BET} and influences the surface N/C atomic ratio. Also it can block the active centers of catalyst, leading to its deactivation.

We have selected the temperature interval of Py decomposition predominantly via the catalytic route. The close values of A_{BET}, about 300+/-50 m^2/g (Fig. 2), and TEM data show that mainly CFC is formed at 550-700°C.

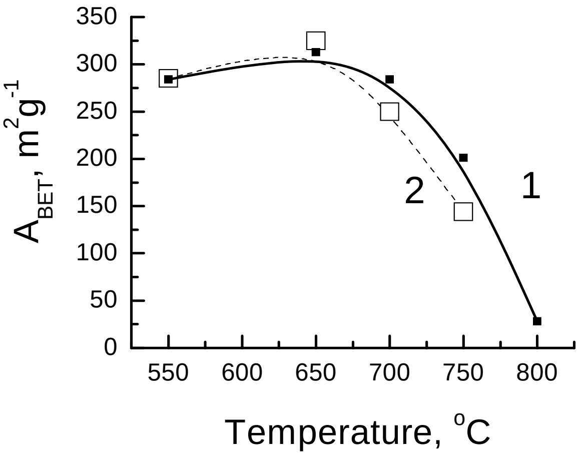

Fig.2. Specific surface area of N-CFC versus the temperature of Py/H_2 decomposition. Time of decomposition: 2,25 h (curve 1), 4,50 h (curve 2).

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PP-I-20

SYNTHESIS OF NITROGEN-CONTAINING CARBON NANOFIBERS: NITROGEN INCORPORATION, STRUCTURAL AND TEXTURAL PROPERTIES

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Carbon nanofibers (CNF) are perspective materials as catalyst supports [1-2]. Modification of CNF with nitrogen atoms enables to vary and control their adsorptive and electrical properties. Therefore synthesis of nitrogen-containing carbon nanofibers (N-CNF) is a progressive field of nanotechnology. Despite the present publications on the preparation of N-CNF the role of nitrogen in the nanofibers growth and physicochemical dependencies of the formation of structure and texture of N-CNF are not clearly established.

The present work is devoted to the development of method for synthesis of N-containing carbon nanofibers and to the investigation of physicochemical dependencies of the N-CNF formation and their properties.

Nitrogen-containing CNF were prepared by the decomposition of ethylene/ammonia mixtures over high-loaded metal catalysts at 550 – 675°C. Catalysts of the following chemical composition were tested: $65Ni-25Cu-Al_2O_3$, $85Fe-5Co-10Al_2O_3$, $62Fe-8Co-30Al_2O_3$, $75Co-25Al_2O_3$ and $72Co-3Mo-25Al_2O_3$. Ammonia content in the reaction mixture was varied from 25 to 75 vol. %. The synthesized N-CNF were characterized by XRD, TEM, XPS, N_2 adsorption, elemental analysis methods. Influence of reaction parameters, such as composition of catalyst and gas mixture, reaction temperature and process duration, on the properties of synthesized carbon material was studied.

It was found that nitrogen content in N-CNF as well as their structural and textural properties are strongly dependent from the synthesis conditions. Comparison of activity of different catalysts in C_2H_4/NH_3 decomposition was made for the selection of the best catalytic system for N-CNF preparation. The highest yield of CNF with the highest nitrogen content was produced over $Ni-Cu-Al_2O_3$ catalyst. Ammonia concentration in the reaction mixture has a great effect on the nitrogen content in N-CNF which can reach value up to 8 wt. %. It was found that lower synthesis temperature favour higher nitrogen concentration in N-CNF. Two different states of surface nitrogen in N-CNF were determined by XPS: pyridinic (BE 398.5 eV) and graphitic (BE 400.8 eV). The ratio of the states is affected by synthesis duration: significant decrease of the percentage of pyridinic nitrogen was observed when the time on stream increased from 1 to 20 h and graphitic nitrogen became the main state in N-CNF produced after 20 h.

Prepared N-containing CNF are the graphitic mesoporous materials as confirmed by XRD, XPS, TEM and N_2 adsorption methods. The surface area varies within the interval of 30 – 350 m^2/g, while the pore size between 5 – 19 nm, depending on the synthesis conditions (Fig. 1). Correlation between the values of surface area and interlayer distance d_{002} in the course of reaction time was observed: maximum BET area of N-CNF with minimum d_{002} were attained at 1 – 2 h. TEM studies showed that formation of helical nanofibers with diameter ranges between 60 and 100 nm takes place during the decomposition of C_2H_4/NH_3 mixtures over Ni-Cu-Al_2O_3 catalyst (Fig. 2). Nanofibers have a ‘herringbone’ structure with graphite layers arranged at an angle of 45 – 75° to fiber axis.

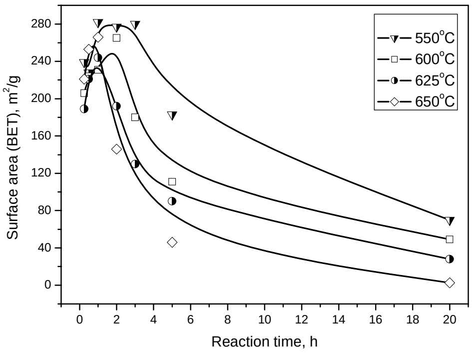

Fig. 1. Dependence of surface area of N-CNF on time on stream for the decomposition of 75%C_2H_4/25%NH_3 mixture on Ni-Cu-Al_2O_3 catalyst at different temperatures.

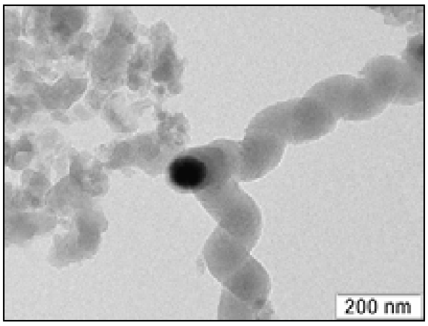

Fig. 2. TEM image of N-CNF grown after 1 h decomposition of 75%C_2H_4/25%NH_3 mixture on Ni-Cu-Al_2O_3 catalyst.

Thus, method of synthesis of nitrogen-containing carbon nanofibers by decomposition of C_2H_4/NH_3 gas mixture on metal catalysts was developed. Influence of the reaction conditions on the nitrogen content and properties of N-CNF were studied. Carbon nanofibers with nitrogen content up to 8 wt. % were prepared. In more detail the experimental results and discussion will be presented in full paper.

Acknowledgements

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PP-II-21

THE CARBON CARRIERS FOR CATALYSTS DECOMPOSITION OF HIGH-TOXIC ORGANIC-CHLORINE COMPOUNDS

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The aim of this research is to produce a new method of formation of nano-sized active cluster centers within pores of a carbon support (CS) under the influence of microwave irradiation (MWI). Besides the solution of vital fundamental problems the investigation is supposed to contribute the production of ecologically pure method of catalytic decomposition of high-toxic organic-chlorine compounds.

The investigation of the influence of MWI on CS and on formation of catalytically active centers in support pores was carried out on the original microwave equipment in the group of catalytic nanotechnologies in A.V. Topchiev Institute of Petrochemical Synthesis RAS. It was established that in carrier pores under the effect of MWI, there takes place a high-velocity destruction of preliminary absorbed in support pores metallic-complexes compounds - precursors to catalytically active clusters, while the support, being a solid body, doesn’t undergo thermal destruction. The irreversible stabilization of atoms and metal clusters becomes possible through the presence in CS of nano-sized micro- and mezopores, in which clusters are formed. It makes the CSs ideal matrices.

The CS porous structure is the decisive factor in the new method of formation of stable nano-cluster catalysts and dictates the necessity to investigate the influence of MWI on the support in relation to the distribution of pores by size. A number of CSs samples with different structure of pores have been investigated. The correlation between the CS pore structure and the kinetics of its heating was established. It made it possible to suggest the mechanism of microwave energy absorption by porous CS which demands the presence in the support structure of nano-sized pores to form the metal clusters and of macropores to create conditions for high-velocity decomposition of metallic-complexes compounds.

The investigation has been completed under the financial support of RFBR, grant № 05-03-32577

CARBON-SUPPORTED 12-MOLYBDOPHOSPHORIC ACID ($H_3PMo_{12}O_{40}$) FOR THIOPHENE HYDRODESULFURIZATION

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In the oil-processing industry hydrotreating is a large-scale operation applied to remove hetero atoms such as sulfur and nitrogen form organic molecules present in crude oil fractions. The industrially applied hydrotreating catalysts contain molybdenum or tungsten sulfide promoted by cobalt or nickel, supported on alumina. The increasing need for efficient removal of the hetero atoms is a continuous drive for further development of hydrotreating catalysts.

Carbon-supported catalysts have been found to display a higher activity in hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD) reactions than transition metal sulfide supported on conventional carriers such as alumina or silica. The activated carbons are inexpensive carriers that are weakly reactive to loaded active components, stable to feed stock poisons and with high surface area. Recovering of expensive metals by burning of spent catalysts is an additional advantage of carbon as a catalyst support.

A series of activated carbons has been prepared by steam pyrolysis of apricot and cherry stones at 923 – 1073 K for 2 h. Carbon samples prepared at 923 and 973 K from apricot stones and at 1073 K from cherry stones are denoted as C-1, C-2 and C-3, respectively. The activated carbons were intensively washed with destilled water by decantation up to neutral pH reaction of suspension. Finally the samples were dried 6 h at 390 K.

Catalysts were prepared by pore-volume impregnation of the washed carbons with an $H_3PMo_{12}O_{40}$ x H_2O (p.a. Fluka) (HPMo) aqueous solution. The samples were heated for 2 h at 350 K and 4 h at 390 K. The molybdenum content in all samples was 12 wt. %. Hydrodesulfurization of thiophene was used as test reaction. Reduction or sulfidation by H_2S were applied for the catalyst activation. The thiophene conversion was measured at 623 K in a fixed-bed reactor.

The activated carbons were characterized by N_2 adsorption. The isotherms for all samples are typical for carbons with wide pore size distribution. Activated carbons produced from various agricultural by-products showed different pore size distributions, depending on pyrolysis and activation conditions. The adsorption characteristics of the activated carbons produced from various agricultural by-products were found to be different and dependent on the composition and structure of the raw materials. A principal part of micropores has radius about 2 nm. The higher temperature of the carbonization leads to formation of a more fine porous structure. The activated carbons loaded with the HPMo changed their surface and pore distribution. The impregnated species close micropores of radius below 2 nm. The surface area located in the narrowest micropores (smaller than 2 nm) will not be available for loading with the active component. The 12-molybdophosphoric acid adsorbed strongly on activated carbon, and the adsorption involved proton transfer from the HPMo to the carbon.

Results of thiophene conversion show that carbon surface, pore structure and catalytic pretreatment by H_2 or H_2S affect the evolution of hydrodesulfurization activity, which depends on two simultaneously proceeding processes of active site formation and deactivation [1]. Heterogeneity of the high carbon surface makes the distribution of the molybdenum precursor in the catalyst non-homogeneous. The chemical state and surface composition of oxide and used catalysts were revealed by X-ray photoelectron spectroscopy.

The flexibility of the carbon surface is the reason for the changes observed at every step of catalyst preparation. Carbon peculiarities as well as catalyst activation affect initial thiophene conversion. The results show that during H_2S pretreatment of the sample. The hydrogen sulfide reacts with Mo species as well as the carbon sites. The results have shown that the activated carbon with appropriate meso/micropores ratio originated from apricot stones is suitable as catalyst support.

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CARBON SUPPORTS FOR IMMOBILIZATION OF ENZYME GLUCOAMYLASE FOR SWEETENERS PRODUCTION FROM STARCH

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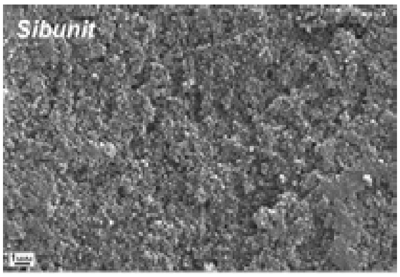
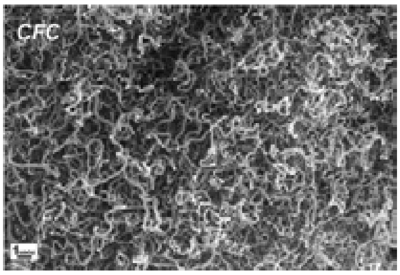
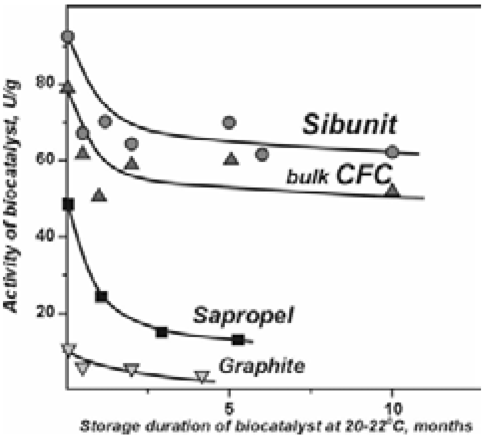
The exploitation of renewable feedstock such as starch to produce the sweeteners for food industry is still of great importance. Now the all stages of starch–feedstock processing relies at homogeneous conditions. The heterogeneous regimes of the starch dextrin hydrolysis to treacle performing with the immobilized glucoamylase are more attractive and feasible for economy. Fist and foremost, the highly stable biocatalysts with the half-life-time ($t_{1/2}$) of 30-120 days are required for implantation of this heterogeneous process into large-scale industry.





Comprehensive investigations for the development of the high stable heterogeneous biocatalysts for dextrin hydrolysis were carried out. Different granulated carbon supports; in particular Sibunit (carbonized soot), bulk catalytical filament carbon (CFC), Sapropel (carbonized lake silt) and Graphite were studied for adsorptive immobilization of glucoamylase. The biocatalytical properties (activity and stability) were found to depend strongly on porous structure and surface morphology. Mesoporous supports like Sibunit and bulk CFC, covered by pyrolytic and filamentous carbon layers (Foto) provided the highest activity and stability of the immobilized glucoamylase in comparison with macroporous Sapropel and Graphite (Fig). The stability of the glucoamylase immobilized on Sibunit was observed to be 105-fold higher than the stability of soluble enzyme. This highly stable biocatalyst did not lose their glucoamylase activity for the more than 30 days under operation conditions of dextrin hydrolysis at 60OC that satisfied the above requirements for commercial available biocatalysts.



PP-I-24

SINGLE WALL CARBON NANOTUBE MATERIAL AS A SUPPORT FOR Pt CATALYST

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Application of single wall carbon nanotubes (SWNTs) as a support for catalysts has several features in comparison to other carbon materials. Purified SWNTs easily aggregate with each other forming microcrystals (ropes) because of strong Van der Waals forces between nanotube walls to be present as highly entangled mats formed by such ropes. Powder of purified SWNTs produced by standard technology from the arc process raw material [1,2] contains mostly nanotube mats in size of several tens of microns. Nevertheless the powder has a large specific surface area of ~ 200 – 400 m^2/g.

Nanotubes themselves and their ropes are very stable structures, which can not be broken into pieces even under long sonication in a liquid. Standard methods of SWNT dispersion by means of ultrasonic treatment in solutions of surface active agents do not lead to a complete dispersion of SWNT into individual nanotubes (nano-dispersion). After sonication the solution contains filaments of different sizes – from separate nanotubes of ~ 1,5 nm in the diameter and less than 1 μm long up to ropes of 0.1 – 0.2 μm in the diameter and a few tens of μm long. Due to strong optical activity of SWNT crystals [3] the level of nanotube dispersion can be easily estimated by polarized light in an optical microscope. One can separate a SWNT dispersion by centrifugation into several fractions, which will contain SWNT ropes of nearly the same sizes. Specific surface area of carbon filaments into such fractions may be varied from ~ 600 m^2/g up to the upper limit for carbon material of ~ 1360 m^2/g (solution of individual nanotubes). The solutions of individual nanotubes and their ropes can be used as a support for catalyst precipitation in wet chemistry. Due to a large specific surface area of carbon nanostructures in the solution the catalyst particles may have small sizes of about 2 – 5 nm even by 10 –20 wt. % loading of metals (Fig.1).

A serious obstacle in the way of SWNT application in the catalysis is the high price of purified SWNTs, which may stay at the level of \$60 - \$100 per 1 gram during the nearest years [1]. Nevertheless in some occasions the high price seems not to be a hindrance. For example, in the polymer electrolyte fuel cell the catalytic and intermediate layers both have to be no thicker than 1 – 3 μm. For preparation of this structure the consumption of SWNT material pro unit area of the electrode would be no more than ~ 0.5 mg/cm^2. Even if the high purity SWNTs produced by the arc technology (at the price of ~ 100 $/g) are used, the price of the catalytic and intermediate layers would be ~ 0,05 $/см^2. For comparison, the carbon paper produced by Ballard Co., USA, is widely used as the gas diffusion layer, and provides the same contribution to the cost of the layer ~ 0,05 $/cm^2.

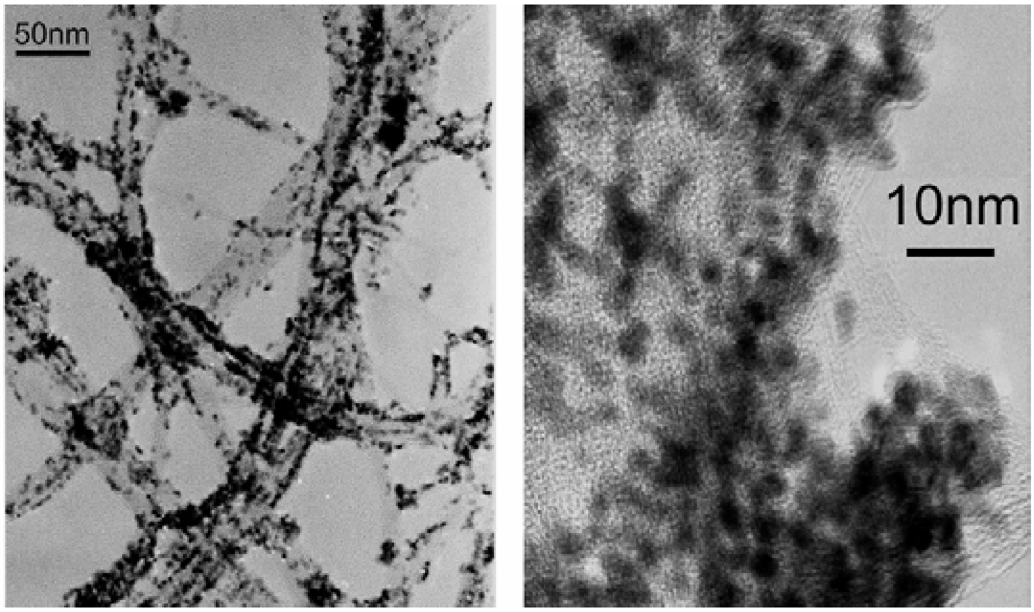

Fig.1. Transmission electron microscopy. The Pt catalytic particles on the surface of SWNT ropes at 10 wt. % Pt loading.

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PP-I-25

POROUS CARBON PRODUCED BY LOW-TEMPERATURE DEHYDRO-HALOGENATION AND HEAT TREATMENT OF CARBON-CHAIN POLYMERS

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Synthesis of porous carbon with high adsorption ability on the basis of carbon-chain halogenated polymers (polyvinylidene fluoride, polyvinylidene chloride, polyvinyl chloride, etc.) has been carried out in three stages: low-temperature processing by the strong bases (dehydrohalogenation) of polymeric precursor and subsequent heat treatments: carbonization (in the inert atmosphere) at temperature up to 400-600 ^{0}C and activation (up to 950 ^{0}C).

For selection of the activation conditions the method of step pyrolysis gas chromatography in various gaseous mediums was used. It has been shown, that the received carbon structures possess high reactivity at the gasification with agents both of oxidizing and reducing character. The conditions of achievement of high values of a specific surface (~1800 m^2/g), porosity (~ 2cm^3/g) and adsorption capacities on benzene vapor (~1100 mg/g) are found as a result.

The dehydrohalogenation was conducted in the polar organic solvents in the presence of alkaline metals hydrates or alcoholates as in a solution of initial polymer when the maximal depth and uniformity of transformation is reached, and in the heterogeneous conditions with preservation of morphology of an initial material, in particular, fibres.

Dehydrohalogenation of polyvinylidene fluoride and polyvinylidene chloride at similar conditions was used earlier for synthesis of linear - chain carbon (carbyne) [1].

According to the data of Raman spectroscopy (He-Ne laser, λ=632,8 nm) the polyene structures (systems of the conjugated double bonds) prevail in the products of chemical low-temperature dehydrohalogenation. At the raised temperatures these structures are easily transformed to typical disordered graphitic carbon in which the porous structure develops at the subsequent gasification.

The investigation of the textural characteristics and properties of produced samples was performed by N_2 (77 K), CO_2 (273 K) and H_2 (77 K) adsorption method. The characterization of microporous structure was based on the theory of volume filling of micropores (TVFMP). The characterization of mesopores was based on the Derjaguin-Broekhoff-de Boer (D-BDB) method with the purpose of calculation of formal pore size distributions (PSD). The received adsorption branches isotherms were additionally processed by the method of the non-local density functional theory (NLDFT).

The samples of porous carbon have clearly demonstrated high volume of ultra- and super-micropores (0.4-0.7 cc/g). The calculated PSD (according to NLDFT-N_2) show the narrow form (0.6-1.2 nm). The mesopores volume is insignificant after heat treatment in the inert medium, but as the result of gasification it reaches greater sizes (up to 1,4 cc/g). It is interesting, that carbonized samples already possess the considerable micropores volume which naturally increases during activation without essential change of their structural heterogeneity.

The received samples possess higher adsorption capacity on hydrogen ($\boldsymbol{\alpha}$) at atmospheric pressure and 77 K (up to 1,8 % mass.) than well-known carbon adsorbents with comparable values of specific surface. A linear relation between values of $\boldsymbol{\alpha}$ and the ultramicropore volume (CO_2 micropore volume) for the synthesized samples of porous carbon was found. The same straight-forward correlation has been obtained for carbon systems with various structure and morphology [2].

The obtained data allow to assume, that the sizes and a positional relationship of the structural elements of porous carbon in a considered case are determined by the low-temperature stage of the synthesis because the stabilized structures with system of the conjugated double bonds are formed.

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PP-I-26

Pt-NANOCLUSTERS SUPPORTED ON CARBON NANOMATERIALS

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Carbon nanomaterials (CNM) are considered as convenient supports for metals nanoclusters because of developed surface, electroconductivity and ability to electrons transfer. Both these properties and synthesis methods readiness in grams scale allow to consider features of platinum nanoclusters fixation onto CNM and show advantages of these materials as a catalysts for redox processes in the present paper.

Products of electroarc graphite evaporation such as X-ray amorphous carbon (AC) after fullerenes extraction, multi-walled carbon nanotubes (MWNT) from cathode deposit spongy part, wherein a graphite rods diameters are 10 mm, current intensity is 100 A, He pressure is 500 Torr and the yields in optimal conditions are 15 and 90 % per evaporated graphite weight; single-walled nanotubes (SWNT) with yield of 10 % per composite of graphite with Ni-Y catalyst weight and carbon nanofibers (CNF) as product of pyrolysis of $C_2H_4/H_2/Ar$ = 30:52:18 % vol. mixtures at 550°C over $LaNi_5$ are used as catalysts supports.

AC and MWNT with specific surface areas 287 and 25 m^2g^{-1} are used without purification . SWNT is purified from AC and catalysts impurities by an alternative stages of HCl conc. treatment and step-like air oxidation (from 300 to 550ºC), that allows to assume of SWNT content about 80 % and specific surface area to 380 m^2g^{-1}. CNF were purified from catalysts impurities by ultrasonic cleaning in HCl conc. during 3 h and sample with trace metal content and specific surface area to 58 m^2g^{-1} is obtained. Used CNM appreciably are differ in a structure and in a reactivity (for example in the air thermogravimetry, fig. 1). So, SWNT, MWNT and CNF include plane or convolute graphene letters in the main but AC contains an alternate unconjugated single and double bonds in five- and six-member rings. SWNT, MWNT and CNF are oxidized by HNO_3 conc. at 70ºC for “anchor” groups introduction. AC is used without pretreatment or brominated with following alkaline saponification. Both Br- and hydroxyl-derivatives of AC with the gross-formula $C_{10}(OH)$ formation are shown by IR-spectroscopy and elemental analysis. These treatment methods allow to increase oxygen-containing groups content in the samples that these groups does not contain at first. Non-oxidative methods of “anchor” groups for Pt-ions introduction that are especially applicable for CNM with graphite-like structure also are developed.

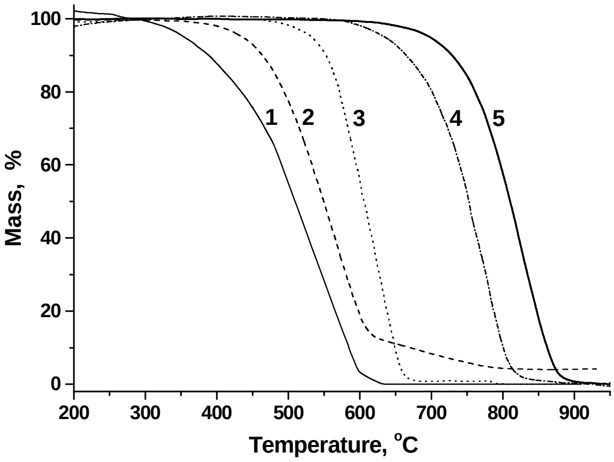
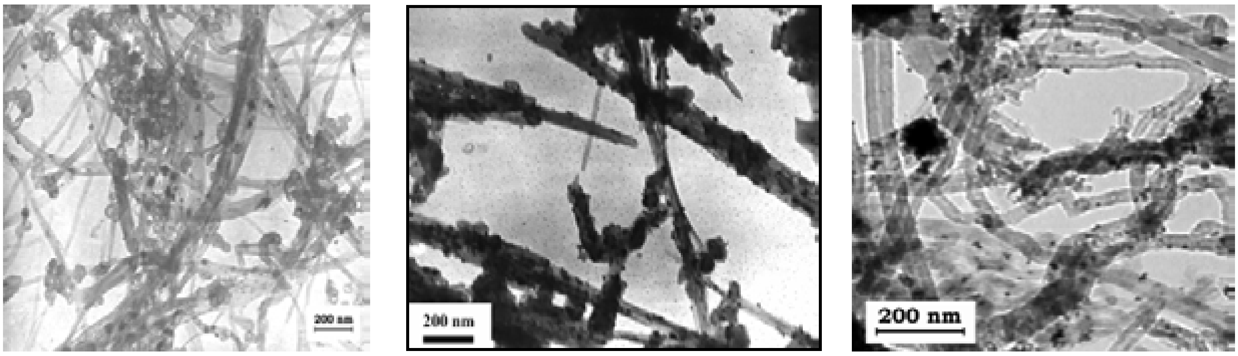


Fig. 1. TG curves for carbon nanomaterials: 1 – AC, 2 – SWNT, 3 – CNF, 4 – MWNT, 5 – graphite.

Platinum fixation onto “anchor” groups that by both IR- and thermogravimetry data are carboxylic, quinoid and hydroxylic are produced from H_2PtCl_6 at addition of base that does not converts $PtCl_6^{2-}$ into $Pt(OH)_6^{2-}$, which have complexes that in water are poor soluble.

The following Pt-containing CNF reduction by $HCOO^-$-ions allows to obtain Pt(0) nanoclusters supported onto CNM with dimensions 5-8 nm determined by both TEM (fig. 2) and X-ray diffraction data that are not separated at ultrasonic machining. Pt(0) clusters obtained by electrodeposition or without “anchor” groups introduction are significantly bigger and not fixing.



a b c

Fig. 2. TEM images of 12 % Pt/CNM: a - SWNT, b - MWNT, c - CNF.

PP-I-27

FeMo CVD CATALYSTS FOR THE SELECTIVE PREPARATION OF SINGLE-WALLED CARBON NANOTUBES

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Nowadays, carbon nanotubes have become a strategic material in the area of nanotechnologies, and an increasing interest exists from the catalysis community [1,2]. Among the different kind of filamentous carbon single wall nanotubes (SWNT), multi wall nanotubes (MWNT) and graphite nanofibers (GNF) can be distinguish. SWNT are often considered as perfect 1D nanostructures so that their peculiar properties have been intensively studied by physicists and chemists. As far as the synthesis processes are concerned, catalytic chemical vapor deposition (C-CVD) seems to be the most promising technique in view of an industrial scale production. Currently, GNF and MWNT can be produced selectively by C-CVD on a large scale. However, for SWNT, catalytic systems performances in terms of selectivity and activity are still relatively low. One of the main challenge for the catalytic growth of SWNT is the control of the catalyst nanoparticles size distribution during the high temperatures (800-1200°C) process.

Chemical vapor deposition is today a well established technique for the preparation of highly dispersed supported metal catalysts [3]. However, only scarce reports described the use of CVD supported catalysts for carbon nanotubes growth [4,5]. Thus, MWNT were produced from acetylene on FeMo/Al2O3 catalysts [4], and we have also reported a very active and selective Fe/Al2O3 catalyst prepared from [Fe(CO)5] for MWNT growth from ethylene [5].

In this work, we report for the first time results dealing with SWNT growth by C-CVD on catalysts produced by fluidized bed organometallic CVD. First results dealing with the catalytic performances of PtRu/SWNT systems for the selective hydrogenation of cinnamaldehyde will be also presented.

The heterobimetallic FeMo/Al_2O_3 CVD catalysts have been prepared from [$Fe(CO)_5$] and [$Mo(CO)_6$]. The SWNT have been prepared by catalytic CVD from methane at 900°C. We demonstrated first that monometallic Fe/Al_2O_3 and Mo/Al_2O_3 systems are not effective for this reaction and that the SWNT synthesis requires the production of small iron particles from the reduction of highly dispersed $FeMoO_4$ phase. Such highly dispersed oxide phase has been obtained from slow oxidation of bimetallic FeMo catalysts. The activity and selectivity towards SWNT production is also strongly dependent on two key parameters: the Fe/Mo molar ratio and the gas phase composition. Low Fe/Mo ratio favours SWNT production. Concerning the gas phase composition, $N_2/H_2/CH_4$ mixtures allows low selectivity towards SWNT whereas Ar/CH_4 mixtures allow to produce SWNT with selectivity as high as 75% (see Table and Figure below).

Finally, after a simple purification step, we have used the SWNT containing material as support for PtRu bimetallic catalysts preparation. Preliminary results concerning the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol with this bimetallic systems show promising results.

Table: Catalyst activity and selectivity

System[a]	**Activity**[b] **(g_C/g_{cata})**	**SWNT selectvity**[c]
Fe	0,1	0
Mo	10	0
Fe_5Mo_{10}	5,5	~30
Fe_4Mo_{10}	5.8	~40
Fe_3Mo_{10}	8,1	~70
Fe_1Mo_{10}	2.9	~75

a) Fe-Mo weight ratio b) from TGA; c) from TGA and TEM observations

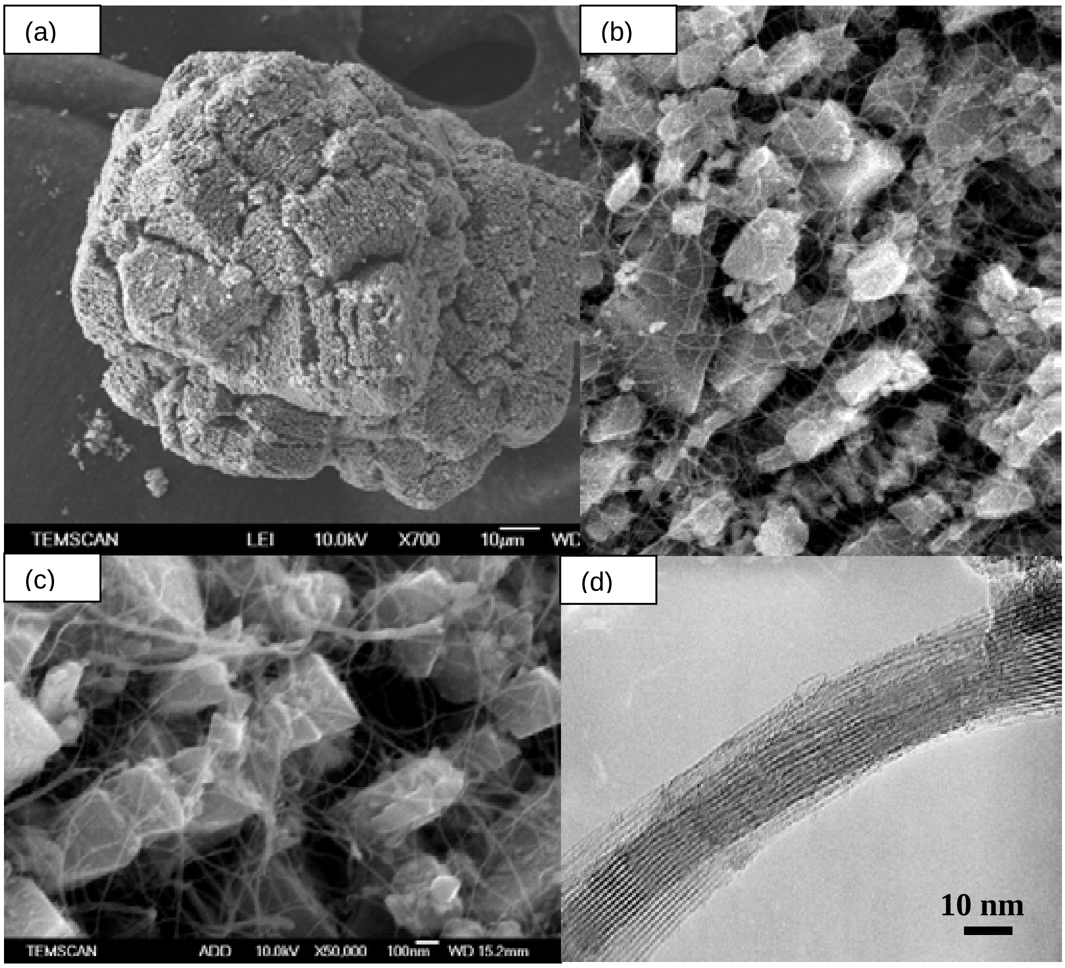

Figure: Micrographs of the product: (a) SEM-FEG of a catalyst grain after C-CVD of methane; (b) higher magnification of the surface; (c) bundles of SWNT on the surface of Fe_xMo_y/Al_2O_3 catalyst; (d) HTEM of SWNT bundles.

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CONTROLLING DIAMETER AND PRESENCE OF DEFECTS OF MULTI WALLED CARBON NANOTUBES BY CVD OVER Fe/Co SBA-15 CATALYSTS

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The use of carbon nanotubes (CNT) opens new perspectives in electronics, sensors, nanoelectromechanical systems, and in the field of catalysis. The diameter and chirality of CNT determine their physical and chemical properties, but still there are limited data on how to control these properties. Limiting to the synthesis of CNT by catalytic hydrocarbon decomposition over metal particles (usually Fe, Co, Ni), because this is one of the preferable methods for larger-scale and low-cost production, it was reported by different authors that the CNT diameter depends on the metal particles size. However, it is unclear whether or not the characteristics and modality of growing of the CNT could also depend on this parameter. Due to the quite different range of reaction conditions, catalyst composition and type of feed used by the different authors in literature, it is also not possible to derive clear information from these results.

In order to contribute to clarify this question, we have prepared FeCo catalytic nanoparticles stabilized inside an ordered mesoporous matrix (SBA-15) or located on the external surface of this mesoporous matrix. The former FeCo particles have uniform size of around 6 nm, the same size of the channels of the SBA-15 we used in this work, while the particles located on the external crystals have a size slightly larger, of around 30 nm, as shown by TEM characterization. Both types of particles have the same composition.

The synthesis of CNT was made by CVD of propane. Under exactly the same reaction conditions, these two type of FeCo nanoparticles give rise to multiwalled carbon nanotubes (MWCNT) with a diameter close to that of the catalyst nanoparticles, but having a different way by which the graphene sheets are rolled up.

The amount and purity of the carbon nanotubes produced by C_3H_8-CVD over Fe/Co SBA-15 catalyst was monitored by temperature programmed oxidation (TPO) in a thermogravimetric apparatus. The yield of carbon nanotubes obtained ranges in the 20-30% wt (with respect to total catalyst), and between 300-500% wt with respect to the active catalytic component.

Quite interesting TEM images reveal that open-ended carbon nanotubes were obtained, while usually CVD methods bring to close-ended carbon nanotubes. The formation of open carbon nanotubes indicates an "End-Growth" mechanism.

Figures 1a and 1b show high resolution TEM images of one of the smallest and largest carbon nanotubes, respectively, with details of the ordering of the carbon walls. While for the smallest carbon nanotubes (8 nm) the graphitic sheets (10 walls) are well ordered parallel to the growing direction of the nanotubes, an apex angle of 45 degree was found for the largest nanotubes, suggesting a different mechanism of growing of the nanotubes (zig-zag and armchair type, respectively) inside and outside the SBA-15 channels. In general, the smallest nanotubes show also a lower presence of defects in the ordering of the graphitic sheets with respect to the largest nanotubes.

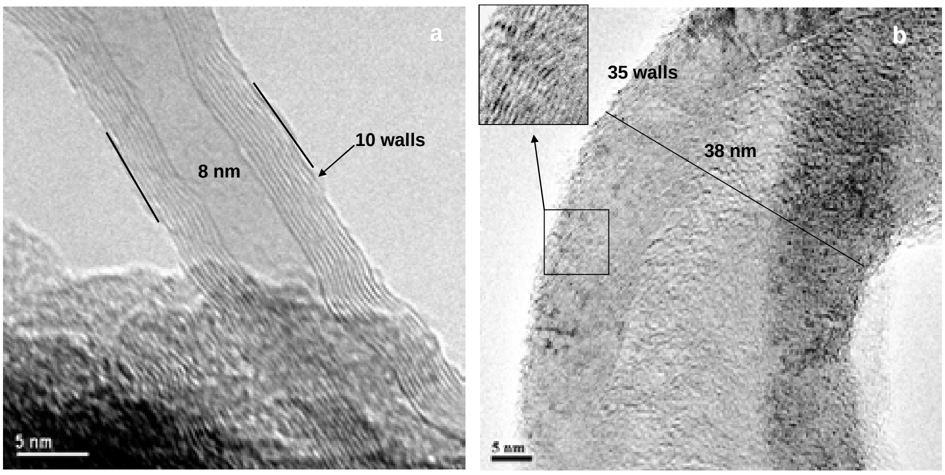

Figure 1. (a) High resolution image of a small carbon nanotube with a detail of the ordering of the carbon walls. (b) High resolution image of one of the largest carbon nanotubes.

In conclusion, this work indicates that the confinement effect due to the localization of catalyst nanoparticles inside the well ordered channels structure of the SBA-15 support may be not only a method to control the dimension of MWCNT, but also a method to control their helicity, the presence of defects and the growing mechanism.

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INFLUENCE OF GAS OXIDATIVE TREATMENT ON MECHANICAL AND CATALYTIC PROPERTIES OF CARBON NANOFIBER COMPOSITE

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Carbon nanofibers (CNFs) produced by catalytic chemical vapor deposition (CCVD) method have shown to be promising candidates for catalysts and catalytic supports, owing to their unique physical and chemical as well as mechanical properties. CNFs as produced are generally in form of fine powders or granules, however, rendering their handling difficult in industrial catalytic reactors. Therefore, it is necessary to transform the nano-structured CNFs into macro-structured catalytic materials. One of the approaches is to intentionally synthesize CNF pellets by shaping process using resin binder, resembling the manufacture process of coal-based activated carbon. Activation is a crucial step for an activated carbon to adapt its textural property and surface chemistry for different purposes, so does the shaped CNFs which are composed of CNFs and the binder-derived carbon. This paper will discuss the influence of gas oxidative treatment on mechanical and catalytic properties of the CNF composite, in order to evaluate the application potential of CNFs in industrial catalysis.

A type of fishbone CNFs is produced in a horizontal quartz tube reactor at 600 °C using 20% (wt) Fe/γ-Al_2O_3 as growing catalyst and CO/H_2 mixture as carbon-containing gas. The CNFs are mixed with a polyglycol-dissolved phenolic resin and then molded using a pellet-compressing machine to produce pellets of designed size and configuration. Carbonization of the polymer binder in pellets is carried out at 800 °C in a flowing Ar stream for 6 hr. The prepared CNF composite is further subjected to gas phase activation for 10 hr using O_2 of different mol-fraction in Ar (2%~10%) at various temperatures (300~450 °C). Side compressive strength of CNF composite pellets is detected on a mechanical testing instrument. Because carbon catalysts have been reported to be highly efficient for oxidative dehydrogenation of ethylbenzene to styrene (ODE), the catalytic performance of the CNF composite is investigated for the ODE reaction in a fixed bed flow reactor. The reaction temperature is set at 380 °C and the gaseous reactants consist of 2% O_2 and 2% ethylbenzene in volume, balanced with Ar.

The experimental results obtained are listed in Table 1, including the weight loss, the side compressive strength, and the catalytic activity and selectivity of the CNF composite after gas oxidative treatment, as compared to the composite without treating. The conversion of ethylbenzene and the selectivity to styrene over the composite given in Table 1 are determined when the ODE reaction has proceeded for about 300 min, nearly reaching a steady state. It is clear that stronger oxidation degree of the composite results in higher catalytic activity but lower mechanical strength.

Table 1 Weight loss, mechanical strength, conversion and selectivity for ODE of the CNF composite

CNF composite	Weight loss (%)	Strength ($N \cdot mm^{-1}$)	Conversion (%)	Selectivity (%)
Untreated	0	31.8	28.1	88.1
300-2%[a]	0.8	24.1	27.8	89.5
350-2%	2.5	19.3	33.1	94.6
400-2%	7.9	13.5	34.2	94.7
450-2%	12.4	16.1	39.9	95.8
300-5%	0.5	24.1	37.2	93.3
350-5%	4.4	15.8	38.0	92.9
400-5%	12.3	6.5	42.5	93.6
450-5%	24.2	2.9	47.6	93.7
300-10%	1.0	22.4	40.2	90.3
350-10%	5.8	15.4	41.5	95.1
400-10%	14.0	6.0	46.7	93.1
450-10%	45.9	-[b]	58.4	89.4

a. 300-2% means the composite is treated at 300 °C with 2% O_2; b. the composite is brittle after treating.

The N_2-physisoption and TPD measurements of the CNF composite are made to find out the variations of the texture and the surface chemistry of the composite treated under different oxidation conditions. The metal content in the composite from growing catalyst is also analyzed. The influence of gas oxidative treatment on the mechanical and the catalytic properties of the CNF composite is discussed on the basis of characterization results.

EXPERIMENTAL VALUES OF THE ENERGY AND ENTROPY CHARACTERISTICS OF THE HYDROGEN-CARBON INTERACTION, RELEVANCE TO THE CARBON CATALYTIC ACTIVITY

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The results of the thermodynamic analysis [1,2] of the most significant experimental data on the hydrogen sorption by graphite and related novel carbon-based nanomaterials (fullerenes, single- and multi-walled nanotubes (SWNT, MWNT), graphite nanofibers (GNF), nanostructured graphites) are presented. The thermodynamic and kinetic (diffusion) characteristics of sorption processes are refined (Table 1), which can be used for optimizing and a better understanding of the carbon catalytic activity (in the Carbo-Cat processes).

Table 1. Some characteristics and mechanisms of chemisorption and diffusion of hydrogen in isotropic graphite and related carbon nanostructures (processes I,II,III,IV), [1,2]

Chemisorption of hydrogen in *sp*^{2} carbon materials	Models of chemisorption and diffusion of hydrogen in the materials; energies of formation of the chemical bonds	Characteristics of chemisorption and diffusion of hydrogen in the materials	Type of the sorption isotherm
Process III (thermodesorption peak) in isotropic (Fig. 8, in [1]) and nanostructured graphites, and GNFs.	Dissociative chemisorption of hydrogen between the graphene layers («reactions» (4)-(7) in [1]). Bulk diffusion of hydrogen atoms, accompanying with a reversible trapping the diffusant by the chemisorption "centers" on the garphene layers, model F* (Fig. 9, in [1]); $\Delta H_{(form.C\text{-}H)III} \approx -243$ kJ/mol(H).	$\Delta H_{(7)III} \approx (1/2\ \Delta H_{(diss.H2)} + \Delta H_{(form.\ C\text{-}H)III}) \approx -19$ kJ/mol(H), $\Delta S_{(7)III}/R \approx -14{,}7\ (-15{,}4)$ ($X_{III\ max} = 0{,}5\ (1{,}0)$); (Eqs. (8)-(10) in [1]). $D_{III} = D_{0III}\exp(-Q_{III}/RT)$, $D_{0III} \approx 3\cdot10^{-3}$ cm^2/s, $Q_{III} \approx (Q_{(latt.)} - \Delta H_{(form.C\text{-}H)III}) \approx 250$ kJ /mol(H); $Q_{(latt.)} \approx 7$ kJ/ mol(H); (Eqs. (11), (12) in [1]).	Sieverts-Langmuir (Eq. (9) in [1]).

Chemisorption of hydrogen in sp^2 carbon materials	Models of chemisorption and diffusion of hydrogen in the materials; energies of formation of the chemical bonds	Characteristics of chemisorption and diffusion of hydrogen in the materials	Type of the sorption isotherm
Process II (TPD peak) in isotropic (Fig. 8, in [1]) and nanostructured graphites, GNFs, defected SWNTs and MWNTs.	«Dissociative-associative» chemisorption of H_2 in the intergrain or defected (surface) regions (“reactions” (13)-(16) in [1]). Diffusion of H_2 in these regions, accompanying with a reversible dissociation and trapping of the diffusant on the chemisorption “centers”, model H (Fig. 9, [1]); $\Delta H_{(form.C=2H)II} \approx -570$ kJ/mol(2H).	$\Delta H_{(16)II} \approx (\Delta H_{(diss.H2)} + \Delta H_{(form.C=2H)II}) \approx -120$ kJ/mol(H_2), $\Delta S_{(16)II}/R \approx -30$ (for $X_{II\,max} = 0{,}5\ (0{,}25)$); (Eqs. (25), (26) in [1]). $D_{II} = D_{0II}\exp(-Q_{II}/RT)$, $D_{0II} \approx 1{,}8\cdot10^3$ cm^2/s, $Q_{II} \approx (Q_{(def.)} - \Delta H_{(16)II}) \approx 120$ k J/mol(H_2); $Q_{(def.)} \approx 10$ k J/mol(H_2); (Eqs. (22), (24), [1]).	Henry-Langmuir (Eq. (25) in [1]).
Process I (TPD peak) in isotropic graphite (Fig. 8, in [1]), SWNTs and MWNTs.	«Dissociative-associative» chemisorption of H_2 in surface layers of the material («reactions» (13)-(16) in [1]). Diffusion of H_2 in these layers, accompanying with a reversible dissociation and trapping of the diffusant on the “centers”, model G or F (Fig. 9, [3]); $\Delta H_{(form\ C=2H,C2=2H)I} \approx -460$ kJ/mol(2H).	$\Delta H_{(16)I} \approx (\Delta H_{(diss.H2)} + \Delta H_{(form.\ C=2H,\ C2=2H)I}) \approx -10$ kJ/mol(H_2), $\Delta S_{(16)I}/R \approx -20$ (for $X_{I\,max} \approx 0{,}5$ (),25)); (Eqs. (20), (21) in [1]). $D_I = D_{0I}\exp(-Q_I/RT)$, $D_{0I} \approx 3\cdot10^{-3}$ cm^2/s, $Q_I \approx (Q_{(surf.)} - \Delta H_{(16)I}) \approx 20$ kJ /mol(H_2); $Q_{(surf.)} \approx 10$ kJ /mol(H_2); (Eqs. (17), (19), [1]).	Henry-Langmuir (Eq. (20) in [1]).
Process IV (TPD peak) in isotropic (Fig. 8, [1]), pyrolytic and nanustructured graphites.	Dissociative chemisorption of H_2 in defected regions of graphite lattice («reactions» (4)-(7) in [1]). Bulk diffusion of H in the defected regions, with the trapping by the «centers», models C, D (Fig. 9, in [1]); $\Delta H_{(form.C\text{-}H)IV} \approx -364$ kJ/mol(H).	$\Delta H_{(7)IV} \approx (1/2\ \Delta H_{(diss.H2)} + \Delta H_{(form.C\text{-}H)IV}) \approx -140$ kJ/mol(H); (Eq. (27) in [1]). $D_{IV} = D_{0IV}\exp(-Q_{IV}/RT)$, $D_{0IV} \approx 6\cdot10^2$ cm^2/s, $Q_{IV} \approx -\Delta H_{(form.C\text{-}H)IV} \approx 365$ kJ /mol(H); (Eq. (28) in [1]).	Sieverts-Langmuir (Eq. as (9) in [1]).

D_{0III}, D_{0II}, D_{0I}, D_{0IV} - the pre-exponential (entropic) factors of the hydrogen diffusion coefficients in the carbon materials corresponding to processes III, II, I, IV.

Acknowledgements

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PP-I-31

TRANSPARENT CARBON COATINGS OF ULTRA FINE DIAMOND

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Carbon coatings were widely used in different fields of technology. Diamond-like coatings are most attractive as they are transparent, inert and stable in aggressive medium. They are usually obtained by CVD method using different organic gas diluted with hydrogen as precursor material. Unlike the CDV techniques which require sophisticated equipment, sol-gel method of deposition of the films may offer an easy and cost effective technology route which may allow one to obtain good quality thin films.

Low-temperature method for depositing Ultra Fine diamond (UFD) films by a simple wet chemical route is presented. UFD is produced from detonation synthesis of explosive substances. It was prepared in an explosion chamber in inert gas atmosphere and explosive substance (3-nitrotoluen, trotil) was kept inside the chamber. After explosion the powder obtained contained about 8 to 20 % of UFD. This powder is undergoes purification by etching of graphite carbon. Finally powder consists of diamond particles with dimensions of 4 – 20 nm and their aggregates.

Suspension of UFD in organic solvents could be obtained by using physical extraction method using organic liquids. Nanoparticles have tendency to diffuse in organic phase from aqua phase. In this process, purification of UFD also takes place because the metal impurities are not extracted into the organic phase while the ultrafine particles of UFD are crossed in organic phase. The calculations based on optical investigation showed that the dimensions of UFD-particles in organic suspensions are in the region of 2-6 nm.

The transparent UFD suspensions in aliphatic and alicyclic carbohydrates were made. The loading of UFD-suspensions varied between 0,03-0,05 g/dm^3 in hexane, octane, toluene. The removal of solvent from suspension allowed reaching their concentration 0.6-1.0 g/dm^3. At the further evaporating the suspensions was loosed the transparency with the initiation of precipitation. The specific conditions for stable suspension obtaining were developed. Different kinds of additions were tested.

Formation of carbon suspensions of the Ultra Fine Diamond (UFD) in organic liquids is a promising area for obtaining useful carbon coating on different substrates. The organic suspensions of UFD had low values of surface tension and could easily wet different substrates to form films by dipping technique. The films were deposited on silicon, quartz and other substrates arranged upright by dip coating technique. The surface of the substrates and the effects of the organic medium stimulated a structural organization. The following evaporation of organic phase on the substrate was carried out at the temperature 300-350 °C, which did not exceed the temperature of diamond oxidation and by thermograph investigations of UFD powders, the mass loss in air started at 500 °C. The choice of organic liquids was determined from their ability to wet the substrate completely and their low temperatures of evaporation. The second factor provided the ability to preserve the nanodiamond without oxidation or graphitization during the film formation. The adhesion of this layer is improved by further process of pyrolysis at a temperature greater than that of the boiling point of dispersion medium. The processes of wetting and pyrolysis were repeated for the preparation of films with desired thickness.

By a method of the fast electron diffraction it was found that the coatings prepared from nanosuspensions of UFD do not show the crystal reflection. The surface of coatings was uniform without ant cracks and voids resembling amorphous structure.

The spectral investigation in UV-VIS-IR region showed that the films have the diamond-like optical properties. It was found that the glasses became more transparent with these UFD coatings on them. In the IR-spectrum (400 - 4000 cm^{-1}) no absorption was observed. Films were transparent through out the whole range of measurement. But for powders of UFD in KBr pellets, the absorption for nitric - extrinsic structures could be identified. In the UV-visible range (200-800 nm) in the reflection spectra of the UFD-coatings on silicon and glass, the absorption below 225 nm was observed. The corresponding band gap would be $\geq$ 5.6 eV. This would mean that the films would contain higher percentage of sp^3 bonded carbon. Thus, the spectral investigations in IR, UV and visible ranges confirm the formation diamond-like structure of UFD-coatings.

From Auger spectrum of film surface indicated the presence of carbon and a small amount of oxygen.

The results of X-ray diffraction measurements on Mo substrate and Mo coated with the UFD-coatings (after examination on internal friction) are shown in Fig.1a and 1b respectively. Fig.1b indicates shows that thermal load on these materials lead to form a carbide phase on the surface of the samples. Formation of carbide is usually favored at high temperatures. Efficiency of cutting tools was found to increase significantly with the use of UFD coating on them.

PP-I-32

CARBON MATERIALS BASED ON CARBON NANOFIBERS

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Active carbons, cokes, carbon fibers are used as sorbents and catalyst supporters. Dispersed carbon materials such as are proposed for this purpose last time very often. The first is the product of pyrocarbon precipitation on soot surface following by activation of the carbon material with steam. This material possess high adsorptive surface. The second is generated by hydrocarbon decomposition or disproportionation of carbon monoxide or CO-containing gas mixture at the surface of Fe, Co, Ni-containing catalysts.

Application of “sibunit” and carbon nanofibers in catalysis is prevented by:

- Low adhesion of catalyst active component to graphitic surface “sibunit”;
- The influence of synthesis condition on properties of carbon nanofibers (diameter, level of graphitization, concentration of initial catalyst) and, as result, properties instability.

We suppose that a number of carbon materials, which can be used as sorbents, catalyst supports or catalysts, may be increased by consolidation of production technologies of “sibunit” and carbon nanofibers. The consolidation advantage includes:

1. Carbon nanofiber contains catalyst precursor, on which carbon nanofibers were synthesized. After pyrocarbon precipitation and gasification of less graphite part of this material (carbon nanofiber) the catalyst particle of carbon nanofiber dispose inside cavity. The catalyst adhesion to support increases as result. The catalyst selectivity also must increase, because it depends on the cavity size. Cavity size is equal to carbon nanofiber diameter.

2. Calculations show, that sorbent with cylinder cavities has cavity volume 1.5 times higher than that of sorbent with sphere cavities (adsorptive surfaces are equal). So sorbent, based on carbon nanofibers, must have more adsorptive capacity then “sibunit”.

The results of synthesis of carbon nanofibers possessing required properties and carbon sorbents based on carbon nanofibers are reported. Carbon nanofibers were synthesized from carbon monoxide, and carbon composites (sorbents) from propane-butane gas mixture.

It was detected, that precursor concentration in carbon nanofibers depends on carbon formation rate and synthesis time. Concentration decreases when carbon formation rate or synthesis time increases.

Influence of synthesis temperature, gas flow and gas composition on nanofibers diameter.

- Temperature rise leads to diameter decreasing.
- Nanofiber diameter decreases with decreasing of carbon monoxide concentration in gas mixture.
- Increasing of gas flow leads to diameter increasing.

It is detected, that synthesis temperature increasing and carbon formation rate decreasing leads to formation of more graphitic nanofibers.

The carbon composites synthesis investigations show:

1. Two processes compete at the beginning of carbon matrix formation, when using carbon nanofibers containing precursor metal. Fist – carbon nanofibers growth continues; second - pyrocarbon formation. Then – only pyrocarbon precipitates and forms matrix. If used nanofibers do not include precursor – only pyrocarbon precipitation is observed.

2. Cavity formation and diameter reduction is originated during nanofibers oxidation. Only cavities are formed, when we oxygenate nanofibers pyrocarbon covered. Oxidation rate increases in metal precursor presence.

3. The increasing of process temperature leads to pyrocarbon formation and oxidation rates increasing.

Sorption characteristics of carbon nanofibers and materials based on them have been discussed.

PP-I-33

HYDROGEN PRODUCTION BY THERMOCATALYTIC DECOMPOSITION OF NATURAL GAS: REGENERATION OF CARBONACEOUS CATALYSTS

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Conventional hydrogen production processes (e.g. steam methane reforming) produce large amount of CO_2 emission. One alternative to conventional processes is single-step thermocatalytic decomposition (TCD) of natural gas (NG) into hydrogen and carbon. Due to the absence of oxidants (e.g., H_2O and/or O_2), no carbon oxides are formed during the process, thus obviating the need for water gas shift and CO_2 removal stages, which significantly simplifies the process. Pure carbon is produced as a valuable by-product that can be marketed, thus reducing hydrogen production cost.

The use of carbon-based catalyst for thermal decomposition of natural gas offers several advantages over metallic catalysts: (i) higher fuel flexibility and no sulphur poisoning; (ii) lower price; (iii) the carbon formed can be used as catalyst precursor, so that, the process is self-consistent. One of the main drawbacks for the use of these materials is catalyst deactivation mainly as a consequence of the drastic reduction in catalyst surface area during methane decomposition due to carbon deposition. In principle, the surface area of carbon particulates can be regenerated via their surface treatment with activating agents at elevated temperature. High temperature steam, CO_2 or their mixtures are the most common activating agents in the production of activating carbons from a variety of carbonaceous materials.

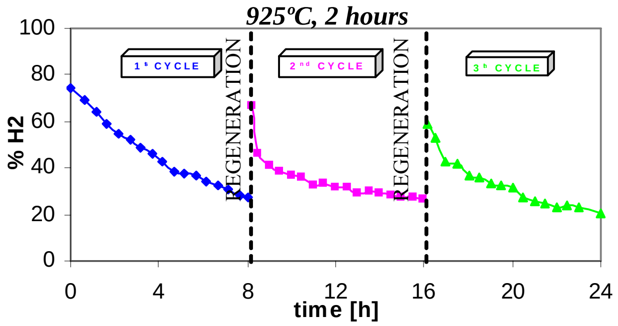
The objective of this work is to study the regeneration of the carbonaceous catalysts for the TCD of methane, using CO_2 as activating agent. In previous works (1, 2), different kinds of activated carbons (AC) and carbon blacks (CB) have been studied in the TCD of CH_4. Among them, a commercial AC –CG NORIT- and a CB –FLUKA 05120, have been selected for the regeneration tests. AC showed an acceptable initial reaction rate but they become rapidly deactivated, while CB with high surface area provided more stable and sustainable hydrogen production.

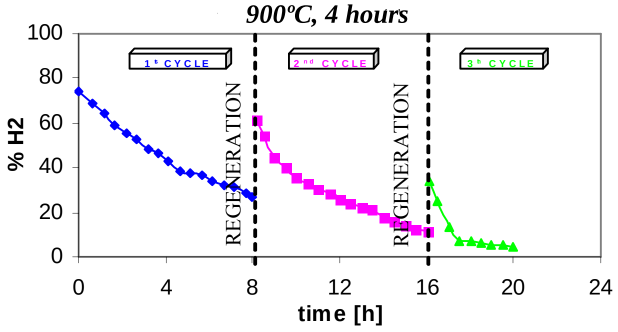
The optimum operation conditions for the catalysts regeneration have been studied, attending to the burn off of the catalysts during the regeneration, which is important for the selfconsistence of the process, and the recovering in the surface area, which is one of the most important factors affecting the activity of these catalysts.

The regeneration tests have been carried out in a bench scale fluidized bed reactor. The following activation conditions have been studied: (1) activating agent: CO_2 (2) activation temperature: 900, 925 and 950º C; (3) carbon residence time: 2 and 4 hours.

Catalyst	Burn off (%)	BET Area (m^2/g)
CG Norit fresh	-	1300
CG Norit deactivated	-	111
CG Norit regenerated 900ºC 2 hours	5	303,6
CG Norit regenerated 900ºC 4 hours	15	606,4
CG Norit regenerated 925ºC 2 hours	30	1287
CG Norit regenerated 925ºC 4 hours	57	1860

Table 1 shows the results obtained for the Activated Carbon-CG NORIT. A lineal relationship between % of weight loss (% of burn off) and surface area can be observed. A compromise between % burn off and surface area recovered must be accomplished in order to assure that the process is self-consistent. For this reason, the optimum regeneration conditions selected were 900ºC- 4 hours and 925ºC- 2 hours. In both conditions, the weight loss is under 30%, taking into account that after each reaction step, 400mg/g carbon is deposited, which corresponds to a 40% of the catalyst mass. The recovering of the surface area is over 50% in both conditions.


925ºC, 2 hours


900ºC, 4 hours

Several cycles consisting in series of reaction with CH_4 and regeneration with CO_2 have been performanced for both selected conditions. As is shown in figure 1, the recovery of the activity for the CG Norit regenerated at 925ºC-2h. is achieved almost completely after three successive reaction–regeneration cycles, while at 900ºC-4h. the catalyst regeneration is not feasible after the second cycle.

Further work is being carried out in order to gain knowledge about the mechanisms of the regeneration process.

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PP-I-34

EXPERIMENTAL ESTIMATION OF PORES VOLUME OF CARBON BLACK AGGREGATES

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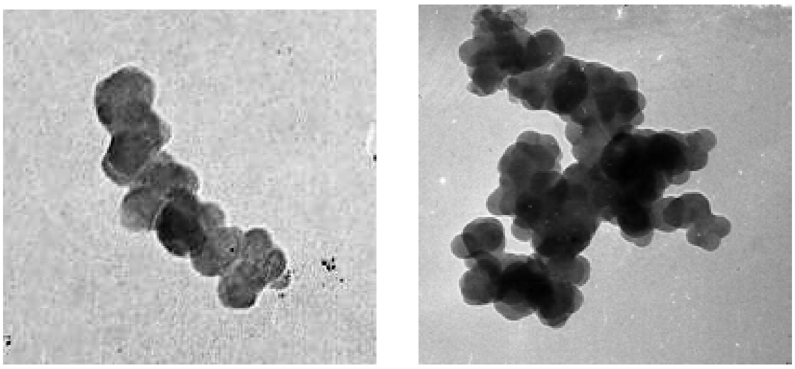
The spherical particles growth in dispersed carbon synthesis from hydrocarbons is accompanied by their conglomeration and carbonizing with obtaining of indivisible aggregates, as it is shown in the electron-microscopic pictures.



With the increase of aggregate size its secondary branching occurs, and polydispersity of aggregates on the sizes is accompanied with their polymorphism. At application of dispersed carbon as filler of rubbers pore volume inside the aggregates stands as container mechanically protected from deformations of rubber [1]. This fact is important for filler intensifying action.

It is necessary to know the size, surface, pore volume and their differential characteristics for porous texture description of dispersed carbon aggregate. True value of voidage in the dispersed carbon aggregate has been calculated as difference of volume occupied by the dispersed carbon aggregate (hydrodynamic) and its firm basis (optical) which were measured by screen analysis [2] and particles size laser spectrometer – analyzer SALD 2001 (SHIMADZU) [3].

In this report the capability of pore volume estimation inside dispersed carbon aggregates by the simple experimental method – titration with viscous liquid dibutylphthalate (DBP) – is shown. At DBP rubbing in dispersed carbon powder to the end point visually fixed at the time of the powder gathering in monolithic mass, sorption space is filled up both inside and outside of aggregate. Taking packing density of the aggregates irrespective of their form and practically identical [2], it is possible to determine the pore volume inside the aggregates according to the quantity absorbed DBP with corrective factors.

The analysis of the volumes calculated by the difference and voidages experimentally measured according to the quantity of absorbed DBP has revealed two areas of DBP_{exp} absorption agreeable to the true voidages, which are described by two linear equations.

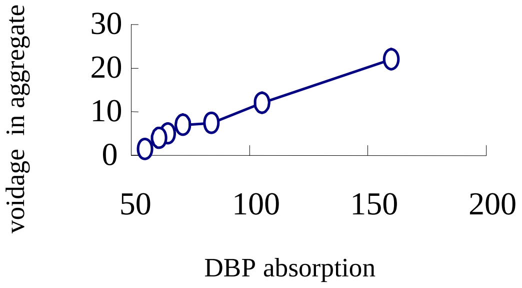


Figure 1. Interrelation of calculated voidages and experimentally fixed ones in the dispersed carbon aggregate.

The regression line angular coefficient of free and DBP occupied aggregates volumes for highly structured technical carbon is 1.95 times less than the same for low-structured one. The observed deviation of the DBP absorption dependence of voidage in aggregate is connected with the diminished density of highly structured carbon black.

For the straight lines combination (Fig. 1) the correction of the DBP_{exp} absorption values exceeding 70 cm^3 /100g is necessary:

$DBP_{true} = 0.5\ DBP_{exp} + 24.7$

Consequently using the above-stated equation the pore volume estimation inside the technical carbon aggregates with the elemental experimental method is possible.

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PP-I-35

THE CHARACTERISTIC SUCH AS FRAME OF DISPERSED CARBON BY THE MACROMOLECULES ADSORPTION METHOD

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For characteristic of dispersed carbon structure type with the macromolecule adsorption method the adsorption of globule polyethylene glycol from aqueous solutions in the range of hydrodynamic diameter d from 1 to 11 nm with carbon black has been studied. From the adsorptive data the surface fractal analysis of active carbon black patterns used at rubber production (foreign marks: N 339, N 375, and domestic ones: P 245, P 234, N-339 which have been recovered by the “traditional” and “advanced” technologies) has been fulfilled.

The surface fractal dimension in macromolecular medium D was determined by the formula:

$n \sim s^{-D}$, where n is the quantity of molecules in monolayer,
s is the cross-section area of the adsorbed substance molecule.

The quantity of molecules in monolayer was calculated from the maximum adsorption values for polyethylene glycol a_∞ (g/g) which were accordingly determined from equilibrium isotherm recovered in static conditions at 298 K according to the formula:

$n = a_\infty N_a / M$, where M is an average molecular weight of polyethylene glycol,
N_a is Avogadro constant.

It is known that surface fractal defines its texture complexities. Fractal values for flat surface are equal to 1, and they approach to 2 for convexo-concave one.

According to reinforcing activity in common destination caoutchouc-based rubbers fillers are arranged abreast similarly to growth row of surface fractal in macromolecular medium.

Modelling parameters

The effect on fractal value in the following directions has been studied:

- spheroid particles size (P 514, P 234, P 145 row);
- degree of aggregates divarication (N 339* > N 375* > N 326; P 145 > P 161);

- surface porosity (P 245$_{\text{intial}}$ and the oxidated one during 10 hours, 20 hours, and 40 hours with the following thermal treatment of oxidated patterns surfaces);
- graphitization at 3000 K (P 245);
- aggregates polydispersion (N-339).

Table 1. Surface fractals of some patterns of dispersed carbon in macromolecular medium.

Dispersed carbon	Surface fractal	Dispersed carbon	Surface fractal
P 514	1,42	N 326	1,49
P 234	1,60	N 375*	1,55
P 245$_{\text{initial}}$	1,62	N 339*	1,80
graph	1,60	P 145	1,88
Oxidated during		P 161	1,74
10 hours		N 234	1,60
20 hours	1,80	P 267-E	1,44
40 hours	1,80	N-339 (1)	
	1,65	unimodal	1,65
		N-339 (2)	
		bimodal	1,65

* Carbon black received by "advanced" technology.

Model identification

The experimental data show selectivity and specificity of the new qualitative method of dispersed carbon structure characterization. Its informational matter is defined by prior items about the presence of dispersion changes of spheroid particles and surface pores, activity and aggregates divarication degree.

The fractal dependence on material polydispersion has not been revealed. The contributions from different measured parameters of modelling to the fractal value have been determined.

It has been discovered that fractal dimension of macromolecules adsorption in the presence of all structure changes possesses the least value as it is shown for P 267-E pattern.

PP-I-36

MODIFICATION OF THE SURFACE OF CARBON MATERIALS BY OZONIZATION

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One of effective methods of oxidizing modification of carbon materials (CM) is ozonization. This method essentially changes a reactionary surface of CM due to formation of oxygen-containing functional groups (OFG). Advantage of gas-phase of ozonization against other strong oxidizers is absence of expensive catalysts and harmful fluid wastes.

The purpose of the work is the research of the effect of ozonization on change of function composition and sorption properties of CM of the various natures.

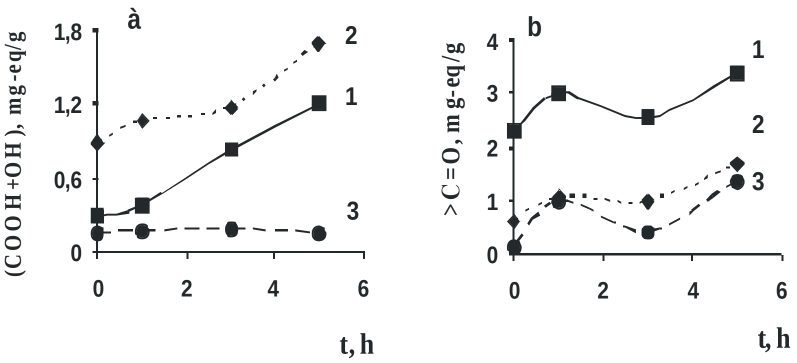
Treatment of CM is carried out in current ozone-oxygen mixtures (1-1,5 % of ozone) in a rotating reactor at 25 ^{o}C. Objects of research are two CM of a natural origin - anthracite (A) and fusains coal of mark D (FD) Kuznetsk coal basin and active carbon (AC) marks AG-OV-1 (Ltd “Sorbent", Perm).

The characteristic of samples:

Sample	Ash, A^d, %	Element composition, % on daf			Function composition, mg- eq/g			Adsorption on iodine, %	S_{BET}*, m^2/g
		C	H	O+N+S	-COOH	-OH	>CO		
AC	33,6	95,2	0,5	4,3	-	0,28	2,29	63,2	690
FD	9,8	91,4	3,0	5,6	-	0,89	0,62	11,5	120
A	4,6	95,0	3,9	3,9	-	0,15	0,12	4,1	2

* The literary data

Ozonization of CM is accompanied by increase of the contents of oxygen and reduction of carbon. Amount of carboxylic and phenolic groups increases in all samples. The contents of carbonyl groups (fig. 1) changes through maximum, that is possible as a result of their secondary oxidation. Ozonization has the greatest influence on CM with the advanced specific surface - AC and FD. It can be connected with both the facilitated diffusion of ozone in volume of particles and catalytic action of mineral ingredients of CM.



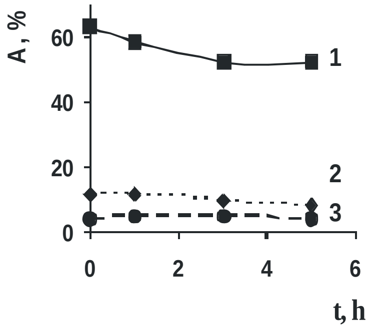


Fig.1 Dynamics of accumulation of groups of acid character (a) and carbonyl groups (b) at ozonization of AC (1), FD (2) and A (3)

Fig.2. Change of magnitude of adsorption of iodine by samples of AC (1), FD (2) and A (3) after ozonization

Intensity of bands of absorption at 3400, 2500-2800, 1700-1750, 1260 sm^{-1}(-OH, >C=O and -C-O-connections of OFG) increases and at 3040, 1600, 690-850 sm^{-1} (-C-H and -C=C-aromatic groups) decreases in IR- spectrums of ozonized samples. It indicates at participation of aromatic fragments of structure of CM in reactions of ozonolysis.

Modification by ozone contributes change of adsorptivity of CM in relation to iodine and pyridine. The reduction of sorptive capacity on iodine (fig. 2) can be caused by the blocking of mouths of pores by educated functional groups. Especially it is typical for highly-porous AC.

The mechanism of sorption of pyridine, as against iodine, is based on specific interacting of substance with surface groups of adsorbent due to formation of hydrogen bonds. Sorption of pyridine after ozonization of CM has positive dynamics. In particular, at ozonization of AC within three hours its adsorptive capacity in relation to pyridine increases in 5 times.

Thus, result of ozonization is accumulation of oxygen-containing groups and change of adsorptivity of CM. The greater activity in relation to ozone has carbon materials with advanced internal surface. Rise of sorption of pyridine by activated carbons after ozonization can be used for cleaning of waste water of the plants of an organic synthesis and medical products.

PP-I-37

ON THE OBTAINING OF CARBONACEOUS MATERIALS DOPED BY NICKEL COMPOUNDS

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Due to the graphite layered structure, different atoms, molecules and ions are able to intercalate into the space between graphite layers in order to form graphite intercalation compounds (GIC). GIC with transition metal chlorides ($NiCl_2$, $CoCl_2$, $PdCl_2$, $PtCl_2$) are the interesting class of inorganic compounds thanks to interesting magnetic properties [1]. The compounds obtained by reduction of GIC-$MeCl_2$ to GIC with metals or their oxides catalyze oxidation reactions of organic compounds [2], these metals without graphite do not show catalytic ability. That is why the purpose of the present work was obtaining of carbonaceous materials doped by nickel compounds with the use of graphite electrochemical oxidation in aqueous solution of nickel nitrate followed by thermal treatment.

The samples were synthesized by anodic oxidation of natural graphite (average size 200 μm, d_0 = 3.35Å) under chronopotentiometric mode (I = 30 mA) in the three-electrode cell. The potentials were measured with the use of Ag/AgCl reference electrode. Aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ were used as electrolyte. Charging curves of graphite sample are smooth in all cases. The potential of graphite electrode increases at first minutes of synthesis. Further polarization is accompanied by insignificant change of potential, the potential value is about 1.5 – 3.2 V for different $Ni(NO_3)_2$ concentration. The synthesis conditions and some characteristics of carbonaceous materials are listed in the table 1.

Table 1. The properties of carbonaceous materials.

$C_{Ni(NO3)2}$, %	Q, A·s/g	d_i, Å	d^{250}_{EG}, g/l	d^{900}_{EG}, g/l	ωNiO, %
52	100	3.37	33	3	10
	500	3.36	6	1	20
	1500	3.36	1	2	45
5.2	100	3.35	34	3	0.8
	500	3.36	17	0.6	1
	1500	3.36	14	1.4	0.6
0.52	100	3.37	62	18	2.2
	500	3.38	56	5	5
	1500	3.37	43	4	7

As one can see in the table, XRD shows that graphite anodic oxidation in the above mentioned electrolyte does not allow to obtain graphite intercalation compound. But the value of d_i increased from 3.35 Å for the initial graphite up to 3.36-3.38 Å for synthesized compounds. Probably, the anodic oxidation and hydrolysis occurs at the same time and the final product is expandable graphite. This material is able to exfoliate at quick heating with the formation of exfoliated graphite (EG). The presence of nickel compounds in the expandable graphite was confirmed by qualitative analysis.

The expandable graphite samples were subjected to thermal shock at 250 and 900 ^oC. Exfoliated graphite is known to be obtained at 900 ^oC [3]. It is necessary to note that synthesized samples are able to exfoliate at 250 ^oC, the bulk density is 1 – 60 g/l and depends on the way of synthesis. The bulk density of EG obtained at 900 ^oC is 1 – 18 g/l. Thus, anodic oxidation of natural graphite under such conditions permits to obtain very light material. The specific area of the exfoliated graphite is 20 – 110 m^2/g.

The content of nickel oxide in the exfoliated graphite was determined quantitatively by incineration of EG in the air flow at 900 ^oC for several hours. XRD analysis of the rest confirmed single phase of NiO. The quantity of nickel oxide in the exfoliated graphite strictly depends on the way of synthesis.

The structural peculiarities of the expandable and exfoliated graphite were investigated with the use of scanning electron microscopy. It was shown that finely-dispersed inclusions of nickel oxide in exfoliated graphite are distributed not homogeneously, and accumulation areas can be observed.

Thus, anodic oxidation of natural graphite followed by thermal treatment allows to obtain carbonaceous materials doped by nickel oxide. These materials are believed to be used as catalysts in different organic reactions.

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CARBON SUPPORTED PALLADIUM CATALYSTS: HIGHLY ACTIVE CATALYTIC SYSTEMS FOR CONTINUOUS HYDROGENATION OF POLYUNSATURATED FATTY ACIDS AND THEIR TRIGLYCERIDES

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Hydrogenation of polyunsaturated fatty acids and their triglycerides over platinum metals is important process in the oil, fat and oleochemical industries that provides a broad assortment of margarines, shortenings, light butters and fats with low trans-isomer content free of carcinogenic nickel [1]. Parallel with it there is an increasing worldwide interest to monounsaturated and saturated fatty acids manufacture for tire and candle production, cosmetic and pharmaceutical industries [2]. To produce saturated fatty acid there is very attractive possibility for industrial application to use the interchangeable raw materials passing through the same effective catalyst. Highly active catalysts on the base of palladium can be proposed to provide selective C=C double bond hydrogenation of sunflower seed oil [3] and methyl linoleate [4]. However reactivity of free fatty acids (FFA) differs from that for esters and FFA saturation demands the higher temperature and elevated hydrogen pressure [5]. Some undesired decarbonylation reaction can occur at the operating conditions to decrease activity of palladium catalyst.

The aim of this work is to study the Pd/C catalyst performance in continuous hydrogenation of rapeseed oil and industrial free fatty acids at different operating conditions.

Samples of Pd/C catalyst with palladium content from 0.5 to 1.0% (wt) were prepared by an incipient wetness impregnation method which includes spraying the solutions H_2PdCl_4 and Na_2CO_3 onto the carbon granules (spheres by diameter of 2÷3 and 4÷6 mm) agitated in a rotating cylinder. The application of activated carbon "Sibunit" as a carbonaceous support has been favored by its high surface area, chemical inertness in acidic media and by the absence of very strong acidic centers on its surface which could promote undesirable isomerization reactions during the catalytic run [6]. Experiments were performed using stainless-steel up-flow reactor at temperature range from 146 to 180^{o}C and elevated hydrogen pressure up to 8 bars. Reagents passed through a pre-heat reservoir and then flowed over the fixed catalyst bed. Hydrogen was metered into the system using a mass flow controller. Condensable products were collected in a water-cooled collector and analyzed by GLC method. To estimate C=C double bond saturation efficiency the melting point of fatty acid hydrogenated products (MPFA) was determined. This characteristic reflects the completeness of fatty acid hydrogenation (61° and 65° of MPFA correspond to full saturation of FFA and rapeseed oil respectively).

The composition of hydrogenated FFA and their triglycerides was shown to depend essentially on palladium metal content. A comparison of catalytic activity of 0.5 and 1.0% (wt) Pd/C shows that the latter is most effective and stable in FFA saturation under mild reaction conditions (Fig. 1). Notable amount of carbon oxide detected by GC analysis at temperature above 160°C indicates that decarbonylation reaction occurs to cause catalyst deactivation. Fatty acids triglycerides are more stable and can be hydrogenated at high temperatures over the catalyst with less 0.5% (wt) palladium content (Fig. 2).

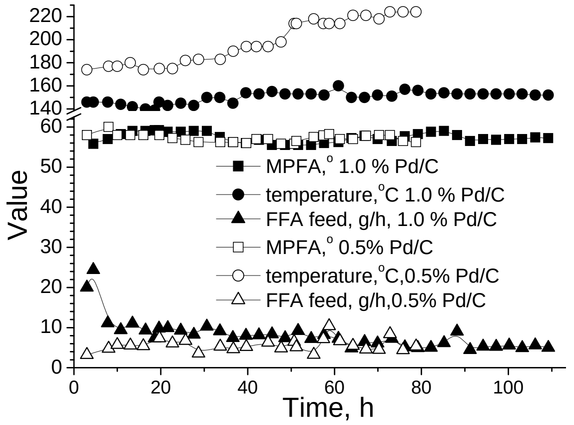

Fig. 1. FFA hydrogenation (Pd/C 0.5% and 1.0% (wt), fr. 2÷3 mm)

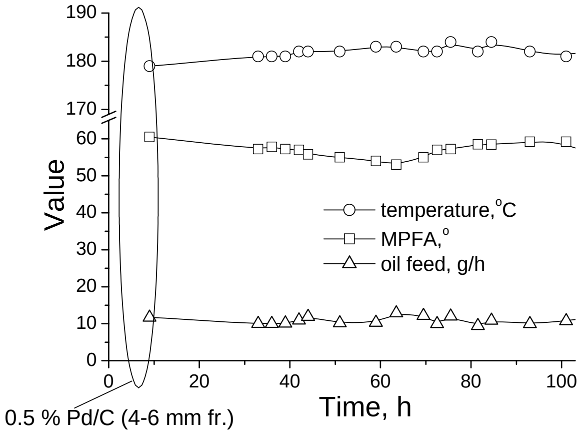

Fig. 2. Rapeseed oil hydrogenation (Pd/C 0.5% (wt), fr. 2÷3 and 4÷6 mm)

The samples of fresh and used catalysts were analyzed by HREM and XRD methods to study palladium catalyst sintering during catalytic runs. The results obtained indicate that Pd dispersion was not changed: average palladium particle size of fresh samples, after long-term hydrogenation of triglycerides and FFA are 4.41, 4.33 and 4.80 nm respectively.

Effect of carbonaceous support grain size on the features of hydrogenation of polyunsaturated fatty acids and their triglycerides in flow reactor with the fixed catalyst bed are studied. Factors responsible for sintering resistance of Pd metal particles on carbon-carbon material support are supposed. The recommendations to prevent catalyst deactivation during fatty acid hydrogenation are suggested.

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PP-I-39

SELF ORGANIZED CARBON POLYCYCLES

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The 21-century will be the century of systemic sciences. It means that universal systemic laws will be used to design objects out of elements and their ensembles. It was supposed by us that elements and ensembles arise as latent faults in objects of previous level.

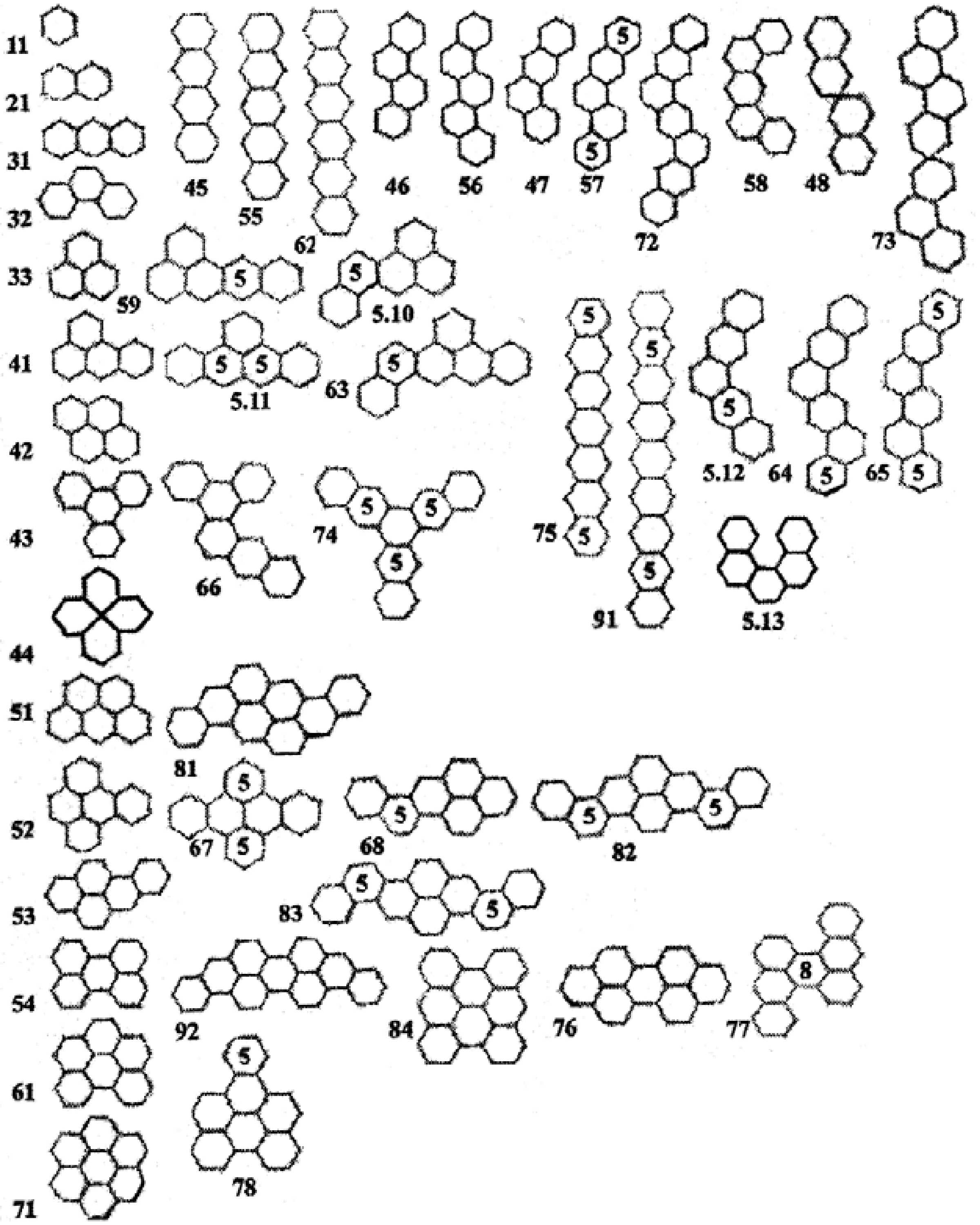
The structure of C graphite consist of Kepler (Archimedean) net 666. This net consists of hexagons that shared all edges. Every vertex is surrounded by 3 hexagons. The net 666 comprise latent bands and ensembles of hexagons. The net 666 is precursor of many new nets and ensembles. It was found by D. Bird (M. Gardner, 1975, B. Grunbaum and G.C. Shephard, 1987) that polycycles consisting of 1, 2, 3, 4, 5 hexagons form 1, 1, 3, 7, 22 ensembles (n-hexes), in all 34. It was revealed (Smirnova N.L., 1976) 13 different ensembles (condensed polycycles or n-hexes) with hexagon surrounded by 0 – 6 hexagons. It was supposed that all these ensembles № 11, 21, 31, 32, 33, 41, 42, 43, 51, 52, 54, 61, 71 (Fig.) are self-organized in nature as structures of inorganic substances and organic molecules. It was found that 19 out of 34 n-hexes and all 13 ensembles were realized. There are 11 n-hexes out of 19 that are comprised in 13 n-hexes. The other 8 n-hexes are №№ 45, 46, 47, 53, 55, 56, 58, 5.13.

We suppose in 1950th that all new structures are self-organized by ordering of the same or different 0, 1, 2, 3-dimensional elements and their ensembles. During this process in all systems superstructures and homological series arise. All new data confirmed this law. In the set of ensembles there is S series of straight homologs, W series of wavy homologs and SW series of partly straight and partly wavy homologs. There are also C series of homologes with central nuclear № 33, 42, 43, 44, 54, 71. One - two 1, 2-hexes are condensed with nuclear: № 33 (59, 5.10, 5.11, 63), № 43 (66, 74), № 42 (52, 53, 67, 68, 82, 83), № 54 (92, 84, 76, 77) and so on. New series of central homologs are self-organized.

Let us denote n-gons as 3 (trigon), 4 (tetragon), 5 (pentagon), 6, 7, 8, 9. Ensembles №№ 31, 32, 33 can consist of 3 cycles aaa, aab, aba, abc. There were found for ensemble № 31 superstructures 555, 556, 565, 566, 656, 667, 676, 677, 767, 668, 576, 658, for ensemble № 32 – 566, 565, 575, 676, 677, 366, 576, for ensemble № 33 – 566, 556. Ensemble № 31 is third member of S series, № 32 is third member W series. There are some members of SW series (№№ 47, 57, 72, 58, 5.12, 64, 65).

Ensembles №№ 31, 45, 55, 62, 75, 91 are homologs of S series. But ensembles № 75 and № 91 of S series are homologs - superstructures with two hexagons substituted by two pentagons. Many ensembles consisting of 5 – 9 cycles are unique superstructures. If one take into account superstructures then 24 ensembles are realized out of 34 and 25 additionally, 49 at all. New members of series and superstructures can be revealed.

n-hexes and their series



PP-I-40

SYNTHESIS AND INVESTIGATION OF HETEROCARBON SUPPORTS AND CATALYSTS ON THEIR BASE FOR OXIDATION-REDUCTION REACTIONS

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The catalytic properties are determined by grain size distribution and dispersion of active component supported on carbon carrier. In one's turn, the distribution and dispersion depends in considerable extent on the support texture and surface chemistry.

Carbon materials surface can be characterized by acid or basic groups and be hydrophilic or hydrophobic. The quantity and strength of these groups depend on the synthesis conditions. But, as a rule, the origin groups of carbon surface: carboxyl, phenol, lactonic, etc which fix initially the precursor molecules, are hold them very weakly. Therefore the bond of these groups with precursor molecules is break on the heat treatment stages. Commonly it is accompanied by thermolysis of precursor molecules and the very surface groups.

As the result the migration of precursor molecules or formed intermediates occurred with the following their collisions and sintering.

By this the dispersion of active component sharply reduces and it leads to the activity decrease.

It is known the high porous oxide supports (Al_2O_3, SiO_2 and others) interact strong with supported precursor molecules preventing their consequent sintering upon heat treatment stages. Therefore it was important to improve the carbon supports properties by introducing in their composition inorganic polar groups in order to stabilize strongly the precursor molecules on the support pore surface.

Besides, it is worth to note that today assortment of porous carbon materials and their quality do not satisfy the customers in such parameters as mechanical strength and stability in aggressive media. In this connection the purposeful synthesis of porous carbon materials of special design as adsorbents and as catalyst supports is actual for chemical and petrochemical processes.

In this work the technology of matrix synthesis of catalyst supports on the base of dispersive and pyrolitic carbon is realized [1].

The pore structure of origin grains of dispersive carbon plays the role of reinforced framework, which determines the space arrangement and the size of microcrystals in forming pyrolitic carbon layers. After that the reinforced framework can be moved off at carbon material activation. As the result the pyrolitic carbon matrix is formed, physics and chemical properties of which are determined by the synthesis conditions [2].

The multistage technology allowed to modify the carbon material by heteroatoms on the stage of carbon-carbon composite formation. This material keeps all the properties which are intrinsic for pyrolitic carbon: mechanical strength, thermo and chemical stability under mesopore part up to 80% of total pore volume and pore sizes 2-10 nm. This material acquired new surface properties, which influenced on the supported catalysts state [3, 4].

In this work the methods of modifying of carbon-carbon composites by heteroatoms are considered and the peculiarities of their microstructure, texture and chemical composition are adduced. The conditions of supporting of active components: Cu, Ru, CeO_2, Ru-Cs on modified sibunits is investigated.

The activity of catalysts on the basis of heterocarbons supports in the reactions of CO oxidation and ammonia decomposition under low temperatures are given.

It is shown that the obtained catalysts activity is on the same level or even on the higher one than the activities of the best catalysts for these reactions.

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PP-I-41

INVESTIGATION OF SURFACE OF ACTIVATED CARBON KM-2 WITH ELECTROSORBED IONS OF ALKALI AND ALKALINE-EARTH METALS

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It is known that applying external potential leads to detectable increasing of the carbon sorption capacity. There are a series of works devoted to adsorption of alkali and alkaline-earth ions by activated carbons, in which the optimum conditions of this process are found. However, the interpretation of these results is difficult due to the complexity of the surface and textural properties of activated carbons, therefore some questions relating to the mechanism of cation electrosorption remain unsolved.

The purpose of this work is the elucidation of the mechanism of the adsorption of alkali and alkaline-earth ions on polarized carbon KM-2.

The investigations of the carbon surface were carried out by method of the potentiometric titration, Auger- and IR-spectroscopy, the X-ray phase analysis, scanning electron microscopy.

The sorption capacity of cathodic polarized carbon with respect to Ca^{2+}, Sr^{2+} and Ba^{2+} ions were 8, 15 and 10 meq g^{-1} respectively. The water washing of these carbons showed that Ca^{2+}, Sr^{2+} and Ba^{2+} ions are adsorbed firmly and are not rinsed with water. The X-ray phase analysis data point to the fact that the strontium ions are on the cathodic polarized carbon surface essentially in the form $SrCO_3$ and partially in the form $Sr(OH)_2$; Ca^{2+} and Ba^{2+} ions are in the form $MeCO_3$. After treatment of carbon samples by hydrochloric acid, 23 %, 50 % and 55 % of the total adsorbed strontium, calcium and barium amounts are removed from the carbon surface. The compounds detected by the X-ray phase analysis must be completely removed after treatment by hydrochloric acid. It is probable that the rest of the adsorbed Ca^{2+},

Sr^{2+} and Ba^{2+} ions are in form of strong compounds which are not removed by treatment by HCl and are not exhibited on X-ray pattern. The assessment of acidic properties was carried out by method of the potentiometric titration and IR- spectroscopy. The pK values of surface functional groups of initial carbon as well as of carbon with adsorbed Ca^{2+}, Sr^{2+} and Ba^{2+} ions were determined from the pH-metric titration curves. There are on the surface of initial carbon acidic groups only. Cathodic polarization leads to partial or total disappearance of acidic surface groups and to appearance of basic surface groups with the different values lgK_{diss}. The obtained results can testify that acidic surface groups don’t take part in adsorption of Ca^{2+}, Sr^{2+} and Ba^{2+} ions on cathodic polarized carbon KM-2. In addition, the insertion of the background ions into carbon structure by cathodic polarization is not observed that is confirmed by Auger spectra.

The sorption capacity of cathodic polarized carbon with respect to Rb^+ ions is 0.75 meq g^{-1}, and with respect to Cs^+ ions is 1.00 meq g^{-1}. The X-ray phase analysis data point to the fact that the rubidium ions are on the polarized carbon surface in the form Rb_2CO_3 and in the compounds that have general formula RbC_x, the latter have the loosened graphite lattice. The intercalation of Rb^+ into space between the carbon layers are not excluded. The results of elemental analysis of these carbon samples show that there are, expect for elements found in initial carbon samples, rubidium ions only. The other ingredients of background solution are not detected.

After water washing and treatment of carbon samples by hydrochloric acid, 23 % of adsorbed rubidium ion amount are removed from the carbon surface. In SEM micrographs of the activated carbon samples with adsorbed rubidium crystal substance, forming conglomerate, can be seen. The conglomerate formation was observed on the X-ray patterns too.

About 46% of electrosorbed Cs^+ ions are removed by water washing and treatment by hydrochloric acid. Elemental analysis of the carbon surface with sorbed cesium shows that on these carbon samples there are background solution ions (K^+). It is possible that under optimal conditions for the cesium electrosorption the electrosorption of K^+ ions takes place too. On the X-ray patterns of such carbons the lines, which can not be uniquely related to one or another chemical compound of cesium or potassium, are detected.

The data obtained in this work are usable for the further development of electrocatalysis and adsorption theory.

Experiments were conducted by use of instrumentation of Analytical Centre for Collective Use of Daghestan Scientific Centre of RAS.

PP-I-42

PREPARATION OF NEW VANADIUM-PHOSHORUS OXIDE CATALYSTS ON CARBON SUPPORTS

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Vanadium-phosphorus oxide (VPO) systems are the most effective catalysts for mild oxidation of n-butane to maleic anhydride [1]. However this fact was not revealed until suitable support for these catalysts was found.. Thus oxide carriers interact strongly with active phase and have negative influence on properties of catalysts. Authors [2] suggested to use materials without oxygen (SiC, BN) to avoid this influence. We present new approaches for: /i/ creation of supports for VPO-catalysts and /ii/ modification of the whole process for preparation of catalysts.

As a supports we used such materials as active carbon (KAU) and carbon nanotubes. Peculiarity and advantage of this approach consist firstly in the fact that carbon is more inert with reference to active phase and secondly that surface carbon atoms play a role of reduce agent in the process of VPO-catalysts synthesis from V_2O_5. Consequently preparation of catalyst can be carried out without adding organic compounds in reaction mixture. All catalysts were synthesized in autoclave.

Active carbon KAU was subjected to preliminary hydrothermal treatment (HTT) by 30-50% H_2O_2 at temperarure 300-360°C for modification of porous structure and oxidation of surface. HTT of KAU leads to increase of surface area S and pore volume V (table) obviously at the expense of formation of both micro- and mesopores. Hemyhydrate of vanadylhydrophosphate $VOHPO_4 \cdot 0,5H_2O$ (HPV) - precursor of catalyst for oxidation n-butane is formed as result of deposition of VPO on active carbon surface. Degree of HPV crystallization (and accordingly size of crystallite D) grows after preliminary HTT of KAU.

Non-porous C-nanotubes were obtained by pyrolysis of ethylene under 650°C [3]. These powders were mixed with water, solutions of H_2O_2 or reaction medium for synthesis of VPO-systems. As a result meso-macroporous materials of aerogels type (V=2,5-4,5 ml/g) were prepared for the first time. Mesoporous supported catalysts with high surface area and pore volume are formed from initial C-nanotubes (table). It is interesting that phase of vanadyl dihydrophosphate $VO(H_2PO_4)_2$ (DHPV) with P/V=2 is crystallized under 170°C whereas phase of HPV with P/V=1 under 200°C. VPO-samples based on oxidized C-nanotubes have weakly developed porous structure.

N	Conditions of treatment	S m^2/g	V ml/g	Phase	I_{001}/I_{220}	D nm
1.	Initial KAU	1305	0,42			
2.	VPO on sample 1 170°C 10 h	722	0,32	HPV	1,1	33
3.	KAU HTT 360°C 30% H_2O_2	1500	0,65			
4.	KAU HTT 350°C 50% H_2O_2	1470	0,66			
5.	VPO on sample 4 170°C 10 h	347	0,34	HPV+V/P-Mica	1,0	28
6.	KAU double HTT 340°C 30% H_2O_2	1440	0,56			
7.	VPO on sample 6 170°C 10 h	770	0,37	HPV	0,9	15
8.	VPO on sample 7 170°C 10 h	480	0,30	HPV	1,0	40
9.	Initial C-nanotubes	185	2,55			
10.	VPO on sample 9 170°C 7 h	44	1,05	DHPV		7
11.	VPO on sample 9 200°C 7 h	36	1,40	HPV	2,7	9
12.	Sample 9 oxidation 20°C 30% H_2O_2	131	4.65			
13.	VPO on sample 12 170°C 7 h	13	0,08	DHPV		
14.	Samle 9 oxidation 250°C 7 h	125	2,65			
15.	VPO on sample 14 170°C 7 h	9	0,09	DHPV		6

Thus we prepared: /i/ micro-, meso- and macroporous carbon materials and /ii/ supported VPO-catalysts with active phase in nanodispersion state. These catalysts is perspective for oxidation of n-butane and oxidative dehydrogenation of light hydrocarbon.

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PP-I-43

A NEW ELECTROCATALYST SUPPORT FOR DIRECT METHANOL FUEL CELLS

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Research on carbon supports for electrocatalysts has been stimulated by intense interest in direct methanol fuel cells (DMFCs) which have recently been considered as one of the most potentially suitable power sources for stationary and portable applications because of their high power density at moderate temperature and their compact design. A desirable electrocatalyst support in fuel cells should possess high surface area, high electric conductivity and suitable pore size to assist electron, proton and mass transfer. Although Vulcan XC-72R appears to be the most commonly used carbon for its compromise of a reasonable surface area and a small amount of micropores, many new nano-sized carbon materials such as single-walled carbon nanotubes, multi-walled carbon nanotubes (MWNTs), carbon nanobeads, carbon nanofibers, carbon nanohorns (CNHs), carbon nanocoils (CNCs), hollow carbon nanoparticles, and ordered mesoporous carbon have been investigated recently, among which CNHs and CNCs-supported electrocatalyst exhibited much higher performance with respect to XC-72R. The performance enhancement was attributed to unique properties and morphology of CNHs and CNCs.

A new carbon nanomaterial (NCM) with high surface area, high degree of graphitization, and suitable pore size was synthesized in our laboratory by homogeneous catalytic reaction. Resorcinol and formaldehyde containing silica gel and iron nitrate (or cobalt, nickel salts) were cured homogeneously in a weak basic medium by adding concentrated ammonia solution. The process of synthesis of NCM is simple, easy to operate and scale-up. The techniques of nitrogen adsorption, transmission electron microscopy, and X-ray diffraction were employed to characterize the physiochemical properties and morphology of the new carbon material. The result of nitrogen adsorption showed that the new carbon material possessed relatively high surface area of more than 200 m^2/g and large size pores, and the TEM image and XRD patterns demonstrated it owned high degree of graphitic characteristics.

30 wt% Pt-15 wt% Ru/NCM catalysts were prepared by modified ethylene glycol (EG) method. It was briefly described as follows: Pt and Ru precursor in basic EG solution were reduced at elevated temperature, then the colloids were added into NCM-EG slurry, hydrochloric acid was added to deposit the metal particles onto the carbon material, after a few hours, the mixture was filtered, then obtained the NCM-supported PtRu catalyst. High-resolution TEM images of PtRu/NCMs indicated that the metal particles were uniformly distributed on the outer surface of this carbon material, and single cell performance showed that maximum power density was higher, and the mass transfer resistance was much low when the carbon material-supported catalyst was used as an anode catalyst as compared to the commercial catalysts from Johnson Matthey Corp with same metal loading. Such unique properties made the carbon material a promising alternative for electrocatalyst support because of its potential to reduce significantly the resistance of mass and electron transfer.

PP-I-44

STUCTURE AND CATALYTIC ACTIVITY OF HEAT TREATED MULTI-WALLED CARBON NANOTUBES (MWNTs)

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Carbon nanotubes have witnessed a great scientific interest during the last decade since their discovery as a by-product in the arc discharge materials in 1991 [1]. Consecutively to their discovery, studies rise on the use of these new nanomaterials in the field of an exciting nanotechnology. Since there numerous potential applications of carbon nanotubes in several domains have been demonstrated covering from the electronic to energy storage devices [2-3]. Among these different potential applications the most promising field seems to be the catalysis field according to recent publications [4-6]. Their specific characteristics offer advantages such as high external surface area, high specific surface area, good electrical and thermal conductivity as well as their high resistance towards acidic or basic media.

The present article is focused on the large scale synthesis of these carbon nanotubes [7] and their structural modification after thermal treatment at high-temperature. The surface behaviour of these nanomaterials will be evaluated in a liquid-phase reaction, i.e., oxidative dehydrogenation of dihydroanthracene into anthracene at relative low reaction temperature.

The MWNTs before and after the thermal treatment were characterised by, TEM, SEM, Raman, XPS and surface area analysis (Figure 1).

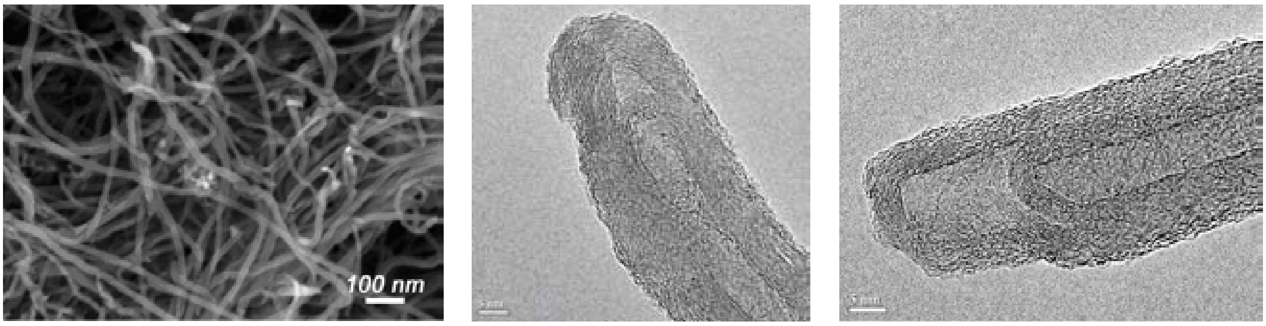

Figure 1. From left to right, TEM and SEM of MWNTs, and TEM of the heat-treated MWNTs

The treatment at 2600°C decreases the specific surface area, removes the oxygenate groups on the carbon surfaces and increases the purity on the MWNTs. The heat treated MWNTs used as catalysts for the 9,10-dihydroanthracene oxidation in anthracene, shows a better catalytic activity compared to MWNTs without post-treatment and to expensed carbon. The carbon graphitization level and the lower oxygen concentration on the heat-treated carbon nanotubes, which favorises the reactants adsorption on the nanotubes surface, increase the di-hydroanthracene conversion into anthracene. Similar results have already been obtained. The authors have observed a conversion reaching 93 % over activated charcoal in the same reaction conditions [8].

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PP-I-45

PREPARATION AND INVESTIGATION OF NANOSTRUCTURAL CARBONACEOUS MICROPOROUS ADSORBENTS FROM THE BIOMASS

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Biomass is one of the most promising among potential energy resources to substitute for fossil fuels and a precursor of various valuable materials. Important sources of biomass are wood and vegetative residues (wheat and corn straw, chaff, rice and oat husk, etc.).

The most abundant solid products of the biomass processing are various types of actives carbons which can be used as effective adsorbents to remove organic and inorganic impurities from liquid and gaseous media.

Microporous carbonaceous materials with a large specific surface area, A, are of particular importance among active carbons. The microporous carbon, due to its large micropore volume, V_μ, is considered now as a potential adsorbent for such poorly adsorbable gases as, for example, hydrogen, carbon monoxide, methane. The currently practicable methods for production of microporous carbons are based mainly on a thermal oxidative treatment of petroleum pitch in nitric and/or sulfuric acid followed by the treatment in melted KOH at 700–800°C in an inert atmosphere [1, 2]. A possibility to produce the same kinds of carbons from a number of carbon-containing precursors (hydroquinone, naphthalene, polychorvinyl etc.) also is demonstrated [3]. However, toxic gaseous and liquid wastes (nitrogen oxides and mineral acids) are produced in considerable quantities in this case.

The best among the currently produced microporous carbons are Maxsorb materials (Kansai Coke and Chemical Co Ltd., Japan), also known as AX-21 (Anderson Develop Co., USA). These carbons have $A_{BET} = 2670 \pm 600$ m^2/g and $V_\mu \sim 1.20$ cm^3/g [1, 2].

The Boreskov Institute of Catalysis proposes a method for synthesis of supermicroporous carbons (SMPC's) with even higher adsorbability via treatment of agricultural high-ash lignocellulose wastes (rice and oats husk, wheat straw). In the new SMPC's, the specific surface area A_{BET} reaches 3460 m^2/g and micropore volume V_μ up to 1.9 cm^3/g at a total of pore volume (not larger than 100 nm), V_Σ, as large as 3.0 cm^3/g. The preliminary carbonization of these wastes in inert atmosphere at 400–450 °C or in a fluidized catalyst bed (FCB) at 450–600 °C allows carbon-mineral composites to be synthesized with the textural parameters shown in Table 1.

Table 1: Characteristics of carbon-mineral composites produced at different temperatures

FCB temperature, °C	A_{BET}, m^2/g	V_{pore}, cm^3/g	Ash, %
450	32	0.04	35
500	176	0.15	56
550	246	0.21	69
600	233	0.22	76

In these composites, the ash residue contains mainly nanospheres of amorphous silica which may behave as a mineral structure-forming agent – template – during the further treatment to synthesize microporous carbons, the carbon nanostructure with 1 to 1.5 nm graphenes being arranged around the template.

The obtained carbon-mineral composites are activated in melted KOH and/or NaOH at 700–900 °C to produce potassium silicates through the interaction between amorphous silica and KOH. After this activation, the materials are cooled and the silicate templates are removed by dissolving in water.

One of the principal parameters affecting the textural characteristics of thus obtained SMPC’s is the activation temperature [3, 4]. Table 2 summarizes the data on properties of SMPC’s synthesized at different temperatures. A_{BET}, V_{pore} and V_{μ} are determined from the nitrogen adsorption isotherms at 77 K.

Table 2: Characteristics of carbonaceous nanostructural SMPC’s materials synthesized at different temperatures

Activation temperature, °C	A_{BET}, m^2/g	V_{pore} /V_{μ}, cm^3/g	Micropore proportion %
700	3170	1.77/1.45	81.9
750	3450	2.01/1.68	83.6
800	3360	2.18/1.87	92.3
850	3170	2.26/1.74	77.0
900	3210	2.97/1.48	49.8

The total pore volume increases with the activation temperature. At the temperatures below 800°C, the increase is due to the micropore formation. At the further temperature elevation, the micropore volume decreases but the mesopore volume increases due to burning processes.

Generally, the specific surface area is proportional to the micropore volumes (Fig. 1). The TEM studies revealed that the SMPC material consists of nanosized individual graphenes arranged in a disordered cell-like structure (Fig. 2).

In the synthesized microporous carbons, not only the specific surface areas and micropore volumes are superior to those of AX-21. The characteristic features of SMPC’s are much narrower pore size distribution and a higher contribution of micropores to the total pore volume (see Fig. 3). The differential surface area *vs* pore size is determined by the Ustinov method [5]; the authors [5] assert that this is the most appropriate method for large surface area carbons.

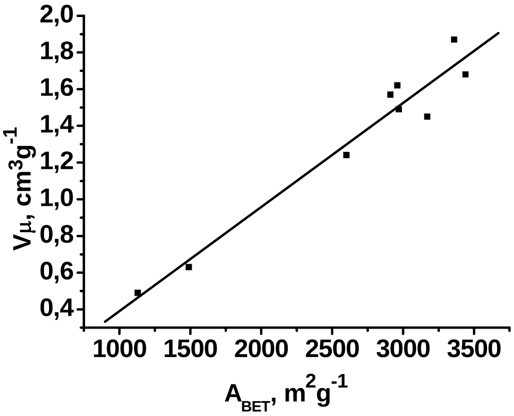

Figure 1: A_{BET} of SMPC's as a function of V_{μ}.

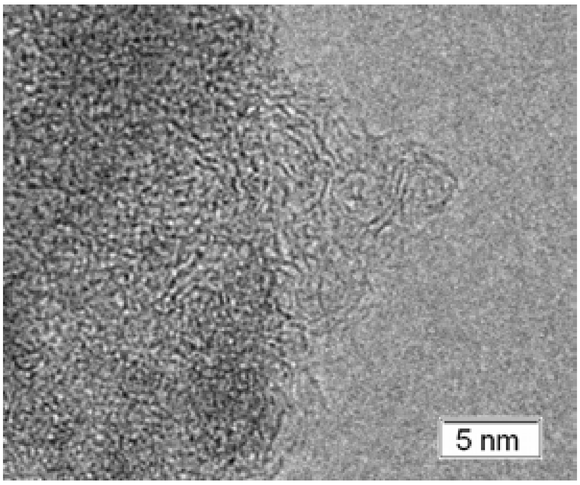

Figure 2: TEM image of a SMPC with $A_{BET} = 3400$ m^2/g, $V_{\Sigma} = 2{,}2$ cm^3/g, $V_{\mu} = 1{,}9$ cm^3/g

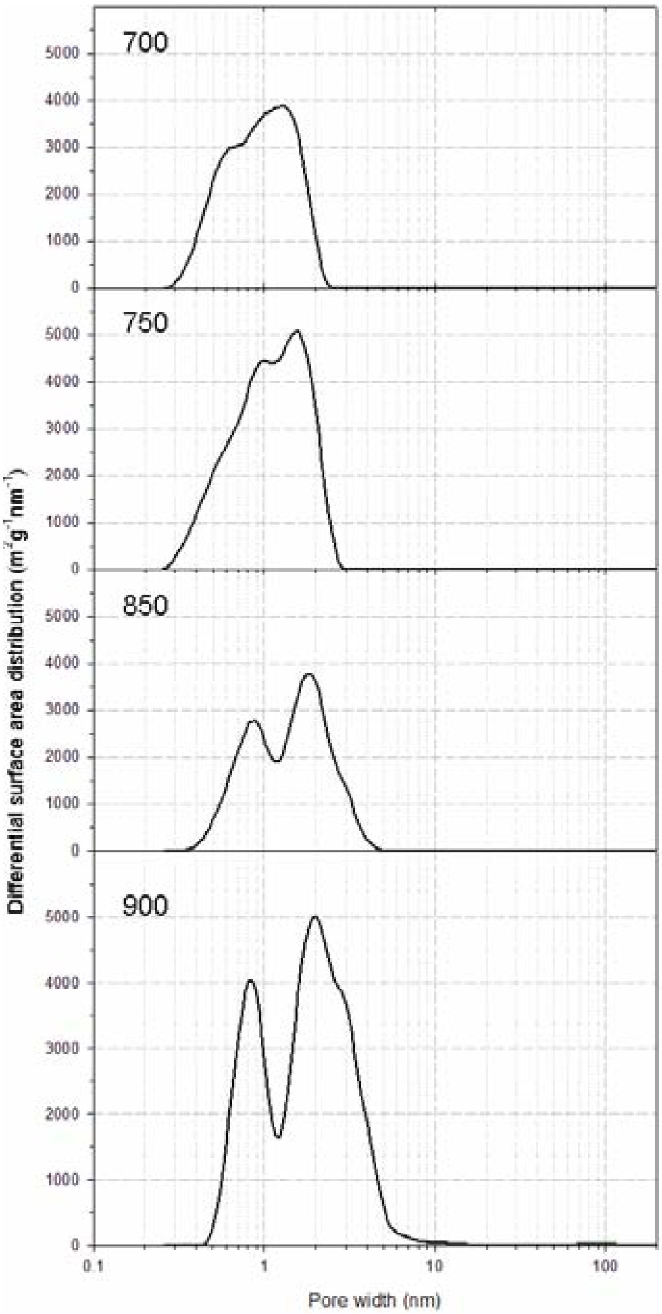

Figure 3: Differential surface area *vs* pore size of SMPC's prepared at different activation temperatures (calculated according to ref. [5]).

Now, the intensive studies are focused on the preparation conditions of the new kind of microporous carbons for their particular applications such as membranes and sorbents for the gas separation and accumulators of power gases (hydrogen, methane etc.)

The search for alternative energy sources for motor vehicles is an urgent problem of our day. The thriving area is the substitution of hydrogen and natural gas for the traditional hydrocarbon fuels for motor vehicles. Therefore, much attention is paid to the development of safe and efficient on-board storage facilities. The adsorptive storage of hydrogen and methane is one of such methods with a good safety. Systems based on SMPC nanomaterials with high sorbability are developed at the Boreskov Institute of Catalysis for the accumulation and storage of hydrogen and methane.

Experimental studies on adsorption of hydrogen and methane demonstrated a considerable sorption capacity of the SMPC materials.

These carbons were shown to absorb up to 65 wt % of methane at room temperature and 60 atm and more than 6 wt % of hydrogen under mild cryogenic conditions (at 77K).

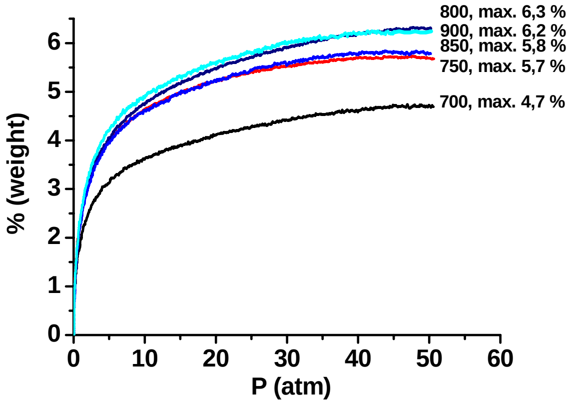

Figure 4: Isotherms of hydrogen adsorption at 77 K for SMPC's synthesized at 700 – 900 °C.

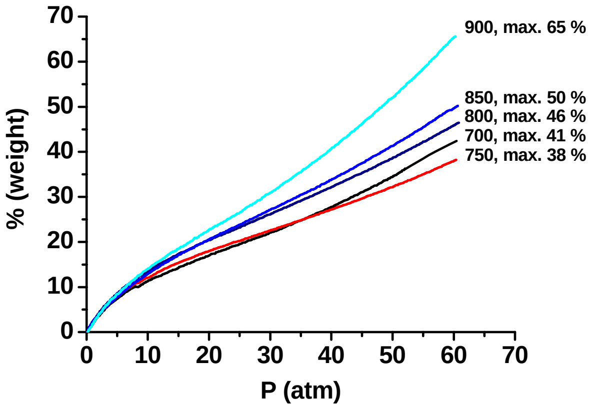

Figure 5: Isotherms of methane adsorption at 293 K for SMPC's synthesized at 700 – 900 °C.

The above data demonstrate that microporous carbons with the very large specific surface area can be synthesized from the high-ash biomass. The samples obtained are superior in their textural characteristics to the known best analogues synthesized by treating petroleum pitch with nitric acid. A correlation between the pore size distribution in the microporous carbons and their sorption capacity with respect to poorly sorbable gases like hydrogen and methane is found.

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PP-I-46

DYNAMIC ANALYSIS OF SORPTION OF TEXTILE DYES SUCH AS METHYLENE BLUE AND BASIC YELLOW 28 ON GRANULAR AND POWDERED ACTIVATED CARBONS

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Removal of dyes and pigments from waste waters of dying and printing industries is a major environmental issue. High surface area activated carbons are usually considered as attractive sorbents, which can be used in waste water treatment in these industries. For the design of such waste water treatment plants, detailed information are needed about the adsorption rates and the sorption rate determining mechanisms of such dyes within the adsorbents having high sorption capacities [1]. In the present study, sorption rates of Methylene Blue and Basic Yellow 28 on granular and powdered activated carbons were investigated by dynamic batch adsorption studies. Effective pore diffusion parameters, which control the sorption rates of these dyes on granular activated carbons and the sorption rate constants on both types of activated carbons were determined from the concentration decay curves of adsorbates in the batch adsorber and by using the moment analysis. Sorption capacities of these sorbents and the adsorption isotherms were also determined. Effects of adsorbate concentration, adsorbent amount and the pH of the solution on the sorption rate and the sorption capacity were investigated.

Some physical properties of the granular and the powdered activated carbons used in this work are given in Table 1.

Table 1. Some physical properties of activated carbons used.

Adsorbent	Surface Area (m^2/g)	Particle Size (cm)	Density (g/cm^3)
Granular Activated Carbon	747	0.112	1.09
Powdered Activated Carbon	741	0.0147	0.76

Moment analysis of the batch adsorber concentration decay curves is a powerful tool for the evaluation of the effective diffusivities and the adsorption equilibrium constants within the porous adsorbents. For two different models, considering the diffusion and adsorption in the pores as seperate terms (Model I) (Eq.1) and as a combined term (Model II) (Eq. 2), the zeroth moment expression, which corresponds to the area under the decay curve of dimensionless concentration within the adsorber were used in the evaluation of effective diffusivities.

$$\mu_o = \frac{R_o^2\left(\varepsilon_a + \rho_p K\right)}{15D_A\left(1 + \frac{w_s}{\rho_p}\left(\varepsilon_a + \rho_p K\right)\right)} \quad (1) \qquad \mu_o = \frac{R_o^2}{15D_A\left(1 + \frac{w_s}{\rho_p}\right)} \quad (2)$$

Here, D_A, R_o and w_s are the effective diffusivity, particle radius and the mass of adsorbent charged per unit volume of the adsorber, respectively. The apparent adsorption equilibrium constant $\rho_p K$ was evaluated from the gradient of the adsorption isotherm at the equilibrium adsorbate concentration.

Sorption results with Methylene Blue showed that, both the sorption capacity and the sorption rate constant values obtained with powdered activated carbon were higher than the corresponding values obtained with granular activated carbon. This was concluded to be due to the much higher pore diffusion resistance in the granular activated carbon. Dissociative chemisorption of the dyes near the pore mouths caused partial closure of the pores. This caused a significant resistance for further sorption at the inner parts of the granular activated carbon. The first order adsorption rate constant of methylene blue obtained with powdered activated carbon was about twice the corresponding value obtained with the granular activated carbon. For granular activated carbon, the sorption rate constant was found to be about 3.2 10^{-4} min^{-1} for w_s values between 0.07 and 0.2 g/l. The diffusion models proposed here gave good prediction of the sorption rate in the granular activated carbon. Especially for Model II (Eq. 2) effective diffusivity was found to be not dependent on concentration. The values of D_A were found to be in the orders of magnitude of 10^{-7} and 10^{-9} cm^2/s for Models I and II, respectively. During the sorption process, pH of the solution did not significantly change. However, the pH was found to be an important parameter on the sorption rate and on the sorption capacity. Among the different adsorption isotherms, Freundlich, Radke-Prausnitz and especially the Toth isotherms gave good fit to the sorption data obtained with both granular and powdered activated carbons. Comparison of the sorption behavior of Methylene Blue and the Basic Yellow 28 showed that both the sorption rate and the sorption capacity values obtained with Basic Yellow 28 were higher than the corresponding values obtained with Methylene Blue.

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PP-I-47

USE OF THE MESOPOROUS NITROGEN-CONTAINING ACTIVATED CARBONS AS THE SUPPORT FOR COBALT/CARBON CATALYSTS IN CO OXIDATION IN HYDROGEN-RICH MIXTURES

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Earlier [1] the opportunity was shown of use of a cobaltous deposit on activated carbon (AC) as a catalyst for CO oxidation in mixtures enriched by hydrogen. Catalysts, synthesized by impregnation of carbon materials with active component may be used in hydrogen mixtures for proton-exchange membrane fuel cells, as CO strongly adsorbs on anode catalysts and substantially decreases the fuel cell performance. The introduction of nitrogen in structure of AC results in rise of its electron-donor ability and in changing of the properties of the catalytic agent in red-ox reactions [2].

The aim of this work is the modification of a surface of mesoporous AC by nitrogen compounds **(AC-N)** and study of catalytic properties of Co compounds supported on AC-N in CO oxidation in hydrogen-rich mixtures.

For preparation of AC-N, AC KAU was used obtained from peach and apricot stones (surface area BET-1150 m^2/g, V_{mi} – 0,48 cm^3/g). Initial carbon KAU was oxidized in 25% HNO_3 at boiling temperature within 4 hour, then, by a procedure, specially designed by the authors, impregnated with water solution of melamine of various ratio melamine:carbon, then subjected to heat treatment at 800^{o}C in a stream of argon. As a result the nitrogen-containing carbons KAU-N with nitrogen content 1-6 % on mass were obtained.

Catalysts were synthesized by impregnation of KAU and KAU-N with a $Co(NO_3)_2$ aqueous solution, then calcined in Ar at 450^{o}C and reduced in flow of H_2. Nominal Co loading was 5 wt.%.

The surface texture of the samples was investigated in gas analyzer NOVA 2200e Cvantachrome instruments at temperature of liquid nitrogen (-196 ºC). Thermal gravimetry analysis was carried out using a Q-1500 “F. Paulik, J. Paulik, L. Erdey” system. The catalytic tests were carried out in flow fixed-bed quartz reactor. The studied reaction mixture contained: 1 vol.% CO, 1 vol.% O_2, 98 vol.% H_2. The analysis of reaction products was carried out by on-line gas chromatograph with conductivity detector.

It was revealed, that the introduction of nitrogen in KAU improves thermal stability of a carbon matrix to a surface oxidizing by oxygen of air up to 450^{o}C and does not result in essential change of its porous structure.

In figure, for example, the temperature dependences of CO oxidation in hydrogen-rich mixture on the studied samples is given. It may be seen from the Figure, that the introduction of nitrogen in a matrix of KAU results in essential increase of activity of catalyst.

Dependence of catalytic activity on the content of nitrogen on the carrier has extreme character. The sample containing 3 mas. % of nitrogen on a surface of carbon matrix is the most active. Over this sample 100 % conversion of CO in a reaction mixture containing 98 % of H_2 is achieved at temperature 160^{o}C. It is necessary to note, that similar influence of the contents of nitrogen in samples on their catalytic activity is revealed in [3] for oxidation of hydrogen sulphide.

It is shown, that activity of the catalyst 5 mas. %. Co/KAU-N with 3 % on mass of nitrogen did not reduce after 25 hours of work.

Thus, the use of nitrogen compound carbon as the support of the cobalt/carbon catalysts in CO oxidation reaction in the hydrogen rich mixtures are the very perspective.

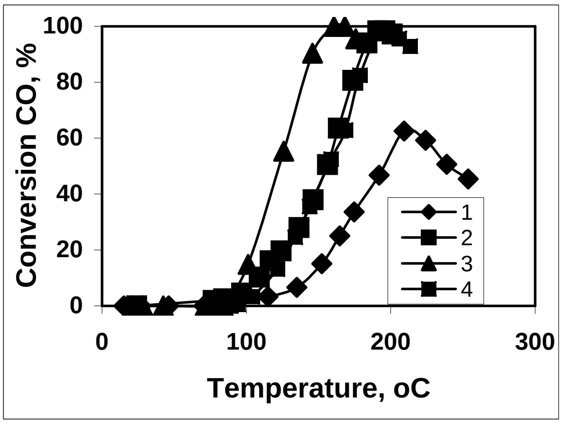

Figure. Dependence of CO conversion in hydrogen-rich mixture from temperature. on: 1 – Co/KAU catalyst, 2 –Co/KAU-N catalyst with 2% on mass nitrogen in carbon matrix. 3 –Co/KAU-N catalyst with 3% on mass nitrogen. . 4 –Co/KAU-N catalyst with 4% on mass nitrogen in carbon matrix.

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PP-I-48

ON THE WETTABILITY OF PLATELET CARBON NANOFIBER BY WICKING KINETIC MEASUREMENT

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Carbon supported catalysts are widely used in industry. The surface and wetting properties of carbon material are vital in catalyst preparation and applications[1]. Moreover, the amphoteric property of carbon should be tuned to a specific reaction.

In recent years, carbon nanofiber (CNF), one of the novel carbon materials, has been used as a potential catalyst support for various types of catalytic reactions. In some cases, CNFs are more competitive than activated carbon owing to their unique characteristics [2]. Recently, *Ros* et al found that fishbone carbon nanofibers oxided by HNO_3/H_2SO_4 had good affinity with water [3]. However, to the best author's knowledge, no systematic study of the wettability of platelet CNF has been reported so far. The present work focuses on the effect of surface modifications of the CNF on their wettability in different solvents, in order to better understand the catalyst preparation and reaction processes.

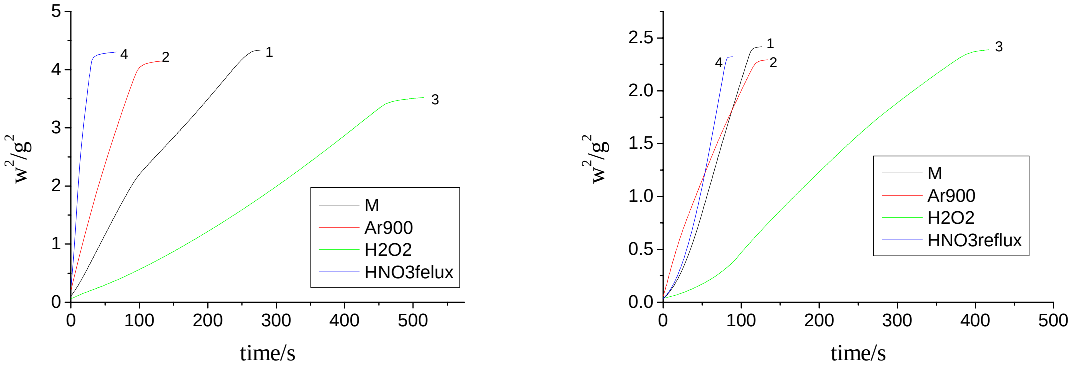
The platelet carbon nanofiber was synthesized by the CCVD method in our laboratory where carbon monoxide (CO) was decomposed on ultrafine iron powders under optimized conditions. The wettability of platelet surface was studied by means of wicking kinetic measurement using a Contact Angle Surface-Tension Instrument (Thermo Cahn Radian Series 3000). A capillary flow technique was successfully applied to characterize the interaction between the CNFs and various solvents [4]. Effects of CNF surface modification on its wettability as well as the wettability of platelet CNF toward various solvents were investigated systematically.

The measured relative wetting contact angles (RWCA) in cyclohexane, acetone, alcohol and water in table 1 showed that the interactions between the CNF surface and the solvent depended very much on the polarity of the solvents. If the contact angle between the as-synthesized platelet CNF cyclohexane is 0°, then its RWCAs in water, acetone and alcohol are 81.6, 45.2 and 24.8°, respectively. It is believed that the small polarity of the CNF surface led to better wettability in non-polar solvents such as cyclohexane than in polar solvents such as water.

Table 1 Characteristics of various solvents and measured relative wetting contact angles

Solvent	Surface tension (mN/m)	Density (kg/m^3)	Viscosity (mpa.s)	Dielectric constant(ε0)	RWCA/°
Water	72.8	998.2	1.005	80	81.6
Ethannol	22.8	789	1.15	24.3	24.8
Acetone	23.7	792	0.32	20.7	45.2
Cyclohexane	25.3	778.6	0.97	2.016	0

Further studies revealed that both the nature of the functional groups on the CNF surfaces and the wettability of the CNF in different solvents could be tailored by different surface modification methods. Fig.1 shows that CNF wettability was increased both in water and in cyclohexane, when it was treated in concentrated nitric acid. When it was treated in peroxide hydrogen, however, its wettability was decreased in both solvents. Interestingly, when it was treated in argon, its wettability was increased in water but decreased in cyclohexane. Temperature programmed desorption analysis of the modified CNFs revealed that the surface affinity changes could be attributed to the surface chemistry changes during modification.



a

b

Fig 1 Influence of surface modification on wettability of CNFs in water(a) and in cyclohexane (b)
as-synthesized CNF; 2. CNF after heated in argon at 900 ^{o}C for 4 h; 3. CNF after treatment in H_2O_2 for 24 h; 4. CNF after being refluxed in concentrated HNO_3 for 0.5 h.

In summary, wicking kinetic measurement is a successful method to determine the CNF's wettability. The described results are important for CNF synthesis and modification as well as its application in carbon-nanofiber-supported catalysts.

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PP-I-49

TAILORING CARBON NANOFIBER SURFACE PROPERTY FOR EFFICIENT Pd/CNF CATALYST IN TA HYDROPURIFICATION

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The unique properties of carbon nanofiber, a novel structured carbon material developed in the past two decades, have generated a large number of applications including selective absorption, energy storage, polymer reinforcement, and catalyst supports [1]. In a previous paper [2], we supported palladium on CNFs and developed a highly active catalyst for terephthalic acid (TA) hydropurification. However we did not focus on the effect of surface property of the CNF support on the catalyst activity for crude TA hydrogenation.

This paper deals with modification and characterization of surface properties of platelet CNFs. The hidden motivation was that surface properties of CNFs could affect not only interactions between the active metal and the support but also the activity of the supported catalyst [3]. Indeed increasing studies on carbon supported catalysts have shown that tailoring of catalyst properties to meet a specific need depends on how the physical and chemical properties of the carbon surface are tuned [4].

CNFs of platelet nanostructure were synthesized in our laboratory using the catalytically chemically vapor deposition (CCVD) with which carbon monoxide was decomposed on ultrafine iron powder under optimized conditions. The as-synthesized platelet CNFs were repeatedly demineralized in 4M HCl at 60 ^{o}C 5 times, each for about 1 h, to remove the remaining iron. The treated CNFs then underwent surface modification to obtain materials of different surface properties by different chemical and thermal treatments including treatment in gas such as air, argon, or hydrogen and in liquid such as hydrogen peroxide, acetone, or concentrated nitric acid. The modified CNFs were designated as C1 to C6 as in Table 1.

CNF supported palladium catalysts (0.5%Pd) were prepared via a standard incipient impregnation method using $Pd(NH_3)_4Cl_2$ as a palladium precursor. Their catalytic performance for the crude TA hydropurification was evaluated based on

4-Carboxybenzaldehyde (4-CBA) conversion. The reactions were carried out in a batch autoclave reactor under conditions similar to those in the industry.

Catalysts on modified CNFs were characterized by SEM, BET, TPD-MS, mass titration and CO chemisorption. Results indicated that physical and chemical properties of platelet CNFs were very different, depending on the modification conditions. Their physical properties such as surface area and porosity were affected more significantly by modification in acetone and concentrated nitric acid than by other modifications, while their chemical properties were more sensitive to each kind of modification method.

Mass titration measured pH_{pzc} (refer to Table 1) revealed that treatment in air and nitric acid generated more acidic group on CNF surface, but treatment in acetone, argon and hydrogen caused more basic surface. TPD analyses showed that the amount of the functional groups on the surface varied with modification conditions. Treatment in air generated the more surface groups, whereas hydrogen treatment created fewest surface groups. Fig.1 shows the catalytic performance of Pd supported on modified CNF for TA hydropurification. Clearly the catalyst activity was very sensitive to the CNF surface property. Further deconvolution of TPD spectra elucidated that the carbonyl group on CNF surface was vital for the catalytic activity of Pd/CNF catalyst for TA hydropurification.

Table 1 Designation of CNF and their pH_{pzc}

symbol	modification method	pH_{pzc}
C0	Purified CNF	6.65
C1	treated in air at 450 °C for 4 h	3.01
C2	Treated in Ar at 900 °C for 4 h	10.22
C3	treated in H_2 at 900 °C for 4 h	11.22
C4	refluxed in HNO_3 for 0.5 h	2.50
C5	treated in H_2O_2 at 25 °C for 24 h	6.63
C6	treated in acetone at 25 °C for 24 h	9.62

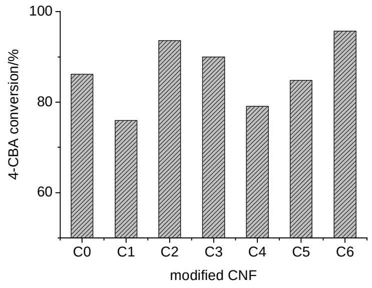

Fig 1 Effect of modification on the catalytic activity of Pd/CNF

In summary, CNF surface chemistry could be tuned by different modification methods. The catalytic activity of CNF supported catalyst could be controlled by tailoring the surface chemical property according to a certain specific application such as TA hydropurification. For TA hydropurification, better activity will be provided when the CNF support is modified in acetone, or thermal treatment in Ar stream at high temperature, e.g. 900 °C.

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PP-I-50

DENSITY FUNCTIONAL CALCULATIONS ON THE FORMATION OF CARBON NANOFIBERS

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Introduction

Carbon nanofiber (CNF) is attracting increased attention. There are two major reasons for studying this particular kind of carbon. On the one hand, filamentous carbon is formed in a temperature range where reactions of great technical importance, e.g., Fisher-Tropsch synthesis, methanation, and steam-reforming, are usually carried out. On the other hand, because of the unique chemical and physical properties induced by the CNF geometric and electronic structure, CNF has been applied in many fields such as catalysts, catalyst supports, gas storage materials, electrodes for fuel cell, and polymer additives. CNFs are synthesized mainly by chemical vapor deposition (CVD). The global evolution of the growth is divided into three stages: firstly, carbon atoms and hydrogen molecules are formed with the decomposition of carbon-containing gas on certain transition metal surface; secondly, the generated carbon atoms dissolve into the metal particle and diffuse through the bulk or along the surface; finally, the carbon atoms precipitate in the form of graphene layer on the rear side of the metal particle. The second stage is generally regarded as the rate-determining step because the activation energy for carbon diffusion is in reasonable agreement with that for the CNF formation in a range of 1.3-1.5eV. However, in fact, the CNF growth mechanism at the atomic scale is still unclear.

As suggested microdiffraction data, the [100] crystallographic direction of the FCC Ni lattice coincided with the filament axis, and (111) planes which were parallel to the graphite sheet accounted for the nucleation of the filament. This point was also confirmed by Yang and Chen who performed both experimental and theoretical studies on carbon filament growth, and verified that the Ni(100) and Ni(110) were among the gas/metal interface, while the Ni(111) and Ni(311) were among the graphite/metal interface. In this paper, the diffusion of carbon atoms on Ni(111) is focused.

Computational details

First-principles calculations based on DFT have been performed by using the CASTEP 3.2 code. The interactions between valence electrons and ion cores are represented by the ultrasoft pseudopotentials (USP) suggested by Vanderbilt, which regards the 4s 3d states as the valence configuration for Ni and 2s 2p states for carbon. Exchange and correlation of the Kohn-Sham theory are treated with the generalized gradient approximation (GGA) functional proposed by Perdew *et al.*. A plane wave energy cutoff of 270 eV is needed to converge the total energy within the tolerance of 2.0e-5 eV/atom. Linear synchronous transit/quadratic synchronous transit (LST/QST) method was performed to search the transition state for the carbon diffusion on the metal surface. The results presented here are based on periodic systems, i.e., a study of the Ni(111) 2 × 2 surface is essentially an infinitely periodic surface composed of these 2 × 2 repeating units.

Results and discussion

Two alternative threefold adsorption sites are considered: one is called the fcc site, the other the hcp site. The difference between them is that there is a Ni atom below the hcp site in the second layer and below the fcc site in the third layer. The obtained adsorption enthalpy of a carbon at the hcp site is 1.17 eV which is 0.05 eV lower than that at the fcc site, indicating that the carbon adsorption at the hcp site is more energetically favorable because of the higher coordination. Two surface diffusion pathways were investigated: the fcc-top-hcp path, a carbon atom moves from the fcc site to the hcp site via an adjacent top site. The second fcc-bridge-hcp path, a carbon atom reaches the hcp site via a bridge site. The activation energy is 2.42 eV and 0.60 eV for the first and second pathway, corresponding to two transition states with a carbon atom over the top site and bridge site, respectively.

Conclusion

During the CNF growth, if the carbon content on the gas/metal interface is low, the carbon surface diffusion adopts the fcc-bridge-hcp pathway. And when the concentration is high, carbon atoms may diffuse along both the two pathways. However, our previous calculation indicates that the activation energy for the carbon bulk diffusion is 1.22 eV at the CNF steady-state growth stage. As a consequence, carbon atoms will diffuse in the bulk Ni under high interface concentration to produce fishbone-type or platelet CNFs while the surface diffusion leads to the formation of tubular CNFs under dilute interface carbon content.

PP-I-51

Pd SUPPORTED ON SURFACE-TREATED CNF AND THEIR CATALYTIC ACTIVITY IN HECK REACTIONS BETWEEN ARYL HALIDES AND OLEFINS

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The olefination of aryl halides (Heck reaction), one of the most important CC coupling reactions in organic synthesis, is mostly catalyzed by palladium complexes in homogeneous solution. Regarding industrial applications, however, these catalysts are expensive for their difficulty to separate Pd from the reaction mixture and their hardness to reuse. Nowadays, the problem concerning separation, recovery of the Pd complexes and thermal stability (high reaction temperatures) have been trying to be overcome by using the heterogeneous palladium system.

As a new kind of carbon materials, carbon monofilament (tubes and fibers), CNT and CNF, has been testified to be a new catalysis material with unique characteristics. In this paper, heterogeneous Pd catalysts were prepared by supporting the Pd precursor on surface treated CNF, and then used in Heck reactions. We attempt to develop a new heterogeneous catalyst for Heck reaction.

The CNF sample was produced by decomposition of CO over a γ-Al_2O_3 supported 20 wt% Ni-Fe alloy. Cuffs, after different kinds of surface treatment, supported palladium catalysts (1%Pd) were prepared by a standard incipient impregnation method using H_2PdCl_4 as palladium precursors. For the sake of comparison, catalysts of Palladium supported on active carbon and graphite were also produced through the same procedure. Heck reaction was conducted in a three-necked flask equipped with a septum and a reflux condenser. The qualitative and quantitative analysis of the reactant was performed by GC.

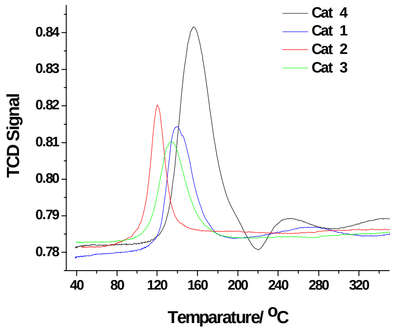

Fig.1 TPR of Pd/CNF

No.	Treatment of CNF	Peak temperature	Pd dispersion[a]	Pd Diameter (nm)[a]	Yield (%)[b]
Cat1	——	140 °C	22.3%	5.8	72
Cat2	HT[c]	118 °C	4.1%	26.4	33
Cat3	HNO3	130 °C	19.2%	6.7	68
Cat4	Acetone	160 °C	24.3%	5.3	78
Cat5	(AC)	——	20.4%	6.4	35
Cat6	(Graphite)	——	17.5%	7.0	25

Table 1. [a] Measured by CO-Chemisorption; [b] Reaction conditions: bromobenzene, styrene, NEt_3, 0.2mol% Pd, DMAc; T=140 °C and t=24h; [c] Heat treatment in 1700 °C for 3h.

The result showed that surface treatment of CNF can import different kinds of oxygenic group on the surface of CNF, and these groups have great impact on the Pd/CNF catalysts, which increase the interaction between the Pd and the CNF surface. As shown in the TPR plots (Fig.1), greater interaction between the metal and the support lead to higher peak temperature. Interestingly, the catalytic activity of Pd/CNF have good correlation between TPR peak temperature, i.e. the activity increased with the increasing peak temperature, which was shown in Fig.1 and Table.1 (Cat1~Cat4).

The pretreatment of CNF also have great impact on the Pd metal dispersion of Pd/CNF. As shown in Table. 1, the Pd metal dispersion measured CO pulse chemisorption varied from 4.1% to 24.3% and the average metal diameters varied from 5.3nm to 26.4. As expected, the higher the metal dispersion, the higher yield of the Heck reaction. The Pd dispersion of Pd/AC and Pd/Graphite was close to Pd on CNF, which was 20.4% and 17.5%, respectively; though the activities of Pd/AC and Pd/Graphite were much lower than Pd/CNF. It might be caused by two reasons. One is that the surface of CNF has great impact on Pd metal interaction with CNF, and hence improves the activity. The other is that the specific microstructure of CNF makes the reactants easier to contact with the active metal which make the reaction fast.

The reusability of the catalysts was also tested. After separation from the reaction mixture of the initial run and washing with CH_2Cl_2, Cat3 was reused for six times in the same reaction condition. The recycled catalyst showed high activity nearly to the first run.

In summery, the CNF supported Pd catalysts exhibit high activity towards the Heck reaction. The activity is improved by the relatively strong metal-support interaction, well dispersed Pd particles and the mesoporous nature of CNF. The catalysts can be easily separated from the reaction mixture and reused after washing without loss in activity. As the Pd/CNF can solve the problems of the traditional homogeneous catalysts, it has a bright future to replace them and enhance the application of Heck reaction in industrial scale.

PP-II-1

FUNCTIONALIZATION OF CARBON NANO BALL FOR BIO-MEDICAL APPLICATIONS

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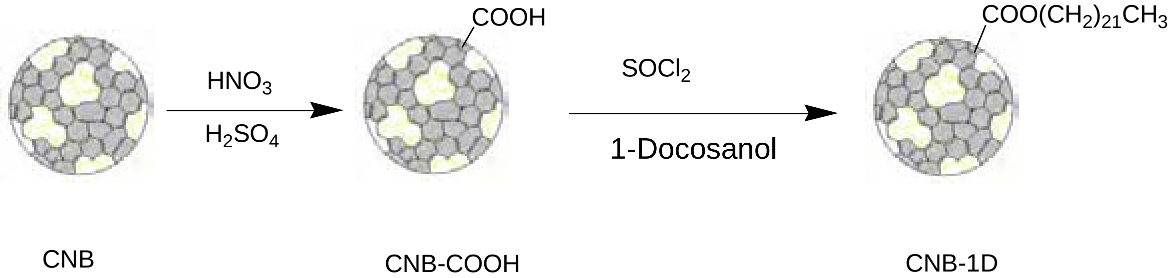
Carbon nano balls (CNBs) are basically hollow core mesoporous shell structures with specific surface area of 1,230m^2/g and the total pore volume 1.27 cm^3/g as determined by nitrogen BET adsorption measurements [1,2] have attracted much attention for potential applications in many fields of science and engineering [3]. Drawing parallel with carbon nano tubes (CNTs) it would be interesting to investigate the utility of CNBs for its application as carrier for drug delivery [4]. The task of drug delivery can be accomplished by means of either physical adsorption of the drug onto CNB or by chemical modification of CNB i.e., through functionalization [5]. The later has been found to be better in terms of better controlled release of the drug than former where the release of the drug can be fast and uncontrolled.

In this report we disclose the functionalization of CNBs by oxidation route and its modification with 1-docosanol, a known antiviral long chain alcohol [6]. In a simple synthetic step the CNBs were oxidized with dilute sulfuric acid nitric acid mixture at 80 ^{o}C for 18 h for generation of carboxyl groups on the surface of CNBs. The oxidized material was treated with thionyl chloride followed by its interaction with 1-docosanol for its chemical linkage with CNBs through ester linkage (**Scheme-1**). The oxidized material and 1-docosanol supported CNB (CNB-1D) were characterized by elemental analysis, ^{1}H and ^{13}C NMR, XPS and SEM analysis. The biological activity of the CNB-1D is in progress and would be communicated in due course.



Scheme-1 Graphical representation for the synthesis of 1-docosanol chemically bound to CNB

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PP-II-2

ACTIVATED CARBON AS CATALYST. EFFECT OF THERMAL TREATMENT ON ITS CATALYTIC PROPERTIES FOR CWAO

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Activated carbon (AC) is a versatile material that typically has been used as adsorbent, but lately certain applications as catalyst have been found. Stüber et al. [1] achieved up to 99% of phenol removal in a slurry reactor, at 160 ºC and 0.7 MPa of oxygen partial pressure, whereas Fortuny et al. [2] obtained 68 % of phenol removal in a fixed bed reactor, at 140ºC and 0.9 MPa of oxygen partial pressure, operating at trickle flow regime, both using a commercial AC as catalyst. Pereira et al. [3] also used a commercial activated carbon as catalyst in the oxidative dehydrogenation of ethylbenzene. However, there is no fully understanding of the characteristics that give catalytic activity to this material. Several researchers have made modifications on certain properties of AC by oxidation in liquid and gas phase. Also thermal treatments in inert atmosphere can be done in order to change its surface chemistry. These surface modifications affect the performance of the activated carbon in their applications. For instance, the adsorption of aromatic compounds can be improved by eliminating oxygen groups from the surface. Regarding to the catalytic activity, Pereira et al [3] found the increase of the amount of carbonyl/quinone groups in the AC surface improves its catalytic activity in the deoxyhydrogenation reaction. In the present study, a commercial AC, with proven catalytic activity for wet oxidation of phenol, was characterised and thermally modified at different temperatures (400, 700 and 900ºC) in order to selectively remove oxygen groups, so that the surface functional groups owning the catalytic activity could be identified. The behaviour of the modified samples was tested for phenol adsorption, and its catalytic performance for phenol CWAO was evaluated in a trickle bed reactor, at 140ºC and 0.2 MPa of oxygen partial pressure. Also thermal treated samples were checked for the decomposition of H_2O_2 –according to the procedure described by Khalil et al [4].

The results from CWAO of phenol show that high oxygen elimination from the surface does not change the catalytic behaviour of the activated carbon. However, the removal of carboxylic groups and the corresponding increase in the amount of lactones lead to a slight increase in the phenol disappearance in steady state. Figure 1 shows that, despite samples AC700 and AC900 have less than 50% of the original oxygen content, the catalytic activity seems to be identical after 72 hours on stream. The results from textural characterisation after being used show a drastic decrease in the surface area, and also that practically 82% of the micropore volume is lost. However, considering that all the AC samples show almost identical steady catalytic activity after 72 hours, the critical factors responsible for the catalytic activity should not entirely depend on the micropore surface area. Regarding phenol adsorption, thermal treated samples show higher adsorption capacity, whereas for H2O2 decomposition, in accordance to Khalil et al [4], the absence of acidic groups favours the H2O2 decomposition, sample AC900 therefore shows the higher decomposition capacity.

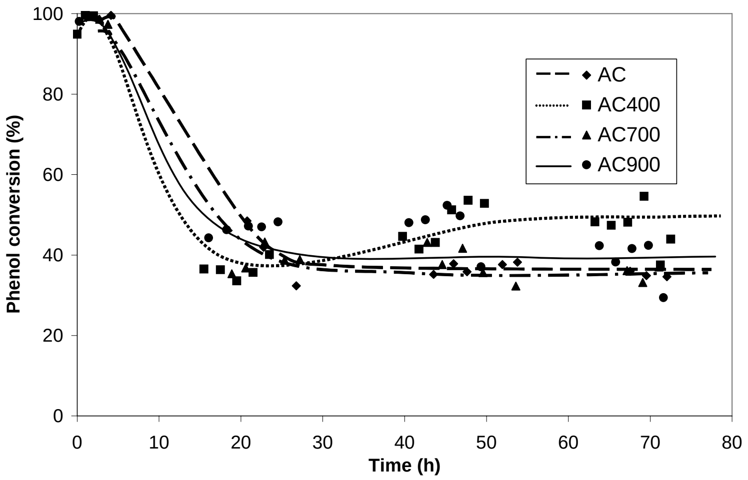

Figure 1. Evolution of the conversion with the time on stream

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PP-II-3

DESIGN AND STUDY OF Ru-CeO_2/CARBON CATALYSTS FOR WET AIR OXIDATION PROCESSES OF INDUSTRIAL WASTEWATER TREATMENT

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Catalytic wet air oxidation (CWAO) is one of the most promising technologies for the treatment of variety organic and inorganic pollutants which may be oxidized into safety compounds. The creation of catalytic reactors for neutralization and purification of industrial waste water with high level of toxicity by CWAO method has required the development of new suitable catalysts. There are two aims to be intensively pursued in developing CWAO catalysts: to increase the catalytic activity on basis of new chemical compositions and to increase the catalyst stability by application of new synthetic materials. Carbon based catalysts (Ru/C, Pt/C, Pd/C CuO/C, Fe_2O_3/C) are preferred over others (Ru/TiO_2, Ru/CeO_2, Ru/ZrO_2, MnO_2/CeO_2, CoO/Bi_2O_3, CuO-ZnO/Al_2O_3, etc.) due to possibility of the use of carbon both as an adsorbent and the catalyst simultaneously. Of particular interest is the development of CWAO catalysts for hard-to-oxidize compounds such as acetic acid, phenol and aniline, which are not biodegradable pollutants due to their high toxicity. In the Boreskov Institute of Catalysis, intensive studies are focused on metal catalysts supported on modifications of porous graphite-like materials of the Sibunit family. Sibunit is superior to conventional active carbons in the stability in aggressive and oxidative media; it behaves as adsorbent and catalyst in liquid-phase oxidation of various compounds with oxygen. Besides, Sibunit is produced in forms (balls of differ size or honeycomb) suitable for the use in chemical reactors of different types.

Carbon-based catalysts (mainly Ru-, Pd-, Pt-, and CeO_2 compositions supported on various types of commercial graphite-like material Sibunit and model Sibunits of different texture, also varying by the type and strength of surface functional groups), have been prepared, characterized and tested in wet air oxidation of aniline, phenol and Cl-phenol. The experiments were performed in batch autoclave reactors of different constructions (V=200 ml and V=500 ml) at T=160 – 200°C and P_{O2} =0.3-1.0 MPa. The most promising results show that the Sibunit-supported catalysts have the highest catalytic activity for oxidation of different molecules and degradation of all the intermediate organic compounds to CO_2. It is necessary to note that the activity of Sibunit is very high, so we have investigated the nature of Sibunit catalytic activity by various methods. After testing and analysis of possible variants (e.g. formation of the radical generating surface species, the presence of catalytically active impurities Fe and Cu, peculiar properties of the Sibunit structure) we have came to the conclusion that the presence of active sites, with O-containing functional groups, explains the Sibunit catalytic activity in some cases. Overall concentration of O-containing groups was measured by IR-spectroscopy and it is equal to 0.1±0.05 mmol/g Sibunit.

The catalytic and adsorptive properties of promoted Ru-CeO_2/C catalysts are considered explicitly as the examples of application of offered principles of design for creation of the catalysts for practical use in clearing of industrial wastewater. Principally, three aims were identified and solved: (1) minimization of Ru loading in the catalyst, (2) introduction of promoters to provide complete oxidation of organic compounds adsorbed on the catalyst surface, and (3) prevention of the leaching of active component. The developed techniques of catalysts synthesis have given us a possibility to solve the indicated problems in the best way.

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PP-II-4

ON THE PREPARATION OF HIGH-DENSITY AND STRONG CARBON NANOFIBER SUPPORT BODIES

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Introduction

Two important pre-requisites have to be balanced for a given catalyst support material: a high bulk density and a high porosity. High bulk density, i.e, mass per reactor volume, results in a more efficient use of the reactor volume and is therefore economically favorable above low density supports. On the other hand, the porosity i.e., accessibility is important in order to avoid mass transport limitations.

Nowadays, new support materials, such as carbon nanofibers (CNF) are available. The properties of CNF potentially surpass those of conventional oxidic supports such as silica and alumina [1,2]. Carbon nanofibers are chemically inert, pure and mechanically strong and thus suitable as catalytic support material. The CNF-bodies consist of entangled individual carbon nanofibers, which are formed during the catalytic growth via decomposition of CO and H_2 on Ni/SiO_2 growth catalysts. An ongoing discussion on the suitability of CNF as catalyst support relates to their claimed low bulk-density.

In this contribution, we show that for CNF supports the density and the porosity can be tuned. The metal loading of the growth catalyst and the growth time of the CNF-bodies are key factors in that respect. Moreover it is shown that these materials hold great potential as catalyst support in slurry, fixed and fluid bed applications.

Results and Discussion

CNF were grown from 5 wt% Ni/SiO_2 and 20 wt% Ni/SiO_2. SEM investigations showed that after CNF growth the formed CNF bodies were enlarged replicates of the original macroscopic Ni/SiO_2 particles. Both CNF bodies showed well defined individual fibers on the outside of the bodies. However the CNF bodies grown from 20 wt% Ni are densely packed on the inside and the fibers are highly entangled; individual fibers were difficult to observe. The bodies grown from the 5 wt% Ni on the other hand are more open on the inside and the straight individual fibers are clearly visible. This can be explained by the growth mode of the

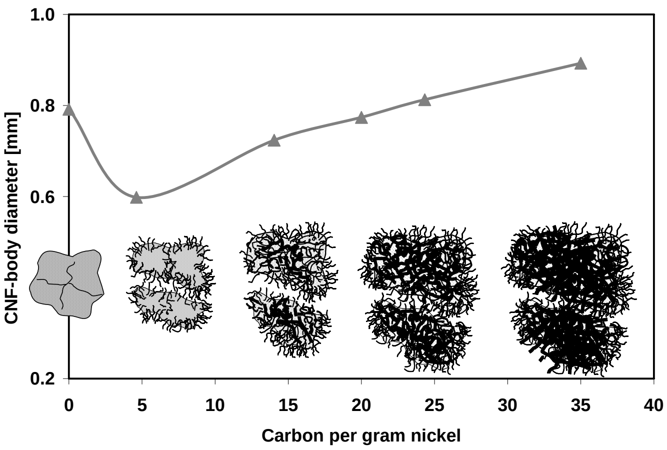

Figure 1: Schematic representation of macroscopic bodies consisting of dense CNF growth from left to right: Ni/SiO$_2$ body with cracks – growing CNF fragmentize the body – start of large diameter growth CNF in interior – further expansion of CNF body.

CNF from both catalysts. The fibers grown from 20 wt% Ni have a large diameter compared to those grown from 5 wt% Ni. This is a result of the more significant sintering of the Ni particles in the 20 wt% growth catalyst as result of the higher metal loading. Thicker fibers grow in a more irregular way, the so called rice shell mechanism [3], resulting in a high entanglement and high bulk density (0.9 g/ml). Note that in the initial stage of growth the starting Ni/SiO$_2$ catalyst breaks in smaller particles as seen in SEM. Next the CNF grow in a highly entangled way resulting in filling up the open space, i.e, forming a high density and strong bodies. This is schematically shown in Figure 1. The thin fibers on the other hand grow in a more straight manner resulting in an open, less entangled structure, with a low bulk density (0.4 g/ml).

Concluding Remarks

CNF can be prepared in high-dense bodies (bulk density 0.9 ml/g). These bodies have a bulk crushing strength of 1.25 MPa. which gives them a great potential as a catalyst support [4]. Both the bulk density and strength of the CNF bodies relates to the metal loading in the Ni/SiO2 growth catalyst.

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PP-II-5

Cu/CARBON XEROGEL CATALYSTS FOR THE SELECTIVE CATALYTIC REDUCTION OF NO BY NH_3: EFFECT OF THE PORE TEXTURE

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Introduction

Recent works reported by Job et al. have shown that the morphology of porous carbon prepared by sol-gel process can be tailored by varying the initial pH of the precursors solution within a narrow range [1]. Carbon supported catalysts are envisaged for the low-temperature Selective Catalytic Reduction (SCR) processes [2]. SCR of NOx using ammonia is commercially used to remove NOx from stationary sources [3]. More recently, this process was developed in the reduction of NOx present in Diesel Truck Exhaust Gas, but with urea as source of NH_3. Few studies concerning SCR of NO by NH_3 have been devoted to Cu/C catalysts [4,5]. Therefore, the goal of this work was to evaluate activity SCR of Cu/C whose carbon support was prepared by sol-gel process and to examine the effect of the support structure on the catalyst performances.

Experimental part

Carbon xerogels were prepared by evaporative drying and pyrolysis of resorcinol-formaldehyde gels. The pore texture of the carbon materials was adjusted as desired by fixing the dilution ratio and the pH of the precursors solution to adequate values. Three supports with very different maximum pore sizes were prepared: one micro-mesoporous with small mesopores (10 nm), one micro-mesoporous with large mesopores (40 nm), and one micro-macroporous (80 nm).

The Cu/C catalysts were obtained by impregnation with $Cu(NO_3)$ solutions. Two impregnation methods were used: (i) the wet impregnation method (WIM), i.e. the immersion of the support in an excess of metal salt solution whose concentration is adjusted so that the amount of liquid that entered the pores contain the metal amount to be deposited on the support; the procedure is followed by filtration and drying; (ii) the impregnation (IMP) using an excess of solvent containing the exact amount of metal to be dispersed on the support, the solvent being removed by evaporation.

Temperature programmed decomposition (TPD_{ec}) was performed on the carbon supports from 298 to 1173 K (10 K/min). SCR catalytic tests with Cu/C catalysts were carried out from 298 to 573 K (4 K/min), respectively. For SCR, the gas mixture was: $NO/NH_3/O_2/He$ = 0.02/0.02/3.00/96.6 with total flowrate = 138 cm^3/min. Each catalytic test was carried out with 0.02 g catalyst. The TPD_{ec} and SCR effluent compositions were monitored continuously by sampling on line to a quadruple mass spectrometer (Pfeiffer Omnistar).

Results

The emission profiles of CO and CO_2 established from the TPDec of the three supports are quite similar (CO : 400μmol.g^{-1}; CO_2 : 170μmol.g^{-1}). The WIM method allows higher metal content compared to the IMP method. The Cu-free carbon samples exhibit a significant activity for the SCR of NO above 533 K due to the direct reaction of carbon with NO. In presence of copper and with a spatial velocity (VVH) = 95000 h^{-1}), the reduction reaction of NO by NH_3 starts between 403 and 433 K and shows a maximum in the 523 – 553 K temperature range. Moreover the SCR efficiency increases both with the copper content and with the pore size of the support.

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PP-II-6

HYDRATION OF α-PINENE OVER ACTIVATED CARBON CATALYSTS

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1. Introduction

Activated carbons are high surface area materials, exhibiting good stability, good mechanical resistance and high porosity. Due to these properties, they are widely used in heterogeneous catalysis as catalysts and catalyst supports [1, 2]. The acid catalysed α−pinene hydration yields a complex mixture of monoterpenes, being the main product, α−terpineol, widely used in the pharmaceutics and perfume industries. Traditionally, mineral acids are used as catalysts, but the effluents disposal leads to environmental problems. These problems can be overcome by use of solid acid catalysts [3-5]. In this work we report the results of the hydration of α-pinene carried out over acidic activated carbons.

2. Experimental

Catalyst samples were prepared from a commercial carbon (NORIT GAC 1210) (sample C0), as follows: C1 – C0 stirred 1 h with HNO_3 5 M at room temperature, washed until neutral pH; C2 – C1 treated with fuming sulphuric acid: heating in fuming sulphuric acid at 90ºC during 24 h, followed by washing until neutral pH. Catalytic experiments were carried out in a jacketed batch reactor equipped with a stirrer, at 50º C. In a typical experiment, the reactor was loaded with 114 mL aqueous acetone (1:1 v/v) and 0.2 g of carbon catalyst. Reactions were started by adding 3.15 mmol of α-pinene. Stirring speed was kept at 800 min^{-1}.

3. Results and Discussion

Figure 1 exemplifies the TPD-MS profiles obtained by monitoring CO_2, CO and SO_2 released upon heating the carbon sample C4, as well as the corresponding deconvolution curves. Surface composition was estimated by integrating the deconvolution bands.

The main product of the acid-catalysed α-pinene hydration over activated carbons is α-terpineol, being also obtained limonene, terpinolene, β-fenchol and isoborneol, as minor products. Figure 2 compares the α-pinene concentration profiles for the experiences carried out with the catalyst samples C0 (as supplied), C1 (only HNO_3 treated) and C2 (treated with fuming sulfuric acid subsequently to the oxidation with HNO_3). It was observed, that the treatment with fuming sulfuric acid improves the catalytic performance of the carbon catalyst. All the oxidised carbon catalysts exhibit good selectivity to α-terpineol (figure 3).

4. Conclusions

Activated carbon based catalysts exhibiting good activity for the hydration reaction of α-pinene, with good selectivity to α-terpineol, could be prepared by acidic treatments. The highest activity with still good selectivity to terpineol (75% at 90% conversion) was achieved with an activated carbon C2.

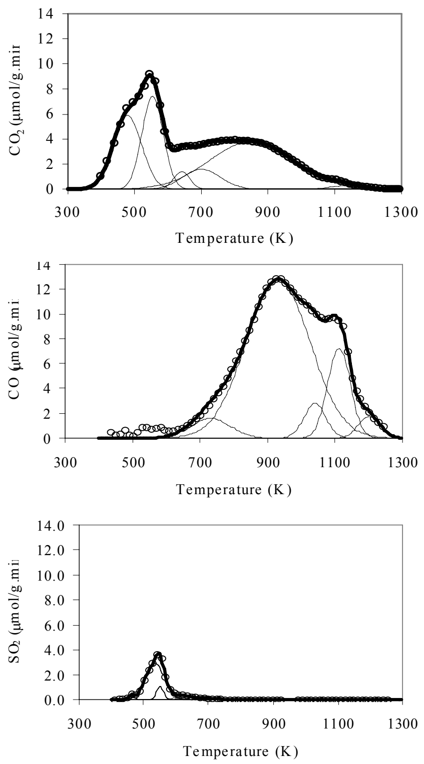

Figure 1 – CO, CO_2 and SO_2 TPD profiles and deconvolution curves for sample C2.

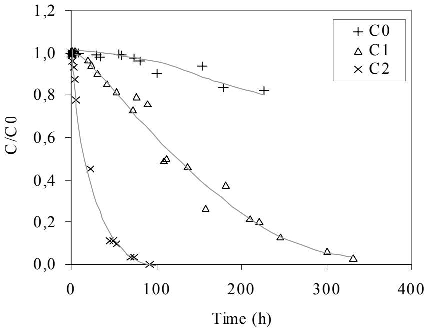

Figure 2 – α-Pinene concentration profiles for the batch experiments carried out with the catalyst samples C0, C1 and C2.

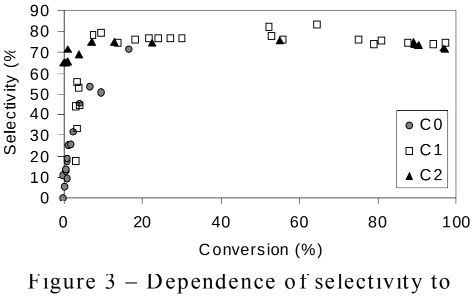

Figure 3 – Dependence of selectivity to α-terpineol on carbon treatment.

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PP-II-7

CONNECTING CARBON FIBRES BY MEANS OF CATALYTICALLY GROWN NANOFILAMENTS: FORMATION OF CARBON-CARBON COMPOSITES

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Carbon fibers are the basic part of the lightweight composite for high-performance materials[1] Depending on the application fields of the material, the filling of the composite can vary from polymeric to inorganic matrixes. Carbon/carbon (C/C) composites belong to the second group and consist of a fibrous carbon substrate embedded in a carbonaceous matrix. Even though the same element forms both of the phases or constituents, a C matrix of a C/C composite comes from two basic processes[2] based on (i) the carbonization of an organic solid or liquid precursor and (ii) the infiltration and densification of gaseous hydrocarbons (CH_4, C_2H_4, C_2H_2, etc.) into textured carbon supports.

The main drawback of the first process is the very high temperature of the thermal treatment (2000-3000°C) necessary to achieve a sufficient order of the C forms[2,3], whereas the problem of the second process is related to the infiltration process, which may be more difficult in the internal part of the composite[2,3].

Metal catalysts are well-known to be active in forming C nanostructures[4] and to reduce the pyrolysis temperature[5]. The catalytic method requires a metal catalyst (usually Ni, Fe, or Co or alloys) supported in the form of nanoparticles on the carbon fibers and a carbon feedstock (hydrocarbon, CO). The catalytic route to the synthesis of C/C composites allows quasicrystalline carbon to be deposited at moderate temperatures (600-1200 °C) with a large carbon yield[6].

As the formation of porous (high surface area) or dense matrixes is governed by the synthesis conditions, in this work the step by step catalytic formation and growth of a carbon matrix on carbon fiber supports is followed by means of SEM, TEM, AFM microscopies, XRD and BET analyses. The aim is to partially contribute to the understanding of the factors affecting the matrix formation. It is shown that nanofilaments growing at the surface of the metal particles are the first products of the synthesis (Fig.1 b). By increasing the reaction time, a porous network of intercrossing filaments, which interconnect the original fibers, is generated (Fig.1 c). At later reaction stages a dense carbon matrix is progressively formed, embedding the carbon substrate with the formation of a dense composite (Fig.1d). Evidence is presented on the role of the metal particles in the formation of the dense carbon matrix.

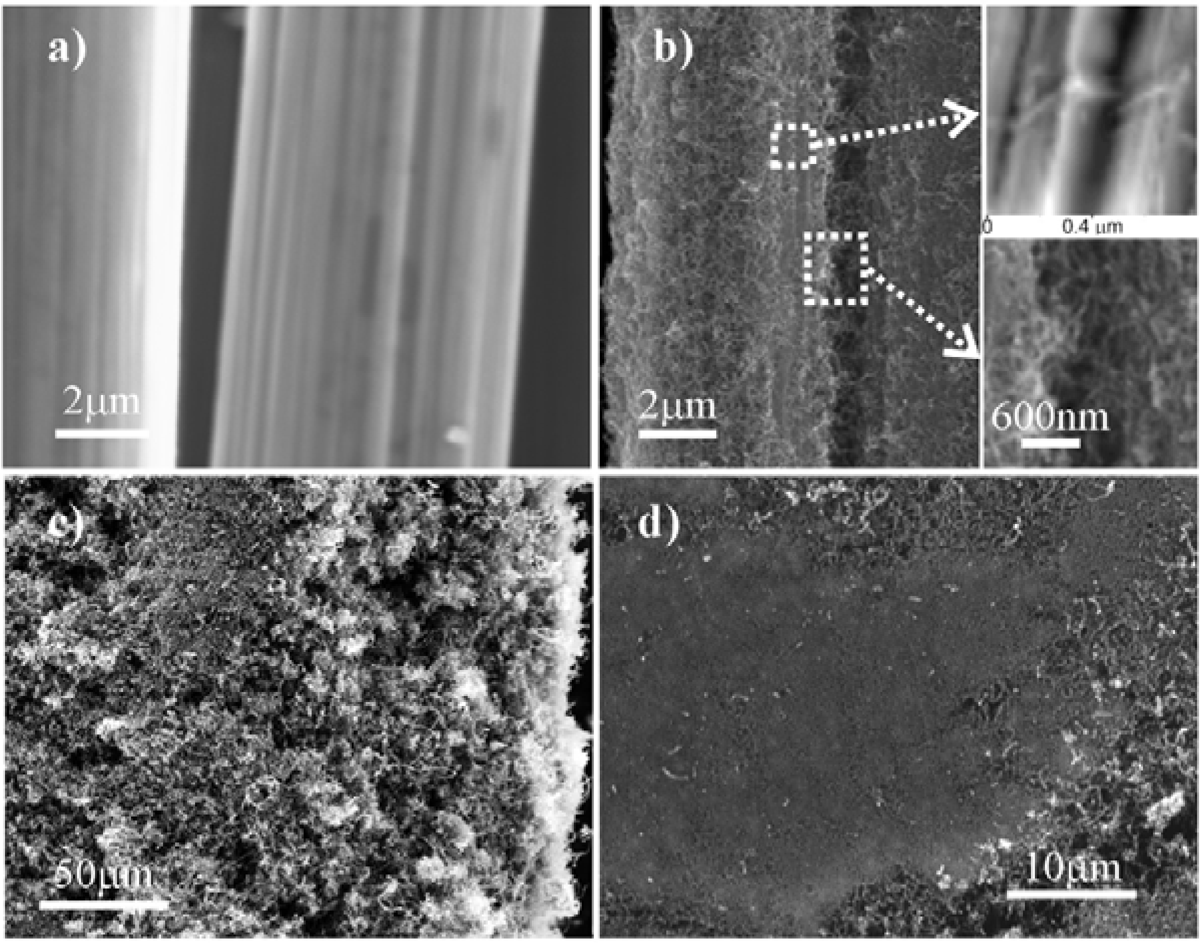

Figure 1

Acknowledgments

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PP-II-8

POROUS CARBONS/ZnO COMPOSITES: SYNTHESIS AND CHARACTERIZATION

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Porous carbons have attracted a great attention in recent years, due to their potential applications in many fields, including catalytic supports, gas storage, molecular sieves, porous electrodes [1]. Organic polymers like as polyacrylonitrile (PAN), phenolic resin, polyimides, poly(p-phenylene vinylene), polyvinyl acetate and polyfurfuryl alcohol (PFA) are commonly used as carbonaceous precursors [2]. Among them, PFA can be easy prepared from a solution of furfuryl alcohol and organic (p-toluenesulphonic, trifluoroacetic) or inorganic ($SnCl_4$, I_2) Brønsted/Lewis acid catalysts [3]. The pyrolysis process of PFA is expected to form non-graphitizing carbons (char formers) with a relatively high carbon yield if compared to other precursors [4,5].

In this contribution it is shown that, starting from furfuryl alcohol and $ZnCl_2$ (Lewis acid catalyst), PFA has been obtained under mild conditions (80-100°C). Subsequent pyrolysis at 500-600°C under controlled atmosphere (N_2/air mixture) gives rise to a highly homogeneous and porous ZnO/carbon composite (Fig.1 a,c), which after a subsequent thermal treatment at higher temperatures in N_2 (800-900 °C) changes into a porous carbon (Fig.1 b,d). The carbon surface is now characterized by a clear presence of pockets. We think that these pockets are the places where ZnO microcrystals were implanted. In other words, ZnO has behaved as a template of the carbon surface.

The formation of an oxide/carbon nanocomposite is very interesting, because it is expected: to improve the abrasion resistance, modify the electrical properties, act as flame retardant and UV stabilizer of the carbon phase. A second element of interest in this novel syntesis route of carbon/ZnO composites, via catalytic dehydroxylation and dehydrogenation, is represented by the presence of ZnO structures with photocatalytic properties for sensing properties. A further element of interest is represented by the formation of an imprinted surface carbon phase, which is originated by reduction of the ZnO microcrystallites implanted on the carbon surface and successive vaporization of metallic Zn.

It is noteworthy that by modifying the thermal treatment, materials with different morphology and properties can be obtained. The surface properties and the structure of the so-obtained materials have been investigated by means of SEM and AFM microscopies, ex-situ EXAFS techniques, XRD analysis and Raman spectroscopy.

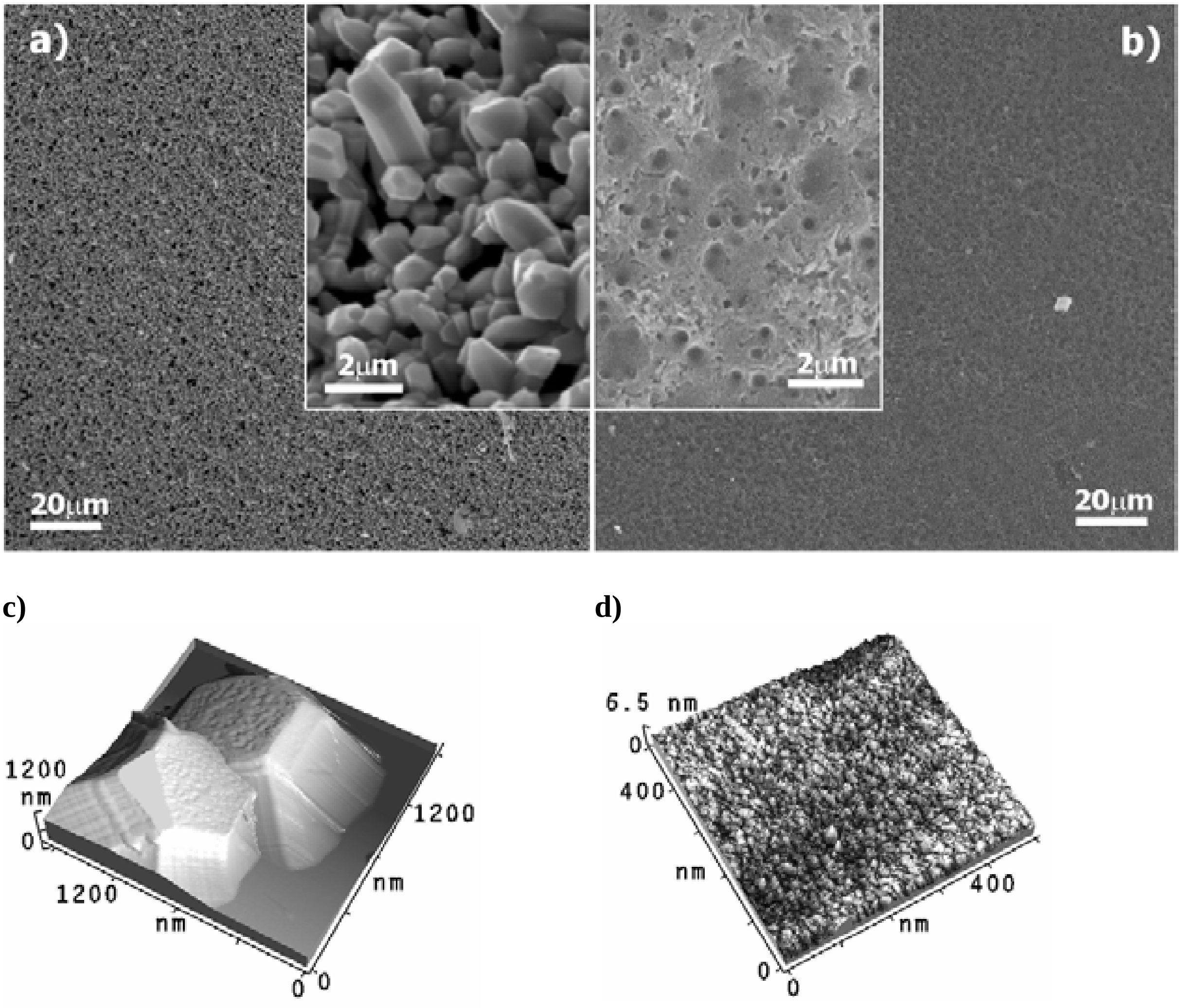

Figure 1: SEM images of the samples obtained at 600°C in N_2/air gas mixture a) and 800°C in N_2 b). Large scale contact-AFM topographies of the samples obtained at 600 and 800°C evidence the presence of protruding ZnO microcrystals c), and of the porous carbon matrix d), respectively.

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PP-II-9

THE USE OF CARBON-BASED ELECTRODES FOR THE ELECTROCHEMICAL TREATMENT OF WASTE WATERS WITH NON-BIODEGRADABLE ORGANIC COMPOUNDS

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The electro-oxidative treatment in an environmental friendly and economically viable method for hardly biodegradables organics molecules and disinfection of waste waters. In the design of any electrochemical solution to a specific industrial problem a suitable cell configuration and an electrode materials must be selected. In the field of electro-oxidation these represent the most important factors for both the direct heterogeneous oxidation/reduction of pollutants and the generation of oxidising agents that react in the homogeneous phase with the pollutants. Carbon based electrodes may play an important role in this field. A good example are the cathodic process for production of hydrogen peroxide where graphite and reticulated vitreous carbon cathodes[1] are used as well as gas diffusion electrodes constituted by a carbon-PTFE layer in contact with a metal mesh as current collector[2]. In this last case the main drawback encountered lies in their short lifetime, induced by the loss of dispersed graphite from the cloth.

Our studies focused on graphite anode for direct oxidation processes of biorefractory organics. These investigations put into evidence the following points:

- operation at low electrode potential (< 1 Vs vs. NHE) for the oxidation of phenolic compounds leads to the formation of adsorbed polymeric material[3] as in the case of oxidation on conductive metals[4], with consequent deactivation of charge transfer process. This implies the necessity to work at electrode potentials higher than those required for water oxidation, where the formation of superficial oxides or adsorbed hydroxyl radicals help preventing the fouling of the electrode.
- Higher electrode potentials lead to lower oxidation kinetics than those typical of other conductive metallic anodes (e.g. Pt-Ti); however, an important difference in the oxidation behavior can be observed compared to these counter parts: the organic molecules can be oxidized without accumulation of cyclic intermediates, since a non

selective path (i.e. leading to carbon dioxide and water) seems to take place preferentially (see the below Figure concerning the abatement of the pharmaceutical Ofloxacin)[5].

- Corrosion effects are unfortunately observed for this electrode as a consequence of high operating potentials and long electrolysis time that come from the ability of carbon to readily adsorb oxygen and desorb oxides of carbon renders it of limited use in high oxidizing environmental.

An enhancement of the demolition oxidative kinetics can though be achieved with the use of three dimensional electrodes consisting of a fixed bed of activated carbon pellets (3D GAC). This electrode configuration is rather attractive and particularly appropriate to treat low concentration solutions[6]. Most of the contributions to the enhancement of the mass transfer coefficient and the limiting current density in the three-dimensional materials come from the increase of the specific surface area (i.e. a more extensive interfacial electrode surface is guaranteed for the electrochemical reaction) and from the induced static mixing. However, after a specific investigation campaign, it was possible to conclude that not all the specific area is useful for the electro-oxidation, supposing that the oxidation kinetics is equal to that of the graphite electrode, the utilized area only a little fraction of the formally available in the whole set of the GAC pellets. This suggests that the process possibly occurs only over the external activated carbon sites of the pellet surface. The reaction between C and O would indeed result in an accumulation of CO + CO_2 at the internal porosity and the occurrence of further reaction steps requires that molecules get rapidly at the reaction front and the products diffuse away from it through the carbon porosity. However, the diffusion rate of organic original molecules and products is smaller than the reaction rate of carbon with oxygen.
Moreover, the structural stability of activated carbon bed is rather low, when working at relative high potentials as in the case of graphite electrode, as testified by the dark colour of the treated solution caused by suspended carbon fine particles, and by a loss of the bed cohesion also due to the oxidation to carbon monoxide/dioxide formation. The measured CO_2 amounts formed from activated carbon pellets oxidation inside the reactor anodic compartment, are proportional to the electric charge passed and are equal to about 12 mg CO_2 /Ah. Conversely, one of the most promising electrode for the electrochemical waste water treatment is the boron-doped diamond, which represents an exciting new carbon material. However, a long way to go is still in front of us to fully understand the relationship between

the physical, chemical, and electronic properties of diamond and its electrochemical performance.

In conclusion, improvement in the characteristics of the carbon electrode materials is thus required to reduce the ageing phenomena and to enhance its application potential in the field of electro-oxidation. An interesting research opportunity can be represented by carbon electrodes protected by coating techniques[7] for electroxidation processes.

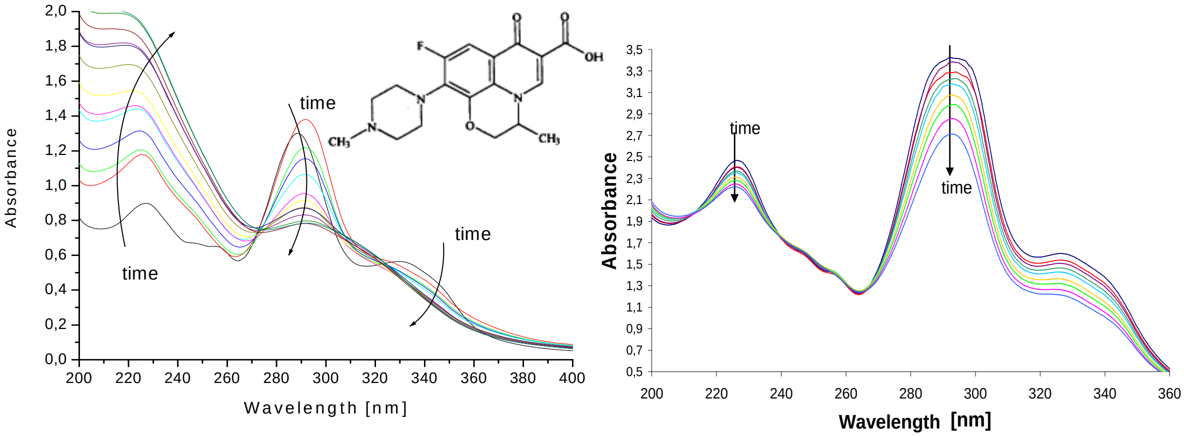

Figure 1 Ofloxacin structure and U.V. spectra for periodically (15 min) withdrawn anolyte samples during the runs in divided cell with: (left) platinised titanium leading to fast oxidation with oxidation intermediates (see increasing peak at low wavelengths) and (right) graphite anode leading to slow oxidation with no reaction intermediates. Current density: 200 A m^{-2}; electrolyte: 0.02N Na_2SO_4.

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STABILITY OF A CARBON CATALYST FLUIDIZED BED

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Maximum heat and mass transfer of catalytic apparatuses can be provide in a fluidized-bed (FB) reactor with carbon spherical particles. Efficiency of a FB reactor (level of conversion) is increased with increasing of FB height. At the same time, in process of FB height increase (and differential pressure), FB itself becomes unstable and undergoes sequentially the following perturbations: spouting, formation of bubbles of Davidson, "piston" boiling [1].

This work is intended to analyse a stability of catalytic FB reactor, to give recommendations how to increase stability when FB height is increased and to check recommendations in experiments with glass models of FB reactors with pyrocarbon catalyst particles 600 µm in diameter. The glass reactor consists of a feeding tube, conic diffuser and cylinder with internal diameter 30 mm. Argon was used as fluidizing gas.

The investigations of FB instability, which has been carried out on glass models, have shown that when the fluidization rate is 0.5-2.0 km/s (Reynolds number of a flow (Re) 130-520, respectively) catalyst particles oscillate under action of turbulent pulsations which intensity is maximum in a FB bottom area (transition from cone to cylinder). The amplitude and frequency of the catalyst particles fluctuations in the top area of FB measured with use of a movie camera were 5 mm and 2 Hz, respectively.

Occurrence of turbulence in the interval of Reynolds numbers when their values is significantly less than 2100-2300 (transition of laminar mode in turbulent in a cylindrical pipe) is explained by the gas rate jump in the cylindrical reactor entrance providing occurrence of turbulence at Re = 81,49 (Orr-Zommerfeld task [2]). If a catalysis process temperature is 300-600ºC then additional rate jump is observed due to expansion of gas, therefore bottom area of FB is located in an area of transition from cone to cylinder due to the maximum turbulence of gas that corresponds to the maximum front of its flowing.

As gas movement is in progress along height of a chemical reactor, stabilization of its temperature, rate hold and composition occurs, the scale of turbulent pulsations decreases, and the flat front of flow becomes parabolic (Gagen-Poiseuille flow in a cylindrical pipe [2]).

Evolution of instability in a top area of FB and localization of FB in an area of the cone - cylinder transition gives the reason to believe that FB stability depends directly on scale of turbulence in a catalytic FB reactor. This assumption has been experimentally proved by experiments on glass tubes with and without additional turbulators. Additional turbulence has been provided with four vertical grooves on the internal surface of a tube. Each groove had the shape of an equilateral triangle in cross-section with 2 mm side.

It was found experimentally that FB stability in standard tubes is realized in a range of particles weight of 9-12 g, and in tubes with turbulators - in a range of 5 – 50 g. At the same time the ratio of FB height to the channel diameter was 1.0-1.3 in the first case and 4.5 in the second case (particles weight 50 g). It is important to note that tenfold change of particles weight in the latter case is realized at constant rate of argon about 60 cm/s). This effect is explained by compensation of viscous friction loss increasing with particles weight increase by reduction of kinetic energy of turbulent pulsations, first of all' due to reduction of pulsations frequency. E.g., if the weight of particles in FB is in a level of 40 – 50, g the amplitude of catalyst particles fluctuations in top area of FB falls up to 3 mm, and frequency up to 0.5 Hz.

Thus, the dependence of FB stability in a catalytic reactor on a level of turbulent pulsations was found and experimentally proved and recommendations how to increase FB stability with increase of a bed height are given.

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CARBON FIBROUS SORBENTS WITH CATION-EXCHANGE PROPERTIES

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The weak cation-exchange properties of many carbon sorbents are explained by the presence of a certain amount of acid groups on the surface of the carbon material because of the oxidizing reactions proceeding in the formation of the carbon structure at high temperatures. The content of the acid groups can be increased by oxidizing modification of the carbon material. In this case the method used determines the chemical behavior and stability of polar groups introduced.

The purpose of the given research is comparison of various ways of the foregoing modification of carbon sorbents. The basic criterion of an estimation of efficiency of the process is stability of acid groups introduced at a typical ion-exchange and regeneration treatments. In our opinion, oxidizing modification of carbon surface can give the greatest effect in case of fibrous materials because the advanced external surface of fibers allows to reach of the most content of polar groups. On the other hand, heat-and-mass transfer at the carbon surface creation is facilitated by the fibrous form of carbon.

As suitable object of the research the carbon fiber based on hydrated cellulose has been chosen. Cellulose is one of the main raw material for producing of activated carbon fibrous materials.

In this work carbon fibrous sorbents (CFS) having cation-exchange properties were obtained by the various ways: (i) by the low-temperature treating it with a strong oxidizing agent - hydrogen peroxide, (ii) by carbonization of the initial cellulose material in the presence of a modifying additives - Mo, Cr, V or W oxides (see recent communication [1]), and (iii) by oxidation of carbon fibers with air or ozone in the absence or presence of the additives aforesaid. For comparison, carbonization of the hydrated cellulose fiber (rayon) was performed in the presence of ammonium chloride (the analog of serial CFS, produced at industrial conditions).

It has been shown that transitional metals compounds can catalyze activation of carbon both with H_2O and CO_2, and increase the concentration of acidic groups on carbon surface.

Mo and V show the most pronounced catalytic activity in activation and maximal content of acidic groups. The similar result has been received at the air oxidation of carbon fiber.

To verify the intactness of the acid groups on the surface of CFS, we run several cycles of ion exchange and regeneration of acid groups by consecutive treating samples obtained with 0.1N NaOH and 0.1N HCl, and washing by water to a neutral reaction. Their total content of acid groups was constant after several cycles of sorption – regeneration. The following table shows the cation-exchange capacity of the samples received.

Total content of acid groups in the CFA samples before and after ion exchange – regeneration cycles (thrice-repeated consecutive treatment with 0.1N NaOH and 0.1N HCl)

Sample	Content of acid groups, mg-equiv./g	
	initial	after 3 cycles of ion exchange
1. Serial CFS based on hydrated cellulose	0.4	1.4
2. CFS based on Mo-doped hydrated cellulose	0.6	1.7
3. Serial CFS oxidized by air, 400°C, 3 h	3.1	3.1
4. CFS based on Mo-doped hydrated cellulose oxidized by air, 300°C, 3 h	4.2	3.1
5. Serial CFS oxidized by 30% H_2O_2, 4 h	2.4	2.0

It has been established, that the sorption of heavy metal ions (for example, Ni^{2+}) essentially depends not only on the content of acid groups, but also from a way of their introduction in carbon material. In other words, fixing of metal ions is appreciably defined by previous history of the sorbent, i.e. by a multiplicity of the factors determining the surface structure of carbon material.

Despite of the high content of the polar groups, the received CFS keep the high ability to adsorption of non-polar organic substances. For example, these samples adsorbs of 300-500 mg/g benzene vapor. Thus one can produce a new type of CFS possessing high adsorption of organic compounds and cation-exchange properties simultaneously.

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CATALYTIC CONVERSION OF METHANE INTO HYDROGEN ON ACTIVATED CARBONS

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By applying different methods of activation a number of activated carbon samples have been obtained from brown coal. The samples have been tested as catalysts in the reaction of methane conversion to hydrogen. The catalytic activity of the activated carbons obtained has been found to depend on the method of activation and to increase with increasing temperature of the process. The catalysts based on activated carbon obtained in the optimum conditions have shown good stability in time, except for a short period at the beginning of the process.

INTRODUCTION

Hydrogen is predicted to be a fundamental fuel in the future. One of the sources of hydrogen is methane (natural gas). The conventional method of hydrogen production via methane steam reforming is however related to production of significant amounts of CO_2, one of the factors responsible for greenhouse effect. Much more promising is the production of hydrogen via catalytic decomposition of methane [1]. The above method is considered environmentally-friendly as the only products of the decomposition are hydrogen and carbon. Good catalysts of the process are carbon materials. .

The main aim of the study reported was to obtain the activated carbon catalysts of high stability and activity in the process of methane decomposition.

EXPERIMENTAL

The precursor of all activated carbon samples studied was Polish brown coal from the Konin colliery. The raw coal of grain size of ≤0.2 mm was subjected to demineralisation by the Radmacher method [2]. The coal sample was activated by KOH [3] and $ZnCl_2/CO_2$ [4]. The catalytic tests were performed at 750, 850 and 950°C in a quartz reactor working on line with a gas chromatograph. All samples were characterised by N_2 adsorption at 77 K.

RESULTS AND DISCUSSION

Selected results of the catalytic tests are presented in Fig. 1 and Fig. 2. As follows from the data in Fig. 1, the catalytic activity of carbon samples activated by KOH strongly depends on the amount of the activating agent. The best results were obtained at the KOH/coal weight ratio of 4:1. The degree of burn-off for this sample was about 80%, and its surface area was very high (2802 m^2/g). The other samples (of lower surface areas) had similar initial activity which however quickly decreased with the time of the process. This is most probably due to a faster filling up of the catalyst's pores by carbon formed as a result of methane decomposition.

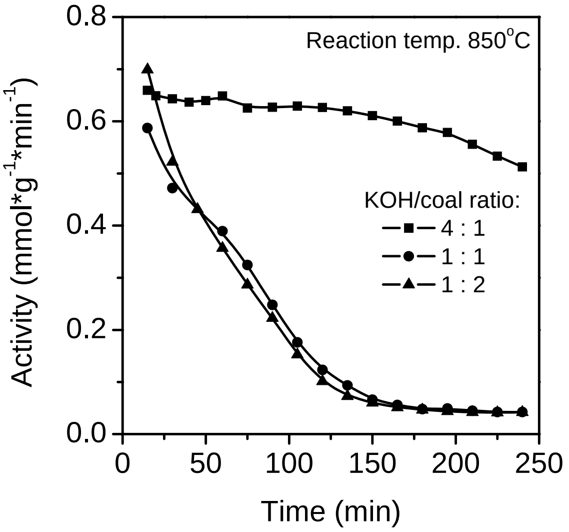

Fig. 1. Catalytic activity as a function of KOH/coal ratio

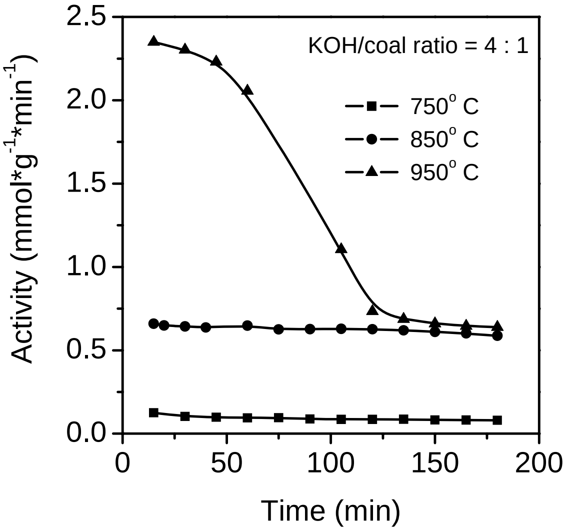

Fig. 2. Catalytic activity as a function of reaction temperature

Fig. 2 presents the effect of temperature on the catalytic activity of the sample activated at the KOH/coal ratio of 4:1. The activity increases with increasing temperature of the reaction. For the process carried out at 950°C, the catalyst activity is very high but quickly decreases to stabilise after about 100 minutes of the reaction. The processes conducted at lower temperatures are characterised by lower degrees of methane conversion to hydrogen, bur the catalyst activity in them is more stable in time.

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THE SORBENTS FOR AIR CLEANING PREPARED FROM BIOMASS

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High temperature combustion, transportations, power plants and other industrial sources emit undesirable pollutants such as SO_2, NO_x and NH_3. Exposure to high levels of nitric oxides and sulphide oxide leads to bronchitis, pneumonia, and susceptibility to infection and alteration to the immune system. It is well known that SO_2 and NO_x are promoters of the acid rain phenomenon and of the photochemical smog. These contaminants can be removed from gases by using adsorptive methods.

The aim of presented work was investigation of the effectiveness of NH_3, SO_2 and NO_x removing from waste gases by sorbents obtained from biomass (corn-cobs and rapeseed straw). The following samples were the subject of investigations:

KKK - char from corncobs received by the microwave heating (time of heating 5 min, temperature of carbonization - 600°C)

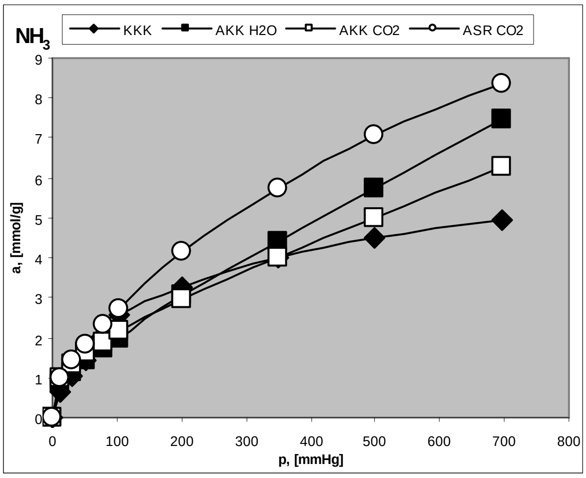
AKK H_2O – active carbon obtained from corn-cobs in the rotation furnace at temperature of 800 °C, using the water vapour as an activation agent (activation time 45 min).

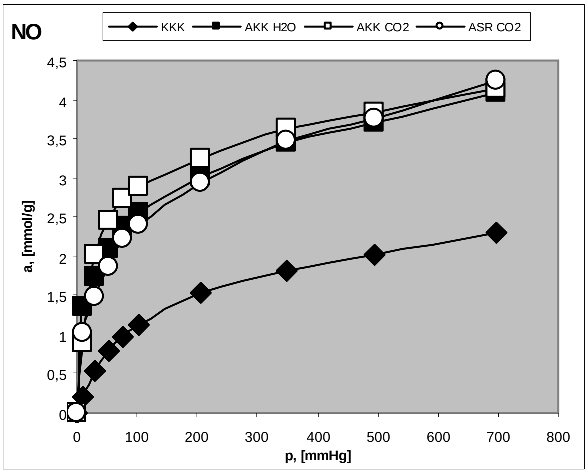
AKK CO_2 - active carbon obtained from corn-cobs in the rotation furnace at temperature of 850 °C, using carbon dioxide as an activation agent (activation time 45 min).

ASR H_2O - active carbon obtained from rapeseed straw in the rotation furnace at temperature of 750 °C, using the water vapour as an activation agent (activation time 25 min).

For measuring of the sorbents porous structure and sorption capacity of ammonia, sulphur dioxide and nitric oxide on char and activation products high-vacuum gravimetric apparatus with a McBain-Bakr quartz spring balances was used. The amount of adsorbed gases is expressed in units of mmoles per g of sorbent. Isotherms of adsorption for ammonia, nitrogen (II) oxide, sulphur dioxide measured on investigated sorbents are illustrated on Fig 1.

The quantities of adsorbed ammonia on examined samples are within the range of 4 – 8 mmol/g of material. The lowest values of sorption of ammonia were found for char prepared from corncobs with the porous system composed mostly of ultramicropores. Whereas, the highest values of sorption of ammonia were found for active carbons obtained from the rapeseed straw and corncobs using water vapour with the greatest micropore volumes. The nitrogen and sulphur oxides are adsorbed on examined materials in quantities of 2 – 7 and 0,5 - 4 mmol/g respectively. It means that one kilogram of sorbent can accumulate from 60 to 220 g of NO_x and SO_2 respectively. The lowest sorption capability was observed for char prepared from corncobs whereas the highest for all investigated active carbons obtained by using water vapour.





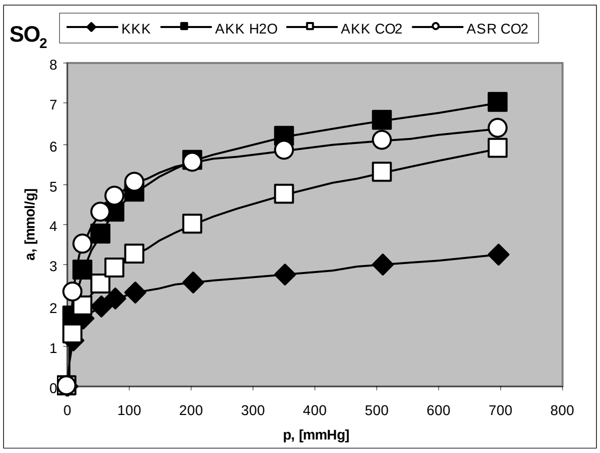


Fig.1. Isotherms of adsorption for ammonia, nitrogen (II) oxide, sulphur dioxide measured on char and active carbons prepared from corn-cobs and from rapeseed straw.

Conclusions

- Sorption ability expressed as quantity of adsorbed gas in milimoles per gram of active carbon diminishes in the following order: NH_3, SO_2, NO. Simultaneously, the quantities of adsorbed gases on active carbons are remarkably higher in comparison with the amount adsorbed on a char.
- Good sorption abilities of sorbents prepared from the biomass with regard of examined gases make them very interesting taking into account their practical application in environmental protection.

MACRO-SHAPING OF CARBON NANOFIBERS : TOWARDS THE DESIGN OF NEW STRUCTURED CATALYSTS SUPPORTS

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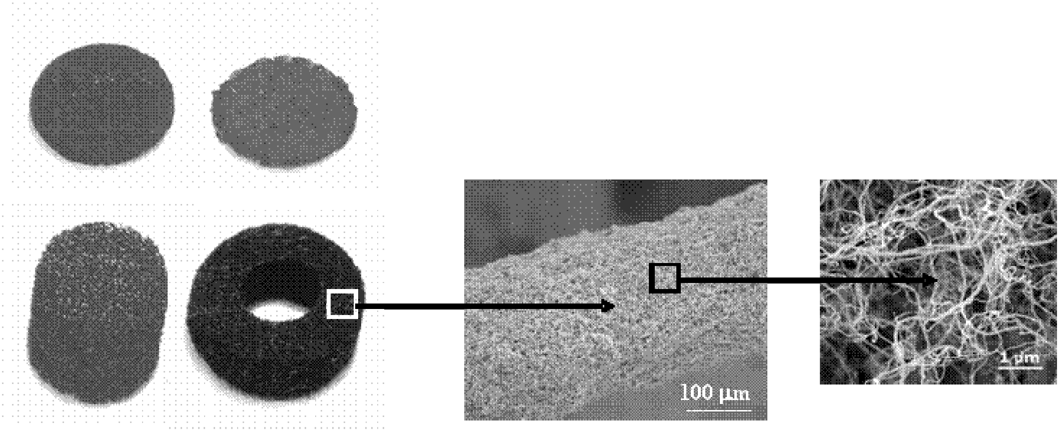
Carbon nanostructures with a 1D dimension, nanofibers and nanotubes, have witnessed a large scientific and industrial interest owing to their exceptional physical and chemical properties [1-3]. Among the different potential applications, the use of these structured carbon nanostructures as catalyst support material seems to be one of the more promising [4]. An increasing need for process optimisation led to the emergence of structured catalyst packings. In reactors containing such packings, the pressure drop, the flow profile, the mass and heat transfer, and the dispersion characteristics of the catalyst are found to improve significantly [5-6]. Therefore in the present work, the synthesis and characterisation of a new type of carbon nanofibers (CNF) composite having a structured macroscopic shape is reported.

CNF having uniform diameter of 30 nm, were produced in a large amount with **yields up to 100 wt%**, the production rate being ***50 g per g of Ni per hour*** via catalytic decomposition of C_2H_6 / H_2 mixture over a nickel (1 wt. %) catalyst supported on graphite microfibers. In addition of producing a large amount of highly pure usually called “fluffy CNF”, the essence of our work was to combine a nano/microscopic ordering with an appropriate design at the macroscale, to produce structured catalytic supports. The shape of this nano/micro and finally macrostructured C/C composite can be modified at will, depending the required purpose (see Figure). This allows its use directly in the existing conventional reactors without the problems linked to the small size of the unsupported CNF. This material displays a relatively high surface area >100m^2/g, essentially constituted by the external surface, and a complete absence of the bottled pores encountered with traditional solid carriers such as alumina, silica or activated charcoal.

This as-synthesized CNF composite was subsequently tested as catalyst support in several reactions like: the decomposition of hydrazine, the Super-Claus reaction, C=C selective hydrogenation, or even itself as a catalyst in the depollution of contaminated water by organics. The catalytic performance of CNF composites is largely superior to that obtained on the state-of-the-art traditional catalysts and the details will be presented in the extended presentation, along with the results obtained on the liquid phase dehydrogenation.



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MESOPOROUS ACTIVATED CARBON AS THE SUPPORT FOR Co/Ni/Fe/CARBON CATALYSTS IN CO OXIDATION

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In recent years active carbon (AC) supported metal-containing CO reacting catalysts are studied. In the literature few works concerning catalytic conversion changes of the chemical nature CM, however, are published at its modifying. The aim of this work is the CO conversion catalytic investigation of a CM modified by Co/Fe/Ni.

A CM activated carbons, KAU and SCN, was used as the starting material. AC KAU (raw material apricot stone) had cleanly carbon surface. Obtained of nitrogen containing resin CA SCN had a nitrogen compound carbon surface. For modifying CM by Co/Fe/Ni metals had been used acid solutions of their nitrate salts. The last ones were impregnated carbons KAU, and SCN within 48 hours. In the further samples dried at 100C, warmed up in argon at 450C and reduced in hydrogen in current of 1 hour at 600C. The covering of a surface CM metal made 5 % wt. accordingly (in recalculation on metal).

The catalytic tests were carried out in flow fixed-bed quartz reactor. The studied reaction mixture contained: 1 vol.% CO, 1 vol.% O_2, 98 vol.% He. The analysis of reaction products was carried out by on-line gas chromatograph with conductivity detector.

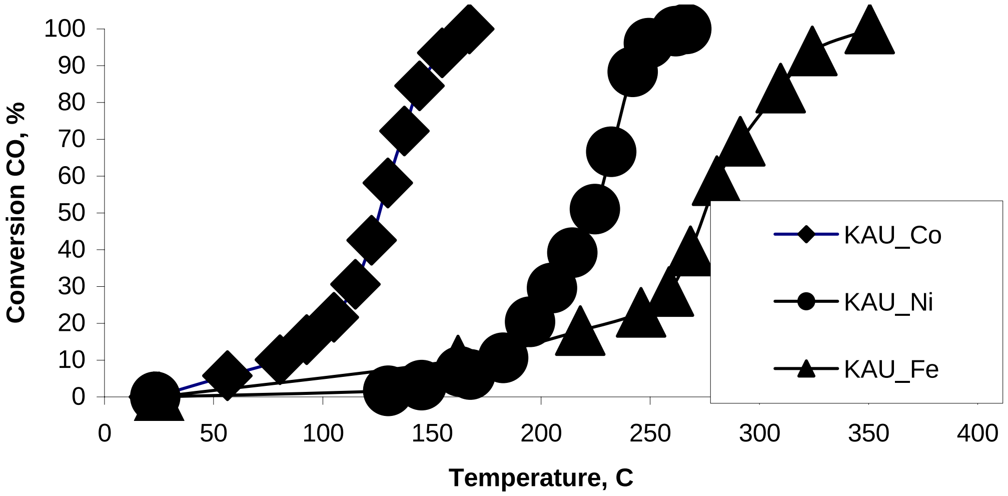

Fig. 1. Curve dependences of conversion CO from temperature on metals modified SM КАУ.

In fig.1 dependences of catalytic activity of metal containing samples CM KAU from reaction temperature are resulted. It is visible, that cobalt containing AC develops the best results in conversion CO. Activity of contacts decreases in a correlation line Co > Ni > Fe.

We have compared catalytic activity of two carbon matrixes SCN and KAU, which had the various nature /an origin (table 1) and have determined the contribution of a cellular structure of nitrogen containing CM on conversion CO.

In the table temperatures of achievement of complete conversion CO on metal-carbon catalysts are presented

Table 1. The temperature of complete conversion CO on metal-carbon catalysts.

Carbon matrix	Temperature of CO complete conversion, C		
	Co	Ni	Fe
KAU	175	249	353
SCN	155	173	475

CA SCN have appeared more active and have effectively reduced temperature of full conversion CO (for Co - 5C, for Ni - 15C and for Fe - 113C). This CA differs not only a cellular structure, but also presence of nitrogen Thus influence of the chemical nature of a surface of CM consists in influence of structure and influence of available heteroatoms (Co and N are most essential).

In this work the modification of a surface of mesoporous AC KAU and SCN by compounds of Co, Ni, Fe was realized. The study of catalytic properties Co/Ni/Fe compounds supported on carbon matrix in CO oxidation was investigated.

EVALUATION OF DIFFERENT ACTIVATED CARBONS AS SUPPORTS FOR THE PALLADIUM CATALYZED HYDROGENOLYSIS OF Z-GROUPS

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The chemical pathways to the complex molecules produced by the fine chemical, pharmaceutical and agrochemical industries often involve multi-step synthesis. Protective groups are commonly used to block reactive sites that would otherwise react in an undesired way. A common protective group for the protection of amines is the Z group, also called Cbz or carbobenzyloxy group. This group can be easily removed by catalytic hydrogenolysis in the presence of a heterogeneous catalyst, preferably palladium on activated carbon [1]. We have developed a useful method to determine the activity of a catalyst by measuring the CO_2 generation rate by means of NDIR detection [2].

One of the factors that affects the activity of palladium on carbon catalysts is the porous structure of the activated carbon used as the catalyst support. For nitrobenzene hydrogenations it was shown that the catalytic activity correlates with the pore size distribution of the activated carbon, concluding that a significant amount of active metal is located in small pores and therefore is unavailable for the catalytic reaction [3]. In the present work, we focused on the effect of pore size on the activity of activated carbon supported palladium catalysts for Z-cleavage reactions, and investigated how the size of the Z-protected compound determines the catalytic activity. Two activated carbons with different pore size distribution as shown by their nitrogen isotherms were used as support (Figure 1). Palladium catalysts were prepared by a Degussa proprietary method in order to achieve a similar palladium particle distribution. Palladium dispersion was measured by CO chemisorption and was determined to be 20% for both catalysts. To check for steric effects coming from the substrate, four different sized Z-group protected compounds were used as test molecules: Z-Glycine **1**, Z-phenylalanine **2**, Z-citrullyl-L-leucine-methylester **3** and Z-O-tert-butyl-L-tyrosyl-D-homocitrullyl-L-leucine-methylester **4** (Figure 2).

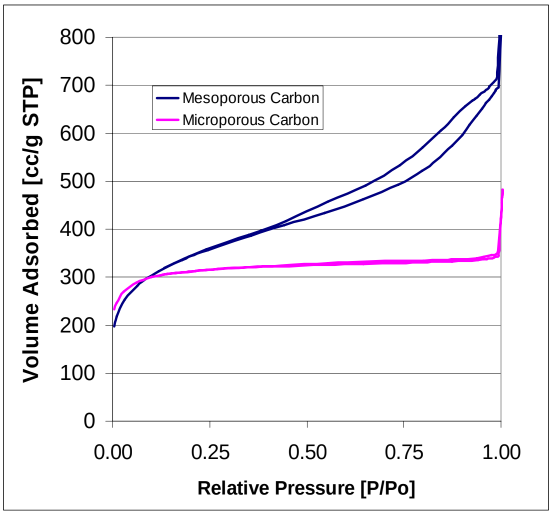

Figure 1: Nitrogen isotherms of meso- and microporous activated carbon

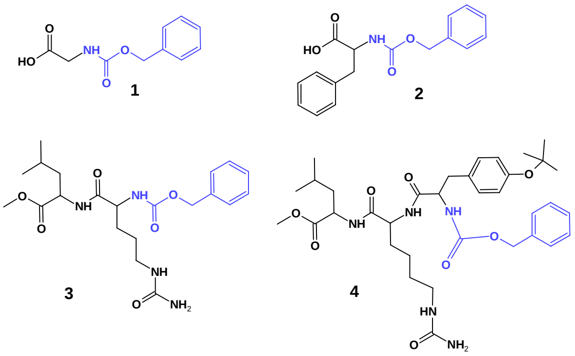

Figure 2: Z-protected test substrates for the catalytic hydrogenolysis

Figure 3 and 4 show the CO2 generation with time. For the mesoporous carbon (Figure 3), there is only a slight difference in activity amongst the different sized Z-protected substrates. The reaction time to convert the higher molecular weight Z-protected substrate takes a little longer compared to the lower molecular weight Z-protected substrates and follows the order 4 > 3 ~ 2 > 1. In figure 4 this effect is more pronounced and it can clearly be seen that the activity decreases with increasing molecule size of the Z-protected compound. A simple explanation for the difference between the two carbon supports is that the smaller pores of the micro porous carbon are not accessible by large organic molecules anymore. For substrate 1 the time to complete the reaction is similar for the microporous and the mesoporous carbon. The size of the substrate 1 is obviously small enough to fit equally good into the pores of both activated carbons.

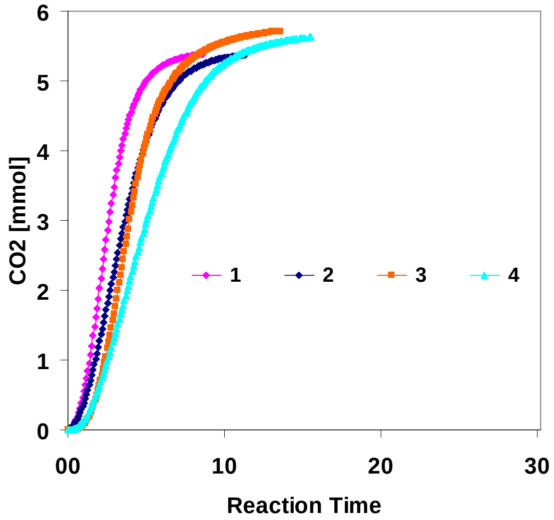

Figure 3: Catalytic activity of Pd catalyst on a mesoporous carbon

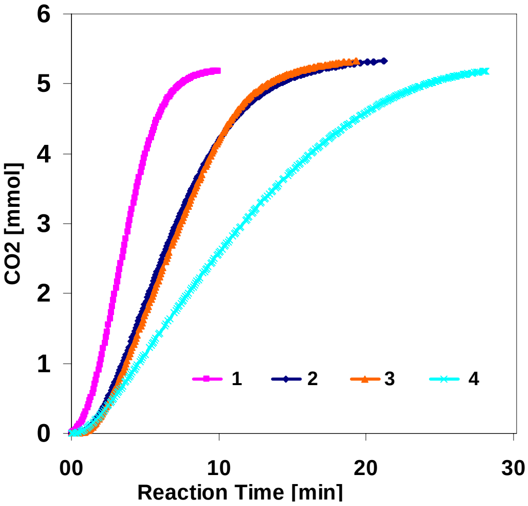

Figure 4: Catalytic activity of Pd catalyst on a microporous carbon

As it would have been expected we could confirm that the pore size characteristics of the activated carbon support is very important when choosing a catalyst. This is not true for all applications, because sometimes other effects than the intrinsic activity of a catalyst determines the overall performance. We have found earlier for a similar hydrogenolysis reaction, the debenzylation of dibenzylether, that the pH of the reaction medium plays a more important role than the catalyst itself [4]. This is not the case for the Z-removal described in this paper and as such this reaction is a very useful tool for screening catalysts.

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PP-II-17

THE ROLE OF 14-ELECTRON INTERMEDIATES IN THE RUTHENIUM ALKYLIDENE-CATALYZED POLYMERIZATION OF NORBORN-2-ENE

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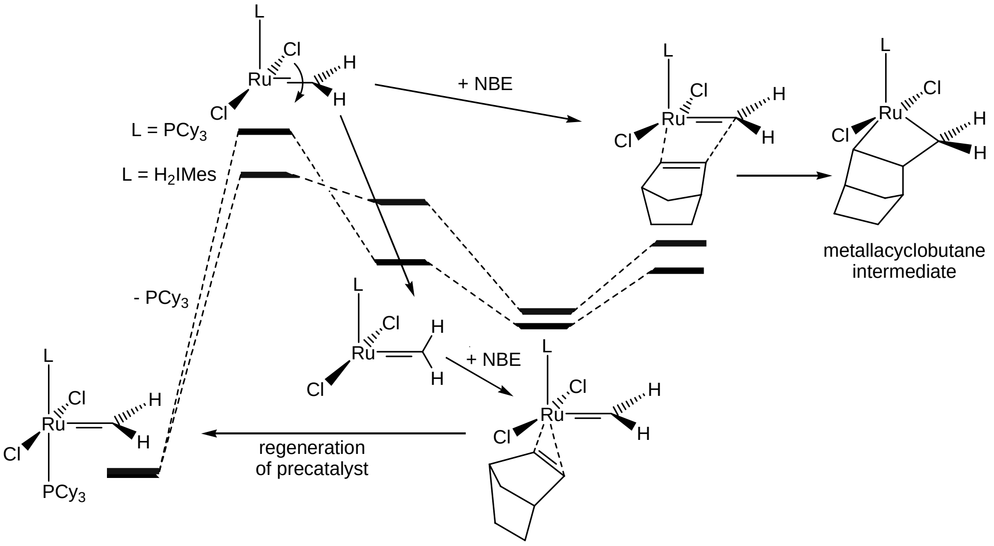
Olefin metathesis is a fundamental reaction for the formation of carbon-carbon double bonds. The activity of the "*first-generation*" ruthenium-based metathesis catalysts $RuX_2(PCy_3)_2(=CH_2)$ (type **I** catalysts) was significantly improved with the "*second-generation*" catalysts $RuX_2(PCy_3)(H_2IMes)(=CH_2)$ (type **II** catalysts), where an N-heterocyclic carbene (NHC) replaces one phosphane group[1]. It was concluded[2] that the greatly increased activity of type **II** catalysts in ring-opening metathesis polymerization (ROMP) origins from the increased reactivity of the four-coordinate 14-electron intermediate $RuX_2(L)(=CH_2)$ produced by phosphane dissociation from type **I** and **II** catalysts. Additionally it was found[3] by comparing the gas-phase reactivity of 14-electron reactive intermediates with experiments that type **II** catalysts show hundred-fold higher activity despite *slower* phosphane dissociation because of a much more-favourable partitioning of the 14-electron active species between entry into the catalytic cycle and return to the precatalyst (by rebinding of phosphane). The gas-phase study[4] findings in ROMP of norborn-2-ene (NBE) are that type **I** catalysts display higher barriers for the conversion of the π-complex into the metallacyclobutane than for phosphane dissociation. In contrast, type **II** catalysts behave as if there was not any significant barrier at all. Moreover, it has been shown by quantum chemical calculations[3] that there are only small differences between the energy surface of first and second-generation catalysts. Thus, there is still no definite answer on the paradox finding that a slower activation step (dissociation of one phosphane ligand) is overcompensated by an improved partitioning into product direction in type **II** catalysts clearing such different activity of type **I** and **II** catalysts. The aim of the present work was to find the rate-limiting critical step in the ROMP of NBE, which could explain the discrepancy between slower phosphane dissociation and higher activity of second-generation catalysts.

Using DFT B3LYP/LANL2DZ (Gaussian03) method, the first step of complex formation between the transition-metal carbene and NBE as well as properties of the active 14-electron intermediate were modelled in dependence on the ligands L used (L=IMes, H_2IMes, tetrahydropyrimidin-2-ylidenes[5,6] and PCy_3) and X (F, Cl, Br, I, and $OCOCF_3$). In agreement with existing X-ray data the most stable structures in type **I** and **II** catalysts have a carbene unit perpendicular to the L-Ru-C plane independent on the ligands X and L. After dissociation of phosphane, a 14-electron intermediate is formed with the carbene unit perpendicular to the L-Ru-C plane, too. However, this 14-electron intermediate $RuX_2(L)(=CH_2)$ is only a local minimum and can transform due to a rather small $Ru=CH_2$ rotation barrier into a more stable one with the carbene unit parallel to the L-Ru-C plane.



The analysis of geometries and frontier molecular orbitals of both conformers of the 14-electron intermediate shows that whereas the conformer with the carbene unit parallel to the L-Ru-C plane leads to a stable π-complex with NBE, the conformer with a carbene unit perpendicular to the L-Ru-C plane is prone to the direct formation of a metallacyclobutane intermediate. Calculations show that the relative stability of these two conformers depends on both ligands L and X. Moreover, the energy difference between two rotational conformations is systematically larger for all calculated 14-electron reactive intermediate of type **I** catalysts than for type **II** catalysts. Consequently, the 14-electron reactive intermediate of type **II** catalysts with the carbene unit perpendicular to the L-Ru-C plane leading to a favourable formation of the metallacyclobutane should be more stable than those of **I**. That should in due consequence lead to much better partitioning into the product direction in type **II** catalysts compared to type **I** catalysts.

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PP-II-18

APPLICATION OF CARBON MATERIAL SIBUNIT AS THE SUPPORT FOR COPPER-CONTAINING CATALYSTS OF ACETALDEHYDE SYNTHESIS

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Development and implementation of high effective and stable catalytic systems is the most important stage of process optimization in chemical industry. The special attention is given to the choice of a support, the material of which should have a number of characteristics, such as a high surface area, advanced porosity, inertness and stability. Recently different carbon materials have been used more widely in heterogeneous catalytic processes.

One of more perspective carbon materials is carbon-carbon composite, which is referred to a new class of carbon composites combining in itself advantages of graphite and active carbons. Another very important advantage of this material is high chemical purity. Fraction of mineral admixtures in sibunit is less than 1%, whereas mineral part of the main gamma of active carbons is 5% and more. This characteristic of sibunit can brings essential influence on selectivity of catalytic systems made on its base.

The next way of chemical industry progressing is development of alternative methods of major organic compounds synthesis, which are characterized by a minimum quantity of harmful waste and are based on renewed sources of raw material. Implementation of such methods into the industry can afford improvement of economical efficiency as well as ecological safety of these compounds production. One of such processes in chemical industry is synthesis of acetaldehyde – the important intermediate of organic synthesis. The main industrial method of acetaldehyde production is ethylene oxidation in the presence of aqueous solutions of palladium and copper chlorides. This method is ecologically adverse and is based on processing of oil raw material. For this reason the production of acetaldehyde by ethanol dehydrogenation is extremely attractive. This process has a number of advantages: absence of poisonous wastes, soft conditions of the process and the use of ethanol as the only raw material, alternative production ways of which from biomass have been under active development recently. However, for effective realization of this process, the development of new active, selective and stable catalytic systems is needed.

Thus, the object of this research was to develop new effective catalysts, based of carbon material sibunit for acetaldehyde synthesis by ethanol dehydrogenation.

Our previous researches have shown that based on sibunit copper-containing catalysts are the most effective for acetaldehyde synthesis. The maximum yield of acetaldehyde reached 69,2% at 375^0C at the presence of catalyst 3%Cu/sibunit. However such systems were unstable in the process conditions. Activity of this catalyst sharply decreased at high temperatures (above 400^0C). One of the ways of increase of catalysts stability is introduction of promotional additives, which interfere of copper sintering. In this connection we investigated expediency of introduction of Cr_2O_3 additives in copper containing catalysts.

Our studies have shown, that chrome oxide possesses of catalytic activity in ethanol transformation. Conversion of ethanol was 58% at 500^0C at the presence of catalyst $3\%Cr_2O_3$/sibunit and the main products were acetaldehyde and ethylene. Thus, the received results have allowed to assume, that the additive of small amounts of Cr_2O_3 can increase activity of the catalyst. For acknowledgement of this assumption we have tested the samples of copper catalysts which contain Cr_2O_3 additives in different quantities.

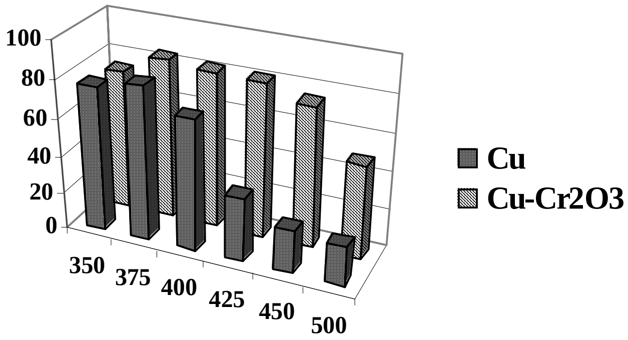

Fig. 1. Ethanol conversion (%)

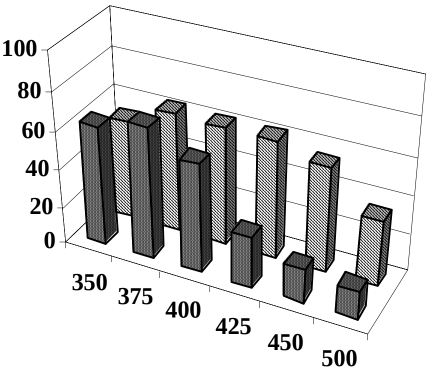

Fig. 2. Yield of acetaldehyde (%)

The best results were obtained in the presence of catalyst, containing copper and chrome oxide in the ratio 20:1. Introduction of Cr_2O_3 in the catalyst has allowed to raise considerably activity of system in the area of temperatures above 400^0C. Alcohol conversion was almost twice above, than at the presence of unpromoted catalyst (Fig. 1). However, selectivity of the process is a little below, that is caused by an intensification of ethylene and 1,3-butadien formation. The maximal yield of acetaldehyde, received at the presence of the catalyst 3%Cu $0,15\%Cr_2O_3$/sibunit, was 63,3 % at 375^0C (Fig 2.).

Besides introduction of the chrome oxide additive has allowed to increase duration of stable work of the catalyst considerably. In the process conditions which provide the maximal yield of acetaldehyde, based on sibunit catalyst, containing 3%Cu and $0,15\%Cr_2O_3$ can work stably not less than 80 hours. While the activity of the system, containing only 3%Cu without any additives, decreased in 30 hours.

PP-II-19

PLATINUM LOADING IN THE BIMODAL MICROPORE SYSTEM OF AN ACTIVATED CARBON

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Introduction

Carbon materials are often used as support for preparing metal-based catalysts because those allow the anchoring of metal particles on a substrate which does not exhibit considerable solid acid-base properties. The most frequently applied activated carbons are very heterogeneous materials and are difficult to characterize in microstructure and reactivity. The extremely valuable advantage of an inert substrate as the carbon consequently has the disadvantage that the active phase is difficult to anchor to the surface. It is hence difficult to create and maintain any useful dispersion of the active phase on carbon. Two more classical ways of the active phase fixation are on oxygen functional groups or on surface defects. The best fixation however is achieved when the catalyst particle digs a small hole in its fixating geometry where it uniquely fits [1].

Recently, the frequency response (FR) method, a sensitive technique for mass transport resistances has been shown to be powerful for investigation the mass transfer kinetics in various sorbents [2]. The aim of this study is to get information about the mass transport behavior of an activated carbon during precious metal loading steps using rate-spectroscopic diffusion studies of propane probe molecule and the catalytic activity in the reaction of cyclohexane hydrogenation compared with the development of the diffusional resistances in the micropores.

Experimental

The 0.71-0.50 mm size granules of a commercial charcoal (BDH Laboratory Supplies, Merck Ltd., UK) were used after an oxidation treatment with 5N HNO_3 at 80 C^o for 3 hours. Pt/carbon catalysts were prepared by impregnation of the parent support with basic (pH = 9) aqueous solution of $[Pt(NH_3)_4]Cl_2$ (Strem Chemicals). The Pt-complex was decomposed in nitrogen flow and the subsequent reduction in hydrogen flow was carried out. Different salt

(NaOH, CsOH and NaN_3) loaded samples were also prepared by impregnation for comparison.

The nitrogen adsorption isotherms were collected using the gas volumetric method in a conventional all-glass BET apparatus for determining the pore size distribution. The mass transport dynamics of propane was investigated by the batch type frequency-response apparatus.

The Pt/carbon catalysts formed in situ after reduction were applied as heterogeneous catalyst in flow-through microreactor to transform cyclohexane between 200 and 420 ^{o}C.

Results and Discussion

The changes in the nitrogen adsorption capacities and in the pore-size distribution of small micropores with diameters 0.64 and 0.92 nm reflected the significant influence of the loadings and treatments. The nitrogen adsorption data were used to determine the microporosity of the sample with the two-term Dubinin-Radushkevich equation. The pore sizes correspond to the thickness of two and three graphite layers, respectively. The distributions of the parallel propane mass transport processes have been also recorded in unloaded and loaded bimodal micropore systems of an activated carbon sorbent after various treatments and modifications. The bimodal size distribution of the micropores and the bimodal character of the FR spectra of intraparticle diffusion suggest that the smaller and the larger micropores of the activated carbon are not interconnected. The macro and mesoporous texture reflects the original texture of the precursor, the carbon source material. The SEM examination suggested that the sorbent was prepared from a coal precursor. Very little porosity existed between the extremely wide macro- and the very narrow micro-pores. Large pores or channels contribute little to the total gas adsorption capacity at low relative pressures but act as important transport pores with low diffusional resistance.

In activated carbons the microporosity responsible for the high surface area may act as physical barrier to the metal particles deposited resulting in the resistance to sintering. This is attributed to deposition of metal particles of high dispersion in narrow pores of the supports, which renders part of the metal surface inaccessible to the organic substrates. Such a blocking effect proved especially significant for Pt catalysts on the activated carbons with the smallest micropores. The possibility of the loss a great part of the catalytically active surface due to the blocking has long been recognised, however, there are not much examples of experimental verification of such a phenomenon. Present results give significant examples.

Conclusion

The results of both static and dynamic sorption measurements in the studied bimodal micropore carbon system can be correlated. Changes in the ratio of two parallel micropore diffusion processes with different time constants distinguished in the FR rate spectra indicate the effect of the loading in the smaller or the larger micropores being not interconnected. An increase of Pt content above 1 % does not influence the propane mobilities in the Pt-loaded activated carbon and also the catalytic activities in cyclohexane dehyrogenation to benzene. It can be concluded that platinum clusters prefer to be located in the narrowest micropores.

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PP-II-20

MEDICAL CARBON ADSORBENTS

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The extraction of toxicants from human body is essential in connection with the growth of production and accumulation of the great variety of chemical substances in the environment and the increased production and consumption of diverse medicines. Therefore it is necessary to develop the accelerated organism cleaning methods.

For these goal various carbon materials were used.

The application of carbon fibrous materials is justified in the processes only where the granulated active carbons can not be used or the specific properties of carbon fibrous materials provide significant vantages, particularly in the following cases:

- sorption of substances in small concentrations;
- sorption from high velocity flows due to the high sorption rate and the possibility of decreasing the flow velocity by the increased sheet filter surface;
- purification of air and water in closed bulks without mixing;
- purification of bioactive media;
- requirement of combined sorption activity and electric conductivity;
- requirement of “soft” form of material, small air dynamic resistance and combined sorption and filtering properties.

Carbon fibrous materials find a wide range of medical applications such as:

- application therapy (sorption layers in bandages and drainages for wounds and burns treatment and for the protection of surfaces from toxicants);
- enterosorption for the medical treatment of various exo- and endogeneous poisonings;
- hemo-, limfo-, plasmo- and liquid-sorption, e.g. the detoxication of conserved blood.

Materials of NDC and graphite with immobilized various medicine substances are perspective as implants for substitution of details of spine in tuberculosis and other fields of the surgery and therapy. For example, the modificated graphite polyethylene terephtalate fibers were used for implants of elements of organs, and the siloxane modificated graphite for temporal shunts, phalanxes were used also, etc.

All examined carbon materials are thermo-, hemo- and radio resistant and can sustain all presently available methods of sterilization.

PP-II-21

THE USE OF ACTIVATED CARBON AS THE SUPPORT OF BIMETALLIC CATALYSTS USED IN CO OXIDATION AND CO HYDROGENATION

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Activated carbon (AC) is a high surface area support with a very unique property. its textural and surface chemical properties can be changed by a simple treatment like oxidation; these changes affect the properties of the resultant catalysts prepared with AC. This paper is an overview of the studies conducted in Catalyst Technology and Reaction Engineering Lab (CATREL) at Boğaziçi University.

Previous studies on AC support and AC supported catalysts had clearly shown the effects of different oxidation treatments on both the chemical and physical properties of AC and catalytic properties of the catalysts [1-3]. The results of CO oxidation and benzene hydrogenation tests conducted on Pt-Sn/AC had pointed out to the changes in metal dispersion, the formation of a Pt-rich alloy, Pt_3Sn, and the resultant high activity in CO oxidation, all of which stems from the formation of oxygen bearing surface groups, especially acidic groups, on oxidized AC.

The current paper concerns the use of AC support in the catalysts for CO oxidation in hydrogen rich streams and CO hydrogenation. Bimetallic Pt-Ce and Pt-Sn systems has been tested for CO oxidation as the continuation of the previous studies mentioned [1-3]; this time CO oxidation activity of the AC supported catalysts were tested for hydrogen rich streams [4]. Another bimetallic system, Ni-Mo, had been tested in CO hydrogenation previously where Al_2O_3 has been used as the support [5-7]. In the current study was used the Ni-Mo system on AC supports. The results clearly indicate the beneficial use of AC as the support. Both in CO oxidation and hydrogenation catalysts, three types of activated carbon, namely (i) grinded and HCl washed activated carbon (AC1), (ii) air oxidized form of AC1 (AC2), and (iii) HNO_3 oxidized form of AC1 (AC3), were prepared and used as catalyst supports.

CO oxidation in H_2-rich streams: The selective oxidation of CO in a H_2-rich gas stream was investigated over a series of Pt-Ce and Pt-Sn catalysts supported on activated carbon (AC). The results have shown that the activities of AC supported catalysts increased with the increase in reduction temperature. Higher conversion levels were observed for 1% CeO_x-1%

Pt /AC and 0.25% SnO_x – 1% Pt/AC catalysts supported on oxidized AC supports compared to those prepared on non-oxidized support. Between these catalysts, the highest activity, ca. 80 per cent CO conversion, is obtained on 0.25% SnO_x-1% Pt/AC2. The results of CO oxidation tests conducted on sequentially impregnated 0.25%SnO_x-1%Pt/AC samples has shown that air oxidized support had the highest activity and selectivity level. This points to the positive effect of the presence of thermally stable surface groups on AC.

CO hydrogenation: We have previously tested bimetallic Ni-Mo/Al_2O_3 for CO hydrogenation, and the results have shown the enhancement in catalytic activity and C_2-C_4 selectivity caused by the synergetic interaction between Ni and Mo. In this study, the same bimetallic system was tested using several AC supports with the aim to exploit the beneficial effects of changes in AC surface chemistry resulting from different oxidation treatments. On these AC supports, three sets of monometallic catalysts with 5wt% Ni and 10wt % Ni loading and three sets of bimetallic catalysts with 5wt% Ni-5wt%Mo and 10wt%Ni-5wt%Mo loading are prepared using the incipient wetness technique. The results of these experiments have shown that (i) the formation of oxygen bearing surface groups enhances both metal dispersion and activity of monometallic Ni/AC samples and (ii) the presence of oxygen bearing surface groups on AC supports increases the activity of the bimetallic Ni-Mo system drastically due to the enhanced interaction between metals caused especially by the changed reduction properties of the catalysts.

ACKNOWLEDGEMENT

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PP-II-22

Ni CVD CATALYST FOR THE SELECTIVE PREPARATION OF SMALL-DIAMETER HERRINGBONE-TYPE GRAPHITE NANOFIBERS AND THEIR USE IN CATALYSIS

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Graphite nanofibers (GNF) constitute an interesting carbon material for catalytic applications. Indeed, in addition to their large mesoporosity, the peculiar orientation of the graphene layers may influence the metal-support interaction [1] and thus, results in specific catalytic activity. As far as the production of GNF is concerned, most of the catalytic CVD processes used afford ill-defined materials. Indeed, GNF diameters distribution is usually large (20-100nm) [2-4] and the resulting specific surface area is often in the range 50-100m²/g [5,6]. These two points can reduce the field of their applications as catalyst support in heterogeneous catalysis. In this work, we report the selective growth of small diameter herringbone-type GNF by C-CVD on catalysts produced by fluidized bed organometallic CVD. First results dealing with the catalytic performances of PtRu/GNF systems for the selective hydrogenation of cinnamaldehyde will be also presented.

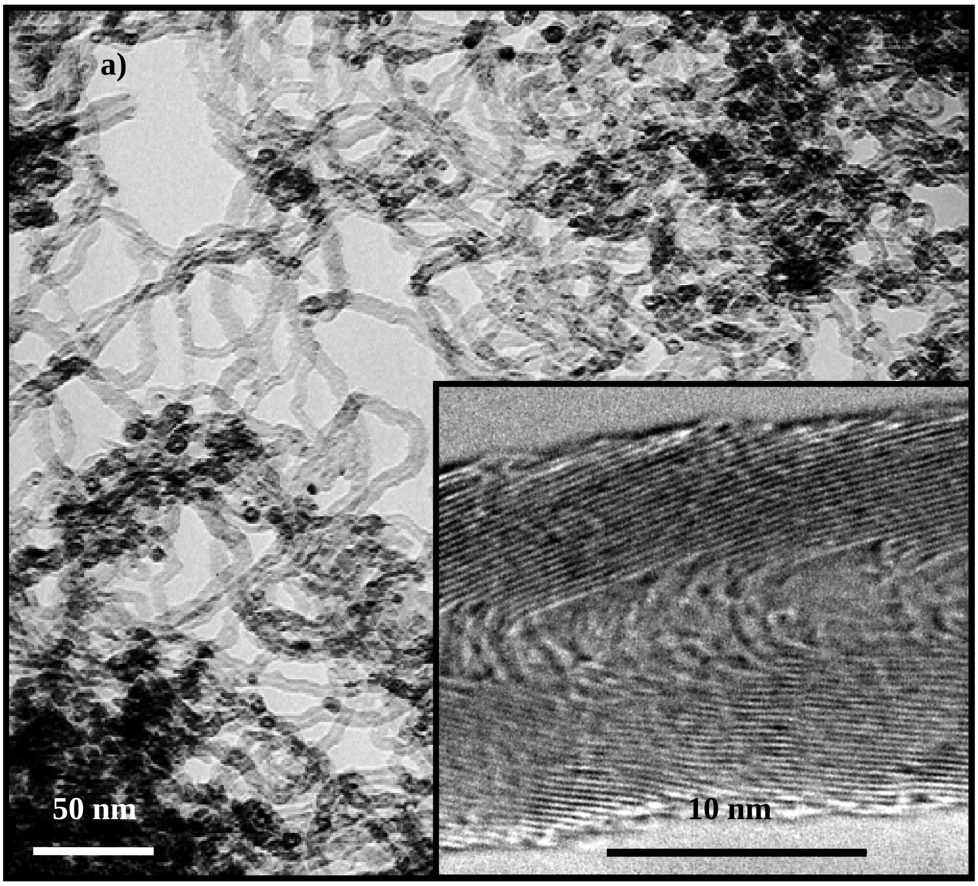
The monometallic Ni/Al_2O_3 OMCVD catalysts for GNF growth have been prepared from nickelocene, $[Ni(Cp)_2]$*. We have demonstrated that the introduction of a partial pressure of H_2 during the OMCVD catalyst preparation allows to produce pure Ni^0 deposits. The GNF have been prepared by catalytic CVD from ethylene at 650°C. We will discuss the influence of some parameters on the quality of the material and on the catalytic performances of the Ni/Al_2O_3 catalysts. We will also present a characterization of the catalyst, the composite material and the purified GNF. These nanofibers are all of the herringbone-type [fig 1a] and present a narrow distribution of diameters around 10-15nm, with a specific surface area of 170m²/g. Finally, we have used the GNF as support for PtRu bimetallic catalysts preparation.

Preliminary results concerning the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol with this bimetallic systems will be presented.

Table 1: Nickel Catalysts performances for the synthesis of nanofibers

System	**Productivity**[a] **($g_{GNF}/g_{Catalyst}$)**	**Catalytic activity ($g_{GNF}/g_{Ni}/h$)**	**Selectvity**[b]	**I_D/I_G**[c]
Ni 4.4%	0.33	7.52	++++	Not measured
Ni 8.3%	1.00	12.08	++++	Not measured
Ni 12.5%	1.22	9.76	++++	0.91

a) from TGA; b) from TEM observation; c) from Raman spectroscopy



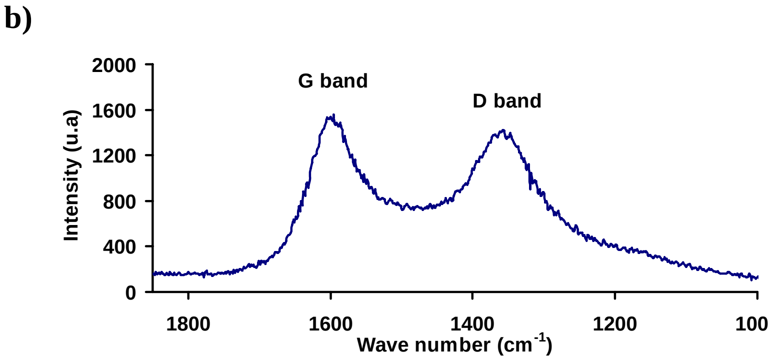


Fig. 1: a) TEM and HRTEM micrographs of the composite material obtained after deposition of carbon b) Raman spectrum of purified nanofibers

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FACTORS DETERMINING THE CATALYTIC PROPERTIES OF ACTIVE CARBONS IN SOME ACID-BASE AND REDOX REACTIONS

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The present and previous investigations make it possible to determine the mechanism of catalytic processes in the presence of carbons both in the liquid and in the vapor phases. Analysis of the results of these investigations help to determine the main factors on which the catalytic properties of the carbons depend: 1) the presence of various functional groups on the surface of the active carbon (-OH,-COOH,=NH, $-NH_2$, $-SO_3OH$, etc); 2) the presence of various modifying additives in the carbon materials (the heteroatoms N, P, S, Me, the ions, oxides, and salts of various metals); 3) the porous structure of the carbon materials, their structural and sorption characteristics; 4) the electrophysical characteristics of the CM and the structure of the carbon .

In the present communication mainly on the basis of the results of investigations carried out in recent years we examine the principal relationships governing certain catalytic processes (table) taking place on the surface of active carbon

Carbons with various chemical types of surface were used for the investigation: activated (anion exchangers) and oxidized (cation exchangers) carbons (OC) from various sources; synthetic materials obtained from polymeric materials (FAU, FOU), nitrogen-containing SKN and SKNO, from various types of wood (DOU), birch (BAU), larch waste products (LAU and LOU), from fruit stones (KAU and KAU_O), natural coals (semicokes KPK), granulated and in cloth form (UT). The oxidized samples of the carbon were modified by ion exchange.

It was established that OC containing various protogenic groups on their surface are best at accelerating many industrially important acid-base reactions: esterification, transesterification, hydrolysis, dehydration, etc. Both model oxidation-reduction processes (the decomposition of H_2O_2) and those with great significance in the chemical industry (the oxidation of cumene, dibenzyl ether, hydrogen sulfide, the decomposition of the oxygen anions of chlorine, etc.) are effectively catalyzed by active carbons. By introducing various modifying additives (metal ions, metal oxides, heteroatoms N, O, P, S and others) and by using carbon from various sources of various chemical surface types it was possible to vary and control the catalytic properties of the active carbon and to produce carbon catalysts with particular characteristics.

Table. Investigated Reactions, Accelerated by Various Carbon Sorbents

Reactions	Experimental conditions	Catalysts
Acid-base		
Esterification of acetic acid with butyl alcohol	Liquid- and vapor-phase synthesis, in static and flow-type circulatory reaction; T=393-723 K, reagent ratio 1:20 to 20:1	FOU, DOU, LOU, BAU$_o$, UT-O, KPKO
Esterification of aliphatic acids with glycerol	Static conditions with agitation under vacuum (1.3.10-3 Pa, 2 h) or in a fluidized bed reactor, T=373-473	DOU, SKNO, BAU$_o$, and their Na forms
Transesterification of edible fats and their mixtures	The same; beef and pork fat, soya, palm, and sunflower oil	DOU, SKNO, BAU$_o$, and their Na forms
Hydrolysis of ethyl acetate	Vapor- and liquid-phase hydrolysis at T=423-673 K in flow-type circulatory reactor and under static conditions (thermostat, agitation, 24 h)	FOU-H, FOU-Me (Me- Na, Ca, Cu, Zn, Fe, Ni, Co, K, Mg)
Dehydration of methanol and isobutanol	Flow-type reactor, 3 h, T= 493-623 K	FOU, DOU
Hydrolysis of vegetable oil	Static conditions, thermostat, agitation, T= 309-323 K, 24 h	SKNO, KAU$_o$, their Zn, F, Co, Mn, and Cu forms
Hydrolysis sucrose, maltose	The same	Ditto, FOU, DOU
Hydrogenation of vegetable oil	Static conditions, agitation with a stream of hydrogen, 1-13 h, T= 433-503 K	Ni-containing FOU and DOU carbons
Oxidation-reduction		
Decomposition of H_2O_2	Static conditions, thermostat, T= 293 and 309 K	FAU, BAU, CKT, AR-3, KAU, SKN, KPK, LOU, their Fe, Co, Ni, Mn, Cu, Cr forms, C+Me$_x$O$_y$ (Me – Mn, Cr, Ni, Fe, Cu)
Decomposition of oxygen compounds of chlorine	Static conditions, agitation in vessels protected from light, T= 295 K	DOU-Co, DOU-Ni
Decomposition of hydroperoxide of dibenzyl ether	Thermostated bubble-type reactor with reflux condenser, 1-6 h, T= 293-323 K	Cation-substituted forms (co, Ni, Mn, Fe, Cu) of DOU, LOU, SKNO
Oxidation of cumene	Gasometric apparatus, agitation, T= 343 K	SKN, FAU, DOU, UT$_o$, their Cr, Fe, Co, Mn, Cu, Ni-forms
Oxidation of H_2S and SO_2	Stationary reactor, agitation, T = 294-309	SKN, UT$_o$, DOU, Cr, Fe, Co, Mn, Cu, Ni -forms

NANOPOROUS CARBON MATERIALS AS EFFECTIVE PREPARATIONS IN MEDICAL PRACTICE

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Carbon hemosorbent VNIITU-1 and carbon enterosorbent VNIITU-2 (nanoporous (mesoporous) carbon sorbents for medical purpose) have been developed and obtained in the Institute of Hydrocarbons Processing SB RAS.

The carbon sorbents obtained on the base of dispersed carbon belong to mesoporous sorbents group. The domination volume of mesopores (the contents mesopores on a surface up to 80%) allows to carry out effective sorption of toxic substances with low and average molecular weight and the molecules size corresponding to the size of sorbent pores.

Sorption activity of carbon hemosorbent VNIITU-1 in relation to chemical standard markers has been investigated (tab. 1).

Table 1. Sorption activity of carbon hemosorbent VNIITU-1 in relation to chemical standard markers.

Standard marker	Molecular weight	Elimination from physiological solution, %
Methylene blue	319	92-98
Vitamin B_{12}	1357	88-90

The essentially new technology of medical purpose carbon materials production has been developed and it is completely appropriate to medicine requirements for the new generation of sorbents. The given technology has allowed to obtain sorbents with the set physico-chemical properties (tab. 2).

Table 2. Physical-chemical characteristics of sorbents.

Parameter name	Parameter norm	
	Carbon hemosorbent VNIITU-1	Carbon enterosorbent VNIITU-2
Spherical granule size, mm	0,70-1,00	0,50-1,00
Total pore volume, cm^3 / g	0,30-0,45	0,35-0,55
Adsorption capacity, g/g	___	Not less than 0,03
Iodine number, g/kg	175-245	200-300
Granule resistance to wear, % per minute, not more than	0,30	0,30

PP-II-24

Carbon hemosorbent VNIITU-1 is applied for toxic substances elimination from blood current at treatment of various diseases. Distinctive features of hemosorbent are the following ones:

- high chemical purity (carbon content is not less than 99,5 %);
- low content of ashes is not more than 0,15 %;
- high mechanical strength of the granules and their spherical form;
- practically full absence of dust on surface and in pores, that gives to the sorbent increased blood compatibility, provide good hydrodynamic of blood clearing process, and inertness in relation to formal blood elements.

The product was awarded with Golden medal at the First International Innovation and Investment Salon (Moscow, 2001).

Carbon enterosorbent VNIITU-2 is used for detoxication of patients with the accumulation of toxic substances in the organism.

Enterosorbent surpasses other sorbents in a number of different unique properties such as:

- high chemical purity (it includes of 99.5 % carbon that is inert to a digestive mucous membrane);
- low content of mineral admixture (ashes);
- high mechanical strength of granules;
- absence of dust;
- practically neutral reaction of surface-active groups;
- high sorptive capacity for toxins of low and medium molecular weight;
- insolubility in biological liquids;
- complete removing from an organism;
- simplicity of application.

The clinical tests of the sorbent were carried out in leading medical centers of Russia. The test results have confirmed a high efficiency of medical sorbents application at treatment of various diseases connected to accumulation of low and medium molecular weight toxins in patient organism.

Carbon sorbents are successfully applied in medical institutions of Russia.

CARBON NANOSTRUCTURAL MATERIALS PRODUCTION

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Carbon nanomaterials (CNMs) – carbon nanofibres (CNFs) and nanotubes (CNTs) have a lot of unique features of great interest for scientists and engineers all over the world. These materials are filament carbon structures with diameter from 1 to hundreds nanometers and with length up to several micrometers. Perfect strength in combination with elastic deformation high values, good electrical conduction and autoelectronic emission ability are typical for CNMs. They can be catalyst carrier, sorbents, supercondenser components and composite materials, additives which improve operating properties of lubricants, ceramics etc.

But the wide use of CNMs is restrained because of their high cost which is connected with the power consumption and complexity of the equipment on using arc and laser thermal methods for the production of these materials.

Tambov Innovative Technological Center for Mechanical Engineering had been carried out research and construction works on the development of CNF technologies and equipment for its industrial-scale production.

The scientists of several institutes of the Russian Academy of Sciences, particularly Ioffe Physical and Engineering Institute, Solid State Physics Institute and High-Molecular Compounds Institute, Voronezh State Technical University, Company “Nanoindustry” and also firms and research institutes in our region were our partners.

As a result of the analysis of the existing methods and techniques for carbon nanostructure obtaining we made a conclusion that catalytic pyrolysis of carbon gases is the most perspective way to produce CNFs in industrial amounts and with low production costs. First they are methane and butane-propane mixtures of the certain ratio.

It is known that in the USA, Japan, China and in some countries of Western Europe CNMs production is organized in industrial amounts but any information about the equipment used is absent in the mass media by clear reasons.

On the first stage of the project realization we carried out complex lab research in carbon gas pyrolysis in different reactors, including those with catalytic vibrofluidized layer where individual 3d-metals served as a catalyst, as well as their binary mixtures and different metals alloys.

Obtained experimental samples are filament nanofibres with diameter from 8 to 60 nm, with length to 3 micrometer and longer, consisting of crystalline nanographite generated in “fish bone” structure. All the fibres have curved shape and the amount of inclusions (catalyst metal elements mainly) doesn’t exceed 1% after appropriate purification (Fig.1). We managed to receive specific CNFs yield – 18-25g per 1g of catalyst, that is a rather perspective result in conditions of industrial production.

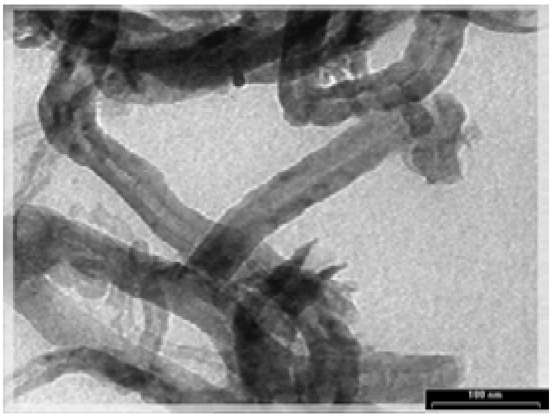

Fig. 1 Nanofibre microstructure photo

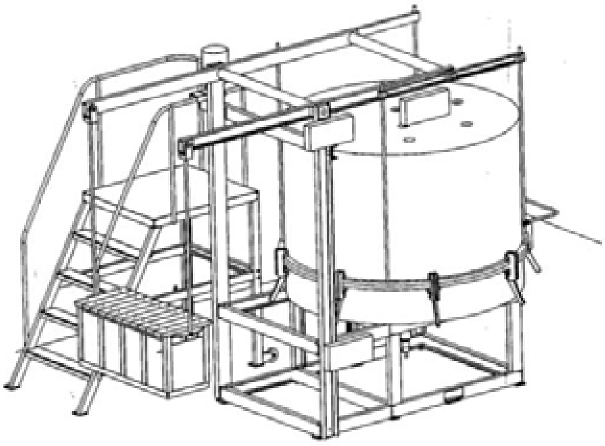

Fig. 2 3d-view of industrial reactor for obtaining of CNFs

High CNMs selectivity was experimentally confirmed and it was expressed in capability of gaining the given properties (morphological and physical and mechanical) in dependence on the technology.

The research and development allowed us creating the technological diagram for CNMs obtaining and to prepare the patent documentation on reactor for the industrial production with the output 2500-3000 kg/year (Fig. 2).

At present “NanoTechCentre” Enterprise (Tambov) was founded aimed at the equipment production and the creation of the CNMs manufacture infrastructures. The manufacture is planned to begin working at the end of 2005.

The technology developed together with CNFs production uses this CNFs technology as a material to produce articles for different engineering purposes: polymer material and antifriction alloy filling compounds, hydrogen storage, filters, adsorbents etc.

The authors are interested in the cooperative research for the large-scale application of obtained CNMs and are ready to give the samples for experiments, to communicate and exchange the information.

GROWTH OF CARBON NANOFIBERS ON METALLIC FILTERS

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During the last decade, carbon nanofibers (CNF) have attracted a lot of interest due to their outstanding mechanical, thermal and electrical properties [1]. The easiest way to grow up carbon nanofibers is by catalytic decomposition of a gaseous carbon precursor. Up to now, the majority of CNF produced by this method needs supported metal catalysts or metals in a powder form. It requires either a step of metal deposition on a support or leads to unsupported CNF, which can be very difficult to handle.

We propose to use metallic filters as supports and catalysts for the carbon nanofibers synthesis. With an adequate metallic composition, it is possible to grow up CNF directly on the filter. This leads to a structured composite material consisting of a filter where the metal wires are surrounded by a layer of CNF. This composite has a graphitic external surface, coming from the nature of the CNF and a high specific surface area due to the small diameter of the nanofibers [2]. Being a combination of two electro- and thermo-conductive compounds, the resulting material keeps these properties. It is suitable for various applications, like a catalytic support, a reinforcement material, or a catalytic electrode.

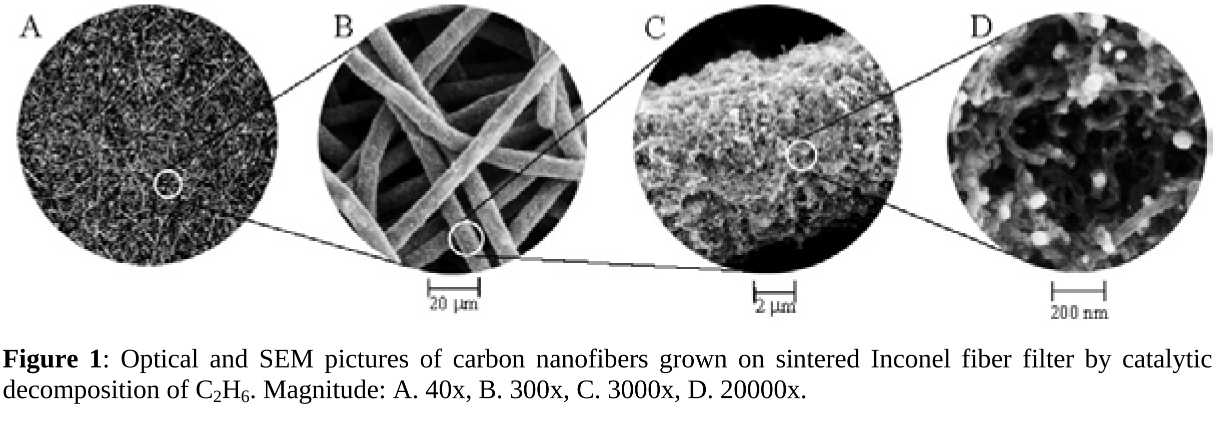

Figure 1: Optical and SEM pictures of carbon nanofibers grown on sintered Inconel fiber filter by catalytic decomposition of C_2H_6. Magnitude: A. 40x, B. 300x, C. 3000x, D. 20000x.

We report hereby the one-step synthesis of a novel composite material consisting of CNF grown on Inconel sintered metal fibers filters (CNF/SMFInconel, Figure 1). The SMF filters have a thickness of 490 μm and consist of fibers of 8 μm diameter. They possess an open macrostructure with a porosity of 81%. Inconel 601 is an alloy of nickel, iron and chromium as the main components. The CNF were produced by catalytic decomposition of ethane on $SMF_{Inconel}$ in the presence of hydrogen in a ratio 15:85 at 1.25 bar. The reaction temperature was varied between 630 and 680°C.

The SMF filters were first oxidized in air at 650°C during 3 hours. This treatment brings a mechanic stress in the metal leading to the formation of cracks and bumps. This surface deformation allows the increase of the surface area and, consequently, the amount of metal in contact with the reactive gas. In order to reduce the oxides, the filters were the treated in hydrogen for 2 hours at 600°C. SEM and XPS analysis of the filters were carried out to investigate the state of the metallic surface of the filters.

The rate of carbon deposition on the filters was measured, showing a fast increase of carbon mass on the sample during the first minutes. Afterwards, a 4 hours period of increasing rate of carbon deposition followed by a deactivation phase was observed.

In order to control the growth of CNF, the kinetics of ethane decomposition on $SMF_{Inconel}$ was studied. Partial orders of 1 and -2 for C_2H_6 and H_2 respectively and an apparent activation energy of 235 kJ/mol were found. These results are at variance with the widely accepted hypothesis of carbon diffusion in the metal as the rate limiting step. SEM studies and the kinetics results suggests a CNF growth mechanism on $SMF_{Inconel}$ with the C - C bond scission as the rate determining step.

All kinetic results and the SEM characterization will be reported and the growth mechanism with will be discussed.

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ACTIVE CARBON AS SUPPORT FOR IMMOBILIZED IONIC LIQUID CATALYSTS

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Activated carbon has been used as a support for transition metal catalysts in many different reactions. Traditionally transition metal particles have been introduced on active carbon support by ionic adsorption, colloid deposition or electroless plating.[1] We introduce a preparation method for heterogeneous catalyst by using an immobilized ionic liquid layer on activated carbon, into which the transition metal particles have been dissolved.[2]

Ionic liquids or room temperature salt melts have been under intensive study recently. Some of the most important features of ionic liquids are neglible vapour pressure, wide liquidus range, unique solvation properties, wide electrochemical window and good ion conductivity.[3, 4] They have also shown good performance in various kinds of catalytic reactions and in preparation of nanostructured materials and nanoparticles for catalysis.[5, 6] However, the wide use of ionic liquids has still been prevented by relatively high cost, limited knowledge of physical and chemical properties and biodegradability. That's why supported ionic liquid catalysts with a catalytic amount of an ionic liquid immobilized on solid surface are a noteworthy alternative from industrial point of view.[7]

Catalyst preparation method was very simple. An ionic liquid and palladium acetylacetonate were dissolved into dry acetone. Solution was poured over the support, which was either pre-dried activated carbon cloth (ACC) Kynol® or active carbon powder (Johnson Matthey). Acetone was evaporated in rotary evaporator, leaving Pd^{4+} ions dissolved in ionic liquid on active carbon support. Catalyst was pre-reduced in the reactor (1 h hydrogen flow at 100 °C). During this pre-treatment, Pd^{4+} ions were reduced to Pd^{2+}, Pd^{+} ions or Pd nanoparticles, depending on the ionic liquid the Pd-precursor was dissolved in. In hydrogenation reactions, Pd has proved to be selective catalyst for carbon-carbon double bond hydrogenation instead of the carbonyl group.

Catalysts were used in the hydrogenation of citral. Citral itself and its different hydrogenation products are used e.g. by the perfumery industry. Citral is also an interesting model compound in hydrogenations because it contains three different double bonds: isolated and conjugated carbon-carbon double bonds and a carbonyl group. During hydrogenation of citral many, competing and consecutive reactions can occur. Reaction scheme for main products is presented in figure 1. Our experiments showed that ionic liquid can improve the hydrogenation reaction rate or affect selectively to the product distribution.

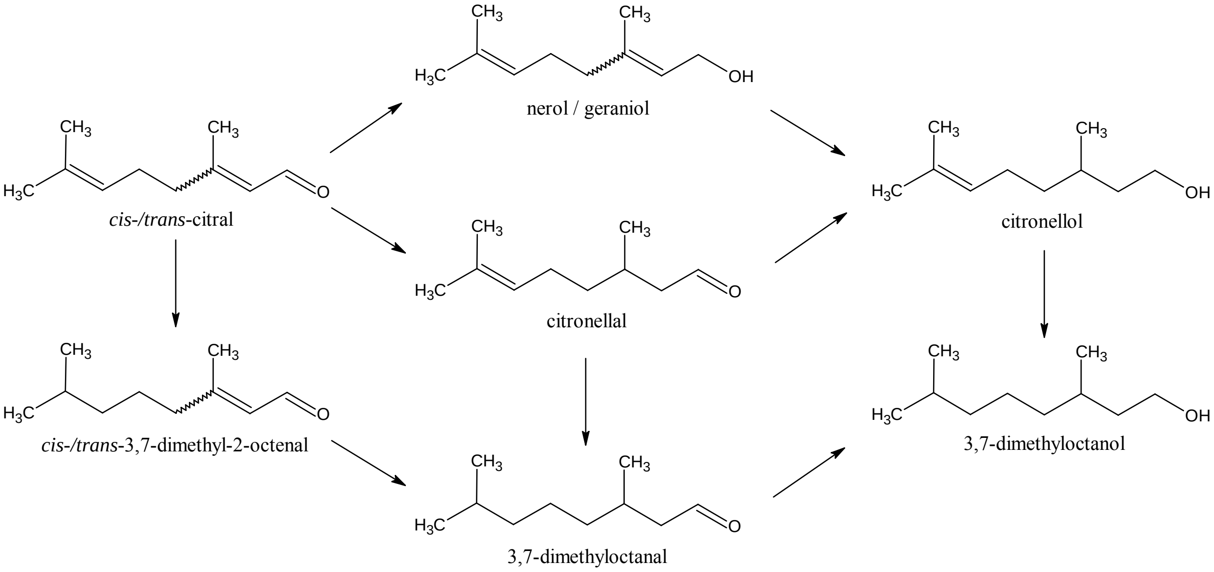

Figure 1: Citral hydrogenation scheme for main products

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USING OF THE DETONATION NANODIAMONDS FOR THE RESTORATION OF THE DEFECTED PIEZOELECTRICAL SUBSTRUCTURES

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The more number of the piezoelectric substructures on the stage of the cleaning, film precipitation, optical lithography on the surface – acoustics waves (SAW) devices production is reject as defective. Really, the whole defection of the substructures using in the technological process exceed 50 percent. The technological process and the piezoelectric substructures do have the more high cost. Therefore the defective substructures are processed with the help of the regrinding and mechanical repolishing. The processing is the removal of the surface layers having the small thickness. For all that the requirement on the surface plane, parallelness, roughness, lack of the mechanical defections on the working surfaces must be observed. The standard schemes of the piezoelectric materials grinding and mechanical polishing (OST 4.054.058-84) do have the high speed of the material surface layers removal. Therefore these schemes with the using of the polishing tool in the form of the polirite (OST 4.054.058-84) or diamond (TU 48-4-244-74) suspensions or the diamond pastes (GOST 25593-83) are not effective in the case of using of the substructures with the small permit on the thickness.

In the present article the new scheme of the defective substructures restoration is suggested.

The observation objects were the defected piezokvarse and lithium niobate substructures with the size of 40 x 20 mm, the thickness of 1,90-1,95 mm and the permit of the thickness – 50-80 µm.

The substructures in the number of 10 were pasted on the metallic disk and were work up by the grinding machine with the pneumatic regulation of pressure on the substructures. The three substructure batches (at 30 each) of the each material were worked up. The four schemes of the substructures processing differ from the abrasive instrument on the mechanical polishing stage. The optical polirite (TU – 48-4244-73) and nanodiamond water suspensions (TU 40-2067910-01-91, TU 40-2067910-04-91) with concentration 10 % mass. were accordingly used in the schemes № 1 and № 2. These suspensions were cleaned of the solid metallic particles and other big aggregates by ultrasound with frequency of 22 kGz during 3 minutes.

The authors of this article have created the polishing pastes and they are used in the schemes № 3 and № 4. The detonation nanodiamonds are used for creation of the polishing pastes with addition of the chemical components [1].

The traditional technological process of treatment of these substructures (OST 4.054.058-84) was changed in the schemes with using of the nanodiamonds. The type of the polishing disk, regimes and consistency of the technological operations were changed as on the grinding as on the polishing stages. The wafer yield was increased on the 20 % and the roughness of the substructures surface was decreased three times by these changes. Outlay of used polishing tool on the whole was decreased by using created pastes as compared with outlay of the suspensions. The polishing properties of these pastes were remained but performance of the process was increased on the 30 % by adding the abrasive micropowders with the size of 5-7 µm and the concentration about 10 % mass.

Thus the observations of the processed substructures have showed the using perspective of the now schemes (№ 3 and № 4) for the defective substructures restoration. The polishing pastes with nanodiamonds are very effective for polishing substructures stage. They improve the surface microrelief and reduce the number of the defective substructures on the polishing stage. For all that the character of the interaction of the tool with the treatment surface may be changed by adding nanodiamonds in the grinding tool with the abrasive micropowder.

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Büchi AG, Uster, Switzerland
Pilot Plants and Pressure reactors

Based in Uster (near Zurich) Switzerland, we deliver customized solutions to the well known global players in Pharma, (Fine) chemicals and Petrochemicals Industry. Our success is based on reliable and well engineered solutions, leading to long live products and satisfied customers. Our products are manufactured in corrosion resistant materials like Borosilicate glass, glass lined steel, stainless steel, Hastelloy, Titanium and Tantalum, allowing us to offer equipment for a wide range of applications.

Glass / Glass lined Pilot Plants – Large Process Equipment

customized to your needs

Büchi AG was founded as glass blowing company. The unique «büchiflex» *flexible* glass connection and exceptional materials, are the key to our success for reliable glass Pilot Plant and also large Process Equipment. It offers excellent vacuum tightness and operator safety as well as fast and simple installation.

Our Glass Pilot product range starts with the mini-pilot 5 (5 liter glass reactors) a completely glass reactor and ends with our «chemreactor 252» (250 liters glass/glass lined steel reactor). For the larger ranges, we offer Process Equipment such as complete glass overheads for big glass lined mixing vessels.

Typical application for our Mini Pilot and Pilot Plant series are:

- (full vacuum) Distillation
- Azeotropic distillation
- Evaporation to any desired consistency
- Multi-component reactions
- Gas dispersion below liquid surface
- Rectification
- Extraction
- Crystallization

in Pilots for scale up, R&D, small scale production, cGMP manufacturing

Operating conditions are:

- -60 to + 200°C (-190 to +250°C)
- Full vacuum to 0.5 bar over pressure (Glass/Glass lined reactor)
- Full vacuum to 10 bar overpressure (with pressure reactor in glass lined steel/ stainless steel, Hastelloy)

Pressure reactors or autoclaves

modular set-up for total flexibility

Observing reactions under pressure, for better understanding, was the starting point of our autoclave series. Today we manufacture pressure vessels in glass, stainless steel, Hastelloy C22, Titanium, Tantalum, Zircon and other customer requested materials.

The modular concept is one of the main features of Büchi pressure reactor systems. It allows the use of reactor vessels made in different materials and for different pressures depending on the application – this within the same equipment. Our magnetic couplings (ATEX) offer safe operation and outstanding reliability.

In combination with our bpc controller (Büchi Pressflow Gasflow Controller for use with Hydrogen and non ideal gases) it is the turn-key solution for accurate, reproducible hydrogenations.

- Pressure reactors from 10 ml to 100 liter, up to 60 bar, -80C …+250°C
- High pressure reactors up to 350 bar, 350 °C
- Distillation overheads for pressure (metal) or vacuum (glass)
- Büchi pressflow glass controller for safe and reproducible hydrogenations
- Certificates and approvals as needed

Пилотные установки и реакторы высокого давления производства компании Büchi AG, Астер, Швейцария

Наша компания располагается в городе Астер, Швейцария, мы разрабатываем современные технические решения, в соответствии с требованиями наших заказчиков, известных во всем мире фармацевтических компаний, а также компаний, работающих в сфере тонких химических технологий и нефтехимии. Успехи компании основаны на использовании богатого опыта в разработке надежных, технически проработанных изделий с продолжительным сроком эксплуатации, отвечающих требованиям заказчиков. Наши изделия изготавливаются из коррозионно-стойких материалов, таких как, боросиликатное стекло, сталь с эмалевым покрытием, нержавеющая сталь, сплав Хастелой, титан и тантал, что дает возможность эксплуатации такого оборудования в широких диапазонах.

Пилотные и промышленные установки из стекла и эмалированных материалов,

(изготавливаются в соответствии с требованиями заказчиков)

Компания Büchi AG первоначально создавалась как стеклодувное предприятие. Применяемые компанией уникальные гибкие соединения «büchiflex» и специальные материалы стали ключевым звеном в создании надежного оборудования для пилотных и промышленных установок из стекла. Такие соединения обеспечивают высокую газоплотность систем, простоту и скорость монтажа, гарантируя при этом безопасность персоналу.
Пилотные реакторы из стекла, выпускаемые компанией, представлены модельным рядом, от 5 до 250 литров. Химический реактор «252» емкостью 250 литров изготавливается из стекла или материалов с эмалиевым покрытием. Компания производит и более крупное технологическое оборудование, например, верхние стеклянные подводки для больших эмалированных смесительных сосудов.

Типичные области, где используются изделия серий «мини» и «пилотные»:

- Дистилляция с применением глубокого вакуума
- Азеотропная перегонка
- Выпаривание до требуемой консистенции
- Многокомпонентные реакции
- Смешивание газа, подаваемого под слой жидкости
- Фракционная перегонка
- Экстракция
- Кристаллизация

Наши изделия широко используются в пилотных установках, для отработки технологического масштабирования, в научно-исследовательских установках, маломасштабном производстве, производстве лекарственных препаратов по нормам GMP.

Условия эксплуатации:

- От -60 до + 200°C (и от -190 до +250°C)
- от глубокого вакуума до 0.5 бар изб. (стеклянные реакторы и реакторы из материалов с эмалевым покрытием)
- от глубокого вакуума до 10 бар изб. (реакторы из эмалированной или нержавеющей стали, или из сплава Хастелой)

Реакторы высокого давления или автоклавы,

(для облегчения пуска технологического процесса выпускаются в модульном исполнении)

Первоначально компания специализировалась на выпуске серийных автоклавов для химических целей. В настоящее время мы производим аппараты высокого давления из стекла, нержавеющей стали сплава Хастелой С 22, титана, тантала, циркония и других материалов в соответствии с требованиями заказчиков.

Одной из отличительных особенностей систем реакторов высокого давления, производимых компанией Büchi, является их модульная конструкция. Это дает возможность использовать в технологических линиях, в зависимости от назначения, реакционные сосуды из различных материалов для различных давлений, заменяя их при необходимости. Муфтовые магнитные соединения АТЕХ, выпускаемые нашей компанией, гарантируют безопасность и обеспечивают надежную работу оборудования.

В комбинации с газовым расходомером высокого давления Büchi PGC (для водорода и неидеальных газов) магнитные муфтовые соединения и модульная конструкция явились идеальным техническим решением конструкции линий воспроизводимой гидрогенизации.

- Реакторы высокого давления от 10 мл до 100 литров на давление до 60 бар, и температуру от -80 °С до +250°С
- Реакторы высокого давления, рассчитанные на эксплуатацию при давлении до 350 бар при температуре 350 °С
- Подводки к ректификационным аппаратам высокого давления (из металла) и к вакуумируемым аппаратам (из стекла)
- Автоматический газовый расходомер высокого давления Büchi PGC для безопасной и воспроизводимой гидрогенизации
- Соответствующие сертификаты и разрешения

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ismaTec	**ISMATEC SA, Zurich, Switzerrland/ ИСМАТЕК, Швейцария** Перистальтические, шестеренчатые и плунжерные насосы; модульные анализаторы для проточно-инжекционного анализа в пищевой промышленности и экологии.
Julabo	**JULABO Labortechnik GmbH, Seelbach, Germany/ ЮЛАБО, Германия** Жидкостные термостаты и криостаты; погружные охладители; водяные бани; лабораторные контроллеры температуры и программаторы.
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A.KRÜSS OPTRONIC	**KRUSS GmbH, Hamburg, Germany/ КРЮСС, Германия** Микроскопы, рефрактометры, спектроскопы, спектрофотометры.
Kühner	**KUHNER AG, Basel, Switzerland/ КЮНЕР, Швейцария** Лабораторные настольные и многоярусные шейкеры; промышленные шейкеры большой производительности; термостатируемые шейкеры.
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Nabertherm®	**NABERTHERM, Linthal, Germany/ НАБЕРТЕРМ, Германия** Лабораторные муфельные печи.

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