RIS CEE-2009

Russian-Indian Symposium

"Catalysis and Environmental Engineering"

ABSTRACTS

Novosibirsk Russia September 13-14, 2009

Novosibirsk-2009

Siberian Branch of Russian Academy of Sciences
Boreskov Institute of Catalysis

Russian-Indian Symposium

“CATALYSIS AND ENVIRONMENTAL ENGINEERING”

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PLENARY LECTURES

PL-1 ÷ PL-7

REACTIVITY OF NOVEL EARLY AND LATE TRANSITION METAL COMPLEXES IN THE POLYMERIZATION AND OLIGOMERIZATION OF ETHYLENE

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Search for new transition metal complexes capable of oligomerizing and polymerizing ethylene continues to challenge the scientific community. Preparation of structurally well defined transition metal complexes capable of imparting diversity to polyolefin structures is a continuing theme in the current literature.

In our laboratories, we have examined several new metals and ligands as catalysts for olefin polymerization. A series of copper (II) Schiff's base complexes have been found to show significant activity for ethylene polymerization. We have also prepared mono-Cp complexes of titanium and zirconium with fluorenyl silyl amido ligands as well as zirconium complexes of novel fluorenyl – alkoxy ligands which show some interesting polymerization behavior. Trans-2-[9-(H) fluorenyl] cyclohexyloxy - *ansa*-η^5-zirconium (IV) complexes were active in the polymerization of ethylene. These catalysts produced a diverse range of branched poly (ethylene) s depending on temperature. At 60°C and 80°C poly (ethylene) s with exclusive long chain branches (>6 C) were formed, whereas, at 100°C short methyl branches were also observed in addition to long chain branching. We have also explored neutral nickel complexes of N^P chelating ligands and examined their behavior towards oligomerization of ethylene. The role of steric crowding around the active center on the reactivity of these complexes was studied.

The lecture will highlight the synthesis of several of these complexes, their structural characterization and a study of ethylene polymerization using such complexes as catalysts.

PL-2

MODERN TRENDS IN THE DEVELOPMENT OF CATALYTIC AFTERTREATMENT SYSTEMS FOR LEAN-BURN AND DIESEL ENGINES

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“Three-way” catalytic converters are extremely effective for neutralization of gasoline engine exhaust gases. However stringency of upcoming environmental legislations, wide spreading of diesel engines, and development of a new generation of lean-burn engines operating under lean conditions (at high air to fuel ratios) require new catalytic systems, which are capable of carrying out several processes simultaneously: selectively reduce nitrogen oxides in the presence of oxygen, oxidize unburnt hydrocarbons and CO, remove soot particles. The modern trends in the development of new aftertreatment catalysts are focused to designing complex catalytic system comprising several components:

1. First, exhaust gases pass trough a deep oxidation catalyst for removal of unburnt hydrocarbons and CO. Additionally this catalyst oxidizes NO to NO_2 thus improving efficiency of NO_x reduction into N_2 over a catalyst for selective catalytic reduction of NO_x (SCR) installed downstream and soot oxidation over particulate filter.
2. Particulate filter is installed on diesel engines between deep oxidation catalyst and SCR catalyst for removal of particulate matter (PM) or soot. It is tempting to improve passive regeneration of particulate filter by designing catalytically active filters, which enhance soot oxidation either by oxygen or by NO_2.
3. NO_x SCR catalyst is usually disposed downstream to oxidation catalyst and particulate filter. Nowadays the most widely used process for selective NO_x reduction is based on the reaction with NH_3 or urea. Alternatively NO_x can be reduced by selective catalytic reduction with hydrocarbons or by NSR (NO_x sorption-reduction) over NO_x trap.
4. Ammonia slip catalyst (or hydrocarbon slip catalyst) is installed downstream to SCR catalyst for elimination of traces of reductant used by SCR catalyst (traces of NH_3 or hydrocarbons)

Development of a competitive catalytic system requires a solution of several tasks for improving its efficiency and cost reduction:

- Lowering the cost of catalytic system by reduction of the amount of noble metal (Pt) or by development of catalyst based on transition metal oxide compositions (without noble metals).
- Replacement of vanadium-containing SCR catalyst by ecologically friendly zeolite-based catalysts.
- Development of a new generation of the catalysts for selective catalytic reduction of NO_x with hydrocarbons.
- Improvement of “life period” and durability of the overall catalytic system by enhancing sulfur tolerance, hydrothermal stability, etc.

PL-3

DEVELOPMENT OF ADVANCED CATALYSTS FOR ENVIRONMENTALLY FRIENDLY METHANE COMBUSTION IN GAS TURBINE CATALYTIC COMBUSTORS

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In this paper we present results on development and study of granulated oxide and low Pd content catalysts for methane combustion and results of test runs in catalytic combustion chamber for small gas turbine providing minimum emissions of NO_x, CO and HC.

The research included the following stages: 1) development of catalysts, 2) kinetic studies of CH_4 oxidation, 3) modeling of processes in a catalytic combustor, 4) design of a model catalytic combustor, 5) pilot testing of catalysts in the model combustor.

The first series of supported catalysts containing 1-2 wt.% Pd have been prepared on ring-shaped alumina modified by CeO_2 [1]. The second series are oxide catalysts: oxides of Mn, hexaaluminates of Mn and La, hexaaluminates doped with 0.5% Pd [2]. Several precursor salts have been screened and metal nitrates have been selected on the basis of stability of catalytic activity and stability tests.

The catalysts were characterized by BET, XRD, H_2-TPR, X-ray microprobe and catalytic activity in CH_4 oxidation. Pilot tests were performed in a model catalytic combustor with 80 mm ID and 400 mm height at the inlet 570°C, mean gas velocity in front of the catalyst package 2 m/s and variation of air/fuel equivalence ratio α from 6.6 to 10.0.

In the as-prepared palladium catalyst, the active component is highly dispersed PdO particles which provide high activity at low temperatures. The Mn-La catalyst contains hexaaluminate structure which exhibits high stability at high temperatures. Doping of Mn-La catalyst with palladium to 0.5 wt.% allows a decrease of ignition temperature by 100°C (from 370 to 270°C) and reduction of CO content in the reaction products from 12-86 to 0-5 ppm.

For efficient methane combustion two-section loading of catalysts in the combustion chamber was designed: a thin bed of highly active Pd-Ce-catalyst in the upstream section and a larger bed of high temperature catalyst in the downstream section.

For modeling the combustion process in the combined catalytic package, calculations were performed for initial gas mixture containing 1.5% methane, the inlet temperature 450°C and different combinations of the bed lengths of Pd-Ce and Mn-La catalysts (20/180, 30/170. 40/160 mm) and also for the mixture containing 3.6% methane, inlet temperature 450°C and 20/180 mm package (Fig. 1). It was shown that at the initial methane concentration 1.5%, the complete methane combustion was attained only at space velocities less than 12000 h^{-1}. At higher space velocities, a high degree of combustion is achieved by increasing the length of the bed of the more active Pd-Ce catalyst. At the initial methane concentration 3.6%, due to high adiabatic temperature rise in the first bed, the combined catalyst package 20/180 mm provides complete methane combustion in a wide range of space velocities 5000 – 35000 h^{-1}.

Based on the results of modeling, the use of the catalyst package consisting entirely of Pd-Ce catalyst gives the best results. However, combined package with Pd-Ce and Mn-La catalysts is more preferable due to optimal design catalyst package design and an increase of its life time because of the presence of thermally stable catalyst in the high temperature zone.

According to calculations, replacement of Mn-La catalyst by its modification doped with 0.5% Pd, in combination with Pd-Ce catalyst (20 mm) in front section results in complete methane combustion in the total range of space velocities studied - up to 60000 h^{-1} at methane concentration 1.5% and inlet temperatures 450-600°C (Fig. 2).

Modeling of the combustion process on the catalysts with different shape and size (spheres, cylinders, rings with different wall thickness) shows that spheres and cylinders produce a higher pressure drop in the combustor in comparison with ring shaped granules. The optimum geometry of the catalyst granule was found to be a ring with dimensions 7x7 mm and a wall thickness 2 mm.

Based on the results of the calculations, optimum conditions for the methane combustion process in the catalytic combustor providing high degree of methane conversion were determined: the use of the combined catalyst package containing 10-20% of highly active Pd-Ce catalyst and 90-80% of thermally stable Mn catalyst in the form of rings of 7 mm diameter and 7 mm height with a 3 mm orifice; methane concentration 1.5% and the inlet temperature of methane-air mixture 450-550°C.

PL-3

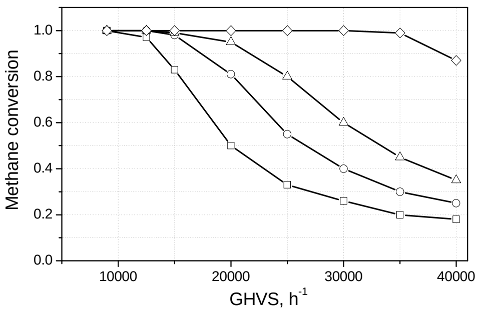

Fig. 1. Methane conversion vs GHSV at the inlet temperature 450°C and different combinations of bed lengths of catalysts Pd-Ce/Mn-La: △-20/180 mm, ○-30/170 mm. □-40/160 mm at C_{CH4} 1.5%; and ◊ - 20/180 at C_{CH4} 3.6%

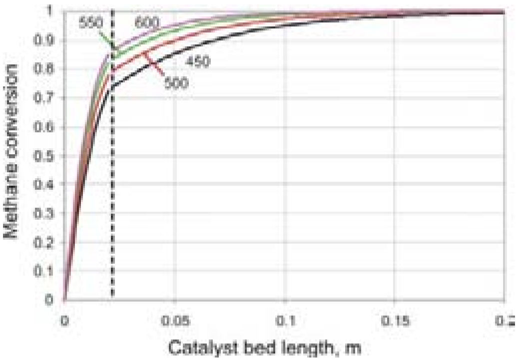

Fig. 2. Profiles of methane conversion across the length of the catalyst package Pd-Ce/Pd-Mn-La 20/180 mm, at C_{CH4} 1.5%, GHSV 60000 h^{-1} and different inlet temperatures: 450, 500, 550 and 600°C

The results of the pilot tests proved to be in good agreement with the results of the modeling. The developed design of the catalyst package provided methane combustion - over 99.97% at α=6.7-10. The level of emissions was as low as: NO_x < 1 ppm, CO < 3 ppm, HC < 10 ppm. The pressure drop of the package was less than 3% of the total pressure (1 atm).

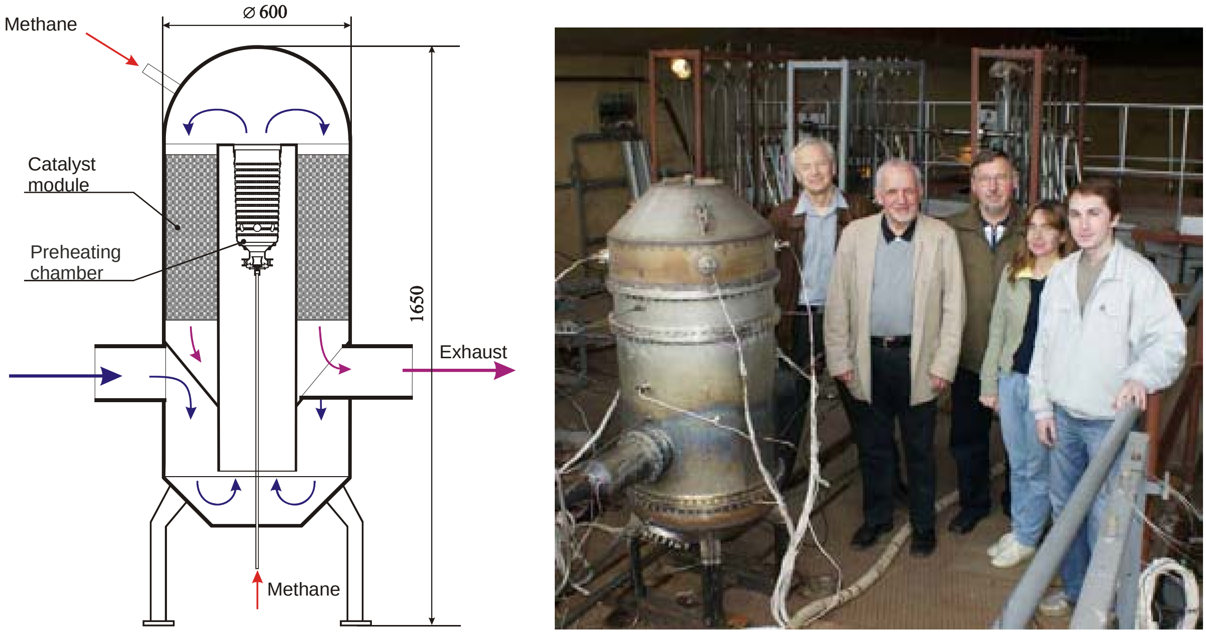

Fig.3. Scheme and photo of the prototype gas turbine catalytic combustor

Modeling and testing of methane combustion in other types of catalyst packages composed of 2 or 3 beds of granulated catalysts different by chemical composition and the shape and/or the size of granules has been performed. Experimental runs with a model combustor and with a prototype combustor with 70 kg catalyst (Fig. 3) demonstrated very good correlation with the results of the modeling. The high efficiency of methane combustion (>99.97%) and low emission of toxic compounds: NO_x < 1 ppm, CO < 10 ppm, HC < 10 ppm can be achieved for all models of catalytic package at variation of the inlet temperature.

ACKNOWLEDGEMENT

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PL-4

CO_2 SEQUESTRATION PAVES NEW WAY FOR ENERGY AND FUEL

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Development of materials with specific reference to usage of biocatalysts, thermal catalysts and photocatalyst have a significant role to play for addressing an important millennium development goal i.e. global warming/climate change. It is indispensable to develop such new advanced materials to address two important mitigative measures related to the global warming i.e usage of low carbon fuel and controlling green house gas (GHG) level. Nature has its own way of tackling GHG. For example, CO_2 in the atmosphere is being stabilized by natural processes like photosynthesis, humification, carbonation etc. However, with alarming increase in the level of CO_2 it is required to re-engineer the materials and biomimic the natural processes to control the growing levels in a cleaner, greener and sustainable manner. In this connection the related ongoing R&D activities includes the following: i) Nanobiocatalysts for biomimetic carbonation and enhanced humification reaction, ii) Mixed oxide based catalysts for biomass conversion iii) Nanosized photocatalytic materials for hydrogen generation.

Nanobiocatalysts for biomimetic carbonation reaction

Efforts are being made at NEERI to mimic the reaction for fixation of anthropogenic CO_2 into calcium carbonate using carbonic anhydrase (CA) as a biocatalyst (Bond et al.). In nature, CO_2 is being sequestered by converting it into naturally occurring minerals like dolomite, calcite etc but this is happening over a geological time frame. Calcium carbonate can be precipitated from aqueous solution, given a suitable saturation of calcium and carbonate ions, and so the issue to be addressed is to produce carbonate ions rapidly from CO_2 and H_2O, a process which first requires the formation of bicarbonate ions. This chemical and engineering problem of enhancing the rate of reaction is being facilitated using carbonic anhydrase as the enzyme and is termed as biomimetic sequestration of carbon dioxide. One of the major issues pertaining to usage of CA is improving its stability and active life. Efforts are being made at NEERI to improvise the half life period using the concept of immobilization and stabilization. Immobilization matrices like metal nanoparticles (Polishettiwar et al), mesocarbon, Barbara's, HMM-Alumina and AlKIT-5 are showing reasonably good CO_2 sequestration capacity of 15.4 mg of $CaCO_3$ / mg of CA, 12.5 mg of $CaCO_3$ / mg of CA, 5.7 mg of $CaCO_3$ / mg of CA, 3.7 mg of $CaCO_3$ / mg of CA, 3mg of $CaCO_3$ / mg of CA as compared to CO_2 sequestration capacity of 12.611 mg of $CaCO_3$ / mg for free enzyme. Also a unique protocol for the synthesis of single enzyme nanoparticles (SENs) has been developed for carbonic anhydrase etc. to stabilize the enzyme activity by encapsulating each enzyme molecule with a hybrid organic/inorganic polymer network based on the work of Kim *et al*. The CO_2 sequestration capacity for SEN is 15.06 mg of $CaCO_3$ / mg of CA as compared to CO_2 sequestration capacity of 12.611 mg of $CaCO_3$ / mg for free enzyme .

Nanobiocatalysts for enhanced humification reaction

A new approach to sequestration is being initiated at NEERI by converting carbon in plant residues to a more stable form generally known as humus using enzymes like tyrosinase (Amonette et al.). This humus is precursor of coal. Immobilization matrices such as metal nanoparticles (Polishettiwar et al), fly ash, bauxite residue, Mn oxide, and mesoporous iron oxide are showing good activity for L-DOPA. The highest activity of 713.53 U/ml has been observed for mesoporous iron oxide as compared to 409.37 U/ml for free enzyme .This maybe attributed to synergistic effect between matrix and enzyme.

Mixed oxide based catalysts for biomass conversion

Efforts are being made to use novel catalysts to promote decomposition of biomass into hydrogen (H_2) and pyrolitic carbon (PyC), with maximium combustion efficiency and minimal waste output. The H_2 produced can be used as a clean fuel whilst PyC waste consists of sequestered carbon. This would facilitate optimal use of cow-dung as a source of hydrogen energy thus avoiding inevitable release of methane, a potential green house gas with higher GWP of 23 as compared to CO_2 (GWP of 1). However, this concept of generation of has it's own share of inherent challenges as the yield of hydrogen is low and the energy content in the biomass is also low.

These problems have been addressed by synthesizing different metal based mesoporous and metal nano particle catalysts (Polishettiwar et al). The results were very much encouraging and it was observed that the synthesized catalysts were superior in their activity as compared to commercial Fe_2O_3 used as a catalyst.. Hydrogen generation was observed to be initiated at a temperature as low as 110^oC and 170^oC. This was inferred from the experimental observations for the new mesoporous catalysts and the new nano sized catalyst in comparison to 250^oC for the commercial Fe_2O_3 catalyst. Also, the maximum hydrogen yield obtained was to the tune of about 1542 μmoles and 1371 μmoles as compared to

1081 μmoles for commercial Fe_2O_3 catalyst and 859 μmoles for cellulose as such. These results have been obtained using cellulose as the biomass substrate.

Nanosized photocatalytic material for hydrogen generation

In order to maximize photocatalytic activity, it is required that the photocatalyst should not only resist recombination reaction but also should have a high specific surface area and, in addition to it, the material has to be active in the visible range (Sinha et al. Sathish et al. Abe et al.). In our previous work we synthesized composite photocatalysts which showed significant photocatalytic activity in the visible range wherein the hydrogen evolution rate of 2730 μmol/h/g of TiO_2 has been achieved (Dubey et al.). New metal nanoparticles (Polishettiwar et al) have been tested for hydrogen evolution reactions. The metal nano particles investigated have shown great potential in photocatalytic hydrogen generation with hydrogen yield in the range of 2250-3000 μmol/h/g of photocatalyst. (Unpublished data).

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PL-5

CATALYSTS DESIGN FOR BIOFUELS: BIODIESEL, GREEN DIESEL, UPGRADED BIOOIL

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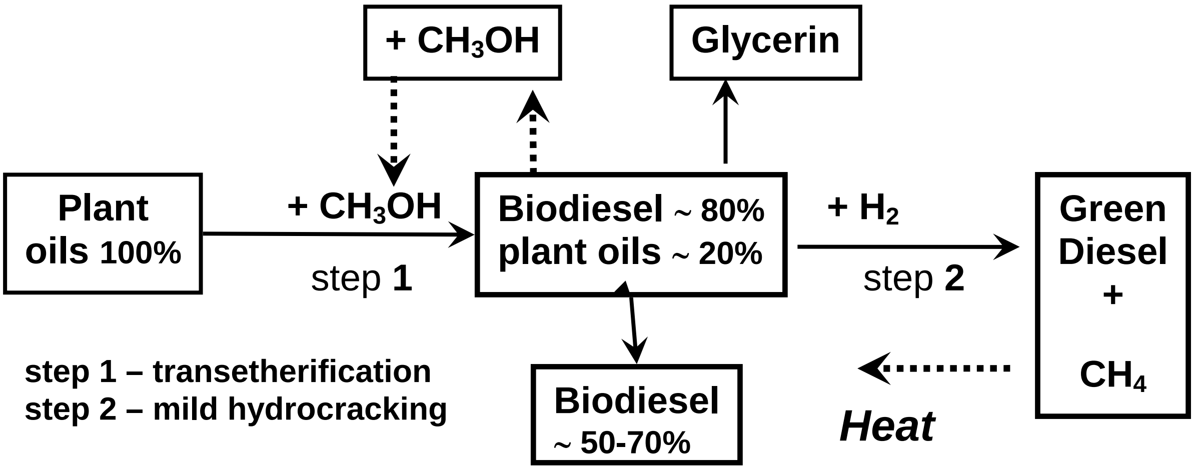
Biomass is a renewable alternative to fossil raw materials in the production of liquid fuels and chemicals. The objective of this work is to develop two-stage technology for biodiesel and green diesel production from lipidic renewables (plant oils, animal fats, algae lipids). The specificity of the work is development of new effective catalysts, adjusted to renewable feedstock. The technology is based on conjugated catalytic processes of transetherification and mild hydrocracking represented on the scheme below:



Main features of developed technology are:

- biofuel production of two types: biodiesel and green diesel;
- varying of biodiesel and green diesel yields depending needs;
- optimization of hydrogen consumption;
- energy-supply of both stages via burning of gaseous products, produced on 2nd step.

PL-5

Catalytic characteristics of the technology include application of heterogeneous basic trasetherification catalysts under 200-220ºC and 2.0 MPa and possibility of multiple catalyst regeneration for the first stage. For the second stage these ones comprise using of non-sulfided and non-noble metal catalysts, mild reaction conditions (300-340ºC and 2.0 MPa H_2) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application.

Thus, developed transetherification and mild hydrocracking processes allow to obtain high-clean biodiesel and green diesel with high cetane number, which can be used as improving additive to traditional fossil diesels. Developed new effective catalysts can be used in processing of non-food lipidic renewables.

HYDROFORMYLATION OF ALKENES IN CONSTRAINED MEDIA

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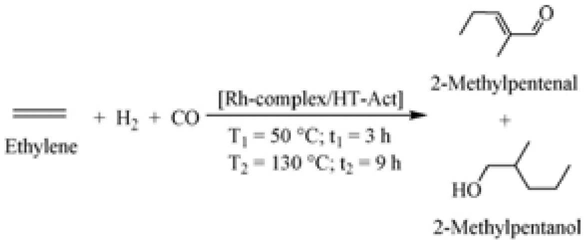
Hydroformylation of alkenes is one of the largest-scale applications of homogeneous catalysis using rhodium or cobalt based catalysts in the chemical industries [1-2]. World production of hydroformylated (oxo) products is nearly 9 million metric tonne per year. Oxo products find applications as solvents, soaps, detergents, plasticizers and intermediates for of fine and perfumery industry. Commercially, carbonyl and phosphine complexes of Co and Rh have been used for hydroformylation of alkenes in homogeneous or biphasic media. There have been attempts to heterogenize these catalysts on inorganic supports for better catalyst recovery and also application in gas phase. In the present paper, as discussed below, hydroformylation studies done to a) impart multifunctionality to the catalysts; b) supporting/intercalating the catalyst complexes inside nanoporous solids namely hydrotalcite and hexagonal mesoporous silica and c) use of biphasic media to push up the reaction rates and facile catalyst recovery will be presented.

Single pot synthesis of C_6 and C_8 oxo products from ethylene and propylene using $HRhCO(PPh_3)_3$ intercalated/supported on hydrotalcite

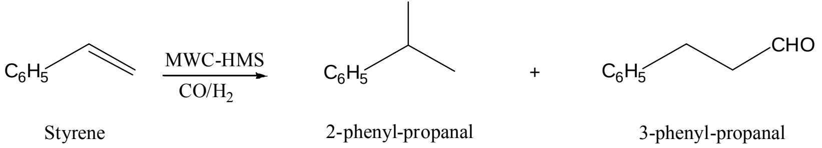
2-Methylpentanol and 2-ethylhexanol are commercially important chemicals. For example, 2-Methylpentanol finds application in pharmaceuticals, fragrances, flavors, cosmetics and as an intermediate for the synthesis of various pharmacologically active compounds [1–3]. 2-Ethylhexanol is used in the production of dioctylphthalate (DOP), other plasticizers is synthesized from propylene. These alcohols are produced using multi-step synthesis involving hydroformylation of alkenes, aldol condensation of aldehydes produces employing hazardous NaOH /KOH followed by hydrogenation of aldol products. Single pot synthesis of these oxo-compounds from ethylene and propylene using eco-friendly $HRhCO(PPh_3)_3$ supported on activated hydrotalcite as a multi-functional catalyst will be discussed [3-4].

PL-6



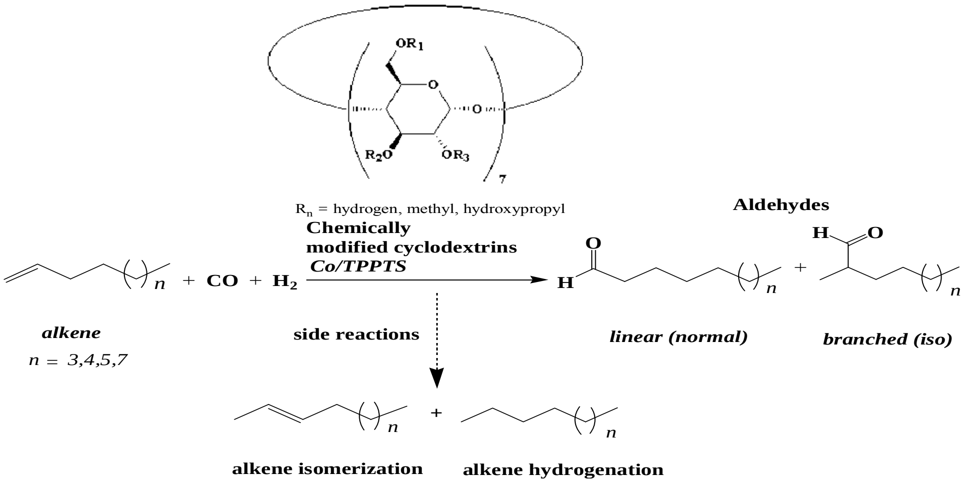
HRh(CO)(PPh$_3$)$_3$ encapsulated mesopores of hexagonal mesoporous silica (HMS) acting as nanophase reactors for effective catalytic hydroformylation of C$_5$-C$_{12}$ alkenes and styrene

HRh(CO)(PPh$_3$)$_3$, rhodium complex encapsulated in the mesopores of HMS was found to be an efficient active for the hydroformylation of C$_5$–C$_{12}$ alkenes. The detail studies performed for a representative olefin, 1-hexene demonstrated that higher selectivity for aldehydes formation occurred at lower temperature with higher *n*/iso ratio. The hydroformylation of 1-hexene was observed to be effected by the parameters: catalyst amount, amount of complex, partial pressure of CO and H$_2$ and temperature. At lower temperatures the selectivity towards aldehydes was higher with higher *n*/iso ratio. The performance of the catalyst is appreciable towards lower temperature and 50°C was found to give best conversion (100%) and selectivity (*n*/iso = 1.4). Similarly, 100% conversion of styrene was obtained yielding aldehydes as the selective products using HMS encapsulated catalyst. Under the employed reaction conditions the selectivity of the desired *iso* aldehyde was more than that of the *normal* aldehyde and the amount of the catalyst and weight ratio of HRh(CO)(PPh$_3$)$_3$ to TEOS were the major contributors in enhancing the selectivity of the *iso* aldehyde. The performance of the heterogeneous catalyst, HRh(CO)(PPh$_3$)$_3$-HMS, was better in the terms of the lower activation energy and higher *iso/n* ratio in comparison of the homogeneous counter part. The catalyst has shown good recyclability and high stability in the studied reaction conditions.



Cobalt catalyzed hydroformylation of 1-octene in the presence of chemically modified cyclodextrins

The cobalt catalyzed hydroformylation of 1-octene in the presence of chemically modified cyclodextrins as a mass transfer promoter was investigated in an aqueous biphasic system. The effect of various parameters, such as the nature of the cyclodextrin and olefin, the temperature, the CO/H$_2$ pressure, the concentration of the cyclodextrin and TPPTS was studied. The results demonstrate that the partially methylated β-cyclodextrin gives good conversion (>92%) and selectivity (>92%) for the hydroformylation of 1-octene without impeding the recovery of the catalytic system.



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PL-7

TiO_2 PHOTOCATALYSIS FOR POLLUTANTS ABATEMENT AND HYDROGEN PRODUCTION

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Inevitable exhaustion of non-renewable energetic and material resources prompts the search for alternative methods of driving chemical reactions. Utilization of photocatalytic processes for carrying out useful chemical reactions seems to be one of the most promising ways of solar light energy conversion [1].

The excitation energy of photocatalyst can be used to initiate electron transfer that results in direct oxidation of organic compounds, production of reactive oxygen species taking part in oxidation as well as oxidation of water to oxygen and reduction to hydrogen. Titanium dioxide in different forms was successfully applied as photocatalyst to carry out oxidation of organic compounds in liquid and gas phase, inactivation and destruction of pathogenic bacteria and water splitting with hydrogen evolution.

The highest activity of TiO_2 in these processes corresponds to different bulk phase and surface composition and particles morphology. Gas phase oxidation proceeds most efficiently over high surface area materials with high surface acidity. Liquid phase oxidation rate is highest for materials with high pore volume and pore diameter, while no correlation with surface area is usually observed. Deposition of platinum nanoparticles by an optimal procedure increases the rates of oxidation in gas and liquid phase as well as enhances inactivation and mineralization of pathogenic microorganisms. Energetic efficiency of air purification can be further improved via combining photocatalytic oxidation and electric discharges as well as gas phase hydrogen peroxide additions.

Hydrogen and oxygen production from water also requires different photocatalysts and co-photocatalysts. Hydrogen generation proceeds faster over anatase TiO_2 with Pt nanoparticles whereas oxygen evolves with higher rate on higher surface area rutile.

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ORAL PRESENTATIONS

Section 1

Catalysis for utilization of non-traditional feedstock and renewable energy sources

OP_{20}-I-1 ÷ OP_{20}-I-10, OP_{10}-I-11 ÷ OP_{10}-I-14

Section 2

Catalytic environmental technologies including industrial and motor waste treatment

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Section 3

Photocatalysis

OP_{20}-III-1 ÷ OP_{20}-III-2, OP_{10}-III-1

SELECTIVE CATALYTIC OXIDATION OF GLUCOSE TO GLUCONIC ACID OVER PLATINUM AND PALLADIUM CATALYSTS SUPPORTED ON SIBUNIT

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Being highly reactive compounds representing the substantial part of biomass carbohydrates are very attractive natural renewable resource for synthesis of complex organic compounds. Selective catalytic oxidation of carbohydrates to valuable aldonic acids is one of the promising routes of sugar feedstock application. Carbon- and alumina-supported Pt, Pd and Pd-Bi catalysts are conventionally used for these processes. Activity of the catalysts and their stability to deactivation depend on the red-ox potential and particle size of the active metal [1].

This work focuses on the comparative investigation of selective oxidation of glucose to gluconic acid over platinum and palladium catalysts based on the mesoporous graphite-like carbon of Sibunit series. Such study is of great interest both from practical and fundamental points of view. The influence of the dispersity of the noble metal particles and preliminary reduction of the noble metal on the performance and deactivation of Pt and Pd catalysts was investigated. Platinum and palladium catalysts supported on the Sibunit were prepared as described earlier [2,3]. All the catalysts were characterized by TEM, low-temperature N_2 adsorption, pulse CO chemisorption and X-ray spectrum fluorescent analysis. The activity of catalysts for the oxidation of glucose dissolved in water was tested in a three-necked glass reactor equipped with a magnetic stirrer (900 rpm) and peristaltic pump for alkali supply (3M NaOH). The experiments were carried out at 60°C, atmospheric pressure and pH = 8.8-9.2. The initial molar ratio of glucose to noble metal was 750:1. Since the surface of noble metal nanoparticles can be partially oxidized, the activity of both not reduced and preliminary reduced catalysts was tested. For reduction the suspension of the catalyst in water was purged with Ar (30 min), H_2 (60 min) and again with Ar (30 min) at 60^{o}C. The reaction over reduced catalysts was carried out in the same suspension. The concentrations of glucose and products of the reaction were measured by HPLC analysis using Shimadzu LC-20 Prominence system equipped with a Phenomenex Luna NH_2 column and diode-array detector.

The influence of the mean diameter of the Sibunit-supported platinum metal particles ($<d_{Pt}>$) on their catalytic activity in the glucose oxidation was studied. It turned out that the specific catalytic activity of the Pt/C catalysts normalized to the platinum surface area is independent on the $<d_{Pt}>$ in the range of 1.1-4.5 nm (according to TEM). The platinum surface area was evaluated by pulse CO chemisorption. Thus there is no particle size effect on the catalytic activity of platinum in the glucose oxidation in contrast to the Pd/C catalysts studied in [1]. Our study of the activity of the 2% Pd/C catalysts also showed that the increase in the palladium particle size results in the increase of the selectivity of gluconic acid formation. The anomalous influence of the palladium metal dispersion on the selectivity of glucose oxidation was earlier described and related to the deactivation processes (‘oxygen tolerance’ of the catalyst).

We have demonstrated that the preliminary reduction of Pd/C catalysts leads to the enhancement of the reaction rate by a factor of 1.5. On the other hand Pt metal particles are much more tolerant to oxidation by air oxygen in comparison with Pd ones. It turned out that the reduced Pt/C catalysts exhibit lower initial reaction rate in comparison with untreated ones (178 mol $h^{-1}\cdot mol_{Pt}^{-1}$ vs. 119 mol $h^{-1}\cdot mol_{Pt}^{-1}$).

Thus in our work we demonstrated that the oxidation state of Pd and Pt influences on their catalytic activity and selectivity of the glucose oxidation. In the case of Pd/C catalysts, an application of preliminary reduced palladium metal particles with low dispersity provides as high yields of the gluconic acid as 83%. On the contrary, the utilization of partially oxidized and highly dispersed platinum metal particles is preferential for Pt/C catalysts.

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STUDY OF CATALYTIC METHODS OF BIOFUELS PRODUCTION FROM WOOD

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The use of biofuels leads to a cleaner and safe environment via reduction of greenhouse gases (CO_2) and toxic gases (NO_x, SO_2), which are produced from fossil fuels. The major processes for plant biomass conversions to the more usable energy forms are gasification, thermal liquefaction and alcohol fuels synthesis. The resent activity in the area of biomass processing is directed towards the rise of yield and quality of biofuels.

The present communication describes catalytic methods of liquid and gaseous biofuels production from wood which were developed by authors. The feedstock materials were pine wood, aspen wood, beech wood, birch wood, lignin, cellulose.

Different processes of wood biomass thermal liquefaction in the presence of catalysts were compared. The low pressure (0.1-0.6 MPa) wood liquefaction processes at 400-500 °C give the moderate yields of liquid products (14-16 % wt.). Catalytic hydrogenation of wood at 15-20 MPa gives the highest yields of bioliquids (46-90 % wt.) at 400-500 °C.

Pyrolysis and hydropyrolysis of polyolefine/wood mixtures in the presence of mechanically activated iron ore catalysts allow to produce liquid products with the yield 40-46 % wt. at 400 °C and medium pressure (3 MPa). Therefore, these processes have good prospects for production of liquid biofuels from waste biomass and plastic mixtures.

The integrated conversion of wood sawdust to liquid hydrocarbons and alcohol fuels was studied. The developed process includes the stages of catalytic delignification of wood by acetic acid – hydrogen peroxide mixture, acid-catalysed hydrolysis of produced cellulosic products to glucose syrup and glucose fermentation to bioethanol. The preliminary removal of C_5-sugars by wood acidic prehydrolysis or by wood treatment by “exploded autohydrolysis” increase on 30-35 % the yield of bioethanol. The low-molecular weight soluble products of lignin oxidative degradation, obtained at the stage of wood delignification can be used for production of components of motor fuels.

For the production of gaseous biofuels the catalytic processes of wood sawdust steam gasification were suggested.

OP_{20}-I-2

The two-stage carbonization-gasification process of syn-gas production from wood sawdust was studied. In the pyrolysis reactor the powdery wood was pyrolized to char product and fuel-gas in fluidized bed of catalyst. The hot char product was treated in the gasification reactor by steam for producing syn-gas. The circulation of hot char-product between carbonization and gasification reactors supplies by heat the steam-gasification process which goes at the low oxygen consumption and produces syn-gas without tar impurities.

The one-stage process of wood sawdust gasification to gaseous mixtures with a high content of methane includes the following steps. Raw material particles feeding to heated fluidized bed of catalyst expose to thermally destruction with the formation of volatile and solid char products. Some part of char reacts with steam, the most fine char particles are burned in a combustion chamber. The heat for gasification process is collected from three sources: from overheated steam, from catalytic methanization of produced syn-gas and from combustion of some part of char product.

The suggested one-step gasification process makes it possible to produce from waste wood the methane-containing gas with calorific value on 30 % higher in comparison with the traditional steam gasification process. Besides, the part of potential heat of the initial raw material, transforming to the potential heat of the produced gas was increased by 10 relative %.

OP$_{20}$-I-3

CATALYTIC CONVERSION OF BIOMOLECULES INTO CHEMICALS

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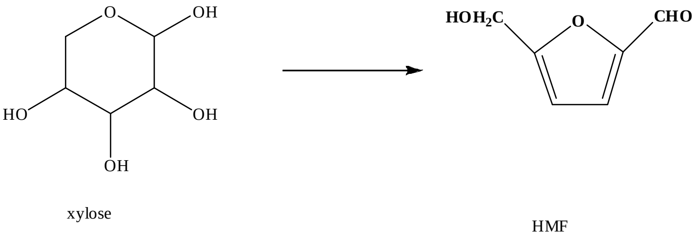
Abstract: Heterogeneous catalysts were used to convert biomolecules (polysaccharide, monosaccharide) into value-added chemicals in a hydrolysis, dehydrocyclization and oxidation reactions. The reactions were carried out using either solid acids or supported metal catalysts and thus replaced the conventional catalysts such as mineral acids and enzymes.

Introduction:

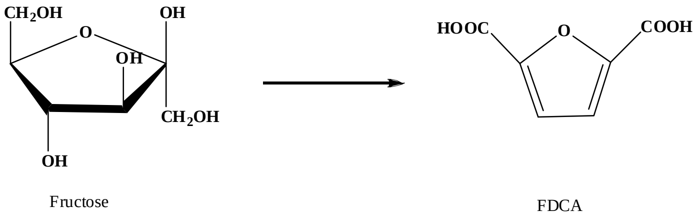
Conversion of renewable biomass into chemicals to secure our future chemical needs is becoming very important due to diminishing fossil feedstock. To achieve sugar molecules from polysaccharides (starch, cellulose, hemicellulose) heterogeneous catalysts can be used. Moreover, once sugars are formed it is very important to efficiently convert those into other value-added chemicals using heterogeneous catalysts.

In our work, we used solid acid catalysts to hydrolyze hemicellulose to yield xylose and arabinose in water media. Investigation of various catalysts revealed that the zeolites and clays are the best catalysts for this reaction. The characterization of the catalysts is done using XRD, TPD, and N2 adsorption-desorption techniques.

Study on the production of furfural from the xylose (monosaccharide) in a cyclodehydration reaction using heterogeneous catalyst is also done.



The reactions are performed using anhydrous organic solvents since presence of water hinders the formation of furfural in higher yields. It is observed that zeolites and sulfated carbon catalysts showed good activity and selectivity.



Besides above reactions, oxidation of fructose and HMF to yield diacid compounds is also carried out in the presence of molecular oxygen and using heterogeneous catalyst. The preliminary results on the reactions will be discussed.

OP_{20}-I-4

GREEN BIODIESEL PRODUCTION: WHAT IS A ROLE OF Pd METAL DISPERSION IN THE CATALYTIC FATTY ACIDS DEOXYGENATION?

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Fatty acids and their esters are renewable raw materials for producing diesel-like hydrocarbons which are known as green biodiesel [1,2]. The most promising catalyst reported in the literature has been Pd/C [3]. The main reaction pathway in deoxygenation of fatty acids results in formation of one carbon shorter hydrocarbons compared to the acid. Other products are gaseous carbon monoxide and carbon dioxide. In case of esters the first reaction step is the formation of a corresponding fatty acid, thereafter the reaction proceeds analogously as for acids.

In the catalytic deoxygenation of fatty acids the effect of metal particle size on activity, i.e. structure sensitivity, has not been previously studied. In the current work the main aim was to systematically study the effect of metal particle size and dispersion on catalytic deoxygenation of a mixture of palmitic and stearic acids.

The catalytic deoxygenation of stearic acid was performed in 300 ml semibatch reactor at 17.5 bar within temperature interval 260-300°C with 5 vol% of hydrogen in helium. The reaction mixture containing typically 0.1 M of a mixture of palmitic and stearic acids, in dodecane was injected into the reactor containing 1 g of prereduced Pd/C catalyst (powder; size < 50 μm to avoid internal diffusion limitations). The samples were silylated in order to analyze by GC.

Four Pd/C catalysts with different metal dispersion supported on mesoporous carbon (Sibunit) were prepared by deposition of palladium hydroxide yielded by hydrolysis of palladium chloride at pH 8-10. The different metal dispersions were achieved by changing the pH of the palladium hydroxide solution [4]. The fresh and spent catalysts were characterized by TEM, nitrogen adsorption, hydrogen TPR and CO TPD techniques in order to reveal the catalytically active sites.

The main liquid phase products were n-heptadecane and n-pentadecane, which were formed parallel. An optimum metal dispersion was found, which was giving the highest catalytic activity in palmitic and stearic acid deoxygenation. The large Pd particles in a sample A (metal dispersion 18%) are not enough active due to their relatively small surface area. On the other hand highly dispersed Pd species in a sample D (metal dispersion 72%) are not sufficiently active because of their strong interactions with the support resulting in the changes of Pd metal structure required for effective deoxygenation of stearic and palmitic acids. The presence of small Pd particles in the samples B (metal dispersion 47%) and C (metal dispersion 65%) provides enough high surface concentration of active Pd atoms in the proper metal structure.

Acknowledgements

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OP_{20}-I-5

PROCESS FOR BIOCRUDE/VEGETABLE OIL CONVERSION TO GREEN DIESEL

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Non-edible and used Vegetable oils, are renewable feedstock for production of bio-fuel, contributing to decreased greenhouse gas emission, decreased dependence on fossil fuels, improvement of rural economics, and increased national security. Biodiesel production by transesterification is currently the primary route to bio-fuel from vegetable oils. However, this process produces byproduct glycerol, and new biodiesel plants require a large capital investment. An attractive byproduct free route, that also offers engine compatibility and feedstock flexibility, using the existing petroleum refinery infrastructure, is vegetables oil hydrotreatment, with petroleum – derived feed stocks such gas oil, to very high cetane diesel fuel. We have developed the process for hydrotreating gas-oil and vegetable oil mixtures, to develop a process for diesel production in the same reactor within a petroleum refinery. Mixtures of gas and soya oil or jatropha oil (5, 10, 25, 40 wt % soya oil or jatropha oil) were hydrotreated at reaction temperature ranging from 350 to 380 ˚C over Ni-Mo, Ni-Co, Ni-W based hydrotreating catalysts at conditions similar to that in refinery diesel hydrotreater. GC analysis showed complete conversion of vegetable oil at the studied temperatures. Detailed hydrocarbon analysis was done to determine the relative yields of all hydrocarbons. The desired diesel range hydrocarbon (C15-C18) yield increased with increasing soya oil ratio in the feed from 5 to 40% which is as expected due to conversion of the triglycerides to the corresponding hydrocarbons. The yield also increased with increasing temperature, reaching a maxima and going down at higher temperatures due to more cracking into smaller components. The yield of the of 250-380˚C fraction (which is the fraction containing n-C15 to n-C18) increases with increasing soya oil content. This cut also increases as the reaction temperature increases from 350 to 370˚C, and then decreases with increasing reaction temperature. The percentage of straight chain alkanes in the 150-250 ˚C cut is less than 16% but does increases with increasing vegetables oil content. The acidity of the various products (TAN) becomes zero after reaction indicating complete conversion of free fatty acids. There is not much change in the pour point of the product after hydrotreating. The cetane number of the obtained product is much higher (1.5-2 times higher) than for diesel which is due to the n-alkanes formed from the vegetable oils. Our research work has resulted in a process by which vegetables oil-gas oil mixture can be converted into liquid alkanes by hydrotreating with standard hydrotreating catalyst.

SELECTIVE CATALYTIC CONVERSION OF NON-EDIBLE OILS AND CO_2 TO FUELS

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Abstract: This presentation reports the current scenario of various solid catalyst systems for production of renewable fuels from (1) non-edible oils and (2) CO_2. Transesterification of vegetable oils with lower alcohols (methanol and ethanol, for example) produces fatty acid alkyl esters (first generation biodiesel). Non-edible oils contain significant fraction of free fatty acids, water, phospholipids and other matter along with fatty acid glycerides. Oligomerization and alkylation of esters and etherification of glycerol are competing reactions to transesterification/esterification. Selective transformation of non-edible oils to biodiesel over solid catalysts is a challenging task. CO_2 is the end product in energy generation processes. It is produced along with CH_4 in biomass gasification. Its conversion back to fuels either by catalytic and photocatalytic methods is desirable. The present scenario of solid catalyst system for the production of renewable fuels (biodiesel, hydrocarbons and alcohols) from non-edible oils and CO_2 will be discussed.

Introduction:

Majority of the world’s energy needs are supplied through petrochemicals, coal and natural gas (fossil fuels), with the exception of hydroelectricity and nuclear energy. But these non-renewable energy sources are finite i.e., these sources are sufficient for less than 100 years at the present rate of consumption. The indiscriminate extraction and consumption of fossil fuels have led to a reduction in petroleum reserves. Now, the world is confronted with the twin crises of fossil fuel depletion and environmental degradation. But diesel fuels have an essential function in the economy of a country. The increasing demand for energy and environmental awareness has prompted a lot of research to produce *alternative fuels from renewable resources* that are environmentally more acceptable. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. One possible alternative to fossil fuel is the use of non-edible and waste oils of plants and animals. The second alternative is to convert back CO_2, a greenhouse gas to fuels. Catalysis and solid catalysts play a crucial role in these transformations to renewable fuel production.

Vegetable oils and animal fats are comprised of one or more fatty acids glycerides. Reaction of vegetable oils with lower alcohols (methanol and ethanol, for example) produces fatty acid alkyl esters (biodiesel). Biodiesel is a biodegradable, cleaner burning, renewable alternative to petrodiesel. It leads to ~25% reduction in the emissions of harmful pollutants like carbon monoxide, nitrogen and sulfur oxides and other particulate matter. Its use becomes attractive, however, only when its cost of production becomes competitive to protroleum-based diesel. Utilization of non-edible oils and fats instead of edible oils and replacement of conventional homogeneous acid and/or alkali with solid catalyst would help in the reduction of their cost of production [1, 2]. Non-edible oils contain significant amount of free fatty acids, water, phospholipids and other impurities which can poison and deactivate the catalysts. Although significant amount of work has gone to development of solid acid/base catalysts most of them are active only for transformation of refined edible oils but not for non-edible oils. Compared to the conventional homogeneous catalysts, the reactions over solid catalysts require higher temperatures and pressures. This requirement leads to unwanted side reactions e.g., oligomerization and alkylation of fatty acid alkyl esters and etherification of glycerol. Design of a solid catalyst which operates at moderate conditions and at the same time gives high purity fatty acid alkyl esters is highly desirable. This first generation biodiesel produced by transesterification reaction meets all the requirement of petroleum design except for pour point. Deoxygenation and hydroisomerization of fatty acid alkyl esters leads to improved quality second generation biofuel. This talk will summarize different catalysts systems including the double metal catalyst composition developed at NCL for production of high purity biodiesel.

Carbon dioxide is the end product of energy generation processes [3]. It is thermodynamically stable and kinetically inert. Its conversion back to chemicals and fuels would be an energy intensive process and requires catalysts for its activation. Gasification of biomass produces CH_4 and CO_2. While efforts are in progress to develop efficient solid adsorbents for CO_2 separation, conversion of CO_2 and CH_4 and CO_2 mixtures to fuels either by chemical or photochemical means is an important research area and a challenging task. Catalysts known as on today are either less efficient or deactivate due to coking. Development of more efficient catalysts for conversion of CO_2 to fuels (e.g., hydrocarbons and oxygenates) is still a challenging research area. The present scenario of the catalysts systems for CO_2 transformation to fuels will be presented.

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GREEN METHODOLOGY TO SYNTHESIZE NANOSTRUCTURED MATERIALS FOR PHOTO(CATALYTIC) APPLICATIONS

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Abstract: Positively charged polypeptides and related polyamines directly mineralize ZnO in a wet-chemical method under “green” conditions of room temperature and neutral pH. The polyamines not only act as mineralizing agents for ZnO nanoparticles, but also self-assemble the nanoparticles to form spindle and rod-like morphologies. The entrapped polyamines also facilitate formation and stabilization of metallic Ag nanoparticles on ZnO for use in photocatalysis. Further, these polyamines can undergo counterion condensation in certain salt solution to form polymer aggregates, and these ionically cross-linked polymer aggregates can template the assembly of silica nanoparticles forming ordered microcapsule structures at ambient conditions. The microcapsules were used to efficiently entrap Pd nanoparticles for use as catalyst in various hydrogenation reactions.

Introduction:

Bio-inspired synthesis has been emerging as an important environmentally friendly “green” route to generate inorganic materials with controlled morphologies by using bio-extracts or related molecules as structure directing agents. In this work we report a facile bio-inspired method to synthesize ZnO nanostructures at room temperature and neutral pH conditions using polypeptides and polyamines as the additives for their use in photocatalysis.

ZnO a versatile semiconductor with a wide direct band gap of 3.37eV, and has potential photocatalytic applications. Proteins or biomolecules are rarely employed for mineralization of ZnO because of their complexity and the demand of extremely mild experimental conditions necessary to preserve their physical and chemical properties. Instead, many have used synthetic polymers as substitutes to prepare ZnO nanostructures with different shapes, sizes, and crystal phases.[12] Herein, we use positively charged simple polypeptides and polyamines to directly catalyze ZnO formation in a wet-chemical method under “green” conditions [1]. Interestingly, the polyamines not only act as mineralizing agents for ZnO nanoparticles, but also self-assemble thus formed nanoparticles to generate spindle and rod-like morphologies at these ambient conditions (Figure 1). To make these structures photocatalytically active in visible light we modified the procedure to include silver nanoparticles in an *in situ* reduction method to deposit the respective metal nanoparticle on ZnO.

Thus prepared materials were tested for photocatalytic activity in decomposing atrazine (2-chloro-4-(ethylamine)-6-(isopropylamine)-s-triazine) a widely used herbicide for industrial weed control. Its use is banned by European Union because of its persistent groundwater contamination, but it is still used in U.S. Also, its carcinogenic effect has led several researchers to develop new wastewater treatment processes that are capable of promoting its complete degradation. The microbial degradation of atrazine is relatively slow process, with a half life of 60-100 days. In this regard photocatalytic degradation of atrazine using semiconductor metal oxides appears to be an efficient alternative.

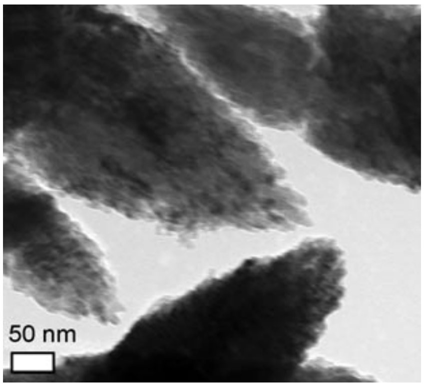

Figure 1. HRTEM images of ZnO spindles prepared with poly-allylamine as the mineralizer at RT, pH 7.4 and a reaction duration of 15 h.

In another methodology, we used these polyamines to make silica based microcaspule structures for use as a stabilizing support for catalytic metal nanoparticles. We used a tandem two-step selfassembly method, in which, cationic polyamines form supramolecular aggregates with multivalent counter-ions via crosslinking, and then negatively charged nanoparticles deposit around the aggregates to form a multilayer thick shell [2]. For encapsulation of Pd nanoaprticle, first the microcapsules were prepared by assembling silica nanoparticles directed by ionically cross-linked polyamine aggregates of Poly L-Lysine and trisodium citrate. Then the Pd salt was absorbed into the shell and reduced to metallic nanoparticles by adding sodium borohydride. Thus prepared palladium nanoparticles assembled microcapsules were used as catalyst for various hydrogenation of nitro group to amine at room temperature. The encapsulated Pd nanoparticles were accessible by the reactant and very active for the conversion. In the microcapsule structures while the polyamine stabilizes the palladium nanoparticles, the silica nanoparticles provide the required mechanical stability. Moreover, the catalyst was efficiently recoverable by simple centrifugation and the separated catalyst could be reused with similar catalytic activity for the hydrogenation reaction.

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NANOPOROUS MATERIALS AND THEIR APPLICATION IN CATALYSIS

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The discovery of periodic nanoporous materials with one- and three-dimentional channels in early 1990s has opened wide range of opportunities in ordered porous solids. The development of such materials of well-defined geometry with precise and easily controllable pore shape and size is of great importance in many areas of modern science and technology. Mesoporous molecular sieve materials are new generation ordered nanoporous materials, analogous to microporous zeolites and zeolite-type molecular sieves, having high surface area, large pore opening and huge pore volume. On the one hand, the unique flexibility in terms of synthetic conditions, pore size tuning, high surface area, large internal hydroxyl groups, framework substitution, etc. of the so-called mesoporous materials have created new avenues not only in catalysis but also in the areas of advanced materials, environmental pollution control strategies and separation processes.

On the one hand, the preparation of high quality materials with designed pore structures is of paramount importance for many applications in areas including nanomaterials, catalysis, adsorption and separation. In designing such materials, several characteristics of pore structure may be addressed, which include their shape, size and interconnectivity. On the other hand, the metal incorporated variant of mesoporous molecular sieve-based catalysts have drawn significant attention as they can be used to perform certain important organic transformation, viz., oxidation, reduction, acid-and base-catalyzed reactions, etc., more efficiently than the corresponding microporous materials or supported metal oxide systems. Moreover, these catalysts systems show remarkable results for the selective oxidation/reduction reactions in an elegant and rapid manner with excellent yields and good recyclability. These processes are highly successful, versatile, and more importantly eco-friendly, and that the chosen catalyst systems show very minimal or no leaching of the active metal ions as compared to almost all the meta-containing heterogeneous catalysts reported so far. Thus, the novel mesoporous-based catalysts show promise, and the opens-up further scope and new possibility for the organic synthesis of molecules having importance in drug and fine chemicals industry. Furthermore, the development of a process that is less damaging to the environment is an important subject in chemical research.

Green chemistry efficiently utilizes (renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products. In this context, catalysis arguably the most important tool and that the waste problem in the chemical industry can largely be eliminated by the widespread application of catalysis — homogeneous, heterogeneous and enzymatic — and alternative reaction media. In this presentation, the recent progress on the development of numerous nanoporous structures and their applications in catalysis will be discussed.

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RICE HUSK AS A PRECURSOR OF MICRO- AND MESOPOROUS CARBONACEOUS ADSORBENTS AND CATALYST SUPPORTS AND CARBON-SILICA NANOCOMPOSITE MATERIALS

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Rice husk (RH) is widely known as a difficult to process large-tonnage agricultural waste because of high content of silica (up to about 23 wt % [1]). From the other hand, this fact can transform RH from a waste to valuable source of carbon- and silica-containing materials with developed porous structure. In this work RH is considered as a precursor of three types of carbon-containing porous materials: carbon-silica nanocomposites, meso- and microporous carbons.

The first stage of the RH processing is carbonization in a fluidized catalyst bed (FCB) reactor (contact time of milled RH with the catalyst bed $\tau \sim 1$ s) with obtaining of the carbon-silica nanocomposites. In the dependence on carbonization temperature, the prepared composites possessed specific surface area $A_{BET} = 30 - 250$ m^{2}g^{-1}, total pore volume $V_\Sigma = 0.04 - 0.22$ ml g^{-1} and silica content 33 – 76 wt % with homogenously distributed carbon and silica phases [2]. These composites can find such applications as cheap bifunctional adsorbents and catalyst supports.

As it seemed that silica phase of the nanocomposites might play a role of template in carbon phase, it was decided to try to use the composites as a precursor of carbons with predominantly mesoporous texture. The composites were mixed with powdered equimolar mixture of Na_2CO_3 and K_2CO_3 with the following thermal treatment at 750 – 1000^{o}C. This approach has allowed to obtain mesoporous carbons with A_{BET} up to 1700 m^{2}g^{-1}, V_Σ up to 1.5 ml g^{-1} and volume mesopore quota more than 80 %. The average pore diameter of the materials was 2 – 4 nm. The mesoporous carbons are intended to be employed as adsorbents and catalyst supports.

The traditional template synthesis method includes the following steps: synthesis of template mesoporous SiO_2, impregnation of SiO_2 by carbonaceous precursor, carbonization at 500 – 1000^{o}C and the last – remove the template SiO_2 by HF or NaOH [3].

The obtaining carbon materials possess texture properties comparable with the properties of carbons from RH. Nevertheless, the traditional way of the materials synthesis is more difficult, expensive and includes the using of a lot of chemicals.

It was also discovered that the carbon-silica composites can be precursors of microporous carbons with high specific surface area – more than 3000 m^2g^{-1} in accordance with BET model. By KOH activation method microporous carbons with A_{BET} up to 3500 m^2g^{-1}, V_{Σ} up to 3.0 ml g^{-1} and V_{μ} up to 1.9 ml g^{-1} were obtained at 700 – 900°C. Tests of the adsorptive properties of the materials relating to H_2 (at 77 K and 50 bar) and methane (at 273 K and 60 bar) have showed high adsorptive capacities of the materials on these gases. They have adsorbed up to 6.3 wt % of H_2 and 41 wt % of CH_4 [4].

The analogies of the materials – microporous carbons, such as Maxsorb (Kansai Coke and Chemical Co Ltd., Japan) are produced from petroleum coke and pitch also by KOH activation at 700 – 800°C but through a preliminary treatment of the precursors by concentrated nitric acid that leads to mordant and toxic wastes. In addition, these materials possess lower texture characteristics (A_{BET} about 2700 m^2g^{-1}, V_{μ} about 1.2 ml g^{-1}) [5]. A comparison of the technical conditions leads to a resume that the proposing method is cheaper and environmentally more appropriate.

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OP$_{20}$-I-10

BIO-GLYCEROL HYDROGENOLYSIS VS. DEHYDRATION UNDER LIQUID PHASE CONDITIONS

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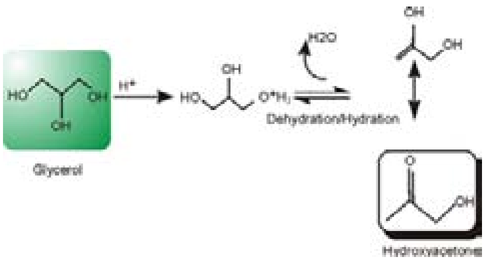
An inevitable depletion of petroleum oil feedstock and its prices souring high, has recently put a tremendous thrust on the production of biodiesel via transesterification of vegetable oils. In this process, glycerol is a co-product and its conversion to value added products becomes an important component of the whole process economics.[1] Bio-glycerol is a highly functionalized molecule, which can serve as a key renewable feedstock for several value added products and intermediates. One such application of bio glycerol is its selective hydrogenolysis to 1,2-propanediol. It is a major commodity chemical with an annual production of over 1 billion pounds in US at a price of about \$0.72/lb with a 4% annual growth in the market. Typical uses of PG are in unsaturated polyester resins, functional fluids (antifreeze, de-icing, heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, flavours, fragrances, personal care products etc. 1,2 PG is formed via acetol intermediate which also can be a starting material for various other valuable products.



Scheme 1.

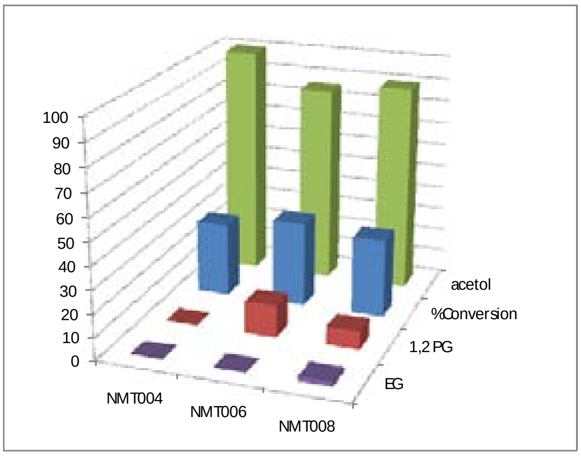


Figure 1: Catalyst screening for dehydration of glycetol to acetol

OP_{20}-I-10

Scheme 1 shows the reaction pathway of hydrogenolysis of glycerol in which hydroxyacetone (acetol) is an intermediate which on further hydrogenation gives selectively 1,2 propylene glycol. Selective dehydration of glycerol to acetol is also important because i) acetol itself is a starting material for several products; ii) A two step process with complete selectivity to PG can be developed starting from acetol since, the dehydration step does not require hydrogen and also the kinetics of both these steps being different, formation of several undesired side products can be eliminated as compared to the single step hydrogenation route. In our work, dehydration of glycerol was studied in a 300 ml Parr reactor under nitrogen atmosphere with 20-80 wt% glycerol in both water and in an organic solvent in a temperature range 180-250^o C for 3h.[2] As shown in Figure 1, our catalyst gave selectively acetol by liquid phase dehydration of glycerol under inert atmosphere. A systematic study on the effect of various process variables on glycerol conversion and selectivity to acetol has also been studied.

Single step hydrogenolysis of glycerol to 1, 2 PG was investigated over various compositions of copper chromite catalysts in a high pressure batch reactor at 220^{o}C and 500- 1000 psi H_2, using both water and 2-propanol as solvents. It was found that NMT006 catalyst gave the highest conversion of 40% in 5 h, with 97% selectivity to 1,2 PG in 2-propanol solvent while NMT004 catalyst was found to be efficient in both 2-propanol as well as water solvents. It is interesting to note that the selectivity to the intermediate acetol was higher in water than that in 2-propanol. It is also important to note that with our copper chromite type catalysts, formation of other side products such as propanols, methane etc. due to excessive hydrogenation, were completely eliminated. Our nano-structured copper based catalysts prepared by us (without Cr, having particle size, <50 nm) catalyst showed the highest glycerol conversion of 39% (5h) as well as highest slectivity (88%) to 1,2 PG as compared to bulk (without Cr) and Cu-Cr catalysts under the same reaction conditions.[3]

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LOW-WASTE BENZOGUANAMINE PRODUCTION BY CATALYTIC REACTION OF N-CYANOGUANIDINE WITH BENZONITRILE

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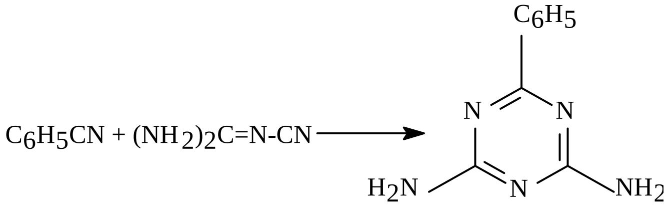
It is known that benzoguanamine (6-phenyl-2,4-diamino-1,3,5-triazine) is usefull raw material for production of amino resins and flame retardants [1]. But the commercial production of benzoguanamine is absent in Russia. The best method of benzoguanamine preparation is the reaction of N-cyanoguanidine with benzonitrile in the presence of basic catalysts [1]:



The reaction offers high yield of benzoguanamine (>90%) and minimum of by-products.

We have researched this reaction to develop scientific basis of commercial production of benzoguanamine. The reaction was carried out in a constant-temperature reactor with a mixer and a reflux condensor. Temperature of reaction (100-190^{o}C), benzonitrile/N-cyanoguanidine ratio (from 1:1 to 1:1,6) , reaction time (0,5-5 h), catalyst (KOH, piperidine, $Ba(OH)_2$, sodium 2-methoxyethylate) and solvent (2-methoxyethanol, benzyl alcohol and dimethylsulfoxide) were varied. The best results were obtained in using of 2-methoxyethanol and dimethylsulfoxide as a solvent and KOH as a catalyst. Using of more weak bases decreases the yield of benzoguanamine. The yield of benzoguanamine was changed slightly when reaction time was varied from 1 to 5 hours.

The results of our investigation will be used to develop low-waste benzoguanamine production in Russia.

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OP_{10}-I-12

PECULIARITIES OF COMPETITIVE HYDROGENATION AND ISOMERISATION OF FATTY ACID METHYL ESTERS AT THE PRESENCE OF PLATINUM GROUP METALS

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Hydrogenation of biomass oils and fatty acid methyl esters is used to improve oxidation stability and to enhance the melting point and viscosity of the hydrogenated products. In this connection a control of the extent of *cis-trans* isomerization during the double bond hydrogenation is an important object.

Hydrogenation of vegetable feedstocks at the presence of platinum group metals is carried out at the milder conditions (low temperature and hydrogen pressure) in comparison with Ni catalysts to produce oils both for food and for industrial application [1]. In the previous work on methyl linoleate hydrogenation over Pd/MgO [2, 3] it was shown that at methyl linoleate conversion up to 95 % the reaction product is the mixture of *cis*- and *trans*-isomers of methyl oleate while methyl stearate is practically missing in the reaction mixture. The *cis-trans* isomerization rate increases sharply after complete methyl linoleate conversion to methyl oleate.

In the present work for studying of competitive hydrogenation and *cis-trans* isomerization of unsaturated fatty acids methyl esters over carbon supported VIII group metals the monounsaturated oleic acid methyl ester was chosen as model compound.

The liquid phase hydrogenation and isomerization of *cis* methyl oleate over Pd/C, Ru/C, Rh/C, Pt/C and Ir/C catalysts were investigated in the temperature range of 298-373 K and hydrogen pressure within 1-10 bar using *n*-octane as a solvent. The platinum group metals supported on carbon catalysts were prepared by the deposition-precipitation method on the carbon support Sibunit as already reported [4] and characterized by N_2 physisorption, XRD, HREM. GLC, ^{13}C-NMR and FTIR techniques were employed to characterize the reaction products.

The initial hydrogenation rates of methyl oleate over Pd/C, Ru/C, Rh/C, Pt/C and Ir/C catalysts are presented on Fig. 1. It is shown that the most active catalysts for the *cis* methyl oleate hydrogenation are the Pt/C and Rh/C catalysts. The Ir/C catalyst has the low catalytic activity in hydrogenation. Over the studied catalysts the processes of *cis* methyl oleate double bond isomerization and hydrogenation took place concurrently. Among the studied catalysts based on Group 8 metals the highest catalytic activity in the *cis* methyl oleate hydrogenation with minor methyl elaidate formation is revealed over Pt catalyst.

The tentative reaction scheme of *cis* methyl oleate hydrogenation and *cis*-*trans* methyl oleate isomerization was proposed for the kinetic modeling. A good agreement between the estimated kinetic curves and the experimental data for the isomerization and hydrogenation of methyl oleate over group 8 metals supported on carbon was obtained. The estimated kinetic parameters calculated for all investigated catalysts (Pd/C, Rh/C, Pt/C, Ru/C and Ir/C) and the effective activation energies, E_a^*, for the methyl oleate hydrogenation and *cis*-*trans* isomerization steps are obtained from effective kinetic constants at various temperatures using the Arrhenius equation.

The effects of the catalyst amount, stirring rate, *cis* methyl oleate concentration, reaction temperature, and hydrogen pressure on the *cis*-*trans* isomerization rate during methyl oleate hydrogenation were investigated. The highest catalytic activity in the *cis* methyl oleate hydrogenation with minor methyl elaidate formation is revealed over Pt/C catalyst. It is concluded that fatty acids methyl esters hydrogenation over platinum metals at mild conditions is the promising way for selective *cis* methyl oleate preparation.

Acknowledgements

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OP_{10}-I-13

ECOLOGY-FRIENDLY WAY OF 1,2-PROPANEDIOL SYNTHESIS FOR BIOMASS DERIVED LACTIC ACID

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Commercial production of propylene glycol is currently petroleum-based and involves the high pressure and high temperature hydrolysis of propylene oxide manufactured by either chlorohydrin’s process or the per-oxidation process. A catalytic method starting from lactic acid obtained by fermentation of crude biomass is perspective way of 1,2-propanediol synthesis. However it is well known that catalytic hydrogenation of carboxylic acid to corresponding alcohols is very difficult process, which requires high pressure and temperature. For example, the hydrogenation of lactic acid to propylene glycol over Ru-containing catalyst was carried out at 145 bar and 423 K to reach necessary for noticeable lactic acid conversion and selectivity to propylene glycol [1].To decrease the pressure the previous esterification may be used, because the hydrogenation of corresponding esters is usually conducted in milder conditions [2,3]. Copper chromite is the one of effective and widely used catalysts of alkyl formates hydrogenation [4]. However, copper chromite shows significant activity in butyl lactate hydrogenation only at elevated pressure up to 200 bar in autoclave [5].

According to [6] silica-supported copper prepared by incipient wetness impregnation is a high selective catalyst to convert lactic acid carboxylic group to 1,2-propanediol hydroxyl one at low hydrogen pressure. Lactic acid hydrogenation over 10 wt. % Cu/SiO_2 catalyst leads to 7.3 % conversion and selectivity to propylene glycol about 75 % at hydrogen pressure 1 bar. Disadvantage of this catalyst is low productivity to the desired propylene glycol.

The goal of the present work is to study catalytic behaviour of silica-supported copper catalysts in vapour phase hydrogenation of lactic acid and hydrogenolysis of methyl- and butyl lactates in order to develop high selective catalytic process of 1,2-propanediol synthesis in mild reaction conditions at temperature range 233-493 K and pressure 1 atm.

The main products of lactic acid hydrogenation were 1,2-propanediol and propanoic acid, while hydrogenolysis of alkyl lactates leads to 1,2-propanediol, hydryxoacetone and corresponding alcohol, methanol or butanol. Also in reaction mixture were presented 1-propanol, 2-propanol, 2-hydroxypropanal in total amount less than 2 wt. %.

To study the activity of Cu-Si catalysts the copper loading in catalyst was varied from 14.2 wt. % to 45.5 wt. %. Conversion of substrate is monotone increasing with grow of copper content, while selectivity to propylene glycol decreases slightly. Precursor of the catalyst 45.5 wt. % Cu/SiO_2 has a structure of mineral chrysocolla with Cu:Si atomic ratio of one to one. Reduction of chrysocolla leads to formation of highly dispersed metallic copper particles, which take part in hydrogenation process. Further experiments was conducted over the most active 45.5 wt. % Cu/SiO_2 catalyst.

To estimate the optimal reaction conditions the temperature dependence studies were conducted. It was obtained, that increase of temperature leads to increase of substrate conversion as overall reaction rate grow, but selectivity to desired PG decreases due to increase of byproducts formation.

Effect of residence time on composition of reaction mixture was studied. It was found, that concentration of substrate is decreased and concentrations of main products is increased with increasing residence time. It is noteworthy, that ratio between 1,2-propanediol and propanoic acid in the case of lactic acid hydrogenation and 1,2-propanediol and hydroxyacetone in the case of alkyl lactate hydrogenolysis was not depending on residence time. The data obtained allow assuming, that formation of 1,2-propanediol and propanoic acid passes throw parallel independent pathways, while hydroxoacetone is thermodynamically equilibrated with 1,2-propanediol.

The optimal conditions of 1,2-propanediol synthesis was found. The most active catalyst 45.5 wt. % Cu/SiO_2 at 473 K provides 95% lactic acid conversion and 65% 1,2-propanediol selectivity. In similar conditions methyl lactate conversion was 98% with 1,2-propanediol selectivity equal to 78%.

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OP$_{10}$-I-14

BIFUNCTIONAL HOMOGENEOUS CATALYSTS FOR ORGANIC COMPOUNDS OXIDATION IN TWO-PHASE SYSTEMS

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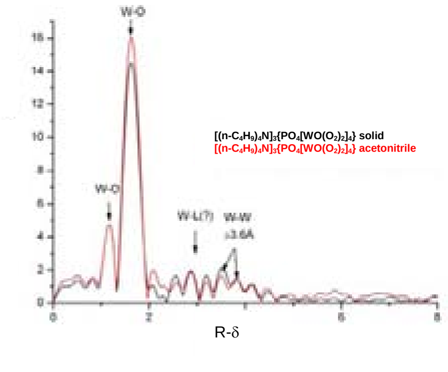
Oxidative catalysis is a field of chemistry where transition metal complexes have found a wide utility. The use of the catalytic properties of metal complexes is of particular importance in the performance of liquid-phase reactions in two-phase systems.

It is of common knowledge that peroxopolyoxotungstates (PPOT) formed in systems $H_2O_2 – H_3PO_4 – Na_2WO_4$ and $H_3PW_{12}O_{40} – H_2O_2$ [1] are usually used for oxidation of various organic substrates (such as olefins, alcohols, aromatic hydrocarbons) with hydrogen peroxide. In situ catalyst synthesis results in the formation of a mixture of $\{PO_4[WO(O_2)_2]_4\}^{3-}$, $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ and $\{HPO_4[WO(O_2)_2]_2\}^{2-}$. Note that $\{PO_4[WO(O_2)_2]_4\}^{3-}$ (tetra(oxodiperoxotungsto)phosphate) exhibits the highest catalytic activity. We synthesized and characterized a number of catalysts based on the above efficient anion and quaternary ammonium salts (QAS) active as phase-transfer catalysts. The application of such catalytic systems permits one to develop the new efficient methods of synthesis of valuable aliphatic and aromatic epoxides as well as mono-, di- and polycarboxylic acids by direct oxidation of different organic substrates with hydrogen peroxide.

The prepared peroxopolyoxotungstophosphate catalysts were studied by structural analysis using the EXAFS method permitting exploration of the neighboring atom surrounding upon treatment of the fine structure of the X-ray absorption spectra of these atoms in the substance. Spectra were taken on a VEPP-3 electron storage ring (EXAFS spectroscopy station of the Siberian Synchrotron Radiation Center) with the electron energy 2 GeV and the current 90 мA, which operated in the "fluorescence" mode.



We succeeded in demonstrating that the distance indicated in the picture as W-W corresponds with the distance W-W equal to 3.54 Å with the coordination number equal to one.

Modeling of the W-L distance as the W-P distance results in interatomic spacing equal to 3.33 Å, that comes to an agreement with the corresponding distance in the similar Mo-containing anion - $\{PO_4[MoO(O_2)_2]_4\}^{3-}$. Furthermore, data on the structural analysis obtained by EXAFS spectroscopy suggest that structures of tungstophosphate peroxopolyoxo complexes do not undergo transformation or destruction under conditions of cyclohexene oxidation with hydrogen peroxide.

Thus, the bifunctional homogeneous catalysts exhibit high efficiency in the oxidation of organics with hydrogen peroxide in the two-phase systems (organic phase – aqueous phase). The reaction predominantly proceeds in the organic phase. Peroxopolyoxotungstate complexes containing an organic cation are very soluble in the organic phase and act as active transport agents of oxygen to the substrate. Regeneration of these complexes proceeds at the interphase during interaction with hydrogen peroxide. An increase in the interfacial area is obtained by vigorous mixing of the two-phase system in the “catalytic duck” type reactor.

The work was supported by RFBR Project 09-03-00395.

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OP_{20}-II-1

OXIDATION OF LIGNIN MODEL COMPOUNDS OVER SBA-15 CATALYSTS

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Lignin is an aromatic biopolymer, which occurs as an integral cell wall constituent of all vascular plants including the herbaceous varieties. Chemically, it is a polymer of phenyl propanoids and largest abundant aromatic biomass available on earth. The structure of lignin suggests that under controlled degradation it can yield a spectrum of low molecular weight aromatic compounds, i.e., it can serve as a renewable resource of chemical feedstock. However, the structural complexity of lignin in wood tissues seriously hinders studies of its degradation mechanism. The common way for elucidation of lignin reaction pathways is to use oligomeric (mostly dimeric) phenyl propane structures as lignin models. The current pathways available for the lignin degradation are by use of photochemical energy, gamma irradiation, photo-catalysis and homogeneous catalysis using metal complexes or polyoxometalates. However, these processes are non-selective and often cannot be recycled. In this regard, heterogeneous catalytic systems based on molecular sieves appear to be a promising alternative for selective degradation of lignin structure.

In the present study we have chosen two lignin model molecules, i.e., the monomer [1-(4-hydroxy-3-methoxyphenoxy)-ethanol, apocynol] and dimer [1-(4-hydroxy-3-methoxyphenoxy)-2-(2-methoxyphenoxy)-propane-1,3-diol]. Microwave assisted oxidation of the lignin model monomer apocynol, 1-(4-hydroxy-3-methoxyphenoxy)-ethanol was carried out over mesoporous SBA-15 catalyst using H_2O_2 as oxidant to produce acetovanillone, vanillin and 2-methoxybenzoquinone. Reaction conditions were optimized in order to obtain acetovanillone selectively, which serves as a raw material for 3,4-dimethoxybenzoic acid, a building block for synthesis of the smooth muscle relaxant mebeverin [1]. SBA-15 was found to be inactive for the oxidation of dimeric compound. Under conventional heating reactions were sluggish and gave poor yields of a mixture of products. Further, we studied the microwave assisted oxidation of apocynol catalysed by Co(salen)/SBA-15 catalayst. The catalyst was prepared by immobilizing

[N,N′-bis(salicylidene)ethane-1,2-diaminato]Cobalt(II), Co(salen) complex on to the periodic mesopore channels of siliceous SBA-15. Powder X-ray diffraction, DRUV–VIS, FT-IR, AAS and TG-DTA spectra revealed that Co(salen) is anchored onto the inner surface, presumably through silanol groups. The activity of the Co(salen)/SBA-15 was investigated for the oxidation of apocynol in the presence of hydrogen peroxide as oxidant. Complete degradation of apocynol was obtained after 40 min of reaction under microwave irradiation, compared to a poor 57% degradation after 24 h under conventional heating [2]. Co(salen)/SBA-15 was found to be very selective in conversion of lignin model dimeric phenolic compound to 2-methoxy phenol.

The use of increased amount of catalyst, reusability the catalyst, role of different solvents and use of other mesoporous catalysts have also been attempted [3].

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OP$_{20}$-II-2

ADSORPTIVE CATALYTIC PROCESSES FOR HYDRODECHLORINATION OF POLYCHLORINATED AROMATIC COMPOUNDS

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Polychlorinated aromatic compounds (PCAC) are very toxic substances. Processing and recycling of these compounds are complicated not only by their thermal and chemical stability, but also by formation of very hazardous pollutants - dioxines. The adsorption technologies developed for waste treatment of the industry do not solve a problem of the further recycling highly toxic PCAC. The analysis of various methods of processing PCAC has shown that the most perspective is the catalytic hydrogenolysis process. The goal of the research work is development of universal adsorptive-catalytic process of water purification from toxic chlorocontaining pollutants allows consecutively (1) to adsorb toxic compounds from water or organic solutions and (2) to process theirs is the catalytic hydrogenolysis reaction in multiphase condition.

The supported palladium catalysts were prepared by impregnation method using aqueous solutions of metals chloride following reduction by sodium borohydride. The following materials were used as supports: carbonaceous material «Sibunit» and active carbons MeKS, FAS, AG-2000 (FGUP «ENPO «Neorganika», Elektrostal) with different specific area and porous structures.

The adsorption step of polychlorinated aromatic compounds and emulsions was carried out in glass cone flask under room temperature and external mixing. Initial and final concentrations of polychlorinated aromatic compounds were determined by ultraviolet spectroscopy.

The hydrodechlorination of chlorobenzene and dichlorobenzene by gaseous hydrogen was carried out at 20 or 50°C in a glass temperature-controlled internal mixing reactor in water or in multiphase reaction medium: organic solvents (2-propanol and toluene) and aqueous solution of KOH. The reaction products were analyzed by gas-liquid chromatography analysis (GLC analysis) and ultraviolet spectroscopy.

During this research work the adsorption step of chlorobenzene (CB) and dichlorobenzene (DCB) from water solutions was studied and it was shown, that the quantity of adsorbed CB and DCB and a kind of adsorption isotherms are in a good according with porous structure of carbon adsorbents. The most effective adsorbents are microporous carbons with the high surface area MeKS, FAS, AG-2000. On the basis of the given carbons, palladium catalysts were synthesized and their activity in liquid-phase hydrodechlorination of CB by molecular hydrogen in different condition was studied.

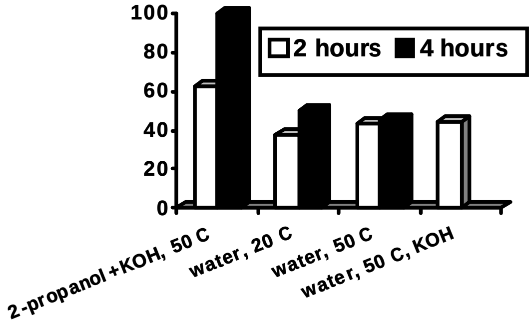

Fig.1. Dechlorination degree of CB on 1% Pd/AG-2000 in different condition

Experimental data represented on Fig.1 shown that hydrodechlorination only in water is not efficient. It may be caused by strong adsorption of CB in the micropores of support. Using of multiphase reaction medium (2-propanol and aqueous solution of KOH) allows achieving complete dechlorination not only for CB and DCB, but also for polychlorinated aromatic compounds as hexachlorobenzene. It was shown that 2-propanol is the most optimal organic solvent for hydrodechlorination. Obtained results permit to suppose that 2-propanol is not only solvent, but reagent too.

Conclusions

It was shown that two steps technology: (1) adsorption of chlorobenzene and dichlorobenzene on adsorptive catalysts and (2) hydrogenolysis of chlorobenzene in multiphase system is very efficient purification from toxic chlorocontaining pollutants.

The authors gratefully acknowledge the Russian Foundation for Basic Research (№ 07-03-01017-a) for their financial support.

OP$_{20}$-II-3

ULTRA-DEEP DESULPHURIZATION OF DIESEL FUELS ON BIFUNCTIONAL Pt-ZEOLITE CATALYSTS

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Prospective implementation of low sulphur (10 ppm, EURO-V) motor fuels is the main motivation for the development of novel advanced catalysts for ultra-deep hydrodesulphurisation of diesel fuel. The Pt and Pd catalysts supported on zeolite-containing materials [1-3] are considered as candidate for second stage of two-stage ultra-deep hydrodesulphurisation of motor fuels when the oil fraction is already mostly desulphurized (to 50 ppm S) over sulphide CoMo/Al_2O_3 and NiMo/Al_2O_3 catalysts. Indeed, the Pt(Pd)-zeolites are demonstrated to be excellent for hydrodesulphurisation of oil fractions with low concentrations of sulphur and aromatic compounds [2].

Current communication is devoted to preparation of the monometallic Pt-zeolite catalysts and study of their catalytic performance in deep desulphurisation of diesel fuels as function of preparation route, acid-base properties of supports, and active component composition. The state and morphology of noble metal particles investigated by FTIR of adsorbed CO, XPS, and HRTEM will be discussed.

The preparation of Pt-zeolite catalysts, including choice of the noble metal precursor and loading (1.0-1.8 wt.%), was optimized for maximizing the catalytic activity in thiophene hydrodesulphurisation and benzene hydrogenation. According to data obtained by HRTEM, XPS, EXAFS and FTIR spectroscopy of adsorbed CO, the catalysts contain finely dispersed Pt nanoparticles (2-5 nm) located on montmorillonite and zeolite surfaces as: Pt^0 (main, ν_{CO}= 2070-2095 cm^{-1}), $Pt^{\delta+}$ (ν_{CO}= 2128 cm^{-1}) and Pt^{2+} (ν_{CO}= 2149-2155 cm^{-1}). It was shown that the Pt-state depends on the Si/Al zeolite ratio, montmorillonite presence and Pt precursor. The use of H_2PtCl_6 as the precursor (impregnation) promoted stabilization of an oxidized Pt state, most likely $Pt(OH)_xCl_y$. When $Pt(NH_3)_4Cl_2$ (ion-exchange) was used, the Pt^0 and hydroxo- or oxy-complexes $Pt(OH)_6^{2-}$ or PtO_2 were formed. The addition of the Ca-montmorillonite favoured stabilization of $Pt^{+\delta}$. The Cl^- ions inhibit reduction of oxidized Pt state to Pt particles.

The Pt-zeolite catalyst demonstrates high efficiency in ultra-deep desulphurization of DLCO (Table). The good catalyst performance in desulphurization/hydrogenation activity and sulphur resistance can be explained by the favorable pore space architecture (Fig.) and the location and the state of the Pt clusters. The bimodal texture of the developed zeolite substrates allows realizing a concept for design of sulphur-resistant noble metal hydrotreating catalyst proposed by Song C [4].

Table. DLCO composition and performance of 1Pt(Cl)ZM-45 catalyst in hydrogenation of desulphurised Light Cycle Oil (6 MPa, 300°C, LHSV – 1h^{-1} and hydrogen-to-feed ratio – 450 NL/L).

Catalyst	S in feed, ppm	Hours on stream	H, wt%	CN	MA, wt%	PA, wt%	TA, wt%	S, ppm	D 15°C	k$_a$, h^{-1}
DLCO Feed	**1.2**	**-**	**12.66**	**35**	**30**	**2.2**	**32.2**	**-**	**0.8646**	**-**
crushed	**20**	**132**	**13.20**	**32.9**	**17.14**	**1.03**	**18.17**	**0**	**0.8305**	**0.57**
	20	**144**	**13.20**	**32.8**	**17.28**	**1.04**	**18.32**	**0**	**0.8304**	**0.56**
crushed	**50**	**312**	**12.96**	**31.2**	**22.19**	**1.32**	**23.51**	**0**	**0.8353**	**0.32**
	50	**324**	**12.96**	**30.9**	**22.66**	**1.37**	**24.03**	**0**	**0.8352**	**0.29**

H – hydrogen, wt.%; CN – cetane number; MA – monoaromatics, wt.%; PA – polyaromatics, wt.%; TA – total aromatics, wt.%; D – density at 15°C.

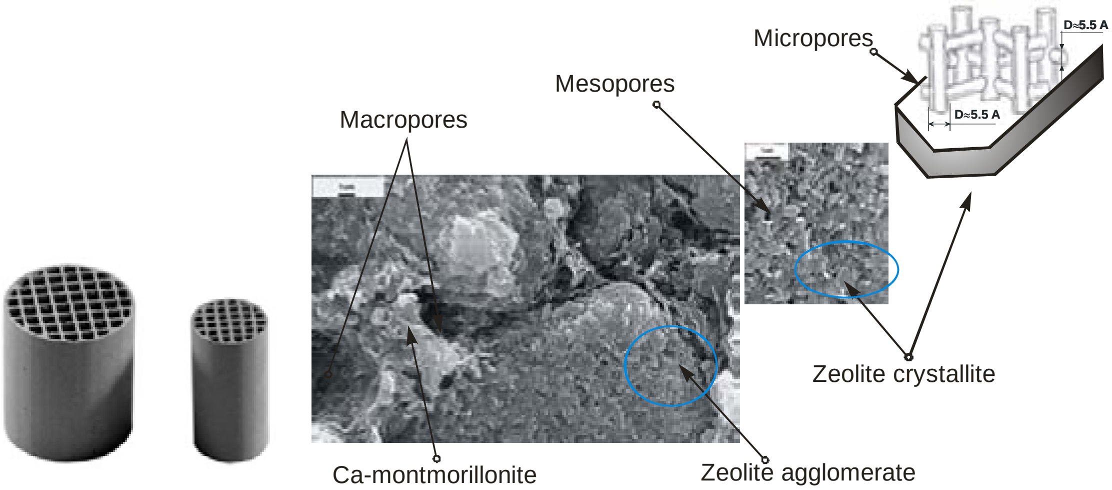

Fig. Scheme of pore structure of Pt-zeolite-monolithic catalyst

Acknowledgements

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OP$_{20}$-II-4

CONCEPT OF ACID-BASE CATALYSIS BY METAL SULFIDES

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The molecular and electronic structure of the active component of the sulfide hydrodesulfurization (HDS) catalysts is considered. The active component consists of a single slab of MoS_2 (WS_2) with Ni or Co atoms being located in its edge plane. The essential element of active component is hydrogen occluded into the MoS_2 matrix, which localizes in the center of “empty” trigonal prism of a MoS_2 matrix made from six sulfur atoms under Ni (Co) atom at the distance of 1.5 Å. Occluded hydrogen appeared in the active component during the catalyst sulfidation as a result of its oxidative addition to the Ni (Co) atoms. This occluded hydrogen creates an electronic d^6 configuration of Ni(IV) or Co(III) atoms, which are the Lewis acid sites with two vacant d_{z2} and d_{xy} orbitals. Therefore, these active centers can adsorb donor molecules of thiophene.

The activation of hydrogen occurs on the couplet sulfur atoms at the edge planes of a single MoS_2 (WS_2) slab. The driving force of this process is the presence of the S –S chemical bond at the terminal sulfur atoms that restrict an electrically neutral macromolecule of the active component and act as the Lewis basic sites. An excess of electron density is transferred from these atoms to a hydrogen molecule, which results in its homolytic dissociation. The high rate of catalytic transformation is ensured by the fast transfer of electrons and protons along the system of chemical bonds within an electrically neutral macromolecule of the active component.

OP_{20}-II-5

NEW GENERATION OF CATALYTIC TECHNOLOGIES FOR ENVIRONMENTAL PROTECTION ON THE BASE OF FIBER-GLASS CATALYSTS

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Novel catalysts comprising noble metals (Pt and Pd), supported on fiber-glass woven support [1] has attained a lot of attention recently both from theoretical and applied points of view. The research investigations [2] showed that such catalysts demonstrate unique catalytic properties in many catalytic reactions, connected with the ability of the glass fibers to stabilize the transient metals in the glass bulk in a highly-dispersed form. It results in increased catalytic activity and extra-high catalyst resistance to deactivation in aggressive reaction media. Notably, excellent catalyst performance is achieved at very low noble metal content (0.01-0.05% wt.) thus providing quite reasonable pricing for the catalyst. Moreover, specific heat/mass transfer properties [3], original geometry, high flexibility and high mechanical strength of such catalysts give the way to develop really new catalytic processes and novel reactor designs. All these features open interesting applications of fiber-glass oxidation catalysts in many areas, first of all, in the area of environmental protection.

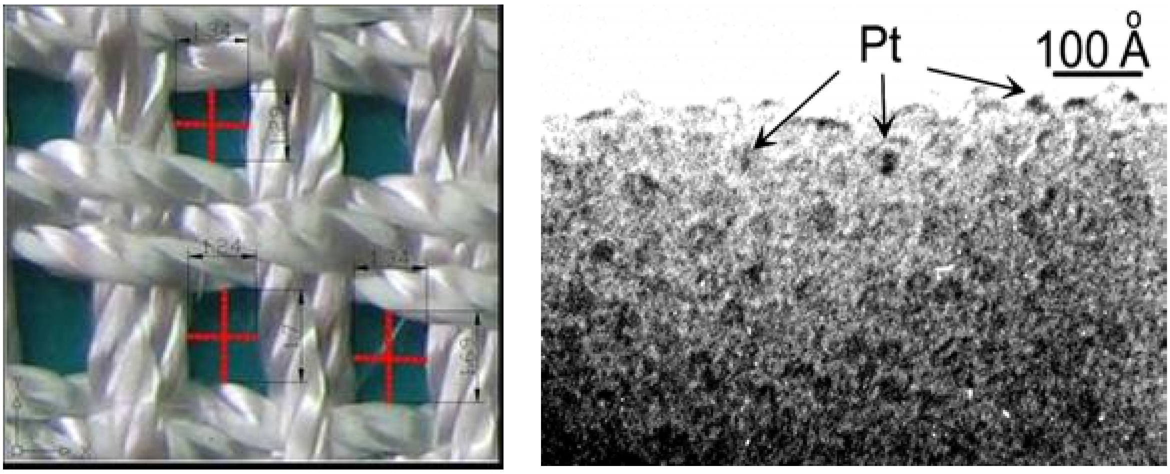

Figure 1: View (left) and internal structure (right) of the fiber-glass based catalysts

The presentation is dedicated to the successful research and development (from fundamental research issues to pilot and semi-industrial tests) of different catalytic oxidation processes based on application of fiber-glass catalysts for solution of different environmental problems, namely:

- purification of automotive exhausts;
- incineration of VOCs (volatile organic compounds) in waste/went gases;
- utilization of chlorinated VOCs and dioxins abatement;
- SO_2 oxidation for purification of waste gases and for conditioning of flue gases of coal-fired powerplants.

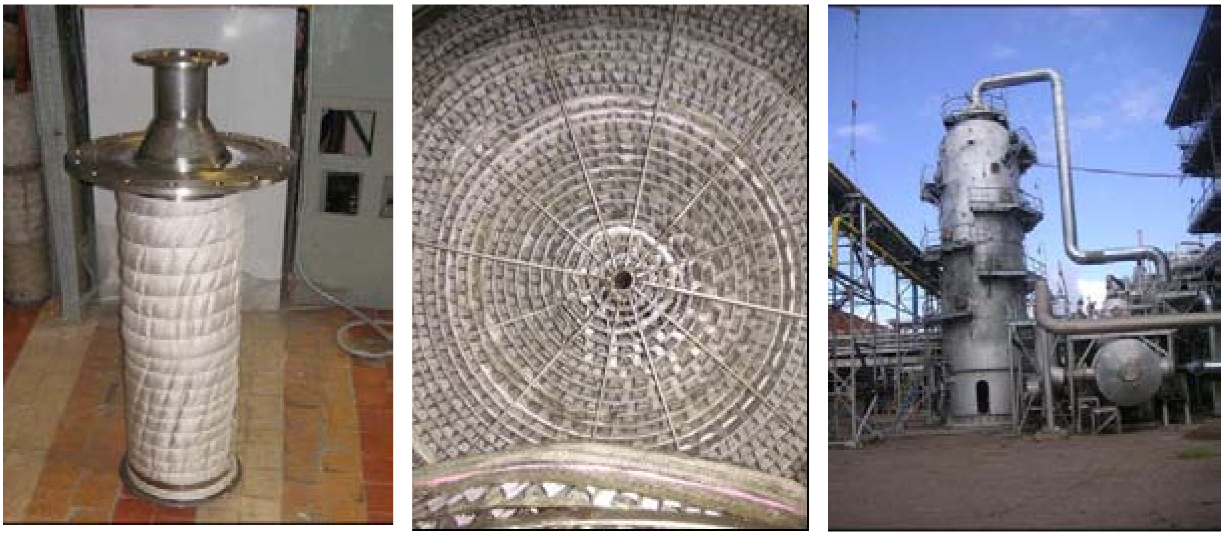

Figure 2: The device with radial bed of fiber-glass catalyst fabric for incineration of chlorinated VOCs (left), spiral-type catalyst block for purification of diesel exhausts (middle) and industrial reactor for incineration of VOC in waste gases (right)

Performed tests have demonstrated the high efficiency of the proposed processes on the base of fiber-glass catalysts, which may become a new generation of novel highly-efficient technologies for solution of environmental protection and resource-saving tasks.

Authors express their gratitude to the Russian Ministry for Science and Education and to the International Scientific-Technological Centre for the financial support of the research.

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DESIGN OF MONOLITHIC CATALYSTS FOR AUTOTERMAL/STEAM REFORMING OF NATURAL GAS AND BIOFUELS

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Transformation of fuels (fossil fuel, biofuels) into syngas or hydrogen is one of the most important tasks of catalysis in the energy-related fields. Catalysts comprised of precious metals and/or Ni supported on complex oxides with a high lattice oxygen mobility are known to be very efficient and stable to coking in autothermal/steam reforming of a variety of fuels including oxygenates [1]. Monolithic substrates with a good thermal conductivity are promising for providing an efficient heat transfer within the reactor to prevent emergence of hot spots/cool zones deteriorating performance [2]. This work presents results of research aimed at design of such catalysts and characterization of their performance parameters at the pilot-scale level.

Several types of heat-conducting substrates including compressed Ni-Al foam, fechraloy foil or gauze protected by corundum layer (either segregated by controlled oxidation or supported via blast dusting) and Cr-Al-O microchannel cermets were used. Stacked flat and corrugated bands of foil were winded into the Arkhimed spiral forming triangular channels. After spark-welding of tungsten rods as electrical current inlets, such a monolithic substrate was used for evaporation of liquid fuels sprayed via a nozzle. Monolithic substrates of planar or cylindrical shapes were washcoated with a slurry of $Ln_x(Ce_{0.5}Zr_{0.5})_{1-x}O_{2-y}$ mixed oxides (Ln = La, Pr, or Sm, x = 0÷0.3) prepared via Pechini route with addition of peptizers and surfactants (loading up to 10÷20 wt.%). Precious metals (up to 1 wt.% of Pt, Pd, Ru), and/or Ni (up to 10 wt. %) with respect to Ln-Ce-Zr-O were supported by incipient wetness impregnation.

Monolithic catalysts were tested in a pilot tubular stainless steel reactor equipped with the electric current heated fuel/water evaporation unit and heating coils to change the catalyst temperature in the reactions of autothermal (ATR)/steam (SR) reforming of natural gas, acetone, ethanol, anisol and sunflower oil. The molar ratios of H_2O/C and O_2/C in the feeds were varied in the range of 1÷7 and 0÷0.5, respectively; the gas flow rate was up to 2 m^3/h (contact times 5-70 ms) and temperature measured at the end of monolith was changed from 500 to 900 ^oC.

For all types of studied fuels, stable autothermal performance with the maximum temperature at foil monolith up to 1000 ^oC was maintained with the inlet feed temperature as low as 200 ^oC. In these conditions, the oxygen slip was not observed at all contact times. The maximum syngas yield was up to 45% with H_2/CO ratio increasing from ~ 0.8 to 1 with increasing water content up to 10%. In products, along with CO_2 (in the range of 4-6%) some amount of CH_4 (1-2%) and olefins (up to 1%) were observed. This demonstrates occurrence of cracking reactions as well.

For longer contact times, and especially for feeds with too high oxygen content, ignition of fuels at the thermal shield was observed followed by the excessive carbon deposition at walls in the inlet part of the reactor.

In the reactions of oxygenates SR the highest yield of syngas (up to 80% of H_2 + CO content in the converted feed) was achieved for systems with Pr-La-Ce-Zr-O complex oxide promoted by Ni and Pt, only CH_4 being observed as by-product.

At a proper optimization of contact times and feed composition, no coking was observed for hours-long pilot tests even for sunflower oil as a fuel. No carbon build-up was observed for the monolithic evaporator as well. Addition of stack of gauzes or thin–foil monolith after thick-foil monolith allowed improving syngas yield and removing residual olefins from products. No spallation or cracking of the active components supported on metallic substrates was revealed.

Pilot-scale tests of structured catalysts on heat-conducting metal/cermet substrates with supported doped ceria-zirconia complex oxides promoted by precious metals and/or Ni in the reactor equipped with an original evaporator/mixer of water and liquid biofuels revealed their high and stable performance. This provides new possibilities for transformation of a variety of fossil fuels and biofuels into syngas for the fuel cell application.

This work was supported by Integration project 57 of SB RAS –Belarus National Academy of Sciences.

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FIXED BED CATALYTIC NOZZLES FOR THE COMBUSTION OF FUELS AND WASTES

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Catalytic oxidation of fuels is known to be promising as environmently benign process of the heat manufacture for different purpose including domestic ones [1]. This process can be used for the deep oxidation of solid wastes of the industries, agriculture and communities with the relatively low formation of the secondary toxic compounds, while the conventional combustion occurs at the high temperatures up to 1200-1600°C leading to formation of the "heat' nitrogen oxides, benzpyrenes etc.

Earlier, the low temperature process ($T \leq 700°C$) of catalytic oxidation of fuels using inert fluidized heat transfer material and fixed bed catalyst for heating liquids had been developed [2]. As a heat transfer material from the catalyst to the heat exchanger, sand was used. For the fixed catalyst bed, the conventional oxide ceramic shaped as rings established between grids was chose. The fixed bed catalyst layer prevents the formation of bubbles. As a result, this process permits to increase the conversion of fuels and diminish concentration of CO, nitrogen oxides and other wastes at the pipetailes. But this process suffers from the low attrition resistance of the ceramic catalyst the lost of the catalyst reaching 0.3-0.5 g per day. The metal-based catalysts like honeycombs made from metallic foil can not be useful because the active component of these catalysts is concentrated in the surface layer and is not stable in the flow of sand. Also, this method is difficult to use for the oxidation of the fluidized solid wastes containing al lot of mineral nonoxidable additives.

For the purpose, a novel composite ceramo-metal (cermet) catalyst with enhanced attrition resistance had been developed. These cermets consist of the macroporos oxide matrix (MeO_x; Me = Cr, Fe, Ni, Cu, Mn, Al) with a randomly distributed metal particles (Cr, Fe, Ni and MAl_x). The macropores (up to few tens microns) provide the low diffusion resistance inside catalysts but prevents the contact of the sand with the active component situated in these pores. The cermets can be shaped as rings, plates and honeycombs, the latter - with a large portion of free space (large channels) providing low pressure gap.

As is seen from the Table, the cermet catalysts provide compatible level of activity with the conventional ceramic catalysts. It should be mentioned that the activity of the catalysts is enough to ignite the process at the temperatures lower than 500°C which is of great importance. The long term tests in the reaction media containing sand revealed the high attrition resistance of the cermet catalysts after 100 hours of time on run.

Table

Some catalytic properties of cermet catalysts

№	Metal particles	Oxide matrix	Activity in the octane oxidation*			
			T, ^0C	Catalyst volume, cm^3	Conver-sion, %	Remaining CO, vol.%
1	Fe, $FeAl_x$	FeO_x, Al_2O_3, CuO	500	3.8	93,0	< 0,01
			700		98,9	< 0,01
2	Cr, $CrAl_x$	CrO_x, Al_2O_3, $CuMnO_x$	500	10.0	96,9	< 0,01
			700		99,6	< 0,01
3	no, (ceramic catalyst ИК-12-70)	$CuCrO_x$, $MgAlO_y$	500	10.0	98,0	< 0,01
			700		99,4	< 0,01

*GHSV~30 l/h, oxygen content -7 vol.%, octane content – 2.15 g/l.

The cermet-type fixed bed catalytic nozzles are also promising for the oxidation of the solid particulate fuels like lignite, dung and peat as well as wastes.

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NiMo/Al-MCM-41 AND SBA-15 CATALYSTS. EFFECT OF THE PREPARATION METHOD ON THE STRUCTURAL STABILITY AND HYDROTREATING ACTIVITY

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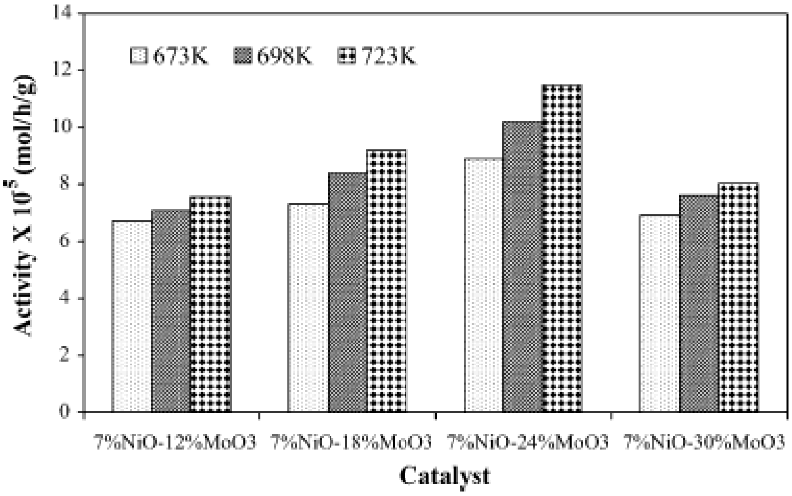
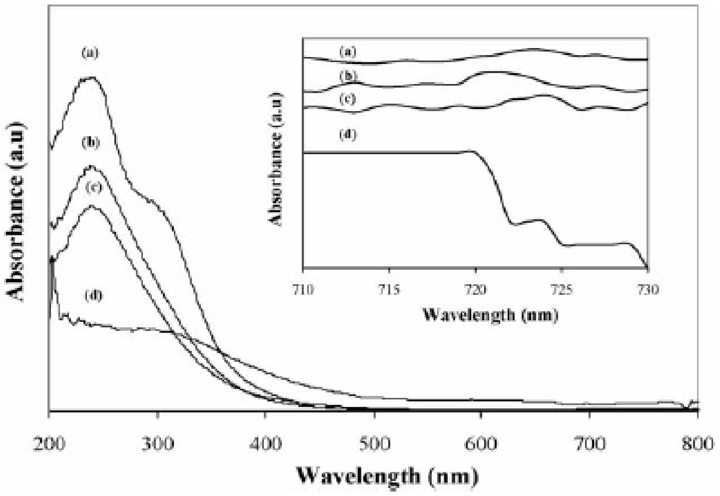
The increasing concerns of global environment have stimulated the demand for cleaner fuels. The removal of sulfur and nitrogen from gasoline and diesel oil is becoming increasingly urgent because of more stringent environmental regulations in many countries and a worldwide decrease in the quality of available petroleum feed stocks. Catalytic hydrotreating is one of the important secondary processes developed to improve the quality of petroleum crude for hydrocracking. Polyaromatic nitrogen compounds such as quinoline, indole, benzothiophene and thiophene are the main nitrogen and sulfur containing compounds in oil fractions. The presence of these compounds in petroleum crude can permanently destroy the active sites of the hydrocracking catalyst, which are responsible for catalytic cracking. In hydrotreating reaction, catalyst Mo (W) is active metal, whereas Ni (Co) is referred to as promoter for hydrotreating. For the past two decades, g- Al_2O_3 supported Ni-Mo catalyst has been used under very severe conditions of temperature and hydrogen pressure. The support effect of g-Al_2O_3 on Ni-Mo catalysts for HDN has been discussed elsewhere in detail. Research has shown that the proper choice of support is of great importance for the enhancement of catalytic hydrotreating in general and to work under less severe reaction conditions in particular. After the discovery of mesoporous materials, MCM- 41 has received increasing attention due to its very high surface area and regular pore dimensions. MCM-41 alumino silicate favors a high dispersion of the active species while increasing the accessibility of the large molecules of the gas feed containing heteroatoms to the catalytic active sites. In the recent years, the interest is focused on employing zeolites and mesoporous materials like MCM-41, AlSBA-15etc., as supports for HDS catalysts. The results of studies made with respect to effect of active component loading and preparation method on the cleavage of aromatic carbon – nitrogen will be presented.

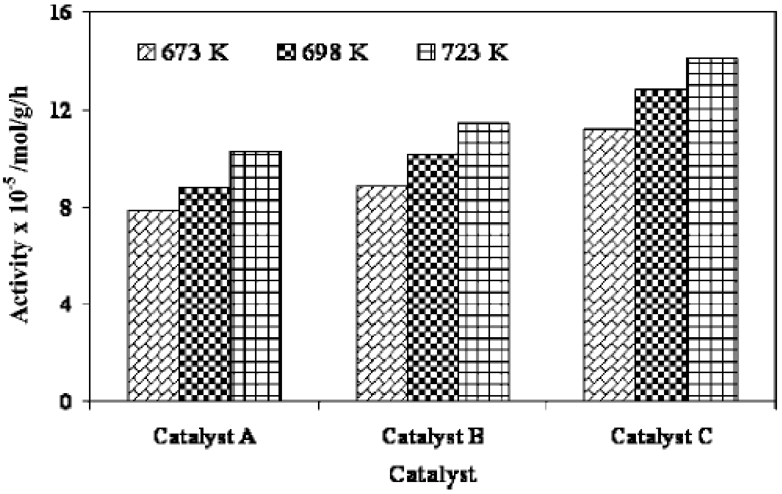
OP$_{20}$-II-8



Effect of loading MoO_3
on MCM-41on the catalytic
activity for o-toluidine.
Reaction conditions : activity
between 150 and 210 min;
LHSV = 0.75 h^{-1};
o-toluidine = 4.2 x 10^{-4} mol/h;
H_2 flow rate = 50 cm^3/min (1 atm)

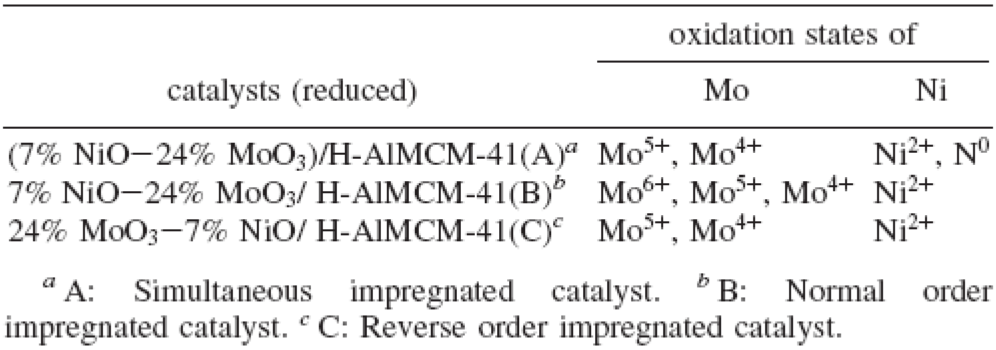


UV-Vis DRS spectra of
7 wt.% NiO-x% MoO_3/AlMCM-41:
(a) 24 wt.% MoO_3,
(b) 18 wt.% MoO_3
(c) 12 wt.% MoO_3 and
(d) 30 wt.% MoO_3.



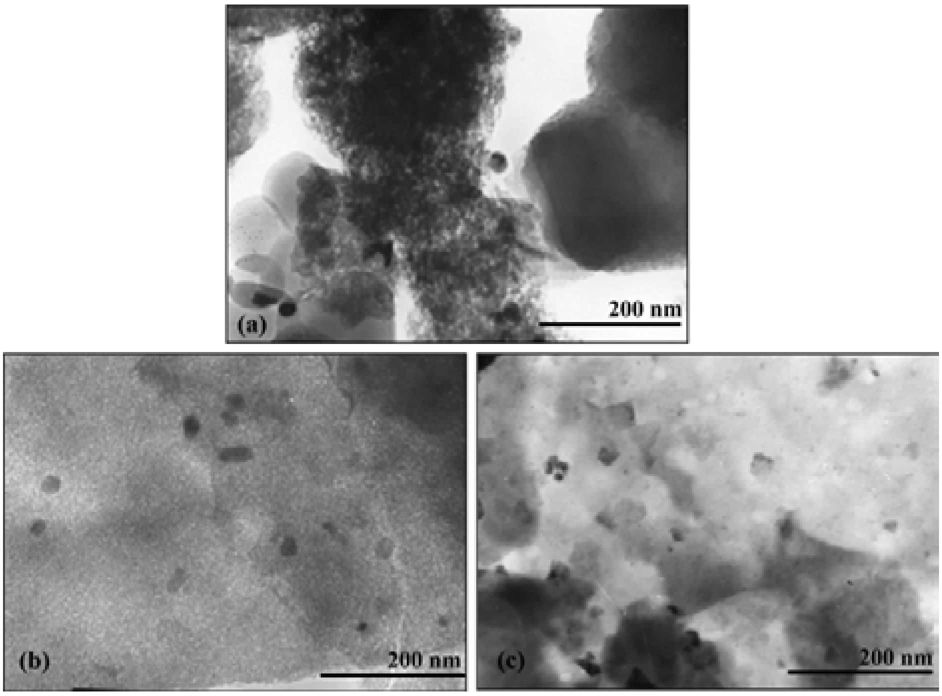
Effect of temperature on the catalytic activity for o-toluidine HDN: Influence of the impregnation method. Reaction conditions : Activity between 150-210 min; LHSV = 0.75 h^{-1}; o-toluidine = 4.2 x 10^{-4} mol/h; H_2 flow rate = 50 cm^3/min (1 atm). Catalysts : A, $(NiO.MoO_3)$/H-AlMCM-41 ; B, NiO-MoO_3/H-AlMCM-41; C, MoO_3-NiO/H-AlMCM-41.

Various Oxidation States Present in NiO-MoO3/ H-AlMCM-41 Catalysts



catalysts (reduced)	oxidation states of Mo	 Ni
(7% NiO−24% MoO$_3$)/H-AlMCM-41(A)[a]	Mo^{5+}, Mo^{4+}	Ni^{2+}, N^0
7% NiO−24% MoO$_3$/ H-AlMCM-41(B)[b]	Mo^{6+}, Mo^{5+}, Mo^{4+}	Ni^{2+}
24% MoO$_3$−7% NiO/ H-AlMCM-41(C)[c]	Mo^{5+}, Mo^{4+}	Ni^{2+}

[a] A: Simultaneous impregnated catalyst. [b] B: Normal order impregnated catalyst. [c] C: Reverse order impregnated catalyst.



TEM images of reduced (a) catalyst A, (b) catalyst B, and (c) catalyst C.

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OP$_{10}$-II-9

A COMPARISON OF MICRO- AND MESOPOROUS Fe-CONTAINING MATERIALS FOR THE CATALYTIC WET PEROXIDE OXIDATION

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Nowadays, the increasing water utilization in industrial and agricultural activities leads to the expansion of wastewater containing pollutants, such as phenol and dyes, which are of the main chemical pollutants. Fenton type homogeneous catalytic systems ($Fe^{2+}/Fe^{3+}/H_2O_2$) are known active catalysts for their complete oxidation (or mineralization) with H_2O_2 that produce CO_2 and H_2O. Iron-containing materials have attracted considerable attention as heterogeneous replacement of homogeneous systems due to their Fenton like behaviour. We review herein major aspects of our research in this field for iron-containing high-surface-area pillared clays (Fe,Al-PILC) and iron-containing mesoporous molecular sieves (Fe-MMM-2 and Fe,Al-MMM-2). Keggin type cation $[FeAl_{12}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ ($FeAl_{12}^{7+}$) was used for preparing these samples.

Fe,Al-PILCs were prepared from naturally occurring montmorillonites from Mukhortala (Buryatia) by exchanging interlayer ions to $FeAl_{12}^{7+}$ cation [1]. Fe-MMM-2 and Fe,Al-MMM-2 were synthesized via sol-mesophase rout under weak acidic conditions [2]. XRD, low-temperature N_2 adsorption, IR, DR-UV-vis and DRIFT spectroscopic techniques, were used for characterization of these materials.

Catalyst design principles are summarized and discussed to illustrate the effective development of catalysts that would meet the requirements of the catalytic application (Table). The following parameters influencing textural, physicochemical, catalytic properties of the catalysts and stability to leaching of metal from the solid are considered: *a)* iron and aluminum content in the samples; *b)* agglomeration and isolation of iron ions; *c)* pH of the synthesis mixture due to the region of mixed polyoxocation $FeAl_{12}^{7+}$ existence is limited. It has been established that the catalytic activity in oxidation of pollutants such as phenol and monoazo dye acid chrome dark-blue (ACDB) with hydrogen peroxide strongly depends on the presence of isolated iron species, which are stable to leaching. The increase in iron loading and pH of the synthetic mixture lead to iron agglomeration, which, in turn, results in reduction of the catalytic activity of Fe-containing systems and in the increase of iron leaching. Activity of Fe-MMM-2 is lower than that of Fe,Al-MMM-2 due to the lower surface acidity. Activity of Fe,Al-MMM-2 is higher than that of Fe,Al-pillared clay due to the higher surface acidity and the decrease of diffusion limitation.

Table
Phenol and ACDB oxidation with H_2O_2 in the presence of Fe-containing samples

Sample [a]	A_{BET} $m^2 \cdot g^{-1}$	d_{10} [b] nm	PhOH oxidation [e]		ACDB oxidation [e]	
			Time [c], h	Leaching of Fe [d], wt. %	Time [c], h	Leaching of Fe [d], wt. %
Without catalyst	-	-	> 30	-	> 30 h	-
Fe-MMM-1(1.0)	852	3.8	1.5 7 [f]	< 0.1 -	-	-
Fe-MMM-2(2.4)	930	3.8	10	0.2	80	17.6
Fe,Al-MMM-2(2.4)	1518	3.9	3.5	6.7	200	15.3
Fe,Al-MMM-2(4.4)	1315	3.8	2.5 1.0 [f] 2.5 [k]	< 0.1 < 0.1 < 0.1	60	1.0
Fe,Al-PILC(4.4)	215	1.8	1.5 [f]	< 0.1	420	0.3

[a] pH of the synthesis mixture is given in bracket ; [b] d_{10} – interlayer spacing; [c] Time of 100% conversion of phenol and ACDB; [d] the amount of iron leached from Fe-containing sample to solution (based on the initial iron content; [e] Reaction condition: phenol, 1 mM; H_2O_2, 14 mM; catalyst 1 $g \cdot L^{-1}$, pH 6.2, 60^0C; and ACDB, 0.1 mM; H_2O_2, 60 mM; catalyst 1 $g \cdot L^{-1}$, pH 5.8, 40^0C; [f] 50^0C; [k] 40^0C

Acknowledgement

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OP_{10}-II-10

DEVELOPMENT OF CATALYST FOR THE SELECTIVE CO_2 HYROGENATION TO CO

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Biomass-derived fuels and other chemicals are considered as a basic element for sustainable development in the modern world. In recent years, production of biodiesel – one of the main biofuel types - has been growing exponentially in many countries. Biodiesel is produced from vegetable oils and fats by catalytic reaction with an alcohol, typically methanol, which yields glycerine as a by-product. As every ton biodiesel roughly consumes 100 kg methanol and produces the same amount of crude glycerine, the world's methanol demand increases while on the other hand the glycerine market becomes glutted. An interesting option addressing the surplus of glycerine and the request for methanol is to produce methanol from the crude glycerine by the biodiesel producer itself: they will then be less dependent on the methanol spot price, there is a (partial) security of supply of methanol, and their own by-product is used as a green, sustainable feed product.

Process of crude glycerine reforming to produce methanol for re-use in biodiesel plants may consists of three catalytic stages: reforming of glycerine in supercritical water, reverse water gas shift reaction and methanol synthesis. The present work addresses the development of a catalyst for selective CO2 hydrogenation to CO (reverse water-gas shift, RWGS) towards the optimum gas composition for methanol synthesis (i.e., with the highest possible CO and a low CO_2 content).

Based on scientific literature data [1-3] and available sources on commercial WGS catalysts, we prepared a series of about 20 RGWS catalysts, tested them for catalytic performance and selected the most active ones presented below.

The Cu-Fe/$CeZrO_2$, Fe/$CeZrO_2$, $CeZrO_2$, ZnO/Al_2O_3, Mn/$CeZrO_2$ catalysts were synthesized by coprecipitation of copper, cerium, iron, zinc, zirconium, manganese and aluminum salts taken at the given rations by 5% solution of K_2CO_3. The resulting precipitates were filtered, washed with distilled water, dried in air at 100°C for 12 h and calcined at 700°C for 3 h.

The Cu/CeZrO$_2$, Pt/CeZrO$_2$ catalysts were synthesized by incipient impregnation of CeZrO$_2$ (prepared by coprecepitation of cerium and zirconium salts) by copper or platinum salt water solution. Samples were dried at 100^{o}C for 12 h and calcined at 700^{o}C for 3 hours.

Catalysts were evaluated in a fixed bed flow reactor with gas analysis on line. Reaction conditions: CO/CO$_2$/H$_2$/H$_2$O =5/30/60/5, GHSV=10000 h^{-1}, pressure 1 atm., temperature 300-700^{o}C. Prior to reaction, the catalysts were reduced at 300^{o}C in reaction mixture for 1 h. The fresh and spent catalysts were characterized by means of TPR, TPO, TPD, XRD, XPS and TEM techniques.

Thermodynamic calculations showed that pressure increase results in preferable methane formation. Therefore, special efforts were made to develop a catalyst highly active for RWGS reaction and inactive for the reaction of CO and CO2 methanation.

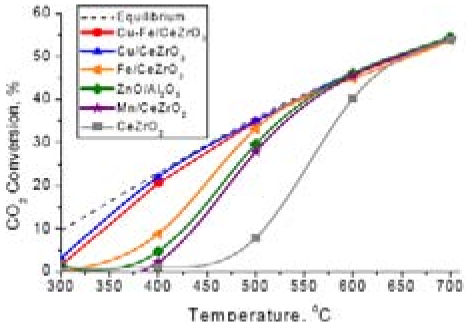

Fig.1 The temperature dependence of CO$_2$ conversion.

Fig. 1 presents the results of catalytic performance studies. Cu- and Cu-Fe-based catalysts showed the best RWGS activity. Equilibrium CO$_2$ conversion on Cu-Fe/CeZrO$_2$ and Cu/Ce-ZrO$_2$ was achieved at 400°C. Fe/CeZrO$_2$, Mn/CeZrO$_2$, ZnO/Al$_2$O$_3$ showed a lower activity. Pt/CeZrO$_2$ catalyst had activity in the methanation reaction.

In the long-term experiments, Cu/CeZrO$_2$ rapidly deactivated, whereas Cu-Fe/CeZrO$_2$ demonstrated stably and high activity, which remained unchanged even after sample exposure to the air at an ambient conditions. Moreover, neither methane, nor other hydrocarbons were detected among the products of the reaction on the Cu-Fe/CeZrO$_2$ catalyst.

The studies by XRD and HR TEM methods revealed that during pretreatment in the reaction mixture, the catalyst undergoes a structural change that leads to the formation of iron carbides Fe$_3$C and Fe$_5$C$_2$ which may be considered as a part of the active component composition.

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OP_{10}-II-11

THE ROLE OF OXYGENATES ON THE SURFACE OF CARBON - BASED CATALYSTS IN THE WET AIR OXIDATION OF ORGANIC CONTAMINANTS

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This work was focused on the investigation of the possible correlations between the amount and the chemical nature of the oxygenated species present at the surface of carbon – based catalysts and the catalytic activity of such catalysts in the wet air oxidation (CWAO) of phenol.

Two series of catalysts based on a mesoporous graphite-like Sibunit-4 carbon were studied. The first series consisted in pure carbons and was prepared by oxidation of the Sibunit-4 carbon with oxygen (without/with water vapor), nitric acid (at 90/100^{o}C), hydrogen peroxide (for 30 min/2 days), sodium hypochlorite (for 20 min/3.5 h). The catalysts were characterized by BET, XPS and pH_{PZC}. The amount and the chemical nature of the oxygenated species on the carbon surface were determined via Boehm titration. The second series (carbon-supported ruthenium catalysts) was obtained by incipient wetness impregnation of the first series with a solution of $Ru(NO)(NO_3)_3$ and reduction under flowing hydrogen at 300°C. The good dispersion of the metal particles for all Ru/Subunit catalysts was confirmed by XRD. All samples were evaluated in the CWAO of phenol at 140 and 160ºC under 50 bar total pressure, using air as the oxidant.

The total amount of oxygenated species and the amount of carboxylic groups turned out to evolve in parallel and increased as follows: oxygen (without water) < H_2O_2 (30 min) < H_2O_2 (2 h) < oxygen (with water) < HNO_3 (90^{o}C) < sodium hypochlorite (20 min) < HNO_3 (100^{o}C) < sodium hypochlorite (3.5 h). Similar results were observed in the CWAO of phenol for both series. The catalytic activity in the phenol oxidation appeared to be inversely proportional to the amount of carboxylic group at the catalyst surface: the highest oxidized samples demonstrated the lowest activity. To explain this trend, we proposed that some scavenging of the active species by the carboxylic surface groups occurred.

Acknowledgements. This research was supported by the Russian Foundation of Basic Research (grant 09 - 03-93114) and program "Laboratoire Franco-Russe de Catalyse" (LFRC). Elena Polyanskaya gratefully acknowledges the French Embassy in Moscow for financial support.

OVERALL WATER SPLITTING OVER Pt/TiO_2 CATALYST WITH Ce^{3+}/Ce^{4+} SHUTTLE CHARGE TRANSFER SYSTEM

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Hydrogen as a high-energy fuel has attracted attention all over the world already for several decades. Indeed, production of hydrogen via the cleavage of water into H_2 and O_2 by sunlight is one of the most promising and desirable ways for the photochemical conversion and storage of solar energy [1]. For pure hydrogen production, we suggest to use inorganic donors of electrons, for example Ce^{3+} ions. The cyclic interfacial electron transfer can be carried out if Ce^{3+} ions are oxidized into Ce^{4+}: Ce^{4+} can be reduced back to Ce^{3+} via its photocatalytic reduction with the simultaneous oxidation of water to dioxygen.

We used aqueous solution of $Ce_2(SO_4)_3$ for hydrogen, and $Ce(SO_4)_2$ for photocatalytic oxygen production. Oxygen and hydrogen were obtained in different experiments. Water suspension with catalyst and $Ce_2(SO_4)_3$ or $Ce(SO_4)_2$ was placed in a sealed thermostatic oxygen-free reactor and illuminated by a 1000-W high-pressure mercury lamp under continuous stirring. The concentration of H_2 and O_2 was measured by means of a gas chromatograph. The concentrations of Ce^{3+} and Ce^{4+} were determined by a Lambda 35 UV/Vis-spectrometer. Platinized commercial Degussa P25 with 1 % wt. of Pt was used as a photocatalyst.

Oxygen is shown to evolve from the Ce^{4+} solution at the action of UV-irradiation and in the presence of semiconductor catalyst; hydrogen is shown to evolve from Ce^{3+} solution under UV-irradiation without any catalyst, but the rate of photocatalytic hydrogen production was higher than the rate of non-catalytic production of hydrogen. The full conversion of $Ce(SO_4)_2$ into $Ce_2(SO_4)_3$ with the simultaneous quantitative oxygen evolution was attained (Fig. 1).

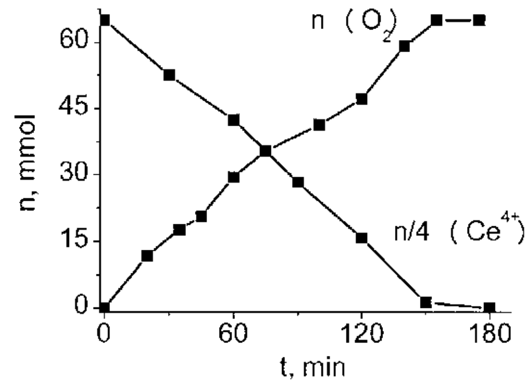

Figure 1: Dependence of the quantity of oxygen evolved on the time of the UV irradiation. Photocatalyst – 1% Pt/TiO_2 Degussa P25 [2].

The rate of the photocatalytic hydrogen production was lower than the rate of photocatalytic oxygen production on the same photocatalyst and in the same irradiation conditions. The influence of the initial substrate concentration, acidity and catalyst loading on photocatalytic oxygen and hydrogen production was studied. The dependences of both hydrogen and oxygen production on the initial concentration of the cerium cations have a maximum. The kinetic equation for the rate of the photocatalytic oxygen production was proposed; the constants in this equation were calculated. The mechanism of the photocatalytic hydrogen production is more complicated. The optimal catalyst loading for the photocatalytic oxygen and hydrogen production is not the same due to the difference in the adsorption of Ce^{3+} and Ce^{4+} on the photocatalyst surface. Both hydrogen and oxygen evolve with the high rate in acidic media. Optimal conditions for photocatalytic reactions were found and explained.

The experiments on photocatalytic water splitting with the separate evolution of O_2 and H_2 in the same reactor were conducted. Separate catalysts should be used for the hydrogen and oxygen production in the shuttle redox Ce^{3+}/Ce^{4+} system.

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HYDROXYL RADICAL FORMATION UPON THE PHOTOLYSIS OF IRON-RICH CLAY IN AQUEOUS SOLUTIONS

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Clay minerals have been developed as heterogeneous catalysts for the remediation of wastewater [1, 2]. Clay-induced photochemistry can play an important role in self-purification of natural aqueous systems. Feng et al. [1] reported heterogeneous catalysts containing a bentonite-clay-based Fe nanocomposite which was employed for the photo-Fenton discoloration and mineralization of an azo-dye Orange II. Ramerez et al. [2] demonstrated Fenton-like oxidation of Orange II solutions using heterogeneous catalyst based on saponite clay. Both Fenton-like and direct photooxidation of organic impurities assisted by iron-rich clays are of great interest.

The goal of this work was to study the primary photochemical processes for the iron-rich clay montmorillonite KSF. Chemical composition of KSF is shown in Table 1. When KSF is dissolved in water, the suspension with pH 3 is formed, and iron is partially leached to the solution bulk. Both Fe(III) and Fe(II) cations were found in the solution. The main dissolved forms of Fe(III) in the solution were $Fe(SO_4)^+$, $Fe(SO_4)_2^-$ and $Fe(OH)^{2+}$ complexes. Fe(II) formed Fe_{aq}^{2+} and $FeSO_4^-$ complexes. UV spectra of the solutions were found to coincide with that of $Fe(OH)^{2+}$ and $Fe(SO_4)^+$, which are almost identical in the near UV spectral region.

SiO_2	Al_2O_3	SO_3	Fe_2O_3	MgO	CaO
49.1	16.3	22.3	4.76	4.3	2.3

Table 1. Major chemical composition (%) of KSF.

Earlier, KSF was used as a catalyst for numbers of organic synthesis reactions, an absorbent and an ion-exchange material in the removal of heavy metals from solutions [3]. KSF assisted photooxidation of Orange II was demonstrated in [4]. The mechanism of clay-assisted photolytic oxidation of organics was proposed to include the formation of $^{\bullet}OH$ radical [5], but no direct evidence of this suggestion was provided.

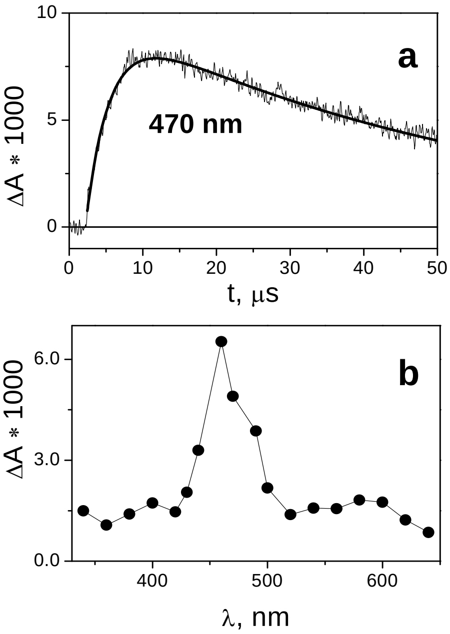

Fig. 1. Laser flash photolysis (355 nm) of KSF in H_2O (10 g/Liter, pH 3, cuvettee 1 cm, Ar saturated sample) in the presence of 1×10^{-3} M MV^{2+}.

a – an example of a kinetic curve;

b – intermediate absorption spectrum 7.2 μs after laser pulse.

In the current work the formation of hydroxyl radical upon the photolysis of KSF was observed in the laser flash photolysis experiments. Laser flash photolysis setup with the excitation by a YAG laser (355 nm, 5-6 ns, 40 mJ/pulse) was used. Methyl viologen dication (MV2+), which was known as an acceptor of hydroxyl radicals, was used in order to capture the radicals. The typical kinetic curve and intermediate absorption spectra are shown in Figure 1. The spectrum belongs to MV•(OH)2+ radical cation. The rate constant of $MV^{\bullet}(OH)^{2+}$ formation ($(3.1\pm0.3)\times10^{8}$ $M^{-1}s^{-1}$) coinsides with the literature data for the reaction between $^{\bullet}OH$ radical and MV^{2+}. It means that the formation of radical cation seems to occur in the solution bulk. This assumption was verified in the experiments with the centrifuged samples. The removal of the particulate matter did not affect the value of $MV(^{\bullet}OH)^{2+}$ intermediate absorption. This fact gives evidence that the dissolved Fe(III) (forming $Fe(OH)_{aq}{}^{2+}$ complexes) is responsible for the formation of $^{\bullet}OH$ radicals upon the photolysis of aqueous clay samples.

Finally, the current work gives evidence of $^{\bullet}OH$ radical formation upon KSF photolysis by means of a direct time-resolved method. The most probable mechanism of a hydroxyl radical formation is the photolysis of $Fe(OH)_{aq}{}^{2+}$ complex in the solution bulk.

The work was supported by FRBR (Grants №№ 08-03-00313, 09-03-00330, 08-03-92205-GFEN) and Program of Integration projects of SB RAS 2009-2011 (grant № 70.

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PHOTOCATALYTIC OXIDATION OF GASEOUS NITROGEN CONTAINING SPECIES

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The air purification contaminated with low concentrations of N-containing organic admixtures is an actual problem because such species are widely used in industry, spacecrafts and for military purposes. For example 1,1-dimethylhydrazine (UDMH) is the popular rocket propellant whereas diethyl cyanophosphate (DECP) is the simulant of dangerous chemical warfare agent tabun. Some inorganic species as nitric acid and NO_x are also not healthy. Therefore the kinetics of TiO_2 mediated photocatalytic oxidation, final products and intermediates distribution and mass balance of these species were the subject of investigation.

Gas-phase photocatalytic oxidation (PCO) of UDMH vapor in batch reactor using TiO_2 as the photocatalyst was studied with FTIR in situ method. FTIR technique is the only method which allows one to detect intermediate species in the gas phase and on the catalyst surface in the course of the experiment (in situ). Different TiO_2 based photocatalysts were synthesized in the present work by the TiO_2 impregnation with transition metal oxides (NiO, V_2O_5, MoO_3, Fe_2O_3) and TiO_2 doping with noble metals like Ag, Au, Pt, Pd by the chemical and photochemical deposition methods.

Carbon dioxide, water, nitric acid and nitrogen were detected as the main products of UDMH PCO. Adsorbed N_2O species was detected as the main surface intermediate. The basic nitrogen-containing product of reaction is molecular nitrogen that is a prominent aspect from the point of view of ecology.

The investigation of dark adsorption of DECP on the TiO_2 surface revealed that almost complete hydrolysis of P-CN fragment proceeds quickly giving the diethyl phosphate and HCN.

$$(C_2H_5O)_2P(O)CN + H_2O \rightarrow (C_2H_5O)_2P(O)OH + HCN$$

The obtaining phosphorous acid ester is practically non-volatile and is quantitatively adsorbed on the TiO_2 surface, whereas cyanhydric acid (HCN) is desorbing into the gas phase giving the 3310 cm^{-1} absorption band.

Only 85% of DECP carbon was converted into the CO_2 form after the 300 min PCO in a static reactor. The rest carbon remained in the form of gaseous HCN which was supported by mass balance calculation and IR spectrum of gas phase after the PCO was finished.

The next experiments were aimed into the enhancing of HCN adsorption on the TiO_2 surface to increase its PCO rate. For this purpose, some methods of TiO_2 modification were used: 1) Ag^+ (1%) ions precipitation by $AgNO_3$ deposition; 2) The transition metals (Au, Ag 1 wt.%) were deposited on the TiO_2 by chemical and photochemical reduction methods.

An interesting behavior of FTIR surface spectra of the Ag/TiO_2 photocatalyst synthesized by the photoassisted $AgNO_3$ reduction was observed. The 2162 cm^{-1} absorption band immediately appeared after the DECP adsorption equilibrium was established. This band was constantly shifting to the higher wavenumber values after the PCO reaction was started transforming into the 2202 cm^{-1} absorption band. Finally the 2202 cm^{-1} absorption band was almost disappeared as the PCO reaction completed.

The best results were demonstrated by 1% Ag/ TiO_2 and 1% Au/ TiO_2 obtained by photochemical deposition method. DECP to CO_2 conversion was measured to be 98% for the first 300 min of PCO.

The ammonia PCO was investigated for a set of photocatalysts modified with noble metals and transition metals oxides. Nitrous oxide N_2O was registered as the gaseous PCO product. The formation of dinitrogen N_2 another gaseous PCO product was estimated from the mass balance. Adsorbed nitrites NO_2^- and nitrates NO_3^- were registered as surface intermediate and final product of NH_3 PCO. The best activity was demonstrated by unmodified high surface area anatase form TiO_2.

Photocatalytic oxidation of UDMH, DECP proceeds till complete mineralization in a static reactor with carbon dioxide, surface nitrates, phosphate, ammonium and molecular nitrogen as the major final products.

HCN was demonstrated to be the only toxic gaseous intermediate of DECP PCO forming as the DECP hydrolysis product. Diethylphosphate, acetic and formic acids were registered as the surface intermediates. The formation of surface cyanide complexes with Ag and Au ions could be responsible for the fast removal of HCN from the gas phase and its further photooxidation.

The pure unmodified TiO_2 (anatase, $S_{BET} \approx 350$ m^2\g) turned out to be the best photocatalyst for oxidation of NH_3 giving only 7% of initial NH_3 quantity converted into N_2O. Long-term experiments were carried out to determine the photocatalysts stability in PCO of NH_3. All the catalysts exhibited stable performance; the rate of deactivation was low due to transformation of NH_3 nitrogen mainly into N_2.

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POSTER PRESENTATIONS

PP-1 ÷PP-10

EFFECT OF THERMO-PHYSICAL PROPERTIES AND TEXTURE OF HEAT SHIELD ON THE TEMPERATURE IN A SHORT CONTACT TIME REACTOR

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Most of the current energy supply system, in which fossil fuel is used, causes many environmental problems: air pollution, acid gas emissions, and the emission of greenhouse gases. Due to these, and potentially more demanding future restrictions, there is a need to improve existing power generation processes. An attractive alternative for small scale processing of hydrocarbon fuels is production of hydrogen-rich gas and catalytic combustion in the compact catalytic reactors near the point of usage. The oxidation processes carried out on structured catalysts (e.g. gauzes and monoliths) at the short contact time (≤0.1 s) are autothermal and nearly adiabatic because the exothermic reactions heat the gases and the catalyst from a low inlet temperature to typical operating temperatures of about 1000 - 1500 K. Placing some heat shield in front of the catalyst would reduce the rate of radiation heat transfer from the hot catalyst upstream towards the inlet the reactor. In this work we studied effect of thermo-physical properties and texture of heat shield on the time-dependent distribution of the temperature in the inlet zone of the reactor, over the hot front face of the catalyst, by means of mathematical simulation.

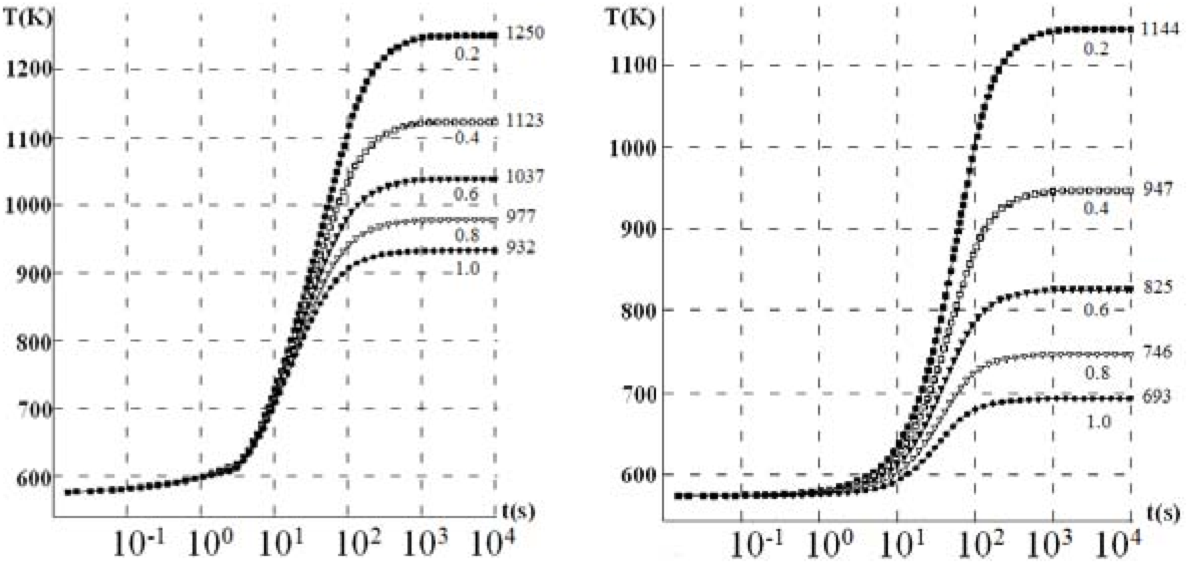

Fig. 1. Dynamic of maximal (left) and mean temperature (right) for the heat shield made of metal foam with $\varepsilon = 0.5$ for the different superficial velocities.

PP-1

In the physical model air-fuel mixture with the temperature of 473 K and uniform distribution is fed into a metallic tube of 50 mm ID and 7 mm thick. After 100 mm of path the gas mixture enters porous matrix media (heat shield) of 10 mm thick followed by the catalytic monolith with the front face temperature of 1473 K. The mathematical description can be condensed to a two-dimensional quasi-homogeneous reactor model with accounting for both the conductive-radiative heat transfer and heat exchange in the metallic tube, gas phase and porous matrix of heat shield. The he following parameters were varied: superficial velocity of the gas media, porosity ε, heat conductivity and heat capacity of the heat shield matrix.

Figure 1 shows dynamics of the maximal (left) and mean temperature (right) for the metal heat shield depending on the inlet velocity of the gas flow. The temperature field within the heat shield at steady state is demonstrated in Fig.2.

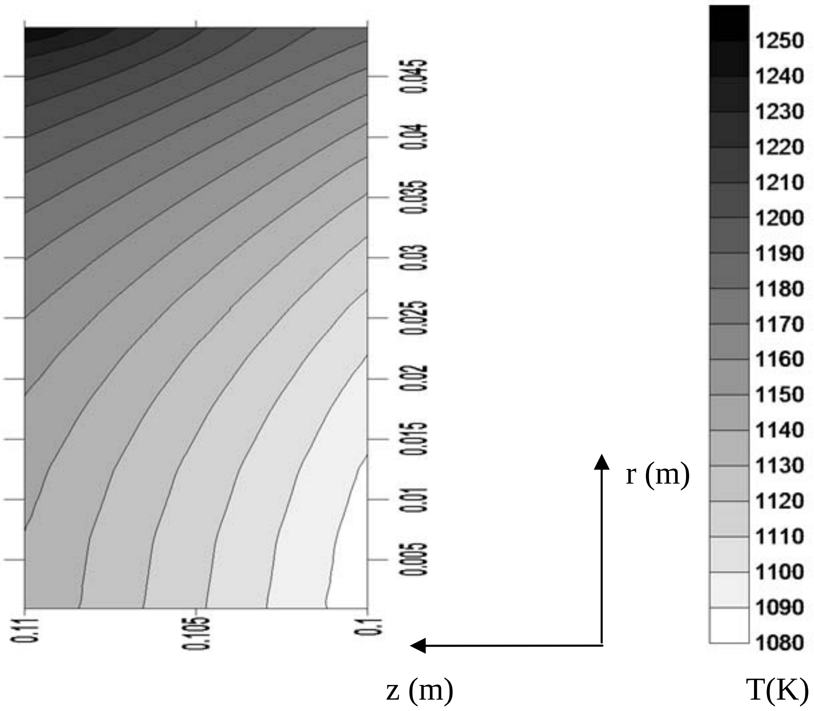

Fig. 2. Two – dimensional distribution of the temperature in the metal heat shield at steady state.

It was found that time scale for steady state distribution of the temperature is about 1000 s. The phenomenon should be taken into account at the process performance in respect of its safety. The temperature in the heat shield may be high enough to initiate the undesired reactions in front of the catalyst also. From the parameters varied superficial velocity of the feed is the main parameter affecting the temperature within the inlet zone of the short contact time reactor. Low conductivity heat shield facilitates larger temperature range in front of the hot catalyst.

THE DIRECT METHANE OXIDATIVE CARBONYLATION INTO OXYGENATES CATALYZED BY RHODIUM CHALCOGEN HALIDES

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The modern process for the commercial conversion of natural gas to valuable organic compounds involves stages of steam methane reforming to H_2–CO mixture, high-temperature conversion of H_2–CO mixture to methanol and subsequent synthesis of organic compounds. Depending on reaction conditions (temperature, pressure, gas mixture), the chemical nature, crystal and porous structure of catalysts, C_1 oxygen-containing compounds (OCC), C_2 hydrocarbons, aromatic compounds can be synthesized from methane. The direct synthesis of alcohols, aldehydes, acids, ethers, etc from methane, carbon monoxide and oxygen may be an alternative root to the energy-consuming multistage natural gas conversion process.

Very few reports have been published on simple heterogeneous catalytic systems for the direct oxidative carbonylation of methane to organic oxygenates. Earlier we had studied the gas phase carbonylation of methane in the presence of molecular oxygen over pure carbon carriers and carbon supported rhodium chalcogen halides as only carbon supports are stable among other carriers (SiO_2, Al_2O_3, ZrO_2, MgO, SiO_2) in non-aqueous chalcogen chloride media [1].

In the present we have studied the gas phase methane oxidative carbonylation in the presence of molecular oxygen over silica materials, including their mechanical mixtures with rhodium chalcogen chlorides obtained in non-aqueous inorganic media. The formation of Rh_4SCl_7, $Rh_4S_9Cl_2$, $Rh_4Se_5Cl_3$ and Rh_3Se_3Cl solids was confirmed by elemental analysis, IR absorption spectroscopy, XPS and X-ray diffraction. Silica, vanadium-, and molybdenum-containing mesoporous molecular sieves have been used as supports. We have found that productivity of oxygenates (methanol, methyl acetate and acetic acid) depends mainly on the method of the catalyst preparation and the type of the support.

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PP-3

CATALYTIC OXIDATION OF ORGANIC COMPOUNDS WITH HYDROGEN PEROXIDE IN TWO-PHASE SYSTEMS

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We synthesized and characterized [1] the catalysts based on the tetra(oxodiperoxo-tungsto)phosphate ($\{PO_4[WO(O_2)_2]_4\}^{3-}$ with quaternary ammonium cations. Such catalytic systems provide efficient synthesis of a number of important aliphatic and aromatic epoxides as well as mono- and dicarboxylic acids by direct oxidation of different organic substrates with hydrogen peroxide in two-phase systems. Since W-peroxocomplexes have a significant place in the organic substrate oxidations, the present study was aimed at *in situ* synthesis of oxoperoxo-W containing organic ligands – tertiary phosphine oxides and testing of their catalytic activity in oxidation reactions of cyclooctene, benzyl alcohol. Tertiary phosphine oxide ligands (tris[2-(2-pyridinyl)etnyl]phosphine oxide, 1-diphenyl-1-[2-(1-ethyl-imidazol)-1-hydroxymethyl]phosphine oxide, 1-diphenyl-1-[2-(1-vinylimidazol)-1-hydroxy-methyl]-phosphine oxide). Oxidation of benzyl alcohol was performed in a two-phase systems (organic phase - aqueous phase) at 80°C upon varied [W] / [L], [Sub] / [Cat] and [Ox] / [Sub] ratios. Epoxidation of cyclooctene was performed at 60°C in a two-phase system.

Thus, the experiments showed that the bifunctional homogeneous metal complex catalysts based on the peroxopolyoxotungstatophosphates combined with organic ligands such as tertiary phosphine oxides can be recommended for the selective oxidation of organic substrates with hydrogen peroxide in two-phase systems.

The oxidation reactions of benzyl alcohol and cyclooctene were used to illustrate the prospects of tungstatophosphoric acid and tris[2-(2-pyridinyl)etnyl]phosphine oxide or 1-diphenyl-1-[2-(1-ethylimidazol)-1-hydroxymethyl]phosphine oxide as precursors of peroxopolyoxotungstate catalysts. It was established that the presence of groups with an unsaturated C=C bond in the phosphine oxide molecule adversely affect both the conversion degree and selectivity of the oxidation reactions.

This study was financially supported by the Department of New Material Chemistry of the Russian Academy of Sciences (Project No 5.7.3)

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PP-4

DEVELOPMENT OF A TiO_2/AC COMPOSITE PHOTOCATALYST FOR AIR AND WATER PURIFICATION

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Introduction

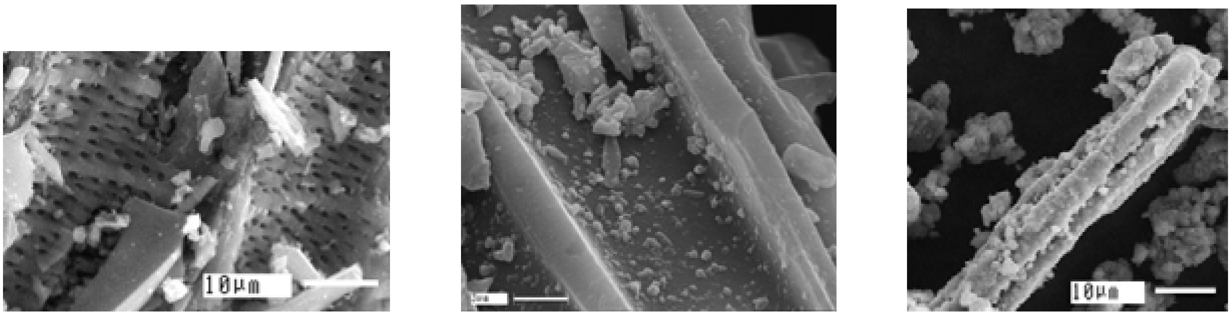
The application of heterogeneous photocatalysis in environmental purification has been widely studied in recent decades. TiO_2 is known as the most effective and intensively investigated photocatalyst for purification of air and water from organic pollutants. However, several shortcomings exist like the deactivation of photocatalyst, poor adsorption of some types of organic compounds. As a result of such restrictions it usually requires a long time period for complete purification and prevents the large-scale applications of photocatalysis.

At the same time the adsorption properties of TiO_2 based photocatalysts could be significantly improved due to its modification. TiO_2 deposition on activated carbon (AC) is one of the promising methods [1,2]. AC in the TiO_2/AC photocatalysts can act as a center where organic molecules can adsorb before transferring to TiO_2 due to the concentration gradient [1].

Results

A TiO_2 supported on activated carbon (TiO_2/AC) composite photocatalysts was synthesized by thermal hydrolysis of $TiOSO_4$ in the presence of AC. Several TiO_2/AC samples with different TiO_2 content and one pure TiO_2 sample for reference purpose were chosen. Data of TiO_2 content in prepared samples indicate that a small amount of TiO_2 escape from the AC surface during synthesis because calculated TiO_2 contents in samples (20, 30, 50, 70 and 80 wt. %) are very close to measured values.

SEM technique revealed that the TiO_2 deposition leads to formation of 3-5 μm in size crystallites on the AC surface (Fig. 1, B) which became completely covered with TiO_2 particles at the TiO_2 content about 80 wt.% (Fig. 1, C).



A B C

Figure 1. SEM images of AC (A); 20 wt.% TiO_2/AC (B); 80 wt.% TiO_2/AC (C)

Gas-phase photocatalytic oxidation (PCO) of some organic pollutants: acetone (Ac), cyclohexane (Cyc), diethyl sulfide (DES) in a static reactor using TiO_2/AC samples as the photocatalyst was studied. FTIR *in situ* method was used for the analysis of gas-phase products. The IR spectra of the gas phase were periodically taken for PCO results monitoring. Carbon dioxide and water were detected as the main products of Ac and Cyc PCO in gas phase. In Ac PCO best of all TiO_2/AC samples were 80%-TiO_2/AC and 70%-TiO_2/AC. The 70%-TiO_2/AC sample demonstrated better results in cyclohexane vapors removal than pure TiO_2. In DES PCO the best photocatalytic active and less deactivated is 70%-TiO_2/AC sample.

Finally the PCO of phenol in aqueous phase with a continuous flow reactor using TiO_2/AC and commercial P25 as the photocatalysts was investigated. TiO_2/AC photocatalyst was synthesized by thermal hydrolysis of $TiOSO_4$ and AC – “sibunit”. Total organic carbon (TOC) analyzer was used for analysis of evolutions of organic carbon concentration during the PCO experiment. It was demonstrated that there occurs the adsorption and further photocatalytic phenol oxidation. Process of phenol PCO is more effective using the TiO_2/AC sample in comparison with the commercial sample P25 as TiO_2/AC sample possesses the best adsorption properties.

Conclusions

TiO_2/AC samples were synthesized with various TiO_2 content by thermal hydrolysis of $TiOSO_4$ solution in the presence of AC particles. Samples are stable under the UV irradiation and photocatalytically active. The synthesized samples were tested in the experimental air and water cleaning processes and demonstrated fast removal of pollutants with its subsequent complete mineralization.

Acetone, cyclohexane and diethyl sulfide vapors PCO demonstrated that such samples have high initial capacity and even their photocatalytic activity could be higher than for pure unmodified TiO_2 of the same origin.

Process of phenol PCO in aqueous solution is more effective using the TiO_2/AC sample in comparison with the commercial sample P25.

Acknowledgements

This work was financially supported by the NATO (“Science for Piece”, grant 981461) and ISTC (grant 3305).

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GOLD IN ENVIRONMENTAL CATALYSIS: SELECTIVE VAPOUR-PHASE α-PINENE ISOMERIZATION TO CAMPHENE OVER Au CATALYSTS

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Fundamental understanding of environmentally friendly and selective nanosized gold materials active as catalysts in the sustainable production of the fine chemicals from biomass products is recently under growing interest. It was believed for a long time that Au was devoid any catalytic activity. Bulk gold is in general regarded as poorly active as a heterogeneous catalyst, but when gold is deposited on a proper metal oxides as ultra-fine particles its chemistry changes [1].

Terpenes are inexpensive renewable starting materials that are widely used in the synthesis of the fine chemicals [2]. For example, camphene is valuable product for the pharmaceutical and perfumery industry. The main source for camphene production is the α-pinene isomerization, which is the main component in turpentine [3]. The traditional way to transform the α-pinene to camphene is the reactions over TiO_2 that gives rather low camphene yields from 35% to 50%. The present work relates to the gold catalysts application for the isomerization of α-pinene to camphene.

The objective of this work is to study vapour-phase α-pinene to camphene isomerization at the presence of supported over different supports gold catalysts.

Gold catalysts over different metal oxides and carbon support were prepared by DP method. The activity of the supports as well as selectivity and stability of the catalysts were tested in the glass up-flow reactor at atmospheric nitrogen pressure in temperature region 180-210^{o}C. It has been established that basic supports CeO_2 and also Al_2O_3, modified by basic type oxides (for example rare-earth oxides CeO_2, La_2O_3), are inert in the reaction, however gold catalysts on these supports quickly deactivate during reaction. Different Al_2O_3 supports and carbon material Sibunit have shown a catalytic activity in the reaction. However, after neutralization by alkaline treatment Al_2O_3 support lost activity and the catalysts on their base Au/γ-Al_2O_3 exhibited a high and stable activity (conversion of α-pinene (98-99 %) and camphene selectivity (80-90%)). At the same time the ratio camphene/cymene increased up to 8,5 compared to 2,0 for the pure support and did not depend on preparation method. Thus, active Au/Al_2O_3 catalytic system for the α-pinene isomerization to camphene with conversion 99% and selectivity about 60-90% was found.

The effect of temperature, residence time and initial α-pinene concentration on the α-pinene conversion and the camphene selectivity over the most stable catalyst 2.2% Au/γ-Al_2O_3 was studied. Experimental data showed that the main products are formed by parallel ways. The selectivity to products did not depend on the reaction temperature in the range 463-483 K, therefore activation energies of products formation were approximately the same. Reaction rate was close to first-order on α-pinene. The values of rate constants at different temperatures were found. The calculated value of the activation energy of reaction (51 kJ/mol) is comparable with the literature data for TiO_2 catalyst [4]. It was found that an increase in α-pinene concentration in the initial mixture causes stronger catalyst deactivation.

The spent catalyst was studied by FT-IR spectroscopy, TEM and DTA-TG. It was found that predominant coke formation and an insignificant amount of oligomers on the catalyst surface may cause the catalyst deactivation, which is reversible. The catalyst activity can be regenerated completely by the oxygen treatment.

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CATALYTIC WET PEROXIDE OXIDATION OF ORGANIC CONTAMINANTS OVER Cu/ZSM-5 CATALYSTS

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Catalytic wet peroxide oxidation (CWPO) is one of ecologically attractive catalytic processes aimed at deep oxidation of toxic poorly biodegradable organic. The homogeneous catalytic systems composed of transition metal ions (Fe, Cu) in spite their efficiency in oxidation of various organic have well-known drawbacks such as the need for removing the precipitated catalyst from the treated water and the production of metal-containing waste sludge. These drawbacks can be overcome by using heterogeneous catalysts, among them metal-exchanged zeolites, which are recoverable and reusable. The CWPO of different organic substrates over the Fe/ZSM-5 zeolites is studied enough. The information concerning catalytic properties of Cu/ZSM-5 zeolites is practically unavailable.

Here, we report on our study on the influence of the chemical composition and structure of the Cu/ZSM-5 catalysts on the performance of such catalysts as well as their stability to leaching of Cu in the wet peroxide oxidation of different organic pollutants.

The catalyst samples were prepared by ion exchange (IE) from the protonic form of ZSM-5. We varied the Al/Si ration (17, 30, 45) and content of active metal (0.3 – 3 wt.% of Cu) in catalyst composition. The prepared catalysts were characterized by ICP, EPR, XRD, DR UV-Vis and tested in CWPO of formic acid at pH ca. 3 and organic dyes (*Rhodamine G*) at pH ca. 4-5 using a batch reactor.

The results of catalysts characterization showed that depending on chemical composition we can prepare samples containing mainly Cu-isolated ions and copper-oxide nanoclusters in zeolite channels and samples containing mainly CuO nanoparticles on the zeolite surface.

Most active in the CWPO of formic acid as well as *Rhodamine G* appeared to be catalysts Cu/ZSM-5 with Al/Si ratio equal 30 which contain Cu-ions mainly in zeolite channels. Stability of such catalyst was demonstrated in 5 cycles of CWPO of formic acid.

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PP-7

ENVIRONMENTAL APPLICATIONS OF ACTIVE CARBON “SIBUNIT”

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“Sibunit” material differs from other active carbons by its structure. Its skeleton is comprised by the fairly regularly ordered graphite layers. As a result, Sibunit contains few micropores (less than 10% of total pore volume) and many mesopores (up to 40% of total pore volume). The hidden advantage of Sibunit is its strong stability in oxidizing media, as shown by the C-oxidation investigation in strong NaOH-aqua-O_2 solutions at elevated temperatures and by the TGA data.

Abnormally rapid organics sorption on Sibunit allows intensification of various adsorption - desorption processes, and minimizes the time of sorbent recover. Thus, Sibunit was tested in the processes of aromatics extraction from industrial waste waters. Material appears to work as a pump for the organics-water separation. Dissolved aniline removal degree goes up to 99%. Sibunit pilot tests as applied for organics removal from the waste waters of hydrometallurgy nickel and tungsten demonstrate that processes go under mild conditions without organic compounds destruction.

Sibunit as a support for Pd-C catalyst may also be used for NO_2^- and NO_3^- ions removal from the drinking and waste waters by their reduction to N_2 by H_2. These processes were first investigated by Varlop and Tacke [1]:

$$2\,NO_2^- + 3\,H_2 \rightarrow N_2 + 2\,OH^- + 2\,H_2O\ ,$$

$$2\,NO_3^- + 5\,H_2 \rightarrow N_2 + 2\,OH^- + 4\,H_2O$$

Detailed reaction mechanism is not yet known, and support role seems to be mostly important. On one hand support surface should be large and resistant to oxidative, acidic (for alkali evolve neutralization) and also alkali medias. On the other hand, its pores should be large enough for the reagents transport and for the acidity gradients prevention.

Sibunit combined with polynuclear hydroxocomplexes of Pd(II) [2] and Cu(II) provide a stable catalyst for nitrite and nitrate ions reduction. Reaction rates obtained with Sibunit supported catalyst are shown to be higher than over the SiO_2, Al_2O_3 and plastics catalysts.

All above mentioned systems allow water purification to European drinking water standards.

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ADSORPTION AND PHOTOCATALYTIC OXIDATION OF ORGANIC COMPOUNDS OVER AEROSOL PARTICLES

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Solid aerosol particles are important constituents of the Earth and other planets atmosphere as well as interstellar space. Chemical and photochemical reactions taking place over aerosol particles can have a significant contribution to the atmospheric chemistry of minor atmospheric components like halogenated hydrocarbons and other greenhouse gases [1].

Another reason for an increased interest to adsorptive and photocatalytic processes over aerosols is small diffusion distances and times for molecules to reach aerosol particles surface. For aerosol particles concentration 10^6 cm^{-3} in air characteristic diffusion time is as short as 1 ms if a molecule has a diffusion coefficient 0.025 cm^2s^{-1}. Such short times make high concentration aerosols a powerful mean of ultrafast air purification.

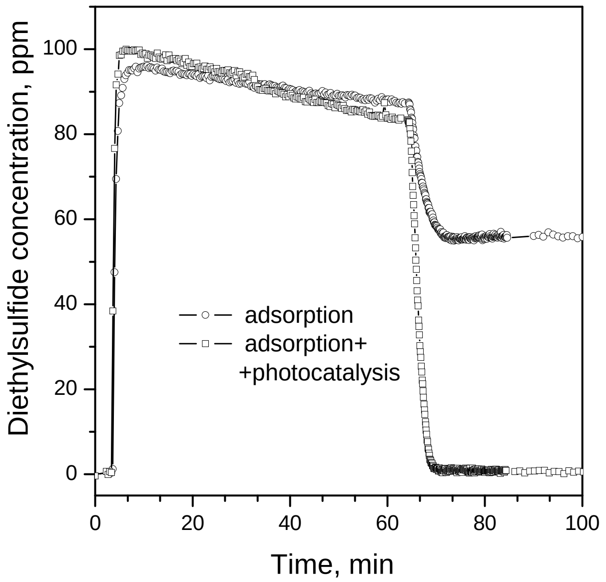

Figure 1. Removal of diethyl sulfide vapor from air by adsorption and photocatalytic oxidation over TiO_2 aerosol.

The present study centers at measurements of rates of adsorption and photocatalytic oxidation over TiO_2 and Fe_2O_3 aerosol particles for model organic compounds such as acetone, dimethyl methylphosphonate (DMMP), diisopropyl phosphonofluoridate (DIPF), diethyl sulfide (DES) and 2-chloroethyl ethylsulfide (CEEES). The results demonstrate very high quantum efficiencies for oxidation over aerosol particles.

Aerosols were generated inside a 0.1 m^3 Plexiglas chamber using a sonic method. Approximately 5 g of TiO_2 (Hombikat UV 100) or Fe_2O_3 (Nanocat Mach I) was loaded into an aerosol generator before the experiments. Organic compounds were injected into the chamber as liquids and evaporated there. Concentration of the initial compound and reaction products was measured using an FT-IR spectrophotometer Vector 22 (Bruker) equipped with a long path gas cell. Aerosol production and release into the chamber was started after the concentration of a gas phase organic compound had stabilized. Maximum concentration of TiO_2 aerosol was reached after the spraying ended at 10 min and was equal to ~ 10^6 cm^{-1}. Nearly all the loaded powder was aerosolized during this period. Adsorption experiments were performed in the dark while photocatalytic oxidation employed a 22 W torroidal UV lamp located at the center of the chamber. About one half of the emitted UV light is absorbed by the TiO_2 aerosol.

The organic compounds under study underwent quick adsorption over TiO_2 or Fe_2O_3 aerosol after the start of its release into the chamber's air. While gaseous acetone and DES underwent only partial adsorption, complete removal was observed for DMMP and DIPF with characteristic time below 3 min.

Photocatalytic oxidation resulted in complete air purification and deep oxidation into CO_2 with overall quantum efficiencies up to 40%. The highest rate of photocatalytic removal was observed for DES (Fig. 1). While dark adsorption removed only 35%, photocatalytic oxidation removed 95% of gaseous DES in 4 min. DMMP underwent irreversible adsorption over aerosols due to the hydrolysis with a fast (τ~0.5 min) and slow (τ>100 min) formation of gaseous methanol. Photocatalytic oxidation allowed to complete air purification in <100 min.

In conclusion, photocatalytic oxidation over TiO_2 aerosol was shown to proceed with high quantum yields, which confirms possible contribution of this process to atmospheric chemistry. Adsorption and photocatalytic oxidation over aerosolized nanosized catalyst was proved to provide complete air purification within few minutes. The rate of adsorption over aerosol particles is limited by the rate of aerosol production and can be increased further.

Partial support of this research by funds of projects ISTC 3305, NATO SfP 981461, SB RAS Integration #70 and 36 as well as RAS Presidium #27.56 is gratefully appreciated.

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CATALYTIC COMBUSTION OF SEWAGE SLUDGE, INCLUDING WASTE OF MUNICIPAL SERVICES

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The traditional circuit clearing constructions of city includes stages of primary upholding, biological oxidation, secondary upholding. The result of the cleaning is formation of solid waste products such as sludge after primary upholding and superfluous active silt after secondary upholding. Average characteristics of waste products of different cities in Russia and India are differed a little. The average characteristics of silt: humidity (after mechanical free from water) - 60-85%, ash value (on dry substance) - 30-60%, the contents of an organic part (on dry substance) - 50-60%, heating calorific value of an organic part - 20-25 MJ/kg. The mineral part contains alkali metals, alkaline-earth metals, Si, Al, Fe, S, Se, P, Cl and heavy metals (Cu, Cr, Mn, V, Sn, Pb, Cd, Hg) are present also. The organic part also contains N, S, P, Cl. The presence in structure of deposits of heavy metals is caused by activity of the industrial enterprises which drains in many cities and mix up with sewer waters.

Now the basic methods of recycling of waste deposits are thermal processing of ones. Preliminary dehydrated mechanically up to 65-72 % humidity sewage sludge is dried up to humidity of 5 %. Sewage sludge burns in the rotating furnace or the chamber furnace. For maintenance of steady sewage sludge burning the temperature in furnace is supported at a level 1200-1300°C. Hence, there are increased requirements to constructional materials and necessity of the big charge of additional fuel. The presence of fusible mineral substances complicates ash removal. There is a big problem of maintenance of completeness of combustion of combustible components and liquidations of secondary pollution of an atmosphere with CO, nitrogen and sulfur oxides, toxic compounds such as benzapyrenes and dioxines. Application furnaces with the fluidized bed of an inert material (sand, ashes) for burning of wastes allows to lower temperature of burning of waste products up to 800-1000°C and to remove a number of lacks of high-temperature burning. However and in this case it is not excluded formation slag of mineral substances in fluidized bed, and there is high level of concentration of harmful substances in departing gases.

Developed in the Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Science the technology of combustion of solid fuels and waste products in the fluidized bed of catalyst of deep oxidation of organic substances allows to exclude the majority of lacks of traditional ways of combustion. The presence at reactionary system of the catalyst allows: to lower temperature of burning of organic raw material with 1000-1200°C up to 500-700°C, keeping thus high speeds of burning and providing full combustion of waste products without excess of air. The catalyst is the solid heat-carrier and provides high factors heat and mass exchange. In comparison with the known ways of combustion these features enable: considerably to lower the requirements to thermochemical properties of constructional materials of devices and to lower their erosive deterioration; to reduce losses of heat through walls of devices; to facilitate considerably the start of system in work and management of process; to lower explosion hazard of devices; to achieve high (up to 10^8 kcal/m^3 hour) thermal stress of volume combustion spaces and, hence, considerably to lower dimensions, weight and metal consumption of designs; to reduce losses of heat with departing gases and due to chemical incompleteness of combustion of organic waste products; to carry out process of combustion in an auto thermal mode, i.e. without use of additional fuel at humidity of waste of deposits less than 75%; to liquidate or sharply to lower emissions of toxic products in an atmosphere.

Executed in the Boreskov Institute of Catalysis research on finding-out of features of burning of sewage of a pulp and paper industry, petroleum refinery, a municipal services in fluidized bed of the catalyst of deep oxidation of organic substances have shown, that, in comparison with the fluidized bed of an inert material (sand), the presence of the catalyst essentially reduces the temperature of burning of volatile substances and also the coke rests. The degree of burning out of carbon achieves 98-99% at temperature 650-750°C and time of contact less than 1s. In departing gases practically there are no products of incomplete combustion (CO, benzapyrene, dioxine), and also sulfur oxides. The level of emissions of NO_x does not exceed 50 mg /m^3. (At burning waste products in a layer of an inert material, the concentration of NO_x achieves 800 mg/m^3).

Reducing contact time of waste with a layer of the catalyst and temperature, it is possible to limit process only by burning of the volatile substances and carbonization of coke rests. Formed thus solid carbonized products possess advanced porous structure with a specific surface of 200-400 m^2/g and have good adsorption properties at sewage water cleaning from the dissolved toxic compounds, relatives on properties activated coal. At simple additional acid updating these products can be used as effective coagulants. It allows realizing cyclic process of processing of waste with subsequent use of a carbonized solid product for adsorption-coagulation sewage water treatment. Excess of a solid product is removed from a cycle and used as adsorbent. Such technology of sewage treatment completely excludes use expensive and scarce coagulant and flocculating agent.

PHOTOADSORPTION AND PHOTOCATALYSIS PHENOMENA OVER TITANIUM DIOXIDE PARTICLES PRODUCED BY POWDERING OF RUTILE CRYSTAL

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Most solid particles of atmospheric aerosol result from the long-time dispersion of different crystal minerals of the lithosphere under tropospheric conditions. Thus, aerosol particles are microcrystals with a sufficiently ideal crystalline structure as opposite to particles of the powder-like adsorbents (photoadsorbents) and catalysts (photocatalysts) produced in laboratory and industrial conditions. The powder-like samples can be expected to have properties differing from those of the artificially produced compounds. In accordance with the published data, photocatalytic reactions on semiconductor oxides of metals [1], as well as photosorption processes on oxides insulators [2], include a transfer stage to the surface of holes and (or) electrons formed under illumination. Consequently, the probability of the event that free carriers will reach the surface and change the surface atoms reactivity of the lattice or adsorbed atoms and molecules depends on the conditions of the carriers transport in the bands (valence band and conductivity band). At small sizes of microcrystalline particles (high dispersion oxides insulators γ-Al_2O_3 and SiO_2 with a specific surface of 150 and 300 m^2/g, respectively), these bands fail to be formed and the photosorption activity relative to halogen-containing organic compounds is not observed [2].

It is known that powdered samples of metal oxides having more fine crystal structure of nanoparticles exhibit a tendency to larger a photocatalytic activity [3]. For example, titanium dioxide prepared by the plasmotrone method (P25 from Degussa) has nonporous structure and consist of rutile and anatase. Such P25-Degussa is better photocatalyst than rutile or anatase or a mixture of rutile and anatase having high porosity and high specific area. Moreover photoelectric effects and photoelectrochemical efficiencies amount to maximum values for crystalline samples of TiO_2, ZnO, SnO_2 [4]. The powder of crystalline microparticles may be prepared from metal oxide crystals.

The rutile crystal produced by the Czochralski method was cleaved and grinded in a corundum mortar. The specific surface of TiO_2 was equal 1.6 m^2/g. Before studies of oxygen photoadsorption and carbon dioxide photodesorption only the vacuum degassing at room temperature was performed. In gas phase and on the titanium dioxide surface the water molecules were always present during measurements.

The quantum yield quantities and spectral dependencies of oxygen photoadsorption and carbon dioxide photodesorption on titanium dioxide were determined. The quantum yields amounted to following values:

a) surface absorption region (465 nm) -- 0,7 % (O_2), 0,35 % (CO_2);

b) band to band absorption region (340 nm) – 0,75 % (O_2), 0,55 % (CO_2).

Also, the photochemical activity of industrial and laboratory preparation TiO_2 was investigated. The oxygen photoadsorption quantum yields over industrial TiO_2 were equal:

a) surface absorption region (465 nm) -- 0,03 %,

b) band to band absorption region (340 nm) – 0,15 %.

Closely approximating to these values the quantum yields were stated over titanium dioxide produced by a laboratory preparation.

It is concluded that the photochemical activity under tropospheric solar irradiation (λ>300 nm) over titanium dioxide, produced by fine grinding of rutile crystal under ambient air, is essentially higher than the photochemical activity on titanium dioxide prepared in traditional ways.

Also, it is supposed that the sharp increase of the quantum yield in the range of TiO_2 surface absorption relative to oxygen is connected with the increase of deep surface levels formed at a break of the Ti–O bonds when producing powder-like oxide from a monocrystal.

It can be expected that the photochemical properties of other oxides produced from natural minerals (MgO from periclase, SiO_2 from quartz, Al_2O_3 from corundum, etc.) will seriously differ from the properties of compounds produced in laboratory or industrial conditions. The formation of oxide particles from minerals under natural conditions is accompanied by the formation of photochemically active solid tropospheric aerosol.

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ABSTRACTS

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