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Monolith honeycomb supports and catalysts

ABSTRACTS

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Monolith Honeycomb
Supports and Catalysts

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Session A

DESIGN OF MONOLITH HONEYCOMB SUPPORTS AND CATALYSTS FOR CATALYTIC APPLICATION. EMISSION CONTROL TECHNIQUES AND CATALYTIC COMBUSTION OF FUELS

The Monolithic Catalyst: Future Generations

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The first commercial application of a monolith as a catalyst support was for off the road vehicles i.e. mining equipment, etc. in the early 1970's. The Pt/ γ-Al_2O_3 was deposited on the channel walls of a laid up ceramic structure made by American Lava, Division of 3-M Corporation (1, 2). This technology provided the foundation for the use of monoliths for the much larger automobile gasoline catalytic converter market in 1975. The washcoating technology, monolith thermal shock resistance, catalyst poisoning, gas flow models, low pressure drop designs, canning and mounting, etc., all were useful in scaling up the technology. The first commercial automobile catalyst supports were either particulate beads of γ-Al_2O_3 or extruded cordierite monoliths upon which the active catalytic coating of Pt and Pd were deposited. The unburned hydrocarbons and carbon monoxide were converted to carbon dioxide and water as they passed through the exhaust train. In 1979 the need for NO_x reduction led to the development of the three way catalyst or TWC which required new catalyst compositions (notably Pt and Rh), an O_2 sensor in the exhaust and a sophisticated feed back engine control strategy. Higher driving speeds and the need for improved fuel economy in 1986 led to operating conditions which increased thermal stresses requiring further advances in the high temperature chemistry of the catalyst and monolith. Today we are seeing the emergence of catalysts in which less expensive Pd can replace large amounts of Pt and Rh which further improve the quality and durability of the emissions while increasing catalyst life to 100,000 miles with temperature excursions up to 1100 °C. It has been a remarkable journey for catalytic chemistry, monolith development and systems engineering (3). Cordierite monoliths are the substrates of choice with increased cell densities i.e. > 400 cpsi, and thin walls, i.e. 0.05 inches, allowing the catalyst system to function more efficiently with lower pressure drop. There is now an emerging use of metallic monoliths with large thin walls i.e. 0.002 inches and open frontal areas exceeding 90% for those markets where pressure drop must be kept to an absolute minimum (4).

The positive experience of the monolith supported catalyst has led to many new generations of commercial applications expanding its ancestral tree as shown in Table 1 (3).

Table 1: Monolith Catalyst Applications Derived from Automotive Technology

* *1968: catalysts to abate (oxidize) hydrocarbon solvents, oxygenates, petrochemicals*

* *1980: extensive use of selective reduction of* NO_x *for power plants*

* *1981: abatement of upper atmospheric ozone which enters the air intake system in high flying commercial aircraft*

* *1982: wood stove catalysts*

* *1983: non-selective reduction of* NO_x *from rich burn engines*

* *1985: reduction of hydrocarbon and carbon monoxide from gas turbine co-generation plants*

* *1988: catalytic oxidation of halogenated hydrocarbons from chemical plants*

* *1994: catalysts to control diesel particulate and gaseous emissions in trucks and passenger cars (5)*

* *1994: oxidation of non-methane hydrocarbons, carbon monoxide and particulates from lean burn natural gas fueled vehicles (6)*

* *1995: decomposition of* N_2O *from chemical facilities (7)*

* *1995: reducing vegetable oils and gas emissions from restaurants (8,9)*

The need for the next generation of monolithic catalyst technologies will extend well into the 21st century (10). New applications will continue to increase the need for improved materials.

A. Gasoline Catalyst/Emission Control System

a) controlling cold start hydrocarbon emissions by any combination of the approaches listed below:

1. close coupled (manifold mounted) catalyst
2. electrically heated catalyst systems
3. hydrocarbon traps
4. exhaust gas igniters

b) increasing use of metallic and thin walled ceramic supports
    1. for high performance vehicles requiring ultra-low pressure drop
    2. pre-coated metal foil to give more uniform washcoats
    3. electrically heated monoliths

c) improved thermal stability for more aggressive driving cycles
    1. inclusion of aggressive driving cycles in the U.S. Federal Test Procedure simulating high speed and acceleration with air conditioning in operation

d) partial lean burn engines with NO_x trap/TWC system
    1. operation of the engine prtially lean for fuel economy with a NO_x trap incorporated into the catalyst

e) full lean burn engines
    1. lean NO_x catalysts using fuel derived hydrocarbons for reduction.

f) near zero emission vehicles
    1. more highly efficient catalysts

B. Diesel Engines

a) 4-way catalysts
    1. high selectivity for NO_x reduction using fuel derived hydrocarbons (11)
    2. high activity for particulate reductions, conversion of gaseous emissions of CO and HC and low selectivity towards oxidation of SO_2 to SO_3

b) catalytic reduction of dry soot
    1. catalyzed filters
    2. fuel additives (12)

C. Stationary Combustion

a) process technology for near zero emission catalytic combustion (13)
b) high temperature stable materials (14)
c) high surface area monoliths (15, 16)

D. Small Appliance Engines

a) controlling emissions from two/four cycle engines i.e., lawn mowers, snow blowers, weed whackers, etc. (17)

E. Low Temperature Catalysts

a) environmental catalysts active at or near room temperature (18)

The lecture will describe the next generation of mobile and stationary applications of monolithic supported catalytic systems.

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OP-1

Combustion of Volatile Organic Compounds. Comparison of catalytic membranes loaded with Pt and with metallic oxides of perovskite structure.

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Introduction

The need to obtain a clean, efficient way to curb VOC emmisions is widely recognized. Catalytic oxidation is being intensely researched as a promising alternative for the removal of VOCs, because of its flexibility and low energy requirements, compared to thermal oxidation. The requirements to be met are stringent: Catalytic combustion must efficiently achieve essentially complete conversion of a wide variety of products, which are often present as mixtures, and do so over a broad range of concentrations and feedrates.

The usual approach involves the use of highly active, nonselective catalysts (i.e., noble metals), or less active, lower-cost catalysts such as single metal oxides (Cu, Ti, V, Co, Ni, Mn), and mixed oxides with a perovskite structure (e.g., La-Cr, La-Co, La-Fe, La-Mn, etc.). Another point to consider is the mode of contact, important in any catalytic system, but critical for processes such as VOC combustion, where reactant concentrations are measured in the ppm range.

In this work, the feasibility of using ceramic membranes for the complete combustion of volatile organic compounds has been investigated. To this end, the performance of different catalytic membranes ($Pt/\gamma\text{-}Al_2O_3$, $LaCrO_3/\gamma\text{-}Al_2O_3$, $LaCoO_3/\gamma\text{-}Al_2O_3$, $LaCrO_3$ and $LaCoO_3$), working in the Knudsen diffusion regime has been compared.

Membrane development and experimental details

The membranes were prepared from commercial microfiltration membranes (SCT). The starting material were 1.5 mm thick, 10 mm o.d. asymmetric ceramic tubes (SCT). Two different lines of membrane development were followed:

i) For catalytic membranes including Pt or oxides supported on $\gamma\text{-}Al_2O_3$, a first stage consisted of several cycles of filtration of a boehmite sol followed by calcination at 600°C, with a double objective: Attaining a sufficient amount of support material and modify the initial porous structure to obtain Knudsen diffusion. The second stage consisted in introducing the active phase. In the case of Pt/γ-Al_2O_3 membranes this was carried out through wet impregnation with chloroplatinic acid, followed again by drying and calcination steps (450°C, 2 hours), and finally by activation with H_2 (400°C, 2 hours). For the $LaCrO_3$/γ-Al_2O_3 and $LaCoO_3$/γ-Al_2O_3 membranes, the incorporation of the mixed oxide involved a first impregnation with $La(NO_3)_3$, plus calcination at 500°C for 10 hours to form La_2O_3. A second impregnation with the corresponding nitrates (either Co or Cr) ensued, after which calcination at 1000°C for 24 hours resulted in the formation of the perovskite.

ii) For catalytic membranes including unsupported $LaCrO_3$ and $LaCoO_3$, the initial microfiltration membrane was impregnated with a solution containing organic salts (citrates) of the metals in the appropriate proportions. This allowed the formation of perovskite at a lower temperature (ca. 800°C), as confirmed by XRD analysis. In this case, Knudsen flow was obtained from repeated crystalization within the membrane structure, and addition of γ-Al_2O_3 was not required.

In addition to XRD measurements, the membranes were characterized by BET surface measurements, H_2 chemisorption, mercury intrusion porosimetry, TG, SEM-EDX and permeation measurements. The reaction system consisted of a feed section in which a mass flow controlled stream (air) was saturated with the selected organic compound and mixed with a second mass flow controlled air stream to give the desired final concentration (from 500 to $1x10^4$ ppm), and a reaction section, with the above described catalytic membrane. The feed mixture entered the membrane tube side and then permeated across the membrane wall. After reaction, the exit stream was directed to an on-line gas chromatograph (FID detector), and to CO and CO_2 analyzers, which were used to check carbon balances.

Results

The membrane reactors used were efficient in the removal of VOCs by combustion. Total combustion temperatures were below 200°C for Pt-based membranes under most of the conditions investigated, while higher values were found for the perovskite membranes, as could be expected. In both cases, the membranes used were able to sustain prolongued experiments, without any apparent loss of mechanical integrity.

OP-2

COMPARATIVE INVESTIGATIONS OF HONEYCOMB AND FOAM STRUCTURE CATALYST SUPPORT TO PURIFY EXHAUST GASES FROM INTERNAL COMBUSTION ENGINES (ICE)

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Lately honeycomb and foam monolith catalysts have been preferably used for high-efficiency processes. Both type catalysts enable one to realize catalytic gas purification with high linear filtrate flow rates (5÷10 m/sec or up to 10^5 1/h) under slight pressure drops (up to 500 mm of water column). In honeycomb catalysts near-laminar regimes of gas flow in channels are realized even at a flow rate of up to 10 m/sec [1], which results in external diffusion limitations. In foam supports a turbulent filtration condition is established at a rate of 1m/sec. Therefore some researches studying the problems of monolith catalyst supports use show a number of advantages of foam supports ensuring a more efficient use of active component [2, 3].

Operating parameters of monolith catalysts for purification of ICE exhaust gases (hydraulic losses, catalytic activity, service life) depend on physical and mechanical properties and structure of a primary support as well as on volume concentration and physical and chemical properties of secondary support and catalytically active components. The primary support whose physico-mechanical and hydrodynamic properties and structure (porosity, channel size, heat conductivity, thermal stability, high-temperature strength) govern the catalyst service life and efficiency of external diffusion processes is of considerable importance in gas purification.

In the present work an attempt to reveal a significance of the spatial structure of the primary support in gas purification has been made. Operating parameters of monolith catalysts of various structures (geometrical block sizes - diameter and height, volume concentration of the secondary support and catalytically active component are the same) may be compared only on simultaneous measurement of four parameters of gas purification: volume rate of exhaust gases, 1/h; hydraulic losses on the block, mm of water column; conversion degree for a toxic component, %; conversion temperature, °C.

Monolith catalysts of honeycomb and foam structure (channels and cells of size 1÷5 mm), prepared by coating monolith supports of the corresponding structure with γ-Al_2O_3 (5÷50 g/l) and catalytically active components - palladium, platinum (0,5÷3,2 g/l), copper-chromium (10÷15 g/l) - have been studied. A comparative investigation of catalytic activity during CO, CH, NO_x and soot conversion was performed at gas flow rates of $4{\cdot}10^4 \div 9{\cdot}10^4$ 1/h, pressure drops of 100÷500 mm of water column, and conversion temperatures of 250÷450°C.

From the investigations the following conclusions have been drawn:

1. At equal volume rates of exhaust gases and pressure drops (the latter equality can be provided by choosing appropriate cells and honeycomb) the temperature corresponding to the same conversion degree is lower by 100÷150 °C for foam catalysts as compared with the honeycomb ones.

2. At the same conversion degree and volume flow rates the pressure drop on the foam monolith is lower by 20÷30% than that on the honeycomb monolith.

3. In contrast to the honeycomb structures, the elements of the foam structures not coated with catalytically active components can efficiently retain solid particles which can be further easily (e.g. electrochemically) regenerated.

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PL-2

Development of a catalytic honeycomb burner for furnaces

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Catalytic combustion was mostly used for small sized heaters at the early stage of its development, but recently many studies on catalytic combustion have focused on the development of combustors with high combustion intensity such as combustors for gas turbines and boilers. Objective of this study is to develop an industrial catalytic burner using Pd/NiO catalysts supported on gamma alumina washcoated honeycomb.

The honeycomb(cordierite) of 400 cells/in^2 was washcoated by a stabilized alumina. The Pd/NiO catalysts were prepared by impregnation with aqueous nickel and palladium salts, drying and calcining at 800 °C for 4 hours. Its maximum heat-resisting temperature is about 900 °C.

We designed the catalytic burner of 10 cm x 10 cm with this honeycomb catalyst, and performed experiment in order to obtain the optimal operating conditions for stable catalytic combustion by analyzing catalytic combustion region, temperature distribution, and combustion efficiency. When the honeycomb catalyst was 30 mm in thickness, stable catalytic combustion was obtained at the operating conditions of excess air ratio 1.25 - 1.75 and heat flux 7 - 14 kcal/h.cm^2.

On the basis of the acquired operation conditions for stable catalytic combustion, long term test of the catalytic burner was performed. Its results showed that when the maximum temperature of the catalyst layer was about 1,000 °C, its life time was 620 hours, but when the maximum temperature was under 900 °C, it was run longer than 1,400 hours.

In order to apply the catalytic burner to industrial processes using LNG, it was tested at a furnace that is used for calcination of ceramic products such as pottery and china. The maximum room temperature within the furnace was maintained under 1,000 °C. As the catalytic burner can be run at fuel rich mixture of over equivalence ratio 1.0, that is, reduction atmospheres, one can obtain typical benefits when it is used at the furnace. Total 24 sets of catalytic burners were assembled into the furnace. They showed good results that their temperature distributions within the catalyst layer were improved comparing with the case of respective catalytic burners before assembly.

Catalytic combustion of methane on perovskite porous monoliths

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Catalysts based on mixed oxides of 3d and rare-earth elements with perovskite structure are promising for high-temperature processes like fuel combustion due to their high thermostability [1]. As honeycomb are required in order to minimize pressure drop across the catalytic bed, a preparation procedure of active components in powdered form with subsequent shaping of honeycomb monolith has been developed [2]. In this work the kinetics of methane combustion on either powder or monolith catalysts was investigated. The catalytic results are discussed with respect to some properties of monoliths such as active component content, porous structure, concentration of surface oxygen adsorbed, cell geometry.

The preparation procedure of perovskite powders, containing La-Ce or Dy-Y or La with Mn, Fe or Ni, by mechanochemical and plasmochemical methods and their shaping to monoliths has been described earlier [2,3]. The samples were characterized in terms of surface area and porosity. Temperature programmed desorption (TPD) of oxygen after treatment in air at 1000°C was carried out with a Micromeritics TPD/TPR 2900, connected with a mass-spectroscopic analyzer Hiden Analytical HPR 20, using helium as a carrier.

Kinetic tests of methane combustion were carried out with a fixed-bed flow reactor loaded with 1.5 g of either perovskite powder or pieces of monolith (1-2 channels, about 20 mm in length), and fed by a gas mixture containing 0.4% CH_4 and 2% O_2 in He, or 1% CH_4 in air. The outlet reactor gas composition was determined by on-line continuous analyzers for CH_4, O_2, CO, CO_2 and NO_x .The concentration of reagents was changed in the ranges 0.1-2% for CH_4 and 0.8-20% for O_2; the temperature varied from 300 to 900°C; and space velocity from about 15000 to 60000 h^{-1}. Either differential or integral reactor conditions were used for the kinetic measurements, limiting temperature gradients along the catalytic bed.

Preliminary tests performed at relatively low methane conversion values, in the region of dominant heterogeneous reaction, indicated an order of reaction close to one for CH_4 and to zero for O_2. The kinetic model fits with sufficient approximation the conversion data for both feeding conditions. The values of apparent energy of activation were in the range 25.4-29 kcal/mol for powders and 18.8-28.3 kcal/mol for monoliths. This differences in the values of apparent activation energy is likely due to the limiting effect of diffusion.

The kinetic analysis was improved by power law modelling of methane combustion rates measured under differential conditions. Fractional orders around 0.8 and 0.2 were evaluated, respectively for CH_4 and for O_2. Comparison with Mars-Van Krevelen model was also performed.

It was found that, for a given rare-earths oxides system (La-Ce or Dy-Y), the specific catalytic activity (SCA) of powder catalysts was in the order Mn>Ni>Fe. La-Ni system, prepared through the plasmochemical route, was found to be the most active, likely due to high concentration of extended defects, which not annealed upon calcination and laboratory test procedure. Almost the same order of activity was found for the monolith catalysts.

The comparison of SCA per gram of pure active components in powder and monolith form showed comparable levels of activity almost for all samples of either La-Ce or Dy-Y based systems, likely due to the relatively high porosity of monolith samples (pore volume of 0.22-0.28 cm^3/g and specific surface area of 46-74 $m^2 7g$).

All TPD spectra of monoliths showed 1 or 2 peaks at $T < 500°C$ due to oxygen desorption; one peak at T=700-800°C was detected for Mn and Fe containing catalysts and a more large signal due to decomposition of the original perovskite structure was checked up at T=900-1000°C. A good correlation between the amount of oxygen desorbed until to 500°C and SCA at 500°C was established.

It was found that in the absence of catalyst the selectivity to CO shows a maximum with temperature, which shifted to lower values by increasing the concentration of methane in the gas feed. In the presence of monoliths the selectivity to CO decreases by about 5-10 times, passing still through a maximum at a temperature closer to that of ignition of homogeneous processes.

The effect of monolith geometry passing from two triangular (4.5x4.5x4.5 mm) to one square (4.5x4.5 mm) channel and from wall's thickness of about 1.2 to 2 mm results in decreasing both activity and selectivity, the ignition temperature being lower of about 25-30°C. The ignition temperature ($T_{10\%}$) over monoliths was generally lower of about 150-200°C, if compared with that of empty reactor, making possible to use them even for ignition of gas feed at the inlet of reactor. It need to be mentioned that the apparent density of monoliths prepared with perovskite powders is higher with respect to those prepared by impregnation. So, the activity per unit volume of that type of catalysts should be higher, an important feature in the case of space limitations.

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OP-4

A STUDY OF MONOLITH CATALYSTS FOR HIGHLY EXOTHERMIC REACTIONS

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An innovative potential advantage of monolith catalysts is related to the good heat transfer properties which can be obtained via proper choice of material and geometry. In view of this and considering their characteristic low pressure drop it has been proposed to use metallic monolith in chemical processes that demand for effective heat transfer to the external environment [1]. However heat transfer mechanisms in such catalyst have not been sufficiently explained and studies are needed develop thermal design methods.

In our previous work on heat transfer properties of honeycomb structures by a pseudo-continuous approximation we derived correlations for the calculation of effective heat conductivities of the monolith matrix as a function of material properties and microgeometry (channel shape and void fraction) [2]. Comparison with the effective conductivities of packed beds showed promising advantages of monolith catalysts when metallic materials are used for the support; however lower void fractions must be used with respect to those typical of monoliths for environmental applications. In this work we extend the continuum model to account for the occurrence of a catalytic heterogeneous exothermic reaction and apply it to the simulation of a multitubular reactor with external cooling loaded with monolithic catalysts. The scope is to develop general criteria for the design of monolith catalysts suited for this purpose.

By means of model simulations we have performed a parametric analysis of an externally cooled single tube. loaded with a monolith catalyst. Values of dimensionless parameters in model equation have been derived from typical characteristics of packed beds in industrial multitubular reactors for highly exothermic processes [3]. The effect of the following catalyst design parameters has been investigated: activity; microgeometry (fraction of void (ε), active phase (ξ) and support (σ)); support conductivity. As a general result the calculated temperature profiles of the catalyst show close analogy with those of packed beds [3,4]. Along the axial coordinate the temperature rapidly increases and reaches a maximum near the reactor inlet, then gradually decreases. The extent of the maximum temperature grows from the wall to the axis of the tube, thus originating a typical hot spot which progressively smoothens on increasing the effective radial conductivity by enhancing the wall thickness and/or the material conductivity of the support.

To assess the potential of the monolith reactor simulations have been performed constraining the average exit conversion at 0.95. In figure 1 the results are reported in the ξ-σ plane, which is representative of the microgeometry of a coated monolith catalyst, with the diagonal as the physical limit corresponding to zero void fraction. The solid lines are the loci of the monolith geometries required to achieve the target conversion at given catalyst activity and support conductivity. The dotted lines connect the points with a maximum catalyst to the gas inlet temperature ratio (T_{mc}/T°) of 1.3, regarded as an optimum design target. Two sets of curves are presented corresponding to catalysts with low and high activity. With low active catalysts considerable amounts of active phase are required to achieve the target conversion. As a result limited volume fractions are available for the support which is mainly responsible for the removal of reaction heat via thermal conduction. Accordingly T_{mo}/T^{o} can be limited below the target level only using highly conductive material for the support and unpractical (low void fraction) monolith geometries. On increasing the catalyst activity much smaller fractions of active phase are required whereas only a slight increment of the support fraction can compensate for the more intensive production of heat. In this case using highly conductive materials feasible catalyst geometries can be adopted (e.g. ε=0.7, ξ=0.138, σ=0.162 with k_s=70 W/mK). These results point out that through a proper choice of materials and a suitable design of the geometry, the combination of low pressure drops and good heat transfer properties secured by monolith catalysts could afford for significant improvement of existing catalytic processes with highly exothermic reactions.

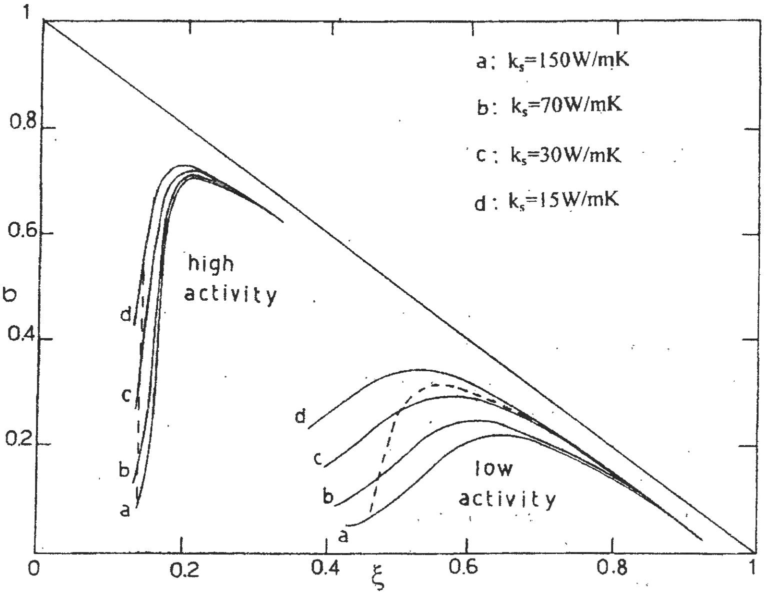

Figure 1: Design of catalyst geometry to achieve 0.95 conversion

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Monolith Catalysts for Medium Temperature Combustion of Methane

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Mixed oxide catalysts represent a valuable alternative to noble metals catalysts in catalytic fuel combustion in view of their thermal stability. Catalyst features are known to depend on the preparation technique. The goal of the paper is to develop high performance catalysts for medium temperature (800-1200°C) combustion of methane.

Powdered oxide catalysts consisting of $LaMnO_3$ supported on alumina with lanthana additive have been prepared by both conventional incipient wetness impregnation technique (impregnated catalyst), and a new procedure providing concentration of an active component precursor from the solution on the surface of support (sorptive catalyst) as well as some sodium introduction in the catalyst composition.

BET surface area of the support, impregnated and sorptive catalysts calcined at 1200°C is, respectively, 53, 21 and 15 m^2/g. Catalytic activity of the samples has been tested in methane oxidation with air (1 vol.% methane in air, SV=48000 h^{-1}) in a microreactor at 400-800°C. The sorptive catalyst is more active in comparison to the impregnated one, temperature of 50 % methane conversion being 40 K lower.

X-ray analysis has revealed $LaAlO_3$ perovskite and hexaaluminate crystal phases in the support as well as in catalysts. X-ray pattern of the sorptive catalyst has also shown peaks of $NaAlO_2$ crystal phase. Perovskite is a major crystal phase in

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the support and the sorptive catalyst, whereas hexaaluminate dominates in the impregnated catalyst. The amount of $LaAlO_3$ perovskite in the impregnated and the sorptive catalysts is, correspondingly, half and five as much as that in the support. The composition of hexaaluminate is $LaAl_{11}O_{18}$ and $LaMnAl_{11}O_{19}$, correspondingly, for the support and the impregnated catalyst. In the sorptive one sodium along with manganese is involved in the hexaaluminate composition.

Coordination of manganese ions was studied by ESDR. Reactivity of surface oxygen of the samples have been established by TPR with CO, and found out to be in agreement with methane complete oxidation activity data.

Catalytic activity tests have been performed with monolith catalysts consisting of $La_xSr_{1-x}B_yB'_{1-y}O_3$ (B=Mn, Co; B'=Ni, Fe) supported on cordierite honeycombs washcoated by alumina with lanthana additive. Active components were applied via sorptive technique. BET surface area of monolith honeycomb catalysts calcined at 1200°C is 1-3 m^2/g.

Preparation technique of sorptive catalysts with homogeneous distribution of supported active component precursor and some sodium introduction in a catalyst composition is a manner to stabilize perovskite crystal structure in catalysts at elevated temperatures.

BLOCK CATALYSTS FOR FLAMELESS COMBUSTION OF FUELS AND CLEANING OF INDUSTRIAL GASEOUS EXHAUSTS FROM TOXIC ORGANIC COMPOUNDS

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The fundamental researches of the influence of perovskite structure oxide compounds composition on their activity in the processes of flameless fuel combustion (methane, propane, buthane, kerosene, etc) were performed. The peculiarity of these catalysts is in their high efficiency in these processes with nearly full absence of NOx and CO in combustion products that predestines their use as alternative catalyst for flame burning process, which is characterised by great amount of toxic exhausts.

The parameters of flameless combustion process of methane are shown in Table 1. The catalysts of this type provide quantitative methane combustion without NOx and CO production, which is reached by varification of combustion conditions.

Table 1. Catalytic flameless combustion process parameters on La-Zr block catalysts of perovskite type. (Volumetric flow rate 25000 h^{-1})

Methane: Air ratio	T, °C produced in the catalyst block	Product composition of flameless combustion of methane, %		
		NO_X	CO	CH_4
1:8	950	0,0	0,72	0,300
	960	0,0	0,62	0,300
	960	0,0	0,45	0,300
1:9	970	0,0	traces	0,055
	920	0,0	traces	0,080
	880	0,0	0,0	0,110
1:10	910	0,0	0,45	0,500
	910	0,0	0,45	0,545
	910	0,0	0,40	0,490

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The possibility of using block perovskite catalysts for cleaning industrial gaseous exhausts from NOx, CO and different toxic compounds was shown. Thus under introduction of different organic admixtures from 1000 ppm to 15 vol.% (Table 2) into air-fuel flow nearly complete conversion (abt. 70-100%) of these admixtures occurs.

Table 2. Different organic compound conversion at flameless methane combustion process (methane - organic compound : air = 1:8, volumetric flow rate 11000 h^{-1}).

Organic compound	Boiling point., °C	Conversion,%	NOx content in combustion products, ppm
Benzene	80,1	98	0
Toluene	110,6	99	0
Acetone	56,0	99,9	0
Aniline	184,4	100	55
Diethyl ether	34,5	99	0
Diethylamine	55,5	93	1660
Nitrobenzene	210,9	70	0
Nitromethane	101,2	94	1100
Mixture of n-hexanol-45% n-hexylamine-55%	100,0	100	40
Chloroform	61,2	84	in the products of HCl combustion

The worked-out catalytic systems based on perovskites provide high process stability and chemical resistance to the hydrofluoric and hydrochloric acid vapours that makes possible to use them for reburning the fluorine- and chlorine- organic exhausts (e.g. freon destruction, solving dioxine problem.)

PERSPECTIVES OF DEVELOPMENT OF MONOLITHIC CATALYSTS FOR ENVIRONMENT PROTECTION AND FUEL COMBUSTION AT BIC

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In a number of Western firms the technique of honeycomb extrusion from cordierite is developed as a top level technology, and there are numerous achievements in preparation of catalysts on metal foil monoliths. During last two decades monolithic honeycomb catalysts have been successfully used most commonly in the following processes:

- control of automobile exhaust pollutants;
- selective reduction of nitrogen oxides in flue gases from power stations;
- oxidation of VOC in industrial off-gases;
- ozone decomposition in airplane air intake systems;
- multiphase processes, e.g. hydrogenation of oils in liquid phase.

Valuable experience in application of monolithic catalysts for some new processes is accumulated:

- methane oxidative dimerization;
- direct oxidation of H_2S to sulfur;
- ammonia oxidation in the process of nitric acid production.

There are some new promising applications in oil and gas processing industries arising too.

We consider as the forthcoming scientific objectives of our research the following:

1. Deposition of catalytically active oxide coatings, e.g. perovskites, on Corning type low BET surface area cordierite monoliths;
2. Deposition of multicomponent catalytically active compositions on ceramic and metal foam materials;

3. Extrusion of monoliths with high specific surface area for low temperature catalytic processes;
4. Elaboration of extrusion technique for manufacture of monoliths from new carbon and oxide catalytically active materials;
5. Development of plasma methods for coating of metal foils with catalytically active materials;
6. Development of monolithic catalyst for methane steam reforming;
7. Development of monolithic catalysts for ethylbenzene dehydrogenation to styrene;
8. Preparation of new monolithic adsorbents for capturing of hydrocarbons and nitrogen oxides from automotive exhausts;
9. Synthesis of membrane layers, comprising catalysts for total oxidation of hydrocarbons and H_2S dissociation, upon tubular membrane supports.
10. Development of new coatings for enzyme immobilization on ceramic honeycomb and foam type monoliths.

Development of a new monolith catalyst for methanol removal from exhaust gases

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Cordierite and mullite type ceramic monoliths are used as supports for noble metal catalysts for VOC control.

These supports have high thermal and mechanical stability, but the specific surface area and volume of pores are rather small for the preparation of impregnated catalysts.

A thin oxide layer (usually γ-Al_2O_3) washcoating of the walls of monolith channels increases specific surface area and allows synthesis of impregnated catalysts.

Nevertheless, this preparation method have some drawbacks and the main of these are the following:

- low resistance to attrition of washcoating layer leading to loss of oxide material and noble metals during exploitation;
- additional stages of washcoating, drying and calcining.

The goal of this work is development of an effective ceramic monolith support and catalyst preparation for removal of methanol from exhaust gases.

The main stages of this work include:

- preparation and study of monolith ceramic supports;
- development of impregnation method for the preparation of Pt catalyst;
- study of the main properties of the catalysts, using XRD analysis, IR- spectroscopy, SEM, XR spectral microanalysis, etc;
- catalytic activity testing in the model reaction of butane oxidation and in the oxidation of methanol.

The Table presents properties of the optimal catalyst wich demonstrated high conversion of methanol. This catalyst was recommended for industrial application.

The batch of 0,3m^3 of the monolithic catalyst has been manufactured and loaded in to an industrial reactor at Tomsk Petrochemical Complex.

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The properties of optimal catalyst. Table.

SUPPORT			CATALYST		
phase composition	monolith geometry	S_{BET}, m^2/g	Pt, wt.%	catalytic activity	
				$W^{300} \bullet 10^2$, C_4H_{10}, $cm^3/g \bullet s$	Convers. of methanol at 180^0C, %
α-SiO_2 + α-Al_2O_3+ $MgSiO_3$	75x75x150mm channel 2,2x2,2mm wall thickness 0,4mm	13	0,3	0,56	98,5

SYNTHESIS OF THE PALLADIUM CATALYSTS ON POROUS NICKEL BLOCKS FOR COMPLETE OXIDATION OF CO AND MIXTURE OF ORGANIC SOLVENTS

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Waste gases of plastic, paint and cable industry can include up to 200-300 mg/m^3 of toluene, xylene, cresol, solvent, CO or their mixtures. Complete catalytic oxidation of admixtures on supported oxides or mixed Pd catalysts is used to clean these gases. Metal plates and nichrom netting covered with Pd black are used as catalysts in the cable industry. Effectiveness of these catalysts is decreased because of Pd exfoliation and carrying away of palladium during the cleaning process.

The P-5 mixed palladium catalyst on granulated Al_2O_3 has been developed at the Institute of Organic Catalysis and Electrochemistry. This catalyst is used for waste gases cleaning in the processes of wire enameling at Samara and Rostov plants of cable industry. To reduce gas-dynamic resistance we have developed the method of P-5 catalyst supporting on porous block ceramic cordierite.

The results of complete oxidation of CO and mixture of organic solvents over palladium catalysts supported on the foamy nickel (K- 20 type) blocks are presented in this report. The characteristics of the blocks are the following: block's channel size - 5 mm, density - 0.3 g/cm^3, porosity - 96,5%, air penetrability - 5,5·10^{-8} m^2). CO concentration in the stream was determined by GIAM-15 gas analyzer.

KhPL-4 chromatograph was used to identify the sum of organic compounds.

The temperature of 70% conversion of CO is 195-200°C at the 0.3-0.6 mas.% Pd/Al_2O_3 concentration in catalysts. The increase of Pd/Al_2O_3 content on blocks up to 1.5-3.0 mas.% leads to the decrease of conversion temperature to 180°C. Oxidation of solvent is 75-100% at 300°C and 0,3-3,0 mas.% concentration of Pd/ Al_2O_3.

Disadvantage of palladium catalysts on porous nickel blocks is a low thermal stability because of oxidation of Ni (up to 30% at 700-800 °C) into nickel oxides. This process reduces mechanical strength of the contacts. To increase thermal and mechanical stability of catalysts the modification of nickel blocks has been carried out. Modification of support with Ce, Zn, Zr leads to a decrease of the temperature of 70% oxidation of CO in the following order: Pd = Pd-Ce (195°), Pd-Zr(185°), Pd-Zn (170°).

Oxidation of the mixture of organic solvents also increases on catalysts modified with Zn, Ce, Zr at 300°C from 79 to 99 - 100%.

However after heating of the palladium catalysts promoted with Ce or Zr at 800° during 25h in air their effectiveness in the reaction of solvent oxidation decreases sharply at 250-300°C. The activity remains unchangeable only in the presence of $Pd/Al_2O_3/Zn/Ni/$. It is shown that effectiveness of oxidation of CO and a mixture of organic solvents on this catalyst is close to that of P-4 and P-5 catalysts supported on Zn/Ni carrier at $W=(20-60)10^3h^{-1}$.

Pilot testing of P-4 and P-5 palladium catalysts, supported on porous Ni blocks and promoted with Zn on the plant of Russian Research Institute of Cable Industry have been carried out. The contacts provide high extent of oxidation (88-96%) at 350-500°C and 77 x 10^3h^{-1} volume rate and concentrations of organic solvent of 50-400ml/h. The developed catalysts on porous Ni blocks in the shape of slabs were recommended for commercial use in purification of gas of cable production.

Catalysts for Diesel engines with high emission of soot particles

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Summary

It is well known that solid particles emitted by Diesel engines are among the most dangerous constituents of exhaust gases produced by motor-cars. It has been found that the solids contain over 10000 chemicals compounds. The most hazardous of them are the mutagenic and cancerogenic cyclic aromatic hydrocarbons. That is why in the closest future many countries will increase their legal requirements in respect to emission of solid particles, so called "Diesel soot". One of many activities, aimed at reduction of emission of the Diesel soot, is purification of exhaust gases. The most effective seem to be the solutions based on "catching" and further combustion of soot in regenerable catalytic filters. However, up-to date effective and economic filter/catalysts are not produced. Facing at the need for reduction of emission, to meet the future legal requirements, many renowned manufacturers begun implementation of simple flow-through oxidation catalysts in the form of typical open monoliths with a washcoat and an oxidation catalyst. The catalysts, operating at temperatures over 100°C, provide combustion of the hydrocarbons, which otherwise (below 50°C) would participate in emission of Diesel soot. The possibility for application of such catalysts for older heavy duty engines of city busses in Wroclaw Communal Enterprise has been examined by the Laboratory of Surface Engineering of Wroclaw Technical University. Exhaust gas compositions of the busses with and without catalysts were compared for various loads of the engines. There were examined new, used and regenerated catalysts. It has been noted however, That in case of the catalysts characterised by reduced activity (used, regenerated) further locking of active centers by soot resulted in emission of hydrocarbons. Particularly, emission of aldehydes and aromatic hydrocarbons considerable increased.

Simultaneously, there were also tested filter/catalysts designed by the Laboratory of Surface Engineering of Wroclaw Technical University. The filter/catalysts, developed for the older engines still used for communal transport purposes, consist of a catalytic filter for catching of soot particles, an electric heating system for boosting of regeneration of the filter during

operation of the bus and catalysts providing oxidation of carbon oxide and hydrocarbons. The filter consists of a pack of compressed heat-resisting steel wool covered by V/Cu catalytic layer, which reduces ignition temperature of soot below 400°C. The filter/catalysts were characterised by small flow resistance and by approx. 80% effectiveness of combustion of soot particulates. Currently, mechanical design of the filter/catalysts is somewhat modified, to prevent collecting of soot in dead voids what may result in too exothermic combustion of the Diesel soot.

PECULIARITIES OF METHANE DEEP OXIDATION ON MONOLITH CATALYSTS OF VARIOUS COMPOSITION

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INTRODUCTION

The problem of methane catalytic combustion as an alternative to conventional thermal combustion, becomes topical today. It is worthy of noting that although methane is one of the most hardly oxidized hydrocarbons, its world's resources are enormous. Besides, methane used as a fuel can help to reduce the green house effect.

In the present paper we report on the methane deep oxidation over monolith catalysts with a wash coating of various chemical and phase composition. We have elucidated the peculiarities and regularities of methane oxidation regarding the catalyst type and its active component.

EXPERIMENTAL

The methane deep oxidation was studied in a flow setup under the conditions as follows: mixture: 1% CH_4 in air; temperature: 150-900°C, volume space velocity: 1000 h^{-1}. The initial reaction mixture and reaction products were analyzed by GC.

We have studied monolith ceramic catalysts whose washcoatings have various compositions, while the active component is based on a mixture of noble metals. The main properties of supports and catalysts are given in Table 1.

RESULTS AND DISCUSSION

Figure 1 presents a typical curve of methane conversion vs. temperature (sample 1). It is evident that hysteresis is not typical for sample 1 (the catalyst is not activated during the run), while samples 2 and 3 demonstrate high catalyst activation resulting in a 50°C decrease of temperature for a 50% conversion. This is apparently caused by the chemical composition of the washcoat. For sample 1, the activity increases if the catalyst is reduced under more severe conditions in the reaction of NO reduction with hydrocarbons, while samples 2 and 3 after operation in a HC-SCR process do not show considerable changes in their activity during methane oxidation.

Table 1.

Sample	Support		Washcoat			Active component	
	Phase	S_{BET}, m^2/g	Composition	Content wt. %	S_{BET}, m^2/g	Pt, wt.%	Pd,wt.%
1	Al-Si-O	11	12% La_2O_3 / TiO_2	5,0	11,3	0,55	0,27
2	Al-Si-O	3	12% La_2O_3/ Al_2O_3	6,1	5,5	0,40	0,20
3	Al-Si-O	11	20% Al_2O_3 + 80% ZrO_2	5,4	18,0	0,40	0,20

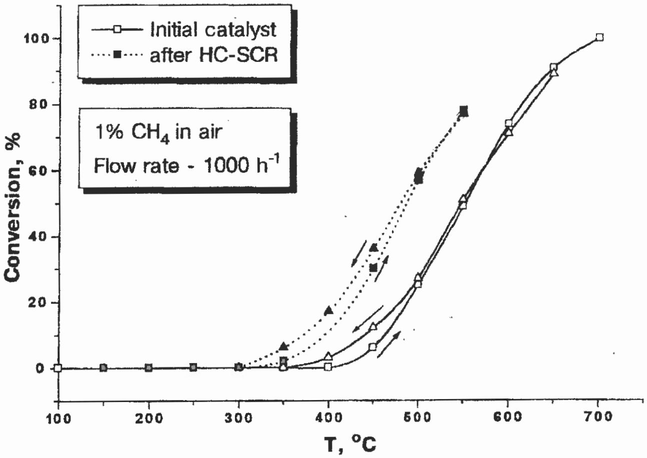

Fig. 1. The methane conversion vs. temperature (sample 1).

These differences in activity and mechanism of catalysts activation in the deep methane oxidation are presumably associated with changes in the chemical composition and valence states of the active component elements as well as in the composition of washcoat.

MONOLITHIC CATALYST FOR ABATEMENT OF CARBON MONOXIDE FROM FLUIDIZED BED CATALYTIC COMBUSTOR

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At Boreskov Institute of Catalysis a method of environmentally clean fuel burning and destruction of hazardous organic wastes using flameless catalytic fluidized bed combustion at low temperature (600-750°C) has been developed [1, 2]. Recently this method was shown to be promising for development of technology of environmentally safe destruction of mixed liquid organic wastes containing radionuclides. This research and development project is supported by the International Science and Technology Center (Project No 110) and carried out in cooperation with a number of nuclear processing enterprises of Russian Ministry of Atomic Energy (Minatom) [2-5].

During study of the process of catalytic fluidized bed combustion of model mixtures simulating mixed organic radioactive wastes (industrial oils, extractants, etc.) in the experimental setup it was revealed that some wastes require rather high temperature to achieve complete oxidation: 750-790°C. The increase of temperature leads to the increase of NO_x emission (up to 120 mg/m^3). At lower temperatures the concentration of NO_x decreases but simultaneously the increase of CO concentration is observed. For the removal of CO admixture from flue gas a new process scheme including catalytic reactor for CO oxidation to CO_2 (CO abater) was developed and tested. At the Boreskov Institute of Catalysis platinum containing catalyst on monolithic honeycomb aluminosilica support was elaborated and prepared. This catalyst is specially designed to remove CO from dust loaded gases. The catalyst is a rectangular monolith with a large number of parallel channels separated by thin walls on which the active component is supported. The characteristics of the support and catalyst are presented in Table 1. CO abater was installed after the cyclone to decrease abrasive deterioration of monolithic catalyst by dust particles from fluidized bed reactor. The amount of the catalyst in the CO abater is 3.6 dm^3 (8 monoliths).

Study of catalytic destruction of organic wastes from nuclear material processing plants in the setup with catalytic CO abater was carried out. The concentration of CO in the flue gas after fluidized bed reactor was 30-400 mg/m^3. CO abater provides CO removal over 95% at a temperature of 230-250°C and V = 6000 h^{-1}, thus decreasing CO concentration below maximum allowable value - 20 mg/m^3.

Table 1. Characteristics of monolithic honeycomb catalyst for CO oxidation

Characteristics	Unit	Value
Dimensions	mm	72 x 72 x 75
Channel size	mm	2,2 x 2,2
Wall thickness	mm	0,45
BET area	m^2/g	10-15
Mass of one monolith	g	290
Pressure drop at V = 6000 h^{-1}	mm of water	< 4
Composition		0,3%Pt/ Al_2O_3, SiO_2, $MgSiO_3$

Table 2. Results of gas analysis upon catalytic combustion of oil sludge

Point of taking probes (after)	T, °C	CO mg/m^3	NO_x mg/m^3
Fluidized bed reactor	790	28 32 30	118 123 116
CO abater	235	0 0 0	116 120 100
Fluidized bed reactor	710	123 121 125	38 38 38
CO Abater	240	0 0	38 45

Table 2 illustrates how harmful emissions can be controlled by the example of catalytic fluidized bed combustion of oil sludge. The three-fold decrease of NO_x emission can be attained by the decrease of temperature from 790 to 710°C. The resulting increase of CO concentration is unessential, as CO is almost totally oxidized in CO abater.

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Session B

SCR-NO_x CONTROL.
ADVANCED CATALYTIC APPLICATIONS

Understanding of Deactivation Behavior of DeNOx Catalysts as a Key to Advanced Catalyst Applications

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Experience gathered with supported vanadium oxide catalysts based on titania and promoted mainly by tungsten or molybdenum which have been chosen for commercial SCR applications using ammonia as the reducing agent has shown that more comprehensive knowledge is required for advanced applications.

Despite the impressive success achieved to date with industrial application of these catalysts in terms of activity, selectivity and service life, it must still be borne in mind that the interrelationship of surface structures, description of active centers and reaction mechanisms as well as deactivation as an important tool to understand catalytic processes needed for an advanced catalysts application have not yet been defined to a satisfactory extent. The causes of deactivation of DeNOx catalysts are therefore clearly of great interest and investigations focus on various aspects pertinent to developers in both the academic and the industrial realm.

The acceleration of the DeNOx reaction via heterogeneous catalysis usually presupposes adsorption of at least one of the reaction partners to form products in a further step which should be desorbed completely. Investigations on SCR reaction kinetics have revealed that the steps involving the reaction of NO with NH_3 can be described with acceptable accuracy using a hyperbolic modeling technique based on Eley-Rideal [1]. By applying a different set of parameters to this model, the reaction can also be described in the presence of water vapor concentrations exceeding 4 vol.%. This model also supports the mechanistic suggestion of a pronounced adsorption and a weal deposition of NO on the catalyst. The Langmuir-Hinshelwood mechanism, by contrast, presupposes a reaction between adsorbed NH_3 and adsorbed NO. The relative importance of these mechanisms in SCR catalysis is currently open to conjecture because without isotopically-labeled reaction partners, for example, it cannot be clearly demonstrated which of the adsorption locations are ultimately responsible for the selectivity of the SCR reaction. Chen et al [2] describe the SCR mechanism by chemisorption of NH_3 on Brönsted sites, binding NO to the chemisorbed NH_3 and then desorption of N_2 and H_2O, followed by oxidation of a surface hydroxyl group to a vanadyl group. It has been pointed out that the SCR activity is directly related to the Brönsted acidity of the catalyst. Even though water is a product of the SCR reaction, the effect of accumulated adsorbed water vapor on SCR reactivity is to weaken the Brönsted acidity and hence decrease the SCR reactivity. Comparison of poisoned catalysts, both dry and wetted, has validated this concept. In the case where SO_2 had a promoting effect, it was attributed to SO_2 increasing the Brönsted acidity of the surface.

By contrast, F. C. Lange et al. [3] postulate the lack of Lewis acid sites, on which the adsorption of ammonia takes place, in a context possibly connected with the loss of SCR activity. The results were obtained from titania supported tungsten oxide and molybdenum oxide catalysts. This unavoidably opens the discussion of the deactivation steps in which there is competition for adsorption sites required by the SCR reaction path.

The reaction partners which compete for these adsorption sites are ultimately substances contained in the flue gas. Flue gas constituents are primarily dependent on the fuel itself and plant conditions. The harmful compounds have been subdivided into groups of alkali metal oxides (i. e. Na, K, Cs, Li, Mg), heavy metal oxides (i.e. Pb, Se, Cd), sulfur dioxide, chlorides, phosphorous and arsenic oxides. In terms of their heavy metal content, low-ash hard coals clearly differ from high-inerts coals and brown coals [4]. Potential flue gas emissions can be influenced by combustion control (temperature, dwell time), fly ash grain size distribution, enrichment of metals in the grain fractions and the degree to which a given fraction can be removed by flue gas cleaning measures. These considerations must, in addition to combustion control, also allow for the dust removal technique used and thus overall metal emissions. It is evident that a number of variable factors determine which flue gas constituents the catalyst is exposed to.

Volatile constituents which can act as catalyst poisons have an impact on catalyst activity and selectivity. In the performance of causality investigations, a distinction between these effects and those which are merely mechanical blockage of the active catalyst surface by deposits which either partially or completely impair access of the SCR reaction partners to the catalytically active surface. Compounding of these two effects, as is the case with flue gases containing arsenic, only indicates that there is an exponential correlation between arsenic oxide adsorption and the relative activity constant k/k_o for supported vanadium oxide catalysts when exposed to As_2O_3 [5]. Attempts to explain the deactivation by loss of surface area turned out to be unsatisfactory [6], because decreasing activity and surface area cannot be readily correlated. Here it was determined that catalysts based on tungsten oxide are deactivated more rapidly than catalysts based on molybdenum oxide.

Owing to its limited detection depth of only a few atomic layers, X-ray photoelectron spectroscopy (XPS) was considered the method most suitable for analyzing the elements adsorbed by catalyst. Apart from weak arsenic and sulfur signals, no elements were initially identified in the overview spectrum. However, increases in the arsenic Auger signals between 1210 and 1220 eV can be observed with increasing exposure time. All catalyst specimens contaminated with arsenic after power plant exposure exhibit doublet peaks in the region of the $L_3M_{45}L_{45}$ signal [7]. The signals for arsenic were attributed to the valence numbers +3 and +5 due a physical mixture of As_2O_3 or As_2O_5 and the catalyst before exposure to flue gas. After about 400 h exposure time, the titanium fraction has decreased to almost just over a third of its initial value. Since this does not change after further exposure, it was assumed that the catalyst surface contamination process had been completed. Surprisingly, this does not apply to the elements sulfur and arsenic. By contrast this proves that arsenic deposits originate, at least from this point in time onward, exclusively from the gas phase, since the arsenic entrained by the flue dust would otherwise result in an increase in X_{si}. The surfaces not accessible for surface sensitive XPS analysis due to their convolution in deeper layers were investigated with X-ray absorption spectroscopy (XAS) after power plant exposure [8]. The arsenic absorption edge in the XANES range was attributed to pentavalent arsenic by investigation with reference compounds (As, As_2O_3, Ag_3AsO_4, $KAsF_6$ and As_2O_5). As^{5+} detected with XAS can also be detected with XPS if the catalyst surface is mechanically removed and deeper layers of the catalyst bulk are exposed for analysis. It was postulated that As^{5+} is bound as isolated arsenate to TiO_2 (anatase) by surface hydroxyl groups. It was not possible to directly demonstrate the presence of a W-O-As or Mo-O-As compound with XAS techniques. Despite formation of pentavalent arsenate from As_2O_3, tungsten remains hexavalent. The same applies to molybdenum. Its adsorption edge and energetic level after exposure to arsenic remain unchanged [8, 9]. But the number of Lewis sites detected by adsorption of ammonia decreases after exposure of TiO_2 supported tungsten oxide or molybdenum to arsenic oxide. Poisoning of the samples leads to the formation of a new type of hydroxyl group while the original hydroxyl groups disappear [3, 9]. In spite of the lack of evidence the chemical interaction between arsenic and molybdenum involving oxygen, As_2O_3 was mixed with MoO_3 in a separate experiment and allowed to react at 430°C in fused quartz ampoules. Single crystals of $MoAs_2O_7$ were taken from this material, which comprises $As_4Mo_3O_{15}$ [10], MoO_3 and $MoAs_2O_7$ [11]. This experiment was repeated in the presence of titania. It was necessary to gear the mixing ratios to the detection threshold of X-ray diffraction and thus these data were unavoidably outside the range of industrial SCR catalysts.

The formation of V-O-As was examined and referred to hydrated vanado (IV) and vanado (V) arsenates. The reduction of V_2O_5 to $VO(AsO_3)_2$ caused by As_2O_3 can be suppressed in the temperature range between 360 - 500°C [12] if MoO_3 is added to V_2O_5. Powder mixtures of MoO_3 and V_2O_5 were melted in quartz ampoules [13]. The mixing ratios were chosen such that they correspond to those of industrial SCR catalysts. The phase composition was analyzed before and after the As_2O_3 reaction. It was not possible to detect a crystalline composite oxide phase in which As is involved. As the carried oxides V_2O_5 and MoO_3 are highly dispersed, it was not possible to investigate these changes on the TiO_2 (anatase) surface for industrial SCR catalysts by means of X-ray diffraction analysis.

With respect to these results, Siemens has developed a plate-type catalyst which is especially suitable for applications downstream of high-grade coal furnaces and for extreme service conditions, such as for high-dust and erosive-dust flue gases. The catalyst material and design in terms of the deactivation phenomena has been optimized to improve catalytic efficiency. Empirical results demonstrate that such measures are necessary to achieve acceptable operating behavior and have also been reported elsewhere [14].

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OP-12

ANALYSIS OF PLATE-TYPE MONOLITH SCR-DeNO$_X$ CATALYSTS

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Introduction

The SCR technology for the abatement of NO$_x$ from power plant flue gases by means of ammonia as reducing agent is based on the use of monolithic catalysts. The literature has widely addressed the analysis of the SCR reactor with honeycomb-type monoliths[1]; instead, comprehensive studies about the behavior of plate-type SCR catalysts have not been reported yet, probably due to the the absence of a standard approach in the lab-scale test and analysis of these systems. Both honeycomb and plate-type monoliths are characterized by the two-dimensional repetition of an elementary cell, the channel; this has typically a square section in the case of honeycombs but an odd-shaped geometry (the section is composed by a rectangular and a sine portion, as shown in Figure 1) in the case of plates. The former configuration has small channel openings (3 - 6 mm); this makes the commercial honeycombs suitable to a reduction in size down to a scale (3x3, 4x4 channels) which is compatible with laboratory testing but is still representative of the full scale behavior. In principle, this allows the direct utilization of the activity data for pilot or indutrial design of the SCR reactor. On the contrary, in the case of plate-type catalysts only pilot-scale testing preserves the original geometry.

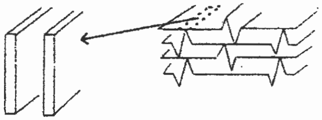

Figure 1- Test-slabs vs. industrial plate-type catalyst.

On a laboratory scale, the plates have to be cut in small slabs and the channel geometry is altered. This raises two issues: (i) the evaluation of intrinsic activity data from such an idealized configuration, (ii) the development of a methodology for estimating the overall performance of the catalyst under industrial conditions. In this work, a systematic lab-scale study of commercial plate-type catalysts is presented; the investigation involved both the DeNOxing performances and the activity in the oxidation of SO$_2$ to SO$_3$ of the plates, tested in the form of slabs. A kinetic treatment which accounts for the effects of trasport phenomena associated with the specific design of the testing reactor is developed and estimates of the intrinsic kinetic parameters are provided. Finally, evaluation of the plate performance inside an industrial reactor is attempted.

Activity testing and kinetic analysis.

The activity of different commercial plate-type catalysts in the DeNO$_X$ reaction and in the oxidation of SO$_2$ to SO$_3$ has been extensively investigated. Two slabs of catalysts, as shown in Figure 1, were placed inside the test reactor to form three parallel channels with rectangular cross-section. Evidence has been collected about the dependence of NO conversion and SO$_3$ formation on the major operating variables: temperature, Area Velocity, feed composition. A model of the SCR process inside the testing reactor has been developed, based on the following assumptions: (i) the partitioning of the total flow rate in the three reactor channels is controlled by the distributed pressure losses, (ii) mass transfer in the channels is analogous to heat trasfer in rectangular ducts with two or three adiabatic walls (corresponding to the non-reactive walls of the testing unit), (iii) the $DeNO_X$ reaction rate is represented by Eley-Rideal kinetics (reaction between adsorbed ammonia and gas-phase NO), (iv) SO_2 oxidation is first order in SO_2 concentration, is inhibited by ammonia and slightly promoted by NO, (v) the $DeNO_X$ reaction is severely limited by pore diffusion, which is described according to Wakao-Smith "random pore model", (vi) SO_2 oxidation occurs in a purely chemical regime. A good match between experimental data and model calculations has been obtained and the intrinsic kinetic costants of $DeNO_X$ reaction and SO_2 oxidation have been estimated. In particular, the kinetic analysis allowed to evaluate the extents to which the catalyst intrinsic activity, its morphological characteristics and the geometrical configuration contribute to the overall performance of the plate-type catalysts herein studied. These results provided a basis for the comparison among different commercial catalysts, which is independent from the specific geometry of the channels obtained in the industrial assembling.

Evaluation of the plate performance under industrial conditions.

A preliminary estimation of the plate performance under industrial conditions can be attempted assuming a simplified channel shape with realistic dimensions. Figure 2 compares the lab-scale results with simulations based on the schematization of the real plate-type monolith in rectangular ducts with cross-section size 6x60 mm. It is shown that, for equal values of AV, the activity data obtained with test slabs tend to overestimate the real performance of the plates. This is due essentially to the short diffusion path that the reactants undergo in the test-reactor, which favors the overall NO conversion. Such results are confirmed also by a more rigorous description of fluidodynamics and mass transfer phenomena inside the commercial plates (Figure 1); this was obtained addressing the numerical solution of momentum and mass balance equations within the oddly-shaped domain of the real monolith channel using finite-element techniques.

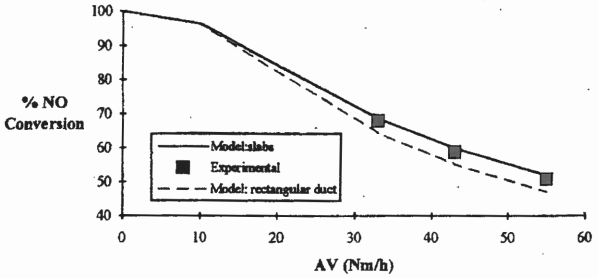

Figure 2 - Comparison of calculated NO conversions over lab-scale and industrial plate catalysts. T=350°C, NH3/NO = 1.1, NO = 500 ppm, SO_2 = 0 ppm.

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OP-13

New mechanism based on the nature of copper ion and reaction intermediates during hydrocarbon SCR of NO by Cu/ZSM-5

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Introduction : The nature of Cu/ZSM-5 during SCR of NO including the mechanistic study was extensively investigated because of importance in removing NOx. The following questions are still controversial : (1) What is the role of Cu ions for the formation of reaction intermediates, especially in the activation of hydrocarbon? (2) What is the role of carbonaceous species containing N? (3) How does the reaction between NO_2 and hydrocarbon proceed? *In-situ* XPS, IR spectra of CO adsorbed on Cu ions, TPD and micropulse study were used to answer thses questions and to propose a new mechanism.

Experimental : Cu/ZSM-5 was prepared by ion-exchange of Cu ions in aqueous solution of copper(II) acetate with Na-ZSM-5 (Si/Al = 31). X-ray photoelectron spectra were acquired in LHS 10 surface analysis system (Leybold Co.) equipped with multiplate channel detector. Cu/ZSM-5 was pretreated in the high pressure reaction cell directly mounted on analysis chamber and transferred to analysis chamber without contacting air. IR spectra were acquired during the reaction ($NO/propene/O_2$ = 3300ppm/3300ppm/6.7%) in *in-situ* DRIFTS cell connected to gas flow system consisted of mass flow controller and 4-port valve with electric actuator. After the reaction was quenched by He, IR spectra were acquired after CO adsorption at room temperature. Details of TPD and TPO studies were decribed elsewhere [1].

Results and Discussion : Figure 1 shows the IR spectra of CO adsorbed on Cu(I) after reaction at various temperatures. The band of CO adsorbed on Cu/ZSM-5 pretreated with He only at 773K was appeared at 2157cm^{-1}. A new band was appeared after SCR reaction at 2136cm^{-1}. As shown in Table 1, the intensity of IR peak at 2157cm^{-1} increased with temperature, but that of peak at 2136cm^{-1} increased up to 350°C and then decreased. XPS results indicated that at 350°C, Cu(I) ion was oxidized to Cu(II)-oxygen species, which was decomposed with Cu(I) and O_2 above 773K. This explains why the activity of Cu/ZSM-5

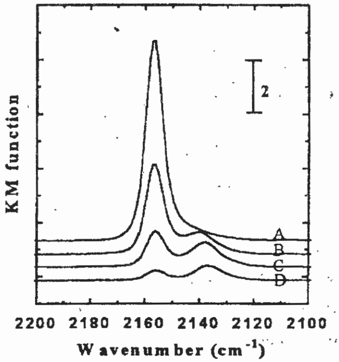

Figure 1. DRIFT spectra of CO adsorbed on Cu/ZSM-5: after the reaction at (a) 773, (B) 673, (C) 623 and (D) 523K

Table 1. Normalized peak areas of IR absorption peaks of adsorbed CO.

Normalized Peak Area	SCR Reaction Temperature (°C)			
	250	350	400	500
peak at 2136cm^{-1}	0.12	0.17	0.16	0
peak at 2157cm^{-1}	0.04	0.21	0.45	1

catalyst decreased above 773K. There exist two kinds of Cu ions during SCR reaction. Since these Cu ions have a different redox properties, these species are distinguished from each other in the role for SCR of NO. It is suggested that the Cu species corresponding to 2157cm^{-1} are responsible for activating NO to NO_2 and those corresponding to 2136cm^{-1} are responsible for activating hydrocarbon according to results of Shpiro *et al.* [2] and Masai *et al.*[3].

When Cu/ZSM-5 pre-reacted with NO/propene/O_2 at 673K was reacted with NO and O_2 at 673K, NCO species and NO_2 could be present on the different kinds of sites suggested by fore-mentioned IR result. The rate of increase in the normalized intensity of the peak assigned to NO_2 is higher than the decreasing rate of peak corresponding to NCO species as shown in Figure 2, indicating that vacant Cu(II) sites producing NO_2 from NO and O_2 are present and that NCO species are slowly converted to N_2, CO_2 and H_2O. Our micropulse study indicated that NO_2 species present on Cu ions are reduced to N_2 by propene even in the absence of oxygen. Our TPO results showed that carbonaceous species containing N are produced on the catalyst in the presence of oxygen. Based on these results, a new two-site mechanism (Cu and Cu* ions) is suggested as follows:

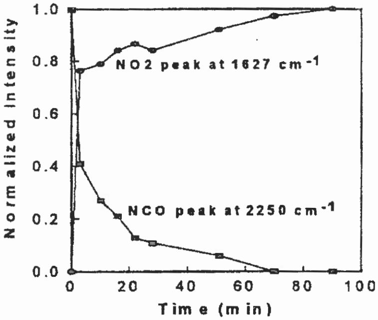

Figure 2. Intensity of IR bands at 1627 and 2250 cm^{-1} as a function of reaction time at 673K between surface species produced during SCR at 673K and NO/O_2

$Cu(I) + O_2 \leftrightarrow Cu(II)\text{-}O$
$Cu(II)\text{-}O + NO \rightarrow Cu(II)\text{-}NO_2$
$Cu(II)\text{-}NO_2 + C_3H_6 \rightarrow Cu(I) + N_2 + CO_2 + H_2O$
fast

$Cu^*(II) + C_3H_6 \leftrightarrow Cu^*(I)\text{-}CxHy$
$Cu^*(I)\text{-}CxHy + O_2 \rightarrow Cu^*(I)\text{-}CxHyO$
$Cu^*(I)\text{-}CxHyO + NO \rightarrow Cu^*(I)\text{-}R\text{-}NCO$
$Cu^*(I)\text{-}R\text{-}NCO + O_2 \rightarrow Cu^*(II) + CO_2 + N_2 + H_2O$
very slow

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OP-14

Zeolites Grown on a Metal Carrier - a New Low-Pressure DropDeNOx Reactor Packing

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Introduction

To assess the feasibility of zeolites as deNOx catalyst, it is not sufficient to study activity, selectivity and stability alone. Attention should also be given to the way the zeolite crystals are to be incorporated in the reactor. Standard techniques to contain zeolitic crystals in reactors are not suitable for industrial NOx removal. Zeolite crystals themselves are too small to be applied without some kind of binder. Normally, zeolite crystals are pelletized in an amorphous matrix. However, when these pellets are too large, much of the catalyst is not used, due to diffusion limitation. When, on the other hand, pellets are too small, an unacceptably high pressure drop over the reactor would result.

An elegant solution to this problem is to fix zeolite crystals to a geometrically well defined support, such as a monolithic structure. In this way a low pressure drop, high catalyst activity and dustproof operation are obtained. Instead of glueing the zeolite crystals to the surface by means of a washcoat, it has been shown possible to grow zeolite crystals *in situ* on a stainless steel support[1,2]. This technique has been shown successful for ZSM-5 and mordenite[3]. In this work we describe the preparation of this novel type of reactor packings covered with zeolite beta (BEA).

Synthesis

Packings were produced by cutting strips of fine meshed AISI 316 stainless steel gauze, measuring 0.04 x 1m. These strips were thoroughly cleaned by boiling in ethanol, followed by a treatment in hydrogen peroxide solution. The strips were rolled up and placed in Teflon lined autoclaves, filled with a synthesis mixture of the following molar composition: $Al_2O_3/SiO_2/OH^-/H_2O/R_2O$ = 1/100/15/1140/15. R represents the template molecule used: dimethyl-dibenzyl ammonium chloride, according to a patent of Rubin *et al.*[4]. Synthesis temperature was 135°C and synthesis time was five days, during which the autoclaves were rotated. After synthesis, the strips were rinsed with water and dried. The increase in weight was *ca.* 2 %, at a total weight of 8.30 g.

The strips were subsequently calcined in air at 550°C. Cupric ions were introduced by exchange in a 0.01 M cupric acetate solution for four hours, during which the solution was refreshed four times.

Results

Figure 1 shows a SEM picture of one wire of the covered gauze (diameter=35 µm). It was found that gently scratching the surface did not destroy the zeolite layer. Also the thermostability was investigated by submerging a sample of the produced packing from an oven at 100°C directly into boiling nitrogen. The crystals remained firmly attached to the surface.

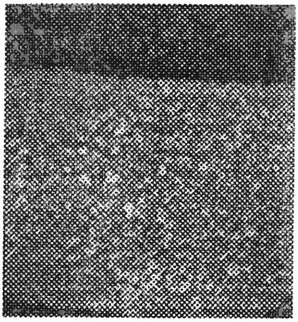

***Figure 1** SEM picture of a wire covered with zeolite beta. Diameter of the wire is 35 µm.*

Direct XRD measurement of the packing did not produce sensible results, the layer of zeolites being too thin. However, XRD measurement of particles collected from the resulting synthesis mixture matched the calculated BEA XRD pattern. Further characterization was done by comparing FT-IR spectra of crystals on the packing, to those of zeolite beta powder. Nitrogen adsorption measurements yielded a BET surface of 400 $m^2/g_{zeolite}$, which agrees with data found in literature[5].

From ICP-AES analysis the Si/Al ratio was found to be 42. The Cu/Al ratio was 3.2, this figure probably being too high due to cupric acetate solution remaining on the packing after ion exchange.

Catalytic Testing

A Cu-BEA packing was tested as a deNOx catalyst using ammonia as reductant:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

The equipment used consisted of an internal recycle reactor, ensuring good contact between the gases and the packing. A gas mixture of the following composition was introduced in the reactor, using mass flow controllers: 100 ppmv NO, 1000 ppmv NH_3 (excess), 5 vol% O_2 and balance nitrogen. The space velocity based on zeolite crystal volume was as high as $2.7 \cdot 10^6$ h^{-1}. Measurements were done at temperatures from 150 to 350°C. The conversions measured are given in Figure 2.

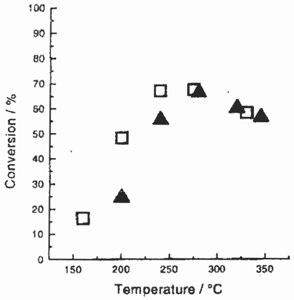

Figure 2 NO conversions at GHSV = $2.7 \cdot 10^6$ h^{-1}. □: first run up; ▲: second run up

Maximum conversion was 70% at 270°C, which is high at the given GHSV. Depending on the shape of the structured packing and the covering of the zeolite crystals, the GHSV in its conventional definition, *i.e.* based on the total volume of the reactor embodying the packing, will be lower. For example, for a packing shaped in 'metal monolith' form with 600 cpsi it will be 10800 h^{-1}.

The zeolite coverage of the tested packings was relatively low (1.56 g/m^2). Optimization of the synthesis conditions has led to a coverage improvement by a factor of 10.

Current Work

At the moment we investigate larger packings covered with *in situ* grown ZSM-5 zeolite in a large flow setup. Important conclusions so far are that it is possible to produce large stable packings with a homogeneous *in situ* grown zeolite covering and that these packings show a high activity for deNOx reactions.

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OP-15

OXIDATION OF CO AND REDUCTION OF NO BY CARBON MONOXIDE AND PROPENE IN THE PRESENCE OF OXYGEN ON COPPER-CONTAINING ZEOLITE CATALYSTS

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It is known at present that catalysts obtained from base metals on zeolite supports are characterised by high efficiency and are proposed for processes of NO reduction by carbon monoxide and hydrocarbons.

The results of NO reduction by carbon monoxide and propene or their mixture at different oxygen concentrations and of CO oxidation on copper-containing catalysts, supported on silicone nitride blocks produced at ISM of Ukrain Academy of Sciences ($S_{sp} \approx 1$ m^2 /g, square channels – 1.4×1.4 mm, wall thickness 0,4 mm, bulk weight 0,57÷0,64 g/sm^3, free section - 70%) are represented in this papers. Synthetic ZSM-5 zeolite, natural zeolites of clinoptilolit type from Ust-Kamenogorsk (UK), Chan-kanai (Chk) and Sary-Ozek (SO) deposits of the Kazakhstan were used as secondary supports.

Supporting on blocks 11-12% of secondary support (5-10 mm dispersity) was carried out by 5-7 fold impregnation from suspension in aluminium- or silicon-containing binders. The reactions were carried out in a flow reactor at a space velocity of $(25\div35)\cdot10^3 h^{-1}$ and a linear increase of temperature from 100 to 450 °C. Concentrations of CO, C_3H_6 were determined using GIAM-15 and NO – 344XL-01 gas analyzers.

Study of the influence of the method of preparation of 3% copper catalyst on zeolites supported on Si_3N_4 on the activity has shown that 70% oxidation of CO is achieved already at 180-200 °C on specimens prepared by impregnation of the support by the mixture of the aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ with dodecane. Using sorption impregnation from the same solution increases this temperature by 80-180 °C. The efficiency of 3% Cu contacts depends on the nature of secondary supports, and $T_{\alpha_{CO}}$= 70% increases in the following order independently of the binder: ZSM-5(180°) ≤ UK(200-220°) ≤ ChK(200-240°) ≤ SO(230-240°).

The reduction of NO on a copper contact on Chk zeolite supported on Si_3N_4 with an aluminum-containing binder has shown the reduction rate to increase with temperature and to be 100% at 450 °C and O_2 concentration from 0 to stoichiometric one (0,11.% by vol.). Further increase in $[O_2]$ hinders the reduction of NO, whereas the conversion of CO increases reaching 99% in the oxidation area. The "window" of oxygen (Δ) concentration in which simultaneous cleaning of the mixture from CO and NO by $\geq$ 70% is provided, is 0,15. The temperature of NO reduction by carbon monoxide up to $\geq$ 70% on 3% Cu catalysts on different secondary supports increases in the following order:

ZSM-5 (285°) $\leq$ Chk (300°) $\leq$ UK (340°) $\leq$ SO(425°).

Use of propene as NO reductant increases Δ to 0,30 at 450 °C. At stoichiometric $[O_2]$ the reduction of NO by propene up to 70% occurs at a higher temperature (415°C) than for CO (300 °C) due to difficulties in propene activation.

Study of NO reduction by CO+C_3H_6 mixture on 3% Cu/Chk/Si_3N_4 catalyst has shown the conversion of all toxic components by 70% at 450° to occur at 0,94 to 1,21% vol.(Δ=0,27) O_2 concentration. At a stoichiometric content of oxygen, NO is reduced by 70% at 390 °C and CO and C_3H_6 are oxidized at 350°.

Thus use of propene or its mixture with CO as a reductant of NO extends Δ two times at 450 °C and increases the temperature of 70% conversion of CO, NO, C_3H_6 at $[O_2]$ stoichiometric ($\alpha \to 1$) by $\approx$ 100°.

KINETICS OF SELECTIVE REDUCTION OF NO BY PROPANE ON Cu-ZSM-5 HONEYCOMB MONOLITH CATALYST

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Recently, many efforts were focused on investigation of reaction of selective catalytic reduction (SCR) of NO by propane on various metal-containing catalysts. Among wide type of catalysts investigated in this reaction considerable attention is attracted to copper-containing zeolites, especially Cu-ZSM-5. This catalyst has been used as a model system in many different studies. Using such well-defined catalyst to study a new catalytic system has several advantages, for instance, that it can help to minimize uncertainties in the experiments at the beginning stage and to optimize the selection of experimental parameters and also that experimental results can be easily related to its known properties. So the kinetic of reagents interaction upon catalyst surface was studied in detail on Cu-ZSM-5 [1]. The data concerning structure of surface intermediates [2] and the analytical dependencies for the reaction rate as functions of reagent's concentrations were obtained. For the most part of papers the reaction was studied in kinetic region though in practice diffusion regimes were usually used.

In the present work we have studied the kinetic of SCR NO by propane in the presence of oxygen on the honeycomb monoliths with various channel cross-section. The honeycomb monoliths were prepared from copper exchanged zeolite (Cu-ZSM-5, 1.3% Cu, Cu/Al=0.28) that were done by the traditional ion-exchange procedure between H-ZSM-5 (Si/Al=19.5) and aqueous solution of copper acetate (0.07M) and by solid-phase synthesis. In latter case the mechanic mixture of zeolite and copper carbonate was calcined at 750°C.

The dependencies of the reaction rate as a function of reagent's concentration and temperature have been obtained in kinetic, diffuse and transition regions. The comparative analysis of the data obtained has been carried out on honeycomb monoliths and grain of catalysts. Influence of geometry of the monoliths on heat- and mass-exchange as well as on activity and selectivity of catalyst has been studied.

The mathematical kinetic model of SCR NO with propane describing experimental data in wide range of conditions has been developed.

The estimation of applicability of the model for selective catalytic reduction of NO by propane in real exhaust gases has been carried out.

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OP-17

New DeNOx Concepts and Configurations for Power Plant Applications

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Of the post-combustion NOx control techniques available for reducing emissions from fossil fired power plants, selective catalytic reduction (SCR) or selective noncatalytic reduction (SNCR) have been used most extensively. In addition to these measures, which in the meantime have become the established state-of-the-art, new concepts and configurations are currently being tested and operated. This essentially involves a modified arrangement of the catalyst material in the flue gas path and combining various NOx control techniques. Four distinct hybrid SCR plant concepts are presented and the experience gathered in actual power plants discussed. As this approach to overall high efficiency and low-cost NOx control does not require additional space for a stand-alone SCR reactor, it is especially well suited to those power plants which require retrofitting under restricted space conditions.

DEVELOPMENT OF THE METHOD FOR PREPARATION OF WASHCOATED MONOLITH CATALYSTS FOR SCR NO_x BY AMMONIA

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Selective catalytic reduction (SCR) of NO_x by ammonia is an efficient method of exhaust gas purification from NO_x . The oxide systems V_2O_5-TiO_2 [1], CuO-TiO_2 [2], ion exchange zeolites Cu-ZSM-5 [3], Co-ZSM-5 [4], etc. are the examples of high-activity catalysts for this process. In spite of the numerous studies in the field of monolith catalysts made of bulk active components there is less information on synthesis and structural studies of supported or washcoated on ceramic monolith catalysts. In [5] the catalyst samples were prepared by washcoating active component on a metal monolith.

In this work we present the results on the development of the method for preparation of the washcoated SCR-catalysts based on ceramic monolith honeycomb support. The washcoating layers contained the active phase or served as a raw material for its formation. Various oxide and zeolite-containing systems [1-4] were used as active phases.

It has been shown that when the washcoating layers based on V_2O_5-TiO_2 and CuO-TiO_2 are used it is preferable to prepare an active phase before the formation of secondary coating. In the case of Me-zeolite-containing catalysts it is advisable to perform ion exchange after the secondary coating application, sample drying and calcination.

The method for testing attrition resistance of washcoated monolith honeycomb supports and catalysts has been developed. It was shown that the proposed procedure for preparation of washcoated catalysts ensures high attrition resistance of secondary layers.

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Session C

HIGH TEMPERATURE MONOLITH SYNTHESIS

PL-5

Hexa-aluminate Materials for High-Temperature Catalytic Applications

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ABSTRACT

Hexa-aluminates are representatives of a broad range of structurally related layered metal oxides having the general formula $BAl_{12}O_{19-x}$, where B is a divalent or trivalent cation (e.g., Ba^{2+}, Sr^{2+}, and La_{3+}). Hexa-aluminates are of current scientific interest for their use in high temperature catalytic materials because of their crystal structure comprising of spinel-like blocks separated by mirror planes containing large cations. The crystal growth occurs slowly by stacking of each spinel block along c-axis which strongly influences retention of high surface areas at elevated temperatures.

The method of preparing hexa-aluminates (e.g. hydrothermal, sol-gel, nitrate precipitation, combustion, etc) also influences their surface area and ultimate catalytic activity. Based on an extensive review of the materials previously prepared as well as those prepared by the authors, we discuss the effects that crystal chemistry and method of preparation have on the phase distribution, catalytic activity, and surface area of these materials at high temperature.

A survey of previous hexa-aluminate synthetic approaches indicates that a variety of cations can be substituted for both the B-site and Al-sites in the $BAl_{12}O_{19-x}$ general hexa-aluminate formula. For example, some of the compositions relevent to catalytic applications included $BaMn_bAl_{12-b}O_{19-x}$, $Ba_{1-a}K_aMnAl_{11}O_{19-x}$, $Sr_{1-a}M_aMnAl_{11}O_{19-x}$ (M = La^{3+},K^+, or Ca^+), and $LnMAl_{11}O_{19-x}$ (Ln = trivalent lanthanide cation; M=Mg^{2+}, $Mn^{2+/3+}$, $Fe^{2+/3+}$, Ni^{2+}, Cu^{2+}).

Depending on the composition, the crystal structure of hexa-aluminates generally fall in two categories: magnetoplumbite (MP), typified by $PbFe_{12}O_{19}$, and β-alumina (β). Both the MP and β-hexa-aluminate structures consist of spinel blocks made up of Al-site cations separated by intermediate mirror plane layers which contain the relatively larger β-site cations. In the ideal MP structure, the mirror plane consists of an β-site cation, an Al-site and three O^{2-}anions.

The specific aspects of the hexa-aluminate crystal chemistry that influences whether the MP of B form is stabilized are still not completely clear. The ionic radius and valence of the β-

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site cation may be significant contributors. However, accommodation of the β-site cation in the mirror plane of the MP structure may also be partially accomplished through distortions of the coordination environment of the Al-site cations occupying or near the mirror plane. It is interesting to note that the substitution of one of the Al-site cations in B $BaAl_{12}O_{19-x}$ with M^{2+}/M^{3+} transition metal cations stabilizes the MP $BaMAl_{11}O_{19-x}$ phases (M= transition metal). Similarly, although $KAl_{12}O_{19-x}$ occurs as the β structure, $KMnAl_{11}O_{19-x}$ is stable as the MP structure. The phase distribution, surface area, and base catalytic activity of hexa-aluminates are greatly influenced by these crystal chemistry effects. However, to date, even a rudimentary understanding of the effects of crystal chemistry on the properties of these materials has not yet been obtained.

For materials used in catalytic applications, it is often tempting to initially assume that the catalytic activity of a material should scale with its surface area. However, for the sol-gel prepared $BaMAl_{11}O_{19-x}$ hexa-aluminates (M= Cr^{3+}, $Mn^{2+/3+}$, $Fe^{2+/3+}$, $Co^{2+/3+}$, and Ni^{2+}) calcined at 1300°C for 5 hours, there was no apparent correlation between the surface area of a material and its catalytic activity. Various researchers have suggested that the base catalytic activity of these hexa-aluminates were more appropriately dictated by the redox chemistry of the transition metal used in their formulation rather than surface area of the material.

Fixing the redox chemistry of sol-gel prepared hexa-aluminates by substituting Mn for Al in $Ba_{1-a}M_aMnAl_{11}O_{19-x}$ (M= K^+, La^{3+}, and Sr^{2+}) and $Sr_{1-a}M_aMnAl_{11}O_{19-x}$ (M= K^+, La^{3+}, and Ca^{2+}), we have found that there was a strong correlation between the surface area of the hexa-aluminate after calcining at 1300°C for 5 hours and its average β-site cation field strength: decreasing the field strength produced a significant increase in surface area. We believe that increasing the field strength of the β-site cation increases the stability of the mirror plane and hence increases the tendency for hexa-aluminate crystal growth along the c-axis with a concomitant decrease in surface area.

These and other issues concerning the chemistry, structure, and properties of hexa-aluminates will be presented and discussed.

OP-19

THE USE OF THERMOCHEMICAL TREATMENT FOR IMPROVEMENT OF HEAT RESISTANCE OF METAL BLOCKS SERVING AS CATALYST CARRIERS IN TAIL GAS NEUTRALIZATION SYSTEMS OF INTERNAL COMBUSTION ENGINES

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The switch-over from ceramic catalyst carriers to more promising metal carriers (metal blocks) in fumes neutralization systems of internal combustion engines is hampered by a number of technical and economic factors. Among others, two main problems can be distinguished: development of a workable efficiently doped metal strip (foil) with a high heat resistance at temperatures up to 1200 °C and creation of an efficient technology for strengthening of the blocks by brazing or welding.

A thin (50 μm) foil is produced from FeCrAl alloys containing (15-23) mass % Cr and up to 5 mass % Al. A further increase in the aluminum content in order to improve heat resistance of the foil and extend the service life of the metal blocks is associated with great technological difficulties. The proposed solutions of this problem (for example, cladding or aluminizing of a semi-rolled foil, rolling of a multilayer semi-rolled foil and subsequent vacuum annealing, or sputtering of aluminum on the foil surface) considerably increase the cost of the foil and, ultimately, of the metal blocks. A possible option to the above-mentioned methods used to raise heat resistance of the metal blocks is a thermochemical treatment (aluminizing) of the foil in the ready metal blocks.

The researchers at the Institute of Metal Physics RAS and the Ural Electrochemical Plant have performed a series of systematic studies into aluminizing of metal blocks in fluorine-activated gaseous media. The choice of a contactless gas aluminizing method where metal blocks do not touch the saturated powder mixture has been substantiated experimentally. Using this method, it is possible to saturate with aluminum cellular products having intricately shaped ducts and simultaneously ensure a high quality of the foil surface. We have analyzed saturation of thin foils made of X15IO5, X20IO5 and X23IO5 alloys and the block shell made of the 12X18H10T steel depending on the aluminizing temperature and time, the powder mixture composition, and the presence of a carrier gas. The studies have led to optimization of the technology for saturation of the metal blocks in their shells, providing a through aluminizing of the foil accompanied by formation of a qualitatively new material with (8-10) mass % Al.

The main problem encountered in aluminizing of full-scale metal blocks is to ensure a more uniform saturation of the foil with aluminum in different cross-sections of the block. We have designed a laboratory installation, which allowed a flow-through gas aluminizing of the metal blocks using a neutral carrier gas (helium or argon). A weak flow of the gas (~3-6 l/min per metal block) provides conditions for transport of gaseous aluminum compounds along the ducts in the metal blocks and removal of gas reaction products from the reaction zone. As a result, the aluminum concentration gradient in the aluminized strip along the block does not exceed 2 %. After aluminizing the foil acquires heat resistance properties, which are 5 to 8 times higher than those of the starting material.

More over, aluminizing in the activated gas atmosphere leads to diffusion welding of the corrugated and flat strips at their contact points. Put another way, in addition to improvement of heat resistance, two more problems are solved: strengthening of the cellular structure of the block and welding of the structure to the shell. The structural strength (axial displacement resistance) is close to that of the brazed block. Dilatometric measurements showed that after aluminizing the difference in the thermal expansion coefficients of the X20IO5 alloy and the 12X18H10T steel decreases from 30 % to 10 %. As a consequence, heat resistance of the welded joint between the strip and the shell is largely increased.

THE SHORT-TERM IMPREGNATION AS AN ADVANCED TENDENCY IN TECHNOLOGY OF CERAMIC MONOLITH HONEYCOMB CATALYSTS

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Method of impregnation for carrier is basic in technology of ceramic monolith catalysts. Conventional method of impregnation is characterized by resistance of porous structure of carrier material to impregnation process, incomplete utilization of solution components and a long time of impregnation procedure [1]. Indicated limitations may be easily eliminated by realizing the impregnation procedure under partly submersion of carrier to solution under definite impregnation volume (short-time impregnation) with following impregnation by water or water-alcohol mixture, if necessary.

It is believed, that under common version of monolith carrier impregnation, metal oxide distribution takes place in uniform manner upon altitude of carrier and its average concentration is calculated by traditional methods. In case of partial submersion of carrier into solution its volume sufficiently quickly is impregnated by salt solution and additional impregnation or well-known procedure of curing water drying will allow much part of salt solution to migrate in direct to top section of monolith block.

Additional impregnation stimulates process of initial impregnation and promotes nonuniform distribution of active components (metal or its oxides) through the carrier volume. In these conditions ratio of oxides concentration on monolith border (top to bottom) as the factor of irregularity (F) exceeds 2,5-3. Previously developed simple gravimetric method permits to calculate metal oxides concentration for any part (point) of monolith block with honeycomb structure [2].

Proposed technology permits to regulate and control catalyst composition along the height of carrier, holds true universal versatile nature and therefore may be use for preparation of any catalyst of definite composition on ceramic carrier. Due to singularity of honeycomb structure essential economy of active ingredients can be obtained (on the first place of noble metals) without general index of catalyst activity lowering.

OP-20

At our point of view the new technology may be applied with success for preparation of monolith catalysts for neutralization of exhaust gases of gasoline motors. Taking into account specificity of complex cleaning of exhaust gases, when oxidation and reduction of topical ingredients of gases should be realized within the length of one monolith of honeycomb structure, the necessity is appeared to concentrate active components (metal oxides) at definite part of carrier.

The short-time impregnation was tested at preparation of real catalyst for exhaust gases neutralization, when active components were promoted by microadditives of palladium dioxide. Nonuniform deposition of palladium dioxide along the carrier height (F=3.5-4) led not only to noble metal economy, but also to decrease of operation temperature of neutralization per 40-50 °C, thus increasing final degree of carbon monoxide conversion.

The experiments with real exhaust gases show, that on catalyst containing zirconium dioxide as second support and palladium dioxide as promoter (0.008% mass. and 0.06% mass) the effect of carbon monoxide oxidation degree rising during passing of exhaust gas across such monolith catalyst in the direction of promoter concentration growth takes place. Possible explanation of this effect may be the increasing of palladium active centers number on the direction of cleaning gas motion and reduction of unreacted amount of carbon monoxide (by the principle of "vers-flow" in the system gas - active centers) at the same time.

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Session D

INDUSTRIAL APPLICATION OF MONOLITH CATALYSTS AND SUPPORTS

MONOLITHIC HONEYCOMBS IN INDUSTRIAL CATALYSIS

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The necessity to accommodate low pressure drop at high gas hourly space velocities, as in the catalyst systems for auto-exhaust emission control, led to the development of monolithic honeycomb catalysts. Ceramic monoliths with a washcoat layer on it, containing the active catalytic component, have become an integral part of the underside of tens of millions of automobiles on the road today. The monolith geometry and its modifications are seeping in into some other catalytic processes also, notably for NOx abatement by selective catalytic reduction (SCR) and for catalytic combustion (CC) [1-5]. SCR is a curative solution, while CC is a preventive solution, to the NOx problem.

Metal monoliths are produced by rolling alternate plain and corrugated sheets of steel or other alloys, while ceramic monoliths are often made by extrusion. Metal monoliths have the inherent superiority of higher thermal conductivity and mechanical strength, greater resistance to thermal shocks and mechanical jerks or vibrations, lower pressure drop due to thinner walls, and possibly higher cell density.

For applications as in low-temperature or high-temperature catalytic combustion, we have selected a special alloy steel (Fecralloy) monolith, the surface of which is fully covered by whiskers of alpha-alumina. These ceramic whiskers provide a firm reinforcing and anchoring (up to 1270 K) for a washcoat layer brought over the monolith, reducing the tendency of the washcoat otherwise to crack, blister or chip off [5-7]. The sol-gel technique is eminently suited to bring down a washcoat layer on the metal (or ceramic) monolith. Colloidal sols, being a suspension of nanometre-scale solid particles in an aqueous medium, have the following unique advantages: a) ready availability of sols of various particle sizes and of different materials such as silica, alumina, zirconia, and titania; b) the possibility to control the surface area, porosity, washcoat thickness, thermal stability and such properties by simple preparation techniques, as shown by Zwinkels et al. [6-7]; c) the use of water as a medium implies easy and safe handling and avoiding the hazards of organic solvents or metal alkoxides.

PL-6

The controllable properties of a washcoating gel, in particular the surface area and thickness of the resulting washcoat, strongly influence the ultimate catalytic activity. Hence the activity of a monolithic catalyst can be fine-tuned for optimal performance. A multi-monolith catalyst system can be tailor-made to have progressively increasing or decreasing catalytic activity from the reactor inlet to the outlet and thus bring a more desired temperature profile over the whole catalyst bed. Such applications should be possible not only for the extreme conditions demanded as in catalytic combustion for gas turbines, but also for exothermic processes at relatively milder conditions such as catalytic combustion of VOC's and selective and partial oxidation or hydrogenation in hydrocarbon processes. This could be a new handle to control the temperature profiles and selectivity in fixed bed operations and to prevent hot spots or run-away temperatures. The inherently higher thermal conductivity of metal monoliths is always an advantage. In endothermic reactions as in steam reforming, this results in a higher conversion than that in a comparable packed-bed operation. In steam cracking to produce olefins and aromatics, even an inert ceramic insert in the cracking coil can lead to a better heat transfer and a higher conversion than in the normally empty coil. Some other recent developments on the use of monolith catalysts will also be presented in this survey.

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HYDROGENATION OF SUNFLOWER METHYL ESTERS USING A NICKEL-BASED MONOLITHIC CATALYST

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INTRODUCTION: The dominating industrial process for vegetable oil harding uses slurry batch reactors with nickel catalysts. A high selectivity for hydrogenating trienes and dienes compared to monoenes is usually required. Reaction conditions favoring high selectivity will also favor high net formation of *trans*-isomers from the naturally found *cis*-isomers. A low level of *trans*-fatty acids in the product is preferred, as they are suspected to have the same effect on humans as saturated fats, *i.e.* increase the likelihood of cardiovascular diseases.

External mass transfer of hydrogen is often rate limiting for the slurry batch process, and the monolithic catalyst may therefore be an alternative. The effect of internal mass transfer limitations can be avoided by using thin layers of washcoat. Both higher selectivites and higher productivity (per m^3 reactor) may be achieved by using a monolithic reactor, as well as better integration with the continuous steps in the margarine production.

Many natural oils contain compounds that poisons the hydrogenation catalyst, and especially sulfur-containing compounds may reduce the activity severely. Using fixed bed reactors, it is important to avoid strong poisoning of the catalyst or to find a way to regenerate the catalyst, preferably *in situ*.

EXPERIMENTAL: Methyl esters of sunflower oil (ME-SF) were hydrogenated in monolith catalysts with cocurrent downflow of ME-SF and hydrogen. The hydrogen was internally recirculated, while the ME-SF was recirculated through an external loop. The reactor was operated in batch mode with respect to the ME-SF. The monolithic catalysts tested were prepared by washcoating corderite supports (400 cpsi) with α-alumina. The α-alumina powder had previously been impregnated with a $Ni(NO_3)_2$-solution and calcinated. The nickel content was measured by AAS and the dispersion of the metal by CO-adsorption. The catalyst was reduced *in situ*, for 14 hours at 425°C in pure H_2, before the first experiment in the series. Various different methods were used in order to regain the same initial activity for the catalyst after an experimental run.

The reaction temperature was 60-180°C, and the hydrogen pressure was varied between 2 and 5 bar.

Catalyst deactivation due to sulfur poisoning was studied by adding small amounts of allylisothiocyanate (AITC) to the reactor during an experiment.

RESULTS: The nickel catalyst produced higher amounts of *trans*-isomers at high temperature and low hydrogen pressure. The selectivity for hydrogenating the diunsaturated methyl esters *vs.* the monounsaturated methyl esters also increased at high temperatures and low hydrogen pressures. The activity of the monolithic catalyst decreased with repeated use despite using different methods for reactivating the catalyst.

External mass transfer was not rate limiting at the experimental conditions used, but internal mass transfer was rate effecting at high loadings of nickel and/or a thick washcoat layer.

Repetitive additions of AITC were made to the same monolithic catalyst under several hydrogenation experiments. When the sulfur compound was added in an amount less than the estimated number of surface nickel atoms, only a small and temporary decrease in reaction rate could be observed. The reaction rate decrease considerably only when the sulfur compound was added in larger amounts than the equivalent number of free metal atoms did. The net formation rate of *trans*-isomers was higher for the catalyst after exposure to AITC. After poisoning, the activity of the catalyst could be partly restored, and the "reactivation" was possibly caused by reduction of oxidized Ni, and not by removal of sulfur or sulfur compounds from the poisoned catalyst.

A model based on Langmuir-Hinshelwood type of kinetics was fitted to the experimental data. Based on the experimental results, the performance of a full-scale monolithic catalyst reactor used for the hydrogenation of edible oils was simulated in a computer program. The external and internal mass transfer was modeled, and the simulations predicted higher productivity per m^3 reactor than the conventional stirred batch reactors.

OP-22

LIQUID-PHASE METHANOL SYNTHESIS IN MONOLITH REACTOR

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Monolith Reactors have been extensively applied in many fields such as automotive exhaust's purification, industrial tail gas treatment, and fuel combustion. Liquid-phase methanol synthesis process has been developed in several kinds of chemical reactors such as slurry-column reactors and fluidized-bed reactors as well as trickled-bed reactors.

Compared with a conventional trickled-bed reactor and a slurry reactor as well as a fluidized-bed, the advantage of the monolith reactor is the both internal and external mass transfer resistances are low, no entrainment of the catalyst can arise, and pressure drops in the monolith reactors are very low. Cybulski et al. developed a mathematical modeling of a monolith reactor in liquid-phase methanol synthesis. The modeling simulated the 'monolith' process for various solvents such as tetraglyme (tetra ethylene glycol dimethyl ether), Witco 40 oil and so on and for different operation conditions. The results of the modeling showed that the productivity of the monolith reactor in liquid-phase methanol synthesis was superior to other reactors. Thus, we believe that the monolith reactor is an attractive alternative of other kinds of chemical reactors in liquid-phase synthesis.

Liquid-phase methanol synthesis experiments are performed at 50 bar and 523 K in a monolith reactor. After measuring, mixing, and heating, hydrogen, carbon monoxide, and carbon dioxide gases are put into the reactor. After being compressed to 50 bar and heated to 523 K, liquid flows through monolithic catalyst cocurrently with gaseous reactants. After reaction gas-phase mixture is separated from liquid and then goes to a GC for analysis. Liquid phase is depressurized and then flashes in order to separate product methanol and other gaseous components absorbed in it. Then liquid cycles back into the reactor. Methanol concentration in liquid is analyzed both before and after flashing. Various liquids, such as tetraglyme, Witco 40 oil, are chosen as solvents absorbing reaction heat and product methanol. Different rates of hydrogen to carbon (carbon monoxide + carbon dioxide) are tested.

Experimental results are discussed and compared with results of Cybulski 's modeling.

OP-23

CATALYTICAL-SORPTIVE REMOVALOF SULFUR DIOXIDE USING CARBON MATERIALS

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One of the most effective method of low concentrated sulfur dioxide removal from air is a catalytical sorption, wich allows not only to clear gases, but also to rid of secondary pollutants and to get a sulfuric acid as a collateral product. The application of carbon materials for the purpose of this process is restrained by low durability and reception complexity of entire carbon monolith sorbents. In this report an opportunity of using of active carbon layers upon ceramic monolyth carriers for catalytical-sorptive removal of sulfur dioxide from air is considered.

The research of sulfur dioxide sorption upon carbon sorbents was carried out in a tubular flow reactor. The UV-spectrophotometric analysis of a gas phase was used. The process was carried out under isothermal conditions.

The outlet sulfur dioxide concentration curves were received as a result of experiments. In view of influence of replacement of air from reactor they were used to evaluate true outlet curves and sorbtive-kinetical characteristics of the process. The evaluation was carried out using the model developed for the given process under the appropriate boundary conditions.

Samples of carbon, put on ceramic honeycomb and foam carriers were used. An active carbon has been put on by two ways. On the first variant, the active carbon was fixed upon a surface of the ceramic carrier by resin and then was thermodestructed in vacuum. On the second variant, the carbon was growed by catalytical hydrocarbon pyrolysis upon nickel.

The kinetics of catalytical hydrocarbon pyrolysis upon a surface of monolith carriers was investigated. It was shown, that the amount of covered carbon can be controlled by amount of nickel compounds.

As a result of experiments it was found out that the best adsorption on all samples is observed in temperature range 98÷105 °C. An adsorption practically linearly grows with increase of carbon amount produced by catalytical hydrocarbon pyrolysis. From received outlet curves for each moment of the time adsorption rate and mass-transfer factor were determined.

For samples, synthesized by binding of active carbon, the adsorption correlates with amount of active carbon, used for synthesis and practically does not depend on amount of carbon, formed by resin binding pyrolysis.

It was found out, that in the case of external diffusion the Nusselt criterion linearly depends on Reinolds criterion both for foam samples, and for honeycomb ones.

Conclusions

- The samples with carbon materials put on ceramic monolith carriers were synthesized. The kinetics of catalytical hydrocarbon pyrolysis on nickel compounds was investigated. It was shown, that the amount of covered carbon can be controlled by nickel compounds amount.
- For investigated samples the greatest sorption capacity is on samples with fiber carbon received by catalytical propan pyrolysis on nickel compounds put on a surface by a homogeneous precipitation method.
- The sorption capacity is directly proportional to active carbon amount on a sample;
- Optimum temperature is 98÷105 °C;
- Flow diffusion mass transfer is described by the criterion equation $Nu=A+B*Re$

OP-24

THE METHANE STEAM REFORMING UPON HONEYCOMB AND FOAM-STRUCTURED NICKEL CATALYSTS

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The peculiarities of methane steam reforming upon nickel foam and honeycomb catalysts are discussed in this report. An influence of the support and way of catalyst preparation on its activity is shown.

The basic industrial way of the hydrogen production for synthesis of ammonia, methanol, fuels etc is a catalytical reforming of a natural gas. As a rule the nickel catalysts are used for these processes.

Now the granulated catalysts are used for this process in industry. The active component of this catalysts does not have high specific activity. The probable ways to increase the catalyst specific activity is using of the monolith catalysts. These catalysts have wide application in various chemical processes. It is possibly to use a monolith catalysts for the methane steam reforming.

In this research the alpha-alumina foam and honeycomb carriers were applied. The catalysts samples activity in the methane steam reforming was studied at atmospheric pressure in the laboratory flow reactor in temperature range 550÷900 °C, at steam/methan ratio 1,9÷9,1 and at volumetric flow rate range 5000÷70000 h^{-1}. The original software is used for analysis results processing, for material balance calculation and for kinetic parametres evalution. The calculated values of apparent activation energy and pre-exponential parameter of Arrhenius equation correspond to known values.

Conclusions:

- The methane steam reforming upon all samples of monolith catalysts is determined by the chemical kinetics.
- There are separate groups of dependences of the catalyst activity on active component concentration. They are determined by method of the active component coating and type of catalysts carriers.
- The maximal degree of an active component using is reached upon foam-structured catalysts, which have a surface site of an active component and maximum diffusion limitations decrease.
- The maximum catalytic activity is reached upon the samples synthesized by a homogeneous precipitation from solutions, which determine the allocation and distribution of an active component.

PL-7

APPLICATION OF MONOLITHIC REACTORS IN MULTIPHASE CATALYTIC PROCESSES IN THE CHEMICAL PROCESS INDUSTRY

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Multiphase reactors are commonly applied in the chemical process industry. The two major fields of application are hydrotreatments in the petroleum industry and liquid phase hydrogenations in chemicals manufacture. Trickle-bed reactors are commonly used for hydrotreatment, though main drawbacks are pressure drop and potential maldistribution. The slurry reactor is the workhorse in the fine chemicals industry. Its major drawbacks are the problems of scale-up and catalyst separation.

A systematic comparison will be presented between conventional technology, i.e. slurry and trickle flow reactors, and monolithic reactors. It will be shown that in many respects monolithic reactors are potentially superior. A limitation is, however, that experience is very limited and that, as a consequence, design rules hardly exist. Specific attention will be given to the problem how to feed a system of channels with dimensions in the mm range. It is clear that a thorough hydrodynamic analysis is essential. Included in the discussion will be the option to carry out the reaction in a mode not possible for packed beds, viz., the countercurrent mode. In theory, this way of operating has distinct advantages.

A number of examples of practical relevance will be treated, in particular the potential for monolithic reactors in selective hydrogenations will be illustrated. These will include selective hydrogenation in the Fine Chemical Industry, Pygas hydrogenation, hydrodesulfurization, hydrodearomatization. Furthermore, potential applications will be discussed for reactions where catalyst deactivation resulting from unfavorable kinetics plays a dominant role. It will be shown that dependent on the kinetics structured reactors might be the best solution.

OP-25

Hydrodynamics of the Down-Flow, Gas-Liquid Monolithic Reactor

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Scope

The development of design rules for the gas-liquid monolithic reactor operated in co-current down flow. The design rules include: even distribution of gas and liquid, scale-up, operating flow rates, start-up procedures and catalyst configuration (stacking).

Introduction

Monoliths used in Chemical Engineering are porous blocks which contain a large collection of parallel channels, running all the way through the material. The interior of the channels of monoliths is frequently covered with a catalyst-impregnated washcoat (porous oxide), to provide a large surface area for reaction.

Monoliths can provide attractive alternatives to trickle-bed and slurry-column technologies. Obvious advantages of monolithic reactors are the absence of on-line solids handling, low pressure drop and high geometrical-surface-to-volume ratios. Furthermore, a feature unique to monolithic packings is the linear nature of the bed, which prevents all redistribution of gas and liquid. This can greatly enhance the safety of some exothermic catalytic processes that are conventionally performed in trickle-bed reactors. So far, inexperience with gas-liquid distribution in monolithic reactors has been a major disadvantage.

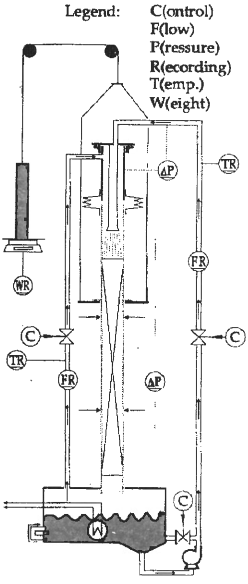

Fig. 1 Experimetal set-up

Experiments

The monoliths used here are made of cordierite (extruded ceramics) and contain channels of square cross-section, with an hydraulic diameter of 1.1 mm. Some 2,500 steady-state measurements of pressure drop and liquid holdup were performed using *air/water* in monoliths of 0.15 to 0.76 m long. The novel way of on-line holdup measurement, using the weight of the monolith (Fig. 1), proved very valuable, for it allowed the quality of the gas-liquid distribution to be determined experimentally.

Homogeneous distribution of gas and liquid was achieved using a shower-type liquid distributor, provided the superficial liquid velocities were sufficiently high (Eq. (1)). Under such ideal conditions, a naturally occurring aerated liquid layer on top of the monolith provides virtually perfect distribution of liquid from 109 jets into 4800 monolith channels.

OP-25

Results

Assuming a constant bubble-rise velocity of 0.136 m s^{-1} and a minimum liquid holdup of 0.45, the following condition for the occurrence of a stable foam layer on top of the monolith was derived:

$$u_{LS}/(\mathrm{m\ s^{-1}}) > 0.079 + 0.82\ u_{GS}/(\mathrm{m\ s^{-1}}). \qquad (1)$$

The criterion is valid for all measurements preformed. It ensures *continuity of the liquid phase* at the entrance to the monolith, which is synonymous to the occurrence of a foam layer. Furthermore, the presence of a foam layer allows monoliths to be stacked with spacings in between subsequent sections. The foam layer that appears on top of every monolith down the line, ensures the even distribution of gas and liquid.

The frictional pressure drop in monoliths is raised significantly by the presence of gas bubbles in otherwise liquid-filled channels. The additional pressure drop is caused by two mechanisms:

1 - the laminar liquid velocity profile inside a channel is flattened at every interface with a gas bubble, causing larger velocity gradients and increased wall shear and

2 - gas bubbles are deformed on entering a monolith channel, which causes additional drag.

Accounting for both effects, the pressure drop in a single channel was modelled successfully. When gas and liquid are evenly distributed (i.e. Eq. (1) is satisfied), all channels behave identically, and the single-channel pressure drop is representative for the monolith as a whole.

Hydrodynamic stability is determined by the condition

$$\partial(-\mathrm{d}P/\mathrm{d}L)/\partial u_{LS} > 0 \qquad (2)$$

It implies increased resistance to flow at increased liquid flow rates. Regions where Eq. (2) is not satisfied (greyed-out in Fig. 2) are characterised by reversed flow in some channels. This is indeed observed in the experiments. The reversed flow destroys the initial distrubution of gas and liquid and is to be avoided in practice.

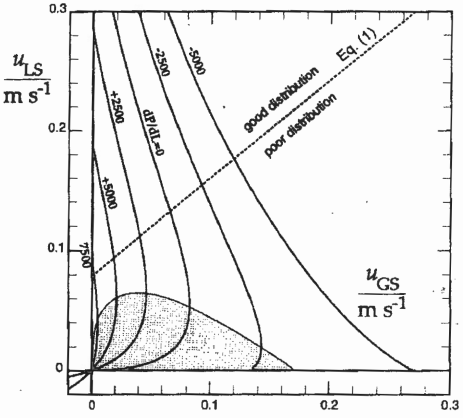

Fig 2 Design map for air/water flow in monoliths

Conclusions

1) Hydrodynamics are the key to the design of monolithic gas-liquid reactors.

2) A liquid-continuous foam layer can be used to achieve uniform distribution of gas and liquid.

3) Unstable regions of operation exist that will destroy even a perfectly homogeneous initial distribution of gas and liquid.

OP-26

Development of Laboratory Reactors for Testing Monolithic Catalysts in Liquid-Phase Hydrogenations

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Introduction

Conventional reactors for liquid-phase hydrogenations are fixed-bed and slurry reactors. The monolith technology forms an interesting alternative. A monolithic catalyst provides low pressure drops, large external surface areas and short diffusion distances. Due to the high regularity of the monolith structure, a uniform liquid distribution is possible which substantially can reduce the risk of hot-spots and run-aways.

A monolith reactor is typically operated in the Taylor flow regime (see also Figure 3). Gas and liquid pass the channels in alternating slugs, which are separated from the wall by a thin liquid film. This film provides low axial dispersion and low mass transfer resistance from the gas/liquid interface to the catalytic wall. Mass transfer is further enhanced by the forced circulation within the liquid slugs.

Scale-up of a monolith reactor is, in principle, straightforward. A uniform and stable distribution of the fluid over the cross-section of the monolith can be realized by creating a froth layer on top of the monolith (1).

The overall objective of this work is to demonstrate the feasibility of using monolith reactors in the selective hydrogenation of aromatic aldehydes to their corresponding alcohols. Important aspects are the kinetics and the mass transfer characteristics, and dedicated laboratory reactors have been developed.

Internal recycle reactor

The Screw Impeller Stirred Reactor (SISR, see Figure 1) is a multi-purpose reactor for catalyst performance testing. The monolith is placed in the annular space between the inner and outer tube. A screw impeller is used to circulate gas and liquid through the monolith. At a sufficiently high impeller speed a froth layer is formed on top of the monolith.

The reactor is also suitable for slurry experiments. For this purpose the inner part of the reactor is replaced by a conventional stirrer and baffles.

The first reaction studied is the selective hydrogenation of benzaldehyde to benzyl alcohol. The adequate operating conditions are determined by checking the influence of the liquid loading and the stirrer speed on the reaction rate (see Figure 2).

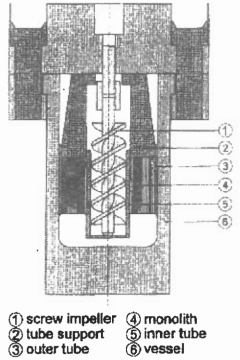

Figure 1: Screw Impeller Stirred Reactor

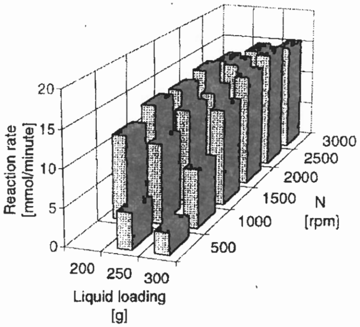

Figure 2: Determination of adequate operating conditions

External recycle reactor

In order to study mass transfer characteristics under reaction conditions a so-called Taylor set-up has been developed. The reactor containing the monolithic catalyst consists of a long narrow tube (see Figure 3). Liquid enters the reactor through a perforated plate. In this way a uniform liquid distribution can be realized. A displacement pump is used for the recirculation of the liquid, giving flexibility in the frequency and the amplitude of the pulsating flow. The window of stable and uniform flow is established.

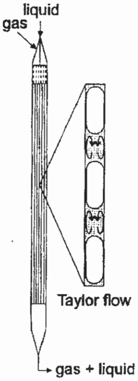

Figure 3: Reactor of Taylor set-up

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Study of massive and metal foam supported perovskite catalysts by IR spectroscopy

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It is well known that perovskites with $LaCoO_3$ as active component possess high activity in methane oxidation. Monolith perovskites can be successfully applied in combustion processes with high gas flows. Perovskite catalysts supported on honeycomb type or foam supports exhibit good mechanical strength and show low pressure drop and, therefore, will perform successfully in combustion processes.

This work is devoted to the preparation and investigation by IR spectroscopy of massive and metal foam supported perovskite catalysts. Impregnation techniques and polymer coating methods were applied to deposit the $LaCoO_3$ catalyst on a Ni foam surface [1], whereas massive $LaCoO_3$ catalysts were synthesized by use of a co-precipitation technique. The adsorption of CH_4 on a massive $LaCoO_3$ catalyst was studied by FTIR, while NO and CH_4 adsorption on $LaCoO_3$ catalysts supported on Ni foam were studied by DRIFT. In this latter case the special DR cell was designed to allow the study of the perovskite catalysts supported on metal foams without changing the original geometry of catalysts. NO adsorption was used to characterize the surface properties of the supported perovskite catalysts. The data on adsorption of methane on supported perovskite catalysts are also very important as these catalysts are developed for the application in methane combustion processes.

The NO adsorption at room temperature has revealed that there are two types of active centers in $LaCoO_3$ catalysts supported on metal foams both by impregnation and polymer coating techniques. IR spectra of adsorbed NO on perovskite catalyst synthesized by polymer coating techniques included two bands: a band at 1920 cm^{-1} relating to the NO adsorption on high valence cations and a band at 1610 cm^{-1} which can be assigned to nitrates. The IR spectrum of adsorbed NO on perovskite catalyst synthesized by impregnation technique also consisted of bands related to the NO adsorbed on high valence cations (1925 cm^{-1} band) and nitrates (1625 cm^{-1} band). However, it was revealed that the surface of catalysts synthesized by impregnation technique is covered by strongly bound carbonates. Treatment of catalysts in oxygen at 500°C and outgassing at 700° C led to the partial destruction of carbonates. The IR spectrum of adsorbed NO on treated catalyst included a band at 1630 cm^{-1} relating to nitrates. A band corresponding to adsorption of NO on high valence cations was shifted to lower wavenumbers region (1900 cm^{-1}) while a new band at 1800 cm^{-1} appeared. These changes in IR spectra can be related to the appearance of highly reduced cations after application of the treatment described above.

The CH_4 adsorption at low temperatures (-100°C) on the massive $LaCoO_3$ perovskite indicated the presence of two bands (3016 and 1506 cm^{-1}) in the IR spectrum corresponding to the stretching and bending vibrations of methane in the gas phase respectively. Further treatment of the sample in methane led to the appearance of a 3008 cm^{-1} band corresponding to physically adsorbed methane and to a decrease in the relative intensity of the bands at 3016 and at 1506 cm^{-1}. The adsorption of CH_4 at elevated temperatures (150-550°C) did not show significant changes in IR spectrum in the range of absorption of carbonate complexes because of the presence of strongly bound carbonates on the catalyst surface that could not be destroyed by pretreatment. However, the heating of the catalyst up to temperatures higher than 350°C led to the appearance of bands in the range of 2300 – 2360 cm^{-1} which can be related to the vibrations of carbon dioxide. The IR spectrum of $LaCoO_3$ catalysts supported on metal foam by means of impregnation technique consisted of bands corresponding to gas phase methane only. Other species were below the detection limit due to the presence of strongly bound carbonates on the catalyst surface as well.

In conclusion, IR data show that there are two types of active centers in perovskite catalysts supported on metal foam. The interaction of methane with perovskite catalysts proceeds via physical adsorption. Noticeable interaction of methane with the catalyst leading to the formation of reaction products is found to start at 350°C. The detailed description of the mechanism of the methane interaction with catalysts under experimental conditions was difficult due to the presence of strongly bound carbonates on the surface of perovskite catalyst.

Acknowledgement. The research was subsidized by a grant of the Dutch Organization for Scientific Research, NWO, in a R & D programme established between the Netherlands and the Russian Federation.

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ON THE METHOD FOR DETERMINATION OF METAL OXIDE CONCENTRATION THROUGH MONOLITH CERAMIC CARRIER

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As a rule, amount of metal oxide on carrier is determined by means of well-known gravimetric analysis or by decreasing of concentration of active components in the solution of impregnation, taking into account increment of initial carrier mass. The active component considers to be distributed uniformly over total volume of carrier. But in reality the active ingredients, such as metal oxides, are distributed along the carrier far from regularity. Common method of calculation does not make it possible to define and control alternate catalyst composition along the monolith carrier height.

We proposed a simple method for determination of oxide metal concentrations in any part of carrier on the preparation stage [1]. The basis of our method is well-known regularity that decomposition of dry salt to solid phase (oxide) (a) and gas phase (c) is realised according to stoichiometric rule for a given salt. As consequence the stable interrelation takes place between (a) and (c) as

$$K=a/c \qquad (1)$$

Taking into account the equation $A+D=(A+a)+c$ the relation for calculation of the amount of metal oxide (q) after impregnation from single component solution is:

$$q_i=a/(A+a)=K[(A+D)/(A+a)-1] \qquad (2)$$

where (A+D) - algebraical sum of carrier mass with dry salt mass, (A+a) - algebraical sum of initial carrier mass with metal oxide mass, K - factor of the proportionality for given solution. If monolith carrier is impregnated with two component solution relation 1 is used applicable for new conditions:

$$a_1=K_1\,c_1 \text{ and } a_2=K_2\,c_2, \qquad (3)$$

where K_1 and K_2 -are factors of proportionality for solutions (1) and (2), respectively; c_1 and c_2 - equivalent masses of gas phases of components (salts) 1 and 2, and a_1 and a_2 - the oxide masses of components 1 and 2. With the allowance for principle of quality additivity (values K, c, a) the relation for calculation of oxides concentration q_1 and q_2 have next final form

$$q_1=K_1/(K_1 - K_2)\{K_{1,2}[(A+D)/(A+a)-1]-[K_2c/(A+a)]\} \tag{4}$$

$$q_2=K_2/(K_2 - K_1)\{K_{1,2}[(A+D)/(A+a)-1]-[K_1c/(A+a)]\} \tag{5}$$

Thus, for both cases (eq. 2, 4, 5) it is necessary to define only the mass of oxides with carrier (A+a), the mass of carrier with dry salt (A+D), factors K_1, K_2 and $K_{1,2}$.

The analysis of relations shows, that there is no necessity for determination of initial mass of carrier before impregnation procedure. Due to this characteristics we can determine the amount of metal oxide at any part of carrier. For this purpose carrier has to be air drying after impregnation, cutting to N parts, once again air drying up to constant mass and calcinated [1]. If the carrier impregnation takes place from solution of three or four ingredients, the course of analysis is similar, but preliminary and conventionally the solution components have to be separate to two pairs (for example 1+2 and 3 or 1+2 and 3+4) with following second conventional division it to two parts.

Presented results open up possibilities for determination of distribution character of metals or metal oxides along the carrier altitude as functions of impregnation conditions, and therefore catalyst design with variable composition of active component along the carrier altitude or catalyst for the purpose of any catalytic reaction.

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Session E

FUNDAMENTALS OF LABORATORY DEVELOPMENT AND TECHNOLOGY OF HONEYCOMB MONOLITHS

PL-8

HIGHSPEED PLASMA SPRAYING TECHNOLOGY OF MANUFACTURING CATALYTIC NEUTRALIZERS AND THEIR PRACTICAL REALIZATION

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The analysis of a ecological situation of large cities of Russia shows: in spite of decrease of production volume of the industrial undertakings, the level of pollution remains high and even constantly grows.

The increase scales of pollution of atmosphere by the technological systems of an oil refining, gas and wastes of chemical industry, in condition of constant deficit of energy resources does necessary development and introduction of the most modern and effective methods of decrease of polluting by toxic substances, new functional materials and technologies of their manufacturing, which will allowed wider using for the decision of ecologycal problems and creation of highcapacity sources of energy, heterogeneous catalysts of a new type.

In CRISM "Prometey" was developed and inculcated the original highspeed plasma spraying method of catalytic covers on a base of oxide alumina, which allows creation of material with high porous and high adhesion with a surface of the catalyst carrier. This method is protected by the russian and foreign patents.

Also, in CRISM "Prometey" was projected and mastered installation BPL-500, which allows to realize a technology of felling of net various configuration and dimensions (for example, square and rhombic cell from titanium, steels of different classes, alloys on a basis of cupper and pure metals) in a tape.

The specified technology allows to produce net substrates by productive method and in a combination with technology of highspeed plasma spraying to create effective porouse and volumetric-porous catalyst of optimum structure.

We developed technology of manufacturing of block catalytic neutralizer of gaseous wastes of engines of internal combustion and industrial wastes, distinguished by high mechanical durability and efficiency, allowing to decrease toxic of gaseous wastes to 85 %; technology of manufacturing of volumetric-porous catalyst carriers for a petrochemical industry ; technology of manufacturing of chemical sources with specific power up to 350 Wt-h/kg, activated by ecologycally pure electrolytes.

OP-29

NEW MECHANOCHEMICAL METHODS FOR THE PREPARATION OF CORDIERITE AND THE CATALYSTS SUPPORTED ON THEM

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Cordierite has been used most frequently for fabrication of high-temperature-resistant supports with monolithic honeycomb structure [1,2]. It is well-known that during cordierite synthesis the intermediate product $MgAl_2O_4$ is formed increasing the temperature of cordierite production up to 1400 °C. Variation in the composition of precursor mixture does not strongly influence this process [3]. Mechanochemical synthesis of complex oxides was shown to be very effective escpecially when hydrated oxides are used [4].

The support usually has a low surface area, and a sufficiently large one is obtained by applying a washcoat the catalytically active phase can be deposited on. The aluminium, lantanum or transition metal oxides are used as a washcoat on a cordierite support [1]. Catalysts prepared with the iron (111) oxalate exhibit the higher activity than those prepared from another commercial iron compounds [5].

In the present work the mechanochemical method was applied to synthesize cordierite. Mechanical activation of the precursors was pefomed in the planetary ball mill AGO-2. After mechanical treatment the samples were annealed at different temperatures. To fabricate honeycomb the activated precursor mixture or obtained cordierite powder were plasticized, extruded and sintered at 1260 °C. The cordierite support was impregnated in the excess of different solutions, dried and heated to form active component.

As the oxide initial mixture was used, the formation of intermediate products (spinel, α-Al_2O_3, α-cristobalite, Mg_2SiO_4) was observed and no cordierite was produced at 1260 °C. The replacement of oxides in the precursor mixture on gibbsite and H_2SiO_3 resulted in the formation of cordierite with increased cell parameters and spinel impurity after annealing at the same conditions. To reduce the admixed spinel content in cordierite the preparation procedure was changed. Mechanically activated mixture of MgO and H_2SiO_3 was preheated at 1000 °C to form magnesium silicates. After that, the new portion of H_2SiO_3 and gibbsite were added to reagent mixure with reactivation in mill followed by calcination at 1260 °C. By this procedure the cordierite with ASTM cell parameters was obtained.

The commercial cordierite synthesis is known to base on employment of talc, kaolinite and gibbsite as precursors. Their mixture is calcined at 1300-1400 °C for 40-60 h. Its preliminary mechanical activation in AGO-2 followed by calcination resulted in the cordierite occurrence even at 1100 °C, the complete formation being realized at 1260 °C.

Hence, preliminary mechanical activation of the precursor mixtures in high-stress planetary ball mill during cordierite synthesis allowed to decrease the temperature and the duration of the calcination and to improve the cordierite purity.

The prepared cordierite supports with the iron oxide washcoat posses low catalytic activity in butane and CO oxidation (sample 1 in table). The supporting of Pt by impregnation with H_2PtCl_6 aqueous solution on this washcoat slightly increase the catalytic activity (sample 2). The new impregnation procedure as well as modifying of the iron oxide washcoat make it possible to rise up the catalytic activity. In this manner the highly active catalysts with low doping of noble metal or without it were obtained (sample 3-6).

Table

The rate of complete butane oxidation at 350 °C (W) and the temperature of CO-conversion x% (T_{CO}) of the catalysts on cordierite monoliths 10×10 mm

Sample	$W \cdot 10^2$	T_{CO}, °C			
	$cm^3/s \cdot g$	X = 25%	50%	75%	85%
1 - $Fe\text{-}O/St_1$*	<0.001				
2 - $Me/Fe\text{-}O/St_1$	0.006	268	278	285	288
3 - $Me/Fe\text{-}O/St_1$	1.9	190	200	205	207
4 - $(Fe\text{-}O)_m/St_1$	1.3	150	180	210	220
5 - $(Fe\text{-}O)_m/St_2$	0.23	205	240	300	370
6 - $Me/(Fe\text{-}O)_m/St_2$	0.17	195	208	214	218

*St_1 - monolith with cell size 1×1 mm, 49 cells per cm^2, surface area 0.1 m^2/g, pore volume 0.19 cm^3/g; St_2 – monolith with threeangle cell 4 mm, 4.7 cells per cm^2, surface area 0.25 m^2/g, pore volume 0.15 cm^3/g.

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OP-30

PROSPECTS OF MONOLITHIC SUPPORTS CARRIERS FOR DEHYDROGENATION CATALYST

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OAO NII «Yarsintez»

Effective catalysts are used in processes of production of important monomers for rubbers and plastics production with catalytic dehydrogenation.

Comparison of different companies processes shows that the achieved level is high and differs insignificantly. The selection of technology is defined by construction expenses. Design of reactor or facilities which depends on applying catalysts usually forms the significant part of equipment cost. Thus, in reactors of radial type, where perforate cups manufacturing demands large economic expenses, transition to block catalysts would give a possibility to reduce the equipment cost. In this connection we' ve considered some varients of constructions of reactors with fixed catalyst bed tested the blocks in ethyl benzene into styrene dehydrogenation process. One of the varients tested was the catalyst of Kazanskii engineering centre «New technologies».

T °C	KMIC catalyst		Industrial catalyst	
	X	γ	X	γ
600	11,0	94,3	65,0	96,0
620	17,7	93,6	78,0	94,5
640	26,3	92,1	84,5	93,8

X - conversion; γ - selectivity

In this concrete example not high conversion is explained by non-optimum catalyst composition and insufficiently vast surface. We are faced with the problem not only to form the block acceptable in shape and to study the behaviour of block catalyst of optimum composition in process of long exploitation, but also to solve many other questions. However, the direction is seemed to us prospective and the work will be continued.

OP-31

INFLUENCE OF Fe_2O_3 ON THE CATALYTIC ACTIVITY AND THERMOSTABILITY OF Zn - Cu - Co CONTAINING OXIDE SYSTEMS

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The high cost and deficiency of Pt containing catalysts for complete catalytic oxidation of CO and hydrocarbons prevent their wide application. The substitution of platinum catalysts by the oxide systems permits to solve the problem of motor transport exhaust gases and waste gases of industry to great extent. Earlier investigated Zn, Cu, Co oxide catalysts [1,2] supported on the metallic carrier of honeycomb structure had a catalytic activity as high as for industrial Pt containing catalysts. However, their practical use is impeded in consequence of low thermostability.

The aim of this work is to investigate the influence of Fe_2O_3 additions on the catalytic activity and thermostability of earlier investigated Zn, Cu, Co-containing oxide systems. The catalysts were prepared by the thermo-decomposition method of metals nitrates mixture. The catalytic activity was studied by the flow catalytic method. Analysis of the reaction products were carried out by chromatography. The mixture of 1% CO in the air was used as the reaction one.

The conditions of the experiment were as follows: the temperature interval 100-850°C, volumetric flow rate of gaseous mixture supply 10000 h^{-1}.

The substitution of Co by Fe atoms was shown to increase thermostability of the catalyst, but, simultaneously, it decreases the catalytic activity due to the reduction of the Co^{3+} ions quantity in the octahedral coordination. The change of Fe_2O_3 content with the initial ratio of active components being constant does not influence the catalytic activity. At the same time thermostability of the catalyst increases. The absence of the influence of Fe_2O_3 on the catalytic activity can be taken as an evidence of the fact that Fe_2O_3 is not included in the composition of the catalyst active component. According to the data of the thermographic and X-ray phase analysis Fe_2O_3 is the texture promoter, which prevents the conglomeration of the catalyst.

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HYDRAULIC LOSSES ON MONOLITH CATALYST SUPPORTS OF FOAM AND HONEYCOMB STRUCTURE

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Honeycomb catalyst supports are widely used in high-speed catalytic processes (conversion rate reaches 10^5 1/h) permitting use of catalysts on monolith supports. In spite of a superior complex of physico-chemical and hydrodynamic characteristics, such supports have an essential disadvantage: even when a filtrate flow rate is $5 \div 10$ m/sec (which corresponds to the Reynolds number $Re=10^2 \div 10^3$), the near-laminar flow mode is realized in the structure channels. This results in limiting heat and mass transfer between a gas and the catalyst. In this respect foam supports hold great advantages over hoheycomb ones. Such supports are also characterized by high specific strength, rigidity and permeability but ensure flow turbulization even at filtrate flow rates lower than 1 m/sec. This is evident from the linearity violation for the function $\Delta p/h=f(v)$ even under such conditions. Many researchers note that the flow turbulization results in the higher coefficient of external diffusion for foam catalysts as compared with the honeycomb ones.

Hydraulic losses on the honeycomb supports representing a complex of parallel-flow permanent-section channels are caused by drag friction losses, inlet and outlet resistance and may be estimated with a high accuracy using the Darcy-Veisbah equation.

Mechanism of flow braking in foam supports is more complicated. In this case hydraulic losses are caused not only by drag friction but also by losses under the stream expansion-compression and change in the flow direction in a cell. Therewith the contribution of inertia losses is predominant under conditions typical of automotive catalytic converters.

Analytical equations for hydraulic characteristics of conventional porous permeable materials, derived by simulating these structures as complexes with straight cylindrical channels, provide 1-2 orders error.

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The report presents the obtained data on the hydrodynamic characteristics of foam materials:

- experimental dependences of hydraulic losses on the structural characteristics of foam materials in various filtrate flow rate ranges;
- equations for estimation hydraulic losses on foam catalysts;
- comparative analysis of hydraulic losses on honeycomb and foam catalysts.

Preparation of honeycomb supports and catalysts via hydrolyzates and co-hydrolyzates of alkoxides.

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The preparation of oxide coatings and the preparation of honeycomb supports and catalysts are two important directions of an application of the alkoxide sol-gel process in catalysis. Oxides generated from alkoxides and their hydrolyzates have many attractive properties (purity, higher porosity and thermal stability, lower formation temperatures, *etc*).

We have been working in these two directions for some years. Polymers synthesized by hydrolysis or co-hydrolysis of different alkoxides $E(OR)_n$ (E - chemical element, for example, Al, Si, Mg, Ti, Zr; R - alkyl) were used for producing protective coatings on honeycomb supports from stainless steel. In some cases RO-groups were substituted by chelating groups for increasing hydrolytic stability of the polymers. Thin protective films (1-10 μm) were prepared by dipping the supports into solutions of polymers in different alcohols, drying at 20-100 ^{0}C and heating up to 500 - 600 ^{0}C. The cycle of coating and heating was repeated 1-5 times. The deposited ZrO_2, ZrO_2-SiO_2 and ZrO_2-Y_2O_3 coatings had good protective properties during thermoxidation of the stainless steel at 600-900 ^{0}C. Moreover, these coatings are good substrate for a deposition of alumina with high surface area because ZrO_2 is the high chemically inertness material.

Extrusion masses were obtained from mixtures of thermostable fine oxide powers (alumina, mullite, cordierite, caoline, *etc*) and from solutions of polymers in alcohols. The honeycomb supports were extruded from these masses. The rapid hydrolysis with formation of an oxide network, having binding properties, takes place when the extrusion is carried out in humid atmosphere. Organic binders, for example, methyl cellulose, may not be used in this case. The temperature of thermal treatment was at about 600 °C that is sufficient for producing strong supports.

Co-hydrolyzates of the $Si(OR)_4$-$Ti(OR)_4$ and $Si(OR)_4$-$Zr(OR)_4$ systems were modified with triethanolamine for solubility in water. Cloths or sheets from thermostable fibers (silica, stainless steel, asbestos) were impregnated with water solutions of these co-hydrolyzates, dried off at the temperature up to 100 °C and then they were corrugated at 150 - 200 °C. The honeycomb supports were collected from corrugated and non-corrugated sheets. The catalytic coatings on these supports can be supported by traditional methods, for example, by the impregnation technique. Addition of the thermodecomposed salts of the catalytically active metals to solutions of co-hydrolyzates is more comfortable. The high active honeycomb catalysts for the CO oxidation to CO_2 have been prepared by this way.

Preparation and study of thermally stable washcoat aluminas for automotive catalysts.

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Porous and thermally stable washcoating layer on mechanically strong support is an important component in both oxidative and three-way catalyst used for car tail gas cleaning. Usually for the preparation of this layer aluminas modified by La, Ce, Zr, Si etc. are used. As it was shown in [1-3] the properties of modified aluminas depend on the method of additives introduction.

In this work we present the results on the preparation and study of model systems modified by La, Ce and Zr alumina as well as of monolith supports washcoated by optimal compositions of alumina and additives.

It is shown, that lanthanum β-aluminate and perovskite type $LaAlO_3$ are formed depending on La_2O_3 concentration (2 - 12wt%), its introduction method and calcination temperature. It is known also that these compounds may serve as suitable catalysts for total oxidation.

Our data shown that ceria and zirconium are less effective additives to increase thermal stability of alumina. Nevertheless it is known that ceria stabilises the dispersion of Pt particles in automotive catalysts and zirconia allow to protect rhodium in these catalysts, and our data approve that washcoating by alumina modified by ZrO_2 is more stable for attrition.

Preparation procedure was developed for washcoating of thermally stable layers on alumina ceramic and cordierite monolith honeycomb supports. Attrition resistance of washcoated modified monolithic supports was tested by specially developed equipment and physico-chemical properties of prepared samples were studied.

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OP-35

ALUMINUM FOIL-BASED HONEYCOMB METALLOCERAMIC CATALYST

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Honeycomb metal-base catalysts are of a special interest owing to high mechanical strength and thermoconductivity. When such metal as stainless steel is used, the problem of the coating layer spallation emerges [1] due to the difference in the thermal expansion coefficients between metal and oxide as well as corrosion of metal. Among promising metal/oxide systems, alumina/aluminum pare deserves a special attention due to a higher density of oxide as compared with metallic Al. As a result, oxide layer grown on the aluminum foil has a good adhesion and protective properties. However, before any practical application, thermal stability of such oxidic layer must be improved [2]. In the work presented, this problem was solved due to detailed studies of the formation mechanism of a porous oxidic layer on the Al foil.

The preparation of the catalyst included next stages: 1) coating of the aluminum foil by the Al_2O_3 layer in the course of the anodic-spark oxidation (ASO) [3]; 2) deposition of the secondary oxide layer from suspension containing aluminum hydroxide; 3) thermal stabilization of the washcoat by impregnating with salts of the rare-earth elements; 4) supporting of the active component. The honeycomb structure was shaped by stacking flat and corrugated sheets of foils (thickness ca 0.3 mm) either into a rectangular monolith or winding them into the Arkhimed spiral. In such way triangular channels ca 3x3x3 mm were formed. The catalyst has the apparent density ~1ml/g. The catalytic activity in the reaction of butane (steady state concentration of Bu in air 0.2 vol.%) and CO oxidation (300^0C, initial concentration - 1 vol.% of CO in air) was determined in the batch-flow kinetic installations. The process of the oxide layer formation was studied by using scanning electron microscopy (BS-350 "Tesla").

At the very beginning of ASO the dense, nonporous, thick (3-5 mm) oxide layer on the surface of foil was found to appear. This layer was not continuous: a part of the surface was covered by disordered layer with a microblock, disordered structure. Within such regions cylindrical pores and cracks are visible. These pores could be the current channels where microarcs are generated [3]. As the time of oxidation increases, lateral growth of a dense oxide layer occurs without any appreciable change of its thickness. When all surface is covered by a dense layer, a density of pores and microcracks declines. Across the layer, the oxide layer thickness remains nonuniform being somewhat lower at the boundaries where pores are concentrated. After this stage moisture capacity of the composite is equal ~0.07 ml/g and specific surface area ~0.1 m^2/g . After deposition of alumina on the support from suspension meso- and microporous structure was formed. After this stage the water capacity of the composite was 0.15-0.20 ml/g and specific surface area ~5-7 m^2/g. The impregnation of the oxidic layer by salts of the rare-earth elements allowed to stabilize porous structure even after calcination up to 700^0C for 2-6 h. The obtained metalloceramic was used as a support for active components based upon platinum metals and/or transition metal oxides (see Table):

Catalyst (support)	Active component	Activity, $W\cdot10^2$ (ml butane/g s) after calcination at			
		600^0C		700^0C	
	(wt.%)	400^0C	500^0C	400^0C	500^0C
Honeycomb (stainless steel)	Pt (0.12)	0.3	2.1	0.2	2.0
SHPAK-0.5 (alumina)	Pd (0.5)	1.5	4.1	1.5	4.1
Honeycomb (Al_2O_3/Al)	Pd (0.2)	1.4	7.9	0.4	4.8
	MnO_x (2.5)	1.5	4.6	0.1	1.2

As can be seen from the Table, the metalloceramic-based catalysts have very high activity and satisfactory thermostability as compared with values typical for stainless steel and aluminas support. A degree of CO oxidation over Pd-containing metalloceramic catalyst changes from ~100 to 89% as the space velocity increases from 50,000 to 300,000 h^{-1}. The catalyst is also stable to corrosion in water vapor (18 h, 500^0, 42 vol.% H_2O) , the activity being unchanged, and is stable for a heat shock up to 900^0C.

Hence, the catalyst developed may be promising for processes of the exhaust gas purification at temperatures up to 700^0C , especially for diesel engines, as well as for other processes, where the alumina supported catalysts are used.

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CATALYSTS FOR NEUTRALIZATION OF GASEOUS WASTES FROM AUTOMOBILES

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For improvement of ecological situation with gaseous wastes from automobiles block type catalyst are widely employed. One of them is the catalyst on the basis of high porosity cellular materials (HPCM), such as nickel, chromium, ceramics, etc. [1,2]. HPCM posses good physico-mechanical properties: permeability according to GOST 25283-82 is 10^{-8}- 10^{-3} m^2, porosity 85÷95%, compression strength 0.2÷100 MPa, density 0.1÷1.5 g/cm^3.

Catalysts are produced through applying on HPCM a layer of gamma-alumina with modifying additions (oxides of rare-earth elements) and catalytically active phase of platinum group (Pt, Pd, Rh and its compositions) metals.

An efficiency of catalysts with platinum-rhodium active phase to gaseous wastes from automobiles was tested in automobiles 1G-2126, VAZ-21072, GAZ-24-10 in regime of oxidation without capacity of addition air at warm up state according to procedure of ECE N 83 (15-04). It appears to be 80÷100% to CO, 75-99% to CH, 35-90% to NO_X, 55-90% to CH+NOx. Service life of catalyst is 80000 km.

Tests of catalytic activity of the samples based on HPCM, carried out according to the demands of HONDA corporation, show high degree of conversion to exhaust gases (table) at volume work load 60000 h^{-1}.

Table.

Catalytically active phase on HPCM block	Conversion at 400 °C, %		
	hydrocarbon	CO	NO
Pt, Rh, La	99	96	93
Pd, Rh, La	98	97	82
Pd, Rh, La, Ce	99	97	92
Catalysts SHR-E N.E. CHEMCAT	99	96	60

On comparison with foreign catalytic blocks produced by Kemira Catalyst (Europe) and Corning Glass Works (USA) our catalysts based on HPCM has three times smaller mechanical volume for a mass of a block equal to 1 kg, and therefore its cost at equal cleaning of exhausts from hydrocarbons, oxides of carbon and nitric is less (100 USD at engine' volume up to 2.5 liters; Kemira Catalyst -200 USD; Corning Glass Works - 250 USD).

Catalytic blocks based on HPCM has specific surface 10÷100 m^2/g, content of precious metals is 0.1÷0.5 mass % for general mass of a block, working temperature for oxidation of CO is 120÷800 °C and 250÷500 °C for reduction of nitric oxides.

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POSTER SESSION

IMPLANTED ACTIVE PHASE ON SURFACE OF METAL BLOCK CATALYST IN ABSENCE OF OXIDE LAYER

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The structure of active phase implanted on surface of metal block catalyst, manufactured by methods of powder metallurgy (PM), and containing no oxide layer has been analyzed using the methods of X-ray structural analysis and electron microscopy. Catalytic activity of blocks in model reactions of toxic components neutralization in exhausted gases of automotive transport was estimated.

Relative density of carrier is 0.05÷0.15, permeability 0.000000001 m^2, specific surface 0.1÷0.5 m^2/g [I]. Average size of coherent scattering Pd areas was established: D=12÷15 nm for 0.3% Pd, D=15÷20 nm for 0.5% Pd. Maximum possible value of active surface of dispersed Pd is 40÷50 m^2/g.

On the surface of metal block carrier, containing 0.5% Pd, the single rough conglomerates of 0.8÷2 mkm size, considerable amount of dispersed particles with the sizes about 100 nm, and also more dispersed fraction with particles sizes outside of resolution REM 20÷25 nm possibilities were revealed. Particles sizes on catalysts surface with 0.3% Pd were beyond the resolution and close to sizes of areas coherent scattering.

Temperature of catalysts strikes in oxidizing reaction of CO did not exceed 120÷130°C, 80% of oxidizing took place at 300°C. Principle opportunity to disperse active phase on surface of metal block catalyst in absence of oxide layer was shown. Absence of oxide layer allows to reduce labour intensity of manufacturing and cost of block catalyst, to raise thermal stability and permeability.

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PP-2

On the mechanism of flow of carbon-black dispersions

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A technology for production of monoliths has been developed at the Omsk Department of Boreskov Institute of Catalysis [1]. The technology involves preparation of plastic paste from dispersed carbon and a binder, extrusion of it through a die of complex shape, thermal treatment of the extrudates in controlled gas media. The basic problem in designing the technology was to determine conditions for extrusion of the carbon paste providing the required shape and size of the extrudates. To accomplish this problem, it was necessary to find criteria of optimization of the carbon paste composition and of choosing the deformation regimes.

For fabrication of extrudates from inorganic catalyst mixtures, the mechanostructural class of pastes is used as a criterion for optimization of rheological parameters of molding stocks [2]. The plastic slurries of the 1 or 2 mechanostructural classes were found to reveal satisfactory adaptability at the molding stage. Although the point position at the deformation triangle provides insufficient information on the structural features of a dispersed system and its flow mechanism, that makes it inappropriate for optimization of the composition of the carbon slurries. There is an alternative approach to optimization of the composition of molding stocks using determination and analysis of flow curves of plastic slurries [3].

In terms of this approach we performed thorough analysis of deformation curves recorded using a shear plastometer with a parallel shearing plate at fixed loading within the range of shearing stress of 1.96 through 6.98 din/cm^2.

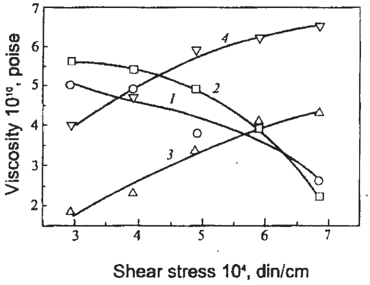

Fig.1. Viscosity of carbon-black pastes with dispersion media of various compositions as a function of shear stress

1 – water;
2 – 5% PVA dispersion in water;
3 – 6% PAA solution in water;
4 – 6% dextrin solution in water

The carbon slurries obtained by mixing carbon plack (CP), having trade mark П-514, with a dispersion medium were examined. Aqueous emulsion of polyvinyl acetate (PVA) and aqueous solutions of a linear elastic-chain polymer, polyacrylamide (PAA), or a rigid-chain polymer, dextrin, were used as the dispersion media. The concentration of CB was kept constant at 33% in all the mixtures.

Fig.1 shows two manners of behavior of carbon-black dispersions as shear increases; the viscosity may either increase (dilatancy properties, curves 1 and 2) or decrease (thixotropic properties, curves 3 and 4), that is mainly determined by the nature of the dispersed medium.

Hydrodispersion of CB (curve 1) reveals pronounced thixotropic properties, its viscosity becomes a half of the initial one under the action of the applied shear. The introduction of PVA making a stable dispersion with water results in practically no change in the rheologic behavior of the mixture under shear against the carbon black–water system. The Newtonian flow behavior is characteristic of both media, water and aqueous dispersion of PVA, that is the result of the absence of three-dimensional fluctuation cross-linking network between the molecules of the dispersion medium. As the Newtonian fluid is filled with carbon black particles to the concentration of above 30%, a three-dimensional structure is formed in the suspension due to dispersive interaction of all the paste constituents. This structure is easy destroyed under shear to cause the observed decrease in the viscosity.

The introduction of water soluble polymers, for example PAA and dextrin, in amount of above 6% to the dispersion medium produces several times increase in viscosity and arising a non-Newtonian flow behavior. That is an evidence for appearance of aggregates and associated complexes of water and the polymer in the solution. They form a rather strong coagulation structure which is not destroyed completely under shear. These speculations are also supported by the absence of a region of the lowest constant viscosity in the flow curve of PAA and dextrine solutions.

An increase in viscosity upon applying shear stress is characteristic of the flow of carbon-black pastes with the non-Newtonian dispersion media (curves 3 and 4). In this case not destruction of the initial three-dimensional structure of the carbon-black dispersion but its rearrangement, enlargement and strengthening become predominant processes, that just the reason for thickening the cross-linking network and, thus, for an increase in the viscosity under shear. It should be noticed that the flow of carbon-black pastes with a non-Newtonian dispersion medium resembles that of carbon-black dispersions in diluted rubber solutions in toluene [4].

The study of extrusion molding of monoliths from carbon-black pastes showed a satisfactory workability of dilatancy carbon-black dispersions, which provide fabrication of high quality fault-free extrudates, while the mixture composition should be optimized based on analysis of the flow curve.

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PP-3

NOVEL MONOLITH CATALYSTS AND NEW FIELDS OF MONOLITH APPLICATION

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An approach previously proposed for the preparation of monolith catalysts as composite materials allowed to synthesize a number of novel monoliths.

Monolith catalysts on the basis of vanadium/titanium composition have been developed. Zeolite ZSM-5 was introduced in the catalyst and this factor has allowed to reduce the possible ammonia slip through under possible fluctuations of the initial reagents concentrations at the expense of the additional catalyst "capacity" with respect to ammonia.

The compositions of intermediate products of radioceramic production have been studied and proposed for practical application. It has been shown that oxide composition on the basis of α-Al_2O_3 with a high concentration of organic compounds as a binder allows to prepare the monoliths with a complicated geometric shapes. In particular, the procedures of "crimping" and "designing" of monolith from separate elements have been applied as well.

The procedure has been proposed for honeycomb monolith preparation on the basis of the wastes of granular sibunit production, i.e. the "siftings" of the main production with particle size <10 mkm.

The new monoliths and previously developed ones have been approbated in a number of novel non traditional applications: monoliths as reactors for closed and resource saving biotechnological processes (enzyme immobilization, hydrocarbon bioconversion), photochemical hydrocarbon oxidation, preparation of adsorbents for potable water production from air, partial hydrocarbon oxidation.

THE CATALYSTS FOR SELECTIVE REDUCTION OF NITROGEN OXIDES IN INDUSTRIAL EXHAUSTS

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The results of the activity research of oxide catalysts, which are widely used in petrochemical processes and don't contain noble metals, and also original catalytic compositions on their basis in the reaction of selective reduction of nitrogen oxides with methane, propane, and/or carbon monoxide in the presence of oxygen are given.

In the reaction of selective reduction of NO with carbon monoxide the mentioned catalysts provide nearly full conversion of nitrogen oxide within 350÷300 °C temperature range.

The fractional conversion of NO into N_2 at reduction with propane is 90-99% at 400÷500 °C.

The results of the influence of reducer (CO or C_3H_8)/oxygen ratio on the value of NO conversion showed that at increase of the partial pressure of the reducer in the system more complete reduction of nitrogen oxide into nitrogen is observed. The reactions of hydrocarbon oxidation and conversion of carbon monoxide into CO_2 run quantitatively at 250÷500 °C temperature range. The proposed process is notable for the possibility of cleaning the gaseous exhausts with low NOx concentrations in tough oxidation conditions at high volume rates.

The worked-out catalytical systems showed high effectivity in the process of simultaneous removing of several toxic components: NO_x, CO, hydrocarbons from model gas mixtures as well as from real exhausts of automobile transport.

The possibility of applicating this catalytical system on metal block surface of comb structure with saving their initial activity was shown. The obtained results could be used for producing block catalysts for cleaning the automobile transport exhausts.

PP-5

STUDY OF THE CATALYSTS FOR BENZENE HYDROGENATION, BASED ON REINFORCED PORE-METAL SUPPORTS

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Metal supports, due to their thermal properties, in particular, high heat conductivity, show promise for the processes occurring with heat release. Using metal supports permits one to perform efficient heat pick up and eliminate the hot spots and sintering of catalysts.

The present work considers the features of the formation of the pore-metal nickel-aluminium supports reinforced with a stainless-steel net [1] and of the supported nickel catalysts based on them. We have studied the supports prepared by sintering powdered metal nickel and aluminium in the ratio of 90 wt.% Ni to 10 wt.% Al. After heating at 800°C in hydrogen flow the specific surface area of the supports is 0.5-1 m^2/g, the pore volume is 0.8-1.2 cm^3/g, and the dominant pore radius is 30-70 μm. According to the data of the X-ray phase analysis, the samples contain the phases of nickel, solid solution of aluminium in nickel and α-Al_2O_3. To increase the specific surface area and active-component dispersity, ≈10 wt.% alumina was supported on the above pore-metal sample by impregnation with the aluminium nitrate solution and its subsequent decomposition. The supported catalysts were prepared by the sample impregnation with the combined solution of nickel and chromium nitrates, followed by heating in hydrogen flow at 330°C and reduction in the nitrogen-hydrogen mixture at 400°C. In most cases the nickel and chromium oxide contents were 15 and 0.5 wt.%, respectively.

To elucidate the behavior of the supported-nickel distribution over the surface, the sample was studied by the scanning electron microscopy. It has been found that the supported nickel is distributed over the surface as a net with 0.5-1 μm long and 0.1-0.2 μm thick units consisting of the intergrown spherical 0.05-0.15 μm particles (Fig. 1a). Fig. 1b, c presents the microphotographs of the original support and the support covered with alumina, respectively.

The prepared catalysts were tested in the gas-phase benzene hydrogenation. The catalysts provide the high-efficiency benzene conversion and are of great practical interest.

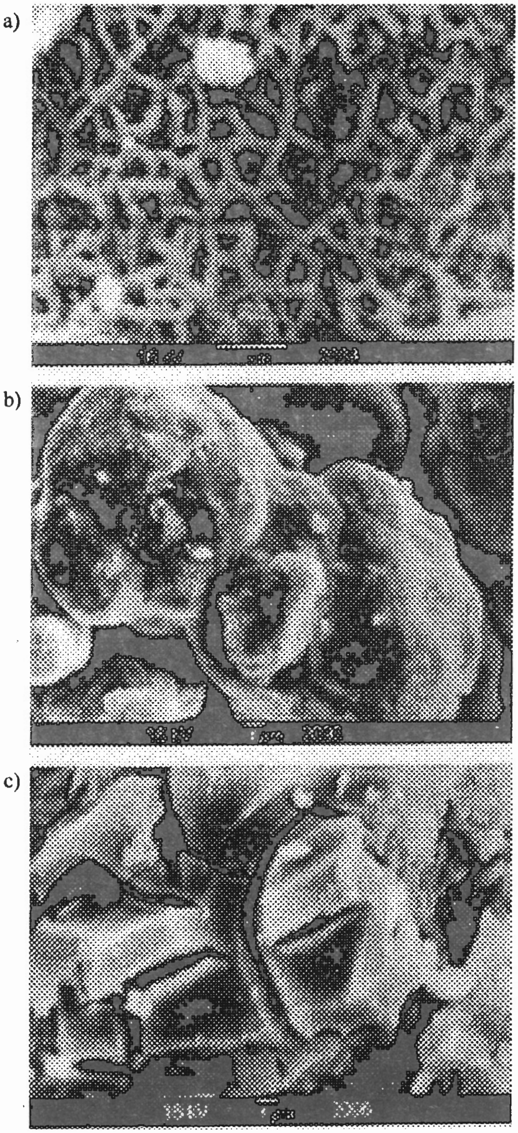

Fig. 1. Electron-microscopic photographs of the samples.
a - supported nickel catalyst;
b - original support;
c - support covered with alumina.

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PP-6

MONOLITHIC CATALYST FOR PURIFICATION OF WELDING EXHAUST

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Welding is accompanied by the following kinds of harmful effects: generation of welding dust, yielding of injurious gases (CO, N_xO_y, HF). Under manual welding the electrodes evolve depending on the type of the latter from 0,332 to 2,7 HF, from 0,23 to 9,64 CO, from 0,8 to 1,95 N_xO_y (g/kg of electrode).

An installation has been designed and manufactured for cleaning the waste gases of welding productions. The installation includes: a draught agitator, a mechanical filter with solid particles sump, gases neutralization unit. Gases neutralization unit consists of three successively connected honeycomb blocks. Honeycomb blocks were manufactured from plastic ultraporcelain mass (the content of Al_2O_3 - 81%). The measure of sells for the first and the second blocks 7 x 7 mm, for the third block - 4 x 4 mm. The cells of the first block were filled with sorbent to absorb gases. Mixture tertiary treatment from the oxides of nitrogen and carbon was performed by catalytic method. To this end the mixture was heated in the second block up to 250°C and than passed through the third block, the walls of the block being covered with a layer of platinum catalyst.

The results of the test are presented in the table. The content of injurious substances at the installation exit does not exceed limiting permissible concentration.

Concentration in air, mg/m^3					
Parameters at filter entrance			Parameters at filter exit		
CO	N_xO_y	NF	CO	N_xO_y	NF
106	30	18	15	0,4	0,3
			Cleaning degree, %		
			85,8	98,6	98,3

PILOT TESTS OF HIGH-TEMPERATURE MONOLITH OXIDE CATALYST IC-12-83 IN NH_3 OXIDATION

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Recently considerable attention was focused on substituting Pt and its alloys by cheap oxide catalysts not only in environment-control processes, but in some industrial processes, such as the oxidation of NH_3 to NO_x during HNO_3 production. The data obtained [1,2] evidence that the partial substitution of Pt gauzes with oxide catalysts (a two step process) is very promising for the nitric acid production. Oxide catalysts, however, should possess the properties as follows: high activity, selectivity, and good resistance to temperature and poisoning. Mixed oxides of transition and rare-earth metals with a perovskite structure are very suitable for the purpose due to their structure peculiarities. A number of publications consider perovskite oxides in the ammonia oxidation. Yet, there is no industrial catalysts for this process [3,4]. On the other hand, at the Boreskov Institute of Catalysis a monolith honeycomb oxide catalyst with a perovskite structure (IC-12-83) was designed for high-temperature oxidation processes [5,6].

Here we present our study on the catalytic properties of the monolith honeycomb catalyst IC-12-83 in the ammonia oxidation.

The perovskite catalyst was synthesized by kneading an active $LnMnO_3$ component powder and alumina-based binder in acid media (HNO_3, CH_3COOH) to obtain plastic paste [5,6]. The paste was extruded through the spinnerets designed and manufactured at the Boreskov Institute of Catalysis. To improve the paste rheology, we add ethylene glycol. The alumosilicate fibers reinforcement was used to obtain good resistance to thermal shock. After extrusion, the "green" catalysts were dried under controlled humidity conditions at optimized temperature (up to 110 °C), and then calcined at 900 °C. Thus obtained monoliths exhibit the following properties: specific surface area, about 30 m^2/g; integral pore volume, about 0.3 cm^3/g, and crushing strength, about 8-10 MPa. Monoliths were manufactured as microhexagon (~15 mm edge sizes, ~ 2.5 mm triangular channels, and ~ 1 mm wall thick) for laboratory studies, and as square monoliths (75x75 mm, 50 mm in length, ~ 2 mm walls thick, and 4 mm square channels) for pilot tests.

Catalytic activity in the high-temperature (800-1000°C) ammonia oxidation (initial NH_3 concentration in air equals 10 %) was determined in a fixed-bed flow reactor for (i) the catalytic system (catalysts were placed behind a Pt gauze), (ii) Pt gauze solely, and (iii) perovskite catalyst solely, selectivities 1,2, and 3, respectively. Gas space velocities and selectivities are given in the Table. No ammonia was observed in gases passed through the catalytic system. Pilot tests of a 0.4 m^3 catalyst batch in combination with incomplete loading of Pt gauzes were carried out in an UKL-7 industrial reactor at Cherepovets and Berezniki NPO "AZOT".

Table

Catalysts Activity

Catalyst	T,°C	V,m/s	Selectivity		
			1	2	3
Microhexagon	925	1.25	95.3	86.8	
	850		92.1		
	940		92.5		79.6
	900		95.6		75.4
	905	2.26	92.1		
Square monolith	900	1.25	95.6	85.7	45.6
Square monolith after industrial reactor	980/1060	1.25			57.7
Square monolith after thermal shock	900	1.25			55

The catalysts used in ammonia oxidation offer great promise for industrial application, since they exhibit high selectivity and stability in the process. If the catalyst is used with a Pt gauze, the selectivity reaches 95.5-96.5 %. At 900 °C and space velocity of 1.25 m/s, no ammonia slip was detected.

In 1995, the Chemical Pilot Department has manufactured two batches (2x0.2 m^3) of such monolith catalyst for Cherepovets and Berezniki NPO "AZOT". While preparing the catalyst for industrial tests, we managed to adopt the preparation procedure to the conditions of the Chemical Pilot Department. The batches manufactured as the second part of the catalytic system were placed into an UKL-7 reactor according to the Instructions derived by the State Institute of Nitrogen Industry. During a year operation, the catalyst system showed a 94% and above selectivity (actual selectivity equals 92.5%-93.5%). Moreover, the relative Pt losses decreased by 20% .

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PP-8

HONEYCOMB MONOLITHS AS SUPPORTS FOR IMMOBILIZATION OF MICROORGANISMS BY ADSORPTION

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Using honeycomb monoliths for immobilization of various microorganisms is a new promising trend to obtain heterogeneous biocatalysts for practical implementation in biotechnology and ecology. Here the monoliths serve both as adsorbent and column reactor through whose channels solutions of substrates of interest flows or circulates.

The present work aims at studying honeycomb monoliths for adsorptive immobilization of various microorganisms, including methanotrophs. The non-growing cells of the latter can directly oxidize gaseous hydrocarbons (methane and propylene) to valuable oxy-products (methanol and propylene oxide) under mild conditions. The selectivity of these biotech processes does not depend on the initial substrate conversion and is close to 100%.

The honeycomb monoliths were prepared by extrusion moulding of the plastic masses, consisting of basic composition materials (TiO_2, Al_2O_3, Fe_2O_3), inorganic and organic binding components and plasticizers, as cylinders 10 mm in diameter and 50-70 mm in length with square-section channels 0.7x0.7 mm.

The studies have shown that in order to use the honeycomb monoliths in biotechnology these supports should fulfil certain requirements. First they should be stable in aqueous media and not disintegrate during long function. The monoliths calcined at a temperature of not below 900°C satisfy this requirement. The honeycomb monolith material should be also nontoxic for bacteria cells. We have studied the influence of monolith material on the morphology and viability of microorganisms of various taxonomic groups (bacteria, yeast, filamentous fungi) and also on the biocatalytic activity of methanotrophs after their contact with the supports. The results show that the supports containing iron, vanadium and copper are highly toxic for most microorganisms, reduce the viability of cells in populations and significantly inhibit the intracellular enzymatic activity. The monoliths based on alumina, titania and aluminosilicate modified with cobalt ions practically have no deactivation effect on the cells of the microorganisms studied.

The adsorption properties of the monoliths and the biocatalytic activity and stability of the immobilized methane-utilizing microorganisms (methanotrophs) have been studied in detail using the TiO_2- and α-Al_2O_3-based honeycomb supports (Table).

Monolith basic composition material	Adsorption, mg of dry cells per g of monolith	Per sent of biocatalytic activity retained after contact of cells with monolith , %	Initial rate of propylene bioepoxidation, nmole of propylene oxide / min/ mg of dry cells	Stability: time of operation till complete biocatalyst deactivation, h
TiO_2	2.6	100	4.7	10
α-Al_2O_3	1.1	60	2.2	8

Thus, the studies have shown that the honeycomb monoliths based on alumina, titania and aluminosilicates are the promising supports for immobilization by adsorption of various microorganisms to develop heterogeneous biocatalysts for practical implementation in biotechnology and ecology.

PP-9

PILOT–INDUSTRIAL PRODUCTION OF A MONOLITH OXIDE CATALYST FOR NITRIC ACID INDUSTRY

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Nowadays nitric acid is manufactured via ammonia oxidation on the gauzes containing 85–95% of platinum. At the gauze operation life of less than one year, platinum irrevocable losses through chemical and mechanical ablations attain 30% (referred to one ton of 100 % nitric acid, these come to 0.155 g of platinum).

To reduce platinum losses, the State Institute of Nitrogen Industry (SINI) has developed a two–stage ammonia oxidation process. This implies a substitution of some platinum gauzes by a pelletized oxide catalyst. Nevertheless, high pressure drop (about 1000 mm of water column) and considerable catalyst attrition (1 g of catalyst per 1 ton of HNO_3) limit wide catalyst application in the nitric acid production.

In order to decrease pressure losses and to increase the efficiency of the second stage of ammonia oxidation to nitrogen oxide, the Boreskov Institute of Catalysis has developed a formulation of the catalyst based on the oxides of rare–earth elements and produced a pilot batch of catalysts formed as honeycomb monoliths [1]. According to industrial tests in a UKL–7–76 reactor (120,000 tons of nitric acid per year), the catalyst proved to be highly selective and stable.

The aim of the present study is to refine the formulation of the moulding paste, to optimize technology of the efficient catalyst production and to organize pilot line of the catalyst manufacturing (10 tons per year) at the Boreskov Institute of Catalysis. Since rare–earth raw materials are expensive, as basic component we used iron oxides from various plants. The final choice of iron oxide source was based upon analysis of the chemical composition, paste moulding properties, thermal shrinkage, mechanical and other properties of the catalyst.

Powdered iron oxide of the metalware production was found to exhibit the optimal technological parameters and ensure high catalyst selectivity.

A scheme of monolith honeycomb catalyst production includes the stages as follows:

(1) raw materials pretreatment
(2) mixing of the initial components of paste;
(3) extrusion of the moulding paste;
(4) drying of extrudates;
(5) calcination.

Beside iron oxide, some additional components, viz. hydrated alumina, mullite–silica fibers, and solution of organic plasticizers were added to the moulding paste. The moisture content of the paste was 22–24 wt.% . The paste plasticity was found to depend on the added plasticizer as well as on the component loading sequence and time of mixing. For the stage of extrusion we studied the effect of the extruder type, air evacuation degree of plastic pastes, the moulding die design, compacting pressure and rate of extrusion through a die. The optimal moulding conditions of honeycomb monoliths with a square cross–section of 75x75 mm, walls thickness equal to 2.2 mm, channel sizes being 5.2x5.2 mm were obtained. After drying in a climatic chamber at room temperature, the monoliths were dried in the flow of air at 60 °C and then calcined under programmed rise of temperature.

The effect of the thermal treatment conditions on the specific surface, mechanical strength, and thermal stability were elucidated. Testing of pilot catalyst batches in real conditions (SINI, Moscow), allowed us to elaborate recommendations for the catalyst loading and operation regimes in the industrial reactor of ammonia oxidation. More than 2 m^3 of the IC–42–1 catalyst were produced and sold to load 12 UKL–7 type reactors of nitric acid production. The results of this work performed at the pilot–chemical shop of the Boreskov Institute of Catalysis made it possible to start the pilot catalyst production.

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PP-10

NEW FIELDS OF OXIDE MONOLITH APPLICATION

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Technologies of materials and design production by extrusion method on the basis of oxide, carbide systems intended for various purposes have being developed at the Institute of Technical Chemistry of the Ural Branch of the Russian Academy of Sciences.

Seeking to maintain the extrusion process, possibilities of application of the basic groups of binders and plasticizers, currently used and proposed for application to mould ceramic materials with complex spatial structure have been analyzed. Specific binding compositions for various oxide systems (e.g. on the basis of Al_2O_3 or TiO_2) have been selected and developed.

Optimization of component ratio in plasticized masses was carried out on the basis of studies of their mouldability and rheological characteristics, using the procedures developed .

Plasticized masses mouldability was determined by express-method with an original device.

Conditions for.producing materials and designs of complex spatial structure have been revealed on the basis of studies of mouldability and rheological characteristics of plasticized masses. Mass shear stress was chosen as one of the basic criteria of optimal technological properties of plastic mass.

Specific range of feasible alteration of shear stresses was used in strength analysis to determine unit pressure on the moulder tool.

Numerical results for predicting elastic and strength characteristics of designs with regular macrostructure under various loading conditions have been obtained and confirmed.

Honeycomb structure designs with penetrable walls, so called materials with regular micro- and macrostructure, have been produced.

Micropore structure was moulded by introducing close - cut fractionated foaming agents - polymethylacrylate and technical carbon - into the composition of plasticized mass.

A computer model based on the determination of spherical particles in three-dimensional space with dispersion medium properties was used to describe the formation of spatial structures from dispersive components.

As a result of studies performed, we have produced a number of products on the basis of oxide systems dealing with water treatment. They are: honeycomb labyrinth-shaped filter body and proportioning chlorination canister.

Characteristics of products are : microporosity - 30 %, with pore size 0,4 - 0,6 mkm; microporosity - 60 % with pore size 10 -12 mkm. Macroporosity - 85 % (with cell size 30 x 30 mm). The above products have been made and are delivered to customers.

PP-11

ON THE PREPARATION OF TiO_2-BASED HONEYCOMB MONOLITHS

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Introduction.

In the frame of our activities on the Selective Catalytic Reduction of NO_x by NH_3 [1] we have recently prepared by extrusion a number of $DeNO_x$-SCR catalysts. In this context we have attempted a systematic and fundamental approach to the extrusion of titania-based ceramic pastes with the aim of elucidating the role of the different stages of the paste extrusion process, and the effects of paste composition on the rheology of the paste and on the morphological, and mechanical characteristics of the honeycomb monoliths.

Results and discussion.

Preparation of the honeycomb monoliths - The honeycomb catalysts have been manufactured starting from tungsta-titania powder and minor amounts of bentonite and glass fibres as inorganic ligands and strengthening agents. The powder components were mixed together in the dry state. Water with small amounts of organic additives such as poly-ethylene-glycol (PEG) and methyl-hydroxy-ethyl-cellulose (MHEC) was then added to the solids to impart plasticity and to provide effective lubrication during extrusion. In few preparations a high shear mixing stage has been applied. This was accomplished by extruding the resulting ceramic paste through a die plate mounted after the end of the screw. This operation was repeated three times. Then the rheological measurements were performed by using a slit capillary devise. The ceramic paste was processed in a single screw laboratory extruder equipped with a die of size and cross sectional shape appropriate to that of the honeycomb product. The extruded monoliths were dried and calcined.

Wet and high shear mixing - The rheological and morphological data indicate that the stages of wet mixing and high shear mixing favour the break down of the agglomerates in the starting commercial tungsta-titania powders to single particles and ensure that these are fully covered with the liquid phase, thus avoiding flow perturbation during extrusion due to particles de-agglomeration.

Extrusion: effect of paste composition - Morphological measurements showed that small if any de-agglomeration of the particles is achieved in the pastes with high water content (e.g. 40% w/w on a wet basis) whereas de-agglomeration occurs to a great extent in the pastes with low water content (e.g. 28% w/w). The rheological data unambiguously prove that this is due to the higher viscosity of the paste that generates higher stresses during mixing. Likewise a similar effect is observed when applying the high shear mixing stage to the paste with sufficiently low water content. As expected the changes observed in the morphology of the final materials when decreasing the water content, or when applying all the steps of the high shear mixing stage, result in superior crushing strength characteristics of the monoliths.

Concerning the organic additives MHEC acts primarily as a binder. In view of its excellent water solubility and of its effectiveness to reduce the surface tension of aqueous solutions, this compound yields improved wetting of the solid particles and favors compacting of the particles when the liquid phase is removed. On the other side PEG acts as a lubricating agent whereas it affects only to a minor extent the morphological and mechanical properties of the finished product, provided that its content is not too large.

Bentonite and glass fibres were used as inorganic additives. In the case of pastes with low water contents on increasing the content of bentonite higher shear stresses are measured at a given shear rate and steeper rheological curves are observed in a log-log plot diagram (shear stress vs shear rate). On the other side the radius and the volume of the largest pores increase significantly on increasing the clay content in spite of the higher shear stresses. This has been explained by considering that the more pronounced velocity profiles in the pastes with high clay contents, that is associated with the steeper rheological curves, may cause inadequate joining of the adiacent layers of the ceramic paste within the die land during extrusion. This eventually accounts for the higher porosity of the finished products and in turn for the slightly lower crushing strength characteristics. This effect is attenuated by the presence of bentonite that acts as an inorganic binder.

SEM photographs demonstrated that glass fibres are oriented in the direction of the extrusion; the fibres are needed to ensure high axial crushing strength to the finished materials.

Drying and calcination - It has been observed that a careful control of temperature and humidity is required in the drying stage of the extruded green bodies. The procedure that has been adopted involves: i) drying at r. t. under saturated moisture conditions for several hours. In this step excess water, i.e. water in excess to that required to fill the intraparticles pores and the pores when the particles touch, is slowly avaporated and most of the shrinkage of the green body occurs; ii) further drying at room temperature in air for several hours. In this step most of the water present inside the pores is removed while no significant additional shrinkage of the material is observed; iii) heating up to 110°C to complete the evaporation of water, again with no significant shrinkage of the material.

DTA-TG measurements prove that any organic material left in the paste is burnt out above 160 °C. Calcination at 550-600°C is appropriate for obtaining honeycomb monoliths with good structural, morphological and mechanical properties.

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PP-12

SOL-GEL METHOD OF SUPPORTED CATALYSTS PREPARATION

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The usual methods of active components entering on ceramic blocks (impregnation by appropriate salt solution or suspension deposition) have the following disadvantages:

- ecologically harmful compounds emission during salt thermal decomposition;
- difficulties in achievement of the homogeneous distribution of the active component on the surface of the carrier;
- insufficient adhesion of the solid particles to the support in the case of suspension applying;
- composition and structure of the multicomponent active compound on the surface of the support defined mainly by reactions taken place during catalyst thermal treatment and are difficult to control. To avoid these disadvantages new sol – gel method of supported catalysts preparation was developed.

The main stages of sol – gel method of catalyst preparation are following:

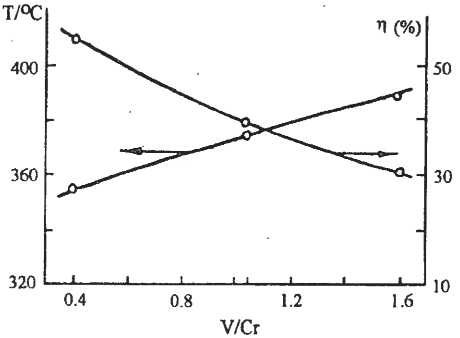
1. Preparation of aqueous sol forming solution of the transition metals oxides.
2. Impregnation of the support by sol forming solution.
3. Liquid – phase sol formation under controlled thermotreatment conditions.
4. Sol coagulation on the surface of the carrier and partly in the liquid phase.
5. Catalyst drying and calcination.

Peculiarity of this method is that the formation of the structure of the multicomponent active compound takes place on the stage of sol formation in aqueous solution. Precipitation from solution by sol coagulation on the surface of support provides formation of the strong – binded fine dispersed layer of active component even in the case of low surface area supports. When peroxide solutions are used as a sol forming system no toxic exhaust gases and waste water are produced.

Set of γ – Al_2O_3– supported complex vanadium – chromium catalysts was synthesized according to sol – gel method suggested and tested in the process of selective catalytic reduction of nitrogen oxides with ammonia.

In the 300 – 400°C temperature range of catalysts thermotreatment active components are X – ray amorphous. The phase composition of Al_2O_3 - V_2O_5 - Cr_2O_3 system at higher temperature is described elsewhere [1].

At the space velocities of gases normally used in industry (10000 – 30000 h^{-1}), the catalysts under consideration are highly active in the 280 – 330°C temperature range at $V_{(NH_3)}/V_{(NH_3)theor}$ ratio equal to 1. The degree of NO_X reduction under these conditions is more than 90%. At GSV of 65000 h^{-1} the catalysts obtained according to sol – gel technology suggested exhibit also high activity (degree of NO_X conversion is > 80% at 340 °C). Analysis of data obtained implies that the optimal temperature of the process and the degree of reduction of nitrogen oxides depend on the vanadium: chromium ratio in the catalysts (fig.).



Dependence of NO_X reduction at 230°C and dependence of the optimal temperature of the process on V/Cr molar ratio at $V_{(NH_3)}/V_{(NH_3)theor} = 1$.

Developed sol – gel method of supported catalysts preparation is ecologically sound and can be used for industrial application.

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PP-13

CORRELATION "MOULDING MASS PROPERTIES - EXTRUSION CONDITIONS - OPERATIONAL CHARACTERS" -FOR MONOLITH SUPPORTS AND CATALYSTS

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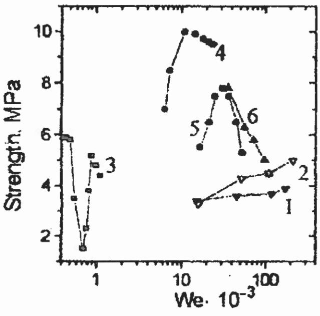
Early in our researches [1-3] it was noted that a moulding masses for monolith supports and catalysts extrusion must possess certain set of rheological properties. Besides mass properties the extrusion conditions have great influence on the operational character of a ready-made product [3,4).

Mass properties and extrusion conditions may be connected by the Weisseaberg number (***We***):

$$We = \Theta Q / R^3 \sim = \Theta v / R,$$

where Θ - relaxation period of moulding mass; Q and v - volume and line velocity of extrusion respectively; R - reduction radius of spinneret. The experimental dependence **Strength** = f(We) and **Pore Volume** = f(We) have extremum behaviour (fig. 1,2). Most strongly the Weissenberg number affect the mechanical strength.



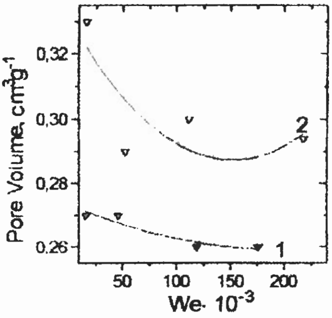


Fig. 1. Dependence of mechanical strength of supports and catalysts from Weissenberg number.

Fig. 2. Dependence of pore volume of supports and catalysts from Weissenberg number.

Systems: 1 - alumina-silica ceramic; 2 - high-alumina ceramic; 3 - ZnO-Surfactants; 4 - Fe_2O_3-H_2CrO_4-Surfactants;5 - Fe_2O_3-H_2CrO_4; 6 - Al_2O_3-HNO_3

Consequently, for each system the mass properties - extrusion conditions relation exists which affords optimal operational characters of supports and catalysts, These outlines are high-priority for honeycomb monolith.

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PP-14

COMPOSITION, CATALYTIC ACTIVITY AND TOXICOLOGICAL HYGIENIC PROPERTIES OF POLYOXIDE RAW MATERIAL USED TO PREPARE MONOLITH HONEYCOMB SCR CATALYST

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The possibility of preparation of the effective industrial monolith and/or granulated SCR catalyst on the basis of polyoxide raw material (power station waste: the washing sewage's precipitate so -called "schlamm") is shown (Refs. /1-4 /).

For the purpose of industrial production of the catalyst authors investigated:

- chemical composition of raw material and active ingredients quantitative distribution along the depth and area of storage reservoir;
- influence of the schlamm composition on the catalyst activity;
- toxic and hygienic properties of raw material and catalyst.

To determine chemical composition of polyoxide schlamm and its distribution along the depth and area of storage reservoir which has volume 200,000 m^3 more than 100 samples were studied. Composition was defined by means of spectral photometry method.

It was shown that schlamm contains a considerable quantity of catalytically active metal oxides like Fe_2O_3, V_2O_5, NiO; admixtures of active oxides like WO_3, Cr_2O_3, Mo_2O_3, CuO and Al_2O_3 and SiO_2 which may be used as active supports.

The estimation of active ingredients distribution along the depth of storage reservoir has shown that its quantity distribution strongly depends to a great extent both on the thickness and on the area of schlamm precipitate. For example, the quantity of Fe_2O_3 is changing from 9 to 38% mass, V_2O_5 from 1 to 15% mass, NiO - from 0.25 to 4% mass.

To determine influence of active ingredients quantity on the catalyst activity we prepared and tested the industrial monolith honeycomb catalysts containing 50% of the schlamm and having a different composition.

Investigation of catalyst was carrying out in following conditions: NO_X concentration at the entrance of the flowing quartz reactor - 0.1 % vol.; oxygen concentration in the gas - 5 % vol., volume ratio NH_3/NO_x = 1.0, volumetric flow rate - 8,000 (1/h), gas temperature -250-400°C, transport gas - the air. NOx concentration at the entrance and exit was determined by means of spectral photometry method.

Results of the experimental catalyst activity determination are shown on the Figure (P.2) in comparison with BASF company's catalyst. For the BASF catalyst, temperature increase is accompanied by activity increase; for experimental catalyst, the dependency has an extreme character with maximum (56-66%) at 370-390 °C.

As one can see from the Figure, there is no correlation between the schlamm composition and the activity of catalyst based on this schlamm type. At the same time, the deviation of catalyst activity at 300 ÷400 °C is equal to ± 5 ÷ 7 % of mean value, that is insignificantly more than for BASF catalyst (± 5 %).

The results obtained allow to make following conclusions:

- the change of quantity of iron, vanadium and nickel oxides containing in the schlamm in the range 20÷36%, 2÷12% and 0.5÷4% , accordingly, was not accompanied by change of the activity of catalysts prepared on the base of this raw material. Changing of catalyst activity varies in the range equal to experimental error;
- it is not necessary to control the quantity of active ingredients containing in the schlamm after the industrial processing of raw material;
- a considerable change of active substance quantity give a possibility to produce catalysts having various composition for different technological processes, for example, the catalyst which contain a small quantity of vanadium oxide for the removal of NO_X from sulfur - rich gases. Toxicological and hygienic investigations of the schlamm and catalysts on its base were carried out /5/. Tests showed that raw material and catalyst may be classified as untoxic and undangerous substances of Class IV (by standard of Russian Federation, GOST 12.1.007-76).

For the dust forming from the schlamm and catalyst temporary provisional sanitary standard - tentative undangerous influence level for industrial zone air - equal to 4.0 mg /m^3 is advisable. Generally accepted rules for secure work should be observed at industrial production of the catalyst on the basis of power station wastes.

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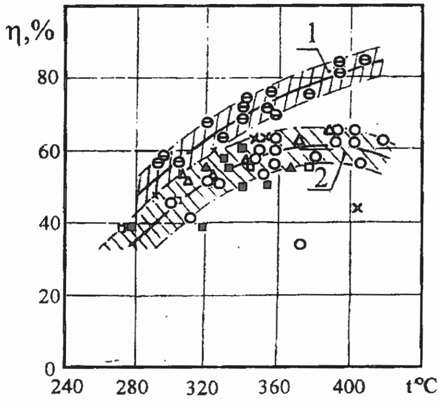

FIGURE: Activity of BASF catalyst (I) and catalyst on the basis of power station waste (II).

Θ - BASF; x - sample No.1 (see Table); Δ - 2; O - 3; ▲- 4; ▬ - 5; □ - 6.

Table. Composition of some schlamm samples.

No.	OXIDES QUANTITY, % mass.			
	GENERAL	Fe_2O_3	V_2O_5	NiO
1	22.9	20.3	2.1	0.5
2	31.3	25.7	5.0	0.6
3	38.5	32.9	5.0	0.6
4	39.6	31.7	6.2	1.7
5	42.4	36.5	2.1	3.8
6	42.5	26.0	12.3	4.2

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PP-15

Composite monolith for energy saving production of fresh water from the atmosphere: preliminary results

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Stable water supply is a vital point for civil settlements in many territories with dry climate and/or deficit of natural water resources. Yet, the Earth's atmosphere is a huge reservoir of water with the humidity exceeding 10 g/m^3 even for desertic areas. Recently at the Boreskov Institute of Catalysis a new energy saving method of fresh water production has been suggested and tested at a lab-scale [1,2]. The essential point of the method is the use of new selective water sorbents (SWS) which allow significant improvement of the process parameters respect to those for common adsorbents like silica gel, alumina, etc.

A typical SWS is a two-phase system which consists of a porous host matrix and a hygroscopic substance (commonly an inorganic salt) impregnated into pores (for more details see [3-8]). Prominent water sorption (up to 0.8 g of sorbed water per 1 g of a dry sorbent) and low regeneration (desorption) temperature (about 60-90°C) make these materials attractive for fresh water production in sorption systems. Water vapour is sorbed during night time at respectively low temperature and high humidity. Water desorption and condensation is carried out during day time at higher temperature (for instance, using low-grade solar energy).

Even first lab-tests have demonstrated a promising output of about 1.5-2 kg of water from 4 kg of the dry SWS material per day. On the other side, an essential part of the input energy appears to be consumed for the atmospheric air passing throughout the fixed bed of the granulated sorbent. Thus, an application in such system monolith sorbents with low hydrodynamic resistance promises a further energy saving and system optimization.

In this communication we present preliminary results on the synthesis of the selective water sorbent with ceramic monolith as a host material and calcium chloride as hygroscopic salt. Ceramic monolith was prepared via extrusion procedure. Initial powders were mixed together with plasticifizers. The ceramic mixture with moisture 23-27% was extruded through the dies with square side 75 mm, using a VP-100 extruder. After conventional thermal treatment a monolith with specific surface area of 70 m^2/g and specific pore volume of about 0.5 cm^3/g was obtained. Then the monolith was filled with aqueous calcium chloride solution and dried at 200°C to remove residual water.

Dynamic parameters of the water production using synthesized sorbent have been measured with the lab-scale unit over the following range of the parameters: absorption temperature - +15 - +30°C, desorption temperature - +55 - +90°C, relative humidity - 30 - 80%, air flux - 0.2 - 0.6 m^3/h, dry sorbent weight - 750 g.

It has been demonstrated that sorption capacity of this monolith may reach 200 g of water that is about 0.27 g per 1 g of the dry monolith. It is worthy to note that more than 85% of the sorbed water can be removed at relatively low temperature T = 80-90°C that allows the sorbent to be used for energy saving fresh water production. Unfortunately, the monolith sorption capacity has been reached so far is much lower than that for mesoporous silica gel KSK (0.7-0.8 g/g) [1,2] due to the relatively small monolith pore volume. That is why the pore volume enlargement is an important matter for our further investigations. The increase of the latter value up to 1 cm^3/g is expected to cause a raise in the water productivity of the new monolith sorbent up to 1 kg of water per 2.5 kg of the dry material per day at condensation temperature T =15°C.

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PP-16

CATALYTIC FILMS EPITAXIALLY DEPOSITED ONTO CERAMIC HONEYCOMB AND OBTAINED BY MODIFIED SOL-GEL TECHNIQUES

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New perspective methods for directed synthesis of multicomponent catalysts and ceramics in the form of thin films and covers supported on ceramic honeycomb are described and discussed. The technique is based on modified sol-gel methods. The alkoxides, acetylacetonates, acetates and stearates of metals of III, IY, YI and YIII groups are used as the molecular precursors [1].

It has been shown earlier, that an interaction of organic molecular precursors with sols is accompanied by the exchange reactions of lygands that take place even on the stage of the existence of parent solution (PS). Later on the X-ray amorphous gels are formed during aging and treatment of PS. Even on the stage of PS, the local structure of newly born aggregates consists of heterometallic polyhedra, connected by organic lygands, with characteristic sizes of 1.2-3.0 nm and interatomic distances which are just the same as in the target complex oxide systems [2-5]. Heat treatment of gels at temperatures of 250-500 °C causes the removal of organic lygands followed by formation, for a variety of reasons, of single-phase complex oxide catalysts or ceramics [4-6].

Structural peculiarities of the single-phase complex oxide catalysts and ceramics, obtained by modified alkoxysynthesis, are those that transition metal ions form epitaxial layers modifying surface structure of ZrO_2, TiO_2, $ZrTiO_4$, Al_2O_3 but not penetrate deeper into the host lattice. The latter favors the development of modified technology for directed synthesis of multicomponent ceramics and catalytical films deposited only on the surface of ceramic block designs.

The purpose of this work is to describe the scientific bases for obtaining complex oxide catalysts for combined CO and CH (hydrocarbon) oxidation and NO_x decomposition. Molecular complexes $Ti(O\text{-}nBu)_4$ and $Cu(acac)_2$ were used as precursors for obtaining catalytical covers and films deposited on the surface of ceramic block designs ZrO_2, TiO_2, $ZrTiO_4$, Al_2O_3. Partial chelation of $Ti(O\text{-}nBu)_4$ by acetylacetone was shown to stabilize sols, to ensure anatase-based single phase $Cu_xTi_{(1-0.5x)}O_2$ ($x<0.04$) and to exhibit the highest activity in CO and CH oxidation; the mean crystal size does not exceed 17 ± 3 nm at that. The structural studies of Cu-O/TiO_2 catalysts by X-Ray diffraction, EXAFS, XPS and magnetic susceptibility methods have shown, that surface ions Ti^{4+} are located in the vicinity of grain boundary of the anatase structure and isomorphically substituted by Cu^{2+} octahedral ions. During heat treatment and catalytic tests a considerable part of surface Cu^{2+} ions is reduced to Cu^{1+} valence state.

At x >0.04, the formation of cupric oxide and titania gives evidence to phase separation. At temperatures T<150 °C, an overall CO conversion over complex oxide $Cu_xTi_{(1-0.5x)}O_2$ depends on parameter x and on mean crystal size "d": with increasing x and decreasing "d" activity remarkably increases. Terminal (non-bridged) oxygen of the bond Cu=Os (O surface), surface anion vacancy VS, related to the reduced Cu^{1+} state and surface labile species Os are suggested as catalytical active centers and intermediates [7]. At temperatures T >150-200 °C, the participation of lattice oxygen in the reaction mechanism is postulated.

Organic sols of metalcontaining (I, IY and YIII groups) precursors possess significant adhesion properties and thus, being drawn onto a surface of ceramic and metallic honeycomb, permit fast formation of supramolecular layers without considerable energy expenditures. Highly effective catalytic covers supported on honeycomb made of corrosionless alloys were obtained on the basis of the above approach.

The obtained honeycomb catalysts showed 70 - 95% conversion of CO, NO_x and hydrocarbons at temperatures 110 - 300 °C and space velocity 20000 - 30000 h^{-1}. The reaction mixture contains 0.3 - 0.5 vol.% CO, 600 -1500 ppm C_3H_6, 380 - 430 ppm NO_x and 3 - 17 vol.% O_2 (the other is N_2).

Thus, the use of the above modified alkoxysynthesis provides possibility for development of low energy and material saving technologies for obtaining catalytic block designs exhibiting bifunctional ability and containing no nobel metals.

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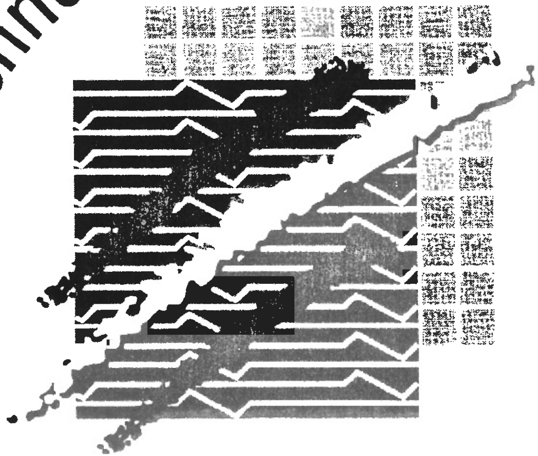

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