Boreskov Institute of Catalysis of Siberian Branch
of Russian Academy of Sciences, Russia

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

Chinese Academy of Sciences

Scientific Council on Catalysis of Russian Academy of Sciences, Russia

Russian Catalytic Society

Chinese Catalytic Society

3-d Russia-China Seminar on Catalysis

Novosibirsk
April 26-28, 2003

ABSTRACTS

Part 1

Novosibirsk-2003

SEMINAR ORGANIZERS

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ORGANIZING COMMITTEE

Co-Chairs:

Valentin N. Parmon,	**Boreskov Institute of Catalysis, Russia**
Valerii V. Lunin,	**Lomonosov Moscow State University, Russia**
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Weishen Yang,	**Dalian Institute of Chemical Physics, China**

Seminar Secretary:

Tatiana V. Zamulina	**Boreskov Institute of Catalysis, Russia**

SCIENTIFIC PROGRAM

The Seminar program includes presentations (20 min) in the following topics:

- **Natural Gas Conversion**
- **Biomass Conversion**
- **Energy Related Catalysis**

TIME-TABLE

April 26, Saturday		**April 27, Sunday**	**April 28, Monday**
Arrival day	9.00	Registration	
	9.30	Seminar Opening	
	10.00	OP-1 Xinhe Bao	OP- 16 Weishen Yang
	10.20	OP-2 Sadykov	OP-17 Varfolomeyev
	10.40	OP-3 Can Li	OP-18 Shudong Wang
	11.00	**COFFEE BREAK**	
	11.20	OP-4 Lapina	OP-19 Vasenin
	11.40	OP-5 Wenzhao Li	OP-20 Zhongmin Liu
	12.00	OP-6 Ismagilov	OP-21 Yakovleva
	12.20	OP-7 Chumakova	OP-22 Molchanov
	12.40	OP-8 Tarabanko	Concluding remarks
	13.00	**LUNCH**	
	15.00	OP-9 Wenjie Shen	**CONCERT**
	15.20	OP-10 Kerzhentsev	
	15.40	OP-11 Gongxuan Lu	
	16.00	**COFFEE BREAK**	**POSTER PRESENTATIONS**
	16.20	OP-12 Simonov	
	16.40	OP-13 Chenglin Sun	
	17.00	OP-14 Galanov	
	17.20	OP-15 Gagachev	
	17.40	Discussion	
	18.00	**WELCOME RECEPTION**	

3-d Russia-China Seminar on Catalysis

April 26-28, 2003

Scientific Program

April 27, Sunday

9.30 Seminar Opening

ORAL PRESENTATIONS

10.00 OP-1
Xinhe Bao
RESEARCH AND DEVELOPMENT OF NATURAL GAS CONVERSION IN DALIAN INSTITUTE OF CHEMICAL PHYSICS (DICP)
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, China

10.20 OP-2
Sadykov V.A., Lunin V.V.*, Kuznetsova T.G., Alikina G.M., Frolova Yu.V., Lukashevich A.I., Potapova Yu.V., Muzykantov V.S., Veniaminov S.A., Rogov V.A., Kriventsov V.V., Kochubei D.I., Moroz E.M., Zuzin D.I., Zaikovskii V.I., Kolomiichuk V.N., Paukshtis E.A., Burgina E.B., Zyryanov V.V., Uvarov N.F.**, S. Neophytides***, E. Kemnitz******
METHANE SELECTIVE OXIDATION INTO SYNGAS BY THE LATTICE OXYGEN OF CERIA-BASED FLUORITE-LIKE OXIDE SOLID SOLUTIONS
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
**Lomonosov Moscow State University, Moscow, Russia*
***Institute of Solid State Chemistry SB RAS Novosibirsk, Russia*
****Institute of Chemical Engineering & High Temperature Processes, Patras, Greece*
*****Institute for Chemistry, Humboldt- University, Berlin, Germany*

10.40 OP-3
Can Li
ADVANCES IN UV RAMAN SPECTROSCOPIC STUDIES ON CATALYSTS AND CATALYST PREPARATION
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian, China

11.00 COFFEE BREAK

11.20 OP-4
Khabibulin D.F., Lapina O.B., G. Garcia Cortez*, M.A. Bañares*
STRUCTURE-ACTIVITY RELATIONSHIPS OF ALUMINA-SUPPORTED V-Mg-O CATALYSTS FOR THE OXIDATIVE DEHYDROGENATION OF PROPANE
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
**Institute of Catalysis and Petrochemistry, Madrid, Spain*

11.40 **OP-5**
Xuebin Liu, Wenzhao Li, Hengyong Xu, Yanxin Chen and Qingjie Ge
HOMOGENEOUS AND HETEROGENEOUS CONTRIBUTIONS TO LIGHT ALKENES PRODUCTION FROM THE CATALYTIC OXIDATIVE CRACKING OF HEXANE
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

12.00 **OP-6**
Ismagilov Z.R., Kerzhentsev M.A.
CATALYTIC FUEL COMBUSTION. RESULTS OF 20 YEAR FUNDAMENTAL STUDIES, ACHIEVEMENTS IN PRACTICAL APPLICATION AND FUTURE PROSPECTS
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

12.20 **OP-7**
Chumakova N.A., Drobyshevich V.I.*, Tsyrulnikov P.G., Yausheva L.V.*, Noskov A.S., G. Eigenberger*****
COAL MINE VENT GASES UTILIZATION FOR HIGH-TEMPERATURE HEAT PRODUCTION IN CATALYTIC REVERSE-PROCESS: MATHEMATICAL MODELING
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
**Institute of Computational Mathematics and Mathematical Geophysics, Novosibirsk, Russia*
***Omsk Department of Boreskov Institute of Catalysis, Russia*
****Institute of Chemical Process Engineering, University of Stuttgart, Germany*

12.40 **OP-8**
Tarabanko V.E., Chernyak M.Yu., Kuznetsov B.N.
THE CATALYTIC CONVERSION OF CARBOHYDRATES INTO THE LEVULINIC ACID AND 5-HYDROXYMETYLFURFURAL DERIVATIVES
Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk

13.00–
15.00 LUNCH

15.00 **OP-9**
Baocai Zhang, Xiaolan Tang, Yong Li, Yide Xu, Wenjie Shen
BIO-ETHANOL STEAM REFORMING OVER CERIA-SUPPORTED Ni and Ir CATALYSTS
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian, China

15.20 **OP-10**
Kruchinin V.N., Kerzhentsev M.A., Ismagilov Z.R., Korotkikh V.N., Zabortsev G.M., Ostrovskii Yu.V.*, Veringa H.J.**
THE BIOMASS PYROLYSIS AND GASIFICATION IN FLUIDIZED BED CATALYTIC REACTORS
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
**Novosibirsk State Design-Exploratory Institute VNIPIET, Novosibirsk, Russia*
***ECN, Petten, The Netherlands*

15.40 **OP-11**
Yushui Bi, Gongxuan Lu
INVESTIGATION OF CO OXIDATION OVER Pd/NaZSM-5 SUPPORTED CATALYST MODIFIED BY Fe
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China

16.20 **COFFEE BREAK**

16.20 **OP-12**
Simonov A.D., Yazykov N.A., Vedyakin P.I., Parmon V.N.
CATALYTIC HEAT SUPPLY INSTALLATIONS OPERATING ON LIQUID AND SOLID FUELS
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

16.40 **OP-13**
Ying Sun[a,b], Min Yang[a], Wei Wang[b], Chenglin Sun[a]
Cu-Zn-Al MIXED OXIDE CATALYSTS PREPARED VIA HYDROTALCITE-LIKE PRECURSORS FOR WET AIR OXIDATION OF PHENOL
[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China*
[b] *Dalian Railway Institute, Dalian, China*

17.00 **OP-14**
Galanov S.I., Smirnov M.Yu., Sidorova O.I.*, Kurina L.N.
THE EFFECT OF HIGHER HYDROCARBONS AND HYDROGEN SULFIDE ON THE PROCESS OF ETHYLENE SYNTHESIS FROM METHANE
Tomsk State University, Tomsk, Russia
**Institute of Petroleum Chemistry SB RAS, Tomsk, Russia*

17.20 **OP-15**
Gagachev V.V., Madirbaev V.J., Sharafutdinov R.G., Zarvin A.E.
THE METHANE CONVERSION INITIATED BY THE ELECTRON BEAM PLASMA IN THE GAS-JET REACTOR
Institute of Thermophysics of SB RAS, Novosibirsk, Russia

17.40 **DISCUSSION**

April 28, Monday

10.00 **OP-16**
Haihui Wang, You Cong, Weishen Yang
PARTIAL OXIDATION OF METHANE (POM) TO SYNGAS IN TUBULAR $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ MEMBRANE REACTOR
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

10.20 **OP-17**
Varfolomeyev S.D., Kalyuzhnyi S.V.
BIOCATALYTIC CONVERSION OF BIOMASS: MECHANISMS AND APPLICATIONS
Lomonosov Moscow State University, Moscow, Russia

10.40 OP-18
Shudong Wang, Liwei Pan
STUDY ON A COMPACT PLATE-FIN STEAM REFORMER FOR FUEL CELL SYSTEM
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

11.00 COFFEE BREAK

11.20 OP-19
Vasenin N.T., Matus E.V., Tsykoza L.T., Ismagilov I.Z., Anufrienko V.F., Kerzhentsev M.A., Ismagilov Z.R.
ESR and DRES STUDIES OF ACTIVE COMPONENT FORMATION IN Mo/HZSM-5 METHANE DEHYDROAROMATIZATION CATALYST
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

11.40 OP-20
Zhengang Sun, Zhongmin Liu, Lei Xu, Yue Yang, Yanli He
HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF TWO ORGANICALLY TEMPLATED TRIVALENT METAL-CONTAINING ZIRCONIUM PHOSPHATES
Department of Natural Gas Chemistry & Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

12.00 OP-21
Yakovleva I.S., Isupova L.A., Tsybulya S.V., Chernysh A.V., Alikina G.M., Rogov V.A., Kolomiichuk V.N., Ivanov V.P., Boldyreva N.N., Sadykov V.A.
METHANE FLAMELESS COMBUSTION ON SUBSTITUTED PEROVSKITES $(La_{1-x}Ca_xFeO_{3-y}, La_{1-x}Sr_xFeO_{3-y})$
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

12.20 OP-22
Molchanov V.V., Chesnokov V.V., Buyanov R.A., Zaitseva N.A.
CATALYSTS FOR DECOMPOSITION OF NATURAL GAS INTO HYDROGEN AND CARBON MATERIALS. NEW AREAS OF APPLICATION FOR FILAMENTOUS CARBON
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

12.40 CONCLUDING REMARKS

13.00–
15.00 LUNCH

16.00–
18.00 POSTER PRESENTATIONS

1. **Andreev D.V., Makarshin L.L., Parmon V.N.**
   DIRECT RESISTANCE HEATING OF CATALYST VERSUS ITS EXTERNAL HEATING: METHANOL DEHYDROGENATION ON METAL COPPER
   Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

2. **Bondareva V.M., Andrushkevich T.V.**
OXIDATIVE DEHYDROGENATION OF ETHANE OVER HETEROPOLY COMPOUND WITH KEGGIN STRUCTURE
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

3. **Danilova I.G., Chuvilin A.L., Litvak G.S., Paukshtis E.A.**
CATALYTIC AND PHYSICOCHEMICAL PROPERTIES OF OXIDATIVE CONDENSATION PRODUCTS IN THE OXIDATIVE DEHYDROGENATION OF PROPANE BY SULFUR DIOXIDE OVER Al-Si-OXIDE CATALYSTS
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

4. **Dultsev F.N., Vasilyeva L.L.**
THE EFFECT OF CATALYZING ADDITIVES ON SOL-GEL FORMATION PROCESS AND ON THE PROPERTIES OF MODIFIED POLYSILOXANE LAYERS
Institute of Semiconductor Physics SB RAS, Novosibirsk, Russia

5. **Dultseva G.G., Dubtsov S.N., Dultsev E.N., Skubnevskaya G.I.**
FORMIC ACID AS A CATALYST FOR GAS-TO-PARTICLE PHOTOCONVERSION IN FORMALDEHYDE VAPOUR
Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia

6. **Galanov S.I.*, Mutas I.N., Kurina L.N.*, Popov V.N.**
THE CATALYST OF OXIDATION OF NATURAL GAS
Tomsk State University, Tomsk, Russia
**Institute of Petroleum Chemistry SB RAS, Tomsk, Russia*

7. **Ismagilov Z.R., Anufrienko V.F.**
SOME FEATURES OF TRANSFORMATIONS IN AHM/HZSM–5 CATALYSTS FOR SYNTHESIS OF BENZENE AND OTHER AROMATICS FROM METHANE: ESR RESULTS
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

8. **Koltsov N.I.**
THE ELEMENTARY SCHEMES DESCRIBING ISOLA AND MUSHROOM IN KINETICS OF CATALYTIC REACTIONS
Chuvash State University, Cheboksary, Russia

9. **Kovalenko G.A., Perminova L.V., Komova O.V., Simakov A.V., Khomov V.V., Rudina N.A.**
HETEROGENEOUS BIOCATALYSTS FOR THE SWEETENERS PRODUCTION
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

10. **Kriger V.G., Kalensky A.V., Miklin R.M., Zakharov Yu.A.**
SELF-ORGANIZATION PHENOMENA AT SOLID STATE DECOMPOSITION OF HEAVY METAL AZIDES
Kemerovo State University, Kemerovo, Russia

11. **Krivoruchko O.P., Larina T.V., Anufrienko V.F., Kolomiichuk V.N., Paukshtis E.A.**
DETECTION OF NANODISPERSED Co^{2+} HYDROXIDE CONTAINING CATIONS IN THE TETRAHEDRAL COORDINATION
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

12. **Kundo N.N., Faddeenkova G.A.**
    ENERGETIC USE OF COKE GAS AND OF COAL GASIFICATION GASES
    Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
13. **Kuznetsova S.A., Danilov V.G., Taraban'ko V.E., Kuznetsov B.N.***
    FINE CHEMICALS FROM LARCH WOOD BIOMASS OBTAINED BY INTEGRATED CATALYTIC AND EXTRACTION PROCESSES
    Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia
    **Krasnoyarsk State University, Russia*
14. **Lazareva E.V., Aleshina G.I., Van'kova N.E., Plyasova L.M., Popova G.Ya., Andrushkevich T.V.**
    PARTIAL OXIDATION OF PROPANE ON V_2O_5-MoO_3-BASED CATALYSTS
    Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
15. **Mysov V.S., Ione K.G.**
    BIFUNCTIONAL CATALYSTS FOR THE SYNGAS CONVERSION TO LIQUID HYDROCARBONS
    SEC "ZEOSIT" SB RAS, Novosibirsk, Russia
16. **Pashkov V.V., Chesak S.V., Belyi A.S.**
    SIMULTANEOUS TRANSFORMATION OF METHANE AND THE HIGHER ALKANES IN CONDITIONS OF CRACKING REACTION
    Omsk Department of Boreskov Institute of Catalysis SB RAS, Omsk, Russia
17. **Simonov A.D., Mishenko T.I., Yazykov N.A., Parmon V.N.**
    CATALYTIC PROCESSING OF RICE HUSK
    Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
18. **Zakharov V.J., Gazenaur E.G., Frolova Ya.S.**
    THE PRODUCTS OF PHOTOCHEMICAL DECOMPOSITION OF THREADLIKE CRYSTALS AZIDES OF SILVER AND LEAD
    Kemerovo State University, Kemerovo, Russia

ORAL PRESENTATIONS

RESEARCH AND DEVELOPMENT OF NATURAL GAS CONVERSION IN DALIAN INSTITUTE OF CHEMICAL PHYSICS (DICP)

Xinhe Bao

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, CAS,
Dalian 116023

After 50 years' exploring and construction, several gas areas are found in different areas of China, particularly in northeast area and west area, such as Talimu in Xinjian province, and the explored and verified geological storage of gas has accumulated to more than 3.0 trillion cubic meters. It is encouraging that thanks to the attention the government pay to and the growing civilian awareness on the sustainable development, environmental protection, and reasonable energy composition, the gas market increases rapidly with a quick-rising demand. However, the explored resource of gas is dominantly distributed in the remote areas, which are far from the densely populated and economically developed areas, such as the cities in the east coast and the northeast. To bring remote gas to the market, a pipeline with more than 4000 km in length from Talimu of Xinjian province to Shanghai has been planed and will be built in the coming years. As another option for transferring the energy derived from gases, the in-situ conversion of natural gas to liquid fuels and valuable chemicals has attracted much attention of the government and industry, and several projects related the chemical conversion of natural gas have been approved by different sections of the government in the last years. Among them, one of the very important projects is a so-called state key project for fundamental research with the title of "Catalytic Basis of the Optimal Utilizations of Natural Gas and Coalbed Methane". Several important research institutions in the field of catalysis in China, e.g. Xiamen University, Nanjing University, Taiyuan Institute of Coal Chemistry, Lanzhou Institute of Chemical Physics and Dalian Institute of Chemical Physics, are actively involved in this project. The overall aim of the project is to develop the science and technology of a series of catalytic processes to open up pioneering forms of chemistry and chemical engineering to produce basic petrochemical feedstock from natural gas in petroleum fields and coalbed methane in coalfields in place. The processes will produce higher valued and more portable methanol, ethene, aromatics, oxygenates and high quality liquid fuels. Its foundations are the selective activation of the C-H bond and the control of its reaction, innovative catalytic processes and catalysts, establishing and developing a reaction dynamics theory of catalysis, the understanding from fundamental theory of the key technologies for the optimal use of natural gas and coal-bed methane and to relate this to the key questions of "controlled activation and selective conversion". It also aims to provide scientific fundamentals for further innovative technologies in the above fields and related fields of catalysis. The main topics of this project are: production of synthesis gas and hydrogen from natural gas, production of high quality liquid fuels, methanol and oxygenates via synthesis gas from natural gas, ethene from natural gas, catalytic combustion of methane, production of aromatics and hydrogen from methane under oxygen-free conditions, structure-activity relationship of catalyst and catalytic systems and *in situ* characterization of reaction dynamics, and the identification of the reaction intermediates and reaction mechanisms of catalytic reactions.

As the center of excellent for natural gas conversion, Dalian Institute of Chemical Physics has been appointed to be the leading institute for this program. More than twenty scientists from the fields of catalysis and chemical engineering are working on the different topics, including novel routes for manufacturing syngas, direct synthesis of dimethylether (DME), modification of F-T catalyst and upgrade of F-T products and integrated processes with organic and inorganic membranes as well as novel processes of direct conversion of methane into methanol, ethylene and aromatics. In this report, a brief introduction of the state key project mentioned above will be presented, and much attention will be focused on the research and development of natural gas conversion in DICP, with emphasizes in the introduction of now processes, including the integration of POM with air as oxidant for the production of syngas and the direct synthesis of dimethylether (DME), and new route for one-step synthesis of diesel distillates with modified F-T catalysts. In the present presentation, some new progresses in the process of non-oxidative dehydrogenation of methane to produce light aromatics and hydrogen will be also described.

METHANE SELECTIVE OXIDATION INTO SYNGAS BY THE LATTICE OXYGEN OF CERIA-BASED FLUORITE-LIKE OXIDE SOLID SOLUTIONS

V.A. Sadykov, V.V. Lunin*, T.G. Kuznetsova, G.M. Alikina, Yu.V. Frolova, A.I. Lukashevich, Yu.V. Potapova, V.S. Muzykantov, S.A. Veniaminov, V.A. Rogov, V.V. Kriventsov, D.I. Kochubei, E.M. Moroz, D.I. Zuzin, V.I. Zaikovskii, V.N. Kolomiichuk, E.A. Paukshtis, E.B. Burgina, V.V. Zyryanov, N.F. Uvarov**, S. Neophytides***, E. Kemnitz******

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Catalytic oxidation of methane (natural gas) into syngas by oxygen transferred through the membranes comprised of complex oxides with mixed ionic-electronic conductivity is now considered as a vial option in the natural gas conversion technologies. In such a way, pure syngas not diluted by nitrogen can be produced by using air as oxidant, while avoiding expensive cryogenic process of oxygen separation. Ceria-based electrolytes possess a good ionic conductivity at moderate temperatures, while electronic conductivity can be imparted either by partial reduction or forming nanocomposites with precious metals (Pt, Ag etc). Another promising option is methane conversion into syngas by the lattice oxygen of ceria–based mixed oxides in red-ox cycles, with reoxidation of reduced systems by air or even by water or carbon dioxide.

This paper presents results of work aimed at design and characterization of catalysts for those processes comprised of ceria modified by Zr, La, Sm or Bi and promoted by Pt. Main idea is to enhance the oxygen mobility in the lattice of ceria by incorporating dopant cations while increasing the rate of methane dissociation by supporting Pt.

Samples of mixed ceria-based oxides containing up to 50 at. % of a dopant were prepared via Pechini or mechanical activation (MA) routes and calcined at temperatures in the range of

500-700 °C. For $Ce_{0.5}Zr_{0.5}O_2$ system, up to 30 % of Me^{4+} cations were substituted by La^{3+}. Pt (up to 1.4 wt. %) was introduced by the incipient impregnation method. Samples were characterized by X-ray diffraction (XRD), X-ray radial electronic distribution (RED) and EXAFS using a synchrotron radiation, TEM, UV-Vis, Raman, SAXS, FTIRS of lattice modes and adsorbed CO, conductivity measurements (the latter for pressed and sintered samples). Oxygen mobility up to 700 °C was estimated by using isotope exchange both in dynamic and isothermal conditions and by isothermal reduction by CO in pulse and flow modes. Methane oxidation by the lattice oxygen of those systems into syngas and combustion products was characterized in both isothermal and temperature-programmed regimes up to 900 °C.

For all dispersed samples, the structure corresponds to that of the fluorite-like solid solution. The tetragonal distortion of the local oxygen environment around both Ce and guest cations was revealed by EXAFS, RED (splitting of peaks corresponding to Me-O and Me-Me distances) and FTIRS of lattice modes (splitting of the Me-O band). Progressive disordering of the coordination sphere with the dopant content is reflected in decline of the coordination numbers (EXAFS, RED) and intensity of the Raman band at ~ 490 cm^{-1}. Disordering is usually more pronounced for samples prepared via MA route, for which microstrains are abundant. At a given temperature, for ceria samples doped by Me^{3+} cations, conductivity increases with the substitution up to a certain level (specific for a dopant and a preparation route) followed by decline. This feature is usually assigned to association of vacancies with dopant cations into complex defects.

Oxygen mobility in the lattice of oxidized samples estimated by the isotope exchange and isothermal samples reduction by CO varies non-monotonously with the substitution degree declining at a high dopant content. Incorporation of La into Ce-Zr-O system decreases the surface and lattice oxygen mobility and reactivity by rearranging the structure and decreasing concentration of anion vacancies. Samples modification by Pt does not affect appreciably dynamics of the oxygen exchange, though decreasing the rate of oxygen diffusion from the bulk to the surface of reduced samples, probably, due to its incorporation into the subsurface layer. Several peaks corresponding to removal of the surface and bulk oxygen followed by the lattice rearrangement are usually present in H_2 TPR curves. Peaks in the range of 300-500 °C can be assigned to reduction of bulk Ce^{4+} cations which have dopant cations as neighbors, such dopant as Bi^{3+} being reduced to metal as well. A high-temperature (700-800 °C) H_2 TPR peak corresponding to reduction of bulk Ce^{4+} without neighboring dopant cations declines by intensity and shifts to lower temperatures with the dopant content, the latter feature correlates with the lattice disordering. In CH_4 TPR the low-temperature peaks usually corresponds to methane combustion, while the high–temperature ones (at ~700-900 °C) – to methane oxidation into syngas. Modification of Sm-, Zr-, Zr+La-doped samples by Pt shifts H_2 and CH_4 TPR peaks to lower temperatures and increases syngas selectivity, which is explained by facilitation of hydrogen and methane dissociation. In contrary, on Bi-doped samples Pt supporting decreases the rates of reduction while favoring methane combustion. Hence, Bi cations in the surface layer of ceria-based solid solution are able to efficiently activate reductants by itself. Analysis of results revealed that the rate of methane transformation into syngas by the lattice oxygen of ceria-based systems is controlled by the methane dissociation and not by the oxygen diffusion.

Even at moderate (500 °C) temperatures, for Pt modified ceria samples doped with considered here cations, up to 5 monolayers of reactive oxygen is easily removed by methane generating CO and hydrogen with a high selectivity without any carbon accumulation. Deep samples reduction was found to be accompanied by the surface layer reconstruction leading to development of the microdomain structure and decreasing the near-surface oxygen mobility. Samples reoxidation by water or carbon dioxide at the same temperature restores the oxygen capacity producing more hydrogen or CO. Repeated redox cycles do not deteriorate the samples performance. Hence, modified ceria-zirconia systems are promising efficient catalysts of methane conversion into CO and hydrogen in the unsteady-state conditions of redox cycles. A high mobility and reactivity of their bulk oxygen makes them also suitable materials for design of membrane catalysts for methane oxidation into syngas by the oxygen of air selectively transferred through their lattice.

Acknowledgements

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ADVANCES IN UV RAMAN SPECTROSCOPIC STUDIES ON CATALYSTS AND CATALYST PREPARATION

Can Li

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Introduction

There are a number of potential advantages of Raman spectroscopy over other techniques available for catalysis studies. The main limitations of conventional Raman spectroscopy are the relatively low sensitivity and the fluorescence interference. The latter is an even severe problem for the characterization of many real catalysts which often show strong fluorescence arising from the surface species like carbonaceous species derived under working conditions. The fluorescence is nearly absence in the region when the wavelength is shorter than 300 nm. So the fluorescence interference can be avoided by shifting the excitation laser from the visible region where for conventional Raman spectroscopy to the UV region (below 300 nm) where without fluorescence interference. The fluorescence is left behind in the visible region while the Raman spectrum is moved out from the fluorescence region to the UV region. So the fluorescence interference can be avoided for most catalysts in the UV Raman spectroscopy,[1,2] this open the possibility for characterizing the catalysts which are difficult to obtain the visible Raman spectra mainly because of the strong fluorescence interference. Another advantages of UV Raman spectroscopy may be the resonance Raman enhancement in some Raman bands because the UV laser could frequently excite the electronic states of samples.

Results and Discussion

Using UV Raman spectroscopy, we have studied sulfated zirconia,[3] coked FCC catalysts,[4] zeolites and alumina-supported oxides[2,5] that all have strong fluorescence background in their visible Raman spectra, but free of fluorescence interference in the UV Raman spectra. The UV Raman spectroscopy opens the possibility for characterizing those catalysts that are difficult to study by conventionally used visible Raman spectroscopy. This also allows us to study catalysts under working conditions with in-situ Raman spectroscopy.

One of the very interesting issues in transition metal substituted zeolites or molecular sieves is to identify the framework transition metal ions. The charge transfer transition between the framework oxygen atom and framework transition metal atom, namely, p.> d. transition falls in the 200-350 nm region for most zeolites with the framework transition metal atoms (e.g., 220 nm for TS-1, 250 nm for Fe-ZSM-5, and 270 nm for V-MCM-41). Thus, it is possible to identify the framework transition metal atoms based on the UV resonance Raman effect. We have studied the transition metal ions in the framework of molecular sieves using the UV resonance Raman spectroscopy. For examples, titanium ions in TS-1,[6] iron ions in Fe-ZSM-5[7] and vanadium ions in V-MCM-41[8] were successfully identified. Recent study on Fe-ZSM-5 shows that UV Raman spectroscopy can follow the synthesis of Fe-ZSM-5 from the very beginning of the zeolite synthesis through the formation of Fe-ZSM-5.

The visible Raman study of the supported molybdate has been limited to the low loading of molybdate because of the low sensitivity and the strong fluorescence interference of the conventional Raman spectroscopy. Our recent studies showed that UV resonance Raman spectroscopy is a very sensitive technique for the characterization of the coordination structures of supported molybdate even with extremely low loading even down to 0.1 wt% MoO_3. This makes it possible to get the information of the interaction between the surface molybdate species and the support particularly when the concentration of the surface molybdate species is very low. The low concentration of supported vanadium oxide can be also detected by UV resonance Raman spectroscopy.

Zirconia exhibits three different phases: monoclinic (m-ZrO_2), tetragonal (t-ZrO_2) and cubic (c-ZrO_2). t-ZrO_2 is a metastable phase of ZrO_2 at low temperatures and it changes into m-ZrO2 at elevated temperatures. Stabilized tetragonal zirconia is considered as an important structure for ceramics and sulfated zirconia catalyst. But the phase transformation from the metastable tetragonal (t) phase to the monoclinic (m) phase of crystalline ZrO_2 prevents its applications from a broader temperature ranges. Many studies have addressed the factors that affect the phase transformation of tetragonal zirconia, however, past investigations provided the information mainly on the bulk of ZrO_2. We present our recent results[10] about UV Raman spectroscopic studies on the phase transformation of zirconia, sulfated zirconia and yttrium oxide doped zirconia. It is found that the UV Raman spectroscopy is a surface sensitive technique for zirconia because zirconia has UV absorption. The UV Raman spectra together with visible Raman spectra and XRD patterns indicate that the phase transformation starts from the surface region of the particle and then extends into the bulk. Recent advances in UV Raman spectroscopic characterization of catalysts show that this new technique can successfully follow the detailed structural evolution of a catalyst under the synthesis procedure.[11-13]

Acknowledgements

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STRUCTURE-ACTIVITY RELATIONSHIPS OF ALUMINA-SUPPORTED V-MG-O CATALYSTS FOR THE OXIDATIVE DEHYDROGENATION OF PROPANE

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Alumina-supported V-Mg-O catalysts were prepared as model systems to understand structure-activity/selectivity relationships of bulk V-Mg-O catalysts. Total V+Mg loading on alumina was 20 atoms per nm^2 of alumina support. The atomic V/Mg ratio ranged from 1/4 to 4/1. The catalysts were characterized by XRD, Raman spectroscopy and ^{51}V-NMR. The catalysts were evaluated for propane oxidative dehydrogenation of propane to propylene. Propane conversion increases as V/Mg ratio increases up to 1/1 (Figure 1), mainly due to propylene formation, which reaches 3.5 % yield for 1V/1MgAl and levels off for higher V loading values.

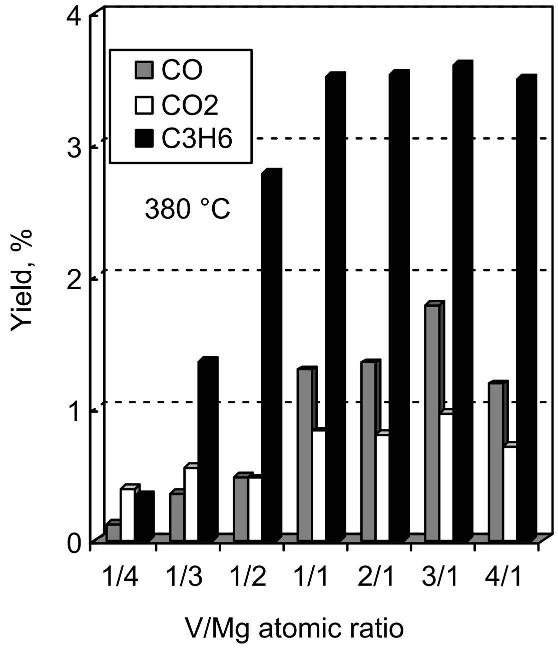

Figure 1. Yields during propane ODH at 380°C. Catalyst weight 100 mg, total flow 45 ml/min, reaction feed: $C_3H_8/O_2/He$ = 1/6/4.

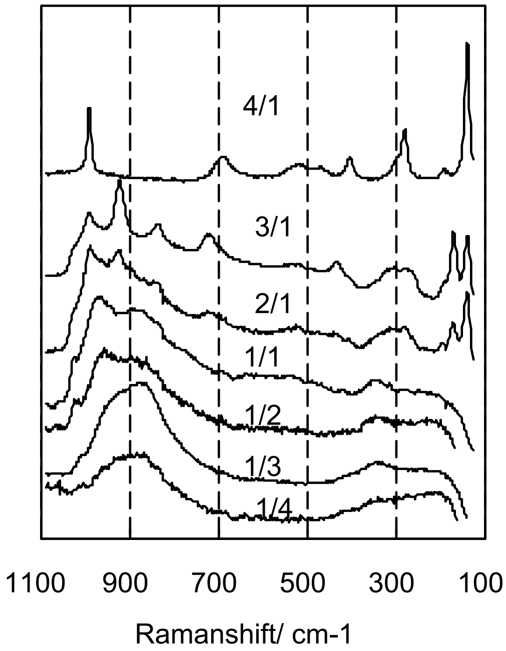

Figure 2. In situ Raman spectra of dehydrated V-Mg-O/Al_2O_3 catalyst at different V/Mg atomic ratios.

X-ray diffraction patterns of all the catalysts only show the presence of alumina support, thus, supported V-Mg-O phases are either amorphous or too small to generate diffraction pattern. Raman spectra show the presence of micro-crystalline aggregates (Figure 2). At the lowest V concentrations a broad Raman band is present near 900 cm^{-1}. It does not correspond to any known phase, but could be the overlapping of broadened bands of magnesium metavanadate, which occur at 949, 904, 879 and 849 cm^{-1}. Such broadening may be due to a distortion of its structure caused by its small size. As V/Mg ratio increases, new Raman bands evidence the formation of magnesium pyrovanadate. V_2O_5 crystallites are evident at V/Mg ratio 2 and above; V_2O_5 is the only phase present at V/Mg ratio of 4. A new Raman band is evident at 1030 cm^{-1}, sensitive to hydration. This band is characteristic of the stretching mode of the terminal V=O bond of dispersed vanadium oxide species and is clearly visible for 1V/2MgAl, 1V/1MgAl and 2V/1MgAl. The ^{51}V MAS spectra consisted of superimposed patterns of spinning sidebands representing up to 6 vanadium sites from five species (Figure 3). “Type 1” prevails in the sample 1V/4MgAl. NMR parameters of this vanadium site are similar to those in $Mg_3(VO_4)_2$ the changes is quadrupolar constant and chemical shielding anisotropy must be due to distortions of the structure due to dispersion of $Mg_3(VO_4)_2$ over the support. Then, . -$Mg_2V_2O_7$ passes through a maximum in the sample 1V/2Mg (25%). Sample 1V/2Mg possesses a new type of vanadium species “type 2” with isotropic shift –500 ppm and axial value of chemical shielding anisotropy. This species passes through a maximum for 1V/1Mg (37%) and is sensitive to hydration, typical for dispersed vanadium oxide species. Additional amounts of vanadium afford $Mg(VO_3)_2$, which is not very abundant (< 5%). Finally, V_2O_5 dominates at higher vanadium loadings. Both characterizations evidence the formation of dispersed vanadium oxide species for the samples that show the most important increase in propane ODH. Thus, it appears that dispersed vanadium oxides must be directly involved in the rate-determining step for this reaction.

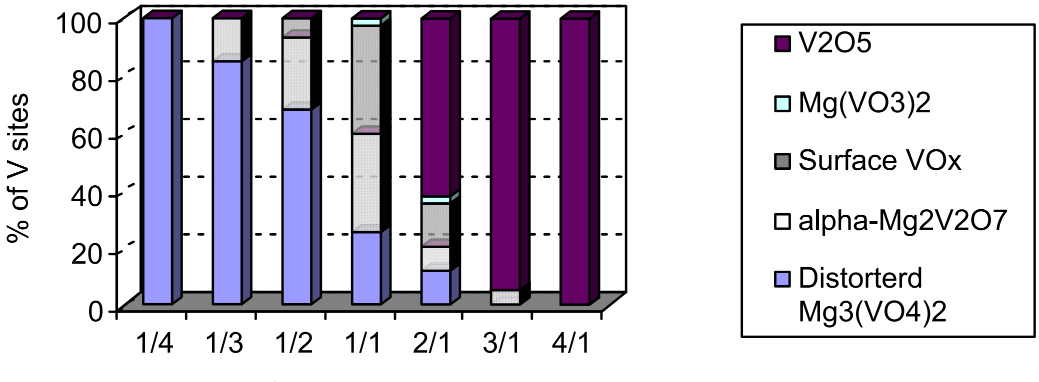

Figure 3. Distribution of V species determined by ^{51}V-NMR in dehydrated V-Mg-O/Al_2O_3.

Acknowledgments

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HOMOGENEOUS AND HETEROGENEOUS CONTRIBUTIONS TO LIGHT ALKENES PRODUCTION FROM THE CATALYTIC OXIDATIVE CRACKING OF HEXANE

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Introduction

Catalytic route is considered as a promising alternative way to traditional pyrolysis in light alkenes production from hydrocarbons. Due to its low activation energy and chemical equilibrium shift with oxygen introduction, alkenes production from catalytic oxidative dehydrogenation of corresponding light paraffins has attracted much more attention in last ten years. It was also found that homogeneous reaction contributes to the total effect of a catalyst in this field [1]. However, no enough attention has been taken to catalytic oxidative course for light alkenes production from heavy hydrocarbons, and especially to homogeneous contributions in it[2]. Not only dehydrogenation but also cleavage of C-C bonds becomes important in the oxidative course of higher hydrocarbons. In this paper, light alkenes production from catalytic oxidative cracking (COC) of hexane was investigated using three typical catalysts: HZSM-5 (solid acid catalyst), 10%La_2O_3/HZSM-5 and Li_2O/MgO (basic catalyst). The homogeneous contribution to oxidative cracking of hexane, which can be called gas phase oxidative cracking (GOC) of hexane (C6), was also considered.

Results and discussion

In a quartz reactor, pyrolytic cracking of C6 without oxygen is inconspicuous below 650ºC. For example, at 500ºC and 650ºC, the conversion of C6 in pyrolysis is only 0.99% and 5.75%, respectively. However, in the GOC process, the cracking is greatly accelerated by the presence of oxygen even at relatively low temperature (see Figure 1). It should be noted that not CO_2 but CO prevail in the COx produced in the GOC process (see Table 1). Based on the above results and the thermodynamic calculation of autothermic reaction with C6 / O_2 = 0.8, CO_2 emission from GOC process is near 90% lower in theory than that from pyrolysis, in which enormous CO_2 is released due to the external burning of a great deal of fuel. Our detail work has shown that the GOC process seems to be an environmentally benign and efficient new route for alkenes and CO (a valuable petrochemical feedstock) production from higher hydrocarbons such as heavy oil and residual oil.

Table 1 Selectivity to CO and CO_2 in the GOC of C6

Temperature. (ºC)	Selectivity (%)	
	CO	CO_2
450	13.87	1.71
500	15.42	0.98
560	15.41	0.76
600	14.99	0.73
650	15.18	0.70

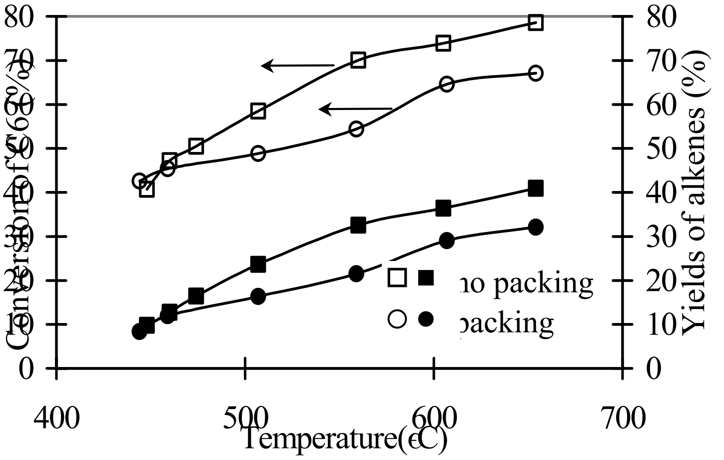

Figure 1 Conversion and yield in the GOC of C6 with/ without quartz packing. $C6/O_2$=0.8(mol), oxygen/nitrogen=22/23 (ml/min, NTP)

The selectivity to alkenes in the GOC process is lower than that in pyrolysis, although the conversion of C6 and yield of alkenes in the GOC process are higher at relatively low temperature. The COC process was expected to increase the selectivity to alkenes. Quartz particles have been generally used to limit the extent of homogeneous reactions. However in our experiment conditions, packing of quartz particles has only some effect in inhibiting homogenous reactions. Therefore the following work on the COC process was performed without complete remove of homogeneous contribution.

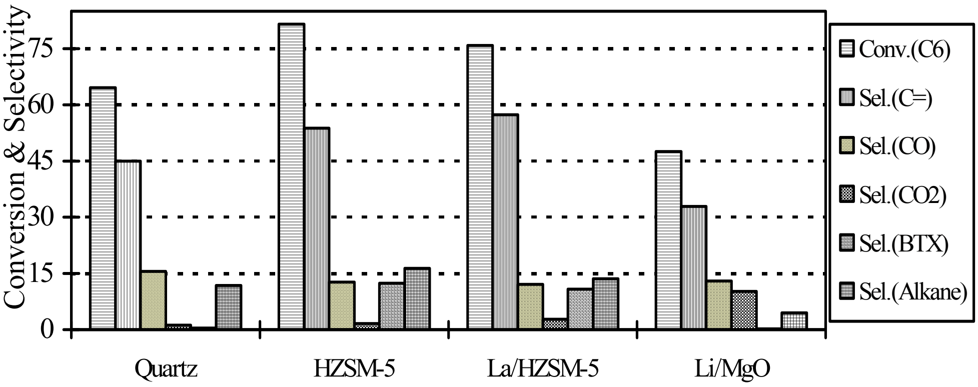

Figure 2 COC of hexane over three representative catalysts. Reaction temperature 600ºC, GHSV (h^{-1})=15000, $C6/O_2$=0.8(mol), oxygen/nitrogen=22/23 (ml/min, NTP)

The catalytic reaction became remarkable only when the reaction temperature is over 550ºC, below which the remained GOC process's contribution was so much that it concealed the catalytic reactions. The catalytic results at 600ºC are shown in the Fig 2, conversion of oxygen was 100% in all cases. Due to easy rupture of C-C bonds with the solid acid catalyst, both the conversion of C6 and selectivity to alkenes increased in the COC process with HZSM-5 and La/HZM-5. Much undesired aromatic (mainly toluene) were also produced because of secondary reactions. The HZSM-5 modified with La showed a little higher selectivity to alkenes but lower conversion of C6 than those with unmodified HZSM-5, it could be explained by the change of acid strength and depression of alkanes and undesired aromatics. The aim for choosing Li/MgO catalyst is to utilize its ability in dehydrogenation. Unfortunately, reactivity sharply decreased and the selectivity to CO_2 increases significantly in the COC of hexane at 600ºC with basic catalyst, Li/MgO. The basic catalyst seemed apt to limit homogenous reaction and promote total oxidation reaction. The selectivity to CO remained nearly constant in all COC cases, which can be attributed to the remained GOC contribution. Based on above considerations, the solid acid catalyst modified by the rare earth mental exhibits promising ability in the COC of higher hydrocarbons in which GOC process' contribution could not be ignored.

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CATALYTIC FUEL COMBUSTION. RESULTS OF 20 YEAR FUNDAMENTAL STUDIES, ACHIEVEMENTS IN PRACTICAL APPLICATION AND FUTURE PROSPECTS

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Catalytic combustion is proved effective technique for clean combustion of fuels. It is fundamentally different from traditional flame combustion because fuels are oxidized flamelessly on the surface of catalysts at relatively low temperatures: 400-1000 °C.

For the past 20 years extensive R&D work on catalytic fuel combustion over various catalysts has been carried out in our laboratory.

The fundamental research was conducted in two main directions:

- study of kinetics and mechanism of catalytic combustion of organic compounds of various nature (hydrocarbons, alcohols, amines, etc);
- synthesis and characterization of novel efficient combustion catalysts containing both transition metal oxides and noble metals. Methods of catalyst preparation in shape of granulated, honeycomb, fibrous, foam material supported, etc. have been developed.

In this lecture, results of systematic studies of kinetics of catalytic combustion of various organic compounds: hydrocarbons, alcohols, amines and other nitrogen containing compounds will be presented.

Our approach is methodical studies in homologous series of organic molecules over oxide and noble metal catalyst. The study of reaction intermediates with application of isotopic C^{14} labeled compounds (alcohols, aldehydes, carbonic acids and CO), kinetic isotope effect measurement and traditional kinetic studies allowed elucidation of the reaction mechanism for n-alcohols.

It was found that at high temperatures reactions of catalytic combustion could proceed via so-called heterogeneous-homogeneous mechanism. Free radicals are formed on the catalyst surface from adsorbed molecules and desorb into the gas phase where they undergo further transformations. Original studies of free radicals generation upon interaction of a series of alcohols and amines with oxygen over Pt and oxide catalysts were carried out. ESR identification of radicals was performed. Kinetic dependencies of radical accumulation were determined. The rate of radicals formation over the catalysts studied at 600-1000 K is in the range of 10^{10}-10^{12} particles/$m^2 \cdot s \cdot torr$, which is sufficient for initiation of gas phase reactions over catalysts under conditions of catalytic fuel combustion.

A very attractive feature of catalytic combustion is the possibility to reduce drastically NO_x emissions. Rather low temperature of catalytic combustion allows nearly complete elimination of thermal NO_x. The problem of fuel NO_x control was reliably solved by studying kinetics of oxidation of a series of nitrogen containing compounds, choosing selective catalysts and providing conditions of predominant conversion of fixed nitrogen to N_2.

Based on fundamental studies, four main types of processes and apparatuses for catalytic fuel combustion were developed:

1. Catalytic heat generators (CHG) based on the use of fluidized bed of granulated spherical catalyst particles with a capacity of 10-1000 kW. The CHGs provide high heat efficiency due to the use of fluidized bed and catalysts with high performance. Pilot and industrial CHGs were tested with various fuels: natural gas, diesel fuel, residual oil, etc. They were shown to be efficient for heat production, drying and thermal treatment of powder materials, treatment of dust loaded off-gases, treatment of waste water containing organic admixtures and hazardous organic wastes, e.g. mixed waste containing radionuclides and toxic rocket fuels, such as unsymmetrical dimethylhydrazine (UDMH).
2. Catalytic air heaters working on natural gas with a capacity 70-850 kW. Air heater performance is based on two-stage combustion. At the first stage flame combustion proceeds under fuel rich conditions at . =0.95-0.98. Then the combustion products with additionally injected air pass into the second chamber equipped with an assembly of honeycomb monolithic catalyst. The catalyst provides total oxidation of CO and HC and reduction of NO_x. The purified flue gas is further diluted with air behind the catalyst and ejected from the apparatus to heat premises.
3. Catalytic gas burning domestic space heaters with a capacity of 2-3 kW. Two types of heaters were developed: for combustion of city gas from cylinders and natural gas. The active component comprising combination of transition metal oxides and Pt is supported on silica-alumina fiber mat (Termocat-1), or on multichannel ceramic plates (Termocat-2, 3). The original construction and use of high performance catalytic materials provides complete burning of fuel and concentrations of NO_x and CO in flue gases below sanitary standards.
4. Catalytic water-heating boiler based on foam catalysts with a capacity of 20 kW. The boiler works with natural gas. It operates with original catalysts supported on highly porous foam materials and catalytic heat exchangers. The heat efficiency of the boiler is 88-94%. The concentrations of CO and NO_x in the flue gas are below 5 mg/m^3.

The future prospects of application of catalytic combustion for gas turbine catalytic chambers, fuel cell reformers, etc. will be discussed.

COAL MINE VENT GASES UTILIZATION FOR HIGH-TEMPERATURE HEAT PRODUCTION IN CATALYTIC REVERSE-PROCESS: MATHEMATICAL MODELING

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This study is a part of joint cooperation project which aims at utilizing the methane content of vent air from coal mines for high temperature heat production and simultaneously to convert the greenhouse gas methane to less harmful compounds. The work was performed under financial support of European Commission in the framework of the Programme INCO-2 (contract No. ICA2-CT-2000-10035).

First suggestion to use the periodic reversals of reaction mixture flow in a catalytic fixed bed with a view of high-temperature heat production was done in 1985 (RU Patent No. 1160201). The subsequent studies on the matter have brought to light some technical difficulties in the process application. First of all, it concerns the periodic changes of the hot gas flow direction in the heat-exchanger placed in the central part of the reactor..

In our study the theoretical analysis of another flow sheet has been done by means of mathematical modeling under the assumptions of well known two-phase mathematical model of the heat and mass transfer processes in a fixed bed of catalyst or inert material. In the scheme, a part of the hot gas stream is directed from the high-temperature central zone of the reactor into a heat exchanger and after that passed to atmosphere. The rest stream goes throw the second catalyst bed as in a conventional reverse-process. Now the stream route in the heat exchanger is invariable in time. We used the kinetic parameters of methane oxidation on the Pd catalyst, and compared with the data of methane oxidation over the Mn-oxide catalyst.

In the report a detailed parametric survey of the influence of different control parameters on the heat utilization efficiency is presented. Namely, we considered inlet methane concentration (0.3-2.0 vol.%), catalyst and inert particles sizes, lengths of catalytic and inert fixed beds. The study of the process operation stability in dependence of inlet methane concentration and degree of the high temperature heat utilization has been done.

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THE CATALYTIC CONVERSION OF CARBOHYDRATES INTO THE LEVULINIC ACID AND 5-HYDROXYMETYLFURFURAL DERIVATIVES

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Hexose carbohydrates, like cellulose, sucrose and fructose are known to produce levulinic acid (LA) and 5-hydroxymethylfurfural (HMF) in the acid media under rigorous conditions (above 160 °C). Levulinic acid is applied for the polymer production and in other different fields of chemical industry and researches. LA is also formed at moderate temperatures about 100 °C and high acidity of the solutions, but such processes have not been comprehensively studied. The low yield of the products is the great problem of the processes, and the main aim of this work is to increase the selectivity of the acid-catalyzed conversion of carbohydrates applying the alcohols as extractants of the products.

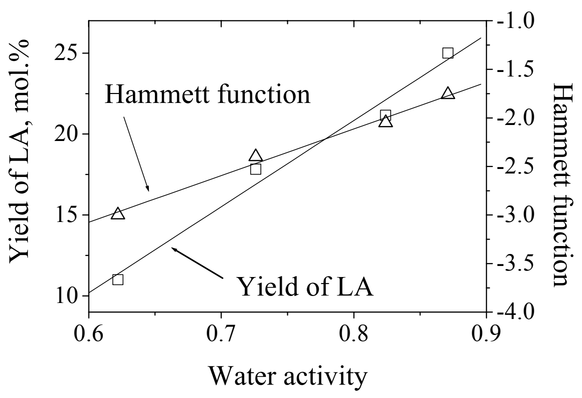

Fig. 1. Influence of water activity and Hammett acidity function on the yield of LA (concentration of glucose – 0.25 M, 98 °C, HCl concentration in the range of 5 – 8 M).

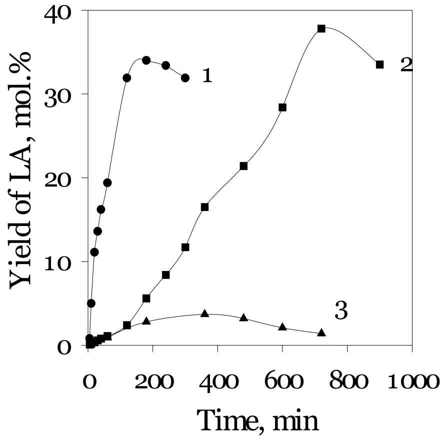

Fig. 2. The influence of the acid nature on the kinetics of levulinic acid formation from glucose (0.35 M) at 98 °C and H^0 = -2.6: 1 – 7.2 M HCl, 2 – 5.8 M H_2SO_4, 3 – 10 M H_3PO_4.

The rate of LA formation from glucose slightly depends on HCl concentration, but selectivity of the process strongly increases with raising the water activity (Fig. 1) estimated as the ratio of vapor pressure of the solution and pure water. Such selectivity gain can be explained by decreasing the contribution of pathways connected with the reactant and intermediate condensation into humic substances when raising the water activity. It should be noted that under the discussed conditions the acidity function H^0 is approximately proportional to the water activity (Fig. 1).

Hydrochloric acid is twelve times more active, than sulfuric acid at the same H^0, but the selectivities of the LA formation are practically the same in both cases (35 – 38 mol. %). Phosphoric acid is too weak for application as the catalyst of the process: the maximum yield of levulinic acid does not exceed 5 mol. %, and the rate of process is small (Fig. 2). To explain these ratios of the rates and yields one may take into account the known approximate connection between H^o and activities of H_2O and H_3O^+ :

$$H^0 = a - \lg (X(H_3O^+)/X(H_2O)) \qquad (1)$$

According to the equation (1) the necessary H^0 value can be attained either by increasing $X(H_3O^+)$ for the strong acids or by decreasing $X(H_2O)$, the water activity, in the case of weak acids. The comparison of the results presented in Fig. 1 and 2 shows that the water activity, but not Hammett acidity function, is responsible for the selectivity of the levulinic acid formation. Sulfuric acid like hydrochloric one permits to attain good selectivity of producing levulinic acid.

Butanol is the efficient and available extractant for levulinic acid (the distribution coefficient k = 4). It forms stable two-phase system with water, but concentrated sulfuric (above 5,1 M) and hydrochloric acids are known to give homogeneous solutions with the alcohol. To prevent homogenization we apply the mixture of sodium sulfate and sulfuric acid as the catalyst (sodium bisulfate with or without the addition of sulfuric acid). This approach allows creating the stable two-phase system water – butanol with good catalytic activity.

The main products of the acid-catalyzed sucrose conversion in the presence of butanol are butyl levulinate and 5-butoxymethylfurfural. Their structures are confirmed by GC-MS, ^{13}C and ^1H NMR spectra. Under optimum conditions (4.6 M $NaHSO_4$) the total yield of the products attains 60 mol. % from sucrose and 83 mol. % from fructose. The method developed is much more efficient than the known synthesis from chloromethylfurfural.

To increase the selectivity of the process by extracting the products from the reaction mass the flow unit was constructed and the process of the carbohydrate acid conversion in the flow of butanol was studied. The main problem of such process is the extraction of fructose or intermediate of its conversion, and these effects do not permit to attain good yields of the products.

Acknowledgements

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BIO-ETHANOL STEAM REFORMING OVER CERIA-SUPPORTED Ni and Ir CATALYSTS

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Introduction

Among the various fuels which can be converted to hydrogen to be used in fuel cells for mobile and stationary applications, alcohols are very promising candidates because they are easily decomposed in the presence of water and generate an H_2-rich mixture suitable for fuel cells. Compared to methanol, renewable ethanol, as a source of hydrogen, can be manufactured by fermentation of crops which consume carbon dioxide, thus offering a nearly zero emission of CO_2. However, only a limited number of reports have appeared in the open literature dealing with the reforming of ethanol due to the relatively sever reaction conditions and less well-formulated catalysts. Supported Ni, Cu, Pt, Rh, Co and other metal oxides were reported to be active, but often resulted in poor selectivity for hydrogen and high operation temperature was required to achieve total ethanol conversion. The reaction behaviors were also strongly affected by both the active metal and the support used. Here, we reported hydrogen production from bio-ethanol steam reforming over ceria-supported Ni and Ir catalysts characterized by high selectivity toward hydrogen production and lower operation temperatures.

Results and Discussion

The Ir/CeO_2, Ni /CeO_2, and $Ir-Ni/CeO_2$ catalyst were prepared by the deposition-precipitation method. Briefly, the CeO_2 support ($96m^2g^{-1}$) was first suspended into the solutions to H_2IrCl_6 and $Ni(OAc)_2$ or their mixtures, followed by the addition of an 0.25M Na_2CO_3 aqueous solution at 348K until the pH value of the mixed solution reached 9.0. The obtained solids were then dried overnight at 383K and calcined at 673K. Steam reforming of ethanol was carried out in a fixed-bed reactor and the composition of the reactor effluent was analyzed by the on-line chromatographs.

Table.1 summarized the production distributions and hydrogen yields over Ir/CeO_2, Ni/CeO_2, and $Ir-Ni/CeO_2$ catalysts together with the bare CeO_2. It can be seen that Ir/CeO_2

catalyst showed extremely high selectivity for hydrogen even at 623 K with the formation of CO around 1%. While, the Ni/CeO_2 catalyst only exhibited marginal ethanol conversion and deactivated rapidly soon after the reaction was started. Interestingly, the Ir-Ni/CeO_2 catalyst gave much less hydrogen yield even though the loading of Ir was not changed, probably caused by the addition of nickel. Another feature of this low temperature operation is that methane was formed as the dominant byproduct up to 40%, mainly through ethanol decomposition. However, the CO formation was just around 1% in either case. When the reaction temperature was raised to 773K, Ir/CeO_2, Ni/CeO_2, and Ir-Ni/CeO_2 catalysts all gave similar hydrogen yields and C-containing product distributions. No significant difference in activity, selectivity, and stability can be observed during the runs lasted for 12 hours. The common feature at this operation temperature is that the remarkable decrease in the formation of methane combined with the great increase in the production of CO, suggesting the reforming of methane either with CO_2 or with steam was occurred as a major reaction. If a comparison is made for the reaction behaviors of Ir/CeO_2 catalyst between 623 K and 723K, it can be found that there is no large change in hydrogen yield except the occurrence of methane reforming reactions. From a practical point of view, this catalyst is preferred based on its high activity at lower temperatures and high selectivity toward hydrogen production with less CO formation. However, the significant dependence of Ni-containing catalysts indicated that higher operation temperature is needed to achieve reasonable hydrogen yield, but accompanied by the higher CO formation more than 5%. In summary, the Ir-Ni/CeO_2 catalyst exhibited high activity and selectivity for steam reforming of ethanol to hydrogen production at low temperatures and is a good candidate to be used in ethanol reforming processors. However, the Ni/CeO_2 catalyst can only give good performance at high temperatures. A detailed understanding of the catalytic mechanism is undergoing.

Table 1 Reaction results of CeO_2-supported Ir and Ni catalysts for ethanol steam reforming[*]

Temp./ K	Catalyst	Ethanol conv./ %	H_2 yield/%	C-containing product distribution/%					
				CO_2	CO	CH_4	C_2H_4	CH_3CHO	CH_3COCH_3
623	Ir-Ni/CeO_2	100	39.7	60.5	0.8	38.8			
	Ir/CeO_2	100	75.4	73.7	1.1	25.2			
	Ni/CeO_2	---	---	---	---	---			
	CeO_2	14.6	11.4	19.6	2.5	0.8		47.6	29.2
773	Ir-Ni/CeO_2	100	77.8	88.2	5.2	6.6			
	Ir/CeO_2	100	71.7	87.3	5.5	7.2			
	Ni/CeO_2	100	78.3	84.5	6.9	8.2			
	CeO_2	100	17.6	29.6	2.3	26.1	41.9		

[*] Atmospheric pressure, $C_2H_5OH/H_2O/He = 1/9.6/89.4$, catalysts were pre-reduced with hydrogen at 873K.

THE BIOMASS PYROLYSIS AND GASIFICATION IN FLUIDIZED BED CATALYTIC REACTORS

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Biomass is considered as the main renewable resource for energy production. Amongst well-known methods of biomass processing (pyrolysis, liquefaction, gasification, combustion) catalytic gasification is of primary interest [1, 2].

Pyrolysis and gasification processes are based on endothermic reactions demanding supply of heat to the reaction zone. Therefore, the introduction of catalytic heat generator (CHG) into the technological cycle of these processes can be a prospective approach [3-5]. Total combustion of fuels in a catalytic fluidized bed of CHG is achieved at relatively low temperatures 600-750 °C. The application of CHGs allows to prevent formation of soot and carcinogenic hydrocarbons and to abate emissions of CO and NO_x.

The goal of this work was to study the processes of biomass pyrolysis and gasification in experimental facilities containing CHG reactors. Three setups used in this work were different by the way of conducting the pyrolysis and gasification processes.

In the *setup 1* the reactor contains fluidized bed (FB) of spherical total oxidation catalyst. The height of the FB being 50 cm. Initially the reactor is heated up by combustion of kerosene in lower part of FB and biomass is fed directly into the hot FB at the height of 40 cm. The *setup 2* contains two FB reactors. Lower reactor is for kerosene catalytic combustion and upper reactor loaded by inert bed material (. -Al_2O_3). The biomass is fed into the FB of the upper reactor. The *setup 3* contains two cylindrical FB reactors of different diameter. The reactor of smaller diameter is placed into the bigger one, so combustion of fuel proceeds in the annulus providing heat transfer through the wall into the FB of inert material in the internal reactor where biomass gasification proceeds. For the studies semolina is taken as a biomass model object, with the following chemical composition (wt. %): hydrogen 6.92;

carbon 39.18; nitrogen 1.81; ash 1.17. The combustion catalyst $Cu_xMg_{1-x}Cr_2O_4$/. -Al_2O_3 (IC-12-73) is used in the experiments. The inert bed material used in the setups 2 and 3 is granulated . -Al_2O_3.

All setups are equipped with the system for on-line continuous gas sampling for GC analysis.

Experimental results

The GC analysis of the reaction products from the reactors showed that the gas formed at biomass pyrolysis and gasification contains substantial amounts of hydrogen, methane, carbon monoxide and carbon dioxide. The relative amounts of these gases depended on the feed rates of the biomass, air and fuel and the temperature of the process and was in the range (vol. %): hydrogen – 2-7; carbon monoxide – 3-18; methane – 1-15; carbon dioxide – 7-14 (Table 1).

Table 1. Amounts of the products of biomass pyrolysis and gasification.

Feed rates of gases, fuel and biomass					T, °C	The gaseous products			
Air, m^3/h	biomas, kg/h	N_2 m^3/h	Fuel, kg/h	H_2O, g/h		H_2, % vol.	CO, % vol.	CH_4, % vol.	CO_2, % vol.
EXPERIMENTAL SETUP 1									
1.5-2	0.2-0.3	1.0	0.1-0.2	-	650-750	2.3-4.2	3.6-4.3	0.5-2.7	7.0-8.5
EXPERIMENTAL SETUP 2									
6.0	0.6-2.1	2.5	0.3	-	650-750	1.5-5.1	3.2-4.3	0.2-0.8	10-12
5.0	0.5-0.6	1.0	0.2-0.3	20-80	650-700	3.8-6.8	6.3-12	0.7-1.6	14-15
EXPERIMENTAL SETUP 3									
8.2	1.7-7.3	-	1-1.5	-	650-700	6.2-8	10.7-18	1.1-2.6	12.6-15
8.2	4.1-8.3	-	1-1.5	0.5-1.8	600-700	5.5-9	7-15	0.9-2	3.5-13

The composition of the gaseous products of these processes was shown to depend substantially on the experimental conditions and the biomass feed rate.

Acknowledgement. This work was supported by NWO grant 2000.

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INVESTIGATION OF CO OXIDATION OVER Pd/NaZSM-5 SUPPORTED CATALYST MODIFIED BY Fe

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Low temperature CO oxidation has attracted considerable attentions because of its significance in environmental protection, fuel cell, reduction of hazardous substances in tobacco, air- purification for respiratory, CO gas sensors and closed-cycle CO_2 lasers. Up to now, catalysts for CO oxidation consist mainly of metal oxides with variable oxidation states and supported noble metals (such as Pd, Pt, Au, etc.) on reducible oxides or on inert oxides. However, catalyst based on NaZSM-5 zeolite for CO oxidation is less studied. We have reported the results of CO oxidation using Pd/NaZSM-5 and Pd-Ce/NaZSM-5 supported catalysts [1,2] and found that they are good for the CO oxidation. In this paper, the results of CO oxidation over Fe_2O_3-modified Pd-Fe bimetallic supported catalysts based on NaZSM-5 prepared by impregnation method have been reported. It is found that the addition of Fe_2O_3 to the catalyst can enhance its activity remarkably.

Experimental

Pd, Fe, and Pd-Fe/NaZSM-5 supported catalysts were prepared by impregnation method as the ref. [1,2]. According to the contents of Pd and Fe (wt%), the catalysts were labeled as 0.8Pd/NaZSM-5, 0.8Pd-0.5Fe/NaZSM-5, 0.8Pd-2.5Fe/NaZSM-5, 0.8Pd-5Fe/NaZSM-5, 0.8Pd-10Fe/NaZSM-5 and 10Fe/NaZSM-5, respectively. Some of the 0.8Pd-10Fe/NaZSM-5 catalysts were further reduced at 400 °C in the stream of hydrogen gas with a rate of $25ml/min^{-1}$ for 3 h, and then cooled in hydrogen atmosphere to room temperature. Catalytic activity measurements were performed in a fixed bed reactor (i.d. 5mm) under atmospheric pressure. 150 mg of catalysts with the average diameter of 0.5-1mm was used each time. The total flow rate of the feed gas (0.8% CO, 25.3% O_2, in N_2 balance) was $25ml/min^{-1}$.

Results and Discussion

Experiment results indicated that Pd /NaZSM-5 or Fe/NaZSM-5 catalyst itself shows low activity, and the light-off temperatures (T_{50}) of them are 173.1°C and 189.1°C, which correspond to the minimum CO complete oxidation temperature (T_{100}), 180°C and 210°C respectively. The addition of Fe_2O_3 improves the activity significantly, and the activity increases with the increase of Fe-loading amounts as well as increase of reaction temperature. T_{50} data are 132.6°C, 60.6°C, 46.3°C, 29.1°C for the catalysts with 0.5wt%, 2.5wt%, 5wt% , 10wt% of Fe, and the T_{100} data are 145°C, 85°C, 70°C, 47°C, respectively. XRD results illustrate that the introduction of the hematite type Fe_2O_3 improves the dispersion of PdO species over the NaZSM-5 support, which is responsible for the high activity of Pd-Fe bimetal catalysts. Furthermore, the introduction of the second component, Fe modifies the interfaces of metal-metal and metal-NaZSM-5 and produces some synergism interactions between Pd and Fe. Some specific active centers at the interface were identified by XPS, which facilitate the activation of CO and O_2 molecules on Pd and Pd-Fe interface and therefore make the reaction proceed easily [3,4]. The lattice oxygen of Fe_2O_3 and PdO participates in the oxidation of CO, and the reduced surfaces of Fe_2O_3 and PdO can be rejuvenated by taking oxygen from the feed gas.

High space velocity of the feed gas results in a lower performance for CO oxidation. H_2 pre-reduction will also decrease the activity. XRD results indicate that the Fe crystalline phase in the reduced 0.8Pd-10Fe/NaZSM-5 catalyst presents in the form of α-Fe, while in the bulk phase Fe may be in the form of FeOOH and Fe^0. Pd in the reduced catalyst exists as Pd^0. In our previous work we found that H_2-reduction of Pd-NaZSM-5 catalyst will convert the surface Pd^{4+} gradually to Pd^{2+} and Pd^0, which will influence the catalytic performance. Based on the catalytic experiment results, we consider that the deactivation of the catalyst is mostly associated with the reduction change of Fe_2O_3 and Pd species in the reduced Pd-Fe/NaZSM-5 catalyst.

The Pd-Fe catalyst is sensitive to moisture in the feed gas. Although the directly calcined and the reduced 0.8Pd-10Fe/NaZSM-5 catalysts can completely convert CO to CO_2 at room temperature, the high activity can only maintain for less than 0.5 h and then deactivates almost completely, which may be arised from the occupation of active sites by H_2O molecules. The mechanism of deactivation is not clear and further study is in progress.

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CATALYTIC HEAT SUPPLY INSTALLATIONS OPERATING ON LIQUID AND SOLID FUELS

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At the present stage of the power industry development, the economy of power production and its environmental purity become a problem of critical importance. Traditional power installations, based on flame combustion of fuels, are among the major sources polluting the environment with heat and harmful substances (CO, nitrogen oxides, sulfur, benzpyrenes and other). The cost of equipment for the exhaust gases detoxication is comparable to the cost of basic process equipment of power installations.

The new technology of fuel combustion, offered by the Boreskov Institute of Catalysis in industrial scale, allows to avoid many disadvantages of the high-temperature fuel combustion. The technology is based on a combination of four principles: use of heterogeneous catalysts for complete oxidation of combustibles; combustion of fuels in a fluidized bed of the catalyst particles; combustion of the fuel without a substantial air surplus; overlapping the processes of the heat release and removal within the same fluidized bed.

Compared with the known methods of combustion, the catalyst allows to decrease the temperature of organic fuel combustion from 1000-1200 °C to 300-700 °C; to decrease requirements for thermochemical stability of construction materials and to reduce their erosion; to diminish heat losses through apparatus's wall; to improve explosion safety of the installations; to reach high values of power loading of the fuel oxidation and thus to decrease significantly the design size, weight and metal consumption; to exclude secondary endothermic reactions forming toxic products. Basing on the new technology, a variety of the apparatuses for the liquids heating and evaporation, for materials drying and heating, for detoxication of industrial emissions (gaseous, liquid and solid), and for a number of other processes have been designed. Pilot catalytic heat supply installations (KTU) have being used since the early 1980s to heat the auxiliary and constructed buildings. Since 1993, 26 industrial KTU units operate successfully and reliably at different facilities of Novosibirsk Region, Russia, all working parameters being at the designed level. Automatic feedback between the temperature of circulating water and the fuel consumption allows to minimize the latter, regarding the heat yield and temperature of outside air. The content of toxic substances in the KTU flue gases does not exceed sanitary norms and corresponds to the quality certificate issued by the regional sanitary inspection. Until now no information is available on the KTU failures or customer's reclamations.

The important advantage of catalytic combustion in the fluidized catalyst bed is an opportunity to burn efficiently the solid fuels (coal, peat) as well. The data on operating of KTU with solid fuels (brown coal, peat and biomass) are given in the work.

Cu-Zn-Al MIXED OXIDE CATALYSTS PREPARED VIA HYDROTALCITE-LIKE PRECURSORS FOR WET AIR OXIDATION OF PHENOL

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Catalytic wet oxidation (CWO) is an emerging technology for treating wastewaters that are either too dilute to incinerate, or too concentrated and toxic for bio-degradation. The efficiency of several noble metal catalysts (including Pt, Pd, Ru, Rh and others) for the catalytic wet oxidation (CWO) of various pollutants has been demonstrated in many studies. However, these noble metals are expensive, thus affecting greatly the economy of the corresponding noble metal catalysts. Alternatively, great efforts have been devoted to the employing of transition metal oxides (including oxides of Cu, Fe, Co, Mn, Ni, Sn and other oxides in various combinations), but the main drawback is their leaching by the corrosive reaction mixtures.

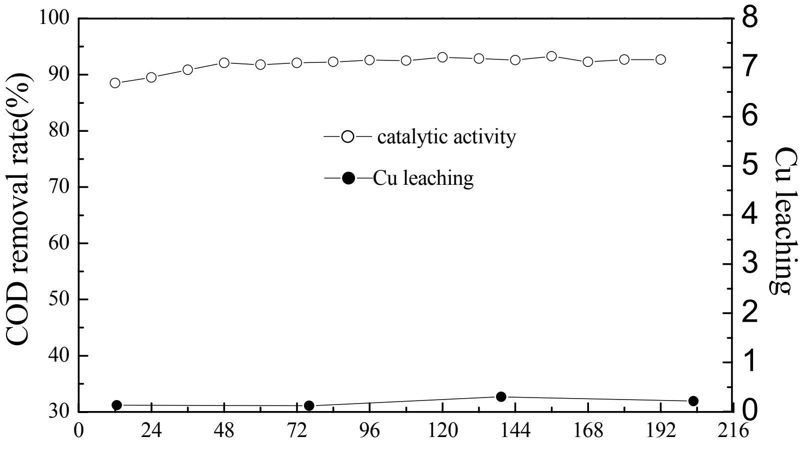

FIG. 1. Phenol COD removal rate and Cu leaching during the lifetime test

The activity and stability of the CuZnAl mixed oxide catalysts prepared by thermal decomposition of hydrotalcite-like compound (HTlc) precursors were studied for the CWO of phenol. The samples were characterized, and it was proved that the HTlc precursors were indispensable starting materials to render satisfactory stabilities to the mixed oxide catalysts, and that it is necessary for the calcination temperature to be tuned in order to achieve the optimal catalytic behavior desired. It was found that catalysts prepared with HTlc precursors and calcined at 973K exhibited remarkably high activity and stability.

The results in FIG. 1 show that no loss in activity after a continuous running of 192 hours, and the Cu leaching was less than 0.3ppm during the reaction process.

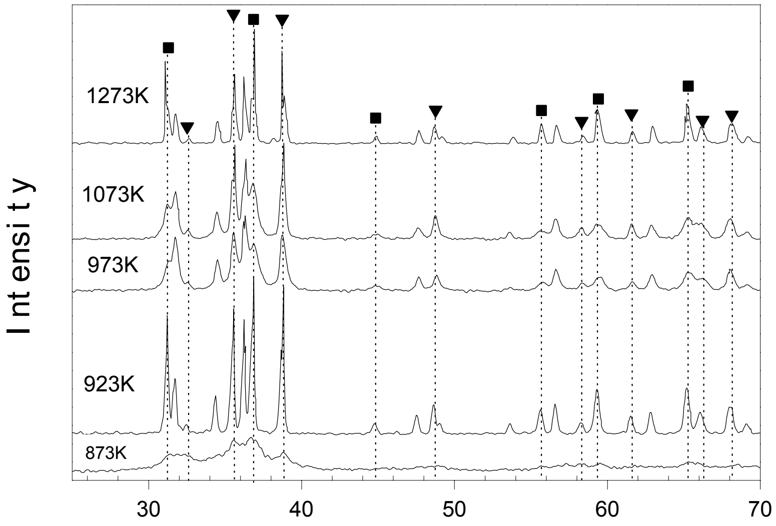

FIG. 2. X-ray diffraction patterns of the $CuZnAlCO_3$-HT samples calcined at different temperatures for 8h; (■)$CuAl_2O_4$; (▼)CuO

Cryatalline phases of the samples after calcination at different temperatures were determined by XRD (FIG. 2). The sample which had been heat-treated at 973K, formed inapparent peaks which correspond to consolidated phases due to the intensive interaction between the CuO phase and the spinel phase. This may be the most plausible interpretation for the stability X-ray patterns of the catalysts before and after TPR are depicted in FIG. 3. After the TPR, the only phase detected was spinel phase, while the CuO phase disappeared completely. It suggests that the inapparent peaks in the diffraction patterns before the TPR correspond to the consolidated phase formation of the CuO phase and its carrier (the spinel phase), thus confirming the findings of FIG. 2.

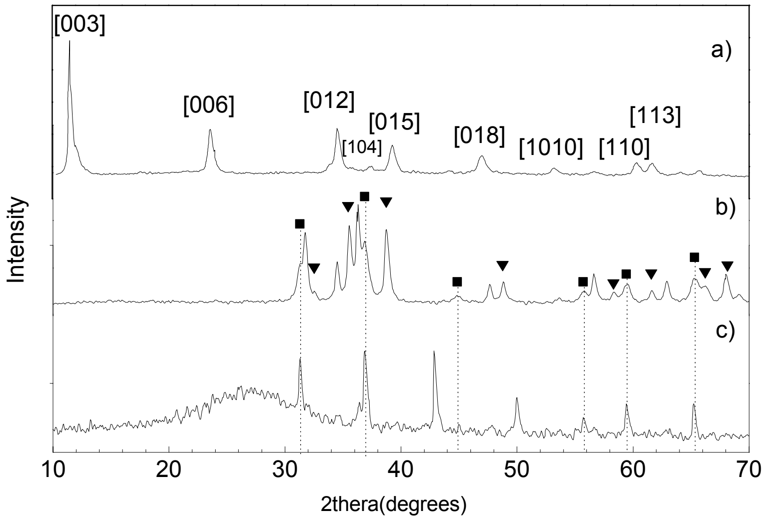

FIG. 3. X-ray patterns of samples: b) after calcined at 973K; c) after TPR; (■) $CuAl_2O_4$; (▼) CuO.

FIG. 4. shows the sample, on heating to 700 °C, the peak shifted to a higher temperature than that of the other peaks. This phenomenon is attributed to the fact that the strong interaction between the CuO phase and the spinel phase can cause the CuO to become less reducible.

In virtue of their activity and stability, the catalysts of mixed oxides prepared via HTlc precursors for the CWO becomes a promising direction.

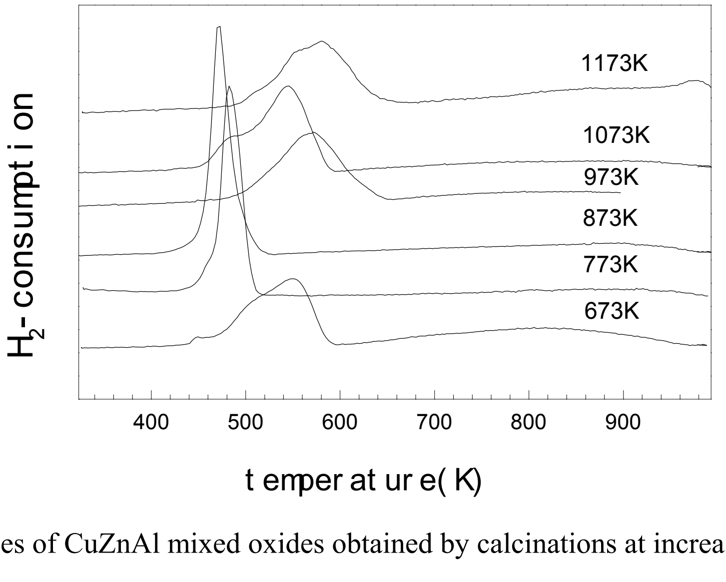

FIG. 4.TPR profiles of CuZnAl mixed oxides obtained by calcinations at increasing temperatures

THE EFFECT OF HIGHER HYDROCARBONS AND HYDROGEN SULFIDE ON THE PROCESS OF ETHYLENE SYNTHESIS FROM METHANE

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Since natural gas contains higher hydrocarbons and hydrogen sulfide, it was of interest to elucidate their influence on the process of oxidative conversion of methane. The addition of 2.4 % vol. of ethane to the methane-air mixture does not lead to the increase in the yield and ethylene concentration in reaction gases, but allows to obtain high ethylene concentration at lower temperatures, to decrease the reaction temperature by 40-60 °C and to reduce contact time (Table). Addition of propane in concentration of 1.2 % vol. to methane-ethane mixture (transition to natural gas) results in the increase of ethylene concentration in reaction gases up to 5.5 %. vol. (Table). At low reaction temperatures (600-650 °C) there is no propylene in the products. At the same time aromatic compounds are present, and the catalyst is carbonized, that results in the loss of activity. Thus, ethane and propane introduction promotes significant increase in process productivity at lower temperatures in comparison with the pure methane. Upon using the methane-ethane-propane mixtures it is necessary to control the reaction temperature (for the catalyst 14 mol % NaCl/K_2SnO_3 it should not be lower 740 °C) carefully, because of the formation of compaction products and deactivation of the contact. In the case of methane- ethane mixture temperature decrease does not lead to coke formation.

Study of the hydrogen sulfide influence on the parameters of the process of oxidative processing of natural gas has shown that elemental sulfur is accumulated at the reactor outlet. This may be connected with the decomposition of mercaptans, hydrogen sulfide and reduction of sulphur dioxide. Simultaneous reactions of sulfur oxidation-reduction and oxidative methane dimerization lead to the decrease in ethylene yield. After finishing of H_2S feeding in reaction mixture, a catalyst restores the former activity. This indicates that sulphur does not block the active centers and irreversible catalyst poisoning does not occur.

Table.

Influence of higher hydrocarbons on the concentration ($C_{C_2H_4}$,%) and productivity (P, g ethylene/g cat.•h) for ethylene.

Catalyst	Reagent ratio	T, °C	. , s	$C_{C_2H_4}$, % vol	P
14%mol NaCl/ K_2SnO_3	CH_4/air=1/1	780	0.8	1.8	0.50
		800	0.4	2.5	1.40
		800	1.0	2.85	0.64
		740	1.0	2.5	0.56
	CH_4+(2.4%C_2H_6)/air=1/1	780	0.8	2.5	0.70
		800	0.4	2.7	1.52
		740	0.2	4.5	5.00
		780	0.2	5.0	5.65
	CH_4+(2.4%C_2H_6) +(1.2%C_3H_8)/air=1/1	800	1.0	5.1	1.16
		780	0.8	1.8	0.50
		800	0.4	2.5	1.40
		800	1.0	2.85	0.64

In the case of periodic input of methane and oxygen (batch process) to Mn–Li–P-contacts addition of ethane to methane increases the yield of ethylene. The concentration of ethylene in reaction gases increases from 2.5 % up to 3.5 –4.6 % vol., the selectivity being 65-100 %. The high selectivity to ethylene is usually observed after 20-minutes cycle.

THE METHANE CONVERSION INITIATED BY AN ELECTRON BEAM PLASMA IN THE GAS-JET REACTOR

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The experimental researches of the composition of subsonic and supersonic flows of methane mixtures with carbon dioxide activated by an electron beam are performed. The measurements are carried out by a method of the molecular-beam mass-spectrometry in the experimental setup VS-4 at the Institute of Thermophysics SB RAS.

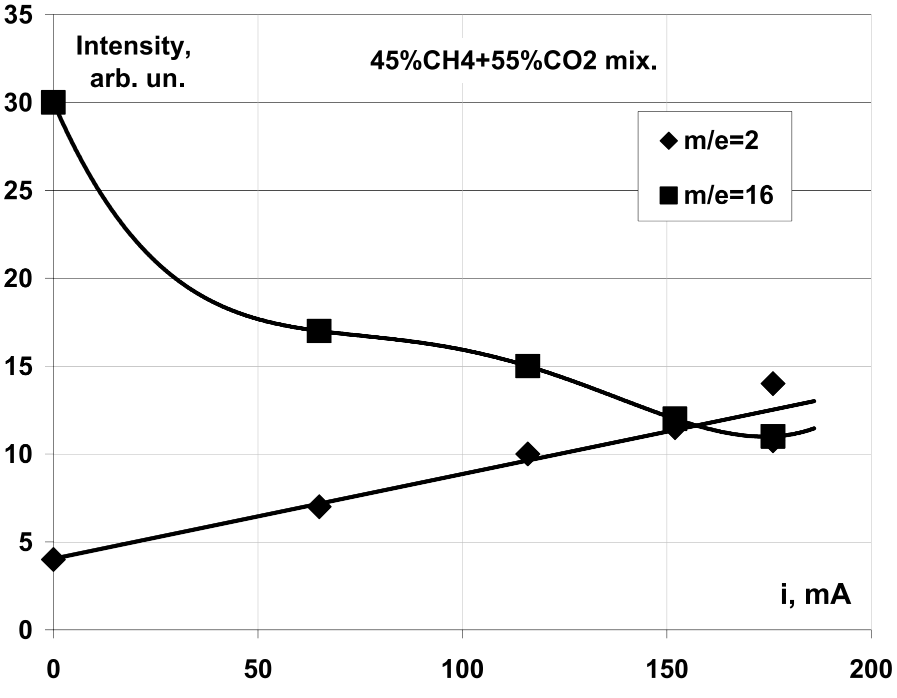

Fig. 1.

For the activation of plasmachemical reactions we used an electron gun with a hollow cathode. The jet of reagents was formed through the supersonic ring nozzle. Along its axis we injected an electron beam. The picking of a sample from a jet was carried out by using the molecular-beam generator. The analysis of a sample at a various parameters of a flow and electron beam was made by using the monopole mass spectrometer. In figure 1 the dependencies of the intensities of an ion peaks of methane (CH_4^+) and hydrogen (H_2^+) on an electron beamof electrons are shown. The increase of a quantity of an electrons in a flow results in the reduction of concentration of methane. Thus the concentration of molecular hydrogen grows. It is shown, that this effect is caused by a fast ion-molecular interaction in a flow activated by an electron beam. The dependencies of the factors of conversion and processing of methane to hydrogen from parameters of a flow and an electron beam are obtained. In figure 2 the dependence of the factors of conversion on capacity of an electron beam is given. The comparison of parameters of methane conversion using an electron beam plasma with the data of works using other methods of conversion is carried out. It is shown that the application of high-energy electron beam results in a shift of the function of secondary electrons energy distribution and, as a consequence, results in an acceleration of chemical reactions and an increase of a factor of methane conversion to hydrogen.

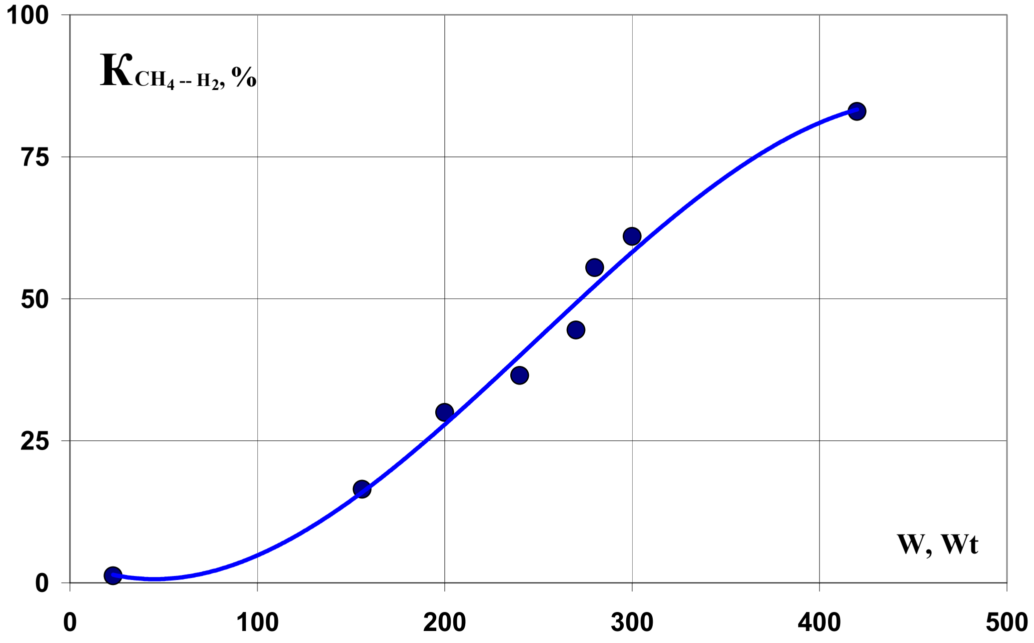

Fig. 2.

The work is supported by the grant of the Ministries of the Industry, Science and Technologies of the Russian Federation (project No 06-05).

PARTIAL OXIDATION OF METHANE (POM) TO SYNGAS IN TUBULAR $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ MEMBRANE REACTOR

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Introduction

Huge amount of natural gas resource has never been developed due to its remoteness and small scale of individual gas fields. Gas-to-Liquids (GTL) technology can convert such stranded gas reserves into easily transportable liquid fuels. The technology consists of two primary stages such as syngas generation stage and liquid fuel production stage. The cost of the former is approximately 60% of the total and its cost reduction has significant impact on the applicability of GTL process. Because of its compactness and energy efficient feature, ceramic membrane reactor using mixed-conduction oxygen permeable membrane would have significant cost reduction potential of syngas generation process.

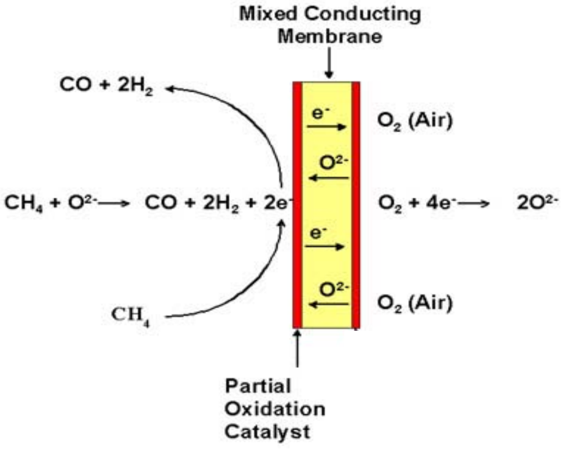

Fig.1 Schematic diagram of the dense oxygen-permeable membrane reactor for partial oxidation of methane to syngas

Using air as an economical oxygen source, dense oxygen-permeable reactor has potential applications in methane partial oxidation to syngas, as shown in Fig. 1. It has been shown that coupling the dense oxygen-permeable membrane with POM reaction can allow directly using air as the oxygen source for the POM reaction, thus realizing coupling of the separation of oxygen and catalytic oxidation in one process. This coupling of separation and

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reaction in one reactor simplifies process operation and reduces production cost, and opens a new route for the POM reaction.

Experiments

BSCF oxide powder was synthesized by a combined citrate and EDTA complexing method. The membrane tube was prepared by plastic extrusion. Detail information for the preparation of BSCF oxide powder and the membrane tube were present in reference[1]. The oxygen permeation and POM were carried out in a shell-and –tube reactor, which had been describe in the literature[2].

Result and discussion

The membrane tube was employed in the reactor for partial oxidation of methane to syngas.

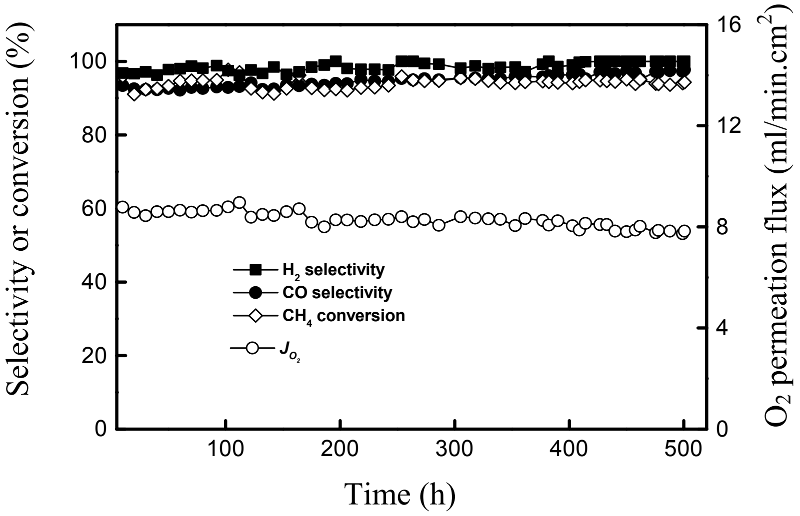

Fig. 2. Long-term performance of reaction in the tubular membrane reactor at 875°C.
The feed (pure methane) flow rate in the tube side is 45.28ml/min, the flow rate of air in the shell side is 300ml/min.

Fig. 2 shows the results obtained in tubular membrane reactor over 500 hours. The pure methane was used as the feed during this period. The flow rate of pure methane in the tube side is 45.28ml/min, the flow rate of air in the shell side is 300ml/min. The reaction temperature is 875 °C. Throughout the run, methane conversion was about 94% with higher than 95% CO selectivity. Relatively stable oxygen permeability was obtained, and the oxygen permeation flux was higher than 8.0ml/min.cm^2. During the 500h operation the oxygen permeation fluxes dropped about 10%.

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BIOCATALYTIC CONVERSION OF BIOMASS: MECHANISMS AND APPLICATIONS

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Biomass, mathematic models, anaerobic biomineralization, immobilized cells

Experimental research and mathematic model of methanogenesis. The processes of methane formation by anaerobic methane generating microbial consortions were experimentally studied in detail. Currently, methanogenesis from various individual compounds (alcohols, organic acids, aromatics, amino acids, proteins and peptides) was studied kinetically with chromatographic detection of all available intermediates and final compounds. Basic chemical reactions were revealed and major groups of microorganisms identified. From experimental results, the mathematic model of the process was constructed based on changes over time of all necessary reaction components. Description includes the construction and analysis of multi-dimensional systems of differential equations. The elaborated model adequately describes the observed experimental data and affords prognosis for mutagenesis process over the time.

Anaerobic conversion of xenobiotics. Processes of anaerobic biomass conversion were used to degrade various classes of xenobiotics. We studied the processes of biomineralization of xenobiotics of various classes including azodyes, aromatic amines, thioglycols, methylphosphonic acid etc. Biodegradation dynamics was studied, major intermediates revealed and technological grounds for wastewater purification created.

Self-immobilized and cryoimmobilized cells as a new type of biocatalysts. A principal step in intensification of biocatalytic processes with participation of microbial cells is the creation of catalysts based on immobilized cells. Certain conditions (the ascending flow of liquid in the reactor and the selected pressure) instigate a unique phenomenon of self-organization of methanogenic microbial consortion – formation of biomass aggregates (self-immobilization) – resulting from microbiological, chemical and physical processes occurring at the interface of liquid and solid phases. The core of the formed aggregates consists of acetate-utilizing methanogens having morphologic features permitting them to generate the formed structures with other bacteria or the mixed colonies. The aggregates so formed are dense granules (1 – 5 mm diameter). Self-immobilization of cells afforded a 50-fold intensification of methanogenesis.

We elaborated the technique for entrapment of cells in synthetic polymer gels via cryostructuring. A unique feature of this task is to demonstrate the capacity of the catalysts to run the reactions for a few years without notable loss of activity. The possibilities of catalysis by cryoimmobilized cells are demonstrated on reactions for deriving the monomers for biodegradable polymer materials (lactic acid), for production of acetic acid, ethanol and amino acids.

<u>Biocatalytic conversion of CO_2; new resource technologies</u>. Anaerobic conversion processes provide new biocatalytic reactions. Of great interest are the technologies for catalytic conversion of carbon dioxide, a pollutant causing global ecological changes. We offered three possible procedures for conversion of CO_2 to yield acetic acid:

$$CO_2 + CH_4 \longrightarrow CH_3COOH \quad (1)$$

$$2CO_2 + 4H_2 \longrightarrow CH_3COOH + 2H_2O \quad (2)$$

$$2CO_2 + 2H_2O \longrightarrow CH_3COOH + O_2 \quad (3)$$

The first reaction presents the methanogenesis key reaction reversible at high pressures. The second reactions can be feasible by using cryoimmobilized cells of acetate-generating bacteria. Reaction 3 runs upon using electrocatalytic decomposition of water and biocatalytic reduction of CO_2 in electrochemical mode.

STUDY ON A COMPACT PLATE-FIN STEAM REFORMER FOR FUEL CELL SYSTEM

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Abstract

A compact plate-fin steam reformer (PFR) consisting of closely spaced plate-fins, where endothermic and exothermic reactions take place in alternate chamber is studied. In the PFR, which is based on a plate-fin heat exchanger, the catalytic combustion of the fuel cell anode off gas (AOG) was used to supply the necessary heat for the reforming reaction. One reforming chamber in which the hydrogen is produced, two vaporization chambers and two combustion chambers are integrated in one unit of the PFR. The PFR is very compact, easy to be placed on board and scaled up. The effects of the ratio of water/methanol on the performance of the PFR were investigated, and the distribution of temperature in different chambers was studied. In addition, internal plate-fins and external catalytic combustion were applied to enhance the heat transfer of the PFR, so that both high methanol conversion ratio and low CO concentration were accomplished.

Keywords: Plate-fin steam reformer; Methanol; Steam reforming; Hydrogen; On board; Fuel cell

ESR AND DRS STUDIES OF ACTIVE COMPONENT FORMATION IN THE Mo/HZSM-5 METHANE DEHYDROAROMATIZATION CATALYST

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The catalytic reaction of methane dehydroaromatization into benzene and other aromatic hydrocarbons without oxygen over the Mo/HZSM–5 type zeolite catalysts was discovered in 1993 [1]. Such catalysts are prepared via the ammonium heptamolybdate (AHM) $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ deposition on the zeolite HZSM–5, with subsequent thermal activation in methane medium at the temperatures up to 700 °C. A large number of spectroscopic methods was used to study the changes in electronic and molecular structure of these catalysts during the reaction. For example, recently the analysis of Electron Spin Resonance (ESR) spectra of AHM/HZSM–5 system after activation by methane with an inert gas additive ($9.5\%N_2/CH_4$) was conducted [2].

Earlier in the works [3, 4] ESR method was used to study the thermolysis of bulk AHM in the air up to 500 °C, and two principal types of Mo^{5+} ions were detected. The Mo^{5+} ions of the first type, with rhombic anisotropy of g–factor, are present in the tetrahedral oxygen coordination, and are stabilized as characteristic structural defects in the forming rhombic phase of MoO_3 oxide (denoted as T–type ESR spectra: $g_x = 1.958$, $g_y = 1.048$, $g_z = 1.877$). The Mo^{5+} ions of the second type, with axial symmetry of the oxygen surroundings, are existing due to the molybdenum stabilization as polymolybdate structures (denoted as PM–type ESR spectra: $g_{.} = 1.936$, $g_{||} = 1.895$). They are characterized by the appearance of molybdenyl bond $[Mo=O]^{3+}$, leading to the axial spectrum. It is also possible to assign these spectra to the phase of hexagonal MoO_3, similar to the polymolybdate structures [5].

In this work the ESR method was used to study the AHM/HZSM–5 (10 wt.% Mo) samples after thermolysis in the flow of methane–argon mixture at temperatures 300, 400, 500, 600, 700 °C for 1, 2, 5 h. The data will be compared with earlier results of our ESR study of AHM/HZSM–5 system after thermolysis in the air using similar temperatures and times, with the aim to show the similarities and differences in the action of methane and air.

The spectra of samples after 1 and 2 h of treatment with the mixture 10%CH_4/Ar at 300 and 400 °C are non–uniform and wide in the vicinity of g_z, containing the superposition of several spectra – types T, PM and a new spectrum. This spectrum appears in the pure form both at 77 and 293 K scanning temperatures already after thermolysis at 500 °C. It can be assigned to the two types of Mo^{5+} ions in axially–distorted coordination with the following parameters: $g_{.}^{(1, 2)} = 1.935$, $g_{||}^{(1)} = 1.910$, $g_{||}^{(2)} = 1.895$. These new states are not the above–mentioned Mo^{5+} ions of T and PM types, though the values of their parameters are close [6]. The nature of observed spectra becomes more understandable, if one will suppose, that in the process of sample thermolysis takes place alkylation of Mo^{5+} ions in the methane medium (with Mo–C bond formation). At the temperatures 300–400 °C and short times of thermolysis (1–2 h) can preferentially proceed the reduction of Mo^{6+} ($4d^0$–ions) to Mo^{5+} ($4d^1$–ions) by methane molecules, and thus there is practically no alkylation. However further thermolysis at higher temperatures 400–500 °C can lead to the alkylation of Mo^{5+} ions, which becomes apparent in the spectra as widened axially–anizotropic signals. As it follows from [2], such spectra are vanishing after sample thermolysis at 700 ^{o}C, which is probably associated with the transformation of molybdenum alkyl complexes into molybdenum carbide – Mo_2C.

The Diffuse Reflectance Spectroscopy (DRS) was used to monitor the appearance of molybdenum ions in the more reduced states than Mo^{5+}. The DRS experiments were performed under the same conditions as ESR experiments, and the results of both types of experiments will be compared.

Acknowledgements

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HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF TWO ORGANICALLY TEMPLATED TRIVALENT METAL-CONTAINING ZIRCONIUM PHOSPHATES

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Metallophosphates have attracted a lot of interest in the past decades [1]. Among them, zirconium phosphates are very attractive materials for their applications in ion-exchange, intercalation, ion conductivity, catalysis and molecular sorption [2, 3]. The fluoride route has recently led to the first zirconium phosphate fluoride (ZrPO-1) with three-dimensional open-framework structure by using the organic amines as templates [4]. More recently, Férey et al. reported the synthesis and ab initio structure determination of a new three-dimensional mixed-valence oxyfluorinated titanium phosphate MIL-15 [5], and two organically templated mixed-valent Ti^{III}/Ti^{IV} phosphates with open-framework structures were also synthesized [6, 7]. This indicated that the synthesis of M^{III}/M^{IV} phosphate with an three-dimensional open framework structure was possible.

Herein we report the organically templated trivalent metal-containing zirconium phosphates FeZrPO-8 and AlZrPO-8, which were synthesized hydrothermally by using 1,6-diaminohexane (DAH) as the structure-directing agent. This work represents the first zirconium homologue to the well-known metal-containing aluminium phosphate molecular sieves (MeAlPO-n) [8]. $FeZrPO_4$-8 was hydrothermally prepared from a starting mixture of $Fe(NO_3)_3{\cdot}9H_2O$, $ZrOCl_2{\cdot}8H_2O$, DAH, ammonium fluoride, phosphoric acid (85%) and distilled water in the mole ratio of 1:3:6:3:6:300. For AlZrPO-8, $Al(NO_3)_3{\cdot}9H_2O$, $ZrOCl_2{\cdot}8H_2O$, DAH, ammonium fluoride, phosphoric acid (85%) and distilled water were mixed in the mole ratio of 1:3:6:3:6:300. This mixture was sealed in a 100mL Teflon-lined stainless steel autoclave with a filling capacity of ~70% and heated at 463K for 7 days under autogenous pressure.

XRD patterns of the two as-synthesized samples show that the recovered products are of high crystallinity, and a single intense peak is observed at low angle, corresponding to d-spacing of 15.25 and 15.20Å in FeZrPO-8 and AlZrPO-8 phases, respectively. From the XRD powder diffraction measurement, the as-synthesized materials are proved to be a new phase, and the variations of trivalent metal ions incorporation do not leading to changes of the crystal structure. ^{31}P MAS NMR spectrum of AlZrPO-8 gives two peaks at –14.7 and –24.6 ppm with a relative intensity ratio of 1:3. On the basis of the previous studies in zirconium or titanium phosphates [9], we assigned the NMR peaks at –14.7 ppm to the HPO_4 group and –24.6 ppm to the PO_4 group. The ^{27}Al MAS NMR spectrum of AlZrPO-8 gives sharp peaks at –20.6 ppm, which is assigned to Al in octahedral enviromental [10]. Since no Al-containing impurities were found in the X-ray diffractographs and by ^{27}Al MAS NMR spectroscopy, we assigned this signal to Al occupying the octahedral Zr sites in AlZrPO-8, and thus confirmed the partly substitution of Zr^{4+} by Al^{3+} in the AlZrPO-8 framework. The IR spectra of the two samples clearly show two typical sharp peaks at ~1550 and ~1620 cm^{-1}, which is indicative of the presence of the 1,6-diaminohexane molecules in their protonated form. The broad bands observed in the region 1100-900cm^{-1} are associated with the asymmetric stretching vibrations of PO_4 units [6, 11]. The thermal behavior of the title compounds have been investigated by using X-ray thermodiffractometry, which indicated that the inorganic framework of the compounds are thermally stable up to ~400 °C.

Further investigation is in progress to solve the structure of the as-synthesized compounds, and to expend the field of microporous phase based on zirconium phosphate.

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METHANE FLAMELESS COMBUSTION ON SUBSTITUTED PEROVSKITES ($La_{1-x}Ca_xFeO_{3-y}$, $La_{1-x}Sr_xFeO_{3-y}$)

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Mixed oxides with perovskite-like structure (such as $LaFeO_3$, $LaCoO_3$, $LaMnO_3$) appear to be promising for high-temperature process of methane combustion due to their good thermal stability and reasonable reactivity. Lanthanum substitution by alkaline-earth cations in the perovskite structure is well known to strongly affect the catalytic properties of these oxides. Thus, for $La_{1-x}Sr_xFeO_3$ perovskites, the maximum of intrinsic catalytic activity was obtained for the sample with x=0.2 [1, 2]. As was revealed in numerous previous studies including our own, for cation-modified perovskite-like systems, their phase composition, microstructure and catalytic performance in deep oxidation processes depend not only upon the lanthanum substitution degree, but on the preparation route as well. In this work, detailed investigation of the surface/bulk composition, structure, catalytic properties and reactivity of $La_{1-x}Sr_xFeO_{3-y}$ and $La_{1-x}Ca_xFeO_{3-y}$ (0 . x . 1) oxides prepared by the mechanochemical activation (MCA) route was carried out using XRD, differential dissolution method, SAXS, SIMS. Samples were prepared from starting compounds (La_2O_3, Fe_2O_3, CaO or $SrCO_3$,) using preliminary mechanical treatment for 3 minutes in the high power planetary mills followed by calcination at 900 or 1100 °C for 4 hours.

Catalytic performance in methane oxidation of Ca– and Sr-substituted $LaFeO_3$ was found to depend in a different way upon the lanthanum substitution degree, though in the presence of O_2 in the gas phase only combustion products were observed.

For Ca-modified system, specific catalytic activity (SCA) reaches its maximim for the sample with x=0.5 (Fig. 1a). H_2 and CH_4 TPR were applied to estimate the amount and reactivity of the surface/lattice oxygen forms. H_2 TPR studies revealed the presence of reactive (weakly bound) oxygen in $La_{1-x}Ca_xFeO_{3-y}$ perovskites easily removed by hydrogen at temperatures up to 200 °C, its amount reaching maximum at x=0.5. According to SAXS data, for this substitution degree, a maximum of the interphase boundaries density was observed. Such a correlation between SCA of Ca-substituted ferrites and the amount of reactive weakly bound oxygen implies that active centers are associated with the outlets of interphase boundaries. According to FTIRS of adsorbed NO data, this weakly bound oxygen could be adsorbed on clusters of coordinatively unsaturated Fe^{3+} and Fe^{2+} cations formed at outlets of interphase boundaries.

In contrary, for Sr-substituted lanthanum ferrite, SCA in CH_4 oxidation declines with a Sr content reaching a constant value for x >0.2 (Fig. 1b). Specificity of the effects of La substitution for Ca or Sr in a perovskite structure could be explained by different mechanisms of charge compensation for these systems, namely, preferential generation of oxygen vacancies in the former and Fe^{4+} cations in the latter. A lower activity of Sr-doped system can thus be assigned to a lower surface density of coordinatively unsaturated/clustered Fe^{3+} and Fe^{2+} cations able to adsorb weakly bound oxygen which is the most reactive oxygen form in deep oxidation processes. Indeed, H_2 TPR studies of Sr-substituted system have not revealed presence of any weakly bound oxygen removed by H_2 up to 200 °C. As judged by results of FTIR spectra of adsorbed NO, another reason of SCA decrease in Sr-substituted ferrites probably consists in decline of the density of CH_4 activation centers (coordinatively unsaturated cations) with the Sr content.

Hence, different ways of charge compensation for $La_{1-x}Sr_xFeO_{3-y}$ and $La_{1-x}Ca_xFeO_{3-y}$ systems are reflected in different trends of SCA variation with the La substitution degree.

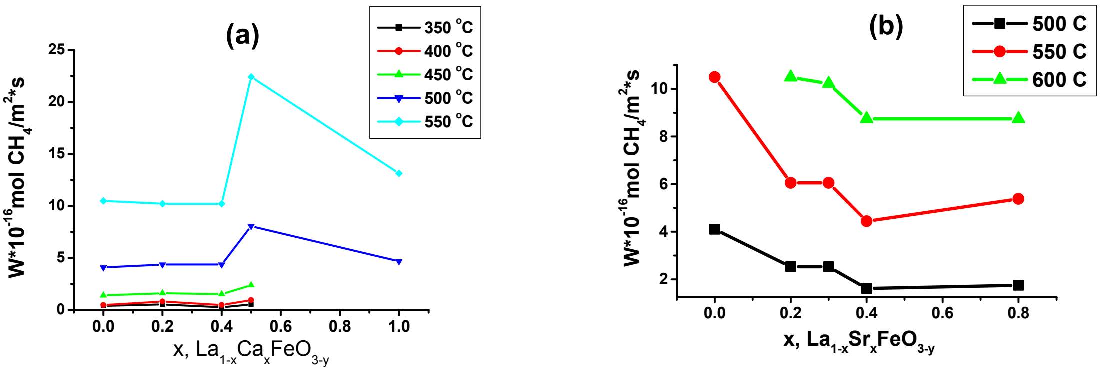

Fig. 1. SCA values in CH_4 oxidation process versus composition (x) for samples of $La_{1-x}Ca_xFeO_{3-y}$ (a) and $La_{1-x}Sr_xFeO_{3-y}$ (b) series (3 min MT, calcined at T=1100 °C/4 h)

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CATALYSTS FOR DECOMPOSITION OF NATURAL GAS INTO HYDROGEN AND CARBON MATERIALS. NEW AREAS OF APPLICATION FOR FILAMENTOUS CARBON

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Catalytic decomposition of hydrocarbons present in natural gases results in the generation of hydrogen and metal-carbon materials. Iron group metals and their alloys act as catalysts in the reaction of hydrocarbon decomposition. The carbon material is formed by graphite-like carbon filaments with metal particles fixed on their ends. Both carbon and the above metals perform certain roles that will be described below.

Catalysts for decomposition of hydrocarbons into hydrogen and filamentous carbon have been developed. Compared to the catalysts prepared by precipitation, our catalysts operate at higher temperatures, which provide both higher degree of methane conversion and yields of hydrogen and a carbon material. The ability of the new catalysts to operate at 700-750 °C permits one to obtain methane-hydrogen mixture containing up to 90% of hydrogen. Varying the composition of the catalysts it is possible to change the structure of the carbon filaments and, thus, the properties of the carbon materials. As a result, a carbon material can obtain some desired properties required for the specific targets such as preparation of sorbents, supports or some constructional materials, etc.

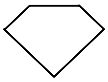
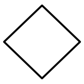
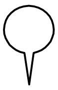
We have developed a waste-less technology for preparation of catalysts for decomposition of natural gas hydrocarbons.

An active search for new domains of the carbon material application is in progress. The material can be successfully utilized as a catalyst and a sorbent.

The authors were the first to study the metal particles bonded to carbon filaments. This resulted in the development of novel catalysts. The active components of such catalysts are metal particles bonded to a carbon filament. In a number of reactions, the filamentous carbon based systems exhibit catalytic properties typical for metal catalysts. The hydrogenation reactions were studied in detail.

The process of filament growth during methane decomposition is accompanied by a stepwise transformation of the particle shape (see Table 1). The deviation of the particle shape from the equilibrium cubic octahedron is accompanied by the formation of defects in the crystal structure, such as twin boundaries, interblock boundaries and micro distortions which are probably associated with the formation of dislocations. A change in the particle morphology and defects provide changes in the catalytic properties. The hydrogenation rate increases due to the formation of defects in the crystal structure, while the selectivity to C_4H_8 increases because of a change in the nature of the crystallographic edges that are open for the reaction medium.

Table 1. Catalytic properties of the carbon material in the butadiene hydrogenation reaction versus morphology of the nickel nanoparticles

Shape of nickel nanoparticles	C/Ni weight ratio	Hydrogenation rate, 10^6 mole $C_4H_6.g_{Ni}^{-1}.s^{-1}$	Selectivity to C_4H_8, mol.%
	1,5	78	47
	10	200	94
	400	2055	98

We have also established new areas for utilization of carbon filaments where their efficiency is determined by their sorption properties. It has been found that carbon materials can effectively purify water from phenol admixtures.

Using hexachlorobenzene it has been shown that toxic chlorinated aromatic compounds can be immobilized on the nanofilaments. After mechanochemical activation of the carbon material with hexachlorobenzene the bond strength is so high that hexachlorobenzene can not be washed off by any solvent.

A high sorption ability has been observed for removal of chlorinated dioxins from gases. Because of the high bonding strength of dioxins, they can not be removed from the sorbents upon heating to 400 °C.

Another promising area for application of the nanofilaments is accumulation of hydrogen. At 120 atm, the filaments sorb as much as 3 mass.% of hydrogen.

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POSTER PRESENTATIONS

DIRECT RESISTANCE HEATING OF CATALYST VERSUS ITS EXTERNAL HEATING: METHANOL DEHYDROGENATION ON METAL COPPER

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Introduction

Microreactors are promising for catalytic production of hydrogen to be used, for example, in fuel cells [1].

In conventional reactors for endothermic catalytic processes, heat is supplied to the catalyst bed from the heated reactor walls due to the heat radiation from the walls, convection and heat conductivity of the bed. There are obvious fundamental limitations on the maximal heat flux density under these conditions that cause insufficient energy release on the catalyst surface to complete the endothermic reaction [2].

In this work experimental studies of the endothermic methanol dehydrogenation were maid to compare the efficiency of direct resistance heating of the catalyst bed against the external heat supply.

Experimental

A thin quartz tube (1.4 mm internal diameter, 28 cm length) with a copper wire coil

A thin quartz tube (1.4 mm internal diameter, 28 cm length) with a copper wire coil (1 mm diameter, 4.5 cm length, made from copper wire of 0.1 mm in diameter) as a catalyst in the inside was used as the reactor. Current leads were made of stainless steel. A cylindrical furnace was used for external heating of the quartz tube. The direct resistance heating was achieved by passing electric current through the copper coil. The temperature was controlled using a thermocouple mounted on the outer surface of the tube and, additionally, by measuring the resistance of the heat-evolving copper coil. Reactants (a mixture of argon and methanol vapor, volume ratio 4:1) were fed at the flow rate of 5 ml/min.

Results

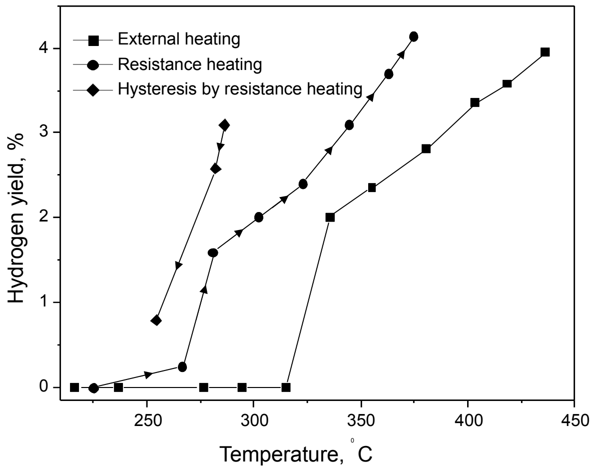

Fig. 1.

The yield of hydrogen as a function of temperature during methanol dehydrogenation on the copper coil is shown in Fig. 1. The reaction is seen to start at a 50°C lower temperature in the case of direct heating by electric current passed through the coil than in the case of external heating, a hysteresis being observed in the former case with hydrogen evolved in a higher amount at the same temperature (according to the thermocouple measurement) during cooling (Fig. 1). Therefore, the yield of hydrogen depends on the procedure used for the catalyst heating and cooling. It looks like the copper coil surface is modified on direct heating that favors the more efficient catalytic reaction. Microscopic studies reveal that some surface microcracks appear on the coil subjected to direct heating but not on the coil heated by the external furnace. Additional experimental data allow us to suppose that the defects are generated on the copper surface under the simultaneous action of the sharp temperature drop (coil – reaction mixture), electric current and the reaction products. The data obtained at alternating the external and direct heating also indicate the higher efficiency of the direct heating due to modification of the copper surface in the course of the catalytic reaction. Notice that the copper coil modified in this way behaves further as a more efficient catalyst irrespectively of the method used for its heating.

Conclusions

1) The endothermic methanol dehydrogenation catalyzed by metal copper is more efficient at the direct resistance heating of the catalyst than at the external convective heating.
2) The direct heating modifies the copper catalyst surface during methanol dehydrogenation that results in lowering of the reaction temperature and an increase in the hydrogen yield.

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OXIDATIVE DEHYDROGENATION OF ETHANE OVER HETEROPOLY COMPOUNDS WITH KEGGIN STRUCTURE

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Introduction

In resent years several studies devoted to heteropoly acids (HPA) and heteropoly salts (HPS) in the oxidative dehydrogenation of light alkanes including ethane were performed [1-3]. Most attention has been concentrated on the properties of the composite HPS and supported HPA.

In the present work we demonstrate the catalytic properties of the bulk PMo and mixed PVMo HPA as well as their sodium salts in oxidative dehydrogenation of ethane (ODE).

Experimental

Solid HPA – $H_{3+X}PV_XMo_{12-X}O_{40}$ (X = 0, 2, 3) and HPS – $Na_3H_2PV_2Mo_{10}O_{40}$, $Na_2H_4PV_3Mo_9O_{40}$ with Keggin structure were prepared· as described in [4].

Catalytic properties were determined in a flow circulating set-up with a chromatography analysis of the reaction mixture. Inlet reaction mixture was 5 C_2H_6 + 5 O_2 + 90 N_2 (% vol.). Reaction temperature was increased stepwise from 300 to 450 °C. In case of PMo HPA influence of oxygen content in inlet reaction mixture on catalytic properties was tested. To compare the catalytic activity we used first-order rate constant of the overall ethane conversion (K, s^{-1}).

Results and discussion

Catalytic properties of the samples are summarized in the Table.

The only selective product is ethylene, carbon oxides (CO and CO_2 mainly) are by-products. At low ethane conversion selectivity is high and exceeds 80%. Increase of ethane conversion is accompanied by remarkable decrease of ethylene selectivity and corresponding growth of COx selectivity. This fact indicates ethylene afteroxidation. Therefore, ODE may be described by triangle consecutive-parallel scheme:

$$\begin{tikzcd} C_2H_6 \arrow[rr] \arrow[dr] & & C_2H_4 \arrow[dl] \\ & COx & \end{tikzcd}$$

· We are grateful Dr. L.G. Detusheva for samples preparation.

Table. Catalytic properties of heteropoly compounds in oxidative dehydrogenation of ethane.

Sample composition	$S_{sp.}$, m^2/g	$T_{r.}$, °C	Contact time, s	Ethane conversion, %	$K\ 10^3$, s^{-1}	Selectivity, %	
						C_2H_4	CO_X
$H_3PMo_{12}O_{40}$	2.0	350	8.6	0.9	1.1	98.0	2.0
		380	8.5	1.6	1.9	98.0	2.0
		400	8.5	2.8	3.4	98.0	2.0
			15.7	5.4	3.6	92.4	7.6
		350[a]	8.3	3.6	4.5	71.1	28.9
		380[a]	8.5	4.2	5.2	64.8	35.2
		400[a]	8.5	6.2	7.8	55.7	44.3
			15.2	9.5	6.9	46.9	53.1
$H_5PV_2Mo_{10}O_{40}$	2.8	350	7.6	6.0	8.4	88.9	11.4
		400	8.6	16.0	22.1	74.4	25.6
			14.5	23.8	21.5	54.5	45.5
$H_6PV_3Mo_9O_{40}$	2.1	300	7.6	3.4	4.7	85.8	14.2
		350	7.9	6.8	9.2	85.8	14.2
			14.1	10.3	8.1	79.1	20.9
		400	14.0	18.8	16.5	64.3	35.7
			8.4	13.5	18.5	80.0	20.0
$Na_3H_2PV_2Mo_{10}O_{40}$	2.2	400	3.4	1.6	4.8	87.0	13.0
		450	3.2	4.0	13.0	33.3	66.7
$Na_2H_4PV_3Mo_9O_{40}$	2.3	350	5.5	2.1	3.9	89.2	10.8
		400	5.2	4.1	8.2	74.5	25.5
		450	5.5	6.2	12.0	20.0	80.0

a – inlet reaction mixture: 5 C_2H_6 + 10 O_2 + 85 N_2 (% vol.).

From the data it follows:

- Substitution of some Mo atoms by V ones results in significant increase of activity, apparently owing to stronger oxidative potential of mixed PVMo HPA [5].
- As the protons are partly replaced by alkali cations the activity and selectivity to ethylene decrease. Similar data were observed in [6] for methane conversion. Selectivity to ethylene at 450 °C decreases sharply due to decomposition of the Keggin structure [4].
- Increase of oxygen content in the inlet reaction mixture is accompanied by growth of activity, while selectivity to ethylene drops essentially because of more profound oxidation of both ethane and ethylene to COx.

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CATALYTIC AND PHYSICOCHEMICAL PROPERTIES OF OXIDATIVE CONDENSATION PRODUCTS IN THE OXIDATIVE DEHYDROGENATION OF PROPANE BY SULFUR DIOXIDE OVER Al-Si-OXIDE CATALYSTS

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The oxidative dehydrogenation of light alkanes is an important process for the effective utilisation of natural gas component. For propane oxidative dehydrogenation by oxygen, the yields of propene are not sufficiently high to satisfy demands of the industrial catalytic processes [1]. It was found that at the oxidative dehydrogenation of propane by sulphur dioxide (**ODP**) the oxidative condensation products (coke) exhibited high catalytic activity. The carbonisation of silica (surface area 40 m^2/g) from 0 to ~ 40 wt % in course of **ODP** at 913 K was accompanied by dramatic increase of propylene yield from 3,4 to 46 mol % [2]. In this work the influence of texture and acidity of Al-Si oxides on the catalytic and physicochemical properties of oxidative condensation products on different supports has been studied**.**

Catalytic tests were carried out in flow-type fixed-bed quarts reactor at atmospheric pressure at 773-973 K at flow rate 3. 60 cm^3/min. Feed gas has following composition: C_3H_8:SO_2:He = 10:10:80 vol. %. The acidity and strength distribution of acidic centers of Al_2O_3, SiO_2 and series Al-Si oxide samples was characterised by low temperature IR–spectroscopy of the adsorbed carbon monoxide [3]. Al-Si oxide with different silica concentration (0.1 to 0.48 Si/Al molar ratio) have been prepared by the procedure reported in [4]. The composition and amount of oxidative condensation products were determined by thermal and chemical analysis and by DRIFTS and electron microscopy.

It was found that filling–up of the reactor only with quartz without catalyst does not lead to any noticeable oxidation under used experimental conditions. Propylene, ethylene, CH_4, oxides of carbon, H_2O, H_2S, and sulfur were the main products during **ODP** over studied catalysts. Catalytic activity and selectivity in **ODP** are determined at initial time (0,2. 0,3 ч.) and after 6 h. time on stream (under the quasisteady state conditions - a period of insignificant changes in the catalytic performance). For all samples, propane conversion and yields to propylene increase with time on stream (Fig. 1). The propylene formation selectivity was found to increase with the increase of Si/Al molar ratio in the catalysts.

It was found that the propylene formation selectivity was decreased with the increase of propane conversion and reaction temperature. The highest yield of propylene was obtained at 873-913 K. The temperature increase causes the increasing of cracking. The product distribution in **ODP** at 913 K as function of contact time was investigated. Upon the decreasing of the contact time, the carbon dioxide and propylene tended to become the main products over the carbonised . -Al_2O_3. The propylene, ethylene and methane tended to become the main products over the carbonised Si-Al oxide catalysts; and the propylene tended to become the main products over the carbonised SiO_2. Formation of the cracking products and carbon oxides increase at high contact time. Maximum yield of olefins over the carbonised Si-Al oxide catalysts is about 52,8 %. The maximum yield of propylene over the carbonised SiO_2 is close to 48,2 %.

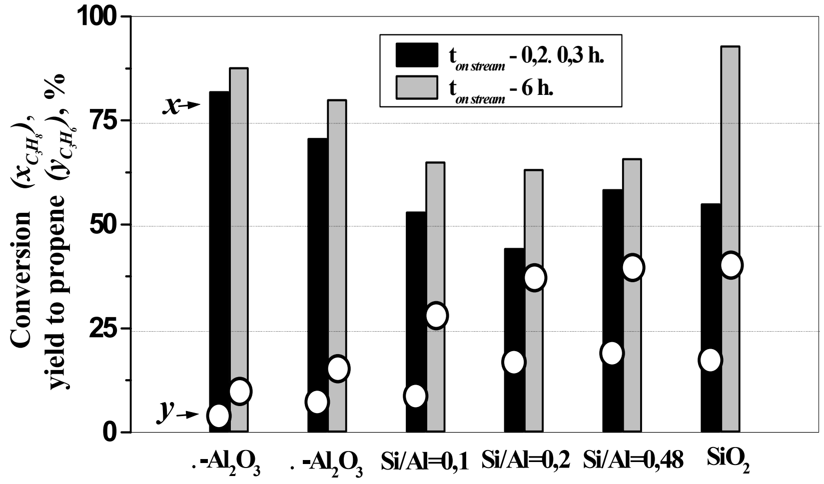

Fig. 1. Conversion of propane (x) and yield of propylene (y) as function of catalysts composition and time of stream: 0.2÷0.3 h, 6 h. (913K, $V_{cat.}$ = 1 cm^3, contact time . = 10 s).

The catalytic activity of oxidative condensation products in **ODP** depends on the C/H ratio of the coke [2]. It was found that the value of maximum exothermic effect of coke elimination increases with increasing the strength of Lewis acidic centers for Al-Si-O catalysts. We suppose that oxidative condensation products are the three-dimensional polymer presented by graphitized and condensed aromatic structures cross-linked by alkyl or sulfur bridges. The quinone, C=S, lactone, carboxyl, and alkyl groups in oxidative condensation products were detected by DRIFTS. There are probably the terminal substituents of polynuclear structures. The sulfate groups were found at the surface of carbonized alunima. It could explain the low selectivity of propylene formation over these catalysts.

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THE EFFECT OF CATALYZING ADDITIVES ON SOL-GEL FORMATION PROCESS AND ON THE PROPERTIES OF MODIFIED POLYSILOXANE LAYERS

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Polysiloxane layers modified with alkyl amines (MAPL) are used for manufacturing sensitive elements of solid sensors for sulphur dioxide [1]. This is explained by the fact that sulphur dioxide, as a weak Lewis acid, forms complex compounds of donor-acceptor type with amines; SO_2 acts as acceptor. The dipole moment of the complex substantially exceeds the geometric sum of dipole moments of the molecules that comprise the complex. Relatively large dipole moments are explained by charge transfer to SO_2, charge redistribution on alkyl amine, and the decrease in the electron density on hydrogen atoms.

The sensitivity (adsorption capacity) of the resulting layers is determined by the surface concentration of adsorption centres that are available for the adsorption of SO_2. In order to increase the sensitivity, it is necessary to synthesize layers with high porosity and large specific surface.

In the present work, the modified layers were obtained using sol-gel technology. The goal of the work was to reveal the formation mechanism of the porous structure of layers.

The hydrolysis and polycondensation of alkoxy silanes are known to be substantially affected by some acidic or alkaline additives. As a rule, the additives act as catalysts accelerating the process rate, as well as the size and structure of the resulting polymers [2].

We investigated the effect of the addition of acids and alkalis on the hydrolysis and polycondensation of diethylaminopropyltriethoxysilane (DEAPTES), which was used as a precursor for the synthesis of layers. We also investigated the properties of layers obtained from different polymeric products, in order to select optimal conditions for the synthesis of high-sensitive and selective layers.

The initial compound for the synthesis of modified polysiloxane layers was anhydrous DEAPTES - $(C_2H_5O)_3$-Si-$(CH_2)_3$-$N(C_2H_5)_2$.

Three types of ethanolic solutions with catalytic additives H_2O, CH_3COOH, and NaOH were prepared. The effect of the additives on the characteristics of hydrolysis and polycondensation was examined by means of liquid chromatography with Milikhrom-1 instrument, with a standard column filled with reverse-phase sorbent LiChrosorb (3 ∝m). A mixture of acetonitrile with water (volume ratio 3:1) was used as elutriator; elution rate was 100 ∝l/min. Examination revealed the catalyzing action of acetic acid on DEAPTES polycondensation. The clusters of the largest size were observed with acetic acid in the ethanolic solution of DEAPTES; the highest polycondensation rate was observed in this case. It is evident that the size of the formed clusters determines the porous structure of the obtained films. To estimate the coagulation rate constant, we solved the system of Smoluchovsky coagulation equations:

$$\frac{\cdot N_1}{\cdot t} = \cdot\ N_1 \sum_{i=1}^{\cdot} \cdot\ {}_{1i} N_1$$

$$\frac{\cdot N_l}{\cdot t} = \tfrac{1}{2} \sum_{i+j=l} \cdot\ {}_{ij} N_i N_j\ \cdot\ N_l \sum_{i=1}^{\cdot} \cdot\ {}_{li} N_l$$

Here $\cdot_{ij}$ is the rate of particle agglomeration, $N_l(t)$ is the concentration of particles consisting of l monomers. Since in the case under consideration the number of equations was about 300, we solved the system of differential equation by the direct numerical method.

Conclusion

The polycondensation process was demonstrated to be catalyzed by acetic acid. The porosity (pore size distribution) of layers obtained by sol-gel technology depends on polycondensation rate, while total number of pores depends on the polymer drying method. Estimations of reaction rate constants suggest that coagulation proceeds in the kinetic region. The adsorption properties of the resulting layers depend on their porosity. Thus, acid catalysis can be applied to govern the properties of resulting layers.

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FORMIC ACID AS A CATALYST FOR GAS-TO-PARTICLE PHOTOCONVERSION IN FORMALDEHYDE VAPOUR

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Formaldehyde H_2CO, known as carcinogen and mutagen, is inevitable intermediate in the exhaust of internal-combustion engines, even of those equipped with afterburners. Additional danger is brought about by the organic particulate matter of breathable size, which we discovered in H_2CO under UV irradiation in air. We detected formic acid as a product of H_2CO photolysis. Acids are known as promoters of aldehyde polymerisation, so they may be initiators of gas-to-particle conversion in H_2CO. In the present study we focus on chemical stages by which formic acid participates in phototransformation of H_2CO into aerosol.

Experimental

Formaldehyde (partial pressure 0.02 – 5 Torr) was photolyzed by a middle-pressure Hg lamp at atmospheric pressure and room temperature in the flow of carrier gas (argon or air; ozone was added in some cases) [1]. Free radical intermediates were identified by means of ESR with spin trapping using specially synthesized aldonitrones as spin traps [2]. The composition of gas and aerosol products was studied with UV absorption spectroscopy and high-performance liquid chromatography. Concentration and size of the generated particles (particle size range 2 – 100 nm) and photonucleation kinetics were measured with aerosol diffusion spectrometer designed and built at the Institute of Chemical Kinetics and Combustion, and tested in international workshops [3].

Results and Discussion

Among gaseous products of photolysis, formic acid was detected only in the presence of oxygen or ozone; [HCOOH] was found to depend on intensity and time of irradiation, initial H_2CO concentration, carrier gas composition. For $[H_2CO]$=1.2 Torr irradiated in air flow, [HCOOH] increases from $4.3 \cdot 10^{14}$ *molec/cm*$^{-3}$ for 1 min irradiation to $9.8 \cdot 10^{14}$ *molec/cm*$^{-3}$ for 100 min. The corresponding yield of nanoparticles increases from $2.2 \cdot 10^{-6}$ to 1.2^{-5}. The mean particle size is changed only slightly from 3 to 4 nm.

Reaction pathways from H_2CO to HCOOH can be outlined with the following scheme:

$H_2CO + h. \rightarrow H + HCO \qquad w_0$

$HCO + O_2 \rightarrow CO + HO_2 \quad 5.6 \cdot 10^{-12}\ cm^3/s$

$HO_2 + H_2CO \rightarrow HOCH_2OO \quad 7.5 \cdot 10^{-14} cm^3/s$

$HOCH_2OO + HOCH_2OO \rightarrow HCOOH + CH_2(OH)_2 + O_2 \quad 7.0 \cdot 10^{-13}\ cm^3/s$

$HOCH_2OO + HOCH_2OO \rightarrow HOCH_2O + HOCH_2O + O_2 \quad 5.5 \cdot 10^{-12}\ cm^3/s$

$HOCH_2O + O_2 \rightarrow HCOOH \quad 3.5 \cdot 10^{-14}\ cm^3/s$

$HOCH_2O \rightarrow H + HCOOH \quad 1.17 \cdot 10^3$

The [HCOOH] calculated by means of numerical modeling of this mechanism is in quantitative agreement with the measured value. To confirm the role of formic acid as an additional catalyst of nucleation, we added HCOOH into the H_2CO flow in argon; actually, the formation of nanoparticles was observed. It should be stressed that aerosol was never formed under H_2CO photolysis in argon without such an additive. However, the acid induces aerosol formation only when added directly into the irradiation zone of reactor. This means that formic acid takes part in gas-phase reactions after photolytic decomposition of formaldehyde; oxygen-containing short-lived free radicals were detected by ESR as spin adducts in Ar when HCOOH was added. These reactions lead to low-volatile products that are converted into nanoparticles. A possible polymerization mechanism can involve HCOOH addition to photolytically excited C=O bond, which simplifies the combination with another aldehyde molecule; the chain may run on till finally the formic acid is detached while the head and tail join each other to terminate the chain.

Conclusion

Thus, formic acid, generated by gas-phase stages of formaldehyde photodecomposition in air, may be a catalyst for gas-to-particle conversion in H_2CO vapour.

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THE CATALYST OF OXIDATION OF NATURAL GAS

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The development of novel methods for a complete hydrocarbon oxidation (reverse-process allowing accumulation of the oxidation heat; high-temperature catalytic combustion of the hydrocarbon feedstock) imposes restrictions on the catalysts: thermal stability and activity. Tin-containing systems promoted by the metals of basic nature are thermally stable catalysts in the reaction of methane coupling at T ~ 800-850 ^{o}C. It has been supposed that by introducing metal ions with an alternate valency (Mn, Ce, Cu, Co and Zn) one may obtain active catalytic systems for a deep hydrocarbon oxidation at the high catalytic activity kept at high temperatures. Along with a high activity, the stability of catalytic properties of the systems at high temperature (600-800 ^{o}C) and in the operation in low-oxygen mixtures was a main criterion. The operation of tin-containing catalysts modified with Co, Zn and Cu in an equimolar hydrocarbon-oxygen mixture at T= 600-800 ^{o}C results in the increase in the specific surface of the catalyst and changes in the activity: increasing of the temperature of 50- and 100% propane conversion and drop in the rate of butane oxidation. The thermal treatment of Ce- and Mn-containing catalysts in hydrocarbon-oxygen reaction mixture leads to the insignificant changes in the specific surface, but in this case the activity in the hydrocarbon oxidation increases from $8.96 \cdot 10^{-10}$ to $30.1 \cdot 10^{-10}$ mol/m^2·s for Mn-SnOx system (at T=200 ^{o}C) and from $22.1 \cdot 10^{-10}$ to $443 \cdot 10^{-10}$ mol/m^2·s for Ce-SnOx system (at T=300 ^{o}C) – the effect of the thermal activation.

Zn-Cu-Co system on metallic carrier (the net, nickel-chrome cellular carrier) is high active in deep oxidation of methane. The operation at the temperature above 500 °C causes the reduction of an activity in two times. The introduction of 20 % Fe_2O_3 to composition Zn-Cu-Co allows to raise the stability of the system. The catalyst works without loss of activity at the temperature 600-700 °C.

Use of Zn-Cu-Co composition loading with 20-40 % SnO_2 anchored on metallic carrier allows to raise thermal stability of systems so that they preserve high activity in deep oxidation of methane at temperatures up to 800–900 °C.

SOME FEATURES OF TRANSFORMATIONS IN AHM/HZSM-5 CATALYSTS FOR SYNTHESIS OF BENZENE AND OTHER AROMATICS FROM METHANE: ESR RESULTS

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In relation to the task of natural gas conversion, a large interest is represented by the discovered in 1993 catalytic reaction of methane dehydroaromatization into benzene and other aromatics over the catalyst Mo/HZSM-5, obtained by the ammonium heptamolybdate (AHM) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ deposition on the zeolite HZSM-5, with subsequent thermolysis (activation) of the catalyst in methane medium at $T \approx 700°C$ [1]. Survey of the results reported up to this moment on the formation of this type of catalysts indicates, that two principal issues still need to be completely solved. First, the features of active centers formation upon thermolysis of AHM/HZSM-5. Second, the features of catalyst deactivation by coke deposits. It is important, that various ESR spectra of coke deposits, appearing upon the formation of catalyst from AHM/HZSM-5, were already observed in work [2], however their detailed interpretation was not given. In this communication, based on the ESR data we will compare the features of thermolysis of AHM/HZSM-5 in methane and of bulk AHM in the air. Our discussion will be based both on the results of work [2] conducted at the Dalian Institute of Chemical Physics CAS, and on the results of experiments conducted at the Boreskov Institute of Catalysis SB RAS (BIC SB RAS) more than 20 years ago [3, 4] and recently.

Comparison of the ESR spectra obtained upon thermolysis of bulk AHM [3, 4] with the spectra obtained in the work [2] for AHM/HZSM-5 system, and also with the recent results obtained at BIC SB RAS shows, that thermolysis of both systems (bulk AHM in the air and AHM/HZSM-5 in methane) in principle is accompanied by the appearance of axial [5] and rhombic spectra of Mo^{5+} ions with corresponding g-factor values. Moreover, analysis of the spectra of such ions taken by us after thermolysis of AHM/HZSM-5 in methane at $T = 300$-$500^{o}C$ indicates, that molybdenum ions in the high oxidation states are not stabilized in the zeolite channels, while the forming polymolybdate and oxide structures are stabilized on the external zeolite surface. Similarly to the work [2], after thermolysis of the AHM/HZSM-5 we have not found spectra of the MoO_4^- hole centers, though earlier their traces were detected for the samples with higher AHM content [3, 4]. The authors of work [2] suggested, that appearance of the super-hyperfine structure (SHFS) from ^{29}Al nuclei is caused by the interaction of Mo^{5+} ions with two aluminum ions in the zeolite channels. Probably, a more justified reason for such SHFS from ^{29}Al nuclei is formation of the nitrogen-containing radicals from ammonium groups, similarly to the SHFS from ^{14}N nuclei in the spectra of MoO_4^- hole centers upon thermolysis of the bulk AHM [3, 4]. Such state of aluminum in the zeolite framework can be defective and capable of capturing the electron, for example upon . -irradiation of the zeolite. It is important, that in contrast with work [2], in the spectra of AHM/HZSM-5 after thermolysis in methane we have not found any paramagnetic centers (PMC) localized at the ^{29}Al nuclei, which would produce SHFS. It is also possible that SHFS from ^{29}Al nuclei in the work [2] was caused by the stabilization of paramagnetic NO molecules, forming upon the oxidation of ammonium groups, on such zeolite defects. Similar stabilization of NO on the oxide TiO_2 is known for a long time [6]. The features of spectra of such PMC are the ratios of g-factors ($g_{.} \sim g_e$, $g_{\parallel} < g_e$), which shows a reasonable match with the spectra in work [2]. After thermolysis of AHM/HZSM-5 in methane, starting by T = 500°C we had also observed an unusual spectrum with parameters $g_{.}^{(1,2)} = 1.935$, $g_{\parallel}^{(1)} = 1.910$, $g_{\parallel}^{(2)} = 1.895$, which are characteristic of Mo^{5+} ions with alkyl bonds, and this allows us to suggest that lower oxidation states of molybdenum are present upon the formation of active catalyst from AHM/HZSM-5.

Acknowledgements

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THE ELEMENTARY SCHEMES DESCRIBING ISOLA AND MUSHROOM IN KINETICS OF CATALYTIC REACTIONS

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Multiplicity of stationary states (MSS) is characterized by an opportunity of realization of several steady regimes of processes under the same conditions of their carrying out. The forms of MSS display are isola and mushroom. Isola is a closed isolated branch of a stationary kinetic curve (Fig. 1a). The main reason of appearance of isola is "rolling - unrolling" of a mushroom curve in Fig. 1b. The isola in the graph of r(C) can be obtained from a kinetic curve having a"singular point”. If one of the parameters changes slightly, this point becomes an isola.

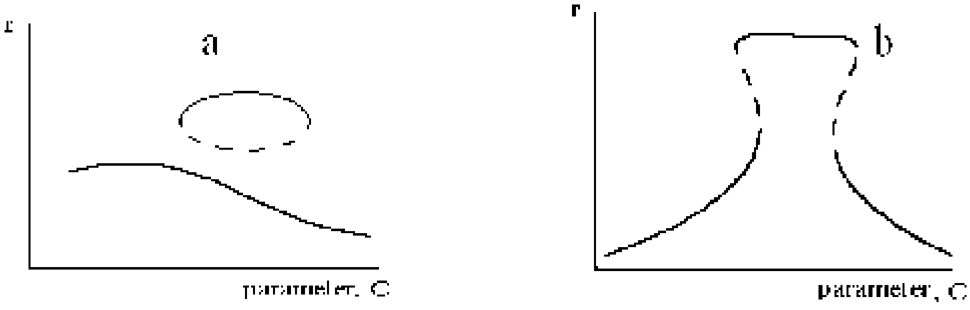

Fig. 1. Multiplicity shapes of steady states: a - isola, b - mushroom (solid lines-steady stationary states, broken lines - unsteady stationary states)

The simplest model of a kinetic curve with isola realization is a A . D reaction proceeding via an intermediate, B, according to the following scheme

$$1.A + 2B + X_1 = X_2 + 3B, \quad 2.B + 3X_1 + X_2 = 4X_1 + D, \qquad \textbf{(1)}$$

which at some parameter values C_B, $r(C_B)$ shows "singular point" (Fig. 2a). If the k_{-1} parameter slightly increases the point turns into an isola (Fig. 2b).

Mushroom behavior (Fig. 1b) can be considered as a monoparameter kinetic curve, which consists of two s-shaped hysteresis branches. This MSS shape rarely appears. There are a few papers in which this critical phenomenon is experimentally described. The kinetic behavior described by mushroom-type curve was experimentally reproduced for benzene [1] and carbon monoxide [2] oxidation on platinum catalysts.

The mushroom shape is a transitional one between isolated and self-crossing kinetic curves. The mushroom shape is connected with the existence of a "singular point". The investigation of stoichiometric conditions of the existence of a "singular point" showed some interesting results. For example, the B_2 . $2B_1$ reaction proceeding via the following scheme

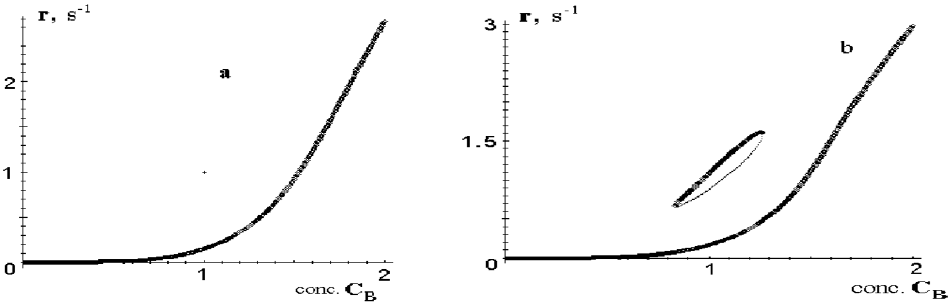

Fig. 2. Kinetic dependencies for scheme (1) at $k_1 = 4$, $k_2 = 67{,}5$, $k_{.2} = 54$ (s^{-1}):
a - monotonous branch with an isolated "special point ($k_{.1} = 0{,}5$)"; b - isola ($k_{.1} = 0{,}51\,s^{-1}$)

$$1.\ B_2 + X_1 = X_2 + B_1,\quad 2.\ X_2 = X_3 + B_1,\quad 3.\ 2X_1 + X_3 = 3X_1, \qquad (2)$$

describes the kinetics with isola under certain conditions (Fig. 3a). If the conditions change, approaching and blending of the isola with a monotonous branch takes place, which finally turns into a mushroom form (Fig. 3b).

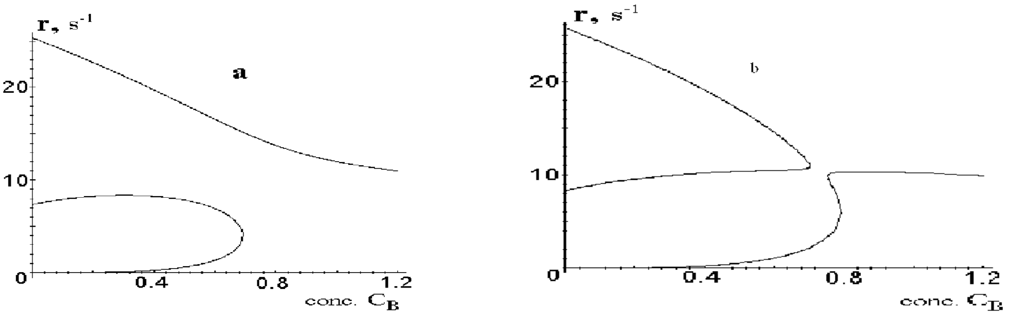

Fig. 3. Isola (a) and mushroom (b) for scheme (2) at: $k_{.1} = 12$, $k_2 = 180$, $k_{.2} = 144$, $k_3 = 405$, $k_{.3} = 81$ (s^{-1}): a - $k_1 = 48$; b - $k_2 = 180$ (s^{-1})

The above-mentioned examples show that kinetic dependencies with isola and mushroom are variable forms of MSS curves, they can turn into one another if the conditions of reaction change. Thus the modelling of complex forms of MSS display in kinetics of catalytic reactions is possible to carry out on a basis of enough simple stage schemes.

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HETEROGENEOUS BIOCATALYSTS FOR THE SWEETENERS PRODUCTION

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The immobilized enzymes are at the heart of innovative biocatalytical processes for biomass conversion performed in continuous *heterogeneous regimes* that are undoubtedly attractive and feasible for implantation in large-scale industry. The R&D of heterogeneous biocatalysts based on immobilized ***glucoamylase*** has been carried out for the key stage of the production of *starch treacle* and *glucose syrup* by the corn and wheaten starch/dextrin hydrolysis. To perform the process for manufacturing of *invert sugar* sweeteners from beet sugar, the biocatalysts based on immobilized ***invertase*** have been developed.

Carbonized ceramics have been synthesized and studied for the immobilization of glucoamylase and invertase. The effect of carbon layer morphology on biocatalytic properties of immobilized enzymes have been studied. *Filamentous carbon* layer (see Fig. 1) have been found to provide the highest long-term and operational stability of immobilized *glucoamylase*. The biocatalyst retained completely the initial activity after 1 year-storage at ambient temperature. The activity of biocatalyst has been kept constant for more than several hundreds hours of continuous starch/dextrines hydrolysis at 50-55 °C.

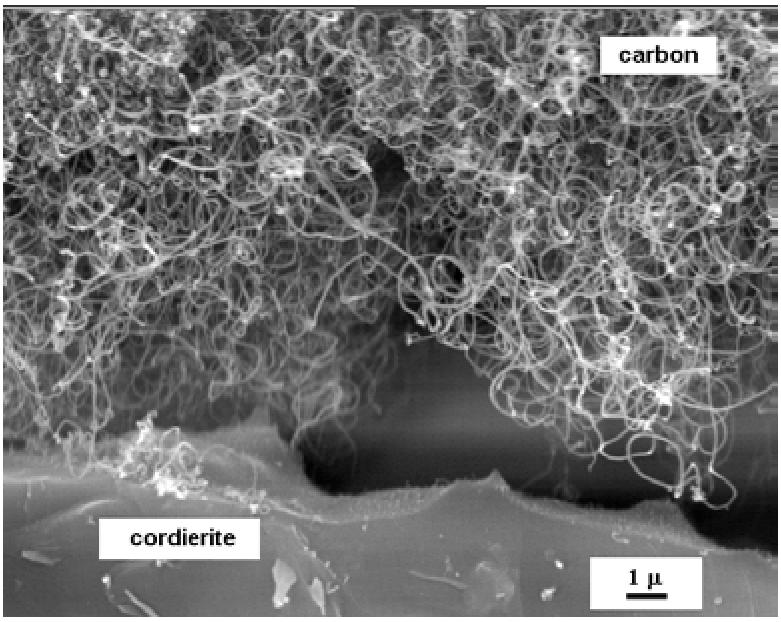

Fig. 1. Filamentous carbon layer on the honeycomb monoliths ceramics

Also, supports coated by catalytic *filamentous carbon* have ensured the highest stabilization of yeast *invertase*: the biocatalyst retained 50% of the initial activity for . 1-year storage at ambient temperature. In spite of that, invertase adsorbed on graphite-like carbon layer (see Fig. 2) has lost biocatalytic activity completely.

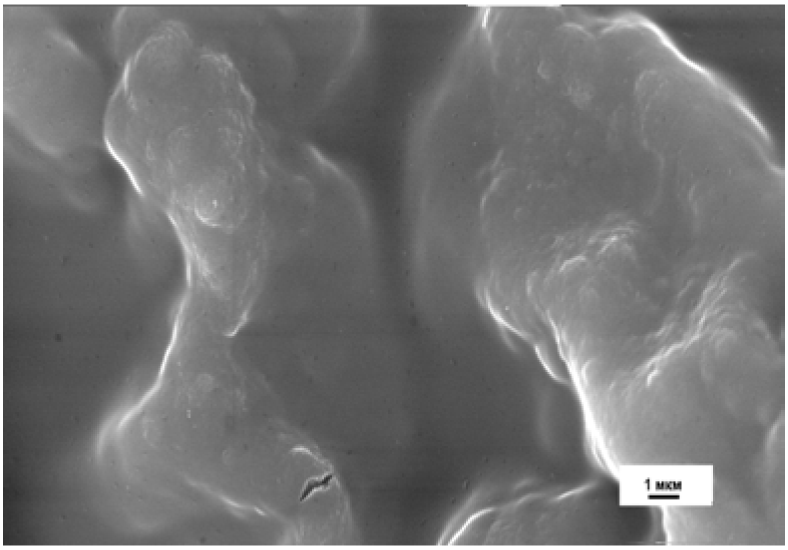

Fig. 2. Graphite-like carbon layer on the foam-like ceramics.

The approaches to control over the morphology of carbon layer and macrostructure of ceramics supports (***honeycomb monoliths*** and ***foam-like*** materials) have been developed to overcome the diffusion restrictions for substrates hydrolysis and to be a basis for the design of novel types of bioreactors.

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SELF-ORGANIZATION PHENOMENA AT SOLID STATE DECOMPOSITION OF HEAVY METAL AZIDES

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To the present time extensive experimental material concerning solid state decomposition of heavy metal azides is accumulated. Solid state decomposition of heavy metal azides was studied under the influence of different external factors in static and pulse modes. As it proved, though the difference of external excitation modes, geometry, and topography of product formation basic regularities of decomposition are sufficiently close that argues general causes of their formation.

Spectral and luminous-current characteristics of silver azide crystal photoconduction were investigated. Samples were illuminated with nonpolarized monochromatic radiation along [001] crystallographic direction in the spectral range of 250–1000 nm and intensity range of $3 \cdot 10^{11}$-$2 \cdot 10^{15}$ $cm^{-2}s^{-1}$ at the room temperature. Photocurrent increases upon the wave length decreasing and run up to maximum value at 390 nm wave length whereupon photoconduction decreases sharply and remains practically steady in short-wave region. It is shown that maximum of photocurrent spectral dependence is defined by increasing of electron-hole generation rate in crystal volume. At the same time generation of recombination centers in short-wave region should result in hysteresis in photocurrent spectra at wave length increasing. On these reasons there should be no maximum on the kinetic dependence of photocurrent. Both conclusions are confirmed experimentally.

Summary:

1. At low intensities of irradiation or wavelengths of incident irradiation more than threshold, kinetic dependencies of photoconduction (.) represent smoothed curves with saturation.
2. At large intensities of irradiation and wavelength less than threshold ones (. $_n$) kinetic dependencies of photoconduction have form of curves with maximum. Time of maximum reaching decreases upon the increasing of irradiation intensity (decreasing of wavelength).
3. There are threshold values of irradiation intensity (J_n) or wavelength of incident light, at which changes of the form of kinetic curve occur.
4. There are no peaks on kinetic dependences of photoconduction at recurrent irradiation with initial intensity. Recurrent irradiation with higher intensity or with . <. $_n$ results in appearance of maximum on kinetic dependences.

5. After reaching the maximum, photoconduction relaxation is observed both at continuous irradiation and at irradiation with dark intervals. This process is observed also at decomposition of many substances.

Mechanism of photo- and radiation processes in silver azide is proposed, based on two main principles:

- Limiting stage of molecular nitrogen formation is destruction of N_6 localized in cation vacancy
- Growth of small silver clusters through electron and ion stages is accompanied by generation of local levels in gap, which play the role of electron-hole pair recombination centers.

Both principles are completely confirmed by experimental data and quantum-chemical calculations of molecular nitrogen formation reaction. Creation of additional recombination centers is much more efficient method of Le Chatellier principle realization than self-compensation effect that is typically used for explanation of deep local center generation in crystals at external actions.

The proposed mechanism permits to explain from unified standpoint not only qualitatively but also quantitatively the regularities of great number of processes: kinetic, spectral, luminous-current characteristics of photoconduction and gas evolving kinetics at thermal, photo- and radiation-chemical decomposition of heavy metal azides.

Changes of the concentration of recombination centers during reaction bring to complex dynamic behavior of system: changes of kinetic curve for photoconduction and rate of radiation-stimulated gas evolving upon the increasing of intensity; photofatigue effect; generation of auto-oscillation and auto-wave process modes. Comparison with the experiment allowed to establish the regularities of metal cluster formation in silver azide. Clusters with odd n are less stable and reaction of its formation is reversible. Effective constants of recombination center growth and destruction in silver azide were determined.

Kinetic analysis has shown that steady state of the model of photo- and radiation decomposition of heavy metal azides is not stable. Consideration of diffusion-drift stages brings to auto-wave modes of the process.

Thus, analysis of solid state decomposition mechanism proposed in the work allowed not only to explain experimentally observed regularities of the process but also to predict a number of new phenomena. This fact is forcible argument in favour of proposed model adequacy.

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DETECTION OF NANODISPERSED Co^{2+} HYDROXIDE CONTAINING CATIONS IN THE TETRAHEDRAL COORDINATION

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Co^{2+} hydroxides have found a wide application as precursors in the synthesis of commercial catalysts (selective and deep oxidation, hydrogenation, etc.). Physicochemical properties of materials significantly change as one proceeds to particles smaller than 10 nm [1-3]. Such nanodispersed systems are likely to exhibit unusual performance in the reactions of adsorption and catalysis [1-3]. In this report we present for the first time data on Co^{2+} ions in tetrahedral oxygen coordination (Co^{2+}_{Td}) for nanodispersed $Co(OH)_2$ hydroxides synthesized by our technique.

The results obtained may be useful in preparation of catalysts and synthesis of high-tech materials, for example, Li-Co rechargeable batteries.

The structural modifications . -$Co(OH)_2$ and . -$Co(OH)_2$ are known for the Co^{2+} hydroxide [4]. The . -$Co(OH)_2$ is a relatively stable hydroxide which contains hexagonal plate crystals of several hundreds nm in size. It has a $Mg(OH)_2$ brucite-like lattice and Co^{2+} ions are located only in the octahedral oxygen coordination. . -$Co(OH)_2$ hydroxide is metastable and has a strongly disordered layered structure. Among the five models suggested for . -$Co(OH)_2$ [4], the model based on the $[M(OH)_{2-x}(H_2O)_x]^{x+}$ hydrotalcite-like structure (which does not contain M^{3+} ions in the hydroxide layer however) has been experimentally substantiated.

UV-VIS DR spectroscopy was used to study Co^{2+} ions electron states in $Co(OH)_2$. The principles of attribution of absorption bands (a.b.) in the UV-VIS DR spectra to different cobalt states and the coordination surrounding were considered in ref. [5]. Typical absorption bands associated with Co^{2+} or Co^{3+} in different crystalline fields of the oxide nature have been recently systematized [6]. For Co^{2+} ions (the electron configuration is d^7, the ground term of free ion is ^4F) in the octahedral coordination, the following transitions are probable: $^4T_{1g}$> $^4T_{2g}$, $^4T_{1g}$> $^4A_{2g}$ and $^4T_{1g}(F)$> $^4T_{1g}(P)$. However, one observes only one band at 19000-20500 cm^{-1} associated with $^4T_{1g}(F)$> $^4T_{1g}(P)$ transition. Note that the first transition lies in the far IR region and we do not observe it. The second is a two-electron transition whose intensity is considerably lower than that of the third transition. For Co^{2+} ions in the tetrahedral oxygen coordination, one can also observe three transitions: $^4A_2$> $^4T_2$, $^4A_2$> $^4T_1(F)$, and $^4A_2(F)$> $^4T_1(P)$, the splitting being much lower. For the same reasons, we have observed only one typical $^4A_2$> $^4T_1$(P) transition manifesting itself as a multiplet at 15000-17000 cm^{-1} [5]. The important difference between $Co^{2+}{}_{Td}$ and $Co^{2+}{}_{Oh}$ is high intensity (10-100 fold) of absorption bands of the Co^{2+} tetrahedral ions.

For . -$Co(OH)_2$ we observed a.b. at 19000 cm^{-1} associated with $^4T_{1g}$(F)> $^4T_{1g}$(P) transition which is typical for Co^{2+} ions in the octahedral oxygen surrounding, which is in complete agreement with the reference data [5]. In the UV region (above 30000 cm^{-1}), the bands of L> M transition of Co^{2+} ions are most likely observed.

We have synthesized nanodispersed $Co(OH)_2$ with particle size being ~1.5 nm. UV-VIS DR spectrum of this sample is characterized by two distinguishing features. First, it does not contain any absorption bands, which may be attributed to the hydroxide structure containing Co^{3+} ions (as CoOOH [6], providing an a.b. at 25000 cm^{-1}). Second, absorption bands of high intensity are unexpectedly registered in the 14500-16000 cm^{-1} region. These bands are conditioned by a multiple nature of $^4A_2$(F)> $^4T_1$(P) transition for Co^{2+} ions in the tetrahedral oxygen coordination [5]. The fact that the spectrum exhibits some multiplicity provides evidence [5] of the ideal tetrahedral coordination of Co^{2+} ions. The presence of $Co^{2+}{}_{Td}$ and $Co^{2+}{}_{Oh}$ ions in our samples can be explained in the following way: the sample consists of two phases, one phase contains only $Co^{2+}{}_{Td}$ ions, the other only $Co^{2+}{}_{Oh}$ ions. The latter phase can be formed, for example, by β-$Co(OH)_2$ crystals. We assume that we have synthesized a new modification of Co^{2+} hydroxide whose particle sizes range from 1.0 to 2.0 nm and the cations are predominantly located in the tetrahedral oxygen coordination designated as . -$Co(OH)_2$.

So, the synthesis of nanodispersed . -$Co(OH)_2$ samples according to our method provided evidence for stabilization of $Co^{2+}{}_{Td}$ ions in the absence of oxide phases and cobalt in other oxidation states, such as Co^{3+}. There is no doubt that the pronounced tetrahedral oxygen coordination of Co^{2+} ions in the nanodispersed $Co(OH)_2$ hydroxides is of much interest for researchers.

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ENERGETIC USE OF COKE GAS AND OF COAL GASIFICATION GASES

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At present the electricity production in Russia is mainly based on combustion of fuels. The proportion of natural gas combusted at thermoelectric power stations is more than 60% in the total fuel balance. However employment of natural gas as fuel may appear uneconomic because of the expected rise in domestic prices, which equal currently approximately one fifth of the world market prices. Therefore the use of coal in the areas remote from the sites of gas and oil extraction seems of particular importance. Among these areas are south of West Siberia and Krasnoyarsk region which are ample of coal resources. The same problems come up in the countries that do not have natural gas and oil resources but only solid fuel. The rise of prices for gas and oil makes it attractive to use coal as the main fuel and feedstock for energetic, metallurgical and chemical industries.

A promising method is gasification of solid fuels to produce synthesis gas or methane (1). The gaseous fuel is easier handled and can be used for gas-vapor energetic facilities with high efficiency of energy transformation. The gaseous products of coal gasification and coking can be used for generation of methane as a substitute for natural gas, production of gasoline and diesel fuel. Projects on application of coke-oven, blast-furnace and converter gases for development of effective energetic facilities are in progress now. They are based on binary cycles including combustion of fuel gas in a gas turbine followed by the stage of heating of water and steam in a boiler. This layout allows the heat energy of the fuel gas in the amount of up to 50% to be converted into electric power.

However, implementation of these technologies requires fine cleaning of gases from dust, tars, unstable chemicals, H_2S, NH_3, HCN that cause catalyst poisoning and corrosion of equipment. The methods of reversible absorption by amine solutions, which are commonly used for desulfurization of natural and oil gas, are inappropriate for coal gases because of their strong contamination with easily condensed chemically unstable resinous compounds.

The liquid-phase oxidative gas treatment in the presence of catalysts is proposed as an integrated method for gas purification. This method is based on catalytic oxidation of hydrogen sulfide absorbed by alkali ammonium or soda solution. The absorptive catalytic method for oxidative gas cleaning has been developed at the Boreskov Institute of Catalysis (2). The method also allows the volatile ash to be removed and the gas temperature to be decreased before the compressor.

The influence of various catalysts on the process of oxidation of alkali solutions of hydrogen sulfide is studied. Soluble derivatives of cobalt phthalocyanine are found most effective (Table); they allow H_2S absorbed from gas to be oxidized to produce elemental sulfur at room temperature at the catalyst concentration as low as several milligrams per liter (3).

Table. Catalytic liquid-phase H_2S- oxidation by oxygen in the presence of soluble derivatives of cobalt phthalocyanine.
t = 25 °C, $[H_2S]_o = 2 \cdot 10^{-2}$ M, volume of liquid 20 ml.

NN	pH	Catalyst	Catalysts concentration x 10^6 M	Expense of oxygen, ml	Rate in half reaction ml O_2/min
1	2	3	4	5	6
	7,3				
1		$CoPc(SO_3Na)_4$	1,02	–	1,90
2		Merox–2	2,60	–	0,44
3		$CoPc(SO_3Na)_2$	1,95	–	0,70
	8,5				
1		$CoPc(SO_3Na)_4$	4,08	6,9	2,25
2		$CoPc(SO_3Na)_2$	3,90	9,6	0,73
3		Merox–2	3,12	7,4	2,23
	9,2-9,5				
1		$CoPc(SO_3Na)_4$	6,13	7,7	2,73
2		$CoPc(SO_3Na)_2$	5,85	9,4	0,24
3		Merox–2	3,12	8,2	0,20

Among the intermediate products of oxidation are polysulfides strongly intensifying the oxidation process. The polysulfide solutions are active in bounding HCN, which must be removed from the cleaned gas.

Experimental studies on purification of coke-oven gas demonstrate potential removal of 95 – 100% of H_2S and HCN from the gas.

A wasteless technology for ecologically friendly combustion of gases evolved at coal coking and gasification can be developed on the basis of the liquid-phase oxidative purification process.

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FINE CHEMICALS FROM LARCH WOOD BIOMASS OBTAINED BY INTEGRATED CATALYTIC AND EXTRACTION PROCESSES

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North regions of Russia have a sufficient quantity of larch trees. But such features of larch wood as an increased content of extractive compounds and its high density create technological problems for the pulping process. From the other hand, the larch biomass contains rather high amount of biologically active compounds. **Therefore production of valuable chemicals is the most profitable way of larch wood treatment.** Up to the present only the production of quercetin dihydrate and arabinogalactan by extractive technique was suggested [1].

This work presents the new ways of larch wood wasteless processing into a big number of valuable chemicals.

Two integrated processes of larch wood processing into fine chemicals have been studied. One of them is based on the combination of following steps: extractive isolation of AG and QDH from wood, catalytic delignification of extracted wood with producing of microcrystalline cellulose and low-molecular-mass lignin.

Both AG and QDH were extracted from larch wood with boiling water. The effect of variation of extraction process operating parameters (time, water/wood ratio, temperature and wood particle sizes) on the yield of AG and QDH was investigated in order to reach the optimum products yield.

MCC was obtained by catalytic delignification of solid residue after wood extraction by hot water using the procedure described in [2]. The first stage of the process included the treatment of extracted wood in static reactor with delignification mixture: $CH_3COOH + H_2O_2$ in the presence of 2% H_2SO_4 at 130 °C and liquor/wood ratio 15:1 during 3 h. Then the spend liquor was replaced by the fresh one (but without H_2SO_4), and pulping was accomplished at the same conditions. Obtained cellulose was washed until pH=7, then dried and ground.

The integrated method of larch wood processing to AG, QDH and MCC allows to obtain the following maximum yields of target products (% wt. on a.d.w.): AG 18,QDH 0.6, MCC 20-21, soluble lignin 12.

Another process of larch wood processing includes the steps of AG and QDH extractive isolation, catalytic oxidation of extracted wood by O_2 into vanillin (V) and cellulose, acid-catalyzed conversion of cellulose to levulinic acid (LA).

Wood sawdust oxidation experiments were carried out in a static reactor at 170 °C, 0.5 MPa in the presence of copper catalyst prepared by dissolution of $CuSO_4 \cdot 5H_2O$ (25 $g.l^{-1}$) in water solution of NaOH (100 $g.l^{-1}$) using the procedure described in [3].

Vanillin yield goes through a maximum with the time of larch wood oxidation. This maximum yield (16-17% wt. on wood lignin) corresponds to 20 min. At the second step of the process levulinic acid was produced by acid-catalyzed conversion of cellulose obtained at the first step. The used process parameters were: temperature 180 °C, liquor ratio 1:8, concentration of sulphuric acid 2% wt. The yield of levulinic acid increased with the growth of process duration from 1 to 3 h. The maximum LA yield was about 10% relative to a.d. wood.

Integrated processing of larch wood to V, LA, AG and QDH gives the following maximum yields of target products (% wt. on a.d.w.): V 5.4, LA 8.6, AG 18, QDH 0.6.

AG is used for sizing and forming of paper, cardboard and for improvement of their quality; as filler in pills and tablets production, etc. QDH posesses antioxidant, antiphlogistic and antihistamine properties. Therefore it has prospects of application in medicine. MCC serves as filtering and filling material in metallurgy, plastics, food industries, in medicine and pharmaceutics and other fields. V and LA have application in medicine and food industry. LA has good prospects of the use in plastics and fine chemicals production.

Acknowledgement

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PARTIAL OXIDATION OF PROPANE ON V_2O_5-MoO_3-BASED CATALYSTS

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Intoduction

At present the promising results for reaction of direct propane oxidation to acrylic acid are obtained over modified V-Mo oxide catalysts [1-4]. The yields of acrylic acid over the catalysts with identical composition amount from 2 to 48% according to the data of various authors. This probably may be caused by complexity of chemical and phase catalyst composition, and by the components interaction in the V-Mo system which depends on method of its preparation.

The aim of the present work is to study the effect of chemical and phase composition of oxide catalysts based on vanadium and molybdenum on their catalytic properties in propane oxidation.

Experimental

Binary Mo-V catalysts were prepared by mixing of aqueous solutions of ammonium paramolybdate and vanadyl oxalate, ternary MoVNb and MoVTe, as well as composite MoVNbTe catalysts – by mixing of aqueous solutions of ammonium paramolybdate, vanadyl oxalate, telluric acid and/or syspension of niobium pentoxide followed by evaporation at 80 °C. Catalysts were subjected to thermal treatment in the temperature range 350-600 °C in the stream of air, nitrogen or reaction mixture.

The catalytic experiments were carried out in a conventional flow quartz tubular reactor (i.d.=8 mm) with a fixed catalyst bed at temperature 380 °C under atmospheric pressure with a reactant molar ratio C_3H_8/H_2O/air - 5/30/75. The reaction products were analyzed using gas chromatography.

The X-ray diffraction patterns (XRD) were obtained using a URD-63 diffractometer with monochromatized Cu-K. radiation.

Results and Discussion

Chemical and phase composition of samples are given in the Table.

Table. Characteristics of Mo-V-based catalysts

Chemical composition	Atomic ratio	Conditions of heattreatment	
		350°C, 2 h, air; 380°C, 5 h in reaction mixture	600°C, 2h, N_2
MoV	1:0.30	MoO_3 (or)[*], VMoO- phase[**]	Mo_5O_{14}, VMoO phase[**]
MoVNb	1:0.30:0.12	MoO_3 (or)[*], Mo_5O_{14}, VMoO phase[**], Nb_2O_5	Mo_5O_{14}, VMoO phase[**]
MoVTe	1:0.30:0.23	MoO_3 (or)[*], TeVMoO phase[***][1-4]	MoO_3 (or)*, TeVMoO phase [1-4][***], VMoO -phase[**]
MoVNbTe	1:0.30:0.12:0.23	MoO_3 (or), TeVMO phase[***], Nb_2O_5	TeVMoO phase[***], . -$TeMo_4O_{13}$, Mo_5O_{14}

[*] MoO_3 (or)- orthorhombic MoO_3, [**] VMo compound from family of related structure compounds of the V_2O_5 type; [***] TeVMoO -phase type M2 [1-4].

The catalytic results obtained upon the oxidation of propane over studied catalysts are shown in the Figure.

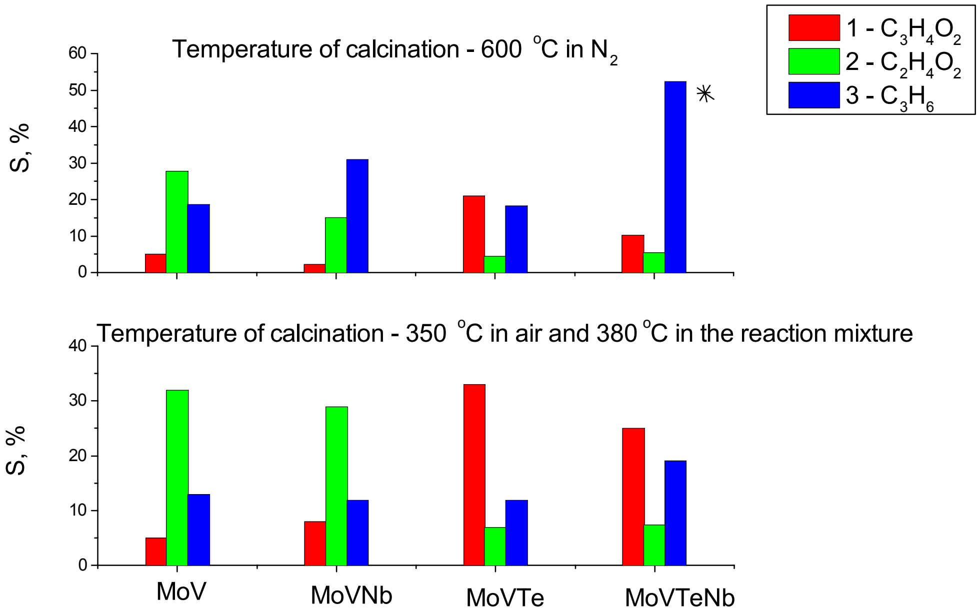

Fig. Variation in selectivities to main products of partial oxidation versus chemical and phase composition of V-Mo based catalysts.
Propane conversion is 12-15% ; * propane conversion - 5%.

Acetic acid and propene are the main products of the selective propane oxidation on VMo and VMoNb samples, plus a small amount of acrylic acid. The incorporation of Te into VMo and VMoNb catalysts results in sharp decrease in selectivity to acetic acid and increase in selectivity to acrylic acid. However, both catalytic activity and selectivity to partial oxidation products depend on the temperature and conditions of calcination. The selectivity to propene for VMo and VMoNb samples calcined at 600°C in N_2 is higher than that for samples treated at 380°C in the reaction mixture (Fig.). The selectivity to acrylic acid over Te-containing catalysts (VMoTe and MoVTeNb) decreases with the increase of heattreatment temperature.

Thus, catalytic properties of V-Mo based catalysts are defined by chemical composition and heattreatment conditions. VMoTe and VMoNbTe catalysts containing orthorhombic MoO_3 and TeVMoO phase [1-4] revealed the best properties in the reaction of propane oxidation to acrylic acid (Fig.).

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BIFUNCTIONAL CATALYSTS FOR THE SYNGAS CONVERSION TO LIQUID HYDROCARBONS

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The Fischer-Tropsch (FT) synthesis has had many applications since it was first reported in 1923 and one of the most important factors in maintaining interest over the past 80 years is its flexibility. For example, FT technology can deliver diesel fuel (Fe- and Co-catalysts), heavy n-alkanes (Ru and Co), olefins (Co/MnO, Fe) etc. The conversion of synthesis gas to hydrocarbons over FT catalysts such as Fe, Co and Ru does not produce liquid fuels with sufficient selectivity and quality. For the last three decades, a great number of works on the selective synthesis of high octane gasoline from CO and H_2 has been carried out with the use of bifunctional catalytic systems composed of a FT component and ZSM-5 zeolite [1-3]. It is of interest to study the conversion of synthesis gas on the different bifunctional catalysts for the production of motor fuels (gasoline, diesel, base oil), aromatic hydrocarbons and medium weight olefins.

In the present paper, we have catalytically examined the one-stage syngas conversion to hydrocarbons in a fixed bed flow reactor. The oxides of Zn, Cr, Fe, Co, Ru in the combination with acid components were applicated as bifunctional catalysts. The influences of the catalysts content, the type of the metal oxides, the type of the acid component (ZSM-5, Beta, SAPO-5, mordenite etc.), mass ratio of the metal oxides to the acid component, pressure (from 5 to 80 atm), temperature (210-420°C), $(H_2\text{-}CO_2)/(CO+CO_2)$ ratio (0.5-10), pilot test run duration (up to 1000 h) on the activity and selectivity of the bifunctional catalysts were shown. The range of reaction parameters and the performance of bifunctional catalysts in hydrocarbons synthesis from CO and H_2 are shown in the Table.

The high quality of gasoline fractions is conditioned by the low content of benzene and of 1,2,4,5-tetramethylbenzene. It is shown that the benzene content doesn't depend on the content of aromatic in the synthesized fuels. This fact is explained by high alkylating ability of the acid component of the bifunctional catalyst. The diesel fractions contain C_{10}-C_{20} branched hydrocarbons (40-60 mass.%) and the content of the aromatic hydrocarbons is less

3 mass.%. The C_1-C_{20} hydrocarbons composition versus carbon atom number differs considerably form Schultz-Flory distribution typical for Fischer-Tropsch products. These differences are caused by the occurring of some reactions on the acid component of the bifunctional catalysts – reactions of hydrogen redistribution, oligomerization, isomerization, alkylation of aromatics [2].

TABLE. The range of reaction parameters and the performance of bifunctional catalysts in hydrocarbons (HC) synthesis from CO and H_2.

Metal component	Co, Ru	Co, Ru	Fe	Fe	Zn, Cr	Zn, Cr	Zn, Cr
Acid component	Wide- and narrow-pore zeolites			ZSM-5	ZSM-5	ZSM-5	Beta, SAPO
H_2/CO	1.5-1.8	1.7-2.0	1.7-2.0	. 2	2-3	1-2	. 2
Pressure, atm	10-30	5-30	10-50	10-50	40-80	40-80	40-80
Temperature, °C	200-220	220-250	240-280	280-360	360-400	380-420	360-420
Selectivity, wt. %							
CH_4	7-12	8-20	4-6	5-8	1-4	4-6	3-6
C_2-C_4	5-9	6-10	7-14	8-16	16-22	20-26	26-34
C_{5+}	82-87	74-85	80-87	76-84	74-82	68-76	60-70
Cutoff in the HC distribution	C_{26} (up to C_{30})	C_{22}	C_{22}	C_{14}	C_{11}	C_{11}	C_{14}
Desired products	diesel, base oil	gasoline, diesel	gasoline, diesel	gasoline	gasoline	aromatics	PMA
I-HC/n-HC ratio							
in gasoline	-	1-2	1-4	5-10	10-20	-	-
in diesel	0.4-1.0	0.8-1.4	1-(>6)	-	-	-	-
C_{5+} Yield, g/m^3 syngas	120-140	90-150	100-150	100-150	90-140	60-140	80-100
C_{5+} Productivity, g/L cat./h	80-200	60-(>300)	70-160	70-160	100-400	40-120	100-140

Thus, in the present paper a possibility of the syngas conversion on the different bifunctional catalysts to high octane gasoline, diesel and base oil fractions with high content of branched hydrocarbons, alkylaromatic and polymethylaromatic hydrocarbons (PMA) as well as medium weight olefins for the production of motor fuels was shown.

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SIMULTANEOUS TRANSFORMATION OF METHANE AND THE HIGHER ALKANES IN CONDITIONS OF CRACKING REACTION

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Reaction of nonoxidizing metane addition to intermediates of alkanes (heptane, tetradecane) conversion has been studied in the presence of polyfunctional catalysts Ni-Sn/Al_2O_3 + Zn/ZSM-5. New experimental data obtained allow to understand the nature of the effects of nonoxidizing methane addition. Alternative paths of methane conversion were simultaneous cracking reactions with breaking of C-C bond and reactions of dehydrocyclization of fragments of alkanes conversion with formation of aromatic hydrocarbons and hydrogen. Experiments were carried out in an autoclave from stainless steel with hashing the reaction medium. Conditions: P=3,0-6,0 MPa, T=250 - 400 ^{0}C, ratio CH_4/alkanes = 3/1 (mol).

In the first series of experiments experimental estimations of the effects of methane addition to intermediates formed in the result of breaking of C-C bond in tetradecane in conditions of high degree (95-100 %) of tetradecane conversion into gaseous C_2 - C_5 hydrocarbons have been carried out. The structure of the products of tetradecane and methane conversion is presented in Table 1.

Table 1

Hydrocarbons	C_1	C_2	C_3	$C_3^=$	C_4	$C_{4=}$	C_5	$C_5^=$	C_6^+	C_{14}
Load	70	-	-	-	-	-	-	-	-	30
Yield, mass %	36	1	7	0	17	1	7	0	38	-

Conditions: P=5,0 MPa, T = 350 ^{0}C, CH_4/C_{14} = 2,5

As the reactions of alkanes cracking are realized with formation of a mixture of paraffins and olefins, experiments on studying a possibility of methane addition to olefins were conducted.

The natural gas purified from microimpurities and propylene was taken as raw material. The following results have been obtained: methane addition to olefins does not occur, but the redistribution of the hydrogen takes place resulting in formation of propane and is further conversion. The similar situation is observed at simultaneous conversion of methane and tetradecane. The amount of paraffin hydrocarbons may be more than 37 % mass of the products.

The experimental estimation of the effects of methane addition to intermediates of reaction of alkanes dehydrocyclization into C^{5+} liquid hydrocarbons has been carried out also. Selectivity of heptane and tetradecane conversion to C^{5+} is adjusted by specially developed technique of preliminary sulfurization of Ni-Sn/Al_2O_3 + ZnZSM-5 catalysts.

The analysis of balance of an initial mixture and reaction products on carbon and hydrogen reveals the absence of significant disbalances (no more than 1-3 % of weights), that testifies the absence of processes of deep dehydrogenization of hydrocarbons ($C_nH_{2n+2} \rightarrow nC + (n+1)H_2$), capable to be a source of hydrogen for saturation of products of tetradecane cracking. Presence of carbon on a surface of the catalyst does not exceed 1-3 % from the whole carbon supplied to reaction. Hence the assumption was made, that reaction of methane dehydrogenating CH_4– -CH_{x+4}-xH and reaction of aromatization of tetradecane or products of its cracking ($C_{14}H_{30}$> $C_{14}H_{10}+10H_2$) may serve as a source of hydrogen for reaction of hydrogenation of products of tetradecane cracking. Presence of aromatic hydrocarbons in the reaction products in amount up to 10 % by weight became the argument for such assumption. Propylene in the ratio ~5 (mol) to tetradecane, $C_3H_6/C_{14}H_{30}$, has been injected into reaction zone (as an acceptor of hydrogen, probably, evolved in reaction) to check the assumption that hydrogen affects the metathesis of methane and tetradecane.

It is necessary to note, that treatment of the catalyst by sulphur-containing chemicals and injection of hydrogen acceptor (propylene) into reaction zone result in double increase in methane conversion. Also it is necessary to note, that formation of alkylaromatic hydrocarbons is observed in significant amounts, as against the experiment without hydrogen acceptor. Probably, the activated methane reacts with intermediates of higher alkanes dehydrocyclization.

CATALYTIC PROCESSING OF RICE HUSK

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Biomass is a most ancient power source. Till now wood fuel remains a main energy source in many countries of the world. Important sources of biomass are vegetative residues (wheaten and corn straw, chaff, rice and oat husk, etc.), solid organic scraps of animal industries, municipal wastes, redundant (excessive) active silt after biological cleaning of waste water. The traditional combustion of biomass in a torch furnace with consequent use of generated heat for the power purposes has an essential disadvantage due to a high level of toxic substances in exhaust gases (CO, nitrogen and sulfur oxides, benzpyrenes and other). The new technology of fuel combustion in the fluidized bed of catalyst, offered by the Boreskov Institute of Catalysis in the industrial scale, avoids many disadvantages of traditional combustion of biomass.

In the present work, some data on catalytic combustion of one of the most widespread vegetative remainders - rice husk are adduced. The rice husk is used not only as a fuel, but also as a source of silicon for semiconductor industry, for synthesis of silicon carbides and silicon nitrides, etc. We studied the rice husk oxidation in the vibrofluidized bed of either a catalyst or an inert material in conditions allowing to reproduce with an adequate accuracy the data on scraps combustion in the dense and unloaded phase of the fluidized bed.

It is found, that the process of the rice husk combustion is localized completely in the bed of the catalyst. In the bed of an inert material the process occurs in a space above the bed; consequently, exhausts contain a fair quantity of CO. Studies on solid products of the rice husk combustion has shown that their texture is determined mainly by silica, which is contained in rice husk as amorphous silica $SiO_2 .nH_2O$. The adsorption ability of these solid products in respect to methylene blue (MB) is investigated. With increasing the process temperature, the value of limiting MB adsorption by the solid products passes through a maximum at the process temperature 600 ^oC. It is found, that the values of the limiting MB adsorption for the solid combustion products in the bed of the catalyst exceed those for solid products obtained in the bed of an inert material.

Under discussion are also some distinctions of the process of rice husk processing in the vibrofluidized beds of either catalyst or inert material.

THE PRODUCTS OF PHOTOCHEMICAL DECOMPOSITION OF THREADLIKE CRYSTAL AZIDES OF SILVER AND LEAD

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It is accepted, that azides of heavy metals (HMA) are decomposed with formation of metal and molecular nitrogen by the simple scheme: $2MN_3 = 2M + 3N_2$, where M - univalent metal. Last experimental researches have shown, that reaction of decomposition in an anionic sublattice of azides has chain character and results in crystal stability, concerning disintegration up to molecular nitrogen of intermediate compound N_6 [1,2]. The present work is devoted to complex research of the products of photochemical decomposition of metal azides; to the experimental proof of an opportunity of synthesis and existence at room temperature of compound N_6.

Irradiation of crystals, in the field of own absorption of azides, was carried out with the help of mercury lamp DRSH-100. Threadlike crystals HMA were irradiated during 35 s ($I = 4{,}078 \cdot 10^{16}$ quantum/cm s) and 50 s ($I = 2{,}855 \cdot 10^{16}$ quantum/cm s) accordingly. The distance between a lamp and a sample was 10 cm. The quantitative analysis of products of photochemical decomposition was carried out by volumometric methods (a method of the Heal [3] and "gas from the butt-end" [4]), controlled decomposition in an anionic sublattice (on a gaseous product formed in reaction). Topography of distribution of products of decomposition investigated both in an anionic (with the use of methods of the analysis of dislocation structures [5]), and cationic (the electronic microscopy platinum-carbon retorts was used) sublattice of azides. Intermediate product of photochemical HMA decomposition was selected after storage of the irradiated samples not less than a day (time necessary for accumulation of sufficient amount of a product) at room temperature.

The results of experimental research show that, at dissolution (0.36 N $Na_2S_2O_3$ aqueous solution for AgN_3 and 3 N CH_3COONH_4 aqueous solution for PbN_6) samples of HMA during 20 hours after UV-irradiation from the reactionary regions (RR), formed by edge dislocations in surface region of a crystal on depth no more than 5 microns, were evolved a gaseous product (more hardly nitrogen) which volume correlates with the time of power influence.

Bubbles a gaseous product (with average diameter 60.70 micron) do not float, and settle on a bottom ditches in which dissolve crystals, and as against molecular nitrogen, are dissolved within 20 minutes. The analysis of an evolved gaseous product of decomposition silver azide with the help of the method developed in our laboratory "spectroscopy of decomposition", which consists in illumination of the formed gaseous product by monochromatic light (monohromator MSD-1, a range of lengths of waves 350.800 nm) has shown, that the irradiation of a gaseous product light with length of a wave 550.10 nm conducts to increase of volume bubble gas no more than three times. At the analysis of an intermediate product of photochemical decomposition lead azide, existence of one more strip (. = 580.10 nm) with increase of volume of an allocated gaseous product in nine and more times is marked. Apparently, products of photochemical decomposition of lead azide contain longer circuits (research of this effect demands development of additional techniques).

Let's note, that time, necessary methodically to evolve an intermediate product of photochemical decomposition of azides as bubble gas, is time of formation of places of a compact arrangement of molecules in reactionary areas (we shall name klaster an intermediate product) This time makes 24-30 hours and it is obvious, is defined ionic by a stage of process (speed of process of an output of ions of metal on a surface of a crystal).

Studies of an intermediate product of photochemical decomposition of silver and lead azides in a solid phase (matrix) has shown presence of one peak appropriate . = 380 nm, in a case of silver azide, and two peaks . = 380 and . = 500 nm, in a case of lead azide, that also testifies, in our opinion, the presence of two products in volume of a sample.

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