Catalytic Isomerisation of Alkanes on Anion-Modified Forms of Zirconium Dioxide

P. N. KUZNETSOV, L. I. KUZNETSOVA and A. V. KAZBANOVA

Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marksa, 42, Krasnoyarsk 660049 (Russia)

E-mail: kpn@icct.ru

Abstract

Results of systematic investigation of the physicochemical features of the formation and isomerising activity of catalysts based on zirconium dioxide modified with sulphate and tungstate anions and various trivalent cations, depending on the composition and preparation conditions, are presented.

Key words: oxide catalysts, anion modification, alkanes, catalytic isomerisation, motor fuel

INTRODUCTION

The basic oil deposits in West Siberia have entered the phase of declining production during the recent years, while the rate of the development of new deposits does not correspond to the rate of reserves reproduction. Deposits in Eastern Siberia, the Republic of Sakha (Yakutia) and Far East are related to the priority deposits in the reproduction and increase in the production of hydrocarbons [1–3].

At the Krasnoyarsk Territory, there are essential resources of hydrocarbon raw material – oil and natural gas [3–6]. According to the State Balance, by 01.01.06 the geological reserves of the bowels of the territory with respect to the sum of categories $C_1 + C_2$ account for 2935.5 million t of oil, 137.21 million t of condensate, and 1181.76 billion m^3 of natural gas; the mineable reserves are 875.2, 80.56 million t and 1181.76 billion m^3, respectively [5]. Estimation of reserves is at the initial stage, and the extent of oil exploration is 4.4 %, gas 7.6 %. The deposits are distributed non-uniformly over territory; aggregative oil and gas bearing regions are distinguished in the generalized form, in particular the north-western region where the Pur-Taz oil and gas bearing region with the largest Vankor deposit is situated, and the south-eastern region where the

western part of the Lena-Tunguska oil and gas bearing province lies, with the largest Yurubchen-Tokhom deposit and large Kuyumba, Sobinsk and other deposits.

The majority of deposits in the Krasnoyarsk Territory, as well as in Eastern Siberia in whole and in Yakutia are oil-and-gas deposits. Almost all the kinds of oil relate to high-quality low-sulphur and light-weight grades. Natural gas from the majority of deposits is almost free from hydrogen sulphide and is distinguished by the increased content of ethane, propane and butane (their total content at the Yurubchen deposit reaches about 11 %), and helium (its weighted mean concentration at this deposits is 0.38 %, and 0.57 % at the Sobinsk deposit) [2, 7]. For comparison, the natural gas of the Orenburg gas condensate deposit processed at the Orenburg helium plant contains only 0.056 % helium.

The commercial production of oil started in the Krasnoyarsk Territory at the end of the year 2009 at the Vankor deposit. The Rosneft Oil Co. is planning to mine there 12 million t of oil in 2010 in order to fill in the Eastern Siberia – the Pacific Ocean oil pipeline; during the subsequent years the production will reach 25 million t. The next stage provides a large-scale development of oil and gas deposits of the Yurubchen-Tokhom zone (on the state balance, there are more than 580 million t of mineable

oil resources, 880 billion m^3 of gas and 69.5 million t of condensate). The construction of the first region of the deposit will be started by the Rosneft Co. in 2010. With the development of this and other deposits, the territory will become a large oil- and gas-mining province of Russia. Efficient development of oil and gas deposits rich in light hydrocarbons and helium requires the systemic approach; from the very beginning it also requires the organization of profound integrated processing of the raw material into high-quality competitive products – motor fuel, chemical compounds, helium and other products with high added cost [3, 4].

Oil refining industry branch is represented in the territory by the Rosneft Achinsk Oil Refinery Plant (AORP) with the processed amount of 6.8 million t in 2008, and with mini plants at the Yurubchen, Paiginsk and Vankor deposits manufacturing motor fuel for local needs. The AORP was put into operation in 1982 with not deep processing layout over the fuel version including atmospheric distillation, hydrofining and catalytic reforming. The set-up for isomerisation was put into operation in 2008; this and other measures aimed at upgrading of the technological scheme allowed one to increase the quality of motor fuel manufactured at the AORP and to bring the ratio of high octane gasoline meeting the Euro-3 standard to 100 %. The programme of measures on the technological modernization of the plant includes the construction of other installations including new catalytic installations for reforming, isomerisation, cracking. By 2012, the amount of oil processing is planned to reach 8 million t.

At present, oil from the deposits of West Siberia is processed at the AORP. In the near-term outlook, oil from the deposits of the Yurubchen-Tokhom district will be supplied to the plant. In this connection, it should be stressed that oil from those deposits, similarly to other deposits of East Siberia, differs substantially in the fractional and hydrocarbon composition from the oil of West Siberian deposits [3]. In particular, benzene fractions of oil from the Yurubchen, Sobinsk and Kuyumba deposits contain mush less isoalkanes, 2 times lower concentrations of naphtene hydrocarbons and two times higher concentrations of normal alkanes [8]. As a consequence, the transition to the new

raw material may cause worsening of the parameters of major processes (isomerisation and reforming) in the production of motor fuel, so the corresponding technological developments will be required.

During the recent years, the demand for high-quality diesel fuel is also increasing because of the growing number of modern cars and trucks with diesel engines. The production of high-cetane and low-solidifying diesel fuel is especially urgent for cold Siberian and northern regions of Russia. The goal to improve the quality of motor fuel manufactured at Russian petroleum processing plants was determined by the Federal law of RF "On Technical Regulation", in particular by the requirements specification approved by the governmental regulation No. 609 of October 12, 2005, establishing the schedule for the transition to more efficient and ecologically safe fuel. The major challenge of home petroleum processing plants in solving this problem is the lag of catalyst production from the world level.

A universal direction of mastering the production of high-quality motor fuel is the development of new modifications of catalysts and the catalytic processes of framework isomerisation of n-alkane hydrocarbons of benzene and diesel fractions into the corresponding branched isomers with high octane and cetane characteristics and lower freezing temperatures and cloud points than those of n-alkanes. The products of isomerisation are the most suitable components for motor fuel meeting all the requirements to the quality and mixing ability. The processes of their obtaining are not connected with substantial capital investment and performance expenses because these processes are carried out at low temperature and pressure of hydrogen; no special production of hydrogen is to be organized because usually the amount of hydrogen from reforming installations is sufficient. The existing industrial processes of alkane isomerisation are intended for processing pentane-hexane fractions the resources of which are available at each petroleum processing plant [9–12].

Isomerisation of n-paraffins into the framework isomers is a reversible exothermal process; low temperatures are favourable to an increase in the yield of high octane isomers,

especially strongly branched ones [13]. Industrial processes are carried out in the region of thermodynamic equilibrium, so the parameters of isomerisation are to a decisive extent determined by the activity of catalysts. Widespread catalysts are those based on zeolites (UOP HS-10, Axens IP-632, Sud-Chemie Hysopar, Russian catalyst SI-1 of Neftekhim Co.), aluminium chloride (UOP I-8, I-80, I-82™, I-84™, I-120, I-120™, 122™, Axens IS-614, IS-614A; Engelgard RD-291 and its analogs NIP-RD, NIP-3A developed by the Russian Olkat Co.) [12]. During the recent years, catalysts based on sulphatized zirconium dioxide become widespread (UOP LPI-100) [9] and Neftekhim CI-2 [10]. New types of catalysts containing no chlorine and combining the advantages of aluminium chloride and sulphatized ZrO_2 are under development and introduction abroad (UOP PI-242 [14]).

At the AORP, low-temperature isomerisation of pentane-hexane fraction (UOP's Penex/DIH process) using platinised aluminium chloride as the catalyst has been realized. The catalysts of such a type are distinguished by high activity; they allow one to obtain high yields of isomerisate. At the same time, they have got essential shortcomings connected with high sensitivity to poisons, impossibility to regenerate them, and the need to introduce chlorine-containing additives into the raw material. These catalysts, similarly to other known industrial catalysts, exhibit low efficiency towards isomerisation of C_{7+} alkanes due to their low selectivity and low stability against deactivation by coke deposits. The concentration of heptane fraction in the raw material should not exceed 3−15 % (depending on the process modification version), benzene concentration should not exceed 3 %.

Catalysts based on sulphatized zirconium dioxide combine the major advantages of aluminium chloride and zeolites. They are close in their catalytic activity to aluminium chloride but similarly to zeolites they are much more stable against the action of admixtures and better able to regenerate. By present, a large amount of data on the physicochemical properties and isomerisation activity of the catalysts based on sulphatized zirconium dioxide and the oxides of some other metals has been published [15−19]. The catalytically active form is represented by fine zirconium dioxide of the metastable tetragonal modification with sulphate groups fixed on its surface and strong Brønsted/Lewis acid centres [15, 18]. A special place is occupied by the anion-modified forms of the dioxide, promoted by di- and trivalent metal cations.

In spite of the large amount of research and the experience of the industrial application of catalysts based on sulphatized zirconium dioxide, the physicochemical regularities of their formation have been studied only poorly. The factors and the nature of the stabilizing action of anion and cation additives and their effect on the acidic and catalytic properties have not been established yet in the final form and remain the subject of active discussion [15, 20−23]. This is to a high extent with the metastable state of the catalytically active form of zirconium dioxide, so that its structural characteristics and catalytic activity are essentially dependent on the method of preparation similar oxide systems modified with WO_4^{2-} and MoO_4^{2-} anions exhibiting increased selectivity for the isomerisation of long-chain alkanes have been studied to much lower extent [15, 16, 24−28]. These systems are of substantial interest for the development of new isomerisation catalysts for obtaining both high octane components of gasoline and low-freezing high cetane components of diesel fuel.
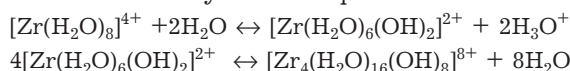
In the present paper we describe the results of systematic investigations of the physicochemical regularities of formation and isomerising activity of catalysts based on zirconium dioxide modified with sulphate and tungstates anions and various trivalent cations, depending on the composition and preparation conditions.

The preparation procedure included synthesis of the hydroxide precursor through precipitation of zirconyl salt (mainly chloride) from aqueous solution under the action of ammonia solution. Cation and anion additives were introduced either at the stage of precipitation or by impregnation of the xerogel. Cations used as the cation promoters were Fe^{3+}, Y^{3+}, Al^{3+}, Mn^{3+} и Sc^{3+} with the atomic fraction of 0.5 to 25 %. Anion modification was performed by impregnating the xerogel with the solutions of sulphuric acid and the salts of tungstic acid. Thermal treatment of dried modified samples of xerogel was carried out in the quartz reactor in the air within temperature range 350−700 °C (usually for 3 h). The following designa-

tions are accepted in the text: for example, $5Al^{3+}/Zr600$ is zirconium dioxide promoted with aluminium cations in the amount of 5 at. % (calculated for the sum of cations) after annealing at 600 °C; $6SO_4^{2-}/5Al^{3+}/Zr600$ is the corresponding sample containing 6 % of SO_4^{2-} groups.

EFFECT OF CATION PROMOTERS ON THE PROPERTIES OF ZIRCONIUM DIOXIDE

After mixing the solution of ammonia with the solution of zirconyl salt, stepwise processes of hydrolysis and polycondensation take place. These processes at first lead to the formation of tetrameric hydroxocomplex:

$[Zr(H_2O)_8]^{4+} + 2H_2O \leftrightarrow [Zr(H_2O)_6(OH)_2]^{2+} + 2H_3O^+$
$4[Zr(H_2O)_6(OH)_2]^{2+} \leftrightarrow [Zr_4(H_2O)_{16}(OH)_8]^{8+} + 8H_2O$

During subsequent hydrolysis of the tetramers and condensation of products, polynuclear hydroxocomplexes and colloid particles of zirconium hydroxide with the composition $[Zr_4O_{8-x}(OH)_{2x} \cdot yH_2O]_n$ are formed.

An important synthesis parameters affecting the structural characteristics of the hydroxide precursor and the dioxide formed from it is the acidity of the environment during the formation of gel. It was established [29, 30] that during the deposition in the alkaline medium under strictly controllable constant pH 9.5 the fraction of mesopores in the resulting xerogel is higher in comparison with the microporous xerogel obtained according to the conventional procedure with the addition of precipitating agent to the solution of zirconyl salt, that is, under the variable pH (from 0.6 to 9.5). After annealing, these samples demonstrate higher specific surface and porosity.

The resulting xerogel $ZrO_x(OH)_{4-2x}$ is a highly dispersed X-ray amorphous substance with the specific surface from 350 to 420 m^2/g with the statistical mean size of globule particles about 3−4 nm. During annealing, the crystallization of the oxide starts at a temperature about 350 °C in two forms: stable monoclinic (M) and metastable tetragonal (T). With temperature rise $T-ZrO_2$ undergoes phase transition at 600 °C; its fraction is about 10 %.

The introduction of promoter cations into the xerogel leads to an increase in the fraction of T-form of ZrO_2 in the product of anneal-

ing; the higher is the concentration of cations, the higher is the extent of this increase [31, 32] (Fig. 1). At the same time, with an increase in the concentration of promoters, the rate of the formation of crystalline phases decreases. For instance, after annealing of the xerogel promoted with Mn^{3+} cations (5 at. %) at 350 °C for 3 h, the oxide phase is X-ray amorphous. The crystalline product containing mainly the T-form of ZrO_2 is formed when temperature is increased to 400 °C. However, with the indicated atomic fraction of the promoter (5 at. %), the T-form is low-stable, and under further temperature rise it undergoes phase transition into the stable M-form (see Fig. 1). An increase in the atomic fraction of M^{3+} cations to 10 % increases the thermal stability of the T-form.

For the system $Al^{3+}/Zr600$ we observed the following regularities of the changes of phase composition depending on the atomic fraction of Al^{3+} [30−32]: at 0.5−1.5 % the prevailing form is M; with an increase in the fraction of aluminium, the amounts of the T-form increases. At the atomic fraction of Al 5−10 %, both metastable modifications of ZrO_2 are formed (including the cubic form) in which the Al^{3+} cations are likely to be present as a solid solution. With an increase in the atomic fraction of Al^{3+} cations, crystallization process slows down; the oxide system $25Al^{3+}/Zr$ conserves the X-ray amorphous state at 600 °C for a long time (not less than 9 h).

Measured crystallite size of ZrO_2 depending on annealing temperature is shown in Fig. 2. The introduced cations brake the growth of crys-
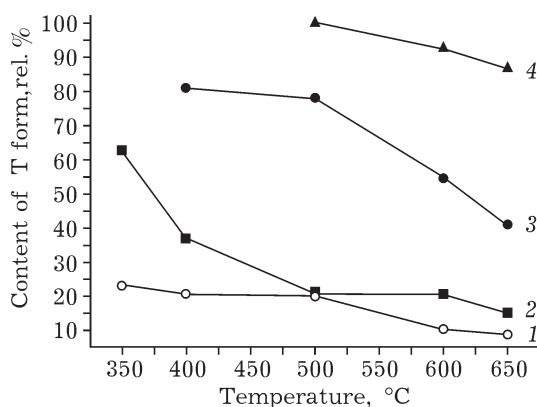

Fig. 1. Fraction of T-form of ZrO_2 depending on annealing temperature for the samples with the atomic fraction of manganese, %: 0 (1), 1.5 (2), 5 (3), 10 (4).
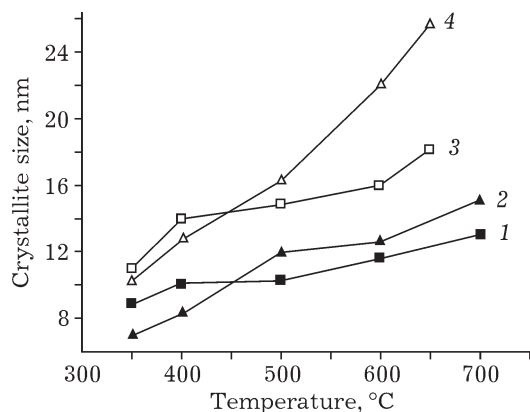
Fig. 2. Change of the size of T-form crystallites of ZrO_2 (1, 3) and M-forms (2, 4) depending on annealing temperature for non-promoted xerogel (3, 4) and the xerogel promoted with Mn^{2+} cations (1, 2).

tallites of both forms but the growth of the crystallites of T form is hindered to a higher extent. After annealing at 700 °C, their size is 13−14 nm, which is much smaller than the critical value for the phase transition (22−27 nm [33]). An increase in the atomic fraction of promoting cations helps the development of specific surface of the oxide system (Fig. 3).

Similar regularities take place also in other Me^{3+}/Zr systems with cations Sc^{3+}, Y^{3+} [32] and generally agree with the existing notions that the stabilization of high-temperature forms of ZrO_2 (tetragonal and cubic) by cation (and anion) promoters at thermodynamically unfavour-
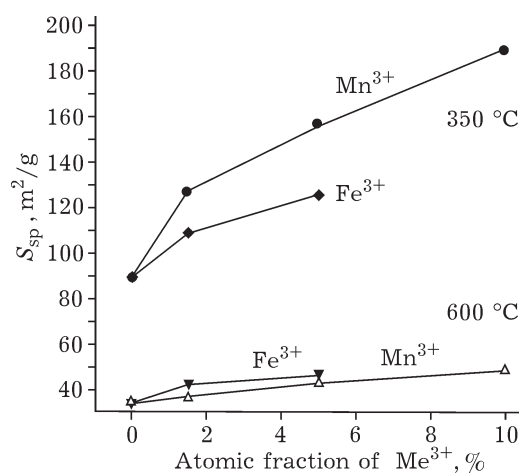
able temperatures is due to hindrance for the growth of crystallites [15, 34−36]. Nanosized crystallites of highly symmetric high-temperature forms, unlike for macrocrystalline forms, are thermodynamically more favourable than the M form due to lower surface energy [33, 34].

Many authors suppose that the formation of the solid solutions of promoter cations in the lattice of the tetragonal ZrO_2 is one of the factors affecting the rate of crystallite growth and the formation of the corresponding phases [15]. The dependence of the fraction of T-form of ZrO_2 formed at 600 °C on the difference between the radii of Zr^{4+} and Me^{3+} cations (atomic fraction 1.5 %) which determines the probability of the formation of solid solutions is shown in Fig. 4. One can see that the larger is the difference between the radii of promoting cations and Zr^{4+} (to one side or another), the stronger is stabilizing action. The most efficient stabilizers of highly symmetric phases are cations Al^{3+} and Y^{3+}, with the size substantially differing from the size of Zr^{4+} cations. The radius of Sc^{3+} cations is 0.83 nm, which is close to the radius of Zr^{4+} cations (0.87 nm), so this is to favour the formation of solid solution. However, it was established that Sc^{3+} cations have a weak effect on the phase composition.

The state and character of the distribution of cations in the oxide phase ZrO_2 were studied [32, 37, 38]. According to the data of XPES [38], in the X-ray amorphous non-crystallized
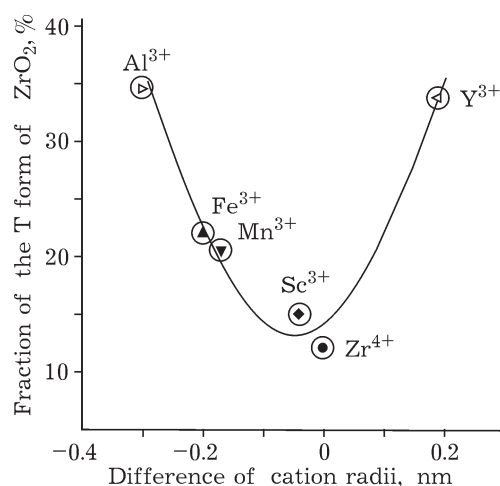

Fig. 3. Change of the specific surface (S_{sp}) of the oxide system depending on the concentration of Fe^{3+} and Mn^{3+} in ZrO_2 after annealing at 350 and 600 °C.

Fig. 4. Dependence of the fraction of T-form of ZrO_2 in the oxide product on the difference of the radii of promoter cations and Zr^{4+}. The atomic fraction of cations is 1.5 %, annealing temperature 600 °C.

sample $5Mn^{3+}/Zr350$ obtained by annealing at relatively low temperature (350 °C) manganese is present on the surface mainly as Mn^{3+} with the Mn/Zr ratio practically corresponding to the volume ratio. The formation of the crystalline T-phase of ZrO_2 at higher temperature (600 °C) is accompanied by partial migration of Mn^{3+} cations into the surface layer where their concentration increases by a factor of 2 in comparison with their concentration in the volume (0.045 to 0.091).

Similar concentrating of cation promoters in the surface layers was observed by means of secondary ion mass spectrometry (SIMS) for the systems with cations Y^{3+} and Fe^{3+} [32, 37] (Fig. 5). Saturation of the surface with Fe^{3+} cations is achieved when their atomic fraction in the sample is 10 %. In all the indicated cases, no formation of the own phases of promoter oxides was detected by means of XPA. Taking into account the data obtained, it may be assumed that the stabilization of the T form of ZrO_2 can be connected with the localization of promoting cations on the surface; they may decrease the surface energy and/or create barriers hindering the surface diffusion of atoms and the growth of crystallites.
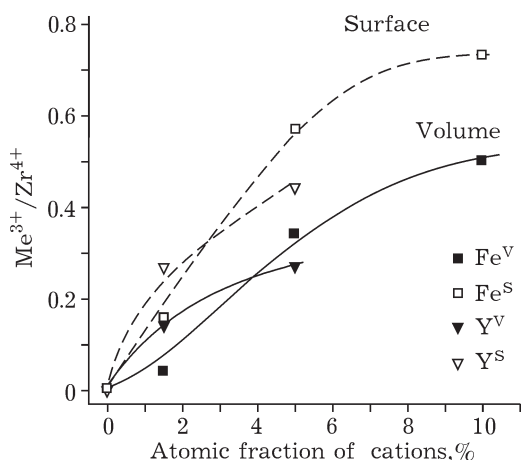
FORMATION OF ANION-MODIFIED ZrO_2 WITH TRIVALENT CATIONS

SO_4^{2-}/ZrO_2 system

The introduction of sulphate groups into the xerogel promotes the crystallization of the T-form of ZrO_2 during annealing. One can see that its amount at 600 °C is in the extremal dependence on the concentration of anion (Fig. 6) [12, 29, 30]. The maximal amount of T-form was obtained for the mass fraction of SO_4^{2-} groups 4–6 %, which is close to the saturation of the monolayer on ZrO_2 surface (6 mass % SO_4^{2-}). The M-form is present in these samples only as insignificant admixture. It must be stressed that the change in the direction of crystallization occurs jumpwise: the prevailing formation of T-form starts at the mass fraction of SO_4^{2-} groups 2.5–3.0 %. As the concentration of SO_4^{2-} groups increases (>6 %), the amount of T-form decreases gradually, and a part of the oxide phase conserves the X-ray amorphous state. For the high mass fraction of sulphate groups (>17–19 %), crystal phases are not formed at all under these annealing conditions. The average size of the crystallites of T-form decreases continuously from 15–18 to 10–11 nm with an increase in the mass fraction of SO_4^{2-} groups to 16.2 %.

The evolution of ZrO_2 texture with variations of the amount of introduced sulphate groups was studied by means of low-tempera-

Fig. 5. Changes of the atomic ratio Me^{3+}/Zr^{4+} in the volume (unbroken lines) and in the surface layer (broken line) of ZrO_2 depending on the atomic fraction of Fe^{3+} and Y^{3+} cations.
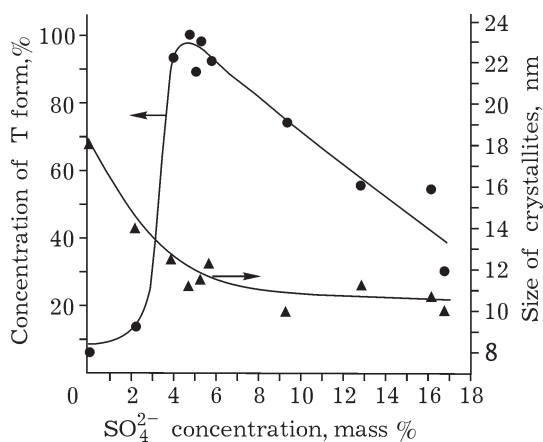

Fig. 6. Effect of sulphate groups on the concentration and size of crystallites of the T-form of ZrO_2 after annealing of sulphatized xerogel at 600 °C.
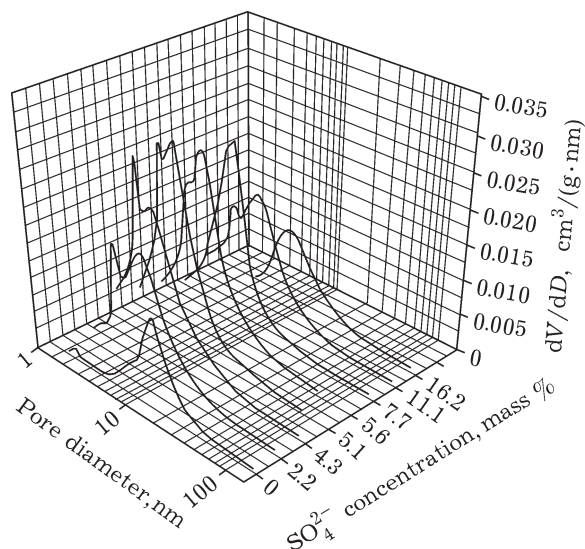
Fig. 7. Distribution of pore volume over sizes in ZrO_2 samples with different mass concentration of SO_4^{2-}.

over size is formed. The maximal specific surface (100–110 m^2/g), minimal average particle size (9.0–10.9 nm) and pore size (5.5–6.5 nm) were obtained when the monolayer coating of the surface was achieved (Fig. 8). The volumes of mesopores are close for different samples (within the range 0.19–0.23 cm^3/g), and the volume of micropores does not exceed 0.01 cm^3/g. After annealing at 500 °C, the specific surface increases to 150 m^2/g, while after annealing at 700 °C it decreases to 70–80 m^2/g.

$SO_4^{2-}/Me^{3+}/ZrO_2$ system

The phase composition of cation-promoted 4–7 $SO_4^{2-}/Me^{3+}/Zr$ sulphatized system, independently of cation concentration, is represented by one nanosized T-form of ZrO_2. At the same time, for corresponding non-sulphatized systems with the atomic fraction of promoter 10 % and more, the cubic form may also be observed. So, the anion promoter has the decisive effect on the formation of the type of crystal structure. An increase in the atomic fraction of cations in the sample hinders its crystallization. For example, the sample with 15 % Al^{3+} after annealing at 600 °C is X-ray amorphous.

An increase in the concentration of cations in sulphatized system leads to the development of the specific surface. For the atomic fraction of Al^{3+} equal to 15 %, it reaches 137 m^2/g (Fig. 9). At the same time, the average diameter

ture nitrogen adsorption. The curves of pore size distribution for various sulphatized samples $SO_4^{2-}/Zr600$ after annealing at 600 °C for 3 h are shown in Fig. 7. One can see that continuous rearrangement of the mesoporous structure occurs with an increase in anion concentration. The samples with the mass fraction of SO_4^{2-} less than 11 % have a bimodal pore size distribution; the position of the maximum for large pores varies within the range 4 to 8 nm depending on anion concentration, while the size of small pores remains 3.0–4.0 nm. With the mass fraction of SO_4^{2-} above 11 %, relatively broad polymodal distribution of pore volume

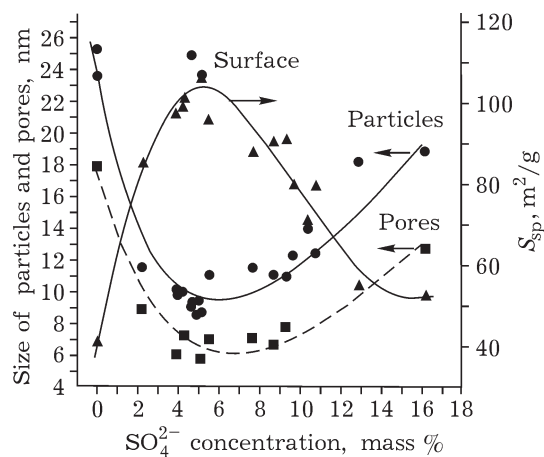Fig. 8. Specific surface, mean size of particles and pores in ZrO_2 depending on the mass concentration of SO_4^{2-}.
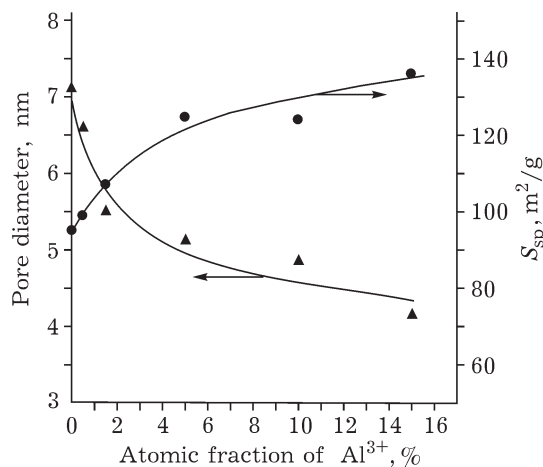

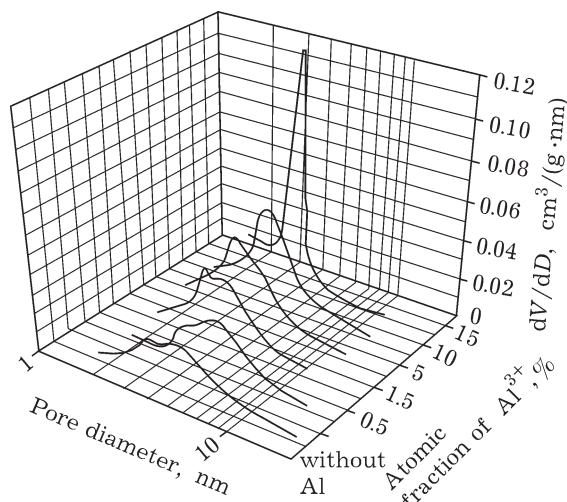Fig. 9. Changes of specific surface, mean pore size of sulphatized ZrO_2 depending on the atomic fraction of Al^{3+}.

Fig. 10. Distribution of pore volume over pore size for sulphatized ZrO_2 with different atomic fractions of Al^{3+}.

of pores decreases (from 7.0 to 4.0 nm), the distribution of pore volume over size becomes more narrow. For 15 at. % Al^{3+}, a sharp transition into the well crystallized porous structure with a narrow monomodal distribution of pore volume over size with the maximum at 3.5 nm occurs in the oxide matrix (Fig. 10).

WO_4^{2-}/ZrO_2 system

Crystallization of zirconium dioxide modified with tungstates anions occurs at higher temperature. Thus, WO_4^{2-} anions exhibit stronger braking action on the crystallization process than SO_4^{2-} anions do. The amount of the T-form after annealing at 700 °C increases
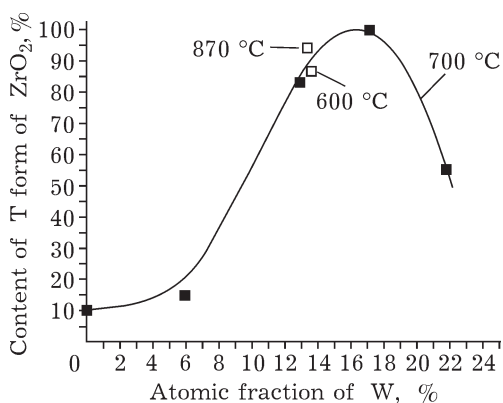

Fig. 11. Changes of the content of T-form of ZrO_2 depending on the atomic fraction of tungsten in the samples annealed at different temperatures.

sharply in the sample with the atomic fraction of tungsten 12.9 % (Fig. 11). Calculated for the surface concentration, this corresponds to 8 at. W/nm^2, which is close to the theoretically calculated monolayer value (6.3 at. W/nm^2). The X-ray diffraction patterns of the samples with tungstates anion content exceeding the monolayer coating exhibit weak reflections of the own phases of tungsten oxide (monoclinic modification at 700 °C and tetragonal modification at 870 °C). The formed nanosized T-form is thermally stable till the temperature of 870 °C.

Depending on the atomic fraction of tungstates anions, the specific surface of WO_4^{2-}/ZrO_2 samples after annealing at 700 °C varies from 69 to 51 m^2/g. The average size of particles calculated from specific surface is within the range 14−20 nm, that is, only slightly differs from the size of crystallites of T-form (130−16 nm).

Acid properties of sulphatized ZrO_2

The acid properties were characterized on the basis of IR spectral data, including the spectral of adsorbed carbon monoxide. Taking into account the known data [15, 39] on the assignment of absorption bands, two major structural types of sulphate groups depending on their concentration were established. For low concentrations corresponding to the coating of 1/3 of monolayer, isolated tridentate sulphate groups with the frequency of stretching vibrations of S=O groups at 1382 cm^{-1} are present on the surface of deeply anhydrous ZrO_2. With an increase in the concentration, they are transformed into binuclear pyrosulphate bidentate groups $S_2O_7^{2-}$ with higher frequency of vibrations (1400 cm^{-1} and higher) [30].

The proton and aprotic acidity was characterized on the basis of IR spectra of OH groups and adsorbed CO molecules depending on the concentration of SO_4^{2-} groups and promoter cations [30, 40]. In the samples containing no cations, with the low mass fraction of SO_4^{2-}, only weak Brønsted/Lewis acid centres are present (LAC and BAC, respectively). With an increase in the concentration of SO_4^{2-}, strong BAC are formed; their strength and surface concentration remain almost unchanged till the mass fraction of SO_4^{2-} equal to 16.2 % (Table 1). At the same time, the amount of strong and me-

TABLE 1

Concentration and force of Brønsted/Lewis acid centres (LAC and BAC, respectively) in SO_4^{2-}/ZrO_2

Concentration of SO_4^{2-}, mass %	LAC (2198−2005 cm^{-1}), μmol/m^2	BAC	
		Concentration, μmol/m^2	Strength of centres, kJ/mol
2.4	0	2.0	1330 (weak)
5.4	1.0	0.9	1240 (medium)
6.4	1.6	0.9	1200 (strong)
			1250 (medium)
7.3	2.5	0.9	1205 (strong)
			1240 (medium)
16.2	5.3	0.8	1205 (strong)
			1250 (medium)

dium LAC (νCO 2198−2005 cm^{-1}) and their surface concentration increase (to 5.3 μmol/m^2).

Cations Al^{3+} and Fe^{3+} affect the characteristics of both Lewis and Brønsted acidity. For instance, with the addition of 1.5 at. % Al^{3+}, the bands νCO at 2211−2213 cm^{-1} are observed in the IR spectra of adsorbed CO, which points to the appearance of very strong LAC. Depending on the amount of introduced cations, the concentrations of LAC (medium and strong) and BAC (with approximately the same strength) pass through the maxima at the atomic fraction of Al^{3+} 5.0−10.0 and 1.5−5.0 %, respectively (Fig. 12). In general, the cation-promoted samples of sulphatized ZrO$_2$ are characterized by the presence of strong LAC and BAC; the concentration of LAC for the majority of samples is 2−3 times higher than that of BAC.
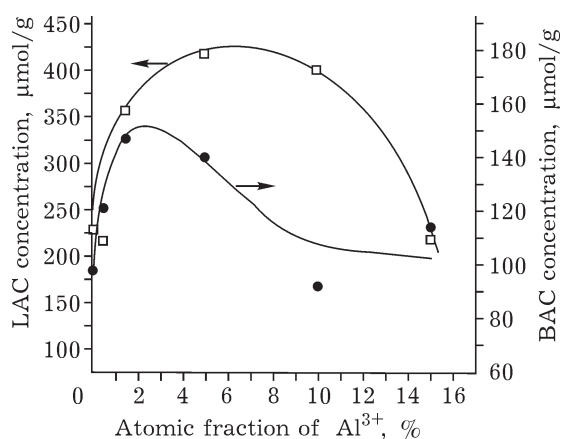

Fig. 12. Change of the acidity of sulphatized ZrO$_2$ depending on the atomic fraction of Al^{3+}.

CATALYTIC ACTIVITY OF ANION-MODIFIED FORMS OF ZrO$_2$ IN THE REACTIONS OF ALKANE ISOMERISATION

Catalysts prepared on the basis of zirconium dioxide modified with sulphate and tungstates groups were tested in the set-up with flow reactor carrying out the processes of isomerisation of individual alkanes from C$_4$ to C$_7$ and the pentane-hexane petroleum fraction.

Sulphatized ZrO$_2$

The dependence of the activity of catalysts on the concentration of SO_4^{2-} groups during isomerisation of n-butane has a complicated character. For the low mass concentration of sulphate groups, their catalytic activity is low. A sharp increase in their activity occurs with the achievement of the concentration approaching the monolayer coating (more than 70−80 %) [30]. Promotion of sulphatized dioxide with cations Fe^{3+}, Mn^{2+}, Al^{3+} leads to an increase in the catalytic activity, isomerisation of n-butane proceeds efficiently in the low-temperature region (145−175 °C) [12]. The highest activity is exhibited by the samples promoted with aluminium, with the atomic concentration of Al^{3+} 1.5−5.0 %. The activity of the samples decreases if a larger amount of aluminium is added.

The comparison of the data on catalytic activity with the characteristics of acidity showed [30, 40] that the most active catalysts contain increased concentration of both LAC and BAC, the number of LAC being 2−4 times larger than the number of BAC. There is no connection be-
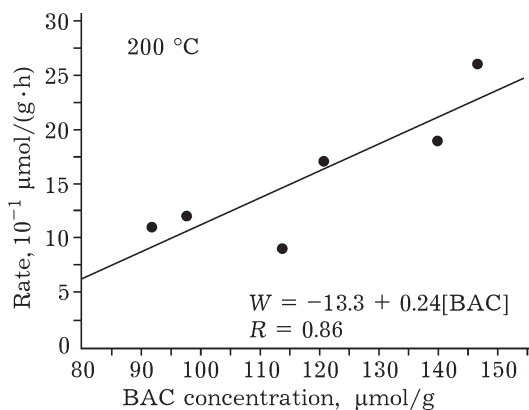
$$W = -13.3 + 0.24[\text{BAC}]$$
$$R = 0.86$$

Fig. 13. Dependence of the initial rate of *n*-butane isomerisation on the catalyst $SO_4^{2-}/Al^{3+}/ZrO_2$ on the concentration of BAC.

tween the reaction rate and LAC content and their force. At the same time, a linear correlation of reaction rate and total concentration of medium and strong BAC is observed (Fig. 13). Taking into account the fact that all the most active samples contain a large number of strong LAC in addition to BAC, we assumed that the catalytic action can be connected with the presence of both types of centres, with the leading role of BAC.

It should be noted that sulphatized ZrO_2 rapidly loses its activity due to the deposition of coke-like products blocking up the acid centres. To prevent the formation of coking products, platinum was introduced into the catalysts. Isomerisation of *n*-butane under the atmospheric pressure of hydrogen proceeds on platinised catalysts in the quasi-steady mode. On the catalyst optimized for composition and preparation conditions, promoted with Al^{3+} cations with platinum in the amount of 0.4 %, isomerisation of *n*-butane proceeds in the low-temperature region at 145−175 °C with almost equilibrium yields of isobutene, with the yield of C_1-C_3 alkanes not more than 6.9 mass % [12, 41, 42].

The parameters of isomerisation of *n*-pentane on platinised catalyst containing 2.5 at. % Al and 7.3 at. % SO_4^{2-} are listed in Table 2. At a temperature of 150 °C and volume flow rate of pentane admission 2.1 h^{-1}, the degree of conversion is 77.3 %; the yield of isopentane is 75.2 %, with the selectivity with respect to isopentane 97.3 %, with respect to the sum of *iso*-C_4-C_5 almost 91 % [12].

Isomerisation of the pentane-hexane fraction on platinised sulphatized ZrO_2 promoted

TABLE 2

Parameters of isomerisation of *n*-pentane on platinised $SO_4^{2-}/Al^{3+}/ZrO_2$. catalysts
Pressure 1 MPa, 150 °C, hydrogen/*n*-pentane = 90 : 10

V, h^{-1}	Degree of *n*-pentane conversion, mass %	Yield of iso-pentane, %	Selectivity, mass %	
			iso-C_5	*iso*-C_4-C_5
1.3	77.9	73.2	94.0	97.2
2.1	77.3	75.2	97.3	98.7

TABLE 3

Parameters of isomerisation of the pentane-hexane fraction of Achinsk PPP on sulphatized ZrO_2 promoted with Al^{3+} cations

Conditions		Mass fraction, %		Octane
T, °C	V, h^{-1}	of isopentane in C_5 fraction	of dimethylbutanes in C_6 fraction	number*
Initial		37.4	0.04	72.2
150	1.5	61.3	13.8	80.9
175	0.8	65.0	44.6	83.9
	1.5	70.4	37.5	84.4
200	1.5	76.7	31.4	84.5

    * Research method.

TABLE 4

Parameters of catalytic activity of Pt/ WO_4^{2-} /ZrO$_2$ catalysts after 30 min of n-heptane isomerisation. Temperature 170 °C, 1 h^{-1}, hydrogen/n-C$_7$ = 3 : 1 (mol.)

Molar fraction of anions, %	Degree of n-heptane conversion, mass %	Yield of heptane, mass %	Selectivity with respect to isoheptanes, mass %
8.0	4.6	3.7	82.0
12.9	60.0	50.1	82.1
17.6	77.6	63.9	82.3
21.9	44.3	38.9	87.7

with aluminium cations proceeds efficiently in the low-temperature region with the yield of isomerisate 96−99 %. At 175 °C and the rate of raw material admission 0.8−1.5 h^{-1}, the concentration of iso-paraffins in the isomerisation product was 73−76 %, the octane number increased by 11.2−12.2 items (up to 83.9−84.4) due to an increase in the concentration of isopentane (from 37.4 to 65−70.4 % in the pentane fraction) and dimethylbutanes (from 0.04 to 37.5−44.6 % in the hexane fraction) (Table 3). It is important to stress that at the optimal temperature, 175 °C, and below it, gas formation did not exceed 3.5 mass %.

Similarly to other known industrial catalysts, sulphatized catalyst is of low efficiency for isomerisation of C$_{7+}$ alkanes due to low selectivity and low stability against deactivation by coke deposits. On sulphatized zirconium dioxide promoted with aluminium cations, n-heptane underwent mainly cracking with the formation of isobutene, isopentane and propane; selectivity with respect to isoheptanes did not exceed 30 %.

The catalytic properties of zirconium dioxide modified with WO_4^{2-} anions are substantially different from those of sulphatized substance. At 200 °C, the degree of n-hexane transformation on the catalysts with the atomic concentration of tungsten 12.9 to 21.9 % reached 80 %, with the selectivity with respect to iso-hexanes 99 %. The degree of n-heptane conversion under the same conditions increased to 88−95 %; the selectivity for iso-heptanes was about 46 mass %. A decrease in reaction temperature to 170 °C resulted in an increase in the selectivity and yield of iso-heptanes. At the optimal concentration of WO_4^{2-} anions in the catalyst (17.6 at. %), the yield of iso-heptanes was 63.9 %, with the selectivity of 82.3 (Table 4).

CONCLUSIONS

The established regularities of the formation of catalytic systems based on zirconium dioxide and the results obtained for sulphatized catalysts give the grounds for the development of the technology of production of industrial catalyst and replacement of the chlorine catalyst of isomerisation of the heptane-hexane fraction applied at the Achinsk Petroleum Processing Plant. The process with the use of sulphate zirconium catalyst is ecologically safe because it excludes the formation of hazardous solid, gaseous and liquid chemical wastes, is devoid of shortcomings connected with the necessity of deep purification of raw material, increased corrosion of equipment, dosing of chlorine-containing compounds in the raw material, purification of "exhaust gas from hydrogen chloride, and utilization of worked out alkaline solutions.

Catalytic systems modified with tungstate anions are of substantial interest for the development of the new isomerisation process in which the heptane fraction may be involved as the raw material, after its extraction from the composition of raw material of reforming. On the one hand, this allows one to sharply decrease the formation of benzene during reforming because it is the heptane fraction that acts as the major benzene-forming component. On the other hand, processing of the alkanes of heptane fraction (with very low octane number) in isomerisation process will allow one to obtain the high octane mixing component. During compounding with the product of reforming, it is possible to manufacture high octane gasoline with low benzene content.

In addition, the development of catalysts for the isomerisation of long-chain alkanes of

diesel fractions is also of interest for obtaining the components of diesel fuel with high cloud point and freezing temperature and with comparatively high cetane number.

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REFERENCES

1 Kontorovich A. E., *Vestn. Ros. Akademii Nauk*, 72, 3 (2002) 206.

2 Kontorovich A. E., Kashirtsev V. A., Korzhubaev A. G., Kurchikov A. R., Likholobov V. A., Safronov A. F., VI Mezhdunar. Konf. "Khimiya Nefti i Gaza" (Proceedings), Tomsk, 2006, pp. 5–7.

3 Kontorovich A. E., *Min. Resursy Rossii. Ekonomika i Upravleniye*, 1 (2009) 12.

4 Kontorovich A. E., Korzhubaev A. G., Filimonova I. V., Eder L. V., *Neft Rossii*, 6 (2008) 22.

5 Serdyuk S. S. (Ed.), Mineralnye Resursy Krasnoyarskogo Kraya: Book 1, Krasnoyarsk, 2002.

6 Sibisov B. V., Ekhanin A. G., *Prirod. Res. Krasnoyar. Kraya*, 4 (2009) 30.

7 Filippov Yu. A., *Ibid.,* 5 (2010) 26.

8 Kuznetsov P. N., Kuznetsova L. I., Tverdokhlebov V. P., *Zh. Sib. Federal. Un-ta. Teckhn. i Tekhnol.*, 2 (2008) 168.

9 Borutskiy P. N., Podkletova N. M., *Kataliz v Prom-sti*, 2 (2002) 86.

10 Kaminskiy E. F., Khavkin V. A., Zharkov B. B., Shakun A. N., *Tekhnol Nefti Gaza*, 38, 1 (2005) 3.

11 Dyupra K., Minkkinen A., *Neftepererab. Neftekhim.*, 10 (1999) 3.

12 Kuznetsov P. N., Kuznetsova L. I., Tverdokhlebov V. P., *Tekhnol Nefti Gaza*, 38, 3 (2005) 20.

13 Zhorov Yu. M., Izomerizatsiya Uglevodorov, Khimiya, Moscow, 1983.

14 Anderson G. C., Rosin R. R., Stine M. A., New Solutions for Light Paraffin Isomerization, UOP LLC, Des Planes, Illinois USA, 2004.

15 Ivanov A. V., Kustov L. M., *Ros. Khim. Zh.*, XLIV (2000) 21.

16 Lavrenov A. V., Basova I. A., Kazakov M. O., Finevich V. P., Velskaya O. B., Buluchevskiy E. A., Duplyakin V. K., *Ibid.*, LI, 4 (2007) 75.

17 Yadav G. D., Nair J. J., *Microporous and Mesoporous Mater.*, 33 (1999) 1.

18 Arata K., *Appl. Catal. A: Gen.*, 146 (1996) 3.

19 Kuznetsov P. N., Kuznetsova L. I., Tverdokhlebov V. P., Sannikov A. L., *Khim. Tekhnol.*, 2 (2005) 7.

20 Karakchiev L. G., Avvakumov E. G., Vinokurova O. B., Gusev A. A., Lyakhov N. Z., *Zh. Neorg. Khim.*, 49, 5 (2004) 820.

21 Karagedov G. K., Shztskaya S. S., Lyakhov N. Z., *Chem. Sust. Dev.*, 14 (2006) 369.
URL: http://www.sibran.ru/English/csde.htm

22 Suresh A., Mayo M. J., Porter W. D., *J. Am. Ceram. Soc.*, 86 (2003) 360 .

23 Kuznetsov P. N., Kuznetsova L. I., Zhyzhaev A. M., Kovalchuk V. I., Sannikov A. L., Boldyrev V. V. , *Appl. Catal. A: Gen.*, 298 (2006) 254.

24 Grau J. M., Yori J. C., Parera J. M., *Appl. Catal. A: Gen.*, 213 (2001) 247.

25 Larsen G., Lotero E., Raghavan S., Parra R., Querini C., *Appl. Catal. A: Gen.*, 139 (1996) 201.

26 Kuba S., Lukinskas P., *J. Catal.*, 216 (2003) 353.

27 Scheithauer M., Jentoft R. E., Gates B. C., Knozinger H., *J. Catal.*, 191 (2000) 271.

28 Shuguang Zhang, Yulong Zhang, John W. Tierney, Irving Wender, *Fuel Proc. Technol.*, 69, 1 (2001) 59.

29 Kuznetsov P. N., Kuznetsova L. I., Zhizhaev A. M., Obukhov Ya. V., Kovalchuk V. I., Tverdokhlebov V. P., Sannikov A. L., *Khim. Tekhnol.*, 1 (2004) 2.

30 Sannikov A. L., Zakonomernosti Formirovaniya Katalizatorov na Osnove Sulfatirovannogo Dioksida Tsirkoniya i Ikh Aktivnost v Izomerizatsii Lyegkikh Alkanov (Candidate's Dissertation in Technical Sciences), Krasnoyarsk, 2007.

31 Kuznetsova L. I., Kolesnikova S. M., Obukhov Ya. V., Yatsinova M. A., Kuznetsov P. N., Zhizhaev A. M., Ivanov V. P., V Ros. Konf. "Nauchnye Osnovy Prigotovleniya i Tekhnologii Katalizatorov" i IV Ros. Konf. "Problemy Dezaktivatsii Katalizatorov" (Thesises), Omsk, 2004, pp. 252–253.

32 Kuznetsov P. N., Kuznetsova L. I., Zhizhaev A. M., in: Fundamentalnye Osnovy Mekhanokhimicheskoy Aktivatsii, Mekhanosinteza i Mekhanokhimicheskikh Tekhnologiy", in E. G. Avvakumov (Ed.), Izd-vo SO RAN, Novosibirsk, 2009, pp. 68–86.

33 Garvie R. C., *J. Phys. Chem.*, 69, 4 (1965) 1238.

34 Gopalan R., Chang C.-H., Lin Y. S., *J. Mater. Sci.*, 30 (1995) 3075.

35 Mercera P. D. L., Ommen V. J. G, Doesburgh E. B. M., *Appl. Catal. A: Gen.*, 57 (1990) 127.

36 Mayo M. J., Suresh A., Porter W. D., *Rev. Adv. Mater. Sci.*, 5, 2 (2003) 100.

37 Kuznetsov P. N., Kuznetsova L. I., Ivanov V. P., Obukhov Ya. V., Kolesnikova S. M., X APAM Topical Sem. and III Conf. "Materials of Siberia. Nanoscience and Technology" (Proceedings), Novosibirsk, 2003, pp. 175–176.

38 Kuznetsov P. N., Kazbanova A. V., Kuznetsova L. I., Mikhlin Yu. L., VII Mezhdunar. Konf. "Khimiya Nefti i Gaza" (Proceedings), Tomsk, 2009, pp. 677–679.

39 Song X., *Catal. Rev. – Sci. and Eng.*, 38 (1996) 329.

40 Kuznetsov P. N., Paukshtis E. A., Kuznetsova L. I., VIII Int. Conf. "Mechanisms of Catalytic Reactions" (Book of Abstracts), Novosibirsk, 2009, vol. II, p. 66.

41 Kuznetsov P. N., Kuznetsova L. I., Tverdokhlebov V. P., Sannikov A. L., I Vseros. Konf. "Khimiya dlya Avtomobilnogo Transporta" (Proceedings), Novosibirsk, 2004, pp. 250–252.

42 Kuznetsov P. N., Kuznetsova L. I., Tverdokhlebov V. P., Sannikov A. L., Obukhov Ya. V., *Izv. Vuzov. Khim. i Khim. Tekhnol.*, 48, 8 (2005) 91.