Major Factors Determining the Activity of Bifunctional Environmentally Safe Catalysts for Hexane Skeleton Isomerisation

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Abstract

A series of environmentally safe highly efficient bifunctional catalysts for hexane skeleton isomerisation was studied. It was demonstrated that the activity of the catalysts is determined mainly by acidic properties. Reaction rate values and selectivity level with respect to target products were determined depending on the concentration of Lewis acid, whereas the content of Brönsted acidic centers was maintained approximately constant. The data obtained could serve as a basis for the development of Russian highly efficient catalysts for light gasoline skeleton isomerisation those could be used for obtaining branched isomers for C_5-C_8 hydrocarbons with the octane number ranging within 92–105.

Key words: bifunctional catalysts, skeleton isomerisation, hexane, sulphated zirconium dioxide

INTRODUCTION

The process of alkane skeleton isomerisation is considered to be the most promising way to increase the octane number of motor fuels: the isomerisation of light gasoline allows obtaining branched isomers with octane number ranging within 92–105 from linear C_5-C_8 hydrocarbons with a low octane number (0–62). For Russia, the contribution of isomerisation processes in different processes increasing the octane number amounts to only 0.2 %, whereas for the USA this value is equal to 5.6 %. In connection with restricting the content of aromatic compounds in the gasoline, the fraction of isomerisation products in commercial fuels in the developed countries are to be increased up to 15 %. The most promising technologies for the isomerisation of paraffins are presented by the developments of the companies such as UOP (the USA) and IFP (France), wherein organochlorine compounds are used [1]. How-

ever, their entering the atmosphere results in the formation of dioxins, the substances those are 10^5 times more toxic than hydrogen cyanide being able of accumulation to cause the formation of cancerous tumours [2].

Searching for environmentally safe ways to carry out the isomerisation of light gasoline, without the use of halogens, is carried out in several directions. Catalysts based on metal oxides treated with various acidic groups such as sulphates [3–9], tungstates [10, 11], as well as catalysts based on the salts of heteropoly acids [12–16] are under wide investigation. It is known that the activity of catalysts based on metal oxides is to a considerable extent dependent on the conditions of preparation. For example, the activity of catalysts based on sulphated zirconia that exhibit the same structure and equal the concentration of the sulphate groups on the surface could be different within an order of magnitude [17].

Nowadays, an issue remains open concerning what the parameters are critical for the

mentioned catalysts: the presence of Brønsted acidic centres (BAC), Lewis acidic centres (LAC), or the presence of both types of the centres on the catalyst surface in the amounts required [18−21]? Recently, a number of authors consider the LAC to participate in the reaction mechanism of skeleton alkane isomerisation [22−24].

The aim of this work consisted in revealing the basic parameters those determine the activity of bifunctional catalysts for hexane skeleton isomerisation.

EXPERIMENTAL

Preparation of catalysts

1 % Pt/WO$_x$/ZrO$_2$. The catalyst was prepared by means of applying the tungsten and chloroplatinic acid according to water-absorbing capacity onto zirconium hydroxide precipitated by ammonia at pH 10. After deposition the sample was dried and calcined in atmospheric air at 700 °C during 3 h.

1 % Pt/SO$_4$/ZrO$_2$. The catalyst was prepared by means of applying sulphuric acid or sulphuric acid salts according to water-absorbing capacity onto zirconium hydroxide precipitated from nitrate solution by ammonia at pH 7.0−9.0. After the application the sample was dried and calcined at a temperature of 630−660 °C, and then it was treated by entering platinum according to water-absorbing capacity from the solution of chloroplatinic acid. The dried sample was then calcined at a temperature above 500 °C for 3 h.

1 % Pt/Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$ (x = 1.0, 1.5, 2.0, 2.5). The catalysts were prepared by means of precipitation method. A solution of cesium nitrate salt (0.1 mol/L) under continuous stirring was poured dropwise to a mixture of phosphotungstic heteropoly acid (0.1 mol/L) and chloroplatinic acid (0.1 mol/L) solutions, taken in the proportion required. The resulting suspension was stirred during 24 h, with further precipitate evaporation and calcination at 300 °C for 3 h.

The microscopic images of calcined samples were obtained using a TESLA Bs-350 field emission microscope.

Studying the catalysts by means of probe molecule IR spectroscopy technique

Pyridine adsorption. The acidic properties of catalysts were studied by means of adsorbed pyridine IR spectroscopy (absorption band at 1540 cm^{-1} for BAC and 1450 cm^{-1} LAC). The samples were pressed to obtain thin tablets containing 30−50 mg/cm^2 of a catalyst. Before the adsorption of pyridine the samples were evacuated in the IR cell at a temperature of 250 °C, then the temperature was lowered down to 150 °C, to adsorb pyridine at a saturation vapour pressure during 15 min. The excess pyridine was removed *via* the evacuation of the samples at 150 °C during 30 min. All the spectra were registered at a room temperature using a Shimadzu-8300 Fourier transform IR spectrometer within the wave number range of 400−6000 cm^{-1} with a resolution of 4 cm^{-1}.

The number of the centres of each type was calculated using the formula as it follows

$$N = A/(\rho A_0) \tag{1}$$

where A is the integral absorption of IR bands inherent in an adsorbate (in this case pyridine) onto Brønsted or Lewis acidic centers, cm^{-1}; ρ is the sample mass normalized to the area of a tablet, g/cm^2; A_0 is the molar absorption coefficient, equal to 3.0 for BAC and 3.5 for the LAC, cm/μmol [25]. The A_0 value was evaluated separately for BAC and LAC by means of the pyridine titration of model systems those exhibit only Brønsted acidity (heteropoly acids) or Lewis acidity (NaX) at certain temperature, when there is no adsorption of pyridine at the cell walls. The measurement technique for A_0 is described in [25, 26].

The strength of proton centers was characterized by PA value calculated from the expression

$$\text{PA} = [\log (3400 - \nu_{\text{NH}})] : 0.0023 - 51 \tag{2}$$

where PA is the proton abstraction energy, kJ/mol; 3400 is the position of the band inherent in unperturbed NH bond in pyridinium ion; ν_{NH} is the "centre of gravity" of pyridinium ion stretching band determined from the band contour within the range of 3400−1800 cm^{-1}; 0.0023 and 51 are empirical coefficients determined from the linear correlation between log (3400 − ν_{NH}) and PA for different Brønsted centres [25].

CO adsorption. In order to study acidic properties we used a technique of adsorbed CO IR spectroscopy (absorption band at 2150−2175 and 2185−2200 cm^{-1} for the BAC and LAC, respectively). The samples were pressed to form thin tablets containing 15−20 mg/cm^2 of a catalyst. The samples were reduced in a hydrogen atmosphere within an IR cell at 200 °C, and cooled then down to −173 °C to perform the procedure of dosed CO adsorption. IR spectra were registered using a Shimadzu 8300 Fourier transform IR spectrometer with the resolution of resolution 4 cm^{-1}.

The number of the centers of each type was calculated from the formula (1) where $A_0 = 0.8$ cm/μmol for the band at 2185−2200 cm^{-1} and 2.6 cm/μmol for the band at 2150−2175 cm^{-1}. The measurement technique for A_0 is described in [25].

Investigation of catalytic properties

The samples of the catalysts prepared by means of the above mentioned methods were tested in the reaction of hexane skeleton isomerisation using a flow-through reactor with a gas chromatographic analysis of gaseous and liquid products. The pressure in the reactor was equal to 3 bar, the temperature was varied within the range of 200−270 °C, the ratio of H$_2$/hexane = 2 : 1. Before the reaction, the catalyst was reduced in a mixture of hydrogen and helium at a temperature of 200 °C during 2 h.

RESULTS AND DISCUSSION

Bifunctional catalysts for the skeletal isomerisation of paraffinic hydrocarbons is typically characterized by realizing a bifunctional isomerisation mechanism where through the formation of intermediate compounds (olefins) occurs on the metal centers as a result of the dehydrogenation reaction, whereas the isomerisation of olefins occurs on acidic centers, where after the hydrogenation of the isomers obtained occurs again at the metal centre [27]. In order to determine the composition of the most active environmentally safe bifunctional catalysts we studied zirconium oxide treated with sulphates and tungstates, as well as cesium salts of phosphotungstic heteropoly acid with platinum additives. With the purpose of eliminat-
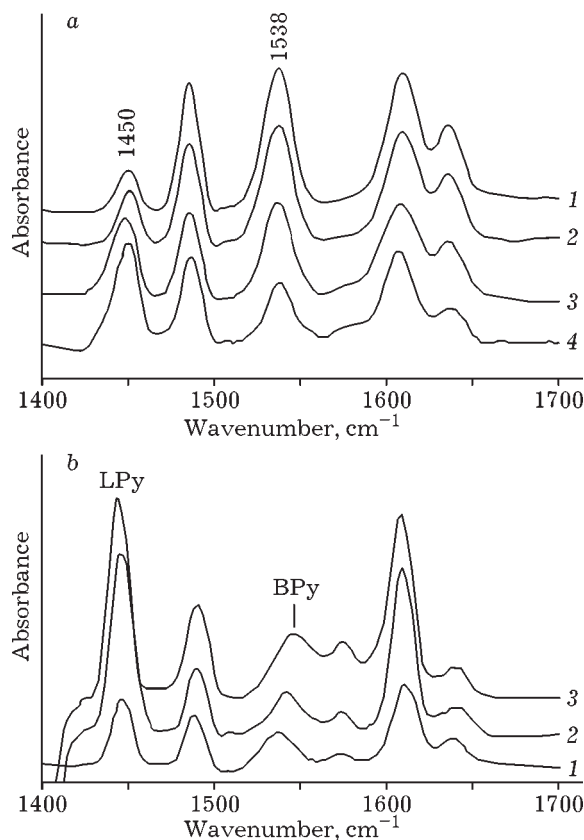

Fig. 1. IR spectra of pyridine adsorbed on the catalysts: a − Pt/Cs$_x$H$_{3-x}$PW$_{12}$O$_{40}$, $x = 1$ (*1*), 1.5 (*2*), 2 (*3*), 2.5 (*4*); b − Pt/WO$_x$/ZrO$_2$ (*1*), Pt/SO$_4$/ZrO$_2$ (*2*, *3*).

ing the influence of the metal centre of the catalyst activity, on the concentration of platinum was not varied.

The results of studying the acidic properties of bifunctional catalysts by means of adsorbed pyridine infrared spectroscopy technique are demonstrated in Figs. 1, 2 and Table 1. The content of the BAC and the LAC on the surface for the samples is 3 to 4 times differing from each other. The greatest amount of BAC (139−118 μmol/g) was registered for the samples Cs$_{1-2}$PW, whereas the maximum amount of LAC (105−110 μmol/g) was observed for the samples based on sulphated zirconia. The proton affinity (PA) presents a relative scale of BAC strength on the catalyst surface. Systems based on acidic cesium salt of phosphotungstic heteropoly acid exhibit much more stronger BAC as compared to SO$_4$/ZrO$_2$ and WO$_x$/ZrO$_2$ systems. The total Lewis acidity of the samples based on SO$_4$/ZrO$_2$ is in a good agreement with the results determined according to ad-
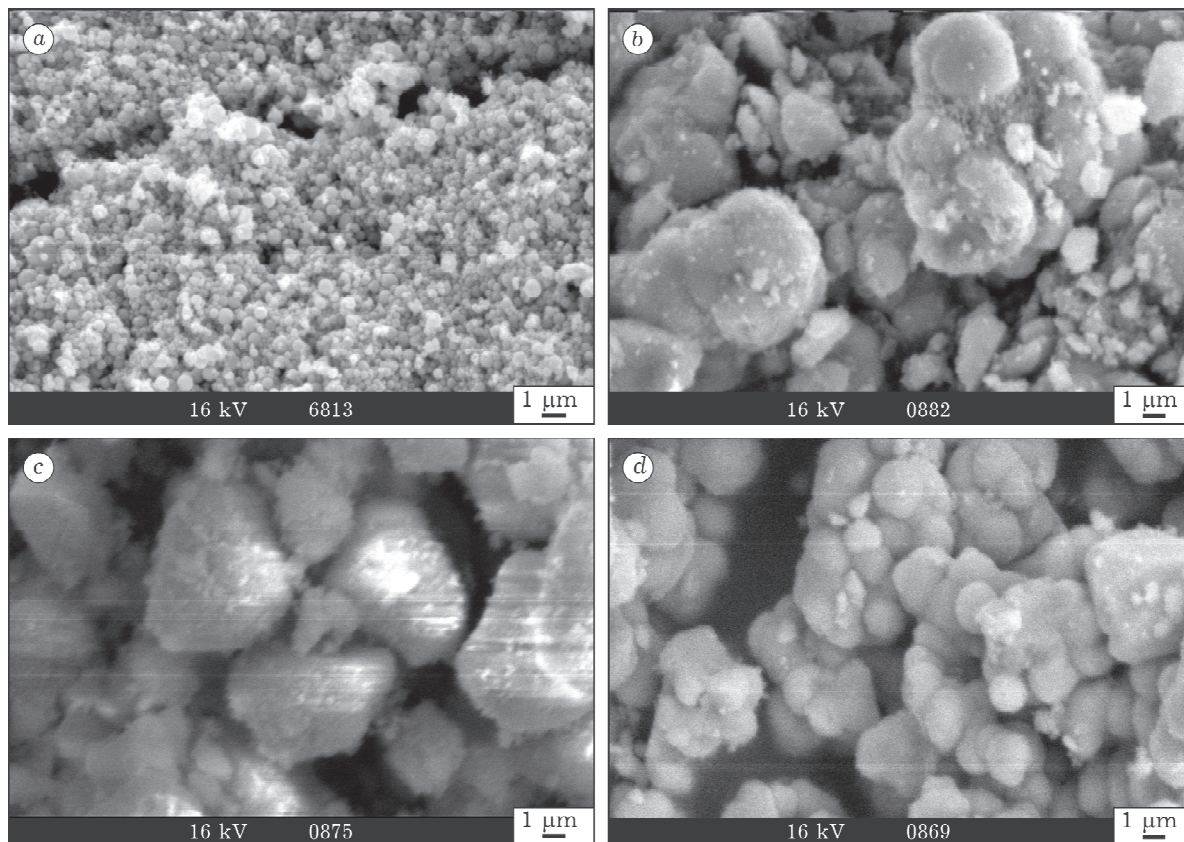
Fig. 2. SEM images of catalyst samples: a − $Pt/Cs_2HPW_{12}O_{40}$; b, c − $Pt/SO_4/ZrO_2$; d − $Pt/WO_x/ZrO_2$.

sorbed pyridine or adsorbed CO IR spectroscopy (100−121 µmol/g) for systems based on sulphated zirconia obtained by means of various methods [28−30].

The concentration values for BAC and LAC on the surface of the catalyst WO_x/ZrO_2 account for 38 and 37 µmol/g, respectively, which is several times lower than those for the other systems under study. These results are in a good agreement with literature data (34−35 µmol/g) [31, 32].

Thus, the results of measuring the acidic properties demonstrated that the catalysts based on sulphated zirconia differ from other systems in significant increasing the amount of LAC.

The specific surface area (see Table 1) significantly differs for catalysts based on acidic cesium salts of phosphotungstic heteropoly acid. However, the system of greatest interest with respect to the alkane skeleton isomerisation such as $Pt/Cs_2HPW_{12}O_{40}$ [14, 15], $Pt/WO_x/ZrO_2$ and $Pt/SO_4/ZrO_2$ are characterized by similar val-

TABLE 1

Specific surface area, concentration and strength of the acidic centres of bifunctional catalysts

Samples	S_{sp}, m²/g	Brønsted acidic centres		Lewis acidic centres
		N, µmol/g	PA, kJ/mol	N, µmol/g
$Pt/Cs_1H_2PW_{12}O_{40}$	37	139	1120	25
$Pt/Cs_{1.5}H_{1.5}PW_{12}O_{40}$	57	128	1120	32
$Pt/Cs_2HPW_{12}O_{40}$	103	118	1150	57
$Pt/Cs_{2.5}H_{0.5}PW_{12}O_{40}$	216	48	1150	63
$Pt/SO_4/ZrO_2$	115	70	1160	110
$Pt/WO_x/ZrO_2$	75	38	1180	37

TABLE 2

Activity and selectivity level of bifunctional catalysts in the hexane skeleton isomerisation with respect to dimethylbutane (DMB)

Samples	T, °C	W, 10^{-8} mol/(g·s)	Selectivity with respect to DMB, %
1 % Pt/Cs$_2$HPW$_{12}$O$_{40}$	200	220	20.6
1 % Pt/WO$_x$/ZrO$_2$	270	200	18.9
1 % Pt/SO$_4$/ZrO$_2$	200	400	23.2

ues of specific surface area (75−115 m^2/g). The images of the surface of these samples (see Fig. 2) demonstrate a significant difference in the formation of the outer surface of the catalysts. The catalysts based on CsPW exhibit a "spongy" texture with a secondary particle size ranging within 100−1000 nm, which particles consist of primary particles with the size of 10−30 nm. The particle size of zirconia treated with sulphates or tungstates are 10 or more times greater than the particle size inherent in the systems based on CsPW.

The catalytic properties of the samples are demonstrated in Table 2. The activity and selectivity level with respect to target products differs to a considerable extent for the catalysts under investigation. The lowest activity level was demonstrated by catalyst Pt/WO$_x$/ZrO$_2$, whereby at 200 °C the reaction rate did not exceed 20 mol/(g·s). Intermediate results were obtained for the catalyst based on heteropoly acid compound Pt/Cs$_2$HPW$_{12}$O$_{40}$. The

greatest reaction rate of hexane skeletal isomerisation was registered for the sample based on sulphated zirconia. The investigation of acidic properties also demonstrated that catalysts based on sulphated zirconia exhibit a significantly greater amount of the LAC as to compare with the other systems. Thus, in order to perform a detailed study of factors those determine the activity of bifunctional environmentally safe catalysts for hexane skeletal isomerisation, we have chosen Pt/SO$_4$/ZrO$_2$ catalyst.

In order to verify the assumption about the key role of LAC in the activity of catalysts on based on sulphated zirconia it was necessary to develop a preparation method which could allow researchers to vary the concentration of the LAC on the catalyst surface so that all the remaining parameters (the concentration of BAC, noble metal content, *etc*.) remain unchanged. We have proposed a novel method for producing a catalyst, which consists in the following: sulphuric acid, or salts of sulphuric acid are applied (according to water absorption capacity) on zirconium-aluminum hydroxide precipitated from the solutions of nitrate salts using ammonia at pH value ranging within 7−11.5. After applying, the sample is dried and calcined at a temperature of 630−660 °C, whereafter the platinum is introduced by applying chloroplatinic acid according to water-absorbing capacity. Dried sample is calcined at a temperature above 500 °C for 3 h with further pelleting and grinding. The catalyst frac-

TABLE 3

Catalyst composition, precipitation pH as well as concentration of Lewis centres (LAC) and Brønsted centres (BAC) on bifunctional catalysts based on sulphated zirconia (SZ)

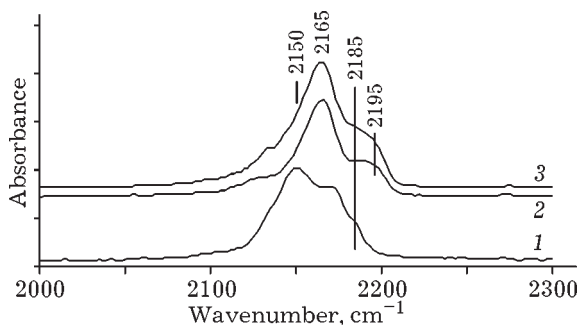| Catalysts	Composition, mass %	pH	N, µmol/g	
			LAC	BAC
SZ-1	0.3Pt/ SO$_4^{2-}$ /Al$_2$O$_3$/ZrO$_2$ (SO$_4^{2-}$ 6, Al$_2$O$_3$ 2.5)	7.0	50	85
				140
SZ-2	0.3Pt/ SO$_4^{2-}$ /Al$_2$O$_3$/ZrO$_2$ (SO$_4^{2-}$ 6, Al$_2$O$_3$ 2.5)	10.0	150	140
SZ-3	0.3Pt^{2-}/ SO$_4^{2-}$ /Al$_2$O$_3$/ZrO$_2$ (SO$_4^{2-}$ 9, Al$_2$O$_3$ 2.9)	11.5	250	170
	0.3Pt/ SO$_4^{2-}$ /ZrO$_2$ (SO$_4^{2-}$ 5.1 [30])	ND	121	37

Note. ND − no data.

Fig. 3. IR spectra of adsorbed CO at a temperature of 100 K and a pressure of 100 Torr for catalysts $Pt/SO_4^{2-}/Al_2O_3/ZrO_2$ obtained under different conditions: SZ-1 (*1*), SZ-2 (*2*), SZ-3 (*3*). For notations see Table 3.

tion of 0.5−1 mm in size is used for loading into the reactor.

Table 3 demonstrates the composition of catalysts based on sulphated zirconia and data concerning the acidic properties, obtained by means of adsorbed CO IR spectroscopy. It can be seen that the variation of sample preparation conditions affects the concentration of the LAC, whereas the content of BAC remains almost unchanged. For comparison, in this table there is a catalyst composition described in [30] presented, with a maximum concentration of the LAC available from the literature (about 120 µmol/L). Figure 3 demonstrates IR spectra of adsorbed CO on the catalysts containing LAC within the range of 50−250 µmol/g.

In the course of studying the kinetics of *n*-hexane isomerisation on superacids [33] it was demonstrated that the process takes place in three stages. The fastest stage is presented by the formation of 3-methylpentane (3MP) from 2-methylpentane (2MP) occurring without changing the number of tertiary carbon atoms. Further, the isomerisation occurs with respect to an equilibrium mixture of methylpentanes up to reaching the equilibrium with 2,3-dimethylbutane (2,3DMB). The isomerisation reaction of *n*-hexane and the formation of 2,2-dimethylbutane (2,2DMB) are characterized by comparable rate values.

Similar results were obtained in the course of *n*-hexane isomerisation on $HF-SbF_5$ catalysts [34]. In this regard, for the calculation of the constants characterizing the activity and selectivity level of the catalyst, we took into consideration the following reaction scheme:

$$n\text{-}C6 \xleftarrow{k_1} 2MP + 3MP + 2,3DMB \xleftarrow{k_2} 2,2DMB \quad (3)$$
$$\downarrow k_3$$
$$C_1 - C_5$$
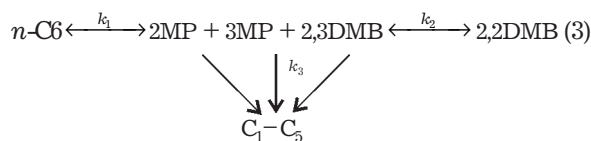
The rate of isomerisation is affected by a number of factors those characterize both the composition of the mixture, and the reaction conditions. However, as it is mentioned in the most of publications, there is first order reaction observed with respect to the reactant within a wide range of contact time value and concentration of reagents.

In order to determine the numerical values of the reaction kinetic rate constants we used a plug flow reactor mathematical model in the following form:

$$\frac{dC_1}{d\tau} = -k_1 C_1 (1 - \frac{C_2}{C_1 K_{e1}})$$

$$\frac{dC_2}{d\tau} = k_1 C_1 (1 - \frac{C_2}{C_1 K_{e1}}) - k_2 C_2 (1 - \frac{C_3}{C_2 K_{e2}}) - k_3 C_3$$

$$\frac{dC_3}{d\tau} = k_2 C_2 (1 - \frac{C_3}{C_2 K_{e2}})$$

$$\frac{dC_4}{d\tau} = k_3 C_2$$

$$\tag{4}$$

$\tau = 0$: $C_1 = C_1^0$, $C_i = 0$, $i = 2, 3, 4$

where $C_1 - C_4$ are the mole fractions of *n*-hexane, of mixture 2MP +3MP + 2,3DMB mixture, of 2,2DMB and the cracking products, respectively; *t* is the contact time value; k_i are the reaction rate constants; K_{ei} are the equilibrium constant for *n*-hexane conversion and the formation of 2,2DMB.

The calculation of kinetic constants was performed as it follows.

1. Basing on the values of *n*-hexane, 2MP, 3MP, 2,3DMB and 2,2DMB entropy and enthalpy, we calculated the thermodynamic equilibrium and determined the equilibrium values of their concentration for each temperature (Fig. 4).

2. Basing on the equilibrium concentration values we determined the equilibrium constant of the stages corresponding to eq. (3).

3. For the preset equilibrium constants, we determined the reaction rate constants basing on the description of experimental data.

Figure 5 demonstrates calculated and experimental data obtained for catalyst SZ-2 (LAC
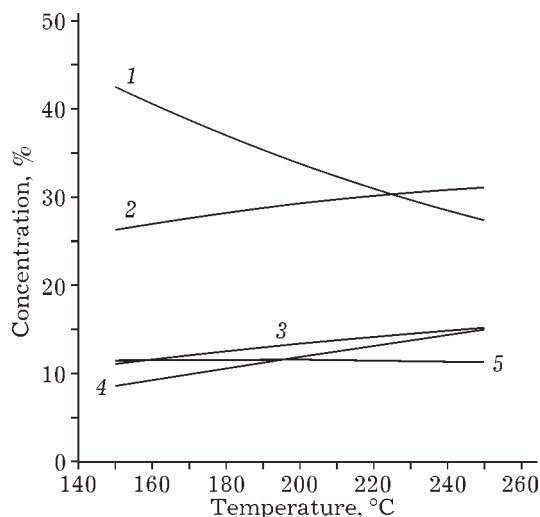
Fig. 4. Equilibrium composition of *n*-hexane isomerisation products depending on temperature: *1* − 2,2DMB, *2* − 2MP, *3* − 3MP, *4* − *n*-C6, *5* − 2,3MP.

150 μmol/g) for different values of contact time and temperature. It can be seen that the results of mathematical modelling describe the experimental data quite well. Likewise we described the literature data and the experimental results for catalysts SZ-2 and SZ-3 at different pressure values (Table 4, Fig. 6).

Figure 7 demonstrates the equilibrium constants and the rate constants of forward reactions in the Arrhenius coordinates. Basing on these data, we estimated the activation energies for the rate constants of forward ($k_1 = 28$, $k_2 = 14.2$ kJ/mol) and reverse (35 and 25.5 kJ/mol, respectively) reactions (see eq. (3)).
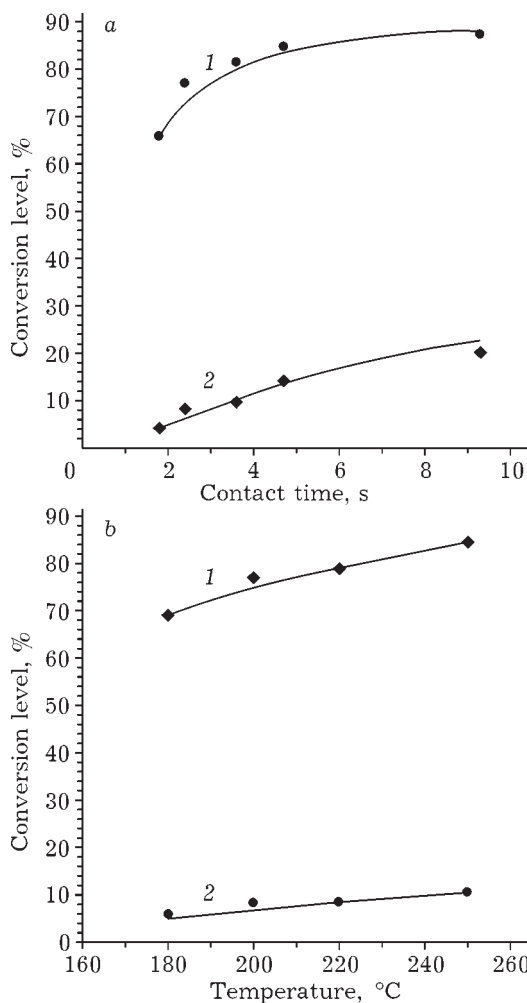

Fig. 5. Conversion level of *n*-hexane (*1*) and the concentration of 2,2DMB (*2*) on the catalyst SZ-2 depending on contact time value (*a*) and temperature (*b*) ($P = 1$ MPa, $H_2/C_6H_{14} = 5$). The dots are standing for the experimental data, the lines denote calculated data.

TABLE 4

Experimental and theoretical kinetic data for *n*-hexane skeleton isomerisation on catalysts SZ-2 and SZ-3 (pressure 0.3 MPa, temperature 200 °C)

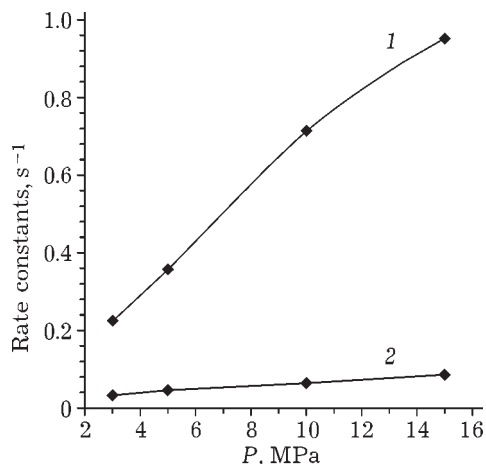| Parameters	SZ-2 (LAC 150 μmol/g)		SZ-3 (LAC 250 μmol/g)	
	Experiment	Calculation	Experiment	Calculation
Concentration of 2,2DMB, %	1.5	1.5	4.6	4.5
Concentration of 2MP + 3MP + 2,3DMB, %	35.1	34.8	59.86	60.0
Conversion of *n*-C$_6$, %	40.3	40.2	69.2	69.3
Rate constants, s^{-1}:				
k_1	−	0.224	−	0.909
k_{-1}	−	0.048	−	0.200
k_2	−	0.033	−	0.073
k_{-2}	−	0.053	−	0.120
Feeding rate of *n*-hexane, h^{-1}	2.79	2.79	4.68	4.68
H$_2$/*n*-C$_6$ ratio	2.09	2.09	1.87	1.87

Fig. 6. Data calculated for changing the rate constants of *n*-hexane isomerisation (*1*) and of 2,2DMB formation (*2*) on the catalyst SZ-2 depending on pressure. *T* = 200 °C.
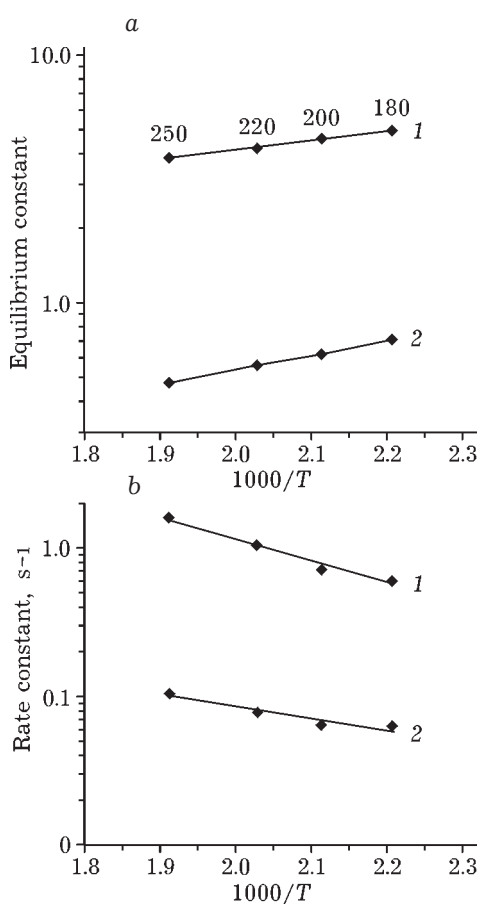

Fig. 7. Equilibrium constants (*a*) and the reaction rate constants (*b*) depending on temperature for the catalyst SZ-2: *1* − *n*-hexane isomerisation stage; *2* − 2,2DMB formation stage.

Data presented in Table 4 demonstrate that the rate constant for the isomerisation of *n*-hexane (k_1) exhibited by the catalyst with the LAC concentration equal to 250 µmol/g is four times higher than that for the catalyst with the LAC concentration of 150 µmol/g. The k_2 constant which characterizes the formation rate of the target product (2,2DMB) for the catalyst with LAC concentration of 250 µmol/g is more than two times greater than the mentioned value for the catalyst with LAC concentration equal to 150 µmol/g. Consequently, the rate of *n*-hexane isomerisation mainly depends on the concentration of the LAC on the catalyst surface.

CONCLUSION

A number of environmentally safe highly efficient bifunctional catalysts for hexane skeleton isomerisation on the base of zirconia treated by sulphates, tungstates, and acidic cesium salts of phosphotungstic heteropoly acids were investigated. It was demonstrated that the main parameter that determines the activity of the catalysts is presented by acidic properties. For the most active catalyst systems based on sulphated zirconia we revealed the reaction rate values and selectivity level with respect to target products depending on the concentration of Lewis acidic centers, whereas the content of Brønsted acidic centers was maintained to be approximately constant.

It was found that the main factor determining the activity of catalysts in the hexane skeleton isomerisation consists in the presence of strong Lewis acidic centers on the surface. Furthermore, it was found that the creation of novel highly efficient catalysts requires for the LAC concentration on the surface to be greater than 150 µmol/g.

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