The Catalytic Properties of Tungstated Zirconia in *n*-Heptane Isomerization

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Abstract—The catalytic properties of zirconia modified with different amounts of tungstate anions in the hydroisomerization of *n*-heptane and its mixtures with benzene or toluene have been studied. It has been found that at a low temperature of 170°C, the yield of isoheptanes reaches 62.8% with a fairly high selectivity of 87.6% on the Pt/WO₄^{2–}/ZrO₂ catalyst prepared by impregnation to contain 17.6 mol % tungstate anions. Under the same conditions, the yield of isoheptanes on a sulfated Pt/SO₄^{2–}/ZrO₂ catalyst is as low as 14.0% with a selectivity of 20.3%. The hydroisomerization process effectively occurs on the tungstated catalyst in the presence of benzene or toluene.

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The efficient use of hydrocarbon resources, such as light hydrocarbon feedstock derived from crude oils and gas condensates, is an urgent problem of the petroleum refining industry. Straight-run gasoline fractions contain significant amounts of *n*-alkanes with a low octane number. One of the effective ways of using them for manufacturing high-performance gasolines is isomerization yielding high-octane skeletal isomers that satisfy all requirements for quality and miscibility. At the same time, the requirements for the environmental characteristics of motor fuels have also sharply increased. Both international and domestic standards for gasolines introduce ever-tightening restrictions on the content of toxic aromatic hydrocarbons, first of all, benzene (up to 1%) [1, 2].

The above factors are responsible for the recent keen demand for process technologies of isomerization of *n*-alkanes to skeletal isomers. These processes are used in the developed countries of Western Europe and in the United States, where the proportion of isomerizates in the gasolines produced is at least 5%; in Russia, it does not exceed 1.5% [3]. Moreover, most of the catalysts used in the existing isomerization units in Russia are imported [2-9]. The development of efficient domestic catalysts for the isomerization of alkanes is one of the important lines in the development of Russian oil refining. The isomerization of alkanes to skeletal isomers is a reversible exothermic process; low temperatures favor the formation of highoctane isoalkanes with a high yield [10]. Therefore, the process performance characteristics are largely determined by catalyst activity.

There are a large number of studies reported in the literature on the synthesis and analysis of the isomerization properties of various types of acid catalysts, including those based on chlorinated alumina, various types of zeolites, mesoporous aluminosilicates and silicates (such as MCM), silicoaluminophosphates (SAPO), salts of heteropoly acids, anion-modified metal oxides, and catalysts based on porous oxides and carbides of molybdenum and tungsten [11-19]. The most active and selective platinized catalysts based on aluminum chloride, which give a possibility to run the process at a low temperature (below 180°C), and those based on high-silica zeolites, which are efficient at higher temperatures (above 250°C), have found wide use in industrial processes [4–7, 20, 21]. New catalysts based on sulfated zirconia have gained acceptance in recent years; they are superior to zeolites in catalytic activity and are highly competitive with chlorinated alumina. In particular, sulfated zirconia catalysts manufactured by Neftekhim are used at some domestic plants [2, 7].

It is noteworthy that currently existing industrial catalysts are used for the isomerization of *n*-butane and low-boiling-point pentane-hexane petroleum fractions. They are not very effective in the isomerization of alkanes with longer hydrocarbon chains because of low selectivity. The catalysts based on zirconia modified with $WO_4^{2-}\,$ and $Mo\,O_4^{2-}\,$ anions are of ever-growing interest for this purpose [5, 13, 22]. However, the physicochemical principles of their formation and catalytic activity are still poorly understood and the data of different authors are often contradictory. In many respects, this can be attributed to the metastability of the active modification of zirconia, which is responsible for the fact that its structural characteristics and catalytic activity substantially depend on the preparation procedure.

The aim of this study is to analyze the influence of the concentration of tungstate anions on the properties of $Pt/WO_4^{2-}/ZrO_2$ catalysts in the *n*-heptane hydroisomerization reaction and to compare them with the properties of sulfated zirconia.

EXPERIMENTAL

The catalysts were prepared by impregnating amorphous zirconium hydroxide with an aqueous solution of ammonium metatungstate $[(NH_4)_6(H_2W_{12}O_{40}) \cdot 18H_2O]$. The thermal treatment of the modified hydroxide was carried out at a temperature of 700°C. Platinum was deposited from a solution of chloroplatinic acid by impregnating calcined oxide samples of WO_4^{2-}/ZrO_2 . The specific surface area was determined using the BET nitrogen adsorption technique. The average pore size was calculated from the desorption branch of the isotherm. The surface area value was used to estimate the average size of particles on the assumption of their spherical shape.

The experiments on the isomerization of *n*-heptane were carried out using a BI-CATflow 4.2(A) catalytic setup (model of the Boreskov Institute of Catalvsis, Siberian Branch, Russian Academy of Sciences) with a flow reactor at atmospheric pressure. The catalyst was charged into the reactor in the form of a fraction with a grain size of 0.2-1 mm. It was activated via heat treatment: first, in an argon stream at a temperature of 350°C and then in hydrogen at 250°C. The space velocity of *n*-heptane was varied from 0.3 to 2 h⁻¹ at a molar ratio of H_2 : *n*-C₇ = 3 : 1. The reaction was run at 170 and 200°C. The isomerization products were analyzed in the on-line mode using a gas chromatograph as part of the catalytic setup equipped with a capillary column and a flame ionization detector. The chromatograms were recorded and processed using the GEPARD software. The values of research octane numbers of the isomerizate were calculated according to the additivity scheme.

RESULTS AND DISCUSSION

According to X-ray diffraction data [22, 23], the synthesized catalysts samples are tetragonal zirconia promoted by tungstate groups in different amounts (5.9 to 21.9 mol %). The ZrO_2 crystallite size is 13–16 nm. Figure 1 shows the specific surface area and the average pore diameter as a function of the concentration of tungstate groups. It is seen that the minimum average pore size of 7–8 nm and the maximum specific surface area of the dioxide of 76–77 m²/g (this corresponds to the average particle size of 12–13 nm) are formed by introducing the tungstate groups in the amount of 12.9–17.6 mol %.

During the isomerization of *n*-heptane on WO_4^{2-}/ZrO_2 (without Pt), we observed a sharp decrease in the conversion during the initial period. A



Fig. 1. Specific surface area and average pore size of $Pt/WO_4^{2-}/ZrO_2$ as a function of the WO_4^{2-} concentration.

quasi-steady state, in which the reaction characteristics vary only slightly over time, was established on the platinized catalysts within 30 min. The process parameters given below refer to this reaction time.

The effect of the concentration of tungstate anions was studied using the example of a set of samples containing 0.5 wt % Pt at a space velocity of 1 h⁻¹ and a temperature of 170°C (Table 1). At a low tungstate content (5.9 mol %), the yield of heptane isomers was as low as 3.1 wt % with a selectivity of 86.3 wt %. An increase in the concentration of tungstate anions led to an increase in the catalyst activity, whereas the selectivity varied only slightly. The maximum yield of heptane isomers of 62.8 wt % was achieved on the catalyst that contained 17.6 mol % WO₄²⁻. The research octane number of the isomerizate produced on this catalyst was 45. A further increase in the concentration

of WO_4^{2-} resulted in a decrease in activity.

A comparison of the data in Fig. 1 and Table 1 shows that the most active catalyst has the highest specific surface area. However, a quantitative comparison of the texture characteristics with the isomerization activity shows that, as the concentration of tungstate anions increases from 5.9 to 17.6%, the specific surface area of the catalysts increases only by a factor of 1.4 (Fig. 1) and the yield of isoheptanes increases by more than a factor of 20 (Table 1). In addition, there is no correlation between the isomerization characteristics and the catalyst pore size, a fact that indicates the absence of internal-diffusion limitation on the reaction. This is also confirmed by the finding in preliminary tests that the reaction characteristics did not vary upon a change in the grain size of the catalysts in the

Sample		$Pt/SO_4^{2-}/ZrO_2$			
Concentration of anions, mol %	5.9	12.9	17.6	21.9	6.5
Conversion of <i>n</i> -heptane, wt %	3.6	60.9	71.7	44.3	68.8
Selectivity for isoheptanes, wt %	86.3	82.2	87.6	87.7	20.3
Yield of heptane isomers, wt %	3.1	50.0	62.8	38.8	14.0
Yield of $C_1 - C_6$ alkanes, wt %	0.5	10.8	8.9	5.5	54.8
C_3/C_4 (mole) ratio	0.91	0.98	1.0	0.98	0.97
Octane number (ON)	2	36	45	25	52

Table 1. Characteristics of *n*-heptane isomerization on the $Pt/WO_4^{2-}/ZrO_2$ and $Pt/SO_4^{2-}/ZrO_2$ catalysts at a temperature of $170^{\circ}C$ and $v = 1 h^{-1}$

range of 0.06 to 1.5 mm. This implies that the isomerizing activity of different $Pt/WO_4^{2-}/ZrO_2$ samples is not determined by textural properties and seems to depend in a certain way on the concentration and state of surface tungstate anions.

The reaction products are mostly composed of methylhexanes and dimethylpentanes as heptane isomers. An increase in the concentrations of WO_4^{2-} groups leads to an increase in the yield of mainly methylhexanes (Fig. 2). In addition to isoheptanes, a small amount of C_1-C_6 alkanes is formed; among

them, C_3 and C_4 alkanes with a ratio close to unity are dominant, which is indicative of the occurrence of the side cracking reaction of the C_7 molecule by breaking the central bond via the carbennium ion mechanism. For comparison, under the same conditions, we tested a Pt/S O_4^{2-}/ZrO_2 catalyst based on sulfated zir-

conia with an optimum concentration of sulfate groups of 6.5 mol % [22]. It was found that the degree of conversion of *n*-heptane on the sulfated catalyst dif-



Fig. 2. Variation in the yield of the heptane isomers methylhexanes and dimethylpentanes as a function of the WO_4^{2-} concentration.

fered little from that on the tungstated sample (68.8 wt % versus 71.7 wt %); however, the yield of the desired isoheptane products was only 14.0 wt %, and the selectivity was 20.3 wt % (Table 1). The dominant reaction was acid cracking, which yielded propane and isobutane in a ratio close to unity.

The data on the effect of space velocity on the characteristics of isomerization on the tungstated catalyst with the optimum composition are given in Table 2. It is seen that as the space velocity increases from 0.3 to $2 h^{-1}$, the conversion of *n*-heptane decreases from 92.0 to 49.7 wt %, the yield of isoheptanes reduces from 68.2 to 46.8 wt %, the octane number decreases from 59 to 27, and the isoheptane selectivity, in contrast, increases from 74.2 to 94.4 wt %. At different space velocities, the C₃/C₄ molar ratio in the cracking product is close to unity.

Thus, the catalyst based on tungstated zirconia with the optimum content of tungstate groups (17.6%) exhibited a relatively high activity and selectivity in *n*-heptane isomerization. Note that in the case of industrial catalysts, including sulfated zirconia, the allowed concentration of heptanes in the feedstock (C_5-C_6 fraction) is at most 10–15% and that of benzene is no more than 1%.

Industrial gasoline fractions of crude oil always contain a significant amount of aromatic hydrocarbons. In order to examine their effect on the isomerization characteristics, the catalyst with the optimum concentration of tungstate groups was tested in the isomerization of *n*-heptane in the presence of 10 wt % benzene and toluene.

The hydroisomerization of the mixtures proceeded almost in the steady-state regime. However, the catalyst activity significantly decreased in comparison with the activity in the reaction with individual heptane. At 170° C, the conversion of heptane in the presence of benzene (10%) was 41.8 wt % against 71.7 wt % in the case of heptane alone (Table 3). As the temperature increased to 200°C, the conversion increased to 75.8 wt % with an isoheptane selectivity of 68.7 wt %. For the mixture with toluene, the conversion characteristics and the yield of heptane isomers decreased by

Table 2. Effect of the space velocity of heptane on the characteristics of isomerization on the Pt/WO₄²⁻/ZrO₂ catalyst. The concentration of WO₄²⁻ is 17.6 mol %; the Pt content is 0.5 wt %; the reaction temperature is 170°C

Characteristics	Space velocity of heptane, h^{-1}				
	0.3	0.5	1	2	
Conversion of <i>n</i> -heptane, wt %	92.0	75.1	71.7	49.7	
Selectivity for isoheptanes, wt %	74.2	85.2	87.6	94.4	
Yield of isoheptanes, wt %	68.2	64.0	62.8	46.8	
ΣDMP/ΣMH	0.35	0.23	0.22	0.18	
C_3/C_4 (molar) ratio	0.98	0.97	1.00	0.96	
Octane number (ON)	59	45	45	27	

Table 3. Characteristics of *n*-heptane isomerization in a mixture with benzene or toluene on $Pt/WO_4^{2-}/ZrO_2$ at 170 and 200°C and $v = 1 h^{-1}$

Reaction temperature, °C	170	200	170	200	200
Feedstock	heptane	heptane	heptane + benzene	heptane + benzene	heptane + benzene
Conversion of <i>n</i> -heptane, wt %	71.7	87.5	41.8	75.8	68.2
Conversion of benzene (toluene), wt %	—	_	99.8	99.9	99.5
Selectivity for isoheptanes, wt $\%$	87.6	61.8	83.8	68.7	71.7
Yield of isoheptanes, wt $\%$	62.8	54.2	35.2	52.1	48.9
Methylcyclopentane	_	_	2.2	4.9	_
Methylcyclohexane	_	_	—	—	3.5
Cyclohexane	—	_	7.6	5.0	—
Dimethylcyclopentanes	—	_	—	—	6.0
C_3/C_4 (mole) ratio	1.0	0.99	0.86	0.97	0.92
Octane number (ON)	45	47	26	42	42

3-8% compared to the mixture with benzene. In this process, benzene or toluene was almost complete consumed for hydrogenation and hydroisomerization to cyclohexane (53 wt %) and methylcyclopentane (47 wt %) or methylcyclohexane (38 wt %) and dimethylcyclopentanes (62 wt %), respectively.

The octane numbers of the products obtained via the hydroisomerization of the mixtures at 200°C decreased by 5 points compared to the heptane isomerizate because of lower yields of the isomers and lower octane numbers of the benzene and toluene hydroisomerization products.

Thus, it has been found that the $Pt/WO_4^{2-}/ZrO_2$ catalyst containing 17.6% WO_4^{2-} is the most efficient. Its isomerization efficiency is manifested in a good general activity (yield of isoheptanes is 62.8 wt %) combined with a quite high selectivity (87.6 wt %) in the low-temperature region of 170°C. It is important

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to note that the isomerization of *n*-heptane on the tungstated catalyst is fairly effective in the presence of a benzene or toluene admixture, which are converted into the respective naphthenic derivatives (methylcy-clopentane, cyclohexane, methylcyclohexane, and dimethylcyclopentane) by 99.7-99.9%.

These results show that catalyst systems based on zirconia modified with tungstate anions are promising for designing a new isomerization process, which can involve components of the heptane fraction. By compounding the isomerizate with reforming products, it is possible to produce environmentally clean highgrade gasolines with a low concentration of toxic benzene.

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