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On the Effect of the Strength of Acid Sites in Heterogeneous Catalysts on the Activity in the Skeletal Isomerization of *n*-Butane

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Abstract—The catalytic activity of three groups of acid catalysts different in the nature and strength of acid sites in the skeletal isomerization of *n*-butane was studied. It was found that the strength of the sites did not correlate with the rate of the reaction.

INTRODUCTION

Presently, the fact that the formation of carbenium ions is a key step in the skeletal isomerization reactions of alkanes is beyond question. These ions can be formed via various reaction paths: the decomposition of carbonium ions formed by the protonation of paraffins, the elimination of a hydride ion from a paraffin molecule at Lewis sites, and the formation of radical cations followed by the elimination of a hydrogen atom. The formation of carbenium ions with the participation of proton and aprotic surface sites has been discussed most intensively in the literature. Both types of these sites occur on the surface of sulfated zirconium oxides, which are the most active catalysts for low-temperature skeletal isomerization [1–3]. However, their role in the reaction is unknown. The results of studies of various classes of catalysts for the low-temperature skeletal isomerization of lower alkanes were presented in a great number of publications. However, based on these data, it is difficult to determine the role of different sites because the strength and concentration of sites and the activity in reactions are absent from publications [4–8].

The aim of this work is to compare the activity of a wide range of acid catalysts, characterized in terms of the strength and activity of sites, in the isomerization of *n*-butane to isobutane. For solving this problem, we used a uniform methodology for the characterization of acid properties and measured the rates of reactions in the same flow-circulation setup. The following three groups of test catalysts with different acid properties were chosen: (I) with only strong surface proton sites ($H_3PW_{12}O_{40}$ heteropoly acid/Sibunit [9]), (II) with simultaneously occurring strong proton and Lewis sites (ZSM-5 zeolite [10], crystalline aluminum sulfate [11], crystalline zirconium sulfate; sulfated alumina [11], sulfated zirconia [3], and fluorinated alumina [12]), and (III) with only Lewis sites of different strength (fluorinated zirconia and zirconium oxides with tetragonal and monoclinic structures).

EXPERIMENTAL

The HZSM-5 zeolite (an SiO_2/Al_2O_3 ratio of 50) was prepared by hydrothermal synthesis and calcined at 500°C [10].

The $H_3PW_{12}O_{40}$ heteropoly acid/Sibunit (henceforth referred to as HPA), which was prepared and characterized by Paukshtis *et al.* [9], was used as a catalyst with strong proton sites.

Crystalline aluminum sulfate and zirconium sulfate were prepared by the calcinaton of the crystal hydrates $Al_2(SO_4)_3 \cdot 18H_2O$ and $Zr(SO_4)_2 \cdot 4H_2O$, respectively, which were preliminarily dried at 110°C, at 500–600°C [13, 14].

Sulfated alumina (SO_3/Al_2O_3) was prepared by the incipient wetness impregnation of γ-Al_2O_3 with a sulfuric acid solution [15].

Zirconium hydroxide and zirconium oxide were used as parent compounds for the preparation of sulfated zirconia (SO_3/ZrO_2). Zirconium hydroxide was obtained by precipitation from an aqueous solution of zirconium oxychloride with an ammonia solution at 65–70°C and a constant pH 8. To prepare crystalline zirconium oxide, the precipitate (hydroxide), which was washed and dried at 110°C, was calcined at 500°C.

The hydroxide and the oxide were sulfated by incipient wetness impregnation with a solution containing a specified amount of sulfuric acid.

Fluorinated alumina and zirconia (F/Al_2O_3 and F/ZrO_2) were obtained by the incipient wetness impregnation of corresponding oxides with an aqueous solution of ammonium fluoride [12].

All of the samples after treatment with solutions were dried in air and then at 110°C; thereafter, they were calcined at different temperatures (from 400 to 600°C) in a flow of dry air.

The concentrations of sulfate sulfur in the sulfated zirconia and alumina were determined. For this purpose, the catalysts were dissolved in hydrofluoric acid

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followed by the removal of the acid and the analysis of the resulting solution by inductively coupled plasma atomic emission spectrometry.

X-ray diffraction analysis was performed on a DRON instrument using monochromatic CuK_α radiation. Diffraction patterns were recorded with a chart recorder at a goniometer rate of 1 deg/min. Phase identification was performed using the ASTM data file.

The specific surface areas of samples were determined from the low-temperature adsorption of nitrogen.

The acid properties were characterized with the use of the IR spectroscopy of adsorbed CO and pyridine [16, 17]. Before adsorption, the samples were evacuated at specified temperatures in the range 400–600°C. Pyridine was adsorbed at 150°C for 15 min at a vapor pressure that corresponded to the saturated vapor pressure at room temperature. Before measuring the spectra, an excess of pyridine was removed by evacuation at 150°C for 15 min. CO was adsorbed in small portions at liquid nitrogen temperature to a total pressure of 10 Torr. The IR spectra of adsorbed pyridine and CO were measured on an IFS-113v spectrometer (resolution, 4 cm^{-1}; number of scans, 64).

The concentration of Lewis sites (N_{CO}, μmol/m^2) was calculated from the intensity of the absorption band of adsorbed CO, and the strength of these sites was characterized by the position of the absorption band maximum (ν(CO)) (the band shifted to the short-wave region as the strength of the sites increased) [16]. The concentration of Brönsted sites (N_{H}, μmol/m^2) was determined from the absorption band intensity of the pyridinium ion. The strength of Brönsted sites (*PA*, kJ/mol) was determined from the shift of the absorption band and characterized by the value of proton affinity (*PA*) in accordance with a published procedure [16, 17].

The activity of the catalysts in the skeletal isomerization of *n*-butane was studied by a flow-circulation method at 150°C and an initial *n*-butane concentration of 24 vol % in a mixture with nitrogen. Before the reaction, the samples were calcined in a catalytic reactor in a flow of dry air at a specified temperature; next, the temperature was decreased to 150°C in a flow of dry and deoxygenated nitrogen. Then the reaction mixture was supplied to the catalyst. The space velocity of *n*-butane feeding was 2000 h^{-1}. The reaction products passed through the loop of a sampling valve of a chromatograph, and they were analyzed at regular intervals. The degree of conversion and the rate of reaction were determined based on the analysis of the reaction products. The activity in the skeletal isomerization was characterized by the maximum rate of the isomerization reaction reached under the specified test conditions.

RESULTS AND DISCUSSION

The table summarizes the acid properties of the test catalysts. It can be seen that both proton and Lewis sites occurred on the surface of the catalysts; the strength and concentration of these sites varied over a wide range mainly depending on the chemical composition of the catalysts.

In the series of the test catalysts, HPA is the strongest Brönsted acid; the strength of its proton sites ($PA = 1120$ kJ/mol) is noticeably higher than the strength of sites in the other catalysts, including HZSM-5. It is well known that the acidity of the latter is close to the acidity of concentrated sulfuric acid. Lewis sites are absent from the surface of HPA. Crystalline aluminum sulfate is the strongest Lewis acid. Sulfated zirconium oxides are weaker Brønsted and Lewis acids. Zirconium oxides are the weakest acids.

Note that the given values of the strength of proton sites in sulfated zirconium oxide and the zeolite are similar. This result is different from published data [3] because of the use of different probe molecules (CO and Py) for testing the strength. The strength of the proton sites of zirconium sulfates determined with the use of pyridine is much higher than that determined with CO. The reason for this discrepancy is related to the interaction of the interaction of Py and CO molecules with surface hydroxyl groups to form a system of hydrogen bonds; this conclusion was discussed by Paukshtis [18].

Based on the results obtained, we can arrange the catalysts in accordance with the strength of sites. The strength of Brönsted sites changes in the order HPA > HZSM-5 = $Zr(SO_4)_2$ = SO_3/ZrO_2 = $Al_2(SO_4)_3$ = $SO_3/Al_2O_3 \geq F/Al_2O_3$, whereas the strength of Lewis sites changes in the order $Al_2(SO_4)_3$ > HZSM-5 > $SO_3/Al_2O_3 \approx Zr(SO_4)_2 \approx F/Al_2O_3 > SO_3/ZrO_2 \approx F/ZrO_2 > ZrO_2$.

The study of the catalytic activity allowed us to conclude that isobutane is the main reaction product (the selectivity is ~99%); propane and pentane (the ratio between them is close to 1, and the total selectivity is no higher than 0.5%) are formed in an insignificant amount in the presence of active catalysts. The deactivation of catalysts was observed in the course of the reaction. The table summarizes the maximum rates of reaction obtained with the test catalysts.

As can be seen in the table, the specific activity changes in the order SO_3/ZrO_2-t-600 > SO_3/ZrO_2-m-600 ≈ SO_3/ZrO_2-m-400 > $F/ZrO_2 \approx Zr(SO_4)_2$ > $Al_2(SO_4)_2 \approx SO_3/Al_2O_3 > SO_3/ZrO_2$-xra. HZSM-5, F/Al_2O_3, HPA, and zirconium oxides were found inactive in the reaction.

A comparison between the strength of proton sites and the activity of catalysts indicates that there is no correlation between these values. Moreover, the strongest proton acid, HPA, is inactive in this reaction, whereas fluorinated zirconia, which has no proton sites, exhibits a noticeable activity. This means that the pro-

Acid properties of catalysts and their activity in the skeletal isomerization of *n*-butane

No.	Catalyst	T_{calc}, °C	S_{BET}, m^2/g	ν(CO), cm^{-1}	N_{CO}, μmol/m^2	*PA*, kJ/mol	N_{H}, μmol/m^2	$w \times 10^6$, mol m^{-2} h^{-1}
I	$H_3PW_{12}O_{40}$/Sibunit	170	20	–	–	1120	2.6	0.005
II	HZSM-5	500	450	2195	0.04–0.09	1170	0.36	0
				2228	0.13–0.19			
	5.0%F/Al_2O_3	500	200	2196	0.43	1180	0.17	0.01
				2211	0.32			
				2223	0.18			
	$Al_2(SO_4)_3$	500	40	2217	1.75	1170	0.42	0.11
				2225	1.50			
				2232	0.50			
	13%SO_3/Al_2O_3	550	240	2196	0.08	1170	0.15	0.10
				2209	0.38			
				2225	0.21			
	$Zr(SO_4)_2$	500	11	2198	1.82	1170	3.0	0.74
				2224	0.91			
	7.7%SO_3/ZrO_2-m	400	33	2181	3.73	1170	0.82	6.7
				2199	2.42			
				2205	0.76			
				2209	0.30			
	5.7%SO_3/ZrO_2-m	600	68	2196	2.78	1170	0.34	7.5
				2200	2.13			
				2205	0.74			
				2209	0.41			
	8.0%SO_3/ZrO_2-xra	400	272	2199	0.51	1170	0.10	0.05
				2208	0.74			
	7.0%SO_3/ZrO_2-t	600	149	2190	1.21	1170	0.19	85
				2200	2.50			
				2210	0.41			
III	2.0%F/ZrO_2	500	44	2187	7.05	–	–	0.82
				2195	2.02			
				2207	0.03			
	ZrO_2-t	430	150	2180	0.77	–	–	0
				2201	0.55			
				2203	0.32			
	ZrO_2-m	900	50	2170	2.48	–	–	0
				2183	1.28			
				2192	0.84			

Note: m and t refer to zirconium oxide with monoclinic and tetragonal structures, respectively; xra is X-ray amorphous.

tonation of butane with the formation of a carbonium ion and its conversion into a carbenium ion does not occur at the surface of the test catalysts. At the same time, the strict dependence of the rate of reaction on the strength of sites was observed in the reactions that occur with the participation of proton sites [19]. The absence of a dependence of the rate of the low-temperature skeletal isomerization reaction of alkanes on the strength of proton sites suggests that proton sites do not participate in a limiting step of the reaction.

The inactivity of catalysts simultaneously containing proton and Lewis sites, for example, zeolite and crystalline aluminum and zirconium sulfates, contradicts the published concept on the necessary participation of both types of sites in the activation of an alkane molecule.

The abstraction of a hydride ion is a possible mechanism of the activation of an alkane molecule at a Lewis site. However, the low activity of aluminum sulfate, which has the strongest Lewis sites, does not support this assumption. Modified zirconium oxides are most active in this reaction. At close strengths and concentrations of both Brønsted and Lewis sites, their specific activity changed by more than three orders of magnitude. Note that this difference manifests itself in catalysts with close chemical compositions. As can be seen in the table, the nature of the modifying anion, the crystal structure of zirconium oxide, and the temperature of calcination are the most important factors affecting activity. Moreover, the activity of sulfated zirconium oxides in this reaction essentially depends on the sulfate content [20, 21]. However, it is not related to the presence of a crystalline phase of zirconium sulfate. The activity of zirconium sulfate is insignificant; however, upon the thermal decomposition of this compound, it dramatically increased and approached the activity of the sulfated oxide with the tetragonal structure [14]. Hence, it follows that either the strength of Lewis sites is not a crucial factor in this process or the Lewis sites with a very narrow strength distribution are required for the reaction to occur. It is likely that the additional participation of other sites is required for the activation of an alkane molecule; that is, the active center is a complex formation whose constituents can be aprotic, proton, and basic sites. In these centers, geometric and energetic factors can play a considerable role because not only the geometric similarity of a complex active center and the reactant molecule but also an optimum energy of their interaction are required for the reaction to occur. In this case, the rate of reaction would be expected to be a sharp extremal function of the strength of active centers because changes in the nature of the anion and the cation, as well as insignificant changes in the crystal lattice, could result in changes in the structure of this center. It is likely that this unique situation occurs in sulfated zirconia with the tetragonal structure. To understand this situation, the catalytic behavior of systems with similar properties should be studied. We intend to perform such a study.

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