Isomerization of *n*-butane on the SO_4/ZrO_2 catalyst promoted by IV Period metals

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The catalytic activity of superacidic systems based on SO_4/ZrO_2 and modified by IV Period metals in isomerization of *n*-butane was studied. At low temperatures of the reaction, the introduction of Fe³⁺, Sc³⁺, Co²⁺, or Zn²⁺ ions (1%) increases the yield of isobutane by 1.5 times due to the activation of *n*-butane on the sites created by the promoting ions. The addition of Cr³⁺, V⁴⁺, or Mn²⁺ (1%) decreases the catalytic activity because of a decrease in the catalyst acidity, most likely, due to the reduction of surface sulfur species. The influence of the nature of the support and surface additives of SiO₂. TiO₂, and ZrO₂ on the activity and selectivity of the catalytic system in *n*-butane isomerization was studied.

Key words: *n*-alkane isomerization, *n*-butane, superacids, SO_4/ZrO_2 , catalysts, modification by Fe³⁺, Se³⁺, Co²⁺, Zn²⁺, Mn²⁺, Cr³⁺, and V⁴⁺.

Isomerization of lower alkanes is one of the urgent problems of oil processing and petrochemistry.¹ It has been established that catalytic isomerization requires strong acidic sites. Such sites have been found in some zeolites² and in systems based on metal oxides promoted by anions of strong acids (SO_4^{2-} and WO_4^{2-}).^{3,4}

In previous works, we have studied the catalytic properties of zeolite catalysts modified by metals, metal oxides, and anionic additives⁵ and specific features of the mechanism of isomerization of *n*-butane and *n*-hexane on superacidic catalysts of the SO_4/ZrO_2 type,^{6,7} which can be an alternative to zeolite systems. In addition, SO_4/ZrO_2 catalysts are close in activity to chlorinated alumoplatinum systems. It is known that the introduction of modifiers can be used for increasing the activity and selectivity of catalysts. The main attention of researchers is concentrated on investigation of superacidic systems containing Fe and Mn,⁸⁻¹⁰ whereas only several works are devoted to the influence of other modifiers.^{11,12}

In this work, we studied the influence of different modifying cations and SiO_2 , TiO_2 , and ZrO_2 additives introduced into the support on the activity and selectivity of SO_4/ZrO_2 -based catalysts in *n*-butane isomerization.

Experimental

Samples of $Zr(OH)_4$ with a specific surface (S_{sp}) of 150 m² g⁻¹ (Magnesium Electron Co., XZ0706/03) and 300 m² g⁻¹ (hereinafter, $Zr(OH)_4$ -300; synthesized in the Insti-

tute of Chemistry of Surfaces of the National Academy of Sciences of the Ukraine, Kiev) were used as supports.

To obtain the SO_4/ZrO_2 system (SO_4/ZrO_2 -300), SO_4^{2-} anions were supported on zirconium hydroxide pre-dried at 120 °C for 2 h ($Zr(OH)_4$ -300) by treatment with a 1 N aqueous solution of H_2SO_4 ; the concentration of SO_4^{2-} anions in the sample was 5 wt.%. The samples were dried at 120 °C for 6 h and calcined in a dry air flow at 400-800 °C for 2 h.

The catalysts containing Fe^{3+} were prepared by the impregnation of $Zr(OH)_4$ with a mixture of a 1 N aqueous solution of H_2SO_4 and a 0.3 M aqueous solution of $Fe(NO_3)_3$; the concentration of SO_4^{2-} anions in the sample was 5 wt.%, and the metal concentration was 1-2 wt.%. The catalysts containing Mn^{2+} , Zn^{2+} , Sc^{3+} , V^{4+} , Co^{2+} , or Cr^{3+} were synthesized by a similar procedure from nitrates of the corresponding salts. The samples were dried at 120 °C for 6 h and calcined in a dry air flow and at 650 °C for 1 h.

The catalysis modified by SiO₂, TiO₂, or ZrO₂ were obtained by the treatment of the noncalcined 1% Fe/SO₄/ZrO₂ system with tetraethoxysilane, TiCl₄, or a solution of Zr(OAc)₄ in ethanol, respectively. The samples were dried at 120 °C for 6 h and calcined in a dry air flow at 600 °C for 2 h.

n-Butane isomerization was carried out in a flow-type installation at 150–270 °C and atmospheric pressure in a He flow. The loading of the catalyst was 1 cm³, the volume flow rate of *n*-butane was 300 h⁻¹, and the molar ratio He : n-C₄H₁₀ = 4 : 1. The reaction products were analyzed by GLC on columns packed with Silipor 600 or Al₂O₃.

Results and Discussion

Influence of the modifier nature on the catalytic activity. Our experiments showed that all catalytic systems were active in *n*-butane isomerization in the ab-

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Fig. 1. Activity (1-5) and selectivity (1'-5') of nonmodified SO₄/ZrO₂ (1, 1') and SO₄/ZrO₂ catalysts modified by Zn (2, 2'), Sc (3, 3'), Fe (4, 4'), and Co (5, 5') in *n*-butane isomerization at different temperatures (here and in Figs. 2 and 3, Y is the yield of isobutane, and S is the selectivity with respect to isobutane).

sence of hydrogen. Dilution of hydrocarbon with helium is necessary to suppress cracking processes resulting in catalyst deactivation. Nonmodified SO_4/ZrO_2 exhibits a noticeable activity already at 190 °C (conversion >5%). The temperature increase results in an increase in the yield of *n*-butane, which reaches a maximum at 240---260 °C. The highest yield of isobutane (27.7 wt.%) was obtained at 240 °C. The selectivity with respect to isobutane remains high at all temperatures used, although it somewhat decreases as the temperature increases (Fig. 1).

The modifiers can be classified into two groups by the influence of catalyst activity. For the systems modified by Fe³⁺, Sc³⁺, Co²⁺, and Zn²⁺ ions (see Fig. 1), the maximum of activity is shifted toward lower temperatures (190–230 °C) as compared to that in the nonpromoted system. The introduction of modifiers of the second group (Fe³⁺-Mn²⁺, Cr³⁺, V⁴⁺) (Fig. 2) considerably decreases the catalyst activity: the yield of isobutane does not exceed 4–10 wt.% and remains unchanged when the temperature increases to 260 °C.

All catalytic systems are characterized by high selectivity with respect to isobutane (80-95%). The main



Fig. 2. Activity (1-4) and selectivity (1'-4') of nonmodified SO₄/ZrO₂ (1, 1') and SO₄/ZrO₂ catalysts modified by Fe-Mn (2, 2'), V (3, 3'), and Cr (4, 4').

data on *n*-butane isomerization are presented in Table 1.

When the SO_4/ZrO_2 system is modified by Fe^{3+} ions, the introduction of 1 wt.% Fe^{3+} increases the yield of isobutane to 30.4 wt.%, although the high selectivity is retained (Fig. 3). A twofold increase in the Fe^{3+} concentration results in a considerable decrease in the catalyst activity, and the yield of isobutane decreases to 10-12 wt.%.

To elucidate the influence of modifying additives on the catalytic activity, one should determine the nature of centers responsible for the activation and transformation of n-butane and estimate the possible effect of the modifiers on these centers.

It has previously been shown that the isomerization of *n*-butane can proceed via two mechanisms depending on the catalyst nature. The first of them is observed for nonpromoted SO_4/ZrO_2 through the formation of a $[C_8^+]$ intermediate on strong Brönsted acidic sites (BAS).^{6,7,13} The second mechanism includes the stages of dehydrogenation---isomerization of C_4H_{10} and is characteristic of bifunctional catalysts containing Pt and moderately strong BAS.^{6,7,14} The first mechanism is more convincing, because the reaction does not require

Catalyst	T/°C	X (%)	Yield of re	S (%)		
			C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	C ₅ H ₁₂	
SO ₄ /ZrO ₂	190	5.4	0.1	5.1	0.2	94.4
	225	26.1	1.3	22.9	1.9	87.7
	240	34.0	3.1	27.7	3.2	81.5
1% Fe/SO ₄ /ZrO ₂	190	35.0	2.0	30.4	2.6	86.9
	210	29.4	1.6	25.7	2.1	87.4
1% Sc/SO ₄ /ZrO ₂	190	19.8	0.5	18.6	0.7	93.9
	230	33.2	2.3	28.2	2.7	84.9
1% Co/SO ₄ /ZrO ₂	190	29.9	1.2	26.8	1.9	89.6
	210	27.6	1.5	24.1	2.0	87.3
$1\% \text{ Zn/SO}_4/\text{ZrO}_2$	190	24.3	0.9	22.3	1.1	91.8
	230	25.3	1.5	21.9	1.9	86.6
1% Fe + 1% Mn/SO ₄ /ZrO ₂	250	11.2	0.7	9.8	0.7	87.5
	270	12.0	[.0	10.0	1.0	83.3
1% Cr/SO ₄ /ZrO ₂	250	4.5	0.1	4.3	0.1	95.6
	270	5.2	0.3	4.9	Traces	94.2
1% V/SO ₄ /ZrO ₂	230	4.5	0.2	4.1	0.2	91.1
	250	5.6	0.3	5.0	0.3	89.3

Table 1. Isomerization of *n*-butane on SO₄/ZrO₂ catalyst modified by IV Period metals ($v_{vot} = 300$ h⁻¹, molar ratio He : *n*-C₄H₁₀ = 4 : 1)

Note. The following designations are used here and in Table 2: T is temperature, X is conversion of n-butane, and S is selectivity with respect to isobutane.

hydrogen, which is necessary for n-alkane isomerization in the presence of bifunctional systems.

The data in Fig. 4 show that all the superacidic catalysts are characterized by a linear dependence of the yield of isobutane on the conversion of n-butane. Therefore, isomerization, disproportionation, and cracking occur in



Fig. 3. Influence of the temperature of *n*-butane isomerization on the yield of isobutane (1, 2) and selectivity of the reaction (1', 2') on 1% Fe/SO₄/ZrO₂ (1, 1') and 2% Fe/SO₄/ZrO₂ (2, 2') catalysts.

parallel on catalysts of this type. It can be assumed that n-butane isomerization occurs on the same specific sites in the cases of all of the catalysts. Mainly BAS are responsible for the catalyst activity, and the isomerizing ability of the system should depend on their strength.

The enhanced acidity of the SO_4/ZrO_2 system was shown¹⁵ to be connected with the surface S^{6+} compounds. The modifiers that decrease the catalyst activity



Fig. 4. Yield (Y) of isobutane as a function of the conversion (X) of *n*-butane for superacidic systems studied within the 190-250 °C temperature range.

Catalyst	<i>Т/</i> °С	X (%)	Yield of re	S (%)		
			C ₃ H ₈	<i>i</i> -C ₄ H ₁₀	C ₅ H ₁₂	
1% Fc/SO ₄ /ZtO ₂	210	29.4	1.6	25.7	2.1	87.4
1% Fe/SO ₄ /ZrO ₂ -300	210	9.3	0.4	8.6	0.3	92.5
1% Fe/SO ₄ /ZrO ₂ + 1% SiO ₂	190 230	11.2 10.1	0.4 0.4	10.3 9.1	0.5 0.6	92.0 90.1
1% Fe/SO ₄ /ZrO ₂ + 3% SiO ₂	230	1.4	0.1	1.3	Traces	92.9
1% Fe/SO ₄ /ZrO ₂ + $3%$ TiO ₂	230	10.5	0.5	9.4	0.6	89.5
$1\% \text{ Fe/SO}_4/\text{ZrO}_2 + 3\% \text{ZrO}_2$	210	9.6	0.3	9.0	0.3	93.8

Table 2. Influence of the support nature on the activity of iron-containing superacidic catalysts ($v_{vol} = 300 \text{ h}^{-1}$, molar ratio He : $n \cdot C_4 H_{10} = 4$: 1)

(V, Cr) are introduced into the system at the intermediate stage of oxidation of V⁴⁺ and Cr³⁺. During pretreatment they can interact with active sites and oxidize to V⁵⁺ and Cr⁶⁺ due to a decrease in the oxidation state of sulfur. It can be expected that due to the Mn²⁺ \rightarrow Mn⁴⁺ transition, excess Mn²⁺ in the 1% Fe + 1% Mn/SO₄/ZrO₂ system exerts a similar effect. According to the published data,¹⁰ an increase in the activity of this system is observed only at a specified ratio of Fe³⁺ to Mn²⁺ (1.5% Fe and 0.5% Mn), whereas manganese systems containing no iron are inactive. The data obtained coincide with the results for the Pt-promoted systems in which sulfur was also reduced¹⁵ due to reaction with Pt⁰.

The modifiers that are metal ions in the highest oxidation states $(Zn^{2+}, Fe^{3+}, Sc^{3+}, and Co^{3+})$ have no noticeable effect on the oxidation state of sulfur. In several cases, a decrease in activity can be related to the partial exchange of protons of BAS on the metal ions. At the same time, the metal cations and particles of metal oxides can additionally activate alkane molecules and thus increase the catalytic activity of the system.

Effect of the support on the catalytic activity. Table 2 presents data on the isomerization of *n*-butane on 1% $Fe/SO_4/ZrO_2$ catalysts prepared on the basis of the SO_4/ZrO_2 and SO_4/ZrO_2 -300 supports and on systems obtained by treatment of the SO_4/ZrO_2 surface with compounds that form the oxides ZrO_2 , TiO_2 , and SiO_2 . The treatment of the catalyst surface was aimed at stabilization of the surface sites formed by SO_4^{2-} groups and prevention of their destruction and removal from the sulfur surface in a hydrocarbon reducing medium. Some decrease in the catalyst activity and an increase in its stability were expected.

The use of SO_4/ZrO_2 -300 as the support results in a decrease in the yield of isobutane by 3--4 times as compared with that for the SO_4/ZrO_2 -based catalyst. The activity can decrease due to a change in the nature of the hydroxide at the stage of preparation, which results in transition of the system surface to a phase that does not form active sites during promotion with sulfur.

The introduction of the surface additives SiO_2 , TiO_2 , and ZrO_2 also results in a considerable decrease in the catalyst activity in *n*-butane isomerization, and the yield of isobutane does not exceed 10–11 wt.%. It can be assumed that the additives of oxides block the active sites, and the latter become inaccessible for alkane molecules, which impedes the formation of the bimolecular transition complex $[C_8^+]$. Therefore, the support nature strongly affects the catalytic activity of the SO₄/ZrO₂-based systems. To prepare an active catalyst, amorphous Zr(OH)₄ should be used. The catalyst activity decreases when the surface additives SiO₂, TiO₂, and ZrO₂ are introduced.

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