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Effect of the Sulfate Sulfur Content and the Preparation Procedure on the Catalytic Properties of Sulfated Zirconium Oxide

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Abstract—The effects of the composition and the procedure of preparing sulfated zirconium oxides on their catalytic properties in the reactions of 1-butene isomerization to 2-butenes and isobutanol dehydration were studied. The activity was found to depend on the nature of parent zirconium oxide, the sulfate sulfur content, and the temperature of calcination. Catalysts prepared from a crystalline oxide exhibited the highest activity. Their activity depends on the sulfate sulfur content. The calcination of catalysts at temperatures higher than 400°C resulted in a detectable loss of sulfate. The activity of sulfated oxides prepared from an amorphous oxide was noticeably lower; it depended only slightly on the temperature of calcination and sulfate sulfur content. The catalytic behavior of the sulfated oxide in both of the reactions is indicative of the absence of superstrong proton sites. Based on the results, assumptions on the nature of formed surface compounds were made.

INTRODUCTION

The ability of sulfated zirconium oxides to catalyze the skeletal isomerization of alkanes at low temperatures generated considerable interest in them, and several reviews on this subject matter were published [1–5]. However, although a great body of data was obtained, many problems remain unsolved. This is especially true in regard to the nature of the active components of solid superacids and to the mechanisms of their action. The occurrence of proton and aprotic acid sites on the surface of these catalysts was found [6–8]; however, the superacidity of these systems was not established by direct measurements. Because the reaction mechanism of skeletal isomerization is unknown, many problems associated with the formation of catalyst acid sites in the course of preparation are still unclarified. To elucidate the roles of various factors in the course of preparation of these catalysts and in the formation of these unique properties, it is of interest to study their behavior in typical catalytic reactions of the acid type, which occur by a known mechanism, and whose rates depend on the strength of sites.

The aim of this work was to examine the effects of the concentration of sulfate ions and the nature of the parent zirconium oxide on the catalytic properties of sulfated zirconia.

The activity of catalysts was studied in the model reactions of double bond migration in 1-butene and of isobutanol dehydration. It was found previously [9] that the former reaction occurs at the proton sites of catalyst surfaces. The latter reaction mainly occurs at proton sites; to a lesser degree, it also occurs with the participation of a pair of aprotic and basic sites, and the isomeric composition of butenes formed in this case is different. The rates of both reactions depend on the strength and concentration of sites. It was found that the activity with respect to the number of proton sites increases proportionally to the strength of sites [10]. In binary silicate catalysts [11], the activity and strength of a proton site is almost independent of the ratio between components, whereas is depends on the nature of the metal.

The SOH group is the carrier of proton sites in sulfate catalysts; in crystalline sulfates, its activity depends only slightly on the nature of the metal [12]. In crystalline aluminum sulfate and sulfated aluminum oxides, the activity of proton sites is almost independent of the concentration of these groups [13]. Taking into account these facts, we intended to obtain data on the proton-donor properties of sulfated zirconium oxides by studying their activity in the above reactions. A change in the total activity will reflect a change in the concentration of proton sites depending on the composition of catalysts and on various factors of their preparation.

EXPERIMENTAL

Zirconium hydroxide and zirconium oxide were used as starting compounds for the preparation of sulfated zirconia. Zirconium hydroxide was prepared from a zirconium oxynitrate solution by precipitation with an aqueous ammonia solution at 65–70°C and a constant value of pH 9. The precipitate (zirconium hydroxide), which was washed and dried at 110°C, was calcined at 500°C to obtain crystalline zirconium oxide.

The hydroxide was sulfated by the treatment with a sulfuric acid solution on filter in accordance with a published procedure [1] or by incipient wetness impregnation using a solution containing a given amount of sulfuric acid. Zirconium oxide was also sulfated by the latter method. In this case, the duration of the interaction between the oxide and sulfuric acid was varied (2 and 30 h). In the subsequent text, the interaction for 30 h is referred to as prolonged. After drying at 110°C, the samples were calcined in a flow of dry air at different temperatures (from 400 to 650°C).

Sulfated zirconium oxides were analyzed by the dissolution in hydrofluoric acid followed by the removal of the acid and the analysis of the solution by inductively coupled plasma atomic emission spectrometry (ICP AES).

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

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

The catalytic activity of samples in the reactions was studied by the flow-circulation method. The reaction rate ($w_{\rm iso}$) under standard conditions at 220°C, 20% conversion, and a butene concentration of 7 vol % in a mixture with nitrogen was taken as a measure of activity in 1-butene isomerization. The activity in alcohol dehydration was measured at 300°C and an initial alcohol concentration of >30 vol %. When the stationary alcohol concentrations is higher than 30 vol %, the reaction rate is independent of the concentration of the component; that is, the reaction is of zero order. In this case, the reaction rate constant is equal to the reaction rate ($w_{\rm deh}$). This value was taken to characterize activity in the dehydration reaction. Before testing, the catalysts were calcined in a flow of air at a given temperature and then evacuated at 400°C and a pressure of ~10^{-2} torr. Thereafter, the temperature was decreased to a reaction temperature in a nitrogen flow.

Table 1. Catalytic properties of zirconium oxide treated with sulfuric acid

$[SO_3]_0$, wt %	$T_{\rm calcination}$, °C	$[SO_3]$, wt %	S, m^2/g	$w_{\rm iso}(w_{\rm deh})$*, mol (g Cat)$^{-1}$ h^{-1}
1.1	400	0.5	100	0.2 (0.02)
	500	0.5	102	0.25 (0.02)
	650	–	83	0.1
3.9	400	1.8	83	1.9
	500	–	101	0.6
	650	1.1	100	0.9 (1.5)
5.2	250	–	79	1.6
	400	3.3	93	3.9/2.9
	500	2.8	97	2.5
	650	2.4	94	1.4 (1.5)
10.4	400	7.7	39	2.0
	500	4.9	74	2.2
	650	1.5	100	1.7
15.3	400	12.2	50	2.7 (3.3)
	500	9.8	52	2.7
	650	2.0	100	–
20.1	250	–	24	1.7
	400	20.3	27	2.2 (3.4)
	500	19.0	33	1.6
	650	2.7	110	1.8
6.0**	400	5.7	63	1.3
	600	3.6	68	0.9
9.0**	400	9.0	55	0.85
	600	5.7	49	0.84

* $w_{\rm iso}$ is the reaction rate of isomerization at a 20% conversion of 1-butene; $w_{\rm deh}$ is the reaction rate of dehydration.

** The catalysts were prepared by the prolonged interaction of zirconium oxide and sulfuric acid.

RESULTS AND DISCUSSION

Samples containing from 1.1 to 20 wt % SO_3 were prepared based on zirconium oxide, and samples containing up to 10 wt % SO_3 were prepared based on zirconium hydroxide. Tables 1 and 2 summarize their compositions and properties. The concentrations $[SO_3]_0$ of sulfate sulfur added in the course of preparation on a calcined zirconia basis are given in Tables 1 and 2. As can be seen in Table 1, the temperature of calcination significantly affected the sulfate sulfur content of samples prepared based on crystalline zirconium oxide. Sulfate was partially degraded in the course of catalyst calcination; the higher the temperature of calcination, the greater the loss of sulfate. After calcination at 650°C, the residual sulfate content was no higher than 2.7 wt % SO_3.

The specific surface areas of samples dramatically decreased as the SO_3 content increased. The specific surface areas of samples calcined at different temperatures were almost equal at similar SO_3 contents.

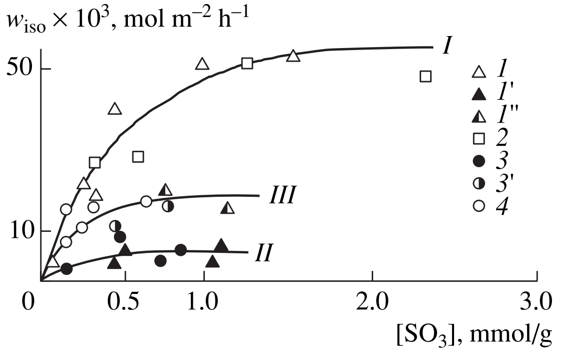

Fig. 1. Effect of the concentration of sulfate sulfur in catalysts prepared from (*I*) zirconium oxide or (*II*) zirconium hydroxide and (*III*) by the prolonged interaction and calcined at (*1*, *1*', *1*'') 400, (*2*) 500, (*3*, *3*') 600, or (*4*) 650°C on the specific activity of the catalysts in the reaction of 1-butene isomerization.

The calcination of catalysts based on zirconium oxide at 650°C, which was accompanied by the degradation of a portion of sulfate, resulted in the regeneration of the initial oxide surface area. At an SO_3 concentration of 0.5–3 wt %, the surface area was 93–110 m^2/g; this value is consistent with the surface area of the parent crystalline oxide.

The interaction of sulfuric acid with zirconium hydroxide results in the formation of sulfate compounds, which are more thermally stable and exhibit more developed specific surface areas (Table 2).

The X-ray diffraction patterns of the resulting samples exhibited only reflections due to ZrO_2 over the entire ranges of SO_3 concentrations and calcination temperatures. The formation of crystallized zirconium sulfate in a detectable amount was not observed. The crystal structure of ZrO_2 in catalysts depends on the nature of the zirconium compound used for sulfation. The monoclinic modification of ZrO_2 was retained over the tested range of the temperatures of calcination of sulfated zirconium oxide prepared from the crystalline oxide. The sulfated oxide prepared from zirconium hydroxide up to calcination temperatures of 400°C was X-ray amorphous. As was repeatedly mentioned in the literature [4], thermal treatment at higher temperatures resulted in the formation of highly dispersed tetragonal ZrO_2. This modification of ZrO_2 was also retained at a maximum of the tested calcination temperatures (650°C).

Table 2. Catalytic properties of zirconium hydroxide treated with sulfuric acid

$[SO_3]_0$, wt %	$T_{calcination}$, °C	$[SO_3]$, wt %	S_{sp}, m^2/g	w_{iso}, mol (g Cat)$^{-1}$ h^{-1}
3.3	400	3.5	480	0.5
	600	0.31	32	0.005
4.5	400	4.2	171	0.85
	600	3.9	107	1.1
7.0	400	5.1	99	1.3
	600	–	–	0.8
8.0	600	6.2	168	0.46
10.0	400	8.25	272	0.52
	600	6.70	168	0.84

Tetragonal and monoclinic zirconium oxides are almost inactive in the reaction of 1-butene isomerization. The samples exhibited a detectable activity after supporting even a small amount of sulfate. The catalyst activity depends on the SO_3 content and the temperature of calcination. The total activity increased with the SO_3 content of the sample calcined at 400°C (Table 1); it reached a weakly pronounced maximum at ~3.3 wt % SO_3 and then decreased. An increase in the calcination temperature, which was accompanied by the decomposition of a portion of sulfate, resulted in a decrease in the activity of catalysts.

Figure 1 demonstrates the specific activity as a function of the concentration of sulfate ions in the samples. As can be seen, it is described by saturation curves for all of the obtained series of samples. The maximum activity depends on the preparation procedure. The sulfated oxides prepared by the short-time interaction of the oxide with sulfuric acid exhibited the highest activity (curve *I*). The samples prepared by the interaction of the oxide with sulfuric acid for a longer time were less active (curve *II*). The samples prepared by the sulfation of the hydroxide exhibited the lowest activity (curve *III*). In a particular catalyst preparation procedure, the activity depended on only the concentration of sulfate sulfur.

Figure 2 shows the activity per mole of sulfate sulfur as a function of sulfate sulfur concentration in the test samples. The activity of sulfated zirconium oxide increased from 0 to 9 h^{-1} as the SO_3 content was increased up to ~0.15 mmol/g; it reached a maximum value at an SO_3 content of 1.4–2.5 wt % and then dramatically decreased (curve *I*). The extremal curve indicates that not all of the sulfate groups are the sources of protons. It is likely that, at low sulfate contents, the oxide is sulfated in a surface layer with the polydentate binding of sulfate anions. A decrease in the activity at high sulfate contents can be explained by the assumption that the surface composition remains unchanged, whereas an excess of sulfate sulfur penetrates into near-surface oxide layers and does not participate in the reaction. In the region of the maximum activity, the surface coverage with sulfate anions is ~75% on the assumption that the anion occupies an area of 25 Å^2 [14].

In the catalysts prepared by the sulfation of zirconium hydroxide, the activity per mole of sulfate sulfur plotted as a function of sulfate concentration has a similar shape (Fig. 2, curve *II*); however, the activity changes on a much smaller scale. Because the reactivity of the hydroxide toward sulfuric acid is higher than that of the oxide, it is believed that in this case bulk sulfates are formed; however, at present, there is no evidence for their occurrence. Actually, the highly dispersed oxide in a low-temperature tetragonal modification is formed; this is possible because of the stabilizing effect of sulfate anions. The samples resulting from the prolonged interaction of zirconium oxide with sulfuric acid approached the sulfated oxide based on the hydroxide in their properties. The low activity of both catalysts can indicate that the polydentate binding of sulfate ions is predominant in these catalysts. This hypothesis is supported by data on the strength and concentration of proton sites in the catalysts of both sample series with similar concentrations of sulfate sulfur [8]. At calcination temperatures equal to 400 and 600°C, the concentrations of proton sites in catalysts based on zirconium oxide were higher by factors of 4 and 3.5, respectively. However, the strengths of proton sites in these catalysts were equal (PA = 1170 kJ/mol), and the reaction rates of 1-butene isomerization referenced to the concentration of proton sites were similar. These rates were insignificantly higher than those for amorphous and crystalline aluminosilicate catalysts [10].

Because aprotic sites occur on the surface of these catalysts along with proton sites, it is of interest to follow the behavior of the catalysts in a model reaction that occurs at not only proton but also aprotic sites. The dehydration of alcohols is a reaction of this kind. It occurs either by a carbenium ion mechanism at proton sites or with the participation of a pair of aprotic and base sites. Information on reaction pathways can be obtained from the products of isobutanol dehydration. Previously, it was found using a wide range of catalysts that a mixture of all butenes with an *n*-butene concentration of 33–40% is formed at proton sites. Isobutylene is formed at the paired sites [9, 15].

Zirconium oxide exhibits a low activity in isobutanol dehydration; its specific activity is equal to 2×10^{-5} mol m^{-2} h^{-1}. The sulfated oxide exhibits a high catalytic activity, which depends on the amount of supported sulfate and on the temperature of calcination (see Table 1), as in the case of 1-butene isomerization. This catalytic activity increases with the sulfate sulfur concentration in the sample.

All isomeric butenes are the products of isobutanol dehydration. The concentration of *n*-butenes is 26–28% regardless of the composition of catalysts and the temperatures of calcination. In this respect, the behavior of sulfated zirconium oxide is analogous to that of all of the bulk and supported sulfates tested [12, 17, 18].

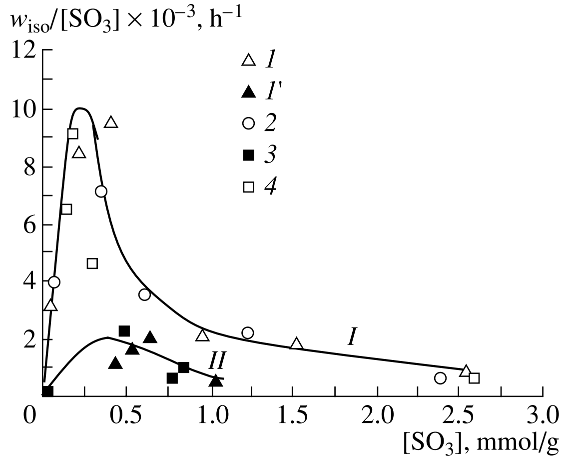

Fig. 2 Effect of the concentration of sulfate sulfur in catalysts prepared from (*I*) zirconium oxide and (*II*) zirconium hydroxide and calcined at (*1, 1'*) 400, (*2*) 500, (*3*) 600, or (*4*) 650°C on the activity in the reaction of 1-butene isomerization.

The results suggest that the specific activity of sulfated zirconium oxides is higher than the activity of aluminosilicate catalysts by a factor of ~5 [10] and that they are among the best catalysts for isobutanol dehydration. However, their specific activity (0.015–0.125 mol m^{-2} h^{-1}) is close to that of sulfated aluminum oxides (0.01–0.1 mol m^{-2} h^{-1}) over the tested range of SO_3 concentrations [18]. The reaction products formed on these catalysts exhibited the same composition, which is different from the composition of products formed on silicotungstic heteropoly acid (35–37% *n*-butenes), which bears only proton sites. The above data are indicative of the participation of the aprotic sites of the sulfated oxide in alcohol dehydration; however, the contribution of these sites is the same as that in sulfated aluminum oxides, which are not superacid catalysts. For superstrong aprotic sites, a considerable increase in the rate of dehydration and a decrease in the concentration of *n*-butene in the reaction products would be expected.

The results obtained in both of the reactions are unambiguously indicative of the absence of both proton and aprotic superstrong sites. This conclusion is consistent with the results obtained by the IR spectroscopy of adsorbed pyridine and CO [6, 8, 19].

We found that the catalytic properties of sulfated zirconium oxide vary over a wide range depending on a number of factors. The main factors affecting the properties of catalysts are the following: the composition of catalysts, the nature of the parent oxide, the temperature of calcination, and the duration of the interaction of a sulfuric acid solution and the oxide in the course of sulfation.

The most probable sources of proton sites are SOH groups. Because both of the reactions occur at proton sites, the effects of the above factors are primarily due to changes in the concentration of SOH groups. Based on this approach, processes that occur in the preparation of sulfated zirconium oxide can be represented as described below. On the treatment of zirconium oxide with a sulfuric acid solution, the components react to form various sulfates. Based on the catalytic behavior and thermal stability, it is believed that at least normal and acidic sulfates are formed. Because acid sulfates are less thermally stable compounds, they undergo degradation as the temperature of calcination is increased. This is evident from a decrease in the concentration of sulfate sulfur and in the activity with calcination temperature (see Table 1). The behavior in the isomerization reaction (Figs. 1, 2) suggests that the surface composition remained almost unchanged at the concentrations of sulfate anions higher than 0.5–0.7 mmol SO_3/(g Cat). A further increase in the amount of supported sulfuric acid results in either an increase in the thickness of a surface sulfate layer or the formation of dispersed zirconium sulfates rather than changes the surface composition. The ratio between surface and bulk sulfates also depends on the nature of the parent oxide. Because of a higher reactivity of the hydroxide, the concentration of bulk sulfates is higher in this series of catalysts, as follows from their lower specific activities.

The results demonstrated that the specific activity of catalysts based on zirconium oxide in the model reactions is higher than the activity of hydroxide-based catalysts. Although the strengths of proton and aprotic sites in the catalysts of both series are similar, their behaviors in the reaction of *n*-butane skeletal isomerization were different; catalysts based on zirconium hydroxide are much more active [14, 20]. Thus, it follows that skeletal isomerization takes place at more complex centers than single proton or paired (aprotic–basic) sites at which the model reactions occur.

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