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Catalytic Properties of the Thermal Decomposition Products of $Zr(SO_4)_2 \cdot 4H_2O$

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Abstract—The catalytic activity of the thermal decomposition products of $Zr(SO_4)_2 \cdot 4H_2O$ in the reactions of 1-butene isomerization to 2-butenes, isobutanol dehydration, and *n*-butane skeletal isomerization was studied. Their behaviors in typical acid reactions and in skeletal isomerization were found to be considerably different. In the first two reactions, which occur with the participation of proton sites, the activity of zirconium sulfates was an extremal function of hydrate calcination temperature. Zirconium sulfate calcined at 400–550°C was the most active catalyst. The reasons for such behavior are discussed. In the skeletal isomerization of *n*-butane, crystalline zirconium sulfate was practically inactive, and it became active only after degradation. The results suggest that the activation of *n*-butane molecules did not occur at proton sites.

INTRODUCTION

Sulfated zirconia is classified with superacid solids because of its ability to catalyze the skeletal isomerization of alkanes at low temperatures (20–100°C) [1–3]. Despite the great number of relevant publications, the mechanism of action of this class of catalysts is not clearly understood. However, there is no doubt that the interaction between catalyst components with the formation of surface sulfates is responsible for the appearance of high activity. In this context, it is of interest to study the activity of zirconium sulfate (a compound with known chemical composition and structure) and its thermal decomposition products in the skeletal isomerization of alkanes. The assumed superacidity raises the question of the relationship between the catalytic properties of sulfated zirconia and the properties of well-studied catalysts in heterolytic reactions whose rates depend on the strength of acid sites.

In this work, we studied the catalytic properties of the thermal decomposition products of $Zr(SO_4)_2 \cdot 4H_2O$ in the reactions of 1-butene isomerization to 2-butenes, isobutanol dehydration, and *n*-butane skeletal isomerization. As found previously [4, 5], the first reaction primarily occurs at proton sites, and the second occurs at both proton sites and paired (aprotic–base) centers. The rates of these reactions increase with the strength of active centers. Changes in the activity of the test catalysts in these reactions and in *n*-butane skeletal isomerization can give us an insight into the mechanism of the skeletal isomerization reaction.

EXPERIMENTAL

The starting compound used for preparing anhydrous crystalline zirconium sulfate was $Zr(SO_4)_2 \cdot 4H_2O$ synthesized according to the published procedure [6]. The samples were calcined in a drying oven at temperatures lower than 200°C for 10 h or in a muffle furnace at higher temperatures for 4 h.

The samples were studied by thermal and X-ray diffraction (XRD) analysis. The specific surface area and catalytic activity of the samples were also measured.

The XRD 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.

Catalytic properties in the reactions of 1-butene isomerization to 2-butenes, isobutanol dehydration, and *n*-butane skeletal isomerization were measured in a gradientless flow reactor under standard conditions. The isomerization of 1-butene was performed at 220°C and an initial 1-butene concentration of 7 vol % in a mixture with nitrogen. The activity was characterized as the rate of reaction at 20% olefin conversion [4]. The reaction rate of alcohol dehydration was measured at 300°C and an initial alcohol concentration of 10–50 vol % and characterized by the rate constant of reaction [5]. The reaction of *n*-butane skeletal isomerization was studied at 150°C and an initial *n*-butane concentration of 24 vol % in a mixture with nitrogen. The activity in the skeletal isomerization was characterized by a maximum reaction rate attained in the transformation of *n*-butane under the test conditions.

Before testing, the catalysts were calcined in the reactor in a flow of air at a given temperature and then evacuated at a pressure of ~10^{-2} torr. Thereafter, the setup was filled with dry nitrogen, and the temperature was decreased to a reaction temperature in a nitrogen flow.

Effect of the calcination temperature of zirconium sulfate hydrate on the specific surface area (*S*) and the reaction rates (*w*) of 1-butene isomerization, isobutanol dehydration, and *n*-butane isomerization

Calcination temperature, °C	S, m^2/g	w, mol g^{-1} h^{-1}		
		1-butene	isobutanol	*n*-butane
270	4.8	0.40	–	–
300	7.3	0.73	–	–
350	7.0	0.75	0.3	–
400	8.3	0.83	1.7	1.1×10^{-6}
450	5.0	0.73	–	–
500	11	2.50	2.4	1.2×10^{-6}
550	12	4.20	–	7.0×10^{-6}
600	48	7.00	6.5	8.2×10^{-6}
700	104	2.60	3.9	1.5×10^{-3}

RESULTS AND DISCUSSION

Endothermic effects at 185, 220, and 290°C due to water removal and an endothermic effect at 775°C due to sulfate decomposition were observed on heating $Zr(SO_4)_2 \cdot 4H_2O$. The decomposition began at 660°C and ended at 820°C. The weight losses up to 325°C corresponded to the removal of 3.94 mol of water; 0.06 mol was removed at higher temperatures without a pronounced effect.

According to XRD data, the crystal hydrate calcined at 300°C was anhydrous crystalline zirconium sulfate, whereas the calcination at 600°C afforded a mixture of the crystalline sulfate and tetragonal zirconia. A sample calcined at 700°C was a mixture of tetragonal and monoclinic zirconia with 4.3 wt % SO_3.

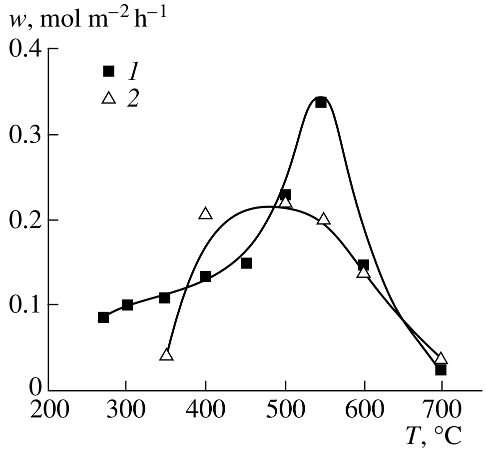
The table summarizes the specific surface areas of the crystal hydrate calcined at different temperatures. It can be seen that the surface area of zirconium sulfate was low (5–11 m^2/g). It noticeably increased after calcination at temperatures higher than 550°C because of sulfate decomposition and zirconia formation. The sample calcined at 700°C, which had the lowest concentration of sulfate sulfur, exhibited the highest surface area. Thus, the specific surface area can serve as a criterion for the phase purity of zirconium sulfate.

The thermal decomposition products of zirconium sulfate hydrate exhibited a catalytic activity in the reaction of 1-butene isomerization. In the course of reaction, an insignificant decrease in the activity (by no more than 5% in 1 h), which is typical of acid catalysts, was observed. The hydrate calcination temperature affected the activity and the dependence of the reaction rate on the steady-state concentration of 1-butene. The order of reaction was equal to 0 on samples calcined at 270 and 300°C, whereas the order of reaction was equal to 1 on samples calcined above 450°C. Within the intermediate range of sample calcination temperatures, the order of reaction on these samples varied from 0 to 1. In this respect, the behavior of zirconium sulfate is similar to that of aluminum sulfate [7].

Owing to the different orders of reaction, the activities of catalysts were compared using the reaction rate (*w*) measured under standard conditions at a 20% conversion of 1-butene (see Experimental). The table summarizes the results.

The reaction products are *cis*-2-butene and *trans*-2-butene. The ratio between them depends only on the conversion of 1-butene, and it is independent of both the calcination temperature of the initial hydrate and the degree of catalyst deactivation. As the conversion of 1-butene increased, the concentration ratio between *cis*-2-butene and *trans*-2-butene proportionally decreased to an equilibrium value. The initial ratio of the above linear function was 0.90 ± 0.05, as determined by extrapolation to zero conversion. Thus, a mixture of 2-butenes, which contained both of the isomers in almost equal amounts, was the primary product of 1-butene isomerization on crystalline zirconium sulfate.

In the tested range of calcination temperatures, the activity referenced to 1 g of catalyst changed by a factor of almost 20 and reached a maximum value in a sample calcined at 600°C (see table). The figure demonstrates the specific activity as a function of the calcination temperature of the initial hydrate. As can be seen, in this case, the activity is an extremal function of hydrate calcination temperature. However, in the range of existence of the crystalline sulfate (300–550°C), this change was not so high (by a factor of ~3.5). It follows that the calcination temperature not only affected the catalytic properties by changing the specific surface area, but it also had a certain effect on the state of the surface and its active centers. It was found previously that double bond isomerization primarily occurs at proton sites and the reaction rate depends on their strength and concentration. This is a test reaction for surface proton sites [4]. Based on these facts, it is believed that residual water has an inhibiting effect in samples calcined at lower temperatures, as was observed in aluminum sul-



Effect of the temperature of zirconium sulfate calcination on the specific activity in the reactions of (*1*) 1-butene isomerization and (*2*) isobutanol dehydration.

fate [7]. Water adsorbed on a proton site either fully blocks it or dramatically decreases its strength. Both of these processes can decrease the catalytic activity and affect the kinetic characteristics of the reaction. It is impossible to distinguish them based on the results of this study.

A decrease in the specific activity of samples after high-temperature calcination is associated with sulfate degradation. The activity of a sample containing 4.3 wt % SO_3 prepared by sulfate calcination at 700°C (0.025 mol m^{-2} h^{-1}) was close to the activity of sulfated zirconia containing the same amount of sulfate sulfur calcined at 500°C (0.03 mol m^{-2} h^{-1}) [8]. A decrease in the activity in the reaction that occurs at proton sites after the high-temperature treatment of sulfates is due to sulfate degradation (after thermal treatment at 600°C, a low-temperature tetragonal modification of zirconia was present in the sample along with the crystalline sulfate, whereas the residual concentration of sulfate sulfur after treatment at 700°C was 4.3 wt %), which decreased the concentration of proton sites with no change in their quality. This assumption is based on the following facts:

(1) The activity (and, consequently, strength) of proton sites in anhydrous crystalline Al, Ga, and Zr sulfates depends only slightly on the nature of the cation [9].

(2) In anhydrous crystalline $Al_2(SO_4)_3$ and sulfated aluminum oxides containing different amounts of sulfate sulfur calcined at 400–650°C, the activity of proton sites has a constant value regardless of composition and calcination temperature. On a proton affinity (PA) scale, the strength of these proton sites is 1170 kJ/mol [10].

(3) It was found by the IR spectroscopy of adsorbed CO and pyridine that the strength of proton and aprotic sites in sulfated zirconium oxides prepared by different procedures is close to that in crystalline zirconium sulfate [11, 12].

Considering these facts, one would hardly expect the strength of proton sites in the high-temperature decomposition products of zirconium sulfate to be significantly different.

A possible reason for the lower activity of high-temperature samples is butene oligomerization, which also occurs at proton sites and depends on their strength. This assumption is inconsistent with the behavior of a wide variety of acid catalysts with different strengths of acid sites in the above reaction. As catalysts do not undergo deactivation instantaneously, their activity in double-bond isomerization depends on the reaction rate extrapolated to the onset of reaction. If it is believed that the strongest sites are deactivated instantaneously, it is unlikely that a relationship between the strength of sites and the activity of a single site similar to that described previously [13] can be obtained. This relationship also describes data obtained more recently with sulfated zirconia and very strong solid acids, such as heteropoly acids, the strength of proton sites in which is 1120 kJ/mol on a PA scale.

Zirconium sulfate also exhibited high activity in the reaction of isobutanol dehydration. Its behavior in this reaction (the stability of its activity and the composition of reaction products) is analogous to that of aluminum sulfate [7]. The calcination temperature of the initial crystal hydrate and the catalyst deactivation in the course of reaction had no effect on the composition of the initially formed products. The reaction products are all possible butenes; the fraction of normal olefins is 25–26%, and it is independent of both the temperature of sample calcination and the conversion of the alcohol. The reaction rate per 1 g of catalyst is an extremal function of hydrate calcination temperature. It reached a maximum in a sample calcined at 600°C. The maximum difference in the activity within the tested range of calcination temperatures was by a factor of ~20 (see table).

The figure demonstrates the specific activity as a function of hydrate calcination temperature. It can be seen that the specific activity of calcination products remained constant over a wide range of hydrate calcination temperatures (400–550°C). The activity dramatically decreased at both higher and lower temperatures of calcination. A decrease in the activity after high-temperature treatment was due to sulfate degradation and the formation of a zirconium oxide, which is inactive in this reaction. It is likely that a crystal hydrate also occurred at a low temperature. In the case of this reaction, the specific activities of the sulfate calcined at 700°C and sulfated zirconia [8] are similar.

Thus, anhydrous crystalline zirconium sulfate is a highly active catalyst in the reactions of 1-butene isomerization and isobutanol dehydration. A common feature in the behavior of the above catalyst in these reactions is that the specific activity is an extremal function of sulfate calcination temperature (figure). The most probable reason for the inconstancy of the specific activity in the region of the crystalline sulfate is the presence of a small amount of firmly bound water on the surface. Water, which is a stronger base than 1-butene, forms hydrogen bonds with S–OH groups, which are active in the reaction, and 1-butene cannot cleave these bonds. The removal of water by increasing calcination temperature increased the activity. A maximum activity can also be attained by long-term calcination at a lower temperature, as was found with aluminum sulfate [7]. The basicity of the alcohol is higher than the basicity of water. Therefore, the alcohol can displace water from a hydrogen-bonded complex followed by protonation, and the reaction of alcohol dehydration can occur. However, this does not exclude the possibility of crystal hydrate formation in the fine pores of zirconium sulfate in the course of alcohol dehydration.

Note that, in terms of specific activity, crystalline zirconium sulfate calcined at 400–550°C is the most active catalyst among the catalysts tested previously in these reactions [4, 5]. Crystalline aluminum sulfate is closest in activity in the reaction of 1-butene isomerization. The maximum activities of the above catalysts differed by a factor of 1.7, whereas the concentration of proton sites on aluminum sulfate was higher by a factor of 1.6, as measured using the IR spectra of protonated pyridine [9, 10]. The activity of a proton site on crystalline zirconium sulfate was higher than the activity of a site on aluminum sulfate by a factor of 2.7. It follows that the strengths of proton sites on both of the crystalline sulfates differed only slightly, and zirconium sulfate has no strong (superacidic) sites, which are assumed to occur on sulfated zirconia.

The samples calcined at 400–700°C were taken for testing the activity in the reaction of *n*-butane skeletal isomerization. The table summarizes the results. As can be seen, the activity of samples calcined at 400–600°C was insignificant and much lower than the activity of sulfated zirconium oxides, which is $\sim(6–15) \times 10^{-3}$ mol g^{-1} h^{-1}. The activity in this reaction appeared only after calcination at 700°C, when the sulfate underwent degradation (the residual concentration of sulfate sulfur was 4.3%). This activity was comparable to the activity of sulfated zirconia in a tetragonal modification.

The behaviors of zirconium sulfate in typical acid reactions (1-butene isomerization and isobutanol dehydration) and in the skeletal isomerization of *n*-butane were different, and they should be discussed in terms of the possible mechanism of action. If the skeletal isomerization of butane takes place at proton sites, the reaction rate should be low because of a low basicity of the reactant. However, this assumption is inconsistent with a dramatic increase in the activity of sulfate thermal decomposition products, which have a much lower concentration of proton sites, as evidenced by a lower activity in the reactions of 1-butene isomerization and isobutanol dehydration. Judging by the invariability of the composition of alcohol dehydration products, aprotic sites did not qualitatively change upon the thermal decomposition of crystalline zirconium sulfate. The concentration of strong acid sites can only decrease with decreasing sulfate sulfur content of the sample. Thus, the activation of an *n*-butane molecule occurs via a mechanism other than the protonation of reactant molecules. Activation sites are almost absent from the surface of crystalline zirconium sulfate. They are formed on the surface of sulfated oxides prepared by the thermal decomposition of crystalline zirconium sulfate or by the sulfation of a hydroxide followed by high-temperature calcination.

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