ISSN 0023-1584, Kinetics and Catalysis, 2010, Vol. 51, No. 3, pp. 438–443. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © M.O. Kazakov, A.V. Lavrenov, M.S. Mikhailova, N.A. Allert, T.I. Gulyaeva, I.V. Muromtsev, V.A. Drozdov, V.K. Duplyakin, 2010, published in Kinetika i Kataliz, 2010, Vol. 51, No. 3, pp. 457–462.

Hydroisomerization of Benzene-Containing Gasoline Fractions on a $Pt/SO_4^{2-}-ZrO_2-Al_2O_3$ Catalyst: I. Effect of Chemical Composition on the Phase State and Texture Characteristics of $SO_4^{2-}-ZrO_2-Al_2O_3$ Supports

M. O. Kazakov, A. V. Lavrenov, M. S. Mikhailova, N. A. Allert, T. I. Gulyaeva, I. V. Muromtsev, V. A. Drozdov, and V. K. Duplyakin

Institute of Hydrocarbons Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia

e-mail: max@ihcp.oscsbras.ru

Received March 27, 2009

Abstract—A series of $SO_4^{2-}-ZrO_2-Al_2O_3$ oxide supports containing from 18.8 to 89.1 wt % alumina was prepared by mixing sulfated zirconia hydrate (weight ratio $ZrO_2 : H_2SO_4 = 9 : 1$) and pseudoboehmite followed by calcination at 650°C. For the subsequent use of the supports to optimize the acid and hydrogenating properties of bifunctional hydroisomerization catalysts of the $Pt/SO_4^{2-}-ZrO_2-Al_2O_3$ type, the formation of these catalysts in the course of thermal treatment and their texture characteristics and phase composition were studied. It was found by chemical and thermogravimetric analysis that the addition of pseudoboehmite to sulfated zirconia hydrate resulted in a decrease in sulfur losses in the course of support production from 55.0 to 2.0% with respect to its nominal amount. As the alumina content was increased from 18.8 to 89.1 wt %, the specific surface area and the pore volume of the support increased nonadditively with respect to mechanical mixtures of sulfated zirconia and γ-alumina (from 155 to 197 m^2/g and from 0.24 to 0.52 cm^3/g, respectively); in this case, a maximum deviation was 18–21%. The experimental results can be explained by chemical interactions between the initial components of the supports. The results of thermogravimetric and X-ray diffraction analysis suggest that the reaction products are sulfated alumina and a sulfated $ZrO_2-Al_2O_3$ solid solution.

DOI: 10.1134/S0023158410030171

INTRODUCTION

The development of technologies for benzene removal from both straight-run gasoline and, primarily, reformed gasoline is currently a crucially important task for the development of catalytic processes for the manufacture of environmentally friendly fuel. Benzene hydroisomerization is considered the simplest and most efficient process [1, 2], in the course of which the hydrogenation of benzene and the isomerization of the resulting cyclohexane to methylcyclopentane occur as consecutive reactions. The capabilities of the hydroisomerization of the light fractions of reforming products, which mainly consist of C_5–C_7 hydrocarbons and include to 30 wt % benzene, have been studied in most detail [3]. In this case, the octane number of liquid hydroisomerization products did not decrease even at almost complete benzene conversion, as compared with the initial benzene-containing fraction.

Bifunctional systems based on platinum supported on the surfaces of various solid acids (zeolites [4–7], heteropoly acids [2, 8], sulfated zirconia [2, 9], and tungstate-containing zirconia [1, 2, 5]) have been actively studied as catalysts for the hydroisomerization of benzene and its mixtures with C_5–C_7 alkanes. In this case, the occurrence of ring-opening side reactions (which lead to a decrease in the octane number) and alkane hydrocracking reactions (which decrease the yield of liquid hydroisomerization products) belong to the disadvantages of hydroisomerization; these disadvantages can be associated with an imbalance between the acid and hydrogenation functions of the used catalysts. For example, it is evident that the level of the acid properties of the $Pt/SO_4^{2-}-ZrO_2$ system, which is an efficient catalyst for C_4–C_6 alkane isomerization [10], is excessive for the hydroisomerization of benzene in a mixture with C_5–C_7 alkanes because the processes of *n*-heptane and cyclohexane isomerization on this catalyst are accompanied by the formation of considerable amounts of C_3–C_4 light alkanes as hydrocracking and hydrogenolysis reaction products [9, 11]. On the other hand, the hydrogenation activity of platinum on the surface of sulfated zirconia is much lower than the activity of platinum supported on γ-alumina [12]; this can prevent the complete conversion of benzene.

The aim of this work was to optimize the acid and hydrogenating properties of a bifunctional catalyst based on platinum and sulfated zirconia for the hydroisomerization of benzene-containing gasoline fractions by the introduction of alumina into the composition of this catalyst.

It is well known that the acidity level of the SO_4^{2-}–ZrO_2–Al_2O_3 systems can be either higher or lower than the acidity of unmodified sulfated zirconia depending on preparation procedure (coprecipitation or mixing) and alumina content [13, 14]. According to Zalewski et al. [15], catalysts on a support prepared by the calcination of aluminum hydroxide mixtures with sulfated zirconia hydrate differ from sulfated zirconia by a greater number of acid sites; however, the strength of these sites is lower and is inversely proportional to the amount of the modifier. Thus, it is obvious that the SO_4^{2-}–ZrO_2–Al_2O_3 system that exhibits high selectivity in the reactions of C_7 alkane isomerization and cyclohexane isomerization to methylcyclopentane can be obtained by varying the amount of alumina. At the same time, the presence of alumina favorably affects the hydrogenating activity of supported platinum to approximate it to the activity of alumina–platinum catalysts. Thus, the modification of the traditional Pt/SO_4^{2-}–ZrO_2 system with alumina additives can really be a promising process for the regulation of the ratio between acid and hydrogenating properties. This study was devoted to the experimental substantiation of the efficiency of this process with the use of hydroisomerization reactions as an example.

Here, we report the results of a thermogravimetric study of the formation of SO_4^{2-}–ZrO_2–Al_2O_3 oxide supports with alumina contents from 18.8 to 89.1 wt %, which were prepared by the thermal treatment of the mixtures of sulfated zirconia hydrate and pseudoboehmite and data on the texture characteristics and phase composition of these supports.

EXPERIMENTAL

Zirconia hydrate was prepared by precipitation from a solution of chemically pure zirconium oxy nitrate under the action of a solution of ammonia; the final value of precipitation pH was 10. The resulting precipitate was washed with distilled water to a neutral reaction and treated with a 16% solution of sulfuric acid in an amount that resulted in the weight ratio $ZrO_2 : H_2SO_4 = 9 : 1$. The sulfated zirconia hydrate was mixed with a required amount of commercial pseudoboehmite (ZAO Promyshlennye Katalizatory, Ryazan, Russia). The mixtures were dried at 120°C and calcined at 650°C in a muffle furnace to obtain finished supports (samples of the SZA series). For comparison, sulfated zirconia (SZ), alumina (A), and sulfated alumina (SA) samples were also prepared. For this purpose, sulfated zirconia hydrate, pseudoboehmite, and sulfated pseudoboehmite were also calcined at 650°C.

To determine the concentration of SO_4^{2-} ions, the weighed portions of samples were dissolved in a mixture of acids (HF, $HClO_4$, and HCl) on heating in accordance with a published procedure [16] followed by the gravimetric analysis of solutions [17]. The actual ZrO_2 and Al_2O_3 contents of the samples were calculated with consideration for the concentration of SO_4^{2-} and the $ZrO_2 : Al_2O_3$ weight ratio, which was specified in the synthesis and remained unchanged after calcination.

The thermogravimetric analysis of the hydroxide precursors of the supports (after drying at 120°C) was performed on a Netzsch STA 449 C instrument in a flow of a gas mixture containing 20 vol % O_2 + 80 vol % Ar (99.999%) over the temperature range of 25–950°C at a heating rate of 10 K/min.

The isotherms of nitrogen adsorption–desorption at 77.4 K were obtained on an ASAP-2020 analyzer (Micromeritics). The range of relative equilibrium pressures was from 10^{-5} to 0.996. The BET specific surface areas (S_{sp}) were determined over the range of relative equilibrium pressures of 0.05–0.3 from the adsorption isotherm. The pore volume (V_{pore}) was found from the adsorption of nitrogen at a relative equilibrium pressure of 0.990. The pore-size distribution curves were obtained by the Barret–Joyner–Halenda (BJH) method [18] with the use of the desorption branches of isotherms in the calculations. From the S_{sp} and V_{pore} of sulfated zirconia and alumina samples, the values of S_{calcd} and V_{calcd} for the mechanical mixtures of these components were calculated using an additive procedure; the concentrations of the components corresponded to the chemical composition of the synthesized supports of the SO_4^{2-}–ZrO_2–Al_2O_3 type.

X-ray diffraction analysis was performed on a D8 Advance powder diffractometer (Bruker) using CuK_α radiation with a nickel β-filter in the range of 2θ angles from 20° to 80° (scan step, 0.1°; exposure, 20 s). The average size of coherent-scattering regions (CSRs) was calculated using the Selyakov–Scherrer equation from the (101) peak of tetragonal ZrO_2 and the (440) peak of γ-Al_2O_3. The determination error was ±0.5 nm.

RESULTS AND DISCUSSION

Table 1 summarizes data on the nominal and actual chemical compositions of the synthesized oxide support samples based on sulfated zirconia and alumina. As can be seen, the actual sulfur content of a sulfated zirconia sample was lower than the nominal value by a factor of more than 2; that is, 55% of sulfur introduced into zirconia hydrate was likely removed as volatile (H_2SO_4) or gaseous (SO_x) compounds in the course of thermal treatment. At the same time, the actual sulfur content of sulfated alumina, which was prepared by

Table 1. Chemical composition of supports based on sulfated zirconia and alumina

Sample*	Nominal concentration, wt %			Actual concentration, wt %		
	SO_4^{2-}	ZrO_2	Al_2O_3	SO_4^{2-}	ZrO_2	Al_2O_3
SZ	10.0	90.0	0.0	4.5	95.5	0.0
SZA-18.8	8.2	73.5	18.3	6.1	75.1	18.8
SZA-28.1	7.2	65.0	27.8	6.2	65.7	28.1
SZA-37.7	6.3	56.2	37.5	5.7	56.6	37.7
SZA-47.8	5.2	47.4	47.4	4.4	47.8	47.8
SZA-57.9	4.2	38.3	57.5	3.5	38.6	57.9
SZA-67.8	3.2	29.0	67.8	3.1	29.1	67.8
SZA-78.3	2.2	19.6	78.2	2.1	19.6	78.3
SZA-89.1	1.1	9.9	89.0	1.0	9.9	89.1
SA	10.0	0.0	90.0	9.8	0.0	90.2

* Figures in sample designations correspond to actual Al_2O_3 concentrations.

the calcination of pseudoboehmite treated with sulfuric acid, differed from the nominal value by no more than 2% (9.8 and 10.0 wt %, respectively).

In general, these facts can be explained by the interaction of sulfuric acid and pseudoboehmite to form stronger sulfate compounds than those formed upon the sulfation of zirconia hydrate. Data published by Waqif et al. [19], who found that the thermal stability of sulfated alumina is higher than that of sulfated zirconia, can serve as indirect evidence for the above.

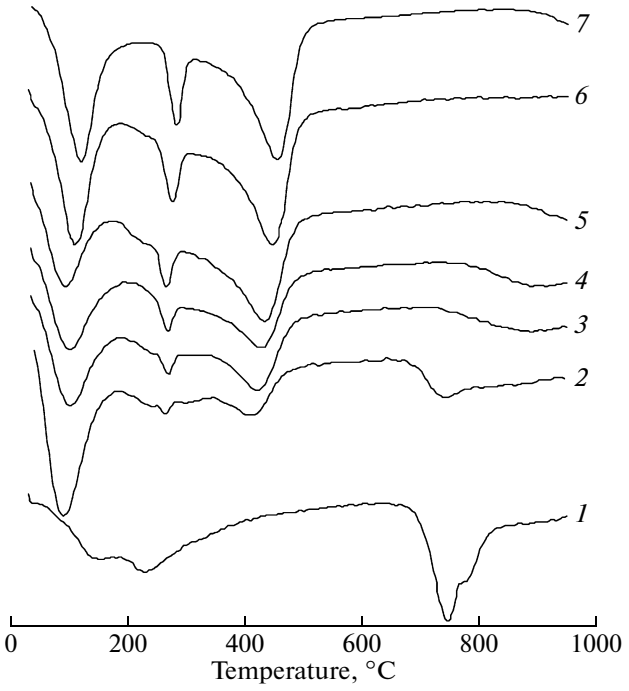

Fig. 1. Differential weight-loss (DTG) curves for the hydroxide precursors of samples based on sulfated zirconia and alumina: (*1*) SZ, (*2*) SZA-18.8, (*3*) SZA-37.7, (*4*) SZA-47.8, (*5*) SZA-67.8, (*6*) A, and (*7*) SA.

The results of the thermogravimetric analysis of sulfated zirconium and aluminum hydroxides and pseudoboehmite (Fig. 1) also supported the conclusion on the higher thermal stability of sulfated alumina. The weight losses of all of the samples in the temperature region to 200°C were due to the removal of physically adsorbed water. In the range of 200–400°C, the weight loss of sulfated zirconia hydrate was due to the removal of chemically bound water, the crystallization of the sample, and the release of sorbed sulfuric acid [20, 21]. In this case, the intense removal of sulfur as oxides started at a temperature of 650–660°C and occurred up to 800–850°C. The DTG curves of sulfated aluminum hydroxide and pseudoboehmite at temperatures to 880°C were identical and exhibited a shape typical of pseudoboehmite [22]. Peaks in the regions of 250–310 and 350–530°C correspond to the formation of γ-Al_2O_3 from pseudoboehmite particles with various degrees of crystallinity. Unlike pseudoboehmite, weight losses were observed in sulfated aluminum hydroxide once again starting from 880°C; this was evidently due to the degradation of the resulting alumina sulfate compounds.

In the formation of more complex SO_4^{2-}–ZrO_2–Al_2O_3 oxide systems, a dramatic decrease in sulfur losses with respect to its nominal amount was observed as a result of mixing sulfated zirconia hydrate with pseudoboehmite and increasing the alumina content. Thus, in the range of Al_2O_3 concentrations from 18.8 to 89.1 wt %, the relative difference between nominal and actual sulfur contents decreased from 25 to 3%. This most likely suggests the formation of sulfated alu-

mina as a constituent of the supports along with sulfated zirconia. The most probable reason for the formation of sulfated alumina under conditions when only zirconia hydrate was treated with sulfuric acid is the gas-phase sulfation of pseudoboehmite or formed alumina with the decomposition products of sulfated zirconia hydrate (H_2SO_4 or SO_x) [23].

From the results of the thermogravimetric analysis of sulfated zirconia hydrate and pseudoboehmite mixtures, which are also shown in Fig. 1, it follows that, in the region to 550°C, the shape of the differential curves of weigh losses mainly depended on the superposition of peaks due to initial components, and it was directly related to the ratio between these components in the mixture. The presence of alumina had a crucial effect only on the removal of sulfur oxides from the system. The clearly pronounced region of their removal at 650–850°C, which is characteristic of sulfated zirconia hydrate, was strongly diffuse even at an Al_2O_3 concentration of 18.8 wt % to reach a limiting analysis temperature (950°C). As the concentration of alumina was further increased, the continuous loss of small sulfur amounts was observed in this region; this can be explained by both a decrease in the nominal sulfur content of the samples and the stronger fixation of sulfur because of the formation of sulfated alumina.

Table 2 summarizes the texture characteristics of the synthesized samples. As can be seen, the specific surface area of the samples increased with the alumina content of the SO_4^{2-}–ZrO_2–Al_2O_3 system; starting from 57.9 wt % Al_2O_3, it became almost equal to S_{sp} of γ-alumina (discrepancies were 7–12 m^2/g). The pore volume of the synthesized sample of sulfated zirconia was no higher than 0.09 cm^3/g. However, after the addition of 18.8 wt % alumina, the V_{pore} dramatically increased (by a factor of 2.6) to reach 0.24 cm^3/g. At an Al_2O_3 content of 67.8 wt % or higher, the total pore volumes of the supports differed only slightly from the pore volume of γ-alumina and was as high as 0.48–0.52 cm^3/g. Note that the experimental values of specific surface areas and pore volumes of the synthesized samples of the SO_4^{2-}–ZrO_2–Al_2O_3 system were much higher than the values calculated using an additive scheme for the mechanical mixtures of sulfated zirconia and alumina. At an Al_2O_3 content of 28.1–37.7 wt %, positive deviations were as high as 18–21 rel. %.

Figure 2 shows pore-size distribution curves for sulfated zirconia, γ-alumina, and SO_4^{2-}–ZrO_2–Al_2O_3 samples. Sulfated zirconia was characterized by a unimodal distribution; mesopores with diameters from 3 to 5 nm made the main contribution (more than 60%). In the SO_4^{2-}–ZrO_2–Al_2O_3 sample containing 18.8 wt % alumina, larger mesopores with sizes from 5 to 25 nm appeared; because of this, V_{pore} increased by a factor of >2, as compared with that of sulfated zirconia. The

Table 2. Texture characteristics of samples based on sulfated zirconia, sulfated alumina, and their mechanical mixtures

Sample	S_{sp}, m^2/g		V_{pore}, cm^3/g	
	experimental	calculated	experimental	calculated
SZ	110	110	0.09	0.09
SZA-18.8	155	130	0.24	0.18
SZA-28.1	172	139	0.27	0.22
SZA-37.7	182	148	0.33	0.26
SZA-47.8	188	158	0.39	0.30
SZA-57.9	197	168	0.40	0.35
SZA-67.8	202	177	0.48	0.39
SZA-78.3	202	187	0.49	0.43
SZA-89.1	197	197	0.52	0.48
A	209	209	0.53	0.53

pore-size distribution curves for the samples with Al_2O_3 concentrations of 67.8 wt % or higher exhibited a clearly pronounced bimodal character: mesopores from 3 to 5 nm in diameter at a maximum of 3.7–

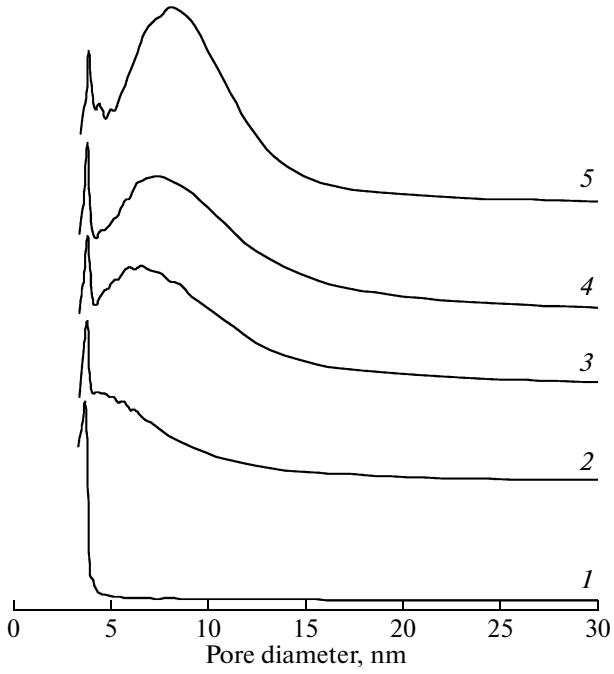

Fig. 2. Pore-size distribution in samples based on sulfated zirconia and alumina: (*1*) SZ, (*2*) SZA-18.8, (*3*) SZA-47.8, (*4*) SZA-67.8, and (*5*) A.

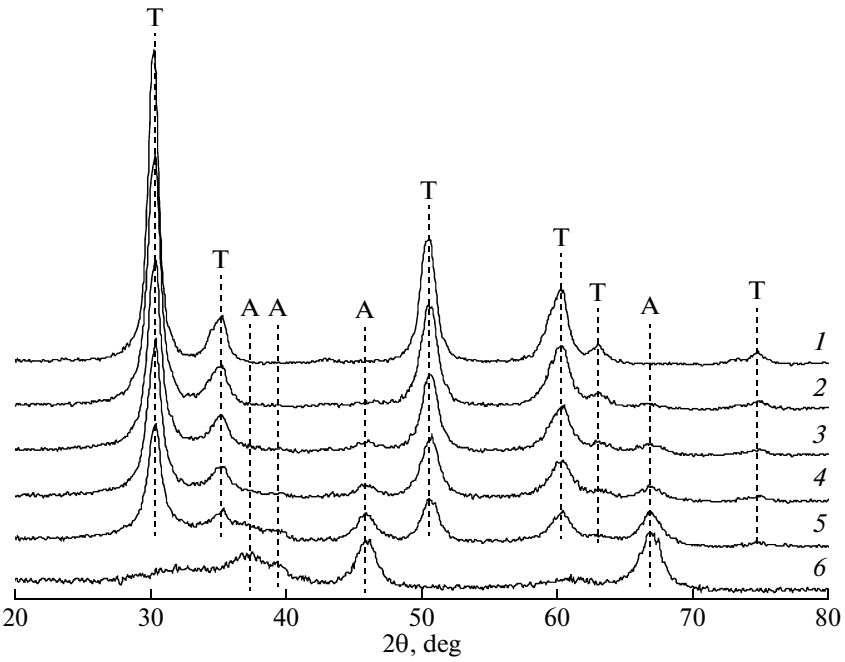

Fig. 3. Diffraction patterns of samples based on sulfated zirconia and alumina: (*1*) SZ, (*2*) SZA-18.8, (*3*) SZA-28.1, (*4*) SZA-47.8, (*5*) SZA-67.8, and (*6*) A. T and A refer to the tetragonal modification of ZrO_2 and γ-Al_2O_3, respectively.

3.8 nm and from 5 to 25 nm in diameter at a maximum of 7.5–8.0 nm.

Thus, changes in the pore space of the SO_4^{2-}–ZrO_2–Al_2O_3 system depending on its chemical composition can be explained only qualitatively by an increasing contribution of γ-alumina, which has a higher intrinsic porosity. The positive deviations of the experimental values of S_{sp} and V_{pore} for the SO_4^{2-}–ZrO_2–Al_2O_3 samples with respect to the values calculated using an additive model can be a consequence of the chemical interaction between the initial components used for the preparation of the supports, for example, by analogy with the ZrO_2–Al_2O_3 system [24]. From the above results of chemical and thermogravimetric analysis, it follows that sulfated alumina can be a product of this interaction.

Figure 3 shows the diffraction patterns of the SO_4^{2-}–ZrO_2–Al_2O_3 samples together with the diffraction patterns of sulfated zirconia and γ-alumina. In the sample of sulfated zirconia, only a tetragonal ZrO_2 phase was identified with a particle size of about 9 nm in terms of CSR. The diffraction patterns of SO_4^{2-}–ZrO_2–Al_2O_3 exhibited signal typical of a γ-Al_2O_3 phase along with reflections due to tetragonal ZrO_2; the intensity of these signals increased with the alumina content of the supports, and the size of CSRs was 6–7 nm. In this case, the particle size (in terms of CSR) of the tetragonal ZrO_2 phase in the SO_4^{2-}–ZrO_2–Al_2O_3 systems was 7–8 nm; that is, they were more dispersed than tetragonal ZrO_2 present in the sample of sulfated zirconia. This can be evidence for the formation of a tetragonal ZrO_2 phase stabilized with alumina, probably, as a ZrO_2–Al_2O_3 solid solution [24]. Evidently, this phase state of sulfated zirconia along with sulfated alumina is responsible for the experimental values of texture characteristics.

The results of the above studies allowed us to assume that the following processes occur in the formation of the SO_4^{2-}–ZrO_2–Al_2O_3 system in the course of calcination of a mixture of sulfated zirconia hydrate and pseudoboehmite at 650°C: (1) the dehydration and crystallization of sulfated zirconia hydrate accompanied by the release of sulfuric acid vapor and sulfur oxides, (2) the dehydration of pseudoboehmite with the formation of sulfated alumina as a result of the interaction of pseudoboehmite with the decomposition products of sulfated zirconia hydrate, and (3) the formation of a sulfated solid solution of ZrO_2–Al_2O_3.

ACKNOWLEDGMENTS

We are grateful to Leading Engineer N.V. Antonicheva for performing thermal analysis and Junior Researcher T.V. Kireeva for performing chemical analysis.

This work was supported by the Council of the President of the Russian Federation for Support of Young Scientists and Leading Scientific Schools (project no. NSh-5797.2008.3).

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