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Hydroisomerization of Benzene-Containing Gasoline Fractions on a Pt/SO_4^{2-}–ZrO_2–Al_2O_3 Catalyst: III. The Hydrogenating Properties of the Catalyst

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Abstract—The properties and state of platinum in Pt/SO_4^{2-}–ZrO_2–Al_2O_3 catalysts with various alumina contents have been investigated in benzene hydrogenation as a model reaction using IR spectroscopy, temperature-programmed reduction, and H_2 chemisorption. As the Al_2O_3 content is raised, the hydrogenating activity of the catalyst increases, which is due to the increasing proportion of metallic platinum on the surface.

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The hydroisomerization of benzene-containing gasoline fractions [1, 2] is carried out to obtain environmentally friendly motor fuels with a reduced concentration of aromatic hydrocarbons, particularly benzene. In this process, benzene is removed via hydrogenation and the associated decrease in the octane number of the gasoline fraction is counterbalanced by the isomerization of the resulting cyclohexane into methylcyclopentane. The hydroisomerization process is made efficient by employing a bifunctional catalyst. The hydrogenating capacity of this catalyst ensures practically complete benzene conversion, and its acidic properties favor selective isomerization of cyclohexane and of the C_6 andC_7 *n*-alkanes that are present in the feedstock.

We demonstrated in our previous reports [3, 4] that preparation of the SO_4^{2-}–ZrO_2–Al_2O_3 system by combining sulfated zirconia with pseudoboehmite followed by calcination of the mixture at 650°C makes it possible to regulate the structural, textural, and acidic properties of the product. For selective *n*-heptane and cyclohexane isomerization over the Pt/SO_4^{2-}–ZrO_2–Al_2O_3 catalyst in the temperature range favorable for hydroisomerization (250–300°C), the optimum alumina content of the support is 67.8 wt %.

The Pt/SO_4^{2-}–ZrO_2 catalyst is far inferior to Pt/Al_2O_3 in hydrogenating activity [5]. It is to be expected that the presence of alumina in the Pt/SO_4^{2-}–ZrO_2–Al_2O_3 system will change not only the acidic properties of the catalyst, but also its hydrogenating properties, bringing them up to the level characteristic of platinum/alumina catalysts. Here, we report an IR spectroscopic, temperature-programmed reduction, and H_2 chemisorption study of the effect of the alumina content of the Pt/SO_4^{2-}–ZrO_2–Al_2O_3 catalyst on the state of platinum and its hydrogenating properties in benzene hydrogenation as a model reaction.

EXPERIMENTAL

The procedures used to prepare the supports SO_4^{2-}–ZrO_2–Al_2O_3 (SZA-*x*, where *x* is the Al_2O_3 content, wt %), sulfated zirconia (**SZ**), alumina (**A**), sulfated alumina (**SA**), and supported platinum catalysts (Pt/SZA-*x*, Pt/A, Pt/SZ, Pt/SA) and to determine their chemical composition were described in our earlier publications [3, 4].

We measured the amounts of platinum sorbed by different supports from 0.9 mmol/l chloroplatinic acid solution at a solution-to-support weight ratio of 20 : 1. The platinum content of the final catalyst samples at complete hexachloroplatinate ion sorption was 0.3 wt %. The H_2PtCl_6 concentration in the solution during platinum sorption measurements was monitored spectrophotometrically [6]. The degree of sorption of platinum by the catalyst (DS_{Pt}, %) was calculated as

$$DS_{Pt} = 100(0.9 - C_{Pt})/0.9, \quad (1)$$

where C_{Pt} is the platinum concentration (mmol/l) in the solution after sorption.

The hydroxyl cover of the surface of the initial supports was studied by IR spectroscopy. Spectra were recorded on an IR Prestige 21 Fourier-transform IR

Table 1. Chemical composition of the catalysts

Catalyst*	Chemical composition of the support, wt %			Pt content, wt %
	SO_4^{2-}	ZrO_2	Al_2O_3	
Pt/SZ	4.5	95.5	0.0	0.32
Pt/SZA-18.8	6.1	75.1	18.8	0.30
Pt/SZA-37.7	5.7	56.6	37.7	0.29
Pt/SZA-47.8	4.4	47.8	47.8	0.28
Pt/SZA-57.9	3.5	38.6	57.9	0.27
Pt/SZA-67.8	3.1	29.1	67.8	0.29
Pt/SZA-78.3	2.1	19.6	78.3	0.26
Pt/SZA-89.1	1.0	9.9	89.1	0.26
Pt/A	0.0	0.0	100.0	0.30
Pt/SA	9.8	0.0	90.2	0.28

* The numbers in catalyst designations indicate the actual weight percentage of Al_2O_3.

spectrometer (Shimadzu). Samples, pressed into pellets with a density of 0.020–0.030 g/cm^2, were placed in the measurement cell and were calcined at 400°C in vacuo for 2 h. Measurements were taken at room temperature in the wavenumber range from 3500 to 3850 cm^{-1} (4 cm^{-1} resolution) via coaddition and averaging of 50 spectra.

The spectra of CO adsorbed on catalysts were recorded on an FTIR-8300 Fourier-transform IR spectrometer (Shimadzu) between 700 and 6000 cm^{-1} (4 cm^{-1} resolution) via coaddition and averaging of the results of 100 scans. Samples were pressed into pellets with a density of 0.011–0.025 g/cm^2 and were placed in a quartz cell with CaF_2 windows. The catalysts were activated by calcination in air at 400°C and then in vacuo followed by reduction with hydrogen (250 mbar) at 300°C for 0.5 h and pumping at 25°C. The reduction procedure was repeated three times. The reduced samples were conditioned in vacuo by raising the temperature to 500°C in steps and by holding them at 500°C for 0.5 h. Carbon monoxide (1000 Pa) was adsorbed at the liquid-nitrogen temperature, and the sample was then heated to 25°C.

Temperature programmed reduction (TPR) followed by the determination of the amount of H_2 chemisorbed by the sample was carried out on an AutoChem II 2920 chemisorption analyzer (Micromeritics) fitted with a thermal-conductivity detector. Before being examined by TPR, the samples were calcined at 400°C in flowing air. The reductive medium was a hydrogen + argon mixture (10 vol % H_2). TPR was performed between 35 and 300°C at a temperature ramp rate of 10°C/min. The amount of hydrogen chemisorbed (H/Pt ratio) was determined in a pulse mode after the sample was cooled to room temperature and was then blown with argon.

The hydrogenation of benzene (99.99 wt % C_6H_6) was studied in a fixed-bed catalytic reactor at pressures of 0.1 and 1.5 MPa, 200°C, a benzene WHSV of 4.0 h^{-1}, and a hydrogen-to-hydrocarbon molar ratio of 8 : 1. Before the hydrogenation reaction, the catalysts were activated in flowing hydrogen at 300°C. The products of the reaction were analyzed on-line on a Khromos-1000 gas chromatograph equipped with a capillary column (100 m, DB-1 phase) and a flame ionization detector. The reaction mixture was sampled 1 h after the benzene supply to the reactor was turned on.

Benzene conversion (x_{benz}, %) was calculated using the formula

$$x_{\text{benz}} = 100\left(W_{\text{feed}} - W_{\text{prod}}\right)/W_{\text{feed}}, \qquad (2)$$

where W_{feed} and W_{prod} are the weight fractions of benzene in the feed and in the product mixture according to gas chromatography data.

RESULTS AND DISCUSSION

The hydrogenating properties and state of platinum in the Pt/SO_4^{2-}– ZrO_2–Al_2O_3 system were studied on samples containing 18.8 to 89.1 wt % alumina (Table 1). The initial ZrO_2 : H_2SO_4 weight ratio was invariable in the synthesis of all samples [3]. Raising the Al_2O_3 content of the catalyst caused a decrease both in the ZrO_2 content (from 75.1 to 9.9 wt %) and in the sulfur content (from 6.1 to 1.0 wt % in terms of SO_4^{2-} ions). For comparison, we examined alumina and sulfated zirconia and alumina samples and Pt-containing catalysts supported on these materials. The platinum content of the catalysts was 0.26–0.32 wt %.

Changes in the chemical composition of the SO_4^{2-}–ZrO_2–Al_2O_3 support should lead to changes in the mechanism of Pt fixation from H_2PtCl_6 solution and to the formation of catalysts differing in the strength of metal–support interaction and in the degree of dispersion of the supported metal. The binding of the hexachloroplatinate complexes to the oxide supports is most likely due to their ligand exchange reaction with basic hydroxyl groups on the support surface [7]. If this is the case, an increase in the basicity of the support within certain limits will be favorable for stronger chemical interaction between the platinum complexes and the oxide surface and for a smaller particle size of the supported metal in the finished catalyst.

It was demonstrated earlier that raising the Al_2O_3 content of the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ catalyst reduces its acidity [4]. Because of the marked amphoterism of aluminum oxide, this should be accompanied by an increase in the number of basic sites at least on the surface of the initial $SO_4^{2-}–ZrO_2–Al_2O_3$ support. The IR spectra of the chemically different supports (Fig. 1) indicate that, as the alumina content is increased, the intensity of the absorption bands of terminal OH groups (3767 and 3789 cm^{-1}), which are characteristic of γ-Al_2O_3 and possess basic properties [8], progressively increases. In the frequency range examined, the spectrum of SZ shows only an absorption band at 3651 cm^{-1}, which is due to bridging, acidic OH groups [9]. Thus, as the Al_2O_3 content of the $SO_4^{2-}–ZrO_2–Al_2O_3$ system is increased, the nature of the surface gradually changes from acidic to mixed—acidic and basic.

The changes in the chemical properties of the surface in the $SO_4^{2-}–ZrO_2–Al_2O_3$ system that are induced by an increasing Al_2O_3 content and, accordingly, the changes in the way the platinum complexes are fixed from the H_2PtCl_6 solution in catalyst synthesis have been confirmed by determination of the degree of sorption of platinum. Sulfated zirconia and alumina and the supports containing up to 18.8 wt % Al_2O_3 practically do not sorb platinum from the H_2PtCl_6 solution (Table 2), because their surface is largely covered by acidic hydroxyl groups. Raising the Al_2O_3 content to 47.8 wt % generates, on the surface of the mixed oxide support, appreciable amounts of hexachloroplatinate ion sorption sites, which, as was mentioned above, are basic hydroxyl groups. As a consequence, the degree of sorption of platinum is 35% for the Pt/SZA-47.8 catalyst and 81% for the sample containing 67.8 wt % Al_2O_3. The density of the basic OH group coverage of the alumina surface is sufficiently high to ensure platinum fixation by sorption alone. Therefore, raising the alumina content of the $SO_4^{2-}–ZrO_2–Al_2O_3$ system leads to an increase in the proportion of platinum fixed on the support surface via sorption.

We used the TPR method to investigate how the hydrogen uptake dynamics in the reduction of the catalysts depends on the chemical composition of the support and of the way in which platinum is fixed on the surface. The TPR profiles for Pt/SZA, Pt/SZ, and Pt/A samples are presented in Fig. 2. Note the radical distinctions between the reduction of the platinum compounds supported on Al_2O_3 and the reduction of those supported on $SO_4^{2-}–ZrO_2$. The main hydrogen uptake region for the platinum/alumina sample is in the 150–300°C range, showing a peak around 225°C. The specific hydrogen uptake (moles of H_2 per mole of Pt) in this case is 1.8, suggesting that platinum (in terms of PtO_2) is reduced to an extent of 90%. Hydrogen uptake by Pt/SZ begins approximately at 90°C. In this case, it is impossible to accurately determine the temperature range in which platinum reduction

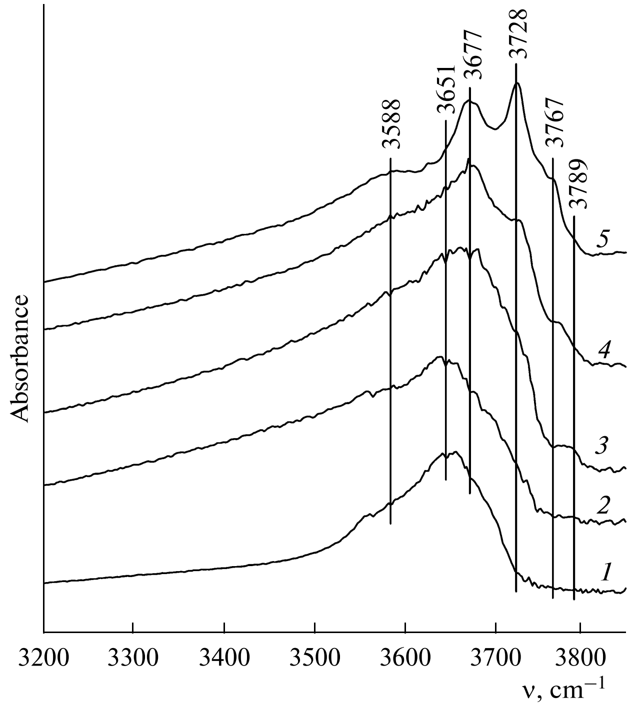

Fig. 1. IR spectra of the supports in the absorption region of hydroxyl groups: (*1*) SZ, (*2*) SZA-18.8, (*3*) SZA-47.8, (*4*) SZA-67.8, and (*5*) A.

Table 2. Degree of sorption of platinum in catalysts of different chemical compositions and their chemisorbing and hydrogenating properties

Catalyst	DS_{Pt}, %	H/Pt, mol/mol	x_{benz}, %
Pt/SZ	0.0	0.00	1.8
Pt/SZA-18.8	0.0	0.00	2.0
Pt/SZA-47.8	35.0	0.00	6.1
Pt/SZA-57.9	–	0.14	–
Pt/SZA-67.8	81.0	0.44	40.7
Pt/A	100.0	0.85	97.1
Pt/SA	0.0	0.00	3.0

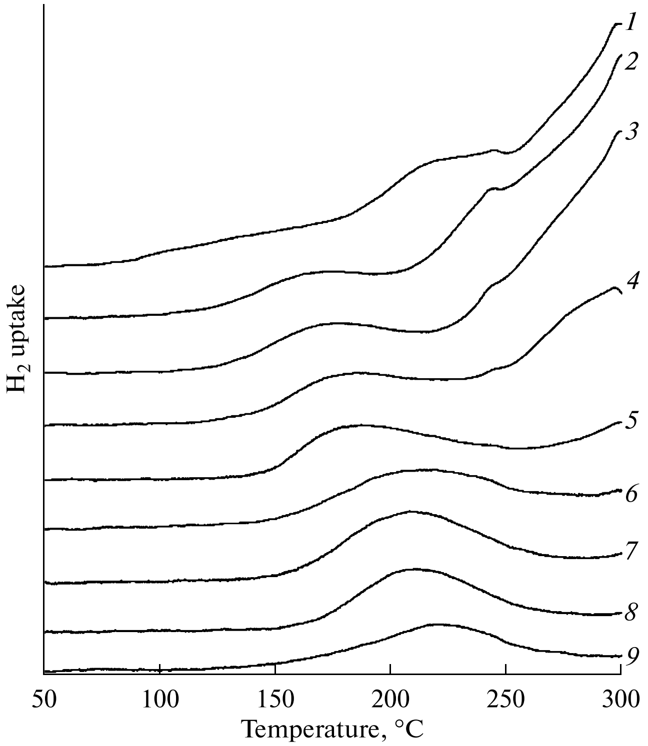

Fig. 2. TPR profiles of the catalysts: (*1*) Pt/SZ, (*2*) Pt/SZA-18.8, (*3*) Pt/SZA-37.7, (*4*) Pt/SZA-47.8, (*5*) Pt/SZA-57.9, (*6*) Pt/SZA-67.8, (*7*) Pt/SZA-78.3, (*8*) Pt/SZA-89.1, and (*9*) Pt/A.

occurs because this process overlaps with the reduction of sulfate compounds present in the catalyst. Experimental evidence of the latter process taking place is that the specific hydrogen uptake for the Pt/SZ sample is 12, exceeding the stoichiometric amount of hydrogen required for the total reduction of platinum oxide by a factor of 6.

The observed distinctions between the TPR profiles are due to the difference between the states of platinum in Pt/A and Pt/SZ subjected to oxidative treatment. While the platinum/alumina system contains Pt(IV) oxide species, the metal on the SZ surface may undergo partial reduction at the oxidative treatment stage [10–12]. Thus, it is likely that, as Pt/SZ is treated with hydrogen, platinum reduction only comes to completion and this process is catalyzed by the Pt particles having formed at the calcination stage. This is why hydrogen uptake becomes noticeable at a comparatively low temperature of 90°C. The hydrogen uptake observed at 180°C is due to the reduction of sulfate groups rather than platinum on the Pt/SZ surface.

For all Pt/SZA samples, it is possible to distinguish between the temperature ranges in which the reduction of platinum compounds and sulfate groups takes place. Platinum reduction in the Pt/SZA samples containing 18.8–57.9 wt % Al_2O_3 occurs between 110 and 255°C. As the Al_2O_3 content is increased, the TPR peak shifts from 170 to 185°C. These data indicate an increase in the proportion of platinum strongly bound to the surface. The onset of the reduction of the sulfur compounds shifts from 205 to 260°C, and the specific hydrogen uptake decreases to 3.7. This is due both to the decrease in the initial sulfur content of the material and to sulfur being more strongly bound to alumina [3].

The TPR profiles of the group of Pt/SZA samples containing 67.8 to 89.1 wt % Al_2O_3 do not differ significantly from that of Pt/A. The platinum reduction peaks in these profiles are observed near 210°C, only 15°C below the temperature at which the corresponding peak in the TPR profile of Pt/A occurs. The specific hydrogen uptake observed for these Pt/SZA samples is 2.2–2.6.

The fraction of accessible platinum in reduced samples was estimated by carrying out hydrogen chemisorption in the pulse mode. Hydrogen chemisorption on Pt/SZ, Pt/SA, and Pt/SZA containing up to 47.8 wt % Al_2O_3 was not detected (Table 2). This is due to the fact that these catalysts contain sulfur compounds that can poison Pt both at the oxidative treatment stage and during reduction [11, 13, 14]. The amount of chemisorbed hydrogen (H/Pt molar ratio) in the Pt/SZA-57.9 and Pt/SZA-67.8 samples is 0.14 and 0.44, respectively. The largest amount of H_2 is chemisorbed by the Pt/A sample: H/Pt = 0.85. The observed trend is likely due to the decrease in the total sulfur content, the corresponding weakening of the poisoning effect of sulfur, and the increase in the proportion of platinum bound by sorption. The latter cir-

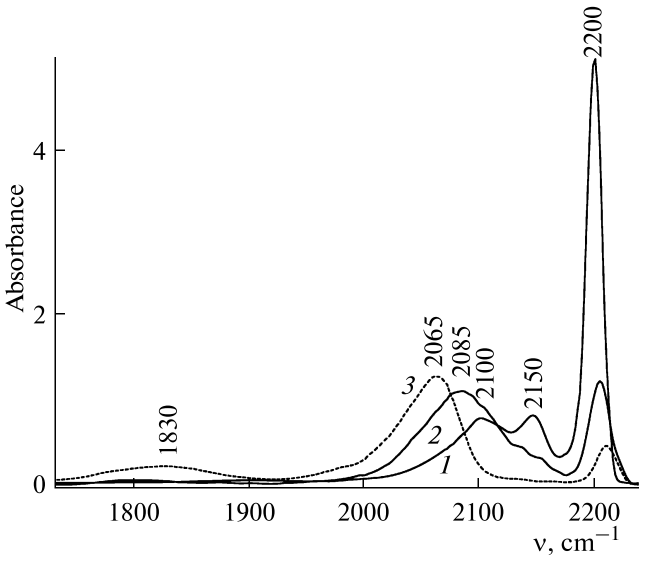

Fig. 3. IR spectra of adsorbed CO (10 mbar, 25°C): (*1*) Pt/SZ, (*2*) Pt/SZA-18.8, (*3*) Pt/SZA-67.8, and (*4*) Pt/A.

cumstance is favorable for a decrease in the platinum particle size and, accordingly, enhances hydrogen chemisorption.

Figure 3 shows the IR spectra of CO adsorbed on Pt/SZ, Pt/SZA-67.8, and Pt/A. The absorption band at 2200–2208 cm^{-1}, present in all spectra, is due to CO complexes with Lewis acid sites of the catalysts [8, 15]. This band is strongest in the spectrum of Pt/SZ, much weaker in the spectrum of Pt/SZA-67.8, and least intensive in the spectrum of Pt/A.

The spectrum of Pt/A shows an absorption band at 2065 cm^{-1}, which arises from vibrations of CO linearly adsorbed on Pt^0, and a broad band at 1830 cm^{-1}, which is due to the bridging CO species adsorbed on Pt^0 [16, 17]. Carbon monoxide adsorption on Pt/SZ gives rise to absorption bands at 2100 and 2150 cm^{-1}, which are similar in intensity and are due to the linear complexes of CO with Pt^0 and with positively charged platinum species, respectively [18, 19]. In the spectrum of Pt/SZA-67.8, the vibration frequency of CO adsorbed on platinum metal particles (2085 cm^{-1}) is intermediate between the corresponding frequencies observed for Pt/A and Pt/SZ. The IR spectroscopic, TPR, and hydrogen chemisorption data suggest that the proportion of Pt^0 on the surface of the reduced catalysts increases in the following order: Pt/SZ < Pt/SZA < Pt/A.

Table 2 presents catalytic activity data for the samples tested in benzene hydrogenation at atmospheric pressure. The results of these catalytic tests correlate with hydrogen chemisorption data. Since the benzene hydrogenation reaction is structure-insensitive, the increase in catalytic activity in the Pt/SZ < Pt/SZA < Pt/A order can be explained only by the increase in the number of platinum metal sites on the surface of these catalysts.

Thus, as the alumina content of the Pt/SO_4^{2-}–ZrO_2–Al_2O_3 system is raised, the benzene hydrogenation activity of the catalyst increases. The observed changes in the hydrogenating properties of the catalyst are due to the increasing proportion of platinum in the metallic state on the catalyst surface. There are two plausible causes of these changes. The first is that raising the alumina content of the Pt/SO_4^{2-}–ZrO_2–Al_2O_3 system obtained by combining sulfated zirconium dioxide hydrate (with a fixed $ZrO_2 : H_2SO_4$ ratio) with pseudoboehmite reduces the amount of sulfur compounds in the catalyst. In turn, this decreases the probability of platinum poisoning at the final calcination and reduction stages. The second supposed cause is that raising the Al_2O_3 content of the catalyst changes the acid–base properties of the support surface and the way in which the platinum precursor is bound to the surface. These changes strengthen the platinum–support interaction, and this can make the platinum particles more resistant to poisoning by sulfur compounds [20].

It was established earlier [4] that the Pt/SZA-67.8 catalyst favors the selective isomerization of *n*-heptane and cyclohexane in the temperature range from 250–300°C, which is thermodynamically favorable for the hydroisomerization process. However, a necessary condition for efficient hydroisomerization is complete benzene hydrogenation under the action of supported platinum. At atmospheric pressure, the benzene conversion over Pt/SZA-67.8 does not exceed 40.7% (Table 2). By a special-purpose experiment conducted at 1.5 MPa, we established that benzene can be completely hydrogenated over the Pt/SZA-67.8 catalyst. Therefore, the Pt/SO_4^{2-}–ZrO_2–Al_2O_3 system with an alumina content of 67.8 wt % is a promising catalyst for hydroisomerization of benzene-containing gasoline fractions.

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