ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 4, pp. 573–578. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © M.O. Kazakov, A.V. Lavrenov, I.G. Danilova, O.B. Belskaya, V.K. Duplyakin, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 4, pp. 583–588.

Hydroisomerization of Benzene-Containing Gasoline Fractions on a $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ Catalyst: II. Effect of Chemical Composition on Acidic and Hydrogenating and the Occurrence of Model Isomerization Reactions

M. O. Kazakov[a], A. V. Lavrenov[a], I. G. Danilova[b], O. B. Belskaya[a], and V. K. Duplyakin[a]

[a] *Institute of Hydrocarbons Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia*

[b] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

e-mail: max@ihcp.oscsbras.ru

Received March 23, 2010

Abstract—The acidic and hydrogenating of $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ samples containing from 18.8 to 67.8 wt % Al_2O_3 as a support constituent were studied by the IR spectroscopy of adsorbed CO and pyridine, and the model reactions of *n*-heptane and cyclohexane isomerization on these catalysts were examined. The total catalyst activity in the conversion of *n*-heptane decreased with the concentration of Al_2O_3; this manifested itself in an increase in the temperature of 50% *n*-heptane conversion from 112 to 266°C and in an increase in the selectivity of isomerization to 94.2%. In this case, the maximum yield of isoheptanes was 47.1 wt %, which was reached on a sample whose support contained 67.8 wt % Al_2O_3. A maximum yield (69.6 wt %) and selectivity (93.7%) for methylcyclopentane formation from cyclohexane were also reached on the above catalyst sample. This can be explained by lower concentrations of Lewis and Brønsted acid sites in the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ system, as compared with those in $Pt/SO_4^{2-}–ZrO_2$. The experimental results allowed us to make a preliminary conclusion that the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ catalyst whose support contains 67.8 wt % Al_2O_3 is promising for use in the selective hydroisomerization of benzene-containing gasoline fractions in the thermodynamically favorable process temperature range of 250–300°C.

DOI: 10.1134/S0023158411040057

INTRODUCTION

The hydroisomerization of benzene-containing fractions is an efficient process for benzene removal to obtain environmentally friendly up-to-date gasoline components [1, 2]. A bifunctional catalyst for the consecutive reactions of benzene hydrogenation to cyclohexane and cyclohexane isomerization to methylcyclopentane is required for the hydroisomerization process. In this case, the hydroisomerization catalyst should have balanced acidic and hydrogenating functions to minimize the occurrence of ring opening (leading to a decrease in the octane number) and alkane hydrocracking (decreasing the yield of liquid hydroisomerization products) side reactions. In our previous work [3], we proposed the introduction of aluminum oxide into a catalyst as a method for regulating the ratio between the acidic and hydrogenating properties of a bifunctional hydroisomerization catalyst based on platinum and sulfated zirconium dioxide.

A series of $SO_4^{2-}–ZrO_2–Al_2O_3$ oxide supports containing from 18.8 to 89.1 wt % Al_2O_3 was prepared by mixing sulfated zirconium dioxide hydrate and pseudoboehmite followed by calcination at 650°C and the formation of these supports in the course of thermal treatment and their texture characteristics and phase composition were studied.

This paper is devoted to the optimization of an alumina content of the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ system in terms of its level of acidic properties and hydrogenating, which is required for selective hydroisomerization. To solve this problem, we used the IR spectroscopy of adsorbed CO and pyridine molecules and performed acid-controlled model reactions of *n*-heptane and cyclohexane isomerization [4–6].

EXPERIMENTAL

The procedures used for the preparation of the samples of $SO_4^{2-}–ZrO_2–Al_2O_3$ supports, sulfated zirconia, and alumina and their main physicochemical characteristics were described previously [3]. To prepare finished catalysts, the supports were impregnated with a solution of H_2PtCl_6 to reach a 0.3 wt % platinum concentration in the final sample, dried at 120°C, and

calcined at 400°C in a flow of air. To determine the concentration of platinum, weighed portions of the samples were dissolved in a mixture of acids (HF, H_2SO_4, and HCl). The concentration of platinum in the solution was determined by spectrophotometry in accordance with a published procedure [7].

The acidic and hydrogenating of the samples were studied using the IR spectroscopy of adsorbed probe molecules in accordance with published procedures [8, 9]. The spectra were measured on a FTIR-8300 spectrometer from Shimadzu in the range of 700–6000 cm^{-1} with a resolution of 4 cm^{-1} and a scan number of 100. The samples were pressed into waters with a density of 0.011–0.025 g/cm^2 and placed in a quartz cell with windows of CaF_2. The sample activation was started with calcination at 400°C in an atmosphere of air and then in a vacuum. Thereafter, a reductive treatment was performed in the presence of H_2 (250 mbar) at 300°C for 0.5 h followed by evacuation at 25°C. The procedure of reduction was repeated three times. Then, the samples were trained in a vacuum with a stepwise increase in the temperature to 500°C and an exposure of 0.5 h at 500°C. The samples were tested with the use of the sequential adsorption of a portion of CO at a temperature of liquid nitrogen (–196°C). Pyridine was adsorbed at 150°C with the subsequent desorption at the same temperature for the removal of its weakly bound species. The concentration (C, μmol/g) of Lewis acid sites (LASs) was evaluated from the integrated intensity of an absorption band due to adsorbed CO in the region of 2180–2208 cm^{-1} (A_0 = 0.8 or 0.8–1.1 cm/μmol for $Pt/SO_4^{2-}–ZrO_2$ or [$Pt/SO_4^{2-}–ZrO_2–Al_2O_3$-67.8 and Pt/Al_2O_3). The concentration of Brønsted acid sites (BASs) was determined from the integrated intensity of an absorption band due to the pyridinium ion with a maximum at 1544 cm^{-1} (A_0 = 3.5 cm/μmol) using the equation

$$C = A/A_0, \quad (1)$$

where A is the observed integrated absorption of a band, and A_0 is the integral absorption coefficient [9].

The isomerization reactions of *n*-heptane (99.3 wt % purity) and cyclohexane (99.8 wt % purity) were performed in a catalytic fixed-bed flow reactor at a pressure of 1.5 MPa, a weight hourly space velocity of 4.0 h^{-1}, a hydrogen : hydrocarbon molar ratio of 5, and temperatures of 100–300°C. The compositions of products were determined by on line analysis with the use of a Khromos GKh-1000 gas chromatograph equipped with a capillary column (100 m in length; stationary phase, DB-1) and a flame-ionization detector.

In the calculation of isomerization characteristics, the amount of hydrogen (AH, wt %) consumed in the process was taken into consideration. The value of AH was determined from data of the gas-chromatographic analysis of the feed and product mixtures based on a balance on carbon and hydrogen with the use of the equation

$$AH = C_{\text{feed}} \times (HC_{\text{product}} - HC_{\text{feed}}), \quad (2)$$

where C_{feed} is the weight fraction of carbon in the feed (%), HC_{product} is the H : C weight ratio for the product hydrocarbon mixture, and HC_{feed} is the H : C weight ratio for the feed. The conversion of the initial hydrocarbon (X, %) was calculated using the equation

$$X = \left(100 \times W_{\text{feed}}^{\text{IH}} - (100 + AH) \times W_{\text{product}}^{\text{IH}}\right) \Big/ W_{\text{feed}}^{\text{IH}}, \quad (3)$$

where $W_{\text{feed}}^{\text{IH}}$ is the weight fraction of the initial hydrocarbon (%) in the starting mixture, as determined from gas-chromatographic analysis data, and $W_{\text{product}}^{\text{IH}}$ is the weight fraction of the initial hydrocarbon (%) in reaction products, as determined from gas-chromatographic analysis data. The yields of gaseous and liquid isomerization products (Y, wt %) were determined from the general equation

$$Y = (100 + AH) \times W_{\text{product}}/100, \quad (4)$$

where W_{product} is the weight fraction of a corresponding component (%) in reaction products, as determined from gas-chromatographic analysis data. Selectivity for the formation of isomerization products was calculated from the equation

$$S = \left((100 + AH) \times W_{\text{product}} - 100 \times W_{\text{feed}}\right) \Big/ \left(W_{\text{feed}}^{\text{IH}} - (100 + AH) \times W_{\text{product}}^{\text{IH}}/100\right), \quad (5)$$

where W_{init} is the total weight fraction of corresponding components (%) in the feed mixture, as determined from gas-chromatographic analysis data.

RESULTS AND DISCUSSION

For varying the acidic properties and hydrogenating of the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ bifunctional system (Pt/SZA), we used the samples of supports containing from 18.8 to 67.8 wt % alumina to prepare this system (Table 1). Sulfated zirconia and alumina with platinum supported on their surfaces (Pt/SZ and Pt/A, respectively) served as reference samples. The platinum content of the catalysts was at a level of 0.28–0.32 wt %.

The preliminary selection of samples with an optimum alumina concentration for selective hydroisomerization and the indirect estimation of changes in their acidic and hydrogenating were based on data concerning the behavior of catalysts in the model reactions of *n*-heptane and cyclohexane isomerization.

Figure 1 shows data on the effect of temperature on the *n*-heptane conversion on chemically different catalysts. It can be seen that the samples different in alumina concentrations, including the Pt/SZ reference

Table 1. Chemical composition of catalyst samples

Sample*	Chemical composition of the support, wt %			Concentration of Pt, wt %
	SO_4^{2-}	ZrO_2	Al_2O_3	
Pt/SZ	4.5	95.5	0	0.32
Pt/SZA-18.8	6.1	75.1	18.8	0.30
Pt/SZA-47.8	4.4	47.8	47.8	0.28
Pt/SZA-67.8	3.1	29.1	67.8	0.29
Pt/A	0	0	100	0.30

* Numerals in sample designations correspond to actual concentrations of Al_2O_3.

Table 2. Catalytic properties of samples in *n*-heptane isomerization

Sample	T_{50}*, °C	Selectivity, %				Yield, wt %		
		C_1–C_4	C_5	C_6	iso-C_7	C_1–C_4	C_{5+}	iso-C_7
Pt/SZ	112	12.7	0.6	0.6	86.5	6.9	93.3	43.3
Pt/SZA-18.8	120	12.2	0.5	0.5	87.2	6.2	94.0	43.6
Pt/SZA-47.8	152	15.3	0.5	0.5	84.0	8.0	92.2	42.0
Pt/SZA-67.8	266	5.4	0.2	0.5	94.2	3.0	97.1	47.1

* Temperature of 50% *n*-heptane conversion.

sample, can provide a similar *n*-heptane conversion of up to 80% but in different temperature intervals. An increase in the concentration of Al_2O_3 as a constituent of catalyst samples is accompanied by a decrease in the overall activity in *n*-heptane conversion, and a specific temperature should be chosen to both initiate the reaction and reach a required conversion. On the Pt/SZ and Pt/SZA-18.8 samples, a 30–35% *n*-heptane conversion was observed even at 100°C. As the concentration of alumina was increased to 47.8 wt %, the reaction temperature of about 135°C was required for maintaining the same activity. For the Pt/SZA-67.8 sample, the range of working temperatures for *n*-heptane isomerization was above 200°C. The alumina–platinum catalyst had the lowest activity, which provided *n*-heptane conversion of no higher than 13% even at 300°C. Thus, the results of the acid-controlled model reaction of *n*-heptane isomerization suggest a gradual decrease in the acidity of the Pt/SO_4^{2-}–ZrO_2–Al_2O_3 system with increasing alumina content.

For all of the samples, C_1–C_4 light alkanes, C_5 and C_6 alkanes, and isoheptanes (iso-C_7) were observed as the main products of *n*-heptane conversion. From the standpoint of the hydroisomerization of light benzene-containing gasoline fractions, only the formation of isoheptanes can be considered as the target process of *n*-heptane conversion, which is responsible for the retention of the octane number of liquid products and, most importantly, the yield of these products. Therefore, for a correct comparison between tested catalyst samples in terms of a ratio between their activity and selectivity for the formation of isoheptanes, we found by interpolation the reaction temperatures at which a 50% n-heptane conversion were reached (T_{50}) and calculated the corresponding product yields and selectivity for the formation of different groups of products. Data given in Table 2 indicate that an increase in the alumina content leads to an increase in the values of T_{50}. The most significant changes in the

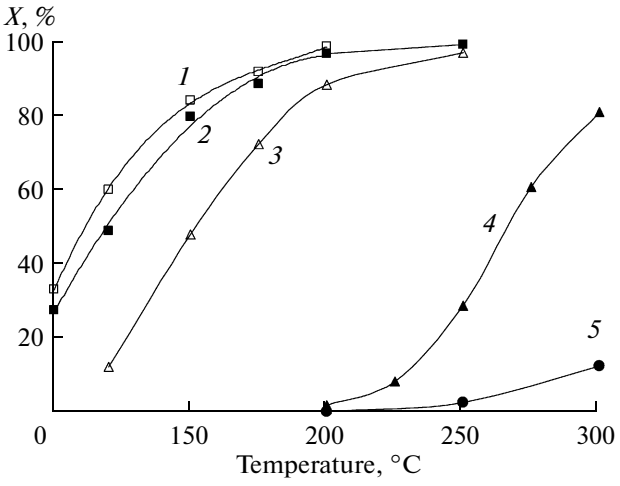

Fig. 1. The temperature dependence of the *n*-heptane conversion (*X*, %) for catalysts with various concentrations of Al_2O_3: (*1*) Pt/SZ, (*2*) Pt/SZA-18.8, (*3*) Pt/SZA-47.8, (*4*) Pt/SZA-67.8, and (*5*) Pt/A.

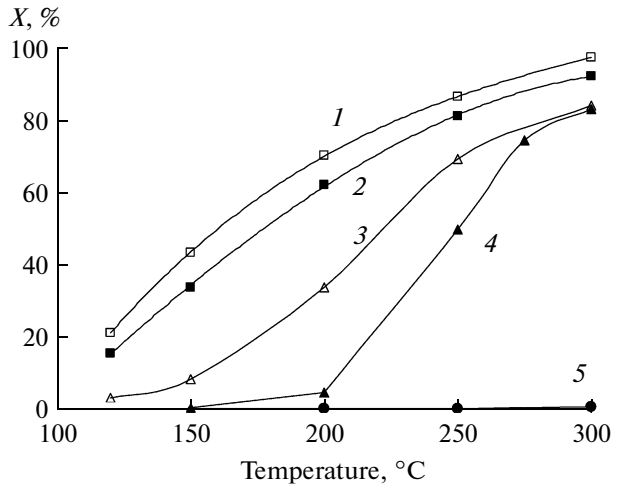

Fig. 2. The temperature dependence of the cyclohexane conversion (X, %) for catalysts with various concentrations of Al_2O_3: (*1*) Pt/SZ, (*2*) Pt/SZA-18.8, (*3*) Pt/SZA-47.8, (*4*) Pt/SZA-67.8, and (*5*) Pt/A.

value of T_{50} occurred in the samples containing 47.8 and 67.8 wt % Al_2O_3. As compared with Pt/SZ, the values of T_{50} for these samples increased by 40 and 154 K, respectively. The 50% n-heptane conversion cannot be achieved on the Pt/A sample under the test temperature conditions. However, selectivity for the formation of isoheptanes on all of the samples containing to 47.8 wt % Al_2O_3 had similar values of no higher than 87.2%. In contrast to this, the Pt/SZA-67.8 sample was characterized by 94.2% selectivity for isomerization. In this case, T_{50} was 266°C for this sample. This is a completely positive fact because the temperature range of 250–300°C is thermodynamically more favorable for cyclohexane isomerization to methylcyclopentane, which forms the basis for compensating losses in the octane number of liquid hydroisomerization products, which appeared as a result of benzene conversion into cyclohexane. According to published data [10], the equilibrium methylcyclopentane : cyclohexane ratio is 3.7, 4.4, or 5.2 at 250, 275, or 300°C, respectively.

The results of the second model reaction—the isomerization of cyclohexane into methylcyclopentane—also confirm the possibility of regulating the catalytic properties of the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ system by changing the concentration of alumina and selecting a catalyst composition to provide the selective formation of target liquid products. As can be seen in Fig. 2, the influence of the chemical composition of catalyst samples on their activity in the conversion of cyclohexane qualitatively coincides with the influence found for the reaction of *n*-heptane isomerization. An increase in the Al_2O_3 content of the catalyst samples was also accompanied by a decrease in the total activity in cyclohexane conversion. In this case, the introduction to 18.8 wt % Al_2O_3 had no principal effect on process characteristics. A further increase in the concentration of Al_2O_3 resulted in the strong differentiation of samples in terms of general activity and the selectivity. Cyclohexane, which is a more stable hydrocarbon than *n*-heptane under the conditions of acid catalysis, did almost not undergo conversion on the alumina–platinum catalyst up to a maximum process temperature of 300°C. The Pt/SZ and Pt/SZA-18.8 samples provided maximum methylcyclopentane yields of 57.1 and 52.9 wt %, respectively, at a temperature of 200°C (Table 3). In this case, $C_1–C_4$ light alkanes and C_6 alkanes, which resulted from hydrocracking reactions, were the main by-products. As a result, the methylcyclopentane : cyclohexane ratio was no higher than 1.9. As in the case of *n*-heptane isomerization, the Pt/SZA-67.8 sample can be considered the most effective catalyst of cyclohexane isomerization. At a temperature of 275°C, the yield of methylcyclopentane on this catalyst was as high as 69.6 wt % at a methylcyclopentane : cyclohexane ratio of 2.7. Light ($C_1–C_5$) and heavy (C_{7+}) conversion products were detected in trace amounts. The selectivity for the formation of methylcyclopentane and C_6 naphthene ring-opening products was 93.7 and 5.8%, respectively.

The strength and concentration of LASs for the Pt/SZA-67.8 catalyst, which is most effective in the isomerization of *n*-heptane and cyclohexane, were

Table 3. Catalytic properties of samples in cyclohexane isomerization

Sample	$T^*_{max, MCP}$, °C	$Y^{**}_{max, MCP}$, wt %	Yield of C_{5+}, wt %	Selectivity, %				
				$C_1–C_4$	C_5	C_6 alkanes	MCP	C_{7+}
Pt/SZ	200	57.1	98.9	2.0	0.8	12.5	81.7	3.5
Pt/SZA-18.8	200	52.9	99.3	1.5	0.6	10.6	85.3	2.3
Pt/SZA-47.8	250	61.6	99.4	1.2	0.6	7.0	89.3	2.1
Pt/SZA-67.8	275	69.6	99.9	0.4	0.1	5.8	93.7	0.3

* Temperature at which a maximum yield of methylcyclopentane was reached.

** Maximum yield of methylcyclopentane.

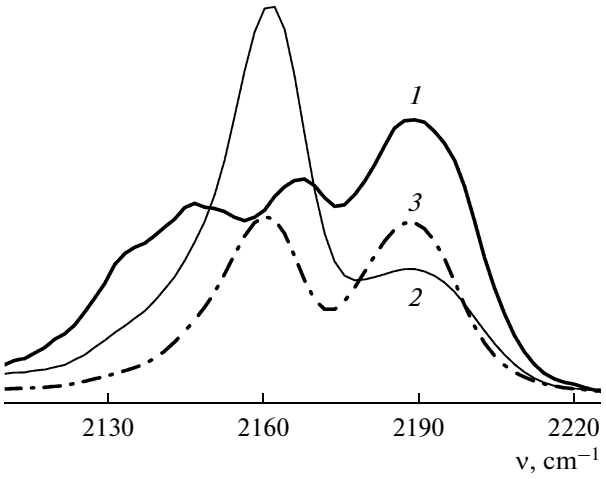

Fig. 3. IR spectra of adsorbed CO (10 mbar; −196°C): (*1*) Pt/SZ, (*2*) Pt/SZA-67.8, and (*3*) Pt/A.

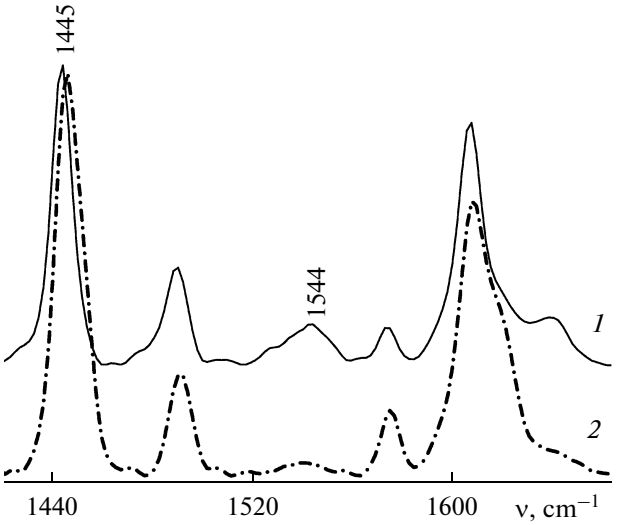

Fig. 4. IR spectra of adsorbed pyridine: (*1*) Pt/SZ and (*2*) Pt/SZA-67.8.

evaluated based on data on the IR spectra of adsorbed CO and compared with those for the Pt/SZ and Pt/A samples (Fig. 3). After the adsorption of CO, absorption bands with frequencies (ν(CO)) in the range of 2180–2208 cm^{-1} corresponding to the complexes of CO with LASs of different strengths; absorption bands at 2168–2171 cm^{-1}, which correspond to the complexes of CO with BASs; absorption bands at 2160–2162 cm^{-1}, which characterize the complexes of CO with weakly acidic hydroxyl groups; and also absorption bands at 2133–2148 cm^{-1}, which are due to the absorption of physically adsorbed CO molecules, were observed in the spectra of all of the samples. In all cases, the presence of only medium-strength LASs (absorption bands with ν(CO) of 2204–2208 cm^{-1} for Pt/SZ, 2202–2208 cm^{-1} for Pt/SZA-67.8, and 2202–2204 cm^{-1} for Pt/A) and weak LASs (absorption bands with ν(CO) of 2194, 2188, and 2180 cm^{-1} for Pt/SZ and 2192 cm^{-1} for Pt/SZA-67.8 and Pt/A). Figure 4 shows the IR spectra of adsorbed pyridine obtained for the Pt/SZ and Pt/SZA-67.8 samples. As well as upon the adsorption of CO, absorption bands corresponding to the complexes of pyridine molecules with the BASs (1544 cm^{-1}) and LASs (1445 cm^{-1}) of the catalysts were detected. The amounts of BASs in the test catalyst samples were estimated from the intensity of an absorption band due to protonated pyridine with a maximum at 1544 cm^{-1}.

Table 4 summarizes data on LAS and BAS concentrations for the Pt/SZ, Pt/SZA-67.8, and Pt/A catalysts. The Pt/SZ sample was characterized by the highest level of both LAS and BAS concentrations. In this case, more than 82% LASs belonged to the sites giving weakly bound complexes with CO. The total amount of LASs in the alumina–platinum system was found lower than that in Pt/SZ by a factor of 1.7, whereas the fraction of weak LASs increased to 92%. We failed to detect the presence of BASs in the Pt/A sample based on the adsorption of pyridine; this is fully consistent with published data on the absence of BASs whose strength is sufficient for the formation of pyridinium ions from the surface of alumina [11–13]. As expected, the Pt/SZA-67.8 sample occupied an intermediate position according to its acidic properties. The amount of BASs in this sample was smaller than that in the Pt/SZ sample by a factor of 3.5, and it was almost proportional to the decrease in the concentration of ZrO_2 in its composition by a factor of 3.3

Table 4. Acidic and hydrogenating of catalyst samples according to IR-spectroscopic data for adsorbed CO and pyridine

Sample	LASs, μmol/g		Total LASs, μmol/g	BASs, μmol/g
	medium-strength (2200–2208 cm^{-1})*	weak (2180–2194 cm^{-1})*		
Pt/SZ	115	530	645	32
Pt/SZA-67.8	60	250	310	9
Pt/A	29	350	379	0

* Frequencies of absorption bands due to adsorbed CO.

(29.1 against 95.5 wt %, respectively). As compared with Pt/SZ, the total amount of LASs decreased by a factor of only 2, and it was lower than that in the alumina–platinum catalyst. However, the ratio between the amounts of medium-strength and weak LASs in the Pt/SZA-67.8 sample corresponds to the ratio found for the Pt/SZ sample. Thus, the introduction of alumina into the $Pt/SO_4^{2-}–ZrO_2$ system leads a decrease in the number LASs and BASs, which is obviously related to the effect of its dilution with a component having a lower intrinsic acidity. The nonadditive change in the concentration of acid sites, in particular, LASs, observed in this case can be caused by the interaction of system components, the manifestations of which were noted earlier in a study of chemical and phase compositions and also the texture characteristics of $SO_4^{2-}–ZrO_2–Al_2O_3$ supports [3].

The decrease of *n*-heptane and cyclohexane conversions in the course of isomerization with the concentration of Al_2O_3 in the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ system can be related to the decrease in the number of acid sites. However, the higher selectivity reached at comparable conversions on the samples with higher alumina contents cannot be explained by only a change in the number of acid sites. Because methane and ethane were almost absent from the resulting hydrocarbon gases, the reactions of hydrogenolysis made a minimum contribution and the C–C bond cleavage occurred by the mechanism of hydrocracking; that is, it was related to the acid function of the catalyst. Data published by Zalewski et al. [14] indicate that the average strength of acid sites decreased as the concentration of alumina in the $SO_4^{2-}–ZrO_2–Al_2O_3$ system was increased. It is likely that this fact is responsible for the increase in selectivity for the isomerization reactions of *n*-heptane and cyclohexane observed in this work.

As a result of the studies, we found that the introduction of Al_2O_3 by adding aluminum hydroxide to sulfated zirconia hydrate can be an effective method for regulating the acidity and choosing the composition of a $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ catalyst designed for the effective hydroisomerization of benzene-containing gasoline fractions. In the course of model reactions, it was found that a catalyst whose support contained 67.8 wt % Al_2O_3 was most effective in the isomerization of *n*-heptane and cyclohexane. The high yields and selectivity for the formation of isoheptanes and methylcyclopentane, which are the target products of model isomerization reactions, obtained on this catalyst over a temperature range of 250–300°C suggest that this catalyst is promising for use in the hydroisomerization of real feeds. To confirm this conclusion, it is necessary to study the hydrogenating properties of the $Pt/SO_4^{2-}–ZrO_2–Al_2O_3$ system. The results of this study will be published elsewhere.

ACKNOWLEDGMENTS

We are grateful to N.A. Allert and T.V. Kireeva for their participation in performing the experiments.

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).

REFERENCES

1. Benitez, V.M., Grau, J.M., Yori, J.C., Pieck, C.L., and Vera, C.R., *Energy Fuels*, 2006, vol. 20, p. 1791.
2. Miyaji, A. and Okuhara, T., *Catal. Today*, 2003, vol. 81, p. 43.
3. Kazakov, M.O., Lavrenov, A.V., Mikhailova, M.S., Allert, N.A., Gulyaeva, T.I., Muromtsev, I.V., Drozdov, V.A., and Duplyakin, V.K., *Kinet. Katal.*, 2010, vol. 51, no. 3, p. 457 [*Kinet. Catal.* (Engl. Transl.), vol. 51, no. 3, p. 438].
4. Moreno, S., Sun Kou, R., and Poncelet, G., *J. Catal.*, 1996, vol. 162, p. 198.
5. Molina, M.F., Molina, R., and Moreno, S., *Catal. Today*, 2005, vol. 107–108, p. 426.
6. Wakayama, T. and Matsuhashi, H., *J. Mol. Catal. A: Chem.*, 2005, vol. 239, p. 32.
7. Ginzburg, S.I., Gladyshevskaya, K.A., Ezerskaya, N.A., et al., *Rukovodstvo po khimicheskomu analizu platinovykh metallov i zolota* (Handbook for the Chemical Analysis of the Platinum Metals and Gold), Moscow: Nauka, 1965.
8. Paukshtis, E.A. and Yurchenko, E.N., *Usp. Khim.*, 1983, vol. 52, no. 3, p. 426.
9. Paukshtis, E.A., *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize* (Infrared Spectroscopy in Heterogeneous Acid–Base Catalysis), Novosibirsk: Nauka, 1992.
10. Zhorov, Yu.M., *Termodinamika khimicheskikh protsessov* (Chemical Thermodynamics), Moscow: Khimiya, 1985.
11. Hughes, T.R. and White, H.M., *J. Phys. Chem.*, 1967, vol. 71, p. 2192.
12. Segawa, K. and Hall, W.K., *J. Catal.*, 1982, vol. 76, p. 133.
13. Datka, J., Turek, A.M., Jehng, J.M., and Wachs, I.E., *J. Catal.*, 1992, vol. 135, p. 186.
14. Zalewski, D.J., Alerasool, S., and Doolin, P.K., *Catal. Today*, 1999, vol. 53, p. 419.