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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Effect of the Acidity of a Zeolite and Its Modification with Cerium and Zirconium on the Activity and Thermal Stability of Pd/beta in the Reaction of Deep Toluene Oxidation

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Abstract—Acidities of beta zeolites with various moduli and the catalytic activities of Pd/beta in the reaction of deep toluene oxidation were compared.

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It is known that ecologically important reactions of carbon monoxide oxidation and afterburning of hydrocarbons widely use supported palladium catalysts in which aluminum oxide and zeolites frequently serve as supports [1, 2]. The practical importance of these catalysts has particularly increased recently because of the rise in the price of platinum. As a result, a most important task for manufacturers of catalysts for detoxication of automobile exhaust gases is to replace platinum in catalysts with palladium to a greater extent. In modern automobiles equipped with afterburners, most part of the hydrocarbon exhaust (~80%) is produced at the so-called "cold start" [3], with the most noxious part of the exhaust composed of aromatic compounds. It is for this reason that the reaction of deep toluene oxidation is used as a test reaction for assessment of catalyst properties.

Typical catalysts for deep oxidation of hydrocarbons are Al_2O_3-supported palladium catalysts. The electronic state of palladium in these catalysts widely varies with the preparation and process conditions. If the reaction mixture contains an excess amount of oxygen, palladium may be simultaneously present as crystals of metallic palladium, phase oxide PdO, and Pd–Al_2O_3 "interaction phases" [4, 5]. Presumably, it is correct to designate these catalysts as PdO_x/Al_2O_3, where x may vary from 0 to 1. A disadvantage of this catalyst is in its comparatively low activity at temperatures below 300°C. Promising for the low-temperature range are Pd-zeolite catalysts, which exhibit high activity and thermal stability [6]. An increase in the thermal stability of catalysts supported by Al_2O_3 [7] and zeolites [8] is favored by presence in their composition of zirconium(IV) and cerium(IV) oxides, which preclude a decrease in the specific surface area of the support on raising the calcination temperature and prevent caking of particles of the active component.

In view of the promise shown by palladium catalysts on zeolite supports, the aim of this study was to examine the activity and thermal stability of Pd–zeolite catalysts in the reaction of deep toluene oxidation and to determine how addition of cerium and zirconium oxides affects the catalyst properties.

EXPERIMENTAL

As supports served zeolites of the beta structural type with silicate moduli (SiO_2/Al_2O_3) of 11 and 25 (Angara Plant of Catalysts and Organic Synthesis Open Joint-Stock Company) and 36 (Tosoh, USA), preliminarily calcined at 600°C for 4 h.

Cerium and zirconium were introduced into the zeolites by (1) impregnation with $Ce(NO_3)_3$ or $ZrO(NO_3)_2$ solutions and (2) ion exchange of the supports with $Ce(NO_3)_3$ or $ZrO(NO_3)_2$ solutions at a temperature of 80°C under permanent agitation for 6 h [9]. The samples obtained were calcined at 600°C for 4 h.

PdO_x was deposited by treating a zeolite with an aqueous solution of the ammonia complex $[Pd(NH_3)_4]^*(NO_3)_2$ [10]. The palladium content of the zeolites was 1 wt %. Pd-Catalysts were calcined at 600 or 800°C for 4 h. The samples were also subjected to a hydrothermal treatment in a flow of nitrogen containing 10% H_2O at 800°C for 25 h.

An X-ray phase analysis of the zeolites was made on a DRON-3 X-ray diffractometer (monochromatized CuKα radiation with a β-filter placed after a sample and before the counter). The samples were analyzed by powder diffraction method in the Bragg–Brentano configuration.*

A temperature-programmed desorption of ammonia (NH3-TPD) of zeolite samples was performed on an Autosorb-1-C/TCD device (Quantachrome Instruments, FL, USA). A sample was activated by heating in a flow of oxygen at 600°C for 1 h and subsequent keeping in a flow of helium for 1 h. After the sample cooled in the flow of helium to 125°C, adsorption of ammonia was performed. The physically adsorbed ammonia was removed by vacuum treatment art 125°C. NH_3 was desorbed by raising temperature at a rate of 10 deg min^{-1} from 125 to 600°C in a flow of helium.

27Al NMR spectra were measured with a Bruker Avance-400 spectrometer at a frequency of 104.2 MHz, with magic-angle spinning (MAS) at a frequency ν = 10 kHz. The spectra were obtained by Fourier transform of the free induction decay (FID). The FID was excited with a single-pulse sequence, with delay between the pulses of 0.3 s. The signal from the $Al(H_2O)_{3+6}$ ion was used as the external reference for the scale of chemical shifts. The spectra of the samples were calculated with account of the second-order quadrupole interaction on the basis of the perturbation theory. The simulation parameters are listed in Table 1.

Table. 1. 27Al NMR simulation parameters for beta (SiO_2/Al_2O_3 = 11)

Al^{3+} coordination type	δ_{iso}, ppm.	C_Q, MHz
$AlO_6(1)$	1	1.7
$AlO_6(2)$	8	6.7
AlO_5	18	3.5
$AlO_4(1)$	55	1.9
$AlO_4(2)$	59	2.5
$AlO_4(3)$	66	5.4

Table 2. Relationship between the acidity of zeolites and the catalytic activity of Pd/beta

SiO_2/Al_2O_3	Calcination (600°C)		Hydrothermal treatment	
	acidity, μmol $g1^{-1}$	$T_{50\%}$, °C	acidity, μmol g^{-1}	$T_{50\%}$, °C
11	884	235	405	256
25	908	237	414	233
36	770	189	347	283

The catalytic activity of the samples in the reaction of complete toluene oxidation was determined by the flow-through method in a microreractor having the form of a steel capillary 3.0 mm in diameter and 200 mm long. The starting gas mixture contained 0.015 vol % toluene, 0.5 vol % O_2, and 10 vol % H_2O in nitrogen. The time of contact between the gas mixture and a catalyst was 0.015 s. The degree of toluene conversion was found from

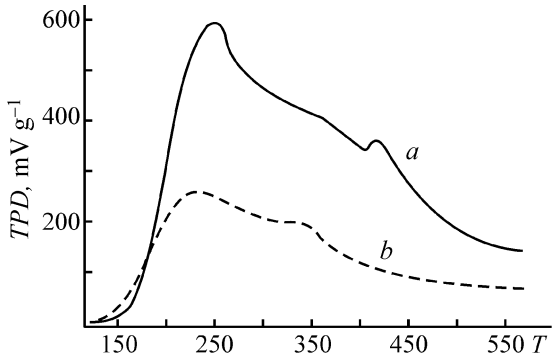

Fig. 1. General appearance of NH_3-*TPD* spectra of beta zeolites after (*a*) calcination (600°C) and (*b*) hydrothermal treatment (800°C, 10 vol % H_2O in N_2, 25 h. (*TPD*) Signal from the heat-conductivity detector and (*T*) temperature.

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the difference of the toluene concentrations before and after the reactor in the temperature range 150–300°C with the use of a flame-ionization detector. The temperature of 50% steady-state conversion of toluene, $T_{50\%}$, served as a measure of the catalytic activity.

NH_3-*TD* curves of beta zeolites after calcination (600°C) and hydrothermal treatment are shown in Fig. 1. The NH_3-*TPD* data and the results of catalytic tests of Pd/beta are compared in Table 2.

It can be seen that, upon calcination at 600°C with a decrease in the integral acidity of the zeolite, the catalytic activity of Pd/beta increases. According to [11], the most active state of palladium in deep-oxidation catalysts is the PdO phase in which the Pd–Pd bond is still preserved. This state is characteristic of a less dispersed palladium. In the case under study, this phase occurs with higher probability for beta-36 zeolite, which contains in a lower concentration ion-exchange groups (–Al–OH–Si–) determining the initial dispersity of palladium. Indeed, as shown in [12], the acidity of a zeolite predetermines the dispersity and oxidation state of palladium and thereby affects its catalytic activity in oxidation of hydrocarbons. Presumably, the smaller, compared with other samples, active surface area of palladium in Pd/beta-36 is compensated for, because of the higher degree of crystallization, by the more active state of supported palladium, with the oxide PdO_x formed on Pd crystals. However, hydrothermal treatment of this sample deactivates it in the reaction of toluene oxidation to a greater extent. A probable reason is that the active component undergoes caking because of the decrease in the number of acid centers of the zeolite, which stabilize PdO_x.

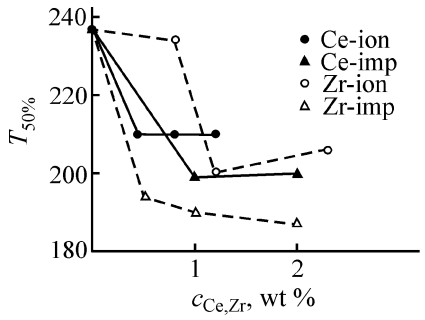

Fig. 2. Dependence of the catalytic activity of 1% Pd/beta-25 in toluene oxidation, $T_{50\%}$, on the method of introduction and content $c_{Ce,Zr}$ of cerium (zirconium).

Hydrothermal treatment leads for all of the samples to a more than twofold decrease in the concentration of acid centers in the zeolites, which is presumably due to dealumination of the zeolite structure. An X-ray phase analysis of the zeolites demonstrated that, in this case, the intensities of peaks corresponding to different planes are redistributed, but, on the whole, the zeolite structure is not changed fundamentally, compared with the samples calcined at 600°C. As noted in [13], the dealumination of a zeolite impairs the catalytic activity of Pd/zeolite samples. The reason is that the specific surface area of the zeolite sharply decreases and palladium undergoes caking. Indeed, values of $T_{50\%}$ for toluene conversion increase upon a hydrothermal treatment of Pd/beta-11 and Pd/beta-36 samples. However, the catalytic activity of Pd/beta-25 remains at the same level despite the considerable decrease in the acidity of the zeolite.

The effect of cerium and zirconium present in a catalyst on its catalytic activity is considered for the example of Pd/beta-25 sample, which is the most stable against a hydrothermal treatment. The results of catalytic tests of samples calcined at 600°C are presented in Fig. 2.

It was shown by varying the content of cerium (zirconium) in the catalyst that modified samples have a lower $T_{50\%}$ of toluene conversion, compared with the starting (600°C) Pd/beta-25. This means that presence of these additives makes the catalytic activity of Pd/beta higher. The extent to which $T_{50\%}$ decreases for Pd/Ce(Zr)/beta depends on the way in which cerium (zirconium) is introduced into a catalyst. For catalysts for which zeolite is modified by the impregnation method (imp) the increase in the catalytic activity exceeds that for samples into which the additives were introduced by the ion-exchange method (ion). For example, introduction of a modifying additive in an amount of 1 wt % results in that $T_{50\%}$ decreases relative to the starting Pd/beta catalyst by 25–35°C for ion-exchange samples, and by 35–50°C for impregnated samples. The highest activity in toluene oxidation is observed, among these catalysts, for Pd/Zr-imp/beta-25, for which $T_{50\%}$ is 190°C, being 237°C for the starting Pd/beta-25.

The observed difference in catalytic activity between the ion-exchange and impregnated samples is due to the interaction of palladium particles with ZrO_2 or CeO_2. According to [10, 14], this interaction favors an increase in the catalytic activity of palladium catalysts in oxidation of hydrocarbons because oxygen has high

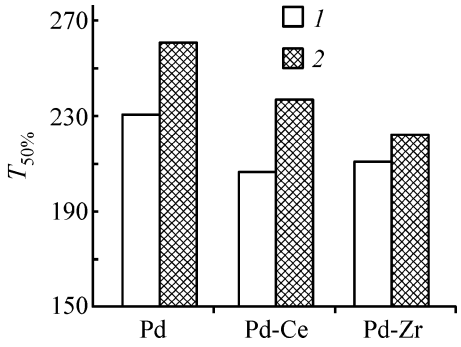

Fig. 3. Catalytic activities of 1% Pd/beta-11 and 1% Pd/Ce(Zr)/beta-11 in toluene oxidation, $T_{50\%}$, before and after hydrothermal treatment. (*1*) 800°C and (*2*) 800°C, 10% H_2O in nitrogen, 25 h; the same for Figs. 4, 5.

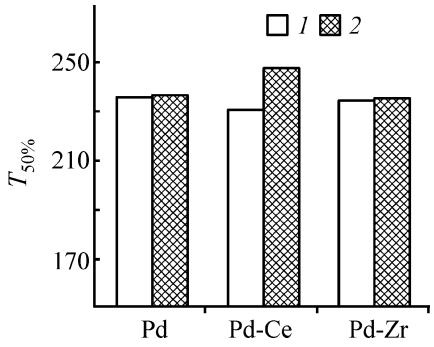

Fig. 4. Catalytic activities of 1% Pd/beta-25 and 1% Pd/Ce(Zr)/beta-25 in toluene oxidation, $T_{50\%}$, before and after hydrothermal treatment.

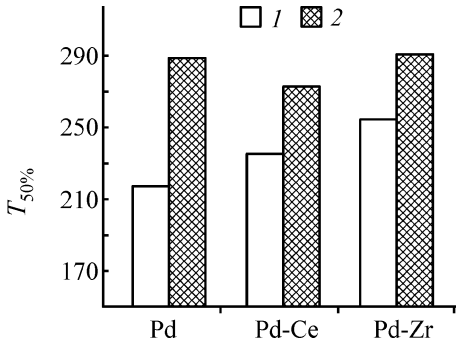

Fig. 5. Catalytic activities of 1% Pd/beta-36 and 1% Pd/Ce(Zr)/beta-36 in toluene oxidation, $T_{50\%}$, before and after hydrothermal treatment.

mobility in these oxides and can form bridges between palladium atoms, thereby making weaker the palladium–oxygen bonding on the surface of PdO_x particles. It can be assumed that, as a result of the ion exchange, the interaction between the modifier and the active component is weakened by their spatial separation. In samples produced by the impregnation method, the interaction probability is higher because, upon a thermal treatment, these particles are mostly situated on the outer surface of zeolite crystals.

The effect of the hydrothermal treatment on the catalytic activity of Pd/Ce(Zr)/beta was considered for samples based on zeolites with different aluminosilicate moduli at a modifier content of 1 wt %. According to the results of catalytic tests, Pd/beta-11 samples containing cerium (zirconium) additives show (Fig. 3) a lower $T_{50\%}$, compared with an unmodified sample, both upon calcination at 800°C and after a hydrothermal treatment at the same temperature.

Thus, presence of cerium and zirconium makes higher the catalytic activity of Pd/beta-11 and improves its stability against hydrothermal treatment. In this case, the catalytic activity decreases upon a prolonged treatment for all the samples; however, the deactivation is less pronounced for modified samples. For example, $T_{50\%}$ of toluene conversion is reached for the Ce- and Zr-containing catalysts 25 and 39°C earlier, respectively, compared with the unmodified Pd/beta.

In the case of Pd/beta-25, the original advantage in the catalytic activity of modified samples is eliminated upon calcination at 800°C and after a hydrothermal treatment: their catalytic activities remain almost unchanged and are comparable with the catalytic activity of Pd/beta-25 catalyst (Fig. 4).

For Pd/beta-36, introduction of cerium (zirconium) into the catalyst makes the catalytic activity lower than that of the unmodified sample; upon hydrothermal treatment, all the catalysts show deactivation (Fig. 5).

Thus, an increase in the silicate modulus of a zeolite diminishes the positive effect of cerium and zirconium additives on the catalytic activity of Pd/beta and its stability against hydrothermal treatment.

For Pd/Ce(Zr)/beta-11, the effect of cerium and zirconium introduction on structural changes in the zeolite in hydrothermal treatment was examined using the 27Al NMR technique. 27Al MAS NMR spectra of beta zeolites before and after hydrothermal treatment are shown in Fig. 6. The spectra were obtained under identical conditions and their intensities are given relative to the spectrum of the starting zeolite. The presence in the 127Al spectrum of lines associated with

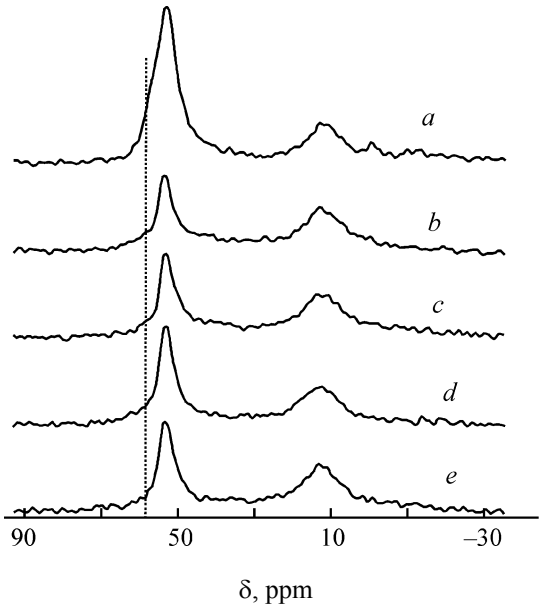

Fig. 6. 27Al MAS NMR spectrum. (δ) Chemical shift. (*a*) beta-11, 600°C (4 h); after a hydrothermal treatment: (*b*) beta-11, (*c*) 1% Pd/beta-11, (*d*) 1% Pd–1% Ce/beta-11, and (*e*) 1% Pd–1% Zr/beta-11.

$AlO_4(1)$ and $AlO_4(2)$ centers, with chemical shifts δ_{iso} of 55 and 59 ppm, characterizes different T-positions of aluminum in the zeolite [15], and, thus, corresponds to structural aluminum in the composition of the zeolite. The other lines present in the spectrum are related to extraskeletal (nonstructural) aluminum.

After a hydrothermal treatment, a substantial change in the intensity of lines characteristic of skeletal aluminum is observed for all the samples. The line with δ_{iso} = 59 ppm (shown by dashed line) nearly completely disappears, and the intensity of the line with δiso 55 ppm, which corresponds to tetrahedral aluminum $AlO_4(1)$ in the zeolite structure, substantially decreases. The known reason is the dealumination of the zeolite: egress of aluminum from the zeolite skeleton, caused by the action of water vapor at a high temperature.

Table 3. Relative intensities of the $AlO_4(1)$ line with a chemical shift of 55 ppm for hydrothermally treated samples based on beta-11

Sample	I_{rel}
beta, 600°C	1
Hydrothermal aging *:	
beta	0.42
1%Pd/beta	0.57
1% Pd-1% Ce/beta	0.67
1%Pd-1%Zr/beta	0.7

* Hydrothermal aging at 800°C and 10 vol % H_2O in N_2.

According to the data in Table 3, the relative intensity of the line associated with tetrahedral aluminum in the zeolite skeleton increases, for samples subjected to hydrothermal treatment, in the following order: beta < 1% Pd/beta < 1% Pd–1% Ce/beta < 1% Pd–1% Zr/beta. Apparently, the presence of cerium(III) and zirconium(IV) does not completely prevent dealumination of the zeolite, but hinders this process by improving the stability of the zeolite structure and leads to an increase in the catalytic activity of Pd/Ce(Zr)/beta-11 upon a prolonged hydrothermal treatment.

CONCLUSIONS

(1) The effect of the acidity of a beta zeolite on the catalytic activity of Pd/beta depends on thermal treatment conditions. Upon calcination at 600°C, the catalytic activity of Pd/beta in toluene oxidation increases as the acidity of the zeolite becomes lower, with the opposite dependence observed after a hydrothermal treatment (800°C, 10% H_2O in nitrogen, 25 h).

(2) Introduction of cerium(III) and zirconium(IV) into Pd/beta-11 improves its catalytic activity and hinders dealumination of the zeolite in a hydrothermal treatment. As, however, the silicate modulus of the zeolite becomes higher, this effect is not observed.

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