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Effect of the Acid–Base Properties of the Support on the Activity of Pd–Zeolite Catalysts for CO Oxidation

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Abstract—The effect of the acid–base properties of zeolite Y on the activity of palladium–zeolite catalysts for CO oxidation was studied. The modification of the support with basic additives was found to improve the catalyst activity. A linear correlation between the ratio between the amounts of O_2 and CO adsorbed on the surface of palladium and the catalyst activity was established.

INTRODUCTION

The dependence of the activity of metal–zeolite catalysts on the acid–base properties of the support was found for a number of reactions. For example, an increase in the acidity of zeolite Y resulted in an increase in the activity of Pt- and Pd-containing zeolite catalysts in the reactions of ethane and *n*-pentane hydrogenolysis [1–3] and an increase in the base properties of zeolite L enhanced the activity of Pt-containing catalysts in the hydrogenation of benzene and the reforming of *n*-hexane [4, 5].

Grafe *et al.* [6] demonstrated that the catalytic activity of Cu-, Mn-, and Fe-containing zeolite catalysts in ethanol oxidation decreased with increasing acidity of the catalyst. Borko *et al.* [7], who studied the effect of the acid properties of natural mordenite modified with transition metal cations on the catalytic activity in the deep oxidation of methane, found that the catalyst activity increased upon additional alkali treatment.

Previously [8], we found that an increase in the acidity of zeolite Y resulted in a decrease in the activity of the Pd–zeolite catalyst in the reaction of CO oxidation.

In this context, it was of interest to study the effect of the base properties of zeolite Y on the activity of a palladium–zeolite catalyst in CO oxidation.

EXPERIMENTAL

Zeolite NaY with a silica modulus (SiO_2/Al_2O_3) of 4.8 (sodium concentration of 3.46 mmol/g) was used for preparing the stock catalyst 0.5%Pd/NaY. Palladium was introduced into the support by the method of ion exchange using a solution of tetraamminepalladium(II) chloride $[Pd(NH_3)_4]Cl_2$. For this purpose, a weighed portion of powdered zeolite was kept in a water–ammonia solution of tetraamminepalladium(II) chloride with a palladium concentration of 0.0125 g/ml for 1 h at room temperature under continuous stirring; the pH of the solution was maintained within the range 8–10. After the ion exchange, the catalyst mass was washed with distilled water to a negative reaction for Cl^- ions and dried at room temperature for 8 h and then at 120°C for 2 h. Next, the resulting mass was pressed as pellets and crushed, and a fraction with a particle size of 0.5–1.0 mm was taken. The stock catalyst thus prepared was activated by calcination in air at 400°C (3 h) and then reduced in a hydrogen flow at the specified temperature for 3 h.

The acid properties of the support were enhanced by decationizing the zeolite, and the base properties were enhanced by introducing K^+, Rb^+, or Cs^+ cations into the zeolite or by supporting alkali metal carbonates.

To obtain samples with the same dispersity of palladium, the decationization of the catalyst and the modification of the support with cations or alkali metal carbonates were performed after reductive treatment of the stock catalyst.

The samples were decationized by treatment with a 0.1 M NH_4Cl solution at room temperature followed by calcination in a helium flow at 400°C.

The exchange of Na^+ for K^+, Rb^+, or Cs^+ cations was performed by the treatment of a reduced catalyst with an excess of a 1 M KCl, RbCl, or CsCl solution, respectively. After the exchange, the samples were washed with distilled water to a negative reaction for Cl^- ions, dried at room temperature, and calcined at 400°C in a helium flow.

The fraction of the exchange of Na^+ cations for K^+, Rb^+, or Cs^+ cations was determined from the sodium concentrations in spent solutions. The exchange fractions for K^+, Rb^+, Cs^+, or H^+ are indicated by the numerical values of zeolite symbols.

Potassium, rubidium, and cesium carbonates were introduced into the catalysts 0.5%Pd/KNaY, 0.5%Pd/RbNaY, and 0.5%Pd/CsNaY by impregnating the samples with a solution of the corresponding alkali metal carbonate in a given concentration. After drying, the samples were calcined in a helium flow at 400°C.

The table summarizes the composition of the synthesized catalysts.

The sorption volume of the test samples was determined chromatographically using the sorption of argon (5% argon mixture in helium at –196°C).

The thermal desorption of CO and oxygen was performed in a vacuum unit with mass-spectrometric detection of the products desorbed into a gas phase on an MX-1320 mass spectrometer. Before thermal-desorption measurements, the samples were evacuated to a residual pressure of 10^{-7} torr at room temperature for 30 min, heated to 400°C, and cooled to room temperature. Carbon monoxide (15 torr) or oxygen (100 torr) was admitted into the samples thus prepared; then, the samples were evacuated to 10^{-7} torr and thermal-desorption spectra were measured in the temperature range from 20 to 200°C. The temperature during programmed-temperature measurement of the spectra was increased at a rate of 15°C/min.

The particle size of reduced palladium was determined by transmission electron microscopy (TEM) on a JEM-100CX instrument.

The activity of synthesized catalysts was determined in a flow reactor at a gas hourly space velocity of 20 000 h^{-1} (1 vol % CO in air).

RESULTS AND DISCUSSION

The sorption volumes of palladium catalysts based on sodium, potassium, rubidium, and cesium forms of zeolite Y differ insignificantly (from 0.26 to 0.23 cm^3/g). However, the sorption volume considerably decreased upon supporting alkali metal carbonates (to 0.10–0.15 cm^3/g) depending on the amount of supported salts (see the table).

According to the TEM data, the dispersity of palladium was the same in all of the synthesized catalysts. The predominant particle size of the reduced metal was 30–60 Å. The formation of reasonably large palladium clusters, which are most likely localized on the outer surface of zeolite crystallites [9], resulted from the severe conditions of the redox treatment of the catalysts.

Data shown in Fig. 1 indicate that the exchange of Na^+ cations in the parent zeolite for K^+, Rb^+, or Cs^+ cations resulted in an insignificant increase in the catalyst activity. Thus, the temperature of 50% conversion on the most active catalyst 0.5%Pd/CsNaY was lower than that on the catalyst 0.5%Pd/NaY by only 12°C. At the same time, on going from the sodium form to the decationized form of zeolite, the catalyst activity dramatically decreased (the temperature of 50% conversion was higher than that on the stock catalyst by 38°C, curve *5*).

The catalyst modification with alkali metal carbonates resulted in a detectable increase in the activity (Fig. 2). Note that in this case, the activity of 0.5%Pd/KNaY, 0.5%Pd/RbNaY, and 0.5%Pd/CsNaY catalysts increased upon addition of the corresponding alkali metal carbonates to 0.6–0.7 mmol/g. A further increase in the added carbonate amount decreased the catalyst activity.

Rubidium carbonate exhibited the strongest modifying effect. Thus, upon addition of 0.65 mmol/g potassium, rubidium, and cesium carbonates to 0.5%Pd/KNaY, 0.5%Pd/RbNaY, and 0.5%Pd/CsNaY catalysts, the temperatures of 50% CO conversion were lower than that on the stock catalyst by 27, 53, and 51°C, respectively (Fig. 2).

According to current concepts [10, 11], the base sites of zeolites are [M^+, $(AlO_4)^-$] fragments in which oxygen ions possess an excessive negative charge because of electron-density donation by alkali metal cations. These oxygen ions are weakly basic sites. Our results suggest that alkali metal cations exert a weakly pronounced modifying effect. It is evident that the high activity of catalysts modified with alkali metal carbonates results from the presence of strong base sites con-

Composition and sorption volumes of the test catalysts (Pd content 0.5 wt %)

No.	Support	M_2CO_3 content, mmol/g	Sorption volume of the catalyst, cm^3/g
1	NaY	–	0.26
2	0.70 HNaY	–	0.27
3	0.65 KNaY	–	0.25
4	0.61 RbNaY	–	0.24
5	0.58 CsNaY	–	0.23
6	2.5% K_2CO_3/0.65 KNaY	0.18	0.24
7	5% K_2CO_3/0.65 KNaY	0.36	0.23
8	9% K_2CO_3/0.65 KNaY	0.65	0.21
9	15% K_2CO_3/0.65 KNaY	1.09	0.19
10	20% K_2CO_3/0.65 KNaY	1.45	0.17
11	25% K_2CO_3/0.65 KNaY	1.81	0.15
12	5% Rb_2CO_3/0.61 RbNaY	0.22	0.23
13	10% Rb_2CO_3/0.61 RbNaY	0.43	0.21
14	15% Rb_2CO_3/0.61 RbNaY	0.65	0.19
15	20% Rb_2CO_3/0.61 RbNaY	0.87	0.17
16	25% Rb_2CO_3/0.61 RbNaY	1.08	0.15
17	5% Cs_2CO_3/0.58 CsNaY	0.15	0.21
18	10% Cs_2CO_3/0.58 CsNaY	0.31	0.19
19	15% Cs_2CO_3/0.58 CsNaY	0.46	0.17
20	21% Cs_2CO_3/0.58 CsNaY	0.65	0.15
21	25% Cs_2CO_3/0.58 CsNaY	0.77	0.13
22	35% Cs_2CO_3/0.58 CsNaY	1.08	0.10

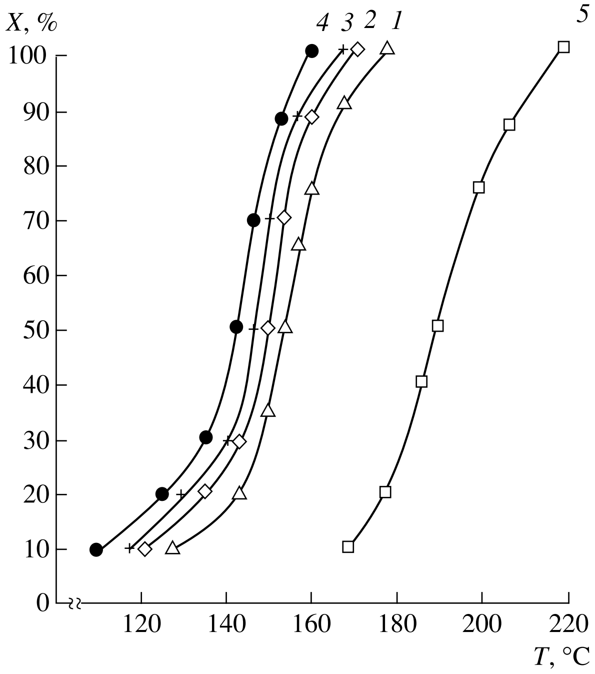

Fig. 1. Conversion of CO as a function of temperature for Pd–zeolite catalysts in (*1*) sodium, (*2*) potassium, (*3*) rubidium, (*4*) cesium, and (*5*) decationized forms.

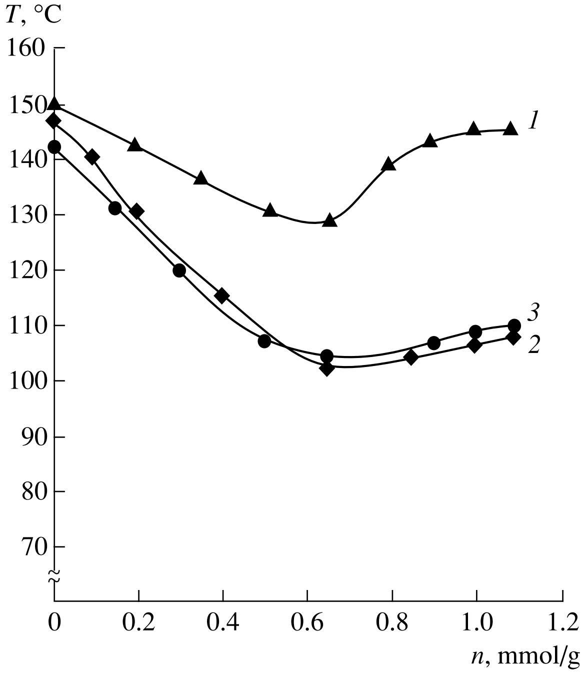

Fig. 2. Temperature of 50% CO conversion as a function of alkali metal carbonate content (*n*) for Pd–zeolite catalysts modified with (*1*) K_2CO_3, (*2*) Rb_2CO_3, and (*3*) Cs_2CO_3.

stituted of carbonate ions CO_3^{2-} [12]. The basicity of the carbonate ion and hence zeolite increases with the cation radius [10].

The catalysts

$$0.5\%Pd/9\%K_2CO_3/0.65KNaY,$$
$$0.5\%Pd/15\%/Rb_2CO_3/0.61RbNaY$$

and $$0.5\%Pd/21\%/Cs_2CO_3/0.58CsNaY$$

contain potassium, rubidium, and cesium carbonates, respectively, at 0.65 mmol/g each. As can be seen from Fig. 2 the catalyst modified with rubidium carbonate is much more active than the catalyst modified with potassium carbonate; this is likely due to an increase in the support basicity.

Catalyst modification with cesium carbonate would further enhance the support basicity and, hence, the catalyst activity. However, the activity of such a catalyst was found to be about the same as that of a rubidium-modified catalyst.

Note that equal molar concentrations of potassium, rubidium, and cesium carbonates in catalysts (0.65 mmol/g for samples 8, 14, and 20 in the table) correspond to different weight concentrations due to differences in molecular weight and have different volumes due to differences in density. A considerable decrease in the sorption volume is a consequence of this; for the above samples, the sorption volumes are 0.21, 0.19, and 0.15 cm^3/g, respectively. This results in a decrease in the rate of mass-exchange processes due to diffusion limitations. As a result, a positive contribution made by the addition of cesium carbonate to an increase in the sample basicity is compensated by a negative contribution due to diffusion limitations. It is likely that the decrease in catalyst activity at concentrations of the modifying additives higher than 0.6–0.7 mmol/g (Fig. 2) also resulted from a decrease in the sorption volume.

Previously [8], we hypothesized that the observed decrease of catalyst activity in the reaction of CO oxidation on going from Pd/NaY to Pd/HNaY is due to the formation of electron-deficient palladium by a shift of electron density from the metal to the support; this shift increases with the zeolite acidity. The reverse donation of electron density from the support to the metal can take place with an increase in the support basicity [13]. The presence of electron-excessive palladium in a catalyst will affect the adsorption properties and catalytic activity.

The results of catalytic studies suggest that the synthesized Pd–zeolite catalysts exhibit activity at low temperatures (<220°C). It is well known that the presence of weakly bonded CO and O_2 species adsorbed at palladium centers is responsible for the reaction of CO oxidation on supported palladium catalysts in this temperature range [14, 15].

The measurements of thermal desorption demonstrated that CO adsorbed on the surface of Pd–zeolite catalysts at room temperature desorbs in the low-temperature region (20–200°C) in different amounts and at

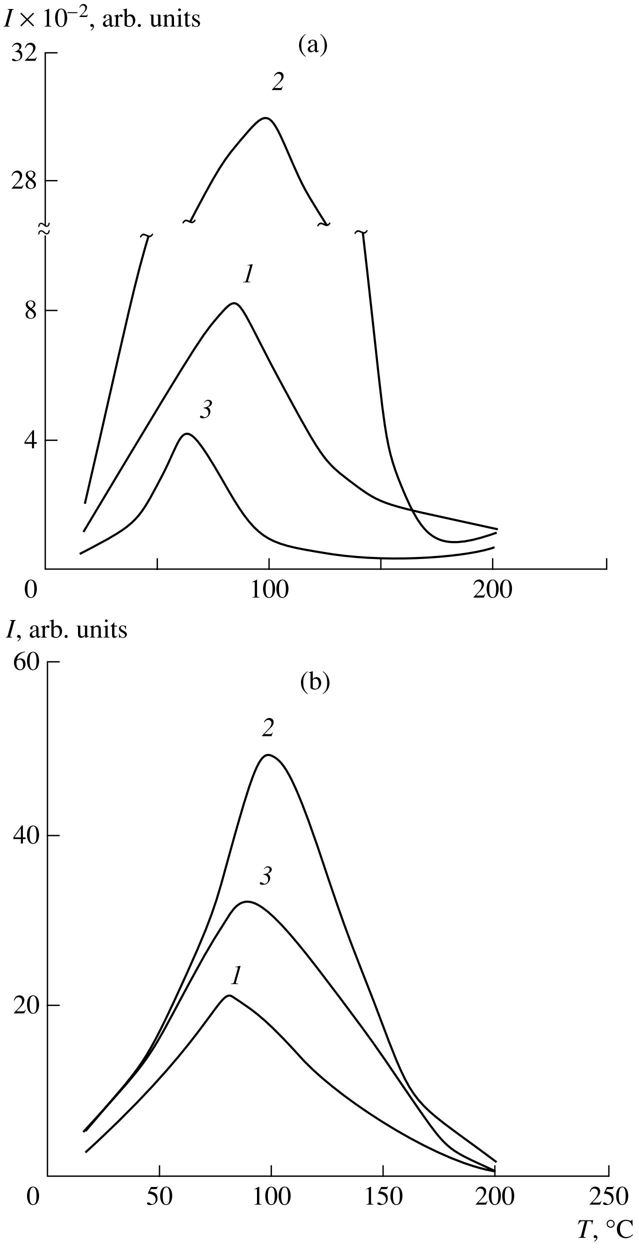

Fig. 3. Spectra of (a) CO and (b) O_2 temperature-programmed desorption from the surface of Pd–zeolite catalysts: (*1*) 0.5%Pd/NaY, (*2*) 0.5%Pd/HNaY, and (*3*) 0.5%Pd/15%Rb_2CO_3/0.61RbNaY.

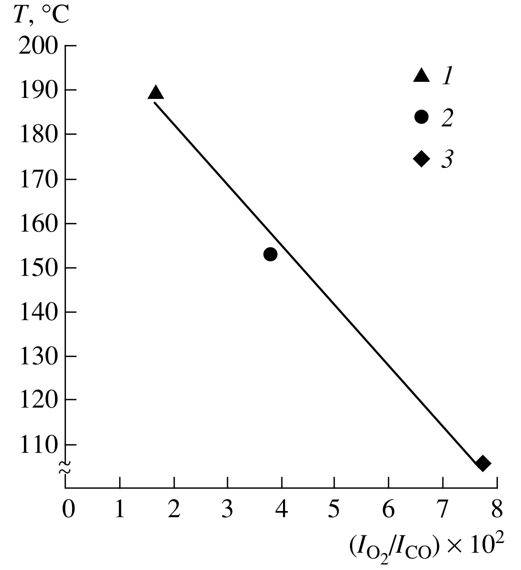

Fig. 4. Temperature of 50% CO conversion as a function of the ratio between the thermal-desorption peak intensities I_{O_2}/I_{CO} for Pd–zeolite catalysts: (*1*) 0.5%Pd/HNaY, (*2*) 0.5%Pd/NaY, and (*3*) 0.5%Pd/15%Rb_2CO_3/0.61RbNaY.

different maximum temperatures (T_{max}) depending on the acid–base properties of the support (Fig. 3a).

Thus, the catalysts 0.5%Pd/HNaY, 0.5%Pd/NaY, and 0.5%Pd/15%Rb_2CO_3/0.61RbNaY are characterized by a high-intensity peak with T_{max} = 100°C, a less intense peak with T_{max} = 80°C, and a low-intensity peak with T_{max} = 60°C, respectively. These data indicate that an increase in the support acidity results in an increase in the Pd–CO bond strength and in a dramatic increase in the amount of adsorbed carbon monoxide, which is likely due to an electron deficiency in the palladium. At the same time, an increase in the support basicity weakened the Pd–CO bond and decreased the amount of adsorbed carbon monoxide, which is probably due to an electron excess in the palladium.

The spectra of thermal oxygen desorption (Fig. 3b) are characterized by peaks with T_{max} ~ 100, 80, and 90°C for the catalysts 0.5%Pd/HNaY, 0.5%Pd/NaY, and 0.5%Pd/15%Rb_2CO_3/0.61RbNaY, respectively. Note that the amount of oxygen adsorbed on the surface of palladium being smaller than the amount of adsorbed CO by one order of magnitude is common for test catalysts. Because the reaction rate is limited by the adsorption and activation of both components, the activity of catalysts under study should be sensitive to the ratio of O_2 and CO adsorbed on the metal surface.

Figure 4 demonstrates the temperature of 50% CO conversion on palladium catalysts as a function of the ratio between the thermal-desorption peak intensities of adsorbed amounts of O_2 and CO, which are expressed in arbitrary units in Fig. 3. These data suggest a linear correlation between the catalyst activity and the value of I_{O_2}/I_{CO}. Therefore, this ratio can be used to predict the activities of different supported metal catalysts in this reaction.

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