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Synthesis and Physicochemical Characterization of Palladium–Cerium Oxide Catalysts for the Low-Temperature Oxidation of Carbon Monoxide

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Abstract—The effect of CeO_2 preparation procedure on the electronic and structural states of the active component of Pd/CeO_2 catalysts and their activity in the low-temperature reaction of CO oxidation was studied. The following two nonequivalent states of palladium were detected in the catalysts having low-temperature activity using XPS and IR spectroscopy: $Pd^0(Pd^{\delta+})$ as the constituent of a palladium-reduced interaction phase and Pd^{2+} as the constituent of a palladium-oxidized interaction phase $Pd_xCeO_{2-\delta}$. It was found that the procedure used for preparing a CeO_2 support considerably affected the formation of these phases and quantitative ratios between them. It was demonstrated that the palladium-oxidized interaction phase was responsible for low-temperature activity, whereas the palladium-reduced interaction phase was responsible for activity in the region of medium and high temperatures.

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INTRODUCTION

Palladium–cerium oxide catalysts make it possible to oxidize CO at a low temperature. The fundamentals of their catalytic action are of great interest.

It is well known that individual palladium, individual cerium oxide, or palladium dispersed on inert supports like SiO_2 and Al_2O_3 does not exhibit low-temperature activity. Low-temperature activity appears upon supporting Pd onto transition metal oxides. In the series of oxides of this type, cerium oxide exhibited the strongest interaction with the active component [1]. In spite of considerable progress in the development of commercial catalysts for the low-temperature oxidation of CO, many fundamental aspects of the catalytic action of Pd–Ce oxide catalysts remain poorly understood. Thus, there are no reliable published data on the electronic and structural state of the active component that is responsible for the formation of an optimum catalyst. The key problems are associated with the interaction of palladium with cerium oxide, the determination of the structure, catalytic activity, and redox properties of surface compounds and phases. It is believed that the structural and morphological properties of the support surface dramatically affect the metal–support interaction.

The aim of this work was to study the interaction of the active component with the surface of different CeO_2 samples and the determination of the electronic and structural state of palladium in catalysts having high low-temperature activity in the reaction of CO oxidation.

EXPERIMENTAL

The samples of 1% Pd/CeO_2 catalysts differed in the procedures used in the preparation cerium dioxide.

Cerium dioxide was prepared from cerium(III) nitrate by the following three procedures: (1) the thermal decomposition of cerium nitrate in air under conditions of temperature-programmed heating to 450°C (henceforth, these samples are referred to as CeO_2-T), (2) the precipitation of CeO_2 with ammonium hydrocarbonate (CeO_2-PC), and (3) the precipitation of CeO_2 with an aqueous ammonia solution at certain pH and temperature followed by filtration and precipitate washing with distilled water until the absence of nitrates from the filtrate (CeO_2-PA). The resulting samples were initially dried in air and then in a drying oven at 110°C for 2–14 h. Thereafter, they were calcined in air at 450°C for 4 h. For supporting 1% Pd, the support was incipient wetness impregnated with an aqueous solution of palladium nitrate and then dried and calcined at 450°C for 4 h. The specific surface areas of Pd/CeO_2-T, Pd/CeO_2-PC, and Pd/CeO_2-PA catalysts were 80, 17, and 113 m^2/g, respectively.

The catalytic properties of the synthesized samples in the reaction of CO oxidation with oxygen were studied using the temperature-programmed reaction (TPR) method. The experiments were performed in an automated system with a flow reactor using the

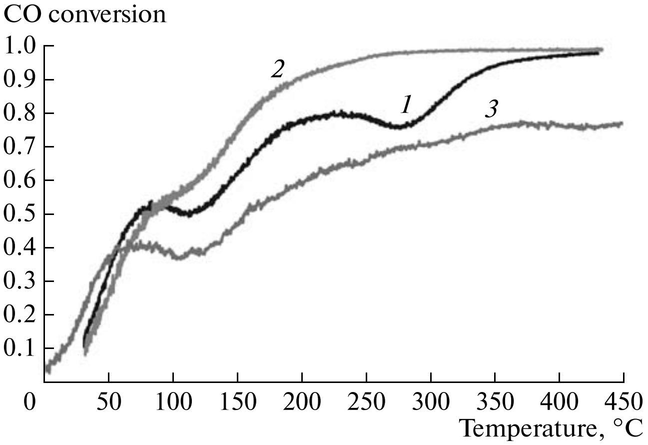

Fig. 1. The temperature dependences of CO conversion for the initial catalysts calcined at 450°C: (*1*) Pd/CeO_2-T, (*2*) Pd/CeO_2-PC, and (*3*) Pd/CeO_2-PA.

mass-spectrometric analysis of a gas mixture. The initial sample (a fraction of 0.5–0.25 mm) after calcination in air was placed in a stainless steel reactor, and the reaction mixture containing 0.2 vol % CO, 1.0 vol % O_2, 0.5 vol % Ne, and the balance helium was introduced at a rate of 1 l/min at an initial temperature of 25°C. The space velocity of the reaction mixture was 240000 h^{-1}. The sample was heated in the reaction mixture to 450°C by increasing the temperature at a rate of 10 K/min.

The XPS analysis was performed on an ES300 instrument (Kratos Analytical, the United Kingdom) using MgK_α radiation ($h\nu = 1253.6$ eV). For the measurements of the spectra, the samples were ground and supported onto an indium substrate. The spectra were calibrated using the U''' component of the Ce 3*d* line ($E_b = 916.7$ eV). In the measurements of the precision spectra the core photoelectron lines, the binding energy was changed at a step of 0.1 eV with a constant analyzer transmission energy of 25 eV.

The IR spectra were recorded on a FTIR 8300 spectrometer from Shimadzu over the spectral region of 700–6000 cm^{-1} with a resolution of 4 cm^{-1}. The powdered catalyst samples were pressed into pellets without a binder ($\rho \approx 0.02$ g/cm^2). The pellets were placed in an IR-spectroscopic quartz cell with NaCl windows and trained in accordance with a standard procedure: initially in air at 673 K and then in a vacuum at 298 K (pressure lower than 10^{-6} bar). For comparison, the samples were also trained in a reducing atmosphere (H_2) at 673 K and then in a vacuum at 298 K. The adsorption experiments were performed at a CO pressure of 0.2 mbar at room temperature. The spectra given below were normalized to the pellet thickness (ρ in g/cm^2).

RESULTS AND DISCUSSION

We studied the catalytic activity of samples different in CeO_2 preparation procedures. Figure 1 shows the temperature dependences of CO conversion on Pd/CeO_2-T, Pd/CeO_2-PC, and Pd/CeO_2-PA catalysts, as found by the TPR method. It can be seen that all of the catalysts exhibited almost the same activity below 50°C. However, their activity at a higher temperature was different and decreased in the order Pd/CeO_2-PC > Pd/CeO_2-T > Pd/CeO_2-PA. The temperature dependence of CO conversion was characterized by the occurrence of two maximums, which suggest different mechanisms of CO oxidation and/or active sites of different nature. Note that the catalytic activity was indirectly related to the specific surface area of the support. Thus, at the early steps of the initiation of reaction, the Pd/CeO_2-PA catalyst with a high specific surface area ($S_{BET} = 117$ m^2/g) exhibited an advantage, whereas the catalyst with S_{BET} = 17 m^2/g exhibited the highest activity in the regions of medium (100–200°C) and higher (>200°C) temperatures.

Figure 2 shows the Pd 3*d* XPS spectra, which characterize the state of the active component on the above three supports. The spectra of the Pd/CeO_2-T and Pd/CeO_2-PC catalysts contained two doublets of approximately the same intensities. The binding energies of the Pd 3$d_{5/2}$ peak components of a doublet were 336.2 and 337.9 or 336.4 and 338.1 eV in the spectra of the samples shown in Figs. 2a and 2b, respectively. These states cannot be ascribed to the presence of palladium oxide because their E_b differ from the value of 336.8–337.0 eV, which is characteristic of PdO [2–4]. Moreover, the characteristic plasmon peak of PdO, whose position corresponds to $E_b \approx 345$ eV, was absent from the spectra. The state of Pd with a binding energy of 336.2–336.4 eV can be ascribed to the presence of Pd^0 ($Pd^{\delta+}$) clusters and nanoparticles as the constituents of a palladium-reduced interaction phase. This phase consists of palladium clusters containing several atoms. The clusters are small so that, in addition to a size shift of the Pd 3*d* line toward higher binding energies [5], the electron density on these clusters decreased because of the polarizing effect of surrounding oxygen ions [6]. Nanosized PdO is characterized by a similar binding energy; however, there is no great difference between palladium oxide and palladium metal at these small particle sizes localized on the surface of an oxide support. In fact, quasi-metal charged (suboxidized) clusters should be considered at these small sizes. According to HRTEM data, these palladium structures are flattened because they occur in an epitaxial contact with the support surface, which mainly consists of the (111) faces of cerium oxide. The observed shift of the Pd 3*d* line for small metal clusters supported onto oxide carriers (E_b = 336.2–336.4 eV) with respect to the line of the Pd metal state (E_b = 335.2 eV) was due to both the cluster charging effect because of the presence of an oxygen environment and

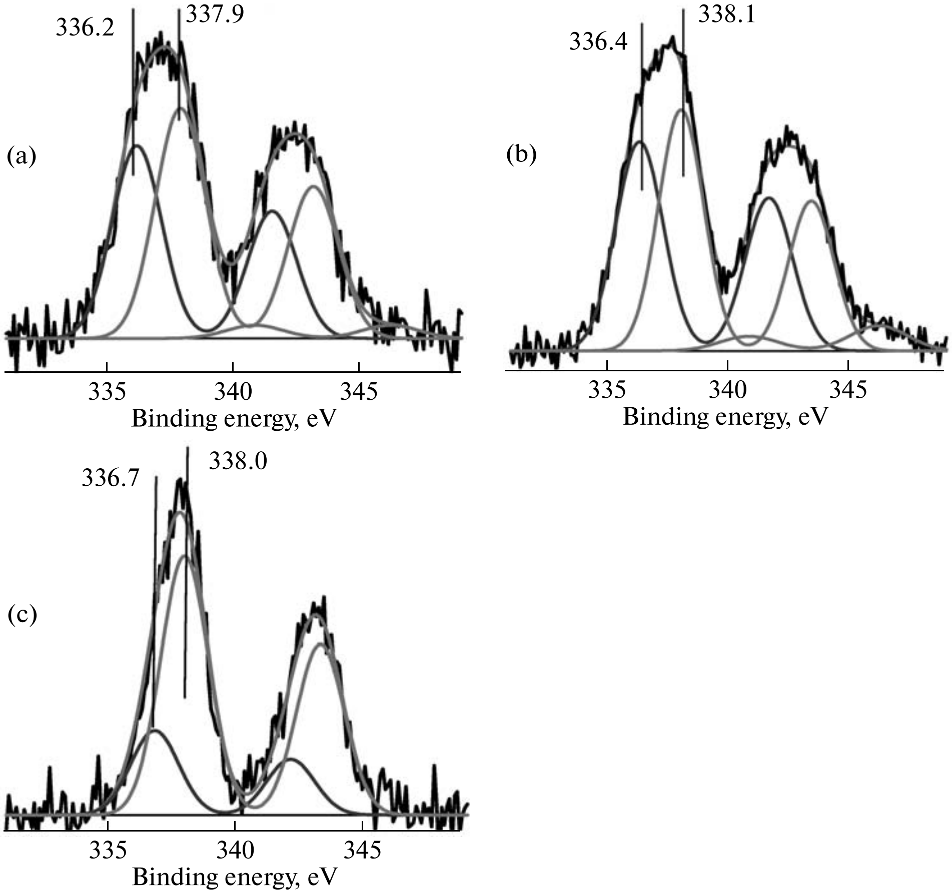

Fig. 2. XPS spectra of the Pd 3*d* line of the initial samples calcined at 450°C: (a) Pd/CeO_2-T, (b) Pd/CeO_2-PC, and (c) Pd/CeO_2-PA.

the relaxation effects of photoionization [7–9]. The state with E_b = 337.9–338.1 eV can be attributed to Pd^{2+} as the constituent of a palladium-oxidized interaction phase. These are atomically dispersed palladium ions, which are dissolved in the near-surface layers of the support lattice. This state of palladium is strongly electron-deficient.

The Pd 3*d* spectrum of the Pd/CeO_2-PA catalyst (Fig. 2) is different from the two previous spectra. It contains a well-defined component with E_b(Pd $3d_{5/2}$) = 338.0 eV, which was attributed to the palladium-oxidized interaction phase. The intensity of the second component with a lower E_b was much smaller, and it can be recognized only using a spectra deconvolution procedure. Note that the binding energy of this component (336.7 eV) is higher than the E_b of low-energy components in the Pd 3*d* spectra of the Pd/CeO_2-T and Pd/CeO_2-PC catalysts. This suggests a very small size of Pd metal clusters (as small as dimers) in the Pd/CeO_2-PA catalyst. We believe that this catalyst did not contain clusters completely oxidized to the state of PdO because E_b(Pd $3d_{5/2}$) = 336.7 eV is somewhat lower than the value characteristic of PdO.

Thus, in the spectra of the Pd/CeO_2-T and Pd/CeO_2-PC samples, the positions of components and ratios between them are almost the same; this suggests approximately the same distribution of palladium by oxidation states. The fraction of $Pd^0(Pd^{\delta+})$ clusters in the Pd/CeO_2-PA catalyst was much lower. In this case, palladium mainly occurred in the state of Pd^{2+} as a constituent of the palladium-oxidized interaction phase.

We studied the surface state of active component particles on the surfaces of supports prepared in accordance with different procedures using Fourier transform IR spectroscopy with adsorbed CO as a probe molecule. In the spectra of CO adsorbed on the support surfaces at 25°C, only a low-intensity absorption band at 2180 cm^{-1} was present, which corresponded to the adsorption of CO at Ce^{4+} ions. This allowed us to use IR spectroscopy for the identification of the ionic and metallic states of Pd in the supported catalysts.

Absorption bands at 1900, 1995, 2060, 2085, and 2115 cm^{-1} were observed in the IR spectra of CO adsorbed on the Pd/CeO_2-PC and Pd/CeO_2-T samples in the region of CO-group stretching vibrations (Fig. 3, spectra *2*, *3*). At the same time, the spectrum

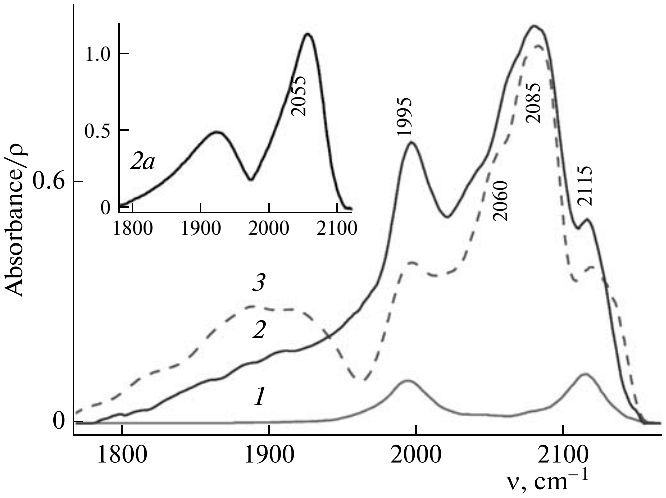

Fig. 3. IR spectra of adsorbed CO (25°C; CO pressure, 0.2 mbar): (*1*) Pd/CeO_2-PA, (*2*) Pd/CeO_2-T, (*3*) Pd/CeO_2-PC, and (*2a*) Pd/CeO_2-T prereduced in H_2 at 400°C. All of the samples were precalcined at 450°C.

of CO on the Pd/CeO_2-PA sample exhibited only absorption bands at 1995 and 2115 cm^{-1}, and the intensity of an absorption band in the range of 2050–2090 cm^{-1} was very low (Fig. 3, spectrum *1*).

A broad low-intensity absorption band with a maximum at 1900 cm^{-1} can be attributed to bridging CO complexes with Pd metal particles. An absorption band in the region of 2050–2090 cm^{-1} is usually attributed to linear CO complexes with Pd metal particles [10, 11]. For comparison, Fig. 3 shows the spectrum of CO adsorbed on the Pd/CeO_2-T sample, which was prereduced in an atmosphere of H_2 at 400°C (spectrum *2a*). It contains absorption bands at 1920 and 2055 cm^{-1}, which belong to bridging and terminal CO complexes with Pd^0, respectively. Thus, an absorption band at 2060 cm^{-1} can be attributed to the linear complexes of CO with Pd metal. The absorption band intensity of the linear complexes of CO with Pd metal is much higher than the absorption band intensity of bridging CO adsorption species; this is characteristic of small palladium clusters [11] and consistent with XPS data.

As the pressure was increased, the absorption band at 2085 cm^{-1} in the spectra of CO on the Pd/CeO_2-PC and Pd/CeO_2-T samples shifter toward higher frequencies (2095 cm^{-1}), and it was easily eliminated upon short-term evacuation. Consequently, this band can be attributed to the linear complexes of CO with $Pd^{\delta+}$ atoms. The $Pd^{\delta+}$ atoms are boundary atoms; they occur on the periphery of clusters in a direct contact with the support. Because of this, they acquire a charge due to the neighboring oxygen atoms.

Absorption bands at 1995 and 2115 cm^{-1} were observed upon the adsorption of CO on all of the Pd/CeO_2 samples regardless of support preparation procedures. These bands are due to the bridging and terminal complexes of CO with Pd^+, respectively [12]. Typically, these bands are the main absorption bands due to the complexes of CO with the surface of palladium in the spectrum obtained on the Pd/CeO_2-PA catalyst. Taking into account XPS data on the presence of Pd^{2+} as a constituent of the palladium-oxidized interaction phase (E_b(Pd $3d_{5/2}$) = 338.0 eV), we can reasonably hypothesize the formation of –O–Pd–Pd–O– structures immediately in the regions where the palladium-oxidized interaction phase occurred. These structures resulted in the appearance of a doublet with E_b(Pd $3d_{5/2}$) = 336.7 eV in XPS spectra.

Thus, IR spectroscopy allowed us to detect the presence of weakly charged palladium metal clusters on the surface of Pd/CeO_2-PC or Pd/CeO_2-T, unlike Pd/CeO_2-PA. Palladium mainly occurred in an oxidized state on the surface of Pd/CeO_2-PA.

The above experimental data allowed us to conclude that the temperature of the onset of reaction initiation in the oxidation of CO on the test catalysts mainly depended on the presence of palladium in the state of Pd^{2+} as a constituent of the palladium-oxidized interaction phase. In addition, small metal clusters played an important role; the presence of these clusters was necessary for the adsorption and activation of CO. The size of the metal clusters can be of considerable importance for two reasons. First, the smaller the cluster size, the greater positive charge is concentrated on palladium atoms and the lower the heat of adsorption of CO, which is required for the onset of initiation. Second, at a small metal cluster size, the access of CO to active oxygen in the palladium-oxidized interaction phase is facilitated, and the reaction can take place at maximally low temperatures. At medium temperatures (above 100°C), the high activity of the catalyst is also due to the occurrence of small $Pd^0(Pd^{\delta+})$ metal clusters as the constituents of palladium-reduced interaction phase. The presence of metal clusters as the constituents of palladium-reduced interaction phase with a higher heat of adsorption of CO is responsible for sufficient surface coverage with carbon monoxide and its interaction with both the surface oxygen of the palladium-oxidized interaction phase and with gas-phase oxygen. Finally, at high temperatures (above 200°C), the surface of catalysts can be more reduced under steady-state conditions up to the formation of greater metal clusters, that is, Pd^0 nanoparticles, which are responsible for the high conversion of CO.

The activity of the sample on the support prepared by the precipitation of CeO_2 with ammonium hydrocarbonate in the region of medium and high temperatures was higher than that of the sample on the support prepared by the thermolysis of cerium nitrate because of an increased surface concentration of Pd on the support with a small specific surface area. The low activity of the catalyst on the support prepared by the precipitation of CeO_2 with ammonia was related to a high concentration of Pd as a constituent of the palladium-oxidized interaction phase and a very low fraction of Pd metal clusters as the constituents of the palladium-reduced interaction phase; these clusters are responsible for the oxidation of CO at temperatures higher than 100°C.

In this work, we studied the effect of CeO_2 preparation procedure on the electronic and structural state of the active component in Pd/CeO_2 catalysts and their activity in the reaction of low-temperature CO oxidation. The following two nonequivalent states of palladium were detected in the catalysts that exhibited low-temperature activity with the use of XPS and IR spectroscopy: $Pd^0(Pd^{\delta+})$ as a constituent of the palladium-reduced interaction phase, which consisted of small $Pd^0(Pd^{\delta+})$ clusters on the support surface, and Pd^{2+} as a constituent of the palladium-oxidized interaction phase $Pd_xCeO_{2-\delta}$. The support preparation procedure exerted a considerable effect on the formation of these phases and the quantitative ratio between them. Thus, in the precipitation of CeO_2 from $Ce(NO_3)_3$ with ammonia, the palladium-oxidized interaction phase, which is characterized by a high low-temperature activity and a low activity at higher temperatures, was mainly formed. The formation of $Pd^0(Pd^{\delta+})$ metal clusters as the constituents of the palladium-reduced interaction phase was observed in the preparation of CeO_2 by thermolysis and in the precipitation of it with ammonium hydrocarbonate. These catalysts are characterized by not only a high low-temperature activity and a considerable activity at temperatures higher than 100°C.

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