

State of Active Components on the Surface of the $\text{PdCl}_2\text{--CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ Catalyst for the Low-Temperature Oxidation of Carbon Monoxide

D. N. Titov^a, A. V. Ustyugov^a, O. P. Tkachenko^b, L. M. Kustov^b, Ya. V. Zubavichus^c, A. A. Veligzhanin^c,
N. V. Sadovskaya^d, I. V. Oshanina^a, L. G. Bruk^a, and O. N. Temkin^a

^a Moscow State Academy of Fine Chemical Technology, Moscow, 117571 Russia

^b Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 117334 Russia

^c Kurchatov Institute Russian Research Center, Moscow, 123182 Russia

^d Karpov Institute of Physical Chemistry, Moscow, 103064 Russia

e-mail: Denisish26@yandex.ru

Received July 8, 2011

Abstract—The state of the active constituents of the freshly prepared $\text{PdCl}_2\text{--CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst for the low-temperature oxidation of the carbon monoxide by molecular oxygen was studied by X-ray absorption spectroscopy (XAS), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and diffuse reflectance IR Fourier transform spectroscopy (DRIFTS). It was shown that copper in the form of a crystalline phase of $\text{Cu}_2\text{Cl}(\text{OH})_3$ with the structure of the mineral paratacamite and palladium chloride in an amorphous state occurred on the surface of $\gamma\text{-Al}_2\text{O}_3$. According to XAS data, the local environment of palladium consisted of four chlorine atoms, which formed a flat square with an increased distance between palladium and one of the chlorine atoms. The evolution of the local environments of copper and palladium upon a transition from the initial salts to the impregnating solutions and chlorides on the surface of $\gamma\text{-Al}_2\text{O}_3$ was considered. The role of $\gamma\text{-Al}_2\text{O}_3$ in the formation of the $\text{Cu}_2\text{Cl}(\text{OH})_3$ phase was discussed. It was found by the DRIFTS method that linear (2114 cm^{-1}) and bridging (1990 and 1928 cm^{-1}) forms of coordinated carbon monoxide were formed upon the adsorption of CO on the catalyst surface. The formation of CO_2 upon the interaction of coordinated CO with atmospheric oxygen was detected. Active sites including copper and palladium were absent from the surface of the freshly prepared catalyst.

DOI: 10.1134/S0023158412020140

INTRODUCTION

The low-temperature ($15\text{--}100^\circ\text{C}$) oxidation of carbon monoxide by oxygen is of fundamental scientific interest because it is one of the simplest oxidation reactions and can be used to establish general laws governing oxidation processes. Furthermore, CO is among the most abundant toxicants. It is released into the atmosphere as a result of natural cataclysms (fires and volcanic eruptions) and human activity (industrial and automobile emissions). Respirators, shielding hoods, and gas masks whose important component is a catalyst for CO oxidation are used to protect people from carbon monoxide in emergency situations.

Among the low-temperature catalysts for this reaction, supported metal complex catalysts are least studied; catalysts based on palladium and copper compounds are the most promising catalysts of this group [1, 2]. At present, there is no general idea of the mechanism of the low-temperature oxidation of carbon monoxide with the participation of such catalysts and of the role of particular components of the catalytic system. It was believed [3–6] that catalytic activity is

due to the solution of Cu(II) and Pd(II) salts occurring in the pores of the support. It was hypothesized that, by analogy with well-studied homogeneous liquid-phase systems [7–10], palladium performs the main function of CO oxidation and the role of Cu(II) is the reoxidation of the reduced form of palladium. In turn, reduced copper is oxidized by oxygen. The strong dependence of catalyst properties on the nature of the support is evidence against the hypothesis that the $\text{PdX}_2\text{--CuX}_2/\text{support}$ catalytic system, where $\text{X} = \text{Cl}^-$, Br^- , or NO_3^- , is in the liquid state [11–14]. If the function of Cu(II) is actually the reoxidation of reduced palladium compounds, the possibility of contact between copper and palladium on the surface (for electron transfer) should exist. The mechanism of this interaction is one of the most interesting aspects of this process. It is likely that halide or hydroxide bridges between copper and palladium facilitate electron transfer [15]. If copper and palladium are bound into a complex, direct electron transfer from the coordinated carbon monoxide to Cu(II) with the participation of

Pd(II), that is, the occurrence of a catalytic process without the reduction of Pd(II) cannot be excluded.

The sample obtained by supporting copper(II) chloride onto the surface of γ -Al₂O₃ was inactive in CO oxidation up to 100°C [14]. However, if palladium(II) chloride is supported together with metal chlorides MCl₂ (where M = Mn or Ni) and MCl (where M = Li, Na, K, or H), which are not oxidizing agents, onto the same support, the resulting samples show the ability to oxidize CO at room temperature in stoichiometric amounts with respect to Pd(II) chloride [14]. Therefore, Cu(II), as in the solutions, plays an important role in the mechanism of the process: it facilitates the catalytic action of palladium in CO oxidation. It is likely that this function of copper can be executed only via the direct interaction of copper and palladium compounds. This interaction occurs readily in solution because of the high mobility of reacting species, whereas Cu(II) and the reduced form of palladium (or palladium hydride) on the surface of the support can interact most readily when they are bound in a complex. The mixed complexes of palladium and copper were detected in nonaqueous solutions [16].

What is known about the state of palladium and copper on the surface of supports? The PdCl₂—CuCl₂/activated carbon (or Al₂O₃ or another support) catalytic system, which is similar to our system, was studied by powder X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) [6, 11, 12, 17–22]. It turned out that, on the surface of the freshly prepared catalysts, copper occurred as a constituent of two crystalline phases—Cu₂Cl(OH)₃ and CuCl₂ · 2H₂O; the concentration of the Cu₂Cl(OH)₃ phase correlated with the catalytic activity of the system in the oxidation reaction of CO with oxygen [21]. The oxidation number of palladium was 2+, and chloride ligands were present in the environment of palladium [6, 12, 17–19, 21, 22]. With the use of in situ diffuse reflectance IR spectroscopy in an atmosphere of CO, it was found [4, 23] that the δ -Al₂O₃ surface contained the carbonyl chlorides PdCl₂(CO), (PdClCO)_n, and Cu(CO)Cl and also small amounts of terminal and bridging CO groups bonded to palladium metal particles, which likely resulted from the contact of the PdCl₂—CuCl₂/ δ -Al₂O₃ catalyst with CO and water vapor.

The mechanism of CO oxidation in the solutions of palladium complexes was studied adequately [7–10, 24–26]. Mechanisms analogous to the Wacker process mechanism (oxidation of alkenes in systems based on Pd(II) in water and nonaqueous solvents) were considered as the main mechanisms. As shown in the scheme, the following was hypothesized: (a) The kinetic functions are separated in such a way that the alkene is oxidized by Pd(II), the reduced form of palladium (or a hydride complex) is oxidized by the cocatalyst (Cu(II), Fe(III), heteropoly acid, quinone, etc.), and the cocatalyst undergoes regeneration with the participation of an oxidizing agent (O₂, H₂O₂, etc.). (b) A Pd⁰ compound can participate in CO ox-

idation to activate the oxidizing agent (O₂). (c) Pd⁰ can be oxidized simultaneously with CO, but it can also perform a catalytic function to activate oxygen. In the latter case, the role of the cocatalyst is not obvious. In addition, Golodov et al. [7] found that Pd(I) complexes, which are more active catalysts for the oxidation of carbon monoxide than Pd(II) complexes, can form in the solutions of Pd(II) upon the interaction of Pd(II) with carbon monoxide. It is also reasonable to use these hypotheses in the examination of the mechanism of the low-temperature oxidation of carbon monoxide on heterogeneous catalysts.

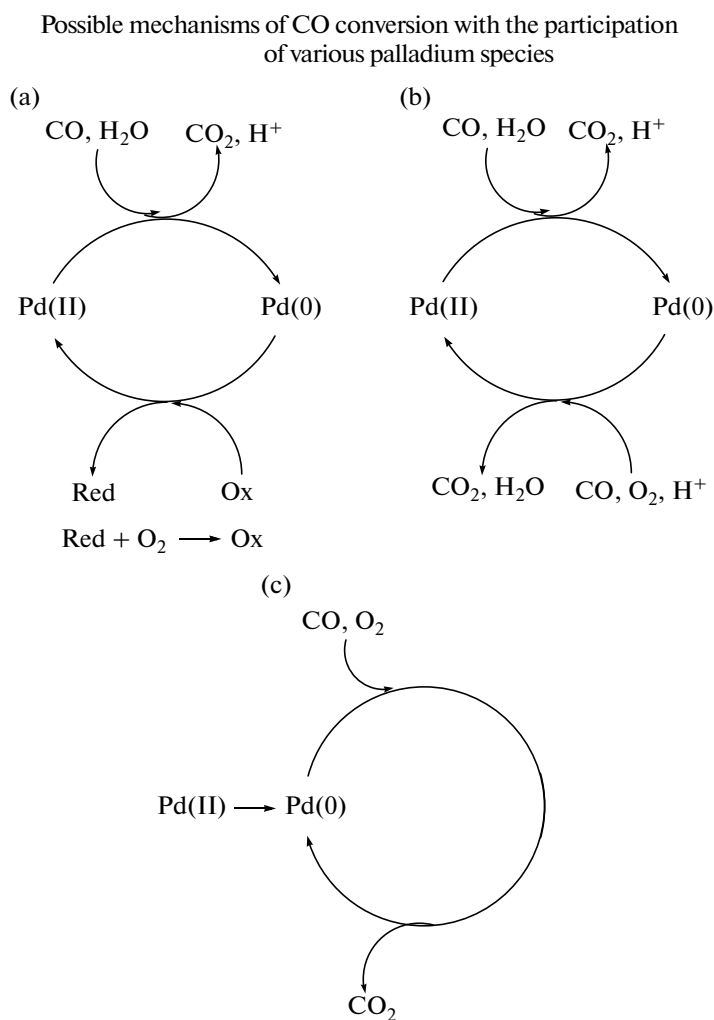
Here, we report a systematic study of the PdCl₂—CuCl₂/ γ -Al₂O₃ catalyst.

EXPERIMENTAL

Three samples were investigated by physical methods. Sample 1—the granules of γ -Al₂O₃ (State Standard GOST 8136-85) of size 0.5–1 mm (BET specific surface area of 219 m²/g)—was used as the support in the preparation of samples 2 and 3. Samples 2 (CuCl₂/ γ -Al₂O₃) and 3 (PdCl₂—CuCl₂/ γ -Al₂O₃ catalyst) were prepared by the cold impregnation of sample 1 with an aqueous solution of CuCl₂ (CuCl₂ · 2H₂O, GOST 4167-61) and with an aqueous solution of the salts PdCl₂ (PdCl₂, Technical Specifications TU 2625-048-00205067-2003) and CuCl₂, respectively [27]. The catalyst contained 1.5 wt % Pd and 3.5 wt % Cu on a γ -Al₂O₃ basis. Solutions with the same concentration of CuCl₂ were used to prepare samples 2 and 3.

Samples 1–3 were studied by powder X-ray diffraction with the use of synchrotron radiation. FujiFilm ImagingPlate photosensitive plates served as a two-dimensional detector; the diffraction patterns were digitized with the aid of a FujiFilm BAS-5000 scanner with a space step of 100 μ m. The radiation wavelength was 0.46416 Å, the distance between the sample and the detector was 230 mm, and the exposure time was 30 min. The study was carried out at room temperature. The two-dimensional diffraction patterns were primarily processed using the Fit2D program [28].

The state and structure of catalytic system components were studied by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) techniques. The *K*-edge X-ray absorption spectra of copper and palladium in samples 2 and 3 and also in the reference compounds CuCl₂ · 2H₂O (s) and PdCl₂ (s) and their aqueous solutions, which were used in the impregnation of the support in the course of the sample preparation, were obtained. The spectra were recorded at room temperature. The synchrotron radiation beam was monochromated with the aid of a channel-cut Si(111) monochromator, and ionization chambers filled with nitrogen (*K* edge of Cu absorption) or argon (*K* edge of Pd absorption) were used as detectors. The IFEFFIT program package was used in the processing of the EXAFS spectra [29]. The photoelectron scattering amplitudes and phases were



Scheme.

calculated using the FEFF program [30]. All of the measurements were carried out at the Structural Materials Science Station of the Kurchatov Center of Synchrotron Radiation and Nanotechnologies [31].

The microstructure of the samples was studied by scanning electron microscopy (SEM) on a 7500 F high-resolution scanning electron microscope with a field emission cathode from JEOL (Japan). The images were obtained in the low-energy secondary electron mode. The Gentle Beam mode at accelerating voltages of 1 and 2 kV (400 V at the sample surface) was additionally used.

A NICOLET Protege 460 spectrometer equipped with a diffuse reflectance attachment designed at the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, was used to characterize the samples by diffuse reflectance Fourier transform IR spectroscopy (DRIFTS) in the range of 6000–400 cm^{-1} with a step of 4 cm^{-1} [32]. Granular samples were placed in an ampoule with a KBr window equipped with a two-way glass vacuum valve. CaF_2 powder was

used as the standard. Before the measurement of the spectra, samples **1–3** were held in a vacuum at room temperature for 4 h for removal of physically adsorbed water (the pressure in the ampoule with the sample was 2×10^{-8} Torr). Carbon monoxide was used as the probe molecule for evaluating the electronic states of palladium and copper. The ampoule with the sample was initially evacuated; then, carbon monoxide was introduced into it at room temperature and an equilibrium pressure of 20 Torr. In the study of sample **3** (catalyst) under the conditions of CO oxidation, the measurements were conducted in a narrow wavenumber interval of 2450–1700 cm^{-1} . CO was introduced into the ampoule at room temperature and kept at an equilibrium pressure of 30 Torr for 50 min. Thereafter, air was admitted into the ampoule at atmospheric pressure.

RESULTS AND DISCUSSION

As was noted above, the phase composition and structure of the samples were studied by powder X-ray

diffraction with the use of synchrotron radiation. The diffraction pattern of the γ - Al_2O_3 support had a number of broad peaks characteristic of this nanocrystalline material (Fig. 1). In particular, the four most intense reflections were observed at the following scattering angles 2θ (interplanar spacing d is given in parentheses): 11.08° (2.40 Å), 11.61° (2.29 Å), 13.51° (1.97 Å), and 19.08° (1.40 Å). These reflections correspond to the (311), (222), (400), and (440) indices of a face-centered cubic lattice with the parameter $a \approx 7.92$ Å. The positions, widths, and relative intensities of the reflections in the diffraction pattern of the γ - Al_2O_3 support measured in this work are close to published data [33, 34].

In addition to the peaks of the γ - Al_2O_3 phase, the diffraction patterns of samples 2 and 3 contained narrow intense reflections at scattering angles 2θ (d in parentheses) of 4.87° (5.47 Å), 9.64° (2.76 Å), and 11.74° (2.27 Å), which makes it possible to identify this additional crystalline phase as the rhombohedral modification of $\text{Cu}_2\text{Cl}(\text{OH})_3$ (space group R-3m, paratacamite). A comparison of the experimental diffraction patterns of samples 2 and 3 with the theoretical curve calculated based on published crystallographic data for the paratacamite phase [35] confirmed this conclusion. We did not observe significant differences between the diffraction patterns of samples 2 and 3; therefore, the introduction of palladium into the catalytic system did not affect the composition of the dominant crystalline phase containing copper. Similar results were obtained earlier for the PdCl_2 – CuCl_2 /activated carbon (or Al_2O_3) catalytic systems [6, 11, 12, 17–22].

The microstructure of samples 1–3 was studied by SEM. The experimental results (Figs. 2–4) are consistent with the above data: it is likely that the microcrystals of the phase $\text{Cu}_2\text{Cl}(\text{OH})_3$ with the structure of paratacamite (space group R-3m) are present only in samples 2 and 3, and they form island aggregates up to 10 μm in diameter on the surface of γ - Al_2O_3 (Figs. 3 and 4). In sample 3, the number of faceted nanocrystals is much greater.

Nanocrystal faces in sample 3 (Fig. 4) are rhombic, characteristic of a simple rhombohedron, and this is also consistent with the crystallization of trigonal $\text{Cu}_2\text{Cl}(\text{OH})_3$ on the surface of γ - Al_2O_3 . It is possible that the simultaneous presence of copper and palladium in sample 3 contributes to the crystallization of $\text{Cu}_2\text{Cl}(\text{OH})_3$ and increases the particle size.

The oxidation numbers and symmetry of the coordination spheres of palladium and copper in the initial salts and impregnating solutions and on the surface of the support were determined by XANES. Figure 5 shows the Pd K -edge XANES spectra for a number of samples. The absorption maximum in each spectrum corresponds to the $1s \rightarrow 5p$ electron transition. The spectra are similar in the shapes and positions of the main absorption maxima. This fact suggests that the electronic states of Pd in the solid salt PdCl_2 , in an

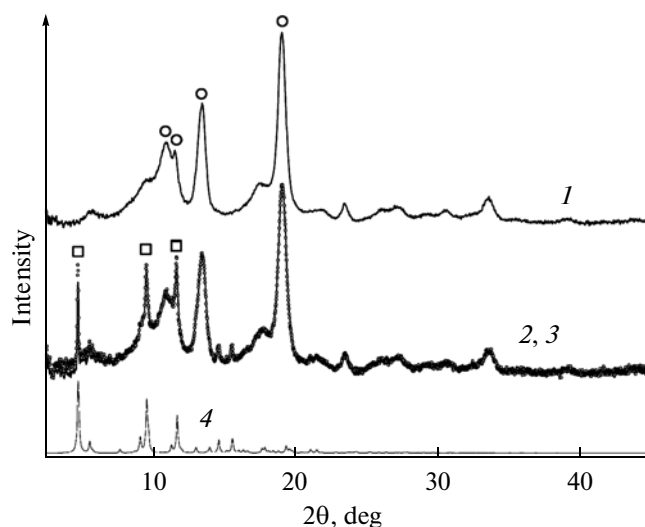


Fig. 1. Diffraction patterns: (1) sample 1 (the support γ - Al_2O_3), (2, solid line) sample 2 (CuCl_2/γ - Al_2O_3), (3, dotted line) sample 3 (the catalyst PdCl_2 – CuCl_2/γ - Al_2O_3), and (4) paratacamite (calculated). The reflections used in the phase identification of γ - Al_2O_3 and paratacamite are labeled with circles and squares, respectively.

aqueous solution of PdCl_2 (in the presence of CuCl_2), and on the surface of the γ - Al_2O_3 support do not differ significantly. It is most likely that the oxidation state of Pd(II) and its square-planar coordination environment of chlorine atoms remained unchanged in the course of catalyst preparation.

Figure 6 shows the Cu K -edge XANES spectra. The absorption maximum corresponds to the $1s \rightarrow 4p$ electron transition. The secondary peaks and shoulders correspond to electron transitions to unoccupied orbitals in accordance with dipole selection rules. The very weak pre-edge resonance at $E \approx 8976$ eV is due to the formally dipole-forbidden $1s \rightarrow 3d$ electron transition, which appears because of the partial p – d hybridization and quadrupole contribution. It reliably suggests the presence of Cu(II) compounds. The spectra of two aqueous solutions and supported samples 2 and 3 are indistinguishable in pairs within the experimental error. The asymmetric peak shape with a pronounced low-energy shoulder in the spectra of the supported catalysts and the reference compound $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (s) is indicative of a mixed oxygen–chlorine environment of the copper atoms [12, 17, 21, 36]. In the aqueous solutions of CuCl_2 , where the hydrolysis and activation of CuCl_2 occur, the mixed oxygen–chlorine environment is replaced by a pure oxygen environment. The observed shape of the spectra is close to that expected for the tetragonal pyramidal coordination of copper atoms to oxygen atoms.

More detailed information on the parameters of the local environments of copper and palladium atoms in samples 2 and 3 and in the solutions of precursors was obtained by the quantitative analysis of EXAFS

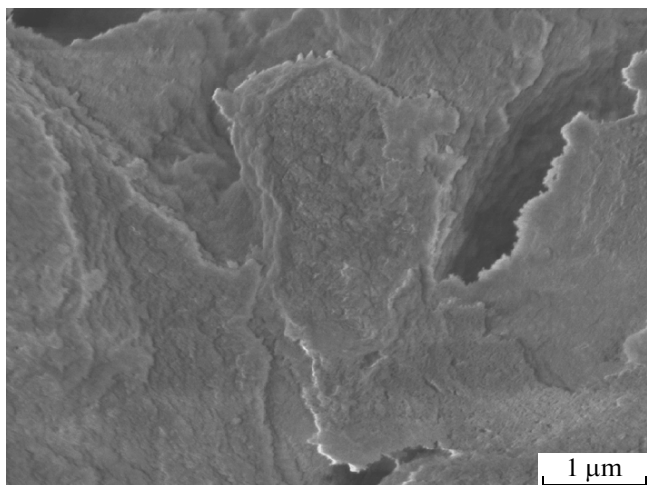


Fig. 2. SEM image of the surface of sample **1** (magnification factor of 20000).

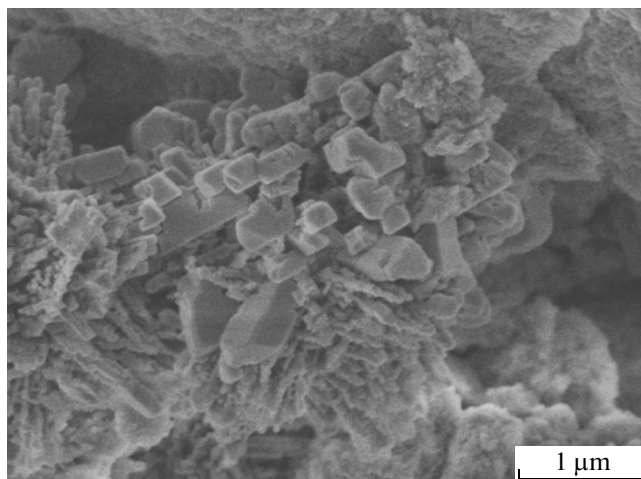


Fig. 3. SEM image of the surface of sample **2** (magnification factor of 25000).

spectra. Figure 7 and Table 1 summarize the results of the processing of the Pd *K*-edge EXAFS spectra. In the PdCl₂ salt sample, the local environment of palladium is the same as is observed in the crystal structure of the β-modification of PdCl₂ [37], which includes Pd₆Cl₁₂ hexamers with octahedrons of palladium atoms in the apexes connected together by μ₂-chloride bridges (Table 1). Each Pd atom is coordinated to four chlorine atoms as a square. It is likely that isolated square-planar [PdCl₄]²⁻ fragments occurred in the aqueous solution of PdCl₂ and CuCl₂ (Table 1). Copper atoms were not detected in the local environment of the palladium atoms. The square-planar environment of palladium with chlorine atoms remained in the catalyst (sample **3**); however, the best convergence between the experimental and theoretical spectra was achieved for a local chlorine environment of palla-

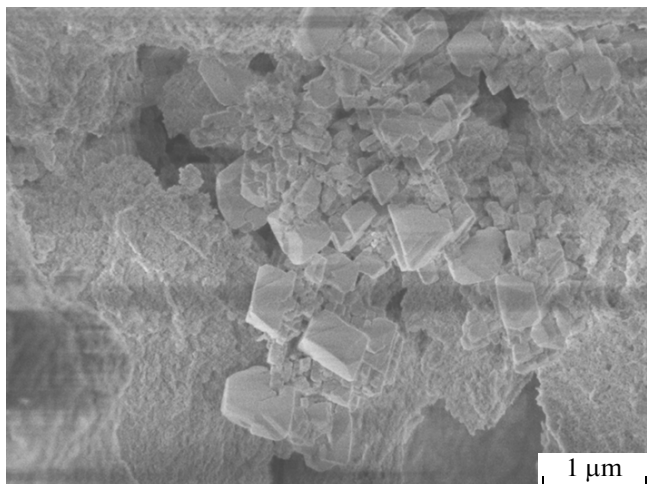


Fig. 4. SEM image of the surface of sample **3** (magnification factor of 20000).

dium at an increased distance between palladium and one of the chlorine atoms (Table 1). The radial atomic distribution curve for the catalyst exhibited long-range order peaks in the range of 3–4 Å; however, they cannot be described as contributions from the Pd–Pd or Pd–Cu atomic pairs, but they are consistent with the presence of lighter atoms, for example, aluminum, which may indicate the formation of Pd–Cl–Al bridging bonds with ion-exchange positions of the support upon chemisorption.

Figure 8 and Table 2 summarize the results of processing the Cu *K*-edge EXAFS spectra. The EXAFS spectrum of the reference compound CuCl₂ · 2H₂O (s) are in good agreement with the structural data [38] (Table 2). The environment of copper is a flat square formed by two chlorine atoms and the two oxygen atoms of water, and the structure is actually built from such isolated squares. Two additional secondary Cu...Cl interactions occurred; because of this, the coordination polyhedron of copper atoms is completed to a tetragonal bipyramid and infinite piles of CuCl₂O₂ squares form.

In the solutions of CuCl₂ (both in the absence and in the presence of palladium), the environment of copper atoms changes to pure oxygen environment. This environment is tetragonal bipyramidal owing to the Jahn–Teller effect. This is typical of copper(II) compounds [39, 40]. In other words, according to EXAFS data, there are two nonequivalent distances: equatorial and axial (Fig. 8, Table 2). As for the local environment of copper, there are no noticeable differences between the solutions.

The EXAFS data for catalysts **2** and **3** are fully consistent with the results of the diffraction study that indicate the formation of a crystalline phase of paratacamite Cu₂Cl(OH)₃: the structural model of the first three coordination spheres of copper atoms, built on the basis of crystallographic data for paratacamite

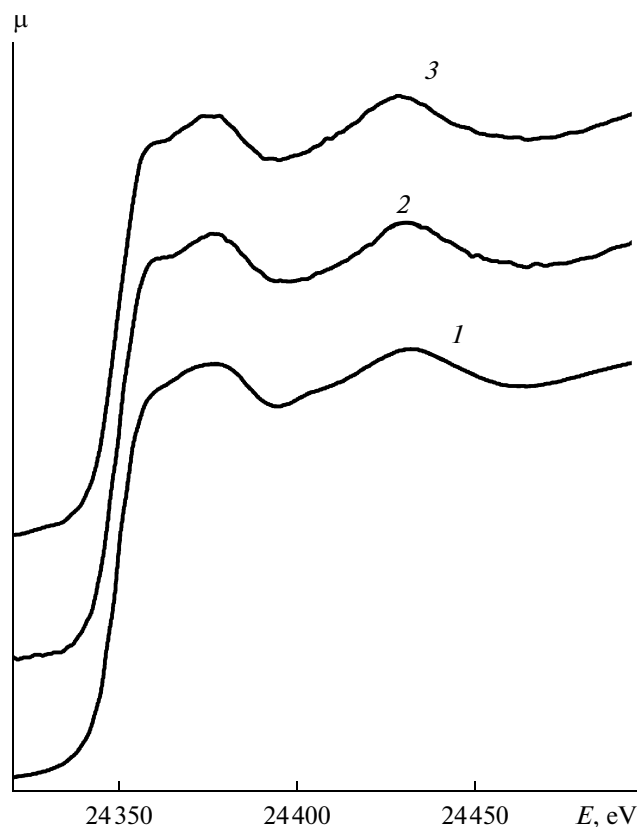


Fig. 5. Pd *K*-edge XANES spectra: (1) the initial salt PdCl_2 , (2) an aqueous solution of PdCl_2 and CuCl_2 , and (3) sample 3 (the catalyst $\text{PdCl}_2\text{--CuCl}_2/\gamma\text{-Al}_2\text{O}_3$).

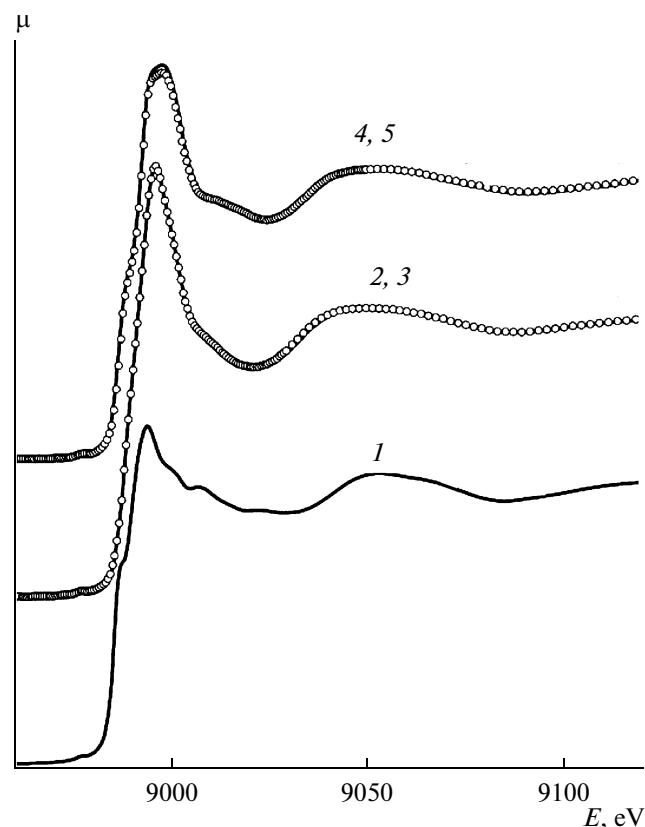


Fig. 6. Cu *K*-edge XANES spectra: (1) the initial salt $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, (2, solid line) an aqueous solution of CuCl_2 , (3, points) an aqueous solution of PdCl_2 and CuCl_2 , (4, solid line) sample 2 ($\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$), and (5, points) sample 3 (the catalyst $\text{PdCl}_2\text{--CuCl}_2/\gamma\text{-Al}_2\text{O}_3$).

[35], makes it possible to describe the experimentally observed EXAFS curve with a high accuracy.

Thus, unique conditions for the formation of $\text{Cu}_2\text{Cl}(\text{OH})_3$ on the surface of $\gamma\text{-Al}_2\text{O}_3$ appear upon the supporting of CuCl_2 (sample 2, $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$) or CuCl_2 together with PdCl_2 (sample 3, the $\text{PdCl}_2\text{--CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst) from an aqueous solution. In the former case, 75% of the initially introduced chloride ions should be replaced, and a lower percentage of these ions should be replaced in the latter case because part of the chloride ions is bound to $\text{Pd}(\text{II})$ (according to the Pd *K*-edge EXAFS data, the local environment of palladium is composed of four chlorine atoms). The basic properties of the $\gamma\text{-Al}_2\text{O}_3$ surface are favorable for more complete hydrolysis of CuCl_2 in the impregnating solutions used in the preparation of samples 2 and 3.

In the diffuse reflectance IR spectra of samples 1 (Al_2O_3) and 2 ($\text{CuCl}_2/\text{Al}_2\text{O}_3$) recorded in the presence of carbon monoxide at room temperature, there are no bands characteristic of the stretching vibrations of the $\text{C}\equiv\text{O}$ bond in the CO molecule (Fig. 9). At the same time, in the spectrum of sample 3 ($\text{CuCl}_2\text{--PdCl}_2/\text{Al}_2\text{O}_3$) obtained under the same conditions, there are

three bands: an intense band at 1928 cm^{-1} and less intense bands at 1990 and 2114 cm^{-1} .

According to published data [4, 41–43], the vibration frequencies lower than 1800 cm^{-1} are due to $\text{Pd}(\text{II})$ complexes with an inserted CO group, which is similar in properties to the carbonyl group in organic compounds. The vibration frequencies in the $1800\text{--}2000\text{ cm}^{-1}$ range correspond to $\text{Pd}(\text{I})$ complexes with a bridging CO group. The vibration frequencies higher than 2000 cm^{-1} correspond to $\text{Pd}(\text{II})$ complexes with a terminal CO group. The $1800\text{--}1890\text{ cm}^{-1}$ frequency range is characteristic of CO molecules coordinated as bridges in the of Pd^0 clusters. The vibration frequencies of CO groups on the surface of palladium metal can occur in the $1800\text{--}1880$, $1800\text{--}2000$, and $2050\text{--}2120\text{ cm}^{-1}$ ranges, which are characteristic of the tri-coordinated, dicoordinated, and terminal CO molecules, respectively [4]. There are no data concerning structurally characterized $\text{Pd}(\text{I})$ complexes with terminal CO groups and $\text{Pd}(\text{II})$ with bridging CO groups. The $2050\text{--}2120\text{ cm}^{-1}$ range is characteristic of $\text{Cu}(\text{I})$ with the terminal CO groups. Adequate information on the complexes of $\text{Cu}(\text{II})$ with carbon monoxide is absent from the literature.

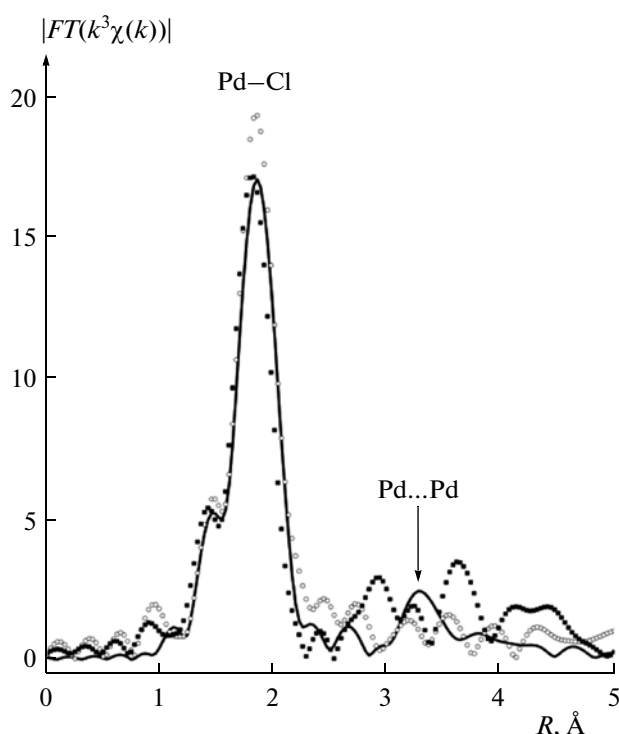


Fig. 7. Radial distribution curves of atoms obtained by the Fourier transform of the Pd *K*-edge EXAFS spectra: (solid line) PdCl₂ (s), (open circles) an aqueous solution of PdCl₂ and CuCl₂, and (solid circles) sample 3 (the catalyst PdCl₂–CuCl₂/γ-Al₂O₃).

Based on published IR spectroscopic data for adsorbed CO, it can be assumed that, in the IR spectrum of sample 3, the band at 2114 cm^{−1} corresponds to the terminal form of CO adsorbed on coordinatively unsaturated Pd(II) atoms and/or on metallic Pd⁰ and/or on Cu(I). The absorption bands at 1990 and 1928 cm^{−1} characterize the adsorption of CO in bridg-

ing form on Pd(0) and/or Pd(I). We believe that the coordination of CO in bridging form on Pd⁰ (band at 1990 cm^{−1}) and on Pd(I) (band at 1928 cm^{−1}) is more probable. It is likely that the medium-intensity band at 1990 cm^{−1} is due to the symmetrical vibrations of bridging CO groups on Pd(I) and the strong band at 1928 cm^{−1} is due to asymmetric vibrations, for example, as in the case of the dimeric anion [Pd₂(CO)₂Cl₄]^{2−} (bands at 1973 and 1922 cm^{−1}) [44]. It is likely that the reduced forms of palladium and copper result from the reduction of Pd(II) and Cu(II) with carbon monoxide in the presence of a small quantity of water, which remained on the surface of sample 3 after vacuum treatment (according to the Pd *K*-edge (Fig. 5) and Cu *K*-edge (Fig. 6) XANES data, copper and palladium in sample 3 are in the oxidation state 2+). Note that the amount of carbon monoxide introduced into the ampoule with the sample is insufficient for the complete reduction of Pd(II) to Pd(I) or Pd⁰ and of Cu(II) to Cu(I). We failed to detect carbon dioxide coordinated on the surface or CO₂ in the gas phase as the CO oxidation product; this may be explained by the resulting amount of CO₂ being too small to be detected. The absence of absorption bands due to the coordinated CO group from the IR spectra of the sample of CuCl₂/γ-Al₂O₃ in an atmosphere of CO and also the experiments carried out to test the catalytic activity of this sample suggest that copper(II) in the form of Cu₂Cl(OH)₃ with the structure of paratacamite on the surface of γ-Al₂O₃ does not oxidize CO to CO₂ to any noticeable extent under the conditions of our experiments in the absence of palladium. Palladium catalyzes the oxidation of carbon monoxide by copper(II).

The IR spectrum shown in Fig. 9 is stable for 50 min. Upon contact with air, the gradual changes shown in Fig. 10 occur. The absorption band at 2346 cm^{−1}, which is characteristic of physically

Table 1. Local environment parameters based on the results of the treatment of Pd *K*-edge EXAFS spectra

Sample	Atomic pair	Coordination number	<i>r</i> , Å	σ ² , Å ²	<i>R</i> _f
PdCl ₂ (s)	Pd–Cl	4	2.29 (2.30–2.31)*	0.0027	0.007
	Pd–Pd	4	3.28 (3.28–3.33)*	0.0146	
	Pd–Cl	1	3.37 (3.34)*	0.0013	
	Pd–Pd	1	3.72 (3.77)*	0.0040	
	Pd–Cl–Pd–Cl	2	4.57 (4.60–4.62)*	0.0026	
Solution of CuCl ₂ + PdCl ₂	Pd–Cl	4	2.28	0.0022	0.030
	Pd–Cl–Pd–Cl	2	4.56	0.0050	
Catalyst 3 (PdCl ₂ –CuCl ₂ /γ-Al ₂ O ₃)	Pd–Cl	3	2.26	0.0015	0.019
	Pd–Cl	1	2.36	0.0015	

Note: *r* is the interatomic distance, σ² is the Debye–Waller parameter, and *R*_f is the uncertainty factor. The coordination numbers have integral values characteristic of the hypothetical structure models; they were not refined.

* Interatomic distances according to crystallographic data [37] are given in parentheses.

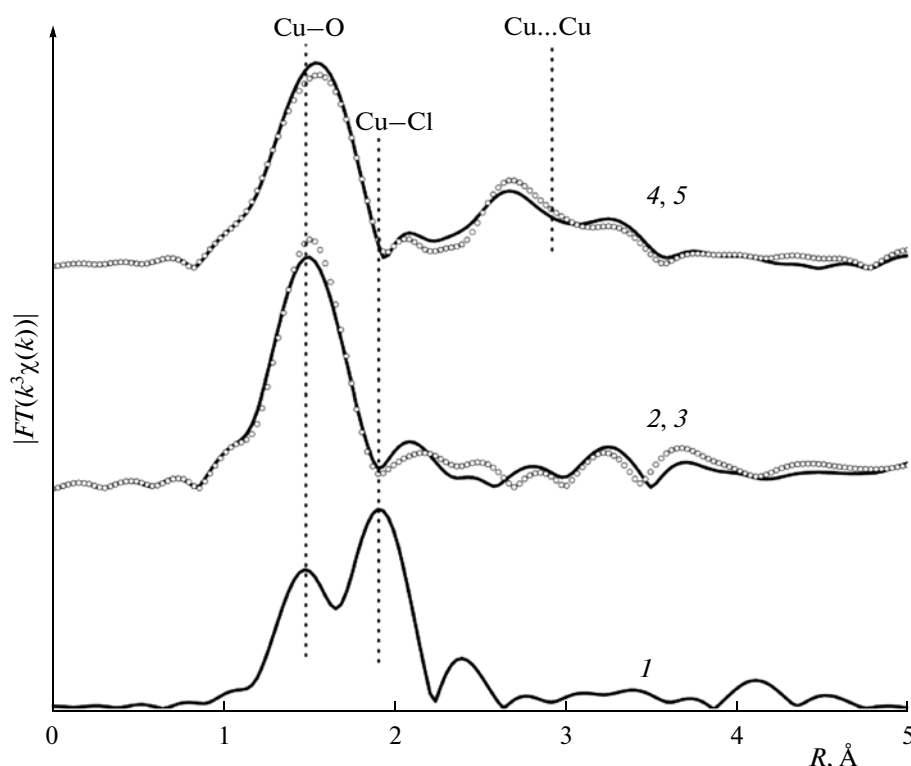


Fig. 8. Radial distribution curves of atoms obtained by the Fourier transform of the Cu *K*-edge EXAFS spectra: (1) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (s), (2, solid line) an aqueous solution of CuCl_2 , (3, circles) an aqueous solution of PdCl_2 and CuCl_2 , (4, solid line) sample 2 ($\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$), and (5, circles) sample 3 (the catalyst $\text{PdCl}_2\text{-CuCl}_2/\gamma\text{-Al}_2\text{O}_3$).

adsorbed CO_2 , appears already after 1 min [43]. The intensity of this band grows to 7 min, and then it does not change up to the 32nd minute, whereas absorption bands due to CO groups gradually disappear. This suggests the direct participation of oxygen in the formation of CO_2 from CO.

Note that the above results coincide to a certain extent with the earlier [4] and latest [23] data on catalysts with similar compositions and preparation procedures; however, there are essential differences. For example, according to Shen et al. [23], the intense bands at 2162 and 2126 cm^{-1} are the main absorption bands in the diffuse reflectance IR spectra of an analogous catalyst in contact with carbon monoxide. Shen et al. [23] assigned these absorption bands to the CO group adsorbed on Pd(II) and Cu(I), respectively. In the spectra of catalyst 3, which were measured under similar conditions (Figs. 9, 10), the band at 2162 cm^{-1} was absent, but there was a band at 2114 cm^{-1} , which was assigned to the terminal CO group on Pd(II) and/or on metallic Pd⁰ and/or on Cu(I). The strongest band in our spectrum was the band at 1928 cm^{-1} , which was assigned to the bridging CO group coordinated to Pd(I) and/or Pd⁰. This band was missing in the spectra of the analogous catalyst [23], and so was the band at 1990 cm^{-1} , which was also assigned to the bridging CO group coordinated to Pd(I) and/or Pd⁰. Similar

absorption bands occurred in the published spectra of catalysts prepared by cold impregnation with the use of aqueous ammonia [23] and also in the spectrum of an analogous catalyst published by Choi and Vannice [4]. Choi and Vannice [4] additionally observed a weak band at 2158 cm^{-1} (at a low partial pressure of CO or under reaction conditions), which was assigned to terminal CO groups on Pd(II), and a shoulder at 2080 cm^{-1} , which is due to the vibrations of terminal CO groups on Pd⁰. Unlike Choi and Vannice [4], we did not observe the reduction of Cu(II) with carbon monoxide in the $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ sample under mild conditions and the appearance of a band at 2120 cm^{-1} , which is due to the terminal CO group coordinated to Cu(I). Note that Shen et al. [23] also observed the formation of CO_2 (the appearance of a band at 2300–2400 cm^{-1}) in the gas phase upon passing CO + O₂ and CO + O₂ + H₂O mixtures through the catalyst.

Thus, in accordance with data obtained for the $\text{PdCl}_2\text{-CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst (sample 3) before its contact with the reagents by XRD (Fig. 1), XAS (Figs. 5–8, Tables 1, 2), and SEM (Fig. 4), the crystalline phase of $\text{Cu}_2\text{Cl}(\text{OH})_3$ with the structure of paratacamite (space group R-3m) occurred on the surface of $\gamma\text{-Al}_2\text{O}_3$. The reflections corresponding to the crystalline phases of palladium were absent from the diffraction patterns of the catalyst (sample 3) (Fig. 1). This fact sug-

Table 2. Local environment parameters based on the results of the treatment of Cu *K* edge EXAFS spectra

Sample	Atomic pair	Coordination number	$r, \text{\AA}$	$\sigma^2, \text{\AA}^2$	R_f
CuCl ₂ · 2H ₂ O	Cu–O	2	1.95 (1.94)*	0.0045	0.030
	Cu–Cl	2	2.27 (2.28)	0.0035	
	Cu–Cl	2	2.86 (2.93)	0.0148	
Solution of CuCl ₂	Cu–O _{eq}	4	1.97	0.0043	0.021
	Cu–O _{ax}	2	2.29	0.0210	
Solution of CuCl ₂ + PdCl ₂	Cu–O _{eq}	4	1.97	0.0044	0.018
	Cu–O _{ax}	2	2.30	0.0203	
Sample 2 (CuCl ₂ /γ-Al ₂ O ₃)	Cu–O	2	1.99 (1.98)	0.0026	0.016
	Cu–O	3	2.05 (2.11)	0.0266	
	Cu–Cl	1	2.85 (2.79)	0.0065	
	Cu–Cu	4	3.09 (3.06)	0.0186	
	Cu–Cu	2	3.47 (3.41)	0.0093	
Sample 3 (PdCl ₂ –CuCl ₂ /γ-Al ₂ O ₃)	Cu–O	2	1.99 (1.98)	0.0028	0.016
	Cu–O	3	2.09 (2.11)	0.0400	
	Cu–Cl	1	2.89 (2.79)	0.0072	
	Cu–Cu	4	3.09 (3.06)	0.0157	
	Cu–Cu	2	3.47 (3.41)	0.0116	

Note: See Table 1 for notation.

* The interatomic distances r given in parentheses correspond to crystallographic data [35, 38].

gests that either the amount of these phases is lower than the detection limit of this technique or palladium is in the amorphous state. According to XAS data, the local environment of palladium is a planar square of four chlorine atoms with an increased distance between palladium and one of the chlorine atoms. It is likely that palladium interacts with the accessible electrophilic centers of γ-Al₂O₃ through this chlorine. According to EXAFS data, there is no direct contact between palladium and copper.

We found using XAS that the oxidation numbers of palladium and copper remained unchanged in the course of the preparation of the PdCl₂–CuCl₂/γ-Al₂O₃ catalyst. However, a change in the local environment of copper occurred: it was tetragonal pyramidal in CuCl₂ · 2H₂O (s) (the coordination polyhedron in the form of a tetragonal pyramid—two chlorine atoms and two oxygen atoms of water in the equatorial plane formed a flat square and two chlorine atoms were located in the axial position); in the impregnating solutions of CuCl₂ (both in the absence and in the presence of palladium, because of the local environment of copper being essentially the same in these solutions) it was purely tetragonal pyramidal oxygen; however, a somewhat irregular oxygen environment with secondary Cu...Cl interactions occurred in the

catalyst. The coordination environment of palladium did not undergo substantial changes on passing from the solid salt PdCl₂ (a flat square of chlorine atoms) to palladium in sample 3 (four chlorine atoms with an increased distance between palladium and one of the chlorine atoms). Analogous data on the states of copper and palladium in the catalytic systems with similar compositions and preparation procedures were obtained previously [6, 11, 12, 17–22]. In this work, we observed, for the first time, an increase in the distance between palladium and one of the four chlorine atoms in the freshly prepared catalyst and demonstrated the evolution of the local environment of copper and palladium on passing from the initial salts to the impregnating solutions and chlorides located on the surface of γ-Al₂O₃.

In the presence of water vapor and carbon monoxide, the reduction of copper and palladium and the coordination of carbon monoxide on the catalyst surface yield terminal and bridging carbonyl groups. The carbonyl compounds of palladium are the most probable intermediate products. The conversion of carbon monoxide coordinated to palladium into carbon dioxide involves oxygen and water, which is consistent with previously obtained kinetic data [45].

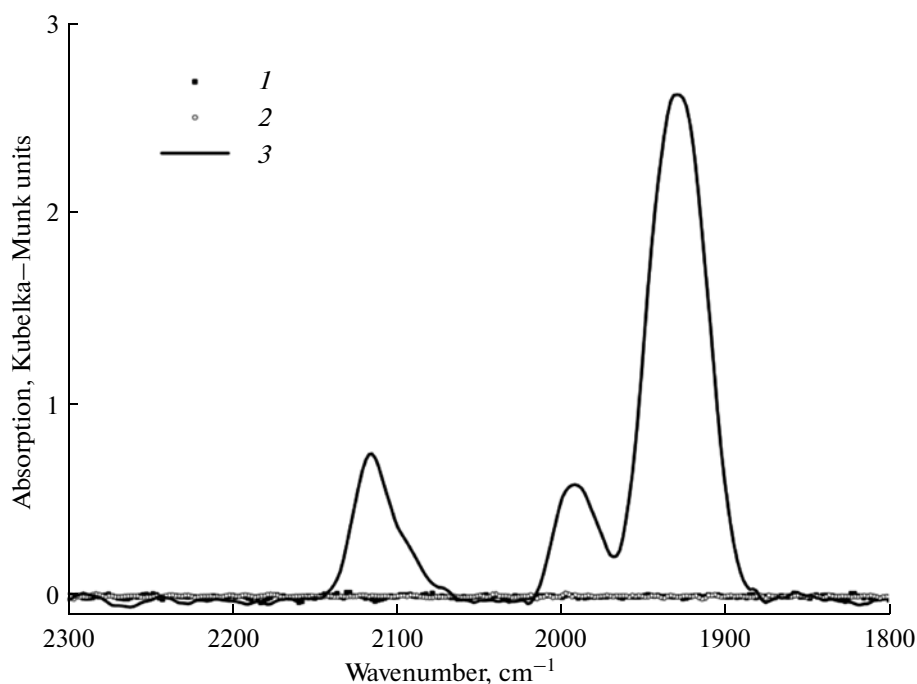


Fig. 9. Diffuse reflectance IR spectra of samples (1) 1, (2) 2, and (3) 3 at an equilibrium CO pressure of 20 Torr and room temperature.

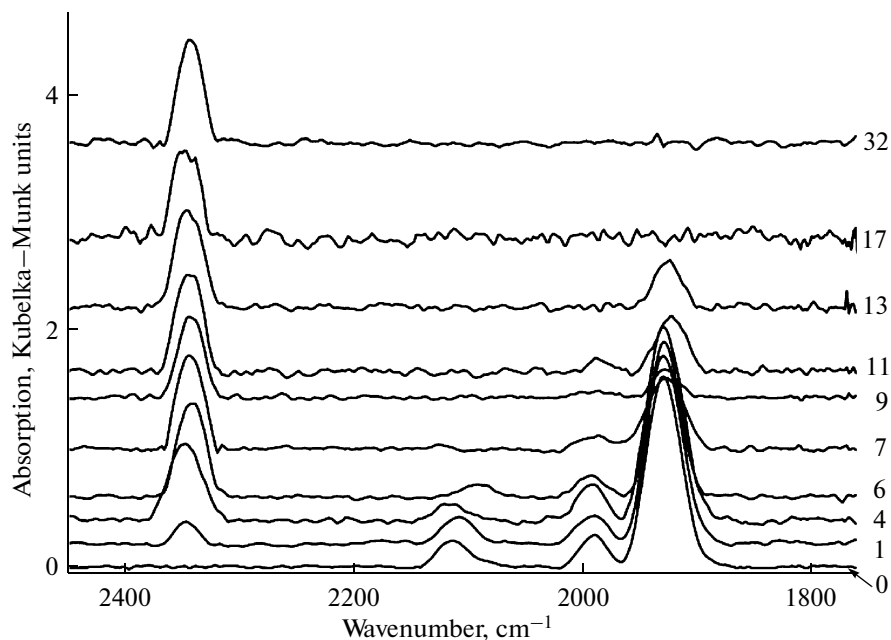
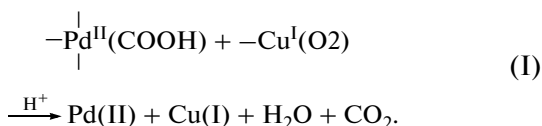


Fig. 10. Diffuse reflectance IR spectra of sample 3 (catalyst $\text{PdCl}_2\text{--CuCl}_2/\gamma\text{-Al}_2\text{O}_3$), which are indicative of the conversion of coordinated CO with the participation of atmospheric oxygen at room temperature and atmospheric pressure. The numbers to the right of the spectra specify the sample–air contact time (min).

The above results do not provide an unambiguous insight into the role of copper in the mechanism of the process. If $\text{Cu}_2\text{Cl}(\text{OH})_3$, which occurs on the surface in the crystalline state, oxidizes Pd^0 or another form of palladium, for example, a hydride complex, then, contact between the crystals of $\text{Cu}(\text{II})$ hydroxide chlo-

ride and the palladium compound is necessary. However, the possibility of this contact or the presence of the mixed complexes of palladium and copper in the freshly prepared catalyst does not follow from our data. Another possible function of copper is activation of oxygen by $\text{Cu}(\text{I})$ complexes with the subsequent

interaction of this complex, for example, with the hydroxycarbonyl complex of palladium according to the reaction

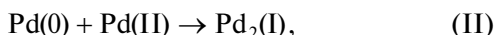


However, either the presence of Cu(I) and Pd(II) as a single complex or the possibility of their interaction on the surface of the support is necessary for fulfilling this function. But we cannot exclude the possibility of forming the mixed complex in the course of the process.

The formation of an active site of the catalyst for CO oxidation by oxygen can involve the following steps:

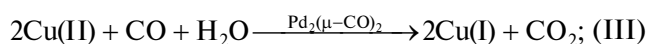
reduction of Pd(II) in the presence of H₂O and CO;

surface diffusion of the reduced complex of Pd⁰ and its interaction with Pd(II) yielding Pd₂(I) according to the reaction



with the Pd₂(I) complex stabilized by bridging carbonyl groups in the form of Pd₂(μ-CO);

catalysis of the partial reduction of Cu(II) to Cu(I) by the Pd₂(μ-CO)₂ complex in the interaction of Cu(II) with H₂O and CO,



formation of the active site Pd₂(I)–Cu(I)_n as a result of these reactions (similar to the formation of the complex [(PdCl₂)₂CuCl₂(DMF)₄]_n in the Wacker oxidation of alkenes in the DMF–H₂O system [16]) or the surface sites Pd₂(I) and Cu(I)_n, which are not connected with chemical bridges (electron carriers).

Our forthcoming studies will be aimed at explaining the mechanisms of the formation of the active site of catalysis and the action of the catalyst.

ACKNOWLEDGMENTS

We are grateful to Cand. Sci. (Chem.) N.A. Prokudina for the measurement of the specific surface area of γ-Al₂O₃.

This work was supported by the Government of Moscow and by the Russian Foundation for Basic Research (project no. 11-03-00118-a). Synchrotron studies were performed at the shared facilities of the Kurchatov Center of Synchrotron Radiation and Nanotechnologies (state contract no. 16.552.11.7003).

REFERENCES

1. Rakitskaya, T.L., Ennan, A.A., and Paina, V.Ya., *Katalizatory nizkotemperaturnogo okisleniya monooksida ugleroda* (Low-temperature Carbon Monoxide Oxidation Catalysts), Moscow: TsINTIKhIMNEFTEMASH, 1991, p. 40.
2. Kuznetsova, L.I., Matveev, K.I., and Zhizhina, E.G., *Kinet. Katal.*, 1985, vol. 25, no. 5, p. 1029.
3. Desai, M.N., Butt, J.B., and Dranoff, J.S., *J. Catal.*, 1983, vol. 79, p. 95.
4. Choi, K.I. and Vannice, M.A., *J. Catal.*, 1991, vol. 127, p. 489.
5. Golodov, V.A., Sokolsky, D.V., and Noskova, N.F., *J. Mol. Catal.*, 1977, vol. 3, nos. 1–3, p. 51.
6. Lee, J.S. and Park, E.D., *Top. Catal.*, 2002, vol. 18, nos. 1–2, p. 67.
7. Golodov, V.A., Sheludyakov, Yu.L., Di, R.I., and Fokanov, V.K., *Kinet. Katal.*, 1977, vol. 18, p. 234.
8. Spitsyn, V.I., Fedoseev, I.V., Ponomarev, A.A., and Elkin, A.I., *Zh. Neorg. Khim.*, 1978, vol. 23, no. 2, p. 454.
9. Golodov, V.A., Kuksenko, E.L., and Taneeva, G.V., *Kinet. Katal.*, 1982, vol. 23, no. 1, p. 248.
10. Golodov, V.A., Kuksenko, E.L., Taneeva, G.V., Alekseev, A.M., and Geminova, M.V., *Kinet. Katal.*, 1984, vol. 25, no. 2, p. 330.
11. Kim, K.D., Nam, I.-S., Chung, J.S., Lee, J.S., Ryu, S.G., and Yang, Y.S., *Appl. Catal., B*, 1994, vol. 5, p. 103.
12. Park, E.D. and Lee, J.S., *J. Catal.*, 2000, vol. 193, p. 5.
13. Kotareva, I.A., Oshanina, I.V., Kuz'micheva, G.M., Turkova, T.V., Khaidarova, E.R., Zhanavskina, S.M., Bruk, L.G., Kaliya, O.L., and Temkin, O.N., *Vestn. MITKhT*, 2007, vol. 2, no. 4, p. 72.
14. Titov, D.N., Karandina, O.A., Oshanina, I.V., Zubavichus, Ya.V., Veligzhanin, A.A., Bruk, L.G., and Temkin, O.N., *Tezisy dokl. III Ross. konf. "Aktual'nye problemy neftekhimii"* (Proc. III Russian Conf. on Topical Problems of Petroleum Chemistry), Zvenigorod, Moscow oblast, 2009.
15. Rakitskaya, T.L. and Paina, V.Ya., *Kinet. Katal.*, 1992, vol. 33, nos. 5–6, p. 1121.
16. Hosokawa, T., Nomura, T., and Murahashi, S.-I., *J. Organomet. Chem.*, 1998, vol. 551, p. 387.
17. Lee, J.S., Choi, S.H., Kim, K.D., and Nomura, M., *Appl. Catal., B*, 1996, vol. 7, p. 199.
18. Choi, S.H. and Lee, J.S., *React. Kinet. Catal. Lett.*, 1996, vol. 57, no. 2, p. 227.
19. Yamamoto, Y., Matsuzaki, T., Ohdan, K., and Okamoto, Y., *J. Catal.*, 1996, vol. 161, p. 577.
20. Koh, D.J., Song, J.H., Ham, S.-W., Nam, I.-S., Chang, R.-W., Park, E.D., Lee, J.S., and Kim, Y.G., *Korean J. Chem. Eng.*, 1997, vol. 14, no. 6, p. 486.
21. Park, E.D. and Lee, J.S., *J. Catal.*, 1998, vol. 180, p. 123.
22. Park, E.D. and Lee, J.S., *Stud. Surf. Sci. Catal.*, 2000, vol. 130, no. 3, p. 2309.
23. Shen, Y., Lu, G., Guo, Yu., Wang, Y., Guo, Ya., and Gong, X., *Catal. Today*, 2011, vol. 175, no. 1, p. 25.
24. Zhir-Lebed', L.N. and Golodov, V.A., *Trudy IOKE* (Institut organicheskogo kataliza i elektrokhemii im. D.V. Sokol'skogo) AN KazSSR, *Gomogennyi Katal.*, 1973, vol. 4, p. 85.

25. Likholobov, V.A., Zudin, V.P., Eremenko, N.K., and Ermakov, Yu.I., *Kinet. Katal.*, 1974, vol. 15, no. 6, p. 1613.
26. Zudin, V.N., Likholobov, V.A., and Ermakov, Yu.I., *Kinet. Katal.*, 1977, vol. 18, no. 2, p. 524.
27. RF Patent 2267354, 2006.
28. Hammersley, A.P., *FIT2D V9.129: Reference Manual, V3.1*, ESRF Internal Report ESRF98HA01T, 1998.
29. Ravel, B. and Newville, M., *J. Synchrotron Radiat.*, 2005, vol. 12, p. 537.
30. Ankudinov, A.L., Ravel, B., Rehr, J.J., and Conradson, S.D., *Phys. Rev. B: Condens. Matter*, 1998, vol. 58, p. 7565.
31. Chernyshov, A.A., Veligzhanin, A.A., and Zubavichus, Y.V., *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2009, vol. 603, p. 95.
32. Kustov, L.M., *Top. Catal.*, 1997, vol. 4, p. 131.
33. Zhou, R.-S. and Snyder, R.L., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, vol. 47, p. 617.
34. Tsybulya, S.V. and Kryukova, G.N., *Phys. Rev. B: Condens. Matter*, 2008, vol. 77, p. 024112.
35. Fleet, M.E., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1975, vol. 31, p. 183.
36. Lamberti, C., Bordiga, S., Bonino, F., Prestipino, C., Berlier, G., Capello, L., and D'Acapito, F., Llabrés i Xamena, F.X., and Zecchina, A., *Phys. Chem. Chem. Phys.*, 2003, vol. 5, p. 4502.
37. Dell'Amico, D.B., Calderazzo, F., Marchetti, F., and Ramello, S., *Angew. Chem. Int. Ed.*, 1996, vol. 35, p. 1331.
38. Brownstein, S., Han, N.F., Gabe, E.J., and le Page, Y., *Z. Kristallogr.*, 1989, vol. 189, p. 13.
39. Ohtaki, H. and Radnai, T., *Chem. Rev.*, 1993, vol. 93, p. 1157.
40. Beagley, B., Eriksson, A., Lindgren, J., Persson, I., Pettersson, L.G.M., Sandstrom, M., Wahlgren, U., and White, E.W., *J. Phys.: Condens. Mater*, 1989, vol. 1, p. 2395.
41. Vargaftik, M.N., Stromnova, T.A., and Moiseev, I.I., *Zh. Neorg. Khim.*, 1980, vol. 25, no. 2, p. 236.
42. Temkin, O.N. and Bruk, L.G., *Usp. Khim.*, 1983, vol. 52, no. 2, p. 206.
43. Davydov, A.A., *IK-spektroskopiya v khimii poverkhnosti okislov* (IR Spectroscopy Applied to Oxide Surface Chemistry), Novosibirsk: Nauka, 1984.
44. Goggin, P.L., Goodfellow, R.J., Herbert, I.R., and Orpen, A.J., *J. Chem. Soc., Chem. Commun.*, 1981, p. 1077.
45. Kotareva, I.A., Oshanina, I.V., Odintsov, K.Yu., Bruk, L.G., and Temkin, O.N., *Kinet. Catal.*, 2008, vol. 49, no. 1, p. 18.