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Catalysis of Carbon Tetrachloride Conversion by Copper Complexes with Monoethanolamine Immobilized on the Surface of Silica

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Abstract—The catalytic properties of silica-immobilized copper complexes with monoethanolamine in reactions of CCl_4 addition to 1-octene and combined metathesis of C–Cl and C–H bonds in the CCl_4–decane system were studied. The catalytic activity was found to be an extremal function of metal concentration. The increase of activity during the addition of CCl_4 to octene as the metal content was decreased to ~0.3 wt % can be explained by an increase in the fraction of mononuclear copper complexes of differing composition. Further changes in activity were due to the formation of metal complexes with various ligand environments. A comparison between EPR data and catalytic properties suggested that the most active catalysts contained a considerable number of divalent copper complexes with a coordination environment of four nitrogen atoms, which are more effective than oxygen at increasing electron density on copper ion; this facilitated the reduction of Cu(II) to Cu(I). The above complexes are unstable because the ligands are rigidly fixed on the surface and strained structures are formed. Ligands in the coordination sphere of the metal can be readily replaced by substrate molecules, which exhibit weak solvating power.

INTRODUCTION

Copper complexes with monodentate donor ligands immobilized on the surface of mineral supports are catalysts for reactions involving halogenated hydrocarbons: carbon tetrachloride addition at multiple bonds, combined metathesis of C–H and C–halogen bonds, and isomerization of chlorinated olefins [1–3]. Recent data suggest that it is possible to develop highly active catalysts based on linear polycopperorganosiloxanes (PCOSs) that are chemically immobilized on silica or zirconia surfaces [4, 5]. In these systems, catalytic activity was found to be an unusual extremal function of surface transition-metal concentration; in this case, a change in the specific activity can be as high as two orders of magnitude, depending on metal content. A technique for controlling the rates of catalytic reactions consists of varying surface metal concentrations. In this context, it is of importance to determine the nature of the most active centers of immobilized catalysts, to reveal factors responsible for extremal relations between catalytic activity and surface metal concentration, and to find general rate laws. Bifunctional ligands such as amino alcohols, as well as PCOSs, facilitate the strong fixation of copper complexes on oxide supports due to the formation of covalent Si–O–C bonds; in addition, they provide an opportunity to monitor the effects of concentration and structure factors on catalytic activity.

Previously, we studied the addition of CCl_4 to olefins (reaction (I)) in the presence of copper complexes with monodentate donor ligands (phosphines, thioethers, and DMF) and found that it mainly occurs via a radical chain mechanism [1]. In the presence of dissolved and immobilized complexes of copper and other metals, the interaction of CCl_4 with decane (reaction (II)) also occurs via a radical mechanism with the formation of a mixture of secondary chlorodecanes (the yield of 1-chlorodecane was negligibly small) [6]. In both cases, it is likely that a metal complex plays the role of a renewable initiator. As a result of this, reactions (I) and (II) exhibit the properties of both radical chain and catalytic processes.

$$CCl_4 + C_6H_{13}CH{=}CH_2 \longrightarrow C_6H_{13}CH(Cl)CH_2CCl_3, \quad \text{(I)}$$

$$CCl_4 + C_{10}H_{22} \longrightarrow CHCl_3 + C_{10}H_{21}Cl. \quad \text{(II)}$$

In this work, we studied the catalytic properties of silica-immobilized copper complexes with monoethanolamine in reactions of CCl_4 addition to 1-octene and combined metathesis of C–Cl and C–H bonds in the CCl_4–decane system.

EXPERIMENTAL

Organic substances were purified in accordance with standard procedures. Chemically pure CCl_4 was dried and distilled from P_2O_5. Acetonitrile of analytical grade was distilled from calcined $CaCl_2$ at 80°C. 1-Octene from Merck was distilled from sodium metal. KSK-2 silica gel (S_{sp} = 250 m^2/g) was calcined in air and then in a vacuum at 450–500°C. Modification with monoethanolamine (MEA) was performed from a gas phase by heating the silica gel in MEA vapor at 150–160°C for several hours, followed by evacuation to a pressure of ≤10^{-2} Torr to remove the liberated water and an excess of the alcohol. Immobilized complexes were synthesized in an acetonitrile solution with the use of CuCl. For varying the metal content, the modified silica gel was placed in solutions with different copper concentrations and the resulting suspensions were stirred at 45–50°C for 2 h. Next, the silica gel was filtered off and washed with acetonitrile for the removal of excess copper chloride.

The concentration of organic matter in the resulting catalysts was determined by elemental analysis, and the concentration of copper ($[Cu]_0$) was determined by titrimetry and atomic absorption spectrometry.

Heterogeneous samples were examined by EPR spectroscopy and diffuse-reflectance UV spectroscopy on an SF-14 spectrophotometer.

The EPR spectra were measured on a Varian E-3 X-band radiospectrometer (100-kHz high-frequency modulation) at 77 K. The g-factors of complexes were determined by the measurement of hyperfine structure (HFS) components of Mn^{2+} ions in MgO simultaneously with the EPR spectra of copper ions. Calibration of the g-factor scale was performed by the simultaneous measurement of the spectra of a diamagnetically diluted solid solution of Mn^{2+} ions in MgO (the apparent values of the g-factors of the third and fourth components and the splitting between them were $g_3 = 2.0328 \pm 0.0001$, $g_4 = 1.9812 \pm 0.0001$, and $\Delta H_{3-4} = 86.76 \pm 0.05$ G, respectively) and a 0.001 M solution of the $[Cu(H_2O)_6](NO_3)_2$ complex in a mixture of D_2O and CD_3OD at 77 K ($g_{\parallel} = 2.424 \pm 0.005$, $g_{\perp} = 2.092 \pm 0.005$, and $A_{\parallel} = 117 \pm 3$ G [7]).

The number of paramagnetic centers in the test samples was determined by comparing the area under the absorption curve of a reference standard (a single crystal of $CuCl_2 \cdot 2H_2O$) with the test sample, corrected to identical measurement conditions. The areas were determined with the use of authoring software and an automated data system.[1]

The constancy of measurement conditions in the resonator of the EPR spectrometer was monitored by recording the spectrum components of an intermediate standard (Al_2O_3 containing Cr^{3+}) simultaneously with the spectrum of the test sample. The relative error in determining the concentration of paramagnetic Cu^{2+} ions was ~ ±10%.

The catalytic experiments were performed in sealed evacuated ampules with intense stirring, under reaction rate conditions independent of the stirring rate. The procedure used for the analysis of products by gas–liquid chromatography was described in detail elsewhere [1]. The activity of catalysts was determined from the initial rates of reactions in standard experiments: 0.02 g of a heterogeneous catalyst, 0.05 ml of 1-octene, and 0.45 ml of CCl_4 at 130°C in the addition reaction and 0.05 g of catalyst, 0.2 ml of *n*-decane, and 0.4 ml of CCl_4 at 160°C in the metathesis. The method of initial rates and the linearization of kinetic curves were used for calculating the kinetic parameters of the addition reaction. The reactant concentration was varied over the range of $[CCl_4]$ from 0.4 to 1.25 mol/l; the catalyst weight was varied from 0.006 to 0.06 g. At low concentrations of CCl_4, *n*-nonane was used as a solvent. To calculate the apparent activation energy, the reaction temperature was varied over the range 110–140°C.

RESULTS AND DISCUSSION

The catalysts synthesized were blue or bluish-green finely dispersed powders. At a low metal content (<0.1 wt %), the color was light yellow. The diffuse-reflectance spectra of samples with high metal contents exhibited broad low-intensity bands in the region 580–680 nm, which correspond to the complexation of bivalent copper with amino alcohol molecules. In this case, the parent CuCl is rapidly oxidized in air in the presence of amino alcohol, which is a typical donor ligand. An analogous phenomenon was observed previously in the interaction of CuCl with thioethers [1].

Silica gel containing up to 7 wt % organic compounds can be obtained by surface modification. The copper concentration that can be obtained on the surface of a modified support from concentrated solutions of CuCl in acetonitrile was determined, as was the total composition of heterogeneous complexes with the amino alcohol. At a ~5 wt % concentration of the organic compound, the maximum concentration of copper in the samples was ~2.5 wt %. With consideration for the molecular weights of the components ($M_{MEA} = 61$, $A_{Cu} = 64$), the composition of the complex was Cu/MEA ≈ 1 : 2.

By analogy with published data [9], we believe that, in the course of immobilization, amino alcohol molecules interact with the surface of silica gel resulting in the formation of an Si–O–C ether group. As a result of this, the coordination of the copper ion to the amino alcohol mainly occurs through the amino group. This structure of grafted complexes with the amino alcohol is essentially different from that of an individual analog [9]. A complex prepared from solution consists of Cu(II) ions and two molecules of a chelating ligand, which are arranged in the equatorial plane; as a rule, either solvent or water molecules occur in the axial position with respect to the metal ion. It is likely that a change in the structure of the heterogenized complex, as compared with that of the homogeneous complex, is responsible for the considerable increase in catalytic activity in the test reactions of CCl_4 addition to olefins and C–Cl bond metathesis.

In the presence of the test heterogeneous catalysts, the selective formation of the addition product (1,1,1,3-tetrachlorononane) was observed in the reaction of 1-octene with CCl_4. Figure 1 demonstrates typical

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[1] We are grateful to Professor A.Kh. Vorob'ev (Faculty of Chemistry, Moscow State University) for permission to use the data acquisition and processing system developed by him.

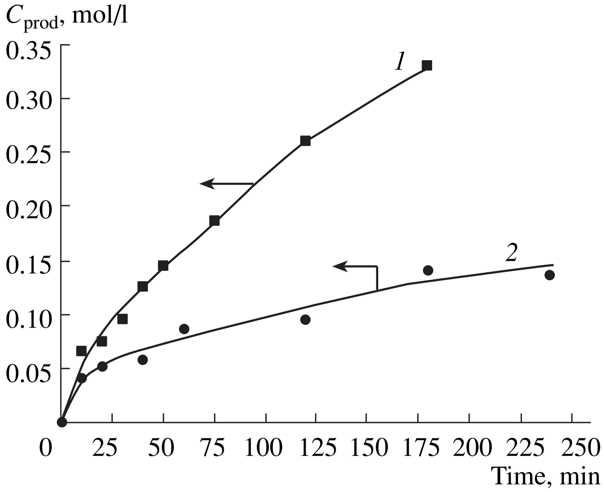

Fig. 1. 1,1,1,3-Tetrachlorononane buildup curves for the reaction of 1-octene with CCl_4 at 130°C on catalysts with different surface copper concentrations (ω(Cu) = (*1*) 0.24 and (*2*) 0.48%). $[C_8H_{16}]$ = 0.64 mol/l; $[CCl_4]$ = 9.3 mol/l; and m_{Cat} = 0.02 g.

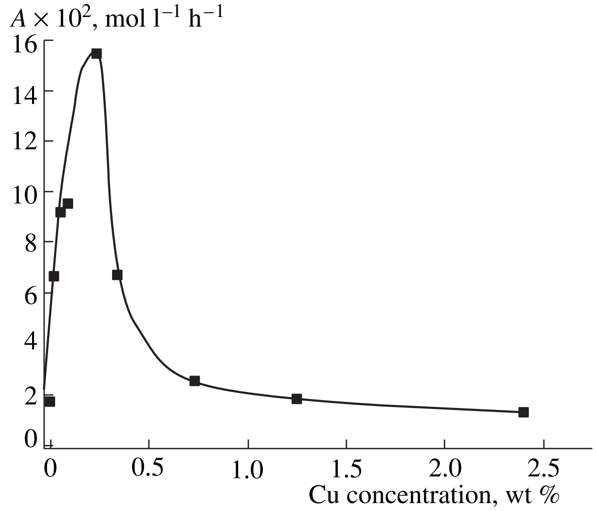

Fig. 2. Dependence of the initial rates of CCl_4 addition to 1-octene on the copper content of catalysts. [Ol] = 0.6 mol/l; $[CCl_4]$ = 9.3 mol/l; V_s = 0.5 ml; and m_{Cat} = 0.02 g.

buildup curves for this product. When there is an excess of CCl_4, the reaction is described by a first-order rate equation. The determination of reaction order with respect to the catalyst and CCl_4 by the method of initial rates allowed us to obtain the rate equation $w = k[\text{O1}][CCl_4][\text{Cat}]$, where w is the reaction rate and [Ol], $[CCl_4]$, and [Cat] are the concentrations of the corresponding reactants. In the test temperature range, the apparent activation energy was ~80 kJ/mol, as found from the $\ln w_0$–$1/T$ linear relationship. An analogous rate equation and similar apparent activation energies were obtained in a study of catalysts based on ruthenium and molybdenum complexes with donor ligands; these catalysts are characterized by a “coordination” reaction mechanism of addition to olefins [10].

With the use of catalysts with different surface concentrations of immobilized copper complexes in the addition reaction, an extremal relation between activity and metal concentration was obtained (Fig. 2). The activity (*A*) was characterized by the initial rate of the reaction at a constant solid catalyst weight. In the test complexes, an increase in catalytic activity was observed up to a metal concentration of 0.1 wt %. A further increase in the metal content of the catalyst resulted in a decrease in activity.

The table summarizes data on the activity of catalysts in the reaction of decane with CCl_4. These data indicate that the reaction rate (w_0) on a catalyst containing 0.06 wt % Cu was higher, by a factor of 1.5, than the reaction rate on an analogous catalyst containing 1.25% Cu; this corresponds to an increase in the specific activity by a factor of 30, in terms of 1 g of copper.

An extremal relation between the activity of heterogeneous metal-containing catalysts and the metal content is a widely occurring phenomenon [11, 12]. It could be due to the following two reasons: first, a nonuniform distribution of metal ions on the surface and the formation of areas with high local concentrations, in which a portion of the catalytic complex is inaccessible to substrate molecules; second, a change in the composition of active centers depending on metal concentration. In our opinion, the second reason is more probable in this case. Because catalysts with a minimum copper content were most active, it was of undoubted interest to study their structure and composition using EPR spectroscopy.

Figure 3 demonstrates typical EPR spectra of copper(II) complexes with MEA supported on SiO_2. At $[\text{Cu}]_0 \le 0.3$ wt %, practically all copper complexes were detected by EPR spectroscopy, and the g-tensor parameters ($g_{\|} > g_{\perp} > 2.000$) determined from the spectra were characteristic of Cu(II) complexes with distorted octahedral structures (symmetry group D_{4h}) [13, 14]. At $[\text{Cu}]_0 \ge 0.3$ wt %, not only isolated copper(II) complexes but also associates with high local concentrations of Cu(II) ions occurred in the samples. Strong magnetic dipole–dipole and spin-exchange interactions between Cu(II) ions occurred in these associates [15], and the fraction of associates increased with total copper concentration in the samples. As would be expected, the probability of formation not only of areas with high local concentrations but also of Cu(II) complexes with structurally different ligand environments increased with the surface concentration of copper ions; this manifested itself in both a broadening of the HFS components of the EPR spectrum and a more complex shape of the spectrum (Fig. 3).

Note that only a portion of the Cu(II) ions in the samples is detected by EPR spectroscopy. Figure 4 shows how the amount of Cu(II) changed as the total

Dependence of the initial rate of the reaction of decane with CCl_4 and of the specific activity of catalysts on the concentration of copper

Concentration of Cu, wt %	w_0, mol l^{-1} h^{-1}	Specific activity, mol product (mol Cu)$^{-1}$ h^{-1}
0.06	0.050	64
0.23	0.040	13
1.25	0.033	2

Note: $[C_{10}] = 1.87$ mol/l; $[CCl_4] = 6.9$ mol/l; $V_s = 0.6$ ml; and $m_{Cat} = 0.05$ g.

copper content of the samples was increased. It can be seen in Fig. 4 that at $[Cu]_0 < 0.3$ wt % practically all copper ions in the sample were paramagnetic. As the total copper content was increased ($[Cu]_0 > 0.3$ wt %), the amount of Cu(II) ions detected by EPR spectroscopy remained approximately constant, whereas the amount of diamagnetic copper ions ($[Cu]_{diam}$), which are EPR undetectable, increased: the value of $[Cu]_{diam}$ at $[Cu]_0 = 2.4$ wt % was higher than the value of [Cu(II)] by a factor of ~10.

As found previously, the availability of personal computers makes it possible to analyze with a sufficient degree of reliability EPR spectra that are the superposition of spectra due to several types of complexes [16–18]. We used an analogous approach in this work. In our opinion, spectrum *4* in Fig. 3 is the superposition of broad anisotropic singlet spectrum *5* and spectrum *6*, whose shape is similar to that of spectrum *2*, with consideration for the noise level of the experimental spectrum. It can also be seen in Fig. 3 that the spectrum of a sample with 0.1 wt % copper (spectrum *3*) can be represented as the superposition of the spectrum of a sample with 0.02 wt % copper (spectrum *1*) and spectrum *2* with an integrated intensity ratio between spectra *1* and *2* close to 1 : 2.5. In spectrum *2*, HFS components with a parallel orientation due to two types of complexes (B and C) can be distinguished, which are different from an A-type complex in magnetic-resonance parameters. Thus, even at a very low surface copper concentration on the support (~0.1 wt %), various Cu(II) complexes with MEA occurred simultaneously in the samples.

We attempted to characterize the structures of complexes A, B, and C based on a comparison of the spin-Hamiltonian parameters found for these complexes with known published data. The magnetic-resonance

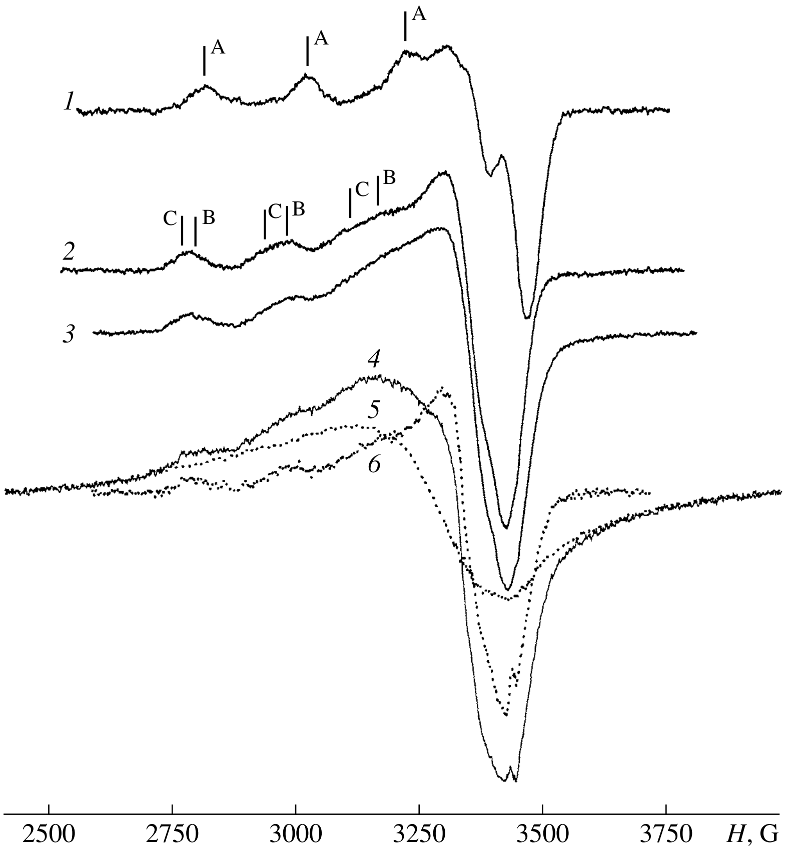

Fig. 3. EPR spectra ($T = 77$ K) of copper(II) complexes with MEA supported on SiO_2 at [Cu], wt %: (*1*) 0.02, (*3*) 0.1, and (*4*) 2.4. Spectrum *2* was obtained by subtracting spectrum *1* from spectrum *3*. Spectrum *4* was represented as the superposition of singlet *5* and multiplet *6*.

parameters of complexes with the principal axis of a polyhedron parallel to the direction of an external magnetic field were most informative.

It is our opinion that only complexes of the A type with the parameters $A_{\parallel}^{A}$ = 20.2 ± 0.3 mT, $g_{\parallel}^{A}$ = 2.203 ± 0.004, and $g_{\perp}^{A}$ = 2.048 ± 0.004 were present on the surface of the support at the lowest copper concentration (0.02 wt %). In samples with $[Cu]_0 > 0.05$ wt %, the amount of A-type complexes remained approximately constant, but complexes of the B and C types appeared, and their fraction rapidly increased; the spin-Hamiltonian parameters of these complexes were close to $A_{\parallel}^{B}$ = 18.5 ± 0.4 mT, $g_{\parallel}^{B}$ = 2.228 ± 0.005, $A_{\parallel}^{C}$ = 17.1 ± 0.4 mT, and $g_{\parallel}^{C}$ = 2.263 ± 0.005.

A comparison of the parameters obtained in this experiment with well-known parameters of Cu(II) complexes with MEA in glassy solutions at 77 K [19] demonstrated that the parameters of complex A are close to the corresponding values of the $[Cu(NH_2)_4(H_2O)_2]^{2+}$ tetraamine structures with nitrogen atoms in the equatorial plane of the polyhedron ($A_{\parallel}$ = 19.9 ± 0.3 mT, $g_{\parallel}$ = 2.203 ± 0.005, and $g_{\perp}$ = 2.051 ± 0.005). It is likely that the high density of $\equiv SiOCH_2CH_2NH_2$ groups grafted onto the surface of SiO_2 is responsible for the occurrence of A-type structures, although their fraction is comparatively small.

The values of $g_{\parallel}$ and $A_{\parallel}$ for B-type complexes are close to those of $[Cu(OCH_2CH_2NH_2)_2(H_2O)_2]$ complexes, in which the Cu(II) ion is bound to the N atoms and $-O^-$ groups (deprotonated hydroxy groups) of two MEA molecules ($A_{\parallel}$ = 18.8 mT; $g_{\parallel}$ = 2.235) [20]. The difference in the values of $g_{\parallel}$ is most likely due to the replacement of $-O^-$ groups or H_2O in the coordination sphere of Cu(II) in the corresponding complexes in solution by the oxygen atoms of surface silanol groups. The values of $g_{\parallel}$ and $A_{\parallel}$ close to those of B complexes can also be observed in Cu(II) complexes with three amino group nitrogen atoms in the coordination sphere [14].

The parameters of a complex of the C type are very close to the values $A_{\parallel}$ = 17.5 mT and $g_{\parallel}$ = 2.269, which were assigned by Molochnikov and Radionov [20] to structures with two nitrogen atoms in the octahedral coordination environment of the copper ion. In our opinion, other sites in the coordination sphere may be occupied by the oxygen atoms of silanol groups and water adsorbed onto the surface of silicon dioxide.

Figure 5 illustrates typical changes in EPR spectra in the course of the catalytic addition reaction and after completion of the reaction and storage of the catalysts in air for 48 h. After the addition of reactants to a dry catalyst, the spectrum was similar in shape to those described previously with somewhat narrower components; however, all the characteristic features were retained (spectrum *1*). The heating of samples under conditions of catalysis resulted in a rapid decrease in the EPR signal, and less than 10% of the copper ions remained paramagnetic after heating for 20 min (spectrum *2*). After heating for 50 min, the signal of Cu(II) ions was absent from the spectrum, and only a narrow low-intensity line with a *g*-factor of ~2.003 was observed. At present, we have no data for determining the nature of the paramagnetic center that exhibits such an EPR spectrum. Paramagnetism was not restored in the samples upon extended storage in sealed ampules at room temperature after the reaction. However, if the catalyst was dried in air for 48 h after the reaction, a new spectrum appeared (Fig. 5, spectrum *3*) with an integrated intensity that approximately corresponded to that of the initial sample before the reaction. A considerable change in the shape of the EPR signal is indicative of a significant rearrangement in the coordination sphere of the Cu(II) ion. In this case, the ligand molecule (MEA) did not participate in complex formation; it is most likely that it underwent considerable destructive transformations in the course of the catalytic process. A similar transformation of catalyst structures resulting in a loss of initial ligands was also previously observed [21–23].

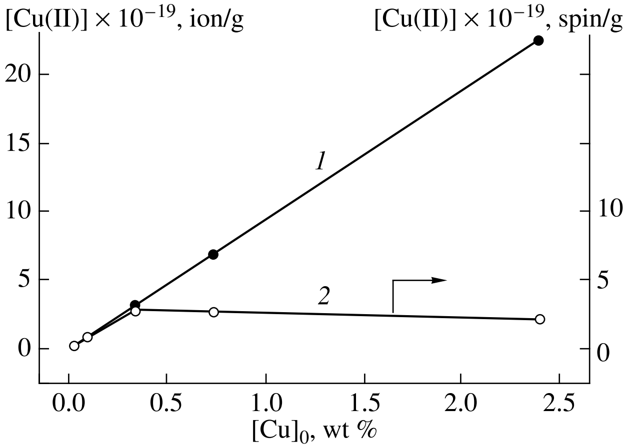

Fig. 4. Dependence of (*1*) the total amount of Cu(II) ions and (*2*) the number of paramagnetic Cu(II) ions on the concentration of copper in Cu–MEA–SiO_2 samples.

An increase in the activity of catalysts in the reaction of CCl_4 addition to 1-octene as $[Cu]_0$ was decreased to ~0.3 wt % can be explained by an increase in the fraction of mononuclear copper complexes of various compositions. It is likely that further changes in activity were due to the formation of metal complexes with different ligand environments. As follows from a comparison between EPR data and catalytic properties, the most active catalysts contained a considerable amount of bivalent copper complexes in the coordination environment of four nitrogen atoms. As compared with oxygen, these nitrogen atoms are more effective in increasing electron density on the copper ion; this facilitates the reduction of Cu(II) to Cu(I). The formation of

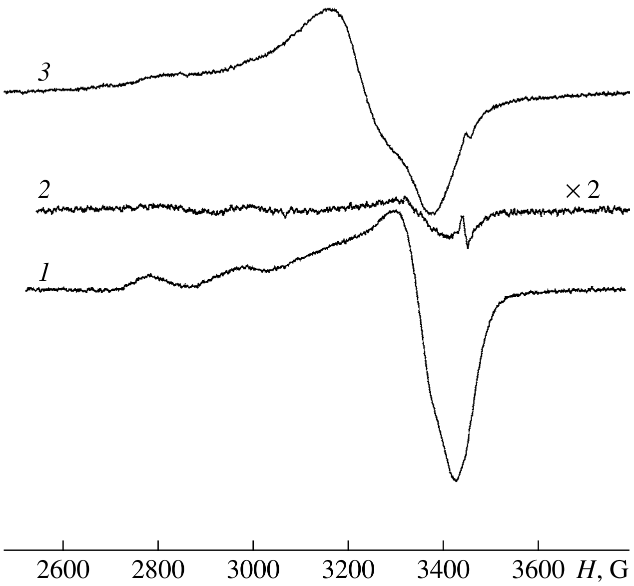

Fig. 5. EPR spectra of Cu–MEA–SiO_2 complexes at $[Cu]_0 \approx 0.3$ wt %: (*1*) the catalyst after the addition of reagents, (*2*) after heating for 20 min at 130°C, (*3*) the catalyst dried in air for 48 h after the reaction.

these structures on the surface of silica gel was due to the polymolecular adsorption of MEA [7]. As a result of this, areas with high local concentrations of amino alcohol were formed; a portion of these molecules was retained on the surface by the formation of intermolecular hydrogen bonds. The above complexes are unstable, and they can readily degrade even at room temperature because of the rigid fixation of a portion of the ligands on the surface and, probably, the formation of strained structures. The EPR data suggest a decrease in the concentration of A-type complexes over time in the samples stored in sealed evacuated ampules. The precursors of catalytically active complex species containing the metal in the coordination environment of a smaller number of ligands can be formed in the transformation of complexes A; this is of paramount importance for the subsequent coordination of weakly solvating substrates, such as the test chloroalkanes and hydrocarbons. Analogous effects were observed in a study on the catalytic activity of linear PCOSs immobilized on silica. The coordination number of the metal was found equal to two in the most active PCOS-based catalytic systems with a minimum surface concentration of organometallic oligomers [5].

Thus, we believe that the test reactions in the presence of the heterogeneous catalysts synthesized occur on the above copper-containing complexes of various compositions. It is believed that the first step in the interaction of CCl_4 with simple olefins and alkanes in the presence of copper complexes is the reduction of Cu(II) to Cu(I) by donor ligands [24]. We also observed the reduction of copper (a gradually decreased signal until its complete disappearance from the EPR spectrum) in the absence of reagents at temperatures close to the reaction temperature. The next step in the catalytic reaction is the interaction of reduced complex species with CCl_4

$$CCl_4 + Cu(I) \longrightarrow CCl_3^{\bullet} + Cu(II)Cl.$$

With free-radical initiation (for example, with the use of organic peroxides), the addition of CCl_4 at a multiple bond occurs via a free-radical mechanism resulting in the formation of various products of radical recombination and telomerization. In the presence of transition metal complexes, the reaction occurs via another so-called “coordination” mechanism [1, 10, 25]. In our case, this is evidenced by the high selectivity and kinetic features of the process.

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