Kinetics and Catalysis, Vol. 46, No. 6, 2005, pp. 861–866. Translated from Kinetika i Kataliz, Vol. 46, No. 6, 2005, pp. 909–914.
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Catalytic Activity of Immobilized Transition Metal Complexes with Monoethanolamine in Carbon Tetrachloride Addition to Multiple Bonds

V. V. Smirnov*, I. G. Tarkhanova*, A. I. Kokorin, and D. S. Tsvetkov***
** Moscow State University, Moscow, 119899 Russia*
*** Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 117977 Russia*

Received November 11, 2004

Abstract—The rates of CCl_4 addition to octene-1 in the presence of monoethanolamine complexes with Mn, Cu, V, Co, and Ni ions immobilized on the surface of silica have been determined. The majority of catalysts exhibit an inverse dependence of relative catalytic activity on surface metal concentration. Changes in the total concentrations and ligand environments of paramagnetic ions in the course of reaction are studied by EPR spectroscopy for copper- and vanadyl-containing catalysts. It has been found that the activity of complexes correlates with the rate of reduction of a metal ion in the course of a catalytic reaction.

INTRODUCTION

The addition of carbon tetrachloride to multiple bonds is a promising route to various functionalized hydrocarbons. Previously, we studied the catalysis of this process by copper complexes with amino alcohols and hydroxy amino acids chemically immobilized on the surface of silica [1, 2]. With the use of this reaction as an example, we demonstrated that the activity of the catalytic system can be varied over a wide range by varying surface metal concentration. The aim of this work was to generalize regularities that were found previously in systems containing other transition metals and to perform a comparative analysis of the nature of the activity of these systems.

As a model reaction, we studied the addition of CCl_4 to octene-1:

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

Because the key step of this radical reaction is the formation of the $CCl_3^{\bullet}$ radical due to the reversible oxidation of a low-valent metal ion,

$$CCl_4 + M^n \longrightarrow CCl_3^{\bullet} + M^{n+1}Cl, \qquad (II)$$

we studied the activity of complexes of the following metals, which can readily change their oxidation state under conditions of a catalytic reaction: Cu, Mn, Co, Ni, V, and Fe. We found that complexes of all of the above metals were active in reaction (I). The process occurred selectively: tetrachlorononane was the only reaction product. The exception was an iron complex. It exhibited low selectivity, which was comparable with that of peroxide initiators, at high activity: telomers and the products of chlorine substitution for hydrogen were formed along with the addition product. The catalytic effects of the iron complex are dramatically different from those of the other tested metals; therefore, they are not considered in this work. Of the other tested systems, Mn(II) complexes were found to be the most active along with copper-containing complexes, whereas a complex of vanadyl (VO(II)) was found to be the least active. Using the most and least active catalysts as examples, we performed a comparative EPR study of the structure of complexes and their evolution in the course of a catalytic process.

EXPERIMENTAL

Organic reagents were purified by standard procedures: CCl_4 was dried and distilled from P_2O_5, and octene-1 was distilled from sodium metal. Monoethanolamine (MEA) from Merck was used without further purification. Silica gel KSK as sand (S_{sp} = 300 m^2/g) was calcined in air and then in a vacuum at 450–500°C. Modification with the amino alcohol from a gas phase was performed by heating the silica gel in MEA vapor at 150–160°C for several hours, followed by evacuation to a pressure of $\leq 10^{-2}$ Torr in order to remove liberated water. To prepare immobilized complexes, we used metal chlorides ($CuCl_2$, $MnCl_2$, $CoCl_2$, $NiCl_2$, and $VOCl_2$), which were purified in accordance with standard procedures and then pumped to remove water and volatile compounds. $VOCl_2$ was synthesized by the reduction of vanadyl oxide in an atmosphere of $SOCl_2$; in turn, vanadyl oxide was prepared by the decomposition of ammonium vanadate. In the synthesis of samples with various surface metal concentrations, modified silica gel was placed in acetonitrile solutions with different chloride concentrations and the resulting suspensions were stirred at 45–50°C for 2 h using a magnetic stirrer. Next, the silica gel was filtered off and washed with acetonitrile for the removal of an excess of metal salt. The concentration of organic matter in the resulting catalysts was determined by elemental analysis, and the concentrations of metals were determined by titrimetry and atomic absorption spectrometry.

The IR spectra of solid samples (as KBr pellets) were measured on a spectroscopic system based on an Infralum FT-801 instrument. The concentration of individual hydroxyl groups on the surface of SiO_2 was determined from the intensity of the absorption band at 3750 cm^{-1} in accordance with a published procedure [3].

The catalytic experiments were performed in sealed evacuated ampules with intense stirring under conditions in which the rate of reaction was independent of the rate of stirring. The reaction was performed under standard conditions: 0.02 g of a heterogeneous catalyst, 0.05 ml of octene-1, and 0.45 ml of CCl_4 at 130°C. The yields of reaction products were determined by chromatography on an LKhM 3700 instrument with a flame-ionization detector and a column with the nonpolar phase SE-30. The specific activity (turnover number per hour) was determined as the ratio of the initial rate of tetrachlorononane formation to metal concentration: $A = w_0/[M]$, h^{-1}.

EPR spectra were measured on a Varian E-3 radiospectrometer in thin-walled quartz ampules 4.0 mm in diameter at 77 K. Spin Hamiltonian parameters for VO^{2+} ions were calculated taking into account second-order corrections [4]. Diphenylpicrylhydrazyl ($g_0 = 2.0036$) and Mn^{2+} ions in an MgO matrix were used for the accurate calibration of magnetic field intensity.

The number of paramagnetic centers in a sample was determined by the double integration of spectra and a comparison of the spectra with the spectrum of a standard (a single crystal of $CuCl_2 \cdot 2H_2O$ with a known number of spins). The experimental EPR spectra were treated with the use of a PC program, which was developed and kindly provided by Professor A.Kh. Vorob'ev.

RESULTS AND DISCUSSION

Immobilized catalysts based on metal complexes with MEA are stable in air; the catalytic activity remained constant for at least a few weeks. To determine the nature of complex binding to the surface, the catalysts were studied by adsorption and spectroscopic techniques at all of the steps of the synthesis. It was found that, in accordance with published data, the treatment of silica with MEA resulted in the covalent binding of a considerable portion of modifier molecules to the surface due to the interaction of silanol groups and the hydroxyl groups of the amino alcohol with the formation of the Si–O–C bond [5]. In particular, this was evidenced by an irreversible decrease in the concentration of isolated hydroxyl groups on the surface of SiO_2. Thus, the concentration of isolated OH groups was $\sim 15 \times 10^{19}$ g^{-1} after MEA treatment. After treatment with a copper salt solution and the removal of an excess of MEA and the solvent by the evacuation of the resulting samples, the concentration of hydroxyl groups increased to $(30–70) \times 10^{19}$ g^{-1} depending on surface copper concentration.

A comparison between the surface areas of the initial and modified silica gels (300 and 120 m^2/g, respectively) demonstrated that part of the amino alcohol was accumulated in pores to produce regions with high local concentrations of MEA and to decrease the total surface area of the sample.

Previously [1], it was found by EPR spectroscopy that, at surface copper concentrations lower than 0.3 wt %, copper was entirely bound as mononuclear complexes containing from two to four nitrogen atoms in the coordination sphere. The rate of the catalytic reaction reached a maximum with catalysts containing 0.2–0.3 wt % of the metal. A further increase in the surface metal concentration did not result in the formation of new mononuclear complexes with MEA [1]. The quantitative analysis of the spectra indicated that the concentration of hydroxyl groups on the surface of SiO_2 decreases as the concentration of the metal is increased from 0.3 to 1.3 wt %. In the specified range of metal concentrations, the rate of reaction on the copper-containing catalysts decreased several times, whereas the turnover number per mole of metal (relative activity) decreased by two orders of magnitude. On this basis, it is believed that the excess metal is adsorbed as an inactive compound, for example, a hydroxy chloride, at hydroxyl rather than amino groups of the modified surface of silica. It is likely that analogous processes also occur in other metal-containing systems.

Figure 1 demonstrates data on the activity of catalysts based on Cu, Mn, Co, and VO. As in the case of previously studied copper-containing systems, the rate of catalytic reaction reached a maximum with the use of catalysts containing 0.2–0.35 wt % metal. The activity of nickel complexes was found to be low; therefore, we did not study these systems in detail. The catalysts were arranged in the following order according to activity under comparable conditions: Cu ≈ Mn > Co > Ni ≈ VO. It was of interest to analyze the factors responsible for the activity of metal ions. For this purpose, we performed a comparative analysis of the structures of copper and vanadyl complexes (the most and least active systems, respectively) and their evolution in the course of catalytic reaction. Interest in the catalytic behavior of vanadium complexes is also due to the fact that they are inhibitors for a number of radical processes, as is well known from published data [6]. The activity of vanadyl derivatives in the reactions of olefins with CCl_4 was not observed previously [7]; we were the first to detect this activity.

Figure 2 shows the EPR spectra of paramagnetic VO^{2+} complexes supported onto the surface of SiO_2 at various vanadyl concentrations in the catalysts. Figure 3

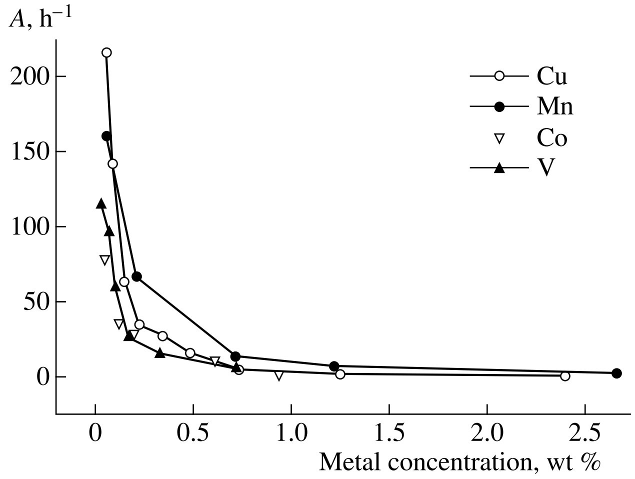

Fig. 1. Dependence of the specific activity of catalysts on the concentration of Cu, Mn, Co, or V ions supported on SiO_2.

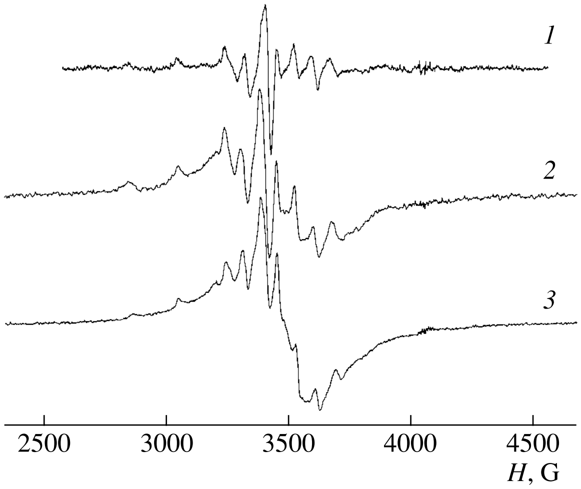

Fig. 2. EPR spectra of paramagnetic VO^{2+} complexes supported on SiO_2 at the following vanadium concentrations, wt %: (*1*) 0.07, (*2*) 0.17, and (*3*) 0.72. $T = 77$ K.

demonstrates that, at a vanadium concentration of ~0.25 wt %, the spectrum was a superposition of a multiplet signal due to VO^{2+} ions (whose contribution is ~30%) and a broad singlet characteristic of V^{4+} sites bound into "associates" by strong spin exchange interactions (whose contribution is ~70%) [8–10].

The spin-Hamiltonian parameters of isolated V^{4+} ions, which were determined with consideration for second-order corrections [4], are $g_{\parallel} = 1.950 \pm 0.005$, $g_{\perp} = 1.988 \pm 0.003$; $A_{\parallel} = 19.0 \pm 0.5$ mT, and $A_{\perp} = 6.84 \pm 0.3$ mT. These parameters are somewhat different from both published data for VO^{2+} complexes supported onto nanocrystalline SiO_2 ($g_{\parallel} = 1.931$, $g_{\perp} = 1.985$, $A_{\parallel} = 19.14$ mT, and $A_{\perp} = 7.14$ mT) [10] and values measured in the $[VO(H_2O)_5]^{2+}$ vanadyl complexes containing only water molecules in the coordination sphere ($g_{\parallel} = 1.934$, $g_{\perp} = 1.980$, $A_{\parallel} = 20.1$ mT, and $A_{\perp} = 7.3$ mT) [9–12]. We explain the difference from the values of $A_{\parallel}$ measured previously [11] by the fact that we used vanadyl chloride rather than vanadyl sulfate in this work. After the adsorption of vanadyl chloride on silica, one or two chloride ions can remain constituents of an adsorption complex.

The second possible explanation of the differences is that the nitrogen atoms of the amino groups of MEA grafted to the surface of SiO_2 can enter into the coordination sphere of VO^{2+} ions. Indeed, Larin *et al.* [13] analyzed published data [14–16] for nine metal complexes and demonstrated that, in the case of the *trans* arrangement of two N atoms in VO^{2+} complexes, the average values are $A_{\parallel}^{trans} = 18.15 \pm 0.15$ mT and $g_{\parallel}^{trans} = 1.948 \pm 0.003$, whereas $A_{\parallel}^{cis} = 17.73 \pm 0.20$ mT and $g_{\parallel}^{cis} = 1.953 \pm 0.004$ in the case of the *cis* arrangement. Differences between the value of $g_{\parallel}$ measured in this work and the above value can be due to the fact that the primary amino group of MEA is noticeably different in electron-donor properties from the Schiff's bases studied previously [13–16]. An ultimate conclusion on the composition of paramagnetic complexes of VO^{2+} immobilized on the surface of SiO_2 cannot be drawn as yet based on EPR data.

Great line widths in the EPR spectra of isolated vanadyl complexes on the surface of silica have

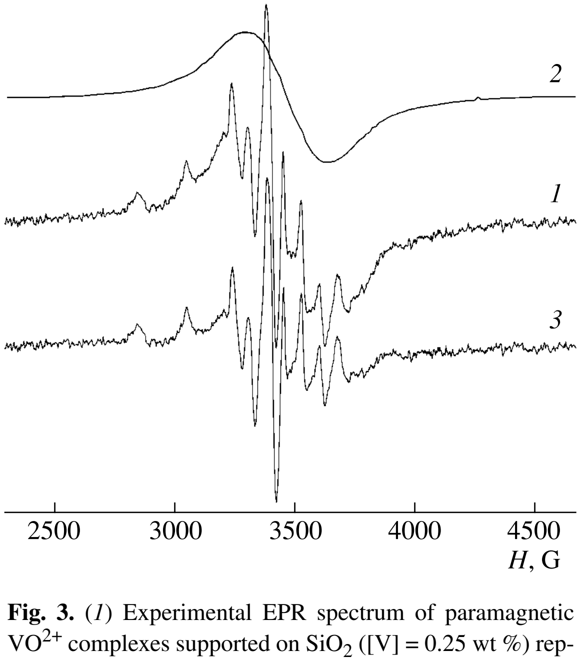

Fig. 3. (*1*) Experimental EPR spectrum of paramagnetic VO^{2+} complexes supported on SiO_2 ([V] = 0.25 wt %) represented as a superposition of (*2*) singlet and (*3*) multiplet spectra. $T = 77$ K. Spectrum *3* is obtained by subtracting spectrum *2*, which is analogous to that measured by Kokorin *et al.* [10], from spectrum *1*.

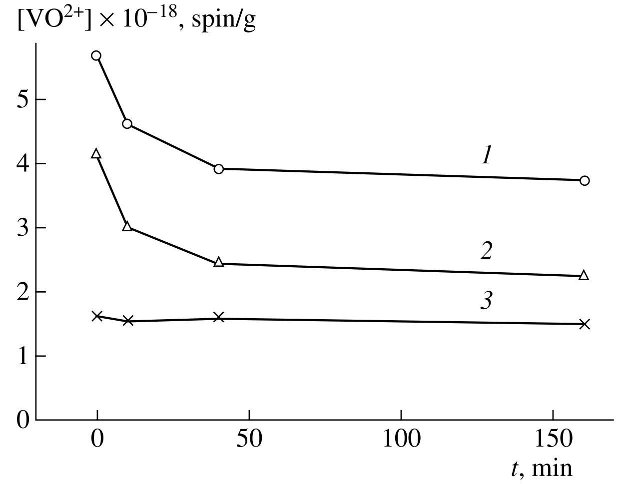

Fig. 4. (*1*) Total concentration of paramagnetic vanadyl complexes supported on SiO_2 at [V] = 0.25 wt % and the amounts of (*2*) associated and (*3*) isolated VO^{2+} ions as functions of the duration of the catalytic process at 130°C.

engaged our attention: 4–5 and ~2.5 mT for parallel and perpendicular components, respectively, of the complexes in a magnetic field. This can be due to either the presence of several types of complexes with similar EPR parameters or a comparatively high local concentration of vanadyl ions. The former cause seems more likely to us because, on the assumption of a uniform distribution, the average distance between isolated VO^{2+} ions on the support surface at the $VOCl_2$ concentrations used in this work cannot lead to a dipole–dipole line broadening of 15–25 G (1.5–2.5 mT) [16].

Vanadyl ions in associates formed on the support surface give rise to a singlet EPR spectrum (Fig. 3) with the g factor $g_0 = 1.986 \pm 0.006$ and the width $\Delta H \approx 34.5 \pm 1.0$ mT. The value of g_0, which is close to $\langle g \rangle = (g_\parallel + 2g_\perp)/3 = 1.975$, allowed us to assume that the structure and composition of paramagnetic centers in isolated VO^{2+} complexes and associates are identical or very similar. The ratio of the isolated paramagnetic complexes ($\langle VO^{2+}_{isol} \rangle$) to the associates ($\langle VO^{2+}_{assoc} \rangle$) depends on the total amount of ions adsorbed on the support. Thus, for a sample with 0.25 wt % vanadyl, $\langle VO^{2+}_{isol} \rangle / \langle VO^{2+}_{assoc} \rangle$ was equal to ~0.4, whereas less than 20% isolated and more than 80% associated VO^{2+} ions were present in a sample with a vanadium content of 0.72 wt %.

Paramagnetic vanadyl complexes, which exhibited a singlet EPR spectrum, occurred in regions with high local $\langle VO^{2+}_{assoc} \rangle$ concentrations, which can be estimated for the region of an exchange narrowing of the spectrum from the relationship [8, 9]

$$\nu_s = K_s(\langle VO^{2+}_{assoc} \rangle)^2 = 3.0 \times 10^{11}(\Delta H)^{-1}. \qquad (1)$$

Here, ν_s and K_s are the frequency and rate constant of static spin exchange in a solid, respectively; $K_s = 1.8 \times 10^8$ s^{-1} (g-ion/l)$^{-2}$ for VO^{2+} vanadyl ions in a vitrified state at 77 K; ΔH is the line width in G; and VO^{2+}_{assoc} is measured in mol/l [8]. Substituting the experimental value of ΔH into Eq. (1), we readily obtain $VO^{2+}_{assoc} \approx 2.2$ mol/l. Hence, in the case of a bulk distribution of VO^{2+} ions in the sample, the average distance $\langle d_{assoc} \rangle$ between paramagnetic ions in regions with high local concentrations is ~9.1 Å in accordance with $\langle d_{assoc} \rangle = (\langle VO^{2+}_{assoc} \rangle)^{-1/3}$.

Because the number of paramagnetic complexes in the sample (7.64×10^{18} spin/g) and the specific surface area ($S \approx 100$ m^2/g) are known, the average distance $\langle r \rangle$ between VO^{2+} ions on the support surface can be easily calculated. This distance is ≈3.6 nm, which is much greater than the value of $\langle d_{assoc} \rangle$ in regions with high local concentrations of VO^{2+}. Thus, paramagnetic vanadyl ions occurred as both isolated mononuclear complexes homogeneously distributed over the surface and closely spaced associated complexes in the catalyst.

In the course of the catalytic reaction, the EPR spectrum underwent changes due to a decrease in the total concentration of paramagnetic vanadyl complexes supported onto SiO_2 (Fig. 4). The amount of associated vanadyl ions was approximately halved, whereas the amount of isolated ions remained approximately constant in the course of the catalytic process. In this case, the EPR spectrum of isolated vanadyl complexes remained unchanged within the limits of measurement accuracy. These results are essentially different from the data obtained previously in our study on the evolution of Cu-containing systems. First, note that the number of paramagnetic V^{4+} ions was no higher than 60% of the total metal concentration even in samples with a minimum amount of vanadium ions. Consequently, the remainder of the metal occurred in another oxidation state of 5+ or 3+. The test catalytic reaction can occur because of V^{4+}–V^{3+} or V^{5+}–V^{4+} transitions. In any case, we would observe a detectable change in the concentration of VO^{2+} in the course of catalytic reaction. For comparison, note that the almost complete reduction of Cu^{2+} was observed at the initial step of the reaction in the case of copper-containing samples [1].

As follows from Fig. 5, the heating of a copper-containing catalyst in a reaction mixture resulted in a decrease in the EPR signal and then in the complete disappearance even at the early step of the reaction. After the completion of the reaction and the removal of the catalyst into air, the EPR spectrum appeared once again. However, a considerable change in the shape of the signal was observed for a spent Cu-containing catalyst; this change suggests a considerable rearrangement of the coordination sphere of the copper(II) ion. As found previously [1], the ligand (MEA) underwent decomposition under these conditions. As mentioned above, the shape of the spectra of vanadyl-containing catalysts under analogous conditions remained almost unchanged. This fact is indicative of an extremely high stability of isolated vanadyl complexes in the course of a catalytic process. This allowed us to assume that the above species do not participate in the reaction. Indeed, two processes should occur in turn for the formation of an active catalyst species and the subsequent catalytic reaction in the system: the reduction of the metal ion under the action of ligand molecules and the oxidation of the metal with carbon tetrachloride. The high rate of the above processes, as was the case in the presence of copper-containing catalysts, was responsible for the high activity of the catalyst. In the case of vanadyl-containing systems, no detectable structural changes, which are indicative of ligand decomposition, were observed in the metal complex. The change in the concentration of VO^{2+} was smaller than 30% of the total vanadyl content of the sample (Fig. 4). Thus, it is our opinion that the high stability of vanadyl-containing complexes under reaction conditions is responsible for the low activity of the test heterogeneous catalysts. We believe that the capacity of transition metals to rapidly change their valence under the action of reaction mixture components is also a criterion of activity for the other metal complexes tested. As a first approximation, the redox potentials of corresponding ions can serve as a quantitative characteristic. In this case, of course, it should be taken into account that the value of this potential significantly depends on the coordination environment of the metal. An increase in the number of nitrogen-containing functional groups in the coordination sphere of the metal results in an increase in electron density on the ion; in this case, electron transfer occurs more readily. These relations have been thoroughly studied using ion-exchanger catalysts for the oxidation of sulfur-containing compounds as an example [17].

As applied to reactions with the participation of CCl_4, we observed similar behaviors in a study of the catalytic activity of polymetalorganosiloxanes with linear and framework structures immobilized on the surface of silica [18]. We studied the evolution of linear and frame systems in the course of thermal treatment using siloxanes containing Cu(II) and organic substituents at the Si atom as an example. We found that the reduction of copper with a smaller number of oxygen atoms in the coordination environment occurred much more easily in linear siloxanes than in frame analogs. The higher thermal stability of the latter compounds correlates with their low catalytic activity in the test reaction.

Thus, the nature and concentration of a transition metal on the surface of silica modified with the amino alcohol play a key role in the formation of catalytic systems active in the addition of CCl_4 to a multiple bond. In this case, manganese- and copper-based catalysts containing 0.1–0.2 wt % metal on the surface exhibited maximum activities.

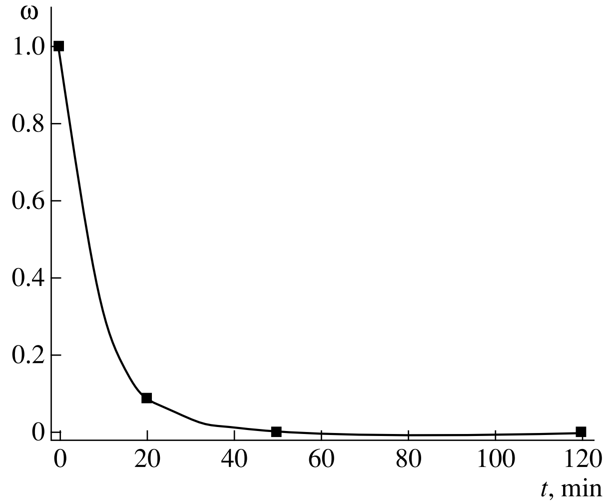

Fig. 5. Concentration of paramagnetic copper complexes supported on SiO_2 at [Cu] = 0.3 wt % as a function of the duration of a catalytic process at 130°C. ω is the fraction of paramagnetic complexes with reference to the total metal content.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 03-03-32863). The spectroscopic system used in this study was constructed within the framework of a program of the Ministry of Industry and Sciences of the Russian Federation for improving the instrumental facilities of scientific institutions. We are grateful to E.V. Vlasenko and N.A. Zubareva (both of Moscow State University) for their assistance in the determination of the surface areas of samples and in the measurement and processing of IR spectra, respectively.

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