III INTERNATIONAL CONFERENCE
"CATALYSIS: FUNDAMENTALS AND APPLICATIONS"

Influence of the Nuclearity of Copper(II) Chloride Complexes on Their Activity in Catalytic C–Cl Bond Metathesis

E. N. Golubeva[a], V. I. Pergushov[a], A. I. Kokorin[b], D. I. Kochubey[c], V. V. Kriventsov[c], and N. A. Zubareva[a]

[a] Faculty of Chemistry, Moscow State University, Moscow, 119992 Russia
[b] Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia
[c] Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
e-mail: legol@mail.ru
Received February 6, 2008

Abstract—Catalytic systems containing mainly mononuclear ($CuCl_4^{2-}$) or dinuclear ($Cu_2Cl_6^{2-}$) tributylbenzyl-ammonium chlorocuprates are prepared by adsorption on silica surfaces of different structures (Aerosil and Silokhrom). Using ESR, XANES, and electronic spectroscopy, the $CuCl_4^{2-}$ ions are shown to be reduced rapidly under conditions of C–Cl bond metathesis, whereas the dinuclear chlorocuprates are relatively stable. A correlation between the number of copper ions in the chlorocuprate anion and its catalytic activity is established: the mononuclear complexes are several times more active than their dinuclear counterparts.

DOI: 10.1134/S0023158408050194
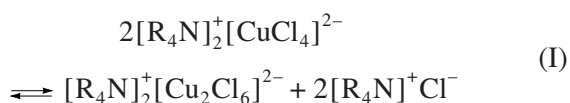
INTRODUCTION

Copper complexes of various compositions are catalysts for many halohydrocarbon transformations, for example, addition to a multiple bond [1], the metathesis of the carbon–halogen bond [2], and alkyl halide isomerization [3]. These reactions are generally characterized by an extreme dependence of their rate on the metal ion content [4–6] and on the ratio of the components in the catalytic mixture [3, 4, 7] and by the existence of an induction period [7–10]. This is evidence that catalysis by the copper complexes has a complicated, multistep mechanism and that there may be a considerable difference between the catalytic activities of catalysts similar in composition and structure. For instance, the existence of an induction period usually indicates the formation of an active site directly involved in the catalytic cycle from the catalyst precursor. The duration of the induction period is determined by the rate of this process. If the active site is rapidly formed under catalytic reaction conditions, then no induction period will be observed in the kinetic curves.

A maximum in the reaction rate as a function of the total metal content under fixed conditions, primarily the concentrations of the ligands and reactants, was observed for heterogeneous [5, 6] and homogeneous [4] catalytic radical reactions of halohydrocarbons, such as C–Cl bond metathesis and CCl_4 addition to a multiple bond. The possible causes of this extreme dependence arising from variations in the metal ion-to-ligand concentration ratio ([M]/[L]) are the following: (1) change in the coordination number of the central ion, (2) change in the ratio between the ligand molecules and the other possible complexing agents (solvent and reactants) in the coordination sphere of the metal ion, and (3) change in the nuclearity of the complex.

It was believed previously that a decrease in the activity of the catalytic system with an increase in the [M]/[L] ratio is primarily due to the third factor, i.e., the increase in the proportion of high-nuclearity complexes, which are less active than their mononuclear counterparts [4, 5, 11]. However, no reliable proof was obtained for this hypothesis.

In this work, we attempted to establish a correlation between the number of copper ions in the complex and its catalytic activity using, as an example, C–Cl bond metathesis catalyzed by tributylbenzylammonium chlorocuprates(II) of different nuclearities, namely, $[(C_4H_9)_3N^+CH_2C_6H_5]_2[CuCl_4]^{2-}$ and $[(C_4H_9)_3N^+CH_2C_6H_5]_2[Cu_2Cl_6]^{2-}$ (hereafter, $[R_4N^+]_2[CuCl_4]^{2-}$ and $[R_4N^+]_2[Cu_2Cl_6]^{2-}$, respectively) immobilized on the silica surface. This catalytic system was chosen for the following reasons. Firstly, the coordination number of chlorocuprates is always four, regardless of the [M]/[L] ratio [12]. Secondly, there is no chemical or coordinative interaction of the components of the system (carbon tetrachloride, n-alkanes, and the hydroxyl groups of the Silokhrom surface) with the copper(II) ion [13, 14]. In addition, we believe that the immobilization of the complexes on the support should retard the establishment of equilibrium [15, 16]

$$2[R_4N]_2^+[CuCl_4]^{2-}$$

$$\rightleftharpoons [R_4N]_2^+[Cu_2Cl_6]^{2-} + 2[R_4N]^+Cl^- \qquad (I)$$

in the solution, resulting in the domination of the mononuclear or dinuclear chlorocuprate species. This would reveal the difference between their reactivities.

EXPERIMENTAL

Carbon tetrachloride (high-purity grade) was purified by distillation from P_2O_5, and *n*-decane (high-purity grade) was distilled from sodium metal. The purity of organic substances was checked by GLC. The purity of CCl_4 was 99.9%, and the purity of *n*-decane was ~98% (2% is accounted for by the skeletal isomers of decane). The chemicals were stored in an argon atmosphere over molecular sieve 4 Å.

Anhydrous copper(II) chloride was prepared from the crystalline hydrate $CuCl_2 \cdot 2H_2O$ by azeotropic distillation with benzene [17]. Tributylbenzylammonium chloride $(C_4H_9)_3N^+CH_2C_6H_5 \cdot Cl^-$ $(R_4N^+Cl^-)$ was synthesized from equimolar amounts of tributylamine and benzyl chloride by heating them in a sealed tube at 268 K for 24 h [18]. The resulting colorless crystals were washed with benzene and dried in vacuo. Silokhrom, which is a mesoporous silica support with a uniform pore size distribution (mean pore diameter of about 10 nm), a specific surface area of ~100 m²/g, and an average pore size of ~0.4 mm, was heated to 150°C within 5 h under reduced pressure (10^{-3} Torr) to remove the adsorbed water. Aerosil (nonporous silica support with a specific surface area of ~140 m²/g and a particle diameter of ~10 nm) was dehydrated by the same method. Dry substances were stored in airtight glassware in vacuo.

The diffuse reflectance spectra of the supported chloride complexes in the wavelength range from 400 to 700 nm were recorded on an SF-14 spectrophotometer.

ESR spectra were recorded on an E-3 *X*-band radio spectrometer (Varian) at 77 K. The *g* factor scale was calibrated against a dilute solid solution of Mn^{2+} ions in MgO (according to VNIIFTRI data, the effective values of the *g* factors of the third and fourth components and the splitting between them are $g_3 = 2.0328 \pm 0.0002$, $g_4 = 1.9812 \pm 0.0002$, and $\Delta H_{3-4} = 86.76 \pm 0.05$ G, respectively) and a solution of copper(II) nitrate (10^{-3} M) in the glassy matrix $CD_3OD : D_2O = 50$ at 77 K ($g_\parallel = 2.424 \pm 0.005$, $g_\perp = 2.092 \pm 0.005$, $A_\parallel = 117 \pm 3$ G [19]). The number of paramagnetic centers in the samples was determined by a comparative method using a $CuCl_2 \cdot 2H_2O$ single crystal as a standard. The relative accuracy of the determination of the number of Cu^{2+} paramagnetic ions in the sample was ±10%.

The Cu *K*-edge XANES spectra were recorded at the EXAFS Station of the Siberian Center of Synchrotron Radiation. A VEPP-3 electron booster with an electron beam energy of 2 GeV and a current of 70–90 mA was used as the radiation source. The X-ray radiation energy was controlled using a Si(111) monochromator. XANES spectra were recorded with ~0.2 eV energy increments using a special-purpose cell in the transmission and fluorescence modes in an inert atmosphere.

The copper(II) chloride complexes were immobilized on the silica supports as follows. Copper(II) dichloride (0.036 g) and $R_4N^+Cl^-$ (0.315 g) were dissolved in chloroform (30 ml). The support (Aerosil or Silokhrom, 20 ml) was added to a solution containing $CuCl_2$ and $R_4N^+Cl^-$ (8.9×10^{-3} and 3.37×10^{-2} mol/l, respectively; $[Cl^-]_\Sigma : [Cu(II)]_\Sigma = 5.8$), and the mixture was stirred for 1 h and was left to stand for 24 h. Next, the support with the adsorbate was separated from the solution by filtration and was dried in an inert atmosphere. The copper content of the catalyst supported on Aerosil and Silokhrom was determined by the titrimetric method [2] to be 0.42 and 0.74 wt %, respectively.

In order to carry out the metathesis of the C–Cl bond and obtain the corresponding kinetic profiles, a heterogeneous catalyst (silica-supported quaternary ammonium chlorocuprate, 0.1 g) and a mixture of the reactants (CCl_4 : *n*-decane = 1 : 10) were loaded into a glass tube and the tube was sealed and heated to a preset temperature. The samples were predegassed by multiple cycles consisting of freezing to 77 K, pumping to 10^{-3} Torr, and thawing at room temperature. As was found earlier [20], these experimental conditions ensure that the reaction is kinetically controlled. One hour after the beginning of the reaction, the tubes were unsealed in a chamber filled with dry argon and were placed in cells for spectral measurements and XANES analysis. ESR spectra were recorded in the absence of the reactants in sealed ESR tubes placed in a thermostat (temperature control accuracy of ±1 K) at 423–448 K. At certain intervals, the tubes were cooled to 77 K and placed in the ESR spectrometer.

The starting liquid substances and reaction solutions were analyzed on an LKhM chromatograph (model 3700) equipped with a flame-ionization detector. The components of the mixture were quantified versus the total amount of all stoichiometrically related components.

RESULTS AND DISCUSSION

Structure of the Chlorocuprates on the Silica Surface

In order to determine the composition and structure of supported tributylbenzylammonium chlorocuprates, the copper(II) chloride complexes on supports with the same chemical composition but different surface structures and porosities (nonporous Aerosil and mesoporous Silokhrom) were studied by electronic spectroscopy, ESR, and XANES.

The diffuse reflectance spectra of the supported tributulbenzylammonium chlorocuprates are shown in
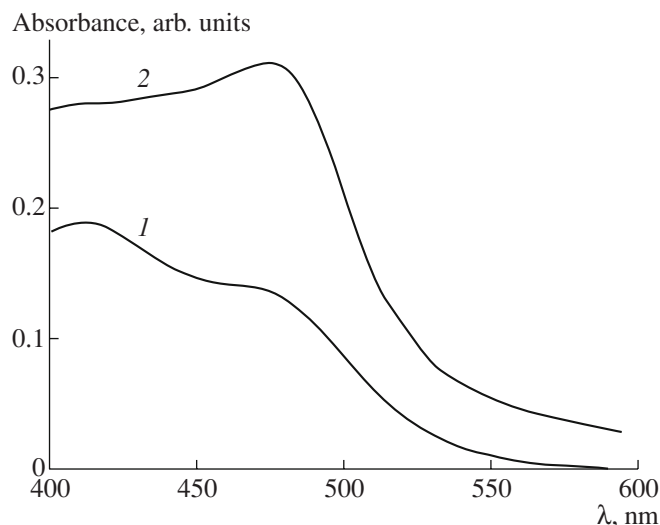
Absorbance, arb. units

Fig. 1. Diffuse reflectance spectra of tributylbenzylammonium chlorocuprates supported on (*1*) Aerosil and (*2*) Silokhrom.

Fig. 2. ESR spectra of the chlorocuprates recorded at 77 K: (*1*) Aerosil surface (sample weight of 0.013 g) and (*2*) Silokhrom surface (sample weight of 0.022 g). Spectrum *3* was obtained by the subtraction of spectrum *1* from spectrum *2*.

Fig. 1. In these spectra, one can distinguish two absorption bands with maxima at 410 and 480 nm, which are due to $n \longrightarrow d$ transitions in the $CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$ anions, respectively [12, 15, 16]. A comparison between the band intensities shows that mononuclear-to-dinuclear chlorocuprate ratios on the two different silica supports are different: the mononuclear chlorocuprate $[R_4N]_2^+[CuCl_4]^{2-}$ dominates on Aerosil (Fig. 1, curve *1*), while Silokhrom is dominated by the dinuclear complex $[R_4N]_2^+[Cu_2Cl_6]^{2-}$ (Fig. 1, curve *2*). The absence of absorption at 600–700 nm, which is typical of $d \longrightarrow d$ transitions in copper complexes with oxygen- and nitrogen-containing ligands [21, 22], is evidence that the silanol groups on the silica surface do not enter the first coordination sphere of the Cu(II) ions.

The ESR spectra of the supported tributylbenzylammonium chlorocuprates are shown in Fig. 2. The spectrum of the complexes on the Aerosil surface (Fig. 2, curve *1*) is characterized by an axially anisotropic *g* tensor, whose components have effective values of $g_\parallel^{eff} = 2.43 \pm 0.01$ and $g_\perp^{eff} = 2.076 \pm 0.005$, and by an unresolved hyperfine structure (HFS) in the region of $g_\parallel$. The ESR spectra of Cu(II) complexes containing chloride anions and oxygen atoms of water hydroxyl groups in their first coordination sphere show a well-resolved HFS in the $g_\parallel$ region [23–25]. Therefore, the absence of an HFS in the spectra presented in Fig. 2 suggests that the oxygen atoms of the silanol groups do not enter the first coordination sphere of the copper(II) ions. In addition, curve *1* in Fig. 2 is similar to the spectrum of the tetrachlorocuprate anion, which, in weakly polar media, is a tetragonally distorted tetrahedron with D_{2d}
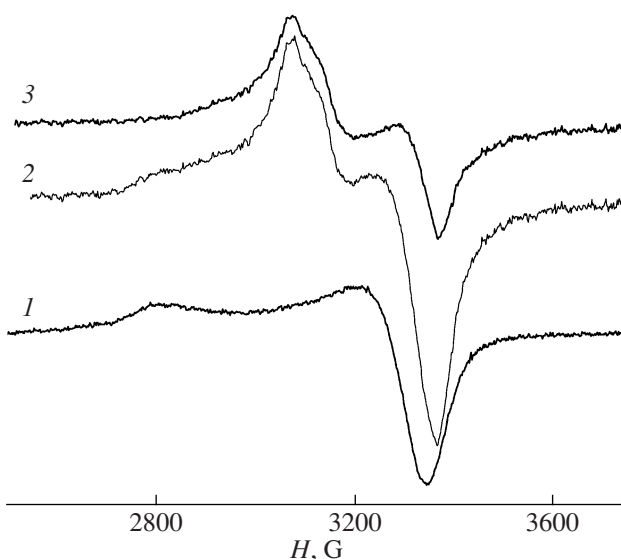
symmetry [15]. The fraction of Cu(II) ions detectable by ESR is about 85% of their total amount. It was shown earlier that the dinuclear chloride complex $Cu_2Cl_6^{2-}$ in similar systems is undetectable by ESR [15]. Thus, the results obtained by ESR agree with the electronic spectroscopy data. They indicate that the dominant copper species stabilized on the Aerosil surface is the mononuclear copper(II) chloride complex $CuCl_4^{2-}$.

Conversely, the complexes adsorbed on Silokhrom contain about 60% Cu(II) ions undetectable by ESR. We believe that these ions are present as the dinuclear chlorocuprate $Cu_2Cl_6^{2-}$. This does not contradict the diffuse reflectance data. Spectrum *2* in Fig. 2, which is due to the copper(II) complexes on Silokhrom, is likely a superposition of two spectra: one of them is similar to the spectrum of the $CuCl_4^{2-}$ complex (point group D_{2d}) stabilized on Aerosil, and the other (spectrum *3*), characterized by the triaxial anisotropy of the *g* tensor, can be obtained by the subtraction of the spectrum of $CuCl_4^{2-}$ (Fig. 2, curve *1*) from the initial spectrum. The components of the *g* tensor of the difference spectrum have the following values: $g_1 = 2.244 \pm 0.005$, $g_2 = 2.183 \pm 0.005$, and $g_3 = 2.024 \pm 0.005$. Presumably, this signal can arise from the $CuCl_4^{2-}$ anion with a lower symmetry of the coordination environment.

Independent information on the coordination symmetry and oxidation state of the metal complexes was obtained by the XANES method [26, 27]. The Cu
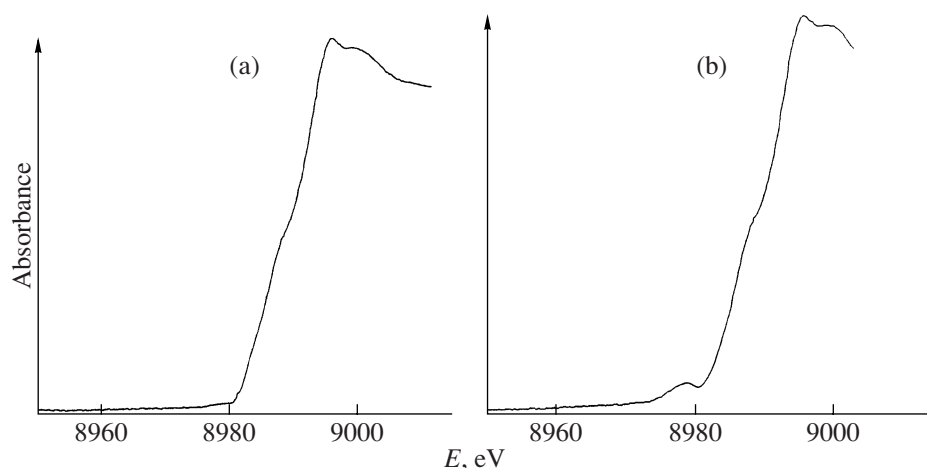
Fig. 3. The Cu *K*-edge XANES spectra of the chlorocuprates adsorbed on (a) Aerosil and (b) Silokhrom.

K-edge XANES spectra of the supported chlorocuprates are shown in Fig. 3. They are similar to the spectra of crystalline chlorocuprates [28, 29] and characterized by intense absorption due to the dipole-allowed transition $1s \longrightarrow 4p$ in the copper(II) ion and by a low-intensity band at 8975–8980 eV corresponding to the forbidden transition $1s \longrightarrow 3d$. The absence of an intense signal with a maximum at ~8984 eV due to the $1s \longrightarrow 4p$ transition in the Cu(I) compounds [5, 30] indicates that almost all copper ions in the starting samples are divalent. The higher intensity of the $1s \longrightarrow 3d$ forbidden transition at 8980 eV in the complexes supported on Silokhrom indicates a considerable distortion of the $CuCl_4^{2-}$ anion [28], which is in agreement with the ESR data.

Thus, our results show that the Aerosil surface is dominated by the mononuclear chlorocuprate $[R_4N]_2^+ [CuCl_4]^{2-}$, whereas the Silokhrom surface is dominated by the dinuclear complex $[R_4N]_2^+ [Cu_2Cl_6]^{2-}$. In both cases, the hydroxyl groups of the silica surface are not included in the first coordination sphere of copper.

The different behaviors of the supports of the same chemical composition are likely due to the difference between the structures of their surfaces. Equilibrium is rapidly established on the nonporous Aerosil particles upon the adsorption of the chlorocuprates from the solution. At the same time, the Silokhrom surface is a system of branched pores from which the mother liquor cannot be removed by filtration, and, hence, the chlorocuprates are adsorbed only with gradual solvent evaporation, which can shift equilibrium (I).

Reactivity and Catalytic Activity of the Chlorocuprates Immobilized on the Silica Supports

As was stated above, the chlorocuprates can serve as catalysts of C–Cl bond metathesis, for example,

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

This reaction is a multistep chain radical process including several catalytic redox steps [4, 5, 31]. When the initial catalyst is a copper(II) complex, another step appears, specifically, the reduction of the metal ions under the reaction conditions [4, 5, 31]:

$$Cu(II) + Red \longrightarrow \{Cu(I)\}, \quad (III)$$

where Red is the reducing agent. The reactants, ligand, counterion, or other components of the catalytic system can act as reducing agents, and the rate of this step determines the duration of the induction period.

It was demonstrated earlier that the Cu(II) ions are reduced rapidly (within 5–10 min) to Cu(I) under the conditions of catalytic C–Cl bond metathesis ($T = 433$–453 K) in solutions of tributylbenzylammonium chlorocuprates in chloroform. This reduction also occurs in the absence of the substrates, namely, *n*-decane and carbon tetrachloride [5]. It was assumed, but not proved, that the counterion is the reducing agent.

For this reason, we studied the heat-induced transformations of the quaternary ammonium chlorocuprates stabilized on the silica surface without other reagents. The heating of the tributylbenzylammonium chlorocuprates supported on the Aerosil surface to 423 K results in the disappearance of the $n \longrightarrow d$ transition band in the electronic spectrum accompanied by a visually observable decrease in the intensity of the sample color. The intensity of the ESR signal decreases simultaneously (Fig. 4, curve *1*). As the tributylbenzylammonium chlorocuprates supported on Silokhrom were heated, the ESR signal from the tetrachlorocuprates also weakened (Fig. 4, curve *2*). However, the color of the sample and its intensity remained almost
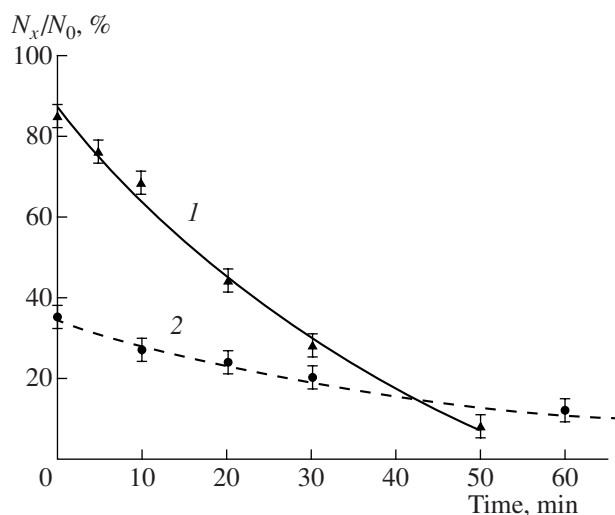
Fig. 4. Time evolution of the fraction of the Cu(II) ions detectable by ESR in the chlorocuprates supported on (*1*) Aerosil and (*2*) Silokhrom; $T = 423$ K.

Fig. 5. Kinetics of chlorodecane accumulation in the presence of the chlorocuprates supported on (*1–3*) Aerosil and (*4*) Silokhrom; $T = (I)$ 448, (*2*) 438, (*3*) 428, and (*4*) 438 K; $[CCl_4]_0 = 0.49$ mol/l; $[C_{10}H_{22}]_0 = 4.9$ mol/l.

unchanged and the band at 480 nm, which is due to the dinuclear chlorocuprate $[R_4N]_2^+ [Cu_2Cl_6]^{2-}$ remained in the electronic spectrum. The XANES spectra also remained almost unchanged. Therefore, the paramagnetic mononuclear tetrachlorocuprate is reduced on the silica surface upon heating, whereas the diamagnetic dinuclear complex is almost irreducible under these conditions.

The accumulation curves of the product of C–Cl bond metathesis (chlorodecane) in the presence of the tributylbenzylammonium chlorocuprates supported on Aerosil and Silokhrom are presented in Fig. 5. All of them indicate an induction period. In our opinion, this is due to the reduction of the Cu(II) complexes under the reaction conditions and the formation of catalytically active and sterically unhindered Cu(I) complexes on the Aerosil surface.

The chlorocuprates on the Silokhrom surface are stabilized mainly in dimeric form and are almost irreducible under the reaction conditions. In our opinion, this is the cause of the low rate of the catalytic process. In addition, the lower catalytic activity of the mononuclear copper complex on Silokhrom as compared to the similar complex on the Aerosil surface can be due to the steric screening of the active sites by other species, for example, the $Cu_2Cl_6^{2-}$ anion.

Thus, the nuclearity of the copper(II) complexes at the stage of their reduction and active site formation is the most important factor determining the reactivity of the chlorocuprates: the mononuclear tetrachlorocuprate $CuCl_4^{2-}$ is several times more reactive than the $Cu_2Cl_6^{2-}$ anion. A similar situation was observed in the similar reduction of the Cu(II) monoacetaes and diacetates by organic radicals: the rates of the process involving the
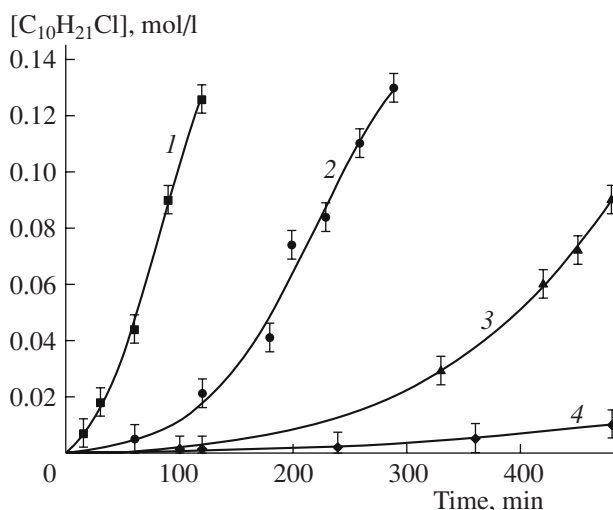
mononuclear and dinuclear complexes differed by more than five orders of magnitude [32]. The results of this work additionally confirm that the redox properties of the copper complexes depend on their nuclearity.

ACKNOWLEDGMENTS

REFERENCES

1. Asscher, M. and Vofsi, D., *J. Chem. Soc.*, 1968, p. 947.
2. Golubeva, E.N., Kokorin, A.I., Zubareva, N.A., et al., *J. Mol. Catal. A: Chem.*, 1999, vol. 146, p. 343.
3. Rostovshchikova, T.N., Kokorin, A.I., Smirnov, V.V., and Pergushov, V.I., *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 6, p. 1395.
4. Kharitonov, D.N., Golubeva, E.N., Pergushov, V.I., et al., *Kinet. Katal.*, 2001, vol. 42, no. 5, p. 741 [*Kinet. Catal. (Engl. Transl.), vol. 42, no. 5, p. 673*].
5. Kharitonov, D.N., *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Moscow: Moscow State Univ., 2003.
6. Smirnov, V.V., Tarkhanova, I.G., Kokorin, A.I., et al., *Kinet. Katal.*, 2005, vol. 46, no. 1, p. 80 [*Kinet. Catal. (Engl. Transl.), vol. 46, no. 1, p. 72*].
7. Rostovshchikova, T.N. and Pergushov, V.I., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 1, p. 12.
8. Rostovshchikova, T.N. and Pergushov, V.I., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 6, p. 985.
9. Tarkhanova, I.G., Smirnov, V.V., and Rostovshchikova, T.N., *Kinet. Katal.*, 2001, vol. 42, no. 2, p. 216 [*Kinet. Catal. (Engl. Transl.), vol. 42, no. 2, p. 193*].
10. Golubeva, E.N., Nevskaya, S.M., Vorontsov, V.V., and Abdrashitov, Ya.M., *Izv. Akad. Nauk, Ser. Khim.*, 1997, no. 10, p. 1835.

11. Golubeva, E.N., Kokorin, A.I., and Smirnov, V.V., *Kinet. Katal.*, 1998, vol. 39, no. 6, p. 908 [*Kinet. Catal.* (Engl. Transl.), vol. 39, no. 6, p. 834].

12. Smith, D.W., *Coord. Chem. Rev.*, 1976, vol. 21, p. 93.

13. *Comprehensive Coordination Chemistry*, Wilkinson, G., Ed., Oxford: Pergamon, 1987.

14. Golubeva, E.N. and Zubareva, N.A., *Kinet. Katal.*, 2004, vol. 45, no. 6, p. 917 [*Kinet. Catal.* (Engl. Transl.), vol. 45, no. 6, p. 867].

15. Golubeva, E.N., Kokorin, A.I., Kochubei, D.I., et al., *Kinet. Katal.*, 2002, vol. 43, no. 3, p. 440 [*Kinet. Catal.* (Engl. Transl.), vol. 43, no. 3, p. 408].

16. Kharitonov, D.N. and Golubeva, E.N., *Kinet. Katal.*, 2003, vol. 44, no. 4, p. 563 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 4, p. 513].

17. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemicals), Moscow: Khimiya, 1974.

18. Zelikman, V.M. and Smirnov, V.V., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 10, p. 1672.

19. Kokorin, A.I., Vengerova, N.A., Kirsh, Yu.E., and Zamaraev, K.I., *Dokl. Akad. Nauk SSSR*, 1972, vol. 102, no. 3, p. 597.

20. Smirnov, V.V., Levitskii, M.M., Nevskaya, S.M., and Golubeva, E.N., *Kinet. Katal.*, 1999, vol. 40, no. 1, p. 86 [*Kinet. Catal.* (Engl. Transl.), vol. 40, no. 1, p. 76].

21. Zamaraev, K.I., Nizel'skii, Yu.N., Lipatova, T.E., et al., *Teor. Eksp. Khim.*, 1971, vol. 7, no. 5, p. 776.

22. Lever, A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1984.

23. Larin, G.M., Minin, V.V., Levin, B.V., and Buslaev, Yu.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, no. 6, p. 1223.

24. Plyusnin, V.F. and Usov, O.M., *Zh. Obshch. Khim.*, 1985, vol. 55, no. 7, p. 1455.

25. Larin, G.M., Minin, V.V., Levin, B.V., and Buslaev, Yu.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, no. 12, p. 2725.

26. Penner-Hahn, J.E., *Coord. Chem. Rev.*, 1999, vols. 190–192, p. 1101.

27. Kochubei, D.I., *EXAFS-spektroskopiya katalizatorov* (EXAFS Spectroscopy of Catalysts), Novosibirsk: Nauka, 1992.

28. Sano, M., Komorita, S., and Yamatera, H., *Inorg. Chem.*, 1992, vol. 31, no. 3, p. 459.

29. Pickering, I.J. and George, G.N., *Inorg. Chem.*, 1995, vol. 34, no. 12, p. 3142.

30. Guerreiro, E.D., Gorriz, O.F., Rivarola, J.B., and Arrua, L.A., *Appl. Catal., A*, 1997, vol. 165, p. 259.

31. Smirnov, V.V. and Golubeva, E.N., *J. Mol. Catal.*, 2000, vol. 158, p. 487.

32. Kochi, J.K. and Subramanian, R.V., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 21, p. 4856.