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Addition of Carbon Tetrachloride to Olefins in the Presence of Copper Complexes with Polyfunctional Ligands Chemically Immobilized on the Surface of Silica

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Abstract—Homogeneous and heterogeneous catalysts containing copper complexes with amino alcohols and hydroxy amino acids were synthesized. Heterogenized systems were immobilized on the surface of silica by covalent bonding of the hydroxyl groups of ligands to the silanol groups of silica. The resulting complexes were active in the reactions of CCl_4 addition to multiple bonds of olefins. In the case of 1-octene, the activity of heterogeneous catalysts was an extremal function of metal concentration on the surface, whereas a symbatic relationship was observed for a chlorinated olefin (allyl chloride). The above effects were explained by the participation of different copper complexes, in particular, of different nuclearity, in reactions with different olefins.

INTRODUCTION

It is well known that surface-immobilized metal complex systems occupy an intermediate position between homogeneous and typical heterogeneous catalysts. In some cases, they combine a comparatively high activity of the former with the simple separation of catalysts from reactants characteristic of the latter [1]. The immobilization of complexes on oxide supports most often results in a decrease in activity. Therefore, the cases where immobilized metal complexes are more active than complexes of analogous composition in solution are of particular interest. In particular, such a behavior is typical of copper complexes with monoethanolamine (MEA) chemically immobilized on the surface of SiO_2. These complexes are efficient catalysts for CCl_4 conversion, including its addition at multiple bonds. Another special feature of catalysts based on the complexes of copper and MEA is an extremal relation between catalytic activity and surface metal concentration [2]. It was of interest to find whether this behavior is extended to copper complexes with other polyfunctional ligands and whether the molecular structure of an olefin correlates with the above properties of copper-containing catalysts.

In this study, the test materials were copper complexes with chelating donor ligands immobilized on the surface of silica. The following compounds were used as chelating ligands: amino alcohols (MEA and diethylaminoethanol (DEAE)) and hydroxyl amino acids (serine (2-amino-3-hydroxypropionic acid) and hydroxyproline (4-hydroxy-2-pyrrolidinecarboxylic acid)). The chemical immobilization was performed by the interaction of the hydroxyl groups of ligand molecules with surface silanol groups with the formation of the Si–O–C bond. The addition of CCl_4 to chemically different olefins (1-octene and allyl chloride) was chosen as model reactions:

$$CCl_4 + CH_2{=}CHC_6H_{13} \longrightarrow CCl_3CH_2CHClC_6H_{13}, \quad (I)$$

$$CCl_4 + CH_2{=}CHCH_2Cl$$
$$\longrightarrow CCl_3CH_2CHClCH_2Cl + CH_2{=}CHCH_2CCl_3 \quad (II)$$
$$+ \text{heavy unidentified products}$$

With the use of homogeneous reactions with the participation of the above olefins as an example, it was found previously that, in the presence of copper complexes, the composition of products and the mechanism of addition changed on going from simple alkenes to chlorinated olefins. In the case of chlorinated olefins, it is believed that polynuclear structures participate in the reaction, whereas they are likely inactive in the addition of CCl_4 to simple alkenes [3].

EXPERIMENTAL

Organic substances were purified in accordance with standard procedures. Acetonitrile of analytical grade was distilled from calcined $CaCl_2$ at 80°C. Chemically pure allyl chloride was distilled, and a fraction was taken at 45–46°C. Chemically pure CCl_4 was dried and distilled from P_2O_5. Chemically pure 1-octene was distilled from sodium metal.

Amino alcohols and amino acids from Merck were used without additional purification. Silica gel KSK (S_{sp} = 250 m^2/g) was calcined in air and then in a vacuum at 450–500°C. Modification with amino alcohols (MEA and DEAE) was performed by heating the silica gel in modifier vapor at 150–160°C for several hours. Next, the samples were evacuated to remove water liberated in the reaction; the liberated water was condensed in a trap cooled with liquid nitrogen. DEAE was also supported from toluene or xylene solutions by boiling for several hours with the continuous removal of water as an azeotropic mixture with the solvent. To support hydroxyproline and serine, the silica gel was impregnated with amino acid solutions in acetonitrile or *tert*-butanol; next, the solvent was removed in a vacuum, and the resulting samples were thermostatted at 150–180°C and then treated analogously to the samples modified with MEA.

Surface copper complexes with immobilized ligands were synthesized in an acetonitrile solution with the use of CuCl, which is readily soluble in this solvent. For varying metal concentration on the surface, 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 the catalyst was washed with acetonitrile for the removal of an excess of copper chloride unreacted with the modified support.

The concentration of organic matter in the resulting catalysts was determined by elemental analysis, and the concentration of copper was determined by titrimetry and atomic absorption spectrometry.

The solutions of metal complexes were prepared in accordance with standard procedures [4–8]. For the synthesis of complexes with MEA and serine, ethanol was used as a solvent; complexes with DEAE and hydroxyproline were prepared in acetonitrile solutions. CuCl was used as the parent copper compound. The resulting compounds were identified by IR spectroscopy after solvent removal. The samples were prepared in Vaseline oil; the spectra were measured on a spectroscopic system based on an Infralum FT-801 instrument.[1] The structure of heterogeneous catalysts was studied by EPR, UV, and IR (KBr pellets) spectroscopy. The EPR spectra were measured on a Varian E-3 X-band radiospectrometer (100-kHz high-frequency modulation) at 77 K. The treatment of the experimental EPR spectra, including the determination of the absolute concentrations of paramagnetic centers, was described in detail elsewhere [2]. The relative error in the determination of the concentration of paramagnetic Cu^{2+} ions was ~±10%. The diffuse-reflectance visible spectra were measured on an SF-14 spectrophotometer over the range 400–700 nm.[2]

The catalytic experiments were performed in sealed evacuated ampules. The samples were placed in an air thermostat equipped with a device for rotating the ampules at a variable rate with the changeable sense of rotation. The experiments were performed under conditions that provided the independence of results on the rate of rotation and changes in the sense of rotation. The activity of supported catalysts was determined from the initial rates of reactions under standard conditions: 0.02 or 0.05 g of a heterogeneous catalyst (containing from 0.05 to 4 wt % Cu) in the addition of CCl_4 to 1-octene or allyl chloride, respectively; 0.05 ml of an olefin; and 0.45 ml of CCl_4 at 130°C. The procedures used in the catalytic experiments in solutions and in the GLC analysis of products were described in detail elsewhere [3]. The samples containing soluble complexes were prepared with the above amounts of reagents, and the catalyst was added in an amount corresponding to $[Cu] = 2 \times 10^{-2}$ mol/l. The products were analyzed on a Kristall-2000M chromatograph with a flame-ionization detector and an SE-30 column.

RESULTS AND DISCUSSION

The composition of copper complexes with the above ligands isolated from solution was fully consistent with published data [4–7]. The complex of copper with DEAE has 1 : 1 composition; in complexes with other ligands (L), Cu/L = 1 : 2 (copper is divalent in these complexes; analogous complexes with Cu^+ were not described in the literature because Cu^+ is oxidized to Cu^{2+} in the presence of the above ligands). The complexes were identified based on a comparison between the IR spectra of complexes and parent amino derivatives [7, 8].

The copper complexes synthesized in solution exhibited a color characteristic of the complexes of amino derivatives. Depending on a particular ligand and synthetic conditions, this color varied from bluish green to violet. The heterogenized samples with high copper contents were also blue or bluish green. At low metal concentrations (<0.1%), the color of the samples was light yellow. The diffuse-reflectance spectra of samples with high metal contents exhibited broad bands in the region 580–680 nm. Absorbance in this region is indicative of the complexation of divalent copper with amino derivative molecules.

Surface modification by the above method allowed us to obtain silica gel containing 3–7 wt % organic matter depending on the nature of the ligand. Using silica gel samples with MEA as an example, we analyzed the surface concentration of free hydroxyl groups by IR spectroscopy (region of 3750 cm^{-1}) in the course of the catalyst synthesis. The thermally treated starting silica gel contained 3.6 mmol of OH groups per gram, whereas after the reaction with MEA (0.1 ml per gram of SiO_2) it contained 0.23 mmol of OH groups per gram. Chemisorbed amino alcohol molecules were not removed from the surface of silica gel after its treatment with a CuCl solution in acetonitrile: the concentration of hydroxyl groups in the prepared catalyst was 0.5–1 mmol of OH groups per gram. According to published data [9], in the immobilization of amino alcohol molecules on the surface of silica gel, one of the functional groups (hydroxyl) of the ligand reacts with sur-

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[2] We are grateful to Cand. Sci. (Chem.) N.A. Zubareva for her assistance in the measurement and interpretation of diffuse-reflectance spectra.

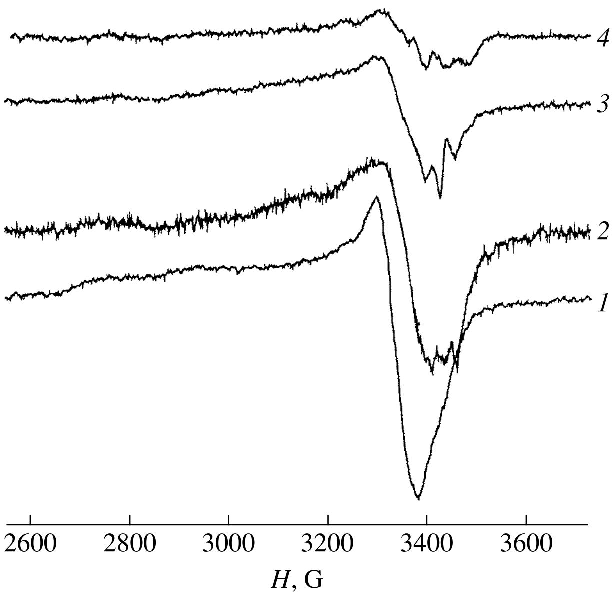

Fig. 1. EPR spectra of copper(II) complexes with diethylaminoethanol supported on SiO_2 at [Cu] = (*1*) 1.24, (*2*) 0.18, (*3*) 0.09, and (*4*) 0.06 wt %.

face hydroxyls to form the Si–O–C group, which is incapable of complexing with metal ions. As a result, the coordination of copper to amino alcohols in surface complexes primarily occurs through the amino group. In the case of amino acids, the structures and compositions of dissolved and heterogenized complexes should be similar because amino acid molecules are grafted to the surface through the hydroxyl group, which does not participate in complexation, whereas amino and carboxyl groups participate in the formation of chelate complexes [6, 7, 9]. Nevertheless, regardless of the ligand chosen, the EPR spectra and catalytic properties of individual and immobilized complexes are essentially different. This result is expected: even with the same composition of coordination environments, which is likely the case in amino acid complexes, the preimmobilization of ligands on the surface can affect the structure of the complex, as compared with the analog that occurs in solution. As a result, structures with enhanced reactivity and catalytic activity can be formed.

Yield (%) of 1,1,1,3-tetrachlorononane in the reaction of CCl_4 addition to 1-octene in the presence of homogeneous and immobilized catalysts

Catalyst	Homogeneous catalyst	Catalyst/SiO_2
Cu–monoethanolamine	56	85
Cu–diethylaminoethanol	48	64
Cu–hydroxyproline	32	51
Cu–serine	39	75

Note: 130°C; reaction time, 3 h; [Cu] = 2×10^{-2} mol/l; [CCl_4] = 9.1 mol/l; [Ol] = 0.7 mol/l.

The results of an EPR study are a good illustration of the structural difference between homogeneous and heterogenized copper complexes with DEAE. The $(CuCl \cdot DEAE)_2$ complex, either dissolved in CCl_4 or isolated as a solid from solution, does not give EPR signals, although divalent copper ions are present in this complex. It is most likely that the EPR-silent complex is binuclear with comparatively closely spaced copper ions; this is consistent with published data [5]. However, the complex prepared by the interaction of copper chloride with DEAE-modified silica gel exhibited an EPR spectrum characteristic of isolated Cu^{2+} ions (Fig. 1). A similar spectrum of the individual complex dissolved in CCl_4 was observed only on boiling the solution for a long time.

Figure 1 shows typical spectra of heterogenized complexes at various copper contents. The absence of clearly pronounced hyperfine structures from the spectra in the region of parallel components (low fields) at comparatively narrow perpendicular components of the complexes in a magnetic field (high fields) suggests the simultaneous occurrence of various structurally different complexes even at minimum copper concentrations. The fractions of various complexes changed with changes in the copper concentration on the surface. It is of interest that, unlikely the SiO_2–Cu–MEA system [2], the formation of paramagnetic associates with a high local concentration of Cu^{2+} complexes did not occur in this case. The signal amplitude indicated that, at a copper concentration of <0.1 wt %, at least 20–25% ions occurred as EPR-detectable mononuclear complexes. The fraction of copper that cannot be determined by EPR spectroscopy increased as the surface metal concentration was increased. Thus, at a total concentration of 1.24 wt %, the fraction of “diamagnetic” copper was higher than the fraction of EPR-detectable copper by a factor higher than 20.

We found that a change in the structure of complexes upon immobilization increased their catalytic activity, as compared with dissolved complexes. The table summarizes the activity of the test homogeneous and heterogenized catalysts in the addition of CCl_4 to 1-octene. As can be seen, the activity of heterogenized samples was always higher than that of homogeneous samples, all other factors being the same. For complexes with MEA and serine, this could be explained by a low solubility of the complexes in the reaction solution; however, we also observed an analogous phenomenon in DEAE and hydroxyproline complexes, whose solubility is sufficiently high. In our opinion, the above increase in the reactivity of heterogenized complexes because of structural changes in the course of formation with the participation of surface-immobilized ligands can be responsible for differences in the catalytic activity. In particular, the conversion of a portion of polynuclear complexes into mononuclear species can belong to changes of this kind. This provides additional possibilities for the coordination of substrate molecules. This possibility is of particular importance for reactants, including CCl_4, that weakly interact with metal ions.

When the reaction was performed in the presence of catalysts with different copper concentrations, the observed activity was an extremal function of metal concentration. Figures 2a and 2b show data obtained for grafted complexes with MEA and DEAE. As can be seen in Fig. 2, the position of a maximum is practically independent of the nature of the amino alcohol. Previously, we found that this dependence of the activity of heterogeneous catalysts containing copper and MEA on metal concentration can be explained by a change in the composition of active centers [2]. With the use of EPR spectroscopy, it was found that complexes containing different numbers of amino groups in the coordination sphere could predominate in the system depending on the surface concentration of the metal. Mononuclear complexes were predominant at copper concentrations lower than 0.3 wt %, whereas the metal occurred as polynuclear structures at higher concentrations. It is likely that in the case of DEAE a set of complexes with different catalytic properties was also formed. In this case, the most active species were mononuclear structures, which contain the greatest number of amino groups in the coordination sphere of the metal. A decrease in the activity of samples in the reaction of CCl_4 addition to octene with increasing metal concentration can be explained by a decrease in the fraction of mononuclear complexes. Data obtained in another reaction, the addition of CCl_4 to allyl chloride, are also in favor of this explanation.

The composition of the products of CCl_4 addition to allyl chloride in the presence of the test copper complexes was unusual. With traditional (for example, peroxide) initiation, an addition product and hexachloroethane (because of the recombination of trichloromethyl radicals) are formed in the system (this was supported by our control experiments with benzoyl peroxide as an initiator). In our case, the product composition was different and analogous to that observed previously in the presence of copper complexes with monodentate donor ligands (phosphines and thioethers). It is not typical of a traditional free-radical mechanism: an olefin containing the trichloromethyl group was formed along with the addition product [3] (see the formulas of the products at the beginning of this paper). Moreover, in this case, as follows from Fig. 2c, an increase in the surface copper content of the catalyst increased catalytic activity, as distinct from the reaction with 1-octene.

Tarkhanova *et al.* [3] found that, in catalytic reactions with the participation of chlorinated olefins in the presence of copper complexes, the formation of polynuclear copper catalyst–substrate complexes is a key step. In our case, the appearance of an unsaturated polychlorinated hydrocarbon can be explained by the reaction of allyl and CCl_3 radicals formed in the coordination spheres of two closely spaced copper ions. The formation of an addition product can also occur in both the coordination sphere of mononuclear complexes, as with 1-octene, and in a polynuclear complex due to the transfer of two chlorine atoms from copper to the $CH_2{=}CHCH_2CCl_3$ olefin:

$$[L_nCuCl]_2Cl_2 + CH_2{=}CHCH_2CCl_3 \longrightarrow [L_nCuCl]_2 + CCl_3CH_2CHClCH_2Cl. \quad (III)$$

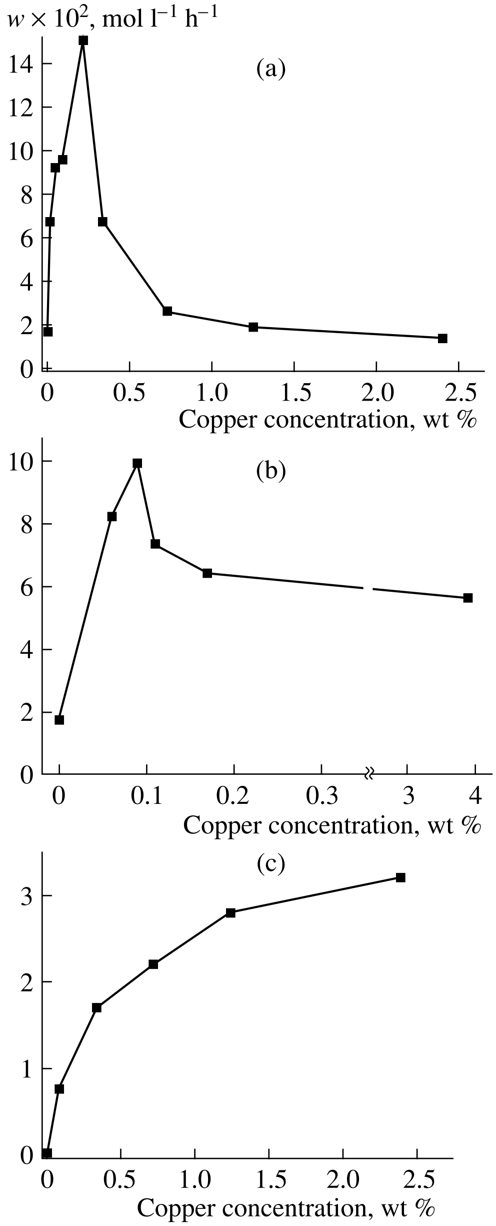

Fig. 2. Activity of catalysts in the reactions of CCl_4 addition to (a) 1-octene and (c) allyl chloride in the presence of the copper complex with monoethanolamine and (b) to 1-octene in the presence of the copper complex with diethylaminoethanol.

Samples with high copper contents, that is, those with the predominance of polynuclear complexes, exhibited the highest activity in this reaction. Therefore, we believe that the addition product is mainly formed in reaction (III).

Thus, systems active in CCl_4 reactions with olefins can be prepared using the procedure for the synthesis of heterogeneous catalysts based on polydentate ligands (amino alcohols and hydroxy amino acids) chemically immobilized on the surface of silica gel. By varying metal concentration on the surface of a modified support, we can obtain primarily mononuclear or polynuclear structures, which exhibit different catalytic properties in the reaction of CCl_4 with olefins. The activity of the resulting catalysts significantly depends on the nature of the olefin: samples with a low concentration of copper, in which mononuclear complexes are predominant, are most active in reactions with 1-octene; in the case of a chlorinated olefin, when the formation of polynuclear copper catalyst–substrate complexes is a key step of reaction, catalysts with high metal concentrations exhibit the highest activity.

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