Supported complexes of cupric chloride with DMF as catalysts in the reaction of CCl_4 with *n*-decane*

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The complex of cupric chloride with DMF immobilized on the surface of silica gel exhibits high catalytic activity in the reaction of tetrachloromethane with *n*-decane. The fact that the reaction is inhibited by phenols and oxygen implies that it occurs by a radical mechanism. The immobilized catalyst that contains copper atoms connected through chlorine bridges and organic donor ligands is the most effective.

Key words: catalysis, polynuclear copper complexes, supported catalysts; kinetics, *n*-decane, tetrachloromethane.

Polynuclear bridged complexes of copper can be regarded as functional analogs of the active sites of copper-containing enzymes.[1] These complexes are much more active as catalysts in many organic reactions including syntheses and transformations of halo-derivatives.[2] The immobilization of complexes of this type on the surface of inorganic supports makes it possible to stabilize the most active structures and to control their catalytic activities.[3] In particular, the use of heterogenized polynuclear copper complexes with amides made it possible to accomplish reaction in the CCl_4—alkane systems, which can be regarded as chlorination of alkanes with tetrachloromethane[4]

$$CH_4 + RH \longrightarrow CHCl_3 + RCl\,.$$

In the present work, we have studied the catalytic chlorination of *n*-decane with CCl_4 in the presence of copper(II) complexes with DMF supported on silica gel. Complexes of copper(II) with DMF appear to be promising homogeneous precursors of efficient catalysts, because mononuclear neutral complexes of Cu^{II} are still unknown even in pure DMF.[5] Complexes of copper(II) with pyridine are normally mononuclear; preparation of analogous polynuclear structures requires the use of more complicated procedures than those used in the case of DMF.[6] The number of Cu atoms in polynuclear complexes can vary from two to four. The formation of heterovalent associates and complexes containing O atoms also cannot be ruled out. Complexes of Cu^{II}, for example, the complex of composition $(CuCl_2)_2 \cdot (DMF)_4$, can be easily synthesized, identified, and fixed on the surface of various supports.

Experimental

Anhydrous copper(II) chloride was prepared by azeotropic drying of the corresponding crystal hydrate.[7] The complex $(CuCl_2)_2 \cdot (DMF)_4$ was synthesized by the known procedure.[8] Granulated silica gel with a specific surface area of 250 m^2 g^{-1} and an average pore radius of 50 Å containing no iron ions was used as the support. Silica gel was placed in a solution of the complex in chloroform, and the mixture was allowed to stand for 24 h. Then the granules of the catalyst (catalyst I) were exposed to air for an additional 10 h until the solvent was completely evaporated. This material contained 3 % (w/w) copper. Catalyst II was prepared by keeping catalyst I at 10^{-3} Torr and at 433 K; catalyst III was obtained by applying $CuCl_2$ on γ-aminopropyl silochrome (with a specific surface area of 35 m^2 g^{-1} and a concentration of NH_2 groups of 0.08 mmol g^{-1}); $CuCl_2$ was applied from a 5% solution in ethanol. The content of copper was 6.2%. Kinetic experiments were carried out in sealed glass ampules at a pressure ranging from 8 to 10 atm.[9] The volume of the gas phase was approximately equal to the volume of the solution. In some of the experiments oxygen was removed from the solution and from the surface of the catalyst by repeating the "freezing to 77 K—evacuation to 10^{-3} Torr—thawing to 20 °C" cycle many times. When ionol was used as the inhibitor, the ionol : copper molar ratio did not exceed 0.1, which made it possible to rule out the effect of complex formation between the catalyst and ionol on the catalytic activity. The reaction products were analyzed by GLC on 3700 and Chrom-5 chromatographs with a flame ionization detector (the length of the columns was 2.5 m, SE-30 (5%) and PEG-1000 (10%) were used as stationary phases, and Chromaton was used as the support; the temperature was programmed as follows: T_1 = 238 K (3 min), T_2 =

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393 K (10 min)). The temperature of the detector was 423 K. The reaction products were identified using reference compounds; quantitative analysis was carried out by the method of internal normalization. The sensitivity of the detector was determined with respect to CCl_4—chloroform standard mixtures with variable ratio of the components. IR spectra were recorded in the 4000—200 cm^{-1} range on Specord M80 and Specord M82 instruments for pellets with KBr and for suspensions in vaseline oil. The ESR spectra of the supported complexes were recorded on a Varian E3 spectrophotometer.

Results and Discussion

The reaction of CCl_4 with *n*-decane was carried out at 433 K; the CCl_4 : decane molar ratio was 4 : 1 and the content of catalyst I was 10 % (w/w). The major (>99%) product of transformation of CCl_4 is chloroform; traces of dichloromethane are also formed. *n*-Decane is mostly converted into secondary monochlorodecanes and 1-chlorodecane; the latter compound is formed in small quantities, not exceeding 3—5% of the overall amount of the products. When the degree of conversion is high, mixtures of isomeric dichlorodecanes and traces of hexachloroethane are also formed. The solution remains transparent even when the degree of conversion of decane is close to 70%; no significant resinification is observed, and copper complexes do not pass into the solution. The material balance was calculated from the equations

$$[C_{10}H_{22}]_0 - [C_{10}H_{22}] = \Sigma[C_{10}H_{21}Cl] + \Sigma[C_{10}H_{20}Cl_2],$$

$$[CCl_4]_0 - [CCl_4] = [CHCl_3] + \Sigma[C_{10}H_{21}Cl] + 2\ \Sigma[C_{10}H_{20}Cl_2]$$

taking into account that $[C_2Cl_6] << [CHCl_3]$ is obeyed with an accuracy of ±2% for degrees of conversion of the alkane of up to 70%.

The known previous attempts to carry out a similar reaction in the CCl_4—cumene system with thermal (500 K) or photochemical initiation have been less successful,[10] because, in addition to chloroform and products of chlorination of the side chain of cumene, the reaction yielded substantial amounts of HCl, dicumyl, and other condensation products as well as products of chlorination of the nucleus.

Figure 1, *a* shows a typical kinetic curve for the reaction. After the initial induction period, the reaction accelerates and then, at large degrees of conversion, it sharply decelerates.

The effect of the composition and structure of the catalyst can be clearly followed by juxtaposing the variation of the reaction rate with the variation of the IR spectra of the catalyst during the process. It can be seen from Fig. 2 that, in addition to the absorption bands corresponding to the support (marked by asterisks), the spectrum contains an intense compound band with a maximum at 1670 cm^{-1} associated with the stretching vibrations of the C=O bond in the DMF incorporated in the complex.[11] According to a previous publication,[11] a similar band is observed in the spectrum of the crystalline complex $(CuCl_2)_2 \cdot (DMF)_4$.

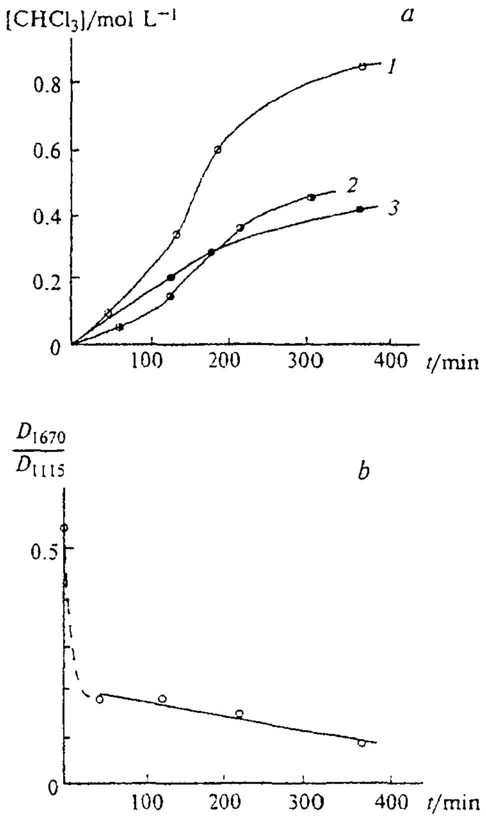

Fig. 1. *a*, Kinetic curves for the accumulation of chloroform in the decane—CCl_4 system at 433 K without additives (*1*), in the presence of 0.1% ionol (*2*), and in the presence of O_2 (*3*). *b*, Time variation of the proportion of DMF in catalyst I.

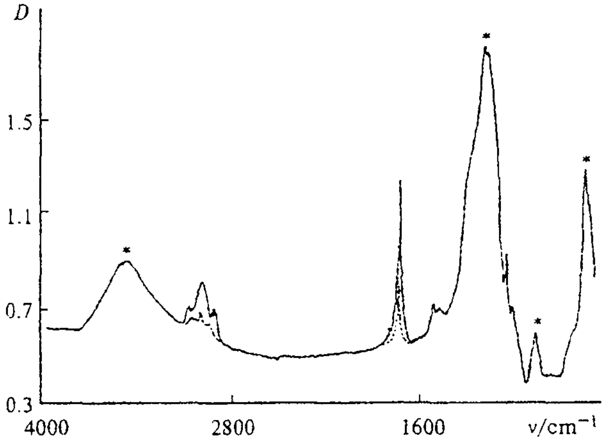

Fig. 2. IR spectra of catalyst I.

In the low-frequency region, the IR spectrum exhibits bands with maxima at 226, 270, and 290 cm^{-1}. The former two bands can be assigned to the stretching vibrations of the bridging Cu—Cl bonds, while the latter band can be attributed to the terminal Cu—Cl bond.[5] This makes it possible to believe that the binuclear unit consisting of copper atoms is not destroyed upon immobilization of the complex.

During the first minutes of the reaction, the content of DMF in the supported catalyst sharply decreases (see Figs. 1, *b* and 2). In addition to the band at 1670 cm^{-1}, absorption in the 1660—1655 cm^{-1} region, typical of $(CuCl_2)_2 \cdot (DMF)_4$ and of other bridged Cu^{II} complexes with DMF, is observed. Simultaneously, the reaction sharply accelerates. Possibly, more active new complexes including those containing copper ions in different oxidation states are formed on the surface.

Under the conditions of homogeneous catalysis by the dissolved complex of Cu^{II} with DMF, the reaction affords resins and suspensions of solid particles but virtually no chloroform or chlorodecanes. Under heterogeneous conditions, the decrease in the content of DMF and the decrease in the activity occur much more slowly.

Evidently, during the reaction, the supported catalyst forms fairly quickly an active form stabilized by the interaction with the surface. Subsequently, this active complex slowly decomposes.

The rate of the catalytic process is influenced by the addition of typical inhibitors of radical reactions, *viz.*, phenols and O_2. Figure 1, *a* shows the kinetic curves for the reaction carried out in the presence of ionol and oxygen. It can be seen that in these cases, the degree of conversion decreases approximately twofold (Table 1). In addition, in the presence of O_2, substantial amounts of high-molecular-weight colored products are formed. The selectivity of the process with respect to chloroform decreases: a mixture of dichloromethane and chloromethane is formed in 1—5% yield. These results can be explained by assuming that the reaction occurs by a radical mechanism. The copper-containing complex acts apparently as a renewable initiator of the process. Evidently, the fact that secondary products of substitution predominate among the decane derivatives formed also attests to a free-radical reaction mechanism. This assumption is also supported by the fact that minor amounts of the product of recombination of trichloromethyl radicals, *viz.*, hexachloroethane, are formed in the reaction.

Table 1. The degrees of conversion of *n*-decane in the presence of various copper-containing immobilized catalysts and additives

Catalyst	Content of Cu (% w/w)	Additive	Degree of conversion of decane (%)
I	3.0	None	51
I	3.0	0.1% ionol	26
I	3.0	O_2 atm.	29
II	3.0	None	12
III	6.2	O_2 atm.	23

Note. Reaction conditions: T = 433 K, $[CCl_4]$: [decane] = 4 : 1, 6 h.

We showed that the catalytic activity of the immobilized copper complex with DMF markedly decreases when the complex loses the ligand. Catalyst II, which was prepared by prolonged evacuation of catalyst I at 433 K and contained virtually no DMF, is substantially less active than the starting material (see Table 1). In addition, in this case, the reaction yields up to 10% chloro-derivatives of methane and HCl. Similar results were obtained when the catalyst that had already worked for six hours was repeatedly used with fresh portions of the reagents. The activity of the catalyst is restored when DMF is added to it in a twofold molar excess with respect to copper, which corresponds to the ratio of these components in the complex precursor. Thus, the presence of donor ligand molecules, for example, DMF, in the coordination sphere of the supported complex is necessary for the preparation of an active and selective catalyst.

The data on the catalytic activity of a mononuclear catalyst, *viz.*, a complex of copper(II) chloride with γ-aminopropyl silochrome (catalyst III), are listed in Table1. In this case, the specific (with respect to copper) activity of the catalyst proved to be somewhat lower. Among other reasons, this can be due to the fact that effective catalysis requires that several Cu atoms bound through bridge atoms interact within one binuclear or polynuclear unit.

Thus, to obtain an active and selective copper catalyst, the following conditions should be fulfilled: the presence of bi- or polynuclear unit of Cu atoms, the presence of a donor ligand, and immobilization of the catalyst on the surface of the support, needed to stabilize complexes that are unstable in solution.

The possibility to convert CCl_4 relatively quickly and highly selectively into industrially valuable products opens up new prospects for solving the problem of its utilization, which appeared after the Montreal convention on the protection of the ozone layer was signed.

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