Copper (II) chloride–dmf catalytic system in solution and on silica

E.N. Golubeva [a,*], A.I. Kokorin [b], N.A. Zubareva [a], P.S. Vorontsov [c], V.V. Smirnov [a]

[a] *Chemistry Department, Moscow State University, 119899 Moscow, Russian Federation*
[b] *N.N. Semenov Institute of Chemical Physics RAS, 117421 Moscow, Russian Federation*
[c] *Karpov Institute of Physical Chemistry, 103064 Moscow, Russian Federation*

Abstract

The connections between composition and formation conditions of catalysts based on immobilised complexes of Cu(II) and dmf as precursors and their catalytic activity in C–Cl bond metathesis in system $CCl_4-n-C_{10}H_{22}$ were studied. High activity and selectivity could be obtained providing that a lamina of dmf containing mononuclear copper complexes forms in pores of a support. It was shown that the composition and structure of surface complexes does not depend on concentrations of copper ions or dmf in precursor solution. The loss of catalytic activity when the support cannot fix the lamina (e.g., charcoal in contrast with silica) is observed. The key stage of catalysis could be a reduction of Cu(II) to Cu(I). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Copper complexes are active in C–Cl bond activation, especially for reactions with partition of CCl_4 [1]. Reduction of CCl_4 to useful products such as $CHCl_3$ by simple and cheep organic H-donors, e.g., alkanes, was studied earlier without significant success [2–4]. There-fore, we showed earlier that selective activation of CCl_4 in presence of supported Cu complexes

and *n*-alkane, e.g., decane, takes place in rather narrow range of conditions of preparation and use of the catalyst [5]. The reaction can be classified as C–Cl bond metathesis:

$$RH + CCl_4 \rightarrow RCl + CHCl_3 \qquad (1)$$

Useful products — chloroform and chloroparaffins — are formed in the reaction. The factors of controlled formation of an effective catalytic system based on copper salts, dmf and inorganic supports are analysed in this paper.

It is known that Cu(II) forms a number of complexes of different composition with dmf

and chloride anions [6]. The mononuclear complexes in crystal form are unknown, only bi-, tri- and polynuclear structures were discovered [7]. On the contrary, all possible combinations of mononuclear neutral or charged particles are observed in solution of Cu^{2+} and chloride ions in dmf.

The situation for the $CuCl_2$–dmf system is rather difficult — it was shown earlier that different kinds of complex can exist in the solution [6]. We failed to find data for a composition of the complexes in pure dmf in literature, all the more for mixtures of dmf with chloroorganic solvents. Data [6] were obtained in presence of high concentrations of different inorganic salts, which strongly influence the composition of the solution. Above all, it is important to determine what kinds of particle exist on the surface of different kinds of inorganic support after various procedures of catalyst formation.

2. Experimental

Copper(II) chloride was dehydrated by azeotropic drying of corresponding crystal hydrate with benzene. Solvents and substrates were purified by known procedures [8]. All solutions were prepared and kept in atmosphere of dry nitrogen. Silica (silica gel with a specific surface area of 250 m^2 g^{-1}, silochrome (100 m^2 g^{-1}) and activated charcoal (250 m^2 g^{-1})) were dried in vacuum 10^{-3} Torr at 473 K. Catalysts were synthesized by impregnation of the supports in solutions of $CuCl_2$ in mixture $CHCl_3$–dmf. Then, granules were exposed in a flow of dry nitrogen.

The EPR spectra were detected with a Varian E-3 X-band spectrometer in quartz tubes (4 mm in diameter) at 77 K. Magnetic field was graduated by the spectrum of Mn^{2+} in the MgO matrix and by the DPPH signal with $g_0 = 2.0036$. The spin-Hamiltonian parameters $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$ have been calculated from the EPR spectra according to recommendations [9]. The

amount of adsorbed Cu(II) ions was calculated by double integration of the EPR spectrum of the sample and its comparison with such one for the reference: monocrystalline of $CuSO_4 \cdot 5H_2O$ with a known number of spins.

Electron spectra of solutions were recorded on Shimadzu UV3100, spectra of diffusal reflection of powders on LOMO SF-4, IR-spectra of tabletted catalysts on Karl Zeiss UR-4 spectrophotometer. Images of particles on the surface of high-ordered pyrographite (HOPG) were obtained with AFM P4SPM MDT.

The reaction of C–Cl bond metathesis was carried out in glass ampoules. The samples were released from dissolved gases by repeating the cycle ''freezing to 77 K — evacuation to 10^{-3} Torr — thawing to 20°C'' many times. Then, the ampoules were disconnected with fire and put into a thermostat with mixing technique. The temperature range was 130–200°C. The reaction products were analysed as in Ref. [5].

3. Results and discussion

Solutions of copper (II) chloride in dmf or mixtures of dmf with $CHCl_3$ have a green or green–yellow colour. Typical UV–Vis spectrum of the solution are shown on Fig. 1a. The most informative absorption is in a region 300–500 nm and it is assigned to a superposition of n–d transitions in chloride complexes of Cu(II) [10]. We estimated concentrations of the complexes containing Cu^{2+}, dmf and chloride anions in dmf–chloroform mixture 1:1 subject to the extinction coefficients calculated in Ref. [6] for pure dmf. It was found out that the content of $CuCl_4^{2-}$ is negligible, and the concentration of $[CuCl_3(dmf)_n]^-$ is less than 10%. About 50% of Cu ions are in form $CuCl_2(dmf)_m$, the rest are cationic copper complexes. It is surely difficult to estimate the proportion between the cationic complexes of different composition, because Ref. [6] presents discrepant values of their extinction coefficients.
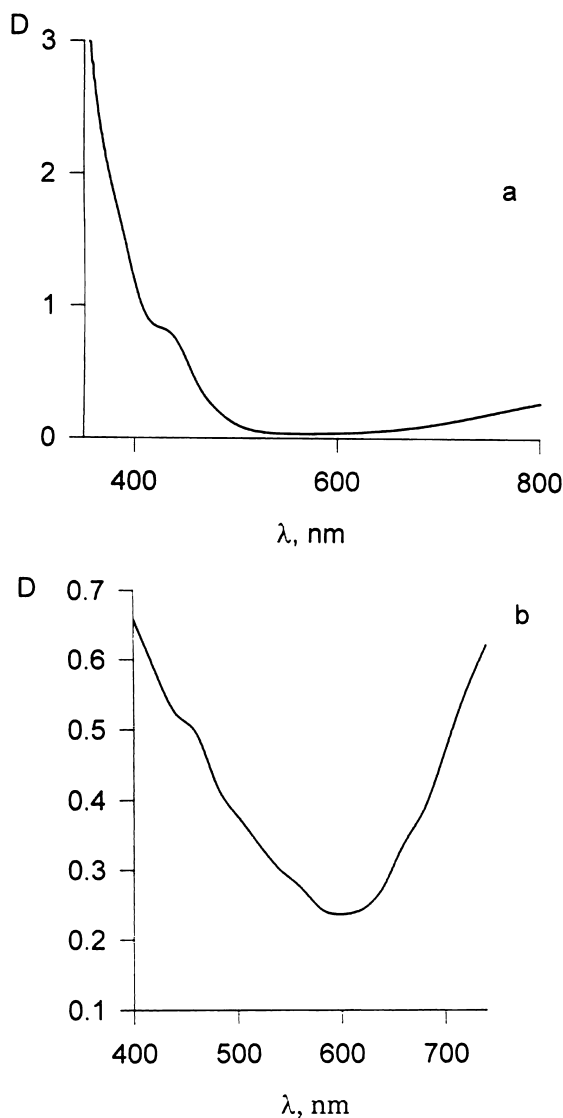
Fig. 1. (a) UV–Vis spectrum of $CuCl_2$ solution in mixture dmf:$CHCl_3 = 1:1$, [Cu] $= 5 \cdot 10^{-2}$ M; (b) Vis spectrum of supported complexes of $CuCl_2$ with dmf on silica, [Cu] $= 0.7\%$ (w/w).

Typical EPR spectra of $CuCl_2$ in the mixtures of dmf and $CHCl_3$ are shown in Fig. 2. Analysis of these spectra in the mixture 1:1 demonstrates that Cu^{2+} complexes of three types (I–III) occur in the mixtures. The distribution of the complexes strongly depends on the ratio between [dmf] and [$CHCl_3$] (Fig. 2). Parameters of the spin-Hamiltonian (Table 1) are typical for the Cu^{2+} complexes, which are characterised by the axial symmetry of the coordination sphere (a slightly distorted octahedron (a tetragonal bipyramid)) with $g_{\parallel} > g_{\perp} > 2.0$. We attributed II as a neutral complex [$CuCl_2(dmf)_m$], I as [$CuCl_3(dmf)_n$]$^-$ anion, and III as [$CuCl(dmf)_p$]$^+$ cation by the dependence of the intensities of the corresponding lines in electronic and EPR spectra on the dmf concentration. Such attribution is in a good agreement with the EPR parameters of the similar complexes in aqueous solutions, where H_2O molecules are located in the polyhedron structure instead of dmf molecules [11]. The absolute values of $g_{\parallel}$ and $A_{\parallel}$ for the relative complexes are different, but the main tendency of changes of these parameters is quite the same (Table 1). We did not observe a signal in a half-field (the forbidden transition), which could prove the existence of bi- or polynuclear copper complexes.

With increasing of the dmf concentration in a solution, one can observe the EPR spectrum of a new complex IV (Figs. 2 and 3). We assume that IV does not contain Cl^- anions in the coordination sphere, because the portion of this complex increases significantly in a solution of $CuCl_2$ in pure dmf. It follows from the shape of the spectrum that the complex IV has essentially another configuration, comparing with I–III, with tri-axial anisotropy of the spin-Hamiltonian parameters of the EPR spectrum: $g_1 = 2.345$; $A_1 = 0.01232$ cm^{-1}; $g_2 \approx 2.10$; $g_3 = 2.005$; $A_3 = 0.00665$ cm^{-1}. The most probable structure of IV is a slightly distorted trigonal bipyramid, well known for many five-coordinated copper (II) complexes with various mono-, bi- and polydentate ligands [12–14]. Principle possibility of such a structure in the systems copper–dmf follows from the X-ray data [15]. It is necessary to mention that compounds II and III are also existing in a pure dmf solution, though the structures IV form the main portion of copper complexes (Figs. 2 and 3).

Thus, it was shown that at least four types of copper containing complexes exist in studied solutions. They are in equilibrium, which can be
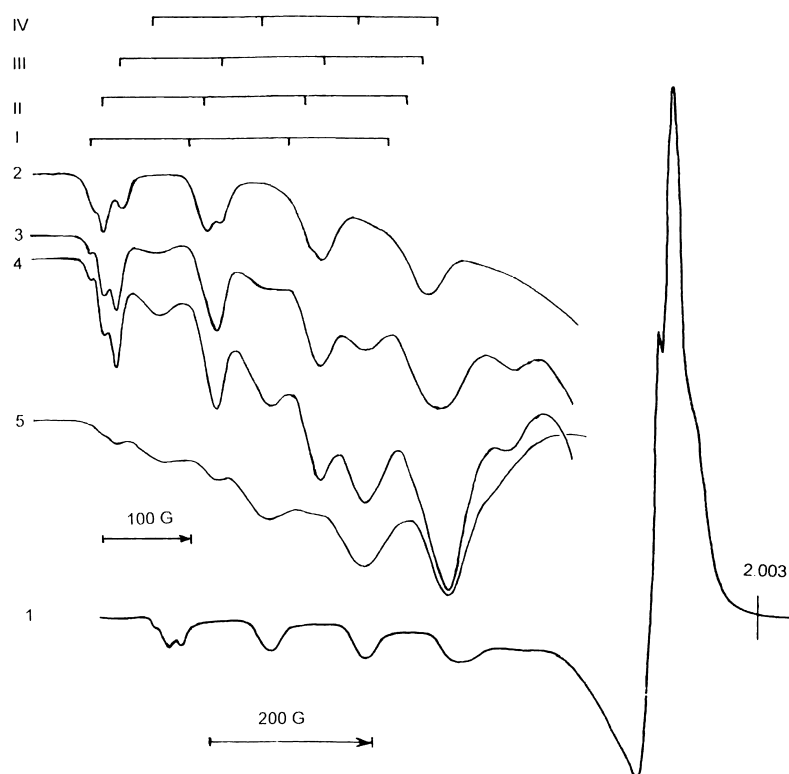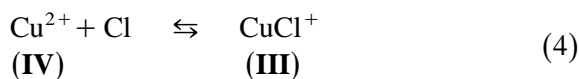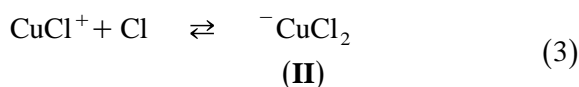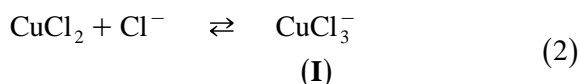
Fig. 2. EPR spectra of frozen at 77 K in mixtures dmf:CHCl$_3$ = 1:1 (1); 1:8 (2), 3:1 (3); 8:1 (4) and 1:0 (5). [Cu^{2+}] = 5.9 · 10^{-2} M.

described by following equations (dmf molecules are emitted for simplification):

$$CuCl_2 + Cl^- \quad \rightleftarrows \quad CuCl_3^- \qquad (2)$$
$$(\mathbf{I})$$

$$CuCl^+ + Cl \quad \rightleftarrows \quad {}^-CuCl_2 \qquad (3)$$
$$(\mathbf{II})$$

$$Cu^{2+} + Cl \quad \leftrightarrows \quad CuCl^+ \qquad (4)$$
$$(\mathbf{IV}) \qquad\qquad\qquad (\mathbf{III})$$

The specific absorbtion of copper ions does not take place when silica is put in the solutions. In this case, attached systems form only after removing of volatile solvent.

Microanalysis of the supported system shows that chloroform removes completely during continuous exposition in atmosphere of dry nitrogen at room temperature. On the contrary, significant amounts of dmf are remained in pores of the support. The dmf–Cu ratio on the surface is about 10–30 and depends on dmf concentration in precursor solution. Obviously, dmf forms on the surface of a lamina containing copper complexes.

IR-spectra demonstrate rather hard interaction between dmf and surface functional groups.

Table 1
Spin-Hamiltonian parameters of Cu(II) complexes, measured at 77 K

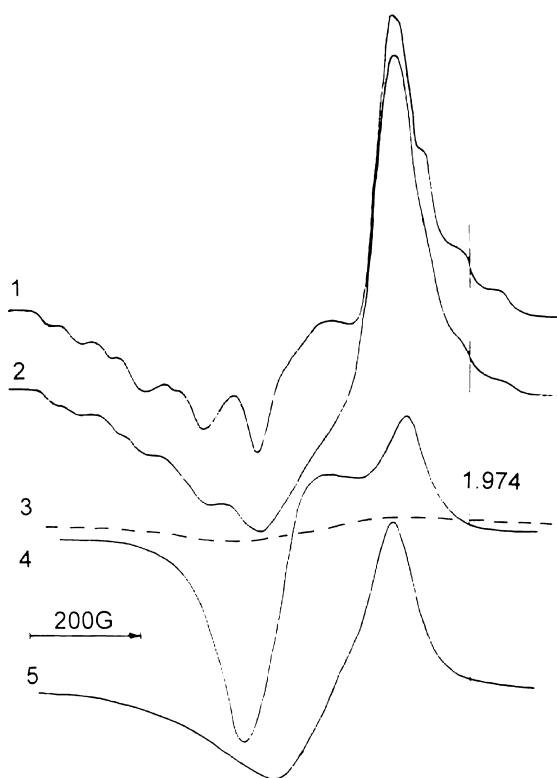| Complex	$(A_{\parallel} \pm 2)10^4$, cm^{-1}	$g_{\parallel} \pm 0.005$	$g_{\perp} \pm 0.005$
I	131.2	2.419	–
II	133.0	2.406	–
III	126.2	2.392	–
SiO$_2$–CuCl$_2$(dmf)$_n$	127.0	2.394	–
(Initial)	121.0	2.355	–
(After the reaction)	–	–	2.079
[CuCl$_4$(H$_2$O)$_2$]$^{2-}$, [2]	137.6	2.297	2.035
[CuCl$_3$(H$_2$O)$_3$]$^-$, [2]	144.9	2.312	2.038
[CuCl$_2$(H$_2$O)$_4$]$^{2-}$, [2]	153.2	2.333	2.038
[CuCl(H$_2$O)$_5$]$^+$, [2]	146.9	2.372	2.040
[Cu(H$_2$O)$_6$]$^{2+}$, [2]	127.4	2.427	2.041

Fig. 3. EPR spectra of CuCl$_2$ in dmf (1) and adsorbed on silica (2–6): initial catalyst (2); treated at 70°C (3), 120°C (4), 150°C (5) and after catalysis (6). T = 77 K.

A strong wide band at 1655–1660 cm^{-1} belongs to bound dmf but distinguishes from the absorbtion of dmf in complexes with cupric chloride (1645 cm^{-1} due to data [16]). An availability of an absorbance at 3300–3450 cm^{-1} referring to vibrations of strongly bound silanol groups shows that dmf is fixed in the pores owing to a formation of hydrogen bonds with surface hydroxyl groups.

Concentrating of dmf in pores of silica results in a fact that a composition of copper containing complexes on the support in most cases is not dependent on the composition in the solvent-precursor and is similar to one in pure dmf. This follows, first of all, from comparison of the EPR spectra of the adsorbed compound with that one recorded in a pure dmf solution (Fig. 3): they are qualitatively identical. Broadening of the EPR spectrum lines in the case of

adsorbed complexes is the evident result of much higher local concentration of the complexes attached to the surface of the SiO$_2$ carrier, comparing with the average concentration in a solution.

The likeness of the complexes in solutions and on silica is illustrated by a comparison of electron spectra, too. A spectrum of a diffusive reflection of the immobilised complexes of cupric chloride with dmf is given on Fig. 1b. The spectrum is similar to the Vis spectrum in solution e.g., a shoulder about 450 nm assigned to the absorbance of CuCl$_3^-$ is the same.

The supported complexes synthesised by the procedure described above are effective catalysts in a reaction of carbon tetrachloride with decane

$$C_{10}H_{22} + CCl_4 \rightarrow C_{10}H_{21}Cl + CHCl_3 \qquad (5)$$
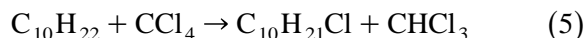
A very high selectivity is obtained in presence of these catalysts. The single product of CCl$_4$ transformation is CHCl$_3$ (> 99%). C$_{10}$H$_{22}$ gives a mixture of C$_{10}$H$_{21}$Cl with selectivity more than 95 mol% (the rest is mainly
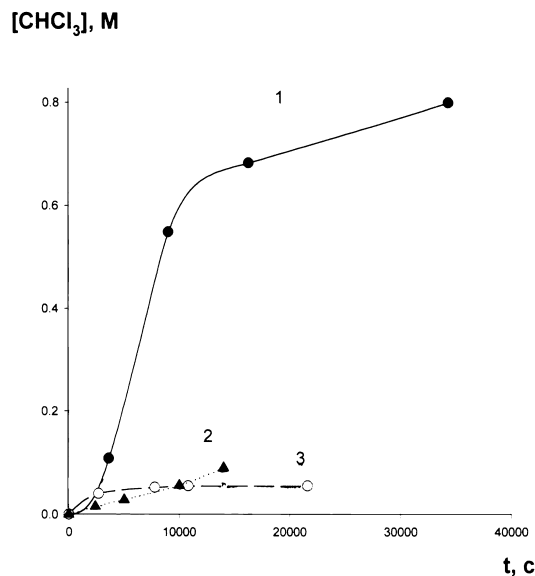
[CHCl$_3$], M

t, c

Fig. 4. Kinetic curves of CHCl$_3$ accumulation in reaction (5) in presence of Cu (II) complexes with dmf (a) on silica, [Cu] = 1.8% (w/w); (b) catalyst (a) treated at 70°C; (c) on charcoal, [Cu] = 2.0% (w/w); T = 160°C.

$C_{10}H_{20}Cl_2$). The yields of hydrogen chloride and methylene chloride are less than 1%.

A typical kinetic curve of the reaction is s-shaped (Fig. 4). A complicated form of the curve indicates changes of state and activity of the catalyst during the process.

The EPR study showed that less than 1% of copper complexes continued being paramagnetic after the reaction (Fig. 3). It is connected with the reduction of Cu(II) ions to Cu(I): addition of air into the reactor led to fast recovery of the initial intensity of the signal consequently to oxidation of Cu(I) by molecular oxygen. Reduction of copper (II) complexes at high temperatures could be realised by their reaction with dmf molecules. Metathesis auto-acceleration might be explained by higher activity of Cu(I) in comparison with Cu(II). In fact, the content of dmf on silica during the first hour of the catalytic process is reduced by about one-half. Another reasons of dmf loss could be thermal desorbtion of excessive dmf or thermal decomposition of dmf complexes with copper. The outlay of dmf is likely the reason for the decrease of the catalytic activity. It is proved by a direct experiment — a treatment of the catalyst partially lost its activity by new portions of dmf followed by a reduction of the initial activity.

A previous removing of dmf by continuous heating at 70°C in a stream of a dry nitrogen results in a significant decrease of the activity (Fig. 4). Just in parallel one could observe that more than 99% of Cu^{2+} ions became formally diamagnetic. It is seemingly connected with formation of polynuclear compounds of copper (II) with a system of coupled electron spins after removal of the main part of the dmf molecules. Such an absence of paramagnetism by Cu(II) compounds is well known, for instance, for the hydroxide Cu(II) complexes adsorbed on SiO_2 [17,18] and in some enzymes. It is of importance that in such a case, contact with atmo-
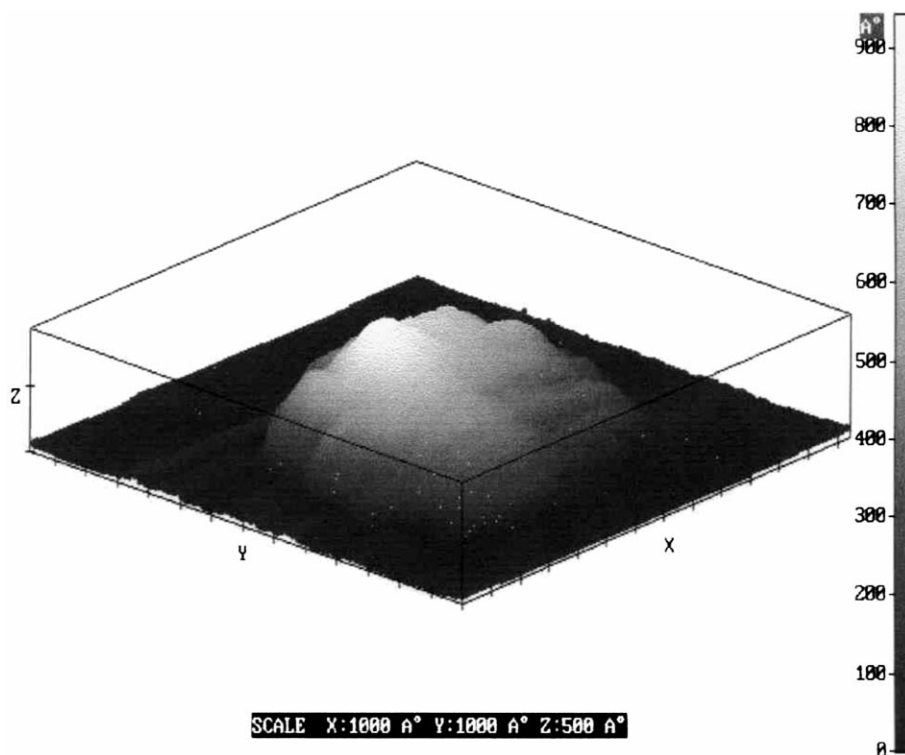

Fig. 5. The image of aggregate of $CuCl_2$ complex with dmf on the HOPG surface, obtained with AFM technique.

spheric O_2 does not lead to recovery of the EPR spectrum, which is coming only after further heating of the sample till 120°C (Fig. 3).

Therefore, the presence of the dmf lamina in silica pores in which mobile mononuclear copper complexes exist is the most important factor responsible for the catalytic activity. The stability of the lamina should depend upon the strength of interactions between dmf and surface groups of a particular support.

In order to check this statement, we studied the structure, thermal stability and activity of complexes of cupric chloride with dmf immobilised on carbon supports. The latter does not contain surface functional groups able to complex with dmf or Cu^{2+} ions.

The structure of particles on the surface of HOPG was studied by AFM techniques. The image of the surface complex aggregate is given in Fig. 5. It is rather large — up to 1000 Å. It could be the complex $[CuCl_2(dmf)_2]_2$, which crystallised from the precursor solvent in absence of any supports.

The catalytic activity of samples supported on charcoal is very low in spite of the Cu content on silica and in it is similar. The reaction practically terminates after 5% conversion. The destruction of the catalytic system and appearance of cupric chloride film on walls of reaction vessel are observed. It should be mentioned that copper complexes do not desorb from silica.

From these results we can formulate necessary conditions for the effective catalysis of metathesis. The first is the presence in pores of a support of a lamina of dmf, which plays different important roles. First of all, it might reduce Cu(II) to Cu(I), second, it prevents the formation of polymeric low active structures. A control experiment shows that the role of dmf is not only to reduce Cu(II). Cuprous chloride supported on silica is low active in the reaction. The second condition — a support should be able to retain the lamina on its surface, thus the surface active hydroxo- or another functional groups are necessary. Earlier, we mentioned

another important fact — oxygen should be absent for successful metathesis [5]. It could be explained by inhibiting radical steps or oxidation of Cu(I). A more trivial but important factor is the appropriate thermal conditions of the process because the reaction proceeds selectively only in a very narrow temperature range (160–180°C). At lower temperatures, the velocity is insufficient while at higher temperatures, metathesis is non-selective and a lot of HCl and resins are formed.

The data presented do not allow us to determine the nature of the catalytic activity. It is not clear whether the active particles are complexes of monovalent copper (nevertheless, complexes of Cu(I) with dmf are not described in literature) or mixed-valenced complexes as in the case of catalytic isomerization of dichlorobutenes [19]. Further experiments should help us to answer these questions.

Acknowledgements

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