

Competitive Complexation in the Copper(II) Chloride–*N,N*-Dimethylformamide–Aerosil System

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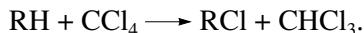
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Abstract—Competitive complexation in the copper(II) chloride–*N,N*-dimethylformamide (DMF)–Aerosil system was studied by IR spectroscopy. It was found that adsorption from organic solutions containing copper(II) chloride and DMF resulted in the formation of the following three types of DMF complexes: self-associates of DMF, DMF complexes with surface hydroxyl groups, and DMF complexes with Cu(II) ions. The removal of DMF resulted in the sequential degradation of, initially, self-associates; next, complexes with silanol groups; and, finally, complexes with copper ions.

INTRODUCTION

The complexes of copper(II) chloride with *N,N*-dimethylformamide (DMF) immobilized on silica surfaces act as catalysts for the C–Cl bond metathesis [1–3]



The systems containing a 10- to 30-fold amount of DMF with respect to copper ions exhibited the highest activity [2]. In this case, the calculated surface coverage is several times higher than a monolayer. It was hypothesized that a DMF film was formed on the surface of the support. It is likely that the complexes of copper(II) ions with DMF and chloride anions were concentrated in this film, and their composition was analogous to the composition of complexes in a DMF solution [3]. However, the mechanism of immobilization of these complexes is not conclusively established. In this study, we used adsorption IR spectroscopy in order to determine the nature of complexes formed during the adsorption of CuCl₂ with DMF on the surface of Aerosil.

EXPERIMENTAL

Copper(II) chloride was dehydrated by azeotropic drying with benzene [4] followed by evacuation to 10^{–3} Torr. DMF was purified in accordance with a standard procedure [4]. Aerosil with a specific surface area of 136 m²/g was subjected to thermal vacuum treatment (calcination at 450°C in air and evacuation at 200°C and 10^{–3} Torr) for the removal of adsorbed water. Next, Aerosil was pressed into pellets at a pressure of ~20 kg/cm² to decrease light refraction at particle interfaces. The Aerosil pellets were placed in a vacuum cell analogous to that described in [5], and the cell was attached to a vacuum unit combined with an IR spectrophotometer. The adsorption of DMF was performed by admitting its vapor to an evacuated Aerosil pellet. The supported copper chloride complexes with DMF were prepared by the impregnation of Aerosil pellets with the

solutions of CuCl₂ and DMF in a molar ratio of 1 : 30 in methylene chloride in an inert atmosphere followed by the removal of the volatile solvent in a flow of dry nitrogen. The IR spectra were measured on an UR-20 spectrophotometer.

RESULTS AND DISCUSSION

The DMF–SiO₂ system. The IR spectrum of Aerosil after thermal treatment contained only a single absorption band in the region of the stretching vibrations of free hydroxyl groups at the surface of Aerosil with a maximum at 3750 cm^{–1} [5] (Fig. 1, curve 1). After the adsorption of DMF vapor, the band due to the stretching vibrations of free hydroxyl groups of the support (3750 cm^{–1}) almost completely disappeared,

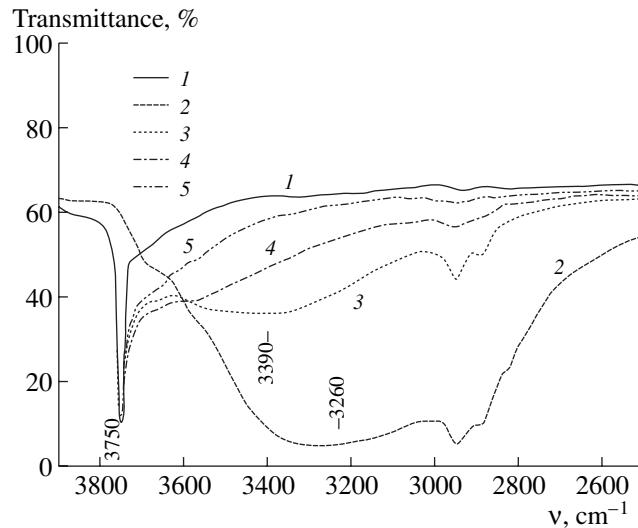


Fig. 1. IR spectra of (1) Aerosil and (2) Aerosil after the adsorption of an excess of DMF followed by vacuum treatment at (3) room temperature, (4) 100°C, or (5) 200°C.

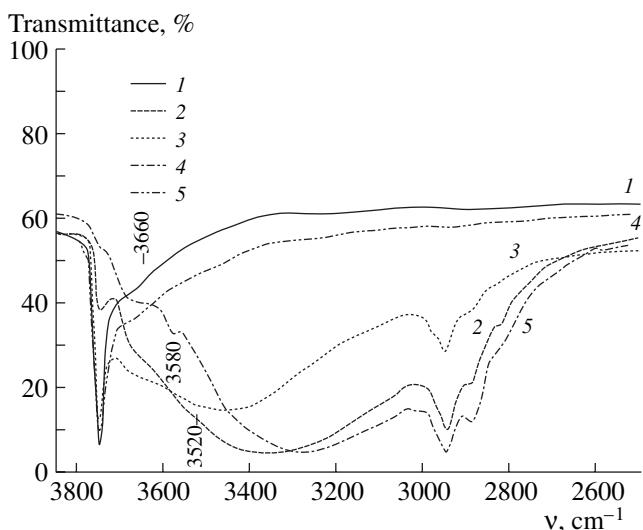


Fig. 2. IR spectra of (1) Aerosil, (2) Aerosil after the adsorption of a copper chloride complex with DMF followed by evacuation at (3) room temperature or (4) 420°C, and Aerosil (5) after the adsorption of an excess of DMF vapor onto sample 4.

and absorption appeared as a superposition of broad bands with a maximum at about 3260 cm⁻¹, which belongs to the stretching vibrations of bound hydroxyl groups [5] (Fig. 1, curve 2). After evacuation at room temperature, DMF was partially desorbed. In this case, the intensity of the absorption band at 3260 cm⁻¹ decreased, and its maximum shifted toward higher frequencies (Fig. 1, curve 3); the intensity of an absorption band due to the stretching vibrations of free silanol groups also increased. The effect of surface coverage on the position of the absorption band maximum of bound hydroxyl groups is well known [5]. It is our opinion that, in this case, an increase in $\Delta\nu(\text{OH})$ with an increase in the amount of adsorbed DMF can be explained by the simultaneous coordination of silanol groups to several adsorbate molecules in polymolecular layers, which causes a stronger disturbance in the OH bond. The shifts $\Delta\nu(\text{OH}) = 350\text{--}490\text{ cm}^{-1}$ are characteristic of silanol groups coordinatively bound to strong oxygen-containing donors (according to Kiselev and Lygin [5], $\Delta\nu(\text{OH}) = 300\text{--}500\text{ cm}^{-1}$).

The spectra of DMF adsorbed on the surface of Aerosil exhibited a shift in the band due to the stretching vibrations of the CO bond ($\nu(\text{CO})$) from 1685 cm⁻¹ (DMF in a liquid phase [6]) to 1665 cm⁻¹ upon adsorption. The band due to the stretching vibrations of the

CN bond ($\nu(\text{CN})$) shifted from 1510 cm⁻¹ in solution to 1490 cm⁻¹ on the surface. In the region of the deformation vibrations of methyl groups ($\delta(\text{CH}_3)$), two bands with maximums at 1412 and 1437 cm⁻¹ appeared (in liquid DMF, $\delta(\text{CH}_3) = 1445\text{ cm}^{-1}$). It is likely that DMF adsorption on Aerosil occurred by the coordination interaction of silanol groups and the oxygen atom of the amide group; this interaction is characteristic of various amide complexes [7]. The energy of formation of complexes with hydrogen bonds at nitrogen atoms is more than 10 kcal/mol lower [8]. A considerable change in the frequency of stretching vibrations of the C–N bond can be due to partial conjugation of this bond with the lone electron pair of the oxygen atom [7, 9].

After evacuation at 100°C, the intensity of the absorption band of free hydroxyl groups on the surface of Aerosil was close to the initial value, whereas the absorption band of bound hydroxyls was weakly pronounced (Fig. 1, curve 4). At 200°C, the spectrum was almost completely restored to its original condition (Fig. 1, curve 5); this fact suggests that the adsorption of DMF on Aerosil is reversible.

The CuCl₂–DMF–SiO₂ system. The IR spectra of copper(II) chloride complexes with DMF immobilized on Aerosil exhibited a considerable decrease in the absorption intensity of free hydroxyl groups as compared with the initial support, and the appearance of a broad intense absorption band due to the stretching vibrations of bound silanol groups (Fig. 2, curves 1, 2). However, in this case, the absorption band of free OH groups did not completely disappear; this can be related to steric hindrances that appear on the adsorption of more bulky particles. In this case, $\Delta\nu(\text{OH})$ was about 400 cm⁻¹. Moreover, in the region of high frequencies, a shoulder with a maximum at 3660 cm⁻¹, which can be attributed to the stretching vibrations of intraglobular OH groups, and unclearly defined bands at 3550, 3580, and 3620 cm⁻¹ appeared. A band due to the stretching vibrations of the CO bond split into three components with maximums at 1685, 1660, and 1640 cm⁻¹ (Fig. 3, curve 1). A comparison of these results with published data and with the results given in the above section (see table) suggests that the first value corresponds to the $\nu(\text{CO})$ of the DMF molecule in a liquid phase, where DMF occurs as self-associates (A). It is likely that the second maximum corresponds to the DMF molecule coordinatively bound to the surface hydroxyl groups of Aerosil (B), whereas the third band is characteristic of DMF in a complex with copper(II) chloride (C). The

Positions of absorption-band maximums in the IR spectra of DMF

System	$\delta(\text{CH}_3)$, cm ⁻¹			$\nu(\text{CN})$, cm ⁻¹	$\nu(\text{CO})$, cm ⁻¹		
DMF in a liquid phase [6]	1445	–	–	1510	–	1685	–
DMF–SiO ₂	1440	–	1412	–	1490	–	1665
CuCl ₂ (DMF) ₂ [6]	1448	1432	1420	1520	1496	–	1644
CuCl ₂ –DMF–SiO ₂	–	1437	1412	–	1495	1685	1660
						1660	1640

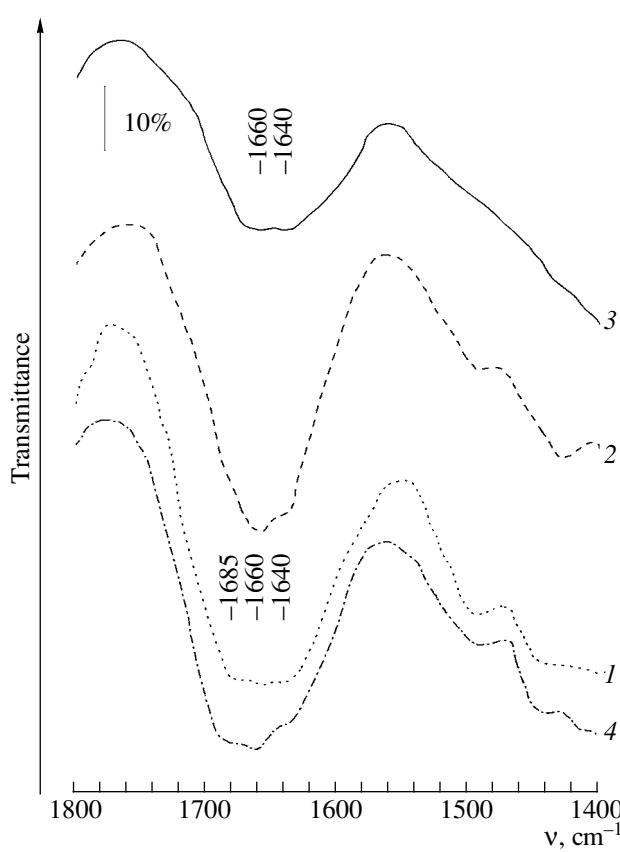


Fig. 3. IR spectra of (1) DMF in the copper(II) chloride-DMF-Aerosil system, sample 1 after evacuation at (2) room temperature or (3) 420°C, and (4) sample 3 after the adsorption of an excess of DMF vapor.

absorption band maximums of the CN groups of the DMF molecule shifted toward low frequencies (table). The partial desorption of DMF occurred even after evacuation at room temperature. In this case, the band maximums of bound OH groups at 3550, 3580, and 3620 cm^{-1} were retained in the IR spectrum (Fig. 2, curve 3). After evacuation at 420°C (Fig. 2, curve 4), the band intensity of free hydroxyl groups of Aerosil was practically restored. In the region of the stretching vibrations of the carbonyl group, a band with a maximum at 1685 cm^{-1} disappeared, whereas bands at 1660 and 1640 cm^{-1} were present in the spectrum even after evacuation for a long time at 420°C, even though their intensities decreased (Fig. 3, curve 3). The color of the sample changed from greenish yellow to dark brown. Consequently, in the presence of copper(II) chloride, DMF can be retained on the surface of Aerosil under more severe conditions. In this case, a portion of DMF molecules interacted with copper(II) ions ($\nu(\text{CO}) = 1640 \text{ cm}^{-1}$), and the other molecules interacted with silanol groups ($\nu(\text{CO}) = 1660 \text{ cm}^{-1}$).

Thus, the desorption of DMF self-associates (**A**) bound to the Aerosil surface and copper(II) ions due to nonspecific interactions occurred first. In this case, as

demonstrated previously, the composition of surface copper(II) complexes with DMF was changed, and the complexes lost their mobility [2]. The DMF molecules coordinatively bound to silanol groups (**B**) were removed under more severe conditions. DMA formed the strongest complexes with copper(II) ions. Because the band due to the stretching vibrations of hydroxyl groups on the surface of Aerosil shifted by no more than 200 cm^{-1} in the case that these species were predominant on the surface, nonspecific adsorption of the complexes occurred. The restoration of the spectrum of the hydroxyl groups of Aerosil after the thermal vacuum treatment of a supported copper(II) chloride complex with DMF indicates that the major portion of the oxygen atoms of silanol groups does not enter into the coordination sphere of Cu(II) even after the removal of DMF. This was also evidenced by a color change in the sample to brown, which is characteristic of the chloride complexes of copper. It is likely that, during a deficiency in DMF, CuCl_2 molecules form polynuclear complexes or microcrystals with chloride-bridging groups. This hypothesis was supported by the fact that copper ions were almost completely removed from silica surfaces after treatment with acetone.

The addition of DMF vapor to a sample after thermal treatment restored the initial color of the pellet. The general shape of the vibrational spectrum in the region of OH-group absorption (Fig. 2, curve 5), as well as in the region of carbonyl-group absorption (Fig. 3, curve 4), was restored; this fact suggests the regeneration of forms **A**, **B**, and **C**.

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