A STUDY OF THE REACTION OF COPPER(II) IONS IN HYDRATED Y ZEOLITE WITH SODIUM 8-MERCAPTOQUINOLINATE AND 8-HYDROXYQUINOLINATE

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The reaction of Cu^{2+} ions from Y zeolite cavities with sodium 8-mercaptoquinolinate (tox) or 8-hydroxyquinolinate (ox) was studied in aqueous solutions by EPR and electronic absorption spectroscopy, X-ray powder diffraction measurements, and scanning electron microscopy. The Cu^{2+} ions migrate towards the support surface to form $[Cu(tox)_2]$ or $[Cu(ox)_2(H_2O)_2]$ complex crystals. Owing to the low solubility of the complex, grains of the $[Cu(tox)_2]$ crystallites gradually grow over the support surface. Better soluble than $[Cu(tox)_2]$, the $[Cu(ox)_2(H_2O)_2]$ complex crystallizes separately from the carrier in the form of long needles.

Zeolites find wide use as supports for transition metal complexes. Attention has been paid largely to cationic complexes bonded inside the zeolite cavities[1,2]. In fact, however, the complexes can also be localized on the external zeolite surface. Their formation and state on the surface depend on the reaction conditions and on the transition metal ion involved. ESCA studies of the reaction of diacetyl dioxime with Co^{2+} or Ni^{2+} ions in X zeolite have given evidence that the $[MeL_2]$ complexes are formed on the external surface of the support if hydrated zeolite is used, whereas the complexes are localized inside the cavities if the reaction is conducted in dehydrated zeolite[3]. Reacted with 1,2-dicyanobenzene in partly hydrated X zeolite, transition metal ions form phthalocyanine complexes both on the external surface of the zeolite and inside its cavities[4]. The ability of ions to form complexes on the external surface increases in order $Co^{2+} < Ni^{2+} < Cu^{2+}$. Hydrated Y zeolites containing exchanged transition metal cations were reacted[5,6] with stable anionic cyanide complexes, emerged in the form of amorphous "islets" on the external surface of the support. Their subsequent reduction led to finely dispersed supported metal catalysts.

As part of a study of complexes on zeolites, we have investigated the preparation of supported complexes of copper(II) with 8-mercaptoquinoline (tox) and 8-hydroxyquinoline (ox) which are of interest, *e.g.*, from the point of view of their reactivity with oxides of nitrogen as potential catalysts[7]. In this work we are concerned with the reaction of the two chelating ligands in their anionic forms with Cu^{2+} ions from supercavities of hydrated Y zeolite. Since the potential use of supported complexes

depends on their state on the support surface, the formation of the copper(II) complexes and their interaction with the surface are examined by means of spectral and powder X-ray diffraction measurements in conjunction with scanning electron microscopy.

EXPERIMENTAL

Sodium 8-mercaptoquinolinate dihydrate (Reakhim, USSR) and 8-hydroxyquinolinate (Labora Brno) were used. The copper complexes, $[Cu(tox)_2]$ (Cu calculated: 16·55%; found: 16·22%) and $[Cu(ox)_2(H_2O)_2]$ (calculated: 16·38% Cu, 9·3% H_2O; found: 15·96% Cu, 9·0% H_2O) were prepared by routine procedures[8,9]. CuNaY zeolites with different concentrations of the exchanged Cu^{2+} ions were prepared by reacting 50 g NaY zeolite (Research Institute for Petroleum and Hydrocarbon Gases; $SiO_2/Al_2O_3 = 5·4$) with 1 000 ml of aqueous solution of copper(II) nitrate for 4 h at room temperature. With concentrations of $Cu(NO_3)_2$ of 0·01 and 0·1 mol l^{-1}, the copper(II) content was 0·20 and 0·84 mmol per g zeolite, respectively, which corresponds to the exchange of 12·5% and 52·5% Na^+ by Cu^{2+}, respectively (henceforth labelled CuNaY(12) and CuNaY(52), respectively). The exchanged zeolites were washed thoroughly with water and dried freely in air. The copper content was determined by atomic absorption spectroscopy after decomposing the zeolite in hydrochloric acid.

The hydrated CuNaY zeolites were reacted with excess sodium salts of the chelating ligands in aqueous solutions. The colour of the zeolite changed from light-blue to brown for sodium 8-mercaptoquinolinate and to yellow-green for 8-hydroxyquinolinate immediately after the mixing. The system was stirred for 4 h and allowed to stand overnight. One g of CuNaY(12) was reacted with 0·33 g of sodium 8-mercaptoquinolinate dihydrate (1·51 mmol) or sodium 8-hydroxyquinolinate (1·97 mmol) dissolved in 100 ml of water, and the same quantity of CuNaY(52) was reacted with 1·0 g of the two substances (4·56 and 5·98 mmol), respectively, each in 200 ml of water. The system with sodium 8-mercaptoquinolinate was held under nitrogen to prevent oxidation of the free ligand to the disulphide. The products, henceforth referred to as $[Cu(tox)_2]/NaY$ and $[Cu(ox)_2]/NaY$, were washed thoroughly with water and dried freely in air.

The electronic absorption spectra in nujol mulls were scanned on a Specord M 40 spectrophotometer over the region of $12\,000-30\,000\,cm^{-1}$. The EPR spectra of the polycrystalline substances were measured on a Varian E-4 instrument in the X band at 77 and 295 K using DPPH as a standard for the determination of the g factors. The powder X-ray diffraction patterns were obtained with a Philips PW 1050 diffractometer using Ni-filtered CuK_α radiation. The scanning electron microphotographs were taken on a Jeol JSM-35 instrument.

RESULTS AND DISCUSSION

For hydrated CuNaY zeolite the band maximum for the $d-d$ transition lies at $12\,500\,cm^{-1}$, corresponding to the $[Cu(H_2O)_6]^{2+}$ complex inside the zeolite cavities. For the supported $[Cu(tox)_2]/NaY$ complex, the $d-d$ transition appears as a shoulder at approximately $15\,000\,cm^{-1}$, whereas the $[Cu(ox)_2]/NaY$ system gives rise to a $d-d$ transition band at $15\,400\,cm^{-1}$. Intense bands of the $\pi \to \pi^*$ transitions within the ligands appear in the short-wavelength regions of the spectra. The electronic spectra of the complexes on the zeolites resemble those of the $[Cu.$ $.(tox)_2]$ and $[Cu(ox)_2(H_2O)_2]$ complexes (Table I).

In the EPR spectrum, hydrated CuNaY(12) zeolite exhibits a nearly symmetrical singlet line at 295 K, whereas an axial spectrum is observed at 77 K (Table I; Fig. 1, curve 1). The parameters of the spectrum correspond to the copper(II) aqua complex of tetragonal symmetry, localized inside the supercavities of the zeolite[10]. The well--resolved hyperfine structure in the parallel region $(A_\parallel = 13 \text{ mT})$ indicates that exchange interactions between the Cu^{2+} ions are negligible[11]. After the reaction of such zeolite with the chelating ligands in their anionic forms, the EPR spectra resemble those of the corresponding polycrystalline complexes (Table I; Fig. 1, curves 2, 3). The spectral data give evidence that the reaction of sodium 8-mercapto-quinolinate or 8-hydroxyquinolinate with the Cu^{2+} ions from the supercavities results in the formation of the $[Cu(tox)_2]$ and $[Cu(ox)_2(H_2O_2)]$ complexes, respectively.

Inasmuch as the chelating ligands in their anionic forms are unable to enter the cavities of the negatively charged lattice of the zeolite, the reaction with the Cu^{2+} ions takes place on the external surface of the support. It follows from the temperature dependence of the EPR spectra of hydrated CuNaY zeolite that the Cu^{2+} ions inside the supercavities are freely mobile at room temperature, their state being similar to that in aqueous solutions, and so they can migrate easily towards the external surface of the support; the negative charge of the zeolite is compensated by the sodium ions from the ligand salt. The reaction of copper(II) with the ligand leads to the insoluble complex, so the concentration of free Cu^{2+} ions on the surface decreases and the equilibrium shifts in favour of the migration. The EPR spectra of the products were devoid of the signal of the starting Cu(II) aqua complex, hence, the above reaction proceeds quantitatively. The EPR spectral patterns of the products are affected considerably by the interactions between the Cu^{2+} which smooth the hyper-

TABLE I

Parameters of the electronic absorption spectra and of the EPR spectra measured at 77 K

Complex	Electronic spectra			EPR spectra			
	$\tilde{\nu} \cdot 10^{-3}$ cm^{-1}			$g_\perp$ g_0	$g_\parallel$	$\bar{g}^a$	ΔB^b mT
CuNaY(12)			12·5	2·070	2·398	2·185	
$[Cu(tox)_2]/NaY(12)$	24·0	20·0	15·0 sh^c	2·048	2·141	2·079	
$[Cu(tox)_2]$	24·0	20·0	15·0 sh	2·038	2·147,	2·075	
$[Cu(ox)_2]/NaY(12)$	24·2		15·4 sh	2·122			10·5
$[Cu(ox)_2(H_2O)_2]$	25·0		15·4	2·129			12·5

^{a} $\bar{g} = [(g_\parallel^2 + 2g_\perp^2)/3]^{1/2}$; ^{b} peak-to-peak width of the singlet spectrum; ^{c} shoulder.

fine structure. This implies that the complexes are not atomically dispersed over the support surface. Inasmuch as the spectral parameters of the complexes on the zeolites and of the solid complexes approach each other closely, the interaction of the complexes with the support can be assumed to be weak. This is also borne out by the fact that the complexes are extractable from the support with chloroform.

The powder X-ray diffraction patterns (Fig. 2) show that the crystal structure of the zeolite lattice is not affected markedly by the substitution of Na^+ by Cu^{2+} or by the reaction of Cu^{2+} with the ligands. In addition to the diffractions due to the zeolite, the $[Cu(tox)_2]/NaY$ and $[Cu(ox)_2]/NaY$ systems also exhibit diffractions whose intensities are proportional to the copper content of the zeolite. From this it can be inferred that the latter diffractions are caused by crystallites of the surface copper(II) complexes. The positions of the lines of $[Cu(tox)_2]/NaY$ coincide with those of the synthetic $[Cu(tox)_2]$ complex (Fig. 2). The diffractions from the surface complex of the $[Cu(ox)_2]/NaY$ system correspond to interplanar spacings of 0·80 and 0·36 nm and they are not identical with those from the $[Cu(ox)_2(H_2O)_2]$ complex
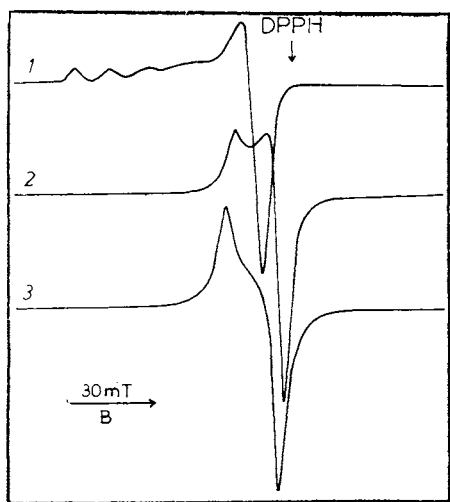

FIG. 1

EPR spectra measured at 77K. *1* CuNaY(12), *2* [Cu(tox)$_2$]/NaY(12), *3* [Cu(tox)$_2$]
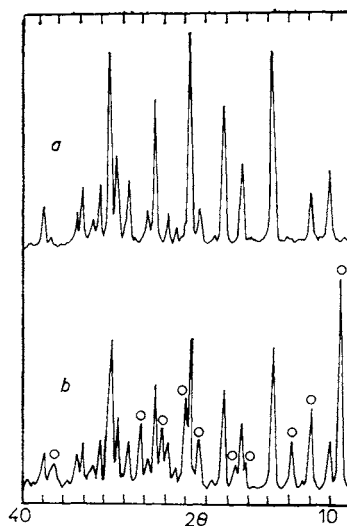
FIG. 2

Powder X-ray diffraction patterns. *a* NaY, *b* [Cu(tox)$_2$]/NaY(52). ○ diffractions corresponding to the [Cu(tox)$_2$] complex; the diffractions at $2\Theta = 11·9°$ and $22·8°$ are sums of diffractions of zeolite and [Cu(tox)$_2$] complex

prepared. According to ref.[9], the $[Cu(ox)_2(H_2O)_2]$ complex can be prepared, in dependence on the reaction conditions, in two modifications exhibiting different diffraction patterns.

Data on the microstructure of the systems formed were derived from their scanning electron microphotographs (see page 1906 at the end of this issue). $CuNaY(52)$ zeolite consists of spherical particles about $0.8 - 1.5 \mu m$ in diameter (Fig. 3a). After the reaction of this zeolite with sodium 8-mercaptoquinolinate, crystallite grains of $[Cu(tox)_2]$ complex about $0.4 - 0.6 \mu m$ in size are observed to grow over the surface (Fig. 3b). This implies that the reaction of Cu^{2+} with the ligand occurs on the external surface of the support. In the conditions used, the zeolite surface is covered by a layer of hydration water. The planar $[Cu(tox)_2]$ complex, which can form adducts with Lewis bases via axial coordination[12], then cannot coordinate directly to the oxygen donor atoms of the zeolite. Owing to the mutual affinity of the complex particles, their nucleation on the uneven zeolite surface and growth of crystallites of the deposited complex take place.

In the $[Cu(ox)_2]/NaY(52)$ system, needles of the $[Cu(ox)_2(H_2O)_2]$ complex, $2 - 3 \mu m$ long, are observed besides the zeolite particles (Fig. 3c). The crystallites of the complex are not apparently joined with the zeolite. The rough surface of the zeolite particles facilitates the formation of crystallization centres. So the nucleation can be assumed to occur on the surface also in this case, the crystal growth, however, proceeds in the solution. This difference between the systems with 8-mercaptoquinolinate and 8-hydroxyquinolinate can be explained in terms of the different solubility of the complexes. $[Cu(tox)_2]$ is less soluble than $[Cu(ox)_2(H_2O)_2]$ ($pK_s = 36.87$ and 29.57, respectively[13,14]). With a higher solubility of the product, the concentration of free Cu^{2+} ions in the reaction system is higher and these can diffuse farther away from the support surface before the complex particle is formed and incorporated into the lattice of the growing crystal. Also the small $[Cu(tox)_2]$ crystallites, the size of which is smaller than that of the zeolite particles, can interact with the support more efficiently than the long needles of the $[Cu(ox)_2(H_2O)_2]$ complex.

It can be concluded that the reaction of the mobile copper(II) ions from the supercavities of hydrated Y zeolite with sodium 8-mercaptoquinolinate or 8-hydroxyquinolinate in aqueous solutions, where the sodium ions provide charge compensation of the zeolite lattice during the migration of the Cu^{2+} ions, results in the formation of crystalline products whose composition is analogous to that of the product obtained from Cu^{2+} and the ligand in aqueous solutions. The interaction of the crystallites of the complex with the surface of the support depends on the solubility of the complex and morphology of the crystallites.

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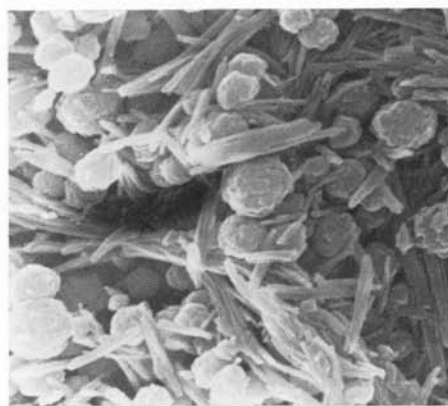
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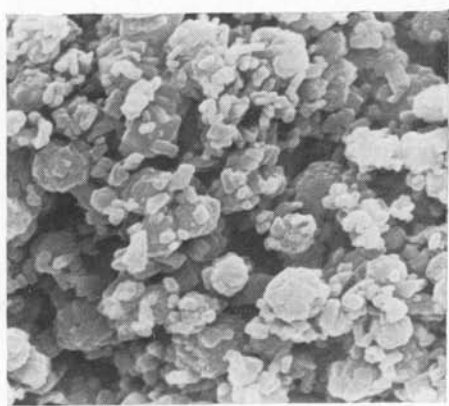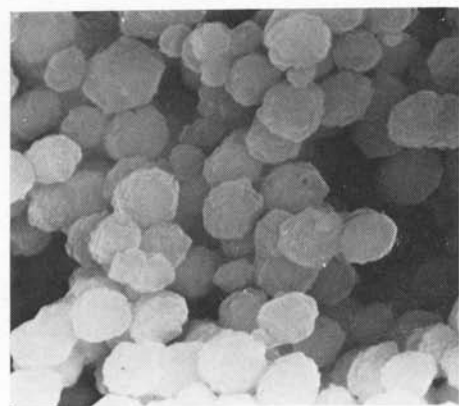
FIG. 3

Scanning electron microphotographs of CuNaY(52) (a), [Cu(tox)$_2$]/NaY(52) (b) and [Cu(ox)$_2$]/ /NaY(52) (c)