EPR study of the reaction of 8-quinolinol with copper(II) ions in Y zeolites with different degree of hydration

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Dedicated to Associate Professor Dr. J. Krätsmár-Šmogrovič in honour of his 60th birthday

According to the results of EPR spectroscopy associates of the complex molecules [Cu(ox)₂] are formed on the external surface of the carrier by the reaction of 8-quinolinol (Hox) with highly mobile Cu(II) aqua complexes exchanged in the supercavities of fully hydrated Y zeolite. The reaction of Hox with Cu(II) exchanged zeolite Y, dehydrated *in vacuo* at 20 °C, 200 °C, and 400 °C, leads to segregated molecules of the [Cu(ox)₂] complex fixed on zeolite. When the content of water in zeolite is lowered, migration of Cu(II) ions from the exchange sites on the walls of the cavities to the places, where they react with bulky molecules of Hox, becomes slower and the association of complex molecules is hindered. A small content of water in zeolite dehydrated at 200 °C accelerates remarkably the reaction of Cu(II) with Hox in comparison with the zeolite fully dehydrated at 400 °C. When the samples with fixed segregated molecules of the complex [Cu(ox)₂] were rehydrated, the complex molecules formed associates in the hydrated layer on external surface of the zeolite.

В соответствии с результатами исследования методом ЭПР-спектроскопии, ассоциаты комплексных молекул [Cu(ox)₂], которые образуются в результате реакции 8-хинолинола (Hox) с высокоподвижными аквакомплексами Cu(II), внесенными в полости полностью гидратированного цеолита Y, располагаются на внешней поверхности носителя. Реакция Hox с Cu(II)-замещенным цеолитом Y, дегидратированным в вакууме при 20 °C, 200 °C и 400 °C, приводит к одиночным молекулам комплекса [Cu(ox)₂], закрепленным на цеолите. При снижении содержания воды в цеолите замедляется мигрирование ионов Cu(II) из центров обмена на стенках полости к местам, где они вступают в реакцию с объемными молекулами Hox и, таким образом, препятствуется ассоциации молекул

комплекса. Небольшое содержание воды в цеолите, дегидратированном при 200 °C, значительно ускоряет реакцию Cu(II) с Hox по сравнению с цеолитом, полностью дегидратированным при 400 °C. При регидратации образцов с закрепленными одиночными молекулами комплекса [Cu(ox)₂], комплексные молекулы образуют ассоциаты в гидратированном слое на внешней поверхности цеолита.

In the last years much attention has been paid to the study of the first row transition metal complexes with chelating ligands, as ethylenediamine and 2,2′-bipyridine, bound in zeolites [1—4]. Such cationic complexes are held in cavities of negatively charged frameworks of zeolites by electrostatic forces. However, fixation of neutral complex molecules with chelating ligands on zeolite was also reported [5, 6]. According to [7], the degree of hydration of zeolite strongly influences the location of neutral complexes formed by the reaction of Co(II) and Ni(II) ions exchanged in zeolite X with diacetyldioxime. When the reaction was carried out in hydrated zeolite, bis(diacetyldioximato)Co(II) and -Ni(II) complexes fixed on the external surface were obtained. However, when the reaction was performed in dehydrated zeolite, complexes encaged in the cavities of zeolite were formed.

In our previous study [8] it has been found that the reaction of Cu(II) exchanged fully hydrated zeolite Y with sodium 8-quinolinolate in aqueous solution led to crystallites of bis(8-quinolinolato)copper(II) dihydrate in the form of long needles not joined with the surface of the carrier. A two-phase system was formed in this way. The Cu(II) ions moved from the zeolite into the surrounding aqueous medium, where a growth of crystallites proceeded. Therefore in this work the reaction of 8-quinolinol (Hox) with Cu(II) exchanged zeolite Y was performed under such conditions that no migration of Cu(II) ions from zeolite into the surrounding medium was possible. The influence of the water content in zeolite on the reaction rate of the formation of Cu(II) complex with 8-quinolinol and on the properties of this surface complex was studied.

Experimental

The Cu(II) exchanged zeolite (CuNaY) was prepared by the reaction of NaY zeolite (Research Institute for Petroleum and Hydrocarbon Gases; $SiO_2/Al_2O_3 = 5.4$) with aqueous solution of $CuNO_3 \cdot 3H_2O$ (Lachema, Brno, anal. grade) at room temperature for 4 h. The concentration of copper(II) nitrate was 0.01 mol dm⁻³ and the ratio of the reaction solution to zeolite was 20 cm³ g⁻¹. Before ionic exchange pH value of the reaction solution was 5.1. After completing the reaction pH reached 7.2. The exchanged zeolite was filtered off, washed thoroughly with water and dried freely in air. The copper content was determined by

atomic absorption spectroscopy (AAS 1 spectrometer, Zeiss, Jena) after the decomposition of zeolite in hydrochloric acid. It was found to be 0.20 mmol Cu per g zeolite, which corresponds to the exchange of 12.5 % Na^+ for Cu(II) ions.

The Cu(II) complexes with 8-quinolinol on zeolite were prepared by a direct reaction of CuNaY of different degree of hydration with 8-quinolinol (Lachema, Brno, anal. grade). After mixing the zeolite with Hox, the samples were sealed in EPR tubes.

1 g CuNaY hydrated in air was mixed with 0.3 g Hox (stoichiometric ratio $n(Cu):n(Hox) = 1:10$).

1 g CuNaY was dehydrated at room temperature and a pressure of ca. 4 Pa for 20 h. Then it was mixed with 0.5 g Hox (stoichiometric ratio $n(Cu):n(Hox) = 1:17$) in vacuo or in atmosphere of argon at normal pressure.

1 g CuNaY was dehydrated at a pressure of ca. 4 Pa. The temperature was raised with the rate 100 °C h^{-1} from room temperature to 200 °C or 400 °C. When the chosen temperature was reached, the samples were heated in oxygen at normal pressure for 1 h and subsequently evacuated for 1 h. After cooling to room temperature, CuNaY was mixed with 0.5 g Hox in vacuo or in argon atmosphere.

Since the complete removing of the excess of Hox, which did not react with Cu(II), but remained adsorbed on zeolite, was very difficult even at prolonged evacuation of samples at elevated temperatures, the excess of 8-quinolinol was not removed from the reaction medium. Its presence did not interfere with EPR measurements.

The EPR spectra were recorded on Varian E-4 spectrometer in X band at room temperature. Varian strong pitch was used as a standard for the determination of g factors.

Results

CuNaY hydrated in air showed a singlet asymmetric line with $g_0 = 2.160$ in the EPR spectrum (Fig. 1 a). Immediately after mixing of CuNaY with Hox in air the colour of the sample turned from light blue to yellow green and in the EPR spectrum a broad signal with the values of g factors $g_1 = 2.158$ and $g_2 = 2.053$ was observed (Fig. 2 a).

CuNaY dehydrated at room temperature (mass loss was 11.4 %) showed a superposition of two axial EPR spectra with the parameters: I $A_{\parallel} = 13$ mT, $g_{\parallel} = 2.361$, $g_{\perp} = 2.069$; II $A_{\parallel} = 15.5$ mT, $g_{\parallel} = 2.323$, $g_{\perp} = 2.043$ (Fig. 1 b). After the reaction with Hox, an axial EPR spectrum with the parameters $A_{\parallel} = 18.5$ mT, $g_{\parallel} = 2.229$, $g_{\perp} = 2.060$ was observed (Fig. 2 b). The reaction was completed within one day after mixing CuNaY with Hox in vacuo and within ten days when the reaction proceeded in argon atmosphere.

CuNaY, dehydrated at 200 °C lost 24.9 % of its mass and exhibited a superposition of two EPR signals with the parameters: I $A_{\parallel} = 11.5$ mT, $g_{\parallel} = 2.382$, $g_{\perp} = 2.062$; II $A_{\parallel} = 15.5$ mT, $g_{\parallel} = 2.323$, $g_{\perp} = 2.036$ (Fig. 1 c). The reaction of CuNaY with Hox was completed within three days in vacuo. The EPR spectral parameters

of the formed complex are $A_\parallel = 18.4$ mT, $g_\parallel = 2.230$, $A_\perp(^{14}N) = 1.5$ mT, $g_\perp = 2.052$ (Fig. 2c). This spectrum was simulated with the program COMTAR [9]. When the reaction proceeded in argon atmosphere a presence of unreacted Cu(II) ions could be also observed in addition to the EPR spectrum of the $[Cu(ox)_2]$ complex even after three months.

CuNaY dehydrated at 400 °C lost 25.2 % of its mass and the parameters of its EPR spectrum were identical with those obtained for the sample degassed at 200 °C. The reaction of CuNaY with Hox also resulted in a complex having identical EPR spectral parameters. But in this case the reaction proceeded considerably slower than with the zeolite evacuated at 200 °C. When the reaction
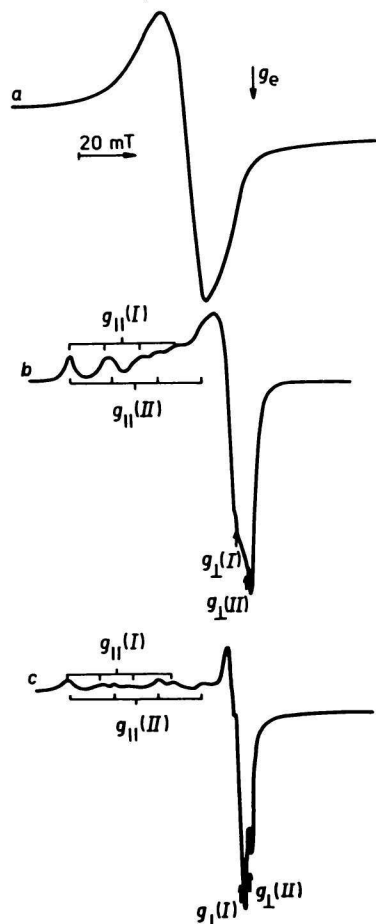

Fig. 1. EPR spectra of Cu NaY zeolite hydrated in air (a); dehydrated at 20 °C (b); dehydrated at 200 °C (c).
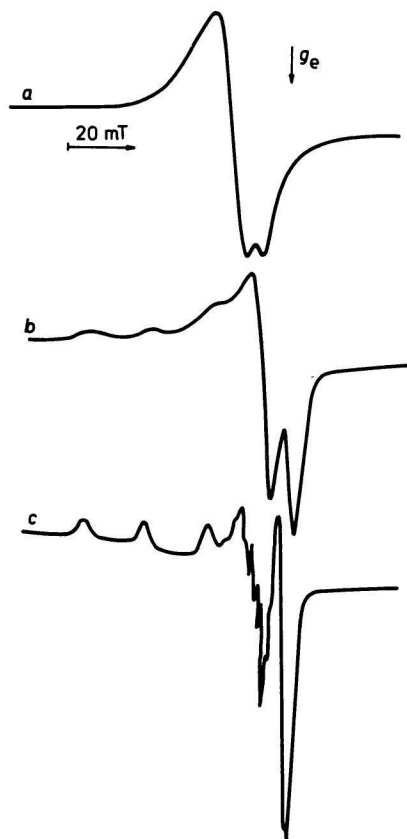
Fig. 2. EPR spectra of CuNaY zeolite after the reaction with 8-quinolinol: CuNaY hydrated in air (a); CuNaY dehydrated at 20 °C (b); CuNaY dehydrated at 200 °C (c).

was carried out *in vacuo*, the presence of small amount of unreacted Cu(II) besides the [Cu(ox)$_2$] complex could be observed even three months after mixing the starting substances. In argon atmosphere the most of the Cu(II) ions did not react with Hox even after three months and the EPR signal of the [Cu(ox)$_2$] complex was very weak.

The obtained surface [Cu(ox)$_2$] complexes can be extracted from the zeolite with organic solvents as chloroform, benzene or ethanol.

Discussion

The reaction of 8-quinolinol with Cu(II) ions exchanged in cavities of Y zeolite results in formation of bis(8-quinolinolato)copper(II) complex on zeolite. The EPR spectral parameters of the surface complexes are similar to those reported for this complex [10]. The water content in zeolite strongly influences the reaction rate of the complex formation as well as the mutual interactions of complex molecules on the surface.

The fully hydrated Cu(II) exchanged zeolite reacts immediately with Hox. 8-Quinolinol sublimes and the partial pressure of its vapour in air is sufficiently high to make possible a fast reaction of Hox with Cu(II) ions in zeolite. The EPR spectrum of obtained [Cu(ox)$_2$] complex is significantly influenced by exchange interactions operating between Cu(II) ions in surface complex molecules, which form associates. Such interactions smooth the hyperfine structure of the spectrum and only peaks that reflect "crystal" values of g factors appear [11, 12]. The van der Waals size of the planar chelate complex [Cu(ox)$_2$] is *ca.* 0.9×1.4 nm [13]. The formation of associates of such bulky complex molecules is not possible in the supercage of Y zeolite with a free effective diameter of *ca.* 1.3 nm [14], but only on the external surface of the carrier. The motionally averaged EPR spectrum of Cu(II) ions in the hydrated zeolite before its reaction with Hox shows that highly mobile [Cu(H$_2$O)$_6$]$^{2+}$ aqua complexes have been exchanged in the supercavities. They easily migrate towards the external surface of zeolite, where the complex [Cu(ox)$_2$] is formed by the reaction with Hox. Protons originating from Hox substitute Cu(II) ions for the charge compensation of the zeolite framework. As the surface is covered by a layer of adsorbed water molecules, the neutral complex molecules move in this layer and form associates.

As it has been shown [15, 16], in the process of dehydration, the Cu(II) aqua complex moves towards specific sites on the walls of the supercavity and loses its free mobility. With increasing dehydration, Cu(II) complexes with reduced water content are formed. They migrate towards specific positions in the sodalite cage and hexagonal prism of the zeolite [16]. The CuNaY zeolite dehydrated at room temperature contains a considerable amount of water. In the EPR spectrum of this

sample two axial signals of Cu(II) species located on two sites with different symmetries on the walls of the cage are observed. Spectra with such parameters can be assigned to distorted octahedral Cu(II) complexes (spectrum *I*) and distorted tetrahedral Cu(II) complexes (spectrum *II*) in zeolite [16]. This zeolite reacts readily with Hox and the complex [Cu(ox)$_2$] is formed. It exhibits an axial EPR spectrum with resolved hyperfine structure from copper nuclei in the parallel region. In contrast to the fully hydrated zeolite, the exchange interactions between Cu(II) ions are weak. The water content in zeolite is sufficient to make possible a migration of Cu(II) ions to the places, where they react with bulky molecules of Hox. But the water content is too low to make possible an effective association of the [Cu(ox)$_2$] molecules. We have no direct experimental evidence on the location of the [Cu(ox)$_2$] complex. Since its size is slightly greater than the free diameter of the supercavity and since it can be extracted from the carrier with organic solvents, we assume that [Cu(ox)$_2$] is located on the external surface of zeolite, where its solvation can take place.

The CuNaY zeolite degassed at 200 °C contains only a small amount of water. The EPR spectrum points to a presence of Cu(II) ions located on two sites with different symmetries in zeolite. Spectrum *I* can be assigned to distorted octahedral Cu(II) complexes and spectrum *II* to distorted tetrahedral Cu(II) complexes in zeolite [16]. The reaction with Hox results in a [Cu(ox)$_2$] complex with a resolved hyperfine structure from copper nuclei in parallel region of the EPR spectrum and from nitrogen nuclei in the perpendicular region. It is an indication that the exchange interactions between Cu(II) ions are further reduced in comparison with the sample degassed at room temperature. The strongly reduced water content allows only a slow migration of Cu(II) ions from the exchange sites on the walls of the cavities to the places, where [Cu(ox)$_2$] is formed. As the most water is removed from the surface, an effective axial interaction of planar chelate complex molecules with the oxygen atoms of zeolite can be assumed. The [Cu(ox)$_2$] molecules are segregated over the surface and do not form any associates.

The mass loss of 0.3 % of CuNaY zeolite under its heating between 200 °C and 400 °C can be explained by the full removing of physically adsorbed water. Infrared spectroscopy has shown [17, 18] that the physically adsorbed water was removed from NaY zeolite by evacuation at 300 °C and from CuY zeolite (fully exchanged with Cu(II) ions) at 230 °C. The parameters of the EPR spectrum of fully dehydrated CuNaY zeolite are identical with those obtained for CuNaY evacuated at 200 °C. It indicates the same location and coordination of Cu(II) ions in both samples. The reaction with Hox results in segregated [Cu(ox)$_2$] complexes bound to the surface of the carrier. However, the migration of Cu(II) ions is strongly hindered and the reaction with Hox proceeds very slowly. The reaction was not completed even after three months. It can be concluded that water molecules offer a convenient path for migration of Cu(II) ions in zeolite. It has been already

reported [5, 6] that the best conditions for the reaction of transition metal ions with chelating ligands are provided in partially dehydrated zeolites.

The reaction of Cu(II) exchanged zeolites with Hox proceeded considerably slower at higher partial pressure of argon in reaction mediums. Argon probably impedes the diffusion of Hox vapours to the places on zeolite, where $[Cu(ox)_2]$ is formed.

The rehydration of zeolites containing fixed segregated molecules of $[Cu(ox)_2]$ with atmospheric moisture leads to broadening of EPR spectra and smoothing of the hyperfine structure from nitrogen nuclei. If the zeolite samples with fixed complexes were suspended in water and then filtered off, broad lines typical of $[Cu(ox)_2]$ complexes with exchange interactions operating between Cu(II) ions were observed in the EPR spectra. The water molecules formed a layer on the surface of the zeolite and in this layer an association of the complex molecules took place.

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