Preparation of highly dispersed copper oxide by thermal destruction of binuclear Cu^{II} monofluoroacetate in zeolite Y cavities

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Thermal destruction of the binuclear monofluoroacetate complex $Cu_2(CH_2FCOO)_4$ deposited on zeolite Y was studied by the TG—DTA and ESR methods. Large particles of copper oxide are not formed and fine dispersion of CuO in the matrix is observed due to low temperatures of the destruction of the supported complex (240—250 °C) and restriction of the process mainly to large cavities of the zeolite.

Key words: clusters, zeolite, copper oxide, TG—DTA, ESR spectroscopy.

Nanoclusters of metals and oxides supported on materials with a developed surface are of great interest as highly active and selective catalytic systems whose properties are close to those of molecular catalysts due to the high dispersion of the particles of the active component. However, the conventional method for preparing supported catalysts by the reduction or oxidation of a precursor compound, which was pre-adsorbed on the support, to the metal or oxide does not provide a sufficiently high degree of dispersion of this component. Therefore, the method for preparation of cluster catalysts has received recognition in recent years. In this method, polymetallic homo- or heteronuclear complexes with labile organic or carbonyl ligands are used as precursors. These complexes decompose in reductive or oxidative media at comparatively low temperatures, which makes it possible to prepare systems with a highly dispersed metal or oxide.[1—5] At the same time, the use of zeolite molecular sieves as supports for the preparation of cluster systems provides additional advantages because the probability of the aggregation of the active component and loss of dispersion is much lower in micropores of these matrices than those in macropores of standard supports.

In this work, we studied the thermal decomposition of binuclear copper(II) monofluoroacetate adsorbed on zeolite Y in inert and oxidative media.

Experimental

Binuclear copper(II) monofluoroacetate tetrahydrate $Cu_2(CH_2FCOO)_4 \cdot 2H_2O$ was synthesized from monofluoroacetic acid and basic copper(II) carbonate according to the following procedure. A 50% aqueous solution of monofluoroacetic acid (a 1.5-fold excess as compared to the stoichiometric amount) was poured to copper carbonate. The resulting solution was evaporated *in vacuo* at 100 °C, and precipitated light-green crystals of the monohydrate were separated from the mother liquor and dried *in vacuo*.

Zeolite NaY with a SiO_2/Al_2O_3 molar ratio of 5 was used as the support. The powdered support was pressed to pellets that were calcined in air at 550 °C and crushed. The fraction of the zeolite particles 0.25—0.5 mm in size was used.

Copper monofluoroacetate was supported on zeolite from its aqueous solution by impregnation to incipient wetness. The amount of the complex in the solution used was selected to adjust the metal concentration in the sample (hereinafter designated as CuFAc/NaY) to ~1 wt.%. Chemical analysis showed that the obtained sample contained 1.1 wt.% copper.

Thermogravimetric and differential thermal analyses were carried out on a Netzsch STA-409 derivatograph in a flow of dry nitrogen or air (75 mL min^{-1}). A weighed air-dry sample was ~50 mg, and the heating rate was 2.5 deg min^{-1}.

ESR spectra were obtained on a Bruker EMX radiospectrometer in the X-range with a high-frequency modulation of 100 kHz. The values of g factors were determined by the simultaneous measurement of the frequency (SHF) and intensity of the magnetic field. ESR spectra were simulated, and double normalized integrals (DI/N) were calculated by the SYMFONIA and WIN-ERP programs (Bruker). ESR spectra of samples evacuated to a pressure of 10^{-5} Torr were recorded at 77 K. In addition, we obtained the ESR spectra of the individual starting complex $Cu_2(CH_2FCOO)_4$ supported from a dilute aqueous solution on an ashless paper filter followed by drying at 20 °C.

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Results and Discussion

The sorbate molecules of the precursor complex can freely enter the pores of the zeolite support and occupy positions in large cavities. The approximate estimation of the effective size of the $Cu_2(CH_2FCOO)_4$ molecule gives a value of ~0.5 nm, which is much less than the free diameter of the "windows" leading to the large cavities of zeolite. However, each cavity with a diameter of ~1.1 nm can accomodate at most two molecules of this size.

Since the copper concentration in the CuFAc/NaY sample amounts to 1 wt.%, the amount of the guest-complex in zeolite does not exceed 15 molecules per 100 large cavities (approximately two molecules per unit cell). For this arrangement of the complexes, the average distance between the $Cu_2(CH_2FCOO)_4$ molecules cannot exceed 2.5 nm. It follows from these estimations that the large cavity cannot contain more than one molecule of the complex and copper is present in the sample mainly as isolated binuclear complexes. The last conclusion is indirectly confirmed by the TG—DTA results presented in Fig. 1, in which the thermogravimetric data are presented as differential curves for clarity.

In the derivatograms obtained in both nitrogen and air (see Fig. 1), the first endothermic peak in the 50—200 °C interval with a maximum at 170 °C coincides with a similar peak in the DTG curve corresponding to a loss of ~25 wt.% of the sample, which allows us to attribute this peak to the removal of the physically sorbed water. However, the heating of the sample at higher temperatures in an inert and oxidative medium gives substantially different results. It is seen in Fig. 1 (curve *3*) that heating in nitrogen is accompanied by the appearance of a very broad exothermic peak in the 200—700 °C interval, and no change in the weight of the sample is observed in the temperature region of >400 °C. Therefore, the thermolysis of copper monofluoroacetate in an inert atmosphere affords only solid nonvolatile products: CuO and Cu_2O and, perhaps, metallic copper because the acetate groups can play the role of reducing agent. At the same time, the organic part of the metal complex intensely burns to form volatile products (carbon oxides and water) in the oxidative medium at 220—280 °C (Fig. 1, curve *4*), which is reflected in the DTG curve as an exothermic peak at 250 °C. It is noteworthy that the weight loss of the CuFAc/NaY sample containing 1.1 wt.% copper is 1.51 wt.% due to oxidation in the 220—900 °C interval; the theoretical weight loss upon complete conversion of the monofluoroacetate that is contained in this sample corresponds to 1.57 wt.%. This indicates that, on heating the CuFAc/NaY sample, trapped copper monofluoroacetate does not sublime and leave the zeolite support. Instead it undergoes thermolysis and oxidation.

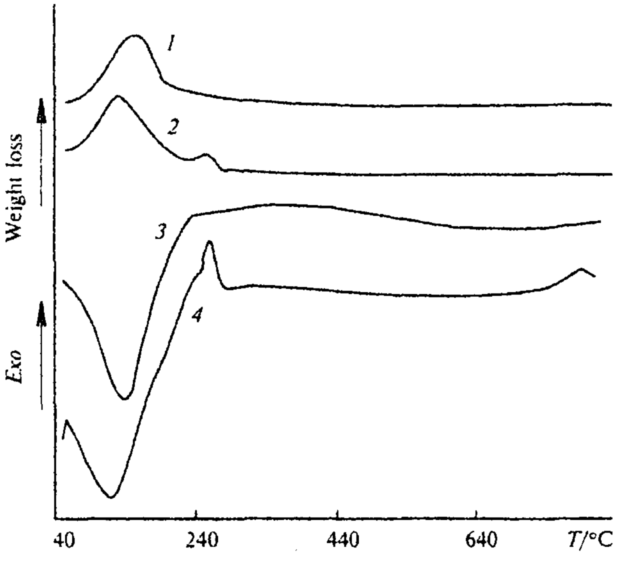

Fig. 1. DTG (*1*, *2*) and DTA curves (*3*, *4*) for CuFAc/NaY sample obtained in a nitrogen (*1*, *3*) and air (*2*, *4*) flow.

Thus, based on the thermogravimetric data, the thermal decomposition of Cu^{II} monofluoroacetate in the cavities of the zeolite support resembles that of copper acetate[6]:

$$2\ Cu(AcO)_2 = 3\ AcOH + 2\ Cu + CO_2 + C.$$

Under the oxidative conditions, the metallocomplex is completely transformed into the corresponding oxides without noticeable formation of fluorides.

The ESR method provides more detailed data on the valent and coordination state of the copper atoms in the starting complex and the products of its thermooxidative degradation. The experimental and model ESR spectra for the individual complex CuFAc, starting air-dry sample CuFAc/NaY, and samples obtained from the latter by various treatments are presented in Fig. 2, *a*, *b*; Fig. 2, *a* also shows schemes of transitions of the hyperfine structure (HFS) of the ESR spectra for the Cu^{II} ions. The parameters of the ESR spectra are presented in Table 1.

In detailed analysis of the spectra they can be assigned to the Cu^{II} ions that give a signal with the axial symmetry with the partially resolved HFS from the ^{63}Cu and ^{65}Cu nuclei.

The ESR spectrum of the individual complex $Cu_2(CH_2FCOO)_4$ supported on a paper from a strongly dilute aqueous solution (spectrum *1* in Fig. 2, *a*) is a superposition of two ESR signals (see Table 1: sample **1**, signals I and II). These signals are related to the isolated copper(II) ions with parameters characteristic of octahedral ligand coordination with slightly different tetragonal distortion.[7] This result is understandable if we keep in mind that binuclear Cu^{II} complexes partly transform into mononuclear complexes in dilute aqueous solutions.[8]

The deposition of the $Cu_2(CH_2FCOO)_4$ complex on zeolite NaY also can result in the appearance of signals

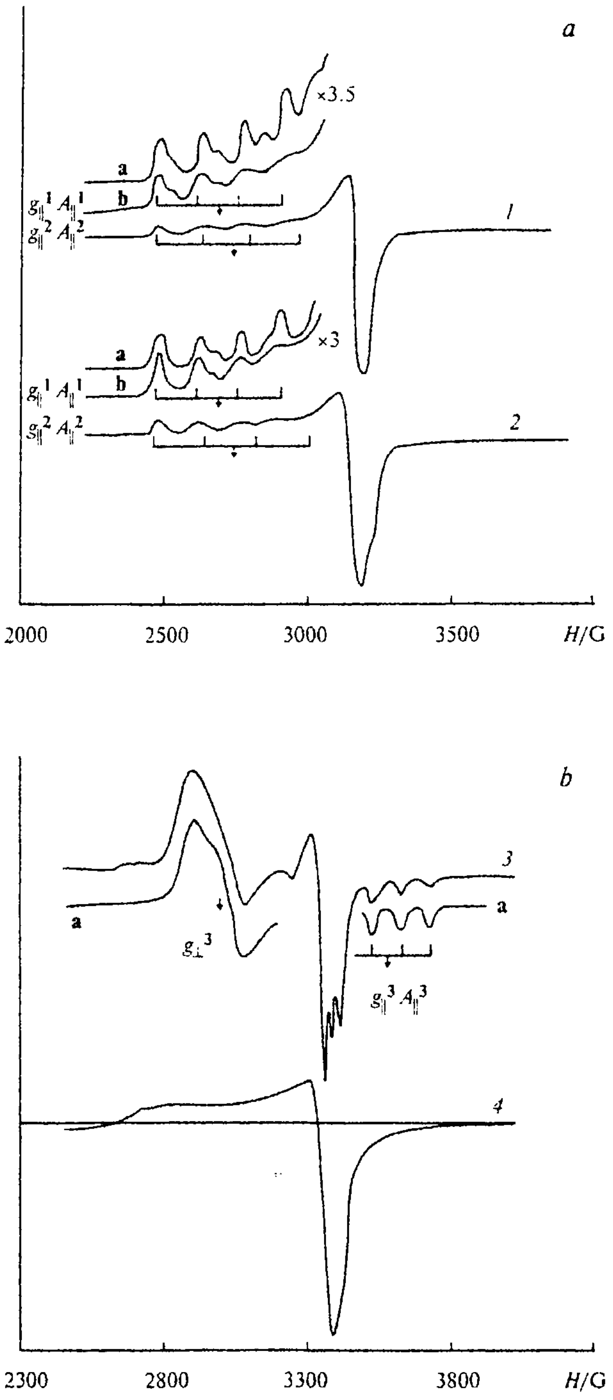

Fig. 2. ESR spectra of copper(II) ions in the $Cu_2(CH_2FCOO)_4$ complex (*a*) supported on a paper filter (*1*) and on zeolite NaY (*2*) and in the CuFAc/NaY sample (*b*) after oxidation in air at 300 (*3*) and 800 °C (*4*). The numbers of spectral curves correspond to the numbers of the samples in Table 1. The model spectra are shown by thin curves and designated by letter **a**, and the 3—3.5-fold amplified parts of the spectra are designated by letter **b**; some HFS transitions obtained by simulation are presented as schemes.

Table 1. Parameters of the ESR spectra of Cu^{II} for the starting complex $Cu_2(CH_2FCOO)_4$ and samples after various treatments

Sample	Conditions of treatment	Signal	$A_{\|}$ /G	$g_{\|}$	$g_{\perp}$	$DI/N \cdot 10^{-3}$
1	$Cu_2(CH_2FCOO)_4$	I	147	2.340	2.071	—
	on filter	II	136	2.375		
2	Air-dry	I	129	2.378	2.073	5.79
	CuFAc/NaY	II	173	2.325		
3	Oxidation	I	—	—	2.072	5.06
	of sample **2**	II	—	—		
	at 300 °C	III	98	1.940	2.305	
4	Oxidation of sample **3** at 800 °C	I	116	2.39	2.07	2.8

from two noticeably different copper ions (spectrum *2* in Fig. 2, *a*). One of the copper ions (see Table 1: sample **2**, signal I) retains the octahedral coordination with weak tetragonal distortion. The copper ions that occupy the S_{II} position in the zeolite Y structure give a similar signal. The signal from another copper ion (see Table 1: sample **2**, signal II) is close in spectral parameters to the signal from the planar-square Cu^{II} complexes observed[9] after deep dehydration of the ion-exchanged forms of zeolites CuX and CuY.

The oxidation of the sample in an air flow at 300 °C results in the appearance of a new signal from the paramagnetic centers (see Table 1: sample **2**, signal III) in the ESR spectra (spectrum *3* in Fig. 2, *b*). This signal is characterized by an inverse ratio of the components of the *g* factor ($g_{\perp} > g_{\|}$) as compared to those in the initial spectra. This indicates that the local symmetry of the copper(II) cations substantially changes during the oxidative decomposition of the complex inside the zeolite cavity.

After the oxidation of the sample at 800 °C, signal III disappears and the ESR spectrum is broadened but still retains all specific features of the spectra characteristic of isolated copper ions (spectrum *4* in Fig. 2, *b*). Due to the strong broadening of the HFS components, it is difficult to determine the ESR parameters of these centers, and their approximate estimations are presented in Table 1 (sample **4**). Note that no ESR signal that could be assigned to large agglomerates including Cu^{II} ions was observed under any conditions of thermal treatment of the sample.

Thus, our data indicate that the copper oxide formed by thermal oxidative decomposition of Cu^{II} monofluoroacetate pre-adsorbed in large cavities of zeolite Y occurs in a highly dispersed state close to molecular dispersion, which persists even after high-temperature oxidative treatment.

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