Preparation and properties of highly dispersed copper oxide in a zeolite matrix*

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Highly dispersed CuO clusters inserted into a zeolite matrix were prepared by oxidative degradation of the $(\mu_4\text{-O})L_4Cu_4Cl_6$ tetranuclear complex (L is *N,N*-diethylnicotinamide) preadsorbed on a dehydrated NaX zeolite from a solution in anhydrous dichloromethane. The catalytic activity of the CuO/NaX catalyst thus obtained in the oxidation of CO is an order of magnitude higher than that of massive CuO.

Key words: zeolites, clusters, metal complexes, carbon monoxide, oxidation, catalysis by copper oxide, active oxygen.

Small clusters of metals or metal oxides constitute a valuable group of catalytic systems. These systems behave as typical molecular catalysts, because the particles of the active component are uniform. As a rule, cluster catalysts exhibit high specific activities (per unit weight), because the active component is highly dispersed.[1,2]

A conventional method for the preparation of cluster catalytic systems is based on thermal or redox decomposition of polynuclear complexes of transition metals with sufficiently labile ligands after their preliminary adsorption on supports.[3,4] Since a complex precursor can be converted into the active component of a catalyst at a low temperature, aggregation and enlargement of small particles of metal or metal oxide during the preparation is avoided, and this ensures a high degree of dispersion of this component. For example, tetranuclear complex $(\mu_4\text{-O})L_4Cu_4Cl_6$ (L is *N,N*-diethylnicotinamide), whose ligands are fairly labile and can be removed at temperatures below 100 °C, can serve as the precursor.[5] When a solution of this complex in an aprotic medium is brought into contact with a zeolite, only the core of this complex, $(\mu_4\text{-O})Cu_4Cl_6$, is adsorbed on the molecular sieve even at room temperature. The subsequent reduction or oxidation of this core affords a metallic or oxide tetranuclear cluster, respectively.[6]

Zeolites have some advantages as matrices for the preparation of cluster catalysts over macroporous solids, and their use opens wide opportunities for combining high activity of clusters with the molecular-sieve effect of the support in catalytic reactions.[7]

In the present study, we synthesized and studied the catalytic systems based on a type X zeolite and the Cu^{II} tetranuclear complex mentioned above.

Experimental

The initial copper complex $(\mu_4\text{-O})L_4Cu_4Cl_6$ (L is *N,N*-diethylnicotinamide) was prepared by a procedure described previously.[8] The NaX zeolite (with a $SiO_2 : Al_2O_3$ ratio of 2.3) was used as the matrix. A powder of the air-dried zeolite was pressed in pellets without a binder, calcined for 6 h at 550 °C, cooled, and crushed; for the subsequent work, granules with a size of 0.5—1 mm were selected. Dichloromethane was washed with concentrated H_2SO_4 and water and dried over a calcined CaA sieve.

Granules of NaX (~3 g) were dehydrated *in vacuo* for 6 h at 450 °C, cooled to ~20 °C, and transferred into a dry box that had been purged with dry nitrogen for 12 h. All the subsequent operations were performed in this box. A solution containing the Cu complex (1.33 mmol) in anhydrous CH_2Cl_2 was added at ~20 °C to ~1 g of the zeolite. Then the support with the adsorbed complex was separated from the mother liquor, washed with the solvent, and dried for 12 h at 60 °C and 10—15 Torr. After that, the zeolite with the adsorbed complex was kept for 10 h in a flow of oxygen at 220 °C. Similar operations were carried out using two more samples of the zeolite (1 g each) and 0.66 and 0.33 mmol of the complex, respectively. The resulting catalysts were analyzed for copper by dissolving a weighed portion of the material in a mixture of concentrated H_2SO_4 and HNO_3 followed by spectrophotometry of this solution in the presence of pyridylazoresorcinol.[9]

The content of active oxygen in the samples was determined by high-temperature "titration" with carbon monoxide. The catalyst (~100 mg) was placed in a quartz reactor (3 mm i.d.) and kept for 2 h at 450 °C in a flow of dry N_2 (30 mL min^{-1}). After that, 8—10 pulses of pure CO were introduced into the flow of the carrier gas, and the amount of

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CO_2 evolved was determined by GLC. A blank experiment was carried out under similar conditions using pure NaX zeolite.

The model reaction of oxidation of CO with molecular oxygen was studied in a gradientless reactor at 450 °C and an overall pressure of 0.103 MPa. A weighed portion of the catalyst was placed in a glass reactor, and the temperature was increased to 550 °C in a flow of dry air purified from CO_2; this flow was passed at this temperature for 2 h, then the reactor was cooled to the working temperature, and a stoichiometric mixture of thoroughly dried CO and O_2 was introduced; the flow rate of the reagents was 2420 $cm^3\ h^{-1}\ g^{-1}$. Gradientless conditions, which was ensured by a recirculation ratio (the ratio of the velocities of the flow and circulation) of ≥200. The composition of the reaction mixture was determined by GLC; the total degree of conversion found from the difference between the concentrations of CO at the inlet and the outlet of the reactor was no more than 15% in all cases; this was attained by choosing appropriate weight portions of the catalyst.

The catalytic activity of the samples was characterized by the rate of oxidation of CO, which was calculated using the averaged results of 8—10 analyses of the reaction mixture performed during the first two hours of the experiment from the following equation:

$$r = v_0 \cdot C_0 \cdot y,$$

where r/mmol $s^{-1}\ g^{-1}$ is the reaction rate; v_0/$cm^3\ s^{-1}\ g^{-1}$ is the flow rate of the reaction mixture; and y is the degree of conversion. The reaction rate found in this way depends only on the velocity of the introduction and does not change upon variation of the velocity of circulation; this is a sufficient criterion for providing gradientless conditions in the reaction system.

In addition to the catalysts based on the zeolite support, a sample of CuO was also studied; this sample was prepared by treatment of a solution of $Cu(NO_3)_2$ with an equivalent quantity of ammonia followed by drying of the precipitate, calcination in air for 10 h at 800 °C, and grinding to a particle size of 0.5—1 mm. The specific surface area of the CuO sample prepared by this procedure was found to be 8.6 $m^2\ g^{-1}$ based on the adsorption of nitrogen at 77 K.

Results and Discussion

The results of chemical analysis of CuO/NaX samples are presented below:

Catalyst	3CuO/NaX	9CuO/NaX	14CuO/NaX
CuO (% (w/w))	3.36	9.44	14.30.

Copper oxide can be quantitatively supported on the zeolite by varying the precursor/support ratio at the first stage of the preparation of the catalyst. An oxygen storage capacity (OSC) for the samples studied determined by high-temperature "titration" of the catalysts by carbon monoxide (Table 1) with the contents of copper in these samples indicates that the OSC per 1 g of the catalyst for CuO/NaX is rather close to that for individual copper oxide, although the quantities of the CuO itself in these systems differ, at least, by an order of magnitude. An even more unexpected finding is that almost all the oxygen incorporated in the CuO particles on the zeolite support reacts with CO. Evidently, this is due to the fact that copper oxide in CuO/NaX is highly dispersed; thus, one can expect that these catalysts would exhibit abnormally high activities in the oxidation of CO.

Table 1. Content (mmol g^{-1}) of active oxygen and copper in the samples

Catalyst	O	Cu	Cu : O*
CuO/NaX	0.40	0.42	1.05
9CuO/NaX	1.04	1.19	1.18
14CuO/NaX	1.53	1.86	1.22
CuO	1.04	12.60	12.10

* Atomic ratio.

Table 2. Catalytic activity of samples in the oxidation of CO at 450 °C

Catalyst	Reaction rate/mmol s^{-1}		ACA*
	per g of the Cat	per g of CuO	
3CuO/NaX	$0.75 \cdot 10^2$	$2.23 \cdot 10^3$	$1.78 \cdot 10^2$
9CuO/NaX	$1.84 \cdot 10^2$	$1.95 \cdot 10^3$	$1.55 \cdot 10^2$
14CuO/NaX	$2.01 \cdot 10^2$	$1.36 \cdot 10^3$	$1.08 \cdot 10^2$
CuO**	19.40	19.40	$3.00 \cdot 10^2$

* The atomic catalytic activity is exspressed in molec. s^{-1} (at Cu)$^{-1}$.

** The calculation was carried out under the assumption that the surface concentration is $5 \cdot 10^{18}$ of Cu atoms m^{-2}.

In fact, the activity of CuO/NaX per 1 g of the catalyst (Table 2) proves to be 4—10 times higher than the corresponding value found for bulk CuO. This result is in good agreement with the data on the OSC in these samples (see Table 1), which is additional evidence of the highly dispersed state of copper oxide in CuO/NaX.

It is also noteworthy that the atomic catalytic activities (ACA) of CuO/NaX and CuO related to one active site, which is represented apparently by a copper atom incorporated into an oxide cluster, are, conversely, values of the same order of magnitude (see Table 2). It should be emphasized that comparison of these materials based on their specific catalytic activities (SCA), *i.e.*, activities related to a unit surface area, are in this case not valid, since for microporous zeolites and catalysts based on them, the specific surface area, which is found, for example, from the adsorption of N_2, is only an effective characteristic having no sufficiently clear physical meaning, as in the case of meso- and macroporous solids. For this reason, we did not estimate SCA for the systems considered in this study.

It was of interest to compare the present results for the oxidation of CO in the presence of the catalysts under consideration with the data obtained previously[10] for the copper forms of Y type zeolites (CuY) and for individual copper oxide. It was found previously[10] that the values of ACA per surface Cu atom for CuY are 2—5 orders of magnitude smaller than those for CuO.

Similar results for the ion-exchanged copper-zeolite catalysts were also obtained by other researchers,[11,12] who found that the differences between the ACA of zeolites and individual copper oxide, manganite, and copper chromite amount to 2—4 orders of magnitude. The results obtained[10—12] indicate that, first, the oxidation of CO involves the O atoms of the solid surface, *i.e.*, a stepwise mechanism of catalysis is realized, and, second, the mobility of the O atoms of the zeolite framework at temperatures of the catalytic reaction is much lower than that of the oxygen atoms in oxides and spinels. This, in turn, implies that the high activity of the CuO/NaX catalysts studied in this work is not due to the presence of Cu atoms as exchange cations that could have resulted from the solid-phase ion exchange between CuO and the zeolite matrix.[13,14]

On the other hand, owing to the features of copper cationic forms of zeolites, "nonequivalent" ion exchange can hardly be avoided during their preparation. Consequently, copper is not only incorporated in the zeolite as individual Cu^{2+} ions but also forms structures like $Cu^{2+}—O^{2-}—Cu^{2+}$ in which the bridging O atom is much more mobile than the framework oxygen. The presence of these extra-lattice O atoms in zeolites containing transition metal ions has been proved by ESR, IR, and Mössbauer spectroscopy and by magnetic measurements.[15—18]

The presence of the extra-lattice oxygen in the zeolite catalysts accounts, in particular, for the increase in the ACA with respect to the oxidation of CO for the samples of copper-containing zeolites, characterized by close total contents of copper but obtained at different pH of the exchange solutions. The maximum ACA value for the Cu-zeolites amounts to $0.9 \cdot 10^2$ mmol s^{-1} per copper atom[18] and is achieved when the pH of the exchange solution is higher than 8; for the sample of individual CuO, the ACA is $2.8 \cdot 10^2$ mmol s^{-1} per Cu atom.[18] Comparison of these values with the ACA found in this study for CuO/NaY samples and for individual CuO (see Table 2) shows that they are fairly close. Thus, it can be concluded that the nature of the active sites of the CuO/NaX catalysts synthesized by the oxidative degradation of the metal complex precursors is apparently similar to that of the Cu-zeolites in which copper occurs, at least partly, as bridged cluster structures.

Thus, our results together with those obtained in the previous study[18] in which the catalytic oxidation of CO was carried out in the presence of Cu-containing systems prepared by various methods can be regarded as one more example illustrating G. K. Boreskov's fundamental idea that the catalytic activity of atoms of a particular element incorporated in various structural fragments of a solid does not depend on the method used for the preparation of the catalyst and is essentially constant, and the efficiency of the unit weight of the catalyst is determined only by the specific surface area.

At the same time, the trend of the ACA values to decrease with increasing the content of CuO in the CuO/NaX samples (see Table 2) indicates that the diffusional restriction for the reactant molecules in narrow channels of the zeolite matrix is also significant. This finding can be regarded as indirect evidence supporting the assumption that clusters of the active component are localized in micropores rather than on an external surface of the zeolite matrix. In addition, it provides an explanation for the fact that the ACA values of Cu-containing zeolite catalysts are lower than those for individual copper oxide (see Table 2 and published data[18]). In fact, owing to diffusion retardation in the micropores of a zeolite matrix, the ACA value found experimentally can be markedly underestimated as compared to the value found for a nonporous catalyst, copper oxide. From this viewpoint, it would obviously be of interest to use mesoporous systems such as the MSM-41 type molecular sieves as supports, because in the channels of these materials the diffusion limitations can be minimized and cluster catalytic systems can exhibit their maximum potential.

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