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The Nature of Cu/ZSM-5 Catalyst Activity in NO Reduction by Propane

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Copper(II) ions on the surface of Cu/ZSM-5 are found to be active sites for NO reduction by propane in an oxidizing atmosphere.

Copper ion-exchanged zeolites Cu/ZSM-5 have been reported to be highly active both for direct decomposition of NO[1–3] and for catalytic reduction of NO by hydrocarbons or CO in an oxidizing atmosphere.[4,5] However, the nature of the surface sites which are active in these reactions, as well as the reaction mechanisms, are not yet well understood.[6–8] In this paper we attempt to describe the different states of copper ions in ZSM-5 zeolites and to explain their role in the catalytic reduction of NO by propane in the presence of oxygen.

Copper-containing samples were prepared (see ref. 9) based on HZSM-5 zeolites (SO_2:Al_2O_3 ratio 40) with 0.15–2.8% copper and on NaHZSM-5 zeolite with 2.86% copper. They will subsequently be referred to as CuZ(1) and CuZ(2). The activity of these samples in NO reduction by C_3H_8 was tested in a mixture of 0.1% NO, 0.08% C_3H_8 and 5% O_2 at space velocity 20 000 h^{-1}. The reagents and products were analysed chromatographically and by a Beckman gas analyser. The experiments were carried out on catalysts pre-oxidized (873 K, O_2, 1 h) and pre-reduced (823 K, H_2, 1 h) *in vacuo* or under flow conditions. Coordination of isolated Cu^{2+} ions was determined by EPR at room temperature. The quantity of Cu^{2+} ions was obtained from a correlation between the integrated EPR spectrum and the spectrum of $CuSO_4{\cdot}5H_2O$. The quantity of Cu^+ ions was obtained from TPD spectra after CO adsorption (it is well known[5] that at temperatures >300 K, CO forms strong bonds only with Cu^+ ions). The amount of associated copper (Cu_{as}) in the oxidized catalysts or of metallic copper in the reduced ones was determined as

Table 1 NO conversion on Cu/ZSM-5 zeolites.

Zeolite	Copper concentration (wt.%)	NO conversion (%)		
		673 K	773 K	873K
CuZ(1)	0.15	15	22	28
	1.3	40	47	35
	1.7	35	60	55
	2.8	30	65	63
CuZ(2)	2.86	0	30	35

the difference between the total amount of copper and the sum of Cu^{2+} and Cu^{+}. EPR, TPD and IR spectroscopy were used to study the reagent molecules during their interaction with the catalyst.

The activity of catalysts studied at various amounts of copper and temperatures is presented in Table 1. It is seen that at temperatures >673 K, NO reduction is rather effective. It should be noted that the conversion of NO does not depend strongly on the amount of copper in the sample if the concentration of copper is $>1\%$. Clear zeolites (without copper) are practically inactive at 673–873 K. After catalytic testing the gas mixture was pumped or substituted by N_2 gas and the EPR spectrum of the catalyst was studied. The quantity of Cu^{2+} ions in the samples after reaction and after oxidation at 873 K are practically the same. This fact allows us to suggest that the oxidized state of Cu^{2+} is an active site in the catalysts.

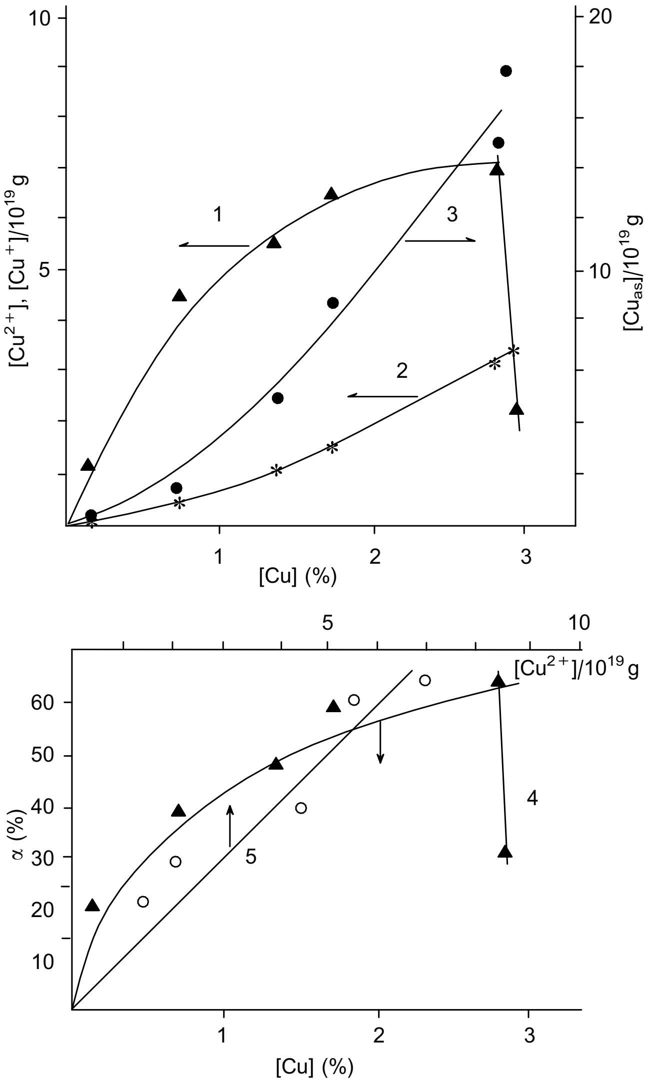

Fig. 1 The distribution of copper states: 1, Cu^{2+}; 2, Cu^{+}; 3, Cu_{as} and NO conversion at $T = 773$ K *versus* 4, Cu and 5, Cu^{2+} concentration in oxidized samples.

To check this assumption we have investigated the state of copper over the oxidized sample *in vacuo*. The EPR spectra showed that the bivalent copper in the CuZ(1) samples was located in square pyramidal and square plane configurations. Cu^{2+} ions in the CuZ(2) sample were detected only in a square pyramidal configuration. In Fig. 1, the quantity of different Cu ions is plotted *versus* the copper concentration in the samples. It is seen that NO conversion correlates well with Cu^{2+} ion concentration in the samples (curves 1, 4 and 5). To explain this correlation we have studied the interaction of different copper ions with reagents.

We did not manage to record the absorption bands of nitrosyl complexes in the transmission and diffuse reflectance IR spectra (NO content in the flow was changed from 0.1–20%, temperature from 300–783 K, the state of samples from oxidized to reduced). Only absorption bands of nitrate–nitrite surface complexes (1570 and 1430 cm^{-1}) were recorded. At the same time, in the TPD spectra of NO at least three peaks at $T_m = 350$, 420 and 650 K were observed. The first peak (at 350 K) is due to NO desorbed from zeolite because it was also detected on zeolite without copper. The second NO peak was detected at 410–430 K. Its intensity correlates well with the quantity of Cu^{+} ions in the sample. The peak intensity increased during the reduction of the samples or on increasing the copper concentration. The nitrate–nitrite complexes decompose at 650 K with the release of NO and NO_2 at 650 K (the third peak).

Adsorption of NO at room temperature causes a decrease in the Cu^{2+} signal in the EPR spectra. The lines of the spectrum associated with hyperfine interaction between the unpaired electron and the copper nucleus ($I = 3/2$) disappear. This effect can be explained by dipole–dipole interaction in the weak NO–Cu^{2+} complex (it is destroyed during pumping at 300 K). The EPR signal of the NO–Cu^{+} complex has been studied at $T = 77$–273 K.[10] We did not observe it at $T > 293$ K; the same effect is observed during adsorption of O_2, but in TPD spectra the O_2 peaks are absent.

The interaction of O_2 and NO with the samples at the reaction temperature is entirely different. In Fig. 2, the intensity of the EPR signal of Cu^{2+} ions is plotted *versus* the number of NO or O_2 pulses supplied to the reduced 1.3%

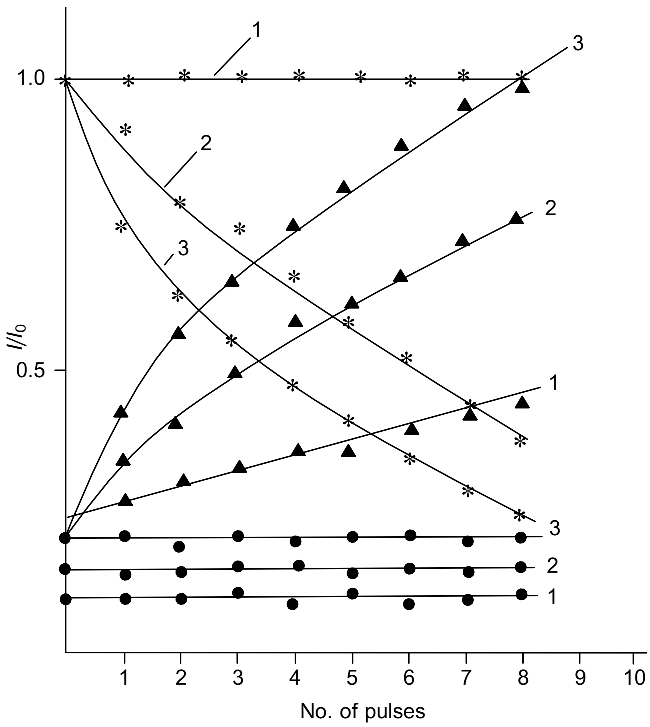

Fig. 2 The intensity of the EPR signal of 1.3% CuZ(1) sample at $T = 293$ K and $P = 10^{-4}$ Pa after treatment with pulses of gases: O_2 (▲) and NO (●) at various temperatures: 1, 470 K; 2, 693 K; 3, 853 K, and C_3H_8 (*): 1, 593 K; 2, 723 K; 3, 943 K.

CuZ(1) at different temperatures. The pressure in the pulse was $P = 1.3$–133 Pa and exposure time $t = 5$ min. After exposure gas was pumped and the pressure was maintained at 10^{-4} Pa. It is evident that the NO adsorption does not cause any increase in the Cu^{2+} signal, *i.e.*, NO does not oxidize the reduced copper. Oxygen from the pulses is strongly adsorbed and the EPR signal of Cu^{2+} ions increases (see Fig. 2). Similar results were also obtained for other samples.

All the data discussed allow us to suggest that the activation of NO and O_2 over the samples studied is not due to the presence of Cu^{2+} ions in the sample. The activation occurs when NO interacts either with zeolite itself or with Cu^{+} ions. This is also confirmed by other investigations.[2,3] The activation of O_2 is likely to occur when oxygen interacts with reduced forms of Cu (Cu^{+}, Cu^{0}).

TPD spectra, after C_3H_8 adsorption at room temperature on pre-oxidized or pre-reduced samples, revealed one peak of C_3H_8 at $T_m = 370$ K. The same peak is also observed after C_3H_8 adsorption on the zeolite without copper. We did not record any absorption bands in the IR spectra after adsorption of C_3H_8. In Fig. 2, the intensities of EPR signals are plotted *versus* the number of C_3H_8 pulses ($P = 1.3$ Pa, $t = 5$ min) fed to the oxidized sample at different temperatures. It is seen that the EPR intensity of Cu^{2+} ions starts to change only after heating of the sample to 600 K. In this case, as in the case of the catalyst interaction with hydrogen the reduction of Cu^{2+} ions occurs.

All the data obtained allow us to draw some conclusions concerning the observed correlation between the activity of the catalysts in the NO reduction by propane and the concentration of isolated Cu^{2+} ions in the samples. It is clear that the rate of NO reduction is not determined by activation of NO molecules during adsorption. It probably depends upon the rate of the sequential transformation of adsorbed species over isolated Cu^{2+} ions. We cannot totally deny the influence of synergetic effects during the reaction of the real gas mixture with the catalyst. Note also that our investigation does not support conclusions about active surface carbon-containing particles.[6] No active carbon particles were found by EPR in the catalyst after reaction.

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