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Effect of copper cations on the formation of radicals in the adsorption of olefins and benzene on Cu/ZSM-5 zeolite

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Isolated Cu^{2+} cations in ZSM-5 zeolite produced oligomeric radicals from propylene and did not result in the formation of radicals in the adsorption of ethylene and benzene.

Nitroxyl organic compounds were asserted[1] to play an important role in the selective catalytic reduction of NO_x by hydrocarbons in an excess of oxygen. Oligomeric radicals can participate in the formation of nitroxyl compounds. Oligomeric radicals were observed on H-ZSM-5[2] and Cu/ZSM-5[3] zeolites. However, the role of copper cations in the formation of oligomeric radicals in the adsorption of olefins was not studied. This work is devoted to this problem.

The preparation of zeolites and the EPR procedure are described in detail elsewhere.[4] EPR measurements were carried out *in vacuo* ($P = 10^{-4}$ Pa) at room temperature in H-ZSM-5 ($SiO_2/Al_2O_3 = 40$) and 0.15–2.86% Cu/ZSM-5 zeolites after the treatment with oxygen at 970 K and $P = 200$–500 Pa for 1 h. The concentrations of adsorbed molecules were determined by hydrocarbon desorption upon heating of the samples to 800 K.

The EPR spectra of oligomeric R· and benzene $(C_6H_6)\cdot$ radicals (Figure 1, curves *1* and *2*) were observed during adsorption of olefins (C_2H_4 or C_3H_6) and benzene at room temperature and $P = 200$ Pa on the H-ZSM-5 sample. The concentration of radicals in the sample was determined by double integration of the EPR spectrum followed by the comparison with the data obtained using $CuSO_4 \cdot 5H_2O$ and Mn^{2+}–MgO reference samples. The A value [hyperfine coupling constant (HFC)] was calculated from the ratio $A = (H_n - H_1)/(n - 1)$, where H_1 and H_n are the field strengths for the first (1) and last (n) lines of the HFC spectrum. The radical concentrations and g and A values are presented in Table 1. Similar spectra and parameters have been obtained previously.[2,5,6]

The oligomeric radical is stable, because its spectrum (Figure 1) remained unchanged after evacuation of the olefin. The intensity of the spectrum of the benzene radical decreased by a factor of 10 when C_6H_6 was evacuated for 10 min. The spectra of oligomeric radicals can be observed within the temperature range 300–450 K. Curve *1* in Figure 2 presents the intensities of the spectrum of the radical (J/J_{max}) observed after heating of the sample *in vacuo* for 10 min. The repeated adsorption of the olefin on the sample heated at temperatures higher than 450 K does not result in the formation of radicals.

The introduction of copper into H-ZSM-5 zeolite by ion exchange produces isolated Cu^{2+} cations, which are localized near lattice Al^{3+} cations.[7] The spectrum for the 1.3% Cu/ZSM-5 sample is presented in Figure 3 (curve *1*). An analysis of the spectrum shows that copper cations in zeolite occur in both square pyramid [$g_{\|}^{(1)} = 2.33$, $A_{\|} = 170$ G] and square planar [$g_{\|}^{(2)} = 2.29$, $A_{\|} = 180$ G] coordination. The admission of propylene at $T = 293$ K decreased the intensity of the signal from copper cations (Figure 3, curve *2*), and the spectrum of the oligomeric R· radical appeared. The spectra of the R· radicals on H-ZSM-5 and 1.3% Cu/ZSM-5 coincide. In addition, the intensity of the signal of the R· radicals decreased as the sample was heated *in vacuo*. These data are similar to those for H-ZSM-5 (Figure 2, curve *2*). These data indicate that the oligomeric radicals are localized at analogous sites in zeolite channels.

The dependences of the concentrations of the radicals on the copper content in the sample in the adsorption of propylene and benzene are presented in Figure 4. It can be seen that the presence of copper in zeolite exerts different effects on the formation of R· and $(C_6H_6)\cdot$ radicals. For example, the concentration of R· radicals increased by an order of magnitude as the copper content in the sample increased from 0.15% to 1.3%. A further increase in the copper content in the sample resulted in a decrease in the EPR signal from the R· radicals and in changes in their spectra, which are manifested as the disappearance of HFC lines.

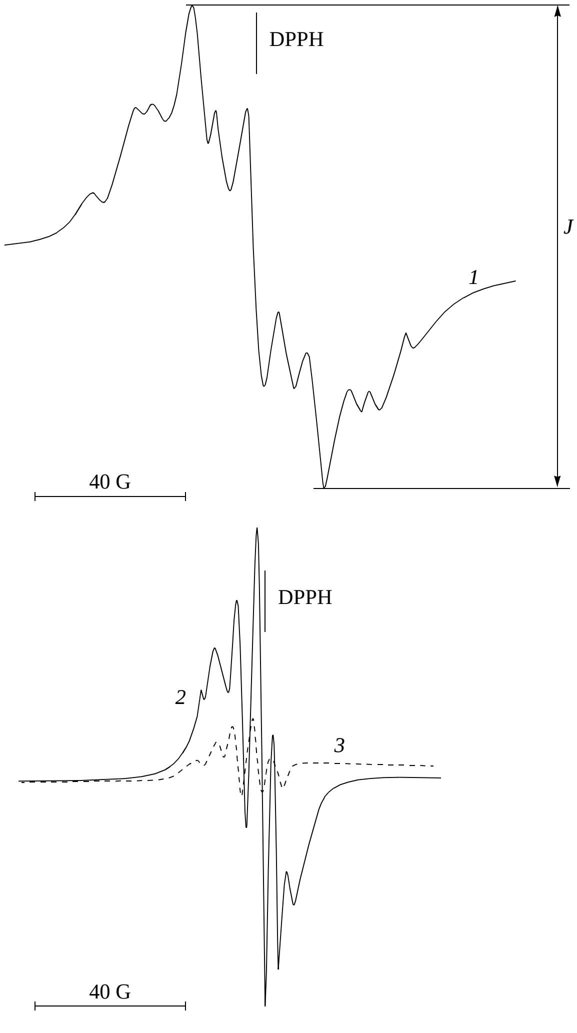

Figure 1 EPR spectra of (*1*) the oligomeric radical after propylene adsorption and the $(C_6H_6)\cdot$ radical (*2*) in a benzene atmosphere and (*3*) after evacuation of benzene at 293 K.

Table 1 Concentrations of adsorbed molecules and radicals on H-ZSM-5 zeolite.

Molecule	$N_{ad}/10^{-20}$ g^{-1}	Radicals	$N_s/10^{-15}$ g^{-1}	g	A/G
C_2H_4	0.5	R	7.0	2.004	8.0
C_3H_6	6.0	R	8.7	2.004	8.0
C_6H_6	4.0	(C_6H_6)	7.4	2.004	4.5

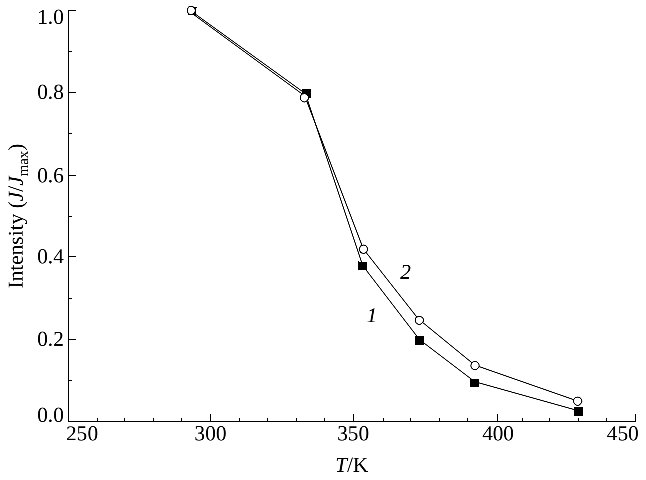

Figure 2 Relative intensities of the spectrum of R· radicals on (*1*) H-ZSM-5 and (*2*) 1.3% Cu/ZSM-5 after heating of the samples at different temperatures *in vacuo* for 10 min.

In the case of benzene, an increase in the copper content in zeolite resulted in a decrease in the concentration of benzene radicals. Seven HFC lines were observed only in the spectra of the radical on 0.15–0.25% Cu/ZSM-5 samples, whereas they were not observed in the samples with the copper content of 1.3–2.86%.

In the ethylene adsorption, the concentration of the oligomeric radicals decreased, as in the case of benzene radicals, with increasing copper content in the samples.

Note that oligomeric radicals are formed in the adsorption of propylene on reduced Cu/ZSM-5 samples, whereas no radicals were observed in the adsorption of the hydrocarbons on H-ZSM-5 zeolite heated in H_2 (970 K, P = 200 Pa, 1 h).

Olefinic and benzene radicals are formed at the sites created upon heating of H-ZSM-5 zeolite in oxygen at $T > 600$ K (oxidative centres), and they are deactivated by hydrogen under these conditions. The nature and properties of these oxidative centres were considered in refs. 8 and 9. We believe that these centres are formed due to the cleavage of stressed Si–O–Al bonds. The concentration of these centres in H-ZSM-5 zeolite (SiO_2/Al_2O_3 = 40) can be estimated from the concentration of the radicals observed. It does not exceed 10^{16} g^{-1} (Table 1). This value is 0.02% of the concentration of Al^{3+} cations in the zeolite, which is consistent with the concentration of oxidative centres in H-ZSM-5 estimated in ref. 9.

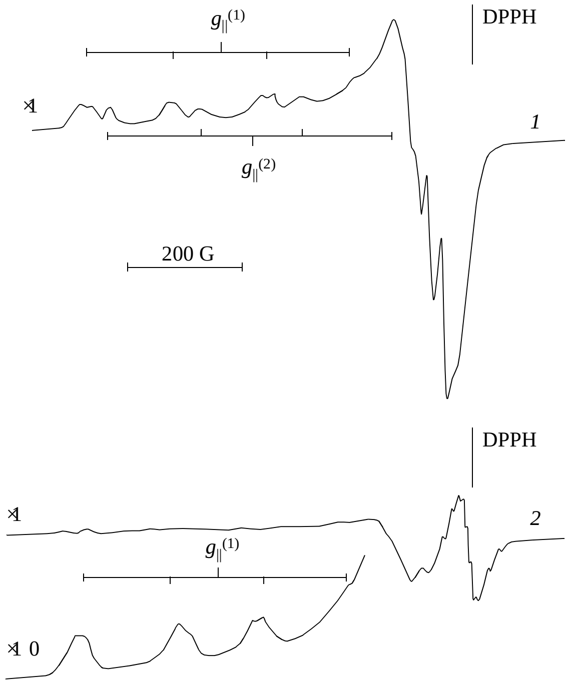

Figure 3 EPR spectra of (*1*) pre-oxidized 1.3% Cu/ZSM-5 zeolite and (*2*) the sample after adsorption of propylene at 293 K and P = 200 Pa.

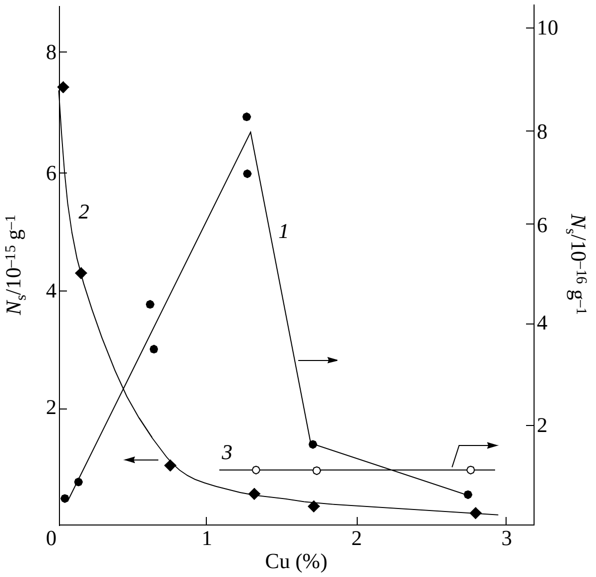

Figure 4 Dependences of the concentrations of (*1*) oligomeric radicals and (*2*) (C_6H_6)· radicals for oxidized samples and of (*3*) oligomeric radicals for reduced samples on the copper concentration.

When copper ions are introduced into H-ZSM-5, some of them interact with the oxidative centres to change the capability of generating radicals. The newly formed surface centres lose the ability to generate radicals upon interaction with benzene and ethylene.

The study of the copper state in oxidized 0.15–2.86% Cu/ZSM-5 zeolites shows[4] that the concentration of isolated copper cations linearly increased with the copper content of the zeolite. The concentration of oligomeric radicals also increased (Figure 4). A decrease in the concentration of isolated Cu^{2+} cations in the 1.3% Cu/ZSM-5 sample during its thermal treatment with hydrogen also results in a decrease in the concentration of radicals (Figure 4, curves *1* and *3*). This fact suggests that oligomeric radicals are formed at isolated Cu^{2+} cations during propylene adsorption.

The fact that isolated copper ions did not produce radicals during the interaction with benzene and ethylene and did form them during the interaction with propylene can be explained by the difference in the ionization potentials of the molecules,[2] which is higher for benzene and ethylene than for propylene.

We have found previously[4] that isolated Cu^{2+} cations are the active centres for NO reduction on copper-containing zeolites. The measurements in 1.3% Cu/ZSM-5 zeolite showed that the ratio between the numbers of oligomeric R· radicals and isolated Cu^{2+} cations does not exceed 2×10^{-3}. In addition, the ratio between the numbers of radicals and adsorbed propylene molecules (Table 1) is 10^{-4}. The data obtained show that the temperature region of the existence of radicals (300–450 K) (Figure 2) is lower than that of the occurrence of the reaction (450–750 K).[4,10]

These data do not allow us to consider the oligomeric radicals as intermediates in the selective reduction of NO_x by hydrocarbons in an excess of oxygen on Cu/ZSM-5. It is noteworthy that the conclusion was drawn without taking into account possible contributions from radical ion reactions.

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