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# Interaction of an $NO + O_2$ gas mixture with Cu/ZSM-5 catalyst, studied by EPR and TPD

**Alexander N. Il'ichev,* Anatoly A. Ukharsky and Valery A. Matyshak**

*N.N.Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russian Federation.*
*Fax: +7 095 938 2156*

**At 293 K the $NO_2$ molecules formed in an $NO + O_2$ gas mixture are found to oxidize the copper ions in Cu/ZSM-5 from $Cu^+$ to $Cu^{2+}_{isol}$ and to become stabilized on isolated $Cu^{2+}_{isol}$ ions at temperatures < 620 K, changing the coordination of the latter to a square planar configuration in which one of the ligands is the $NO_2$ molecule.**

Catalytic reduction of $NO_x$ by hydrocarbons in an oxidizing atmosphere appears to be the most efficient process for removing $NO_x$ from exhaust gases. However, the commonly used copper-based catalyst does not possess a high enough efficiency. Therefore, investigations of the reaction mechanism and of the nature of the active sites and intermediates remain to be carried out. Stabilization of $NO_x$ on the catalyst as well as its reaction with hydrocarbons are important steps in $NO_x$ reduction, which have already been explored.[1,2] Recently,[3,4] we observed the existence of a correlation between the activity of the catalyst and the concentration of $Cu^{2+}_{isol}$ ions during NO reduction by propane in an excess of oxygen. It was noted then that propane reduces $Cu^{2+}_{isol}$ ions at 600 K and oxygen oxidizes $Cu^+$ ions to $Cu^{2+}_{isol}$ at temperatures >400 K. Adsorption of NO did not change the state of copper in the catalyst. No complexes were detected on Cu/ZSM-5 zeolite. In the present work a study was carried out of the reaction between Cu/ZSM-5 catalyst and an $NO + O_2$ gas mixture.

The preparation of Cu/ZSM-5 samples (the concentration of the supported copper was 0.15–2.8% wt.) was described in ref. 4. In this paper typical results are given for 1.3% Cu/ZSM-5 catalyst. The coordination and concentration of $Cu^{2+}_{isol}$ ions was determined by EPR. The concentration of $Cu^+$ ions was evaluated from TPD data after adsorption of CO molecules.[4] The interaction of gas molecules with zeolites was studied by TPD (heating rate was 12 K $min^{-1}$) and EPR. The EPR measurements were carried out on reduced and oxidized samples in a vacuum or in a gas atmosphere at 293 K. The samples were reduced by $H_2$ and oxidized by $O_2$ at 800 K and $P = 0.8$ kPa, for 1 h. The concentrations of $Cu^+$ and $Cu^{2+}_{isol}$ ions did not change upon heating the samples even to 900 K at a pressure of $10^{-4}$ Pa.

EPR spectra of the 1.3% Cu/ZSM-5 catalyst after oxidation and reduction are presented in Figure 1 (curves 1,2). In the oxidized sample the concentration of $Cu^{2+}_{isol}$ ions is $6\times10^{19}$ $g^{-1}$ and of $Cu^+$ ions it is $0.9\times10^{19}$ $g^{-1}$. In the reduced sample the concentrations of $Cu^{2+}_{isol}$ and $Cu^+$ are $1.2\times10^{19}$ and $5\times10^{19}$ $g^{-1}$, respectively. The rest of the supported copper (40%) was found to be bound on the outer surface.[4] According to ref. 5, spectra 1 and 2 show that the isolated $Cu^{2+}_{isol}$ ions in the zeolite are arranged in square pyramidal ($g_{||} = 2.34$ $A_{||} = 177$, $g_\perp = 2.07$ $A_\perp = 13$) and square planar ($g_{||} = 2.29$ $A_{||} = 184$, $g_\perp = 2.04$ $A_\perp = 25$) configurations. The adsorption of NO or $O_2$ results in a decrease of hyperfine (hf) line intensity without any change their $g$ tensor (these spectra are presented by dashed lines). By pumping out the gas from the reactor at 293 K the spectrum is restored to its original form. This phenomenon has been observed by other investigators. As suggested in refs. 4 and 6 the unstable complex was formed by interaction of NO or $O_2$ with a $Cu^{2+}_{isol}$ ion. We did not detect the spectrum of the $Cu^+$–NO complex at 293 K, $P = 0.1$–800 Pa and a concentration of $Cu^+$ ions equal to $0.1–10\times10^{19}$ $g^{-1}$, the EPR spectrum of this complex was observed at 77–273 K in ref. 7.

The EPR spectra of the catalysts change more significantly during the adsorption of a 1:1 $NO + O_2$ gas mixture ($P = 0.8$ kPa, $T = 293$ K). Figure 2 shows typical spectra (the range of the $g_\perp$ volume is given) of a pre-reduced catalyst during adsorption at different time intervals. From Figure 2, the intensity increases during the first 25 min (see spectra 1–4).

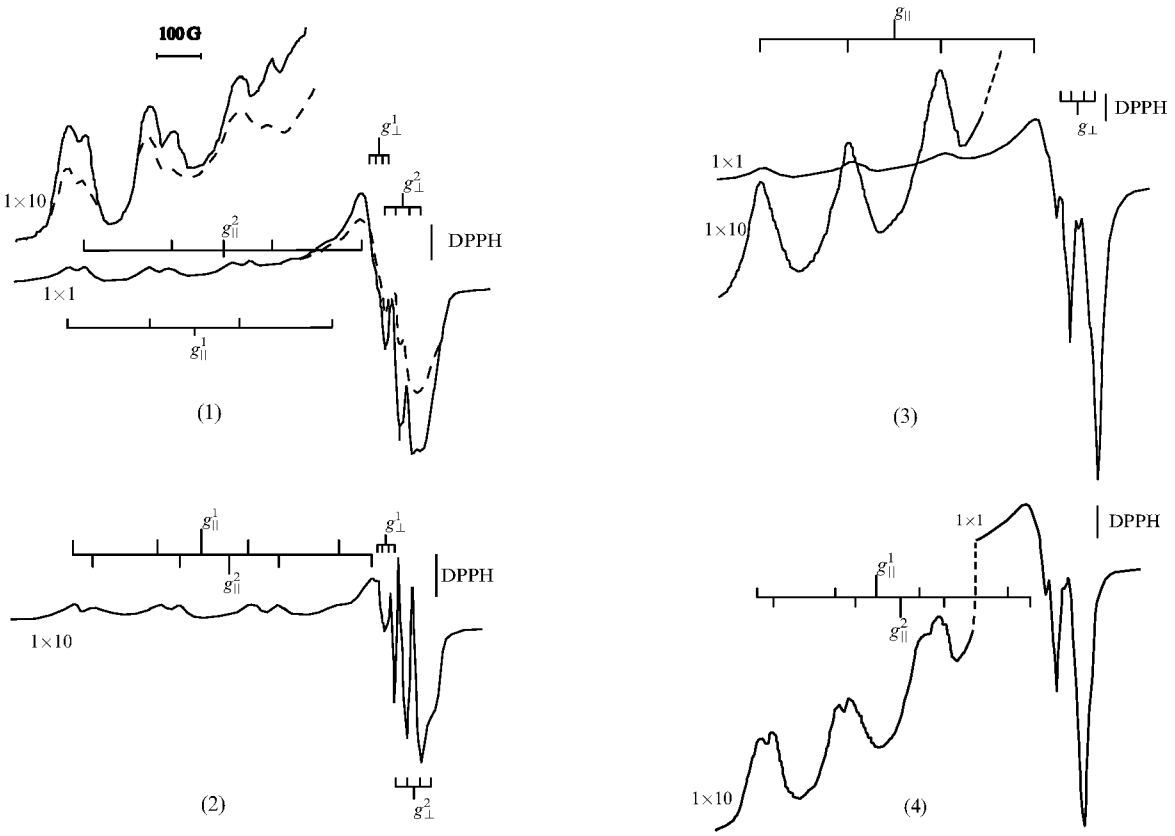


**Figure 1** EPR spectra of the oxidized (1) and reduced (2) catalyst; the same after $NO + O_2$ adsorption on the reduced (3) and oxidized (4) catalyst ($P = 10^{-4}$ Pa, $T = 293$ K).

This shows that the concentration of $Cu^{2+}_{isol}$ in the sample increases. After the next 10 min a new spectrum appears (curve 5). Then the intensity decreases and hf lines disappear (curves 6–8). This change of the spectrum (6–8) seems to be due to a weak interaction between $Cu^{2+}_{isol}$ ions and NO, $NO_2$ or $O_2$ molecules, since pumping out of the gas results in appearance of the same spectrum (5). Note that $NO + O_2$ adsorption on the oxidized sample does not substantially change its spectrum during the first 20 min (no oxidation takes place). Then the spectrum changes similarly to that observed in the case of the pre-reduced sample during adsorption for more than 20 min. Recently, similar spectra have been obtained for copper-containing samples even at 600 K under flow conditions.[8] Comparison of spectra presented in Figure 1 (curves 1,2 and 3,4, *i.e.* before and after $NO + O_2$ adsorption on the sample) shows that the configuration of $Cu^{2+}_{isol}$ ions during $NO_2$ adsorption changes. The parameters: $g_{||} = 2.30$ $A_{||} = 184$, $g_{\perp} = 2.04$ $A_{\perp} = 25$ are calculated from the spectra 3,4. They characterize $Cu^{2+}_{isol}$ ions located in a square planar configuration. In spectrum 4 (the pre-oxidized sample) parameters: $g_{||} = 2.34$ $A_{||} = 177$ are also present. This suggests that a part of the $Cu^{2+}_{isol}$ ions remain in a square pyramidal coordination. We suggest that the change in the spectrum is due to the interaction of $Cu^{2+}_{isol}$ ions located both in pyramidal and square planar configurations with $NO_2$ molecules ($NO_2$ molecules are always present in an $NO + O_2$ mixture). This interaction seems to result in the formation of a complex which will subsequently be referred to as $Cu^{2+}_{isol}$–$(NO_2)_x$.

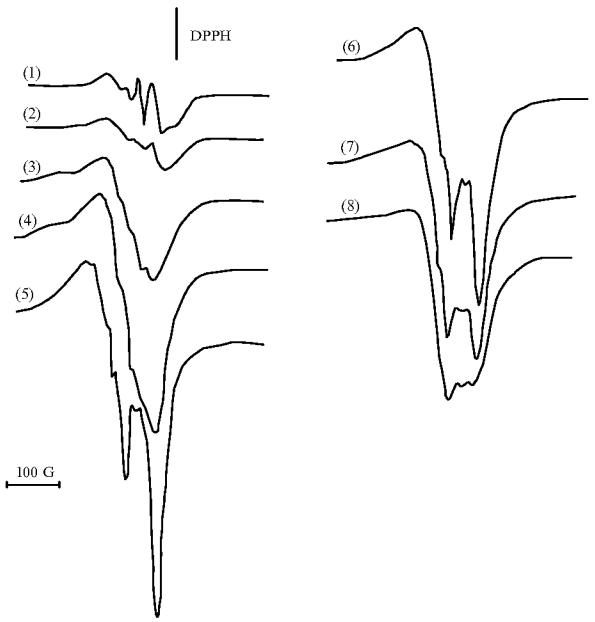


**Figure 2** EPR spectra of the catalyst during adsorption of an $NO + O_2$ mixture ($P = 0.8$ kPa, $T = 293$ K) recorded at $t = 0$ min (1), 2 (2), 13 (3), 24 (4), 30 (5), 36 (6), 39 (7), 50 (8).

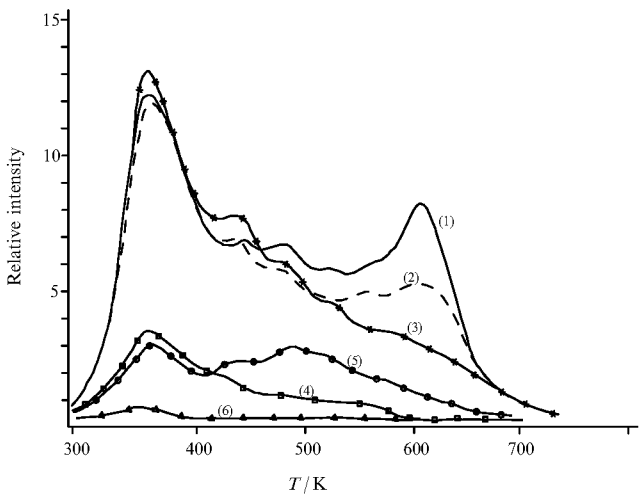


**Figure 3** TPD spectra after $NO + O_2$ adsorption on the reduced (1), oxidized (2) catalyst and zeolite without copper (3) ($P = 0.8$ kPa, $T = 293$ K, adsorption time 50 min). Spectra after adsorption of NO (4), NO, then $O_2$ (5) and $O_2$ (6) for the reduced catalyst.

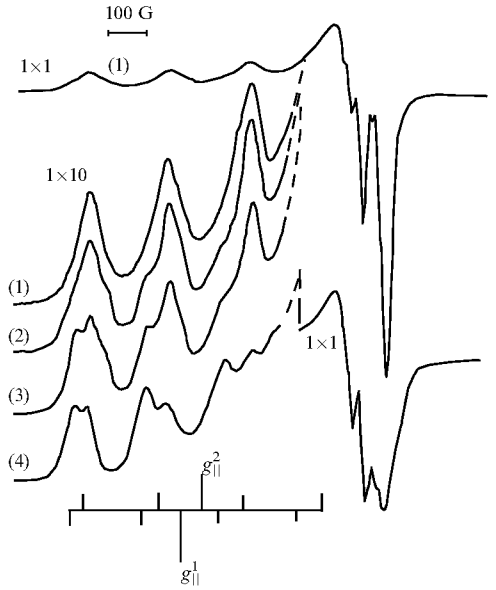


**Figure 4** EPR spectra recorded during TPD investigation at 293 K (1), 453 K (2), 573 K (3), 643 K (4).

Further study of this complex was made with the help of the TPD technique. Catalyst and Cu-free zeolite samples were dosed for 50 min with $NO/O_2$ at 0.8 kPa and 293 K. The samples were then evacuated and the TPD spectra recorded up to 800 K at a heating rate of 12 K $min^{-1}$. From Figure 3, curve 3 (for the zeolite without copper) the TPD spectrum has peaks at $T=370$ and 400–480 K. For Cu-containing zeolites the TPD spectra have an additional peak at 620 K. For the pre-reduced sample this peak is larger than for the pre-oxidized one (see curves 1,2). The number of molecules $g^{-1}$ of the catalyst desorbing at temperatures corresponding to these peaks are $7\times10^{19}$ and $4\times10^{19}$ $g^{-1}$, and these values correspond to a concentration of $Cu^{2+}_{isol}$ ions in the oxidized sample equal to $6\times10^{19}$ $g^{-1}$. Note that an increase or decrease of copper concentration in the zeolite leads to a similar change of the peak intensity only at 620 K.

In addition, the desorption of NO and $O_2$ from samples was studied after separate adsorption of these gases under the same conditions as previously. The data obtained are shown in Figure 3 (curves 4,6). The TPD peaks of $O_2$ and NO at 350 and 370 K are due to desorption of these gases from the zeolite matrix.[4] The intensities of these peaks are 25 and 4 times less than those observed after joint $NO+O_2$ adsorption over both pre-reduced and pre-oxidized samples. An additional wide peak appeared at 480 K when $O_2$ gas was adsorbed subsequent to NO adsorption ($T=293$ K, $P=0.8$ kPa). This peak is present in the TPD spectrum after adsorption of the $NO+O_2$ gas mixture (see curves 3,5).

Consequently, after $NO+O_2$ adsorption on Cu-containing zeolite, peaks at 370 and 480 K are observed due to $NO_2$ desorption from the zeolite matrix. The peak at 620 K is caused by $NO_2$ desorption from $Cu^{2+}_{isol}$ ions.

EPR and TPD spectra were studied simultaneously. They show that the $Cu^{2+}_{isol}$–$(NO_2)_x$ complex decays at a high temperature. As shown in Figure 4 in case of the pre-reduced sample the spectrum of the $Cu^{2+}_{isol}$–$(NO_2)_x$ complex changes when the temperature of the sample is >480 K. A new spectrum appears which is related to $Cu^{2+}_{isol}$ ions situated in both the pyramidal and square planar configurations in the original cation positions (curves 3,4). After the TPD experiment the concentrations of $Cu^{2+}_{isol}$ and $Cu^{+}$ ions in the sample coincide with those of $Cu^{2+}_{isol}$ and $Cu^{+}$ ions in the pre-oxidized catalyst.

This suggests that the TPD peak at 620 K is due to the decomposition of $Cu^{2+}_{isol}$–$(NO_2)_x$ complex with $x=1$, since the number of desorbed molecules in this peak coincides with the number of $Cu^{2+}_{isol}$ ions in the pre-oxidized sample. This decomposition is realized through the rupture of the $Cu^{2+}_{isol}$–$(NO_2)$ bond. The $Cu^{2+}O$–NO bond does not break because upon NO adsorption the previous complex is not formed. The activation energy of this reaction is equal to 145 kJ $mol^{-1}$ (as determined by the method described in ref. 9).

All these data suggest that oxidation of $Cu^{+}$ to $Cu^{2+}_{isol}$ proceeds even at room temperature at the expense of $NO_2$ molecules present in the $NO+O_2$ gas mixture. The oxidation seems to be due to dissociation of the $NO_2$ molecule on the $Cu^{+}$ ion. Upon interaction of $NO_2$ molecules with $Cu^{2+}_{isol}$ ions a new EPR spectrum appears, the parameters of which show that the coordination of $Cu^{2+}_{isol}$ ions corresponds to a square planar configuration (this was confirmed in ref. 10). The square planar configuration is likely to be formed from an $NO_2$ molecule and three oxygen atoms from the zeolite: $(O)_3$–Cu–$(NO_2)$. Note that the complex formed more effectively with $Cu^{2+}_{isol}$ ions located in the lower coordination. The high reactivity of these ions in ZSM-5 was noted in ref. 11. The change of their coordination during adsorption of different molecules was observed in ref. 12.

The complex decomposes at 620 K with an activation energy of 145 kJ $mol^{-1}$. In this case the $Cu^{2+}_{isol}$–$(NO_2)$ bond is broken, the $NO_2$ molecule desorbs and the $Cu^{2+}_{isol}$ ion becomes positioned at the cation position in the channel, where the copper ion and oxygen atoms of the matrix form square pyramidal and square planar configurations.

We have detected the $Cu^{2+}_{isol}$–$(NO_2)$ complex by IR spectroscopy and considered it to be an intermediate in NO reduction by propane.[13] This complex is formed and is stable at the same temperatures as the complex mentioned above. This indicates that the active nitrite structure in $NO_x$ reduction by propane can be formed by the interaction of a $Cu^{2+}_{isol}$ ion and an $NO_2$ molecule. The question concerning the activation of propane is not yet clear, although, as noted in ref. 1, the activation of hydrocarbons can take place due to the interaction of $NO_2$ with the hydrocarbon. This may explain the existence of a correlation between the activity of the catalyst and the concentration of $Cu^{2+}_{isol}$ ions.

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