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The Interaction of NO with Copper Ions in ZSM5: An EPR and IR Investigation

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The interaction of nitric oxide with copper ZSM5 zeolites at room temperature has been studied by EPR and FT–IR spectroscopy in the aim of investigating the surface intermediates involved in the decomposition of NO to N_2 and O_2. Particular care has been devoted to obtaining a catalyst in a well-defined oxidation state, i.e., with one of the two ionic forms of copper (Cu^{2+} or Cu^+) clearly prevailing on the other. The interaction of NO with Cu^{2+}/ZSM5 yields a reversibly adsorbed nitrosylic adduct easily desorbed upon pumping at 333 K. The species is diamagnetic and bears a partial positive charge. Cu^+ is unstable under NO pressure and undergoes oxidation at room temperature. In the early stages of the interaction a paramagnetic nitrosyl of Cu^+ is formed having a partial negative charge on NO. This species evolves with time (or NO pressure) towards a diamagnetic dinitrosyl capable of eliminating N_2O with simultaneous oxidation of the site to Cu^{2+}.

INTRODUCTION

The catalytic decomposition of NO is an area that has attracted a great deal of attention over the past decade. The catalytic removal of NO_x compounds from the exhaust streams of various combustion sources is particularly important because of the contribution of these compounds to acid rain and smog formation (*1*).

In particular, the decomposition of NO into N_2 and O_2, although thermodynamically favourable over a wide range of temperatures, needs an efficient catalyst for appreciable reactivity. Among the many potential catalysts so far developed, Cu^{2+}-exchanged zeolites have shown pronounced activity for the reaction (*2–4*). Unlike previous catalysts, the activity of Cu^{2+}- exchanged zeolites is not inhibited by oxygen present in the feed gas or produced in the decomposition (*1*). In particular, Cu^{2+}/ZSM5 has attracted a lot of attention because of its sustained actvity over long periods and because of its ability to act as a photocatalyst at 275 K (*5*) as well as a thermal catalyst in the temperature range 723 to 873 K (*6, 7*).

However, despite the great deal of work carried out on this catalyst, a detailed understanding of the basic interaction between the NO and the catalytic sites is not yet available. In particular, as recently reported by Li and Hall (*8*) "... we know essentially nothing about the surface intermediates involved in the reaction."

The aim of this paper is to provide spectroscopic evidence for the nature of the primary intermediates formed by contact of NO with Cu/ZSM5 at room temperature, i.e., at temperature conditions similar to those of the photocatalytic process (*5*), but sufficiently lower than those of the thermal decomposition to avoid interference due to fast reactions in the gas phase. The spectroscopic techniques adopted in this study are FT infrared spectroscopy and electron paramagnetic resonance (EPR). The two techniques are complementary because the for-

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mer one allows detailed analysis of the adsorbate vibrations whereas the latter is capable of detecting paramagnetic sites (such as Cu^{2+}) or paramagnetic surface adducts.

Particular emphasis is given to preparation of systems that are as well defined as possible in terms of the prevailing oxidation state of the copper. This is not a particularly easy task because the interconversion between Cu^{2+} and Cu^{+} ions is known to occur readily for surface-supported copper ions (for example, during treatments under vacuum or upon adsorption of gases (*9, 10*). Moreover, it will be shown that in the case of copper/ZSM5 systems, it is impossible to prepare samples containing exclusively one of the two oxidation states of copper because traces of the other oxidation state are practically always present in the sample. Therefore we have performed separate experiments on the adsorption of very small doses of NO on samples predominantly containing Cu^{2+} and Cu^{+}. This allows a clearer examination of the species formed in the early stages of the interaction of NO with Cu^{+} or Cu^{2+}. This specific interaction of NO with either the reduced or oxidised form of Cu/ZSM5 is of vital importance for a better understanding of the whole catalytic transformation, based on the redox behaviour of the ionic copper sites, even though it is known that high efficiency real catalysts are slightly different than the solids employed in the present study since they contain a level of copper in excess of the exchange capacity of the zeolite (*7*).

Finally, the dependence of these surface species to various parameters such as time and NO pressure is discussed.

EXPERIMENTAL

Two samples of Cu^{2+}/ZSM5 (Si/Al ratio = 23.3) having different copper loadings were prepared by ion exchange with an aqueous solution contaning $Cu(NO_3)_2$.

After washing and drying in air, the copper loading of the two samples was determined (following dissolution of a weighed amount of the exchanged zeolite) by means of an inductively coupled plasma emission spectrometer (Plasma 300 from Allied Analytical System). The copper contents resulting were 1.9 and 0.13 wt% for the two samples, respectively.

Prior to spectral recording both samples were treated as follows: slow evacuation at 523 K overnight, then evacuation at 873 K for 1 h. To obtain samples in which either Cu^{2+} or Cu^{+} prevail, the two catalysts were oxidised or reduced, according to the following procedures.

(1) Oxidised sample (hereafter referred to as Cu^{2+}/ZSM5): Oxygen (100 Torr) was admitted to the sample (previously dehydrated) at 673 K for 1 h. The sample was cooled to room temperature in the oxygen atmosphere, and O_2 was removed by evacuation at 298 K. Evacuation of O_2 at higher temperatures would result in a partial reduction of copper.

(2) Reduced sample (hereafter referred to as Cu^{+}/ZSM5): Hydrogen (100 Torr) was added to the sample (dehydrated) at 603 K for 30 min. The sample was evacuated at this temperature and then cooled to room temperature under a dynamic vacuum.

NO was purified by the freeze–pump–thaw technique before contact with the sample. Very small doses of NO (corresponding to the vapour pressure at 77 K) were initially adsorbed onto both samples at 298 K. Higher doses were admitted after spectra recording.

X-band EPR spectra were recorded on a Varian E-109 spectrometer equipped with dual cavity, at 77 K. The g values were measured by comparison with Varian pitch (g = 2.0028).

For IR measurements, the sample was compressed into self-supporting discs ($\approx$10 mg cm^{-2}) and placed in a special vacuum cell, where it underwent all activation and adsorptive treatments in a strictly *in situ* configuration. Spectra were recorded at 298 K at a resolution of 2 cm^{-1} on a Bruker IFS

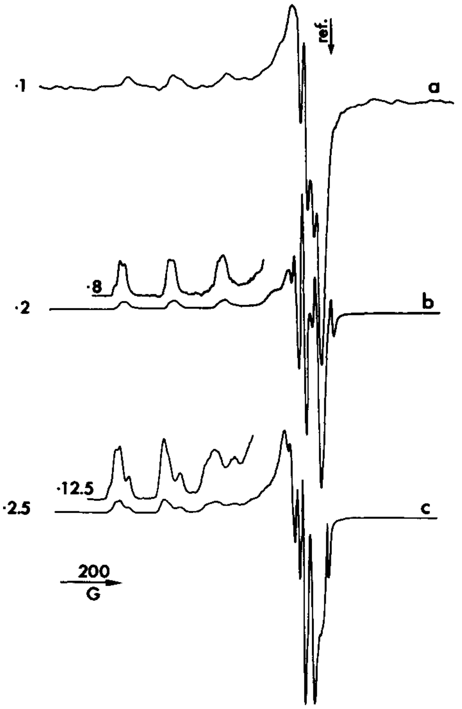


FIG. 1. EPR spectra of Cu^{2+}/ZSM5 (1.9 wt% Cu) dehydrated for 1 h at (a) 298 K, (b) 673 K, and (c) 873 K. Spectra recorded at 77 K.

113 v spectrometer equipped with an MCT detector.

RESULTS

1. EPR OF Cu/ZSM5

Freshly prepared Cu/ZSM5 samples exhibit an axial, broad, and scarcely resolved EPR spectrum typical of hydrated Cu^{2+} ions in a zeolitic framework. The spectra of high and low loaded samples were similar, but for the intensities of the signals.

Thermovacuum treatment at increasing temperatures produces a change in the spectral profile due to the progressive appearance of various distinct Cu^{2+} species and, in parallel, a decrease in the signal intensity, indicating a partial reduction of Cu^{2+} to Cu^{+}. The effect of dehydration temperature on the spectral profile of the Cu^{2+}/ZSM5 system (1.9 wt% Cu) is shown in Fig. 1. The reduction of the Cu^{2+} ions in zeolites by thermovacuum treatment has already been reported (*9*, *10*). Activation by thermal treatment at 673 K produces two Cu^{2+} species the features of which, although scarcely resolved, are visible in the spectrum of Fig. 1b. The observed spectrum is similar to that reported by Anderson and Kevan (*11*) for Cu^{2+}-doped NaH–ZSM5. Further evacuation to 873 K produces a third distinct Cu^{2+} site. The spin-hamiltonian parameters of these three sites (labelled A, B, and C) are similar to those previously reported by Sendoda and Ono (*12*) for Cu/ZSM5 evacuated at the same temperature and are given in Table 1.

The reducibility of Cu^{2+} in ZSM5 is markedly different from that of other supported Cu systems. In fact, in Cu/SiO_2 and Cu/PVG (porous Vycor glass), a thermal treatment at 773 K is sufficient to reduce all the Cu^{2+} ions (*13*) and in Cu/Y zeolite, CO (30 Torr) at 773 K is required to complete the reduction (*14*). In the case of Cu/ZSM5, hydrogen (100 Torr) at 603 K is necessary to reduce the bulk of the Cu^{2+} ions. The high degree of stability of the copper ions in ZSM5 is thought to be due to the extra stabilization appended by the lattice framework of ZSM5.

The spectra of the oxidised and reduced samples, prior to NO admission, are shown in Figs. 2a and 2b, respectively. The spectrum of Fig. 2a closely resembles that of the freshly prepared Cu^{2+}/ZSM5 sample: it is very intense, broad, and poorly resolved due to the high copper (II) content and the

TABLE 1

Spin-Hamiltonian Parameters for Cu^{2+} Ions in Partially Reduced Cu^{2+}/ZSM5, Thermally Treated at 873 K

(I)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
Species A	2.31	2.04	157	26
Species B	2.30	2.05	163	26
Species C	2.27	2.07	173	14

Note. *A* values are given in gauss.

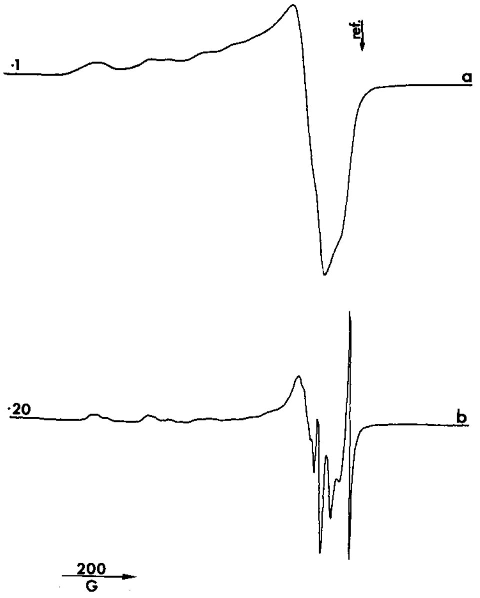


FIG. 2. EPR spectra of the (a) oxidised sample (Cu^{2+}/ZSM5) and (b) reduced sample (Cu^+/ZSM5) prior to NO adsorption. Recorded at 77 K.

consequent dipolar interaction between neighbouring copper centres. The spectrum of the reduced sample (Fig. 2b) shows that the intensity of the Cu^{2+} EPR signal is weak (more than one order of magnitude lower than that of the initial spectrum), indicating that most (but not all) of the copper ions are in the reduced state. This is demonstrated also by the observation on the same sample, of the photoluminesence spectrum (*15*) of Cu^+ ions (*16*). A sharp isotropic peak around the free electron value is also visible in Fig. 2b, likely due to small amounts of carbon radical impurities formed during the reduction.

1a. Effects of NO Treatment

Cu^{2+}/ZSM5. The addition of NO to the oxidised samples produced an immediate decrease of the EPR signal due to Cu^{2+} centres. The extent of this decrease depends on the pressure of NO employed: at low pressures (less than 1 Torr) the signal intensity is reduced by a factor of about 10 and the intensity is then reduced further under progressively higher NO pressures.

Cu^+/ZSM5. Cu^+ is a diamagnetic ion and thus not visible by EPR. The interaction of nitric oxide with Cu^+ ion depends on NO pressure. At high pressures (5–30 Torr) oxidation of the Cu^+ sites occurs; Cu^{2+} ions are created immediately, in both the high and low loaded samples, as monitored by the immediate appearance of a Cu^{2+} EPR signal upon NO addition. The intensity of this Cu^{2+} signal is, however, one order of magnitude lower than the original intensity of the fully oxidised Cu^{2+}/ZSM5 sample.

At low NO pressures (less than 1 Torr) a paramagnetic species was formed on the Cu^+/ZSM5 (0.13 wt%) system, the EPR spectrum of which is shown in Fig. 3a. A species with the same spin-hamiltonian parameters was also observed on the high loaded sample (1.9 wt% Cu) shown in Fig. 3b. However, due to the appreciable amount of Cu^{2+} ions remaining after the reductive treatment of the high loaded sample, the spectrum of Fig. 3b turns out to be the superimposition of a Cu^{2+} signal and of that due to the newly formed paramagnetic species. Note that the interference from residual Cu^{2+} ions in Fig. 3a is minimal because of the lower overall copper loading. The spectrum of the new species is basically understood in terms of an axial spectrum ($g_1 = g_\parallel$, $g_2 = g_3 = g_\perp$) whose g components are split into partially overlapped quartets because of the hyperfine interaction between the unpaired electron and the Cu nucleus (^{63}Cu and ^{65}Cu have a nuclear spin of $\frac{3}{2}$). A further splitting of some Cu hyperfine lines into triplets is also observable, due to the interaction with the nitrogen nucleus (^{14}N, $I = 1$).

Spectra similar to those in Fig. 3 were previously observed by Naccache *et al.* (*14*) and Chao and Lunsford (*17*) after NO interaction with Cu^+/Y zeolite and in Cu^+/SiO_2 by Anpo *et al.* (*13*). The paramagnetic species responsible for this signal was identified as a nitrosylic adduct on Cu^+, i.e., Cu^+NO. The spin-hamiltonian parameters of the nitrosylic adduct in Cu^+/ZSM5 (deduced by

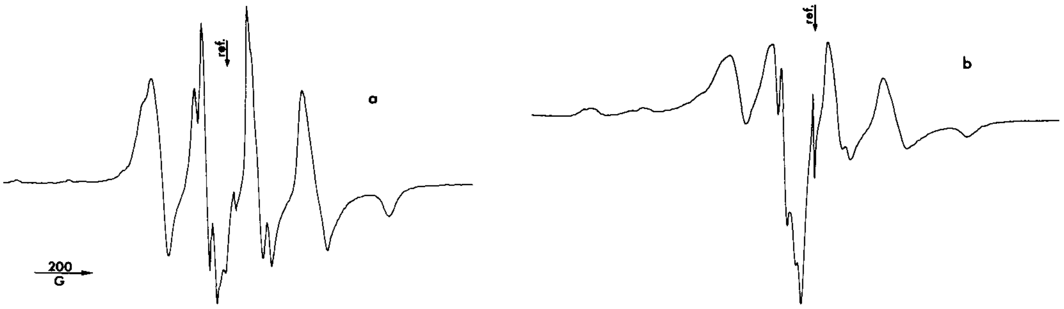


FIG. 3. (a) EPR spectrum of the Cu$^+$NO complex at 77 K on the low loaded Cu/ZSM5 sample (0.13 wt% Cu). NO (0.5 Torr) added at 298 K. Spectrum recorded at 77 K. (b) EPR of Cu$^+$NO at 77 K on the high loaded sample (1.9 wt% Cu), with residual Cu^{2+} ions present. No (0.5 Torr) added at 298 K.

computer simulation of the experimental spectrum) are comparable, but not identical to those reported for various systems. All the values are reported in Table 2.

2. INFRARED SPECTRA OF Cu/ZSM5

2a. *Effects of NO Pressure*

Cu^{2+}/ZSM5. The infrared spectra of the high loaded Cu^{2+}/ZSM5 sample under increasing pressures of NO (0.07 → 26 Torr) are shown in Fig. 4. At low NO pressures, the main features of the spectra are bands at 1912 and 1811 cm^{-1}. The band at 1912 cm^{-1} increases foremost in the spectrum as the NO pressure is increased, while additional bands begin to appear at 1734 and 1827 cm^{-1}. The latter bands grow simultaneously and in parallel with a corresponding decrease of the 1811 cm^{-1} band. The spectrum obtained upon NO contact with the lower loaded sample was similar, but for the presence of bands at 1630 and 1889 cm^{-1}. These extra bands are due to NO interacting with residual sodium (Na) cations that remain after the incomplete ion exchange of the parent Na/ZSM5 zeolite, as confirmed by the IR spectra of NO on Na/ZSM5 under similar conditions. The influence of NO/Na$^+$ contact was not apparent in the high loaded sample because of the high exchange levels of Cu^{2+} for Na$^+$ ions.

The spectrum recorded at the highest NO pressures is by far dominated by the band

TABLE 2

Spin-Hamiltonian Parameters for Cu$^+$NO in Different Systems

System	g	$g_{\perp}$	A	$A_{\perp}$	Ref.
ZSM5	1.87	2.0053	187.5(Cu) 18(N)	176.6(Cu) 29(N)	This work
Y zeolite	1.89	2.009	240	190	(15)
Y zeolite	1.74	2.019	—	175	(14)
SiO_2	1.94	2.030	183	118	(13)

Note. Spectra recorded at 77 K. A values are given in gauss.

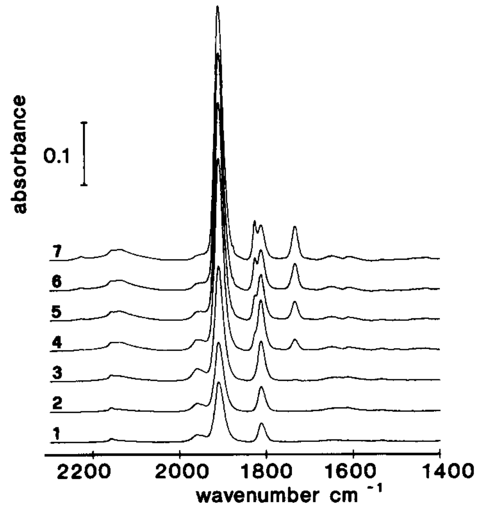


FIG. 4. IR spectra of Cu^{2+}/ZSM5 (1.9 wt% Cu) treated with NO at 298 K. Curves 1–7: P_{NO} was gradually increased from 0.07 to 26 Torr.

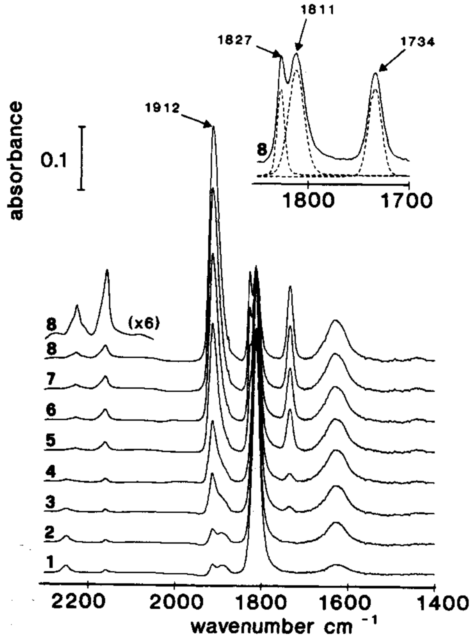


FIG. 5. IR spectra of Cu$^+$/ZSM5 (0.13 wt% Cu) treated with NO at 298 K. Curves 1–8: P_{NO} was gradually increased from 0.07 to 26 Torr. The inset shows two blown-up segments of the spectrum at P_{NO} of 26 Torr.

at 1912 cm^{-1}, whereas the bands at 1827 and 1734 cm^{-1} are more intense than the parent band at 1811 cm^{-1}, and minor bands are observed at 2157 and 1630 cm^{-1} (broad).

Cu$^+$/ZSM5. The infrared spectra due to the contact of NO (from 0.07 to 26 Torr) with Cu$^+$/ZSM5 is shown in Fig. 5. The spectrum turns out to depend strongly on the pressure of NO used, in agreement with the EPR experiments relative to the reduced Cu/ZSM5 system. Figure 5 shows that at low NO pressures (less than 1 Torr) the situation is very different from that observed on Cu^{2+}/ZSM5: there is a dominant band at 1811 cm^{-1} with other minor bands at 1911, 1888, 1635, 2158, and 2249 cm^{-1}. However, as the NO pressure is increased from 0.07 to 26 Torr of NO, the spectral profile changes and progressively appears similar to that of the Cu^{2+} state. In particular there is a band pair at 1734 and 1827 cm^{-1} (already described for the Cu^{2+}/ZSM5 sample), which grows in parallel with the band at 1912 cm^{-1}, while the band at 1811 cm^{-1} declines. At 26 Torr the bands at 1734, 1812, 1827, and 1912 cm^{-1} dominate the spectrum, which looks very similar to the corresponding one in Fig. 4, except for additional bands at 1635 and 2159 cm^{-1}, which appear to grow with time and with increasing NO pressure.

2b. *Effects of Time of Contact and Evacuation*

Cu^{2+}/ZSM5. There was no visible change in the EPR spectrum after evacuation of NO from Cu^{2+}/ZSM5 at room temperature. But upon evacuation at 333 K, i.e., a temperature comparable to that most likely induced in the sample by the IR beam, the Cu^{2+} signal was completely restored to its original intensity. This indicates the complete reversibility of the Cu^{2+}/NO interaction at this temperature. The EPR spectrum of the Cu^{2+}/ZSM5 system under NO (>1 Torr) did not change with time, indicating that the copper(II) NO diamagnetic complex is stable with respect to time. Also the IR spectrum of the Cu^{2+}/ZSM5 samples in contact with NO does not change with time, as no appreciable spectral differences were observed after 5 days. The IR spectrum depends however on NO evacuation: a gradual evacuation of the gas reduces the bands at 1912, 1734, and 1827 cm^{-1} with an initial increase of the band at 1811 cm^{-1}, whereas after complete evacuation, all the bands are eliminated.

Cu$^+$/ZSM5. Evacuation at 333 K of NO from the Cu$^+$/ZSM5 sample completely destroys the EPR spectrum of the Cu$^+$NO species, shown in Figs. 3a and 3b. The removal of this signal is accompanied by the simultaneous appearance of a Cu^{2+} signal, the intensity of which is by far higher (about five times) than that of the residual Cu^{2+} always present on the starting reduced Cu$^+$ sample.

A tendency of the Cu$^+$ state to be oxidised by coordinated NO is observed with respect to the time of contact. In fact as the time of NO contact increases (under a constant NO pressure of less than 1 Torr), the Cu$^+$NO signal decreases, while a Cu^{2+} signal is formed and increases. The final EPR spectrum (either after NO evacuation or after 2 days of contact) closely resembles the spectrum observed in the case of Cu^{2+}/ZSM5.

Similar evidence is observed in the IR. The initial spectrum of the Cu^{+}/ZSM5 system treated with 0.07 Torr of NO is characterized by the band at 1811 cm^{-1} mentioned above and shown in Fig. 5. This band decreases and finally disappears after 2 days of contact (not shown in the figure), and the final spectrum is similar to that typical of the Cu^{2+}/ZSM5 system treated with NO (26 Torr); i.e., it is dominated by the 1912 cm^{-1} band, which is the IR fingerprint of the interaction of NO with Cu^{2+}. Evacuation at 333 K of NO from a Cu^{+}/ZSM5 sample that still exhibits the signal at 1811 cm^{-1}, as the main spectral feature, destroys the latter band. Subsequent NO additions to this evacuated sample yield as the main spectrum feature the band at 1912 cm^{-1} indicating that the Cu^{2+} state has been produced upon NO evacuation from the Cu^{+} specimen. This unambiguously indicates (as inferred on the basis of the parallel EPR experiment, reported above) that Cu^{2+} oxidised sites are produced by contact and successive evacuation of the Cu^{+}-reduced sample after employing a very small dose of nitric oxide (<1 Torr). In particular, Cu^{2+} ions seem to be the result of the decomposition of the Cu^{+}–NO adduct which is characterized by the EPR spectrum in Fig. 3 and the IR band at 1811 cm^{-1}.

DISCUSSION

The NO molecule has an unpaired electron in a degenerate antibonding orbital with a relatively low ionization energy of 9.5 eV. Electron transfer of this unpaired electron from the antibonding orbital of NO to empty or partially filled 3*d* orbitals of transition metal ions can then occur easily, followed by lone pair donation from NO and π backbonding to the NO orbitals, generating a nitrosyl complex. Although the molecular orbital structure of the nitrosyl is rather complex, the process can be conveniently schematized as

$$Me^{x+} + NO \rightleftharpoons Me^{(x-1)+}NO^{+}.$$

This reaction is widely documented (*18*) and seems to be the reaction responsible for the marked decrease of the Cu^{2+} signal intensity, in the EPR spectrum of the Cu^{2+}/ZSM5 system:

$$Cu^{2+} + NO \rightleftharpoons [Cu^{+}NO^{+}].$$

The nitrosyl is diamagnetic because of spin pairing between NO and Cu^{2+}, and so its formation would result in the intensity decrease of the Cu^{2+} paramagnetic signal, as indeed observed. A fraction of the total Cu^{2+} sites, still visible in the EPR after NO adsorption, is thus unreactive or inaccessible to the NO molecules.

The band at 1912 cm^{-1}, which is the principal one in the IR spectrum of the Cu^{2+}/ZSM5 system, is thought to correspond to this diamagnetic complex. A similar band was observed by Naccache *et al.* (*14*) at 1918 cm^{-1} for NO contacted with Cu^{2+}–Y zeolite and assigned to a $Cu^{+}NO^{+}$ complex.

The bond order in the free NO molecule is $2\frac{1}{2}$. Removal of one antibonding electron, by coordination to a transition metal ion, producing NO^{+}, increases the bond order and results in a shorter and stronger bond because the electron is removed from an antibonding orbital. A stronger bond should produce a vibrational frequency above 1875 cm^{-1}, i.e., above the vibrational frequency of the free NO molecule: the band at 1912 cm^{-1} would thus correspond to a partially positive NO species, as expected for $[Cu^{+\delta+}NO^{\delta'+}]$ (*19*) (where $\delta + \delta' = 1$). This notation implies in fact that, although a spin pairing has occurred, as revealed by EPR, the charge donation from NO to Cu^{2+} centres is far from being complete, as the observed IR frequency is slightly higher than that of NO gas and definetly lower than that of the NO^{+} species (NO^{+} frequency = 2345 cm^{-1}) (*20*).

Moreover, the reversible behaviour of the band at 1912 cm^{-1} with respect to evacuation is consistent with the effect observed in the EPR: evacuation of NO produces a corresponding increase in the Cu^{2+} signal intensity. It is clear that $[Cu^{+\delta+}NO^{\delta'+}]$ (i.e., a complex with a reversible partial charge from NO to the Cu^{2+} centres) is the main initial product of the interaction between NO and Cu^{2+} ions in Cu/ZSM5 and that it is stable, at least under the experimental conditions of the present work.

In the case of Cu^+/ZSM5, the main product formed in the early stages of the interaction with NO is a nitrosylic adduct on Cu^+ (it can be written as Cu^+NO), which exhibits the EPR spectrum shown in Figs. 3a and 3b. This species is thought to be responsible for the IR band at 1811 cm^{-1} (Fig. 5), which initially dominates this spectrum. Again the correspondance between the EPR and IR spectral features is found on the basis of the intensities and of the behaviour upon NO evacuation. Arguments in support of this Cu^+NO complex are as follows:

The paramagnetic species in Figs. 3a and 3b appears to have axial symmetry, with two partially overlapping hyperfine quartets. The hyperfine structure indicates that the unpaired electron interacts with a copper nucleus ($I = \frac{3}{2}$ for ^{63}Cu and ^{65}Cu) producing four hyperfine lines. A further splitting of some single copper hyperfine lines also into three lines is instead due to the interaction of the paramagnetic electron with ^{14}N ($a_{\perp N} = 29$ G, and $a_{\parallel N} = 18$ G, $I(^{14}N) = 1$). This latter coupling due to nitrogen was not observed for similar NO adducts on Cu^+ in Y zeolites (*14, 17*). The g values of the nitrosyl adduct observed on Cu^+ are typical of species formed upon NO adsorption on non-d cationic centres, which occurs without electron transfer to the cation (*21–23*). The spectrum of adsorbed NO is observable in such a case due to the removal of the degeneracy in the highest occupied π antibonding orbital of NO, by the cationic electric field (*23*). The $Me^{(x-1)+}NO^+$ structure typical of transition metal nitrosyls and observed in the case of the Cu^{2+}–NO interaction is absent in the case of NO on Cu^+/ZSM5 because of the $3d^{10}$ closed shell structure of Cu^+, which cannot undergo electron transfer to d orbitals.

The nature of the adduct is thus determined by the balance between the σ donation from the 5σ NO lone pair and π backbonding to the π antibonding NO orbitals. The IR frequency of the adduct (1811 cm^{-1}) is slightly lower than that of the free NO molecule, and this implies that a partial electron transfer from Cu^+ to NO does indeed occur, resulting in a slightly negatively charged nitrosyl. On the other hand the observed stretching frequency (1811 cm^{-1}) is lower than that of the free molecule but by far higher than that reported for the NO^- ion (1100 cm^{-1}) (*24*) and in a cryogenic matrix (1358–1374 cm^{-1}) (*25*). Frequencies of $\approx$1815 cm^{-1} for mononitrosyl complexes, which do not imply a net charge transfer, have also been observed with other systems, e.g., Cr^{2+}–NO (*26*).

After the initial formation of Cu^+NO at low NO pressures, the successive stages of NO interaction with Cu^+ can be observed in Fig. 5: as the NO pressure is increased a second molecule can adsorb at the Cu^+NO site, creating a dinitrosyl, with stretching bands at 1734 and 1827 cm^{-1}. (This is clearly seen to occur also in Fig. 4 on the small fraction of Cu^+ ions, where the band pair only appears as the pressure is increased.) Upon further increase of the NO pressure, Fig. 5 shows that the concentration of dinitrosyls grows (growth of the twin peaks at 1734 and 1827 cm^{-1}), with the simultaneous decrease of the mononitrosyl Cu^+NO species (single peak at 1811 cm^{-1}). Evacuation of NO reveals that this step is reversible, as the 1734 and 1827 cm^{-1} bands are destroyed and the 1811 cm^{-1} band is restored. Dimeric NO species with a *cis*-configuration are known to adsorb, in cryogenic matrix, at $\approx$1870 and $\approx$1710 cm^{-1} (*27*) and have been observed at the surface of various catalysts. The intensity ratio of the symmetric and asymmetric stretching modes of the dinitrosyl species formed in Cu^+ are shown by the inset of Fig. 5. Using the integrated intensities for the asymmetric and symmetric stretching modes, as obtained through a band simulation program (*26, 28*), we have

$$\left[\frac{\bar{I}as}{\bar{I}s}\right]^{1/2} = 1.2738,$$

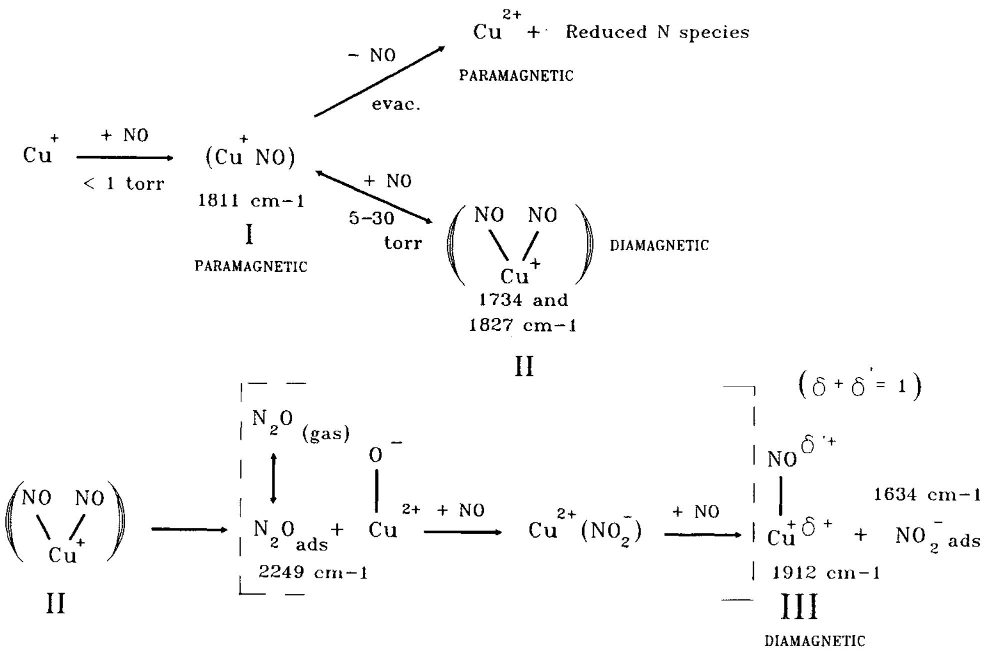
and α (the angle of oscillation between the two NO molecules) = 104°, which is a realistic figure for asymmetric *cis*-$(NO)_2$ complexes on a surface site. Note that the two NO stretching modes have rather different half band widths, as normally observed in the condensed phase (*20*). If we use the non-integrated intensities (I_{max}), we would observe an angle of $\alpha \approx 90°$, i.e., a figure close to that observed for $(NO)_2$ in the gas phase, and any effect due to the coordination at Cu^+ surface centres would be lost.

In parallel with the pressure dependence of the dinitrosyl species, the intensity of the 1912 cm^{-1} band also grows at higher NO pressures eventually becoming the dominant feature of the spectrum of the Cu^+/ZSM5 specimen (Fig. 5). This band is the same band observed in the spectra of the Cu^{2+}/ZSM5 system (Fig. 4) and is typical of NO interaction with Cu^{2+}, resulting in the formation of $[Cu^{+\delta+}NO^{\delta'+}]$, as detailed above. The appearance of the latter band, in Fig. 5, indicates that the Cu^+ sites undergo oxidation in the presence of a high NO pressure. This fact is also confirmed by the appearance of a Cu^{2+} signal in the EPR spectrum of Cu^+/ZSM5 after the adsorption of 5–30 Torr of NO. Since the $Cu^{+\delta+}NO^{\delta'+}$ adduct is not EPR visible, the observed Cu^{2+} ions (exhibiting a low spectral intensity) should correspond to the fraction of oxidised sites not capable of NO adsorption (see IR section).

The mechanism of the whole oxidative process can be understood by examining the other bands observed in Fig. 5, which provide spectroscopic evidence for the oxidative intermediates. The 2249 cm^{-1} band is typical of adsorbed N_2O (*29*) (N oxidation No. = +1) whereas the 2158 cm^{-1} band likely belongs to a $NO_2^{\delta+}$ molecule (N oxidation No. ≈ +3) adsorbed in a quasi-linear configuration (*30*). The band observed at 1634 cm^{-1} can also be attributed to an oxidised adsorbed species, i.e., to nitrites or pseudo nitrites (NO_2^-). The nitrite formation parallels that of the 1912 cm^{-1} band (the band characteristic of the oxidised state of copper). The interaction of NO with Cu^+/ZSM5 is thus a complex redox process. The oxidation of the site likely occurs by N_2O elimination from the dinitrosyl, followed by further successive reactivity of the site with NO, according to Scheme 1.

Elimination of N_2O from the copper dinitrosyl(II) occurs via the oxidation of the site to Cu^{2+} leaving a reactive oxygen intermediate that can easily react with additional NO to give NO_2^- (1634 cm^{-1}). Elimination of N_2O from an adsorbed nitrosyl pair has already been observed in the case of NO adsorbed on Ca^{2+} zeolites (*23*). The Cu^{2+} site remaining after the oxidation and N_2O elimination is then available for the coordination of another NO molecule to give the $[Cu^{+\delta+}NO^{\delta'+}]$ nitrosyl(III) typical of an oxidised Cu^{2+} sample (which is the main final result of the oxidation process), as supported by the appearance of the band at 1912 cm^{-1}. The formation of Cu^{2+} sites also occurs by evacuation of the reduced sample (see Scheme 1) under a low NO pressure when Cu^+NO(I) is the most abundant species present at the surface (Section 2b). This is unambiguously proved, both by the appearance of a Cu^{2+} signal in the EPR spectrum after NO evacuation and by the IR spectrum after NO readsorption that exhibits the 1912 cm^{-1} band typical of a NO adduct on Cu^{2+}. The interpretation of the mechanism of this second oxidation process is not straightforward and requires a careful analysis of the evacuated gas phase to identify the nature of the nitrogen species. (Work is currently in progress on this last point.)

Some discrepancies apparently exist between the present picture of NO chemistry on ionic copper sites and that proposed by



SCHEME 1

Iwamoto *et al.* (*29*) who previously observed bands at 1734, 1811, and 1827 cm^{-1} for NO on a partially reduced Cu/ZSM5 system. The bands at 1734 and 1827 cm^{-1} were assigned to $(NO)_2^-$ or dinitrosyls and the 1811 cm^{-1} band was assigned to an NO^- species; it was suggested that these bands were the intermediate species involved in the NO decomposition. According to Iwamoto *et al.* all three bands decreased simultaneously in intensity with time, under a constant pressure of NO (42 Torr). This intensity trend is different from that observed in our experiments, where the 1827 and 1734 cm^{-1} bands increased at the expense of the 1811 cm^{-1} band and vice versa (Fig. 4). In our opinion, the apparent different behaviour is due to the pressures of NO employed in the respective experiments. This hypothesis was confirmed by adding a high pressure of NO (26 Torr) to the Cu/ZSM5 sample: all three bands decreased simultaneously, as in the case described by Iwamoto *et al.* However, the use of very small doses of NO allowed us to show that the mononitrosyl (1811 cm^{-1}) and the dinitrosyl (1734 and 1827 cm^{-1}) on Cu^+ are not formed independently but are two species formed on the same site and interconvert into one another following the gas pressure. At high pressures both mono- and dinitrosyl complexes exist at the same time, and, as the decomposition proceeds, both nitrosyl sites are destroyed resulting in the decrease of all three bands simultaneously. At the lower pressures the decomposition follows the reaction scheme shown above.

Furthermore, by comparison of the result of adsorption onto oxidised and reduced samples of Cu/ZSM5, it is possible to single out the adducts typical of Cu^{2+} and Cu^+, respectively, and to describe the oxidative mechanism and its pressure dependence on the reduced site.

CONCLUSION

At ambient temperatures, NO typically reacts with Cu^{2+}/ZSM5 leading to a diamagnetic mononitrosyl characterized by a partial electron transfer from the molecule to the transition metal ion. The adduct, the NO stretching frequency of which is 1912 cm^{-1}, is reversibly formed at the temperature of the IR beam.

The interaction of NO with Cu^{+}/ZSM5 is characterized by the initial formation of a mononitrosyl which forms without electron transfer to the copper. The mononitrosyl (formerly Cu^{+}NO) is paramagnetic and characterised by a typical EPR spectrum. The IR stretching frequency of 1811 cm^{-1} indicates that the adsorbed NO molecule is slightly negative. The formation of this species is the first step in the formation of a dinitrosyl and of an oxidation process that occurs through the disproportionation of the dinitrosyl species and leaves Cu^{2+}, N$_2$O, and NO$_2^-$. The reduced state of Cu^{2+} in the Cu/ZSM5 catalyst is therefore deduced to be unstable under NO pressure at room temperature.

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REFERENCES

1. Li, K., and Hall, W. K., *J. Phys. Chem. Lett.* **94**(16), 6145 (1990).
2. Iwamoto, M., Yokoo, S., Sakai, K., and Kagawa, S., *J. Chem. Soc. Faraday Trans 1* **77**, 1629 (1981).
3. Iwamoto, M., Yahiro, H., Kutsuno, T., Bunyu, S., and Kagawa, S., *Bull. Chem. Soc. Jpn.* **62**, 583 (1989).
4. Iwamoto, M., Yahiro, H., and Tanda, K., "Successful Design in Catalysis," p. 219. Elsevier, Amsterdam, 1989.
5. Anpo, M., Nomura, T., Shioya, Y., Giamello, E., Murphy, D., and Che, M., *in* "9th International Conference on Catalysis."
6. Iwamoto, M., Furukawa, H., Mine, Y., Uemura, F., Mikuriya, S., and Kagawa, S., *J. Chem. Soc., Chem. Commun.*, 1272 (1986).
7. Iwamoto, M., Yahiro, H., Mine, Y., and Kagawa, S., *Chem. Lett.*, 213 (1989).
8. Li, Y., and Hall, K., *J. Catal.* **129**, 202 (1991).
9. Jacobs, P. A., DeWilde, W., Schoonheydt, R., Uytterhoeven, J. B., and Beyer, H., *J. Chem. Soc. Faraday Trans 1* **72**, 1221 (1976).
10. Jacobs, P. A., and Beyer, H., *J. Phys. Chem.* **83**, 1174 (1979).
11. Anderson, M. W., and Kevan, L., *J. Phys. Chem.* **91**, 4174 (1987).
12. Sendoda, Y., and Ono, Y., *Zeolites* **6**, 209 (1986).
13. Anpo, M., Nomura, T., Kitao, T., Giamello, E., Murphy, D., Che, M., and Fox, M. A., *Res. Chem. Intermed.* **15**, 225 (1991).
14. Naccache, C., Che, M., and Ben Taarit, Y., *Chem. Phys. Lett.* **13**(2), 109 (1972).
15. Anpo, M., *in* "Photochemical Conversion and Storage of Solar Energy," p. 307. Kluwer, Dordrecht, Netherlands, 1991.
16. Anpo, M., *et al.*, to be published.
17. Chao, C. C., and Lunsford, J. H., *J. Phys. Chem.* **76**(11), 1546 (1972).
18. Gray, H. B., Bernal, I., and Billing, E., *J. Am. Chem. Soc.* **84**, 3404 (1972).
19. Nakamoto, K., *in* "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed., p. 309. Wiley-Interscience, New York, 1986.
20. Laane, J., and Ohlsen, J. R., *Progr. Inorg. Chem.* **27**, 465 (1980).
21. Lunsford, J., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 22, p. 265. Academic Press, New York, 1972.
22. Che, M., and Giamello, E., *in* "Spectroscopic Characterization of Heterogenous Catalysis" (J. L. G. Fierro, Ed.), Vol. 57, Part B, p. B265. Elsevier, Amsterdam, 1990.
23. Addison, W. E., and Barrer, R. M., *J. Chem. Soc.*, 757 (1955).
24. Johnson, B. F. G., and McCleverty, J. A., *in* "Progress in Inorganic Chemistry" (A. F. Cotton, Ed.), Vol. 7, Interscience, New York, p. 311, 1966.
25. Tevault, D. E., and Andrews, L., *J. Phys. Chem.* **77**, 1646 (1973).
26. Garrone, E., Ghiotti, G., Morterra, C., and Zecchina, A., *Z. Naturforsch.* **42b**, 728 (1987).
27. Guillory, W. A., and Hunter, C. E., *J. Chem. Phys.* **50**, 3516 (1969).
28. Kung, M. C., and Kung, H. H., *Catal. Rev.-Sci. Eng.* **27**, 425 (1985).
29. Iwamoto, M., Furukawa, H., and Kagawa, S., *in* "New Developements in Zeolites Science and Technology" (Y. Murakami, Ed.), p. 943. Elsevier, New York, 1986.
30. Neben, J. W., McElroy, A. D., Klodowski, H. F., *Inorg. Chem.* **4**, 1796 (1965).