Co-adsorption of nitrogen monoxide and nitrogen dioxide in zeolitic de-NOx catalysts

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Room temperature adsorption and temperature programmed desorption (TPD) of NO, NO with O_2, and NO after NO_2 saturation were investigated for Na/Y, Na/ZSM5, Cu/ZSM5 and SiO_2 gel. The adsorbates were characterized by TPD, using mass spectrometry to identify the desorbed molecules. In the presence of O_2, the adsorption of NO and NO_2 is non-additive; co-desorption of nearly equal amounts of NO and NO_2 takes place suggesting the formation of a complex with an overall composition N_2O_3 within the zeolite. Since SiO_2 gel does not adsorb NO nor NO_2, the adsorption capacity of the zeolites is a function of their specific structure. The oxidation of NO to NO_2 is catalyzed by Na/Y and Na/ZSM5.

Keywords: adsorption; TPD; NO; NO_2; Na/Y; Na/ZSM5; Cu/ZSM5; SiO_2

1. Introduction

Decomposition of nitrogen oxide, though favored by thermodynamics is negligible at low temperatures in the absence of an appropriate catalyst [1]. Among the known catalysts, transition metals and their oxides require very high temperatures before appreciable conversion occurs [2]. Nitrogen oxide is, however, decomposed to N_2 and O_2 at temperatures near 400°C over Cu/ZSM5, as was discovered by Iwamoto [3]. At present the mechanistic functions of Cu and of the zeolite in this unique catalyst are incompletely understood. The same materials also catalyze the reduction of NO_x with e.g. propane; this reduction is strongly enhanced by the simultaneous presence of O_2, suggesting that coexistence of NO and NO_2 is essential in this catalysis [4,5].

The formation of N_2 from NO obviously requires rupture of N–O bonds and formation of N–N bonds. The sequence of these events is different for reduced transition metals such as Rh, and for catalysts containing metal ions. For NO adsorption on Rh(111) van Santen has shown that NO dissociation occurs on an ensemble of five contiguous Rh atoms [6]. No such clusters exist in Cu/ZSM-5 under oxygen rich or "lean" conditions, as Cu ions are not each other's closest

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neighbors. Therefore, the rupture of N–O bonds is likely to be preceded by formation of N–N bonds. This holds for all catalysts working in an oxidizing atmosphere. Since future technology favors lean conditions for automobiles, the catalysis of "lean NO_x" abatement is likely to include reaction steps in which N–N bonds are formed either between NO ligands of the same catalyst site, or between NO_{ads} and $NO_{2,ads}$.

Earlier, Addison and Barrer reported that nitric oxide disproportionates to N_2O_3 and N_2O [7] over Ca/Y zeolite. They found that N_2O is easily released from the zeolite, but an adduct of NO and NO_2 was retained. Kasai and Bishop found that the adsorbed complex did not give an EPR signal; they assumed that it was present inside the zeolite as an ion pair, $NO^+ + NO_2^-$ [8].

The research of the present paper was motivated by the question whether formation of an N_2O_3 adduct inside zeolite cavities could be a step initiating N–N bond formation in the reaction network of catalytic decomposition or reduction of NO_x. If an adsorbed N_2O_3 complex is an intermediate in these reactions, an important function of the zeolite in this catalysis might be to stabilize this adduct. This implies that adsorption of NO should be enhanced in the presence of NO_2 and, hence, of O_2.

Data on adsorption and desorption of NO, either alone or with O_2, and of NO_2 will be reported for the zeolites Na/ZSM-5 and Na/Y and on Cu/ZSM5. The adsorbates are characterized by TPD, using mass spectrometry to identify the desorbed molecules.

2. Experimental

2.1. CATALYST PREPARATION

The Cu/ZSM5 sample was prepared via ion exchange at room temperature. A 0.15 M $Cu(OAc)_2$ solution was added dropwise to a Na/ZSM5 (UOP lot #13923-60) slurry. The slurry was stirred for 24 h before being vacuum filtered. The product was washed with doubly deionized water, then air dried. This process was repeated twice. The sample was crushed to >60 mesh. Elemental analysis via inductively coupled plasma atomic emission spectroscopy gave the following data per Cu/ZSM5 unit cell (u.c.): $Cu_{2.6}[(AlO_2)_{4.57}(SiO_2)_{91.43}]\cdot 16H_2O$; Na/ZSM5 u.c.: $H_{1.51}Na_{3.06}[(AlO_2)_{4.57}(SiO_2)_{91.43}]\cdot 16H_2O$; Na/Y u.c.: $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]\cdot 240H_2O$.

2.2. PRETREATMENT

In the dynamic flow mode, adsorption measurements were made using a quartz reactor charged with 200 mg of zeolite on a porous frit. Each sample was pre-treated in a similar manner. The sample was calcined from 20 to 500°C at 0.67°C/min in 200 ml/min UHP O_2 flow. The temperature was held at 500°C for 2 h, then cooled to room temperature in oxygen flow. The sample was then heated from 20 to 500°C at 8°C/min in 30 ml/min UHP He, then cooled to room temperature in helium flow.

2.3. ADSORPTION STUDIES

All measurements were made on a temperature programmed system attached to a Dycor Quadrupole Gas Analyzer mass spectrometer (TP-MS). For "NO only" experiments, a mixture of NO (0.4%) in He at 60 ml/min was used; for "$NO + O_2$" experiments, a mixture of NO (0.4%) and O_2 (1.0%) in He was used. Upon bypassing the reactor, the background signal was measured before exposing the zeolite to the gas mixture. Computer monitoring of the mass spectra began once the background signal equilibrated. The gas flow was then switched so that the mixture passed over the reactor bed. Once equilibrium was reestablished, the reactor was sealed and computer monitoring of the mass spectra ended. Adsorption temperature was 22°C.

To test the non-additive adsorption of NO in the presence of NO_2, sodium-exchanged zeolites were first saturated with NO_2 before being exposed to a dilute NO stream. For these experiments, a mixture of NO_2 (0.47%) and O_2 (1.25%) in He was used. After saturation, the Na/ZSM5 sample was purged at 0°C with 30 ml/min UHP He while the Na/Y sample was purged at 50°C. The same procedures for adsorption and desorption measurements were used as in the "NO only" method described above, except the adsorption temperature was 0°C for Na/ZSM5 and 22°C for Na/Y. Samples studied were Na/ZSM5, Na/Y, silica gel (Aldrich grade 62, 60–200 mesh, 150 Å, 300 m^2/g).

2.4. DESORPTION STUDIES

The sealed reactor was cooled to −78°C using a dry ice/acetone bath. The sample was then purged for 30 min with 30 ml/min UHP He. After purging for 30 min, the dry ice/acetone bath was removed, and the sample was heated from −78 to 500°C at 8°C/min. Once the bath was removed, computer monitoring of the mass spectra began. A complication of the simultaneous analysis of NO and NO_2 is the high extent of fragmentation of the latter; its main fragment being the NO^+ ion. We determined the 30/46 mass ratio for NO_2 during desorption using calibrated mixture of NO_2 and O_2 in He. (Oxygen was included to prevent NO_2 from dissociating.)

3. Results

The following terminology will be used for the types of N–O bond fission processes discussed in this work:

decomposition: conversion of NO to $N_2 + O_2$;

disproportionation: conversion of NO to N_2O and N_2O_3 [7];

dissociation: all other chemical processes encompassing N–N or N–O bond rupture e.g. $NO_2 \rightleftharpoons NO + \frac{1}{2}O_2$;

fragmentation: decomposition, inside the ionization chamber of the mass spectrometer, of parent ions into ionic fragments of lower mass.

3.1. METAL-FREE ZEOLITES

Whereas no adsorption of NO or NO_2 was detected on SiO_2 gel, both gases are appreciably adsorbed by Na/ZSM5 and Na/Y. Both zeolites adsorb less NO than NO_2. The quantity of NO desorbed following the "NO only" adsorption, has been calculated and is presented in table 1.

TPD is used to probe for adsorbed complexes of NO and NO_2. Fig. 1 shows the TPD following exposure to "NO + O_2". At 85°C, nearly equal molar amounts of NO and NO_2 are released from Na/ZSM5 (fig. 1a); the quantities derived from the integrated curves are: 3.8 NO/u.c. and 3.7 NO_2/u.c. This desorption occurs at a similar temperature as in the "NO only" experiment. The co-desorption of NO and

Table 1
TPD data

Catalyst	T_{des} (°C)	NO_x/unit cell	NO_x/cation
following adsorption of NO at 22°C			
Na/Y	60	1.3 NO/u.c.	0.2 NO/Na
	180	<0.1 NO_2/u.c.	≪0.1 NO_2/Na
	450	≪0.1 NO_2/u.c.	≪0.1 NO_2/Na
Na/ZSM5	90	0.2 NO/u.c.	<0.1 NO/Na
	250	<0.1 NO_2/u.c.	<0.1 NO_2/Na
Cu/ZSM5	80	4.8 NO/u.c.	1.85 NO/Cu
	400	1.4 NO_2/u.c.	0.54 NO_2/Cu
following "NO + O_2" exposure at 22°C			
Na/Y	160	8.3 NO/u.c.	0.15 NO/Na
	160	9.6 NO_2/u.c.	0.17 NO_2/Na
Na/ZSM5	85	3.8 NO/u.c.	1.24 NO/Na
	85	3.7 NO_2/u.c.	1.21 NO_2/Na
	360	0.1 NO_2/u.c.	<0.1 NO_2/Na
H/ZSM5	85	7.3 NO_2/u.c.	2.45 NO_2/u.c.
Cu/ZSM5	85	4.5 NO/u.c.	1.73 NO/Cu
	85	6.9 NO_2/u.c.	2.65 NO_2/Cu
	400	2.2 NO_2/u.c.	0.85 NO_2

NO_2 suggests decomposition of a sorbed complex $[NO + NO_2]$, though in this case the value of T_{des} is not different from that after the "NO only" experiment. The desorbed amount is, however, an order of magnitude greater than after adsorption of NO alone. For Na/Y (fig. 1b), the evolution at 160°C corresponds to 8.3 NO/u.c. and 9.6 NO_2/u.c. With this zeolite T_{des} has been shifted to higher temperature by 100°C, indicating a strong interaction of NO with NO_2 and the zeolite. The quantity of NO evolved is also an order of magnitude larger in the presence of O_2 than in its absence. Clearly, NO is oxidized by O_2 to form NO_2 over these zeolites, and co-adsorption of NO and NO_2 takes place, which is non-additive. The data are compiled in table 1.

The adsorption capacity of H/ZSM5 was also investigated. H/ZSM5, like Na/ZSM5, absorbs little NO indicating that H/ZSM5 cannot catalyze the dispropor-

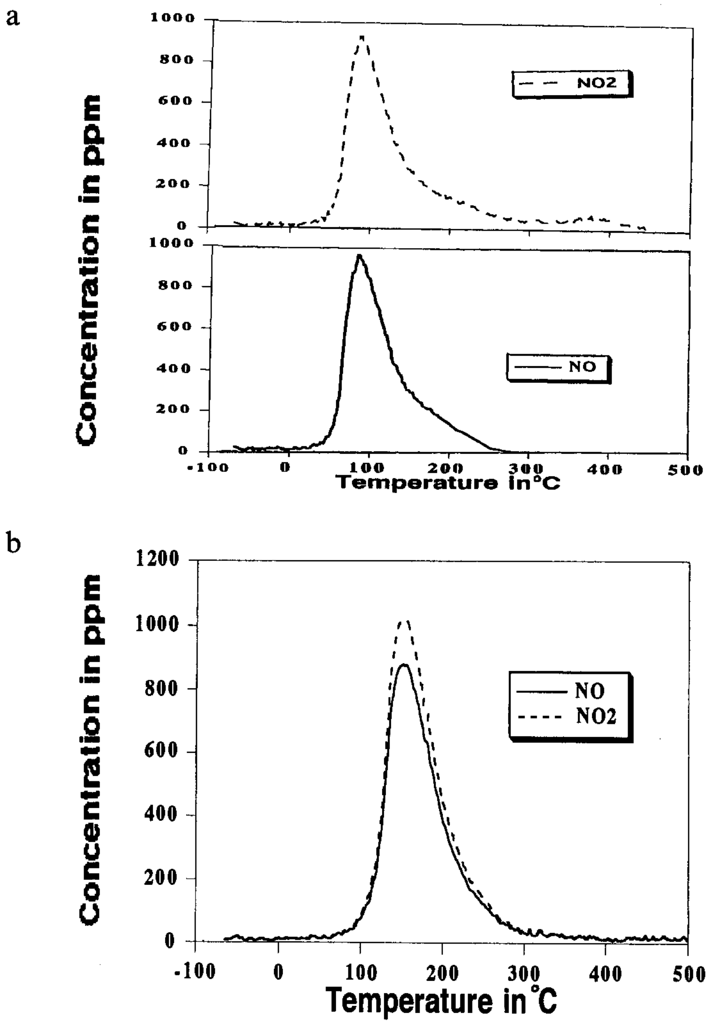


Fig. 1. TPD from (a) Na/ZSM5 and (b) NaY following exposure to "NO + O_2" at 22°C.

tionation reaction. In the presence of O_2, much NO_x is sorbed. From the TPD experiment this sorbed species was found to be solely NO_2. The total quantity of NO_x retained by the H/ZSM5 sample was the same as the Na/ZSM5 sample with identical T_{des}, 80°C. This datum is presented in table 1.

Fig. 2a shows the TPD spectrum from Na/ZSM5 after saturation with NO_2 at room temperature. The peak at 85°C corresponds to 7.3 NO_2 per unit cell. A second peak, corresponding to 0.4 NO_2/u.c. is registered at 380°C. Before exposing the NO_2-saturated sample to NO, the system was purged at 0°C with UHP He. This temperature was chosen to prevent significant NO_2 desorption which starts near 40°C, as follows from fig. 2a. Fig. 2b shows the TPD spectrum from Na/ZSM5 following NO adsorption after NO_2 saturation. The NO_x desorbed at 80°C corresponds to 7.3 NO_2/u.c. and 1.9 NO/u.c. There remains an NO_2 peak at 380°C

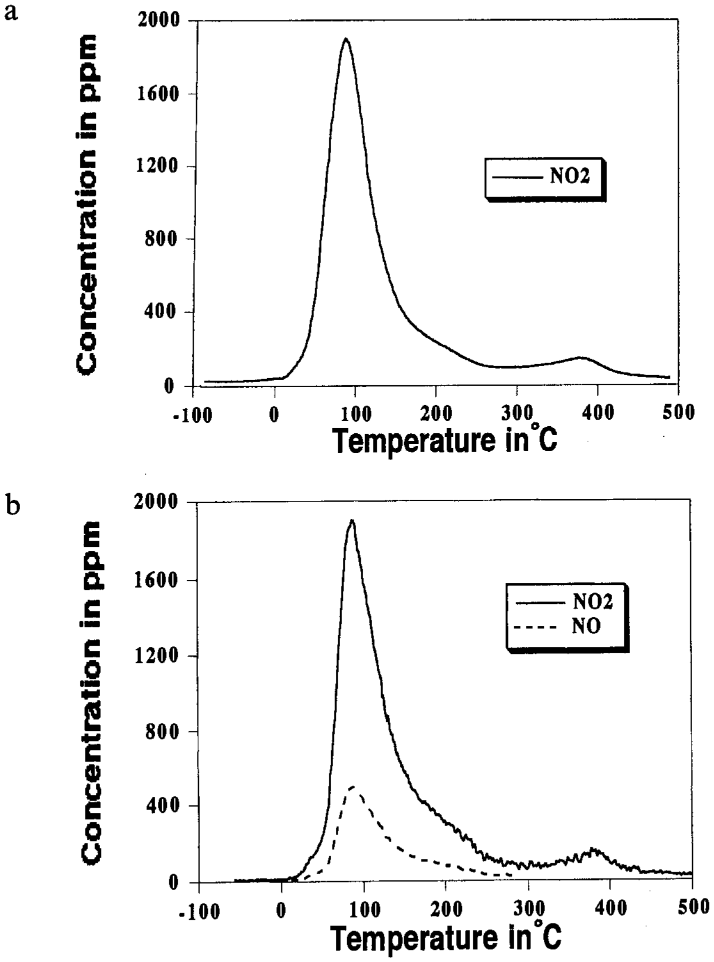


Fig. 2. (a) TPD from Na/ZSM5 following NO_2 saturation at 22°C. (b) TPD from Na/ZSM5 following NO adsorption at 0°C after NO_2 saturation at 22°C.

which corresponds to 0.4 NO_2/u.c. These data are compiled in table 2. Clearly, the sample saturated with NO_2 is able to adsorb additional NO without, however, reaching the $NO/NO_2 = 1/1$ ratio observed with the "NO + O_2" experiment.

Conspicuous color changes were observed in these experiments. After saturating with NO_2, the sample was yellow-brown. Upon NO exposure, the color changed to blue-green, and became light blue after cooling to −78°C. The yellow-brown color is reminiscent of NO_2, while the light blue color is indicative for N_2O_3. As no other blue complex is known for nitrogen oxides, this color change suggests that NO and NO_2 are present as N_2O_3.

Fig. 3a shows the TPD spectrum from Na/Y saturated with NO_2. The peak at 140°C corresponds to 18.5 NO_2/u.c. In order to determine if NO can be adsorbed by the saturated surface, the sample was saturated with NO_2, purged at 50°C, cooled to 22°C, then exposed to NO. Fig. 3b shows the TPD spectrum from Na/Y following NO adsorption after NO_2 saturation. The peak at 120°C corresponds to 17.6 NO_2/u.c. and 1.8 NO/u.c. After saturation with NO_2, the sample was, again, yellow-brown. Upon exposing it to NO, the color changes to blue-green and becomes light blue at −78°C, though the color change was less dramatic. These data are compiled in table 2.

3.2. Cu/ZEOLITES

The mass spectra for the adsorption of NO by Cu/ZSM5 from "NO only" and from "NO + O_2" are shown in fig. 4. They indicate some decomposition of NO, although formation of N_2 and N_2O could not be quantified from the mass 28 and

Table 2
TPD data following NO_2 saturation at 22°C

Catalyst	T_{des} (°C)	NO_x/unit cell	NO_x/cation
NO_2 only			
Na/Y	140	18.5 NO_2/u.c.	0.33 NO_2/Na
Na/ZSM5	85	7.3 NO_2/u.c.	2.4 NO_2/Na
	380	0.4 NO_2/u.c.	0.1 NO_2/Na
silica gel	–	none	none
after additional exposure to NO [a]			
Na/Y	120	17.6 NO_2/u.c.	0.31 NO_2/Na
	120	1.8 NO/u.c.	0.03 NO/Na
Na/ZSM5	80	7.3 NO_2/u.c.	2.4 NO_2/Na
	80	1.9 NO/u.c.	0.6 NO/Na
	380	0.4 NO_2/u.c.	0.1 NO_2/Na

[a] Na/ZSM5 adsorption at 0°C after degassing at 0°C for 30 min; Na/Y adsorption at 22°C after degassing at 30°C for 30 min.

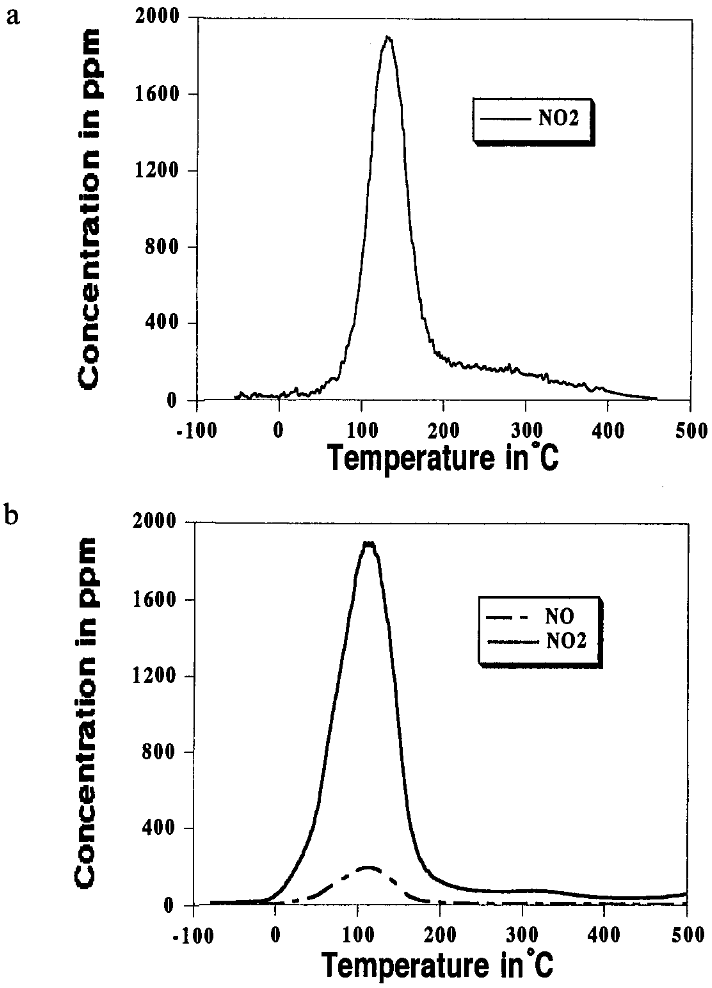


Fig. 3. (a) TPD from Na/Y following NO_2 saturation at 22°C. (b) TPD from Na/Y following NO adsorption at 22°C after NO_2 saturation at 22°C.

the mass 44 signals. Cu/ZSM5 is found to adsorb NO in the absence of O_2 in the gas mixture. Fig. 4a shows the change in the mass 30 signal versus time during the "NO only" experiment. Unlike the desorption spectra during the "NO + O_2" experiments for the sodium exchange zeolites, the dip is symmetric. Fig. 4b shows the change in the mass 30 and 32 signals during the "NO + O_2" experiment. Note that in the present flow experiments all gas phase concentrations below the value during the bypass mode signify positive adsorption rates. The figure shows that initially the rate of NO adsorption is high (TPD proves that in this stage the adsorbate is mainly NO); this is followed by adsorption of O_2, which is remarkable, as in the absence of NO, O_2 adsorption is not detected for this oxidized catalyst. In this stage the rate of NO adsorption decreases, but remains finite. This is followed

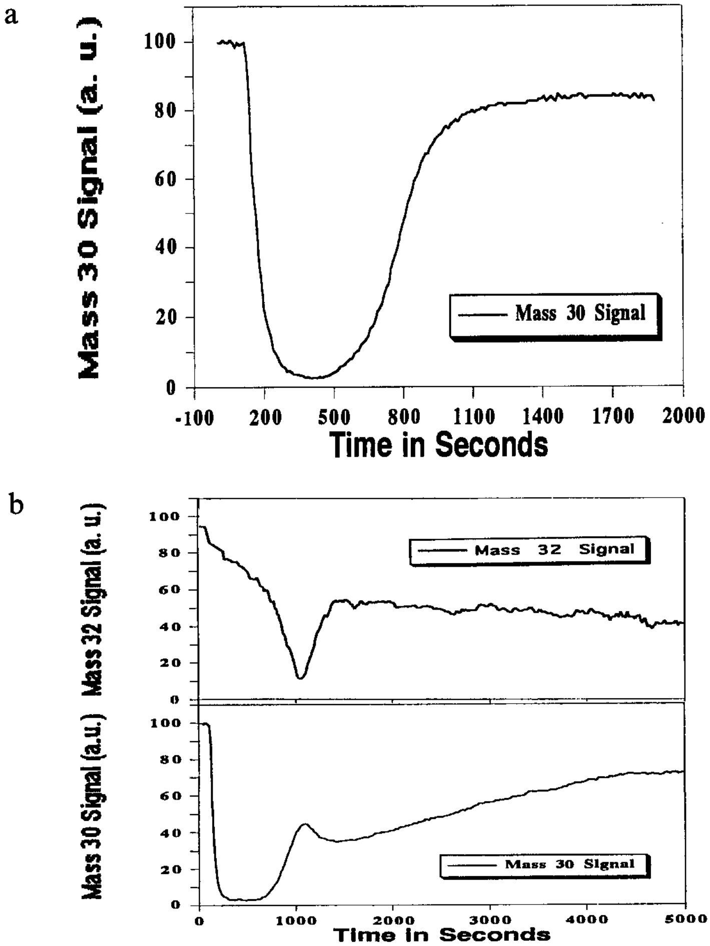


Fig. 4. (a) Time dependence of the mass 30 signal during "NO only" exposure over Cu/ZSM5 at 22°C. (b) Time dependence of the mass 30 and mass 32 signals during "NO + O_2" exposure over Cu/ZSM5 at 22°C.

by a third stage in which NO adsorption becomes rapid again. This suggests that $NO_{2,ads}$ which in all likelihood is formed during the second stage by Cu catalyzed oxidation of NO, accelerates the adsorption of additional NO. This indicates, again, formation of an NO + NO_2 adduct inside the zeolite.

Fig. 5 shows the TPD spectra after the "NO only" and the "NO + O_2" adsorption experiments. For "NO only" (fig. 5a), there are two large mass 30 peaks. The lower temperature peak at 80°C corresponds to 4.8 NO/u.c. At 400°C, there are simultaneous NO and O_2 evolutions. The mass 30 signal peak corresponds to 1.4 NO/u.c. and the mass 32 peak corresponds to 0.82 O_2/u.c. These peaks have been attributed to the evolution of NO_2 which has dissociated into NO and O_2 [9,10]. However, this should lead to an NO/O_2 ratio of 2 : 1 not 1.7 : 1. The differ-

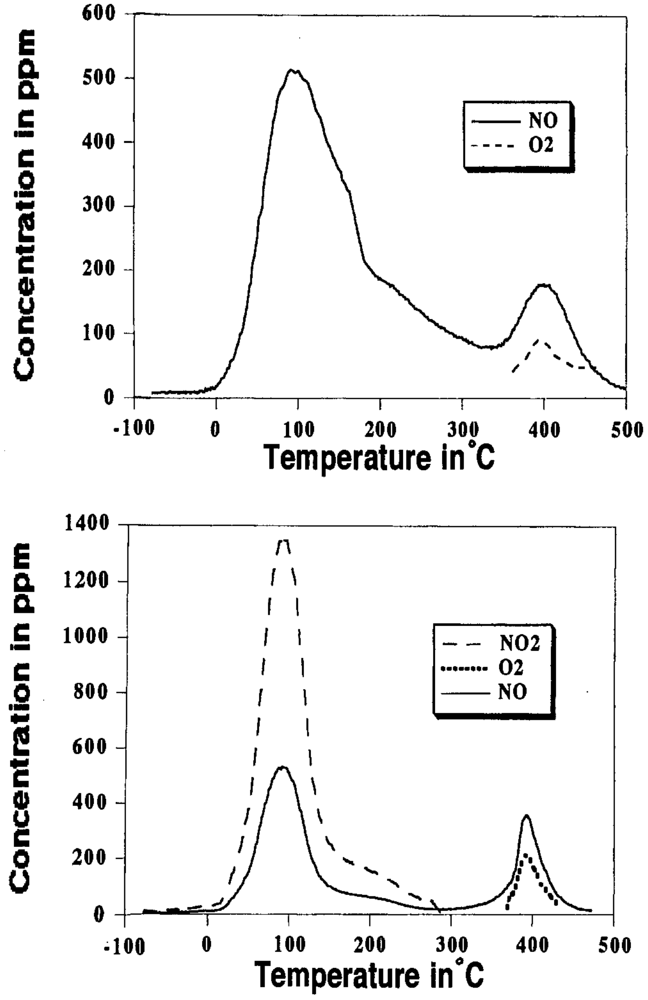


Fig. 5. (a) TPD from Cu/ZSM5 following NO adsorption at 22°C. (b) TPD from Cu/ZSM5 following "NO + O_2" exposure at 22°C.

ence between the calculated and observed ratios might be caused by O_2 evolution from the extra-lattice oxygen formed during the decomposition reaction, or by dissociation of nitrato complexes, $2NO^-_{3ads} \rightleftharpoons O^{2-}_{ads} + 2NO + 1\frac{1}{2}O_2$ [9]. As in the "NO only" experiments, there are two peaks during the TPD from the "NO + O_2" (fig. 5b). The lower peak at 85°C corresponds to 4.5 NO/u.c. and 6.9 NO_2/u.c. The quantity of NO evolved is relatively the same as the lower temperature peak from fig. 5a. Therefore, NO adsorption is not competitive in the presence of O_2. The higher temperature peak at 400°C corresponds to 2.2 NO_x/u.c. Again, the NO to O_2 ratio is 1.7. Since Na/ZSM5 has a markedly lower adsorption capacity per unit cell, the increase in NO_x evolution is attributed to the presence of copper. These data are reported in table 1.

4. Discussion

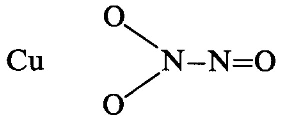
As silica gel does not adsorb appreciable quantities of NO or NO_2, the significant adsorption capacity of the zeolites reflects their specific structure, in particular the presence of unshielded ions.

Neither Na/ZSM5 nor Na/Y is capable of catalyzing the decomposition or disproportionation reactions at room temperature [11]. With both zeolites the adsorption of NO is markedly enhanced by co-adsorbing NO_2. This proves that both adsorbates are not competing for the same sites, but an attractive interaction apparently exists between them. This is shown most clearly after NO and O_2 exposure. For Na/Y the NO T_{des} increases by 100°C. Also, after saturation with NO_2 Na/ZSM5 and Na/Y zeolites adsorb NO which is detected both by the TPD profile and by the change in color. When the copper-free zeolites are exposed to a gas containing both nitrogen oxides, NO and NO_2 are adsorbed in a molar ratio near 1 : 1. This lends some justification to the notion that inside the zeolite the molecules have formed a complex with the overall formula N_2O_3. If true, this may be an entity similar to the gaseous molecule of that composition or it may be an ion pair. Kasai and Bishop assumed that an ion pair is formed which is stabilized by electrostatic interaction inside the zeolite [8]. In the case of Na/Y the attractive interaction between the NO + NO_2 monomers is especially clear from the 100°C shift of the T_{des} and that T_{des} was highest when the NO : NO_2 was 1 : 1. The absence of a large shift in T_{des} for Na/ZSM5 indicates the effect of NO_2: the dissociative desorption of N_2O_3 occurs at or near the same temperature at which NO_2 alone desorbs as seen in tables 1 and 2.

Which zeolite adsorbs more NO_x depends on the normalization of the data; per unit cell more NO_x is present in Na/Y, per Na^+ the sorption capacity of NaZSM5 for this entity exceeds that of Na/Y by almost an order of magnitude. Zeolite Y and ZSM5 are structurally different; Y contains sodalite and supercages while ZSM5 has intersecting channels. Per unit cell, there are 8 sodalite cages in zeolite Y and 4 intersections in ZSM5 (roughly one intersection per 24 tetrahedra). If we normalize the NO_x content along these lines, there is one N_2O_x ($x = 3$ or 4) dimer per sodalite or per intersection. This normalization may prove to be more useful when speculating reaction intermediates. From the data by Addison and Barrer, Kasai and Bishop also found 1 N_2O_3 dimer per sodalite cage after the disproportionation reaction over Ca/Y [8].

The results also show that reaction between NO and O_2 to form NO_2 is mediated by the zeolites, also in the absence of Cu.

The adsorbed quantities are significantly enhanced by the presence of Cu, as is to be expected. At present we can only speculate on the nature of the complexes that are formed between N_2O_3 and Cu^+ or Cu^{2+} ions. Quantum mechanical calculations by Kishner et al. [12] show that the N–N bond in N_2O_3 is of sigma type with high p-type character. The N–N bond order is reduced by the oxygen lone pair antibonding delocalization onto the nitrogens. It is, therefore, conceivable that the interaction of the N_2O_3 molecule with an electron accepting Lewis site such as a Cu ion, will strengthen the N–N bond. If so, a bidentate complex of Cu and N_2O_3:



might be visualized as a potential intermediate in NO_x reduction to N_2O and N_2. This is, however, pure speculation at this stage.

5. Conclusions

In the presence of O_2, NO and NO_2 are adsorbed by the sodium form of the zeolite. The adsorption is not competitive, but an attractive interaction exists between NO and NO_2, and between N_2O_3 and either zeolite. A NO/NO_2 ratio near unity, detected in TPD suggests formation of a complex of the overall composition N_2O_3.

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References

[1] Howard and F. Daniels, J. Phys. Chem. 62 (1958) 316.
[2] J.M. Fraser and F. Daniels, J. Phys. Chem. 62 (1958) 215.
[3] M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya and S. Kagawa, J. Chem. Soc. Chem. Commun. (1986) 1272.
[4] M. Iwamoto, *Proc. Meeting of Catalytic Technology for Removal of Nitrogen Monoxide*, Tokyo 1990, p. 17.
[5] W. Held, A. Konig, T. Richter and L. Puppe, SAE Paper 900496 (1990).
[6] R.A. van Santen, Presented at the Northwestern University Chemistry Colloquium, Evanston, IL, 8 April 1994.
[7] W.E. Addison and R.M. Barrer, J. Chem. Soc. (1955) 757.
[8] P.H. Kasai and R.J. Bishop, J. Am. Chem. Soc. 94 (1972) 5560.
[9] Y. Li and J.N. Armor, Appl. Catal. 76 (1991) L1.
[10] G. Ansel, A. Diwell, S. Golunski, J. Hayes, R. Rajaram, T. Truex and A. Walker, App. Catal. B 2 (1993) 81.
[11] C.C. Chao and J.H. Lunsford, J. Am. Chem. Soc. 93 (1977) 71.
[12] S. Kishner, M.A. Whitehead and M.S. Gopinathan, J. Am. Chem. Soc. 100 (1978) 1365.