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TPD study of the interaction of oxygen and NO with reduced Cu/ZSM-5

Zhiqun Wang, Andrey V. Sklyarov, George W. Keulks *

Department of Chemistry, Advanced Analysis Facility, University of Wisconsin-Milwaukee, Milwaukee, WI 53201, USA

Abstract

The adsorption and desorption of oxygen and NO over reduced 103% Cu/ZSM-5 were studied by means of TPD and TPD-FTIR. The oxygen TPD patterns with adsorption temperatures from − 100 to 500°C contained at least three desorption peaks which showed strong temperature dependence. The results of $^{18}O_2$-TPD and kinetic oxygen desorption–adsorption experiments revealed that dissociative adsorption of oxygen starts above 200°C. At lower temperature, oxygen adsorbs mainly in molecular form. The amount of oxygen adsorbed at low and higher temperatures correspond to the ratio of 0.15 O_2/Cu and 0.17 O/Cu, respectively. The results of NO TPD indicated that about 80% of the copper sites are active for NO adsorption. The adsorbed NO can be partially desorbed as NO below 300°C. During the process of NO adsorption, some of the NO molecules react with ELO to form NO_2 which can be desorbed around 400°C. The co-adsorption of NO and oxygen suggested that oxygen and NO compete for the same part of copper sites. These results indicate that oxygen adsorption, NO decomposition and NO_2 formation happen at the same type of copper site which is believed to be the copper center bonded with ELO.

Keywords: Cu/ZSM-5; TPD; NO decomposition; oxygen desorption; NO desorption; NO_2 formation

1. Introduction

Since the pioneer work of Iwamoto et al. [1], many studies have been made on Cu/ZSM-5, the most active catalyst for NO decomposition to date. Several mechanisms have been proposed; these can be grouped into two categories: the redox mechanism proposed by Iwamoto et al. [2], and Hall and Valyon [3,4] and nonredox mechanism proposed by Shelef [5]. Although most of the experimental data favors the former, which involves a Cu^{2+}/Cu^{1+} cycle coupled with the formation of O and the release of O_2, the exact nature of the active sites, the reaction intermediates and the reaction pathway remain debatable.

In ESR studies [6,7] on samples with high Si/Al ratios and exchange levels below 70%, the data showed that the sample contains two types of isolated cupric sites with different coordination. When the exchange level was higher than 100%, ESR studies [8,9] revealed that the two types of isolated cupric sites also exist. It is well documented that the so-called extra lattice oxygen (ELO) is introduced into the overexchanged Cu/ZSM-5 as OH bridged Cu^{2+} dimers or $[CuOH]^+$ [9–11]. Upon heating, these dimers lose water molecules and form Cu^{2+}–O^{2-}–Cu^{2+} and other species. Lei et al. [9] have

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* Corresponding author.

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suggested that the oxygen bridged copper dimers are ESR silent. Therefore, the literature data has shown that at least three types of copper sites may exist on the surface of excessively exchanged Cu/ZSM-5.

A study of the desorption of oxygen from Cu/ZSM-5 [12] suggested that the low temperature release of oxygen may explain the superiority of Cu/ZSM-5 versus CuY and other catalysts. But the active centers for oxygen adsorption were not defined. As shown by Iwamoto [13] the desorption of oxygen from CuY, which also contains ELO is unambiguously due to the collapse of Cu^{2+}–O^{2-}–Cu^{2+} species. We may ask ourselves whether or not a similar reaction is also responsible for the oxygen desorption over excessively exchanged Cu/ZSM-5. May oxygen be adsorbed in a molecular form or exist only as oxygen atoms?

On an excessively exchanged Cu/ZSM-5 sample, Iwamoto et al. [14] discovered that about 94% of the copper ions introduced by ion exchange are active for NO adsorption. Are the active centers for NO adsorption and decomposition the same? Are oxygen and NO adsorbed on the same copper centers? In the reaction mechanism proposed by Hall and Valyon [15] and Spoto et al. [16], NO–Cu–NO_2 species formed upon adsorption of NO are considered as possible reaction intermediates. A detailed TPD and TPD-FTIR study of NO adsorption on Cu/ZSM-5 might possibly give more straightforward evidence of the formation of NO_2.

In the present study, TPD and TPD-FTIR techniques have been applied to further understand the adsorption of oxygen and NO on Cu/ZSM-5. Attention is focused on the active sites responsible for oxygen and NO adsorption and the species formed.

2. Experimental

2.1. Catalyst preparation and characterization

The Cu/ZSM-5 catalyst was prepared from HZSM-5 (Si/Al = 17, PQ Co.) by ion exchange with 0.05 M copper acetate solution at room temperature. The pH value was about 5.5. After the ion exchange, the product was filtered and washed with deionized water. The samples obtained were dried at 120°C overnight and then calcined at 500°C under atmosphere for 10 hours. Atomic Absorption analysis showed a copper content of 2.8 wt% or an exchange level of 103%.

2.2. TPD studies

All the TPD measurements were carried out on a TPD system (base vacuum 10^{-7} Torr) equipped with a quadrupole mass spectrometer (Spectra Instruments). In order to remove water and possible hydrocarbon from the surface, after being mounted in a quartz reactor between quartz-wool plugs, the fresh Cu/ZSM-5 sample was treated in vacuum (10^{-6} Torr) at 500°C for two hours and then exposed to O_2 (600 Torr) at the same temperature for another two hours.

Two types of sample pretreatment were used prior to adsorption: (1) vacuum treatment ($< 10^{-6}$ Torr) at 500°C for 10 hours followed by cooling to adsorption temperature in vacuum; and (2) treatment in O_2 (600 Torr, UHP, Gas Tech) at 500°C for 10 hours followed by cooling to adsorption temperatures in the atmosphere of O_2. The two samples are termed as "reduced sample" and "oxidized sample", respectively.

After pretreatment, the samples were exposed to O_2 or NO (Matheson, 99.5%) (100 Torr) for one hour at the desired temperature for adsorption before evacuated for three minutes at the same temperature, and then, the sample was cooled down to room temperature within 10 minutes in vacuum. Another 20 minutes of evacuation was performed to remove the residue gas phase O_2 or NO. Finally the programmed heating at a rate of 8°C/min was started. The composition of the desorbed gas was continuously monitored by the mass spectrometer. The MS signal was recorded at 30 amu (NO), 32 amu (O_2), 28 amu (N_2), 44 amu (N_2O) and 46 amu (NO_2). The amount of desorbed gas was calculated based on the integrated area of corresponding TPD spectra. All the TPD spectra were obtained on reduced samples except as specified elsewhere.

2.3. FTIR measurements

The FTIR spectra were recorded using a Mattson 5000 Galaxy FTIR Spectrometer equipped with a diffuse-reflectance attachment and an environment chamber from Spectra-Tech. The resolution was set at 4 cm^{-1}. The catalyst powder samples were pressed into a sample holder with a chromel–alumel thermocouple in contact with the catalyst bed. Prior to the adsorption of NO at room temperature, the samples were treated in a flow of He (or O_2) at 500°C for more than five hours and cooled down to room temperature in He (or O_2). Then a flow of 0.4% NO/He was introduced into the system. After adsorption for 30 minutes, the sample was purged with pure He at the same temperature for 15 minutes and then the programmed heating was started with a heating rate of about 5°C/min. The DRIFT spectra were recorded at selected temperatures. Different spectra at corresponding temperatures obtained from He treated sample were used as reference.

3. Results and discussion

3.1. Oxygen adsorption and desorption

The O_2 TPD spectra from the reduced Cu/ZSM-5 after O_2 adsorption at different temperatures are shown in Fig. 1. As the parent H-ZSM-5 does not show any apparent oxygen desorption peaks, the adsorption of oxygen on the Cu/ZSM-5 may be ascribed to the presence of copper centers. When oxygen was adsorbed at −100°C (Fig. 1a), at least three different states of adsorbed oxygen are present indicated by the appearance of three TPD peaks (or shoulders) below 200°C. As the adsorption temperature (T_{ad}) was increased to 100, 300 and 500°C, while these three desorption peaks (or shoulders) were always present, the position of the oxygen desorption peaks showed a strong temperature dependence as seen in Fig. 1b–1d. When oxygen was adsorbed at −100°C and 500°C, the total amount of oxygen desorbed from the surface corresponded to $O_2/Cu = 0.15$ and $O/Cu = 0.17$, respectively. These results are in an agreement with the three types of copper sites detected by Photoluminescence [17] and ESR [18] on a highly reduced sample. In comparison, on a fully oxidized sample, Valyon and Hall [12] observed four oxygen desorption peaks at 125°C, 218°C, 410°C and 540°C, respectively.

In order to determine the forms of oxygen adsorbed at different temperatures, TPD experiments using $^{18}O_2$ (10 Torr) (Cambridge Isotope Laboratories, 98%) at various adsorption temperatures were carried out. Prior to the adsorption, the sample was treated at 500°C under high vacuum (10^{-6} Torr) for 10 hours to remove the adsorbed $^{16}O_2$ from the surface. The results obtained are shown in Fig. 2. After the adsorption at 30°C (Fig. 2a), only $^{18}O_2$ desorption was detected. The small amount of $^{16}O^{18}O$ detected in the gas phase is due to the impurity of $^{16}O^{18}O$ in the $^{18}O_2$ gas used. This result suggests that at temperatures below 30°C, oxygen is adsorbed mainly in molecular form. As the adsorption temperature was increased up to 300°C, besides the dominant $^{18}O_2$ signal, two obvious desorption peaks of $^{16}O^{18}O$ were observed (Fig. 2b). The desorption of $^{16}O_2$ was also detected around 400°C maybe because of the release of lattice oxygen. In the TPD profile of $^{18}O_2$ with an adsorption temperature of 500°C (Fig. 2c), stronger signals of $^{16}O^{18}O$ was recorded. These results suggested that at higher temperature ($\geq$ 300°C), the gas phase oxygen easily exchanges with the lattice oxygen and, therefore, oxygen adsorbs mainly in atomic form. The high desorption peaks of $^{18}O_2$ suggest that a great deal of lattice oxygen (O^{16}) was exchanged by gas phase oxygen (^{18}O) during the process of adsorption at 500°C, and during the desorption process, ^{18}O atoms recombined to form $^{18}O_2$ and desorbed into gas phase.

To confirm our conclusions, a temperature-programmed desorption–adsorption experiment was performed over a sample presaturated with oxygen at 30°C with 10^{-3} Torr oxygen in the gas phase. As demonstrated in Fig. 3, oxygen desorption was detected from 30°C to 225°C. This result indicates that the molecular oxygen adsorbed at room temperature can be removed from the surface below 225°C. Above this temperature, the oxygen pressure dropped significantly revealing another type of activated oxygen adsorption was taking place. These adsorbed oxygen species can be desorbed only at temperatures higher than 460°C. The relatively sharp decrease of the oxygen pressure around 225°C shows that the adsorption of oxygen at this temperature is a relatively fast process even at an oxygen pressure as low as 10^{-3} Torr. During the cooling process after the temperature of the sample reached 800°C, at least two types of oxygen adsorption processes were observed as shown in Fig. 3. These results clearly show that two forms of oxygen can be adsorbed on the surface of reduced Cu/ZSM-5: weakly bonded or molecular oxygen that can be desorbed at temperatures below 225°C, and strongly bonded or atomic oxygen which can be formed during the adsorption at higher temperature. At elevated temperature, e.g., 500°C, oxygen is adsorbed mainly in atomic form.

Keeping the above results in mind, we can now go back to the amount of oxygen adsorbed at low and high temperatures in molecular and atomic forms, respectively. As shown before,

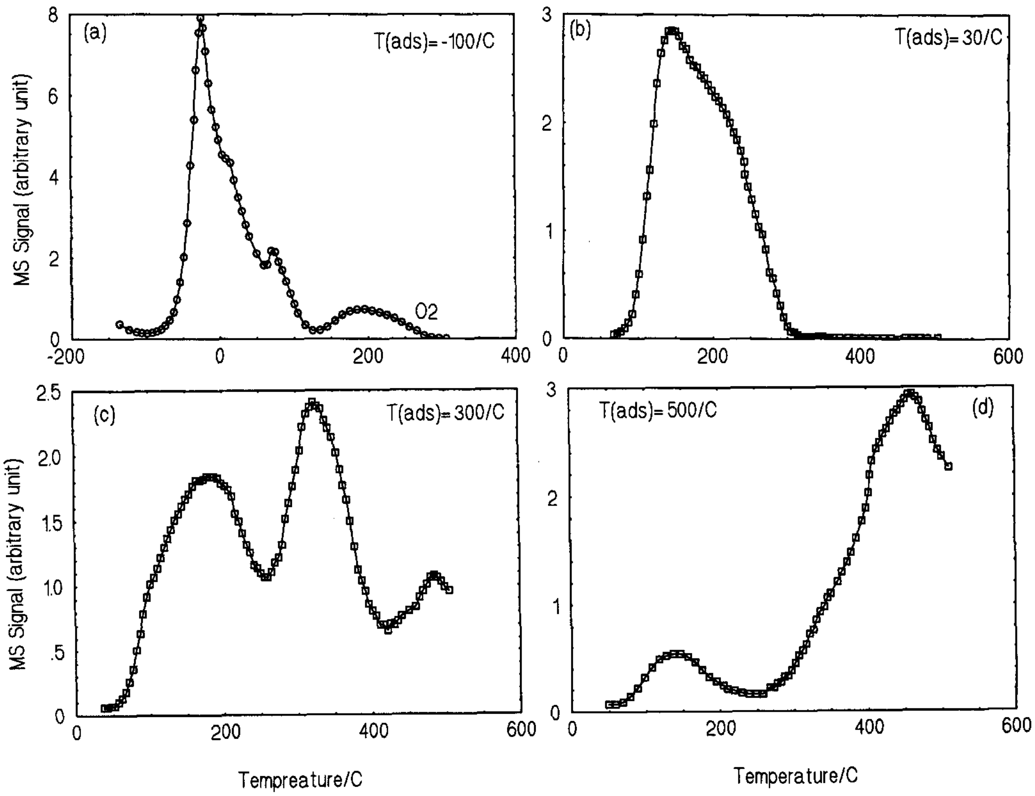


Fig. 1. TPD profiles of O_2 (32 amu) from reduced Cu/ZSM-5 at various adsorption temperatures: (a) − 100°C, (b) 30°C, (c) 300°C, and (d) 500°C. The sample was pretreated in vacuum (10^{-6} Torr) at 500°C for 10 hours and cooled to adsorption temperature in vacuum where 100 Torr of O_2 was introduced for adsorption (30 minutes). The temperature was raised at a rate of 8°C/min. The sample was 0.1 g.

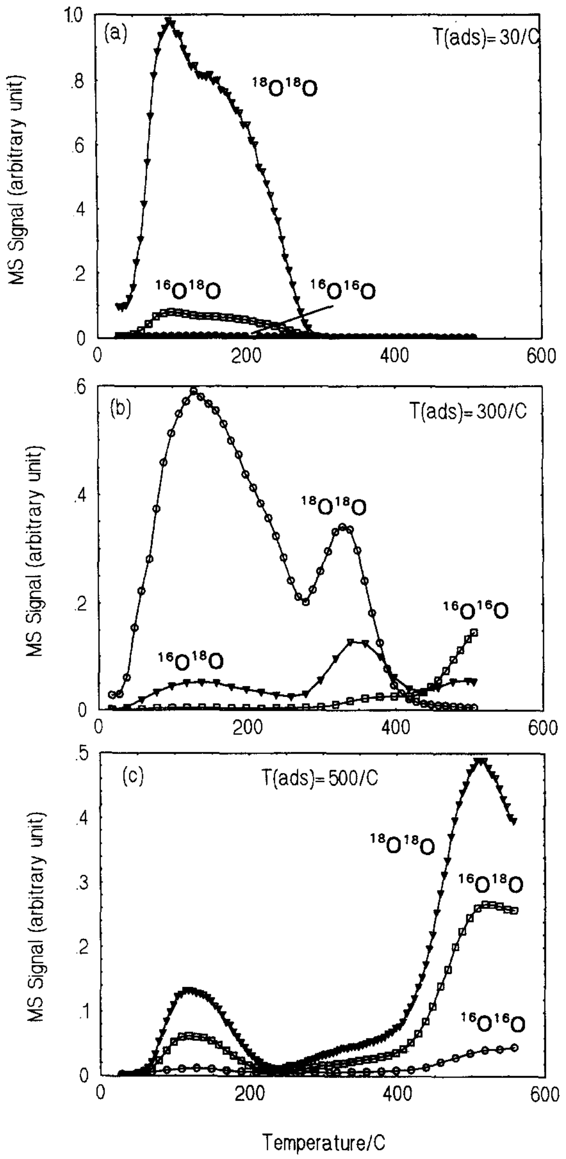


Fig. 2. TPD profiles of $^{18}O_2$ from reduced Cu/ZSM-5 at various adsorption temperatures: (a) 30°C, (b) 300°C, and (c) 500°C. Oxygen pressure for adsorption: 10 Torr.

the total amount of oxygen adsorbed at − 100°C and 500°C, is 0.15 O_2/Cu and 0.17 O/Cu, respectively. This reveals that less than 20% of all the copper centers introduced by ion exchange are active for oxygen adsorption. If taking into account of the dimers possibly involved in the oxygen adsorption, this ratio may be higher. It also may suggest that the oxygen adsorption always occurs on the same type of copper centers, either in molecular or in atomic form, depending on the adsorption temperature.

On a Cu/ZSM-5 sample with a higher exchange level (Si/Al = 14, exchange level 114%), Valyon and Hall [12] found that the desorbed oxygen amounted to about 0.2 O/Cu. As the exchange level of our sample is 103%, these results may indicate that on an excessively exchanged (≥ 100%) Cu/ZSM-5, no matter how high the exchange level is, only the particular 20% of the copper centers are active for oxygen adsorption.

The presence of extra-lattice oxygen (ELO) in CuY and excessively exchanged Cu/ZSM-5 has been widely discussed [10,11,13]. As shown by Iwamoto et al. [10], in Cu/ZSM-5, the ELO is held as $[Cu^{2+}–O^{2-}–Cu^{2+}]$. This part of the copper ions can be self-reduced to Cu^{1+} with the evolution of $\frac{1}{2}O_2$ upon thermal treatment in vacuum. These copper species can be reversibly reproduced by the high temperature treatment in an oxygen atmosphere.

In a TPD experiment using a sample with an exchange level of 15.6% (Si/Al = 15), no oxygen desorption and therefore no oxygen adsorption was detected. Thus, it may be assumed that only on the excessively exchanged Cu/ZSM-5, the copper centers which hold ELO are responsible for the oxygen adsorption. In another words, during the thermal treatment of excessively exchanged Cu/ZSM-5 under vacuum,

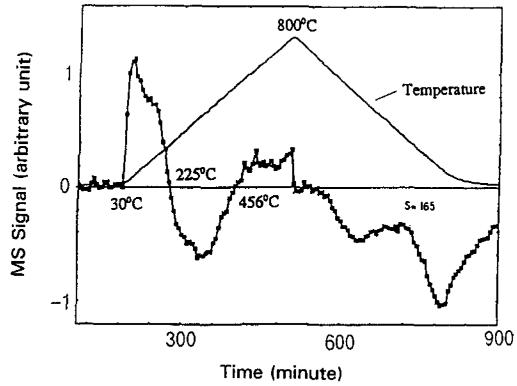


Fig. 3. Temperature programmed desorption–adsorption profile of oxygen with 10^{-3} Torr O_2 in the gas phase. The reduced sample was saturated with oxygen at room temperature.

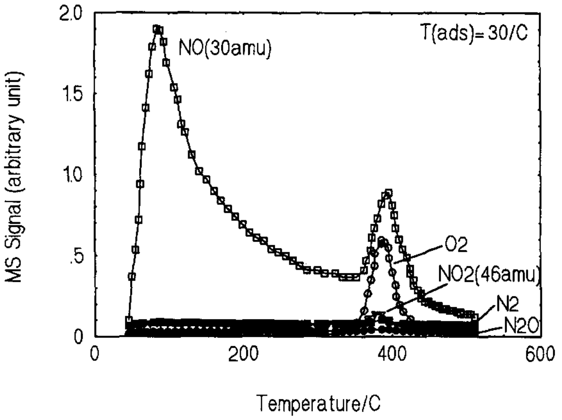


Fig. 4. TPD profile of NO from reduced Cu/ZSM-5. Adsorption temperature: 30°C. NO pressure for adsorption: 100 Torr. Adsorption time: 30 minutes.

some of the ELO was removed and at the same time, some of the Cu^{2+} was reduced to Cu^{1+}. When oxygen was introduced at high temperature (e.g., 500°C) for adsorption, these Cu^{1+} species were reoxidized to Cu^{2+} and atomically adsorbed oxygen bonded with these Cu^{2+} centers to form ELO. In this sense, the redox capability of copper ions in excessively exchanged Cu/ZSM-5 is responsible for the adsorption and desorption of oxygen.

3.2. NO adsorption and desorption

After exposure of the reduced sample to NO at room temperature, two major NO (30 amu) desorption peaks were detected at 90 and 390°C with possibly unresolved peaks in between in the TPD profile (Fig. 4). Weak signals of NO_2 and N_2O desorption were also recorded with peak temperatures close to those of NO desorption. Room temperature decomposition of NO was also observed as shown by the presence of N_2 desorption through all the temperature range, which was also observed by Li and Armor [18]. Another important feature that should be specified is that oxygen desorption was seen only with one desorption peak at 390°C which is always a few degrees ahead of the high temperature desorption peak of 30 amu. As shown before, when oxygen is adsorbed below 250°C, the desorption of molecularly adsorbed oxygen was completed below 350°C. But at high temperatures, oxygen molecules can be adsorbed dissociatively on the surface. These adsorbed atomic oxygen could be desorbed at temperatures higher than 400°C as shown in Fig. 2 and Fig. 3. Therefore, the evolution of oxygen with a desorption peak around 390°C in the TPD profile after NO adsorption was ascribed to the decomposition of NO that occurs even at room temperature followed by recombination of atomic oxygen and desorption as molecular oxygen at high temperature.

The amount of NO adsorbed at room temperature corresponds to a ratio of 0.8 NO/Cu. As the $Cu(NO)_2$ species are hardly detectable in the FTIR spectra after NO adsorption for 30 minutes, this result indicates that most of the copper centers (80%) are active for NO adsorption at room temperature, whereas only 20% of

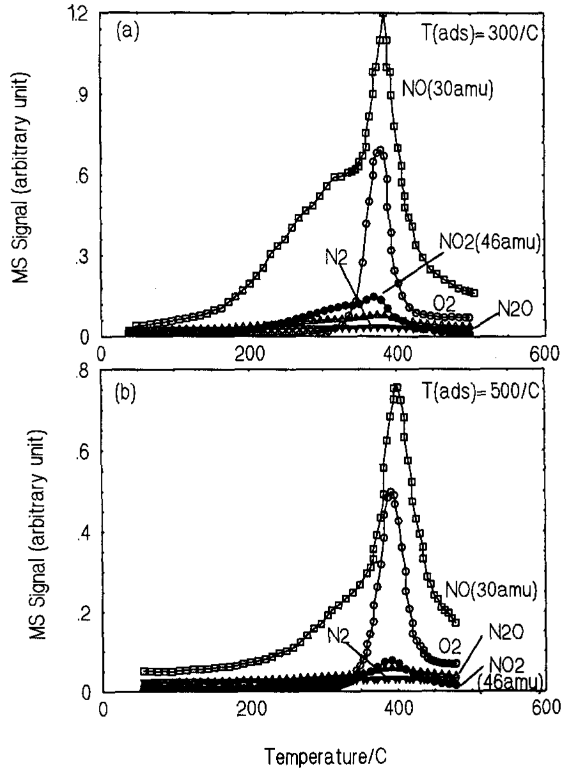


Fig. 5. TPD profiles of NO from reduced Cu/ZSM-5. Adsorption temperatures: (a) 300°C, and (b) 500°C.

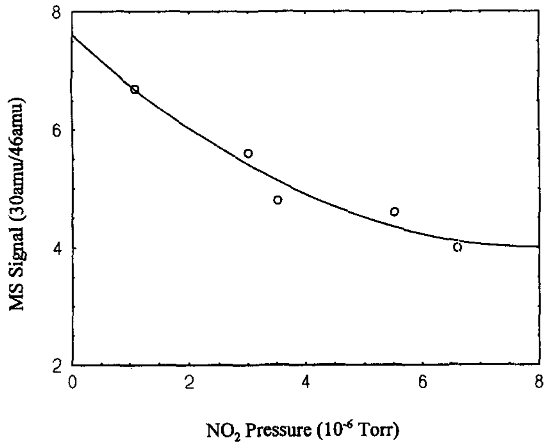


Fig. 6. Calibration of the ratio of the MS fragmentation pattern of 46 amu (NO_2) to 30 amu (NO) at various NO_2 pressures.

them are active for oxygen adsorption as shown by the results of oxygen TPD. It should be noted that the total amount of high temperature desorbed NO (30 amu) and oxygen correspond to about 0.2 NO/Cu and 0.2 O/Cu after the NO adsorption at different temperatures.

When the adsorption temperature was increased from room temperature to 300 and 500°C, the 100°C desorption peak disappeared while the intensity of 390°C peak showed no temperature dependence (Fig. 5). A pronounced shoulder appeared in the 350°C region. When the adsorption temperature reached 500°C, besides the weak shoulder around 350°C, only the 390°C desorption peak was detected. It should be noted that in the TPD profiles with various adsorption temperatures, the oxygen desorption peak around 390°C was always observed.

In the NO TPD experiments of Iwamoto et al. [14] and Li and Armor [18], no NO_2 was detected in gas phase after the NO adsorption. At the same time, the IR bands of NO_2 and NO_3 adsorbates were shown to disappear around 380°C. The higher temperature desorbed NO around 360°C detected in their TPD experiments were thought to be due to the catalytic decomposition of the adsorbed NO_2 or NO_3 species. In other words, it was believed that the NO_2 or NO_3 species formed on the surface of the catalysts could not be desorbed as NO_2, rather it was decomposed into NO and O and formed the detected 30 amu desorption peak around 360°C.

If this is the case, after the adsorption of NO at a temperature as high as 500°C, which is much higher than the required temperature of NO_2 decomposition and corresponding NO desorption, there should be little NO_2 formation on the surface and therefore there should be no strong NO (30 amu) desorption peak detected. This is contrary with our experimental data shown in Fig. 5b.

Based on the above reasons, it was assumed that the so-called NO desorption around 390°C detected in our experiments is just MS fragmentation of desorbed NO_2. To confirm this assumption, the contribution of MS fragmentation of NO_2 to 30 amu signal was measured at various NO_2 pressure (Fig. 6). These data show that the MS fragmentation pattern not only depends on the NO_2 pressure in the gas phase and the type of MS Spectrometer used; the design of the ion source also plays a critical role in the process of fragmentation. By comparison of the 30 amu/46 amu (NO/NO_2) ratio at various NO_2 pressure taken from the calibration curve (Fig. 6) and the data taken from the TPD profile of NO (Fig. 4) around 390°C (Table 1), it is believed that the high temperature 30 amu desorption peak is not due to the decomposition of the adsorbed NO_2 and formation of NO. Instead, it is ascribed to the MS fragmentation of gas phase NO_2 desorbed from the surface. In

Table 1

Comparison of the 30 amu/46 amu (NO/NO_2) ratios at various NO_2 pressures. The data were taken from the calibration run and Fig. 4 around 390°C

NO_2 pressure (10^{-n8} Torr)	30 amu/46 amu (NO/NO_2) (calibration)	30 amu/46 amu (NO/NO_2) (experimental)
1.1	6.8	6.4
1.0	8.0	7.3
0.9	10.1	8.0
0.8	11.7	10.8
0.7	12.4	11.7

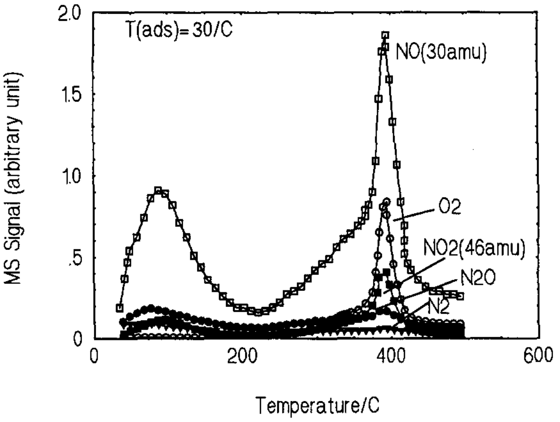


Fig. 7. TPD profile of NO_2 from reduced Cu/ZSM-5. The sample was saturated with NO at room temperature before the intrduction of NO_2. Adsorption temperature: 30°C.

other words, the NO_2 or NO_3 species formed and adsorbed on the surface at lower temperature can be desorbed as NO_2 at higher temperature.

To support our conclusions further, after NO_2 was adsorbed at room temperature on a sample saturated with NO at room temperature, a TPD experiment of co-adsorbed NO and NO_2 was performed. Two 30 amu desorption peaks were observed (Fig. 7). In comparison with the TPD profile of pure NO, the intensity of the low temperature peak was only half of that, whereas the high temperature peak was doubled. This confirms that the high temperature desorption peak of 30 amu came from the adsorbed NO_2. This result also may suggest that NO and NO_2 were adsorbed on the same type of copper centers. Again, a simultaneous evolution of oxygen and NO_2 (recorded as 30 amu peak by the mass spectrometer) was detected at 390°C. This suggests the close correlation of the active center for oxygen adsorption and that for NO_2 formation and adsorption. Based on the discussion before, it is believed that NO was adsorbed on the reducible copper centers and reacted with ELO to form NO_2.

In summary, the TPD data show that during the adsorption of NO at various temperatures, two types of stable adsorption species exist on the surface of Cu/ZSM-5, i.e., NO and NO_2/NO_3. The adsorbed NO species can be completely desorbed below 300°C, whereas the NO_2 species are stable up to at least 400°C.

It has been proposed by Li and Hall [19] that the ability of relative low-temperature oxygen release of Cu/ZSM-5 plays a major role in the catalytic reduction and decomposition of NO. At present, although ESR and Cu^{1+} photoluminescence studies [6,8,17] revealed several types of copper sites on the surface of Cu/ZSM-5 treated under different conditions, the clear identification of the active sites for oxygen and NO adsorption and reaction has still not been found. To shed light on this question, a TPD experiment was carried out after the adsorption of NO at room temperature on a reduced sample saturated with oxygen at the same temperature (Fig. 8). If there are different copper sites for oxygen and NO adsorption, we would expect low temperature oxygen desorption as observed in Fig. 1b besides the NO desorption. However, as can be easily seen from Fig. 8, the TPD spectrum is almost identical with that of pure NO adsorption. This result indicates that oxygen and some of the NO compete for the same type of adsorption sites. As it has been shown that in an excessively exchanged Cu/ZSM-5, only the copper centers which hold the ELO are responsible for the oxygen adsorption, it can be con-

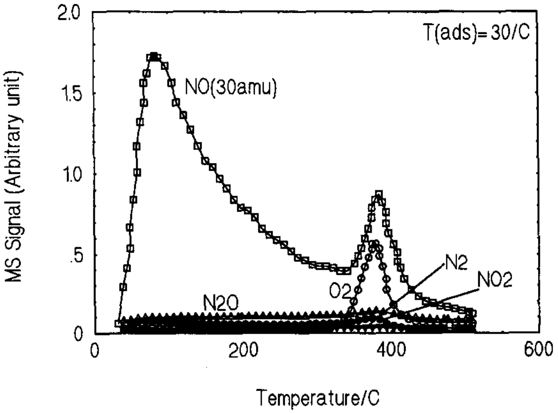


Fig. 8. TPD profile of NO from reduced Cu/ZSM-5. NO was adsorbed at room temperature on a sample saturated with oxygen at the same temperature.

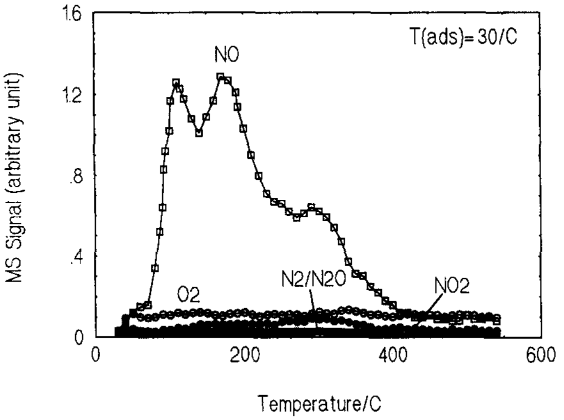


Fig. 9. TPD profile of NO from reduced 15.6% exchanged Cu/ZSM-5. Adsorption temperature: 30°C.

cluded that some of the NO competes with oxygen for this type of copper site.

From the above experiments, it also can be concluded that the adsorption of NO is stronger than that of molecular oxygen, since the adsorbed oxygen can be replaced by NO.

In order to investigate the nature of the copper sites involved in NO decomposition, NO TPD experiments were performed on a sample with an exchange level of 15.6% (Fig. 9). It is well known [6,7] that in a sample of Cu/ZSM-5 with an exchange level less than 100%, almost all the copper ions are highly isolated. In Fig. 9, three different desorption peaks were detected at 108, 210 and 290°C. These results may be consistent with the three different copper sites detected in an in situ ESR study carried out on a 56% exchanged Cu/ZSM-5 [6]. An important feature specified in this TPD profile is that there is no simultaneous evolution of oxygen and NO at 390°C as detected in all the TPD profiles of excessively exchanged samples. It has been shown that the 390°C NO desorption peak at 30 amu is mainly due to the MS fragmentation of the desorbed NO_2. Therefore, it is clear that there is no NO_2 formation during the NO adsorption and desorption process on this 15.6% exchanged sample. Furthermore, the absence of oxygen desorption indicates that there is little NO decomposition happening on this sample. An experiment of oxygen adsorption and desorption was also performed over this sample with no detectable oxygen desorption was observed. Therefore, it is assumed that on this under exchanged sample, all copper ions are highly isolated and can not be reduced by thermal treatment under vacuum. Based on the above discussion, it may be concluded that on an excessively exchanged Cu/ZSM-5, which is the most active catalyst for NO decomposition and reduction, not only the copper centers which hold the ELO are reducible and responsible for the adsorption of oxygen, but also only this part of copper centers is involved in the NO decomposition and NO_2 formation. Another conclusion may also be reached that the reaction of NO_2 formation is always closely related with the NO decomposition.

3.3. TPD-FTIR study of NO adsorption and desorption

A number of detailed FTIR studies of the NO adsorption on Cu/ZSM-5 can be found in literature [2,3,16], although some ambiguous assignments of certain bands still exist. In order to obtain more straightforward evidence for our conclusions obtained from the TPD experiments, a FTIR study of the temperature pro-

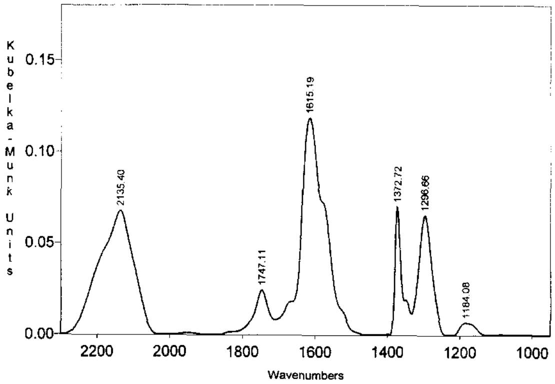


Fig. 10. FTIR spectrum from NO adsorbed on reduced Cu/ZSM-5 at room temperature. The adsorption was performed in flowing NO/He for 30 minutes after which 30 minutes of He purge was carried out. NO partial pressure: 3 Torr.

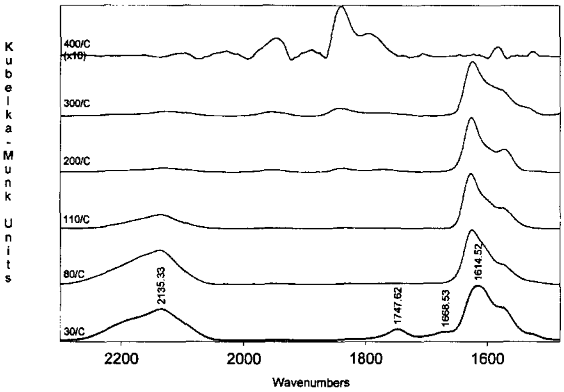


Fig. 11. FTIR spectra of NO over reduced Cu/ZSM-5 at different temperatures. NO was initially adsorbed at room temperature for 30 minutes followed by He flush for 30 minutes. The temperature was raised at a rate of 5°C.

grammed desorption of NO was performed over the excessively exchanged sample after adsorption of NO at room temperature. As it has been found that the FTIR spectra of adsorbed NO and the intensities of particular peaks often change with the pretreatment conditions of the sample, adsorption time, temperature and NO pressure, the FTIR spectra were taken under similar conditions under which the TPD experiments were carried out (adsorption time, adsorption temperature). In this case, it can be assumed that equilibrium was reached on the surface, therefore, only the adsorption species with high stabilities left on the surface before the spectra were taken.

The FTIR spectrum taken from a reduced sample at room temperature is presented in Fig. 10. Bands at 2135, 1747, 1615, 1372, 1296, 1184 cm^{-1} were apparent. Several shoulders around, 1915, 1650, 1580 cm^{-1} were also observed. Bands between 1615 and 1184 cm^{-1} have been assigned to adsorbed NO_2, or nitro-, nitrito- and nitrato- complexes [3,20]. The 1747 cm^{-1} band may be assigned to adsorbed N_2O_4. As the temperature increased, the very weak band at 1915 cm^{-1}, which was assigned to $Cu^{(2-\delta)+}$–$NO^{\delta+}$ [2,3], disappeared around 80°C contributing a part of the low temperature NO desorption observed in the TPD profiles. The intensity of the band around 1615 cm^{-1} increased with the increase of temperature until 200°C where the 2133 cm^{-1} band disappeared at this temperature (Fig. 11). The 1615 cm^{-1} band, which is due to the presence of NO_2 or NO_3 species [3,20], was stable up to 300°C and then disappeared at higher temperature. The NO_3 species suggested by the 1568 cm^{-1} band can be detected even at 400°C. These results revealed the presence of NO_2 /NO_3 species on the surface of Cu/ZSM-5 as a rather stable intermediate or side product of the NO decomposition. At 400°C, several other adsorbed species with very low concentration still exist on the surface indicated by the very weak IR peaks. Assignments of these bands are not available at this moment.

The assignment of the band around 2133 cm^{-1} has been studied carefully by Hoost et al. [21] who assigned it to the adsorption of NO on Bronst acid sites or the ZSM-5 framework based on an IR study of $^{15}N^{18}O$ adsorption. Our data show disagreement with this assignment.

On an oxidized sample, the 2133 cm^{-1} band was basically not found (Fig. 12), whereas the 1750, 1677 and 1607 cm^{-1} bands were observed and then disappeared around 100 and above 300°C, respectively. If the 2133 cm^{-1} band is due to the NO adsorption on the OH sites of zeolite framework, it should be able to be detected even on an "oxidized" sample. In

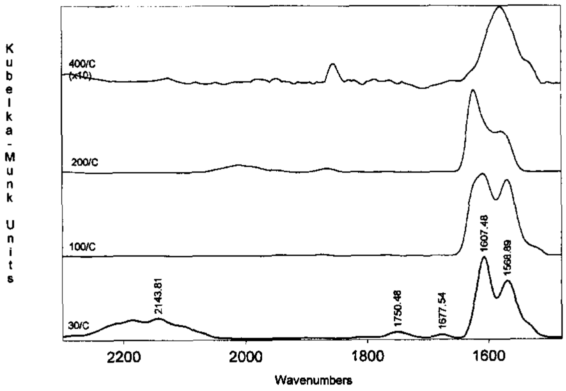
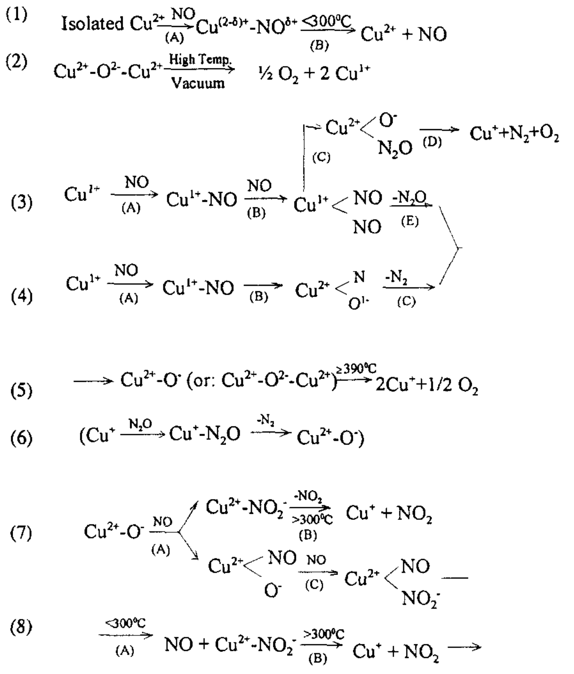


Fig. 12. FTIR spectra of NO over oxidized Cu/ZSM-5 at different temperatures. NO was initially adsorbed at room temperature. The sample was oxidized in oxygen (600 Torr) at 500°C for 10 hours and cooled to room temperature in oxygen.

our TPD profile of NO, the low temperature desorption of NO completed around 200°C and no NO_2 formation was observed below this temperature. Therefore, the 2133 cm^{-1} band may be due to some NO related species adsorbed on Cu^{1+} centers. The nature of this species is not clear at this moment.

Based on the above results and discussions, the reactions happening during the processes of NO adsorption and desorption over Cu/ZSM-5 may be briefly described as the following: NO adsorbed on the surface and is decomposed into its elements and leave an oxygen atom behind. During this process, Cu^{1+} is oxidized into Cu^{2+}. The upcoming NO can react with this adsorbed oxygen or ELO to form NO_2. This adsorbed NO_2 can be desorbed at higher temperature and remove one oxygen atom from the surface. At the same time, Cu^{2+} is reduced into Cu^{1+}. In other words, NO may act as oxidizing agent at low temperature and reducing agent at high temperature. The following reaction scheme (Scheme 1) may hopefully reveal the reaction chemistry happening on the surface during the NO adsorption and desorption over excessively exchanged Cu/ZSM-5.



Continued

Scheme 1. Reaction scheme.

4. Conclusions

At least three types of copper sites were detected by our TPD experiments which are active for oxygen adsorption on excessively exchanged Cu/ZSM-5. The copper centers which are active for oxygen adsorption either in molecular or atomic form account for about 20% of all the copper ions. At temperatures below 250°C, oxygen is adsorbed mainly in molecular form, whereas the dissociative adsorption of oxygen happens at temperatures higher than 300°C. The copper centers bonded with ELO which can be reduced by thermal treatment under vacuum are responsible for oxygen adsorption and desorption.

Although almost all the copper centers are accessible for NO adsorption, only the 20% of the copper centers mentioned above are mainly involved in NO decomposition and NO_2 formation. NO and oxygen molecules compete for the same copper centers; furthermore, the adsorption of NO is stronger than that of oxygen. The NO molecules adsorbed on isolated copper centers can be completely desorbed below 300°C. The NO molecules adsorbed on ELO-bonded copper centers can react with ELO to form NO_2. The NO_2 formed exists on the surface as a rather stable intermediate or side product until at least 300°C where the adsorbed NO_2 can be desorbed into gas phase. In the reaction mechanism, NO may act as oxidizing agent at low temperature and reducing agent at high temperature.

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