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An *in situ* infrared study of NO reduction by C_3H_8 over Fe-ZSM-5

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The interactions of NO, O_2 and NO_2 with Fe-ZSM-5, as well as the reduction of NO by C_3H_8 in the presence of O_2, have been investigated using *in situ* infrared spectroscopy. The sample of Fe-ZSM-5 (Fe/Al $= 0.56$) was prepared by solid-state ion exchange. NO adsorption in the absence of O_2 produces only mono- and dinitrosyl species associated with Fe^{2+} cations. Adsorbed NO_2/NO_3 species are formed via the reaction of adsorbed O_2 with gas-phase NO or by the adsorption of gas-phase NO_2. The reduction of NO in the presence of O_2 begins with the reaction of gas-phase C_3H_8 with adsorbed NO_2/NO_3 species to form a nitrogen-containing polymeric species. A reaction pathway is proposed for the catalyzed reduction of NO by C_3H_8 in the presence of O_2.

Keywords: selective catalytic reduction, SCR, Fe-ZSM-5, zeolites, NO_x reduction with propane

1. Introduction

Recent studies have demonstrated that Fe exchanged into H-ZSM-5 is active for the reduction of NO by either C_3H_8 or i-C_4H_{10} [1–6]. The activity of Fe-ZSM-5 is negligible in the absence of O_2, but rises to a maximum when approximately 2% O_2 is present in a feed containing NO and i-C_4H_{10} [5]. Infrared observations have revealed that NO_2/NO_3 species are present at 573 K when a mixture of NO and O_2 is passed over Fe-ZSM-5, and that these species will react with C_3H_8 or i-C_4H_{10} to form a nitrogen-containing organic deposit [5]. The latter deposit reacts with NO_2 and O_2, and has been proposed as an intermediate in the reduction of NO by alkanes [5]. As yet unresolved issues include the mechanism by which NO_2/NO_3 species are formed on Fe-ZSM-5, the temperature at which NO_2/NO_3 begin to undergo reduction, and whether adsorbed NO might undergo reduction as well. The present study was undertaken to address each of these issues. To this end, *in situ* infrared spectra were obtained as a function of temperature in various mixtures of NO, O_2, NO_2, and C_3H_8.

2. Experimental

Fe-ZSM-5 was prepared via solid-state ion exchange, in a manner similar to that described by Chen et al. [3,4]. Na-ZSM-5 obtained from Alsi-Penta was first converted to the NH_4^+ form by aqueous ion exchange with ammonium nitrate. About 10 g of the zeolite was added to a 120 ml solution of 1.0 M ammonium nitrate. This mixture was stirred at 298 K for 12 h, then filtered and washed. To ensure complete displacement of Na^+ by NH_4^+, the exchange procedure was repeated two more times. NH_4^+-ZSM-5 was then transformed to H-ZSM-5 by calcining at 823 K for 8 h in air. The calcined H-ZSM-5 was then transferred to a glove box without contacting air and mechanically mixed with the appropriate amount of $FeCl_3$ required for the desired exchange level. While still in the glove box, this mixture was placed into a sealed reactor. The reactor was then removed from the glove box and placed in a furnace. A flow of He was passed through the reactor as it was heated at a rate of 0.25 K/min to 583 K, the sublimation temperature of $FeCl_3$. Upon reaching 583 K, the reactor was held at this temperature for 4 h. The sample was then cooled to room temperature, removed from the reactor, and washed with water until the precipitation of AgCl was not detected upon addition of $AgNO_3$ to the residual water. Finally, the Fe-ZSM-5 was dried in an oven overnight at 393 K. Elemental analysis of the catalyst determined the Si/Al ratio to be 25 and the Fe/Al ratio to be 0.56 with a residual Na/Al ratio <0.04.

For infrared spectroscopy, the Fe-ZSM-5 was pressed into a 20–50 mg self-supporting wafer and placed into a flow-through infrared cell (volume $= 0.126$ cm^3) similar to that described by Joly et al. [7]. Spectra were recorded on a Digilab FTS-50 Fourier transform infrared spectrometer at a resolution of 4 cm^{-1}. Typically, 64 or 256 scans were coadded to obtain a signal-to-noise ratio of at least 10 to 1. A reference spectrum of Fe-ZSM-5 in He, taken at the same temperature as the experimental spectrum, was subtracted from each spectrum. The temperature of the sample was raised at a rate of 1.0 K/min when infrared spectra were recorded under the conditions of temperature-programmed desorption or reaction. The total gas flow rate was typically 100 cm^3/min.

Unless otherwise specified, prior to each experiment the catalyst was: (1) heated at 773 K in 4.2% CO for 2 h, (2) heated at 773 K in He for 1 h, and (3) cooled to room temperature in He. This pretreatment procedure is based on our previous work [8], which showed that CO reduction will disperse Fe present in FeO_x particles, formed during oxidation of the fresh catalyst, to isolated cation exchange sites.

To determine its activity the catalyst was placed in a quartz microreactor. Reactants were supplied via mass flow controllers and the product composition was determined by gas chromatography. A molecular sieve 5A column was used to separate NO, O_2, N_2, and CO. A Porapak Q column was also employed to separate CO_2 and C_3H_8. Typical reaction mixtures contained 2,000 ppm NO, 2,000 ppm C_3H_8, and 2.0% O_2, with the balance He. A 300 mg catalyst sample was used with a total flow rate of 150 cm^3/min, resulting in a GHSV = 15,000 h^{-1} (based on an apparent bulk density of the zeolite of 0.5 g/cm^3). Prior to each activity experiment the catalyst was: (1) heated in He at 773 K for 2 h and (2) cooled to the desired reaction temperature in He. The conversion of NO was based on the amount of N_2 formed and the conversion of C_3H_8 was based on the amount of CO_2 and CO formed.

For the present studies, 4.99% NO in He, 1.03% NO_2 in He, 10.1% O_2 in He, and 1.04% C_3H_8 in He were obtained from Matheson. UHP helium was obtained on-site. He, NO, and the C_3H_8/He mixture were passed through an oxysorb trap, an ascarite trap, and a molecular sieve trap, in that order, for additional purification. The O_2 was passed through an ascarite and a molecular sieve trap.

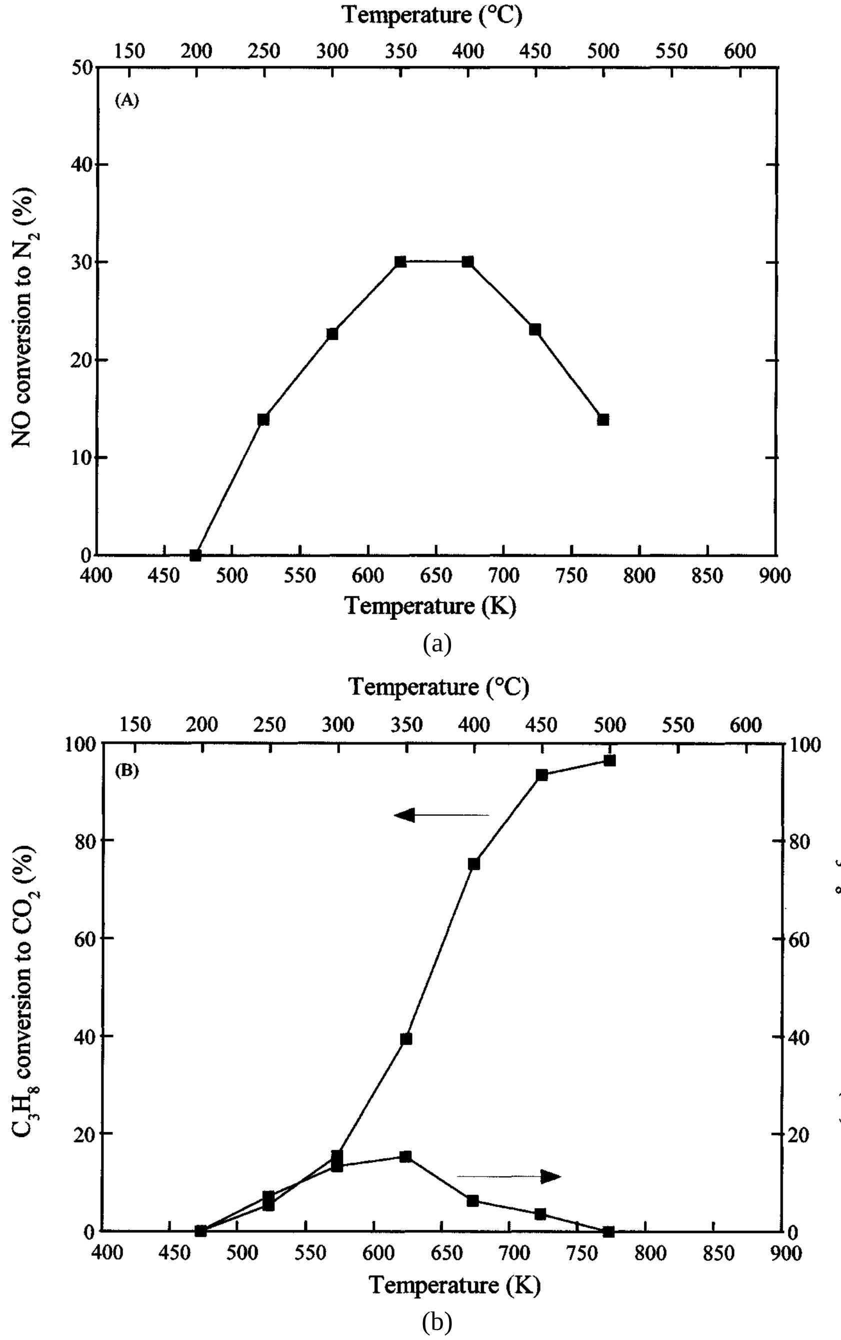
3. Results

The activity of Fe-ZSM-5 for NO reduction by C_3H_8 is shown in figure 1. Figure 1(a) shows the conversion of NO to N_2 as a function of temperature. NO reduction to N_2 begins at temperatures greater than 473 K, and the temperature of maximum NO conversion to N_2 is 623 K. Figure 1(b) shows the conversion of C_3H_8 to CO and CO_2. While the conversion of C_3H_8 to CO_2 reaches nearly 100% at 773 K, the conversion to CO exhibits a maximum with temperature, similar to that observed for the NO conversion to N_2 in figure 1(a).

Figure 2 shows the infrared spectrum taken at room temperature after a 20 min exposure of the catalyst to 5,000 ppm NO in He. Four bands are observed at 2133, 1876, 1856, and 1806 cm^{-1} with shoulders at 1917 and 1767 cm^{-1}. The bands at 1917 and 1806 cm^{-1} are assigned to $Fe^{2+}(NO)_2$ and the bands at 1876, 1856, and 1767 cm^{-1} are assigned to Fe^{2+} mononitrosyl [$Fe^{2+}(NO)$] species [8–10]. In a prior study of NO adsorption on Fe-ZSM-5 [8], it was concluded that the bands at 1917, 1806, and 1767 cm^{-1} are associated with Fe^{2+} located at α charge-exchange sites occurring in the straight channels of ZSM-5, whereas the bands at 1876 and 1856 cm^{-1} are associated with Fe^{2+} located in less accessible β and γ charge-exchange sites [11]. While the assignment of the band at 2133 cm^{-1} has been the subject of significant discussion in the literature [12–15], strong evidence has been presented recently [16] suggesting that this band is due to NO^+ acting as the charge-compensating species at a cation exchange site (e.g., Z^-NO^+).

Figure 2 also shows a series of infrared spectra acquired during the temperature-programmed desorption (TPD) of NO into a He carrier gas following NO adsorption at room temperature. Purging the sample in He for 5 min at 298 K results in a decrease in the intensity of the bands at 2133, 1917, and 1806 cm^{-1} and an increase in the band at 1767 cm^{-1}, while the intensity of the bands at 1876 and 1856 cm^{-1} remains unchanged. During the temperature ramp, the features at 2133, 1917, and 1806 cm^{-1} decrease in intensity and disappear by 373 K. The band at 1767 cm^{-1} first increases in intensity and reaches a maximum at 323 K. For temperatures above 373 K, this band decreases in intensity until it is no longer visible at 573 K. The bands at 1876 and 1856 cm^{-1} decrease in intensity with temperature and are no longer present on the surface at 573 K. Above 323 K, a small, broad feature is observed centered at 1616 cm^{-1}. This band is tentatively assigned to NO_2 associated with Fe^{n+} [5] and it disappears above 523 K. While not shown, the spectra acquired when NO is maintained in the gas phase while increasing the temperature are similar to those observed in figure 2. However, the intensity of the bands due to $Fe^{2+}(NO)_2$ is higher than that observed in He alone and the three mononitrosyl species which yield features at 1876, 1856, and 1767 cm^{-1} are observed to temperatures greater than 573 K. Also not shown is the spectrum obtained when NO adsorbed at room temperature undergoes temperature-programmed desorption in C_3H_8 instead of He. In this case, the spectra observed at each temperature are identical to those attained with He as the carrier gas (figure 2), indicating that adsorbed NO does not react with C_3H_8.

Figure 3 shows the spectra for NO temperature-programmed desorption into 1% O_2 following NO adsorption for 20 min at room temperature from a gas stream containing 5,000 ppm NO in He. With the exception of a small decrease in the intensities of the bands at 1917, 1856, and 1806 cm^{-1}, a 5 min exposure to O_2 at room temperature results in a spectrum similar to that observed after a He purge (figure 2). Increasing the temperature generally results in an acceleration of the desorption of species from the surface relative to TPD in He alone. Similar to NO TPD in He, the features at 2133, 1917, and 1806 cm^{-1} disappear by 373 K. However, the Fe^{2+} mononitrosyl species, characterized by the band at 1767 cm^{-1}, does not increase in intensity with temperature, and is much less stable, desorbing at a temperature 200 K lower than that observed during NO TPD in He. The band at 1856 cm^{-1} is also attenuated in the presence of O_2 and desorbs from the surface by 373 K. The most stable nitrosyl species is associated with the band at 1876 cm^{-1}, and it disappears above 423 K. As observed in figure 2, the species observed at 1616 cm^{-1} is again present between 373 and 523 K and the peak exhibits a similar shape and intensity compared to that observed during NO TPD in He.



(a)

(b)

Figure 1. NO conversion to N_2 (a), and C_3H_8 conversion to CO_x (b) as a function of temperature. Reaction mixture: NO 2,000 ppm, C_3H_8 2,000 ppm, O_2 2.0%. Total flow rate = 150 cm^3/min, GHSV = 15,000 h^{-1}.

A series of spectra recorded during the temperature-programmed reaction (TPR) in 5,000 ppm NO and 1% O_2 is presented in figure 4. The spectrum observed following a 20 min exposure to NO and O_2 at room temperature exhibits several new features not previously observed. In addition to the bands due to NO^+ (2133 cm^{-1}) and $Fe^{2+}(NO)$ (1876 cm^{-1}), bands are apparent at 1620 and 1577 cm^{-1}, with shoulders at 1635, 1602, and 1549 cm^{-1}. The bands at 1602 and 1577 cm^{-1} are in the region typically assigned to nitrates [17]. It has been observed that alkyl ammonium and cesium tetranitroferrates (e.g., $(X)[Fe(NO_3)_4]$, X = Et_4N or Cs) exhibit bands for monodentate NO_3 near 1600, 1560, and 1490 cm^{-1} [18]. However, bands in this region have also been assigned to both mono- and/or bidentate NO_3 in previous studies of metal-exchanged zeolites [19–22]. Since this issue is not clear, the bands at 1602 and 1577 cm^{-1} are assigned to either mono- or bidentate NO_3 groups. Based on previous studies on Co- and Mn-ZSM-5, the band at 1549 cm^{-1} is assigned to an Fe–ONO group, although it is noted that this frequency is relatively high for this type of ligand [17] and it is possible that this feature is also due to a nitrate group. The band at 1635 cm^{-1} is attributed to some form of adsorbed NO_2, though the exact structure is not known. Finally, the band

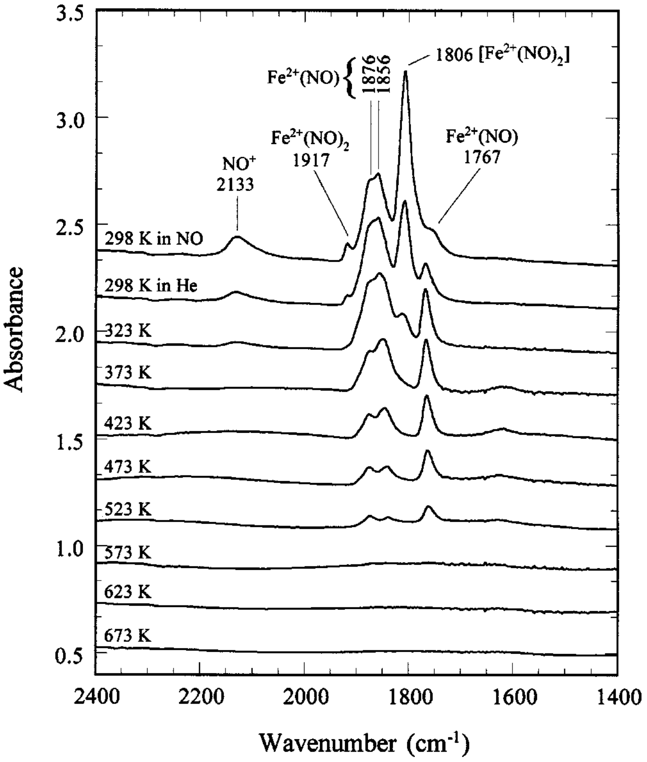


Figure 2. Infrared spectra acquired during the temperature-programmed desorption of NO into He following the room-temperature exposure of the catalyst to 5,000 ppm NO for 20 min.

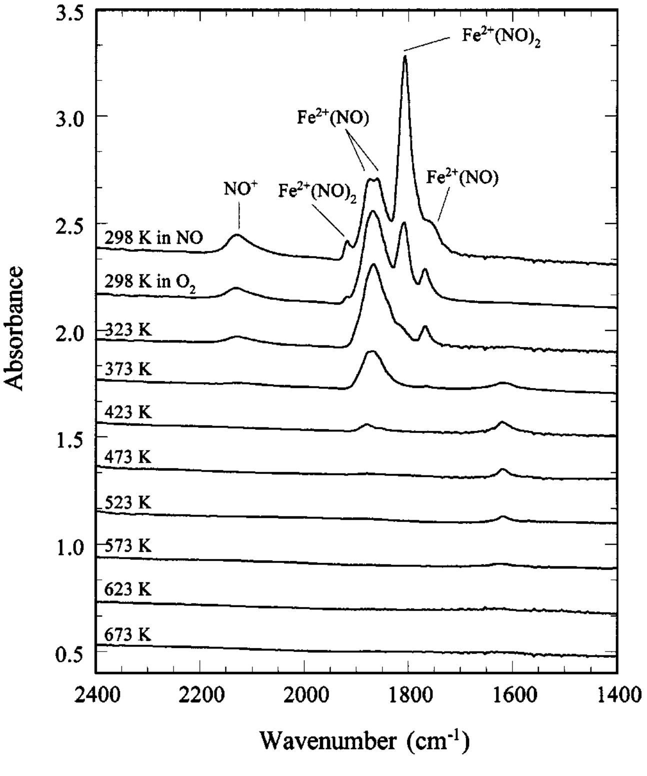


Figure 3. Infrared spectra acquired during the temperature-programmed desorption of NO into 1% O_2 following the room-temperature exposure of the catalyst to 5,000 ppm NO for 20 min.

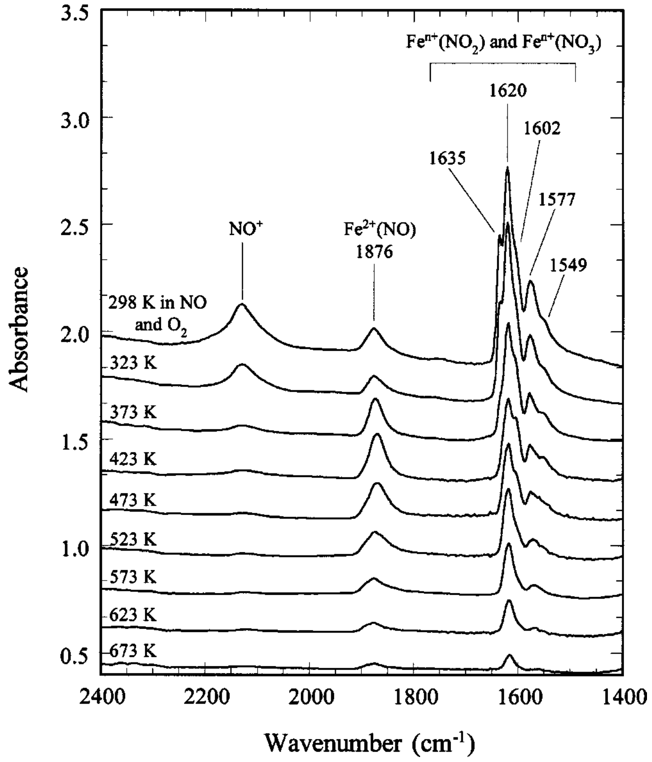


Figure 4. Infrared spectra taken during a temperature ramp while 5,000 ppm NO and 1% O_2 is passed over the catalyst after it had been exposed to this mixture for 20 min at room temperature.

at 1620 cm^{-1} is assigned to a nitro group associated with and Fe^{n+} cation [5] which is very close to the frequency of vibration of gaseous NO_2 of 1610 cm^{-1} [17].

An increase in temperature in the presence of NO and O_2 (figure 4) results in the disappearance of the band due to NO^+ above 373 K while the feature due to the Fe mononitrosyl at 1876 cm^{-1} first passes through a maximum at 423 K and then decreases in intensity and is still observed at 673 K. With increasing temperature, the features at 1549, 1602, and 1635 cm^{-1} decrease in intensity and are no longer observed at 523 K. At this temperature, the only features remaining in the region between 1640 and 1540 cm^{-1} are the bands at 1620 and 1577 cm^{-1}, due to NO_2 and NO_3 species, respectively. A further increase in temperature above this point results in a decrease in the intensity of both species with the band due to the nitrate at 1577 cm^{-1} disappearing above 623 K while the feature at 1620 cm^{-1} is still present at 673 K.

The results presented in figure 4 suggest that NO_2 species will be present on the surface when NO and O_2 are present in the gas phase together, however, the results of figure 3 suggest that little, if any, adsorbed NO reacts with gas-phase O_2 to form adsorbed NO_x species. Hence, since the formation of NO_2 can occur homogeneously, it was of interest to establish whether adsorbed NO_2 could be formed without both NO and O_2 present in the gas phase. Thus, a third experiment was designed in which, prior to the experiment, the catalyst was heated at 773 K in 10% O_2 for 3 h, cooled to 313 K in 10% O_2, and then purged

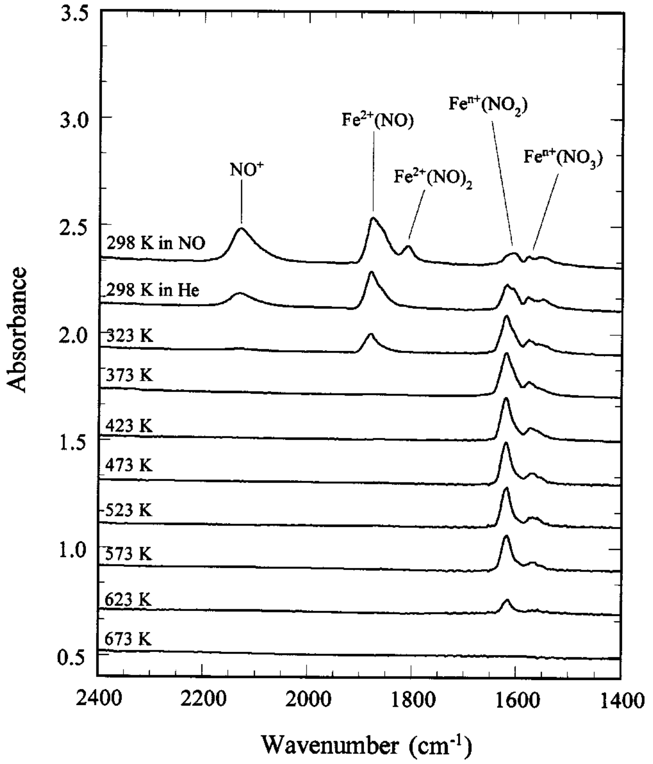


Figure 5. Infrared spectra acquired during the temperature-programmed desorption of NO into He following pretreatment in oxygen. The catalyst was exposed to 5,000 ppm NO in He for 20 min at room temperature prior to the temperature ramp.

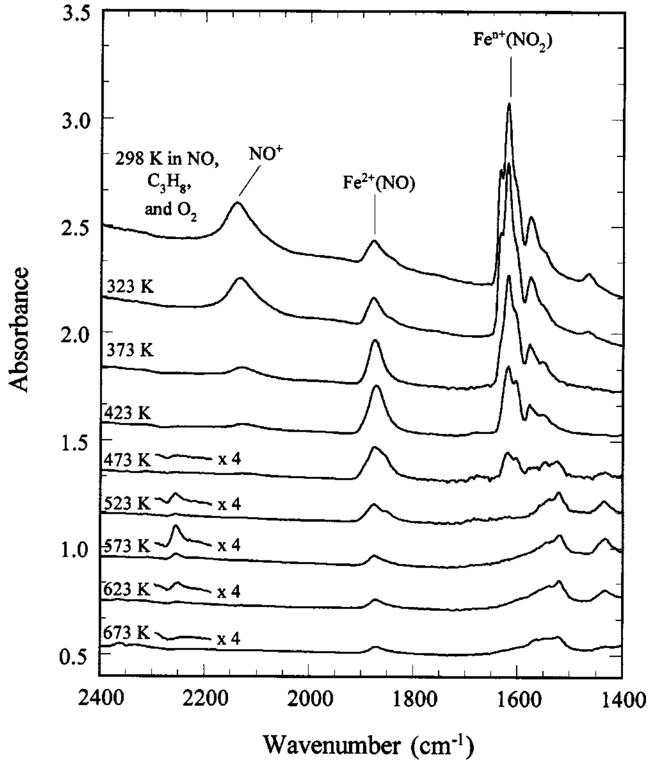


Figure 6. Infrared spectra taken during a temperature ramp while a gas stream containing 5,000 ppm NO, 5,000 ppm C_3H_8 and 1% O_2 is passed over the catalyst after it had been exposed to this mixture for 20 min at room temperature.

and cooled to room temperature in He. Following this pretreatment an NO TPD was performed. The purpose of this experiment was to ascertain whether NO_2 could be formed via reaction of adsorbed O_2 with gas-phase NO. The results are shown in figure 5. A significant decrease in the intensity of the peaks between 1750 and 1920 cm^{-1} due to Fe^{2+} nitrosyls is observed relative to the spectrum acquired following a standard pretreatment (figure 2). Based on previous work, the change in intensity of these species is likely due to the formation of Fe^{3+} species which do not readily adsorb NO [8]. Also observed at room temperature are bands at 1620 and 1577 cm^{-1} due to NO_2/NO_3 species. A He purge results in the complete removal of iron dinitrosyl species from the surface, along with a decrease in the intensity of the NO^+ species and an increase in the concentrations of NO_2/NO_3 species. Both the NO^+ and $Fe^{2+}(NO)$ are weakly bound to the surface and disappear by 323 and 373 K, respectively. The intensity of the band at 1577 cm^{-1} due to NO_3 is relatively constant as the temperature is raised, and this species finally desorbs above 573 K. However, the band at 1620 cm^{-1} due to NO_2 increases in intensity with temperature, reaches a maximum at 373 K, and then remains on the surface to temperatures as high as 623 K.

Figure 6 shows a series of infrared spectra acquired during temperature-programmed reaction in 5,000 ppm NO, 5,000 ppm C_3H_8, and 1% O_2. With the exception of a band observed at 1465 cm^{-1} due to the bending vibrations of $–CH_2$ and $–CH_3$ groups in gas-phase C_3H_8 [23], the spectrum observed at room temperature in the presence of the entire reaction mixture is virtually identical to that observed in NO and O_2 (figure 4). As the temperature is increased from room temperature to 423 K, the spectra in figure 6 remain identical to those shown in figure 4. Above 423 K, the addition of C_3H_8 to the reaction mixture has a significant effect on the concentration and type of species present on the catalyst surface. The only exception is the band at 1876 cm^{-1}, which is unaffected by the presence of C_3H_8 at all temperatures. The feature at 1620 cm^{-1} is dramatically attenuated in the presence of C_3H_8 beginning at 473 K and completely disappears by 523 K. It is not clear whether the presence of C_3H_8 has an effect on the band at 1577 cm^{-1} as several new bands appear in the region from 1400 to 1600 cm^{-1}. It has been proposed that these bands are due to a nitrogen-containing polymeric deposit which may be an intermediate in the formation of nitrogen [5]. Finally, beginning at 523 K a new band appears at 2254 cm^{-1} (see inset with expanded peaks) and at 623 K a doublet due to CO_2 is observed at centered at 2349 cm^{-1}. It has been proposed for Co-, Mn-, and Pd-ZSM-5 [22,24,25] that bands observed in the region from 2250 to 2300 cm^{-1} are due to isocyanate species associated with framework Al, and hence the band observed at 2254 cm^{-1} is tentatively assigned to NCO species.

To investigate the behavior of adsorbed NO_2, temperature-programmed desorption/reaction experiments were

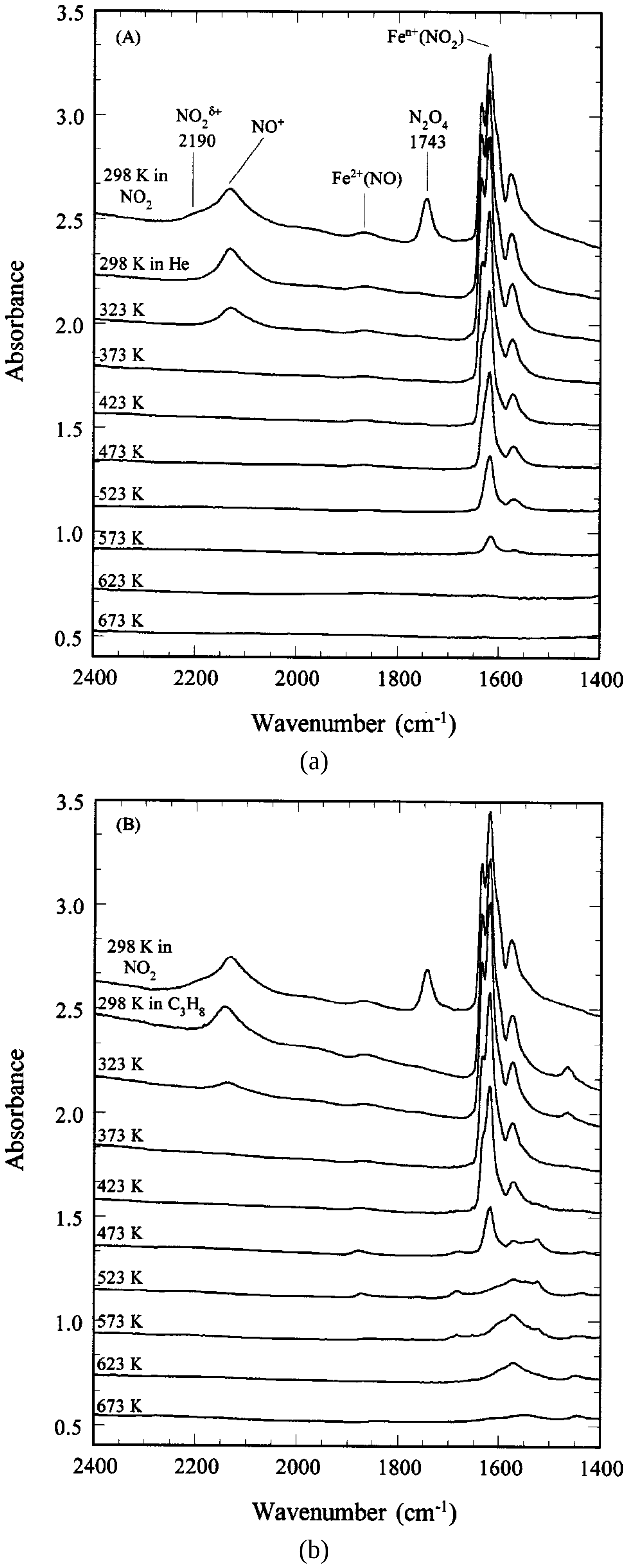


Figure 7. Infrared spectra acquired during the temperature-programmed desorption of NO_2 into He (a) and 5,000 ppm C_3H_8 (b) following the room-temperature exposure of the catalyst to 5,000 ppm NO_2 for 20 min.

performed using NO_2 as the adsorbate. Figure 7 (a) and (b) shows the results observed following the room-temperature adsorption of NO_2 from a gas stream containing 5,000 ppm NO_2 in He, followed by the desorption, as the temperature is increased from room temperature to 673 K, into either He (figure 7(a)) or C_3H_8 (figure 7(b)). The spectrum observed following room-temperature exposure to NO_2 is similar to that observed when a mixture of NO and O_2 is passed over the catalyst (figure 4). Two additional features are present at 2190 and 1743 cm^{-1}, and the band at 1876 cm^{-1} is barely detectable. The feature at 2190 cm^{-1} is most likely due to $NO_2^{\delta+}$ [26,27] while the feature at 1743 cm^{-1} can be assigned to N_2O_4 [28]. Purging in either He or C_3H_8 at room temperature results in the removal of the bands at 2190 and 1743 cm^{-1} and, in the case of C_3H_8, the appearance of the band due to $-CH_2$ and $-CH_3$ groups at 1465 cm^{-1}. As the temperature is raised, NO^+ desorbs from the surface above 323 K, similar to what was observed in figures 2–6. Also, similar to the results observed in figure 4, the features due to NO_2/NO_3 species at 1620 and 1577 cm^{-1} remain on the surface up to 573 K. When C_3H_8 is present in the carrier gas, the feature due to $Fe^{n+}(NO_2)$ is strongly attenuated above 423 K and is completely removed by 523 K, and features due to a nitrogen-containing polymeric deposit are observed between 1400 and 1600 cm^{-1}. These trends are similar to those observed in figure 6 for TPR of a feed mixture containing NO, O_2, and C_3H_8.

4. Discussion

The spectra presented in figures 6 and 7 clearly demonstrate that C_3H_8 reacts with adsorbed NO_2/NO_3 species and that the temperature at which this process begins (>423 K) is similar to that for the onset of the steady-state reduction of NO in the presence of O_2 and C_3H_8. The observation of NO_2/NO_3 as the relevant adsorbed intermediate in NO reduction by alkanes over Fe-ZSM-5 is in agreement with what has been reported for i-C_4H_{10} [5]. While adsorbed NO co-exists with adsorbed NO_2/NO_3, no evidence was found for the reduction of adsorbed NO even at elevated temperatures.

The importance of adsorbed NO_2/NO_3 raises the issue of how these species are formed. Figure 3 shows that NO_2/NO_3 species are not formed via the reaction of O_2 with adsorbed mono- or dinitrosyls associated with Fe^{2+}. NO_2/NO_3 species are formed, however, when either NO reacts with adsorbed O_2 (figure 5) or NO and O_2 are co-adsorbed at room temperature (figure 4). In the latter case, the spectrum for the adsorbed NO_2/NO_3 species is identical to that observed upon room-temperature adsorption of NO_2. These results indicate that the formation of adsorbed NO_2/NO_3 species is due to the reaction of gas-phase NO with adsorbed O_2 or to the adsorption of NO_2 formed in the gas phase by the homogeneous reaction of NO with O_2.

Figure 8 illustrates a possible mechanism for the reduction of NO by C_3H_8 in the presence of O_2. Iron present as Fe^{2+} (actually $Fe^{2+}(OH^-)$) reacts with O_2 to form $Fe^{3+}(O_2^-)$. Reaction of this species with NO results in the formation of either $Fe^{3+}(O^-)(NO_2)$ or $Fe^{3+}(NO_3^-)$. Upon

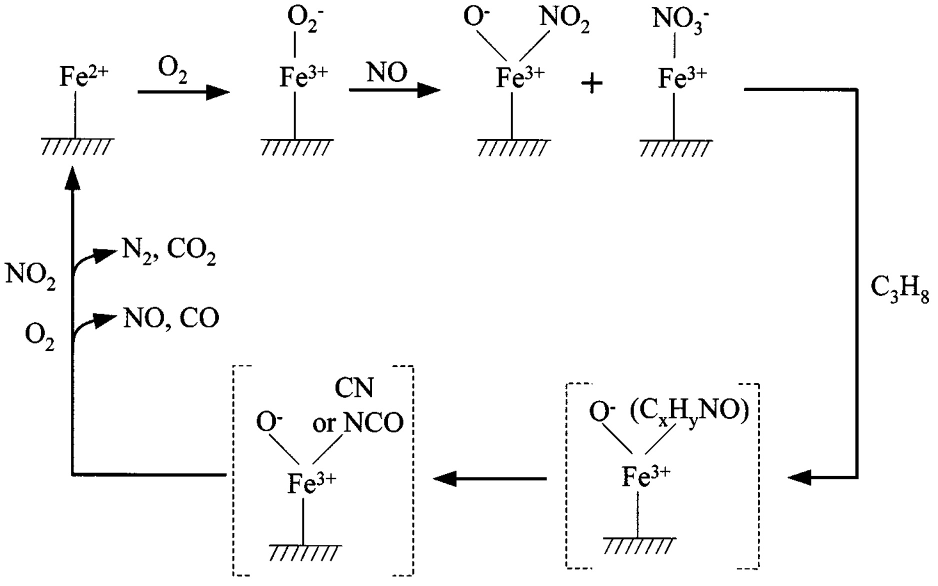


Figure 8. Proposed mechanism for the reduction of NO by C_3H_8 over Fe-ZSM-5.

reaction of these NO_2/NO_3 species with C_3H_8, an intermediate designated as C_xH_yNO is formed. The presence of this intermediate is supported by the observation of infrared bands in the region between 1400 and 1600 cm^{-1} at temperatures above 423 K (see figures 6 and 7(b)), the temperature above which steady-state reduction of NO is observed (see figure 1). It is proposed that CN and NCO species are formed as products of the reaction of C_xH_yNO with NO_2 and O_2. While only the latter species has been observed for Fe-ZSM-5, the former has been reported as a highly active intermediate in the reduction of NO by CH_4 over Co-, Mn-, and Pd-ZSM-5 [21,22,24,25]. The CN and NCO can then react with NO_2 or O_2 to form nitrogen and carbon-containing combustion products, while the reduction of Fe^{3+} to Fe^{2+} is assumed to occur via the reduction of the O^- with the CN or NCO.

5. Conclusions

In situ infrared observations of NO reduction by C_3H_8 in the presence of Fe-ZSM-5 indicate that adsorbed NO_2/NO_3 species are active intermediates, whereas adsorbed NO is not. NO_2/NO_3 species are formed via the reaction of NO with adsorbed O_2 and by the adsorption of NO_2 formed in the gas phase via homogeneous reaction of NO with O_2. The reaction of gas-phase C_3H_8 with adsorbed NO_2/NO_3 species results in the formation of a nitrogen-containing deposit. It is proposed that CN or NCO species derived from this deposit act as intermediates and that the oxidation of these species results in the formation of N_2 and CO_2 (see figure 8).

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References

[1] X. Feng and W.K. Hall, Catal. Lett. 41 (1996) 45.
[2] X. Feng and W.K. Hall, J. Catal. 166 (1997) 368.
[3] H.-Y. Chen and W.M.H. Sachtler, Catal. Lett. 50 (1998) 125.
[4] H.-Y. Chen and W.M.H. Sachtler, Catal. Today 42 (1998) 73.
[5] H.-Y. Chen and W.M.H. Sachtler, J. Catal. 180 (1998) 171.
[6] I.-C. Hwang and A.T. Bell, unpublished results.
[7] J.F. Joly, N. Zanier-Szyldowski, S. Colin, F. Raatz, J. Saussey and J.C. Lavalley, Catal. Today 9 (1991) 31.
[8] L.J. Lobree, I.-C. Hwang, J.A. Reimer and A.T. Bell, J. Catal., in press.
[9] K. Segawa, Y. Chen, J.E. Kubsh, W.N. Delgass, J.A. Dumesic and W.K. Hall, J. Catal. 76 (1982) 112.
[10] L.M. Aparicio, W.K. Hall, S. Fang, M.A. Ulla, W.S. Millman and J.A. Dumesic, J. Catal. 108 (1987) 233.
[11] B. Wichterlová, J. Dedecek and Z. Sobalík, in: *Proc. of the 12th Int. Zeolite Conference*, eds. M.M. Treacy, B.K. Marcus, M.E. Bisher and J.B. Higgins (Materials Research Society, Baltimore, 1998) p. 941.
[12] M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, J. Phys. Chem. 96 (1992) 9360.
[13] E. Giamello, D. Murphy, G. Magnacca, C. Morterra, Y. Shioya, T. Nomura and M. Anpo, J. Catal. 136 (1992) 510.
[14] J. Valyon and W.K. Hall, J. Phys. Chem. 97 (1993) 1204.
[15] T.E. Hoost, K.A. Laframboise and K. Otto, Catal. Lett. 33 (1995) 1105.
[16] K. Hadjiivanov, J. Saussey, J.L. Freysz and J.C. Lavalley, Catal. Lett. 52 (1998) 103.
[17] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1997).
[18] C.C. Addison, P.M. Boorman and N. Logan, J. Chem. Soc. (1965) 5146.
[19] A.W. Aylor, S.C. Larsen, J.A. Reimer and A.T. Bell, J. Catal. 157 (1995) 592.
[20] B.J. Adelman, T. Beutel, G.-D. Lei and W.M.H. Sachtler, J. Catal. 158 (1996) 327.
[21] A.W. Aylor, L.J. Lobree, J.A. Reimer and A.T. Bell, in: *Studies in Surface Science and Catalysis*, Vol. 101, eds. J.W. Hightower,

W.N. Delgass, E. Iglesia and A.T. Bell (Elsevier, Amsterdam, 1996) p. 661.
[22] A.W. Aylor, L.J. Lobree, J.A. Reimer and A.T. Bell, J. Catal. 170 (1997) 390.
[23] N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy* (Academic Press, New York, 1964).
[24] L.J. Lobree, A.W. Aylor, J.A. Reimer and A.T. Bell, J. Catal. 169 (1997) 188.
[25] L.J. Lobree, A.W. Aylor, J.A. Reimer and A.T. Bell, J. Catal. 181 (1999) 189.
[26] J.C. Evans, H.W. Rinn, S.J. Kuhn and G.A. Olah, Inorg. Chem. 3 (1964) 857.
[27] J.W. Nebgen, A.D. McElroy and H.F. Klodowsky, Inorg. Chem. 4 (1965) 1796.
[28] G.M. Begun and W.H. Fletcher, J. Mol. Spectrosc. 4 (1960) 388.