Spectroscopic evidence for a nitrite intermediate in the catalytic reduction of NO_x with ammonia on Fe/MFI

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The mechanism of selective catalytic reduction (SCR) of NO_x with NH_3 over Fe/MFI was studied using *in situ* FTIR spectroscopy. Exposing Fe/MFI first to NH_3 then to flowing $NO + O_2$ or using the reversed sequence, invariably leads to the formation of ammonium nitrite, NH_4NO_2. *In situ* FTIR results in flowing $NO + NH_3 + O_2$ at different temperatures show that NH_3 is strongly adsorbed and reacts with impinging NO_x. The intensity of the NH_4NO_2 bands initially increases with temperature, but passes through a maximum at 120 °C because the nitrite decomposes to $N_2 + H_2O$. The mechanistic model rationalizes that the consumption ratio of NO and NH_3 is close to unity and that the effect of water vapor depends on the reaction temperature. At high temperature H_2O enhances the rate because it is needed to form NH_4NO_2. At low temperature, when adsorbed H_2O is abundant it lowers the rate because it competes with NO_x for adsorption sites.

KEY WORDS: selective catalytic reduction of NO_x; NO_x reduction with ammonia; IR detection of surface ammonium nitrite; Fe/MFI catalyst

1. Introduction

Selective catalytic reduction (SCR) of NO_x with hydrocarbons over Fe/MFI† is of interest because of the high activity and durability of this catalyst [1–3]. It has been proposed that NO is first oxidized; chemisorbed NO_2 groups and NO_3^- ions have been identified by FTIR. They react with hydrocarbons to form a nitrogen-containing deposit, which after some rearrangements exposes amine-like groups. Chemical interaction of these $R{-}NH_2$ groups with NO or NO_2 results in formation of N_2 molecules with one N atom from the deposit, the other from NO. This mechanism suggests that use of ammonia as the reductant will permit a "shortcut" bypassing the difficult formation of $-NH_2$ groups in a carbonaceous deposit. Indeed, experimental results show that the rate of NO reduction is much faster with NH_3 than with hydrocarbons [4–7]. Isotopic labeling proves that one N atom in each N_2 molecule is from the NH_3, the other from the NO [7]. The consumption ratio of NO and NH_3 at low temperature is near unity. Sun *et al.* [7] proposed a mechanistic pathway in which NO is first oxidized to N_2O_3, which reacts with NH_3 and H_2O to ammonium nitrite. This NH_4NO_2 intermediate easily decomposes to $N_2 + H_2O$.

Reduction of NO_x with ammonia over vanadia/titania catalysts has been studied by Topsøe *et al.* [8–10]. Also, in that case a consumption ratio of unity is found. These authors propose that ammonia is initially adsorbed on Brønsted acid sites followed by its partial oxidation. Reaction with impinging NO results in formation of $N_2 + H_2O$. Interestingly, in this model it is the NH_3, not the NO, which is assumed to be partially oxidized in order to achieve the stoichiometry of the overall process: $2NO + 2NH_3 + \frac{1}{2}O_2 = 2N_2 + 3H_2O$. Also, this model predicts that one N atom in each N_2 comes from NH_3, the other from NO.

While there is no reason to exclude the possibility that a given reaction uses different paths on different catalysts, this state of the problem motivated us to do additional experiments to discriminate between these models. In the present work, *in situ* FTIR has been used to identify reaction intermediates on the same Fe/MFI catalyst as in the previous work [7].

2. Experimental

2.1. Catalyst preparation

H-MFI was obtained from Na-MFI, provided by UOP (Si/AL = 19, Lot No. 99499506001) by conventional ion exchange with a diluted ammonium nitrate solution, followed by calcination at 500 °C in an oxygen flow. The Fe/MFI catalysts were prepared by sublimation of the $FeCl_3$ onto H-MFI, as previously described [1–3]. Elemental analysis by inductively coupled plasma (ICP) atomic emission shows that the Fe/Al ratio is near unity and the sodium concentration is below 10^{-3} ppm. The infrared spectra in the hydroxyl

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† The MFI zeolite is often called ZSM-5 for its industrial trademark.

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stretching region of H-MFI, before and after sublimation of $FeCl_3$, show Brønsted acid sites vanished after sublimation. After washing and calcination, 20% of the original Brønsted acid sites are regenerated.

2.2. *In situ FTIR*

A Nicolet 60S FTIR spectrometer equipped with a liquid nitrogen-cooled MCT detector was used to monitor adsorption and desorption of NO, NO_2, and NH_3 at constant or variable temperature. Spectra were taken by accumulating 64 scans with a spectral resolution of $1\,cm^{-1}$. The catalyst wafers of 8–$10\,mg/cm^2$ were placed into a flow-through quartz cell sealed with NaCl windows. The sample was pre-heated *in situ* in the IR cell before any adsorption and reaction. When reaction was monitored, the spectrum of Fe/MFI in helium flow, taken at the same temperatures, was used as a reference and subtracted from the actual spectrum measured under the same flow conditions.

After calcination of Fe/MFI at 450 °C in flowing O_2/He (10%) with a flow of 30 ml/min, the catalyst surface was purged with UHP He at RT for 1 h to remove physically adsorbed O_2. The IR spectra were registered at RT as a function of time upon exposing the NH_3-loaded Fe/MFI to a feed of $NO\,(0.5\%) + O_2\,(3\%) + He$. Likewise, IR spectra were recorded upon exposing Fe/MFI covered with adsorbed NO_2 or NO_3^- groups, further lumped together as NO_y groups, to a flow of NH_3 (0.5%) in He. Spectra were also registered under flowing $NO\,(0.1\%) + NH_3\,(0.1\%) + O_2\,(2\%) + He$, while the temperature was raised from RT to 400 °C with a ramp of 4 °C/min. In this case, the temperature was kept constant for 5 min at some values for spectra collection. Transient IR spectra of the catalytic reduction of NO_x with ammonia were registered at a number of temperatures.

3. Results

Adsorption of NH_3 on Fe/MFI is very strong. As shown in figure 1, both NH_4^+ ions and coordinated NH_3 molecules are observed. Strong bands at $1464\,cm^{-1}$, $1700\,cm^{-1}$, $1620\,cm^{-1}$, a shoulder peak at $1495\,cm^{-1}$, and a broad band in 3000–$3500\,cm^{-1}$ were registered in flowing $NH_3 + He$. Another wide band was observed in 2400–$2850\,cm^{-1}$. Ammonia reacts with strong Brønsted acid sites and also sites of lower acid strength (Fe–OH, Si–OH). Accordingly, the intensity of the bands at $3680\,cm^{-1}$ (Fe–OH) and $3740\,cm^{-1}$ (Si–OH) decreases. The negative peaks at 3610, 3680 and $3740\,cm^{-1}$ indicate formation of NH_4^+ on Brønsted acid sites and the iron hydroxyl groups (Fe–OH) which are part of the dinuclear $[HO{-}Fe{-}O{-}Fe{-}OH]^{2+}$ ions proposed previously [1–3]. The bands at 1464 and $1700\,cm^{-1}$ are due to the symmetric and asymmetric bending vibration (δs, δa) of NH_4^+, respectively [11–13]. The $1620\,cm^{-1}$ band is assigned to the asymmetric bending (degenerate deformation) vibration of the N–H bonds in NH_3 coordinated to Lewis acid sites [11], *i.e.*, Al^{3+} and Fe^{3+} ions. The multiple broad vibrational bands at higher wave numbers are attributed to the N–H stretching vibration of NH_4^+ and NH_3. The bands at 3300–$3500\,cm^{-1}$ are attributed to the coordinatively bonded NH_3, while bands in the 2500–$3300\,cm^{-1}$ region are often assigned to NH_4^+ [11,14,15]. Upon increasing the temperature, the overall intensity of NH_3 and NH_4^+ decreased, but the negative band at $3610\,cm^{-1}$ increased first, then decreased, indicating some weakly adsorbed ammonia is transferred to Brønsted sites. The bands of NH_3 at $1960\,cm^{-1}$ and $2180\,cm^{-1}$ which were identified by Russell [16] as combination bands disappeared gradually, while all other species persisted at high temperature. However, the intensity of the bands at 3375 and $3290\,cm^{-1}$ initially increased, then passed through a maximum at about 160 °C. At 400 °C, NH_4^+ ions and coordinated NH_3 molecules persist on the surface of the Fe/MFI catalyst.

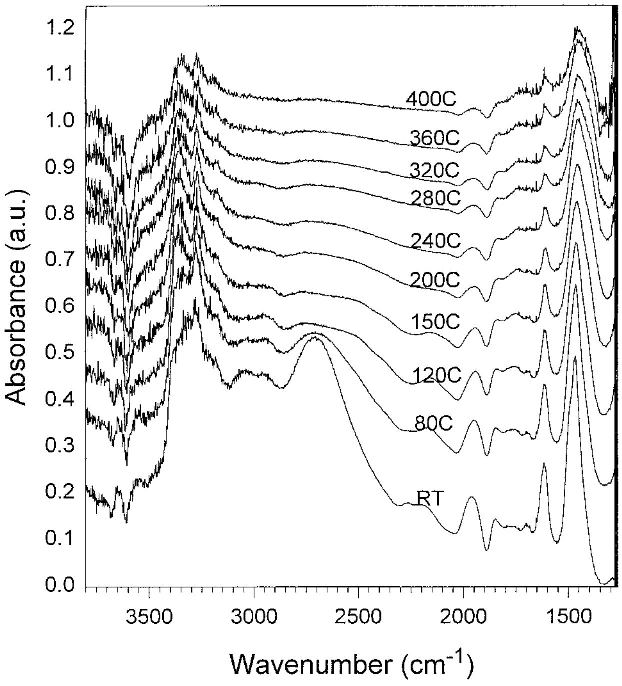

Figure 1. FTIR spectra of NH_3 adsorbed on Fe/MFI, taken during temperature-programmed desorption in He flow.

In figure 2, spectra are shown of Fe/MFI that was exposed first to NH_3 and subsequently to a flow of $NO + O_2$ at room temperature. A band at $1320\,cm^{-1}$ rapidly appeared; its intensity increased then decreased, while the band at $1300\,cm^{-1}$ monotonously increased with exposure time. The bands at $1320\,cm^{-1}$ are assigned to nitrite groups [17]. Upon purging with He, the bands at 1300 and $1865\,cm^{-1}$ immediately disappeared, indicating a species of low stability unlike the bands caused by NO

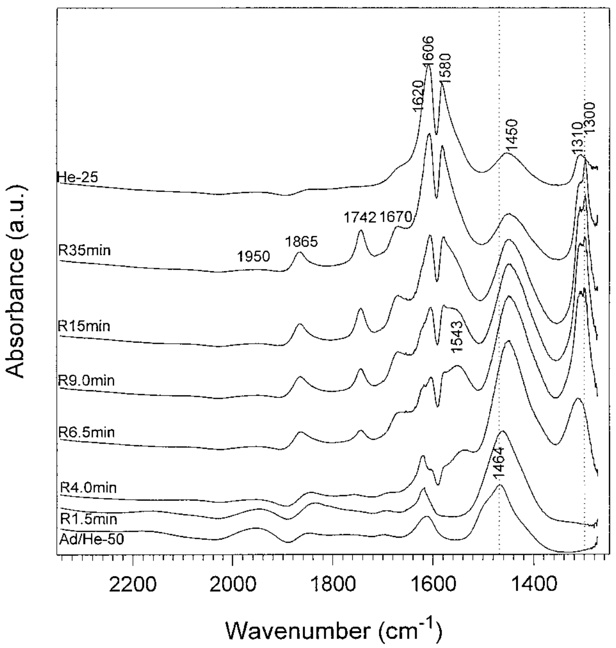

Figure 2. FTIR spectra taken at room temperature after exposing a flow of NH_3 to Fe/MFI followed by purging with He for 30 min (a); subsequently exposed to a flow of 0.5% NO + 2.0% O_2 + He for 1.5 min (b); 4 min (c); 7 min (d); 9 min (e); 15 min (f); 35 min (g); and He purged for 25 min (h).

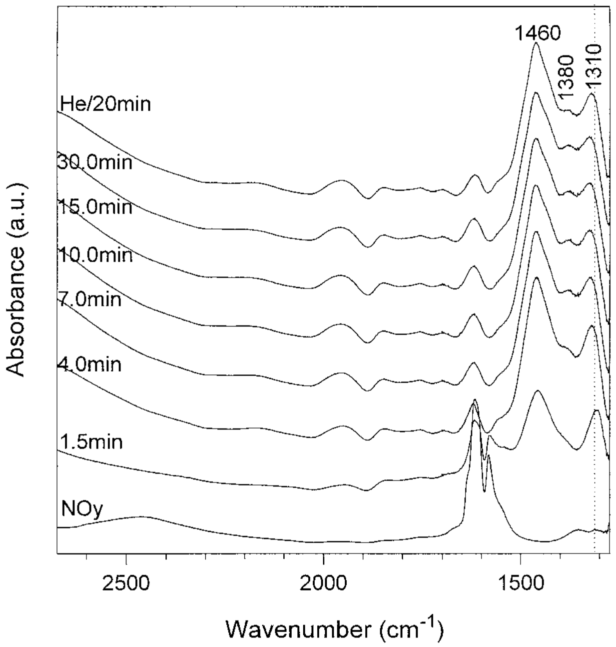

Figure 3. FTIR spectra taken at room temperature after exposing a flow of NO (0.5%) + O_2 (2.0%) + He to Fe/MFI followed by purging with He for 30 min (a); subsequently exposed to a flow of 0.5% NH_3 + He for 1.5 min (b); 4 min (c); 7 min (d); 10 min (e); 15 min (f); 30 min (g); and He purged for 25 min (h).

or NO_y groups, which are quite stable even at 200 °C. We assign the bands at 1300 and 1865 cm^{-1} to N_2O_3 vibrations, following Chno *et al.*, who showed that the antisymmetric N_2O_3 molecule with an O=N–NO_2 structure should display three stretching vibrational modes: $\nu_{as}(NO_2)$ at 1652 cm^{-1}, $\nu_s(NO_2)$ at 1305 cm^{-1} and $\nu_{(NO=O)}$ at 1832 cm^{-1} [18]. For N_2O_3 adsorbed on a zeolite, the stretching vibration bands have been detected at 1930–1880 cm^{-1} ($\nu_{N=O}$), 1590–1550 cm^{-1} ($\nu_{as}(NO_2)$), and 1305–1290 cm^{-1} ($\nu_s(NO_2)$) [17]. More specifically, we demonstrated in our previous work [19] that N_2O_3 adsorption on Fe/MFI leads to the vibrational bands at 1876 and 1297 cm^{-1}. Due to the influence of adsorbed ammonia, these bands are slightly shifted; they appear at 1865 and 1300 cm^{-1} respectively. The intensity of the NH_4^+ band at 1464 cm^{-1} increased first, then decreased, while the frequency shifted downward by 25 cm^{-1}. Although no additional NH_3 was supplied to the catalyst, the intensity of this band was found to increase with exposure of NO + O_2 while its position shifted. These changes indicate that a new species is formed in which NH_4^+ is bonded to a new ligand, such as an NO_2^- group. Indeed, the concurrent changes in the intensities of the NH_4^+ and NO_2^- adsorption peaks suggest formation of NH_4NO_2. Accordingly, the intensity of the NH_4^+ (1450 cm^{-1}) and NO_2^- (1320 cm^{-1}) bands decreases with exposure time, indicating that the NH_4^+ and NO_2^- groups are being consumed. Upon flushing with He, the band ascribed to N_2O_3 decreased rapidly. This is in conformity with the observation that N_2O_3 can exist at RT on the catalyst surface only in the presence of NO + O_2. The band at 1670 cm^{-1} increased first, then gradually decreased with exposure time, as did the band at 1310 cm^{-1}. This band appears neither in flowing NO + O_2 nor NH_3, which eliminates its assignment to NO, NO_y, NH_3 or NH_4^+. Its assignment to the nitrite ion (NO_2^-) combined with ammonia is supported by Tanaka *et al.* [20], who report that organic nitrite compounds, such as *i*-butane nitrite, have a vibrational band at 1650 cm^{-1}. It stands to reason that the nitrite band at 1670 cm^{-1} will appear when the NH_3-loaded Fe/MFI is exposed to NO + O_2 at RT. In our previous work with NO + O_2 + hydrocarbons the bands of the NO_y groups (NO_2 and NO_3^-) at1578 cm^{-1} dominated the spectrum, but in the present work with an ammonia-containing feed NH_4^+ was still detectable besides the NO_y groups; in addition N_2O_4 (1742 cm^{-1}) and NO (1865 cm^{-1}) were observed after feeding NO + O_2 for 30 min. Upon exposing the Fe/MFI covered with NO_y groups to flowing NH_3/He for 30 min, most NO_y groups are quickly displaced by NH_3 and NH_4^+ (see figure 3). The strong peak at 1320 cm^{-1}, which only emerges after exposing the NO_y-loaded catalyst to flowing NH_3 + He, indicates that nitrate ions have been transformed into nitrite ions. Partial reduction of nitrate ions (NO_3^-) to nitrite ions (NO_2^-) had been proposed previously [7].

Upon admitting the reactant mixture (1000 ppm NO, 1000 ppm NH_3, and 2.0% O_2) while raising the temperature, the bands of NH_4^+ at 1467 and 1615 cm^{-1}

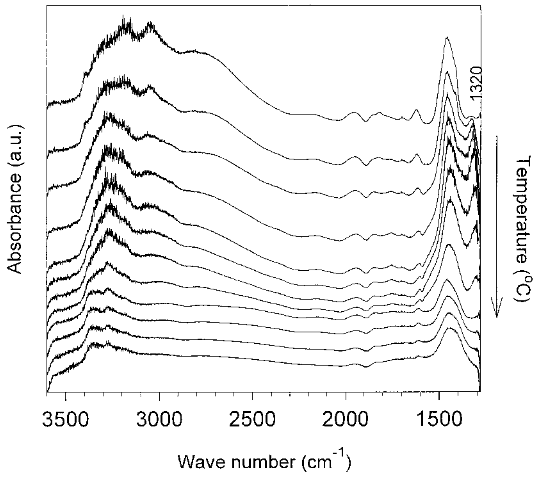

Figure 4. FTIR spectra taken during a temperature ramp in gas flow of 0.1% NO + 0.1% NH_3 + 2.0% O_2 + He over Fe/MFI.

immediately appear, while no NO^+, NO, NO_2 or NO_y is observed (see figure 4). Under reaction conditions the catalyst surface will thus be mainly occupied with ammonia or ammonium ions, which react with impinging molecules. Indeed an Eley–Rideal kinetics was found to be valid [21]. As shown in figure 5, the intensity of the NO_2^- band at 1320 cm^{-1} first increases with temperature; after reaching a maximum at 120 °C, it decreases, gradually. This concentration change of a surface complex with temperature is of relevance for the reaction mechanism. While some weak bands might be masked by adsorbed ammonia, these data strongly suggest that NH_4NO_2 is a true reaction intermediate in the formation of N_2.

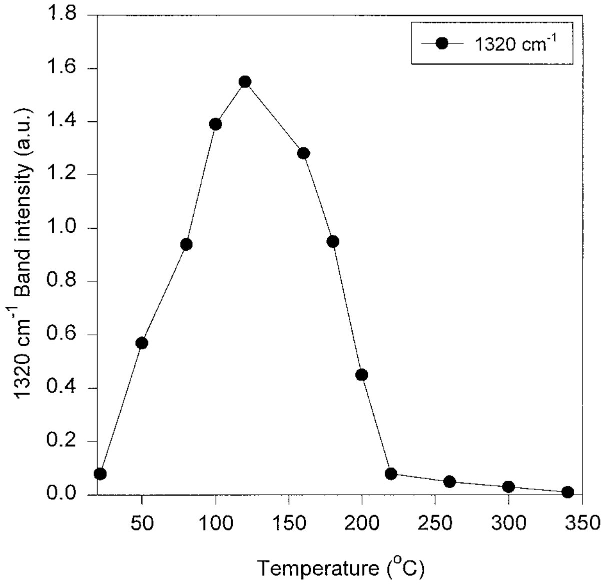

Figure 5. Intensity of IR band at 1320 cm^{-1} as a function of reaction temperature.

4. Discussion

Ammonia is strongly adsorbed on Fe/MFI, both as NH_4^+ ions and coordinated NH_3 molecules. With increasing temperature, the bands due to Brønsted acid sites first decrease, then increase; the intensity ratio of the bands at 3360 and 3300 cm^{-1} exhibits the same change. Apparently, adsorption of NH_3 on Brønsted acid sites increases with temperature and part of the coordinated or weakly adsorbed NH_3 molecules are transferred to Brønsted acid sites. At higher temperature, however, the NH_4^+ ions will decompose.

The FTIR results provide direct evidence that nitrite ions are intermediates in the formation of N_2. This follows from the observation that nitrite bands at 1320 cm^{-1} and 1670 cm^{-1} are formed upon either exposing the NH_3-loaded Fe/MFI to NO + O_2 or the NO_y-loaded Fe/MFI to NH_3 or the catalyst to the combined feed gas. Another clue is the change with time of the intensity of the bands upon exposing the NH_3-loaded Fe/MFI to flowing NO + O_2. The intensity first increases with time, then decreases, while adsorbed NH_3 is gradually consumed. *In situ* FTIR spectra further show that the band intensity at 1320 cm^{-1} increases with reaction temperature, then decreases after passing through a maximum at 120 °C. Obviously, the formation rate of the nitrite increases with temperature, but so does its subsequent decomposition to $N_2 + H_2O$. The result of this kinetics is that the surface concentration of NH_4NO_2 reaches a maximum at 120 °C. It is also of relevance that the band intensity of NH_4^+ (1464 cm^{-1}) initially increases although no additional NH_3 was supplied. It is plausible that the degenerate deformation band of the NH_4^+ ion, which is usually IR inactive, becomes observable when the NH_4^+ ion loses symmetry by interaction with either the zeolite or another ligand. The observed enhancement of the intensity and the downward shift of the NH_4^+ band indicate indeed that NH_4^+ ions interact with NO_2^- groups. The NO_2^- ions are generated by NO oxidation to N_2O_3, followed by combination with surface water.

The nitrite band at 1320 cm^{-1}, which did not exist on NO_y loaded Fe/MFI, immediately emerges after exposure to flowing NH_3/He. This indicates that adsorbed NH_3 reduces NO_y to NO_2^-, as proposed previously [7]. The change of the band intensity at 1320 cm^{-1} reveals the change of surface nitrite concentration. Upon purging with He, this peak gradually decreased. These results strongly suggest that N_2 is formed via decomposition of ammonium nitrite.

Ammonia and nitrite ions are the dominating features in the FTIR spectrum under flowing $NH_3 + NO + O_2$. The model that adsorbed ammonia reacts with impinging NO or NO_2 is in accordance with the kinetic data reported by Komatsu *et al.* [21], *i.e.* zero order in ammonia and first order in NO. The temperature dependence of the NO_2^- band fits the model that nitrite formation increases, but at high temperature its decomposition prevails. As shown previously [7], the consumption ratio of NO and NH_3 close to unity is in agreement with both the mechanistic model of the ammonium nitrite ions and the above IR results.

N_2O_3 though detected at RT in a $NO + O_2$ flow is, of course, not stable at higher temperature. It does however, swiftly react with H_2O and NH_3 to form ammonium nitrite. As mentioned, water vapor promotes the reaction rate at high temperature when the concentration of adsorbed water is low. At low temperature when the surface water and hydroxyl groups are abundant, water merely acts as a competitor for sites, thus lowering the reaction rate as found experimentally [4–7]. This finding is, however, not compatible with the model of N_2 formation by NO impinging onto an activated ammonia [8–10]. That model can therefore be disregarded for the Fe/MFI catalyst.

Other authors working on similar catalysts have assumed that nitrate ions NO_3^- are acting as intermediates [21,22]. While this chemistry is well established for NO reduction with hydrocarbons, we reject such a mechanism for ammonia as the reductant on the basis that it is well known that ammonium nitrate decomposes to N_2O, not N_2. Moreover, the nitrate ion is thermally much more stable than the nitrite ion and, therefore, unable to decompose with the required rate at a temperature where the SCR of NO with ammonia is known to be fast.

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