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An FTIR Study on the Mechanism of the Reaction between Nitrogen Dioxide and Propene over Acidic Mordenites

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Nitrosonium ions, NO^+, are formed upon reaction between NO, NO_2, and the Brønsted acid sites of H–MOR. It is shown that the NO^+ ions are highly reactive towards propene, forming propenal oxime at 120°C. At temperatures above 170°C, propenal oxime is dehydrated to acrylonitrile. A mechanism is proposed to explain the acrylonitrile formation. The nitrile can be hydrolysed to yield adsorbed ammonium ions, which are known to be efficient in reducing nitrogen oxides to nitrogen. The dehydration of propenal oxime appears to be the rate determining step in nitrile formation. © 1999 Academic Press

INTRODUCTION

The reduction of NO_x to nitrogen in the exhaust gas of diesel and lean-burn engines currently attracts great interest both in applied and fundamental research. Concerning the mechanism of this reaction, there seems to exist agreement that NO is first oxidised to NO_2, which is then reduced to nitrogen in a reaction with the hydrocarbon. Several authors have proposed that the reaction between NO_2 and the hydrocarbon is catalysed by the acid sites of catalysts like Co/H–ZSM-5 (1, 2) or Pd/H–ZSM-5 (3). This appears likely, because NO_2 can be easily reduced to N_2 by hydrocarbons over undoped, acidic zeolites and the activity towards this reaction increases with increasing acid site concentration (1, 4).

In studies applying FTIR spectroscopy, several authors have observed a band at ca. 2133 cm^{-1} upon adsorption of NO under oxidising conditions or of NO_2 on H–ZSM-5 (5–8). The assignment of this band was discussed controversially. Recently, Hadjiivanov *et al.* (8) have shown that this band can be assigned to nitrosonium ions, NO^+, chemisorbed on the catalyst according to the following reaction:

$$NO + NO_2 + 2\,H^+ \rightleftharpoons 2\,NO^+ + H_2O. \qquad [1]$$

The water formed in this reaction was represented by bands at 3699, 3534, and 1630 cm^{-1}, while the loss of Brønsted acid hydroxyl groups of the zeolite was displayed in a decrease of the band at 3610 cm^{-1}. The authors emphasised that apart from NO^+, no other stable adsorbates were observed upon adsorption of NO_x and proposed that NO^+ might be an important intermediate of NO_x reduction under lean conditions over H–ZSM-5.

We report in the present contribution on the results of a FTIR study on the adsorption of NO_x on a H–MOR catalyst and on the reaction between the NO_x derived adsorbates and propene. It was our aim to elucidate the relevance of adsorbed NO_x species for the $DeNO_x$ reaction and to obtain a more advanced insight into the reaction mechanism.

EXPERIMENTAL

The catalyst used was a mordenite (MOR) in its ammonium form (Zeolyst International). The fresh sample had a surface area of 500 $m^2\,g^{-1}$ and a Si/Al ratio of 10. To transform it into the H form, the zeolite was heated at a rate of 20 K min^{-1} to 550°C for 2 h in air.

FTIR spectra were recorded in the transmission mode (Biorad FTS-60 A spectrometer). Forty milligrams of the zeolite were pressed to a thin self-supporting wafer and mounted into a quartz cell which was equipped with CaF_2 windows. The cell was heated by a heating tape wound around the walls of the cell. The temperature was measured by a thermocouple located close to the sample. The cell could be evacuated to high vacuum (10^{-5} mbar) by a turbomolecular pump. Prior to the IR experiments, the catalyst was heated *in vacuo* to 450°C for 0.5 h to remove adsorbed water. Subsequently, the cell was cooled to the relevant reaction temperature, and a spectrum of the activated zeolite was recorded. These spectra were used to calculate difference spectra characteristic for the adsorbates after the adsorption/reaction experiments.

For studying the surface species formed upon exposure of the catalyst towards NO_2 at 120, 200, and 300°C, the valve to the vacuum pump was closed and 50 mbar of a gas mixture of 10% NO_2 (98%) in He (99.999%) were introduced to the cell. All gases were supplied by Messer–Griesheim GmbH and used without further purification. After ca. 10 min of adsorption, the cell was again evacuated to remove gas-phase

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species and to monitor the desorption of adsorbed species with time. To study the reactivity of the surface species towards C_3H_6 at 120, 200, and 300°C, 30 mbar of a gas mix of 10% C_3H_6 (99.95%) in He (99.999%) were introduced after certain times of desorption *in vacuo*. The changes of the surface species were monitored with time.

Spectra were collected averaging 64 scans at a resolution of 2 cm^{-1} to obtain a good signal-to-noise ratio. The time required for one spectrum was ca. 40 s and the time indicated in the time-resolved experiments is the midpoint of data collection.

RESULTS AND DISCUSSION

Adsorption of NO_x

After introduction of 5 mbar NO_2 for 10 min and 30 s of subsequent evacuation at 120°C, positive bands at 2202, 1641, 1589, and 1314 cm^{-1}, and a broad band between ca. 3500 and 2600 cm^{-1} were visible in the difference spectrum (Fig. 1). The negative band due to the Brønsted acid hydroxyl groups of the zeolite had two maxima at 3618 and 3585 cm^{-1}. This spectrum is similar to the spectra recorded by Hadjiivanov *et al.* upon coadsorption of NO and O_2 on H–ZSM-5 at room temperature, where a negative band was observed at 3610 cm^{-1} and positive bands at 2133 and 1630 cm^{-1} (8). The authors had proposed that the bands at 2133 and 1630 cm^{-1} can be assigned to NO^+ ions and to adsorbed H_2O, respectively, both being formed according to Eq. [1], the consumption of Brønsted acid sites being reflected in the negative band at 3610 cm^{-1}.

During evacuation of the cell at 120°C for 15 min, the intensity of all bands decreased with time. The integrated intensities of the bands at 1640 and around 3600 cm^{-1} correlated linearly with the integrated intensity of the band around 2200 cm^{-1} (Fig. 2), showing that the species giving rise to these bands correlated with each other, as implied by Eq. [1]. However, both lines shown in Fig. 2 have a significant offset when extrapolated to zero intensity of the 2200 cm^{-1} band. While this offset may be due to the difficulty of defining a proper baseline for the 3600 cm^{-1} band, in the case of the 1640 cm^{-1} band another explanation has to be found. On admitting NO_2 and subsequent evacuation at 300°C (Fig. 3), the disappearance of the bands was sufficiently fast to achieve complete removal of the 2200 cm^{-1} band within 60 min (spectrum d, Fig. 3). While the negative band due to the Brønsted hydroxyls was also removed

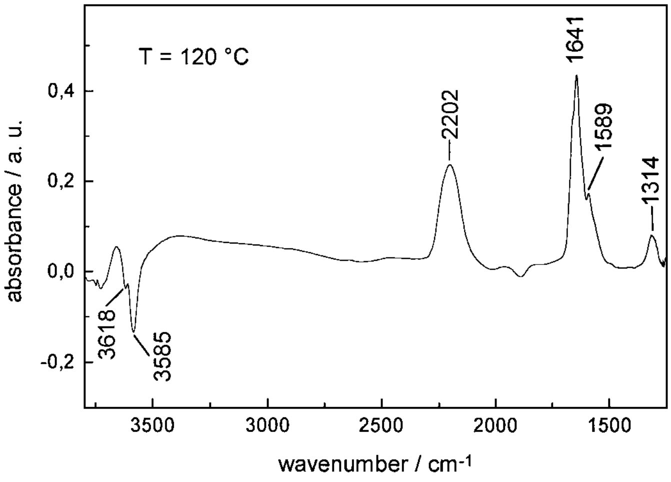

FIG. 1. FTIR spectrum recorded upon 30 s of evacuation after exposure of H–MOR to 5 mbar NO_2 for 10 min.

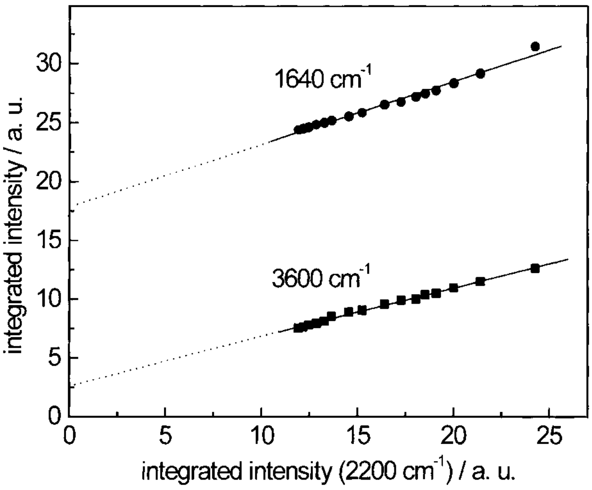

FIG. 2. Integrated intensities of the positive band at 1640 and the negative band at ca. 3600 cm^{-1} versus the integrated intensity of the band at ca. 2200 cm^{-1}.

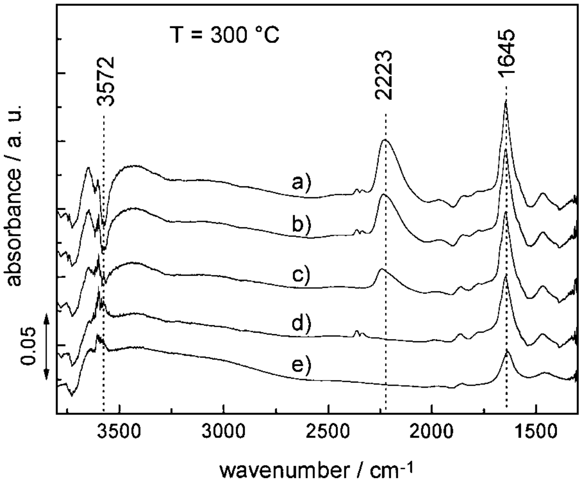

FIG. 3. Variation of the IR spectra with time after adsorption of 5 mbar NO_2 at 300°C and subsequent evacuation for 30 s (a), 1 min 20 s (b), 5 min 30 s (c), 60 min (d). Spectrum (e) was obtained after exposing the activated catalyst to 20 mbar H_2O for 5 min at 300°C and subsequent evacuation for 10 min.

after 60 min, the intensity of the 1645 cm^{-1} band did not decrease to zero. Comparison of spectrum d, Fig. 3, with spectrum e, which was obtained after adsorption of H_2O at 300°C, shows that the remaining surface species was mainly adsorbed H_2O. Wakabayashi *et al.* observed a band at 1633 cm^{-1} and a broad band between 3500 and 2200 cm^{-1} upon adsorption of low amounts of water at 30°C on a H–ZSM-5 containing Lewis acid sites (9). The authors assigned these bands to the δ(HOH) and ν(OH) vibration, respectively, of water species bonded to Lewis acid sites. Spectra d and e, Fig. 3, are similar to their spectrum and therefore the band at ca. 1645 cm^{-1} can be assigned to the δ(HOH) vibration of water adsorbed on Lewis acid sites. Wakabayashi *et al.* could show that Lewis acid sites, as opposed to Brønsted acid sites, are the preferred adsorption sites for water in zeolites.

The presence of residual water after complete removal of the 2200 cm^{-1} band is inconsistent with removal of NO^+ by reversal of Eq. [1], because complete removal of NO^+ ions should also lead to a complete removal of water. We believe that the remaining water is additional, nonstoichiometric water which was adsorbed on the zeolite during the admission of NO_2. It should be emphasised that during exposure of the zeolite to NO_2 the valve to the vacuum pump was closed. During that time, water desorbing from the walls of the vacuum system was not pumped off, and it is likely that the partial pressure of water increased by several orders of magnitude. Therefore, the additional water observed upon subsequent evacuation can be interpreted as an experimental artefact. Furthermore, the formation of stable nitrates on Fe or Na ions present in the commercial zeolite might also contribute to the band around 1645 cm^{-1}: inorganic nitrates absorb between 1650 and 1200 cm^{-1} (11).

Taking the above observations together, we believe that the observed spectra can be explained by the formation of NO^+ and H_2O according to reaction [1], which was first proposed by Hadjiivanov *et al.* (8). The complete assignment of the bands observed at 120°C is given in Table 1.

TABLE 1

Assignment of the Bands Observed upon NO_2 Adsorption on H–MOR at 120°C

Wavenumber/cm^{-1}	Assignment
3618	Brønsted hydroxyl groups in the main channels
3585	Brønsted hydroxyl groups in the side pockets
3500–2600	ν(OH) of water adsorded on Lewis acid sites
2202	Chemisorbed NO^+
1641	δ(HOH) of water adsorbed on Lewis acid sites (possibly superimposed on $\nu(NO_3^-)$ of nitrates formed on Fe and Na impurities)
1589	$\nu(NO_3^-)$ of nitrates formed on Fe and Na impurities
1314	δ(OH) of zeolite hydroxyl groups perturbed by H-bonding to adsorbed water (8, 10)

As we initially introduced NO_2 into the cell, the NO necessary for reaction [1] must have formed by thermal decomposition of the NO_2, possibly catalysed by the zeolite. The equilibrium between NO_2 and NO shifts to NO with increasing temperature: the partial pressure of NO in equilibrium with 5 mbar NO_2 is 0.12 mbar at 120°C and 2.3 mbar at 300°C (calculated for $p_0(NO_2) = 5$ mbar, $V =$ const.). In fact, gas phase NO was present in the cell at 300°C during admission of NO_2, as evidenced by the observation of a rotovibrational structure centred around 1876 cm^{-1}, the stretching frequency of gas phase NO (11).

It is noteworthy that the negative band due to Brønsted hydroxyl groups (Fig. 1) is split into two components. Zeolite mordenite has two different types of Brønsted acid sites, one located in the large main channels and one in the side pockets. Maache *et al.* found that the acidic hydroxyl groups in the main channels absorb at 3612 cm^{-1} and those in the side pockets at 3585 cm^{-1} (12). Therefore, the two negative bands observed at 3618 and 3585 cm^{-1} (Fig. 1) can be attributed to a consumption of hydroxyl groups in the main channels and in the side pockets, respectively. The number of acid sites is higher in the main channels than in the side pockets. Therefore, if reaction [1] would proceed at an equal probability on both types of sites, the intensity decrease at 3618 cm^{-1} should be larger than that at 3585 cm^{-1}. Figure 1 shows that the opposite was observed. It may, therefore, be concluded that formation of NO^+ is favoured in the side pockets of the zeolite, possibly because the NO^+ ions are better stabilised in the small side pockets due to a stronger interaction with the anionic framework.

The frequency of the maximum of the band due to NO^+ ions was higher at 300°C than at 120°C (compare Figs. 3 and 1, respectively) and increased upon extended evacuation (Fig. 3). It is possible that the stretching frequency of NO^+ is influenced by the coverage of the zeolite surface with adsorbed species. At short times of evacuation, it may be assumed that the coverage of the zeolite with NO^+ was relatively high. Due to the low Si/Al ratio of the zeolite used, the NO^+ ions would be in close proximity to each other, and the action of repulsive forces between the NO^+ ions is likely. This repulsive interaction might lower the stretching frequency of NO^+. As the coverage of the surface with NO^+ decreased due to the back reaction in Eq. [1], the remaining NO^+ ions became more and more isolated, thus absorbing at higher wavenumbers.

Hadjiivanov *et al.* observed the NO^+ ions chemisorbed on H–ZSM-5 at 2133 cm^{-1}, while in the present study on H–MOR bands at wavenumbers above 2200 cm^{-1} occurred. It is known that the stretching frequency of NO^+ in nitrosonium salts varies with the anion: in $NO^+HSO_4^-$ it is observed at 2340 cm^{-1}, while in $NO^+AlCl_4^-$ the frequency is 2236 cm^{-1} (11). This was related to the varying degree of electron transfer into the antibonding π^* orbital of NO^+ (11). A similar explanation might hold for the observed frequency shift between H–MOR and H–ZSM-5. The stronger acidity of H–MOR compared to H–ZSM-5 (13) might be related to this subject.

Reaction between NO^+ and C_3H_6

As described above, the intensity of the band due to NO^+ decreased with time upon evacuation due to the back reaction of Eq. [1]. The spectral changes observed in the 2000–2300 cm^{-1} region during evacuation and subsequent addition of 3 mbar C_3H_6 at 120, 200, and 300°C are shown in Figs. 4a–4c, respectively. At all temperatures, the band around 2200 cm^{-1} disappeared fast upon admission of C_3H_6, indicating that NO^+ reacted readily with C_3H_6 even at 120°C. At 300°C, a new band appeared at ca. 2280 cm^{-1} immediately upon reaction of NO^+ with C_3H_6 (Fig. 4c). Formation of this band was slow at 200°C and was not observed within the time interval studied at 120°C (Figs. 4b and 4a, respectively).

Comparison of the spectra after reaction of NO^+ and C_3H_6 (Fig. 5a) at 300°C and after adsorption of acrylonitrile (Fig. 5b) shows that the band observed at ca. 2280 cm^{-1} can be assigned to the stretching vibration of a nitrile (C≡N) group, because the band observed upon reaction appears at almost the same position as the band which can be assigned to the C≡N group of acrylonitrile. Therefore, it is certain that nitriles are formed in the reaction between NO^+ and propene. This finding is in excellent agreement with our observation that in the continuous flow reaction between 1000 ppm NO_2 and 1000 ppm C_3H_6 over acidic zeolites, acrylonitrile is formed as a side product (4). We have proposed that acrylonitrile is an intermediate in NO_2 reduction to N_2 (4).

As nitriles can be hydrolysed to ammonia (14), we studied the reaction of water with both the nitrile surface compound formed from NO^+ and C_3H_6 and with adsorbed acrylonitrile. In both cases, the band at ca. 2280 cm^{-1}, assigned to the stretching vibration of the C≡N group, disappeared upon

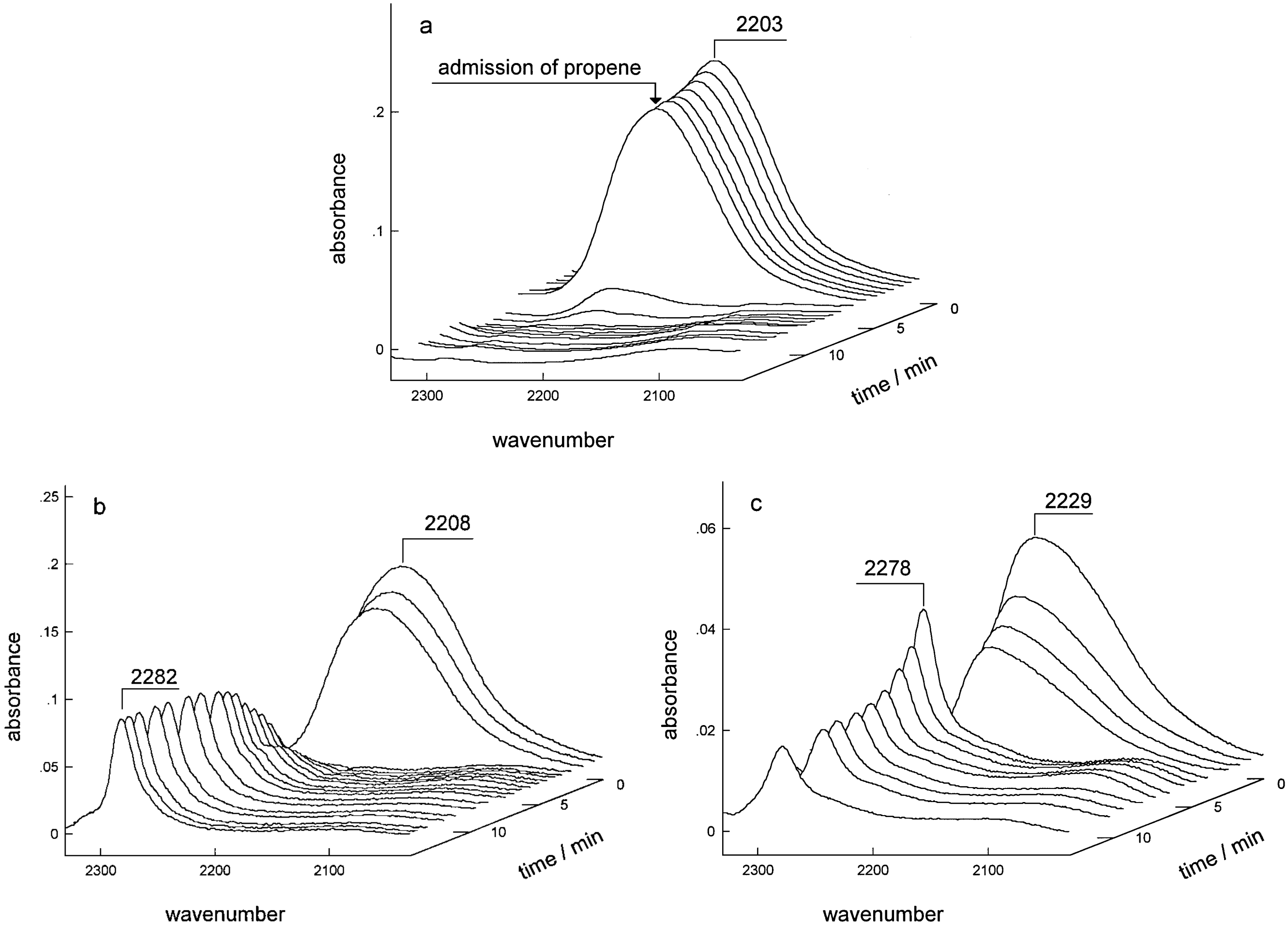

FIG. 4. Reaction of NO^+ with propene at 120°C (a), 200°C (b), 300°C (c). At each temperature, the zeolite was exposed for ca. 10 min to 5 mbar NO_2 and subsequently, the cell was evacuated (time zero in the figures). After 6 min (a), 2 min 10 s (b), 3 min 30 s (c) of evacuation, 3 mbar C_3H_6 were introduced to the cell. The spectra are background corrected.

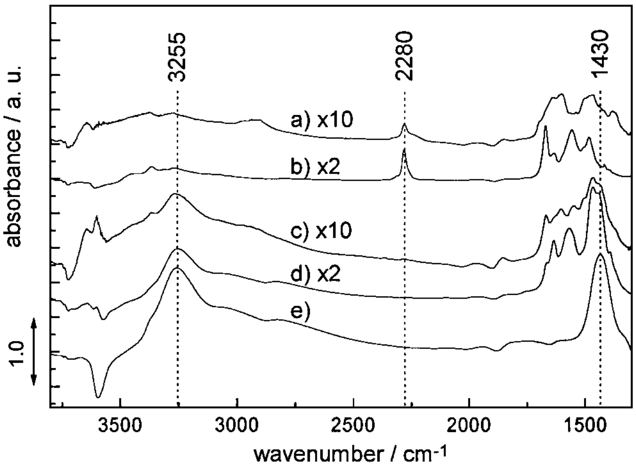

FIG. 5. Spectra recorded after (a) sequential reaction between NO$^+$ and C_3H_6 at 300°C and subsequent evacuation, (b) exposure of a fresh sample to 5 mbar acrylonitrile for 5 min at 300°C and subsequent evacuation, (c), (d) addition of 20 mbar H_2O for 10 min at 300°C to a and b, respectively, and subsequent evacuation, (e) adsorption of 5 mbar NH_3 at 300°C for 10 min and subsequent evacuation.

contact with water (Figs. 5c and 5d), and a new band was formed at ca. 3255 cm^{-1}. By comparison with the spectrum obtained after adsorption of ammonia at 300°C (Fig. 5e), the band at 3255 cm^{-1} can be assigned to the symmetrical stretching vibration of adsorbed ammonium ions. This is another analytical indication that the band formed at 2280 cm^{-1} upon reaction of NO$^+$ with C_3H_6 is in fact a nitrile, since it can be hydrolysed to ammonia. Furthermore, this supports our previous finding that the acrylonitrile formed in the NO_2/C_3H_6 reaction over acidic zeolites can be hydrolysed to ammonia and that the ammonium ions are the intermediate surface species which reduce NO$_x$ to N_2 (4, 15).

Formation of nitrile species, i.e., of acrylonitrile if C_3H_6 is used as reducing agent, in the reaction between NO$^+$ and C_3H_6 can be envisioned according to the following mechanism:

$$\mathrm{NO_2 + NO + 2\,H^+ \rightleftharpoons 2\,NO^+ + H_2O} \quad [1]$$

$$\mathrm{2\,NO^+ + 2\,CH_3\text{-}CH{=}CH_2 \rightleftharpoons 2\,[CH_3\text{-}CH\text{-}CH_2\text{-}NO]^+} \quad [2]$$

$$\mathrm{2\,[CH_3\text{-}CH\text{-}CH_2\text{-}NO]^+ \rightleftharpoons 2\,CH_2{=}CH\text{-}CH_2\text{-}NO + 2\,H^+} \quad [3]$$

$$\mathrm{2\,CH_2{=}CH\text{-}CH_2\text{-}NO \rightleftharpoons 2\,CH_2{=}CH\text{-}CH{=}NOH} \quad [4]$$

$$\mathrm{2\,CH_2{=}CH\text{-}CH{=}NOH \rightleftharpoons 2\,CH_2{=}CH\text{-}C{\equiv}N + 2\,H_2O} \quad [5]$$

First, NO$^+$ ions are formed by a reaction between NO, NO_2, and the Brønsted acid sites (reaction [1]). The electrophilic NO$^+$ ions add to the double bond of propene to yield a carbocation (reaction [2]). Dissociation of one proton from the carbocation yields 3-nitroso propene (reaction [3]). Nitroso compounds with α hydrogen are known to be unstable and undergo tautomerisation to their respective oximes (reaction [4]) (14). Propenal oxime can be dehydrated to acrylonitrile (reaction [5]), this reaction is catalysed by the acid sites of the zeolite (14). The sum of reactions [1] to [5] gives:

$$\mathrm{2\,C_3H_6 + NO + NO_2 \rightarrow 2\,CH_2{=}CH\text{-}C{\equiv}N + 3\,H_2O} \quad [6]$$

This mechanism explains the role of acid sites in the reaction: both the formation of nitrosonium ions and the dehydration of propenal oxime are acid catalysed reactions. The ability of the Brønsted acid sites to convert the neutral nitrogen oxides NO and NO_2 which are radicals into electrophilic nitrosonium ions is remarkable. Several authors have proposed that in the DeNO$_x$ reaction the initial reaction between nitrogen oxides and the hydrocarbon is a radical type process (16–18). Our finding, however, implies that over acidic catalysts, the reaction mechanism is shifted from the radical type chemistry of gas-phase NO$_x$ to a polar mechanism involving electrophilic ions. This effect of acidic catalysts is known from liquid-phase organic chemistry. While the gas-phase nitration of aromatics occurs via a radical type mechanism, involvement of nitronium (NO_2^+) and nitrosonium (NO$^+$) ions is most likely when the nitration is carried out in the liquid phase in the presence of acids like concentrated H_2SO_4 (19).

The complete spectra recorded immediately before and after the addition of C_3H_6 to the NO$_x$-derived adsorbates at 120°C are shown in Fig. 6. After the reaction, a broad band had formed between ca. 3350 and 2600 cm^{-1} and new bands at 1458 and 1414 cm^{-1}. The band at 1641 cm^{-1} which was assigned to adsorbed water did not change significantly in intensity upon reaction, showing again that the species giving rise to that band (H_2O) is a different one than that giving rise to the band at 2200 cm^{-1} (NO$^+$). Interesting changes

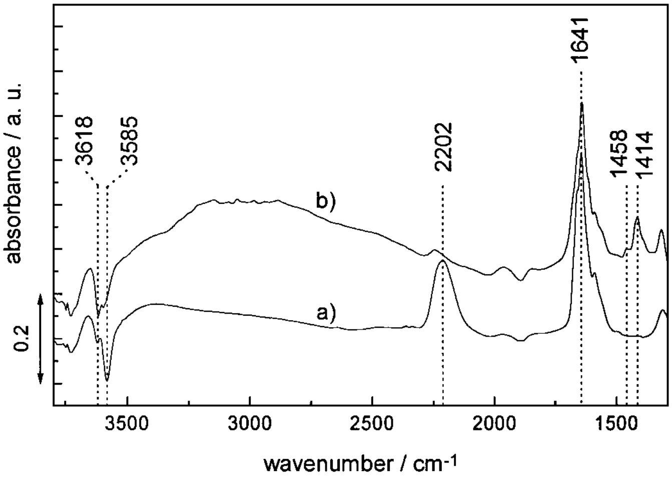

FIG. 6. Spectra recorded (a) immediately before and (b) 30 s after admission of 3 mbar C_3H_6 to chemisorbed NO$^+$ at 120°C.

occur in the region of the acidic zeolite hydroxyl groups. The negative band at 3585 cm^{-1} (OH groups in the side pockets) decreases in intensity upon addition of C_3H_6, while the negative band at 3618 cm^{-1} (OH groups in the main channels) increases in intensity. It seems, therefore, that the NO^+ ions in the side pockets react with propene in the main channels to yield a compound which remains adsorbed on the hydroxyl groups in the main channels, possibly because this propene-derived species is too large to enter the side pockets. The hydroxyl groups in the side pockets are restored during this reaction and therefore the intensity of the negative band at 3585 cm^{-1} decreases.

The broad band observed between 3350 and 2600 cm^{-1} is typical for the stretching vibration of OH groups strongly H-bonded to acid sites (20). It is, therefore, likely that the compound formed in the reaction between NO^+ and C_3H_6 at 120°C, which gives rise to this broad band and to the bands at 1458 and 1414 cm^{-1}, is the propenal oxime formed in reaction [4] of the above mechanism. In line with this assignment, no strong bands due to sp^3 hybridised C–H vibrations (2800–3000 cm^{-1}) were visible, because propenal oxime does not contain such bonds. The band at 1414 cm^{-1} might correspond to the δ(O–H) vibration of the OH–group of propenal oxime: while the δ(O–H) vibration of, e.g., acetone oxime in the gas phase occurs at 1340 cm^{-1}, it is shifted to 1477 cm^{-1} in the crystalline state or in solution (21).

If this assignment is correct, it should be possible to transform the oxime produced at 120°C to acrylonitrile by heating the catalyst. This could in fact be verified experimentally. Spectrum a of Fig. 7 was obtained after 5 min exposure of the catalyst to 3 mbar C_3H_6 and 5 min evacuation in the sequential experiment at 120°C. The difference to spectrum b, Fig. 6 is that now bands at 3000–2800 cm^{-1} and around 1500 cm^{-1} due to the C–H stretching and bending vibrations, respectively, of propene derived adsorbed hydrocarbons are present, which is due to the prolonged exposure of the catalyst to gas-phase propene (22). The broad band between 3350 and 2000 cm^{-1} and the band at 1414 cm^{-1} due to propenal oxime was still visible. The catalyst was then heated to 300°C, and IR spectra were recorded during heating. At ca. 170°C (spectrum c, Fig. 7), i.e., at about the same temperature, where the catalyst starts to exhibit significant activity in NO_2 reduction to N_2 (4), the intensity of the broad band due to the OH group of propenal oxime started to decrease and a band at 2280 cm^{-1} started to grow due to the formation of a nitrile. It may therefore be concluded that the dehydration of propenal oxime is the rate determining step in formation of acrylonitrile from C_3H_6 and NO_2.

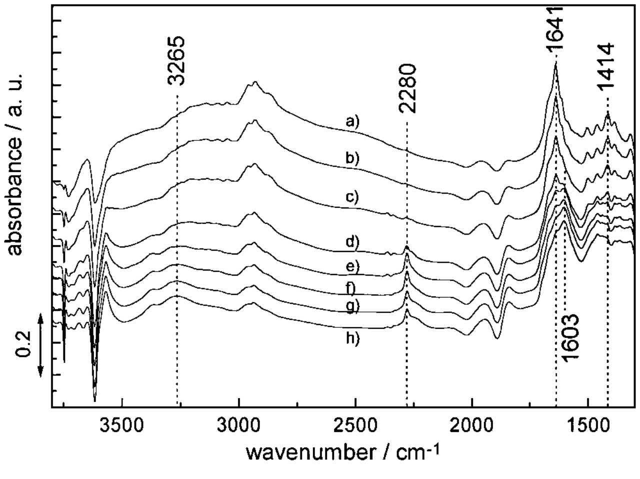

FIG. 7. Spectra recorded (a) after admission of 3 mbar C_3H_6 to chemisorbed NO^+ at 120°C for 5 min and subsequent evacuation for 5 min, and upon subsequent heating of the catalyst at (b) 135, (c) 170, (d) 200, (e) 245, (f) 275, (g) 288, and (h) 300°C.

The intensity of the nitrile band reached a maximum at ca. 275°C (spectrum f, Fig. 7) and decreased upon further heating. At the same time, a new band appeared at ca. 3265 cm^{-1}, which can be assigned to the stretching vibrations of adsorbed ammonium ions, formed by hydrolysis of the nitrile by adsorbed water. The ammonium ions obtained from hydrolysis of acrylonitrile are most likely the surface species which reduce NO_x to N_2 in the NO_2/C_3H_6 reaction under continuous flow conditions (4).

CONCLUSIONS

It was shown that nitrosonium ions, which are formed upon reaction of NO_2 with NO over acidic zeolites, are likely to be important intermediates of NO_x reduction over this type of catalyst: they react rapidly with propene, thereby forming acrylonitrile. Hydrolysis of acrylonitrile yields adsorbed ammonium ions, which are known to reduce NO_x to nitrogen efficiently. Furthermore, the results show that the acid sites of the catalyst are important catalytic centres for the formation of acrylonitrile. The involvement of acid sites appears to shift the mechanism from radical type processes in the case of gas-phase nitrogen oxides to an electrophilic mechanism involving chemisorbed nitrosonium ions.

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