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FT-IR study of $NO + O_2$ co-adsorption on H-ZSM-5: re-assignment of the 2133 cm^{-1} band to NO^+ species

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Whereas NO adsorption at room temperature on activated H-ZSM-5 (Si/Al = 29) caused only negligible changes in its IR spectrum, addition on O_2 to NO led to the appearance of bands at 2133 and 977 cm^{-1}. Concomitantly, the number of acidic zeolite OH groups decreased while H_2O hydrogen-bonded to zeolite OH groups developed. Introduction of small amounts of $^{18}O_2$ did not change the 2133 cm^{-1} band wavenumber, nor the use of a partly deuteroxylated D–H-ZSM-5 sample. In such a case, HOD formation was detected. The results obtained evidence that the 2133 cm^{-1} band, generally considered as characterizing NO_2^+ species, is, in fact, due to NO^+ species occupying cationic positions in the zeolite. The 977 cm^{-1} band is attributed to the $O_{lattice}$–NO^+ vibration. A scheme of the NO^+ formation, involving NO_2 molecules as NO oxidizing agent, is proposed.

Keywords: nitrogen oxides, nitrosonium ion, DeNOx, H-ZSM-5, IR spectroscopy

1. Introduction

When the possibility of selective catalytic reduction of nitrogen oxides by hydrocarbons (HC-SCR) was established [1,2], this provoked an immense interest in characterizing the nature of the different NO_x adspecies formed on catalyst surfaces. In particular, many studies [3–16] on the $NO + O_2$ co-adsorption on zeolites and metal-exchanged zeolites appeared since the latter are promising HC-SCR catalysts. In general, IR spectroscopy is used to determine the nature of the surface species. However, the interpretations of various bands proposed by different authors are often quite contradictory. A typical example is the band at ca. 2133 cm^{-1} which has been assigned to NO_2^+ [4–6,8,9,11,17–22], $NO_2^{\delta+}$ [12,23], NO_2 [3,10,24], NO^+ [13] or N_2O [25].

To the best of our knowledge, the 2133 cm^{-1} band was first reported by Iwamoto et al. [17] (who observed it at 2125 cm^{-1}) in a study of NO decomposition on a Cu-ZSM-5 sample. The authors found this band to be slowly developing with time when the catalyst was placed in a NO atmosphere. They proved, by ^{15}N isotopic substitution experiments, that the corresponding species contained only one N atom. Based on the classical works of Chao and Lunsford [26,27], the band was assigned to NO_2^+ species located on copper ions. Valyon and Hall [24] reported that the band was also observable when the catalysts were exposed to low pressures of NO_2 and attributed it to NO_2 adsorbed on Cu^{2+} ions. The same authors later noted that the band at 2130 cm^{-1} was observed after NO adsorption on oxidized Cu-ZSM-5 even at 173 K, but appeared neither after NO adsorption on reduced catalysts, nor after NO_2 adsorption [28]. They suggested that the species would be formed by a reaction of NO with surface deposited oxygen and might be important intermediates in NO decomposition.

A careful investigation of the 2133 cm^{-1} band was performed by Hoost et al. [5]. They observed the band when using H-ZSM-5 and found a strong correlation between its development and the intensity decrease of the band at 3610 cm^{-1} due to the zeolite acidic OH groups. Since the 2133 cm^{-1} band was also observed (with a lower intensity) from NO_2 adsorption, it was assigned to adsorbed NO_2^+. Following the papers of Iwamoto et al. [17] and Hoost et al. [5], many other authors [4,6,8,9,11,18–21] also attributed the band to NO_2^+ species.

Szanyi and Paffett [10] reported that the 2133 cm^{-1} band was observed on H-ZSM-5 and Me–H-ZSM-5 zeolites when a small amount of oxygen was added to NO and confirmed the results of Hoost et al. [5] about the strong correlation between the increase of its intensity and the intensity decrease of the 3610 cm^{-1} OH band. In addition, they reported that the well-known A–B features of the A–B–C structure of H-bonded hydroxyls concomitantly appeared. Thus, the authors proposed the 2133 cm^{-1} band to be due to NO_2 strongly bound to the acidic zeolite hydroxyls.

The data on the stability of the species characterized by the 2133 cm^{-1} band, as reported by various authors, differ dramatically. Thus, a full removal of the band was reported after evacuation or helium purge at room temperature [3] or at 323 K [20], whereas other authors found the band to be stable up to 673–723 K evacuation [8,12,21,28].

Taking into account these rather contradictory results, the fact that a frequency of 2133 cm^{-1} is not typical of NO_2 [29,30] and that NO_2^+ in salts adsorbs at higher frequencies, namely, in the 2392–2360 cm^{-1} range [29], we re-

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investigated the $NO+O_2$ co-adsorption on H-ZSM-5 using isotopic substituted samples as $^{18}O_2$ and a D–H-ZSM-5 zeolite. The reported results led us to propose another interpretation involving the formation of NO^+ species and water.

2. Experimental

The H-ZSM-5 sample had a Si/Al ratio of 29. Heavy water consisted of 99.9% D_2O. $^{18}O_2$ (isotopic purity = 97.26%) was supplied by Enriso-Top. Both $^{16}O_2$ (99.99%) and $^{18}O_2$ were additionally purified prior to adsorption by passing through a liquid nitrogen trap. NO (99.9%) was additionally purified by fraction distillation.

IR spectroscopy studies were carried out with a Nicolet-MX-1 FTIR spectrophotometer at a spectral resolution of 4 cm^{-1}. The number of scans was 128. A self-supporting pellet was prepared from the sample and activated directly in the IR cell. The latter was equipped with a gas burette, allowing the introduction of small and well known amounts of adsorbates. The vacuum apparatus used had a residual pressure lower than 10^{-5} Torr. Before the adsorption measurements, all performed at room temperature (r.t.), the pellet was activated by 1 h calcination at 673 K and 1 h evacuation at the same temperature.

3. Results

The IR spectrum of the activated H-ZSM-5 mainly presents, in the ν(OH) region, two narrow bands with maxima at 3742 and 3610 cm^{-1}, which characterize silanol groups and the acidic zeolite –Al–(OH)–Si– hydroxyls, respectively.

The adsorption of water was carefully investigated in order to specify the interpretation of the spectra obtained during $NO + O_2$ co-adsorption (see below). Subsequent introduction of small doses of water on the sample caused the following changes in the IR spectrum (figure 1):

(i) development of bands due to molecularly adsorbed water [30]: $\delta(H_2O)$ at 1623 cm^{-1}, $\nu_{as}(H_2O)$ at 3700 cm^{-1} and $\nu_s(H_2O)$ at 3552 cm^{-1}.

(ii) gradual decrease in intensity of the band at 3610 cm^{-1} and a parallel appearance and rise in intensity of three broad features at ca. 2880, 2464 and near 1700 cm^{-1}, due to the well known A–B–C structure produced by hydrogen-bonded hydroxyls, and two bands at 1350 and 872 cm^{-1} (not shown) assigned to the δ(OH) and γ(OH) modes of the H-bonded zeolite hydroxyls. A plot showing the 3610 cm^{-1} band intensity loss variation versus the intensity rise of the B feature (chosen because of its high intensity) is presented in figure 2(a).

Introduction of NO, purified before used and at a relatively low equilibrium pressure (1 Torr), on the activated sample did practically not change its spectrum. However, a careful inspection of the subtracted spectra indicated the presence of two very weak bands at 1830 and 1637 cm^{-1} (reported, also, in [10]) and assigned to small amounts of N_2O_3.

Admission of one small dose of oxygen (ca. 1 μmol) into the IR cell containing the H-ZSM-5 pellet, placed under 1 Torr NO, induced the following changes in the IR spectrum (figure 3):

(i) appearance of a band at 2133 cm^{-1}, which increased in intensity with time;

(ii) parallel development of a band at 977 cm^{-1};

(iii) concomitant decrease in intensity of the band at 3610 cm^{-1}; and

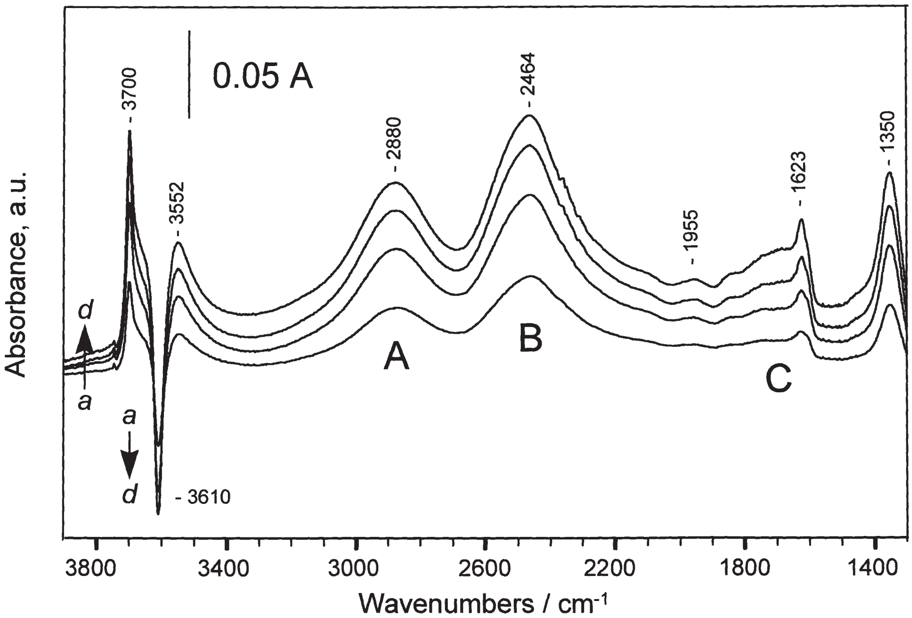


Figure 1. Changes in the IR spectra of activated H-ZSM-5 after successive introduction of 1 (a), 2 (b) and 3 μmol of H_2O.

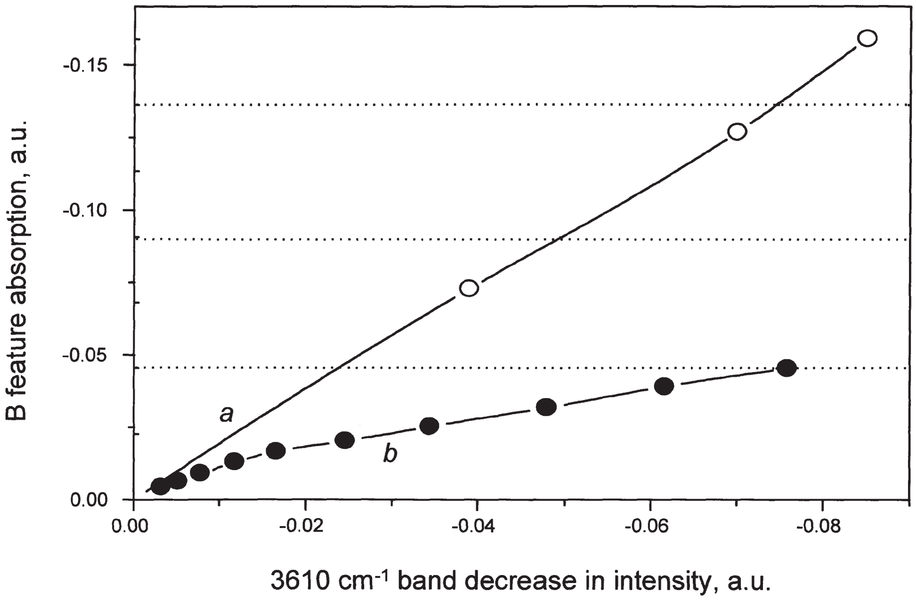


Figure 2. Variation of the intensity of the B band versus the intensity loss of the 3610 cm^{-1} band after adsorption of water (a) and co-adsorption of NO and O_2 (b) on H-ZSM-5.

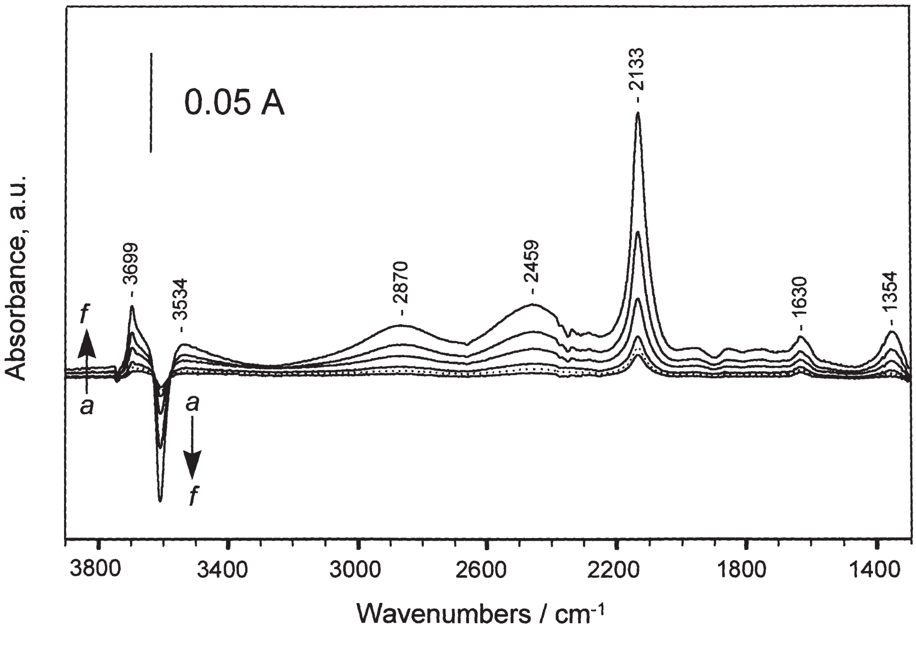


Figure 3. Changes in the IR spectra of H-ZSM-5 under 1 Torr NO after introduction into the IR cell of increasing amounts of O_2. Introduction of 1 μmol O_2 (a) and the same spectrum after 5 min (b); successive introduction of 2 (c), 4 (d), 8 (e) and 16 μmol (f) of O_2.

(iv) development of bands at 3699, 3534 and 1630 cm^{-1}, which were assigned (see above) to molecularly adsorbed water, as well as of the features characterizing the H-bonded zeolite hydroxyls (2870, 2459, 1354 and 872 cm^{-1}).

The increase in amount of O_2 introduced into the IR cell or in the contact time provoked the intensity increase of the band at 2133 cm^{-1}, whereas the described concomitant changes of the other bands developed. The decrease of the 3610 cm^{-1} band intensity versus the increase of the B band is ca. 3 times faster (figure 2(b)) than the same feature observed after water adsorption (figure 2(a)). This means that only $1/3$ of the acidic OH groups interact with water, the disappearance of the remaining part of the band being associated with another phenomenon.

In order to obtain more information about the nature of the species characterized by the 2133 cm^{-1} band, co-adsorption of NO and $^{18}O_2$ was studied. The first portions of $^{18}O_2$ successively introduced into the cell containing the sample and 1 Torr of NO caused the same changes in the IR spectrum as those observed with non-labelled oxygen (figure 4). The only difference we were able to note was the red shift of a small part of the 3699 cm^{-1} band to 3690 cm^{-1}.

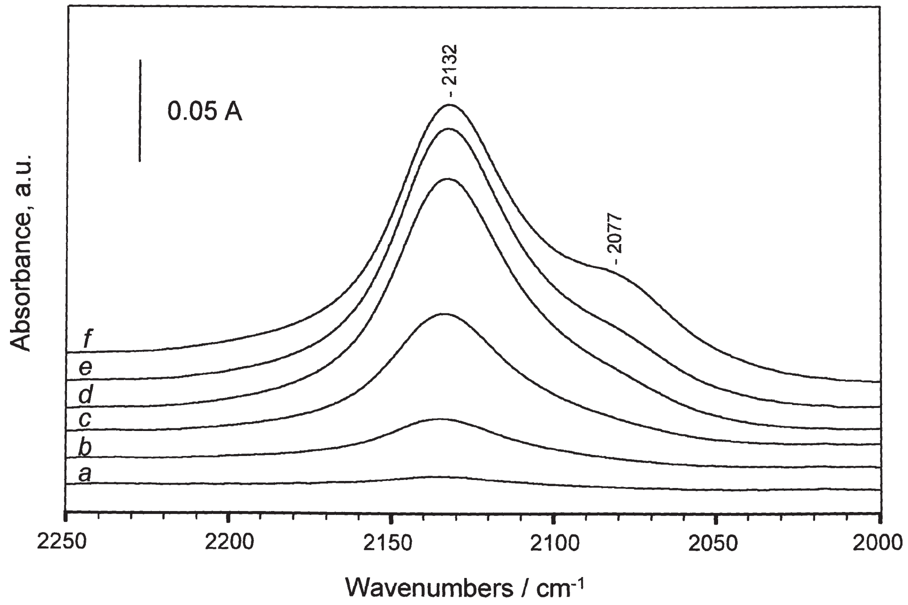


Figure 4. Changes in the IR spectra of H-ZSM-5 under 1 Torr NO after introduction into the IR cell of increasing amounts of $^{18}O_2$. Introduction of 2 (a), 4 (b), 20 (c) and 40 μmol (d) of $^{18}O_2$; $^{18}O_2$ partial pressure of 1 (e) and 5 Torr (f).

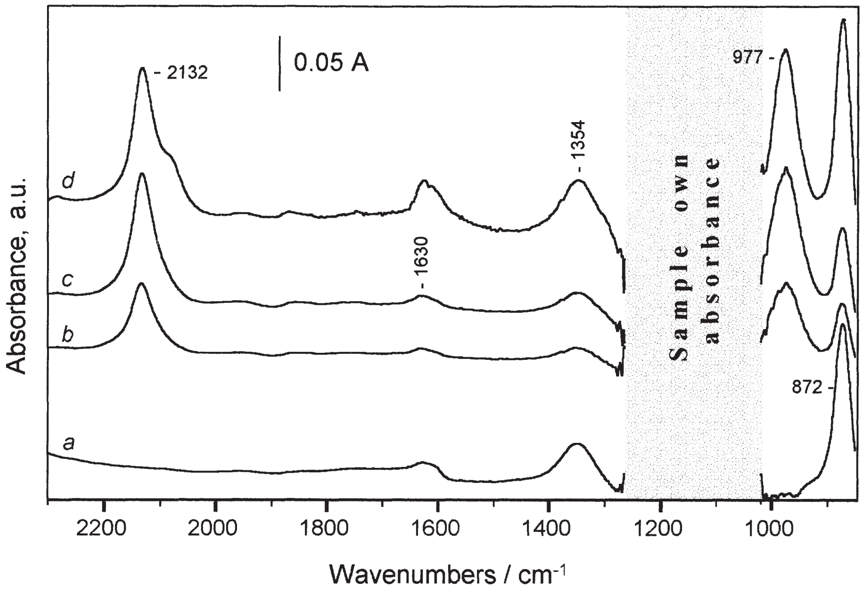


Figure 5. Changes in the IR spectra of H-ZSM-5, notably in the 1000–800 cm^{-1} region, after introduction of 1 μmol H_2O (a), or co-adsorption of NO with 8 (b) and 16 μmol (c) $^{16}O_2$ or with 5 Torr $^{18}O_2$ (d).

This 10 cm^{-1} red shift coincides with the calculated isotopic shift for ^{16}O–H to ^{18}O–H stretching vibrations. Thus, the results prove that a small fraction of the water produced contains labelled oxygen. It was only after attaining some equilibrium pressure of introduced oxygen that a new shoulder at 2077 cm^{-1} began to develop (figure 4(e)), partly at the expense of the 2133 cm^{-1} band. This new band coincides in position with the calculated N–^{16}O $\rightarrow$ N–^{18}O shift of the N–O stretching mode. Thus, the shifted value proves that the 2133 cm^{-1} species contained oxygen, whereas the appearance of only one additional band after the isotopic substitution implies that only one oxygen atom participates in the species formed. No changes were observed for the band at 977 cm^{-1} (figure 5), i.e., no ^{18}O participates in its corresponding vibration.

Since the appearance of the 2133 cm^{-1} feature occurs at the expense of the 3610 cm^{-1} OH group band, we may suppose that one or more protons are included in the structure of the species under consideration. To check that, NO and O_2 co-adsorption experiments were performed on a partly deuteroxylated sample (the reason not to use a fully D-exchanged zeolite was the possibility to detect the δ(H–O–D) mode which would be an additional proof of water formation). The H-ZSM-5 sample was placed in an atmosphere of 5 Torr D_2O and heated for 1 h at 400 °C. After this treatment, the O–H band decreased in intensity, and new bands with the expected isotopic shift appeared instead ($3742 \rightarrow 2760$ cm^{-1} and $3610 \rightarrow 2662$ cm^{-1}). Co-adsorption of NO and O_2 (using the already described procedure) on the D–H-ZSM-5 sample led to the appearance of the same band at 2133 cm^{-1}, the other bands in the spectrum coinciding well with the expected H–D shift. Whereas the 1630 cm^{-1} band was poorly observable, a new band, at 1416 cm^{-1}, assigned to the δ(H–O–D) mode [29,30], was observed (spectrum not shown). The results show that no hydrogen atom participates in the structure of the 2133 cm^{-1} band species.

4. Discussion

It is known [31] that the NO molecule has three electron pairs occupying bonding orbitals and one unpaired electron situated on a π antibonding orbital. As a result, the N–O bond order is 2.5. Another electron pair is situated on the 5σ non-bonding (or weakly antibonding) orbital and makes NO a weak electron donor, i.e., a weak Lewis base. Coordination of a NO molecule to a Lewis acid via the nitrogen atom is accompanied by a partial charge transfer and an increase in bond order, as in the case of CO. Formation of a back π bond, although not so easily as with CO, is also possible, and this causes a decrease in the N–O stretching mode. Thus, it is generally accepted to denote the partial charge transfer either by $NO^{\delta+}$ or $NO^{\delta-}$. With time, the δ sign has been often omitted, and many examples are found in the literature about coordinated NO denoted as NO^+ or NO^-. That is why it is often believed that NO^+ is spectrally detected in the region about 1900 cm^{-1}.

The electron of the NO molecule which is situated on the antibonding orbital can easily be donated [31], and thus, the formed NO^+ ion will be characterized by a bond order ≈ 3, which induces a very different spectral behavior than that of NO. Indeed, the isolated nitrosonium ion has been reported to absorb at 2220 cm^{-1} [30]. However, in salts the frequency is shifted, and the values reported vary from 2391 to 2165 cm^{-1} [29]. On the contrary, when NO accepts an electron and forms NO^-, this electron occupies the antibonding orbital, the N–O bond order becomes 2 and the N–O stretching frequency falls to 1353 cm^{-1} [29].

Our results on $NO + {}^{18}O_2$ co-adsorption clearly prove that the 2133 cm^{-1} band implies only one oxygen atom. Since it has already been demonstrated by other authors using ^{15}NO that the species unambiguously contains only one nitrogen atom [5,9,17,22], evidently it is a N–O species. The high frequency of the characteristic band suggests a high N–O bond order, close to 3, which implies that the species under consideration is a NO^+ cation.

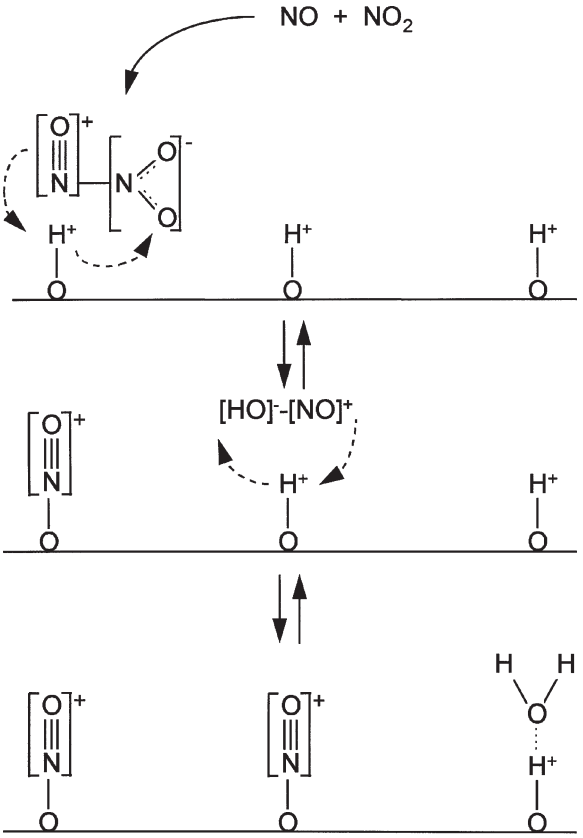
Since NO^+ is a charged fragment, the only suitable place for its localization is the cationic position in the zeolite. In this case, an $O_{lattice}$–NO^+ vibration should be observed in the region about 1000 cm^{-1} [29]. We detect it at 977 cm^{-1}. The ^{18}O-substitution experiments prove that the oxygen introduced into the gas phase does not participate in this vibration, which is in agreement with the assignment of the band to the $O_{lattice}$–NO^+ stretching mode.

The plots presented in figure 2 imply that the disappearance of the 3610 cm^{-1} OH groups occurs at the expense of two phenomena: formation of H_2O molecules which are H-bonded to the zeolite hydroxyls, and one more process. The following equilibrium can be proposed:

$$2NO + (1/2)O_2 + 2O_{lattice}\text{–}H^+ \rightleftharpoons H_2O + 2O_{lattice}\text{–}NO^+$$

Here, two protons from the acidic OH groups are exchanged by NO^+ to form one water molecule which is H-bonded to another zeolite hydroxyl. This scheme is in excellent agreement with the experimentally observed reaction stoichiometry (see figure 2). The parallel formation of water and the 2133 cm^{-1} band species has previously been suggested by Aylor et al. [12] on the basis of the existence of a band at 1630 cm^{-1} which was not shifted after ^{15}N substitution.

The following scheme of the process can be suggested:



Scheme 1.

Note that the NO_2 formation is slow which explains the slow appearance of the 2133 cm^{-1} band.

It was already noted that the stability of the 2133 cm^{-1} band, as reported by various authors, dramatically varies following the experimental conditions. Isolated NO^+ is an ionic species, and its thermal stability should be significant. However, it easily interacts with water to regenerate the acidic OH groups and form N_2O_3. Thus, the mobility of water on the sample would determine the stability of NO^+. One may expect that conditions favouring water trapping would stabilize NO^+. Indeed, the band is reported to be stable in metal-exchanged zeolites [8,12,21,28] where the metal cations coordinate the evolved water and thus act as water traps. Higher equilibrium pressures of NO and O_2, at which the N_2O_4 being formed could replace the water from the sample [10], would also stabilize the NO^+ cation.

Finally, we should like to emphasize that NO^+ is the only stable NO_x surface species on H-ZSM-5 and is most probably an important intermediate in the SCR of NO_x on this type of catalyst. This is in excellent agreement with the suggestion of Halasz et al. [32], who proposed that the HC-SCR active sites of H-ZSM-5 involve the Brønsted acidic bridging hydroxyls. In addition, our results could explain the fact that H-ZSM shows a SCR activity only under dry conditions [33], since, in the presence of water, the concentration of NO^+ cations strongly decreases.

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