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Operando FTIR study of reaction pathways of selective catalytic reduction of NO_x with decane in the presence of water on iron-exchanged MFI-type zeolite

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Abstract

The reaction mechanism of selective catalytic reduction of NO_x with decane on acid and iron-exchanged MFI-type zeolite was investigated by operando FTIR spectroscopy and a special reactor cell enabling the use of water–bearing gas mixtures. Water has a dramatic influence on the reaction pathway. The formation of organic nitro and nitrite compounds does not proceed via chemisorbed states of NO_x as observed in SCR with dry gases.

Keywords: Operando FTIR; SCR; Fe-MFI zeolite; Selective catalytic reduction of NO_x

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1. Introduction

Previous IR spectroscopic investigations of hydrocarbon–SCR reactions on transition-metal zeolites were mostly conducted with synthetic gas mixtures lacking water. The studies revealed the important catalytic role of chemisorbed states of NO_x and of the hydrocarbon in the formation of organic nitrogen compounds as reaction intermediates [1,2]. Sadykov et al. reviewed the literature on SCR by methane, propane, and propene and concluded that inorganic surface nitrate complexes are key reaction intermediates [3]. The rate-limiting step of hydrocarbon–SCR was proposed to be the reaction between surface nitrates and hydrocarbons or their activated fragments, leading to the formation of organic nitro compounds [3]. Wang et al. observed chemisorbed states of NO_2/NO_3^- (denoted NO_y) in the ligand sphere of Fe^{3+} and Co^{2+} cations in zeolites [4]. These NO_y complexes can react with isobutane [4] and are able to abstract hydrogen atoms from hydrocarbons [5–7]. Variation of hydrocarbon–SCR performance was ascribed to differences in the nature of the NO_y ligands, depending on the transition metal and the zeolite [4]. In propene–SCR on Cu-ZSM-5, NO_2 reacts with an allylic intermediate originating from propene adsorption on Cu^{2+} ions [8]. Recombination of alkyl radicals with NO_x leads to nitro, nitrite, and nitroso compounds. FTIR signatures of organic nitro and nitrite compounds were also observed in propene–SCR on silica-supported platinum [9]. Above 150 °C on an iron zeolite, carbonaceous deposits containing low-valence nitrogen atoms are formed through the reaction of hydrocarbons with NO_2 [10]. The transformations of the initially formed organic nitrogen compounds are rapid and lead to a variety of organic functional groups, including nitriles, isocyanates, amides, and amines. Upon exposure of this nitrogen-containing organic deposit to NO_x, nitrogen is released, as, for example, in propene–SCR over Cu/ZSM-5 [11–13]. An isotopic labeling study of isobutane–, propene–, and propane–SCR over Fe/ZSM-5 zeolite revealed that one N atom in every N_2 molecule formed stems from the deposit and the other one from NO_2 [14]. On Ag/Al_2O_3 catalyst, or-

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ganic nitrite compounds were found to decompose to surface nitrates and partly oxidized hydrocarbons [15].

In practical applications of hydrocarbon–SCR, gas streams contain large water concentrations. In an experiment by Hadjiivanov et al., Fe-ZSM-5 catalyst was exposed to 100 Pa D_2O, followed by 1000 Pa NO and subsequently 1000 Pa O_2 with evacuation between consecutive steps. From that study it was concluded that nitrates can be formed on a D_2O-covered Fe-ZSM-5 catalyst under a sufficiently large NO pressure. The stability of the surface nitrates in the presence of a trace amount of D_2O led those authors to propose that practical propane–SCR proceeds through a reaction of the hydrocarbon with chemisorbed NO_x [16].

Recently we investigated the decane–SCR reaction on Fe/H-MFI in the presence of water. The catalyst was subjected to temperature cycles between 150 and 550 °C with heating and cooling at ca. 10 °C/min. NO_x removal and N_2 formation were traced separately. The NO_x removal from the gas stream over the catalyst showed two maxima, at ca. 225 and 325 °C. The first maximum corresponded to NO_x trapping not leading to N_2. Nitrogen formation set in after the first NO_x removal maximum, and peaked around 350 °C. During the cooling phase, NO_x removal slightly exceeded N_2 formation, such that over the entire temperature cycle, NO_x removal and N_2 formation were in agreement. Thus with temperature ramping, the hydrocarbon SCR process could be divided into two steps. First at low temperature there was trapping of NO_x, presumably by formation of organo nitrogen compounds [2]. Subsequently at high temperature there was nitrogen formation.

Reaction cells for in situ FTIR generally are not suitable for handling hydrated gases because of reaction with the KBr windows. Recently, the technical problems linked with the handling of hydrated gases in operando FTIR spectroscopic investigation of solid catalysts were largely overcome [17]. For handling hydrated gas mixtures, a special reactor cell with minimized dead volume can be used in which the gas flow is forced through the catalyst wafer in the longitudinal direction to minimize the contact of the gas with the windows [17]. In the work we report here we used the FTIR setup and investigated the low-temperature NO_x trapping during decane–SCR over Fe/H-MFI in the presence of water.

2. Experimental

The Fe/H-MFI zeolite catalyst was prepared according to an existing procedure [18]. The NH_4-zeolite was mixed and intensively ground with an appropriate amount of $FeCl_2 \cdot 4H_2O$ salt in a mortar. The resulting powder mixture was slowly heated under a gentle flow of a dry air to 550 °C at 0.5 °C/min and maintained at this temperature for 6 h. The solid was cooled and washed with de-ionized water until no chloride ions were detected in the eluted water. The zeolite was dried at 80 °C overnight. The Si/Al ratio of the zeolite was 11.4, and the Fe/Al atomic ratio was 0.25. The catalyst contained residual Brønsted acidity, leading to a sample notation Fe/H-MFI. The sample was an active hydrocarbon–SCR catalyst [19]. FTIR spectra were recorded in the transmission mode with a Nicolet Magna 550 FT-IR spectrometer. The gas flow rate in the FTIR cell was ca. 25 ml/min. Difference spectra were obtained by subtraction of the initial spectrum after pretreatment of the catalyst pastille from all spectra recorded in subsequent adsorption and reaction periods. In operando FTIR spectroscopy experiments, the gas composition at the outlet of the reactor cell was simultaneously analyzed by quadrupole mass spectrometry (Balzers TCP 121). Volumetric determination of the NO_x adsorption capacity of the catalyst was done in lab scale reactor setup with on-line NO_x analysis (chemiluminescence detector Ecophysics 700 EL ht) [20]. A temperature of 150 °C was imposed on the catalyst to try and prevent the reaction intermediates to be investigated from being converted to nitrogen.

3. Results and discussion

In the in situ FTIR experiments, the catalyst wafer was exposed to a gas stream containing NO_x, decane and again NO_x in presence of oxygen. The experiments were performed in the absence of water and in the presence of 2% water. The spectra obtained in the absence and in the presence of water are presented as parts (a) and (b), respectively, of the figures to facilitate comparison.

3.1. NO_x and decane adsorption on Fe/H-MFI zeolite in the absence of water

An iron MFI zeolite catalyst wafer was mounted in the FTIR cell, heated at 150 °C, and brought into contact first with a gas mixture of 1000 ppm NO_2 and 6% O_2 in argon. Difference FTIR spectra taken during saturation of the catalyst with NO_2 in the absence of water are displayed in Fig. 1a. In the 1300–2000 cm^{-1} spectral range, a complicated absorption spectrum developed. Absorptions at 1633 cm^{-1} with shoulders at 1657, 1619, and 1598 cm^{-1} are assigned to nitro groups, and those around 1575 cm^{-1} to nitrate groups [21]. An absorption band at 1882 cm^{-1} attributed to iron-nitrosyl species [21] quickly appeared and disappeared again. Very weak bands at 2133 cm^{-1} assigned to NO^+ and at 2175 and 1760 cm^{-1} assigned to N_2O_4 could also be discerned (outside the spectral range shown). The observation of N_2O_4 suggested the presence of N_2O_3 as well, but the spectral fingerprints of this molecule expected at 1555 and 1882 cm^{-1} were probably masked by those of the other species, such as iron-nitrosyl at 1882 cm^{-1} and nitrate at 1575 cm^{-1}. If any N_2O_3 formed at all, it must have disappeared upon saturation of the catalyst with NO_x, since the band at 1882 cm^{-1} disappeared at that point (Fig. 1a). In the last recorded spectrum, there was absorbance in the region of

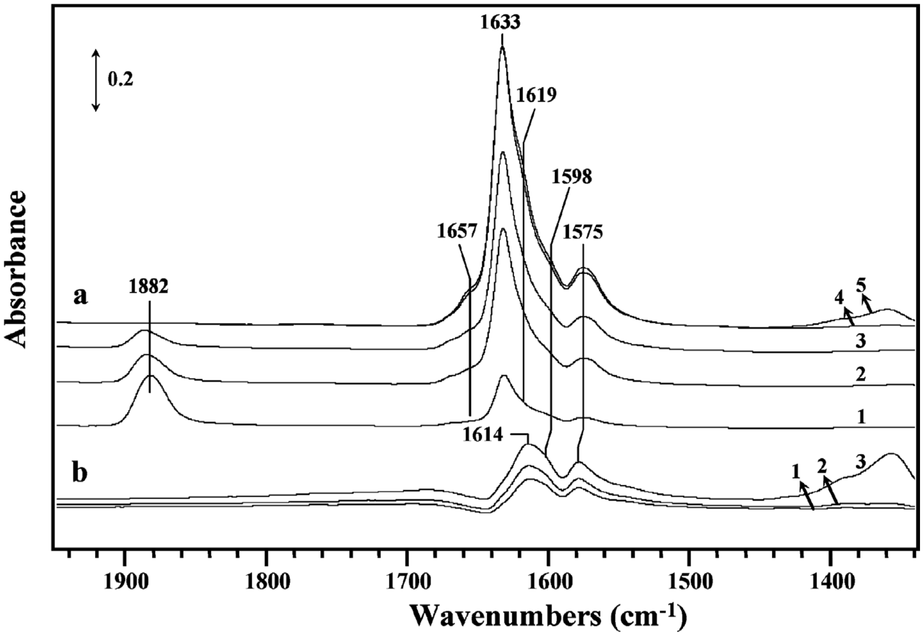

Fig. 1. Difference FTIR spectra of NO_2 adsorption on Fe/H-MFI zeolite in the absence (a) and in the presence of 2% water (b) of H_2O. Spectra in (a) were taken at the following times (min): (1) 2.1, (2) 3.0, (3) 3.4, (4) 10, (5) 31; and in (b) at: (1) 3.4, (2) 6.4, (3) 31. Gas composition, 1000 ppm NO_2 and 6% O_2 in argon.

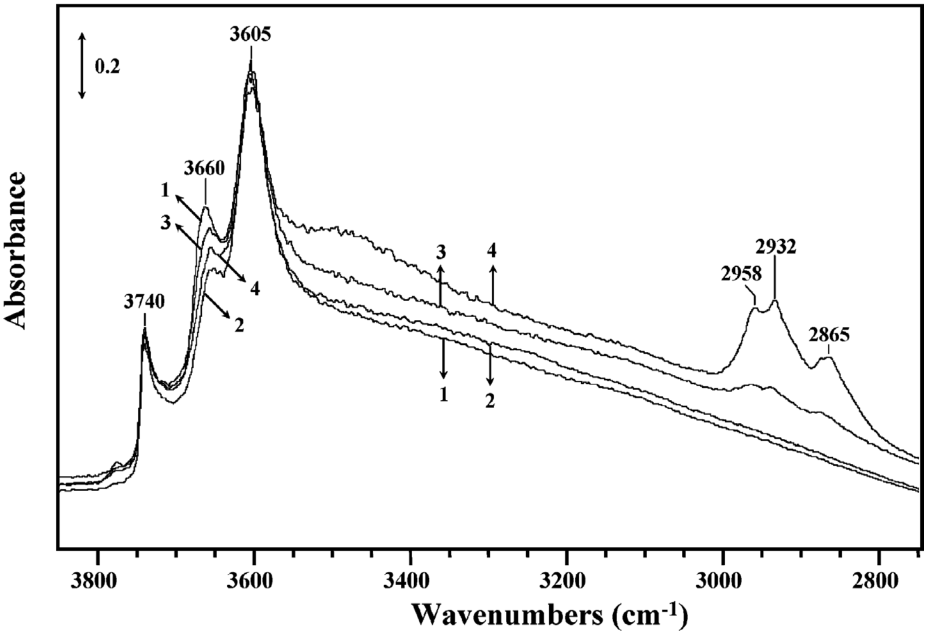

Fig. 2. FTIR spectra of Fe-H-MFI zeolite (1) after activation at 400 °C in dry helium, (2) after NO_2 adsorption in absence of water (gas mixture of 1000 ppm NO_2 and 6% O_2), (3) subsequent decane adsorption for 20 min, and (4) 45 min from a gas mixture of 150 ppm decane and 6% O_2 in argon.

1300–1400 cm^{-1}, which we ascribe to nitrate formation in the KBr windows of the cell. Based on the late appearance of these signals, we assume that the 1500–1650 cm^{-1} spectral region recorded earlier did not contain any spectral contributions of the cell windows. The evolution in the spectral range of the OH stretching region is displayed in Fig. 2. Exposure of pretreated Fe-MFI catalyst to 1000 ppm NO_2 and 6% O_2 caused a decrease in the intensity of the band at 3660 cm^{-1} (spectrum 2 compared with 1). As the band at 3660 cm^{-1} is assigned to hydroxyl groups on iron [10,14,22], the spectra reveal the coordination of NO_x with iron sites. The weak band at 3775 cm^{-1} associated with extraframework Al was also affected by the adsorption of NO_x. The adsorption of NO_x scarcely affected the 3740 and 3605 cm^{-1} vibrations assigned to terminal and bridging hydroxyl groups of the aluminosilicate zeolite.

After saturation of the catalyst with NO_x, a gas mixture consisting of argon with 150 ppm decane and 6% O_2

was passed through the cell. The introduction of decane was evident from C–H (3000–2800 cm^{-1}) stretching vibrations (Fig. 2, spectra 3 and 4). In the OH stretching region the band at 3660 cm^{-1} grew again upon decane feeding (Fig. 2, spectrum 3). The restoration of the Fe–OH spectral feature was probably due to reaction of decane with adsorbed nitro groups. In the later spectrum 4 the absorbance around 3660 cm^{-1} was weakened again. A broad feature at 3450–3550 cm^{-1} developed, pointing to weak perturbation of OH groups by hydrogen bridging with the hydrocarbon. Upon decane adsorption, an absorbance developed around 1878 cm^{-1} (Fig. 3a, spectrum 1). This signal was assigned to iron-nitrosyl complexes likely formed through the reduction of surface nitro/nitrate species by decane.

After 30 min of decane adsorption, the catalyst wafer was exposed 1000 ppm NO_2 in argon with 6% O_2 (Fig. 3a, spectra 2–6). The absorbance around 1878 cm^{-1} due to iron-nitrosyl complexes increased quickly, showing that NO_2 was at least partly reduced to NO through reaction with adsorbed hydrocarbon. A wealth of absorption bands spanning the spectral range of 1340–1850 cm^{-1} appeared. Bands at 1633, 1619, and 1575 cm^{-1} can be attributed to chemisorbed nitro and nitrate species. These bands can contain contributions from NO_x chemisorbed on iron and from organic intermediates with N=O groups. Bands at 1595, 1575, and 1540 cm^{-1} are tentatively ascribed to organic nitroso and nitro compounds. The asymmetric and symmetric stretching of C–NO_2 is expected at 1590–1530 and 1390–1350 cm^{-1}, respectively. Interpretation of the region 1300–1400 cm^{-1} is hampered by the strong absorption by ionic nitrates at 1385 cm^{-1} accumulating on the cell windows. The N=O stretching of nitroso compounds gives rise to absorptions in the region of 1620–1540 cm^{-1}. Asymmetrical and symmetrical stretching vibrations of carboxylate groups are found in the same spectral regions where –NO_2 absorbs. The wavenumbers of stretching vibration modes of N=O bonds in organic nitrites are around 1650–1620 cm^{-1} [23], very similar to those of the bending vibration of water at 1630–1640 cm^{-1}. NO_x molecules chemisorbed at Fe sites can also display absorption bands around these wavenumbers. Tanaka et al. demonstrated that organic nitrite formed on Pt/SiO_2 in the reaction of propene with NO and O_2 absorbs at 1655 cm^{-1} [9]. IR absorption bands assigned to N=O in various nitrite compounds, listed in Table 1, illustrate the position of these signals in IR spectra. Nitrite has two absorptions around 1640 cm^{-1}. The lower wavenumber absorption is the least intense one [24]. The C=O double bond absorbs at wavenumbers higher than those of the nitrites. Given the overwhelming evidence of the ease with which NO_2 reacts with alkenes found in the literature [26], C=C absorptions situated in the lower frequency part of the C=O spectral range are probably very faint. Carbonyls belonging to acetic anhydride vibrate around 1850 cm^{-1}, but absorption around this wavenumber might be due to nitrosyl species in complexes of Fe^{3+} cations as well. Bands around 1755 cm^{-1} can be attributed to carbonyl groups belonging to esters and lactones.

The formation of water through oxidation of decane with NO_2 was evaluated based on difference spectra in the OH stretching region (Fig. 4). The disappearance of the band at 3605 cm^{-1} assigned to the bridging Si–OH–Al hydroxyls and the appearance of a broad absorption band spanning the range of 3000–3500 cm^{-1} upon reaction of adsorbed decane with NO_2 indicates the formation of water (Fig. 4, spectrum 3). Consequently, also in the bending region, water provides a contribution to the bands at 1630–1640 cm^{-1}. The water was only slowly removed from the cell (Fig. 4, spectrum 3). This latter spectrum also revealed NO_x chemisorption at Fe sites through the erosion of the absorption around 3665 cm^{-1}. The absorption band around 1633 cm^{-1} comprises a contribution of water and chemisorbed NO_x. In Fig. 3a, the weak bands at 1655 cm^{-1} can be assigned to nitrite, the bands centered around 1682 cm^{-1} to carbonyl. Table 2 provides an overview of bands observed in this specific spectral region in operando FTIR experiments reported in the literature. Also noteworthy is the formation of nitrile species (2282 cm^{-1}) during the reaction of NO_2 with adsorbed decane (Fig. 4). The spectra of Fe-MFI type zeolite in the presence of NO_2 and decane obtained in this work are similar to those obtained with other hydrocarbons on similar iron zeolites in other reported studies.

3.2. NO_x and decane adsorption on Fe/H-MFI zeolite in the presence of water

A catalyst pellet was mounted in the cell, heated at 150 °C, and permeated with a gas mixture of 1000 ppm NO_2, 6% O_2, and 2% water in argon. The sequence of difference FTIR spectra is presented in Fig. 1b. Compared with the spectra obtained in the absence of water (Fig. 1a), the absorbances in the 1500–2000 cm^{-1} region assigned to nitro and nitrate species were much weaker. This observation suggests that water suppresses NO_2 chemisorption on the catalyst. Note that also in this instance the IR absorbance due to potassium nitrate in the cell windows at 1300–1400 cm^{-1} arose in the latest recorded spectrum only. The NO_2 adsorption capacity of Fe-MFI zeolite in the presence of water was verified volumetrically. At 150 °C, Fe-MFI zeolite equilibrated in a gas mixture of 1000 ppm NO_2, 6% O_2, and 12% water adsorbed ca. 8.7 μmol/g of NO_2, which is negligible compared with the iron content of 312.5 μmol/g.

After saturation of the catalyst in the FTIR cell with NO_2, the cell was flushed with hydrated argon with 6% oxygen. The FTIR signals of nitro/nitrate species in the 1500–1700 cm^{-1} region gradually faded (Fig. 5), showing that the chemisorbed NO_2 can be evacuated by reaction with water. While the absorbance in the 1500–1700 cm^{-1} range ascribed to NO_x chemisorbed on the catalyst decreased, the absorbance at 1300–1400 cm^{-1} ascribed to nitrate on the cell windows increased.

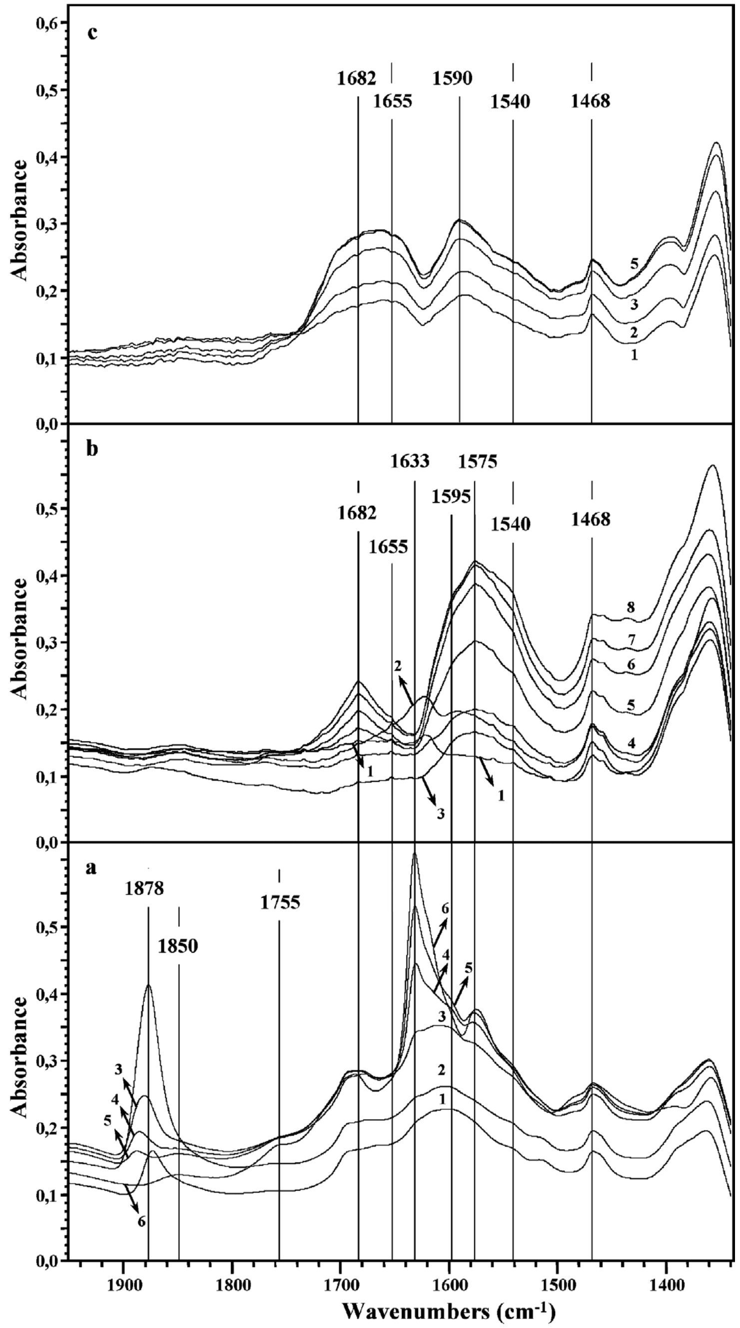

Fig. 3. Difference FTIR spectra of NO_2 reaction with pre-adsorbed decane on Fe/H-MFI in the presence (a) or absence (b) of H_2O and on H-MFI in the presence of H_2O (c). Spectra in (a) were taken at the following times (min): (1) 0.4, (2) 2.6, (3) 6.4, (4) 8.1, (5) 9.8, (6) 31, in (b) at: (1) 0.4, (2) 1.7, (3) 3.0, (4) 3.4, (5) 6.4, (6) 12, (7) 17, (8) 31, and in (c) at: (1) 0.8, (2) 5.6, (3) 16, (4) 26, (5) 31. Gas composition for decane pre-adsorption, 150 ppm decane, 6% O_2 and 0 or 2% water in argon. Gas composition for subsequent NO_2 reaction, 1000 ppm NO_2, 6% O_2 and 0 or 2% water in argon.

Subsequently, a stream of 150 ppm decane, 6% oxygen, and 2% water in argon was admitted to the cell. Given the very small amount of NO_x that is adsorbed on Fe/H-MFI zeolite from the hydrated gas stream, only very weak and ill-defined bands can be discerned in the spectral region of 1500–1700 cm^{-1} (spectrum 1 in Fig. 3b compared with Fig. 3a).

After 30 min of decane adsorption, the catalyst wafer was exposed to 1000 ppm NO_2 in argon with 6% O_2 and 2% water (Fig. 3b, spectra 2–8). In contrast to the experiment with dry gas (Fig. 3a), absorptions around 1878 cm^{-1} assigned to iron nitrosyl groups are not observed when water is present, confirming the poor NO_x chemisorption in the presence of water. Bands at 1595, 1575, and 1540 cm^{-1} that were tentatively ascribed to organic nitroso and nitro compounds appear to be slightly more intense than in the absence of water. In the presence of water bands at around 1755 and 1850 cm^{-1}, which were attributed to esters or lactones

Table 1
Positions of absorption bands of nitrites [23,24]

Compound	Absorptions (cm^{-1})		Compound	Absorptions (cm^{-1})	
Propyl nitrite	1665	1615	Pentyl nitrite	1640	1600
Isobutyl nitrite	1670	1610	*sec*-Butyl nitrite	1660	1610
Isopentyl nitrite	1640	1600	*tert*-Butyl nitrite	1625	
Octyl nitrite	1645	1600	Decyl nitrite [25]	1655	1615

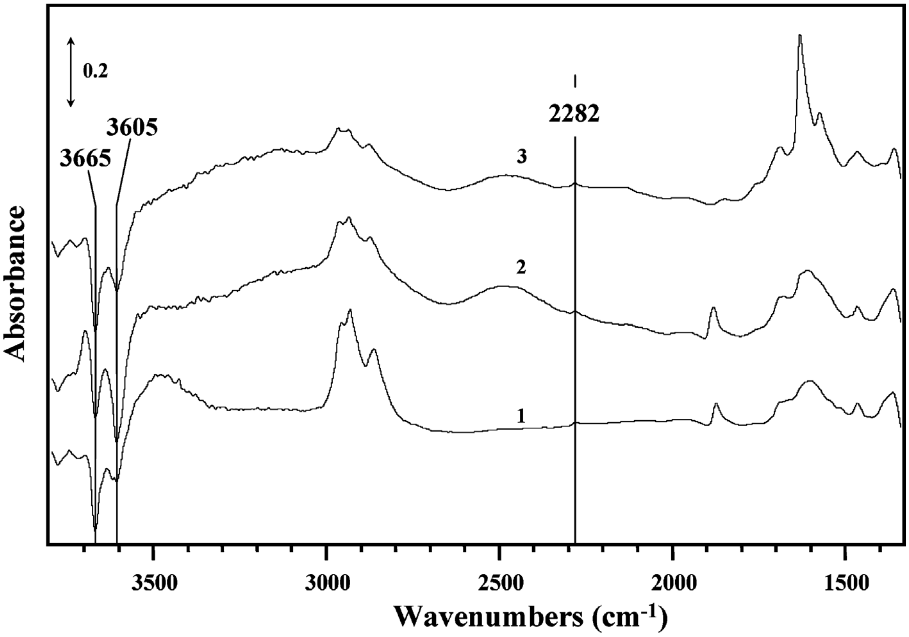

Fig. 4. Difference FTIR spectra on Fe-H-MFI zeolite at consecutive stages of the experiment in absence of water: (1) after 30 min of decane adsorption, (2) after subsequent exposure to NO_2 for 6 min, and (3) for 31 min. Gas compositions are those of Fig. 3.

Table 2
IR absorbances in the spectral region 1600–1700 cm^{-1} reported in literature

Absorption band (cm^{-1})	Assignation	Catalyst	Reagents	Ref.
1662	Nitritopropane	CuO/Al_2O_3	C_3H_6, NO, O_2	[27]
1655	Nitritopropane	Pt/SiO_2	C_3H_6, NO, O_2	[9]
1670	Organic nitrite	Ni/Na-MOR	C_3H_6, NO, O_2	[28]
1640	δ(HOH) in water	Cu-ZSM-5	C_3H_6, NO, O_2	[8]
1635	C=O in aldehyde	Ag/Al_2O_3	C_2H_5OH, NO, O_2	[29]
1680	*tert*-Butyl nitrite	Fe/ZSM-5	*iso*-C_4H_{10}, NO, O_2	[30]
1683	Butyl nitrite	Fe/ZSM-5	*n*-C_4H_{10}, NO, O_2	[30]
1650	Nitrite or C=O	Co/Al_2O_3, Ag/Al_2O_3	C_3H_6, NO, O_2	[31]
1611 and 1689	*tert*-Butyl nitrite	Co/Al_2O_3, Ag/Al_2O_3	*tert*-Butyl nitrite	[15]
1641	δ(HOH) in water	H-MOR	C_3H_6, NO_2	[1]
1682	Organic nitrite	Na/H-MOR	C_3H_6, NO, O_2	[32]
1630	NO_2, NO_3^-	Na/H-MOR	C_3H_6, NO, O_2	[32]
1625	NO_2, NO_3^-	Fe/ZSM-5	C_4H_{10}, NO, O_2	[14]

and acid anhydrides, respectively, were not observed either (Fig. 3b). Esters, lactones, and acid anhydrides, if formed, are hydrolyzed in the presence of water (compare bands at about 1755 and 1850 cm^{-1} in Figs. 3a and b). Organic nitrites are expected to hydrolyze in the presence of water to partially oxidized hydrocarbons and nitrous acid [33]. The difficulty in discriminating between nitrite and carbonyl bands already discussed obstructs further interpretation of the spectra.

The quantity of NO_2 that is converted into organic nitrogen compounds was determined volumetrically with a fixed-bed reactor unit as follows [2]. A sample of 1.2 g of iron zeolite was loaded first with 2.285 mg of decane from a gas mixture of 150 ppm decane in helium with 6% O_2 and 12% water. Because of the iron loading, the effective pore size of the MFI zeolite is decreased such that decane does not penetrate the micropores [34]. The quantity of decane fed when spread as a monolayer is sufficient to cover the external

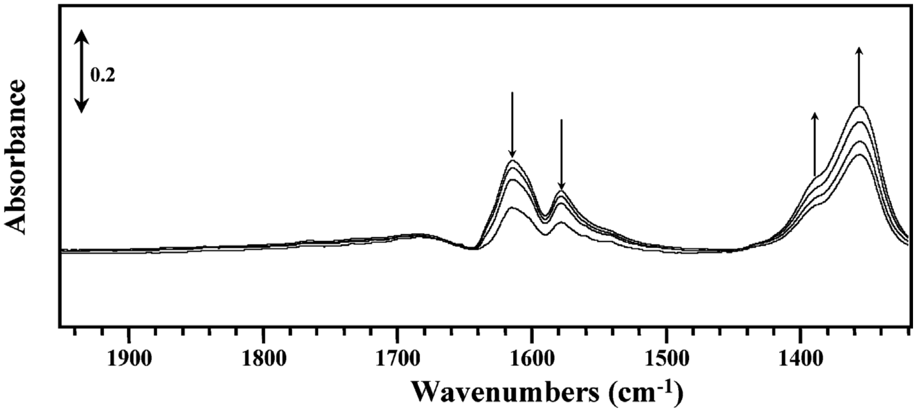

Fig. 5. Sequence of difference FTIR spectra on Fe/H-MFI zeolite after saturation with NO_2 from a gas mixture of 1000 ppm NO_2, 6% O_2 and 2% water in argon and evacuation with a gas mixture composed of 6% oxygen, 2% water and argon.

specific surface area of this zeolite, that is, 12.7 m^2 g^{-1}. Subsequently, a gas mixture with 1000 ppm NO_2, 6% O_2, and 12% H_2O was sent over the catalyst bed until NO_x uptake ceased. The quantity of NO_2 that was trapped corresponded to ca. 3.3 molecules of NO_2 reacted per molecule of decane. When the NO_x in the gas mixture was fed as NO instead of NO_2, at 150 °C there was no NO_x uptake, showing that NO_2 is the reactive NO_x species.

3.3. NO_x and decane adsorption on acid MFI zeolite devoid of iron in the presence of water

NO_2 adsorption experiments were performed with the parent acid MFI zeolite devoid of iron. Acid MFI did not adsorb any NO_2 in the presence of water, as indicated by the absence of IR absorption bands in the region of 1500–1700 cm^{-1} upon exposure to 1000 ppm NO_2 in argon with 6% O_2 and 2% H_2O (spectrum not shown). In a subsequent experiment, decane was pre-adsorbed, and NO_2 reacted with it under the gas compositions already mentioned in the experiments with the Fe-containing catalyst. IR spectra similar to the ones observed in the experiment with Fe/H-MFI zeolite developed (Fig. 3c compared to b). Bands at 1595, 1575, and 1540 cm^{-1} that were tentatively ascribed to organic nitroso and nitro compounds are observed, as are bands at 1682 and 1655 cm^{-1} assigned to carbonyl and nitrite compounds, respectively. Nevertheless, the intensities of the various bands are different for experiments with acid MFI and Fe/H-MFI. For instance, the bands around 1682 and 1655 cm^{-1} are more intense on acid MFI (Fig. 3c compared with b), suggesting that the species giving rise to these bands are converted more easily on Fe/H-MFI. This experiment with the acid form of the zeolite teaches that the formation of organic nitro or nitroso compounds does not require NO_x to be chemisorbed at iron sites before reaction with the hydrocarbon. There is another experiment in the literature revealing the reaction of NO_2 with the hydrocarbon on an acid zeolite. Nanba et al. monitored with IR spectroscopy the product gas from C_2H_4–SCR on H-FER, in which NO_x was fed as NO_2, and detected nitro-ethylene formation [35].

Based on this FTIR study, the following reaction mechanism could be at work in hydrocarbon–SCR on iron zeolites. Especially with long paraffin such as decane displaying high adsorption enthalpies, SCR in wet gases begins with hydrocarbon physisorption followed by activation through hydrogen abstraction by NO_2 to form nitrous acid. The organic radical reacts with NO_2 into nitro and nitrite organic compounds; the latter is hydrolyzed in the presence of water. Nitrous acid from the hydrolysis of nitrites and from hydrogen abstraction by NO_2 is decomposed to water, NO_2, and NO. Alternatively, the organic radical may be oxidized by NO_2 to an alkoxy radical, which subsequently may undergo β-scission to give an aldehyde and another radical. This reaction and the recombination of the organic radical with molecular oxygen to a peroxy radical both initiate partial oxidation of the adsorbed hydrocarbon. Hydrolysis of nitrous acid and direct oxygen transfer from NO_2 to the radical explain the reduction of a significant part of the NO_2 concentration to NO upon reaction with hydrocarbons.

Iron is not required for the initial steps of the reaction between NO_x and decane in the presence of water at 150 °C. This is in agreement with the observation that acid zeolites devoid of iron are effective catalysts for NO_x reduction, provided NO_x is fed as NO_2 [2]. A possible corollary of this is that in the presence of water the catalytic role of iron is restricted to the oxidation of NO into NO_2. However, it cannot be excluded that iron may intervene in the conversion of some partial oxidation products farther down the reaction scheme toward N_2 formation.

4. Conclusion

From the insignificant NO_2 adsorption on iron zeolite in the presence of water and the similarity of the FTIR spectra of iron and acid zeolite upon reaction of NO_2 with pre-adsorbed decane, we conclude that it is unlikely that the initial reaction between NO_2 and the hydrocarbon molecule would be preceded by chemisorption of NO_x on iron sites, contrary to what has been observed in the absence of water.

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References

[1] T. Gerlach, F.-W. Schütze, M. Baerns, J. Catal. 185 (1999) 131.
[2] R. Brosius, J.A. Martens, Top. Catal. 28 (2004) 119.
[3] V.A. Sadykov, V.V. Lunin, V.A. Matyshak, E.A. Paukshtis, A.Ya. Rozovskii, N.N. Bulgakov, J.R.H. Ross, Kinet. Catal. 44 (2003) 379.
[4] X. Wang, H.-Y. Chen, W.M.H. Sachtler, J. Catal. 197 (2001) 281.
[5] Y. Li, J.N. Armor, J. Catal. 150 (1994) 376.
[6] T. Beutel, B.J. Adelman, G.-D. Lei, W.M.H. Sachtler, Catal. Lett. 32 (1995) 83.
[7] D.B. Lukyanov, G. Sill, J.L. d'Itri, W.K. Hall, J. Catal. 153 (1995) 265.
[8] N.W. Hayes, R.W. Joyner, E.S. Shpiro, Appl. Catal. B 8 (1996) 343.
[9] T. Tanaka, T. Okuhara, M. Misono, Appl. Catal. B 4 (1994) L1.
[10] H.-Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, J. Catal. 186 (1999) 91.
[11] J. Connerton, R.W. Joyner, M. Stockenhuber, Chem. Commun. (1997) 185.
[12] M. Guyon, V.Le. Chanu, P. Gilot, H.P. Kessler, G. Prado, Appl. Catal. B 8 (1996) 183.
[13] N.W. Hayes, W. Grünert, G.J. Hutchings, R.W. Joyner, E.S. Shpiro, Chem. Commun. (1994) 531.
[14] H.-Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, J. Catal. 180 (1998) 171.
[15] V. Zuzaniuk, F.C. Meunier, J.R.H. Ross, J. Catal. 202 (2001) 340.
[16] K. Hadjiivanov, H. Knözinger, B. Tsyntsarski, L. Dimitrov, Catal. Lett. 62 (1999) 35.
[17] T. Lesage, C. Verrier, P. Bazin, J. Saussey, M. Daturi, Phys. Chem. Chem. Phys. 5 (2003) 4435.
[18] M. Kögel, V.H. Sandoval, W. Schwieger, A. Tissler, T. Turek, Catal. Lett. 51 (1998) 23.
[19] M. Kögel, R. Mönnig, W. Schwieger, A. Tissler, T. Turek, J. Catal. 182 (1999) 470.
[20] A. Sultana, R. Loenders, O. Monticelli, C. Kirschhock, P.A. Jacobs, J.A. Martens, Angew. Chem. Int. Ed. 39 (2000) 2934.
[21] H.-Y. Chen, El-M. El-Malki, X. Wang, R.A. van Santen, W.M.H. Sachtler, J. Mol. Catal. A 162 (2000) 159.
[22] T. Voskoboinikov, H.-Y. Chen, W.M.H. Sachtler, Appl. Catal. B 19 (1998) 279.
[23] W.W. Simons (Ed.), The Sadtler Handbook of Infrared Spectra, Sadtler Research Laboratories, Philadelphia, 1978.
[24] C.J. Pouchert (Ed.), The Aldrich Library of Infrared Spectra, second ed., Aldrich Chemical Company Inc., Milwaukee, WI, 1975.
[25] B.S. Svetlov, B.A. Lur'e, S.I. Myasnikova, N.S. Khersonskii, Kinet. Catal. 15 (1974) 1252.
[26] A.V. Stepanov, V.V. Veselovsky, Russ. Chem. Rev. 72 (2003) 327.
[27] Y. Chi, S.S.C. Chuang, J. Catal. 190 (2000) 75.
[28] B.I. Mosqueda-Jiménez, A. Jentys, K. Seshan, J.A. Lercher, Appl. Catal. B 46 (2003) 189.
[29] T. Chafik, S. Kameoka, Y. Ukisu, T. Miyadera, J. Mol. Catal. A 136 (1998) 203.
[30] H.-Y. Chen, T. Voskoboinikov, W.M.H. Sachtler, Catal. Today 54 (1999) 483.
[31] F.C. Meunier, V. Zuzaniuk, J.P. Breen, M. Olsson, J.R.H. Ross, Catal. Today 59 (2000) 287.
[32] A. Satsuma, T. Enjoji, K. Shimizu, K. Sato, H. Yoshida, T. Hattori, J. Chem. Soc., Faraday Trans. 94 (1998) 301.
[33] J.A. Martens, A. Cauvel, A. Francis, C. Hermans, F. Jayat, M. Remy, M. Keung, J. Lievens, P.A. Jacobs, Angew. Chem. Int. Ed. Eng. 37 (1998) 1901.
[34] S. Boulard, P. Gilot, D. Habermacher, R. Brosius, J.A. Martens, Top. Catal. 30 (2004) 49.
[35] T. Nanba, A. Obuchi, H. Izumi, Y. Sugiura, J. Xu, J. Uchisawa, S. Kushiyama, Chem. Commun. (2001) 173.