

NO adsorption on ex-framework [Fe,X]MFI catalysts: novel IR bands and evaluation of assignments

G. Mul*, J. Pérez-Ramírez, F. Kapteijn, and J.A. Moulijn

Industrial Catalysis, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands

Received 6 December 2001; accepted 7 February 2002

IR spectra of NO adsorbed on isomorphously substituted [Fe,Al]MFI, [Fe,Ga]MFI and [Fe]MFI after steaming at 873 K in 30 vol% H_2O are presented. On *ex*-[Fe,Al]MFI, NO adsorption leads to bands at 2133 cm^{-1} and a doublet at 1886 and 1874 cm^{-1} . The 2133 cm^{-1} band is assigned to NO^+ occupying cationic positions in the zeolite structure. Of the doublet, the 1874 cm^{-1} band is much more susceptible to reaction with O_2 than the 1886 cm^{-1} band, yielding adsorbed NO_2 with an absorption frequency of 1635 cm^{-1} . After evaluation of the constitution of the catalyst and (sometimes contradictory) literature assignments, the 1886 cm^{-1} band is assigned to NO adsorbed on Fe ions located in isolated positions, and/or $(FeO)_n$ clusters inside the zeolite channels, whereas the 1874 cm^{-1} band is proposed to be induced by 2 nm $FeAlO_x$ nano-particles. The *ex*-[Fe,Ga]MFI catalyst showed a similar absorption pattern (doublet), which is shifted to lower wavenumbers (1881 and 1867 cm^{-1}), suggesting that both frequencies are affected by the vicinity of Ga (or Al) to the Fe site involved. The absence of bands at 1765 and 1835 cm^{-1} suggests that the isolated sites causing these absorptions are in the Fe^{III} state in *ex*-[Fe,Al]MFI and *ex*-[Fe,Ga]MFI. For the *ex*-[Fe]MFI sample, which did not contain any 2 nm FeO_x nano-particles, an NO absorption band at 1854 cm^{-1} is assigned to mono-nitrosyl on extra-framework oligonuclear $(Fe^{II}O)_n$ species in the zeolite channels.

KEY WORDS: NO adsorption; infrared; assignment; FeMFI; Fe-ZSM-5; Fe-silicalite; isomorphous substitution; *ex*-framework method.

1. Introduction

Fe-based zeolite catalysts are currently extensively studied, because of high activity in (i) $deNO_x$ -SCR [1–5], (ii) N_2O -mediated selective oxidation of benzene to phenol [6,7] and (iii) catalytic N_2O decomposition [8–11]. Recently we reported a high performance in the latter reaction of a specific FeZSM-5 catalyst prepared *via* an *ex*-framework method [10]. One of the most interesting features of this catalyst for practical application in tail-gas of *e.g.* nitric acid plants is the positive effect of NO on the N_2O decomposition rate. This positive effect by NO has also been observed for other catalysts prepared using the same *ex*-framework method, but replacing Al by Ga (Fe-gallosilicate) or excluding Al in the synthesis gel (Fe-silicalite). These samples are generally denoted as *ex*-[Fe,Al]MFI, *ex*-[Fe,Ga]MFI and *ex*-[Fe]MFI [12]. We have addressed the mechanism of the NO-assisted N_2O decomposition over *ex*-[Fe,Al]MFI by applying pulse-response techniques (Multitrack) and transient *in situ* FT-IR spectroscopy [13]. NO adsorbs very strongly on the catalyst surface, inducing the formation of NO_2 and enhancing the desorption rate of oxygen upon reaction with N_2O . In the course of that investigation, multiple NO bands were observed in *in situ* FT-IR spectra around 1880 cm^{-1} , which were not previously assigned in the literature.

In this paper we will further address the interpretation of NO adsorbed on *ex*-[Fe,Al]MFI, *ex*-[Fe,Ga]MFI and *ex*-[Fe]MFI catalysts, using an overview of the available literature and information on the structure of isomorphously substituted iron MFI catalysts. An extensive investigation on the nature of the active sites using XRD, TGA-DSC-MS, gas (Ar, N_2) physisorption, NH_3 -TPD, ^{27}Al and ^{29}Si MAS-NMR, DR/UV-vis, TEM, H_2 -TPR, EPR, ^{57}Fe Mössbauer, and electrochemical response techniques is reported elsewhere [14].

2. Experimental

2.1. Material preparation

The isomorphously substituted iron MFI zeolites were synthesized hydrothermally using tetra-propylammonium hydroxide as the template [6]. For the preparation of [Fe,Al]MFI, a solution of the silica source (tetraethyl-orthosilicate, TEOS, Acros, 98%), the template (tetrapropylammonium hydroxide, TPAOH, Fluka, 20% in water), and NaOH was added to a mixture of aluminum(III) nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Merck, 99%) and iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck, 98.5%). The molar ratios between components were $H_2O/Si = 45$, TPAOH/Si = 0.1, NaOH/Si = 0.2, Si/Al = 36 and Si/Fe = 152. For the preparation of [Fe,Ga]MFI and [Fe]MFI, the Al precursor was replaced by gallium(III) nitrate ($Ga(NO_3)_3 \cdot 9H_2O$, Merck, 99%) or excluded in the synthesis gel, respectively.

* To whom correspondence should be addressed.
E-mail: g.mul@tnw.tudelft.nl

The solutions were transferred to a stainless steel autoclave lined with Teflon and kept in a static-air oven at 448 K for 5 days. The crystalline materials were filtered and washed with deionized water. The as-synthesized samples, in which Fe(III) is isomorphously substituted in the zeolite framework, were calcined in air at 823 K for 10 h and then converted into the H form by three consecutive overnight exchanges with an ammonium nitrate solution (0.1 M). This was followed by calcination at 823 K for 5 h. Finally, the catalysts were treated in flowing steam at ambient pressure (water partial pressure of 300 mbar and 30 ml min⁻¹ of N₂ flow) at 873 K during 5 h, yielding *ex*-[Fe,Al]MFI, *ex*-[Fe,Ga]MFI and *ex*-[Fe]MFI.

2.2. IR characterization

The FT-IR measurements were performed using an *in situ* IR cell with CaF₂ windows. This cell was designed and built at the University of Amsterdam. Gas could be fed to the cell (volume 3.8 ml) using a 4-way valve (Valco), which was configured to select two separate gas feeds. Using a volumetric flow of 30 ml min⁻¹, the cell was completely refreshed in about 10 s after switching the valve. For the IR measurements, the catalyst was prepared in the form of self-supporting wafers (~70 mg cm⁻²) at pressures of 3–4 tons cm⁻². Spectra were recorded using a Nicolet Magna IR 860 spectrometer equipped with a nitrogen cooled MCT detector and a rapid scan interferometer. The catalysts were pretreated in He at 573 K for 30 min before conducting further experiments. Unless stated otherwise, spectra were recorded against a background of the sample at the reaction temperature in He at 4 cm⁻¹ resolution, using co-addition of 48 scans. Transient experiments were performed using a rapid scan collection mode. Again 48 scans were co-added for each spectrum using scan length minimization, leading to a complete spectrum collection time of 7.7 s.

The purity of the gases applied (5 vol% NO in He, O₂, and He) was >99.998%. The gas feed was dried before use over a molecular sieve column. NO adsorption spectra were recorded at temperatures ranging from 373 to 573 K in a flow of 30 ml min⁻¹ 5 vol% NO in He. Using rapid scan analyses, transients in absorption intensities upon switching the gas composition from 5 vol% NO in He to 5 vol% O₂ in He at 473 K were analyzed.

3. Results

3.1. Characterization

The chemical composition of the steamed catalysts determined by ICP-OES is shown in table 1. The Fe loadings of all the microporous materials are very similar

Table 1
Chemical composition of the crystalline samples used in this study

Catalyst	Si/Al or Si/Ga ^a	Si/Fe ^a	Fe ^a (wt%)
<i>ex</i> -[Fe,Al]MFI-LC	31.3	121.7	0.67
<i>ex</i> -[Fe,Ga]MFI-LC	32.6	144.2	0.58
<i>ex</i> -[Fe]MFI-LC	—	129.8	0.68

(~0.6 wt%). Also the amount of Ga was adjusted to correspond to the Si/Al ratio (~31) of the [Fe,Al]MFI. The applied synthesis procedure leads to similar catalysts and is an excellent procedure to compare MFI catalysts with different framework composition. The nature of the Fe species is different in the three catalyst compositions. In *ex*-[Fe,Al]MFI and *ex*-[Fe,Ga]MFI the presence of FeMO_x nano-particles (M = Al, Ga) of 1–2 nm can be inferred from TEM micrographs (figure 1). These nanoparticles are absent in the *ex*-[Fe]MFI sample, even after steaming.

3.2. IR spectra of *ex*-[Fe,Al]MFI

NO adsorption at 423 K on *ex*-[Fe,Al]MFI yields absorption bands at wavenumbers 2133, 1886 and 1874 cm⁻¹ (figure 2). This figure also shows the dynamics of the NO adsorption bands upon reaction with O₂. The gas-phase composition was changed from 5 vol% NO in He to 5 vol% O₂ in He at 473 K. It can be clearly observed that the NO species absorbing at 1874 cm⁻¹ shows a higher reactivity toward oxygen than the species at 1886 cm⁻¹, while also the 2133 cm⁻¹ band rapidly

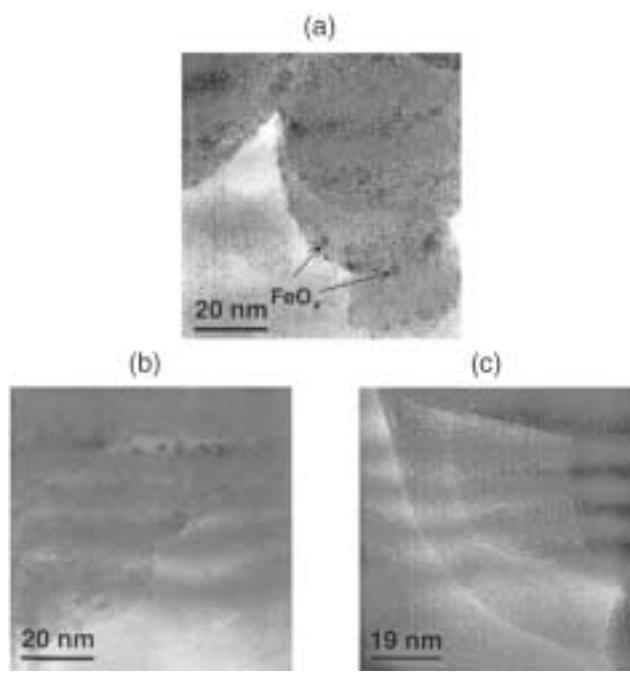


Figure 1. TEM micrographs of (a) *ex*-[Fe,Al]MFI, (b) *ex*-[Fe,Ga]MFI and (c) *ex*-[Fe]MFI.

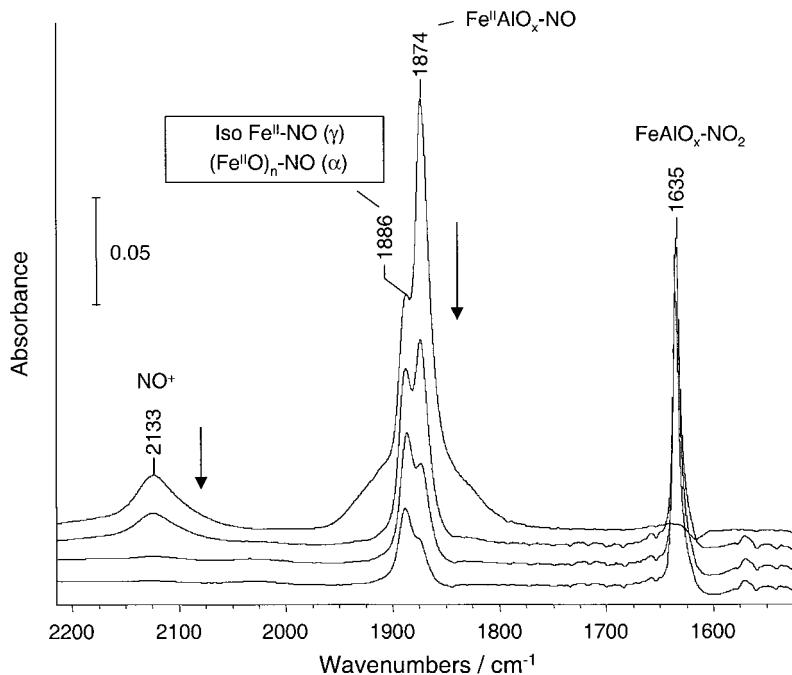


Figure 2. Rapid scan spectra of *ex*-[Fe,Al]MFI in 5 vol% O₂ in Ar after NO adsorption at 423 K. The 1634 cm⁻¹ band goes through a maximum: bottom to top: in NO, and in O₂, after switching from NO at 31, 63, and 94 s.

disappears. Furthermore, a new absorption frequency arises at 1635 cm⁻¹. Changing the gas phase back to NO rapidly restores the original spectrum (not shown). Similar intensity changes can be observed by exposing the catalyst with adsorbed NO to N₂O, as previously reported [13]. Figure 3 shows the effect of exposing adsorbed ¹⁵NO on *ex*-[Fe,Al]MFI to 5 vol% O₂ in He, compared with a similar experiment in ¹⁴NO. Clearly a shift in wavenumbers of approximately 35 cm⁻¹ of the

various absorption bands can be observed, and a new band develops at 1598 cm⁻¹ for ¹⁵NO, rather than at 1635 cm⁻¹ for ¹⁴NO.

3.3. IR spectra of *ex*-[Fe,Ga]MFI

To further assess the effect of the composition of *ex*-[Fe,Al]MFI on the NO adsorption frequencies, Al³⁺ was replaced by Ga³⁺ in the preparation of the zeolite

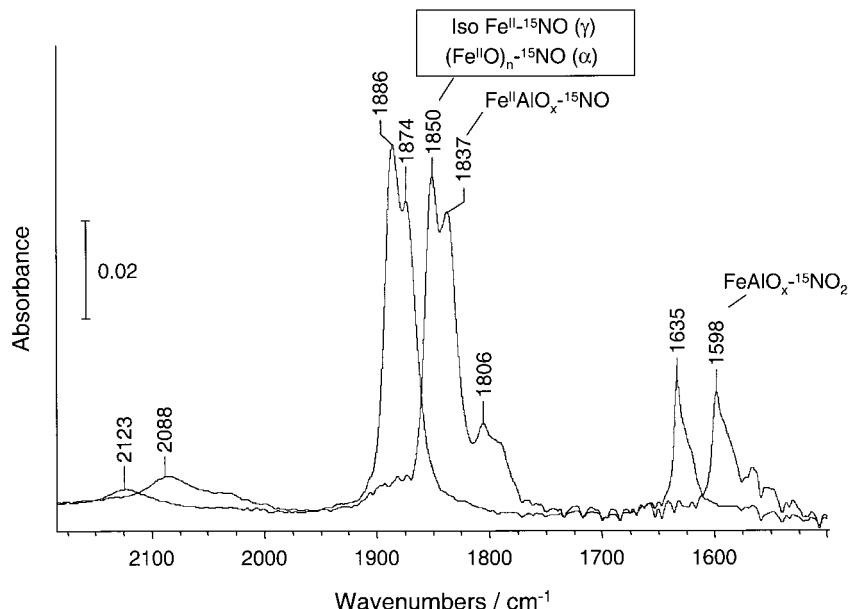


Figure 3. Spectra of adsorbed NO on *ex*-[Fe,Al]MFI at 423 K, 1 min after switching from 5 vol% NO in He to 5 vol% O₂ in He. The same procedure was repeated for 10 vol% ¹⁵NO in He.

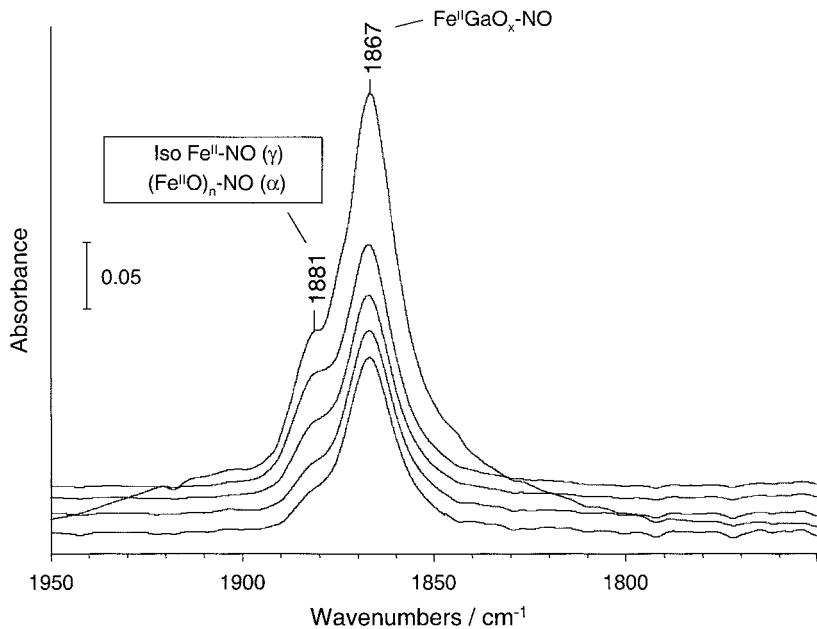


Figure 4. Spectra of adsorbed NO on *ex*-[Fe,Ga]MFI, recorded at 423 K. Top to bottom: in NO/He, in He after 1, 2, 4 and 6 minutes.

by hydrothermal synthesis, yielding *ex*-[Fe,Ga]MFI. The spectra of NO adsorbed on *ex*-[Fe,Ga]MFI show a similar doublet as observed in “regular” *ex*-[Fe,Al]MFI (figure 4), but the doublet has shifted to lower wavenumbers. The absorptions are located at 1867 and 1881 cm^{-1} . The 2133 cm^{-1} band of the *ex*-[Fe,Ga]MFI sample was observed with very low intensity at

2112 cm^{-1} (not shown). For this material also the desorption of NO in He is presented in figure 4. The two bands show approximately equal stability, since the intensity ratio hardly changes. This was confirmed by deconvolution of the doublet (not shown). The effect of temperature on the absorption frequencies is shown in figure 5. An increasing temperature induces

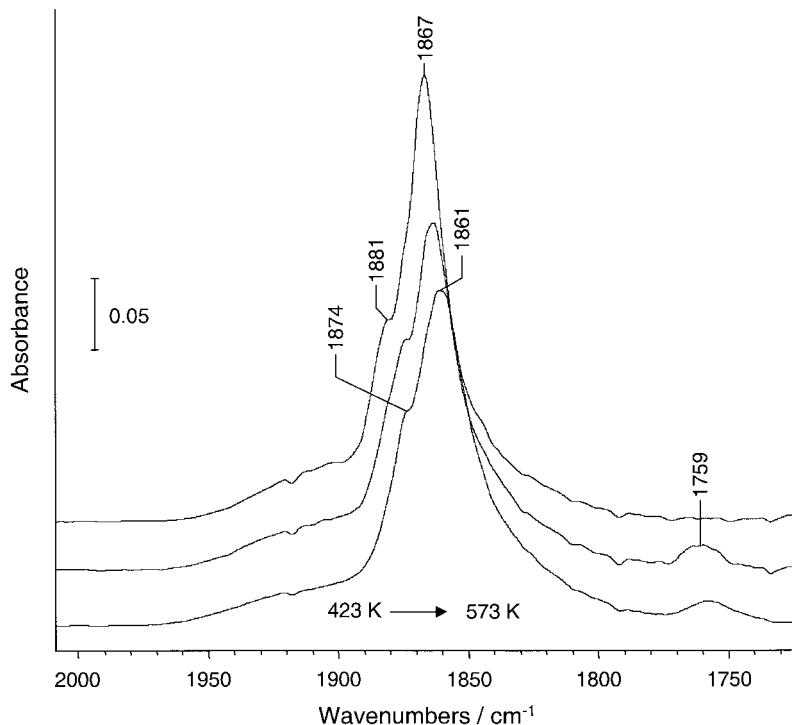


Figure 5. Spectra of adsorbed NO on *ex*-[Fe,Ga]MFI, recorded at 423, 523 and 573 K, respectively.

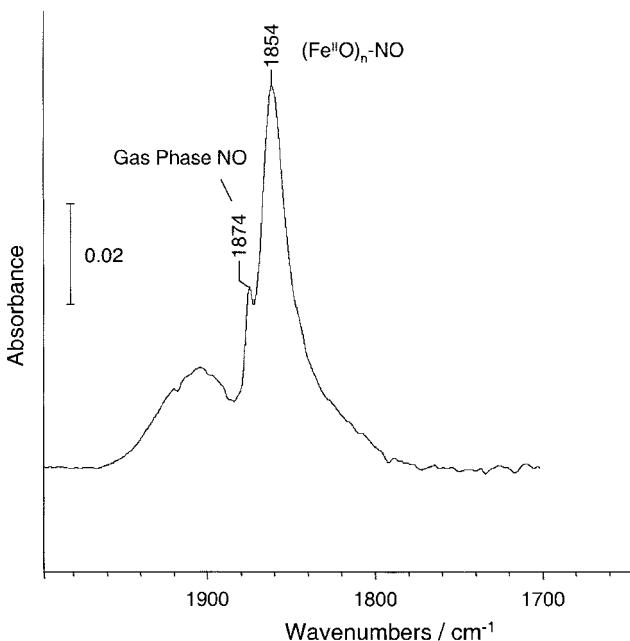


Figure 6. Spectra of adsorbed NO on *ex*-[Fe]MFI in 5 vol% NO/He, recorded at 423 K.

a shift of the NO absorption frequencies to lower wavenumbers.

3.4. IR spectra of *ex*-[Fe]MFI

The spectra of NO adsorbed on *ex*-[Fe]MFI are shown in figure 6. When recorded at 423 K, the absorption frequencies are located at 1854 cm^{-1} , with a small shoulder at 1874 cm^{-1} . Changing the feed from 5% NO in He to He results in a rapid desorption of NO and disappearance of the bands involved. A comparison of the spectra of the different samples is presented in figure 7.

4. Discussion

4.1. Introduction

The Fe species in the steamed samples analyzed in this paper are of different constitution. An extensive description of the analytical results of the catalysts is presented elsewhere [14]. The major differences between the catalysts, as can also be inferred from the TEM figures shown in figure 1, can be summarized as follows. It should be mentioned that, in this discussion, we will call Fe_4O_4 [16] and $(\text{FeO})_n$ ($n < 5$) [17] “oligonuclear clusters”, and FeMO_x ($\text{M} = \text{Al, Ga}$) [18,19] “nano-particles”.

1. The *ex*-[Fe,Al]MFI and *ex*-[Fe,Ga]MFI samples contain an extensive amount of nano-particles, mainly in the oxidation state Fe^{3+} . A minor fraction is already reduced to Fe^{2+} in the steaming procedure. In view of (i) the low loading of Fe in the materials, (ii) the large amount of particles observed in the TEM micrograph shown in figure 1 and (iii) the large extent of dealumination of the framework, it can be inferred that a significant amount of Al (or Ga) should be incorporated in the FeO_x nano-particles. Therefore, the nano-particles are denoted as FeMO_x (with M being Al or Ga) in the discussion. At the same time a significant amount of Fe is still present in isolated sites and oligonuclear clusters, of which the oxidation state can be either Fe^{2+} or Fe^{3+} , depending on the temperature and gas phase environment [14].
2. *Ex*-[Fe]MFI does not contain any FeO_x nano-particles. Both isolated species and clusters in the channels of the MFI structure are mainly present in this catalyst in the oxidation state of Fe^{2+} .

Various (recent) papers describe spectra and assignments of NO adsorbed on Fe-zeolites extensively. For

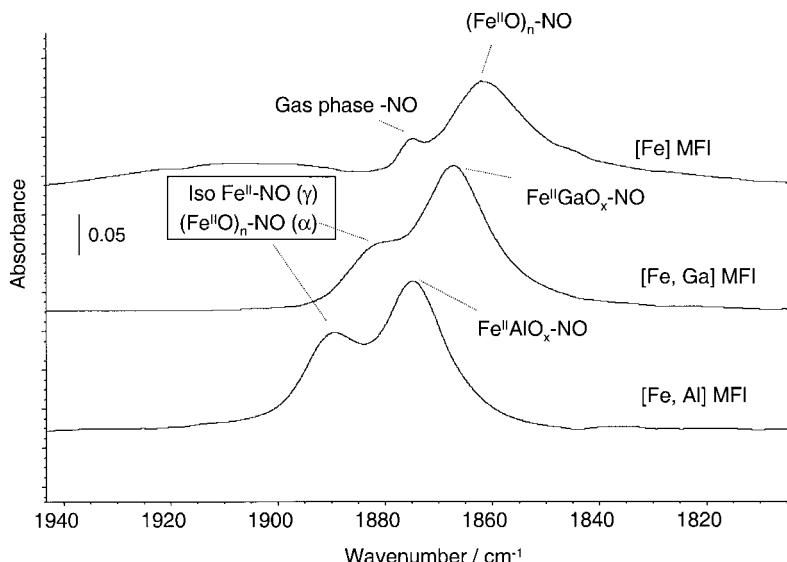


Figure 7. Spectra of adsorbed NO on *ex*-[Fe,Al]MFI, *ex*-[Fe,Ga]MFI, and *ex*-[Fe]MFI recorded at 423 K.

liquid ion-exchanged ZSM-5 samples, the assignments given by Hadjiivanov *et al.* [1,20], Lezcano *et al.* [19], Segawa *et al.* [21] and Joyner *et al.* [16] are representative, while Lobree *et al.* [18] discuss assignments for samples prepared by solid state ion exchange *via* sublimation. Spoto *et al.* [17] extensively describe NO absorption frequencies for ex-framework Fe-silicalite (calcined in air at 973 K). These papers will be used for the discussion. Other papers discussing the mechanism of lean deNO_x catalysis, *e.g.* [3,5], suggest that there is consensus on the assignments of the bands of adsorbed NO on Fe-ZSM-5 catalysts. It will be shown that in fact there is in several cases disagreement among references [16–21]. Different assignments have been proposed in relation to the absence or presence of multiple NO molecules on the same site and the location of the Fe sites causing specific NO absorptions. In the following, the assignments for each individual absorption will be discussed separately. Table 2 gives an overview. Figure 8 is an adaption of the figure presented by Lobree *et al.* in [18], and illustrates the different Fe species in MFI materials and corresponding wavenumbers of adsorbed NO.

4.2. The band around 2133 cm⁻¹

The origin of the 2133 cm⁻¹ band has recently been discussed extensively by Hadjiivanov *et al.* [20] for an ion-exchanged Fe-ZSM-5 catalyst, and this band is assigned to positively charged NO, occupying cationic positions in the zeolite structure [20]. The stability of this NO species is relatively low, and usually the 2133 cm⁻¹ band is not observed at temperatures higher than 573 K. The presence of Ga, rather than Al, in the framework, leads to an absorption band of much weaker intensity at lower wavenumber, suggesting that the amount and nature of the cationic positions is

Table 2
Assignments of the vibrations discussed in this paper

Wavenumber (cm ⁻¹)	Assignment	Catalyst	Reference
2133	Cat [*] -NO ⁺	Fe-ZSM-5	[20]
1910	Fe ^{II} (NO) ₂ (α)	Fe-Y	[21]
	Fe ^{II} (NO) ₂	Fe-ZSM-5	[18,19,20]
	Fe ^{II} (NO) _{n>2} (α)	Fe-silicalite	[17]
1880	Fe ^{II} (NO), Fe ^{II} (NO) (γ)	Fe-Y	[21]
	Fe ^{II} (NO) (γ)	Fe-ZSM-5	[18]
	Fe ^{II} (NO)	Fe-ZSM-5	[19,20]
	Fe ^{II} O ₄ -NO (α)	Fe-ZSM-5	[16]
1850	Fe ^{II} (NO) Iso (β)	Fe-Y	[21]
	Fe ^{II} (NO) (β)	Fe-ZSM-5	[16,18]
	Fe ^{II} O _x -*(NO) (α)	Fe-ZSM-5	[19]
	(Fe ^{II} O) _n -*(NO) (α)	Fe-silicalite	[17]
	and Fe ^{II} (NO) _{n>2} (α)		
1800	Fe ^{II} (NO) ₂ (α)	Fe-Y	[21]
	Fe ^{II} (NO) ₂	Fe-ZSM-5	[20]
	Fe ^{II} (NO) ₂ (α)	Fe-ZSM-5	[18,19]
	Fe ^{II} O ₄ -*(NO) ₂ (α)	Fe-ZSM-5	[16]
	Fe ^{II} (NO) _{n>2} (α)	Fe-silicalite	[17]
1765	Fe ^{II} (NO) ₂ (α)	Fe-silicalite	[17]
	Fe ^{II} (NO) (α)	Fe-ZSM-5/Fe-Y	[18,21]
	Fe ^{II} -NO	Fe-ZSM-5	[16,19,20]
1635	Adsorbed NO ₂	Fe-ZSM-5	[2]

affected by the trivalent ion. A band at 2133 cm⁻¹ was not observed for the *ex*-[Fe]MFI sample.

4.3. The band around 1910 cm⁻¹

A band around 1910 cm⁻¹ has been reported by various authors, and was assigned to a di-nitrosyllic entity on isolated highly accessible Fe^{II} sites in ion-exchanged Fe-ZSM-5 [18] and Fe-Y zeolites [21]. This band is associated with the bands at 1805 and 1765 cm⁻¹ (figure 8, to be discussed later). In agreement with Lobree, we interpret “highly accessible” as being

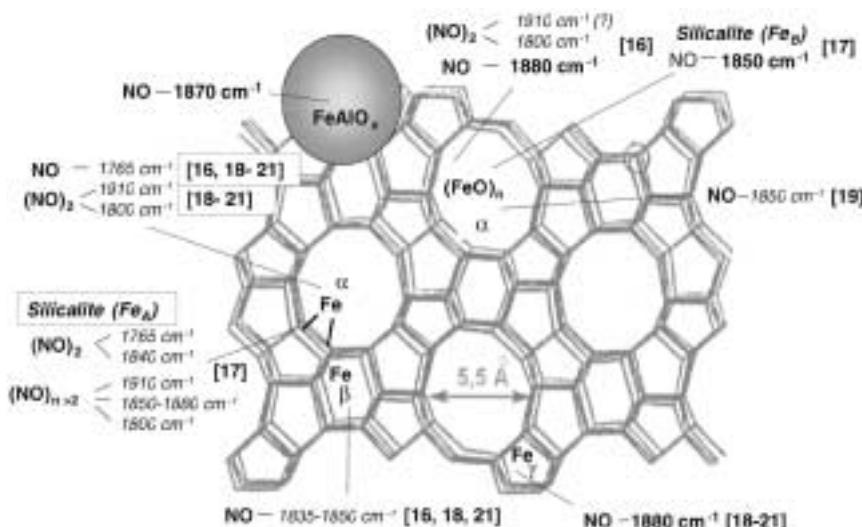


Figure 8. Schematic representation of the Fe-containing sites in the MFI structure. The wavenumbers shown in bold are the assignments for the spectra in this paper, while those in italics are only related to spectra presented in the literature.

located in the α sites of the zeolite. The same frequency has been assigned to poly-nitrosyls on Fe-silicalite [17] on highly unsaturated isolated Fe^{II} sites (labeled Fe_A [17], figure 8). Again, these should be located in the α sites of the zeolite. Whether poly-nitrosyls can exist on Fe-MFI catalysts is, however, still a matter of controversy [17,19]. Finally, a peculiar behavior of this band has been reported by Long and Yang [5], where the 1876 cm⁻¹ band (discussed in the next section) was split at high temperatures (573–673 K), into an absorption band at 1906 cm⁻¹, together with a band 1852 cm⁻¹. Although the authors claim that these bands are related to absorbed species, it is likely that in fact the gas-phase spectrum of NO is recorded, which contains a maximum at these frequencies. In our spectra, we believe that the (broad) tailing contribution around 1910 cm⁻¹ is due to gas-phase NO. Adsorbed di-nitrosylc or poly-nitrosylc NO is absent. This can have various reasons. Either (i) the isolated Fe site in α positions is not present in our steamed MFI samples, (ii) the site is in the Fe^{III} state, or (iii) the site has become inaccessible by the steaming procedure. The latter explanation is not very likely in view of pore volume measurements [14], while EPR measurements show the presence of Fe species in isolated sites in the Fe^{III} state [6,14]. It is therefore most likely that the isolated sites in α positions are in the Fe^{III} state during our IR measurements. In any case, the absence of this band is in agreement with the absence of the 1805 and 1765 cm⁻¹ bands, as will be discussed later.

4.4. The bands around 1880 cm⁻¹

Bands around 1880 cm⁻¹ have often been observed in the spectra of NO adsorbed on zeolite and oxide-supported Fe catalysts, but the assignment is ambiguous. The 1880 cm⁻¹ band has been assigned to mono-nitrosylc species associated with isolated Fe sites either in the 3+ state (Fe^{III}-NO) [21], or 2+ state (Fe^{II}-NO) [3,19]. Among others, Segawa *et al.* [21] assigned this band to isolated Fe^{III}-NO in Fe-Y zeolites, based on the presence of this band (at 1870 cm⁻¹) after the sample was pretreated with O₂ at elevated temperatures. Also the dynamics of this band upon *in situ* oxidation of the sample containing adsorbed NO was in agreement with this assignment. On the other hand, Lezcano *et al.* [19] argued that the assignment to isolated Fe^{III}-NO is questionable, since the few known stoichiometric nitrosyl complexes of Fe³⁺ all show NO absorption frequencies higher than 1900 cm⁻¹. It was furthermore inferred by Hadjiivanov *et al.* [20] that the 1880 cm⁻¹ band must be related to isolated Fe^{II}-NO complexes to explain the formation of NO⁺ leading to the absorption at 2133 cm⁻¹. Indeed the last authors observed a parallel in peak intensity between the 2133 cm⁻¹ and the band at 1878 cm⁻¹. Other researchers tend to agree with the assignment to isolated Fe^{II}-NO, including Lobree *et al.* [18].

Besides the oxidation state of the Fe species causing the 1880 cm⁻¹ absorption, the location and nature of the Fe site is also a matter of controversy. Lobree *et al.* [18] locate the specific Fe site involved in the 1880 cm⁻¹ NO absorption in γ positions in the zeolite framework. Joyner *et al.* [16] on the other hand associate this band with NO on an (Fe^{II}O)_n oligonuclear cluster (of composition Fe₄O₄), which should be located in the α position. Furthermore, Joyner *et al.* [16] correlate this band to the absorption at 1803 cm⁻¹ (to be discussed later) which is suggested to be the corresponding di-nitrosyl. Hadjiivanov *et al.* [1] do not discuss the location of the (isolated) Fe^{II}-NO sites, but disagree with Joyner *et al.* on the issue of the 1803 cm⁻¹ band, specifically stating that this band (located at 1814 cm⁻¹) is involving different Fe species than those causing the 1880 cm⁻¹ band [1].

Before further discussing the assignment of the bands around 1880 cm⁻¹ in the spectra shown in figures 2–6, it should be mentioned that the absorption around 1880 cm⁻¹ in spectra shown in the literature is usually rather broad. Variations in the location of the maximum of 5–10 cm⁻¹ are quite common (e.g. Hadjiivanov *et al.* [1] identify the same absorption band at 1876 and 1882 cm⁻¹). The exact location changes with temperature and NO partial pressure [16], as can also be seen from figure 4. In other publications discussing the 1870–1880 cm⁻¹ bands, shoulders on the main absorption frequency can usually be observed. Of all the publications, only Lezcano *et al.* [19] clearly state the presence of multiple bands, but these authors do not discuss or assign this shoulder. Finally, it should be mentioned that high-intensity bands in the region of 1870–1890 cm⁻¹ have never been observed or discussed for the spectra of Fe-silicalite presented in the literature, while a small band can be observed in the spectrum of steamed Fe-silicalite shown in figure 5.

In view of the previous literature overview and the presence of a variety of Fe species in our samples [14] the interpretation of the doublet around 1870–1880 cm⁻¹ can only be speculative. In view of the isotopic shift presented in figure 3, it is clear, however, that the bands are related to mono-nitrosylc species, in agreement with the literature. Moreover the dynamics of the bands in oxygen (figure 2, adsorbed NO is converted to adsorbed NO₂) show the involvement of two different species. On the other hand, non-oxidative desorption occurs with approximately equal rates (figure 4). In view of the constitution of *ex*-[Fe,Al]MFI and *ex*-[Fe,Ga]MFI a contribution of Fe^{II}MO_x (M = Al, Ga) nano-particles to the absorption pattern is likely. These nano-particles are located on the external surface of the zeolite crystals. Species similar to those present in materials prepared by ion exchange, *i.e.* isolated Fe^{II} in γ positions or (FeO)_n oligonuclear clusters in α positions, apparently also contribute to the absorption pattern. Unfortunately, at this stage it is not possible to discriminate between isolated Fe^{II} in γ positions or

$(\text{FeO})_n$ oligonuclear clusters in α positions, since both species are present in the investigated MFI materials [14]. The higher reactivity of the NO species absorbing around 1870 cm^{-1} toward oxygen (or N_2O) suggests that the lower frequency band is related to the nanoparticles located on the outside of the zeolite crystals, and the high-frequency band at 1880 cm^{-1} to the species inside the zeolite pores. The dynamics of the species in non-oxidative desorption suggest that the stability of NO adsorbed on $\text{Fe}^{\text{II}}\text{AlO}_x$ particles and on either the oligonuclear clusters or the Fe^{II} sites in zeolite channels is quite similar.

Besides the susceptibility towards oxygen, an argument presented by Segawa *et al.* [21] can also be used to assign the low wavenumber absorption to FeAlO_x particles. It was inferred that if the NO molecule has freedom to attain a bent configuration, the NO absorption frequency will be located at lower wavenumbers. Since NO adsorbed on particles has more freedom to bend than NO adsorbed on sites in the zeolite framework, the assignment is consistent with this argument.

Ex-[Fe,Ga]MFI showed similar bands to *ex*-[Fe,Al]MFI, but at somewhat lower wavenumbers. Apparently the absorption character of NO is affected by Al or Ga in the MFI samples, which is in perfect agreement with other characterization techniques summarized in section 4.1 [14].

To finalize the discussion of the NO absorption bands in the 1880 cm^{-1} region, in the spectrum of NO adsorbed on *ex*-[Fe]MFI only a very small contribution of the band at 1874 cm^{-1} is observed (figure 5). This is in agreement with the absence of nano-particles in this material after steaming. It can be inferred that this band is related to gas phase NO, since this band has never been previously observed or discussed in papers related to Fe-MFI samples [17].

4.5. The band at $1835\text{--}1860\text{ cm}^{-1}$

Bands at $1835\text{--}1860\text{ cm}^{-1}$ have been reported in many studies. The frequencies where this band is observed encompass a larger range than the band at 1880 cm^{-1} . In view of literature reports, it is clear that bands in this region of the spectrum need to be assigned to Fe^{II} species [19]. However, the location of these specific sites is again a matter of controversy. The absorption band at around 1852 cm^{-1} has been assigned to mono-nitrosyl on Fe sites in Fe-Y with intermediate accessibility by Segawa *et al.* [21] (identified as β sites in ZSM-5 (figure 8)). It is, on the other hand, argued by Lezcano [19] that the band observed by these authors at 1838 cm^{-1} is related to FeO_x “particles” (it seems the authors mean oligonuclear clusters) in the zeolite channels, referring to the work of Joyner *et al.* [16]. It is proposed that these species are formed during calcination from Fe^{2+} either in cationic positions or from traces of iron oxalate (used as iron precursor in the preparation of

over-exchanged Fe-ZSM-5) occluded in the zeolite pore network [19]. Careful reading of the paper of Joyner *et al.* [16], however, reveals that these authors assign the band at 1841 cm^{-1} specifically to NO on isolated Fe^{2+} , and not to FeO_x clusters. Lobree *et al.* [18] agree with Joyner *et al.* [16] and assign this band to mono-nitrosyl on Fe sites, specifically in β positions in the zeolite framework. Finally, Spoto *et al.* [17] argue that in Fe-silicalite this band is composed of NO adsorbed on two families of Fe sites (Fe_A and Fe_B). The Fe_A site is highly coordinatively unsaturated and allows the adsorption of at least two NO molecules, the absorption of which contributes to the 1839 cm^{-1} band. On Fe_B sites, which are discussed to be the $(\text{FeO})_n$ oligonuclear clusters, the 1839 cm^{-1} band is assigned to a mono-nitrosyl. It is argued that the Fe_B sites can be converted in Fe_A sites by reaction with water [17].

Comparison of the spectra shown in figure 7 indicates that only the silicalite sample contains a band at 1854 cm^{-1} . In view of the elevated temperature where the spectrum was recorded and the absence of other bands (besides the 1874 cm^{-1} , which was previously assigned), it is most likely related to mononitrosyls on $(\text{FeO})_n$ extra-framework species (Spoto's Fe_B sites [17]), rather than poly-nitrosyls. Assuming the validity of the assignments of Segawa *et al.* [21], Lobree *et al.* [18] and Joyner *et al.* [16] of the band around 1850 cm^{-1} to isolated species in Fe-ZSM-5 prepared by ion-exchange methods (solid state and liquid ion exchange, respectively), extraction of Fe from the framework by steaming induces an Fe^{III} state of this particular isolated species in *ex*-[Fe,Al]MFI and *ex*-[Fe,Ga]MFI.

4.6. The band at $1800\text{--}1820\text{ cm}^{-1}$

Segawa *et al.* [21] assigned an 1815 cm^{-1} band to a di-nitrosyl based on a linear relationship between the (low) intensity of the 1915 cm^{-1} band and the intensity of the 1815 cm^{-1} band. The corresponding mono-nitrosyl is located at 1765 cm^{-1} (to be discussed later). Based on this assignment, Lobree [18] *et al.* and Hadjiiivanov *et al.* [20] assign this band to di-nitrosyls in α positions (the larger pores). Spoto *et al.* [17] observed a band at similar position after NO adsorption on calcined Fe-silicalite, which was assigned to a poly-nitrosyl, rather than di-nitrosyl species, based on the dynamics of the bands at 1914 , $1880\text{--}1850$ and 1808 cm^{-1} on the one hand, and the 1839 cm^{-1} and 1765 cm^{-1} (di-nitrosyl) on the other. Arguments based on stability were given by Lezcano *et al.* [19] to exclude the existence of poly-nitrosyls and to suggest that the dynamics can be a matter of coincidence. While the previous citations give the impression that isolated Fe sites in α positions are involved in the 1815 cm^{-1} absorption, Joyner *et al.* [16] assign this band to a di-nitrosyl on an $(\text{FeO})_4$ cluster, based on an intensity correlation between the 1880 cm^{-1} band and the 1815 cm^{-1} band for four different samples at similar NO pressure.

In all the spectra shown in the present contribution, the 1815 cm^{-1} band has not been observed, while clearly bands in the 1880 cm^{-1} region are dominant. This suggests that the assignment of Joyner *et al.* [16] is less likely than the assignments of others to isolated sites in α positions. In agreement with the argument given for the absence of the 1910 and 1850 cm^{-1} bands, the absence of the 1815 cm^{-1} band is most likely related to the steaming procedure, which induces the formation of Fe^{III} , rather than Fe^{II} sites.

4.7. The band around 1765 cm^{-1}

Spoto *et al.* [17] observed this band on Fe-silicalite samples and assigned this band to a di-nitrosyl (see previous section). Lezcano *et al.* [19] exclude the assignment to di-nitrosyls on Fe-ZSM-5, based on experiments with ^{15}NO which show a characteristic shift of a mono-nitrosyl. Although correlations between an increasing 1765 cm^{-1} band and a decreasing 1815 cm^{-1} band have been found [21], Lezcano observed that the intensities of the bands at 1922 , 1813 and 1750 cm^{-1} increase linearly with coverage, excluding interplay between mono-nitrosyl (1765 cm^{-1}) and di-nitrosyl (1805 cm^{-1} and 1912 cm^{-1}) as suggested by Segawa *et al.* [21] and Lobree *et al.* [18]. An explanation for the discrepancy of the observation by Lezcano *versus* Segawa and Lobree is, however, not provided [19]. The band is assigned to a low spin $\text{Fe}^{\text{I}}\text{-NO}^+$ complex [18,19,21]. Joyner *et al.* [16] agree with this assignment, but neither correlate this band to the di-nitrosyls at 1805 – 1810 and 1910 cm^{-1} , as previously discussed.

Again the absence of the 1765 cm^{-1} band in our spectra indicates that after steaming the isolated site in α positions is in the Fe^{III} state. Some further comments are needed on the absence of the band at 1765 cm^{-1} in our steamed [Fe]MFI sample. Regarding the silicalite sample, apparently the morphology is quite different from the sample investigated by Spoto *et al.* [17], and contains a significantly higher fraction of mainly $(\text{FeO})_n$ extra-framework species, rather than isolated sites. Apparently the calcination procedure of Spoto *et al.* [17] leads to less excessive clustering and oxidation of isolated Fe sites than our steaming procedure.

4.8. The band around 1635 cm^{-1}

Bands in the 1635 cm^{-1} region have been observed by many people analyzing lean deNO_x chemistry over Fe-ZSM-5 by FT-IR spectroscopy [1–3]. Usually bands are rather broad and show a multiple character. Chen *et al.* [3] cannot assign this band with certainty, but assume a band at 1625 cm^{-1} to be related to a nitro group ligated to an iron ion. Another band at 1570 cm^{-1} , observed by these authors, is associated with nitrate groups [3]. Bands around 1620 cm^{-1} and below have also been extensively described by Hadjiivanov *et al.* [1]. The band at

1620 cm^{-1} has been assigned to bridging nitrates, and a band at 1575 cm^{-1} to bidentate nitrates [1]. The (sharp) 1635 cm^{-1} band was neither observed nor discussed by these authors [1,3]. Lobree *et al.* [2] describe the dynamics of adsorbed NO with oxygen. These authors observed a band at 1635 cm^{-1} , besides the bands at 1620 cm^{-1} and below (nitro groups). The 1635 cm^{-1} band is tentatively assigned to some form of adsorbed NO_2 , though the exact structure is not known. Surprisingly, in the experimental conditions used by Lobree *et al.* [2], the adsorbed NO_2 species at 1635 cm^{-1} was never formed when exposing preadsorbed NO to O_2 , while this is clearly the case in our studies (figure 2, and spectra in [13]). This is related to the short analysis time in our experiment (this was a rapid scan collection) and might be related to a relatively high stability of the NO_2 species on the nano-particles in our samples. The isotopic shift (from 1635 to 1598 cm^{-1}) shown in figure 3 is in perfect agreement with the assignment to adsorbed NO_2 . Furthermore, the spectra in figure 2 show a correlation between the decreasing 1874 cm^{-1} band and the increasing band at 1635 cm^{-1} upon exposure of the adsorbed NO to $5\text{ vol}\%$ O_2 in He. It can therefore be inferred that the NO_2 species is located on the same site as NO adsorbing at 1874 cm^{-1} , which was previously discussed to be the FeMO_x ($\text{M} = \text{Al, Ga}$) nano-particle.

5. Conclusions

Strong adsorption of NO was observed at elevated temperatures (400–650 K) on various ex-framework [Fe]MFI catalysts at around 1870 and 1880 cm^{-1} . The first band is assigned to NO adsorbed on FeMO_x ($\text{M} = \text{Al, Ga}$) nano-particles, and the second to oligonuclear $(\text{FeO})_n$ clusters in α positions and/or isolated sites in γ positions of the zeolite. Other bands typically observed for ion-exchanged catalysts were *absent* in our spectra, suggesting that the isolated species involved in these vibrations were oxidized to Fe^{III} upon steaming. An observed shift in wavenumbers of the NO adsorbed on *ex-[Fe,Al]MFI* compared with *ex-[Fe,Ga]MFI* suggests that Al or Ga might be present in the FeMO_x particles, which is in agreement with the extensive dealumination (or Ga removal) of the MFI framework. The steamed silicalite sample did not contain any particles, as observed by TEM, and therefore the 1853 cm^{-1} band is assigned to $(\text{FeO})_n$ clusters, which are likely to be present in the α positions of the MFI matrix.

Acknowledgments

G.M. gratefully acknowledges a fellowship granted by the Royal Netherlands Academy of Arts and Sciences. Bart v.d. Linden is acknowledged for assistance in the

set-up of the IR/MS equipment. The authors would like to thank Prof. A. Bliek (University of Amsterdam) for allowing us to use the *in situ* IR cell. This research was financially supported by the council for chemical science of the Netherlands Organization for Scientific Research (CW-NWO).

References

- [1] K. Hadjiivanov, H. Knozinger, B. Tsyntsarski and L. Dimitrov, *Catal. Lett.* 62 (1999) 35.
- [2] L.J. Lobree, I.-C. Hwang, J.A. Reimer and A.T. Bell, *Catal. Lett.* 63 (1999) 233.
- [3] H.-Y. Chen, T. Voskoboinikov and W.M.H. Sachtler, *J. Catal.* 180 (1998) 171.
- [4] A.A. Battiston, J.H. Bitter and D.C. Koningsberger, *Catal. Lett.* 66 (2000) 75.
- [5] R.Q. Long and R.T. Yang, *J. Catal.* 194 (2000) 80.
- [6] A. Ribera, I.W.C.E. Arends, S. deVries, J. Perez-Ramirez and R.A. Sheldon, *J. Catal.* 195 (2000) 287.
- [7] G.I. Panov, A.K. Uriarte, M.A. Rodkin and V.I. Sobolev, *Catal. Today* 41 (1998) 365.
- [8] C. Sang and C.R.F. Lund, *Catal. Lett.* 73 (2001) 73.
- [9] F. Kapteijn, J. Rodriguez-Mirasol and J.A. Moulijn, *Appl. Catal. B: Env.* (1996) 25.
- [10] J. Perez-Ramirez, F. Kapteijn, G. Mul and J.A. Moulijn, *Chem. Commun.* 8 (2001) 693.
- [11] G. Grubert, M.J. Hudson, R.W. Joyner and M. Stockenhuber, *J. Catal.* 196 (2000) 126.
- [12] J. Perez-Ramirez, G. Mul, F. Kapteijn and J.A. Moulijn, *J. Catal.* submitted (2001).
- [13] G. Mul, J. Perez-Ramirez, F. Kapteijn and J.A. Moulijn, *Catal. Lett.* 77 (2001) 7.
- [14] J. Perez-Ramirez, G. Mul, F. Kapteijn, J.A. Moulijn, A. Domenech, A. Ribera, A.R. Overweg and I.W.C.E. Arends, *J. Catal.* submitted (2001).
- [15] P. Marturano, L. Drozdova, A. Kogelbauer and R. Prins, *J. Catal.* 192 (2000) 236.
- [16] R.W. Joyner and M. Stockenhuber, *J. Phys. Chem. B* 103 (1999) 5963.
- [17] G. Spoto, A. Zecchina, G. Berlier, S. Bordiga, M.G. Clerici and L. Basini, *J. Mol. Catal. A: Chemical* 158 (2000) 107.
- [18] L.J. Lobree, I.-C. Hwang, J.A. Reimer and A.T. Bell, *J. Catal.* 186 (1999) 242.
- [19] M. Lezcano, V.I. Kovalchuk and J.L. d'Itri, *Kinet. Catal.* 42 (2001) 104.
- [20] K. Hadjiivanov, J. Saussey, J.L. Freysz and J.C. Lavalley, *Catal. Lett.* 52 (1998) 103.
- [21] K. Segawa, Y. Chen, J.E. Kubsh, W.N. Delgass, J.A. Dumesic and W. Keith Hall, *J. Catal.* 76 (2001) 112.