FTIR and UV–Vis characterization of Fe-Silicalite

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Abstract

FTIR and diffuse reflectance UV–Vis spectroscopies were used to investigate the nature of the extra-framework iron species in Fe-Silicalite using NO as probe molecule. After removal of the template at 773 K, ferrous species present in two different coordinative states, namely Fe_A^{2+} and Fe_B^{2+}, were mainly detected. The Fe_A^{2+} species are highly coordinatively unsaturated and can form a $[Fe_A(NO)_n]^{2+}$ (with $n > 2$) polynitrosyl complex characterized by IR bands at 1914, 1880–1850, and 1808 cm^{-1} and by an electronic transition at 23,000 cm^{-1}. Upon reducing the NO pressure, this complex is transformed into a $[Fe_A(NO)_2]^{2+}$ dinitrosyl characterized by a doublet of IR bands at 1839 and 1765 cm^{-1}. Fe_B^{2+} is less coordinatively unsaturated and forms only $[Fe_B(NO)]^{2+}$ mon}nitrosyl (absorbing in the IR at 1839 cm^{-1} and at 26,500 and 17,500 cm^{-1} in the UV–Vis). Upon dosage of H_2O, the Fe_B^{2+} species becomes able to uptake further NO ligands to give new polynitrosyl species spectroscopically indistinguishable from those formed on the Fe_A^{2+} species. Based on these results, some hypotheses about the structure of Fe_A^{2+} and Fe_B^{2+} are advanced. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Isomorphous substitution of a small fraction of Si^{4+} by Fe^{3+} in the MFI framework of Silicalite and ZSM-5 zeolites leads to Fe-Silicalite and Fe-ZSM-5, materials which are known to show catalytic activity in a number of chemical processes. Among them, we mention isomerization, conversion, and dehydrogenation reactions [1–3], reduction of NO by hydrocarbons [4] and selective oxidations [5–7]. For most of

these reactions, the catalytic activity is thought to be related to extra-framework iron species (iron oxides or oxohydroxides aggregates) formed by Fe extraction during the post-synthesis thermal treatments [8–10] and acting either independently or in synergy with protonic — Fe(OH)Si — sites (Brønsted acid).

A certain number of papers have been published concerning the characterization of Fe-exchanged zeolites, i.e., of systems where iron is introduced in the zeolitic channels and cavities from an *external* source (see for instance Refs. [11–15]). Less information is, on the contrary, available on the nature of the encapsulated iron species formed by migration from framework to extra-framework positions. Some of us have

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shown that in ''as prepared'' (still containing the template) Fe-Silicalite iron is present as isolated Fe^{3+} located in the framework in tetrahedral symmetry [16,17]. Template burning (with associated water production) causes the breakdown of some framework $Fe-O$ bonds and induces formation of oxidic aggregates [17]. At 773 K, this phenomenon involves only 20–25% of the Fe^{3+}, whereas at 973 K almost all Fe^{3+} species are concerned. The adsorptive properties towards CO, N_2, H_2O and NH_3 were also investigated [17,18]. The consequences of template removal by calcination on the Fe-ZSM-5 structure have also been studied by Fejes et al. [19]. A quasi-linear decrease of isomorphously substituted framework Fe^{3+} vs. the temperature of treatment was found resulting in the formation of extra-framework highly dispersed iron-oxides. The role played by extra-framework iron in N_2O decomposition on Fe-ZSM-5 has been extensively studied by Panov et al. [20–22]. Following these authors, N_2O decomposition occurs on extra-framework iron microclusters and leads to surface reactive oxygen species (α-oxygen). These species are responsible for the selective oxidation of benzene to phenol and methane to methanol, which are performed by the N_2O/Fe-Silicalite and N_2O/Fe-ZSM-5 systems under mild conditions [5–7]. Structural analogies between the extra-framework iron clusters in MFI-type Fe-zeolites and the binuclear iron clusters encountered in the active sites of methane mono-oxygenase [23] have been outlined [24,25].

From the analysis of the literature data briefly discussed above, it is however evident that the mechanism of formation as well as the real nature of the extra-framework species in MFI-type Fe-zeolites is far from being completely understood. As shown in this paper, useful additional information can be gained by the study of their surface properties by means of adsorption of probe molecule. In particular, FTIR data concerning the interaction of NO with Fe-Silicalite treated at moderately high temperature (773 K) are illustrated here. Some preliminary UV–Vis results are also shown and briefly discussed.

2. Experimental

The Fe-Silicalite samples (Si/Fe = 50) used in these experiments were synthesised in the EniTechnologie laboratories. Burning or decomposition of the template was performed either in air at 773 K or under vacuo at the same temperature. In the first case, as cooling at room temperature in air after removal of the template causes readsorption of water and other impurities, before NO dosage the samples were outgassed under high vacuum (final pressure ca. 10^{-5} Torr) up to 773 K in the same cell used for the FTIR or UV–Vis measurements. It is worth to note that very similar IR spectra of adsorbed NO were obtained in the two cases (burning of the template in air and subsequent outgassing under vacuo or decomposition under vacuo). This indicates that the two procedures lead to similar systems.

The IR experiments were carried out on a Bruker IFS 66 FTIR instrument equipped with a cryogenic MCT detector and running at 2 cm^{-1} resolution. The Fe-Silicalite samples were in form of self-supporting pellets suitable for measurements in transmission mode. All the IR spectra reported in the following are background-subtracted.

The diffuse reflectance UV–Vis spectra were obtained on a Varian Cary 5 spectrometer on powdered samples.

NO, carefully purified by distillation in order to remove other undesired nitrogen oxides, was dosed from a vacuum line permanently attached to the measurements cells. The same system was also used for dosing H_2O from the gas phase.

3. Results and discussion

The IR spectrum of a Fe-Silicalite sample (previously outgassed at 773 K) in equilibrium

at room temperature with 10 Torr of NO is reported in Fig. 1 (dotted line). In the same figure, the effect of gradually decreasing the NO equilibrium pressure is also illustrated.

The following can be commented:

(i) At maximum NO coverage, the spectrum is dominated by an intense absorption at 1808 cm^{-1} superimposed to a second band centered at 1839 cm^{-1}. Less intense features appear at 1914 and 1765 cm^{-1} together with a broad absorption covering the 1880–1850 cm^{-1} range.

(ii) Upon decreasing the NO pressure, the bands at 1914 and 1808 cm^{-1} are gradually and parallely eroded and finally disappear. This process is accompanied by the simultaneous (and parallel) intensification of the components at 1839 and 1765 cm^{-1} (which finally dominate the spectrum: dashed line in Fig. 1) and by the
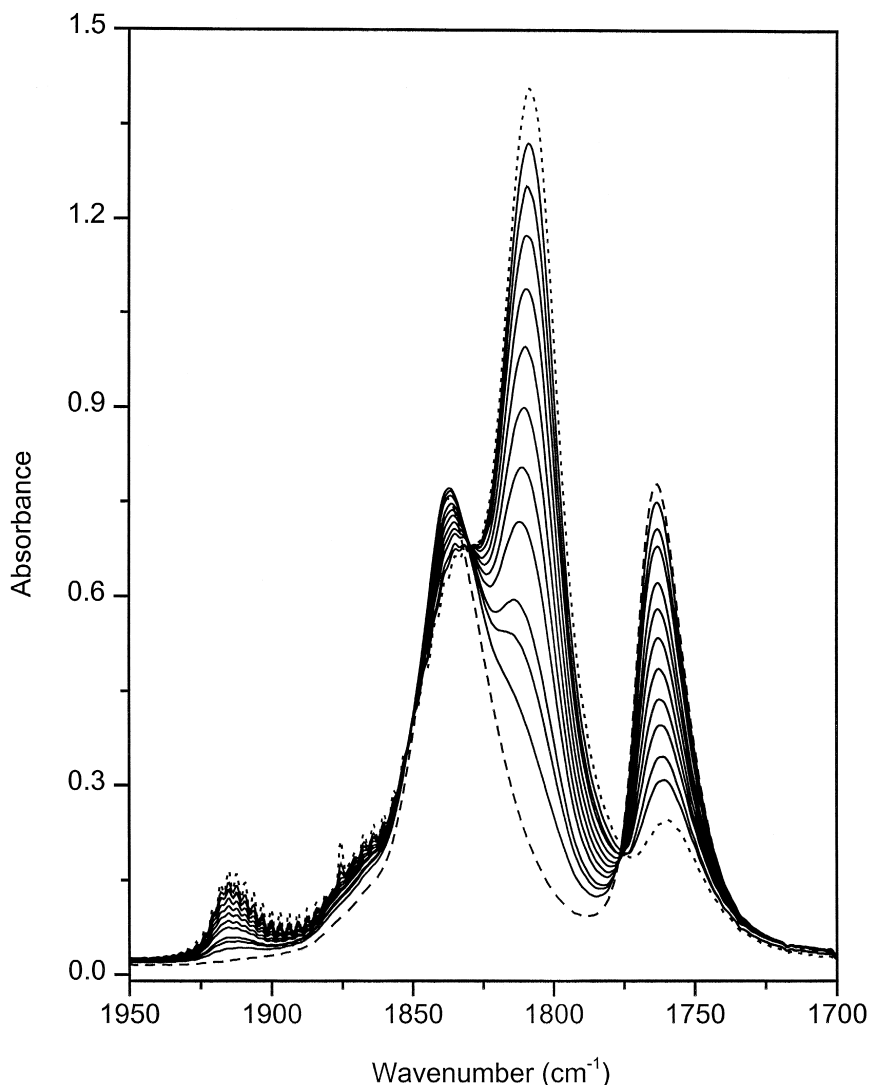

Fig. 1. FTIR (background-subtracted) spectra of NO adsorbed at room temperature on Fe-Silicalite (previously outgassed at 773 K). Dotted line: in the presence of 10 Torr of NO. Dashed line: after outgassing for 15 min at the IR beam temperature. Full lines: intermediate NO coverages.

appearance of three isosbestic points at ca. 1850, 1825, and 1775 cm^{-1}. The fate of the absorption at 1880–1850 cm^{-1} is less clear.
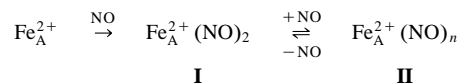
(iii) The doublet at 1839 and 1765 cm^{-1} is not destroyed even after outgassing the sample under high vacuum for 15 min at the IR beam temperature.

It is worth noticing that initial spectrum (dotted line in Fig. 1) can be completely recovered by readmission of NO (results not shown for sake of brevity).

Similar bands have been already reported for the NO adsorption on silica-supported iron oxide [26]. In particular, a doublet appearing at 1910 and 1810 cm^{-1} and a single band at 1750 cm^{-1} were respectively assigned to di- and mononitrosyl species formed on fourfold coordinated Fe^{2+} centers strongly interacting with the support, while a band at 1830 cm^{-1} was assigned to a mononitrosyl complex on sixfold coordinated Fe^{2+} at the surface of small iron-oxide particles [26]. An equilibrium between $[Fe(NO)_2]^{2+}$ (characterized by a couple of IR bands at 1917 and 1815 cm^{-1}) and $[Fe(NO)]^{2+}$ (absorbing at 1767 cm^{-1}) complexes has been also hypothesised to explain the pressure dependence of the spectra of NO adsorbed on Fe–Y zeolite [12]. On the same system, a band at 1845 cm^{-1} was assigned to mononitrosyl complexes on more coordinated ferrous ions [12]. Similar spectral features have been observed on other iron-exchanged zeolites (Mordenite and ZSM-5) and a similar interpretation has been given [13].

In agreement with these literature data, we assign the bands at 1914, 1880–1850, 1839, 1808, and 1765 cm^{-1} to nitrosyl complexes formed on extra-framework (or partially extra-framework, vide infra) ferrous species. The assignment to reduced iron centers is further supported by the experimental observation that these bands are nearly absent on Fe-Silicalite samples oxidised by treatment with O_2 at 500 K or with N_2O at 523 K (results not shown). Based on the results described above in (ii), a different interpretation is however given here as far as the nature (number of involved NO ligands) and the

equilibria between different nitrosyl species are concerned. We think, in fact, that the spectral features of Fig. 1 can be more reasonably interpreted on the basis of the following reaction involving the same Fe^{2+} centers (hereafter Fe_A^{2+}):

$$Fe_A^{2+} \xrightarrow{\ NO\ } \underset{\mathbf{I}}{Fe_A^{2+}(NO)_2} \underset{-NO}{\overset{+NO}{\rightleftharpoons}} \underset{\mathbf{II}}{Fe_A^{2+}(NO)_n}$$

where complex **I** is responsible for the doublet at 1839 and 1765 cm^{-1} and complex **II** for that at 1914 and 1808 cm^{-1} (and possibly for the absorption in the 1880–1850 cm^{-1} range). This interpretation better explains the strict proportionality between the decrement of the bands at 1839 and 1765 cm^{-1} and the increment of the bands at 1914 and 1808 cm^{-1}. Definite support to the assignment of the doublet at 1839 and 1765 cm^{-1} to a dinitrosyl complex will be given in the following on the basis of the isotopic substitution experiments.

Some significant difference in spectra of the NO/Fe-Silicalite system are observed on samples containing preadsorbed H_2O. To illustrate this point, in Fig. 2 the spectra obtained at maximum NO coverage (part a) and after prolonged outgassing at room temperature (part b) on a ''usual'' sample (simply outgassed at 773 K, dotted curve) are compared with those obtained on a Fe-Silicalite sample previously contacted with 5 Torr H_2O at room temperature, evacuated under high vacuum for 10 min at the IR beam temperature and finally contacted with NO (full line curve). On the sample pretreated with H_2O the following can be noticed.

(i) The bands at 1914, 1880–1850, 1808, and 1765 cm^{-1} have gained intensity in both the spectra at high (part a of Fig. 2) as well as at low (part b of Fig. 2) NO coverage.

(ii) The gain in intensity of the bands quoted in (i) is paralleled by a decrement of the absorption at 1839 cm^{-1} (part a of Fig. 2).

(iii) At low NO coverage, the band width of the absorption at 1839 cm^{-1} is reduced to ca. one-half with respect to that found on the H_2O-
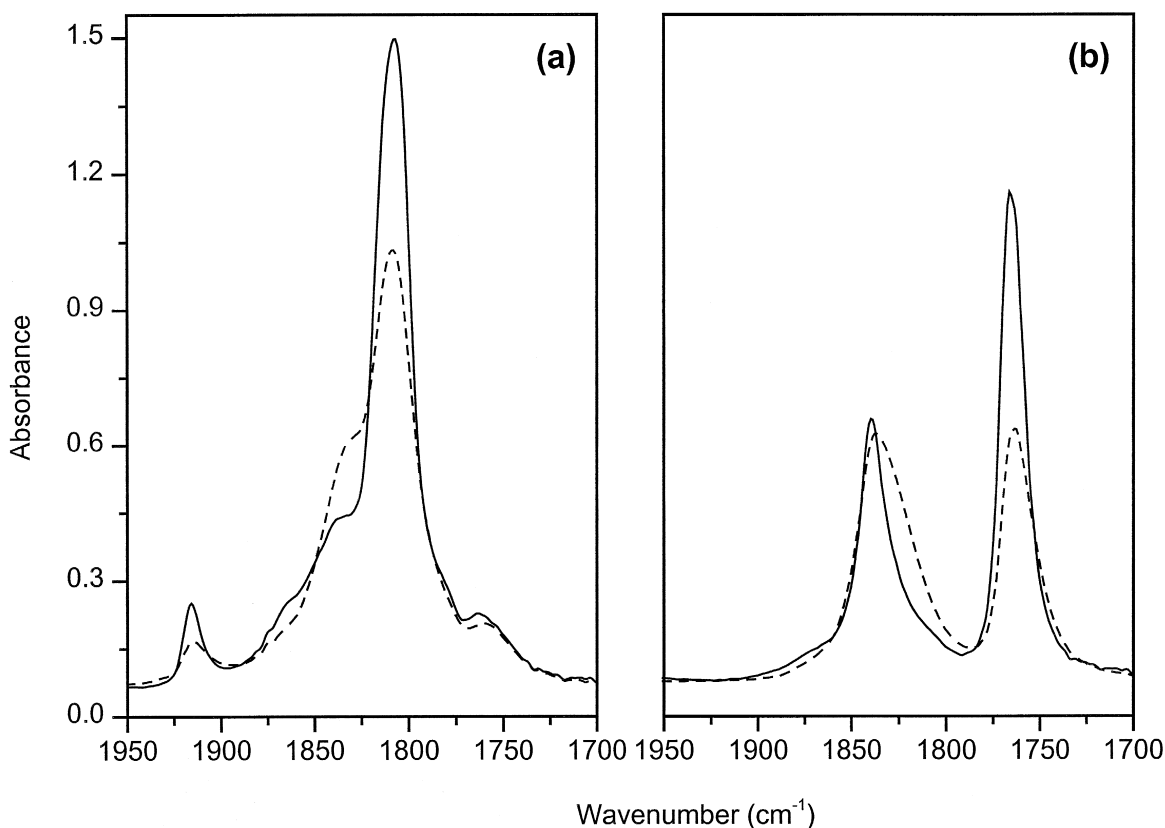
Fig. 2. Comparison between the IR spectra of the NO/Fe-Silicalite (dotted lines) and NO/H$_2$O/Fe-Silicalite (full lines) systems. Part a: spectra in presence of 10 Torr NO in the gas phase. Part b: after outgassing for 15 min at the IR beam temperature.

free sample (part b of Fig. 2). This leads to the conclusion that the absorption at 1839 cm^{-1} has a composite nature and is originated by the superposition of at least two distinct components, one of which is selectively depleted by H$_2$O adsorption.

To explain these findings, we hypothesise that, beside Fe$_A^{2+}$, a second family of ferrous centers is present (hereafter Fe$_B^{2+}$). On the H$_2$O-free samples, this species forms, by addition of NO, a [Fe$_B$(NO)]$^{2+}$ mononitrosyl complex (absorbing at 1839 cm^{-1}). Upon dosage of H$_2$O, Fe$_B$ becomes able to uptake further NO ligands to give polynitrosylic complexes, which are spectroscopically indistinguishable from those formed by the Fe$_A^{2+}$ sites.

In order to establish the stoichiometry of complexes **I** and **II**, isotopic substitution experi-

ments have been performed using pure ^{14}NO, pure ^{15}NO and a 1:1 ^{14}NO/^{15}NO isotopic mixture. The spectra obtained for complex **I** on a sample previously contacted with H$_2$O (and hence not disturbed by the manifestation of the [Fe$_B$(NO)]$^{2+}$ complex) are compared in Fig. 3.

We can observe that the doublet at 1839 and 1765 cm^{-1} (^{14}NO) is shifted at 1803 and 1729 cm^{-1} when pure ^{15}NO is adsorbed (with an isotopic shift of 36 cm^{-1}). In the presence of the 1:1 ^{14}NO/^{15}NO mixture, the isotopic pattern consists of two triplets with components at 1839, 1827, and 1803 cm^{-1} and 1765, 1744, and 1729 cm^{-1}. It is most noticeable that in both the triplets the intensity ratio of the components is ca. 1:2:1. These data undoubtedly confirm the dinitrosylic nature of complex **I**. The isotopic pattern due to complex **II** (not reported
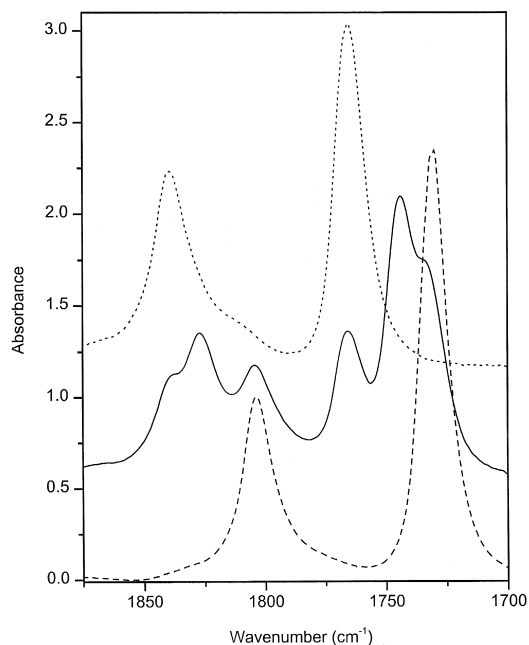
Fig. 3. FTIR spectra of ^{14}NO (dotted line), ^{15}NO (dashed line), ^{14}NO/^{15}NO 1:1 isotopic mixture (full line) adsorbed at low coverage on Fe-Silicalite outgassed at 773 K.

here for sake of brevity) appears to be much more complicated and its exact interpretation is still in progress. However, we can anticipate that it is in broad agreement with that expected for a trinitrosylic stoichiometry.

In Fig. 4, the diffuse reflectance spectrum of a Fe-Silicalite sample outgassed at 773 K (dashed line) is compared in the 32,500–13,500-cm^{-1} region with the spectrum obtained after dosing 10 Torr NO at room temperature (full line). The effect of reducing the NO pressure is also illustrated (dashed lines).

We can observe that dosage of NO results in the appearance of three bands at 27,500, 23,000, and 17,500 cm^{-1}. The intensity of the band at 23,000 cm^{-1} diminishes upon decreasing the NO pressure (hence, showing the same behaviour of the IR bands assigned to complex **II**, see Fig. 1): its assignment to electronic transitions involving the $[Fe_A(NO)_n]^{2+}$ species is therefore straightforward. The intensity of the bands at 27,500 and 17,500 cm^{-1} seems, on the contrary, not dependent on the NO equilibrium

pressure. They are therefore assigned to the $[Fe_B(NO)]^{2+}$ complex. It is noteworthy that, upon decreasing the NO coverages, no absorptions seem to develop associated with complex **I**. The absence of bands associated with this species (whose formation is clearly revealed by the IR spectra; see Fig. 1) could be related to a higher local symmetry of the $[Fe_A(NO)_2]^{2+}$ complex with respect to the $[Fe_A(NO)_n]^{2+}$ one resulting in a reduction of the electronic extinction coefficient [27].

The above assignment is further supported by the electronic spectra obtained upon NO adsorption on Fe-Silicalite pretreated with H$_2$O. In fact, as shown in Fig. 5, where the background-subtracted spectra of the NO/Fe-Silicalite (full line) and NO/H$_2$O/Fe-Silicalite (dashed line) systems are compared, in the presence of H$_2$O
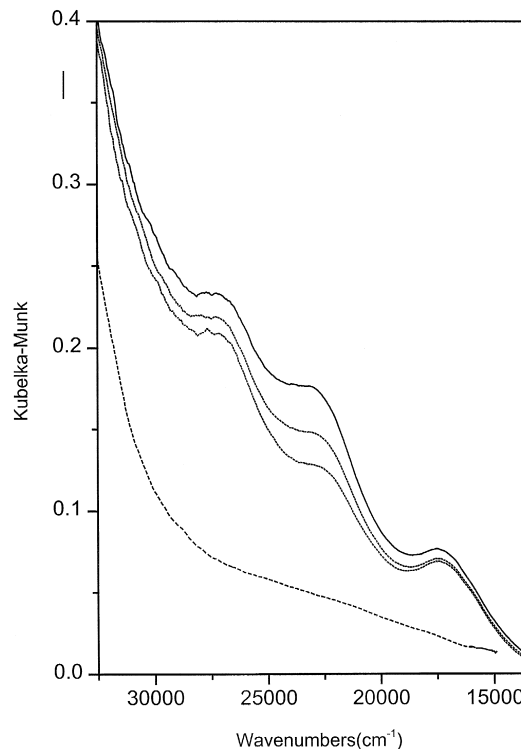

Fig. 4. UV–Vis diffuse reflectance spectra of NO adsorbed on Fe-Silicalite. Dashed line: spectrum of Fe-Silicalite outgassed at 773 K. Full line: spectrum after dosage of 10 Torr NO at room temperature. Dotted lines: effect of lowering the NO equilibrium pressure.
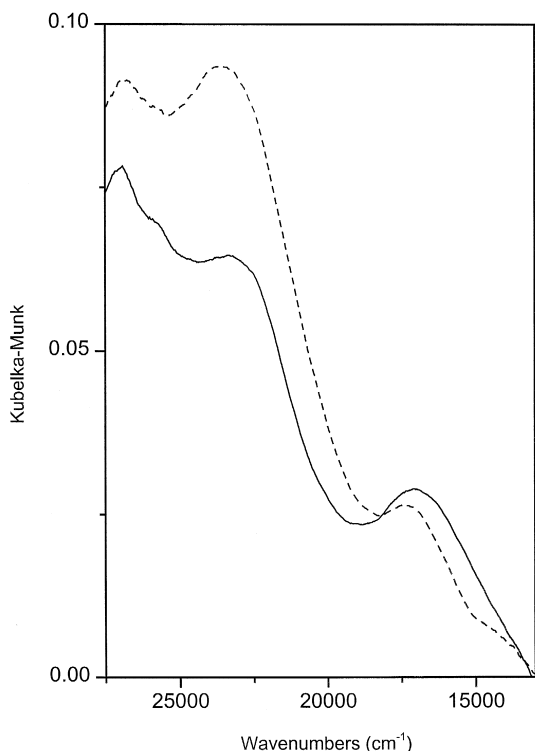
Fig. 5. Comparison between the background-subtracted UV–Vis diffuse reflectance spectra of the NO/Fe-Silicalite (full line) and NO/H_2O/Fe-Silicalite (dashed line) systems.

the bands at 27,500 and 17,500 cm^{-1} are reduced in intensity, whereas that at 23,000 cm^{-1} shows an opposite behaviour. These findings are in close correspondence with those of the IR experiment illustrated in Fig. 2 and confirm the hypothesis that water transforms F_B^{2+} into a new species having adsorptive properties towards NO similar to those of the Fe_A^{2+} center (although not necessarily the same local structure).

We underline that the electronic bands observed in the present work show broad analogies with those found by Lange and Klier [27] on the NO/Fe(II)-A system. On this basis, they can be analogously attributed to d–d transitions of Fe^{2+} ions. However, the high intensity of these peaks suggests that the observed transitions involve states where p–d admixture is also present. A more precise assignment, which is in

any case outside the limited scope of this paper, needs further experimental work.

The experimental results illustrated here clearly show that dislodged iron is present in the channels of Fe-Silicalite in a reduced state as Fe(II). As during the zeolite synthesis iron is introduced in tetrahedral framework positions as Fe(III), the occurrence of a self-reductive process, possibly with oxygen release, must be necessarily invoked. Of course, we are not able to state if self-reduction is either accompanying the extraction stage or is occurring in a second time. It has been however shown that the reverse process, i.e., the facile oxidation of Fe(II) to Fe(III) by O_2, requires at least cation pairs in close proximity [28,29]. On this basis, we hypothesise that the self-reduction process involves oxidic (or oxohydroxidic) aggregates primarily formed as a consequence of the thermal treatments.

Concerning the nature of the Fe_A and Fe_B species, it is a matter of fact that they show a completely different propensity towards the adsorption of NO ligands (at least a trinitrosyl can be, in fact, formed by the former and a mononitrosyl only by the latter). This is a clear indication of different coordinative states, higher for Fe_B with respect to Fe_A. We suggest that Fe_A are isolated, low coordinated iron centers (probably mononuclear) grafted to the framework, while Fe_B species belong to $(FeO)_n$ extra-framework (or partially extra-framework) clusters which can be broken up by H_2O to give more reactive Fe_A-type species. This attribution is certainly in agreement with the very well-defined nature of the spectra of adsorbed NO, which more closely resemble those usually obtained of ordinary stoichiometric compounds in homogeneous conditions rather than those usually obtained on surfaces.

4. Conclusions

The IR and UV–Vis spectra of NO adsorbed on Fe-Silicalite reveal that the thermal treatment

at 773 K devoted to the template burning leads to formation of two different extra-framework ferrous species (Fe_A^{2+} and Fe_B^{2+}). The Fe_A^{2+} centers can form $[Fe_A(NO)_n]^{2+}$ polynitrosyl complexes containing at least three NO ligands: this suggests that they are low coordinated iron(II) species. The high definition of the IR spectra of adsorbed NO, which resemble those of homogeneous analogues, is indicative of high structural definition of these centers. Adsorption of NO on Fe_B^{2+} gives $[Fe_B(NO)]^{2+}$ mononitrosyl only, as expected for a less coordinatively unsaturated species belonging to clustered $(FeO)_n$ structures.

Dosage of H_2O leads to at least partial disruption of the clustered structures.

Acknowledgements

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