Analysis of Fe species in zeolites by UV–VIS–NIR, IR spectra and voltammetry. Effect of preparation, Fe loading and zeolite type

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Abstract

Three procedures were employed for the preparation of Fe-zeolites with ZSM-5 (MFI), ferrierite (FER) and beta (BEA) structures: ion exchange from FeCl₃ solution in acetyl acetonate and solid-state ion exchange from FeCl₂ using an oxygen or nitrogen stream. A combination of UV–VIS–NIR spectra, IR spectra of skeletal vibrations and of adsorbed NO, as well as voltammetry provided information on the type of Fe species introduced. Single Fe(III) ion complexes (Fe(H₂O)₆/C0xOx) in hydrated zeolites were reflected in the charge-transfer bands at 33100, 37300 and 45600 cm⁻¹. The single Fe(II) ions at cationic sites in evacuated zeolites yielded (through perturbation of framework T–O bonds) characteristic bands (910–950 cm⁻¹) in the region of the skeletal window. These Fe(II) ions with adsorbed NO were also reflected in vibrations at 1880 cm⁻¹. Dinuclear Fe–oxo complexes yielded the Vis band at 28200 cm⁻¹. Voltammetry indicated the presence of Fe oxides (hematite) through the reduction peak at ~0.7 V. Such oxide-like species were also reflected in the absorption edge at 19800 cm⁻¹, and a doublet at 11000 and 11800 cm⁻¹ in the Vis spectra. Fe(II)–NO vibrations at 1840, 1810 and 1760 cm⁻¹ belonged to the undefined exposed Fe cations, probably originating from supported oxides. Using an ion exchange procedure, employing FeCl₃ in acetyl acetonate, exclusively Fe ions at cationic sites could be introduced at low concentrations (Fe/Al < 0.1). At higher Fe loadings, dinuclear Fe–oxo complexes were formed preferably in Fe-ZSM-5, but were absent in Fe-beta. Exclusively single Fe species could not be prepared at Fe concentrations above Fe/Al > 0.2; all three types of Fe species, single Fe ions, dinuclear Fe–oxo complexes and Fe oxides were formed.

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Keywords: Fe-zeolites; UV–VIS spectra; IR spectra; Voltammetry; Fe complexes

1. Introduction

Fe species in silicon rich zeolites with pentasil ring structures, particularly of ZSM-5, have recently attracted a great deal of attention due to their unique activity in oxidation of benzene to phenol with N₂O [1,2], N₂O decomposition, and stable activity in selective catalytic reduction of NOₓ (SCR-NOₓ) with alkanes in the presence of water vapour [3–7]. Attempts are currently being made to identify the structure of Fe species in these zeolites in order to analyse the activity of specific Fe species in these reactions. However, due to the highly variable chemistry of iron in an environment of oxygen-containing ligands and the simultaneous presence of various types of Fe species, whose populations depend on the procedure of Fe zeolite preparation and treatment, such relationships have not yet been unambiguously established. Moreover, there are indications...
that some specific Fe species might exhibit extremely high activity in hydrocarbon hydroxylation with N₂O, which makes it necessary to analyse Fe-zeolites with low iron contents of hundreds of ppm [1].

The ion exchange of Fe ions from Fe salt solutions is not simple for two reasons. From the aspect of the zeolite, the exchange of trivalent Fe ions in silicon-rich zeolites is difficult because of the insufficient local negative framework charge to balance a bare trivalent cation. In relation to the source of the Fe ions, the Fe(III) ions in aqueous solutions are mainly present as [Fe(H₂O)₆]³⁺, [Fe(OH)₂(H₂O)₆]²⁺, and [Fe(H₂O)₆(OH)₂]²⁺ single-ion aquo-complexes, as well as dimeric forms present as [Fe₂(μ-O)(H₂O)₈]⁴⁺ oxo-bridged complexes or [Fe₂(μ-O)₂(H₂O)$_5$]⁴⁺ di-oxo-bridged complexes. In high concentrations of non-acidified Fe(III) salt solutions, Fe ion polymerisation leads to α-Fe₂O₃ or α-FeO(OH) [7].

Therefore, in addition to attempts to introduce trivalent Fe ions, a number of preparation methods employed divalent iron. Fe-zeolites of ZSM-5 and ferrierite structures have been successfully prepared by several methods. Fe(II) ion exchange using an aqueous solution of FeSO₄ [4,8], FeC₂O₄ [4,8] or Fe(NO₃)₂ [9], as well as a solution of anhydrous FeCl₂ in acetyl acetone were employed [10]. In addition, a method of sublimation of FeCl₃ through a dry ZSM-5 layer at high temperature, followed by zeolite washing, was suggested by Sachtl et al. [4,5,11]. Finally, “solid-state” ion exchange between solid FeCl₂ [12] or FeCl₃ [4] and the H- or NH₄-zeolites was employed to incorporate iron into the zeolite structure. Thus, volatile iron compounds at temperatures above 300 °C were able to exchange Fe ion species for zeolite protons.

Accordingly, the nature of Fe species introduced and their oxidation state depends mainly on the Fe content and post-preparation zeolite treatment. Lobree et al. [13] found isolated Fe(OH)⁺ species at Fe/Al < 0.2, which underwent dehydration to FeO⁺. For Fe/Al ratios between 0.2 and 0.6, the iron was present in the form of FeOH⁺, whereas the formation of iron oxide, together with a significant amount of Fe(II), was observed above this level. Rauscher et al. [14] reported hematite formation on Fe-ZSM-5, obtained by solid-state exchange with FeSO₄ in nitrogen at a temperature of 500 °C.

Preparation of the exchanged Fe ions at low Fe loadings using FeCl₃ in acetyl acetone yielded three different Fe(II) cationic sites in ferrierite by characteristic IR bands of the anti-symmetric T–O–T mode [15]. The predominant type of the Fe ion (β-type) was located in the elongated six-membered ring of the side channel. At loadings of Fe/Al > 0.1, the α- and a minor amount of γ-type Fe ions were formed, coordinated in the main channel to the six-membered ring composed of two five-membered rings and located in the boat-shaped sites of the ferrierite side channel, respectively.

Based on the Mössbauer spectra of Fe(III) and Fe(II) species in Fe-ZSM-5 zeolites [16,17] and by analogy with the structure of Fe methane monooxygenase [18], Panov et al. proposed the occurrence of dinuclear Fe species in ZSM-5 [17]. They connected these structures with the zeolite activity in benzene oxidation to phenol with N₂O. Prins and co-workers [19] and Sachtl et al. [20] revealed similar dinuclear Fe species in highly loaded Fe-ZSM-5 zeolites by using EXAFS measurements. They assumed these species to be active in SCR-NOₓ with iso-butane under water vapour presence in the reactant stream [3,11].

It follows that, like the complex chemistry of iron in solutions, there are many possible structures of Fe species in zeolites. It is evident that, in most cases, single-di- and trivalent Fe ions, oxo- and hydroxo-complexes, polymeric oxidic species and iron oxide species are present simultaneously.

We attempted to distinguish individual Fe species in zeolites of ZSM-5, ferrierite and beta topologies by UV–VIS–NIR, voltammetry and the FTIR spectra of adsorbed NO. The reference samples with various Fe loadings were prepared by different ion exchange procedures.

For Fe species analysis, UV–VIS–NIR diffuse reflectance (DR) spectroscopy has been employed and represents a promising tool for examination of Fe(III) ions in various structures. This method can distinguish highly dispersed Fe(III) in/on a solid matrix from isolated hydrated and complexed Fe(III) ions through their hydrated oligomers to condensed nano- or microcrystalline Fe oxides or Fe-bearing silicates [21–25]. UV–VIS–NIR spectra are supplemented by the voltammetry of microparticles (VMP) resolving Fe(III) in oxides [26–28]. The IR spectra of skeletal vibrations and of adsorbed NO have been used to identify Fe ions in cationic sites.

2. Experimental

2.1. Parent zeolites

NH₄-MFI-I, NH₄-BEA and NH₄-FER with Si/Al 13.2, 13.5 and 10.8, respectively, were supplied by Unipetrol, Czech Republic. NH₄-MFI-II with Si/Al 12 was kindly provided by AlSi-Penta Zeolithe GmbH, Germany.

2.2. Fe-zeolites

Three procedures, denoted as A, B and C, were employed for introduction of Fe ions into the zeolites, thus yielding Fe-MFI-I-A and Fe-MFI-I-C, Fe-MFI-II-B, Fe-FER-A and Fe-FER-B and Fe-BEA-B and Fe-BEA-C zeolites. These were prepared as follows:
**Fe-zeolites using procedure A.** Parent NH$_4$-zeolite was dried at 150 °C for 4 h and then mixed with a solution of FeCl$_3$ in acetyl acetonate. After 12 h of mixing, the solution was removed, and the solid was dried at RT and heated under vacuum at 350 °C (4 °C/min) for 4 h. The sample was then washed with distilled water and dried in air at RT. Then, the remainder of the organics in the Fe-zeolite were decomposed at 420 °C in an air stream for 6 h.

**Fe-zeolites using procedure B.** The NH$_4$-zeolite was mixed and intensively ground with an appropriate amount of FeCl$_2$·4H$_2$O salt in a mortar. The resulting powder mixture was slowly heated under a gentle flow of 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 Cl$^-$ ions were detected in the eluted water. The zeolite was then dried at 80 °C overnight.

**Fe-zeolites using procedure C.** The dried (at 150 °C) NH$_4$-zeolite was mixed and intensively ground with an appropriate amount of anhydrous FeCl$_2$ in a mortar under nitrogen atmosphere. The resulting powder mixture was slowly heated under a dry nitrogen stream to 550 °C (0.5 °C/min) and kept at this temperature for 6 h. The parameters of Fe ion exchange and the chemical compositions of the parent and Fe-zeolites determined by atomic absorption spectrometry following dissolution of the zeolite samples are given in Tables 1 and 2.

### Table 1
Chemical composition of Fe-zeolites prepared by procedure A, and conditions of Fe ion exchange

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Fe/Al</th>
<th>g FeCl$_3$ per g acetylacetonate</th>
<th>Time (h) × repetition</th>
<th>ml solution per g zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-MFI-I-A</td>
<td>13.0</td>
<td>0.02</td>
<td>0.01</td>
<td>16</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe-MFI-I-A</td>
<td>13.1</td>
<td>0.04</td>
<td>0.02</td>
<td>16</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe-MFI-I-A</td>
<td>13.1</td>
<td>0.06</td>
<td>0.02</td>
<td>16</td>
<td>1.3</td>
</tr>
<tr>
<td>Fe-MFI-I-A</td>
<td>12.9</td>
<td>0.08</td>
<td>0.02</td>
<td>16</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe-MFI-I-A</td>
<td>13.1</td>
<td>0.18</td>
<td>0.02</td>
<td>16 × 3</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe-MFI-I-A</td>
<td>13.5</td>
<td>0.33</td>
<td>0.02</td>
<td>16 × 4</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe-MFI-I-A</td>
<td>13.3</td>
<td>0.53</td>
<td>0.12</td>
<td>16</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe-FER-A</td>
<td>11.1</td>
<td>0.12</td>
<td>0.02</td>
<td>16</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe-FER-A</td>
<td>10.9</td>
<td>0.24</td>
<td>0.02</td>
<td>16 × 2</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe-FER-A</td>
<td>10.9</td>
<td>0.33</td>
<td>0.02</td>
<td>16 × 3</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe-FER-A</td>
<td>11.1</td>
<td>0.39</td>
<td>0.02</td>
<td>16 × 4</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Table 2
Chemical composition of Fe-zeolites prepared by procedures B and C

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Fe/Al</th>
<th>g FeCl$_2$·4H$_2$O per g zeolite</th>
<th>g FeCl$_2$ per g zeolite</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-MFI-II-B</td>
<td>12.3</td>
<td>0.25</td>
<td>0.0326</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>Fe-MFI-II-B</td>
<td>12.5</td>
<td>0.31</td>
<td>0.0652</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>Fe-MFI-II-B</td>
<td>12.3</td>
<td>0.55</td>
<td>0.1304</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>Fe-FER-B</td>
<td>11.2</td>
<td>0.39</td>
<td>0.0736</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>Fe-BEA-B</td>
<td>13.5</td>
<td>0.35</td>
<td>0.0573</td>
<td>–</td>
<td>6</td>
</tr>
<tr>
<td>Fe-MFI-I-C</td>
<td>12.5</td>
<td>0.28</td>
<td>–</td>
<td>0.035</td>
<td>6</td>
</tr>
<tr>
<td>Fe-BEA-C</td>
<td>13.6</td>
<td>0.30</td>
<td>–</td>
<td>0.031</td>
<td>6</td>
</tr>
</tbody>
</table>

### 2.3. UV–VIS–NIR spectroscopy

UV–VIS–NIR diffuse reflectance (DR) spectra of hydrated Fe-zeolites were recorded using a Perkin–Elmer Lambda 19 UV–VIS–NIR spectrometer equipped with a diffuse reflectance attachment with an integrating sphere coated with BaSO$_4$. BaSO$_4$ was also used as a reference. The absorption intensity was expressed using the Schuster–Kubelka–Munk function, $F(R_infty) = (1 - R_infty)^2/2R_infty$, where $R_infty$ is the diffuse reflectance from a semi-infinite layer. Spectra were deconvoluted to the Gaussian bands using the Microcal Origin 4.1 software (Microcal Software, Inc., USA). For details see Refs. [29–31].

### 2.4. Voltammetry

Voltammetry of microparticles (VMP) was performed using the procedure described elsewhere [26,28]. Samples were mechanically deposited on the basal plane of a paraffin-impregnated graphite rod and voltammetric curves were recorded in N$_2$-purged acetic acid–sodium acetate buffer (1:1, 0.2 M total acetates) with a Pt-plated counter-electrode and saturated calomel reference electrode (SCE). All potentials are referred to SCE. Scanning was initiated at the zero-current (open-circuit) potential and continued towards negative potentials at a rate of 3 mV/s to yield the voltammetric peaks of reductive dissolution of the ferric species. The buffer and potential...
program were checked for Fe oxides of varying crystallinity [26]. The interpretation of the peak potentials was based on previous systematic studies of various synthetic Fe oxides and Fe-bearing zeolites [27].

2.5. FTIR spectroscopy

FTIR spectra were monitored at room temperature (RT) on Fe-zeolites after evacuation (10⁻³ Pa) at 450 °C for 3 h in the region of the skeletal vibrations, and after adsorption of NO (4 kPa at RT followed by desorption at RT for 30 min) in the region of the NO vibrational mode. The samples were placed in a carousel sample holder with six samples placed in a glass vacuum cell equipped with NaCl windows. A Nicolet Magna-550 FTIR spectrometer with a MCT-B low-temperature detector were used. For details see Refs. [32,33].

2.6. External and internal specific surface area measurements

Nitrogen adsorption isotherms were determined using an Omnisorp 100 instrument (Coulter) in the continuous flow mode on samples Fe-MFI-II-B, Fe-FER-B and Fe-BEA-B and their parent zeolites. A distinction was made between ultra-micropores ($V_p < 0.7$), with diameters smaller than 0.7 nm, and secondary pores, representing super-micropores (diameters of 0.7–2 nm) and small mesopores (up to 5 nm). Experimental adsorption isotherms were interpreted using the method of Remy and Poncelet [34]. Nitrogen adsorption in the ultra-micropores was described using the Dubinin–Radushkevich equation [35].

The specific external surface area ($S_{ext}$) was determined using the t-Plot method with Aerosil as a reference.

3. Results

3.1. UV–VIS–NIR spectra

Figs. 1 and 2 depict the effect of the method of Fe incorporation and Fe loading on the UV–VIS–NIR spectra of Fe-zeolites. Fe-MFI-I-A zeolites prepared by ion exchange of FeCl₃ in acetyl acetonate at low Fe concentrations exhibited bands with maxima at 37300 and 45600 cm⁻¹ and a weak band at 33100 cm⁻¹ (Fig. 1A). A band at 28200 cm⁻¹ and a low-intensity band around 19800 cm⁻¹ were developed with increasing Fe concentration (Fig. 1B). The band at 28200 cm⁻¹ predominates in the spectra above Fe/Al ratio of 0.20. The maxima of these bands were estimated from the spectra deconvolution to the Gaussian bands, as illustrated in Fig. 3. Fe-FER-A zeolites exhibited all the above bands with comparable relative intensities in the whole range of Fe loading, with the exception of the band at 19800 cm⁻¹, which was not developed (Fig. 1C). Bands below 19000 cm⁻¹ were not observed for all Fe-MFI-I-A and Fe-FER-A samples.
Fe-MFI-II-B, Fe-FER-B and Fe-BEA-B zeolites, prepared by solid-state ion exchange in an air stream, exhibited a characteristic doublet at 11000 and 11800 cm\(^{-1}\) and an absorption edge at 18500 cm\(^{-1}\) (Fig. 2 A and B). On the other hand, in the spectra of Fe-MFI-I-C and Fe-BEA-C, prepared by solid-state ion exchange with anhydrous FeCl\(_2\) under nitrogen, the bands below 19000 cm\(^{-1}\) were not observed (Fig. 2C). Nevertheless, we would like to mention that the sample Fe-MFI-I-C contained less cationic Fe species in comparison with that prepared by procedure A. Fe-MFI-II-B and Fe-MFI-I-C zeolites also exhibited a well-developed band at 28200 cm\(^{-1}\) and weak absorption at 19800 cm\(^{-1}\). These two bands were also observed in the spectra of Fe-MFI-I-C and Fe-BEA-C, prepared by solid-state ion exchange with anhydrous FeCl\(_2\) under nitrogen, the bands below 19000 cm\(^{-1}\) were not observed (Fig. 2C). Nevertheless, we would like to mention that the sample Fe-MFI-I-C contained less cationic Fe species in comparison with that prepared by procedure A. Fe-MFI-II-B and Fe-MFI-I-C zeolites also exhibited a well-developed band at 28200 cm\(^{-1}\) and weak absorption at 19800 cm\(^{-1}\). These two bands were also observed in the spectra of Fe-MFI-I-C and Fe-BEA-C, prepared by solid-state ion exchange with anhydrous FeCl\(_2\) under nitrogen, the bands below 19000 cm\(^{-1}\) were not observed (Fig. 2C).

The presence of the doublet at 11000 and 11800 cm\(^{-1}\) is well documented in the detailed VIS-NIR spectra shown in Fig. 4 and the absorption edge is clearly indicated by the second derivation mode of the spectra (Fig. 5). Note that the Gaussian curves cannot be used for description of the shape of the absorption edge and its wavenumber can be only estimated from the second derivation mode.

Fig. 6 depicts the UV–VIS spectra of selected Fe-zeolites dehydrated in an oxygen stream at 450 °C. In comparison with hydrated Fe-zeolites (Figs. 1 and 2), the changes in relative intensities of only the bands at 33100, 37300 and 45600 cm\(^{-1}\) were observed according to the spectra decomposition. The band at 28200 cm\(^{-1}\) was shifted to higher energies (30000 cm\(^{-1}\)). Changes in its intensity can be explained by changes in the intensity of the band at 33100 cm\(^{-1}\) and/or by the change of the absorption coefficient. The bands at 11000, 11800.

![Fig. 3. Illustration of the decomposition of the experimental UV–VIS spectrum of Fe-MFI-I-A with Fe/Al ratio of 0.24 (——) to the Gaussian curves (---).](image)

![Fig. 4. UV–VIS spectra of (——) Fe-MFI-II-B with Fe/Al ratio of 0.31, (-•-) Fe-BEA-B with Fe/Al ratio of 0.31 and (-••-) Fe-FER-B with Fe/Al ratio of 0.34.](image)

![Fig. 5. Second derivate of UV–VIS spectra of (——) Fe-MFI-II-B with Fe/Al ratio of 0.31, (-•) Fe-BEA-B with Fe/Al ratio of 0.31 and (-••) Fe-FER-B with Fe/Al ratio of 0.34.](image)

![Fig. 6. UV–VIS spectra of Fe-zeolites dehydrated in an oxygen stream, (A) Fe-MFI-I-A with Fe/Al ratio of (——) 0.08 and (——) 0.33, (B) (——) Fe-MFI-II-B with Fe/Al ratio of 0.31 and (-••-) Fe-FER-B with Fe/Al ratio of 0.34 and (C) (——) Fe-MFI-I-C with Fe/Al ratio of 0.28. Inserted spectra of 40 times higher intensity for (A) Fe-MFI-I-A with Fe/Al ratio of 0.33, (B) Fe-MFI-II-B with Fe/Al ratio of 0.31 and (C) Fe-MFI-I-C with Fe/Al ratio of 0.28.](image)
and 18,500 cm\(^{-1}\) were not changed, while the band at 19,800 cm\(^{-1}\) was substantially suppressed.

Complete dehydration of Fe-zeolites is reflected in the absence of the band at 5200 cm\(^{-1}\) (see Fig. 6), corresponding to the combination vibration band \((\delta + \nu)\) of water molecules. On the other hand, the band of the combination vibration ascribed to OH groups only marginally decreased in intensity, but three weak bands around 7000 cm\(^{-1}\) were present in the spectrum. This indicates the presence of OH groups bound to Fe or Al species and of bridging OH groups. No new bands were observed in the NIR region of oxidized dehydrated zeolites, attributable to Fe(II) ions.

### 3.2. Voltammetry

Four peaks occurred on the voltammetric curves of Fe-zeolites, with peak potentials at about 0, -0.4, -0.7, and -0.9 V vs. SCE (Figs. 7 and 8). The most positive peak at 0 V was present only as a very small broad pre-peak in some samples. It should correspond to highly reactive Fe(III) species, more reactive than amorphous Fe\(_2\)O\(_3\). The peak at -0.7 V vs. SCE undoubtedly indicates the presence of highly crystalline hematite [25,26]. This was found in samples from procedure B, i.e. Fe-MFI-II-B, Fe-BEA-B and Fe-FER-B. The major peak at -0.4 V found in Fe-MFI-I-A of high Fe concentration (Fe/Al 0.53) could be identified as poorly ordered, defective nano-crystalline hematite (protohematite), that has much larger electrochemical reactivity than the well-ordered hematite [28]. Another possibility is the formation of \(\beta\)-Fe\(_2\)O\(_3\) or nano-crystalline maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)). It should be noted that the rare polymorph \(\beta\)-Fe\(_2\)O\(_3\) is prepared by heating Cl-containing solid mixtures [36]. However, neither \(\beta\)- nor \(\gamma\)-Fe\(_2\)O\(_3\) were indicated by UV–VIS–NIR spectroscopy. Hence, the peak at -0.4 V can be attributed to nano-crystalline hematite.

In low Fe-loaded samples prepared by procedure A (Fe-MFI-I-A, Fe/Al ratio of 0.08–0.24), there is a complete absence of the voltammetric peaks of the Fe(III) species. Because in Fe-MFI-I-A with Fe/Al ratio of 0.24, the Fe concentration is well above the detection limit of voltammetry of microparticles, the absence of such a peak indicates that single Fe ions in cationic sites, detected by FTIR and UV–VIS spectra, are not available for the electrochemical reaction. As this low-intensity peak occurs in highly loaded Fe-zeolites prepared by solid-state ion exchange (procedures B and C), we suggest that it reflects the presence of Fe(III) ions occluded on the zeolite. The absence of electrochemical response to Fe ions in cationic sites can be caused by their divalent state under electrochemical measurements or difficult electron transport from the electrode to the zeolite [37].

### 3.3. FTIR spectra

FTIR spectra in the transmission window region of Fe-zeolites dehydrated by evacuation (thus containing mostly Fe ions in cationic sites with prevailing divalent state, cf. Ref. [15,38]) reflected the presence of the predominant band at 930 cm\(^{-1}\) for Fe-MFI-I-A zeolites, indicating single Fe(II) ions predominantly in \(\beta\) cationic site. The bands at 915, 930 and 945 cm\(^{-1}\) observed for
Fe-FER-A zeolites indicated the presence of Fe(II) ions in \( \gamma, \beta \) and \( \alpha \) sites, respectively. For details of the site positions, see Ref. [15].

The presence of Fe(II) in the cationic sites of zeolites is also indicated by an intense IR band at 1880 cm\(^{-1}\), characteristic for adsorbed NO on these Fe(II) ions (Fig. 9), as also reported for Fe-MFI zeolites in Refs. [3,13,39]. The other bands at 1840, 1810 and 1760 cm\(^{-1}\) could be ascribed to vibrations of NO adsorbed on the other undefined Fe ions, probably associated with supported Fe-oxide-like species. The assignment of the IR band at 1880 cm\(^{-1}\) is supported by the correlation (not shown in the figure) between the intensity increase of the band at 1880 cm\(^{-1}\) of NO adsorbed on Fe(II) and a decrease in the intensity of the sum of perturbed skeletal bands at 915, 930 and 945 cm\(^{-1}\), caused by coordination of the single Fe(II) ions exclusively to the framework oxygens, as found for Fe-ferrierite [40]. Therefore, it is indicated that Fe-MFI-I-A with a low Fe concentration, Fe/Al = 0.08, contains predominantly single Fe ions in cationic sites. On the other hand, Fe-MFI-II-B with Fe/Al = 0.31 exhibiting additional bands at 1840, 1810 and 1760 cm\(^{-1}\) contains, besides Fe in cationic sites, also a significant concentration of undefined, likely supported Fe-oxide-like species.

### 3.4. Specific surface area

The results given in Table 3 indicate that the ultramicropore volume of the iron-loaded samples is only slightly smaller than in the H-zeolites. Thus the Fe species occupy little space within the zeolite channels and larger Fe species, in case they are formed, do not block the zeolite pores (Table 3). Some secondary porosity developed in Fe-BEA sample during the solid-state introduction of Fe into the zeolite corresponds to the lower structural stability of the BEA structure under the atmosphere formed at Fe chloride sublimation conditions. The number \( n \) of adsorbed \( \text{N}_2 \) layers needed on the walls of secondary pores in order to achieve pore filling is larger in Fe-BEA \( (n_{\text{BET}} = 5.2) \) than in Fe-FER \( (n_{\text{BET}} = 4.5) \) and Fe-MFI \( (n_{\text{BET}} = 2.5) \). Thus, the diameter of the secondary pores decreases in the order Fe-BEA > Fe-FER > Fe-MFI.

### 4. Discussion

#### 4.1. Analysis of Fe species detected by UV–VIS–NIR, voltammetry and the FTIR spectra of skeletal vibrations and adsorbed NO

FTIR spectra in the region of skeletal vibrations with characteristic IR bands of anti-symmetric T–O–T mode [15,38,41] and FTIR spectra of adsorbed NO [15,38,39,42] have already been successfully used for the identification of different cationic sites of polyvalent cations. The skeletal bands at 930 cm\(^{-1}\) for Fe-MFI and the bands at 915 cm\(^{-1}\) and 945 cm\(^{-1}\) for Fe-FER are characteristic for Fe ions located at cationic sites. In addition, the intense band of NO adsorbed on Fe ions around 1880 cm\(^{-1}\) resembles the band for these ions in cationic sites (Fig. 9). Thus, single Fe(II) ions located in cationic sites were present in all the Fe-zeolites dehydrated in vacuum. As in dehydrated Fe-MFI-I-A zeolites with low Fe concentrations (Fe/Al < 0.1), IR bands of NO adsorbed on Fe in cationic sites highly prevailed, it is concluded that Fe-zeolites with low Fe concentration, containing predominantly single Fe ions in cationic sites, can be prepared by procedure A of Fe ion exchange with FeCl\(_3\) in acetyl acetonate.

UV–VIS–NIR spectra of hydrated Fe-MFI-I-A zeolites (Figs. 1 and 2) with Fe loading Fe/Al < 0.1 exhibit UV bands at 33100, 37300 and 45600 cm\(^{-1}\). These high-energy bands can be attributed to ligand-to-metal O-Fe

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Fe/Al</th>
<th>( V_p ) u-( \mu ) (ml/g)</th>
<th>( V_p ) sec (ml/g)</th>
<th>( n_{\text{BET}} )</th>
<th>( S_{\text{ext}} ) (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI-I</td>
<td>–</td>
<td>0.096</td>
<td>0.022</td>
<td>2.0</td>
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<tr>
<td>Fe-MFI-II-B</td>
<td>0.31</td>
<td>0.091</td>
<td>0.024</td>
<td>2.5</td>
<td>13.0</td>
</tr>
<tr>
<td>FER</td>
<td>–</td>
<td>0.131</td>
<td>0.010</td>
<td>4.1</td>
<td>24.0</td>
</tr>
<tr>
<td>Fe-FER-B</td>
<td>0.39</td>
<td>0.126</td>
<td>0.004</td>
<td>4.5</td>
<td>37.0</td>
</tr>
<tr>
<td>BEA</td>
<td>–</td>
<td>0.184</td>
<td>0.012</td>
<td>5.6</td>
<td>151.0</td>
</tr>
<tr>
<td>Fe-BEA-B</td>
<td>0.35</td>
<td>0.170</td>
<td>0.026</td>
<td>5.2</td>
<td>133.0</td>
</tr>
</tbody>
</table>

Fig. 9. FTIR spectra of NO adsorbed on (—) Fe-MFI-I-A with Fe/Al ratio of 0.08 and (–•–) Fe-MFI-II-B with Fe/Al ratio of 0.31.
charge-transfer transitions of Fe(III) ions in the octahedral environment of oxygen atoms [24,43]. Since these three bands form the spectrum of Fe-MFI-I-A zeolites with loading Fe/Al < 0.1, where, according to the IR spectra, single Fe ions in cationic sites are present, these bands can be attributed to the aequous complexes of single Fe ions in hydrated zeolites rather than to small iron oxide clusters or tetrahedrally coordinated Fe species, as suggested in Refs. [44–46]. However, three types of Fe(III) complexes—[Fe(H_2O)_6]^{3+}, [Fe(H_2O)_5(OH)]^{2+}, and [Fe(H_2O)_4(OH)_2]^{2+}, the latter present as three isomers—can be present in aqueous solutions and thus also inside the channels of hydrated zeolites. All these species in aqueous solutions exhibit absorptions only above 30000 cm^{-1}, similar to the samples reported here, but none of them can be directly identified with the spectra of Fe-zeolites. Small differences in the spectra of Fe in aqueous solutions and those in hydrated zeolites can be explained by the replacement of one or more water molecules or OH groups by the framework oxygens. Note that all the Fe zeolites were calcinated during their preparation, followed finally by re-hydration. Thus, it can be concluded that exclusively aqueous/framework oxygen complexes of single Fe(III) ions are present in hydrated Fe-MFI-I-A with Fe/Al < 0.1; they are characterized by charge transfer (CT) bands at 33100, 37300 and 45600 cm^{-1}. Such Fe ions, with these bands, are present in all the investigated Fe zeolites, but greatly predominate in zeolites from procedure A at low Fe loadings. It can also be concluded that the presence of CT bands above 30000 cm^{-1} in the spectra of hydrated Fe-zeolites is in agreement with the presence of the intense FTIR band of adsorbed NO on Fe(II) ions in cationic sites at 1880 cm^{-1} in the spectra of all the Fe-zeolites.

Surprisingly, dehydration of Fe-zeolites in oxygen (see Fig. 6) was not accompanied by any dramatic changes in the UV spectral region. No band disappeared and no new band was found. Small changes in the shape of the spectra can be explained by the re-organisation of framework/extra-framework oxygen ligands containing Fe(III) ion complexes. The presence of three types of OH groups, reflected in the low-intensity combination vibration bands at 7070, 7170 and 7280 cm^{-1} in dehydrated samples, indicates the presence of negatively charged extra-framework ligands containing oxygen atoms. Note that the relatively low intensity of 2v combination vibration bands, compared with the Fe(III) CT bands, reflects a dramatic difference in their extinction coefficients. Thus, preservation of octahedral or pseudo-octahedral sixfold coordination of Fe(III) ions, as well as preservation of their trivalent state by coordination of two OH groups to Fe(III) located in the framework ring containing one Al atom, can be expected for Fe ions located in both the α-site with pseudo-octahedral and in a β-site with bipyramidal coordination of Fe ions. The α-site is located on the wall of the straight channel of the MFI structure, while the β-site is formed by the deformed six-membered ring at the straight and sinusoidal channel intersection; for site identification see Refs. [29,30]. In the case of one OH group coordinated to an Fe(III) ion located in the six-membered ring containing two framework Al atoms, the five-coordinated Fe(III) ions exhibiting deformed C_2v coordination (Fe ions close to the plane of the six-membered ring in a β-site) or square pyramidal coordination (Fe(III) ions in an α-site) can be assumed. The Fe(III) ions with C_2v coordination exhibit CT spectra similar to six-coordinated Fe(III) ions. It should be mentioned that the CT transitions are more sensitive to the nature of the ligands (framework or extra-framework oxygen atoms, and an oxygen atom in a water molecule or OH group) than to the Fe ion coordination. Thus, according to the UV and NIR spectra, single Fe(III) ions bearing one or two OH groups and located in cationic sites are present in all the investigated oxidized/dehydrated Fe samples, but greatly predominate in Fe-zeolites with low loadings prepared by procedure A.

The doublet at 11000 and 11800 cm^{-1} corresponds to the 6^1_A_1g → 4^1T_1g(4G), 4^1T_2g(4G) d-d transitions of Fe(III) ion in an octahedral environment of oxygen-containing ligands (Fig. 4). This can be attributed to Fe(III) ions in hematite [43,47]. The attribution of a strong absorption edge at about 18500 cm^{-1} is also unambiguous. This absorption corresponds to the d–d electron pair transition (EPT), which is unique in this region for Fe(III) ions in hematite [22,43,47,48]. Attribution of these bands to haematite is further supported by the fact that these bands are not affected by zeolite dehydration. Small changes in their intensity, when observed, can be explained by disappearance of the band at 19500 cm^{-1} overlapping the haematite bands. Attribution of these bands to hematite in Fe-MFI-B, FER-B and BEA-B zeolites prepared by procedure B is further confirmed by the presence of a voltammetric peak at ~0.7 V observed for these samples, which is characteristic for hematite (Figs. 7 and 8). In addition to the band at 1880 cm^{-1} of Fe ions in cationic sites, the FTIR spectra of adsorbed NO on these Fe-zeolites also exhibit additional bands at 1840, 1810 and 1760 cm^{-1} (Fig. 9). These bands indicate the presence of NO adsorbed on undefined supported Fe ions, which might originate from oxide-like species. The actual position of EPT depends on the particle size of hematite [48]: hematite with particle size of the order of 100 nm has an EPT band at 18000 cm^{-1}, which shifts to the range of 18200–18900 cm^{-1} when particles are an order of magnitude smaller. Thus, hematite particles with a size of 10–50 nm are present in the above-mentioned zeolites. The ultra-micropore volume of the iron-loaded samples is only slightly smaller than
4.2. Effect of the preparation method, Fe loading and zeolite type on the nature of the Fe species

The presented results and the information given in the literature clearly indicate that, in most cases, the Fe-zeolites contain a wide range of Fe species, which, moreover, can be distinguished only with difficulty. In rare circumstances, only one type of Fe species can be introduced in the zeolite. It is shown here that the procedure of exchange of low concentrations of Fe ions from a solution of FeCl₂ in acetyl acetonate (procedure A) is able to yield Fe ions located predominantly in cationic sites, as identified within the sensitivity of the spectral methods employed in this study. The exchanged single Fe ions are located at α, β and γ cationic sites, which can be distinguished by the characteristic spectra of anti-symmetric T–O vibrations due to perturbation of the skeletal T–O bonds binding the cations at cationic sites (for Fe-FER, the positions of the bands are 930 cm⁻¹ for the β site and 945 cm⁻¹ for the α site). The β site is most populated in all the pentasil ring zeolites, while Fe ions in γ site represent only a minor fraction that can sometimes be monitored only with difficulty.

At higher Fe concentrations, it is possible to prepare Fe-zeolites containing both Fe ions in cationic sites and also oxo- or hydroxo-dinuclear Fe-species, reflected in the UV–VIS band at 28200 and 30000 cm⁻¹ for hydrated and dehydrated zeolites, respectively. Fe-zeolites with such species can be obtained by procedure A using a higher concentration of Fe and also by procedure C, when solid-state ion exchange is performed with FeCl₂ and oxidation of divalent Fe ions during preparation is prevented by using a dry zeolite and a nitrogen atmosphere. With such Fe-zeolites, no UV–VIS bands reflecting Fe oxides and no voltammetric peaks were observed. Thus, a minimum of Fe-oxide phase can be expected to be present in the zeolite.

For all the preparations (procedures A–C) of zeolites with high Fe loadings, single Fe ions in cationic sites, oxo- hydroxo-dinuclear Fe species and iron oxide, mostly of hematite, are formed. Hematite is preferably formed by procedure B, where solid-state exchange was carried out in an air atmosphere and using ferrous chloride with crystalline water, both supporting oxidation of divalent iron to the trivalent state. It should also be noted that, for all the preparations, the inner pore volume is largely preserved, even for Fe-zeolites, where supported iron oxide particles (procedure B) are formed. Such oxides probably migrate to the zeolite crystal surface, where they are responsible for an increase in the secondary pore volume by narrowing the voids between crystallites.

Among the individual zeolite structures, the ZSM-5 zeolite is that one that most readily accommodates single Fe ions in cationic sites as well as dinuclear Fe
complexes. On the other hand, the more open structure of beta zeolite has a much higher tendency to form Fe oxide species. Because of the more open inner channel volume and thus the larger distances between the cationic sites, dinuclear Fe species are not formed in the beta zeolite, in contrast to the ZSM-5 structure, where the distances between the cations are favourable for such pairing.

5. Conclusions

It is concluded that a combination of UV–VIS–NIR, IR spectra of skeletal vibrations and of adsorbed NO, as well as voltammetry can provide information on the type of Fe species in zeolites, i.e. the occurrence of the single Fe ions at cationic sites, Fe–oxo species and Fe oxides. Single Fe(II) ion complexes (Fe(H2O)6−x...OHx) in hydrated zeolites are reflected in the CT bands at 33100, 37300 and 45600 cm−1. These bands exhibit similar positions in dehydrated zeolites, as the ligands also contain oxygen atoms, represented by skeletal oxygens and OH groups. The single Fe(II) ions at the cationic sites are present in evacuated zeolites, where they perturb the framework T–O bonds, yielding characteristic bands in the region of the skeletal window, and are also detected by the vibration of adsorbed NO at 1880 cm−1. However, Fe(III) cations at these sites were not reflected in voltammetric peaks around 0 V, although their reactivity is expected to be high. As these cations are atomically dispersed inside aluminosilicate channels, electron transfer from the electrode might be difficult or they already change their state to divalency. The defined dinuclear Fe–oxo complexes are manifested by the band at 28200 cm−1 in hydrated zeolites, shifting to 30000 cm−1 after dehydration. Voltammetry yields convincing evidence for the presence of Fe oxides, hematite and protohematite, through the reduction peaks at −0.7 and −0.4 V, respectively. Such oxide species are also manifested by the absorption edge at 19800 cm−1, and a doublet at 11000 and 11800 cm−1 in the Vis spectra (but with low intensity). Fe(II)–NO vibrations at 1840, 1810 and 1760 cm−1 correspond to the undefined exposed Fe cations, probably originating from supported oxides.

At medium and high Fe concentrations of Fe-zeolites, these usually contain all the described Fe species. Exclusively single Fe ions can be incorporated into ZSM-5, ferrierite and beta zeolites only at very low loadings, preferably by the procedure employing ion exchange with FeCl3 in acetyl acetonate solution. Also solid-state ion exchange (procedure C) using FeCl3 with an inert atmosphere, preventing oxidation of iron to trivalent state, yields Fe ions predominantly in cationic sites at low concentrations of Fe ions. Dinuclear Fe complexes are formed only in ZSM-5 and ferrierite structures, but they are absent in beta zeolites. This can be explained by the wide channels of the beta structure, which do not yield cation–cation distances suitable for dinuclear complex formation.

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References

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