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New precursor for the post-synthesis preparation of Fe-ZSM-5 zeolites with low iron content

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A new method for preparing ZSM-5 catalysts containing highly dispersed iron species is presented. Iron(III) oxalate was used as the iron precursor in an aerobic aqueous exchange process. The presence of different iron species inside the zeolite pores was investigated by IR spectroscopy of adsorbed NO, which revealed an excellent iron dispersion. The results were compared with those obtained on a Fe-ZSM-5 catalysts prepared by iron(II) chloride sublimation and on samples prepared by controlled migration of framework iron in isomorphously substituted samples.

KEY WORDS: Fe-ZSM-5; Iron(III) oxalate; aqueous exchange; FTIR spectroscopy; $Fe(NO)_n$ complexes.

1. Introduction

The catalytic performances of iron supported ZSM-5 catalysts are incontestable. Nitrous oxide decomposition [1], selective catalytic reduction (SCR) of nitric oxide with hydrocarbons [2] and ammonia [3] and hydroxylation of benzene to phenol with nitrous oxide [4] are by far the most important reactions in which Fe-ZSM-5 catalysts are successfully used.

Starting from the seventies different methods have been proposed for zeolites functionalisation with iron, either during the zeolite synthesis or with post-synthesis methods. The state of iron and the ion exchange level as well as the catalytic performances of Fe-ZSM-5 catalysts strongly depend on the method used for their preparation. Hydrothermal synthesis, solid state and aqueous exchange, sublimation or chemical vapour deposition are frequently used as preparation methods, each of them having its own advantages and drawbacks. Iron precursors are usually inorganic salts, such as $FeCl_3$ [5], $FeSO_4$ [6], $(NH_4)_2Fe(SO_4)_2$ [7], $FeCl_2$ [8], $Fe(NO_3)_3$ [6], $FeCO_3$ [6], organometallic compounds like iron(III) acetylacetonate, iron(II) oxalate [9,10], or even Fe powder and HCl [8].

The preparation methods can be divided into two groups. In the first group all post-synthetic methods are included, which are designed to directly prepare samples containing extraframework Fe sites. The second group consists of isomorphously substituted Fe-zeolites, where the formation of extraframework sites is obtained by controlled migration of Fe from framework to extraframework positions [11,12]. In both cases, depending upon the iron content and the thermal treatments (temperature higher than 773 K), an heterogeneous distribution of different Fe sites is necessarily obtained in the zeolitic channels and cavities (i.e. grafted to the inner surface), or even anchored on the external surface of the zeolite particles. In other words, it is reasonable to hypothesize that isolated, dimeric, oligomeric Fe sites and oxidic/hydroxidic $Fe_xO_y(OH)_n$ aggregates always coexist in Fe-containing zeolites, and that the preparation methods must be designed to tune the sites distribution. For instance, it is evident that high iron content favours clustered species, while isolated Fe sites are expected to dominate in highly diluted samples (see for example the samples with concentrations below 1000 ppm, reported in Refs. [13,14]). Among the various preparation methods, migration of Fe ions from framework to extraframework positions in isomorphously substituted samples, allows a better control of the iron dispersion, because the migration is gradual and because the Fe concentration in the systems is always low [13].

To further complicate the situation, we have to take into account that different oxidation state of Fe can also coexist in the same sample, depending upon the iron precursor used for the exchange and upon the activation conditions (temperature, presence of water, vacuo or He flow). This aspect is also important, since it has been reported that the active sites for N_2O decompositions and benzene hydroxylation are Fe^{2+} ions [4]. Fe^{2+} ions can be introduced in extraframework positions by using a ferrous salt as precursor. In alternative, when iron is initially present as trivalent ion (in samples prepared by post-synthetic methods with ferric salts or in isomorphously substituted Fe^{3+} samples) thermal activation

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treatments (*in vacuo* or He) are known to cause the reduction of (at least) a fraction of iron sites from Fe^{3+} to Fe^{2+} [4,13,15].

The nature of iron species in Fe-ZSM-5 samples is usually investigated by FTIR spectroscopy using NO as probe molecule. This technique was successfully used by several groups [12,15–19] to characterize the exposed sites of different iron containing molecular sieves, and it is based on the capability of grafted and coordinatively unsaturated Fe^{2+} and Fe^{3+} ions to form stable NO adducts ($Fe(NO)_n$, $n = 1, 2, 3$) at room temperature. The maximum number of NO ligands adsorbed by each Fe^{2+} and Fe^{3+} centre represents a direct indication of their coordinative unsaturation and allows to differentiate the exposed Fe species, i.e. extraframework Fe^{2+} and Fe^{3+} ions in isolated positions, in small extraframework clusters (like dinuclear ones) or present at the surface of bigger particles [15]. As a result, the close examination of the spectra of adsorbed NO allows the detailed exploration of all the accessible Fe^{2+} and Fe^{3+} surface sites, both isolated and clustered.

A not secondary advantage of the use of NO as probe of exposed Fe^{x+} sites, is related to the high IR intensity of the $Fe(NO)_n$ complexes: zeolite samples characterized by Fe concentrations as low as 800 ppm could be investigated [18]. This makes the method based on IR spectroscopy of the NO probe the most sensitive and the only one able to investigate the properties of samples containing 150–1000 Fe parts per million. This is particularly relevant because it has been shown that the activity of Fe sites in highly diluted samples (< 1000 ppm) is highest and that their number is compatible with α-oxygen population [13].

Coming back to the preparation methods, one of the most controversial post-synthesis preparation method, known as ‘‘the oxalate method’’, was proposed by Feng and Hall and consists into an aqueous exchange procedure, where iron(II) oxalate is used as precursor [9]. Following this procedure, a saturated solution of iron(II) oxalate was used for the zeolite exchange into a complicated apparatus designed to exclude the oxygen from the system (in order to avoid the oxidation of Fe^{2+} to Fe^{3+} and the subsequent precipitation of FeOOH and/or $Fe(OH)_3$). Notwithstanding the promising results initially obtained, the low reproducibility of the method designed to obtain samples containing only Fe^{2+} was soon evidenced, as deeply discussed by Marturano *et al.* [10]. Our attempts to use FeC_2O_4 for the exchange procedure also failed. In fact, as the salt solubility is very low, FeC_2O_4 precipitates from the solution onto the zeolite and can be almost completely removed by washing the zeolite with water, as already reported in Ref. [10].

The aim of this work is to propose a novel post-synthesis method for preparing highly dispersed Fe-ZSM-5, by aerobic aqueous exchange of H-ZSM-5 with an iron(III) oxalate solution, which is much more soluble than ferrous oxalate. We will show that the new method shows a good reproducibility, allowing the insertion of small amounts of highly dispersed iron species in an easy and reproducible manner. The high dispersion of the iron species will be tested by using NO as probe and compared to that obtained with other methods (Fe-ZSM-5 prepared by solid state exchange with $FeCl_2$ and Fe-based samples from isomorphously substituted Fe-MFI). The former preparation methods have been extensively studied in recent times [6,8], and led, in our laboratories, to better results (as catalytic activity and iron dispersion) with respect to the most commonly used $FeCl_3$ method [5]. The results obtained in this study will be the starting point for catalytic activity experiments regarding SCR of NO_x and N_2O decomposition reactions, in order to compare their activity with that of Fe-zeolites prepared by well-established methods.

2. Experimental

2.1. Materials preparation

Fe-exchanged ZSM-5 zeolites were prepared using two different methods: aqueous and solid state ion-exchange. The parent zeolite, NH_4-ZSM-5 (nominally $SiO_2/Al_2O_3 = 80$, $Na_2O = 0.05\%$ wt) was supplied by Zeolyst International. The protonic form H-ZSM-5 was prepared by calcination at 500 °C in vacuum of the parent zeolite.

For the aqueous ion-exchange equal quantities (0.3 g) of NH_4-ZSM-5 and H-ZSM-5 were added under stirring in two recipients, each one containing 5 mL solution 0.01 M iron(III) oxalate. The solution of iron(III) oxalate was prepared using $Fe_2(C_2O_4)_3 \cdot 6H_2O$ (99%, Aldrich) and deionised water. After 24 h the mixtures were filtered, washed with deionised water, dried in atmosphere and used for further investigations. During the impregnation, the ferric oxalate solution and the zeolite slurries were carefully kept away from light. The scaling-up of the method to larger amount of zeolites (3 g) was verified in subsequent experiments. The same procedure was also used without stirring the solutions. The characterisation results (not reported) showed results equal to those obtained by stirring. Similar results were obtained starting from NH_4-ZSM-5 and H-ZSM-5 zeolites. In the following the sample prepared by the oxalate method will be referred to as Fe-ZSM-5_{oxa}.

Solid state ion-exchange was performed using $FeCl_2$ as iron precursor, and the method was similar to that described by Long and Yang [8]. Sample prepared by the solid state method is referred in the text as Fe-ZSM-5_{ss}.

The Fe-ZSM-5 sample prepared by isomorphous substitution (0.08 Fe wt%, only reported for comparison) was synthesized in the laboratories of Prof. L. Forni (Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano) following the method described by Ratnasamy and Kumar [20]. After the synthesis the catalyst was washed, dried, and calcined in nitrogen and then air at 823 K to remove the organic molecule used as a template. The sample will be referred in the text as Fe-ZSM-5_{syn}.

2.2. Characterization

The IR experiments were performed on a Bruker IFS 66 FTIR instrument equipped with a cryogenic MCT detector and running at 2 cm^{-1} resolution. All the samples under study were in the form of self-supporting pellets suitable for measurements in transmission mode. Before the NO dosage the sample wafers were activated under vacuo at 773 K for 1 h directly in the IR measurement cells. Pure NO, freshly distilled from a NO_x mixture, was dosed on the activated sample at room temperature. After the first dose ($P_{NO} = 15$ Torr), NO was left in contact with the sample for 1 h, and the evolution of the spectra with time was followed by IR (not reported). Afterwards a sequence of IR spectra was recorded by gradually reducing the NO equilibrium pressure in the cell until $P_{NO} = 10^{-3}$ Torr.

The intensity of the NO spectra was "normalized" in terms of thickness of the zeolite pellet by measuring the intensity of the overtone bands in the 2100–1550 cm^{-1} range, which is proportional to the quantity of the siliceous matrix in the IR beam [14]. A second "normalization" of the NO spectra was made on the basis of the Fe content. The most diluted sample (Fe-ZSM-5_{syn}, 0.08 wt%) was chosen as a reference, i.e with a "normalization factor" of 1. The intensity of the bands obtained on the other samples was divided by a "normalization factor" corresponding to the ratio of the iron contents.

Chemical composition was determined by elemental analysis, by means of a Varian Vista Pro Axial ICP spectrometer. Fe-standard solutions were made from Spectrascan-standard (1000 ppm) delivered by Teknolab.

3. Results and discussion

3.1. The ferric oxalate method

The delicate step of the preparation method is to avoid photochemical reduction of Fe^{3+} to Fe^{2+} and the precipitation of FeC_2O_4, a well-known process [21] with applications in hydrometallurgy [22]. The problem of FeOOH and/or $Fe(OH)_3$ precipitation can be avoided since the formation of hydroxoiron(III) complexes as $(Fe_x(OH)_y)^{3x-y}$ does not happen at pH lower than 3 [23]. This requirement (pH < 3) has been fulfilled by using a solution 0.01 M iron (III) oxalate (pH ≈ 2.47). After the exchange, the pH values of the residual solutions were slightly increased, but still below 3 (≈ 2.7).

The speciation of oxalic acid as well as of the iron oxalato complexes (ferric and ferrous) has been extensively studied by Panianis and co-workers [23]. Based on their reports, and considering the measured values of pH before and after the zeolite functionalisation, we assume that the $[Fe(C_2O_4)]^+$ (oxalatoiron (III) ion) is involved in the ion exchange process, as depicted in schemes 1 and 2. The size of this ion could explain the low rate of exchange (*vide infra*). After the exchange procedure the mixtures were filtered, washed with deionised water and dried in atmosphere.

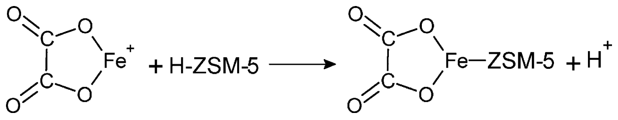
Before every experiment, the samples were activated under vacuo at 773 K for 1 h, this being the standard procedure for zeolite activation in our laboratories. After this treatment, no traces of the oxalate ligands were observed, neither by FTIR or UV-Vis spectroscopies (not reported). The nature of the Fe ions dispersed inside the zeolite channels after the thermal treatments was investigated by using FTIR spectroscopy associated with the use of the NO molecule as a probe (*vide infra*).

Thermal programmed desorption (TPD) analysis was used to follow the products generated during the zeolite activation. CO and CO_2 were observed in the 273–673 K temperature range, together with a major quantity of H_2O (data not reported for brevity). A possible mechanism for the decomposition of the oxalatoiron (III) ion is described in scheme 3. Following this mechanism an extraframework FeO^+ ion (where iron is still trivalent), would be generated as counterion. We anticipate in this section, that extraframework FeO^+ are not the ultimate sites present after the treatment *in vacuo* at 773 K. In fact, the results obtained by FTIR spectroscopy of adsorbed NO, will show that after thermal activation most of the iron sites dispersed inside the zeolite channels are present as Fe^{2+} ions. Possible reduction mechanisms from ferric to ferrous sites will be hypothesized and discussed.

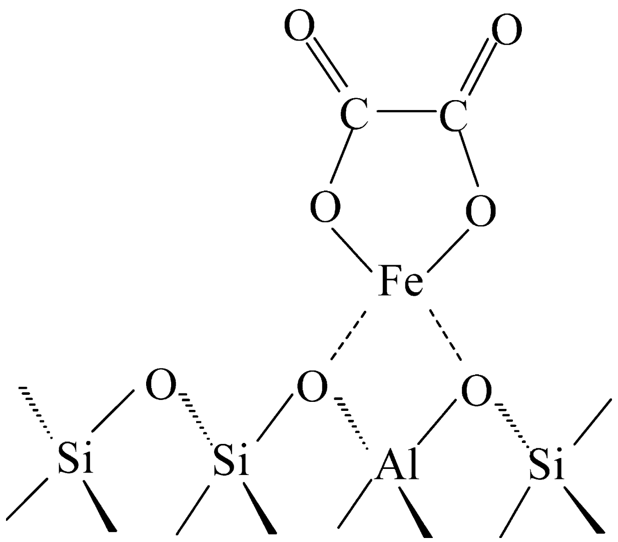
3.2. FTIR spectroscopy in the O–H stretching region

The effect of the ion-exchange processes with $Fe_2(C_2O_4)_3$ and $FeCl_2$ on the population of Brønsted sites is illustrated in figure 1, where the results obtained on the parent H-ZSM-5 zeolite are reported (full line). The spectra have been registered after activation under vacuo at 773 K. They are all composed by two major adsorptions: a sharp peak at 3745 cm^{-1} (with a shoulder at 3720 cm^{-1}) and a band at 3610 cm^{-1}. The sharp peak at 3745 cm^{-1} is due to isolated Si–OH groups present on the external surface of the zeolite particles, while the band at 3610 cm^{-1} is related to Si(OH)Al Brønsted sites.

The main changes caused by the ion-exchange processes are associated with the intensity of the Brønsted Si(OH)Al band at 3610 cm^{-1}. In fact, after ion exchange, the intensity of this band slightly decreases for the aqueous exchanged sample (Fe-ZSM-5_{oxa}, dashed line),



Scheme 1. A possible mechanism for ion exchange in aqueous solution of iron(III) oxalate.



Scheme 2. Proposed structure for iron species in Fe-ZSM-5 after the ion exchange.

$$\mathrm{Fe(C_2O_4)^+} \longrightarrow \mathrm{FeO^+ + CO + CO_2}$$

Scheme 3. Proposed mechanism for thermal decomposition of the oxalatoiron (III) ion.

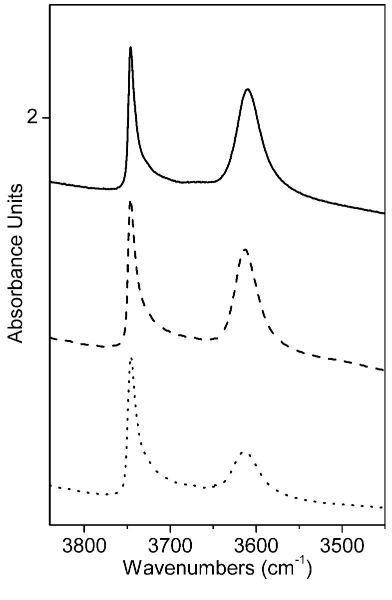


Figure 1. FTIR in the OH stretching region of samples outgassed at 773 K. From top to bottom: H-ZSM-5 zeolite before any exchange (full line); Fe-ZSM-5 prepared through aqueous exchange with iron(III) oxalate (Fe-ZSM-5_{oxa}, dashed line) and by solid state exchange with iron(II) chloride (Fe-ZSM-5_{ss}, dotted line).

and for the sample prepared by the solid state method (Fe-ZSM-5_{ss}, dotted curve). The intensity decrease is more evident for Fe-ZSM-5_{ss}, corresponding to a 65% decrease, while only a 12% decrease is measured in Fe-ZSM-5_{oxa}. The different entity of the OH Brønsted band perturbation in the two samples could be related to the different Fe content of the samples being 3.30 and 0.38 wt% Fe, respectively (table 1). Notice that the exchange of the Brønsted groups by iron cations is not easily achieved in ZSM-5 (characterized by low Al content), especially when ferric precursors are used, since the latter should exchange three vicinal H^+ counterions. However, on the basis of what discussed in section 3.1, we propose for the sample prepared *via* the oxalate method the exchange mechanisms reported in schemes 1 and 2, involving monovalent $Fe(C_2O_4)^+$ cations and a minor fraction of the Brønsted sites. Tentatively, the low percentage of exchange of the sample could be related to the big size of the $Fe(C_2O_4)^+$ cation.

3.3. FTIR spectroscopy of Fe nitrosyl complexes

FTIR spectroscopy of adsorbed NO is a well-established method to explore iron sites dispersed in inorganic matrices, as testified by the rich literature reporting IR spectra of Fe nitrosyl complexes in zeolites [12,16,17,19]. From the literature on iron nitrosyl complexes in different organic and inorganic matrices, it appears that the nitrosyl frequency (ν_{NO}) is strongly influenced by the iron oxidation state. In particular, other conditions being equal, ferric nitrosyl complexes usually show higher ν_{NO} with respect to ferrous ones [24,25]. The ν_{NO} values reported in literature for Fe^{2+} and Fe^{3+} complexes either isolated (usually in homogeneous systems) or at the surface (such as supported oxides) are plotted in figure 2a. The ν_{NO} values were grouped on the basis of the iron oxidation state and of the number of NO ligands. Data concerning nitrosyls of iron ions complexed by ligands such as porphyrins [26–28], imidazole [29] or ditholene [25] were not reported in figure 2a. These ligands, containing N and S atoms usually not present on the surface, are not mimicking the surface complexes.

The number of NO ligands adsorbed by each Fe centre is a direct indication of their local environment. Mononitrosyl complexes of Fe^{2+} and Fe^{3+} ions can be formed on surface sites carrying a single coordination vacancy, which are present at the surface of clusters and particles. On the contrary, polinitrosyl complexes can only be formed at exceptionally unsaturated sites, with a small number of ligands in the coordination sphere. These sites are most probably isolated and grafted. For this reason they can be considered as indicative of atomic dispersion. Another corollary deriving from comparison of the data reported in figure 2 and the experimental ones (*vide infra*) is that the ratio between the intensity of the bands of the mononitrosyl species and the polinitrosyl ones cannot be used to directly quantify the clustered/isolated ions ratio. In fact, the mononitrosyl bands, being associated only with the exposed ions at the surface of clusters, cannot give information on the sub-surface atoms, and thus on their number.

Table 1
Chemical composition of the samples

Sample	Fe (wt%)	Al (wt%)
Fe-ZSM-5_{ss}	3.30	1.02
Fe-ZSM-5_{oxa}	0.38	1.02
Fe-ZSM-5_{syn}	0.08	2.26

To further complicate the situation, from figure 2 it clearly appears that the IR spectroscopy of $Fe^{x+}(NO)_n$ is extremely complex, since bands due to $Fe^{3+}(NO)$, $Fe^{2+}(NO)$, $Fe^{2+}(NO)_2$ and $Fe^{2+}(NO)_3$ complexes are found in a limited spectral range (1950–1700 cm^{-1}) and are often superimposed. This explains the lively discussion about the Fe-nitrosyl bands assignment found in literature [12]. The assignment of the different nitrosyl components could be possible only by performing experiments with 1:1 $^{14}NO/^{15}NO$ mixtures [17, 30]. These experiments definitely confirmed the assignment to $Fe^{2+}(NO)_2$ and $Fe^{2+}(NO)_3$ complexes of the two couples of bands reported in figure 2 (*vide infra* for a more detailed assignment).

In figure 2b the typical nitrosyl bands formed upon NO adsorption on the Fe-ZSM-5_{oxa} sample, prepared with the oxalate method and subsequently activated *in vacuo* at 773 K are reported. From comparison with figure 2a, we can try to assign the complex spectroscopy in the 1950–1700 cm^{-1} range. More in detail (see table 2 for a summary of the assignments):

i) the broad and asymmetric adsorption at 1880 cm^{-1}, practically unperturbed by the decrease of P_{NO}, is assigned to $Fe^{3+}(NO)$ complexes formed on the surface of clusters;
ii) the couple of bands at 1918 and 1807 cm^{-1}, gradually decreasing with P_{NO}, is related to $Fe^{2+}(NO)_3$ complexes;
iii) the pair at 1846/1767 cm^{-1}, growing upon NO removal, is assigned to $Fe^{2+}(NO)_2$;
iv) the 1:1 transformation of the couple at 1918 and 1807 cm^{-1} into the one at 1846/1767 cm^{-1} by dec reasing P_{NO}, is testified by the presence of three well-defined isosbestic points at 1852, 1838 and 1776 cm^{-1};
v) the previous transformation has been explained with the $Fe^{2+}(NO)_3 \rightleftharpoons Fe^{2+}(NO)_2$ equilibrium [17, 30];
vi) the Fe^{2+} species able to add up to 3 NO ligands are isolated species;
vii) a small component around 1840 cm^{-1} is assigned to $Fe^{2+}(NO)$ species, formed on the surface of small clusters.

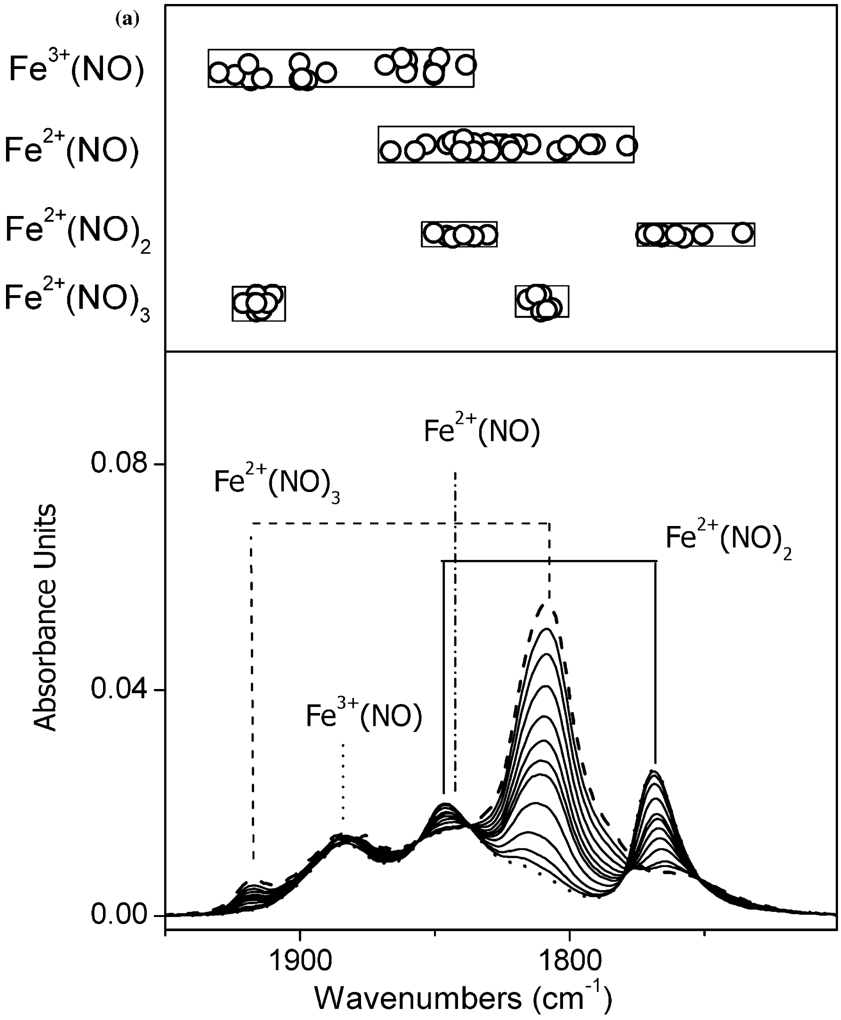


Figure 2. Part (a): Frequencies of ν_{NO} in different Fe nitrosyl complexes formed in mononuclear homogeneous systems or on supported oxides. Data were taken from: Refs. [15,30–46] for $Fe^{3+}(NO)$ complexes; Refs. [15,17,18,35,47–52] for $Fe^{2+}(NO)$; Refs. [15,17,18,35,48,50–52] for $Fe^{2+}(NO)_2$; Refs. [15,17,18,30,35,48,50,53] $Fe^{2+}(NO)_3$ ones. Part (b): FTIR spectra of NO dosed at room temperature (decreasing P_{NO} from 15 Torr, dashed line spectrum to 10^{-3} Torr, dotted line spectrum) on Fe-ZSM-5_{oxa} sample previously activated *in vacuo* at 773 K.

Notice that the previous assignment implies that, in the sample prepared by the ferric oxalate methods, Fe^{2+} extraframework sites are formed upon activation *in vacuo* at 773 K. This indicates that a reduction from Fe^{3+} (ferric oxalate) to Fe^{2+} sites has occurred during thermal activation. This phenomenon will be discussed in the following section.

3.4. Comparison of IR nitrosyl bands formed on different Fe- samples

The results obtained by IR spectroscopy of adsorbed NO on sample prepared by the ferric oxalate method (Fe-ZSM-5_{oxa}, figure 3b) are compared in figure 3 with two other "classical" Fe-ZSM-5 samples, activated in the same conditions (773 K *in vacuo*). More in detail, results obtained on Fe-ZSM-5_{ss} (prepared by solid state exchange with $FeCl_2$) and on Fe-ZSM-5_{syn} (isomorphously substituted sample) are reported in figure 3a and 3c, respectively. All spectra were normalized with respect to the iron content crossed by the IR beam, as detailed in the experimental section.

Sample Fe-ZSM-5_{ss} (figure 3a) was chosen as a reference for "classical" post-synthesis exchanged samples, following the procedure reported in Ref. [8]. This method lead, in our lab, to better results (in terms of

Table 2
Assignment of the ν_{NO} to iron complexes

Complexes	Frequencies	Assignment
$Fe^{3+}(NO)$	1880 cm^{-1}	clustered sites
$Fe^{2+}(NO)$	1840 cm^{-1}	clustered sites
$Fe^{2+}(NO)_2$	1918 and 1807 cm^{-1}	isolated sites
$Fe^{2+}(NO)_3$	1846 and 1767 cm^{-1}	isolated sites

Note: The reported frequencies were measured on sample Fe-ZSM-5_{oxa} previously activated *in vacuo* at 773 K.

iron dispersion and preliminary catalytic tests) with respect to the most commonly used $FeCl_3$ method [5]. Similar results were also obtained by aqueous exchange with the Mohr salt (not reported) following the recipe suggested in [7]. Notices that all these "classical" exchanged samples are characterized by an intense orange-red colour, suggesting the presence of Fe_2O_3 aggregates, while Fe-ZSM-5_{oxa} is white.

The second sample used for comparison (Fe-ZSM-5_{syn}, figure 3c), is a highly diluted isomorphously substituted sample. This sample was chosen for direct comparison because the very low iron content (800 ppm) allows to consider it as a model system, were isolated Fe^{2+} sites are the predominant species [14]. We anticipate that the iron dispersion obtained in this sample is among the highest reported the literature, allowing to infer that almost every Fe atom is involved in the formation of active α oxygen [4, 13, 14]. The colour of this sample is white, even after activation at high temperature.

Coming to the discussion of the spectra of figure 3, the first observation regards the overall intensity of the bands, which is increasing in the in the order Fe-ZSM-5_{ss} < Fe-ZSM-5_{oxa} < Fe-ZSM-5_{syn}. Since NO is probing all the exposed iron sites, the intensity of the nitrosyl bands can be used, to a first approximation, to estimate the fraction of accessible Fe sites, and thus give an indication on the dispersion of iron ions [14, 15, 18]. Notice that the intensity of the bands is lowest for the sample with the higher Fe amount (Fe-ZSM-5_{ss}, figure 3a), indicating that in this sample a major fraction of Fe ions is silent, i.e. inside Fe_xO_y aggregates. The intensity of the bands obtained on Fe-ZSM-5_{oxa} is quite close to that of sample of Fe-ZSM-5_{syn}, considered as a model system, where the highest iron dispersion is obtained. This suggests that the present version of the oxalate method allows good iron dispersion.

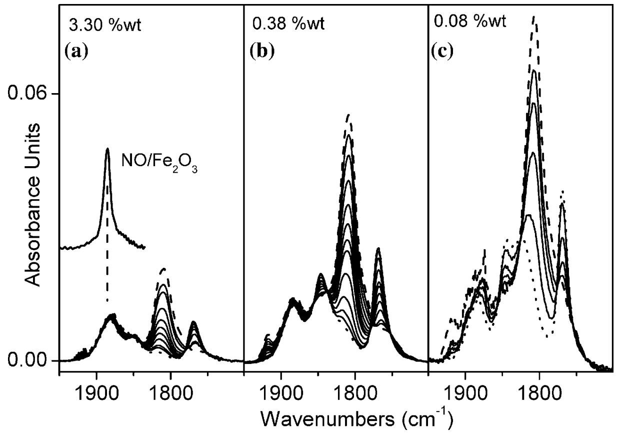


Figure 3. FTIR spectra of NO dosed at room temperature (decreasing P_{NO} from 15 Torr, dashed line spectrum to 10^{-3} Torr, dotted line spectrum) on (a) Fe-ZSM-5_{ss}, (b) Fe-ZSM-5_{oxa}, and (c) Fe-ZSM-5_{syn}, samples previously activated *in vacuo* at 773 K. Spectra were normalized with respect to the pellet thickness and with respect to the iron content as detailed in the experimental section. Top spectrum of part a): 15 Torr of NO on Fe_2O_3 sample (ex-goethite) outgassed and oxidized at 773 K.

Coming to the band at 1880 cm^{-1}, we think that it is related to Fe^{3+}(NO) complexes formed on clustered species. This assignment is not only supported by the data of figure 2a, but also by direct comparison with the result obtained upon NO adsorption on Fe_2O_3 sample (ex-goethite, oxidized at 773 K, top spectrum in figure 3a). The relative intensity of this feature increases in the order: Fe-ZSM-5_{ss} > Fe-ZSM-5_{oxa} > Fe-ZSM-5_{syn}, as expected. All these observations strongly suggest that the amount of clustered species increases in the order: Fe-ZSM-5_{syn} < Fe-ZSM-5_{oxa} < Fe-ZSM-5_{ss}. Due to the superimposition of the different components, it is not possible to clearly quantify the behaviour upon iron concentration of the component at around 1840 cm^{-1}, assigned to Fe^{2+}(NO) complexes on aggregates.

We can thus conclude that the oxalate method allows the preparation of Fe-zeolite with a good iron dispersion, standing comparison with very diluted sample prepared by isomorphous substitution, which showed the best performances in selective oxidation reactions [13, 14].

As a last remark, we underline the fact that in all samples extraframework Fe^{2+} sites are present after activation *in vacuo* at 773 K. The presence of Fe^{2+} sites is not surprising in the Fe-ZSM-5_{ss} sample, since ferrous chloride was used as iron precursor. On the contrary, Fe^{3+} ions were the starting point in both Fe-ZSM-5_{oxa} and Fe-ZSM-5_{syn}. The reduction of framework Fe^{3+} ions to extraframework Fe^{2+} sites during thermal activation in controlled atmosphere (vacuo or He flow) is a well-known phenomenon for isomorphously substituted systems [4, 13, 15]. Notwithstanding the fact that many author reported this phenomenon, a plausible mechanism for this reduction has never been proposed.

Concerning the oxalate sample, a plausible mechanism for the thermal decomposition of the $Fe(C_2O_4)^+$ cations is reported in Scheme 3. In this scheme, the 3+ oxidation state of iron is maintained. However, FeO^+ ion cannot be considered as the final species present inside the zeolite channels after the thermal activation, because we have seen that NO probes Fe^{2+} species. We so infer that FeO^+ ion undergoes reduction at high temperature *in vacuo*. We were not able to draw a mechanism for the reduction of FeO^+ ions to the Fe^{2+} sites, able to adsorb 3 NO molecules. We can just hypothesize that the mechanism is similar to that acting during thermal activation of isomorphously substituted samples.

As a final remark, we anticipate that, concerning the isolated Fe^{2+} species described above, we are not dealing with a unique species, but with one family of oxo-iron species, characterized by different local structures and levels of coordination, as already proposed in Ref. [15]. The formation of these species is strongly related to the method of iron exchange, the nature of iron precursors, the thermal treatment, the aluminium content of the zeolite matrix and, not the last, with the amount of iron in the zeolite. Notice that in the samples reported in this work, the position of $Fe^{2+}(NO)_n$ nitrosyl bands is found at distinctly higher frequency with respect to those reported for the same complexes on Al-free Fe-silicalite [15]. This is in agreement with the hypothesis that Fe species are formed in the immediate vicinity of framework Al, as observed in Ref. [18] and depicted in scheme 3.

4. Conclusions

Fe-ZSM-5 sample containing highly dispersed iron species can be easily prepared by aerobic aqueous ion exchange in 0.01 M iron (III) oxalate solution. Low iron content zeolites (0.38 wt% Fe) were obtained, and the reproducibility of the results was checked. The achieved iron content seems to be not sensitive to the counter-ion of the parent zeolite, similar results being obtained for protonic and ammonia form of the matrix. The presence of different iron species inside the zeolite pores was investigated by IR spectroscopy of adsorbed NO. The results were compared with those obtained on a sample prepared by solid state exchange with $FeCl_2$, and by isomorphous substitution during the synthesis. The former sample showed better results (in terms of iron dispersion and catalytic activity) in our laboratories when compared to the most famous $FeCl_3$ CVD method. The latter was considered as a "model" sample, characterized by well-defined isolated extraframework Fe^{2+} sites. In all the samples a mixture of clustered and isolated sites was observed, the former giving mononitrosyl complexes and the latter polinitrosyl ($Fe(NO)_n$, $n=2$, 3) ones. The fraction of clustered sites was found to be higher in the sample prepared by solid state exchange with FeCl2, while that of isolated sites was major in Fe-ZSM-5_{syn}. On the basis of the characterization results, we report that the sample prepared by the new method showed an iron dispersion close to that of the latter catalyst. We can thus conclude that the oxalate method allows the preparation of Fe-zeolite with good iron dispersion, standing comparison with very diluted sample prepared by isomorphous substitution, which showed the best performances in selective oxidation reactions [13, 14].

In conclusion, our method allowed the formation of a major fraction of well-dispersed isolated Fe species, likely formed in the close vicinity of framework Al. The concurrent formation of clustered Fe species could not be totally avoided. However, the concentration of clustered species seems less important with respect to the sample prepared by classical methods (solid state exchange with $FeCl_2$). The ferric oxalate method is thus promising for the preparation of catalysts for the one-step oxidation of benzene to phenol, where the presence of low iron content is crucial. The catalytic activity of the Fe-ZSM-5_{oxa} catalysts in different reactions (N_2O decomposition and $deNO_x$ with hydrocarbons) is the subject of our further investigations.

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