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Catalytic activity of Fe ions in iron-based crystalline and amorphous systems: role of dispersion, coordinative unsaturation and Al content

Gloria Berlier, Gabriele Ricchiardi, Silvia Bordiga, Adriano Zecchina *

Università di Torino, Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Via P. Giuria 7, 10125 Torino, Italy
INSTM UdR di Torino Università, Via P. Giuria 7, 10125 Torino, Italy
NIS Center of Excellence, University of Torino, Italy

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Abstract

Different Fe-based materials, where iron ions are anchored on crystalline and amorphous siliceous supports are studied by FTIR spectroscopy of adsorbed NO and in the N_2O decomposition reaction test. The influence of Al concentration is also considered. We show that the coordination state of Fe dramatically changes when Fe is anchored on crystalline or amorphous matrices. In crystalline Fe-ZSM-5 and Fe-silicalite samples highly coordinatively unsaturated and isolated Fe sites are present, which form $Fe^{2+}(NO)_2$ and $Fe^{2+}(NO)_3$ complexes upon NO contact. The presence of oxidic clusters, forming $Fe^{2+}(NO)$ complexes, whose relative concentration strictly depends upon the presence of Al and the concentration of Fe, is also evidenced. Fe-ZSM-5 sample ($Si/Fe = 1120$) mainly contains isolated Fe^{2+} ions characterised by high coordinative unsaturation. This sample also shows the highest activity in N_2O decomposition, indicating that isolated and coordinatively unsaturated Fe sites are the most active precursors for the catalytic reaction. It is thought that adsorbed oxygen is formed, upon N_2O decomposition, on both isolated and oxidic clusters, forming ferryl groups in the former case and bridged structures in the latter.

Keywords: Fe-ZSM-5; α-Oxygen; $Fe(NO)_n$ complexes; IR spectroscopy; N_2O decomposition

1. Introduction

Fe-containing zeolites (in particular Fe-silicalite and Fe-ZSM-5) are currently the subject of an animated scientific debate due to their catalytic activity in the one-step conversion of benzene to phenol using N_2O as oxidising agent. This reaction represents a promising and environmentally friendly alternative to the commonly used three-step process via cumene, since N_2 is the only co-product [1,2]. The catalysts are isomorphously substituted zeolites containing very low iron amounts, which become active after severe thermal treatments leading to migration of iron from framework to extraframework positions [3–6]. Migration induced by treatments in vacuo at high temperature is also accompanied by extensive reduction of iron from ferric to ferrous ions as documented in Refs. [6,7]. The so-formed extraframework iron sites are thought to be the precursors of the catalytically active sites: they are able to decompose N_2O with formation of the so-called α-oxygen, which is assumed to play the key role for selective oxidation of benzene [4,7].

The nature of the iron sites responsible for N_2O decomposition is still under debate. The more controversial point regards their nuclearity, which can have important consequences on the structure of active adsorbed oxygen (α-oxygen). In fact, if dinuclear structures or small clusters are responsible (as proposed by many authors [8,9]), α-oxygen is most likely an $O^=$ bridged species like in methane monooxygenase [10]. If only isolated iron ions are the active sites, oxygen interacts with a single iron site, and the α-oxygen could be analogous to oxygen in the ferryl group of heme enzymes [11]. As isolated and oxidic clusters could be simultaneously present, it can be plausibly inferred that both types of oxygen types are formed on the same sam-

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[*] Corresponding author. Fax: +39-011-6707855.
E-mail address: adriano.zecchina@unito.it (A. Zecchina).

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ples. The presence of catalytically active isolated Fe sites has been recently documented by the group of Bell on the basis of DFT [12–14] and EXAFS investigations [15]. The same conclusion can be found in the late works coming from the group of Sachtler, where combined FTIR measurements and catalytic tests showed the higher activity of mononuclear Fe sites [16,17]. Dubkov et al. have proposed an intermediate situation [7], hypothesising that α-sites are binuclear complexes in which each Fe^{2+} atom is independently absorbing a single oxygen atom forming two $Fe^{3+}O^{-}$ groups.

A second important point of debate is the role of Al in determining the structure of the sites and their catalytic activity. It is in fact well known that the activity of Al-containing Fe-ZSM-5 is higher than the analogous Al-free Fe-silicalite with the same iron content [4,18,19]. This led some authors to conclude that Al can catalyse the reaction by creating strong acidic sites [20,21] or that the effective active sites are Al Lewis sites [22–24]. However, these hypotheses have never been proved, while the main role of iron was invariably confirmed [18,25]. In a recent paper, Hensen et al. proposed that the active sites are extraframework Fe–Al–O entities [26], whose structure has not been elucidated. A mononuclear Fe ion, interacting with a zeolite portion containing Al in close vicinity, has been proposed by Ryder et al. [12,13] and Liang et al. [14] on the basis of DFT calculations. The exhibited role of Al in stabilising extraframework mononuclear Fe sites has been elucidated by the EXAFS studies of Choi et al. [27]. Moreover, Wichterlová et al. showed that Fe–oxo structures, acting as counterions in proximity of framework Al^{3+}, are characterised by high catalytic activity [28]. All these results are in good agreement with our findings that extraframework isolated Fe^{2+} ions with one or two atoms of Al in the immediate vicinity could be the precursors of the active sites in partial oxidation reactions [29].

A third point of debate concerns the coordination state of iron in the active sites. One of the methods for investigating the coordinative unsaturation of dispersed metal ions involves the use of suitable probe molecules, able to interact with the exposed and accessible ions. In previous papers we demonstrated that NO is an efficient probe for Fe sites, since it is able to monitor and 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 [6,29–31]. In fact NO shows high affinity toward coordinatively unsaturated Fe^{2+} and Fe^{3+} ions, leading to the formation at room temperature of well-defined and stable complexes $Fe(NO)_n$ ($n = 1, 2, 3$), characterised by strong IR activity [6,29,31]. The maximum number of NO ligands adsorbed by each Fe^{2+} and Fe^{3+} centre represents a direct indication of their coordinative unsaturation [6]. For all these reasons the NO probe allows the detailed and comprehensive exploration of *all* the accessible Fe surface sites. Of course, Fe sites not located in surface positions (and hence surely not active, such as bulk atoms in Fe_xO_y particles or Fe^{3+} located in framework positions) escape this probing procedure.

In a series of experimental studies, it has been established that isolated and low coordinated Fe^{2+} sites, in extraframework positions of Fe-silicalite zeolite, originate $Fe^{2+}(NO)_2$ and $Fe^{2+}(NO)_3$ complexes adsorbing at 1835/1764 and 1915/1810 cm^{-1}, respectively [6,30]. When Al-containing Fe-ZSM-5 samples were studied, the IR bands corresponding to the same complexes were found at higher frequency: 1845/1769 cm^{-1} for $Fe^{2+}(NO)_2$ and 1919/1812 cm^{-1} for $Fe^{2+}(NO)_3$ [29]. Fe^{2+} sites at the surface of clusters (mainly observed in Fe-silicalite samples) formed only $Fe^{2+}(NO)$ compounds, adsorbing in the 1825–1835 cm^{-1} range, while exposed Fe^{3+} sites originated $Fe^{3+}(NO)$ complexes adsorbing in the 1910–1875 cm^{-1} range [6]. Like observed for homogeneous nitrosyl analogues [32–34], the ν_{NO} bands were characterised by high extinction coefficients and high dependence upon the valence state of iron. The high intensity of these bands allowed the investigation of very diluted samples, i.e., with a concentration of iron below the detectability limit of most characterisation techniques.

The same technique was used to study Fe-based amorphous samples, such as high surface area Fe/SiO_2 and Fe-MCM-41 [31]. On this kind of samples NO mainly revealed the presence of two surface Fe sites characterised by low coordinative unsaturation. The first type of surface species, likely present at the surface of small oxidic clusters, is only able to adsorb one NO molecule, giving $Fe^{2+}(NO)$ complexes adsorbing at 1774 cm^{-1}. The second type originates (upon varying NO pressure) $Fe^{2+}(NO)$ and $Fe^{2+}(NO)_2$ compounds, resulting in IR nitrosyl bands at 1830 and 1876/1805 cm^{-1}, respectively [31]. The lower number of NO molecules adsorbed by Fe sites on amorphous supports (as compared to the crystalline case) shows how the coordinative degree of the metallic ions can be easily tuned by changing the crystallinity of the matrix.

In this work, the procedures already described are used to get information on the influence of Al concentration upon the accessibility and coordinative state of Fe ions grafted on different supports (crystalline and amorphous). The spectroscopic results were then correlated to the catalytic activity in the N_2O decomposition reaction, used as simple reaction test for exploring the activity of exposed Fe^{x+} sites. This reaction has been chosen among all catalysed by Fe-based materials because of its simplicity. The comparison of the characterisation and activity results on the same samples represent a first attempt to close the gap between characterisation and catalysis.

2. Experimental

Fe-silicalite and Fe-ZSM-5 samples were prepared in the laboratories of Prof. L. Forni (Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano) following the method described by Ratnasamy and Kumar [35]. These samples showed surface areas between 500 and 540 cm^2/g, as described in detail in Ref. [36]. After the synthesis the catalysts were washed, dried, and calcined in nitrogen and then in air at 823 K. Their chemical composition was determined by elemental analysis, as described in [36].

The Fe/SiO_2 material was prepared by wet impregnation of a high surface area silica (Aerosil, 296 m^2/g) with a solution of $Fe(NO_3)_3$. The concentration of the nitrate solution was calculated in order to obtain a 0.7 wt% in Fe. A solution of $Al(NO_3)_3$ was used to prepare the Al_2O_3/SiO_2 sample, which was subsequently impregnated with a solution of $Fe(NO_3)_3$ in order to obtain the $Fe/Al/SiO_2$ sample used in the experiments. The calculated amounts of Al and Fe corresponded to 1 and 0.34 wt%, respectively. The chemical composition of the amorphous samples was successively confirmed by EDX analysis on a SEM Stereoscan 400 Oxford apparatus.

Prior to FTIR experiments, the samples were compressed into 1.5 × 1.5 cm pellets for high temperature activation in vacuum. Pellets were weighted and their thickness carefully measured. Prior to catalytic tests, powdered samples were activated in a nitrogen flow at the desired temperature.

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. Suitable measurement cells were used allowing in situ thermal treatments and dosing of NO. NO, carefully purified by distillation, was initially dosed at room temperature ($P_{NO} = 15$ Torr); the equilibrium pressure was reduced step by step, thus allowing to obtain a sequence of IR spectra corresponding to decreasing NO coverage. The first spectrum collected just before the initial gas dosage was used as a reference for obtaining the background-subtracted spectra, that are reported in the following.

The intensity of the NO spectra was "normalised" in terms of weight and thickness of the siliceous matrix following two procedures. The first one is based on the weight and thickness of the pellets, carefully measured before and after every experiment. The second procedure is based on 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. This normalisation is very precise when Fe-ZSM-5 and Fe-silicalite are compared (because we are dealing with the same crystalline matrix). The same holds for the comparison of silica-based materials. Comparison of silicalite and silica-based materials with this method is not precise (because the overtone bands have different width). For this comparison only the first method was used. We estimate that this normalisation is sufficiently accurate to allow semiquantitative considerations.

A second "normalisation" of the NO spectra was made on the basis of the Fe content. The most diluted sample (Fe-ZSM-5, 0.08 wt%) was chosen as a reference, i.e., with a "normalisation factor" of 1. The intensity of the bands obtained on the other samples was divided by a "normalisation factor" corresponding to the ratio of the iron contents.

The catalytic N_2O decomposition was carried out in a fixed-bed reactor connected to a gas chromatograph equipped with TCD detector for the analysis of reactant and product gases. Before every run the catalysts were activated in nitrogen flow. The reaction was carried out in the temperature range from 673 to 900 K. Different feed compositions were used, that is 100 vol% N_2O, 50, 3.3, and 1.5 vol% N_2O in He. The activity of the catalysts was investigated using different amounts of catalyst (100 and 200 mg) and different total flows, resulting in GHSV = 600, 900, 3600, and 27,000 h^{-1}. Since the results were qualitatively similar along the whole range of experiments (as far as the activity comparison is concerned), we only report about the results obtained using 3.3 vol% of N_2O in He, total flow of 150 cm^3/min, resulting in GHSV = 27,000 h^{-1}. N_2O decomposes stoichiometrically into N_2 and O_2 and neither NO nor NO_2 was detected during the experiments. To compare the activity per Fe atom in the different catalysts, turnover frequency values, calculated as number of N_2 molecules produced per second per atom of Fe, were also reported.

Volumetric analysis (N_2 adsorption at 77 K) was performed on the catalysts after the catalytic tests and no mesoporosity formation was observed.

3. Results and discussion

Two different typologies of Fe-containing samples were considered: (a) crystalline MFI zeolites and (b) amorphous silica-based samples. In both cases Al-free and Al-containing samples were considered. In the following, Al-free MFI zeolite will be referred to as Fe-silicalite, and Al-containing zeolite as Fe-ZSM-5. Regarding the amorphous materials, Fe/SiO_2 and $Fe/Al/SiO_2$ samples will be considered. The chemical composition of the various samples is displayed in Table 1. Notice that Fe-ZSM-5 sample is characterised by a very low Fe content ($Si/Fe = 1120$). The choice of such diluted samples is justified, since the low iron content surely minimises the presence of dimeric and larger oxidic clusters and optimises the concentration of isolated sites. In other words, in our hope the Fe-ZSM-5 sample could be considered as a single-site model catalyst, where the presence of isolated Fe ions is predominant.

3.1. Activity in N_2O decomposition

N_2O decomposition was carried out in a wide range of experimental conditions, that is in the temperature range

Table 1
Chemical composition of the samples

Sample	Fe (wt%)	Al (wt%)
Fe-silicalite	1.33	–
Fe-ZSM-5	0.08	2.26
Fe/SiO_2	0.70	–
$Fe/Al/SiO_2$	0.34	1.00

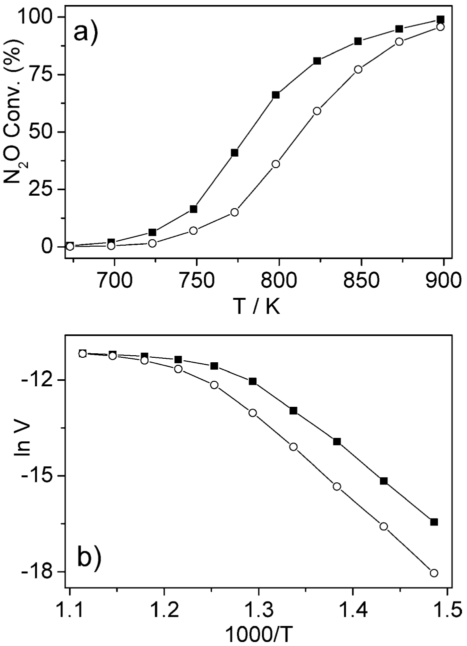

Fig. 1. (a) N_2O conversion (%) of samples Fe-ZSM-5 (■) and Fe-silicalite (○) previously activated at 1073 K, in the 673–900 K temperature range, 3.3 vol% N_2O in He (GHSV = 27,000 h^{-1}). (b) Corresponding plot of the natural logarithm of the reaction rate against the inverse of reaction temperature.

from 673 to 900 K, using different feed composition, different amounts of catalyst, and different total flows. Since the results were qualitatively similar along the whole range of experiments (as far as the activity comparison is concerned), we hereafter report about the results obtained using 3.3 vol% of N_2O in He, GHSV = 27,000 h^{-1}, on the catalysts previously activated at 773 and 1073 K.

The increase of activity with reaction temperature is compared in Fig. 1a for samples Fe-silicalite and Fe-ZSM-5 previously activated at 1073 K. This is a general trend, as reported by several authors [19,37–40]. From Fig. 1a the higher activity of Fe-ZSM-5 with respect to Fe-silicalite, along the whole temperature range, is verified. These results are qualitatively similar to those recently reported by Pérez-Ramírez et al. [19]. From the data of Fig. 1a we calculated the corresponding reaction rate, assuming the isothermicity of the catalyst bed (which has been verified, as the amount of catalyst is very small). This approximation only holds for low conversion levels (that is, a differential reactor), which in our case is true at low temperatures [41]. The calculated reaction rate was plotted against the inverse of temperature in Fig. 1b. By assuming a first reaction order for N_2O decomposition [37,42], this plot can be considered an Arrhenius diagram, allowing the discrimination between kinetic and diffusion controlled regimes [42]. In particular, the low temperature range, where the conversion is low and linearly increases with temperature, can be considered as the kinetic regime where the reaction rate is not affected by diffusion phenomena. From the data of Fig. 1 we infer that the reaction is kinetically controlled in the 673–800 K range. In conclusion we confirm that the Fe-ZSM-5 sample is more active than Fe-silicalite (and the amorphous materials) in the whole range of temperatures.

A more detailed analysis of the activity and stability of all the catalysts at a given temperature (773 K) is hereafter reported. By comparing the activity of the four catalysts in the same experimental conditions, we firstly notice that the activity of the catalysts increases upon increasing the activation temperature (Table 2). This fact is not surprising for Fe-based zeolites where iron (introduced during the synthesis) is at first mainly present in framework positions: it is in fact a general finding that high temperature activation favours the migration of Fe into extraframework positions, thus generating a higher concentration of active Fe sites [7,26–43]. The migration of Fe into extraframework positions is the consequence of the breaking of framework Fe–O–Si bonds, caused by the synergic action of temperature and traces of water present inside the zeolitic channels [5,6,44]. The same explanation does not hold for the amorphous M/SiO_2 (M = Fe or Fe/Al) materials, where all iron is ab initio in extraframework positions being grafted to the external silica surface or clustered in form of small iron oxide particles [31,45]. We could thus suggest that dehydroxylation and surface rearrangements, induced by high temperature activation, are favouring the general increase of activity with activation temperature.

The behaviour of the catalytic activity with time is variable. In Fig. 2 the catalytic activities in N_2O decomposition (reaction temperature = 773 K, GHSV = 27,000 h^{-1}) of the four samples previously activated at 1073 K are compared. From Fig. 2 we see that the activity gradually increases with time (this is particularly evident for the Fe-ZSM-5 catalyst). This trend is quite unusual, since most often a slow deactivation to steady state was reported [46]. We also observed

Table 2
Catalytic activity in N_2O conversion after different activations

Sample	N_2O conversion (%)[a]		T.O.F. (s^{-1})[b]	
	773 K	1073 K	773 K	1073 K
Fe-silicalite	7.6 ± 0.7	15.4 ± 4.8	$6 \times 10^{-3} \pm 5 \times 10^{-4}$	$0.01 \pm 6 \times 10^{-4}$
Fe-ZSM-5	6.9 ± 0.8	41.8 ± 2.5	$0.07 \pm 8 \times 10^{-3}$	0.43 ± 0.07
Fe/SiO_2	1.1 ± 0.4	4.5 ± 0.7	$6 \times 10^{-4} \pm 2 \times 10^{-4}$	$2 \times 10^{-3} \pm 4 \times 10^{-4}$
Fe/Al/SiO_2	0.7 ± 0.2	4.2 ± 0.9	$1 \times 10^{-3} \pm 3 \times 10^{-4}$	$6 \times 10^{-3} \pm 1 \times 10^{-3}$

[a] The average N_2O conversion (%) was calculated along the 100–1000 min of reaction.

[b] Turnover frequency values were calculated as number of molecules of N_2 produced per second per atom of Fe.

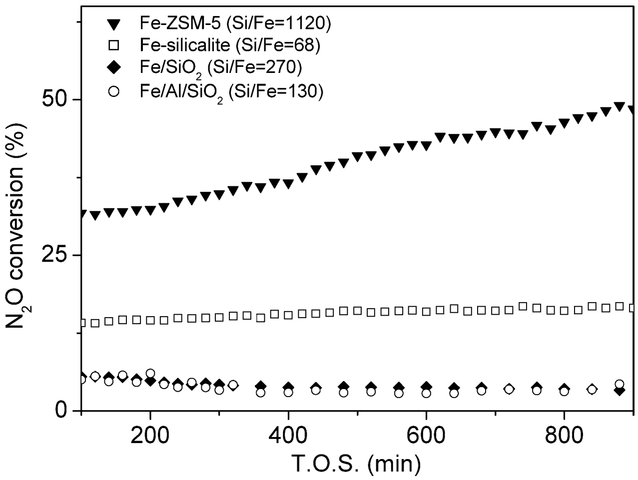

Fig. 2. N_2O decomposition at 773 K (GHSV = 27,000 h^{-1}) over the various catalysts activated at 1073 K: ▼, Fe-ZSM-5; □, Fe-silicalite; ○, $Fe/Al/SiO_2$; and ◆, Fe/SiO_2.

a decay of activity with time in other experiments. In particular, low space velocities and pure N_2O feed most often resulted in slow deactivation, while by increasing the space velocity (using He as a diluent) the slight increase observable in Fig. 2 was often observed. Notwithstanding the large number of experiments we were not able to obtain a fully reproducible behaviour. This suggests that the activity is controlled by many fine parameters. This is not unexpected, since our previous work regarding the systematic characterisation of a large series of samples showed how the distribution and nature of Fe sites hosted in zeolitic matrices can seriously change upon small variations in the activation conditions [6]. In our opinion, the same explanation could hold for the small changes of activity during the reaction: structural rearrangements (such as aggregation or changes in the local environment of Fe sites) could play a role also during the first steps of the reaction, depending upon the experimental conditions.

N_2O decomposes stoichiometrically to N_2 and O_2 (within the experimental error) following the reaction scheme:

$$2N_2O \rightarrow 2N_2 + O_2. \tag{1}$$

A possible pathway for N_2O decomposition and oxygen recombination is the following:

$$N_2O + ()_\alpha \rightarrow N_2 + (O)_\alpha, \tag{2}$$

$$2(O)_\alpha \rightarrow O_2, \tag{3}$$

where by $()_\alpha$ we indicate the active sites, and by $(O)_\alpha$ mobile and reactive oxygen species. In agreement with many authors [7,9] this reaction pathway should occur on clustered (at least dimeric) Fe species because they are expected to allow more facile oxygen adsorption, migration, and recombination. An alternative reaction pathway is as follows:

$$N_2O + ()_\alpha \rightarrow N_2 + (O)_\alpha, \tag{2'}$$

$$(O)_\alpha + N_2O \rightarrow N_2 + O_2. \tag{3'}$$

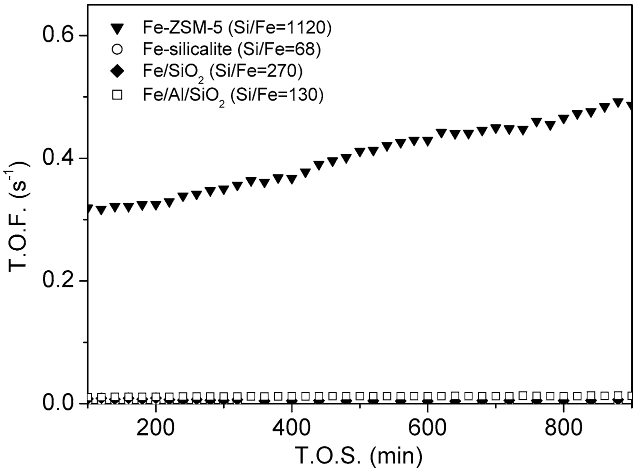

Fig. 3. Turnover frequency values for N_2O decomposition at 773 K (GHSV = 27,000 h^{-1}) over the various catalysts activated at 1073 K: ▼, Fe-ZSM-5; ○, Fe-silicalite; □, $Fe/Al/SiO_2$; and ◆, Fe/SiO_2. The T.O.F. values were calculated as number of molecules of N_2 produced per second per atom of Fe.

Paths (2′) and (3′), not requiring the migration of atomic oxygen on the surface, do not necessarily imply the presence of oxidic clusters and hence could be favoured on very diluted samples, where isolated Fe^{x+} sites are the dominant species.

From the data plotted in Fig. 2, the higher activity of Fe-ZSM-5 with respect to the other catalysts is evident. Since the iron content of the Fe-ZSM-5 sample is very low ($Si/Fe = 1120$), in this case we can reasonably assume that the formation of aggregates is minimised. We can thus infer that isolated Fe sites are mainly involved in the catalytic activity. As the catalytic activity slightly increases along the reaction, structural rearrangements cannot be excluded. From Fig. 2 it can be inferred that the activity of Fe-silicalite, although higher than that of the amorphous samples, is sensibly lower with respect of Fe-ZSM-5. Since the Fe content of this sample is higher than that of Fe-ZSM-5 (by a factor of 16.6), it could be argued that only a fraction of the total iron content is in this case active, for instance as the consequence of a too extensive clustering process. However, catalytic tests performed on highly diluted Fe-silicalite samples ($Si/Fe = 440$, not reported) showed a very low activity as well: this is indicating that dilution alone is not sufficient to obtain a high concentration of active sites and that the presence of Al is crucial.

The difference between the activities of the four samples is further amplified when the turnover frequency values (T.O.F.) are reported (Fig. 3). T.O.F. values were calculated as number of N_2 molecules produced per second per Fe atom. From this comparison it is emerging that the activity per Fe atom of Fe-ZSM-5 is one order of magnitude higher with respect to Fe-silicalite and two orders of magnitude higher with respect to the amorphous samples. A first conclusion deriving from the catalytic results illustrated in Figs. 2 and 3 is that isolated, or less likely small clusters

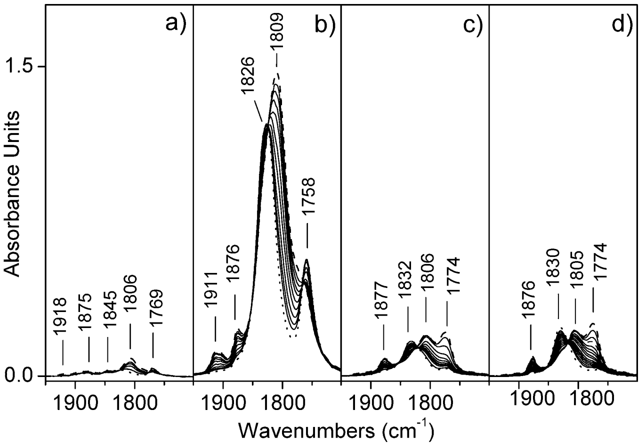

Fig. 4. FTIR spectra of NO dosed at room temperature (decreasing P_{NO} from 15 Torr, dashed line spectrum to 10^{-3} Torr, dotted line spectrum) on various catalysts activated at 1073 K: (a) Fe-ZSM-5, (b) Fe-silicalite, (c) $Fe/Al/SiO_2$, and (d) Fe/SiO_2.

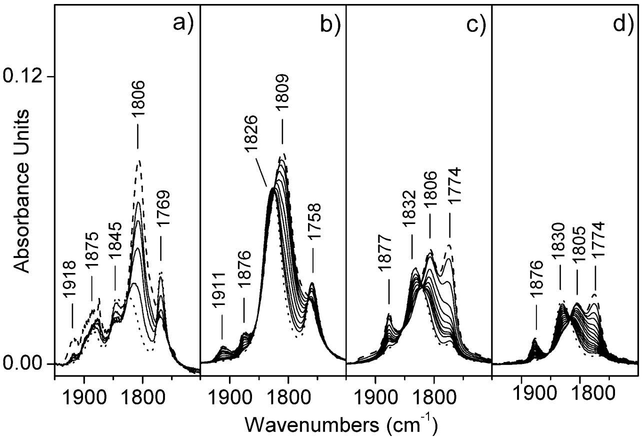

Fig. 5. Normalised FTIR spectra of NO dosed at room temperature (decreasing P_{NO} from 15 Torr, dashed line spectrum to 10^{-3} Torr, dotted line spectrum) on various catalysts activated at 1073 K: (a) Fe-ZSM-5, (b) Fe-silicalite, (c) $Fe/Al/SiO_2$, and (d) Fe/SiO_2. The spectra intensity was normalised with respect to the iron content. Fe-ZSM-5 sample (0.08 Fe wt%) was chosen as reference.

of Fe ions, are the precursors of the sites active in N_2O decomposition. Large oxidic clusters or particles are, on the contrary, less active. From the comparisons we draw also a second conclusion: Al is playing a definite role in determining the activity of Fe ions. From this it is inferred that the catalytic sites must contain both Fe and Al, as also proposed in Refs. [12–14,27–29]. Finally, the activity per Fe atom of the amorphous samples is almost nil, indicating that the crystalline character of the support is a fundamental factor in determining the catalytic activity.

3.2. *FTIR of adsorbed NO*

In Fig. 4 the FTIR spectra (normalised for the pellet weight and thickness) obtained from room temperature adsorption of NO on the four catalysts are reported. For an easier comparison we also report (Fig. 5) the same spectra after further normalisation of the adsorptions with respect to the iron content. The scope of this comparison is to:

(i) evaluate the accessibility of iron centres;
(ii) evaluate the valence state;
(iii) evaluate the coordination state;
(iv) ascertain if a correlation between catalytic activity, and coordination state of Fe centres (as probed by NO) is existing.

As a first observation we underline that the overall intensity of the NO bands obtained on Fe-ZSM-5 and Fe-silicalite, after normalisation with respect to the iron content (see Fig. 5a and 5b) are substantially similar. This indicates that the fraction of *accessible* Fe sites on the two samples is roughly the same. Consequently, the different activity of the Fe-silicalite and Fe-ZSM-5 sample in N_2O decomposition cannot be simply explained in terms of the fraction of accessible sites. A detailed analysis of the type of exposed sites (isolated and clustered Fe^{2+} and Fe^{3+}) is consequently needed.

In particular, the FTIR spectra of adsorbed NO indicate:

(a) On both crystalline samples the di-nitrosyl ⇄ tri-nitrosyl transformation, characteristic of isolated Fe^{2+} ions in extraframework positions, is observable upon varying NO pressure (scheme (4)),

$$Fe^{2+}(NO)^2 \underset{-NO}{\overset{+NO}{\rightleftarrows}} Fe^{3+}(NO)_3. \tag{4}$$

The $Fe^{2+}(NO)_2$ complexes (visible at low NO pressure, dotted lines in Fig. 5a and 5b) originate IR bands at 1845 and 1769 cm^{-1} on Fe-ZSM-5 (Figs. 4a and 5a) and at 1826 and 1758 cm^{-1} on Fe-silicalite (Figs. 4b and 5b). $Fe^{2+}(NO)_3$ complexes dominate the spectra at high NO pressure (dashed curve) and are responsible for the bands at 1918 and 1806 cm^{-1} on Fe-ZSM-5 and at 1911 and 1809 cm^{-1} on Fe-silicalite. From these findings it is concluded that isolated Fe sites in Fe-ZSM-5 and Fe-silicalite samples are not identical and give different $Fe(NO)_2$ and $Fe(NO)_3$ complexes (see Table 3). This observation, also reported in Ref. [29], indicates that the isolated Fe^{2+} ions in Fe-ZSM-5 are influenced by Al^{3+} in very close proximity, as also suggested by different authors [12–14,26–28]. This observation is in agreement with the literature concerning the vibrational spectroscopy of nitrosyl complexes [32,33]. It is in fact known that the ν_{NO} of $Fe(NO)_n$ complexes is influenced by the electronic state of the central metal, the electron-poor centres (associated with smaller back-donation) giving the higher frequencies. This is in accord with the electron withdrawing effect of Al, which is decreasing the electron density of vicinal Fe centres. Notice that the blue-shift of the bands obtained on Fe-ZSM-5 with respect to Fe-silicalite is very clear for the $Fe^{2+}(NO)_2$ components and for the high energy mode of the $Fe^{2+}(NO)_3$ complexes. On the contrary, the low energy component of the $Fe^{2+}(NO)_3$

Table 3
Position of the maxima (cm^{-1}) and assignment of the FTIR nitrosyl bands formed on the crystalline samples described in this work

	$Fe^{2+}(NO)$	$Fe^{2+}(NO)_2$	$Fe^{2+}(NO)_3$	$Al^{3+}/Fe^{3+}(NO)$	$Fe_A^{2+}(NO)_2$[a]
Fe-ZSM-5	–	1845 and 1769	1918 and 1806	1875	–
Fe-silicalite	1826[b]	1826[b] and 1758	1911 and 1809[c]	–	1876 and 1809[c]

[a] Typical complexes observed on amorphous complexes.

[b,c] These bands are formed by the sum of two different components: their maxima position is thus not reliable.

Table 4
Position of the maxima (cm^{-1}) and assignment of the FTIR nitrosyl bands formed on the amorphous samples described in this work

	$Fe_A^{2+}(NO)$	$Fe_A^{2+}(NO)_2$	$Fe_B^{2+}(NO)$
$Fe/Al/SiO_2$	1832	1877 and 1806	1774
Fe/SiO_2	1830	1876 and 1805	1774

complexes (maximum position at 1806 cm^{-1} for Fe-ZSM-5 and at 1809 cm^{-1} in Fe-silicalite) is not reliable since influenced by the superimposition of different adsorptions: the band due to $Fe^{2+}(NO)$ complexes (vide infra) and the high frequency mode of the $Fe^{2+}(NO)_2$ ones. As a final observation, notice that the fraction of isolated centres on Fe-ZSM-5 is about twice that observed on Fe-silicalite (Fig. 5a and 5b). This indicates that the presence of Al is favouring the dispersion of Fe, as also observed by Choi et al. [27].

(b) Fe sites characterised by lower coordinative unsaturation are also observed on the crystalline samples. These species, able to adsorb only one NO molecule, were assigned to Fe^{2+} ions on small oxidic clusters. The corresponding $Fe^{2+}(NO)$ complexes on clusters absorb in the 1825–1835 cm^{-1} interval and are more abundant on Fe-silicalite sample ($Si/Fe = 68$, Fig. 5b). It is worth noticing that the concentration of oxidic clusters (band in the 1825–1835 cm^{-1} range) is very low on Fe-ZSM-5 sample ($Si/Fe = 1120$), where isolated Fe^{2+} ions characterised by high coordinative unsaturation represent the major fraction of exposed sites. From this it is confirmed that the relative concentration of isolated and clustered species is strictly dependent upon the presence of Al and upon Fe concentration.

Coming to the minor features detected on the crystalline samples, the weak band at 1876 cm^{-1} clearly visible on Fe-silicalite (Fig. 5b) closely reminds that formed on the amorphous samples (see next section and Tables 3 and 4) and its presence was explained by assuming a local amorphisation of the zeolitic support as a consequence of high temperature thermal treatments [31]. Finally, the band at 1875 cm^{-1} (not very intense in relative terms) observed on Fe-ZSM-5 (Fig. 5a) has been assigned to $Al^{3+}(NO)$ and/or $Fe^{3+}(NO)$ adducts [29].

It is important to underline that previous experiments on samples oxidised with N_2O at 673 K showed that the capacity of *all* Fe sites (i.e., isolated and clustered) to adsorb NO is dramatically inhibited by the presence of adsorbed oxygen from N_2O decomposition [6]. This observation has direct implications on the structure of active adsorbed oxygen, which is expected to be similar to the ferryl species observed on heme systems on isolated ions [11], and is similar to oxygen in methane monooxygenase on oxidic clusters [10].

At this point of the discussion, we can draw the following conclusions:

(i) thermal treatments in vacuo at high temperature generate highly dispersed Fe sites on both Fe-ZSM-5 and Fe-silicalite;
(ii) isolated Fe^{2+} ions are (in relative terms) more abundant on Fe-ZSM-5 than on Fe-silicalite;
(iii) isolated Fe^{2+} sites on Fe-ZSM-5 are in close proximity of Al, which acts as electron withdrawing centre and hence influences the chemical properties of Fe;
(iv) comparison of the spectroscopic and catalytic results suggests that the high activity of Fe-ZSM-5 in N_2O decomposition is associated with isolated Fe^{2+} extraframework ions in close proximity of Al. This observation does not automatically exclude that clustered oxo–iron species are also playing a role in N_2O decomposition. In fact, it only indicates that the reaction on isolated centres is faster than that occurring on clustered sites, in agreement with what was recently proposed by Pirngruber et al. [46].

(c) Coming to the amorphous $Fe–SiO_2$ and $Fe/Al/SiO_2$ samples (Fig. 5c and 5d), the overall intensity of the IR bands is, after normalisation with respect to the iron content, about half of that obtained on the crystalline samples. This indicates a lower fraction of accessible Fe sites, as expected for amorphous samples where the formation of oxidic clusters grafted on the surface of silica has been often reported [45]. However, similarly to what is observed on crystalline materials, the difference in intensity is not so dramatic to explain the observed difference in catalytic activity. Hence, also in this case a detailed analysis of the type of exposed sites, in terms of coordination state, is necessary,

$$Fe_A^{2+}(NO) \underset{-NO}{\overset{+NO}{\rightleftharpoons}} Fe_A^{2+}(NO)_2. \tag{5}$$

The nitrosyl bands obtained on the two amorphous samples are substantially similar, and will be discussed together. Four main bands are observed, at 1877, 1832, 1806, and 1774 cm^{-1}. The intensity of the bands is strictly dependent upon NO pressure as follows: by decreasing NO pressure the bands at 1877, 1806, and 1774 cm^{-1} decrease, while the band at 1832 cm^{-1} grows. To give a correct interpretation of these complex bands, two-dimensional correlation spectroscopy (2DCOS, not reported) was used.

The spectra can be interpreted by assuming that on the amorphous surface two types of Fe^{2+} sites are present. The first type (hereafter Fe^{2+}_A) can adsorb up to 2 NO molecules (bands at 1877 and 1806 cm^{-1}), and is reversibly transformed into a stable mono-nitrosyl adduct (band at 1832 cm^{-1}) by decreasing the NO pressure, as reported in the scheme (5). The second type (hereafter Fe^{2+}_B) can only adsorb one NO molecule, giving the IR band at 1774 cm^{-1}

$$Fe^{2+}_B \underset{-NO}{\overset{+NO}{\rightleftharpoons}} Fe^{2+}_B(NO). \qquad (6)$$

By comparing this results with those obtained on the crystalline samples it is clear that on Fe–SiO_2 and Fe/Al/SiO_2 samples tri-nitrosyl complexes are totally absent. This indicates that Fe ions on amorphous matrices are characterised by a lower coordinative unsaturation. This could be explained either by the flexible nature of the siliceous matrix (where Fe ions can easily sink, to increase their coordination state) or by the formation of oxidic clusters. In this case the presence of Al does not sensibly affect the frequency of the nitrosyl bands, since only a very small blue-shift of the bands in Fe/Al/SiO_2 is observable. The intensity of the bands obtained on the Fe/Al/SiO_2 samples (after normalisation of the iron content) is possibly suggesting that the presence of Al also in this case slightly favours the dispersion of Fe.

The previous observations give further support to the hypothesis that the most active sites are isolated Fe ions characterised by high coordinative unsaturation, in agreement with what was recently proposed by Pirngruber et al. [46]. Fe sites formed on amorphous matrices, even if well dispersed and accessible to the interaction with NO, show almost nil catalytic activity in N_2O decomposition because their coordinative unsaturation is lower. Hence, the crystalline character of the zeolite support is essential to stabilise extraframework Fe sites characterised by high coordinative unsaturation and catalytic activity.

4. Conclusions

In conclusion, we have shown that Fe coordination degree dramatically changes when Fe ions are anchored at the surface of crystalline or amorphous silica-based supports. The accessibility of iron, on the contrary, is not very much affected (at least for Fe concentration below 1.3%). In particular, Fe ions supported on amorphous silica show a higher coordination degree with respect to the Fe sites present on crystalline zeolitic materials. The results of testing the activity of Fe-catalysts in the N_2O decomposition reaction show that Fe centres anchored on crystalline materials exhibit higher activity than those grafted on amorphous materials. This observation suggests that there is a definite correlation between coordination state and catalytic activity.

Within the crystalline materials, both isolated and clustered extraframework Fe ions were observed, whose concentration depends upon the presence of Al and the amount of Fe. The isolated extraframework Fe sites, on both Fe-silicalite and Fe-ZSM-5, are characterised by high coordinative unsaturation being able to add up to 3 NO molecules. The clustered ions, instead, form only $Fe^{2+}(NO)$ complexes. In the Fe-ZSM-5 sample ($Si/Fe = 1120$) the concentration of oxidic clusters is minimised in favour of the isolated ones, while the opposite occurs on Fe-silicalite ($Si/Fe = 68$). Moreover, the isolated Fe^{2+} sites formed on Fe-silicalite and Fe-ZSM-5 are not identical, as testified by the different frequency at which the corresponding $Fe^{2+}(NO)_n$ complexes absorb. By comparison with the literature concerning nitrosyl complexes, it is concluded that Al centres act as electron withdrawing centres, decreasing the electronic density of vicinal Fe ions.

Fe-ZSM-5 sample ($Si/Fe = 1120$) shows the higher catalytic activity, suggesting that highly coordinatively unsaturated and isolated Fe centres are catalytically active in N_2O decomposition. This conclusion does not exclude that clustered sites are also involved in N_2O decomposition, but simply indicates that the reaction is faster on isolated Fe ions. Finally, adsorbed oxygen is formed by N_2O decomposition on both isolated and clustered Fe sites. It is inferred that in the first case ferryl groups are formed, while in the second adsorbed oxygen has bridged nature.

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