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The role of Al in the structure and reactivity of iron centers in Fe-ZSM-5-based catalysts: a statistically based infrared study

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Abstract

A statistical analysis of the infrared data obtained upon absorption of NO on a large number of Al-free Fe-silicalite and Fe-ZSM-5 samples highlighted the influence of Al on the formation and stabilization of extraframework iron species and shed more light on the superior activity of Fe-ZSM-5-based catalysts. It was concluded that Al favors the dispersion of extraframework iron species and that isolated Fe^{II} species with one or two Al atoms in the immediate vicinity are the active sites in partial oxidation reactions. The structure of the α-oxygen species adsorbed on iron centers is also briefly discussed.

Keywords: Fe-ZSM-5; α-oxygen; $Fe(NO)_n$ complexes; IR spectroscopy; Partial oxidation catalyst

1. Introduction

The one-step conversion of benzene to phenol using N_2O as oxidizing agent is a promising and environmentally, friendly alternative to the commonly used three-step process via cumene [1,2]. This reaction is catalyzed by Fe-MFI zeolites (both Al-free Fe-silicalite and Fe-ZSM-5) which are isomorphously substituted zeolites containing very low iron amounts [3–5]. The conversion yield of the Al-containing Fe-ZSM-5 and the Al-free Fe-silicalite is qualitatively similar even if, at the same iron content, Fe-ZSM-5 shows higher activity [4–6]. Both catalysts become active only after severe thermal treatments ($T > 773$ K) which cause the migration of iron into extraframework positions and its partial reduction to Fe^{II} [3,7–12]. This migration, favored by the presence of traces of water [10], is certainly associated with profound reconstruction of the framework at the vacant positions. The extraframework iron species formed in this way are thought to be the catalytically active sites where N_2O is decomposed with formation of the so-called α-oxygen, which is the active species in the selective oxidation reactions [4,5,7,10]. However, the characterization of the extraframework Fe^{II} structures and of the oxygen species adsorbed on them has represented an extremely difficult task probably because of the low iron concentration in the active catalyst [4–6]. It is a matter of fact that the results obtained in different laboratories or even in the same laboratory on the same sample have shown a substantial variability from one experiment to the other. This can be rationalized by considering that on samples characterized by such low concentration of iron sites, slightly different activation conditions can have profound consequences on the migration of iron into extraframework positions and its successive grafting on the channel wall sites [7,10–12].

With regard to the structure of α-oxygen, two main hypotheses can be advanced. (i) α-Oxygen is essentially an O^{2-} species bridged to two Fe^{II}s located in adjacent positions as in methane monooxygenase [13,14]. This hypothesis implies that the active sites for partial oxidation reactions using N_2O as oxidant are Fe^{II}–Fe^{II} dimers as hypothesized for instance by Marturano et al. [15,16]. (ii) α-Oxygen is interacting with a single iron center. In this case the homogeneous analogue is the ferryl group observed in many enzymatic systems [17–21]. This hypothesis implies that the presence of Fe^{II}–Fe^{II} dimers in the catalysts is not a necessary prerequisite for α-oxygen formation.

Dubkov et al. [5], on the basis of Mössbauer spectroscopy and determination of the α-site concentration, have ad-

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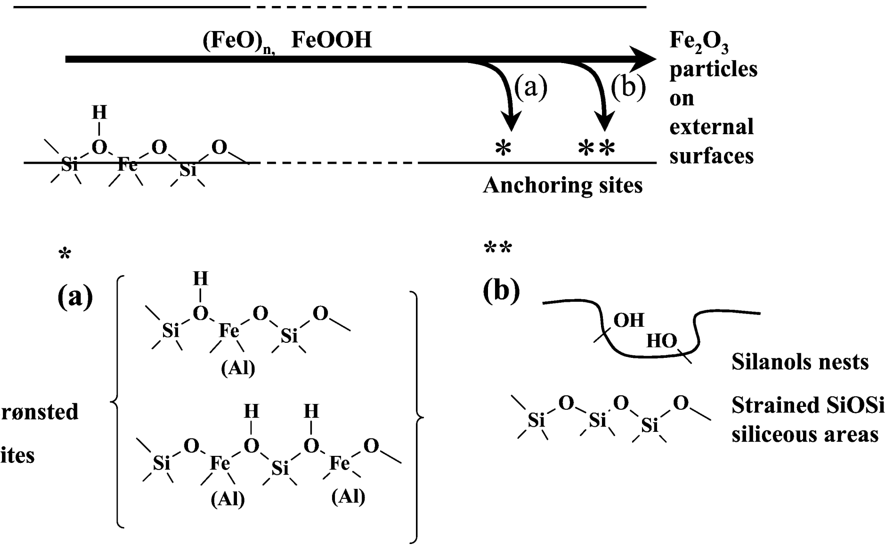

Scheme 1.

vanced the intermediate hypothesis that α-sites are binuclear complexes in which both Fe atoms are able to absorb a single oxygen atom in the form of O^- (or as a ferryl group). Notice that while this model on the one hand keeps the dimeric structure, it on the other hand accepts the hypothesis that each Fe^{II} of the pair is acting as an isolated center. In other words the hypothesis that α-oxygen is a bridging O^{2-} species is ruled out. In this regard, the recent work of Bell's group [22] is worth noticing. They have proposed a new molecular precursor strategy to prepare a series of single-site catalysts that possess isolated iron centers supported on mesoporous silica.

Recently, we reported a characterization of extraframework iron species formed in Fe-silicalite upon activation in vacuo based on a multitechnique approach [10–12]. This work definitely showed that the nature and the distribution of the extraframework iron species are highly sensitive to the iron concentration, to the activation temperature, to the duration of the thermal treatments, and to the dynamic vacuum conditions (which presumably control the presence of water traces). This conclusion justifies the limited reproducibility of the results obtained on low-concentration Fe-MFI catalysts. Moreover it suggests that a complete understanding of catalyst structure can be obtained only by means of a systematic approach based on the statistical analysis of the results obtained on many samples apparently treated in the same way. Scheme 1 shows the structure of the Fe^{II} species formed by migration into extraframework positions and successive grafting to different reactive centers located on the walls of the channels. Two structures with regard to different anchoring sites have been considered: Brønsted sites (structure a) associated with residual M^{III} in the lattice ($M = Al$ or Fe) and silanol nests (structure b).[1]

Due to its strong affinity toward Fe^{II} and because of the high intensity of the ν_{NO} bands [10–12,24–27], the NO molecule is a very sensitive probe for the study of the oxidation and coordination state of iron in Fe-silicalite. In Fe-silicalite we distinguished at least three families of ferrous species [10–12] whose structure can be written as $L_2N_nFe^{II}$, where L is the oxygen of framework Si–O or Fe^{III}–O moieties chemically linked to Fe^{II}, and Ns are vicinal SiOSi groups only electrostatically linked to Fe^{II}. Depending upon the number of N ligands in the pristine $L_2N_nFe^{II}$ structures, the Fe^{II} species form, upon contact with NO, $L_2N_3Fe^{II}(NO)$, $L_2N_2Fe^{II}(NO)_2$, and $L_2NFe^{II}(NO)_3$ complexes characterized by high-intensity and well-defined IR spectra [10–12, 28,29]. Following Scheme 1 and the results of the probing experiment with NO, the extraframework species exposed to interaction with gases behave as mononuclear structures. In fact, although these structures are probably characterized by the presence of Fe^{III}–Fe^{II} or Fe^{III}–Fe^{II}–Fe^{III} dimers and trimers, only Fe^{II} ions are exposed to the interaction with bases. Notice also that Fe^{III}–Fe^{II} and Fe^{III}–Fe^{II}–Fe^{III} structures can be formed in situ by simultaneous interaction of FeO and FeOOH species with strained silanol nests (see Scheme 1b and Scheme 2). In the case of species formed by interaction of FeO with Brønsted sites (see Scheme 1, structure a and Scheme 3), there are dimers or trimers where one (or two) iron species (Fe^{III}) is (are) in the framework (and hence inactive) and the other (Fe^{II}) is exposed to the gas interaction. This is in agreement with previously documented results [10–12,28,29]; in fact both structures, when probed by NO, behave as single centers. This is the reason that they cannot readily be distinguished by IR spectroscopy.

Following this idea, the dimeric and trimeric structures should progressively disappear in the samples treated at the

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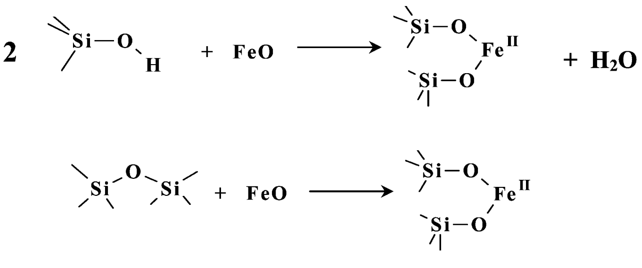
[1] Note that for Fe-silicate, $M^{III} = Fe^{II}$ always, while for Fe-ZSM-5, M could be either iron or aluminum. Sites containing two M^{III} centers have considered preferential sites for hosting divalent cations by Wichterlová and Dedecek [23].



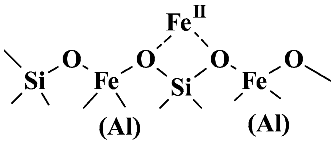
Scheme 2.

highest temperatures (because under these conditions all iron migrates progressively into extraframework positions) and the anchored species become predominant (Scheme 1b). As final observation it must be noted that the peaks of the nitrosylic species are clearly detected even on samples characterized by Fe/Si ratios as low as 1000. It is thus concluded that NO is a very sensitive probe for iron species. In fact the number of the inserted NO groups provide information about the accessibility and coordinative unsaturation of the active centers even in samples where the vast majority of the physical methods fail because of the too low iron concentration.

In this work the same approach based on the NO probe has been extended to the study of the homologous Al-containing Fe-ZSM-5 catalysts, with the aim to understand the role of Al in the formation of extraframework iron species and in the conferring of superior activity to the Fe-ZSM-5 catalyst in the partial oxidation of benzene with N_2O [4,6]. To this aim we have studied the IR spectroscopy of absorbed NO on a series of low-concentration Fe-ZSM-5 samples with different Fe and Al contents and with activation at different temperatures. For comparison, iron was also introduced by postsynthesis gas-phase exchange in the Al-containing H-ZSM-5 and H-Y matrices. The data were analyzed and treated by a statistical approach and compared with those previously obtained on Fe-silicalite samples [10–12,28,29].

2. Experimental section

Four Fe-silicalite catalysts (Si/Fe = 25, 50, 150, and 350) were prepared following the method of Szostak et al. [30]. Four Fe-silicalite samples (Si/Fe = 68, 90, 133, and 440) and six Fe-ZSM-5 samples with different Si/Fe and Si/Al ratios (see Table 1) were prepared by the hydrothermal method described by Ratnasamy and Kumar [31]. To broaden the statistical representation of our systematic study, samples from three different synthesis laboratories have been used: (i) SnamProgetti, (ii) EniChem (now PolimeriEuropa), and (iii) Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano. All samples were washed, dried, and calcined at 823 K. The ion-exchanged samples were prepared, in our laboratories, starting from the corresponding H-ZSM-5 (Si/Al = 15) and H-Y (Si/Al = 2.5) zeolites using a $FeCl_2$ precursor. The samples were prepared by mixing the zeolite with $FeCl_2$ under controlled atmosphere in a quartz pipe and successively outgassing it at 673 K for 1 h. Before the IR experiment the Fe-silicalite and Fe-ZSM-5 samples were outgassed under high vacuum at 773 and 973 K, while the exchanged samples were activated only at 773 K.



Scheme 3.

Table 1
Chemical composition of the investigated samples

N	Sample	Si/Fe	Si/Al	*N*	Sample	Si/Fe	Si/Al
1	Fe-silicalite	440	∞	9	Fe-ZSM-5	1818	26
2	Fe-silicalite	350	∞	10	Fe-ZSM-5	1300	50
3	Fe-silicalite	150	∞	11	Fe-ZSM-5	1120	18
4	Fe-silicalite	133	∞	12	Fe-ZSM-5	530	26
5	Fe-silicalite	90	∞	13	Fe-ZSM-5	75	19
6	Fe-silicalite	68	∞	14	Fe-ZSM-5	30	30
7	Fe-silicalite	50	∞	15	Fe/H-ZSM-5[a]	86	15
8	Fe-silicalite	25	∞	16	Fe/H-Y[a]	64	2.5

[a] Exchanged samples.

The IR experiments were carried out on a Bruker IFS 66 FTIR instrument equipped with a cryogenic MCT detector and running at 1 cm^{-1} resolution. The samples were in the form of self-supporting pellets suitable for measurements in transmission mode. Measurement cells allowing in situ thermal treatments and dosing of NO were used. NO, carefully purified by distillation, was dosed at room temperature ($P_{NO} = 15$ Torr) and the equilibrium pressure was reduced step by step. An IR spectrum was recorded at each step. The last spectrum typically corresponds to 15 min outgassing at room temperature (residual pressure lower than 10^{-3} Torr). The zeolite spectrum collected before gas dosage was used as reference for obtaining the background-subtracted spectra reported in Fig. 1. All the IR spectra were normalized with respect to the iron content. See the experimental section of [10] for a more detailed discussion.

3. Results and discussion

Fig. 1 illustrates the behavior, upon changes of the NO equilibrium pressure (P_{NO}), of the nitrosyl bands obtained on a Fe-ZSM-5 sample (No. 10 of Table 1) previously activated at 973 K. As a first observation, it is worth noting the "molecular definition" of the spectra (in terms of half-width) which resembles those of homogeneous complexes. This means that the adsorbing sites have well-defined mononuclear structure and exhibit a low degree of heterogeneity. The spectra mainly comprise two pairs of bands: the first pair, at 1917 cm^{-1} (T_1) and 1813 cm^{-1} (T_2), gradually decreases by reducing P_{NO}; the second pair, at

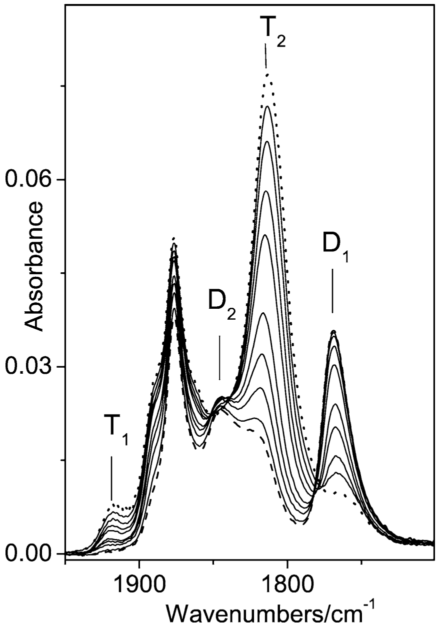


Fig. 1. IR spectra of NO dosed at room temperature on Fe-ZSM-5 sample (No. 10 of Table 1; previously activated at 973 K) collected by reducing P_{NO} from 15 Torr (dotted spectrum) to 10^{-3} Torr (dashed spectrum).

1845 cm^{-1} (D_2) and 1769 cm^{-1} (D_1), grows and finally dominates the spectra after outgassing at room temperature. A sharp and quite intense peak (not totally disappearing upon reduction of P_{NO}) is also observed at 1876 cm^{-1}. The observed spectra are quite similar to those found on the Fe-silicalite [10–12,28,29], the major difference being represented by the peak at 1876 cm^{-1}, which has been interpreted with regard to NO adsorbed on trigonal $\mathrm{Al}^{\mathrm{III}}$ and $\mathrm{Fe}^{\mathrm{III}}$ sites. The detection of extraframework $\mathrm{Al}^{\mathrm{III}}$ sites indicates that, under the adopted severe treatment conditions, both $\mathrm{Fe}^{\mathrm{III}}$ and $\mathrm{Al}^{\mathrm{III}}$ are migrating. Even if in the here investigated Fe-ZSM-5 samples (Table 1) the Fe/Al ratio is $\leqslant 1$, the much higher stability in the MFI framework of $\mathrm{Al}^{\mathrm{III}}$ with respect to $\mathrm{Fe}^{\mathrm{III}}$ heteroatoms implies that migration into extraframework positions is greater for iron than for aluminum in any sample. The main bands (T_1, T_2, D_1, and D_2) associated with NO on $\mathrm{Fe}^{\mathrm{II}}$ centers are ascribed to isolated dinitrosylic and trinitrosylic species in mutual equilibrium [10–12,28,29]:

$$\mathrm{Fe}^{2+}(\mathrm{NO})_2 \underset{-\mathrm{NO}}{\overset{+\mathrm{NO}}{\rightleftharpoons}} \mathrm{Fe}^{2+}(\mathrm{NO})_3. \tag{1}$$

In particular the $\mathrm{Fe}^{\mathrm{II}}(\mathrm{NO})_2$ complex is responsible for the D_2 and D_1 bands at 1845 and 1769 cm^{-1}, while $\mathrm{Fe}^{\mathrm{II}}(\mathrm{NO})_3$ is associated with the T_1 and T_2 bands at 1917 and 1813 cm^{-1} [10–12,28,29]. This assignment has been confirmed by adsorption on a Fe-silicalite sample of an isotopic $^{14}\mathrm{NO}/^{15}\mathrm{NO}$ mixture [28]. As observed on Fe-silicalite, the presence of mononitrosylic species is also detected (component around 1835 cm^{-1} [10]. These species, which absorb only one NO even at the highest dosages, are thought to be less coordinatively unsaturated and hence less reactive.

A superficial comparison of these spectra with those obtained on the Al-free samples treated in an analogous way [10–12,28,29] leads to the conclusion that essentially the same nitrosylic species on $\mathrm{Fe}^{\mathrm{II}}$ truly isolated centers (or behaving as isolated centers as those in Scheme 3) are present in both samples. There are, however, small but nevertheless significant differences, which must be noted. In particular, (i) the frequencies of the nitrosylic bands shown in Fig. 1 are slightly (but still significantly) higher than those measured on Al-free samples and (ii) their intensities are definitely larger by a factor of about 1.5 with respect to those observed on Al-free samples containing the same amount of Fe.

As the frequency and intensity differences are not large, we have repeated the same experiment on a large number of samples to confirm the validity of this observation. As far as the intensity is concerned, the observation initially made after inspection of the spectra shown in Fig. 1 appears of general validity for the whole set of samples. In fact, the intensification is observed on all investigated samples although not always by the same factor. This scattering of data is not unexpected when the difficulties in reproducing exactly the same experimental condition already discussed are considered. As already discussed, the spectroscopic features of NO complexes formed on Fe-silicalite and Fe-ZSM-5 (see Fig. 1) are typical of dispersed and highly coordinatively unsaturated $\mathrm{Fe}^{\mathrm{II}}$ species. As a consequence, stronger IR bands reflect a higher fraction of dispersed active sites. The presence of stable trivalent framework species (such as $\mathrm{Al}^{\mathrm{III}}$ in Fe-ZSM-5) prevents the aggregation of extraframework $\mathrm{Fe}^{\mathrm{II}}$ species, increasing the number of dispersed and coordinatively unsaturated active species. The adopted statistical approach based on a large number of experiments (20 for Fe-silicalites and 17 for Fe-ZSM-5) allows us to reach the following firm conclusion: *the presence of framework* $\mathit{Al}^{\mathit{III}}$ *favors the dispersion of exposed extraframework* $\mathit{Fe}^{\mathit{II}}$ *centers*. In this regard, the recent paper of the Panov group [6], reporting a study on the effect of different $\mathrm{M}^{\mathrm{III}}$ framework atoms ($\mathrm{M}^{\mathrm{III}} = \mathrm{Al}^{\mathrm{III}}$, $\mathrm{Ga}^{\mathrm{III}}$, and $\mathrm{B}^{\mathrm{III}}$) on the catalyst activity, is noteworthy.

Fig. 2 shows the percentage occurrence of any measured frequency for the T_1 and D_1 peaks. In Figs. 2a and 2b, the data referring to Fe-ZSM-5 are shown in the bottom section while those referring to Al-free Fe-silicalite are shown in the top section. These two bands have been chosen for comparison (one for each pair of bands representative of the $\mathrm{Fe}^{\mathrm{II}}(\mathrm{NO})_3$ and $\mathrm{Fe}^{\mathrm{II}}(\mathrm{NO})_2$ complexes) since they are spectroscopically isolated (i.e., not sensibly superimposed on other absorptions, while the D_2 and T_2 bands often are, see Fig. 1) and hence their frequencies can be directly estimated from those measured on the apparent maxima. By comparing the top and bottom sections of Fig. 2 it can be observed that, when $\mathrm{Al}^{\mathrm{III}}$ is present in the framework (bottom section) the frequencies of the D_1 and T_1 bands are

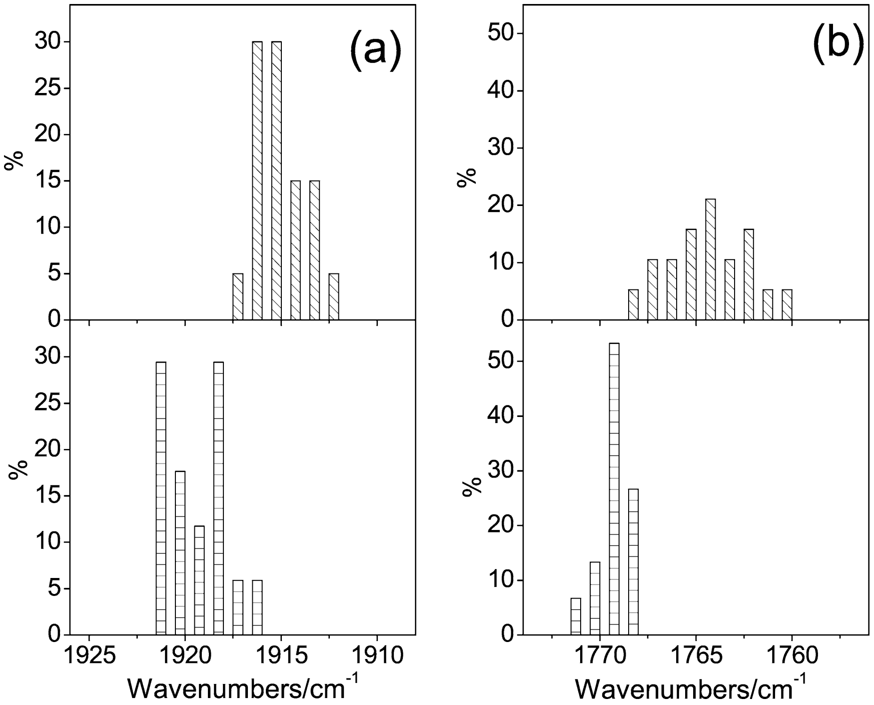


Fig. 2. Relative fraction of the frequency observed for the T_1 (a) and D_1 (b) components of the $Fe^{II}(NO)_3$ and $Fe^{II}(NO)_2$ adducts (taken at 15 Torr and 10^{-3} Torr, respectively) along the 18 samples listed in Table 1. Top and bottom sections refer to Al-free Fe-silicalite and Fe-ZSM-5 samples, respectively. For some samples the experiment has been repeated more than once [9,28], resulting in 20 IR experiments for Fe-silicalites and 17 for Fe-ZSM-5. See Table 2 for analysis.

statistically higher with respect to those observed on Al-free samples (top sections of Fig. 2): $\langle T_1 \rangle = 1914.8 \pm 1.3$ and 1919.2 ± 1.6 cm^{-1} for Al-free and Al-containing systems, while $\langle D_1 \rangle = 1764.1 \pm 2.2$ and 1769.0 ± 0.8 cm^{-1} for Al-free and Al-containing systems (see Table 2). As is known from the literature concerning the vibrational spectroscopy of nitrosylic complexes of transition metal ions [32–34], the ν(NO) is influenced by the electronic state of the central metal, the electron-poor centers (associated with smaller back-donation) giving the highest frequencies. This is the reason that the nitrosyls of Fe^{III} have frequencies higher than those of Fe^{II} [10–12,32–34].

On this basis it is deduced that Fe^{II} ions in the immediate vicinity of the framework Al^{III} in a $L_2N_nFe^{II}$ center (for instance formed by initial interaction of a Brønsted site containing one or two Al with FeO species followed by restructuring, as shown schematically in Schemes 1a and 3), should have smaller backbonding character toward NO. The resulting nitrosylic species should show higher stretching frequency, as experimentally observed. The fact that $[Fe_nCl_m]^+$ species or their oxidic derivatives, $[Fe_nO_m]^+$, can act as charge-balancing counter-ions is well evidenced by the results of studies on $CuCl_3$-exchanged ZSM-5 samples [15,35].

Table 2
Quantification of the statistical study performed on the results summarized in Fig. 2

IR band	System	$\bar{\nu}_{max}$ (cm^{-1})	$\bar{\nu}_{min}$ (cm^{-1})	$\langle\bar{\nu}\rangle$ (cm^{-1})	σ (cm^{-1})
T_1	Fe-silicalite	1917	1912	1914.8	1.3
T_1	Fe-ZSM-5	1921	1916	1919.2	1.6
D_1	Fe-silicalite	1768	1760	1764.1	2.2
D_1	Fe-ZSM-5	1771	1768	1769.0	0.8

For each selected IR band (T_1 and D_1) and for each hosting system (Fe-ZSM-5 and Fe-silicalite) the range where frequencies have been observed ($\bar{\nu}_{max}$–$\bar{\nu}_{min}$), the mean value $\langle\bar{\nu}\rangle$ and the corresponding standard deviation have been reported.

In conclusion, the shift of the nitrosylic bands to higher frequency is an indication of the presence of framework Al^{III} in the immediate vicinity of Fe^{II}. As Al-containing Brønsted structures are the preferential anchoring sites, *we are now able to explain at the same time the upward frequency shift and the simultaneous increase of intensity* of IR bands of Fe^{II}-nitrosyl complexes. In fact, the presence of Al, ensuring a relevant concentration of anchoring sites for dislodged Fe^{II} species, prevents iron aggregation. About the detailed structure of the Al-containing $L_2N_nFe^{II}$ centers we can only say that Fe^{II} sites in this structure are highly coordinatively unsaturated (because they can adsorb up to three NO molecules). This behavior is reminiscent of that of Cu^I in Cu^I-ZSM-5, where the Cu^I counter-ion is able to coordinate up to three CO or two NO molecules [36–38]. The closest Fe^{II}-based analogue, where Fe^{II} is acting as a divalent charge-balancing counter-ion, is shown in Scheme 3.

This picture is of some utility also for explaining (at least partially) the superior activity of Fe-ZSM-5 with respect to Al-free Fe-silicalite in the benzene to phenol conversion.

In fact when due consideration is made about the superior stability of Al^{III} in the MFI framework with respect to Fe^{III} (i.e., the presence of stable M^{III} framework species being a prerequisite for high Fe^{II} dispersion), the higher and more persistent activity of Fe-ZSM-5 occurs as a direct consequence. Of course an indirect consequence of this picture is that *dimeric Fe^{II}–Fe^{II} species do not seem to play an essential role as catalytic centers* (because Fe-ZSM-5-based catalysts, where the Fe^{II}–Al^{III} pairs and Al^{III}–Fe^{II}–Al^{III} trimers are expected to predominate, are definitely more active than Fe-silicalite-based catalysts).

The obtained picture has important consequences also on the structure of α-oxygen. In fact, if dimeric Fe^{II}–Fe^{II} species do not play fundamental roles in Fe-ZSM-5-based catalysts, it must be necessarily inferred that the hypothesis that α-oxygen is a bridging O^{2-} species is not supported by the experimental data. This is in agreement with the recent conclusion of the Panov group [5]. This implies that the α-oxygen, being adsorbed on a single iron species, should be similar to that of the ferryl-type species $(FeO)^{2+}$ or that of the $Fe^{III}O^{-}$ group [5], where the bond distance between iron and oxygen is lower than that typical of the single bond. *In other words, the structure of iron in Fe-ZSM-5 is more reminiscent of the eme complexes than of monooxygenase*. Although these considerations indicate that the Al-containing centers are preferential active sites for partial oxidation reactions in Fe-ZSM-5 samples, a contribution to the catalytic activity of the Fe^{III}-containing centers Fe^{III}–Fe^{II}–Al^{III} (Schemes 1b and 3) and of the anchored Fe^{II} sites formed to silanol nests is not excluded (Schemes 1a and 2).

4. Conclusion

On the basis of a statistical analysis of the IR data obtained upon absorption of NO on a large number of Fe-silicalite and Fe-ZSM-5 samples and the characteristics of NO complexes formed on dispersed and highly unsaturated Fe^{II} species, two main differences have been highlighted. (i) A systematic blue shift of the N-O stretching frequencies of the $Fe^{II}(NO)_3$ and $Fe^{II}(NO)_2$ adducts formed on Fe-ZSM-5 samples has been observed, reflecting the presence of a trivalent framework cation (Al^{III}) in the immediate vicinity of the adduct. (ii) It was observed that the intensity of the IR bands, normalized to the iron content, are higher in Fe-ZSM-5 samples by a factor of about 1.5.

The higher benzene conversion yield, per Fe atom, systematically observed in Fe-ZSM-5 samples with respect to Fe-silicalites has been explained with regard to a higher fraction of dispersed and coordinativaly unsaturated Fe^{II} species. It was thus concluded that framework Al^{III} favors the dispersion of extraframework iron species and that isolated Fe^{II} species, with one or two Al atoms in the immediate vicinity, are active sites in partial oxidation reactions. It is concluded that α-oxygen species are formed on isolate iron adsorbing centers.

Acknowledgments

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