

Evolution of Fe³⁺ from Framework to Extra-Framework Species in Fe-Silicate as a Function of the Template Burning Temperature

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Abstract We report a XAFS study of the Fe³⁺ local environment in Fe-silicalite as a function of the template burning temperature. We investigate the structural changes of the zeolitic structure, upon thermal treatments and interaction with NH₃. Our XAFS results show that, before template burning, Fe³⁺ are in tetrahedral symmetry with 4 oxygens at 1.85 Å, while after template removal and in vacuum conditions, they exhibit a distorted tetrahedral symmetry with 3 oxygens at 1.87 Å, and one at 2.10 Å; dosage of NH₃ partially restore the tetrahedral symmetry of the site. These results are strongly supported by parallel IR, Raman, UV-Vis, TPR and EPR investigations and by recent theoretical simulations.

1. RESULTS AND DISCUSSION

Isomorphous substitution of a small fraction (1-2 wt%) of Si⁴⁺ with Fe³⁺ in silicalite framework, leads to the Fe-silicalite (Fe-S) structure [1,2]. The presence in the zeolitic framework of Fe³⁺ species causes the appearance of an extra negative charge in the framework which must be compensated by protons in the form of bridged hydroxyls having an acidic strength very close to that observed in H-ZSM-5. It has been reported that the stability the tetrahedral symmetry in the framework for the two structures is very different [2]: in fact template burning in Fe-S with the associated water production is sufficient to cause the breaking of some bonds connecting iron with the oxygens of the framework and to induce migration of the iron into extra-framework positions [2-4]. Because of this, a decrease of the framework iron species and the simultaneous appearance of oxidic micro aggregates are observed after calcination in an percentage increasing with the burning temperature [4,5]. Since the catalytic properties of Fe-S are strictly related to the characteristics of framework and/or extra-framework species, the determination of the location and of the aggregation state of iron species is of paramount importance in the characterization of acidic, catalytic and shape-selective properties of Fe-S (see e.g. the introduction of ref. [4] and quoted refs.). Consequently it is a matter of primary importance to follow the framework zeolite evolution upon thermal treatments, starting from a virgin sample still containing the template up to the final sample calcined at high temperature. In this contribution we have investigated the structure of both framework or extraframework sites by means of XANES and EXAFS spectroscopies on a pure Fe-silicalite after different treatment stages *i.e.*: an Fe-S as synthesized (indicated as FeS), and samples calcined in air at 773 and 973 K (indicated as FeSC1 and FeSC2). For the last two samples the modification of the iron environment upon NH₃ dosage will also be discussed.

XAFS spectra have been collected in the transmission mode, at the EXAFS3 beam line of LURE in Orsay (F), equipped with a double crystal Si(311) monochromator (calibrated with a Fe foil) and air filled ionization chambers. Sampling step was 0.3 and 2.0 eV for XANES and EXAFS spectra respectively. The former were background subtracted with a linear function in the energy range 7090 - 7110 eV; the spectra were then normalized to unity in the continuum at 7190 eV. The latter were analyzed following standard procedures [6] using Michalovicz programs [7]: polynomial function (third degree) has been used to extract $\chi(k)$; k^3 weighted FT were computed in the range 4-13 Å⁻¹ using a Kaiser window with $\tau = 3$. Data analysis were obtained in the frame of single scattering curved wave approximation extracting the experimental phase shift and amplitude functions from (FePO₄) model compound.

Fe³⁺ K-edge absorption spectra is characterized by a small pre-edge peak due to $1s \rightarrow 3d$ transitions. In ideal systems having a perfect octahedral symmetry these transitions are Laporte forbidden, nevertheless in real systems, where distortions from the perfect octahedral symmetry are very common, the loss of the inversion center and a partial mixing of p and d levels is often observed with subsequent gain of the pre-edge transitions intensity. On the contrary, systems with tetrahedral symmetry, having no inversion center and strong $d-p$ mixing, are characterized by an intense peak in the pre edge region due to the allowed transition from the ground state A_1 to the final state T_2 [3,4,8,9]. We have thus used the normalized intensity of the XANES $1s \rightarrow 3d$ pre-edge peak to qualitatively discuss the symmetry of iron species present in the investigated samples. Reported in Fig. 1 are the pre edge peak regions of FeS, FeSC1 and FeSC2 spectra (spectra obtained in the presence of NH₃ are reported as dashed lines, while those obtained in vacuo are shown as full lines). For sake of comparison Fig. 1 also reports the pre-edge region of two model compounds with tetrahedral (FePO₄) and octahedral (Fe₂O₃) coordination. The pre-edge spectra of Fe-S samples are characterized by a well-defined single peak whose intensity, energy and full width at half maximum (FWHM) is sensitive to calcination treatments and to adsorbates interaction [3,4,10]. The qualitative agreement of pre-edge data obtained for FeS and FeSC1 samples with those of FePO₄ (which is considered a good model compound for tetrahedrally coordinated Fe³⁺ species) indicates that a high concentration of nearly perfect tetrahedrally coordinated Fe³⁺ species is present in these systems. From the previous considerations, it is evident that the pre edge peak intensity is directly related to the percentage of Fe³⁺ in tetrahedral coordination (which substitute for Si⁴⁺ in the

framework). From Fig. 1 it is evident that on passing from sample FeS to FeSC1 and especially to FeSC2, the pre-edge peak intensity decreases, and the FWHM increases. The progressive intensity decrease induced by calcination (small in FeSC1 and large in FeSC2) accompanied by a clear broadening, indicates that the calcination procedure causes a progressive migration of framework Fe^{3+} species towards extra-framework positions with formation of oxidic microaggregates. The persistence of a distinct (although broadened) single pre edge peak, without the splitting pattern characteristic of the model compounds with octahedral symmetry [9] (see Fe_2O_3) suggests that the fraction of large oxidic aggregates containing a high percentage of octahedral Fe^{3+} is still very low. The low concentration of bulky species is not surprising: in fact, if Fe_2O_3 clusters are formed inside the zeolite channels and at their intersection (diameter: 5.5 Å), only microaggregates with less than 3-5 Fe_2O_3 units can be formed, which contain a negligible proportion of Fe^{3+} with octahedral configuration and a large fraction of low coordinated surface ions. NH_3 dosage on FeSC1 and FeSC2 induces a parallel intensity increase of the pre edge peak: this suggest that the amount of Fe^{3+} ions interacting with adsorbates is analogous in FeSC1 and FeSC2. EXAFS analysis has been performed on FeS and FeCS1 (in vacuo and in presence of NH_3) samples and corresponding fits are reported in Fig. 2. Main results can be summarized as follows: i) FeS sample is characterized by the presence of Fe^{3+} 4-fold coordinated with a Fe-O distance of 1.85 Å; ii) for FeSC1 in vacuo a two-oxygen shell fit is needed (3 oxygens at 1.86 Å and 1 at 2.07 Å), in agreement with simulations carried out using the standard lattice energy minimization [12]; iii) EXAFS spectrum of FeSC1 sample in the presence of NH_3 is fitted with a single oxygen-shell (4 atoms at 1.86 Å) corresponding to an Fe^{3+} surrounding more homogeneous than in the FeSC1 sample in vacuo: in particular both coordination number and distances are compatible with tetrahedral Fe^{3+} species in $[\text{FeO}_4]^-$ units hydrogen bonded to protonated ammonia. In conclusion: i) In FeSC1 most of the Fe^{3+} species are in the framework with a distorted tetrahedral symmetry (in vacuo) ii) FeSC1 contains also extra-framework species in the form of oxidic clusters with very small dimensions where almost all Fe^{3+} species are exposed. These ions seem to reach a distorted tetrahedral symmetry in presence of ligands. iii) In FeSC2 nearly all the Fe^{3+} ions are in extra-framework position and form aggregates containing a high concentration of surface ions which can interact with adsorbates assuming distorted tetrahedral symmetry. The evidence that in FeSC2 sample highly dispersed low-coordinated extra-framework Fe^{3+} species are present, is in perfect agreement with the high catalytic activity of this zeolite in oxidation reactions. These data are strongly supported by parallel investigation using UV-Vis [3,4], IR and Raman [4,11], TPR, and EPR data [4], and by IR spectroscopy of CO and N_2 dosed at 77 K [5]. The helpful assistance of F. Villain is acknowledged.

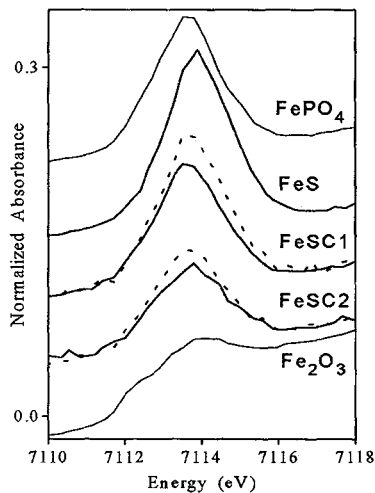


Figure 1: XANES pre edge peaks: dashed curves are referred to samples in interaction with 60 Torr of NH_3

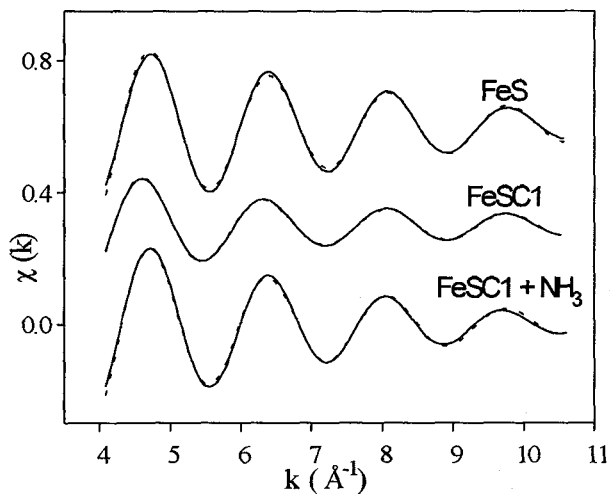


Figure 2: First shell filtered experimental $\chi(k)$ (solid lines) and corresponding fits (dashed lines)

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