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Iron Location in Fe-Silicalites by Synchrotron Radiation Single Crystal X-ray Diffraction

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We report the first structural evidence, obtained by synchrotron radiation single-crystal X-ray diffraction experiments, of the presence of preferential substitution sites for iron heteroatoms hosted in the MFI framework of a Na–Fe-silicalite sample. The location of Fe^{III} at sites T(9) and T(10) is inferred on the basis of (i) an increase of the average T–O distance greater than 3 σ ; (ii) the presence of two peaks (2.28 and 0.67 e/Å³) in the electron density map near T(9) and T(10) in a niche of the sinusoidal channel, interpreted as the corresponding Na⁺ counterion coordinated to framework oxygens; (iii) the higher anisotropy of the thermal displacement parameters observed for T(9) and T(10), which is related to the substitutional disorder of iron insertion. Independent data obtained on single crystals of Fe-silicalite samples synthesized with NH₄⁺ and K⁺ counterions confirm the results obtained on the sodium derivative.

In the past decade MFI-type¹ materials have shown a tremendous impact as new shape-selective industrial catalysts having tunable acidic strength. In fact, the isomorphous substitution of Si by other tetrahedrally coordinated elements such as B^{III},² Al^{III} (ZSM-5 zeolite),³ Ti^{IV} (Ti-silicalite or TS-1),⁴ Ga^{III},⁵ and Fe^{III} in small amounts (1–3 wt %), provides new materials showing specific catalytic properties in oxidation and hydroxylation reactions related to the coordination state of the heteroatom.⁷ Moreover, when trivalent metals are present in tetrahedral (T) sites, the zeolite framework has a net negative charge which can be balanced by a number of bridged Si(OH)M^{III} protons (M = B, Al, Fe, Ga), effectively yielding microporous solids with Brønsted acidity. Since the acidic strength of the OH group depends on the nature of the trivalent heteroatom, the choice of M^{III} critically affects this property of the material (Al > Fe \sim Ga \gg B).⁸ The charge can be balanced by other cations (Na⁺, K⁺, Cs⁺, etc.), instead of protons, yielding microporous solids with Lewis acidity.

Fe-silicalite proved to be a remarkable catalyst for several reactions; among them we recall: the oxidation of benzene to phenol,⁹ the conversion of ethylbenzene,¹⁰ the *m*-xylene isomerization,¹⁰ the NO_x decomposition¹¹ and the conversion of methanol into light olefins.¹²

From a structural point of view, the relevant question still remains open whether there are preferential substitution T sites, among the 12 nonequivalent sites of the orthorhombic MFI cell. Because of its industrial relevance, most of the published data refer to TS-1. Since only very small fractions of heteroatoms can be isomorphously inserted into the framework, the determination of the substitution sites is rather difficult. Moreover metal-substituted silicalites are in general powdered materials and almost all structural studies have been performed by the less accurate powder XRD technique. For these reasons the

debate concerning the possible presence of preferential substitution T sites has been mainly limited to the field of computational chemistry.^{13–18} Some authors concluded that the energy differences for the insertion of the heteroatom in different T sites is too small and thus substitution should be randomly dispersed on all the sites.¹³ Others claimed T8^{14,15} or T2 and T12¹⁵ as preferential sites for the Ti insertion. The most recent results obtained by Sauer and co-workers,¹⁸ are of relevant novelty since they highlight how all previous computational results, performed by simulating the zeolite structure in a vacuum, should be considered with care; in fact, hydration must be taken into account when discussing Ti substitution in the framework sites because, in the presence of water, the stability differences among different Ti sites are much larger (up to 40 kJ mol^{–1}) than in the dehydrated state and also the order of the stability of the different Ti substitution sites in TS-1 changes with hydration.

To the best of our knowledge, the only published experimental attempt to contribute to this debate comes from Lamberti et al.,¹⁹ who reported a synchrotron radiation powder XRD study on different Ti-silicalites, but no clear evidence was obtained. In a subsequent work²⁰ they have repeated the experiment at lower temperature and a weak evidence that titanium has a preferential tendency to occupy sites T10 and T11 and to avoid sites T4 and T12 was found. Coming to indirect evidences, we recall that the calorimetric study of Bolis et al.²¹ reported an evolution of the heat of adsorption of ammonia on TS-1 typical of heterogeneous surfaces, suggesting either a random distribution or a portioning of Ti in more than one preferential site. A powder neutron diffraction study of Ti- and Fe-silicalites was presented at the last IUCr meeting²² and 5 substitution sites were indicated for Ti, while only the T8 site was indicated for Fe. A powder neutron diffraction study of Ti-silicalites from our group will be available soon.²³

We have recently synthesized high quality Fe-silicalite samples incorporating a relatively large fraction of iron (higher than 2 wt %) and exhibiting crystals of comparatively large dimensions ($\sim 15 \times 15 \times 40 \mu\text{m}^3$).²⁴ Such dimensions were sufficient to allow an accurate single crystal study using the

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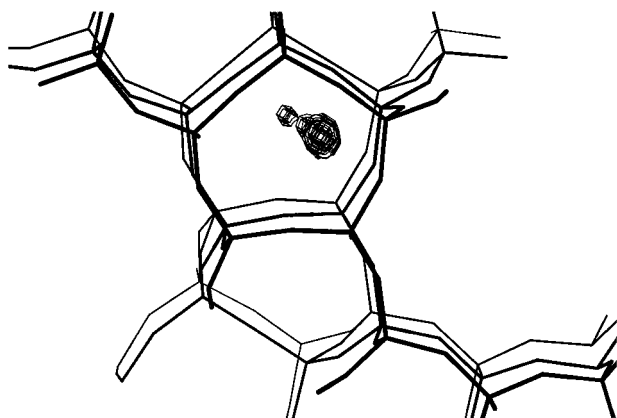


Figure 1. Maxima in the difference electron density map corresponding to the two positions of the counterions, $\text{Na}1^+$ and $\text{Na}2^+$. The framework skeleton around these peaks is also shown. SC indicates the straight channels almost normal to the projection plane.

highly collimated and intense X-ray flux emitted by the bending magnet BM1 at the ESRF. The crystals are twins, but the twin law could be easily found. Since it is well-known that template burning, even under mild conditions, causes a partial migration of Fe^{III} species from framework into extraframework positions,⁶ we had no choice but performing our diffraction studies on the as synthesized crystals, containing the tetrapropylammonium (TPA) template.

The refinement of the Na^+ –Fe-silicalite²⁵ structure, allowed also the location of the disordered TPA template at the intersection of the straight and sinusoidal channels, as found in ZSM-5 by Van Koningsveld et al.;²⁶ the type of disorder is also very similar to that reported by these authors.

The results of our analysis on the Na^+ derivative²⁵ gave a number of convincing indications on the possible substitution sites:

1. The localization in the difference electron density maps of a relevant peak²⁷ ($2.28 \text{ e}/\text{\AA}^3$, Figure 1), which can be attributed to the extraframework $\text{Na}1^+$ counterion, implies that framework Fe^{III} species must be inserted in the adjacent T sites. Besides, a second smaller peak ($0.67 \text{ e}/\text{\AA}^3$, Figure 1) can also be interpreted as a less populated $\text{Na}2^+$ site. When this information was introduced in the refinement, a significant improvement of the agreement factors was observed. The two peaks are in a niche of the sinusoidal channel at more than 5 \AA from the nearest carbon atom of the template (they cannot be mixed up with the disordered propyl chains of TPA) and, as typical for cations, are surrounded by oxygen atoms of the framework. Both peaks are at about 0.5 \AA from the crystallographic mirror plane [Figure 2; $\text{Na}1^+ - \text{Na}1^+(m) = 0.99 \text{ \AA}$, $\text{Na}2^+ - \text{Na}2^+(m) = 1.08 \text{ \AA}$ and $\text{Na}1^+ - \text{Na}2^+(m) = 1.07 \text{ \AA}$]. It is worth pointing out that the total population of Na^+ cations was found to be about 2.1 atoms per unit cell, a very reasonable value, slightly lower than the value of 2.5 Fe atoms per unit cell indicated by elemental analysis.²⁸

2. A significant lengthening of the T–O distances (Figure 3), with respect to ZSM-5,²⁶ is a second indication of the most probable substitution sites. When a Si atom is substituted by an Fe the T–O distance increases from 1.6 to 1.9 \AA and the coordination sphere around the site increases of about 40%. It can be expected that such a large increase will induce distortions or defects in the zeolitic framework.

3. The detection of an excess of electron density due to Fe^{III} substitution is problematic, because of its spread probably due to the different location of Si and Fe in the tetrahedral sites and because of the mentioned distortions and defects. Nevertheless,

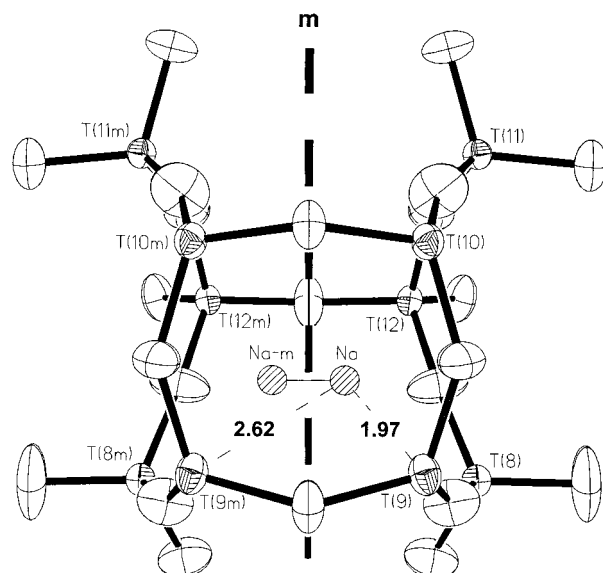


Figure 2. View of part of the Fe-silicalite framework, in the region where the counteraction is found ($\text{Na}2^+$ is omitted for clarity), showing the crystallographic mirror plane *m* and the thermal ellipsoids at the 50% probability level.

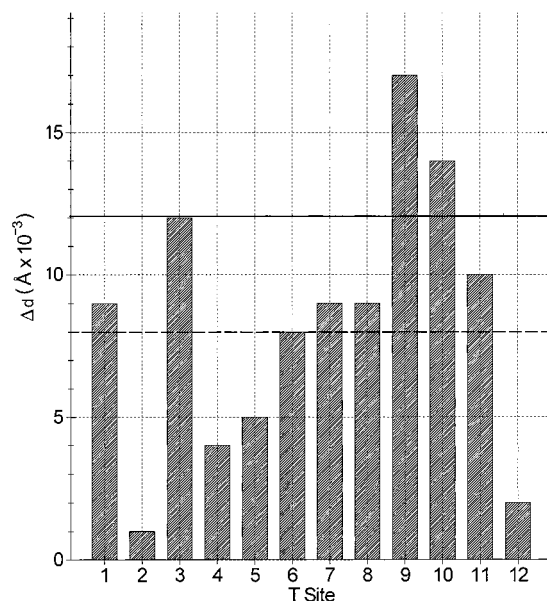


Figure 3. Differences Δd between the average T–O distances found in the present Fe-silicalite and the corresponding average distances in ZSM-5,²⁶ for the 12 independent T sites. Dotted and continuous horizontal lines represent $2\sigma(d)$ and $3\sigma(d)$ values respectively

it has been possible to localize some residual electron density on some of the T sites.

From these evidences we can derive the following conclusions:

1. Site T9 and T10 are the most probable substitution sites, because (i) they are located close to the Na^+ cations, (ii) the lengthening of the T9–O and T10–O distances is the most significant, and (iii) a residual electron density of $0.34 \text{ e}/\text{\AA}^3$ and of $0.19 \text{ e}/\text{\AA}^3$ is present at sites T9 and T10, respectively. Besides, T9 shows the maximum anisotropy in the thermal displacement parameters, which is an expected phenomenon related to the substitutional disorder induced by iron insertion. The T9– $\text{Na}1^+(m)$ (1.97 \AA) and T10– $\text{Na}2^+$ (1.93 \AA) distances appear to be unreasonably short and need some explanation (cf. Figure 2). Indeed these are “virtual” (X-ray) distances in the sense that

they correspond to distances between scarcely populated Na^+ cations and time and space averaged T positions, which are determined (with 98% weight) by a situation where Fe and Na are absent. The T9– Na^+ and T10– $\text{Na}^{2+}(m)$ distances are 2.62 and 2.64 Å, respectively. When, for instance, an Fe is present at a given T9 site the charge will be balanced by the Na^+ counterion at more than 2.6 Å, but as we have seen, substitution introduces considerable distortions and/or defectivity in the neighboring framework and in particular in T9(m) that can locally be actually absent or far away from Na^+ . Indeed, defects in these silicalites are common²⁹ and in our samples they have been evidenced by IR and NMR.

2. All other T sites are far away from Na^+ and Na^{2+} and the lengthening of the T–O distances is less significant [$\Delta d < 3\sigma(d)$]. A small degree of substitution at some of these sites is not detectable, but cannot be excluded. In particular the relatively large Δd value and the residual electron density of $0.28 \text{ e}/\text{\AA}^3$ at T3 may suggest this site as a possible substitution site. Some degree of random substitution is suggested by the positive Δd value found for all T sites, in agreement with the results of the theoretical calculations¹³ which indicate that the energy differences of T substitution at different sites are rather small. Furthermore, random substitution would also yield an entropy gain.

To our knowledge this is the first example of an experimental location of the position of the counterion in a substituted MFI framework zeolite, which, together with the analysis of the T–O distances and the residual electron density at the T sites, yields a rather convincing indication of the Fe^{III} substitution sites. Our results differ from those reported by Eckert et al.,²² in the sense that we have no evidence of a preferred substitution at T8. Nevertheless, a different substitution pattern in samples prepared in different experimental conditions cannot be ruled out.¹⁵ We are aware that all our evidences are indirect, but even with good quality synchrotron single-crystal data, it was not possible to obtain the direct location of the heteroatoms. As an attempt at achieving this result, we have been assigned beamtime to carry out an anomalous dispersion experiment.³⁰

The detailed analysis of the other M^+ derivatives is still in progress, but the preliminary results, a full account of which will be given elsewhere, confirm the present findings.

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