

XAS Investigation of Iron Substitution in Triclinic FeAPO-34

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Abstract

Iron-modified aluminophosphate with a triclinic form of the chabazite topology FeAPO-34, synthesized hydrothermally from a fluoride medium, is analyzed by Fe K-edge XANES and EXAFS. XANES analysis reveals that the as-synthesized sample contains approximately equal amounts of Fe(II) and Fe(III) cations, while the oxidation state of iron in the template-free sample is Fe(III). EXAFS analysis confirms the incorporation of iron into different framework sites of the as-synthesized FeAPO-34 with triclinic symmetry. In the template-free FeAPO-34 with rhombohedral symmetry, iron cations are located on tetrahedral sites, forming catalytically active acid and redox centers.

1. Introduction

The isomorphous substitution of aluminum sites in the framework of microporous aluminophosphates ($\text{AlPO}_4\text{-}n$, n denotes structure type) by small amounts of transition metal ions generates catalytically active acid and redox centers. In this way heterogeneous catalysts can be produced. The degree of incorporation of the metal atoms depends on the particular structure of the aluminophosphate.

In the triclinic form of aluminophosphate with chabazite topology ($\text{AlPO}_4\text{-}34$) successful substitutions of aluminum with Co, Mn, Ni and Zn cations were reported, producing $\text{CoAPO-}34$, $\text{MnAPO-}34$, $\text{NiAPO-}34$ and $\text{ZnAPO-}34$ aluminophosphates [1–3]. The aluminophosphate with triclinic form of chabazite topology ($\text{AlPO}_4\text{-}34$) can be synthesized from fluoride medium using morpholine or piperidine as structure-directing agents [4, 5]. There are three inequivalent aluminum sites in the framework of $\text{AlPO}_4\text{-}34$. Two aluminum sites are tetrahedrally coordinated while the aluminum at the third site is octahedrally coordinated with two fluoride atoms in addition to four oxygens. The fluoride ions bridge two Al atoms in a 4-ring connecting double-6-rings of the structure and thus break the rhombohedral symmetry of chabazite [4]. After the thermal treatment the template- and fluoride-free material adopts the rhombohedral symmetry of chabazite topology in which all aluminum atoms are tetrahedrally coordinated [5]. The framework structure of this phase reforms the triclinic symmetry of chabazite in the presence of water [6].

In this paper we examine the incorporation of iron into the framework of triclinic $\text{AlPO}_4\text{-}34$. We synthesized hydrothermally the FeAPO-34 aluminophosphate. XRD analysis confirmed that the as-synthesized sample had triclinic symmetry, while the framework of the template-free sample adopted the rhombohedral symmetry. The elemental analysis of the as-synthesized sample indicated isomorphous substitution of the framework aluminum by iron. Detailed information on the Fe cation location, however,

was difficult to obtain by XRD, since Fe concentration was very low and Fe cations were randomly distributed in the structure. Therefore we used Fe K-edge XANES and EXAFS analysis to probe directly the valence state and the local environment of Fe cations in the as-synthesized and template-free FeAPO-34 samples.

2. Experimental

We synthesized hydrothermally triclinic FeAPO-34 from a fluoride medium using piperidine as a structure-directing agent [3]. A template-free sample was obtained by calcination in oxygen flow at 500 °C for 3 hours.

X-ray absorption spectra were measured in the transmission mode at E4 beamline of HASYLAB synchrotron facility at DESY in Hamburg. The E4 station provided a focused beam from an Au-coated toroidal mirror and a Si(111) double crystal monochromator with about 1 eV resolution at the Fe K-edge. Harmonics were effectively eliminated by a plane Au-coated mirror, and by a slight detuning of the monochromator crystals, keeping the intensity at 60% of the rocking curve with the beam stabilization feedback control. Powder samples of the as-synthesized and template-free FeAPO-34 materials and reference samples were prepared on multiple layers of adhesive tape and mounted on a sample holder in a vacuum chamber of the beamline, so that during measurements the samples were kept in high vacuum. The standard stepping progression within [–250 eV ... 1000 eV] region of the Fe K-edge was adopted with an integration time of 2 s/step. The exact energy calibration was established with the simultaneous absorption measurements on the Fe metal foil.

3. Results and discussion

The Fe XANES spectra of the FeAPO-34 samples and reference compounds Fe(III)PO_4 , Fe(II)SO_4 , Fe(0) with known oxidation numbers are extracted by a standard procedure (Fig. 1) [7]. The zero energy is taken at the first inflection point in the Fe metal spectrum (7112 eV), i.e., at the 1s ionization threshold in the Fe metal. The shape of the K-edge and the pre-edge resonances is characteristic of the local symmetry of the investigated atom and can be used as a fingerprint in identification of its local environment [7, 8]. Tetrahedrally coordinated atoms are recognized by a single pre-edge peak, which can be assigned to the 1s → 3d transition, as for example in the FePO_4 reference sample. The characteristic tetrahedral resonance is present in the template-free FeAPO-34 demonstrating that iron cations are incorporated into the tetrahedral sites. In the case of the as-synthesized sample

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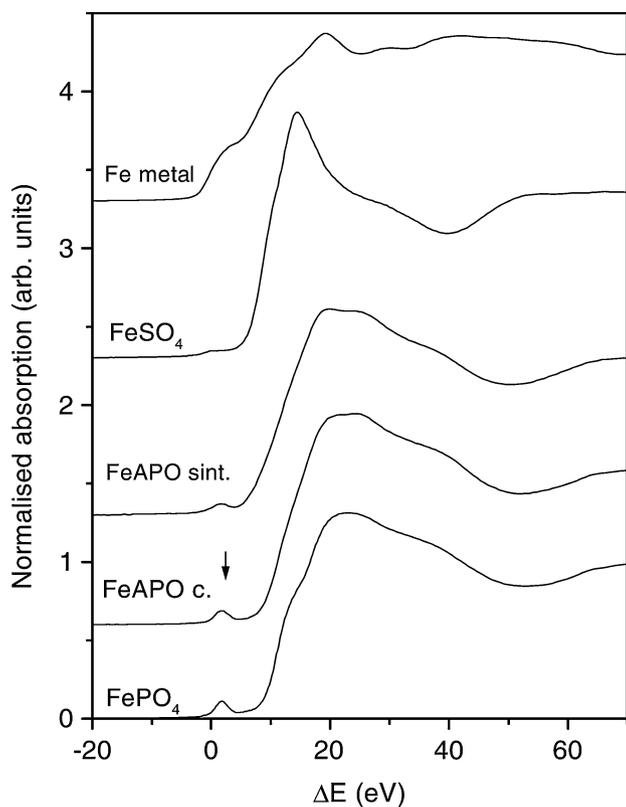


Fig. 1. Normalized Fe K-edge XANES spectra of the as-synthesized and template-free FeAPO-34 and reference samples: FePO₄, FeSO₄ and Fe metal. The zero energy is taken at the 1s ionization threshold in the Fe metal (7112 eV). The pre-edge resonance characteristic for tetrahedrally coordinated atoms is marked by the arrow.

the pre-edge peak is weaker, which indicates that only a fraction of iron cations in the sample occupy tetrahedral sites.

A change in the valence state of metal cations during calcination can be deduced from the energy shift of the Fe absorption edge. The precise energy position of the edge is taken at the edge inflection point, which can best be determined in the derivative spectrum (Fig. 2). A linear relation between the edge shift and the valence state has been established for the atoms with the same type of ligands [7–9]. From the spectra of the reference samples (FeSO₄ and FePO₄) with known iron oxidation states, we derive a Fe K-edge shift of about 3.0 eV per valence state. The Fe XANES spectra of the FeAPO-34 samples clearly indicate oxidation of iron cations during the calcination: the Fe K-edge in the template-free sample is shifted for 1.5 eV when compared to that in the as-synthesized sample. We obtained an average iron valence of about +2.5 in the as-synthesized and +3 in the template-free sample. The as-synthesized FeAPO-34 thus contains about the same amount of Fe(II) and Fe(III) cations, while during calcination all Fe(II) cations in the sample oxidize to Fe(III).

The Fe K-edge EXAFS spectra were quantitatively analyzed for the coordination number, distance, and Debye-Waller factor of the nearest coordination shells of neighbor atoms. The analysis was performed with the University of Washington UWXAFS package [10] using FEFF6 code [11] for ab initio calculation of scattering paths. The k^3 weighted Fourier transform magnitudes of Fe EXAFS spectra calculated in the k -range from 4.5 to 11.5 Å⁻¹ are shown in Fig. 3, together with the best fit EXAFS models.

In the case of the as-synthesized FeAPO-34 sample the fit of the first coordination shell shows that iron is coordinated on average

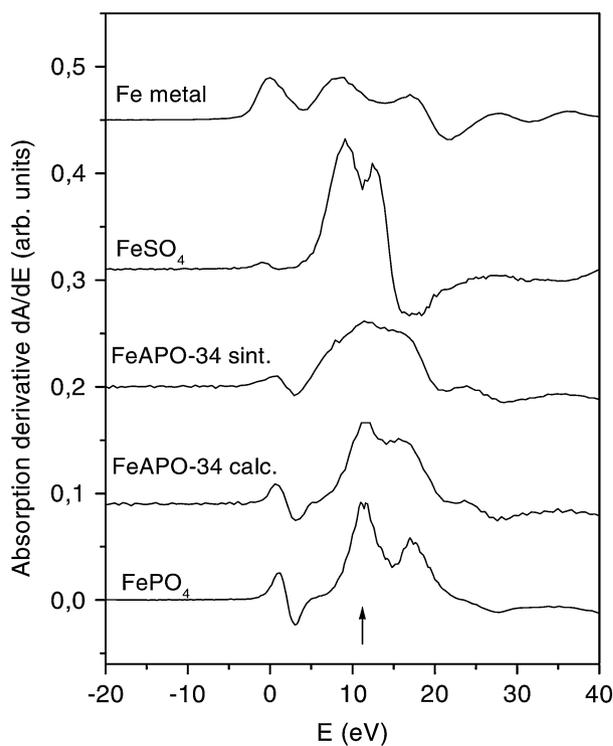


Fig. 2. Absorption derivative of the Fe K-edge profile of the as-synthesized and template-free FeAPO-34 and reference samples from Fig. 1. Vertical arrow is plotted at the energy position of Fe K-edge in FePO₄ sample.

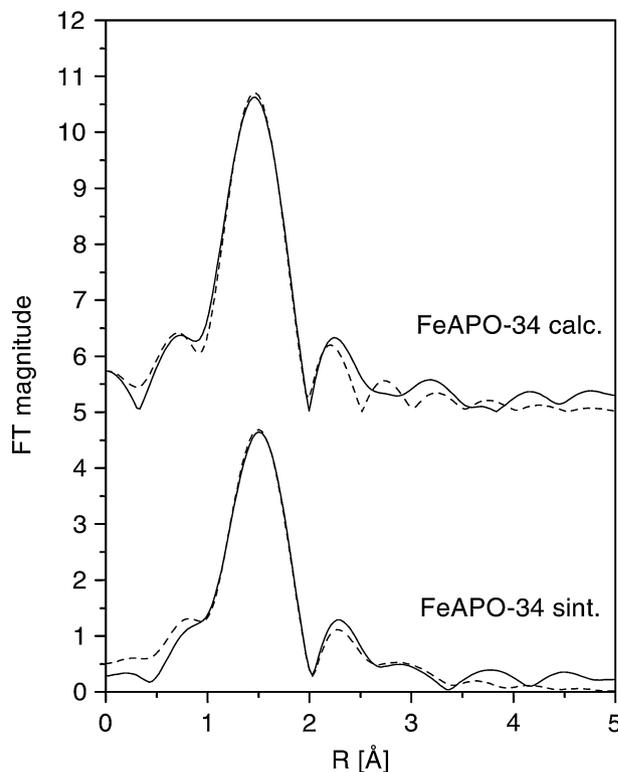


Fig. 3. Fourier transforms of k^3 -weighted EXAFS spectra of the as-synthesized and template-free FeAPO-34 (experiment—solid line, EXAFS model—dotted line).

to five oxygen neighbors at 1.92 Å. This average Fe-O distance is consistent with Fe-O distances (1.91 Å) reported earlier for FeAPO-18 sample [12]. In addition, about 0.3 fluorine atoms on average are found at 2.18 Å. A presence of phosphorous atoms is

Table I. Structural parameters of nearest coordination shells around iron in the as-synthesized and template-free FeAPO-34: neighbour atom, number of atoms (N), distance (R), and Debye-Waller factor (σ^2). Uncertainties of the last digit are given in the parentheses.

Neighbour atom	N	R (Å)	σ^2 (Å ²)
as-synthesized (triclinic)			
O	4.9(5)	1.92(1)	0.007(2)
F	0.3(2)	2.18(1)	0.002(1)
P	0.6(4)	3.13(1)	0.002(1)
template-free (rhombohedral)			
O	3.8(5)	1.86(1)	0.004(1)

indicated in the second coordination shell at about 3.1 Å. Best fit parameters are listed in Table I.

This result supports isomorphous substitution of framework aluminum by iron in the as synthesized sample, as suggested by elemental analysis. Iron cations replace aluminum at all three inequivalent aluminum sites (tetrahedral and octahedral) in the framework of the triclinic AlPO₄-34 framework. In view of the limited sensitivity of the EXAFS signal it should be noted that fluorine neighbor atoms, expected on octahedral sites, cannot be reliably distinguished from oxygen atoms.

In the template-free sample we found four oxygen neighbors at a shorter distance of 1.86 Å in agreement with previously reported values for tetrahedrally coordinated Fe(III) cations [13]. This is in agreement with the rhombohedral symmetry of the template-free sample after the evacuation, when water molecules are removed from the pores. Taking into account also the XANES results we

can conclude that in the template-free sample iron is incorporated into the tetrahedral framework sites in the form of Fe(III). The results are additionally supported by the IR spectroscopic analysis of adsorbed CO at 100 K, which gives clear evidence that the acidic Brønsted and redox centers are present in the template-free FeAPO-34 sample [3].

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