

EXAFS and XANES study of the incorporation of Mn cations into a chabazite-like AIPO molecular sieve

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The incorporation of Mn(II) cations into a chabazite-like MnAIPO material is studied with Mn K-edge XANES and EXAFS. Both methods show that Mn(II) is inserted exclusively into the tetrahedrally coordinated aluminum sites. Calcination and rehydration of the as-synthesized MnAIPO cause a partial oxidation of Mn(II) as well as a change of its coordination geometry to a distorted octahedron.

Keywords: Aluminophosphate molecular sieves, MnAIPO, Mn EXAFS, Mn XANES

Aluminophosphate-based molecular sieves (AIPO) have attracted great attention due to their enhanced structural and composition diversity, in particular transition-metal modified AIPOs. They combine two important phenomena: catalytic activity of the transition metal modified solids and the shape selectivity of the zeolitic host. In this paper we study the incorporation of Mn(II) into a chabazite-like MnAIPO material. The Mn K-edge EXAFS and XANES spectra measured on the as synthesized and the calcined and rehydrated MnAIPO samples are used to determine the oxidation number and location of the manganese cations in the framework.

The material with stoichiometric formula: $(\text{Mn}_{0.05}\text{Al}_{0.95}\text{PO}_4)_6(\text{C}_5\text{H}_7\text{N})_2\text{F}_2$ is synthesized hydrothermally (Rajič *et al.*, 1997). After calcination in air at 800°C for 2 h the product is rehydrated in controlled-humidity atmosphere.

Powdered samples of the as-synthesized and rehydrated-calcined material and of reference compounds ($\text{Mn}^{\text{II}}\text{O}$, $\text{K}_3[\text{Mn}^{\text{III}}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, $\text{Mn}^{\text{IV}}\text{O}_2$, and Mn^0 metal) with well-defined oxidation numbers were prepared on multiple layers of adhesive tape with the total absorption thickness of $\mu\text{d} \sim 2$ above the K-edge and Mn K-edge jump of 0.1 in the MnAIPO samples. Their absorption spectra were measured at the HASYLAB synchrotron facility at DESY (Hamburg, Germany). The EXAFS II station provides a focused beam from a Au-coated mirror and a Si(111) double-crystal monochromator with 1.5 eV resolution at Mn K-edge. Harmonics are effectively eliminated by a plane Ni coated mirror. Reference spectra are taken on empty tapes. Exact energy calibration is established with the simultaneous absorption measurements on the Mn metal foil.

Table 1

The energy shift ΔE_K of the edge point and an average Mn oxidation number in the MnAIPO and reference samples. Uncertainty of the last digit is given in parentheses.

Sample	ΔE_K (eV)	Mn oxidation number
MnAIPO, as-synthesized	7.5(2)	+2.5(3)
MnAIPO, rehydrated-calcined	8.4(2)	+2.7(3)
MnO	5.7(2)	+2
$\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	9.3(2)	+3
MnO_2	13.5(2)	+4

The normalized Mn XANES spectra of the MnAIPO and reference samples (Fig. 1) are extracted by standard procedure (Wong *et al.*, 1984). The zero energy is taken at the first inflection point in Mn metal spectrum at 6539.0 eV, the 1s ionization threshold in Mn metal.

A single pre-edge peak in the XANES spectra of both MnAIPO samples indicates that Mn atoms occupy sites without a center of inversion. However, the intensity of the peak is much lower than in systems with a regular $[\text{MnO}_4]$ species where Mn atoms are tetrahedrally coordinated (Bianconi *et al.*, 1991). This indicates that the coordination geometry of Mn atoms in the samples is distorted.

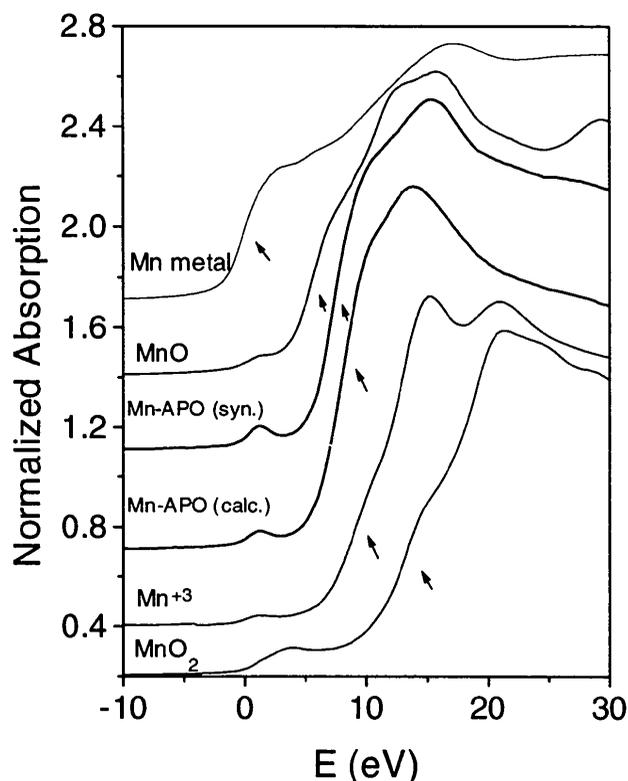


Figure 1

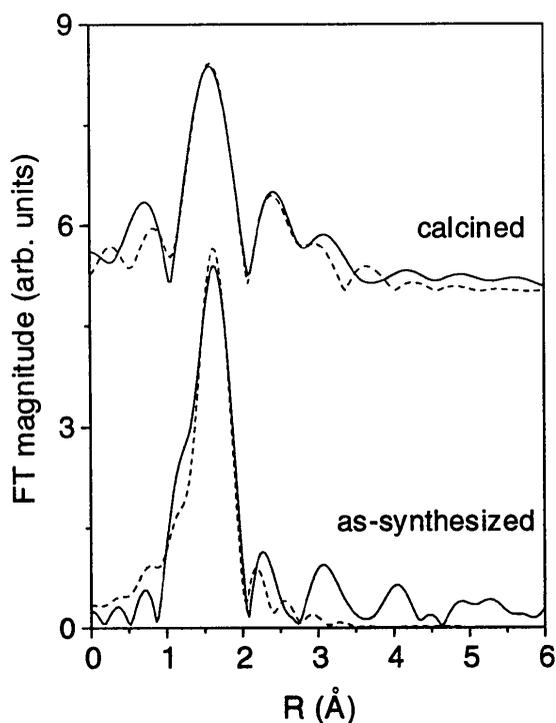
Normalized Mn K-edge profiles, displaced vertically, for the MnAIPO and reference samples. Arrows denote position of the Mn K-edge. Energy scale is relative to the Mn K-edge of the metal (6539.0 eV).

Table 2

Parameters of the first coordination sphere of Mn atoms in the MnAlPO samples: N – number of oxygen atoms; R - metal-oxygen distance, and σ^2 - Debye-Waller factor. Best fit is obtained with a ΔE_0 of -5(4) eV for the as-synthesized and -1(4) eV for the calcined sample. Uncertainty of the last digit is given in parentheses.

As-synthesized			Rehydrated-calcined		
N	R (Å)	$\sigma^2(\text{Å}^2)$	N	R (Å)	$\sigma^2(\text{Å}^2)$
4.0(4)	2.02(2)	0.005(1)	4.0(4)	2.10(2)	0.005(1)
/	/	/	2.0(4)	2.37(2)	0.003(1)

The valence state of an atom shifts the position of the absorption edge. Of various edge features the edge point defined by the position of the second peak in the derivative spectrum is chosen as most sensitive to the oxydation state (Wong *et al.*, 1984). The shift in the edge points of the Mn samples (arrows in Fig. 1) is evident, even between the AlPO samples before and after calcination/rehydration. In quantitative analysis a linear relation between the edge shift and the Mn oxidation is established from the data on the reference samples (Table 1), in analogy with similar empirical relations for other elements in oxides (Wong *et al.*, 1984, Pantelouris *et al.*, 1995, Arčon *et al.*, 1998). The relation gives an average Mn oxidation number of 2.5 for the as-synthesized and 2.7 for the rehydrated/calcined MnAlPO.

**Figure 2**

Fourier transforms of k^3 weighted EXAFS spectra of the as-synthesized and rehydrated-calcined MnAlPO samples calculated in the k range of 4.5 - 12 Å^{-1} and 4.5 - 10 Å^{-1} respectively. FEFF models of four tetrahedrally coordinated oxygens and four plus two octahedrally coordinated oxygens, respectively, are fitted in the first shell R range of 1.3 Å to 2.3 Å . Experiment – (solid line); fit – (dotted line).

EXAFS analysis of the MnAlPO samples has been performed with the University of Washington analysis programs using FEFF6 code for ab-initio calculation of scattering paths (Stern *et al.*, 1995, Rehr *et al.*, 1992). Fourier transforms of k^3 weighted EXAFS are shown in Fig. 2. In the first coordination shell of the Mn atom four oxygen atoms at 2.02 Å are identified in the as-synthesized sample, in accord with the presumed insertion of Mn cations into the AlPO framework. In the rehydrated-calcined sample four oxygens are found at 2.10 Å and further two at 2.37 Å , indicating a distorted octahedral geometry of Mn sites.

Both XANES and EXAFS show that Mn(II) is inserted exclusively into the tetrahedrally coordinated aluminum sites. The average Mn oxidation number of 2.5 obtained for the as-synthesized MnAlPO indicates that upon crystallization of MnAlPO a part of Mn(II) is oxidized to Mn(III). The calcination/rehydration treatment induces a partial oxidation of Mn(II) to Mn(III) as well as a change of its coordination geometry to a distorted octahedron.

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