

Incorporation of Mn, Co and Zn cations into large-pore aluminophosphate molecular sieves MeAPO-50

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Large-pore metal modified aluminophosphate molecular sieves MeAPO-50 (Me=Co,Zn,Mn) were synthesised by hydrothermal crystallisation using di-n-propylamine as structure directing agent. EXAFS and XRD analysis show that cobalt(II), manganese(II) and zinc(II) are incorporated into the non-phosphorus tetrahedral framework sites of MeAPO-50 on the threefold-axis site, and on a site in a general position in the unit cell. Results of both methods on distribution of the metal over the two sites are compared.

Keywords: aluminophosphate molecular sieves MeAPO-50, Mn, Co, Zn EXAFS

1. Introduction

In recent years the interest in metal-substituted large-pore aluminophosphates MeAPO-*n* (where Me = Co, Zn, Mn and *n* denotes a specific structure type) molecular sieves has increased because of their use in catalytic reactions with molecules of kinetic diameter greater than 0.7 nm (Davis, 1994). The catalytic properties of these materials depend both on structure and on the transition metal, i.e. its location and oxidation state.

Large-pore molecular sieve MeAPO-50 with a unidimensional 12-ring channel system has a free aperture between 0.7 and 0.8 nm crossed-linked through 8 rings (Bennet, 1988). The unique feature of this structure type is the high amount of metal cations incorporated into the framework. Metal cations inhabit the MeAPO-50 framework on two nonequivalent non-phosphorus tetrahedral sites. The first site (Me-1) on a general position with multiplicity of 6 is preferably occupied by Al and by a small amount of transition metal, while the second site (Me-2) on the threefold axis with multiplicity 2 is occupied mainly by the substituting metal cations.

In this paper we study the incorporation and distribution of Co, Zn, and Mn cations into the MeAPO-50 molecular sieves by EXAFS and XRD methods at the maximum amount of transition metal necessary for the formation of the MeAPO-50 structure. In case of Mn, the distribution of metal cations at the minimum amount of transition metal is analysed for comparison.

2. Experiment

Large-pore CoAPO-50 and ZnAPO-50 products are synthesised by hydrothermal crystallisation in the presence of di-n-propylamine as a structure directing agent. The Me/Al ratio of 0.36 is used in the reaction gel to obtain the product with the maximum amount of transition metal. Details of the synthesis are described elsewhere (Ristić *et al.*, 1999). MnAPO-50 is synthesised by the same procedure (Novak Tušar *et al.*, 2000) but with the Mn/Al ratio of 0.40 and 2.0 to obtain the product with the minimum (1-MnAPO-50) and the maximum amount of metal (2-MnAPO-50), respectively.

Elemental analysis of the products was carried out by EDAX (Energy dispersion analysis by X-ray) analytical system TRACOR EDX, attached to the scanning electron microscope JXA-840A.

Single-crystal XRD analysis was performed on CoAPO-50 and MnAPO-50 products, on Rigaku AFC5R rotating-anode diffractometer using CuK α radiation. The least-squares refinement of the hexagonal unit cell parameters was performed on 23 reflections in the range from 13.8 to 30.6 $^{\circ}$. TeXsan program package (Molecular Structure Corporation, 1995) was used for all calculations. Data on ZnAPO-50 product crystal structure are obtained by Rietveld refinement of powder XRD patterns.

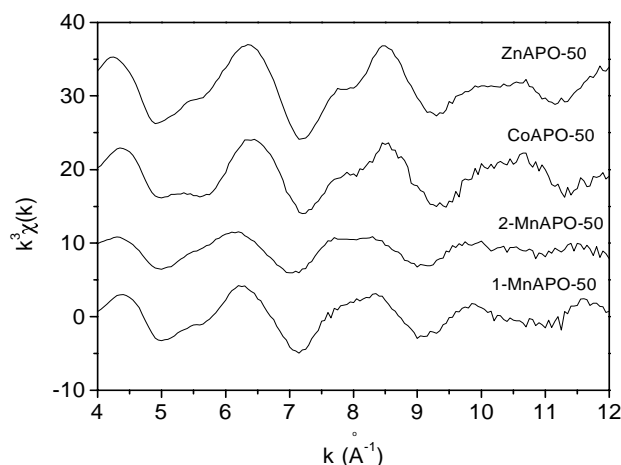


Figure 1

The Zn, Co and Mn k^3 EXAFS spectra measured on ZnAPO-50, CoAPO-50, 1-MnAPO-50 and 2-MnAPO-50 samples.

Powdered samples of the as-synthesized materials were prepared on multiple layers of adhesive tape with the total absorption thickness of $\mu\text{d} \sim 2$ above the K-edge. Their absorption spectra were measured at the HASYLAB synchrotron facility at DESY (Hamburg, Germany). The E4 station provides a focused beam from an Au-coated mirror and an Si(111) double-crystal monochromator with 1.5 eV resolution at Mn K-edge. Harmonics were effectively eliminated by a plane Au coated mirror and by a slight detuning of the monochromator crystals using the beam stabilization feedback control. The standard stepping progression within 1000 eV region of K edge of the incorporated metal (Co, Mn, Zn) was adopted. The monochromator scale was calibrated in energy by a simultaneous absorption measurement on a thin foil of the

respective metal. EXAFS signal of the samples was obtained after removal of a reference spectrum measured on empty tapes.

3. Results and discussion

The formation of a pure structural type MeAPO-50 is confirmed for all samples by XRD analysis. The elemental analysis proves the incorporation of the metal cations into non-phosphorous sites, as evident also from the stoichiometric formulae (Table 1). The occupancies of each site by metal cations obtained by XRD analysis are also shown. The data for ZnAPO-50 are less reliable since they are obtained from powder diffraction data.

Table 1

Stoichiometric formulas from elemental analysis, percentage of metal cations (p) on Me-1 and Me2 site, and fraction of metal (w1) on Me-1 site from XRD.

Sample		p ₁ [%]	p ₂ [%]	w ₁
1-MnAPO-50*	(Mn _{0.36} Al _{0.64})PO ₄	16 (2)	97 (2)	33(5)
2-MnAPO-50	(Mn _{0.48} Al _{0.52})PO ₄	29 (2)	97 (2)	47(5)
CoAPO-50	(Co _{0.46} Al _{0.54})PO ₄	17 (2)	100 (2)	34(5)
ZnAPO-50**	(Zn _{0.40} Al _{0.60})PO ₄	10 (5)	90 (5)	25(18)

*(Novak Tušar *et al.*, 2000); *(Ristić *et al.*, 1999).

The EXAFS spectra were analysed by UWXAFS and FEFF6 code (Stern *et al.*, 1995, Rehr *et al.*, 1992) in the k-range 4 – 12 Å⁻¹, using k³ weight and a Hanning window. The k³ weighted Co, Mn and Zn K-edge EXAFS spectra of the samples are shown in Fig. 1.

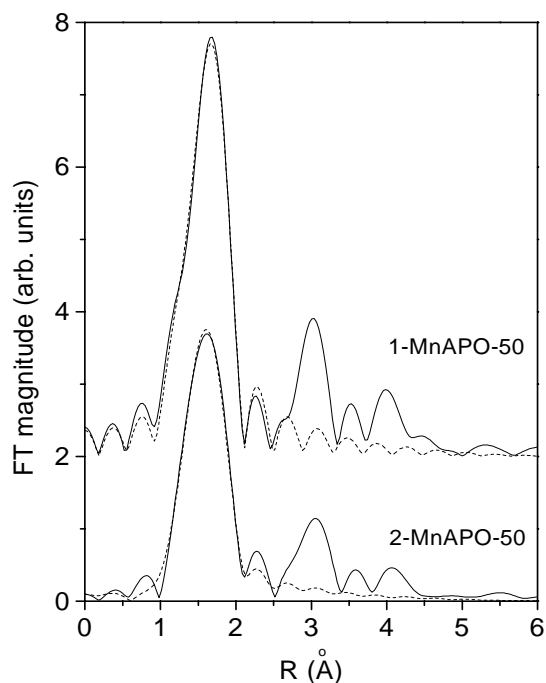


Figure 2

Comparison of the k³ weighted FT magnitude of EXAFS spectra measured on 1-MnAPO-50 and 2-MnAPO-50, (solid line) with the FEFF model of the first peak (dashed line).

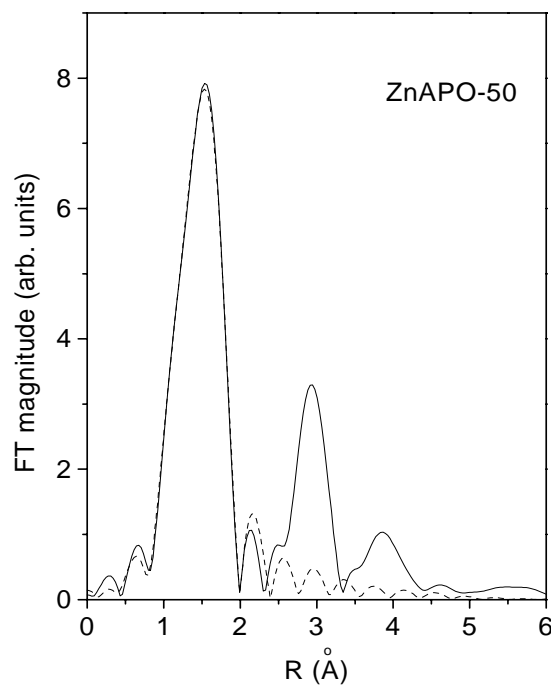
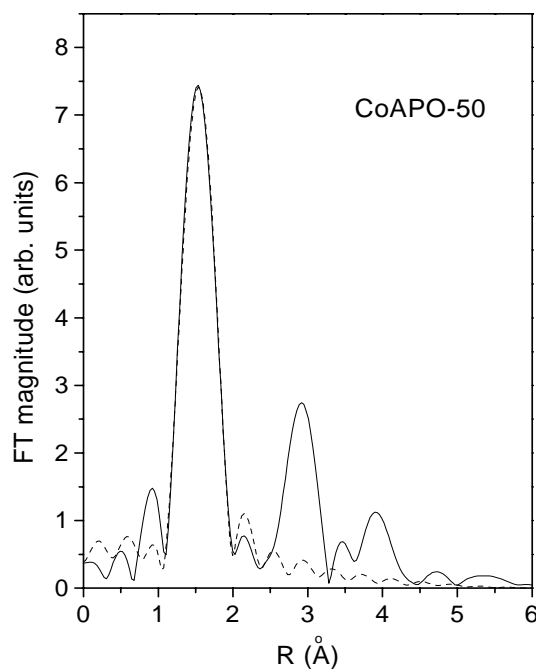


Figure 3

Comparison of the k³ weighted FT magnitude of EXAFS spectra measured on CoAPO-50 and ZnAPO-50 (solid line) with the FEFF model of the first peak (dashed line).

For a quantitative analysis a separate FEFF6 model of the local structure around both sites (Me-1 and Me-2) is constructed, based on 1-MnAPO-50 crystallographic data (Novak Tušar *et al.*, 2000). Mn²⁺ cation is tetrahedrally coordinated by four oxygen atoms, but with significantly different Mn-O distances 1.76 Å and 2.04 Å for Me-1 and Me-2 site respectively. Thus, the analysis of the first coordination

shell in the EXAFS spectra in the R range of 1.0 Å to 2.3 Å is sufficient for determination of distribution of the metal cation over both sites.

In modeling the EXAFS spectra, the scattering paths of the two sites are combined. The ratio of the occupancies of the two sites is varied together with a common Debye-Waller factor σ^2 for the first coordination shell. In addition, variable relative expansions $\Delta R/R$ for each site are used to provide the relaxation of the Me-O distances from the above Mn-O values obtained from MnAPO-50 diffraction data. An excellent fit is found for all the EXAFS spectra. The results are shown in Table 2. The quality of the fit is demonstrated on Figs. 2 and 3.

Table 2

Parameters of the first coordination shell of metal cation on each metal site in the crystal structure of MeAPO-50 samples: w – fraction of metal at each site. $\Delta R/R$ – lattice expansion relative to XRD 1-MnAPO-50 data (Novak Tušar, 2000) at each metal site, and σ^2 – Debye-Waller factor. Uncertainty of the last digit is given in parentheses

Sample	Metal site	w [%]	$\Delta R/R$ (Å)	σ^2 (Å ²)
1-MnAPO-50	Mn-1	18(5)	-0.08(1)	0.002(1)
	Mn-2	82(5)	0.02(2)	0.002(1)
2-MnAPO-50	Mn-1	26(5)	-0.05(1)	0.003(2)
	Mn-2	74(5)	0.03(1)	0.003(2)
CoAPO-50	Co-1	22(7)	-0.08(1)	0.005(3)
	Co-2	78(7)	-0.02(1)	0.005(3)
ZnAPO-50	Zn-1	22(2)	-0.12(1)	0.0025(8)
	Zn-2	78(2)	-0.02(1)	0.0025(8)

Co and Zn cations are incorporated into both crystallographic sites Me-1 and Me-2 with significant predominance of the latter. The result is similar for the minimum-Me 1-MnAPO-50 sample. In 2-MnAPO-50 sample with the maximum amount of the metal the occupation of the Me-1 site is increased.

These results of EXAFS analysis agree with X-ray diffraction structure data of the products, where Me-2 site is found to be almost completely populated with metal cations, while on the Me-1 site Al prevails. This site accommodates Mn occupation between the lower and upper limit of MeAPO-50 structure viability.

However, precise quantitative agreement of the two methods is not yet achieved.

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