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Local structure of Zr incorporated in ETS-10 titanosilicate

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Introduction

ETS-10 is one of crystalline microporous titanosilicates with corner-sharing SiO_4 tetrahedra and TiO_6 octahedra linked through bridging oxygen atoms [1], which leads us to a great interest in the ion-exchange or adsorption characteristics of the material. Here we studied on the substitution of framework sites with Zr and the local structure of Zr in ETS-10 structure.

Experimental

ETZrS-10 was hydrothermally synthesized from the gel with a chemical composition of $5\ SiO_2 \cdot TiO_2 \cdot 0.3\ ZrO_2 \cdot 3\ NaOH \cdot KF \cdot 75\ H_2O$ at 473 K for 45 h, using Ludox® TM-40 colloidal silica and P25 titania powder as Si and Ti source, respectively. XRD was performed to confirm the crystallinity of the material. Zr K-edge spectra were collected at BL-10B in a transmission mode and the data were analyzed by REX 2000 (Rigaku).

Results and discussion

XRD patterns proved that the obtained products contained mainly ETS-10 phase and only small amount of anatase TiO_2 by-phase. Elemental analysis indicated that Zr/Ti ratio in the product was 0.30, comparable to that in the mother gel.

Fig.1 shows the Fourier transforms of the k^3-weighed EXAFS oscillation of ETZrS-10 material. The curve-fitting results are summarized in Table 1. The obtained coordination numbers of Zr-Ti and Zr-Si are consistent with that one Zr atom links with two OTi and four OSi, namely in a (4Si, 2Ti) coordination environment. We examined whether other structural models, such as $Zr(OSi)_4$ (4Si) and $Zr(OSi)_3(OTi)_1$ (3Si, 1Ti), substituting tetrahedral Si, and $Zr(OZr)_6$ (bulk zirconia), would fit our EXAFS results; however none of them led to good fitting results. This strongly indicates that Zr atom substituted framework octahedral Ti isomorphously, being isolated. Interestingly, our findings are quite different from the observations by Eldewik et al. on the substitution with cobalt [2]. According to their results, Co substituted tetrahedral Si at (3Si, 1Ti) site. This difference of the site might be caused by the larger ionic radius of Zr^{4+} than that of Co^{2+}.

Table 1 Results of curve fitting analysis

Scattering atom	N	R / Å	dE / eV	DW / Å	R / %
O	4.429	2.092	-1.122	0.055	5.7
Ti	1.509	3.801	-12.322	0.068	
Si	3.458	3.481	9.345	0.060	

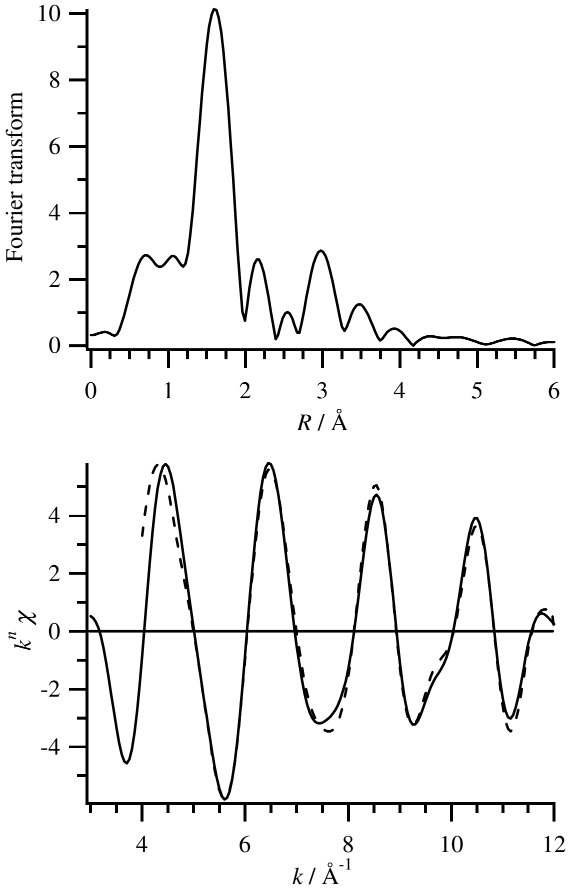

Fig.1 Fourier transform (a) and the fit to back Fourier transforms (b) of ETZrS-10. Solid line: experimental data, dashed line: simulated data.

References

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