

Distribution of aluminum over different T-sites in ferrierite zeolites studied with aluminum valence to core X-ray emission spectroscopy

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Zeolites are microporous crystalline aluminosilicates commercially used as catalysts. Their framework is composed of corner sharing TO₄ tetrahedra with the central T-site occupied either by a silicon atom or an aluminum atom. Replacing a silicon atom with an aluminum atom introduces a local negative charge at the T-site which can be stabilized by protons or cations. These positively charged species confer the catalytic activity to the zeolite. The catalytic activity is therefore directly related to the positioning of aluminum atoms within the framework. The determination of the location of aluminum atoms at individual T-sites and their mutual arrangement, however, remains an open question in zeolite structural analysis.

We have recently performed a series of non-resonant Al valence to core (VtC) X-ray emission spectroscopy (XES) measurements on zeolite samples of type ferrierite [1]. Four samples (FER-PYRR, FER-BMP-TMA, FER-PYRR-TMA, and FER3) prepared with different structural directing agents [2] exhibit different positioning of aluminum inside the framework and thus represent an ideal set of samples to study the sensitivity of the technique with respect to aluminum distribution. The emission measurements were performed at the SLS PHOENIX I beam line with the energy of the incoming photon beam tuned well above the Al K-edge, at 2.5 keV. The VtC X-ray emission spectra were measured in high energy resolution using the von Hamos X-ray spectrometer of Fribourg [3] equipped with an ADP(101) crystal and a back-illuminated CCD detector.

The Al VtC XES spectra of the samples indicate minor differences in the intensity and position of the main emission peak. As indicated by our theoretical calculations, an increased intensity of the Kβ_x feature in the emission spectra can be linked to a higher occupation of a crystallographic position referred to as the T3 site by a single aluminum atom. A fitting procedure of experimental spectra with theoretical spectra corresponding to aluminum occupation of different T-sites indicates that the maximal and minimal occupation of the T3 site by an aluminum atom corresponds to the FER-PYRR and FER3 samples, respectively, which confirms the results from previous works [3]. This study thus suggests that valence to core X-ray emission spectroscopy can be applied to help determine the occupation of aluminum at crystallographic T-sites in zeolites.

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[2] A. B. Pinar et. al., Microporous Mesoporous Mater., **193**, 111-114, (2014)

[3] J. Hoszowska et. al., Nucl. Instr. Meth. Phys. Res. A, **376**, 129-138, (1996)