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Report:

X-ray Standing Waves (XSW) were applied to determine the crystallographic structures of zeolites and the elemental distribution over the alumina-silica framework in particular. Aim was the assignment of aluminum atoms on the crystallographic T-sites (these sites are called T-sites, because of the tetrahedral coordination of the atom that occupies this site, which is aluminum or silicon in case of zeolites), which remains one of the challenges in zeolite structure determination. Because the aluminum atoms are associated with the catalytically active sites in zeolites, knowledge of their distribution over the zeolite crystals is of paramount importance for understanding structure-performance relationships. These relationships aid the design and construction of improved catalysts.

In an X-ray diffraction experiment, the phase information is lost; XSW determines both the phase and amplitude of the Fourier coefficients of the atomic distribution functions in an element specific way. The simultaneous detection of the fluorescence emitted by the sample using an energy-dispersive detector [1] enabled the distinction of the lattice elements silicon and aluminum and the extra-framework cations of which calcium is the most abundant. In the experiments, we attempted to extend the application of XSW imaging beyond surfaces and one-dimensional structures to solving three-dimensional structures.

A single crystal of a zeolite was mounted on a Huber six-circle diffractometer and an X-ray beam of 6.0 keV focused to 50 μm was used. The first zeolite that we attempted was a large crystal (of about 100 μm) of synthetic zeolite ZSM-5. Although the scanning electron microscopy pictures had suggested these were single crystals, the diffraction patterns indicated they were twinned. Moreover, the amount of aluminum was insufficient to detect its modulation while scanning the Bragg reflections. Using a microfocused beam [2] in future experiments will enable the use of smaller crystals that have higher Si/Al ratios and are of better quality.

Figure 1. Natural crystal of zeolite Scolecite mounted on a sample holder.

Subsequently, zeolites Mesolite and Scolecite were investigated. Figure 1 shows a Scolecite crystal mounted. These natural crystals were about 1 cm in size. Various Bragg reflections were scanned and the modulations in the fluorescence signals of aluminum, silicon, calcium, and phosphor were detected. Figure 2 shows the modulation that we observed. The figure shows an XWS-scan of the (040) and (006) Bragg reflections in Scolecite. These reflections were chosen because of their orientation that enables the distinction of different crystallographic sites, their intensities, and high reflectivities. The black dots represent the Bragg reflections, which shows that the single crystal was of reasonable quality. The aluminum and silicon signals show different modulation; In case of the (040) reflection, they had an opposite phase. This

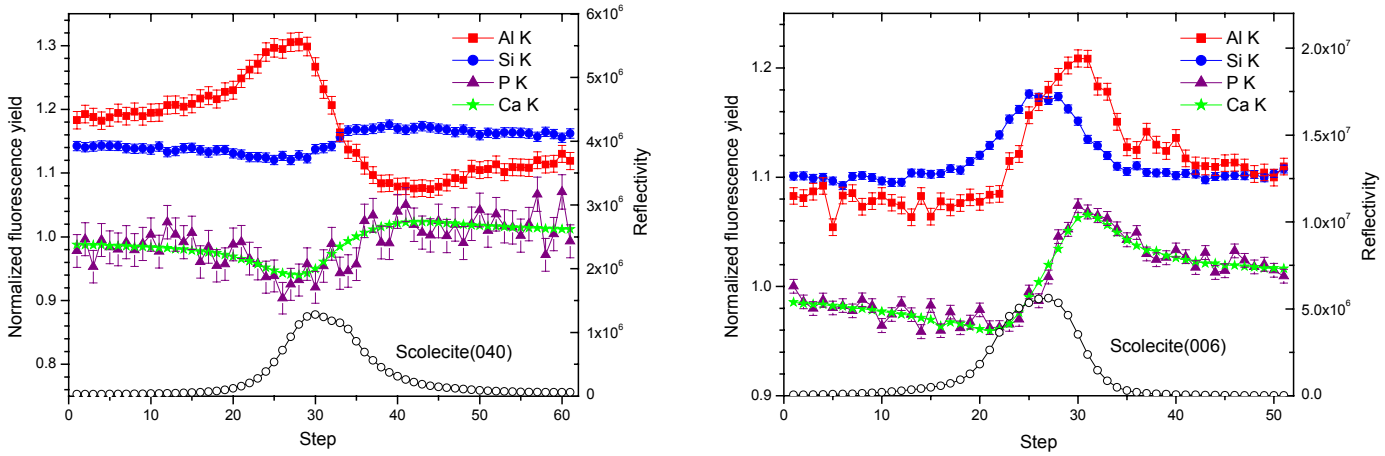

Figure 2. X-ray reflectivity and modulations in the fluorescence yield as function the Bragg reflections (040) and (006) in zeolite Scolecite.

unambiguously proves that these elements are differently distributed over the crystallographic T-sites and that there is significant ordening in aluminum and silicon over this zeolite framework. Also the extraframework cations showed modulation while scanning the Bragg reflection. This shows that these atoms are ordered in the micropores of the zeolite crystal. Two reflections were scanned for each zeolite. Using the crystal structures of these zeolites, we are currently analyzing the data to quantitatively determine the occupation of aluminum over the crystallographic sites. This information will be combined with additional structural information we obtained on these crystals, such as ^{29}Si and ^{27}Al MAS NMR.

These first XSW measurements on zeolites proved that its application provides unique information not only about the framework composition and atom distribution but also about the extra-framework species in the pores of the zeolites. Further application of XSW to smaller crystals, which are readily synthesized in the laboratory could become a practical tool in the determination of zeolite structures, and other materials when conventional diffraction methods fail.

References

[1] L. Cheng et al. *Phys. Rev. Lett.* **90 (**2003) 255503-1-4
[2] M. Drakopoulos et al. *Synchr. Rad. News* **17 (**2004) 37