



In situ investigations of framework materials using neutron scattering

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Many framework materials contain rigid polyhedral units, such as metal-centered octahedral and tetrahedral units, which have the ability to articulate about flexible joints between the polyhedra in response to changes in pressure, temperature and composition. For example, zeolites, naturally occurring aluminosilicates and related microporous framework materials, have molecule-sized cavities, which make these thermally- and acid-stable solids applicable to chemical processes as diverse as catalysis, gas separations and ion exchange. The selectivity of zeolitic materials is tied to the geometry of the framework, and the positions of cations and solvent molecules in the channels. Determination of the crystal structures therefore is important for understanding the properties of these materials, and for tailoring them to better suit a particular process. *In situ* neutron powder diffraction is often an important technique for these studies, since processes such as ion exchange and dehydration are more applicable if they are performed under the “operating conditions” of interest.

Some of the neutron’s unique properties make these studies possible. The penetrating power of the neutron makes design of experimental apparatus for *in situ* work more straightforward. Often competition between water molecules and cations in zeolitic cavities leads to unusual behavior upon hydration; the neutron’s sensitivity to water, and particularly hydrogen, in the presence of heavy elements such as lead and cadmium, allow us to follow the *in situ* mechanism of ion movement in certain zeolites as they are heated, dehydrated and rehydrated. Depending on the results of

competition between cations and water for occupancy of sites close to the apertures of zeolites, cations can locate and relocate to occupy blocking positions that exclude sorption to the interior of the zeolitic channels. This process has been observed in a number of naturally occurring and synthetic materials.

This work is made more difficult by the relatively poor diffraction patterns seen from these materials, since they usually exhibit significant amounts of disorder. Distinguishing between partially occupied metal sites is challenging and is sometimes facilitated by the joint use of synchrotron X-ray and neutron powder diffraction. The use of single crystals would greatly aid in many of these studies. Single crystal neutron scattering however is notoriously difficult on many earth materials because they tend to crystallize in the size range $< 300 \mu\text{m}$. The advent of more powerful sources, newer generation area detectors, and the prospects for focusing beams to $100 \mu\text{m}$ suggests that *in situ* single crystal studies on smaller samples may now be possible.

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