

Two-in-one: XRD and Raman diagnostics combined

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Introduction

Changing demands in industry make tailor-made zeolites necessary especially in view of their wide use and high potential as catalysts and adsorbents. For this, detailed knowledge of the crystallization processes and also the catalytic mechanisms is absolutely essential. We designed a unique combined XRD-Raman system with high flexibility allowing closure of the diagnostic gap between molecular short range interaction and long range structure.

As examples, two research topics which will greatly profit by the two-in-one approach.

Experimental

To meet scientific demands, the machine (Diffram) is designed with a unique flexibility in diffractometer and Raman parts. For zeolite and guest-host analysis the Raman setup allows the choice of different excitations in the ultraviolet and the visible electromagnetic spectrum. This avoids well known fluorescence problems and opens the possibility to exploit resonance Raman effects. A triple spectrometer which can be operated in additive or subtractive mode makes optimization of intensity versus resolution feasible. The XRD diffractometer combines the three most common measurement configurations: Transmission, Bragg-Brentano and micro-diffraction geometry. This is achieved using focusing optics and variable source-sample-detector distances.

Results

The all-silica molecular sieve Silicalite-1 is chosen as a model for zeolite formation studies. Silicalite-1 is crystallized by heating a clear solution of tetraethylorthosilicate and aqueous tetrapropylammonium hydroxide as template. The latter directs silica condensations towards specific precursor silicate polyanions, of which the largest one has a connectivity approaching the MFI framework topology. These units locally enrich and condense in a self-assembly process which eventually results in a zeolite. Raman spectroscopy is very sensitive to follow the formation of these molecular silicate-species, and specifically the template-silicate interaction. X-rays contribute to the study from the moment of particle formation, manifesting in the low angle region till onset of crystallization detectable in Bragg scattering.

A recent example for guest-host (active site) studies, is analysis of a Ru-complex in a Y zeolite. Preliminary results show a change in the active trimer-structure with the inclusion into the zeolite and also modifications during the ad- and desorption of NO_x. The sensitivity of the Raman spectrum towards changes in metal-coordination helps understanding the local processes during ad- and desorption

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