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Report:

Introduction

The formation and stability of aluminium rich zeolites critically depends on the type and concentration of the inorganic, alkaline (earth) cations in the synthesis batch (Figure 1).[1] Although essential in a large number of verified synthesis recipes, the structure directing role of these cations during the transformation of an amorphous gel into a final crystalline framework, is yet to be elucidated. In this experiment, clear zeolite precursor solutions containing Rb^+ cations only, were investigated to gain insight in the first stages of zeolite formation. Rather than complex gels, the particular synthesis system formulated at our lab, produces clear solutions ideally suited for SAXS, EXAFS and NMR analysis of the zeolite precursor oligomers. The influence of the silica, alumina and water content on the size of the aluminosilicate oligomers and changes in Rb^+ coordination was explored.

Revealing the role of inorganic cations in zeolite formation is necessary to control the crystallization of high alumina zeolites, that have applications in adsorption and catalysis of small molecules. Extensive characterization of the precursor solution, synthesis evolution and final frameworks already has been done for the K containing system, and is currently extended to the Rb system.In literature there are only few reports about the templating role of Rb. This experiment could show how the Rb cation directs the nucleation of zeolitic products.

Experimental set-up

As this was our first Rb-EXAFS experiment, a number of samples with simple, known structures, such as RbOH, RbCl, $RbNO_3$, Rb_2CO_3, Rb_2HPO_4 and $Rb_2Ge_4O_9$, were measured as a reference. Clear zeolite precursor solutions with composition 0-0.5 SiO_2: 1 RbOH: 0-0.026 Al_2O_3: 4-12 H_2O were prepared at the ESRF. The Rb K-edge XAS was measured on all liquid samples in transmission mode from 15 to 16 keV.

Finally, a set of different solid zeolite samples (MER; CHA, KFI, MOR), either made in presence of RbOH, or exchanged with Rb-salt after synthesis, was investigated. While the solid samples were measured in capillaries or were

pelletised, liquid films of suitable thickness were obtained by using a plastic spacer in plastic bags, and then mounted on the sample holder. The commonly used Kapton tape did not resist the strongly alkaline RbOH samples.

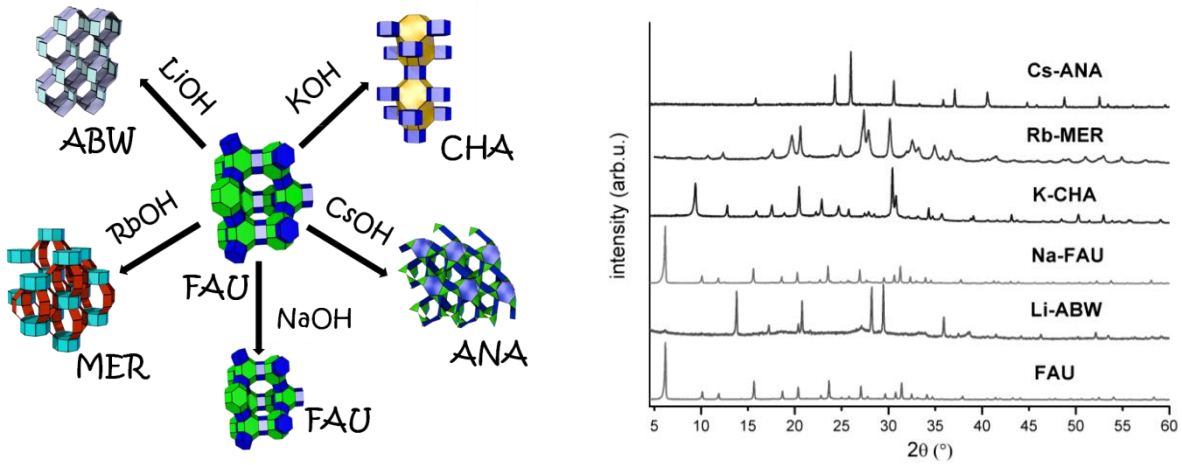

Figure 1: Illustration of the structure directing effect of alkaline cations on zeolite (trans)formation. The different framework types, identified by XRD, are obtained by exposing zeolite Y (FAU) to MOH solution (1 M) at 95°C

Preliminary results

Preliminary inspection of the datasets demonstrated an overall excellent signal to noise ratio. In the liquid samples, the effect of different water content is easily distinguished, while the effects of a variation of the Al content was not evident. As expected, the extraction of the EXAFS signal is severely hampered due to the presence multi electron excitations[2]. To tackle this hurdle, complimentary techniques such as SAXS (at COK, Leuven) and HEXS (ID15B, SC3807) were performed on identical samples to determine the size and connectivity of the zeolite precursor species. Combination of these results with the XAS data recorded will be evaluated as a route to implement a more reliable way of background subtraction.

For the study of final solid zeolite materials, frameworks were chosen which underwent a full structure characterization at COK. The spectra recorded for different zeolite types significantly differed, and interestingly, also differences were observed between the Rb-containing zeolites directly synthesized in RbOH, and the same framework types obtained in the Rb-form by post-synthesis ion-exchange. In addition, also time series of products obtained during exposure of FAU type zeolite to RbOH, leading to MER type zeolite, were measured. For several of these structures, high resolutions diffraction data is available. For these datasets, rietveld refinement can be combined with the XAS analysis, thereby providing an additional route to verify and improve the procedures for extraction of the exafs signal.

References

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