



	Experiment title: Investigation of the structure and mechanism of formation of colloidal zeolite A using SAXS and WAXS	Experiment number: CH-1538
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Report:

Introduction

The aim of this experiment was to investigate the structure and mechanism of formation of zeolite LTA colloidal particles formed in situ under hydrothermal conditions. The combination of SAXS/WAXS and USAXS was shown to be particularly powerful for following the development of structure on different length scales, during the nucleation, growth and subsequent crystallisation of the zeolite.

In the synthesis procedure, two precursor solutions of silicate and aluminate were used. (These solutions are transparent and contain oligomeric species). It was shown that when mixed, these species react to give aluminosilicate clusters (this process occurs during an "induction period"); these clusters subsequently grow and eventually nucleate to form crystalline zeolite LTA.

The precursor solutions also contain two different cations: Sodium and tetramethylammonium (TMA). TMA is important as a "structure-directing" cation to obtain exclusively the zeolite LTA structure. However the TMA/Na ratio has a profound effect on the kinetics and the reaction mechanism, which is not understood. The importance of TMA on the mechanism has been explored in the present experiment.

WAXS

In figure 1, WAXS profiles of in situ samples taken from a zeolite synthesis mixture at 353 K containing a high organic template concentration are shown. After six hours a broad Gaussian band centred at $Q = 2.0 \text{ \AA}^{-1}$ is observed. This can be ascribed to an amorphous aluminosilicate phase, which constitutes the colloidal particles

formed during the induction period. After 18 hours, broad diffraction features appear, which are superimposed on this broad band. These indicate the nucleation of zeolite phase –which takes place within the colloidal particles. After 24 hours, these diffraction features grow and the broad band disappears which indicates the amorphous phase is consumed during crystal growth. All the diffraction peaks can be indexed to the zeolite LTA structure as indicated.

SAXS / UAXS

Typical combined SAXS and USAXS (Bonse – Hart) results for samples produced at 353 K under comparable conditions of high TMA/Na ratio are shown in figure 2. Initially, (a), the scattering is very weak and can be ascribed to small oligomeric silicate/TMA units (other results not shown here). After 3 hours, (b) – (d), the SAXS develops indicating the formation and growth of colloidal particles. These appear to be relatively monodispersed (~10% polydispersity) as indicated by maxima in $P(Q)$ observed in the range $Q > 4.10^{-3} \text{ \AA}^{-1}$. These curves have been fitted to the $P(Q)$ for spheres as illustrated in figure 3. (N.B. values of R_s derived from the full curve fitting and R_G are in reasonable accord). After longer times (>12 hours) when crystallisation occurs, results from SEM show the transformation to particles with a cubic shape and this results in less satisfactory fits to the $P(Q)$ for spheres.

An initial, and tentative analysis of the zeolite formation mechanism, suggests that two stages occur. During the first (induction period) there is a nucleation of oligomers to form amorphous alumino-silicate particles. These particles then grow by accretion of further oligomeric species, as evidenced by the linear relationship between $I(Q)Q^2_0$ and R_s^6 (figure 4.). In the second stage nucleation of the crystalline zeolite occurs within the particles. Consumption of the amorphous phase proceeds with simultaneous distortion of the isotropic spherical particles to give cubic colloidal crystals.

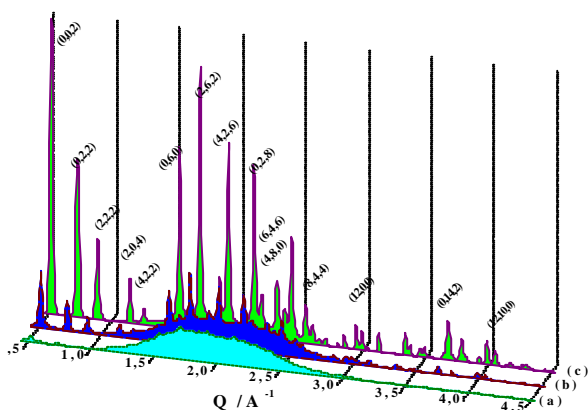


Fig. 1. WAXS profiles of in situ samples produced in a zeolite LTA synthesis mixture at 353K after different times (a) 6 hours, (b) 18 hours, (c) 24 hours. At 18 hours, after an induction period, diffraction peaks are evident. After 24 hours all the peaks can be indexed to the LTA structure as shown. In this synthesis mixture the organic template (TMA), concentration ratio is : $[TMA]/([Na]+[TMA])=0.93$.

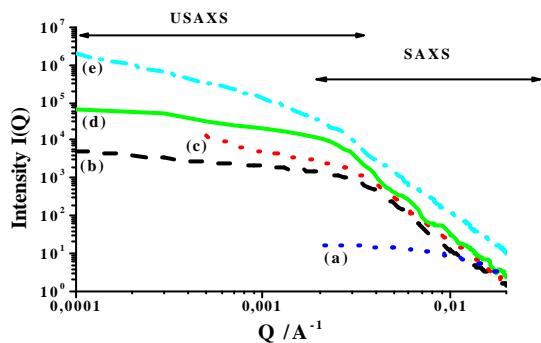


Fig. 2. Combination of SAXS and USAXS for samples produced after different times in a zeolite LTA synthesis mixture at 353K. Synthesis times are (a) 1 hour, (b) 3 hours (c) 6 hours, (d) 12 hours (e) 24 hours. (a) to (d) correspond to an in situ sample of colloidal particles in water (~8% w/w), (e) corresponds to the dried powder composed of crystalline cubic particles.

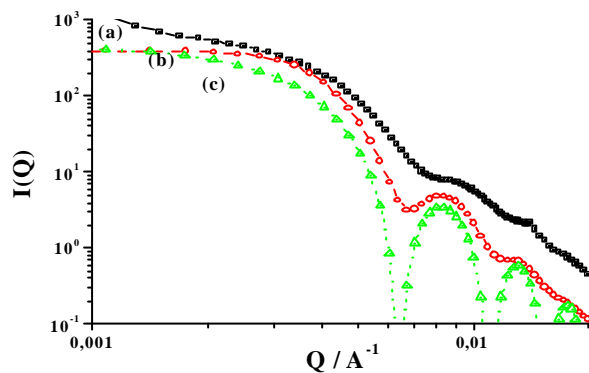


Fig. 3. (a) SAXS for a diluted colloidal sample formed after 3 hours as in figure 2. The curves in (b) and (c) correspond to the form factor $P(Q)$ for spherical particles of radius $R_s = 60 \text{ nm}$ with polydispersity 0 and 10% respectively.

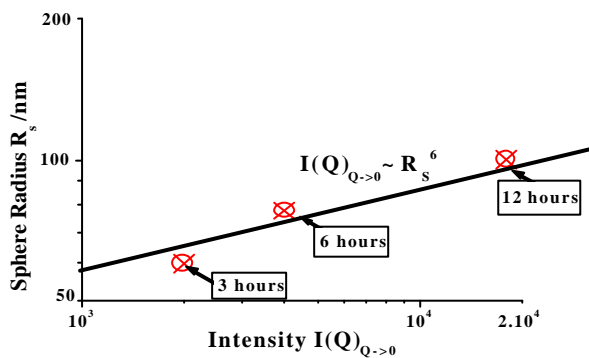


Fig. 4. Dependence of R_s on intensity $I(Q)_{Q \rightarrow 0}$ determined experimentally after progressive time of synthesis (3h, 6h and 12hours). The continuous line corresponds to a R_s^6 dependence on $I(Q)_{Q \rightarrow 0}$ which obtains for a mechanism of nucleation and particle growth.