The Crystallization of a Layered Silicate Clay as Monitored by Small-Angle X-ray Scattering

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Introduction

The mechanism of formation of clays is of interest because of the use of synthetic layered silicates as heterogeneous catalyst supports and in various other technological applications.[1,2] A full understanding of the mechanism would help direct tailored synthetic processes. The complete crystallization of a 2:1 magnesium silicate smectite clay called hectorite takes just 48 hours at 100ºC. The formation has been monitored by several *ex situ* techniques.[3] We have now exploited small-angle x-ray scattering (SAXS) to access different size regimes, length scales, and time frames and thereby add information to the overall scenario of a clay crystallization mechanism.

Materials

The typical method for *in situ* hydrothermal crystallization of organohectorite clays is to create a 2 wt% gel of silica sol, $Mg(OH)^2$, LiF, and organic in water and to reflux for 2 days. Complete details can be found elsewhere.[4,5,6] The organic for these crystallization studies is tetraethylammonium chloride (TEA). The mixture is refluxed for up to 48 h and then centrifuged and the products are washed and air-dried. Small aliquots for *ex situ* time-resolved studies are removed at various times during the crystallization. Powder samples are isolated after centrifuging, washing, and drying. Wet gels are saved as is without further washing.

SAXS Analysis

The SAXS instrument at the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) undulator beamline ID-12 at the Advanced Photon Source was utilized.[7] For the *ex situ* gel studies, wet aliquots were transferred to 1.5-mm quartz capillary tubes. The SAXS data were collected in 5-min. exposures. Controls of pure silica and brucite sols were also run in capillaries. For the *in situ* study, a small portion of unreacted clay gel was transferred to a capillary tube and sealed. This capillary was placed in a home-built furnace assembly such that the gel was directly in the beam path and heated to100ºC. SAXS data were collected in 2-min scans separated by 5 msec for the first 2 h, then as 10-min scans for the remaining 10 hs. Monochromatic x-rays at 10.0 keV were scattered off the sample and collected on a 19 x 19 cm^2 position-sensitive two-dimensional gas wire detector. The scattered intensity has been corrected for absorption, scattering from a blank capillary containing only water (or scattering from blank Scotch tape for the powder studies), and instrument background. The instrument was operated at a sample-to-detector distance of 67 cm to obtain data at $0.04 < Q < 0.7$ $Å^{-1}$ (high Q) and at 389 cm for the range $0.007 < Q < 0.16$ $Å^{-1}$ (low Q). Whereas Kapton windows were used for the lower-Q range data, Mylar windows were used for the higher Q range because Kapton does not have diffraction peaks in this region. For *ex situ* powder studies, the samples were sealed in Scotch tape "cells." A newer nine-element mosaic CCD detector (15 x 15 cm^2) with a maximum of 3000 x 3000 pixel resolution was used for these samples. This detector can better accommodate the high scattering intensities of these powders and required only 0.1-s exposure times. Other parameters were enhanced as well: An evacuated sample chamber was utilized and the effective Q-range was 0.002-.07 $Å^{-1}$ (the sample-to-detector distance was 296 cm in this configuration).

Results and Discussion

Results from the high-Q SAXS using aliquots show that data for both isolated dried powders and wet gels are consistent with each other. This has implications for SAXS sample preparation in that for convenience either form (wet or dry) can be used. Scattering from the starting material, silica sol (seen at ~0.08 $Å^{-1}$) gradually disappears as the clay crystallizes and scatters in the basal spacing region (0.4 $Å^{-1}$, 15 Å) and is visibly evident at about 6 hs. This data is consistent with *ex situ* XRD, TGA, and IR data in that all these techniques show clay crystallites beginning to form after about 4 hs of reaction. The first *in situ* study of clay crystallization of any kind was performed by *in situ* SAXS. Data were collected every 2 min for 2 h, then every 10 min for 10 h in the high-Q range. Results are consistent with the *ex situ* data.

In the low-Q regime, powder samples are more informative, especially at the very early crystallization times, than gel samples. There are two large humps in the mid-Q range of the scattering curve of the unreacted starting material, which consists primarily of silica sol and brucite, at 0.02 $Å^{-1}$ and 0.035 $Å^{-1}$. There is a significant reduction of these humps after just 30 min of reaction time. The curves from 1 to 48 h can be fit using an extension of the unified equation developed by Beaucage[8] for multiple structural levels, with parameters inserted for a lamellar disc. This in essence treats the system as fractal aggregates of lamellae. The data for the 0-h sample cannot be fit to this equation. The power-law exponents, lamellar radii, and lamellar particle thicknesses for all of the powder aliquots were determined from the Beaucage fits. There is a linear progression in power-law exponent from 2.39 to 3.32 up to the 14-h time frame. From earlier atomic force microscopy (AFM) data, we proposed[5] that layers of brucite progress to particles of clay layers with tendrils of silica "glue," and that these further progress to more cemented aggregates of particles of clay layers. More specifically, the AFM data show that between 4 and 8 hs nucleation of the clay crystallites is occurring, and that at some point between 8 and 14 h the nucleation is complete. At times longer than 14 h, particles appeared to primarily coalesce and form substantially larger aggregates. We propose that the change in the low-Q power-law value also is reflecting the whole particle at early stages of clay nuclei. These nuclei have silica tendrils that create a more open structure. As crystallization proceeds, the particles become more cemented, dense agglomerates. An increase in lamellar thickness from 136 Å at 0.5 h to 201 Å at 48 h corresponds to an increase from 9 to 13 average stacked TEA-clay layers, and also reflects the enhanced XRD signals observed with crystallization time.[4] A possible scenario describing how this crystallization mechanism proceeds has now been developed.[9]

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