

Silane Modification of Hectorites

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Introduction

Mesoporous lamellar clays may be obtained commercially, obtained from natural sources, or prepared especially to give desired properties (e.g., composition, porosity, cation exchange capacity). After the desired hectorite has been acquired, it may be further tailored in several ways to vary the counter cation species, incorporate organic intercalants, or form more complex organo-inorganic nanocomposites. The various modifications may be used to provide the optimal interaction between clay matrices and biological molecules. It is envisioned that judicious tailoring of clays may lead to the coupling of clay catalytic processes with enzymatic reactions.

We examined the utility of a post-clay crystallization synthetic route for modifying clay matrices on the basis of the chemisorption of organosilanes to the siloxane clay layer surface [1]. The effects of reaction time, reaction temperature, and the alkyl chain length of the organosilane were examined by small-angle x-ray scattering (SAXS) and thermal gravimetric analysis.

Methods and Materials

Laponite RD, a synthetic hectorite from Southern Clay Products of Gonzales, Texas, was used as received. All other reagents were purchased from Aldrich.

Postcrystallization modification was based on the method of Okutomo et al. [1]. Briefly, C₈-laponite was

prepared by the reaction of laponite suspended in a mixture of chlorodimethyloctylsilane and rigorously dry toluene under a dry nitrogen atmosphere. The solid product was collected by centrifugation and washed sequentially with toluene, acetone, and water. Chlorodimethyloctadecylsilane and aminopropyl-triethoxysilane were used to prepare C₁₈- and NH₂-laponite.

Thermal gravimetric analysis (TGA) measurements were obtained on an EXSTAR6000 from Seiko Haake Instruments. The samples were measured against an α -alumina standard under an O₂ flow rate of 100 mL/min with a temperature ramp of 10°C/min to 900°C. Total combustible organic content was calculated by measuring the weight loss over a temperature range of approximately 200-600°C.

Powder SAXS samples were spread evenly in a thin layer on a piece of transparent plastic tape, then sandwiched with another layer of tape. These samples were placed on the sample holder perpendicular to the x-ray beam.

Results and Discussion

Several samples of each reaction type were prepared. Of these, a few were selected for SAXS analysis on the basis of the amount of organic species measured by TGA. These samples are described in Table 1. The degree of reaction may be gauged by the amount of organic species

Table 1. Summary of sample preparation and analysis results.

Sample	Reactant ^a	Reaction condition ^b	Reaction time (h)	Wt% organic by TGA	d-spacing (Å)
a	C ₈	reflux	250	13.2	19.7
b	C ₈	reflux	500	15.9	17.4
c	C ₁₈	r.t.	500	11.5	17.0
d	C ₁₈	r.t.	1000	na ^c	17.4
e	C ₁₈	reflux	500	23.3	17.5
f	NH ₂	r.t.	500	7.3	16.9
g	NH ₂	r.t.	1000	14.1	17.4
h	NH ₂	reflux	500	11.8	17.3

^aC₈ = chlorodimethyloctylsilane, C₁₈ = chlorodimethyloctadecylsilane, and NH₂ = aminopropyl-triethoxysilane.

^breflux = reaction carried out at temperature at which toluene boils, r.t. = reaction carried out at room temperature.

^cna = no TGA could be performed.

incorporated in the solid product. TGA results show that the reaction proceeded more quickly at elevated temperatures than at room temperature.

The SAXS data (Fig. 1) show various changes in the d-spacing of these lamellar samples. SAXS results are summarized and corresponding sample descriptions are provided in Table 1. Laponite RD prior to organosilane reaction displays a d-spacing of typically 14-15 Å, depending on the amount of adsorbed water. All of these samples displayed an increased d-spacing as a result of the intercalation of the organosilane. As each reaction proceeded, the d-spacing of the clay expanded further, with the exception of the C₈-laponite sample at reflux for 250 h. For sample "a," the elevated water content (20 wt% as opposed to 3-5 wt% for the rest of the samples) induced swelling of the clay in addition to the effect of intercalation of the organosilane. More detailed analysis of these samples may be done at a later date by using a different Q range.

SAXS and TGA data show that this reaction may be used to modify the interlayer space, or gallery, of laponite and possibly other hectorites. Further characterization of the interaction between the organosilane and clay layers is underway.

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References

[1] S Ohtutomo, K. Kuroda, and M. Ogawa, Appl. Clay Sci. **15**, 253-264 (1999).

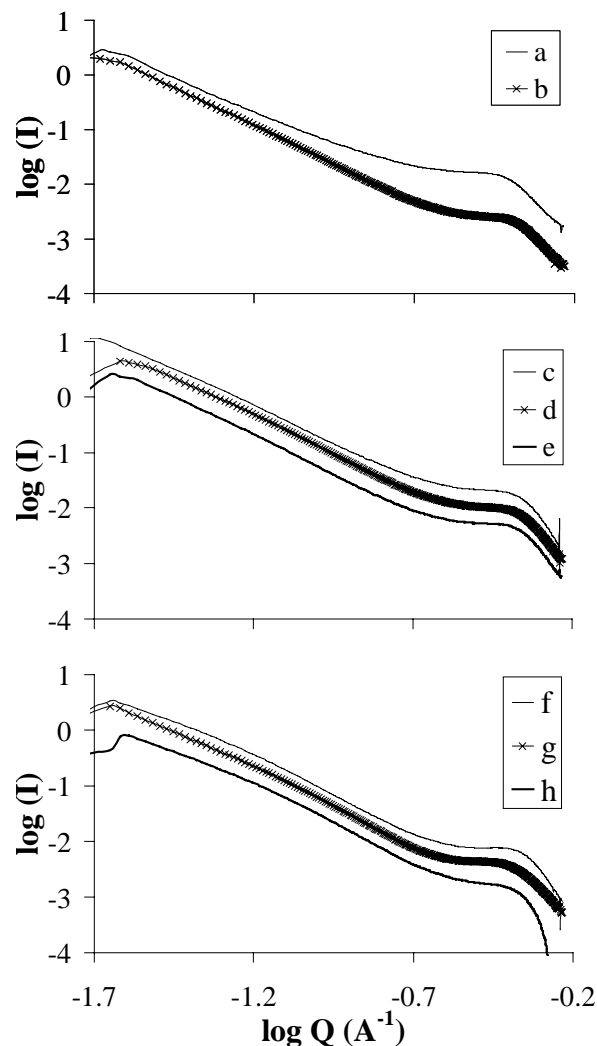


FIG. 1. SAXS data collected for samples as described in Table 1.