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Development of Nanoscale Synthetic Hectorite Clays

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Pre-service Teacher Intern 2006

Overview

This project seeks to:

- Synthesize clays using established methods
- Develop alternate methods for synthesizing clays
- Combine alkoxysilanes and organoalkoxysilanes in various mixtures in order to create materials with various organo-group densities grafted to the silicate surface

Clays are silicates of sheet-like structure, with gallery spaces filled with water. The sheets are usually aluminosilicate or magnesium silicate composition.

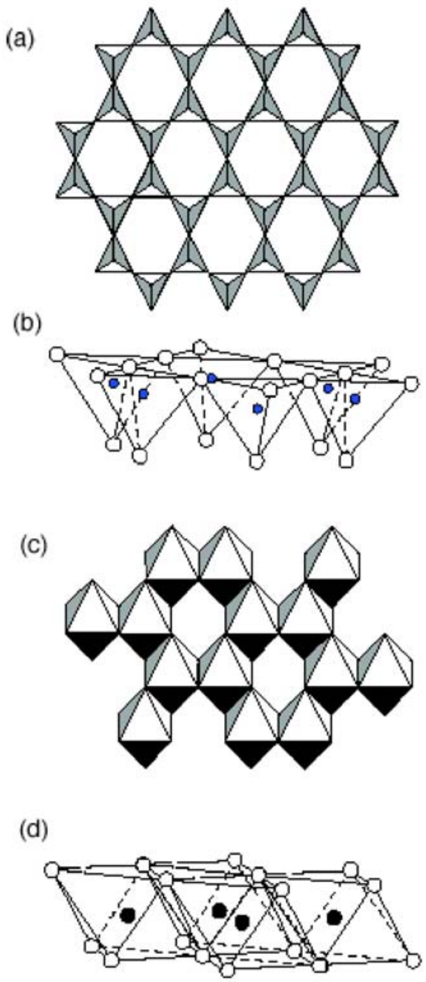
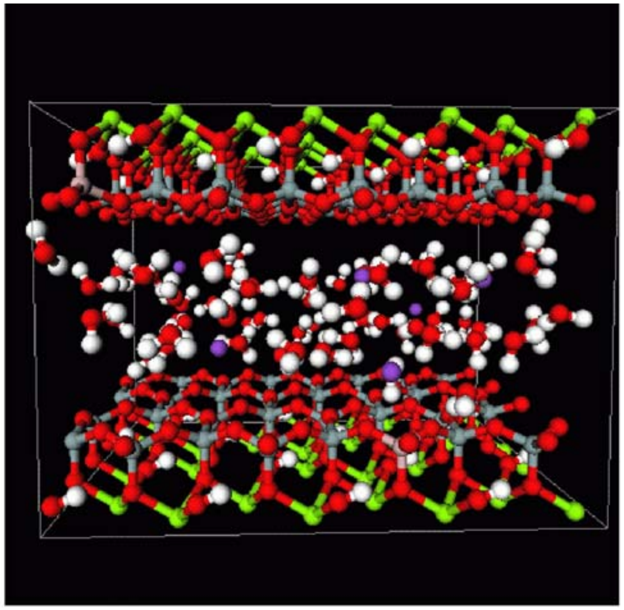
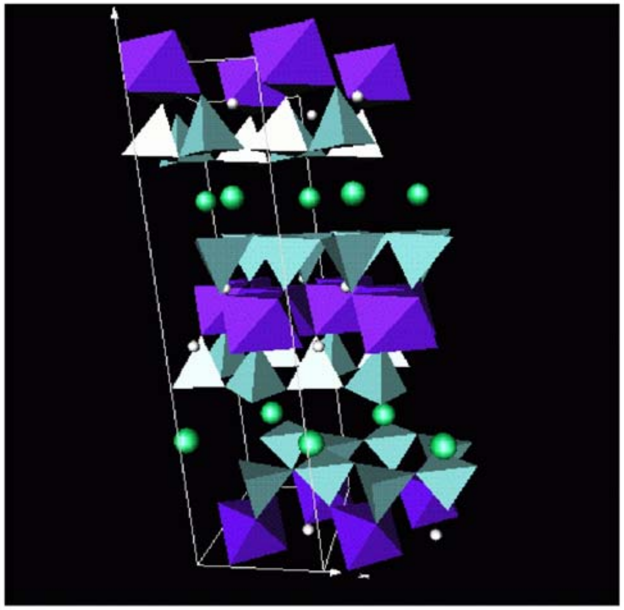


Figure 1. A clay $[Si_4O_{10}]^{4-}$ tetrahedral sheet in (a) top view and (b) side view, and a clay octahedral sheet in (c) top view and (d) side view.

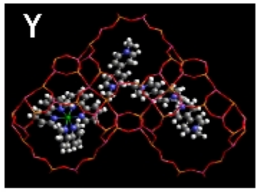


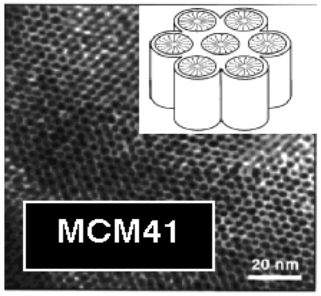
Montmorillonite

(“ball & stick” model)



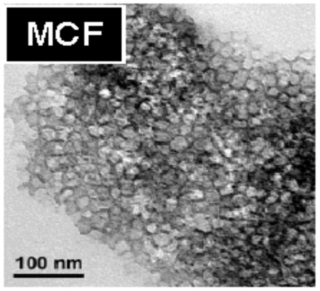
Muscovite Mica (“polyhedral” model)

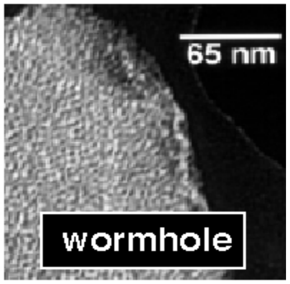




Zeolites: microporous (< 2 nm), highly selective, hindered transport, small molecule chemistry, 3-D

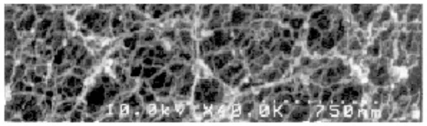
Periodic Mesoporosity: 2-50 nm, 1-D channels
e.g. mesoporous silicas (MCMs);
subject to blockage

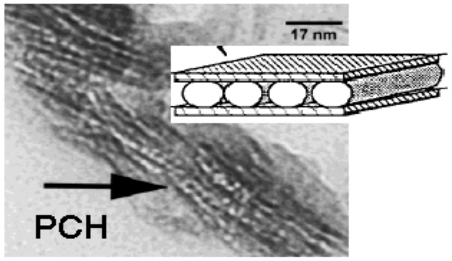




Non-Periodic Mesoporosity: 2-50 nm, 3-D “wormholes”
e.g. mesoporous cellular foams (MCFs), similar to aerogels, selectivity for large molecules possible

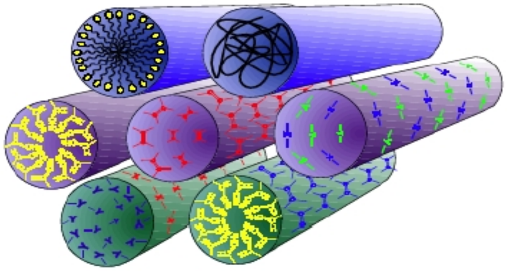
Macroporosity: > 50 nm,
e.g. ultraporous aerogels, aluminas, high diffusion rates, lower selectivity





Layered Silicates: 2-D clays, pillared clays = microporous;
porous clay heterostructures (PCH) = supermicropores (2-3 nm);
mesostructured synthetic clays = MSCs (2-20 nm)

Hybrid Organic-Inorganic Mesoporous Silicates:
grafting or co-condensation can tune surface properties & reactivity; "nanoscopic reactors" for catalysis, metal sorption, polymerization, biological molecules, etc.



Clay Research Applications

CATALYSIS

high surface acidity and surface area

original oil-refining catalysts prior to zeolites

ENVIRONMENTAL ISSUES

high cation exchange capacities, sorption, molecular sieving

metal ion fixation

pesticide fixation/degradation

POLYMER-CLAY NANOCOMPOSITES

exfoliation of individual layers, 1 nm slabs, within polymeric matrices

1 - 10 wt% loading levels

mechanical reinforcement/strengthening, gas barriers, flame retardants,

ablative & rheological enhancement

CARRADO ET AL., CHEMICAL TRANSFORMATION MECHANISMS

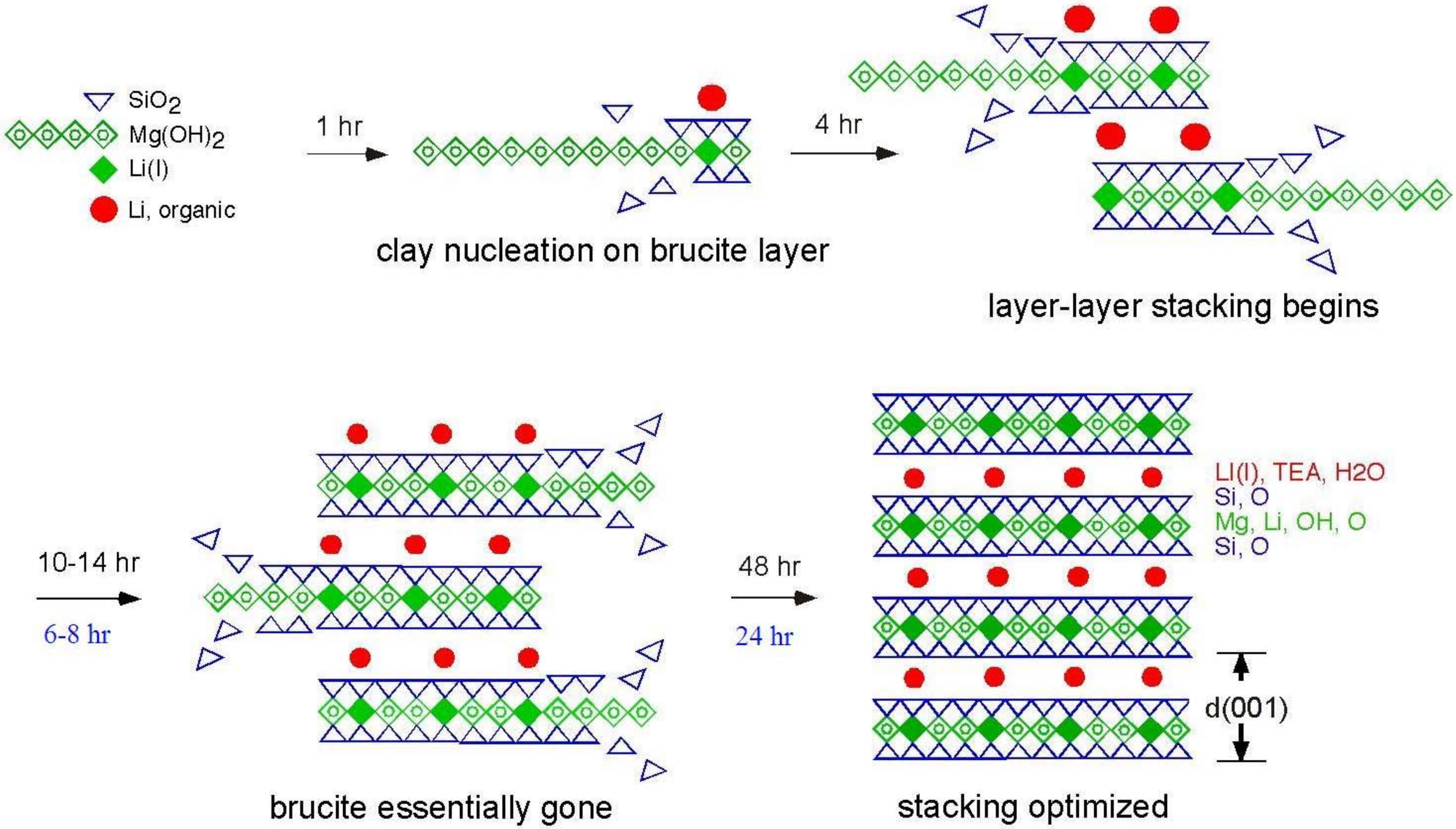
Clays Synthesized with Established Methods

Three clays were synthesized at full boil reflux-

- Tetraethyl ammonium hectorite (TEA)
- Tetraethoxysilane, tetraethylorthosilicate hectorite (TEOS)
- Silica-Lithium-Hectorite (SLH)

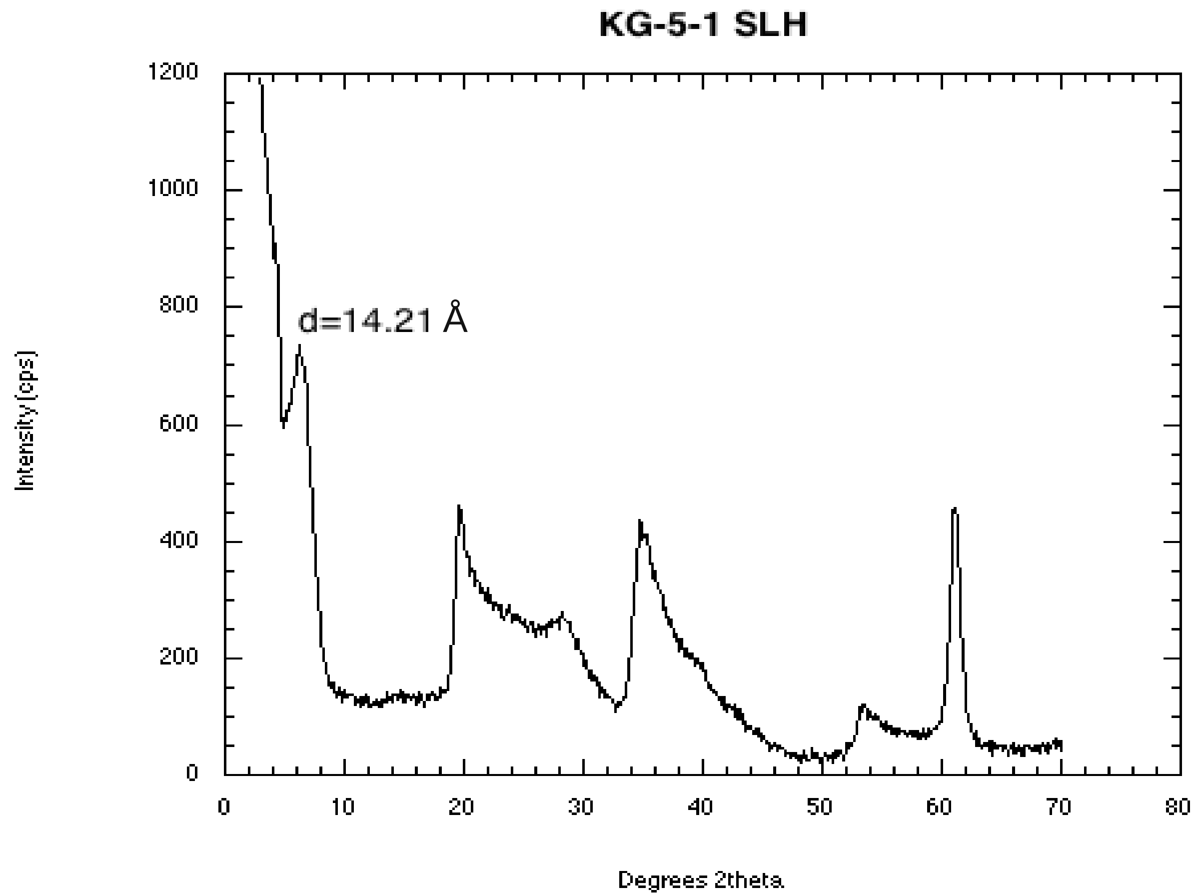
The clays were characterized by X-ray powder diffraction (XRD) and thermal gravimetric analysis (TGA).

The silica sol-derived hectorite clay crystallization model (*Chem. Mater.*, **2000**, *12*, 3052)

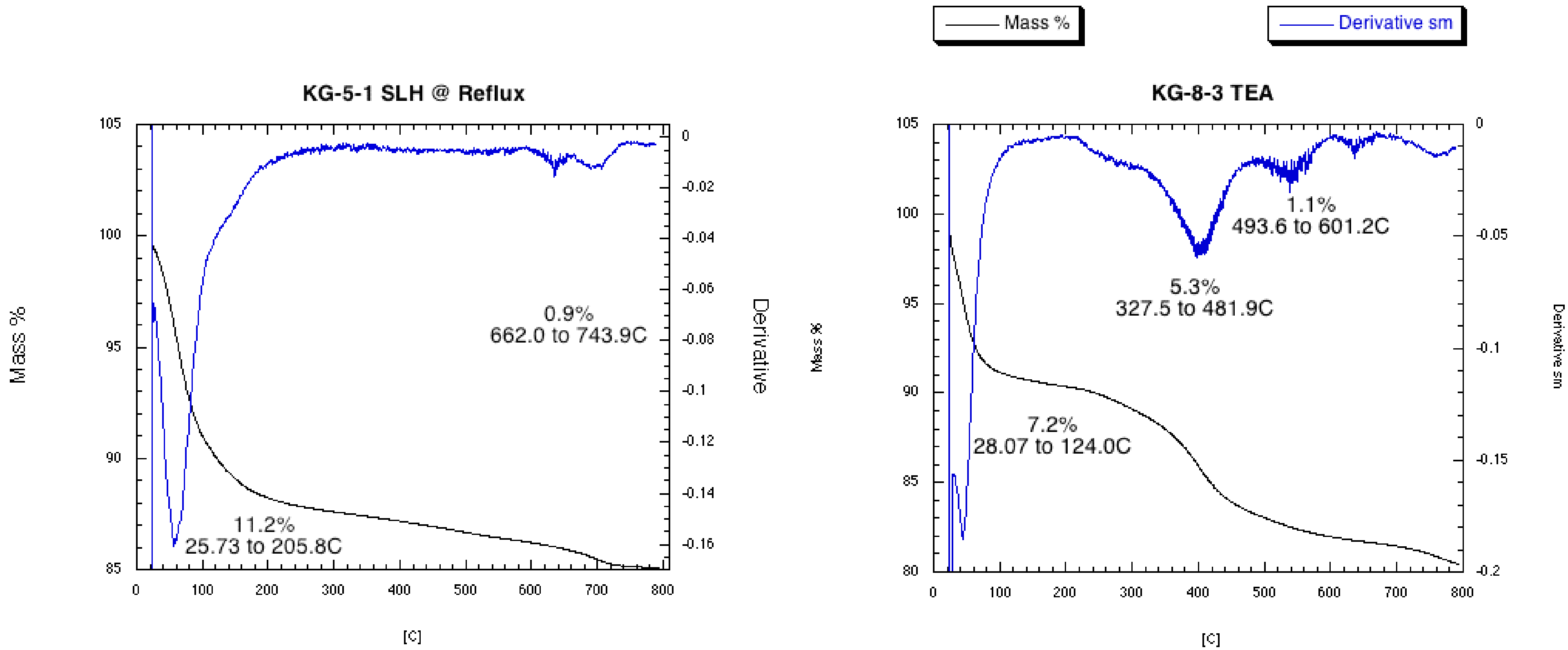


Results

- Each of the clays were analyzed and shown to be synthesized successfully.



Results



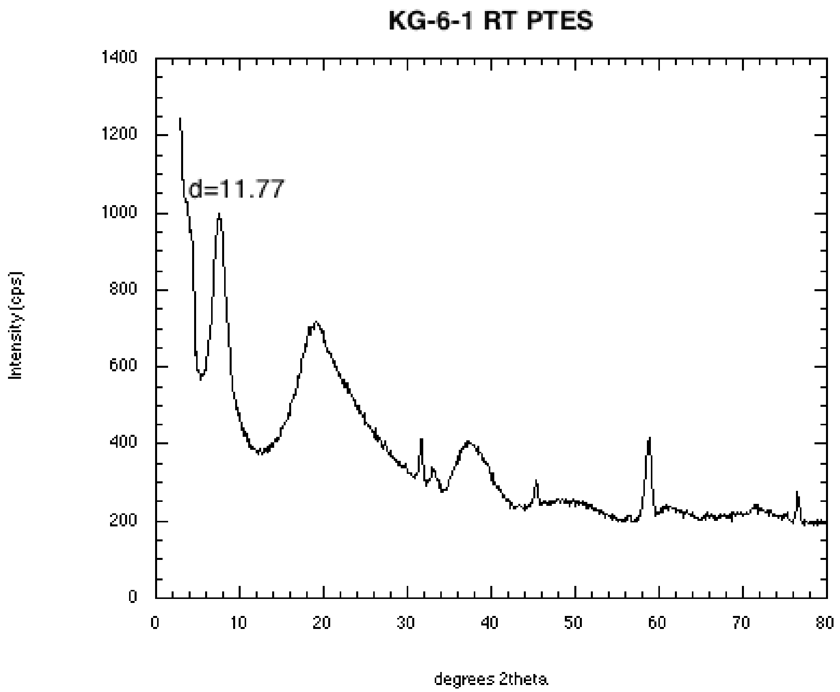
The flat portion of the derivative curve between 200 and 600°C in the graph of KG-5-1 indicates low weight loss due to the absence of organic material. The weight loss in KG-8-3 at 400°C indicates organic content.

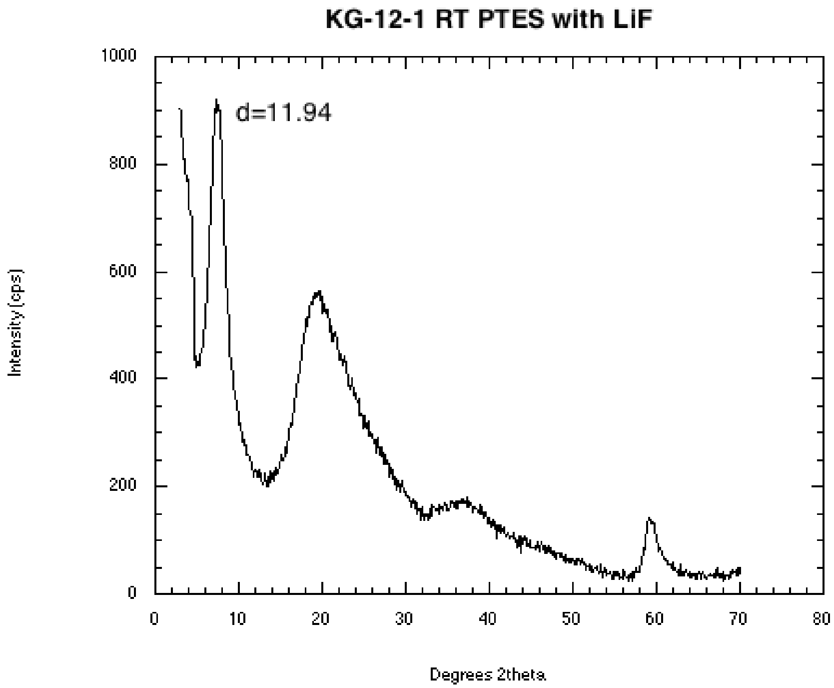
Mann Preparation of Clays at Room Temperature

- S. Mann, "Synthesis, characterization, and reactivity of layered inorganic-organic nanocomposites based on 2:1 trioctahedral phyllosilicates," Chem. Mater., vol 9, pp. 1071-1073.
- Phenyltriethoxysilane (PTES) and TEOS clays were synthesized at room temperature.
- Analysis by XRD and TGA.

Results

- PTES XRD indicated impurities.
- Repeated prep with LiF modification.

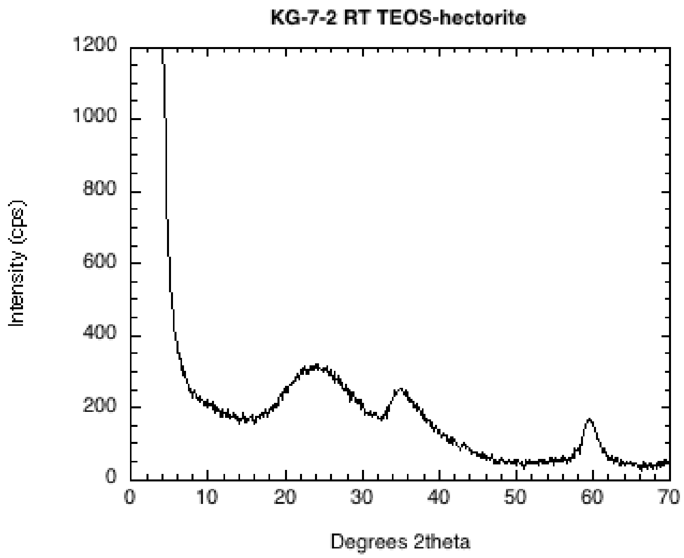




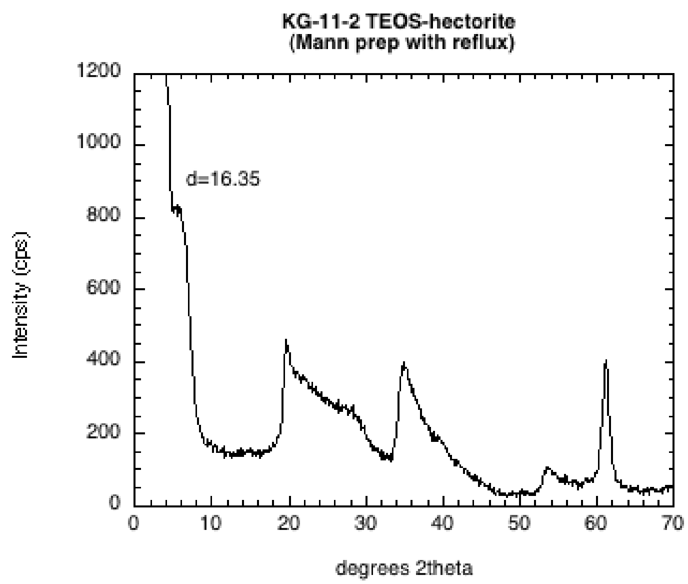
- No impurities
- Ion exchange capacity

Results

- TEOS prep failed



- Repeated TEOS clay synthesis with Mann prep and reflux modification

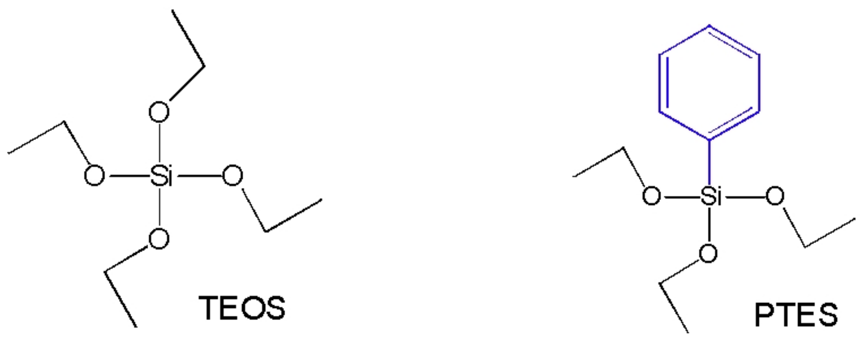


- Success!
- Since refluxing helped the TEOS prep, would it also help the PTES?

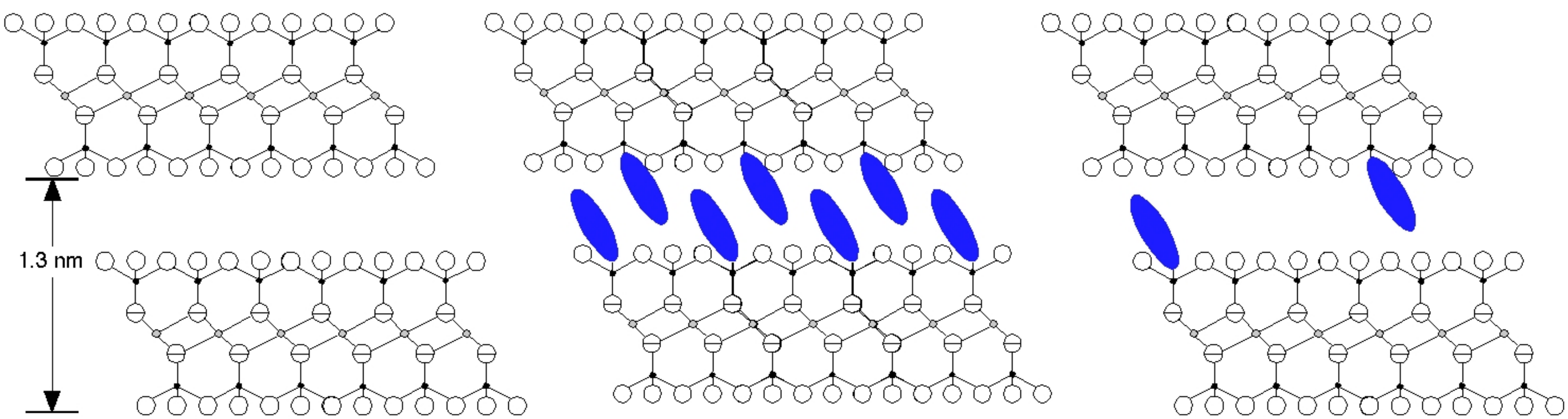
Varying the TEOS/PTES RATIOS

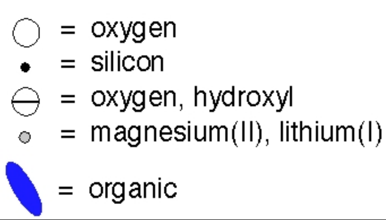
- Why is it useful to be able to accomplish this?
- Affinities for polymeric molecules in polymer-clay nanocomposite applications
- Clays were synthesized using the Mann prep with the added reflux step and three ratios of TEOS to PTES

TEOS (tetraethoxysilane) and/or PTES (phenyltriethoxysilane) + $Mg(OH)_2$ + LiF + H_2O $\xrightarrow[\text{1-5 days}]{100^{\circ}C}$ hectorite clay



various TEOS/PTES ratios

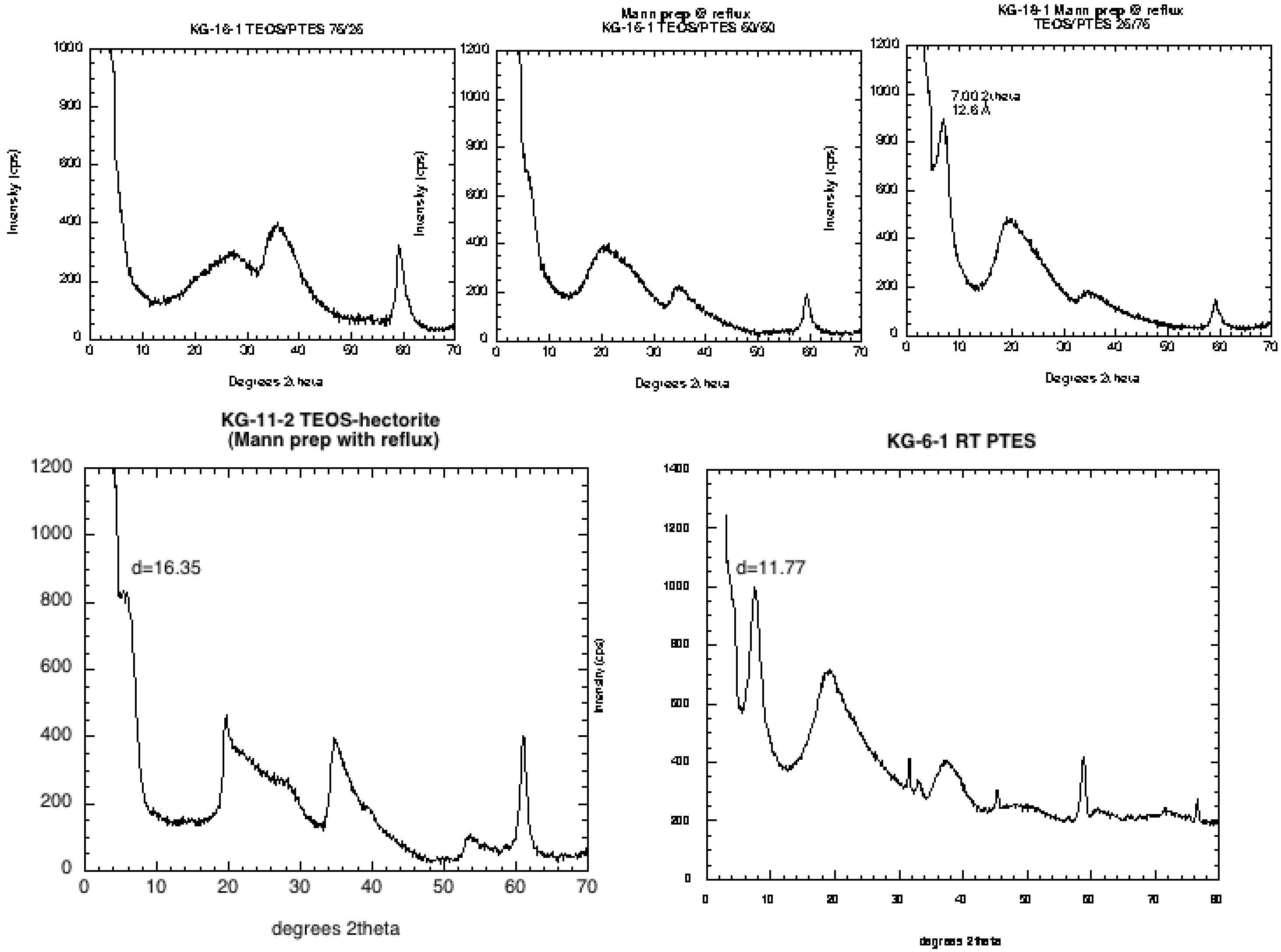


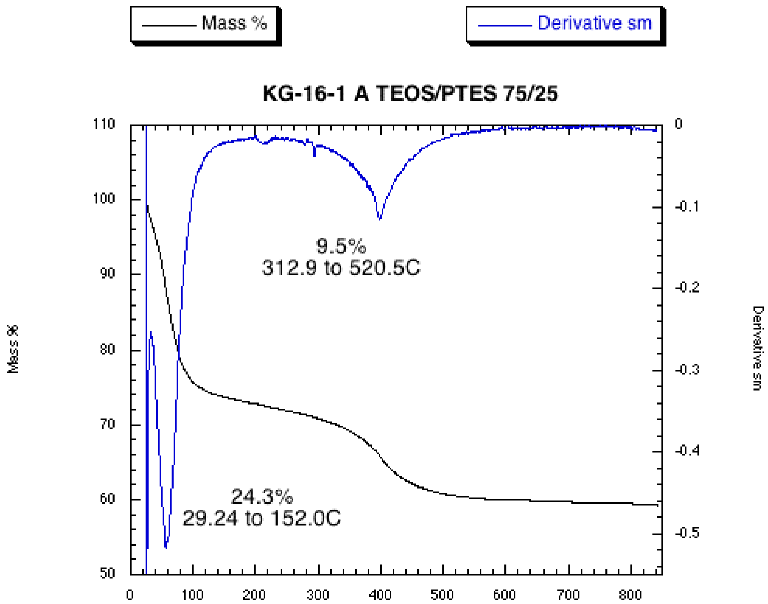


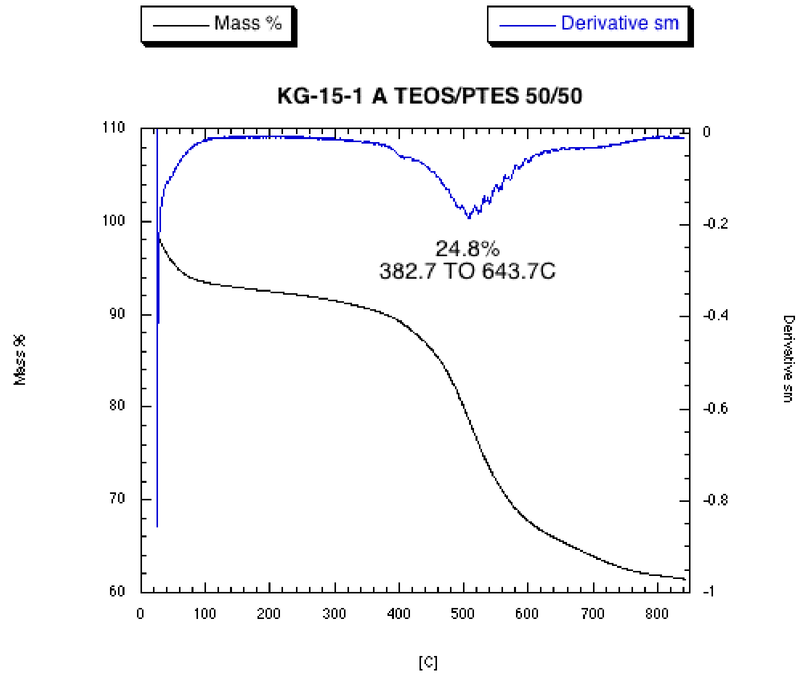
Chem. Mater. 2001, *13*, 3766

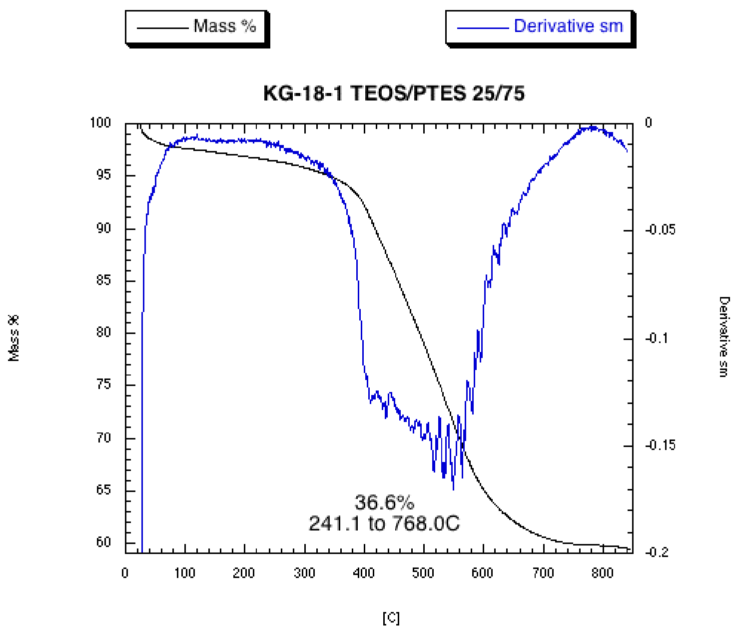
Results

- XRD shows that clay is made in each case









The TGA graphs show increased weight loss around 500°C with higher organic ratios.

Summary

- The hectorite clays synthesized with the established reflux prep were shown to have the desired structure and composition
- The Mann prep resulted in impurities and failed clays, which were both corrected by altering the preparations.
- The Mann prep with an added reflux step allows for easy varying of organic/inorganic ratios.

Over the Next 2 ½ Weeks…

- I will attempt to create hectorite clays with varying amounts of TEOS/PTES using the established reflux prep
- I will determine the effects of refluxing PTES clays synthesized with the Mann prep
- N_2 porosimetry?

Acknowledgements

- DOE Office of Science
- PST internship
- Kathleen Carrado