

## Synthesis of Layered Silicates from Sodium Silicate Solution

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In recent years, layered silicate have been used extensively to design new nanomaterials by interlayer modification.<sup>1-5</sup> Magadiite ( $\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot 9\text{H}_2\text{O}$ ) and kenyaite ( $\text{Na}_2\text{Si}_{22}\text{O}_{45}\cdot 10\text{H}_2\text{O}$ ) have potentially great value as basic material to design and construct new nanomaterial with desired function because they have excellent adsorption and ion exchange property characteristic of clay minerals. Although these materials were found naturally in various regions, they were also synthesized under hydrothermal condition.<sup>6-9</sup> These minerals was generally synthesized by commercial silica like as silica gel, silica powder and colloidal silica. The production cost has to be reduced for conventional application in industrial field.

We report the noble synthetic route leading to magadiite and kenyaite by using sodium silicate solution and fluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ). The use of sodium silicate and  $\text{H}_2\text{SiF}_6$  solution as silica source can reduce the production cost greatly. Although sodium silicate solution is the cheapest raw material among silica sources, the synthesis using sodium silicate solution has been not conducted yet.  $\text{H}_2\text{SiF}_6$  solution is also obtained from byproduct in phosphorous fertilizer process and has a role as silica source as well as acid. Here, it was difficult to use directly sodium silicate solution as silica source because their strong alkalinity dissolve again silicate framework.

Our synthetic strategy was focused on using precipitated silica slurry (PSS) as starting material for synthesis. PSS was prepared by direct reaction of sodium silicate solution with inorganic and organic acids such as fluorosilicic acid, sulfuric acid, hydrochloric acid, acetic acid, tartaric acid and oxalic acid. PSS were prepared by dropping slowly sodium silicate solution (38 wt%) to 100 mL of each acid solutions (9-12 wt%) to final pH 7 with stirring at 70 °C. The molar ratios of  $\text{SiO}_2 : \text{H}_2\text{O}$  in resultant PSS were within the range of 1 : 10-15. Water and NaOH were added additionally to each PSS to allow molar ratio of  $\text{SiO}_2 : \text{NaOH} : \text{H}_2\text{O} = 1 : 0.2 : 20$ . Suspensions with molar ratio of  $\text{SiO}_2 : \text{NaOH} : \text{H}_2\text{O} = 1 : 0.2 : 20$  were allowed to digest without stirring at 150 °C for 48-96 h in a stainless steel autoclave. The solid products were separated by filtration, washed with deionized water, and air-dried at 60 °C. Identification of samples were carried out by X-ray powder diffraction using Rigaku Rotaflex diffractometers equipped with  $\text{CuK}\alpha$  radiation and SEM

(Scanning electron microscopes, Jeol, JSM-840A). The chemical composition of magadiite and kenyaite were determined by energy dispersive X-ray spectrometer analysis (EDS, Link system AS1000-85S) and thermogravimetric analysis (TGA, 10 °C/min to 900 °C, 100 cc/min  $\text{N}_2$  purge).

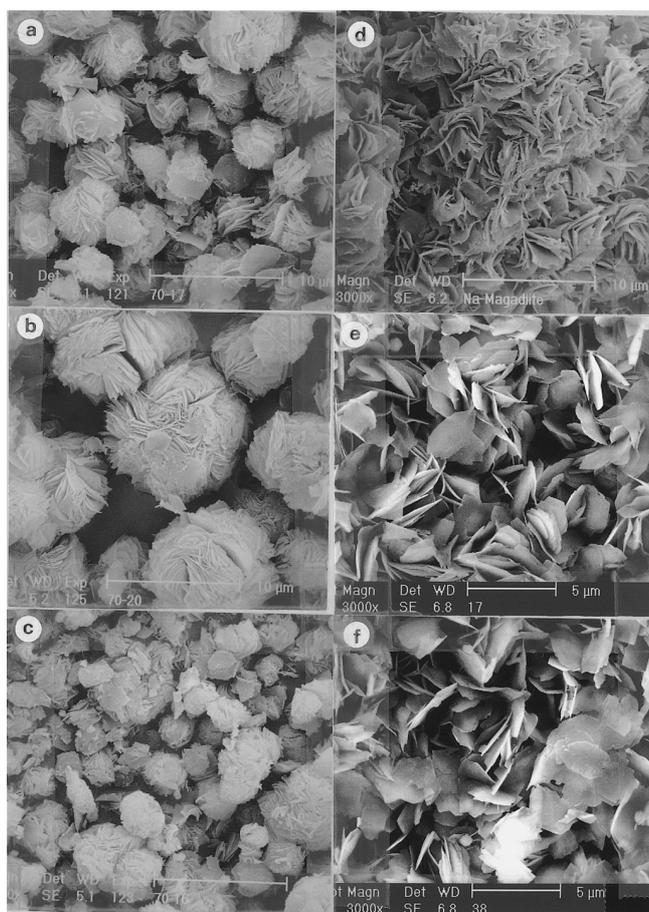
Various anions such as  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CH}_3\text{COO}^-$ ,  $^- \text{OOCCH}(\text{OH})\text{CH}(\text{OH})\text{COO}^-$  and  $^- \text{OOC-COO}^-$  exist in PSS suspension. These anions may influence on the crystallization of magadiite and kenyaite. The behavior of silicate species in the presence of various anions is not well understood. Previous studies<sup>10,11</sup> reported that  $\text{F}^-$  ion can have a role like  $\text{OH}^-$  ion in polycondensation of  $\text{Si}(\text{OH})_4$ . Fletcher and Bibby<sup>8</sup> also reported that the formation of layered silicate could be affected by anions such as  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$  and  $\text{CH}_3\text{COO}^-$ . Soaking of PSS from various acids, as shown in Table 1, guaranteed highly crystalline magadiite and kenyaite. At the soaking for 48 h, magadiite was formed preferentially regardless of acid types used. As reaction time increases from 48 to 96 h, magadiite was transformed into kenyaite. Previous studies<sup>6-9</sup> reported that amorphous silica, in alkaline hydrothermal condition, was transformed into magadiite, and magadiite transformed into kenyaite, and

**Table 1.** Products from PSS prepared by the reaction of sodium silicate with various acids

Acid species	Reaction time (h)	Products <sup>a</sup>
Fluorosilicic acid	48	Magadiite
	96	Highly crystalline kenyaite
Sulfuric acid	48	Magadiite
	96	Abundant magadiite; 10% Kenyaite <sup>b</sup>
Hydrochloric acid	48	Magadiite
	96	Kenyaite
Phosphoric acid	48	Magadiite
	96	Kenyaite; 10% magadiite
Acetic acid	48	Magadiite
	96	Kenyaite
Oxalic acid	48	Magadiite
	96	
Tartaric acid	48	Magadiite = Kenyaite
	96	Magadiite
Commercial $\text{SiO}_2$	96	Magadiite = Kenyaite
		Magadiite

All synthesis carried out with molar ratio of  $\text{SiO}_2 : \text{NaOH} : \text{H}_2\text{O} = 1 : 0.2 : 20$ . <sup>a</sup>Identifications by X-ray powder diffraction (see text). <sup>b</sup>10% represents the minimum detectable limit of the mineral by the analytical method employed.

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**Figure 1.** SEM morphologies of Na-magadiite (a, b, c and d) and Na-kenyaite (e and f) prepared from various acids-sodium silicate systems. (a): HCl, (b): H<sub>2</sub>SO<sub>4</sub>, (c): tartaric acid, (d): commercial SiO<sub>2</sub>, and (e) (f): H<sub>2</sub>SiF<sub>6</sub>.

then kenyaite to quartz. In particular, when molar ratio of SiO<sub>2</sub>/Na was above 7, kenyaite crystal was formed directly from amorphous silica.

In particular, kenyaite was easily formed in H<sub>2</sub>SiF<sub>6</sub> and acetic acid system. Other acids resulted in mixed phase of magadiite and kenyaite, allowing transformation into kenyaite after 96 h. However, the synthesis using commercial SiO<sub>2</sub> without anions did not produce kenyaite by 96 h soaking. This indicates that magadiite can be transformed easily to kenyaite in the presence of anions such as F<sup>-</sup>, Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, <sup>-</sup>OOC-COO<sup>-</sup> and <sup>-</sup>OOCCH(OH)CH(OH)COO<sup>-</sup>. The preparation of kenyaite may have great value because they are more stable and swellable than magadiite. Various SEM of layered silicate from PSS are shown in Figure 1. Magadiite (a, b, c and d) exhibit well characteristic morphology of

loosely packed aggregates of well-developed platelets. However, kenyaite (e and f) exhibit peculiar particle morphology separated with each small platelet different from those of magadiite. In general, morphology of kenyaite is very similar to magadiite. Smaller and divided particle is very important in industrial aspect because they can result in more effective dispersion. Here, magadiite particles (a, b and c) from PSS are smaller than that (d) from commercial silica. These phenomena may be attributed to the difference in particle size between silica sources. Particle size of SiO<sub>2</sub> suspended in PSS was about 10 nm, whereas commercial SiO<sub>2</sub> was about 100 μm. Decrease of particle size can accelerate dissolution of silica, resulting in rapid increase of Si(OH)<sub>4</sub> in the solution. This can lead to form abruptly a large number of silicate nucleus, reducing Si(OH)<sub>4</sub> to need in the growth of silicate crystal. Kenyaite and magadiite from PSS had unit cell composition Na<sub>1.96-2.1</sub>Si<sub>13-16</sub>O<sub>27-29</sub>·7~10H<sub>2</sub>O and Na<sub>1.95-2</sub>Si<sub>20-22</sub>O<sub>40-43</sub>·8~10H<sub>2</sub>O, respectively, which are compared favorably with approximate composition reported by the previous studies.<sup>6,7,9</sup>

In conclusion, sodium silicate solution could use effectively as silica source to obtain magadiite and kenyaite by neutralizing with acids. Results showed that anions such as F<sup>-</sup>, Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, <sup>-</sup>OOC-COO<sup>-</sup> and <sup>-</sup>OOCCH(OH)CH(OH)COO<sup>-</sup> existed in PSS suspension could accelerate the formation of kenyaite. In particular, layered silicate particles are well separated and smaller than that from commercial silica. Synthesis using sodium silicate solution should be promising route leading to the preparation and application of magadiite and kenyaite because of great economical merit and additional effect like the control of particle size.

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