

Direct synthesis of Na-kenyaite from amorphous silica

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무정형 실리카로부터 Na-kenyaite의 직접합성

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Abstract Amorphous silica was hydrothermally reacted for 48~120 h at 170~180°C in molar ratios of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 2\sim 20$ and $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 200\sim 250$. Na-kenyaite nuclei were formed directly from amorphous silica without formation of Na-magadiite nuclei in wide range with $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3\sim 20$. Above $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 10$, Na-kenyaite always produced with a residual amorphous silica. Well-crystallized Na-kenyaite without residual amorphous silica were obtained in the range of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3\sim 10$. Morphology of Na-kenyaite exhibited that a large spherical and loosely packed aggregates changed into the smaller and individual platelets according to increase of reaction time.

요 약 $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 2\sim 20$, $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 200\sim 250$ 인 몰 비 조건에서 무정형 실리카를 170~180°C, 48~120시간에 걸쳐 수열반응 시켰다. $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3\sim 20$ 의 몰 비 조건에서 Na-kenyaite 결정은 중간 생성물인 Na-magadiite 결정의 생성을 거치지 않고 무정형 실리카로부터 직접 형성되었다. $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 10$ 이상의 몰 비에서는 항상 Na-kenyaite와 함께 무정형 실리카가 잔류물로 남아있었다. 전자 현미경으로 관찰한 Na-kenyaite 결정 모양은 꽃잎 모양의 판들이 모여서 이루어진 둥근 다발과 같은 형태를 보여주었으며, 반응시간이 경과하면 결정 다발은 개개의 판들로 나누어진 보다 작은 조각들로 분리된 모양을 보여주었다.

1. Introduction

Layered silicates such as makatite ($\text{Na}_2\text{Si}_4\text{O}_{10} \cdot 5\text{H}_2\text{O}$), magadiite ($\text{Na}_2\text{Si}_{11}\text{O}_{29} \cdot 9\text{H}_2\text{O}$) and kenyaite ($\text{Na}_2\text{Si}_{22}\text{O}_{45} \cdot 10\text{H}_2\text{O}$) have growing interests due to their catalytic, adsorptive and ion-exchange properties [1, 2]. These materials exhibit the acid-resistance and the thermal stability, because of structural characteristics without aluminium in the network unlike zeolite or clay minerals.

Recently, silica-pillared derivatives from these layered silicates were introduced by a few researchers [3-12]. For the silica pillaring through inter-layer, silicate sheets consisting of layered silicates must keep too firm to collapse in elevated temperature and acidic condition. Kenyaite have most stable

structure among the other Al-free layered silicates, because silicate sheets consisted of 4-fold SiO_4 tetrahedra layers [13]. Kenyaite were primarily found by Eugster [14] in the lake beds of the lake Magadi in Kenya. Other occurrences have been continually reported in various regions [15, 16]. The synthetic kenyaite were also prepared under hydrothermal conditions. Beneke and Lagaly [17] indicate that the formation of kenyaite at 100°C was required a several months, but crystallizing time of kenyaite at the elevated temperature decreased greatly, accompanying formation of quartz. Recently, effects of carbonate on the formation of kenyaite were reported by a few researchers [18-20]. Previous works indicated that the kenyaite was formed by way of magadiite from amorphous silica. This

imply that the pure and well crystallized kenyaite is very difficult to obtain by controlling reaction time because kenyaite is formed with intermediate such as magadiite in the course of amorphous silica to quartz.

In spite of applicability and structural stability, the research on the synthesis of kenyaite are rarely conducted. We now report that Na-kenyaite could be obtained directly from amorphous silica by controlling SiO_2/Na ratio. Recently, Kosuge et al. [19] reported that (K, Na)-kenyaite could form directly from amorphous silica in limited $\text{SiO}_2/(\text{Na}, \text{K})$ ratio, but no one has reported on the direct formation of Na-kenyaite in wide range of SiO_2/Na ratio. The direct synthesis of Na-kenyaite from amorphous silica without intermediate such as magadiite may be a promising route leading to obtain industrially a large amount of pure synthetic Na-kenyaite.

Table 1
Representative runs to synthesize Na-kenyaite from SiO_2 , NaOH, Na_2CO_3 and H_2O suspensions

Run No.	Temp. (°C)	Time (hour)	Molar ratio of starting materials		Products ^b
			SiO_2/B^a	$\text{H}_2\text{O}/\text{B}^a$	
1	180	48	20	200	A>Ke
2		72			A>Ke
3		96			A>Ke
4	170	48	15	200	A>Ke
5		72			A>Ke
6		96			A>Ke
7		120			A>Ke
8	180	72			A<Ke
9		82			A<Ke
10		96			A<Ke
11	170	48	10	200	A<Ke
12		72			Ke
13		96			Ke
15	180	48			Ke
16		72			Ke
17		96			Ke
18	170	48	7	200	A<Ke
19		72			Ke
20	180	48			Ke
21		72			Ke
22	170	48	5	200	Ke
23	180	48			Ke
24		72			Ke<Q
25	170	48	3	200	Ke
26	180	24			Ke
27	170	48	2	200	Ma<Ke

^aB = NaOH + Na_2CO_3 (Molar ratio of NaOH to Na_2CO_3 is 1/3).

^bKe = Na-kenyaite, Ma = Na-magadiite, A = amorphous silica, Q = quartz, a inequality represent a relative magnitude of quantity.

2. Experimental

Materials used were silica gel (Wako gel Q-63), NaOH and Na_2CO_3 of analytical reagent grade. Synthesis were carried out in stainless steel autoclave without stirring for 24~120 h at 170~180°C in various molar ratios of reactants under autogeneous pressure. Two thirds of the NaOH in molar ratio was replaced by the Na_2CO_3 , the composition of reactants and reaction conditions were shown in Table 1. Reaction products were filtered, and washed with deionized water in order to remove excess NaOH or Na_2CO_3 , and then dried at 40°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 compositions of synthetic Na-kenyaite were determined by EDS (Energy dispersive X-ray spectrometer, Link system AS1000-85S) and TGA (Thermogravimetric analyzer, Dupont 9900). EDS analysis was carried out using electron beam with the sample of carbon-coated pellet. For the quantitative analysis of silica and sodium, quartz and sodium chloride were used as references.

3. Results and discussion

Table 1 shows reactant condition and results of XRD analysis for synthetic samples. Results were

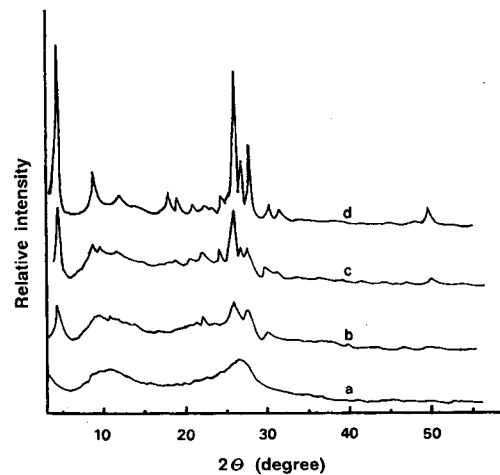


Fig. 1. XRD patterns of synthetic Na-kenyaite according to reaction time at 170°C. Molar ratio of reactant mixture: $\text{SiO}_2/\text{NaOH} + \text{Na}_2\text{CO}_3 = 10$, $\text{H}_2\text{O}/\text{NaOH} + \text{Na}_2\text{CO}_3 = 200$. (a) 15 h. (b) 2 h. (c) 48 h. (d) 72 h.

selected among about 50 experimental runs. All synthetic conditions were allowed a direct crystallization of Na-kenyaite from amorphous silica without crystallization of Na-magadiite. Figure 1 shows typically the XRD patterns for the crystallization of Na-kenyaite against reaction time in molar ratio of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 10$, $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 200$ at 170°C . Amorphous silica exists only at the reaction for 15 h, but after 24 h, the separation of peaks become clearly. The characteristic peaks of well crystallized Na-kenyaite appears after 72 h. It is well known that Na-kenyaite gradually crystallized around the crystalline nucleus formed with a given induction period after melting of amorphous silica. When amorphous silica dissolve with $\text{SiO}_2/\text{NaOH} + \text{Na}_2\text{CO}_3$ ratio enough to form Na-kenyaite nuclei, Na-kenyaite nuclei could form preferred to Na-magadiite nuclei, and successive dissolution of silica proceed to the growth of crystalline Na-kenyaite. This implies that what type of nuclei forms in the initial stage could determine a sort of final product. Therefore, the formation of Na-kenyaite nuclei with higher $\text{SiO}_2/\text{NaOH} + \text{Na}_2\text{CO}_3$ ratio in reactant mixture.

Comparing XRD patterns for Na-kenyaite crystallized against $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3)$ ratio for 72 h at 170°C in fixed molar ratio of $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3)$, Na-kenyaite nuclei forms preferentially in wide range of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 2\sim 20$. However, above $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 15$, Na-kenyaite always produce with a residual amorphous silica. This implies that reactant solution is supersaturated with amorphous silica during all reaction period, affording dissolved $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3)$ ratio enough to produce Na-kenyaite nuclei. When water needed to hydrolysis is not enough, whatever soaking time is long, amorphous silica may be remained. We observed that above $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 20$, final reactant solution is changed with gel without water. This bring about a relative decrease of water according to increase of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3)$ ratio. Well-crystallized Na-kenyaite without residual amorphous silica were obtained in the range of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3\sim 10$. Also Na-magadiite crystals were formed between 2 and 3 in $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3)$ ratio.

Table 2 exhibits composition of synthetic Na-kenyaite calculated by water loss, silica and sodium (%) from TGA and EDS analysis. The unit cell composition of synthetic Na-kenyaite is in agreement

Table 2
Compositions of synthetic Na-kenyaite

Sample	Weight percent (%)			Atomic ratios	
	Na_2O	SiO_2	H_2O	Na	Si
Synthetic Na-kenyaite	4.2	83.0	12.5	1.96	20



Fig. 2. Scanning electron micrographs of synthetic Na-kenyaite according to reaction time. Molar ratio of reactant mixture: $\text{SiO}_2/\text{NaOH} + \text{Na}_2\text{CO}_3 = 10$, $\text{H}_2\text{O}/\text{Na}_2\text{CO}_3 = 200$. (a) 48 h, (b) 72 h, (c) 96 h.

with $\text{Na}_{1.96}\text{Si}_{20}\text{O}_{40.8} \cdot 10\text{H}_2\text{O}$, which compares favorably with approximate composition of $\text{Na}_2\text{Si}_{20}\text{O}_{41} \cdot 10\text{H}_2\text{O}$ supported by the early work of Beneke and Lagaly [17]. Figure 2 shows a various type of morphology for synthetic Na-kenyaite against soaking time from the scanning electron micrographs. Figures show that the Na-kenyaite crystals shaped initially like a large spherical and loosely packed aggregates change into the smaller and individual platelets according to increase of soaking time. Figure 2 (a) exhibits well that amorphous silica is still remained among well-crystallized Na-kenyaite crystals shaped like a spherical packed aggregates. Figure 2 (b) shows a well-developed Na-kenyaite crystals shaped like a spherical and loosely packed aggregates only, exhibiting that amorphous silica disappear after lapse of time. Figure 2 (c) also exhibits that the morphology of Na-kenyaite change into individual platelets. This implies that the control of time may be allow the filmy layered silicates, in which eight-membered ring "micropores" are in the a-b plane.

4. Conclusions

Conclusionally a direct formation of Na-kenyaite nuclei from amorphous silica was happen in wide range with $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3\sim 20$. Above $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 20$, Na-kenyaite always produce with a residual amorphous silica. Well-crystallized Na-kenyaite crystals without residual amorphous silica were formed in the range of $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 3\sim 10$. Morphology of Na-kenyaite exhibited that a large spherical and loosely packed aggregates changed into the smaller and individual platelets during lapse of time.

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