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Hydrothermal synthesis of Mn-kaolinite using NaOH or KOH and characterization

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ABSTRACT

Mn-kaolinite containing both Mn and Al in the octahedral sheet was prepared under hydrothermal conditions of 100–200 °C for 6–96 h by using Al-nitrate, Mn-carbonate, silicic acid and aqueous solutions of NaOH or KOH. The synthetic phases were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray Absorption Near Edge Structure (XANES) spectroscopy. The results showed that the best hydrothermal conditions to prepare well-crystallized Mn-kaolinite were 100–175 °C for 2 days using either NaOH or KOH and the Mn species was mostly present as Mn^{3+} as determined by XANES spectroscopy.

1. Introduction

The presence of elements other than Si and Al in kaolinite is rare in nature, although, some elements such as Fe^{3+} (Herbillon et al., 1976; Mestdagh et al., 1980; Cuttler, 1981; Stone and Torres Sánchez, 1988; Delineau et al., 1994; Gaite et al., 1997; Balan et al., 1999) and Cr^{3+} (Brookins, 1973; Maksimovic and Brindley, 1980; Maksimovic et al., 1981; Singh and Gilkes, 1991; Mosser et al., 1993) were found to substitute for Al. Kaolinite was synthesized hydrothermally by many investigators (Ewell and Insley, 1935; Norton, 1939; Huertas et al., 1993; Iriarte et al., 2005). Mg-rich and Mg–Ni-rich kaolinites were synthesized in hydrothermal experiments (Bentabol et al., 2006). Co-kaolinite was synthesized at 200 °C under hydrothermal conditions (Bentabol et al., 2009). Regarding the synthesis of kaolinite under alkaline conditions, Na^+ ions were found to induce the formation of smectite and/or zeolite as intermediate phases, which could be transformed into kaolinite (De Kimpe, 1976). Therefore, kaolinite was synthesized by using K^+ ions in the alkaline solution apparently because K^+ prevented the formation of zeolite and/or smectite (De Kimpe et al., 1981).

Mn-kaolinite containing both Mn and Al in the octahedral sheet (referred to hereinafter as Mn-kaolinite) was recently prepared for the first time by Komarneni's group using silicic acid, aluminum nitrate, manganese carbonate and aqueous solution of KOH (Choi et al., 2009) under hydrothermal conditions. Choi et al. (2009) stated that the best conditions for the hydrothermal synthesis of Mn-kaolinite were 100 °C for 24–96 h and 200 °C for 24–48 h. The present work is part of detailed studies of Mn-kaolinite synthesis with Mn element substituting for Al using KOH or NaOH to generate alkaline conditions. The present authors did not find any studies of Mn-kaolinite synthesis using aqueous solution of NaOH in the literature. Therefore, the main objective of the present work was to find the best conditions for synthesis of Mn-kaolinite under different aqueous solutions of NaOH and compare the results with those prepared using KOH. Moreover, the effect of NaOH or KOH concentrations in the starting materials on the preparation of Mn-kaolinite was also investigated here.

2. Materials and methods

The alkali hydroxides used in the synthesis of Mn-kaolinite were NaOH (Alfa Aesar, purity: 97%) and KOH (EM Science, purity: 85% minimum). The starting chemical components were silicic acid (Aldrich Chemicals Company, purity: 99.9%), Al-nitrate (Fisher Scientific, purity: 98.8%) and Mn-carbonate (Aldrich Chemicals Company, purity: 99.99%) as sources of Si, Al and Mn, respectively. All chemicals were mixed with aqueous solutions of NaOH or KOH in Teflon vessels (125 ml capacity) of stainless steel Parr reactors. Parr reactors were heated in the temperature range of 100 to 200 °C for 6–96 h. After hydrothermal treatment, the vessels were cooled to room temperature. The solid and liquid phases were collected in centrifuge tubes. The solids and solutions were separated by centrifuging. After removal of the liquids, the synthetic solids were washed with distilled water and ethanol several times to remove any remaining soluble salts. The solid products were subjected to drying at 65 °C. The dried samples were gently ground and

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homogenized in an agate mortar with a pestle. In order to determine the yields, the mass of the solid reaction products was determined.

The solid phases were characterized by using X-ray diffractometer. XRD was carried out on the synthetic products using a Scintag X-ray diffraction unit with CuKα radiation in the 2θ range of 5–40 at a scanning speed of 5° min^{-1}. The morphology and particle size were determined by a field emission scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan) on samples coated with very thin carbon and by a transmission electron microscope (TEM; Model 2010, JEOL, Tokyo, Japan). The oxidation and coordination state of Mn was determined by XANES spectroscopy. The X-ray absorption spectroscopy (XAS) experiments at the Mn K-edge were performed with the X-ray absorption fine structure (XAFS) facility installed at beamlines 7C in the Pohang Accelerator Laboratory, Korea. The XAS data were collected at room temperature in a transmission mode. All the present spectra were calibrated by measuring the spectra of Mn metal foil simultaneously with those of the samples. A Si(111) double crystal monochromator was employed to monochromatize the X-ray photon energy.

3. Results and discussion

3.1. Mn-kaolinite syntheses using NaOH

Table 1 shows the starting chemicals and the hydrothermal conditions used to prepare Mn-kaolinite at three different concentrations of NaOH while keeping the other chemicals constant. Crystallization as a function of treatment time showed that very well-crystallized Mn-kaolinite was obtained after 48 h at 100 °C (Fig. 1) and after 12 h at 150 °C (Table 1). Thus the crystallization of Mn-kaolinite increased with increasing duration (Table 1), as expected. Mn-kaolinite crystallized at all the three concentrations of NaOH. Weak or no Mn-kaolinite existed at 200 °C (Table 1) probably because the Mn-kaolinite is not stable at this temperature (Fig. 2). TEM and SEM images of synthetic products prepared with NaOH at temperatures of 100°, 150° and 200 °C for 48 h are shown in Fig. 3. The Mn-kaolinite sample prepared at 100 °C showed pseudohexagonal and needle-like morphology (Fig. 3A) while the sample prepared at 150 °C also showed similar morphologies (Fig. 3B). However, the 150 °C sample showed more needles and the particles were well defined (Fig. 3B) compared to the 100 °C sample (Fig. 3A) probably because of better crystallization at the higher temperature. TEM image of synthetic product prepared with NaOH at a temperature of 200 °C for 48 h is shown in Fig. 3C. By increasing the temperature of synthesis to 200 °C in NaOH, crumpled foil-like morphology was formed (Fig. 3C) and this product was found to be amorphous by XRD (Table 1; Fig. 2) with a concentration of 6.38 Na_2O moles.

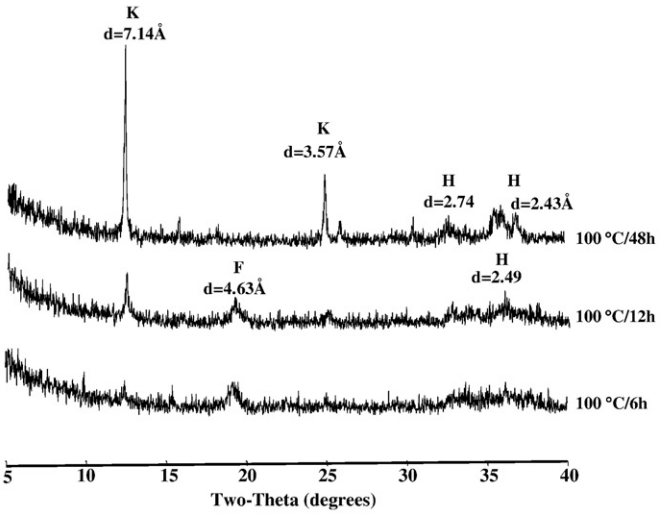

Fig. 1. XRD patterns of Mn-kaolinite prepared from NaOH at a hydrothermal temperature of 100 °C using a composition of 6.38 Na_2O:0.135 Al_2O_3:0.99 MnO:1.02 SiO_2:2222 H_2O. K = Kaolinite ($Si_2Al_{2-x}Mn_xO_5(OH)_4$); H = Hausmannite ($Mn_3O_4$); F = Feitknechtite (MnOOH).

The influence of Mn-carbonate and Al-nitrate as starting materials in the preparation of Mn-kaolinite using NaOH was also investigated. Without Mn-carbonate addition, no crystallization of kaolinite or any other solids occurred at 100 °C for 48 h. On the other hand, without Al-nitrate addition, slight or no crystallization of Mn-kaolinite occurred at 100 °C for 48 h (Fig. 4). These results are consistent with those of Choi et al. (2009), who previously reported similar results with the use of KOH, i.e., kaolinite did not crystallize with just Si–Al composition.

3.2. Mn-kaolinite syntheses using KOH

The hydrothermal conditions to prepare Mn-kaolinite using various concentrations of KOH and the other chemicals are shown in Table 2. It is clear from Table 2 and Fig. 5 that well-crystallized Mn-kaolinite was formed at 100 °C by increasing reaction time to 48 h. The morphology of this Mn-kaolinite is ill-defined as can be seen from the TEM picture (Fig. 6). Crystallization of Mn-kaolinite decreased but mica ($d = 10.18$ Å) crystallization predominated after treatment at

Table 1
Hydrothermal syntheses of Mn-kaolinites using different concentrations of NaOH.

Gel composition[a]	Temperature (°C)	Time (h)	Phases detected by XRD	% yield of solids including Mn-kaolinite
1. 6.38 Na_2O, 0.135 Al_2O_3, 0.99 MnO, 1.02 SiO_2, 2222 H_2O	100	6	Weak kaolinite	63
	100	12	Sharp kaolinite	63
	100	48	Very sharp kaolinite[b]	68
	150	6	Weak kaolinite	71
	150	12	Very sharp kaolinite	73
	150	24	Very sharp kaolinite	61
	150	48	Very sharp kaolinite[c]	64
	200	24	Weak kaolinite	79
	200	48	No kaolinite	63
2. 12.76 Na_2O, 0.135 Al_2O_3, 0.99 MnO, 1.02 SiO_2, 2222 H_2O	100	48	Very sharp kaolinite	57
	150	24	Very sharp kaolinite	58
	150	48	Very sharp kaolinite	53
	200	48	No kaolinite	47
3. 156 Na_2O, 0.135 Al_2O_3, 0.99 MnO, 1.02 SiO_2, 2222 H_2O	200	24	No kaolinite	47
	200	48	Weak kaolinite	47
	200	96	No kaolinite	50

[a] Chemical sources are NaOH, Al-nitrate, silicic acid and Mn-carbonate in all cases.
[b] Sh-28 sample used for XANES spectrum.
[c] Sh-29 sample used for XANES spectrum.