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ScienceDirect

Microporous and Mesoporous Materials 106 (2007) 284–297

MICROPOROUS AND MESOPOROUS MATERIALS

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High resolution solid-state NMR studies on dissolution and alteration of Na-montmorillonite under highly alkaline conditions

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Received 16 November 2006; received in revised form 5 March 2007; accepted 6 March 2007
Available online 14 March 2007

Abstract

Dissolution and alteration of Na-montmorillonite (Na-mon) under highly alkaline conditions have been studied by high resolution solid state ^{27}Al/^{29}Si MAS and ^{27}Al 3Q MAS NMR. Six altered samples were prepared by treating Na-mon in a highly alkaline $Ca(OH)_2$ solution (0.01 M: M = mol dm^{-3}) from 1 week to 3 months. The 3Q MAS NMR spectra of non-altered and altered samples indicated the existence of one octahedral Al site (Al^{VI}) and two tetrahedral Al sites (Al_a^{IV}, Al_b^{IV}). The Al_a^{IV} and Al_b^{IV} sites were assigned to Q^3(3Si) and Q^4(4Si) units, respectively. The Al_b^{IV} site of altered samples was ascribed to formation of analcime on the basis of powder X-ray diffraction patterns and ^{27}Al MAS NMR spectra. The average isotropic chemical shifts and the quadrupolar products remained constant before and after the alkaline treatment. The ratio of Al_a^{IV}/Al^{VI} indicated that the tetrahedral Al is more easily dissolved than the octahedral one. Therefore, we proposed a model that octahedral sites of Na-mon are exposed due to partial removal of external tetrahedral sites. ^{29}Si MAS NMR spectra showed that tetrahedral sheets of the Na-mon mainly consist of Q^3(0Al) and Q^3(1Al) units, and that the estimated bond angles (Si–O–Si) and bond lengths (Si–Si) are not affected by alkaline alteration. Furthermore, the full widths at half-maximum (FWHMs) of ^{29}Si NMR peaks corresponding to Q^3(0Al) and Q^3(1Al) sites were constant before and after the highly alkaline treatment. These results suggest that the coordination structure around tetrahedral Si is not largely changed by the alkaline treatment.

Keywords: Solid state NMR; ^{27}Al 3Q MAS; ^{27}Al/^{29}Si MAS; Na-montmorillonite; Alkaline condition; Microscopic change

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1. Introduction

Na-montmorillonite (Na-mon) is a typical smectite constructed by a stack of 2:1 layers. In the layer, one Al-rich octahedral sheet is sandwiched by two Si-rich tetrahedral ones. Interlayer Na^+ ions can be replaced by multivalent cations such as K^+, Ca^{2+}, Ln^{3+} (Ln = lanthanoid), and UO_2^{2+} [1–3]. The good catalytic actions [4] and the swelling with absorption of water [5] have been utilized in industrial applications.

Na-mon is a main constituent mineral of bentonite, which has been considered as buffer materials of the artificial barrier in geological disposal of high-level radioactive wastes (HLW) [6,7]. In the application, the hydro-dynamic and surface properties of Na-mon play an important role for notably inhibiting the migration of radioactive ions.

However, the dissolution and alteration of buffer materials are serious problems for safety assessment of geological disposal of HLW. Highly alkaline solutions are predicted to penetrate into the buffer materials in actual conditions of the repository. This is due to that pH of ground water increases (pH = 10–13.5) accompanying the continuous contact with the cement materials used for repository facilities [8,9]. As stated by Inoue et al. [10], the alkaline solutions generated by the long term-contact (>10^4 y) of ground water with cement materials contain a large quantity of Ca^{2+} ions. Therefore, understanding the alteration behavior of Na-mon in highly alkaline $Ca(OH)_2$

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doi:10.1016/j.micromeso.2007.03.008

solutions is important for the long-term safety assessment of the geological disposal system.

The dissolution behavior and mineral transformation of the Na-mon under alkaline conditions have been studied not only for radioactive waste management [11–15], but also for cement aggregate reaction [16,17] and the diagenic illite–smectite transformation [18]. Montes-H et al. [19] proposed a model for predicting the long-term chemical transformation of bentonite. However, local structural changes of Na-mon during alkaline alteration are not explored yet. Furthermore, the dissolution behavior of tetrahedral and octahedral sheets in Na-mon has not been analyzed quantitatively. The microscopic changes are important for examining effects of alkaline treatment on the crystal structure of Na-mon.

High resolution solid-state NMR allows us to characterize the local structures around the observed nuclei. Unlike the powder X-ray diffraction (XRD), solid state NMR is a powerful tool for structural analyses of both crystalline and non-crystalline materials. In the magic angle spinning (MAS) method, the line broadening effects due to dipole–dipole interaction and chemical shift anisotropy are removed by rotating solids at an angle of 54.4° to the direction of the static magnetic field [20]. Hence, the MAS NMR has been applied to the characterization of zeolite [21] and structural analyses of other silicate minerals [22–25]. Furthermore, the recent use of high magnetic field and fast spinning rate in MAS NMR enables us to obtain high resolution spectra of aluminosilicates. In fact, the high resolution ^{27}Al MAS NMR has been used in structural analyses of weathered kaolinite [26] and altered montmorillonite [27].

The MAS NMR spectra of half integer quadrupolar nuclei ($I \geqslant 3/2$) are broadened by second order quadrupolar interactions when the quadrupolar coupling constant is in the order of several MHz. The multiple quantum (MQ) MAS NMR method was developed by Frydman and Harwood [28] to obtain high resolution NMR spectra of quadrupolar nuclei by controlling the multiple quantum coherences. Using MQ MAS NMR method, we can determine the isotropic chemical shifts (δ_{iso}) and quadrupolar products (P_{Q}), which are important parameters to inspect the local structural distortion. As shown by Crosson et al. [26], the δ_{iso} and P_{Q} values cannot be estimated by conventional MAS NMR measurements unless several kinds of NMR spectrometers with different magnetic fields are available. MQ MAS NMR has been recently applied to the structural analyses of porous materials and glasses abundantly containing quadrupolar nuclei [29–38]. In earth sciences, MQ MAS NMR has been used to analyze the structures of the peraluminous glasses and potassium silicates [39,40]. These studies are helpful to investigate the generation of Si and Al networks in silicate melts. Furthermore, MQ MAS NMR has been used in the structural analyses of layered silicates such as clay minerals [23,41,42]. Ohkubo et al. [41] applied ^{27}Al 3Q and 5Q MAS NMR to the structural analysis of Na-mon, and discussed the local structure of Na-mon.

In this study, we have applied the combination of ^{27}Al/^{29}Si MAS and 3Q MAS NMR for discussing the microscopic changes of Na-mon under highly alkaline conditions. Moreover, macroscopic changes were clarified by using the X-ray diffraction (XRD), X-ray fluorescence (XRF) spectroscopy, and inductively coupled plasma optical emission (ICP-OES) spectroscopy. The changes in surface conditions of Na-mon were also examined by means of scanning electron microscopy (SEM) observation and the N_2 adsorption–desorption experiments. Based on macroscopic and microscopic analyses, we characterized the secondary phase and quantitatively discussed the dissolution behavior of the octahedral and tetrahedral Al in Na-mon.

2. Experimental

2.1. Sample preparation

The initial Na-mon used for the alteration experiments is Kunipia F (Kunimine Industries Co. Ltd.), which is prepared by purifying the Tsukinuno Na-mon supplied by the Japan Clay Science Society (JCSS-3101). In Kunipia F, small amount of quartz (<1%) is contained as the impurity.

To investigate the structure of pure Na-mon, we prepared a sample defined as Kunipia-P by further purifying the Kunipia-F. The purification was performed according to the method developed by Sato [43]. Kunipia-P was used only for XRD and solid state NMR measurements, because of its limited amount.

Highly alkaline solution (pH = 12.6) was prepared by dissolving $Ca(OH)_2$ in deionized water (0.01 M: M = mol dm^{-3}). Then, the alkaline solution (250 g) and Na-mon (10.0 g) were put into TPX (Mitsui Chemicals, Inc.) bottles and mixed sufficiently. Because TPX formerly known as poly-methyl-penten-polymer is stable under acidic and alkaline conditions, the contamination of Si, Al, and other elements from the bottles was avoided.

All bottles were placed in a thermostat at constant temperature (80 ± 1 °C) and humidity (60 ± 2%). Although all bottles were sealed with caps, a small amount of water was escaped from the boundary between the cap and body part of the bottles because of the increase in internal pressure. Thus, to make up the loss, deionized water (<2 g) was added to each bottle every week. The Kunipia-F was contacted with $Ca(OH)_2$ solution for 1–4 weeks, 2 months, and 3 months, respectively. Here, the time was defined as contact time. Each sample was labeled in order of the contact time as Mon1w, Mon2w, Mon3w, Mon4w, Mon2m, and Mon3m, respectively. The pH of the solution decreased with increasing the contact time and became constant (10.8 ± 0.2) at the contact time of 1 month. After the elapse of each contact time, suspensions were transferred to centrifuge tubes. Solid phases were separated from supernatant liquids by the centrifugation at 3500 rpm for 24 h. Then, deionized water of 30 ml was added to the solid phases in the centrifuge tube, and the centrifugation was carried out again to collect the dissolved ions. The