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Research paper

Metal occupancy and its influence on thermal stability of synthetic saponites

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ABSTRACT

Due to high surface acidity and thermal stability, saponite has important applications in various fields. In this study, saponites with different Mg/Zn ratios (0–6) and a fixed Si/Al ratio of 5.43 were synthesized under hydrothermal condition. The resultant synthetic saponites were characterized by using XRD, FTIR, TG, SEM and MAS NMR. The characterization results demonstrated that, with a decrease of Mg/Zn ratio, both the crystallinity and layer stacking order of saponite were increased, and rose-like morphology was observed in Zn-saponite. Al^{3+} preferentially occupied tetrahedral sites in *Si*-O tetrahedral sheet in all synthetic saponites. A decrease of Mg/Zn ratio in octahedral sheet could improve the substitution extent of Al^{3+} for Si^{4+} and resulted in an increase of Al(IV)/Al(VI) ratio in the resultant saponite, which might be a crucial factor to control the crystal growth of saponite. The dehydroxylation temperature of saponite depended strongly on the Mg/Zn ratio and the replacement of Al^{3+} for Mg^{2+} and Zn^{2+} in octahedral sheets, due to their different bond strength. A 'one-to-one' mode was proposed for the substitution of Al^{3+} for Mg^{2+} and Zn^{2+} in octahedral sheets of the synthetic saponites.

1. Introduction

Saponite is a kind of 2:1 type trioctahedral phyllosilicate, belonging to smectite group clay minerals. In its unit layer, a central $MgO_4(OH)_2$ octahedral sheet is sandwiched by two *Si*-O tetrahedral sheets via sharing oxygen. The ideal structural formula of saponite can be expressed as $M+X\,[Si_{4-x}Al_x][Mg_3]O_{10}(OH)_2\cdot nH_2O$, where *M* is the exchangeable interlayer cation, *x* ($0.2 \le x \le 1.2$) is the fraction of aluminum present in *Si*-O tetrahedral sheet, and *n* is the number of water molecules (Kloprogge et al., 1994; Vogels et al., 2005a; Costenaro et al., 2013). As shown by saponite formula, negative charges for saponite layers are created mainly by the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet, which are compensated by exchangeable interlayer cations such as Na^+, Ca^{2+}, and Mg^{2+}. The octahedral sites are generally occupied by Mg^{2+} in nature, and can be substituted by other cations such as Al^{3+}, Fe^{3+}, Li^+, Mn^{2+}, Ni^{2+}, and Zn^{2+} (Mackenzie, 1957; Rodriguez et al., 1994; Varma, 2002).

Due to the high surface acidity and thermal stability, saponite has many important applications in a number of fields, including clay-based polymer nanocomposites and heterogeneous catalysts (Varma, 2002; Casagrande et al., 2005; Liu and Breen, 2005). However, the chemical composition and physicochemical properties of natural saponites are extremely variable, which depend on the chemical compositions of the mother rocks, the genesis process and the provenance (Utracki, 2007). Thus, natural saponite cannot meet the requirements in some fields such as catalysts, in which the chemical composition and surface property are required to be homogeneous (Artok et al., 1993; Chevalier et al., 1994). The composition and property variability of natural saponites strongly limits their industrial applications. For this reason, different methods have been developed to synthesize saponites with well-controlled chemical composition and property (Farmer et al., 1991; Kloprogge et al., 1993; Vogels et al., 1997; Kawi and Yao, 1999; Jaber et al., 2005; Higashi et al., 2007; Bisio et al., 2008; Vicente et al., 2010). More importantly, saponite-type clay minerals can be obtained by synthesis ways, which are rare in nature but have unique property and morphology (Zhang et al., 2010).

Saponites with various metals in octahedral sheet (i.e., Mg^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}) have been successfully synthesized, and their structure and properties (e.g., specific surface area, lateral size, order of layer stacking) were investigated (Brtndle and KrrKewe, 1979; Brat and Rajan, 1981; Decarreau et al., 1992; Grauby et al., 1994; Reinholdt et al., 2005; Trujillano et al., 2015). Vogels et al. (2005b) proposed that

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the compositions of the octahedral and tetrahedral sheets had significant influences on the structure and physicochemical property of synthetic saponites. For example, the crystal size of Mg-saponite is smaller than that of Zn-saponite, and the average stacking degree of the saponite layers is higher in Zn-saponite than that in Mg-saponite. Correspondingly, Mg-saponite has higher micropore volume and specific surface area than Zn-saponite (Vogels et al., 1995; Vogels et al., 2005b). Meanwhile, Mg-saponite had higher Brönsted acid density than Zn-saponite (Leliveld et al., 1998). However, saponite containing both Zn^{2+} and Mg^{2+} in octahedral sheets displayed better catalytic activity in alcohol decomposition and cumene cracking (Prikhod'ko et al., 2003). These differences on the structure and property of synthetic saponite may be controlled by the occupancy of Al^{3+} in saponite, besides the effects of the nature of Mg^{2+} and Zn^{2+} and their distribution. The substitution of Al^{3+} for Si^{4+} is critical for growth of saponite crystals (He et al., 2014) and can produce Brönsted acid sites (Suquet et al. 1981). Prikhod'ko et al. (2003) suggested that the preferential occupancy of Al^{3+} in the tetrahedral sheet of Mg- and Zn-saponite only occurred when the atomic ratio $Si^{4+}/Al^{3+} \geq 12$ (Prikhod'ko et al., 2003). However, He et al. (2014) demonstrated that Al^{3+} preferred to occupy tetrahedral sites instead of octahedral ones in Mg-saponite with different Si/Al ratios. Moreover, both the saponite crystallinity and the layer stacking order are controlled by the distribution fraction of Al^{3+} in tetrahedral and octahedral sheets (i.e., the ratio of Al(IV)/Al(VI)). It is noteworthy that, in a ternary system of octahedral sheet (i.e., Mg-Zn-Al), the ratio of Mg/Zn may have a significant effect on the distribution of Al^{3+} in tetrahedral and octahedral sheets and a further influence on the structure and property of the resultant saponite, which has not been systematically investigated.

Hence, the main aim of this study is to investigate metal distribution and its influence on thermal stability of synthetic saponites with different Mg/Zn ratios. The saponites were synthesized under hydrothermal condition and characterized by using a combination of techniques, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), scanning electron microscopy (SEM), and ^{27}Al and ^{29}Si solid-state magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS NMR). The insights about the effect of Mg/Zn ratio on the occupancy of Al^{3+} in tetrahedral and octahedral sheets and the thermal stability of synthetic saponites are of high importance for synthesis and application of synthetic saponite.

2. Experimental

2.1. Sample preparation

Saponite samples with a fixed ratio Si/Al/(Mg + Zn) of 1.18, and Mg/Zn ratios of 6, 4, 2, and 0, respectively, were prepared by modifying a previously reported method (Kawi and Yao 1999).

A general synthesis procedure is as follows: A mixture of 4.00 g of NaOH and 9.00 g of $NaHCO_3$ was dissolved in 125 mL deionized water. Then, 24.00 g of sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) solution was added to the buffer solution under vigorous stirring (Solution A). Desired amounts of $MgCl_2 \cdot 6H_2O$, $ZnCl_2$ and 3.80 g of $AlCl_3 \cdot 6H_2O$ were dissolved in 12.5 mL of deionized water (Solution B). With continuous stirring, Solution B was slowly added into Solution A until a uniform gel was eventually formed. The gel was then transferred to a polytetrafluoroethylene-lined autoclave and heated at 200 °C for 72 h. The obtained products were denoted as Sap-Mg6Zn0, Sap-Mg4Zn2, Sap-Mg2Zn4, and Sap-Mg0Zn6, respectively.

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

Randomly oriented powder XRD patterns were collected from 3° to 80° (2θ) at a scanning rate of 1° (2θ) min^{-1} on a Bruker D8 Advance diffractometer with Ni-filtered CuKα radiation (λ = 0.154 nm, 40 kV, and 40 mA).

2.2.2. Thermogravimetric analysis (TG)

TG analysis was conducted on a Netzsch STA 409PC instrument. Approximately 10 mg of the sample was heated in a corundum crucible. The sample was heated from 30 to 1000 °C at a heating rate of 10 °C/min under a highly pure N_2 atmosphere (60 cm^3/min).

2.2.3. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of the samples were recorded on a Bruker Vertex-70 Fourier-transform infrared spectrometer. The specimens were prepared for measurement by mixing 0.9 mg of the sample powder with 80 mg of KBr and pressing the mixture into a pellet. Over 64 scans were collected for each measurement at a resolution of 4 cm^{-1}.

2.2.4. Field-emission scanning electron microscopy (FE-SEM)

SEM images were recorded on a Hitachi SU8010 cold field emission scanning electron microscope (FESEM, SU8010, Hitachi, Japan) at 1.5 kV accelerating voltage and at a working distance (WD) of 5.0 mm.

2.2.5. Magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR)

^{27}Al and ^{29}Si MAS NMR spectra were obtained on Bruker AVANCE III 600 spectrometer at resonance frequencies of 156.4 and 119.2 MHz, respectively. ^{29}Si MAS NMR spectra with high-power proton decoupling were recorded on a 4 mm probe with a spinning rate of 12 kHz, a π/4 pulse length of 2.6 μs, and a recycle delay of 80 s. The chemical shifts of ^{29}Si were referenced to tetramethylsilane (TMS). A 4 mm HX double-resonance MAS probe was used to measure ^{27}Al MAS NMR at a sample spinning rate of 14 kHz. The spectra were recorded by a small-flip angle technique with a pulse length of 0.5 μs (<π/12) and a 1 s recycle delay. The chemical shift of ^{27}Al was referenced to 1 M aqueous $Al(NO_3)_3$. The deconvolution of ^{27}Al and ^{29}Si MAS NMR spectra was undertaken using a Gauss–Lorentz cross-product function applied by the PEAKFIT software package. The positions and areas of peaks were obtained until the squared correlation coefficients $r^2 \geq 0.995$.

3. Results and discussion

3.1. Crystallinity and morphology of the synthetic saponites

XRD patterns of the synthetic samples (Fig. 1) displayed the characteristic (001) reflections at ca. 6.5° (2θ) with the d-values of ca. 13.0 Å. All d-values of the (060) reflections were equal to or larger than 1.53 Å, suggesting that trioctahedral saponite was successfully synthesized (Grauby et al., 1993). With a decrease of Mg/Zn ratio, the basal reflection intensity was prominently increased with a decrease of the full width at half maximum, implying an increase of crystallinity and layer stacking order (He et al., 2014). Meanwhile, a small quantity of hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) formed in the case of Sap-Mg0Zn6, where no Mg^{2+} was added in the preparation solution. The appearance of hemimorphite was probably due to a high pH value and high Zn^{2+} concentration in the reaction system (Yokoyama et al., 2006).

The synthetic Mg-saponites (Sap-Mg6Zn0) exhibited plate-like morphology with curved edges (Fig. 2), which was typically able to be observed in raw clay minerals, especially in smectite family of clay minerals (Cravero et al., 2000; Christidis, 2001). With decreasing in the Mg/Zn ratio, there were more curved edges in Sap-Mg4Zn2 (Fig. 2b) than those in Sap-Mg6Zn0. Well-known rose-like morphology was displayed in Sap-Mg2Zn4 and Sap-Mg0Zn6 (Ma and Pierre, 1999).