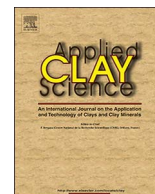




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Research paper

Hydrothermal transformation of mixed metal oxides and silicate anions to phyllosilicate under highly alkaline conditions

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ABSTRACT

Mixed metal oxides (MMO) were transformed to phyllosilicate in the presence of silicate anions under hydrothermal conditions. The product was shown to be saponite with a trioctahedral layer structure by characterization with XRD, FTIR, ²⁷Al and ²⁹Si MAS NMR, HRTEM and TG-DTG. The formation of saponite was through a rehydration-dissolution-precipitation pathway, involving the critical steps such as the reconstruction of MMO to hydrotalcite (Ht), exsolution of Al³⁺ from Ht, condensation of metasilicate anions with Ht, and finally crystallization of saponite. Isomorphous substitution of Al³⁺ for Si⁴⁺ in silicate oligomers is the key for the above conversion, which generated the negative charge necessary for the condensation between the silicate oligomers and Ht surface and the formation of 2:1 saponite TOT layers. High pH value (over 14.0) favored the condensation of silicate oligomers and led to crystallization of saponite. Thus, we report a novel method for the crystallization of saponite.

1. Introduction

The dissolution and precipitation of minerals are always accompanied by the enrichment and migration of atoms on their surfaces in the earth's surface environment (Hochella, 1990). It was previously disclosed that the chemical exchange in basalt rocks (mainly composed of SiO₂, Al₂O₃, MgO, Fe₂O₃, Na₂O etc.) and hydrothermal alteration by seawater are closely related to the formation of secondary minerals and the origin of seafloor heavy-metal deposits (Bischoff and Dickson, 1975; Seyfried Jr and Bischoff, 1981). Experiments using synthetic basaltic glasses and Mg-rich solution in laboratory revealed the formation of hydrotalcite-like compounds (Htlc) and other subcarbonates during the earlier period of reaction but subsequently most of them were transformed to phyllosilicate when the reaction time was extended (Abdelouas et al., 1994). These studies provided theoretical foundations for the alteration of nuclear waste glasses, which is of high importance in nuclear waste disposal (Ewing, 1979; Byers et al., 1984).

Hydrotalcite (Ht), Mg₆Al₂(OH)₁₆CO₃·mH₂O, is a naturally occurring but rare anionic clay with positive charges in its layers. These positive charges result from partial substitution of Mg²⁺ by Al³⁺ in its brucite-

like octahedral layer and are balanced by anions in the interlayers. Natural Ht are usually formed during the weathering of basalts or precipitation in saline water sources (Auerbach et al., 2011). Unlike clays, they are seldom found in large or commercially useful deposits (Auerbach et al., 2011). In laboratory, however, Ht can be readily synthesized through coprecipitation reactions in alkaline solutions either at room temperature and pressure or under hydrothermal conditions (Tao et al., 2006). Previous research showed that many kinds of reactants, such as metal salts, physically mixed MgO and Al₂O₃ oxides or chemically mixed MgAl double oxides (MMO) can be used as precursors for the synthesis of Ht (Chibwe and Jones, 1989; Hibino and Tsunashima, 1998; Xu and Lu, 2005; Tao et al., 2010). However, Mg/Al was not the only cation pair to form Htlc, which are also well-known as layered double hydroxides (LDHs). Dozens of Htlc consisting of other cation pairs with different molar ratios were previously reported, including divalent-trivalent cation pairs (e.g., Mg/Al, Co/Al, Ni/Fe, Zn/Cr, Fe/Fe etc.), some monovalent-trivalent pair (e.g., Li/Al) or divalent-tetravalent pair (e.g., Zn/Ti) etc. The interlayer anions can be inorganic anions (e.g., CO₃²⁻, SO₄²⁻, PO₄³⁻, NO₃⁻, Cl⁻ etc.) (Duan and Evans, 2006) as well as organic anions (e.g., anionic surfactant) (Tao et al.,

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2009). This large family of Htlc have positively charged layers and excellent ion exchange capacities, with wide applications as adsorbents, ion exchangers, pharmaceuticals, catalysts or catalyst supports etc. (Dimotakis and Pinnavaia, 1990; Cavani et al., 1991; Hermosin et al., 1996; Choudary et al., 2002; You et al., 2002; Hutson et al., 2004; Domingo et al., 2006).

After calcination in the temperature range of 300–500 °C, Htlc is converted to mixed metallic oxides (MMO). For Ht, a periclase phase (MgO) was produced in which some of the Mg^{2+} was substituted isomorphously by Al^{3+} along with a small amount of amorphous Al_2O_3 (Tao et al., 2010). It is well-known that MMO readily converts to Ht layered structure when treated with alkaline solutions and anions such as carbonate, chloride etc. through reconstruction. This unique calcination-reconstruction by rehydroxylation and rehydration is also known as “structure memory effect”. This effect may enable them to undergo significant structural responses to geological and environmental changes as in the case of smart materials with structural memory (Roy and Gupta, 2003; Erickson et al., 2005).

Although, the source materials, metal cations pairs and hosted interlayer anions can be varied in a wide range, Htlc intercalated with silicate anions were rarely reported for either natural minerals or synthetic phases. The reason may be that silicate anions are readily polymerized in aqueous solutions (Schutz and Biloen, 1987; Yun, 1995; Depège et al., 1996; Baskaran et al., 2013), which would promote further transformation of neoformed Htlc into other minerals (e.g. phyllosilicate) in alkaline solutions rather than intercalation into Htlc. This might be one of the reasons for the rarity of Htlc deposits in alkaline geological environments. It is worth mentioning that, during the above mentioned conversions, non-equivalent isomorphous substitutions always occur, which would reverse the layer charge of mineral from positive to negative (Yun, 1995). This kind of charge reversal may significantly influence the surface enrichment and migration of the environmental ions (Hochella, 1990).

Herein, we report for the first time the structural reconstruction of Htlc through the intercalation and in-situ polymerization of metasilicates followed by the formation of phyllosilicate under hydrothermal conditions. A combination of characterization techniques, including X-ray diffraction (XRD), ^{27}Al and ^{29}Si solid-state magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS NMR), and transmission electron microscopy (TEM) were used to confirm the above transformation and its mechanism. The new findings of this research are relevant for understanding the stability of hydrotalcite, heterogeneous nucleation and growth of hydrotalcite and silicate minerals, and the formation processes of the hydrothermal saponite deposits.

2. Experimental methods

2.1. Materials

Synthesized Ht with a chemical formula of $Mg_2Al(OH)_6CO_3 \cdot mH_2O$ was purchased from Shaoyang Tiantang (Hunan, PR China), in which, the concentrations of MgO and Al_2O_3 were 30_{wt%} and 20_{wt%}, respectively. Sodium metasilicate nonahydrate ($Na_2SiO_3 \cdot 9H_2O$) was purchased from Aladdin (Shanghai, PR China) with a purity of $\geq 98\%$. The other chemicals, such as NaOH, $NaHCO_3$ etc. were of analytical reagent (AR) grades and purchased from Guangzhou Chemical (Gangzhou, PR China). All the materials and chemicals were used, as received. The mixed metal oxides (MMO) were obtained by calcination of Ht at 500 °C for 6 h.

2.2. Experimental procedure

Generally, 33.80 mmol of $Na_2SiO_3 \cdot 9H_2O$, 90.00 mmol of NaOH and 66.20 mmol of $NaHCO_3$ were dissolved in 100 ml DI water. Then, 2.47 g MMO (containing 30.00 mmol Mg^{2+} and 15.70 mmol Al^{3+}) was put into the above mentioned freshly prepared alkaline solution. After

thoroughly stirring, the mixture was transferred to a polytetrafluoroethylene-lined autoclave (with a capacity of 200 ml) and hydrothermally treated at 160 °C for different times ($t = 0, 1, 2, 4, 6, 12, 18, 24, 48,$ and 72 h). In all the reaction procedures, the pH values were over 14.0 as measured before and after hydrothermal treatment. The obtained gel-like mixtures were washed with DI water several times by centrifuge-washing until the supernatant reached neutral pH and then the gel was dried at 80 °C followed by grinding prior to characterization. The obtained products were marked as MMO-t where $t = 0, 1, 2, 4, 6, 12, 18, 24, 48,$ and 72 h.

2.3. Analytical techniques

Randomly oriented powder X-ray diffraction (XRD) patterns were collected between 1° and 65°(2 θ) at a scanning rate of 1° min⁻¹ on a Bruker D8 Advance diffractometer with Ni-filtered $CuK\alpha$ radiation ($\lambda = 0.154$ nm, 40 kV and 40 mA). Fourier transform infrared (FTIR) spectra were obtained using a Bruker VERTEX 70 Fourier transform infrared spectrometer. All spectra were collected at room temperature over the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and by using 64 scans. High resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL 2010 high resolution transmission electron microscope, which was operated at an accelerating voltage of 200 kV. Specimens were prepared by dispersing the samples in ethanol and ultrasonically treating them for 5 min. A drop of the resultant suspension was placed on a porous carbon film supported by a copper grid, after which the ethanol was evaporated. Both ^{27}Al and ^{29}Si Magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS NMR) experiments were performed 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 $\pi/4$ pulse length of 2.6 μ s, 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 μ s ($< \pi/12$) and a 1 s recycle delay. The chemical shift of ^{27}Al was referenced to 1 M aqueous $Al(NO_3)_3$. Peak component analysis was undertaken using a Gauss–Lorentz cross-product function applied by the Peakfit software package. A minimum number of component bands was obtained with squared correlations ≥ 0.995 . TG analyses were performed on a Netzsch STA 409PC instrument. Approximately 15 mg of ground sample was heated in a corundum crucible from 30 to 1000 °C at a heating rate of 10 °C/min under a pure N_2 atmosphere (60 cm³/min). The differential thermogravimetric (DTG) curve was derived from the TG curve.

3. Results and discussion

3.1. XRD patterns

After calcination, a series of d_{hkl} peaks corresponding to Ht (Tao et al., 2010) were replaced by characteristic reflections of periclase (\blacklozenge , PDF#: 45-0946) (Fig. 1a). A small sharp reflection at ca. 29.5°(2 θ) and a weak reflection at ca. 35°(2 θ) were attributed to calcite (\blacklozenge , PDF#: 05-0586) and aluminum oxides (\circ , PDF#: 37-1462), respectively. The formation of these phases indicated that Ht structure was destroyed and MMO was formed.

Rehydration of MMO in alkaline solution was a very rapid process. A typical and well-ordered layer structure with a basal spacing (d_{003}) of 0.78 nm appeared after hydrothermal treatment of MMO for only 1 h (Fig. 1b). This pattern matches well with Ht phase (\blacklozenge , PDF#: 41-1428), except that the location of reflection shifted slightly to the higher angle, due to the lower Mg/Al ratio in this case. Considering that the Ht layer is 0.48 nm, the interlayer spacing was calculated as 0.30 nm. The XRD result indicated that the intercalated anions were mainly CO_3^{2-} (Cavani

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