



Research paper

Insights into the physicochemical characteristics from vermiculite to silica nanosheets

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ABSTRACT

Mesoporous silica nanosheets (SiNSs) were prepared from acid-treated vermiculite (Verm). The influences of acid concentration and reaction time on the structural and textural properties of acid-treated samples were investigated. The physicochemical characteristics of SiNSs were studied by X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR), N₂ adsorption-desorption techniques, zeta potential, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), and ²⁹Si and ²⁷Al nuclear magnetic resonance (NMR). XRF study indicated that acid-treatment leads to the removal of the aluminum and magnesium from the octahedral sheets along with other impurities. XRD, SEM and HRTEM measurements supported that treatment with moderate concentrated acid and reaction time favor the formation of translucent and monodispersed SiNSs, which have been reported rarely. Acid-activation with 2 M HCl for 12 h gave a maximum value of specific surface area (764 m² g⁻¹) with zeta potential of -38.9 mV. FTIR and NMR spectroscopic analyses demonstrated the formation of active groups (Si-OH groups) on the surface of SiNSs. The SiNSs thus obtained by acid-treatment can be used as promising catalyst supports, adsorbents, and morphology-controlling reagents of nanomaterials.

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1. Introduction

Silica materials with a large specific surface area and high mechanical strength have been widely used as supporter of functional materials (Angelos et al. 2007; Gutierrez et al. 2011), nanoscaled filler in polymer nanocomposites (Frisch and Mark 1996), adsorbent (Ho et al. 2003), and so on (Vallet-Regi et al. 2011). Many studies on the preparation of silica have been reported from original work (Okada et al. 2005; Ciriminna et al. 2013), especially for the silica materials with abundant active-sites (for example, silanol groups). However, most of the routes to obtain activated silica are either complicated or costly. Selective leaching of clay minerals by acid-treatment is a simple technique for preparation of silica materials.

Clay minerals are excellent raw materials for preparing porous silica materials because of their special layered silicate structures and abundant reservations. Preparation of silica materials from clay minerals by acid-treatment is the most commonly used technique to enhance the chemical and physical properties of clay minerals, which replaces exchangeable cations with H⁺ ions while Al³⁺ and other cations escape from both tetrahedral and octahedral sites, leaving the SiO₄ groups largely intact (Komadel and Madejova 2006). This process generally

increases the specific surface area and acidic sites of the clay minerals and eliminates mineral impurities with partial dissolution of the external layers (Ishii et al. 2005; Lai et al. 2010; Okada et al. 2010). At present, among these layer silicate minerals, montmorillonite, vermiculite and kaolinite were paid more attention.

Vermiculite (Verm) is one of the most investigated clay materials from a structural viewpoint. In the family of naturally occurring 2:1 aluminosilicate clay minerals, Verm is a very important member. Verm is widely available, easily handled, odorless, and low-cost material. Owing to its remarkable properties, vermiculite and modified vermiculite are commonly used in agricultural (as fertilizer carrier, adsorbent, etc.), industrial (as fire protection, acoustic and thermal insulator, additive in concrete and plaster, packaging material, etc.), and environmental (as adsorbent) applications (Duman and Tunc 2008; Duman et al. 2015). The 2:1 layer of vermiculite is composed of an MgO₂(OH)₄ octahedra sheet symmetrically coupled to a tetrahedral sheet of silica. The positive charge deficiency is compensated by the hydrated exchangeable cations Mg²⁺, Ca²⁺, Na⁺ and K⁺ located in the interlayer space between the parallel 2:1 layers (Brigatti, 2006).

The unique sandwich structure endows Verm with some excellent physicochemical properties. Verm can be considered as raw materials for preparing porous silica via simple acid-leaching method. Despite the large number of studies on Verm leaching, the typical procedures utilize HCl, H₂SO₄ or HNO₃ as a leaching agent (Temuujin et al. 2003;

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Chmielarz et al. 2014; Santos et al. 2015), but the most of product are undefined morphology of silica or partially leached clay mineral, and much less information is available on the preparation of silica nanosheets (SiNSs) with only one dimension (their thicknesses) in nanoscale and monodispersed morphology from Verm (Zhao et al. 2008). In our previous exploratory study, the silica nanolayers, which is essentially delaminated and chemically functionalized was obtained from Verm by acid-treatment, have been successfully used as supporter of TiO₂ nanoparticles and hard-template controlling the morphology and growth of TiO₂ single crystals (Wang et al. 2012; Wang et al. 2013), respectively.

In the work, we further investigated the influences of acid concentrations and acid-treatment time on the physicochemical properties of as-prepared SiNSs, respectively. The main purpose of the work was to evaluate the changes of textural, structural, surface properties and morphology of Verm during acid-leaching process, which is important to understand the contribution of the physicochemical characteristics on its further functionalization and practical applications.

2. Experimental section

2.1. Materials

Verm from Yuli (300 mesh, Xinlong Vermiculite Co. Ltd., Yuli, Xinjiang, China) was used as the starting material. Its main chemical composition is tabulated in Table 1. Hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd., 36 ~ 38%) was used without further purification. Milli-Q water (18 MΩ cm) was used for preparation of all solutions.

2.2. Acid-treatment

A series of acid-treated samples was prepared as follows. 25 g of the as-received Verm was dispersed into 1 L of HCl solution at various concentrations (0.5, 1, 2, 3, and 4 M), and the resulting slurry was magnetically stirred at 50 °C for 8 h. The resulted dispersion was then separated by filtering and washed thoroughly with deionized water several times until the filtrate had a pH value of 6.8. Following this, the obtained solid material was dried at 100 °C for 12 h. The final acid-treated product after grinding was a fine powder that was whiter than the starting Verm.

To investigate effect of acid-treatment time, the acid-treated samples were also prepared at 2 M HCl solution for various reaction times (2, 4, 8, 12, and 16 h). All other experimental conditions were kept the same. For simplification, hereafter the acid-treated samples were denoted as “Verm” followed by the acid concentration and the acid-treatment time used in the reaction. For instance, Verm-0.5-8 means the sample prepared with a 0.5 M HCl and a reaction time of 8 h.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded using a D8 Advance X-ray diffractometer (Bruker, Germany) (40 kV, 40 mA) with nickel-

filtered Cu Kα radiation ($\lambda = 1.54056 \text{ \AA}$) (scan range, 5 ~ 60° 2θ; step size, 0.022°; scan speed, 0.2 s/step; counting time, 108 s; slit width, 0.6 mm). Chemical analyses of the samples were determined by X-ray fluorescence (XRF) spectroscopy (XRF-1800, Japan). Fourier transform infrared spectroscopy (FTIR) measurements were conducted on a Nicolet is50 instrument at a resolution of 4 cm⁻¹ using KBr. N₂ isotherms were obtained at 77 K using a specific surface area and pore size analyzer (QUADRASORB IQ, Quantachrome, USA.). The specific surface areas (S_{BET}) were calculated using the Brunauer-Emmett-Teller (BET) equation within a relative pressure range (P/P_0) of 0.05–0.30. The pore volume (V_p) was determined from the amount of N₂ adsorbed at the highest relative pressure of $P/P_0 \approx 0.99$. The pore diameter (D_p) was defined by applying the Barrett-Joyner-Halenda (BJH) model to the desorption isotherm. Prior to the analysis, the samples were degassed at 120 °C for 3 h under vacuum. The zeta potentials of the different solids dispersed in water were measured in Zetasizer Nano ZS90 equipment (Malvern Instruments Ltd., UK). Samples were prepared at a concentration of 1 mg mL⁻¹ and the measurement was taken at 25 °C. Before taking each measurement, sample was sonicated for 1 min to preclude aggregation. The zeta potential was achieved by Laser Doppler Microelectrophoresis (Malvern's patented M3-PALS technology). The morphology of the sample was observed with scanning electron microscopy (SEM, Zeiss Supra55VP, Japan) using an In-Lens detector operated at an accelerating voltage of 20 kV. The method of making an SEM preparation was to sprinkle a small amount of powder onto the SEM tape, making sure the sample was spread evenly over the surface of the SEM stub then sputtered coat with Pt in vacuum to improve conductivity and image contrast. High resolution transmission electron microscopy observation was carried out using a JEM-2010F (HRTEM, JEOL, Japan) operated at 200 kV. The method of making an HRTEM preparation was to place a carbon-coated 200-mesh TEM copper grid on a filter paper and with a pipette allow one drop of the sample dispersion of ethanol to fall onto the TEM grid. The sample was dried in a vacuum oven at room temperature. Solid state ²⁹Si and ²⁷Al MAS Nuclear magnetic resonance (NMR) experiments were performed at room temperature in a Bruker-400 spectrometer. For each run, approximately 30 microgram of the solid sample was put into a MAS probe. The ²⁹Si spectra were acquired using a 90° pulse (pulse length 2 μs) and a recycle delay of 2 s, and were referenced to tetramethylsilane (TMS). The ²⁷Al spectra were acquired using a 15° pulse (pulse length 1 μs) and recycle delay of 1 s, and were referenced to Al(H₂O)₆³⁺. The spinning frequency was set to 8 kHz and 12 kHz for ²⁹Si and ²⁷Al spectra, respectively.

3. Results and discussion

Table 1 shows the chemical analysis of the main components of the as-received and acid-treated samples. Apparently, the SiO₂ content increased greatly after treatment with 2 M HCl for the same acid-treatment time (8 h) and reached a composition of almost 82%, which can be ascribed to the dissolution of the other components. After treatment with 4 M HCl, the products were almost pure SiO₂. A high acid concentration caused an initial sharp increase of SiO₂ content, but above about 95%, the increase became more gradual. In other words, increasing the HCl concentration from 3 to 4 M produced the similar lixiviation of the solids, without significantly alternating their compositions. However, a low acid concentration did not give a fully leached structure. The data also revealed that Mg²⁺ was removed faster than Al³⁺ and disappeared completely after 8 h treatment of Verm with 4 M HCl, which can be attributed to the fact that it is more difficult to dissolve Al because it is in the tetrahedral sheet. Thus, acid-treatment of Verm significantly changed its chemical composition due to partial leaching of cations located mainly in the octahedral sheet of layered silicates, especially at moderate concentrations. Similar behavior of elements during acid-treatment process of Verm was described by Temuujin et al. (Temuujin et al. 2003).

Table 1
Content of the main elements and textural properties of Verm and acid-treated samples.

Sample	SiO ₂ (wt.%)	MgO (wt.%)	Al ₂ O ₃ (wt.%)	S_{BET} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)
Verm	38.8	23.6	13.9	5	0.017
Verm-0.5-8	45.3	16.1	7.21	498	0.305
Verm-1-8	60.6	10.2	5.52	592	0.371
Verm-2-8	82.3	0.75	1.02	751	0.554
Verm-3-8	95.4	–	0.55	697	0.520
Verm-4-8	96.5	–	–	629	0.418
Verm-2-2	78.5	8.83	3.65	632	0.395
Verm-2-4	80.2	7.55	2.58	686	0.461
Verm-2-12	95.5	0.10	0.31	764	0.602
Verm-2-16	97.8	0.05	0.07	753	0.604

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