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Research paper

Nanoporous-walled silica and alumina nanotubes derived from halloysite: controllable preparation and their dye adsorption applications

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ABSTRACT

Acid/alkali selective-etching chemistry cooperated with a pre-calcination treatment are proposed and demonstrated, to process natural halloysite nanotubes (Hal) into nanoporous-walled silica or alumina nanotubes. The phase transformation behavior of Hal under the different condition of calcination was investigated. Acid or alkaline aqueous solution was used to selectively remove alumina or silica in the tube wall of pre-calcined Hal with resultant developed nanopores. Microporous/mesoporous-walled silica nanotubes of specific surface area (S_{BET}) up to 414 m^2/g were obtained by acid-etching Hal pre-calcined at 850 °C. Mesoporous-walled alumina-rich nanotubes of S_{BET} up to 159 m^2/g were developed by alkali-etching Hal pre-calcined at 1000 °C. In the experiment the materials exhibit enhanced adsorption for methylene blue (MB) in aqueous solution of elevated pH. Theoretical modeling based on the concepts of Langmuir, Freundlich and Redlich–Peterson was applied for their isotherms. The optimized monolayer MB adsorption capacities of 427 mg/g for silica and 249 mg/g for alumina products were achieved, showing potential in low-cost and high-efficient adsorbents.

1. Introduction

Nanoporous materials are of great interests for scientific research and technical applications, with the benefits of well-defined nanoscale pores able to efficiently discriminate and interact with molecules and clusters. The International Union of Pure and Applied Chemistry (IUPAC) defines nanopores into three categories: micropores (diameter <2 nm), mesopores (2–50 nm) and macropores (>50 nm). Increasing efforts in the area of nanoporous materials have been driven by the rapid-growing wide applications, such as biotechnology, molecule adsorption/separation, energy storage/conversion, catalysis, and photonics (Schuth and Schmidt, 2002; Wan and Zhao, 2007; Liang et al., 2008; Ren et al., 2012; Li and Zhao, 2013; Ma et al., 2013).

The production of nanoporous materials can be through either artificial synthesis or natural development. The synthesized mesoporous materials, with various kinds of frameworks such as carbon (Liang et al., 2008; Ma et al., 2013), silica (Wan and Zhao, 2007), metal oxide (Ren et al., 2012) or their hybrids (Guo et al., 2014), have been studied for two decades. Nevertheless, it is also acknowledged that many artificial nanoporous materials are suffering from high cost, complexity and pollution during the fabrication process, which thus hinders their wide applications. In contrast, the natural nanoporous materials are generally with low cost and environmental-friendly, benefiting from their richness in reserves and easiness in acquisition. Nowadays, many kinds of nanoporous minerals have been recognized and utilized, such as the microporous zeolite (Davis and Lobo, 1992) and sepiolite (Galan, 1996), the mesoporous halloysite (Joo et al., 2013; Kogure et al., 2013; Tan et al., 2013), and the macroporous pumice (Thomas et al., 1994) and diatomite (Khraisheh et al., 2004). Among all the natural nanoporous minerals, halloysite is of particular importance due to its unique tubular morphology, similar to the carbon nanotube. Halloysite generally exhibits a nanotube shape of 500–1000 nm in length and 10–100 nm in inner-diameter. The tube wall is consisted of curved layers of crystalline aluminosilicate belonging to the monoclinic system. The layer unit contains a corner-shared tetrahedral [SiO_4] sheet, stacked with an edge-shared octahedral [AlO_6] sheet with internal aluminol group (Al–OH). A water monolayer also exists between the adjacent two layers. The general stoichiometry of halloysite is expressed as $Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$, where n equals 6 for 10 Å halloysite and 2 for 7 Å halloysite (Oya et al., 1987; Barrientos-Ramirez et al., 2009; Abdullayev et al., 2012; Kadi et al., 2012; Zhang et al., 2012; Kogure et al., 2013). The interlayer water in 10 Å halloysite evaporates easily in the dry air with the resultant generation of 7 Å halloysite (Yuan et al., 2012; Ouyang et al., 2014) (Reaction (1)).

$$Al_2O_3 \cdot 2SiO_2 \cdot 6H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 4H_2O \qquad (1)$$

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In the past decade, there are many halloysite-related works, such as halloysite-based adsorbents (Viseras et al., 2008; Zhao and Liu, 2008; Kiani et al., 2011; Kadi et al., 2012; Kiani, 2014), catalysts (Barrientos-Ramirez et al., 2009; Li et al., 2013), advanced ceramics (Fu and Zhang, 2005), polymer nanocomposites (Liu et al., 2013; Pasbakhsh et al., 2013; Carli et al., 2014; Sarifuddin et al., 2014; Yang et al., 2014), hard template (Zhou et al., 2011), and drug loading and releasing (Tan et al., 2014). Nonetheless, the halloysite nanotubes (abbreviated as Hal hereafter) feature a solid tube wall of tens of nanometers in thickness, which restricts the Hal with a confined specific surface area S_{BET} of around 50 m^2/g (Zhang et al., 2012).

The enlargement of the specific surface area of nanotubes by thinning the tube wall or constructing nanopores within the solid wall can improve their performance in interface-relative implementations. Recently, researchers have reported the progress of the nanoporosity improvement of Hal. For instance, Abdullayev et al. (2012) has applied the direct Hal treatment with sulphuric acid to selectively etch the aluminum oxide and enlarged the nanotube lumen diameter from 15 to 25 nm, with the specific surface area increased from 40 to 250 m^2/g. Zhang et al. (2012) alternatively treated Hal with sulphuric acid and also improved the specific surface area from 48 to 267 m^2/g by selectively etching the alumina. The silica-rich nanotube products were obtained in their works accordingly. Wormlike nanopores existed in the tube wall and lead to the enhanced specific surface area. Nevertheless, specific surface area (about 250 m^2/g) is yet restricted in the reported nanoporous-walled silica nanotubes prepared from directly acid-etching Hal. Considering the chemical difference between silica and alumina, Hal-based nanoporous-walled alumina nanotubes may also be obtained from Hal by the selective etching of the silica component in alkaline solution. This difference has been observed by White et al. (2012) during the research on the stability of the raw Hal in acidic and alkaline aqueous solution.

In this paper, the authors proposed and demonstrated both the nanoporous-walled silica nanotubes, with effectively improved specific surface area, and a new type of nanoporous-walled alumina nanotubes originated from the raw Hal. The raw Hal was firstly heat-treated for activation and then treated by acid or alkali to selectively etch the alumina or silica component. Microporous/mesoporous-walled silica nanotubes with improved specific surface area up to 414 m^2/g were obtained while mesoporous-walled alumina nanotubes with the specific surface area up to 159 m^2/g. The effects of the thermal and chemical treatments on the composition, morphology and porosity characteristics of Hal were investigated. The adsorption performance of the nanoporous-walled silica or alumina nanotubes towards methylene blue, that is a cationic dye model, was also evaluated.

2. Experimental

2.1. Materials

In the work, the Hal material was purchased from Danjiangkou Shunhe Clay Co. The concentrated hydrochloric acid (HCl, A. R.), sodium hydroxide (NaOH, A. R.) and methylene blue (MB, A. R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the materials were used directly, without any further purification.

2.2. Preparation of nanoporous-walled silica or alumina nanotubes from Hal

Hal went through a thermal treatment and then was etched by acid or alkaline aqueous solution. It changes into nanoporous-walled silica or alumina nanotubes. Hal was calcined for 4 h at a temperature of 750–1150 °C with a heating rate of 10 °C/min. Then the calcined Hal (5 g) was magnetically stirring-mixed with 100 mL of 5 mol/L HCl (or 2 mol/L NaOH) aqueous solution in a sealed glass (or Teflon) vessel at 80 °C for 6 h. Finally, the resultant solid was filtered, washed with deionized water, and dried at 110 °C overnight. The HCl (or NaOH) etched sample was labeled as Hal-x-HCl (or Hal-x-NaOH), where x represents the pre-calcination temperature.

2.3. Batch adsorption test on methylene blue

Two representative samples, Hal-850-HCl (nanoporous-walled silica nanotubes) and Hal-1000-NaOH (nanoporous-walled alumina nanotubes), were chosen to investigate the adsorption behavior of methylene blue (MB). 20 mg of each adsorbent (dried at 110 °C overnight) was added into 20 mL MB solution in a 40 mL sealed vessel. The initial MB concentration was set at 100, 150, 200, 300, 400 or 550 mg/L, and the pH of solution was adjusted from 2 to 12 by HCl or NaOH solutions. The obtained mixture solution was shaken at a speed of 170 rpm for 24 h at 25 °C to attain equilibrium. Once the solution was centrifuged at 3800 rpm for 20 min, the supernatant liquid was characterized by the UV–Vis spectrophotometer (DR6000, HACH, US) at the wavelength of 664 nm to measure the MB concentration in solution. The amount of MB adsorption at equilibrium Q_e (mg/g) was calculated by the following Eq. (2):

$$Q_e = \frac{(C_0 - C_e)\ V}{M} \tag{2}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of MB in solution, respectively. V (L) is the volume of solution, and M (g) is the dosage of dried adsorbent.

2.4. Characterization and analysis

The samples are characterized by the X-ray powder diffraction (XRD) technique and the XRD patterns were recorded by the Rigaku D/Max-3B diffractometer using CuKα radiation at 35 kV and 40 mA. Thermo-gravimetric/differential scanning calorimetry (TG-DSC) measurements were conducted using a Netzsch STA409 PG/PC apparatus at a heating rate of 10 K/min in air atmosphere. Nitrogen adsorption/desorption isotherms at 77 K were measured by the Micromeritics TriStar 3020 porosimeter. All samples were pre-outgassed at 150 °C for 6 h under flowing nitrogen. The total specific surface area (S_{BET}) was calculated using the Brunauer–Emmet–Teller (BET) method. The micropore surface area (S_{micro}) was determined by the t-plot method and the mesopore surface area ($S_{external}$) was obtained by subtracting S_{micro} from S_{BET}. The total pore volume (V_t) was calculated at the relative pressure p/p_0 of 0.97. Similarly, the micropore volume (V_{micro}) was determined by the t-plot method and the mesopore volume (V_{meso}) was obtained by subtracting V_{micro} from V_t. The pore size distributions were analyzed by the Barrett–Joyner–Halenda (BJH) method. Field emission scanning electron microscopy (SEM) analysis were performed using the Magellon 400 electron microscope. Field emission transmission electron microscopy (TEM) analysis was conducted on the JEOL 200CX electron microscope operated at 200 KV.

3. Results and discussion

3.1. Design of constructing nanopores in the Hal tube wall

The tube wall of Hal is a crystalline layered aluminosilicate with interlayer water. Its layer unit is consisted of a tetrahedral [SiO_4] sheet stacked with an octahedral [AlO_6] sheet, precisely similar to that of kaolinite. It is known that calcination activates the aluminosilicate network of kaolinite and improves its activity in the reaction with acid or alkali (Okada et al., 1995; Belver et al., 2002; Lenarda et al., 2007). Likewise, a temperature-dependent change of the Hal structure also happens in calcination (Yuan et al., 2012; Ouyang et al., 2014). Therefore, a thermal treatment will allow the activation of the aluminosilicate network of Hal nanotube wall. A subsequent treatment of acid or alkali