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Research paper

Template-free preparation of mesoporous silica and alumina from natural kaolinite and their application in methylene blue adsorption

Zhu Shu [a], Tiantian Li [a], Jun Zhou [a,*], Yun Chen [a], Dongxue Yu [a], Yanxin Wang [b,*]

[a] Faculty of Materials Science and Chemistry, China University of Geosciences, 430074 Wuhan, PR China
[b] School of Environmental Studies, China University of Geosciences, 430074 Wuhan, PR China

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ABSTRACT

A facile top-down strategy of preparing mesoporous materials directly from natural minerals by selective-etching was proposed. Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), a cheap and abundant clay mineral, was chosen and processed into mesoporous materials with well-defined mesopores (2–6 nm) and high specific surface areas (170–430 m^2/g). In the process, kaolinite was activated by heat-treatment, and then etched by an acid or alkali solution according to its chemical and crystalline features. The activated amorphous alumina or silica component was selectively etched by acid or alkali, respectively, and nanopores were generated in-situ as a result. The pore sizes and specific surface areas can be controlled by the calcination and etching conditions. The as-prepared mesoporous silica and alumina materials showed favorable adsorption abilities towards methylene blue with the monolayer adsorption capacity up to 362 mg/g. The template-free preparation of mesoporous materials directly from natural clay minerals may help to promote not only the development of clay products but also the wide application of mesoporous materials with encouraging economic and environmental benefits.

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1. Introduction

Mesoporous materials were well-known and highly attractive for the defined mesoporosity (mesopores of 2–50 nm in diameter) and large specific surface areas (abbreviated as SSA hereafter), which benefited their wide applications in adsorption, separation, catalysis, drug delivery and so on (Sen et al., 2006; Vallet-Regi et al., 2007; Shi, 2013). Traditional approaches for synthesizing mesoporous materials generally followed the template route, i.e. using surfactant micelles as the soft-template or utilizing mesoporous/meso-sized inorganic materials as the hard-template to obtain mesopores in the final product after the template being removed. Additionally, industrial chemicals were used as raw materials to form the meso-structured framework in general. The template route was proved powerful and feasible in producing various mesoporous materials such as mesoporous silica, carbon, metal oxide and their hybrids/compositions (Yang et al., 1998; Kleitz et al., 2003; Wan and Zhao, 2007; Ren et al., 2012; Crossland et al., 2013). However, it is also well-known that the templates were extremely costly and their consumption highly raised the cost of these mesoporous materials. Thus, in order to cost-effectively produce mesoporous materials, increasing attempts were conducted to develop facile template-free routes. For instance, Shi' group proposed a template-free strategy to synthesize various types of mesoporous metal oxides by the controlled thermal decomposition of oxalate precursors (Yu et al., 2008; Shu et al., 2013). Tao et al. synthesized highly mesoporous carbon foam with a high SSA via a facile, cost-effective and template-free Pechini method (Tao et al., 2013). Nevertheless, these meso-structured frameworks were still mainly synthesized from industrial chemicals that are generally not cheap and hard-processed from natural minerals, the most-original resource supporting the world. Therefore, it is of great interest to prepare mesoporous materials directly from natural minerals via a template-free route, in consideration of the encouraging economic and environmental benefits.

As a matter of fact, in view of the chemical and structural features, many minerals may be potential candidates for template-freely processing mesoporous materials. For example, the clay minerals generally have a layer structure and the layer unit is consisted of a corner-shared tetrahedral sheet and an edge-shared octahedral sheet stacked at a ratio of 1:1 or 2:1 (Bergaya and Lagaly, 2001; Bergaya et al., 2006; Duarte-Silva et al., 2014; Ndlovu et al., 2014). Each tetrahedron consists of a cation, mainly Si^{4+}, Al^{3+} and Fe^{3+}, coordinated to four oxygen atoms, and each octahedron comprises a cation, usually Al^{3+}, Mg^{2+} and Fe^{3+}, coordinated to six oxygen atoms. Considering the acidity–alkalinity difference between Si^{4+} and $Al^{3+}/Mg^{2+}/Fe^{3+}$, the acid or alkali etching may be applied on the clay minerals to selectively remove the metal oxide or SiO_2 component, respectively. Afterwards, nanopores are expected to form in situ. In fact, kaolinite (abbreviated as Ka hereafter), a clay mineral with a 1:1 layer structure consisted of a $[SiO_4]$ tetrahedral sheet and a $[AlO_6]$ octahedral sheet in the layer unit (Bergaya et al., 2006), was previously thermal-activated

* Corresponding authors at: 388 Lumo Road, 430074 Wuhan, P.R. China. Tel.: +86 13018015320; fax: +86 27 67883731.
E-mail addresses: zhoujun@cug.edu.cn (J. Zhou), yx.wang1108@gmail.com (Y. Wang).

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and acid-treated into catalysts or adsorbents which were found to be nanoporous with enlarged specific areas up to 219 m^2/g (Belver et al., 2002; Lenarda et al., 2007; Panda et al., 2010; Auta and Hameed, 2012). However, these researches mainly focused on the catalysis or adsorption performance of as-obtained materials while the nano-porosity issue was not concerned. Thus, the evaluation mechanism of nanoporous structure was not clear, the size of nanopores lacked control, and the obtained SSA was still limited. Moreover, the idea of preparing mesoporous materials from minerals was not definitely proposed yet.

In this work, the idea of constructing mesoporosity in natural minerals by selective etching was proposed. Natural Ka was processed into mesoporous materials of high SSA, controlled pore sizes and different frameworks via a facile template-free route of selective acid or alkali etching. The evaluation mechanism of mesoporosity was investigated and the effect of processing parameters on the mesoporosity was studied. Additionally, the adsorption abilities of as-processed Ka-based mesoporous materials towards methylene blue (MB), a model of cationic dye pollutant, were investigated.

2. Experimental

2.1. Materials

The used Ka was purchased from China Kaolin Clay Co., Ltd. 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 without further purification.

2.2. Preparation of mesoporous materials from Ka

Ka firstly underwent a thermal treatment and then was etched by acid or alkali into the mesoporous materials. In detail, the Ka was calcined for 2 h at a temperature of 750–1200 °C using a heating rate of 10 °C/min. Then, 5 g of the calcined Ka was magnetically stirring-mixed with 100 mL HCl (or NaOH) aqueous solution in a sealed glass (or Teflon) vessel. The etching temperature was controlled at 60, 80 or 100 °C. The initial HCl concentration in solution was set at 2, 3, 5, 7 or 9 mol/L and the initial NaOH concentration was 1, 2, 3 or 4 mol/L. 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 Ka-x-HCl (or Ka-x-NaOH), where x represented the calcination temperature.

2.3. Batch adsorption studies towards methylene blue (MB)

Several HCl or NaOH etched samples were chosen as adsorbents for the MB adsorption application. 20 mg of adsorbent dried at 110 °C overnight was mixed with 20 mL of MB solution in a sealed vessel (40 mL), which was placed in a water-bath shaker with a speed of 170 rpm for 24 h at 25 °C to attain equilibrium. After the solution was centrifuged at 4000 rpm for 20 min, the final MB concentration in the liquid phase was determined by UV–Vis spectrophotometer at the maximum wavelength of 664 nm for MB. The amount of the MB adsorbed at equilibrium Q_e (mg/g) was calculated using the Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentration of MB at initial and equilibrium, respectively; V (L) is the solution volume and W (g) is the mass of the dried adsorbent used.

To investigate the effect of solution pH on adsorption, an initial MB concentration of 100 mg/L was used and the initial pH of MB solution was varied from 2 to 12. Either HCl or NaOH solution (0.1, 1.0 or 5.0 mol/L) was used for the adjusting of solution pH. In the subsequent adsorption isotherm studies, a constant initial solution pH of 8 was used and a set of initial MB concentrations of 100, 150, 200, 300, 400 and 550 mg/L was employed.

2.4. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max-3B diffractometer using Cu Kα radiation at 35 kV and 40 mA. Thermogravimetric/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 on a Micromeritics TriStar 3020 porosimeter. All samples were outgassed at 150 °C for 6 h under flowing nitrogen before measurements. The total SSA (S_{BET}) was calculated by the Brunauer–Emmet–Teller (BET) method, the micropore SSA (S_{micro}) was determined by the t-plot method and the mesopore SSA ($S_{external}$) 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, 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 was performed on a Magellon 400 electron microscope. Field emission transmission electron microscopy (TEM) analysis was conducted on a JEOL 200CX electron microscope operated at 200 kV.

3. Results and discussion

3.1. Design of constructing nanopores in Ka

It is a known fact that, Ka is a clay mineral with a 1:1 layer structure consisted of a $[SiO_4]$ tetrahedral sheet and a $[AlO_6]$ octahedral sheet in the layer unit with resistances to acid/alkali in general. Thus, a thermal treatment is adopted to break the Al–O and Si–O binds of Ka. Afterwards, H^+ (or OH^-) may be used to selectively remove the activated Al_2O_3 (or SiO_2) component of the calcined Ka and to develop nanopores in situ.

3.2. Characterization of the Ka and its calcined counterparts

The used Ka was of typical plate shapes (Fig. 1A) and composed of well-crystallized Ka crystals (PDF 89-6538) and traces of illite (PDF 26-0911) and quartz (PDF 86-1630) impurities (Fig. 1B). Its DSC curve (Fig. 1C) showed an endothermic peak at 533 °C and an exothermic peak at 1016 °C. The endothermic peak at 533 °C is related to a large weight loss of about 13% as indicated by the TG curve (Fig. 1C), and can be assigned to the well-known dehydroxylation process (reaction (2)), after which the crystalline Ka becomes the metakaolin which is an amorphous solid. This phase transformation has been deeply studied and is also proved by our XRD results of samples calcined at 700–900 °C (Fig. 1B) (Lambert et al., 1989; Badogiannis et al., 2005). However, the calcination at further increased temperatures of 1000–1100 °C led to the reorganization of the oxide network which was finally composed of poorly crystallized γ-Al_2O_3 (PDF 10-0425), mullite (PDF 15-0776) and an amorphous phase rich in silica (Fig. 1B). This transformation can be expressed as reaction (3) as documented previously (Lambert et al., 1989). Moreover, the calcination at 1200 °C resulted in the enhanced crystallization of mullite and the disappearing of γ-Al_2O_3, the latter of which is supposed due to the competition for the aluminium resource by the former (Fig. 1B). In addition, the thermal treatment hardly changed the SSA (shown in Table 1) or the flaky morphology (shown in Fig. 1A, D and E) of Ka in spite of the variation of calcination temperature from 700 to 1100 °C.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \quad (2)$$

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