



Research paper

Template-free synthesis of kaolin-based mesoporous silica with improved specific surface area by a novel approach

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ABSTRACT

A novel template-free method is proposed and demonstrated to develop the facile top-down strategy of preparing mesoporous materials from natural minerals. In the process, kaolin was pre-calcined, alkali-activated and finally acid-etched into mesoporous silica (MS) of improved specific surface area (604 m²/g) and large pore size (4.41 nm) at the maximum probability. The characterizations of XRF, XRD, TG, FT-IR, SEM, TEM and N₂ adsorption/desorption were carried out and the material evolution mechanism was clarified. The as-resulted MS showed favorable adsorption ability toward methylene blue with the monolayer adsorption capacity up to 652.9 mg/g, indicating its promising potential in adsorption application. The template-free method proposed may benefit not only the clay products but also the wide application of mesoporous materials cost-effectively.

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1. Introduction

Mesoporous materials are highly attractive for the defined mesoporosity (mesopores of 2–50 nm in diameter) and large specific surface areas (S_{BET}), which benefit their wide applications in adsorption, separation, catalysis, drug delivery and so on (Tanev et al., 1994; Corma, 1997; Sen et al., 2006; Slowing et al., 2007; Vallet-Regí et al., 2007; Shi, 2012). The traditional synthesis of mesoporous materials is generally based on the template strategy. In this case, surfactant micelles or meso-sized inorganic materials are applied as the templates to form the meso-structured framework with fine-grade industrial chemicals, and the final mesoporous materials are obtained after the templates being removed. The template strategy proves powerful and feasible, but the consumption is considerable high for the extremely costly templates and industrial chemicals. Thus, it would be of great interest for the facile top-down strategy of preparing mesoporous materials without any templates or industrial chemicals. Following this, the selective etching and the substitution of natural minerals for industrial chemicals have been widely studied, considering the reserve-richness and low-cost features of natural minerals.

Several clay minerals such as montmorillonite, halloysite and kaolinite have been utilized as raw materials to template-freely prepare mineral-based mesoporous silica through selective acid-etching route.

For instance, Pesquera et al. (1992) and Mendioroz et al. (1987) modified montmorillonite by the acid treatment and obtained nanoporous silica of S_{BET} up to 391 and 416 m²/g, respectively. Abdullayev et al. (2012) and Zhang et al. (2012) treated the natural mesoporous nanotubes, halloysite, with H₂SO₄ solutions and improved the S_{BET} from about 40 to 270 m²/g. Auta and Hameed (2012) applied the acid treatment on the kaolin and prepared a microporous silica-rich material with a S_{BET} of 92 m²/g. Moreover, it was confirmed that a proper pre-calcination can weaken the acid resistance of kaolin and promote the acid-treating progress. Lenarda et al. (2007) prepared mesoporous silica of the increased S_{BET} up to 288 m²/g by acid-treating the kaolin pre-calcined at 850 °C for 2 h. Perissinotto et al. (1997) and Okada et al. (1998) pretreated kaolin at 600 °C and acid-etched it into nanoporous silica of increased S_{BET} up to ~330 m²/g. Li et al. (2011) obtained a porous silica with a S_{BET} of 357 m²/g by acid-dissociating the alumina of 900 °C-calcined kaolin. Shu et al. (2014) acid-etched 850 °C-calcined kaolin and improved the S_{BET} to 430 m²/g.

Nevertheless, the reported mineral-based mesoporous silica is still limited in specific surface area (<430 m²/g for the kaolin-based ones), which is far behind those developed by the template strategy (600–1000 m²/g for MCM-41, SBA-15, KIT-6, etc.) (Xu et al., 2012; Lee et al., 2014; Meléndez-Ortiz et al., 2014; Ruiz-Hitzky and Aranda, 2014). Thus, it is still of much significance to develop new technologies to greatly improve the specific surface area of mineral-based mesoporous materials.

In this study, the authors proposed and demonstrated a novel approach to template-freely synthesize mesoporous silica of highly enlarged specific surface area (604 m²/g) from a natural kaolin. The

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process was addressed in detail. The characteristics of the final product coupled with the starting material and intermediate counterparts were systematically analyzed. The mechanism for the evolution of mesoporosity was revealed. The adsorption behavior of as-synthesized mesoporous silica toward methyl blue (MB), a model of cationic dye pollutant, was also investigated.

2. Experimental

2.1. Raw materials

Concentrated hydrochloric acid (HCl, A. R.) and sodium hydroxide (NaOH, A. R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. The kaolin was obtained from China Kaolin Clay Co. All raw materials were used directly without any further purification.

2.2. Preparation of mesoporous silica from kaolin

The kaolin was activated into metakaolin (MK) by calcination at 850 °C for 4 h. Then 5 g of MK was submitted to 100 mL of 4 mol/L NaOH aqueous solution in a sealed Teflon vessel and stirred for 0.5 h at 80 °C. After the filtration, purification with deionized water and drying at 110 °C, an alkali-treated metakaolin (AMK) was obtained. Finally, 5 g of AMK was etched by 100 mL of 5 mol/L HCl aqueous solution for 6 h at 80 °C in a sealed glass vessel and then filtered, washed with deionized water and drying at 110 °C overnight to obtain the final mesoporous silica (MS).

2.3. Adsorption test

The adsorption ability of the as-obtained mesoporous silica (MS) on methylene blue (MB) was evaluated. Twenty milligrams of MS dried at 110 °C overnight was mixed with 20 mL of MB solution in a sealed vessel (40 mL). The vessel was placed in a water-bath shaker with a speed of 170 rpm for 24 h at room temperature to attain equilibrium. After the solution was centrifuged at 3800 rpm for 20 min, the final MB concentration in the liquid phase was determined by a UV-vis spectrophotometer (DR6000, HACH, America) at the wavelength of 664 nm. 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 concentrations of the adsorbate at initial and equilibrium, respectively; V (L) is the volume of solution and W (g) is the mass of adsorbent.

To investigate the effect of solution pH on adsorption, an initial MB concentration of 400 mg/L was used, and the initial pH of MB solution was varied from 2 to 12 with an interval of 2. Either HCl or NaOH solutions were used for the adjusting of solution pH. In the subsequent adsorption isotherm study, a constant initial solution pH of 10 and a set of initial MB concentrations of 100, 150, 200, 300, 400, 550, 600, 700, 800, 900 and 1000 mg/L were employed.

2.4. Characterization

The chemical compositions of materials were analyzed by an AXIOSmAX X-ray fluorescence (XRF) spectrometry. X-ray powder diffraction (XRD) patterns were recorded by a Rigaku D/Max-3B diffractometer using $\text{CuK}\alpha$ 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 20 K/min in air atmosphere. FT-IR spectra were recorded in the region 4000–400 cm^{-1} in a Nicolet 6700 infrared Fourier transform spectrometer, using the KBr pellet technique (1% samples by mass in KBr). Field emission scanning electron microscopy (SEM) analysis were 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.

Nitrogen adsorption/desorption isotherms at 77 K were measured on a Micromeritics TriStar 3020 porosimeter. All samples were outgassed at 250 °C for > 8 h under flowing nitrogen before measurements. The total specific surface area (S_{BET}) was calculated by 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, 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.

3. Results and discussion

3.1. Characteristics of the as-prepared mesoporous silica

The obtained product (MS) is dominant in silica with an amorphous structure as confirmed by the XRF (shown in Table 1) and XRD (shown in Fig. 1) analyses. The N_2 adsorption–desorption isotherm (plotted in Fig. 2) is a typical Langmuir IV curve with a hysteresis loop, evidencing MS to be well-defined mesoporous. The mesoporous structure is also illustrated by the TEM observation (shown in Fig. 3b). In detail, it possesses a specific surface area as high as 604 m^2/g and a large pore size of 4.41 nm at the maximum probability (shown in Fig. 2 and Table 2), both of which are much superior to the properties of the kaolin-based nanoporous materials reported in literatures (shown in Table 2).

3.2. Development of MS

In this section, the starting material (kaolin), the intermediate counterparts (MK and AMK) and the final product (MS), were all characterized and compared to investigate the mechanism of the transformation from kaolin to the final mesoporous silica.

3.2.1. Evolution of crystalline degree

XRD patterns shown in Fig. 1 reveal that the kaolin mainly consists of kaolinite, while traces of quartz impurity can be also observed. No

Table 1
Chemical compositions of the materials (mass%).

Samples	Chemical compositions										
	$n_{\text{Si}/\text{Al}}^a$	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	TiO_2	P_2O_5	LOI^b
Kaolin	1.02	45.79	38.07	0.55	0.53	0.20	0.07	0.13	0.32	0.46	13.82
MK	1.02	52.73	43.84	0.63	0.61	0.23	0.08	0.15	0.37	0.53	0.77
AMK	1.02	43.77	36.37	0.35	0.41	11.77	0.12	0.01	0.32	0.03	6.84
MS	12.99	87.93	5.74	0.17	0.17	0.06	0.08	0.04	0.66	0.02	5.11

^a $n_{\text{Si}/\text{Al}}$: the mole ratio of Si to Al.

^b LOI: loss on ignition.

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