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Synthesis and CO_2 adsorption property of amino-functionalized silica nanospheres with centrosymmetric radial mesopores

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ABSTRACT

Amino-functionalized silica nanospheres with centrosymmetric radial mesopores were successfully prepared using the anionic surfactant N-lauroylsarcosine sodium (Sar-Na) as template and 3-aminopropyltrimethoxysilane (APMS) as co-structure directing agent. The template was efficiently removed by extraction either using a basic solution of monoethanol amine (MEA) in ethanol or an acetonitrile solution acidified with HCl. The synthesized mesoporous silica materials were characterized by the FT-IR, TG-DTA, XRD, N_2 adsorption–desorption and TEM techniques. CO_2 adsorption at 25 °C was evaluated by a volumetric method, and CO_2 desorption was studied by the TPD technique. The results indicate that, compared to the sorbent treated with acidic-acetonitrile, the sorbent treated with the MEA–ethanol solution has a much higher adsorption capacity towards CO_2, exhibits a higher degree of reversibility in the adsorption process, and has a much higher CO_2/N_2 selectivity.

1. Introduction

It is well known that carbon dioxide (CO_2) has become an important global issue due to the significant and continuous rise in anthropic CO_2 emissions to the atmosphere and their connection with global climate change. Therefore, it is necessary to reduce CO_2 concentration significantly from the current level [1]. At present, the main available approaches for CO_2 capture and separation include the use of solid sorbents such as activated carbons and zeolites [2–4] and amine solution absorption technologies [5–7]. The major drawbacks of the use of amine solutions for CO_2 separation on an industrial scale include the large amount of energy required for regeneration of the amine solutions, equipment corrosion, and absorption solvent degradation in the presence of oxygen [5–7]. Adsorption with solid sorbents would be preferable over amine solution absorption because of the inherent properties associated with ease in handling of solids [8–11]. In particular, amino-functionalized mesoporous silicas (AFMS) are ideal candidates for capturing CO_2 from combustion flue gas, due to the reversible formation of ammonium carbamates and/or carbonates during CO_2 adsorption, as well as due to uniform, large pores, and high surface area [12–14]. Recently, plenty of research work has been carried out on AFMS sorbents for CO_2 adsorption. For example, Jones and coworkers synthesized an organic/inorganic hybrid amine-tethered silica material, the so-called SBA-HAS, with high amine loadings capable of reversibly binding CO_2 with high adsorption capacity [15]. Sayari and coworkers synthesized amine-bearing pore-expanded MCM-41 silicas and used them as CO_2 sorbents [16,17]. To obtain CO_2 sorbents with high amine loadings, mesoporous silicas were impregnated with polyethyleneimine (PEI) or tetraethylenepentamine (TEPA) [9,18].

The co-condensation [10,12] and post-grafting [13,14] of functional silanes are commonly applied to the preparation of AFMS. However, certain drawbacks are associated with both methods. The post-grafting method typically results in an inhomogeneous surface coverage due to organic moieties congregating near the entries of the mesopores and the exterior surfaces [12]. The co-condensation method may lead to situations where some of the functional groups are embedded in the silica network [19,20]. Co-condensation of organosilanes with terminal organic groups is also disadvantageous, because the terminal groups destabilize the framework [21]. Therefore, it is necessary to develop a method to synthesize meso-materials with a highly symmetrical amino-group distribution.

Anionic surfactant-templated mesoporous silicas (AMS) have attracted much attention because of the extremely regular arrangement of the functional groups introduced by the co-structure directing method [22]. To obtain the AFMS from the AMS, solvent extraction methods [23–27] are often used owing to necessity of preserving amino groups. Kim et al. [25] synthesized the AFMS

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using acidic-acetonitrile as extractive solvent for CO_2 separation. As CO_2 sorbents, amino groups in the AFMS must be free, so in their synthesis alkalis such as NaOH and KOH were used to recover the basicity of amino moiety in a post-treatment step. Recently, a mesoporous silica with free amino groups was prepared via an alkali-ethanol extractive system by Che's group [27]. Those authors found that using a monoethanol amine (MEA) solution in ethanol as extracting agent gave a good result, based on the XRD, N_2 adsorption–desorption, and FT-IR characterizations, and the optimal MEA concentration was 3.3 mol/l. More recently, Wang et al. [28] prepared spherical silicas with radially oriented mesopores, and suggested that the prepared materials could be suitable for adsorption-based separations, because all the mesopores in the materials were connected to each other, leading to better adsorption properties. However, their synthesized materials have not been used as sorbents for further investigations.

In this work, AMS nanospheres with centrosymmetric radial mesopores were synthesized using N-lauroylsarcosine sodium (Sar-Na) as template and 3-aminopropyltrimethoxysilane (APMS) as co-structure directing agent (CSDA). Two different extraction procedures were used to remove the templating agent from the as-synthesized materials, namely extraction with alkaline MEA-ethanol solution and extraction with HCl-acidified acetonitrile solution. Various techniques such as FT-IR, TG-DTA, XRD, N_2 adsorption–desorption, SEM, and TEM were used to characterize the synthesized materials. Eventually, in view of a possible use of these sorbents for CO_2 removal, their adsorption–desorption properties towards CO_2 were investigated in detail.

2. Experimental

2.1. Chemicals

N-lauroylsarcosine sodium (Sar-Na) was purchased from Merck, and tetraethyl orthosilicate (TEOS) and 3-aminopropyltrimethoxysilane (APMS) were from Acros and Aldrich, respectively. Hydrochloric acid (0.1 mol/l) was prepared from 37% fuming hydrochloric acid (Sinopharm Chemical Reagent Co., Ltd., Shanghai). All the other reagents were used without further purification.

2.2. Synthesis

The AMS was prepared by the method developed by Wang et al. [28]. In a typical synthesis, 2.0 mmol Sar-Na was completely dissolved in 70 ml deionized water under stirring at room temperature. Afterwards, 13 g of 0.1 mol/l HCl solution was added to the Sar-Na solution under vigorous stirring for 1 h, and then a mixture of 3.0 ml TEOS and 0.20 ml APMS was added to the above prepared solution under vigorous stirring for 10 min. The resulting mixture was aged at room temperature for 2 h and the synthesis was then carried out hydrothermally without agitation in a closed 100 ml reaction kettle placed in an oven at 80 °C for 20–48 h. The products were filtered and the solids were washed with deionized water. The washed solids were then dried for 10 h at 80 °C prior to a further analysis or use.

The surfactant in the dried sample was removed by an ion-exchange extraction method [27]. Typically, 1.0 g of the synthesized AMS was dispersed in a mixture solution of 100 ml ethanol and 3.3 mol/l MEA (ca. 25.2 g) at 25 °C by agitation and then the mixture was refluxed at 90 °C for 12 h. The solids were recovered by filtration, washed with ethanol, dried, and the above extraction procedure was repeated. The resulting solid is referred to as Sample A. In analogy to the preparation of Sample A, the same amount of the AMS was dispersed in a solution of 100 ml acetonitrile and 10.42 g of ca.35 wt.% HCl (aq.) using the same procedure described for the synthesis of Sample A, and the resulting solid is referred to as Sample B.

2.3. Characterization

The FT-IR spectra were recorded on a Nicole Nexus 670 spectrometer with a resolution of 4 cm^{-1} using the KBr compression method and the *in situ* FT-IR spectra were obtained with an MCT detector. The powdered X-ray diffraction (XRD) patterns were performed on a PHILIPS PW3040/60 powder diffractometer using CuKα radiation ($\lambda = 0.15406$ nm). Morphology and particle sizes of samples were examined with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. SEM images were obtained using a Hitachi S-4800 instrument operating at 50 kV, and TEM images were obtained on a 2100 JEOL working at 200 kV. The amounts of nitrogen introduced to the mesoporous silica samples were measured on a Vario ELIII elemental analyzer. The thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C thermogravimetric analyzer with a temperature ramp of 10 °C/min in air. The measurements of N_2 adsorption–desorption were performed on a Micromeritics ASAP 2020 apparatus at −196 °C, and the specific surface areas of the investigated samples were calculated using the multiple-point Brunauer–Emmett–Teller (BET) method in the relative pressure range $p/p_0 = 0.05–0.3$. The pore size distribution curves were computed using the Barrett–Joyner–Halenda (BJH) method and the average pore sizes were obtained from the peak positions of the distribution curves.

2.4. CO_2 and N_2 adsorption

The isotherms of CO_2 and N_2 adsorption were measured on Micromeritics ASAP 2020 at 25 °C. The sample cell was loaded with ca. 250 mg of the sorbent. After the sorbent was outgassed in vacuum at 120 °C for 12 h in order to remove any adsorbed impurities, the adsorption run was carried out using highly pure CO_2 (99.999%) and N_2 (99.99%) in a pressure range from 0.01 to 101 kPa.

2.5. CO_2 TPD

The temperature-programmed desorption (TPD) of CO_2 was performed on a Micromeritics AutoChem II chemisorption analyzer. The sample cell was loaded with ca. 150 mg of the sorbent and then was heated in flowing helium at 120 °C for 2 h. After it was cooled to 25 °C, a CO_2 flow with a rate of 30 ml/min was introduced to the sample cell for CO_2 adsorption for 40 min. To remove the weakly adsorbed CO_2, the sample was swept using flowing helium with a rate of 30 ml/min at 25 °C for 1 h. Afterwards the TPD experiment was carried out in flowing helium with a rate of 30 ml/min from 25 to 140 °C with a temperature ramp of 3 °C/min. After temperature was cooled to 25 °C, the next run for CO_2 adsorption and TPD experiments were performed following the same procedure.

3. Results and discussion

3.1. Template removal

The FT-IR spectra of the as-synthesized sample and Samples A and B are shown in Fig. 1. The amounts of the surfactant and the CSDA in the samples can be reflected from the intensity of bands around 2852 and 2932 cm^{-1}, which can be associated with the symmetrical and asymmetrical stretching vibrations of the methylene groups of the surfactant and the CSDA, respectively [27]. From