



Swelling-agent-free synthesis of rice husk derived silica materials with large mesopores for efficient CO₂ capture



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HIGHLIGHTS

- Biporous MS-400(25) with large mesopores was prepared without swelling agents.
- Using silicate waste of rice husk as precursor reduces the chemical costs.
- MS-400(25) made from agricultural waste can be a potential CO₂ adsorbent.

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ABSTRACT

Swelling-agent-free synthesis of silica materials with large mesopores were developed using silicate from rice husk ash (RHA) as an alternative silica precursor in this study. Unlike the conventional methods for preparing large-pore silica materials in which toxic and expensive additives were employed as swelling agents, the obtained silica materials with large mesopores could be facilely prepared via a simple temperature-controlled approach without adding pore expanders. The fusion and hydrothermal temperature effects on the structural properties of obtained mesoporous silicas were investigated by the XRD, nitrogen adsorption–desorption, SEM and TEM analyses. The obtained mesoporous MS-400(25), which was fabricated using rice husk fused at 400 °C and treated with sodium hydroxide at 25 °C, exhibited bimodal meso-porosities (2.7 and 24 nm) and large pore volume (1.92 cm³/g). The bi-porosities mainly originated from the intra-particle mesostructure within silica particles and the inter-particle porosity between the aggregated nano-sized silica particles, respectively. The synthesized silicas were applied as the supports of adsorbents for CO₂ capture. The adsorption tests clearly revealed that the tetraethylenepentamine (TEPA) impregnated MS-400(25) material could achieve CO₂ adsorption capacity of 173 mg/g under 10% CO₂ at 75 °C, which was the best sorbents among all samples due to its relatively large pore volume.

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1. Introduction

The mitigation of global warming due to CO₂ emission is of great importance in environmental protection. Among available technologies, the use of amine-based solid sorbents for controlling CO₂ emission has attracted considerable attention, particularly in post-combustion processes where CO₂ is captured at low temperature and low pressure [1–4]. In comparison with conventional amine-based solvent scrubbing, the use of solid sorbents shows great potential to reduce the cost of capture process and lessen the energy penalty [5,6]. Therefore, the development of efficient and low-cost CO₂ sorbents will undoubtedly enhance the competitiveness for CO₂ capture applications [7,8].

Recently mesoporous silicas with tunable pore texture and unique surface chemistry via functionalization are considered as promising adsorbents for CO₂ capture [9]. Progress has been made by functionalizing various amine-based polymers on several supports including MCM-41, SBA-15, HMS, KIT, MSU, mesoporous silica spherical particles and mesocellular foams [10–16]. And high sorbent capacity and selectivity have been achieved for CO₂ capture. More recently, research works have shown that the pore size and pore volume of silica support play important roles in sorbent performance [17–19]. Supports with high pore volume can accommodate a greater amount of amines in the pores, and a large pore size is desirable for rapid diffusion of CO₂ in the pores. In this regard, mesocellular foams and mesoporous silica with large pore size and good pore interconnection appear to be more efficient than the other mesoporous silica supports [19–21].

Silicon alkoxide and sodium silicate are common silica sources [22,23]. However, the commercial fabrications of silica sources are

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highly energy-consuming and associated with high temperature, high pressure and strong acidity process [24,25], which is expensive and unfriendly to the environment. In addition, in the preparation of silica supports with large pores and hierarchical structures for efficient CO₂ capture, the use of toxic and expensive swelling agents such as trimethylbenzene (TMB) and ammonium fluoride are required [26,27]. Thus the industrial applications of current methods would have certain limitations in terms of environment, energy and economic concerns.

The recycling of silicon or silica-containing wastes as alternative precursors for preparing mesoporous silica instead of using commercial agents may provide an excellent opportunity to prepare the sorbents economically and minimize the waste production as well. Rice husk (RH) is one of the major agricultural wastes around the world, and it has been demonstrated to be a potentially feasible resource for synthesizing silica-based materials [28–30]. With the aim of lowering manufacturing cost and green synthesis for CO₂ adsorbent, a series of polyethyleneimine-immobilized uni-modal and/or bi-modal porous silicas were prepared from rice husk ash with biopolymer of chitosan as a pore structure-directing agent [31]. However, the maximum pore volume of their prepared silica support was only 1.08 cm³/g, which could only accommodate ca. 50 wt.% amines. From the viewpoint of both lowering cost and green synthesis, it is highly desirable to develop a simple and scalable approach to prepare silica supports with large pore volume and large pore size.

In this study, the fabrication of mesoporous silica materials with different mesopore sizes and large pore volumes were prepared by using sodium silicate solution as silica source via a simple temperature-controlled approach. The sodium silicate solution, which is extracted from rice husk ash (RHA), has been demonstrated to be a potentially feasible resource for synthesizing silica-based materials. The synthetic process is simple, cost-effective and environmentally benign since no extra pore expander and post-pore-expansion treatment are necessary, which significantly simplifies the scale-up synthesis. The pore structure and morphology of the obtained silica materials are presented and discussed. Moreover, an attempt has also been made to apply these mesoporous silica for immobilization of tetraethylpentaamine (TEPA) as sorbents and investigate their structure vs. performance relationship for CO₂ capture.

2. Experimental section

2.1. Silica extraction and material preparation

In order to figure out the effect of fusion temperature on structural properties of the obtained MS materials, the rice husk (RH) was fused under 400, 550 or 700 °C, respectively, and the obtained rice husk ash (RHA) was then mixed with aqueous NaOH solution at 25 °C for 24 h for the extraction of silica. The resulting mixture was then centrifuged to separate supernatant and sediment. The silicate supernatant was then utilized as the silica precursor for the synthesis of mesoporous silica materials. Mesoporous silicas were synthesized by the hydrothermal treatment method using the silicate supernatant extracted from RHA as the silica precursor and cetyltrimethylammonium bromide (CTAB) was employed as the structure-directing template in the synthesis. The molar composition of the gel mixture was 1 SiO₂: 0.2 CTAB: 0.89 H₂SO₄: 120 H₂O. In a typical procedure, 63 ml of waste silicate solution was acidified by adding approximately 40 ml of 4N H₂SO₄ to bring down the pH to 10.5 with constant stirring to form a gel. After stirring, 7.28 g of CTAB (dissolved in 25 ml of DI water) was added drop by drop into the above mixture and the combined mixture was stirred for three additional hours. The resulting gel mixture

was transferred into a Teflon coated autoclave and kept in an oven at 145 °C for 36 h. After cooling to room temperature, the resultant solid was recovered by filtration, washed with DI water and dried in an oven at 110 °C for 8 h. Finally, the organic template was removed by using a muffle furnace in air at 550 °C for 6 h. The synthesized mesoporous silica was denoted as MS-X(25), where X corresponds to the fusion temperature of raw RH under 400, 550 or 700 °C, with the following silica extraction temperature at 25 °C.

On the other hand, for studying the effect of extraction temperature on structural properties of the obtained MS materials, the RH was fused under a fixed temperature of 400 °C, the fused RHA was then mixed with aqueous NaOH solution at different hydrothermal temperatures of 25, 40, or 105 °C, respectively, to extract silica from fused RHA. The resulting mixture was then centrifuged to separate supernatant and sediment. The silicate supernatant was then utilized as the silica precursor for the synthesis of mesoporous silica, with similar procedures described above. The synthesized mesoporous silica was denoted as MS-400(Y), where 400 denotes the fusion temperature and Y corresponds to the silicate extraction (hydrothermal) temperature of either 25, 40, or 105 °C.

For comparison purpose, the preparation of MCM-41(NaSi) and SBA-15(NaSi) from commercial silicate precursors via conventional hydrothermal process was presented as well [8]. The synthesis of MCM-41(NaSi) was carried out using pure chemicals of sodium metasilicate nanohydrate (Na₂SiO₃·9H₂O) with CTAB as the structure-directing template. The molar composition of the gel mixture was 1SiO₂: 0.2 CTAB: 120 H₂O: 0.89 H₂SO₄. Mesoporous SBA-15 was synthesized using a tri-block copolymer, EO₂₀-PO₇₀-EO₂₀ (Pluronic P123, BASF) as the template and sodium silicate solution (~14% NaOH, ~27% SiO₂, Aldrich) as the silica source. The molar composition of the gel mixture was 1SiO₂: 0.01 P123: 286 H₂O: 0.7 H₂SO₄.

2.2. Characterization

The specific surface area, specific pore volume and average pore diameter (BJH method) of the samples were measured by N₂ adsorption–desorption isotherms at 77 K using a surface area analyzer (Micromeritics, ASAP 2000). All the samples were degassed for 6 h at 350 °C under vacuum (10⁻⁶ mbar) prior to the adsorption experiments. The powder X-ray diffraction (XRD) analyses were made to reveal the crystalline structure of mesoporous materials, and the diffractograms of the mesoporous samples were recorded in the 2θ range of 2–80° in steps of 0.6 degree with a count time of 60 s at each point. The morphology of the materials was observed via the SEM (HITACHI-S4700) images. TEM images of the samples were observed with a JEOL JEM 1210 TEM instrument operated at 120 keV, prior that the samples (5–10 mg) were ultrasonicated in ethanol and dispersed on carbon film supported on copper grids (200 mesh).

2.3. Functionalization and CO₂ adsorption tests

The above mesoporous silica materials were functionalized with amine reagent of tetraethylpentaamine (TEPA) via the wet impregnation method to enhance their CO₂ capture capacity. In a typical process, all silica supports were thermally pretreated at 120 °C for 1 h. Meanwhile, TEPA was mixed with ethanol and the resulting solution was stirred for 30 min. After pretreatment, the silica adsorbents were dispersed into a flask containing TEPA solution and the mixture was then refluxed at 80 °C for 2 h. After cooling to room temperature, the obtained materials were dried at 100 °C for 2 h. The nitrogen loading of the aminated material was evaluated by a thermo-gravimetric analyzer (TGA, Netzsch TG209 F1, Germany).

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