Microporous and Mesoporous Materials 213 (2015) 22–29

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Fast synthesis of mesoporous silica materials via simple organic compounds templated sol–gel route in the absence of hydrogen bond

Linzhou Zhuang [a], Beibei Ma [a], Siyu Chen [a], Xunan Hou [a], Shuixia Chen [a, b, *]

[a] *PCFM Lab, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China*
[b] *Materials Science Institute, Sun Yat-Sen University, Guangzhou 510275, PR China*

ARTICLE INFO

Article history:
Received 15 August 2014
Received in revised form
16 March 2015
Accepted 6 April 2015
Available online 14 April 2015

Keywords:
Mesoporous silica
Organic compound template
Fast sol–gel
Preparation

ABSTRACT

As simple organic compounds that contain no hydroxyl, amino or carboxyl groups cannot assemble with the siliceous species through hydrogen bond or electrostatic force, they have not been applied as templates to prepare mesoporous silica materials before. However, in this work it was found that only if the organic compound can form homogeneous solution with ethanol and water can it successfully lead the formation of mesopores under the catalysis of 5% ammonium hydroxide (NH_4OH) solution. The effects of template type, template amount and NH_4OH solution concentration on the pore structure of the prepared porous silica were comprehensively studied. The pore size had no direct correlation with the molecular size of the template, but it could be easily adjusted in the range of 2.4–6.6 nm through changing the template amount. When using 5% NH_4OH solution as the catalyst, the gelation time of siliceous species was ultrashort and therefore the template aggregates could be trapped in the three-dimensional SiO_2 matrixes to function as the pore-forming agents. However, when the concentration of NH_4OH solution was excessive high, like 15%, the gelation reaction was over intense and mesopores cannot be formed in the prepared silica. The mesoporous silica materials prepared in this new sol–gel route can be used as good supports of CO_2 adsorbents. Through loading PEI into the mesopores of the silica materials, the solid amine adsorbents could be easily prepared, and they can keep remarkable CO_2 adsorption ability even after 10 adsorption–desorption cycles.

1. Introduction

Intense efforts have been focused on ordered mesoporous silica materials since the discovery of the M41s family of mesoporous molecular sieves. These mesoporous silica materials showed different structural and textural characteristics and could be applied in various fields, including catalysis, drug delivery, molecular host, separation and adsorption [1–3]. M41s possess well-ordered pore structures, tunable pore sizes that range from 2.0 to 10.0 nm, large surface areas, and high pore volumes [4]. In the preparation process of M41s, the surfactant molecules like cetyltrimethylammonium cation were employed as structure-directing agents, and the mesopores could be formed through the self-assembly between siliceous species and surfactant and the gelation of the siliceous species [4,5]. This self-assembly process was based on the electrostatic interaction. Afterwards, different types of surfactants like anionic-, neutral-, and acid treated surfactants were applied as templates to elaborately design the pore structures of mesoporous silica materials, so that new families of mesoporous silica materials (such as SBA [6,7], MSU [8,9], and FSM [10]) could be obtained. Among these routes, the one that uses nonionic surfactants as templates is especially important, because this electrically neutral S^0I^0 self-assembly pathway applies the weak hydrogen bond between templates and siliceous species to lead the formation of mesopores, instead of electrostatic force [11]. Indeed, it is strongly complementary to the electrostatic interaction pathway in the preparation of mesoporous silica. However, even all these methods can successfully prepare well-ordered mesospores, their weaknesses like long preparation period, expensive template cost and narrow range of template choice severely restrict their industrial application.

Wei et al. developed a new low-cost nonsurfactant route to prepare the mesoporous silica materials [12]. In this route, the nonsurfactant organic compounds like citric acid, malic acid, tartaric acid [13–15], menthol [16], D-glucose, D-maltose [12,17,18],

---

* Corresponding author. PCFM Lab, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, PR China.
E-mail address: cescsx@mail.sysu.edu.cn (S. Chen).

http://dx.doi.org/10.1016/j.micromeso.2015.04.007
1387-1811/

urea [19,20], fatty alcohols [21] and cyclodextrin [22] could be employed as templates, and via HCl-catalyzed hydrolysis, gelation of siliceous species and removal of the templates, the silica materials with interconnected mesopores can be prepared [20]. Their pore volumes and pore sizes can be easily adjusted by varying the amount of added templates [23]. The authors claim that it is the hydrogen bonding between the nonsurfactant template aggregates and the siliceous species that directs the formation of mesopores [12,13]. However, because of the necessity of hydrogen bonding, the applicable templates here are limited to the organic compounds that contain hydroxyl, amino or carboxyl groups. Besides, NaOH was commonly used in this route to neutralize the silicate-template solution, and in most cases it led to a long gelation period, which could be as long as tens of days [16–18]. The narrow range of template choice and long preparation period is the key constraints of this route in the industrial application.

As ammonium hydroxide (NH_4OH) has been proved that it can accelerate the gelation speed of siliceous species in the preparation of microporous silica xerogel monoliths [24], in this work we tried to use NH_4OH solution as gelation catalyst to prepare mesporous silica materials. Moreover, to extend the range of template choice, we even made an effort to use simple organic compounds containing no hydroxyl, amino or carboxyl groups as the templates. These organic compounds can be cyclohexane (CH), methyl cyclohexane (MCH), and limonene (LM) and so on. N_2 adsorption–desorption and transmission electron microscope (TEM) results indicated that the pore structures of these mesoporous materials were similar to those of materials prepared by Wei et al. However, our fast sol–gel route should differ from the nonsurfactant route as the applied simple organic compounds here cannot form hydrogen bond with the siliceous species. For better using this fast sol–gel route to prepare mesoporous silica materials, its synthesis mechanism and influence factors have been comprehensively investigated. This fast sol–gel route is believed to be a facile, economical, and environmental-friendly route to produce mesoporous materials.

2. Experimental section

2.1. Reagents

Tetraethyl orthosilicate (TEOS, >99%), cyclohexane (CH, 99.5%), methyl cyclohexane (MCH, 99%), (R)-(+)-limonene (LM, 95%), DL-menthol (MINT, 99%), and polyethylenimine (PEI, $Mw = 1800$) were purchased from Aladdin Chemistry Co., Ltd., China. Ethanol (AR), hydrochloric acid (HCl, 37%), ammonium hydroxide (NH_4OH, 29%), tetrahydrofuran (THF, AR), hexane (AR), n-butyl bromide (BBM, 98%), 1, 2-dichloroethane (DCE, 99%) and benzaldehyde (BA, AR) were from Guangzhou Chemical Reagent Factory, China. All reagents were used without further purification. 0.1 M HCl solution and 1%, 5% NH_4OH solution were prepared from HCl (37%) and NH_4OH (29%).

2.2. Synthesis of mesoporous silica materials

As a typical procedure, first, 7.7 g 0.1 M HCl solution and 13.8 g ethanol were mixed in a three-neck round bottom flask at room temperature. Then, 20.8 g TEOS was slowly added into the flask with moderate stirring. After stirring for 30 min, the mixture became homogeneous, and it was stirred at 70 °C for another 5 h. Upon cooling to room temperature, 12.2 g of this prehydrolyzed mixture was slowly added into a mixed solution of ethanol (5.0 mL)-simple organic compounds (the amount of CH, MCH, LM or MINT can be 0.5–4.0 g) under agitation. Next, about 1.0 mL 5% NH_4OH solution was added to adjust the *pH* of the silicate-template mixture to 6, and a *pH* meter was used to monitor its *pH*. Gel occurred as soon as the NH_4OH solution was dropped into the transparent mixture. The adding speed of NH_4OH solution could be as high as 0.1 mL s^{-1} at first, but when the *pH* reached up to 5, the adding speed should be much lower. During the NH_4OH solution adding and stirring process (300 rpm), the mixture got increasingly stickier and finally solidified into white powder. The powder was then placed in a fume hood overnight for drying. Finally, the template was removed by heating the powder at 150 °C for 3 h with an electric furnace under air flow. For comparison, a series of control samples were also prepared according to the above procedure, except that 1% NH_4OH was used to adjust the *pH* of the silicate-template solution to 6.

2.3. Characterization

N_2 adsorption–desorption isotherms at −196 °C was measured with an automatic gas adsorption instrument (ASAP2020, Micromeritics Corp., USA) in a relative pressure range from 10^{-6} to 1. V_{total} was calculated based on the N_2 amount adsorbed at $P/P_0 = 0.95$. S_{BET} and pore size distribution were calculated through Brunauer–Emmett–Teller (BET) method and density functional theory (DFT) method, respectively. The average pore size was calculated by Barrett–Joyner–Halenda (BJH) analysis from the desorption branch of the isotherms. Scanning electron microscope (SEM, S4800, Hitachi, Japan) was used to observe the morphology and microstructure of the samples, while transmission electron microscope (TEM, JEM-2010HR, JEOL, Japan) was applied to observe their pore structure. Elemental analysis (EA, Analysen systeme GmbH Elementar Vario EL, Germany) was applied to determine the nitrogen, carbon and hydrogen contents of the solid amine adsorbents. The crystal structure of the silica materials was determined by small-angle powder X-ray diffraction (XRD, D8 ADVANCE, BRUKER Textile Technologies GmbH & Co. KG, Germany) at a scan rate of 1.0° min^{-1} in the range of 0.8–8.0°.

2.4. Preparation of PEI-impregnated mesoporous silica materials

2.0 g PEI was dissolved in 5.0 mL ethanol after stirring for 15 min, and then 2.5 g mesoporous silica material (prepared using CH, MCH or LM as template) was added into the solution. The mixture was continuously stirred at 80 °C for 2 h and then centrifuged at 11000 rpm for 5 min. After being dried at 70 °C for 12 h, the adsorbent can be obtained, and denoted as CH-PEI, MCH-PEI or LM-PEI.

2.5. CO_2 adsorption procedures

2.0 g of the solid amine adsorbent was placed into an adsorption column ($\Phi = 1.3$ cm), and dry N_2 gas was introduced into the column for 20 min at a rate of 30 mL min^{-1} to remove the air and residue water. Then to measure the CO_2 adsorption amount of the adsorbent, dry CO_2/N_2 mixed gas was introduced into the column at a rate of 30 mL min^{-1}, and the CO_2 inlet/outlet concentrations were determined by an Agilent 6820 gas chromatograph equipped with a thermal conductivity detector. After CO_2 adsorption, the adsorbents were regenerated by N_2 flow at 95 °C for 20 min.

3. Results and discussion

3.1. Preparation of mesoporous silica materials using NH_4OH solution of different concentrations as catalysts

Under the catalysis of NH_4OH solution of different concentrations, two series of silica materials were prepared using 2.0 g CH,