

Rapid synthesis of ordered mesoporous silica with the aid of heteropoly acids

Yongming Luo^{a,b}, Zhaoyin Hou^a, Rongtao Li^c, Xiaoming Zheng^{a,*}

^a Institute of Catalysis, Department of Chemistry, Zhejiang University (Xixi campus), Hangzhou 310028, PR China

^b Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650093, PR China

^c Faculty of Chemical and Bioengineering, Kunming University of Science and Technology, Kunming 650093, PR China

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Abstract

Well-ordered mesoporous SBA-15 sieves have been rapidly synthesized with the aid of heteropoly acids (abbreviated to HPAs). The promotable role of HPAs on SBA-15 formation has been confirmed by controlling the same synthesis conditions and the hydrothermal stability of corresponding reaction product was found to improve remarkably. The interaction between the EO moieties of template and tungstic or molybdic species (such as octahedral molybdic species), originated from the HPAs dissociation in the syntheses media, was expected to play a crucial role in promoting rapid nucleation and enhancing the tendency for mesoscopic ordering to occur. The synthesis route might be applicable to other nonionic surfactants, liquid acids and silica sources, which should provide promising method for synthesis of a large number of ordered mesoporous sieves with variety structure.

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1. Introduction

Mesoporous molecular sieves SBA-15 with two-dimensional hexagonally ordered arrays of channels, discovered by Stucky and coworkers [1,2], has attracted much attention for potential applications as versatile catalysts and catalyst supports [3–9], template [10–15] and separation materials [16] because of its appealing textural properties and high surface area, and appreciable thermal and hydrothermal stability. Generally, it is synthesized under strongly acidic conditions ($\text{pH} < 1$) [1], using liquid acids as pH adjuster, nonionic amphiphilic poly(alkyleneoxide) triblock copolymer such as poly(ethyleneoxide) – poly(propyleneoxide) – poly(ethyleneoxide) as a structure-directing agent and tetraethoxysilane (TEOS) as a silica source

[1–19]. In order to obtain highly ordered SBA-15, large amounts of toxic liquid acids such as HCl, HNO₃ and H₂SO₄ were used, which would cause serious corrosive and other environmental problem. On the other hand, it is well-known that most zeolites are synthesized by hydrothermal methods, which generally suffer from the drawback of long crystallization times [20,21]. Therefore, in past several years, much effort has been devoted to develop the new route for synthesis of SBA-15, which involved reducing liquid acids concentration or shortening thermal treatment (or reaction) time [17,22–24]. For example, Komarneni et al. [17] prepared well-ordered mesoporous SBA-15 within 2 h by using microwave hydrothermal instead of conventional hydrothermal method, while the high concentration of HCl was required under such short thermal treatment time. Ryoo et al. [22] reported that the HCl concentration of SBA-15 synthesis media could be decreased significantly by adjusting the molar ratio of SiO₂ to P123. However, the corresponding thermal treatment time is as long as 24 h or even more under low

* Corresponding author. Tel.: +86 571 88273272; fax: +86 571 88273283.

E-mail addresses: luoyongming@tsinghua.org.cn (Y. Luo), xmzheng@dial.zju.edu.cn (X. Zheng).

concentration of HCl media, particularly when TEOS was used as silica source. Stucky and coworker reported the thermal treatment time required for synthesis of ordered SBA-15 would obviously increase, if the molar of HCl to Si is lower than 0.59 and without any promoter's addition [23]. Therefore, substantially reducing HCl concentration, shortening thermal treatment time, and whilst maintaining the well-ordered structure is a challengeable task. Previous literatures [23,24] reported that addition small amounts of fluoride or fluorocarbon-surfactant would result in both substantially reducing the concentration of HCl and without compromising thermal treatment time and well-ordered mesostructure.

In this communication, we expound a new route for rapid synthesis of SBA-15 in low concentration of HCl media. Compared with the conventional synthesis method, [1,2] the HCl concentration of reaction mixture solution is only 3.6% and the total H^+ originated from both HCl and HPAs dissociation is about 4%. Under such low concentration HCl media, small amounts of HPAs such as phosphomolybdic acid (HPMo), phosphotungstic acid (HPW), or silicotungstic acid (HSiW) was added into the synthesis media, which results in significantly enhancing the crystallization process for SBA-15 formation and the corresponding thermal treatment time was obviously shorten within 3 h. The interaction between the EO moieties of template and tungstic or molybdic species might enhance long-range Coulombic interactions to the coassembly process and/or result in the assembly of mesoporous SBA-15 through a $(S^0Mo^-)I^+$ synthesis route (where S^0 is the template P123, Mo^- is the octahedral molybdic species, and I^+ is silicate cation, respectively). In addition, we found that HPAs can be easily recycled to synthesize SBA-15, and corresponding reaction product shows higher hydrothermal stability.

2. Experimental section

Materials: Nonionic triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) was purchased from Aldrich. Phosphomolybdic acid, phosphotungstic acid and silicotungstic acid with principal composition of $H_3PO_4 \cdot 12MoO_3 \cdot 24H_2O$, $H_3PO_4 \cdot 12WO_3 \cdot 24H_2O$ and $H_4SiO_4 \cdot 12WO_3 \cdot 24H_2O$ (abbreviated to HPMo, HPW and HSiW, respectively), were obtained from J& K Chemical. Tetraethoxysilane (TEOS) and concentration hydrochloric acid (c-HCl, 36 wt %) were provided by Shanghai chemical reagent Company of China.

Synthesis Procedures: The following general procedure was used to prepare highly ordered mesoporous SBA-15 samples described in this communication. P123 was used as a structure-directing agent and TEOS as a silica source, and heteropoly acids as novel promoters. In a typical synthesis batch, 4.0 g of P123 was dissolved in 105 g of distilled water with vigorously stirring at room temperature for 3 h, then the calculated amounts of HPMo (0.64 g) was added into the solution to keep the molar ratio of Si/Mo = 12.4. After P123 and HPMo were dissolved com-

pletely, 8.55 g of TEOS and 0.75 ml c-HCl (36 wt%) were added dropwise to the above mixture solution. The chemical composition of the reaction mixture was 4 g P123 copolymer: 0.041 mol TEOS: 0.00028 mol HPMo: 0.0087 mol HCl: 5.83 mol H_2O . Subsequently, the mixture was stirred at 38 °C for 20 h and thermally treated at 96 °C for 6 h, respectively. The reaction products were filtered, washed and dried at 45 °C for 48 h. Finally, the samples were calcined at 550 °C in air for 8 h. To investigate the influence of thermal treatment time on SBA-15 formation under the synthesis media, samples thermally treated at 96 °C for 0, 3, 12, and 24 h were characterized using XRD and N_2 adsorption–desorption.

Recycle use of HPAs procedures: All filtered and washed solution of the first synthesis process was collected, and the solution was concentrated to 105 ml under vacuum at 55 °C. In addition, 1 g P123 was added to the above concentrated solution with vigorously stirring at room temperature. After P123 was dissolved completely, 8.55 g of TEOS and 0.75 ml c-HCl were added dropwise to the mixture solution. The following steps of synthesis procedure were similar to the above report.

The hydrothermal stability of the synthesized samples was investigated by mixing ca. 0.5 g of the calcined sample with 100 g deionised water and heating in a closed bottle at 100 °C under static conditions. After hydrothermal treatment, the samples were filtered, washed with deionised water and dried at 110 °C overnight.

Characterization: XRD patterns were recorded on a Rigaku D/max 2550PC diffractometer (Rigaku, Japan) using $Cu K\alpha$ radiation, operating at 40 kV and 300 mA. N_2 adsorption–desorption isotherms were obtained at –196 °C on an Omnisorp–100CX apparatus (USA). Prior to analysis, all samples were degassed in high vacuum for 2 h at 250 °C. BET surface areas were calculated from the linear part of the BET plot. Pore size distribution (PSD) were calculated by the Barret–Joyner–Halenda model, and the total pore volumes were estimated from the N_2 uptake at $P/P_0 = 0.994$. Transmission electron microscopic images were obtained on a JEM-2010HR microscope (JEOL, Japan). UV–VIS spectra were measured using a spectrometer (Shimadzu UV-2401, Japan), and distilled water was used as reference. The parameters (0.5 nm spectral band width, 0.1 s signal averaging time, and 0.5 nm data interval) were used to record the data. FT–IR spectra of the samples in the form of KBr pellets were recorded by using a Nicolet 560 IR spectrometer.

3. Result and discussions

Representative small-angle powder XRD patterns for as-synthesized and calcined mesoporous SBA-15 (sample 1) are presented in Fig. 1. A well resolved pattern with a prominent peak (100) and two weak peaks (110) and (200) are detected in the 2θ region of 0.5° to 2° for both of them, which matches well with the patterns reported for ordered mesoporous SBA-15 prepared with conven-

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