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Direct synthesis of homogeneous Zr-doped SBA-15 mesoporous silica via masking zirconium sulfate

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ABSTRACT

Incorporating zirconium is one of the most widely applied method to functionalize the inert mesoporous silica. However, the conventional zirconium precursors are are costly and poisonous, and zirconium distributes unevenly in Zr-SBA-15. Herein, a homogeneous Zr-doped SBA-15 material (Zr-SBA-15) has been synthesized by employing the low-cost and nontoxic zirconium sulfate as metal precursor. Furthermore, different coordinating ligands including cholamine, diethanol amine, triethanolamine, pentaerythritol, lactic acid and oxalic acid were used as masking agent to mask zirconium sulfate. The masking effects of coordinating ligands on zirconium sulfate were investigated in the synthesis of Zr-SBA-15. It was found that the introduction of coordinating ligands has a remarkable masking effects on preventing the rapid hydrolysis of zirconium sulfate. The obtained Zr-SBA-15 shows an uniform zirconium dispersion (EDS mapping results) with outstanding texture property (S_{BET} of 806 m^2 g^{-1}, D_{BJH} of 6.6 nm and V_{BJH} of 0.99 cm^3 g^{-1}). Computational simulations was performed for qualitative comparison of masking ability, and the validity of experimental results was theoretically confirmed as well.

1. Introduction

Mesoporous material is a kind of porous material. According to the definition of International Union of Pure and Applied Chemistry (IUPAC), material with less than 2 nm pore diameter is defined as microporous material; the one with the diameter in the range of 2–50 nm is regarded as mesoporous material; if its diameter is greater than 50 nm, it is known as macroporous material [1].

Mobil synthesized mesoporous material (M41S) for the first time in 1992. However, M41S type of mesoporous material shows poor chemical and hydrothermal stability due to smaller pore size and thinner pore wall [2]. In order to improve the defect of M41S, Zhao and his coauthor [3] invented a lager pore size mesoporous material SBA-15, which possess a well-aligned pore channel structure, high specific surface area, excellent thermal stability. But because pure silica mesoporous material lacks acidity and possesses poor hydrothermal stability, it was limited in the application of adsorption, separation and catalysis field [4]. Inorganic metal oxide owns outstanding mechanical stability and can avoid swelling to a great extent in solvent conditions, thus metal inorganic supports facilitate the superior thermal stability of silicon mesoporous material [5]. It is necessary to introduce metal elements into silica based mesoporous material for the creation of the active sites [6]. Incorporation of zirconium into silica mesoporous material has caused wide attention owing to its unique catalyzing [7], adsorbing [8,9] and separating property [10].

"Direct synthesis" and "Post-synthesis grafting" are two typical strategies for the incorporation of metal heteroatoms into silica mesoporous material. "Post-synthesis grafting" route are relatively complicated and usually results in channel blockage [11]. Comparatively, "Direct synthesis" is relatively convenient in synthetic process and Zr-SBA-15 exhibits homogeneous Zr dispersity [12].

However, the existing problems as to metal element doped mesoporous material is that of the metal source. Metal salt is prone to hydrolyze, while the silicon source hydrolysis speed is relatively slow leading to incongruous hydrolysis rate between the metal and silicon source. As a result, the metallic element doped unevenly

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[13]. Thus, it is crucial to control hydrolysis and condensation of the silicon or metal source in order to obtain uniform metal doping silica mesoporous material [14]. In this context, Zhang et al. [15] proposed a direct synthesis method to prepare Ti-SBA-15, in which the hydrolysis of the TMOS was accelerated by NH_4F. The results showed that fluoride is capable of promoting the hydrolysis of silicon source. Francois Berube [16] synthesized Ti-SBA-15 by post-grafting approach, in which the titanium precursor was modified with acetylacetone. The results indicate that acetylacetone can efficiently reduce the hydrolysis rate of tetrapropylorthotitanate, finally preventing the formation of the anatase in Ti-SBA-15. In addition, Zheng and his coauthor [17] prepared Ti-SBA-15 in the existence of zinc acetate. It was found that zinc acetate lessened the hydrolysis reaction of $TiCl_3$ in acidic condition, which was attributed to the stabilization of COO^- for $TiCl_3$. Luan [18] and his coauthor synthesized and incorporated variable amount of titanium into silica SBA-15 via incipient-wetness impregnation with titanium isopropoxide in ethanol followed by calcination. It was found that, to a certain extent, -OH groups of ethanol exhibit a retarding action for the hydrolysis of titanium precursor, at low titanium loading (Ti 1 atom % relative to silicon), titanium ions are monatomically dispersed.

In previous work, several strategies have been used for the homogeneous Zr-doped SBA-15 mesoporous silica. Masaru and his coauthor [19] reported the synthesis of Zr-SBA-15 via post-grafting method with $ZrO(NO_3)_2$ as zirconium precursor employing vapor-induced internal hydrolysis (VIH) method to control the hydrolysis rate of zirconium precursor. Concretely, Zr-SBA-15-i with different zirconium content was prepared by wet-impregnation, then Zr-SBA-15-i was kept inside a Teflon-Lined autoclave containing NH_3/H_2O solution in 60 °C for 0.5 h. Finally, Zr-SBA-15-i samples with uniform Zr distribution were obtained after drying and calcinating. Li [20] carried out a direct synthesis of Zr-SBA-15 with alcohol and $Zr(NO_3)_2$ mixture solution as zirconium precursor, using the -OH groups of ethanol as metal coordinating ligands. In this case, the zirconium dispersed uniformly and connected into the framework of SBA-15 successfully with Zr/Si molar ratio lower than 0.38. However, when Zr/Si molar ratio becomes larger, the tetragonal ZrO_2 phase was formed.

In the present work, the most commonly used zirconium precursors are zirconium isopropoxide [21], zirconium oxychloride [22] and zirconium nitrate [23]. However, zirconium isopropoxide and zirconium oxychloride are all costly and poisonous. Moreover, zirconium nitrate is rather expensive and easier to hydrolyze in aqueous. Therefore, zirconium sulfate is a potential zirconium precursor. Owing to its low-cost and nontoxic it is deemed to be extensively applied in industrial field. We expect that the development of a new zirconium precursor material with low-cost and eco-friendly property, and masking metal source is a promising strategy for preparation of homogeneous zirconium doped silicon mesoporous material.

In this work, we present a new method by employing low-cost and non-poisonous zirconium sulfate instead of the conventional zirconium precursor. Utilizing several kinds of metal coordinating ligands to mask zirconium sulfate, the hydrolysis rate of the zirconium sulfate was reduced during Zr-SBA-15 synthetic process, consequently avoiding the formation of zirconium dioxide particle in Zr-SBA-15 samples (Scheme 1). The X-ray powder diffraction, nitrogen adsorption-desorption isotherms, transmission electron microscopy and energy disperse spectroscopy mapping, X-ray photoelectron spectra, inductively coupled plasma atom emission spectroscopy and fourier infrared spectrometer were used to investigate the physicochemical properties of the synthesized Zr-SBA-15 samples. Molecular simulation, as a theoretical analyze tool, was applied for quantitative analysis of masking ability.

2. Experimental

2.1. Materials

Triblock copolymer P123 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)) with average molecular weight of 5800, which was used as structure-directing agent, was purchased from Aldrich. Tetraethoxysilane (TEOS) ($C_8H_{20}O_4Si \geq 98.0\%$) and zirconium sulfate ($Zr(SO_4)_2 \cdot 4H_2O \geq 98.0\%$), which were used as silica source and zirconium precursor, were obtained from Kermel and Tianjin Guanfu Fine Chemical Research Institute Co., Ltd, respectively. Cholamine, diethanol amine, triethanolamine, pentaerythritol, lactic acid and oxalic acid were used as coordinating ligands to retard the hydrolysis rate of zirconium sulfate. Cholamine ($NH_2(CH_2CH_2OH)$ 98.0%–100.5%), diethanol amine ($NH(CH_2CH_2OH)_2 \geq 99.0\%$) and oxalic acid ($C_2H_2O_4 \cdot 2H_2O \geq 99.5\%$) were purchased from Tianjin Hengxing Chemical Reagent Co., Ltd. Triethanolamine ($N(CH_2CH_2OH)_3 \geq 85.0\%$), lactic acid ($CH_3CH(OH)COOH$ 85.0–90.0%) and sodium chloride ($NaCl \geq 99.5\%$) were provided by Tianjin Hongyan Chemical Reagent Co., China. Also, pentaerythritol ($C(CH_2OH)_4 \geq 98.0\%$) was supplied by Tianjin Fuchen Chemical Reagent Co., China."

2.2. Synthesis of Zr-SBA-15

Zr-SBA-15 materials were synthesized using triblock copolymer P123 as structure-directing agent, TEOS as silicon source and zirconium sulfate as zirconium source. In addition, cholamine, diethanol amine, triethanolamine, pentaerythritol, lactic acid and oxalic acid were considered as metal coordinating ligands to mask zirconium sulfate, finally reducing the hydrolysis of the zirconium source. The synthesis was performed with the initial ratio of the composition according to 1.0 TEOS/0.017 P123/1.0 NaCl/0.1 $Zr(SO_4)_2$/0.2 ligands/220 H_2O.

In a typical synthesis, 2.0 g P123 and 1.18 g NaCl were added into 60 mL deionized water. The mixture solution was stirred under 40 °C water bath until P123 dissolved entirely. After that, 4.5 mL TEOS was added and the resulting solution was stirred for 4 h at 40 °C for the prehydrolysis of TEOS.

Thereafter, the zirconium precursor was prepared by coordinating ligands (cholamine, diethanol amine, triethanolamine, pentaerythritol, lactic acid and oxalic acid) and zirconium sulfate at the given molar ratio. Coordinating ligands were dissolved in 20 mL deionized water, and 0.72 g $Zr(SO_4)_2$ was then added. The mixture solution was stirred with a magnetic stirrer until the solution turns transparency. The transparent solution thus obtained was added into the prehydrolysis solution. The resulting mixture was stirred for 24 h at 40 °C and subsequently was hydrothermally treated for an additional 24 h at 90 °C. After that, the reactant was cooled to room temperature and the precipitated products were then filtered, washed with deionized water, dried at 50 °C. Finally, the solid products were calcined at 250 °C for 3 h and 500 °C for another 3 h with heating rate of 5 °C/min, and further heated at 600 °C for 1 h with a 1 °C/min heating rate to obtain Zr-SBA-15.

The Zr-SBA-15 samples synthesized with cholamine, diethanol amine, triethanolamine, pentaerythritol, lactic acid and oxalic acid were denoted as a, b, c, d,e and f, respectively.

2.3. Characterization

XRD patterns were recorded using D8 Advance (Bruker) powder diffractometer with Cu-Kα (0.154 nm) radiation operated at 45 kV and 45 mA, over a 2θ range from 0.5° to 5, with a step size of 0.01° and a counting time per step of 2 s. The wide angle XRD patterns