Journal of Physics and Chemistry of Solids 86 (2015) 1–4

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

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

One-step synthesis of hydrophobic mesoporous silica and its application in nonylphenol adsorption

Yanling Zhao [a], Jinliang Song [b,*], Dong Wu [c], Tao Tang [d], Yuhan Sun [c,d]

[a] School of Materials Science and Engineering, University of Jinan, Jinan 250022, PR China
[b] Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, PR China
[c] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China
[d] Low Carbon Energy Conversion Center, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201203, PR China

ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form
6 May 2015
Accepted 16 June 2015
Available online 18 June 2015

Keywords:
Nanostructures
Chemical synthesis
Surface properties
Nuclear magnetic resonance

ABSTRACT

Highly CH_3-functionalized mesoporous silica with nearly spherical morphology was synthesized under acidic conditions by co-condensation of two different silica precursors polymethylhydrosiloxane (PMHS) and tetraethoxysilane (TEOS) in the presence of triblock copolymer P123 as template. XRD, N_2 adsorption–desorption, HRTEM, SEM and ^{29}Si MAS NMR were used to identify its highly-ordered mesopore array structure, nearly spherical particle morphology and CH_3 functionalization of the as-synthesized material. The resulting hydrophobic mesoporous silica possessed regular mesochannel arrays, indicating that the introduction of PMHS had little impact on the formation of an ordered mesostructure. Also, PMHS played an important role in morphology control and organic functionalization, ensuring nearly spherical particle morphology and high CH_3 functionalization degree of the obtained mesoporous silica material. As compared with pristine mesoporous silica SBA-15, the hydrophobic mesoporous silica showed the higher adsorption performance when they were used as adsorbents to remove organic pollutant nonylphenol at a very low concentration from aqueous solution.

1. Introduction

A wide variety of toxic inorganic and organic chemicals are discharged to the environment as industrial wastes, causing serious water, air and soil pollution. With regard to organic pollutants in aquatic ecosystems, phenols are considered priority pollutants since they are harmful to living organisms even at ppb levels [1,2]. Alkylphenolic chemicals such as nonylphenol, which are biodegradation products of alkylphenol polyethoxylate resin, have been found to be the major estrogenic contaminants to induce feminizing effects in fish [3].

Adsorption-based processes may lead to one of the most efficient routes for removal of toxic substances. The fundamental and great challenge is developing highly efficient adsorbents. In this regard, ordered mesoporous materials may be the answer in the future. They possess intrinsic high specific surface areas, regular and tunable pore sizes, large pore volumes, as well as stable and interconnected frameworks with active pore surfaces for modification or functionalization [4–7]. Recent research has revealed that the sorption efficiency of porous inorganic materials, such as clays and mesoporous silica, could be improved by grafting organic functional groups on these inorganic substrates via stable covalent bonds. Owing to the fact that the organic functional groups have a strong affinity for a certain class of toxic contaminants, the grafted adsorbents can capture the contaminants selectively even if their concentrations are extremely low [8].

Nevskaia et al. [9] studied the adsorption of nonylphenol on commercial microporous activated carbons and concluded that the introduction of surface OH groups enhanced nonylphenol adsorption because the adsorption process occurred via hydrogen bonding between OH groups on the nonylphenol micelles and on the carbon surface. Inumaru et al. [3] reported that octylsilane-grafted hexagonal mesoporous silica could remove low-concentrated nonylphenol in water with high efficiency comparable to that of activated carbon, while the adsorbent showed no detectable uptake of phenol. They subsequently investigated the molecular selective adsorption of alkylanilines and alkylphenols on alkyl-grafted MCM-41 and gave evidence of novel organic–inorganic cooperative molecular recognition in the nanostructure [10]. Inumaru et al. [11] also compared the molecular selective adsorption of alkylphenols and alkylanilines by alkyl-grafted

---

[*] Corresponding author.
E-mail address: jlsong1982@yeah.net (J. Song).

http://dx.doi.org/10.1016/j.jpcs.2015.06.011
0022-3697/© 2015 Published by Elsevier Ltd.

mesoporous alumina to that by alkyl-grafted mesoporous silica and found that the differences in the inorganic pore wall (alumina and silica) were very influential on the adsorption properties. Yang et al. [8] developed a new efficient sorbent by grafting the external surface of γ-alumina (γ-Al_2O_3) nanofibers with octyl groups for removal of highly diluted 4-nonylphenol from water and attributed the superior sorption efficiency to the improved accessibility of the sorption sites and the numerous large interconnected voids formed in the aggregation of the randomly oriented γ-Al_2O_3 nanofibers.

Some adsorbents have been attempted to remove trace nonylphenol from water as mentioned above. Unfortunately, there is still little research reported on nonylphenol adsorption by mesoporous adsorbents, and the few mesoporous adsorbents were modified by post-grafting organic groups, in which method increases the number of synthetic steps and leads to organic functions unevenly distributed throughout the pore surface [12,13]. Herein, a promising hydrophobic mesoporous silica was fabricated under acidic conditions by a one-step synthetic route using polymethylhydrosiloxane and tetraethoxysilane with triblock copolymer P123 as template. Thus-obtained material possessed nearly spherical particle morphology, well-ordered mesochannel arrays and texture with highly CH_3-functionalized surface. To compare its adsorption performance with that of pristine mesoporous silica SBA-15, they were used to remove highly diluted nonylphenol from aqueous solution.

2. Experimental

2.1. Synthesis

The starting materials employed in this work included tetraethoxysilane (TEOS, 99%, TSR), polymethylhydrosiloxane (PMHS, 99%, $\overline{M}_w =$ 2700–5400, Acros.), Pluronic P123 triblock copolymer (EO_{20}–PO_{70}–EO_{20}, $\overline{M} =$ 5800, Aldrich). All the chemical agents were used as received without further purification.

In a typical synthesis under ambient conditions, 2 g of P123 was completely dissolved in 60 mL of a 2 mol/L HCl solution at 40 °C. 3.1 g of TEOS and 3.1 g of PMHS were added together to the above solution under vigorous stirring. After 24 h of stirring at 40 °C, the reaction mixture was allowed to age at 100 °C for another 24 h under quiescent conditions. Then the white precipitate was recovered by filtration, washed with deionized water, and dried at 80 °C. Finally, the template was removed by Soxhlet extraction with ethanol for 48 h.

2.2. Characterization

^{29}Si MAS NMR experiments were performed on a Varian Infinityplus-300 spectrometer using 7.5 mm probe under magic-angle spinning. Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS diffractometer using Cu Kα radiation. N_2 adsorption–desorption isotherms were measured at 77 K on a Micromeritics Tristar 3000 Sorptometer. The samples were degassed at 353 K and under a vacuum of 10^{-6} Torr for at least 12 h prior to the measurement. The specific surface areas were calculated using the multiple-point Brunauer–Emmett–Teller (BET) method. The pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model. The pore channels were observed by high-resolution transmission electron microscopy (HRTEM) images on JEOL JEM-2010. Field emission scanning electron microscopy (FESEM) images were obtained on LEO 1530VP.

2.3. Adsorption of nonylphenol in aqueous solution

In typical adsorption experiments, 15 mg of the adsorbent was added into 55 g of an aqueous solution of nonylphenol with an initial concentration of 4.9 ppm. After adsorption with stirring for a given time, the supernatant solution was separated by millipore filter (0.22 μm) and the residual nonylphenol was analyzed using a Shimadzu UV-3150PC spectrophotometer at 278 nm.

3. Results and discussion

3.1. ^{29}Si MAS NMR

The ^{29}Si MAS NMR spectrum of the hydrophobic mesoporous silica displays five main resonance signals at −36.6, −57.0, −66.9, −102.7 and −111.1 ppm (see Fig. 1), corresponding to D^2 [CH_3(H)–Si*$(OSi)_2$], T^2 [CH_3–Si*$(OSi)_2$(OH)], T^3 [CH_3–Si*$(OSi)_3$], Q^3 [Si*$(OSi)_3$(OH)] and Q^4 [Si*$(OSi)_4$], respectively. Among all the resonance signals, the existence of the D^2 peak was due to the incomplete hydrolysis of Si–H groups in PMHS. It is well-known that with NaOH as the catalyst, the active Si–H groups in PMHS could be rapidly hydrolyzed to form Si–OH groups which would come into the subsequent co-condensation with the hydrolyzate of TEOS. Because of the weaker catalysis of HCl and the strong interfacial tension between oil phase and water phase induced by the introduction of PMHS into acidic aqueous solution, the incomplete hydrolysis of Si–H groups in PMHS took place and led to the D^2 peak.

The $(D+T)/(D+T+Q)$ ratio calculated from the normalized peak areas [14] was 0.628, namely, the CH_3 functionalization degree of the hydrophobic mesoporous silica was as high as 62.8%, which exceeded the conventional methyl group loading in mesoporous silica SBA-15 framework by one-step synthesis. Thus, the introduction of PMHS into the synthetic system realized high CH_3 functionalization degree of the obtained material.

3.2. Structural characteristics

The small-angle XRD pattern of the hydrophobic mesoporous silica shows a well-resolved peak and two small peaks indexable as (100), (110), and (200) reflections associated with *p6mm* hexagonal symmetry (see Fig. 2), indicating a well-ordered hexagonal mesopore array structure similar to that of SBA-15. As shown in Fig. 3, the N_2 adsorption–desorption isotherm of the hydrophobic mesoporous silica displays a type IV isotherm, being characteristic of a mesoporous solid. The hysteresis loop is slightly different from H1 type, as the desorption isotherm does not coincide with the adsorption isotherm in the relative pressure (P/P_0) range of 0.8–

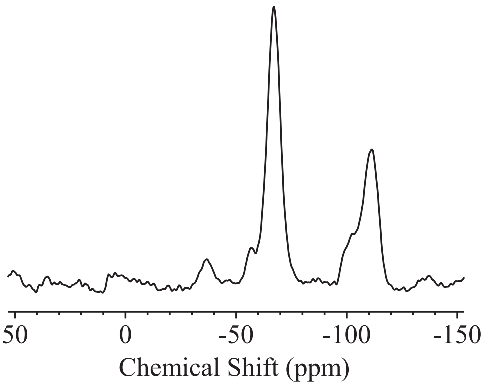

Fig. 1. ^{29}Si MAS NMR spectrum of the hydrophobic mesoporous silica.