Rapid Sonochemical Synthesis of Spherical-shaped Mesoporous SBA-15 silica and Ti-incorporated SBA-15 Silica Materials

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Received December 6, 2002; Accepted January 13, 2003

Abstract: Mesoporous SBA-15 silica materials were synthesized in short time from one hour ultrasonic irradiation, followed by 1~3 h gelation in acidic media. The particle morphology of these sonochemically synthesized mesoporous materials was nearly spherical. Titanium was directly incorporated into SBA-15 silicate framework through sonochemical co-condensation of Ti(O-iPr)4 and Si(OEt)4. The Ti-incorporated SBA-15 silica exhibited good catalytic activity for the oxidation of 2,6-di-tert-butyphenol.

Keywords: sonochemistry, ultrasound, mesoporous silica, Ti-incorporation, SBA-15

Introduction

Since the development of MCM-41 and MCM-48 silicas by the Mobil Oil researchers in 1992 [1], many mesoporous inorganic materials have been prepared using various types of organic templates [2-4]. Self-assemblies of surfactants and block copolymers have been frequently applied as templates in the synthesis. Among them, hexagonal MCM-41 materials have been most frequently applied as catalytic supports and other purposes [5,6].

In 1998, Stucky group reported the fabrication of hexagonal mesoporous SBA-15 silica materials with wide range of pore sizes through acid-catalyzed sol-gel processing of tetraethyl orthosilicate (TEOS) in the presence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EOm-POn-EOm) triblock copolymer template [7]. The large pore size of over 5 nm combined with regular hexagonal pore arrangement made the material very unique for various applications [8-13]. The long preparation time, mostly from the long gelation time, for these mesoporous materials would hamper their extensive applications. There are several reports on the rapid synthesis of mesoporous materials, including microwave-assisted synthesis [14-19].

Sonochemistry has been intensively applied in materials chemistry area [20-23]. Sonochemistry arises from acoustic cavitation, which consists of the formation, growth, and implosive collapse of bubbles, when a high intensity ultrasound is applied in a liquid [20,21]. The collapse of bubbles generates localized hot spots with transient temperatures of ~5000 K, pressures of ~1800 atm, cooling rates in excess of 10¹⁰ K/s. Using these extreme conditions, various nanostructured materials have been synthesized [24-30]. Ultrasound was successfully applied in the sol-gel processes [31,32]. Ultrasonic irradiation of Si(OEt)4 (TEOS) in water with an acid catalyst produced a silica "sonogel". A common solvent (for example, ethanol for TEOS as a precursor) is required in conventional sol-gel processes due to the immiscibility of the precursors with water. Such solvents can become problematic because they may cause cracking during drying. These volatile co-solvents become unnecessary with sonication due to enhanced mixing. The gelation time for sonogel formation was much shorter than that of silica gels prepared from conventional sol-gel process. The silica sonogel generally exhibited higher density than the conventionally prepared gel. The particle size and pore size distribution of sonogels were quite different from those of conventionally prepared silica gels. In view of

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mesoporous silica synthesis, we paid particular attention to the short gelation time for the acid-catalyzed sol-gels. Very recently, Gedanken and coworkers successfully applied ultrasound to synthesize MCM-41 silica materials in basic medium [33]. And the same group also have synthesized several other mesoporous materials through ultrasonic irradiation [34-36]. The titanium incorporated SBA-15 with good hydrothermal stability could be used as a versatile selective oxidation catalyst for many larger reactants. But the strong acidic media in the synthesis of SBA-15 have hampered direct incorporation of titanium into the SBA-15. Very recently, Komarneni and coworkers successfully synthesized Ti incorporated SBA-15 via a “direct synthesis” procedure which involves the addition of a titanium source under microwave-hydrothermal conditions [17]. Herein we would like to report the rapid synthesis of SBA-15 silica and Ti-incorporated SBA-15 silica materials from the ultrasonic irradiation of inorganic precursors and organic template materials in acidic media.

Experimental

Synthesis of SBA-15 Silica Materials

The composition of the starting reaction mixture for SBA-15 silica materials were the same as that in the previously reported literature [7]. 4 g of P123 (Pluonic 123) was dissolved in an 150 mL of aqueous 1.6 M HCl solution. This solution was stirred with slight heating until P123 was completely dissolved. After then, 0.041 mol of TEOS was added to the homogeneous solution with stirring for a few minutes. The resulting homogeneous solution was subjected to ultrasonic irradiation for one hour in an open glass container (Sonic & Materials VCX600, 20 kHz, 13 nm Ti horn). After one hour ultrasonic irradiation, the solution temperature was measured to be 65°C. The resulting milky solution was aged at 85°C for one hour. The solution was filtered and washed with distilled water and EtOH several times until the solution pH reached 7. The as-synthesized material was dried at 100°C, and finally calcined under air flowing at a heating rate of 1°C/min up to 550°C and then maintained at this temperature for 5.5 h.

Synthesis of Ti-Incorporated SBA-15 Silica Materials

4 g of P123 (Pluonic 123) was dissolved to 150 mL of aqueous 1.6 M HCl solution. This solution (A) was stirred with slight heating until P123 became completely dissolved. Solution (B) was prepared by adding 0.0082 mol of Ti(O-i-Pr)4 (TTIP) to 10 mL of 10 M aqueous HCl solution. After the solution became clear, 0.041 mol of TEOS was added. When the temperature of this precursor solution became RT, the solution (B) was added dropwise to the solution (A) under ultrasonic irradiation and kept sonicated for 2 h. After the sonication, the bulk temperature was measured to be 60°C. The resulting milky solution was aged at 95°C for 2 h with vigorous stirring. The solution was filtered and washed with distilled water and EtOH several times until the solution pH reached 7. The as-synthesized material was dried at 100°C, and finally calcined under air flowing at a heating rate of 1°C/min up to 550°C and then maintained at this temperature for 5.5 h.

Characterization

N2 adsorption and desorption isotherms were collected at STP on a Micromeritics ASAP2010 Gas Adsorption Analyzer after the mesoporous materials were degassed at 200°C at 30 µtorr for 5 h. Pore size distributions were determined from N2 adsorption isotherms. X-ray diffraction (XRD) patterns was obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode and Cu Kα radiation (λ = 0.15418 nm). Small-angle X-ray scattering was acquired on a Bruker GADDS with general area detector diffracting system. The mesostructures and particle morphologies are observed by a transmission electron microscope (TEM, JEOL EM-2000 EX II) and a scanning electron microscopy (SEM, JEOL JSM-840A). UV-vis spectroscopic measurements were proceeded on a Varian CARY 3 E double beam spectrometer and dehydrated MgO as a reference in the range of 190-800 nm.

Results and Discussion

XRD pattern of the sonochemically prepared sample through one-hour sonication and one-hour gelation (Figure 1a) revealed a well-defined characteristic P6mm hexagonal structure of SBA-15 silica. The relative peak intensity of the (100) peak from the sonochemically prepared sample was higher than that of the conventionally prepared sample of 48-h gelation (Figure 1b). XRD patterns of the conventionally prepared sample of 24 h and 12 h gelation times (Figure 1c and 1d) exhibited much lower intensity, confirming that long gelation time of over 48 h are required for the fabrication of SBA-15 silica through the conventional procedure. The nitrogen adsorption-desorption isotherms of the sonochemically synthesized SBA-15 silica shows a typical H1-type hysteresis loop at high relative pressure, suggesting that the material possesses very regular mesoporous channels (Figure 2). The corresponding pore size calculated by the BJH (Barrett, Joyner, and Halenda) method revealed uniform pore size distribution with mean pore diameter of 6.5 nm. The BET surface area and mesopore volume of the sonochemically prepared SBA-15 were 760 m2/g and 0.76 cm3/g, respectively, which are comparable to
Figure 1. X-ray diffraction (XRD) patterns of SBA-15 silica materials after calcinating at 500°C: (a) sonochemically synthesized sample (1 hr sonication followed by 1 h gelation at 85°C), (b) conventionally synthesized sample from 48 h gelation, (c) conventionally synthesized sample from 24 h gelation, and (d) conventionally synthesized sample from 12 h gelation.

Figure 2. Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution of the sonochemically synthesized SBA-15.

solvent (dimethyl formamide) was added in the reaction mixture [37]. Synthesis of these sphere-shaped mesoporous materials is important for their applications in chromatographic separations and catalysis [38]. Titanium incorporated zeolite and mesoporous materials were extensively applied as epoxidation of alkenes and solid acid catalysis [5,6]. Recently Ti-incorporated SBA-15 silica with maximum Ti loading of 6 wt% was produced from the post synthetic grafting technique [39]. UV-VIS and Raman spectra of the material, however, revealed that Ti ions are distributed over tetrahedral and octahedral sites and significant amount of TiO$_2$ species was also observed. We have tried to synthesize Ti-incorporated SBA-15 silica material from the sonochemical co-condensation of TEOS and Ti(O-iPr)$_4$ (TTIP) in the presence of P123 triblock copolymer self-assembly under ultrasonic irradiation. The overall synthetic procedure is

Figure 3. (a) Transmission electron microscopy (TEM) and (b) Scanning electron microscopy (SEM) of the sonochemically synthesized SBA-15 silica.
similar to the previously described sonochemical synthesis of SBA-15 silica, except a variable amount of TTIP was added in the reaction mixture. The highest Ti incorporation of 1.5 wt%, determined by X-ray fluorescence spectroscopy, was achieved, when the reaction mixture of 3:1 = TEOS:TTIP (molar ratio) was applied. Various characterizations revealed that the sonochemically synthesized titanium incorporated SBA-15 silica kept hexagonal structure of SBA-15 (Figure 4 and Figure 5).

The sonochemically synthesized Ti-SBA-15 silica with 1.5 wt% Ti incorporation exhibited BET surface area of 680 m² g⁻¹, mesopore volume of 0.65 cm³ g⁻¹, and mean pore size of 6.5 nm (Figure 6). The UV-VIS spectrum of the sonochemically prepared sample (1.5 wt% Ti, Figure 7a) revealed that nearly all Ti ions are located at tetrahedral sites and the overall spectral pattern was quite similar to that of titanium silicalite-1 (TS-1, Figure 7b).

FT-IR spectra of the sonochemically prepared Ti-SBA-15 materials exhibited characteristic Si-O-Ti peak at 960 cm⁻¹, demonstrating the successful incorporation of Ti into silicate framework (Figure 8). The ²⁹Si MAS NMR spectrum of the material (0.5 wt% Ti) exhibited peaks attributed to Si(OSi)₄ (Q⁴, δ ~108 ppm) and (OH)Si(OSi)₃ (Q³, δ ~103 ppm) with relative integrated area of 68:32. No peak attributable to Q² and Q¹ was observed in the spectrum, demonstrating high degree of silica condensation (Figure 9).

Preliminary catalytic performance of the sonochemically prepared 1.5 wt% Ti-incorporated SBA-15 silica was tested for oxidation of a bulky aromatic compound 2, 6-di-tert-butylphenol, which has been frequently used as a probe reaction for redox molecular sieves of mesoporous structures [5,6,40]. The experiment was conducted at 337 K for 2 h using 10 mmol of substrate, 100 mg of catalyst, 10 g acetone as a solvent, and 33 mmol H₂O₂.
catalytic activity was comparable to the best-performed mesoporous Ti-incorporated silica, 1.5 wt% Ti-HMS silica of 18.1% conversion tested under the same conditions.

Conclusions

The syntheses of SBA-15 silica and Ti-incorporated SBA-15 were achieved under ultrasonic irradiation. The XRD studies revealed that well-ordered SBA-15 silica materials could be synthesized by one hour sonication followed by one hour gellation. In comparison, using conventional synthetic procedure more than 48 h gellation was required to synthesize the same materials with a similar mesostructure ordering. Scanning electron microscopy (SEM) shows spherical morphology of the sonochemically prepared samples.

Titanium incorporated SBA-15 silica materials have been synthesized from the sonochemical co-condensation of Ti(O-iPr)4 and Si(OEt)4. The UV-VIS and IR spectra of the sonochemically prepared sample showed that titanium was incorporated in the tetrahedral sites of the SBA-15 silicate framework. The catalytic activity of this material is comparable to Ti-HMS in the oxidation of 2,6-di-tert-butylphenol.

Acknowledgement

We are grateful to the Korea Research Foundation (KRF-2001-041-D00172) for their financial support.

References