

Synthesis of Novel Mesoporous Silica Materials with Hierarchical Pore Structures

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1. Introduction

Porous materials with various pore sizes in the range of micropore (< 2 nm), mesopore (2-50 nm), and macropore (> 50 nm) are attractive due to their many emerging applications such as catalysts, separation systems, and low dielectric constant materials [1-3]. The discovery of new M41S mesoporous silica families with pore sizes larger than 2 nm in diameter in 1992 extended the applications into much wider pore ranges, bringing in a new prosperous era in porous material research [4]. The synthesis of these silica materials has been mainly accomplished through a self-assembly between surfactant molecules and inorganic species under various pH conditions. Recently, core-shell nanoparticles with a silica core and mesoporous shell under basic conditions were synthesized using the silica nanoparticles as a core, and a silica precursor (TEOS) and cationic surfactant (CTABr) as a material for the formation of the mesoporous shell [5]. The resultant materials were very monodisperse in size and showed a narrow pore size distribution in the range of *ca* 2-3 nm in diameter, depending on the alkyl-chain length of the surfactants used.

In this work, the mesoporous shell coated-fumed silicas (denoted as MS@M-5s) were synthesized by using fumed silica instead of the silica nanoparticle as a core based on previous reports. Also, the structural properties of the MS@M-5s such as the specific surface area and pore volume were easily controlled by varying the amount of the silica precursor and surfactant. The resultant materials exhibited a BET surface area of *ca* 279-446 m²/g and total pore volume of *ca* 0.64-0.74 cm³/g and showed a narrow pore size distribution (PSD) due to the removal of the organic surfactant molecules.

2. Methods and Results

2.1 Synthesis of the mesoporous shell coated-fumed silicas (MS@M-5s)

The mesoporous shell coated-fumed silicas were synthesized based on previous reports. The mixture solution consisting of aqueous ammonia (NH₄OH, 28 wt.%, 0.3 ml), deionized water (DI H₂O, 20 ml), and absolute ethanol (abs. EtOH, 10 ml) were vigorously stirred for 10 min. 0.3 g of the fumed silica (M-5) was added into the above mixture solution and stirred for 30 min. The surfactant solution was dissolved in a 1:2 mixture of EtOH and DI H₂O was added dropwise.

After stirring for 30 min, TEOS was added to the above reaction mixture at ambient conditions and stirred for 1 h more, and the reaction mixture was then aged at 343 K for 1 day. In the preparation of the MS@M-5-*x* (where *x* is the sample number of the MS@M-5s), their structural properties were easily controlled by varying the amount of CTABr (0.12-0.36 g)/TEOS (0.215-0.645 ml). From the resultant suspension solution, as-synthesized MS@M-5s were retrieved by centrifugation, and then dried at 343 K overnight. The as-synthesized samples were calcined at 823 K for 5 h under an air atmosphere to remove the organic surfactant molecules.

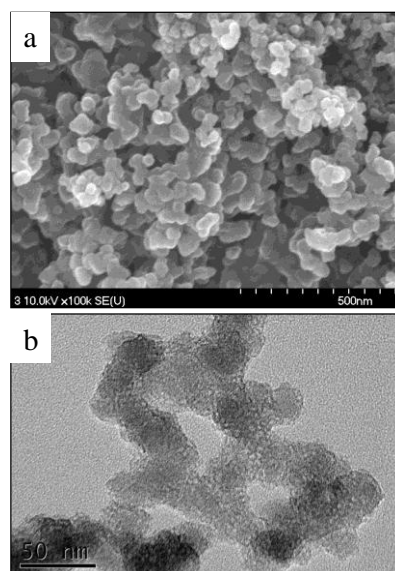


Fig. 1. Representative (a) SEM and (b) TEM images of the calcined MS@M-5-3 prepared using CTABr (0.36 g) and TEOS (0.645 ml).

2.2 SEM and TEM Images Analysis

The fumed silica used in this work exhibited network structures consisting of primary particles with a size of *ca* 30-50 nm in diameter. Fig. 1 shows the representative SEM and TEM images of the calcined MS@M-5-3 prepared using CTABr (0.36 g) and TEOS (0.645 ml). Although the SEM image showed a similar morphology with the fumed silica, the TEM image showed that a mesoporous shell was formed on the surface of the fumed silica. The thickness of the mesoporous shell was easily controlled by varying the amount of CTABr/TEOS.

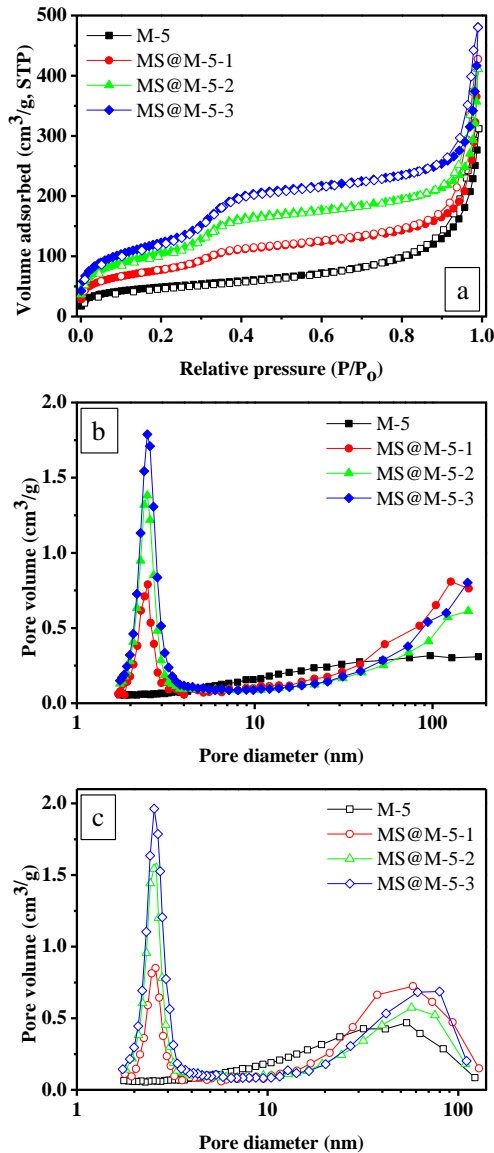


Fig. 2. (a) Nitrogen sorption isotherms at 77 K and their corresponding (b) adsorption and (c) desorption PSD curves for MS@M-5-x, respectively.

2.3 Structural Property Measurements

Nitrogen sorption isotherms and their corresponding PSD curves were measured to investigate the structural properties of the calcined MS@M-5s, which are shown in Fig. 2. All the samples prepared in this work exhibited a type IV isotherm characteristic of mesoporous materials according to the IUPAC nomenclature due to the presence of uniform mesopores with the exception of the fumed silica (Fig. 2a). The volume adsorbed for the MS@M-5s at $P/P_0 = ca$ 0.2-0.4 increased with an increase in the amount of CTABr/TEOS used. Also, the resultant materials showed a narrow pore size distribution within a range of ca 2-3 nm in diameter due to the removal of the organic surfactant. The broad pore size distribution within the range of ca 10-100 nm as shown in Fig. 2(c) may be attributed to the textural porosity between the MS@M-5

particles. The structural properties such as BET surface area, total pore volume, and pore size of all the samples are summarized in Table I.

Table I: Structural properties of the M-5 and calcined MS@M-5-x

Sample name	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Pore Diameter (nm)		
			11.0 ^a	16.9 ^b	15.3 ^c
M-5	176	0.48	11.0 ^a	16.9 ^b	15.3 ^c
MS@M-5-1	279	0.66	9.5 ^a	11.1 ^b	10.3 ^c
MS@M-5-2	379	0.64	6.7 ^a	6.8 ^b	6.7 ^c
MS@M-5-3	446	0.74	6.7 ^a	6.4 ^b	6.2 ^c

^a Adsorption average pore width (4V/A by BET)
^b BJH adsorption average pore diameter (4V/A)
^c BJH desorption average pore diameter (4V/A)

3. Conclusions

The synthesis of novel mesoporous silica materials with hierarchical pore structures has been demonstrated using the fumed silica as a core. The structural properties of these materials are easily controlled through varying the amount of surfactant and silica precursor. These resultant materials can provide hard templates for the fabrication of new nanostructured materials such as polymer, carbon, and metal oxide as well as new functional materials for many applications such as absorbent, purification and separation, catalysis, and chromatography.

The preparation of a chemical gel decontaminant or foam using the novel mesoporous silica materials synthesized in this work for removal of the radioactive waste from the surfaces of nuclear facilities is currently under progress.

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