Simple preparation of silica and alumina with a hierarchical pore system via the dual-templating method

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Abstract
Silica and alumina with macro-meso-type hierarchical pore systems are synthesized by dual templating using both surfactants and polystyrene (PS) spheres. After calcination, scanning electron microscope images show uniform macropores with a diameter of approximately 200 nm. This size coincides with that of the original PS spheres. The density of the macropores increases with the amount of added PS spheres in the precursor solutions. Transmission electron microscope images, small-angle x-ray scattering spectra and N₂ adsorption–desorption isotherms reveal the formation of ordered mesoporous structures in the macropore walls. Also, the existence of micropores (less than 2 nm in size) was confirmed from the large N₂ uptake at low relative pressures.

Keywords: mesoporous material, macroporous material, silica, alumina, hierarchical pore system

1. Introduction
Recently, it has been shown that porous materials have diverse applications such as heterogeneous catalysis, adsorbents and molecular separators. Mesoporous silica particles (from 2 to 50 nm pore size) were first reported in 1990 [1]. Mesoporous materials have consequently served as molecular sieves and also have applications in drug delivery and biosensing. On the other hand, macroporous materials (more than 50 nm pore size) possess excellent chemical, mechanical and thermal stability and have varied applications as a catalytic support in fuel cells, hydrogen storage materials and molecular separators.

Considering the extremely widespread use of mesoporous and macroporous materials, hierarchically ordered particles, having a bimodal distribution of pores, may become more important than unimodal mesoporous systems. In most chemical applications involving catalysis, a bimodal system would be more helpful because the interconnections between small pores and large pores enhance the internal surface area. Furthermore, a bimodal structure has the advantage that the reagents and products can pass through both macropores and mesopores.

Various methods for synthesizing hierarchical structures have been proposed [2–10]. In many conventional studies, hierarchical porous systems were formed in two steps: the formation of a template containing closely packed colloidal crystals followed by the penetration of a surfactant-based sol–gel precursor [4–8]. One-step synthesis has also been conducted; however, a special surfactant (‘KLE’ and an ionic liquid) [9] or surface-functionalized polymer spheres [10] are required in that case. Furthermore, the conventional strategies do not necessarily result in the desired multimodal structure owing to the formation of an amorphous silica region [6, 7]
and/or a lack of interconnectivity among the poorly packed macropores [10]. Very recently, we reported the simple preparation of hierarchical porous silica spheres through the aerosol-assisted multicomponent assembly of both polymer latex spheres and surfactants [11]. However, this process was limited to only silica systems and required special equipment.

Compared with silica, alumina is more attractive because of its broad applications in the catalysis field. The functionality of alumina can be enhanced by adding mesoporous properties, such as a high surface area, large pore volume and uniform pore size. Several studies on ordered mesoporous alumina [12, 13] and the synthesis of hierarchical alumina [14–16] have been reported; however, the macropores were not uniform in size and their packing was insufficient [14–16].

In this paper, we report the one-step synthesis of hierarchical silica without any special techniques or chemicals. Suspensions consisting of surfactants, polystyrene (PS) spheres, a silica source and solvents were prepared. While both PS spheres and surfactants were simultaneously assembled though solvent evaporation, a silica polymerization reaction was carried out. After the removal of the PS spheres and surfactants, macro-meso-type hierarchical porous silica was obtained. Because of its simplicity, this procedure can be applied to a wide range of other inorganic materials. We also applied this procedure to alumina and succeeded in obtaining a hierarchical sample with close-packed macropores.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS, extra-pure reagent), hydrochloric acid (pH 2) and concentrated hydrochloric acid (35 wt%) were purchased from Nacalai Tesque, Inc. Aluminum tri-n-butoxide was purchased from Kanto Chemical Co., Inc. Ethanol (99.5% purity, Koso Chemical Co., Ltd was used as the solvent. Triblock copolymers Pluronic F127 and P123 were obtained from Sigma–Aldrich Inc. Polystyrene spheres with an average diameter of 200 nm (Chemisnow MP-2701) were obtained from Soken Chemical and Engineering Co., Ltd.

2.2. Synthesis of bimodal silica and alumina

To prepare the silica precursor solution, 28 ml (26 g) of TEOS was added to the ethanol solvent (13 ml). Then, HCl (pH 2, 12.5 ml) was added dropwise. This mixture was subjected to vigorous stirring at room temperature for 30 min until a clear solution was obtained. In a separate beaker, Pluronic F127 (7.9 g) was added to 12.5 ml ethanol and mixed thoroughly in a hot water bath. After the complete dissolution of F127, the two solutions were mixed and subjected to vigorous stirring for 30 min at room temperature. To prepare the alumina precursor solution, we used the method of Fan et al [12]. P123 (1.6 g), acetic acid (2.3 ml), concentrated hydrochloric acid (1.0 ml) and aluminum tri-n-butoxide (2.5 g) were dissolved in ethanol (30 ml) and then stirred for 5 h.

In parallel with the above preparation of the precursor solutions, the PS powder was mixed with ethanol. The amount of PS powder was as follows: 2.2 g (sample A), 4.7 g (sample B), 6.5 g (sample C), 8.6 g (sample D), 10.8 g (sample E), 20.8 g (sample F) and 26.8 g (sample G) for the silica samples and 11.9 g (sample H) for the alumina sample. The PS spheres were well dispersed by ultrasonication. After that, the PS solutions were added to the above-described precursor solutions. They were then poured into Petri dishes to evaporate the solvent at room temperature for at least 72 h. Finally, the obtained white particles were calcined at 500 °C for 8 h (silica) or 5 h (alumina).

2.3. Characterizations

Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of each sample were obtained using a Hitachi S-4800 field-emission SEM and a JEOL-J3000F TEM, respectively. For TEM measurement, the accelerating voltage of the electron beam was 200 kV, and powder samples were dispersed in ethanol by ultrasound and mounted on a microgrid. Small-angle x-ray scattering (SAXS) spectra were obtained with a NANO-Viewer spectrometer (Rigaku). N2 adsorption–desorption isotherms were measured using a Quantachrome Autosorb-1 analyzer. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were applied to estimate specific surface areas and pore size distributions, respectively. The chemical composition of each sample was examined using an energy-dispersive x-ray spectrometer (EDX) attached to the SEM.

3. Results and discussion

Figure 1 shows SEM images of each sample after calcination. To find a suitable weight ratio of surfactants to PS spheres, several silica samples were synthesized by changing the amount of added PS spheres (samples A–G). In sample A, which has the lowest amount of PS, macropores were isolated within the silica matrix. With increasing amount of PS (samples B–F), the macropores tended to accumulate, and in some parts became closely packed. These packed macropores were connected by windows, which is attributed to the closely packed arrangement of the PS spheres (i.e. contacts). Sample G, with the greatest amount of PS, possessed three-dimensionally closely packed spherical macropores over the entire area (figure 2(a)). The size of macropores was about 200 nm, which coincided with the particle size of the original PS spheres. This situation appears to be similar to the formation of ordered macropores between PS and ceramic particles by a heterocoagulation method [17, 18].

The mesostructural ordering was determined through a combination of SAXS, TEM and N2 adsorption–desorption isotherms. SAXS profiles for each sample are shown in figure 3. Each sample exhibited a broad peak at approximately 2θ = 1°, revealing the mesostructural ordering derived from the assembly of surfactants. Sample G had a peak at 2θ = 0.9°, from which the pore–pore distance was estimated.
Figure 1. SEM images of silica (A–G) and alumina (H) samples. The amounts of PS powder were as follows: (a) sample A (2.2 g), (b) sample B (4.7 g), (c) sample C (6.5 g), (d) sample D (8.6 g), (e) sample E (10.8 g), (f) sample F (20.8 g), (g) sample G (26.8 g) and (h) sample H (11.9 g).

to be 10 nm. In general, in SAXS spectra, the peaks broaden and their intensities decrease as the ordering of domains decreases. In sample A (with the lowest amount of PS), because the mesoporous silica region was large (figure 1(a)), the size of the ordered domains was larger, thus resulting in stronger peaks. However, as the amount of doped PS spheres
was increased, the mesopore regions between the macropores were reduced in size, which explains why the peaks broadened and their intensities decreased.

The \( \text{N}_2 \) adsorption–desorption isotherm of sample G is displayed in figure 4. The isotherm is of type IV with a hysteresis loop. A large \( \text{N}_2 \) uptake was observed at low relative pressures, indicating the presence of micropores (less than 2 nm in size). The micropores originated from the hydrophilic tails of the triblock polymer (i.e. F127) \([6, 7]\). The calculated BET surface area was 356 m\(^2\) g\(^{-1}\) and the mesopore size was calculated to be 4.1 nm by the BJH method.

TEM images of sample G (figures 5(a) and (b)) revealed that cage-type mesopores were closely packed in the macropore walls. No tubular mesochannels could be observed. By tilting the sample grid during TEM observation, the presence of cage-type spherical mesopores was confirmed. This finding neatly supports the conclusion that spherical mesopores of uniform size were closely packed. Note that, in our sample, ordered mesostructures were created even near the edge of the macropores. No distortion of the uniform-size mesopores was observed, although it was previously reported that a domain without mesopores existed around the macropore windows \([6, 7]\). The pore-to-pore distance was estimated to be 10 nm from TEM images, which is in good agreement with the SAXS result. The thickness of the mesoporous walls was estimated to be 6 nm (i.e. the pore-to-pore distance is 10 nm and the mesopore size is 4 nm).

By adopting the most suitable weight ratio described above, an alumina sample with hierarchical ordered pores was successfully synthesized (sample H in figure 1). The macropores (200 nm in size) were connected with windows (figure 2). The SAXS pattern also had a single peak at \( 2\theta = 1.0^\circ \), revealing structural order on the mesoscopic scale (figure 3). The pore-to-pore distance of the mesoporous structures was calculated to be 9.0 nm, which is consistent with the estimation from the TEM images (figures 5(c) and (d)). Similarly to silica sample G, cage-type mesopores with a uniform size were clearly observed. No domain without mesopores existed inside the macropore walls. The crystallinity of alumina is poor, as indicated by the broad selected-area electron diffraction rings (inset of figure 5(d)) \([13]\). Polycrystals were formed in mesopore walls during the calcination process used for the removal of PS...
spheres and surfactant. The BET surface area was measured to be 329 m² g⁻¹ from the N₂ adsorption–desorption isotherm. This BET surface area is similar to that of mesoporous γ-alumina (without macropores) [13]. Consequently, the one-step synthesis of other metal oxides with a hierarchical porous structure can be accomplished by suitably adjusting the weight ratio of the surfactant to PS spheres.

4. Conclusions

We succeeded in synthesizing silica with a hierarchical structure in a single step. The obtained products had three types of pores (macropores, mesopores and micropores) originating from PS spheres, triblock copolymer spheres and the tails of the copolymer, respectively. In contrast to conventional studies [6, 7], our materials had ordered cage-type mesoporous structures within the macropore walls. This synthesis procedure was also applied to alumina, resulting in the successful preparation of hierarchical alumina. This simple synthesis method can be utilized to fabricate various types of hierarchical metal oxides.

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