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Influence of the Ammonium Hydroxide Concentration in Morphological Control of Mesoporous Silica Particles

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1. Introduction

The discovery of new M41S mesoporous silica families in 1992 extended the applications into much wider pore ranges, bringing in a new prosperous era in porous material research [1]. The synthesis of these mesoporous silicas has been mainly accomplished through a self-assembly between surfactant molecules and inorganic species under various pH conditions [2-4]. Meanwhile, many studies have been conducted on the application as catalysts, adsorbents, and packing materials for separation columns due to their unique properties such as high specific surface area, large pore volume, tuneable pore size, and narrow pore size distribution. The pore sizes of these materials can be easily controlled by changing the alkyl-chain length of the surfactant used. However, the control of the morphology and the pore structure is not so common. The morphological control of these materials in particular is one of the major challenges for their industrial application. Recently, the mesoporous silica materials with various shapes such as fibers, films, polyhedral particles, and spheres have been reported. In our previous study, the core-shell nanoparticles with a silica core and a mesoporous shell under basic conditions were synthesized using the silica nanoparticles as a core and tetraethylorthosilicate (TEOS)-cetyltrimethylammonium bromide (CTABr)-NH_4OH-H_2O-C_2H_5OH system [5].

In this work, we report the synthesis of the most well-known hexagonal MCM-41 among three main mesophases in the M41S families using TEOS-CTABr-NH_4OH-H_2O system. Also, in the control of the morphology and pore structure of the mesoporous silica materials, the influence of the NH_4OH concentration was investigated.

2. Methods and Results

2.1 Synthesis of mesoporous silica materials with various morphologies

To synthesize the mesoporous silica materials with various morphologies, the mixture solution consisting of CTABr (0.24 g), NH_4OH (28 wt.%, 0.25-3.00 ml), and DI H_2O (30 ml) were vigorously stirred for 30 min until a clear solution. Then, TEOS (98 %, 0.43 ml) was added into the above mixture solution and stirred for 60 min. The reaction mixture was then aged at 343 K overnight. From the resultant suspension solution, as-synthesized samples 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.

2.2 SEM Images Analysis

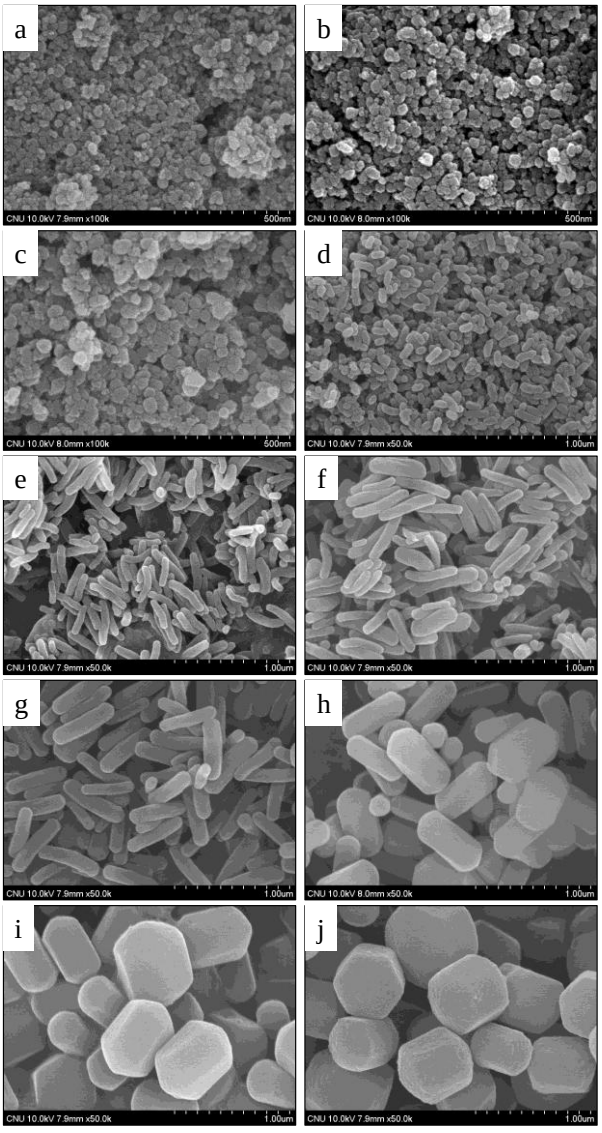

Fig. 1. SEM images of the calcined samples synthesized by varying the amount of the NH_4OH. (a) 0.25 ml, (b) 0.30 ml, (c) 0.40 ml, (d) 0.50 ml, (e) 0.75 ml, (f) 1.00 ml, (g) 1.50 ml, (h) 2.00 ml, (i) 2.50 ml, and (j) 3.00 ml, respectively.

The morphologies, particle sizes, and pore structures of the obtained mesoporous silica materials show a high

dependence on the amount of the NH_4OH used in this work. Fig. 1 shows SEM images of the calcined samples synthesized by varying the amount of the NH_4OH (0.25-3.00 ml). As shown in the SEM images, when the amount of the NH_4OH was less than 0.50 ml, the morphologies of the mesoporous silica materials exhibited irregular shapes (Fig. 1a-c). On the other hand, the morphology of the silica materials according to the increase of the amount of the NH_4OH was replaced by rod-like shapes (Fig. 1d-g) and hexagonal shapes (Fig. 1h-j).

2.3 TEM Images Analysis

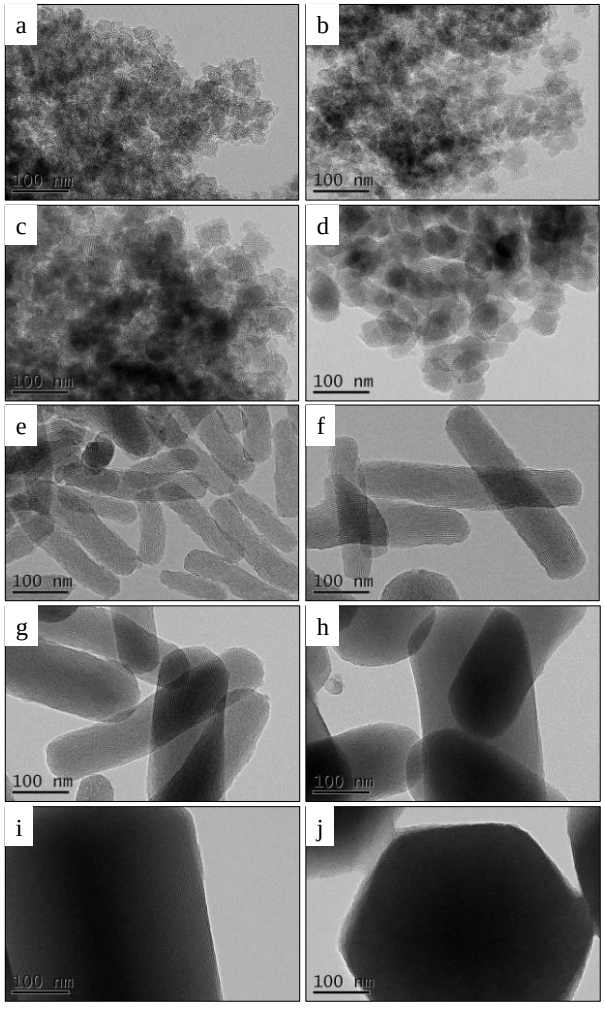

Fig. 2. TEM images of the calcined samples synthesized by varying the amount of the NH_4OH. (a) 0.25 ml, (b) 0.30 ml, (c) 0.40 ml, (d) 0.50 ml, (e) 0.75 ml, (f) 1.00 ml, (g) 1.50 ml, (h) 2.00 ml, (i) 2.50 ml, and (j) 3.00 ml, respectively.

The morphologies and pore structures of the mesoporous silica materials are clearly revealed by TEM. The silica materials synthesized using the amount of the NH_4OH below 0.5 ml show disordered mesostructures, where nanoparticles with irregular shapes of ca 30-50 nm in diameter can be seen (Fig. 2a-b). Although the silica material synthesized using the amount of the NH_4OH (0.40 ml) shows an irregular shape, the pore structure exhibits the existence of ordered hexagonal array (Fig. 2c). The rod-like shapes and highly ordered hexagonal array were obtained when using the amount of the NH_4OH in the range of 0.50-1.50 ml (Fig. 2d-g), showing that the hexagonal shapes were synthesized by using the amount of the NH_4OH over 1.50 ml (Fig. 2h-j).

3. Conclusions

The mesoporous silica particles with various morphologies, particle size, and mesopore structures under the reaction condition of TEOS-CTABr-NH_4OH-H_2O system were synthesized by varying the amount of the NH_4OH. The resultant silica materials showed various morphologies such as irregular, rod-like, and hexagonal shapes. The concentration of the NH_4OH played a key role as a basic catalyst for the controlled synthesis of the ordered mesoporous silica materials.

These materials will find many applications such as adsorption of VOCs and radioactive wastes produced in a nuclear facility as well as purification and separation process, catalysis and electrode materials. Also, these materials can be used to stabilize foam for the removal of radioactive wastes. Further research for the removal of the radioactive wastes using the novel functionalized mesoporous silica materials is currently under progress.

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