J Mater Sci (2008) 43:2362–2366
DOI 10.1007/s10853-007-2022-y

NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Microwave-assisted sol–gel process for production of spherical mesoporous silica materials

Miki Inada · Akira Nishinosono · Kai Kamada · Naoya Enomoto · Junichi Hojo

Received: 5 November 2006 / Accepted: 20 July 2007 / Published online: 13 November 2007

Abstract Spherical mesoporous SiO_2 and SiO_2–TiO_2 particles were synthesized by sol–gel method using W/O emulsion under microwave irradiation. In SiO_2 system, W/O emulsion was prepared by mixing partially hydrolyzed $Si(OC_2H_5)_4$ aqueous solution including $C_{18}TAC$ as template with *n*-hexane solution including polyglycerol polyricinalate as emulsifier. In SiO_2–TiO_2 system, $Ti(OC_2H_5)_4$ capped by acetylacetone was added to the aqueous phase. In both cases, spherical products were synthesized by heating of W/O emulsion for 30 min under microwave irradiation. The specific surface area and pore size of spherical products were 800 m^2/g and 1.6 nm, respectively, which indicates that the spherical products are mesoporous. These results suggest that sol–gel reaction in water phase proceeds rapidly because microwave quickly and selectively heats up the aqueous solution.

Introduction

Mesoporous silica has been receiving a lot of attention. Regularly-oriented mesopores form by a sol–gel process using the self-assembly of organic surfactant as template [1]. The deposited SiO_2 is amorphous. It's known that the gas adsorbability of mesoporous silica is remarkably enhanced by the addition of other metal oxides forming acidic points. Among a variety of metallic elements, Ti is famous as most effective additive to generate acidic points in silica [2–4]. The sol–gel process using metal alkoxides is useful to achieve homogeneous distribution of the second component into Si–O network. There is, however, a problem in the difference of hydrolysis rate between various starting alkoxides. The authors have studied the process factors on formation of SiO_2–TiO_2 mesoporous materials from Si and Ti alkoxides, and found that the way for homogenization is the partial hydrolysis of Si alkoxide before the addition of Ti alkoxide [4–6]. Homogeneous SiO_2–TiO_2 mesoporous materials were also synthesized by using acetylacetone as capping agent of Ti alkoxide to inhibit the separate deposition of TiO_2 in the recent study. This method is one-step process and suitable to obtain SiO_2–TiO_2 materials.

Because of the large surface area, the mesoporous silica is useful as adsorbent in gas or liquid phase, and various functions are expected by combining with other oxides for catalytic applications. Generally, mesoporous materials obtained by sol–gel method are glassy and have an irregular form. For application of mesoporous materials to catalyst or support, the control of morphology is important. In this study, we propose a novel synthesis method, so-called microwave-emulsion method, for the synthesis of spherical mesoporous silica.

The emulsion method is one of the effective synthesis methods for spherical particles [7]. The W/O emulsion is composed of oil phase as matrix and water phase in micelle surrounded by surfactants as emulsifier. Spherical particles are synthesized by heating of W/O emulsion including reactants in water phase. Since the size of droplet in W/O emulsion is decided by molar ratio of surfactant to water and mixing, the particle size of product can be controlled.

M. Inada · A. Nishinosono · K. Kamada · N. Enomoto · J. Hojo (✉)
Faculty of Engineering, Department of Applied Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
e-mail: jhojo@cstf.kyushu-u.ac.jp

The microwave technique has been extended as one of hydrothermal processes for synthesis of fine oxide powders [8], showing some interesting phenomena such as promotion of reaction, smaller crystallite size, and so on [9–16]. Microwave is absorbed directly into solvent having large dielectric loss like water, and enables the rapid heating compared to a conventional heating process in which the container is heated from the outside. The short-time reaction is preferable for efficient industrial production because the long-time reaction consumes more energy. In addition, the most noteworthy phenomenon by microwave irradiation is the selective heating of high-dielectric media, especially water.

In the microwave-emulsion method, *n*-hexane was used as oil phase, because *n*-hexane does not absorb microwave, and aqueous solution including silica source and template of mesopores as water phase. When microwave is irradiated to the W/O emulsion, water phase is heated selectively and sol–gel reaction proceeds in water phase, resulting in formation of mesoporous silica. In addition, spherical particles may form because of selective heating of water phase in micelle and cooling by oil phase.

In this study, spherical mesoporous silica was synthesized by the microwave-emulsion process as new morphology control method to investigate the microwave effect for the formation of mesoporous spheres of SiO_2 and SiO_2–TiO_2 using acetylacetone as capping agent.

Experimental procedure

Synthesis of spherical mesoporous silica

Spherical mesoporous silica was synthesized by sol–gel method using W/O emulsion under microwave irradiation. Figure 1 shows the flow chart for synthesis of spherical mesoporous silica. *n*-Hexane was used as matrix solvent of W/O emulsion because *n*-hexane does not absorb microwave. First, oil phase was prepared by mixing 50 mL of *n*-hexane and 10 wt.% of polyglycerol polyricinalate (PP) as emulsifier. Water phase was prepared as follows: 2.21 mL of $Si(OC_2H_5)_4$ (TEOS) was mixed with 10 mL of diluted HCl water (pH = 2) including stearyltrimethylammonium chloride (C_{18}TAC) as template at 50 °C. The composition was set at TEOS:C_{18}TAC:H_2O = 1:0.28:56 in mol. In order to prepare water phase, this TEOS aqueous solution was stirred for 1.5 h at 50 °C and then 5 mL of H_2O was added. The water phase was mixed with oil phase under stirring, resulting in W/O emulsion. In the conventional heating method, the W/O emulsion was put into a glass flask equipped with a reflux condenser, and heated using a water bath at 60 °C under stirring with a magnetic stirrer. The microwave heating process was performed by using the MARS5X (CEM Co.) microwave digestion system. The maximum power of microwave could be selected to be 300, 600 or 1200 W and the power was automatically varied from 0% to 100%, controlled according to setting temperature or pressure. The microwave frequency was 2.45 GHz, which is the same as that in domestic microwave ovens. In the microwave heating method, the reaction was carried out in a sealed Teflon vessel under stirring with a magnetic stirrer and the reacting temperature was set at 60 °C. After heating, the precipitate was separated by centrifugation. The produced powder was washed with ethanol and distilled water, and then dried at 100 °C. In order to remove the organic residue, the dried products were calcined at 500 °C for 4 h in air.

Synthesis of spherical mesoporous SiO_2–TiO_2

SiO_2–TiO_2 mesoporous particles were prepared by adding $Ti(OC_2H_5)_4$ (TEOT) to the water phase with TEOS and C_{18}TAC. TEOT was capped with acetylacetone to control the reactivity, because the hydrolysis rate of TEOT was higher than that of TEOS. First, TEOT was mixed with acetylacetone in dry N_2 at the ratio of TEOT to acetylacetone = 1:2 in mol. After stirring for 30 min, the capped TEOT was added to the solution of TEOS, C_{18}TAC and diluted HCl water (pH = 2). The composition of the TEOS solution was the same as in the mesoporous silica formation as above (TEOS:C_{18}TAC:H_2O=1:0.28:56 in mol). The Ti/Si molar ratio in the composite was changed from 0.1 to 1.0. This mixture was heated at 50 °C for 1.5 h under stirring. After then, 5 mL of H_2O was added to the TEOS–TEOT aqueous solution. The water phase was mixed with *n*-hexane including PP to form W/O emulsion. The W/O emulsion was heated at 60 °C under microwave irradiation.

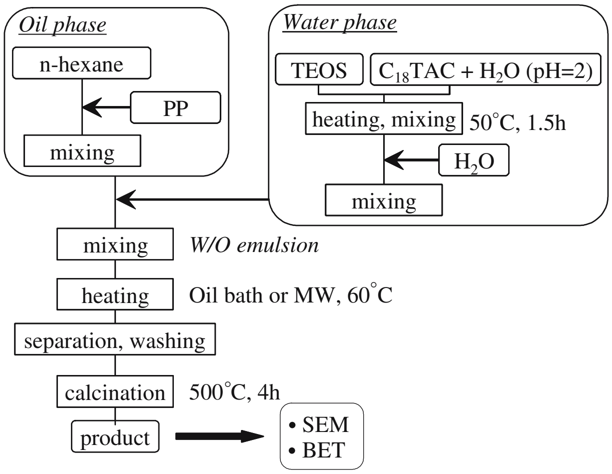

Fig. 1 Flow chart for synthesis of spherical mesoporous silica

The final product was washed, dried and calcined by the same processes as mentioned above.

Characterization

The morphology of products was observed by scanning electron microscopy (SEM; S-5200, Hitachi Co.). The specific surface area and average pore size of calcined products were determined from N_2 adsorption isotherm by the BET method (Belsorp 18SP, BelJAPAN, Inc.).

Results

Synthesis of spherical mesoporous silica

Effect of microwave heating

In both synthesis methods, the same N_2 adsorption isotherm was obtained as shown in Fig. 2. The specific surface area and average pore size were 840 m^2/g and 1.64 nm, respectively, indicating that the products were mesoporous including micropore and C_{18}TAC worked as template in water droplets. The SEM images of products are shown in Fig. 3. In the microwave heating method, spherical particles with smooth surface were observed, whereas irregular particles with rough surface were formed by the conventional heating method. These results indicate that the rapid and selective heating by microwave irradiation is effective to make spherical particles. When the microwave power was set at 300, 600 and 1200 W and the reaction time at 5 min, 30 min and 4 h, the particle morphology was not changed. Even at 5 min, the spherical mesoporous silica was formed under microwave irradiation. This is due to the rapid heating by microwave.

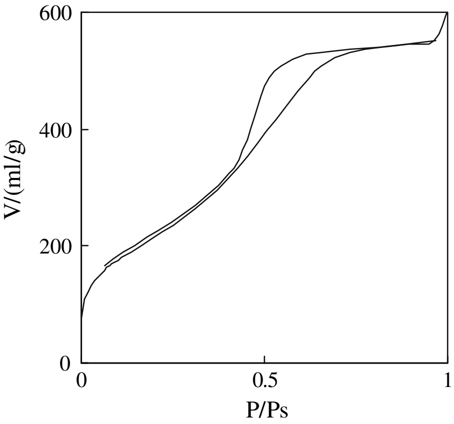

Fig. 2 N_2 adsorption isotherm of product by microwave heating method

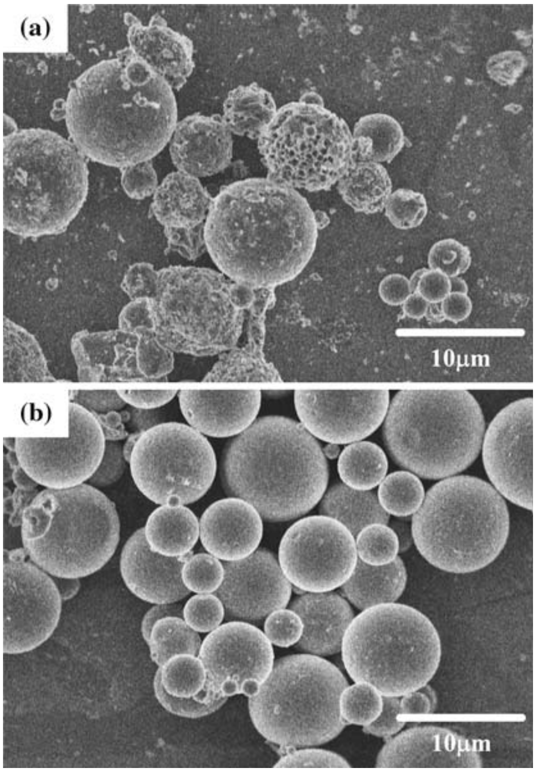

Fig. 3 SEM images of products by (**a**) conventional heating method and (**b**) microwave heating method

Effect of concentration of reactants

In order to investigate the effect of concentration of reactants, the amount of TEOS, additive water or *n*-hexane was changed. In all cases, as-prepared W/O emulsion was stable. The SEM images of products are shown in Fig. 4. When the amount of TEOS increased, the agglomerates of spherical particles were observed. This result indicates that SiO_2 was released from water droplets during sol–gel reaction because much amount of SiO_2 formed by hydrolysis of TEOS. The much amount of irregular particles was observed when the amount of additive water increased or the amount of *n*-hexane decreased, meaning that the emulsion was broken by microwave heating although as-prepared W/O emulsion was stable.

Synthesis of spherical mesoporous SiO_2–TiO_2

Figure 5 shows the SEM images of products in SiO_2–TiO_2 system. In the SiO_2–TiO_2 system also, the spherical mesoporous particles were synthesized at Ti/Si molar ratio of 0.1. At Ti/Si = 0.1, the specific surface area and average pore size were 800 m^2/g and 1.6 nm, respectively. These results agreed with those in SiO_2 system, indicating that the product in SiO_2–TiO_2 system was also mesoporous. When

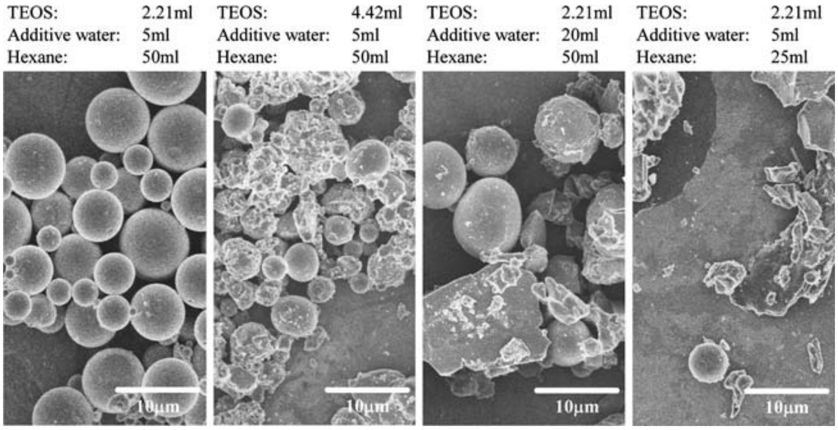

Fig. 4 SEM images of products by microwave heating method at different concentration of reactants

the amount of Ti-source increased, the particle shape tended to become irregular. This may be due to the change in stability of W/O emulsion in the starting solution. In addition, the specific surface area decreased as Ti/Si molar ratio was higher than 0.1 (Fig. 6). This result suggests that mesoporous structure was broken by increase in the amount of Ti-source.

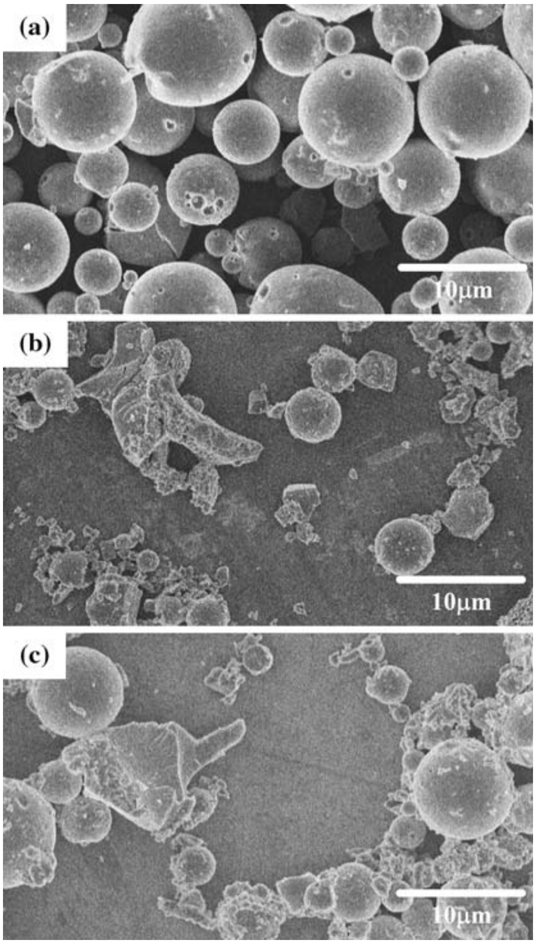

Fig. 5 SEM images of products in SiO_2–TiO_2 system: (**a**) Ti/Si = 0.1, (**b**) Ti/Si = 0.5, (**c**) Ti/Si = 1.0

Discussion

In order to investigate the effect of microwave for synthesis of spherical mesoporous silica, the change in temperature with time under microwave irradiation was examined for *n*-hexane, water, and W/O emulsion (Fig. 7). In this section, the W/O emulsion was prepared by mixing 5 mL of water and 50 mL of *n*-hexane including 10 wt.% of PP. The maximum microwave power and temperature were set at 300 W and 60 °C, respectively. Under microwave irradiation, the temperature of *n*-hexane did not change, whereas that of water rapidly increased, went over 60 °C within 1 min and then settled at the temperature. These results depend on the dielectric loss of each solvent. In the case of W/O emulsion, the temperature went over 60 °C within 3 min and then settled. When microwave is irradiated to W/O emulsion, water phase is selectively heated and the temperature of water droplets may rise up over 60 °C in the early stage. On the other hand, the elevation of temperature in oil phase depends on thermal conduction from water

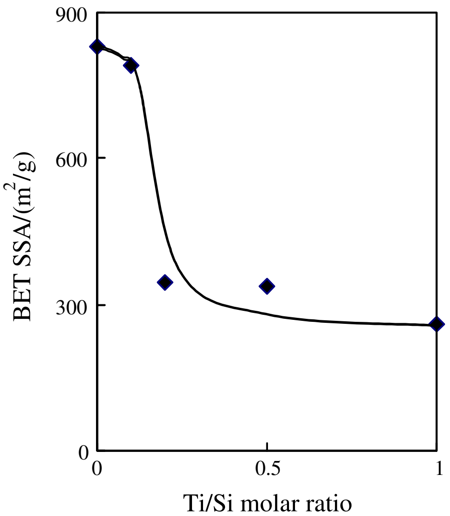

Fig. 6 Change in specific surface area with Ti/Si molar ratio

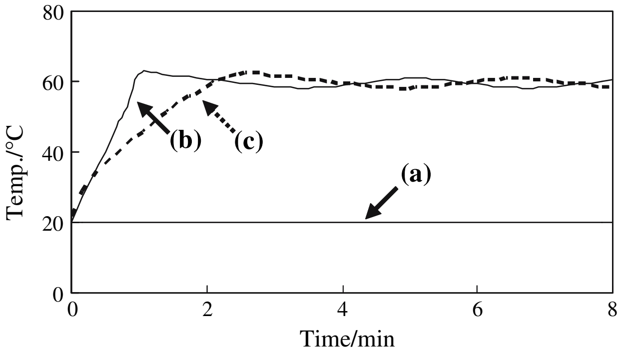

Fig. 7 Change in temperature with time under microwave irradiation: (**a**) *n*-hexane, (**b**) water, (**c**) W/O emulsion

phase because oil phase does not absorb microwave. Therefore, the inner region of water droplets is heated rapidly by microwave irradiation and the interfacial region between water and oil phases is cooled by oil phase. W/O emulsion becomes unstable with raising temperature because the emulsifier molecules move actively on the surface of water droplets. The cooling of the interfacial region is useful to keep the W/O emulsion stable. In addition, the rapid heating of water droplets enables the short-time reaction to form rigid mesoporous structure. This is the mechanism for the formation of spherical mesoporous silica from W/O emulsion under microwave irradiation.

The stability of W/O emulsion depends on the concentration of reactants. When the amount of TEOS is large, the formed SiO_2 tends to agglomerate. C_2H_5OH forms during hydrolysis of TEOS, and the existence of C_2H_5OH makes the W/O emulsion unstable because of reduction of hydrophobic effect of emulsifier to water phase. The molar ratio of emulsifier to water is important to keep the stability of W/O emulsion. This ratio decreases relatively with increasing amount of water phase and decreasing amount of oil phase, resulting in the formation of irregular shape particles. The spherical shape is broken by increasing amount of Ti-source. This is also explained by the existence of acetylacetone released from the capped Ti-source similarly to C_2H_5OH released from Si-source. The specific surface area of SiO_2-TiO_2 system decreases with an increase in Ti content. According to the previous work for preparation of mesoporous SiO_2–TiO_2 [4–6], Ti is incorporated into Si–O network at small Ti content, whereas TiO_2 forms separately at large Ti content, leading to the decrease in specific surface area. The stable coordination number of oxygen is four for Si–O bonding and six for Ti–O bonding. The difference in the coordination number limits the solubility of Ti–O bond into Si–O network, and tends to form TiO_2 clusters. This may be the reason for restriction of the formation of mesoporous structure.

Conclusions

In this study, spherical mesoporous SiO_2 and SiO_2–TiO_2 could be synthesized by novel synthesis method, so-called microwave-emulsion method. When the W/O emulsion was heated by microwave irradiation, spherical silica particles were obtained. The specific surface area and average pore size were 840 m^2/g and 1.64 nm, respectively, indicating that the spherical product was mesoporous. On the other hand, the irregular silica particles were formed by conventional heating under the same conditions. In the present reaction system, $C_{18}TAC$ works as mesopore-forming template in water droplets, and PP works as surfactant to emulsify the water phase including silica source in oil phase. Since the dielectric constant of n-hexane is lower than that of water, the emulsified water droplets are selectively heated. This is the mechanism for the formation of spherical mesoporous silica particles in the sol-gel process under the microwave irradiation.

References

1. Kresge CT, Leonowicz ME, Roth WJ, Vrtuli JC, Beck JS (1992) Nature 359:710
2. Zheng S, Gao L, Zhang Q, Guo J (2000) J Mater Chem 10:723
3. Zheng S, Gao L, Zhang Q, Zhang W, Guo J (2001) J Mater Chem 11:578
4. Li XY, Uehara M, Enomoto N, Hojo J (2001) Trans Mater Soc Jpn 26(2):499
5. Li XY, Uehara M, Enomoto N, Hojo J (2001) J Ceram Soc Jpn 109(10):818
6. Enomoto N, Kawasaki K, Yoshida M, Li XY, Uehara M, Hojo J (2002) Solid State Ionics 151:171
7. Masui T, Adachi K (1999) Bull Ceram Soc Jpn 34:93 (in Japanese)
8. Somiya S, Roy R (2000) Bull Mater Sci 23:453
9. Katsuki H, Furuta S, Komarneni S (1999) J Am Ceram Soc 82:2257
10. Katsuki H, Komarneni S (2001) J Am Ceram Soc 84:2313
11. Wu DS, Han CY, Wang SY, Wu NL, Rusakova IA (2002) Mater Lett 53:155
12. Bellon K, Chaumont D, Stuerga D (2001) J Mater Res 16(9):2619
13. Bondiol F, Ferrari AM, Leonelli C, Siligardi C, Pellacani GC (2001) J Am Ceram Soc 84(11):2728
14. Zhou J, Zhu J, Liao X, Fang J, Zhou M, Chen H (2002) Mater Lett 53:12
15. Potdar HS, Deshpande SB, Deshpande AS, Gokhale SP, Date SK, Khollam YB, Patil AJ (2002) Mater Chem Phys 74:306
16. Newalkar BL, Komarneni S, Katsuki H (2001) Mater Res Bull 35:2347