Preparation of mesoporous materials with adjustable pore size using anionic and cationic surfactants

Ji Won Park [a], Dong Sin Jung [a], Myung Eun Seo [b], Sang Youl Kim [b],
Won-Jin Moon [c], Chae-Ho Shin [d], Gon Seo [a],*

[a] *School of Applied Chemical Engineering and The Center for Functional Nano Fine Chemicals, Chonnam National University, Gwangju 500-757, Republic of Korea*
[b] *Department of Chemistry and School of Molecular Science, Korea Advanced Insitute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon, Republic of Korea*
[c] *Korea Basic Science Institute Gwangju Center, Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea*
[d] *Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 361-763, Republic of Korea*

Abstract

The mesopores of mesoporous materials prepared with the anionic surfactant *N*-lauroyl-L-glutamic monosodium salt (AS) were enlarged by adding the cationic surfactant hexadecyltrimethylammonium bromide (CS) to the micelles of AS at pH 9. The ζ-potential of the micelles in the synthetic mixtures and the physical state of the assembled surfactants in the mesopores were examined by a light scattering spectrophotometer, ^{1}H ^{13}C CP-MAS NMR and DSC. The average pore diameters of the mesopores increased from 2.8 nm to 6.2 nm with increasing the content of CS. CS molecules inserted to the micelles composed of AS molecules, resulting in the enlargement of mesopores. However, the addition of too much CS interfered with the formation of the micelles. As a result, no mesoporous materials were produced when the ratio of CS to AS was above 80%.
© 2007 Elsevier Inc. All rights reserved.

Keywords: Mesoporous materials; Cationic and anionic surfactants; Pore size

1. Introduction

The use of mesoporous materials as catalysts and adsorbents has been extensively studied in an attempt to make use of their uniform mesopores and large surface areas. Even large molecules with diameters of above 1 nm, which cannot enter into zeolite pores, can be adsorbed on the inner surface of mesopores. Their low resistance to mass transfer in mesopores improves their performance as catalysts and adsorbents. Furthermore, the short residence time of reactants and products in mesopores compared to zeolite pores maximizes their selectivity to the desired products in consecutive catalytic reactions [1].

Most of mesoporous materials are prepared with the micelles formed by cationic surfactants that are used as templates in the formation of mesopores [1–5]. The variation in the sizes and shapes of the templates leads to the formation of mesoporous materials with different pore sizes and structures. Anionic and nonionic surfactants are also employed as templates, but the preparation condition such as the type of silica sources and pH of the synthetic mixtures are considerably different in this case [6,7]. The mesoporous materials that are prepared using anionic surfactants show chiral properties in their pores, and thus, they attract much attention as adsorbents that are useful in the separation of chiral molecules [8,9].

The size of the mesopores is very important in the application of mesoporous materials, because the pore size is a primary factor in determining the access of materials to

---

their mesopores. Various methods have been suggested to control the pore sizes of mesoporous materials, when cationic surfactants are used as templates. Increasing the length of the carbon chains of cationic surfactants is a typical way to increase in the size of micelles [10–12]. The addition of 1,3,5-trimethylbenzene and triisopropylbenzene is also effective in increasing the size of micelles, through their insertion into the micelles of cationic surfactants [13,14]. Alkanes such as *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane and *n*-dodecane and *N,N*-dimethylhexadecylamine which can interact with the micelles of cationic surfactants, also lead to the enlargement of the mesopores [15,16]. The specific hydrothermal treatment of mesoporous materials is an another method of obtaining stable and enlarged mesopores [17,18].

Although the increase in the length of the carbon chains of anionic surfactants definitely results in the enlargement of the mesopores, the extent of the enlargement is not sufficient due to the difficulty in the preparation of long chain surfactants. Furthermore, the addition of alkylbenzenes and amines to the synthetic mixtures of mesoporous materials containing anionic surfactants is usually ineffective in enlarging their pore sizes. Since they interact directly with the anionic surfactants, they are not to be inserted into the micelles.

Micelles composed of anionic surfactants have a similar level of uniformity to those prepared using cationic surfactants. Therefore, the regularity of the mesopores prepared using anionic surfactants is also high compared to those prepared using cationic surfactants, although only a part of the silica source, 3-aminopropyltriethoxy silane (APTES), interacts with the polar ends of anionic surfactants [19–24]. The silica chains formed from tetraethylorthosilicate (TEOS) through the hydrolysis of the silyl groups and the condensation of the hydrolyzed hydroxyl groups, do not interact with the micelles composed of anionic surfactants. These micelles combine with APTES and the silica chains formed from the TEOS connected to APTES and covered the surface of the micelles with silica. Therefore, the addition of other materials such as alkylbenzenes, amines and alkanes to anionic surfactants may be harmful to the formation of mesoporous materials because they lower the regularity of the micelles.

Recently ordered mesoporous materials have been synthesized using mixture of surfactants such as cationic/nonionic [25] and cationic/anionic surfactants [26]. These mixtures give rise to mesoporous materials with well defined pore sizes and morphologies. Mixtures of surfactants with different charges allow a wide variety of silica sources and synthetic conditions for the preparation of mesoporous materials. The surface properties of the pore walls is also different according to the type of surfactant used [7].

Since the functional groups of anionic and cationic surfactants have opposite electric charges, they attract each other during the formation of the micelles. The similarity of the non polar carbon chains of the surfactants enhances their miscibility. The mixture of anionic and cationic surfactants, therefore, produces micelles with a stable structure and a uniform size, which can be used as templates for the formation of mesoporous materials. In addition, the insertion of cationic surfactant molecules into the micelles composed of anionic surfactants increases their sizes, resulting in the enlargement of the mesopores of the resultant mesoporous materials.

In this study, we used the mixtures of anionic and cationic surfactants as templates for the preparation of mesoporous materials. The enlargement of the mesopores was observed with increasing the content of cationic surfactant in the micelles of the anionic surfactant. On the other hand, the excessive addition of cationic surfactants to the anionic surfactants interferes with the formation of the mesoporous materials. The role of the cationic surfactant as an enlarging additive for the mesopores was discussed and a model for the structure of the micelles composed of anionic and cationic surfactants was also suggested.

2. Experimental

2.1. Preparation of mesoporous materials

Mesoporous materials were prepared through the hydrothermal reaction of the synthetic mixtures composed of silica sources, surfactants and solvents. The preparation of the mesoporous materials using the mixtures of anionic and cationic surfactant was performed according to the procedure described in the literature [26]. The anionic surfactant used in this study was *N*-lauroyl-L-glutamic acid monosodium salt (Ajinomoto Co. Inc., 99%, abbreviated hereafter as AS), while the cationic surfactant used was hexadecyltrimethylammonium bromide (Johnson Matthey Co., 98%, abbreviated here after as CS).

The surfactants were dissolved in a mixture of deionized water and ethyl alcohol (EtOH, Daejung, 99.8%). The content of EtOH in water was adjusted to be 10 wt%. The formation of micelles from AS and CS was examined by an electrophoretic light scattering spectrophotometer (Otsuka, ELS-8000). The ζ-potential of the micelle was measured with a He/Ne laser with a wavelength of 648 nm.

The synthetic mixtures of the mesoporous materials were prepared by dropping this silica sources onto the surfactant solution which contained micelles. TEOS (Aldrich 98%) and APTES (Aldrich 97%) were employed as the silica sources. The compositions of the synthetic mixtures prepared herein can be described as like xAS:yCS:0.6TEOS:0.4APTES:20EtOH:180H$_2$O, where x and y denoted the molar compositions of the anionic and cationic surfactants, respectively. The molar compositions of AS and CS in the mesoporous materials that were prepared are listed in Table 1. The pH of the synthetic mixtures prepared with AS and CS was adjusted to 9.0 by adding a solutions of hydrochloric acid (Daejung 35%), and these mixtures were aged by stirring them at 25 °C for 24 h. The hydrothermal reaction of these mixtures was carried out at 100 °C for

Table 1
Molar compositions and reaction conditions of synthetic mixtures in the preparation of mesoporous materials

	AS (x)	CS (y)	CS/AS molar ratio	Crystallization temperature (°C)	Gel pH	S_{BET} (m²/g)
MMAS-100[a]	0.100	–	0.00	100	9.0	960
MMAS-80[a]	0.100	0.025	0.25	100	9.0	700
MMAS-67[a]	0.100	0.050	0.50	100	9.0	740
MMAS-57[a]	0.100	0.075	0.75	100	9.0	520
MMAS-50[a]	0.100	0.100	1.00	100	9.0	390
MMAS-33[a]	0.100	0.200	2.00	100	9.0	260
MMCS-100[b]	–	0.050	–	80	11.3	1020

[a] Molar composition of a synthetic mixtures for MMAS:xAS:yCS:0.6TEOS:0.4APTES:20EtOH:180H$_2$O.
[b] Molar composition of a synthetic mixture for MMCS:0.05CS:1.0TEOS:0.5NaOH:5.0EtOH:150H$_2$O.

24 h under autogenesis pressure in an autoclave to produce mesoporous materials. For comparison, a mesoporous material prepared using CS only was synthesized from a mixture composed of TEOS and CS, as described in the literature [27]. The pH of the mixture was adjusted to be 11 by adding a solution of hydrochloric acid before aging it at 25 °C for 24 h. The hydrothermal reaction was carried out at 90 °C. After washing the filtrates with deionized water, they were dried at 100 °C for 24 h. Finally, mesoporous materials prepared using anionic and cationic surfactants were obtained by removing the surfactants by calcination at 550 °C in an air stream for 6 h.

The mesoporous materials prepared using AS and CS were denoted as MMAS-m, where m represents the mole percentage of AS to the total surfactants. A low value of m indicates a large content of CS in the micelles. The mesoporous material prepared using AS only is referred to as MMAS-100, while that prepared using CS only is referred to as MMCS-100.

2.2. Characterization of mesoporous materials

The XRD patterns of the mesoporous materials were recorded on a high resolution X-ray diffractometer (XRD, Rigaku D/MAX Ultima III). Their diffraction patterns were obtained by using Cu Kα radiation with a Ni-filter at 40 kV and 40 mA.

The arrangement of the mesopores of the mesoporous materials was observed by means of a transmission electron microscope (TEM, FEI Co., Tecnai F20) operated at 200 kV.

A volumetric adsorption measurement system (Mirae SI nanoPorosity-XG) was employed to measure the adsorption/desorption isotherms of nitrogen on the mesoporous materials. The samples were evacuated at 200 °C for 2 h before exposing them to nitrogen at 77 K. Their surface areas were calculated by the BET equation and their average pore diameter by the BJH method.

The melting behavior of the assembled surfactants in the mesopores of the mesoporous materials was examined using a differential scanning calorimeter (DSC, TA Instrument, DSC Q100). The temperature of the samples was increased from −40 °C to 160 °C with a ramping rate of 10 °C/min in nitrogen atmosphere.

The ^{1}H–^{13}C cross polarization-magic angle spinning (CP-MAS) NMR spectra were measured on a Bruker AVANCE 500 spectrometer at a spinning rate of 10.0 kHz. The operating ^{13}C frequency was 125.77 MHz with a π/2 rad pulse length of 5.0 μs, a contact time of 2.9 ms, and a recycle delay of 5 s. Two thousand scans were accumulated and ^{13}C chemical shifts were referenced to TMS.

3. Results and discussion

3.1. Preparation of mesoporous materials using the mixtures of AS and CS

The arrangement of the mesopores in the mesoporous materials are strongly dependent upon the types of surfactants used. Fig. 1 shows the XRD patterns of the mesoporous materials prepared with AS and CS. The sharp peak at $2\theta = 2.3°$ of the mesoporous material prepared using CS only, MMCS-100, indicates the presence of highly ordered mesopores. On the other hand, the peak at $2\theta = 2.2°$ of MMAS-100 was neither sharp nor strong compared to that of MMCS-100. It is certain that the mesoporous material
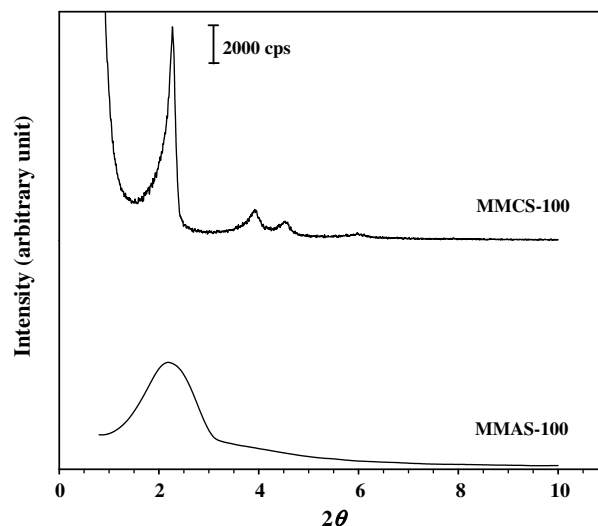

Fig. 1. X-ray diffraction patterns of MMAS-100 and MMCS-100 mesoporous materials.

prepared using AS only also has mesopores, but their uniformity is low compared to the mesoporous materials prepared using CS only. Since the surface charge of micelles composed of cationic surfactant is positive, the partially negative oxygen atoms of the silica chains condensate on them with high regularity, producing a very regular arrangement of mesopores. Since the surface charge of micelles composed of anionic surfactants is negative, the oxygen atoms of the silica chains with their partially negative charges do not interact with the micelles. Only the amine groups of APTES mixed with TEOS interact with the micelles. The hydroxyl groups of APTES and TEOS formed through the hydrolysis of the silyl groups combine with each other, producing silica chains which cover the micelles composed of anionic surfactants. Therefore, the regularity of the silica chains composed of APTES and TEOS covering the micelles of AS must be low. As a result, the mesoporous material MMAS-100 shows a small and wide diffraction peak compared to that of MMCS-100.

The mesoporous materials prepared using the mixtures of anionic and cationic surfactants show different XRD patterns according to the content of CS in the micelles. As shown in Fig. 2, MMAS-80 and MMAS-67 showed diffraction peaks at around at $2\theta = 2°$ whose intensity is comparable to that of MMAS-100. The addition of CS to AS did not inhibit the formation of the mesopores unless its content of CS was too high. The intensity of the peak associated with the mesopores, however, was slightly weak in the case of MMAS-57. The peak became considerably

smaller in the case of MMAS-50, and was not observed at all in the case of MMAS-33. This means that the excessive addition of CS to AS interferes with the formation of the mesoporous materials.

The diffraction peaks associated with the mesopores of the mesoporous materials prepared using the mixtures of AS and CS shifted to a lower value with increasing the content of CS. In the case of MMAS-100 prepared using AS only, the peak appeared at $2\theta = 2.3°$, whereas in the case of MMAS-80 prepared using the mixture of AS and CS it appeared at $2\theta = 1.8°$. This peak was observed at $2\theta = 1.5°$ in the case of MMAS-67 and at $2\theta = 1.0°$ in the case of MMAS-50. The shift of the 2θ value of the peak to a lower value with increasing the content of CS corresponds to the increase in the diameters of the mesopores. The co-addition of CS and AS increases the diameters of the micelles, resulting in the enlargement of the mesopores.

The enlargement of the mesopores of the mesoporous materials prepared using the mixtures of AS and CS is clearly observed on their adsorption isotherms of nitrogen. Fig. 3 shows the adsorption/desorption isotherms of nitrogen on the mesoporous materials at 77 K. Since the amounts of nitrogen adsorbed above a P/P_o ratio of 0.8 were similar on MMAS-100, MMAS-80, MMAS-67 and MMAS-57, it can be concluded that their volumes of mesopores were similar, regardless of the content of CS in the surfactants. On the other hand, the relative pressure at which a sharp increase in the nitrogen adsorption was
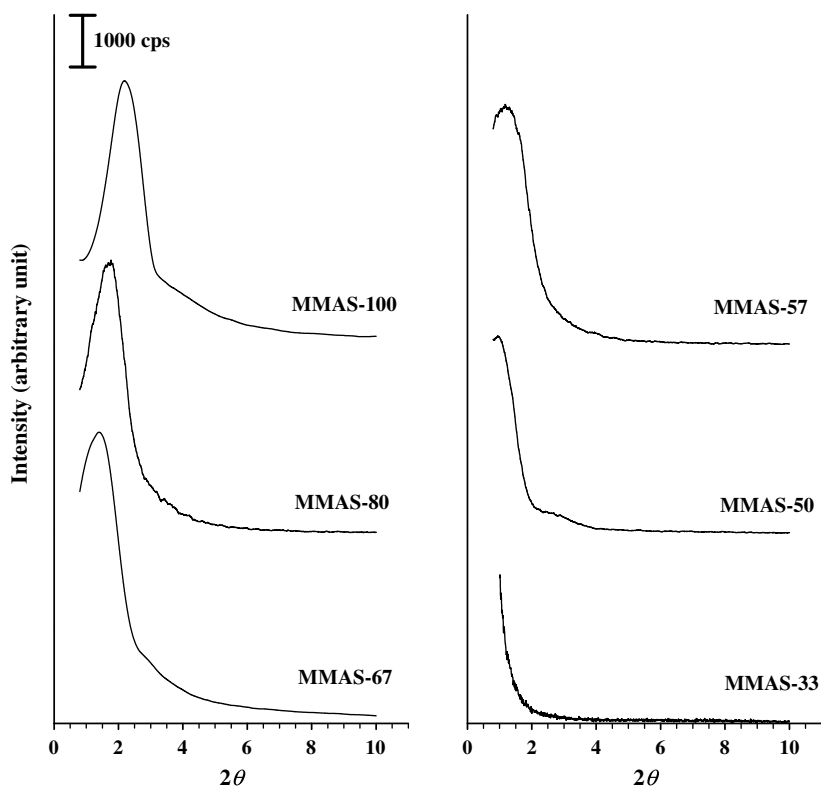

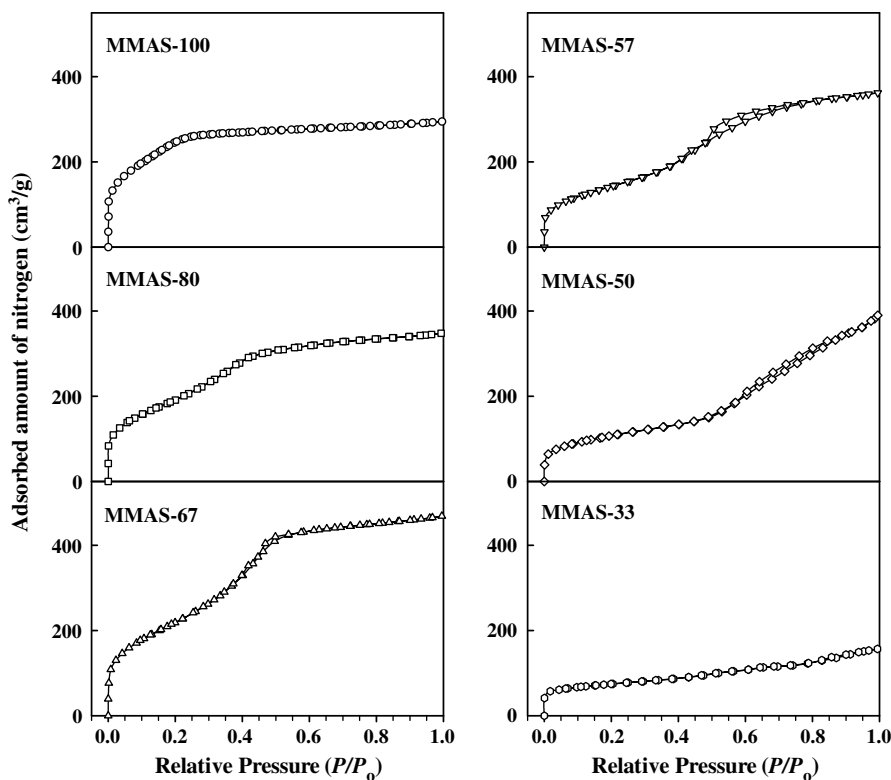Fig. 2. X-ray diffraction patterns of MMAS mesoporous materials.

Fig. 3. N$_2$ adsorption isotherms of MMAS mesoporous materials.

observed shifted toward a higher pressure with increasing the content of CS. The capillary condensation of nitrogen in the mesopores confirms their presence and the shift to a higher pressure with increasing the content of CS indicates the enlargement of the mesopores. However, the flat isotherm of nitrogen on MMAS-33 in the case of the mesoporous materials prepared using the mixture with a high content of CS revealed the absence of mesopores on this material. These isotherms showed that the addition of CS to AS was very effective in increasing the diameter of the mesopores unless the content of CS was excessively high. The specific surface areas of MMAS-100 and MMCS-100 were high around 1000 m^2/g, indicating high regularity of their mesopores. The increase in the added amount of CS lowers the specific surface area of MMAS mesoporous materials prepared. The specific surface area of MMAS-33 prepared from the synthetic mixture containing 77% CS was small as 260 m^2/g. The low specific surface area of MMAS-33 also indicated the absence of mesopores on it.

The pore size distributions of the MMAS mesoporous materials calculated from their adsorption isotherms of nitrogen clearly showed the increase in the diameter of the mesopores caused by the addition of CS, as shown in Fig. 4. The average pore diameter shifted toward a larger value with increasing the content of CS. There were no mesopores on MMAS-33 when content of CS was too high. MMAS-57 had the largest mesopores among the mesoporous materials prepared using the mixtures

of AS and CS. The excessive content of CS in the surfactants in the case of MMAS-57 induced a wide pore size distribution, indicating poor regularity of the mesopores. The contents of AS and CS in the synthetic mixture of MMAS-57 were 0.100 and 0.075 mol per mol of SiO$_2$, respectively. A higher content of AS than that of CS was required to prepare regular mesopores under these synthetic conditions.

The TEM photos of the MMAS mesoporous materials showed the changes in the size and arrangement of the mesopores according to the content of CS. As shown in Fig. 5, MMAS-100 prepared using AS only showed worm-like disordered mesopores with a small diameter. The arrangement of the mesopores was not altered on MMAS-67 prepared using the mixture of AS and CS, but the increase in the diameter of the mesopores was certain. There was no regularity in the arrangement of the mesopores of MMAS-50 prepared using a 1:1 mixture of AS and CS. However, the mesoporous material prepared using CS only, MMCS-100, showed nicely ordered mesopores. No diffraction spot was observed on the MMAS mesoporous materials due to their worm-like disordered mesopores.

3.2. The role of CS in enlarging the mesopores

Since the sizes of the mesopores are determined by those of the micelles composed of surfactants used in the preparation of the mesoporous materials, the increasing in the
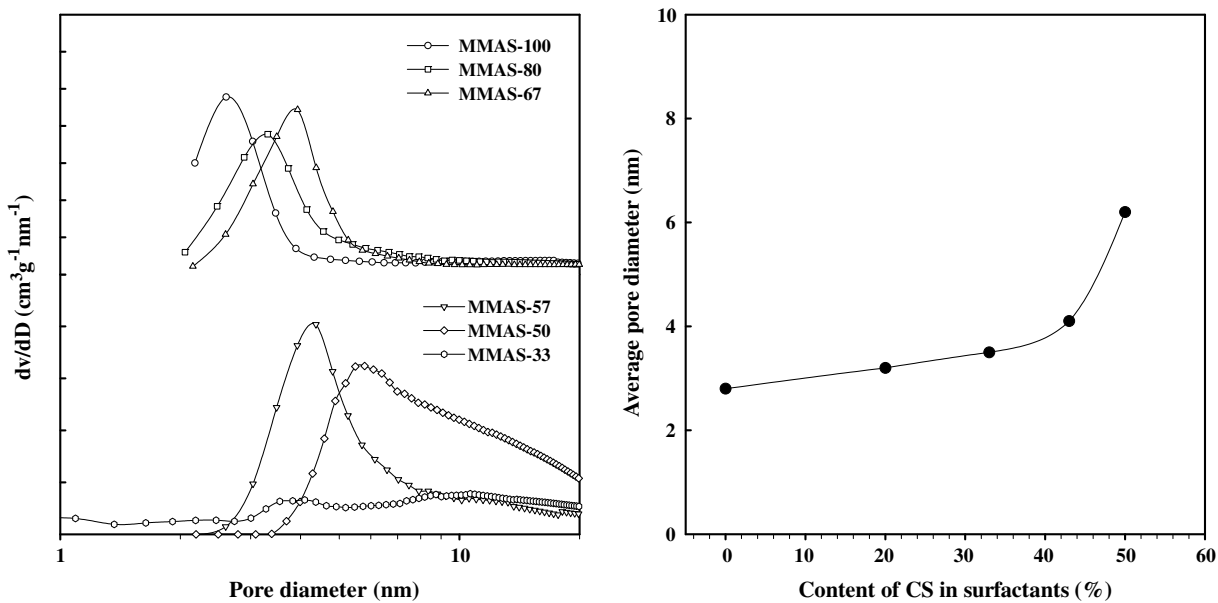
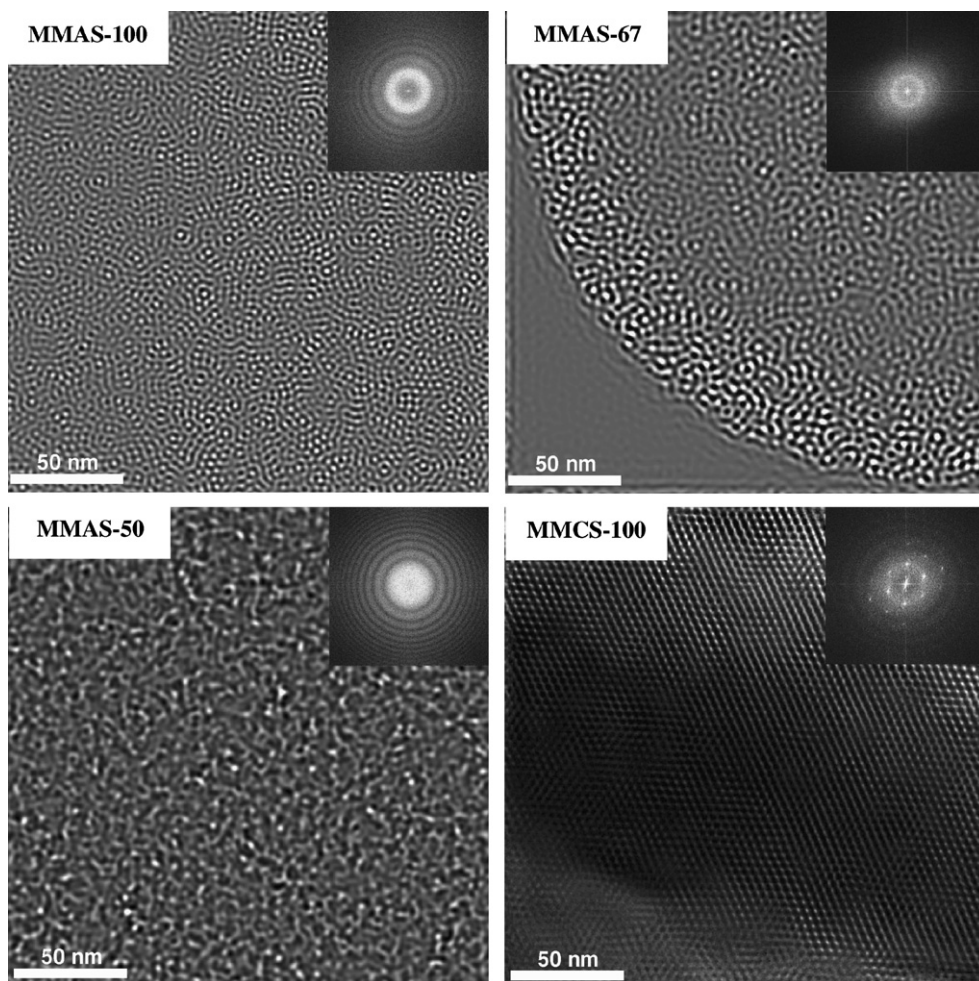Fig. 4. Pore size distributions of MMAS mesoporous materials.

Fig. 5. TEM images of MMAS and MMCS mesoporous materials.

size of the micelles is the primary requirement to obtain enlarged mesopores. Therefore, the variation in the sizes of the micelles with the content of CS provides some clues to the role of CS in enlarging the mesopores. The average diameters of the MMAS mesoporous materials deduced from Fig. 4 were in the ranged of 2.8–6.2 nm. We tried to determine the sizes of the micelles by a conventional electrophoretic light scattering spectrophotometer, but they were too small to be measured.

The electric charges at their ends of AS and CS are opposite, being negative and positive, respectively. The micelles composed of AC and CS also have different surface charge. The addition of CS to the micelles composed of AS, therefore, induced a considerable increase in the ζ-potential as shown in Fig. 6. The micelles composed of AS only showed a negative ζ-potential of −19 mV, but the addition of CS induced a gradual increase in the ζ-potential to −5 mV. This means that the negative surface charge of the micelles composed of AS was partially neutralized by the positive charge of CS. A part of
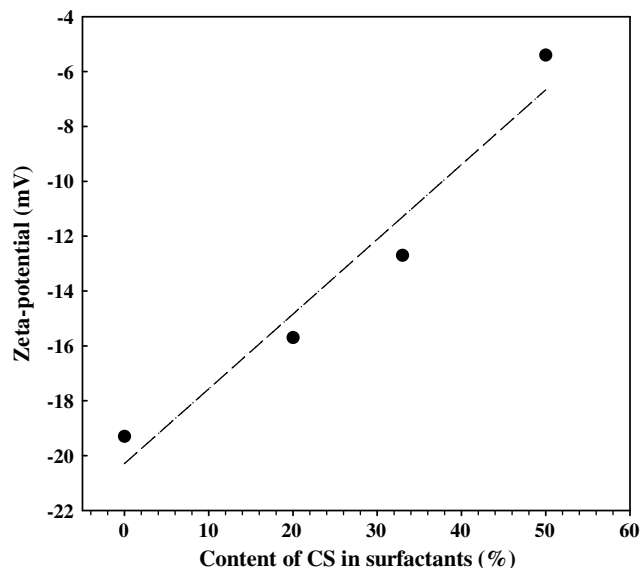

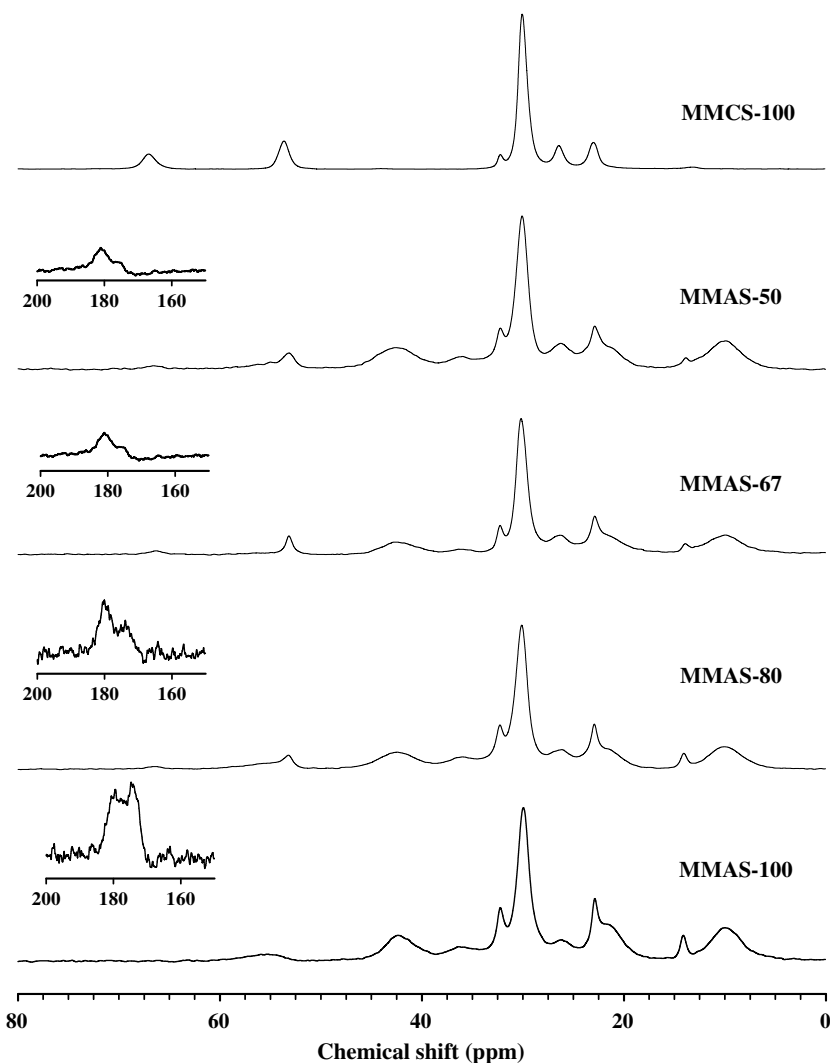Fig. 6. ζ-potentials of micelles formed from the mixtures of AS and CS surfactants.

Fig. 7. ^{13}C MAS NMR spectra of assembled surfactants in the mesopores of MMAS and MMCS mesoporous materials.
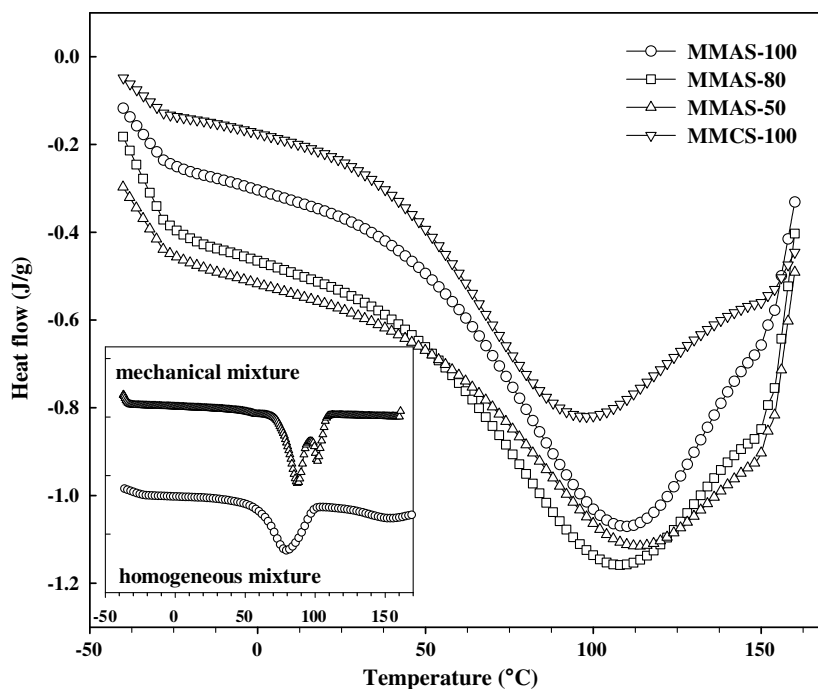
Fig. 8. DSC curves of MMAS and MMCS mesoporous materials.

the carboxylic groups of AS interacts with the quaternary ammonium groups of the inserted CS molecules, increasing the ζ-potential of the micelles.

The interaction between AS and CS during the formation of the micelles can be examined by means of a $^{1}H–^{13}C$ CP-MAS NMR study of the assembled surfactants in the mesopores of the MMAS mesoporous materials. Fig. 7 shows the $^{1}H–^{13}C$ CP-MAS NMR spectra of the assembled surfactants in the mesopores of the MMAS mesoporous materials prior to their calcination. The large peaks at 28 ppm are associated with the carbon atoms of the nonpolar carbon chains. The peak at 55 ppm was ascribed to the carbon atoms combined with the quaternary ammonium groups of CS and the peaks at 14 ppm and 22 ppm to the carbon atoms of the methyl groups at the ends of AS. The large peaks at 28 ppm were the same for all of the samples, regardless of the content of CS, while the peak at 55 ppm increased and the peaks at 22 ppm and 14 ppm decreased with increasing the content of CS in the surfactants. The changes in the peak heights without an associated shift indicated the homogeneous mixing of AS and CS in the formation of the micelles. The considerable decrease in the peak around 180 ppm associated with the carbon atoms of the carboxylic groups with increasing content of CS showed the existence of an interaction between the carboxylic groups of AS and the quaternary ammonium groups of CS. However, the chemical shifts of other peaks associated with the carbon atoms of AS and CS remained unchanged, regardless of the mixing ratio. The polar groups of AS and CS interact with each other, but their carbon chains are assembled in a similar manner to the micelles composed of AS only.

The method of assembling the AS and CS surfactants in the mesopores of the MMAS mesoporous materials influences their melting transition. Fig. 8 shows the DSC curves of the MMAS and MMCS mesoporous materials. The mechanical mixture of AS and CS showed two peaks at 88 °C and 101 °C, but the homogeneous mixture prepared by dissolving them in ethanol followed by drying showed a single peak at 80 °C. The mixtures of AS and CS assembled in MMAS-50 and MMAS-80 also showed single peaks, but the temperatures at the minima were around 110 °C. The single peaks in the DSC curves of the MMAS mesoporous materials indicated the homogeneous mixing of AS and CS in the mesopores. However, the interaction between the surfactant molecules and pore wall increases the temperature for the melting transition by 30 °C.

4. Conclusions

The addition of CS to the synthetic mixtures of mesoporous materials prepared using AS at pH 9 was very effective in enlarging their mesopores. The average diameters of the mesopores increased from 2.8 nm for MMAS-100 prepared using AS to 6.2 nm for MMAS-50 prepared using an equimolar mixture of AS and CS. The CS added to the synthetic mixtures was inserted into the micelles composed of AS, resulting in the enlargement of the size of micelles, but a high content of CS in the surfactants interfered with the formation of the micelles and made it impossible to produce regular mesopores. The proposed structure of the micelle composed of AS and CS was helpful in explaining the enlargement of the mesopores and the increase in the

ζ-potential with increasing the content of the CS in the preparation of mesoporous materials.

Acknowledgments

References

[1] C.T. Lresge, M.E. Leonowiez, W.J. Roth, J.C. Varituli, J.S. Beck, Nature 359 (1992) 710.
[2] A. Corma, N. Fornes, M.T. Navarro, J. Perez-Pariente, J. Catal. 148 (1994) 569.
[3] P.T. Tanev, T.J. Pinnavaia, Science 267 (1995) 865.
[4] S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia, Science 269 (1995) 1242.
[5] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024.
[6] J.M. Kim, S.K. Kim, R. Ryoo, Chem. Commun. (1998) 259.
[7] R. Ryoo, S.H. Joo, J.M. Kim, J. Phys. Chem. B 103 (1999) 7435.
[8] A.E. Garcia-Bennett, O. Terasaki, S. Che, T. Tatsumi, Chem. Mater. 16 (2004) 813.
[9] S. Che, Z. Liu, T. Ohsuna, K. Sakamoto, O. Terasaki, T. Tatsumi, Nature 429 (2004) 281.
[10] S. Namba, A. Mochizuki, M. Kito, Chem. Lett. (1998) 569.
[11] S. Namba, A. Mochizuki, M. Kito, Stud. Surf. Sci. Catal. 117 (1998) 257.
[12] P. Van Der Voort, M. Mathieu, F. Mess, E.F. Vansant, J. Phys. Chem. B 102 (1998) 8847.
[13] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Shephard, S.B. McCullen, J.B. Higgins, J.C. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[14] T. Kimura, Y. Sugahara, K. Kuroda, J. Chem. Sco. Chem. Commun. (1998) 559.
[15] J.L. Blin, C. Otjacques, G. Herrier, B.-L. Su, Stud. Surf. Sci. Catal. 129 (2000) 75.
[16] A. Sayari, M. Kruk, M. Jaroniec, I.L. Moudrakovski, Adv. Mater. 10 (1998) 1376.
[17] Q. Huo, D.I. Margolez, G.D. Stucky, Chem. Mater. 8 (1996) 1147.
[18] A. Sayar, P. Liu, M. Kruk, M. Jaroniec, Chem. Mater. 9 (1997) 2499.
[19] T. Yokoi, H. Yoshitake, T. Tatsumi, Chem. Mater. 15 (2003) 4536.
[20] S. Che, A.E. Garica-Bennett, T. Yokoi, K. Sakamoto, H. Kunieda, O. Terasaki, T. Tatsumi, Nat. Mater. 2 (2003) 801.
[21] A.E. Garica-Bennett, K. Lund, O. Terasaki, Angew. Chem. Int. Ed. 45 (2006) 2434.
[22] A.E. Garcia-Bennett, N. Kuoferschmidt, Y. Sakamoto, S. Che, O. Terasaki, Angew. Chem. Int. Ed. 44 (2005) 5317.
[23] C. Gao, Y. Sakamoto, K. Sakamoto, O. Terasaki, S. Che, Angew. Chem. Int. Ed. 45 (2006) 4295.
[24] C. Gao, H. Qiu, W. Zeng, Y. Sakamoto, O. Terasaki, K. Sakamoto, Q. Chen, S. Che, Chem. Mater. 18 (2006) 3904.
[25] K. Suzuki, K. Kenichi, H. Imai, J. Am. Chem. Soc. 126 (2004) 462.
[26] T. Ohkubo, T. Ogura, H. Sakai, M. Abe, J. Colloid. Interf. Sci. 312 (2007) 42.
[27] I.S. Paulino, U. Schuchardt, Stud. Surf. Sci. Catal. 141 (2002) 93.