Original Paper

Effect of Short-Chain Alkylamine on Micelle Structure in MCM-41 Synthesis Process

Hyoung-Ho LEE[1], Junji SHIBATA[1], Ji-Whan AHN[2] and Hwan KIM[3]

[1]Department of Chemical Engineering, Kansai University, Osaka 564-8680 Japan
[2]Institute of Geoscience & Mineral Resources, Taejon 305-350, South Korea
[3]School of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea

Abstract

It was found that MCM-41 mesostructure can be strengthened by using ethylamine as a mineralizer in our previous study. The addition of ethylamine causes structural changes at the same time. In this report, important factors deciding micelle formation and possible changes in conformation of micelle when small amphiphilic materials co-exist are discussed. Incorporation of short-chain alkylamine in micelle is predicted by the energetical consideration if alkylamine is in neutral state and has an adequately hydrophobic chain part. Ethylamine which is supposed to be neutral in the pH range above pK_a is found to incorporate in micelle when alcohol coexists together and increases hydrophobicity of ethylamine by forming complex with it. The same phenomenon takes place even without the addition of alcohol when alkylamine having a longer alkylchain such as propylamine and butylamine is used because of increased hydrophobicity.

**Key words:** mesoporous, MCM-41, alkylamine, micelle, cosurfactant

Introduction

Various mesoporous silicates[1–4] have been developed since the discovery of MCM-41 by scientists at Mobil Oil Co. in 1992[5,6]. The poor structural stability is a critical weakness which retards their industrial consumption. Various studies are being carried out to solve the problem[7–10]. In our previous report[11], ethylamine (EA) was added to synthesize MCM-41 molecular sieves with high structural stability. The samples have walls approximately 2 nm thick, and consequently do not lose their structure entirely even after heat treatment at 1273 K. Some indications are found that the added ethylamine takes part in the micelle-forming process which decides the final structure of mesoporous materials. This means that the enhancement of structural stability by the addition of ethylamine may be accompanied by some changes in mesostructure.

In this report, more detailed study was carried out to trace a change in mesostructure caused by alkylamine addition and the micelle-forming process is discussed in terms of related energy change to understand the phenomenon. The purpose of this research is to understand the interaction between silicate precursor and alkylamine to achieve structural stability and mesoporosity.

Experimental

The amounts of ethylamine or ethanol (EtOH) were subject to variation, while the cetyltrimethylammoniumbromide (CTAB)/Si was fixed. The composition of synthesis mixture had the following molar ratio;

1Si-xEA-0.5CTAB-100H$_2$O-yEtOH
(x = 0.2, 0.5, 1, 2; y = 0, 1, 2, 4)
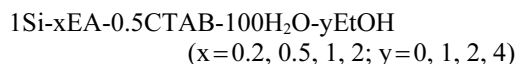
Tetraethylorthosilicate (TEOS), CTAB and EA were obtained from Aldrich. Ethanol was obtained from Haymann. All chemicals were reagent grade and used without further purification. Initially, solution 1, which was composed of H$_2$O, CTAB and EA, and solution 2, which was composed of ethanol and TEOS, were mixed for 1.8 ks individually, and then solution 2 was added to solution 1 in drops for a period of 0.6 ks. The resultant solu-

tion was further stirred for 7.2 ks at room temperature. Then the solution was transferred to a 250 cm³ Teflon bottle with a sealing cap and left in an oil bath filled with silicon oil at 373 K for 1 day. The product was filtered and washed twice with plenty of deionized water, dried in an oven at 353 K overnight, and calcined at 823 K for 21.6 ks to remove the remaining surfactant.

Several short-chain alkylamines (AA) were used in the process without the addition of ethanol. Ethylamine (EA, C=2), propylamine (PA, C=3) and butylamine (BA, C=4) were adopted with the products of Aldrich. The amounts of the alkylamines were varied and CTAB/Si ratio was fixed. The composition of synthesis mixture can be summarized as the following molar ratio;

1Si-xAA-0.5CTAB-100H$_2$O (x=0.2, 0.5, 1, 2)

The synthesis process was the same as described above except for the exclusion of ethanol in this case.

Small-angle X-ray scattering (SAXS) data were collected for all samples on a Bruker GADDS diffraction system with a general area detector at 40 kV and 30 mA with Cu-Kα radiations (λ=1.5418 Å).

Results and discussion

In our previous report[11], it was reported that mesoporous silicate stable in structure with a wall thickness of about 2 nm can be produced by using ethylamine instead of NaOH in the MCM-41 preparation process. Ethanol is added together as a cosolvent in the process. In this study, it is reported that there is a mesostructural change due to ethanol addition.

Figure 1 shows the SAXS patterns of the samples prepared with different amounts of ethanol and ethylamine additions. Distance between pores decreases with an increase in ethylamine amount when ethanol is added together. Alcohol is known to form a complex with amine and substantially increase the hydrophobicity of hydrocarbon
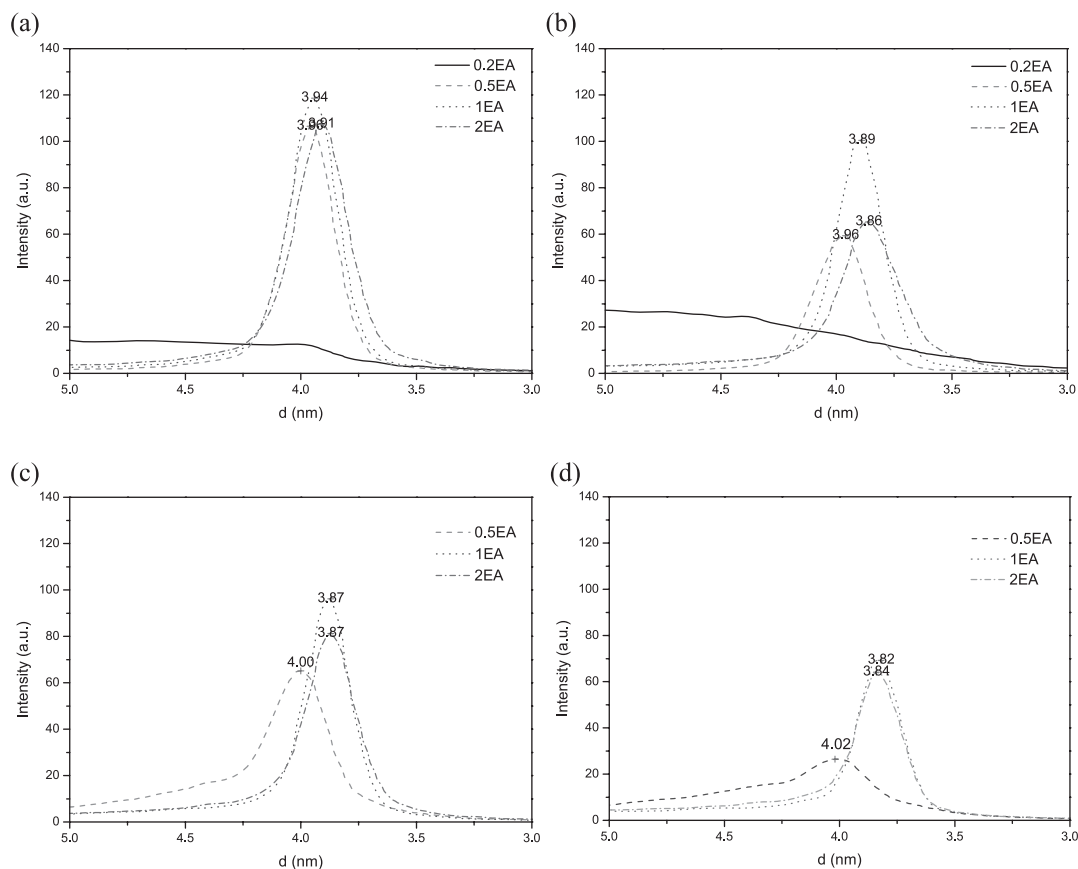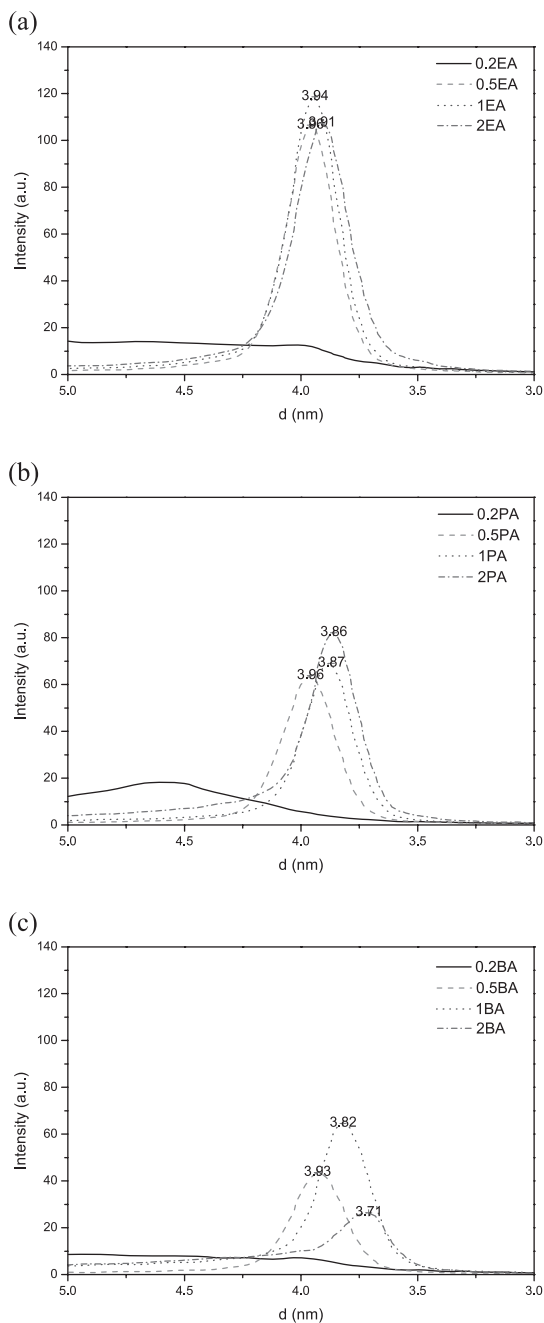

Fig. 1 SAXS patterns of products obtained from initial mixtures of various ethylamine and ethanol concentrations in case of ethanol/Si ratios of (a) 0, (b) 1, (c) 2 and (d) 4.

groups without changing the state of head parts considerably[12–14]. In order to confirm that it is related with hydrophobicity of alkylamine, it is tried to prepare mesoporous silicates using various alkylamines having different hydrophobicity while excluding ethanol. Hydrophobicity increases in the order of ethylamine, propylamine and butylamine. SAXS patterns of the products are shown in Fig. 2. The same tendency of decrease in pore-to-pore distance is noticed with increasing hydrophobicity of alkylamine. It is suggested that alkylamine takes part in templating mesostructure as a cosurfactant. Alkylamine molecules used in this study are smaller than the CTAB molecule. If the alkylamine incorporates into micelles together with CTAB, micelles will contract by small surfactants and consequently resulting mesostructure will contain smaller mesopores. To understand why this phenomenon happens in connection with hydrophobicity of alkylamine, the energy change accompanying micelle formation is discussed.

There are three principal factors related to the energy change of micelle formation. One comes from the interaction between the head groups of surfactants organized into micelle. Head group interactions mainly represent the electrostatic repulsion between the charged units of the cationic surfactants such as CTAB. Energy change attributable to this repulsion, designated as ΔG_h, means an obstacle to the formation of micelle. The other two factors result from the interactions between the tail groups. The hydrophobic and bulky tail groups usually experience both the hydrophobic (van der Waals) attraction and the steric repulsion between them. They are designated as ΔG_{t1} and ΔG_{t2}, respectively. Then, Gibbs free energy change of micelle forming, ΔG_m can be described by the following general equation;

$$\Delta G_m = \Delta G_h + \Delta G_{t1} + \Delta G_{t2}$$

Hydrophobic parts tend to hide themselves from the hydrophilic media by bonding together and the accompanied energy decrease corresponds to ΔG_{t1}. This energy change provides a driving force for micelle formation. There are retarding forces for micelle formation, which are related with ΔG_{t2} and ΔG_h. Micelles containing polymers with highly-charged head groups are unstable. Energy will increase with the charge of head unit, which is described by ΔG_h. Another retarding element against micelle formation is the steric hindrance between tail groups. ΔG_{t2} is always positive and increases with bulkier chains. For a stable micelle, ΔG_m is equal to zero and ΔG_{t1} is the

Fig. 2 SAXS patterns of products obtained with addition of various alkylamines, (a) ethylamine, (b) propylamine and (c) butylamine.

biggest value among the three factors mentioned. When a short-chain alkylamine molecule coadsorbs with a CTAB molecule, conformation of the surfactants constituting micelles changes. Both the hydrophobic attraction and steric hin-

drance between tail groups decrease. This is unfavorable for maintaining micelle because ΔG_{t1}, which provides a driving force for micelle formation, decreases to a greater degree than ΔG_{t2}. If less hydrophobic amines are involved, replacement is less likely to happen. It accounts for the above phenomenon.

Surface charge density of the protonated amine's head group is larger than that of CTAB because the size of the amine head group is smaller than that of CTAB. The coadsorption of protonated ethylamine with CTAB will increase the electrostatic repulsion between head groups, ΔG_h, leading to an unfavorable process. On the contrary, coadsorption of neutral ethylamine will relax the repulsive state by screening the charges between CTAB head groups and decrease ΔG_h, suggesting this could be a desirable process. Therefore, the energy increase by ΔG_{t1} change can be compensated for by ΔG_h decrease with neutral ethylamine. If the ethylamine is positively charged, ΔG_h and ΔG_{t1} both change in an unfavorable way due to the participation of ethylamine in the micelle, and the process will not
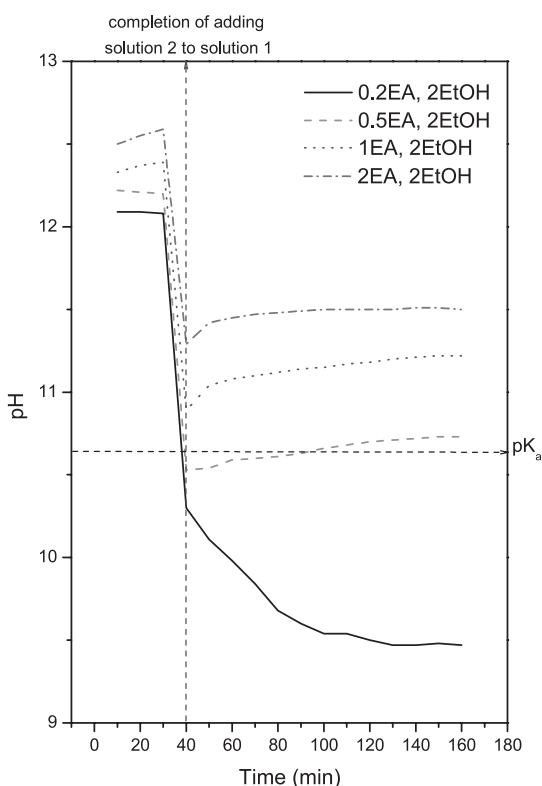
happen.

It can be decided from pH of solution if the included alkylamine is neutral or protonated. Figure 3 shows pH change occurring in the synthesis mixture during the initial stage of reaction. Because micelle formation is known to be completed in a few minutes, it is thought that the solution with EA/Si=0.5 and the solution with EA/Si=1 are below and above pK_a, respectively while micelles are formed. Alkylamine has the following reaction in solution;
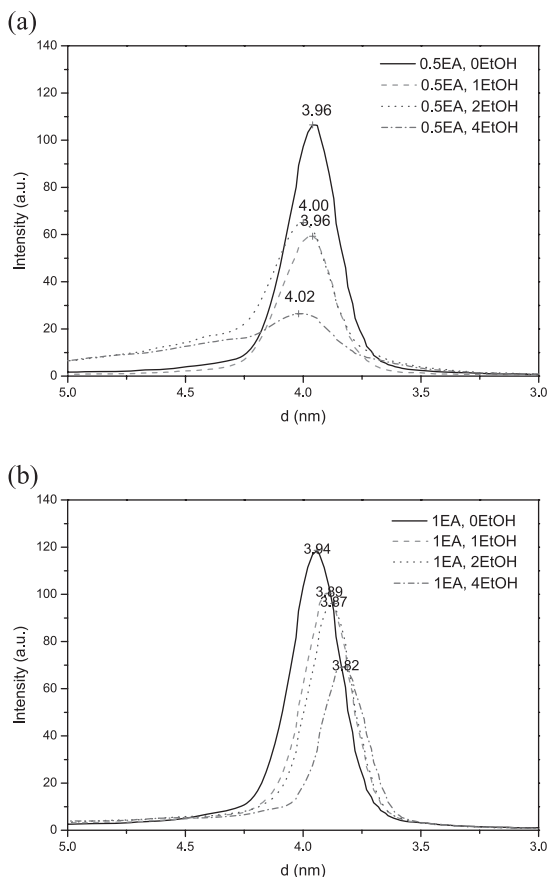
$$RNH_3^+ \rightleftarrows RNH_2 + H^+$$
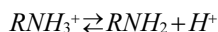
pK_a has the following meaning for the above reaction;

$$pH = \log\frac{[RNH_2]}{[RNH_3^+]} + pK_a$$

It can be deduced from the above equation that neutral species of alkylamine predominates at pH above pK_a and protonated species predominate at

(a)

(b)

Fig. 4 SAXS patterns of products obtained from mixtures of various ethanol concentrations and EA/Si ratios of (a) 0.5 and (b) 1.

Fig. 3 The pH profile during initial mixing in the synthesis mixture of ethanol/Si=2.

Hyoung-Ho LEE, Junji SHIBATA, Ji-Whan AHN and Hwan KIM

(a)

(b)
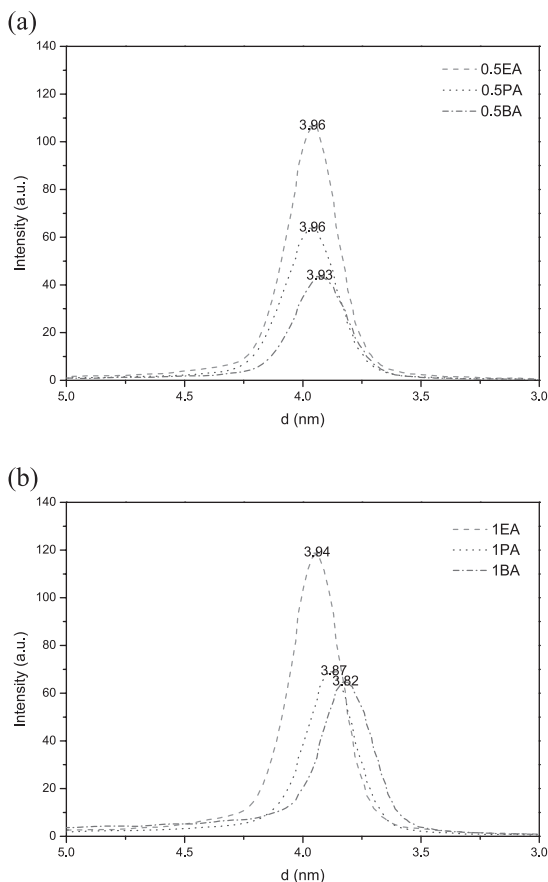
Fig. 5 SAXS patterns of products obtained with addition of alkylamines having different chain lengths when alkylamine/Si ratio is (a) 0.5 or (b) 1.

pH below pK$_a$. 1EA/Si solution contains neutral alkylamine as the major part while neutral alkylamine and protonated alkylamine are almost the same in number in 0.5EA/Si solution.

Figure 4 shows SAXS patterns of samples obtained using different amount of ethanol additions for 0.5EA/Si solution and 1EA/Si solution. There is a definite tendency predicting cosurfactant incorporation, the decrease in pore-to-pore spacings shown in the patterns of 1EA/Si series, which can not be observed in those of 0.5EA/Si. Figure 5 shows SAXS patterns of samples obtained using different kinds of alkylamines for alkylamine/Si=0.5 solution and alkylamine/Si=1 solution. Regardless of difference in hydrophobiciy, every alkylamine has almost the same pK$_a$, and the pH profiles of reaction do not show any difference among these amines. When conditioned at the pH above pK$_a$, in which neutral amines predominate over protonated ones, the interplanar spacings de-

crease according to the chain length of alkylamines. This does not happen for a pH condition not exceeding pK$_a$; no change in the interplanar spacings according to the chain length of alkylamines.

It can be concluded that ΔG_h and ΔG_{t1} have a decisive effect on cosurfactant incorporation of alkylamine; if alkylamine possesses adequate amount of hydrophobicity and its head part is neutral in charge, it incorporates into micelle as a cosurfactant and micelle contracts consequently.

Conclusion

More detailed study was carried out to trace a change in mesostructure caused by alkylamine addition and the micelle-forming process is discussed in terms of related energy change to understand the phenomenon. The aim of this research is to understand the interaction between silicate precursor and alkylamine to achieve structural stability and mesoporosity.

Incorporation of short-chain alkylamine in micelle is predicted by the energetical consideration if alkylamine is in neutral state and has an adequately hydrophobic chain part. Ethylamine which is supposed to be neutral in the pH range above pK$_a$ is found to incorporate in micelle when alcohol coexists together and increases hydrophobicity of ethylamine by forming complex with it. The same phenomenon takes place even without the addition of alcohol when alkylamine having a longer alkylchain such as propylamine and butylamine is used because of increased hydrophobicity.

Acknowledgement

References

1. P.T. Tanev, T.J. Pinnavaia: Science, **267**, pp. 865–867 (1995)
2. S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia: Science, **269**, pp. 1242–1244 (1995)
3. D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky: Science, **279**, pp. 548–552 (1998)
4. R. Ryoo, J.M. Kim, C.H. Ko, C.H. Shin: J. Phys. Chem., **100**, pp. 17718–17721 (1996)
5. C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck: Nature, **359**, pp. 710–712 (1992)

6. 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. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker: J. Am. Chem. Soc., **114**, pp. 10834–10843 (1992)

7. J.M. Kim, S. Jun, R. Ryoo: J. Phys. Chem., **B103**, pp. 6200–6205 (1999)

8. Y. Liu, W. Zhang, T.J. Pinnavaia: Angew. Chem. Int. Ed., **40**, pp. 1255–1258 (2001)

9. Z. Zhang, Y. Han, F.S. Xiao: J. Am. Chem. Soc., **123**, pp. 5014–5021 (2001)

10. D.T. On, S. Kaliaguine: Angew. Chem. Int. Ed., **41**, pp. 1036–1040 (2002)

11. Hyoung-Ho Lee, Ji-Whan Ahn, Hwan Kim: Resources Processing, **51**, pp. 20–24 (2004)

12. M. Kruk, M. Jaroniec, A. Sayari: Microporous Mesoporous Mater., **35–36**, pp. 545–553 (2000)

13. A. Vidyadhar, K. Hanumantha Rao, I.V. Chernyshova: Colloids and Surfaces A: Physicochem. Eng. Aspects, **214**, pp. 127–142 (2003)

14. M.B.N. Monte, J.F. Oliveira: Minerals Eng., **17**, pp. 425–430 (2004)