

Conversion of Fly Ash into Mesoporous Aluminosilicate

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Mesoporous aluminosilicate in the hexagonal phase (MCM-41) has been synthesized from fused fly ash solutions and cationic cetyltrimethylammonium bromide (CTAB) surfactants. We provide direct evidence that an MCM-41 aluminosilicate with a homogeneous chemical composition of Si/Al = 13.4 can be prepared with cationic surfactant. Our results indicate that coal combustion byproducts can be utilized for producing mesoporous molecular sieves even though they contain significant amounts of impurities.

Introduction

Mesoscopic inorganics can be processed by mixing cationic surfactants with an inorganic precursor in aqueous solutions.¹ After calcination, the organic phase is pyrolyzed and the remaining mesoporous inorganic phase contains periodic nanometer size pores that are either hexagonally (MCM-41) or cubically arranged (MCM-48). Most of the mesoporous molecular sieves made thus far have been aluminosilicates or silicates.^{2–4}

The original process studied by the Mobil group used cationic surfactant and anionic inorganic species and produced mostly silicate and aluminosilicate mesoporous materials.¹ The silicon and aluminum sources for these mesoporous materials include sodium silicate, tetraethoxysilane, colloidal silica, Catapal alumina, and sodium aluminate.^{2–4} The wide variety of silicate and aluminate precursors used to form mesoporous materials indicates that the formation is not sensitive to the silicate and aluminum sources.

Fly ash, which is a byproduct of coal burning, contains mostly aluminosilicates. Recently, several authors have studied the conversion of fly ash into zeolites.^{5–7} Shigemoto et al.⁸ increased the yield of zeolites by first fusing the fly ash with NaOH. The reaction of fly ash with NaOH produced a large amount of sodium silicates which dissolve readily in aqueous solutions. In fact, the fusion of alkali-metal hydroxide with aluminosilicates has been a common technique for dissolving Si, Al, and many metallic species for chemical analysis.⁹ More recently, Chang and Shih applied the fusion method for converting a variety of ashes from several utility power plants to zeolites.¹⁰

In this paper, we report our results on converting fly ash into mesoporous molecular sieves. Due to their uniform molecular pore sizes and large surface areas, the mesoporous materials can be very useful for a wide range of applications such as molecular sieves, adsorbents, and catalysts.¹¹ Therefore, converting fly ash into mesoporous materials not only eliminates the disposal problem of fly ash but also turns an otherwise waste material into a useful one.

Because fly ash contains a significant amount of aluminosilicates and a small amount of various metal

oxides, the formation of mesoporous phase from fly ash is not as straightforward as in the case with pure chemicals. For example, the Si/Al molar ratio plays an important role in forming MCM-41 aluminosilicates. Previously, Chen et al.³ showed that MCM-41 aluminosilicate can only be prepared with a Si/Al molar ratio higher than 29 using CTAB surfactant. Since then, there have been several publications^{12–18} indicating the existence of MCM-41 aluminosilicate with a Si/Al ratio lower than 29. However, the Si/Al ratios quoted in most of these publications^{12–17} were the initial ratios in the precursor solutions rather than the actual Si/Al ratios in the MCM-41 phase. Due to the lack of direct microscopic chemical composition evidence, it is inconclusive that Al has been incorporated into the framework of MCM-41. To be conclusive, it is essential to show that aluminum has been incorporated into silica as a solid solution and is not present as segregated alumina particles together with a Si-rich mesoporous phase. Recently, Kloetstra et al.¹⁸ used TEM with EDXS elemental analysis to measure the Si/Al molar ratios in the MCM-41 phase. It was found that the Si/Al ratio of the MCM-41 phase can be as low as 12.

In addition, Vaudry et al.¹⁹ showed that pure alumina mesoporous materials can be synthesized by reacting aluminum alkoxide and carboxylic acids with controlled amounts of water in low-molecular-weight alcoholic solvents. Also, Yada et al.²⁰ showed that the alumina mesoporous phase can be synthesized with a dodecyl sulfate surfactant. At this point, it is not clear that these pure alumina mesoporous materials were actually MCM-41 phases. Furthermore, the surfactants used in these studies were very different from the cationic surfactant CTAB that was used in the present study. Therefore, the effect of how Si/Al ratios on the formation of MCM-41 materials is not completely clear.

Due to the fusion of sodium hydroxide with fly ash, the effect of Na concentration becomes important, perhaps more so than in the case with pure chemical precursors. Although it is known that a high Na content enhances the formation of zeolites,⁸ there is no systematic data concerning the effect of Na on the formation of the MCM-41 phase.

Experimental Procedure

The raw materials for the experiments were class F fly ash from the Conemaugh power plant (Pennsylvania

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Table 1. Chemical Compositions of Untreated Fly Ash and the Precipitates Shown in Figure 4

elements	atom %			
	fly ash (Conemiaugh)	MCM-41	fibril	particle
Si	55.59	91.01	93.81	95.22
Al	31.41	6.8	4.5	3.26
Fe	18.95	0.8	0.44	0.13
Na	0.88	0	0	0
K	3.06	0.17	0.16	0.14
Ca	1.28	0.34	0.22	0.29

Table 2. Concentrations of Si, Al, and Na in Solutions I and II Prepared from Conemiaugh Ash

	Si, ppm	Al, ppm	Na, ppm
I	2740	528	46 000
II	572	161	12 000

Electric Company, New Florence, PA). The chemical composition of the fly ash is shown in Table 1 as determined by energy-dispersive X-ray spectroscopy (EDXS; LINK-ISIS, Oxford Instruments, Concord, MA) in a scanning electron microscope (SEM; 1830 Amray, Bedford, MA). The surfactant used was $C_{16}H_{33}(CH_3)_3NBr$ (cetyltrimethylammonium bromide, CTAB).

Because larger amounts of Si and Al species can be dissolved by the fusion method, we adopted the fusion approach in this study. The fusion process began by mixing fly ash with NaOH powder in a weight ratio of fly ash to NaOH of 1:1.2. The mixed powders were treated at 550 °C for 1 h in air using a heating rate of 1 °C/min from room temperature. After fusion, the powder was mixed with water in a weight ratio of 0.20 to produce the fused fly ash solutions. The fused fly ash solutions were aged for 1 day at room temperature and ambient pressure with stirring. The fused fly ash did not dissolve completely after 1 day of aging. The supernatant of the solution was separated from the sediment by centrifugation. This supernatant solution is referred to as I from hereon. To examine whether all soluble species have dissolved, a second supernatant solution, referred to as II from hereon, was obtained by centrifuging the solution prepared from the sediment of I and water. The chemical compositions of I and II are determined by atomic absorption spectroscopy (Varian AA-1275 Series), and the results are shown in Table 2 for comparison. It can be seen that the concentrations of Si, Al, and Na in II are smaller than that in I. Also, the Si/Al molar ratio changes from 5.2 in I to 3.6 in II. The surfactant solution was prepared by mixing 0.755 g of surfactant, $C_{16}H_{33}(CH_3)_3NBr$, with 2.265 g of distilled water at room temperature. After the surfactants were fully dissolved, 0.5 mL of 4.96 N NH_4OH solution was added to the surfactant solution, and the solution was diluted by adding 13.85 mL of distilled water. The aqueous surfactant solution was then added to 40 mL of supernatant solution and stirred for 30 min. The pH value of the mixed solutions was typically 12.8. The mixed solutions were then hydrothermally cured at 115 °C in a pressure chamber. Powder samples were taken out at various curing times and were washed with distilled water and centrifuged twice. The washed powders were dried between 60 and 80 °C for 12 h. The powders were then heat-treated to 540 °C with a heating rate of 1 °C/min and soaked at 540 °C for 7 h. The structure of the powders was studied by X-ray diffraction (XRD) using ground powders, and the surface area measurements were done by a surface area analyzer

(NOVA 2200, QuantaChrome). Further, the structure, size, morphology, and local chemical composition of the mesoporous aluminosilicates were examined by analytical transmission electron microscopy (TEM; CM 200 FEG, Philips Electronics) attached with an EDXS (PGT, 2000, Princeton Gamma Tech.). EDXS analysis was typically performed at 200-keV accelerating voltage with a 50-nm spot size. TEM samples were prepared by dipping a Cu TEM grid, coated with holey carbon film, into a colloidal suspension of particles dispersed in methanol which were then air-dried and stored in a vacuum chamber.

Results and Discussion

Both I and II were studied for the formation of mesoporous materials. The MCM-41 phase began to form after 100 h of hydrothermal treatment using II. The XRD pattern of the precipitate heat-treated at 115 °C for 150 h and calcined at 540 °C for 7 h is shown in Figure 1. Figure 1 shows that the MCM-41 phase is formed in the mixed solution. The XRD patterns in higher angles ($2\theta > 11^\circ$) indicate that besides the MCM-41 phase there are amorphous silicates in the system. In contrast, using I, after 150 h of heat treatment, no MCM-41 phase was formed. Clearly II is a better solution for producing the MCM-41 phase than I. The reason for the formation of MCM-41 phase in II instead of I may be discussed in terms of the chemical compositions as shown in Table 2. One difference between the two solutions is the Si/Al molar ratio. Different Si/Al molar ratios in the precursor may affect the formation of the MCM-41 phase. In a recent study using pure chemicals,²¹ we found that MCM-41 aluminosilicates can be formed from precursor solutions with Si/Al molar ratios ranging from 1.35 to the limit of pure Si. Therefore, the higher Si/Al molar ratio in I is not expected to prohibit the formation of MCM-41. It is more likely that the difficulty for the formation of the MCM-41 phase in solution I is related to the high concentration of Na ions. A high Na ion concentration in the precursor solutions has been known to favor the formation of zeolites,⁸ which may hinder the formation of MCM-41 phase. In our model study of aluminosilicate MCM-41, the Na concentrations are typically on the order of 10 000 ppm, similar to II. The concentration of ions other than Si, Al, and Na in I and II was not measured except for Fe. It was found that the concentration of Fe in I was negligibly small. We suspect that the low concentration of Fe in I is due to the low solubility of Fe in basic condition. It should be noted that the rate of formation of the MCM-41 phase from II is slower than that of using pure chemicals.¹⁻³ It is speculated that the slower rate of formation in II than in pure chemical solutions is due to the low Si concentration (~600 ppm) in II compared to typical Si concentration (~60 000 ppm) in pure chemical solutions.

It should be emphasized that the fusion of fly ash with NaOH is critical for the formation of mesoporous materials. Previously we have studied the possibility of forming mesoporous materials with fly ash, NaOH solutions, and surfactants. No mesoporous materials were found. It was only when we fused fly ash with NaOH that mesoporous materials are formed. Clearly, the much higher concentration of Si and Al species in the solutions of fused fly ash promotes the formation of mesoporous materials.

The nitrogen adsorption/desorption isotherms for the MCM-41 phase obtained from II heat-treated for 150

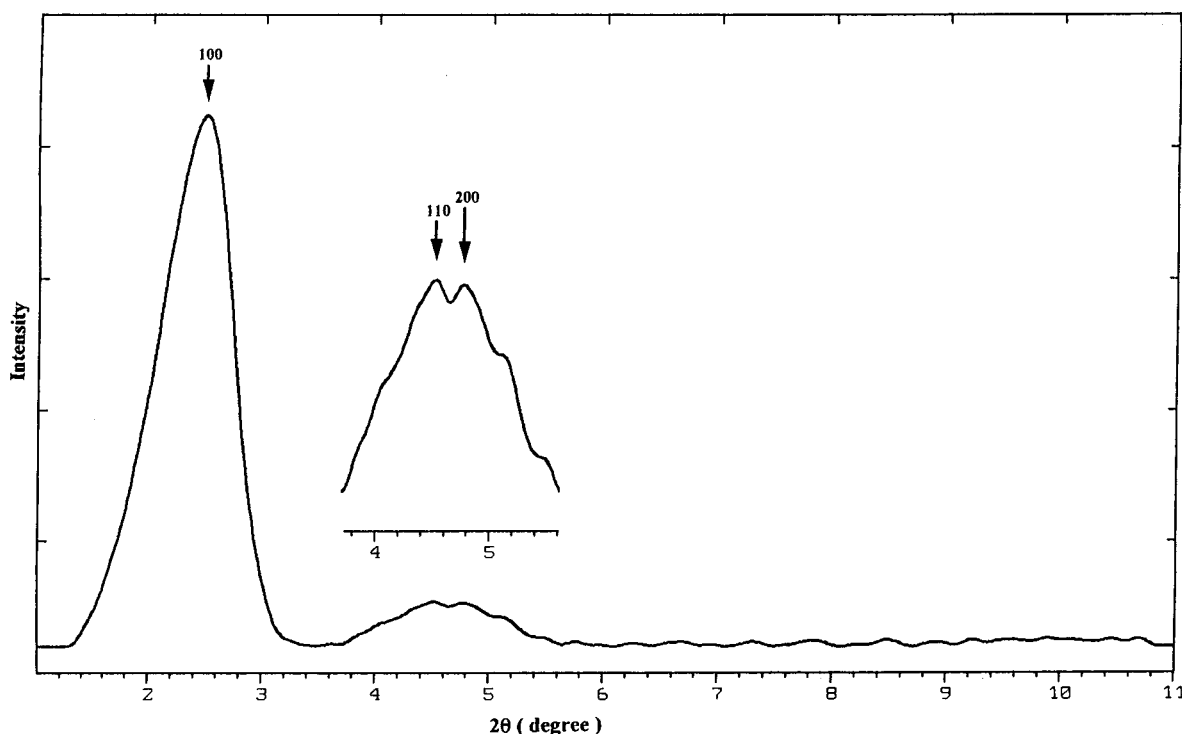


Figure 1. XRD pattern of the aluminosilicate MCM-41 phase precipitated after 150 h of curing. The 110 and 200 peaks were amplified 5 times in the insert.

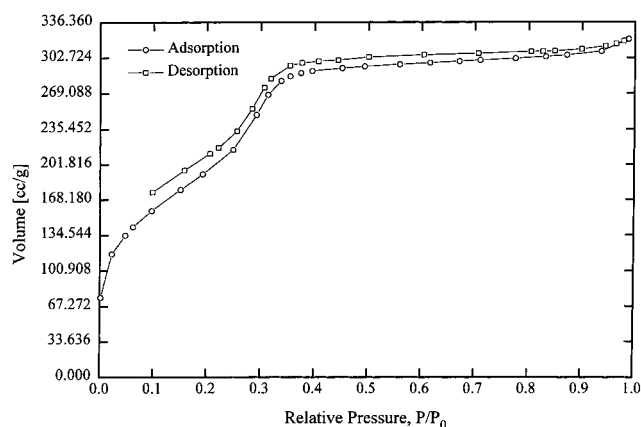


Figure 2. N₂ adsorption and desorption isotherms for the MCM-41 phase. Squares indicate the desorption data and circles the adsorption.

h, as shown in Figure 2, are typical of the MCM-41 phase with a surface area of 735 m²/g. From the TEM study, we find that the MCM-41 phase covers about 40–50% of the area of the sample. The rest are particles and fibrils, as shown in Figure 4. Therefore, the true surface area of the MCM-41 phase may be as high as 1470 m²/g, in close agreement with the results presented in the review paper by Sayari.²² The pore size distribution of the MCM-41 phase is quite uniform and is shown in Figure 3 with an average pore size of 27.4 Å. By using the d_{100} spacing of 35.5 Å obtained from the XRD, we calculated the lattice constant of the hexagonal phase to be $a = (4/3)^{1/2} d_{100} = 41.0$ Å. Therefore, the pore wall thickness is estimated to be 14.0 Å. The TEM image in Figure 4 shows a large piece of plate with particles and fibrils embedded in it. The large plate is the MCM-41 material, and its TEM image at higher magnification is shown in Figure 5. Clear hexagonal patterns of the pores can be seen in Figure 5. The TEM image shows that the size of the pores and the distances between the

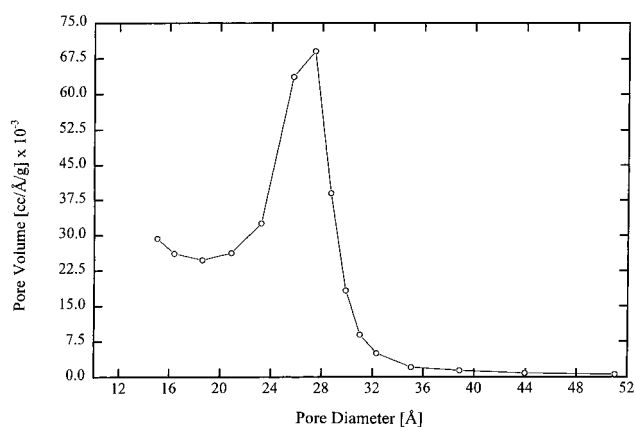


Figure 3. Pore size distribution of the MCM-41 phase.

pores vary in different parts of the micrograph. These variations correspond to the different projection angles from the different areas. As an attempt to see if the lattice constant measured from XRD is reasonable, we measured the lattice constants of the hexagonal patterns from various regions and obtained an average value. The average lattice constant is found to be 39.5 Å, which is slightly lower than the 41.0 Å obtained from XRD.

EDXS analysis of the various regions in Figure 4 was performed, and the results are summarized in Table 1. The MCM-41 aluminosilicates have an average Si content of 91.0 atom %, Al of 6.8 atom %, Fe of 0.8 atom % and small amounts of Ca, K, S, and P. The data were averaged over 10 locations taken from 3 different plates. An interesting observation is that there is no Na detected from either the MCM-41 phase, the fibrils, or the particles. This observation is consistent with the results mentioned earlier that II is more favored to form MCM-41 than I because I is much richer in Na than II. It appears that the MCM-41 phase is incompatible with

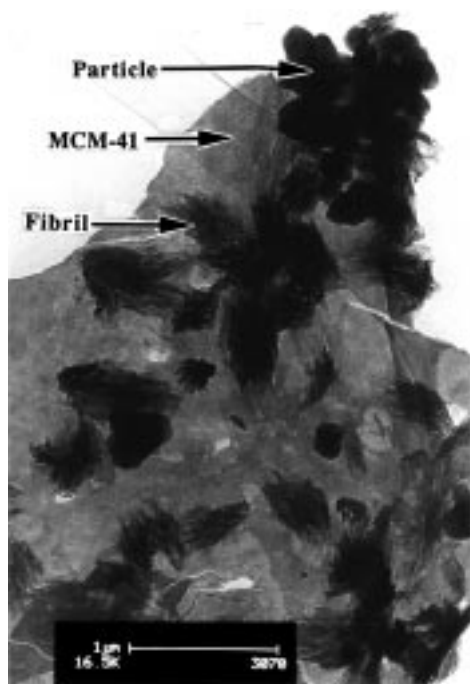


Figure 4. TEM image of precipitates from the supernatant of fused fly ash solution. The lighter piece of plate contains darker particles and fibrils within it. The lighter piece of plate is the MCM-41 phase and is further magnified in Figure 5.

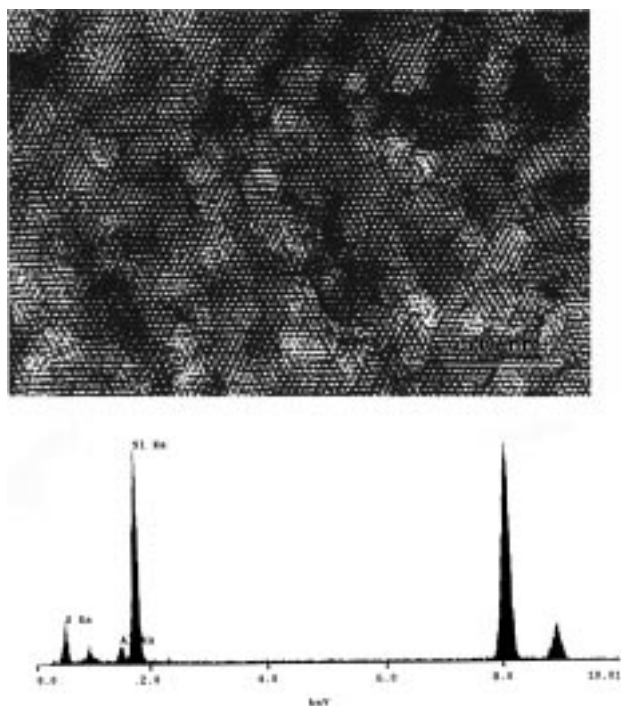


Figure 5. TEM image of the MCM-41 phase precipitated from the supernatant of fused fly ash solution. The EDXS results are also included. The unlabeled peaks belong to the Cu grid.

Na. The Na-free MCM-41 phase may be useful for catalytic applications since Na can poison the Brønsted acid sites in the aluminosilicates.²³ The incorporation of Al in the MCM-41 phase may also be studied by ²⁷Al MAS NMR. However, due to the fact that the precipitates contain several phases including the MCM-41 phase, fibril, and particle, the results of the NMR study cannot provide direct evidence of Al incorporation in the MCM-41 phase. Other phases contain Al as well. TEM

EDXS is more appropriate for the analysis of local chemical composition in the present situation.

The Si/Al molar ratio of the mesoporous aluminosilicates is 13.4, which is much higher than the Si/Al = 1.73 in the fly ash. Apparently the dissolution of silicates is more efficient than that of the aluminum species during the synthesis. The abundance of Si in the supernatant of the fused fly ash solution can be seen from the strong sodium silicate peaks in the XRD pattern of fused fly ash. The chemical compositions in the particles and fibrils that were embedded in the MCM-41 plates are also shown in Table 1. Both the particles and fibrils have a higher Si content than the MCM-41 plate. However, the microstructure of the particles and fibrils was not characterized in the present study. It should be noted that the results in Table 1 and Figures 4 and 5 belong to the precipitates formed in the supernatant. There are still a significant amount of fly ash in the sediment of the fly ash solutions. It is expected that the Al content in the sediment will be much higher than those shown in Table 1. Due to the long curing time, it is not surprising that other phases such as fibrils and particles form in the solution. The fact that fibrils and particles have a higher Si content than the MCM-41 phase indicates that they may be precipitated from regions with higher Si concentrations.

Previously, Chen et al.³ showed that an aluminosilicate MCM-41 can be prepared with a Si/Al ratio as low as 29 without observing the presence of octahedral aluminum. Since then, several publications^{9,10,12–17} indicated the existence of aluminosilicate MCM-41 with Si/Al ratios lower than 29. More recently, Kloetstra et al.¹⁸ showed that the Si/Al molar ratio of MCM-41 aluminosilicates can be as low as 12. The results in Figure 5 show that an MCM-41 aluminosilicate with a Si/Al = 13.4 has been synthesized. The Si/Al ratio of the MCM-41 phase synthesized from fly ash is close to that found by Kloetstra et al.¹⁸ Furthermore, the standard deviation in the Si/Al ratio from the 10 locations that were measured in the sample is only 1.1%, indicating that the Si/Al ratio is quite uniform throughout our sample. Therefore, we not only have converted MCM-41 aluminosilicates from fly ash but also have provided direct evidence that MCM-41 aluminosilicates with a Si/Al = 13.4 can be formed with CTAB surfactant. It is conceivable that, with the recent results of the formation of pure alumina using carboxylic acids¹⁹ or dodecyl sulfate²⁰ as surfactant, MCM-41 aluminosilicates with even lower Si/Al ratios can be made with suitable surfactants.

Table 1 shows that a small amount of impurities is either incorporated into or located in the channels of the MCM-41 aluminosilicates. The impurities include Fe, Ca, K, S, and P. The fact that MCM-41 can be synthesized from fly ash indicates that the impurities in the fly ash are not detrimental to the formation of MCM-41. Therefore, even though there may be significant amounts of impurities in the fly ash, the mesoporous aluminosilicate MCM-41 phase can be synthesized.

In conclusion, it is shown that coal combustion byproducts can be utilized for producing mesoporous molecular sieves with periodic pore structures. Furthermore, direct evidence of Al incorporation in the MCM-41 framework is provided with a homogeneous chemical composition of Si/Al = 13.4.

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