

Mechanism and Morphological Change in Zeolite Formation from Coal Fly Ash

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ABSTRACT

Coal fly ashes include much silica and alumina. They can be converted to zeolites by alkaline treatment. The fly ash was mixed with 2M NaOH aqueous solution and refluxed at about 100°C. The product was identified as zeolite Na-P1 by X-ray diffraction. In the course of reaction, the Si and Al concentrations in the solution and solid phases were analyzed. There was an induction period before the zeolite was detected by XRD. At the early stage of reaction, some amorphous deposits were observed on the surface of fly ash particles by SEM and TEM. The solid state NMR analysis suggested that an amorphous aluminosilicate gel formed as an intermediate and it changed into zeolite crystal.

Key words: Zeolite, Coal fly ash, Hydrothermal synthesis, Morphology, Mechanism

1. INTRODUCTION

A huge amount of coal fly ash has been exhausted from coal-firing power station, and recycling of this ash is an emergent subject. Coal fly ash includes a large amount of silica and alumina. They can be converted into zeolite by a hydrothermal reaction in alkaline solution [1-4]. This is a low-temperature process, requiring less energy than high-temperature processes, and the produced zeolite is useful for ion exchangers and gas adsorbents. However, the type and yield of synthesized zeolite depend on the composition of fly ash source and the reaction conditions. The formation mechanism of zeolite from the fly ash is not clear. In order to synthesize a specific zeolite from any fly ash source, the formation mechanism should be clarified. The purpose in this study is to investigate the formation process of zeolite from coal fly ash.

2. EXPERIMENTAL PROCEDURES

Table 1 summarizes the composition of used fly ash. The total content of SiO₂ and Al₂O₃ was 73wt%. Quartz and mullite were included as crystalline phases,

and aluminosilicate glass as amorphous phase. The particle size was 0.5-100µm. Coal fly ash was treated by conventional refluxing method. Coal fly ash (10g) was mixed with 2M NaOH aqueous solution (80ml) in a 300ml Teflon vessel and refluxed with stirring in a thermostatic oil bath. The oil bath temperature was 120°C. The reacting solution was sampled in the course of reaction and the concentrations of Si and Al in the supernatant liquid were analyzed by ICP-MS. After refluxing, the powder product was centrifuged, washed by deionized water, and dried at about 100°C. The particle morphology was observed by SEM and TEM. The product was analyzed by XRD and ²⁷Al NMR. The change in the amount of synthesized zeolite was investigated with the peak intensity ratio of zeolite to MgO used as standard. The cation exchange capacity (CEC) was measured for NH₄⁺ and Ca²⁺.

Table 1 Composition of coal fly ash (wt%)
bulk of fly ash

SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	Others
38.3	34.8	11.0	8.1	7.8

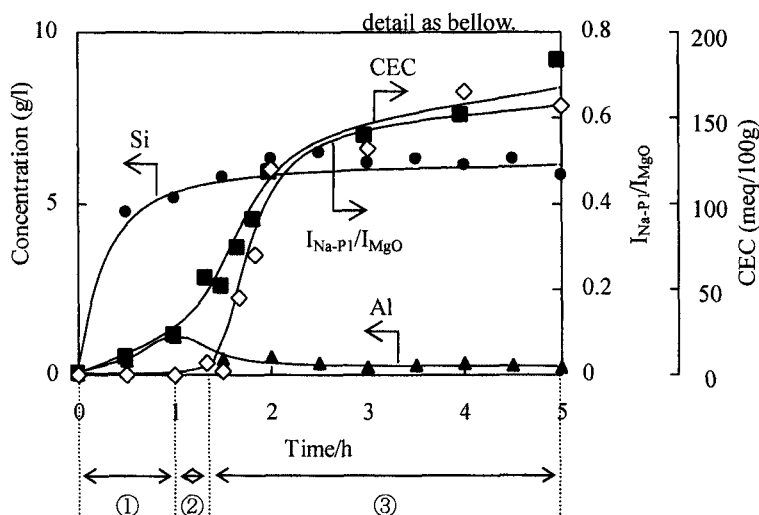


Fig. 1 Analyses of liquid and solid phases in the course of reaction.

3. RESULT AND DISCUSSION

3.1 Formation Process of Zeolite

When coal fly ash was treated with 2M NaOH, zeolite Na-P1 ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$) formed. By XRD, the peaks of quartz and mullite were still remained after alkaline treatment. To investigate the formation process of zeolite from coal fly ash, the liquid and solid phases in the course of reaction were analyzed. Figure 1 shows the change of Si and Al concentrations in liquid phase, zeolite content and CEC value for NH_4^+ of solid product with time. The Si concentration increased rapidly and became constant at the early stage of reaction. The Al concentration reached the maximum at 1h and then decreased. After the Al concentration started to decrease, the XRD peaks of zeolite Na-P1 appeared and the amount of formed zeolite increased rapidly during 1-2h, and then gradually after 2h. On the other hand, the CEC for NH_4^+ increased immediately after the reaction was started. These results suggest that the formation process of zeolite from coal fly ash is explained as follows: 1) dissolution of the fly ash into alkaline solution (Step 1 in Fig.1), 2) formation of intermediate gel because zeolite Na-P1 was not observed by XRD but the CEC for NH_4^+ increased at the early stage of reaction (Step 2 in Fig.1), 3) nucleation and crystal growth of zeolite (Step 3 in Fig.1).

In order to confirm the formation steps, the solid phase at the initial stage of reaction was examined in

3.2 Comparison between XRD and CEC

The CEC for Ca^{2+} was measured and compared with the changes in the amount of zeolite detected by XRD and the CEC for NH_4^+ (Fig.2). Before 60min, the XRD peaks of zeolite Na-P1 did not appear. The coal fly ash itself had a small CEC for Ca^{2+} . The CEC for Ca^{2+} was constant until 60min, whereas that for NH_4^+ increased. These results indicate that NH_4^+ ion was adsorbed on an amorphous aluminosilicate at the early stage. After 60min, the amount of zeolite Na-P1 and the CEC increased significantly with time. This is due to the crystallization and crystal growth of zeolite.

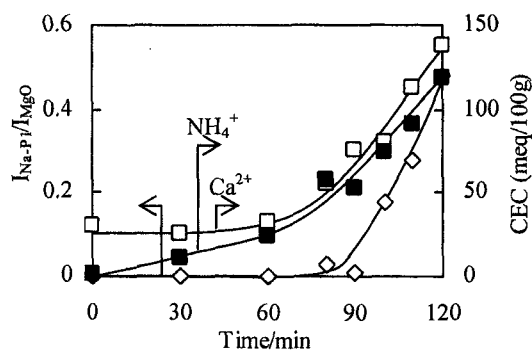


Fig. 2 Change in zeolite yield and CEC with time.

3.3 ^{27}Al NMR

Figure 3 shows the ^{27}Al NMR spectra of treated fly ash. Al has three types of coordination by oxygen. The peaks are located at 0, 35 and 65ppm, assigned to 6-coordinate, 5-coordinate and 4-coordinate Al-O bonds, respectively. The X -coordinate Al-O bond is defined as AlO_X ($X = 4, 5, 6$) below. With the original coal fly ash, the peaks were detected at 0ppm and 50ppm. The 50ppm peak is the overlapped one of AlO_5 and AlO_4 peaks. The AlO_5 can exist in glass phase but not in crystalline phase of the fly ash. As the reaction time was longer, the 50ppm peak shifted to 65ppm and the 0ppm peak became weak, indicating that the content of 4-coordinate Al-O increased by reaction. These results suggest that the glass network of original ash was changed into crystal structure of zeolite.

Figure 4 shows the change in the ratio of AlO_X peak area with time. Before 60min, there was no zeolite structure detected by XRD. The AlO_5 peak ratio was constant until 40min. However, the AlO_6 peak became weak and the AlO_4 peak became strong. These results indicate that the AlO_6 content decreases during dissolution of the glass phase and changes closely to zeolite structure, but the AlO_5 content still exist because the deposit is amorphous gel at the early stage. The AlO_5 may exist in amorphous glass of original fly ash and aluminosilicate gel after treatment. During the reaction at 40-60min, the AlO_5 peak ratio decreased remarkably and the increase in AlO_4 peak ratio was large. This is due to the crystallization of intermediate gel into zeolite. After 60min, zeolite was detected by XRD and the AlO_5 peak completely disappeared. This indicates the crystal growth of zeolite.

3.4 Morphology of treated fly ash

Figure 5 shows the SEM photographs of original and treated fly ash particles. The original fly ash consisted of spherical particles having smooth surface. At 40min, any crystalline product was not detected by XRD, but some deposits were observed on the surface of fly ash particle. The deposits may be an amorphous intermediate gel. After 60min, the XRD peaks of zeolite appeared and the deposits became large with time. This indicates the crystallization of zeolite. Finally, after 120min, the surface of fly ash was

completely covered by zeolite. During the reaction at 60-120min, the crystal growth of zeolite occurred.

In order to confirm the crystallinity of deposit, the TEM observation was carried out (Fig.6). At 40min, some fluffy matter was observed on the surface of fly ash particle. The electron diffraction showed a halo pattern. These matters were shrunk by electron beam irradiation. These results indicate that the structure was amorphous. At 60min, the crystalline phase was observed in a part of amorphous gel. This means that the embryos form on the amorphous intermediate gel and grow to crystalline zeolite.

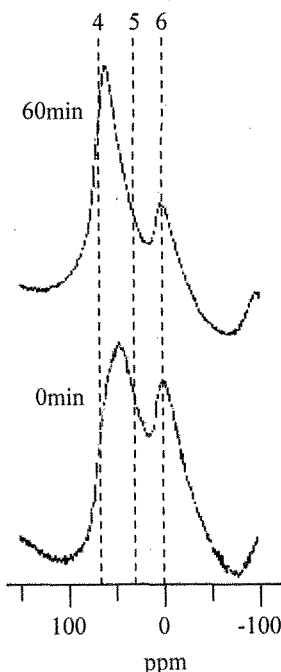


Fig. 3 ^{27}Al -NMR spectra of treated fly ash

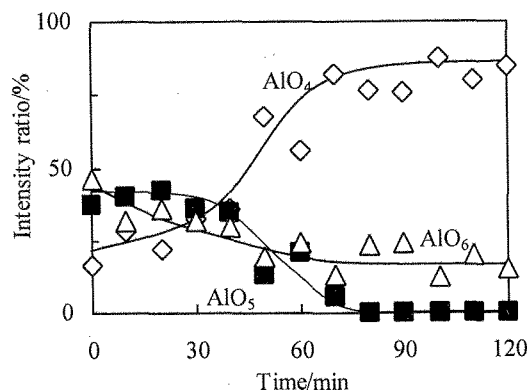


Fig. 4 Change in Al-O coordination state.

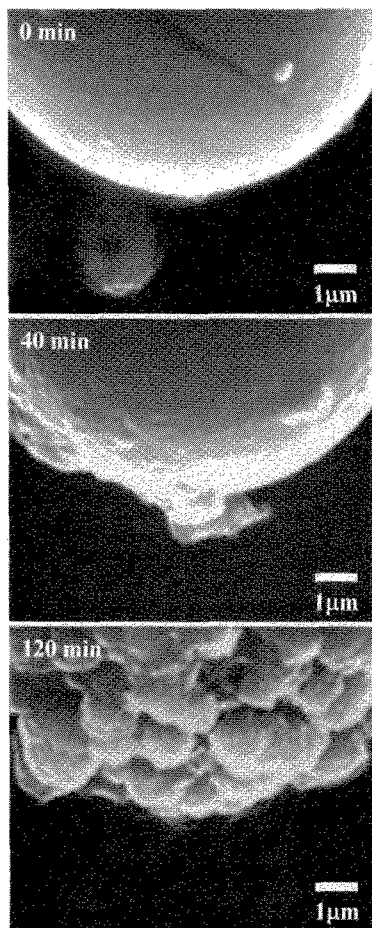


Fig. 5 SEM photographs of treated fly ash.

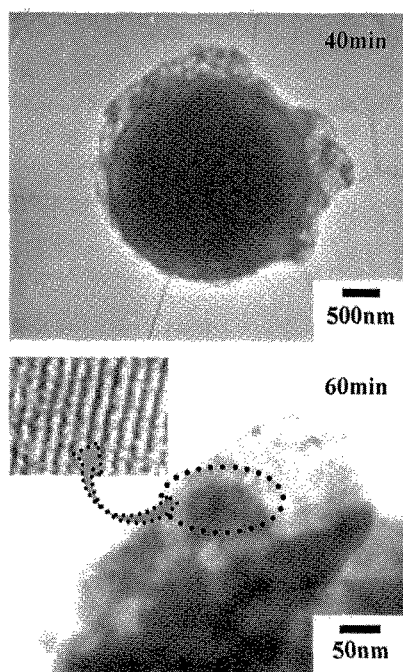


Fig. 6 TEM photographs of treated fly ash.

4. CONCLUSIONS

The formation process of zeolite from coal fly ash is composed of three steps. The first step is the dissolution of Si and Al into alkaline solution. At 40 min, zeolite structure was not detected by XRD, but some deposits were observed by SEM. The electron diffraction of these deposits showed a halo pattern. The presence of aluminosilicate network was indicated by spectroscopic analyses with ^{27}Al NMR. These results suggest that the intermediate aluminosilicate gel forms by deposition from dissolved Si and Al at the second step. The final step is the nucleation and crystal growth of zeolite. This is clearly understood from the rapid increase in the amount of formed zeolite and the CEC value after 60 min.

References

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