Zeolite X Produced by Hydrothermal Treatment of Fly Ash in an Alkaline Solution

Fumihiko Ogata, Yuka Iwata, and Naohito Kawasaki*
Faculty of Pharmacy, Kinki University 3-1-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan
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Fly ash (FA) was hydrothermally treated in an alkaline solution to produce zeolite X (Z-FA). The properties of the FA and Z-FA were then investigated. The FA consisted of spherical particles of various diameters. The X-ray diffraction patterns of FA and Z-FA showed that the FA mainly consisted of mullite crystals (3Al2O3·2SiO2), while the Z-FA consisted of zeolite crystals. The specific surface area (23.3 m²/g) and pore volume (57.6 µL/g) of the Z-FA were greater than those of the FA (2.7 m²/g and 12.7 µL/g, respectively). The pH of the FA and Z-FA were 7.94 and 9.81, respectively. [DOI: 10.1380/ejssnt.2014.23]

Keywords: Fly ash; Hydrothermal treatment; Alkaline solution; Zeolite X

I. INTRODUCTION

Japan generated 11 million tons of coal ash, the inorganic residue arising from coal combustion processes, in 2006. Coal ash consists of mainly fly ash (FA), bottom ash, slag, and by-products of fluidized bed combustion and flue gas desulfurization [1]. Although about 97% of FA is reused in cement and concrete mixtures, the production of cement has decreased over time, making recycling of FA a significant problem [2]. Although previous studies have reported the evaluation of the moisture content in adsorbents produced from FA [3] and the recovery of rare metals from FA [2, 4], a useful method for recovering FA has not yet been established. Since the Great East Japan Earthquake of March 11, 2011, the focus of energy production in Japan has shifted away from nuclear power toward coal-generated power. The FA generated at coal-fired power plants was mostly wasted before the earthquake; however, more FA is expected to be generated in the future. Hence, developing a useful method of recycling FA is of paramount importance. There have been many reports to date on the use of adsorbents produced from waste FA. In addition, the extraction efficiencies of adsorbents from FA are dependent on factors such as the contents of non-reactive phases (mainly hematite, magnetite, and lime), chemically resistant aluminum–silicate phases such as mullite and quartz, and the grain size distribution [1, 5]. Querol et al. reported an example of different zeolitic materials obtained by applying the same synthesis conditions to different fly ashes with similar bulk SiO2/Al2O3 ratios. Therefore, it is the SiO2/Al2O3 ratios of the glass matrix and not the bulk ratios that exert an important influence on the type of zeolite obtained [1]. However, to the best of our knowledge, there have been no reports on zeolite synthesis with FA obtained from the Tachibana-wan Thermal Power Station (in Japan). We developed an adsorbent by hydrothermally treating FA obtained from the Tachibana-wan Thermal Power Station in an alkaline solution and investigated its characteristics.

II. EXPERIMENTAL METHODS

A. Materials

FA was obtained from the Tachibana-wan Thermal Power Station (Shikoku Electric Power Inc., Japan). The main components of FA are SiO2 and Al2O3, which comprise 70-80% of the total weight. The other minor components of FA are Fe2O3, CaO, MgO, Na2O, K2O, and rare earth metals [2]. Zeolite X (Z-FA) was produced by hydrothermally treating FA in an alkaline solution [3]. FA (0.5 g) was added to 40 mL of a 3.0 mol/L sodium hydroxide solution, and the mixture was subsequently heated at 93°C for 60 h. The suspension was filtered through a 0.45-µm-pore-diameter membrane filter. The residue was washed with distilled water and dried at 110°C for 24 h.

B. Characteristics

The morphologies and crystallinities of the FA and Z-FA were studied using scanning electron microscopy (SEM; JSM-5500LV; JEOL, Japan) and X-ray diffractometry (XRD; MiniFlex II; Rigaku, Japan), respectively. The yield percentage of the Z-FA was calculated using the weight of the Z-FA before and after calcination. The ash content was measured using the method reported in a previous study (JIS M8812). FA or Z-FA (1.0 g) were each heated in a muffle furnace at 815°C for 1 h. The ash content was calculated using the weight of the ash before and after heat treatment. The surface functional groups (i.e., acidic or basic) were determined using the following method also stated in previous studies [6, 7]. FA or Z-FA (0.1 g) were mixed with 20 mL of a 0.05 mol/L solution of either sodium hydroxide or hydrochloric acid. The suspension was shaken at 100 rpm at 25°C for 24 h. The excess base or acid in 5 mL of the filtrate, obtained using a 0.45-µm-pore-diameter membrane filter, was titrated with a 0.01 mol/L solution of either hydrochloric acid or sodium hydroxide, respectively. Methyl red and phenolphthalein were used as indicators.

The specific surface area and pore volume were measured using a specific surface analyzer, NOVA4200e (Yuasa Ionics, Japan) and determined based on nitrogen adsorption/desorption isotherms. The pH values of the...
solutions containing FA or Z-FA were measured using the following method. FA or Z-FA (0.1 g) were each added to 50 mL of distilled water and maintained at 25°C for 2 h. The suspensions were subsequently filtered using a 0.45-μm-pore-diameter membrane filter. The solution pH was measured using a digital pH meter (Mettler Toledo, Japan).

The pH_{pzc} of the samples was measured as follows, as also stated in a previous study [8]. 50 mL of a 0.01 mol/L sodium chloride solution was placed in a closed vial. The pH was adjusted to either 2 or 12 by adding a 0.1 mol/L solution of either hydrochloric acid or sodium hydroxide, respectively, and 0.1 g of each sample was then added. The solutions were agitated at room temperature for 48 h. The final pH values of the solutions were then measured. The pH_{pzc} is the point where the curve pH_{final} vs. pH_{initial} crosses the line pH_{final} = pH_{initial}.

III. RESULTS AND DISCUSSION

A. Properties of FA and Z-FA

SEM images of the FA and Z-FA are shown in Fig. 1. The FA consisted of spherical particles of various diameters. The XRD patterns for the FA and Z-FA (Fig. 2) show that the FA mainly consisted of mullite crystals (3Al_{2}O_{3}-2SiO_{2}) while the Z-FA, on the other hand, consisted of zeolite crystals. These results indicate that hydrothermally treating the FA in an alkaline solution transformed the FA into Z-FA. Querol et al. reported that the synthesis of zeolites from Spanish fly ashes (obtained from power plant in Spain) at laboratory and pilot plant scales. NaP1 zeolite, Faujasite, Zeolite A was produced from Spain fly ash by alkaline hydrothermal treatment. The characteristics (the SiO_{2}/Al_{2}O_{3} ratios of the glass matrix) of fly ash obtained from the Tachibana-kan Thermal Power Station or power plants in Spain are completely different from each other. The optimization of synthesis yields have to be specific for each fly ash due to differences in mineralogical and chemical compositions [5]. Therefore, zeolitic product produced from fly ash depends on the physico-chemical characterization. Zeolites are crystalline aluminum–silicates with group I or II elements as counterions. Their structure is made up of a framework of [SiO_{4}]^{4-} and [AlO_{4}]^{5-} tetrahedra linked to each other at the corners by sharing their oxygen atoms. The tetrahedra form a three-dimensional network, with many voids and open spaces. It is these voids that define the many special properties of zeolites, such as the adsorption of molecules in these huge internal channels of voids [1]. Zeolites may be found in natural deposits, generally associated with the alkaline activation of glassy volcanic rocks, or they can be synthesized from a wide variety of high-Si and -Al starting materials. As a consequence of the peculiar structural properties of zeolites, they have a wide range of industrial applications, mainly based on ion exchange, gas adsorption, and water adsorption [9]. Zeolite X has a large pore size (7.3 Å) and a high cation exchange capacity (5 meq/g), which make this zeolite an interesting molecular sieve and a high-cation-exchange material [1]. Therefore, it is important to investigate the properties of adsorbents (Z-FA) produced from FA. The properties of the FA and Z-FA are shown in Table I. The yield of Z-FA was 86.2%. Sakamoto et al. reported that the yield percentage of zeolites synthesized from allophane (volcanic ash in south Kyushu) was approximately 50% without pretreatment [10]. These results indicate that the method of synthesizing Z-FA from FA obtained from the Tachibana-kan Thermal Power Station used in this study was useful for producing zeolite X. The factors affecting the conversion efficiency are primarily the contents of calcium and unburned carbon in the ash from incineration because these components are converted to small, low-density floating materials in alkali solutions [11].

The surface functional groups, specific surface area, pore volume, and pH_{pzc} are closely related with adsorption capability. The number of acid functional groups on the Z-FA surface decreased and the number of base functional groups on the Z-FA surface increased (Z-FA: pH 10.4) and the pH of the FA solution increased (7.2) because a 3.0 mol/L solution of sodium hydroxide was used to hydrothermally treat FA.

The percentages of ash in FA and Z-FA were 95.6 and 84.5%, respectively. A previous study reported that zeolite X produced by hydrothermally treating FA in an alkaline solution had water in its pores. In this study, the water molecules in the Z-FA pores were evaporated upon heating before the contents of Z-FA were analyzed; the heating contributed to the decreased ash content in the Z-FA produced.

The specific surface areas and total pore volumes of the FA were 2.7 m^{2}/g and 12.7 μL/g, respectively, and those of Z-FA were 23.3 m^{2}/g and 57.6 μL/g, respectively. The mean pore diameters of the FA and Z-FA were 189.8...
TABLE I: Properties of FA and Z-FA.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Yield (%)</th>
<th>Acid consumption (mmol/L)</th>
<th>Basic consumption (mmol/L)</th>
<th>Ash (%)</th>
<th>pH</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (μL/g)</th>
<th>Mean pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>—</td>
<td>0.54</td>
<td>0.28</td>
<td>95.6</td>
<td>7.2</td>
<td>2.7</td>
<td>0.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Z-FA</td>
<td>86.2</td>
<td>0.44</td>
<td>3.22</td>
<td>84.5</td>
<td>10.4</td>
<td>23.3</td>
<td>1.2</td>
<td>37.7</td>
</tr>
</tbody>
</table>

FIG. 3: Determination of the pHₚₚₑ of the FA and Z-FA. Filled circles and squares denote FA and Z-FA, respectively.

...and 98.9 Å, respectively. These results suggest that hydrothermally treating FA in an alkaline solution led to significant pore development in the Z-FA, resulting in a novel adsorbent. Moreover, the specific surface area of zeolite synthesized from coal fly ash using a NaOH/Na₂CO₃ solution (63.6 m²/g) was greater than that of the zeolite X obtained in this study (23.3 m²/g). These results are attributable to the components of fly ash [12].

Figure 3 shows how pHₚₑ is determined for the FA and Z-FA. pHₚₑ is the pH at which the net particle charge becomes zero, and it is an important parameter in describing surface behavior. The pHₚₑ values of FA and Z-FA were 7.94 and 9.81, respectively. The pHₚₑ value of 9.81 indicates that Z-FA has a zero charge at pH = 9.81. Therefore, it shows a positive charge density on its surface for a solution of pH less than 9.81 and a negative charge density for a solution of pH greater than 9.81. The surface charge of the adsorbent affects the adsorption of gas, water, and heavy metals. The surface charge is thus an important characteristic of an adsorbent.

IV. CONCLUSIONS

Zeolite X (Z-FA) was produced by hydrothermal treatment of FA in an alkaline solution. The FA consisted of mullite crystals (3Al₂O₃·2SiO₂), whereas the Z-FA consisted mainly of zeolite crystals. The specific surface areas and total pore volumes of the produced Z-FA were 23.3 m²/g and 57.6 μL/g, respectively. These results suggest that hydrothermally treating the FA in an alkaline solution leads to significant pore development in the Z-FA, resulting in a novel adsorbent.