Conversion of fly ash into zeolite: Effect of reaction temperature

S.H. Hanipah, N. H. Othman, S.N.M. Hanapi, N.Idrus
Faculty of Chemical Engineering
University Teknologi MARA
Malaysia

Abstract—The conversion of fly ash into zeolites has become an important waste management issue in recent years. Zeolites may be easily obtained from fly ash by the relatively cheap and fast hydrothermal conversion process. Raw fly ash is pretreated with hydrochloric acid at the determined optimum pre-treatment temperature, time and ratio of 80°C, 1 hour and 25:5 (ml/g), respectively. Zeolite was then synthesized by mixing the pretreated fly ash with sodium hydroxide solution in a ratio of 150 g: 300 ml at various reaction temperatures: 90, 150, 210 and 350°C. XRD analysis of the fly ash with treatment and the structure of the as-synthesized zeolite indicates little change in the crystalline structure of the fly ash, although peak intensities of most components appear to decrease with increasing synthesis temperature. Evaluation of the particle size distribution of the zeolite material indicates that at higher temperatures a bimodal distribution and improved particle size uniformity manifest. In conclusion, the best zeolite material was obtained at 350°C.

Keywords—fly ash, zeolites.

I. INTRODUCTION

Large quantities of coal ash are produced in electric power plants throughout the world every year. The amount of coal ash formed is approximately 500 million tons per year and is predicted to increase. Efficient disposal of coal fly ash has been a worldwide issue, because of the massive amounts of ash produced and its harmful effects on the environment. A technique to reduce coal fly ash disposal is the synthesis of zeolites from fly ash, which has consequently received extensive attention over the last decade. Due to their uniform pore sizes and large surface areas, zeolites are very useful materials in a wide range of applications such as ion exchange, molecular sieving, gas adsorption and catalysis [1]. Synthetic zeolite products still contain significant amounts of residual fly ash and zeolites, such as sodalite and analcime, usually exhibit a less desirable more condensed structure (low pore volume). The presence of non-zeolite phases in the converted product limits cation exchange capacity (CEC) and greatly hinders the potential application of synthetic zeolites from coal fly ash [1].

II. EXPERIMENTAL

A. Materials and chemicals

1) Fly ash and chemicals

The coal fly ash used in this study was obtained from the Sultan Abdul Aziz Power Station in Kapar, Selangor. Solidified fly ash suspended in the exhaust gases is collected by electrostatic precipitation [2]. The acquired fly ash is generally spherical in shape. The preparation of the fly ash and consequent conversion into zeolite material rewaried the following chemicals: Hydrochloric acid (HCl) (Raml, 2M, 95.5%) and Sodium Hydroxide (NaOH) (ChemAR, 40 g/mol MW)

B. Fly ash pretreatment

Raw fly ash was pretreated based upon the method developed by Wang et al. [3] and Querol et al. [4] using acid-washing, whereby a mixture of hydrochloric acid and fly ash in a ratio of 25 mL: 5 g was placed in a water bath and continuously agitated at 80°C for 1 hour. The resultant fly ash was then filtered, washed multiple times with distilled water and then dried at 100°C for 24 hours.

C. Process of zeolites synthesis

Sodium hydroxide was mixed with the pre-treated fly ash in a ratio of 150 g: 300 mL [5,6,7]. The resultant mixture was milled and fused at: 90, 150, 210 and 350°C for 1 hour, cooled to room temperature and stirred for 1 hour. The precipitate was then washed multiple times with distilled water to remove excess sodium hydroxide. The final zeolite material was then filtered and dried at 100°C for 24 hours.

D. Zeolite characterization

1) X-Ray diffraction (XRD) Study

The crystalline structure of the raw and pretreated fly ash, as well as the synthesized zeolite, were analyzed using a Rigaku D/Max -200PC X-Ray Diffractometer.

2) Particle Size and specific surface area study

The particle size distribution of the zeolite particles was determined using a Malvern Hydro 200MU, whereby light scattering is used to measure particle size and surface area.

III. RESULTS AND DISCUSSIONS

A. Effect of Pre-Treatment on Fly Ash

1) X-ray diffraction analysis

Hydrochloric acid (HCl) was used to reduce the concentration of iron and alkali oxides present in the fly ash, which predominantly found in the outer part of the ash particles, and also to promote leaching of the Al₂O₃, which increased the relative SiO₂ content of the reaction mixture. Fly ash contains SiO₂, Al₂O₃ and several other undesirable components,
including potassium oxide (K₂O), titanium dioxide (TiO₂), magnesium oxide (MgO), sodium oxide (Na₂O) and calcium oxide (CaO) in synthesized zeolites. Some of these components act as poisons during the catalytic application of zeolites.

XRD patterns are a consequence of the diffraction of X-rays by different crystal planes which are unique to the crystalline form of the analysed material. The peak intensities can be used as a semi-quantitative measurement of the quantity of different crystalline phases exhibited by a material. Pretreated fly ash exhibits only three notable differences to the raw fly ash; at 29, 37.5 and 43°, Figure 1. It is evident from Figure 1 that the fly ash is composed of a number of oxides including phosphorous, sulphur, titanium and magnesium. Changes in relative peak intensity, presence and position indicate crystalline transitions; in Figure 1 it is of note that peaks for sulphur dioxide and magnesium oxide are exhibited in the region of 29° and 43° in the raw fly ash, respectively, but are absent after acid treatment; yet corresponding peaks are exhibited in the regions of 43° and 37.5°. This would indicate that sulphur dioxide and magnesium oxide are still present in the fly ash, but their crystalline forms have been modified and this may play an active role in the properties of the final zeolite material. It should be noted that the composition of the fly ash pre- and post-treatment appears consistent with respect to the minerals present, but there is some crystalline modification of sulphur and magnesium oxide as a consequence of acid washing [10].

B. Effect of synthesis temperature on zeolites properties

1) X-ray diffraction analysis

The XRD patterns for the zeolites synthesized at 90, 150, 210 and 350°C are presented in Figures 2 from which it is evident that there are no significant variations in peak distribution or position, but there is a slight relative reduction in peak intensities with increasing temperature, which might indicate reduced amounts of crystalline material. This may be a consequence of transition from the hematite phase to the zeolite phase. Hui et al. [1] stated that higher synthesis temperatures enhance the crystallinity of zeolites; however it also increases the conversion of metastable zeolites into more thermodynamically stable zeolite phases, e.g. hydroxyl-sodalite. It is known that the synthesis of zeolites depends on the rate of gel dissolution, the number and distribution of nuclei in the gel, and the crystal growth rate during hydrothermal treatment. All of which in turn depend on other factors, including temperature, time and alkalinity.
2) **Particle size analysis**

The particle size distributions for the synthesized zeolite material at 90, 150, 210 and 350°C are presented in Figure 3 from which it is evident that higher synthesis temperatures yield broader size distributions and bimodality begins to manifest. It may therefore be hypothesized that increasing the synthesis temperature increases gel dissolution of nuclei and crystal growth in accordance with the work of Hui et al. [1], thus instigating a particle size transition culminating in larger particles. Further to this, according to Keka et al. [8] sodium hydroxide acts as an activator during zeolite synthesis, promoting the formation of soluble silicate and aluminate salts, which are active in zeolite formation during hydrothermal treatment; and the activation of silicon on the outer surface of particles may be responsible for the increase in zeolite particle size.

3) **Specific surface area analysis**

The specific surface areas of the synthesized zeolites are presented in Figure 4 and it is apparent that the maximum specific surface area (0.14 m²/g) is achieved at a synthesis temperature of 210°C. This is a consequence of a greater number of smaller particles, <10 µm, which increases the surface area, but which at a synthesis temperature of 350°C is offset by a greater number of larger particles, >110 µm.
Acid pretreated fly ash has been successfully converted into zeolite material, according to XRD analysis in Figure 1, during which changes in the crystalline form of sulphur dioxide and magnesium oxide were exhibited. The zeolite material produced possessing the most desirable properties was synthesized at 210°C and resulted in a material with the largest specific surface area of 0.14 m$^2$/g and a particle size distribution, which exhibited the onset of a possible bimodal distribution due to surface silicon activation and the dominance of crystal growth at synthesis higher temperatures.

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