



## A NOVEL AND GREEN APPROACH OF SYNTHESIS AND CHARACTERIZATION OF NANO-ADSORBENTS (ZEOLITES) FROM COAL FLY ASH: A REVIEW

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### ABSTRACT

Coal fly ash (CFA) is the waste product of combustion of coal in a coal-fired power station. The global annual production of CFA is about 800 million tons and this amount is predicted to increase in the future. However, the global recycling rate of CFA is only 15% posing important challenges in waste management. In India, more than 120 million tons of fly ash is being generated annually with more than 65,000 acres of land being occupied by ash ponds. Several approaches have been made for proper utilization of fly ash, either to reduce the cost of disposal or to minimize the environmental impact. One of the approaches is the conversion of fly ash to zeolites, which have wide applications in ion exchange, as molecular sieves, catalysts and adsorbents. Zeolites have extensive applications in basic science, petrochemical science, energy conservation/storage, medicine, chemical sensor, air purification, environmentally benign composite structure and waste remediation. However, the uses of zeolites in these areas, especially environmental remediation, are restricted due to prohibitive production cost. Efficient recycling and resource recovery from coal fly ash has been a major topic of current international research interest, aimed at achieving sustainable development of human society from the view points of energy, economy and environmental strategy. For zeolite, this novel production method allows a reduction by half of the total production time while maintaining a high degree of crystallinity of zeolite which exists in a narrower particle size distribution.

**Key words:** Coal fly ash, Zeolite, Degree of crystallinity, Molecular sieves.

### INTRODUCTION

Coal fly ash (CFA) is the waste product of combustion of coal in a coal-fired power station. The global annual production of CFA is about 800 million tons and this amount is predicted to increase in the future<sup>1</sup>. However, the global recycling rate of CFA is only 15% posing important challenges in waste management. At present, efficient disposal of CFA is a worldwide issue because of its massive production and its harmful effects on the environment<sup>2</sup>. Resource recovery from CFA can be one of the approaches to speed up reuse of CFA, since the major chemical compositions contained in CFA are SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (60-70 wt. % and 16-20 wt. %, respectively)<sup>3</sup>. Although CFA has been reused in highway construction, land reclamation and restoration of eroded soil, the demand for such applications is still limited<sup>4</sup>. Converting CFA into useful zeolites is one of the approaches to recycle CFA. However, most of the studies applied a long

conversion time (1-3 days) to produce zeolites from coal fly ash and the materials produced still contained a significant amount of residual CFA<sup>5-8</sup>. Thus, the potential applicability of the zeolites is greatly reduced.

In India, more than 120 million tons of fly ash is being generated annually with more than 65,000 acres of land being occupied by ash ponds. Several approaches have been made for proper utilization of fly ash, either to reduce the cost of disposal or to minimize the environmental impact. One of the approaches is the conversion of fly ash to zeolites, which have wide applications in ion exchange, as molecular sieves, catalysts and adsorbents.

Fly ash is mainly composed of some oxides derived from inorganic compounds, which remain after combustion of the coal. The amounts of the main components of ash viz., SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, show few variations with the type of coal. The similar chemical composition of fly ash and some volcanic rocks prompted several research groups to attempt making zeolite from fly ash<sup>9</sup>. In general, zeolite synthesis processes involve the addition of a caustic agent to the fly ash slurry at higher temperatures. In 1985, Holler and Wirsching utilized fly ash as the raw material for synthesis of zeolite using hydrothermal method. After that, a number of researchers have used this process successfully, varying the hydrothermal temperature within the range of 333–573 K<sup>9</sup> synthesized hydroxy-sodalite by conventional hydrothermal process in the temperature range 353–363 K for 3-24 h. He succeeded in converting about 30% of the original fly ash to hydroxy-sodalite with high cation exchange capacity compared to the original fly ash. However, major attempts on zeolitization of fly ash have been made from 1990 onwards.

Mondragon *et al.*,<sup>10</sup> investigated on possible uses of coal fly ash, in general and synthesis of zeolites from it, in particular, but like most other investigators, they also tried the hydrothermal method. Adsorption property of the treated fly ash was reported to be similar to that of commercial 13X zeolite. Shigemoto and co-workers<sup>11</sup> also synthesized zeolite by using a similar method. They have developed fusion followed by hydrothermal treatment method to synthesize low silica NaX type zeolite from fly ash. Fusion of the alkali-fly ash mixture facilitates the formation of highly active Na-aluminates and silicates, which are readily soluble in water and enhance zeolite formation. Using fusion followed by hydrothermal process, the investigators developed low silica, X-type zeolite selectively. Addition of sodium aluminate to the fly ash before fusion brought the success in obtaining Na-A zeolite also.

Lin and Hsi<sup>12</sup> extensively investigated effects of the hydrothermal reaction parameters such as temperatures, molarity of caustic reagents and reaction time on the properties of the treated fly ash and also optimized the reaction parameters to obtain best quality product. They carried out experiments in open as well as in closed systems at elevated pressure (500 psi) and temperatures as high as 473 K. The synthesis of zeolite was also studied with fly ash of varying chemical composition, which was not investigated in previous works.

Shih and Chang<sup>13</sup> investigated the effects of curing temperature and chemical composition on formation of two types of zeolites; zeolite A and faujasite, from Class F fly ash at lower temperature (only 311 K), but, the treatment time required for synthesizing zeolite A by them was longer enough, more than 3 days. Yoshida and Inoue synthesized a similar type of zeolite A at 363 K and they observed that at higher temperature zeolite A began to disappear and zeolite P started to form.

Querol and co-workers<sup>14</sup> used KOH and NaOH as activators to synthesize zeolite using both open and closed system. They have carried out experiments from fly ashes of varying compositions, collected from different power plants. Their results have shown higher conversion efficiency of NaOH than that of KOH solutions, even at higher KOH concentrations (1 × 0 M and 473 K). Quartz and mullite could not be dissolved substantially and remained in the fly ash. Higher pH of the solution also showed better zeolite synthesis efficiency. Mainly zeolite NaP1, NaP derivatives and Phillipsites have been synthesized by NaOH and KOH activation.

Querol *et al.*,<sup>14</sup> reported microwave-assisted method for zeolite synthesis from coal fly ash. Yields and zeolite types obtained from the microwave and conventional experiments have been reported to be very similar, but the activation time has been drastically reduced by using microwaves (from 24–48 h to 30 min). Chang and Shih<sup>15</sup> established the alkali fusion followed by hydrothermal treatment as a general method for synthesis of a particular type of zeolite from different sources of fly ash. They have also compared their results with simple hydrothermal treatment (without fusion) and have concluded that the fusion approach is a better process which can be applied to fly ash of wide composition ranges. In the year 2000, the same research group published another paper in which they described fusion method to synthesize zeolites X, Y and A. They also showed the capability of fusion method to synthesize a specific zeolite selectively by varying the reaction parameters.

Park and co-workers<sup>16</sup> developed a new method for synthesizing zeolite under molten conditions without any addition of water. However, complete zeolitization of fly ash could not be accomplished by this molten salt method, probably due to low temperature and insufficient contact of NaOH with raw materials. The molten salt product was of irregular morphology, in which zeolites could not be identified by their characteristic morphological shapes. On the other hand, well-developed polycrystals were observed in the hydrothermal product. These results indicate that the crystal growth in molten-salt state is somewhat limited compared to that in hydrothermal products. Based on the above discussion, it can be concluded that alkali fusion followed by hydrothermal treatment is the most reliable method of obtaining faujasite (Na–X and Na–Y) type zeolite selectively from fly ash of different compositions. It was, therefore, thought desirable to convert fly ashes from some of the Indian thermal power plants to zeolites, which could be used as catalysts for some industrially important reactions, by alkali fusion followed by hydrothermal treatment.

All the above cited references and researchers used the conventional techniques for synthesis of the zeolites from coal fly ash and have the synthesis time is ranging between 1-3 days. The research done by Hui and Chao<sup>17</sup> gives an overview of production of zeolites from CFA by a novel and green approach to reduce the energy consumed and the waste generated in the production process, which can be an important contribution to the large scale production of zeolites. Environmental and economic aspects of conversion of CFA into zeolites were also discussed.

## EXPERIMENTAL

### Materials

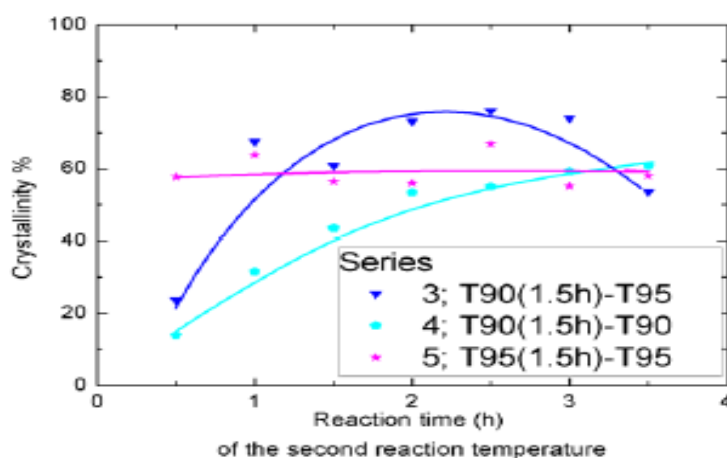
The CFA used in this project was obtained from a power plant in the southern part of China and was used in each experiment after pretreatment at 120°C for 30 min in an oven. The size of the CFA, determined by a particle size analyzer (Coulter LS230), covers a range from 0.04 to 600 µm and with an average diameter of 20.7 µm. The chemical composition of the CFA and CFAZ was analyzed by XRF (JEOL JSX-3201Z) and is listed in Table 1. The amounts of crystallized and amorphous SiO<sub>2</sub> in the CFA are 3.9 and 46.2 wt. % respectively, which was assayed by a quantitative X-ray diffraction (XRD) method<sup>18</sup>. The specific surface area of the CFA is 1.4 m<sup>2</sup>/g.

### Production of zeolite from coal fly ash

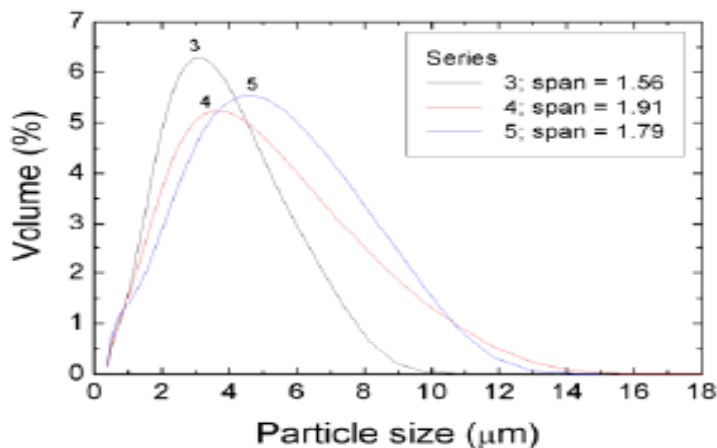
A novel and fast method was developed by Hui *et al.*<sup>19</sup> to produce a pure form, single-phase and high-crystalline zeolite from CFA compared to the methods reported in the literature. Briefly, a mixture of 30 g of CFA and 300 mL of 2 M NaOH solution in a 1 litre sealed polypropylene bottle was kept in an oil bath at 100°C for 2 h under stirred conditions (300 rpm). Then, the solution was separated from the mixture by a filtration process. The molar ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> : Na<sub>2</sub>O/SiO<sub>2</sub> : H<sub>2</sub>O/Na<sub>2</sub>O in the solution was adjusted to 1.64 : 8.09 : 56.51 by adding 100 mL of aluminum solution. With the addition of the aluminum solution, single-phase and high-crystalline zeolite could be easily produced from the solution compared to the case

without the addition of the aluminum solution. The solution was then stirred (500 rpm) for 30 min at room temperature (25°C) and kept at its first reaction temperature of 90°C for 1.5 h and subsequently at the second reaction temperature of 95°C for 2.5 h. The precipitated sample was separated from the mixture by a filtration process and washed with deionized water until the pH of the solution was around 10. The sample was kept in an oven and dried at 100°C for 12 h. It took 6.5 h to produce 7.5 g of pure zeolite powder from the CFA, denoted as CFAZ (coal fly ash zeolite).

Compared with the zeolite A prepared under a constant reaction temperature, the proposed method (step-change of reaction temperature) reduced the total production time by half without compromising its quality. For example, as shown in Fig. 1, series 3 lead to higher crystalline zeolite A compared to series 4 and 5 if the reaction time in the second stage was in the range of 1–3 h. Series 3 also consumed less energy than series 5 in the production process. In addition, a narrower particle size distribution (PSD) of series 3 was obtained by applying the step-change of reaction temperature, as shown in Fig. 2. The step-change of reaction temperature during the production process may have the potential for producing a high crystalline and reduced particle size of zeolite crystal (series 3) which is a significant parameter that may affect the performance in several applications related to catalysis, diffusion, adsorption, ion exchange, etc. Detailed information about the production of zeolite A from the CFA can be found in our previous work<sup>19</sup>.



**Fig. 1:** The effect of step-change of reaction temperature on the percentage crystallinity of zeolite A



**Fig. 2:** Particle size distribution (PSD) curves of the zeolite, A samples. Sample parameter: series 3 (T90 (1.5 h)-T95 (3.5 h)), series 4 (T90 (1.5 h)-T90 (3.5 h)) and series 5 (T95 (1.5 h)-T95 (3.5 h))

### Characterization of samples

The pH values of the aqueous solutions were measured with a Mettler-Toledo meter (MP 120). The bulk elemental composition of the samples were determined by a JEOL X-ray reflective fluorescence spectrometer (XRF, JSX 3201Z). Powder X-ray diffraction (XRD) patterns of the samples were obtained using a powder diffractometer (Philips PW 1830) equipped with a  $\text{CuK}\alpha$  radiation. The accelerating voltage and current used were 40 kV and 20 mA, respectively. The scanning range of  $2\theta$  was set between  $2^\circ$  and  $50^\circ$ , with a step size of  $0.02^\circ$  and  $0.01^\circ/\text{s}$ . Nitrogen adsorption/desorption was carried out at 77 K using the Coulter SA3100 nitrogen physicasorption apparatus. The volume of adsorbed nitrogen was normalized to standard temperature and pressure (STP). Prior to the experiments, the samples were dehydrated at  $150^\circ\text{C}$  for 3 h. The BET surface area was determined from the linear part of the BET plot ( $p/p_0 = 0.05-0.2$ ). Surface morphology of the samples was analyzed by scanning electronic microscopy (SEM, JEOL 6300) coupled with energy dispersive X-ray analysis (EDAX). In the SEM analysis, the samples were coated with a thin layer of gold and mounted on a copper stab using a double-stick tape.

The particle size measurements were performed by laser beam scattering technique (Coulter LS230). From the particle size distribution (PSD) curves obtained, the sizes of which 10%, 50% and 90% (by volume) of the particles in the samples were smaller could be determined. In this study, these particle sizes (by volume) were denoted by  $d(0.1)$ ,  $d(0.5)$  and  $d(0.9)$  respectively. The particle size of which 50% of the particles in the sample were smaller represented the average crystal diameter. Size span of the zeolite A samples were calculated by using the following equation:

$$\text{Span} = [d(0.9) - d(0.1)]/d(0.5)$$

Where span is a measure of the width of the size distribution and smaller span values are obtained when narrower distribution exists.

## RESULTS AND DISCUSSION

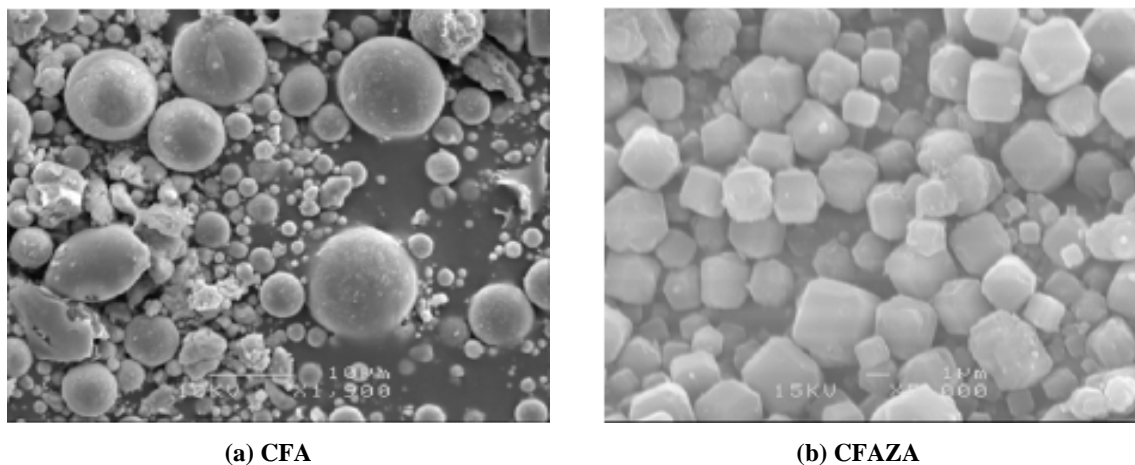
### Characterization of the adsorbents

Table 1 shows the chemical composition of the CFA and the zeolite A produced from CFA (CFAZA). As shown in Table 1, the BET surface area of CFAZA is 13-fold from the CFA. This increase in BET surface area is due to crystallization of zeolite crystals on the outer surface of the CFA. The BET surface area of CFAZA is similar to the value reported in literature<sup>15</sup>.

**Table 1**

Composition (Wt. %)	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{Fe}_2\text{O}_3$	$\text{Cr}_2\text{O}_3$	$\text{CuO}$	$\text{ZnO}$	$\text{NiO}$	$\text{CoO}$	BET surface area ( $\text{m}^2/\text{g}$ )
CFA	50.09	24.91	0.14	11.77	0.40	7.60	--	--	--	--	--	1.4
CFAZA	43.34	35.71	19.75	--	0.25	0.8	--	--	--	--	--	54.8

Fig. 3 shows the morphology of the CFA and CFAZA. The CFA consists of smooth spheres of diameter of 0.04 - 600  $\mu\text{m}$  and has a mean diameter of 20.7  $\mu\text{m}$ . These particles were formed from the cooling of molten products after the combustion of clay compounds in the original coal. The morphology of the CFAZA was chamfered-edged cube. The chamfered-edged cube morphology was due to the initial  $\text{SiO}_2/\text{Al}_2\text{O}_3$  concentration used in the production process. The particle size of the CFAZA was observed 1-3  $\mu\text{m}$  with a mean diameter of 2  $\mu\text{m}$ .

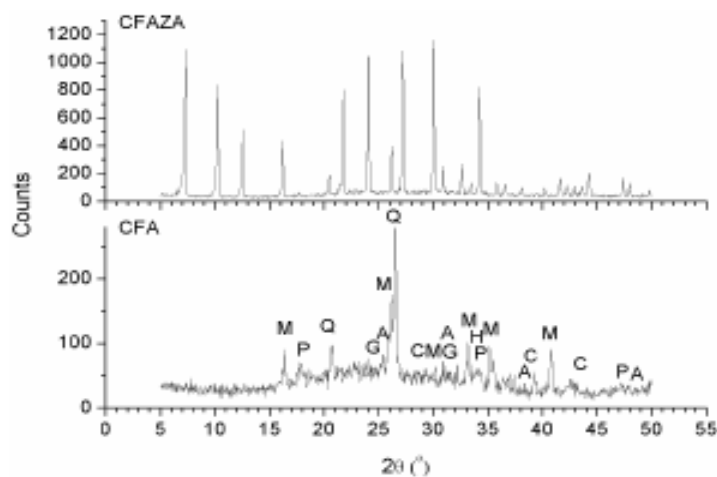


(a) CFA

(b) CFAZA

**Fig. 3: SEM pictures of the CFA and CFAZA**

Fig. 4 shows the XRD patterns of the CFA and the CFAZA. The crystalline species in the CFA sample are quartz, mullite, calcite, portlandite, anhydrite, hematite and gehlenite as identified by the sharp peaks, while the presence of the amorphous phases of  $\text{SiO}_2$  are identified by the presence of a broad diffraction peak (near  $2\theta = 24^\circ$ ). Quartz and mullite were produced during the thermal decomposition of clay minerals such as kaolinite during combustion. CFAZA was identified as a single phase zeolite A (JCPDS card 43-0142).



**Fig. 4: XRD pattern of the CFA and CFAZA. (M, Q, C, P, A, H and G represent mullite, quartz, calcite, portlandite, anhydrite, hematite and gehlenite, respectively)**

### **Environmental and economic aspects of production of zeolite A from coal fly ash**

A waste material CFA from coal-burning power plants into zeolite A may have several important implications on the environment and economy<sup>17</sup>. In terms of the environment, the increased use of CFA can reduce the need for additional landfill space and conserve natural resources. For example, a ton of CFA, compressed to 70 pounds per cubic foot, normally takes up approximately 28 cubic feet of landfill space. Each ton of recycled CFA reduces the use of one ton of virgin resources (e.g. limestone, gypsum, sand and soil) in the same applications<sup>4</sup>. It has been shown that CFA can be reused in highway construction, land reclamation and restoration of eroded soil<sup>20</sup>; however, the demand for reuse of ash in such projects is limited. Instead of dumping the ash in landfill sites or lagoons, converting it into zeolite A can provide another way to protect the environment.

In term of the economy, zeolite produced from CFA can provide a new source of revenue for power production companies and eliminate previous expenses associated with the disposal of CFA. A detailed cost analysis of the feasibility of the production of zeolite A from coal fly ash can be referred to the literature<sup>17</sup>. Pure form zeolites produced from CFA may provide cost-effective alternative to commercial zeolites in applications of pollution control and energy generation and storage.

## CONCLUSION

Many new developments in zeolites science are driving the use of zeolites substitutes in many applications such as air and water purification, gases adsorption and catalysis. These developments include the development of new type of zeolite, production of zeolite from waste materials and carbonzeolite hybrid materials. This novel and green method produces 7.5 g of pure zeolite A powder from the CFA in 6.5 h. Compared with the zeolite A prepared under a constant reaction temperature, this method (step-change of reaction temperature) reduces the total production time by half without compromising its quality. In views of environmental and economic aspects, production of zeolite A from CFA may provide cost-effective alternative to commercial zeolites in many applications.

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