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Siliceous fly ash utilization conditions for zeolite synthesis

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Abstract: Fly Ash is a coal combustion product partly disposed of in landfills since it finds no other application. Recycling this solid is of great benefit in terms of quality, cost effectiveness and environment. The chemical and mineralogical composition of siliceous fly ash makes it an attractive and economic raw material for the synthesis of zeolites. Zeolites are microporous, aluminosilicate minerals characterized by a three-dimensional network of tetrahedral units produced industrially on a large scale. In this work synthetic X and A-type zeolite with high crystallinity and high value of surface area were synthesized by pre-fusion method followed by hydrothermal treatment at various conditions. The data indicate that zeolitic products were obtained using NaOH while no zeolitic material was crystallized using KOH and LiOH. Pre-treatment of fly ash with acid before being used in the synthesis of artificial zeolites is considered an important parameter for the purity phase of zeolites. Without sodium aluminate additions, synthetic zeolite A was not formed. The results confirm that temperature, crystallization time, SiO_2/Al_2O_3 ratio, type of water (distilled water and seawater), are also important parameters influencing type of zeolite synthesized. Zeolite X was used as novel catalyst for alkylation of phenol using diethyl carbonate.

Keywords: fly ash; synthesis; zeolite structure; crystallinity

1. Introduction

The major generators of industrial solid wastes are the by-products of combustion power plants producing coal fly ash. In the last few decades, worldwide coal consumption has been monitored. The main consummator being China, followed by India, United States and Russia [1] Accumulation of massive amounts of such residues, if not managed properly causes serious environmental, aesthetic, economic and social problems. The re-evaluation of "wastes" in which significant energy has been invested and lost through disposal via their conversion into sustainable construction materials and products is probably the best way to recover this energy [2].

Fly ash is one of the waste by-products with major potential for recycling. Until today, several approaches have been carried out in aim to increase the utilization and reducing its negative impacts. Fly ash offers a large spectrum of utilization possibilities ranging from underground mining to building and cement industry [3,4]. Furthermore, the synthesis of mesoporous silica from fly ash has also attracted interest due to the resulting material characteristics [5].

Fly Ash is mineralogically characterized by the presence of amorphous materials and mixture of Ferro-aluminosilicate minerals. The high content of silica and alumina makes it a suitable raw material for the synthesis of high value zeolitic material.

Since the last millennium, zeolites are known as a "magic rock". Zeolites are hydrated aluminosilicate minerals with a three-dimensional open structure. They consist of SiO_4 and AlO_4 tetrahedra which gives it an anionic framework with the negative charge of Al being compensated by extra framework cations (positively charged ions), some being Na^+, K^+, Ca^{2+} Mg^{2+} and water molecules. Porous structure is large enough to be able to accommodate the guest ionic and molecular species. It is also possible to produce zeolite structures that do not appear in nature. Therefore, converting fly ash into zeolite is expected to resolve the problem of disposal of fly ash at least partially and thereby minimize its impact on environment.

In the last decade, fly ash was used as raw materials for obtaining zeolites type; X [6,7], A [6, 7 8,9] or P [10], competing with zeolites made from pure industrial chemicals, which is of great importance for the sustainable resource management [11]. Developing green techniques with cost-effective and eco-friendly routes for the synthesis of zeolite from FA it is very significant for the economy and sustainable technology. Furthermore, the synthesis of zeolite from fly ash has also attracted interest due to the resulting material characteristics [12, 13].

Two well-known methods are commonly applied, namely the conventional hydrothermal method by using an alkaline medium, and the hydrothermal process with fusion pre-treatment at high temperatures. The fusion method gains advantages of speed of reaction [14], and purity of the final product [15] whereas the hydrothermal method has the advantage in terms of the consistent pattern of zeolite product. Synthesis conditions for each of the methods are different; they include pretreatment with acid [16], various alkali sources [17], molarities of alkaline agents [18], solution/ solid ratio [19], temperature [6], reaction time [20], pressure, type of incubation [21] and type of water [22,23].

In this project, different conditions determining the synthesis of zeolites from fly ash were investigated. The synthetic products were characterized in terms of mineralogy and morphology.

2. Materials and Methods

Materials

The main raw material, coal fly ash (Class F type) sample was supplied from the BauMineral Gmb, a German power plant company. Sodium hydroxide, sodium aluminate and hydrochloric acid were purchased from Sigma Aldrich, respectively ≥ 97.0% purity, anhydrous pellets, 99.9% $NaAlO_2$ powder and ASC, reagent 37% HCl.

Zeolite synthesis procedure

Initially raw fly ash (FA) was added to HCl, with 20% w/w acid concentration under the acid/FA ratios of 15 ml acid/g FA [16]. The mixture was constantly stirred at the rate of 300 rpm at 80 °C for 2 h. Once stirred, the solid sample was filtered and repeatedly washed with distilled water until the solution reached the neutral pH and then dried overnight at 90°C in oven. The fly ash was mixed with sodium hydroxide anhydrous pellets, in a weight ratio NaOH/FA of 0.75 and 1.25 by initially grinding the fly ash with sodium hydroxide. Subsequently, the mixture was fused at 550 °C for 1 h in a muffle furnace. Once cooled down, the product was crushed and was added NaAlO2 to make the ratio $NaAlO_2$/FA of 0.5 and 1 to investigate the effect of the ratio of Si/Al the mixture was dispersed in a weight ratio of 1/5 ml of seawater or distilled water. Crystallization was then performed under static condition (40, 60 and 90 °C) for 1-72 h. The crystal products were separated and washed several times with distilled water for a pH of around 10–11. The wet solid was finally dried overnight at 105 °C and then calcined at 550 °C for 5 h and used as previously described.

Characterization methods

The X-ray fluorescence (XRF) (PANalytical AXIOS Spectrometer) was applied for the chemical composition of major chemical constituents and trace elements. The mineral characterizations of both fly ash and zeolite products were determined by powder X-ray diffraction (XRD) using a Philips X'Pert vertical diffractometer, using cooper radiation Cu-Kα. The morphology and the chemical composition of the main mineral components were determined using electron scanning microscope (SEM). The equipment used was a Zeiss Supra 40 scanning microscope. The specific surface area of the zeolite samples was determined applying N2 adsorption - desorption technique involving Brunauer-Emmett-Teller (BET), Sorpty 1750 Fison instrument, after a preliminary degassing step under vacuum at 150 °C.

3. Results

The chemical composition of fly ash determined by means of X-ray fluorescence (XRF) contains mainly 78 % SiO_2 + Al_2O_3, whereas the impurities consist of metallic oxides such as Fe_2O_3 and CaO. Other elements including K_2O, TiO_2, SO_3 and MgO are present on trace, Table 1 (defined as class F coal fly ash corresponding with ASTM C618. Fly ash was treated with acid-washing to dealuminate and reduce the concentration of iron and alkali oxides and to enhance Si and Al compositions. XRF data (Table 1) indicate that most of the impurities (Fe_2O_3, CaO, and other impurities were removed by FA treatment with 20%w/w of hydrochloric acid in liquid ratio (acid / fly ash solution of 15 mL acid / 1 g FA) thus enhancing SiO_2 + Al_2O_3 compositions. Table 1 shows that the amount of silicon increased by acid treatment, thus increasing the mass ratio of SiO_2/Al_2O_3 which was 1.8% before acid treatment and became 2.25% after treatment. This is also confirmed by XRD data (Figure. 1) which mainly confirms the presence of amorphous phase by giving wide elevations in the 2θ range of 20-35°. Meanwhile the main crystalline phase consists mainly of quartz (SiO_2) (Ref. 01-089-8936) and mullite ($Al_6Si_2O_{13}$) (Ref. 00-015-0776) where sharp points are observed.

Table 1. Chemical composition of raw and acid-treated fly ash analyzed by XRF.

Chemical composition (wt. %)	Fly ash raw	Fly Ash acid treatment
SiO_2	50.96	61.66
Al_2O_3	27.45	24.20
Fe_2O_3	7.02	5.47
CaO	4.22	1.07
K_2O	3.34	3.21
TiO_2	1.74	1.92
SO_3	1.52	0.18
MgO	1.28	0.75
Na_2O	0.92	0.68
P_2O_5	0.77	0.23
SiO_2/Al_2O_3	1.86	2.55

The SEM image in Figure 1 shows the typical fly ash morphology characterized by most spherical particles which consist of cenospheres and plerospheres. XRD data in Figure 1 indicate that the mineral composition of fly ash does not change with the acid treatment showing the presence of mullite and quartz, as well as the large amount of amorphous materials. The specific surface, instead, slightly increases after the treatment with acid, from 1.5 m^2 / g to 2.9 m^2 / g. Figure 1 also displays XRD patter of FA after fusion at 550 °C for 1 hour with NaOH. The profile indicates the formation of sodium silicate (Na_2SiO_3) (Ref. 00-016-0818) and silicon oxide dealuminate (Al_2SiO_5) (Ref. 01-088-0890).

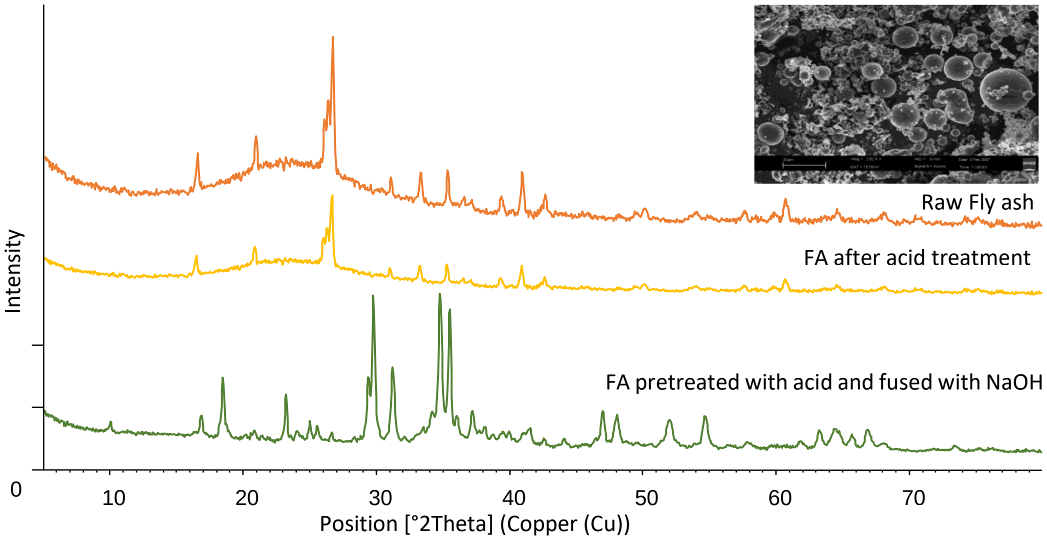

Figure 1. X-ray diffraction patterns of raw fly ash, fly ash pretreated with acid, fly ash pretreated with acid and fused with NaOH/FA 1.25 at 550 °C for 1 h. Top right, Scanning electron microscopy image of raw fly ash.

On the other hand, these newly formed compounds dissolve in water much more easily than quartz and mullite in the initial FA. Dissolution of FA and alkaline aluminosilicate phases released ionic species which were activated at the nucleation sites. As condensation of aluminum and silicon ions occurred, the surface of the FA particles was covered with the precipitate of an aluminosilicate gel. After some time, the zeolite phases were crystallized, using NaOH as an activator. All zeolite products were obtained when NaOH was used as an activator Figure 2a, whereas no zeolite material was crystallized using KOH and LiOH (Figure 2b, c).

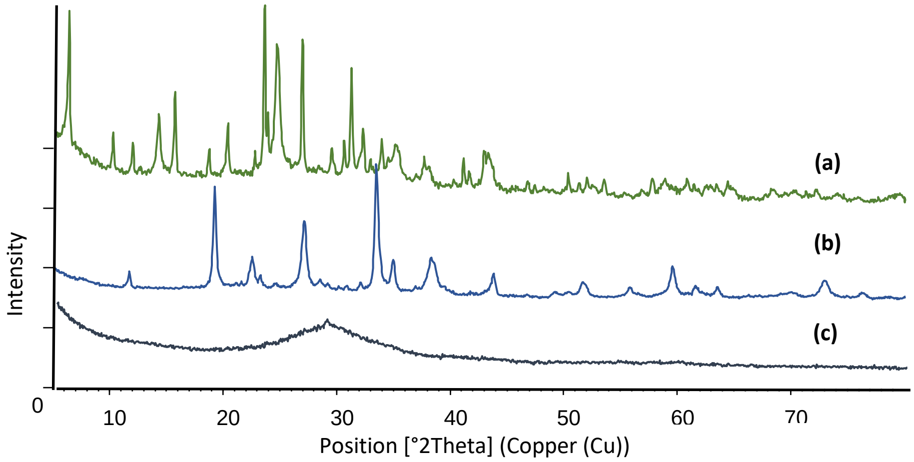

Figure 2. X-ray diffraction patterns of products synthesized from fly ash using as an activator: (a) NaOH; (b) KOH; and (c) LiOH.

XRD data show the presence of amorphous/geopolymer phase in the sample treated with KOH as activator(Figure 2b); and lithium silicate (Li_2SiO_3) when LiOH was used Figure 2c. A and X-type zeolites after NaOH pre-fusion treatment followed by Figure 3, instead, shows the products after NaOH pre-fusion treatment followed by hydrothermal process. In detail, X-type zeolite (Figure 3, top) formed after

FA pre-treated with hydrochloric acid, followed by the fusion process at 550 °C for 1 h (NaOH) / FA = 1.25); crystallization temperature 60 ° C; crystallization time 72 hours and distilled water as solution. In detail, the X-ray diffraction pattern shows that the generated X zeolite has a high crystallinity and is pure phase. The surface area (BET) for this synthetic product was 412 m^2 / g. The diffraction peaks of the powder pattern are well described by $Na_{71}(Si_{121}Al_{71})O_{384}$ crystal structure (Ref. 00-150-7214).

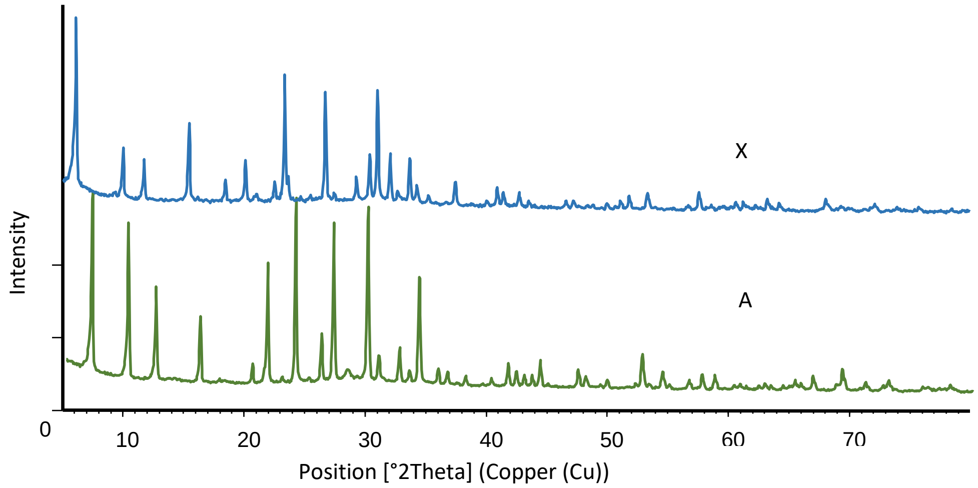

Figure 3. X-ray diffraction patterns of synthesized zeolite from fly ash type Zeolite X (top) and Zeolite A (bottom).

The addition of sodium aluminate ($NaAlO_2$ / FA = 1.0) combined with higher crystallization temperature (90 °C) and higher incubation time (6 hours) determined the formation of A-type A (Figure 3 bottom). Zeolite A was synthesized using the following experimental conditions: FA pre-treated with hydrochloric acid (HCl) followed by the fusion process at 550 °C for 1 h (NaOH / FA = 1.25), addition after calcination of sodium aluminate at the ratio $NaAlO_2$ / FA = 1, the crystallization temperature is 90 °C; crystallization time 6 hours using distilled water as solution in 1/5 solid / liquid ratio. The XRD model shows that zeolite A is characterized by a very high crystallinity phase (80-97%) with yield up to 71%. However, the results show that the surface area of this zeolite is 30 m^2 / g (BET) much lower than X-type zeolite. The diffraction peaks of the powder pattern are well described by $Na_{12}(Al_{12}Si_{12}O_{48})(H_2O)_{27}$ crystal structure (Ref. 00-8104-214).

Both zeolite X and zeolite A belong to the cubic system. Synthesis conditions strongly influenced the morphology of the synthesis products. Figure 4 a shows SEM micrograph of typical octahedral crystals of zeolites X (Figure 4a) and cubic shape of zeolite A (Figure 4b).

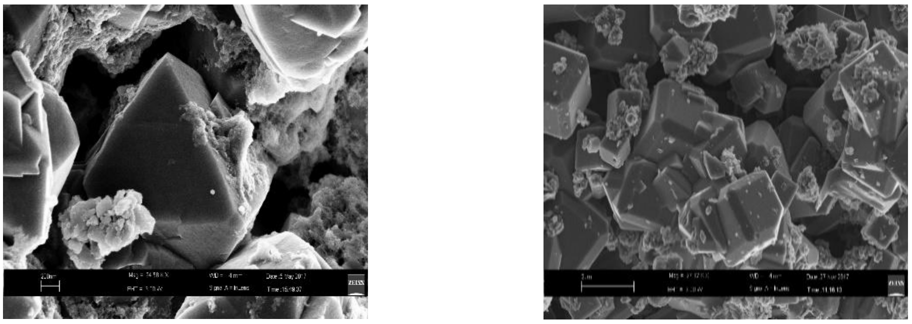
(**a**) (**b**)

Figure 4. Scanning electron microscopy (SEM) images of (a), zeolite type X (b), zeolite type A

Zeolite have been successfully synthesized from fused fly ash by using seawater as a crystallization medium. Using distilled water zeolite X with a specific surface area 412 m^2/g was formed, meanwhile when sea water was used was synthesized zeolites type X a lower specific surface area 362 m^2/g.

4. Discussion and conclusion

Zeolite samples were synthesized from fly ash through fusion followed by hydrothermal treatment. FA contained a reasonable fraction of Si and Al, which is considered a potential raw material for the synthesis of zeolite. Several other components act as poison during the catalytic applications of zeolites [20]. Fly ash particles are mostly spherical in shape with a relatively smooth surface structure. Cenospheres show a large variation in their dimensions and plerospheres expose smaller spheres [23]. Fly ash treated with acid-washing to dealuminate and reduce the concentration of iron and alkali oxides, results agree with that of [16, 24], who reported that heavy metals show a high leachability in acid condition. Fe_2O_3 is closely bound to ash and does not break down easily, while the CaO content in FA is highly soluble and purifies almost more than half of the content, specifically CaO was 4.2% before acid treatment and reached 1.1% after acid treatment. The untreated carbon fly ash had a purity of 79% (Na_2O, SiO_2 and Al_2O_3), while the HCl treatment provided a purity of the material of up to 87% (Na_2O, SiO_2 and Al_2O_3). From the results it is observed that the acid pre-treatment of the fly ash before being used in the synthesis of artificial zeolites is considered an important parameter for the purity of the zeolite phase.

Conversion of FA to zeolite materials using an alkaline fusion, followed by hydrothermal treatment revealed that KOH and LiOH showed a poor efficiency to activate FA, compared to the case where NaOH was used as activator as reported by [25]. Na^+ cations also play a very important role during zeolitization because they stabilize the sub-building units of zeolite frames and are fundamental to the synthesis of zeolite under hydrothermal conditions [20]. On the other hand, K^+ solution promotes the slow rate of crystallization in KOH solutions and it is therefore the suppression factor for zeolite synthesis [26]. The synthesis of zeolites X was favored by the value 1.7 of the mass ratio SiO_2 / Al_2O_3 or otherwise expressed in the molar ratio of 2.9 which is suitable for the synthesis of zeolite X. These results agree with those of [27] who reported that zeolites such as (Na-X, Na-Y) formed in the Si / Al molar ratio of more than 1 in this case concrete molar ratio Si / Al was 1.35. The synthesis of zeolites A is attributed to the modified Si / Al ratio with the addition of $NaAlO_2$ which enables the synthesis of zeolites A instead of zeolites X. It is worth mentioning here that the synthesis of type A zeolite requires much shorter crystallization time (starting from 4 hours compared to the synthesis of type X zeolites which requires 72 hours. The Si / Al molar ratio for the synthesized zeolite A is calculated at 0.98, this agrees with [27] who reported also that zeolites A are formed in the Si / Al molar ratio around the value 1.

Meanwhile, crystallization is the process that forms the crystal framework of the zeolite, which occurs faster at higher crystallization temperatures such as 90°C, but the highest phase purity is obtained at 60°C. The crystallinity of zeolite X increases progressively in the crystallization temperature range from 40°C to 60°C. The surface area increased from 44 to 412 m^2/g as the crystallization temperature increased from 40 to 60 °C, and then dropped to 318 m^2/g at 90 °C. The use of seawater improves the zeolite synthesis, and the action is more pronounced at lower incubation temperature. When sea water is used instead of distilled water to produce X-type zeolite, the newly formed mineral has lower purity and specific surface area but higher catalytic activity than when distilled water was used [12].

In short time of crystallization 24 h, low temperature 60 °C and low ratio of NaOH/FA 0.75, the use of sea water was favorable compared to distilled water in the synthesis of zeolite type X. However, it was confirmed from XRD profile, when it was used sea water, time of crystallization 72 h, crystallization temperature 90 °C and ratio of NaOH/FA 1.25, sodalite was generated together with, an undesired secondary.

Synthetic zeolites were tested as heterogeneous basic catalyst in the gas-phase alkylation of phenol with diethyl carbonate (DEC). It was obtained phenol conversions up to 95% with a selectivity to phenetole higher than 85% thus demonstrating that the catalytic activity of the zeolites synthesized from fly ash i very high.

Results obtained show that the method described is clean, cost-effective, and environmentally friendly. The stability of the catalyst and the applicability of our innovative synthetic zeolites for catalytic application as heterogeneous basic systems makes zeolite synthesis from FA an alternative for the common commercial catalysts used in industries.

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Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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