

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 the 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 a pre-fusion method followed by a hydrothermal treatment under 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, SiO₂/Al₂O₃ ratio and type of water (distilled water and seawater) are also important parameters influencing type of zeolite synthesized. Zeolite X was used as a novel catalyst for the alkylation of phenol using diethyl carbonate.

Keywords: fly ash; synthesis; zeolite structure; crystallinity

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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 producer 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. To date, several approaches have been carried out aiming to increase the utilization of fly ash and reducing its negative impacts. Fly ash offers a large spectrum of utilization possibilities ranging from underground mining to the building and cement industry [3,4]. Furthermore, the synthesis of mesoporous silica from fly ash has attracted interest due to the resulting material's characteristics [5].

Fly ash is mineralogically characterized by the presence of amorphous materials and the 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 have been 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. The 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 the disposal of fly ash, at least partially, and thereby minimize its impact on the environment.

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

Two well-known methods are commonly applied, namely the conventional hydrothermal method using an alkaline medium, and the hydrothermal process with fusion pre-treatment at high temperatures. The advantages of the fusion method are its speed of reaction [14], and the purity of the final product [15] whereas the hydrothermal method has an advantage in terms of the consistent pattern of zeolite produced. Synthesis conditions for each of the methods are different; they include pretreatment with acid [8], various alkali sources [16], molarities of alkaline agents [17], solution–solid ratio [18], temperature [6], reaction time [19], pressure, type of incubation [20] and type of water [21,22].

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

2.1. Materials

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

2.2. 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 [8]. 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 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 to NaAlO_2 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 conditions (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.

2.3. 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 copper radiation Cu-K α . 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), using a Sorptly 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 % SiO₂ + Al₂O₃, whereas the impurities consist of metallic oxides such as Fe₂O₃ and CaO. Other elements including K₂O, TiO₂, SO₃ and MgO are present in trace amounts, shown in 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 (Fe₂O₃, 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 SiO₂ + Al₂O₃ compositions. Table 1 shows that the amount of silicon was increased by acid treatment, thus increasing the mass ratio of SiO₂/Al₂O₃ 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 2 θ range of 20–35°. Meanwhile the main crystalline phase consists largely of quartz (SiO₂) (Ref. 01-089-8936) and mullite (Al₆Si₂O₁₃) (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 ₂ O ₃	27.45	24.20
Fe ₂ O ₃	7.02	5.47
CaO	4.22	1.07
K ₂ O	3.34	3.21
TiO ₂	1.74	1.92
SO ₃	1.52	0.18
MgO	1.28	0.75
Na ₂ O	0.92	0.68
P ₂ O ₅	0.77	0.23
SiO ₂ /Al ₂ O ₃	1.86	2.55

The SEM image in Figure 1 shows the typical fly ash morphology characterized by the 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 following the acid treatment showing the presence of mullite and quartz, as well as a large number of amorphous materials. The specific surface, instead, slightly increases after the treatment with acid, from 1.5 m²/g to 2.9 m²/g. Figure 1 also displays the XRD pattern of FA after fusion at 550 °C for 1 h with NaOH. The profile indicates the formation of sodium silicate (Na₂SiO₃) (Ref. 00-016-0818) and silicon oxide dealuminate (Al₂SiO₅) (Ref. 01-088-0890).

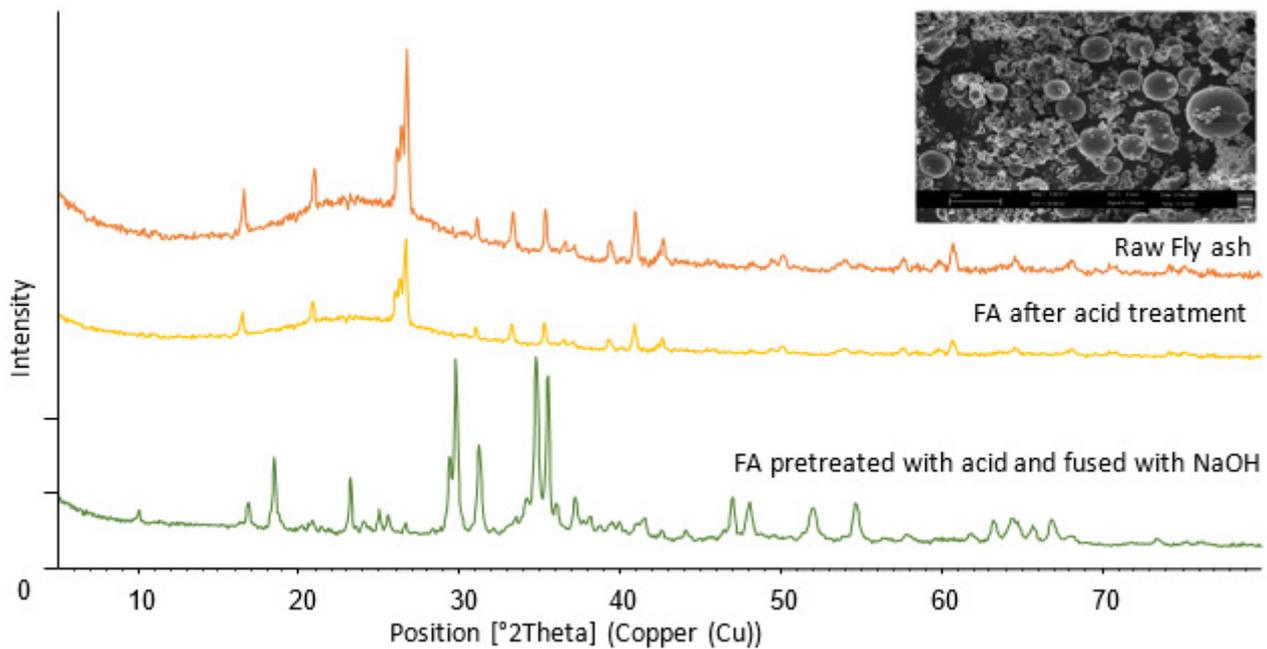


Figure 1. X-ray diffraction patterns of raw fly ash, fly ash pretreated with acid, fly ash pretreated with acid and fused with NaOH/FA 1.25 at 550 °C for 1 h. Top right, Scanning electron microscopy image of raw fly ash.

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 or LiOH (Figure 2b,c).

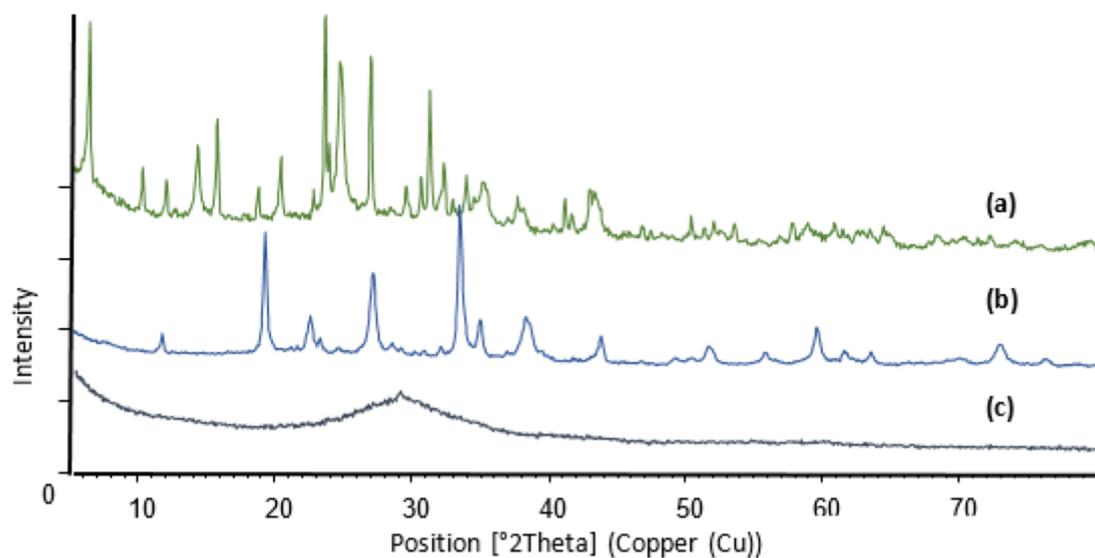


Figure 2. X-ray diffraction patterns of products synthesized from fly ash using as an activator: (a) NaOH; (b) KOH; and (c) LiOH.

XRD data show the presence of an 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). Figure 3 shows A- and X-type zeolites after NaOH pre-fusion treatment followed by the hydrothermal process. In detail, X-type zeolite (Figure 3, top) formed after FA was pre-treated with hydrochloric acid followed by the fusion process at $550\text{ }^\circ\text{C}$ for 1 h ($\text{NaOH}/\text{FA} = 1.25$), with a crystallization temperature $60\text{ }^\circ\text{C}$, crystallization time of 72 h and distilled water as the 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 $412\text{ m}^2/\text{g}$. The diffraction peaks of the powder pattern are well described by $\text{Na}_{71}(\text{Si}_{121}\text{Al}_{71})\text{O}_{384}$ crystal structure (Ref. 00-150-7214).

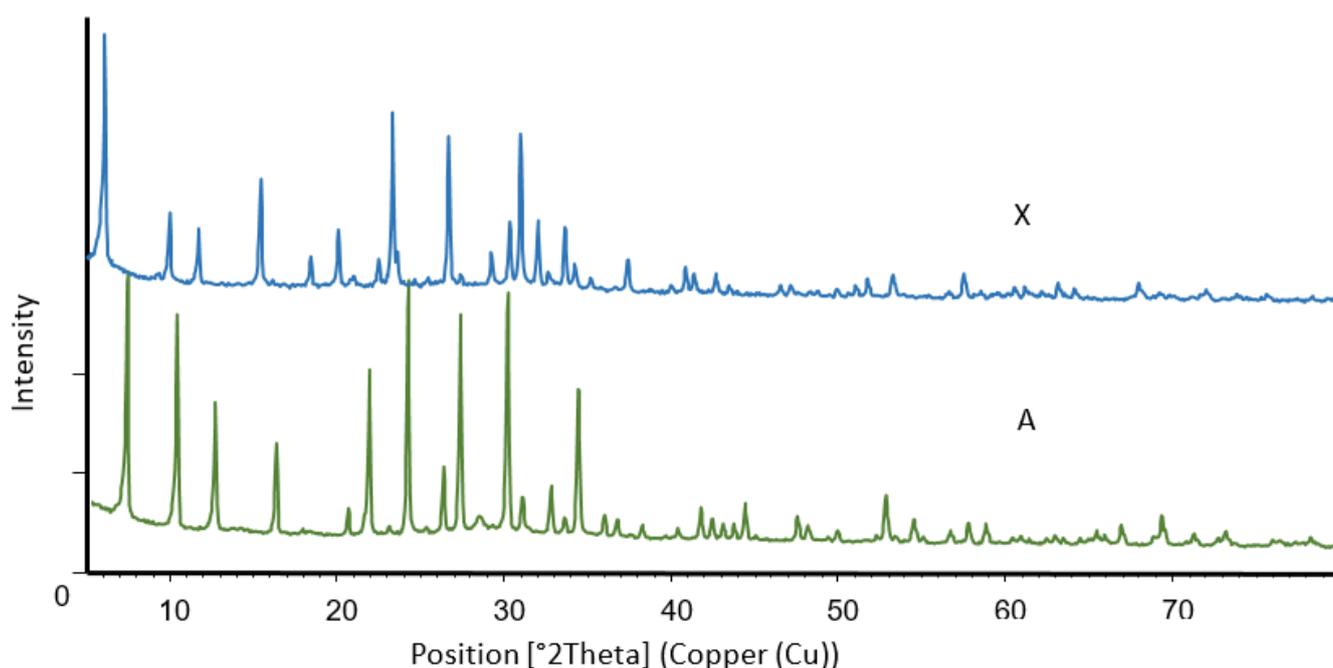


Figure 3. X-ray diffraction patterns of synthesized zeolite from fly ash type Zeolite X (**top**) and Zeolite A (**bottom**).

The addition of sodium aluminate ($\text{NaAlO}_2/\text{FA} = 1.0$) combined with a higher crystallization temperature ($90\text{ }^\circ\text{C}$) and higher incubation time (6 h) determined the formation of A-type (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 $550\text{ }^\circ\text{C}$ for 1 h ($\text{NaOH}/\text{FA} = 1.25$), the addition after calcination of sodium aluminate at the ratio $\text{NaAlO}_2/\text{FA} = 1$, the crystallization temperature at $90\text{ }^\circ\text{C}$ and a crystallization time of 6 h using distilled water as the 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 $30\text{ m}^2/\text{g}$ (BET) much lower than X-type zeolite. The diffraction peaks of the powder pattern are well described by $\text{Na}_{12}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48})(\text{H}_2\text{O})_{27}$ 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 4a shows an SEM micrograph of typical octahedral crystals of zeolites X (Figure 4a) and cubic shapes of zeolite A (Figure 4b).

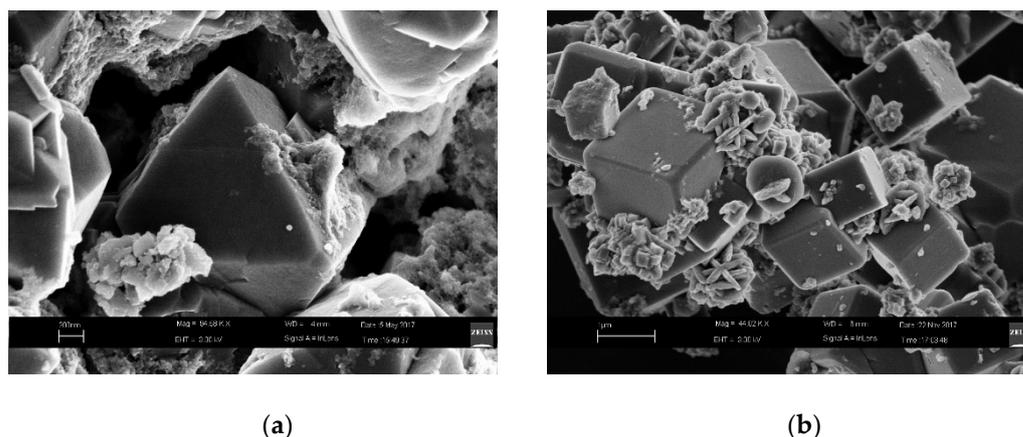


Figure 4. Scanning electron microscopy (SEM) images of (a), zeolite type X (b), zeolite type A.

Zeolite have been successfully synthesized from fused fly ash by using seawater as a crystallization medium. Using distilled water, zeolite type X with a specific surface area of 412 m²/g was formed; meanwhile, when sea water was used this created zeolite type X with a lower specific surface area of 362 m²/g.

4. Discussion and Conclusions

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 [19]. 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 [22]. Fly ash was treated with acid washing to dealuminate and reduce the concentration of iron and alkali oxides. Results agree with those of [7,8], who reported that heavy metals show a high leachability in acid condition. Fe₂O₃ is closely bound to ash and does not break down easily, while the CaO content in FA is highly soluble and purifies 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% (Na₂O, SiO₂ and Al₂O₃), while the HCl treatment provided a purity of the material of up to 87% (Na₂O, SiO₂ and Al₂O₃). 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 [23]. 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 [19]. On the other hand, K⁺ solution promotes the slow rate of crystallization in KOH solutions and is therefore the suppression factor for zeolite synthesis [24]. The synthesis of zeolite X was favored by the value 1.7 of the mass ratio SiO₂/Al₂O₃, otherwise expressed in the molar ratio of 2.9, which is suitable for the synthesis of zeolite X. These results agree with those of [25] who reported that zeolites such as (Na-X, Na-Y) formed in the Si/Al molar ratio of more than 1; in this case the concrete molar ratio Si/Al was 1.35. The synthesis of zeolite A is attributed to the modified Si/Al ratio with the addition of NaAlO₂ 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 h compared to the synthesis of type X zeolites which requires 72 h). The Si/Al molar ratio for the synthesized zeolite A is calculated at 0.98, this agrees with [25] 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 m²/g as the crystallization temperature increased from 40 to 60 °C, and then dropped to 318 m²/g at 90 °C. The use of seawater improves the zeolite synthesis, and the action is more pronounced at lower incubation temperatures. 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 is used [12].

With a short crystallization time of 24 h, low temperature at 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 the XRD profile, that when sea water was used, with a crystallization time of 72 h, a crystallization temperature of 90 °C and a ratio of NaOH/FA 1.25, sodalite was generated together with an undesired secondary.

Synthetic zeolites were tested as heterogeneous basic catalysts in the gas-phase alkylation of phenol with diethyl carbonate (DEC). This 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 is 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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