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Siliceous fly ash utilization conditions for zeolite synthesis

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Silvana Gjyli [1,*], Arjan Korpa [2], Valdet Teneqja [2], Dritan Siliqi [3], Claudia Belviso [4*]

[1] Department of Industrial Chemistry, Faculty of Natural Sciences, University of Tirana, 1000 Albania;
[2] Department of Chemistry, Faculty of Natural Sciences, University of Tirana, 1000 Albania;
[3] Istituto di Cristallografia, Consiglio Nazionale delle Ricerche, 70126 Bari, Italy;
[4] Institute of Methodologies for Environmental Analysis - IMAA-CNR, Tito Scalo (PZ), 85050 Italy;
* Corresponding author: vanagjyli@yahoo.com (S.Gj); claudia.belviso@imaa.cnr.it (C.B)

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

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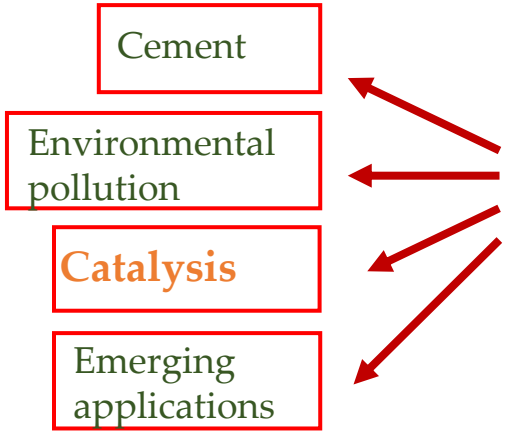
Zeolites are hydrated aluminosilicate minerals with a three-dimensional open structure.

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.



Zeolites are used in several applications because of their special structure and properties.

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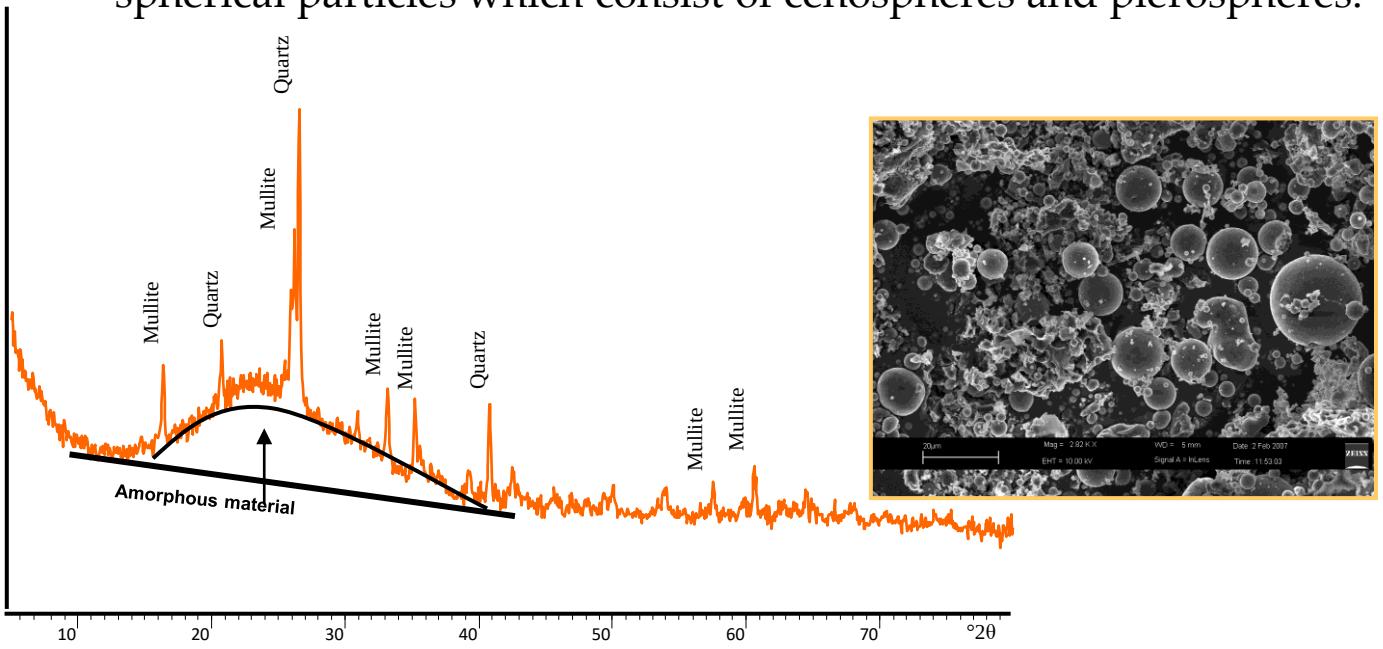
Waste fly ash can be employed for the synthesis of zeolites;

Fly ash contains abundant aluminosilicate and silicate phases; it is typically composed of:

- amorphous materials, ranging from 34% to 80 %, and
- crystalline phases (e.g., quartz, mullite, hematite, etc.

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.

The SEM image shows the typical fly ash morphology characterized by most spherical particles which consist of cenospheres and plerospheres.



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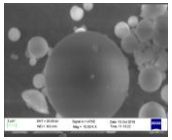
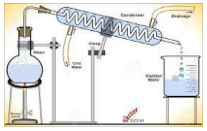
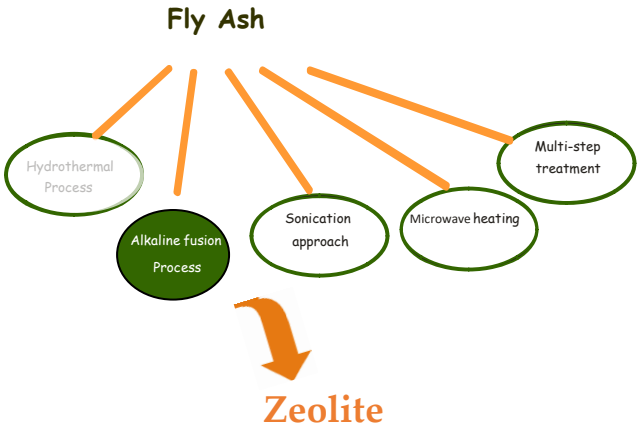
The experiments were carried with:

- Silicious fly ash (FA 
- Alkaline pre-fusion hydrothermal process
- With and without fly ash HCl treatment
- NaOH/fly ash with different ratio
- Crystallization temperature from 40°C to 90°C 
- Incubation time ranging from 1h to 72h 
- Distilled water or seawater as incubation solution 
- With and without $NaAlO_2$ addition 



Main parameters studied:

- Acid pre-treatment of fly ash before the fusion and hydrothermal process
- NaOH, KOH, LiOH pre-fusion hydrothermal process
- NaOH/FA and Si/Al ratio
- Study of the effect of seawater vs. distilled water on the type and purity of zeolite
- With and without $NaAlO_2$ addition

Results and Discussion

The chemical composition of fly ash determined by means of XRF, contains mainly 78 % SiO_2 + Al_2O_3, whereas the impurities consist of metallic oxides such as Fe_2O_3 and CaO defined as class F coal fly ash corresponding with ASTM C618. Fly ash was treated with acid-washing XRF data (Table 1) indicate that most of the impurities (Fe_2O_3, CaO, were removed, thus increasing the mass ratio of SiO_2/Al_2O_3 which was 1.8% before acid treatment and became 2.25% after treatment.

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

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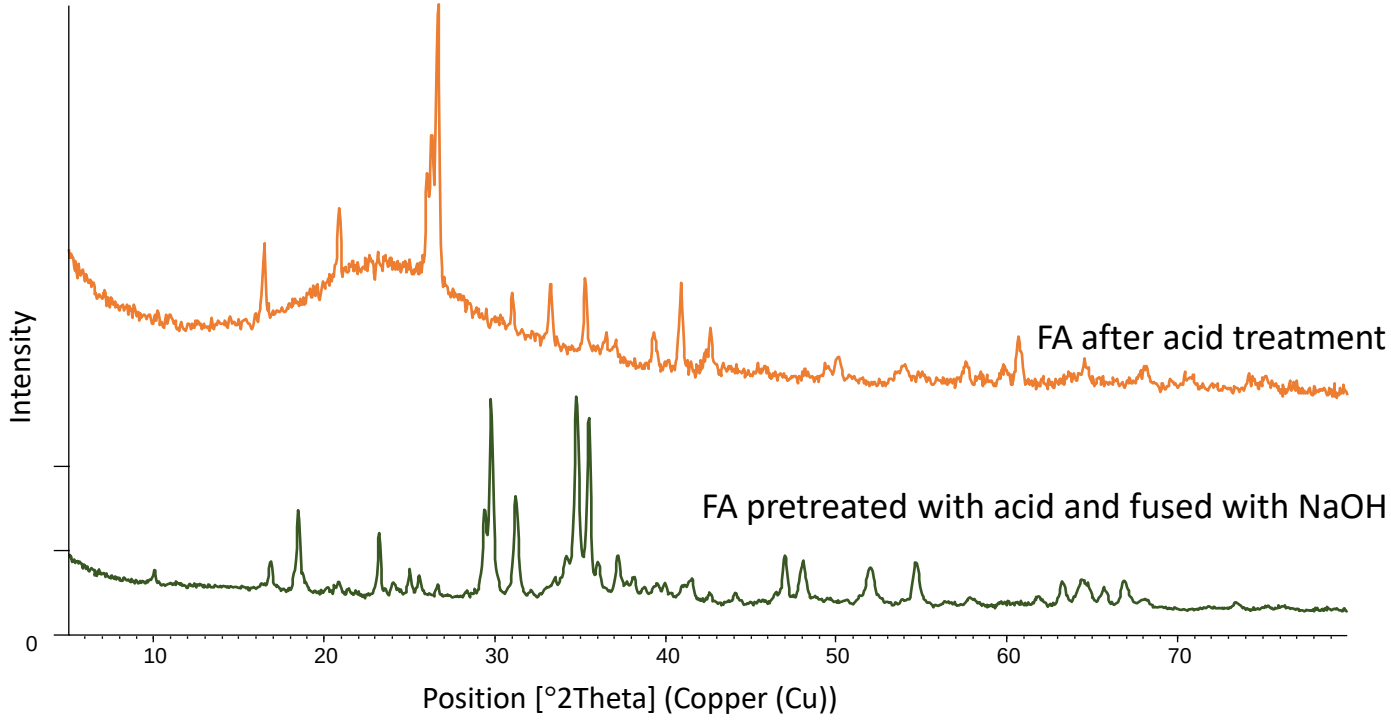
XRD data indicate that the mineral composition of fly ash does not change with the acid treatment. The untreated carbon fly ash had a purity of 79% (Na_2O, SiO_2 and Al_2O_3), while the HCl treatment provided a purity of the material of up to 87% (Na_2O, SiO_2 and Al_2O_3). The specific surface, instead, slightly increases after the treatment with acid, from 1.5 m^2/g to 2.9 m^2/g.

XRD patter displays also 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).



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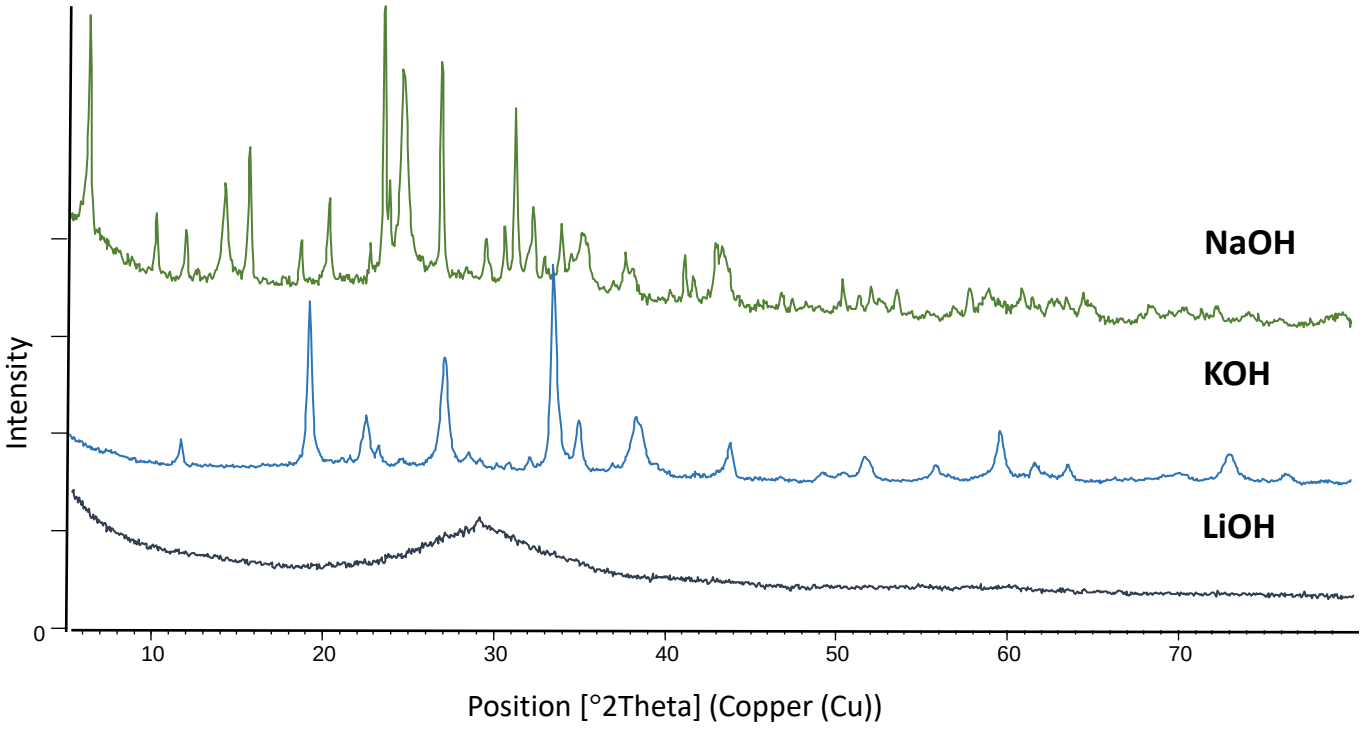
Conversion of FA to zeolite materials using an alkaline fusion, followed by hydrothermal treatment revealed that KOH and LiOH showed a poor efficiency to activate FA, compared to the case where NaOH was used as activator. XRD data show the presence of amorphous/geopolymer phase in the sample treated with KOH as activator and lithium silicate (Li_2SiO_3) when LiOH was used.

All zeolite products were obtained when NaOH was used as an activator. A and X-type zeolites after NaOH pre-fusion treatment followed by hydrothermal process.



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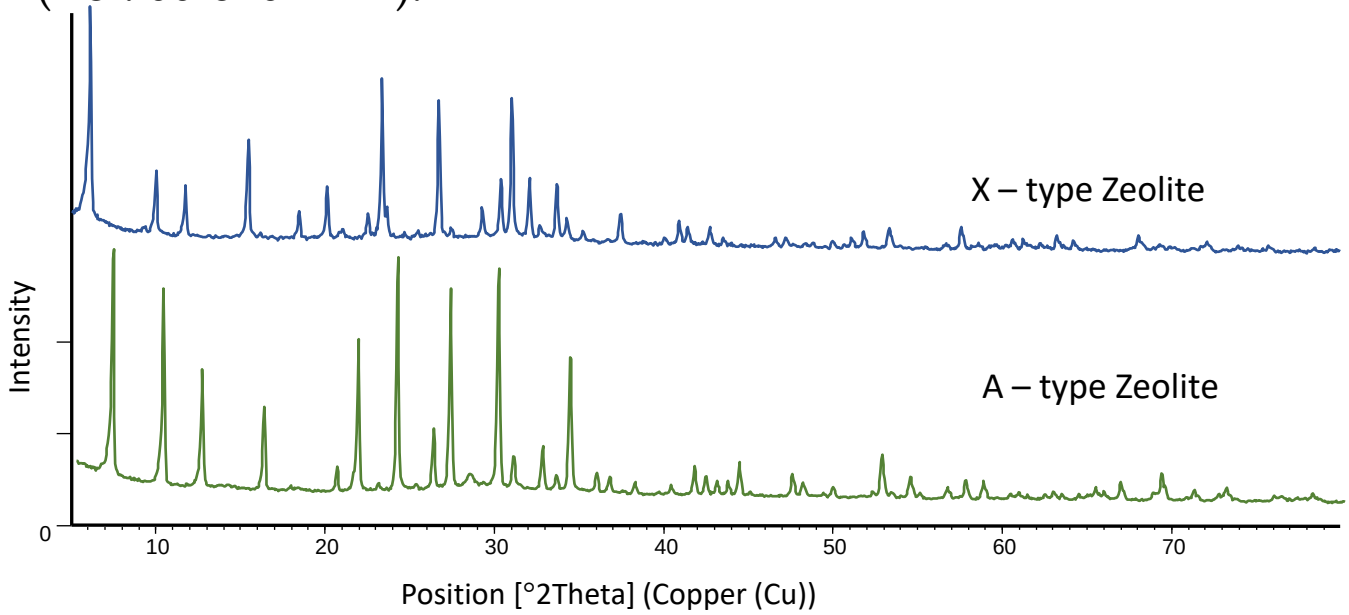
X-ray diffraction pattern shows that the generated **X zeolite** has a high crystallinity and is pure phase. The surface area (BET) for this synthetic product was 412 m^2/g. The diffraction peaks of the powder pattern are well described by $Na_{71}(Si_{121}Al_{71})O_{384}$ crystal structure (Ref. 00-150-7214).

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.

XRD model shows that **zeolite A** is characterized by a very high crystallinity phase (80-97%). 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).



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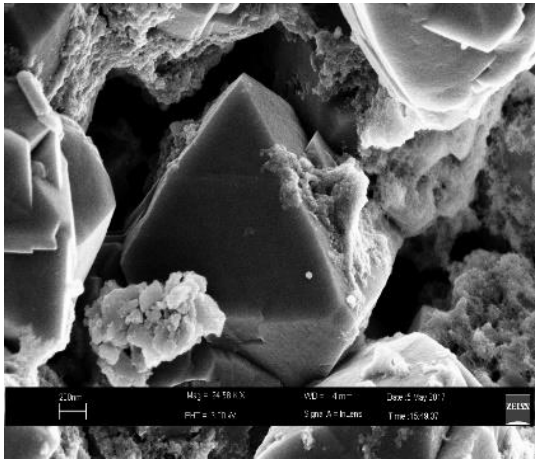
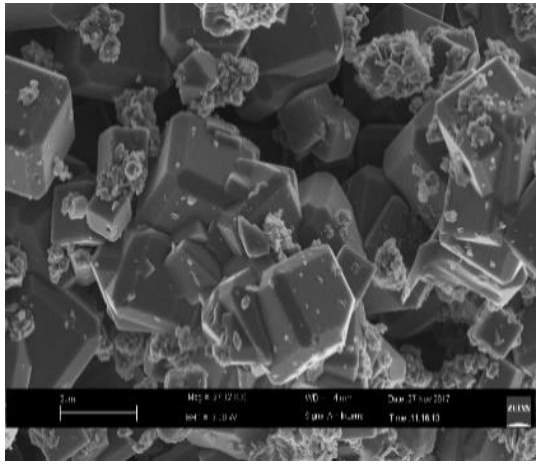
Both **zeolite X and zeolite A** belong to the cubic system. Synthesis conditions strongly influenced the morphology of the synthesis products.

SEM micrograph shows the typical octahedral crystals of zeolites X (Figure a) and cubic shape of zeolite A (Figure b).



(a)



(b)

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.

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.

The surface area of type X zeolite increased from 44 to 412 m^2/g when increasing the crystallization temperature from 40 to 60°C, and then dropped to 318 m^2/g at 90°C.

In short time of crystallization 24h, 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. 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.

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Conclusions:

- The zeolites were synthesized from waste coal fly ash through dissolution of alkali-fused aluminosilicates, followed by hydrothermal treatment.
- Acid-washing pre-treatment and synthesis conditions have a significant effect on the type and properties of the synthesized zeolite product.
- Without addition of $NaAlO_2$ the zeolite A could not be synthesized.
- When sea water is used instead of distilled water the zeolite type X has lower purity and specific surface area.
- The NaOH/FA ratio of 1.25 seems to be advantageous for type X zeolites than the NaOH/FA ratio of 0.75.

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- The optimal synthesis conditions for zeolite X were fly ash pre-treatment, NaOH/FA ratio of 1.25, fusion at 550°C for 1h, crystallization 60°C for 72 hours and employment of distilled water.

- The optimal synthesis condition for zeolite A were fly ash pre-treatment, NaOH/FA ratio of 1.25, fusion at 550°C for 1h, $NaAlO_2$/FA ratio of 0.5, crystallization 90°C for 72 hours and employment of sea water.

- The methods described are clean, cost-effective, and environmentally friendly.

- 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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