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Effect of acid pre-treatment on zeolite synthesis from fly ash: preliminary data

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Abstract

Fly ash is a by-product of thermal power plants partly disposed of in landfills. It is composed of minerals and amorphous substances, i.e., quartz, mullite, hematite and magnetite, unburned coal particles and amorphous aluminosilicate. Zeolites are tectosilicates characterised by a three-dimensional network of tetrahedral units that form a system of interconnected pores. The substitution of silicon with aluminium produces a net negative charge which is balanced by the presence of an extra cation in the framework. Due to their structure and their excellent ion exchange and sorption properties, zeolites are useful in a number of applications. Many literature data have documented fly ash conversion into zeolite.

The purpose of this study was to investigate the effect of different parameters on properties of zeolite formed from fly ash. With this aim, crystallization time (from 1 to 72 h), alkaline ratio (0.75 and 1.25), type of water (distilled water and seawater), and action of acid treatment were investigated. The experiments were performed at 40, 60, 90 °C. The synthetic products were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray fluorescence spectrometry(XRF), Infrared spectroscopy (IR), and Brunauer- Emmett-Teller (BET) method.

The results cofirm that the investigated parameters have significant effects on the structural properties of zeolite synthesised.

Keywords: Fly Ash; Acid Pre-Treatment; Zeolite Synthesis

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1. Introduction

A huge quantity of fly ash is produced from many coal thermal power plants in the world. The management of fly ash therefore is becoming both economics and environmental issues. However, partly of fly ash has been used as a raw material substitute in the concrete and cement manufacturing (Seung et al., 1999; Korpa et al., 2013), but more than half of it disposed of in landfills. Fly ash poses a great threat to the environment as well as to human health. It is composed of minerals such as quarts, mullite, subordinately hematite and magnetite, residual carbon particles, and a prevalent phase of amorphous aluminosilicate (Hower et al., 1999; Koukouzas et al., 2006). Several investigations have been carried out to recycle this waste in the production of new materials.

Fly ash conversion into zeolite is a particularly interesting process and, in the last few years, it has been proposed as a viable method. The similar chemical composition of fly ash promoted several research groups to attempt making zeolite from this waste material (Querol et al., 2002; Belviso et al., 2009, 2010; Panitchakarn et al., 2014). Zeolites are hydrated aluminosilicate minerals with a three dimensional open structure, they have a uniform pore size, a high cation – exchange capacity (CEC) and a large surface area, which make them interesting adsorbents, catalyst and ion exchangers (Gliozzi et.al., 2015).

In this study a sample of fly ash from Germany thermoelectric power plant was used for synthesizing zeolites. The high degree of conversion as well as the many properties including the ion-exchange, point to a broad spectrum of applications of zeolite materials in industrial and environmental engineering.

2. Materials and methods

1.1 Characterization

The experiments were performed using a sample of fly ash (FA) obtained from the BauMineral GmbH Company in Germany. The chemical characterization for major chemical constituents and trace elements was carried out by X-ray fluorescence (XRF) using PANalytical AXIOS Spectrometer. The mineralogical characterizations of both fly ash and zeolite products were performed by powder X-ray diffraction (XRD; Rigaku RINT-2200) using copper radiation Cu-Kα, 2θ ranging from 2-70 and step size 0.02°. Morphological observations were performed using scanning electron microscopy (SEM; Zeiss Supra 40). Infrared spectroscopic analysis of the prepared zeolite and fly ash was carried out with Alpha Bruker FT-IR spectrometer in the range 400-4000 cm^{-1}. The specific surface area of the zeolite samples was determined by N_2 adsorption-desorption technique using Brunauer-Emmett-Teller (BET), by a Carlo Erba model Sorpty 1750 instrument, after a preliminary degassing step under vacuum at 150 $^{\circ}$C.

1.2 Acid-washing pre-treatment procedure

FA was initially added to HCl, with 20% w/w acid concentration under the acid/FA ratios of 15 ml acid/g FA (Panitchakarn et al., 2014). The mixture was stirred constantly at the rate of 300 rpm at 80 °C for 2 hr. After that, the solid sample was filtered off from the acid solution and washed repeatedly with deionised water until the solution reached neutral pH and then dried overnight at 90 °C in oven.

1.3 Zeolite synthesis procedure

Zeolite synthesis was performed applying the method developed by (Ruen-ngam et al., 2009) based on pre-fusion hydrothermal method. Pre-treated fly ash was mixed with NaOH to make the ratio NaOH/FA of 0.75 and 1.25. Next, the mixture was fused at 550 °C for 1 h in furnace. The product, after cooling down, was crushed and dissolved in ratio 1:5 ml of seawater or distilled water. Crystallization was then performed under static condition (40, 60 and 90 °C) for 1-72 hr. The crystal products were separated and washed several times with distilled water to bring pH to 10 –11 and then dried overnight at 80 °C.

2. Results and Discussion

The XRD pattern of fly ash (Figure 1) shows that the main crystalline phases are mullite and quartz. However, large amount of amorphous material (approximately 80%) represents the principal source of Si and Al for this raw material. SEM observation (Fig. 1) shows the typical fly ash morphology characterized by spherical particles.

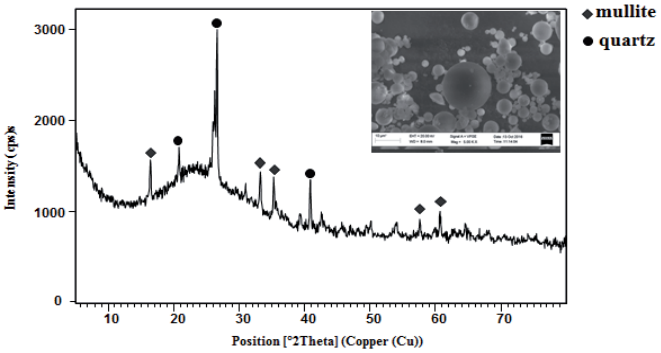

Fig. 1. XRD pattern and SEM image of fly ash

X-ray fluorescence analysis confirms that the main components of the original CFA are silicon and aluminium, whereas the impurities consist of Fe and Ca. Other elements are present on trace including K_2O, TiO_2, SO_3 and MgO (Table 1).

Table 1. Chemical composition of fly ash and fly ash treated with acid analysed by XRF

Chemical Composition (wt%) of Fly Ash				Chemical Composition (wt%) of Fly Ash treated with acid			
Major Oxide	Concentation %wt	Minor oxide	Concentation %wt	Major Oxide	Concentation %wt	Minor oxide	Concentation %wt
SiO_2	50.96	V_2O_5	0.14	SiO2	61.66	ZrO2	0.12
Al_2O_3	27.45	BaO	0.14	Al2O3	24.20	SrO	0.09
Fe_2O_3	7.02	SrO	0.1	Fe2O3	5.47	NiO	0.07
CaO	4.22	NiO	0.07	K2O	3.21	BaO	0.07
K_2O	3.34	MnO	0.06	TiO2	1.92	ZnO	0.06
TiO_2	1.74	ZrO_2	0.06	CaO	1.07	V2O5	0.06
SO_3	1.52	ZnO	0.05	MgO	0.75	MnO	0.04
MgO	1.28	Cl	0.05	Na2O	0.68	Cl	0.04
Na_2O	0.92	Cr_2O_3	0.04	P2O5	0.23	PbO	0.03
P_2O_5	0.77	PbO	0.03	SO3	0.18	Rb2O	0.03
		CuO	0.02			CuO	0.02
SiO_2/Al_2O_3	**1.86**	Co_3O_4	0.02	SiO_2/Al_2O_3	**2.55**		
Surface area (m^2/g)	**1.5**	Rb_2O	0.02	Surface area (m^2/g)	**29**		

To produce high-purity zeolite, FA raw material was also subjected to acid-washing aimed to reduce the concentration of iron and alkali oxides and to enhance Si and Al compositions (Shivpuri et al., 2012).

XRD data indicate that zeolite X formed in all the samples after 48-72 h of incubation. High amount of zeolite formed using FA/NaOH ratio 0.75 and seawater. However, the acid treatment improves the zeolite formation using distilled water and Fa/NaOH ratio 1.25 (Fig. 2).

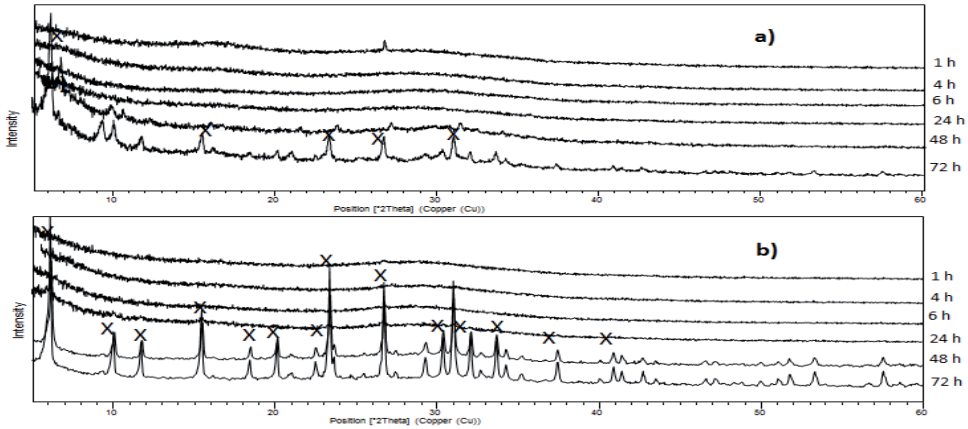

Fig. 2. X- ray diffraction patterns of synthesized zeolite at different time of crystallization, using distilled water, NaOH/FA 1.25, crystallization temperature 60 °C. a) without acid, b) with acid. X =X zeolite

Regarding the temperature parameter, XRD data of acid treated fly ash after incubation at 40, 60 and 90 °C reveal that zeolite X formed only at 90 °C with distilled water (Fig. 3a) whereas significant zeolite synthesis takes place at 60 °C using seawater (Fig. 3b). BET values change from 12 m^2/g for the sample incubated at 40 °C to 323 m^2/g after incubation at 90 °C using distilled water (Fig. 3a). BET values of 247 m^2/g and 172 m^2/g are calculated for the samples incubated at 60 °C and 90 °C, respectively, with seawater. These results could be explained taking into account both the different type of zeolite formed and their amount. However, the results indicate that BET is generally higher in the samples synthesized using acid treated fly ash.

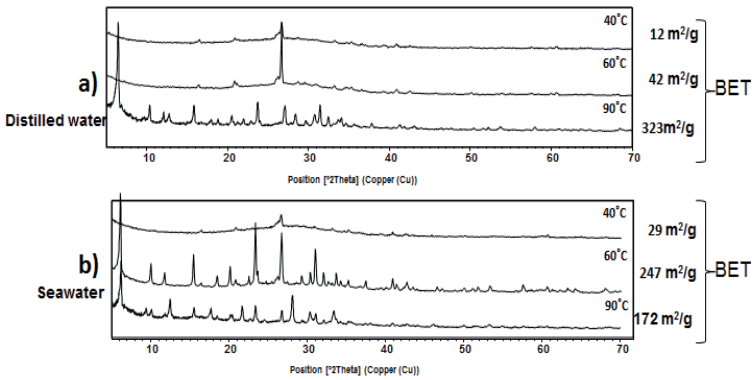

Fig. 3. X- ray diffraction patterns of zeolite crystallization at different temperatures treatment with acid, NaOH/FA 0.75 using : a) distilled water, b) seawater

Representative IR spectra zeolite formed is shown in Figure 4. The two most intense bands at 860–1230 cm^{-1} and 420–500 cm^{-1} confirm the presence of zeolite (Flanigen et al., 1971).

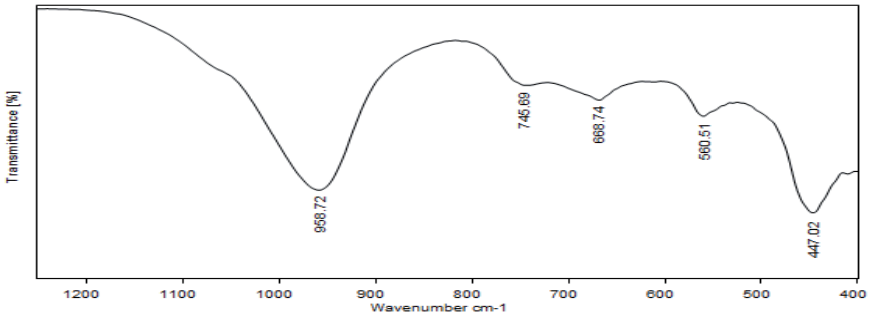

Fig. 4. IR spectra of synthesized zeolite in 1250-400 cm^{-1} wave number region

Finally, the morphology of zeolite formed is shown by SEM images in Figure 5.

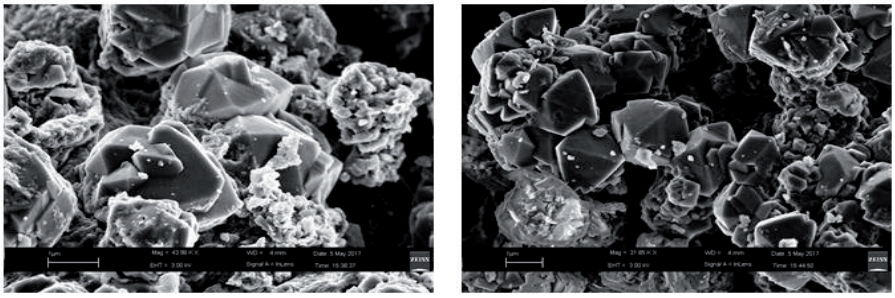

Fig. 5. SEM image of zeolite formed

4. Conclusions

In this work, the effect of various synthesis parameters such as the action of acid treatment, NaOH/FA, crystallization temperature, type of water and time were examined. The data obtained indicate that pretreatment with acid, NaOH/FA weight ratio of 1.25, distilled water, crystallization temperature of 60 °C, and crystallization time of 72 h represent the best condition to form higher amount of synthetic products. Maximum yield of X-type zeolite was as confirmed by XRD patterns, SEM images and FT–IR analysis. Zeolite synthesized from FA without acid treatment show a purity of 79% (Na_2O, SiO_2, and Al_2O_3) and specific area of 186 m^2/g. FA treated with HCl provides the highest purity material (87% of Na_2O, SiO_2, and Al_2O_3), with the specific area of 412 m^2/g, pore size of 4.86 Å and pore volume 0.13 cm^3/g.

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