

Feasibility Study on Synthesis of Zeolite from Coal Wastes of Coal Washing Plants

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ABSTRACT

Zeolite was synthesized from coal tailings and coal fly ash sampled from Zarand coal washing plant, Iran, using H₂O₂-promoted hydrothermal treatment. Samples consisted mainly of SiO₂ and Al₂O₃ which are the main components for the zeolite synthesis. To perform the experiments, appropriate amount of the starting materials were mixed with 240 ml volume of 30% H₂O₂ at room temperature with continuous stirring at 480 rpm. Then, the temperature was gradually raised to and adjusted at 80°C for 180 min. At the end, the treated mixture was filtered and aged in an oven for 15 h at 95°C to give the zeolitic products. The XRD patterns showed semi-quantitative yields of 21.43% and 8.31% for direct and indirect conversions, respectively. Based on XRF analysis, the higher yield of direct conversion could be ascribed to the higher CaO content in coal tailings compared to fly ash.

KEYWORDS

coal tailings, fly ash, zeolite, H₂O₂-promoted hydrothermal treatment.

1. INTRODUCTION

A large number of coal washing plants all over the world generates huge quantities of coal tailings which are discharged and dumped into reclaimed ground or pond. Zarand coal washing plant, Kerman/Iran, for example, discharge nearly 100 thousand tones of coal waste of about 70 percent ash content annually. These materials cause serious environmental problems mainly due to their fine structure and toxic elements, especially sulfur. However, the environmental protection restricts the development of the reclaimed area. Now, the recycling process is an emergent subject. In this regard, small portion of disposal is retreated as raw material for briquette making uses, but huge amounts would still remain as intact [1].

As a technique for recycling coal fly ash produced from electric power plants, synthesis of

zeolites from coal fly ash has received extensive attention over the last decade. Zeolites are crystalline aluminum-silicates, with group I or II elements as counter ions. These crystals are characterized by a three-dimensional pore system, with pores of precisely defined diameter and are made up of a framework of [SiO₄]⁴⁻ and [AlO₄]⁵⁻ tetrahedral linked to each other at the corners by sharing their oxygens as shown in Figure 1 [2,3]. Due to their uniform pore sizes and large surface areas, zeolites are very useful materials for a wide range of applications such as ion exchanger, molecular sieves, gases and water adsorbents, and catalysts [4].

Since the initial studies by Höller and Wirsching [6], many patents and technical articles have proposed different activation methods to synthesize different zeolites from fly ash. Although all the synthesis methods are based

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on hydrothermal alkaline conversion of fly ash, the following types of processes may be used:

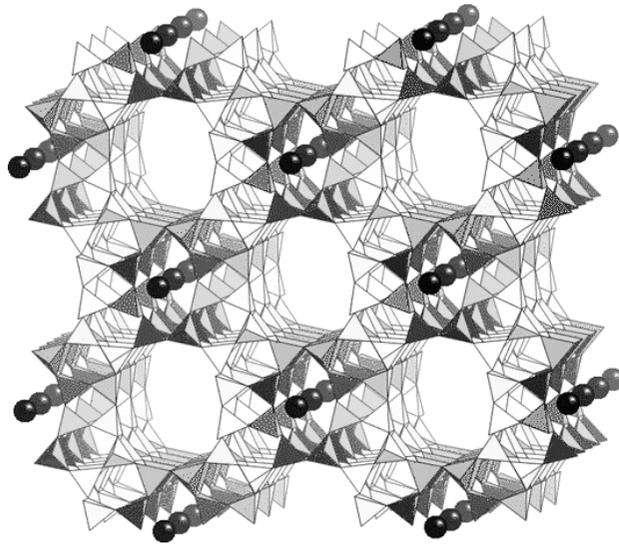


Fig.1: Idealized structure of zeolite framework: SiO_4 and AlO_4 tetrahedral are represented as light and dark colored pyramids, respectively; solid spheres indicate the counter ions [5].

Classic alkaline conversion: This is based on the combination of different activation solution/fly ash ratios, with temperature, pressure, and reaction time to obtain different zeolite types. Referring to the literature, the fly ash activation is usually carries out in digestion bombs or autoclaves, varying the activation agent (mainly KOH and NaOH), temperature (80–200°C), conversion time (3–48 h), solution concentration (0.5–5 M), pressure (the vapor pressure at the temperature selected), and solution/sample ratio (1–20 ml/g), to synthesize up to 13 different zeolites from the same fly ash. The zeolite content of the resulting material varied widely from 40 to 95 percents [2,7–15]. Most of the previously referenced studies demonstrated that the NaOH solutions have higher conversion efficiency than the KOH solutions under the same temperature. This methodology has been applied at a pilot plant scale by Querol et al. [9] for the production of 2.7 tones of zeolite material in 8 h in a single-batch experiment. Table 1 summarizes the zeolite types that may be synthesized from fly ash using classic alkaline conversion under different conditions.

TABLE 1
Zeolite and other neomorphic phases synthesized from fly ash using classic alkaline method

Type and concentration (M) of activation solution	Temperature (°C)	Activation solution/fly ash ratio (ml/g)
NaOH		
0.5–3.0	90–175	10–18
	175–225	NaPl analcime, hydroxyl-sodalite, tobermorite, nepheline-hydroxy
3.0–5.0	150–200	hydroxyl-sodalite, hydroxyl-cancrinite, tobermorite
KOH		
0.5–1.0	150–200	KM, tobermorite
3.0	< 150	linde F, tobermorite
5.0	< 150	linde F, kalsilite, tobermorite
3.0–5.0	> 150	kalsilite, tobermorite
NaOH		
5.0	150–200	1–3 low activation for all temperatures
1.0	150	low activation, NaPl (herschelite)
	200	NaPl and herschelite for 8 h activation
	90	A zeolite
2.0–3.0	150	NaPl (herschelite traces), faujasite (if aging)
	200	NaPl, herschelite
	150–200	herschelite, analcime, hydroxyl-sodalite, hydroxyl-cancrinite
KOH		
2.0	150–200	KM zeolite
5.0	150	KM, chabazite and linde F traces
	200	kalsilite and KM, perialite and tobermorite traces

Alkaline fusion conversion: In this method, an alkaline fusion stage is introduced in the classic alkaline conversion before the conventional zeolite synthesis, resulting in very interesting zeolites such as zeolite A and faujasite. In fusion method, a mixture of fly ash and activation agent (KOH or NaOH) of 1/1.2 wt. ratio is milled, and fused at 500–800°C for 1 h. The resultant fused mixture is cooled and milled again. The powder thus obtained is mixed with certain volume of distilled water and kept in stirring condition for 8–12 h at room temperature. Then the whole mass is transferred into a pressure bomb and kept for 12 h at 100–105°C at autogenous pressure. Finally precipitates are filtered, washed repeatedly with distilled water to remove the remaining activation agent, dried at 110°C, to yield synthesized zeolite. In alkaline fusion conversion, the most important variables are fusion temperature (500–800°C) and the volume of water applied in hydrothermal stage (100–200 ml) [11,16–24].

Dry or molten-salt conversion: To avoid a synthesis process with the generation of waste water, Park et al. [25,26] developed a synthesis strategy based on the use of salt mixtures instead of the aqueous solutions as the reaction medium. This interesting process has limitations since, up to now, only low-CEC zeolites are obtained to the high temperature needed in the activation process.

Multi-stage hydrothermal procedures: To enhance the efficiency of synthesis process, some researchers have tried to improve classic hydrothermal conversion by introducing one or more stages during hydrothermal treatment. These studies are all focused on keeping the Al(III)/Si(IV) ratio in the starting solution as high as possible using an aluminates solution, resulting in zeolite of high ion exchange capacity [4,27–31].

H₂O₂-promoted hydrothermal conversion: Kantiranis et al. [32] developed an open-system method in which a H₂O₂ solution was applied as

activation agent instead of conventional alkaline agents. The process is carried out in an open vessel at 80°C under atmospheric pressure and then, product is filtered and dried at 95°C. The role of H₂O₂ as a dominant factor in the zeolite synthesis is attributed to the oxidation of Fe(II) to Fe(III) and to the oxidative action on the unburned organic matter of the fly ash to prevent the reduction of Fe(III) to Fe(II). Fe(III) is proposed to participate in the reaction with Si–OH and OH–Al groups in the preliminary steps, resulting to the formation of an intermediate group [Fe–(H⁺)O(O–Si)–Al] which then gives Si–O–Al groups and Si–O–Fe groups to a lesser extent, both of which lead to a zeolite structure. Formation of the latter group explains the presence of Fe(III) in the zeolite crystal structure.

In spite of the large amount of studies focusing on the conversion of coal fly ash into zeolite, there is no work considering the directly synthesis of zeolite from coal tailings. The purpose of this study is therefore to assess the possibility of directly synthesize zeolite from coal wastes of coal washing plants. H₂O₂-promoted hydrothermal method was applied to synthesize zeolite due to its superior advantages, i.e. open-system aided and low capital costs, relative to other synthesis alkaline methods.

2. MATERIAL PREPARATION

A carefully chosen sample of coal tailings from Zarand coal washing plant, Iran, was used as starting material for directly synthesis process. The chemical composition of the coal tailings is given in Table 2. For comparative study, a fly ash sample was produced from the tailings. In this regard, 60 samples of 1 g of coal tailings were milled, and then heated up in a porcelain crucible at 850°C for 8 h. Since during combustion the mineral matter of coal undergoes a series of physical and chemical changes, prepared fly ash was chemically analyzed (Table 2).

TABLE 2
Chemical composition (wt%) of the starting and treated materials

Component	Coal tailings (CF)	Direct synthesis product (CP)	Fly ash used by Kantiranis et al. [32]	Fly ash (AF)	Indirect synthesis product (AP)
SiO ₂	49.1	52.6	38.24	57.6	56.9
Al ₂ O ₃	25.8	25.9	13.96	27.9	26.6
CaO	5.5	3.2	25.46	1.9	2.1
Fe ₂ O ₃	5.9	4.6	4.88	4.8	5.7
K ₂ O	5.6	3.8	0.96	3.4	3.3
SO ₃	4.0	5.0	4.26	1.1	1.3
Others*	4.1	4.9	12.24	3.3	4.1

* P₂O₅, TiO₂, MnO, MgO, Na₂O, K₂O, L.O.I.

3. EXPERIMENTAL PROCEDURE FOR ZEOLITE SYNTHESIS

The experiments were performed as follows: 20 g of the prepared fly ash were placed in 500 ml glass beaker and 240 ml volume of 30% H₂O₂ was added at room temperature with continuous stirring at 480 rpm. Then, the temperature was gradually raised to 80°C. The synthesis was performed in an open system using a stirrer-heater equipped with a thermostat (IKA yellow line, Germany) to adjust the temperature to 80±2°C, with continuous stirring for 180 min. At the end of the treatment the slurry mixture was filtered and the solid experimental product was placed into a porcelain-evaporating basin and aged in an oven for 15 h at 95°C. Similar procedure was performed to directly synthesize zeolite from coal tailings. However, to prevent the reduction of Fe(III) to Fe(II) by organic matter of coal tailings, 10 g of coal tailings was mixed with 240 ml of 30% H₂O₂.

4. MATERIAL CHARACTERIZATION

The chemical composition of obtained products was determined by X-ray fluorescence spectrometer (XRF) and is listed in Table 2. In addition, powder X-ray diffraction (XRD) was performed on the starting materials and the treated samples. The samples were scanned over the 3–74° 2θ interval. A semi-quantitative estimation of the abundance (efficiency) of the mineral phases was derived from the XRD data, using the intensity of maximum reflections as follows:

$$R = \frac{P_{\max, P} - P_{\max, F}}{P_{\max, F}} \times 100 \quad (1)$$

5. RESULTS AND DISCUSSION

The chemical compositions and XRD patterns of raw materials and products are given in Table 2 and Figures 2 and 3. Although data in Table 2 shows nearly the same composition for starting and treated materials, the XRD patterns allow us to infer the progress of zeolite synthesis process. The maximum peaks of P_{max,F}=210 and P_{max,P}=255 yield efficiency of 21.43% (Eq. 1) for direct conversion. Whereas, the yield is 8.31% for indirect conversion having maximum peaks of P_{max,F}=325 and P_{max,P}=352. In the case of fly ash, despite the higher total content in SiO₂ and Al₂O₃ which are the main components for the zeolite synthesis (85.5 wt% in total), the fly ash gave lower yield compared to coal tailings. This could be attributed to the higher CaO and K₂O percentages in coal tailings. However, these differences in chemical composition may appear during combustion of coal tailings to obtain fly ash.

The chemical composition of the fly ash used by Kantiranis et al. [32] is also given in Table 2. In spite of the lesser total SiO₂ and Al₂O₃ content of starting material, the yielding of zeolite obtained in Kantiranis et al. experiments, was found to be higher compared to the present study, i.e. 40% vs. 21.43%. Two points leading to this result could be as follows:

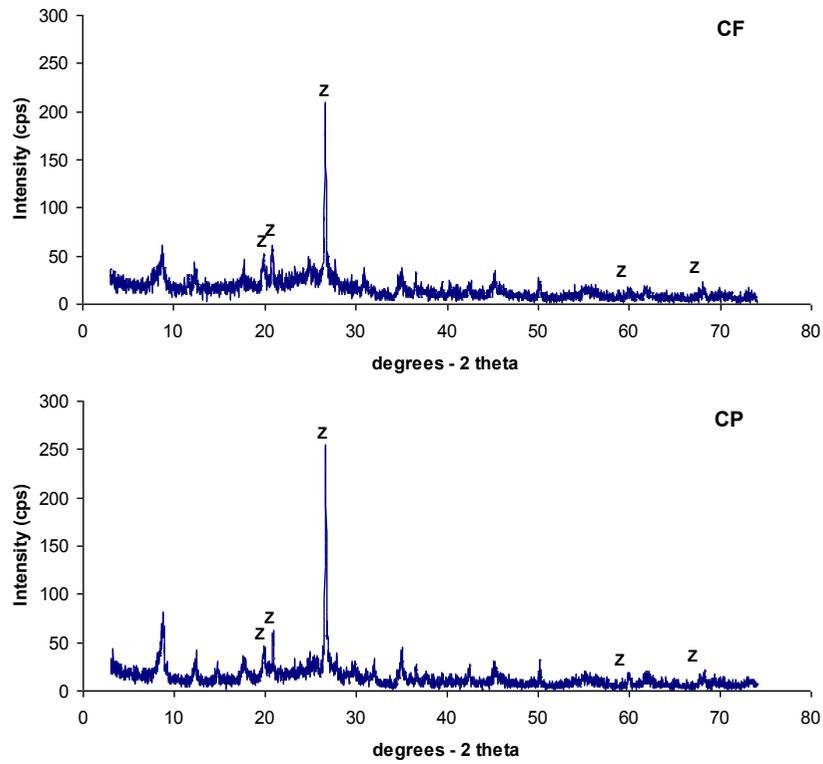


Fig.2: XRD patterns of the coal tailings (CF) and the treated sample (CP).

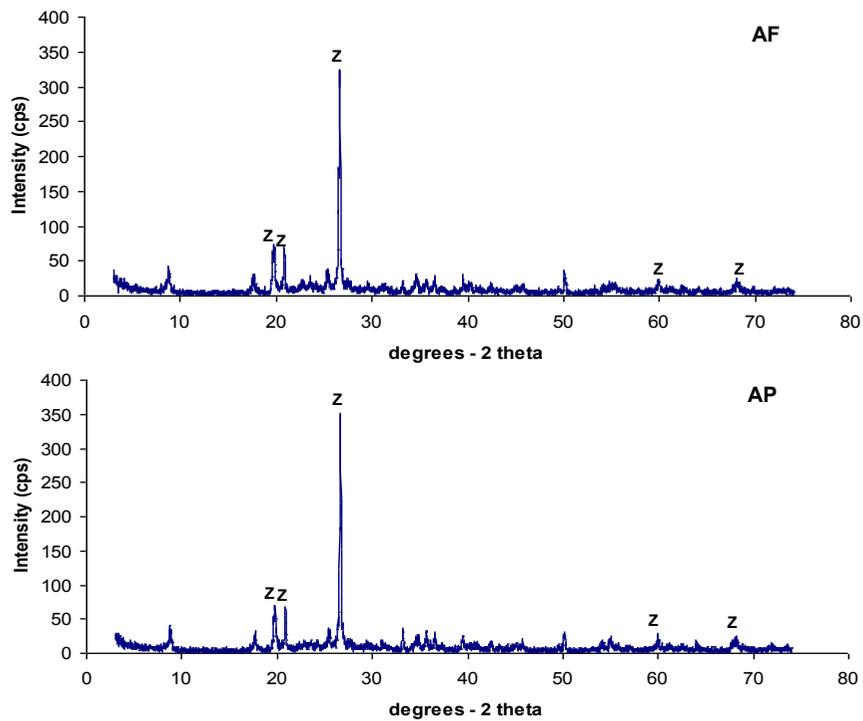


Fig.3: XRD patterns of the fly ash (AF) and the treated sample (AP).

Synthesis conversions, in which KOH and/or NaOH is involved as activation agent, give a multi- or single phase K- or Na-type zeolite. Whereas, a Ca-type zeolite was produced by Kantiranis et al. due to using a high-CaO fly ash. As seen from Table 2, the coal tailing is poorer in CaO in comparison to fly ash used by Kantiranis et al. (5.5% vs. 25.46%), leading to the lesser yield. This is the case for fly ash produced from the coal tailings.

The coal fly ashes discharged from power plants are 99 percentages smaller than 100 μm in particle size. Whereas, starting materials, especially the coal tailings, used in this work were smaller than 200 μm . Hence, the rate of conversion could be expected to decrease in our case study.

As seen in Table 2, XRD results for raw material and product from direct process, i.e. coal tailings, differ more significant than those from indirect process. After H_2O_2 activation stage, liberation degree of organic from mineral materials is expected to increase due to phase transference, resulting in the increase in free coal content in the treated product. This, in turn, causes error in the sample preparation for XRD analysis. Therefore, the result from initial coal tailings seems to be more reliable.

6. CONCLUSIONS

The possibility of synthesis of zeolite from coal tailings and fly ash was investigated using H_2O_2 -promoted hydrothermal conversion. The XRD patterns indicated the formation of zeolite from both initial materials. However, the yielding of treated product in direct process was found to be higher than indirect one, i.e. 21.43% vs. 8.31%. This result was ascribed to the higher CaO content in coal tailings compared to fly ash. Despite the higher total content in SiO_2 and Al_2O_3 which are the main components for the zeolite synthesis (74.9–85.5 wt% in total), the present work gave lesser yields compared to the experiments by Kantiranis et al. [32]. This result could also be ascribed to the higher CaO content of fly ash used by Kantiranis et al.. Results from the present study seemed promising enough to introduce zeolite synthesis as a new technique for recycling the coal wastes discharged from coal washing plants. However, more investigations are

recommended to confirm the industrial applicability of the obtained results, especially concerning the total efficiency and economics.

7. NOMENCLATURE

R semi-quantitative efficiency [%]
 $P_{\text{max,P}}$ peak of maximum intensity in XRD pattern for treated material [cps]
 $P_{\text{max,F}}$ peak of maximum intensity in XRD pattern for raw material [cps]

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9. BIOGRAPHIES



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