Conversion of coal fly ash by-products into high-grade zeolites by a quasi natural crystallization process

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Abstract
This study is focused on a technologically viable approach to obtain zeolite Na-X by aging of lignite coal fly ash (FA) in alkaline solutions at ambient conditions resembling a quasi natural crystallization process. Reaction products were characterized for their phase composition by X-ray diffraction, morphology by scanning electron microscopy (SEM) and surface properties by nitrogen adsorption/desorption isotherms. The effect of the crystallization time was investigated as an important parameter for the extent of zeolitization. The highest yield of zeolite Na-X was achieved by incubating FA in 1.5 mol/l NaOH for one year. However, significant crystallization extent is established after eight months of alkaline aging. Fly ash zeolites (FAZ) obtained by atmospheric crystallization have specific surface values up to 280 m^2/gFAZ.
Keywords: Coal ash utilization, Fly ash zeolite, Zeolite Na-X, Quasi natural crystallization

1. Introduction

Recently, the synthesis of zeolites from coal fly ash (FA) has been extensively studied regarding the process optimization, industrial up scaling and technological commercialization (Querol et al. 2001; Jha and Singh 2016). The obtaining of fly ash zeolites (FAZ) is based on the transformation of aluminosilicates from the raw FA by alkaline activation which undergoes several stages: alkaline dissolution of Si-Al-components; hydrogel formation; crystallization of zeolite phases over the insoluble particles (Querol et al. 2002). Different synthesis methods of FAZ have been studied in the quest to achieve the highest transformation rate in a particular zeolitic phase (Murayama et al. 2002). FA can be converted into zeolites X, A and Y which are the most important zeolite types for practice due to their wide specific surface and large pore sizes. Generally, the zeolites occur in the nature due to the interaction between rock aluminosilicates and sea salts in a course of thousands of years. This natural example provides an idea of simplifying the conversion of FA into zeolites under atmospheric conditions avoiding the external energy and the special equipment required. The equipment convenience and the zero energy demands are of great importance for scaling up the coal ash utilization. This study is aimed at development of a simple and energy-efficient approach to obtaining high grade zeolites by crystallizing mixtures of FA and alkaline solution in ambient conditions, which is a low-cost technique suitable for industrial applications. It is expected that the obtained FAZ are appropriate adsorbents in gas and water purification systems.

2. Experimental

FA sampled from the electrostatic precipitators of the biggest Thermal Power Plant in Bulgaria TPP "Maritza East 2" supplied by lignite coal was used as a raw material for the synthesis of zeolites. Slurries of 10 g FA distributed in 100 ml solution of 1.5 mol/l NaOH were subjected to long-term atmospheric aging resembling a quasi natural zeolitization process. The alkaline treatment was carried out in closed polypropylene containers kept at room temperature. The crystallization rate was investigated at different times of alkaline aging in terms of the structure, morphology and surface properties of the resulting products. Phase composition was studied by X-ray diffraction (XRD) using a Brucker D2 Phaser diffractometer with CuK_{α}-radiation and a Ni filter. Morphological observations were carried out by scanning electron microscopy (SEM), using an apparatus model JEOL JSM6390. Nitrogen adsorption/desorption isotherms were measured at 77 K by a volumetric adsorption analyzer Tristar II 3020, Micromeritics. Samples were preliminary degassed in a set-up FlowPrep 60, Micromeritics, at 260 °C for 4 h under helium flow. Specific surface areas (S_{BET}, m^2/g) were evaluated applying the multi-point Brunauer–Emmett–Teller (BET) model to describe the adsorption isotherms.

3. Results and Discussions

The composition and some physiochemical characteristics of the raw FA have been studied previously (Boycheva et al. 2013). It contains about 76 wt.% SiO_2+Al_2O_3, 9 wt.% Fe_2O_3 and some alkaline, alkaline earth, and transition metal oxides. The duration of FAZ crystallization is given in Table 1. X-ray diffractograms of FA zeolitization products and a reference zeolite Na-X are plotted in Fig. 1. Obviously, the dominant zeolite phase that is crystallized is Na-X

(Faujasite, FAU) and the reflexes of magnetite (MAG) transferred in FAZ from the crude FA are also observed.

Table 1. FAZ crystallization periods

Sample	Crystallization time
FAZ 1	180 days
FAZ 2	240 days
FAZ 3	300 days
FAZ 4	360 days

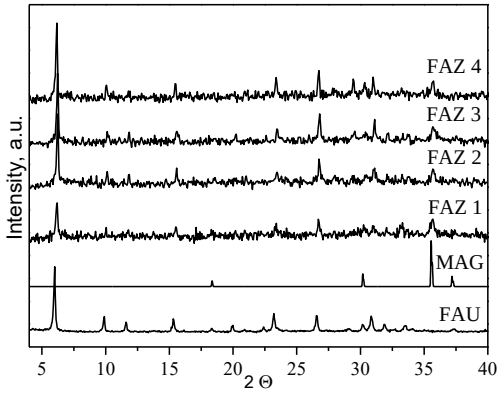

Figure 1. X-ray diffractograms of FAZ obtained at different aging time and patterns of reference phases.

Typical SEM images of the obtained FAZ are shown in Fig. 2. Hexaoctahedral crystallites of micron sizes which are typical morphology for Na-X phase and their agglomerates are observed. Values for the specific surface area (S_{BET}, m^2/g) of FAZ calculated applying BET model in the monolayer adsorption region at p/p_0=0.01-0.05 are summarised in Table 2. The extent of conversion of FA into Na-X zeolite was calculated as a ratio of S_{BET} values of FAZ to the reference Na-X, and was estimated t relatively to the aluminosilicate part of the raw material.

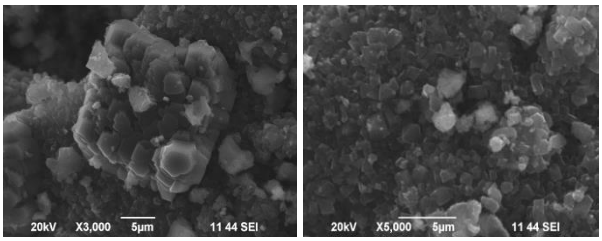

Figure 2. SEM images of FAZ 4.

Table 2. Specific surface and zeolite yield of FAZ

Sample	S_{BET}, m^2/g FAZ	Yield of Na-X, wt %
FAZ 1	36.96	6
FAZ 2	228.82	38
FAZ 3	262.36	44
FAZ 4	279.37	47

4. Conclusions

Our study demonstrates that FA can be converted into zeolite Na-X by alkaline aging at atmospheric condition. This zeolitization process provides energy-free FA utilization approach. Significant conversion rate of the raw aluminosilicates is achieved after eight months, while almost 50 wt % of zeolite Na-X is crystallized for a year. The specific surface of FAZ reaches 280 m^2/g, which is more than twenty times higher than that of the raw FA. The zeolites Na-X obtained by atmospheric crystallization possess suitable surface characteristics to adsorb contaminants from gases and waters.

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