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Synthesis of zeolites at low temperatures in fly ash-kaolinite mixtures

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ABSTRACT

Coal fly ash from an Italian coal-fired power plant, kaolinite from the Source Clay Repository of The Clay Minerals Society, and four derived mixtures were used to synthesize zeolite using hydrothermal treatment at 45 °C in distilled water after alkaline fusion. The results documented that geopolymers, A-type and X-type zeolites were formed in different quantities, depending on the starting material and the duration of the experiment. Zeolite-X was the prevailing phase synthesized using pure fly ash, zeolite-A formed in higher amounts from kaolinite, and comparable amounts of A- and X-type zeolites crystallized, thereby adding 20 and 40% kaolinite to the fly ash, respectively. Zeolite-A as main phase was synthesized already adding 60% or even up to 80% kaolinite to the fly ash. Sodalite occasionally formed from the source materials, whereas zeolite ZK-5 was synthesized from only fused fly ash (100FA). The data indicated that, in addition to the Si/Al ratio of solid source materials, zeolite formation was controlled by the time and chemistry of the solution. The polymerization of alumina-silicate gels changed during the experiments, likely due to the amorphization of metastable zeolites.

1. Introduction

Zeolites are hydrated aluminosilicate minerals that can be synthesized using several source materials, such as fly ash (e.g., [1–11]) and kaolinite (e.g., [12–19]). Experiments using fly ash have been performed with a hydrothermal reaction in alkaline solutions (e.g., [3,4]) and after a fusion pre-treatment (e.g., [9–11]). Microwaves (e.g., [20,21]) and ultrasonic treatments (e.g., [22–26]) have been employed to increase kinetic reactions. The use of kaolinite generally requires calcination at high temperatures (600–1000 °C), and only a few recent studies have introduced pre-fusion treatment with alkalis [17,19,27] or hydrothermal treatment with an NaOH solution [28].

In spite of several papers detailing the synthesis of zeolites using kaolinite or fly ash, there are aspects that are not fully understood. The most relevant aspects are related to the role of Si/Al in the starting material, the crystallization time and temperature and the incubation time. Different literature indicates that zeolite-A was formed with a molar ratio of Si/Al >2 (e.g., [29,30]) or Si/Al < 2 (e.g., [19,31–33]), whereas the zeolite-X was synthesized with pre-fusion at an incubation temperature < 60 °C (e.g., [9–11]) or > 60 °C (e.g., [6]). In terms of the crystallization time, various authors synthesized zeolite-A between 8 and 24 h [34] or after 96 h (e.g., [19]).

In a previous study [19], we documented that the use of almost pure kaolinite is mainly conducive to zeolite-A and to traces of zeolite-X, but if minor amounts of other silicate minerals (e.g., illite and quartz) are associated with kaolinite, the quantity of zeolite-X significantly increases. It has also been ascertained [11] that the presence of Mg and Ca in the contact solution plays a determinant role in the formation of zeolite-X. In addition to the chemical composition of the starting material and the contact solution, the incubation time may favour the crystallization of one type of zeolite with respect to another one (e.g., [35]); furthermore, it has been suggested [11] that the crystallization rates of zeolite-A and zeolite-X change over time. To provide more information about the role of Si/Al and time in controlling the hydrothermal synthesis of zeolites after fusion with NaOH, we performed new experiments by fixing the temperature at 45 °C and ageing a coal fly ash, a pure kaolinite, and four mixtures of these two materials in distilled water for 1–216 h.

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2. Materials and methods

The experiments were performed with coal fly ash (FA) from an Italian thermoelectric power plant that we have used in previous experiments [9–11,25,26] and kaolinite (KGa-2) from the Source Clay Repository of The Clay Minerals Society. These two materials had a similar Si/Al ratio (FA:1.46; KGa-2:1.01), and therefore it changed little in the four mixtures (Table 1). The major element chemical analyses were performed on pressed powder pellets using X-ray fluorescence spectrometry (XRF; Philips PW 1480). It was used a Cr anode tube at 60 kV and 50 mA. The loss on ignition (LOI) was measured by heating the sample at 900 °C for 3 h. The mineralogical composition was determined by powder X-ray diffraction (XRD) using a Rigaku Rint 2200 diffractometer equipped with Cu-Kα radiation (40 kV and 30 mA) and a graphite monochromator. The data collections were performed in the 2θ range 2–54° with step size of 0.02°. The morphological features of the starting and aged materials were observed using a field emission scanning electron microscope (SEM, Zeiss Supra 40). The samples were carbon-sputtered (10 nm thick) in order to avoid charging of the surface. Elemental analyses were performed with an energy-dispersive X-ray spectrometer (EDS, Oxford Inca Energy 350) equipped with a Si(Li) detector.

The starting materials were fused using NaOH (1:1.2 weight ratio) and, with distilled water added, were stirred overnight at room temperature. The suspensions were incubated at 45 °C for 1, 6, 12, 24, 48, 72, 96, 120, 144, 168, 192, and 216 h in separate experiments. The incubation temperature was chosen based on our previous studies [9,10,19], which indicated that a large amount of zeolites formed at 45 °C from fly ash or kaolinite. The solids and solutions were then separated by centrifugation.

The solids were washed with distilled water, dried in an oven at 30 °C and characterized using SEM and XRD. Quantitative mineralogical analyses were not reliable because of the presence of high amount of non-crystalline materials (mainly neoformed geopolymers) that continuously changed their polymerization state during the incubation time. An estimation of each neoformed mineral in the different experiments was performed by comparing the integrated intensities of the selected XRD diffraction lines (X-type zeolite: I_{111} at 6.09° 2θ; A-type zeolite: I_{222} at 7.20° 2θ; sodalite: I_{110} at 13.92° 2θ; zeolite ZK-5: I_{200} at 9.30° 2θ).

The solutions were analysed for Si, Al, Ca, Mg, Na, and K contents using an inductively coupled plasma mass spectrometer (ICP-MS; Perkin Elmer ELAN 9000). Analytical precision was better than 5% except for Ca (<10%).

To obtain information regarding the coordination state of aluminium, the two starting materials (FA and KGa-2) and their fused products (100FA and 0FA) were analysed with a solid state nuclear magnetic resonance spectrometer (Bruker Avance I 400 MHz) using a magic angle spinning technique (MAS-NMR).

Table 1
Mixtures of FA and KGa-2. Si/Al = molar ratio.

Mixture	FA	KGa-2	Si/Al
100FA	100	0	1.46
80FA	80	20	1.35
60FA	60	40	1.25
40FA	40	60	1.16
20FA	20	80	1.08
0FA	0	100	1.01

Si/Al: determined in FA and KGa-2 samples; "calculated" in the mixtures.

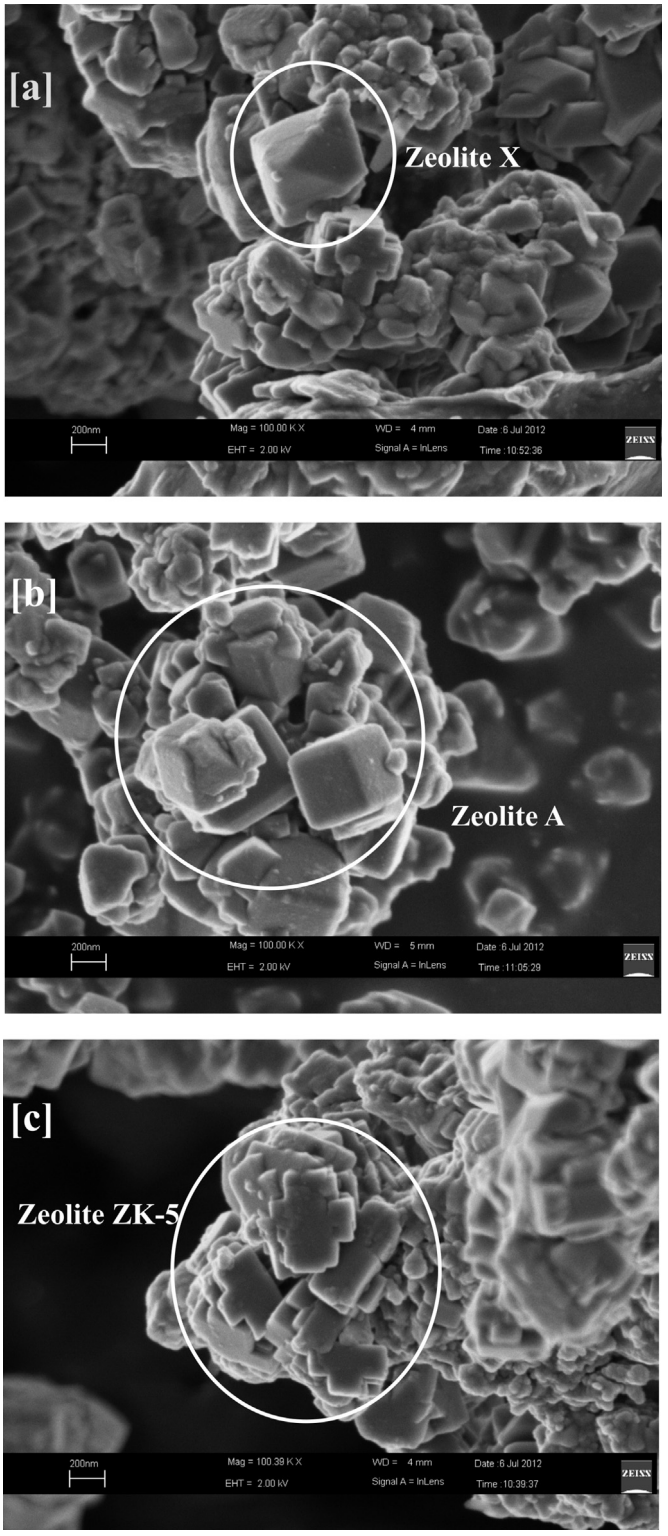

Fig. 1. Selected SEM images of zeolites synthesized using mixtures of fly ash and kaolinite after 48 h of incubation. [a] octahedral crystals of X-type zeolite (40FA sample); [b] cubic crystals of A-type zeolite (0FA sample); [c] typical morphology of zeolite ZK-5 (100FA sample).