

Effect of Na₂O/SiO₂ mole ratio on the crystal type of zeolite synthesized from coal fly ash

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Abstract: Coal fly ash was modified to zeolitic materials by hydrothermal treatment at 90 °C. The zeolite synthesis was studied as a function of the mole ratio of Na₂O/SiO₂ in the reaction mixtures. The results showed that NaP1 zeolite is obtained when the Na₂O/SiO₂ mole ratio was 0.7. Hydroxysodalite is the dominant zeolite phase in modified fly ash treated with a higher Na₂O concentration solution (Na₂O/SiO₂ = 1.3). The IR and XRD methods were used to determine the phases present in the starting sample and in the zeolitic materials.

Keywords: coal fly ash, hydrothermal treatment, zeolitic materials.

INTRODUCTION

It is well known that zeolites have important industrial applications, mainly as ion exchanges, molecular sieves, adsorbents and catalysts. An increased interest has been noted lately in the use of coal fly ash as the starting material for zeolite synthesis. Zeolite synthesis from fly ash has an important potential for the recycling of solid wastes from coal-fired power stations. Furthermore, the conversion of a low-cost waste product into a higher level product is economically justified. Fly ash is composed primarily of aluminosilicate glass, mullite (Al₆Si₂O₁₃) and quartz (SiO₂), hence it provides a ready source of Al and Si, which are necessary for the synthesis of zeolites. The low Si/Al mole ratio in fly ash allows the synthesis of low-Si zeolites with high cation exchange capacities for transition metals and ammonium ions, high selectivity for polar molecules and with large pore volumes.¹ A number of hydrothermal activation methods have been proposed for the conversion of fly ash into zeolites and these studies indicate that, due to the varying compositions of different ashes, the conversion process of the ash has to be changed accordingly.^{2–14}

The present work is an attempt at determining the effect of the Na₂O/SiO₂ mole ratio on the crystal type of zeolite synthesized from coal fly ash from the “Nikola Tesla–B” power station, produced during the combustion of coal (lignite) from the “Kolubara” deposit (Serbia), by the hydrothermal alkaline method.

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EXPERIMENTAL

The raw material for the experiments was fly ash collected from the electrostatic precipitators of the "Nikola Tesla-B" power station. The chemical composition of a representative sample of fly ash is given in Table I. The contents of the major inorganic phase were determined by X-ray analysis (Fig. 1), using a Philips PW 1710 automated power diffractometer with monochromatic $\text{CuK}\alpha$ radiation and an automatic divergence slot, and by the IR spectrophotometric KBr method (Perkin-Elmer infrared spectrophotometer type 397), (Fig. 2).

TABLE I. Chemical analysis of the "Nikola Tesla-B" power station fly ash

Oxide	% wt	mol/100 g of fly ash
SiO_2	52.27	0.869
Al_2O_3	22.34	0.219
Fe_2O_3	6.05	0.038
CaO	6.64	0.118
MgO	4.41	0.109
SO_3	2.74	0.034
P_2O_5	0.085	0.001
TiO_2	1.07	0.013
Na_2O	0.41	0.007
K_2O	1.36	0.014
Loss of ignition	2.34	

Bulk fly ash sample without prior treatment were used for the zeolite synthesis experiments. The activation of fly ash was performed by means of NaOH solution in open system (atmospheric pressure), at 90 °C for 5 h, stirring at 300 min^{-1} . The amount of fly ash used in the experiments was determined by the mole ratios $\text{Na}_2\text{O} : \text{SiO}_2 = 0.7$ or 1.3 and $\text{Na}_2\text{O} : \text{H}_2\text{O} = 25$. The treated samples were filtered and washed with excess distilled water. After drying at 105 °C, the samples were stored in a dessicator over a saturated ammonium chloride solution for two weeks before the IR and XRD analyses (Figs. 3–6).

RESULTS AND DISCUSSION

The chemical analysis of the fly ash used as the starting material in this work showed it to be a high-silica ash with the mole ratio of $\text{SiO}_2 : \text{Al}_2\text{O}_3 = 3.97 : 1$ (Table I).

The main minerals present in the fly ash were quartz, mullite, hematite and amorphous phase as aluminosilicate glass (Fig. 1) The characteristic bands of α -quartz and aluminosilicate phases can be identified in the infrared spectrum of the raw material (Fig. 2, 1075 cm^{-1} , 440 cm^{-1}). The bands of water were not observed. Höller and Wirsching² highlighted the compositional similarity of fly ash to volcanic material, the precursor of natural zeolites.⁹ The major reactive phase concerning the alkaline activation of fly ash is the glass fraction. In the meantime, Querol *et al.*^{6,14} showed that under strong alkaline conditions mullite and quartz are also digested and, consequently, that these are also involved in the conversion of fly ash into zeolites. Namely, all the methodologies developed have

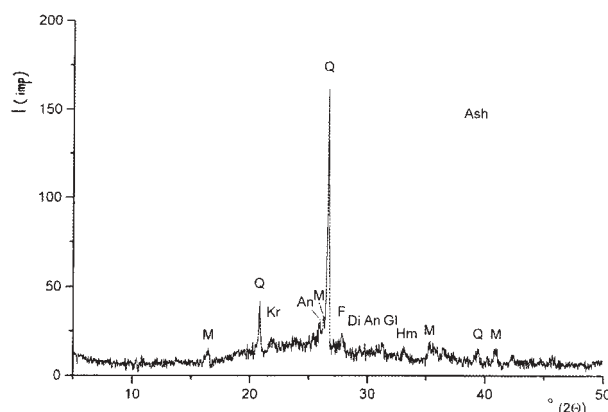


Fig. 1. X-Ray diffraction pattern of fly ash (Q – quartz, M – mullite, Hm – hematite, F – feldspars, Kr – cristobalite, Di – diopside, Gl – gehlenite, An – anhydrite).

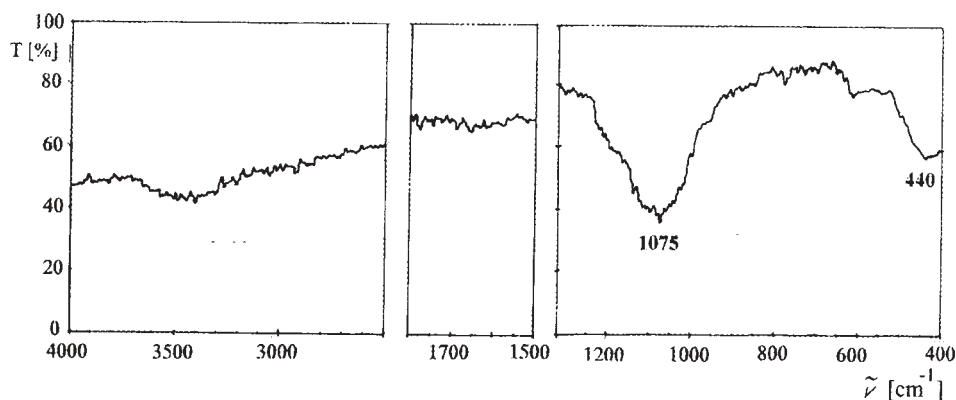
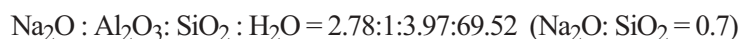
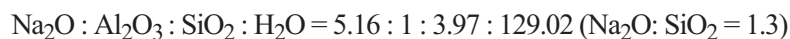


Fig. 2. Infrared spectrum of fly ash.

been based on the dissolution of Al–Si bearing fly ash phases with alkaline solution and the subsequent precipitation of the zeolitic material. It was indicated in earlier studies^{2–14} that the type of synthesized zeolite by hydrothermal treatment depends on the chemical composition of the fly ash, the concentration of the alkaline solution, the alkaline solution/fly ash ratio, the reaction temperature and pressure, as well as the reaction time and speed of stirring the reaction mixture. Bulk fly ash samples from the “Nikola Tesla–B” power station without prior treatment were hydrothermally activated under defined experimental conditions. Mole ratios of the components in the reaction mixture were



or



For the mole ratio of $\text{Na}_2\text{O} : \text{SiO}_2 = 0.7$ a modified fly ash having the XRD pattern shown in Fig. 3 was obtained. The crystalline phases identified in this sample were quartz and mullite which were also present in the unmodified fly ash. This means that under the given experimental conditions these phases were not digested. Besides the residual ash

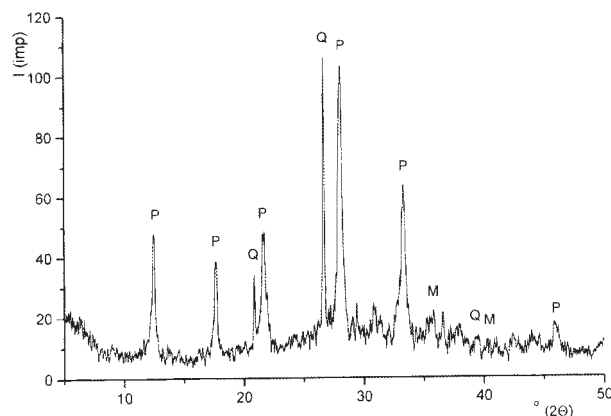


Fig. 3. X-Ray diffraction pattern of 5 h zeolitized fly ash; $\text{Na}_2\text{O}/\text{SiO}_2 = 0.7$ (P – NaP1 zeolite).

phases (quartz, mullite and also the same amount of amorphous phase) new peaks are present in the XRD pattern that match a high silica variety of a NaP^{1,15–18} zeolite phase called NaP1, for which the ideal unit cell content is $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{10}] \times 12\text{H}_2\text{O}$,^{17,19} the best. In the paper, no chemical composition of the zeolitization achieved zeolite was determined, mostly because of the multiphase composition of the zeolitized material. Woolard *et al.*⁸ obtained similar results for fly ash modification at room temperature using NaOH solution of concentrations from 1 M to 3 M. Also, Moreno *et al.*¹⁰ identified NaP1 in fly ash treated at low temperatures ($t < 150$ °C) and reagent concentrations from 0.5 to 1.0 M NaOH. The conditions for the formation of the different NaP phases (high silica NaP, so-called NaP1, NaP2 and low silica NaP) can be found in the literature.^{1,16–21} Generally, pure zeolites can be synthesized from $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ reaction system, *i.e.*, from the $[\text{Na}_d(\text{AlO}_2)_b(\text{SiO}_2)_c \cdot \text{NaOH} \cdot \text{H}_2\text{O}]$ gel.¹ The gel crystallizes in a hydrothermal system at temperatures varying from room temperature to about 175 °C. In some cases, higher temperatures up to 300 °C are used. Low temperature synthetic zeolites (A, P, R, S, X, Y) have been synthesized as pure phases in reaction systems. From a study of the many aluminosilicate gel compositions, relationships between the synthetic zeolite product and the starting reactant mixture composition have been established.^{1,22} It was determined that at temperatures near 100 °C, zeolite P is more readily formed from gels of higher silica content ($\text{Na}_2\text{O}/\text{SiO}_2 = 0.38-0.61$) than zeolite X ($\text{Na}_2\text{O}/\text{SiO}_2 = 0.12-1.5$) or zeolite A ($\text{Na}_2\text{O}/\text{SiO}_2 = 0.8-3.0$). Also, if, after crystallization, zeolite A remains in contact with the mother liquor (≈ 1 M NaOH) recrystallization to zeolite P may occur in 3–10 days. Similarly, zeolite X appears to be metastable with respect to zeolite P. The synthetic P zeolites dominate the synthesis composition fields in the low temperature range (from 100 to 150 °C). For example, Barrer *et al.*²³ used colloidal SiO_2 , NaAlO_2 , sodium silicate and NaOH as reagents to make a reaction mixture with the mole ratios of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 2 : 1 : 3.8 : 94$ for the synthesis of NaP zeolites at different temperatures (60–150 °C). They obtained zeolites with the compositions of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 1 : 1 : (2-5) : 5$. Using the $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 6 : 1 : 8 : x$ system, the moles of SiO_2 in the zeolites varied from 3.2 to 5.3. On the other hand, metakaolins, obtained by the thermal conversion of kaolin-type clays at about 550 °C, are convenient amorphous material for hydrothermal

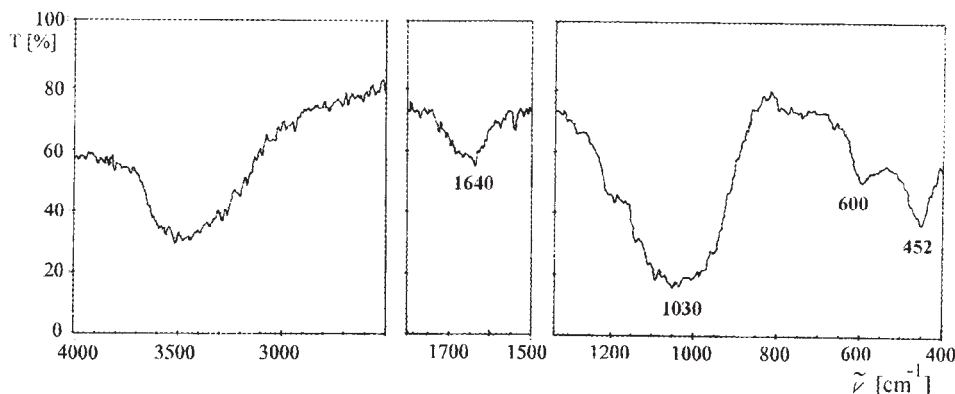


Fig. 4. Infrared spectrum of 5 h zeolitized fly ash; $\text{Na}_2\text{O}/\text{SiO}_2 = 0.7$.

zeolite synthesis. In order to form zeolites, having $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratios greater than 2, additional SiO_2 must be added in the form of sodium silicate or other sources such as colloidal silica. In this way NaP zeolite is obtained using metakaolin, NaOH and sodium silicate (reactant composition $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O} = 4 : 1 : 10 : 120$) by stirring for 3 days at 100°C .¹

The infrared spectrum of the obtained zeolitic material is the result of the overlapping of fly ash phases and new crystal phase vibrations (Fig. 4). The shift of the band maximum at 1075 cm^{-1} in the unzeolitized fly ash spectrum (Fig. 2) to 1030 cm^{-1} (Fig. 4) confirms the tetrahedral coordination of aluminum in the zeolite framework.¹ Namely, in the zeolite spectra this band is the main asymmetric stretching vibration of the tetrahedra, the frequency of which decreases with increasing amount of aluminum in the tetrahedral sites of the aluminosilicate framework of the zeolite. Also, the shoulder in the $1200 - 1150\text{ cm}^{-1}$ region in the pure zeolite spectra is the result of asymmetric stretching vibrations of the external linkages of the primary structural units. The band at 440 cm^{-1} in the fly ash spectrum is shifted to 452 cm^{-1} . For zeolites this band is assigned to a T-O bending mode.¹ In the case of NaP1 zeolite, a secondary building unit is the single 4-ring¹ (S4R), so the very

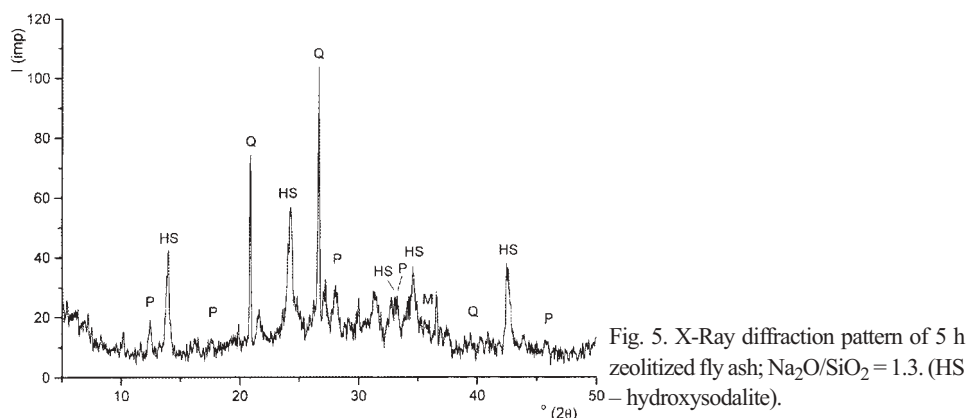


Fig. 5. X-Ray diffraction pattern of 5 h zeolitized fly ash; $\text{Na}_2\text{O}/\text{SiO}_2 = 1.3$. (HS 50 – hydroxysodalite).

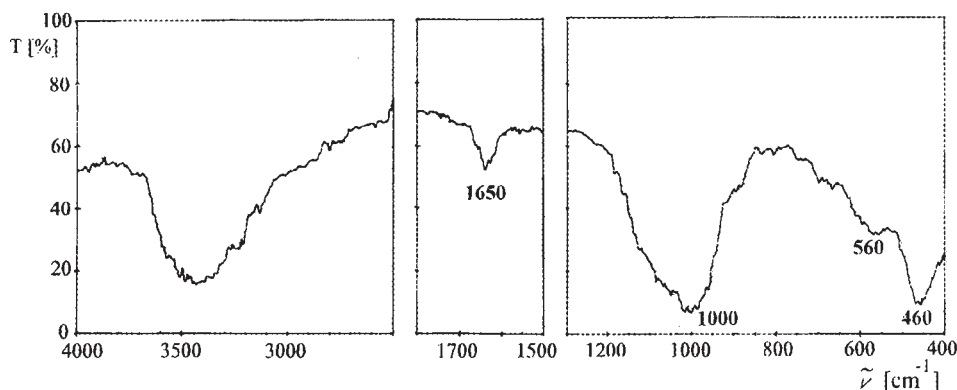


Fig. 6. Infrared spectrum of 5 h zeolitized fly ash; $\text{Na}_2\text{O}/\text{SiO}_2 = 1.3$.

weak band at 600 cm^{-1} is probably a vibration of the double ring of some other zeolite phase present in a small amount. Since there were no bands of water in the fly ash spectrum, the bands of zeolite water at about 3400 cm^{-1} (stretching vibrations) and at 1640 cm^{-1} (bending vibration)¹ in the treated fly ash present a special confirmation that the zeolite has been formed.

When the mole ratio of $\text{Na}_2\text{O} : \text{SiO}_2$ was higher, 1.3, hydroxysodalite (HS) can be identified as the dominant zeolite phase (Fig. 5). According to the obtained results and the XRD data,²⁴ the oxide formula $\text{Na}_2\text{O}_{1.08} \cdot \text{Al}_2\text{O}_3 \cdot 1.68\text{SiO}_2 \cdot 1.8\text{H}_2\text{O}$ fits best for the synthesized HS. The typical oxide formula for hydroxysodalite is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 1.5\text{H}_2\text{O}$, *i.e.*, the typical unit cell contains $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \approx 12\text{H}_2\text{O}$.¹ Querol *et al.*⁷ also synthesized the same type of hydroxysodalite as ours after fly ash activation with 3.0–5.0 M NaOH solutions at $150\text{ }^\circ\text{C}$. Similar results were obtained by Woolard *et al.*,⁸ Lin and Hsi¹² and Singer and Berggaut.¹³ Some of these authors found that the intensities of the hydroxysodalite peaks in the XRD pattern increase with increasing NaOH concentration whereas those for quartz and mullite decrease.¹² Others^{6,13} also noted a decrease in the intensity of the quartz peaks, but observed that the mullite peaks were relatively stable under alkaline treatment. Our result showed that quartz and mullite are also present in the obtained zeolitic material, and that generally they were not involved in the conversion process of fly ash under the given experimental conditions. Weak intensity peaks of NaP1 as another zeolite were detected in the XRD pattern of zeolitized fly ash. According to Singer and Berggaut,¹³ zeolite NaP1 would be the first zeolite to form, but it would be replaced gradually with increasing reaction time by hydroxysodalite. Generally, pure hydroxysodalite can be formed at $\text{Na}_2\text{O}/\text{SiO}_2 = 1$ at low $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios and at about $100\text{ }^\circ\text{C}$.¹ Also, in 1 M NaOH solution, zeolite A converts to zeolite P, but with a large excess of NaOH (about 10 wt% NaOH) it converts to HS.

The infrared spectrum of this sample is also the result of the overlapping of fly ash phases and zeolite vibrations (Fig. 6). The shifts of the band from 1075 cm^{-1} to 1000 cm^{-1} and the band from 440 cm^{-1} to 460 cm^{-1} confirm the formation of a zeolite phases. A secondary building unit of hydroxysodalite is the single 6-ring¹ (S6R), so the weak band at

about 560 cm^{-1} could point to the beginning of the crystallization of a zeolite with double rings. The broad band at about 3400 cm^{-1} and a band at 1650 cm^{-1} are attributed to zeolite water in the zeolitized fly ash.

CONCLUSION

According to the obtained results, it can be concluded that the coal fly ash from the “Nikola Tesla-B” power station, with a $\text{SiO}_2 : \text{Al}_2\text{O}_3 = 3.97 : 1$ mole ratio, is convenient as a starting material for the hydrothermal synthesis of zeolites. By varying the composition of the reaction mixture at a given temperature ($90\text{ }^\circ\text{C}$) during 5 h, control over the type of zeolite formed was achieved.

When the $\text{Na}_2\text{O}/\text{SiO}_2$ mole ratio was 0.7, NaP1 was detected as the zeolite phase in the modified fly ash. At a higher $\text{Na}_2\text{O}/\text{SiO}_2$ mole ratio (1.3), hydroxysodalite (HS) can be identified as the dominant zeolite. A small amount of NaP1 was also found in this zeolitized fly ash.

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ИЗВОД

УТИЦАЈ МОЛСКОГ ОДНОСА $\text{Na}_2\text{O}/\text{SiO}_2$ НА КРИСТАЛНИ ТИП СИНТЕТИЗОВАНОГ ЗЕОЛИТА ИЗ ЛЕТЕЋЕГ ПЕПЕЛА

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Хидротермалним поступком на $90\text{ }^\circ\text{C}$ летећи пепео добијен у термоелектрани (електро-филтерски пепео) модификован је у материјале који садрже зеолиите. У раду је испитивана зависност типа зеолиита синтелизованог применом наведеног поступка од молског односа $\text{Na}_2\text{O}/\text{SiO}_2$ у реакционој смеши. Резултати су показали да се при вредности $\text{Na}_2\text{O}/\text{SiO}_2 = 0,7$ у зеолизираним пепелу формира зеолиит NaP1. Када је тај однос већи ($\text{Na}_2\text{O}/\text{SiO}_2 = 1,3$) као доминантна зеолиитна фаза идентификован је хидроксисодалит. За анализу летећег пепела као полазне сировине као и зеолизираних материјала коришћене су методе инфрацрвене спектроскопије и рендгенске анализе.

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