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THERMAL ANALYSIS OF FLY ASH-BASED ZEOLITES

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Abstract

The paper presents research results on dehydration properties and thermal behaviour of zeolites synthesized from fly ash, applying TG (thermogravimetry), DTG (derivative thermogravimetry) and SDTA (simultaneous differential thermal analysis) methods. In result of the analysis conducted water contents in zeolite samples were defined. On the basis of the data obtained from the thermogravimetric analysis, thermal behaviour of zeolites was assessed.

Keywords: fly ash, thermal dehydration, zeolite

Introduction

The physicochemical similarity of fly ashes to aluminosilicates enables fly ashes to be transformed into materials with a zeolite crystalline structure under appropriate hydrothermal treatment. Research on this subject has been published by many authors [1–7]. These papers have suggested different methods for synthesizing zeolites from fly ash: classic alkaline conversion [1–5], two-stage synthesis procedure [7], alkaline fusion stage prior to the conventional zeolite synthesis [6]. In result of the processes conducted one may obtain the following types of zeolites: Na-A, Na-X, sodalite, analcime, Na-P1.

The major potential application of the obtained zeolites are based on their use as high ion exchangers in industrial waste water and soil decontamination. The zeolites synthesized from fly ash have very promising capacities for the immobilization of environmental pollutants like radioactive waste and ammonium ions [1–5].

Zeolite application possibilities depend on their sorption and catalytic properties as well as on molecular - sieve activity. Due to the fact that these qualities may only be observed in the dehydrated state, it is crucial to research on the behavior of zeolites in the process of dehydration. It is well known that a part of zeolites dehydrates until certain extent with no major changes in their crystalline structure. Thanks to this fact, they may later rehydrate, that is absorb water from the gas or liquid phase. In mineralogy, the water that may be obtained from zeolite in higher temperature and with no changes in the crystalline structure and that may be reabsorbed by the zeolite after the initial

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conditions have been restored is referred to as zeolite water. Molecules of such water have different properties and they are differently placed in the crystalline aluminosilicate network, taking a strictly defined place in the structure [8].

Thermal analysis methods are extremely useful in the research on dehydration properties of zeolites. They provide valuable information on the dehydration process and thermal stability of different types of zeolites as well as on their pore structure and catalytic activity [9–14].

The main objective of the research conducted was to define thermal behaviour and water content of fly ash-based zeolites with the application of TG (thermogravimetry), DTG (derivative thermogravimetry) and SDTA (simultaneous differential thermal analysis) techniques.

Experimental section

Coal fly ash was obtained from an utility power station in Poland (CFB) circulating fluidized bed boiler of 235 MWe in capacity. The fly ash was chemically analyzed and used to prepare the zeolitic materials described below. The main components of coal fly ash were SiO_2 and Al_2O_3. The SiO_2/Al_2O_3 ratio for fly ash used for zeolite synthesis was 1.19. The value of this ratio for zeolite synthesis is very important, as the formation of the particular zeolite species dependents on the Si/Al ratio in the starting material.

Zeolite synthesis reactions were carried out in a Teflon reaction vessel placed within a temperature-controlled furnace, and in a thermostatic bath equipped with a stirrer.
Synthesis processes were run using the following two methods:

- The method of fusion with sodium hydroxide prior to hydrothermal reaction [6]. Sample 1 - fly ash (10 g) and NaOH (12 g) were milled, and then heated up in a platinum crucible at 550°C for 1 h. The mixture obtained in this manner was cooled to room temperature, milled again, and replenished with distilled H_2O (100 mL). Afterwards it was agitated for 12 h at room temperature. After such preparation, the sample was placed at 100°C for 12 h.
- The classical method
  Sample 2 - fly ash (20 g) was mixed with 3.0 mol dm^{-3} sodium hydroxide solution (160 cm^3) and heated at 100°C for 24 h.
  Sample 3 - fly ash (20 g) was mixed with 3.0 mol dm^{-3} sodium hydroxide solution (160 cm^3), (additionally 3 g of salt NaCl was added) and heated at 150°C for 24 h.

After this time, the samples were filtered, washed with distilled water in order to remove the remaining NaOH, and dried at 120°C for 12 h. After drying the samples, the products were characterized by various conventional methods. X-ray diffraction patterns of the zeolite samples were obtained with CuK_α radiation by using a Feifert 3003 diffractometer. The XRD patterns of samples are presented in Fig. 1. Particle morphology was observed by Jeol 5400 scanning microscope [15]. On the basis of

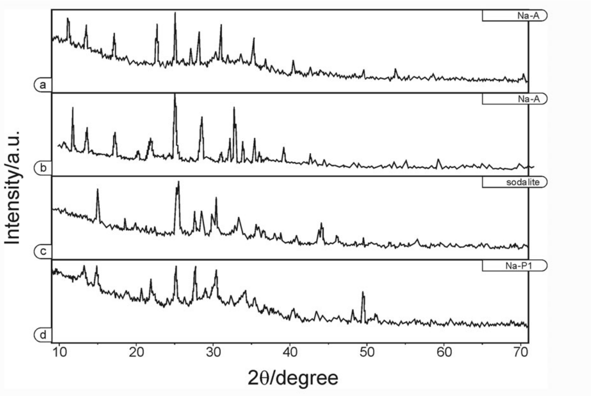

Fig. 1 X-ray diffraction patterns for a – fly ash-based zeolite (Na-A), b – commercial Na-A zeolite, c – fly ash-based zeolite (sodalite), d – fly ash-based zeolite (Na-P1)

the research conducted the presence of well crystallized zeolite Na-A (sample 1), zeolite Na-P1 (sample 2) and sodalite (sample 3) was stated. The contents of zeolites in the samples amounted to about 30% (sodalite) - 60% (Na-A zeolite), the remaining part was residue fly ash.

The effect of temperature on the zeolite samples was studied by a Mettler TGA/SDTA 851e thermobalance. Samples of zeolites were heated in the temperature range 20–1100°C using heating rate of 20°C min^{-1}, with a controlled nitrogen flow of 50 cm^3 min^{-1}. The samples (about 5 mg) was heated in a platinum crucible. For evaluating data Mettler-Toledo Star Softwer was used. This software permits one to evaluate mass changes for a sample (thermogravimetric curve) and Single Differential Thermal Analysis curve (obtained in absence of reference sample by difference of the sample temperature and calculated reference temperature with a mathematical model).

Results and discussion

Figure 2 presents the mass loss of the zeolite Na-A synthesized from fly ash (solid line) and of the commercial one (dashed line) during the process of their heating in nitrogen atmosphere (heating rate, 20°C min^{-1}; flow rate, N_2 50 cm^3 min^{-1}). In both cases the mass loss is a result of moisture and zeolite water desorption. The initial mass loss of the samples, below 100°C, is presumably [9] caused by desorption of physically adsorbed water from within the solid microstructure. Classically synthesized (commercial) Na-A zeolite loses about 18.8% of water while heated up to the temperature of 300°C and 20.4% of water by the temperature of 400°C. Na-A zeolite synthesized from fly ash loses 15.5 and 17.2 % respectively.

Maximum amount of water in Na-A zeolite synthesized from fly ash amounts to 18.3% and is lower than in commercial Na-A zeolite, containing 21.3% of water (according to Breck [8] 22.5%, according to Kosanović [9] 20.17%).

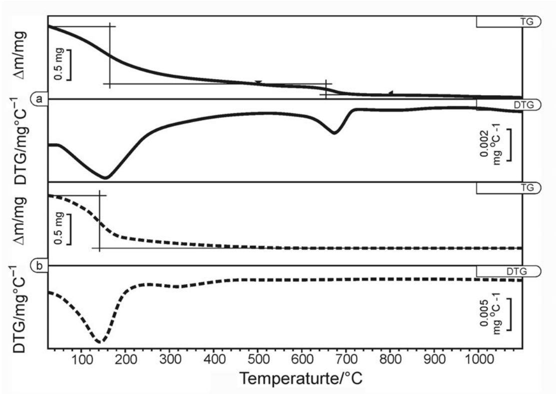

Fig. 2 TG and DTG curves for a – fly ash-based zeolite (Na-A), b – commercial Na-A zeolite

The mass loss was initiated at 30°C and was almost complete at 500°C for both Na-A zeolite synthesized from fly ash and commercial Na-A zeolite.

On the TG curve of Na-A zeolite synthesized from fly ash there are two mass losses. The first one is connected with constant water desorption during the process of heating and is accompanied by an endothermic effect on the SDTA curve (Fig. 3). This phenomenon is characteristic to zeolites (including the Na-A zeolite and it confirms its presence in the sample, being an ash modification).

The second mass loss of Na-A zeolite synthesized from fly ash on the TG curve and the accompanying endothermic effect on the SDTA curve (Fig. 3) point to $CaCO_3$ decomposition. Its presence in the sample has been also confirmed by X-ray analysis, proving that in the sample, being a fly-ash modification, there were residues of SiO_2, $CaCO_3$ ash apart from well crystallized Na-A zeolite.

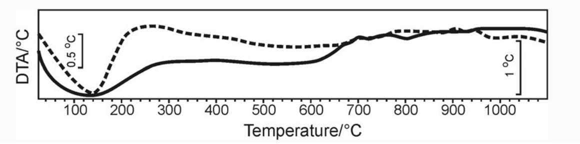

Fig. 3 SDTA curves of Na-A zeolite synthesized from fly ash (solid line) and of the classically synthesized one (dashed line)

Figure 3 presents SDTA curves of Na-A zeolite synthesized from fly ash and of the classic one. In case of SDTA curves, the endothermic effect corresponds to water release from the zeolite structure and the size of its surface speaks about the amount of water loss and temperature limits in which release takes place. It is well known that the endothermic effect in the process of heating zeolites is a consequence of the consumption of the heat needed for dehydration of the hydrated cations positioned in the zeolite framework and the release of water molecules from the channel/void system of the zeolite structure [8, 9].

On the basis of the literature data [8, 9], the temperature of endothermic minimum, decrease together with the increase of the effective diameter of the channels and the heat needed to remove water molecules from zeolite channels decreases with the increase in the effective diameter of these channels.

As the SDTA curve for commercial Na-A zeolite (Fig. 3) shows, maximum changes of the endothermic thermal effect and sudden mass loss caused by desorption of water from Na-A zeolite occur in the temperatures of 140–160°C. Almost total removal of moisture from zeolites is only achieved in the temperature of 500–600°C.

The minimum of the endothermic effect on the SDTA (Fig. 3) and DTG (Fig. 2) curve occurs by slightly higher temperatures in case of Na-A zeolite synthesized from fly ash than the minimum of the endothermic effect on the SDTA curve in case of the 4A commercial zeolite. The temperature of the endothermic minimum on the SDTA and DTG curve equals 140°C in case of commercial zeolite and 155°C in case of Na-A zeolite synthesized from fly ash.

This effect may be explained by the fact that the heat needed to remove water molecules from the pores formed during the process of creating fly ash zeolite is slightly higher than the heat needed to remove water molecules from the channel/void system of commercial zeolite.

Such situation may be caused by lower crystalline level of fly ash-based zeolites, the presence of fly ash residues in them, arrangement of water molecules in the structure, lower pore volume (in comparison to commercial Na-A zeolite) as well as different effective diameter of channels and voids (in case of commercial Na-A zeolite the effective channels diameter is 0.41 μm).

Endothermic peaks of classic Na-A zeolite and fly ash-based zeolite are similar, what proves the zeolite nature of the product obtained from fly ash.

The results obtained confirm that in spite of different material applied to its synthesis, different crystallisation process and thus different contents of some ash residues Na-A zeolite synthesized from fly ash possesses a well developed channel / void system of similar diameters and a high crystallisation degree in comparison to commercial Na-A zeolite.

These slight differences are caused by different synthesis process in case of fly ash zeolites and classic synthesis of zeolites, based on chemically pure reagents such as water glass or silical gel. Although zeolite syntheses from fly ash are conducted similarly to zeolite syntheses with the application of chemically pure reagents - hydrothermal conditions in alkaline environment, mainly in the presence of NaOH or KOH solutions, crystallisation of zeolite from fly ash differs from zeolite syntheses conducted in the standard way. It is mainly due to the fact that the sources of silicon and aluminium in fly ash are less reactive and there are also other contaminating cations.

On the basis of the data obtained during the thermal analysis one may also define thermal stability of the zeolite framework, that is the threshold of thermal stability. SDTA curves are of assistance here. Their endothermic effect corresponds to water release from the zeolite structure and the exothermic effect to the changes in the zeolite structure (zeolite transformation into other amorphous or crystalline phase). On the basis of this effect one may define the limit of single permissible heating of zeolite. Although destruction of crystalline structure is an endothermic process, in case of zeolites exothermic effect is connected with rendering the sample amorphous. It results from the fact that the transition from crystalline to amorphous phase is connected with substantial reduction of the free surface of the dehydrated voids, what follows is that the free energy of the amorphous phase is lower than the dehydrated framework [8]. Two exothermic effects on the SDTA curve of the commercial Na-A zeolite that prove the structure destruction occur in the temperatures of 910 and 950°C.

Although in case of single heating of type A zeolites (4A, 5A) the exothermic effects prove the crystalline structure destruction only in the temperature of about 900°C, according to Breck [8] the upper temperature limit by which the sorption properties of zeolites are not decreased in the long run is 550–600°C.

As far as zeolite behavior during dehydration process is concerned, they may be divided into two groups: zeolites in which there are no major structural changes by dehydration and dehydration curves as temperature functions are constant and zeolites in which there occur structural changes during dehydration processes and dehydration curves are not constant. There may be steps observed. The researched Na-A zeolites (commercial and from fly ash) are characterized by the first dehydration type. The TG, DTG and SDTA curves presented on the Figs 2, 3 confirm this observation.

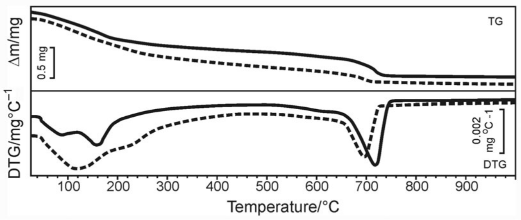

Fig. 4 TG, DTG curves for the modification of fly ash containing Na-P1 zeolite (solid line) and sodalite (dashed line)

Figure 4 presents TG and DTG curves of two other zeolites obtained from fly ash-sodalite and Na-P1. Their contents in the modified ash samples was lower than that of the Na-A zeolite. A large part of these samples was fly ash residue, what confirms the size of the second effect on the DTG curves. Water contents in the samples was the following: in case of the Na-P1 zeolite sample about 14.9%, in case of the sodalite sample 13.9%

Conclusions

On the basis of the research conducted one may state that:

- The loss of water from the zeolite samples generally occurred in the temperature range 30–500°C and was manifested in the SDTA graphs by an extended endothermic effect.
- The water content in the samples of fly ash-based zeolites is lower than in the commercial ones.

- There is no significant difference in the thermal behaviour between the commercial and fly ash-based sample of Na-A zeolite.
- Endothermic peaks of commercial and fly ash-based Na-A zeolite are similar, what proves the zeolite nature of the product obtained from fly ash.
- The minimum of the endothermic effect on the SDTA and DTG curve occurs by slightly higher temperatures in case of Na-A zeolite synthesized from fly ash than the minimum of the endothermic effect on the SDTA curve in case of the 4A commercial zeolite.

Analysis of the experimental data led to the conclusion that zeolite dehydration is a complex process and that defining the influence of particular factors on it is rather difficult. One of the main factors is most probably the zeolite structure. The channel/void system that in case of zeolite synthesized from fly ash is undoubtedly less developed than in case of commercial zeolites synthesized from chemically pure reacting substances. However, the data obtained has also proven the high crystalline level of these samples. Zeolite water molecules play an important role as well. Depending on the zeolite type they have different properties and are placed differently in the crystalline network.

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