Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 413 (2004) 23–29

thermochimica acta

www.elsevier.com/locate/tca

Application of model-free kinetics to the study of dehydration of fly ash-based zeolite

I. Majchrzak-Kucęba*, W. Nowak

Department of Heating, Ventilation and Air Protection, Czestochowa University of Technology,
ul. Dabrowskiego 73, 42-200 Czestochowa, Poland

Received 14 July 2003; received in revised form 29 October 2003; accepted 29 October 2003

Abstract

In the present paper, dehydration kinetics of zeolite Na-A synthesized from fly ash was investigated by means of thermogravimetric analysis. Na-A zeolite was formed from coal fly fash by fusion with sodium hydroxide and succeeding hydrothermal treatment at 100 °C after induction period. The model-free kinetic method was applied to calculate the activation energy of the dehydration process of fly ash-based zeolite as a function of conversion and temperature. The Vyazovkin model-free kinetic method also enabled the definition of time, necessary to remove water molecules from the zeolite structure for a given temperature.

Keywords: Model-free kinetics; Zeolites; Thermal dehydration; Fly ash

1. Introduction

Natural and synthetic zeolites are hydrated aluminosilicates of porous crystalline structure. Wide variety of characteristic features of these compounds has influenced the fact that they are applied in numerous areas of economy. They are especially useful in the processes of drying and cleaning gases, deactivation of radioactive waste as well as in refinery, chemical and paper industries [1].

One of the recent zeolite synthesis possibilities is modification of fly ash conducted in hydrothermal conditions, in alkaline environment, with NaOH or KOH solutions. Modification processes may be conducted with the application of different methods: classic alkaline conversion [2–6], fusion with sodium hydroxide before the hydrothermal reaction [7], two-stage process of obtaining pure zeolites [8]. In result of the processes conducted one may obtain the following types of zeolites: Na-A, Na-X, sodalite, analcime, Na-P1. The zeolites synthesized from fly ash have been used for immobilization of environmental pollutants like radioactive waste, removal of heavy metals and ammonium ions from industrial sludge [2–7].

The research on dehydration kinetics (value of activation energy, conversion rates) is crucial as it is in the dehydration state that zeolites prove their sorption and catalytic qualities or molecular-sieve activity. Numerous factors may influence the kinetics of zeolite dehydration. They include the interaction of H_2O molecules with a framework, of H_2O molecules with other cations and with each other, geometry of zeolite channel/void systems as well as their transformations during the process of dehydration. Stating the influence of particular factors on the dehydration process is rather difficult.

Thermal analysis methods (thermogravimetry, differential thermogravimetry) are widely used in characterization of zeolites and in the process of studying the mechanism and kinetics of zeolite dehydration [1]. The results of thermal analysis can supply very useful information on the processes of dehydration of zeolites and their thermal stability.

The aim of the present study is to investigate the process of dehydration of Na-A zeolite, a product obtained during hydrothermal treatment of fly ash with the application of thermogravimetry and to determine the kinetic parameters of thermal dehydration zeolite by using the Vyazovkin model-free kinetic method.

---

* Corresponding author. Tel.: +48-103334-3250432;
fax: +48-103334-3250933.
E-mail address: izak@is.pcz.czest.pl (I. Majchrzak-Kucęba).

0040-6031/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2003.10.021

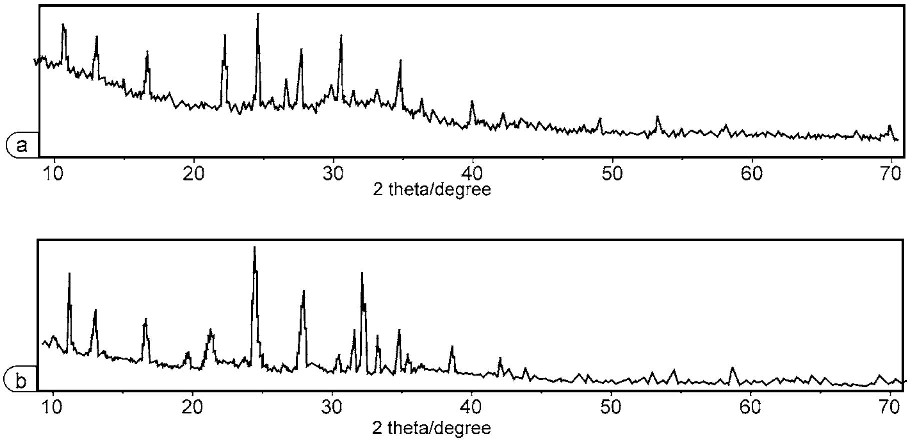


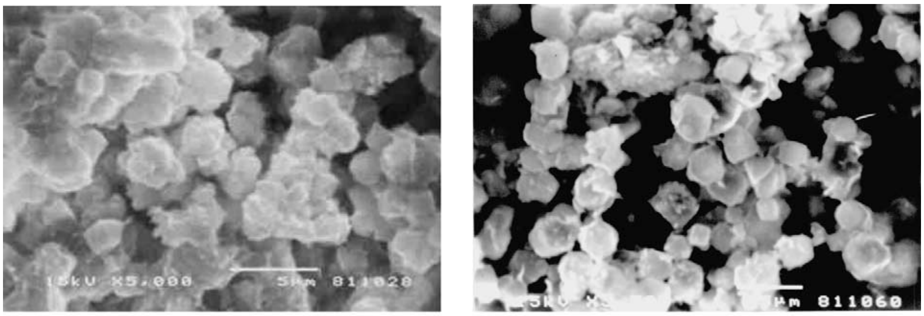
Fig. 1. XRD patterns of Na-A zeolite from fly ash (a) and commercial Na-A zeolite (b).

2. Experimental

In order to obtain zeolite from fly ash, alkaline, hydrothermal activation process was carried out. A sample of fly ash was obtained from an electric power station in Poland (Circulating Fluidized Bed boiler of 235 MWe in capacity). Fly ash was chemically analyzed and used to prepare the zeolitic material. The experiment was performed in a teflon reaction vessel placed within a temperature-controlled furnace and in a thermostatic bath equipped with a stirrer.

The synthesis process was run using the method of fusion with sodium hydroxide prior to the hydrothermal reaction—applying the procedure presented by Shigemoto et al. [7]. In accordance with this method, 10 g of fly ash and 12 g of NaOH was 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 100 ml distilled H_2O. Afterwards, it was agitated for 12 h at room temperature. After such preparation, the sample was placed at 100 °C for 12 h. After this time, the sample was filtered, washed with distilled water in order to remove the remaining NaOH, and dried at 120 °C for 12 h. After drying the sample, the product was characterized by various conventional methods. X-ray diffraction pattern of the zeolite sample was obtained with Cu Kα radiation by using a Feifert 3003 diffractometer. The XRD pattern of zeolite Na-A is presented in Fig. 1a. Particle morphology was observed by JEOL 5400 scanning microscope (Fig. 2a). On the basis of the research conducted, the presence of well crystallized zeolite Na-A (4A) was stated. The contents of zeolite in the sample amounted to about 60%, the remaining part was residue fly ash. Commercial Na-A zeolite has been also applied to the research discussed in the paper. Its X-ray and scanning analyses are presented in Fig. 1b and 2b.

Na-A zeolite synthesized from fly ash has been the subject of thermogravimetric analyses conducted for the purpose of this study. Na-A commercial zeolite results obtained during the same analyses were then compared. The effect of temperature on the zeolite samples was studied by a Mettler TG/SDTA 851e thermobalance. The samples of Na-A zeolites were heated in the temperature range of 20–1100 °C using heating rates of 10, 20, 30 °C min^{-1}, with a controlled nitrogen flow of 50 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. All measurements were blank curve corrected. The samples (about 5 mg) were heated in a platinum crucible. Mettler-Toledo STARe Software was used for evaluating the data. This software permits one to evaluate weight changes of a sample (thermogravimetric curve) and the single differential thermal analysis curve (obtained in the absence of a reference sample by difference of



(a) (b)

Fig. 2. SEM photographs of Na-A zeolite from fly ash (a) and commercial Na-A zeolite (b).

the sample temperature and the reference temperature calculated with the application of a mathematical model).

3. Model-free kinetics

Model-free kinetics is based on an iso-conversional computational technique that calculates the effective activation energy (E) as a function of the conversion (α) of a chemical reaction, $E = f(\alpha)$. Conversion (α), temperature (T) and time (t) are the three factors influencing the reaction rate of a chemical reaction. The reaction rate represented as function of conversion $f(\alpha)$ is different for each process and must be determined experimentally. The model-free kinetics is a computer program option basing on the Vyazovkin theory. In his approach, no model is applied. The data in this approach is gathered during numerous experiments. The approach follows all points of conversion from multiple experiments instead of a single one [9–11]. The theory is based on the assumption that

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha), \tag{1}$$

(where $f(\alpha)$ represents reaction model and $k(T)$ the Arrhenius rate constant) and that the activation energy $E(\alpha)$ is constant for a certain value of conversion α (iso-conversional method). Taking the reaction rate equation, presented as $f(\alpha)$ and dividing by the heating rate $\beta = \mathrm{d}T/\mathrm{d}t$ one obtains:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \Rightarrow \frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{k}{\beta}f(\alpha), \tag{2}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the reaction rate (s^{-1}), k the velocity constant (s^{-1}), α the conversion, and β the heating rate ($\mathrm{K\,s}^{-1}$). Substituting k by the Arrhenius expression $k = k_0 \cdot e^{-E/RT}$ and rearranging gives:

$$\frac{1}{f(\alpha)}\mathrm{d}\alpha = \frac{k_0}{\beta}e^{-E/RT}\mathrm{d}T \tag{3}$$

Integrating up to conversion, α (at the temperature T) gives:

$$\int_0^{\alpha}\frac{1}{f(\alpha)}\mathrm{d}\alpha = g(\alpha) = \frac{k_o}{\beta}\int_{T_0}^{T}e^{-E/RT}\mathrm{d}T, \tag{4}$$

Since $E/2RT \gg 1$, the temperature integral can be approximated by:

$$\int_{T_0}^{T}e^{-E/RT}\mathrm{d}T \approx \frac{R}{E}\cdot T^2 \cdot e^{-E/RT}, \tag{5}$$

Substituting the temperature integral, rearranging and logarithming, gives:

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{Rk_o}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha}, \tag{6}$$

where

$$\int_0^{\alpha}\frac{1}{f(\alpha)} = g(\alpha) \tag{7}$$

This is defined as a dynamic equation, which is used for the determination of the activation energy for all conversion values (α).

4. Results and discussion

Fig. 3 shows the loss of weight of the Na-A zeolite from fly ash during its controlled heating in nitrogen atmosphere (heating rate: 20 °C min^{-1}; flow rate: 50 cm^3 min^{-1}). The first step in the TG curve of Na-A zeolite from fly ash (from 20 to 500 °C), is due to zeolite dehydration process (desorption of moisture and zeolitic water). The water content in the sample of Na-A zeolite synthesized from fly ash is 18.3 wt.% and is lower than in the commercial Na-A zeolite (21.3 wt.%). The second step is caused by the decomposition of $CaCO_3$, being a residue of fly ash. Its presence was also confirmed by X-ray analysis. The first stage of the TG and DTG curves was analyzed for each heating rate in order

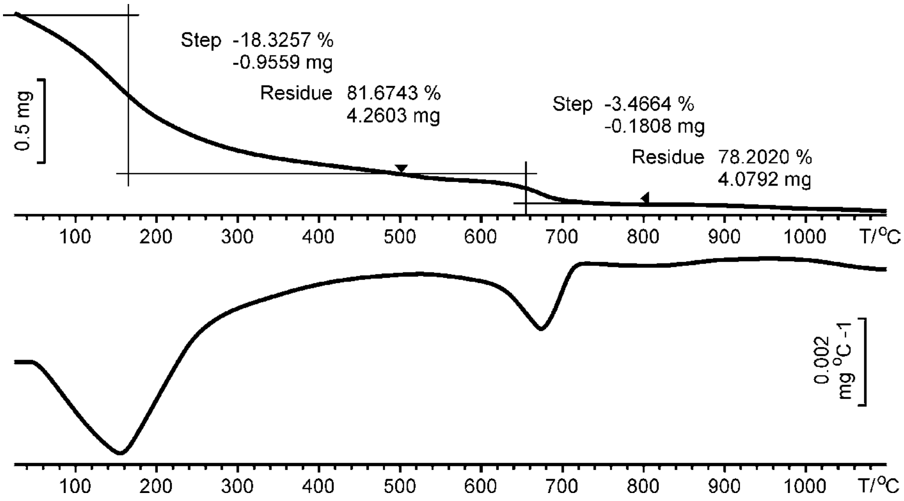


Fig. 3. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of Na-A zeolite (heating rate: 20 °C min^{-1}; nitrogen flow: 50 cm^3 min^{-1}).

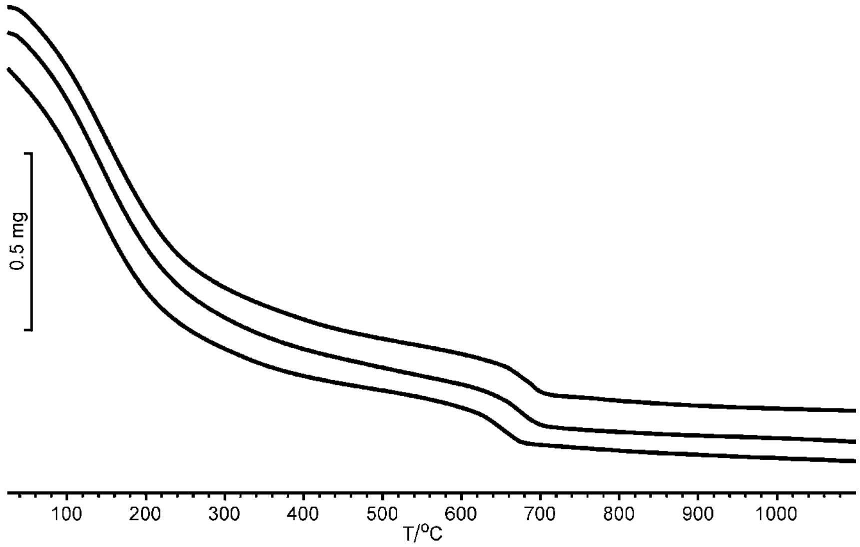


Fig. 4. Thermogravimetric curves (TG) of Na-A zeolite with three heating rates: 10, 20, and 30 °C min^{-1} (from left to right).

to define the right zeolite dehydration temperature range. In case of $\beta = 20\,^{\circ}\mathrm{C\,min^{-1}}$, dehydration occurs in the range of 20–500 °C. The choice of this temperature range resulted also from the fact that in case of Na-A commercial zeolite analyzed for comparison purposes the weight loss caused by the dehydration process occurs in the temperature range from 20 to 500 °C.

Model-free kinetics requires at least three dynamic curves with different heating rates. In the present study these were three heating curves of Na-A zeolite from fly ash and commercial Na-A zeolite obtained in the temperature range of 20–1100 °C. Fig. 4. shows three Na-A zeolite curves obtained from fly ash, while heating from 20 to 1100 °C with heating rates of 10, 20, and 30 °C min^{-1}. The first step in the TG curve (20–500 °C) was chosen for model-free kinetics calculations, as it is this stage that is connected with zeolite dehydration process.

The respective conversion curves were calculated out of the TG measured curves. Conversion curves as a function of temperature are showed in Fig. 5.

In accordance with model-free kinetics, for each conversion α, $\ln \beta / T_{\alpha}^{2}$ was plotted versus $1/T_{\alpha}$, giving a straight line with the slope $-E_{\alpha}/R$; therefore the activation energy was obtained as a function of conversion.

Fig. 6a presents activation energy as a function of percentage conversion for Na-A zeolite synthesized from fly ash and Fig. 6b the relation for commercial Na-A zeolite obtained in result of the same calculations.

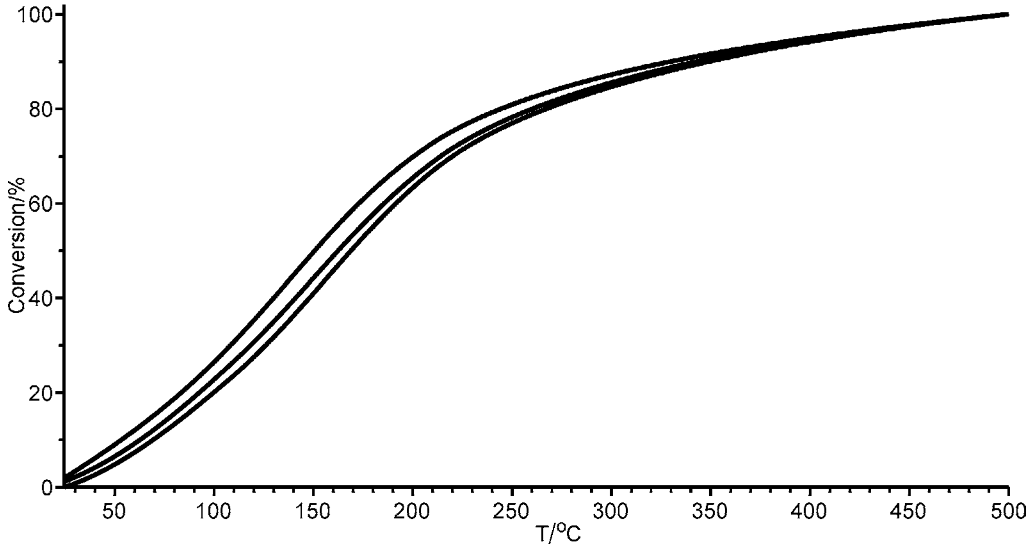


Fig. 5. Conversion curves as a function of temperature for Na-A zeolite dehydration.

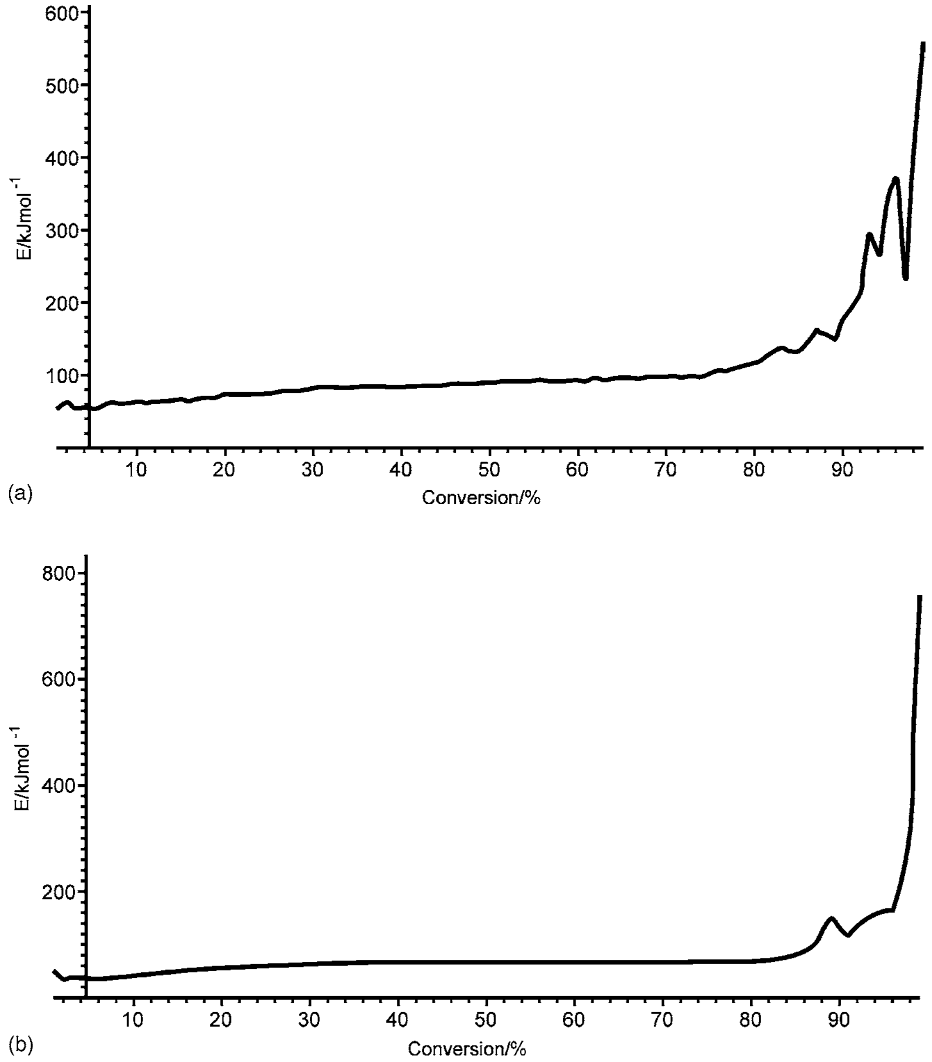


Fig. 6. Activation energy as a function of percentage conversion for: Na-A zeolite from fly ash (a) and commercial Na-A zeolite (b).

As results from Fig. 6a, dehydration of Na-A zeolite from fly ash has a practically constant activation energy of about 60–120 kJ/mol ($\alpha = 0.1$–0.9). The same evaluations were performed for commercial Na-A zeolite. The activation energy for commercial Na-A zeolite (Fig. 6b) is about 40–100 kJ/mol ($\alpha = 0.1$–0.9), and is slightly lower than the value obtained for zeolite from fly ash. It points to the fact that the energy needed to remove water molecules from the pores formed in result of fly ash modification is slightly higher than the energy needed to remove water molecules from the channel/void system of the crystallized zeolite synthesized classically. 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 as well as different effective diameter of channels and voids. The last factor is particularly important as the energy needed to remove water molecules from zeolite voids decreases with the increase of effective diameter of these voids. In case of classically synthesized commercial Na-A zeolite the effective void diameter is 0.41 μm and it is larger than in case of Na-A zeolite from fly ash.

Fig. 7a and b present conversion curves of dehydration of Na-A zeolite synthesized from fly ash and commercial Na-A zeolite as a function of time, for different temperatures. On the basis of the curves obtained for Na-A zeolite from fly ash one may state that the conversion time decreases as a function of temperature. It follows from the graph that at 23 °C it is possible to obtain only 10% conversion for 17.7 min. It is evident from the figure, that a conversion of 90% is reached when the zeolite is stored at 310 °C for 6.5 min.

In case of commercial Na-A zeolite, the process of dehydration is slightly faster (Fig. 7b). At 23 °C, it is possible to obtain 10% conversion for 8.28 min. The time is thus half as long as in case of zeolite synthesized from ash. 90% conversion may be obtained only at 310 °C just like in case of Na-A zeolite synthesized from fly ash. However, it will only take 0.39 min.

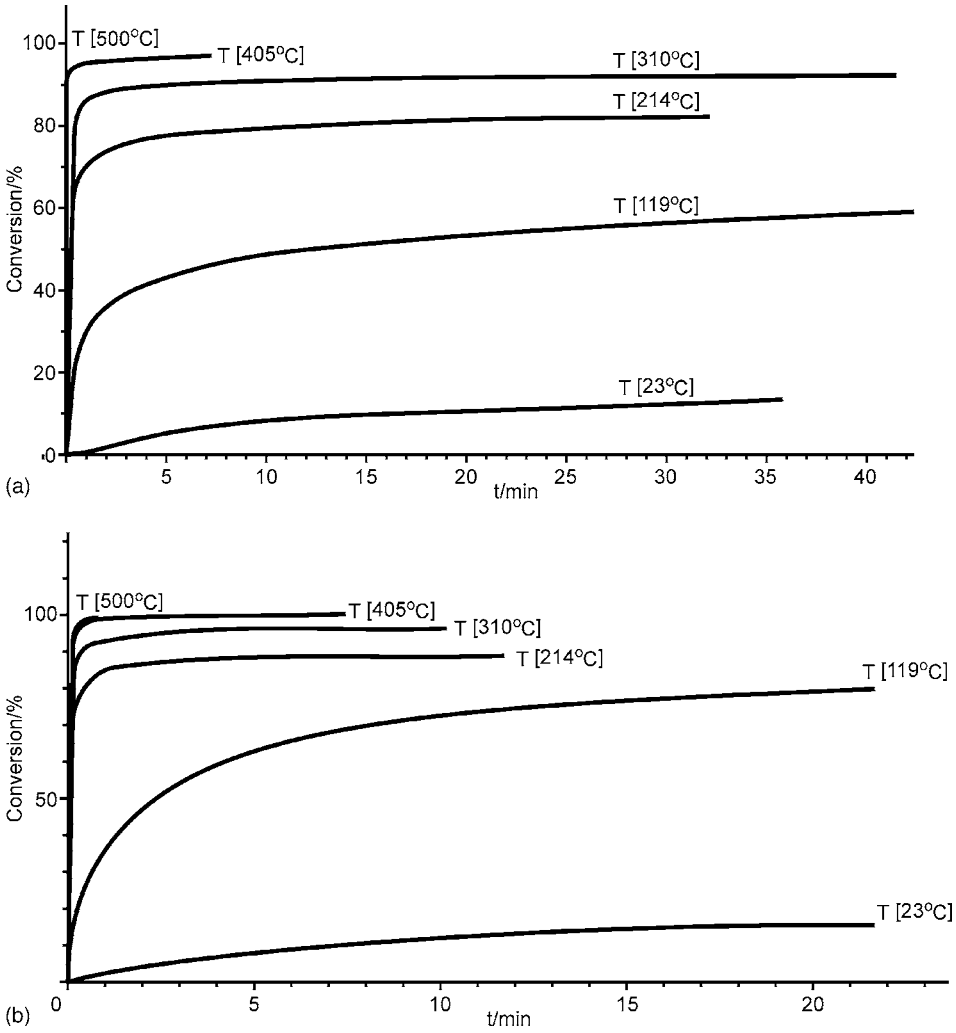


Fig. 7. The conversion curves as a function of time for: Na-A zeolite from fly ash (a) and commercial Na-A zeolite (b).

The results obtained (values of activation energy, conversion curves) confirm that in spite of different material applied to its synthesis, different crystallization process and thus different contents of some fly ash residues, Na-A zeolite synthesized from fly ash possesses a well developed channel/void system of similar diameters and a high crystallization 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 silica 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, crystallization 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.

5. Conclusions

The model-free kinetics applied in the research has proven to be a comfortable evaluation tool in case of zeolite dehydration kinetics, including the Na-A fly ash based zeolite containing also some fly ash residues. The value of activation energy, obtained on the basis of the model in the (α) conversion function amounted to 60–120 kJ/mol for this zeolite. It is similar to the value of activation energy E obtained as a result of identical calculations for Na-A (4A) commercial zeolite. This fact proves the presence of Na-A zeolite with a well developed channel/void system in the sample synthesized from fly ash.

References

[1] D.W. Breck, Zeolite Molecular Sieves—Structure, Chemistry and Use, J. Wiley & Sons, New York, 1974.
[2] F. Mondragon, F. Rincon, L. Sierra, J. Escobar, J. Ramirez, J. Fernandez, Fuel 69 (1990) 263–266.

[3] Ch.-F. Lin, H.-Ch. Hsi, Environ. Sci. Technol. 29 (1995) 1109–1117.
[4] C.H. Amrhein, G.H. Haghnia, T.S. Kim, P.A. Mosher, R.C. Gagajena, T. Amanios, L. De La Torre, Environ. Sci. Technol. 30 (1996) 735–742.
[5] X. Querol, A. Alastuey, A. Lopez-Soler, F. Plana, J.M. Andres, R. Juan, P. Ferrer, C.R. Ruiz, Environ. Sci. Technol. 31 (1997) 2527–2533.
[6] H-L. Chang, W-H. Shih, A general method for the conversion of fly ash into zeolites as ion exchangers for cesium, Ind. Eng. Chem. Res. 37 (1998) 71–78.
[7] N. Shigemoto, H. Hayashi, K. Miyaura, J. Mater. Sci. 28 (1993) 4781–4786.
[8] G.G. Hollman, G. Steenbruggen, M. Janssen-Jurkovicova, Fuel 78 (1999) 1225–1230.
[9] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340–341 (1999) 53–68.
[10] S. Vyazovkin, N. Sbirrazzuoli, Anal. Chim. Acta 355 (1997) 175–180.
[11] S. Vyazovkin, Int. J. Chem. Kinet. 28 (1996) 95–101.