INFLUENCE OF BASE SOLUTION CONCENTRATION ON THE FLY ASH ZEOLITE HYDROTHERMAL SYNTHESIS

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Abstract

Industrial fly ash may be used as the substrate in synthesis of zeolites. The impact of process parameter on the product is high, in relation to this, in the presented work the influence of base concentration, used in the synthesis process, was investigated. It was proved that it is possible to obtain different product of synthesis as well as different yield of synthesis with the use of differentiated concentration of the base solution. The lower pH values resulted in obtaining P1 zeolite while the use of higher concentrations was favorable for the production of sodalite.

Keywords: Zeolite, fly ash, hydrothermal synthesis

1. INTRODUCTION

In relation to high amounts of fly ash being produced in power plants and heat power plants, new directions of this materials use are being searched for. Chemical composition of fly ash enable to use it as a substrate for the synthesis of new materials, one of the proposition is zeolite synthesis. There exist several methods of fly ash conversion into zeolites [1, 2]. The most widespread is hydrothermal synthesis method, due to its relative simplicity. A lot of research indicate that it is possible to obtain zeolites in the hydrothermal process [3, 4]. What is characteristic, is that the change of synthesis parameters may significantly influence the process [4, 5, 6, 7]. The parameter of high importance is the concentration of alkali used in the process. It was experimentally proved that it is possible to receive zeolites in very wide range of concentration values, form value around 2 mol/dm^3 [7] up to 15 mol/dm^3 [8]. Literature data indicate that the increase in alkali concentration influences the process of digestion of raw material [9], what suggest that more condensed solutions would positively influence the reaction outcome. In the performed experiments testing of the influence of change in alkali concentration on the zeolites products was presented.

2. EXPERIMENTAL

2.1. Raw material

For the experiments fly ash form the pulverized coal-fired boiler equipped with SCR installation was selected. For the synthesis fly ash unprocessed samples were collected form main fly ash containers.

2.2. Apparatus

Determination of fly ash oxide composition was performed according to polish standard PN-EN 450, w plasma spectrometer Thermo iCAP 6500 Duo ICP. The mineralogical phase content was examined with the use of XRD diffractometer PANalytical - Empyrean, equipped with radiation source Cu-Kα (λ=1.5406Å). The analysis was performed for the angle ranges 2θ 3-90° with step size 0.02°/min in the ambient temperature. Based on polish standard PN-EN 450-1 loss on ignition analysis was done. Estimated values for the values of fly ash fines were presented, the examination was performed with the use of Hosokawa Alpine 200 LS-N Air Jet Sieve, with the use of 45 µm sieve. The use of air jet sieve Hosokawa Alpine 200 LS-N equipped with sieved 200 µm, 90 µm, 45 µm, 32 µm i 20 µm provided information about the granulometric curve. The samples structure

analysis was performed with the use of Bresser Advanced ICD 10x - 160x Trino equipped with Delta Optical DLT-Cam PRO 5MP USB 2.0.

2.3. Raw material analysis results

Analysis of oxide content (symbol K4M) was presented in **Table 1**. As a result of XRD analysis of raw material diffractogram presented in **Figure 1** was obtained. The presence of mullite and quartz as dominant phases.

Table 1 Oxide content in fly ash

	SiO_2	Fe_2O_3	Al_2O_3	Mn_3O_4	TiO_2	CaO	MgO	SO_3	P_2O_5	Na_2O	K_2O	BaO	SrO	LOI
K4M, %	50.1	6.53	28.3	0.04	1.28	1.37	1.1	0.44	1.16	0.45	2.14	0.16	0.12	6.48

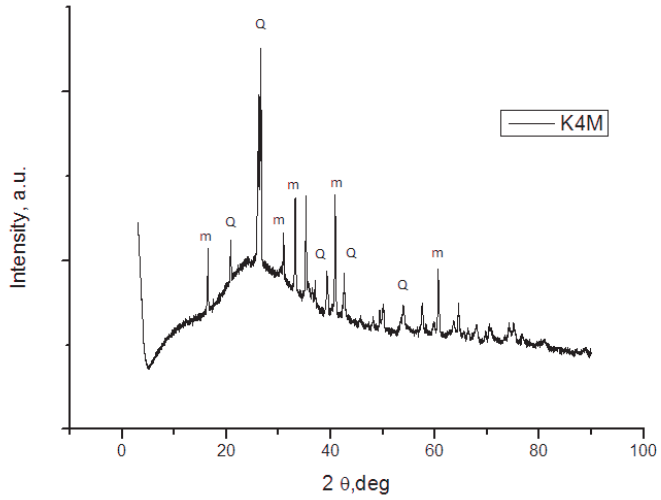

Figure 1 Unprocessed fly ash diffractogram

The examination of loss on ignitron value represented the value of 6.48%, estimated fitness value was 28%, what gives information of high content of fine particles in raw material. Granulometric curve for raw fly ash is presented in **Figure 2**. In the **Figure 2** symbols correspond to fly ash particles size ranges F1 >200 µm, 200 µm> F2 >90 µm, 90 µm> F3 >45 µm, 45 µm> F4 >32 µm, 32 µm> F5 >20 µm, 20 µm> F6. Presented granulometric curve confirms high share if very fine particles fraction in selected for synthesis material.

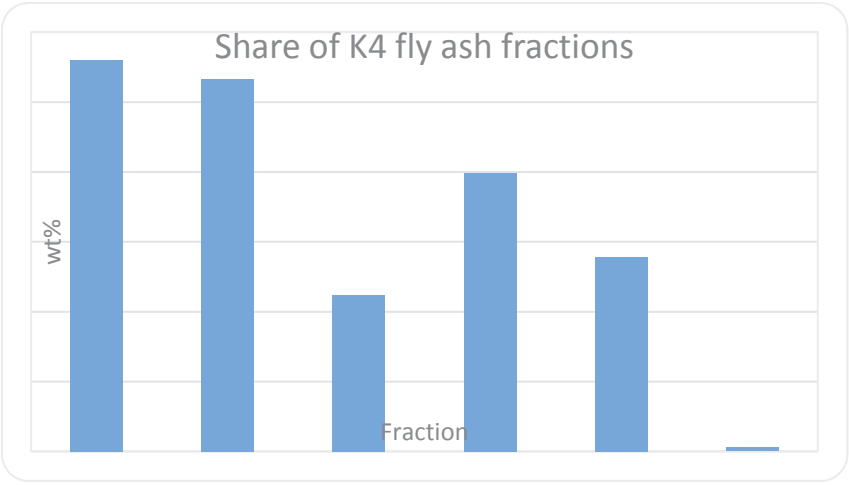

Figure 2 The share of examined fly ash fractions

Photograph of fly ash selected for the synthesis was presented in **Figure 3**.

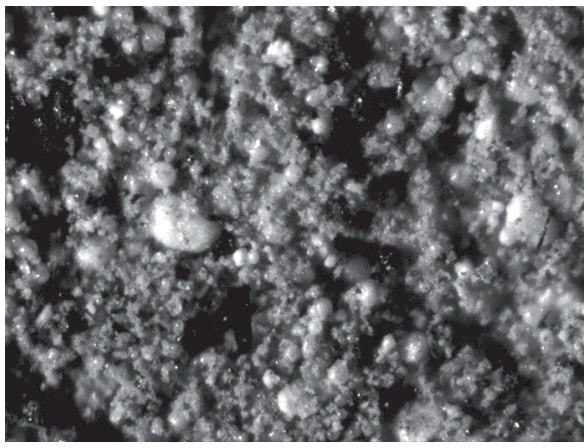

Figure 3 K4M fly ash, magnification 160x

Silica/alumina fly ash ratio is 1.77, what based on literature data, allows to expect that fly ash selected for those experiments will give positive effect in the zeolite synthesis process. The XRD diffractogram analysis show that mullite and quartz, which are silica and alumina source are present. Additionally the amorphous halo in the angle range 20-40 2θ was present, what proves the presence of glassy phase which will undergo digestion in first place [10]. Loss on ignitron value of 6% should not significantly influence the synthesis process, the fitness value as well as granulometric curve giving information of high amount of fine particles allow to expect the raw material to be good substrate for the zeolites synthesis, as fine particles will undergo digestion process in first place. Presented results of raw material analysis provides information that this material is suitable for the synthesis of zeolites out of fly ash.

2.4. Synthesis procedure

In the experiment hydrothermal synthesis of zeolites out of fly ash was performed. For the synthesis below parameters were selected:

- temperature: 90^0C
- time: 24 hours
- fly ash amount: 10 g
- alkali used: 200ml NaOH
- mixing of solution during synthesis: yes
- rinsing with water: five times with the same amount of distillated water
- drying: 105^0C, 6 hours

Five processes of synthesis were performed aimed at determination of the alkali concentration influence on the experiment result. There were selected concentrations of values: 3 mol/dm^3, 3.5 mol/dm^3, 4 mol/dm^3, 4.5 mol/dm^3 i 5 mol/dm^3. The identifiers for received samples were introduced: K4M- result of synthesis in the alkali solution of 3 mol/dm^3 concentration, K4 3.5M result of synthesis in the alkali solution of 3.5 mol/dm^3 concentration, K4 4M- result of synthesis in the alkali solution of 4 mol/dm^3 concentration, K4 4.5M result of synthesis in the alkali solution of 4.5 mol/dm^3 concentration, K4 5M- result of synthesis in the alkali solution of 5 mol/dm^3 concentration.

2.5. Synthesis results

In **Table 2** the identifiers of samples received as a synthesis products were presented along with the type of zeolite synthesized.

Table 2 Symbols of samples and synthesis zeolitic products

Identifiers of samples received as a result of performed synthesis	Alkali concentration, mol/dm^3	Zeolite
K4M	3	P1
K4 3.5M	3.5	P1
K4 4M	4	trace P1, sodalite
K4 4.5M	4.5	Sodalite
K4 5M	5	Sodalite

The products of synthesis were identified with the use of XRD method. Diffractograms of all samples were presented in **Figure 4**.

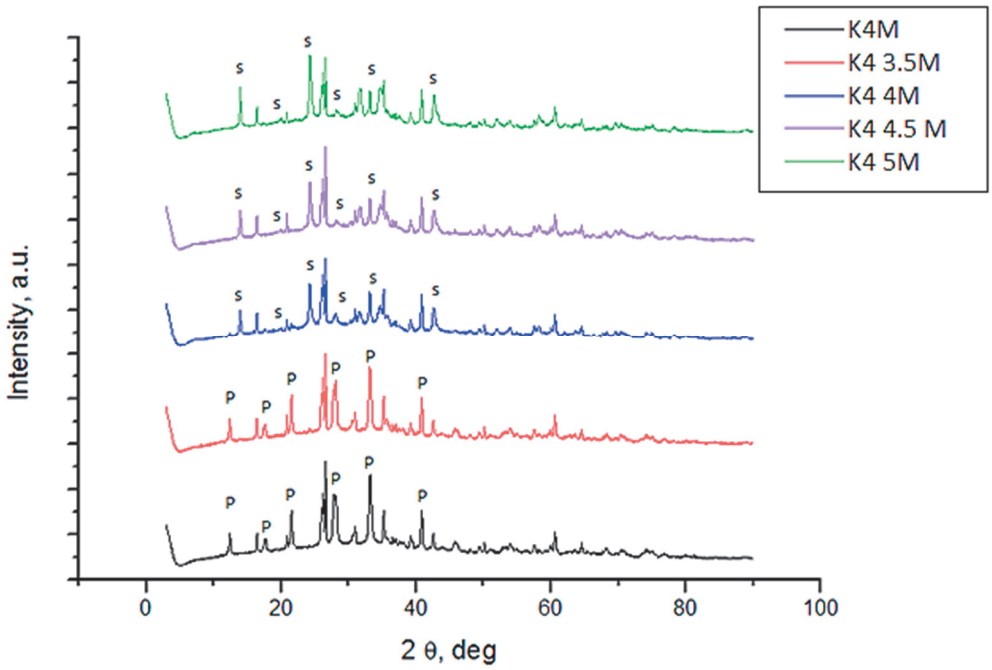

Figure 4 Hydrothermal synthesis products XRD diffractograms

In **Figures 5-9** there are presented pictures of synthesis products.

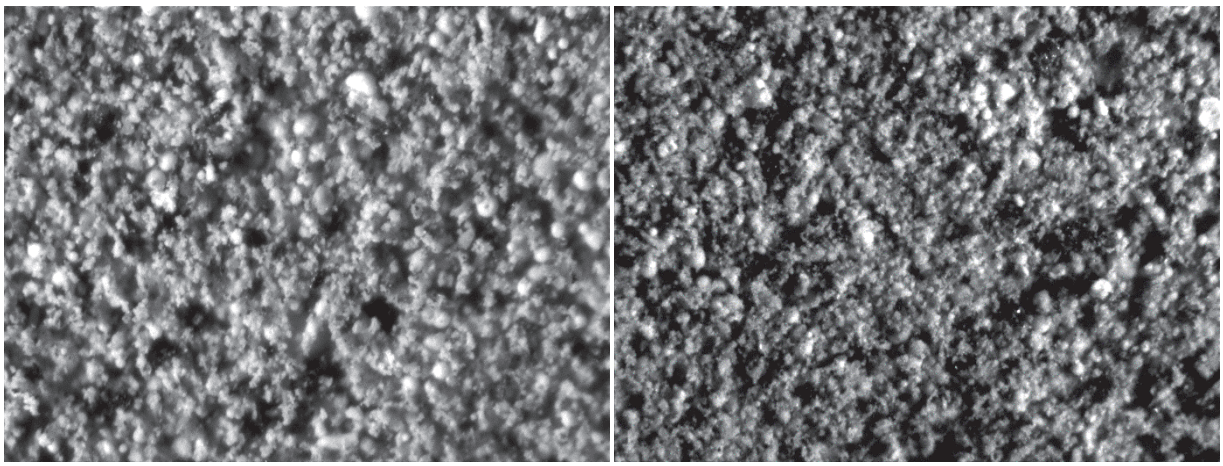

Figure 5 Synthesis product magnification 160x, 1) K4M, 2) K4 3.5M

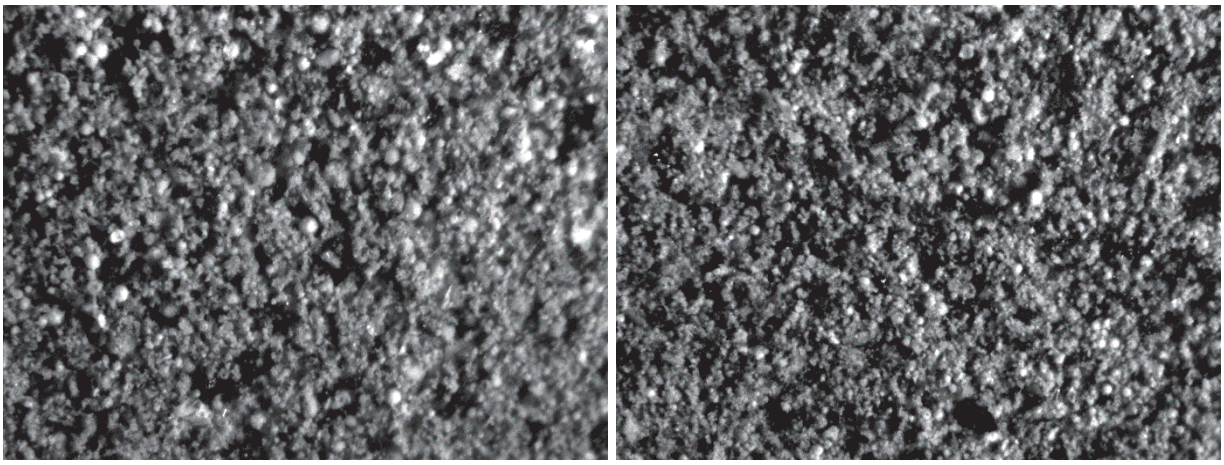

Figure 6 Synthesis product magnification 160x, 1) K4M 4M, 2) K4M 4.5M

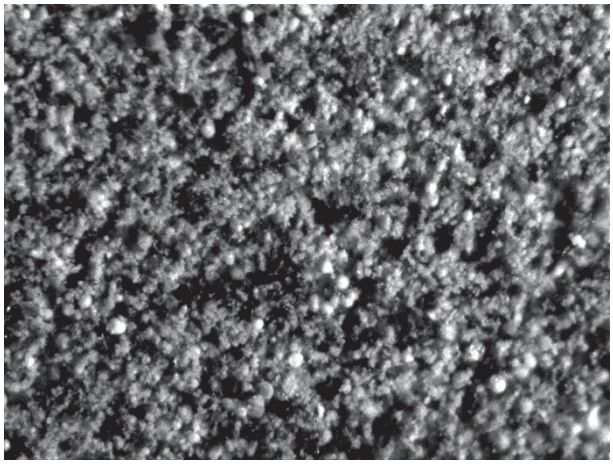

Figure 7 Synthesis product magnification 160x, 1) K4M 5M

2.6. Results analysis

As a result of performed synthesis it was found that it is possible to receive zeolite materials with the use of proposed method, with increasing value of alkali concentration in the ranges 3-5 mol/dm^3. It was proved that the change of alkali concentration results in obtaining different zeolite products as well as different yields of synthesis. With the increasing concentration zeolite P1 which crystallized in sample K4M is disappearing while sodalie occurs. Estimated relative efficiencies, which calculation was based on comparison of areas under the most intensive reflections of appropriate phase [2], lead to identification of decrease of zeolite P1 efficiency in line with trend K4M>K4 3.5M>>K4 4M. In the sample K4 4M only trace reflections from zeolite P1 were found. In samples where higher concentration of base solution was used - 4-5 mol/dm^3 - reflections characteristic for sodalite were found. Once the analogical comparison of reflections intensities was done it was found that the amount of sodalite is increasing in case of higher base solution concentration used. The trend for decreasing amount of sodalite is as follows: K4 5M>K4 4,5M>K4 4M. The observation of samples with the use of optical microscope, there were no significant differences in the morphology of samples found in reaction products. Analyzing the change in relation to raw material, it can be stated that synthesis products were characterized by more fine particles, texture of samples may be described as more uniform.

In relation to application possibilities of using zeolite materials P1, it is intentional to use in experiments base concentration of value 3 mol/dm^3. However, experimental results indicate that in case of will to receive sodalite it will be more beneficial to use higher base solution concentration. Trend observed in the research indicate

that one zeolite phase disappears for the advantage on the other one, with increasing value of base solution concentration. This can indicate that secondary dissolution of zeolite P1 in conditions of higher concentration of base solution and its recrystallization in the form of sodalite. Similar observations were also found by other researchers [3, 11, 12]. Secondary recrystallization is a result of increase of dissolution of building materials, what was noticed and described in other research [9].

3. CONCLUSIONS

Performed experiments proved the possibility of receiving zeolites from fly ash samples from the process of hard coal burning. Series of samples, characterized by differentiated valued of base solution concentration, along with constant remaining parameters, allowed to determine the influence of basicity of solution on the zeolite synthesis process. The results of experiments indicate that it is possible to receive different products as well as highlighted receiving of differentiated efficiencies in relation to synthesis zeolites products. It was fund that the increase in sodium hydroxide up to value 5 mol/dm^3 was more beneficial for the crystallization of sodalie, once lower concentrations (3 mol/dm^3) were preferential for the formation of zeolite P1.

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