Analysis of the influence of fusion synthesis parameters on the SO_2 sorption properties of zeolites produced out of fly ash

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Abstract. Fly ash zeolites are interesting alternative for zeolies produced out of pure chemicals as well as for natural zeolites. It can be applied as SO_2 sorbents out of flue gases. In the work the experiments were aimed at investigation of SO_2 sorption capacity of samples produced out of fly ash in fusion process. The influence of fusion reaction parameters on the type of obtained zeolites and on the efficiency of synthesis was investigated. The samples containing the same types of zeolites, but with different production yield were testes on SO_2 sorption capacity.

1 Introduction

Fly ashes are solid residues form the process of fossil fuels burning, captured from flue gases by electrostatic precipitator. According to its composition may be used in various industrial areas. The examples of its use may be reclamation of mining excavations (brown coal fly ashes), production of solidified ash mixtures for curing of lands, embankments, dumps, local roads and others, production of non-cement binders, Portland clinker production, as an active cement additive, concrete production, the light aggregates production, road building, use in agriculture and gardening, for the self-solidifying filling in mining [1]. Fly ash production in Poland is at a level of around 4,5 mln tonnes [2]. Poland is a country where the reuse of fly ashes is very efficient (87%) [2]. Due to the need of decreasing the amount of fly ash landfills (especially in the countries of lower degree of fly ash use [3]), searching for new processes for fly ash utilization is needed.

The way allowing for the reduction of fly ash landfill sites along with the production of valuable material is the process of zeolite production with the use of fly ashes. Zeolites can be obtained in the processes of: hydrothermal synthesis, fusion synthesis, molten salt synthesis method [4], by the combination of different methods and for example by utilizing microwave and ultrasound energies [5]. The comparison of literature data of particular methods allowed for the selection of fusion method for the research presented in this work. Adoption of this method was dictated by the reports stating that highly efficient zeolite synthesis process can be expected [5,6].

Burning process of fossil fuels is related to the emissions of particulate matter and gaseous pollutants, including sulphur dioxide (SO_2). A common way to capture SO_2 is to use calcium compounds in the dry and semi-dry methods of flue gas purification. It is necessary to search for alternative ways for sulphur dioxide capture out of flue gases. Zeolites as materials used for soil, sewages as well as gases purification [7], can be used as SO_2 adsorbents. The possibility of fly ash zeolites use as SO_2 sorbents would have a positive ecological outcome due to use of waste material as a substrate.

The series of experiments were performed aimed at selecting the best conditions for the zeolites formation. Based on the outcome of synthesis two samples were selected. In the chosen samples the same types of zeolites were present, but the efficiency of zeolite material formation was different.

In the work the SO_2 sorption capacity of material synthesized out of fly ash with the use of fusion method on selected samples was investigated, as well as regeneration properties of received materials.

2 Material and measurements methods

For the research fly ash from one of Polish heat-power plants was selected. Chemical composition analysis have been preformed with the use of XRF method. XRF analysis was preformed with the use of a Philips spectrometer PW 1404 with an X-ray tube equipped with dual Cr–Au anode with a maximum power of 3 kW as the excitation source. The investigated fly ash was marked with symbol L in this work and presents the following the chemical composition: Na_2O-2,3%, MgO-1,769%, Al_2O_3-15,706%, SiO_2-38,449%, P_2O_5-0,743%, SO_3-1,038, K_2O-2,773%, CaO-3,578%, TiO_2-1,001%, V_2O_5-0,044%, Cr_2O_3-0,045%, MnO-0,168%, Fe_2O_3-10,085, NiO-0,024%, CuO-0,085%, ZnO-0,987%, Ga_2O_3-0,006%, As_2O_3-0,023%, Rb_2O-0,014%, SrO-0,047%, Y_2O_3-0,004%, ZrO_2-0,03%, Nb_2O_5-0,003%,

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SnO_2-0,022%, BaO-0,094%, PbO-0,298%. Due to standard specification [8], fly ash L was classified as siliceous fly ash. In literature more widespread classification based on American standard specification [9], classified fly ash L as F class fly ash. The XRD analysis have been also performed. The results of analysis were presented in the figure 1.

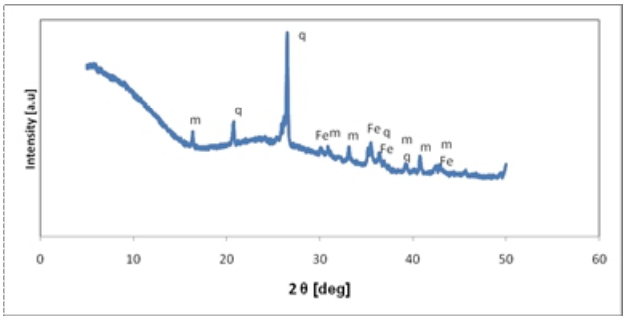

Figure 1. XRD diffractogram of fly ash L (m-mullite, q-quartz, Fe-hemaite/magnetite)

In the experimental part the synthesis of zeolites by the fusion method combined with hydrothermal aging process of solutions was preformed. Synthesis were differentiated in case of the temperature of synthesis process, used fly ash/base ratio and the time during which the aging of solution took place in the evaluated temperature after the fusion process. Received materials were washed to pH~10 and then dried.

The estimated efficiency of zeolite synthesis was calculated with the use of XRD data, based on equation (1) [10]. In the estimated calculations there was no pattern used, the comparison was based on 10 most intensive reflections characteristic for a given zeolite compared with the other synthesized sample- reference sample.

$$WK_{XRD} = \frac{\text{The sum of 10 individual reflections relative intensities of fly ash zeolite}}{\text{The sum of 10 individual reflections relative intensities of commercial zeolite (pattern)}} \times 100 \quad (1)$$

Performed fusions were differentiated in case of the process temperature: Fusion 550 - 550^{0}C, Fusion 600 - 600^{0}C, Fusion 650 - 650^{0}C, Fusion 700 - 700^{0}C. The time of fusion process was in cases of all examined samples the same -1 hour.

3 Results of synthesis

Prepared powders were analysed in order to confirm the presence of zeolite materials with the use of XRD method. The comparision of recieved synthesis products was presented in table 1.

Table 1. Comparison of synthesis results

	6-hour hydrothermal aging time		24-hour hydrothermal aging time	
	Fly ash/base ratio	Zeolite type	Fly ash/base ratio	Zeolite type
FUSION 550	2	-	2	trace X
	1	X, trace A	1	X, sodalite
	0,8	X, A	0,8	X, sodalite
FUSION 600	2	-	2	sodalite
	1	X, A	1	X, sodalite
	0,8	X	0,8	sodalite
FUSION 650	2	-	2	X, A
	1	X, A	1	X, sodalite
	0,8	X	0,8	X, sodalite
FUSION 700	2	-	2	-
	1	X, A	1	sodalite
	0,8	X, A	0,8	sodalite

4 Results of synthesis analysis

After the analysis of results it was fund that the elongation of the hydrothermal aging after the fusion process up to 24 hours, in most cases lead to sodalite formation. In part of the samples zeolite X was present, however it was noticed, based on the analysis of area under the most intensive reflections characteristic for X zeolite phases, that along with the appearance of sodalite reflections, the intensity of reflections characteristic for zeolite X is decreasing, what in approximation gives idea of the amount of formatted zeolite. It is believed that in the 24-hour aging the secondary dissolution of silica-alumina sources takes place (also from zeolite phases) and the recrystallization in the form of sodalite is observed [6].

It was discovered that the used fly ash/base ratio influences the formation of zeolite phases. For the purpose of determination of the best conditions for zeolite formation it was assumed that zeolites of high potential application should be obtained with high estimated efficiency of synthesis. Least of all profitable fly ash/base ratio is 2. The use of fly ash/base ratio of 1 and 0,8 in majority of samples resulted in zeolite formation. While comparing the areas under the reflections characteristic for analyzed phase, conclusions can be drawn that the higher reflections intensity, in approximation representing the zeolite formation efficiency, can be observed for fly ash/base ratio 0,8.

Detailed analysis of results allowed to draw conclusions of the temperature influence on the synthesis process. It was found that the most profitable temperature in relation to efficiency of received zeolite materials is 700^{0}C.

5 Sorption properties of selected samples

Due to possibility of application of zeolites synthesized out of fly ash for adsorption of SO_2, the experiments aimed at determination of sorption capacity of selected samples have been performed.

The experiment was performed in the temperature of 25^{0}C. The analyzed material was not additionally prepared for the sorption experiments. For the analysis two samples were selected, with different quantity of present zeolite. In both samples the presence of zeolite X and A was confirmed. The first sample was received in the fusion preformed in the temperature 700^{0}C, the ratio of fly ash to base was 0,8, the fusion was combined with 6-hour hydrothermal solution aging. This sample in the work was marked with symbol F700-0,8-6. The second sample was marked with symbol F550-0,8-6 and was received in the fusion process performed in the temperature 550^{0}C with the use of fly ash and base ratio of 0,8, combined with 6-hour hydrothermal solution aging. Diffractograms of both samples were presented in figure 2.

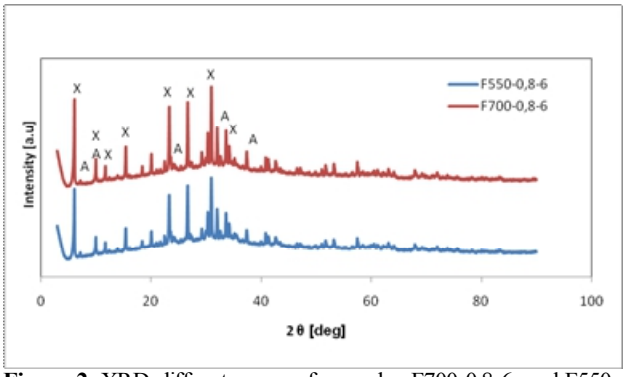

Figure 2. XRD diffractogram of samples F700-0,8-6 and F550-0,8-6 (X-zeolite X, A- zeolite A)

Based on the equation (1) the efficiency of zeolite synthesis was estimated, with the use of commercial zeolites type A and X as reference samples. For sample F700-0,8-6 the efficiency of zeolite X synthesis was approximately 47%, while in the same sample the efficiency of zeolite A synthesis was about 4%. For sample F550-0,8-6 the efficiency of zeolite X synthesis was estimated at 44%, while for zeolite A the value was 7%.

6 Sorption capacity results

The results of sorption capacity experiments performed on selected samples were presented in figures 3 and 4.

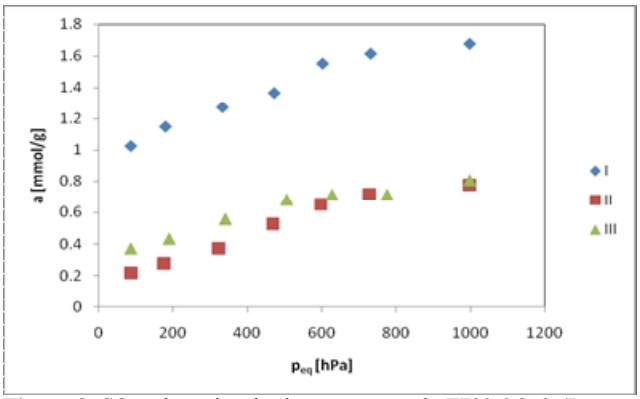

Figure 3. SO_2 adsorption isotherm on sample F700-0,8-6 (I-first sorption cycle, II- second sorption cycle, III-third sorption cycle)

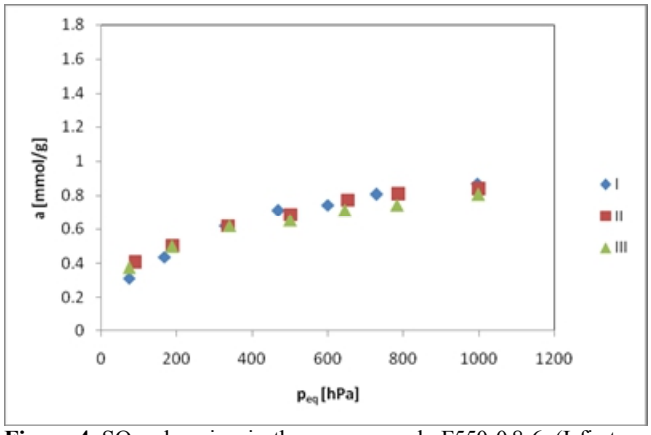

Figure 4. SO_2 adsorpion isotherm on sample F550-0,8-6 (I-first sorption cycle, II- second sorption cycle, III-third sorption cycle)

In table 2 the comparison of SO_2 sorption values were presented.

Table 2. Comparison of SO_2 sorption capacity for investigated samples

Sample name	Cycles of sorption capacity a, mmol/g		
	I	II	III
F700-0.8-6	1.68	0.78	0.81
F550-0.8-6	0.87	0.84	0.81

7 Results of sorption analysis

During the analysis of sorption experiments it was noted that sample F700-0.8-6, characterized by the higher amount of zeolite material synthesized, presented higher SO_2 sorption capacity. It was also observed that after the first sorption-desorption cycle the sorption capacity decreases, but in the following cycles it remained on constant level. Authors noticed similar observations for other samples containing zeolites synthesized out of fly ash [11]. Sorption capacity decrease after the first cycle may be related to permanent connection of sulphur dioxide with the non-reacted fly ash materials. Sample F550-0.8-6 characterized by lower content of zeolite material has presented lower sorption capacity value in relation to SO_2. This trend is consistent with author's predictions, the lower zeolite material amount will result in lower area able to capture SO_2. From the application point of view, sample F550-0.8-6 is highly attractive due to very good regeneration properties of examined material. In the second and third sorption-desorption cycle only slight decrease in the sorption capacity was observed. Authors considered performing additional experiments for sample F550-0.8-6 to be intentional.

8 Conclusions

In the work the investigation of fusion process parameters on the formation of zeolite phases synthesized out of fly ash was presented. The series of synthesis were performed, differentiated in case of fusion temperature, the ratio of amount of fly ash to base used and the hydrothermal aging time after the fusion process.

As a result of performed experiments it was fund that the highest efficiency of zeolites synthesis, estimated as an area under the most intensive reflections for given zeolite, was for the fusion temperature 700^{0}C. This trend was observed for all samples with the same fly ash/base ratio and with the same aging time. The use of fly ash/ base ratio of 0,8 was proven to give the best results, lower efficiency of zeolites formation was noticed for the use of fly ash/base ratio equal 1. With the use of smaller amount of base (ratio 2), in most cases, no zeolite phases were present in the investigated material. The time of hydrothermal aging after the fusion process is believed to have a significant influence on the zeolite formation. It was fund that the time of hydrothermal reaction of 6 hours was more profitable due to formation of zeolite phases of higher application potential. Extended to 24 hours time of hydrothermal aging lead to appearance of sodalite in predominant number of samples. It was stated that formatted zeolite phases in the 6-hour hydrothermal aging, were dissolved and the secondary crystallization took place as a result of which sodalite was formed. Confirmation of this fact are available literature data [6] as well as the fact that in case of presence of different than sodalite zeolite phases (also present in the sample subjected to 6-hour hydrothermal aging), the reflections intensity of this different phase is lower than for analogical sample subjected to 6-hour hydrothermal aging process.

The analysis of sorption properties proved the use possibility of received zeolites for the SO_2 sorption. Selected samples were differentiated in case of the yield of zeolite formation. In case of sample characterized by higher zeolite synthesis efficiency F700-0,8-6, the sorption capacity was 1,68 mmol/g in the first cycle and 0,78 and 0,81 mmol/g in the second and third sorption-desorption cycle accordingly. After the first cycle the decrease in the sorption capacity was observed, while in the second and the third cycle it remained on constant level. For the sample F550-0,8-6 lower sorption capacity was observed 0,87 mmol/g, which is related to the lower amount of zeolite present in the sample. Very good regeneration properties of this sample is highly interesting feature (0,84 and 0,81 mmol/g in the second and third sorption-desorption cycle respectively). Sorption capacity only slightly decreased in the second and the third sorption-desorption cycle, what classified the sample for future research. According to no detailed data in relation to the quantity of zeolite material present in the samples synthesized out of fly ash, the description of efficiency calculation methods and the use of different methodology of the sorption experiments performed in other works aimed at SO_2 sorption analysis of the zeolites synthesized out of fly ash, it is difficult to perform comparative analysis of received values. In general it can be stated that the received in this work values are in the range specified by other authors or are higher [12-14].

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