

Synthesis of zeolites from fly ash with the use of modified two-step hydrothermal method and preliminary SO₂ sorption tests

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Abstract

Synthesis of zeolites from fly ash is an ecologically justified process aimed at the transformation of energy sector waste – fly ash into microcrystalline zeolites of broad possible application field. In this study, the synthesis of zeolites from fly ash by using a modified two-step synthesis was presented. The aim of such a planned experiment was to use the waste solutions from previous synthesis, in such a way that minimalization of negative influence of post-synthesis wastes on environment was possible. Received materials were tested for its sulfur dioxide sorption capacity, indicating its future possible application to capture SO₂ from exhaust gases.

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Keywords

Fly ash, zeolites, modification of two-step synthesis, sulfur dioxide, sorption

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Introduction

According to the European standard EN 450–1, fly ash is a fine grained, loose material, which is predominantly composed of spherical aluminosilicate glass particles, formed as a result of coal burning. It is inorganic, multicomponent, heterogeneous, and to high extend amorphous substance (Sommerville et al., 2013), captured out of flue gas stem by bag filters, cyclones, and electrostatic precipitators (Iyer et al., 2001). Chemical composition of fly ash depends on the type of coal burned as well as combustion process conditions (Ahmaruzzaman, 2010). Despite the fact that in 2014 and 2015, for the first time since 1990, decrease in the global coal production was observed, it is believed that coal, responsible for 40% of the world's electric energy supply, will still play a key role as an energy raw material in global scale (World Energy Resources, 2016). As a result, continuous production of fly ash can be expected. In 2009–2011, around 53% globally produced fly ash was used in other economic processes, while the remaining part was directed to landfills (World Energy Resources, 2016) which are nonecological and noneconomical option. Therefore, searching for alternative methods of effective utilization of fly ash is justified.

One of the uses of fly ash is its transformation into zeolite materials. Fly ashes are mainly composed of silicon and aluminum, which are the main building materials of zeolites. Currently, there are many known differentiated methods of fly ash zeolite synthesis. (Bukhari et al., 2015; Hollman et al., 1999; Park et al., 2000, 2000b; Querol et al., 1997, 2002; Shigemoto and Hayashi, 1993). Undoubtedly, the most discussed is the hydrothermal method, due to its relative simplicity and low energy consumption in relation to broad range of possible products to obtain (Mainganye et al., 2013; Querol et al., 2001; Wdowin et al., 2014).

One of the major environmental problems of hydrothermal synthesis is a waste formed as a result of the process, which is alkaline solution (Behin et al., 2016). Literature research indicates that as a result of fly ash storage on landfills, easy to rinse substances deposited during cooling on ash particles are eluted, negatively affecting the environment (Borm, 1997; Querol et al., 2002; Twardowska and Szczepanska, 2002).

It should be assumed that solutions after fly ash zeolite synthesis will consist of substances that harmfully influence the environment (trace amounts of heavy metals, high pH). The aim of this research was to determine whether it is possible to synthesize fly ash zeolites by hydrothermal method either with the use of solutions from previously conducted zeolite synthesis or with the use of solutions enriched in silicon and aluminum compounds by the use of alternative methods of alkaline treatment of fly ash (for the purpose of comparison), in order to exploit liquid post-process wastes.

According to literature, fly ash zeolites can be used as sulfur dioxide sorbents (Czuma et al., 2016; Grutzeck, 1999; Suchecki et al., 2004; Zarębska et al., 2015).

Due to SO₂ emission that limits restrictions (Directive IPPC 96/60/UE, Directive LCP 2001/80/UE, Directive IED 2010/75/UE, Commission Implementing Decision (EU) 2017/1442 of 31 July 2017), it is justified to search for alternative sorbents. Possibility of application of fly ash zeolites can provide cost effective and ecologically reasonable option,

especially in case of proving usefulness of fly ash zeolites produced with reduction of post-production liquid wastes.

Aims and research hypothesis

The aim of this study was to develop a method allowing to adopt solutions given in the previous fly ash zeolites hydrothermal synthesis reaction. It has been hypothesized that it is possible to obtain zeolite materials out of fly ash using solutions originating from the previously conducted hydrothermal synthesis. Performed research were to high extend based on two-step process of synthesis of zeolites from coal fly ash (Hollman et al., 1999). In this classic two-step method used for the production of fly ash zeolites, two process steps were used. The result of the second step is receiving zeolite materials of high purity. Given the research goals directed at the possibility of using solutions from hydrothermal synthesis method for further experiments, the modification of the two-step method was proposed. The first step in the process was to perform, with the use of unique methodology of synthesis provided by authors, the synthesis of zeolite materials. Solutions obtained in this way from previous syntheses were directed to the next cycle. It was assumed, however, that there is a need for addition of another fly ash portion. Due to the fact that the proposed methodology is preliminary research and one cycle was performed, there was no hydroxide addition.

Two different fly ashes were selected for the experiments and solutions after hydrothermal synthesis. The proposed procedure was aimed at determination of fly ash type influence on the outcome of the process.

Due to the fact that in experiments, additional portions of the ash were provided, synthesis was carried out using two different portions of the ash weight. The purpose of this experiment was to determine how increase in fly ash portion will affect the result of the synthesis. It has been hypothesized that use of a larger quantity of fly ash will have a positive impact on the synthesis of products, as greater amount of zeolite building material will dissolve into solution.

For experiments, there were used solutions from synthesis of fly ash zeolite as a result of which zeolite material was formed (R, RL – descriptions in Figure 3), as well as solution from fly ash zeolite synthesis as a result of which no zeolite was formed (RL2) as a result of too low process temperature applied. Hypothesis was formed that solution RL2 will be appropriate for following synthesis, because of its enrichment in silicon and aluminum ions during synthesis attempt. In order to confirm this assumption, for the purpose of comparison, two additional solutions were prepared utilizing ultrasound (R2) and microwave (R5) energy. As a result of the impact of those energies on fly ash samples in alkaline solutions, enhancement of dissolution of silicon and aluminum sources took place, while enriching solutions in zeolite building materials at the same time. It was assumed that this treatment will positively influence the outcome of synthesis.

Subsequently, on received materials, as well as on raw fly ash, sorption experiments were performed, aim of which was to demonstrate the potential use of these materials as SO₂ sorbents. The research was conducted in the sorption–desorption cycles on the same sample to determine the possibility of its regeneration.

Research material

For the experiments, two types of fly ashes were selected from Polish Power plants (FA1, FA2). Fly ashes used were formed as a result of hard coal burning in pulverized coal-fired

Table 1. Oxide composition of fly ashes selected for synthesis.

Component	Concentration (%)
FA1 fly ash	
Na ₂ O	2.30
MgO	1.77
Al ₂ O ₃	15.71
SiO ₂	38.45
P ₂ O ₅	0.74
SO ₃	1.04
K ₂ O	2.77
CaO	3.58
TiO ₂	1.00
MnO	0.17
Fe ₂ O ₃	10.09
ZnO	0.99
PbO	0.30
FA2 fly ash	
Na ₂ O	3.03
MgO	3.31
Al ₂ O ₃	20.29
SiO ₂	38.91
P ₂ O ₅	0.99
SO ₃	1.81
K ₂ O	2.92
CaO	7.65
TiO ₂	1.24
MnO	0.20
Fe ₂ O ₃	8.95
BaO	0.13

boilers. Chemical composition of these research materials was investigated with the use of an XRF method and with the use of a Philips spectrometer PW 1404. An X-ray tube equipped with dual Cr–Au anode with a maximum power of 3 kW as the excitation source. Results of analysis were presented in Table 1.

The mineral composition was determined via powder X-ray diffraction (XRD) method using a Philips X'pert APD diffractometer (with a PW 3020 goniometer), Cu lamp, and a graphite monochromator. The analysis was performed within the angle range of 5–50 2θ . In the material, the presence of crystalline phases such as quartz and mullite was proved. There is an indication of amorphous phase present as well, due to increase in background in 2θ range 20–30. Diffractograms of fly ashes used for the synthesis were presented in Figures 1 and 2.

For the research, three solutions from previously carried out zeolite synthesis (R, RL, RL2) and the two solutions, which were produced by the use of ultrasonic (R2) and microwave (R5) energy to dissolve the sources of silicon and aluminum in an alkaline medium, were selected. Based on the assumptions of increased amounts of silicon and aluminum ions present in solution after synthesis in which no zeolite was obtained, the authors decided to

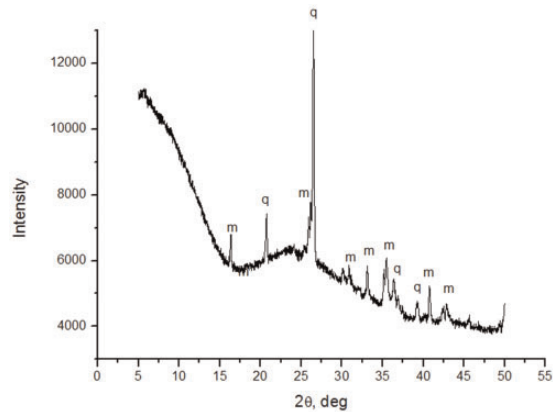


Figure 1. FA1 fly ash diffractogram (q-quartz, m-mullite).

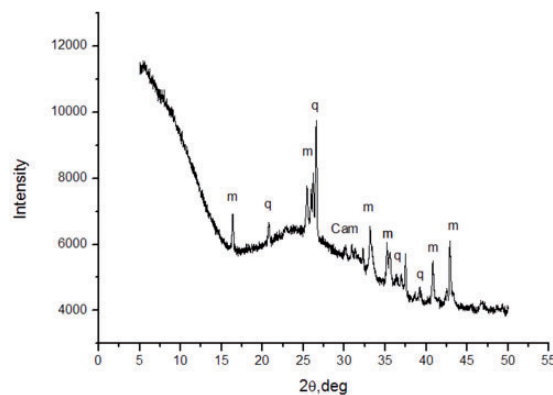


Figure 2. FA2 fly ash diffractogram (q-quartz, m-mullite).

test the effect of using other solutions that have been produced with the aim of enriching the alkaline solution in silicon and aluminum ions. To receive such solutions, ultrasonic and microwave energy was applied. Enrichment of the first solution (referred to as R2) consisted of subjecting the NaOH alkaline solution with fly ash to ultrasound energy in ultrasonic homogenizer. It was assumed that the cavitation energy in the alkaline medium will improve dissolution of silicon and aluminum ions to solution. Second solution (R5) was performed analogously using a microwave reactor, taking into account the advantages of using microwave energy such as fast and continuous material heating rates in all volume, as microwaves penetrate through the walls of the reactor. In such a way, more efficient dissolution of Si and Al sources can be assumed.

The schematic presentation of each solution preparation and its symbols was presented in Figure 3.

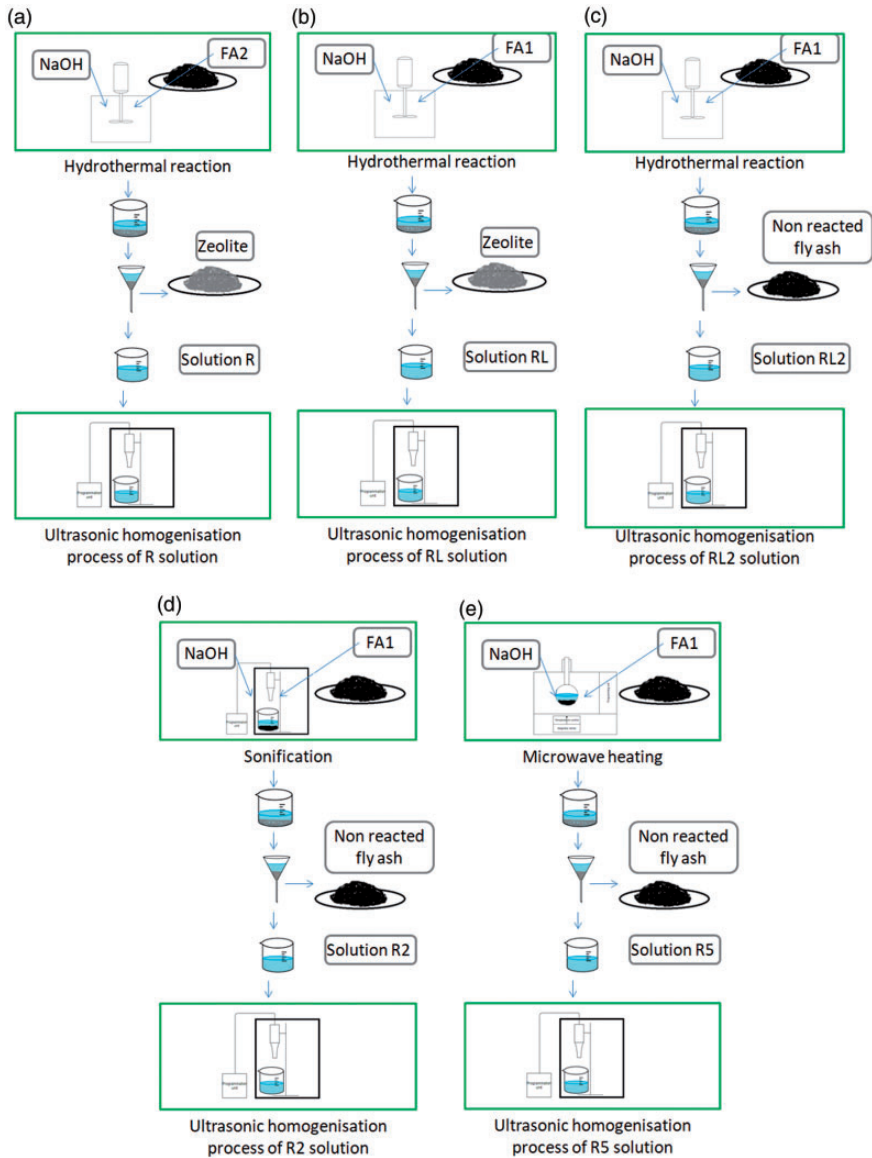


Figure 3. Symbols and schemes of solutions are used in synthesis processes preparation. (a) R solution preparation; (b) RL solution preparation; (c) RL2 solution preparation; (d) R2 solution preparation; (e) R5 solution preparation.

Experimental

Synthesis

In the research, six zeolite syntheses were performed with the use of modified two-step synthesis. Modification of method was forced by the preliminary assumptions, based on

Table 2. Symbols of synthesized samples.

Sample symbol	Fly ash used	Quantity of fly ash (g)	Solution used
A_R	FA2	1,5	R
B_R	FA2	3	R
C_RL	FA1	3	RL
D_RL2	FA1	3	RL2
E_R2	FA1	3	R2
F_R5	FA1	3	R5

which the main aim of the experiment was to use solutions produced as a result of hydrothermal synthesis and specially prepared alkaline solutions enriched in silica and alumina ions. Portions of fly ash were added in the process. It should be noted that the aim of the experiment is not to produce zeolite material of high purity, as in classic two-step synthesis, but analysis of possibility to re-use post-synthesis waste.

Ash sample of 1.5 or 3 g was weighed. The ashes were placed in pre-prepared solutions described in Table 2. As prepared samples were placed in containers and kept at a temperature close to 100°C for 2 days. The samples were then rinsed with distilled water until the pH was about 10 and dried at 105°C. Comparison of prepared samples symbols, quantity, and type of ash used and solutions used were provided in Table 2.

Sorption

Received materials were examined for its SO₂ sorption capacity. For the purpose of comparison, the sorption tests were performed on the raw fly ash to check whether fly ash itself shows sorption properties. Experiments were performed with the use of Sartorius sorption microbalance. Research was performed in room temperature.

Results

Synthesis process results

Received powders were analyzed with the use of XRD method for the purpose of verification of zeolite phases present in samples. In each synthesized samples, zeolite materials were received. Zeolite-type Na-P1 and sodalite were found. Additionally, still increase in background can be noted, which indicate that not all amorphous phase underwent transformation. In Figures 4 to 9, diffractograms were presented for all synthesis products.

Received zeolite phased present in each sample was compared in Table 3.

As additional element, calculations of crystallite size of zeolite P1 for samples B_R and E_R2 were performed. In order to estimate the crystallite size, XRD data (Scherrer method) were used, taking into account the most intensive reflections. Based on data, crystallite sizes were calculated. For sample B_R, the size was 30.2 nm whereas for the sample E_R2, it was 35.5 nm.

In order to confirm the hypothesis of the advantageous effect of the solutions used for the synthesis enrichment, quantification of the presence of aluminum and silicon ions in the solutions used for the synthesis was carried out.

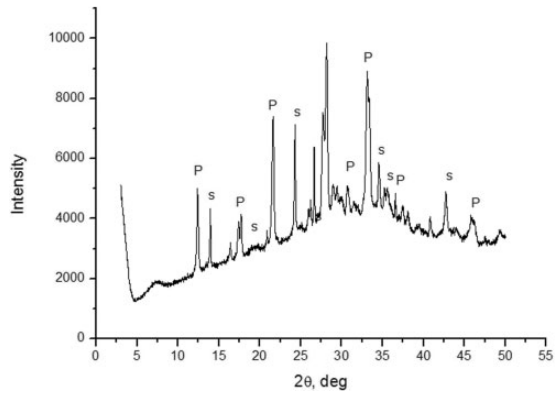


Figure 4. Diffractogram of sample A_R (P-zeolite Na-PI, s-sodalite).

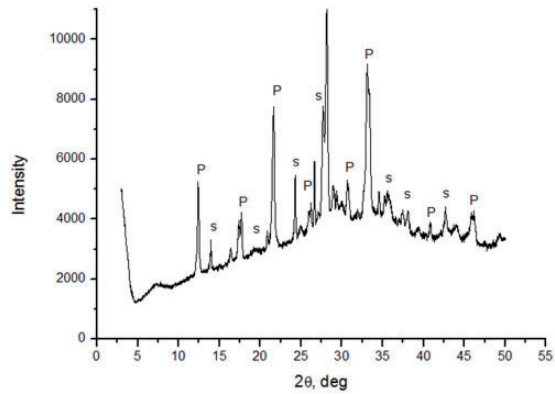


Figure 5. Diffractogram of sample B_R (P-zeolite Na-PI, s-sodalite).

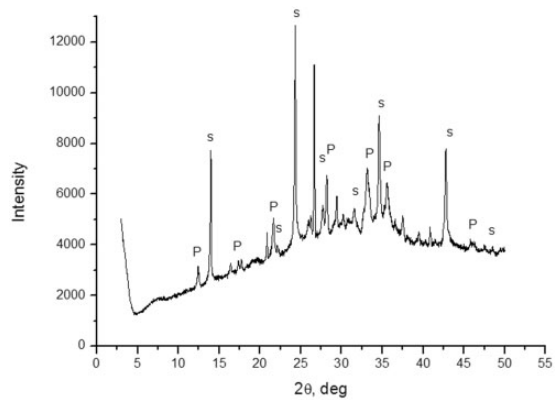


Figure 6. Diffractogram of sample C_RL (P-zeolite Na-PI, s-sodalite).

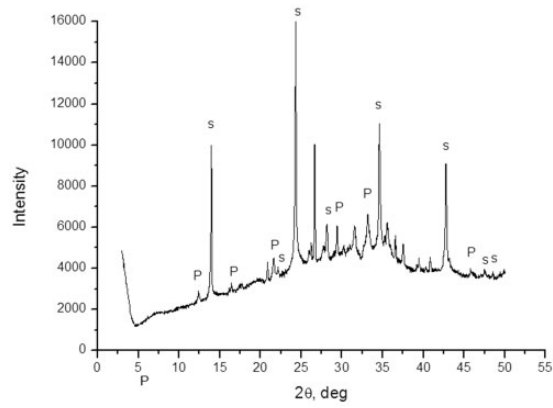


Figure 7. Diffractogram of sample D_RL2 (P-zeolite Na-PI, s-sodalite).

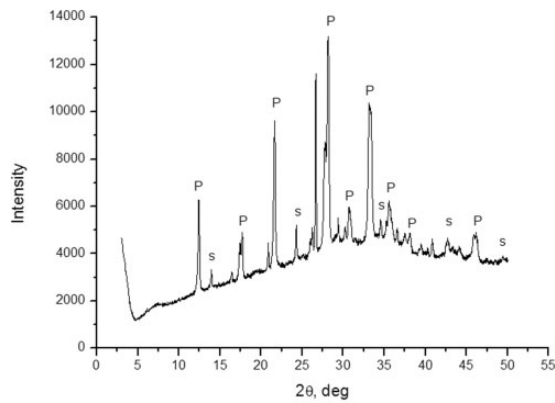


Figure 8. Diffractogram of sample E_R2 (P-zeolite Na-PI, s-sodalite).

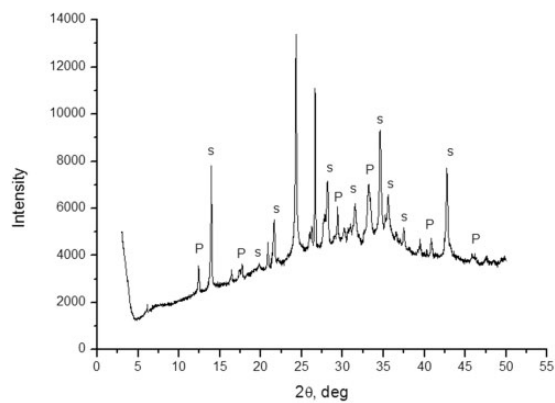


Figure 9. Diffractogram of sample F_R5 (P-zeolite Na-PI, s-sodalite).

Table 3. Comparison of zeolite products of performed synthesis processes.

Sample symbol	Zeolite present in sample
A_R	Na-P1, sodalite
B_R	Na-P1, sodalite
C_RL	Na-P1, sodalite
D_RL2	Na-P1, sodalite
E_R2	Na-P1, sodalite
F_R5	Na-P1, sodalite

Table 4. Comparison of results of qualitative analysis of silica and alumina content in solutions used for synthesis.

Solution symbol	Si (mg/dm ³)	Al (mg/dm ³)	Si/Al
R	562.3	73.34	7.67
RL	126.5	162.8	0.78
RL2	335.0	104.5	3.21
R2	136.3	100.6	1.35
R5	266.3	193.8	1.37

Comparison of the results of quantitative analysis for silica and alumina ions was presented in Table 4. As an additional parameter, Si/Al ratio was calculated.

Sorption experiments results

For the sorption experiments, there were selected samples with symbols B_R and E_R2 as well as raw fly ash samples FA1 and FA2. The choice of sample B_R was directed by the will to investigate sorption capacity of sample received as a result of use of solution from previous hydrothermal synthesis. Sample E_R2 was selected due to high, estimated based on XRD data yield of synthesis of Na-P1 zeolite phase.

In Figures 10 to 13, obtained SO₂ isotherms are presented. Experiments for samples B_R and E_R2 were performed in sorption–desorption cycles, directed at determination of regeneration properties of material. Only sorption isotherms were presented. Experiment was performed in three cycles on each sample. Pressure swing adsorption was used. In case of sorption of fly ash, only one cycle due to negligible sorption capacity was performed.

Data analysis

Zeolite materials were obtained in all performed syntheses. Based on the analysis of XRD data by comparing areas under the most intense reflections characteristic for a given zeolite phase (Mainganye et al., 2013), the most favorable synthesis conditions were estimated. Estimation of synthesis efficiencies was performed separately for Na-P1 zeolite and for sodalite. According to the decreasing amount of Na-P1 zeolite, material samples were presented in series: E_R2 > B_R > A_R > C_RL > F_R5 > D_RL2. For the sodalite, a series of D_RL2 > C_RL > F_R5 > E_R2 > A_R > B_L was obtained.

Such a comparison enables to draw conclusions about the effect of both the solution used for the synthesis, the amount of ash added to the synthesis, and partly the effect of the type

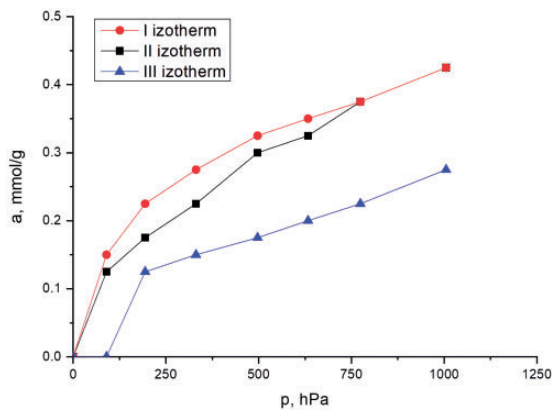


Figure 10. SO₂ isotherms on sample B_R.

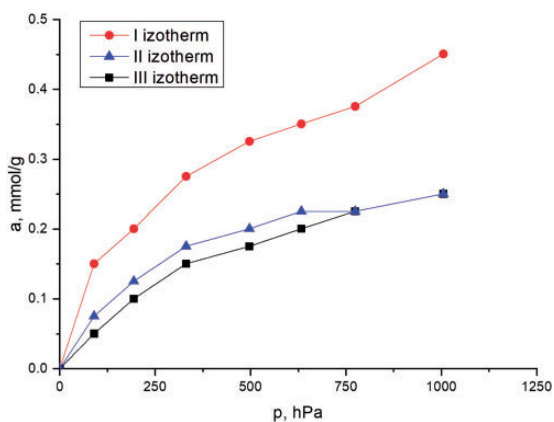


Figure 11. SO₂ isotherms on sample E_R2.

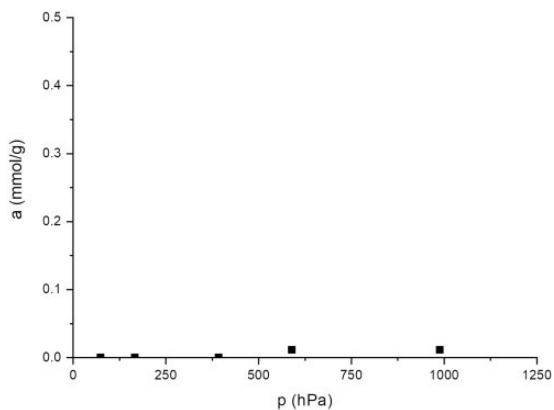


Figure 12. SO₂ isotherms on raw FAI sample.

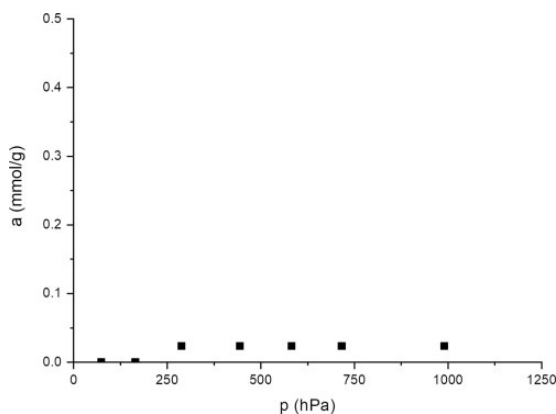


Figure 13. SO₂ isotherms on raw FA2 sample.

of ash used on the result of the synthesis. The obtained results confirm the initial assumption that it is possible to reuse solutions after hydrothermal zeolite synthesis for further cycles of synthesis with addition of fly ash portions.

Analysis of the influence of quantity of fly ash added

For samples B_R and A_R, the aim was to investigate how the amount of fly ash added will affect the synthesis result. For this purpose in those performed synthesis, the only variable parameter was the quantity of fly ash added. Estimated results indicate that higher amount of fly ash added had positive influence on the synthesis of Na-P1 zeolite, while its smaller amount for favorable for sodalite crystallization. The reason for this can be associated with the silicon and aluminum ration in synthesis solution in amounts more adequate for synthesis of zeolite NaP1. Due to literature, the Si/Al ratio of zeolite NaP1 is in the range 0.8–2.0 (Azizi et al., 2013; Bukalaket al., 2009). In solution denoted as R, the Si/Al ratio was the highest, and apparently, the addition of higher amount of fly ash was more favorable for zeolite NaP1 synthesis allowing for appropriate crystallization conditions.

Analysis of fly ash type used

Analyzing samples with symbols B_R and C_RL, the influence of type of fly ash used on the outcome of synthesis can be deduced. In the research, two different types of fly ash were used – FA1 and FA2, for which solutions after hydrothermal synthesis were added, coming from previous synthesis performed with the use of FA1 and FA2 fly ash accordingly. As a result of primary synthesis, in both cases, zeolites were received. It was proved that in case of zeolite Na-P1, more advantageous results were received for FA2 fly ash, once FA1 fly ash presented better conditions for crystallization of sodalite. Si/Al ratios in FA1 and FA2 fly ashes were accordingly FA1-2.5 and FA2-1.9. Literature data indicate that zeolites Na-P1 crystallize as a result of synthesis performed with the use of fly ashes of Si/Al ratio 0.8–2.0 (Bukalaket al., 2009). It should be noted however that authors do not consider this parameter to be crucial as the order of dissolution of silica and alumina sources differs. In the first place, the dissolution of aluminosilicate glass takes place, followed by quartz and mullite (Querol et al., 2001). Value of Si/Al ratio of fly ash itself may be inaccurate due to possibility

of the presence of building materials for zeolite in differentiated forms. This assumption may be proven by relatively high derivations of Si/Al ratio in case of solutions produced from the same fly ashes. Visual estimation of amorphous phase present in samples (XRD diffraction background increase) does not give clear premises for influence of aluminosilicate glass content in fly ashes on the outcome of synthesis. It should be stated that the influence of fly ash type on the synthesis product will be more complicated and will be a result of influence of each components on synthesis, what is proved by literature data (Bukhari et al., 2015; Czuma et al., 2016; Franus and Wdowin, 2011; Mainganye et al., 2013).

Influence of use of solutions after hydrothermal synthesis

The aim of this part of experiment was to investigate whether it is possible to receive zeolites out of fly ash with the use of solutions obtained from previously performed synthesis processes. For samples D_RL2, C_RL, A_R, and B_R, for the synthesis, there were chosen solutions from previous hydrothermal synthesis. Based on the fact that in all synthesized samples, zeolite was present, and the possibility of secondary use of postsynthesis solutions with appropriate assumptions can be proved.

Additional parameter which was investigated was estimation whether the use of solution out of which in first cycle zeolite crystallized (sample C_RL) and the one, as a result of which no zeolite was formed (sample D_RL2), will have decisive influence on received material. Analyzing received data, it was found that in case of Na_P1 zeolite, RL2 solution proved to have more favorable influence on the synthesis outcome. This result was expected taking assumption that during synthesis, dissolution of silica and alumina sources takes place, while zeolite formation is a result of secondary crystallization of zeolite building components (Franus and Wdowin, 2011). In correlation to this, assumption was made that solution after synthesis of zeolite, which use did not lead to formation of zeolites (RL2), was enriched to higher extend in silica and alumina ions, as it was not 'used' for zeolite structure building. What was interesting was the fact that the same solution in connection to sample D_RL2 provided the best conditions for sodalite synthesis. This result is most probably associated with the presence of solution appropriate to the ratio of ions for sodalite crystallization.

Influence of use of solutions enriched in silica and alumina

The use of solution produced with the use of ultrasound energy allowed to receive the highest estimated efficiency of Na-P1 zeolite. This allowed to confirm the hypothesis that unused silica and alumina ions will have a positive influence on the synthesis of zeolite material. The use of solution received in microwave reactor resulted in much worse results; however, authors assume that the process of dissolution of silica and alumina sources could not be fulfilled in relation to technical difficulties of reactor working periods.

Sorption experiments analysis

As a result of performed research, it was found that received zeolite materials can be used as a sulfur dioxide sorbents.

Analyzing sorption data, authors based on assumption that the presence of Na-P1 zeolite will predominantly be responsible for the sorption capacity, while in case of sodalite,

relatively small channel dimensions would limit its share in the sorption process, which could be considered negligible.

Sorption capacity of sample E_R2 represented higher value than of B_R sample in first sorption cycle. This expected outcome is associated with the amount of zeolite material, as according to performed estimations, sample E_R2 contains higher amount of Na-P1 zeolite. In the following cycle sorption capacity value decreased; however, during III isotherm, examination remained at practically the same level. Similar observation was noticed by the authors in previous works (Czuma et al., 2016; Zarebska et al., 2015).

Sorption capacity of sample B_R selected for the sorption experiment due to use for the synthesis R solution from previously performed hydrothermal synthesis indicated slightly lower values of sorption capacity in relation to SO₂ during I sorption cycle. The analysis of II adsorption isotherm was interesting as the value was practically on the same level. Authors observed similar isotherm in one case in different research (Czuma et al., 2016). In case of III isotherm, the decrease in sorption capacity was observed. It should be noted however that the value was higher than for sample E_R2 in case of II and III isotherm.

Values of sorption capacity in I sorption cycle are in good relation to estimated amount of P1 zeolite in samples. The values in following cycles are worth noticing. Authors made attempt to combine differentiated results in following sorption cycles with the zeolite P1 crystalline size. It was found that sample B_R was characterized by smaller crystals. Authors found it highly possible that this parameter was responsible for better regeneration properties of sample. Logically, SO₂ particles would be desorbed more easily in case of smaller crystals.

In order to prove that synthesized zeolites were responsible for sorption capacity of a sample the raw, unprocessed fly ash samples were examined in connection to its sorption properties. The sorption test results indicate that the raw fly ash represents negligible sorption; therefore, sorption capacity of samples B_R and E_R2 was predominantly associated with the presence of zeolite phase.

Conclusions

In case of all performed experiments, the result of synthesis was the crystallization of zeolite phases. In each of performed synthesis, the presence of zeolite P1 and sodalite was confirmed.

It was proved that the estimated efficiency of the process is different; however, it was not possible to find simple analogy of synthesis efficiency with the composition of solutions taken into synthesis. In research, it was confirmed that the addition of higher amount of fly ash for synthesis was more advantageous in case of final efficiency in case of P1 zeolite according to the presence of higher amount of alumina and silica sources. It was also found that the use of different kind of fly ash does have influence on the outcome.

It is possible to synthesize zeolite out of fly ash with the use of solutions constituted as a waste from previous synthesis. It is significant that the solutions formed in synthesis, as a result of which zeolite crystallized, are suitable for further synthesis as this is the first indication confirming the possibility of minimalization of ecological threats associated with production of zeolites out of fly ash. Postproduction waste of hydrothermal synthesis of zeolites is alkaline solution enriched in silica and alumina ions and other components, for example, heavy metals from fly ashes. Due to this fact, research aimed at possibility of limitation, and its influence of natural environment is of high value.

In the performed experiments, there were additionally presented alternative methods of enrichment of solutions in silica and alumina.

Presented sorption experiments allowed to prove that received form fly ash zeolite materials may be used as sulfur dioxide sorbents. It was confirmed that regeneration of investigated material is possible.

Declaration of Conflicting Interests


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