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著者	Walek Tomasz, Saito Fumio, Zhang Qiwu, Kano Junya
journal or publication title	東北大学多元物質科学研究所素材工学研究彙報
volume	63
number	1/2
page range	86-95
year	2008-03-01
URL	http://hdl.handle.net/10097/40582

Zeolite Synthesis from Fly Ash: Current Processes and their Benefits and Drawbacks

By Tomasz Walek*1*2, Fumio Saito*1, Qiwu Zhang*1 and Junya Kano*1

1 Introduction

Power and heat generation based upon coal combustion results in formation of solid, liquid and gas wastes which require additional treatment in separated processes to prevent their direct emission to natural environment. Fly ash is one of the coal combustion solid wastes which deposits cause an environmental problem around the world. In Japan the yearly production of fly ash reaches 8 million tonnes and this value is expected to gradually increase [1]. The highest amount of fly ash - about 50 wt.% - is utilized in Japan in cement and concrete industry but the requirements concerning the quality of fly ash can gradually limit this way of utilization [2]. About 30 wt.% of fly ash produced in Japan is deposited in the sea and 10 wt.% is landfill disposed [1]. It shows that development of new methods of fly ash utilization is therefore of primary importance.

Fly ash composition depends on coal composition and combustion parameters. A range of chemical composition of fly ash is presented in Table 1. The significant amount of Si and Al in amorphous and crystalline phases makes possible to apply fly ash as a source material for synthesis of zeolites.

Table 1 Chemical composition of fly ash

Component	Content, wt.%
SiO_2	21.99 - 71.00
Al_2O_3	10.16 - 42.60
Fe_2O_3	0.98 - 20.21
CaO	0.30 - 26.70
TiO_2	0.49 - 2.95
MgO	0.18 - 2.90
SO_3	0.01 - 2.34
Na_2O	0.02 - 5.93
MnO	0.02 - 0.16
K_2O	0.46 - 4.42
Loss of ignition	1.00 - 15.10

In general, the synthesis process can be summarized as follows. When fly ash is mixed with a base solution at an elevated temperature, Si and Al compounds react with OH- anions present in the slurry and dissolution process begins. Si and Al are gradually released from fly ash and form SiO_4^{4-} and AlO_4^{5-} tetrahedrons. The tetrahedrons constitute basic building units of zeolite crystals. The electric charge of the Al tetrahedrons is negative and in presence of cations (usually Na^+) the Si and Al tetrahedrons start connecting around the cations. The nuclei formed in this way crystallize on the surface of partially dissolved fly ash particles. Such the overlapping of dissolution and crystallization stages causes that the product contains both zeolite crystals and unreacted starting material and not all suitable material is reacted. The number and sequence of the Si and Al tetrahedrons connected around the cations can differ for various types of zeolites with specific types of channels. Both the composition of starting material and the synthesis parameters can influence the crystallization process. The channel-opening diameter can vary from 2.3 to 7.5 Å what determines a potential application of zeolitets.

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*1 Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 980-8577 Sendai, Japan
*2 Department of Environmental and Safety Management, Silesian University of Technology, 44-100 Zabrze, Poland

The product is usually identified by means of X-ray diffractometry and its morphology is analyzed with SEM. The yield of fly ash transformation is semi-quantitatively determined by comparison of a specific parameter of the product with a commercial grade sample of the same type of zeolite. Most frequently cation exchange capacity is used for the comparison and it is usually determined by the ammonium acetate method [3].

Many authors have undertaken various attempts to increase the yield of fly ash zeolitization and a number of different methods of synthesis was developed. Nevertheless, none of the methods has found any application in a large scale. In this paper relations between starting materials, process parameters and type and quality of the product obtained were analyzed to outline benefits and drawbacks of different synthesis methods from the point of view of potential industrial application.

2 Synthesis methods

All known methods of fly ash zeolite synthesis are based upon hydrothermal or molten salt treatment. The hydrothermal treatment procedure has a number of varieties. The differences are usually related to additional pretreatment of starting material, changes of reactional parameters, or separation of the process for few stages conducted at different conditions. Anyhow, the mechanism of interaction of Si and Al compounds with OH- and crystallization in presence of cations is the same for all the methods.

2.1 Classical hydrothermal treatment

Classical hydrothermal alkali treatment of fly ash was investigated by many authors [4–25]. In this process fly ash is mixed with a base solution and heated for a certain time with or without stirring. A process of aging at room temperature for 6-24 h can be additionally conducted before heating. A seeding material or a structure directing agent can also be added to the slurry. Ranges in which the individual reaction parameters change are given in Table 2.

Parameters applied in the process remain unchanged during the reaction. Most frequently NaOH and rarely KOH is used as the base. Instead of using a hydroxide as a mineralizing agent it is also possible to apply NaF, but F- anion is very corrosive to a synthesis equipment [26]. In the next step the solid residue is filtered from the slurry, washed and dried. Depending on the reaction temperature applied the synthesis can be conducted in an open system at atmospheric pressure or in a close system at autogenic pressure. To prevent water evaporation in the open systems a condensation and reflux equipment is used.

The product obtained in this method consists of both zeolite crystals and unreacted fly ash residue. A typical image of zeolite crystals formed on a surface of partially reacted fly ash particle

Table 2 Process parameters of classical hydrothermal treatment of fly ash

Process parameter	Value
Temperature	20-250°C
Reaction time	2h-7days(2-50 months for 20-30°C)
Base solution concentration	0.1-8 M
Fly ash concentration	25-3000g/dm^3

is shown in Fig.1. In this case fly ash was treated at 80°C for 6 days in 1 M NaOH solution [27].

The product contains different single or multiple zeolitic phases and usually it is a combination of zeolites Na-X, Na-P, Na-P1, hydroxy-sodalite, Na-Y, analcime, linde F and phillipsite. The cation exchange capacity reaches in this method 30-260 meq/100 g. The yield of fly ash transformation into zeolite is reported as 10-75 wt.%.

The Si/Al molar ratio of fly ash differs from 1.09-4.80 but it does not strictly determine the type of the zeolite obtained. From the same starting material different types of zeolites can be obtained in different conditions and as well similar products can crystallize from different starting materials. The most important parameters of the synthesis process are the reaction temperature and NaOH concentration, but all the parameters can influence the resulting product in a certain degree and no general relations between the parameters and type and quality of the product obtained are determined.

Fig.1 SEM image of a typical product of the classical alkali hydrothermal treatment of fly ash.

2.2 Microwave assisted hydrothermal treatment

The microwave assisted method introduces a modification of the classical hydrothermal treatment by substituting microwave heating of the reactional slurry for standard heating [28,29]. The process parameters are presented in Table 3. NaOH and KOH are used as bases and the slurry is stirred or remains still.

The reaction time can be significantly shortened in this method, but if the microwave heating is applied during all the synthesis time, crystallization yield is reduced. When microwave heating is applied in an early stage of the synthesis only and then conventional heating is used, the crystallization rate can be effectively improved.

Similarly to the classical hydrothermal treatment the product obtained consists of both zeolite crystals and unreacted fly ash residue. The type of the zeolitic phase depends on the starting material and reactional parameters. In processes with NaOH solution NaP1 zeolite and hydroxy-sodalite are obtained. With use of KOH linde F and kalsilite are formed. The cation exchange capacity reaches 70-100 meq/100g. For reactions where microwave heating was used in the first

Table 3 Process parameters of microwave assisted hydrothermal treatment of fly ash

Process parameter	Value
Temperature	100-225°C
Reaction time	10min-9h
Base solution concentration	1-5 M
Fly ash concentration	40-190g/dm^3

stage of the synthesis and then conventional heating was applied, phases of NaP1 zeolite dominated. The cation exchange capacity in this case increased to 200meq/100g, what indicates 40wt.% transformation of fly ash.

2.3 Hydrothermal treatment with Si/Al ratio modification

In the classical hydrothermal treatment of fly ash not all suitable Si and Al content is utilized. Aluminum is usually present in deficiency and a certain amount of silicon remains unused in the post-reactional slurry. Hence the idea of modification of Si/Al molar ratio of the starting material prior to the synthesis [25, 30–32]. Such the modification allows to utilize most of the suitable material dissolved from fly ash. To adjust the Si/Al ratio Al_2O_3 aerosil powder, $NaAlO_2$ or $Al(OH)_3$ is added as Al source and SiO_2 aerosil powder, Na_2SiO_4 solution or rice husk ash (containing >85 wt.% of Si) as Si source. The additional Al or Si sources are added to fly ash before or during the reaction. The process parameters are presented in Table 4. NaOH solution is used and the slurry is stirred or remains without stirring.

Table 4 Process parameters of hydrothermal treatment of fly ash with Si/Al ratio modification

Process parameter	Value
Temperature	100-210°C
Reaction time	4-48h
Base solution concentration	0.5-5 M
Fly ash concentration	60-125g/dm^3

This process allows for more selective crystallization of a specific zeolitic phases. The product contains single phase of zeolite Na-P1 and Y, or a combination of Na-P1 and hydroxy-sodalite. In the process with use of tetrapropyl ammonium bromide as a structure directing agent zeolite ZSM-5 was obtained [33]. Without use of TPABr zeolite Na-P1 was synthesized in the same conditions. The cation exchange capacity reaches 300 meq/100 g and the yield of fly ash transformation is reported as 59-72 wt.%. Though, the method with Si/Al ratio modification require use of the additional Si or Al source in amount of 10-40% of the initial weight of fly ash.

2.4 Thermal fusion prior to hydrothermal treatment

Hydrothermal treatment of fly ash can be modified by application of thermal fusion of fly ash and NaOH prior to the synthesis [10,19,34–38]. In this process fly ash is mixed with NaOH pellets and grinded to obtain a homogeneous mixture. The mixture is heated in a nickel or stainless steel crucible for a certain time. The resulted fused mass is grinded, mixed with water and stirred. Eventual additions for Si/Al ratio modification or zeolite seeds can be introduced at this time. Additionally, an aging process (room temperature, usually 6-24h) can be applied after fusion. The slurry is next subjected to the hydrothermal treatment with or without stirring. The process parameters are presented in Table 5.

The product consists of both zeolite crystals and unreacted fly ash. Single phases of zeolites A, NaP1, X or hydroxy-sodalite are obtained. The cation exchange capacity can reach 60-250 meq/100g and 30-60 wt.% crystallization is reported.

Table 5 Parameters of the process with thermal fusion prior to the hydrothermal treatment of fly ash

Process parameter	Value
Fusion temperature	550-650°C
Fusion time	1-2h
Hydrothermal treatment temperature	40-105°C
Hydrothermal treatment time	2-24h(3-20 days at 60°C)
Base solution concentration	2-3.5 M
Fly ash concentration	100-660g/dm^3

2.5 Two-stage hydrothermal synthesis with separation of dissolution and crystallization

This method allows to obtain pure crystals of zeolites from fly ash as distinct from the typical zeolite-like material [39–43]. The classical hydrothermal process is interrupted after a certain time and undissolved fly ash is filtered from the solution. In this way the solution contains a certain amount of dissolved Si and Al and no residual fly ash. The Si/Al ratio can be modified in this moment by introduction of additional Si or Al sources. The solution is next subjected to the hydrothermal process during which the crystallization from clear solution takes place. The process parameters are presented in Table 6. NaOH solution is used in the process and the slurry is stirred or remains without stirring during the dissolution and crystallization stages.

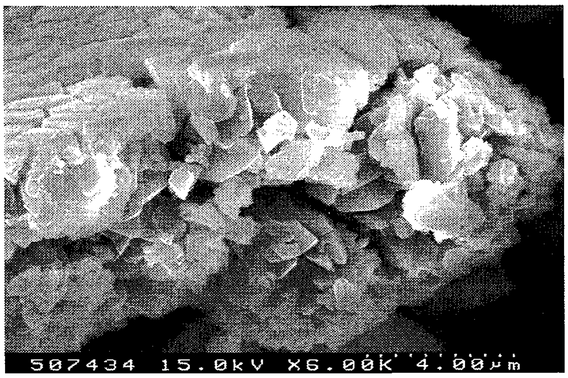

Fig.2 SEM image of pure crystals of single-phase NaP1 zeolite obtained from fly ash in a two-stage process with separated dissolution and crystallization.

In this method two separated types of products are obtained - a solid residue of undissolved fly ash from the first stage, and pure crystals of zeolites from the second stage of synthesis. The crystals are identified as single phases of zeolite A, Na-X, Na-P1 or Na-Y. Figure 2 shows pure crystals of Na-P1 zeolite obtained from fly ash treated at 104°C for 4 h during the first stage and 80°C for 96 h in the second stage [44].

Table 6 Parameters of the process with separation of the dissolution and crystallization stages

Process parameter	Value
First stage temperature	85-105°C
First stage reaction time	2-72h
Second stage temperature	80-95°C
Second stage reaction time	1.5-72h
Base solution concentration	2 M
Fly ash concentration	100-1200g/dm^3

The cation exchange capacity of the products is 360-578 meq/100g what is similar to commercial samples of respective types of zeolites. The efficiency of the process in the meaning of comparison of the weight of the crystals obtained with the weight of the starting material is 5-8 % only.

2.6 Dry molten-salt treatment

In this method the synthesis is conducted under molten conditions without addition of water [45,46]. Fly ash, base and salt is mixed and grinded. NaOH and NH_4F are applied as bases and $NaNO_3$, KNO_3 and NH_4NO_3 as salts. The resulting mixture is heated. The process parameters are presented in Table 7. After the treatment the material is grinded prior to analyses.

Table 7 Process parameters of dry molten-salt treatment of fly ash

Process parameter	Value
Temperature	350°C
Reaction time	3h-3 days

Partially converted fly ash with crystalline phases of hydroxy-sodalite and cancrinite is obtained. The CEC value of the product is 84-160 meq/100g and the yield of transformation reaches ~30 wt.%.

3 Benefits and drawbacks

The main benefit and sole purpose of fly ash zeolite synthesis is transformation of a waste into a useful material which could be applied e.g. for gas adsorption, heavy metal ions removal or soil treatment. The hydrothermal synthesis process is relatively simple and does not require any special equipment. Anyhow, the character and quality of the product obtained still discriminates its application and hence zeolite-like material has not found any large scale application.

Raw fly ash is usually applied in the process without any pre-treatment. Unburned coal or Fe_2O_3 does not influence the reaction, but it presents an undesired ballast material which is also treated in the process and remains in the product. Bulk fly ash also contains a certain amount of impurities originating from a boiler of flue gas ducts. The impurities are usually $>200\mu m$ in diameter [27]. For reactions conducted in the laboratory scale the amount of the ballast is marginal, but in a large scale applications it means a significant loss of energy what definitely decreases profitability of the process. Separation of such the ballast should be performed prior to the synthesis.

The synthesis procedures do not allow for complete utilization of the waste material. In processes described in Sec. 2.1-2.4 and 2.6 the product consists of both crystalline phases of zeolites and unreacted fly ash residue. The coexistence of zeolite crystals and unreacted fly ash cannot be avoided because of the overlapping of the dissolution and crystallization stages. The only method where pure zeolite crystals are obtained is the process with separation of the dissolution and crystallization stages (Sec. 2.5). However, in this method two products are obtained: pure zeolite crystals and undissolved fly ash residue. It significantly decreases a total efficiency of the process. Both the yield of fly ash transformation and the number of subsequent operations required in this process make any industrial application difficult, even though reuse of undissolved fly ash and post-reactional slurry is possible.

Most of the synthesis methods generate an additional liquid waste in the form of post-reactional base slurry which contains some unreacted elements dissolved from fly ash. It means that a next waste material, which also requires a certain treatment, is produced. The only process where water is not used is the dry molten-salt method (Sec. 2.6), but in this case high temperatures applied cause formation of zeolites with small channel-opening diameter what reduces application of the product. Only zeolites with bigger channel-opening diameter (Na-X, Na-Y, Na-P1, Na-A, phillipsite) can be suitable for industrial applications. The problem of formation of zeolites with small channel-opening diameters can also exist in hydrothermal methods.

In the current methods the relations between starting material properties, process parameters and type and quality of the product obtained are not clearly determined. The yield of fly ash transformation is determined by semi-quantitative methods and its average value for classical hydrothermal treatment is ~35 wt.%. Higher average rate (~65 wt.%) is reported for reactions with Si/Al ratio modification, but in this case usually 10-40 wt.% of additional Si or Al source is introduced. The average yield of transformation for dry molten salt processes is ~40 wt.%, but in this case the product is a lump of solid material which requires an additional grinding, what makes it difficult for any large scale usage. Similar difficulties are observed in processes with thermal fusion applied prior to hydrothermal treatment.

4 Concluding remarks

High Si and Al contents in fly ash make possible to apply it as a source material for synthesis of zeolites. A number of methods of fly ash zeolite synthesis was developed and various modifications of the process were investigated to improve the type of crystalline phases or final yield of transformation. Single or multiple phases of different types of zeolites with relatively high CEC values can be obtained. Still, it is necessary to remember that fly ash is a waste material which should be utilized in the most effective and environmental friendly way. The most effective utilization means in this case a complete transformation of the suitable material into a new material that could be favorably applied in another processes. None of the current methods of fly ash zeolite synthesis bears record of such the effective utilization.

The main disadvantage of fly ash zeolite synthesis is overlapping of fly ash dissolution and zeolite crystallization stages. It leads to formation of zeolite crystals on the surface of partially reacted fly ash particles and thus limits further reaction. This disadvantage is eliminated only in the process with separation of fly ash dissolution and zeolite crystallization.

The most promising directions in development of fly ash zeolite synthesis methods are: (i) improvement of the classical hydrothermal treatment to obtain a high crystallinity zeolite-like material (~80 wt.%) with single-phase zeolite of a desired type, (ii) improvement of the process with separation of the dissolution and crystallization stages to completely reuse fly ash undissolved in the first stage of reaction.

Conversion of fly ash into a high crystallinity zeolite-like material or high grade pure zeolite crystals is possible but still not clearly determined. An economical and industrially applicable method of fly ash zeolite synthesis can be a remedy for environmental issues concerning fly ash.

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