II. ENVIRONMENTAL BIOTECHNOLOGY

NOVEL TECHNICAL AND ECONOMICAL SUPERIOR APPROACH FOR SYNTHESIS OF ZEOLITES FROM COAL FLY ASH

Denitza Zgureva, Silviya Boycheva

Abstract. The present paper is aimed on the preparation of zeolites from lignite coal fly ash using a superior synthesis approach that combines the advantages of different established technological schemes. The novel method is directed to improvement of the energy efficiency and the raw material economy, and at the same time resulting in better quality material. Fly ash zeolites of Na-X type were synthesized applying fusion stage of fly ash/NaOH mixtures followed by atmospheric self-crystallization. The obtained zeolite structure was investigated by X-ray diffraction for different periods of crystallization of the reaction mixtures under atmospheric conditions. Comparative studies of three different methods for synthesis of Na-X were performed taking into account the specific energy and the raw material consumption. It was considered that adsorbents of zeolite X type can be obtained by different ways of alkaline conversion of coal fly ash, and that is why the most important issues for the scale production of these materials are the economical aspects of the synthesis.

Keywords: synthesis of zeolites; adsorption; carbon emissions

INTRODUCTION

One of the most investigated issues of the modern world is the environment protection provoked by the continuously increasing consumption of technological resources. The global unsolved ecological problem is the enormous production of greenhouse gases, in the largest quantities from which carbon dioxide (CO₂) is emitted into the atmosphere.

The thermal power plants are the major sources of CO₂ (approx. 40% of total generated CO₂ amount). In the last years, many technologies for carbon capture and storage are intensively studied directed to fuel combustion systems [1, 2]. Three main technological approaches have been outlined, such as pre-combustion capture, modified combustion and post-combustion capture. The post-combustion technology is based on the absorption of CO₂ from organic liquids (mostly amines) [3]. It is the most technical and economical compatible approach to the existing combustion plants, but is hindered by the high consumption of energy for desorption process, as well as the toxicity of these substances. Its negative aspects can be overcome by the development of appropriate solid adsorbents [4].

Zeolites are the most valuable natural and synthetic porous solids suitable for gas adsorption [5], which can be easily obtained from aluminosilicate by-products, such as coal fly ash [6,7]. The highest adsorption ability toward the polar CO₂ molecules has been established for zeolite types A and X due to their large pore size [8,9].

In our previous studies, the synthesis of zeolites type A and X by alkaline conversion of fly ash (FA) from incineration of Bulgarian lignite coals has been studied [10,11]. Sufficient results have been achieved in two different ways of treatment of fly ash mixed with sodium hydroxide as an alkaline activator: (1) hydrothermal activation with a prior stage of calcination at 550 °C; (2) atmospheric self-crystallization. The first method of synthesis gains an advantage with rapidly getting zeolite X for 24 hours, but has a major drawback because of the large energy consumption.

The second approach does not require any additional energy but a long period of 12 months is necessary to obtain zeolite X.

In this study, an alternative method for a hybrid synthesis is considered by the implementation of the scheme: fusion stage of fly ash/NaOH mixtures followed by atmospheric self-crystallization. This superior manner combines the advantages of the above approaches, while overcomes their main disadvantages.

MATERIALS AND METHODS

FA generated by combustion of lignite coals in the biggest power plant in Bulgaria ‘‘TPP Maritsa East 2’’ has been previously studied with respect to its morphology, chemistry and structure. The composition of FA is reported in Table 1. The ratio of crystalline vs. amorphous phase has been found of 57/43.
Table 1. Chemical composition of raw fly ash

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>MnO</th>
<th>ZnO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>weight %</td>
<td>52.66</td>
<td>23.37</td>
<td>8.72</td>
<td>5.75</td>
<td>2.75</td>
<td>2.40</td>
<td>0.06</td>
<td>0.04</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

In our published investigations, FA zeolitization by a double stage fusion-hydrothermal syntheses and atmospheric crystallization has been thoroughly studied.

In this study, mixtures of FA and NaOH were prepared in two different ratios of 1/1 and 1.6/1.0 and were subjected in a double-stage treatment. The first stage of the synthesis was performed at temperature of 550 °C for 1 h in a muffle furnace. Thereafter, the sintered alloys were crushed, mixed with distilled water in a ratio of FA/H$_2$O$_{dist}$=1/10, and were filled into closed polypropylene containers. The second stage is so called “atmospheric self-crystallization”, which was realised at room temperature (approx. 20 °C). Small parts of the suspensions were taken off for analyses after 30, 60, 90, 120 and 180 days. The solid part was separated by filtration, thoroughly washed with distilled water and dried again at room temperature.

Structural analysis of the obtained solid powders was performed by X-ray diffraction (XRD) technique on a Brucker D2 Phaser diffractometer with CuK$_\alpha$-radiation and a Ni filter.

For the evaluation of the economical parameters of the different synthesis approaches, the electricity consumption of the considered processes was estimated with an energy measurement device, Brennenstuhl PM231 E. The obtained results are attributed to the specific consumption per mass unit of FA zeolite (FAZ) in kWh/kg FAZ. The quantities of NaOH and water spent for activation, as well as the energy consumption for drying were also considered in the economical evaluation.

RESULTS AND DISCUSSIONS

XRD patterns of the samples obtained by calcination at 550 °C of FA/NaOH mixtures at a ratio of 1.6/1 are shown on Figure 1. The kinetics of the zeolitization process under self-crystallization in water media was investigated in three stages during the period of 190 days. First analysis of the extracted solid material was performed after 30 days of its incubation. The XRD pattern indicates absence of any crystalline phases excepting the hematite (α-Fe$_2$O$_3$). After 100 days of room temperature synthesis, well-expressed peaks are observed which correspond to the Na-X zeolite phase.

Fig. 1. XRD patterns of samples obtained by calcination at 550 °C of FA/NaOH mixtures at a ratio of 1.6/1.0 for different self-crystallization times, where: X is Na-X zeolite; Hem is α-Fe$_2$O$_3$. 
Third analysis is performed after 190 days, and it can be seen that the intensity of the main peak on the XRD pattern of the Na-X zeolite phase is increased, which indicates an improved yield of FAZ. Other specific peaks of Na-X, such as that at 2 Theta=30.85° is disappeared due to the changes in the crystal growth directions. Further prolongation in the synthesis duration may result in crystallization of more stable zeolitic phases such as chabazite or sodalite.

In Fig.2, the XRD patterns of samples obtained at a FA/NaOH ratio of 1/1 are shown. Increasing NaOH molarities from 1.5 to 2.5 M, the crystallization of zeolite from the reaction mixture is accelerated. The conversion process of FA into X type zeolite is finished just for 30 days, as the intensity of the reflections of Na-X phase for the sample after a month is almost equal to that after longer self-crystallization periods for 90 and 130 days. At these synthesis conditions, the characteristic peaks of α-Fe₂O₃ on the XRD patterns are diminished. This probably due to the higher concentration of the NaOH solution which causes an electrochemical reduction of α-Fe₂O₃ to Fe(OH)₃ and Fe, according to the scheme [12]:

\[
\frac{1}{2} \alpha-\text{Fe}_2\text{O}_3 + 3/2\text{H}_2\text{O} + \text{OH}^- = \text{Fe(OH)}_3^- \quad 1a)
\]

\[
\text{Fe(OH)}_3^- + e^- = \text{Fe(OH)}_3 + \text{OH}^- \quad 1b)
\]

\[
\text{Fe(OH)}_3 + 2e^- \rightarrow 3\text{OH}^- + \text{Fe}^0 \quad 1c)
\]

Thus, the obtained Fe(OH)₃ co-precipitate with sodium silicate and sodium aluminate hydrogel and Fe³⁺-ions incorporates into aluminosilicate zeolite framework or play a role as a charge compensator of AlO₄²⁻-anions.

In our previous studies, preliminary experimental results on CO₂ adsorption onto FAZ with Na-X structure have been reported [13,14]. CO₂ adsorption tests were performed on FAZ synthesized by a two stage fusion-hydrothermal synthesis at FA/NaOH=1/2, FA/H₂O=1/20, calcination for 1 h at 550 °C, 16 hours magnetic stirring, hydrothermal activation for 4 h at 90 °C, and drying for 1 h at 105 °C. FAZ obtained by atmospheric self-crystallization of mixtures of FA/NaOH=1/1 and FA/H₂O=1/10 during 12 months (approx. 360 days) of zeolitization. Promising adsorption capacity was obtained for zeolite samples, prepared by different techniques. Thus, the most important point for application of FAZ for adsorption of CO₂ in large scale systems is the economical superiority of their synthesis approach. The sequences of the different technological schemes of syntheses are presented in Fig. 3.

![Fig. 2. XRD pattern of samples obtained by calcination at 550 °C of FA/NaOH mixture at a ratio of 1/1 and different self-crystallization times, where X is Na-X zeolite structure.](image-url)
The economical and technical parameters of different synthesis manners were evaluated comparing their specific consumption for the production of 1kg FAZ in Table 2 and the corresponding costs in Table 3.

Table 2. Technical and economical comparison of different approaches for synthesis of zeolite X from 1 kg fly ash.

<table>
<thead>
<tr>
<th>Method of FAZ synthesis</th>
<th>Calcination at 550 °C for 1 h kWh/kg FAZ</th>
<th>Magnetic stirring kWh/kg FAZ</th>
<th>Hydrothermal activation at 90 °C kWh/kg FAZ</th>
<th>Drying at 105 °C l/kg FAZ</th>
<th>Distilled water kg/kg FAZ</th>
<th>NaOH kg/kg FAZ</th>
<th>Time of synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two stage fusion-hydrothermal</td>
<td>1.759</td>
<td>0.820</td>
<td>1.742</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>22 hours</td>
</tr>
<tr>
<td>Atmospheric self-crystallization</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>10</td>
<td>1</td>
<td>365 days</td>
</tr>
<tr>
<td>Two stage fusion-atmospheric</td>
<td>1.759</td>
<td>N/A</td>
<td>N/A</td>
<td>10</td>
<td>0.6</td>
<td>1</td>
<td>190 days</td>
</tr>
<tr>
<td>Two stage fusion-atmospheric</td>
<td>1.759</td>
<td>N/A</td>
<td>N/A</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>90 days</td>
</tr>
</tbody>
</table>
Table 3. Comparative cost analysis of different approaches for synthesis of zeolite X from 1 kg fly ash.

<table>
<thead>
<tr>
<th>Method of FAZ synthesis</th>
<th>Cost per unit electric power</th>
<th>Cost per unit NaOH</th>
<th>Cost per unit water</th>
<th>Value (incl. washing)</th>
<th>Total cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two stage fusion-hydrothermal</td>
<td>0.1012</td>
<td>0.4607</td>
<td>5.1129</td>
<td>1.0656</td>
<td>6.6392</td>
</tr>
<tr>
<td>Atmospheric self-crystallization</td>
<td>N/A</td>
<td>N/A</td>
<td>2.5560</td>
<td>1.0635</td>
<td>3.6206</td>
</tr>
<tr>
<td>Two stage fusion-atmospheric</td>
<td>0.1012</td>
<td>0.1780</td>
<td>1.5336</td>
<td>1.0646</td>
<td>2.7762</td>
</tr>
<tr>
<td>Two stage fusion-atmospheric</td>
<td>0.1012</td>
<td>0.1780</td>
<td>2.5560</td>
<td>1.0646</td>
<td>3.7986</td>
</tr>
</tbody>
</table>

The obtained cost values in Table 3 are calculated for a laboratory scale experiments including industrial costs for electrical energy without distribution and water with purification. It could be expected a serious price discount for FAZ produced in large-scale systems supposing that energy efficient processes will be installed in the frame of a Thermal Power Plant by utilization of residual thermal energy, and by concentration and utilization of the exhausted alkaline solution. In addition, cost reduction will be also realized estimating the expenses for fly ash transportation and disposal. Furthermore, carbon capture by solid adsorbents is the most economically efficient and environmentally friendly approach in comparison to the other existing low-carbon technologies.

CONCLUSIONS

Lignite coal fly ash was converted into zeolite of Na-X type applying a novel hybrid approach, which consists of a double stage fusion-atmospheric self-crystallization, combining the advantages of the existed manners for preparation of zeolites from aluminosilicate by-products. A comparative economical evaluation was performed for three different methods for obtaining of zeolite Na-X by alkaline treatment of coal fly ash in laboratory scales. The best results are obtained for the hybride fusion-atmospheric synthesis at a concentration of the alkaline activator corresponding to 1.5–2.5 M NaOH, considering the balance between the specific cost and the time consumption for the production of mass unit of the zeolite. Furthermore, the simultaneous resolving of two global ecological problems, such as fly ash deposition and carbon dioxide capture has an inestimable environment protection benefit.

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REFERENCES


ПОДОБРЯВАНЕ ТЕХНИКО-ИКОНОМИЧЕСКИТЕ ПОКАЗАТЕЛИ НА МЕТОДИТЕ ЗА СИНТЕЗ НА ЗЕОЛИТИ ОТ ЛЕТЯЩА ПЕПЕЛ

Деница Згурева, Силия Бойчева

Резюме. Опазването на околната среда е най-актуалният въпрос на съвременния свят, породен от непрестанно нарастващата конкуренция на технологични ресурси. Един от нерешените в глобален мащаб екологични проблеми е свърхпроизводството на парникови газове, от които в най-големи количества се емитира въглероден диоксид (CO₂).

Основен дял в генерирането на CO₂ заемат инсталацияте за производство на електроенергия (около 40 % от общоизречени въглеродни емисии). През последните години се разработват интензивни технологии за улавяне и подземно депониране на CO₂ от продуктите на горене. Към момента се развиват интересни подходи за улавяне на CO₂ при горивни процеси: чрез модифициране на горивния процес, преди и след изгаряне на горивата. За съществуващите горивни инсталации, технически и икономически най-целесъобразна е следногоривната технология, която се основава на абсорбцията на CO₂ от органични съединения (най-често амини), свързано с високи енергийни разходи за десорбицията процес и токсичните характеристики на тези вещества. Разработването на подходящи твърдофазни адсорбенти ще реши тези две негативни аспекти.

В предишните изследвания сме разгледали възможността за синтез на зеолити от летяща пепел, получена при изгарянето на български лъжнити въглища и последващият им приложение като адсорбенти на въглеродни емисии. От изследваните методи за получаване на високопоръчни зеолити от тип A и X, най-добри резултати са постигнати при два подхода: хидротермална активация с етан на предварително стабилно при 550 °C и атмосферна самокристализация. При всички експерименти, като алкален реагент е използван натриев хидроксид (NaOH). Предимство на първия метод на синтез е бързото получаване на края зеолита структура-24 часа, а основен негов недостатък е разхода на големи количества енергия. При втория подход не се влага никаква допълнителна енергия, но изисква продължителен период до достигане на богата на зеолит X крайна фаза - 12 месеца.
Настоящето изследване предлага алтернативен хибриден метод на синтез, който обединява предимствата на описаните по-горе подходи, като елиминира основните им недостатъци чрез реализиране на ехемата: атмосферна самокристализация с прилагане на етап на предварително стапяне. По този начин се спестява енергията, необходима за хидротермалната активация, а с етапа на предварително стапяне при 550 °С се съкращава четирикратно времето, необходимо за атмосферна самокристализация. Постигнатите резултати подобряват технико-икономическите показатели на процеса на зеолитизация на летящата пепел, с което се намалява себестойността на технологията за следгоривно улавяне на единица маса СО₂.

Ключови думи: синтез на зеолити, адсорбция, въглеродни емисии

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