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Green seed-assisted fly ash zeolitisation at room temperature

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Zeolite X has been successfully synthesised from fly ash produced by combustion of lignite coal at Maritsa Iztok 2 thermal power plant using a two-stage process: fusion with sodium hydroxide followed by hydrothermal treatment at room temperature. NaX zeolite crystallisation started later by decreasing NaOH amount. In order to optimise synthesis process a seed-assisted procedure was introduced. Preliminary synthesised zeolite X from pure chemicals was used as a seed material. On the one hand, seed addition affected synthesis direction to the desired zeolite structure (a monophase zeolite X product) and resulted in reduced synthesis time, but also reduced sodium hydroxide amount upon melting. In this way, zeolitisation may increase cost-effectiveness and eco-efficiency.

Key words: zeolite X, fly ash, zeolite synthesis, seed, green synthesis.

INTRODUCTION

Coal-fired thermal power plants (TPP) are a major source of fly ash (FA). Depending on the type of source and composition of the combustion coal, solid by-product components may vary significantly, but all types of FA include large amounts of silica (amorphous and crystalline) and alumina, both of which are constituent parts of many coal bedrocks. FA world production is over 750 million tons per year [1]. The areas where the production waste from the TPPs is deposited are huge terrains. Due to dusting during drying and release of harmful substances, FA represents an environmental hazard for soils, waters, and air. Discharges of the ash create environmental risks due to increased acid content and infiltration of heavy metals and radioactive elements in the soil. Toxic components in FA depend on the specific structure of the deposit and they may include a variety of the following elements found in negligible quantities: arsenic, beryllium, boron, cadmium, chromium, cobalt, lead, mercury, selenium, thallium, and vanadium. Many approaches to the use of FA have been developed, given their composition and degree of crystallinity. Part of deposited ash is used in the construction of roads and buildings, in the form of gypsum, gypsum board, cement, and concrete, in the ceramic industry, and other building mixes. Zeolite synthesis is another solution to utilise FA [2,3]. Zeolite production from FA results in a good practice with higher added value compared to ash usage as a cement additive [4–6]. In recent years, many studies have also been accomplished on zeolite synthesis from other alternative sources of SiO_2 and Al_2O_3 because the production of synthetic zeolites from pure silica and alumina sources is quite expensive. For alternative sources of silicon and aluminium, industrial waste or geothermal materials rich in Si and Al [7–14] may be used, as well as FA, which is largely composed of silicon and aluminium units. So naturally, one of the approaches to use FA is their zeolitisation. Zeolites synthesised from fly ash have many applications, including ion exchangers, molecular sieves, and adsorbents, similar to the zeolites obtained by conventional methods.

Generally, zeolites represent a group of natural or synthetic crystalline microporous aluminasilicates having a pore size of 0.3 to 2.0 nm [15]. Zeolite pores form a system of channels and cavities with well-defined shape and dimensions. These micro-porous materials are used as adsorbents [16,17], for ion exchange processes [18], and in catalysis [19–22]. Thus, from an environmental point of view the synthesis of coal ash zeolites and their use as adsorbents, catalysts, and ion exchangers is considered one of the most effective applications of fly ash.

FA is fine particles that are trapped by the TPP filters. They are collected by electrostatic or mechanical precipitation. The ash mainly contains amorphous and crystalline silica as well as hematite, mullite, and magnetite [3,23–25]. It has been found that different zeolite structures can be synthesised from the same ash but under different crystallisation conditions, the A, NaX, and NaY zeolites being of utmost importance [26]. One of them, namely NaX

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zeolite, which is an analogue to the natural faujasite, has a great ecological application. This zeolite, characterised by a highly developed specific surface area and numerous pores ranging in size from 5.0 to 7.5 Å, facilitates adsorption of 3.2-Å carbon dioxide molecules. Primarily, NaX zeolite is used as a catalyst in biodiesel production and CO_2 adsorption [27,28].

The purpose of the present work was to synthesise a NaX zeolite structure from fly ash obtained after the combustion of lignite coal at Maritsa Iztok 2 TPP by using a two stages process: fusion with sodium hydroxide followed by hydrothermal synthesis at room temperature. The first step, fusion of the alkaline-ash mixture led to the formation of soluble sodium aluminate and sodium silicate, enhanced zeolite formation, and facilitated the complete utilisation of the waste as a raw material [29, 30]. Hydrothermal activation is the second stage, which usually is held at a relatively high temperature (90–120 °C). The goal of the present study was to perform this stage at room temperature. Synthesis time at room temperature was between two weeks and one month, whereas the crystallisation process at 90 °C took a few hours (4–8). In order to reduce crystallisation time, a seed-induced synthesis procedure was applied. Prelimi-nary synthesised zeolite X from pure chemicals was used as a seed material.

EXPERIMENTAL

Sample preparation

Ash residues, containing 52.66 and 23.37 mass% of silica and alumina, respectively, were subjected to a dual stage fusion-hydrothermal transformation.

Initially, the coal ash was thoroughly homogenised with sodium hydroxide, and then the resulting mixture was poured into a nickel pot. Melting was carried out in a furnace at a temperature of 550 °C for a period of 1 hour. Then distilled water and the seed material were added to the preconditioned sample, and the resulting mixture was placed into a polypropylene vessel. Depending on the NaOH/fly ash ratio and the amount of crystal seed added to the resulting mixture the crystallisation of zeolite NaX was conducted at room temperature from 15 days to two months. The separated sample was filtered and allowed to dry at room temperature. In order to reduce crystallisation time and increase the yield, 1, 2, and 5 wt.% crystalline seed of zeolite NaX were used. Weight percentage was calculated regarding silica and alumina in the fly ash. The obtained solid substance was carefully washed with distilled water and then dried at 105 °C for an hour.

Zeolite seeds were synthesised at 90 °C for 8 h by using pure chemicals from initial gel with the following molar composition: $NaAlO_2$:4SiO_2: 16NaOH:325H_2O.

Samples characterization

Product morphology was observed by scanning electron microscopy (SEM) on a JEOL JSM6390 microscope coupled with an energy-dispersive X-ray (EDX) analyser (Oxford Instruments). Phase identification was performed by X-ray diffraction (XRD) technique on a Brucker D2 Phaser diffractometer with CuK_α radiation and a Ni filter.

RESULTS AND DISCUSSIONS

The hydrothermal synthesis of NaX zeolite from fly ash was carried out at room temperature. In these experiments, synthesis duration varied between 15 and 60 days. Table 1 provides data on the crystallisation time of zeolite X obtained from fly ash without seed and with 1, 2, and 5% seed, respectively, at a different NaOH/FA ratio. The NaOH/FA ratios used were 1.2/1, 1.0/1, 0.8/1, and 0.6/1 (Table 1). Higher amounts of NaOH caused NaX zeolite crystallisation to start much earlier. X-ray powder patterns indicate that the best results were obtained when the amount of sodium hydroxide was higher with NaOH/FA ratio of 1.2/1 or 1.0/1. Such a result could be expected because in this case sodium hydroxide brings about larger amounts of soluble silicates and aluminates from the silica and alumina phases, respectively, present in the fly ash. The latter phases increase their mobility to become able to form zeolite nuclei around which crystal growth takes place to build a zeolite structure. On using a lower amount of sodium hydroxide, however, NaX zeolite synthesis was not successful. X-ray powder patterns of the resulting products synthesised at a NaOH/FA ratio of 1/1 show that a crystalline phase emerged around the 29th day after crystallisation at room temperature (Fig. 1) and a high crystalline product of this zeolite was only reached by the 45th day of synthesis.

On employing a NaOH/FA ratio of 1.2/1 in the studies, the crystallisation of NaX zeolite began about 25 days after synthesis onset.

To reduce crystallisation time and direct synthesis to the desired zeolite structure, a seed-assisted synthesis of NaX zeolite from fly ash was applied by means of 1, 2 or 5 wt.% crystalline NaX zeolite. The weight percentage was calculated regarding the total amount of silica and alumina in the fly ash. NaX zeolite crystallisation at a NaOH/FA ratio of 1.2/1 started earlier on using 1, 2, and 5% seed. Comparing seed-assisted with seed-free NaX zeolite

synthesis, crystallisation with the latter started later for the same NaOH/FA ratio. By applying 1, 2 or 5% by weight of crystalline seed crystals, zeolite crystallisation started 21 days after synthesis onset at room temperature.

Table 1. Dependence of the NaOH/FA ratio on the crystallisation time of NaX zeolite synthesised from fly ash in the presence of 1, 2 or 5% seed at room temperature

NaOH/FA	No seeds	1% crystal seed	2% crystal seed	5% crystal seed
1.2/1	25 days	21 days	21 days	21 days
1	29 days	29 days	29 days	21 days
0.8/1	-	37 days	37 days	24 days
0.6/1	-	-	43 days	37 days

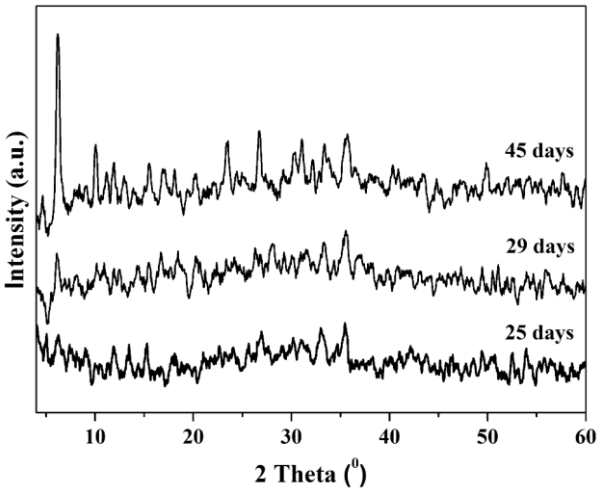

Fig. 1. X-ray powder patterns of NaX zeolite after seed-free synthesis from fly ash at room temperature at a NaOH/FA ratio of 1/1.

On employing a NaOH/FA ratio of 1.2/1 in the studies, the crystallisation of NaX zeolite began about 25 days after synthesis onset.

At a NaOH/FA ratio of 1.2/1 even small amounts of seed made the synthesis of zeolite X most sensitive. Upon addition of 1% seed, the crystallisation time decreased to 21 days, whereas without seed, crystallisation arose after the 25th day. Use of 5 wt.% seed led to a higher degree of crystallinity.

If the NaOH/FA ratio was 1/1 and crystallisation occurred in the presence of 1 or 2% seed, the NaX zeolite started to crystallise before the 29th day. At a higher amount of seed (5%), the crystallisation started earlier than the case with 1 or 2% crystal seed. X-ray powder patterns of the synthesised products give evidence that the NaX zeolite began to crystallise before the 21st day of synthesis (Fig. 2). From these results, it can be concluded that the use of a larger amount of crystal seed favoured a significant decrease in crystallisation time.

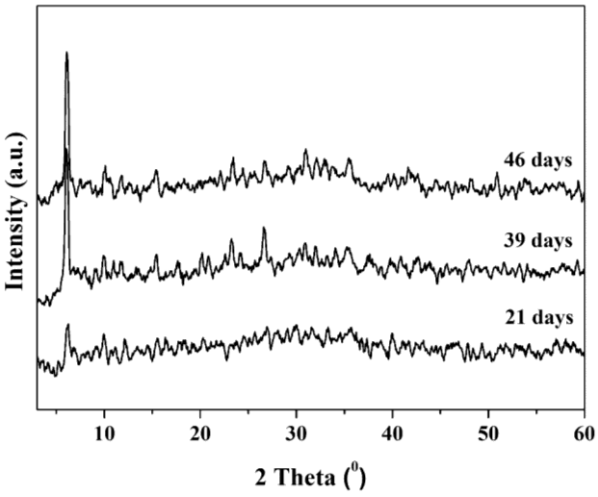

Fig. 2. X-ray powder patterns of NaX zeolite synthesised from fly ash at room temperature in the presence of 5% seeds at a NaOH/FA ratio of 1/1.

Scanning electron microscopy (SEM) was applied to investigate the morphology and size of the crystal particles of NaX zeolite. In Figure 3, a SEM image of NaX zeolite synthesised from fly ash and sodium hydroxide at a ratio of 1/1 in the presence of 5% crystalline seed is presented. From the micrographs, it can be seen that aggregates were formed. The size of the NaX zeolite aggregates varies between 1 and 10 μm, whereas some aggre-gates have sizes in the submicron range (500–1000 nm).

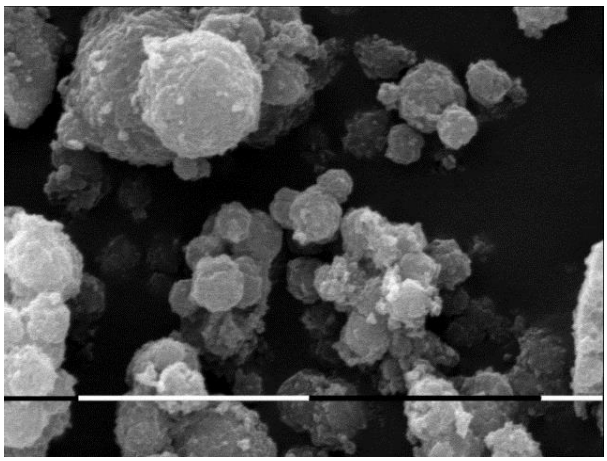

Fig. 3. SEM micrograph of NaX zeolite synthesised from fly ash at room temperature in the presence of 5% of seeds at a NaOH/FA ratio of 1/1 and crystallisation time of 39 days. Bar length 10 μm, magnification 5000.

When the crystallisation time was extended to about 70 days, a product of higher crystallinity was formed. Figure 4 displays an X-ray powder pattern of a product synthesised over a period of 70 days at NaOH/FA ratio of 1/1 in the presence of 2% seeds. It is observed that the product obtained exhibits a higher crystallinity compared with those synthesised for a shorter period.

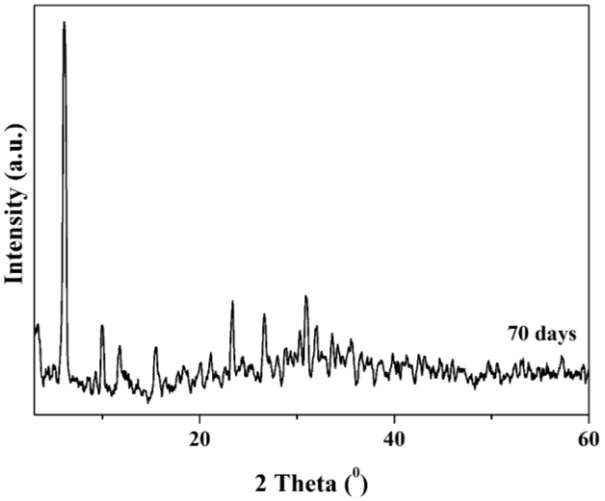

Fig. 4. X-ray powder patterns of NaX zeolite synthesised from fly ash at room temperature in the presence of 2% seeds at a NaOH/FA ratio of 1/1.

On using less sodium hydroxide at NaOH/FA of 0.8/1 without seed, NaX zeolite synthesis failed despite the long crystallisation period of 50 days (Table 1). By adding 1 or 2% crystalline seed to the reaction mixture, the NaX zeolite started to crystallise on the 37th day after synthesis. By use of a larger amount of crystalline seed (5%), significant crystallisation of the zeolite began much earlier, as of the 24th day. Despite the use of a larger amount of seed and crystallisation for nearly 50 days, a completely crystallised NaX zeolite phase was not observed. Figure 5 presents X-ray powder patterns of products synthesised in the presence of 5% seed.

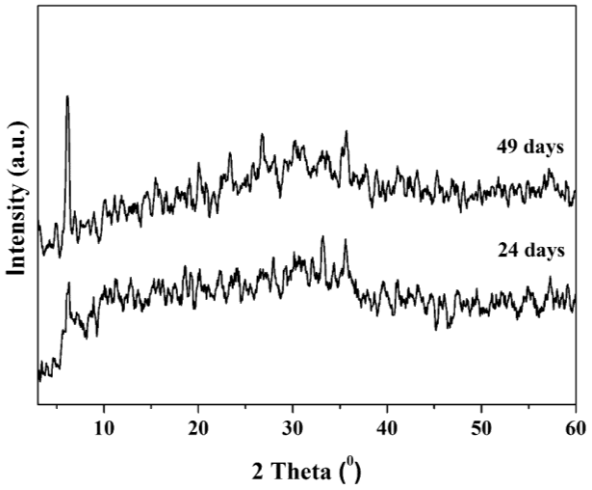

Fig. 5. X-ray powder patterns of NaX zeolite synthesised from fly ash at room temperature in the presence of 5% of seeds at a NaOH/FA ratio of 0.8/1.

At a NaOH/FA ratio of 0.6/1, studies of NaX zeolite synthesis without seed or in the presence of 1% seed were unsuccessful. In these experiments, zeolite crystallisation was not observed despite the long synthesis period of 50 days.

Figure 6 shows X-ray powder patterns of the resulting products synthesised in the presence of 5% crystalline seed. Upon synthesis in the presence of 2% seed, the NaX zeolite started to crystallise only 43 days after synthesis. X-ray powder patterns of the products synthesised in the presence of a higher amount of crystalline seed (5%) indicate that zeolite crystallisation started somewhat earlier, as of the 37th day. From the results obtained, it can be concluded that a larger amount of seed contributes to earlier formation of a zeolite phase.

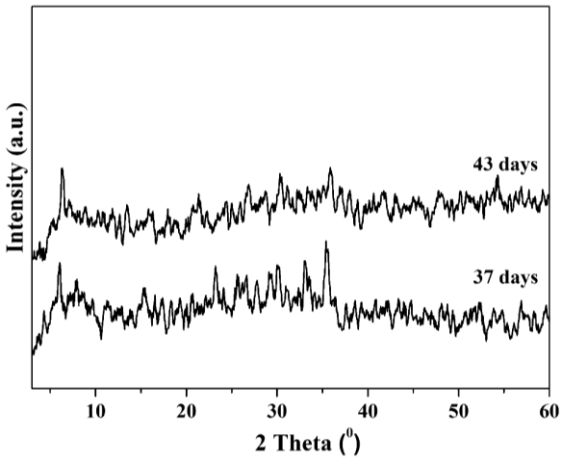

Fig. 6. X-ray powder patterns of NaX zeolite synthesised from fly ash at room temperature in the presence of 5% of seeds at a NaOH/FA ratio of 0.6/1.

It is evident that the lowest NaOH/FA ratio, at which the NaX zeolite is successfully synthesised at room temperature without the presence of seeds, is 1/1. Further reduction of the sodium base at this ratio did not result in a crystalline phase of the zeolite. It was found that by adding crystalline seed to the reaction mixture it is possible to use less NaOH in the zeolite synthesis at room temperature. The results obtained with NaOH/FA ratios of 0.8/1 and 0.6/1 indicate that seeds may result in a crystalline product for longer crystallisation periods of 37–50 days.

CONCLUSIONS

Zeolite X was successfully synthesised from fly ash produced by combustion of lignite coal at Maritsa Iztok 2 TPP using a two-stage process: fusion with sodium hydroxide followed by hydrothermal treatment at room temperature. Added seed directed synthesis to the desired zeolite structure (mono-phase zeolite X), and reduced both synthesis time and used sodium hydroxide amount upon melting. In this way, the process of zeolitisation is economically cost-effective and better eco-efficient.

Seed-assisted crystallisation at room temperature using NaOH/FA ratios of 1.2/1, 1/1, and 0.8/1

provided successful synthesis of the NaX zeolite. Zeolite crystallisation started later on reducing the amount of sodium hydroxide.

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ЗЕЛЕН СИНТЕЗ НА ЗЕОЛИТ ОТ ВЪГЛИЩНА ПЕПЕЛ В ПРИСЪСТВИЕТО НА ЗАРОДИШИ

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(Резюме)

Успешно е синтезиран зеолит X от въглищна пепел, получена чрез изгаряне на лигнитни въглища в ТЕЦ „Марица Изток 2", използвайки двуетапен процес - стапяне с натриев хидроксид, последвано от хидротермален синтез при стайна температура. При намаляване на количеството на NaOH, кристализацията на зеолит NaX започва по-късно. За оптимизиране на процеса на синтез е въведена процедура с използване на зародиши. Кристали от предварително синтезиран зеолит X от чисти химикали се използват като зародиши. Добавянето на зародиши води не само до насочването на синтезата към желаната зеолитна структура (получаване на моно-фазен зеолит X) и до намаляване на времето за синтез, но също и до намаляване на количеството NaOH при стапяне. По този начин процесът на зеолитизация е икономически по-рентабилен и екологично ефективен.