Textural properties vs. CEC and EGME retention of Na–X zeolite prepared from fly ash at room temperature

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Abstract

Zeolite Na–X (FAU type) was synthesized from F-class fly ash in simple and economical way. Several months of storage of fly ash in NaOH solution, at room temperature, without any prior treatment, results in the production of material with ca. 50% content of Na–X zeolite. The most efficient reaction takes place at (OH)− activity of 0.1–0.15 mol (OH)−/g of ash and at S/L ratio of 33 to 67 g/dm³. Higher S/L value causes an accelerating dissolution–crystallization equilibrium attainment. Cl− ion acts as the inhibitor of this reaction.

Na–X crystals show Si/Al ratios of framework in the range of 1.14 to 1.45. Zeolite content controls the micropore volume and the surface area of the samples, limiting the ethylene glycol monoethyl ether (EGME) retention and the cation exchange capacity (CEC) values. The temperature of pre-heating is a crucial factor for the amount of retained EGME. Insufficient dehydration at 250 °C (as in conventional procedure for clays) does not allow EGME molecules to enter all micropores. Pre-heating at 400 °C causes EGME adsorption on all available surfaces. EGME molecule occupation area is ca. 41 Å², using BET algorithm and ca. 52 Å² for Langmuir equation, or package ratio 16 Å³/1 EGME molecule if calculating adsorption as mechanism of micropores infilling. Total CEC value (including sodalite cages) of materials rich in Na–X zeolite, measured using Ba2+ and Mg2+ cations is ca. 2.5 meq/g. Exchange positions available for [Co(NH3)6]3+ cation occur only inside 12-ring space and loops of FAU framework (secondary building unit — SBU). They produce CEC which attains almost 1.2 meq/g, following directly the development of microporous texture. Produced materials reach maximum N2-BET surface area 344 m²/g from 15.3 m²/g of raw fly ash. Simple procedure of EGME retention can be successfully used to determine microporous texture of X zeolite available to organic molecules.

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Keywords: Zeolite X; Fly ash; Synthesis; Nitrogen adsorption; Ethylene glycol monoethyl ether (EGME); Cation exchange capacity

1. Introduction

Zeolite X (FAU; classification and nomenclature after Baerlocher et al., 2001) is a very attractive material for technological and environmental applications. Wide
micropores make it useful for purification and separation of gases and organic components; high exchange capacity allows for adsorption of heavy cations and radionuclides (Breck, 1974). Synthesis of zeolite X has been carried out in various hydrothermal reaction conditions and fly ash was successfully used as a reaction substrate (review by Querol et al., 2002). Most of proposed methods provide X zeolite coexisting not only with residual fly ash phases, but also with other zeolites — types A or P1 (e.g. Amrhein et al., 1996). Pure X zeolite can be synthesized by fusion of fly ash with NaOH (Chang and Shih, 1998; Terzano et al., 2005) or multi-step synthesis (Hollman et al., 1999) that complicates the procedure and increases the cost of synthesis. Mixing raw fly ash with NaOH solutions and heating by one or several days can provide material rich in X zeolite, with a small content of residual phases (Derkowski et al., 2006). Shih and Chang (1996) reduced the temperature of reaction to 38 °C, but received only approx. 20% of X phase.

Searching for a way to lower significantly the costs and simplify the procedure of production of zeolite X from fly ash, we made successful experiments of synthesis of Na–X zeolite at room temperature. Such synthesis, of efficiency comparable to hydrothermal reactions, requires a long time, according to the relationship described by Breck (1974). Crystallization and properties of Na–X zeolite, synthesized at room temperature from pure reagents, have been recently described by Valtchev and Bozhilov (2004). Na–X zeolite produced from fly ash does not achieve such quality as zeolites synthesized from pure chemical reagents, but it can substitute them in less purity-demanding technologies as less expensive material. Commercial synthesis of zeolite X from fly ash at room temperature or at open air (in summer or in hot climate) is likely to become profitable.

The retention of EGME is a useful technique for determination of the total surface area (TSA) of expandable clay minerals (Carter et al., 1965). The microporous texture of zeolites is non-expandable and its size is fixed. Dimension of Na–X micropores is probably wide enough for access of EGME molecules, thus EGME should fill pores in a capillary way and cover as monolayer the glass mesopores and external surface of grains in the produced material (Derkowski et al., 2006).

The cobalt (III) hexamine chloride was already tested for the determination of CEC of Na–X zeolite, bringing unclear results. Material rich in FAU phase showed very different values of CEC while measured by conventional methodology and with [Co(NH3)6]3+ cation, after Orsini and Remy (1976). Zeolites of narrow micropores — sodalite and NaP1 — exhibit very low CEC originating only from external surfaces when using hexamine cobalt (III) complex cation. Materials containing Na–X show CEC values significantly lower than when measured with small cations, but undoubtedly exceeding the external charge (Derkowski et al., 2006).

This study focuses on the transformation of fly ash into material rich in Na–X zeolite, at room temperature and on the determination of its composition and textural properties. Retention of EGME was measured applying the conventional and modified techniques used for phyllosilicate clay minerals, in order to check relations between textural properties and retention. Other aim of this work is to explain the reaction of [Co(NH3)6]3+ cation with charged surface of X zeolite.

2. Materials

Fresh fly ash from the “Elektrociepłownia Kraków” power plant (Cracow, Poland), that was used in the experiments, is a typical F-class fly ash with a following composition: aluminosilicate glass (40–50%), mullite (below 30%), quartz (5–7%), unburned coaly matter (below 7%). Fe oxides, gypsum, calcite, feldspars and apatite are minor components (Fig. 1). The chemical composition of fly ash is as following (wt.%): SiO2 — 47.31, Al2O3 — 25.19, Fe2O3 — 6.95, MnO — 0.08, MgO — 2.88, CaO — 3.84, Na2O — 1.24, K2O — 2.65, TiO2 — 1.01, P2O5 — 0.48, LOI — 7.26 %. The SiO2/Al2O3 wt. ratio of the fly ash is ca. 1.88 and the average SiO2/Al2O3 wt. ratio of its aluminosilicate glass component is ca. 1.6. Weight percent of other components, determined following the EU specifications EN 450, EN 451 and EN 196 are: chlorides — 0.01 wt. %; reactive SiO2 — 26.2 wt.%; free CaO — 0.16. The

Fig. 1. SEM image of morphology of fly ash from ECK power plant: microspheres of aluminosilicate glass (smooth surface, various fractions); iron oxides (rough sphere at upper right side); unburned coaly particle of irregular shape at the bottom.
cation exchange capacity of the raw fly ash is 5.5 meq/100 g (Derkowski et al., 2006).

3. Methods

3.1. Conditions of synthesis

10 g samples of homogenized raw fly ash were treated with solutions of various concentrations of sodium hydroxide and sodium chloride, at solid-to-liquid ratios (S/L) from 25 to 100 g/dm³. The suspensions were stored for 2 to 20 months at room temperature (21–22 °C) and stirred occasionally. Several times during storage, small portions of solids were collected for XRD analysis and other tests. Before the analyses, the solids were washed by centrifuging 4 times with distilled water and dried. All reaction details are given in Tables 1 and 2.

3.2. Analytical methods

The mineral composition of all samples was determined by X-ray diffraction (XRD) using Philips X’pert APD and Thermo XTRA diffractometers. The identification of phases was based on ICDD PDF-2 database and the collection of patterns recommended by International Zeolite Association (Trecay and Higgins, 2001). Random preparations were made from 300 mg of a ground sample. Quantitative analysis of zeolite content was carried out using calculation based on comparison with artificial mixtures of raw ash with commercial 13× molecular sieve (Sigma-Aldrich No 69854) and with AutoQuan® and BGMN Rietveld refinement programs (Bergmann et al., 1998).

Table 1

Products of the first experiment after 7 months of reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution V [ml]</th>
<th>Na⁺ [mole]</th>
<th>(OH⁻)⁻ [mole]</th>
<th>Cl⁻ [mole]</th>
<th>Na–X content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECK 47</td>
<td>400</td>
<td>0.20</td>
<td>0.20</td>
<td>0.00</td>
<td>0</td>
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<tr>
<td>ECK 48</td>
<td>400</td>
<td>0.40</td>
<td>0.40</td>
<td>0.00</td>
<td>0</td>
</tr>
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<td>ECK 49</td>
<td>400</td>
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<td>0.60</td>
<td>0.00</td>
<td>34</td>
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<tr>
<td>ECK 50</td>
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<td>0.80</td>
<td>0.80</td>
<td>0.00</td>
<td>32</td>
</tr>
<tr>
<td>ECK 51</td>
<td>400</td>
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<td>1.00</td>
<td>0.00</td>
<td>42</td>
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<tr>
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<td>0.00</td>
<td>43</td>
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<td>ECK 53</td>
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<td>0.30</td>
<td>0.90</td>
<td>0</td>
</tr>
<tr>
<td>ECK 54</td>
<td>400</td>
<td>1.20</td>
<td>0.60</td>
<td>0.60</td>
<td>20</td>
</tr>
<tr>
<td>ECK 55</td>
<td>400</td>
<td>1.20</td>
<td>0.90</td>
<td>0.30</td>
<td>34</td>
</tr>
<tr>
<td>ECK 56</td>
<td>400</td>
<td>0.70</td>
<td>0.10</td>
<td>0.60</td>
<td>2</td>
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<tr>
<td>ECK 57</td>
<td>400</td>
<td>0.60</td>
<td>0.20</td>
<td>0.40</td>
<td>0</td>
</tr>
<tr>
<td>ECK 58</td>
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<td>0.30</td>
<td>0.20</td>
<td>0</td>
</tr>
<tr>
<td>ECK 59</td>
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<td>0.50</td>
<td>0.20</td>
<td>0.30</td>
<td>0</td>
</tr>
<tr>
<td>ECK 60</td>
<td>400</td>
<td>0.60</td>
<td>0.40</td>
<td>0.20</td>
<td>7</td>
</tr>
<tr>
<td>ECK 61</td>
<td>400</td>
<td>0.70</td>
<td>0.60</td>
<td>0.10</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 2

Products of the second experiment after 100 days and 20 months of reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution V [ml]</th>
<th>Na⁺ [mole]</th>
<th>(OH⁻)⁻ [mole]</th>
<th>Cl⁻ [mole]</th>
<th>Na–X content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EcnT 2</td>
<td>300</td>
<td>1.50</td>
<td>1.50</td>
<td>0.00</td>
<td>3</td>
</tr>
<tr>
<td>EcnT 3</td>
<td>200</td>
<td>1.00</td>
<td>1.00</td>
<td>0.00</td>
<td>14</td>
</tr>
<tr>
<td>EcnT 4</td>
<td>300</td>
<td>1.30</td>
<td>1.00</td>
<td>0.30</td>
<td>22</td>
</tr>
<tr>
<td>EcnT 5</td>
<td>150</td>
<td>0.75</td>
<td>0.75</td>
<td>0.00</td>
<td>2</td>
</tr>
<tr>
<td>EcnT 6</td>
<td>200</td>
<td>0.90</td>
<td>0.75</td>
<td>0.15</td>
<td>6</td>
</tr>
<tr>
<td>EcnT 7</td>
<td>100</td>
<td>0.50</td>
<td>0.50</td>
<td>0.00</td>
<td>14</td>
</tr>
<tr>
<td>EcnT 8</td>
<td>150</td>
<td>0.65</td>
<td>0.50</td>
<td>0.15</td>
<td>10</td>
</tr>
</tbody>
</table>

Observations of the reaction products and the analyses of chemical composition in micro-range were carried out using field emission scanning electron microscope (SEM) HITACHI S-4700 equipped with energy dispersive spectrometry (EDS) system VANTAGE NORAN.

CEC was determined using simple and quick method employing cobalt (III) hexamine chloride, described by Orsini and Remy (1976). This method relies on the measurement of content of cobalt hexamine in solution by VIS spectrometry. Absorbance depends on the amount of [Co(NH₃)₆]³⁺ cation sorbed by the tested material (0.5–1 g) mixed with 25 ml of chloride solution. Selected samples were also measured by conventional methods (Mackenzie, 1951; Gillman, 1979), based on an ion exchange reaction with BaCl₂ and MgCl₂ and subsequent determination of the released cations. The samples were divided into portions (from 33 to 500 mg), which were mixed with 10 ml of 0.1 M solutions and shaken 30 min. Procedure was repeated 5 times The concentrations of the Na, K, Mg and Ca ions in the solution were determined by atomic absorption spectroscopy (AAS) and the values of mean CEC were calculated. Barium-exchanged, washed and dried samples were treated with MgCl₂ solution using the procedure in order to desorb Ba cation and to measure its content with AAS. The CEC values were calculated per weight of a dehydrated sample.

Sorption of EGME (Carter et al., 1965) was carried at room temperature using the “free surface” procedure described by Eltantawy and Arnold (1973). The measurements were repeated 3 or 4 times and average values are reported. The samples for EGME adsorption measurements were preheated at 250 °C overnight, as recommended for clays, and at 400 °C to remove the zeolitic water.

For measurements of the surface area and pore volume the ASAP 2405 instrument (Micromeritics) was used. The instrument performs physical adsorption and desorption of gases using programming provided by
 Micromeritics. All procedures are workable with nitrogen and helium, and also with krypton for low surface areas. Before analysis the samples were degassed at 350 °C for 24 h until the pressure in the tubes is stabilized at 2·10^{-3} mm Hg. The selected degassing temperature should be as high as possible not to cause decomposition of the analyzed material. In the course of analysis pure nitrogen (99.999%) is dosed into each sample in order to obtain the required pressure \( P/P_0 \) (an adequate number of points to calculate the isotherms). During the analysis the entire sample is immersed in a container filled with liquid nitrogen. Nitrogen dosage (adsorption) is continued until the atmospheric pressure is reached, which is followed by the reverse process (desorption).

4. Results

Application of low-temperature (ca. 22 °C) treatment resulted in the synthesis of a Na–X (FAU type, identification based on: ICDD card 38-0237, and Treacy and Higgins, 2001) at the expense of dissolved components of fly ash. The Na–X phase was the only zeolitic structure identified in the reaction products and no other neoformed mineral was found. The residual quartz, mullite and glass phase (noticeable as a slight rise of the XRD background line) occur also in various contents. The glass seems to be the main substrate for zeolite synthesis, as it disappears while Na–X reflections grow; quartz and mullite persist almost unchanged.

The low-temperature synthesis was carried out in two ways. In the first one, constant solid-to-liquid ratio (25 g/dm³) and various concentrations of NaOH and NaCl solutions were applied (Table 1). According to “salt effect” described by Cooks and Pope (1995) and confirmed during synthesis from fly ash (Derkowski and Michalik, in press), the presence of Cl⁻ ion in solution can enhance the crystallization of zeolites. A small quantity of Na–X phase was first detected after 2 months of storage and it increased significantly within the next month. The highest quantity of Na–X phase in the product was found after 7 months of reaction. Longer storage (up to 19 months) did not cause a further crystallization of Na–X phase or dissolution of the residual material. It is clear (Table 1), that the highest contents of Na–X phase were reached at condition of high (OH)⁻ and low Cl⁻ activity.

In the second experiment we tested various S/L ratios (33 to 100 g/dm³) and constant, high concentrations of NaOH (5 M) and NaCl (3 M) solutions. The aim of this step of the study was to shorten the time of synthesis and to lower the use of solutions, maintaining the quality of produced material. No sample showed the Na–X

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exchange with BaCl₂</th>
<th>Ba desorption with MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>EcnT 2</td>
<td>2.367</td>
<td>2.287</td>
</tr>
<tr>
<td>EcnT 5</td>
<td>2.740</td>
<td>2.406</td>
</tr>
<tr>
<td>Sodalite*</td>
<td>1.203</td>
<td>1.114</td>
</tr>
</tbody>
</table>

Values of CEC are given as meq/g.

*See Derkowski et al., 2006.
crystallization after 50 days, but 100 days of the reaction turned to be sufficient for the synthesis (Table 2). As in the previous experiment, crystallization is favored by the absence of Cl− ion in solution and takes place in the whole range of S/L ratio. The fastest crystallization of Na–X is observed at a medium S/L ratio (EcnT 5), but such relationship changes within time of the reaction. After 20 months, the S/L ratio (and – simultaneously – the activity of hydroxyl group) clearly correlates with Na–X content in reaction products. Samples EcnT 2, EcnT 3 and EcnT 5 show the highest contents of Na–X, reaching ca. 50%. The mass of synthesized products differs slightly according to the advance of dissolution of the fly ash components, but remains close to the mass of starting fly ash (10 g).

The SEM images of Na–X crystals are presented in Fig. 2. Three samples representing wide range of the reaction conditions were analyzed with EDS microprobe. Si/Al molar ratio of Na–X phase varies from 1.08 to 1.34. Na–X formulae calculated based on 24 oxygen atoms, are as follows:

Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fly ash</th>
<th>ECK 52 (350 °C)</th>
<th>ECK 52 (200 °C)</th>
<th>ECK 60 (350 °C)</th>
<th>EcnT 3 (350 °C)</th>
<th>EcnT 2 (350 °C)</th>
<th>EcnT 4 (350 °C)</th>
<th>EcnT 5 (350 °C)</th>
<th>EcnT 6 (350 °C)</th>
<th>EcnT 7 (350 °C)</th>
<th>EcnT 8 (350 °C)</th>
<th>13X (350 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S BET</td>
<td>15.3</td>
<td>280</td>
<td>246</td>
<td>40.0</td>
<td>333</td>
<td>344</td>
<td>302</td>
<td>236</td>
<td>286</td>
<td>246</td>
<td>283</td>
<td>544</td>
</tr>
<tr>
<td>S L</td>
<td>19.5</td>
<td>351</td>
<td>309</td>
<td>50.2</td>
<td>417</td>
<td>431</td>
<td>379</td>
<td>409</td>
<td>359</td>
<td>390</td>
<td>355</td>
<td>680</td>
</tr>
<tr>
<td>V mic</td>
<td>0.0005</td>
<td>0.1006</td>
<td>0.0864</td>
<td>0.0125</td>
<td>0.1224</td>
<td>0.1261</td>
<td>0.1086</td>
<td>0.1124</td>
<td>0.0966</td>
<td>0.0827</td>
<td>0.1010</td>
<td>0.2146</td>
</tr>
<tr>
<td>S mic</td>
<td>1.16</td>
<td>226.5</td>
<td>194.5</td>
<td>28.2</td>
<td>275.3</td>
<td>283.7</td>
<td>244.5</td>
<td>252.9</td>
<td>217.6</td>
<td>185.9</td>
<td>227.2</td>
<td>483.7</td>
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<tr>
<td>S ext</td>
<td>14.12</td>
<td>53.70</td>
<td>51.90</td>
<td>11.79</td>
<td>57.34</td>
<td>59.80</td>
<td>57.71</td>
<td>72.85</td>
<td>68.68</td>
<td>59.74</td>
<td>55.96</td>
<td>60.02</td>
</tr>
<tr>
<td>S BH ads</td>
<td>13.54</td>
<td>48.07</td>
<td>48.06</td>
<td>10.40</td>
<td>49.73</td>
<td>53.15</td>
<td>52.94</td>
<td>69.74</td>
<td>65.29</td>
<td>52.14</td>
<td>43.29</td>
<td>51.95</td>
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<tr>
<td>S BH des</td>
<td>19.87</td>
<td>68.17</td>
<td>64.63</td>
<td>13.22</td>
<td>61.95</td>
<td>65.54</td>
<td>63.74</td>
<td>86.99</td>
<td>80.61</td>
<td>65.94</td>
<td>61.84</td>
<td>62.28</td>
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<tr>
<td>S SP</td>
<td>0.0290</td>
<td>0.1418</td>
<td>0.2098</td>
<td>0.0292</td>
<td>0.1341</td>
<td>0.1638</td>
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<td>0.1606</td>
<td>0.0992</td>
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<tr>
<td>S VP</td>
<td>0.2079</td>
<td>0.1455</td>
<td>0.2186</td>
<td>0.0303</td>
<td>0.1351</td>
<td>0.1651</td>
<td>0.1211</td>
<td>0.2091</td>
<td>0.1676</td>
<td>0.1030</td>
<td>0.0893</td>
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</tr>
<tr>
<td>EGME250</td>
<td>14.5</td>
<td>n.a.</td>
<td>n.a.</td>
<td>101.1</td>
<td>113.6</td>
<td>n.a.</td>
<td>121.1</td>
<td>n.a.</td>
<td>94.9</td>
<td>98.6</td>
<td>203.7</td>
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<tr>
<td>EGME400</td>
<td>14.8</td>
<td>108.8</td>
<td>24.3</td>
<td>136.4</td>
<td>126.8</td>
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<td>121.9</td>
<td>139.3</td>
<td>104.5</td>
<td>110.1</td>
<td>223.9</td>
<td></td>
</tr>
</tbody>
</table>

S (surface areas) given in m²/g, V (volumes) in cm³/g.
S BET, S L — BET and Langmuir equations based surface areas.
V mic, S mic, S ext — micropore volume, micropore area, external surface area.
S BH ads, S BH des, V BH ads, and V BH des — BJH cumulative adsorption and desorption surface areas (=S mesopores) and pore volumes (=V mesopores); calculated after Barrett, Joyner and Halenda (1951) equations, using pore size range 17–3000 Å.
S SP, V SP — Single point total surface area (at P/P₀ = 0.199x) and total pore volume (at P/P₀ = 0.98x) of pores less than ca. 115 nm diameter.EGME250, EGME400 — retention of EGME (in mg/g) after pre-heating at 250 and 400 °C.

The crystallization of Na–X from fly ash causes increase of CEC values measured with cobalt (III) hexamine cation, from 0.055 to ca 1.20 meq/g (Table 3). The CEC received by the conventional method is significantly higher. The sums of exchangeable cations, desorbed by Ba were confirmed by the measurement of Ba exchanged with Mg. The Ba desorption procedure brings slightly lower CEC values, probably because of an incomplete desorption. Pure sodalite synthesized from fly ash shows ca 1.20 meq/g (see Table 3; Derkowski et al., 2006).

The adsorption of EGME was measured according to the procedure used for the determination of total surface area (TSA) for phyllosilicates (Carter et al., 1965). Pre-heating of samples was first done at 250 °C, and then a sample mixed with liquid EGME was loaded into a desiccator. Repeated measurements with pre-heating at 400 °C brought significantly higher values of EGME retention. It is clear, that 250 °C is to low temperature for complete dehydration, even if the samples are later stored in vacuum and oversaturated with organic liquid (Table 4). Raw fly ash shows almost equal values of EGME retention after preheating at different temperatures.

Wide range of textural parameters was calculated using N2 adsorption–desorption isotherms (Fig. 3., Table 4). Raw fly ash isotherm belongs to types II and...
IV, with H2/H3 hysteresis loop. Such shape is produced by nonuniform pores frequently formed by granular material (Leofanti et al., 1998). Coaly matter and aluminosilicate glass components may also provide some porosity. Ash attains very small BET surface area, almost whole belonging to external surface. BJH (Barrett-Joyner-Halenda; Barrett et al., 1951) pore size distribution (PSD) calculation is correct for this material, as it uses mesoporous dimension range 17–3000 Å (Fig. 4). Surface area increases significantly after zeolitization and the microporous texture of zeolite structure is responsible for this fact. Isotherm shape changes towards type I with H3 or mixed H2/H3 hysteresis loop. BJH calculations can show only the distribution of non-zeolitic pores — external surface areas of zeolitic samples are very close to BJH cumulative areas. Capillary condensation starts (and evaporation ends) at normal $P/P_0$ value for N$_2$ (77 K) isotherm $\approx 0.42$. PSD curves drawn upon BJH calculation show rise of volume at ca. 25–30 Å pore diameter (Fig. 4). PSD pattern for sample EcnT 6 shows the highest peaks. In the PSD pattern of EcnT 5 the average size 51 Å dominates and higher values are also noticeable, but they all look negligible when compared to microporous texture. Desorption BJH curves evidence significant capillary evaporation in mesopore range.

The sample ECK 52 was measured also after preheating in vacuum at lower temperature (200 °C), than commonly used. Textural properties measured in such conditions were worse than after heating at 350 °C, reaching >85% of BET and micropore characteristics. Parameters referring to the external area remain close to the maximum.

Acid-resistance test of the Na–X produced from fly ash showed that this phase is extremely unstable. Treating with 20% H$_2$SO$_4$ solution (100 g/dm$^3$ S/L ratio) caused complete and instant dissolution of Na–X zeolite. After 24 h of heating at 700 °C, Na–X recrystallizes into carnegeite (PDF card 11-0220).
5. Discussion

5.1. Crystallization

Classical regularity of X zeolite synthesis, described by Breck (1974), can be extended not only to low-temperature, but also to compositionally unstable material. Na–X phase crystallizes from aluminosilicate substrates of wide range of composition, including F class fly ash.

Experiments showed that the synthesis of Na–X phase at room temperature depends strongly on (OH)$^-$ activity. The crystallization takes place when (OH)$^-$ activity is at least 40 mmol (OH)$^-/1$ g ash. Cl$^-$ ion in solution acts as inhibitor of the reaction, instead of enhancing it, as predicted by “salt effect” (Cooks and Pope, 1995). Crystallization follows the dissolution of substrates limited by an equilibrium between (OH)$^-$ and the dissolved phase — this is evidenced by the fastest Na–X synthesis that occurs while high S/L ratio (67 g/dm$^3$) was used. High S/L ratio allows for quick equilibration between solution and ash components, sufficient for Na–X nucleation and crystallization. Quartz and mullite seem to persist during reactions – their activation energies at low-temperature conditions are probably so high, that they do not influence significantly the equilibrium state. Thus, the aluminosilicate glass dissolution rate controls the availability of substrates for the synthesis, as earlier noticed by Querol et al. (1997). Too high S/L ratio stops synthesis because of the lower (OH)$^-$ activity; higher concentration of (OH)$^-$ is hard to apply due to the limited NaOH solubility. Lower S/L ratio causes longer approach to the equilibrium state (“temporary semi-open system”), but can provide more substrates, if (OH)$^-$ activity is high; this leads to a more efficient synthesis in the longer time. Depending on requirements, in order to enhance the efficiency of reaction, the higher S/L parameter should be applied to shorten reaction time or the lower S/L ratio, if the most Na–X abundant material is needed and the time of reaction does not matter.

Zeolite X shows low Si/Al ratio. This provides very high CEC values (exchangeable cations outside framework). Complying a minor part of Al as exchangeable

Fig. 4. BJH adsorption and desorption pore size distributions (Å), in $V/D \times 10^4$. 
cation, framework Si/Al ratio is slightly higher than Si/Al ratio measured in a whole crystal: 1.14 for EcnT 3, 1.20 for Eck 52, and 1.45 for EcnT 8 sample. CEC values of these samples calculated upon framework Si/Al ratios are 6.83, 6.60, and 6.11 meq/g of dehydrated material, respectively. Breck (1974) measured similar value for pure, well-crystallized phase X (6.40 meq/g at Si/Al ratio 1.25), and determined also CEC for the hydrated form (4.70 meq/g). Taking the last value as reference, CEC values determined in the present study confirmed up to 55% of the Na–X phase content, estimated by XRD.

5.2. Textural properties

Increase of the N2-BET surface area clearly depends on the development of microporous texture ($R^2=0.99$, Table 4). Micropore volume and area strictly follow the Na–X content (Fig. 5) but mesopore volume and surface area calculated from the BJH adsorption algorithm are independent on the zeolite content. There is the outlier within regression lines of $V_{mic}$, $S_{mic}$ ($R^2=0.98$, both regressions are linear each other) and $S_{BET}$ ($R^2=0.97$) vs. Na–X content of the sample EcnT 8. The zeolite content seems to be underestimated or there is a microporous phase other than the Na–X, which increases textural parameters of this sample. XRD patterns in Fig. 6 evidence the trace amount of additional phase (probably EMT type) in EcnT 8 sample and in EcnT 6. Interparticle space of the zeolite crystals and residual fly ash components produce hysteresis loops characteristic at such granular materials (Leofanti et al., 1998). The EcnT 5 and EcnT 6 show larger external surface than other samples; for the EcnT 5 such difference is likely produced by a domination of sizes in the range from ca. 50 (BJH adsorption) to 90 (BJH desorption) Å. Sample EcnT 6, which follows strictly Na–X content vs. $V_{mic}$ relationship, shows enlarged $S_{BET}$ value due to increased value of $S_{meso}$.

The lower temperature of pre-heating is insufficient for complete desorption of microporous cavities, providing 15% decrease of expected value. The mesoporous and external surface areas stay almost stable while pre-heating in vacuum was done in the lower temperature.
The isotherms of zeolitic samples show uprise at the highest values of $P/P_0$ and the desorption curves parallel to the adsorption ones — with sudden drop in 0.4–0.5 $P/P_0$ range. These are characteristic artifacts of alkaline-treated zeolites. Tensile strength effect is also responsible for the BJH desorption PSD uniform shape at ca. 40 Å (Groen et al., 2003).

5.3. CEC and EGME retention

The CEC values measured with $[\text{Co(NH}_3\text{)}_6]\text{Cl}_3$ increase with the perfect linearity following to the development of micropore texture (CEC vs. $V_{\text{mic}}$ and $S_{\text{mic}}$, $R^2=0.99$). Due to the great share of $S_{\text{mic}}$ in the total surface area, the linearity for CEC vs. $S_{\text{BET}}$ and $S_L$ may seem to be the derivative of CEC vs. $S_{\text{mic}}$. But $R^2=0.99$ for CEC vs. $S_{\text{BET}}$ exists even for samples with distinctive $S_{\text{ext}}$ values. Thus, it is clear that CEC depends on the total surface area, including external one. The CEC of sodalite, which pore diameter is ca. 0.23 nm, shows only small value related to the external surface, but conventional methods reveal total CEC available for small non-complex cations. The measurement of CEC for two samples rich in Na–X phase using small cations results in the significantly higher values. The difference reflects the molecular sieving properties of Na–X and shows more or less the CEC of pure sodalite. Cation $[\text{Co(NH}_3\text{)}_6]^{3+}$ can exchange only extra-framework sites inside 12-ring channels and cages (SBU exchange positions), while small cations enter both FAU channels and cages as well as sodalite cages building FAU structure. Fig. 5 presents valid but less perfect correlation between CEC and Na–X content ($R^2=0.975$). Apart from the possible inaccurate determination of Na–X content, departures from linearity may originate from the difference in amount of available 0.74 nm channels within FAU structure.

The results of EGME retention show effect of preheating temperature parallel to insufficient dehydration before nitrogen adsorption: samples preheated at 400 °C adsorb more EGME than ones preheated at 250 °C. Thus EGME$_{400}$ values should be considered as the true EGME retention. The temperature 400 °C is sufficient for the complete dehydration and safe to avoid recrystallization of Na–X into other phase (Breck, 1974), while storage in vacuum after 250 °C heating does not dehydrate zeolites completely. Mass of retained EGME (Table 4) linearly correlates with micropore volume and surface area ($R^2 = 0.96$), as well as $S_{\text{BET}}$ and $S_L$ ($R^2 = 0.97$; Fig. 7). The retention of EGME does not correlate with $V_{\text{meso}}$ or with $V_{\text{SP}}$ (micropores+mesopores), however the incomplete dehydration (preheating at 250 °C) allows for the partial EGME-water substitution in micropores and for the adsorption on the available mesopore surface area. The dimension of cylindrical micropores of the Na–X phase is ca. 43 Å$^2$, thus EGME retention inside the structure may be considered as a capillary infilling as well as surface adsorption (Quirk and Murray, 1999). Sample EcnT 6 clearly adsorbs more EGME than textural properties suggest. Such inconsistence may come from an additional phase with large TSA, unavailable for N$_2$ molecules. However, this sample also shows excess of EGME retention vs. CEC, what suggests an existence of a phase of significantly lower layer charge (i.e. smectite) or a molecular sieve which blocks an access of complex ion and gas molecule (zeolite of the narrower micropores, e.g. clinoptilolite — see Tiller and Smith, 1990). Excluding obvious surface adsorption within the mesopores range, the packing ratio in micropores is one EGME molecule per 16.13 Å$^3$ ($R^2 = 0.98$). Calculating directly from the total surface area of samples, EGME molecule occupies ca. 41 Å$^2$, using the BET algorithm and ca. 52 Å$^2$ for the Langmuir equation. Both values are very close to those given by Carter et al. (1965) for EGME on smectite surface (52 Å$^2$) and by Tiller and Smith (1990) for various minerals.

It is clear that EGME retention linearly depends on the Na–X content (Fig. 5). Complying underestimated zeolite percentage in the sample EcnT 8 (excluding outlier), the linear correlation ($R^2$) is 0.97. Such correlation
does not take place while calculating EGME retention after preheating at 250 °C; Na–X content is not the predominant factor.

The EGME retention is linear with respect to the CEC (Fig. 8); these two values correlate but may be independent of each other. Both values increase

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Fig. 7. Relationships between volumes (upper plots) and surface areas (lower plots) of studied samples, and their EGME retention after preheating at 400 °C (left) and CEC values (right). Valid linear correlations are marked with solid (black and white) symbols.

Fig. 8. Correlation of EGME retention with CEC measured by \([\text{Co(NH}_3)_6]^{3+}\) cation (left). Right plot: relationship of EGME occupation area (in \(\mu\text{mol/m}^2\)) vs. charge density (\(\mu\text{eq/m}^2\)).
following the crystallization of the Na–X phase. Beside the development of microporous structure, other factors may subordinately control the variability of EGME retention. EGME is a polar molecule, which adsorption depends on surface available for EGME molecules, the charge density and hydration energy and the actual stage of cations adsorbed on measured surface (Quirk and Murray, 1999). The type of cation compensating anionic charge is predominantly Na, but the remaining cations occurs in various proportions providing not uniform hydration stage. The packing ratio of adsorbed organic molecules inside micropores varies according to the type of cation occupying exchangeable positions in zeolite (Joshi et al., 2001). Moreover, the framework Si/Al ratios vary among studied samples. Positive correlation of the TSA measured with EGME or water retention with the CEC or layer charge was observed so frequently during smectite and illite–smectite studies (i.e. Bigorre et al., 2000) that the correction for CEC-dependent adsorption can be considered. Total charge density of zeolites is several folds higher than of smectites and vermiculites (1.0 density of zeolites is several folds higher than of smectites and vermiculites). What supports opinion about possible dependence of the EGME retention of zeolites on the charge density value. The charge density calculated directly as CEC/$\text{S}_{\text{BET}}$ gives false results for raw fly ash and samples poor in Na–X phase. Cation $[\text{Co(NH}_3\text{)}_6]^{3+}$ can measure the CEC of organic components in fly ash, opposite to EGME, which does not interact significantly with organic matter (Tiller and Smith, 1990; Bigorre et al., 2000), but is retained in the intergranular space and glass surface. Excluding raw fly ash and ECK 60, the plot of EGME occupation area vs. charge density inside 12-fold channels positions and at external surface (Fig. 8) reveals no clear trend.

6. Conclusions

Zeolite Na–X can be easily synthesized in a big quantity from fly ash, without providing heat energy for fusion or the conventional synthesis. The storage in NaOH solution for several months is necessary to obtain material of ca. 50% rich in zeolite, of mass close to the initial mass of fly ash. The most efficient reaction takes place while $\text{(OH)}^{-}$ activity is 0.1–0.15 mol $\text{(OH)}^{-}/1$ g of ash and at S/L ratio from 33 to 67 g/dm$^3$. Higher S/L value accelerates the approach to the dissolution–crystallization equilibrium. The presence of $\text{Cl}^-$ ion in solution inhibits the reaction.

Synthesized at various conditions, the Na–X zeolite shows variability of framework Si/Al ratio in the range of 1.14 to 1.45. Zeolite content controls the micropore volume and the surface area of the samples, limiting EGME retention (from 14.5 to 136.4 mg/g) and CEC values. Temperature of pre-heating is a crucial factor for the amount of retained EGME. Insufficient dehydration at 250 °C (as in conventional procedure for clays) does not allow EGME molecules to enter whole microporous structure. Pre-heating at 400 °C causes EGME adsorption on all available surfaces. EGME molecule occupation area is ca. 41 Å$^2$, using BET algorithm and ca. 52 Å$^2$ for Langmuir equation. Calculating package ratio for infilling micropores by EGME, one EGME molecule occupies ca. 16 Å$^3$. Simple procedure of EGME retention can be successfully used to determine microporous texture of X zeolite available to organic molecules. Total CEC value of materials rich in Na–X zeolite is ca. 2.5 meq/g (including sodalite cages) and depends on cation used in measurements. CEC measured using $[\text{Co(NH}_3\text{)}_6]^{3+}$ cation exhibits only positions inside FAU 12-fold channels, attaining almost 1.2 meq/g, and follows linearly the development of microporous texture. Materials produced from raw fly ash (15.3 m$^2$/g) reach maximum $\text{N}_2$-BET surface area at 344 m$^2$/g.

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