Synthesis of Pure Na–X and Na–P Zeolite from Acid-Extracting Residues of CFB Fly Ash by a Single-Step Hydrothermal Method

Jingjing Zou, Chunbin Guo, Cundi Wei, Fangfei Li* and Yinshan Jiang*

Key Laboratory of Automobile Materials, Ministry of Education, Department of Materials Science and Engineering, Jilin University, 5988 People’s Avenue, Changchun 130025, People’s Republic of China

Acid-extracting residue of circulating fluidized bed (CFB) fly ash is still underutilized leaving disposal problems. In fact, high silica content inside this material opens a possibility to become a potential zeolites precursor. In this study, fine particles of acid residues have been reused to prepare zeolite Na–X and Na–P with high purity and intensity. Acid residue was used to synthesize zeolite Na–X and Na–P using a single–step hydrothermal process. The effects of crystallization time, temperature and sodium hydroxide concentration on the end products were investigated. The results revealed that crystallization time and temperature determined whether or not zeolite Na–X or Na–P was formed. The zeolites were characterized in terms of their mineralogical composition, morphology, and fourier-transform infrared spectroscopy.


(Received December 14, 2015; Accepted February 9, 2016; Published April 8, 2016)

Keywords: coal fly ash, acid residue, sodium–X zeolite, sodium–P zeolite, hydrothermal method

1. Introduction

Coal-fired power plants are producing larger quantities of fly ash annually1–3). Large amount of fly ash is being disposed of in opened landfill sites, creating problems with air, groundwater and soil pollution with harmful elements4–6). Recently, acid extracting alumina from fly ash becomes the main development trend. However, the residue after extracting the alumina presents a new problem: that of solid waste disposal.

The significant content of acid residues is silica, alumina and unburned carbon. Naturally, acid residues contain less chemical components than fly ash or other waste solids, thus these materials produces with lower unrelated component concentration other than silica and alumina. And the amorphous aluminosilicate has the higher activity than the crystalline phase, thus acid residue could easily transfer into pure zeolite at lower alkalinity. Therefore, synthesizing zeolites is an environmental friendly application of the solid waste disposal of acid residues.

In recent years, several strategies in zeolite synthesis using solid wastes as the silica–alumina source have been proposed in order to obtain a pure zeolite other than a mixture of zeolitic materials7–10). The methods are widely recognized as single-step and two-step hydrothermal. In the single-step hydrothermal processing, crystal variety in the end zeolite products become the major drawbacks of this method11–13). In the two-step hydrothermal processing, only the liquid alkali extracts from fly ash were used in the production of the zeolite, which leaves behind yet another solid waste product and gives a very low production yield14–16). Previously, only one type of pure zeolite was utilized in the investigation and it is not clear whether the same methodology was suitable to synthesize two different kinds of pure zeolites from the same raw material.

In this study, we find an effective way to deal with million tons of acid residues and simultaneously finding a cheap raw material to prepare zeolite efficiently. A single-step hydrothermal preparation method for pure zeolite Na–X and Na–P using acid residues at lower alkalinity is developed. The production cost of zeolite could be reduced tremendously using this method on account of the low cost of acid residues and high yield. The effects of the reaction temperature, thermal treatment time, NaOH concentration, and liquid to solid ratios on zeolite quality were studied. Moreover, a purer precursor is always preferred to ensure the quality and reproducibility of the end products using the predetermined zeolitization conditions. Additionally, it is environmentally friendly economically efficient.

2. Experimental Section

2.1 Materials

The coals from the Jungar coalfield in Inner Mongolia of China are unique because the raw coals are highly enriched in boehmite. Both the fly ash and the acid-extracting residues of coal fly ash were collected from the proving ground of Jungar coal-fired Power Plant in Inner Mongolia of China. All the boilers used a same coal; the limestone was always added to the circulating fluidized bed (CFB) during the circulating combustion process. The combustion temperature in the CFB boiler was always lower than that in the conventional pulverized coal (PC) boiler. Therefore, the fly ash has the higher activity than other solid wastes. The samples of pristine fly ash were collected from the economizer of the power plant with electrostatic precipitators during the operation of the boilers because the flue gas along with fly ash was disposed at this power plant. The fly ash was transported to a factory for extracting alumina. Because of alumina extraction yield could reach 80%, various batches of acid residues contain different amount of the silica and alumina content in the acid residues. So we collected the acid residues for different times. About 10 kg acid residues were collected each time. The acid residues were stored immediately in PVC zip lock bags to prevent contamination. Prior to use, the acid residues were washed, then the acid residues were carried out to remove the unreacted acid and later filtered. The filtered sample was

*Corresponding author, E-mail: lifangfei_jlu@163.com
dried at 105°C in an oven and was used for synthesizing the zeolite Na–X and Na–P. The corresponding chemical components are shown in Table 1, which determined at The First Geological Survey, Changchun, Jilin, China. Three replicates of each fly ash samples were conducted and the average data were reported. The uncertainty was estimated to be within ±3% for the chemical components analyzed.

As can be seen in Table 1, main chemical components of acid residues are unburned carbon, alumina and silica, the sum of alumina and silica account for more than 70 wt.% in acid residues. This unique chemistry characteristic makes a suitable raw material for zeolite synthesized.

Figure 1 shows the XRD pattern of acid residue. The peaks at 2θ-values of 26.639° can be indexed to quartz. The broad structure that appears over the range 15° to 25° indicates that amorphous silica and carbon phases are present in the acid residue. The amorphous silica has higher activity than the crystalline silica. This is reason why the zeolites could be synthesized from acid residues at lower alkalinity.

Sodium hydroxide is the obtained from the Beijing chemical reagent factory. All other chemicals are analytical grade reagents and commercially available.

### 2.2 Zeolite X preparation

For precursor preparation, 2.7 g of aluminium hydroxide and 7.5 g of sodium hydroxide were mixed with 60 ml deionized water. Under magnetic stirring at 50°C, the aluminium hydroxide dissolved and the solution became clear. Then the sodium aluminate solution was mixed with 12.7 g sodium water glass for preparing the reaction mixture with Si/Al molar ratio of 2. After 0.5 h stirring, the Na–X precursor preparation can be completed.

Synthesis of zeolite Na–X took a single-step process. All chemicals were directly used as received without any further purification. Typically, sodium hydroxide was dissolved in 50 ml deionized water. Then 3 g of acid residue and the solution were placed in reaction kettle, 3 ml precursor was put into the solution and heated at 70–120°C for 6–24 h. The final procedures were filtering, washing and drying of the precipitates. The effects of the reaction temperature, thermal treatment time and sodium hydroxide concentration on zeolite quality were studied. For the ease of identification, zeolite sample names follow this rule: ZXXTytz which x is the sodium hydroxide concentration in the parent solution (%), y is the hydrothermal temperature in °C and z is the hydrothermal time in hours.

### 2.3 Zeolite P preparation

In the synthesis of zeolite Na–P, a similar process was taken, sodium hydroxide was dissolved in 50 ml deionized water. Then 3 g of acid residue and the solution were placed in reaction kettle, but the hydrothermal temperature was carried out at 110–150°C for 6–10 h without using precursor. The final procedures were filtering, washing and drying of the precipitates. The zeolite sample names follow this rule: ZPXYtz which x is the sodium hydroxide concentration in the parent solution (%), y is the hydrothermal temperature in °C and z is the hydrothermal time in hours.

### 2.4 Characterization of materials

The crystalline phases in the acid residues and synthesized samples were characterized using XRD (DX-2700, Dandong Fangyuan, Dandong, China) with Cu Kα radiation. The acceleration voltage was 35 kV, and the electrical current was 25 mA. The scans ranged from 5° to 50° at 5°/min. FTIR spectroscopy (Nexus-6700 spectrometer equipped with a FTIR-grade KBr beam splitter, Thermo Electron Corporation) was conducted on the samples at room temperature. The spectra were acquired in the range of 4000–400 cm⁻¹ wave-number with 2 cm⁻¹ resolution. The background spectrum for KBr was also recorded under the same conditions for reference. Morphology of acid residues and the products were examined by scanning electron microscope (SEM).

### 3. Results and Discussion

#### 3.1 The effect of hydrothermal time

In here, the influence of time variation on the zeolite crystallization during hydrothermal treatment was investigated. In the case of zeolite Na–X preparation, lower hydrothermal temperature required longer processing time. Figure 2 and 3 shows the XRD pattern and SEM images of Na–X samples obtained at different reaction times. As can be seen from Fig. 2, the shortest preparation time of ZX6T100t3 shows clearly broad amorphous peak in region between 10° and 25° indicating the presence of an abundant amorphous phase and no zeolite phase was already nucleated. And the SEM image of this sample (Fig. 3a) displays irregular shape which is accordance with XRD results. By 6 h hydrothermal treatment at 100°C, flake-like texture with irregular shapes can be observed for ZX6T100t6 sample in Fig. 3(b). Although XRD pattern in Fig. 2 of this sample only exhibit very low broad peak of amorphous phase in 2θ = 20–35°, the Na–X peaks intensity are lower than the longer prepared sample of

---

<table>
<thead>
<tr>
<th>sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>55.74</td>
<td>22.18</td>
<td>2.06</td>
<td>3.21</td>
<td>0.24</td>
<td>1.47</td>
<td>0.13</td>
<td>0.55</td>
<td>0.62</td>
<td>13.8</td>
</tr>
<tr>
<td>residue</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Composition of the acid residue samples/wt%.
ZX6T100t12 indicating incomplete crystal growth. After 12 h crystallization, a large number of loosely packed zeolite crystals were produced, some of which exhibit an octahedral morphology (Fig. 3(c)). Further increasing the curing time, the concentration of zeolite Na–X was getting lower as indicated by the decrease of diffraction intensity and also the diffraction pattern of sodalite was appeared after 24 h treatment. This is because the sodalite has more stable structure than zeolite Na–X.

Note that the zeolites can be divided into seven groups where each group unites the zeolites with the same connections between TO₄ (T refer to Al or Si) tetrahedral¹⁴,¹⁷–²⁰. The primary structural units are the SiO₄ and AlO₄ tetrahedra, while these condary units are combined from these tetrahedral. The structure of the zeolite X is formed by the simple β-cages which are composed of 24T-atoms. Therefore, the structural formation of Na–X zeolite requires longer crystal- lization time due to its more complex and larger polymeric silicate units (D₆R) and sparser structure. The bonds between the β-cages appear through the double T₆-rings (D₆R), and the cavities in the zeolite framework are formed by the simple T₁₂-rings. The Na–A zeolite was the main crystalline phase during the shorter crystallization time. Prolonging the hydrothermal time, the β-cages are connected through the simple T₆-rings directly and then the sodalite is formed.

Meanwhile, preparing pure zeolite Na–P was a lot easier than zeolite Na–X using acid residues. Pure zeolite Na–P can be always prepared in relatively short treatment time. At 130°C of crystallization temperature, zeolite Na–P can be fully crystallized within 6 h with small particle size (<7 μm). Figure 2 shows zeolite Na–P particles which have spherical shape with rough surface. This typical particle shape is consistent with a previous report employing similar preparation method²¹–²³. When the curing time was lengthened into 8 h, the pure phase of zeolite Na–P was still preserved thus no change in crystal structure. Comparing SEM image between Fig. 3(d) and (e) and diffraction pattern in Fig. 4, it can be said that increasing the crystallization time will only grow the particle size without any significant structural changes. The less treatment time dependency for zeolite Na–P nucleation is in good agreement with previous report²⁴,²⁵. It is interesting to note that increasing the crystallization time more than 10 h for zeolite Na–P could decrease the intensity for zeolite Na–P and increase the intensity for sodalite and analcite, which are consistent with the SEM results.
3.2 The effect of hydrothermal temperature

The heat treatment temperature effects become more stringent in hydrothermal reaction especially for preparing pure zeolite Na–X. As shown by diffraction pattern in Fig. 5, the crystallinity of zeolite Na–X sample gradually increased while crystallization temperature was raised from 80°C to 100°C. The higher the temperature, the bigger the energy and the shorter the crystallization time will be\(^{26}\). At the same time, the higher temperature can enhance concentration of chemical group in sol, and it is also beneficial to crystalline. However, 110°C crystallization results in sample with mixture phases of zeolite Na–X and sodalite. Further increasing the crystallization temperature up to 120°C, the peak intensities associated with zeolite Na–X disappeared. The sodalite and zeolite Na–P were seemed to be formed by the conversion of metastable Na–X zeolite into more stable zeolite phase\(^{27}\).

Zeolite Na–P is more stable than zeolite Na–X, thus higher curing temperatures or longer curing time allow the formation of more stable state of this zeolite type without any precursor\(^{28}\). It can be seen that no crystalline Na–P zeolite was detected in the ZP4T90t6 sample (Fig. 4), and the broad peak corresponding to amorphous silica disappeared which means most of the amorphous silicon dissolved in the solution. Further increasing the curing temperature, the concentration of zeolite Na–P was getting higher as indicated by the increase of diffraction intensity and also the diffraction pattern of analcime was appeared after 150°C. The particles of analcime prepared in a microwave field have regular octahedral or polyhedral crystal morphology as well as good crystallization as shown in Fig. 6a.

It is interesting to note that higher treatment temperature creates larger particle size in a particular curing time for both zeolite types. The effect of temperature change on particle size can be observed in SEM micrographs by comparing Fig. 2 and Fig. 6 for Na–X and Na–P.

3.3 The effect of sodium hydroxide concentration

The effect of sodium hydroxide concentration on the zeolite crystallization by a two-step hydrothermal method has been previously studied\(^{28,29}\). For instance, increasing sodium hydroxide concentration in the reaction mixture enhances the kinetic of the zeolite nucleation and crystal growth. For some reasons such as limiting unwanted compound formation and economical consideration, the use of large amount of alkali to optimally synthesize zeolite is not always applicable. Hence, this effect may become handy for the production of zeolite using acid residues by a single-step hydrothermal method.

Compare Fig. 1 and Fig. 7, XRD result shows that Si–O bonds are high activity in the acid residues. Under the alkalinity condition of 4% at 100°C for 3 h, most of Si–O bonds dissolve in the solution and little Al–O bonds dissolve. And the Si/Al molar ratio is much high than 2 in the solution. It is easier to form zeolite Na–P rather than zeolite Na–X. Increasing the alkalinity to 6% and 9%, most of Al–O bonds in the
acid residues dissolved and the total amorphous phase is approximately changed to the total crystalline zeolite Na–X phase. Further increasing alkalinity to 12%, the zeolite Na–X is converted into the Na–P phases. That may be because the precursor dissolved under the condition of high alkalinity. As mentioned earlier zeolite Na–P is more stable and faster to be formed than zeolite Na–X. However, the zeolite Na–P was converted into analcime when the alkalinity was increased to 9% at 130°C. From XRD analysis and SEM images (Figs. 7 and 6), it is clear that increasing alkalinity (from 6% to 12%), the crystallinity increases and the crystals size decreases. Similar results were obtained by S. Bosnar and W. Chandra. However, the increase of alkalinity will result on the reduction of the production yield due to faster zeolite dissolution rate in a higher alkaline condition.

3.4 Spectroscopic analysis

Spectroscopic method provides useful information about the structure of zeolites and other functional group that may be present during synthesis and post treatment. In here, infrared spectroscopy has been performed for selected samples to tract the zeolite formation from the early stages in the synthesis.

The IR spectra of absorption bands due to the formation of structural unit during zeolite crystallization are shown in Fig. 8. A summary of vibration bands of zeolites was reported by Breck. The broad, strong band around 3465 cm\(^{-1}\) was due to the stretching vibration of H\(_2\)O and structural OH groups, indicating the presence of surface hydroxyl groups and physically absorbed water. The acid residues spectra shows typical amorphous alumina silicate which has two broad bands peaked around 1100 and 465 cm\(^{-1}\) that correspond to T–O–T stretching and T–O bending modes (T refer to Si or Al atom). The vibration at 814 and 596 cm\(^{-1}\) is assigned to the Al–O stretch and the stretching modes involving mainly tetrahedral atoms. The absorption bands at around 1100, 814 and 460 cm\(^{-1}\) weaken with time, indicating the amount of amorphous material in the sample gradually decreases (acid residue and ZX6T100t4). This is due to the amorphous phase dissolved in the sodium hydroxide solution. The bands for amorphous phase completely disappear and only pure zeolite absorption bands are observed in the 12 h crystallized sample (ZX6T100t12). For the 12 h sample, the existences of zeolite X phase can be observed by a strong vibrational band at 995 cm\(^{-1}\) correspond to Si–O–Si asymmetrical stretching. The FT-IR results are in good agreement with the XRD results. In addition, the appearance of the new band after 12 h crystallization at 560 cm\(^{-1}\) indicates the formation of double six rings (D6R) which is the main structural subunit of zeolite X.

Note that most of the bands related to zeolite X are sharper for the lower temperature sample suggesting for a better crystal structure and purity. In contrast, the two zeolite P samples with different synthesis temperature exhibit no significant differences of IR absorption spectra in term of intensity and frequency.

4. Conclusion

Pure zeolite Na–X and Na–P have been successfully prepared from acid residues as the silica and alumina sources by a single-step hydrothermal treatment. The effects of crystallization time, crystallization temperature and sodium hydroxide concentration in the synthesis zeolites on the crystalline end products were investigated. These results indicated that well-developed zeolite Na–X could be obtained after 12 h of hydrothermal treatment at 100°C and well-developed zeolite Na–P could be obtained after 6 h of hydrothermal treatment at 130°C, while the high crystallization temperature results in hydroxyl sodalite and analcime developed. Furthermore, the sodium hydroxide concentration was found to play a significant role in the zeolite structure and composition. Optimization of sodium hydroxide concentration and shortening of synthesis times to 12 h and 6 h resulted in highly crystalline Na–X and Na–P without any alien phase. Higher purity and smaller particle size of zeolite were easier to be prepared in a low zeolitization temperature.

Acknowledgment

The authors are grateful for the financial support of the National Natural Science Foundation of China (grant No.41472035 and grant No.51304080).

REFERENCES

219.