In-situ Synthesis of NaY Zeolite with Coal-Based Kaolin

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Abstract: NaY zeolites were in-situ synthesized from coal-based kaolin via the hydrothermal method. The effects of various factors on the structure of the samples were extensively investigated. The samples were characterized by N₂ adsorption, XRD, IR and DTG-DTA methods, and the results show that the crystallization temperature and amount of added water play an important role in the formation of the zeolite structure. The 4A and P zeolites are the competitive phase present in the resulting product. However, NaY zeolites with a higher relative crystallinity, excluding impure crystals and the well hydrothermal stability, can be synthesized from coal-based kaolin. These zeolites possess a larger surface area and a narrow pore size distribution, and this means that optimization of this process might result in a commercial route to synthesize NaY zeolites from coal-based kaolin.

Key words: coal-based kaolin, NaY zeolite, in-situ hydrothermal synthesis

1. Introduction

Coal-based kaolin is simultaneously generated with coal, and it has become a pressing waste disposal problem because it constitutes up to 10%–20% of the total coal yield [1]. It is essential to develop an effective method to exploit this substance and mitigate the environmental burden on coal mining enterprises and coal sites.

Of interest is that kaolin possesses the Si-O or Al-O octahedral and tetrahedral sheets which create a charge imbalance in the 1:1 layer. There is very little substitution in the structural lattice, and thus it has a minimal layer charge and a low exchange capacity. Its surface area and absorption capacity is relatively low, but many of the properties of kaolin can be improved by proper treatment. The main applications of kaolin are for coating paper, functional fillers, plastics, rubber, glass fiber and other materials used in fine chemical engineering. Unfortunately, all of these materials are low value-added products. It is necessary to create a suitable method to utilize kaolin in an environmentally friendly manner that has high commercial value.

Zeolites are widely used in adsorption, separation, catalysis, ion exchange and other processes. Some groups [1–6,11] have already studied the preparation of various zeolites from kaolin or other fly ashes and have made great progress in synthesis of 4A, mordenite, X, Y zeolites, etc. The NaY zeolite is a parent catalyst in catalytic cracking of hydrocarbons and petrochemical processes. In-situ synthesis of NaY zeolites from coal-based kaolin might be the best way to chemically utilize kaolin resources in the future. Although coal-based kaolin is actually a type of natural clay, the Si-O or Al-O octahedral and tetrahedral sheets are inactive to modification under moderate conditions. The key to this process is how to activate kaolin and subsequently hydrothermal synthesis.

In our experiment, NaY zeolites were in-situ synthesized in a hydrothermal system. The effects of various parameters on the properties of the resulting products were systematically investigated. The results prove that pure NaY zeolites with high relative
crystallinity can be effectively synthesized.

2. Experimental

2.1. Synthesis

The kaolin was activated by the addition of sodium hydroxide at 1,123 K for 3 h. The active sample and a certain amount of Na$_2$SiO$_3$, which acts as a reinforcing silicon source, were dispersed in deionized water with gentle stirring for 1 h. Then the mixture was aged at room temperature for a desired period to form gel slurry. The gel slurry was transferred to the stainless-steel autoclave with a Teflon seat to hydrothermally crystallize. Subsequently, the precipitate was filtered, repeatedly washed with deionized water and dried at 373 K overnight.

2.2. Characterization

The synthesized samples were characterized with a nitrogen adsorption analyzer, X-ray diffraction (XRD), infrared spectroscopy (IR), and thermal analysis (TG-DTA).

The nitrogen adsorption of the samples was performed on a Micromeritics 2010 apparatus at liquid nitrogen temperature (77.3 K), and the samples were degassed at 673 K for 4 h prior to adsorption analysis. The micropore distribution and mean pore size were calculated from the gas adsorption using the Horvath-Kawazoe equation, with relative pressure ($p/p_0$) below 0.01. A T-plot calculation was conducted to quantitatively analyze the area and total volume ascribed to micropores.

XRD for structural analysis of the samples was carried out with a Rigaku Dmax-3A X-ray diffractometer using Cu $K_\alpha$ radiation with a tube voltage of 40 kV, a tube current of 30 mA and scanned from 5°–39° (2θ). The reference sample was standard NaY.

Infrared spectra were recorded with an IR Spectrum One made in the US. The resolution was 0.2 cm$^{-1}$, and the sample was pressed with a certain amount of KBr into disks 10 mm in diameter and 0.1 mm thick.

Thermal analysis was carried out using a CDR-1 thermometer. Measurements were performed in a nitrogen flow with a heating rate of 5 K/min.

3. Results and discussion

3.1. The structure of coal-based kaolin

The crystal structure of coal-based kaolin is shown in Figure 1. Evidently, its dominant component is Al$_2$(Si$_2$O$_7$)(OH)$_4$, doped with a small quantity of Fe and trace amounts of Ni, Mn, Cu and Ti. In addition, very little quartz phase exists. Of interest is that this kaolin possesses the Si–O or Al–O octahedral and tetrahedral sheets, which creates a charge imbalance in the 1:1 layer and might be a potential raw material to synthesize zeolites. Unfortunately, the Si–O and Al–O structures in coal-based kaolin are inactive to modification or activation. This means that it is difficult to directly synthesize zeolites, and the kaolin must be pre-activated to change this inert structure [7]. The most effective way to activate such natural clay is to thermally transform the inert phase into the active phase at elevated temperatures in the presence of alkali hydroxide, which might also be useful in subsequent hydrothermal synthesis because the commercial NaY zeolites are synthesized at the basic environment. Herein, the kaolin is treated with sodium hydroxide at 1,123 K.

Further investigation shows that crystal transformation of the coal-based kaolin actually occurs upon thermal activation in the presence of the sodium hydroxide. Under the basic environment, the inert skeletal structure of coal-based kaolin was converted into activated silicate and aluminate, which might be soluble in acidic or basic aqueous solutions. In other words, this coal-based kaolin might be the optimum feed to the in-situ synthesis of NaY zeolites.
3.2. **In-situ synthesis of NaY zeolites from coal-based kaolin**

When coal-based kaolin is thermally activated by the addition of sodium hydroxide to form an active Al-O structure, NaY zeolites can be *in-situ* synthesized by the hydrothermal method. The problem is that the Si/Al ratio in coal-based kaolin is nearly unit and it is too low to directly synthesize Y zeolite. Some silica source must be made up to be suitable for direct crystallization. Sodium silicate was introduced as a reinforcing silicium source prior to hydrothermal synthesis. As shown in Figure 2, the XRD pattern of the synthesized zeolite is a typical crystal structure of a NaY zeolite, which exhibits that it is feasible to *in-situ* synthesize NaY using the hydrothermal method from activated coal-based kaolin.

![Figure 2. XRD pattern of in-situ synthesized zeolites by hydrothermal synthesis](image)

Upon *in-situ* hydrothermal synthesis, the active Si and Al species dissolve in the alkali solution and form the supersaturated solution. They react with each other and reconstruct to form some ring-like structures that are the basic units for zeolite construction [2]. At crystallizing conditions, they form another phase, which might be thermodynamically metastable. It is this reconstruction and recrystallization of Si and Al species that results in the formation a Y-type zeolite skeleton. To optimize the *in-situ* synthesis conditions of coal-based kaolin, we extensively investigated many operating parameters.

3.3. **Effect of crystallization temperature on zeolite formation**

Crystallization temperature is an important parameter in the hydrothermal synthesis of certain zeolites. It might influence the growth velocity, interface reactions of different faces or directions and diffusion rates of active crystal particles. Specific surface area was tentatively introduced to indicate the properties of synthesized Y zeolites and optimize the suitable crystallization conditions because the NaY zeolite with higher crystallinity and uniform structure usually has a higher surface area, especially inner surface area or micropore area. Various surface areas of synthesized NaY zeolites are depicted in Figure 3, which shows that the crystallization temperature plays an important role in the physical properties of NaY zeolites. The specific surface area, micropore area and external area of the samples prepared in the low temperature domain increased with the crystallization temperature and all reach a maximum at 380 K. Then they decreased when the temperature is...
above 380 K. This implies that the lower temperature realm is not only beneficial to formation of the crystal nucleus but also to its hydrothermal stability, which results in the ratio of formation velocity to growth velocity of crystal nucleus increasing. It also suggests that lower temperatures are preferable for the growth of crystal faces, and higher temperatures are positive for interface diffusion. This shows that crystallization at lower temperatures is feasible to synthesize metastable Y zeolite, whereas higher temperatures can synthesize even condensed and thermodynamically stable species. It is noted that the particle size of the resulting product is dramatically reduced and the surface area is accordingly increased at lower temperatures.

From the surface area of the samples synthesized at different temperatures, there must be several crystalline phases existing in the resulting products during the hydrothermal synthesis, which can be shown by the XRD data. The diffraction lines of the XRD patterns illustrate that the 4A and NaP zeolites ($Na_6Al_6Si_{10}O_{32}•12H_2O$) are the competitive phase present in the resulting products. From reaction kinetics, the low temperature is beneficial to the formation of 4A crystalline seeds, but the formation rate of NaY crystalline seeds is effectively accelerated by the increase in temperature. When the temperature is increased to 370 K, pure NaY zeolites with higher relative crystallinity can be obtained. When it is further increased, the zeolite P becomes the predominant phase, and the perfect NaP zeolite can be prepared at 410 K (Figure 4). This means that zeolite P is the even more stable phase in thermodynamics and possesses a condensed skeletal structure.

![Figure 4. Effect of crystallization temperature on synthesized zeolites](image-url)

(a) 363 K, (b) 373 K, (c) 393 K, (d) 413 K
The co-existence of 4A, NaY and NaP occurs due to the remarkable disparity between the rate of the interface reaction and diffusion process at different temperatures resulting in the growth rate diversity among the various crystalline surfaces upon thermal synthesis. The crystallization temperature might affect the sol-gel properties, especially the particle size and electricity of the sol-gel system. With increasing crystallization temperature, particle size will be effectively decreased and the diffusion is also accelerated. Hence, the thermal stable phase is formed. To synthesize metastable Y zeolite, the crystallization temperature must be strictly controlled, and the optimum temperature for the NaY zeolite is 370 K.

The ion exchange between the solid and liquid phase results in the zeolite skeleton composition changing over time. Therefore, the impure crystalline phase can be observed with the crystallization time. Yang et al. [8] also investigated these phenomena.

Most importantly, the pure NaY with higher specific area and perfect crystallinity can be synthesized at optimum conditions. The pore distribution of NaY synthesized from kaolin is shown in Figure 5. The NaY samples possess narrow micropores, which are more concentrated than the commercial NaY.

### Figure 5. Micropore distribution of NaY synthesized from coal-based kaolin

<table>
<thead>
<tr>
<th>Water amount (ml)</th>
<th>Product composition</th>
<th>Relative crystallinity (%)</th>
<th>Surface area (m²/g)</th>
<th>Micropore area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>amorphous</td>
<td>—</td>
<td>94.8</td>
<td>10.1</td>
<td>0.30</td>
</tr>
<tr>
<td>30</td>
<td>mainly amorphous+minim 4A</td>
<td>—</td>
<td>100.8</td>
<td>48.3</td>
<td>0.21</td>
</tr>
<tr>
<td>40</td>
<td>mainly NaY+minim 4A</td>
<td>70</td>
<td>413.9</td>
<td>377.7</td>
<td>0.23</td>
</tr>
<tr>
<td>50</td>
<td>NaY</td>
<td>73</td>
<td>246.7</td>
<td>224.9</td>
<td>0.14</td>
</tr>
<tr>
<td>60</td>
<td>NaY</td>
<td>65</td>
<td>297.3</td>
<td>261.0</td>
<td>0.18</td>
</tr>
<tr>
<td>70</td>
<td>mainly amorphous+minim NaY</td>
<td>—</td>
<td>20.6</td>
<td>—</td>
<td>0.08</td>
</tr>
<tr>
<td>80</td>
<td>amorphous</td>
<td>—</td>
<td>13.6</td>
<td>—</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### 3.4. Effect of water volume on zeolite formation

The pH value of the aqueous solution significantly influences the crystalline pattern of the zeolites. Table 1 compiles the textural characteristics of the resulting products and shows the effect of added water volume upon NaY zeolite synthesis.

The XRD analysis shows that the amount of water exerts a strong influence on the structure of the zeolites prepared from coal-based kaolin. An increase in the water volume from 20 ml to 80 ml can result in an enormous change in the crystalline pattern. When the water volume is below 30 ml the sample has an amorphous pattern. However, the sharp diffusion peak of the NaY zeolites can be exist when the water volume is as high as 40 ml, whilst there are a small number of 4A zeolites accompany with it (shown in Figure 6(a)). Pure NaY can be synthesized by increasing the water volume. It can be obtained when the water volume is 60 ml (shown in Figure 6(b)), whereas the relative crystallinity is lower than 40 ml and 50 ml. The decrease in the relative crystallinity is ascribed to the amorphous pattern mixing in it. When the water volume is above 70 ml, the sample is totally converted into the amorphous pattern. We can see that the water volume plays an important role in the formation of the zeolite prepared from coal-based kaolin.

The functions of water can be described as follows. First, the water volume contributes to the pH value of the colloid system and accordingly influences the external dielectric constant and sizes of gel particles. Second, the pH value influences the sedimentation velocity of gel particles, which results in the change in the gel concentration and the transfer rate of gel particles. This reveals that too much or too little water may inhibit the formation of perfect NaY zeolites from kaolin.
3.5. Effect of crystallization time on zeolite formation

The effect of crystallization time on synthesized NaY zeolites was also extensively investigated. Figure 7 shows that the various surface areas of samples are all low, and specific surface area ascribes to the external area when the crystallization temperature is below 363 K. This is because the crystal products synthesized at low temperatures are mostly amorphous material, which is verified by XRD data. With the time increase, the crystalline particles are manifolded and the surface area is accordingly increased.

3.6. Effect of aging on zeolite formation

Aging is also an important factor for the zeolite synthesis process. The effects of aging conditions on the resulting products are listed in Table 2.

Table 2 indicates that NaY zeolites with a higher surface area could be obtained at the proper aging time. Extended aging times are negative to the synthesis of NaY zeolites because the micropore surface area and relative crystallinity of the samples markedly decreases. The pure NaY with higher relative crystallinity shown in the XRD diffraction patterns can be developed at aging times up to 12 hours. The proper aging time might be favorable for the formation of the skeletal structure, particle size and dielectric properties of the unit cell in the colloid. Furthermore, it would optimize the composition of the reactants in the sol-gel solution, which contribute to the formation of the pure NaY zeolite. However, prolonging the aging time can accelerate the growth and agglomeration of gel particles so that the NaY zeolite possesses a lower micropore volume and surface area.
Table 2. Effect of aging on NaY zeolites synthesis

<table>
<thead>
<tr>
<th>Aging time (h)</th>
<th>Product</th>
<th>Relative crystallinity (%)</th>
<th>Surface area (m²/g)</th>
<th>Micropore area (m³/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>NaY</td>
<td>68</td>
<td>333.8</td>
<td>306.1</td>
<td>0.18</td>
</tr>
<tr>
<td>10</td>
<td>NaY</td>
<td>70</td>
<td>147.9</td>
<td>132.9</td>
<td>0.10</td>
</tr>
<tr>
<td>12</td>
<td>NaY</td>
<td>75</td>
<td>246.7</td>
<td>224.9</td>
<td>0.14</td>
</tr>
<tr>
<td>14</td>
<td>NaY</td>
<td>65</td>
<td>112.7</td>
<td>94.3</td>
<td>0.09</td>
</tr>
</tbody>
</table>

3.7. Hydrothermal stability

The DTA results are shown in Figure 8. The endothermic peak at 470 K is due to desorption of physical adsorption water. The peak of the chemical desorption water exists between 480 K and 700 K. The peak at 840 K is ascribed to the collapse of the NaY skeleton, which is similar to the commercial NaY.

3.8. FT-IR spectra of skeletal vibration

Figure 9 presents the FT-IR spectra of skeletal vibration. It shows that the NaY zeolites synthesized with kaolin have similar skeletal vibration spectra as those conventionally prepared. The band at 3,467 cm⁻¹ is ascribed to the tortuous vibration, and that at 1,637 cm⁻¹ is ascribed to the corresponding covalent bond vibration. The band at 1,000, 790 and 720 cm⁻¹ can be attributed to the inner asymmetric stretching vibration of the TO4 tetrahedron, external and inner symmetric vibration of the TO4 tetrahedron respectively. The bands at 500 cm⁻¹ and 450 cm⁻¹ may correspond to the bend vibration of the T-O band.

Figure 8. TG-DTA diagram of coal-based NaY zeolite

Figure 9. FT-IR spectra of coal-based NaY zeolite sample

4. Conclusion

1. Coal-based kaolin with little quartz is a promising material for NaY zeolite synthesis. The pure NaY zeolites were in-situ prepared by activation treatment using hydroxide sodium and crystallization hydrothermal synthesis under the proper synthesis conditions.

2. The crystallization temperature and pH of the solution play an important role in the formation of the zeolite prepared from coal-based kaolin.

3. There are apparent competition among 4A, NaP and NaY zeolites during the synthesis from coal-
based kaolin. 4A and NaY zeolites are the metastable pattern and NaP is the relative stable one. Thus, it is important to control the reaction parameters to obtain the desired zeolite.

4. Pure NaY with a high relative crystallinity can be prepared from kaolin. The samples possess a larger specific area, sharper pore distribution and good hydrothermal stability.

References