Eco-friendly synthesis of kaolin-based chabazite for CO₂ capture

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Chabazite was successfully synthesized from Kaolin for the first time via a calcination-hydrothermal process. The effects of Si/Al ratio, (OH)⁻/Si ratio, calcination time and hydrothermal time on the synthesis process were investigated one by one, and the final synthesis scheme under this condition was obtained. The adsorption isotherms of CO₂ and N₂ were measured at 30–90°C and 0–120 kPa to measure the gas adsorption properties of chabazite. In this paper, the adsorption capacity of chabazite to CO₂ and N₂ could reach 1.61 and 0.66 mmol/g respectively at 120 kPa and 30°C. In addition, chabazite showed excellent CO₂/N₂ selectivity over the full pressure range.

Key-words : Kaolin, Synthesis, Chabazite, CO₂, Adsorption

1. Introduction

Global warming has brought about possibly permanent alterations to the earth, which has led to the emergence of environment hazards to human health, for instance, natural catastrophes occur more frequently. Scientists rule out the reasons which are causing the high level of warming today, and the increase in CO₂ concentration is considered as the most plausible cause.¹ With the increase of demands for fossil fuels, capturing CO₂ from the exhaust gases has becomes a significant way to solve the dilemma. Adsorption technology, including pressure swing adsorption,¹²,¹³ and temperature swing adsorption,¹⁴,¹⁵ is one of the representative CO₂ capture processes. The development of adsorption techniques in CO₂ capture is, however, dependent on the availability of inexpensive absorbents featuring considerable selectivity of CO₂ over N₂.⁶–⁸ Thus, searching for effective and low-cost absorbents for CO₂ capture is actively pursued.

Chabazite, one remarkable category of tectosilicate minerals, is acknowledged to have promising properties in catalysis, gas separation, pollution abatement, etc.¹⁹ As a typical small-pore zeolite, chabazite has planar structure composed of double 6-ring building units arranged in layers in the sequence of ABCABC and linked by tilted 4-rings.¹⁶ In the framework of chabazite, a number of cations disperse homogeneously near the Al atom to achieve the charge balance. The extra-framework cations lying in the cavities play an important role, which not only brings strong ion exchange capacities, but also enhances the adsorption selectivity of chabazites for gas molecules. Cesium chabazite for instance, show the highest selectivity of CO₂ over CH₄ with important application to natural gas purification.¹¹

Various synthetic procedures for chabazites have been developed recently, including organic template method and interzeolite conversion.¹²–¹⁵ In the organic template method, template agent acts as a guide in the synthesis process. However, the organic structure-directing agent is generally both expensive and toxic, and removal of this agent is a difficult bottleneck problem to solve. By contrast, the conversion method can be achieved by removing and recombining the structural units of other zeolites with similar structures to obtain the target product. This process avoids using poisonous template but has a long synthetic cycle, making it difficult to meet the mass-production requirements. Moreover, this method itself has particular requirements for the precursor zeolites, such as silica-alumina ratio and crystallinity. On the other hand, searching for an affordable raw waste material that is suitable for synthesis of chabazite would effectively cut the cost. However, it seems a tricky task because the synthesis of chabazite is sensitive to the reaction conditions. To the best of our knowledge, only a limited number of raw materials have been reported to be utilized for the synthesis of chabazite.¹³

Kaolin is a widely distributed and low-cost raw material, which has been used commercially for hundreds of years.¹⁶,¹⁷ The main components of kaolin are aluminum oxide and silica, which make it a suitable raw material for synthesizing chabazite as silicon source and aluminum source.¹⁸–²⁰ In this investigation, we used kaolin as a raw material to synthesize chabazite by a calcination and hydrothermal treatment. The critical conditions to obtain high-purity chabazites were optimized, including Si/Al mole ratios, alkaline ash ratio, calcination time, and hydrothermal time. Finally, the product was examined to assess
its properties as an adsorbent for CO₂ capture. The ultimate aim of this study was to develop a cheaper and environmentally method for the synthesis of chabazite.

2. Experimental

2.1 Synthesis

Kaolin used in this experiment was primarily comprised of SiO₂ (52.1 wt %), Al₂O₃ (45.5 wt %), TiO₂ (0.73 wt %), and Fe₂O₃ (0.5 wt %), indicating that it could be a favorable raw material for synthesizing chabazite. The synthesis procedure for chabazite is summarized schematically in the flow diagram (Fig. 1). In a typical procedure, 5 g of kaolin was mixed with SiO₂ powder using different molar ratios of Si/Al molar ratios such as 1.5, 2, 2.5, and 3. Then, potassium hydroxide was added into the resulting mixture to adjust the alkalinity/ash mass ratios to a desired value such as 1, 2, and 3. The mixture was fused in a high temperature oven at 650°C for different time (30 to 75 min). After the calcination process, the resulting sinter was ground and added into distilled water followed by stirring. The slurry was transferred into an autoclave and heated at 95°C for different hydrothermal reaction time (1–4 days). Finally, the precipitates were centrifuged, washed, and dried overnight to obtain chabazites.

2.2 Characterization

The crystalline properties of the as-synthesized samples were examined by X-ray diffraction (XRD) using a Shimadzu X-ray diffractometer, with a scanning rate of 2°·min⁻¹ from 4 to 60°. The microscopic morphology of samples was examined by scanning electron microscopy (SEM). The model of SEM used in this study was ZEISS Ultra Plus. All samples were platinum coated prior to measurement. BET surface areas and gas adsorption isotherms were measured on a surface area analyzer (JW-BK222). Prior to analysis, the chabazites were degassed under vacuum at 300°C for 6 h. The elemental composition of the synthesized sample was determined by X-ray fluorescence spectrometry.

3. Results and discussion

3.1 Synthesis optimization

The optimal conditions for synthesizing chabazite were investigated systematically to obtain chabazites. The Si/Al mole ratio has a great effect on the synthesis of zeolites.²¹,²² Too low or high ratios will cause amorphous phases in the structure, which greatly affects the crystallinity of zeolites. Figure 2 shows the XRD patterns for products obtained at the ratio range from 1.5 to 3. According to the XRD results, when the Si/Al ratio was 1.5, a large bread peak formed at about 30°, suggesting that a large amount of amorphous phase was present in the product. XRD pattern of sample obtained at the ratio of 2 has the diffraction peaks, corresponding with the characteristic signatures of chabazites. However, when Si/Al mole ratio increased to 2.5 or higher, amorphous phase or characteristic peak of mullite appeared. Therefore, the optimum Si/Al mole ratio was 2, wherein chabazite with high purity was obtained.

Appropriate alkalinity has important significance for the synthesis of zeolites.²¹ During calcination and hydrothermal reaction, the alkalinity will affect the hydrothermal rate and polymerization degree, thus affect the synthesis of zeolite. In this study, a plurality of 5 g of kaolin were mixed with 5, 10, 15 and 20 g of KOH, respectively, and then the synthesis experiment of chabazite was carried out according to the ratio of the prepared raw materials. The
Effect of different alkaline ash ratios, in the range of 1 to 4, was investigated by XRD analysis, and the results were shown in Fig. 3. An characteristic peak of mullite was observed, when the alkaline ash ratio was 1. Thus, chabazite did not form at this ratio, due to the low alkalinity of the solution in the hydrothermal reaction. As alkaline ash ratios increased beyond 2, high-purity chabazites were obtained. Furthermore, the crystallinity of chabazite increased as the alkaline ash ratio increased. However, excessive alkali causes the waste of alkali and the increase in the synthetic cost of chabazite. Therefore, the alkaline ash ration of 2 was sufficient for the synthesis of chabazites.

Calcination time is also an important factor for the zeolites synthesis. Insufficient calcination time to destroy completely the crystal structure of the inert substance, will be unfavorable to synthesis of zeolites. On the contrary, if the calcination time is too long, the energy consumption of synthesis process will increase significantly. In order to investigate the influence of calcination time on chabazite synthesis, different calcination time was investigated, and the products were examined by XRD analysis (Fig. 4). The results show that chabazites could be always obtained at this range of calcination time. However, chabazite was heavily contaminated with amorphous phase and mullite when the calcination time was less than 60 min, which could be contributed to that the decomposition of the inert composition of kaolin was not complete. Further extending the calcination time to 75 min, the peaks of characteristic peak of mullite appeared. The best chabazite was obtained at 60 min, and thus, this calcination time of 60 min was used in the following experiments.

XRD patterns of the obtained chabazites at various hydrothermal time are shown in Fig. 5. Combining with the crystallinity and experimental data, the hydrothermal time of 1 day was insufficient, a large amount of silica in the suspension did not participate in the reaction. This stage was in the nucleation of chabazite, where a plenty of new nucleus have not formed, and its crystallinity of product was as low as 55%. As the hydrothermal process progresses, the crystallinity of chabazite increases. In particular, the best chabazite with a high crystallinity of 73% was obtained at the hydrothermal time of 3 days. However, when the hydrothermal time was extended to 4 days, a large amount of mullite was doped in the synthetic sample, which might be due to the excessive reaction time which caused crystal transformation between different zeolites in the alkali solution. It could be concluded that the optimum hydrothermal time for synthesizing chabazite was 3 days.

Based on the experimental results above, the optimal synthesis conditions for chabazite were found as follows: Si/Al mole ratio of 2, alkaline ash ratio of 2, calcination time of 60 min, hydrothermal time of 3 days. The product obtained under these optimal conditions was used in the following experiments.

3.2 Morphological and structural analysis

The SEM morphologies of kaolin and prepared chabazite are shown in Fig. 6, and the observations were carried
at magnifications between 10 and 30 k×. In the image of kaolin [Fig. 3(a)], small flake and platelets with the size of a few micrometers could be distinguished. In comparison, the morphology of chabazite was clearly different from that of kaolin. From the SEM observations in Figs. 6(b) and 6(c), the products had the walnut-like shape with a good symmetry, which was in good agreement with the literature. In addition, amorphous material was hardly noticeable in the SEM images, suggesting the formation of high crystallinity chabazite. X-ray fluorescence was used to detect the mass fraction of the component elements of kaolin and CHA, the detailed detection results shown in Table 1. According to the X-ray fluorescence test results (as shown in Table 1), the chabazite sample synthesized according to the optimal conditions of this study has a silicon to aluminum ratio of 1.81, and its chemical composition can be approximated as K₂Si₉Al₅O₅₆.

\[
a = \frac{m_k \times 45.5\%}{m_c \times 22.1\%}
\]

Where \( m_k \) is the weight of kaolin, \( m_c \) is the weight of the produced sample, and \( a \) is the conversion rate.

### 3.3 Gas adsorption performance

The factors that affect the gas adsorption of chabazite are mainly temperature and pressure, then the effect of temperature and pressure on chabazite needs to be discussed. In this experiment, the chabazite samples were tested by physical adsorbent. As shown in Fig. 7 and 8, the change of pressure and adsorption capacity of CO₂ and N₂ at different temperatures was fitted with Dual-site-Langmuir equation\(^{(23)}\) shown as Eqs. (2)–(4).

\[
n = \frac{MBP}{1 + BP} + \frac{NDP}{1 + DP}
\]

\[
B = b_0 \exp \left( -\frac{Q_B}{RT} \right)
\]

\[
D = d_0 \exp \left( -\frac{Q_D}{RT} \right)
\]

Where \( n \), \( T \), \( Q_B \), \( Q_D \), were respectively the nth-order adsorption amount, adsorption temperature and \( B \), \( D \) double point adsorption heat. \( M \), \( N \) were respectively saturated adsorption capacity of \( B \) and \( D \) points. \( R \) was gas constant. \( b_0 \) and \( d_0 \) were respectively resulting parameters fitted with Dual-site-Langmuir equation. The parameters fitted by isotherms were shown in Table 2.

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Table 1. Kaolin and CHA components of each component mass fraction

| Component | SiO₂ | Al₂O₃ | K₂O | Other ingredients |
|-----------|------|-------|-----|------------------|
| Kaolin    | 52.1 | 45.5  | 0.3 | 2.1              |
| CHA       | 47.3 | 22.1  | 28.3| 2.3              |

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Fig. 6. SEM images for: (a) kaolin, (b, c) prepared chabazite at low and high magnifications.

Fig. 7. CO₂ isothermal adsorption curve at 30, 60 and 90°C.

Fig. 8. N₂ isothermal adsorption curve at 30, 60 and 90°C.
As can be seen from the figure, the amount of gas adsorbed by chabazite increased with increasing pressure. When the pressure was reduced, the CO$_2$ bound to the channel of chabazite would diffuse in the environment. When the pressure increased, the CO$_2$ molecules were more likely to adhere to the pores of the chabazite. The adsorption capacity of N$_2$ and CO$_2$ on chabazite in the case of temperature change, and the amount of gas adsorption decreased with the increase of adsorption temperature. Because the gas molecules had the same level of molecular kinetic energy, when the temperature was low, the molecules had a lower molecular kinetic energy due to chabazite surface adsorption. Most of the gas was fixed on the gas surface, then chabazite adsorption capacity was relatively large. With the increasing of temperature, the kinetic energy obtained by the molecule would increase, and it increased to a certain value. It would get rid of the surface of its bound role into the air, resulting in reduced adsorption capacity.

The isosteric heats of CO$_2$ and N$_2$ adsorption were computed from the equilibrium data measured at 30, 60 and 90°C, which had been fit to the Dual-site-Langmuir equation. Clausius–Clapeyron relationship was introduced as a basis for calculating heat of adsorption.

$$Q_{st} = R \ln \left( \frac{P_2}{P_1} \right) \frac{T_1}{T_2}$$

(5)

Where in this paper, $P_2$ and $P_1$ were respectively 110 and 3 kPa, calculated according to the following Eqs. which was derived from Eq. (2).

According to Eq. (5), the adsorption calorific values of CO$_2$ and N$_2$ under different adsorption capacities were calculated. As shown in Fig. 9, the adsorption heat of CO$_2$ showed a decreasing trend in the range of 0 to 2 adsorption volume, and the adsorption heat of N$_2$ increased slightly with the adsorption amount without any significant change. The relationship between the adsorption heat of CO$_2$ and N$_2$ as a function of adsorption capacity was shown in Eqs. (6)–(8). The CO$_2$ and N$_2$ adsorption ranges tested in this paper were 0–2 and 0–0.4 mmol/g, respectively, and the corresponding adsorption heat ranges were 10.8–12.6 and 1.6–2.2 kJ/mol, both less than 40 kJ/mol. This showed adsorption of CO$_2$ and N$_2$ on synthetic chabazite belonged to reversible physical adsorption. Further details of adsorption heat were shown in Fig. 9.

The choice of adsorbability was another indicator of adsorbent gas adsorption characteristics. In this paper, the method of calculating the adsorption coefficient of CO$_2$/N$_2$ was to divide the adsorption amounts of the two gases at different pressures and the same temperature. The three curves in Fig. 10 represented the CO$_2$/N$_2$ selective adsorption coefficients at 30, 60 and 90°C, respectively. According to the information in the figure, it could be found that in the pressure range of 0 to 60 kPa, the value of the selective adsorption coefficient of CO$_2$/N$_2$ gradually decreased with the increase of the pressure. In addition, at the same adsorption pressure, its value decreased with in-

| Table 2. Parameters fitted with Dual-site-Langmuir |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | $M$             | $t_0$           | $Q_0$           | $N$             | $d_0$           | $Q_0$          |
| CO$_2$         | 0.9            | 5.0E-4          | 12875.8         | 760868          | 1.2E-10         | 1.1E+4         |
| N$_2$          | 26895.3        | 4.5E-58         | 286665.1        | 2.1             | 1.3E-3          | 7.0E-8         |
creasing temperature. The adsorption capacity of chabazite to N\textsubscript{2} was close to the vacuum state, which was the main reason for the smaller adsorption coefficient of CO\textsubscript{2}/N\textsubscript{2} in the low pressure zone. Low pressure was an obstacle to the gas adsorption process, however, because of its strong molecular polarity, CO\textsubscript{2} had a strong ability to overcome this negative factor. In the low-pressure state, the majority of adsorption sites inside chabazite were “vacant”, which was also conducive to the formation of larger adsorption capacity of chabazite to CO\textsubscript{2}. Therefore, under this pressure condition, chabazite had higher CO\textsubscript{2}/N\textsubscript{2} selective adsorption coefficient with respect to the high-pressure state. In the pressure range of 60 to 120 kPa, the selective adsorption coefficient of CO\textsubscript{2}/N\textsubscript{2} mainly concentrated in the range of 4.3 to 6, which was not obviously affected by the pressure change, and its value changes little with the increase of temperature. The main reason for this phenomenon was that in the high pressure range, the amount of CO\textsubscript{2} adsorbed gradually becomes larger, and the adsorption sites at this time were mostly in a full state. Accompanied by a large number of CO\textsubscript{2} molecules were adsorbed, the heat released during the adsorption process on the inhibitory effect began to increase. However, due to its adsorption capacity and adsorption heat, N\textsubscript{2} was less affected by the above factors. It could be seen from Fig. 7 that the isotherm of CO\textsubscript{2} in this range was similar to that of N\textsubscript{2} that it was close to the linear relationship with the pressure value, which was the main reason why the selective adsorption coefficient of CO\textsubscript{2}/N\textsubscript{2} does not change much in the high pressure range.

In order to have a more intuitive understanding of the gas adsorption properties of the synthetic chabazite in this study, the conventional crystallizer synthesized chabazite was prepared for comparison. After comparison, the study successfully increased the CO\textsubscript{2}/N\textsubscript{2} adsorption selectivity coefficient from 1.25 to 4.47. In addition, according to other relevant research experience of our team, if the cations in the chabazite framework were replaced with other species (such as Zn\textsuperscript{2+} or NH\textsubscript{4}\textsuperscript{+}), the improvement effect will be more significantly improved. More importantly, the synthesis cycle of chabazite was also greatly reduced, from 15 days to only 2 days.

4. Conclusions

In this study, chabazite was prepared via calcination and hydrothermal reaction by using low-cost kaolin as a raw material. The optimum conditions for high-purity chabazite were obtained as follows: silica/alumina ratio was 2, alkali-to-ash ratio was 2, hydrothermal temperature at 95°C and a hydrothermal time of 4 days. The synthetic chabazite has the highest purity and the crystallinity is 75%. The adsorption capacity of synthetic chabazite to CO\textsubscript{2} and N\textsubscript{2} could reach 1.61 and 0.66 mmol/g respectively at 120 kPa and 30°C. The selective adsorption coefficient of CO\textsubscript{2}/N\textsubscript{2} could reach as high as 24 under low pressure, basically maintaining at 4.3 to 6 at above 60 kPa, indicating that synthetic chabazite was a kind of adsorbent with potential gas adsorption performance.

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