

Selective adsorption behaviors of CO₂ in small-pore chabazite zeolites

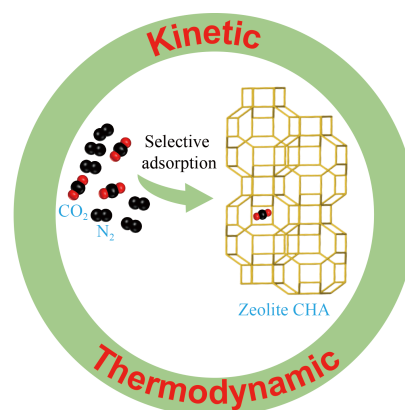
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Abstract: Chabazite-type (CHA) zeolite is considered to be a highly promising CO₂ adsorption material due to its unique pore structure. However, the underlying adsorption kinetics of CHA zeolite still need to be studied to facilitate development of efficient adsorbents. In this study, the preparation method, CO₂ adsorption kinetics, and thermodynamic properties of CHA zeolite are investigated. CHA zeolite is synthesized from hydrogen type faujasite-type (H-FAU) zeolite using a transformation method. By modulating the ratios of $n(\text{KOH})/n(\text{SiO}_2)$, $n(\text{H}_2\text{O})/n(\text{SiO}_2)$, crystallization temperature, and crystallization time during the synthesis process, the optimal synthesis conditions for CHA zeolite are explored based on X-Ray Diffraction (XRD) and scanning electron microscopy (SEM) of the as-synthesized materials. The CO₂ adsorption performance of the prepared CHA zeolite is tested and evaluated using both dynamic and static measurements. Different kinetic models are applied to analyze the kinetic behavior of the adsorption process. Among them, the Avrami equation yields a good fit to illustrate the adsorption process of studied zeolites ($R^2 > 0.99$). With increasing temperature, the adsorption process reaches equilibrium more quickly due to the enhanced adsorption rate. The selectivity also increases with increasing temperature, indicating that the adsorption process of CO₂ on CHA zeolite is mainly controlled by diffusion. Breakthrough data and thermodynamic analysis show that the material's interaction with CO₂ is stronger than that with N₂, yet the CO₂ adsorption is still dominated by physical interactions. The weak adsorption strength between CO₂ and CHA zeolite is conducive to gas desorption. These findings provide a theoretical support for optimizing industrial adsorption operating conditions.

Key words: chabazite; CO₂ adsorption; zeolite crystallization; adsorption kinetics; Avrami model



Accelerated industrialization has driven a sustained increase in atmospheric CO₂ concentrations, which constitutes one of the dominant contributing factors to global climate warming and frequent occurrences of extreme weather events^[1]. In response to this pressing global challenge, both the international and the scientific efforts are overwhelmingly directed towards CO₂ capture and emission reduction technologies. Among various approaches, adsorptive capture stands out as a promising strategy for CO₂ removal, which has garnered extensive

research attention owing to its operational simplicity and relatively low energy consumption^[2–3].

Zeolitic molecular sieves are widely regarded as ideal adsorbents for CO₂ capture with attributes of unique microporous architecture, high specific surface area, excellent thermal and chemical stability, and tunable pore size dimensions. As such, these inorganic porous silicate materials demonstrate great potential in efficient CO₂ capture via physical adsorption mechanisms^[3–5].

As a representative eight-membered ring small-pore

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zeolite, CHA-type framework exhibits remarkable potential in gas adsorption and separation applications due to its distinctive topology and precisely engineered pore architecture. Particularly notable are its exceptional performance characteristics demonstrated in greenhouse gas capture and noble gas purification processes^[6]. Specifically, CHA zeolite exhibit exceptional adsorptive capacity toward critical atmospheric species including carbon dioxide (CO₂)^[7], methane (CH₄)^[8] and nitrous oxide (N₂O)^[9]. This excellent adsorption capacity and separation selectivity are largely attributed to the unique “trapdoor effect” or “molecular sieve effect” of CHA zeolite^[10]. The “trapdoor effect” refers to the ability of the pores or cage-like windows of CHA zeolite molecular sieves to undergo reversible structural dynamic changes under specific conditions based on the size and shape of the adsorbate molecules, thereby achieving selective adsorption and blocking of specific molecules^[11]. This effect allows CHA zeolite to precisely distinguish gas molecules of different sizes and polarities. For example, in CO₂ capture, CHA zeolite can effectively and selectively adsorb CO₂ from a mixed gas stream, while its adsorption capacity for other gases (such as N₂) is relatively low. This characteristic is of great significance for achieving efficient and low-energy greenhouse gas emission reduction. In addition to greenhouse gases, CHA zeolite molecular sieves have also shown significant potential in the field of rare gas separation. For example, in the separation of xenon (Xe) and krypton (Kr), traditional methods such as cryogenic distillation are energy-intensive and complex to operate due to the subtle differences in the molecular size and polarity of the two gases. CHA zeolite molecular sieves can effectively distinguish between these two rare gases by leveraging their pore structure, achieving an efficient Xe/Kr separation. This characteristic of CHA zeolites provides a new approach for nuclear industry waste gas treatment, isotope separation, and the production of high-purity rare gases^[12].

Carbon dioxide, as the leading greenhouse gas, contributes significantly to the greenhouse effect. In their research of carbon dioxide adsorption on CHA zeolite, Clatworthy et al.^[7] synthesized micron- and nano-scale K-CHA zeolites using a hydrothermal method. By comparing the steepness of the breakthrough curves and performing derivative analysis, a comparative study of the adsorption kinetics was conducted to evaluate the relative adsorption rates of nanoscale and microscale CHA zeolites. Studies have found that reducing the size of zeolite crystals can significantly shorten the diffusion path of CO₂ molecules and reduce the diffusion resistance of micropores, thereby enhancing the overall mass transfer performance and effectively improving the efficiency of the rapid separation process. Fu et al.^[13] achieved high adsorption performance by controlling the distribution of Zn²⁺ in the six-membered rings (6MRs) of zeolite: when Zn²⁺ is located at the paired anion sites of 6MRs, the adsorption capacity reaches 0.51 mmol/g (Si/Al≈7), which is 17 times higher than that

of H-type zeolite; after reducing the Si/Al ratio to ~2, the capacity increases to 0.67 mmol/g. By comparing the steepness of breakthrough curves with those of 13X zeolite, the modified Zn-CHA zeolite exhibited relatively faster adsorption kinetics. Cao et al.^[14] synthesized a sunflower-shaped CHA zeolite superstructure (SFS-CHA) through a directional attachment mechanism, which is based on self-assembly of nanocrystals to form a micro-mesoporous hierarchical structure. The material exhibits a CO₂ adsorption capacity of 71.14 cm³/g at 298 K and 0.15 bar, and IAST predicts CO₂/N₂ and CO₂/CH₄ selectivity of 815 and 264, respectively. The normalized adsorption equilibrium time obtained from an Intelligent Gravimetric Analyzer (IGA) was used to compare the adsorption kinetics rates among samples with different morphologies. The relevant dynamic breakthrough experiments indicate that this hierarchical pore structure facilitates the separation performance with an excellent CO₂ adsorption capacity. This study provides a new strategy for the design of high-efficiency adsorbents. Although some aspects of adsorption kinetics in CHA zeolites have been studied, there is still a lack of research that systematically describes the CO₂ adsorption behavior of CHA using kinetic equations. Therefore, this paper uses H-type FAU zeolite molecular sieves as raw materials to explore the synthesis conditions for CHA molecular sieves by crystallization and to study the carbon dioxide adsorption kinetics and thermodynamics of the prepared CHA molecular sieves.

1 Experimental

1.1 Preparation of CHA zeolite

The HY zeolite (SiO₂/Al₂O₃ molar ratio=5) was purchased from the Nankai University Catalyst Co., Ltd. Potassium hydroxide (KOH, 98%, Purchased from Greagent). The deionized water was prepared in the laboratory.

The specific synthesis process is as follows: first, deionized water, potassium hydroxide and HY (SiO₂/Al₂O₃=5) zeolite sieve are added to the polytetrafluoroethylene lining of the hydrothermal synthesis reactor, and then the mixture is continuously magnetically stirred for 1 h at room temperature. Then, the polytetrafluoroethylene liner containing the mixture was placed in a stainless steel high-pressure reactor. The high-pressure reactor was sealed and moved into a preheated oven. After hydrothermal synthesis at 423 K for 48 h, it was taken out and rapidly cooled. The obtained solid sample was taken out, washed with deionized water until neutral, and dried at 373K for 8 h to obtain CHA zeolite.

1.2 Characterization of CHA zeolite

The crystal structure of the synthesized sample was characterized using XRD (Panalytical X'Pert Powder,

Netherlands). The XRD pattern was recorded on a Panalytical X' Pert Powder diffractometer using a Cu K α radiation source ($\lambda=1.5406$ Å) to characterize the powder. The step size was 0.013° and the scan was performed once every $0.109^\circ/\text{s}$ in the 2θ range of 5° – 50° . Gas adsorption tests were conducted at 273 and 298 K using a BSD-660M physical adsorption instrument manufactured by Best Instruments Co., Ltd. The surface morphology and aggregation state of the synthesized samples were observed using a thermal field emission scanning electron microscope (ZEISS Gemini SEM 300). The accelerating voltage was

200 V–30 kV, the resolution was 1.2 nm, and the magnification was 25–200000 to obtain the scanning electron microscope (SEM) images. Elemental quantitative analysis of the HY molecular sieve raw material for crystal transformation was performed using XRF (XRF-1800). The relative crystallinity of the molecular sieve was calculated using Highscore Plus software based on the intensity of the main characteristic peaks ($2\theta=9.45^\circ$, 12.83° , 15.93° , 20.49° , 30.49°) in the XRD pattern. The specific calculation formula is as follows:

$$\text{Relative crystallinity (\%)} = \frac{\text{The sum of the characteristic peak areas of the samples}}{\text{The sum of the characteristic peak areas of the standard samples}} \times 100\% \quad (1)$$

1.3 Gas adsorption performance test

The static adsorption performance was tested using a BSD-660M physical adsorption instrument from BeiShiDe Instruments. First, the test sample was activated at 523 K under vacuum for 6 h, and then its nitrogen and carbon dioxide gas adsorption isotherms were measured at 273 and 298 K, respectively. To examine the CO₂/N₂ separation capability of cha zeolite, the CO₂/N₂ (20:80) adsorption selectivity was calculated based on single-component gas adsorption isotherm data. First, the pure component isotherm data of CO₂ and N₂ recorded at 273 and 298 K were fitted using the Dual-Site Langmuir-Freundlich (DSLFL) model:

$$q = q_{A,\text{sat}} \frac{b_A p^{\nu_A}}{1 + b_A p^{\nu_A}} + q_{B,\text{sat}} \frac{b_B p^{\nu_B}}{1 + b_B p^{\nu_B}} \quad (2)$$

where q is the component molar loading (mol/kg), $q_{A,\text{sat}}$ and $q_{B,\text{sat}}$ are the saturated component molar loadings at adsorption sites A and B (mol/kg), respectively. p is the total system pressure at equilibrium (kPa), while b_A and b_B are Langmuir-Freundlich constant at sites A and B (1 kPa^{-1}). The parameters ν_A and ν_B represent the reciprocal of deviations from an ideal homogeneous surface^[15].

The gas selectivity was calculated based on the Ideal Solution Theory (IAST). Based on the isotherms of the pure components, the adsorption capacity of CHA zeolite for both gases in the CO₂/N₂ (20:80) mixture was determined by applying the fitting equation (Figure S1), and the selectivity was calculated using the following formula:

$$\text{Selectivity} = \frac{q_{\text{CO}_2}/q_{\text{N}_2}}{y_{\text{CO}_2}/y_{\text{N}_2}} \times 100\% \quad (3)$$

where q_{CO_2} and q_{N_2} are the uptakes, and y_{CO_2} and y_{N_2} are the partial pressure of components 1 and 2, respectively^[16].

The dynamic adsorption performance was tested on a specific gas adsorption and separation experimental apparatus (SIRIUS-HG-40G). First, the molecular sieve is compressed into tablets to screen out particles of 40–60 mesh. Then, it is loaded into an adsorption tube and activated at 523 K under vacuum for 6 h before being cooled to room temperature. Pure CO₂ or a mixture of 20% CO₂ and 80% N₂ was introduced into the gas adsorption

separation apparatus at room temperature using a mass flow meter at a specific flow rate. The gas concentration at the end of the penetration column was measured using an online mass spectrometer. The temperature during the experiment was controlled by a circulating water bath. The dynamic gas adsorption capacity and gas selectivity were calculated according to the following equations (4) and (3), respectively.

$$q = \frac{F \times C_0 \times \int_0^{t_i} \left(1 - \frac{C_t}{C_0}\right) dt}{m} \quad (4)$$

where q is the saturated adsorption capacity of a certain component gas; m is the adsorbent mass; C_0 is the gas inlet concentration; C_t is the gas outlet concentration at time t ; t_i is the adsorption time; and F is the total gas flow rate.

1.4 CO₂ adsorption kinetics analysis

The adsorption column breakthrough experiment^[17–18] was conducted on a specific gas adsorption separation experimental apparatus (SIRIUS-HG-40G). CO₂ kinetic curves were measured at 298, 323 and 348 K, and the curves were fitted using pseudo-first-order kinetic equations, pseudo-second-order kinetic equations, and the Avrami kinetic model respectively^[19–20].

Pseudo-first-order adsorption kinetics model, which describes the adsorption process in terms of adsorption capacities, is among the most widely employed rate models in adsorption studies. It is described as follows^[21]:

$$q_t = a(1 - e^{-k_1 t}) \quad (5)$$

where q_t is the adsorption at time t , a is the adsorption at adsorption equilibrium, k_1 is the pseudo-first-order adsorption kinetic parameter and t is time.

Pseudo-second-order adsorption kinetic model is based on the assumption that the adsorption capacity is proportional to the number of occupied active sites on the adsorbent surface^[22]. The model is commonly expressed as:

$$q_t = \frac{a^2 k_1 t}{1 + a k_1 t} \quad (6)$$

where, q_t is the adsorption at time t , a is the adsorption at

adsorption equilibrium, k_1 and k_2 are pseudo-second-order adsorption kinetic parameters, and t is time.

Avrami adsorption kinetic model was initially developed to describe particle nucleation. Recently, this model has been extended to simulate phase transitions and crystal growth in materials, as well as to investigate the dynamic adsorption behavior of solid adsorbents^[18,23–24]. The model is expressed as:

$$q_t = a(1 - e^{-(kt)^n}) \quad (7)$$

where q_t is the amount of adsorbent adsorbed at time t , a is the equilibrium adsorption amount, k is the adsorption rate constant, t is time, and n is the Avrami exponent, which is often in fractional form, and reflects possible mechanism changes in the adsorption process^[25]. The parameter n characterizes the dimensional growth of adsorbed species at the active site, with $n = 2$ corresponding to one-dimensional growth, $n = 3$ indicating two-dimensional growth, and higher values representing progressively higher-dimensional expansion^[26]. For uniform adsorption, where the probability of adsorption is equal across all zones within a fixed time interval, $n = 1$ ^[27]. When $n = 2$, the adsorption process represents an ideal one-dimensional growth initiated from the adsorption site on the adsorbent surface, characterized by continuous formation and a constant rate^[26]. The fractional order of this model arises due to the complexity of the reaction mechanism or the simultaneous occurrence of multiple reaction pathways^[28].

Calculation of adsorption activation energy using the Arrhenius equation^[29]:

$$k = k_0 e^{\left(\frac{E}{RT}\right)} \quad (8)$$

where k_0 is the adsorption rate constant, E is the adsorption activation energy, R is the gas constant, and T is the absolute temperature.

1.5 Thermodynamic analysis of CO₂ adsorption

The adsorption heat of CO₂ is calculated using the Virial equation^[30], and its expression is shown in (9).

$$\ln p = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{j=0}^n b_j N^j \quad (9)$$

In the formula, p is the pressure (unit: bar), N is the adsorption amount (unit: mmol/g), T is the temperature (unit: K); a_i and b_j are temperature-independent Virial coefficients, and m and n are the number of terms required to describe the isotherm.

Based on the above equation, the adsorption heat Q_{st} is calculated using the Virial coefficients a_0 to a_m :

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (10)$$

where Q_{st} is the heat of adsorption and R is the gas constant.

2 Results and discussion

2.1 CHA synthesis conditions

2.1.1 Study of $n(\text{KOH})/n(\text{SiO}_2)$ on synthesis

As shown in Figure 1, the XRD and SEM were applied to investigate the effect of the basicity ratio $n(\text{KOH})/n(\text{SiO}_2)$ on zeolite structure in the synthesis system. When $n(\text{KOH})/n(\text{SiO}_2) = 0.5$, weak CHA zeolite characteristic diffraction peaks can be observed in the XRD pattern, while the SEM image shows that the bulk HY zeolite has agglomerated. This indicates that a higher basicity ratio is required to completely dissolve HY zeolite and convert it into CHA molecular sieve.

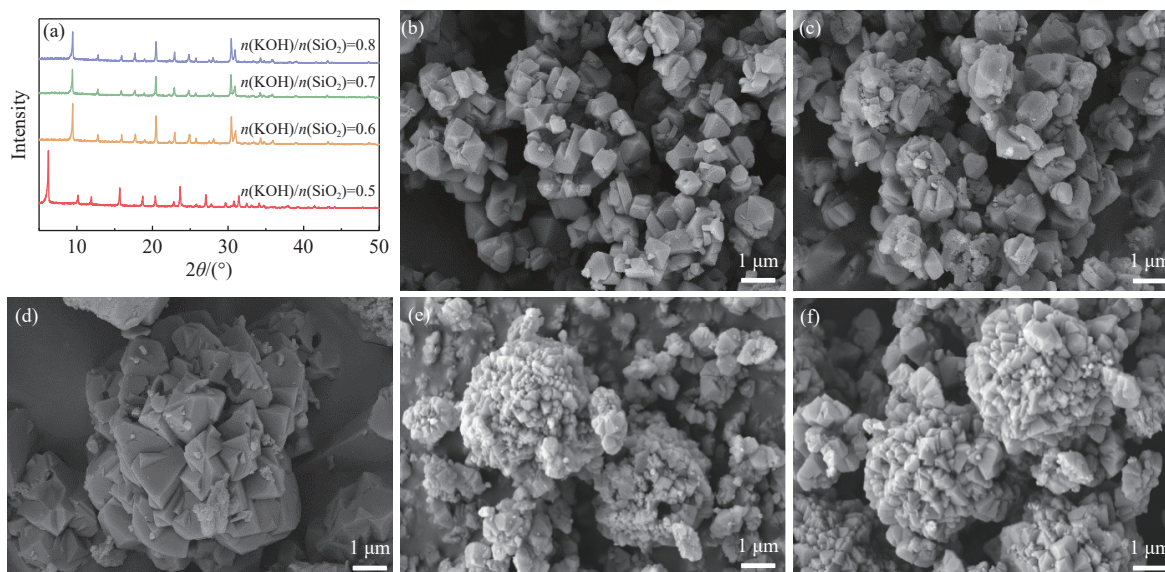


Fig. 1 XRD patterns (a) and SEM images for (b) HY zeolite, (c) $n(\text{KOH})/n(\text{SiO}_2) = 0.5$, (d) $n(\text{KOH})/n(\text{SiO}_2) = 0.6$, (e) $n(\text{KOH})/n(\text{SiO}_2) = 0.7$, (f) $n(\text{KOH})/n(\text{SiO}_2) = 0.8$

When $n(\text{KOH})/n(\text{SiO}_2)$ increases to 0.6, pure-phase CHA zeolite is obtained, and the blocky particles constituting the spiky structure are evenly distributed in the SEM image. However, when the alkalinity ratio was further increased to 0.7 and 0.8, the relative crystallinity of the samples decreased significantly (Table 1), and the blocky particles in the spiky structure tended to be finer, with the diameter of the spheres decreasing (Figure 1). The reduced crystallinity and altered morphology may result from the partial dissolution of CHA molecular sieve caused by excessive alkalinity.

2.1.2 Study of $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ on synthesis

Based on the results in the previous step, the influence of $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ ratios on the structure and morphology of CHA zeolite was studied under the condition of $n(\text{KOH})/n(\text{SiO}_2) = 0.6$. The XRD pattern in Figure 2 shows that as the ratio increases to 110, a distinct characteristic peak of HY zeolite appears at $2\theta=6.2^\circ$. When the ratio is further increased to 130, the intensity of this characteristic peak is significantly enhanced. This is attributed to the

reduced activity of OH^- under high water content, preventing the complete dissolution of HY crystals. At the same time, the probability of the effective collision between K^+ and soluble (aluminum) silicate oligomers (such as four-membered ring structural units) is reduced, hindering the formation of the CHA cage structure. SEM (Figure 2 (b)–(f)) show that as the water content of the system increases, the surface morphology of as-synthesized zeolites exhibits a gradual evolution: under low water content, excessive alkali solution will corrode the CHA crystal nuclei, causing the resultant spheres appear spread out with sparsely protrusion. At a $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ of 110, although the crystal retains a spherical outline, it still contains a large number of blocky fragments and fine HY zeolite particles. When the ratio is further increased to 130, the microspheres are mainly composed of regular hexagonal or smooth sheet-like HY single crystals. It is worth noting that the diameter of the sphere decreases monotonically with increasing water content. The optimal relative crystallinity value was obtained at a $\text{H}_2\text{O}/\text{SiO}_2$ ratio of 90 (Table 1), confirming that this condition is most favorable for the synthesis of CHA molecular sieves.

Table 1 Relative crystallinity of CHA zeolite under different synthesis conditions

$n(\text{KOH})/$ $n(\text{SiO}_2)$	Relative crystallinity ^a /%	$n(\text{H}_2\text{O})/$ $n(\text{SiO}_2)$	Relative crystallinity/%	Crystallization temperature/K	Relative crystallinity/%	Crystallization time/h	Relative crystallinity/%
0.5	—	50	89	393	69	24	29
0.6	100	70	97	403	82	36	81
0.7	94	90	100	413	85	48	100
0.8	87	110	94	423	100	60	90
		130	14	433	80	72	87

^a: The synthesis conditions that yield the highest relative crystallinity are considered the optimal synthesis conditions.

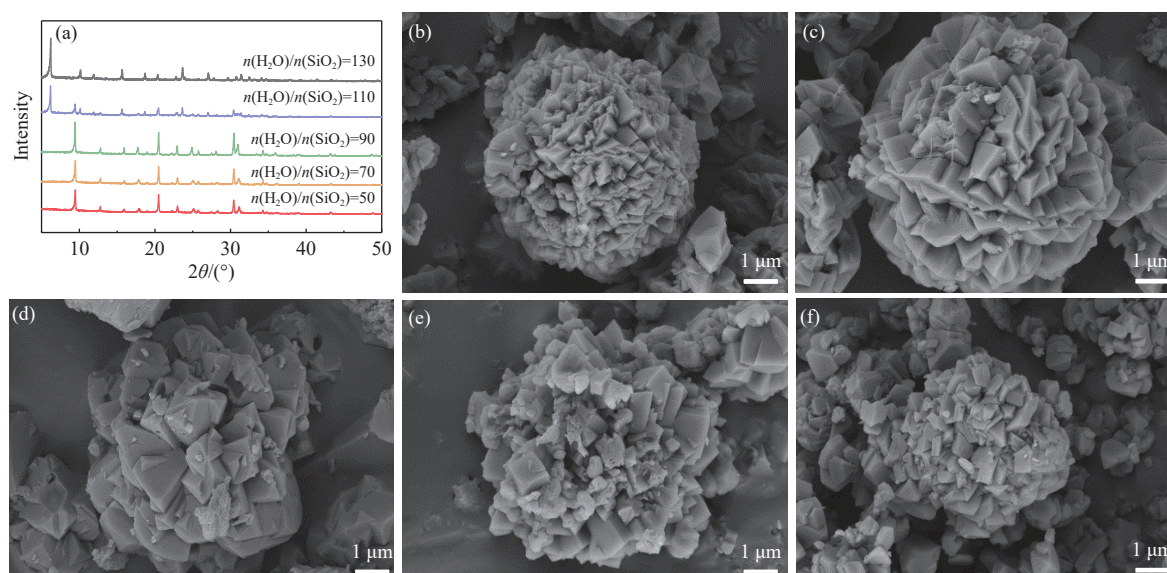


Fig. 2 XRD patterns (a) and SEM images for (b) $\text{H}_2\text{O}/\text{SiO}_2=50$, (c) $\text{H}_2\text{O}/\text{SiO}_2=70$, (d) $\text{H}_2\text{O}/\text{SiO}_2=90$, (e) $\text{H}_2\text{O}/\text{SiO}_2=110$, (f) $\text{H}_2\text{O}/\text{SiO}_2=130$

2.1.3 Study of crystallization temperature on synthesis

Considering the effect of crystallization conditions (Figure 3) and the corresponding performance parameters, it is evident that crystallization temperature plays an insignificant role under optimal time and alkalinity conditions. Within the crystallization temperature range of 393 to 433 K, all characteristic peaks of CHA molecular sieves can be clearly detected in the XRD patterns (Figure 3(a)), indicating that the formation of a pure CHA phase across this temperature range. When the crystallization temperature gradually increases, the relative crystallinity of the product shows a volcanic trend, reaching a peak (Table 1) at 423 K. The relevant SEM images (Figure 3 (b)–(f)) further

revealed the regulatory effect of crystallization temperature on zeolite morphology: at lower crystallization temperatures, the samples exist in the form of scattered small fragments with poor dispersion, and the surface crystal exhibits a primary disk shape. The measured crystal grain size is about 0.8 μm . As indicated by XRD analysis, the scattered fragments are pure CHA. As the synthesis temperature increases, the crystal morphology gradually transforms from disk-shaped and rhomboid to cluster-shaped. The size of the bulk CHA crystals gradually increases and they assemble into spherical aggregates through agglomeration, while the crystallinity of the product increases simultaneously. Among them, the crystals prepared at 423 K exhibited a more symmetrical and regular spherical morphology.

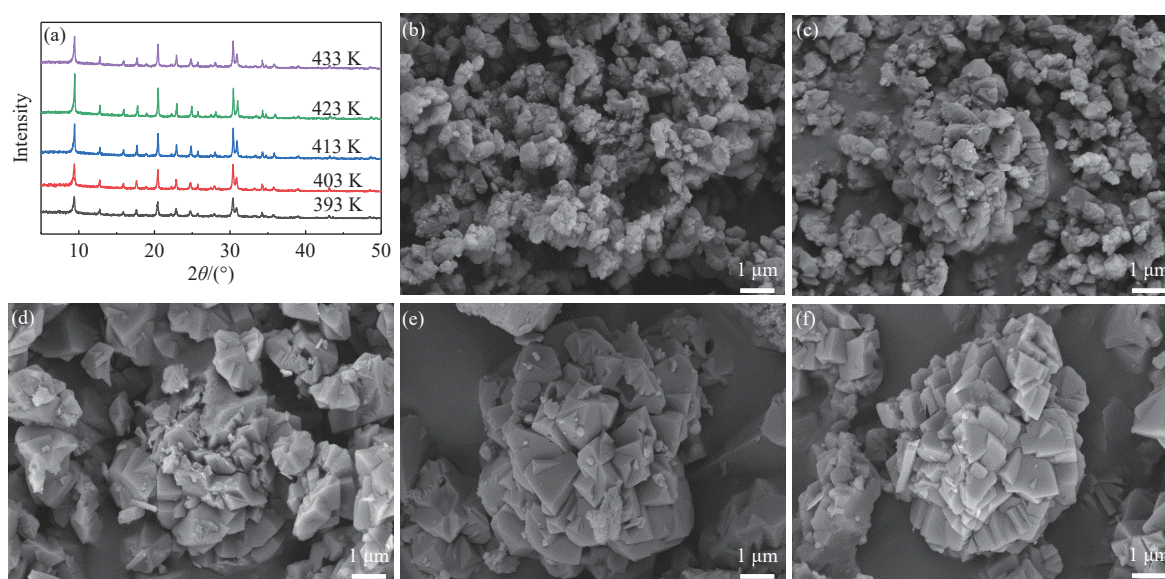


Fig. 3 XRD patterns (a) and SEM images for different synthesis temperature ((b) 393 K, (c) 403 K, (d) 413 K, (e) 423 K, (f) 433 K)

2.1.4 Study of crystallization time on CHA synthesis

As shown in Figure 4 and Table 1, the crystallization process is incomplete after 24 h, as indicated by the presence of FAU phase (from HY zeolite) present in the XRD pattern. When the crystallization time reached 36 h, the intensity of the characteristic peak of HY zeolite decreased significantly, while the characteristic peak of CHA-type molecular sieve began to appear. This phase transformation can be explained by the structure-directing effect of K⁺ during prolonged crystallization. The system reaches crystallization equilibrium at 48 h, with the crystallinity reaching its maximum. At this point, the crystal growth rate and dissolution rate are in dynamic equilibrium. It is worth noting that extending the crystallization time to 72 h resulted in a slight decrease in crystallinity, which is related to the metastable nature of molecular sieves^[31].

Based on the evolution pattern analysis in Figure 4, the crystallization CHA molecular sieve can be divided into four stages: (1) Initial stage (0–24 h): In the early stage of crystallization, HY zeolite dissolves under alkaline conditions^[32–33]. The dissolution rate is affected by various

factors such as temperature, basicity, silica-alumina ratio, and reactant concentration. K⁺ ions may act as structure-directing agents or crystallization aids at this stage, promoting the aggregation and agglomeration of dissolved components (such as silicate and aluminate species) to form amorphous or nanocrystalline intermediates^[32]. (2) Reorganization stage (24–36 h): HY zeolite continues to dissolve, while the internal structure of the spherical aggregates is reconstructed with a pronounced increase in crystallinity. In this stage, the aggregates (or gel particles) formed by the initial dissolved components begin to undergo internal structural rearrangement and crystallization. Meanwhile, the remaining HY zeolite in the solution continues to dissolve, providing more silicon and aluminum sources for the newly formed CHA crystals^[34]. The sharp increase in crystallinity indicates an accelerated formation rate of the CHA phase, with the nuclei of the new phase growing rapidly inside or on the surface of the aggregates. This typically involves the synergistic effect of solution phase transformation and solid-phase rearrangement^[35]. Some studies have also mentioned that under hydrothermal conditions, materials undergo a transformation from

amorphous to crystalline phase over time, accompanied by structural reorganization^[36]. (3) Crystal growth period (36–48 h): During this period, the dissolution of HY zeolite stops, and the system enters the pure crystal growth stage, with the grain size on the surface of the spheres increasing linearly. After most of the precursors dissolve and are converted into CHA crystal nuclei, the system enters the crystal growth-dominated stage^[34]. At this point, the silicon and aluminum species in the supersaturated solution continue to deposit onto the surface of the formed crystal nuclei, resulting in an increase in grain size^[37]. The crystal growth rate may remain relatively stable, resulting in a linear increase in grain size. (4) Late crystallization stage (48–72 h): In the late crystallization stage (48–72 h), since crystal growth has reached its limit, the system undergoes reverse dissolution, which manifests as a reduction in the diameter of the spheres and a decrease in the size of the surface grains^[38].

Based on the analysis presented above, the optimal synthesis conditions for CHA were subsequently determined: $n(\text{KOH})/n(\text{SiO}_2) = 0.6$, $n(\text{H}_2\text{O})/n(\text{SiO}_2) = 90$, crystallization temperature of 423 K, synthesis time of 48 h. This combination of parameters achieves an optimal balance between crystal phase purity, crystallinity, and energy efficiency, laying the foundation for subsequent testing and analysis. Since crystal size and Si/Al ratio significantly impact the adsorption performance of materials, samples with distinct morphologies were selected for preliminary adsorption performance tests (Figure S2) and elemental composition analysis (Table S1). Considering the above factors comprehensively, the CHA sample prepared under the conditions of $n(\text{KOH})/n(\text{SiO}_2) = 0.6$, $n(\text{H}_2\text{O})/n(\text{SiO}_2) = 90$, a crystallization temperature of 423 K, and a synthesis time of 48 h was selected for further detailed analysis of its adsorption performance.

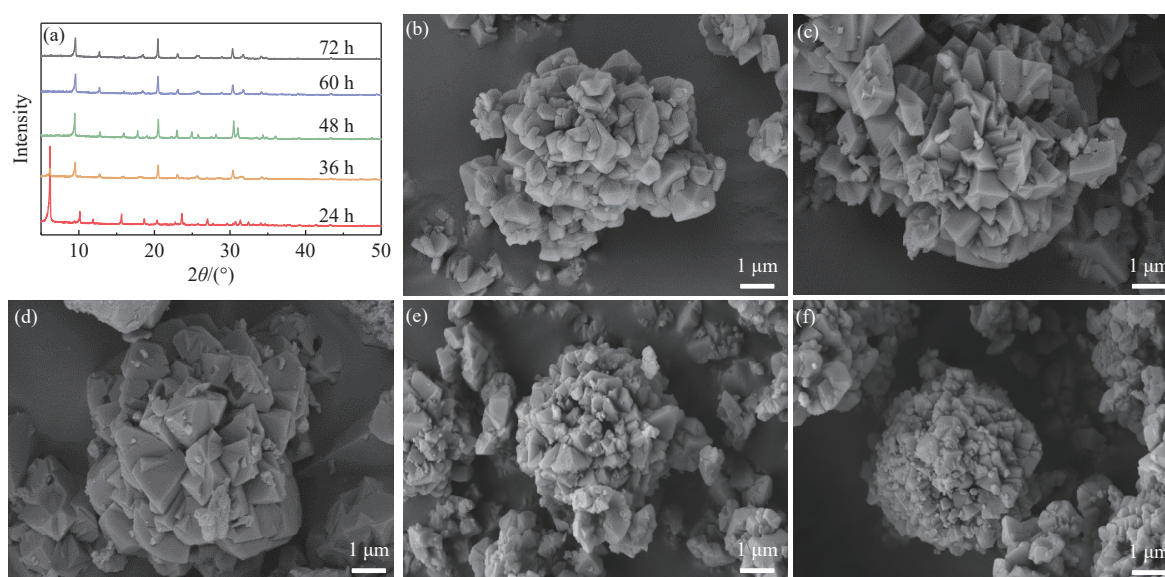


Fig. 4 XRD patterns (a) and SEM images for different synthesis times ((b) 24 h, (c) 36 h, (d) 48 h, (e) 60 h, (f) 72 h)

2.2 CO₂ adsorption performance and mechanism analysis of CHA zeolite

The dynamic and static adsorption properties of the prepared CHA zeolite were tested. As shown in the Figure 5(a), dynamic adsorption tests indicate that within the temperature range of 273–323 K, the adsorption capacity of CHA zeolite decreases with increasing temperature. The gas adsorption capacity decreased from 4.04 mmol/g at 273 K to 3.3 mmol/g at 423 K. The same trend was observed in the static adsorption data as shown in Figure 5(b). The adsorption capacities of CO₂ and N₂ at 298 K were lower than those at 273 K. This reduction may be due to the fact that adsorption is an exothermic process, and the adsorbed CO₂ is desorbed as the temperature increases^[39].

The breakthrough experiments were conducted using a CO₂/N₂ mixture (20:80, V/V) to analyze the adsorption capacity and separation coefficient of CO₂ and N₂

(Figure 5(c)). The breakthrough data revealed distinct adsorption behaviors at key points. At the breakthrough point (5%), the corresponding CO₂ and N₂ uptake were 3.22 and 0.21 mmol/g respectively, with a separation coefficient of 59.96. As the breakthrough process proceeds, the material's selectivity for CO₂ successively decreases at the semi-dry point (50%), flow-dry point (95%), and the equilibrium point, ultimately reaching 26.91% of its value at the equilibrium point. The separation coefficient decreases as penetration progresses. The analysis of the breakthrough curve of the mixed gas should also include an overall analysis of the breakthrough process. The material displayed a prominent selective adsorption for CO₂ with a breakthrough time of 2464.6 s/g, while N₂ reached the flow point much earlier at 106.2 s/g. Comprehensive analysis showed that when the penetration reached 2464.6 s/g, the N₂ gas curve showed a C/C_0 greater than 1. This is because the interaction force between CO₂ and the material is stronger than that between CO₂ and N₂.

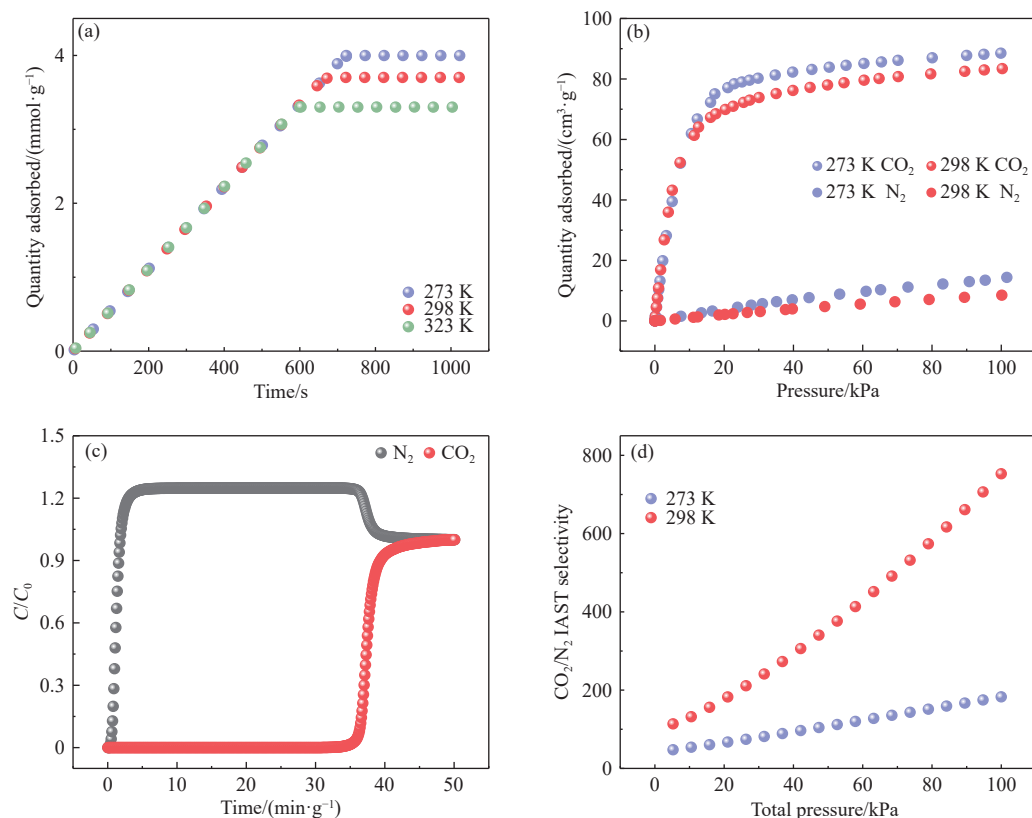


Fig. 5 (a) Adsorption isotherms of CHA zeolite at 273, 298 and 323 K obtained by dynamic method, (b) CO₂ and N₂ adsorption isotherms at 273 and 298 K, (c) Dynamic gas breakthrough curve of the CO₂/N₂ (20:80, V/V) mixture on CHA at 298 K, (d) IAST selectivity of CHA zeolites for the CO₂/N₂ (20:80, V/V) mixture

As adsorption proceeds, CO₂ gas molecules will displace the previously adsorbed N₂ molecules and occupy the adsorption sites. Consequently, the separation coefficient under actual mixed-gas equilibrium conditions is greater than 26.91, the value calculated from individually measured equilibrium uptakes.

For the static data analysis, the adsorption isotherms at different temperatures were fitted using the DSLF equation (Figure S3), the adsorption uptake (Figure S1) and the CO₂/N₂ selectivity under mixed-gas condition (CO₂/N₂=20:80) was calculated using the ideal solution theory (IAST). IAST data show (Figure 5(d)) that at different temperatures (273 and 298 K), the selectivity exhibits a trend of increasing selectivity with increasing adsorption pressure. Furthermore, the selectivity at 298 K is much higher than that at 273 K. This may be because higher temperature promotes gas molecular activity, allowing CO₂ to preferentially occupy more adsorption sites. This indicates that the material's selectivity for gases is primarily driven by kinetic effects^[40].

2.3 Adsorption kinetics analysis of CO₂ in CHA zeolite

A detailed kinetic analysis was performed on the prepared CHA zeolite. The adsorption data at 298 K were fitted and analyzed using pseudo-first-order kinetic equations, pseudo-second-order kinetic equations, and the

Avrami equation (Figure 6(a)). When pseudo-first-order and pseudo-second-order kinetic equations are used, the obtained R^2 is significantly lower (Table 2), indicating that these two models cannot effectively describe the adsorption kinetic characteristics. In contrast, the Avrami equation showed the best fit to the adsorption data with an R^2 of 0.9946, demonstrating its greater suitability for analyzing the kinetic behavior of this system (Figure 6(b)). Upon the Avrami equation, the adsorption rate constant increases continuously with increasing temperature (Figure 6(c), Table 3), indicating that the adsorption rate is enhanced with increasing temperature. This suggests that the adsorption process can reach equilibrium more quickly at higher temperatures. The corresponding adsorption activation energy of CHA zeolite for CO₂ was calculated to be 8.31 kJ/mol (Figure 6(d)). This value indicates that the adsorption process is dominated by physisorption.

2.4 Thermodynamic analysis of CO₂ adsorption in CHA zeolite

In thermodynamic studies of adsorption processes, the heat of adsorption indicating the strength of the interaction between the adsorbate and the adsorbent, is a key parameter for evaluating the energy characteristics of the adsorption process and understanding the adsorption mechanism and designing adsorption cycles.

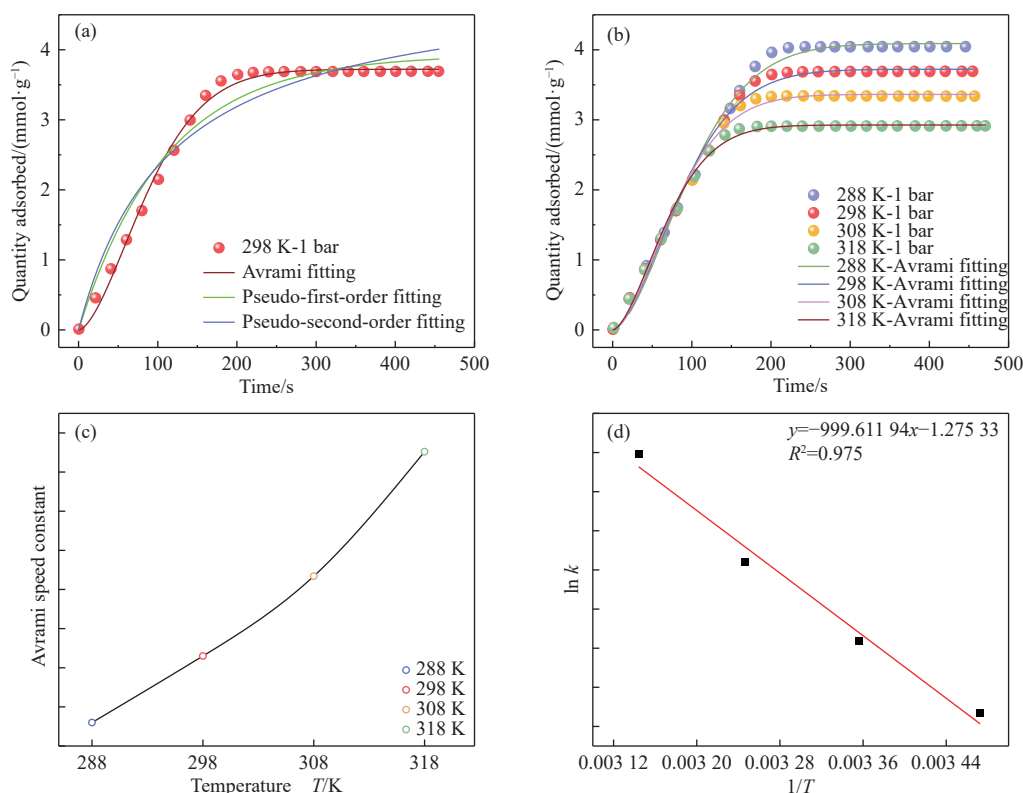


Fig. 6 (a) Fitting curves of different kinetic equations at 298 K, (b) Fitting curves of the Avrami equation at different temperatures, (c) Avrami equation rate constants at different temperatures, (d) Fitting curve of the Arrhenius equation

Table 2 Fitting parameters of different kinetic models for CHA adsorption curves at 298 K temperature

	Pseudo-first-order	Pseudo-second-order	Avrami
Equation expression	$q_t = a(1 - e^{-k_1 t})$	$q_t = \frac{a^2 k_1 t}{1 + a k_2 t}$	$q_t = a(1 - e^{-(k t)^n})$
a	3.92	0.51	3.72
$k(k_1/k_2)$	0.00912	0.16313/0.01681	0.00965
n	—	—	1.64255
R ²	0.9629	0.9331	0.9946

Table 3 Fitting parameters of the Avrami equation at different temperatures

Temperature/K	n	k	R ²
288	1.66845	0.0088	0.9913
298	1.64255	0.00965	0.9946
308	1.65058	0.01067	0.9947
318	1.64152	0.01226	0.9956

In this study, the adsorption heat of CO₂ was calculated by fitting the experimental data to the virial equation using AIM software^[41], enabling an in-depth exploration of the adsorption mechanism.

The virial equation was specifically proposed to describe the relationship between adsorption amount and operational parameters (pressure and temperature), and can be directly used to calculate the heat of adsorption of equal amounts and its behavior under different conditions^[42]. The CO₂ adsorption isotherms at 273 and 298 K were fitted using the virial equation to obtain relevant fitting parameters

(Figure 7). Then, the CO₂ adsorption heat data of CHA molecular sieve were calculated based on the obtained parameters. Adsorption heat data show that the adsorption heat varies with different adsorption amounts, indicating that the CHA molecular sieve has a heterogeneous surface. However, the overall adsorption heat is below 20 kJ/mol (Figure 7), which is considered physical adsorption. Kinetic data also confirm this, showing that the interaction force between CO₂ and CHA is relatively small, which helps reduce the energy consumption of the desorption process.

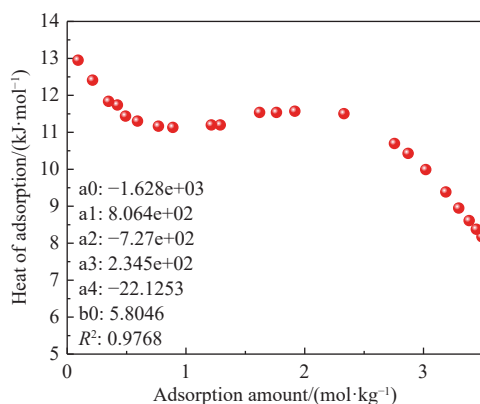


Fig. 7 Heat of adsorption for CO₂ of CHA

3 Conclusion

This study successfully synthesized CHA zeolite under optimized conditions ($n(\text{KOH})/n(\text{SiO}_2) = 0.6$, $n(\text{H}_2\text{O})/n(\text{SiO}_2) = 90$, hydrothermal synthesis temperature 423 K, hydrothermal synthesis time 48 h) using the H-FAU zeolite crystallization method. The CO₂ adsorption performance of CHA zeolite was tested in detail. Dynamic adsorption test data show that under the conditions of 1 bar and 273–323 K, the CO₂ adsorption capacity decreases with increasing temperature, from 4.04 mmol/g at 273 K to 3.3 mmol/g at 323 K. Static adsorption data show that at 1 bar, the CO₂ adsorption capacity also exhibits a decreasing trend with increasing temperature at 273 and 298 K, indicating that the adsorption process is exothermic. Thermodynamic analysis using the virial equation to calculate the heat of adsorption during the adsorption process, further confirmed that the adsorption process is exothermic. In the IAST selectivity calculation, the selectivity of CHA zeolite for CO₂ increases with increasing temperature, indicating that the separation process is mainly affected by diffusion. Furthermore, the breakthrough curve shows C/C_0 bigger than 1 at the end of the breakthrough column, suggesting that the interaction strength between CHA zeolite and CO₂ is greater than that with N₂. These findings provide insights into improving the separation efficiency of CHA zeolite in practical separation processes, demonstrating its significant application potential.

Declaration of Competing Interest

The authors declare no conflict of interest.

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小孔菱沸石选择性吸附 CO₂ 的性能研究

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摘 要: 菱沸石(CHA)由于其特殊的孔道结构被认为是一种极具潜力的 CO₂ 吸附材料。通过对 CHA 沸石吸附过程动力学的了解, 以促进高效吸附剂的开发仍是值得期待的。本研究中对 CHA 沸石的制备方法、CO₂ 吸附动力学以及热力学性能进行了研究。通过沸石间转化的方法, 以 H-FAU 沸石为原料进行沸石间转化合成 CHA 沸石。通过改变合成过程中的 $n(\text{KOH})/n(\text{SiO}_2)$ 、 $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ 、晶化温度以及晶化时间, 根据合成材料的 XRD、扫描电镜数据分析探索出最佳的 CHA 沸石合成条件。对制备 CHA 沸石的 CO₂ 吸附性能分别通过动态与静态方法进行了测试评价。采用不同的动力学模型对吸附过程的动力学行为进行分析, 动力学拟合数据表明, Avrami 方程对吸附过程有较好的拟合效果($R^2>0.99$), 随着温度升高吸附速率增加, 吸附过程更快速地达到平衡。选择性也随着温度的升高而升高, 表明 CO₂ 在 CHA 沸石上的吸附过程主要由扩散过程控制。穿透数据与热力学分析表明, 虽然材料与 CO₂ 之间作用力强于与 N₂ 之间的作用力, 但是对于 CO₂ 的吸附过程仍属于典型的物理吸附, CO₂ 与 CHA 沸石之间较弱的吸附强度有利于气体的解吸。研究结果为优化工业吸附操作条件提供了理论依据。

关键词: 菱沸石; CO₂ 吸附; 沸石转晶; 吸附动力学; Avrami 模型

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