

Study On the Adsorption Performance of Zeolite Molecular Sieve for CO₂

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Abstract. In this paper, CO₂ was used as the target adsorbate to study the adsorption capacity of three kinds of zeolite molecular sieves for CO₂ and the selective adsorption of CO₂/N₂. The results show that the adsorption capacity of NaX zeolite molecular sieve for CO₂ is significantly higher than that of NaA and CaA zeolite molecular sieves.

Keywords: CO₂, zeolite molecular sieve, adsorption capacity.

1. Introduction

Zeolite is a framework-shaped aluminosilicate mineral, which is divided into two types: natural zeolite and artificial zeolite, which are often modified and used as molecular sieves.^[1] Due to the high impurity content and small pore size of natural zeolite, its performance is limited and it is difficult to apply to various fields. Therefore, in actual production and life, synthetic zeolite molecular sieves are more widely used.^[2] Molecular sieve is a kind of adsorbent or film material with uniform micropores, mainly composed of silicon, aluminum and some other metal cations.^[3] Zeolite molecular sieves have uniform pore structure, good hydrothermal stability and strong acid resistance.^[4] Due to its special structure and properties, it has good properties such as sieving molecules, adsorption, ion exchange and catalysis.^[5] At present, it has been widely used in petrochemical field, environmental pollution, food industry, pharmaceutical chemical industry and other fields.^[6] With the development of various industries, zeolite molecular sieves have broad application prospects.^[7] This paper focuses on the application of zeolite in the field of air cleaning and preservation of fruits and vegetables.^[8]

2. Structural characteristics and main properties of zeolite

Zeolite is a general term for porous aluminosilicate crystal ore with a framework-like structure. According to different sources, it can be divided into two categories: natural zeolite and synthetic zeolite.^[9] The general chemical formula of zeolite is: $A_{x/n}(AlO_2)_x(SiO_2)_y \cdot mH_2O$, where m is the number of bound water molecules, x and y are integers, A is an exchangeable cation, and n is the valence state of the cation. The zeolite framework is composed of the most basic structural units silicon-oxygen tetrahedron (SiO₄) and aluminum-oxygen tetrahedron (AlO₄) in different ways through bridging oxygen.^[10] The zeolite framework is negative and neutralized by free cations outside the framework, such as Ca²⁺, Na⁺, K⁺, etc.^[11-13] Zeolite has the same structure and characteristics as a crystal, and its interior is a network of pores.

2.1. Adsorption performance

Zeolite has a large specific surface area, which makes zeolite as an adsorbent have stronger adsorption performance than other types of adsorbents.^[14] The adsorption of zeolite is a physical phenomenon.^[15] The surface force generated by the molecules on the surface of the zeolite attracts the molecules in the fluid to collide with the surface of the adsorbent, and generates molecular concentration on the surface, which reduces the number of such molecules in the fluid and achieves separation and removal.^[16] Purpose. Adsorption does not undergo any chemical change. As long as the molecules concentrated on the surface are dissipated, the zeolite has adsorption capacity again. This process is the reverse process of adsorption, which is called the regeneration process.

The zeolite molecular sieve has a uniform pore size, and it is generally determined by the size of the molecule whether it is adsorbed or not. Only when the molecular dynamics diameter is smaller

than the zeolite molecular sieve pore size can it easily enter the interior of the crystal cavity and be adsorbed. Since the zeolite molecular sieve has a strong polarity in the crystal cavity, it can interact with the molecules containing polar groups on the surface of the zeolite molecular sieve, or induce strong adsorption by polarizing the polarizable molecules. Due to this characteristic, The zeolite molecular sieve can be used as a carrier material to increase the reaction area and promote the reaction.

2.2. Catalytic performance

Zeolite molecular sieve is an environmentally friendly solid catalytic material. Because of its unique regular crystal structure, strong acidity and redox properties, it is widely used in petrochemical, ion exchange and environmental protection and other related industries. For example, HZSM-5 zeolite has attracted wide attention due to its excellent catalytic performance in the reaction of methanol to aromatics; Y molecular sieves have been widely used in petroleum refining and petrochemical fields; It exhibits excellent catalytic performance in the hydroisomerization reaction of long-chain alkanes. With the increasingly severe environmental pollution and energy shortage, people put forward higher requirements for the catalytic performance of catalytic materials.

When the zeolite molecular sieve is used as a catalyst or catalyst carrier, the crystal pore size of the zeolite molecular sieve affects the progress of the catalytic reaction. The size and shape of molecular sieve pores play a selective role in the catalytic reaction, showing a shape-selective catalytic state, which makes zeolite molecular sieves promising as catalytic materials.

2.3. Ion exchange performance

Zeolite molecular sieves have strong ion exchange performance, which usually refers to the exchange reaction between the zeolite molecular sieve framework and the ions in the solution, so that the specific transition metal ions we need are exchanged on the carrier to prepare transition metal zeolite. Generally, it is an alkali metal or alkaline earth metal ion, and the main zeolites used are X zeolite, Y zeolite, beta zeolite, ZSM-5 zeolite, etc. Metal cations are easily exchanged into metal zeolite molecular sieves of various valence states in aqueous solutions of metal salts. The pore size of zeolite molecular sieve can be changed by ion exchange, so as to change its performance and achieve the purpose of shape-selective adsorption and separation of mixtures.

In aqueous solution, due to the different ion selectivity of zeolite molecular sieves, different ion exchange properties can be exhibited. The cations in the zeolite molecular sieve are basically distributed in the zeolite structure in a fixed position. After ion exchange, the number, size and position of the cations in the aqueous solution change. When the ion is reduced, it often causes the vacancy of the site to make the pore size larger; and the ion with a larger radius is easy to be blocked by a certain amount of ions after the ion with a smaller radius is exchanged, so that the effective pore size is reduced.

3. The principle of zeolite molecular sieve

Regarding the difference between zeolite and molecular sieve, the chemical composition is the same. The structure is also similar, the small glass beads can be used to prevent boiling, it has air bubbles on the wall, not zeolite. In fact, the main difference between them is in their use, zeolites are generally natural, with different pore sizes, as long as there are cavities to prevent bumping. The functions of molecular sieves are much more advanced, such as screening molecules, making catalysts, slow-release catalysts, etc., so they have certain requirements on the pore size, and are often artificially synthesized. Sometimes natural zeolites can also be used as molecular sieves. The zeolite molecular sieve is a hydrate of crystalline aluminosilicate metal salt, which has two characteristics: (a). The Lewis center on the surface is very polar; (b). The small dimensions of the cages or channels in zeolites make the gravitational field within them very strong. Therefore, its adsorption capacity for adsorbate molecules far exceeds that of other types of adsorbents. Even if the partial pressure (or concentration) of the adsorbate is low, the amount of adsorption is still considerable. The adsorption

separation effect of zeolite molecular sieve is not only related to the size and shape of adsorbate molecules, but also to its polarity. Therefore, zeolite molecular sieve can also be used for the separation of substances with similar sizes.

Zeolite molecular sieves have the structure and characteristics of crystals, the surface is a solid framework, and the internal pores can play the role of adsorbing molecules. The pores are connected with each other by channels, and the molecules pass through the channels. Due to the crystalline nature of the pores, the pore size distribution of molecular sieves is very uniform. Molecular sieves selectively adsorb molecules according to the size of the pores inside their crystals, that is, adsorption-size molecules and repelling molecules of larger substances, so they are vividly called "molecular sieves".

The function of molecular sieve adsorption or repulsion is affected by the electrical properties of the molecule. Synthetic zeolite has the special function of selective adsorption according to the size and polarity of the molecule, so it can dry or purify the gas or liquid, which is also the basis for the separation of molecular sieves. Synthetic zeolite can meet the wide demand of the industry for adsorption and selective characteristic products, and it is also widely used in synthetic zeolite molecular sieves in industrial separation.

Adsorption is a physical phenomenon in which gaseous and liquid substances (adsorbates) are fixed on a solid surface (adsorbent), which has a large number of microporous active surfaces, and the molecules of the adsorbate are attracted by the adsorbent surface, so as to be fixed on it. Therefore, during adsorption, the pressure should be raised to the highest and the temperature should be lowered to the lowest. During desorption, the pressure should be reduced to the minimum and the temperature should be raised to the maximum.

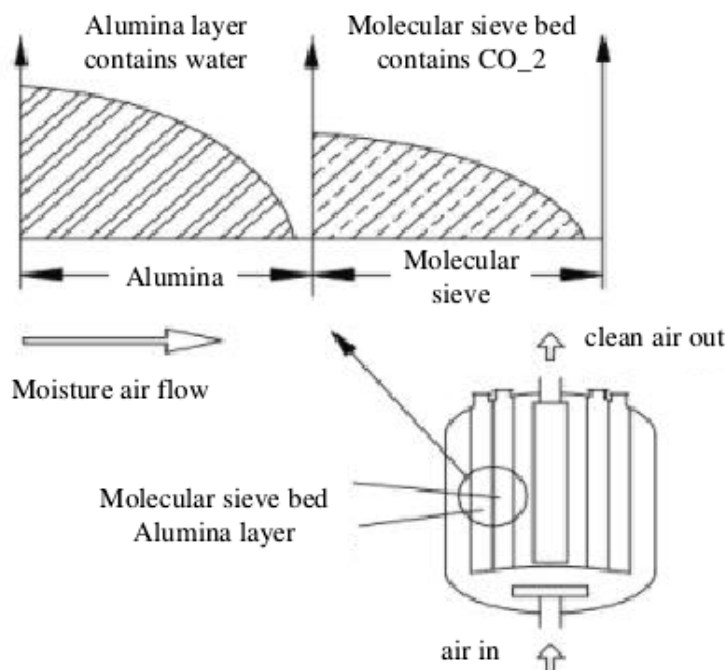


Figure 1. The state of adsorbent before the end of purification

4. Effect of Zeolite Molecular Sieve Type on CO₂ Adsorption Performance

Due to the differences in pore volume and specific surface area of different zeolite molecular sieves, the CO₂ adsorption capacity is affected to a certain extent. In this paper, NaA, CaA and NaX zeolite molecular sieves synthesized from fly ash under the optimal process parameters were selected, and the effects on CO₂ adsorption capacity at 25°C were investigated respectively to determine the optimal CO₂ adsorbent material. Table 1 and Figure 2 are the CO₂ pressure swing adsorption isotherm data table and CO₂ adsorption capacity map of NaA, CaA and NaX molecular sieves, respectively.

It can be seen from Table 1 that the CO₂ adsorption capacity of the synthesized three different types of zeolite molecular sieves has been greatly improved compared with the original fly ash. From the bar graph in Figure 2, it can be clearly seen that the CO₂ adsorption capacity of the original fly ash is only 0.2 mmol/g, while the synthesized NaA, CaA and NaX zeolite molecular sieves have relatively high CO₂ adsorption capacity, at 25 °C The adsorption capacities at the temperature were 3.8mmol/g, 3.3mmol/g and 2.5mmol/g respectively, and the CO adsorption capacity of NaX zeolite molecular sieve was the highest, because the specific surface area (608.1947m²/g) of NaX zeolite molecular sieves The two kinds of zeolite molecular sieves are large, which makes it have a higher adsorption capacity for CO₂; on the other hand, the NaX zeolite molecular sieve has a pore size of 1.3 nm, which is much larger than that of NaA (0.4 nm) and CaA (0.5 nm) type zeolite molecular sieves, making CO₂ molecules can freely enter the pores of NaX zeolite molecular sieve, which is convenient for further adsorption. In addition, for all the prepared zeolite molecular sieve products, the adsorption and desorption isotherms of CO₂ gas are almost at the same position, indicating that the adsorption type of the prepared samples is physical adsorption, which is easy to regenerate. Therefore, it can be concluded from the above analysis that among the NaA, CaA and NaX type zeolite molecular sieves synthesized by fly ash in the experiment, the NaX type zeolite molecular sieve has higher CO₂ adsorption capacity due to its larger specific surface area and pore size. conducive to regeneration.

Table 1. Adsorption capacity of molecular sieves for CO₂ at the same temperature

Model/Pressure	10	30	50	70	90
NaX	3.0 mmol/g	3.3 mmol/g	3.5 mmol/g	3.7 mmol/g	3.8 mmol/g
CaA	2.0 mmol/g	2.5 mmol/g	2.7 mmol/g	3.1 mmol/g	3.3 mmol/g
NaA	1.3 mmol/g	1.7 mmol/g	2.0 mmol/g	2.3 mmol/g	2.5 mmol/g
CFA	0 mmol/g	0 mmol/g	0.1 mmol/g	0.1 mmol/g	0.2 mmol/g

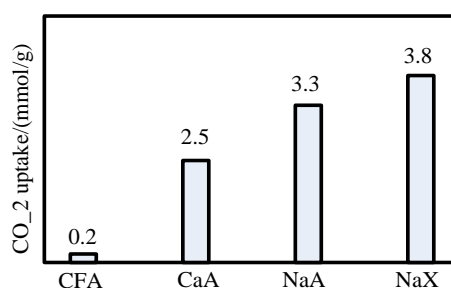


Figure 2. Histogram of CO₂ adsorption capacity of zeolite molecular sieves

5. Conclusion

In this paper, CO₂ was used as the target adsorbate to study the adsorption capacity of different types of zeolite molecular sieves for CO₂, and good results were obtained. However, this paper only studies the adsorption capacity under a single CO₂ atmosphere. It is more widely used, making the fly ash source zeolite molecular sieve a new material for "treating waste with waste and comprehensive utilization". In the follow-up research, the competitive adsorption of CO₂ in the coexistence of multi-component gases can be explored, and the selective adsorption performance of the synthesized zeolite molecular sieve can be more comprehensively evaluated.

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