

Influence of Gas Type on Adsorption Performance of Chabazite

Jiandong Yang, Xin Guo

China Satellite Maritime Tracking and Control Department, Jiangyin 214431, China

Abstract. Chabazite is a kind of aluminosilicate with special structure. In recent years, a large number of related studies have proved that it has good CO₂ adsorption performance. In this paper, the effect of gas species on the adsorption capacity of chabazite at a certain temperature was studied, and the conclusion was drawn: under the temperature of 60°C, the adsorption capacity of chabazite for N₂ was 1.0 mmol/g, and the adsorption capacity for CO₂ was 2.4 mmol/g, there is a relatively large difference in the adsorption capacity of these two gases.

Key words: adsorption capacity, chabazite, CO₂

1. Introduction

Zeolite is an aluminosilicate ore with specific pore structure. Zeolites can be classified into MFI, FAU, BEA, and CHA types according to the extension law of the smallest repeatable unit in the three-dimensional direction. According to the pore size, zeolites can be divided into small pores, medium pores and large pores (the number of ring silicon atoms of small pore zeolite is less than or equal to eight, and the number of ring silicon atoms of large pore zeolite is greater than or equal to twelve). CHA structure zeolite (chabazite) is a zeolite whose primary structural units are silicon-oxygen tetrahedron and aluminum-oxygen tetrahedron, which are connected to form a six-membered ring by sharing oxygen atoms. Therefore, it has a special three-dimensional pore structure and cage structure. At present, it is the gas adsorption performance of the adsorbent that determines the operating efficiency of most CO₂ capture devices. When chabazite adsorbs or desorbs gas, it will be accompanied by the release and absorption of heat. Thermodynamic analysis can further reveal the reaction mechanism of gas adsorbed on the adsorbent, and provide a theoretical basis for improving CO₂ capture efficiency.

Chabazite has unique adsorption and ion exchange properties. The inside of chabazite has channels with uniform pore size and a large number of cavities, which makes the inside of chabazite have a particularly large surface area, which provides the possibility for the adsorption of gas by chabazite. Molecules with similar pore size can enter the chabazite and be adsorbed, while molecules larger than the pore size cannot enter it. The cations inside the chabazite have a certain fluidity. When the chabazite is immersed in a salt solution with metal cations, the cations in the solution will enter the chabazite, thereby replacing the original cations. This property can change its internal pore size as well as the electric field and surface acidity inside the crystal, thereby changing its adsorption.

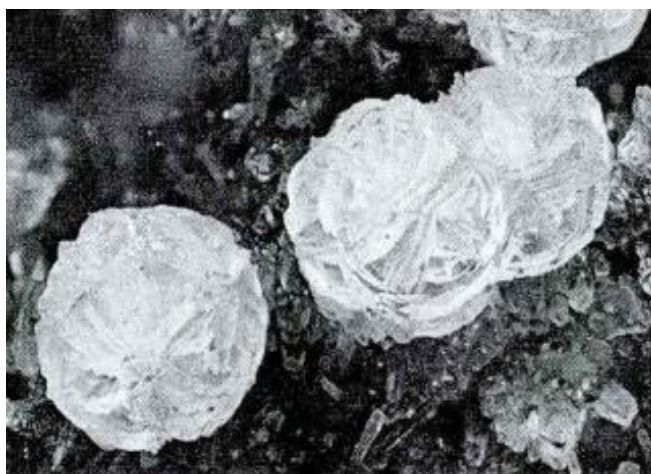


Fig. 1 Chabazite in crystalline state

2. Scheme of Synthesis of Chabazite

2.1. Scheme (A)

Reagents: silica sol; aluminum sulfate; NaOH; N,N,N-trimethyl-1-adamantane ammonium hydroxide.

Instruments: reaction kettle; oven; X-ray diffractometer.

Experiment procedure:

Using silica sol, aluminum sulfate, sodium hydroxide, N,N,N-trimethyl-1-adamantane ammonium hydroxide (R) and deionized water as raw materials, SSZ-13 was synthesized by traditional hydrothermal method. $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{NaOH}:\text{R}_2\text{O}:\text{H}_2\text{O}=40:1:6:5:900$ ratio and mix, after stirring evenly, age at room temperature for 0.5 h, and then pour it into a high pressure reaction kettle with PTFE lining at 155°C Crystallize for 2 to 5 days. After the reaction, it was poured into a beaker, heated to $70\text{--}80^\circ\text{C}$, and then added a certain amount of ammonium chloride for exchange for 2 h, vacuum filtered, and the exchange reaction was repeated 3 times. The separated solid was dried at 120°C , and then calcined with a temperature-programmed temperature to remove the templating agent and water in the crystals to obtain the original powder SSZ-13.

In the experiment, on the basis of the original synthesis, keeping other reaction conditions unchanged, the amount of NaOH and water was changed in turn, and the change of the specific surface area with the reaction time was observed when adding seeds and accelerators.

2.2. Scheme (B)

Reagents: silica sol; sodium meta aluminate or aluminum hydroxide; potassium hydroxide and sodium hydroxide (base raw materials); heterogeneous T-type zeolite.

Instruments: stainless steel reaction kettle; suction filter; X-ray diffractometer.

Adopt heterophase T-type zeolite as crystal seed to induce formation of chabazite without adding organic template agent, and its preparation is as follows:

(a). Prepare raw material liquid $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-Na}_2\text{O-H}_2\text{O}$, the molar ratio of each component is $\text{SiO}_2/\text{Al}_2\text{O}_3=10\text{--}25$, $\text{H}_2\text{O}/\text{SiO}_2=10\text{--}16$, $\text{Na}^+/\text{K}^+=0.1\text{--}0.8$, $\text{OH}^-/\text{SiO}_2=0.85\text{--}1.2$;

(b). The prepared raw material solution is added with 0.1~5wt% T-type zeolite crystal seeds, poured into a stainless steel reaction kettle, and hydrothermally synthesized at $80\text{--}180^\circ\text{C}$ for 6~48 hours;

(c). After the completion of the reaction, boil with 100°C of deionized water, wash away the surface alkali liquor, suction filter, wash to pH 7, and dry at 100°C for 12 hours.

3. The effect of gas species on adsorption capacity

The Dual-site-Langmuir equation can calculate the adsorption heat of N_2 and CO_2 on chabazite under certain temperature conditions. The specific formula is shown in formula (1):

$$q = M_B \frac{BP_n}{1 + BP} + M_D \frac{DP_n}{DP} \quad (1)$$

$$B = b_0 \exp\left(-\frac{Q_B}{RT}\right) \quad (2)$$

$$D = d_0 \exp\left(-\frac{Q_D}{RT}\right) \quad (3)$$

At a certain temperature, the adsorption curve of chabazite is brought into the above equation for fitting, and an approximate predicted trend can be finally obtained. In addition, the isotherms at 363K, 333K, and 303K can also be used to obtain the adsorption heat of chabazite for certain gases by using the Clapeyrm formula. The Clapeyrm formula looks like this:

$$Q_{st} = -R \left(\frac{\partial(\ln p)}{\partial(1/T)} \right)_q \quad (4)$$

Integrating both ends of formula (4), the linear form of formula (4) can be obtained as follows:

$$\ln p = -\frac{Q_{st}}{R} \frac{1}{T} + C \quad (5)$$

Substituting the relevant parameters of the Dual-site-Langmuir equation and the fitting curve into formula (5), the relationship between the adsorption capacity of chabazite for N₂ and the heat of adsorption can be obtained, and it can be proved that chabazite has a certain adsorption capacity range for CO₂. The adsorption heat trend is a downward curve.

According to the weight loss study of chabazite recorded in relevant literature, it can be seen that when the surrounding temperature reaches above 300°C, the chabazite basically does not change in terms of weight, which proves that when the temperature reaches a certain value, the interior of chabazite There is no gas and water anymore. At this time, the weight of chabazite is its real weight, so we usually set 300°C as the activation temperature of chabazite. The basic conditions for the adsorption characteristics test are shown in Table 1.

Table 1. Test Conditions Table

	Initial temperature°C	Termination temperature°C	Heating rate°C/min	Operating time (min)
1	60	60	0	60
2	300	300	0	60
3	30	300	30	9
4	300	60	-10	24

Before the experiment, before completing the adsorption test on the experimental sample, it is necessary to stipulate that the experiment should be carried out under the same conditions, so that it can be compared with other subsequent experiments to obtain more scientific results. The uniform steps for this regulation are:

(a). Turn on the machine and power it up, turning on the switches for all associated ancillary equipment.

(b). Put in N₂ gas at a speed of 30ml/min, and then wait for the flowmeter to stabilize before starting the next step.

(c). Load the sample and place the sample into the device using a gentle handling strategy.

(d). Set the program, such as the speed at which the temperature is raised, and parameters such as how long each temperature lasts.

According to the above steps, the test of the sample to be tested is carried out under a unified standard. The specific details are not described in this article. The adsorption capacity data of chabazite for N₂ and CO₂ at 60°C obtained in the final experimental test are shown in the Table 2.

Table 2. Adsorption capacity of chabazite at 60°C

Sample/time	50 min	100 min	150 min	200 min	250 min
CO ₂	0 mmol/g	0.7 mmol/g	1.4 mmol/g	2.4 mmol/g	2.5 mmol/g
N ₂	0 mmol/g	0.2 mmol/g	0.7 mmol/g	1.0 mmol/g	1.2 mmol/g

It can be seen from Table 2 that the adsorption capacities of the two chabazites for gases are relatively similar. In addition, if the temperature is lowered, the adsorption quantity of chabazite for N₂ and CO₂ will increase, and the adsorption rate of N₂ is lower than that of CO₂. When the state is stable, N₂ is significantly smaller than CO₂ in terms of the amount of adsorption. When the temperature is 60°C, the adsorption capacity of chabazite for N₂ is 1.0 mmol/g, and the adsorption capacity for CO₂ is 2.4 mmol/g. There is a big difference in the adsorption capacity of these two gases.

This is because N₂ is a non-polar molecule, but CO₂ is a triatomic molecule and a polar molecule, so the force on the surface of chabazite on N₂ is much smaller than the intermolecular force of CO₂.

4. Conclusion

Through research, it is known that the force on the surface of chabazite on N₂ is much smaller than the intermolecular force of CO₂. In addition, the molecular diameter of N₂ is 0.36nm, which is larger than the molecular diameter of CO₂, 0.33nm, and the internal pore size of chabazite is 0.34 nm. So it is obvious that CO₂ molecules can easily enter the pores of chabazite and be adsorbed.

References

- [1] High performance CO₂ -perm-selective SSZ-13 membranes: Elucidation of the link between membrane material and module properties[J]. Minseong Lee, Yanghwan Jeong, Sungwon Hong, Jungkyu Choi. *Journal of Membrane Science*. 2020 (prep)
- [2] High performance SSZ-13 membranes prepared at low temperature[J]. Heng'e Qiu, Ye Zhang, Lin Kong, Xue Kong, Xiaoxue Tang, Danni Meng, Ning Xu, Mingquan Wang, Yanfeng Zhang. *Journal of Membrane Science*. 2020 (prep)
- [3] High-performance SAPO-34 membranes for CO₂ separations from simulated flue gas[J]. Bo Liu, Congyong Tang, Xuewen Li, Bin Wang, Rongfei Zhou. *Microporous and Mesoporous Materials*. 2020 (C)
- [4] Synthesis and gas permeation properties of chabazite-type titanosilicate membranes synthesized using nano-sized seed crystals[J]. Sadao Araki, Hiroyasu Ishii, Satoshi Imasaka, Hideki Yamamoto. *Microporous and Mesoporous Materials*. 2020 (C)
- [5] Microstructural control of a SSZ-13 zeolite film via rapid thermal processing[J]. Jinseong Kim, Eunhee Jang, Sungwon Hong, Dongjae Kim, Eunjoo Kim, Hannes Richter, Adrian Simon, Nakwon Choi, Danil Korelskiy, Shahpar Fouladvand, Jaewook Nam, Jungkyu Choi. *Journal of Membrane Science*. 2019 (C)
- [6] Fast synthesis of thin high silica SSZ-13 zeolite membrane using oil-bath heating[J]. Hongbo Tang, Lu Bai, Mingquan Wang, Ye Zhang, Meng Li, Mengxin Wang, Lin Kong, Ning Xu, Yanfeng Zhang, Pinhua Rao. *International Journal of Hydrogen Energy*. 2019 (41)
- [7] Enhanced separation of maximum boiling azeotropic mixtures with extractive heterogeneous-azeotropic distillation[J]. Andras Jozsef Toth, Botond Szilagyi, Eniko Haaz, Szabolcs Solti, Tibor Nagy, Agnes Szanyi, Judit Nagy, Peter Mizsey. *Chemical Engineering Research and Design*. 2019
- [8] Defect-free high-silica CHA zeolite membranes with high selectivity for light gas separation[J]. Pelin Karakili?, Xuerui Wang, Freek Kapteijn, Arian Nijmeijer, Louis Winnubst. *Journal of Membrane Science*. 2019
- [9] Highly Selective SSZ-13 Zeolite Hollow Fiber Membranes by Ultraviolet Activation at Near-Ambient Temperature[J]. Dr. Shaowei Yang, Yeon Hye Kwon, Prof. Dr. Dong-Yeun Koh, Byunghyun Min, Dr. Yujun Liu, Prof. Dr. Sankar Nair. *ChemNanoMat*. 2019 (1)
- [10] Defects-healing of SAPO-34 membrane by post-synthesis modification using organosilica for selective CO₂ separation[J]. Yibing Mu, Huanhao Chen, Huan Xiang, Lan Lan, Yan Shao, Xiaolei Fan, Christopher Hardacre. *Journal of Membrane Science*. 2019
- [11] Tontisirin, Patcharin Worathanakul, Chantaraporn Phalakornkule. *Fuel*. 2017
- [12] Synthesis of a ceramic tile base based on high-alumina fly ash[J]. Hao Wang, Mengguang Zhu, Yongqi Sun, Ru Ji, Lili Liu, Xidong Wang. *Construction and Building Materials*. 2017
- [13] Changes in the CO₂ dynamics in near-surface cavities under a future warming scenario: Factors and evidence from the field and experimental findings[J]. C. Pla, S. Cuezva, E. Garcia-Anton, A. Fernandez-Cortes, J.C. Ca?averas, S. Sanchez-Moral, D. Benavente. *Science of the Total Environment*. 2016
- [14] CO₂ Capture and Ca²⁺ Exchange Using Zeolite A and 13X Prepared from Power Plant Fly Ash[J]. June Thet Soe, Su-Sung Kim, Yu-Ri Lee, Ji-Whan Ahn, Wha-Seung Ahn. *Bulletin of the Korean Chemical Society*. 2016 (4)
- [15] The effects of climate sensitivity and carbon cycle interactions on mitigation policy stringency[J]. Katherine Calvin, Ben Bond-Lamberty, James Edmonds, Mohamad Hejazi, Stephanie Waldhoff, Marshall Wise, Yuyu Zhou. *Climatic Change*. 2015 (1)
- [16] Selective preparation of zeolite X and A from flyash and its use as catalyst for biodiesel production[J]. Vikranth Volli, M.K. Purkait. *Journal of Hazardous Materials*. 2015