Adsorption Evaluation with Zeolites for Gases in the Confined Space

Xin Zheng1,2, Yao Li1, Wenli Li1, Zhen Su3, Jing Xu3, Yan Li3, Aihua Yuan1, Yusong Xu2 and Linzhi Zhai1,*

1School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, P. R. China
2School of Metallurgical and Materials Engineering, Jiangsu University of Science and Technology, Zhangjiagang, P. R. China
3Marine Equipment and Technology Institute, Jiangsu University of Science and Technology, Zhenjiang, P. R. China

*Corresponding author

Abstract: The high humidity characteristics of the confined space challenge the zeolites with good water performance. In this study, the adsorption of N2, CO2, H2, CH4, CO and H2O vapor by zeolites (5A and 13X) were discussed, and the structure of zeolites were characterized by XRD, FTIR and SEM. The adsorption breakthrough curve of CO2 was measured by the fixed bed reactor, and the adsorption characteristics were obtained under different temperatures and gas velocities. The results showed that 13X-2 zeolite had the CO2 adsorption capacity of 100.1 cm3·g-1, which is higher than the others, and the appropriate water stability.

1. Introduction
Recently, human activities become more popular in the confined space. Because of the human body metabolizes activity and material movement, harmful gases are produced. These harmful gases accumulated together, which would endanger the health of the human. Thus, the controlling techniques of the atmosphere in the confined space have aroused great attention[1].

Common gas purification technologies include adsorption, absorption, catalytic combustion, low temperature plasma and photocatalysis[2]. Among of these, adsorption process is a widely used technology, due to its high efficiency, simple operation and reusability[3]. Some adsorbents can be often used, such as include zeolites, metal-organic frameworks, covalent-organic frameworks and activated carbon[4]. Due to the stability and suitable microstructure, some researchers have focused on the zeolites[5]. Paul et al[6] studied the molecular kinetics of gas adsorption in confined space. Singh’s group[7] modified binder-containing zeolite 4A bodies with amine, which greatly improved the adsorption capacity of CO2 to 2.56mmol·g-1. According to SiO2/Al2O3 ratio and pore size, zeolites can be classified into 3A, 4A, 5A, 10X, 13X, Y type, etc[8-14]. Type A and type 13X have been widely used for gas adsorption due to their excellent properties and mature production process. The diameter of internal cavity with zeolite 5A (Na96(Al96Si96O384)·216H2O) is 5 Å, therefore, some molecules with the diameter less than 5 Å can be inhaled into the pores[15]. The effective aperture of zeolite 13X (Na86(Al86Si106O384)·264H2O) is 10 Å[16].

In the confined space, H2O vapor may have a great effect on the adsorption performance of zeolites. Therefore, zeolites should endow high adsorption capacity and good water stability. In this study, to obtain the good adsorbents, zeolites 5A and 13X were discussed. The static adsorption N2, CO2, H2,
CH₄, CO and H₂O vapor were carried out, and the dynamic CO₂ adsorption was performed with a fixed-bed reactor.

2. Experiment

2.1. Materials and Instruments
Zeolites 5A-1, 5A-2, 13X-1 and 13X-2 are purchased from four companies. Gas adsorption, SEM, FTIR, and XRD was measured by physical adsorption instrument (Mike, TriStar II flex 3), scanning electron microscopy (JEOL, JMS-7001F), Fourier transform infrared spectrometer (PittCon, Nicolet-IS10), and X-ray diffractometer (Scintag, XDS2000), respectively. CO₂, H₂, CH₄, CO and H₂O vapor was measured at 298 K.

2.2. Experimental Device
The fixed-bed system consisted of the furnace (Boyuntong, VTL1200) and the mass flowmeter (Shengye, SY-902B). In a typical experiment, the zeolites was filled into the reactor, and then the simulated flue gas with a volume fraction of 10% CO₂ and 90% N₂ was feed. The flow rate of gas and the temperature of the fixed-bed reactor were controlled, and the concentration of CO₂ was detected in each interval time.

3. Results and Discussion

3.1. Characterization
The XRD patterns of zeolites 5A-1, 5A-2, 13X-1 and 13X-2 are shown in Figure 1a. It can be found that the 5A-1 and 5A-2 zeolites display several same characteristic peaks in the range from 5 to 50°, which located at 2θ = 7, 21, 27, and 30°. The good accordance of XRD peaks between 5A-1 and 5A-2 indicates that they have a similar structure. The 13X zeolites depict the peaks at 2θ = 6, 23, and 26°[17]. The FT-IR spectra in Figure 1b showed that the four zeolites showed obvious absorption peaks at around 3480, 1651, 1487 and 995 cm⁻¹. The peaks of 1487, 995 cm⁻¹ and 3480, 1651 cm⁻¹ were assigned to Si-OH and O-H groups, respectively. It should be noted that the 13X zeolites show obviously stronger O-H peaks than those of 5A zeolites. This was possibly because that the 13X zeolites contain more crystal water[18].

SEM images of zeolites are presented in Figure 2. The 5A zeolites exhibited a typical hexahedral shape, while the particle sizes were not uniform. The two 13X zeolites demonstrated an octahedral shape with a narrow size distribution from 1.9 to 2.5 μm.

![Figure 1. XRD (a) and FTIR (b) patterns of the zeolites.](image-url)
3.2. Adsorption

The N$_2$ adsorption-desorption curves were used to evaluate the detailed pore characteristics of these samples, and the pore size distributions were analyzed by the NLDFT model. As shown in Figure 3a, in the area of low relative pressure (P/P$_0$<0.05), N$_2$ adsorption increased rapidly, which could be classified as I-type isotherm, indicating that all the samples contain a large number of micropores$^{[19]}$. In the area of P/P$_0$>0.9, the N$_2$ desorption curve was slightly higher than the adsorption curve, presenting an H3 hysteresis loop, which may be due to the presence of flake or crack holes in the zeolites$^{[20]}$. As shown in Figure 3b, the CO$_2$ adsorption capacity of 5A-1, 5A-2, 13X-1 and 13X-2 are 75.39, 85.55, 87.45 and 100.12 cm$^3$·g$^{-1}$, respectively. As calculated, the CO$_2$ adsorption capacity of 13X-2 zeolite is 32.8, 17.0 and 14.5 % higher than that of 5A-1, 5A-2 and 13X-1 zeolites. The adsorption and desorption curves of zeolite for CO$_2$ almost completely coincide, indicating that adsorbent has good regeneration ability, which is important in the gas adsorption and separation$^{[21]}$. In practice, the adsorption of H$_2$O vapor may have a great effect on the adsorption performance of zeolites. Therefore, the zeolite used in the confined space is required to have a good water stability$^{[22]}$. As shown in Figure 3c, the adsorption capacity of 13X-2 reached up to 323.0 cm$^3$·g$^{-1}$, with the good water stability.

![Figure 2. SEM images of 5A-1 (a), 5A-2 (b), 13X-1 (c) and 13X-2 (d).](image)

![Figure 3. The adsorption of N$_2$ (a), CO$_2$ (b), and H$_2$O (c).](image)

| Sample | BET (m$^2$·g$^{-1}$) | N$_2$ | CO$_2$ | H$_2$ | CH$_4$ | CO  | H$_2$O |
|--------|---------------------|-------|-------|-------|-------|-----|--------|
| 5A-1   | 514.3               | 229.9 | 75.4  | 1.13  | 11.1  | 16.7| 314.0  |
| 5A-2   | 569.2               | 208.9 | 85.5  | 0.90  | 12.2  | 20.7| 357.2  |
| 13X-1  | 581.8               | 226.0 | 87.4  | 0.70  | 9.8   | 11.2| 306.1  |
| 13X-2  | 639.0               | 242.6 | 100.1 | 0.92  | 7.3   | 12.5| 323.0  |

As shown in Table 1, 13X zeolite has the prominent BET surface area of 639.0 m$^2$·g$^{-1}$. The adsorption
of H₂, CH₄, and CO were 0.92, 7.3, and 12.5 cm³·g⁻¹, respectively. The adsorption curve was linearly related to the relative pressure, indicating that H₂, CH₄ and CO adsorbed on the zeolite as a single molecular layer. Because the aluminum in the zeolites has a +3 valence state, it is not balanced with the valence number of the oxygen atoms in the aluminum oxygen tetrahedron, so that the whole aluminum oxygen tetrahedron has a negative charge. In order to remain electrically neutral, metal ions with a positive charge would counteract its negative charge. A strong electric field was generated between positively charged metal ions and negatively charged zeolite skeleton, which makes the adsorption ability of polar substances much stronger than that of non-polar substances. At the same time, due to the strong electric field, a substance containing a double bond or π bond has a considerable adsorption capacity through induced polarization[19]. The order of maximum adsorption for different gases is: H₂O > N₂ > CO₂ > CO > CH₄ > H₂, which is basically consistent with the order of gas molecular polarizability[23].

3.3. Fixed-bed Adsorption

Adsortion breakthrough curves of different zeolites at 60 mL/min and 15 °C are shown in Figure 4a. At the early stage, CO₂ was completely adsorbed in the zeolite bed. With the increase of time, the adsorption of CO₂ reached the saturation point Therefore, the outlet CO₂ concentration slowly increased. The breakthrough curve became flat, indicating that the mass transfer zone reached the end of the fixed-bed reactor[24]. The adsorption breakthrough time of 5A-1, 5A-2, 13X-1 and 13X-2 were 3.9, 4.6, 4.9 and 5.3 min, respectively, which was corresponding to the order of CO₂ adsorption capacity. Form Figure 4b, the breakthrough time extended with the decreasing of gas flow rate. When the flow rate decreased form 60 mL/min to 15 mL/min, the breakthrough time reduced to 17 min. In Figure 4c, with the increase of temperature, the breakthrough point began to move forward (8.4 min at 15 °C to 11.1 min at 40 °C). Therefore, it can be concluded that the mass transfer zone will quickly reach the end of the fixed-bed at higher temperature.

![Figure 4 Adsorption breakthrough curves of zeolites (a), adsorption breakthrough curves of 13X-2 at different flow rates (b) and temperatures (c).](image)

4. Conclusion

In summary, the adsorption capacity of N₂, CO₂, H₂O, H₂, CH₄, and CO by four kinds of zeolites was studied. 13X-2 has the highest BET surface area (639.0 m²·g⁻¹) and excellent microstructure. The CO₂ adsorption capacity of 13X-2 zeolite reached up to 100.1 cm³·g⁻¹, which higher than those of others. In addition, the 13X-2 has the appropriate H₂O adsorption capacity of 323.0 cm³·g⁻¹, indicating a good water resistance. Therefore, zeolite 13X-2 is the better adsorbents for gases in the confined space.

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