Study of RHO zeolite with different cations for CO\textsubscript{2}/CO separation in pressure swing adsorption

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Funding information PetroChina Innovation Foundation, China, Grant/Award Number: 2012D-5006-0403; PetroChina Technology Development, Grant/Award Number: 2014A-2610; National Natural Science Foundation of China, Grant/Award Number: 51702044

Abstract A series of cation-exchanged RHO zeolites, including H-RHO, Li-RHO, Na-RHO, K-RHO, Cs-RHO, Cd-RHO and Pb-RHO, were prepared, and the samples were characterised by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, thermogravimetric analysis, inductive coupled plasma emission spectrometer and N\textsubscript{2}-BET. The CO\textsubscript{2} and CO adsorption behaviours of the samples were measured at 298 K and 0–10 bar. The Langmuir equation was used to fit adsorption isotherms to compare the separation effect of these RHO zeolites. The results show that extra-framework cations can effectively adjust the pore size of RHO. Not only it depends on the size of the cation radius, but other factors also play an important role, such as the position of the cation. Besides, compared with CHA structure, RHO structure has better CO\textsubscript{2}/CO separation performance. In all researched cationic forms of RHO, Li-RHO, Cd-RHO and Pb-RHO have excellent CO\textsubscript{2}/CO separation effects. Among them, the pore size of Cd-RHO is significantly reduced, thereby restricting the entry of CO more effectively, ultimately leading to greater shape selectivity. Cd-RHO not only has the highest CO\textsubscript{2} saturated adsorption capacity and CO\textsubscript{2} working capacity but also has relatively excellent CO\textsubscript{2}/CO selectivity, resulting in the sorbent selection parameter ($S$) is also the largest.

1 | INTRODUCTION

Smelting waste gases and automobile tail gases contain a large amount of CO and CO\textsubscript{2}, so the recovery of CO\textsubscript{2} not only reduces greenhouse gas emissions \cite{1–3}, but CO\textsubscript{2} is also used as an essential raw material for the production of urea, soda ash, and ammonium bicarbonate. Meanwhile, high-purity CO can be used to produce liquid hydrocarbon fuels by the Fischer–Tropsch synthesis method. It can also be widely used to produce various valuable chemical products, such as oxygenated compounds (methanol, ethanol, dimethyl ether etc.) and low carbon olefins \cite{4, 5}. Therefore, as the demand for these chemical products increases year by year, the separation of CO\textsubscript{2} and CO is essential in the chemical industry.

The common methods for separating CO\textsubscript{2} and CO include adsorption, solvent absorption, cryogenic distillation, and membrane separation \cite{6–8}. In these separation methods, adsorption separation has attracted more and more attention due to its relatively high energy efficiency and low cost \cite{9}. With the rapid development of Pressure Swing Adsorption (PSA), it has become the most critical adsorption and separation technology in the chemical industry. Meanwhile, the choice of adsorbent is particularly critical in the separation of CO\textsubscript{2} and CO by PSA technology. The adsorbents commonly used in the study of CO\textsubscript{2}/CO separation include various carbon-based adsorbents, metal-organic framework, and zeolite molecular sieves. Although carbon-based adsorbents have the advantages of low cost and low sensitivity to water, their application is limited owing to the large reactor volume required and the lack of adsorption selectivity for CO\textsubscript{2}/CO mixed gas \cite{10}. For the metal-organic framework, it shows a particularly strong CO\textsubscript{2} adsorption capacity, but the selectivity toward CO\textsubscript{2}/CO mixed gas is also relatively low. In addition, their frameworks are highly susceptible to water vapour, which can lead to deformable frameworks, so they are still far from practical applications \cite{11–14}. Zeolite molecular sieves have the advantages of low...
cost, high thermal stability, high recyclability, large surface area, and easy to adjust the pore size by ion exchange [15]. Therefore, people attach great importance to the study of zeolite molecular sieve for the separation of mixed gas in PSA technology.

ZSM-5 (MFI), Linde Type A (LTA), Faujasite (FAU), and Chabazite (CHA) type zeolites have been reported for CO₂ and CO separation [16]. Their CO₂ adsorption capacity is relatively high, but the CO₂/CO selectivity has not achieved an ideal effect. To solve this problem, an adsorbent with a strong separation ability of CO₂ and CO should be developed. We have previously studied the CO₂/CO separation performance of SSZ-13 with different alkali metal cations. Among them, K-SSZ-13 has a relatively low CO₂ saturation adsorption capacity, but the CO₂/CO selectivity reached 14.52, showing an excellent CO₂/CO separation effect [17]. Besides, many studies have reported the application of RHO zeolite in the separation of CO₂/CH₄ and CO₂/N₂, showing high CO₂ adsorption capacity and separation selectivity [18, 19]. However, few studies report on the CO₂/CO separation performance of RHO zeolite with different kinds of cations and different valence cations in PSA. Therefore, RHO zeolite may be a potential adsorbent for CO₂/CO separation.

The RHO zeolite is an open framework structure with double eight-membered rings uniformly connected to the α-cage [20, 21]. According to the theoretical calculations, the diameter of the eight-membered ring is 0.36 nm, which is just between the kinetic diameters of CO₂ (0.34 nm) and CO (0.38 nm) [22]. Therefore, the small pore eight-membered ring is the crucial position that determines the adsorption and separation performance of RHO zeolite. Adjusting the pore size of the eight-membered ring through cation exchange has the opportunity to enhance the shape selectivity of RHO zeolite, thereby further improving the CO₂/CO selectivity. In this work, we first modify the RHO framework by monovalent cations H⁺, Li⁺, Na⁺, K⁺, Cs⁺ to explore the CO₂/CO separation performance. We also introduced the divalent cations Cd²⁺ and Pb²⁺ with radii close to Li⁺ and Na⁺. The separation effect of RHO zeolites with different cations was compared to search the appropriate adsorbent to separate CO₂ and CO in PSA.

2 | EXPERIMENT

RHO zeolite was synthesised using a hydrothermal method, similar to the report of Chatelain et al. [23]. In 6 g of distilled water, 1.4 g of 18-crown-6 (≥ 98%) was dissolved. Then, 1 g of CsOH (99.9%), 0.6 g of NaOH (≥ 98%), 2.55 g of NaAlO₂ (≥ 98%), and 24 g of colloidal silica (30%) were added to the above solution. The formed gel was aged for 24 h under closing conditions at room temperature. Subsequently, the gel was performed in dynamic conditions at 383 K for 96 h. The obtained solid was filtered and washed with distilled water. Finally, the sample was dried at 373 K overnight and calcined at 823 K for 4 h to remove water and organic template.

As-synthesised RHO zeolite of 3 g was mixed with 150 ml 0.2 M NH₄NO₃, LiNO₃, NaN₂₃, NaNO₃, KNO₃, CsCl, Cd(NO₃)₂, and Pb(NO₃)₂, respectively. They were heated and stirred in a water bath at 353 K for 2 h to prepare for NH₄-RHO, Li-RHO, Na-RHO, K-RHO, Cs-RHO, Cd-RHO, and Pb-RHO, respectively. The obtained solid was filtered and washed with distilled water, and then the sample was dried at 373 K overnight and calcined at 823 K for 4 h. The above steps were repeated twice to get H-RHO, Li-RHO, Na-RHO, K-RHO, Cs-RHO, Cd-RHO, and Pb-RHO, respectively. The ion exchange degree is the percentage of moles of cations exchanged to the original moles of cations in RHO zeolite.

As-synthesised RHO zeolite was characterised by X-ray diffraction (XRD) using an X-ray diffractometer (D/max-2200 PC, 40.0 kV, 30.0 mA) with CuKα radiation, and the data were obtained in the 2θ range of 5–50° with a step of 0.02° and 2 s. Chemical analysis of as-synthesised RHO zeolite was performed by inductive coupled plasma emission spectrometer on an ICPS-7510 spectrometer under the conditions of an acceleration voltage of 3–10 kV and a current of 10 μA. Thermogravimetric analyses (TGA) were performed using an instrument (Diamond TG/DTA Perkin-Elmer SII) with the range from 323 to 1073 K at the heating rate of 278 K/min in airflow. Morphology of as-synthesised RHO, H-RHO, Li-RHO, Na-RHO, K-RHO, Cs-RHO, Cd-RHO, and Pb-RHO was examined by scanning electron microscopy (SEM) using a scanning electron microscope (JSM-6380) and an Oxford ISIS-300 energy dispersive X-ray spectroscopy (EDX). N₂ adsorption-desorption isotherms were measured at 77 K using Beishide 3H-2000PM1.

The adsorption capacity measurements of the cation-exchanged RHO zeolite were performed by using the high-pressure physical adsorption analyser. The sample was first activated at 523 K for 1 h and then cooled to room temperature. The constant temperature cup was raised to maintain the constant temperature of the sample tube, and CO₂ or CO adsorption experiments were carried out at 298 K and 0–10 bar, respectively.

The obtained adsorption data were fitted by Langmuir and Langmuir–Freundlich equations. The Langmuir (1) [24] and the Langmuir–Freundlich (2) [25–27] equations are as follows:

\[
q = \frac{q_m b_p}{1 + b_p} \quad (1)
\]

\[
q = \frac{q_m b_p^{1/n}}{1 + b_p^{1/n}} \quad (2)
\]

where \(q\) is the adsorption capacity of adsorbent (mmol/g), \(q_m\) is the saturation adsorption capacity of adsorbents (mmol/g), \(p\) is the adsorption pressure (bar), \(b\) is the Langmuir constant, \(n\) is a constant associated with temperature and system.

The CO₂/CO equilibrium selectivity (\(\alpha\)) formula is as follows:

\[
\alpha_{1,2} = \frac{q_{m1} b_1}{q_{m2} b_2} = \frac{K_1}{K_2} \quad (3)
\]

in which 1 represents CO₂ gas composition, and 2 represents CO gas composition. Under the condition that the adsorption data meets the adsorption characteristics of Langmuir, \(q_m b\) is
equal to the initial slope of the isotherm, which corresponds to Henry constant ($K$), so the equilibrium selectivity ($\alpha$) is equal to the ratio of the slopes of the initial adsorption isotherms of the two components, that is, $K_1/K_2$ [24].

For the PSA process, the sorbent selection parameter ($S$) is usually used to judge the separation performance of the adsorbent. The better the separation performance, the higher the $S$ value.

$$S = W\cdot \alpha_{1,2} = \frac{\Delta q_1}{\Delta q_2} \cdot \frac{K_1}{K_2}$$

where $\Delta q$ is the working capacity of the corresponding component.

### 3 RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of as-synthesised RHO and cation-exchanged RHO. It is evident that the XRD patterns of these samples match well with the characteristic peaks of the RHO standard pattern (PDF#43-0053), indicating that the pure phase RHO without other impurity crystals has been successfully synthesised. Meanwhile, it can be seen that the diffraction peak intensity of cation-exchanged RHO is slightly weaker than that of as-synthesised RHO. In this study, two calcination operations were performed in the process of ion exchange. Although the calcination process is conducive to the improvement of cation exchange degree, it has a certain influence on the crystallinity of zeolite. This phenomenon complies with the general rules of zeolite treatment. However, compared with the as-synthesised RHO, we find that the diffraction angle of the diffraction peak of the cation-exchanged RHO does not change. This result shows that cation exchange has no effect on the framework structure of RHO. Based on ICP analysis data, the Si/Al ratio of RHO zeolite is 12.1. As can be seen from the TGA and Differential Thermogravimetry Analysis (DTG) curves in Figure 2, the first weight-loss stage is from 323 to 623 K, which is the dehydration of without calcined as-synthesised RHO zeolite, and the second weight-loss stage is from 623 to 823 K, which is the decomposition of 18-crown-6 organic material. After 800 K, there is basically no further weight loss. Therefore, it can be proved that the samples were obtained after optimal thermal treatment. The morphology of as-synthesised RHO and cation-exchanged RHO were analysed by SEM in Figure 3. According to the SEM images, these samples always exhibit complete spherical crystal particles before and after ion exchange with the size of approximately 2–5 μm. However, the surface of the cation-exchanged RHO is relatively rough, so their crystallinity is slightly lower than that of as-synthesised RHO. The RHO crystal structure does not collapse, even though the introduction of cations has a certain effect on the crystallinity, which is consistent with the XRD results. According to the EDX results, high ion exchange degrees are achieved in all the cationic forms of RHO studied. Ion exchange degree of H-RHO, Li-RHO, Na-RHO, K-RHO, Cs-RHO, Cd-RHO, and Pb-RHO is calculated to be 82%, 94%, 78%, 97%, 100%, 54%, and 57%, respectively.

As displayed in Figure 4, the N$_2$ adsorption-desorption isotherms were measured at 77 K. H-RHO has a relatively large N$_2$ adsorption capacity. In contrast, the N$_2$ adsorption capacity of cation-exchanged RHO with a larger radius than H$^+$ is small. According to the calculation of the Langmuir model, the specific surface area for H-RHO (278.79 m$^2$/g) is significantly higher than other cation-exchanged RHO. The actual specific surface area values of these cationic forms of RHO, even H-RHO, have not been fully measured. The ion exchange degree of H-RHO is 82%, which might be since some Na$^+$ and Cs$^+$ in RHO were not exchanged, thus affecting the N$_2$ reaching the adsorption site of H-RHO zeolite. As a result, the specific surface area data obtained by BET is lower than the
actual specific surface area. It can be preliminarily concluded that the pore size of H-RHO is significantly larger than that of other cation-exchanged RHO, and cations with different radii can affect the pore size of RHO.

The adsorption behaviour of pure components CO$_2$ and CO on cation-exchanged RHO was measured at 298 K and 0–10 bar, respectively. The results of fitting the experimental adsorption data using the Langmuir and Langmuir–Freundlich equations are shown in Figure 5, and the fitting parameters are given in Tables 1 and 2. After fitting by the Langmuir and Langmuir–Freundlich equations, the correlation coefficient ($R^2$) of the Langmuir–Freundlich equation is slightly higher than that of the Langmuir equation. The Langmuir equation is given under the assumption that the surface is uniform [24]. In contrast, the Langmuir–Freundlich equation can be regarded as the application of the Langmuir model on the non-uniform surface [25]. Therefore, the adsorption of CO$_2$ and CO gas on RHO zeolite belongs to the non-uniform surface adsorption behaviour. More notably, the correlation coefficient of CO$_2$ and CO adsorption isotherms are both close to 1, indicating that the adsorption data are well fitted by these two equations. Therefore, the use of these two fitting equations is reasonable and reliable, and they are both suitable for analysing the adsorption and separation performance of CO$_2$ and CO on RHO zeolite. The equilibrium selectivity ($\alpha$) is a crucial indicator of mixed gas separation performance. To make the calculation of selectivity
more convenient, in this study, we chose to use the Langmuir equation to fit the adsorption data to analyse the CO₂/CO separation performance of different cation-exchanged RHO.

A common feature of all cation-exchanged RHO is that CO₂ adsorption capacity is higher than CO adsorption capacity over the entire pressure range (Figure 5). The result of high CO₂ adsorption capacity, on the one hand, is due to the relatively small kinetic diameter of CO₂. On the other hand, it is the result of the interaction between the field gradient of RHO zeolite and the quadrupole moment of CO₂ (4.3 × 10⁻²⁶ esu cm²). However, the kinetic diameter of CO is relatively large, and the quadrupole moment of CO (2.5 × 10⁻²⁶ esu cm²) is weaker than that of CO₂, so the CO adsorption capacity is lower.

The order of the CO₂/CO selectivity of RHO with monovalent cations is as follows: Li-RHO > Na-RHO > K-RHO > H-RHO > Cs-RHO (Table 3). For H-RHO, the adsorption capacity of CO₂ and CO is relatively high in the whole pressure range (Figure 5). Because the radius of H⁺ is too small, the pore size of H-RHO is the largest among all RHO zeolites studied such that CO₂ and CO can reach the adsorption site of H-RHO more easily. Ultimately, the saturated adsorption capacity of CO₂ and CO can reach 4.07 and 3.01 mmol/g, respectively. As a result, shape selectivity of H-RHO zeolite is not displayed, so that the CO₂/CO selectivity is relatively small, which is 26.80. For Cs-RHO, the adsorption capacity of CO₂ and CO is extremely small (Figure 5). The existence of the Cs⁺ (0.17 nm) with the largest ionic radius makes the pore size of the eight-membered ring of RHO greatly reduced, and even CO₂ with a relatively small kinetic diameter can hardly pass through the eight-membered ring, so it also does not exhibit shape selectivity. The CO₂/CO selectivity is extremely low, 13.93. This reflects the influence of the cationic radius size on the pore size of RHO, that is, the larger the cation radius, the smaller the pore size of RHO.

In our previous study on CO₂/CO separation of a series of alkali metal cation-exchanged SSZ-13, K-SSZ-13 zeolite showed excellent separation performance. For the same kind of cation in this study, K-RHO, although its adsorption and separation performance is not excellent in the studied RHO, its CO₂/CO selectivity (55.37) is about twice that of K-SSZ-13 (23.46) (Table 3). SSZ-13 is a microporous aluminosilicate zeolite with the CHA structure, and the theoretically calculated pore size is 0.38 × 0.38 nm [26, 27]. The pore size of the RHO structure (0.36 × 0.36 nm) is smaller than that of the CHA structure, so that RHO has greater shape selectivity for CO₂ and CO, and has a better separation effect of CO₂ and CO.

The CO₂/CO selectivity of Li-RHO and Na-RHO, which have better separation effects than K-RHO, is 144.32 and 101.70, respectively (Table 3). They more effectively restrict the entry of CO and have better shape selectivity for CO₂ and CO. Different from the pore size rules of H-RHO and Cs-RHO, we found that the exchange of Li⁺ (0.076 nm) and Na⁺ (0.102 nm) with smaller radius makes the pores smaller and has greater shape selectivity. Although the CO₂ saturated adsorption capacity of Li-RHO is not high, the CO₂/CO selectivity shows the highest value, 144.32, indicating that Li-RHO has a strong restriction on the entry of CO. It has been reported that the extra-framework cations are preferentially distributed in the three positions of single eight-ring, double eight-ring and single six-ring [18, 19]. According to Lozinska et al. [28], Li⁺ is located at the position of the single six-membered rings that are not the eight-membered rings. To coordinate the balance of Li⁺ on the single six-membered rings, the single six-membered rings are distorted, the entire RHO framework and the eight-membered rings as the main window are strongly deformed as well, the window size is reduced, and the shape selectivity is significantly improved. Therefore, it can be regarded that the pore size of RHO is also greatly related to the position of the cation. This critical phenomenon is also well reflected in divalent cation-exchanged RHO (Cd-RHO and Pb-RHO) with radii close to Li⁺ and Na⁺.

It can be seen from Tables 1 and 3 that Cd-RHO and Pb-RHO show relatively excellent CO₂ saturated adsorption capacity and CO₂/CO selectivity. Among them, the CO₂ saturated adsorption capacity of Cd-RHO can be as high as 4.58 mmol/g, and the CO₂/CO selectivity of Cd-RHO is almost similar to

![Figure 4](https://example.com/figure4.png)  
**Figure 4** N₂ adsorption (solid)-desorption (hollow) isotherms at 77 K of H-RHO, Li-RHO, Na-RHO, K-RHO, Cs-RHO, Cd-RHO, and Pb-RHO.

### Table 1

| Adsorbent | CO₂ | CO |
|-----------|-----|----|
|            | qₘ (mmol/g) | b  | R² | qₘ (mmol/g) | b  | R² |
| H-RHO      | 4.07 | 1.348 | 0.99918 | 3.01 | 0.068 | 0.99977 |
| Li-RHO     | 3.52 | 0.738 | 0.98631 | 0.40 | 0.045 | 0.84841 |
| Na-RHO     | 4.05 | 1.464 | 0.99069 | 2.65 | 0.022 | 0.98886 |
| K-RHO      | 3.84 | 3.039 | 0.99091 | 2.81 | 0.075 | 0.99849 |
| Cs-RHO     | 2.64 | 0.579 | 0.96639 | 1.59 | 0.069 | 0.96635 |
| Cd-RHO     | 4.58 | 0.580 | 0.99575 | 0.60 | 0.032 | 0.87663 |
| Pb-RHO     | 3.53 | 0.609 | 0.98081 | 0.47 | 0.044 | 0.91304 |
FIGURE 5  (a) CO$_2$ adsorption isotherms and (b) CO adsorption isotherms for cation-exchanged RHO at 298 K, the solid lines were data simulated by Langmuir equation, (c) CO$_2$ adsorption isotherms, and (d) CO adsorption isotherms for cation-exchanged RHO at 298 K, the solid lines were data simulated by Langmuir–Freundlich equation.

TABLE 2  The Langmuir–Freundlich equation fits the CO$_2$ and CO adsorption isotherms on the cationic forms of RHO

| Adsorbent | qm (mmol/g) | b    | R$^2$ | qm (mmol/g) | b    | R$^2$ |
|-----------|-------------|------|-------|-------------|------|-------|
| H-RHO     | 4.19        | 1.233| 0.99982| 2.61        | 0.077| 0.99993|
| Li-RHO    | 3.05        | 1.063| 0.99856| 0.68        | 0.012| 0.99878|
| Na-RHO    | 3.77        | 2.076| 0.99743| 1.48        | 0.027| 0.99705|
| K-RHO     | 4.06        | 2.292| 0.99671| 2.18        | 0.090| 0.99920|
| Cs-RHO    | 2.63        | 0.581| 0.99014| 1.67        | 0.037| 0.99761|
| Cd-RHO    | 3.74        | 0.850| 0.99847| 0.79        | 0.005| 0.99622|
| Pb-RHO    | 4.04        | 0.485| 0.99838| 0.69        | 0.009| 0.99722|

that of Li-RHO, 138.35. Although the exchange degree of divalent cations Cd$^{2+}$ (54%) and Pb$^{2+}$ (57%) is less than that of alkali metal cations, their adsorption and separation effects are also very prominent. Therefore, it is fully confirmed that the exchange of the divalent cations Cd$^{2+}$ (0.095 nm) and Pb$^{2+}$ (0.119 nm) with radii similar to Li$^+$ and Na$^+$ also significantly reduces the pore size, and the shape selectivity is also significantly enhanced, especially for Cd-RHO.

In the industrial PSA, the adsorption process is performed at 4–6 bar, and the desorption process is performed at 1 bar [15]. Therefore, this study defines the CO$_2$ working capacity as the CO$_2$ adsorption capacity at 6 bar minus the CO$_2$ adsorption capacity at 1 bar. It can be considered that during the PSA working pressure (1–6 bar), the more significant the change in the CO$_2$ adsorption capacity, the more conducive to separation. Meanwhile, the CO$_2$ working capacity is related to the strength of the adsorption between adsorbate and adsorbent. Henry constant can reflect the strength of adsorption. The order of Henry constant of CO$_2$ is as follows: H-RHO, Na-RHO, K-RHO > Cd-RHO, Pb-RHO, Li-RHO > Cs-RHO (Table 3). The Henry constant of CO$_2$ is too high or too low, that is, the adsorption is too strong or too weak, which will lead to a minimal change in the CO$_2$ adsorption capacity within the operating pressure range, making the CO$_2$ working capacity very low. Since the Henry constant of CO$_2$ of Cd-RHO, Pb-RHO and Li-RHO are smaller than H-RHO, Na-RHO and K-RHO, and greater than Cs-RHO, resulting in the Henry constants of CO$_2$ of Cd-RHO, Pb-RHO and Li-RHO are just right. The strength of adsorption is more appropriate, so the CO$_2$ adsorption capacity will vary greatly within the entire PSA working pressure range. Eventually, high CO$_2$ working capacity will be obtained, especially Cd-RHO is the highest, 1.88 mmol/g.

Rege and Yang proposed a simple sorbent selection parameter ($S$) for the PSA separation process to compare the separation effect of two adsorbents for a particular binary gas to determine which adsorbent is more suitable for the separation of the binary gas [29, 30]. The $S$ parameter is extremely
sensitive to the subtle variations in adsorption isotherms [26]. The \( \delta \) parameter is composed of two factors. One is the equilibrium selectivity of the adsorbent, and the other is related to the working capacity. The \( \delta \) parameters of all different cation-exchanged RHO are compared, Li-RHO, Cd-RHO and Pb-RHO are relatively high, among which the \( \delta \) parameter of Cd-RHO can be as high as 3371. It can be considered that Cd-RHO is a very suitable adsorbent for CO\(_2\)/CO separation in PSA.

### 4 CONCLUSION

RHO zeolite was successfully synthesised by hydrothermal synthesis using an 18-crown-6 template agent. The pores of the as-synthesised RHO were modified by ion exchange (H\(^+\), Li\(^+\), Na\(^+\), K\(^+\), Cs\(^+\), Cd\(^{2+}\) and Pb\(^{2+}\)) to study the CO\(_2\)/CO separation performance. The results of adsorption and separation show that RHO structure zeolite is better than CHA structure zeolite in the application of PSA to separate CO\(_2\) and CO. The extra-framework cation can effectively adjust the pore size of RHO. In addition to the radius of the cation, there are other factors that can affect the pore size, such as the position of the extra-framework cation. Among all the cation-exchanged RHO zeolites studied, Li-RHO, Cd-RHO and Pb-RHO exhibit excellent separation performance of CO\(_2\) and CO. For Li-RHO, the CO\(_2\)/CO selectivity is the highest among all zeolites studied, but the CO\(_2\) saturated adsorption capacity is not excellent. For Cd-RHO, the CO\(_2\) saturated adsorption capacity and the CO\(_2\) working capacity are the highest, and the CO\(_2\)/CO selectivity is close to that of Li-RHO, reaching 138.35. Meanwhile, it can be judged from the sorbent selection parameters that Cd-RHO is more suitable for PSA to separate CO\(_2\) and CO.

### ACKNOWLEDGEMENTS

The authors would like to acknowledge the PetroChina Innovation Foundation, China (grant no. 2012D-5006-0403), PetroChina Technology Development (2014A-2610) and the National Natural Science Foundation of China (no. 51702044) for the support for this work.

### REFERENCES

1. Sapchenko, S.A., et al.: Selective gas adsorption in microporous metal-organic frameworks incorporating urotropine basic sites: An experimental and theoretical study. Chem. Commun. 51(73), 13918–13921 (2015)
2. Kim, H., et al.: Highly selective carbon dioxide sorption in an organic molecular porous material. J. Am. Chem. Soc. 132(35), 12200–12202 (2010)
3. Duc, N.H., Chauvy, F., Herri, J.M.: CO\(_2\) capture by hydrate crystallization-a potential solution for gas emission of steelmaking industry. Energy Convers. Manage. 48(4), 1313–1322 (2007)
4. Kauffman, G.B.: Beyond oil and gas: The methanol economy, 2nd updated and enlarged edition. Found. Chem. 15(2), 239–240 (2013)
5. Liu, K., Song, C., Subramani, V. Desulfurization Technologies: Hydrogen and Syngas Production and Purification Technologies. John Wiley & Sons Inc., Hoboken, New Jersey, pp. 219–310 (2009)
6. Rufford, T.E., et al.: The removal of CO\(_2\) and N\(_2\) from natural gas: A review of conventional and emerging process technologies. J. Pet. Sci. Eng. 94-95, 123–154 (2012)
7. Songolzadeh, M., et al.: Carbon dioxide separation from flue gases: A technological review emphasizing reduction in greenhouse gas emissions. Sci. World J. 2014(1), 828131 (2014)
8. Aaron, D., Tsiouris, C.: Separation of CO\(_2\) from flue gas: A review: Separation Science and Technology. Sep. Sci. Technol. 40, 321–348 (2005)
9. Hartmann, M.: Characterization of mesoporous molecular sieves containing copper and zinc: An adsorption and TPR study. Stud. Surf. Sci. Catal. 128, 215–224 (2000)
10. McEwen, J., Hayman, J.D., Yazaydin, A.O.: A comparative study of CO\(_2\), CH\(_4\) and N\(_2\) adsorption in ZIF-8, Zeolite-13X and BPL activated carbon. Chem. Phys. 412, 72–76 (2013)
11. Li, J.R., Kuppler, R.J., Zhou, H.C.: Selective gas adsorption and separation in metal-organic frameworks. Chem. Soc. Rev. 38(5), 1477–1504 (2009)
12. Banerjee, R., et al.: High-throughput synthesis of zeolite imidazolate frameworks and application to CO\(_2\) capture. Science 319(5865), 939–943 (2008)
13. Trickett, C.A., et al.: The chemistry of metal-organic frameworks for CO\(_2\) capture, regeneration and conversion. Nat. Rev. Mater. 2(8), 17045 (2017)
14. Li, J.R., Sculley, J., Zhou, H.C.: Metal-organic frameworks for separations. Chem. Rev. 112(2), 869–932 (2012)
15. Patel, H.A., Byun, J., Yavuz, C.T.: Carbon dioxide capture sorbents: Chemistry and methods. ChemSusChem. 10(7), 1303–1317 (2017)
16. Wilson, S.M.W., Kennedy, D.A., Tezel, F.H.: Adsorbent screening for CO\(_2\)/CO separation for applications in syngas production. Sep. Purif. Technol. 236, 116268 (2019)

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17. Feng, J.W., et al.: Carbon monoxide and carbon dioxide adsorption on alkali metal cation-exchanged SSZ-13 zeolites. Micro Nano Lett. 15(8), 529–534 (2020)
18. Lozinska, M.M., et al.: Understanding carbon dioxide adsorption on univalent cation forms of the flexible zeolite rho at conditions relevant to carbon capture from flue gases. J. Am. Chem. Soc. 134(42), 17628–17642 (2012)
19. Lozinska, M.M., et al.: Cation gating and relocation during the highly selective “trapdoor” adsorption of CO₂ on univalent cation forms of zeolite rho. Chem. Mater. 26(6), 2052–2061 (2014)
20. Pera-Titus, M., et al.: Thermodynamic analysis of framework deformation in Na, Cs-RHO zeolite upon CO₂ adsorption. Phys. Chem. Chem. Phys. 16(44), 24391–24400 (2014)
21. Nenoff, T.M., et al.: Flexibility of the zeolite RHO framework. In situ X-ray and neutron powder structural characterization of cation exchanged BePO and BeAsO RHO analogs. J. Phys. Chem. 100(33), 14256–14264 (1996)
22. Langmi, H.W., et al.: Hydrogen adsorption in zeolites A, X, Y and RHO. J. Alloys Compd. 356-357, 710–715 (2003)
23. Chancel, T., et al.: Synthesis and characterization of high-silica zeolite-rho prepared in the presence of 18-crown-6 ether as organic template. Microporous Mater. 4(2-3), 231–238 (1995)
24. Li, Y.P., et al.: Efficient synthesis of high silica SSZ-13 zeolite via a steam-assisted crystallization process. J. Porous Mater. 26(6), 1879–1888 (2019)
25. Yang, R.T. Sorbent Selection: Equilibrium Isotherms, Diffusion, Cyclic Processes, and Sorbent Selection Criteria: Adsorbents: Fundamentals and Applications, pp. 17–53. John Wiley & Sons Inc., Hoboken, New Jersey Hoboken (2003)
26. Bonenfant, D., et al.: Advances in principal factors influencing carbon dioxide adsorption on zeolites. Sci. Technol. Adv. Mater. 9(1), 013007 (2008)
27. Boot-Handford, M.E., et al.: Carbon capture and storage update. Energy Environ. Sci. 7(1), 130–189 (2014)
28. Lozinska, M.M., et al.: Cation control of molecular sieving by flexible Li-containing zeolite RHO. J. Phys. Chem. C 120(35), 19652–19662 (2016)
29. Rege, S.U., Yang, R.T.: A novel FTIR method for studying mixed gas adsorption at low concentrations: H₂O and CO₂ on NaX zeolite and gamma-alumina. Chem. Eng. Sci. 56(12), 3781–3796 (2001)
30. Rege, S.U., Yang, R.T.: A simple parameter for selecting an adsorbent for gas separation by pressure swing adsorption. Sep. Sci. Technol. 36(15), 3355–3365 (2001)

How to cite this article: Liang D. et al.: Study of RHO zeolite with different cations for CO₂/CO separation in pressure swing adsorption. Micro Nano Lett. 16, 319–326 (2021). https://doi.org/10.1049/mna2.12054