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Tao, Zeyu; Tian, Yuanmeng; Ou, Sze Yiu; Gu, Qinfen; Shang, Jin

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Direct air capture of CO₂ by metal cation-exchanged LTA zeolites: effect of the charge-to-size ratio of cations

Zeyu Tao^{a, b}, Yuanmeng Tian^{a, b}, SzeYiu Ou^a, Qinfen Gu^c, Jin Shang^{a, b, d *}

a. School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

b. City University of Hong Kong Shenzhen Research Institute, Yuexing 1st Road, Shenzhen Hi-Tech Industrial Park, Nanshan District, Shenzhen, PR China

c. Australian Synchrotron (ANSTO), Clayton, Victoria 3168, Australia

d. Low-Carbon and Climate Impact Research Center, School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, PR China

*Corresponding author, email: jinshang@cityu.edu.hk

Abstract

Direct air capture of CO₂ (DAC) has been increasingly recognized as a promising carbon-negative technology. The challenge in deploying energy-efficient DAC lies in effective sorbent materials. In this research, we comprehensively investigated the DAC behavior of LTA zeolites exchanged with different metal cations (Na⁺, K⁺, Mg²⁺, Ca²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Y³⁺, La³⁺, Ce³⁺, Eu³⁺, Tb³⁺, and Yb³⁺) by both static single-component gas adsorption and dynamic mixture gas adsorptive separation tests. We found that a large charge-to-size ratio of cations is critical to imparting a high DAC capacity of LTA zeolites, which is ascribed to the enhanced electrostatic interaction and/or π -back bonding toward CO₂. Meanwhile, a detrimental effect is associated with an excessively large charge-to-size ratio, that is, a significant “shielding effect” of (pre-) adsorbed contaminants (e.g., H₂O and CO₂) on cations (e.g., Mn²⁺ and Mg²⁺) reduce the accessible CO₂ capacity. Ca-LTA featuring Ca²⁺ with an appropriate charge-to-size ratio exhibits the highest DAC capacity (350 ppm CO₂ in the air, 1.20 mmol/g) with fast kinetics and good reusability. These results provide valuable insights for the design of zeolites-based physisorbents for DAC.

Keywords: Direct air capture of CO₂ (DAC), physisorbents, zeolite LTA, metal cations

Introduction

With industrialization and urbanization, the atmospheric carbon dioxide (CO₂) concentration has risen from 280 ppm in the pre-industrial era to more than 400 ppm today.¹ The ever-increasing atmospheric CO₂ concentration has already caused a severe greenhouse effect associated with various climate-related disasters. To mitigate the greenhouse effect, carbon-negative technologies are in urgent demand.^{2,3} Direct air capture of CO₂ (DAC) has been recognized as a promising carbon-negative technology with a bright future and great potential.^{2,4} DAC is a technology able to separate low-concentration (approximately 400 ppm) CO₂ directly from the air. The captured CO₂ can be stored underground permanently or used as feedstocks in the chemical industry (e.g., converted to methanol).⁵

Adsorption technology is a promising approach for DAC.^{6,7} However, the implementation of adsorption-based DAC is often restricted by the lack of effective adsorbents due to the ultra-low CO₂ concentration (400 ppm in the air) that usually leads to a very low DAC capacity.^{8,9} To achieve high DAC capacity, chemisorption that affords strong interaction strength and thus high CO₂ uptake has so far attracted the most attention in the design of DAC adsorbents.^{2,4,10-12} The first reported DAC chemisorbents are alkaline adsorbents, such as bulk and supported inorganic bases.^{2,4} However, their slow adsorption kinetics and high energy consumption (for desorption and regeneration) make it economically challenging for large-scale applications.^{4,8,13} Another type of prominent DAC chemisorbents is amine-modified adsorbents, which feature improved regenerability.^{10,14-16} But the thermal and oxidative degradation of amine are problematic for long-term usage.^{5,9,17-21} Besides, the adsorption kinetics of amine-modified adsorbents are still relatively slow due to the high loading of amine, which is often needed to ensure high CO₂ uptake.^{8,22} Clearly, deployment of large-scale DAC needs further efforts in developing

adsorbents with balanced DAC capacity, sorption kinetics, and reusability, for which physisorbents featuring good structural stability and moderate interaction strength with CO₂ could be a promising alternative.

Physisorbents generally have weaker interaction with CO₂ than chemisorbents, thus allowing for desorption/regeneration with modest energy consumption.^{7,23} But the excessively weak interaction of most physisorbents usually leads to low adsorption capacity toward low-concentration CO₂.^{5,9,18} Metal-organic-frameworks (MOFs) are the most widely studied physisorbents for low-concentration CO₂ adsorption. A few hybrid ultra-microporous materials (HUMs, a group of MOFs) exhibit high (single-component) CO₂ adsorption capacity at low pressure (e.g., NbOFFIVE-1-Ni: 1.8 mmol/g at 0.1 kPa; SIFSIX-3-Cu: 1.24 mmol/g at 0.04 kPa) thanks to their fine-tuned pore size and adsorption sites.²⁴⁻²⁶ However, their CO₂ adsorption capacity in CO₂/N₂ bicomponent mixture (composed of 1000 ppm CO₂ balanced by N₂ with a total pressure of 100 kPa corresponding to the partial pressure of CO₂ at 0.1 kPa) declines substantially (e.g., NbOFFIVE-1-Ni: 1.2 mmol/g, SIFSIX-3-Cu: 0.4 mmol/g), possibly due to the low CO₂/N₂ selectivity and slow CO₂ adsorption kinetics, which presents the challenges in the application of these MOFs in DAC.^{25,26} Moreover, the low long-term stability and high manufacturing cost are also inherent challenges for MOFs in real applications.^{8,25,27}

Zeolites are another type of physisorbents. Zeolites have good structural stability and low manufacturing cost, which have been recognized as promising candidates for CO₂ adsorption and DAC.^{6,7,28-36} Zeolites are equipped with charge-balancing cations accommodated in the pores as effective adsorption sites, which can be tuned to impart appropriate interaction strength (with guest gas molecules), high adsorption capacity, fast adsorption kinetics, and good adsorption-desorption cyclability.^{8,37} Even though it is generally challenging for zeolites to maintain a high

CO₂ uptake in humid conditions due to the competitive adsorption of water molecules, this issue can be solved by engineering approaches via adding a pre-layer of desiccants before the zeolite adsorbents.^{7,27,28} Among the reported zeolites-based physisorbents for DAC, Ca-A, a small pore zeolite (LTA structure) with the lowest Si/Al ratio (Si/Al = 1) and the most abundant Ca²⁺ cations as adsorption sites, had the highest (single-component) CO₂ adsorption capacity (1.8 mmol/g at 0.04 kPa).³⁸ However, the relatively low structural stability (associated with such low Si zeolites) and irreversible adsorption (caused by the excessively abundant Ca²⁺ cations) of Ca-A prevent its large-scale and long-term implementation.^{7,28,38} One possible way to address the above limitations is to appropriately increase the Si/Al ratio and reduce the density of extra-framework cations. Notably, although manipulating the charge-balancing cations by ion exchange is a well-known strategy to tune the adsorption behavior of zeolites, the effects of different metal cations on DAC have not been systematically studied.

In this research, for the first time, we systematically studied different metal cation-exchanged LTA zeolites on low-concentration CO₂ adsorption for DAC. LTA zeolites with Si/Al ratio higher than 1 (3 and 6) featuring high structural stability were synthesized. Different types of metal cations were installed as active adsorption sites in the LTA zeolites via liquid state ion exchange. The cations studied include monovalent alkali metal cations (Na⁺ and K⁺), divalent alkaline earth metal cations (Mg²⁺ and Ca²⁺), divalent (Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺), and trivalent (Y³⁺, La³⁺, Ce³⁺, Eu³⁺, Tb³⁺, and Yb³⁺) transition metal cations, with proton form (H⁺) prepared as the benchmark. Na⁺, Ca²⁺, Mn²⁺, and Ce³⁺ (-exchanged LTA) were selected as the representatives of monovalent alkali metals, divalent alkaline earth metals, divalent transition metals, and trivalent transition metals (also categorized as rare-earth metals), respectively, for more in-depth investigation and discussion. Through comprehensive gas adsorption experiments

(i.e., single-component gas adsorption, mixture gas dynamic breakthrough tests, temperature-programmed desorption, and adsorption-desorption cycles) and characterizations (in-situ DRIFTS and DFT calculations), we identified the best adsorbent and proposed a proper activation/regeneration scheme for DAC. More importantly, we established the effect of the “charge-to-size ratio” of metal cations (in LTA zeolites) on DAC. This research affords valuable insights into further developing zeolite-based physisorbents for DAC.

Experimental

Preparation of adsorbents

LTA zeolites with Si/Al ratios of 3 and 6, respectively, were synthesized following the reported procedures.³⁹ Typically, LTA-3 was synthesized by mixing 4.12 g of tetramethylammonium hydroxide pentahydrate (TMAOH·5H₂O), 1.15 g of sodium aluminate, 6.7 g of H₂O, 20 g of LUDOX HS-40 colloidal silica, and 35 g of TMAOH 25% solution. The mixture was magnetically stirred to be homogeneous and aged in an air convection oven at 78 °C for 6 days. LTA-6 was synthesized by mixing 1.64 g of aluminum sec-butoxide, 10 g of Ludox HS-40, 0.2 g of NaCl, 0.37 g of tetramethylammonium chloride (TMACl), 14.73 g of tetraethylammonium hydroxide (TEAOH), and 7.95 g of diethyldimethylammonium hydroxide (DEDMAOH) 20% solution. The mixture was magnetically stirred to be homogeneous and heated in an air convection oven at 98 °C for 13 days and then at 125 °C for 7 days. The as-synthesized LTA zeolites were calcined at 600 °C for 10 hours in airflow. After that, the zeolites were ion-exchanged in 1 M NH₄NO₃ solution for four times to obtain NH₄-LTA. Proton form LTA zeolites were prepared by the calcination of NH₄-LTA at 550 °C for 10 hours in airflow. Na⁺, K⁺,

Mg²⁺, and Ca²⁺-exchanged LTA zeolites were prepared by liquid state ion exchange from NH₄-LTA in 1 M metal nitrate solution. All the transition metal cation-exchanged LTA zeolites were prepared by liquid state ion exchange from Na-LTA in 0.05 M metal (II) acetate solution (Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺) and 0.05 M metal (III) nitrate solution (Y³⁺, La³⁺, Ce³⁺, Eu³⁺, Tb³⁺, and Yb³⁺). The prepared adsorbents were named M-LTA-N, where M represents the metal cation, and N represents the Si/Al ratio of the LTA framework. For example, the Na-exchanged LTA zeolite with Si/Al ratio of 3 was named Na-LTA-3.

Characterization

X-ray powder diffraction (XRD) was conducted using X'Pert3 Powder, PANalytical, equipped with Cu anode ($\lambda = 0.15406$ nm) and operated at 40 V voltage and 40 mA current within 2θ from 5° to 50° at 0.026° per step to evaluate the crystallinity and phase purity of the zeolite adsorbents. Energy dispersive spectroscopy (EDS) was measured using Oxford Aztec Energy X-MAX 50 attached to a scanning electron microscope (FEI Quanta 450FEG), and inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on an Agilent 720ES to determine the Si/Al ratio and ion exchange degree of adsorbents. N₂ adsorption isotherms at 77 K were measured using a Micromeritics 3Flex to obtain the porous properties of adsorbents. Specifically, the Brunauer-Emmett-Teller (BET) surface area was calculated by the BET theory. Micropore surface area, external surface area, and micropore volume were calculated by the t-plot method. Pore size distribution was calculated by the Horvath-Kawazoe model. Before the adsorption measurement, the adsorbents were activated under a high vacuum (10⁻⁶ pa) at 300 °C for 10 hours to remove the pre-adsorbed impurities. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) during CO₂ adsorption was collected on a Bruker VERTEX 70v (Bruker, Germany) equipped with an MCT detector. 20-30 mg of the adsorbent was placed

into an in-situ chamber and mounted in a PTFE IR cell equipped with a KBr window. The adsorbent was activated at 300 °C for 4 hours in 40 ml/min of continuous Ar flow. The baseline was collected after the adsorbent was cooled down to room temperature. During CO₂ adsorption (5ml/min, 5% CO₂ in Ar), the spectrum was collected every minute with 32 scan times and 4 cm⁻¹ resolution.

Gas adsorption study of adsorbents

The single-component gas adsorption of CO₂ and N₂ at 273 K (0 °C), 298 K (25 °C), and 313 K (40 °C) were measured volumetrically using Micromeritics 3Flex after the adsorbents underwent the same activation condition as described above. The adsorption isotherms of both CO₂ and N₂ were measured from 0.04 kPa to 100 kPa.

The CO₂/N₂ adsorption selectivity was calculated based on the ideal adsorbed solution theory (IAST) using the following equation:^{40,41}

$$\text{Selectivity} = \frac{q_{\text{CO}_2}/q_{\text{N}_2}}{x_{\text{CO}_2}/x_{\text{N}_2}}$$

Where q is the molar amount of gas in the adsorbed phase, and x is the molar proportion of CO₂ and N₂ in the gas phase. In the calculation, the molar proportion of CO₂ and N₂ was considered as 0.04: 99.96 ($x_{\text{CO}_2}/x_{\text{N}_2}$) to simulate the air in which the CO₂ concentration is 400 ppm.

The isosteric heat of adsorption was calculated using the Clausius-Clapeyron equation:⁴²

$$-\Delta H = R \left[\frac{\partial(\ln P)}{\partial(1/T)} \right]_{\theta}$$

where ΔH is the isosteric heat of adsorption (kJ/mol), R is the universal gas constant (8.3145 J·mol⁻¹·K⁻¹), P is the pressure (kPa), and T is the temperature (K).

The DAC column breakthrough dynamic adsorption was conducted using a home-built system. 0.3 g of the zeolite adsorbent was loaded into a stainless-steel column (10 cm in length and 0.4 cm in diameter), and the bed length of the adsorbent was around 3 cm. The fresh adsorbent was activated/regenerated at 500 °C, 300 °C, and 120 °C (respectively) for 4 hours in continuous Ar flow at 40 ml/min. After the adsorbent was cooled to room temperature, 40 ml/min of “dry” air supplied by a compressed air gas cylinder (Linde HK, 350 ppm CO₂ content, around 50-100 ppm water content) was fed into the adsorption column. The CO₂ concentration at the outlet of the column was measured by an FTIR spectrometer (MKS Multigas 6030).

The temperature-programmed desorption (TPD) was conducted using the same setup as the column breakthrough dynamic adsorption. After the DAC column breakthrough test (the adsorbent was activated at 500 °C), the adsorbent was heated to 600 °C at 10 °C/min heating rate in 40 ml/min of N₂ flow. The CO₂ and H₂O concentration at the outlet of the column was measured by an FTIR spectrometer (MKS Multigas 6030).

Density functional theory (DFT) calculations

All density functional theory (DFT) calculations were performed on Australian Synchrotron Compute Infrastructure (ASCI) using vienna ab initio simulation package (VASP) 5.4.4.⁴³ The generalized gradient approximation (GGA) and GGA+U were adopted. A Perdew-Burke-Ernzerhof (PBE) exchange-correlation function was included in the calculation.⁴⁴ Ultrasoft pseudopotentials were used to treat the interactions between the ionic cores and the valence electrons. Zero damping DFT-D3 dispersion correction method of Grimme was chosen for Van der Waals (VdW) interactions of the adsorption between CO₂ and our zeolite adsorbents.⁴⁵ In all calculations, the cutoff energy of the plane wave was set at 550 eV, and the Monkhorst-Pack k-point was used to ensure the total energy convergence within 1 meV/atom.

Results and discussion

Adsorbent characterization

The crystallinity and phase purity of ion-exchanged LTA zeolites were confirmed by XRD (Figure S1). The XRD pattern of each zeolite adsorbent agrees with that of the standard LTA zeolites, which indicates high crystallinity and phase purity.^{39,46} The Si/Al ratio and the degree of ion exchange of our zeolite adsorbents were determined by the analysis of EDS and ICP-OES results (Table S1 and S2). The average Si/Al ratios of LTA-3 and LTA-6 were measured to be 2.5 and 5.5, respectively. The ion exchange degree for most of the alkali metal (i.e., Na⁺ and K⁺), alkaline earth metal (i.e., Mg²⁺ and Ca²⁺), and divalent transition metal (i.e., Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺) cation-exchanged LTA zeolites were determined as over 60%. Notably, Cu²⁺ exhibits an ion exchange degree of over 100%. The observed excessive amount of Cu²⁺ is attributed to the misrepresentation of copper species, i.e., both Cu²⁺ and (Cu-O-Cu)⁺ that exist in the Cu²⁺-exchanged LTA zeolites were deemed to be Cu²⁺.^{47,48} Apart from these, all the trivalent transition metal (i.e., Y³⁺, La³⁺, Ce³⁺, Eu³⁺, Tb³⁺, and Yb³⁺, also categorized as rare earth metals) cation-exchanged LTA zeolites exhibit low ion exchange degree of between 17% to 35%, mainly resulting from the limited diffusion kinetics and steric restriction of the cations in LTA framework, caused by the large size of hydrated rare earth metal cations.⁴⁹⁻⁵² Similarly, the low ion exchange degree of Ni²⁺ in LTA-3 may also be ascribed to the large size of Ni²⁺ acetate tetrahydrate.

N₂ adsorption at 77 K reveals the porous features of our zeolite adsorbents. As shown in Figure S2, all the ion-exchanged LTA zeolites exhibit Type I adsorption isotherm of N₂ at 77 K, which indicates the microporous feature.⁵³ Several porous properties, including surface area, pore

volume, and pore size, are presented in Table S3-S4 and Figure S3. All the ion-exchanged LTA zeolites have comparable surface area and pore volume, except K-LTA-3 and K-LTA-6, both of which show very small (or even negligible) surface area and pore volume. Such phenomenon of K^+ -exchanged small-pore zeolites has been widely reported and attributed to the pore blockage by large K^+ cation.^{31,33} Besides, divalent and trivalent transition metal cation-exchanged LTA zeolites have a slightly smaller specific surface area and pore volume than those of H, Na, Mg, or Ca-LTA (Table S3-S4), which is mainly attributed to the increased molecular weight of the adsorbents. Specifically, the larger molecular weight of transition metals would increase the molecular weight of the LTA unit cell, which results in the increment of the denominator in the specific surface area and pore volume.

Single-component adsorption of CO₂ and N₂

The single-component adsorption isotherms of CO₂ (the target adsorbate for DAC) and N₂ (the dominant component of air) were measured using a volumetric method at 273 K (0 °C), 298 K (25 °C), and 313 K (40 °C) to evaluate the ideal low-pressure (up to 0.5 kPa) CO₂ adsorption capacity and selectivity. The adsorption isotherms are plotted in Figure 1a-1d and S4-S9. The adsorption capacity of CO₂ at 0.04 kPa (corresponding to the partial pressure of 400 ppm CO₂ in the air at 100 kPa total pressure) and N₂ at 100 kPa are listed in Figure 1e-1f and Table S5-S6. To evaluate and compare the contribution of metal cations as primary adsorption sites more explicitly, the unit of adsorption capacity was also converted from mmol/g to the number of gas molecules/unit cell (Figure S10-S15 and Table S7-S8). The results in both units show the same trend of adsorption capacity.

The equilibrium adsorption capacity of CO₂ represents the primary criterion for evaluating DAC adsorbents. As shown in Table S5-S6, H-LTA as benchmarks shows negligible low-

concentration CO₂ adsorption capacity, due to the lack of metal cations as efficient adsorption sites.⁵⁴ Among the studied metal cation-exchanged LTA zeolites, Na-form zeolites are the most widely studied adsorbents for CO₂ capture from flue gas (15% CO₂) and biogas (40-60% CO₂) due to the wide availability of Na-form zeolites and more abundant monovalent Na⁺ (than divalent and trivalent cations) as CO₂ adsorption sites at moderate (partial) pressures (e.g., 15 kPa CO₂ in flue gas and 40-60 kPa CO₂ in biogas).^{39,55-57} We thus chose Na⁺-exchanged LTA zeolites among our adsorbents as a benchmark. Together with monovalent Na⁺, Ca²⁺, Mn²⁺, and Ce³⁺ were selected as the representatives of divalent alkaline earth metal, divalent transition metal, and trivalent transition metal, respectively, for further discussion. According to Figure 1e, Na-LTA-3 shows a small CO₂ adsorption capacity at 0.04 kPa (0.06 mmol/g at 298 K), possibly due to the relatively weak interaction strength with low-pressure CO₂. Notably, Ca-LTA-3 exhibits the highest CO₂ adsorption capacity of 1.12 mmol/g (at 298 K, 0.04 kPa), which is almost 20 times of that on Na-LTA-3. The CO₂ adsorption capacity of Mn-LTA-3 and Ce-LTA-3 at the same condition is 0.35 mmol/g and 0.16 mmol/g, respectively. A similar trend of CO₂ adsorption capacity was also observed on metal cation-exchanged LTA-6 (Figure 1f). Compared with Na-LTA, after the divalent and trivalent metal cations exchange, the low-pressure CO₂ adsorption capacity increased tremendously (Figure 1 and S4-S15, Table S5-S8). The only exception is Cu-LTA, possibly due to the existence of monovalent (Cu-O-Cu)⁺. Such a trend of CO₂ capacity among mono-, di-, and trivalent cations was for the first time observed and demonstrated in the low-pressure CO₂ adsorption on LTA zeolites. It suggests that divalent and trivalent cations can serve as more effective adsorption sites for low-pressure CO₂ capture than monovalent Na⁺ in LTA zeolites. The adsorption capacity of N₂ shows a similar trend (Figure 1 and S4-S15, Table S5-S8) to that of CO₂.

The density of effective adsorption sites is important to the adsorption capacity of low-pressure CO₂ and atmospheric-pressure N₂, which is mainly affected by the ion exchange degree of cations and the Si/Al ratio of LTA zeolites. The ion exchange degrees of trivalent transition metal cations are very low in both LTA-3 and LTA-6 (< 40%, Table S1-S2), with Na⁺ still being the dominant cation in the above adsorbents. Thus, the adsorption capacity on Ce-LTA is higher than that on Na-LTA but lower than that on Ca-LTA and Mn-LTA (Figure 1), because fewer trivalent metal cations (than divalent metal cations) are available to serve as effective adsorption sites in these trivalent transition metal cation-exchanged LTA zeolites. In addition to the ion exchange degree, the density of adsorption sites is also affected by the Si/Al ratio of LTA zeolites. Comparing LTA-6 and LTA-3 shows that the increased Si/Al ratio and reduced cation density significantly reduced the adsorption capacity (Figure 1 and S4-S15, Table S5-S8).

Based on the measured CO₂ and N₂ adsorption isotherms, the IAST CO₂/N₂ (0.04:99.96) selectivity was calculated to evaluate the potential of our LTA adsorbents for DAC. Even though the substitution of monovalent cations by divalent and trivalent cations would improve the (single-component) adsorption capacity of both CO₂ and N₂, our zeolite adsorbents still exhibit high CO₂/N₂ selectivity. Typically, Ca-LTA-3 and Mn-LTA-3 exhibit the highest CO₂/N₂ selectivity among all the LTA zeolites, being 50156 and 2655, respectively (Figure 1e and Table S5). Ca-LTA-3 displays the highest CO₂/N₂ selectivity, together with the superior CO₂ adsorption capacity, suggesting the high potential of our adsorbents for DAC.²⁵

CO₂ adsorption mechanism

To evaluate the interaction strength of the ion-exchanged LTA zeolites toward CO₂, the isosteric heat of adsorption of CO₂ was calculated using the Clausius-Clapeyron equation based on adsorption isotherms at 273 K, 298 K, and 313 K (Table S9). Most adsorbents showed the

isosteric heat of adsorption in the range of 30-40 kJ/mol, indicating a moderate interaction strength toward CO₂. To precisely evaluate the interaction strength of different metal cations toward CO₂, the interaction energies between one CO₂ molecule and different metal cations-exchanged LTA-3 were also calculated using the density functional theory (DFT) (Table S10). It was found that the interaction energy highly depends on the charge-to-size ratio of cations (Figure 2). Specifically, cations with larger charge-to-size ratio displays higher interaction energy toward CO₂ in LTA-3 (Ce³⁺ > Mg²⁺ > Mn²⁺ > Ca²⁺ > Na⁺ > K⁺). As CO₂ is a quadrupolar molecule, zeolites can bind CO₂ via electrostatic interactions (including polarization interaction and quadrupole moment-surface electric field interaction) and Van Der Waals interactions.^{7,58,59} Cations with larger charge-to-size ratio can exert greater polarizing power (for polarization interaction) and stronger surface electric field (for quadrupole moment-surface electric field interaction) in LTA zeolites, thus imparting stronger electrostatic interactions with CO₂.^{23,37} The charge-to-size ratio of the divalent and trivalent metal cations studied herein is much larger than the monovalent Na⁺, leading to higher interaction energy and adsorption capacity toward low-pressure CO₂.

However, a high charge-to-size ratio does not always benefit low-pressure CO₂ adsorption in practice. As shown in Figure 2, Ca²⁺, with a moderate charge-to-size ratio, exhibits the highest CO₂ adsorption capacity. In contrast, even though Mg²⁺ and Mn²⁺ have a larger charge-to-size ratio than Ca²⁺ and display much higher interaction energy (with CO₂), they do not exhibit as high adsorption capacity as Ca²⁺ in the same zeolite support. Such a deviation from the trend of CO₂ adsorption capacity against the charge-to-size ratio of cations is because cations with a large charge-to-size ratio are more vulnerable to be contaminated by the (pre-) adsorbed molecules (H₂O and a small quantity of strongly adsorbed CO₂).^{60,61} In other words, such cations are easier

to be shielded by molecular contaminants that are hard to desorb due to their strong interaction strength. The CO₂ adsorption was thus restrained.⁶² We refer to it as the “shielding effect”. The “shielding effect” of cations with a large charge-to-size ratio was further demonstrated by the TPD and column breakthrough dynamic adsorption results in the following sections.

To investigate the CO₂ adsorption mechanism, the in-situ DRIFTS was conducted on the representative adsorbents, i.e., Na⁺, Ca²⁺, Mn²⁺, and Ce³⁺-exchanged LTA-3 (Figure 3). According to the spectra, most of the CO₂ molecules were physisorbed on our LTA zeolites, as evidenced by the main peak at 2200-2500 cm⁻¹.⁶³⁻⁶⁵ Compared with Na-LTA-3, the red shift of this peak on Ca, Mn, and Ce-LTA-3 indicates a stronger interaction between cations and physisorbed CO₂ molecules. Such an interaction would be derived from the strong electrostatic force exerted by the cations with a large charge-to-size ratio (Ca²⁺, Mn²⁺, and Ce³⁺).^{54,66} Apart from the electrostatic interaction, π -complexation may also contribute to the CO₂ adsorption on Mn²⁺ and Ce³⁺.^{54,66} CO₂ molecules can be adsorbed by transition metal cations via π -back bonding (formed by the back donation of the d-orbital electron to the anti-bonding π^* orbital of gas molecules).^{7,67-69} π -back bonding has been proven to contribute to small molecule adsorption on metal-organic frameworks with open copper(I) centers.⁷⁰ In Ce-LTA-3, the appearance of two peaks at 2331 and 2367 cm⁻¹ is due to the low ion exchange degree of Ce³⁺, which represents the physisorbed CO₂ on the stronger binding Ce³⁺ sites and weaker binding Na⁺ sites, respectively. The peak at around 3710 cm⁻¹ represents the existence of -OH, which results from the adsorption of trace water from the feed gas.⁶³ Meanwhile, the formation of carbonyl groups was evidenced by the appearance of two peaks at 1237-1251 cm⁻¹ and 1658-1705 cm⁻¹, representing the formation of bidentate carbonates and bridged bidentate carbonates (respectively) during CO₂ chemisorption.^{63,71}

The TPD curves of CO₂ and H₂O were measured using the LTA adsorbents following CO₂ adsorption (DAC column breakthrough dynamic adsorption using the “dry” air) to investigate the adsorption strength (of CO₂ and H₂O) and desorption temperature (Figure 4). The quantity of desorbed CO₂ on Ca-LTA-3 and Mn-LTA-3 is much larger than that on Ce-LTA-3 and Na-LTA-3, consistent with their high CO₂ adsorption capacity measured by single-component CO₂ adsorption, thanks to the abundant cations with a large charge-to-size ratio as effective adsorption sites. The results from the DAC column breakthrough dynamic adsorption test will be discussed in the next section. To precisely define the CO₂ desorption behavior, the CO₂ TPD curves were deconvoluted, showing four peaks on both Ca-LTA-3 (80 °C, 116 °C, 160 °C, and 188 °C) and Mn-LTA-3 (70 °C, 107 °C, 147 °C, and 187 °C), respectively. In each case, the two peaks at lower temperatures represent the desorption of physisorbed CO₂, while those two at higher temperatures represent weak chemisorbed CO₂ molecules.⁶³ In contrast, Na-LTA-3 exhibits only one desorption peak at 68 °C, which is consistent with the weaker interaction imparted by Na⁺. For Ce-LTA-3, although most CO₂ desorption occurs at 70 °C, the CO₂ desorption was also detected at three higher temperatures (108 °C, 154 °C, and 188 °C), suggesting the stronger interaction imparted by Ce³⁺ sites than Na⁺. However, the overall DAC capacity of Ce-LTA-3 is limited by the low ion exchange degree and the “shielding effect” associated with the large charge-to-size ratio of Ce³⁺.

The proportions of CO₂ desorption at different temperatures were also quantified based on the TPD results to identify the appropriate regeneration condition for Ca-LTA-3 and Mn-LTA-3 (Table 1). Specifically, 120 °C and 300 °C were selected as two operating temperatures to desorb the physisorbed CO₂ and weakly chemisorbed CO₂, respectively, following a DAC operation on a fresh adsorbent initially activated at 500 °C. As shown in Table 1, majority of the adsorbed

CO₂ can be desorbed at 120 °C (Ca-LTA-3: 61.26%, Mn-LTA-3:78.69%), indicating the moderate interaction strength with CO₂. After increasing the temperature to 300 °C, most of the adsorbed CO₂ can be removed (Ca-LTA-3: 91.57%, Mn-LTA-3: 87.16%). The desorption of H₂O and a tiny amount of CO₂ was observed at a temperature above 400 °C. The desorbed H₂O should come from the H₂O adsorbed from the feed gas (ppm level H₂O content in the “dry” air) and retained following the adsorbent activation step.⁷² The desorbed CO₂ should come from chemisorbed carbonates.^{63,73} Ca-LTA-3 and Mn-LTA-3, which showed superior CO₂ adsorption capacity and good adsorption-desorption cyclability, are recognized as effective DAC adsorbents.

Direct air capture of CO₂ in “dry” air

Ca-LTA-3 and Mn-LTA-3 were selected as promising candidates for the column breakthrough dynamic adsorption and cyclic adsorption-desorption tests to evaluate their DAC capacity and cyclic DAC performance. The tests were conducted using the “dry” air supplied by a compressed air cylinder as feed gas at room temperature. The CO₂ concentration in the “dry” air was measured to be 350 ppm, and the H₂O content was determined as 50-100 ppm (from TPD and cyclic adsorption-desorption results). The CO₂ breakthrough curves of Ca-LTA-3 and Mn-LTA-3 are plotted in Figure 5a and 5c. The DAC capacity and cyclic DAC performance (with the adsorbents activated at 500 °C, 300 °C, and 120 °C, respectively) are illustrated in Figure 5b and 5d. Both Ca-LTA-3 and Mn-LTA-3 display high DAC capacity and good cyclic DAC performance. Notably, Ca-LTA-3 exhibits the highest DAC capacity (1.2 mmol/g, Figure 5b and 5d) among the reported DAC physisorbents in the open literature to the best of our knowledge.^{8,9,22,25,26,38,74} Thanks to the superior DAC capacity and fast kinetics (evidenced by the sharp breakthrough curve, Figure 5a and 5c), one gram of Ca-LTA-3 is able to thoroughly

remove the CO₂ in around 80 liters of “dry” air at room temperature and atmospheric pressure.^{6,75}

Comparing the DAC capacity measured by breakthrough adsorption with the ideal CO₂ adsorption capacity measured using single-component adsorption at the same condition (at 25 °C, using the adsorbents activated at 300 °C) shows that the DAC capacity (Ca-LTA-3: 0.76 mmol/g, Mn-LTA-3: 0.24 mmol/g, Figures 5b) is slightly lower than the ideal CO₂ capacity (Ca-LTA-3: 1.12 mmol/g, Mn-LTA-3: 0.35 mmol/g, at 298 K, 0.04 kPa, Figure 1e). This is mainly due to the lower CO₂ concentration (350 ppm in “dry” air in DAC versus 0.04 kPa - 400 ppm CO₂ in single-component CO₂ adsorption) and the competing adsorption of other components (N₂ and H₂O) in the DAC test.

Notably, the DAC capacity of both Ca-LTA-3 and Mn-LTA-3 highly depends on the activation and regeneration temperatures. An elevated activation temperature is demonstrated to be beneficial to the DAC capacity of Ca-LTA-3 and Mn-LTA-3. According to Figures 5b, fresh adsorbents activated at 500 °C show higher DAC capacity than fresh adsorbents activated at 300 °C and 120 °C, due to the insufficient desorption of the pre-adsorbed H₂O and a tiny amount of chemisorbed CO₂ in the case of the latter two adsorbents.^{60,61} Such a phenomenon can be explained by the TPD results in the last section. After 500 °C activation, more metal cations that were occupied by pre-adsorbed contaminants are recovered as active adsorption sites for DAC. Specifically, the DAC capacity of fresh Ca-LTA-3 activated at 500 °C is 1.2 mmol/g, compared with 0.76 mmol/g after the activation at 300 °C (Figure 5b). In the case of Mn-LTA-3, the adsorbent activated at 500 °C shows more than twice the capacity (0.54 mmol/g) of that activated at 300 °C (0.24 mmol/g). Notably, the extent of increase in DAC capacity due to the increased activation temperature on Ca-LTA-3 is not as much as that on Mn-LTA-3 (Figure 5b). This is

because Mn^{2+} with a larger charge-to-size ratio than Ca^{2+} is easier to be shielded by the pre-adsorbed contaminants and thus more sensitive to the change in the activation temperature. A high-temperature activation at 500 °C not only can increase the DAC capacity but also can improve the regeneration capability. Based on the comparison between Figure 5b and 5d, a 500 °C pre-activation of Ca-LTA-3 and Mn-LTA-3 significantly improves the DAC capacity after 300 °C and 120 °C regeneration, especially for 120 °C. This phenomenon can be ascribed to the greater difficulty in desorbing the pre-adsorbed H_2O than DAC-adsorbed CO_2 , which can also be evidenced by the higher DAC capacity of the fresh adsorbents activated at 500 °C than those activated at 300 °C and 120 °C as well as the TPD curves of CO_2 and H_2O shown in Figure 4.

Cyclic adsorption-desorption is usually driven by pressure change (pressure swing adsorption (PSA)) and/or temperature change (temperature swing adsorption (TSA)) in industrial gas separation processes. PSA is not feasible for DAC because the extremely low CO_2 partial pressure in the air requires the deep vacuum to execute the desorption/regeneration step, which is highly energy intensive. In contrast, TSA is the favorable industrial separation process for DAC.^{11,76,77} In this research, the DAC capacities of adsorbents activated at different temperatures can be used to predict the TSA working capacity. As shown in Figure 5d and S16, Ca-LTA-3 and Mn-LTA-3 exhibits stable TSA working capacity at each regeneration temperature. Notably, based on the comparison between Figure 5b and 5d, an efficient adsorbent activation/regeneration scheme was demonstrated; that is, a pre-activation at 500 °C would significantly improve the TSA working capacity of both Ca-LTA-3 and Mn-LTA-3 treated by moderate regeneration temperatures (e.g., 300 °C and 120 °C) between cycles. Such a strategy would significantly reduce the energy consumption associated with desorption/regeneration.

Compared with the reported DAC physisorbents in the open literature, Ca-LTA-3 exhibits the highest DAC capacity (1.2 mmol/g) and moderate interaction strength (Figure 6, Table S11).^{8,22} Notably, the DAC capacity of Ca-LTA-3 is even higher than many amine-grafted DAC chemisorbents (Table S11). Ca-LTA-3, featuring superior DAC capacity, fast CO₂ adsorption kinetics, high adsorption-desorption cyclability, and good structural stability, is confirmed to be a promising DAC adsorbent.

Conclusion

This research comprehensively investigated the potential of LTA zeolites (Si/Al = 3 and 6) exchanged with different kinds of metal cations (mono-, di-, trivalent cations) in direct air capture of CO₂. It was found that cations with larger charge-to-size ratio display higher interaction energy with CO₂, which is attributed to the enhanced electrostatic interactions and/or π -back bonding interactions toward CO₂. Although a high interaction energy with CO₂ is beneficial to DAC by affording high CO₂ capacity, an excessively large charge-to-size ratio leads to a pronounced ‘shielding effect’ (i.e., (pre-) adsorbed contaminants (e.g., H₂O and CO₂) on cations are difficult to be removed and thus reduces the practical CO₂ capacity) and is detrimental to DAC. Thanks to the appropriate charge-to-size ratio of divalent Ca²⁺, Ca-LTA-3 exhibits the highest DAC capacity of 1.20 mmol/g (350 ppm CO₂ from “dry” air) accompanied by fast adsorption kinetics, ease of regeneration, and high adsorption-desorption cyclability among reported physisorbents. Based on the temperature swing adsorption (TSA) process, a pre-activation at 500 °C was proved to be an effective strategy to improve the TSA working capacity of Ca-LTA-3 and Mn-LTA-3 treated by moderate regeneration temperatures (e.g., 120 °C). This

work reaffirms zeolites as promising adsorbents for direct air capture and affords valuable insights for the future development of zeolite adsorbents in potential large-scale CO₂ capture applications.

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Plain Language Summary

A proper charge-to-size ratio was critical for metal ions as effective adsorption sites in LTA zeolite to afford high CO₂ adsorption capacity for DAC (direct air capture of CO₂). Specifically, Ca²⁺-exchanged LTA zeolite with a Si/Al of 3 shows the highest DAC capacity among the reported DAC physisorbents together with fast kinetics, ease of regeneration, and high adsorption-desorption cyclability.

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