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Achieving highly selective CO₂ adsorption on SAPO-35 zeolites by template-modulating the framework silicon content†

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Small-pore silicoaluminophosphate (SAPO) zeolites with 8-ring pore windows and appropriate acidities/polarities, for example, SAPO-34 (CHA) and SAPO-56 (AFX), have proven to be potential adsorbing materials for selective adsorption of CO₂. However, SAPO-35 zeolites (LEV framework topology) synthesized using conventional templates are less reported for highly selective CO₂ adsorption which might be due to inappropriate Si contents and acidities in the framework. In this work, by using *N*-methylpiperidine (NMP) as a template, SAPO-35 zeolites with various Si contents were synthesized under hydrothermal conditions, which allowed SAPO-35 zeolites with modulated acidities and polarities. The CO₂ adsorption and separation properties of SAPO-35_x (*x*: Si/(Si + P + Al) in molar ratio) were investigated, and a close relationship between the acidity, polarity and CO₂ adsorption and separation capacity was revealed. SAPO-35_{0.14} with the strongest acidity showed the highest CO₂ uptake of 4.76 mmol g⁻¹ (273 K and 100 kPa), and appeared to be one of the best SAPO materials for CO₂ adsorption. Moreover, increased Brønsted acidity can significantly enhance the adsorption selectivity of CO₂ over N₂. At 298 K and 100 kPa, SAPO-35_{0.14} showed the highest CO₂/N₂ selectivity of 49.9, exhibiting potential for industrial processes. Transient binary breakthrough experiments on SAPO-35_{0.14} further proved the efficient separation performance and stable circulation. The results of this study prove that the framework Si content of SAPO-35 zeolites is essential for regulating their CO₂ adsorption performance. This work demonstrates that modulating the silicon content and acidity in SAPO zeolites via a suitable choice of template, as well as polarity, is of great significance for the rational synthesis of zeolites with superior CO₂ adsorption and separation abilities.

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Introduction

The release of greenhouse gases, especially CO₂ arising from fossil fuel combustion, has caused global warming and extreme weather, which upset the balance of the ecosystem. CO₂ capture and separation from effluent gases has thus attracted more and more attention. Flue gas emissions coming from power plants account for 33–40% of total CO₂ emissions, and N₂ is the major component of the flue gas (>70%).¹ Currently, the most widely

adopted technology for the separation of CO₂/N₂ mixed gases, *i.e.*, aqueous amine absorption, causes a large quantity of energy consumption and waste. Thus, it is necessary to promote the development of physical adsorption technologies with lower energy penalty and lower cost, for example pressure swing adsorption (PSA).^{1,2} Among physical adsorption technologies, the investigation and evolution of highly efficient adsorbing materials is the focus of adsorption and separation.³ In recent years, porous solid adsorbing materials such as zeolites,⁴ metal-organic frameworks (MOFs),⁵ zeolitic imidazolate frameworks (ZIFs),⁶ covalent organic frameworks (COFs),⁷ and porous organic polymers (POPs)⁸ have been extensively used in selective adsorption. Among these adsorbents, MOFs show potential because of their controllable structures and functions but are limited by the weak thermal stability and high manufacturing costs.⁹

Zeolites are a famous category of inorganic porous materials with well-defined and stable structures, large surface areas, and various active sites, which have broad applications in the fields of catalysis, ion exchange, adsorption/separation and pharmaceuticals.¹⁰ The large CO₂ adsorption capacity, high structural

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stability and controllable polarity give zeolites great potential for application in gas adsorption and separation of CO₂-containing gas mixtures.¹¹ Zeolites preferentially adsorb molecules with large dipole and quadrupole moments, especially CO₂ (13.4×10^{-40} C m² quadrupole moment), because the frameworks possess strong electric fields, and thus fairly high CO₂ adsorption uptake and selectivity over N₂ (4.7×10^{-40} C m² quadrupole moment) at low pressure, making them promising candidates for applications.^{4a,12} Various factors can influence the adsorption capacity and selectivity of zeolites for CO₂, such as framework composition,¹³ topologies,¹⁴ channel systems,¹⁵ pore size dimensions,¹⁶ pore volumes,¹⁷ exchanged cations,¹⁸ isomorphous heteroatom substitutions,¹⁹ and numbers and distributions of active sites that are related to acidities and polarities.^{12b,20} It is worth noting that the similar kinetic diameters of CO₂ (0.33 nm) and N₂ (0.36 nm) make kinetic separation very challenging.^{9,21} Recently, some small pore zeolites with 8-membered ring windows have been spotlighted and confirmed to be excellent CO₂ adsorbents, since the effective size of their 8-rings can be tuned to ensure the passage of CO₂, but to hinder the slightly larger N₂ molecule, leading to high CO₂/N₂ selectivity.^{4a,14,20,22} As a notable example, the low-pressure separation of CO₂ from N₂ by SSZ-13 zeolite (CHA framework topology) was studied in both acidic and copper-exchanged forms, which exhibited unconventional high selectivity (>70) evaluated by the ideal adsorbed solution theory under ideal conditions for industrial CO₂/N₂ separations.^{4a} The high CO₂ uptake of aluminosilicate zeolites is partly due to their high electrical field gradients. However, aluminosilicate zeolites adsorb CO₂ very vigorously, limiting the ease of their use in cyclic adsorption processes.^{12c,23}

Silicoaluminophosphate (SAPO) zeolites, which are an important category of zeolites, provide equally high CO₂ adsorption capacity as adsorbents at corresponding pressures. Their weaker electrical field gradients lead to highly reversible CO₂ uptake.²⁴ For instance, SAPO-56 displayed a higher CO₂ adsorption uptake (5.42 mmol g⁻¹ at 273 K and 101 kPa) and less water sensitivity than aluminosilicate zeolite 13X. Cyclic adsorption and *in situ* infrared spectroscopy (IR) revealed that SAPO-56 retained 95% of its initial CO₂ capacity after six cycles and that adsorption occurred *via* physisorption.^{24a}

SAPO-35 with LEV topology will be a preferred candidate for CO₂ adsorption and separation due to its structural features. Levyne (LEV) is a typical small pore 8-ring window zeolite belonging to the ABC-6 family constructed by *lev* cages, single 6-rings and double 6-rings, whose window dimensions (0.36 × 0.48 nm) allowing the molecules to diffuse through are very suitable for the separation of CO₂ from N₂.^{24a,25} However, few studies have focused on the investigation of Levyne and its analogues for CO₂ adsorption and separation. The SAPO-35 zeolites were typically synthesized by using hexamethylenimine (HMI) as a template which showed a poor CO₂ adsorption capacity.^{24a} This might be due to the inappropriate Si acidities/polarities in the framework. Herein, by adopting *N*-methylpiperidine (NMP) as a template, a series of SAPO-35 zeolites were synthesized, which exhibited a wider range of Si content from 5% to 23%. The relationship between Si content and CO₂

adsorption and separation abilities was also investigated. By regulating the Si content in SAPO-35 zeolites synthesized using NMP, we found that the sample with moderate Si content showed the strongest Brønsted acidity and polarity, further aiding in CO₂ affinity and separation of the CO₂/N₂ mixture. This work implies that many small pore SAPO zeolites could be explored for gas adsorption and separation applications by template assisted modulation of the Si content to tune the framework acidity and polarity.

Results and discussion

Synthesis and characterization

Three SAPO-35_x samples with different Si contents were synthesized using NMP as a template under hydrothermal conditions at 180 °C. The molar composition of the starting mixture was 1.0 Al₂O₃ : 2.0 P₂O₅ : *n* SiO₂ : 6.15 NMP : 123.8 H₂O (*n* = 0.2, 0.6, or 1.4). The powder X-ray diffraction patterns are all consistent with that of a previously reported zeolite with the LEV topology,²⁵ proving their phase purity (Fig. S1†). The scanning electron microscopy (SEM) images of SAPO-35_x samples show cube-like rhombohedral morphology (Fig. S2†), and the variation of Si content leads to a change of product size from 15 μm to 40 μm. Inductively coupled plasma atomic emission spectrum (ICP-AES) analyses give SAPO-35_x samples with Si contents of 0.08, 0.14 and 0.22 in molar ratio (Table S1†). N₂ adsorption–desorption isotherms were measured at 77 K to characterize the porous properties of SAPO-35_x samples. As shown in Fig. 1, all the samples display characteristic type I isotherms according to the IUPAC classification, confirming their microporous characteristics. As shown in Table S1,† the Brunauer–Emmett–Teller (BET) specific surface areas are calculated to be 493 m² g⁻¹ for SAPO-35_{0.08}, 502 m² g⁻¹ for SAPO-35_{0.14}, and 447 m² g⁻¹ for SAPO-35_{0.22} in the pressure range 0.05–0.30 *P/P*₀. Micropore volumes of SAPO-35_{0.08}, SAPO-35_{0.14}, and SAPO-35_{0.22} are 0.22, 0.22, and 0.18 cm³ g⁻¹ determined by the *t*-plot method, respectively. The above values are similar to those of previously reported SAPO-35

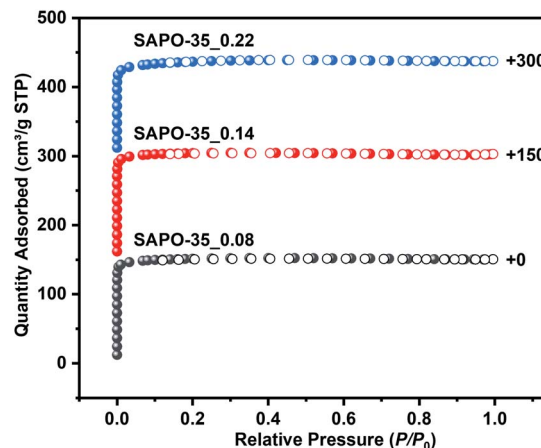


Fig. 1 N₂ adsorption–desorption isotherms of SAPO-35_x samples at 77 K.



zeolites in the literature.²⁶ The decrease of BET specific surface area and micropore volume of SAPO-35_0.22 is based on the decrease in crystallinity, which is also proved by the decrease in XRD peak intensity in Fig. S1.† Temperature-programmed desorption of ammonia (NH₃-TPD) was employed to determine the acidity of the SAPO-35_x samples (Fig. S3†). The desorption temperature indicates the acidic strength, and the peak area indicates the acidic concentration of the samples. Obviously, SAPO-35_0.14 with medium Si content possesses the strongest acid strength and the highest concentration of acid sites among these three samples.

Subsequently, solid-state ²⁹Si MAS NMR spectra were measured to clarify the relationship between Si content and acidity. The silicon substitution proceeds *via* the SM2 mechanism (for low Si content) and SM2 + SM3 mechanism. In case of the SM2 mechanism, only P atoms are substituted, causing Brønsted acidity, while for the SM3 mechanism, an (Al, P) pair is substituted by two Si atoms. When the degree of Si substitution in SAPO zeolites is high enough to generate Si islands, *i.e.*, Si(4Si,0Al), there is a decrease in the acidity of SAPO zeolites.²⁷ ²⁹Si MAS NMR spectra of SAPO-35_x samples are shown in Fig. S4.† The peaks at −90 and −95 ppm in SAPO-35_0.08 can be assigned to the Si(0Si,4Al) unit at the T1 and T2 sites in the SAPO-35 framework, respectively. With the increase of Si content (SAPO-35_0.14; SAPO-35_0.22), the coordination environments of Si become complex, and the peaks for Si(*n*Si,(4−*n*)Al) (*n* = 0 to 4) become overlapped between −90 ppm and −110 ppm. In general, peaks at around −110 ppm can be assigned to Si(4Si,0Al), which appears only in SAPO-35_0.22, leading to its decrease of acidity compared to SAPO-35_0.14.²⁵

CO₂ adsorption

Pure CO₂ adsorption isotherms of SAPO-35_x samples were measured at 273, 283 and 298 K, respectively, to evaluate the CO₂ adsorption abilities of SAPO-35 zeolites with different Si contents and acidity. As shown in Fig. 2 and Table 1, the CO₂ uptakes of these SAPO-35 samples decrease with increase in

temperature, and are always in the order SAPO-35_0.14 > SAPO-35_0.22 > SAPO-35_0.08 at 273, 283, and 298 K and 100 kPa whether in the low-pressure area or in the high-pressure area. The results clearly show that Si contents regulated by the template and the enhanced acidity could strengthen the CO₂ adsorption capacity of SAPO-35 zeolites. Compared with other pure AlPO zeolites and SAPO zeolites, SAPO-35_0.14 (4.76 mmol g^{−1} at 273 K and 100 kPa) appears to be one of the best AlPO/SAPO zeolite adsorbents for CO₂ adsorption (Table S2†), which is superior to aluminosilicate zeolites with the same topology (Na-LEV)²⁸ and most of the SAPO zeolites, proving the potential of SAPO-35 zeolites in CO₂ adsorption.

Obviously, the framework Si content of SAPO-35 zeolites plays an essential role in governing the CO₂ adsorption behaviour of this structure type of small-pore zeolites. To further explore the relationship between CO₂ adsorption properties, Si content and acidity in SAPO-35_x zeolites, the isosteric heats of CO₂ adsorption (*Q*_{st}) for SAPO-35_x zeolites were calculated by fitting the CO₂ adsorption isotherms at 273, 283 and 298 K to the virial equation (Fig. S5†). As shown in Table 1 and Fig. 2d, the *Q*_{st} at zero coverage for SAPO-35_0.14 (29.3 kJ mol^{−1}) is the highest among the three SAPO-35_x samples. The result indicates that increased acidity could strengthen the interaction between the CO₂ adsorbate and the inorganic framework. The regeneration of the adsorbent is one of the most important parameters for practical application. One way to estimate the regeneration of an adsorbent is the determination of the energy released during the adsorption process by means of *Q*_{st}. Excessive *Q*_{st} of aluminosilicate zeolites will be against the desorption of CO₂, thus leading to low regenerability and high-energy cost.^{4a} SAPO-35 zeolites possess medium *Q*_{st} and relatively high CO₂ adsorption, which are beneficial to the application for CO₂ adsorption/desorption.

CO₂/N₂ selectivity predicted by ideal adsorbed solution theory (IAST)

Apparently, CO₂ is more favorably adsorbed than N₂ on all SAPO-35_x samples. The size and electronic properties of CO₂ and N₂ are shown in Table S3.† The kinetic diameter of CO₂ is smaller, and hence it can more easily diffuse into the LEV pore structure (pore aperture of 0.36 × 0.48 nm). More importantly, CO₂ possesses higher polarizability (26.3 × 10^{−25} cm³) and quadrupole moment (13.4 × 10^{−40} C m²), which results in stronger electronic interaction between CO₂ molecules and the inorganic framework.

IAST is one of the most credible theories to predict the multicomponent adsorption equilibrium with only the pure component adsorption isotherms. Herein, IAST was employed to predict CO₂/N₂ selectivity on the basis of the adsorption isotherms of CO₂ and N₂ at 273 and 298 K on SAPO-35_x samples (Fig. 2 and S6†) to investigate the influence of Si content and acidity on the CO₂ adsorption selectivities over N₂. The adsorption capacities are in the order CO₂ > N₂ for each sample, indicating the preferential adsorption for CO₂ over N₂. The Langmuir–Freundlich model fitted isotherm parameters were applied to carry out the calculations. The simulations were

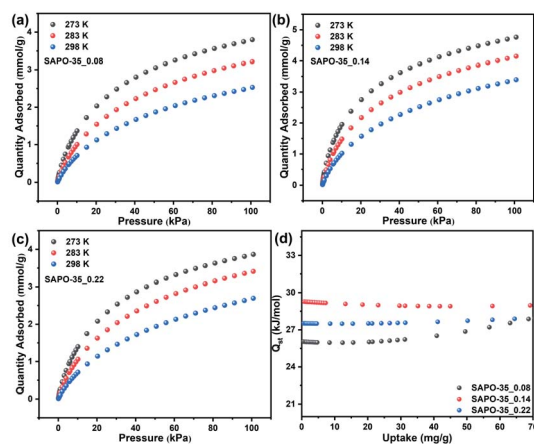


Fig. 2 CO₂ adsorption of (a) SAPO-35_0.08, (b) SAPO-35_0.14, and (c) SAPO-35_0.22 at 273, 283 and 298 K. (d) Isothermic heat of adsorption (*Q*_{st}) for the SAPO-35_x samples.



Table 1 CO₂ adsorption and Q_{st} at zero coverage of SAPO-35_x at 273, 283 and 298 K

Sample	Q_{st} (kJ mol ⁻¹)	CO ₂ at 100 kPa (mmol g ⁻¹)			CO ₂ at 10 kPa (mmol g ⁻¹)		
		273 K	283 K	298 K	273 K	283 K	298 K
SAPO-35_0.08	26.0	3.80	3.21	2.53	1.37	1.00	0.71
SAPO-35_0.14	29.3	4.76	4.15	3.40	1.95	1.48	1.02
SAPO-35_0.22	27.5	3.87	3.41	2.69	1.40	1.06	0.71

conducted on gas mixtures with two different molar compositions (50/50 and 20/80 for CO₂/N₂). The adsorption isotherms were properly fitted by the dual-site Langmuir–Freundlich adsorption model ($R^2 > 0.999$, Fig. S7†). Subsequently, the fitting parameters (Tables S4–S6†) were applied in predicting the multicomponent adsorption with IAST. As shown in Fig. 3, the tendencies in the pressure dependence of IAST selectivity are similar among these three samples, *i.e.*, the selectivity falls rapidly at first and is later followed by a smaller dependence of selectivity on pressure. This is due to the heterogeneous adsorption site distribution on the zeolite cavities.

At lower pressures, the high-energy adsorption sites, *i.e.*, Brønsted acid sites in SAPO-based materials, are preferentially occupied by CO₂ molecules. As a result, the CO₂–adsorbent interaction is more pronounced than that at higher pressures.^{12b,29} SAPO-35_0.14 shows the highest CO₂/N₂ IAST selectivity (49.9) at 298 K compared to the other two samples due to the increased acid strength and acidic concentration (Table 2). Compared to some other types of zeolites and adsorbing materials (Table S7†), SAPO-35_0.14 shows exhilarating

separation selectivities for CO₂/N₂. In addition, Brønsted acid sites are highly polarized hydroxyl groups in zeolite frameworks.^{12a} An increase of the concentration of acid sites generates more energetic adsorption sites for the quadrupolar adsorbate.^{27c} Therefore, SAPO-35_0.14 is accompanied by the strongest electrostatic field. Consequently, the electronic interaction becomes stronger, which leads to the best CO₂ adsorption abilities. What's more, CO₂ is more polar than N₂, and the interaction between CO₂ molecules and the LEV framework shows higher sensitivity with the variation of the electrostatic field, thus SAPO-35_0.14 shows the highest CO₂/N₂ separation selectivity. To compare the separation performance of SAPO-35 made using NMP and HMI as templates, we synthesized SAPO-35 using HMI, named SAPO-35_HMI,^{24a} which possesses the same Si content as the best adsorbent (SAPO-35_0.14). CO₂ and N₂ adsorption of SAPO-35_HMI and CO₂/N₂ IAST selectivity for SAPO-35_HMI at 273 K are shown in Fig. S8 and S9.† A comparison of CO₂ uptake and CO₂/N₂ IAST selectivity for SAPO-35_HMI and SAPO-35_0.14 is summarized in Table S8.† As a result, SAPO-35_HMI shows lower CO₂ uptake

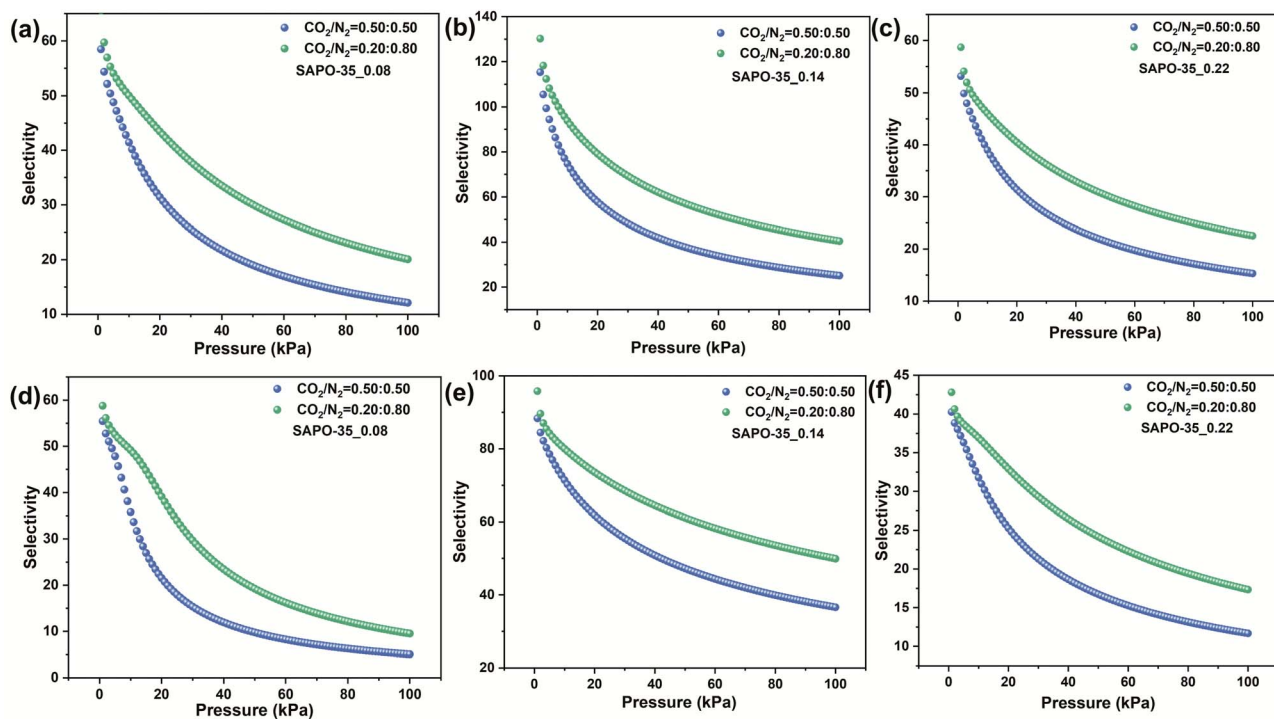


Fig. 3 CO₂/N₂ IAST selectivity for (a) SAPO-35_0.08, (b) SAPO-35_0.14, and (c) SAPO-35_0.22 at 273 K and (d) SAPO-35_0.08, (e) SAPO-35_0.14, and (f) SAPO-35_0.22 at 298 K.



Table 2 CO₂/N₂ IAST separation of SAPO-35_x at 273/298 K and 100 kPa

Sample	CO ₂ /N ₂ at 273 K		CO ₂ /N ₂ at 298 K	
	0.5 : 0.5	0.2 : 0.8	0.5 : 0.5	0.2 : 0.8
SAPO-35_0.08	12.1	20.1	5.1	9.5
SAPO-35_0.14	25.1	40.4	36.6	49.9
SAPO-35_0.22	15.3	22.5	11.7	17.3

and CO₂/N₂ selectivity compared with SAPO-35_0.14, proving the advantage of SAPO-35 zeolite synthesized using NMP as a template in CO₂ adsorption and separation application.

Breakthrough experiments

The breakthrough experiments of SAPO-35_0.14 were performed by utilizing binary CO₂/N₂ (20 : 80 v/v) gas mixtures at 298 K and atmospheric pressure in a fixed bed continuous separation system (Fig. S10[†]), imitating the industrial process conditions of flue gas.^{1b,22} The corresponding breakthrough curves are displayed in Fig. 4. As shown in Fig. 4a, when the CO₂/N₂ mixture at a rate of 3.0 mL min⁻¹ was fed into 5.80 g of SAPO-35_0.14 adsorbent, N₂ eluted first through the column without CO₂ breakthrough. However, the outlet concentration of CO₂ was below the detection limit of the FID until 800 seconds because CO₂ adsorbed on SAPO-35_0.14. When the pores of SAPO-35_0.14 progressively filled with CO₂, CO₂ began to break through the column and diluted the N₂. Hence, dynamic gas separation was achieved by selective CO₂ adsorption to SAPO-35_0.14. In line with equilibrium isotherms, the higher affinity of SAPO-35_0.14 for CO₂ over N₂ led to adequately long differences in breakthrough times. SAPO-35_0.14 is highly selective under dynamic conditions, hence we carried out multiple consecutive tests (Fig. 4b), and the results showed that the adsorption capacity of SAPO-35_0.14 fully recovered to its initial capacity, proving that SAPO-35_0.14 has excellent regeneration. In addition, for CO₂ capture from flue gas, it is important to evaluate the capacity and selectivity of adsorbents in the presence of water. We performed

multiple consecutive breakthrough experiments of SAPO-35_0.14 with a relative humidity of ~40% by using a vapor generator at 298 K and 1 bar. The corresponding breakthrough curves are displayed in Fig. S11.[†] SAPO-35_0.14 well maintains its adsorption and separation abilities and regeneration in the presence of water, indicating the potential of the adsorbent for selective CO₂ adsorption in practical application.

Conclusions

Zeolite materials are widely applied in CO₂ adsorption and separation. In particular, small-pore SAPO zeolites with 8-ring windows and high regenerability are potential candidates. In this work, we have first demonstrated that SAPO-35 zeolites with LEV topology possess excellent CO₂ adsorption and separation abilities. By using *N*-methylpiperidine (NMP) as a template, SAPO-35 zeolites with a broad range of Si contents were prepared, and their CO₂ adsorption/separation properties were investigated. Regulating the Si content can enhance the acidity and polarity of SAPO-35_0.14. Consequently, SAPO-35_0.14 showed a relatively higher CO₂ adsorption uptake of 4.76 mmol g⁻¹ (273 K and 100 kPa) among aluminosilicate zeolites with the same topology (Na-LEV) and most of the SAPO zeolites, showing great potential for CO₂ adsorption. In the meantime, enhanced selectivities of CO₂/N₂ were also observed. Among these, SAPO-35_0.14 showed the highest CO₂/N₂ IAST selectivity of 49.9 at 298 K. SAPO-35_0.14 was also highly selective and was regenerated in transient breakthrough experiments, proving the potential of SAPO-35 zeolite in the practical selective CO₂ adsorption process. This work provides a powerful way to enhance the CO₂ adsorption properties of SAPO zeolites *via* regulating the Si content and acidity, which is of great significance for achieving superior CO₂ adsorption and separation abilities.

Author contributions

X. S. and J. Y. designed and supervised the project; Y. L. and C. W. performed the experiments; Y. Y. checked the data; H. C. and L. L. conducted the adsorption analyses; Y. L. wrote the first draft; X. S. and J. Y. deeply revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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References

- (a) D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058–6082; (b) Y.-S. Bae and R. Q. Snurr, *Angew. Chem., Int. Ed.*, 2011, **50**, 11586–11596.

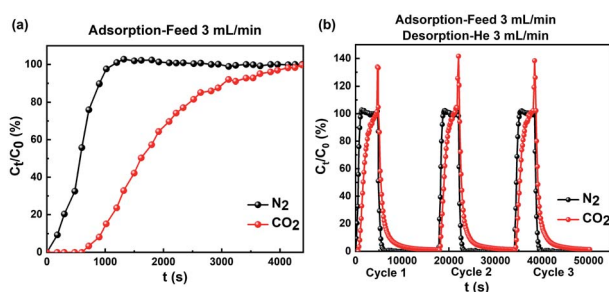


Fig. 4 (a) Experimental binary breakthrough curves for a gas mixture of CO₂/N₂ (20 : 80 v/v) on SAPO-35_0.14 at 298 K and 100 kPa with a total gas flow rate of 3 mL min⁻¹. C₁ and C₀ denote outlet and inlet concentrations, respectively. (b) Multiple consecutive cycles of breakthrough curves for SAPO-35_0.14 with an adsorption/desorption gas flow rate of 3 mL min⁻¹ (CO₂/N₂ 20 : 80 v/v for adsorption and He for desorption) at 298 K and 100 kPa.



- 2 H. A. Patel, J. Byun and C. T. Yavuz, *ChemSusChem*, 2017, **10**, 1303–1317.
- 3 R. Liu, S. Xu, G. Hao and A. Lu, *Chem. J. Chinese Universities*, 2022, **38**, 18–30.
- 4 (a) M. R. Hudson, W. L. Queen, J. A. Mason, D. W. Fickel, R. F. Lobo and C. M. Brown, *J. Am. Chem. Soc.*, 2012, **134**, 1970–1973; (b) S. Smeets, D. Xie, L. B. McCusker, C. Baerlocher, S. I. Zones, J. A. Thompson, H. S. Lacheen and H.-M. Huang, *Chem. Mater.*, 2014, **26**, 3909–3913; (c) Y. Chai, X. Han, W. Li, S. Liu, S. Yao, C. Wang, W. Shi, I. da-Silva, P. Manuel, Y. Cheng, L. D. Daemen, A. J. Ramirez-Cuesta, C. C. Tang, L. Jiang, S. Yang, N. Guan and L. Li, *Science*, 2020, **368**, 1002–1006.
- 5 (a) H.-M. Wen, B. Li, L. Li, R.-B. Lin, W. Zhou, G. Qian and B. Chen, *Adv. Mater.*, 2018, **30**, 1704792; (b) H. Zeng, M. Xie, T. Wang, R.-J. Wei, X.-J. Xie, Y. Zhao, W. Lu and D. Li, *Nature*, 2021, **595**, 542–548.
- 6 A. G. Kontos, V. Likodimos, C. M. Veziri, E. Kouvelos, N. Moustakas, G. N. Karanikolos, G. E. Romanos and P. Falaras, *ChemSusChem*, 2014, **7**, 1696–1702.
- 7 O. F. Altundal, C. Altintas and S. Keskin, *J. Mater. Chem. A*, 2020, **8**, 14609–14623.
- 8 Y. Liu, S. Wang, X. Meng, Y. Ye, X. Song, Z. Liang and Y. Zhao, *Angew. Chem., Int. Ed.*, 2020, **59**, 19487–19493.
- 9 G. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191–214.
- 10 (a) Y. Li and J. Yu, *Nat. Rev. Mater.*, 2021, **6**, 1156–1174; (b) Q. Sun, Z. Xie and J. Yu, *Natl. Sci. Rev.*, 2017, **5**, 542–558; (c) Z. Wang, J. Yu and R. Xu, *Chem. Soc. Rev.*, 2012, **41**, 1729–1741; (d) L. Yu, X. Shang, H. Chen, L. Xiao, Y. Zhu and J. Fan, *Nat. Commun.*, 2019, **10**, 1932; (e) D.-D. Zhou, X.-W. Zhang, Z.-W. Mo, Y.-Z. Xu, X.-Y. Tian, Y. Li, X.-M. Chen and J.-P. Zhang, *EnergyChem*, 2019, **1**, 100016.
- 11 (a) J. Shang, G. Li, R. Singh, Q. Gu, K. M. Nairn, T. J. Bastow, N. Medhekar, C. M. Doherty, A. J. Hill, J. Z. Liu and P. A. Webley, *J. Am. Chem. Soc.*, 2012, **134**, 19246–19253; (b) P. Li and F. Handan Tezel, *Microporous Mesoporous Mater.*, 2007, **98**, 94–101.
- 12 (a) Y. Li, L. Li and J. Yu, *Chem*, 2017, **3**, 928–949; (b) Y. Guo, T. Sun, Y. Gu, X. Liu, Q. Ke, X. Wei and S. Wang, *Chem. Asian J.*, 2018, **13**, 3222–3230; (c) M. Pera-Titus, *Chem. Rev.*, 2014, **114**, 1413–1492.
- 13 Q. Yue, J. Halamek, D. N. Rainer, J. Zhang, R. Bulánek, R. E. Morris, J. Čejka and M. Opanasenko, *Chem. Eng. J.*, 2022, **429**, 131277.
- 14 M. Moliner, C. Martínez and A. Corma, *Chem. Mater.*, 2014, **26**, 246–258.
- 15 J. Yang, J. Li, W. Wang, L. Li and J. Li, *Ind. Eng. Chem. Res.*, 2013, **52**, 17856–17864.
- 16 A. Zukal, M. Shamzhy, M. Kubů and J. Čejka, *J. CO₂ Util.*, 2018, **24**, 157–163.
- 17 (a) J. Gong, C. Wang, C. Zeng and L. Zhang, *Microporous Mesoporous Mater.*, 2016, **221**, 128–136; (b) Y. Wang, Q. Zhang and J. Yu, *Chem. J. Chin. Univ.*, 2020, **41**, 616–622.
- 18 M. M. Lozinska, E. Mangano, J. P. S. Mowat, A. M. Shepherd, R. F. Howe, S. P. Thompson, J. E. Parker, S. Brandani and P. A. Wright, *J. Am. Chem. Soc.*, 2012, **134**, 17628–17642.
- 19 Y. Yu, X. Li, R. Krishna, Y. Liu, Y. Cui, J. Du, Z. Liang, X. Song and J. Yu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 43570–43577.
- 20 H. J. Choi and S. B. Hong, *Chem. Eng. J.*, 2022, **433**, 133800.
- 21 T. D. Pham, M. R. Hudson, C. M. Brown and R. F. Lobo, *ChemSusChem*, 2017, **10**, 946–957.
- 22 X. Wang, N. Yan, M. Xie, P. Liu, P. Bai, H. Su, B. Wang, Y. Wang, L. Li, T. Cheng, P. Guo, W. Yan and J. Yu, *Chem. Sci.*, 2021, **12**, 8803–8810.
- 23 (a) O. Cheung and N. Hedin, *RSC Adv.*, 2014, **4**, 14480–14494; (b) M. Palomino, A. Corma, J. L. Jordá, F. Rey and S. Valencia, *Chem. Commun.*, 2012, **48**, 215–217; (c) R. L. Siegelman, E. J. Kim and J. R. Long, *Nat. Mater.*, 2021, **20**, 1060–1072.
- 24 (a) O. Cheung, Q. Liu, Z. Bacsik and N. Hedin, *Microporous Mesoporous Mater.*, 2012, **156**, 90–96; (b) B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1984, **106**, 6092–6093.
- 25 H. J. Jung, C. H. Shin and S. B. Hong, *J. Phys. Chem. B*, 2005, **109**, 20847–20853.
- 26 (a) I. Pinilla-Herrero, U. Olsbye, C. Márquez-Álvarez and E. Sastre, *J. Catal.*, 2017, **352**, 191–207; (b) I. Pinilla-Herrero, C. Marquez-Alvarez and E. Sastre, *Catal. Sci. Technol.*, 2017, **7**, 3892–3901.
- 27 (a) L. S. de Saldarriaga, C. Saldarriaga and M. E. Davis, *J. Am. Chem. Soc.*, 1987, **109**, 2686–2691; (b) D. Barthomeuf, *Zeolites*, 1994, **14**, 394–401; (c) I. Deroche, L. Gaberova, G. Maurin, M. Castro, P. A. Wright and P. L. Llewellyn, *J. Phys. Chem. C*, 2008, **112**, 5048–5056.
- 28 J. Yang, Q. Zhao, H. Xu, L. Li, J. Dong and J. Li, *J. Chem. Eng. Data*, 2012, **57**, 3701–3709.
- 29 X. Su, P. Tian, D. Fan, Q. Xia, Y. Yang, S. Xu, L. Zhang, Y. Zhang, D. Wang and Z. Liu, *ChemSusChem*, 2013, **6**, 911–918.

