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RESEARCH

CO_2 capture by modified clinoptilolite and its regeneration performance

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Abstract

This study focuses on CO_2 capture by pressure swing adsorption (PSA), with modified clinoptilolite as the adsorbent. Natural clinoptilolite is modified by roasting, by acid pickling, by a combination of acid pickling and roasting, and by ion exchange. Modification by acid pickling–roasting and by ion exchange are found to give the highest CO_2 adsorption capacities, of 730 mL/g and 876.7 mL/g, respectively. It is found that regeneration of clinoptilolite by a combination of vacuum desorption and heating enables recovery of as much as 89% of its previous CO_2 adsorption capacity. To examine the CO_2 adsorption capacity of clinoptilolite when applied to mixed gas, a simulated coking exhaust containing 12% CO_2 and 4% O_2 is used, and it is found that ion exchange modified clinoptilolite achieves a CO_2 removal efficiency of 92.5%. A BET test reveals that acid pickling–roasting and Na^+ modification enhance the porosity of clinoptilolite, thereby improving its adsorption capacity. This work demonstrates the feasibility of applying modified clinoptilolite as an effective adsorbent for CO_2 capture, providing a promising tool for dealing with greenhouse gases.

Keywords Clinoptilolite · Carbon dioxide capture · Pressure swing adsorption (PSA)

1 Introduction

Atmospheric carbon dioxide is the primary carbon source for life on Earth, and its concentration is mainly regulated by photosynthetic organisms, as well as by other natural sources, including volcanoes, hot springs and geysers (Atsumi et al. 2009). CO_2 is present in deposits of petroleum and natural gas, and large amounts are produced by the combustion of these and other fossil fuels, which, together with deforestation (removing a natural sink for CO_2), has led to a rapidly increasing concentration of CO_2 in the atmosphere ever since the Industrial Revolution, accelerating global warming (George et al. 2007; Li 2021). CO_2 also causes ocean acidification, because it dissolves in water to form carbonic acid (Kuffner et al. 2008; Zondervan et al. 2001).

Many widely used industrial processes are feasible for the capture of CO_2, such as absorption, adsorption, low-temperature distillation, and membrane separation, of which adsorption has the advantages of high removal efficiency, easy operation, and reuse of adsorbent. The pressure swing adsorption (PSA) process is a non-cryogenic gas separation and purification technique, based on the pressure dependence of the adsorption capacity of gases by an adsorbent (Chou and Chen 2004). PSA has been successfully applied to the separation of mixed gases, such as CO_2–CH_4–N_2 (Dong et al. 1999) and HO_2–CH_4–N_2 (Gomes and Yee 2002), as well as to CO_2 capture (Rege et al. 2001).

Solid adsorbents for CO_2 capture include carbonaceous materials (e.g., porous carbon-based materials such as activated carbon, graphite and biochar, and newly developed

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carbon-based materials such as graphene, carbon nanotubes, and carbon nanofibers), molecular sieves (e.g., natural and modified clinoptilolites), metal oxides, amino-adsorbents and metal–organic frameworks (MOFs) (Banerjee et al. 2008; D'Alessandro et al. 2010; Kim et al. 2013; Orimo et al. 2003; Titirici et al. 2015; Wilmer and Snurr 2011; Xie et al. 2013; Yang et al. 2021; Zhang et al. 2019; Zhao et al. 2018). Clinoptilolites, which are natural or synthetic crystalline aluminosilicates, are widely used as adsorbents owing to their high abrasion resistance and high thermal stability, as well as their small pore diameters, which provide a high surface area and hence high adsorption capacity. Clinoptilolites have been used to remove various gaseous pollutants (e.g., SO_2, NO_x, CO, and CO_2), as well as radioactive contamination. Previous studies have shown that the adsorption capacity of CO_2 by clinoptilolites increases at higher pressures and lower temperatures (Othman et al. 2006). Modification of natural clinoptilolites can remove impurities and effectively improve their ion exchange capacity and adsorption capacity. Roasting facilitates the release of water from clinoptilolites at high temperature, thereby increasing their adsorption capacity (Huo et al. 2013). Roasting modification of clinoptilolites at 400 ℃ was shown to give a specific surface area of 50.99 m^2/g and a pore volume of 0.08 cm^3/g (Othman et al. 2006). Ion exchange modification was found to increase the CO_2 adsorption capacity of clinoptilolites through cationic exchange between the introduced cations (e.g., Na^+, Li^+, and Ca^{2+}) and the cations present in the clinoptilolites as non-skeletal structure (Baksh et al. 1992).

The work described in the present paper focused on the application of modified clinoptilolites as adsorbents for CO_2 capture by PSA. The modification methods applied to the clinoptilolites included roasting, acid pickling, acid pickling–roasting, and ion exchange. Clinoptilolites prepared under the optimal modification conditions were used for CO_2 adsorption in a simulated coking exhaust. In addition, regeneration of modified clinoptilolites was investigated to evaluate their renewability and adsorption capacity for CO_2.

2 Materials and methods

2.1 Natural clinoptilolite

The natural clinoptilolite used in the present study was sampled from Jinyun City, Zhejiang Province (China), with conchoidal incision, fine consolidation, and compactness. This natural clinoptilolite has a paragenetic composition of quartz, as well as trace amounts of montmorillonite, cristobalite, opal, and chlorite (Kusrini et al. 2019). The chemical composition of the clinoptilolite is shown in Table S1 (in Supplementary Material): its typical unit cell composition was $Na_6[(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$, with an average size of 0.5–2 nm. Other chemicals used in the present study were of analytical pure grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

Scanning electron microscope (SEM) images of clinoptilolite at different magnifications are shown in Fig. S1 (in Supplementary Material). Coarse and irregular framework structures were found, which formed cavities approximately 5 μm in size (Figs. S1c and d: 3000 × and 6000 ×). These aluminum–silicon tetrahedral cavities provided active sites for adsorption and ion exchange, endowing the clinoptilolite with high adsorption capacity for pollutants.

2.2 Modification of clinoptilolite

Natural clinoptilolite of particle size in the range of 0.300–0.391 mm was used for roasting modification. The clinoptilolite was washed several times and placed in an oven at 100 °C for drying. Afterwards, the dried clinoptilolite was transferred into a muffle furnace to be roasted for 1 h, after which the roasting-modified clinoptilolite was cooled to room temperature for further use. The furnace temperature was set variously at 200 °C, 300 °C, 400 °C, 500 °C, and 600 °C to determine the optimal roasting temperature.

Acid pickling modification of natural clinoptilolite (again in the particle size range of 0.300–0.391 mm) was conducted by immersion in aqueous HCl for 40 h. Excessive acid was washed off by distilled water, and the clinoptilolite was dried at 100 °C for further use. Various concentrations of HCl (1 mol/L, 2 mol/L, 4 mol/L, and 6 mol/L) were tested to determine the optimal pickling concentration.

Acid pickling–roasting modification of clinoptilolite was conducted at the optimal roasting temperature determined in the roasting test and with the HCl concentration determined in the acid pickling test. Natural clinoptilolite was ground into different particle size ranges of <0.150 mm, 0.150–0.187 mm, 0.187–0.300 mm, 0.300–0.391 mm, and 0.391–0.800 mm. Samples of the natural clinoptilolite of each particle size range were immersed in HCl for 40 h, washed to remove excessive acid, and then dried at 100 °C and roasted in the muffle furnace for 1 h. The air-cooled acid pickling–roasting modified clinoptilolite was stored for further use.

The acid pickling–roasting modified clinoptilolite was further modified via ion exchange reaction. It was added to nitrate solutions of four cations (Na^+, Cu^{2+}, Mg^{2+}, and Ca^{2+}), and the mixture was placed in a water bath at 85 °C for 24 h. Afterwards, the clinoptilolite was washed, dried at 100 °C, and air-cooled. Various concentrations of each cation were tested (0.1 mol/L, 0.2 mol/L, 0.4 mol/L, and 0.6 mol/L) to determine the optimal combination of concentrations.

2.3 Determination of cation exchange capacity

The cation exchange capacity (CEC) was determined via the ammonium chloride (3%)–ammonium hydroxide (3%) method. Natural or modified clinoptilolite was mixed with 25 mL ammonium chloride–ammonium hydroxide and stood at room temperature for 30 min. Subsequently, 10 drops of polyoxyethylene were added to the mixture, which was then filtered. Excessive ammonium chloride was washed off by ammonium hydroxide until no Cl^- could be detected. Then, 25 mL of calcium chloride (12.5%, weight/volume)–formaldehyde (12.5%, volume/volume) mixture was added, and the resulting condensation reaction between ammonium ion and formaldehyde led to the formation of hydrochloric acid, which was titrated by sodium hydroxide using phenolphthalein as indicator. The CEC (mmol/100 g) was calculated as follows:

$$\mathrm{CEC} = \frac{100C \times V}{m} \tag{1}$$

where C (mol/L) is the concentration of sodium hydroxide, V (mL) is the volume of sodium hydroxide consumed in the titration, and m (g) is the weight of clinoptilolite.

2.4 Design of PSA equipment for CO_2

A schematic of the PSA equipment for CO_2 adsorption is shown in Fig. 1. Mixed N_2–CO_2 gas (58.1%, volume/volume) from the gas tank flows into the adsorption column (20 cm in height and 2 cm in diameter) at a flow rate of 30 mL/min. The CO_2 concentration in the outlet gas is determined by the CO_2 analyzer (Cyes2) every 2 min, until the outlet CO_2 concentration is the same as the inlet concentration.

The CO_2 adsorption capacity was used to evaluate the performance of the modified clinoptilolite. First, the volume of CO_2 adsorbed, V (m^3), was calculated from the breakthrough curve as follows:

$$V = Q\int_{t_1}^{t_2} \left(C_2 - C_1\right)\mathrm{d}t \tag{2}$$

where Q (mL/min) is the flow rate of inlet gas, C_2 (% volume/v) is the concentration of CO_2 at time point t_2, and C_1 (% v/v) is the concentration of CO_2 at time point t_1. The CO_2 adsorption capacity q (mol/g) under standard conditions was then calculated as follows:

$$q = \frac{1000V}{22.4 \times m} \tag{3}$$

where m is the weight of modified clinoptilolite in the adsorption bed (g) and 22.4 L/mol is the molar volume of gas under standard conditions.

2.5 CO_2 desorption and clinoptilolite regeneration

To desorb the CO_2, the modified clinoptilolite was first vacuum-treated (with an oilless vacuum pump, hp-01D) at – 0.02 MPa for 50 min, then heated to 300 °C for 1 h, and finally cooled to room temperature. The CO_2 re-adsorption capacity was determined after desorption, in order to evaluate the performance of the modified clinoptilolite after regeneration.

2.6 CO_2 adsorption in coking exhaust

Acid pickling–roasting–ion (Na^+) exchange modified clinoptilolite was used for CO_2 adsorption from a gas mixture that simulated the coking exhaust from a coking plant in Hebei Province, China that manufactures metallurgical coke. In this plant, coke oven gas is used as coking fuel, and the combusted coking exhaust is released into the atmosphere.

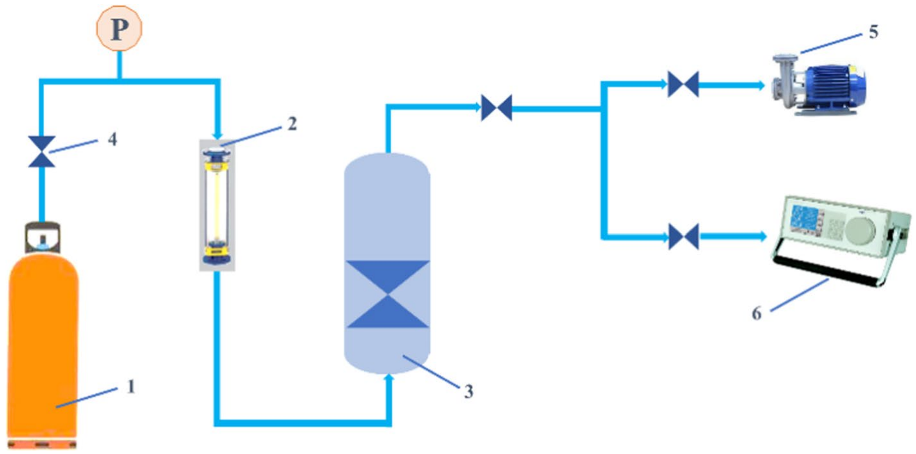


Fig. 1 Schematic diagram of PSA equipment for CO_2 adsorption. 1-gas tank with mixture of N_2 and CO_2; 2-gas flowmeter; 3-adsorption column with modified clinoptilolite; 4-valves; 5-vacuum pump; 6-CO_2 analyzer (Cyes2)

Table 1 Compositions of coke oven gas and coking exhaust

Composition	Gas source	
	Coke oven gas	Coking exhaust
H_2	58.05	0.08
O_2	0.01	4.00
N_2	3.99	83.92
CO_2	2.93	12.00
CH_4	22.89	1.00
CO	9.20	N/A
NO_x	N/A	0.001
Unsaturated hydrocarbon	3.23	N/A

The compositions of the coke oven gas and coking exhaust were determined by gas chromatography (Table 1).

The inlet gas simulating the main composition of the coking exhaust consisted of CO_2 (12% volume/volume), oxygen (4% volume/volume), and N_2 (84% volume/volume). The adsorption pressure was set at 0.4 MPa, and the gas flow rate was 60 mL/min. The adsorption column was filled with 150 g clinoptilolite as the adsorbent. The clinoptilolite was regenerated as described in Sect. 2.5.

2.7 BET test of modified clinoptilolite

The specific surface and pore distribution of the modified clinoptilolite were determined using the Micromeritics Surface Area and Porosimetry System (ASAP2010, USA), with N_2 as the adsorbate. The clinoptilolite was dried at 120 °C and then vacuum-treated at 300 °C for 3 h, after which the adsorption capacity was determined at 77 K. The specific surface of the clinoptilolite was calculated according to the Brunauer–Emmett–Teller (BET) equation (Chai et al. 2019).

3 Results

3.1 Optimization of clinoptilolite modification methods

The CEC was used to evaluate the potential of modified clinoptilolite for CO_2 adsorption, since it reflects the capabilities of ion exchange and porosity in providing active sites for adsorption reactions (Jayarathne et al. 2019; Wang and Wang 2019). The effects of the different clinoptilolite modification methods on the CEC are illustrated in Fig. 2. Increasing the roasting temperature to 300 °C led to a significant increase in the CEC to 69.1 mmol/L, as water and volatile materials in the clinoptilolite escaped, leading to increased porosity (Fig. 2a). Increasing the temperature further, however, led to a rapid decrease in the CEC, to just 49.4 mmol/L at 600 °C. Therefore, the optimal roasting temperature was set at 300 °C. The roasting time also influenced the CEC (Fig. 2b), and it was found that a time of 1.5 h was optimal in terms of achieving a high CEC (75.9 mmol/L) without destroying the structure of the clinoptilolite.

Acid treatment dissolves impurities that block the micropores of clinoptilolite, and pickling in 2 mol/L HCl significantly increased the CEC to 81.9 mmol/L (Fig. 2c). However, higher HCl concentrations led to excessive loss of alumina and destruction of the clinoptilolite structure, with a consequent decrease in the CEC.

For clinoptilolite with particle sizes in the range of 0.300–0.391 mm and modified by a combination of roasting and acid pickling, the CEC of 87.8 mmol/L (Fig. 2d) was significantly increased in comparison with clinoptilolite modified by roasting alone (75.9 mmol/L) or by acid pickling alone (81.9 mmol/L). Although smaller clinoptilolite particle sizes could provide more active reaction sites and larger specific surface area, Fig. 2d shows that further grinding of clinoptilolite to smaller sizes led to only a slight increase in the CEC, and therefore the particle size range of 0.187–0.300 mm was selected for further experimentation.

3.2 Influence of pressure and ion on CO_2 adsorption by acid pickling–roasting modified clinoptilolite

The influence of operation pressure on CO_2 adsorption was investigated, and the CO_2 concentration in the outlet gas is shown versus time for different pressures in Fig. 3. The clinoptilolite was modified by the acid pickling–roasting method. The adsorption capacity of the modified clinoptilolite increased with increasing operation pressure, from 519 mL/g at 0.2 MPa to 730 mL/g at 0.4 MPa. In view of economic considerations, 0.4 MPa was adopted as the optimal operation pressure.

Four cations, namely, Na^+, Cu^{2+}, Mg^{2+}, and Ca^{2+}, each at various concentrations of 0.1 mol/L, 0.2 mol/L, 0.4 mol/L, and 0.6 mol/L, were used for ion exchange modification of

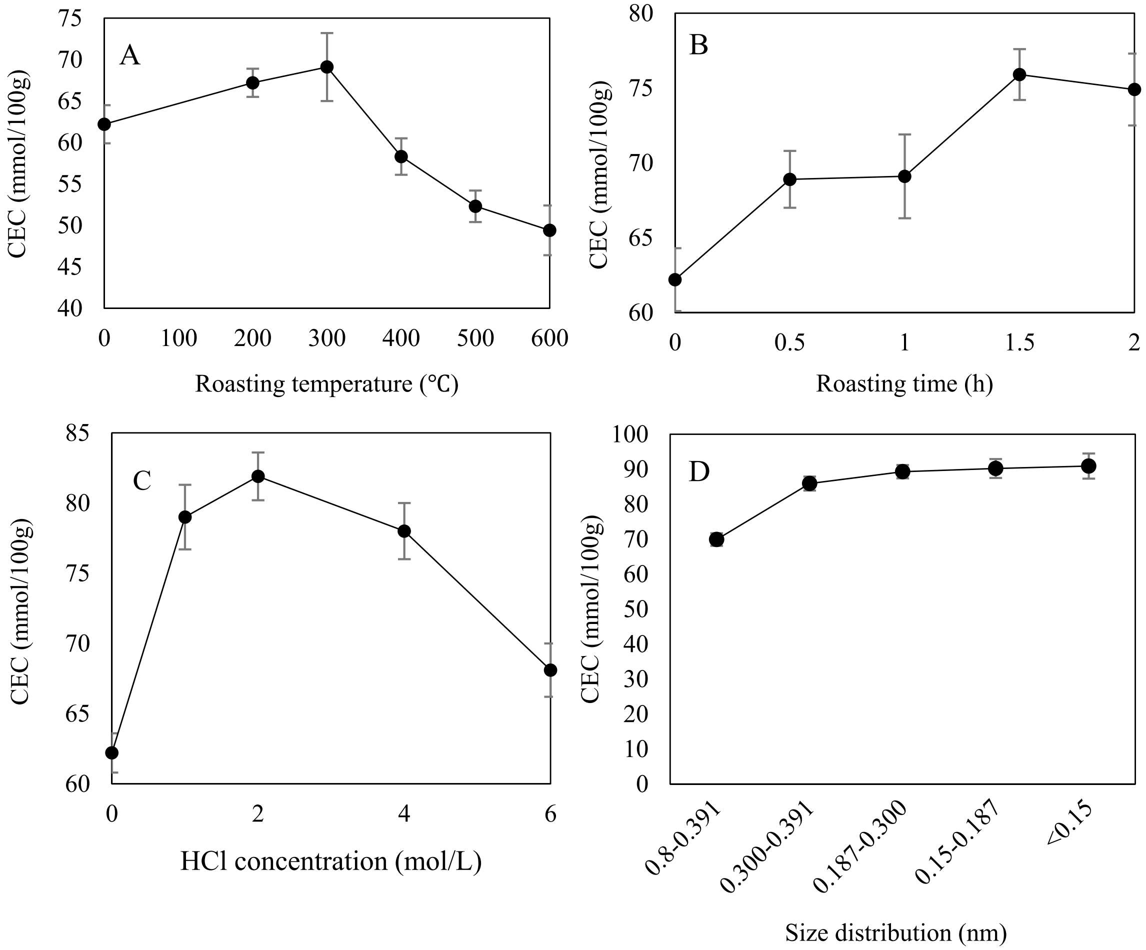
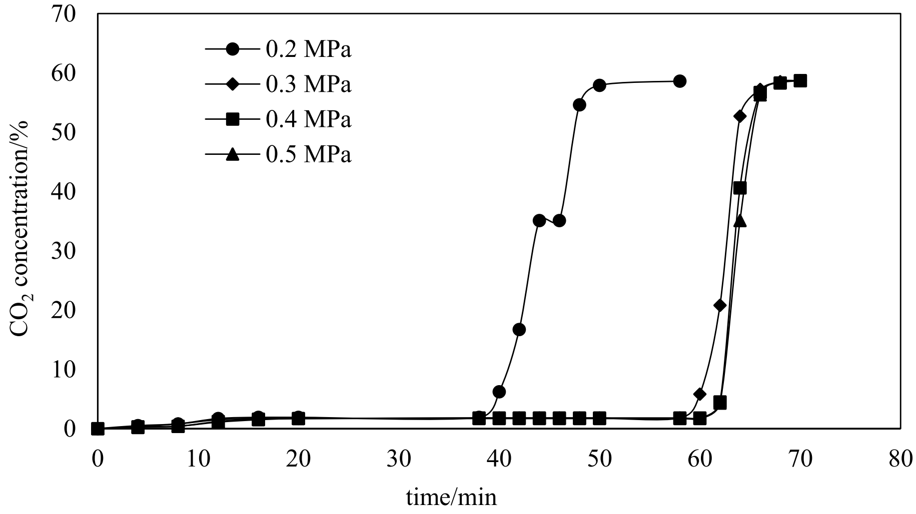


Fig. 2 Influence of different parameters on CEC of modified clinoptilolite **a** roasting temperature **b** roasting time **c** acid concentration **d** size of clinoptilolite

Fig. 3 Influence of operation pressure on CO_2 adsorption of acid pickling-roasting modified clinoptilolite



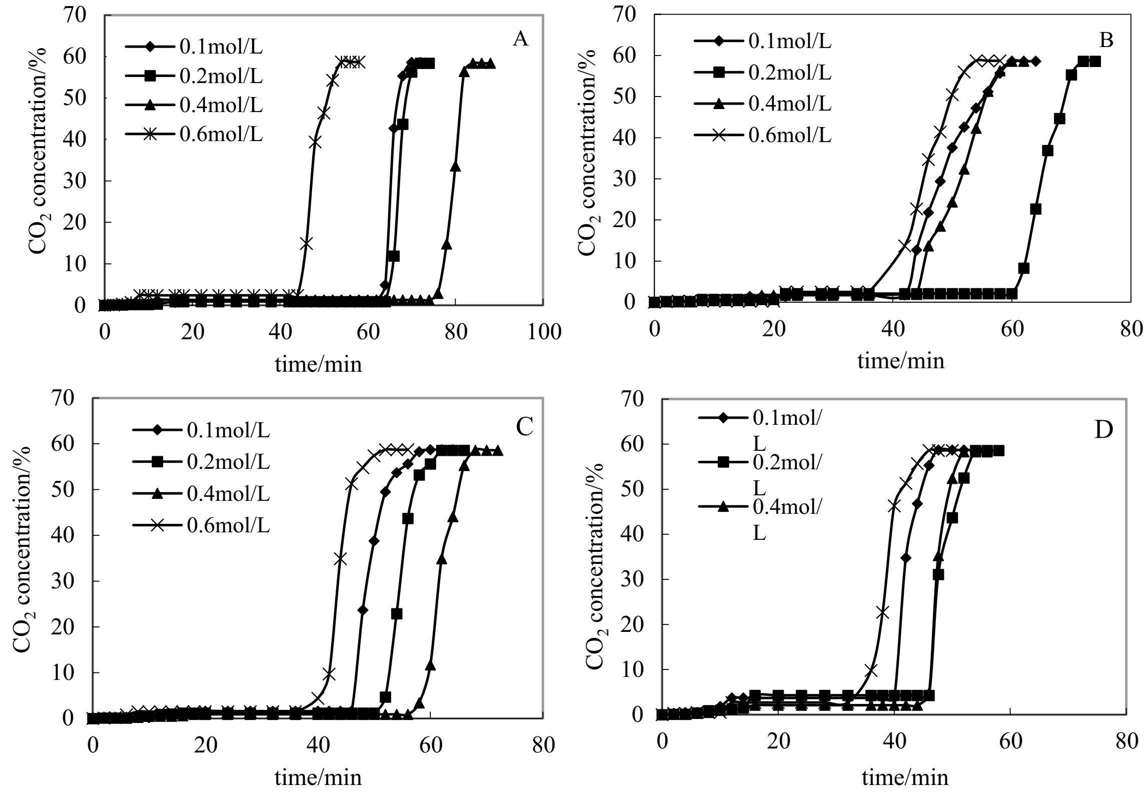


Fig. 4 Influence of cation concentrations on CO_2 adsorption on ion exchange modified clinoptilolite **a** Na^+ **b** Cu^{2+} **c** Mg^{2+} **d** Ca^{2+}

Table 2 CO_2 adsorption capacity after acid pickling-roasting modification

Ions used for modification	Na^+ (0.4 mol/L)	Mg^{2+} (0.4 mol/L)	Cu^{2+} (0.2 mol/L)	Ca^{2+} (0.2 mol/L)
Area of penetration curve	4383.4	3654.7	3767.8	2834.6
CO_2 adsorption capacity (mL/g)	876.7	730.9	753.6	566.9

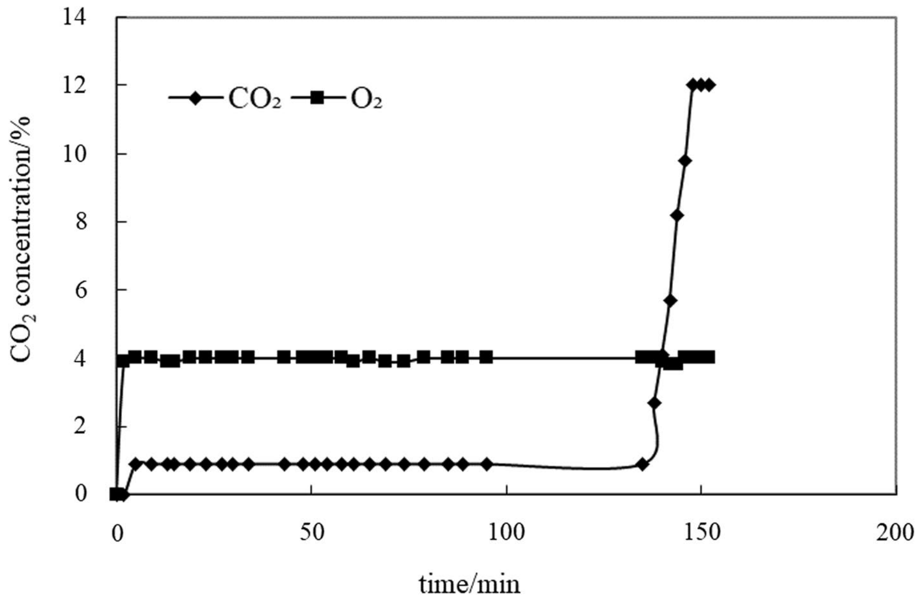


Fig. 5 CO_2 adsorption by Na^+-acid pickling-roasting modified clinoptilolite at the presence of O_2 (4%)

natural clinoptilolite. The CO_2 adsorption capacity of the modified clinoptilolite is shown in Fig. 4 for the different cation concentrations. The optimal concentrations were found to be 0.4 mol/L Na^+ (876.7 mL/g), 0.2 mol/L Cu^{2+} (753.6 mL/g), 0.4 mol/L Mg^{2+} (730.9 mL/g), and 0.2 mol/L Ca^{2+} (566.9 mL/g) (Table 2). Therefore, 0.4 mol/L Na^+ was selected for ion exchange modification of clinoptilolite.

3.3 CO_2 adsorption by Na^+–acid pickling–roasting modified clinoptilolite

A gas mixture with 4% O_2 and 12% CO_2 was used to simulate coking exhaust, in order to investigate the effect of the presence of O_2 on CO_2 adsorption (Fig. 5). Up to a time of 130 min, the O_2 concentration in the outlet gas remained at 4% and the CO_2 concentration at 0.9%, indicating that the Na^+–acid pickling–roasting modified clinoptilolite was suitable for CO_2 adsorption from coking exhaust containing O_2.

3.4 Regeneration of clinoptilolite by vacuum treatment and heating

Vacuum treatment and heating were combined to desorb the CO_2 from the saturated clinoptilolite, in order to evaluate the CO_2 adsorption capacity of clinoptilolite after regeneration (Fig. 6). All the modified clinoptilolites tested showed a slightly decreased CO_2 adsorption capacity after regeneration. Acid pickling–roasting and Na^+–acid pickling–roasting modified clinoptilolites could adsorb 649.8 mL CO_2/g and 780.3 mL CO_2/g, respectively, after regeneration. These results suggest that clinoptilolite as a material for CO_2 adsorption is renewable, and desorption via vacuum treatment and heating is able to recover approximately 89% CO_2 adsorption capacity.

4 Discussion

This study has demonstrated that the use of modified clinoptilolite as an adsorbent offers enhanced CO_2 capture performance. Roasting is a well-established approach for the modification of natural clinoptilolite to improve its adsorption performance. The optimal roasting temperature determined in the present work was 300 °C. Previous studies have shown that roasting at low temperatures (< 300 °C) may lead to incomplete cleaning of the porous surface of natural clinoptilolite, while higher temperatures over 800 °C may destroy the structure of natural clinoptilolite. Thus, roasting at 300 °C could effectively improve the adsorption performance of clinoptilolite without affecting its structure (Figini-Albisetti et al. 2010).

Acid pickling is usually used for the modification of natural clinoptilolite by dealumination. Previous studies have shown that acid pickling can significantly increase both the surface area of clinoptilolite and its Si/Al ratio, thereby enhancing its CO_2 adsorption capacity (Lin et al. 2015; Luo et al. 2022; Strejcova et al. 2020; Wahono et al. 2020; Wojciechowska 2019).

In addition, the present study has found that ion exchange modification of clinoptilolite, particularly with Na^+, can significantly improve its adsorption capacity for CO_2. This is consistent with the results of other recent studies showing that ion exchange modification can achieve the highest removal efficiency for various environmental contaminants, such as fluoride (Nunez et al. 2019), As(V) (Velazquez-Pena et al. 2019), and ammonium and phosphate (Gao et al. 2019), compared with natural clinoptilolite. Ion exchange modification also improves the performance with regard to the purification and separation of valuable gases from mixtures. For example, Hao et al. reported that Na^+ (0.2 mol/L)-modified clinoptilolite showed promise as an adsorbent for the

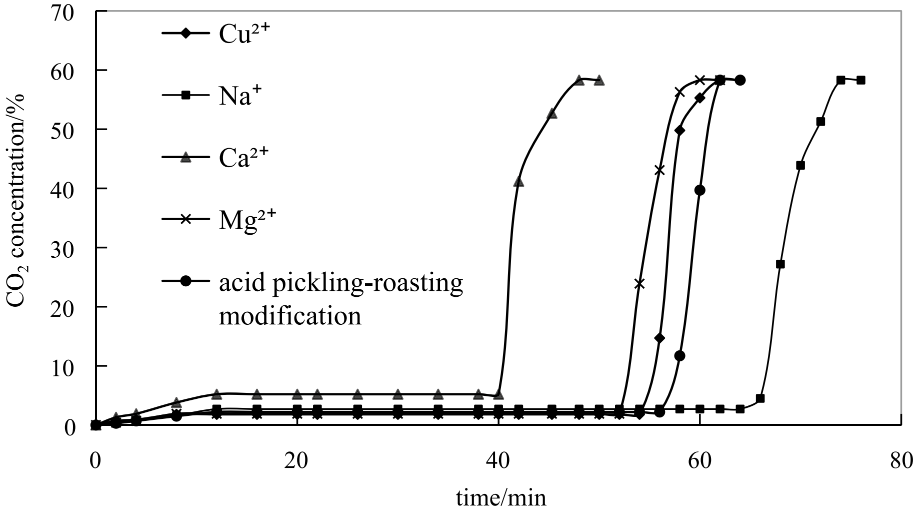


Fig. 6 CO_2 adsorption capacity by regenerated clinoptilolite

Table 3 Distribution of pore volume

Tested samples	Pore volume (cm^3/g)				$\frac{V_1}{V}$ (%)	$\frac{V_2}{V}$ (%)	$\frac{V_3}{V}$ (%)
	Total pore volume	V_1 (2–10 nm)	V_2 (10–30 nm)	V_3 (> 30 nm)			
Natural clinoptilolite	0.808496	0.563575	0.163646	0.081275	69.7%	20.2%	10.1%
Acid pickling-roasting modified clinoptilolite	0.793977	0.529803	0.18903	0.075144	66.7%	23.8%	9.5%
Na^+-acid pickling-roasting modified clinoptilolite	1.03609	0.70762	0.230904	0.097657	68.2%	22.3%	9.5%

Table 4 Distribution of specific surface area

Tested samples	Specific surface area (m^3/g)				$\frac{S_1}{S}$ (%)	$\frac{S_2}{S}$ (%)	$\frac{S_3}{S}$(%)
	Total specific surface area	S_1 (2–10 nm)	S_2 (10–30 nm)	S_3 (> 30 nm)			
Natural clinoptilolite	118.424	99.878	15.591	2.955	84.3%	13.2%	2.5%
Acid pickling-roasting modified clinoptilolite	98.532	80.836	14.884	2.812	82.0%	15.1%	2.9%
Na^+-acid pickling-roasting modified clinoptilolite	113.262	92.785	16.948	3.529	81.9%	15.0%	3.1%

separation of low concentrations of CH_4 from coal bed gas (Hao et al. 2018). Kennedy et al. found that Ca^{2+}-modified clinoptilolite had great potential for CO_2/CH_4 separation owing to its high selectivity, while Fe^{3+}-modified clinoptilolite was more suitable for CH_4/N_2 separation over wider ranges of temperature and pressure (Kennedy et al. 2019).

To unravel the mechanism underlying the enhanced performance of clinoptilolite after acid pickling–roasting modification and Na^+-acid pickling-roasting modification, the pore volume, pore size, and specific surface area of natural clinoptilolite, acid pickling–roasting modified clinoptilolite, and Na^+–acid pickling–roasting modified clinoptilolite were calculated using the BET method, and the results are shown in Tables 3, 4 and 5. Pickling-roasting and Na^+-acid pickling-roasting modification of clinoptilolite both significantly increased the percentage of pore volume of V_2 (10–30 nm) (Table 3), compared with that of natural clinoptilolite. Similarly, although the specific surface areas of the modified clinoptilolites decreased slightly, the percentages of specific surface areas of larger pores (> 10 nm) in the modified clinoptilolites increased by 2.3 %-2.4 % compared with those of natural clinoptilolite (Table 4). These results indicate that modification had effectively removed impurities from larger pores, thereby increasing the surface area and providing more active adsorption sites.

Clinoptilolite serves as a molecular sieve for the adsorption of smaller molecules, and therefore CO_2 (diameter 0.33 nm) can theoretically be adsorbed by clinoptilolite. The modified clinoptilolites had significantly increased mean pore sizes for both large pores and micropores (Table 5), which possibly contributed to their improved CO_2 adsorption performance. Also, the specific surface areas in larger pores were significantly increased in the modified clinoptilolites

Table 5 Specific surface area via BET calculation

Tested samples	BET specific surface area (m^2/g)	Specific surface area in micropores (m^2/g)	Specific surface area in other pores (m^2/g)	Mean pore size (Å)	Mean micropore size (Å)
Natural clinoptilolite	59.0073	52.5079	6.4994	34.8345	6.9181
Acid pickling-roasting modified clinoptilolite	30.9529	22.9205	8.0324	51.3335	8.6601
Na^+-acid pickling-roasting modified clinoptilolite	31.0774	24.1053	6.9721	54.9011	9.8433

(Table 4), indicating that it may be the larger pores that play key roles in CO_2 adsorption, rather than the micropores.

X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) could also be employed to investigate the structure of clinoptilolite before and after its modification, to further explore the mechanisms underlying enhanced CO_2 adsorption capacity. In many previous studies, no changes have been found after modification processes such as roasting below 300 °C and acid modification (Lin et al. 2015; Nunez et al. 2019). In addition, it should be noted that exchangeable cations in clinoptilolite have a strong attraction for CO_2, owing to its quadrupole moment. This is in accordance with the adsorption results obtained here, in which Na^+–acid pickling–roasting modified clinoptilolite demonstrated the highest CO_2 adsorption capacity.

5 Conclusions

The adsorption of CO_2 by modified clinoptilolite was investigated experimentally, and the results showed that modification of clinoptilolite by a combination of acid pickling and roasting or by ion exchange led to the best CO_2 adsorption capacity. Clinoptilolite desorption via vacuum treatment and heating enabled recovery of approximately 89% CO_2 adsorption capacity. The results of a BET test suggested that modified clinoptilolite had significantly increased mean pore size for both large pores and micropores, possibly improving adsorption capacity. This work provides a renewable, easily obtained, and highly effective approach for CO_2 capture and removal, with promise as a tool for the control of air pollution and global warming. Future work should focus on unraveling the mechanisms underlying the improved CO_2 capture performance of modified clinoptilolite, using further characterization methods, such as XRD, XPS, FTIR spectroscopy, and NMR, as well as numerical simulations.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s40789-023-00661-x.

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Author contributions BJ performed the data analysis and wrote the draft manuscript. BZ did the laboratory work. XD designed the experiment and revised the manuscript. YX revised the manuscript.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Atsumi S, Higashide W, Liao JC (2009) Direct photosynthetic recycling of carbon dioxide to isobutyraldehyde. Nat Biotechnol 27:1177-U1142. https://doi.org/10.1038/nbt.1586

Baksh MSA, Kikkinides ES, Yang RT (1992) Lithium type X zeolite as a superior sorbent for air separation. Sep Sci Technol 27:277–294

Banerjee R, Phan A, Wang B, Knobler C, Furukawa H, O'Keeffe M, Yaghi OM (2008) High-throughput synthesis of zeolitic imidazolate frameworks and application to CO_2 capture. Science 319:939–943. https://doi.org/10.1126/science.1152516

Chai D, Yang G, Fan ZQ, Li XL (2019) Gas transport in shale matrix coupling multilayer adsorption and pore confinement effect. Chem Eng J 370:1534–1549. https://doi.org/10.1016/j.cej.2019.03.276

Chou CT, Chen CY (2004) Carbon dioxide recovery by vacuum swing adsorption. Sep Purif Technol 39:51–65. https://doi.org/10.1016/j.seppur.2003.12.009

D'Alessandro DM, Smit B, Long JR (2010) Carbon dioxide capture: prospects for new materials. Angew Chemie-Int Ed 49:6058–6082. https://doi.org/10.1002/anie.201000431

Dong F, Lou H, Kodama A, Goto M, Hirose T (1999) The Petlyuk PSA process for the separation of ternary gas mixtures: exemplification by separating a mixture of CO2–CH4–N2. Sep Purif Technol 16:159–166. https://doi.org/10.1016/S1383-5866(98)00122-1

Figini-Albisetti A, Velasco LF, Parra JB, Ania CO (2010) Effect of outgassing temperature on the performance of porous materials. Appl Surf Sci 256:5182–5186. https://doi.org/10.1016/j.apsusc.2009.12.090

Gao L, Zhang CY, Sun Y, Ma CM (2019) Effect and mechanism of modification treatment on ammonium and phosphate removal by ferric-modified zeolite. Environ Technol 40:1959–1968. https://doi.org/10.1080/09593330.2018.1435729

George K, Ziska LH, Bunce JA, Quebedeaux B (2007) Elevated atmospheric CO_2 concentration and temperature across an urban-rural transect. Atmos Environ 41:7654–7665. https://doi.org/10.1016/j.atmosenv.2007.08.018

Gomes VG, Yee KWK (2002) Pressure swing adsorption for carbon dioxide sequestration from exhaust gases. Sep Purif Technol 28:161–171. https://doi.org/10.1016/s1383-5866(02)00064-3

Hao XF, Li Z, Hu HJ, Liu XQ, Huang YQ (2018) Separation of CH4/N-2 of low concentrations from coal bed gas by sodium-modified clinoptilolite. Front Chem. https://doi.org/10.3389/fchem.2018.00633

Huo H, Lin H, Dong Y, Liu Q (2013) Effects of roasting modification on the characteristics and ammonium nitrogen removal ability of zeolite. J Northeastern Univ (natural Science) 34:1778–1782. https://doi.org/10.12068/j.issn.1005-3026.2013.12.025

Jayarathne A, Wijesiri B, Egodawatta P, Ayoko GA, Goonetilleke A (2019) Role of adsorption behavior on metal build-up in urban road dust. J Environ Sci 83:85–95. https://doi.org/10.1016/j.jes.2019.03.023

Kennedy DA, Mujcin M, Abou-Zeid C, Tezel FH (2019) Cation exchange modification of clinoptilolite -thermodynamic effects on adsorption separations of carbon dioxide, methane, and nitrogen. Microporous Mesoporous Mater 274:327–341. https://doi.org/10.1016/j.micromeso.2018.08.035

Kim JH, Abouelnasr M, Lin LC, Smit B (2013) Large-scale screening of zeolite structures for CO_2 membrane separations. J Am Chem Soc 135:7545–7552. https://doi.org/10.1021/ja400267g

Kuffner IB, Andersson AJ, Jokiel PL, Rodgers KS, Mackenzie FT (2008) Decreased abundance of crustose coralline algae due to ocean acidification. Nat Geosci 1:114–117. https://doi.org/10.1038/ngeo100

Kusrini E, Usman A, Wibowo J (2019) SnOx-impregnated clinoptilolite for efficient mercury removal from liquid hydrocarbon. Arab J Sci Eng 44:189–197. https://doi.org/10.1007/s13369-018-3386-9

Li Q (2021) The view of technological innovation in coal industry under the vision of carbon neutralization. Int J Coal Sci Technol 8:1197–1207. https://doi.org/10.1007/s40789-021-00458-w

Lin H, Liu QL, Dong YB, He YH, Wang L (2015) Physicochemical properties and mechanism study of clinoptilolite modified by NaOH. Microporous Mesoporous Mater 218:174–179. https://doi.org/10.1016/j.micromeso.2015.07.017

Luo LJ, Zheng LB, Zhang XJ, Jiang FZ, Xia LH, Dai JH, Meng DM (2022) The dealuminated zeolites via acid leaching and followed calcination method for removal of hydrophobic bisphenol A. J Solid State Chem. https://doi.org/10.1016/j.jssc.2021.122640

Nunez IL, Perez MV, Dosamante KGA (2019) Clinoptilolite modified by calcium and hydroxyl ions for removal of fluoride from aqueous solution. J Phys Conf Ser 1221:7

Orimo S, Zuttel A, Schlapbach L, Majer G, Fukunaga T, Fujii H (2003) Hydrogen interaction with carbon nanostructures: current situation and future prospects. J Alloy Compd 356:716–719. https://doi.org/10.1016/s0925-8388(03)00175-0

Othman MR, Rasid NM, Fernando WJN (2006) Mg-Al hydrotalcite coating on zeolites for improved carbon dioxide adsorption. Chem Eng Sci 61:1555–1560. https://doi.org/10.1016/j.ces.2005.09.011

Rege SU, Yang RT, Qian KY, Buzanowski MA (2001) Air-prepurification by pressure swing adsorption using single/layered beds. Chem Eng Sci 56:2745–2759. https://doi.org/10.1016/s0009-2509(00)00531-5

Strejcova K, Tisler Z, Svobodova E, Velvarskia R (2020) Characterization of modified natural minerals and rocks for possible adsorption and catalytic use. Molecules. https://doi.org/10.3390/molecules25214989

Titirici MM, White RJ, Brun N, Budarin VL, Su DS, del Monte F, Clark JH, MacLachlan MJ (2015) Sustainable carbon materials. Chem Soc Rev 44:250–290. https://doi.org/10.1039/c4cs00232f

Velazquez-Pena GC, Solache-Rios M, Olguin MT, Fall C (2019) As(V) sorption by different natural zeolite frameworks modified with Fe, Zr and FeZr. Microporous Mesoporous Mater 273:133–141. https://doi.org/10.1016/j.micromeso.2018.07.003

Wahono SK, Stalin J, Addai-Mensah J, Skinner W, Vinu A, Vasilev K (2020) Physico-chemical modification of natural mordenite-clinoptilolite zeolites and their enhanced CO_2 adsorption capacity. Microporous Mesoporous Mater. https://doi.org/10.1016/j.micromeso.2019.109871

Wang JL, Wang SZ (2019) Preparation, modification and environmental application of biochar: a review. J Clean Prod 227:1002–1022. https://doi.org/10.1016/j.jclepro.2019.04.282

Wilmer CE, Snurr RQ (2011) Towards rapid computational screening of metal-organic frameworks for carbon dioxide capture: calculation of framework charges via charge equilibration. Chem Eng J 171:775–781. https://doi.org/10.1016/j.cej.2010.10.035

Wojciechowska K (2019) The influence of desilication/dealumination processes on the physicochemical properties of clinoptilolite. Clay Miner 54:111–119. https://doi.org/10.1180/clm.2019.17

Xie Y, Wang TT, Liu XH, Zou K, Deng WQ (2013) Capture and conversion of CO_2 at ambient conditions by a conjugated microporous polymer. Nat Commun. https://doi.org/10.1038/ncomms2960

Yang Z, Lei Z, Ge B, Xiong X, Jin Y, Jiao K, Chen F, Peng S (2021) Development of catalytic combustion and CO_2 capture and conversion technology. Int J Coal Sci Technol 8:377–382. https://doi.org/10.1007/s40789-021-00444-2

Zhang YH, Zhu CQ, Liu FQ, Yuan Y, Wu HD, Li AM (2019) Effects of ionic strength on removal of toxic pollutants from aqueous media with multifarious adsorbents: a review. Sci Total Environ 646:265–279. https://doi.org/10.1016/j.scitotenv.2018.07.279

Zhao FL, Liu HM, Mathe SDR, Dong AJ, Zhang JH (2018) Covalent organic frameworks: from materials design to biomedical application. Nanomaterials. https://doi.org/10.3390/nano8010015

Zondervan I, Zeebe RE, Rost B, Riebesell U (2001) Decreasing marine biogenic calcification: a negative feedback on rising atmospheric pCO(2). Global Biogeochem Cycles 15:507–516. https://doi.org/10.1029/2000gb001321