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# Promotional effect of NaNO<sub>3</sub>/NaNO<sub>2</sub> on CO<sub>2</sub> adsorption performance of MgO sorbents



Ting Qu<sup>a</sup>, Jinpeng Zhang<sup>a,1</sup>, Jinbo Song<sup>a</sup>, Jieying Jing<sup>a,b,\*</sup>, Wen-Ying Li<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, China
 <sup>b</sup> Shanxi-Zheda Institute of Advanced Materials and Chemical Engineering, Taiyuan 030000, China

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Keywords: Carbon dioxide adsorption Magnesium sorbent Molten salt Cycling stability	The magnesium oxide (MgO) sorbents doped with different NaNO <sub>3</sub> /NaNO <sub>2</sub> molar ratios were prepared to improve their stability over multiple cycles. Regulating the NaNO <sub>3</sub> /NaNO <sub>2</sub> molar ratio effectively improved the CO <sub>2</sub> adsorption performance of the sorbent. The MgO sorbent with the NaNO <sub>3</sub> /NaNO <sub>2</sub> molar ratio of 0.8 exhibited outstanding performance and stability. Characterization and density functional theory calculations confirmed the positive effects of the appropriate NaNO <sub>3</sub> amount in improving the adsorption activity, whereas the suitable NaNO <sub>2</sub> amount slowed the sintering step and improved stability. Notably, the molten salt remained stable during cycling and did not decompose even at high regeneration temperatures, guaranteeing the cyclic stability of the sorbent. Further characterization showed that the CO <sub>2</sub> sorbiton drop in the first few cycles was		

of sorbents, and segregation of molten salt on the sorbent surface.

## 1. Introduction

 $H_2$  energy is useful for realizing zero-carbon-emission energy (Shen, 2023). Currently, 99 %  $H_2$  resources are produced from fossil fuels (e.g., coal and methane) (Cao et al., 2021), thereby emitting large amounts of CO<sub>2</sub> and harmful substances, which place a burden on the environment. Therefore, CO<sub>2</sub> emissions during  $H_2$  production should be reduced (Voldsund et al., 2016; Liu et al., 2021; Hu et al., 2019; Sun et al., 2024).

Water gas shift (WGS) reaction is an essential process in  $H_2$  production. Currently, the generated  $CO_2$  in WGS reactions is usually absorbed by an alcohol-amine solution. As such, this technology has the advantages of high technical maturity and simple scale-up; however, it is limited by its high renewable energy consumption, operating costs, and investment (Gao et al., 2019; Kou et al., 2018; Zhu et al., 2020). Sorption-enhanced water gas shift (SEWGS) is an effective method for producing  $H_2$  while reducing  $CO_2$  emissions. It has attracted considerable attention because it surpasses thermodynamic limitations and can obtain high-purity  $H_2$  in one step compared with traditional WGS. SEWGS integrates a separation process that removes  $CO_2$  and produces high  $H_2$  concentration through Le Chatelier's principle (Cui et al., 2018; Teixeira et al., 2022; Jiang et al., 2022; Sikarwar et al., 2022; Bassani

et al., 2019). In addition, the reaction equilibrium is shifted and the reaction can react at a higher temperature (600 °C) without using a low-temperature-shift catalyst in this process, the  $CO_2$  sorbent is crucial because the amount and rate of  $CO_2$  removal directly determine the degree of intensification of the WGS reaction, which consequently affects the H<sub>2</sub> production and purity.

ascribed to the decline in the active surface owing to the aggregation of MgO particles, incomplete regeneration

As a solid sorbent, MgO has several advantages, such as a high theoretical adsorption capacity (25 mmol/g(CO<sub>2</sub>/sorbent)), low renewable energy consumption, and low availability; therefore, it has great potential in SEWGS reaction (Xu et al., 2021; Hu et al., 2019). In a typical SEWGS cyclic process, MgO adsorbs CO<sub>2</sub> to produce the carbonation product MgCO<sub>3</sub>, which then decomposes at high temperatures to produce MgO used in the cyclic CO<sub>2</sub> absorption process. The Mg–O bond of MgO is difficult to break owing to two main reasons, namely, the high lattice enthalpy of MgO and dense MgCO<sub>3</sub> product layer produced on the MgO surface after absorbing CO<sub>2</sub>, thereby increasing the mass-transfer resistance of CO<sub>2</sub>. As a result, MgO has an extremely low actual adsorption capacity (<0.45 mmol/g(CO<sub>2</sub>/sorbent)) (Rekhtina et al., 2023; Xu et al., 2021).

Several strategies have been proposed to enhance the performance of MgO, such as synthesizing mesoporous MgO (Ruhaimi and Aziz, 2021),

\* Corresponding authors.

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E-mail addresses: jingjieying@tyut.edu.cn (J. Jing), ying@tyut.edu.cn (W.-Y. Li).

<sup>&</sup>lt;sup>1</sup> These authors contributed equally to this work.

screening suitable Mg precursors (Gao et al., 2017; Yang et al., 2018; Ruhaimi et al., 2021), dispersing MgO on porous supports (Zhou et al., 2024), and varying the reaction conditions and doping promoters (Gao et al., 2017; Cui et al., 2020). Among these strategies, molten-salt doping is the most effective. Harada et al. (Harada et al., 2015) obtained the CO2 adsorption capacity of 11 mmol/g(CO2/sorbent) using NaNO3 to modify MgO. Xu et al. (Xu et al., 2024) prepared MgO using waste pyroxene as the raw material and investigated the effect of NaNO3 doping on its properties. The sorbent achieved excellent CO2 adsorption of 36.62 wt% at 320 °C. Wang et al. (Wang et al., 2019) employed NaNO<sub>2</sub> to modify MgO for increased CO<sub>2</sub> adsorption, reaching the adsorption capacity of 11.36 mmol/g(CO<sub>2</sub>/sorbent) after 30 min. Gui et al. (Gui et al., 2024) reported a LiNO<sub>3</sub>-NaNO<sub>3</sub>-KNO<sub>3</sub>-doped MgO sorbent with the maximum CO2 adsorption capacity of 57.1 wt% at 350 °C and CO2 concentration of 80 %. However, most sorbents promoted by molten salts rapidly lose their CO<sub>2</sub> adsorption capacity during cycling. Chen et al., (Chen et al., 2021) noted the significant decrease in the adsorption properties of MgO sorbents promoted by NaNO3, LiNO3, K2CO3, and Na2CO3 from 7.73 mmol/g(CO<sub>2</sub>/sorbent) to 3.41 mmol/g(CO<sub>2</sub>/sorbent) after 15 cycles. Zhao et al. (Zhao et al., 2018) prepared MgO sorbents doped with NaNO<sub>3</sub> and NaNO<sub>2</sub>, whereby the CO<sub>2</sub> adsorption capacity decreased by 54 % after 10 cycles. Therefore, the CO<sub>2</sub> adsorption capacity of moltensalt-doped MgO sorbents should be maintained over long-term cycles.

Previous studies have determined three factors that decline the stability of molten-salt-doped MgO sorbents (Gao et al., 2022; Pang et al., 2021; Rekhtina et al., 2023). First, during the adsorption process, the molten salt on the MgO surface segregates and reassembles, resulting in the instability of molten salt and uncovering of the MgO surface. Second, the carbonation temperature of the sorbent is higher than the Tammann temperature of MgCO<sub>3</sub>, which accelerates the atomic diffusion in the interface between MgCO<sub>3</sub> and the molten salt, inducing the sintering of the sorbent and aggregation of MgO particles. Finally, during the carbonation of MgO to form MgCO<sub>3</sub>, the lattice volume expands, which accelerates the collapse of the pore structure, sintering, and deactivation of the sorbent. Researchers have attempted to overcome these difficulties. Kim et al. (Kim et al., 2014) used a core-shell structure to embed multicore MgO particles into porous carbon nanospheres through a solvent-free process. The isolation effect of the shell inhibited the sintering of MgO particles. Pang et al. (Pang et al., 2023) selected eutectic carbonates with high melting points as accelerators to explore the CO<sub>2</sub> capture performance under high-temperature conditions. After 30 cycles, the sorbent maintained a CO<sub>2</sub> capture rate of 17.9 mmol/g(CO<sub>2</sub>/ sorbent) because of its porous structure after cyclic testing, which enhanced the mass transfer of CO<sub>2</sub> and provided good cyclic stability. Triviño et al. (Trivino et al., 2018) prepared MgO sorbents impregnated with NaNO3 and used commercially available hydrotalcites as stabilizers to improve cycling stability. The sorbent with 30 wt% hydrotalcite had a higher and more stable CO<sub>2</sub> adsorption performance than that without a stabilizer after several cycles because hydrotalcite limits the formation of large and inhomogeneous product crystallites. To the best of our knowledge, the effects of molten salt components during the CO<sub>2</sub> adsorption reaction have not been discussed in depth. Moreover, the mechanism by which molten salts promotes MgO adsorption remains controversial.

In this work, NaNO<sub>3</sub>/NaNO<sub>2</sub>-doped MgO-based sorbent was prepared by ball-milling technique (Wang et al., 2019). The effects of the NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio on the crystallographic structure, surface morphology, and CO<sub>2</sub> adsorption properties were investigated to obtain excellent CO<sub>2</sub> capture performance. Further, the role of the molten salt in the process and overall sorption mechanism was analyzed.

# 2. Experimental methods

#### 2.1. Sorbent preparation

Analytical-grade magnesium carbonate hydroxide hydrate

(4MgCO<sub>3</sub>·Mg(OH)<sub>2</sub>·5H<sub>2</sub>O), sodium nitrate (NaNO<sub>3</sub>), and sodium nitrite (NaNO<sub>2</sub>) were purchased from Shanghai Aladdin Reagent Co., China. MgO-based sorbents doped with different NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratios were prepared by ball-milling technique. In a typical process, MgO powder was prepared by calcining 4MgCO<sub>3</sub>·Mg(OH)<sub>2</sub>·5H<sub>2</sub>O in a muffle furnace by heating from room temperature to 450 °C at the rate of 3 °C/ min and maintaining it for 3 h. The resulting MgO sample was labeled MgO-1. Subsequently, 0.2 g molten salt and 1 g MgO were mixed in a mortar and ground thoroughly (the total amount of MgO doped with NaNO<sub>3</sub>/NaNO<sub>2</sub> was 16.7 wt%). After complete grinding, secondary calcination was performed following the steps of the preceding calcination step. The resulting sorbents are denoted as Sorb-4.0, Sorb-2.4, Sorb-1.6, Sorb-0.8, and Sorb-0.4 according to the NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio x (x = 4.0, 2.4, 1.6, 0.8, and 0.4, respectively). For comparison, single-component molten-salt-doped MgO sorbents, labeled NaNO3-Mg and NaNO2-Mg, were synthesized using the above procedure. Commercial MgO was labeled as MgO-2.

# 2.2. Characterization

The crystal-phase structures of the synthesized sorbents were characterized by X-ray powder diffraction (XRD, Rigaku D/Max-3B) at the scanning speed of 4°/min and scanning range of 10°–90°. The physical and structural parameters of the synthesized sorbents were analyzed using a physical adsorption method (Quantachrome iQ Autosorb-1). The synthesized sorbents were pretreated under a vacuum at 180.0 °C to remove water vapour and other impurities and tested at – 196 °C in a N<sub>2</sub> atmosphere. The Brunauer–Emmett–Teller method was used to calculate the total specific surface area of the synthesized sorbent, and the Barrett–Joyner–Halenda method was used to calculate the total pore volume and average pore size of the synthesized sorbent. Scanning electron microscopy (SEM, TESCAN MIRA4) was used to observe the surface morphologies of the synthesized sorbents at an acceleration voltage of 15 kV.

## 2.3. Sorbent performance tests

The performance of the synthesized sorbents was tested by thermogravimetric analysis (TGA, STA449F5). Approximately 10 mg sorbent was placed in an Al<sub>2</sub>O<sub>3</sub> crucible. Subsequently, isothermal adsorption performance tests were conducted. The sorbent was heated to an adsorption temperature of 340 °C under a N<sub>2</sub> atmosphere (50 mL/ min), immediately switched to an atmosphere of 60 vol% CO<sub>2</sub>/N<sub>2</sub> (50 mL/min), and maintained for 60 min. All the experiments were conducted 3 times and the recorded data were considered credible when the relative deviation was less than 3 %.

The cyclic stability of the sorbent was evaluated after 10 adsorption/ regeneration cycles. First, adsorption using the sorbent was conducted for 60 min at 340 °C in 50 mL/min 60 vol%  $CO_2/N_2$  atmosphere. Subsequently, the temperature was increased to 400 °C and regeneration was kept for 15 min at 50 mL/min in a pure  $N_2$  atmosphere. The  $CO_2$ adsorption capacities and MgO utilization rates of the sorbents were calculated using Equations (1) and (2), respectively.

$$N = \frac{1000m_{\rm ad}}{M_{\rm CO_2} * m_0} \tag{1}$$

where *N* is the adsorption capacity, mmol/g(CO<sub>2</sub>/sorbent);  $m_{ad}$  is the weight increase of the sorbent, mg;  $M_{CO2}$  is the CO<sub>2</sub> molar mass, g/mol; and  $m_0$  is the initial sorbent mass, mg.

$$X = \frac{N}{N^{\theta} * x} * 100\%$$
 (2)

where X is the utilization rate of MgO, %; x is the mass fraction of MgO in the sorbent, %; and  $N^{\theta}$  is the CO<sub>2</sub> theoretical adsorption capacity of MgO, 25 mmol/g(CO<sub>2</sub>/MgO).

# 2.4. Theoretical calculation

The mechanism for the promoted MgO adsorption with NaNO<sub>3</sub>/NaNO<sub>2</sub> doping was elucidated through density functional theory (DFT) calculations. The Perdew–Burke–Ernzerh function in the Vienna Ab Initio Simulation Package (VASP) was used for all spin-polarized DFT calculations (Perdew et al., 1996; Kresse, hafner., 1993). The interaction between the nuclei and valence electrons was described using the projected augmented wave method at a cutoff energy of 400 eV (Perdew and Wang, 1992). Additionally, a general gradient approximation parameterized using Grimme's method (DFT-D3) was used (Grimme et al., 2011). A 3 × 3 × 1 Monkhorst–Pack grid was used for the plate calculation of the Brillouin sampling. The total energy was  $10^{-5}$  eV, and the convergence criterion for the force was 0.02 eV/Å.

The lattice parameter of MgO (4.209 Å) in all models were consistent with that reported in the literature (Pang et al., 2021). After optimizing the lattice parameters of the MgO monomer, the MgO (100) surface of the (2 × 2) periodic supercell was considered for the calculation. To prevent potential interactions between the plates, a 15 Å vacuum plate was set in the z direction (Pang et al., 2021). During the simulation, the bottom surface was fixed, and the top surface was relaxed for modeling. The orbital hybridization and charge redistribution between the atoms after the interaction were analyzed using the projected density of states (PDOS) and charge density difference to determine the interaction mechanism between the substrate and adsorbed material. The strength of the interaction between the substrate and adsorbed substance was evaluated by the adsorption energy ( $\Delta E_{ads}$ ), as shown in Equation (3).

$$\Delta E_{\rm ads} = E_{\rm system} - (E_{\rm substrate} + E_{\rm adsorbate}) \tag{3}$$

where  $E_{substrate}$  is the energy of the substrate (pure and NaNO<sub>3</sub>doped, MgO),  $E_{adsorbate}$  is the energy of the adsorbate (CO<sub>2</sub> molecule), and  $E_{system}$  is the total energy required for the sorbent to attach to the substrate. A negative  $\Delta E_{ads}$  corresponds to a stable configuration.

#### 3. Results and discussion

## 3.1. Properties of the MgO-based sorbents

### 3.1.1. Crystallographic structure

The crystalline structures of the synthesized sorbents are shown in Fig. 1. Notable characteristic peaks of MgO (JCPDS 45–0946) are noted, indicating the high purity of the MgO sorbent without impurities, such as Mg(OH)<sub>2</sub> or MgCO<sub>3</sub>. As shown in Fig. 1b, the synthesized sorbents have two phases, namely MgO (JCPDS 45–0946) and NaNO<sub>3</sub> (JCPDS 36–1474), denoting that different NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratios did not affect the structure. The sorbents contain NaNO<sub>2</sub> (JCPDS 06–0392) (Fig. 1a) before the second calcination step, depicting the oxidization of all NaNO<sub>2</sub> content to NaNO<sub>3</sub> during calcination (Gao et al., 2019). Moreover, the crystallite size of MgO increases after calcination. For

example, the crystallite size of Sorb-0.8 increases from 7.5 nm to 13.8 nm after calcination, corresponding to approximately a two-fold increase. The shrinkage of the composites is ascribed to the low melting temperatures of NaNO<sub>3</sub> and NaNO<sub>2</sub> during calcination, which could increase the grain size of MgO after the secondary calcination.

#### 3.1.2. Sorbent textural properties

The physical and structural parameters of the sorbents are closely related to the adsorption properties (Akgsornpeak et al., 2014). Fig. 2 displays the N<sub>2</sub> physisorption isotherms and pore-size distribution of the sorbents. According to the IUPAC classification, the isotherms of the sorbents are all type IV, and the hysteresis curves are type H3, depicting the dominant mesoporous structure. The mesopores of the sorbents doped with molten salt have a bimodal size distribution at 3–4 and 10–15 nm. Small pores are conducive to the uniform distribution of the molten salt on the MgO surface, whereas large pores can enhance the reachability of  $CO_2$  to small pores and provide a buffer space for volume expansion/contraction during cycling. Therefore, this bimodal pore structure is advantageous for  $CO_2$  adsorption (Cui et al., 2020).

Table 1 summarizes the structural properties of the synthesized sorbents. The specific surface area and pore volume of the sorbents sharply decrease after doping the molten salt owing to the melting of solid NaNO<sub>3</sub>/NaNO<sub>2</sub>, its flow on the surface of MgO, and filling of the mesopores during calcination. This confirms the successful doping of the molten salt. Although the specific surface areas and pore volumes of the sorbents doped with molten salt decrease, they still exceed those of MgO-2. Such mesoporous structures and large specific surface areas are favorable for improving the CO<sub>2</sub> adsorption capacity. MgO prepared by low-temperature (~450 °C) calcination contains several lattice defects or vacancies, which can result in the rapid formation of MgCO3 (Harada et al., 2015).

## 3.1.3. Sorbent surface morphology

The MgO obtained from the calcination of magnesium carbonate hydroxide shows a sheet-like structure (Fig. S1), typically resulting in a large specific surface area. After doping NaNO<sub>3</sub>/NaNO<sub>2</sub>, the alkali metal salt tends to melt and cover the surface of MgO to form smaller particles. By taking into account the pore size distribution and surface morphology of sorbents (Table 1), it is confirmed that the molten salt blocks the pores of MgO and consequently decrease their surface area and pore volume. Fig. 3 further provides the surface morphologies of the synthesized sorbents doped with NaNO<sub>3</sub>/NaNO<sub>2</sub>. All the sorbents exhibit a villi-like porous structure, which could promote the mass transfer of CO<sub>2</sub> and CO<sub>2</sub> adsorption capacity. Furthermore, the NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio does not affect the morphology of the sorbents, leading to similar surface area and pore volume, which is consistent with the pore structure analysis in Table 1.



Fig. 1. XRD patterns of the sorbents (a) before and (b) after calcination.



Fig. 2. (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore-size distribution of the sorbents.

Table 1Structural properties of the sorbents.

Samples	Specific surface area /m²/g	Total pore volume /cm <sup>3</sup> /g	Average pore size /nm	
MgO-1	82.10	0.199	8.3	
MgO-2	19.60	0.206	42.2	
NaNO <sub>3</sub> –Mg	43.60	0.164	15.5	
Sorb-4.0	36.75	0.158	17.6	
Sorb-2.4	38.05	0.156	17.4	
Sorb-0.8	36.07	0.158	18.8	
Sorb-0.4	35.82	0.145	17.4	
NaNO <sub>2</sub> –Mg	33.24	0.140	18.0	

#### 3.2. CO<sub>2</sub> sorption performance

## 3.2.1. Initial CO<sub>2</sub> sorption capacity

The initial performances of the synthetic sorbents were tested at 340 °C under 60 vol% CO<sub>2</sub>/N<sub>2</sub>. Fig. S2a shows that the CO<sub>2</sub> adsorption capacity of all synthesized sorbents is considerably higher than that of MgO-1 (0.6 mmol/g(CO<sub>2</sub>/sorbent)). Moreover, the isothermal adsorption curves of each sorbent exhibit the same three-stage adsorption process. The first stage, which is the initial induction stage ( $\sim$ 3 min), is characterized by the physical adsorption of a small amount of CO<sub>2</sub> on the surface of the sorbents. The second stage, which is the rapid

chemisorption stage, exhibits a rapid increase in the adsorption rate and  $CO_2$  capacity because the temperature exceeds the melting point of the salt, resulting in the melting of salt, which provides channels for the carbonation reaction and reduces the mass-transfer resistance of  $CO_2$ . The last stage, which is the slow reaction stage, that is, the diffusion-controlled stage, depicts the saturation of the sorbent and smoothened adsorption curve (Jo S. I., An Y.I., Kim K.Y., 2017).

As shown in Fig. 4a, the CO<sub>2</sub> adsorption capacity is negatively correlated with the melting point of the doped molten salt. At a carbonation temperature of 340 °C, the enhancement in the CO<sub>2</sub> uptake is stronger for sorbents with lower melting points, which can be attributed to the higher ion mobility of the molten salts with lower melting points (Delise et al., 2020). Mg<sup>2+</sup>, O<sup>2-</sup>, and CO<sub>2</sub> have higher mobility in the environment of molten salt and can diffuse together in a short time to form [Mg<sup>2+</sup>...CO<sub>3</sub><sup>2-</sup>] ion pairs. The MgCO<sub>3</sub> phase precipitates when the target substance exceeds its solubility and reaches supersaturation (dal Pozzo et al., 2019). The NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio has a significant impact on the reaction rate during the rapid reaction stage. As shown in Fig. S2b, the rapid reaction rate initially increases and then decreases with the change in NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio, and the maximum reaction rate can reach 0.36 min<sup>-1</sup>.

## 3.2.2. CO<sub>2</sub> cyclic sorption stability

In the molten state, alkali metal nitrates can be used as effective



Fig. 3. SEM images of the sorbents: (a) NaNO<sub>3</sub>-Mg, (b) Sorb-4.0, (c) Sorb-2.4, (d) Sorb-0.8, (e) Sorb-0.4 and (f) NaNO<sub>2</sub>-Mg.



Fig. 4. (a) Relationship between the adsorption capacity of the sorbent and melting point of molten salt (Delise et al., 2020). (b) Cyclic stability of CO<sub>2</sub> sorption.

phase transfer catalysts, providing reaction sites for the carbonation of MgO and promoting the adsorption of  $CO_2$  by MgO (Zhang et al., 2014). Nitrate in the molten state promotes the adsorption properties of MgO for CO<sub>2</sub>; however, the degree of promotion is significantly different for different salts (dal Pozzo et al., 2019; Qiao et al., 2017). The CO<sub>2</sub> cyclic sorption stabilities of the sorbents are shown in Fig. 4b. The performance of the sorbents decreases as the number of cycles increases. However, notable differences are noted in the stabilities of the sorbents, indicating the different roles of NaNO<sub>3</sub> and NaNO<sub>2</sub> roles in the process. For the individually doped NaNO<sub>3</sub> and NaNO<sub>2</sub> components, the CO<sub>2</sub> adsorption capacity greatly decreases. For example, the CO<sub>2</sub> adsorption capacity of NaNO<sub>3</sub>-Mg decreases from 12.5 mmol/g(CO<sub>2</sub>/sorbent) to 0.9 mmol/g (CO<sub>2</sub>/sorbent) in the first four cycles. However, when a small amount of NaNO<sub>2</sub> is doped into it, that is, a high proportion of NaNO<sub>3</sub> is maintained, such as Sorb-4.0 and Sorb-2.4, the cyclic performance evidently improves, reaching 11.8 mmol/g(CO<sub>2</sub>/sorbent) and 12.6 mmol/g(CO<sub>2</sub>/ sorbent) in the fourth cycle, respectively. Although the CO<sub>2</sub> adsorption capacity increases, no flat trend is observed, and the CO<sub>2</sub> capacity losses after 20 cycles are 52.5 % and 61.7 %, respectively. With an increase in the NaNO<sub>2</sub> doping amount, such as in Sorb-1.6 and Sorb-0.8, the CO<sub>2</sub> adsorption capacity decreases in the first few cycles but the decay slowed down, thereby achieving a stable CO2 adsorption capacity. Sorb-0.8 exhibits excellent performance, which starts to stabilize at approximately 9.5 mmol/g(CO<sub>2</sub>/sorbent), maintaining approximately 70 % of the initial adsorption capacity, at the sixth cycle. When the amount of NaNO<sub>2</sub> doping is excessively high (Sorb-0.4), the adsorption activity and stability decrease. Therefore, NaNO3 is conducive to improving the sorbent activity but its effect declines as the number of cycles increases. Although the addition of an appropriate amount of NaNO<sub>2</sub> reduces the adsorption capacity, it is conducive to slowing the decay of the adsorption capacity.

The thermal stabilities of the sorbents were analyzed to further illustrate their good stabilities. The weight loss of NaNO<sub>3</sub>/NaNO<sub>2</sub> single-

component and co-doped sorbents is shown in Fig. 5. At the regeneration temperature of 400 °C, the weight loss of approximately 7 % of the single-component NaNO<sub>3</sub>/NaNO<sub>2</sub> sorbents doped with MgO is more obvious, whereas the weight loss of Sorb-0.8 is only approximately 1 %, corresponding to water vapor impurities and other substances. Therefore, the NaNO<sub>3</sub>/NaNO<sub>2</sub> co-doped MgO sorbent is more stable during  $CO_2$  cycling.

The stability of the doped molten salt was confirmed by conducting a weight-loss analysis of the NaNO<sub>3</sub>/NaNO<sub>2</sub> mixture with a mass ratio of 1, as shown in Fig. 5b. The NaNO<sub>3</sub>/NaNO<sub>2</sub> mixture starts to decompose at ~ 600 °C and is completely decomposed when the temperature exceeds 800 °C. The residual mass of the substance is 32.5 % of the total mass, and the residual solid phase is mainly Na<sub>2</sub>O, as shown in the chemical formula (4) and (5). The decomposition temperature is higher than the regeneration temperature (400 °C). Thus, NaNO<sub>3</sub>/NaNO<sub>2</sub> is stable during the cyclic test without a weight loss of the molten salt mass owing to the temperature changes during the test. The absence of molten salt weight loss indicates the good stability of the sorbent.

$$2NaNO_3 = 2NaNO_2 + O_2\uparrow \tag{4}$$

$$2NaNO_2 = Na_2O + 2NO\uparrow + \frac{1}{2}O_2\uparrow$$
(5)

The NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio was controlled to improve the stability of the MgO-based sorbent. The  $CO_2$  adsorption capacity is a key index for evaluating sorbents. Compared with the  $CO_2$  sorption performance of MgO doped with molten salt reported in the literature (Table 2), the sorbent obtained in this work has certain advantages in terms of ease of preparation, use of raw materials, and sorbent stability.

Adjusting the NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio effectively enhanced the CO<sub>2</sub> adsorption capacity. Compared with NaNO<sub>3</sub>–Mg and NaNO<sub>2</sub>–Mg, the CO<sub>2</sub> adsorption capacity of Sorb-0.8 increases by 1120 % and 17.4 %, respectively, after 20 cycles. Although the activity and stability are improved, the CO<sub>2</sub> adsorption capacity still decreases in the first few



Fig. 5. Weight loss of (a) different sorbents and (b) NaNO<sub>3</sub>/NaNO<sub>2</sub> mixture.

# Table 2

Added component	Temperature (°C)/Time (min Adsorption	n)/atmosphere Desorption	Number of cycles	Adsorption capacity 1st/last/mmol/g	Ref
LiNO <sub>3</sub> NaNO <sub>3</sub> KNO <sub>3</sub> LiNO <sub>3</sub> NaNO <sub>3</sub> KNO <sub>3</sub> LiNO <sub>3</sub> NaNO <sub>3</sub> KNO <sub>3</sub> NaNO <sub>2</sub> LiNO <sub>3</sub> KNO <sub>3</sub>	350/30/80 % CO <sub>2</sub> 280/30/pure CO <sub>2</sub> 300/60/pure CO <sub>2</sub> 320/60/pure CO <sub>2</sub> 350/60/pure CO <sub>2</sub>	425/10/N <sub>2</sub> 400/15/N <sub>2</sub> 445/60/N <sub>2</sub> 400/10/N <sub>2</sub> 500/10/N <sub>2</sub>	10 10 5 10 20	3.64/1.36 2.91/0.44 11.36/6.82 12.50/6.59 10.40/7.20	(Gui et al., 2024) (Teixeira et al., 2024) (Correia et al., 2023) (Wang et al., 2019) (Lee et al., 2018) This rest:

cycles. Fig. 6a shows the XRD pattern of Sorb-0.8 before and after 10 cycles. The MgCO<sub>3</sub> phase (JCPDS 71–1534) remains in the sorbent after 10 cycles, suggesting that the sorbent is not completely regenerated, MgCO<sub>3</sub> remains to fill the pores, and the active surface area decreases with increasing cycle number (dal Pozzo et al., 2019). In addition, Table S1 shows the notable decrease in the specific surface area and pore volume of the sorbent after multiple cycles, indicating the aggregation of MgO particles and damaged sorbent structure during the cyclic test. A comparison of the surface morphologies of the sorbent before and after 10 cycles shows the segregation of the molten salt after the cycles and that some MgO particles are not covered by the molten salt (Fig. S3), thereby inhibiting the effective utilization of this part of MgO. Therefore, the segregation of the molten salt, aggregation of MgO particles, presence of MgCO<sub>3</sub>, and decrease in the specific surface area and pore size decreases the CO<sub>2</sub> adsorption capacity of the sorbent after cycling, which manifests as a reduction in the effective contact area between MgO and molten salt. In other words, the key to improving the cycle stability of the sorbent is to control the active surface areas of MgO and molten salt to ensure the stability of the molten salt and its even distribution on the MgO surface.

#### 3.3. Adsorption mechanism

The mechanism of NaNO<sub>3</sub> in promoting the MgO adsorption of CO<sub>2</sub> is still unclear in the literature. Gao et al. (Gao et al., 2022) recently explored the adsorption mechanism of molten salt-doped MgO by transient <sup>18</sup>O isotope exchange experiments to describe the promoted effect of NaNO<sub>3</sub> through the decomposition of NO<sub>3</sub><sup>-</sup> into NO<sub>2</sub><sup>+</sup> and O<sup>2-</sup>. The DFT calculation results noted that NO<sub>2</sub><sup>+</sup> promoted carbonation by adsorbing MgO, which reduced the energy barrier for the dissolution of the [Mg<sup>2+…O<sup>2-</sup></sup>] ion pair into NaNO<sub>3</sub>. However, Landuyt et al. (Landuyt et al., 2022) used <sup>18</sup>O labeling experiment to explore the adsorption mechanism, revealing that neither NaNO<sub>3</sub> nor its decomposition products participated in the adsorption reaction. Moreover, the formation of surface carbonate dissolved in the form of [Mg<sup>2+…CO<sup>3-</sup>] ion pairs in the nitrate melt. Meanwhile, DFT and ab-initio molecular dynamics calculations have verified the accuracy of the mechanism and excluded</sup>

the possibility of NaNO<sub>3</sub> in participating in the reaction. Based on the above mechanism, the influence of NaNO<sub>3</sub> on the  $CO_2$  adsorption and electronic properties was further revealed through DFT calculations.

Different models of CO<sub>2</sub> stable adsorption on MgO and NaNO<sub>3</sub> promoted the MgO surface, as shown in Fig. S4. The structural parameters and  $\Delta E_{ads}$  of the models are listed in Table S2 and shown in Fig. 7a. Based on the  $\Delta E_{ads}$  results, more negative  $\Delta E_{ads}$  values of CO<sub>2</sub> on the surface model of NaNO3-doped MgO suggest the easier adsorption of  $CO_2$ . The  $\Delta E_{ads}$  of model (V) is higher than that of the other models, which is mainly attributed to the weaker interaction owing to the  $C_{CO2}$ - $O_{MgO}$  distance of 4.91 Å, as shown Table S2. From the perspective of the adsorption configuration, when CO2 directly interacts with MgO (model (II) and (III)), the structure is more stable and the  $\Delta E_{ads}$  value is more negative. Different trends are observed for CO2 directly adsorbed on the MgO surface (models (II) and (III)) and CO<sub>2</sub> adsorbed on the surface of NaNO3-doped MgO (models (IV) and (V)). Moreover, slight changes in the CO<sub>2</sub> adsorption and inactivation are noted for models (IV) and (V) with the d(C<sub>CO2</sub>–O<sub>CO2</sub>) of 1.17/1.17 and 1.17/1.18 Å, respectively, and  $\angle CO_2(O-C-O)$  of 177.1° and 178.2°, respectively. This indirectly confirms the reaction mechanism, in which NaNO3 does not participate in the reaction but promotes CO<sub>2</sub> adsorption.

The charge transfer and distribution after the adsorption of MgO and NaNO<sub>3</sub>-doped MgO are shown in Fig. 7a. The charge transfer values of models (II) and (III) (0.417 and 0.459e, respectively) are higher than that of model (I) (0.400e), indicating that NaNO<sub>3</sub> doping promotes the charge transfer to CO<sub>2</sub>. Moreover, an extremely weak charge transfer of 0.046e-0.083e is noted between MgO and NaNO3. When CO2 is adsorbed on the MgO surface through its interaction with NaNO<sub>3</sub> (model (IV) and (V)), the charge transfer between MgO and NaNO3 increases to approximately 0.08e, whereas the charge transferred to CO<sub>2</sub> is lower. As shown in Fig. 7b,  $\Delta E_{ads}$  should follow the same trend as the chargetransfer number. However, charge transfer can only confirm the adsorption (Zhao et al., 2024). In particular, more reliable calculations can be obtained by combining the electron density changes with the orbital interactions (Gameel et al., 2018). Fig. 7c and 7d present the PDOS of O in MgO and C in CO<sub>2</sub> before and after the adsorption of CO<sub>2</sub> in models (I)-(V). Fig. 7c shows that MgO near the Fermi level is mainly occupied by P-state O atoms, indicating that MgO acts as an electron



Fig. 6. (a) XRD patterns and (b) pore-size distribution of Sorb-0.8 before and after 10 cycles.



**Fig. 7.** (a) Adsorption energy, electron density distributions and Bader charge transfers of different models. (b) Adsorption energy and charge transfer of different models. PDOS of model (I) and (III), namely after adsorption and after adsorption-NaNO<sub>3</sub>, of the (c) O atom in MgO and (d) C atom in CO<sub>2</sub> before and after CO<sub>2</sub> adsorption (pink areas: charge accumulation, blue area: charge depletion). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. (continued).

donor in the carbonation process, which is consistent with the law of electron-density distributions (Pang et al., 2021). The p-orbital of OMgO splits into several segments with reduced peaks and broadened energy levels after the interaction, and moves towards lower energies. This phenomenon is consistent with the results obtained by Pang (Pang et al., 2021). The peak of the p-state O atom in the NaNO<sub>3</sub>-doped MgO after adsorption shifts towards a lower-energy region, indicating the easier adsorption of CO<sub>2</sub> than that of pure MgO. This result is consistent with that obtained by Zhao et al. (Zhao et al., 2024) on the CO<sub>2</sub> adsorption on CaO. A similar phenomenon was observed before and after the adsorption of CO<sub>2</sub> by the p- and s-states of C, as shown in Fig. 7d. Interestingly, the presence of several formants between  $O_{\mbox{MgO}}$  and  $C_{\mbox{CO2}}$  suggests that the interaction between the two atoms is a mixture of C<sub>CO2</sub>-sp and O<sub>MgO</sub>sp states at approximately - 20 and - 9-0 eV, respectively. In particular, prominent overlapping regions are noted at -7.98, -6.09, and -5.45 eV for pure MgO and - 8.69, -6.85, and - 6.41 eV in NaNO3doped MgO after adsorption. These overlapping regions indicate the formation of stable bonds, confirming the occurrence of chemisorption in the optimized structure. The downward movement of the O electronic states also demonstrates the adsorption process, which is consistent with the results of Zhao (Zhao et al., 2024). In other words, NaNO<sub>3</sub> promotes the adsorption of CO<sub>2</sub> by MgO and converts it into carbonate or bicarbonate substances.

The process of promoting MgO adsorption by the molten salt can be simplified, as shown in Fig. 8. MgO is partially dissolved in molten salt to produce  $[Mg^{2+}..O^{2-}]$  ionic pairs, which reacts with dissolved CO<sub>2</sub> to form  $[Mg^{2+}..CO_3^2-]$  ionic pairs, and then saturates and precipitates into crystalline MgCO<sub>3</sub> phase. CO<sub>2</sub> has high fluidity in molten salts with a low melting point, thereby improving the ion mobility and promoting the rapid production of MgCO<sub>3</sub>. During the reaction, molten salt does not decompose because of the high operating temperature, thereby improving the stability of the sorbent. However, as the cycles progress, the fluidity of the molten salt, aggregation of MgO particles, and presence of MgCO<sub>3</sub> all reduce the active surface area (i.e., the phase interface between MgO and molten salt). As a result, the MgO particles that are not covered by molten salt cannot be effectively utilized, and the cycle stability decreases.

## 4. Conclusions

MgO sorbents with different NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratios were successfully prepared by ball-milling technique. NaNO<sub>3</sub> and NaNO<sub>2</sub> played different roles during the adsorption cycles. NaNO<sub>3</sub> contributed to the initial activity of the sorbent, whereas NaNO<sub>2</sub> mitigated the decline in the sorbent activity during cycling. Therefore, adjusting the NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio can effectively improve the adsorption performance.



Fig. 8. Schematic of the MgO adsorption mechanism.

With the NaNO<sub>3</sub>/NaNO<sub>2</sub> molar ratio of 0.8, superior stability was obtained. In particular, the weight of the molten salt was maintained during cycling, which contributed in improving the stability of the sorbent performance. After 20 cycles, the CO<sub>2</sub> adsorption capacity decreased by only 4.2 mmol/g(CO<sub>2</sub>/sorbent) owing to the decrease in the phase interface between MgO and the molten salt, which was manifested by the aggregation of MgO particles, presence of MgCO<sub>3</sub>, and reduction in the specific surface area and pore size. In addition, the influence of NaNO<sub>3</sub> on the CO<sub>2</sub> adsorption and electronic properties was further revealed through DFT calculations. NaNO<sub>3</sub> was determined to promote the adsorption of CO<sub>2</sub> by MgO and further converted it into carbonate or bicarbonate substances.

#### CRediT authorship contribution statement

**Ting Qu:** Writing – original draft, Methodology, Investigation, Data curation. **Jinpeng Zhang:** Software, Investigation. **Jinbo Song:** Investigation, Data curation. **Jieying Jing:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Wen-Ying Li:** Writing – review & editing, Funding acquisition.

#### Declaration of competing 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.

#### Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

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