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Effect of pre-calcination for modified CaO-based sorbents on multiple carbonation/calcination cycles☆

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ABSTRACT

In the present work, the effect of pre-calcination on carbonation conversion and cyclic stability of modified CaO-based sorbent was investigated by thermogravimetric analyzer (TGA). The modified CaO-based sorbents with CaAc₂ as precursor were respectively doped with different elements (Mg, Al, Ce, Zr and La). The specific surface area, pore volume and pore size distribution were tested by N₂ isothermal adsorption measurements. The phase compositions of sorbents were characterized by X-ray diffraction (XRD). The results showed that the cyclic stabilities of the sorbents were improved by pre-calcination. The pre-calcination was conducted at 900 °C for 5 h in air by the muffle furnace. With pre-calcination, the cyclic stabilities of sorbents could be as high as 96% after 22 cycles, such as CaO-Al, CaO-Ce and CaO-La. After contact with air, the carbonation conversions of spent sorbents with pre-calcination suddenly increased by about one-sixth due to the change of channel structure by hydration. Both the cyclic stability of sorbent and the durability of reactivation were related to the structural stability of sample, especially the stability of mesopores between 2 nm and 5.5 nm. The present work also provided an easy and low-cost method for reactivating the spent CaO-based sorbents.

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1. Introduction

It is widely believed that CO₂ with increased concentration in atmosphere is the main contributor to global warming [1]. Carbon capture and storage (CCS) provides a viable approach to capture CO₂ discharged from fossil fuel power plants which contributes one-third of the anthropogenic CO₂ emissions [2,3]. CaO-based materials become the promising candidate sorbents due to the high adsorption capacity, wide sources, low cost and easy regeneration [4,5]. Calcium Looping is composed of the carbonation of CaO with CO₂ and calcination of CaCO₃ [6] as the reversible reaction (Eq. (1)), which has been from basic research toward successful process demonstration at pilot scale. Heiko and colleagues [7–9] reported that the pilot scales have been erected at IFK in Germany (200 kW_{th}), Technische University Darmstadt in Germany (1 MW_{th}), la Pereda in Asturias-Spain (1.7 MW_t) and so on. In the carbonator of dual fluidized bed system (DFB) (carbonator, 650 °C; regenerator, 900 °C), the CO₂ adsorption efficiency of limestone

could be kept above 85% for long periods, such as 22 h. The simulation results of 505 MW_e coal fired power plant showed that the efficiency penalty was between 4% and 7% points [10] which consumed lower energy than other commercial post-combustion CO₂ capture technologies such as MEA (around 8% to 12.5%).



In spite of low cost, the adsorption capacity of limestone decreased rapidly with the increase of cycle number due to the sintering of CaCO₃ at high temperature [11,12], which is the general weakness of CaO-based sorbents.

There are a lot of methods used to improve the cyclic stability of CaO-based sorbents. The first kind of methods are aimed at seeking the appropriate precursors such as limestone [11], dolomite [13], rice husk ash [14], CaCO₃ [15], and Ca(OH)₂ [16]. However, the natural CaO-based sorbents quickly lost most of the CO₂ capture ability through multiple cycles. The second method is finding the appropriate synthetic methods, such as precipitation method [17,18], sol-gel method [19,20] and flame spray pyrolysis (FSP) [21]. For example, the carbonation conversion of sorbents prepared by sol-gel process increased from 32% to 65% after 20 cycles [19]. The third method is the modification of the natural or synthetic CaO-based sorbents, such as thermal pre-treatment [22], hydration treatment [1,23–25] and incorporation of an

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inert phase [18]. Ozcan *et al.* [22] reported that the adsorption capacity for plaster of Paris sorbent could be kept increasing after more than 200 cycles through the cyclic process of reduction and oxidation at 1070 °C. Wang *et al.* [1] considered the hydration treatment could restore the high adsorption capacity by generating a new oxide structure to decrease crystalline size and increase porosity and specific surface area. Radfarnia *et al.* [26] found that the carbonation conversion of CaO prepared with $\text{Ca}_9\text{Al}_6\text{O}_{18}$ increased from 48% to 78% after 31 cycles. Other metallic oxide were also doped with the CaO-based sorbents, such as Al_2O_3 [11], SiO_2 [2,12,27], MgO [28], CuO [29], TiO_2 [30] and MnCO_3 [31]. The doped metallic oxides helped to improve the cyclic stabilities of CaO-based sorbents in different degrees by increasing the surface area and pore volume.

Since doping is an effective modification method to improve the cyclic stability, the effect of different doping elements on cyclic stability was investigated in previous work [32–36]. With the dopant of Mg, Al, Ce, Zr and La, respectively, the cyclic stability of CaO doped with Al, Ce or La was greatly improved. Furthermore, the adsorption capacity of CaO derived from CaAc_2 was larger than CaO derived from CaCO_3 , CaC_2O_4 and $\text{Ca}(\text{OH})_2$, respectively. However, the effect of improvement was various with different pretreatments for fresh sorbents. The cyclic stabilities of doped sorbents without pretreatment after 20 cycles were unsatisfied [32], while the cyclic stabilities of sorbents with the pretreatment were greatly improved [33–36].

The objective of the present work was to study the effect of pre-calcination on cyclic stabilities of modified CaO-based sorbents, exploring more stable sorbents for the possibility of industrial application. The pre-calcination could help to strengthen the channel structure of CaO and restrain the further sintering. The effect of specific surface area and channel structure on carbonation conversion and cyclic stability of sorbents was investigated in different experimental conditions. In addition, the reactivation mechanism of sorbents after contact with air was studied. It also provided an easy and low-cost method to reactivate the spent sorbents.

2. Experimental

2.1. Sorbent preparation

All the reagents used in present work were analytically pure. CaO was derived from $\text{CaAc}_2 \cdot \text{H}_2\text{O}$ (Chengdu Fuchen, 250 g, >98.0%). The doped element was respectively derived from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Chengdu Kelong, 500 g, 99.0%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Tianjin Fuchen, 500 g, 99.0%), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Tianjin Fuchen, 25 g, 99.0%), $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (Chengdu Kelong, 25 g, 99.0%) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Shanghai Diyang, 500 g, 99.95%). The target mole ratio of Ca and the doping element was 8:2, which was verified as an appropriate doping ratio in our previous work [32–36]. Taking Mg as an example, the preparation of the modified sorbent was shown as follows. The quantitative $\text{CaAc}_2 \cdot \text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in the distilled water at 80 °C. The excess ammonia water (Tianjin Tianli, 500 ml, 25%–28%) was added as precipitant to generate magnesium hydroxide. After the distilled water was evaporated, the absolute ethyl alcohol (Tianjin Fuyu, 500 ml, >99.7%) was added as the solvent. The slurry was stirred overnight and dried at 120 °C to obtain calcium acetate and magnesium hydroxide, marked as CaO-Mg(wd). In our previous work, the sorbent with pre-calcination (900 °C, 5 h) showed the better cyclic performance through pre-calcination with different temperature and time. Therefore, a part of CaO-Mg(wd) was calcinated in the muffle furnace at 900 °C for 5 h to obtain calcium oxide and magnesium oxide, marked as CaO-Mg. This calcination in muffle furnace was called pre-calcination in this paper.

2.2. TGA experiments

The carbonation/calcination cycle experiments were conducted by a STA449F3 thermogravimetric analyzer (TGA). About 10 mg of the

sample was calcinated in nitrogen ($70 \text{ ml} \cdot \text{min}^{-1}$, 99.99%) at 700 °C for 30 min with a heating rate of $20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Then, the carbonation was conducted at 700 °C for 9 min before CO_2 ($30 \text{ ml} \cdot \text{min}^{-1}$, 99.99%) was introduced into the system. The calcination was followed at 700 °C for 20 min without CO_2 . As the slight quantities of samples with slight exothermic reaction in TGA, the higher carbonation temperature compared with DFB in practical pilot scale was beneficial to the greater carbonation conversion. With the short carbonation time, the samples could be almost totally carbonated. The lower calcination temperature helped to retard the sintering of sorbents and achieve energy conservation, which still ensured the complete regeneration of samples.

In the experimental conditions of present work, the oxides of doping elements were regarded as inert support. The carbonation conversion (X) of sorbent was defined as the mole ratio of the actually adsorbed CO_2 and the theoretically adsorbed CO_2 by the effective CaO of sorbent. Taking an example of doping Mg in the following, Eq. (2) shows the definition of carbonation conversion of CaO-Mg (X_{Mg}).

$$X_{\text{Mg}} = \frac{m_t - m_0}{m_0 \times a_{\text{Mg}}} \times \frac{M_{\text{CaO}}}{M_{\text{CO}_2}} \quad (2)$$

m_0 is the mass of totally calcined sorbent before carbonation. m_t is the mass of sorbent when the carbonation carries on the t minute. $m_t - m_0$ means the mass gained by adsorbing CO_2 . a_{Mg} is used to calculate the effective mass of CaO in CaO-Mg as Eq. (3).

$$a_{\text{Mg}} = \frac{n_{\text{Ca}} \times M_{\text{CaO}}}{n_{\text{Ca}} \times M_{\text{CaO}} + n_{\text{Mg}} \times M_{\text{MgO}}} \quad (3)$$

n is the mole number. M is the molar mass. $n_{\text{Ca}}/n_{\text{Mg}}$ is 8:2.

The cyclic stability of sorbent is marked as S_N , shown in Eq. (4). S_N is the ratio of the carbonation conversion in the N th cycle and the carbonation conversion in the 1st cycle. N is the cycle number. Through 22 cycles, the cyclic stability of CaO-Mg is marked as $S_{22}(\text{CaO-Mg})$.

$$S_N = (X_N/X_1) \times 100\% \quad (4)$$

2.3. Sorbent characterization

The pore structure parameters of the sorbents were obtained by N_2 adsorption and desorption isotherms, measured at the temperature of liquid N_2 by QUANTACHROME AUTOSORB-1. Brunauer–Emmett–Teller (BET) equations and Barrett–Joyner–Halenda (BJH) method were respectively used to calculate the specific surface area and the pore volume. The phase compositions of sorbents were determined by X-ray diffraction (XRD; Smartlab) with Cu K α radiation, $\lambda = 0.1542 \text{ nm}$ in the 2θ range of 10° – 80° with a scanning speed of 0.01° .

3. Results and Discussion

3.1. Effect of pre-calcination on cyclic CO_2

Five types of modified CaO-based sorbents were used to study the effect of pre-calcination on the cyclic performance through multiple carbonation/calcinations. In Fig. 1, the 22-cycle performance results of the modified sorbents were presented.

In the 1st cycle, the carbonation conversions of all modified sorbents without pre-calcination were always larger than those with pre-calcination. As CaO was generated by the multi-step decomposition of CaAc_2 (Eqs. (5)–(7)), the generation and escape of a variety of gas was benefit to the formation of porous structure in the process of calcination. The pore size of modified sorbents without pre-calcination was mainly distributed from 3 nm to 5 nm (Fig. 2). The porous structure could decrease the diffusion resistance of CO_2 and increase the chance for

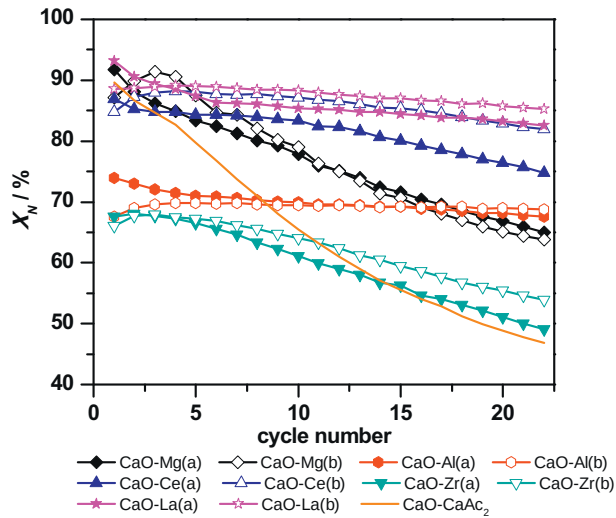
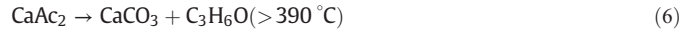


Fig. 1. Carbonation conversions of sorbents through 22 carbonation/calcination cycles: (a) without pre-calcination, (b) with pre-calcination.

CO_2 reacting with CaO inside particles, as Eq. (8), which helped to get the larger carbonation conversion.



After pre-calcination, the carbonation conversions of modified sorbents decreased due to the sintering in the pre-calcination period [33]. As the Tammann temperature of CaCO_3 is 533°C [21], CaCO_3 generated by the decomposition of CaAc_2 might begin to melt in the process of pre-calcination. All the atoms in the lattice began to loosen at 900°C in the muffle furnace. The fusion occurred by adjacent melt CaCO_3 , which resulted in the disappearance of some micropores and mesopores. At the same time, some mesopores with large pores were formed due to the combination of small pores. It was consistent with the change of pore size distribution before and after pre-calcination

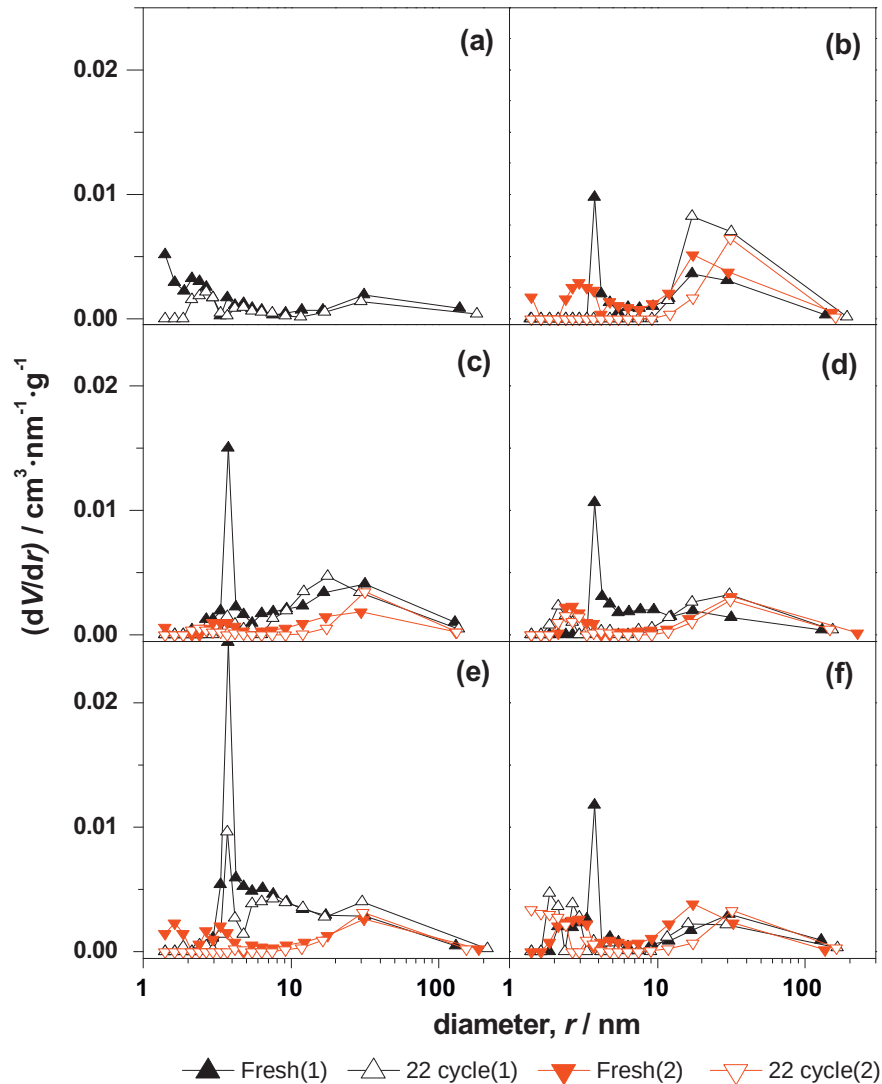


Fig. 2. Pore size distribution of modified sorbents before and after 22 cycles: (a) CaO-CaAc_2 , (b) CaO-Mg , (c) CaO-Al , (d) CaO-Ce , (e) CaO-Zr , (f) CaO-La ; (1) without pre-calcination, (2) with pre-calcination.

shown in Fig. 2. Therefore, either the specific surface area or pore volume of modified sorbents decreased after pre-calcination (Table 1). The increase of diffusion resistance for CO₂ resulted in the reduction of carbonation conversion of sorbents after pre-calcination.

After 22 carbonation/calcination cycles, the carbonation conversions of all modified sorbents decreased in various degrees. However, the decay trend of carbonation conversion for the modified sorbents became slow after pre-calcination.

Before and after pre-calcination, the carbonation and calcination curves of modified sorbents in the 1st, 5th, 10th, 15th and 22nd cycle were shown in Fig. 3. The carbonation consisted of chemical reaction control stage and diffusion control stage, which were also called rapid reaction stage and slow reaction stage. The rapid reaction stage only lasted for about 1 min. Then, the conversion rates of all the five modified sorbents dropped rapidly, which made the carbonation reaction into a slow reaction stage. In the chemical reaction control stage, the carbonation conversions of sorbents without pre-calcination were much greater than those with pre-calcination. After 22 cycles, the decay of carbonation conversions of sorbents without pre-calcination was much sharper than those with pre-calcination. Furthermore, the decomposition rates of all sorbents in the calcination stage became slow after pre-calcination.

La-doped sorbent showed the remarkable performance. Both in the 1st cycle and after 22 cycles, the carbonation conversions were always the largest in the five kinds of modified sorbents. For CaO-La(wd), the carbonation conversion in the 1st cycle was close to the theoretical maximum. Among them, the carbonation conversion in the rapid reaction stage was more than 85%. However, more than one-fourth of the initial carbonation conversion in rapid reaction stage was lost after 22 cycles. Through 22 cycles, the carbonation conversion of CaO-La(wd) dropped from 93.2% to 82.6%. With pre-calcination, the cyclic stability of CaO-La was greatly improved. The carbonation conversion of CaO-La in the 22nd cycle was 85.2%, which was equal to 96.2% of the carbonation conversion in the 1st cycle. The carbonation conversions of CaO-La(wd) in chemical reaction control stage through 22 cycles decreased more obviously than that of CaO-La. The decrease of carbonation conversion in chemical reaction control stage for CaO-La(wd) was particularly sharp in the initial 5 cycles.

For the fresh CaO-La(wd), there was hardly any sintering layer on the surface of particles. Therefore, the carbonation conversion became larger in the rapid reaction stage. With the increase of carbonation number, the sinter gradually occurred. Therefore, the fluffy structure of sorbents without pre-calcination melted and collapsed through a long time at high temperature. Most 4-nm channels were replaced by the channels with smaller size after 22 cycles (Fig. 2(f)). The specific surface area after 22 cycles was only left a half of the original one (Table 1). Vasilije *et al.* [37] found that the sintered area focused on the surface of particles and the thickness of sintered area was an order of magnitude of micrometers. The carbonation conversion in rapid

reaction stage decreased due to the less contact between CO₂ and active CaO. The carbonation conversion rate slowed down when it was difficult for CO₂ to diffuse into the core of particles through the sintered layer. The carbonation conversion decreased obviously. On the other hand, the structure of sorbent with pre-calcination was more stable through multiple carbonations. Although the carbonation conversion in rapid reaction stage decreased after pre-calcination, it was almost kept unchanged from the 1st cycle to the 22nd cycle in Fig. 3(e-2). Before and after 22 cycles, there was much less change of the pore size distribution for CaO-La with pre-calcination than that without pre-calcination shown in Fig. 2(f). Due to the slight sinter in pre-calcination, the sintered layer became a stable framework support to fix other CaCO₃ in a certain area and isolate the contact of more CaCO₃ from each other. Therefore, the further sintering was delayed.

Fig. 4(a) shows that La₂O₃ existed in the fresh La-doped sorbents examined by XRD, which was accorded with the expectation. However, it was an active material rather than inert material for CO₂ uptake as Eq. (9), which was verified by XRD that La₂O₂CO₃ existed in La-doped sorbents after carbonation. In the cycles, La₂O₂CO₃ could be decomposed to La₂O₃ after calcination (Fig. 4(c)) and keep on reacting with CO₂ in the subsequent carbonation stage. Therefore, the calculated α_{La} was smaller than the practical coefficient. The calculated X_{La} was larger than the practical carbonation conversion of pure CaO in La-doped sorbent. Due to the dual effects of CaO and La₂O₃, the calculative X_{La} was much higher than those of other sorbents.



CaO-Mg(wd) presented the largest carbonation conversion in the initial cycle, without regard to CaO-La(wd). Fig. 5 showed that the Mg-doped sorbents were composed of CaO and MgO. In the experimental conditions, MgO were inert for CO₂. There was no extra adsorption ability of CaO-Mg(wd) provided by MgO. However, the pore volume of MgO-doped sorbent was as high as 0.3322 cm³·g⁻¹. The porous structure helped CO₂ to contact and react with CaO more easily before the diffusion control stage. Therefore, the carbonation conversion of CaO-Mg(wd) in rapid reaction stage was great in the 1st cycle (Fig. 3(a-1)), while, X_{Mg} was much smaller than $X_{Mg(wd)}$ due to the sinter of CaCO₃ in pre-calcination stage. Like the other four kinds of modified sorbents, the decomposition rate of CaO-Mg in calcinations became slow after pre-calcination (Fig. 3). Without pre-calcination, the carbonations of CaO-Mg(wd) with porous structure mainly occurred on the surface of particles and channels where CO₂ was easy to arrive. In the process of calcinations, the main decomposition also first occurred in these areas where CO₂ was more likely to escape. The decomposition rate of the surfaces of particles was greater than that deeper inside of particles. After pre-calcination, the slight sintered CaCO₃ on the surface of particles reduced the reaction chance between CaO and CO₂ in the

Table 1

S_{BET} and pore volume of sorbents before and after 22 cycles

Sample	Fresh			After 22 cycles		
	Specific surface area/m ² ·g ⁻¹	Pore volume/cm ³ ·g ⁻¹	Average pore size/nm	Specific surface area/m ² ·g ⁻¹	Pore volume/cm ³ ·g ⁻¹	Average pore size/nm
CaO-Mg(wd)	31.29	0.3322	42.46	26.94	0.2344	34.81
CaO-Mg	30.07	0.2341	31.14	14.56	0.1732	47.56
CaO-Al(wd)	36.28	0.3165	34.89	22.78	0.2109	37.04
CaO-Al	12.98	0.1031	31.77	13.01	0.1348	41.44
CaO-Ce(wd)	19.45	0.1453	29.87	16.41	0.1809	44.10
CaO-Ce	16.20	0.1477	36.45	14.09	0.1802	51.13
CaO-Zr(wd)	39.77	0.2261	22.74	28.42	0.2173	30.59
CaO-Zr	16.68	0.1421	34.06	11.55	0.1365	47.25
CaO-La(wd)	25.49	0.2582	40.52	13.81	0.1412	40.90
CaO-La	21.98	0.1386	25.22	13.33	0.1653	49.59
CaO-CaAc ₂	22.70	0.2204	38.83	9.09	0.1042	45.86

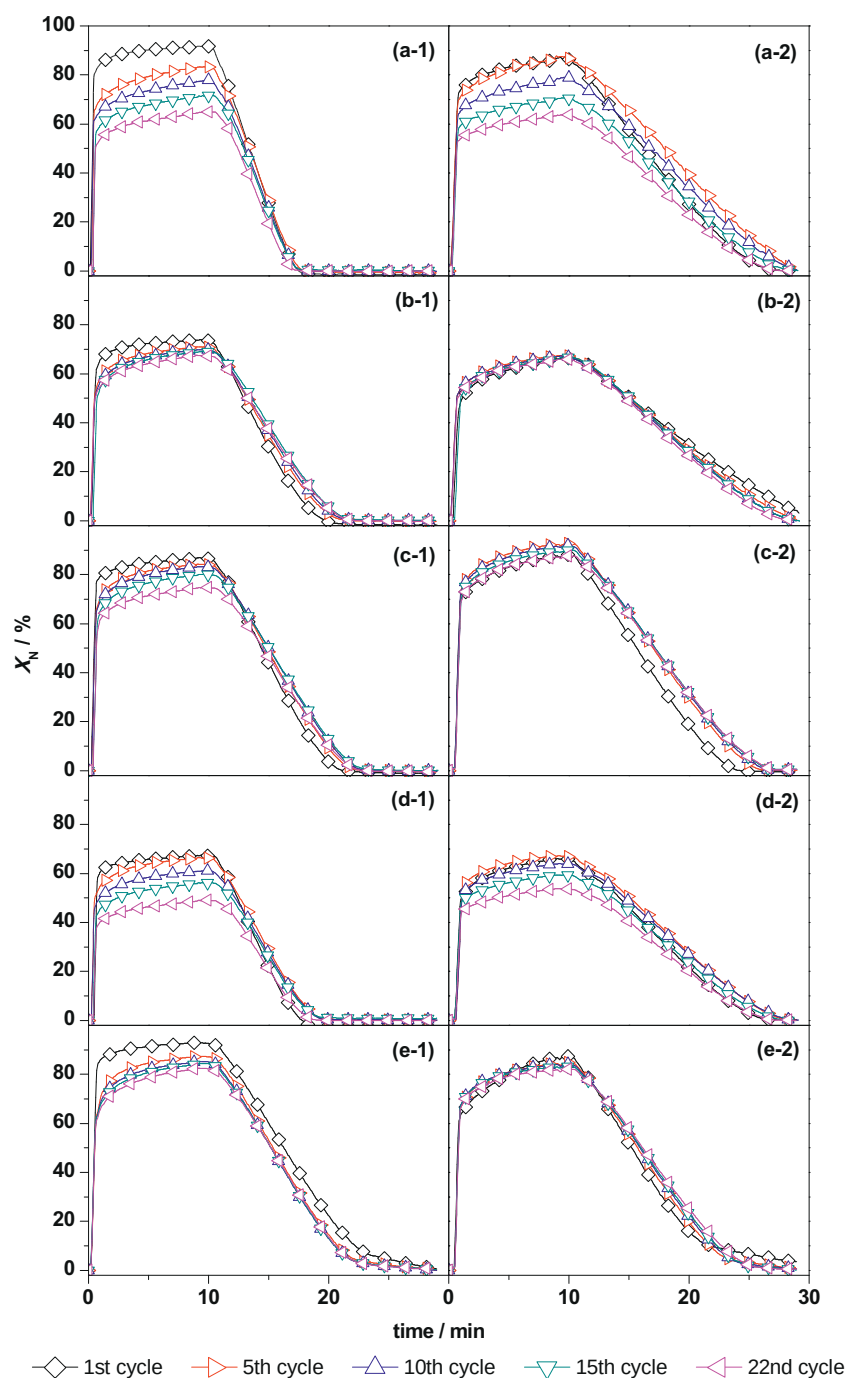


Fig. 3. Carbonation conversions of modified sorbents through different carbonation/calcination cycles: (a) CaO-Mg, (b) CaO-Al, (c) CaO-Ce, (d) CaO-Zr, (e) CaO-La; (1) without pre-calcination, (2) with pre-calcination.

process of carbonation. A part of carbonation could not occur until CO_2 diffused through the channels of CaO-Mg. Therefore, CO_2 decomposed from the inside of CaCO_3 needed more time to diffuse through channels to get outside and to be released. The decomposition rate of CaO-Mg slowed down.

However, the effect of pre-calcination for the cyclic stability was slight for CaO-Mg. Fig. 2(b) shows that there were a lot of mesopores between 3 nm and 5 nm for fresh Mg-doped sorbent. However, they disappeared after 22 cycles due to the sintering of CaCO_3 . There was only a number of mesopores with larger size left. With the smaller molar volume of MgO, the effect of isolating CaCO_3 from each other

was not obvious. The function of the skeleton structure made by MgO was slighter than others.

Different from the Mg-doped sorbent, the decay of carbonation conversion for Ce-doped CaO was much gentler with the increase of cycle number. However, without pre-calcination, the loose porous structure due to the decomposition of CaAc_2 was still much more difficult to be kept through multiple cycles. With the increase of cycle number, the melt CaCO_3 would be much easier to flow down due to the gravity. The vacancy formed by the lost melt CaCO_3 increased the pore size. The pore size of CaO-Ce(wd) after 22 cycles mainly focused on 20 nm to 30 nm shown in Fig. 2(d) while the pore size of the fresh

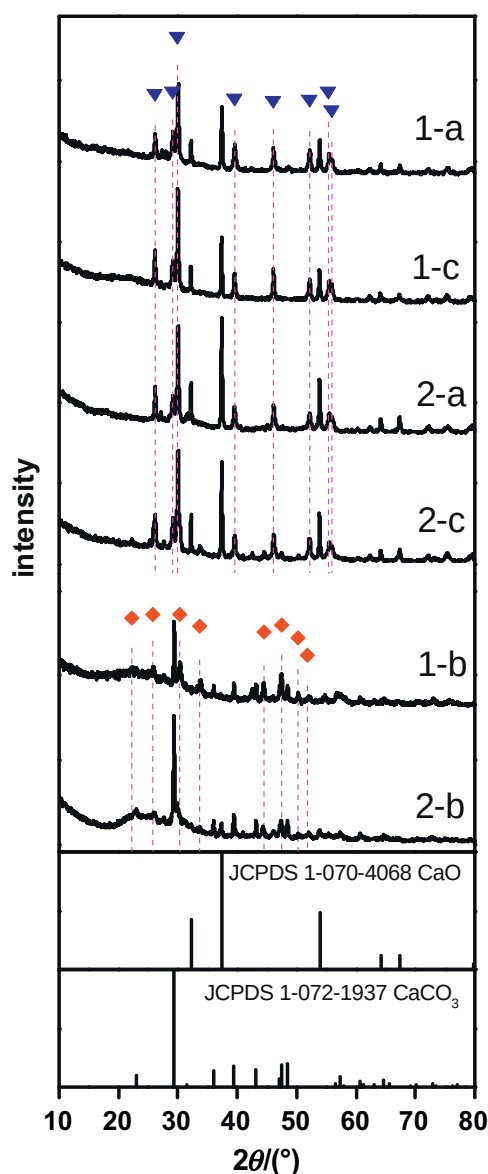


Fig. 4. XRD of CaO-La(wd) (1) and CaO-La (2): (a) fresh sorbents, (b) sorbents after carbonation, (c) calcinated sorbents after 22 cycles.(▼ La_2O_3 , ◆ $\text{La}_2\text{O}_2\text{CO}_3$).

one focused on about 4 nm. On the other hand, some channels became narrow when the original channels were filled with the melted CaCO_3 in part or in whole. It was confirmed that the other most probable pore size of mesopores decreased to 2 nm. Therefore, the CO_2 diffusion resistance increased. After pre-calcination, the cyclic stability of CaO-Ce after 22 cycles increased from 86.0% to 96.7% due to the slight sintering of CaCO_3 in pre-calcination stage. The difference of carbonation conversion rate of CaO-Ce through different cycles was slight as shown in Fig. 3(c-2). As the Tammann temperature was as high as 1064 °C [21], CeO_2 always existed in a stable form through multiple carbonation/calcinations (Fig. 5). The skeleton built by CeO_2 could maintain the stable channel structure. Fig. 2(d) shows that the pore size distribution of CaO-Ce after 22 cycles was in accordance with the fresh one. There was hardly any reduction of the specific surface area and pore volume for CaO-Ce. The cyclic stability after 22 cycles was greatly improved by doping Ce.

There were polarized carbonation conversions of the five kinds of modified sorbents in the initial cycle. The carbonation conversion with smaller numeric value was contributed by sorbents doped with Al and

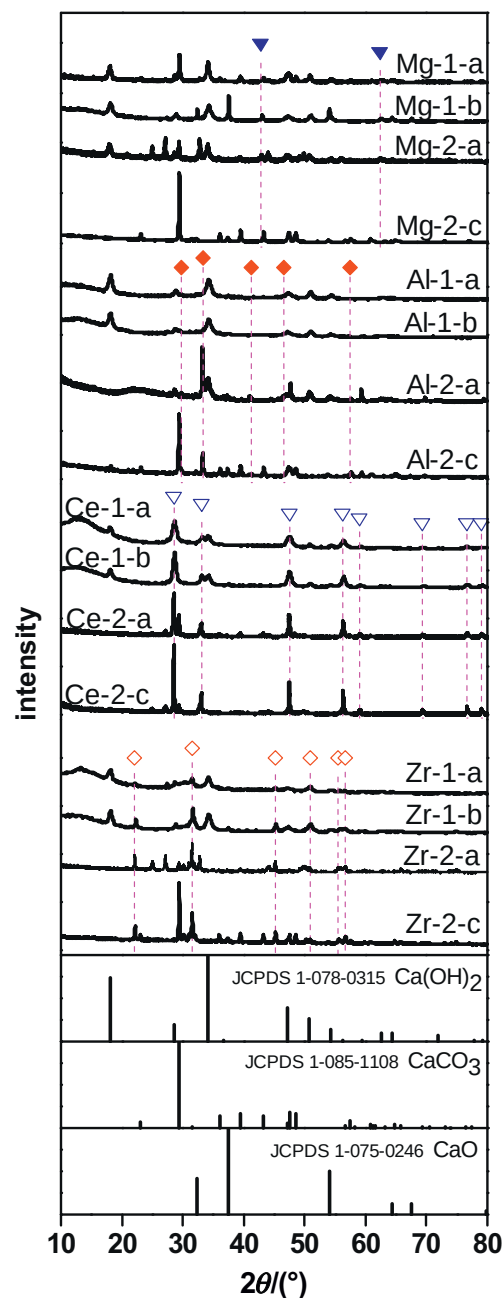


Fig. 5. XRD of modified sorbents with different dopants: (1) without pre-calcination, (2) with pre-calcination; (a) fresh sorbents, (b) calcinated sorbents after 22 cycles, (c) sorbents after carbonation. (▼ MgO , ◆ $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, ▼ CeO_2 , ◆ CaZrO_3).

Zr, respectively. Even the carbonation conversions of sorbents without pre-calcination were much bigger; the CO_2 uptake of fresh CaO-Al(wd) was only about four-fifths of that of fresh CaO- CaAc_2 . As Fig. 5 shows, some effective CaO of Al-doped sorbents could be consumed by reacting with Al_2O_3 as Eq. (10) [38,39]. Even with great specific surface area and pore volume, the decay of $X_{\text{Al(wd)}}$ was due to the gradually consumed CaO with the increase of time at high temperature. After pre-calcination, the poor carbonation conversion of CaO-Al in the initial cycle was resulted from the generation of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ in muffle furnace, which consumed a part of the effective CaO. The $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ could help to build a stable skeleton, which made CaCO_3 evenly dispersed in the certain areas. CaCO_3 was effectively isolated from each other, which could weaken the further sintering of CaCO_3 . The specific surface area and pore volume of CaO-Al were kept stable from

the 1st cycle to the 22nd cycle. There was hardly any decrease of carbonation conversion in either the rapid reaction stage or the slow reaction stage for CaO–Al (Fig. 3(b-2)) with the increase of cycle number. Therefore, the ability of CaO–Al to capture CO_2 completely survived through 22 cycles.



The doping element, Zr, could also react with CaO, similar with Al as the dopant. Fig. 5 showed that CaZrO_3 existed in XRD of Zr-doped sorbents as Eq. (11) [21]. It was much easier to find CaZrO_3 in CaO–Zr(wd) after 22 cycles, which was the result of the gradual sacrifice of some effective CaO by reacting with ZrO_2 with the increase of cycle number. Fig. 2(e) showed that the appropriate mesopores, distributed from 3 nm to 5 nm, played an important role for the carbonation conversion of CaO–Zr(wd). Without pre-calcination, the appropriate mesopores of fresh sorbents were abundant. However, they were reduced sharply through pre-calcination. After pre-calcination, the pore size trended toward either much larger or much smaller due to the melting of CaCO_3 . Since nearly all of ZrO_2 participated in the formation of CaZrO_3 in the muffle furnace, the decay of X_{Zr} due to the CaO consumption by ZrO_2 was much smaller through multiple cycles. With the skeleton structure made by CaZrO_3 and partial sintered CaCO_3 , the decay of carbonation conversion rates for CaO–Zr through 22 cycles in Fig. 3(d-2) was much slighter than that without pre-calcination. S_{22} of CaO–Zr increased from 72.7% to 81.6% after pre-calcination.



3.2. Effect of reactivation in air on cyclic CO_2

The modified sorbents with pre-calcination showed better cyclic stabilities after 22 cycles. The modified sorbents after pre-calcination were used to test the cyclic stability when the cycle number extended to 110. In order to avoid damaging TGA instrument during a continuous long time at high temperature, the 110 carbonation/calcination cycles were conducted by repeating 5 groups of the 22-cycle experiments.

Before the experiments, it was uncertain which dopant could greatly improve the cyclic stability of CaO. Only 1 or 2 groups of 22 cycles were conducted. When all the samples finished the tests and analysis, the sorbents with greater cyclic stabilities would experience the rest of groups, such as CaO–Al, CaO–Ce and CaO–La. CaO–CaAc₂ was used as comparison. Before the rest of groups, the samples could contact and react with the air in the process of placing, which might change the adsorption abilities of sorbents.

Fig. 6 shows the cycle performance of sorbents through 110 cycles. The carbonation conversions of the sorbents in the initial 22 cycles or 44 cycles decreased with the increase of cycle number in different degrees. After the process of placing the spent sorbents in air, there was a sudden increase of carbonation conversion in the subsequent cycle, especially for CaO–CaAc₂, CaO–La and CaO–Ce.

The carbonation conversion of CaO–CaAc₂ after 43 cycles was dropped from 89.6% (1st cycle) to 34.3%. The sharp drop of carbonation conversion was due to the sintering. There was more than a half of specific surface area lost (Table 2) through 43 carbonation/calcination cycles. However, the great carbonation conversion of CaO–CaAc₂ in the 44th cycle was suddenly recovered after contact with air. The schematic diagram was shown in Fig. 7. The hydration and carbonation for CaO occurred due to the presence of the water vapor and CO_2 in the air. $\text{Ca}(\text{OH})_2$ and CaCO_3 could be seen by XRD in our previous work when the calcined CaO sorbent was placed in air after 1 h and 4 days, respectively. Therefore, the volume of particle was expanded by the generated $\text{Ca}(\text{OH})_2$ ($32.9 \text{ cm}^3 \cdot \text{mol}^{-1}$) and CaCO_3 ($36.9 \text{ cm}^3 \cdot \text{mol}^{-1}$) [4] with larger molar volumes. The channels would become narrow or blocked. Before the next carbonation, the calcination of CaCO_3 and $\text{Ca}(\text{OH})_2$

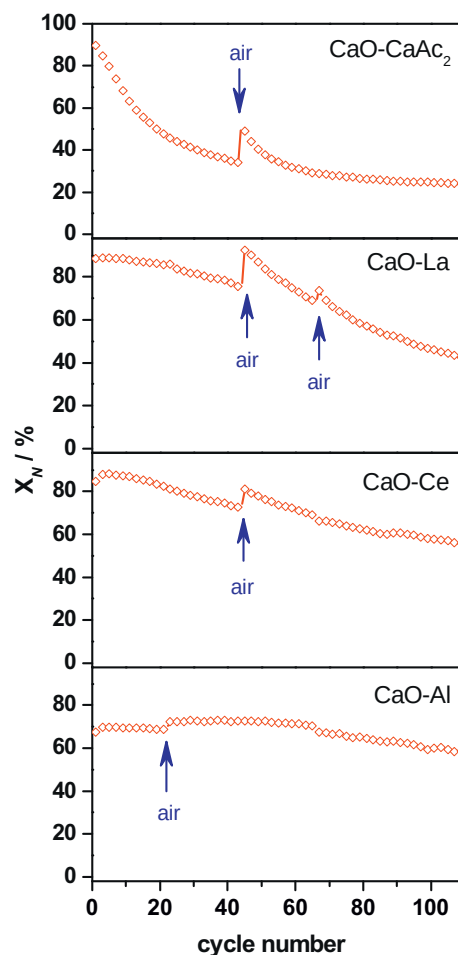


Fig. 6. Reactivation of carbonation conversions in the process of placing in air.

Table 2

S_{BET} and pore volume of sorbents through multiple cycles before and after the reactivation in air

Sample	Cycle number	Specific surface area/ $\text{m}^2 \cdot \text{g}^{-1}$	Pore volume/ $\text{cm}^3 \cdot \text{g}^{-1}$	Average pore size/nm
CaO–Al	1	12.90	0.1188	36.83
	22	13.01	0.1348	41.44
	22 ^①	13.52	0.1424	42.13
CaO–Ce	0	16.20	0.1477	36.45
	44	12.73	0.1716	53.94
	44 ^①	15.67	0.2087	53.28
CaO–La	0	21.98	0.1386	25.22
	44	11.38	0.1415	49.73
	44 ^①	15.05	0.2036	54.11
CaO–CaAc ₂	0	22.70	0.2204	38.83
	43	8.80	0.1046	47.55
	43 ^①	20.36	0.2732	53.67

^① After the reactivation in air.

could release H_2O and CO_2 . The escape of gas could either generate several new channels or broaden the existing channels, which increased the porosity of sorbent [18]. For CaO–CaAc₂, Fig. 8(a) verified that the volume of mesopores in both smaller size and larger size increased after contact with air. Table 2 showed that the specific surface area and pore volume of CaO–CaAc₂ increased by about 1.5 times after contact with air, which was nearly as high as the fresh one. The expanded volume improved the channel structure to reduce the resistance of CO_2 diffusion. The carbonation conversion of CaO–CaAc₂ increased to

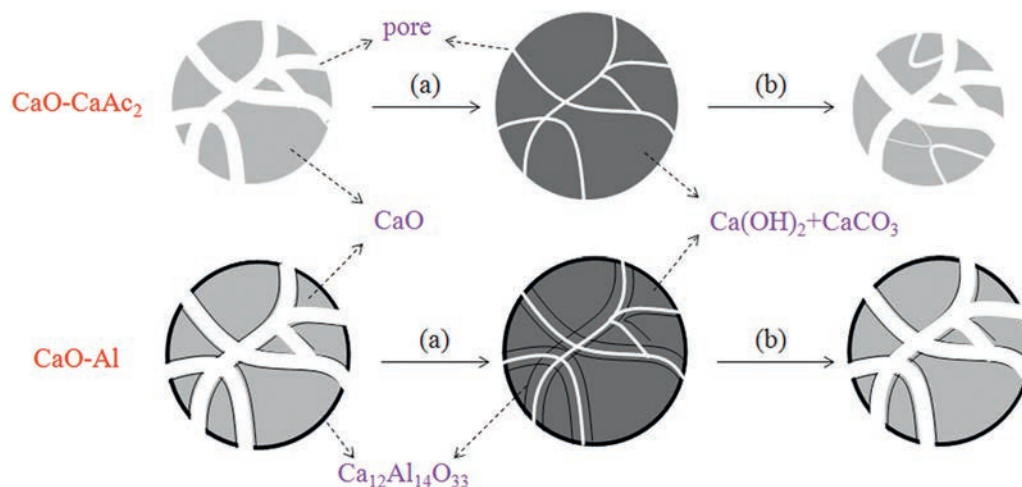


Fig. 7. Schematic diagram of the reactivation by placing in air after multiple cycles for CaO-CaAc₂ and CaO-Al: (a) hydration and carbonation in air, (b) calcination in N₂. (The sorbents in (a) was through 43 cycles while (b) was through 44 cycles.)

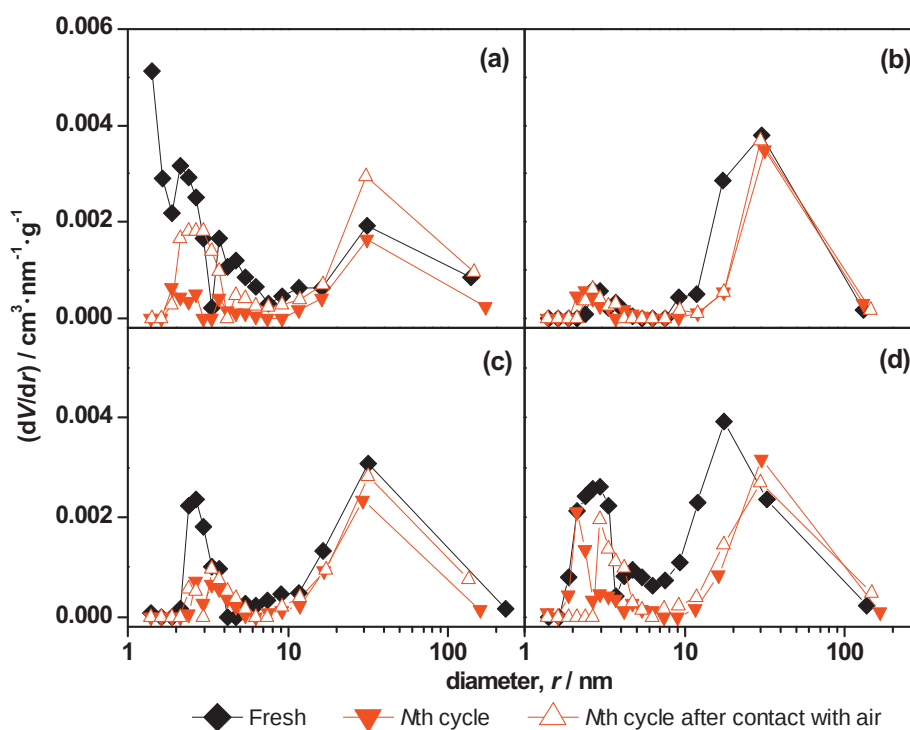


Fig. 8. Pore size distribution of modified sorbents before and after contact with air through multiple cycles: (a) CaO-CaAc₂, N: 43; (b) CaO-Al, N: 22; (c) CaO-Ce, N: 44; (d) CaO-La, N: 44.

51.4% in the 44th cycle, which was double of the one in the 43rd cycle. Wang *et al.* [1] reported the sorbent after 40 cycles was reactivated by hydration–dehydration technology that should be conducted in water at 60 °C without air. The carbonation conversion of reactivated sorbent was almost identical with the fresh one. However, the improvement of carbonation conversion by hydration was not durable. As the channels of CaCO₃ could be melted and collapsed again at 700 °C, the expanded pore was not stable. In present work, the increased carbonation conversion of CaO-CaAc₂ dropped again soon. Only after the subsequent 12 cycles, the carbonation conversion was as little as the one in the 43rd cycle. The carbonation conversion through five groups of 22 cycles was only 24.0%. S_{109} of CaO-CaAc₂ was only 26.8%, which was smaller than S_{109} of CaO-CaAc₂ without contact with air, 36.2% [33]. Although the reactivation of CaO-CaAc₂ in air was not as great as the hydration–

dehydration technology, it also provides an easy and low-cost method for regeneration of the spent CaO-based sorbents.

After 44 cycles, X_{Ce} and X_{La} were still more than 76%. The doped Ce and La helped the sorbents build the skeleton structure. Therefore, the loss of carbonation conversions through the multiple cycles was much smaller than that of CaO-CaAc₂. The hydration and carbonation in the air between the 44th cycle and the 45th cycle helped to improve the channel structure of CaO-Ce. The specific surface area increased due to the reactivation. However, the stable skeleton structure limited both the volume expansion of hydration and carbonation in air and the melt of CaCO₃ in the subsequent cycles. The increasing range of carbonation conversion for CaO-Ce was about 10.7%, which was smaller than that of CaO-CaAc₂. The cycle performance of CaO-La was similar with that of CaO-Ce. However, La₂O₃ could react with CO₂ and H₂O in air.

There was more chance for CaO-La to generate new channels in calcinations stage due to the decomposition of lanthanum carbonate. The increase value of X_{La} was as high as 15.7% between the 44th and 45th cycle. Fig. 8(d) showed that the pore volume of mesopores between 2 nm and 4 nm for CaO-La recovered to the level of fresh one after contact with air. Through the subsequent 14 cycles, the carbonation conversion decreased to the one before the reactivation. With the less time in air, the reactivation for CaO-La became less between the 66th and 67th cycle. Although the carbonation conversions increased after contact with air, the carbonation conversions of all sorbents in the subsequent cycles dropped with the increase of cycle number. After 110 cycles, the cyclic stability of CaO-Ce and CaO-La were respectively 65.5% and 47.7%, which were much greater than that of CaO-CaAc₂.

For CaO-Al, the reactivation of X_{Al} after contact with air was not as obvious as other sorbents. The increased X_{Al} after reactivation was only 3.7%. The stable skeleton structure formed by the inert Ca₁₂Al₁₄O₃₃ helped to fix the CaCO₃ in a certain area and isolate the CaCO₃ from each other. It could effectively prevent the substantial expansion of pore volume when it was exposed to air (Fig. 7). In the calcination stage of CaO-Al after the hydration and carbonation in air, the stable skeleton could limit the melt flow of CaCO₃ and maintain the channel structure as the original one. Table 2 showed that the increase range of specific surface area and pore volume for CaO-Al was the least in the four sorbents after contact with air. Although the poor carbonation conversion in initial cycle was due to the consumption of effective CaO, the cyclic performance of CaO-Al was excellent. The skeleton structure formed by Ca₁₂Al₁₄O₃₃ was stable, which effectively avoided the channel collapse and reduced the decay of carbonation conversion in subsequent cycles. Fig. 6 shows that the carbonation conversions of CaO-Al in the subsequent 44 cycles were greater than the one before the reactivation. X_{Al} was 58.5% through 110 cycles, which was as high as 86.5% of the fresh one. S_{110} of CaO-Al with the stable structure was almost the same with the one without contact with air in the 110 carbonation/calcinations.

When the pore size increased, the diffusion resistance of CO₂ decreased. However, the specific surface area also decreased when the pore volume was constant. There was less chance for CO₂ to react with CaO. The appropriate pore size should be conducive to both CO₂ diffusion and the contact with CaO. Comparing the carbonation conversion in Fig. 6 and pore size distribution in Fig. 8, it was found that the volume of mesopores between 2 nm and 5.5 nm showed more influence on carbonation conversion than the volume of mesopores with larger pore size. For fresh sorbents and spent sorbents before and after reactivation, the pore volume within the different range of diameter was calculated. Fig. 9 showed the effect of pore volume within the different range of diameter on carbonation conversions of the four sorbents. In different range of channel diameter, carbonation conversions of sorbents always increased with the increase of pore volume within the range of 2 nm to 5.5 nm whether in contact with air or not. Through multiple cycles, the cyclic stability of CaO-Al with the stable channel structure formed by Ca₁₂Al₁₄O₃₃ was the most significant in the four sorbents. Meanwhile, the loss of pore volume within the range of 2 nm–5.5 nm of CaO-Al was only 0.000032, which was the least loss of the four sorbents. Therefore, the cyclic stability was in accordance with the stability of pore volume for mesopores between 2 nm and 5.5 nm. Before and after contact with air, the increased carbonation conversion of CaO-Al was only 21.6% of that of CaO-CaAc₂ while the increased pore volume of 2 nm–5.5 nm of CaO-Al was also only 23.6% of that of CaO-CaAc₂. Therefore, the cyclic stability and the extent of reactivation were related to the structural stability of sample, especially the stability of mesopores between 2 nm and 5.5 nm. Furthermore, the mesopores between 2 nm and 5.5 nm might be the appropriate pore size of CaO-based sorbent for CO₂ capture.

4. Conclusions

In present study, the effect of pre-calcination and reactivation in air on the cyclic stability of modified CaO-based sorbents was investigated.

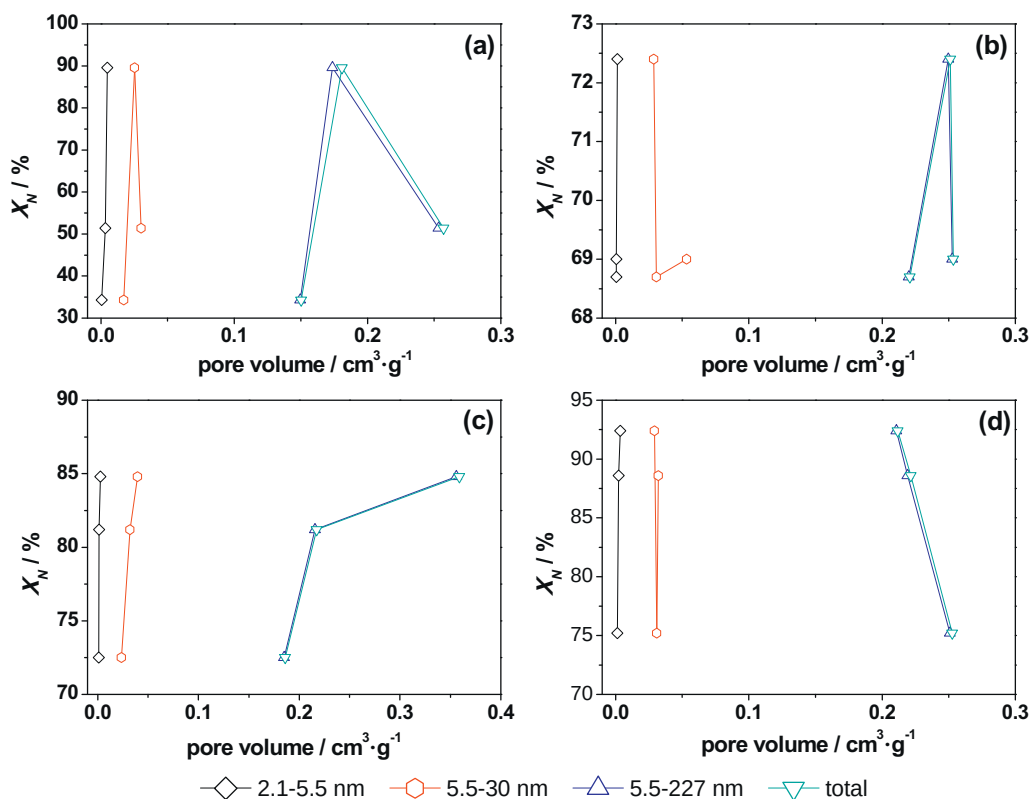


Fig. 9. Effect of pore volume within the range of different diameter on carbonation conversions of modified sorbents before and after contact with air through multiple cycles: (a) CaO-CaAc₂, N: 43; (b) CaO-Al, N: 22; (c) CaO-Ce, N: 44; (d) CaO-La, N: 44.

After pre-calcination, the carbonation conversions of the sorbents in the 1st cycle were generally reduced over twentieth than those without pre-calcination. However, the cyclic stability after 22 cycles was improved due to the slight sintering during the pre-calcination. All the cyclic stabilities of CaO-Al, CaO-Ce and CaO-La were above 96% after 22 cycles.

During the 110 cycles, the carbonation conversions of the spent sorbents with pre-calcination suddenly increased by about one-sixth after contact with air, which was due to the hydration and carbonation in air. It provides an easy and cheap reactivation method for spent CaO-based sorbents. The temporary reactivation of carbonation conversion was obvious for sorbent with unstable structure, such as CaO-CaAc₂. For CaO-Al with stable skeleton structure, the reactivation was unapparent, while the cyclic stability was as high as 86.5% after 110 cycles. According to the change of pore size distribution, it was considered that the mesopores between 2 nm and 5.5 nm played an important role in cyclic stability.

Nomenclature

m_0	sample mass before carbonation, mg
m_t	real-time sample mass while carbonation, mg
S_N	sorbent stability through N cycles
X	carbonation conversion
α	effective mass of CaO in sorbent

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