

KINETICS, CATALYSIS, AND REACTION ENGINEERING

Properties of Ca-Base CO₂ Sorbent Using Ca(OH)₂ as Precursor

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The study concerns evaluation of the properties of Ca-base CO₂ sorbents using Ca(OH)₂ as precursor. The CO₂ sorption capacities of the sorbents are measured using a fixed-bed reactor at different operating conditions. Experimental data show that a pelletized Ca(OH)₂ has a maximum CO₂ sorption capacity of 10.7 mol/kg of sorbent at a temperature of 650 °C and at a CO₂ partial pressure of 0.4 atm. A pellet containing 85 wt % Ca(OH)₂ bound with 15 wt % clay has the stable carbonation capacity 3.45 mol/kg after 10 carbonation–calcination cyclic runs at the temperatures of 500 and 880 °C, respectively. The reasons Ca(OH)₂ precursor sorbent has a higher sorption capacity than CaO precursor and steam enhanced the sorption capacity have been studied. The sorption capacity and durability of Ca(OH)₂ precursor CO₂ sorbent and CaCO₃ precursor sorbent have been studied by TGA. The other influencing factors on the sorbent capacities of Ca(OH)₂ precursor CO₂ sorbents have been briefly studied.

1. Introduction

The sorption-enhanced reaction process (SERP) is an effective technique to enhance steam methane reforming to produce hydrogen and it has developed rapidly during recent years. The SERP process is realized by mixing reforming catalyst with CO₂ adsorbent together in one reactor, breaking reforming reaction, and driving in the direction of producing hydrogen by Le Chatelier's principle. The SERP technique with the advantages of high methane conversion, high-purity hydrogen, and shorter process becomes a low-cost hydrogen-producing process of steam methane reforming (SMR) and has attracted many studies in the past decade.^{1,2}

The high-temperature CO₂ sorbent plays a key role in the performance of the SERP technique. Hydrotalcite-like compounds (HTLcs) as prior high-temperature CO₂ sorbents for SERP with the advantage of easy generation has been studied a great deal, but there is not much interest in using it in the industry because of the low CO₂ working capacity.³ CaO adsorption (or reaction) with CO₂ in terms of stoichiometry shows a big potential in industrial application. CaO used as a CO₂ capturing sorbent in the chemical heat pump, energy storage, and the zero emission coal process provides background research for uses in SERP. The highly exothermic reaction between CaO and CO₂ ($\Delta H^\circ = -178.3$ kJ/mol) is good for the highly endothermic steam methane reforming reaction by combining reaction with adsorption.

The precursors of Ca-base CO₂ adsorbent could be many and showed different sorption capacities. Gupta and Fan⁴ studied adsorption properties with different morphological properties CaO sorbents calcinated from Ca(OH)₂, dolomite, and precipi-

tated CaCO₃ (PCC). With a CaO precursor sorbent, Abanades et al.'s studies showed a carbonation conversion that started from around 70% after decomposition at a temperature of 1050 °C and decreased to lower than 20% after 20 cycles.⁵ Johnson et al.⁶ studied SERP to produce hydrogen with dolomite as the CO₂ acceptor. Li et al.⁷ studied the CaO/Ca₁₂Al₁₄O₃₃ sorbent. Different precursors have a different sorption capacity and until now the unsatisfied durability was a common problem in the application of the Ca-base CO₂ sorbents.

Ca(OH)₂ is one of the available candidates of high-temperature CO₂ capture. However, the properties of sorption capacity and the durability of Ca(OH)₂ precursor sorbent have not been published yet and need to be investigated in detail.

2. Experimental Section

Powders of CaO and Ca(OH)₂ were obtained from Aldrich Chemical Company. CaO and Ca(OH)₂ pellets were prepared by pelletizing the powders of CaO and Ca(OH)₂ to the size of 2–3 mm by pressing at a pressure of 5.6 kg/cm² for 10 min (using CARVER hydraulic unit model #3925). The durability study of Ca(OH)₂ precursors sorbent were prepared by mixing a betonies clay with the powder of Ca(OH)₂ precursor and dampening with a 10 wt % glycol water solution and a cylindrical pellet of 1 mm diameter was formed by an extruder. The pellet sorbent contains 85% Ca(OH)₂ and 15% clay.

A schematic diagram of the apparatus used to study the adsorption capacity of the CO₂ sorbent is illustrated in Figure 1. A quartz tube (Ø 6 × 550 mm) and a stainless steel tube (Ø 12.5 × 350 mm) were used as the fixed-bed reactor. Adsorbent sample pellet with 7–10 g filled in the middle of the reactor. Nitrogen was used as the carrier gas to dilute the CO₂ to a desirable partial pressure. Two mass flowmeters were used to control the flow rates of N₂ and CO₂. N₂ and CO₂ mixed and

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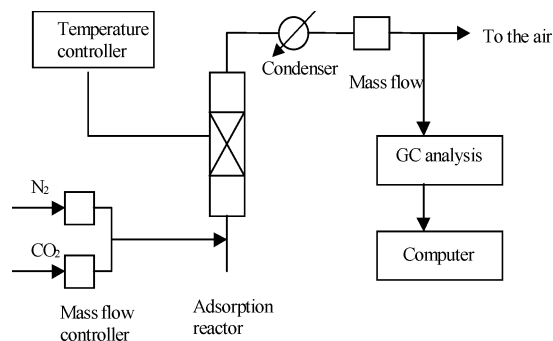


Figure 1. Schematic diagram of the sorption experiments.

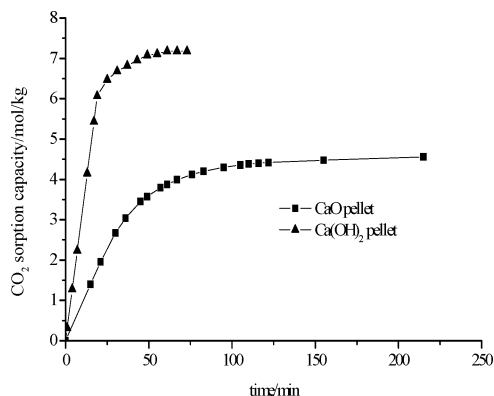


Figure 2. Sorption capacities of CO₂ of different sorbents (CO₂ partial pressure of 0.4 atm).

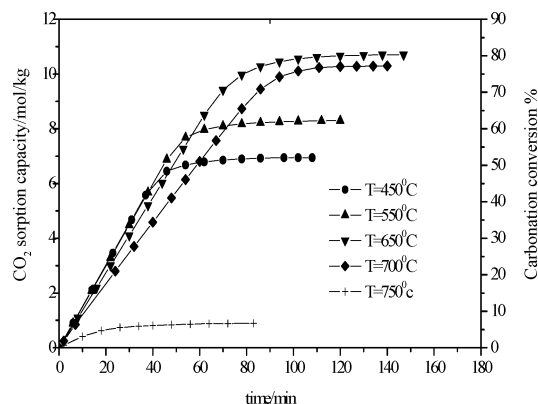


Figure 3. CO₂ sorption capacities and carbonation conversions of Ca(OH)₂ precursor pellet with sorbents at 450 °C (CO₂ partial pressure at 0.4 atm).

entered the reactor from the bottom of the reactor. The temperature of the reactor was controlled by a furnace. The effluent gas was condensed and then analyzed by a gas chromatograph on-line. The time between two samples is 7 min.

3. Results and Discussions

3.1. Adsorption Capacity with Different Temperatures.

Figure 2 showed the CO₂ sorption capacities of pelletized Ca(OH)₂, pelletized CaO at a temperature of 450 °C and at a CO₂ partial pressure of 0.4 atm. It was revealed that the Ca(OH)₂ precursor pellet has a higher sorption capacity of CO₂ than that of CaO with a rapid sorption rate. The carbonation conversion of the Ca(OH)₂ precursor pellet was approximately 51.5% at a temperature of 450 °C, mainly produced in the first reaction control stage.

Figure 3 shows the effect of temperature on the CO₂ sorption capacity and carbonation conversion of Ca(OH)₂ precursor

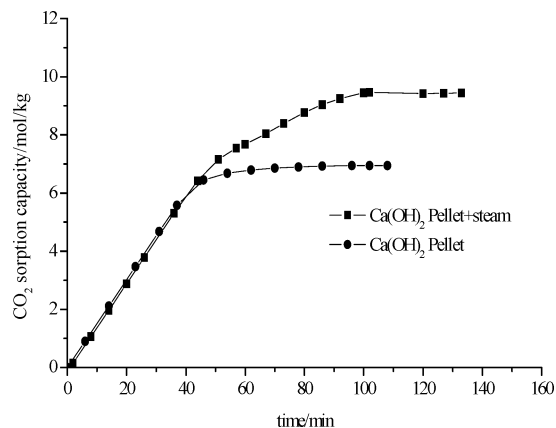


Figure 4. Effect of steam on the CO₂ sorption capacity at 450 °C (CO₂ partial pressure at 0.25 atm, steam 14 mL/min).

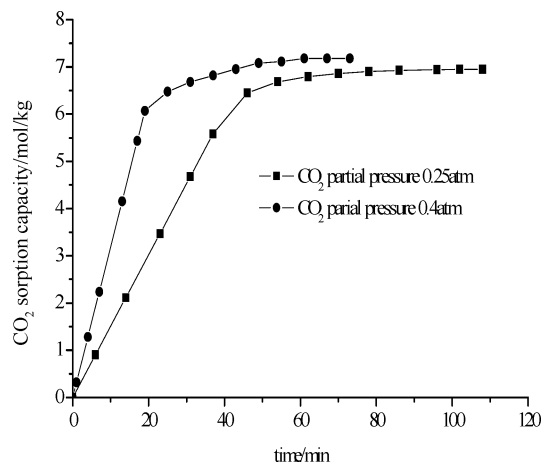


Figure 5. Effect of CO₂ partial pressure on sorption capacity of Ca(OH)₂ pellet at 450 °C.

Table 1. Equilibrium Constants at Different Temperatures and Ambient Pressure

T (°C)	equilibrium constant K_a	
	Ca(OH) ₂ + CO ₂ → CaCO ₃ + H ₂ O	CaO + CO ₂ → CaCO ₃
450.0	8832.4799	7.46×10^4
500.0	2892.6405	1.07×10^4
550.0	1056.8164	1979.0680
600.0	423.7045	443.4878
650.0	183.9851	117.4264
700.0	85.6125	35.8069
750.0	42.3193	12.3173

Table 2. Surface Properties of Two CaO Pellet Samples after Calcination^a

items	Ca(OH) ₂ precursor pellet	CaO pellet
BET surface area (m ² /g)	7.544	2.801
total pore volume (cm ³ /g)	0.058	0.012
average pore diameter (Å)	312.29	173.37

^a Calcination conditions: N₂ flow rate, 15 mL/min; temperature, 500 °C for 3 h.

pellet. The CO₂ sorption capacity increased with the increase of temperature between 450 and 700 °C. It decreases with the increase of temperature in the range between 650 and 750 °C. The maximum CO₂ sorption capacity of Ca(OH)₂ precursor pellet was 10.7 mol/kg at a temperature of 650 °C and under CO₂ partial pressure of 0.4 atm.

3.2. Steam Effect on the Adsorption Capacity. The investigation results of the steam effect on the CO₂ sorption

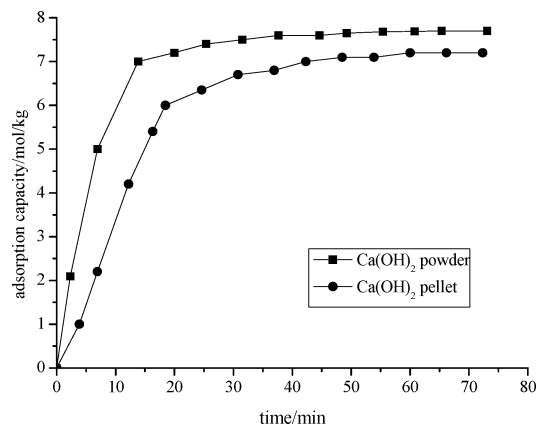


Figure 6. Effect of particle size on sorption capacity at 450 °C (CO₂ partial pressure at 0.25 atm).

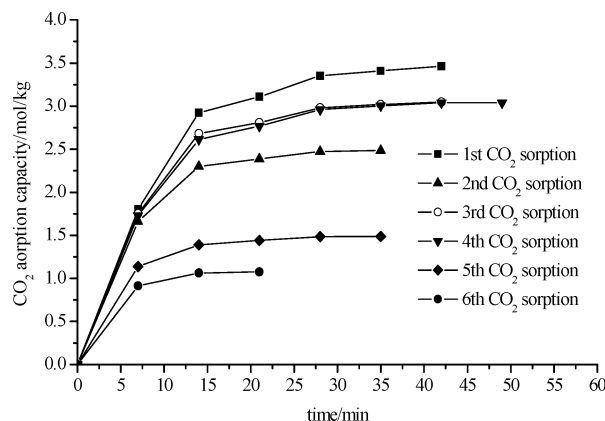
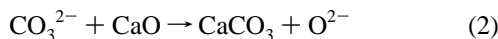
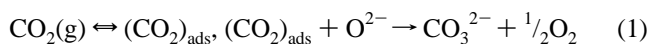


Figure 7. CO₂ sorption capacities of Ca(OH)₂ precursor sorbent with sorption time (Carbonation temperature 650 °C, calcination temperature 750 °C, CO₂ partial pressure 0.5 atm.)

capacity of Ca(OH)₂ precursor pellet are shown in Figure 4. The steam enhancing the CO₂ sorption capacity is obviously seen in Figure 4. There are two plausible mechanisms for the reason of the enhancement of sorption capacity by steam.⁸ One of the proposed mechanisms in the CaO–CaCO₃ inner surface is shown in the following formula:



O²⁻ released from steam can accelerate carbonation. Another possible mechanism was pointed out that the steam first reacts with CaO to form Ca(OH)₂ and then Ca(OH)₂ undergoes carbonation. The reaction formula is as follows:



To explain the experimental studies of 3.1 and 3.2, the equilibrium constant K_a of the reactions of $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ and $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$ have been calculated. With eqs 5–8, and the published parameters and equilibrium constant K_a data of 25 °C,⁹ equilibrium constant K_a at different temperatures was calculated and listed in Table 1.

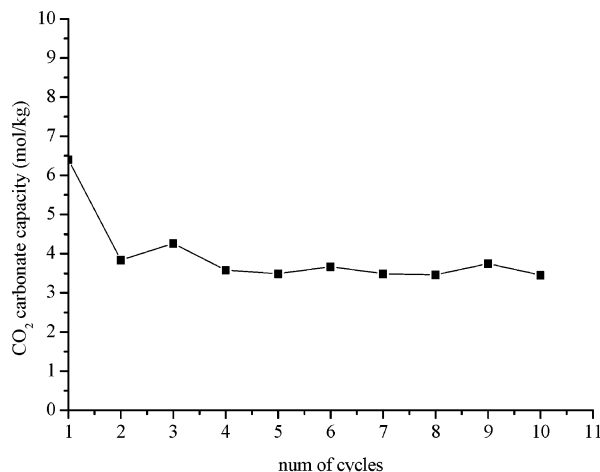


Figure 8. CO₂ sorption capacities of clay-bound Ca(OH)₂ precursor sorbent with number of cycles. (Carbonation temperature 500 °C, calcination temperature 880 °C, CO₂ partial pressure 0.5 atm.)

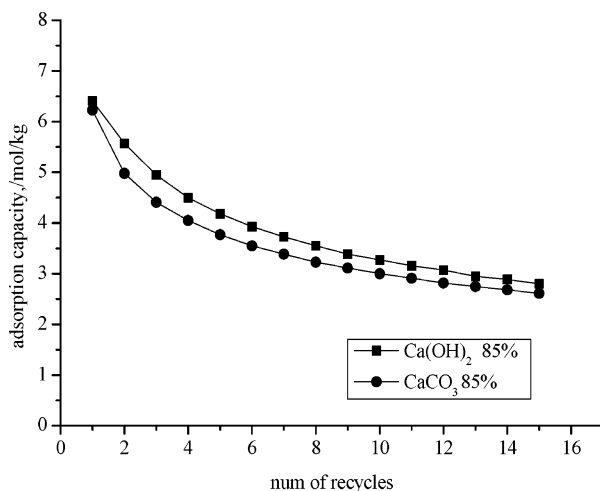


Figure 9. CO₂ adsorption capacities of clay-bound Ca(OH)₂ precursor and CaCO₃ sorbents with number of cycles. (Carbonation temperature 600 °C, calcination temperature 750 °C, CO₂ partial pressure 0.333 atm.)

$$K_a = \exp\left(\frac{-\Delta G^\circ}{RT}\right) \quad (5)$$

$$\left[\frac{\partial \ln K_a}{\partial T}\right]_P = \frac{\Delta H_T^\circ}{RT^2} \quad (6)$$

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \int_{298}^T \left(\sum_i \nu_i C_{p,i}^0\right) dT \quad (7)$$

$$C_{p,i} = a_i + b_i T + c_i T^2 + d_i T^3 + e_i T^{-2} \quad (8)$$

From Table 1, with the temperature increase from 450 to 750 °C, both equilibrium constants K_a of the reactions decrease significantly. For the temperatures lower than 650 °C, equilibrium constant K_a of the CaO reaction with CO₂ is several times higher than that of the Ca(OH)₂ reaction with CO₂, but the sorption rate and sorption capacity of CaO precursor are lower than those of the Ca(OH)₂ precursor. These results are in contrast to the experimental results of sorption capacity increasing with the temperature increasing. It seems that the reactions are controlled by a kinetic process, and not by a thermodynamic process. Further, BET surface area, pore diameter, and pore volume of the two samples were measured by ASAP 2010 and listed in Table 2. From Table 2, the Ca(OH)₂ precursor pellet has a larger surface area than that of the CaO pellet caused by the decomposition of Ca(OH)₂ and release of H₂O. This

illustrated the reason the $\text{Ca}(\text{OH})_2$ precursor pellet has a big CO_2 adsorption capacity and high speed of sorption rate compared to CaO sorbent. Steam released increases the volume of the pore inside the $\text{Ca}(\text{OH})_2$ precursor pellet and enhances sorption. This drives us to a new understanding of the experimental fact of steam enhancing the $\text{Ca}(\text{OH})_2$ sorption shown in Figure 4; the steam as a gas keeps the pore and BET surface area of sorbent during the sorption and has a bigger sorption capacity.

3.3. CO_2 Partial Pressure with the Adsorption Ratio. Figure 5 shows the influence of CO_2 partial pressure on the sorption characteristics. With the increase of the partial pressure from 0.25 to 0.4 atm, the CO_2 sorption rate increased, but the equilibrium sorption capacities are similar in the two cases. As shown in Figure 6, the powder type of $\text{Ca}(\text{OH})_2$ has a faster reaction rate and higher sorption capacity than those of the pellet type. This showed that the CO_2 partial pressure as a kinetic factor influences the diffusion of gas–solid reaction of CaO with CO_2 .

3.4. Durability Study. The durability study of the CO_2 sorbent is very important for industrial application. Initially, a pelletized $\text{Ca}(\text{OH})_2$ sorbent was used in the durability study. Figure 7 shows the results of cyclic runs at a carbonation temperature of 650 °C and a calcination temperature of 750 °C. The sorption capacity sharply decreased after four cyclic runs. The reason may be the sintering of CaO at high-temperature calcinations.

The increase of the $\text{Ca}(\text{OH})_2$ amount gives lower mechanical strength and high sorption capacity for CO_2 . To maintain enough mechanical strength, a pelletized sorbent containing 85 wt % $\text{Ca}(\text{OH})_2$ and 15 wt % clay binder was prepared. Figure 8 shows sorption capacity with multiple cyclic runs going on at a carbonation temperature of 500 °C and a calcination temperature of 880 °C. The carbonation time was about 77 min and the calcination time was about 10 min. The stable carbonation conversion was 30.5% and sorption capacity was 3.45 mol/kg. $\text{Ca}(\text{OH})_2$ precursor sorbent has an approximately 80% conversion to CaO at a temperature of 500 °C. To compare the sorption capacity of the sorbents of 15% clay bound with 85% $\text{Ca}(\text{OH})_2$ precursor and 85% CaCO_3 precursor, a TGA analysis (Perkin-Elmer Pyris 1) was used to test the durability of the sorbent under the conditions of carbonation at 600 °C and regeneration at 750 °C. The experimental results are shown in Figure 9. It has been found that they have a similar durability with the cyclic runs. But sorbent with $\text{Ca}(\text{OH})_2$ precursor has a higher sorption capacity than CaCO_3 precursor based on the same content.

4. Conclusions

The study results show that $\text{Ca}(\text{OH})_2$ precursor is better than CaO precursor and CaCO_3 precursor with higher good sorption capacity. The sorption capacity of $\text{Ca}(\text{OH})_2$ pellet increases with temperature increasing in the range of 450–750 °C, and it

decreases with temperature in the range of 650–750 °C. The maximum CO_2 sorption capacity is 10.7 mol/kg and 93.1% conversion ratio at a temperature of 650 °C and at a CO_2 partial pressure of 0.4 atm. The existence of steam in the mixed gas can enhance the CO_2 sorption capacity of $\text{Ca}(\text{OH})_2$ precursor pellet. $\text{Ca}(\text{OH})_2$ decomposition creates much more surface area since steam released is the reason for both $\text{Ca}(\text{OH})_2$ precursor having a higher sorption capacity and steam enhancing $\text{Ca}(\text{OH})_2$ sorption capacity. The sorption capacity increases with CO_2 partial pressure increasing, and the powder of $\text{Ca}(\text{OH})_2$ has a faster sorption rate with a slightly higher reaction capacity than those of the pellet. The results mean the kinetic influences are much more important than the thermodynamic equilibrium influence.

The experimental study shows that a pellet containing 85 wt % $\text{Ca}(\text{OH})_2$ and 15 wt % clay binder has the same durability as 85 wt % CaCO_3 and 15 wt % clay binder pellet, but the sorption capacity is 0.4 mol/kg higher than the CaCO_3 precursor sorbent because of the stoichiometric advantage of $\text{Ca}(\text{OH})_2$ precursor.

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