Effect of calcium precursors on pelletized property and cyclic CO₂ capture performance

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Abstract. CaO is widely used for capturing CO₂ in large scale application however the work on the manufacture of CaO based pellets for the application of CO₂ capture is relatively limited. In this research investigated the effect of calcium precursors (Ca(OH)₂, Ca(NO₃)₂ and Ca(CH₃COO)₂) and their synthesis method (sol-mixing and wet-mixing) on pelletization. Adsorbent synthesized from Ca(CH₃COO)₂ as a precursor using sol-mixing pelletize to porous spherical provide the best mechanical strength and CO₂ adsorption capacity 0.51 and 0.41 g CO₂/ g CaO at first cycle and tenth cycle respectively. The outstanding cyclic performance of Ca(CH₃COO)₂ sol-mixing can be ascribed to the presence of inert support material i.e. Ca₉Al₆O₁₈ and Ca₁₂Al₁₄O₃₃ with suitable pore volume to prevent sintering of CaO and structure collapsing at high temperature.

1 Introduction

A dramatic increase of carbon dioxide, a known greenhouse gas, in atmosphere is a worldwide environmentally concern. Calcium looping is one of potential technologies for the separation of CO₂ from flue gas mixture. Moreover, it can be applied as a sorbent in sorption enhanced reforming for H₂ production [1]. The CO₂ capture reaction for CaO adsorbent is occurred by the reversible reaction between CaO and CO₂, named carbonation-calcination reaction [2]

Such a calcium looping process involves in multi-cycles carbonation-calcination; however, the makeup flow of fresh sorbent in calcium looping is still required due to the deactivation of it lead to higher operating cost. Consequently, several technologies have been explored for enhancing the CO₂ capture activity of the sorbents, such as steam or water hydration [3-4], incorporation of metal ion using wet mixing method, sol-gel process [5], flame spray pyrolysis technology [6], co-precipitation [7,8]

It is worth to note that, no matter what method was employed, the type of calcium precursor used plays a significant role in the carbonation-calcination performance. The dependent on the type of calcium precursor used is one of interested in this research.

On the other side, because CaO particles are soft and are able to erode quickly in fluidized bed, mass loss is therefore another problem when using a calcination reactor operating in fluidization mode [9]. Also the pelletization has outgrowth in reducing pressure drop more than the powder sorbent when applied in fixed bed adsorpter, which is of more interest for the use in industry; however the work on the manufacture of CaO based pellets for the application of high-temperature CO₂ capture is relatively limited.

It has been reported that the pellet sorbent can increase the mechanical strength for sorbent [10-11]. Moreover, Wu et al. [12] evaluated the use of Ca(OH)₂ as a precursor of Ca-base pellet sorbent for the application of CO₂ capture. Experimental results show that Ca(OH)₂ precursor provides better adsorption capacity than CaO precursor and CaCO₃ precursor, of which 10.7 mol CO₂/kg of adsorbent can be obtained at temperature of 650°C and at CO₂ partial pressure of 0.4 atm. This is due to the decomposition of Ca(OH)₂ which release water creates more surface area. Ridha et al

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studied the effect of pellet size on CO₂ uptake capacity. Natural kaolin and Al(OH)₃ obtained from acid leaching of kaolin were employed as binders. They found the smaller pellets have higher ability to capture about 20% more CO₂ than the larger pellets in the first cycles. However, after a large number of cycles, the effect becomes insignificant. In addition, the pellet with Al(OH)₃ binder has higher thermal stability than that without binder [13].

In this study, a dependent of calcium precursor on pelletization and their carbonation/calcination performance are investigated.

2. Materials and Methods

2.1 Chemicals

Calcium hydroxide (Ca(OH)₂), calcium acetate (Ca(CH₃COO)₂), calcium nitrate (Ca(NO₃)₂), and calcium oxide (CaO) were used as calcium precursors. Aluminium nitrate (Al(NO₃)₃) was used as aluminium precursor. Deionized water and 2-propanol were used as solvent. All chemicals were used as received.

2.2 Preparation of sorbents

Two techniques of mixing method were used to prepare sorbents: sol-mixing and wet-mixing. The synthesis procedure for sol-mixing technique, briefly, calcium precursor was firstly decomposed to pure CaO by calcination in the furnace; at 850°C for calcium acetate precursor and at 900°C for calcium hydroxide precursor. Then CaO was mixed with aluminium precursor in the solution of propanol and stirred for 1 h at 75°C. The reaction was aged for overnight and then recovered by drying in an oven at 120°C for 12 h followed by calcination at 900°C for 1.5 h. In the case of wet-mixing, the solution of calcium and aluminium were mixed and stirred at 75°C for 1 h. The solution was then dried in an oven at 120°C for 12 h, dry white powder was obtained. The obtained material was calcined at 900°C for 1.5 h to form CaO. The ratio of calcium to aluminium was calculated to be 75/25 wt% for all samples. In this work, we denoted the synthetic materials prepared from wet-mixing as -w and from sol-mixing as -s, for example, the adsorbent prepared from wet-mixing method using calcium hydroxide as a precursor was denoted as Ca(OH)₂-w. Pellet-type adsorbents were prepared by mixing water to the powder of CaO-based sorbent with the ratio of 1.5 g/g of sorbent powder. Pellet was prepared by gradually dropping water in powder sorbent and stirred until a gel was obtained. Then the gel was subjected to molding and pressed until a stiff consistency is reached. After shaping, the samples were dried at room temperature for 24 h.

2.3 Adsorbent characterization

Crystallinity of synthetic adsorbents were characterized by powder X-ray diffraction (XRD). The spectra were recorded on a Rigaku, Miniflex II desktop X-ray diffractometer using Cu Kα radiation in the 2θ range of 10-80°C at room temperature. Structure and morphologies of the adsorbents were imaged by scanning electron microscopy (SEM, JEOL JSM-5800 LV). The surface properties, including BET surface area, average pore size, and pore size distribution, were determined by N₂ adsorption/desorption at 77 K, provided by BEL SORP mini II.

2.4 CO₂ adsorption test

CO₂ adsorption capacity was performed by introducing the CaO pellets in a vertical alumina tube placed in the furnace at constant carbonation temperature of 450°C. CO₂ gas was flowed into the reactor at 10 bar, the weight and pressure changes were monitored until it became constant. Regeneration of CaO was performed by heating the sorbent to calcination temperature of 900°C for 1.5 h.

3. Results and Discussion

3.1 Effect of calcium precursor on sorbent characteristic

The synthetic adsorbents were characterized by XRD as shown in Fig.1. All the samples are composed of CaO, Ca₁₂Al₁₄O₃₃, and Ca₉Al₆O₁₈ with different compositions depend upon calcium precursor and synthesis method.

Fig.1: XRD pattern of synthetic CaO-based sorbents.

Fig.2 presents SEM images of the adsorbents CaO-based alumina. The adsorbents obtained by the use of Ca(CH₃COO)₂ as calcium precursor has the smallest size of crystal where the others aggregated to larger particle. Moreover comparing between wet-mixing and sol-mixing of Ca(CH₃COO)₂ precursor, the wet-mixing

exhibit comparatively lower particle size. N_2 adsorption/desorption isotherm measurement was conducted to determine surface properties texture of the sorbents as summarized in Table 1. Two sorbents, $Ca(OH)_2$ -s and $Ca(NO_3)_2$ -w have low surface area and are similar to that of commercial CaO , whereas, $Ca(CH_3COO)_2$ -w and $Ca(CH_3COO)_2$ -s offer distinctive high surface area than others. The significantly increased of specific surface area is in consistent with the results of SEM as smallest particle of the sorbent obtained from calcium acetate precursor via wet-mixing method (Fig. 2b). In addition, using wet-mixing in $Ca(CH_3COO)_2$ -w increased their pore volume remarkably comparing to the sol-mixing of $Ca(CH_3COO)_2$ -s (Table 1).

Fig.2: SEM images of fresh sorbent sample (a) $Ca(NO_3)_2$ -w, (b) $Ca(CH_3COO)_2$ -w, (c) $Ca(CH_3COO)_2$ -s, (d) $Ca(OH)_2$ -s

Table 1: Surface properties of the synthesized materials

Adsorbent	S_{BET} ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)
Commercial CaO	5.6	0.0384
$Ca(NO_3)_2$ wet-mixing	4.5	0.0018
$Ca(CH_3COO)_2$ wet-mixing	16.6	0.2284
$Ca(CH_3COO)_2$ sol-mixing	13.1	0.0525
$Ca(OH)_2$ sol-mixing	7.4	0.0463

3.2 Pelletization of adsorbent

Fig. 3: Photographs of spherical pellet after exposed at $900^\circ C$ for 1 hr: (a) $Ca(NO_3)_2$ -w, (b) $Ca(CH_3COO)_2$ -w, (c) $Ca(CH_3COO)_2$ -s, (d) $Ca(OH)_2$ -s

Thermal stability of the sorbents in pellet form has been examined before performing high temperature CO_2 adsorption test. Thermal stability test has been conducted at $900^\circ C$ similar to the temperature where calcination reaction takes place. Fig. 3 shows thermal resistance of spherical pellets of different preparation techniques. The results show that CaO -based alumina in spherical shape, which was derived from $Ca(OH)_2$ cracked (Fig. 3d) while others can retain their shape and structure (Fig. 3a-c)

3.3 CO_2 adsorption performance

Since the mechanical property of $Ca(OH)_2$ -s was unsuitable, the CO_2 adsorption performance test of $Ca(OH)_2$ -s was neglected in this section. The value of CO_2 sorption capacity of different pellet-type sorbent are shown in Fig. 4. $Ca(CH_3COO)_2$ -w and $Ca(CH_3COO)_2$ -s exhibit higher CO_2 sorption capacity than that of commercial CaO (the values are 0.58, 0.51 and 0.42 $g CO_2 / g CaO$, respectively), while $Ca(NO_3)_2$ had the lowest sorption capacity (0.22 $g CO_2 / g CaO$). Although the understanding is not straightforward, the much lower in total pore volume of $Ca(NO_3)_2$ -w might be a reason of a much lower CO_2 sorption capacity while the surface area also a dominant parameters of the sorption capacity as observed from the tendency of others sorbent. The cyclic carbonation/calcination performance are further tested for three sorbents except $Ca(NO_3)_2$ -w.

Fig 4: CO_2 sorption capacity of pellet sphere sorbents in the first cycle.

As shown in Fig. 5, although $Ca(CH_3COO)_2$ -w can exhibit the highest sorption capacity in the first cycle, the capacity drastically decreased in the 2nd and 3rd cycle. Generally, the presence of $Ca_9Al_6O_{18}$ and $Ca_{12}Al_{14}O_{33}$ inert support material effectively prevents sintering of CaO to some extent during regeneration of sorbent at high temperature. Although, $Ca(CH_3COO)_2$ -w consists of $Ca_9Al_6O_{18}$ inert materials acting as structural supports, a very large pore volume of $Ca(CH_3COO)_2$ -w are hypothesized as a reason for structure collapse after only three cycle carbonation/calcination. This undesirable loss of pellet strength during carbonation/calcination cycles can be explained due to the presence of cracks

and/or structure collapsing in the $\text{Ca}(\text{CH}_3\text{COO})_2$ -w and commercial CaO after three cycles.

Fig 5: Show adsorption capacities of pellet sphere sorbents during carbonation/calcination cycles

4. Conclusion

A screening of potential calcium precursors and their synthesis method for pelletization of CaO-based sorbents for CO₂ capture was conducted in this work. Among calcium precursors including $\text{Ca}(\text{OH})_2$, $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{CH}_3\text{COO})_2$, CaO derived from $\text{Ca}(\text{CH}_3\text{COO})_2$ precursors using both wet- and sol-mixing methods exhibit higher CO₂ sorption capacity than that of commercial CaO. However, the pelletized CaO from $\text{Ca}(\text{CH}_3\text{COO})_2$ wet-mixing and commercial CaO cannot retain their structure after carbonation/calcination for 3 cycles lead to a drastic loss in sorption capacity. $\text{Ca}(\text{CH}_3\text{COO})_2$ sol-mixing exhibit the most carbonation/calcination stability with 0.51 and 0.41 g CO₂/g CaO at first cycle and tenth cycle respectively. The presence of $\text{Ca}_9\text{Al}_6\text{O}_{18}$ and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ with suitable pore volume might be key parameters to prevent sintering of CaO and structure collapsing at high temperature.

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