Ca-Mg-Al-oxide Sorbents Prepared from Hydrotalcite Precursors for CO₂ Capture at Realistic Calcium Looping Conditions

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Abstract. The calcium looping (CaL) process, based on the cyclic carbonation/calcination of CaO sorbents, has been widely investigated recently as a potential technique to capture CO₂ at reduced energy penalty. This process can be used in facilities such as power plants and produce a concentrated CO₂ which is suitable for storage. In recent years, the hydrogen production processes become more important due to the development of sustainable energy. The CaL process can also be combined with reforming process to produce a concentrated stream of H₂ >98 vol. % in a single step, which is known as sorption-enhanced reforming (SER) process, reducing the cost of H₂ production effectively. The capture capacities and multicycle stabilities of sorbents are crucial in these uses. In this study, a series of CaMgAl oxide materials for CO₂ capture, derived from layered-double hydroxides (LDHs), were prepared to test their performances at realistic calcium looping conditions, namely at high CO₂ concentration in the calcination stage. A series of materials with different CaMgAl molar ratios were tested at different regeneration temperatures, regeneration times, and in different CO₂ concentrations at the regeneration stage to find out the optimal treatment conditions. The multicycle capture capacities of these materials were examined and compared with that of limestone. Materials regenerated for 15 minutes at 930°C and 70~100% CO₂ had good performances. The Ca/Al = 7/1 materials possessed well capture capacity and multicycle stability compared with that of limestone. Addition of magnesium oxide can further improve its performance. In the 40 cycles test, although the initial capture capacity of the CaMgAl material was lower than that of the CaAl materials, because of the better stability of the former, its capture performance was better than that of the CaAl material at the end of the loop. These materials have the potential to be applied in hydrogen production and other related processes in the future.

1. Introduction
The greenhouse effect caused by a large amount of CO₂ emissions into the atmosphere has recently received extensive attention, and coal-fired power plants contribute a large part of CO₂ emissions. The CO₂ capture with a calcium looping (CaL) process is one of the solutions, which can effectively reduce the cost of CO₂ capture [1]. The captured CO₂ can be sequestered or reused. The CaL process involves sorption-desorption cycles of CaO according to the following reaction: CaO+CO₂ ⇌ CaCO₃. The capture is a chemical reaction that forms CaCO₃ and is typically performed at 550-700°C in around 15% vol CO₂ at atmospheric pressure. The carbonated sorbent is then subjected to a desorption process, which typically occurs at approximately 900°C in high concentration of CO₂ (70-90% vol) at
atmospheric pressure. Calcination at high temperature causes a marked aggregation and sintering of the CaO nascent grains during the CaCO\textsubscript{3}/CaO transformation, which leads to a drastic decrease of the CaO surface area available for quick carbonation in a subsequent cycle and a loss of capture capacity [1]. This drawback hinders CaL from integrating into industrial plants. Many studies have attempted to solve this problem, including CaO-containing minerals such as limestone and dolomite modified using acid solutions [2], or synthetical preparation of CaO-containing sorbents [3-4]. It was found that a small amount of MgO was beneficial to maintain the stability of the materials [4]. Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, have been widely and intensively studied because they possess both a high surface area and abundant basic sites at their surface. [5-6] However, these materials were rarely tested under harsh conditions. For example, they were usually calcined in the N\textsubscript{2} atmosphere at less than 900°C for regeneration. Recently, hydrogen energy related research has continued to increase because of the increasing demands on renewable energy. Purification of H\textsubscript{2} is an important process in the production of H\textsubscript{2} and consumes a lot of energy. The CaL process can also be combined with reforming process to produce a concentrated stream of H\textsubscript{2} >98 vol. % in a single step. This is known as sorption-enhanced reforming (SER) process, which can reduce the cost of H\textsubscript{2} production effectively [7]. In this study, a series of different proportions of CaMgAl LDHs were prepared, and CaMgO mixed oxides and limestone were used as the control group to investigate the capture performance in realistic CaL environment.

2. Experiments

2.1 Sorbents preparation

Reagents of Ca(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{2} . xH\textsubscript{2}O, Mg(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{2} . 4H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3} . 9H\textsubscript{2}O, NaOH, and Na\textsubscript{2}CO\textsubscript{3} were purchased from Merck Co. Limestone was acquired by a local supplier and was grinded into powder from ore by ourselves. The synthesis procedure was used Ca/Mg/Al = 7/1/1 as an example. An aqueous solution containing calcium acetate, magnesium acetate, and aluminum nitrate was prepared and called A solution, wherein the concentration of calcium acetate was 1 M and the molar ratio of calcium to magnesium to aluminum was 7:1:1. An aqueous solution containing 1.6 M of NaOH and 0.1 M of Na\textsubscript{2}CO\textsubscript{3} was prepared and called B solution. The A solution was heated and maintained at 80°C, then the B solution was dropped into the A solution and still maintained at 80°C. When the addition was completed, the solution was stirred for 30 minutes and then filtered, washed with water, and dried on the oven overnight at 80°C to obtain the precursor powder. The powder was ground and calcined at 600°C for 2 hours to obtain the final product of Ca/Mg/Al = 7/1/1, which represented that the molar ratio of Ca: Mg: Al was 1:1:1. The four different ratios of samples were prepared, which were Ca/Mg/Al = 7/2/1, Ca/Mg/Al = 7/1/1, Ca/Al = 7/1, Ca/Mg = 7/3, respectively.

2.2 Sorbents characterization and evaluation of their performances

The CO\textsubscript{2} adsorption performance of the sample was evaluated with a Netzsch STA TGA. Prior to the adsorption experiment, the sample was pretreated at 750°C for 1 hour in a N\textsubscript{2} stream to remove H\textsubscript{2}O and CO\textsubscript{2} adsorbed on the sample in the atmosphere. A complete cycle test consisted of two steps: carbonation at 750°C in 20% CO\textsubscript{2}/80% N\textsubscript{2} vol/vol for 30 minutes and calcination at 900 ~ 950°C in 70 ~ 100% CO\textsubscript{2}/0 ~ 30% N\textsubscript{2} vol/vol for 15 ~ 30 minutes. A Multi-cycles test was a test that repeated one cycle multiple times. Powder X-ray diffraction (XRD) data were collected using Cu K\textsubscript{\alpha} radiation operated at 50 kV and 40 mA. Diffraction data were recorded at two theta values between 5° and 90° to identify the existing crystalline phases based on comparison with JCPDS diffraction data files.

3. Results and Discussions

In order to investigate the effect of regeneration temperature and time on the degree of regeneration of the sorbent during the procedure, the Ca/Mg/Al = 7/1/1 was carbonated at 750°C in 20% CO\textsubscript{2}/80% N\textsubscript{2} for 30 minutes and was then calcinated at 900°C, 930°C, and 950°C, respectively, in 100% CO\textsubscript{2} for 30 minutes to compare the differences. In Figure 1 it was found that the sample was regenerated faster and more completed with increasing regeneration temperature. The temperature of 900°C was not
sufficient to regenerate the sorbent, and when the temperature was 950°C the rate of regeneration was so high that the regeneration was completed when the temperature was just reached 950°C. However, considering that higher regeneration temperature leads to higher energy consumption and faster sorbent degradation rate, so 930°C was chosen as the regeneration temperature. In addition, because that the sorbent has reached 85% regeneration when the regeneration time was 15 minutes, the regeneration time was selected to 15 minutes based on the energy saving consideration.

Figure 2 shows the effect of the different regeneration atmospheres on the CO₂ capture capacity and stability of the sorbent under 10 carbonation/calcination cycles when the regeneration temperature was 930°C and the regeneration time was 15 minutes. The CO₂ concentration was 70% and 100%, respectively. It was found that the concentration of CO₂ during regeneration had little effect on the performance of the sorbent. The initial capture capacity was 45wt%, the capture capacity of the 10th cycle was 29 wt%, and the stability was 64%. It is considered that the higher the CO₂ concentration during regeneration, the more favorable to obtain the high-purity CO₂ for subsequent sequestration or reuse, so that 100% CO₂ was selected as the regeneration atmosphere.

Figure 3 demonstrates the performances of Ca/Mg/Al = 7/2/1, Ca/Mg/Al = 7/1/1, Ca/Al = 7/1, Ca/Mg = 7/3, limestone during 10 carbonation/calcination cycles test. The carbonation was conducted at 750°C in 20% CO₂/80% N₂ vol/vol for 30 min and calcination at 900–950°C in 100% CO₂ for 30 min. The performance of limestone was found to be the worst. Although its initial capture capacity of 49.2 wt% was the highest of all samples, its capture capacity of the 10th cycle was only 11.4 wt% and therefore, its stability was only 23%. The performance of Ca/Mg = 7/3 was also poor, which capture capacity decreased from 37.9 wt% to 16.5 wt% with stability of 44%. The performances of Ca/Al = 7/1, Ca/Mg/Al = 7/1/1, and Ca/Mg/Al = 7/2/1 were relatively better. Its stability of 10
cycles test was 67%, 63%, and 73%, respectively. It can be found that the addition of magnesium oxide to the Ca/Al = 7/1 has a positive effect on the stability of the sorbent. Although the initial capture capacity of Ca/Mg/Al = 7/2/1 was lower than the other two sorbents because the amount of CaO was diluted, the capture capacity was stably maintained at about 30 wt% from the third cycle. The better stabilities of these three sorbents can be attributed to the presence of layered double hydroxides in their precursors, which is beneficial for maintaining the chemical structures of the sorbents [5]. Although it is verified that MgO can improve the performance of CaO-based sorbents over multiple cycles [4], it possessed limited improvement when it existed alone. On the other hand, if it was co-existing with alumina oxide, the performance over multiple cycles can be further improved.

Figure 3. 10 cycles of carbonation/calcination for the Ca/Mg/Al = 7/2/1, Ca/Mg/Al = 7/1/1, Ca/Al = 7/1, Ca/Mg = 7/1, limestone at 750°C in 20% CO₂/80% N₂ for 30 min and 930°C in 100% CO₂ for 15 min.

Figure 4 demonstrates the results of Ca/Al = 7/1 and Ca/Mg/Al = 7/2/1 over 40 cycles test under the same experimental conditions as the 10 cycles test. It was found that although the initial capture capacity of Ca/Mg/Al = 7/2/1 was worse than that of Ca/Al = 7/1, the capture capacity maintained at about 28~30 wt% from the third cycle, resulting in the capture capacity of Ca/Mg/Al = 7/2/1 was higher than that of Ca/Al = 7/1 from the 13th cycle. The stability of Ca/Mg/Al = 7/2/1 and Ca/Al = 7/1 over 40 cycles test was 69% and 50%, respectively. Hence, the latter had significant advantages over long periods of operation.

Figure 5 is the XRD patterns of Ca / Mg / Al = 7/2/1, Ca / Al = 7/1, Ca / Mg = 3/1, limestone after calcination (a) and after 10 or 40 carbonation/calcination cycles test (b). It also contains the pattern of Ca/Mg/Al = 7/2/1 as prepared. The Bragg reflection peaks observed for the calcined samples correspond to CaCO₃, Ca(OH)₂, and MgO. In addition, the phase of Ca₃Al₂O₆(H₂O)₆ was also formed in Ca/Al = 7/1 and Ca/Mg/Al = 7/2/1. After the samples were calcination, they were placed for a while before analysis. Therefore, the phase of CaCO₃ may be due to the reaction of CaO with CO₂ from the...
atmosphere. The phase of hydrotalcite was found in Ca/Mg/Al = 7/2/1 as prepared, and this phase decomposed to small Ca-Al-O structures, such as Ca$_3$Al$_2$O$_6$(H$_2$O)$_6$, at above 600°C, the structures which contributed to the stability of the overall CaO structure [5]. The Bragg reflection peaks observed for the samples after cycles test correspond to CaO, CaCO$_3$, MgO, and Ca(OH)$_2$. The sample after cycles test was additionally subjected to a calcination procedure, so that there was a CaO phase. Table 1 demonstrates the crystallite sizes of CaCO$_3$ (limestone) or Ca(OH)$_2$ in the calcined samples or CaO in the used samples obtained by the Scherrer Equation. It can be obtained that the crystallite sizes of the synthetic samples after calcination were 11.9 ~ 16.7 nm, which were significantly smaller than that of limestone. On the other hand, the crystallite sizes of the synthetic samples after cycles test were increased to 26.16 ~ 32.56 nm, which were close to that of limestone. This implied that the stability of the materials may be related to the microstructure of pores and cannot be explained solely by the crystallite sizes variation.

![Figure 5. XRD patterns of sorbents with different compositions after calcination (a) and after 10 cycles or 40 cycles test (b) ((a): (1) limestone, (2) Ca/Mg = 3/1, (3) Ca/Al = 7/1, (4) Ca/Mg/Al = 7/2/1, (5) Ca/Mg/Al = 7/2/1 as prepared. (b) limestone, (2) Ca/Mg = 3/1, (3) Ca/Al = 7/1, (4) Ca/Mg/Al = 7/1/1.)](image)

| Sample                  | D (nm)  | Sample                  | D (nm)  |
|-------------------------|---------|-------------------------|---------|
| Ca/Mg/Al = 7/2/1 calcined | 13.19   | Ca/Mg/Al = 7/2/1 used    | 32.56   |
| Ca/Al = 7/1 calcined    | 11.90   | Ca/Al = 7/1 used        | 26.16   |
| Ca/Mg = 3/1 calcined    | 16.69   | Ca/Mg = 3/1 used        | 32.56   |
| limestone calcined      | 35.87   | limestone used          | 33.30   |

4. Conclusions
In this study, a series of CaMgAl oxide materials with different CaMgAl molar ratios for CO$_2$ capture, derived from LDHs, CaMgO mixed oxides and limestone were prepared to test their performances at realistic CaL conditions. They were tested at different regeneration temperatures, regeneration times, and in different CO$_2$ concentrations at the regeneration stage to find out the optimal treatment conditions. The multicycle capture capacities of these materials were also examined. Materials regenerated for 15 minutes at 930°C and 70~100% CO$_2$ had good performances. The Ca/Al = 7/1 materials possessed well capture capacity and multicycle stability compared with that of limestone. Addition of magnesium oxide can further improve its performance. In the 40 cycles test, although the initial capture capacity of the CaMgAl material was lower than that of the CaAl materials, because of the better stability of the former, its capture performance was better than that of the CaAl material at
the end of the loop. This study confirmed that these materials have the potential to be applied in CO\textsubscript{2} capture and hydrogen production in the future.

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5. References
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