Behavior of CaTiO₃/Nano-CaO as a CO₂ Reactive Adsorbent

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This study focuses on the preparation of a CaTiO₃-coated nano-CaO-based CO₂ adsorbent (CaTiO₃-nano-CaO) for the improvement of sorption properties. The CaTiO₃-coated nano-CaO adsorbent was prepared by forming Ti(OH)₄ from the hydrolysis of titanium alkoxide in a nano-CaCO₃ suspended solution. The resulting Ti(OH)₄-coated nano-CaCO₃ was then heated and calcined. Test results from transmission electron microscopy and scanning electron microscopy with energy dispersive X-ray spectroscopy show that an obvious film of TiO₂ was formed on the surface of nano-CaCO₃ after heating. X-ray diffraction analysis also showed that the nano-CaTiO₃ layer was formed at 750 °C, a calcination temperature that causes the reaction of TiO₂ with nano-CaO. The cyclic tests of reactive sorption capacity were conducted in a thermogravimetric analyzer under the following conditions: 0.02 MPa CO₂ partial pressure, carbonation temperature of 600 °C, and calcination temperature of 750 °C. Test results showed that CaTiO₃ coated onto the nano-CaO caused a significant improvement in the capacity for reactive sorption. Nano-CaO that had an optimum content of 10 wt % TiO₂ showed significantly stable CO₂ reactive sorption capacity (5.3 mol/kg) after 40 cyclic carbonation—calcination runs compared to the reactive sorption capacity of CaO without TiO₂ coating (3.7 mol/kg).

1. Introduction

A CO₂ adsorption process that employs a solid CaO-based reactive adsorbent plays an important and effective role in the capture of CO₂ for many industrial purposes. For example, CO₂ sorption enhances reformation for hydrogen production,1–4 promotes CO₂ removal from flue gas,5,6 and can be utilized for chemical heat pumps7 and energy storage systems. Although many materials could be potentially used for CO₂ adsorption, CaO has been identified as the most promising candidate8 because of its stoichiometric reactive sorption capacity, low cost, and the abundance of its natural precursors. However, the natural precursors of CaO-based adsorbents, such as limestone and dolomite that both contain CaCO₃, suffer from the rapid decay of CO₂ reactive sorption capacity during multiple carbonation—calcination reaction cycles. Abanades9 demonstrated a significant decrease in reactive sorption capacity from about 75% during the first carbonation cycle to about 20% in the 14th cycle using 100–800 μm limestone particles.

Aside from its natural precursors, Kuramoto10 reported a drop in the carbonation conversion of reagent grade CaCO₃ and Ca(OH)₂ from 50% in the first cycle to 12.2% in the sixth cycle. Florin11 showed a decline in conversion of CaO adsorbents derived from CaCO₃ (Sigma Aldrich, ≤45 μm) from 69% in the first cycle to only 13% after 50 reaction cycles. Alvarez12 found that the decay of the reactive sorption capacity of limestone (400–600 μm) was accompanied by an obvious decrease in the pore volume and surface area. He attributed these to the occlusion of pores and shrinkage of CaO during cycling, which are consequences of sintering. Fierro13 had proposed a new model to describe the processes of calcination and sintering. He concluded that the main reason for reactive sorption capacity decay is the sintering of CaO during cyclic carbonation—calcination runs. This decay results in subsequent decreases in surface area and porosity and increases in the average CaO particle size.

Several investigations were conducted with the goal of improving the resistance of CaO to sintering. These involved adding MgO,14 as well as Ca₁₂Al₁₄O₃₃, to support the CaO-based CO₂ adsorbent.15 The author found that nano-CaCO₃ had many advantages in comparison to micro-CaCO₃. These advantages include higher reactive sorption capacity, fast reaction rate, and a significant improvement in the durability of the adsorbent.16 The additional investigations have focused on SiO₂-coated nano-CaCO₃ as the precursor of nano-CaO-based CO₂ adsorbents. The use of the sol—gel method produced a good reactive sorption capacity of 6.4 mol/kg of the first cyclic run and 4.7 mol/kg of the 20th cyclic run.17 However, even though the many coating methods provided increased durability during high temperature carbonation and calcination cycles, the overall durability of CaO-based CO₂ adsorbents is still too low for commercial applications.

The hydrolysis method is another technique for preparing metal oxides. Alhar 18 briefly exploited the hydrolysis of [Ca(OC₄H₉)₂] and [Ti(OC₂H₅)₃] to form a mixture of CaO and CaTiO₃. Guo19 studied monodispersed silica siloxa spheres coated with titania by using Ti(OC₂H₅)₄, and Li20 coated TiO₂ on SiO₂ cores via the hydrolysis of tetrabutyl orthotitanate (TBOT). This research reports on the preparation of nano-CaO coated with a nanoscale layer of CaTiO₃ via hydrolysis and calcination to form a CO₂ adsorbent. Its durability performance and reasons for sintering resistance were investigated.

2. Experimental Section

2.1. Reagents and Instruments. Nano-CaCO₃ (>95% purity) with a particle size of 70 nm (Hu Zhou Ling Hua Ltd. China) was used as the CaO-based adsorbent precursor. TiO₂ powder (178 nm, Sinopharm Chemical Reagent Co., Ltd.) and tetrabutyl titanate Ti(OC₄H₉)₄ (Sinopharm Chemical Reagent Co., Ltd.) were used as sources of TiO₂.

A thermogravimetric analyzer (TGA, Pyris1, Perkin-Elmer) was used for reactive sorption capacity measurements. The crystalline phases of the components of the adsorbent were determined using an X-ray diffractometer (XRD, D/MAX-RA, Rigaku, Japan). The morphology of the adsorbent was investigated using a transmission electron microscope (TEM, JEM-
1230, JEOL, Japan) and scanning electron microscope (SEM, S-4800, HITACHI, Japan). The Ti content was measured by energy-dispersive X-ray analysis (EDX, EX350, HORIBA, Japan). Brunauer—Emmet—Teller (BET) surface area and Barrett—Joyner—Halenda (BJH) desorption average pore diameter analyses were conducted by nitrogen physisorption at liquid N₂ temperatures using a Micromeritics ASAP 2020 apparatus.

2.2. Preparation of TiO₂(Nano-CaCO₃). A total of 4.26 g of Ti(OC₄H₉)₄ was dissolved in 25 mL of dehydrated ethanol to form a clear solution. A 9 g portion of nano-CaCO₃ was dispersed in dehydrated ethanol by ultrasonic methods and then mixed with the clear solution to form a suspension. A 3 g portion of distilled water was added dropwise into the suspension while stirring. Solids were collected by vacuum filtration. The solid product was obtained through drying and heat treatment at 500 °C for 3 h. The first obtained sample is designated as sample A₁.

The mechanism of forming Ti(OH)₄ by the hydrolysis of Ti(OC₄H₉)₄ proceeds in the following reactions steps (1) – (4):

\[
\text{Ti(OC₄H₉)₄} + \text{H₂O} \rightarrow \text{Ti(OC₄H₉)₃(OH)} + \text{C₄H₉OH}
\]

(1)

\[
\text{Ti(OC₄H₉)₃(OH)} + \text{H₂O} \rightarrow \text{Ti(OC₄H₉)₂(OH)}₂ + \text{C₄H₉OH}
\]

(2)

\[
\text{Ti(OC₄H₉)₂(OH)}₂ + \text{H₂O} \rightarrow \text{Ti(OC₄H₉)(OH)}₃ + \text{C₄H₉OH}
\]

(3)

\[
\text{Ti(OC₄H₉)(OH)}₃ + \text{H₂O} \rightarrow \text{Ti(OH)}₄ + \text{C₄H₉OH}
\]

(4)

The hydrolyzed product was heated to decompose Ti(OH)₄ to TiO₂ at a temperature of 500 °C according to the following reactions (5) and (6):

\[
\text{H₂TiO₄} \rightarrow \text{H₂TiO₃} + \text{H₂O}
\]

(5)

\[
\text{H₂TiO₃} \rightarrow \text{TiO₂} + \text{H₂O}
\]

(6)

A 9 g portion of nano-CaCO₃ was dispersed in distilled water by ultrasonic methods, and 1 g of TiO₂ powder was stirred into the suspension. The solids were collected by vacuum filtration and dried. The product obtained in this procedure is designated as sample A₁.

3. Results and Discussion

3.1. Properties of the TiO₂/Nano-CaCO₃. 3.1.1. XRD Pattern. To investigate the coating of nano-TiO₂ on the surface of nano-CaCO₃, XRD analysis was performed on sample A₁. TiO₂ was introduced into the CaCO₃ structure by hydrolysis (Figure 1).

3.1.2. TEM Images. TEM images of nano-CaCO₃ and sample A₁ are shown in Figure 2. Sample A₁ exhibited a cubic crystal, according to Figure 2b. Sample A₁, prepared in a dehydrated ethanol environment, exhibited a flocculelike layer on nano-CaCO₃, according to Figure 2a. This layer was composed of a TiO₂ coating. The thickness of the TiO₂ coating was less than 10 nm.

3.1.3. SEM-EDX Images. The SEM images and EDX patterns of the samples A₁ and B₁ are shown in Figure 3. Compared to that of nano-CaCO₃, the particles of sample A₁ had a rough surface layer, where Ti metal was detected by EDX. These confirmed the coating structure. It also confirmed that the hydrolysis product of TiO₂ from titanium alkoxide was indeed formed on the particle surface of sample A₁.

3.1.4. Durability of TiO₂/Nano-CaCO₃ Adsorbents. Durability studies of the CO₂ adsorbents at a carbonation temperature of 600 °C and a calcination temperature of 750 °C on nano-CaCO₃ and the samples A₁ and B₁ are shown in Figure 4. Nano-CaCO₃ recorded a reactive sorption ratio of 84.3% in the

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**Figure 1.** XRD pattern of sample A₁.

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**Figure 2.** TEM images of nano-CaCO₃ and sample A₁.
first run and the lowest reactive sorption ratio at 37.7% in the tenth run. Sample B1 had a higher reactive sorption capacity than nano-CaCO3. This indicated that nano-CaCO3 mixed with TiO2 powder improved the sorption durability of adsorbents. The attenuation trend after 10 runs was also comparable with that of nano-CaCO3. In comparison, sample A1 showed more stable reactive sorption ratios of 80.6% in the first run and 61.4% in the tenth run. These results indicate that adsorbents prepared via the coating method performed better than those prepared via a simple mixing method.

3.2. Properties of CaTiO3/Nano-CaO Adsorbents. Although TiO2-coated nano-CaCO3 had a higher reactive sorption ratio, as shown in sample A1, there was still obvious reactive sorption ratio decay. To improve the durability of sorption, calcination of TiO2/nano-CaCO3 to form CaTiO3/nano-CaO was performed.

3.2.1. CaTiO3 Identification at Different Calcination Temperatures. To investigate the effects of different calcination temperatures on the formation of CaTiO3 from the reaction between CaO and TiO2, XRD was performed. It examined the formation of CaTiO3 from sample A1 at different temperatures. Three temperatures, 750, 800, and 850 °C, were selected for the calcination of sample A1 for 1 h. Results from this experiment are shown in Figure 5. The figure shows that CaTiO3 already formed at 750 °C but retains only a weak characteristic peak. This temperature is much lower than the CaTiO3 formation temperature, 1200 °C, which was reported in a chemistry handbook.22 Thus, this supports the formation of a nanoscale layer of CaTiO3 at a lower temperature. At a temperature of 850 °C, the diffraction peaks of CaTiO3 were much stronger, indicating that nano-CaCO3 had completely decomposed to CaO.

3.2.2. Carbonation/Calcination Durability. The reactive sorption capacity of sample A1, calcined at different tempera-
tures in the range of 750–850 °C, was tested. The sorption capacities after 10 cyclic runs at a sorption temperature of 600 °C and a decomposition temperature of 750 °C are shown in Figure 6. The results show that sample A1 calcined below 800 °C had a low reactive sorption capacity. In contrast, sample A1 calcined at 850 °C showed an increase in CO2 reactive sorption capacity through several initial cycles. This increase in reactive sorption capacity was maintained at 5.3 mol/kg after 10 runs. Manovic disclosed a similar phenomenon called self-reactivation. The results in Figure 6 were consistent with the results shown in Figure 5. Thus, it can be said that sample A1 calcined below temperatures of 850 °C can form a compound with a stable content of CaTiO3 and increased durability of CO2 reactive sorption capacity.

The results of the reactive sorption capacity of the nano-CaO, and samples A2 and B2 are shown in Figure 7. The reactive sorption capacity of nano-CaO increased in the first several cycles then decreased slightly. In particular, sample A2 reached a higher reactive sorption capacity than the other samples within three runs, keeping the same reactive sorption capacity after 10 cycles. The reactive sorption capacities of samples A2 and B2 were much higher than that of nano-CaO. Sample A2, which was prepared by the coating method, was more durable than sample B2 to which TiO2 was added via a mixing method.

A comparison of the multicycle sorption properties of samples A1 and A2 are shown in Figure 8. After 40 cycles, the reactive sorption capacity of TiO2/nano-CaCO3 was lower than that of CaTiO3/nano-CaO, decaying continuously as the cycles continued. On the other hand, samples of CaTiO3/nano-CaO retained their durability through all experimental runs.

The reactive sorption capacity of sample A2 in the tenth cycle was 5.3 mol/kg. The reactive sorption capacity of nano-CaO with a TiO2 coating layer was 1.6 mol/kg higher than that of nano-CaO without the TiO2 coating. One possible reason for this is that CaTiO3 has a higher melting point (2200 K) and this increases the sintering temperature of the adsorbent. As shown in Figure 8, the reactive sorption capacity of A2 slightly increased within 10 runs of carbonation and calcination. From the 10th to the 40th run, the reactive sorption capacity was almost stable. The results of BET surface area measurements on A1 before and after 10 runs are shown in Table 1. The results showed a consistent trend of surface area increase with the increase of reactive sorption capacity.

As shown in Figure 9, SEM morphology analysis showed that CaTiO3/nano-CaO particles have an average size of 80 nm that is maintained after 10 cyclic runs. The CaTiO3 outer layer has high thermal stability and acts as an effective barrier that resists the
sintering of CaO, which keeps the structure of the adsorbent more stable even after long-term exposure to elevated temperatures.

3.3. Effects of TiO2 Content on Cyclic Performances of CaTiO3/Nano-CaO. In order to investigate the effects of TiO2 content on cyclic performances, five samples with different TiO2 wt % were prepared by following the synthesis method of sample A2. Details are listed in Table 2.

TGA test results of reactive sorption capacity are shown in Figure 10. The results showed an optimum TiO2 content of 10% among compounds containing 5, 8, 10, 15, and 20% TiO2. It is surmised that when the TiO2 content was lower than 10 wt %, the TiO2 amount finally produced from hydrolysis was not enough to cover the surface area of nano-CaCO3. Thus, the resistance to sintering became weak after high temperature calcination. In contrast, when the TiO2 content was higher than 10 wt %, some active nano-CaO reacted with TiO2 to form CaTiO3, thus causing the decrease of reactive sorption capacity.

4. Conclusion

The surface of nano-CaCO3 can be coated with a nano-TiO2 film via Ti(OC4H9)4 hydrolysis and using dehydrated ethanol as a dispersant. A layer of CaTiO3 was formed by calcination at temperatures until 850 °C, thus preventing the nano-CaO particles from coming into contact with each other under high temperatures. Good results were obtained of CaTiO3/nano-CaO adsorbent for the durability of reactive sorption capacity as tested by TGA. Under the same conditions, the 10th cyclic run of the synthesized coated adsorbent had a reactive sorption capacity of 5.3 mol/kg, which was 1.6 mol/kg higher than that of the uncoated nano-CaCO3 adsorbent. Nano-CaCO3 coated with 10 wt % TiO2 had a maximum reactive sorption capacity during multiple carbonation–calcination cyclic runs.

Acknowledgment

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Literature Cited


Table 2. Preparation of TiO2 Coated nano-CaCO3

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<tr>
<th>nano-CaCO3 (g)</th>
<th>Ti(OC4H9)4 (g)</th>
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Figure 9. (a) SEM image of sample A2 before multiple carbonation–calcination runs. (b) SEM image of sample A2 after 10 carbonation–calcination runs.

Figure 10. CO2 reactive sorption capacity for sorbents with different TiO2 wt % (carbonation at 600 °C in 0.02 MPa CO2 partial pressure, calcination at 750 °C in N2).


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