

# Properties of a Nano CaO/Al<sub>2</sub>O<sub>3</sub> CO<sub>2</sub> Sorbent

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This project studied the properties of nano CaO/Al<sub>2</sub>O<sub>3</sub> as a high-temperature CO<sub>2</sub> sorbent for its use in an adsorption enhanced reforming reaction. The sorbent containing nano CaCO<sub>3</sub> precursors and aluminum oxide was prepared, and evaluation of the CO<sub>2</sub> adsorption properties by a thermogravimetric analyzer, the results show that nano CaO/Al<sub>2</sub>O<sub>3</sub> has a faster decomposition rate and has a higher CO<sub>2</sub> adsorption ratio than micro CaO/Al<sub>2</sub>O<sub>3</sub>. The maximum adsorption ratio occurs at temperatures of 650 °C under a CO<sub>2</sub> partial pressure of 0.33 atm. Durability studies show that the CO<sub>2</sub> adsorption ratio remains at 68.3% after 50 cyclic runs under a carbonation temperature of 650 °C and calcination temperature of 800 °C, respectively. XRD, SEM, and BET were used for studying the change of micro characteristics of the CO<sub>2</sub> sorbents before and after multiple carbonation–calcination runs. The results showed that the pore size of CaO/Al<sub>2</sub>O<sub>3</sub> sorbents was enlarged and that a new substance (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>) was formed even under a temperature of 800 °C for the function of keeping the compound stable and durable.

## 1. Introduction

Hydrogen has been widely used in petroleum, chemical, energy, and metallurgical industries. Steam-methane reforming is one of the inexpensive techniques to produce hydrogen and has a large share in the hydrogen producing market.<sup>1</sup> CO<sub>2</sub> adsorption enhanced methane reforming (AER) is an emerging technology for directly producing a high concentration of hydrogen and, hence, is becoming a hot research topic.<sup>2</sup> High-temperature CO<sub>2</sub> sorbents are the bottleneck for the AER technique used in industries because the properties of high-temperature CO<sub>2</sub> sorbents strongly affect the cost of hydrogen produced. High-temperature CO<sub>2</sub> adsorbents also have been widely used in the capture of CO<sub>2</sub> from fuel gas to control greenhouse effects. Thus, it is important to study the properties of high-temperature CO<sub>2</sub> adsorbents at the present time.

Research on CaO based CO<sub>2</sub> adsorbents can usually be found to be focused on removing CO<sub>2</sub> from flue gas and energy pumps.<sup>3,4</sup> Recently, the properties of CaO based CO<sub>2</sub> adsorbents and their application in sorption enhanced steam-methane reforming have been studied. Sorbent properties including the CO<sub>2</sub> adsorption ratio, adsorption capacity, and durability under different operation conditions have been studied. Li et al.<sup>5,6</sup> prepared a CaO based CO<sub>2</sub> sorbent mixed with Ca(OH)<sub>2</sub> and Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. The thermogravimetric analysis (TGA) results showed that after 50 carbonation–calcination cyclic runs, the adsorption ratio was retained at 40%. Using an experimental scale fixed bed, Lee<sup>7</sup> evaluated a CaO based CO<sub>2</sub> adsorbent in a temperature range of 650–750 °C, which gave a CO<sub>2</sub> adsorption ratio between 8 and 18%. Wu et al.<sup>8</sup> prepared an adsorbent using micro grade Ca (OH)<sub>2</sub> powder and evaluated its stability. The CO<sub>2</sub> adsorption ratio was 46% after 10 carbonation–calcination cyclic runs.

Nano CaCO<sub>3</sub> normally is used as a packaging material in plastics;<sup>9</sup> however, there not much attention has been paid to the use of CaO based CO<sub>2</sub> sorbents. Wu<sup>10</sup> studied silicon dioxide

coated nano CaCO<sub>3</sub>, giving rise to a CO<sub>2</sub> adsorption ratio of 63.0% after 20 cyclic runs. The results show a significant advantage of using nano CaCO<sub>3</sub> as CaO based precursor. In this paper, the preparation and evaluation of a nano CaO/Al<sub>2</sub>O<sub>3</sub> CO<sub>2</sub> adsorbent were studied in detail.

## 2. Experimental Procedures

**2.1. Agents and Instruments.** Nanometer grade calcium carbonate CaCO<sub>3</sub> (>95%) with a particle size of 70 nm, micro CaCO<sub>3</sub> (>95%) with a particle size of 5 μm, Ca(OH)<sub>2</sub> (>95%) with a particle size of 5 μm, aluminum sol solid, and sodium hexametaphosphate, AR grade were used. Kaoline and Bantomite, industrial grade powders, with particle sizes of lower than 300 mesh were also used.

The following instruments were used: a thermogravimetric analyzer, Pyris1 (PerkinElmer), for adsorption properties measurement, X radial diffractor, D/MAX-2400X (Cu Kα, nm), scanning electron microscope, JEM-1000, and an OMNISORP-100CS instrument for surface area analysis.

**2.2. Sorbent Preparation.** CaO/Al<sub>2</sub>O<sub>3</sub> sorbent preparation (CaO 35%): 5 g of nano calcium carbonate was added in a beaker, and 30 g of aluminum sol was added with stirring to form a liquid in suspension. Two grams of sodium hexametaphosphate was added, and this mixture was strongly stirred to separate the nano calcium carbonate particles in the liquid suspension. Then, the mixture was heated and pressed to the pellet. The other CaO content sorbent can be prepared by adjusting the amount of CaO and aluminum sol.

**2.3. Experimental Methods.** The TGA evaluation system is shown in Figure 1. A total of 0.5 mg of adsorbent was added to a nacelle. The CO<sub>2</sub> gas was switched on to perform adsorption and switched off to perform calcination of the sorbent. The weight data of in situ measurements were transmitted to the computer for analysis. The adsorption ratio and adsorption capacity were calculated. The adsorption ratio is defined as the adsorbed CO<sub>2</sub> mol amount divided by the CaO mol amount. During the CO<sub>2</sub> adsorption operation, there were two gases: CO<sub>2</sub> and balanced N<sub>2</sub>. The flow rate of CO<sub>2</sub> was 20 mL/min, and the flow rate of balanced N<sub>2</sub> was 40 mL/min. Thus, CO<sub>2</sub> shares

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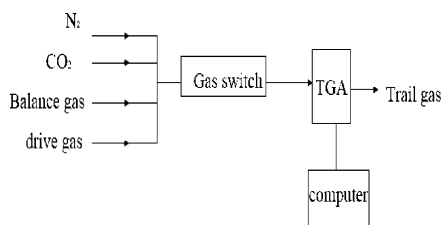


Figure 1. Scheme of TGA as an experimental reactor.

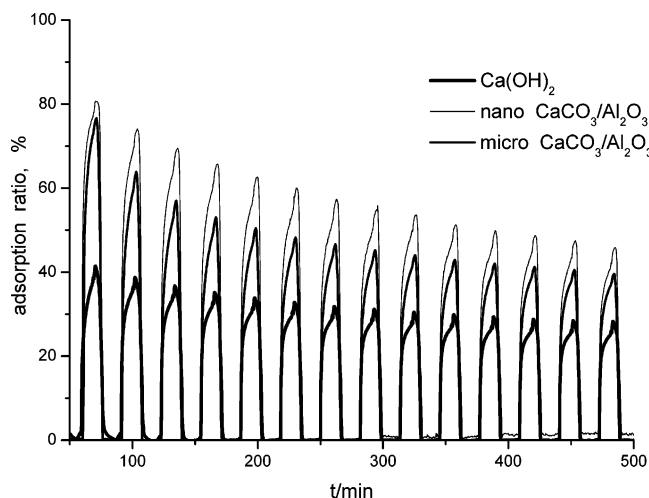


Figure 2. Cycle adsorption performance with different precursors ( $T_{ad} = 600\text{ }^{\circ}\text{C}$ ,  $T_{de} = 800\text{ }^{\circ}\text{C}$ ,  $P_{CO_2} = 0.33\text{ atm}$ , and particle size = 60 to  $\sim 80\text{ }\mu\text{m}$ ).

33% partial pressure. The temperature raise rate of TGA was  $15\text{ }^{\circ}\text{C}/\text{min}$ .

To compare the adsorption properties during the different cyclic runs, the adsorption ratio was defined as each isothermal absorption of the  $\text{CO}_2$  mol amount within 10 min divided by the  $\text{CaO}$  mol amount in the initial mass of sorbent. The adsorption capacity was defined as the isothermal adsorption  $\text{CO}_2$  mol within 10 min divided by the initial mass of sorbent, as presented in eqs 1 and 2

$$\text{adsorption ratio} = \frac{\text{CO}_2 \text{ adsorption mol amount}}{MY/56} 100 (\%) \quad (1)$$

$$\text{adsorption capacity} = \frac{\text{CO}_2 \text{ adsorption mol amount}}{M} 1000 (\text{mol kg}^{-1}) \quad (2)$$

where  $M$  is the initial mass of sorbent, and  $Y$  is the content of  $\text{CaO}$  in the sorbent.

### 3. Results and Discussion

**3.1. Evaluation of Precursors and Binders.** Three types of sorbents were prepared using nano  $\text{CaCO}_3$ , micro  $\text{CaCO}_3$ , and  $\text{Ca(OH)}_2$  as the  $\text{CaO}$  precursor, respectively, according to the sorbent preparation procedure of section 2.2. The TGA instrument was operated at  $600\text{ }^{\circ}\text{C}$  for carbonation for 40 min and at  $800\text{ }^{\circ}\text{C}$  for calcination for 5 min. The results of 15 cyclic carbonation–calcination runs are shown in Figure 2.

As can be seen in Figure 2, the nano  $\text{CaCO}_3$  precursor adsorbent has a higher adsorption ratio than that of the micro  $\text{CaCO}_3$  and micro  $\text{Ca(OH)}_2$  precursor adsorbents. The adsorption ratio of the nano  $\text{CaCO}_3$  precursor adsorbent decreases with cyclic runs, but it remained at 44% after 15 runs, much higher than that of the micro  $\text{Ca(OH)}_2$  precursor adsorbent. On the

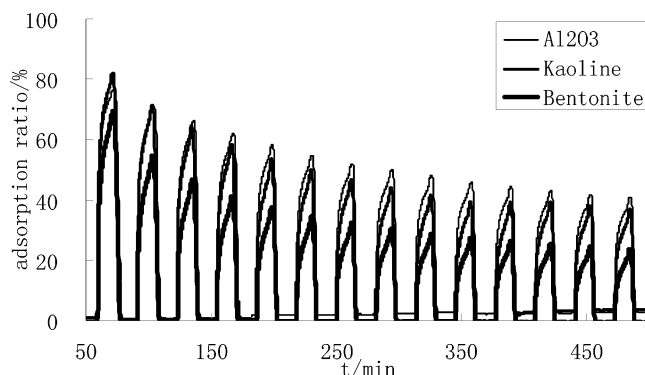


Figure 3. Adsorption ratio for different carriers ( $T_{ad} = 600\text{ }^{\circ}\text{C}$ ,  $T_{de} = 800\text{ }^{\circ}\text{C}$ ,  $P_{CO_2} = 0.33\text{ atm}$ , and particle size = 60 to  $\sim 80\text{ }\mu\text{m}$ ).

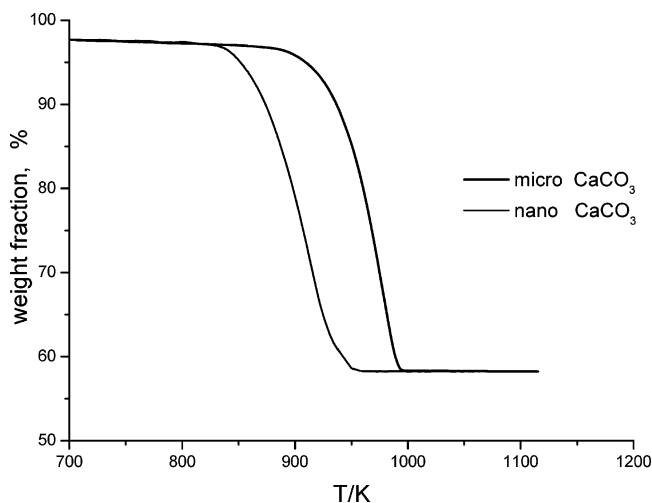


Figure 4. Decomposition curves of nano  $\text{CaCO}_3$  and micro  $\text{CaCO}_3$  decomposition curves (particle size = 60 to  $\sim 80\text{ }\mu\text{m}$ ).

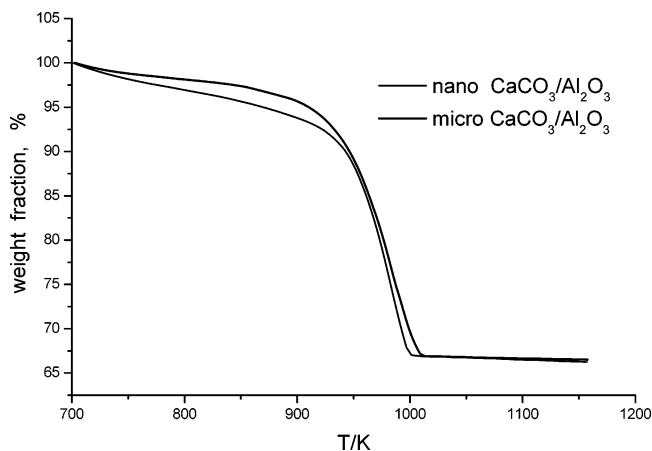
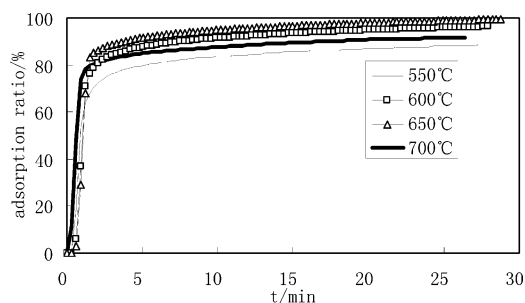


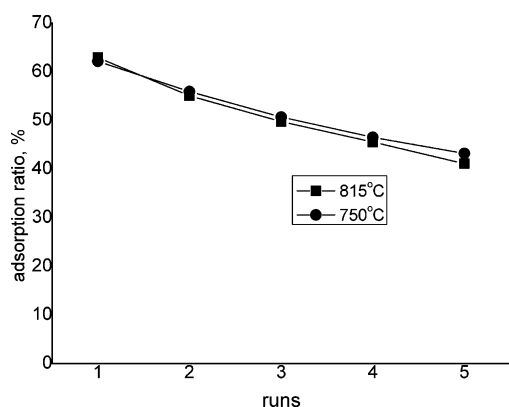
Figure 5. Decomposition curves of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent and micro  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent (particle size = 60 to  $\sim 80\text{ }\mu\text{m}$  and  $\text{CaO} = 35\%$ ).

other hand, the micro  $\text{Ca(OH)}_2$  precursor adsorbent showed more stability for  $\text{CO}_2$  adsorption. The adsorption capacity of each sorbent can be calculated with eqs 1 and 2 with a  $\text{CaO}$  content of 42.0%.

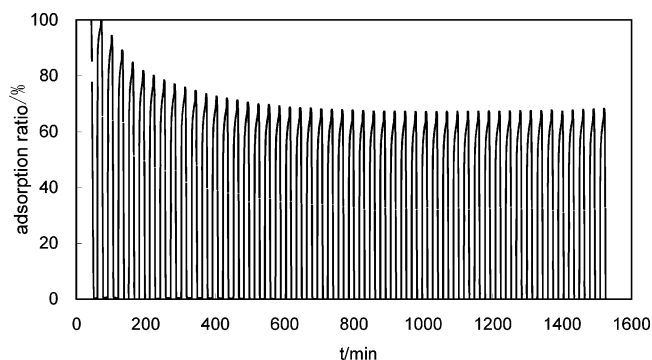
Figure 3 shows the adsorption ratios for a different carrier with a  $\text{CaO}$  content of 42.0% using nano  $\text{CaCO}_3$  as the precursor. The results clearly show that the  $\text{Al}_2\text{O}_3$  carrier is better than Kaoline or Bantonite in terms of adsorption ratio. The possible reason is that Kaoline and Bantonite are powders, otherwise the  $\text{Al}_2\text{O}_3$  carrier uses a sol material. It is advantageous for the separation of nano  $\text{CaCO}_3$  powder to form a suspension



**Figure 6.** Adsorption ratio at different temperatures ( $T_{de} = 800\text{ }^{\circ}\text{C}$ ,  $P_{\text{CO}_2} = 0.33\text{ atm}$ , and particle size =  $60\text{--}80\text{ }\mu\text{m}$ ).



**Figure 7.** Adsorption ratio of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent at different decomposition temperatures ( $T_{ad} = 600\text{ }^{\circ}\text{C}$ ,  $T_{de} = 800\text{ }^{\circ}\text{C}$ ,  $P_{\text{CO}_2} = 0.33\text{ atm}$ , and particle size =  $60\text{ to } \sim 80\text{ }\mu\text{m}$ ).

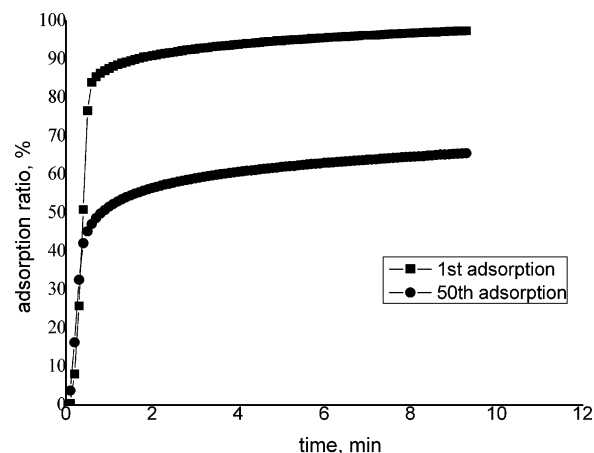


**Figure 8.** TGA data for 50 runs of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent ( $T_{ad} = 650\text{ }^{\circ}\text{C}$ ,  $T_{de} = 800\text{ }^{\circ}\text{C}$ ,  $P_{\text{CO}_2} = 0.33\text{ atm}$ , and particle size =  $60\text{ to } \sim 80\text{ }\mu\text{m}$ ).

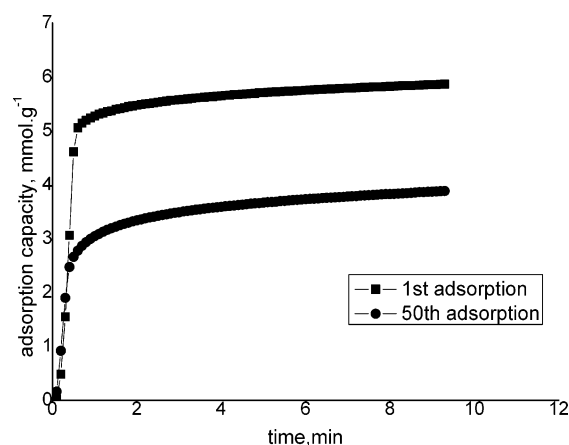
liquid. In this paper, the sorbent prepared by the nano  $\text{CaCO}_3$  precursor with aluminium sol has been studied further.

**3.2. Nano  $\text{CaO}/\text{Al}_2\text{O}_3$  Decomposition and Adsorption Properties.** The decomposition temperature of the  $\text{CO}_2$  sorbent is important for evaluating its feasibility since energy was saved during the regeneration of sorbent. Figure 4 shows the decomposition curves of nano  $\text{CaCO}_3$  and micro  $\text{CaCO}_3$ . The starting decomposition temperature of nano  $\text{CaCO}_3$  is  $879.6\text{ K}$ , and the complete decomposition temperature is  $828.4\text{ K}$ , while the start decomposition temperature of micro  $\text{CaCO}_3$  is  $927.7\text{ K}$ , and the complete decomposition temperature is  $986.6\text{ K}$ . It is clear that nano  $\text{CaCO}_3$  has a lower decomposition temperature because of its higher surface energy.

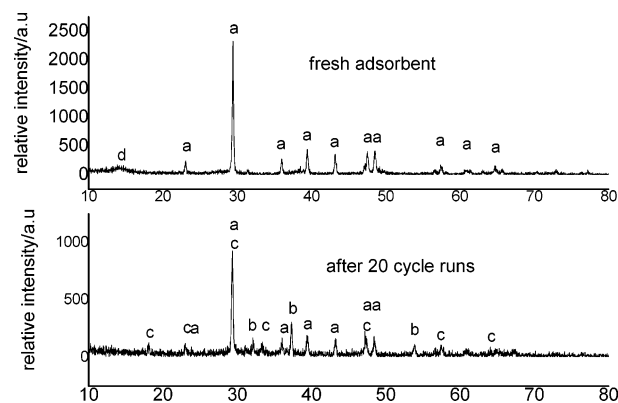
Figure 5 shows the decomposition curves of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  and micro  $\text{CaO}/\text{Al}_2\text{O}_3$ ; the decomposition rate of the nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent is faster than the micro  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent in the beginning of the decomposition, and the nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent has a lower complete decomposition temperature. Even the micro size of the  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent is almost the same for the nano  $\text{CaCO}_3$  precursor and micro  $\text{CaCO}_3$  precursor;



**Figure 9.** Adsorption ratio for the first and 50th adsorption run ( $T_{ad} = 650\text{ }^{\circ}\text{C}$ ,  $T_{de} = 800\text{ }^{\circ}\text{C}$ ,  $P_{\text{CO}_2} = 0.33\text{ atm}$ , and particle size =  $60\text{ to } \sim 80\text{ }\mu\text{m}$ ).



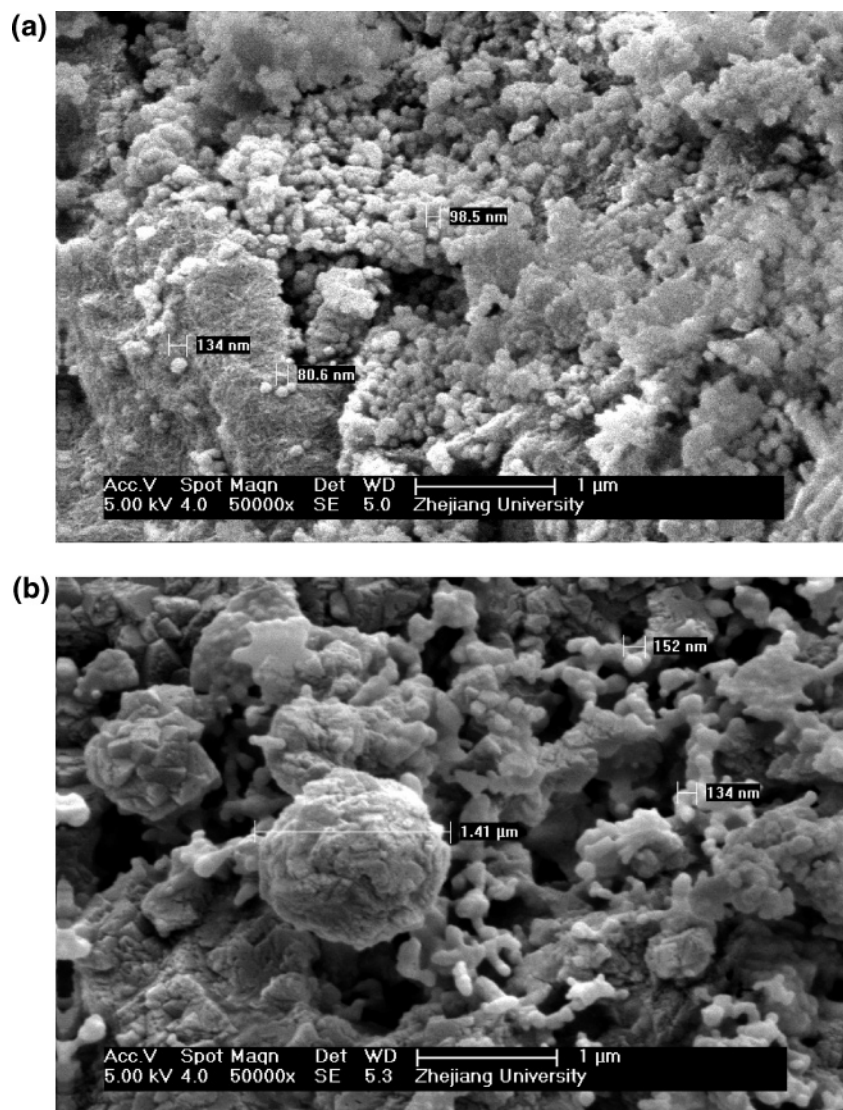
**Figure 10.** Adsorption capacity for the first and 50th adsorption run ( $T_{ad} = 650\text{ }^{\circ}\text{C}$ ,  $T_{de} = 800\text{ }^{\circ}\text{C}$ ,  $P_{\text{CO}_2} = 0.33\text{ atm}$ , and particle size =  $60\text{ to } \sim 80\text{ }\mu\text{m}$ ).



**Figure 11.** Comparison of XRD charts of adsorbents (a:  $\text{CaCO}_3$ ; b:  $\text{CaO}$ ; c:  $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$ ; and d:  $\text{Al}_2\text{O}_3$ ).

however, the nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent has an obvious lower decomposition temperature than the micro  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent. The reason may be that the nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent still shows properties of nano materials since nano  $\text{CaCO}_3$  has a larger surface energy and causes a decrease in the decomposition temperature. A detailed explanation needs further study.

A nano  $\text{CaO}/\text{Al}_2\text{O}_3$  adsorbent containing  $\text{CaO } 33.7\%$  was prepared. The results of the adsorption ratio at  $550\text{--}700\text{ }^{\circ}\text{C}$  for a step batch of  $50\text{ }^{\circ}\text{C}$  are shown in Figure 6. It is clear that the maximum adsorption ratio occurs at  $650\text{ }^{\circ}\text{C}$ . The adsorption



**Figure 12.** SEM image of fresh adsorbent and adsorbent after 20 cyclic runs of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent: (a) fresh adsorbent and (b) adsorbent after 20 cycle runs.

**Table 1. Pore Distribution of Sorbent Before and After 20 Cyclic Runs**

items	av aperture (nm)	total pore volume (mL/g)	surface area ( $\text{m}^2/\text{g}$ )
fresh sorbent	8.631	0.2578	115.5
after 20 cyclic runs	15.18	0.1116	30.57

ratio increases with a temperature increase from 550 to 650 °C and decreases with a temperature increase over 650 °C. This is due to the fact that the decomposition rate of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  is faster over 650 °C (927 K) as shown in Figure 5.

Experiments also show that the decomposition temperature at a high  $\text{CO}_2$  content affects the adsorption ratio. According to the decomposition characteristics of the nano and micro  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbents, the decomposition temperatures of 750 and 815 °C were selected as the decomposition temperatures. On the other hand, a maximum  $\text{CO}_2$  partial pressure of 50% for Pyris 1 was used. The sorbent contains 20%  $\text{CaO}$  from nano  $\text{CaCO}_3$  as the precursor at a heating rate of 15 °C/min. The results are shown in Figure 7. It seems that after five cyclic runs, the decrease of the adsorption ratio between 750 and 815 °C is almost the same. For the fifth cycle, the case of a 750 °C decomposition has a 3–4% increase over the case of 815 °C.

**3.3. Nano  $\text{CaO}/\text{Al}_2\text{O}_3$  Durability Studies and Microstructure.** Furthermore, a TGA analysis result of 50 carbonation–calcination runs of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  is shown in Figure 8. It is clear that the  $\text{CO}_2$  adsorption ratio becomes stable after 15 runs of carbonation and calcination. From Figure 3, the adsorption ratio of the micro  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent drops from 80% of the first cycle to 40% of the 14th cycle. However, the adsorption ratio of the nano  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent drops to 68.3% after 15 cycles as shown in Figure 10. The adsorption ratio and adsorption capacity of nano  $\text{CaO}/\text{Al}_2\text{O}_3$  for the first and 50th runs are shown in Figures 9 and 10.

To find the changes of adsorbent during multiple carbonation and calcination cycles, XRD, SEM, and BET analyses were applied. The XRD results are shown in Figure 11.

The upper chart in Figure 11 shows that when a  $2\theta$  angle equals 15, there is a set of aluminum oxide characteristic peaks (d) for the fresh adsorbent. The lower chart in Figure 11 shows that except for calcium carbonate, there are  $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$  characteristic peaks (c) and a  $\text{CaO}$  peak (b) after 20 cyclic runs, but the aluminum oxide peak (d) disappeared.

The SEM images before and after 20 runs with the  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent are shown in Figure 12. As compared to Figure 12a, Figure 12b, it showed that multi-runs made pore size of particle become larger.



Table 1 shows the BET data before and after 20 cyclic runs with the  $\text{CaO}/\text{Al}_2\text{O}_3$  sorbent. The average pore diameter increased, and the number of small and middle sized pores decreased after 20 cyclic runs. The total pore volume of the adsorbent after 20 cyclic runs was half of the fresh sorbent, and the specific surface area decreased to 1/3 of the fresh sorbent.

On the basis of the results shown in Figures 11 and 12 and Table 1, we conclude that (a) there is a new phase substance  $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  formed and (b) the micro structure of the sorbent is changed after multiple cyclic runs. The interaction between  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  is discussed at a temperature of 800 °C in this paper since 800 °C is the recommended maximum of the calcination temperature. A new substance  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  can be formed even under a temperature of 800 °C.  $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$  can improve the durability of the sorbent, which has been proven by Li et al.<sup>6</sup> However, the difference of this study with reference to ref 6 is that  $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$  can be formed even under a temperature of 800 °C. This is the difference in the properties of the nano  $\text{CaCO}_3$  precursor.

## Conclusion

Using the nano  $\text{CaCO}_3$  precursor and the micro  $\text{CaCO}_3$  precursor to prepare nano  $\text{CaO}/\text{Al}_2\text{O}_3$  and micro  $\text{CaO}/\text{Al}_2\text{O}_3$ , nano  $\text{CaO}/\text{Al}_2\text{O}_3$  has a higher adsorption ratio and adsorption capacity with a lower decomposition temperature. Nano  $\text{CaO}/\text{Al}_2\text{O}_3$  has a maximum adsorption capacity of 6.02 mol/kg at 650 °C and a  $\text{CO}_2$  partial pressure of 0.33 atm. After 50 cyclic runs of carbonation–calcination at 650 and 800 °C, respectively, the adsorption ratio was retained at 68.3%. The reason for more stable durability is that the new substance of  $(\text{CaO})_{12}(\text{Al}_2\text{O}_3)_7$  can be formed even at 800 °C, and the pore size of the sorbent can be enlarged to maintain an available situation. The experimental studies show that the  $\text{CaO}$  based sorbent using nano  $\text{CaCO}_3$  as the precursor has a great potential for application in high-temperature  $\text{CO}_2$  sorption.

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