Development of Superior Sorbents for Separation of CO_2 from Flue Gas at a Wide Temperature range during Coal Combustion

Annual Technical Report (Year 2)

Reporting Period Start Date: July 1, 2004
Reporting Period End Date: June 30, 2005

by

Panagiotis G. Smirniotis

Original date report was issued: 10,02,2005
Date of final revision: 09,30,2005
DoE Award Number: DE-FG26-03NT41810

Chemical & Materials Engineering Department
497 Rhodes Hall
University of Cincinnati
Cincinnati, OH 45221-0012

DISCLAIMER

No patentable subject matter is disclosed in this report.

Abstract

For earlier studies it was found that calcium oxide is a promising sorbent for adsorption of carbon dioxide. $Ca(NO_3)_2 \cdot 4H_2O$, CaO, $Ca(OH)_2$, $CaCO_3$, and $Ca(CH_3COO)_2 \cdot H_2O$ were used as precursors for synthesis of CaO sorbents on this work. The sorbents prepared from calcium acetate ($CaAc_2$-CaO) resulted in the best uptake characteristics for CO_2. It possessed higher BET surface area and higher pore volume than the other sorbents. According to SEM images, this sorbent shows "fluffy" structure, which probably contributes to its high surface area and pore volume. When temperatures were between 550 and 800 ^oC, this sorbent could be carbonated almost completely. Moreover, the carbonation progressed dominantly at the initial short period. Under numerous adsorption-desorption cycles, the $CaAc_2$-CaO demonstrated the best reversibility, even under the existence of 10 vol % water vapor. In a 27 cyclic running, the sorbent sustained fairly high carbonation conversion of 62%. Pore size distributions indicate that their pore volume decreased when experimental cycles went on. Silica was doped on the $CaAc_2$-CaO in various weight percentages, but the resultant sorbent did not exhibit better performance under cyclic operation than those without dopant .Extensive work is under progress to find the influence of refractory dopants to performance of CaO sorbents.

Calcium oxides synthesized by flame spray pyrolysis and high temperature calcination were compared as sorbents of carbon dioxide. Flame made sorbents are solid nanoparticles with specific surface areas as high as 68 m^2/g. At 700 ^oC, all sorbents showed comparable fast carbonation rates during the first minutes and comparable maximum conversion with carbon dioxide during five hours adsorption. All samples showed high carbonation conversion of more than 95% over the first several cyclic adsorption/desorption periods. Experiments of long term cyclic adsorption/desorption showed that the sorbents synthesized from the flame pyrolysis had good durability. Its carbonation conversion was still stable around 50% after 60 cyclic running.

Contents

Captions of Tables and Figures

Table 1.1. Morphological Properties of various sorbents

Figure 1.1. XRD patterns of calcium oxide sorbents prepared from different precursors:
$CaAc_2 \cdot H_2O$, $CaCO_3$, $Ca(OH)_2$, and Aldrich CaO.

Figure 1.2. Uptake of CO_2 over CaO sorbents made with various precursors. Conditions: Temperature of adsorption, 600 °C; Concentration of CO_2, 30 vol % balanced by helium.

Figure 1.3. Pore size distribution of CaO sorbents prepared from $CaAc_2 \cdot H_2O$, $CaCO_3$, $Ca(OH)_2$, and Aldrich CaO.

Figure 1.4. Percent weight change of $CaAc_2 \cdot H_2O$ during calcination. Conditions: Temperature ramp 10 °C/min; Atmosphere: helium.

Figure 1.5. SEM images of CaO sorbents: a, $CaAc_2 \cdot H_2O$-CaO; b, $Ca(OH)_2$-CaO.

Figure 1.6. Particle size distribution of CaO sorbents prepared from $CaAc_2 \cdot H_2O$, $Ca(OH)_2$, $CaCO_3$, and Aldrich CaO.

Figure 1.7. Effect of temperature on adsorption of CO_2 over $CaAc_2$-CaO. Conditions: Temperature of adsorption, 50 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C; Concentration of CO_2, 30 vol % balanced by helium.

Figure 1.8. Adsorption of CO_2 over $CaAc_2$-CaO at initial stage. Conditions: Temperature of adsorption, 700 °C; concentration of CO_2, 30 vol % balanced by helium.

Figure 1.9. Extended adsorption-desorption cycles of CO_2 over $CaAc_2$-CaO (27 cycles w/o water and 17 cycles w/ water). Conditions: Temperature of adsorption-desorption, 700 °C; Concentration of gases, a, 30 vol % CO_2 balanced by helium; b, 10 vol % H_2O (gas) + 30 vol % CO_2 balanced by helium.

Figure 1.10. Pore size distribution of $CaAc_2$-CaO sorbents: after adsorption and desorption at 700 °C.

Figure 1.11. Maximum adsorption values of CO_2 over $CaAc_2$-CaO sorbents doped with 0 to 50 wt % SiO_2. Conditions: Temperature of adsorption-desorption, 700 °C; Concentration of CO_2, 30 vol % balanced by helium

Figure 2.1. Process flow chart of flame pyrolysis.

Figure2. 2. Photos of flame pyrolysis setup and sorbent synthesis Setup (Left up); b) Combustion of premixed oxygen and methane (Right up); c) Combustion of calcium precursor (Down).

Figure 2.3. TEM image of $CaO/CaCO_3$ synthesized by flame pyrolysis method

(Precursor concentration: 0.5 mol/L Ca-naphtenate (4% in min. spirits) xylene solution; Precursor solution flow: 5 ml/min; Oxygen flow: 5 L/min; Methane flow: 400 ml/min).

Figure 2.4. Percent weight change of sorbents by flame pyrolysis method during pretreatment. Conditions: Temperature ramp 10 ^{o}C/min; Atmosphere: helium.

Figure 2.5. The evolution in maximum carbonation conversion with the number of cycles of CaO made from flame spray pyrolysis and high temperature calcination

Figure 2.6. Uptake of CO_2 over CaO sorbents made with various organometallic compounds; T=700 ^{o}C. The precursor in high temperature calcination was calcium acetate. Concentration of gases, a, 30 vol % CO_2 balanced by helium; b, 10 vol % H_2O (gas) + 30 vol % CO_2 balanced by helium.

Executive Summary

Five precursors were used to synthesize CO_2 sorbents in this work. CaO sorbents prepared from calcium acetate monohydrate were identified as the best candidate for the adsorption of CO_2. In a wide operation window of 550-800 ^oC, this sorbent achieved a high carbonation of more than 94%. When the adsorption temperature was 700 ^oC, about 90% of the sorbent reacted with CO_2 within the first 10 min of the carbonation. The $CaAc_2$-CaO also showed capability of maintaining its reversibility over multi adsorption-desorptions, even under the existence of 10 vol % water vapor. In a 27 cyclic adsorption-desorption experiment, the sorbent still sustained fairly high conversion of 62%, of which the adsorptions were conducted under 30 vol% CO_2 (balanced in helium), 700 ^oC and desorptions conducted under helium, 700 ^oC. When "refractory" silica was doped on these sorbents, it didn't apparently enhance durability of the sorbent. Nano scale calcium sorbents were synthesized through flame pyrolysis. These sorbents demonstrated very good durability during long term running. It had about 50% conversion after 60 cyclic performance. Sorbents from several other organometallic precursors were also observed good performance during our work.

The performed work constitutes about 60% of the proposed work and offers a screening for effectiveness in conjunction with the most important operating parameters. Our efforts fall within the budget.

Since we observed that our CaO sorbents from specific precursors or flame pyrolysis method behave satisfactorily, our immediate efforts will concentrate on studying the causes which induced the good performance of these sorbents and to control the synthesis process more efficiently. We also aim at improving the durability of our sorbents moreover by pinpointing specific sorbent particle size, structure, and dopants.

Our long term plans for this project will be to test the best and most durable sorbents in the presence of SO_2. Moreover, we will test our sorbents at conditions used for WGS and syngas applications, gasification.

Part I Calcium Oxide Based Sorbents for Adsorption of Carbon Dioxide at High Temperatures

1. Introduction

Greenhouse gases, such as CO_2 are responsible for global warming. In order to mitigate the greenhouse impact, it's important to sequester CO_2 from stationary sources, such as flue gas from fossil fuel power plants, which account for about one third of all anthropogenic CO_2 emissions (Herzog et al, 2004). Yong et al (2002) and Aaron (2005) reviewed the separation of CO_2 from flue gas. The reversible carbonation and calcination reactions of calcium oxide with CO_2 provided a viable approach for CO_2 capture and separation from high temperature gas streams, such as flue gas, gas stream generated during coal gasification, fuel cell applications, and chemical heat pump (Gupta et al, 2002; Ida et al, 2003; Reddy et al, 2004).

Recently, researchers concentrated on how to enhance the uptake capacity and reversibility of calcium oxide sorbent. In a research attempt to apply CaO for thermal energy storage, Aihara et al (2001) synthesized a reactant of CaO and calcium titanate with molar ratio of 1:1. The molar conversion of CaO was about 60% after ten carbonation-calcination cycles. Gupta and Fan (2002) managed to achieve high CaO sorbent performance by synthesizing it from precipitated calcium carbonate which was prepared from calcium hydrate. In an effort to develop hydrogen production process, Japanese researchers enhanced the reactivity and durability of CaO sorbents by an intermediate hydration treatment during multi cycle operation. More than 85% carbonation of the sorbents was achieved after seven cyclic operations at 973 K under the partial CO_2 pressures of 6.0 or 9.0 MPa. For the sorbents which were not treated by hydration, they exhibited much lower carbonation conversions (Kuramoto and Fujimoto et al, 2003; Kuramoto and Shibano et al, 2003). Reddy and Smirniotis (2004) studied the promotion effect by doping alkali metals on CaO sorbent. They observed that uptake capacity of the sorbent was significantly enhanced when cesium was used as dopant. Moreover, it was noticed that the sorbent has zero affinity to N_2 and O_2.

The objective of this research is to develop high performance sorbents for CO_2 at high temperatures by using various calcium oxide precursors. The reversibility of sorbents will be tested at suitable reaction conditions. The effect of doping silica on sorbent performance was also studied.

2. Experimental

Sorbents preparation. Calcium nitrate tetra hydrate (Fisher), calcium oxide (Aldrich), calcium hydroxide (Fisher), calcium carbonate (Fisher), and calcium acetate monohydrate (Fisher) were used as calcium oxide precursor sources. Calcium oxide sorbents were synthesized by calcination of these precursors as follows. The precursor was heated from 50 ^oC to 750 ^oC with a ramp rate of 10 $^oC/min$ and kept at 750 ^oC for 30 min in the purpose of full calcination of precursors to calcium oxides. During the entire calcination progress, the sample was kept under helium atmosphere. In this work, the calcium oxide sorbents loaded with various weight percentages of silica were synthesized by wet impregnation method. In a typical synthesis, calcium acetate precursor which corresponds to one gram calcium oxide was added to a 100 ml beaker containing 80 ml of DI water. After the calcium acetate was completely dissolved into water under continuously stirring at 70 ^oC, the appropriate amount of silica (based on silica and calcium oxide only) to result in doping levels ranging from 10-50 wt% was then added into the calcium acetate solution. The mixture was then kept under vigorous stirring at 70 ^{o}C until the slurry evaporated to dryness. The product was then ground to fine powder and calcined to SiO_2/CaO with the same calcination procedure as that described previously.

Characterizations. X-ray diffraction (XRD) measurements were employed for the identification of phases of the synthesized calcium oxide sorbents. The XRD patterns were conducted on a Siemens D500 powder X-Ray diffractometer with a CuK_α radiation source (wavelength 1.5406 Å). Aluminum holder was used to support the samples in the XRD measurements.

BET surface area and pore size distribution measurements were performed by using nitrogen adsorption and desorption isotherms at -196 ^{o}C on a Micromeritics ASAP 2010 volumetric adsorption analyzer. The calcium oxide sorbents were degassed at 300 °C for at least three hours in the degassing port of the apparatus before the actual measurement. The adsorption isotherms of nitrogen for BET measurement were collected at -196 ^{o}C by using six values of pressure ranging from about 30 mmHg to 186 mmHg. The pore size distribution measurements were obtained based on BJH method.

Particle-size distribution measurements of the sorbent material were performed with a laser scattering particle distribution analyzer (Malvern Mastersizer S series) and a Malvern dispersion unit controller. Prior to the measurements, the sorbents were subjected to ultrasound treatment.

Scanning electron microscopy (SEM) measurements were done on selected samples to get information of morphology by using a Hitachi S-400 field emission SEM. For a typical sample preparation, 5 mg of the sorbent was added into a plastic bottle which contains 20 ml of methanol. This bottle was then subject to ultrasonic treatment for 20 min. After this treatment, 1–2 drops of this suspension were transferred to the SEM sample holder and dried overnight.

Adsorption-desorption. Adsorption-desorption (carbonation-calcination) experiments were conducted with a Perkin-Elmer Pyris™-1 thermogravimertic analyzer (TGA), a Perkin Elmer thermal analysis gas station (TFGS) and the software of Pyris™ v3.8 from Perkin Elmer. The microbalance of the Pyris™-1 TGA operates as a high gain electromechanical servo system which permits detection of weight changes versus time as small as 0.1 μg. To maintain the TGA balance accurate, the helium flow of 45 ml/min was used as balance purge gas to flow over the sample. The TFGS has four gas channels and can automatically switch on either of them to introduce gas over the sample according to the reaction program. The shift between carbon dioxide and helium together with flows of them was accurately maintained by the FTGS and the reaction program.

All experiments of the adsorption and desorption, including heating the sample, cooling the sample, and shifting gases between CO_2 (99.5%, Wright Bros, Inc.) and helium were programmable and operated batch wise. A small amount of sorbent (weight ranging from 5 to 10 mg) was put in a platinum sample pan and heated to the adsorption temperature at a ramp rate of 10 ^{o}C/min. Once the sample reached the adsorption temperature, the program was automatically switched to adsorption process. After one minute the adsorption progress began, 20 ml/min of the reactant gas CO_2 was automatically switched into the system to alternate the 20 ml/min of sheath helium. When the adsorption process completed, the temperature was increased at a ramp ratio of 10 ^{o}C/min or decreased at 15 ^{o}C/min to the programmed desorption temperature. After one minute the adsorption progress completed, the 20 ml/min of CO_2 was replaced by the 20 ml/min of helium. When the desorption process finished, the temperature was increased at a ramp ratio of 10 ^{o}C/min or decreased at 15 ^{o}C/min to the adsorption temperature. A new adsorption cycle began when the temperature was achieved. In this work, typical adsorption time was set as 300 min in order to get relatively high uptake capacity of CO_2, and desorption time set as 30 min to let the sorbent to be calcinated completely. The desorption time was intentionally kept that short to prevent possible sintering effect of sorbents. During an entire process, the sorbent weight together with the temperature was continuously recorded.

3. Results and discussion.

Calcium oxide sorbents were prepared by calcining various commercially available precursors, namely calcium acetate monohydrate, calcium carbonate, calcium hydroxide, calcium oxide, and calcium nitrate tetra hydrate. For simplicity, they were denoted as $CaAc_2$-CaO, $CaCO_3$-CaO, $Ca(OH)_2$-CaO, Aldrich-CaO, and $Ca(NO_3)_2$-CaO. XRD patterns of these sorbents show that they have the same peaks locating at 2θ of 32.4, 37.6, and 54.2 degrees (Figure 1.1) which are characteristic ones of calcium oxide. This indicates that the chemical composition and physical crystallinity of all these calcium oxide sorbents prepared from different precursors are similar. They might not be the cause for different adsorption and desorption behaviors which will be discussed later.

Characteristic TGA curves of isothermal carbon dioxide adsorption over these sorbents in a 5-hour-adsorption process at 600 ^{o}C are presented in Figure 1.2. Chemistry schemes of calcium oxide carbonation (adsorption) and calcination (desorption) of CO_2 over CaO sorbents are described as follows:

Carbonation (adsorption): $CO_2\ (g) + CaO\ (s) \rightarrow CaCO_3\ (s)$ (1)

Calcination (desorption): $CaCO_3\ (s) \rightarrow CO_2\ (g) + CaO\ (s)$ (2)

If CaO achieved 100% carbonation conversion by following reaction (1), one molar of CaO (56 g) should take one molar of CO_2 (44 g), which is a tremendously large value. However, the reversible reaction (2) restrains the carbonation to reach the stoichiometrical point and the physical structure restricts the carbonation reaction to achieve equilibrium during reasonable experiment time. Both of these effects limit the achievement of 100% carbonation conversion value under the experimental conditions.

To compare performance of all these calcium oxide, adsorption experiments were performed at 600 ^{o}C under CO_2 partial pressure of 0.3 atm. For all the five sorbents, a monotonic increase of CO_2 adsorption was observed (Figure 1.2). With the exception of $Ca(NO_3)_2$-CaO, all the other sorbents exhibited rapid carbonation rates during the initial stage which were followed by an abrupt shift to a relative slower one. During the 5-hour-adsorption process at 600 ^{o}C, $Ca(NO_3)_2$-CaO was carbonated only about 2.5% by CO_2. Under the same adsorption conditions, Aldrich-CaO was carbonated about 25%, $Ca(OH)_2$-CaO carbonated 63 %, $CaCO_3$-CaO carbonated 66%, and $CaAc_2$-CaO carbonated 97%, which was nearly 100% conversion. The reason that the $Ca(NO_3)_2$-CaO exhibited such a low uptake capacity of CO_2 or its carbonation rate was so slow during the experiment condition is that it possessed significantly less BET surface area than the other sorbents. For the $Ca(NO_3)_2$-CaO, the BET surface area was so small that its measurement result was even not available under our test condition (Table 1.1). We observed that the precursor $Ca(NO_3)_2{\cdot}4H2O$ melted and formed solid oxide upon calcination. However, the other precursors still existed as fine powder during and after the calcination process. The cause for the complete melting and sintering of $Ca(NO_3)_2$-CaO is that the calcium nitrate tetra hydrate has a low melting temperature of about 45 ^{o}C. During the calcination, the precursor melted at the very early stages and finally formed solid sorbent instead of powder. This phenomenon prevents the possible formation of pores when the precursor progressed to the calcium oxide. For the Aldrich-CaO, it still existed as fine powder after calcination which justifies its higher CO_2 adsorption capacity than the $Ca(NO_3)_2$-CaO. However, this sorbent doesn't posses many pores and its BET surface area is fairly small (4.2 m^2/g). So, its capacity was constrained to a low value (25%). With $Ca(OH)_2$ and $CaCO_3$, porosity was formed when the precursors decomposed through releasing H_2O or CO_2 (Table 1.1 and Figure 1.3). So, $Ca(OH)_2$-CaO and $CaCO_3$-CaO had better uptake capacity than the previous two sorbents. For $CaAc_2 \cdot H_2O$, its high melting temperature (about 150 ^oC) prevented the precursor from dissolving into the water released by the hydrate itself. The dissociated water evaporated before the precursor dissolved. When this metal organic compound decomposed to calcium oxide through multi steps during calcination, large volume of pores was formed.

The curve of weight versus time in Figure 1.4 depicts progressing process of the $CaAc_2 \cdot H_2O$ to CaO. The various weight plateaus correspond with the desorption of physically adsorbed gases and water, dehydratation to calcium acetate, decomposition to calcium carbonate at about 400 ^oC, and consequent decomposition to calcium oxide around 600 ^oC, respectively. This multi-step decomposition ended in the formation of meso and macro pore structure (Figure 1.3). Structure difference of the sorbents is clearly depicted by SEM images (Figure 1.5). The $CaAc_2$-CaO possesses porous, "fluffy" structure while the $Ca(OH)_2$-CaO has particles which look more compact and solid. These SEM images intuitively revealed that their different pore volumes and BET surface areas are based on their different structures, which finally decided their adsorption performances. It seems carbon dioxide diffused more easily through the "fluffy" structure than through a solid one. Since these sorbents have similar particle size range (Figure 1.6), it's reasonable to propose that the different adsorption performances were induced by their different pore structures and BET surface areas. At 600 ^oC, $CaAc_2$-CaO sorbent exhibited about 97% conversion during the 5-hour-adsorption process of CO_2, the best performance among the five precursors under investigation in this research. This performance might ascribe to its larger surface area and pore volume. In order to appreciate its performance, one should notice that 97% is a significantly high uptake of about 76 wt % CO_2 per mass sorbent.

Except that the $Ca(NO_3)_2$-CaO began the carbonation with a relative slow rate from the initial stage, the other sorbents began with a rapid reaction which was followed abruptly by a much slower one. During the slow reaction regime, the reaction slowed down because CO_2 had to diffuse through the formed $CaCO_3$ layer to reach the unreacted CaO. It's suggested that the shift of the reaction mechanism happened when the surface of sorbent was covered and small pores have been blocked by formation of nonporous carbonate product layer. This layer significantly hinders the inward diffusion of CO_2. According to our results, the ratio between the carbonation rates of the fast reaction regime to those of the slow one is about two orders. This is in accordance with the results of both Hyatt et al (1958) and Barker (1973).

Since the $CaAc_2$-CaO exhibited the best performance for adsorption of CO_2 among the other sorbents being studied, we selected it to study temperature effect on CO_2 adsorption behavior. A set of experiments was conducted at temperatures ranging from 50 to 800 ^oC (Figure 1.7). When the temperatures were equal to or less than 300 ^oC, the reaction rates were fairly slow. These slow rates indicate that the reactions are kinetically controlled at the low temperatures. When the adsorption was conducted under 400 or 500 ^oC, the carbonation curves smoothly shifted from the first regime to the second regime. This suggests that the reaction mechanism transfered from kinetic control to diffusion control or the reaction was being controlled by both mass diffusion and kinetic mechanism. When the adsorption temperatures were between 550 and 800 °C, conversions increased to more than 94% during the five hours adsorption. These observations indicate that the range of 550-800 °C is a suitable wide operation window for the adsorption of CO_2 over the $CaAc_2$-CaO. Under this temperature operation window, the adsorption equilibrium isotherms of carbon dioxide over $CaAc_2$-CaO are quite large when they're compared with those under lower temperatures. It's observed that the curves evolved into plateau stage shortly after the adsorption began. More than 90% of this carbonation happens within the first 10 min of the fast reaction period (Figure 1.8). The fast carbonation might be ascribed to the large BET surface area of $CaAc_2$-CaO and the diffuse control mechanism under higher temperatures. At the initial stage, the diffusion resistance obviously didn't restrain the reaction rate much because large area of sorbent was under exposure to gas phase. This rapid rate offers a great opportunity to use calcium oxide for industrial applications.

Good reversibility is a must for sorbent applications. The $CaAc_2$-CaO was chosen to test sorbent durability. 700 °C was selected as the operation temperature for both carbonation and calcination. At 700 °C, both CaO carbonation and $CaCO_3$ calcination reacted quickly. By using the same temperature for the carbonation and calcination, the continuously heating and cooling of sorbents were avoided between cyclic operations. The calcium acetate monohydrate precursor was calcined for three hours at 700 °C under oxygen in order to get better sorbent reversibility although its adsorption ability would be slightly reduced based on the first carbonation. Figure 1.9 shows that the carbonation conversion of the $CaAc_2$-CaO sorbent remained stable, even when 10 vol % water (vapor) presented in feed gases, at 93% after ten cyclic carbonation-calcinations at 700 °C. When reaction reached 10 cycles, the CO_2 uptake capacity began to decrease slowly in the following cycles. However, after 27 cycles, the sorbent still maintained relatively high conversion (about 62%). The high conversion was ascribed to its "fluffy" structure, high BET surface area, and pore volume. The decreasing of conversion through reaction cycles might be caused by the pore blockage and collapse which induced less surface area and smaller pores. The results in Table 1.1 and Figure 1.10 showed how the BET surface area and the pore volume evolved with the progressing of cyclic adsorption-desorptions. When the reaction cycles increased, the BET surface area and pore volume of sorbent decreased. When the water vapor presented in the system, the uptake capacity decreased faster than that without vapor. It's probably due to that the water "helped" the collapse of pore structure.

Sintering effects deteriorate the uptake capacity of sorbent. However, it is significant only when operation temperature is above Tammann temperature, which is estimated as 0.52 times of the melting point temperature in K. "Refractory" dopants are expected to prevent the sorbent sintering (Aihara et al, 2001). For CaO, SiO_2, and $CaCO_3$, their melting temperatures are 3171 K, 3223 K, and 1603 K, respectively. Here, their Tammann temperatures are corresponding to 1649 K, 1676 K, 834 K, individually. Thus, sintering phenomenon of the former two compounds won't occur while the last one does do at our operation temperature (973 K). The sorbents with five different weight percentages of SiO_2, namely 10 wt %, 20 wt %, 30 wt %, 40 wt %, and 50 wt % of SiO_2 (based on CaO and SiO_2 only) were studied in this work. Figure 1.11 gives the maximum carbonation values of the pure $CaAc_2$-CaO sorbent and the $CaAc_2$-CaO doped with refractory silica at 700 °C in different cycles.

However, the results revealed that the durability performances of the sorbents with silica were not better than those without dopant during the four cyclic adsorption-desorptions operation. Since $CaCO_3$, the product after carbonation does sinter at 700 ^oC (973 K) and sintering effect does hurt sorbent performance, we proposed that sintering effect might not be the main factor which induces adsorption performance decaying in multi cyclic carbonations. The dominant factor that causes the deterioration of carbonation might be the closure of pores and decrease of surface area during the repetitive carbonations and calcinations. So, although SiO_2 might effectively prevent $CaCO_3$ from sintering to each other, it has little impact on the overall sorbent reversibility performance.

Part II CO_2 Sorbents Made by Flame Pyrolysis and Organometallic Precursors at High Temperature Calcination

Experimental.

Flame pyrolysis. CaO sorbent was synthesized with flame pyrolysis method. Calcium oxide precursor (0.5 mol/L Ca-naphtenate (4% in mineral spirits) xylene solution) was fed into reactor through syringe pump at a rate of 5 ml/min. The precursor was dispersed by oxygen gas (5 L/min) before it combusted with premixed oxygen/methane. The experimental setup is shown in Figure 2.1 and Figure 2.2. Sorbents were collected at filter locating above reactor.

High temperature calcination. Precursors were calcined at 750 ^{o}C for 30 min.

Results and discussion.

The sorbent has a BET surface area of 68 m^2/g. Unlike sorbents synthesized by calcining calcium precursors at high temperature, which resulted in porous sorbent, this sorbent is in solid particle form. We propose that the big surface area of this sorbent is ascribed to its nano size (Figure 2.3).

Since the sorbent particle is in nano scale, it's feasible to reaction with CO_2 in air during synthesis and product collection period. By calculating through the weight changing curve of sorbent under thermal pretreatment (Figure 2.4), we found that the collected product contained only about 20% (wt) CaO while it contained about 80% (wt) $CaCO_3$.

To compare durability of the flame-made sorbents and the sorbents ($CaAc_2$-CaO) by calcining calcium acetate at high temperature, which demonstrated very good CO_2 capacity and durability in the cyclic operation in Part I of this report, long term running experiments were performed. One can observe from Figure 2.5 that the flame-made sorbents had comparable capacity during first several cyclic adsorption/desorption. Then, it showed faster decrease in capacity in the following cycles than the $CaAc_2$-CaO. The decrease is probably caused by decrease of void space among solid particles. However, in the continuous cyclic running, the flame-made sorbents exhibited better durability. Its uptake capacity was around 50% after 20 cycles and kept that value in the following 40 cycles. It seems that the solid particle of this flame sorbents circumvented the problem of pore structure collapse and blockage, which caused pore sorbents to deteriorate in the cyclic operation.

Adsorption performance of various sorbents from organometallic compounds was shown on figure 2.6. One can observe that sorbents from calcium propionate, calcium acetylacetonate hydrate, and calcium oxalate hydrate demonstrate very high CO_2 uptake capacity. The causes for their better performance are under investigation.

Part III Conclusions

Five precursors were used to synthesize CO_2 sorbents in this work. CaO sorbents prepared from calcium acetate monohydrate were identified as the best candidate for the adsorption of CO_2. In a wide operation window of 550-800 ^{o}C, this sorbent achieved a high carbonation of more than 94%. When the adsorption temperature was 700 ^{o}C, about 90% of the sorbent reacted with CO_2 within the first 10 min of the carbonation. The $CaAc_2$-CaO also showed capability of maintaining its reversibility over multi adsorption-desorptions, even under the existence of 10 vol % water vapor. In a 27 cyclic adsorption-desorption experiment, the sorbent still sustained fairly high conversion of 62%, of which the adsorptions were conducted under 30 vol% CO_2 (balanced in helium), 700 ^{o}C and desorptions conducted under helium, 700 ^{o}C. Both rapid and high uptake capacity of CO_2, together with good regenerability observed over these sorbents, was ascribed to the high BET surface area and meso and macro porous structure. This structure might be incurred in the progress of precursor decomposing during calcination. When "refractory" silica was doped on these sorbents, it apparently didn't enhance durability of the sorbent. This illuminates that the main factor in decaying adsorption performance is the blockage and collapse of pore structure but sorbent sintering effect in multi cyclic adsorption-desorptions.

Adsorption performance of various sorbents from organometallic compounds, such as calcium acetate, calcium propionate, calcium acetylacetonate hydrate, and calcium oxalate hydrate demonstrated very high CO_2 uptake capacity. Sorbents from some other organometallic compounds, such as calcium 2-ethylhexanonate and calcium isopropoxide, didn't show good performance. The mechanism behind these is still under investigation.

The sorbent synthesized by flame spray pyrolysis has a BET surface area of 68 m^2/g. Its solid nano particles provide large surface area to uptake CO2 at rapid rate and demonstrated good durability during the 60 cyclic adsorption/desorptions. We propose that the nono size provide large area and solid form prevente structure collapse.

Part IV Future Work

The main characteristics we plan to achieve are high performance, great durability, and resistance to SO_2. Our planned work towards these task are as following.

- Investigation of causes which induce some good performance behavior of calcium oxide sorbents from organometallic compound. Investigation of new synthesis method which might induce strong calcium oxide “sponge like” structure.
- Investigation of control mechanism on particle size of flame pyrolysis. Investigation of effect of particle size on CO_2 uptake performance. Investigation of doping refractory compounds on calcium sorbents and the effect on CO_2 uptake performance.
- Investigation of synthesis of sorbent with refractory dopant through wet impregnation method. Investigation of performance of these dopants.
- Investigation of sorbents which repel SO_2 or adsorb it but don’t hurt CO_2 uptake performance much simultaneously.

Acknowledgement

The authors acknowledge U.S. Department of Energy for financial support (Grant Number #: DE-FG03NT41810) and Dr. Jose Figueroa of US DOE (NETL) for very fruitful discussions.

References

Aaron, D., Separation of CO_2 from flue gas: a review. *Separation Science and Technology* **2005,** 40, 321-348.

Aihara, M.; Nagai, T.; Matsushita, J.; Negishi, Y.; Ohya, H., Development of porous solid reactant for thermal-energy storage and temperature upgrade using carbonation/decarbonation reaction. *Applied Energy* **2001,** 69, (3), 225-238.

Barker, R., The Reversibility of the Reaction $CaCO_3$=CaO+CO_2. *J Appl Chem Biotechnol* **1973,** 23, (10), 733-742.

Gupta, H.; Fan, L.-S., Carbonation/Calcination Cycle Using High Reactivity Calcium Oxide for Carbon Dioxide Separation from Flue Gas. *Industrial & Engineering Chemistry Research* **2002,** 41, (16), 4035-4042.

Hyatt, E. P.; Cutler, I. B.; Wadsworth, M. E., Calcium carbonate decomposition in carbon dioxide atmosphere. *Journal of the American Ceramic Society* **1958,** 441, 70-74.

Kuramoto, K.; Fujimoto, S.; Morita, A.; Shibano, S.; Suzuki, Y.; Hatano, H.; Shi-Ying, L.; Harada, M.; Takarada, T., Repetitive carbonation-calcination reactions of Ca-based sorbents for efficient CO_2 sorption at elevated temperatures and pressures. *Industrial and Engineering Chemistry Research* **2003,** 42, (5), 975-981.

Kuramoto, K.; Shibano, S.; Fujimoto, S.; Kimura, T.; Suzuki, Y.; Hatano, H.; Shi-Ying, L.; Harada, M.; Morishita, K.; Takarada, T., Deactivation of Ca-based sorbents by coal-derived minerals during multicycle CO_2 sorption under elevated pressure and temperature. *Industrial and Engineering Chemistry Research* **2003,** 42, (15), 3566-3570.

Reddy, E. P.; Smirniotis, P. G., High-temperature sorbents for CO_2 made of alkali metals doped on CaO supports. *Journal of Physical Chemistry B* **2004,** 108, (23), 7794-7800.

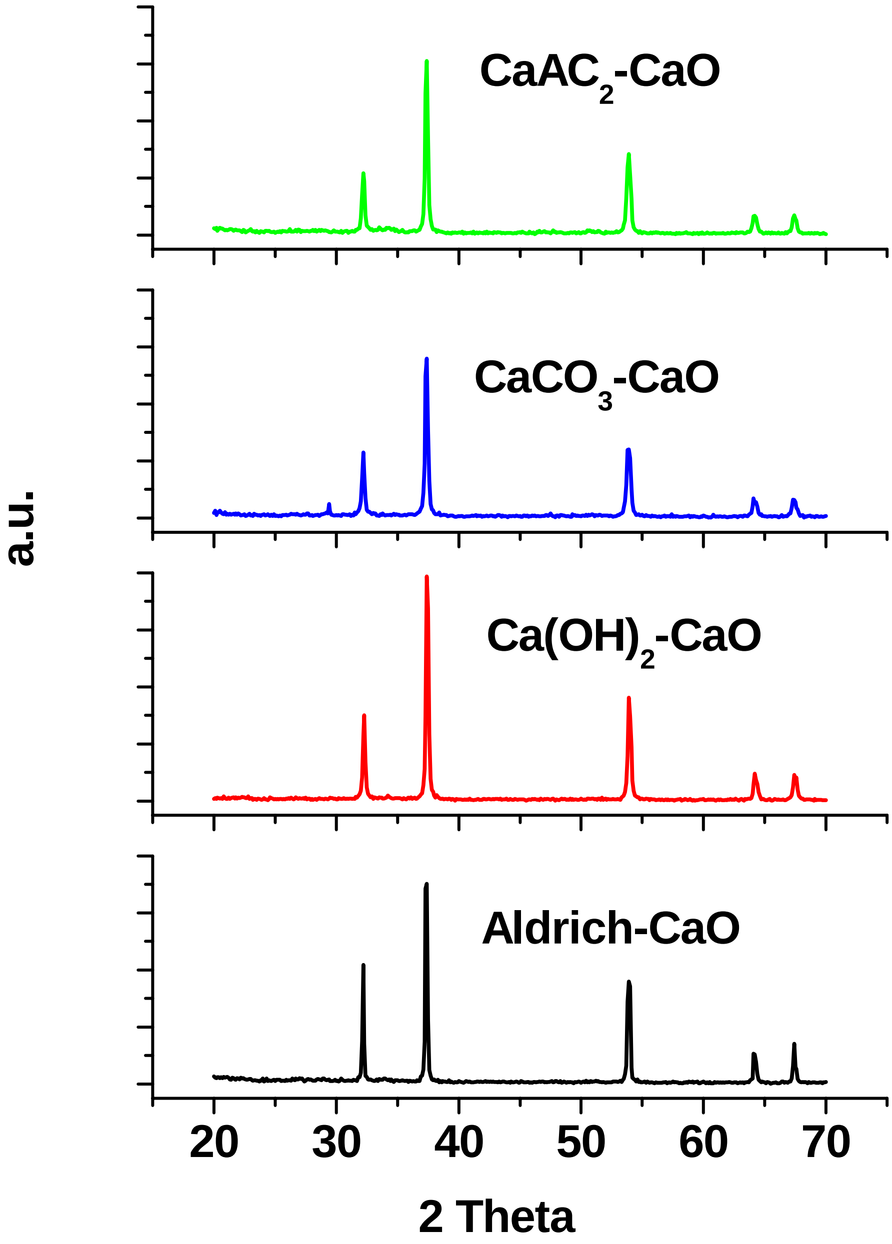
Yong, Z.; Mata, V.; Rodrigues, A. E., Adsorption of carbon dioxide at high temperature--a review. *Separation and Purification Technology* **2002,** 26, (2-3), 195 - 205.

Tables and Figures

Table 1.1. Morphological Properties of various sorbents
(before and after adsorption and desorption)

Sorbents	*BET (m^2/g)*	*Pore volume (cm^3/g)*
$Ca(NO_3)_2$-CaO	n/a	n/a
Aldrich-CaO	4.2	0.02
$Ca(OH)_2$-CaO	13.9	0.15
$CaCO_3$-CaO	5.3	0.08
$CaAc_2{\cdot}H_2O$-CaO	20.2	0.23
$CaAc_2{\cdot}H_2O$-CaO (After 1 cyclic adsorption-desorption at 700 °C)	18.7	0.19
$CaAc_2{\cdot}H_2O$-CaO (After 2 cyclic adsorption-desorption at 700 °C)	19.0	0.19
$CaAc_2{\cdot}H_2O$-CaO (After 4 cyclic adsorption-desorption at 700 °C)	18.3	0.19
$CaAc_2{\cdot}H_2O$-CaO (After 8 cyclic adsorption-desorption at 700 °C)	14.9	0.14

n.a: not available.



CaAC2-CaO
CaCO3-CaO
Ca(OH)2-CaO
Aldrich-CaO
a.u.
20
30
40
50
60
70
2 Theta

Figure 1.1

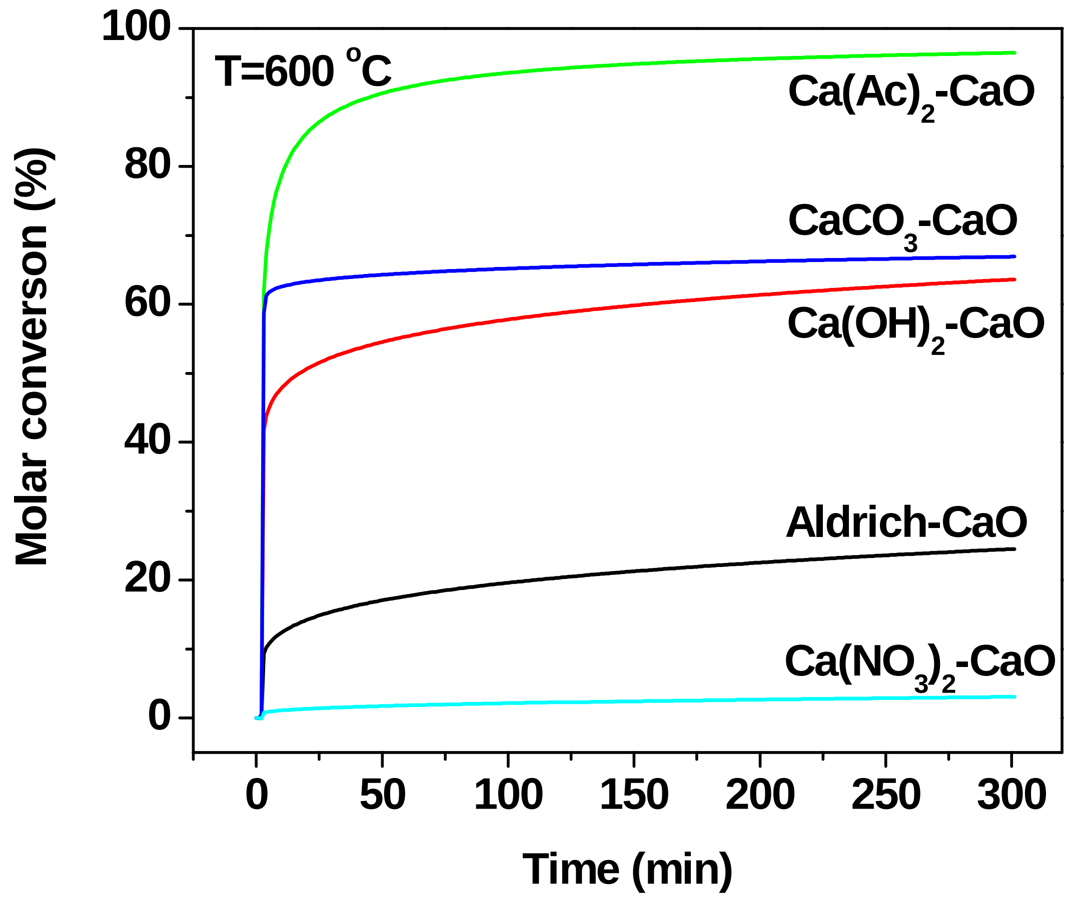

T=600 °C
Ca(Ac)2-CaO
CaCO3-CaO
Ca(OH)2-CaO
Aldrich-CaO
Ca(NO3)2-CaO
Molar converson (%)
0
20
40
60
80
100
Time (min)
0
50
100
150
200
250
300

Figure 1.2

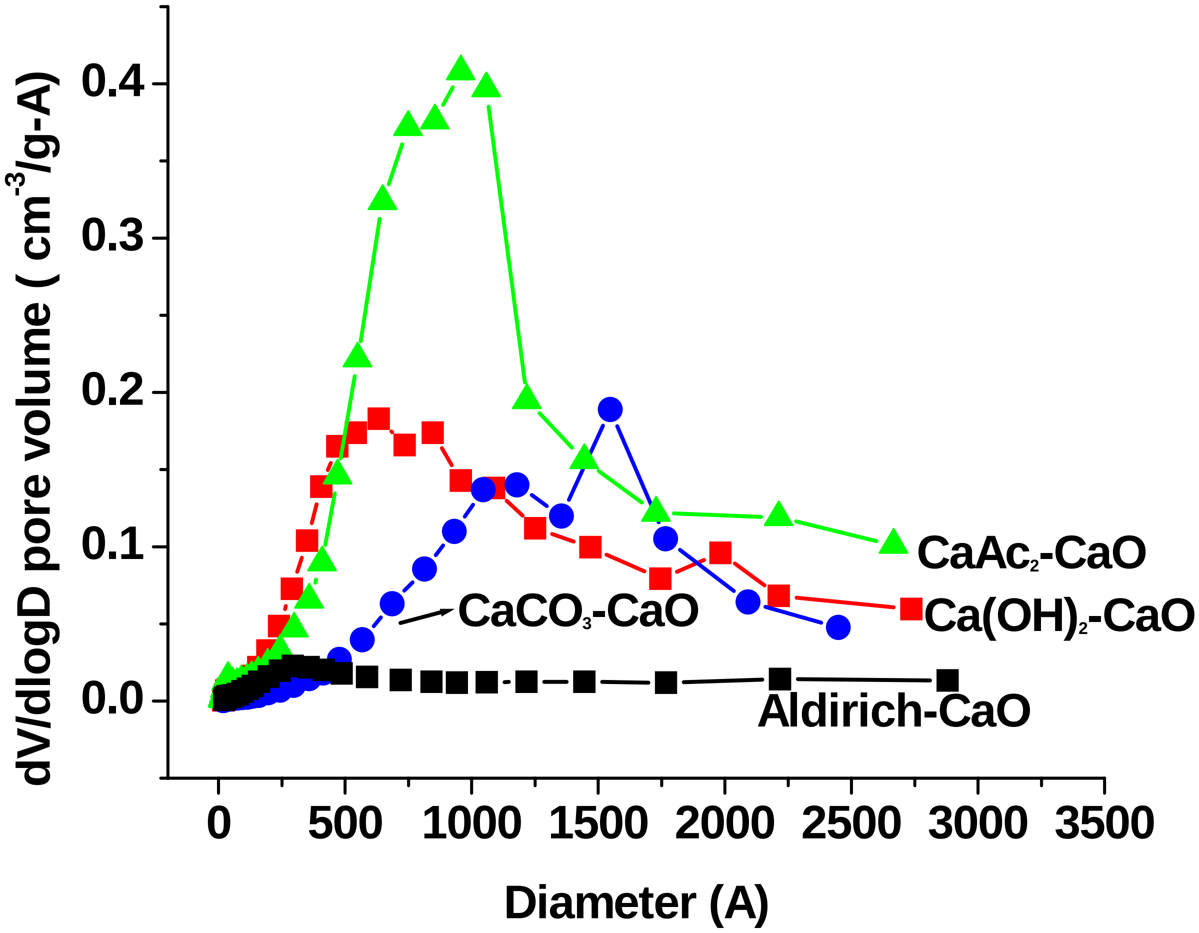
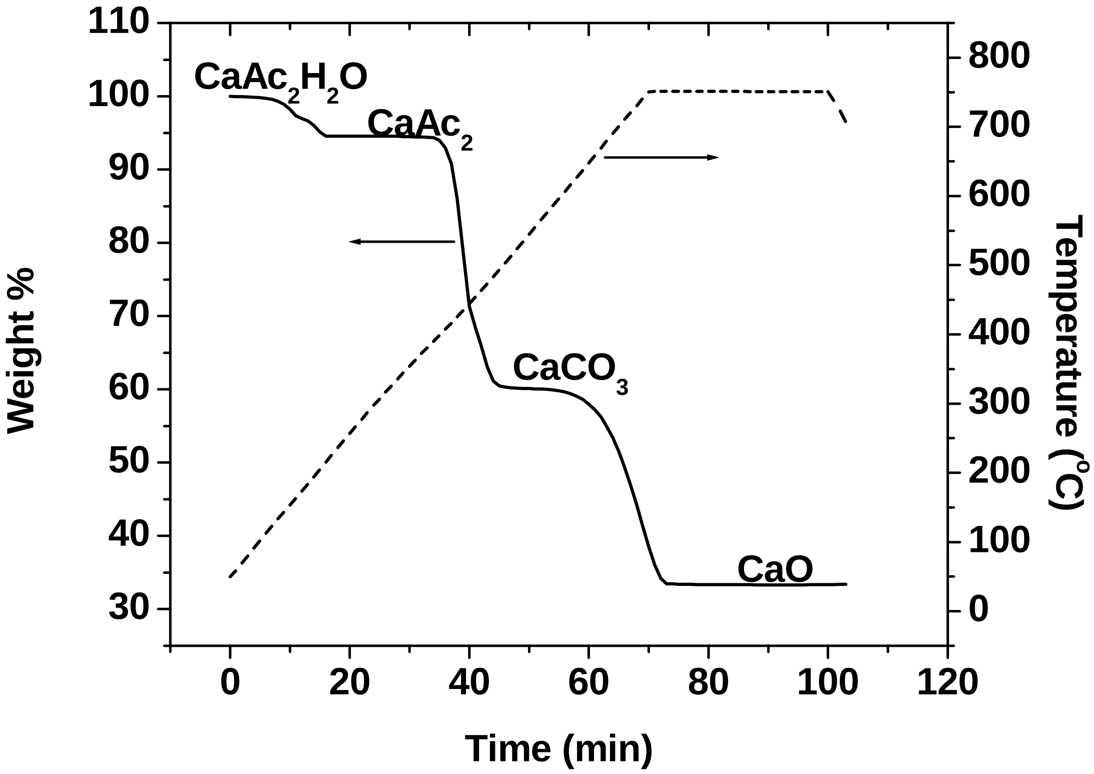

dV/dlogD pore volume (cm-3/g-A)
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
2500
3000
3500
Diameter (A)
CaAc2-CaO
Ca(OH)2-CaO
CaCO3-CaO
Aldirich-CaO

Figure 1.3



110
100
90
80
70
60
50
40
30
Weight %
800
700
600
500
400
300
200
100
0
Temperature (°C)
0
20
40
60
80
100
120
Time (min)
CaAc₂H₂O
CaAc₂
CaCO₃
CaO

Figure 1.4

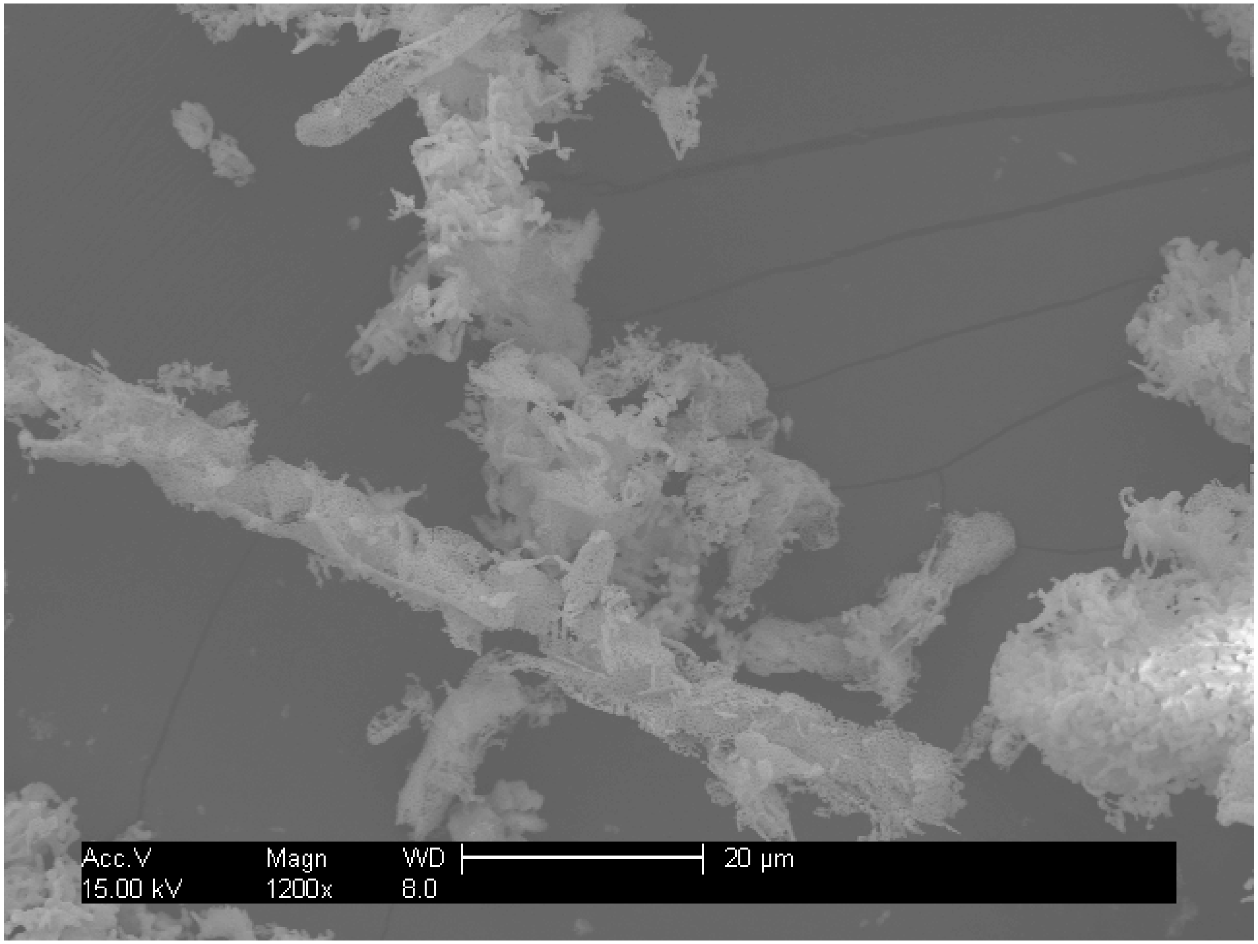


Figure 1.5 (a)

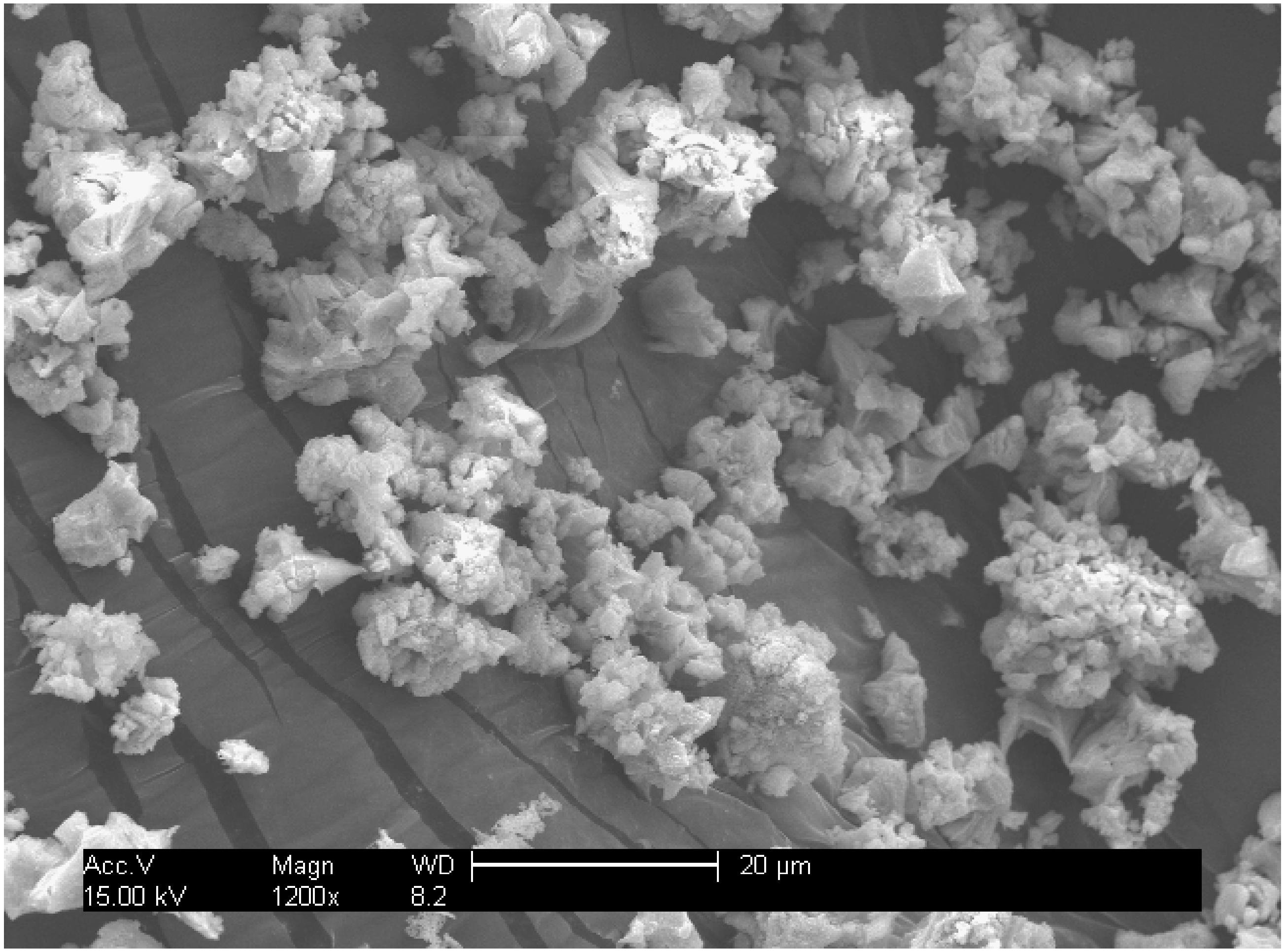


Figure 1.5 (b)

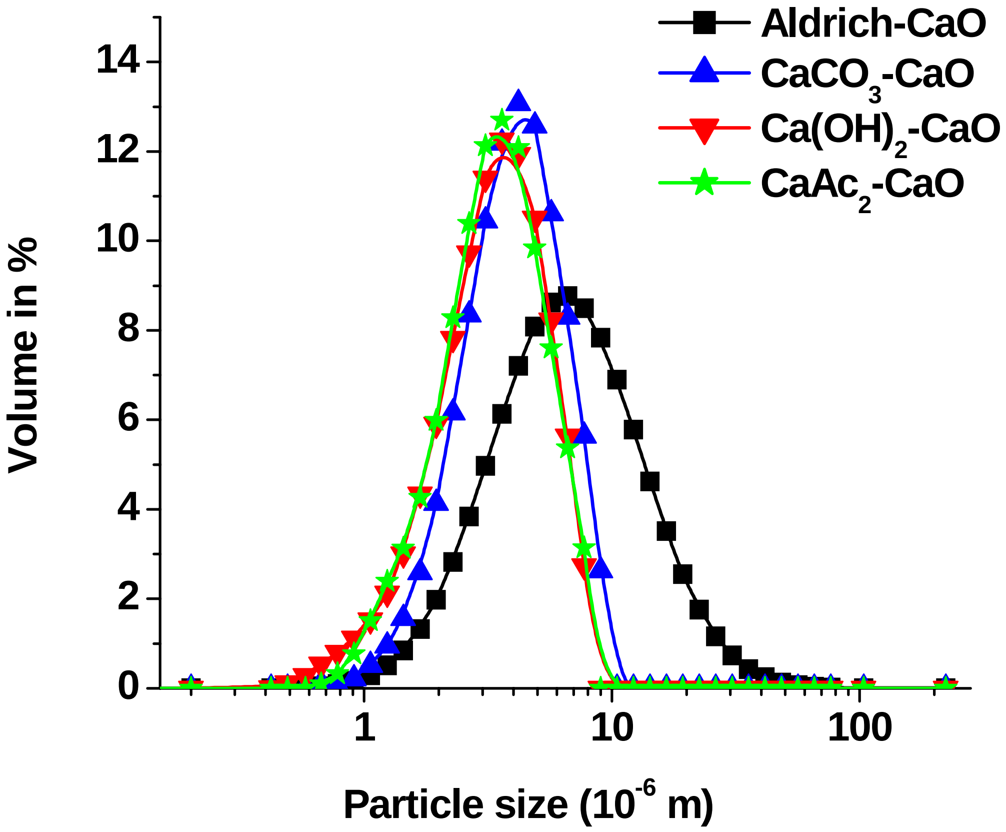

Aldrich-CaO
$CaCO_3$-CaO
$Ca(OH)_2$-CaO
$CaAc_2$-CaO
Volume in %
0
2
4
6
8
10
12
14
1
10
100
Particle size (10^{-6} m)

Figure 1.6

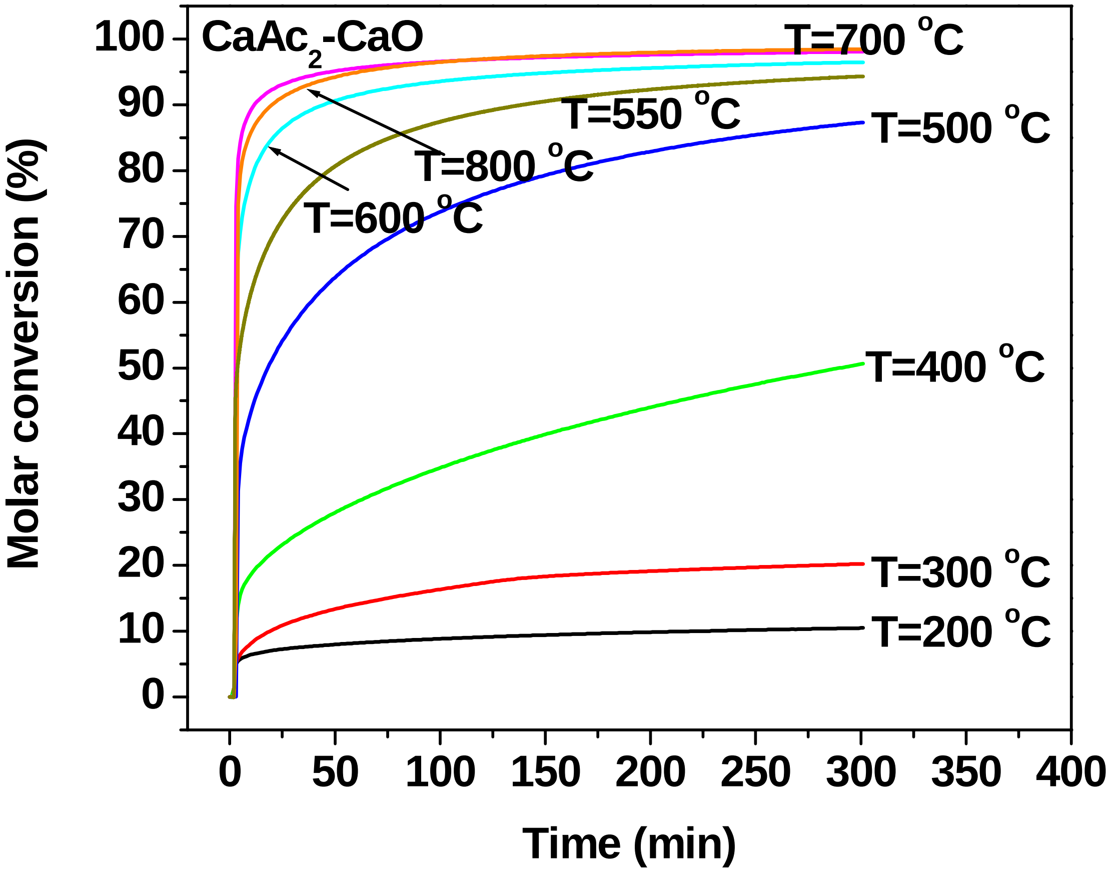

CaAc$_2$-CaO
T=700 °C
T=550 °C
T=500 °C
T=800 °C
T=600 °C
T=400 °C
T=300 °C
T=200 °C
Molar conversion (%)
Time (min)
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

Figure 1.7

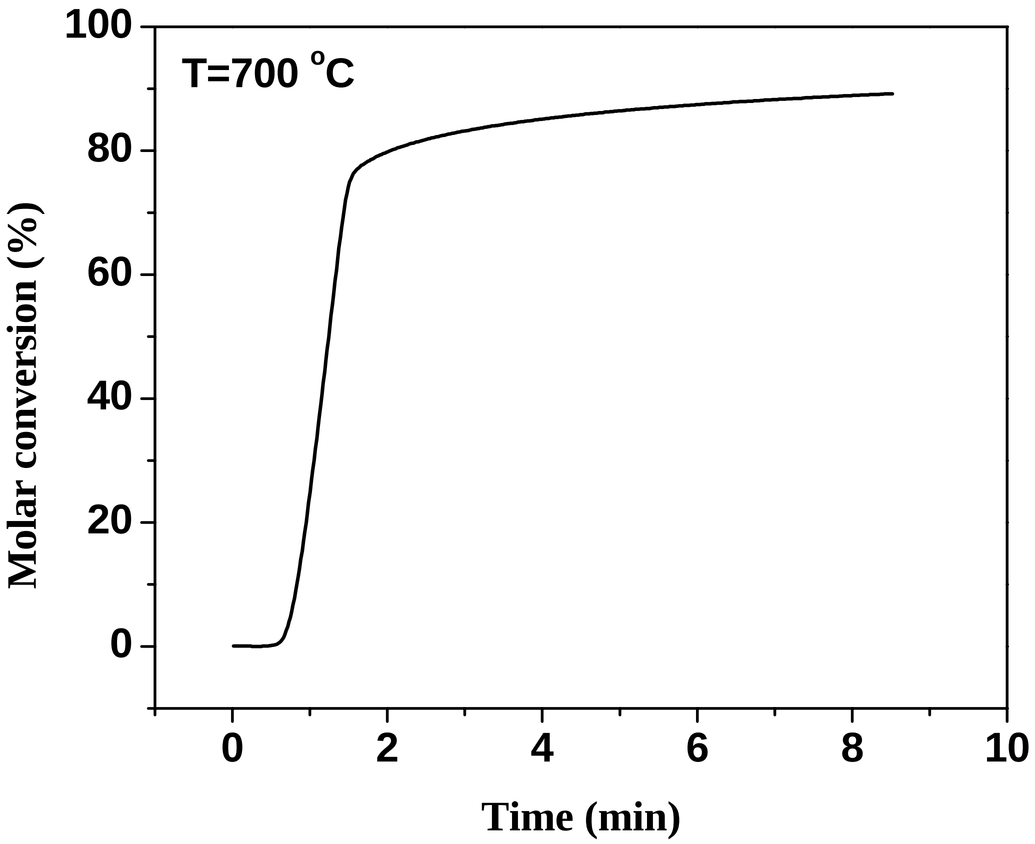


Figure 1.8

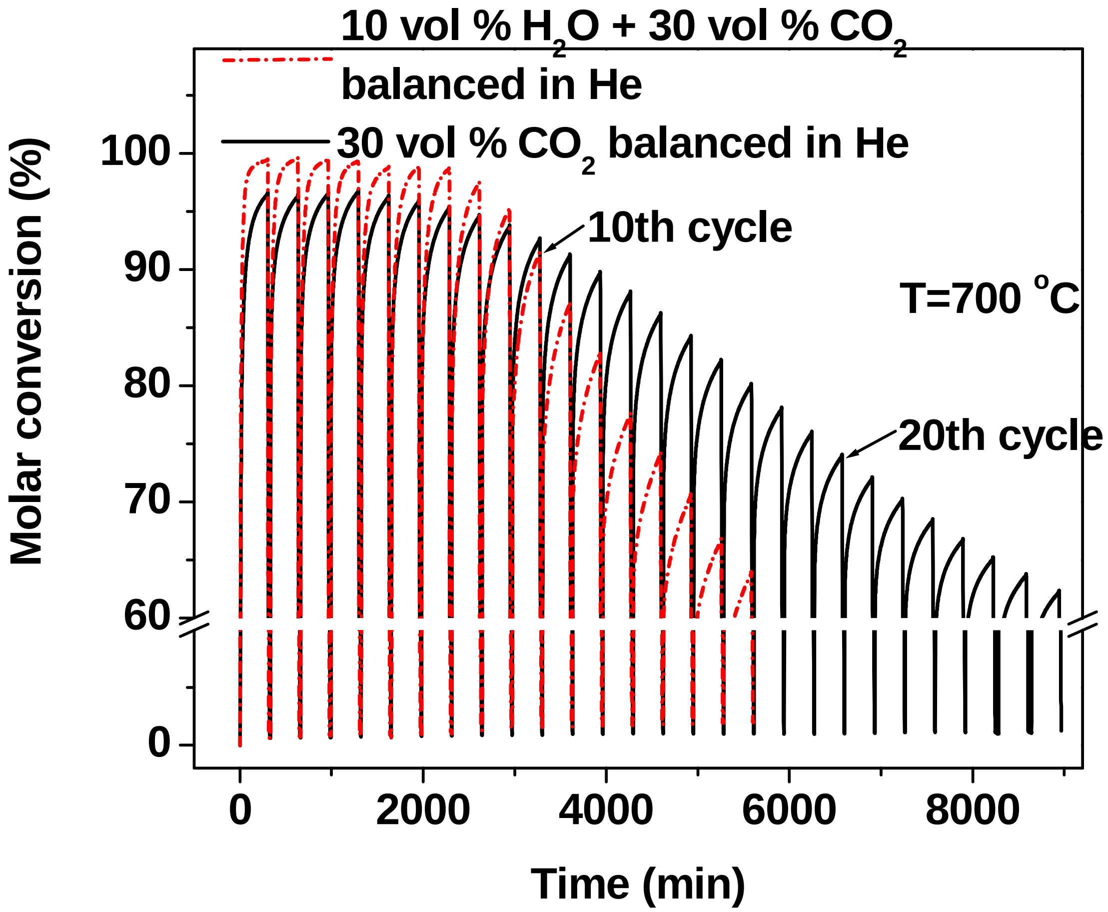

10 vol % H$_2$O + 30 vol % CO$_2$ balanced in He
30 vol % CO$_2$ balanced in He
10th cycle
T=700 °C
20th cycle
Molar conversion (%)
100
90
80
70
60
0
0
2000
4000
6000
8000
Time (min)

Figure1. 9

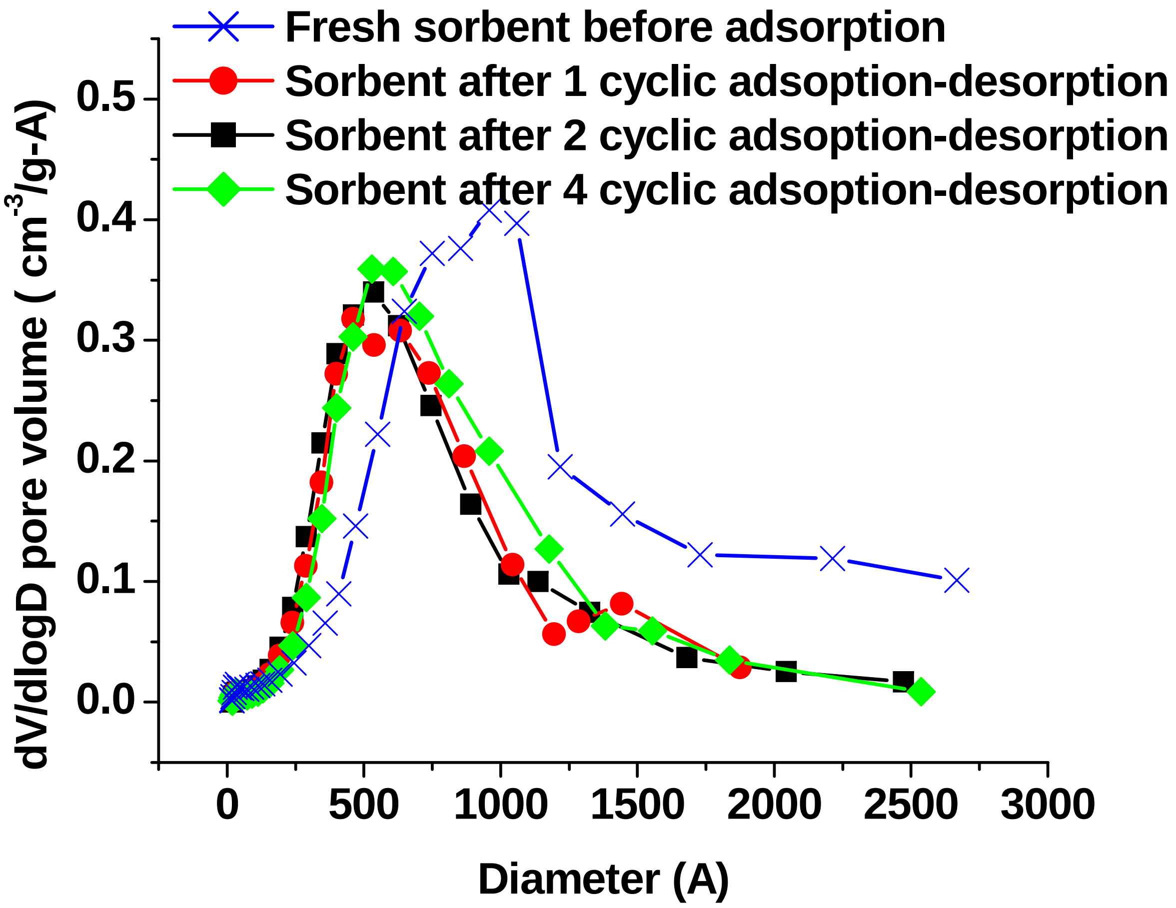
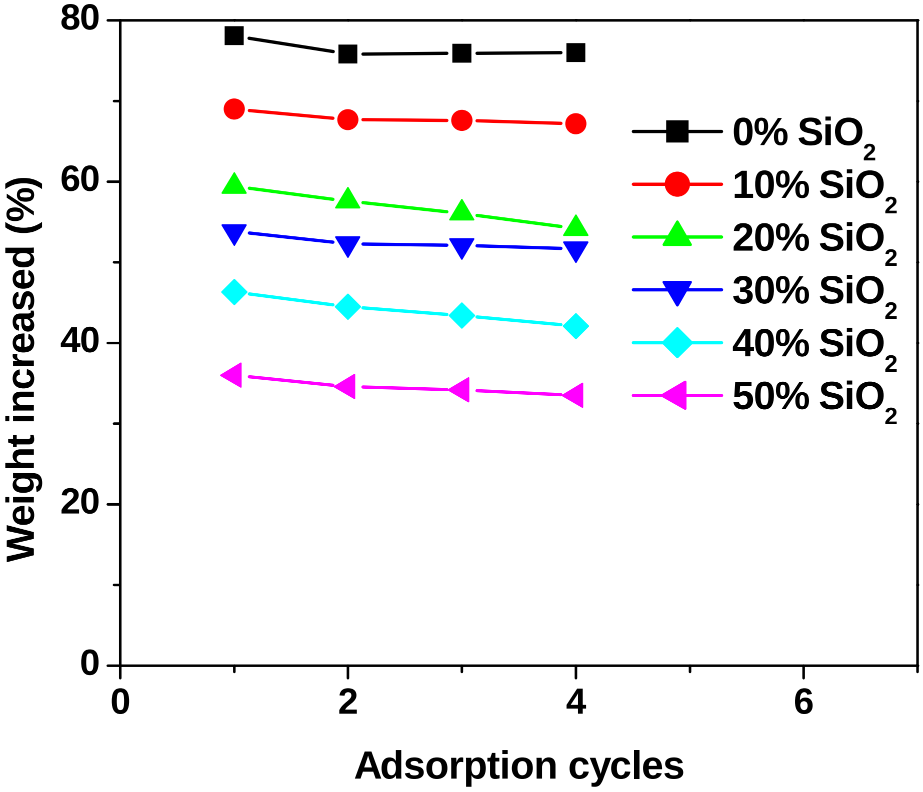

Fresh sorbent before adsorption
Sorbent after 1 cyclic adsoption-desorption
Sorbent after 2 cyclic adsoption-desorption
Sorbent after 4 cyclic adsoption-desorption
dV/dlogD pore volume (cm^{-3}/g-A)
0.5
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
2500
3000
Diameter (A)

Figure 1.10



Weight increased (%)
80
60
40
20
0
0
2
4
6
Adsorption cycles
0% SiO_2
10% SiO_2
20% SiO_2
30% SiO_2
40% SiO_2
50% SiO_2

Figure 1.11

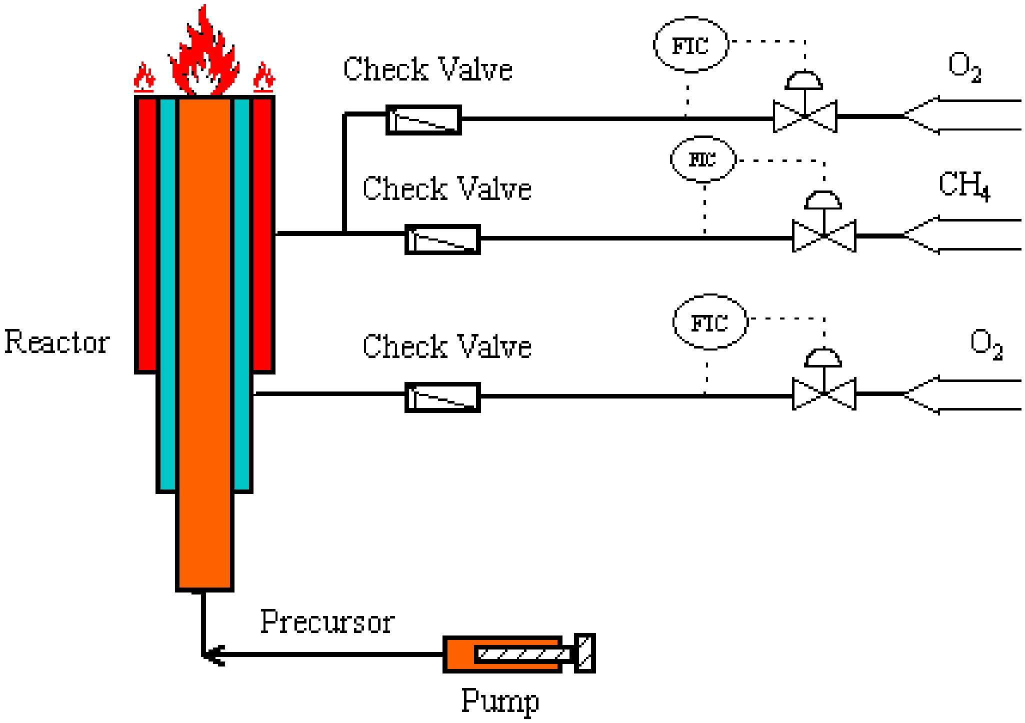

Check Valve
FIC
O_2
Check Valve
FIC
CH_4
Reactor
Check Valve
FIC
O_2
Precursor
Pump

Figure 2.1

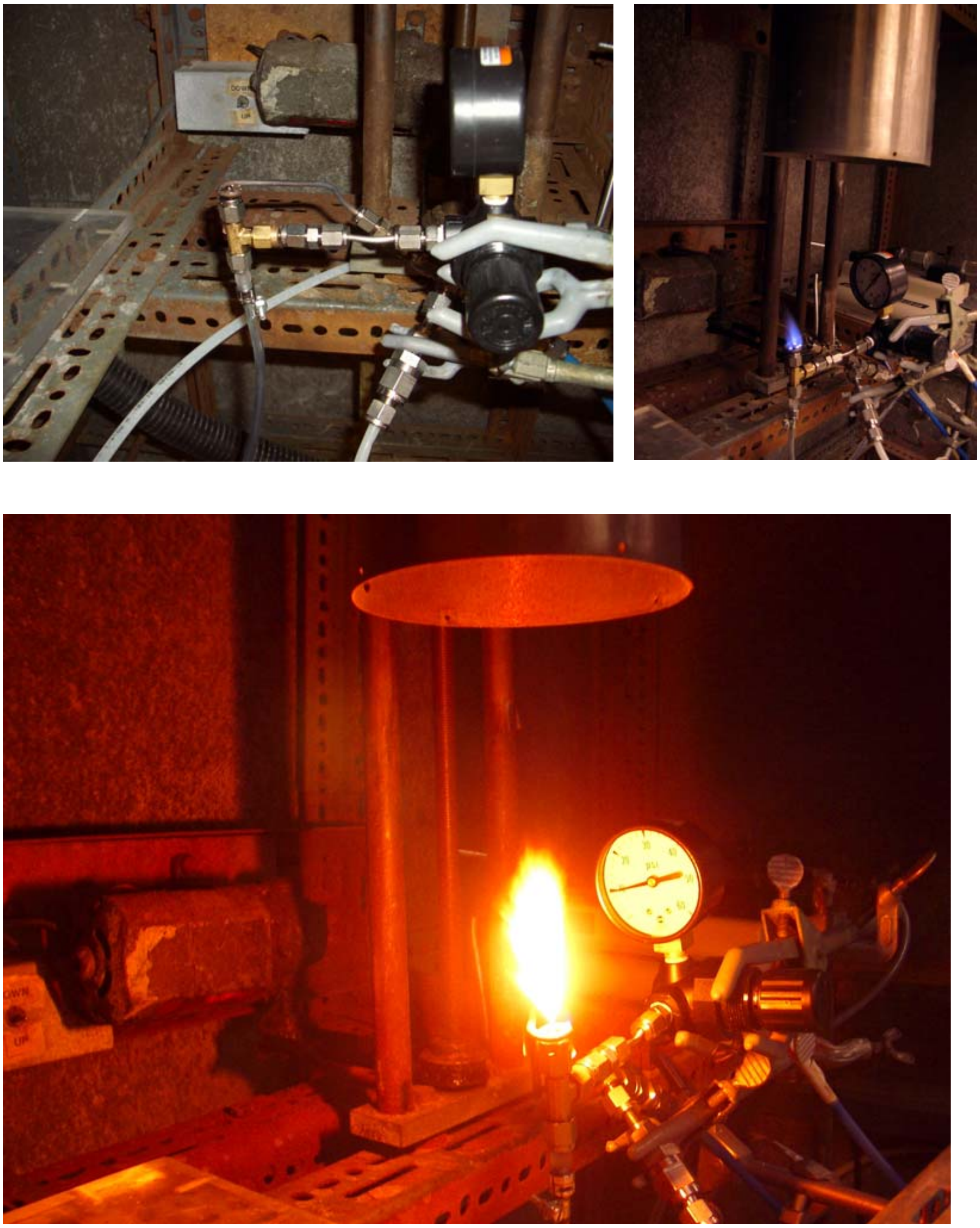


Figure2. 2

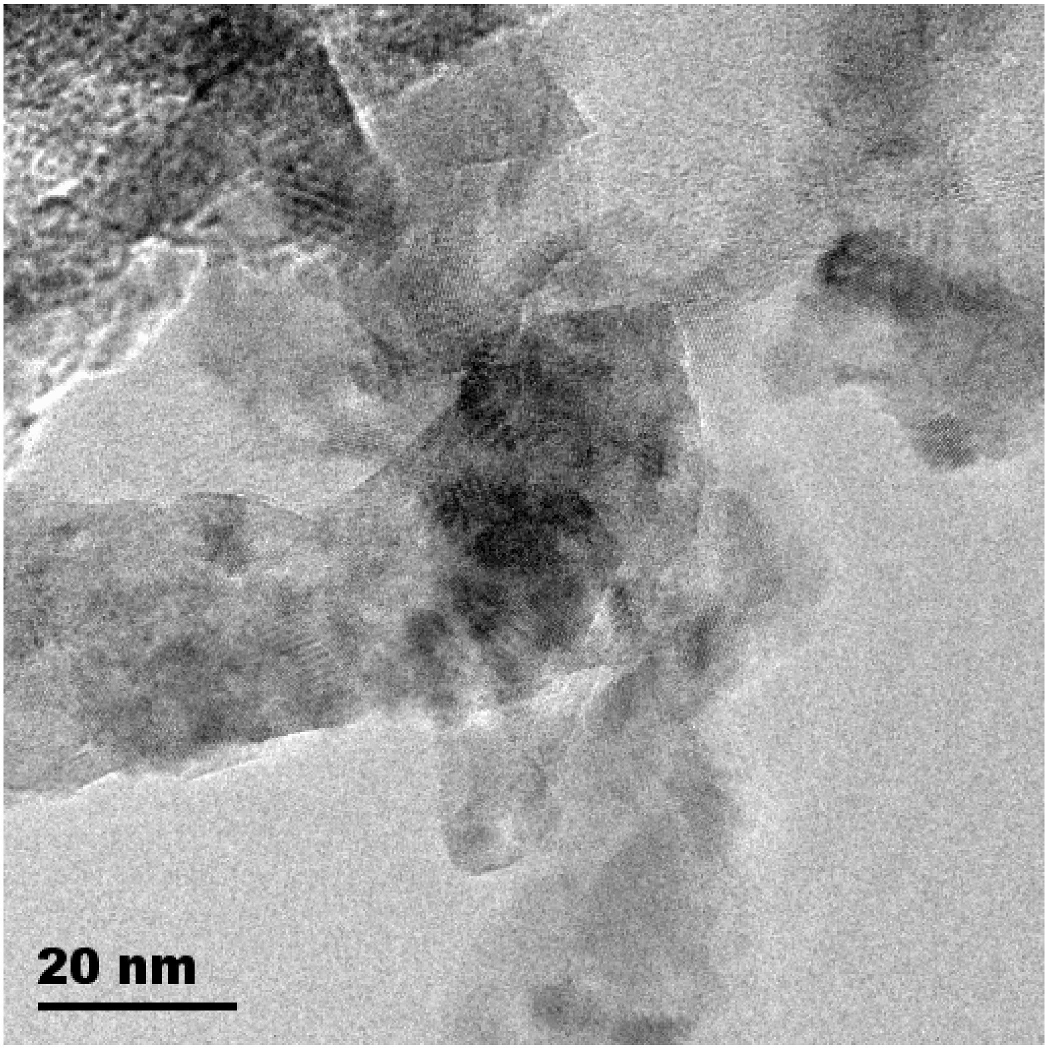


Figure 2.3.

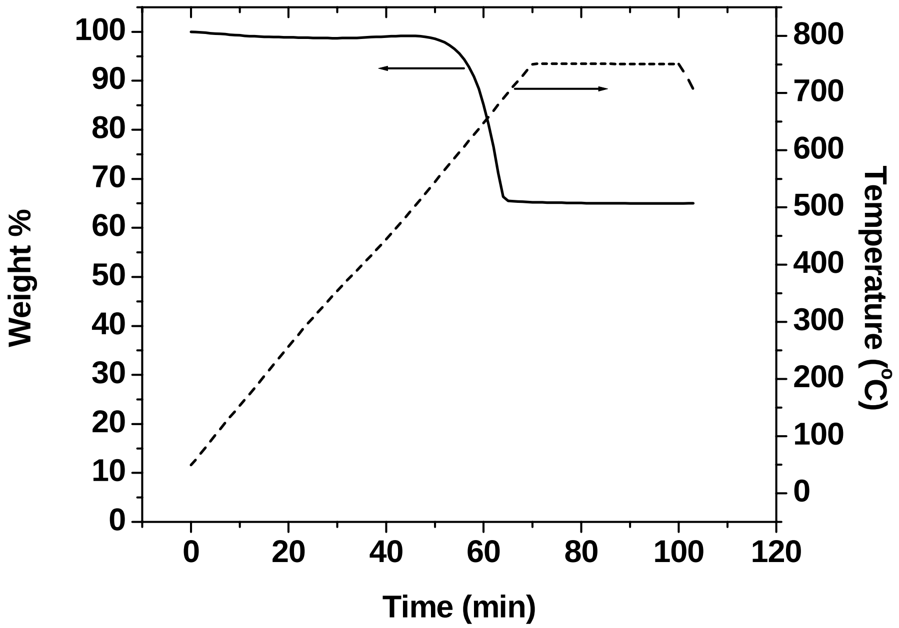

100
90
80
70
60
50
40
30
20
10
0
Weight %
800
700
600
500
400
300
200
100
0
Temperature (°C)
0
20
40
60
80
100
120
Time (min)

Figure 2.4.

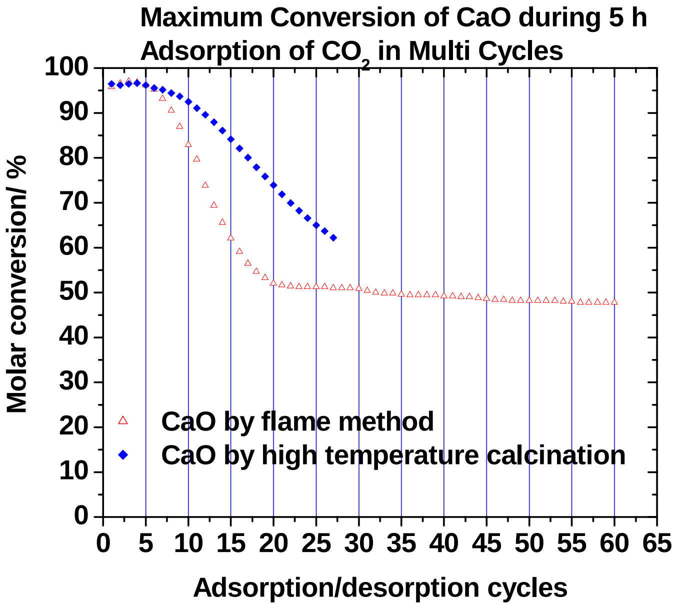

Maximum Conversion of CaO during 5 h
Adsorption of CO_2 in Multi Cycles
Molar conversion/ %
100
90
80
70
60
50
40
30
20
10
0
0 5 10 15 20 25 30 35 40 45 50 55 60 65
Adsorption/desorption cycles
△ CaO by flame method
◆ CaO by high temperature calcination

Figure 2.5

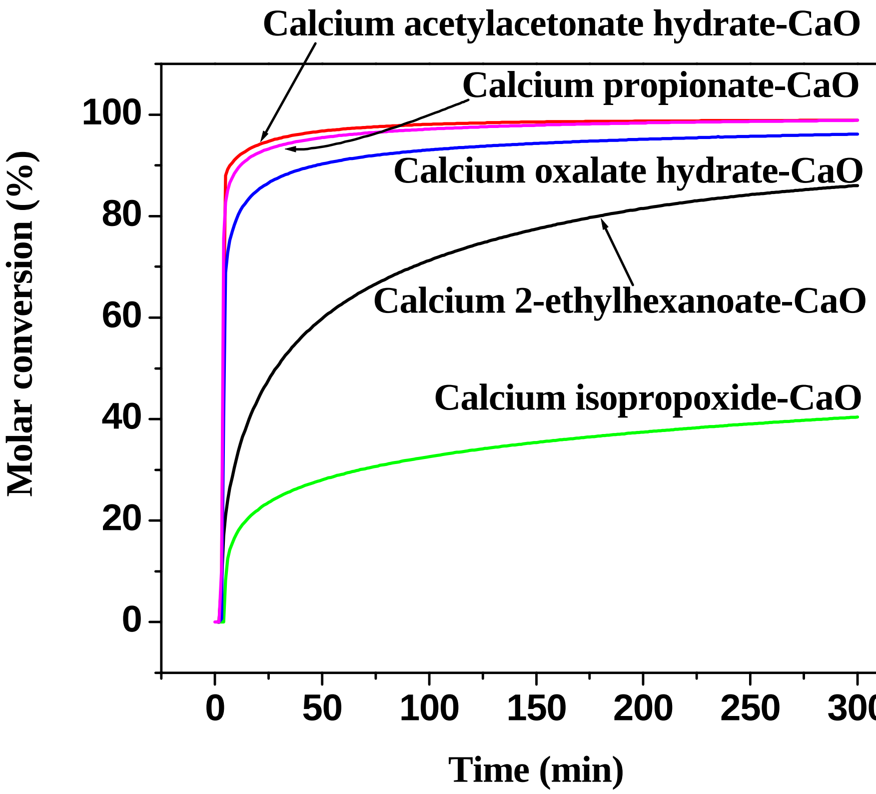

Calcium acetylacetonate hydrate-CaO
Calcium propionate-CaO
Calcium oxalate hydrate-CaO
Calcium 2-ethylhexanoate-CaO
Calcium isopropoxide-CaO
Molar conversion (%)
100
80
60
40
20
0
0
50
100
150
200
250
300
Time (min)

Figure 2.6

US Patent Applications, Refereed Articles, Presentations, and Students Receiving Support from the Grant

US Patent Applications

<u>*Title*</u>: Novel Sorbents for Separaton of CO2 at a Wide Temperature Range, <u>*Date of submission*</u>; 05/07/2001, *Number*: UC Patent Disclosure 101-020.

Journal Articles (peer reviewed)

1) H. Lu, E. P. Reddy, and P.G. Smirniotis, "Calcium Oxide Based Sorbents for Adsorption of Carbon Dioxide at High Temperatures", in preparation for submission to **Industrial & Engineering Chemistry Research,** 2005.

2) H. Lu, E. P. Reddy, and P.G. Smirniotis, "Development of High Temperature Sorbents for Adsorption of Carbon Dioxide", in preparation for submission to **Augewandte Chemie**, 2005.

3) A. Roesch, E. P. Reddy, and P.G. Smirniotis, "Parametric Study of Cs/CaO sorbents with respect to simulated flue gases at high temperatures", **Industrial & Engineering Chemistry Research (2005)**, vol 44, p.6485-6490.

4) M. Hagen, E. P. Reddy, and P.G. Smirniotis, "CO_2 Sorbents based on SiC and CaO at High Temperatures", **Gas Separation and Purification**, in preparation for submission, 2005.

Conference Presentations

This work will be presented at the 2005 AIChE Annual Meeting in Cincinnati, October 2005.

This work was presented only at the 2004 and 2005 Annual Contractors Meeting in Pittsburgh, PA in June 2004 and June 2005, respectively.

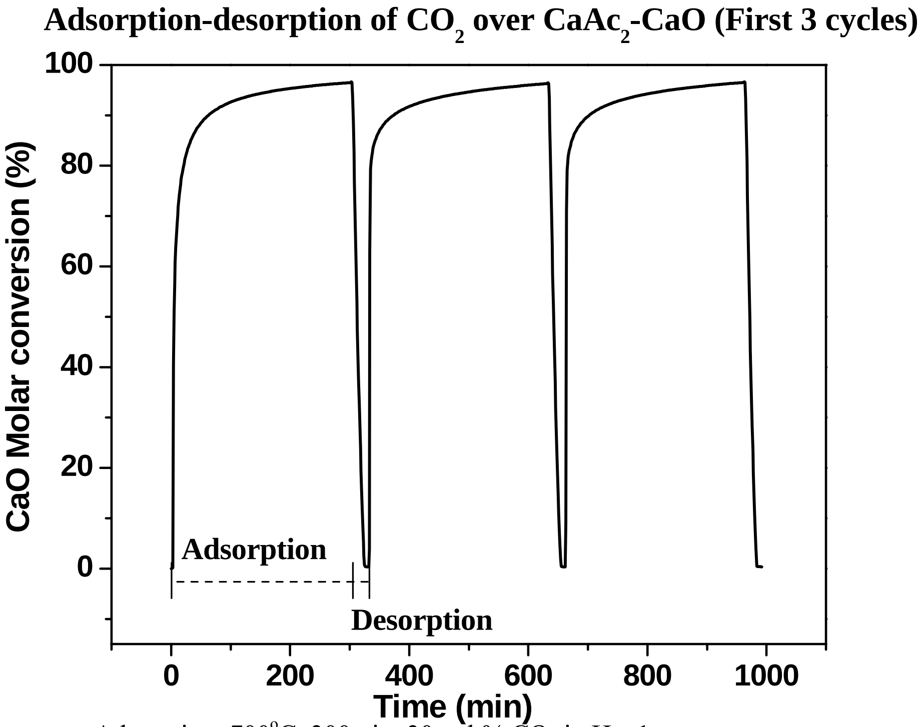
Students received support from the grant.

Graduate Students:

1) Mr. Hong LU, graduate (Ph.D.) student in Chemical Engineering

Appendices

A1. Adsorption-desorption curve of CO_2 over $CaAc_2$-CaO, 700 °C, and 800 °C; Conditions: Temperature of adsorption, 700 °C; Concentration of CO_2, 30 vol % balanced by helium, p=1atm.



Adsorption: 700°C, 300min, 30 vol % CO_2 in He, 1atm

Desorption: 700°C, 30min, He, 1atm

A2. Effect of temperature on adsorption of CO_2 over flame-CaO and $CaAc_2$-CaO. Conditions: Temperature of adsorption, 50 °C, 300 °C, 500 °C, 700 °C, and 800 °C; Concentration of CO_2, 30 vol % balanced by helium, p=1atm.