Development of Superior Sorbents for Separation of CO_2 over a Wide Temperature Range during Coal Combustion

Prof. Panagiotis (Peter) Smirniotis (PI)

Chemical & Materials Engineering Department, University of Cincinnati, Cincinnati, OH 45221-0171

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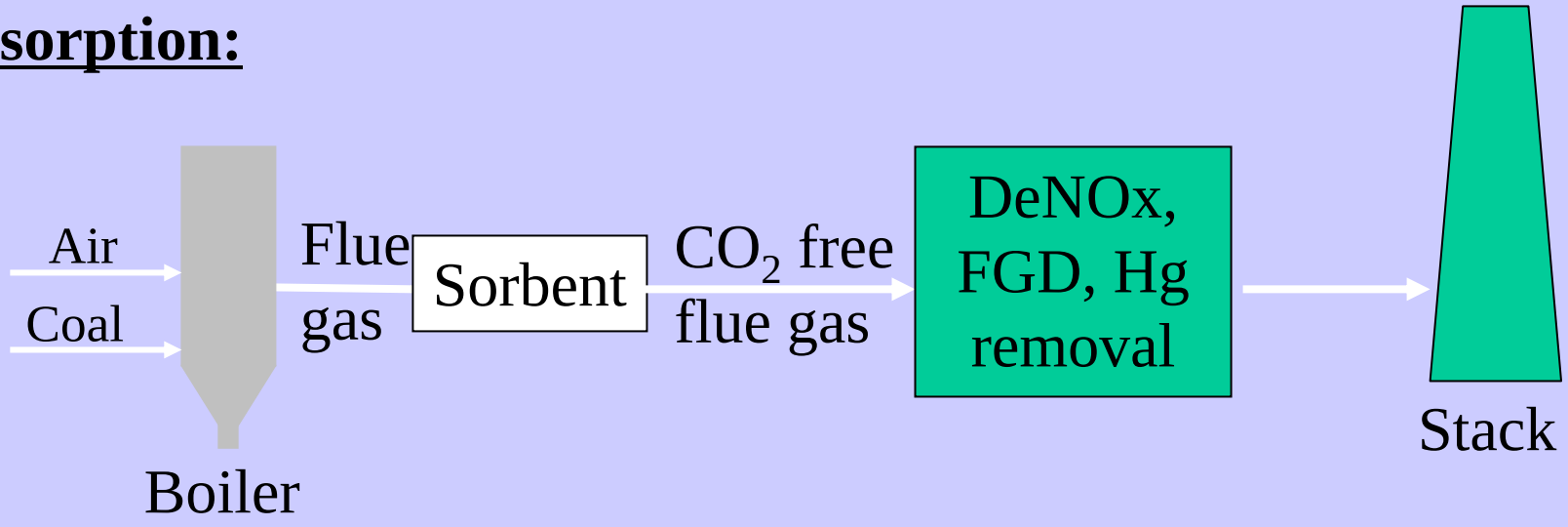
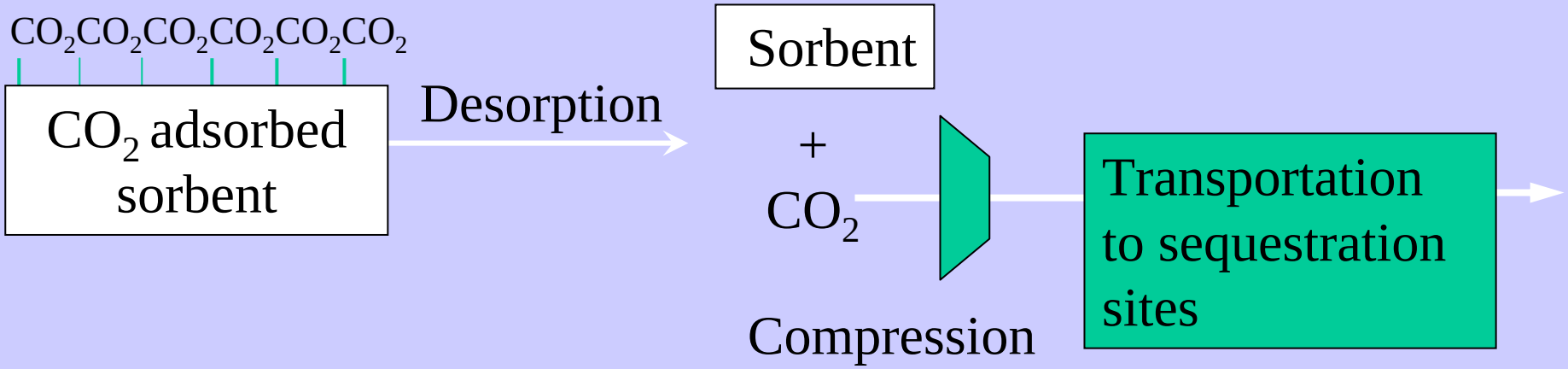
Concept of the CO_2 Separation Process

Adsorption:



Sorbent Regeneration:



Background Review of the Literature and State-of-the Art

Possible methods for CO_2 separation:

- Absorption
- Adsorption
- Cryogenic distillation
- Membrane separation

Most Related References

- Inui et al., *Ind.eng. Chem. Res.*, 27, 1103-1109 (1988)

  High Al zeolites (13 X, Erionite) were used in PSA mode for temperatures lower than 250 ^{o}C.

- Ojo et al., *U.S. Patent* 5, 531,808 (1996)

  Low silicon X faujasite (LSX) exchange with mono-, di-, and tri-valent metals were used.

  It is used to purify gases which are less polar than CO_2. Studies were performed only for very low concentrations of CO_2.

- Suzuki et al., *J. Chem. Eng. Japan*, 30, 954-958 (1997)

  Hydrophobic zeolites were used with success because they repel water. However, the operating temperature is low (T = 60 ^{o}C)

- Aihara et al, *Applied Energy*, 69 (3), 225-238 (2001)

  $CaTiO_3$ was added to CaO by molar ratio 1:1 as inert framework.

- Gupta and Fan, *Industrial & Engineering Chemistry Research*, 41 (16), 4035-4042 (2002)

  CaO sorbents were synthesize from calcium hydrate to get mesopores.

- Kuramoto et al, *Industrial & Engineering Chemistry Research*, 42 (5), 975-981(2003)

  Intermediate hydration treatment was performed between calcination and carbonation.

- Reddy and Smirniotis [1] , *Journal of Physical Chemistry B*, 108 (23), 7794-7800 (2004)

  Alkali metals were dope on CaO sorbents to form superbasic sites.

- Alvarez and Abanades, *Energy & Fuels*, 19 (1), 270-278 (2005)

  Carbonation conversion of CaO sorbent depends on both surface area and geometry.

Limitations of Existing Technologies

- Most carbon dioxide separation methods are used around or under 50°C which is far less than temperature of fuel gas exiting furnace.
- Existing methods demonstrate low capacities: Monoethanolamine (MEA): <6%(wt); Carbon based sorbents: <8%(wt).
- Moreover, the selectivity for CO_2 sorption is low, especially if other polar molecules are present in the mixture.
- Poisons (H_2O, SO_2, etc….) can dramatically decrease their performance.
- Several sorbents adsorb O_2 and N_2.

Need for Development of Highly Active and Selective High Temperature CO_2 Sorbents

- Operation at elevated temperatures to remove CO_2 from hot gas streams
- Sorbents with high capacity are needed
- Sorbents with zero affinity for N_2 and O_2 are needed (both gases constitute more than 77 vol.% of typical flue gas compositions)
- Easy to adapt in existing units
- Low Cost
- Highly reproducible synthesis

Requirements for Operating at Elevated Temperatures

- Operation at severe conditions, namely T>600 ^{o}C in presence of SO_2, NO_x, 10+ vol.% H_2O, etc…..
- High saturation capacity
- Fast kinetics
- High selectivity for CO_2 and minimal affinity for the rest of the gases
- Time stability, durability for large number of cycles
- Excellent regenerability

Original Objectives of this DOE Project (DE-FG26-03-NT41810)

- Integrate the synthesis efforts aiming at developing basic and superbasic supports and sorbents. Enhance the knowledge of functionalizing the surface for obtaining the desirable performance.
- Characterize the synthesized sorbents with numerous state-of-the-art characterization techniques to understand their surface properties and functionality.
- Direct the synthesis and characterizations toward highly durable systems that will ensure stability for regeneration over many hundred cycles at elevated temperatures and severe operation environments.
- Use the obtained information as feed-back to design the most effective sorbents. Test these sorbents with gas mixtures containing CO_2, H_2O, air, NO, SO_2, SO_3, H_2, and CO at selected compositions simulating industrial operation of coal-fired boilers.

Work Performed for this US DOE Award

- Synthesis and screening of alkali metals doped on CaO
  * Wet impregnation technique
- Screening of various CaO precursors
- Characterization with state-of-art techniques

Screening of Metal Oxides and Sorbents

- Thermogravimetric Analysis (TGA)
- Pretreatment at 750°C in the presence of Helium
- 30 vol% CO_2 feed at atmosphere unless otherwise stated
- Selection for further consideration is based on:

  * Saturation capacity

  * Sorption selectivity

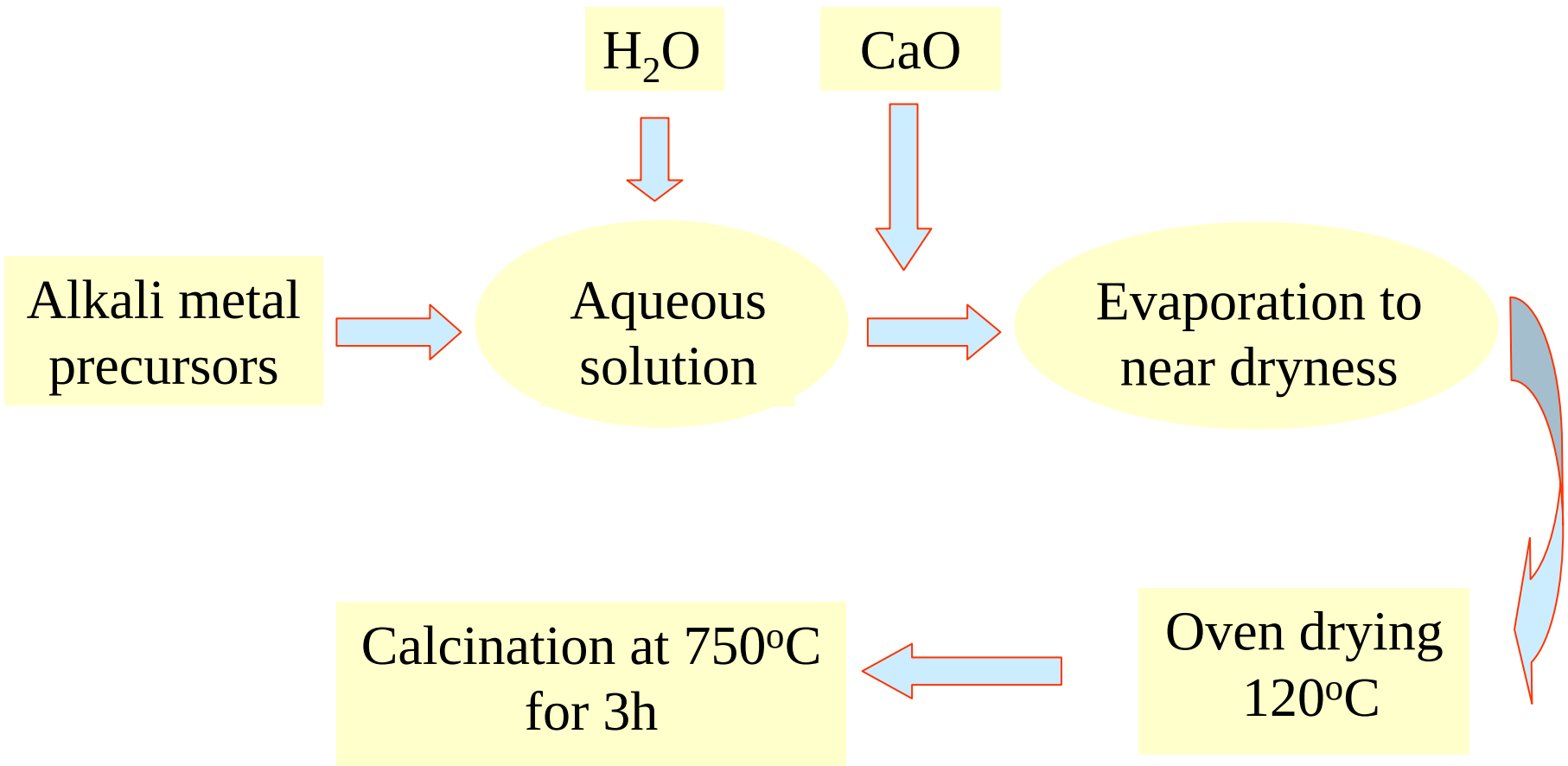
  * Sorption temperature

  * Durability

MAIN RESULTS:

- **CaO chosen as a viable support for sorbents**
- **Cs/CaO was found to be very promising**
- **Calcium acetate was chosen as the most promising precursor for detailed study**

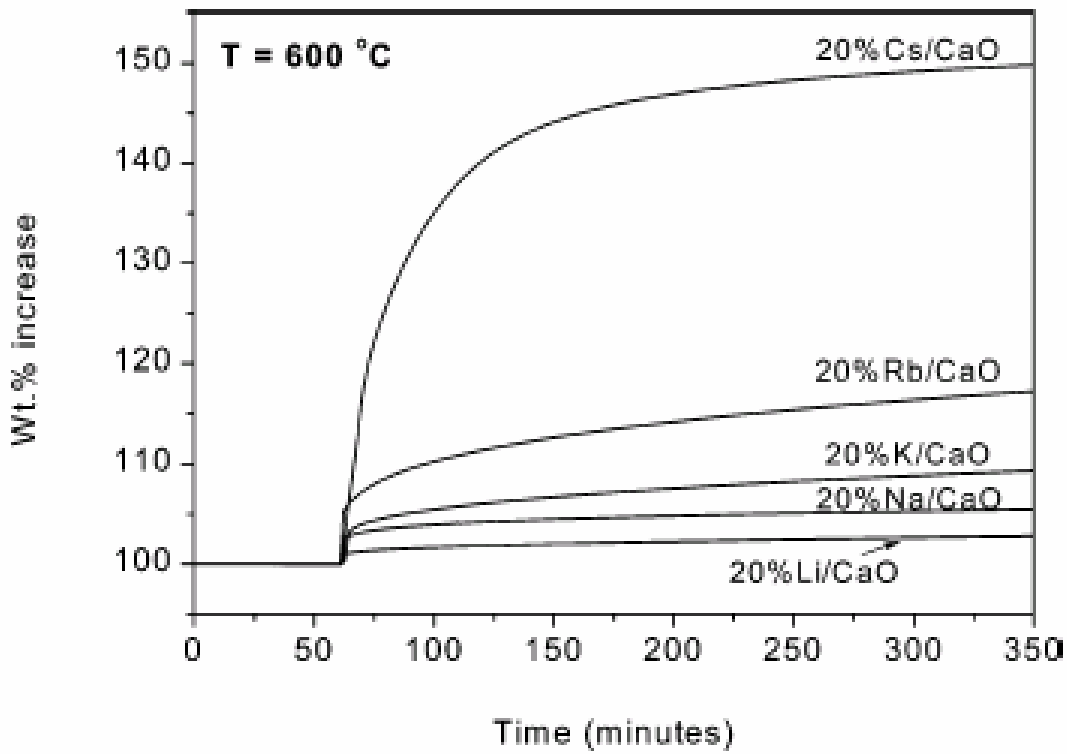
Synthesis of Sorbents



PHASE I
ALKALI METALS ON CALCIUM OXIDE

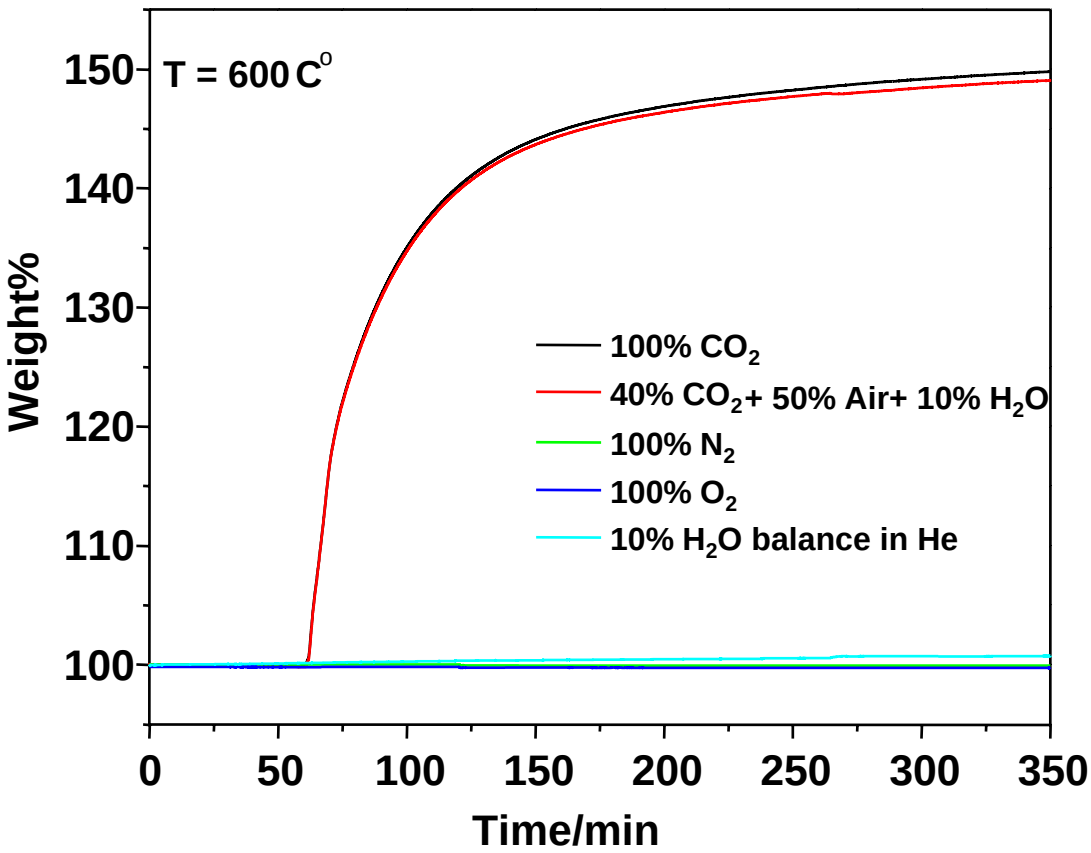
Adsorption of CO_2 over CaO Doped with Various Alkali Metals

30 vol % CO_2 was balanced in He



CaO sorbents doped with Cs showed much higher capacity than those with other alkali metals

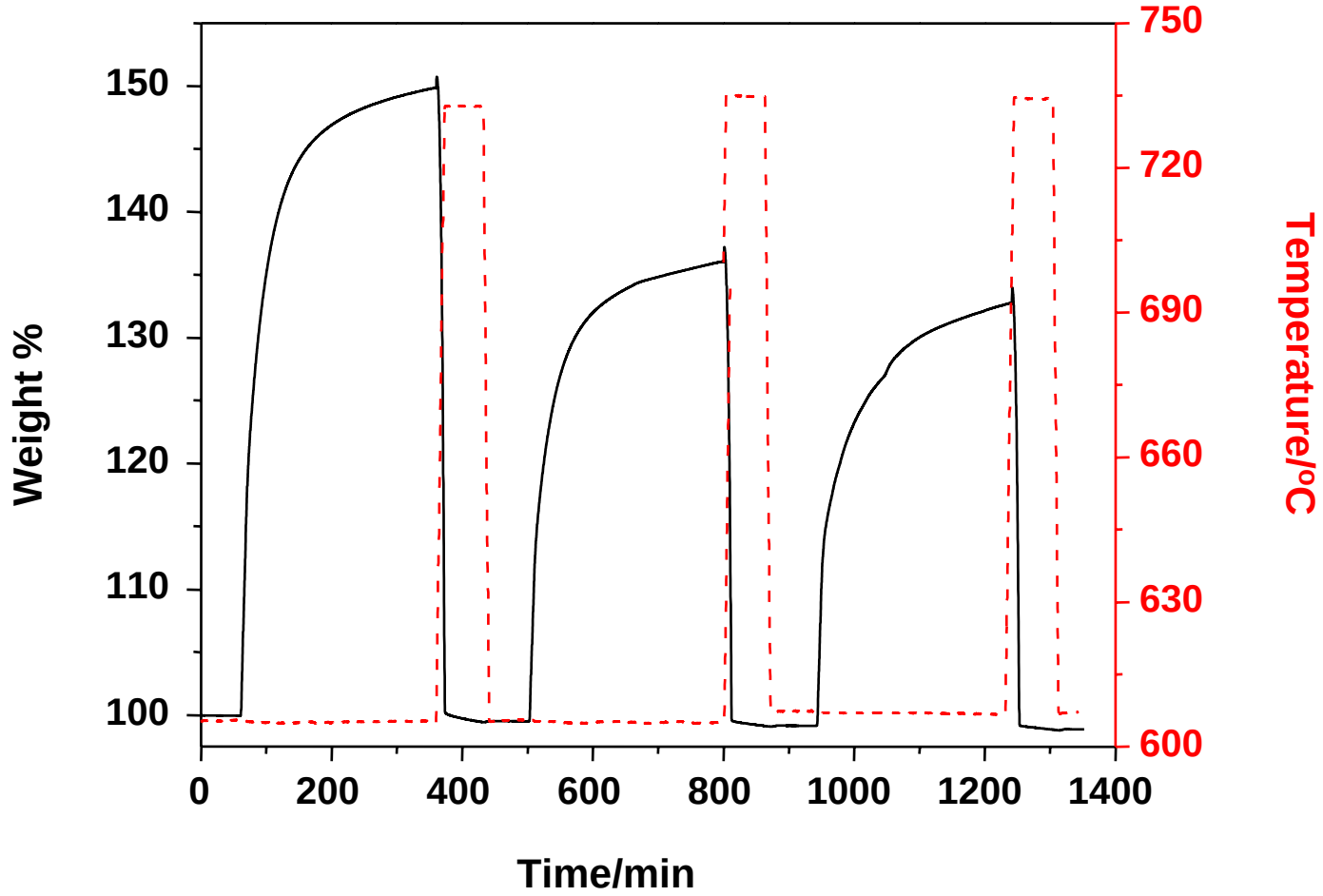
Effect on Adsorption of other Gases over 20 wt% Cs/CaO at 600 ^{o}C



The sorbent has high selectivity for CO_2 over N_2, O_2, and H_2O.

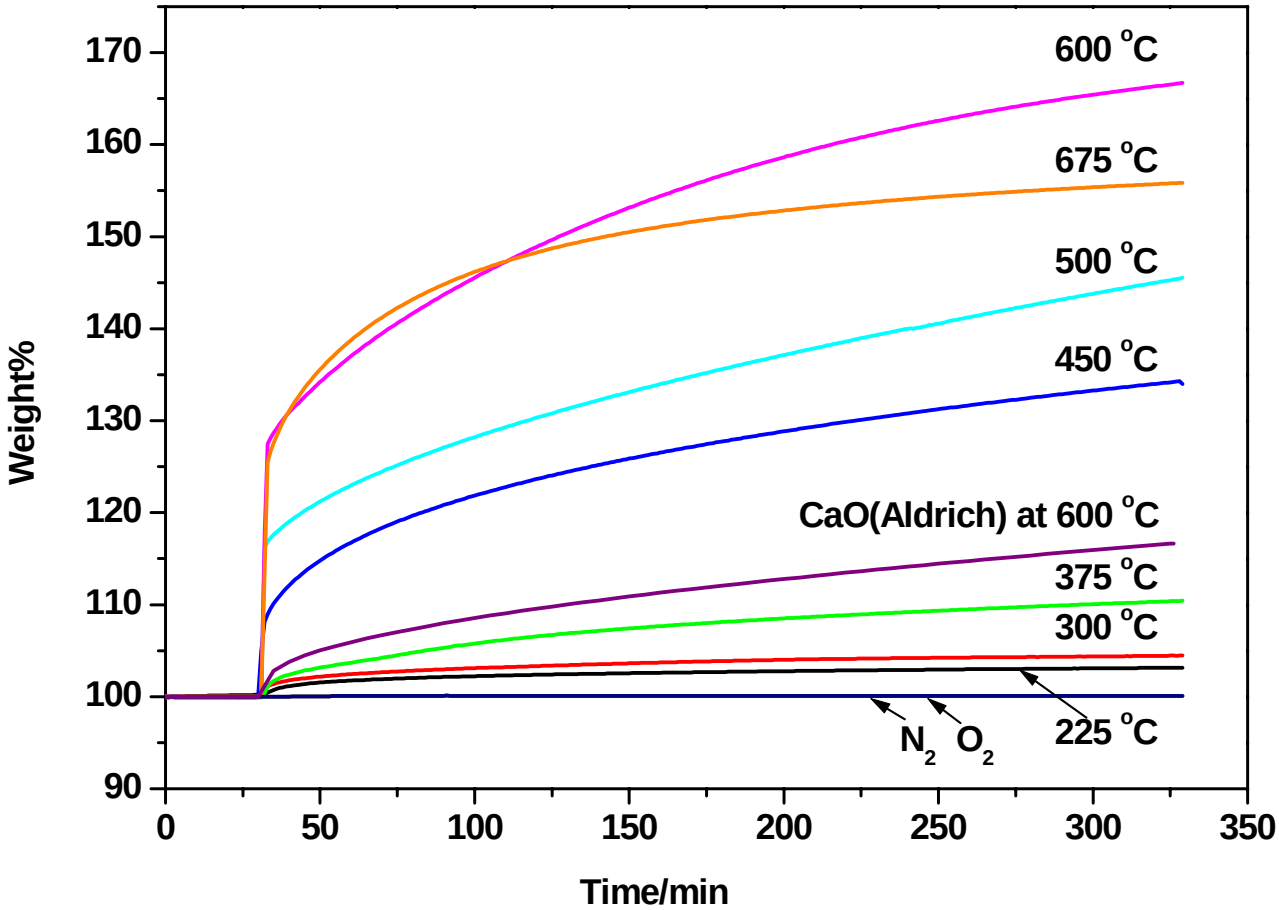
Cyclic Adsorption/Desorption of CO_2 over 20 wt% Cs/CaO at 600 °C

30 vol % CO_2 was balanced in helium.



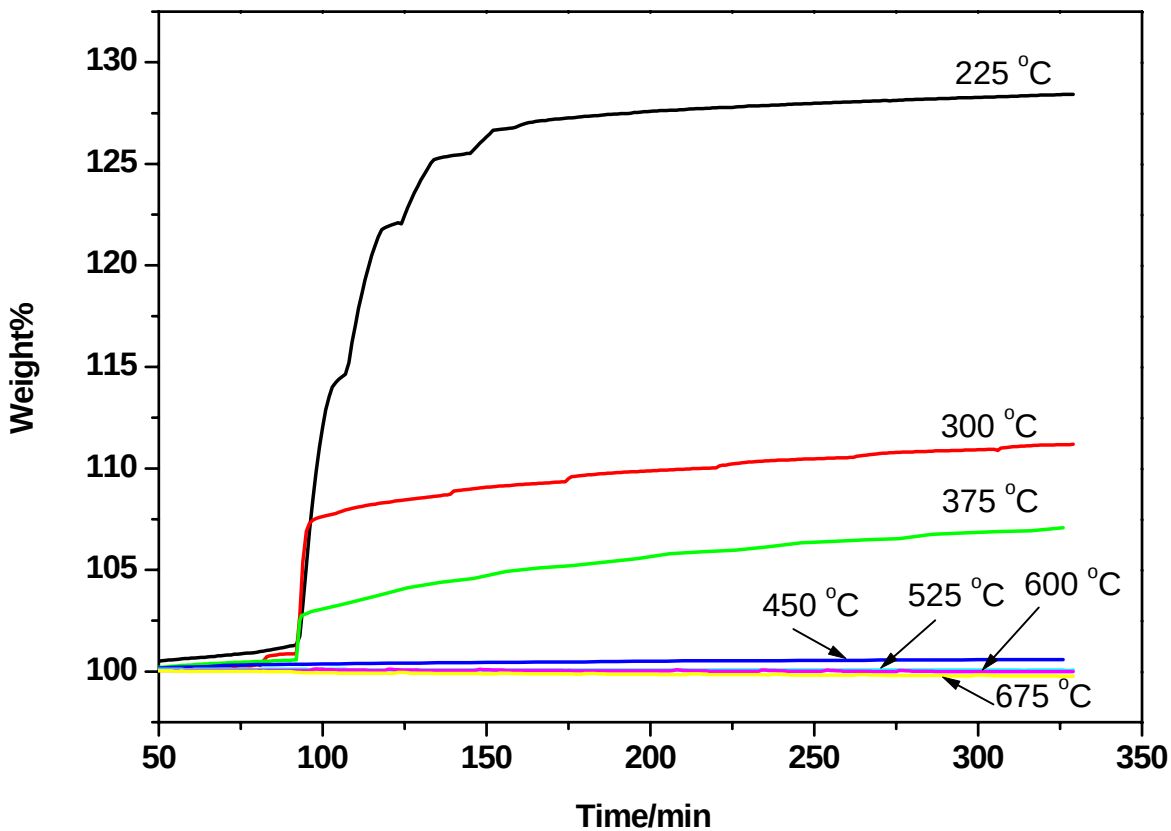
Effect of Temperatures on Adsorption of CO_2 over 20 wt% Cs/CaO

30 vol % CO_2 was balanced in helium.



Effect of Temperatures on Adsorption of H_2O over 20wt% Cs/CaO

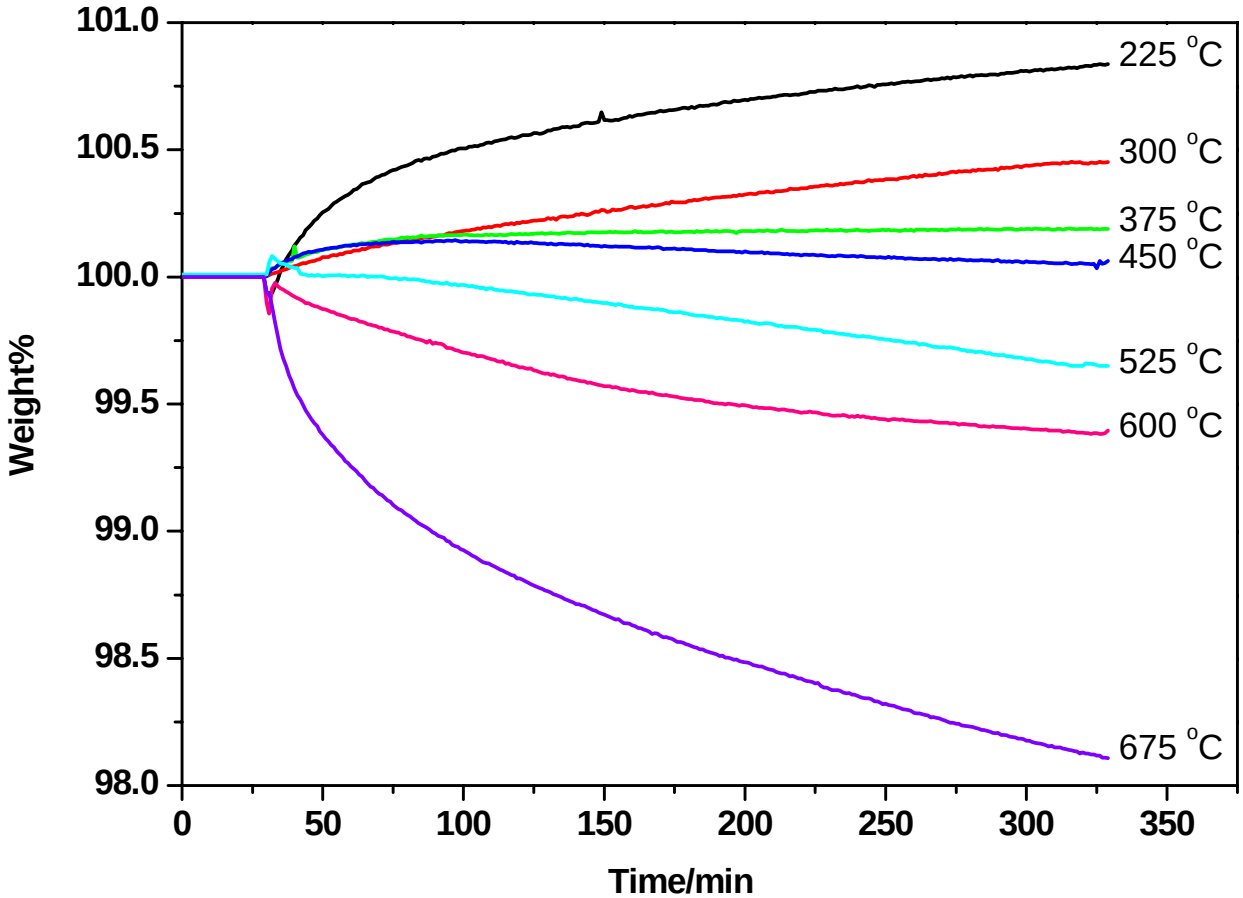
10 vol% H_2O was balanced in helium.



At high temperatures, the sorbent has high selectivity of CO_2 over H_2O.

Effect of Temperature on Adsorption of NO over 20 wt% Cs/CaO

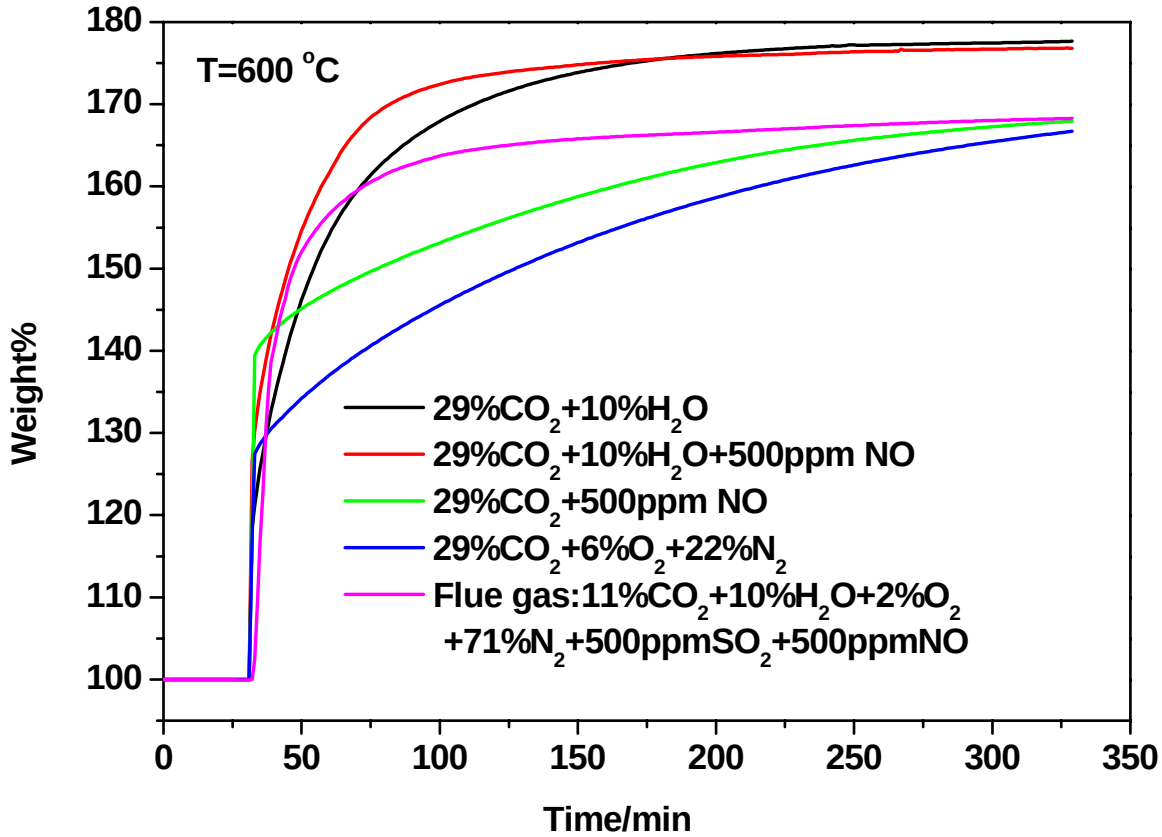
4000 ppm NO was balanced in helium.



At relatively low temperatures，sorbent adsorbed a little NO due to the formation of $CsNO_3$.

Effect of Different Gases on Adsorption of CO_2 over 20wt% Cs/CaO

All gases were balanced in helium.



Even under severe simulated flue gas conditions, the sorbent retained its high capacity.

Proposed Mechanism

Adsorption step:

$$Me^{+}/CaO + CO_2(g) \xrightarrow{600\ ^{o}C} Me_2(CO_3) + CaCO_3$$

Desorption step:

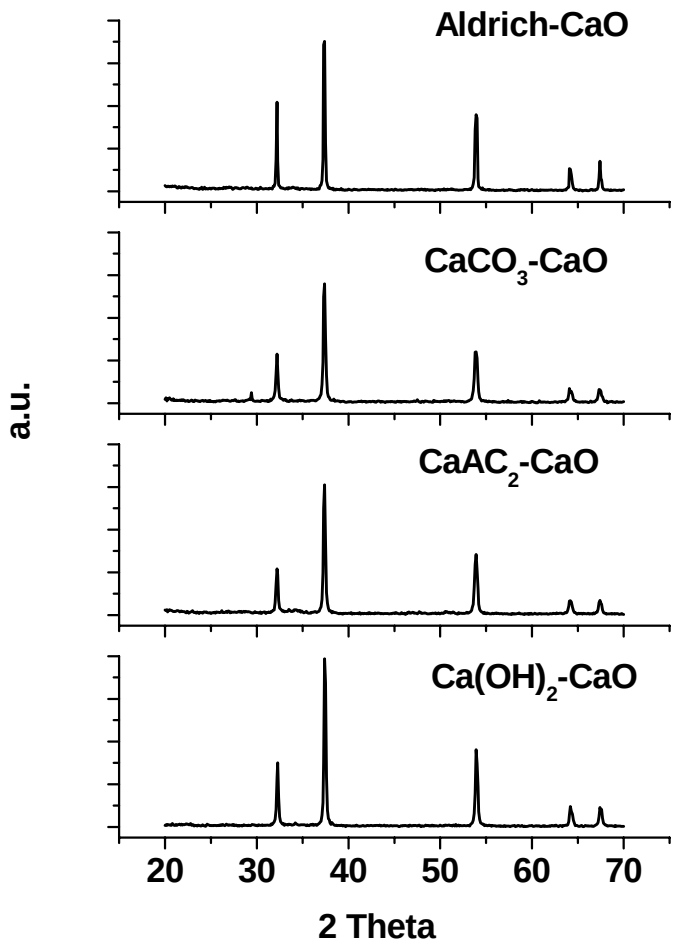
$$Me_2CO_3 + CaCO_3 \xrightarrow{725\ ^{o}C} Me^{+}/CaO + CO_2$$

where:

Me = Alkali metals

PHASE II
CALCIUM OXIDE SORBENTS MADE BY VARIOUS PRECURSORS

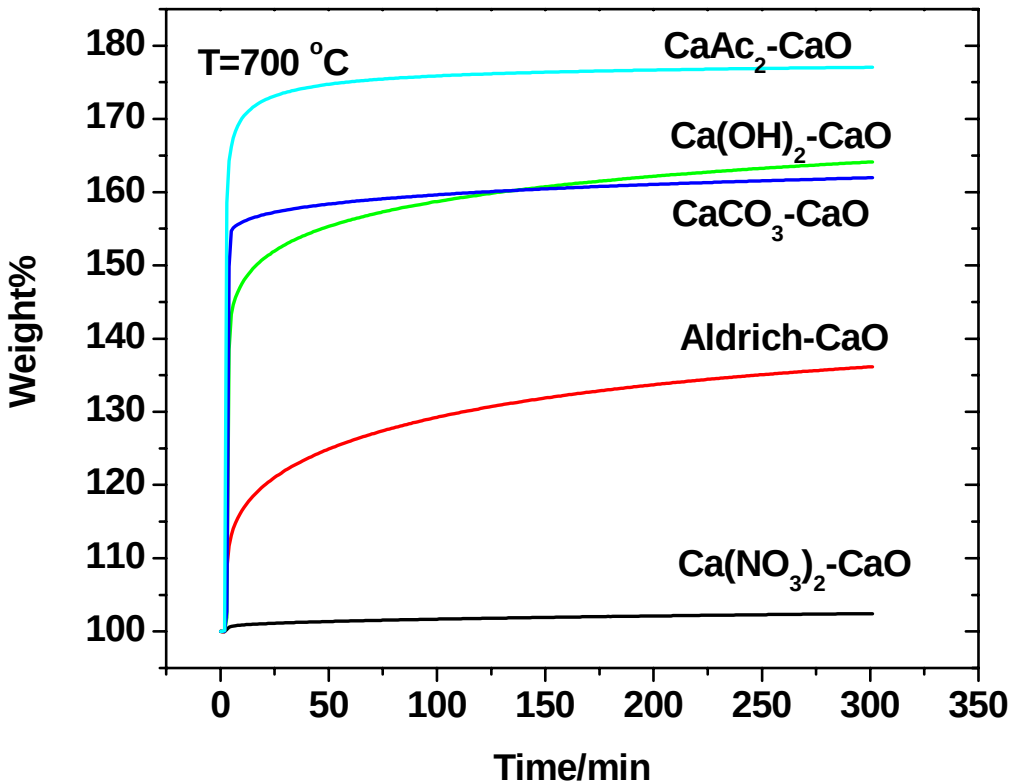
XRD Diffractograms of CaO Prepared with Various Precursors



The same characteristic peaks of calcium oxide sorbents indicate that chemical composition and structural crystallinity were very similar.

Adsorption of CO_2 over CaO Sorbents Prepared with Various Precursors at 700 ^oC

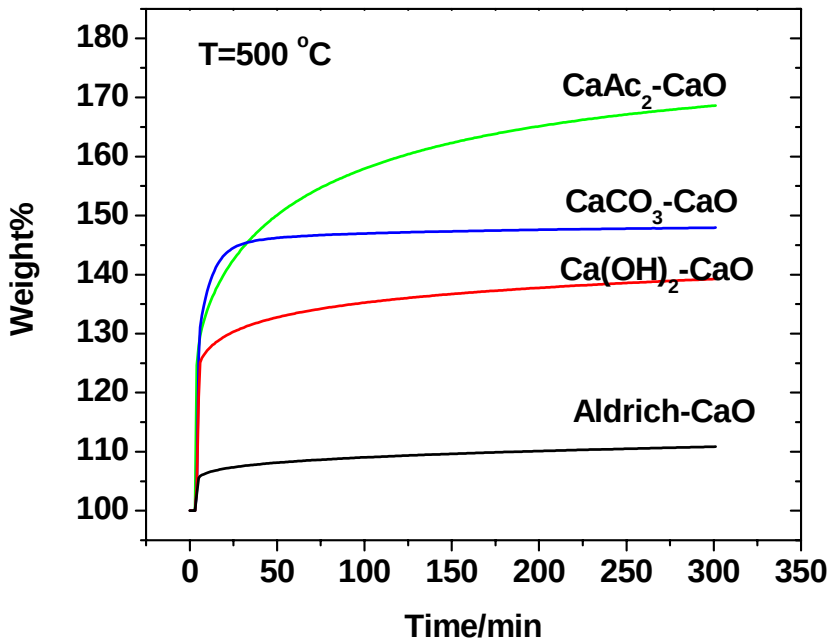
30 vol % CO_2 was balanced in helium.

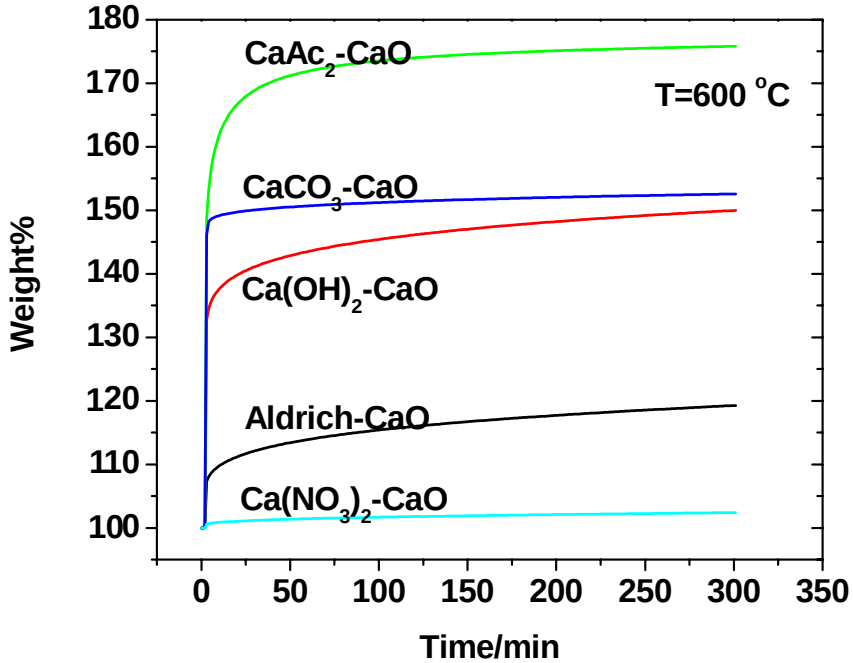


Adsorption behaviors exhibited distinguished two stages: fast and slow. $CaAc_2$-CaO has capacity of more than 75 wt% per mass sorbent, nearly 100% molar conversion.

Adsorption of CO_2 over CaO Sorbents Prepared with Various Precursors at 500 and 600 ^oC

30 vol % CO_2 was balanced in helium.





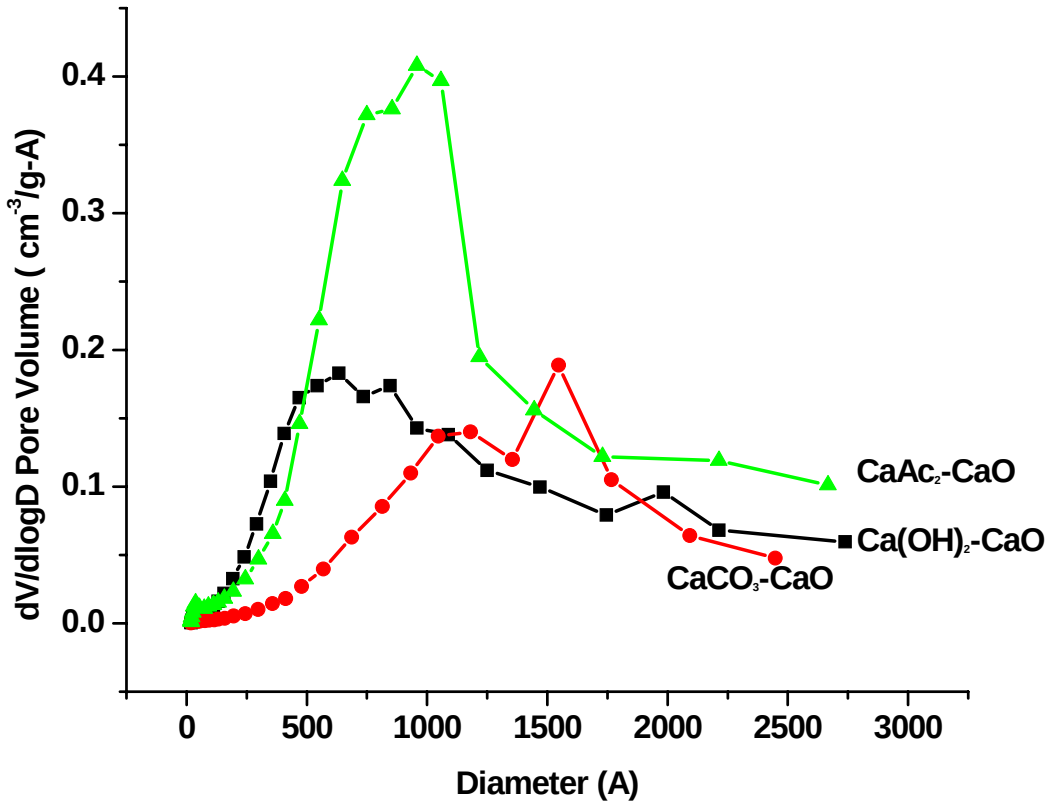
$CaAc_2$-CaO exhibited highest capacity at high temperatures. That capacity corresponds to a sorbent conversion of nearly 100% at 700 ^oC.

Morphological Properties of Various CaO Sorbents

CaO Precursor	BET [m^2/g]	Pore Volume [cm^3/g]
$Ca(NO_3)_2\ 4H_2O$	Not available	Not available
Aldrich-CaO	4.2	0.02
$Ca(OH)_2$	13.9	0.15
$CaCO_3$	5.3	0.08
$CaAc_2\ H_2O$	20.2	0.23

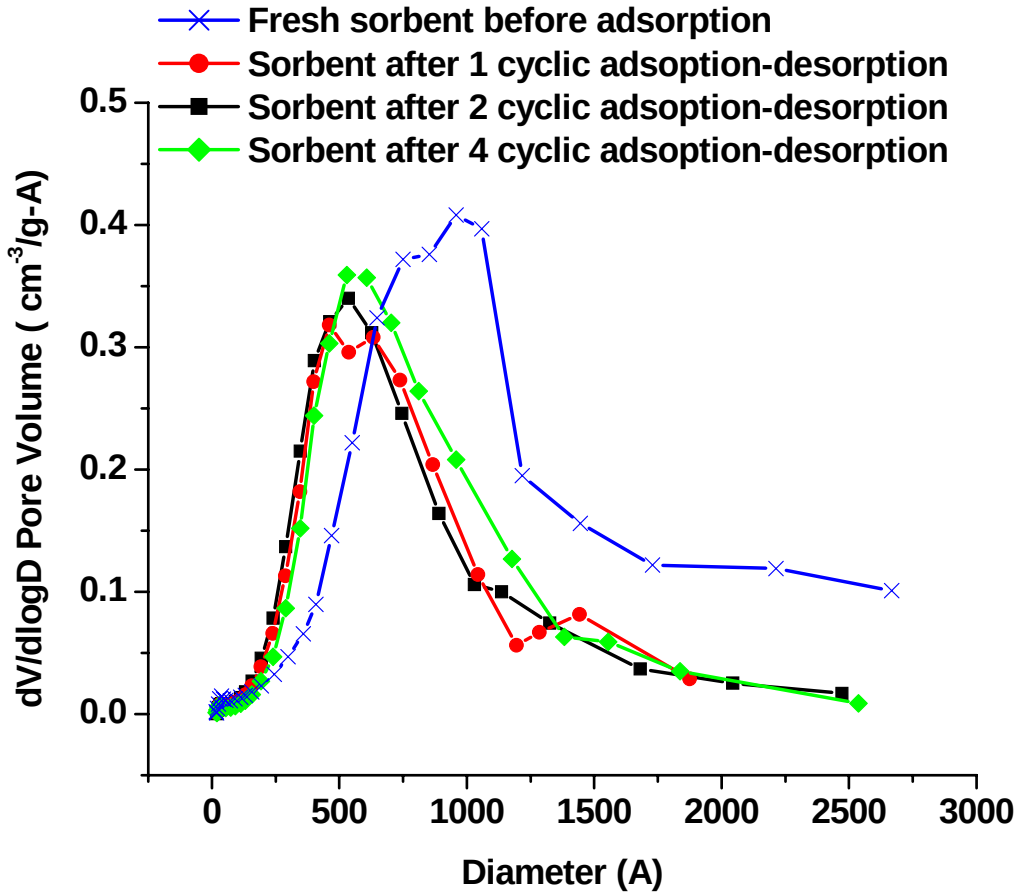
Higher BET surface area and higher pore volume contribute to $CaAc_2$-CaO's high adsorption capacity for CO_2.

Pore Size Distribution of CaO Sorbents with Various Precursors



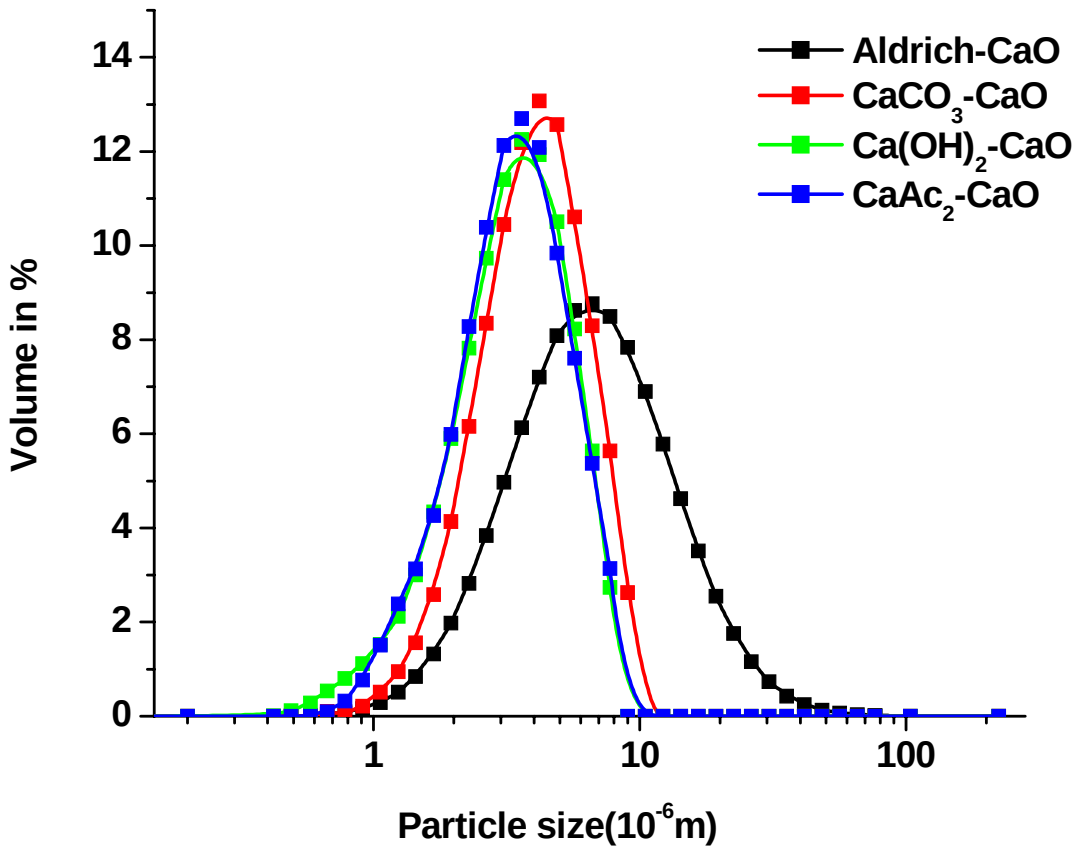
Higher pore volume contribute to $CaAc_2$-CaO's high adsorption capacity for CO_2.

Pore Size Distribution of $CaAc_2$ -CaO Sorbents: before and after adsorption



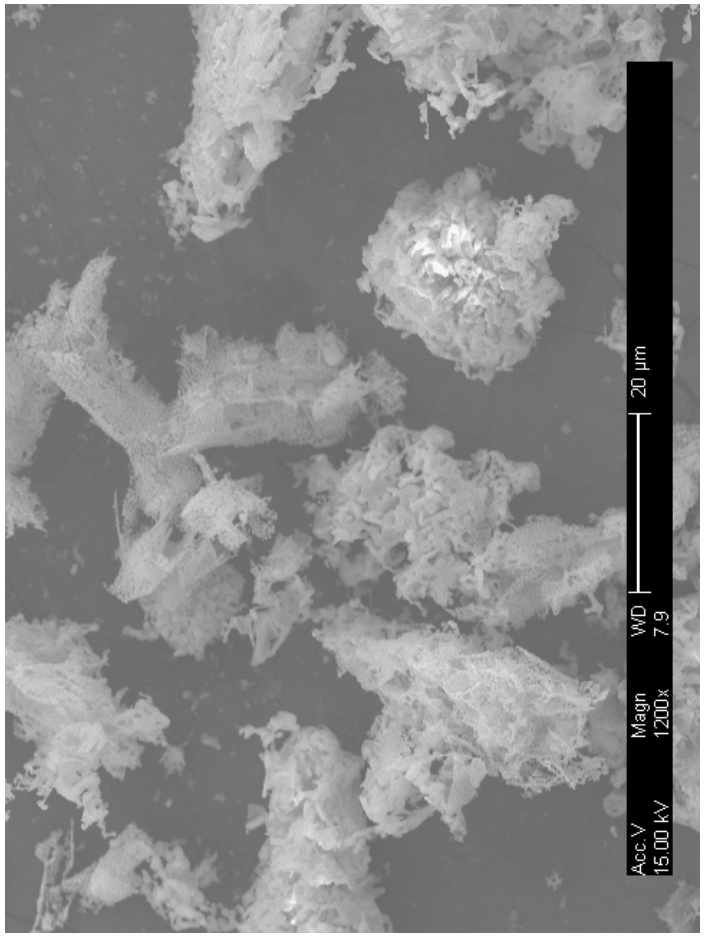
Both pore diameter and pore volume decreased a little when reaction cycles went on.

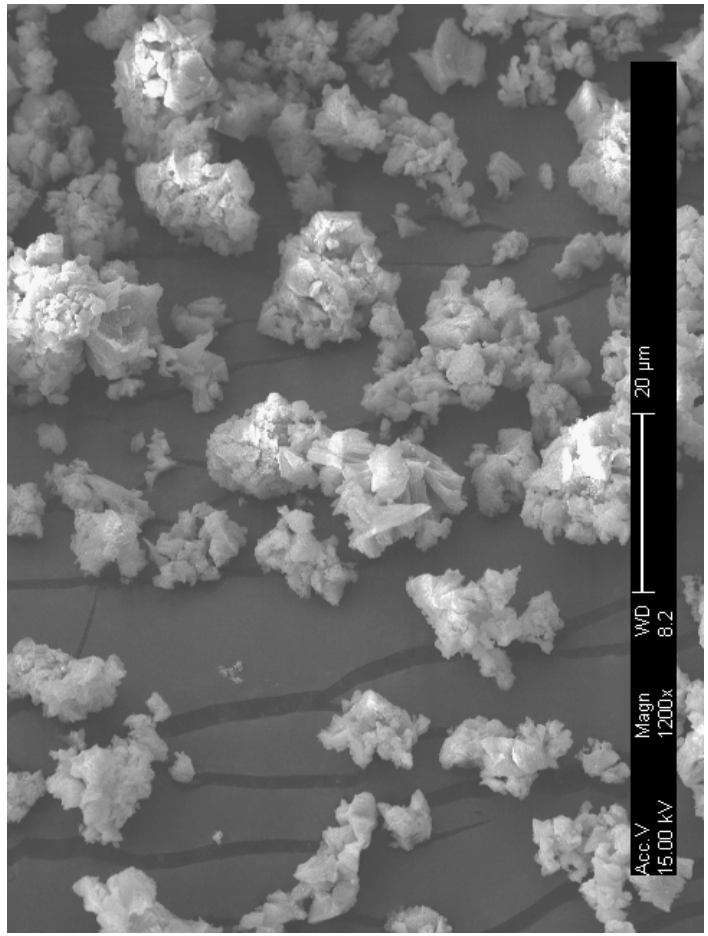
Particle Size Distribution of CaO Sorbents Prepared with Various Precursors



Since all sorbents have similar particle size, it might not be the main factor for different sorbent capacities.

SEM of $CaAc_2$-CaO (Left) and $Ca(OH)_2$-CaO (Right)

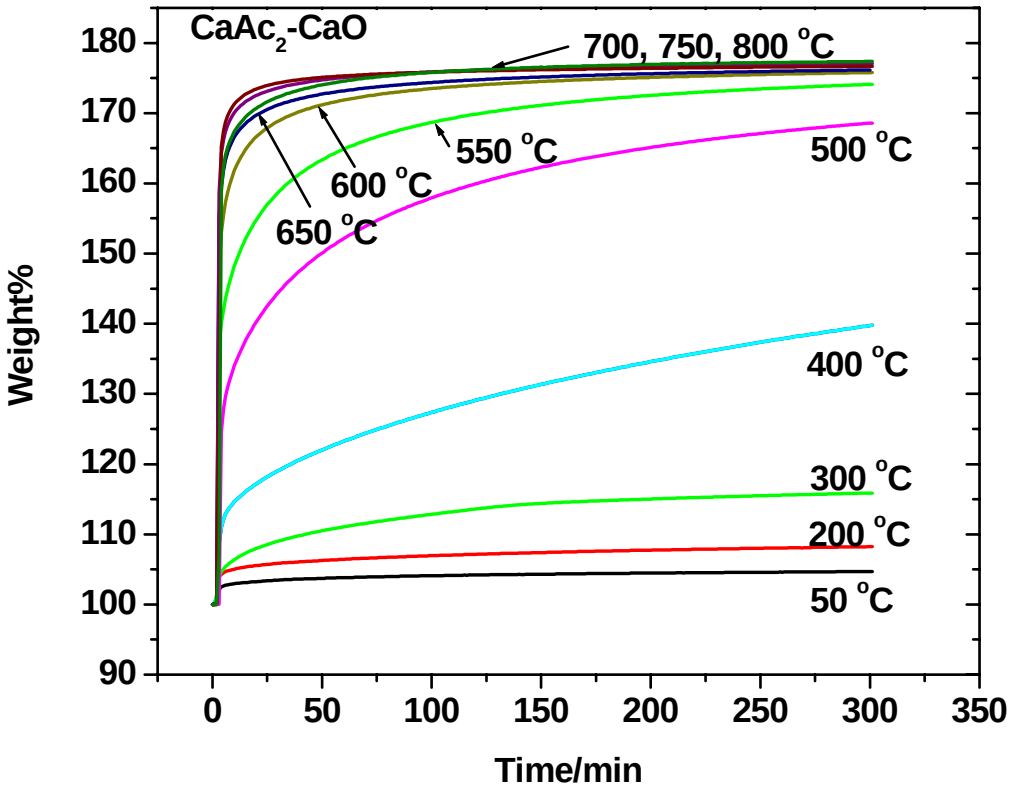




The photos indicate “fluffy” morphology of $CaAc_2$-CaO contributes to its higher CO_2 adsorption capacity than that of $Ca(OH)_2$-CaO.

Effect of Temperatures on Adsorption of CO_2 over $CaAc_2$-CaO

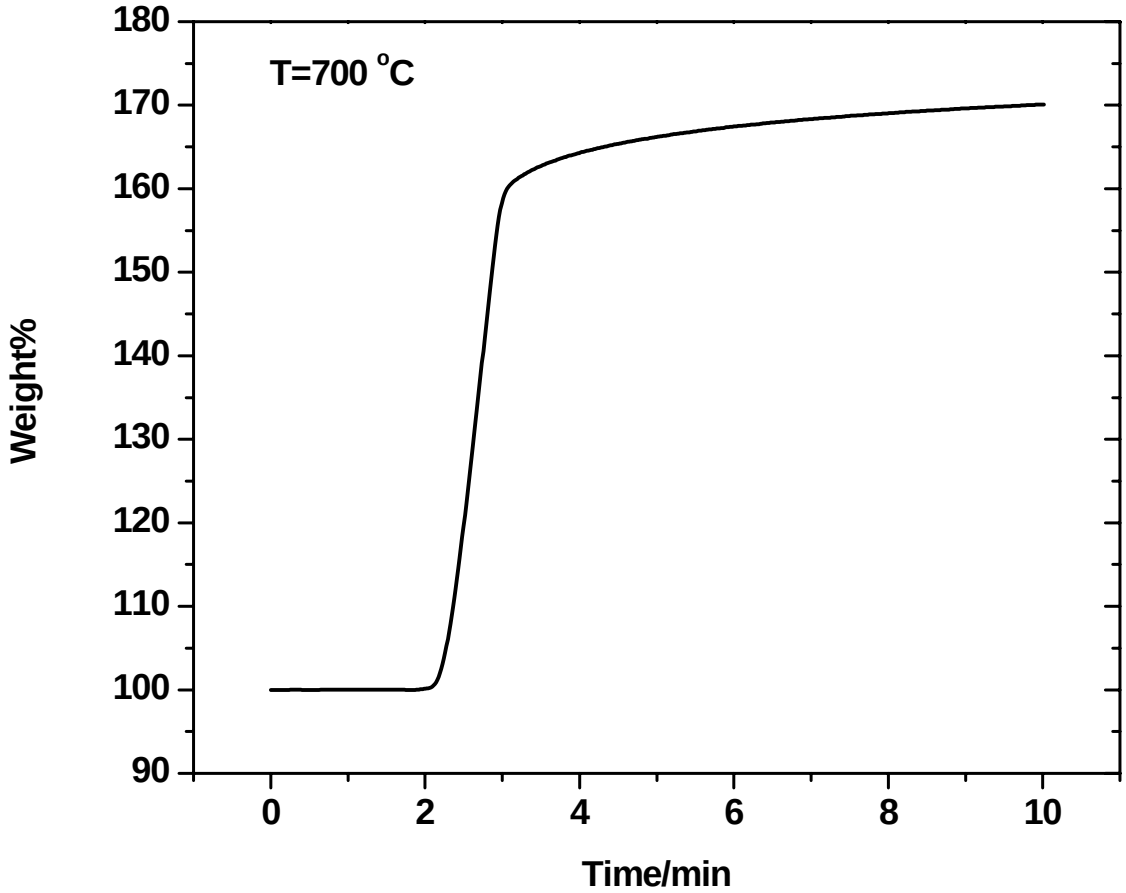
30 vol % CO_2 was balanced in helium.



When T is between 550 °C to 800 °C, sorbent capacity is more than 74 wt% per mass sorbent, which corresponds to 94% CaO conversion.

Adsorption of CO_2 over $CaAc_2$-CaO at the Initial Stage

30 vol % CO_2 was balanced in helium.

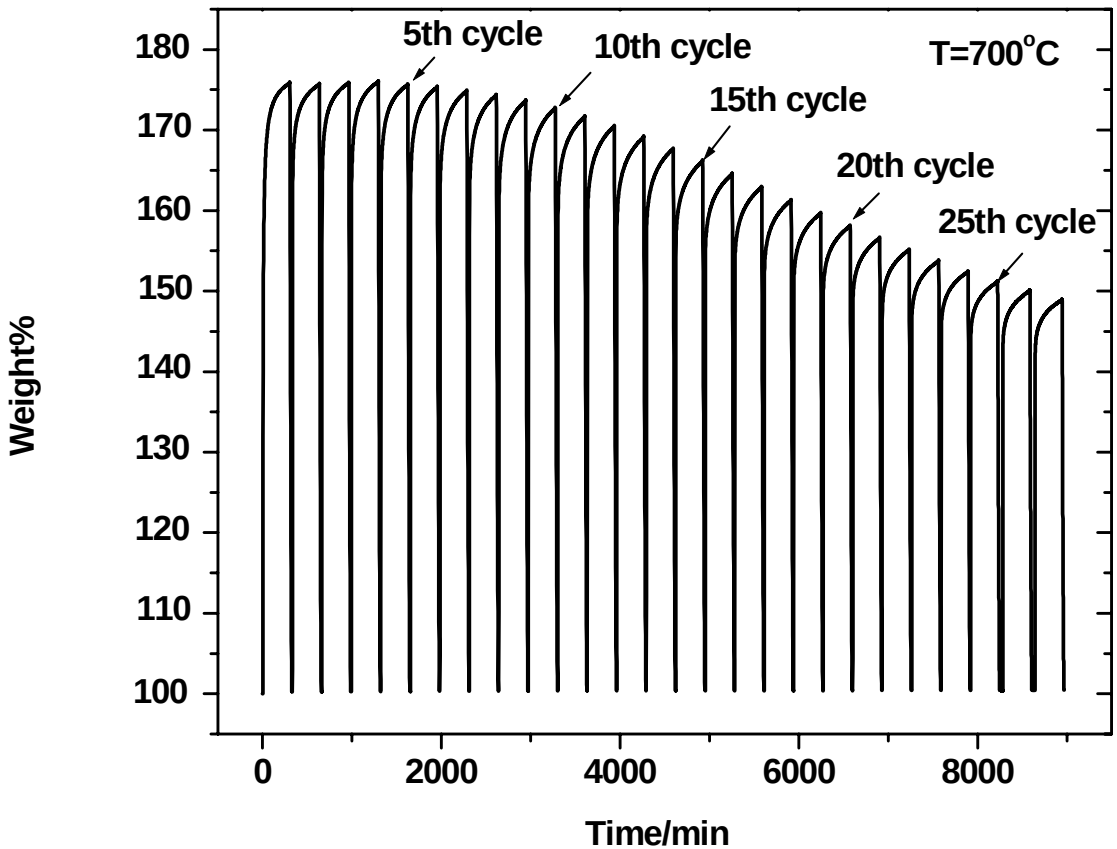


Fast reaction and wide temperature window for operation are important factors for industrial applications

Cyclic Adsorption-Desorption of CO_2 over $CaAc_2$-CaO

Adsorption: 700 ^oC, 300 min, 30 vol% CO_2 balance in He

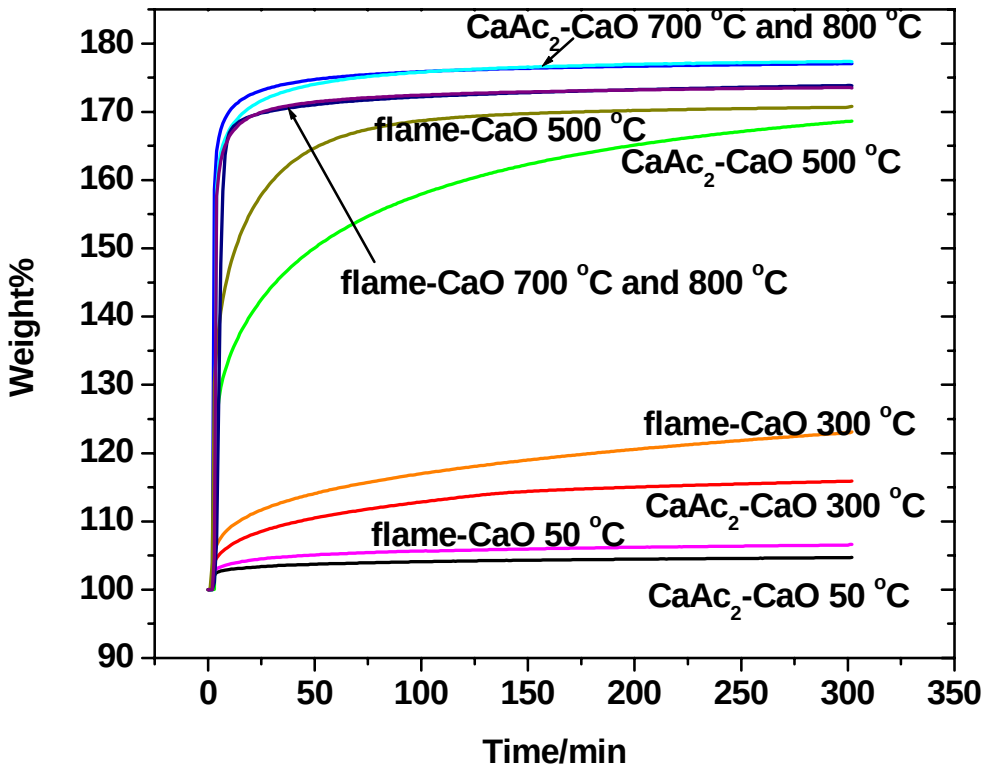
Desorption: 700 ^oC, 30 min, 100% He



Capacity of sorbent kept decreasing after the 8th cyclic reaction. This might be ascribed to pore blockage and structure collapse.

Comparison of Adsorption of CO_2 over $CaAc_2$-CaO and Flame-made (Aerosol) CaO

30 vol % CO_2 was balanced in helium.



High capacity of flame-CaO might be ascribed to its higher surface area which dues to its nano range size but pore structure. Flame-CaO might be a solution for sustainability of sorbent in multi cyclic operation because it circumvents the possibility of pores blockage and structure collapses.

Conclusions and Key Findings

- CaO sorbents can be used at high temperatures (range of 600 to 800 ^{o}C) for CO_2 separation;

- Highly selective for CO_2 sorption (zero affinity for O_2 and N_2, very low affinity for H_2O) when doped with alkali metal;

- Large CO_2 sorption capacities were observed (> **75** wt.% CO_2 /wt sorbent in 5 hours, 90% of which happens at the first half an hour) when use calcium acetate based sorbents;

- CaO sorbents synthesized from calcium acetate have good regenerabilility properties.

Future Work

- Direct the synthesis towards highly durable systems that will ensure stability for regeneration over many hundred cycles at elevated temperatures and severe conditions;

  Emphasis of Flame Spray Pyrolysis (Aerosol)

- Characterize the synthesized sorbents with numerous state-of-the-art characterization techniques to understand their morphological properties and functionality;

- Use the obtained information as feed-back to design the most effective sorbents. Test these sorbents with gas mixtures containing CO_2, H_2O, air, SO_2, SO_3, NO_x, H_2 and CO at selected compositions simulating industrial conditions

Time Schedule

Tasks \ Completed	20 %	40 %	60 %	80 %	10 0%
Synthesis of superbasic sorbents					
Screening of different sorbent precursors					
Synthesis of sorbents by flame spray pyrolysis					
Characterization the synthesized sorbents					
Adsorption studies with CO_2					
Selectivity studies with selected mixtures CO_2 and H_2O, O_2, N_2, SO_x, Air H_2, CO, and NO_x					
Durability studies					
Choose sorbents based on the above tasks					
Testing the optimum sorbents with simulated flue gas					

Future Applications of this Work

Besides application in flue gas separation, these sorbents are also useful in other applications such as:

- Purification of hydrogen from water gas shift (WGS) reactions
- Coal Gasification
- Fuel Cell applications
- Membrane materials
- Automobile applications

Publications

1. E.P. Reddy, and P.G. Smirniotis, "High-temperature sorbents for CO_2 made of alkali metals doped on CaO supports", **Journal of Physical Chemistry B,** 108, 7797-7800 (2004).

2. 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,** *in press 2005.*

IN PREPARATION

3. H. Lu, E.P. Reddy, and P.G. Smirniotis, "Calcium oxide based sorbents for adsorption of CO_2 at high temperatures".
4. H. Lu, E.P. Reddy, and P.G. Smirniotis., "Development of high temperature sorbents for adsorption of CO_2"
5. H. Lu, F.O. Ernst, S.E. Pratsinis, and P.G. Smirniotis, "CO_2 sorbents made by flame spray pyrolysis and high temperature calcination"
6. F.O. Ernst, H. Lu, P.G. Smirniotis, and S.E. Pratsinis, "Complex effects of dopants on adsorption of CO_2 at high temperatures over sorbents made with flame spray pyrolysis "

Acknowledgements

- US Department of Energy for Awarding this Innovative Concepts Phase-I Program (Grant Number DE-FG26-03-NT41810).
- Dr. Jose Figueroa of US DOE (NETL) for very fruitful discussions.