

CaO-Based Sorbents for CO₂ Capture Prepared by Ultrasonic Spray Pyrolysis

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Materials Synthesis

The USP apparatus is represented in Figure S1. The custom nebulizer base was constructed at the University of Illinois at Urbana-Champaign electronics shop and contains a 1.65 MHz fixed frequency piezoceramic. The nebulization cell was constructed from a 57 mm O-ring flat flange (Chemglass, # CG-138-02) which has been modified to taper to a 24/40 ground glass joint at the top. Additionally, the cell was outfitted with a solution addition arm and carrier gas inlet arm. A circular polyethylene membrane (2 mils thickness, cut from a Ziploc[®] bag) was clamped to the nebulization cell and the assembly was centered over the piezoceramic on the nebulizer base. Water was added to couple the piezoceramic to the plastic membrane and any air bubbles trapped under the membrane were removed. Argon was flowed through the nebulization cell at 1 l/min and carried an ultrasonically generated mist through a quartz furnace tube preheated to 600 °C. A 2 in. Vigreux column was inserted between the nebulization cell and furnace tube to make more uniform droplet sizes. After passing through the furnace, the resulting product was collected in four bubblers each containing ~50 mL of ethanol.

The precursor solution was prepared volumetrically by dissolving the appropriate amount of calcium nitrate tetrahydrate (Aldrich, >99%) and aluminum nitrate nonahydrate (Aldrich, >98%) in 95% ethanol such that the correct Al to Ca ratios in the product

were achieved. The products were concentrated by rotary evaporation and dried at ~80 °C for ~12 h prior to characterization.

Materials Characterization

Scanning Electron Micrographs (SEMs) were taken using a Hitachi S4800 SEM at an accelerating voltage of 10 kV. Samples were sputter-coated with Au/Pd alloy before SEM analysis. Transmission Electron Micrographs (TEMs) were taken using a JEOL 2100 Cryo TEM at an operating voltage of 200 kV. Scanning transmission electron micrographs (STEM) were collected using a JEOL 2010F with an accelerating voltage of 200 keV. Elemental Analysis (EA) was done in the Microanalysis Lab at the University of Illinois at Urbana-Champaign on a Perkin Elmer Sciex DRc ICP-MS and a Model CE 440 CHN Analyzer. Powder diffraction patterns were collected using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) with a Seimens Bruker D5000 instrument operating at 40 kV and 30 mA and scanning $2\theta = 10^\circ$ to 90° at a rate of $1.0^\circ/\text{min}$. Surface area (SA) measurements were obtained using a 3-point BET (Brunauer, Emmett, Teller) adsorption curve on a Quantachrome Instruments Nova 2200e Surface Area and Pore Analyzer. Thermogravimetric analysis (TGA) was conducted on a ThermoScientific VersaTherm thermogravimetric analyzer.

Table S1. Pre- and post-calcine surface areas of the sorbents containing various Al/Ca ratios.

Sorbent Al/Ca atomic ratio (Al ₂ O ₃ /CaO mass ratio)	Pre-calcine SA m ² /g	Post-calcine SA m ² /g
0.03 (0.03)	19.6	27.2
0.08 (0.07)	20.4	29.1
0.16 (0.15)	19.8	22.7
0.24 (0.22)	23.7	26.2
0.38 (0.35)	15.9	19.0
0.56 (0.51)	46.4	33.9

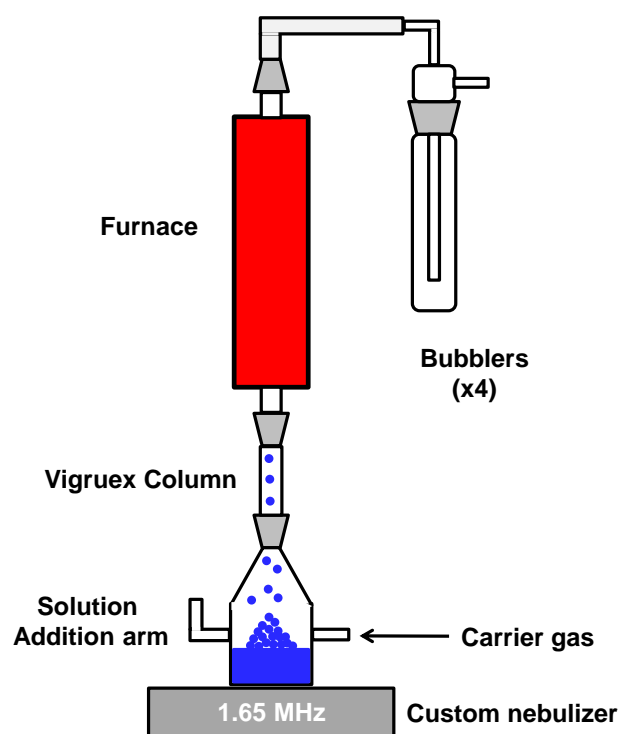


Figure S1. Experimental setup of the USP apparatus.

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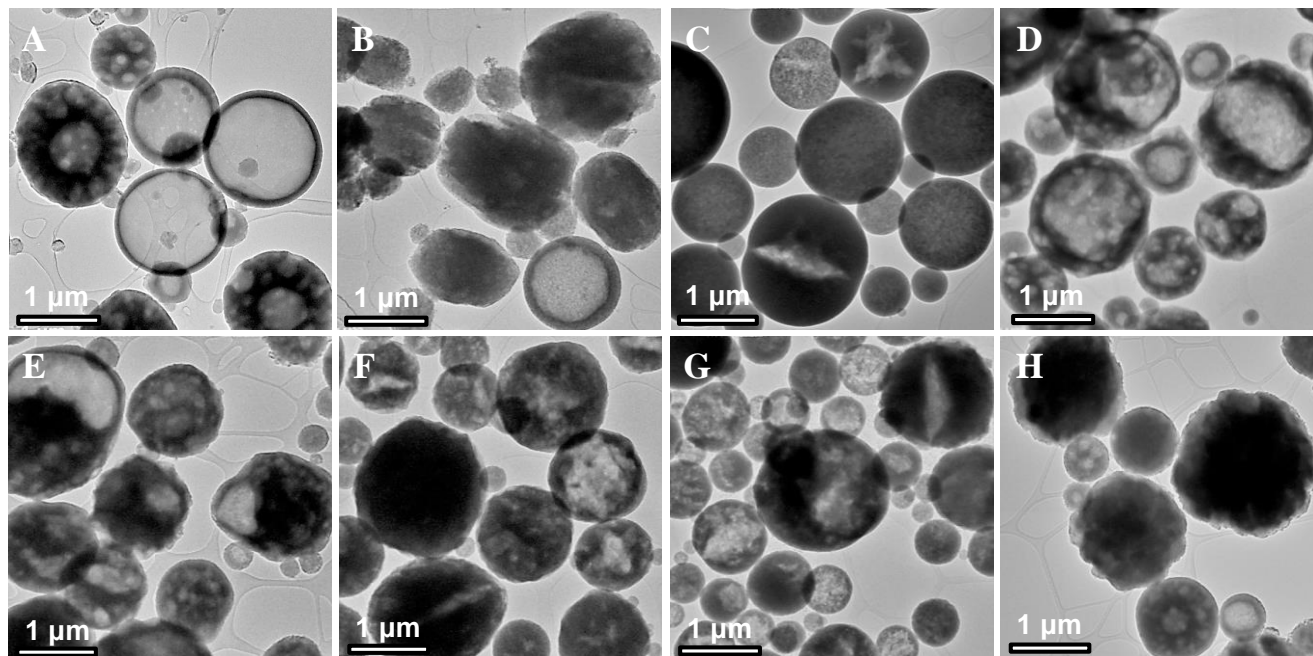


Figure S2. TEM images of Al-containing sorbents with various Aluminum to Calcium ratios. (A) 0 (B) 0.03 (C) 0.08 (D) 0.16 (E) 0.24 (F) 0.38 (G) 0.56 (H) 1.17

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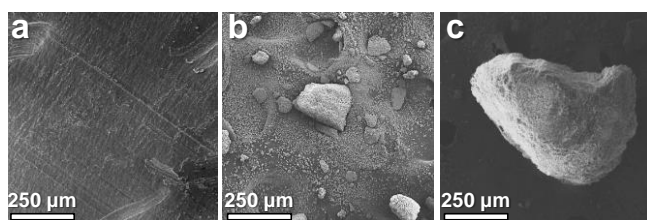


Figure S3. Low magnification SEM images of the sorbent with Al/Ca = 0.16. (a) before cycling, (b) after 2 cycles of calcination/carbonation and (c) after 15 cycles of calcination/carbonation.

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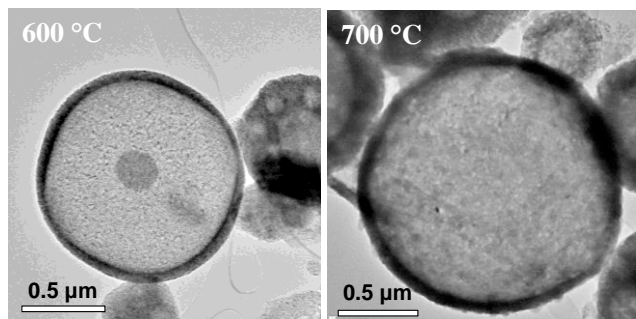
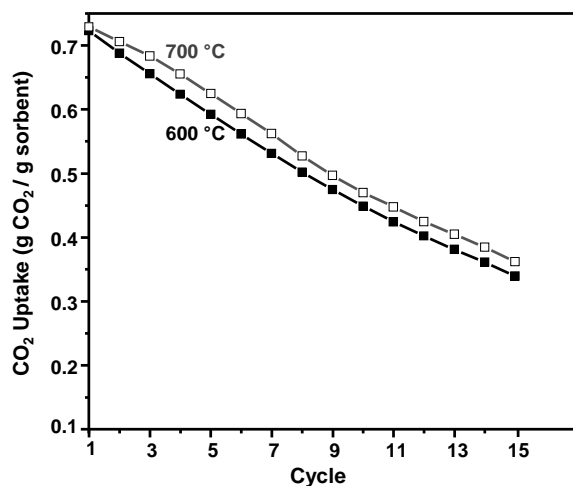


Figure S5. Top panel: CO₂ uptake for pure CaO sorbents synthesized at 600 °C and 700 °C during 15 cycles of calcination/carbonation. Bottom panel: TEM images of the hollow pure CaO sorbent; left, synthesized at 600 °C and right at 700 °C.

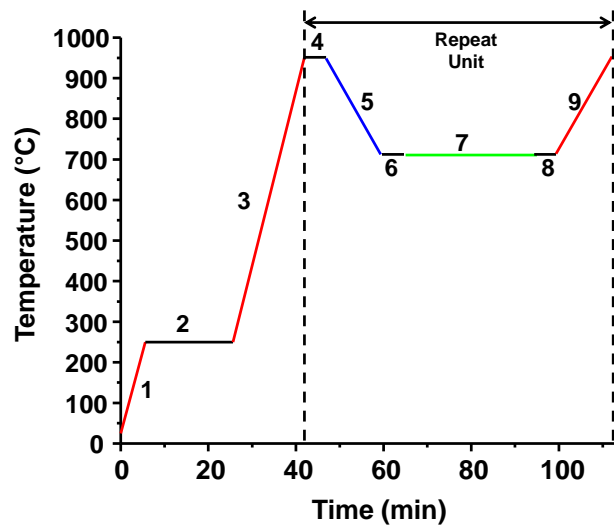
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TGA Protocol

- 15 Each of the materials was subjected to 15 calcination/carbonation cycles on a thermogravimetric analyzer (TGA, a ThermoScientific VersaTherm thermogravimetric analyzer). Approximately 20 mg of sample was loaded into a quartz sample boat. The instrument is controlled using Thermal Analyst Data
- 20 Acquisition Version 3.30.0 VT software which allows the user to program the TGA operation parameters. A typical TGA protocol is shown in Figure S5: (1) heat from room temperature to 250 °C at 40 deg/min under N₂, (2) hold at 250 °C for 20 min under N₂ (this is to remove any water vapor or other adsorbents), (3) heat from 250 °C to 950 °C at 40 deg/min under N₂, (4) hold at 950 °C for 5 min under N₂ (this is the calcination stage), (5) cool from 950 °C to 710 °C at -20 deg/min under N₂, (6) hold at 710 °C for 5 min under N₂, (7) maintain the temperature at 710 °C and switch the gas to CO₂ for 30 min (this is the carbonation stage),
- 35 (8) maintain the temperature at 710 °C and switch the gas back to N₂ for 5 min, (9) heat from 710 °C to 950 °C at 20 deg/min under N₂, and (10) repeat steps 4-9. TGA data was analyzed using ThermoCahn Instruments Thermal Analyst Version 1.3.2.2 software.

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Figure S5. Diagram of the method programmed for multiple carbonation/calcinations cycles. Red corresponds to heating, black to isothermal periods under N₂, blue to cooling, and green to isothermal periods under CO₂.

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Table S2. Comparison of the performance of the sorbents with Al/Ca=0.16 (i.e., 75:25 wt% CaO:Ca₁₂Al₁₄O₃₃) in the literature.

Method of synthesis	Sorbent Source/precursor	Carbonation/ Calcination	CO ₂ uptake at cycle 15 (g CO ₂ / g sorbent)	Retention Ratio (%) cycle 15/cycle 1	Reference
Calcination at 900 °C	CaO powder Al(NO ₃) ₃ ·9H ₂ O in isopropanol	700 °C, 30 min, 20% CO ₂ 850 °C, 5 min, 100% N ₂	~0.48	94	15b
Calcination at 900 °C	Ca(OH) ₂ Al(NO ₃) ₃ ·9H ₂ O in isopropanol	690 °C, 30 min, 15% CO ₂ 850 °C, 10 min, 100% N ₂	~0.22	-	15c
Calcination at 900 °C	CaO Al(NO ₃) ₃ ·9H ₂ O in isopropanol	690 °C, 30 min, 15% CO ₂ 850 °C, 5 min, 100% N ₂	~0.35	-	15d
Ultrasonic Spray Pyrolysis at 600 °C	Ca(NO ₃) ₂ ·4 H ₂ O Al(NO ₃) ₃ ·9H ₂ O	710 °C, 30 min, 100% CO ₂ 950 °C, 5 min, 100% N ₂	0.55	92	This work

Notes and references

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