# CaO –based sorbent development for carbon capture and the study of critical thickness of $CaCO_3$ layer

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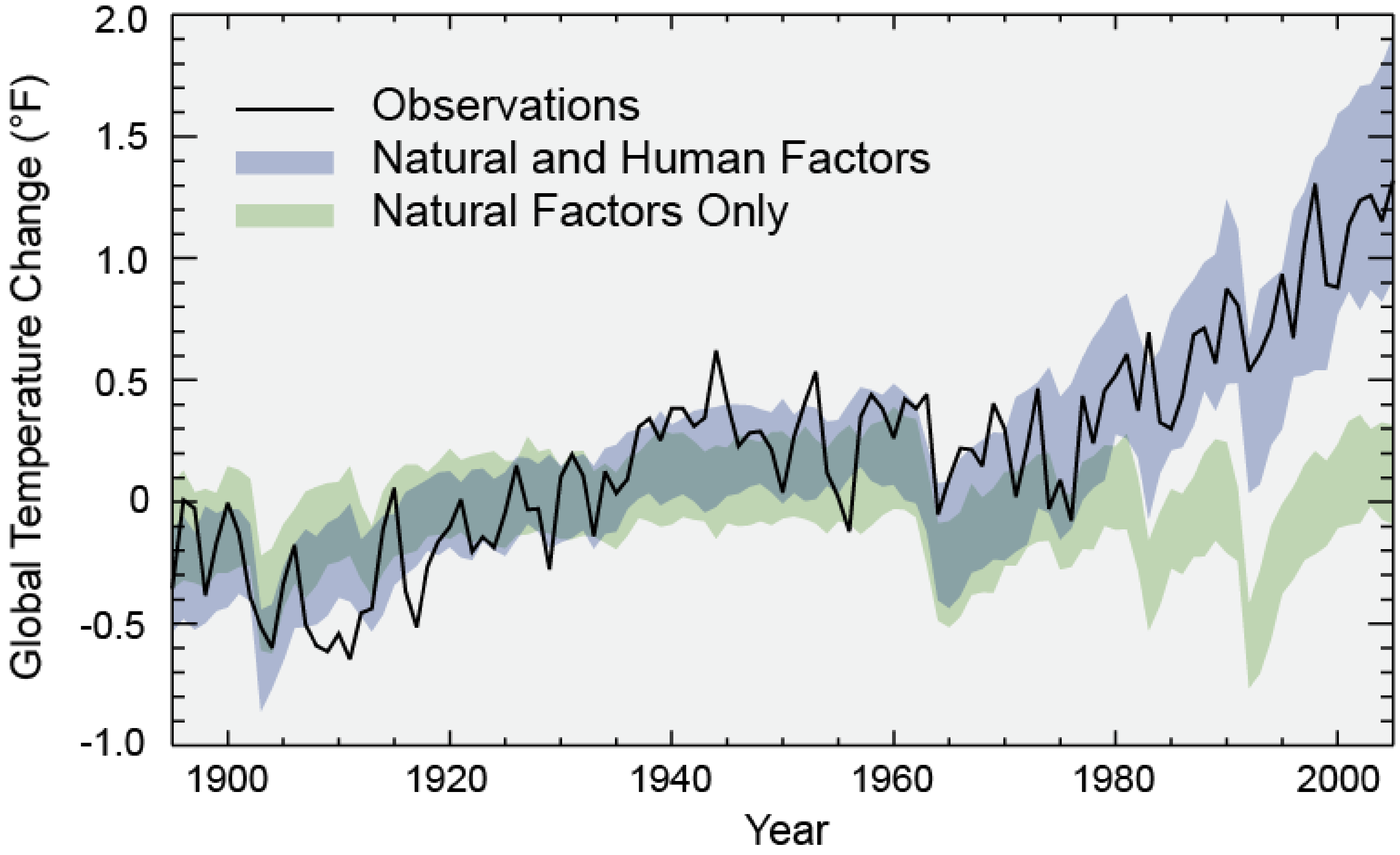
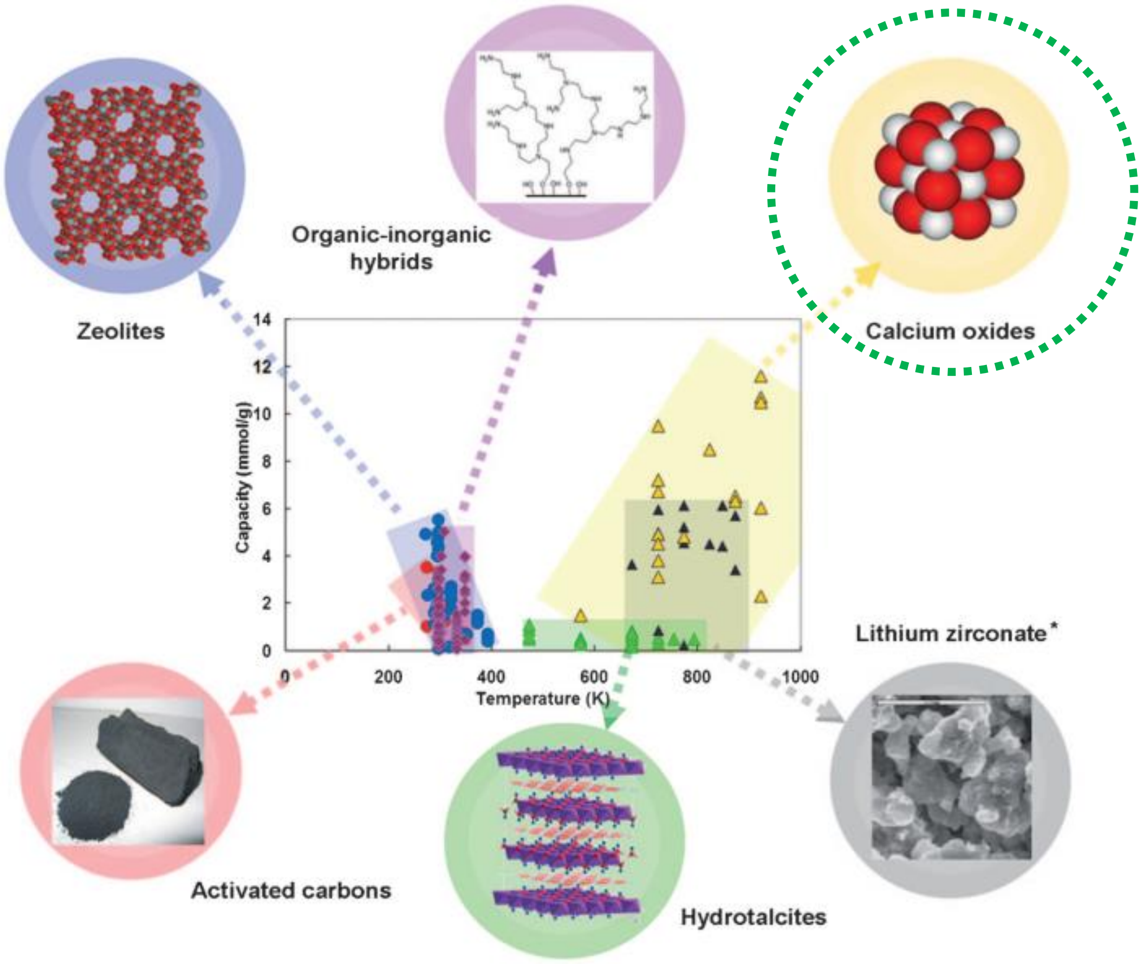
# Background




U.S. National Climate Assessment (2014)

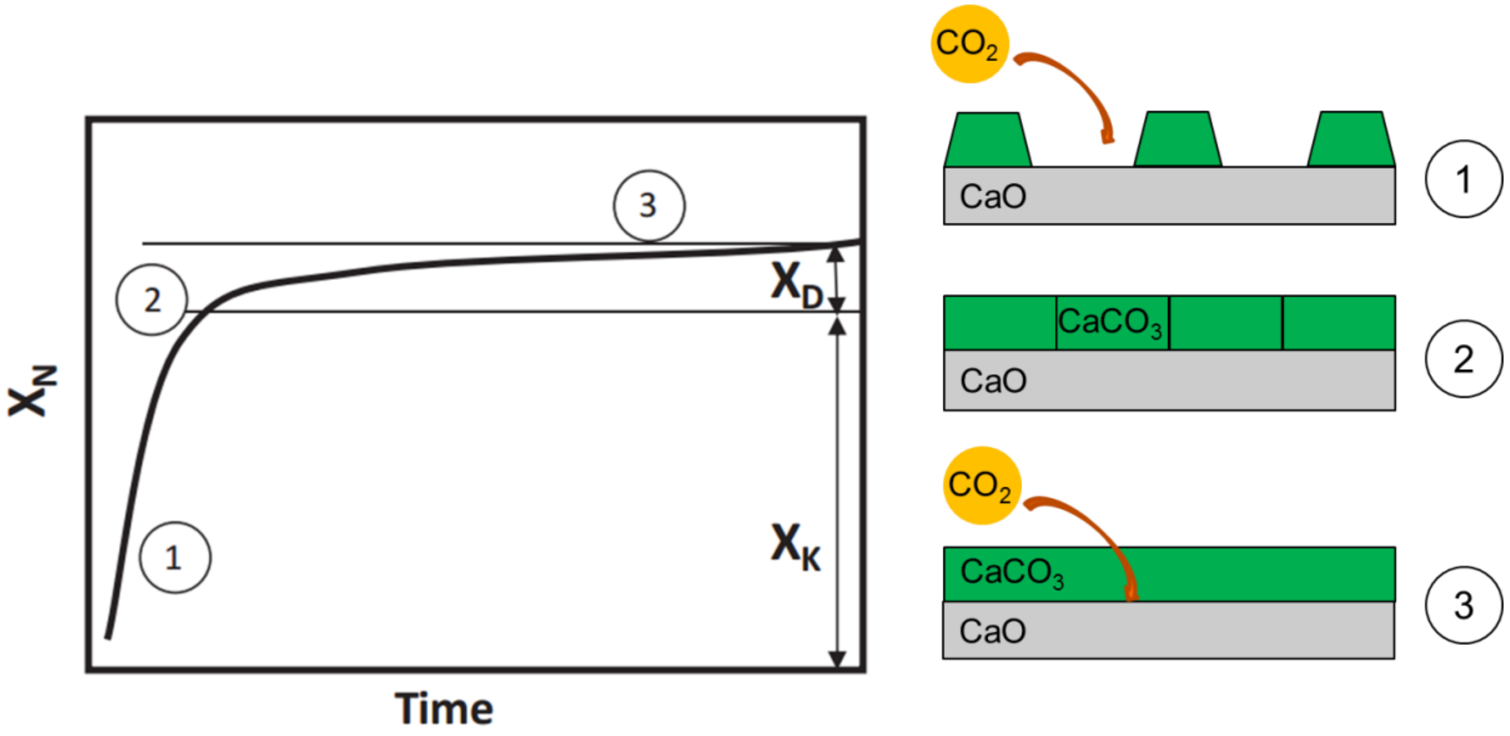



high theoretical capture capacity

low cost

The application of different types of adsorbents at different temperature

ChemSusChem.2009,2:796-854.




No direct measurement or observation of the critical thickness of product layer

$X_N$: the molar conversion in each cycle
$X_K$: the molar conversion in fast reaction stage
$X_D$: the molar conversion in diffusion-controlled stage

B. Arias, J. Abanades and G. S. Grasa, *Chemical engineering journal*, 2011, **167**, 255-261.

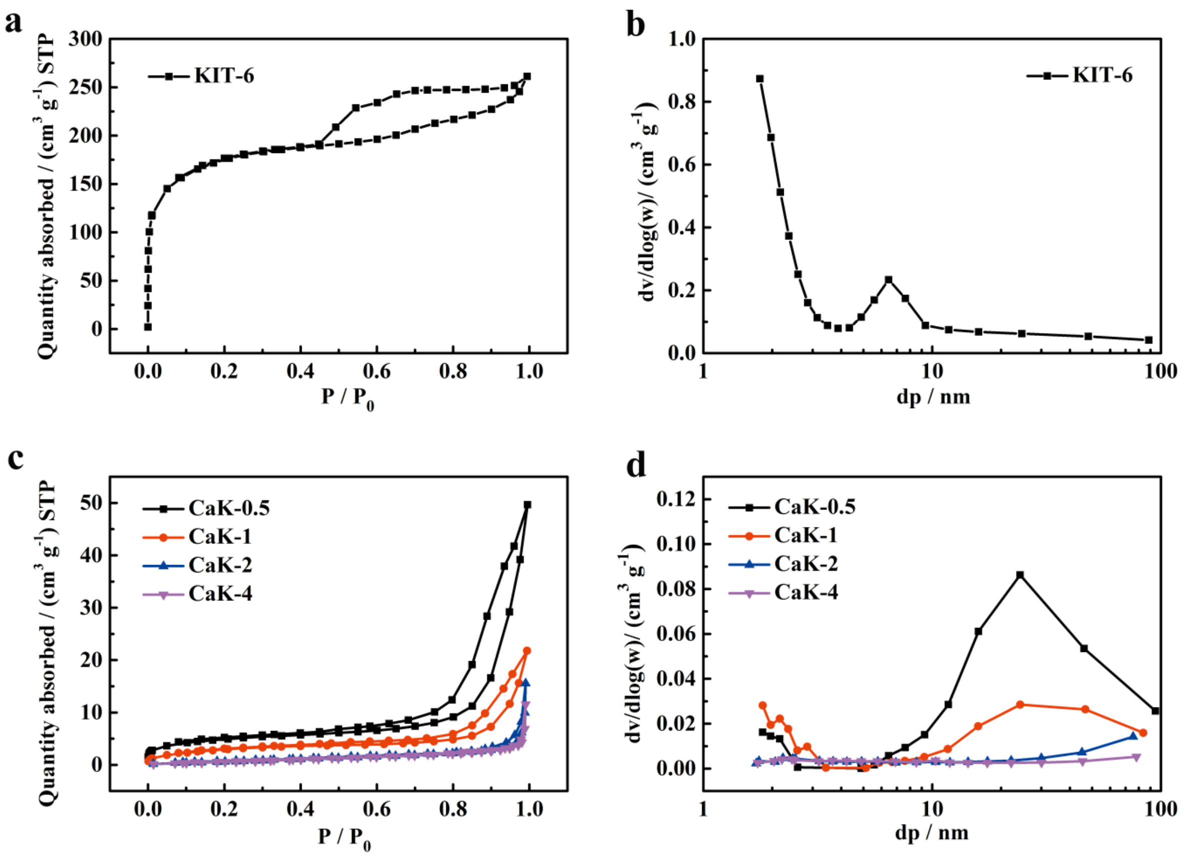
# CaO/KIT-6 materials development

| Sample | CaO | Ave. Size | $CaSiO_3$ | Ave. Size | $Ca_2SiO_4$ | Ave. Size |
|---|---|---|---|---|---|---|
| CaK-0.5 | 0% | n.a. | 100% | 45 nm | 0% | n.a. |
| CaK-1 | 4% | 40 nm | 66% | 35 nm | 30% | 18 nm |
| CaK-2 | 15% | 40 nm | 0% | n.a. | 85% | 30 nm |
| CaK-4 | 54% | 87 nm | 0% | n.a. | 46% | 37 nm |
| CaO | 100% | 120 nm | 0% | n.a. | 0% | n.a. |

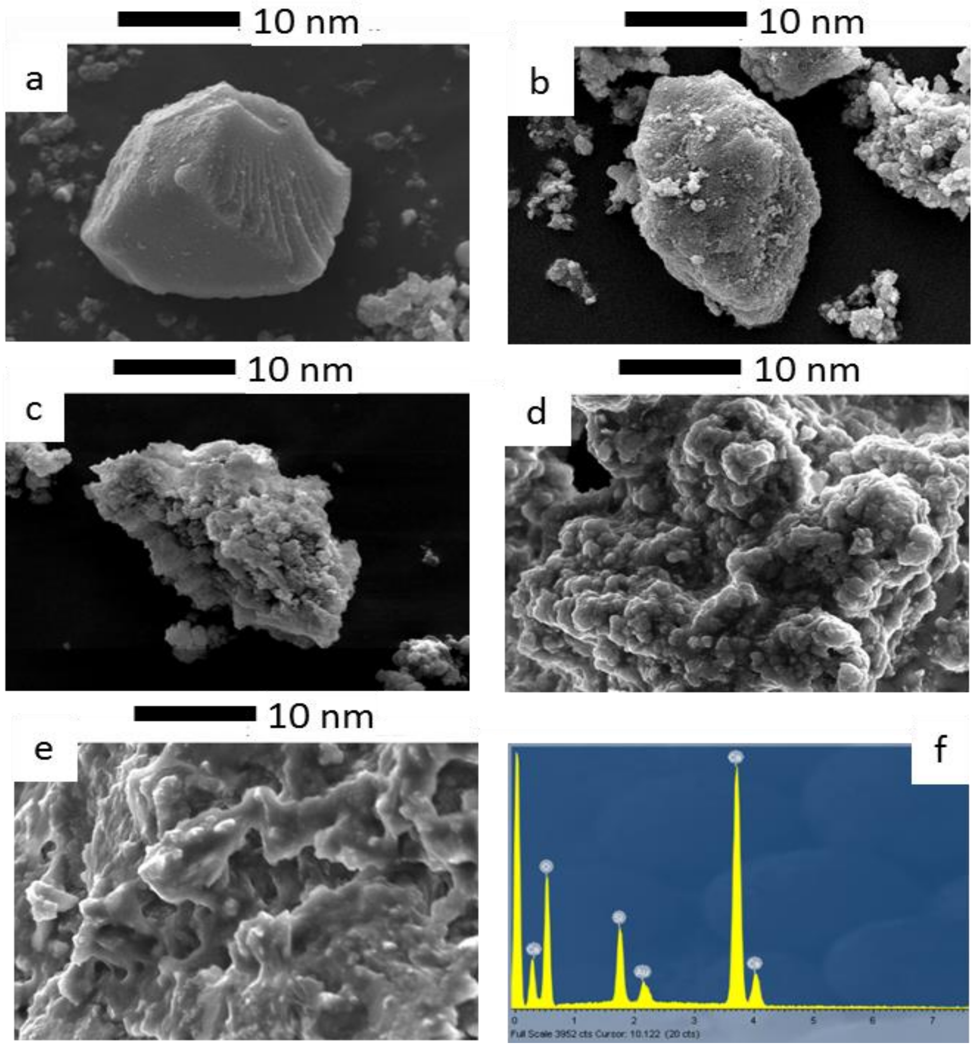
Phase composition and average crystallite size of CaO-based adsorbents

Textural properties derived from different CaO-based adsorbents

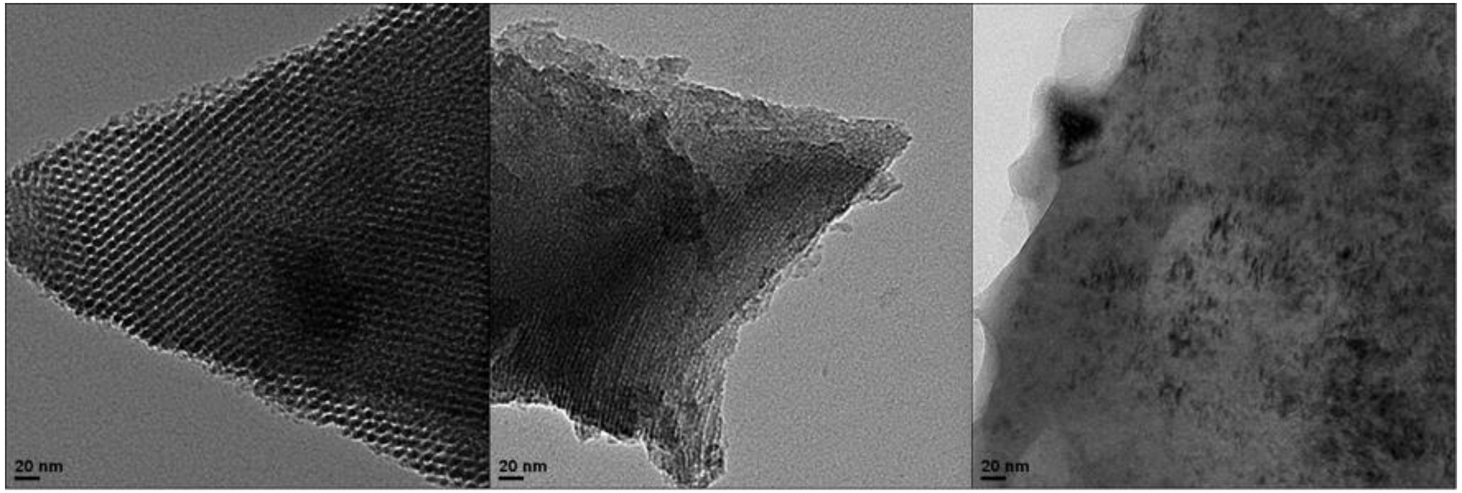
| Samples | $S_{BET}$/ (m²/g) | $S_{micro}$/ (m²/g) | $S_{meso}$/ (m²/g) | $V_{total}$/ (cm³/g) | $V_{micro}$/ (cm³/g) | $V_{meso}$/ (cm³/g) |
|---|---|---|---|---|---|---|
| KIT-6 | 545 | 265 | 280 | 0.40 | 0.11 | 0.29 |
| CaK-0.5 | 16.2 | 8.6 | 7.8 | 0.08 | 0.005 | 0.075 |
| CaK-1 | 11.1 | 7.0 | 4.1 | 0.04 | 0.003 | 0.035 |
| CaK-2 | 2.9 | 1.0 | 1.9 | 0.007 | 0.003 | 0.004 |
| CaK-4 | 2.7 | 1.0 | 1.7 | 0.005 | 0.002 | 0.003 |




$N_2$ adsorption-desorption isotherms (a: KIT-6; c: CaO-based adsorbents) and pore size distribution calculated from the BJH adsorption branch (b: KIT-6; d: CaO-based adsorbents)




SEM images of (a) parent KIT-6, (b) CaK-0.5, (c) CaK-1, (d) CaK-2 and (e) CaK-4, with (f) representative EDX spectra for CaK-2




(a) KIT-6 (b) CaK-2 (c) CaK-4

TEM images of parent KIT-6 and CaK-x adsorbents

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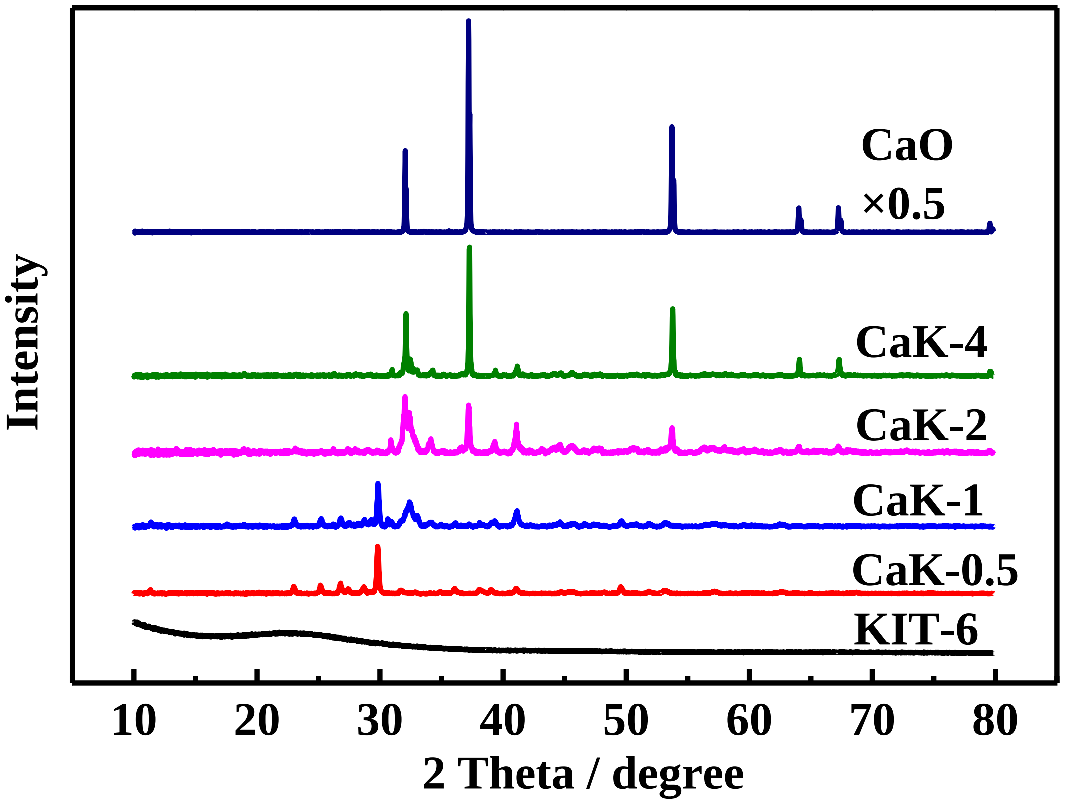
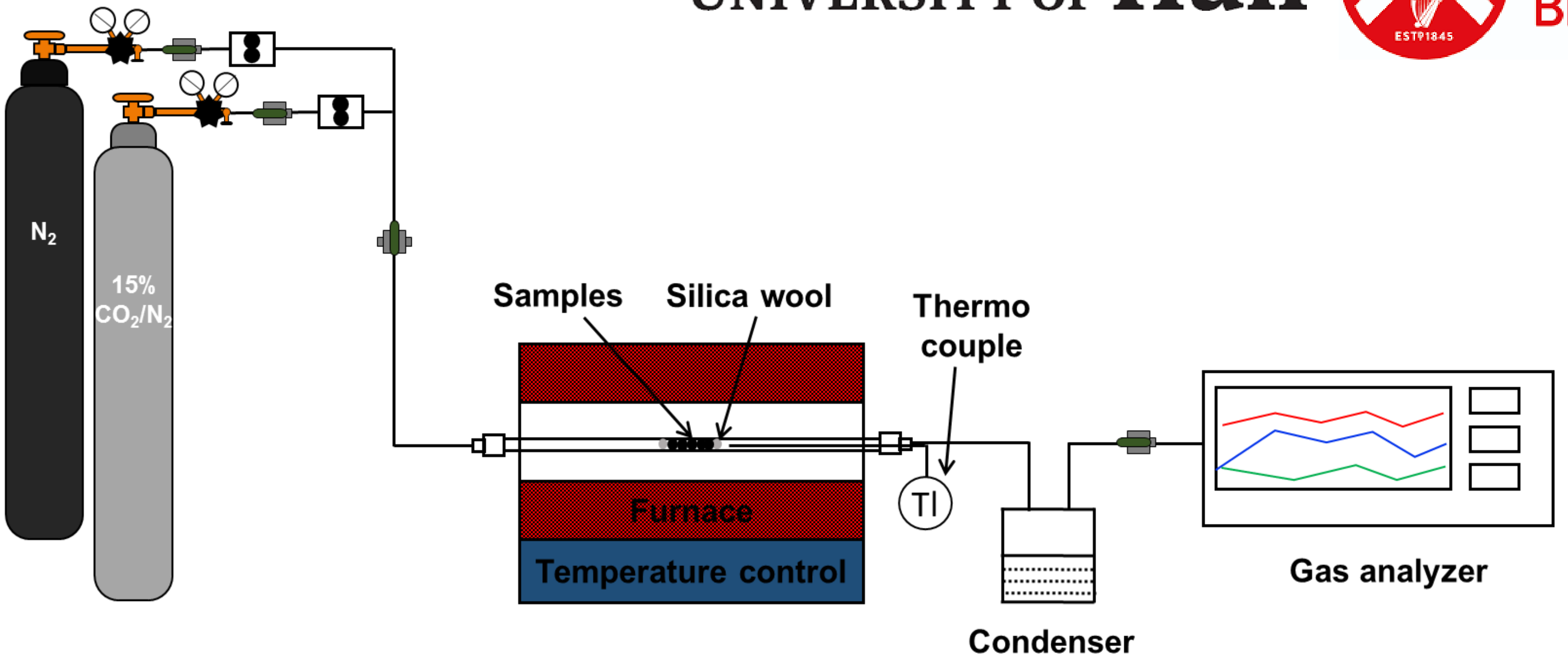



XRD analysis of CaO-based adsorbents




Schematic diagram of the atmospheric carbonation/calcination reactor system (fixed bed)

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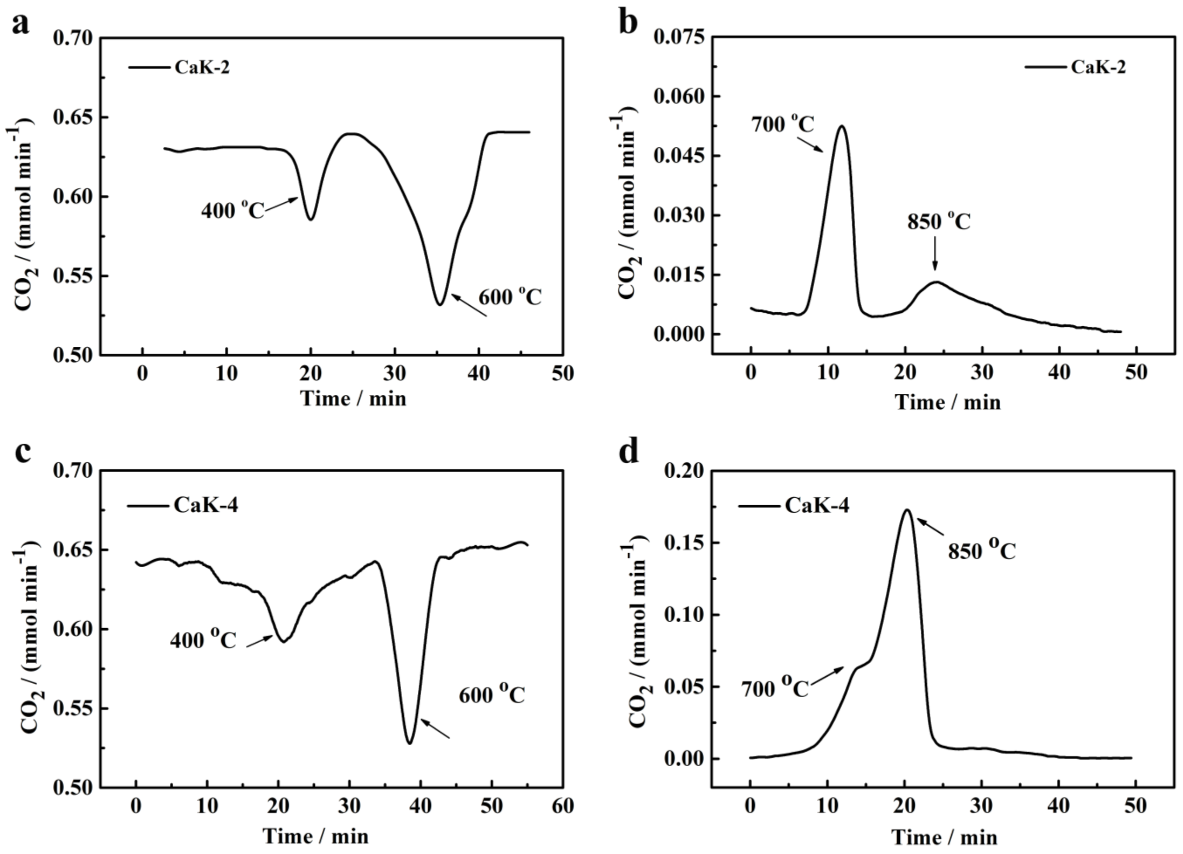
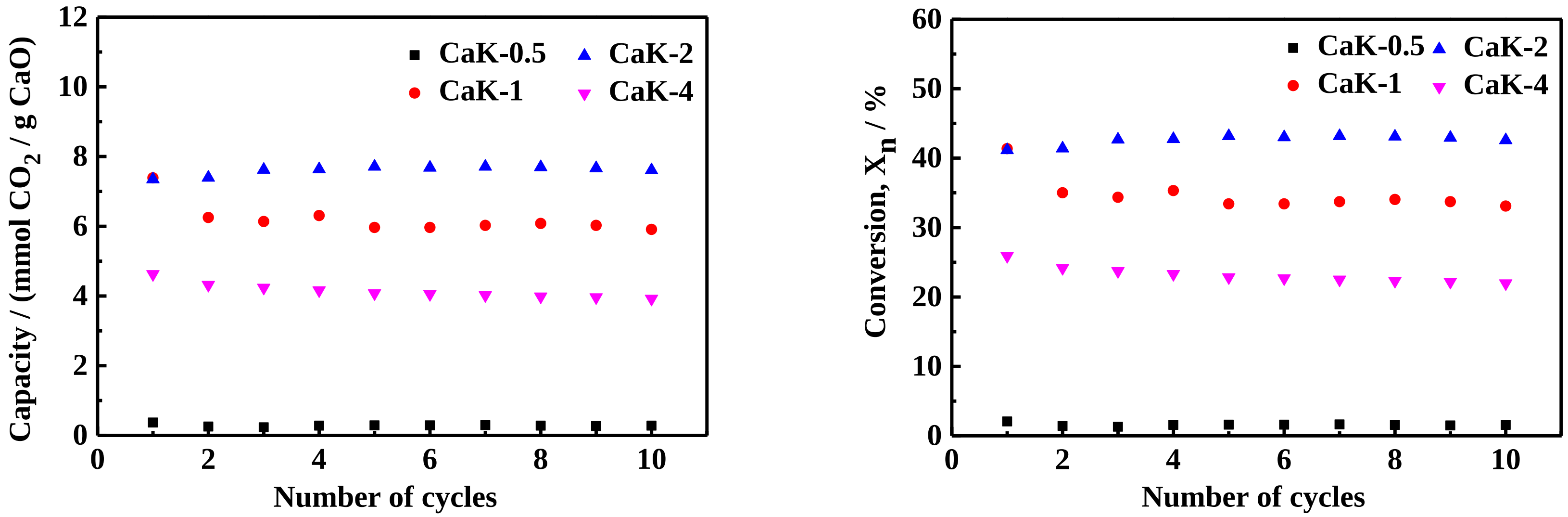


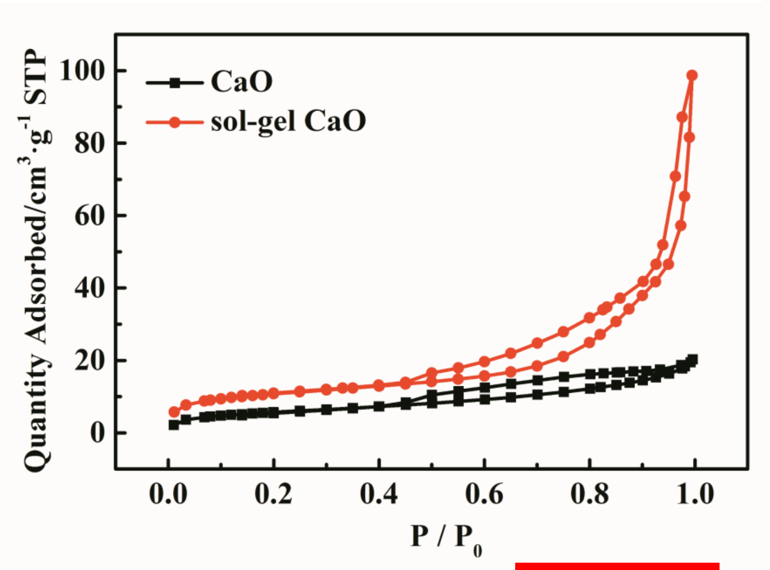

Fixed bed $CO_2$ capture performance of different adsorbents (a: adsorption of CaK-2; b: desorption of CaK-2; c: adsorption of CaK-4; d: desorption of CaK-4)

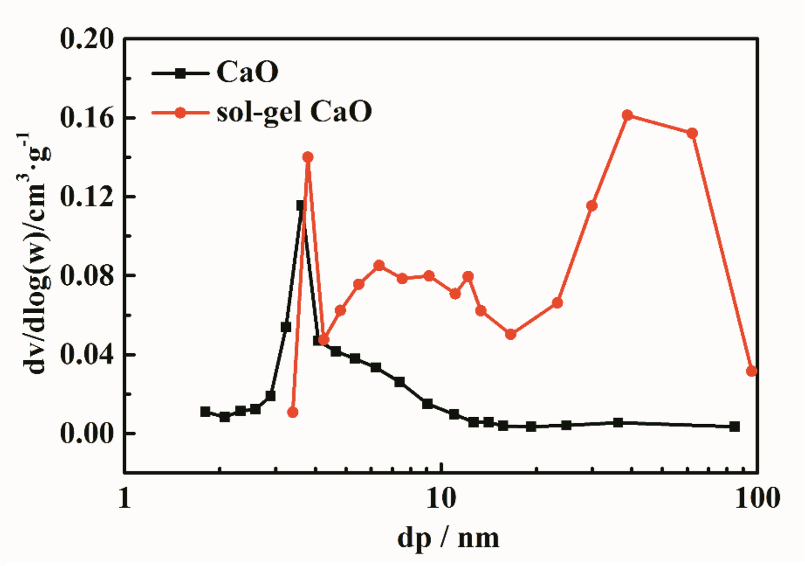


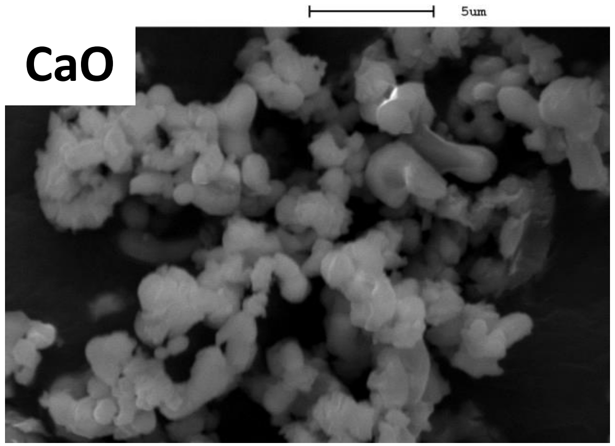

Cyclic capture capacity and conversion of different adsorbents per gram of CaO at 650 ˚C

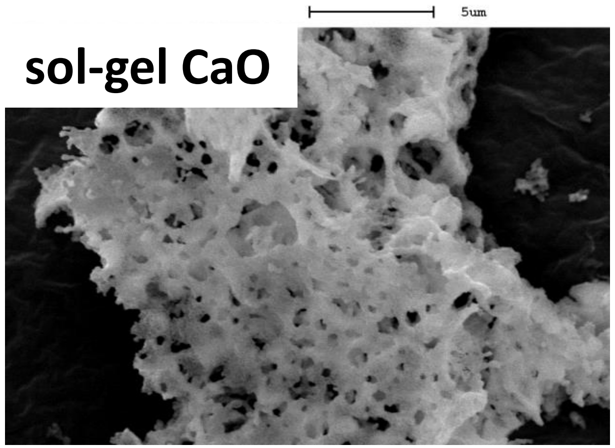
# Carbon capture using two CaO materials

## Characterisations of two CaO adsorbents



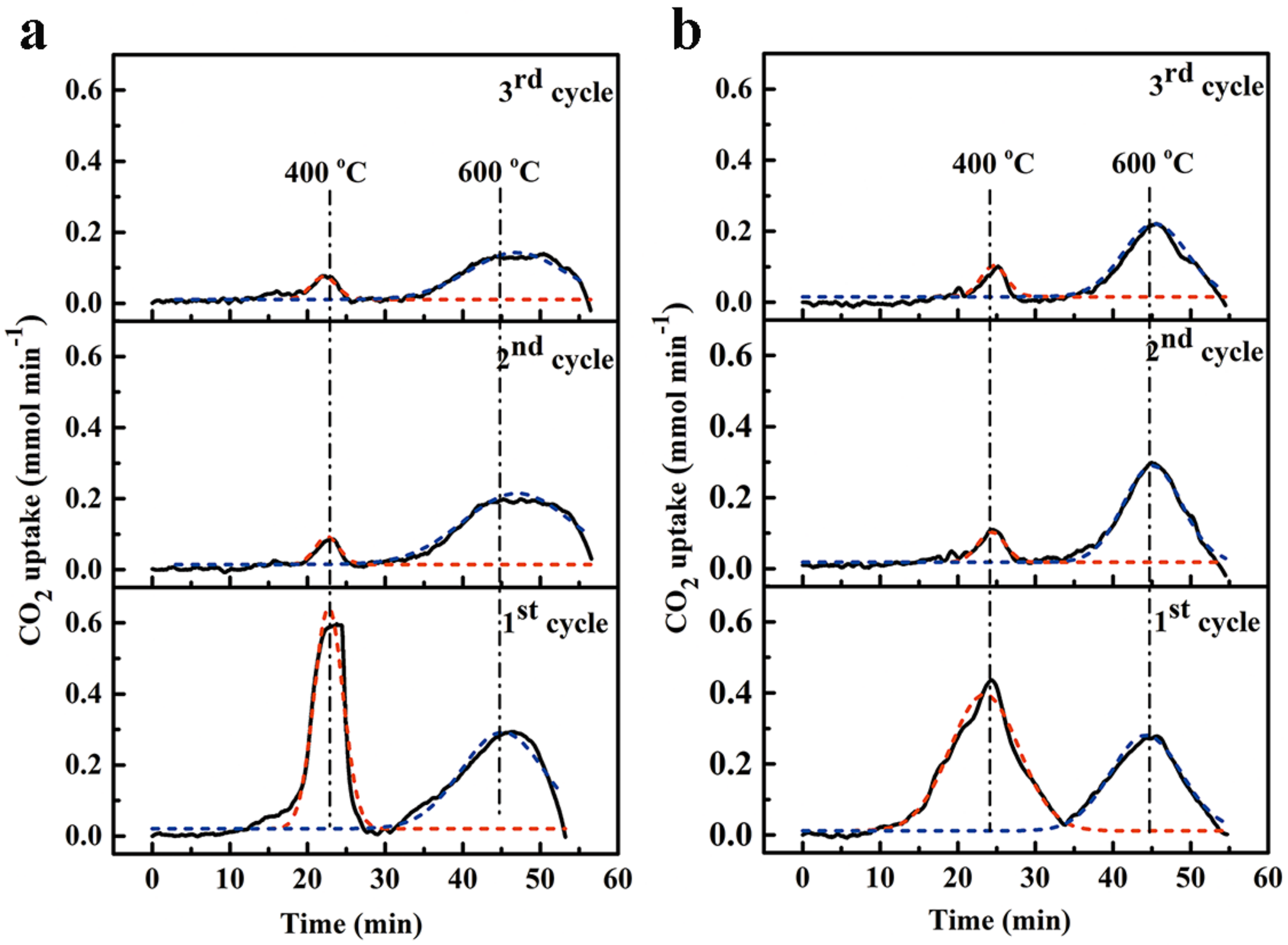




| Adsorbents | $S_{BET}$ ($m^2\ g^{-1}$) | $S_{meso}$ ($m^2\ g^{-1}$) | $V_p$ ($cm^3\ g^{-1}$) | $V_{meso}$ ($cm^3\ g^{-1}$) |
|---|---|---|---|---|
| CaO | 20.96 | 17.26 | 0.0314 | 0.0331 |
| sol-gel CaO | 38.51 | 30.01 | 0.1527 | 0.1511 |

# Carbon capture test of two CaO adsorbents




a) CaO, b) sol-gel CaO, carried out in a fixed-bed reactor

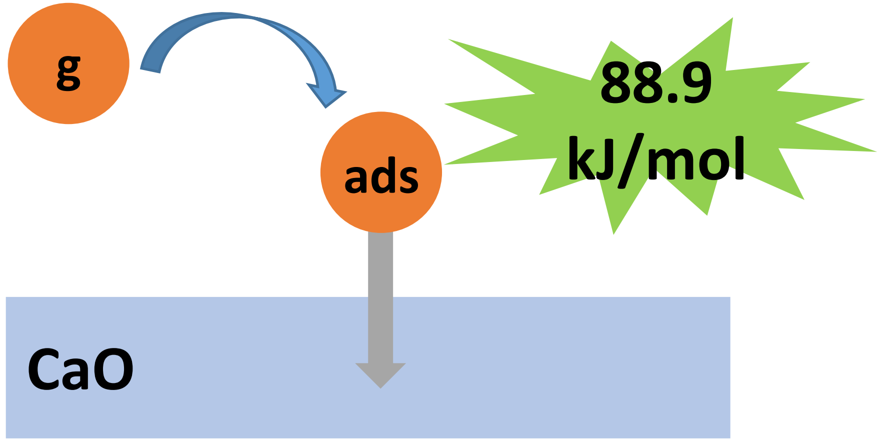
| $CO_2$ uptake (mmol) | 1st cycle | | 2nd cycle | | 3rd cycle | |
|---|---|---|---|---|---|---|
| | 400 ˚C | 600 ˚C | 400 ˚C | 600 ˚C | 400 ˚C | 600 ˚C |
| CaO | 2.92 | 3.63 | 0.30 | 3.51 | 0.27 | 2.03 |
| sol-gel CaO | 4.25 | 3.08 | 0.38 | 2.56 | 0.37 | 2.10 |

$CO_2$ uptake of a commercial CaO and a sol-gel CaO at different temperatures for 3 cycles

(1) T<515 ºC, pore surface:

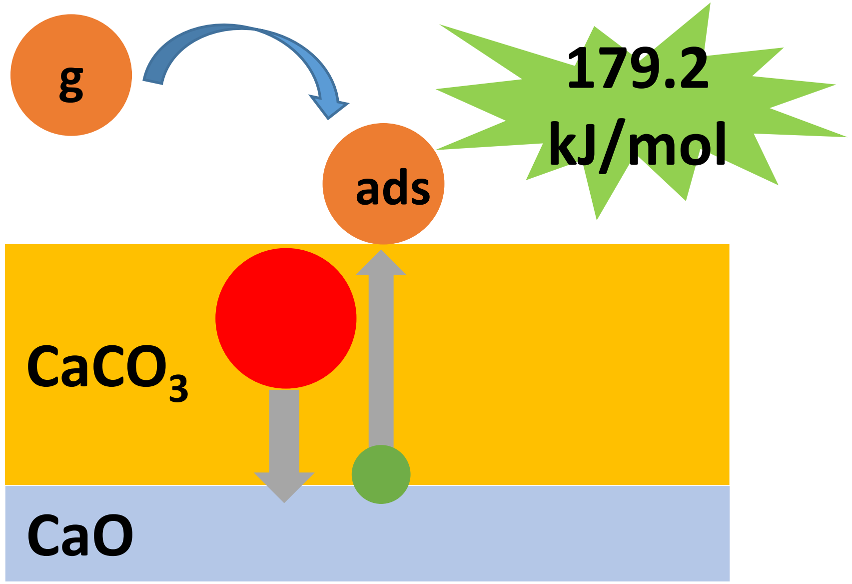
$CO_2\,(g) \rightleftharpoons (CO_2)_{ads}$

$(CO_2)_{ads} + O^{-2} \rightarrow CO_3^{-2}$




(2) T>515 ºC, CaO-CaCO$_3$ interface:

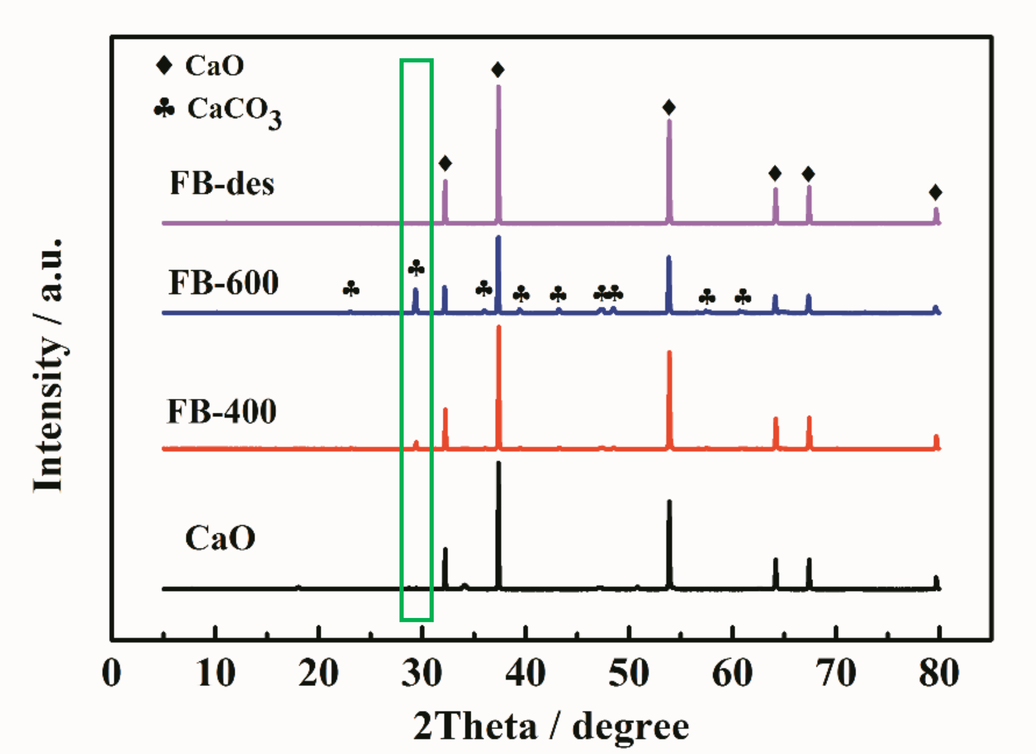
$CO_3^{-2} + CaO \rightarrow CaCO_3 + O^{-2}$

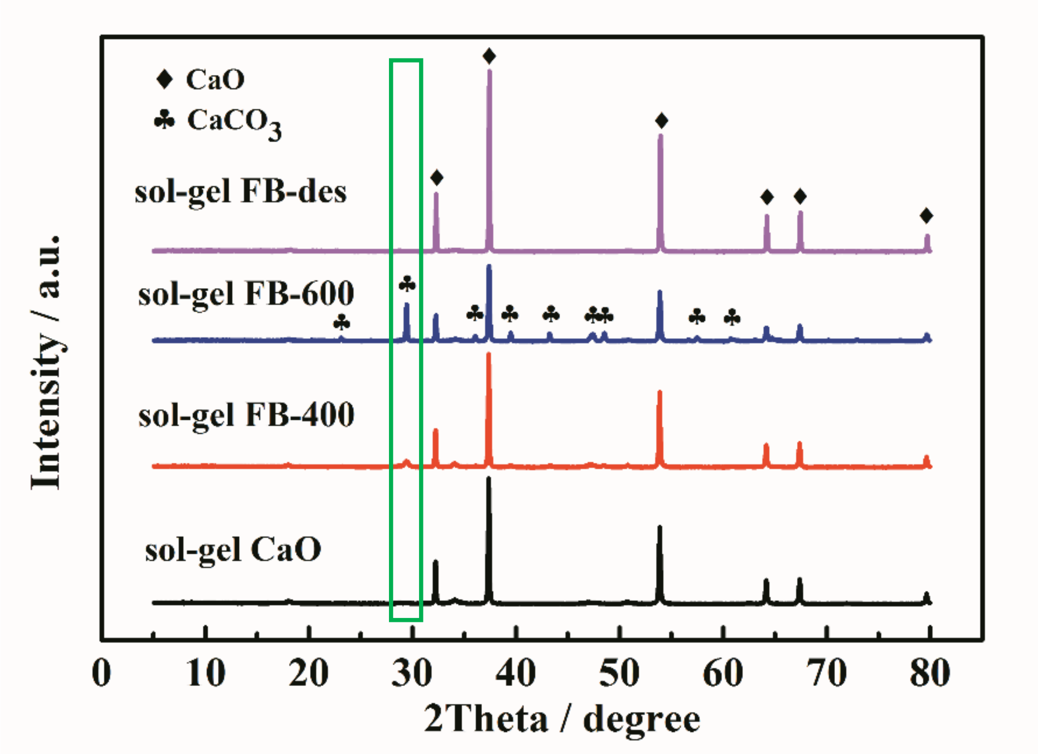




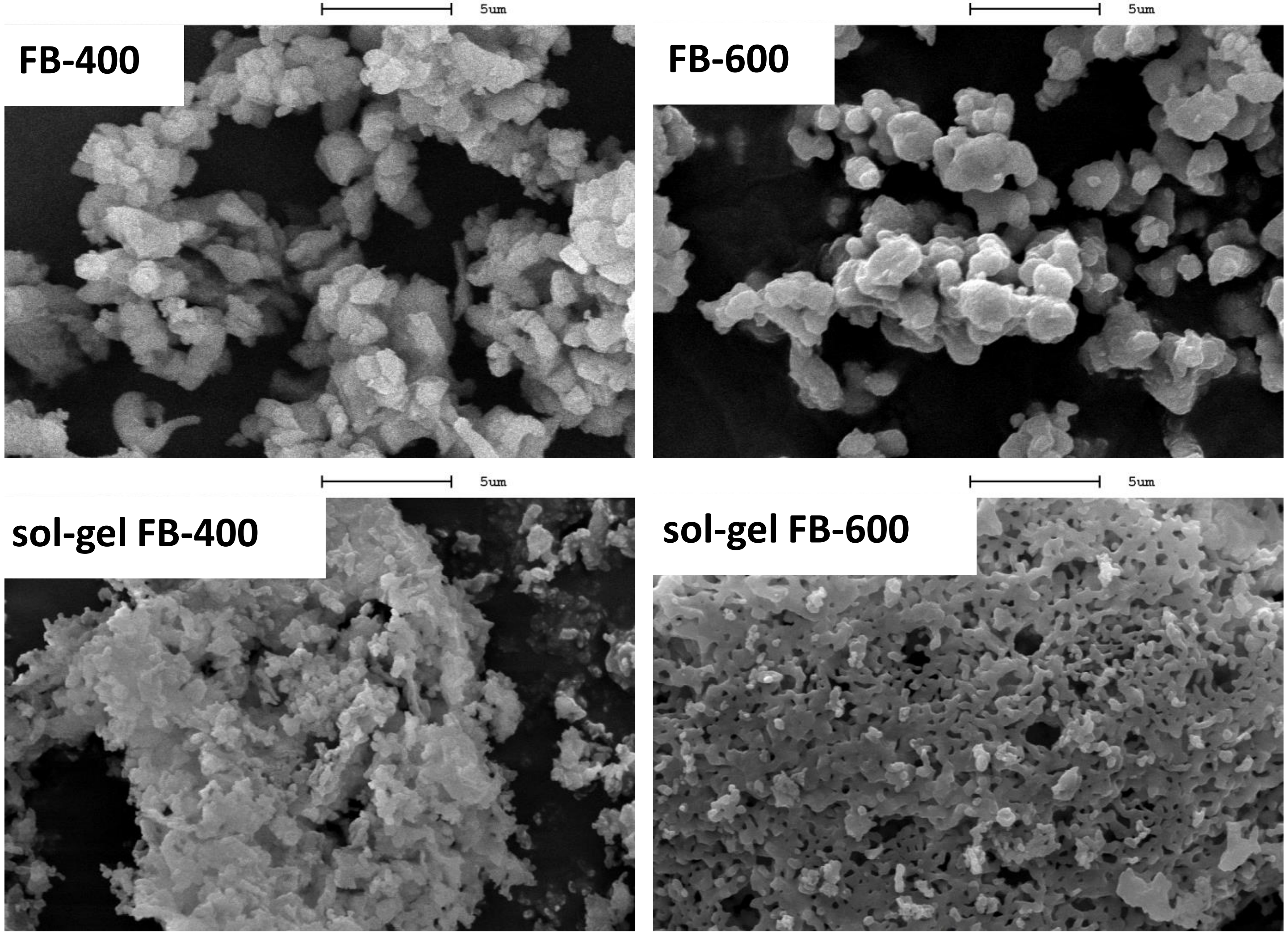
Bhatia, S.; Perlmutter, D. Effect of the product layer on the kinetics of the $CO_2$-lime reaction. *AIChE J* **1983,** (1), 79-86.

# Ex-situ XRD analysis

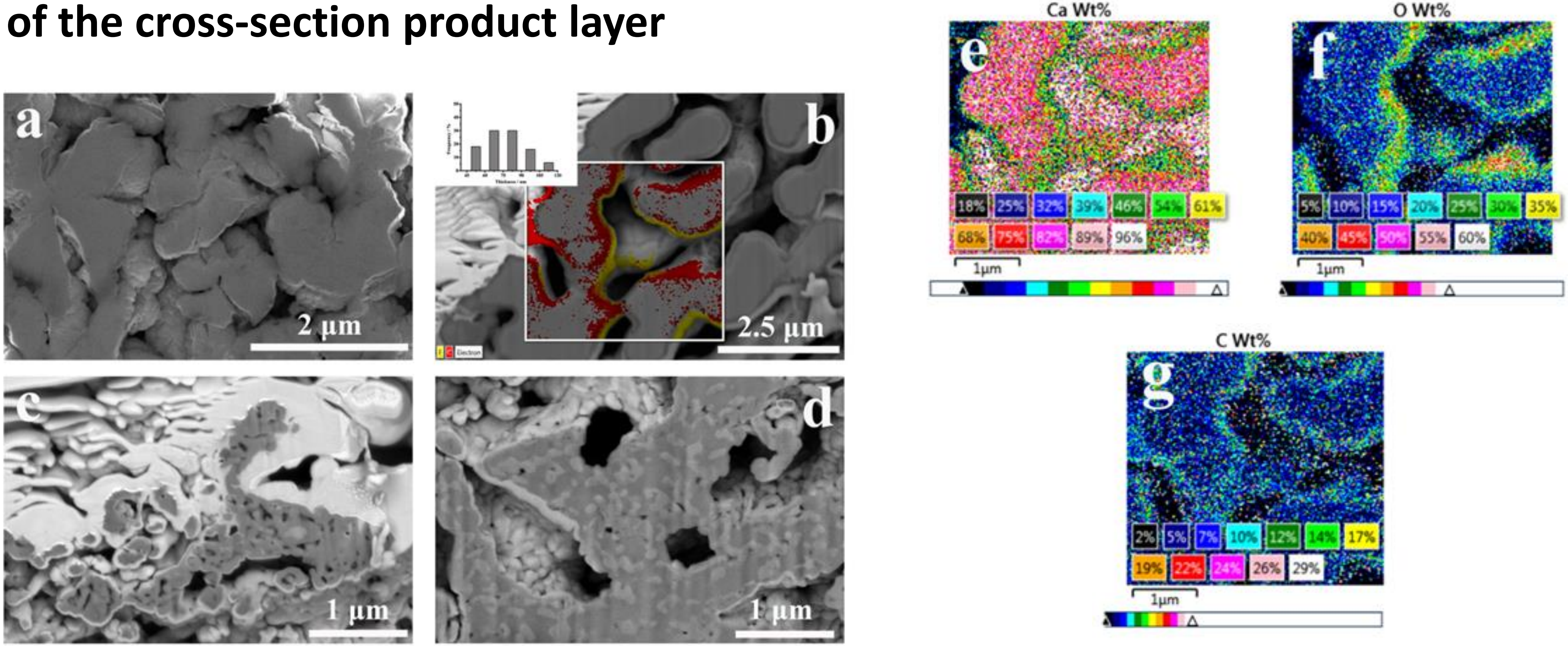


# SEM analysis of carbonated samples

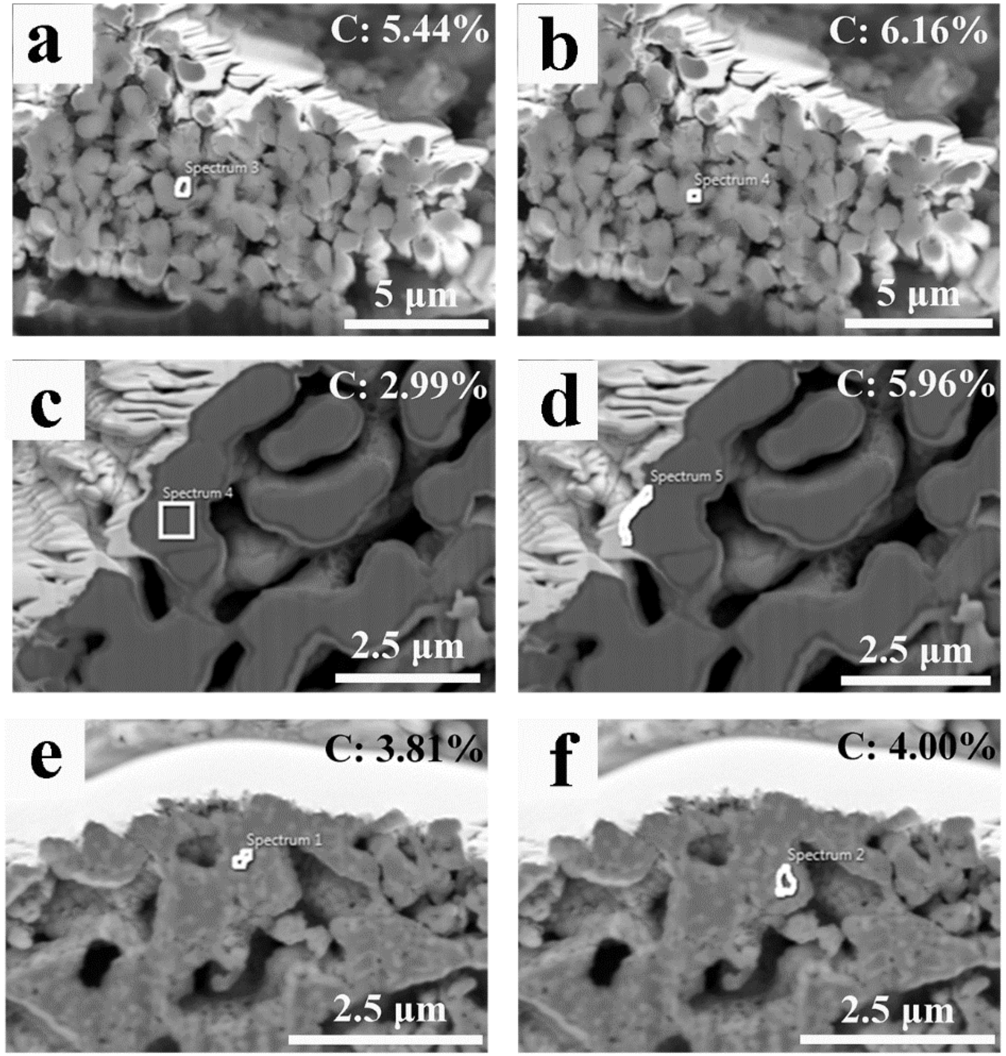


# FIB-SEM images coupled with EDX mapping of the cross-section product layer




a) FB-400, b) FB-600, c) sol-gel FB-400, d) sol-gel FB-600, e) Ca element mapping, f) O element mapping, g) C element mapping

# FIB-SEM images and carbon element content




a) and b) FB-400

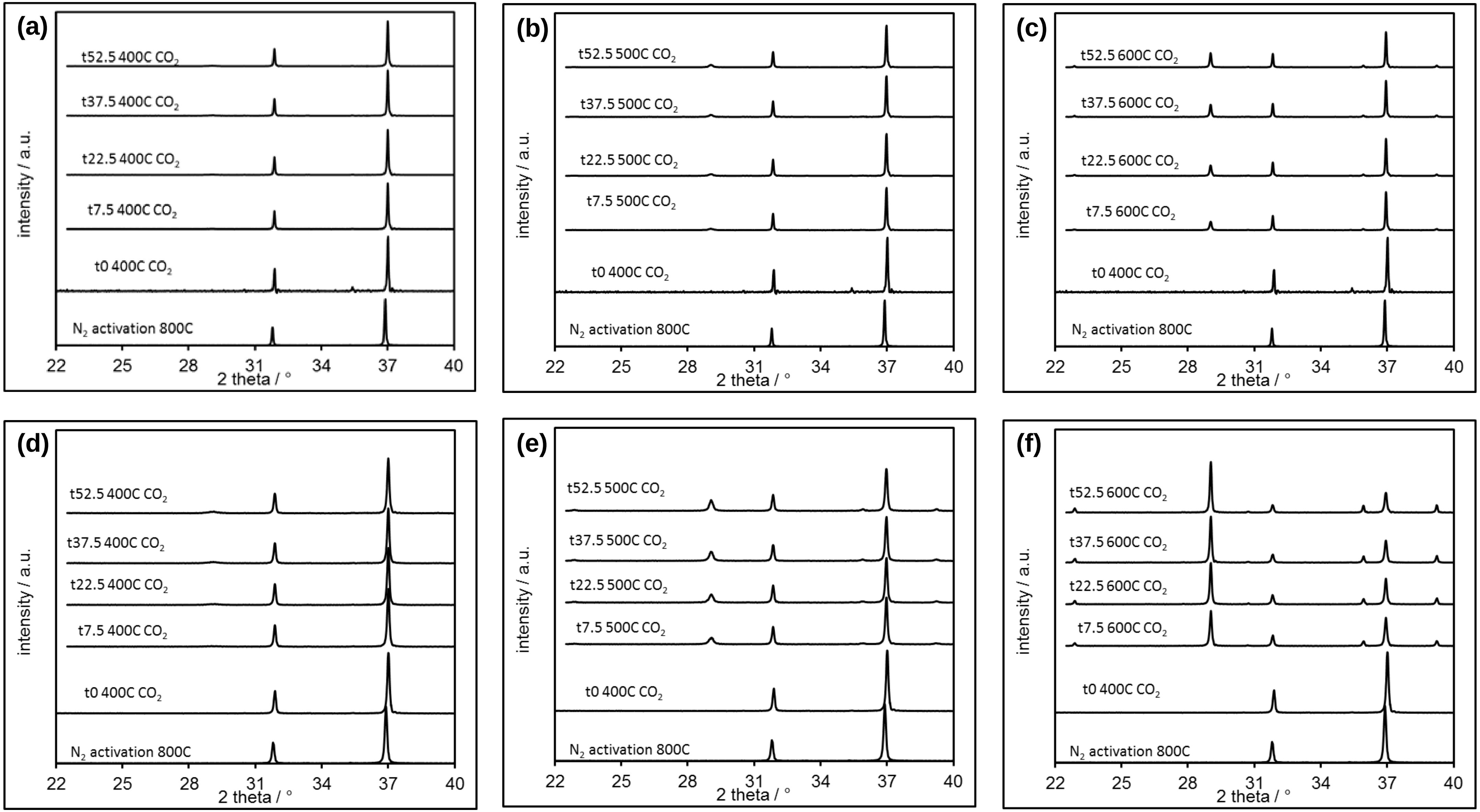
c) and d) FB-600

e) and f) sol-gel FB-600

# In-situ XRD analysis

CaO

sol-gel CaO




a): CaO 400˚C; b): CaO 500˚C; c): CaO 600˚C; d): sol-gel CaO 400˚C; e): sol-gel CaO 500˚C; f): sol-gel CaO 600˚C

# FIB-TEM sample preparation

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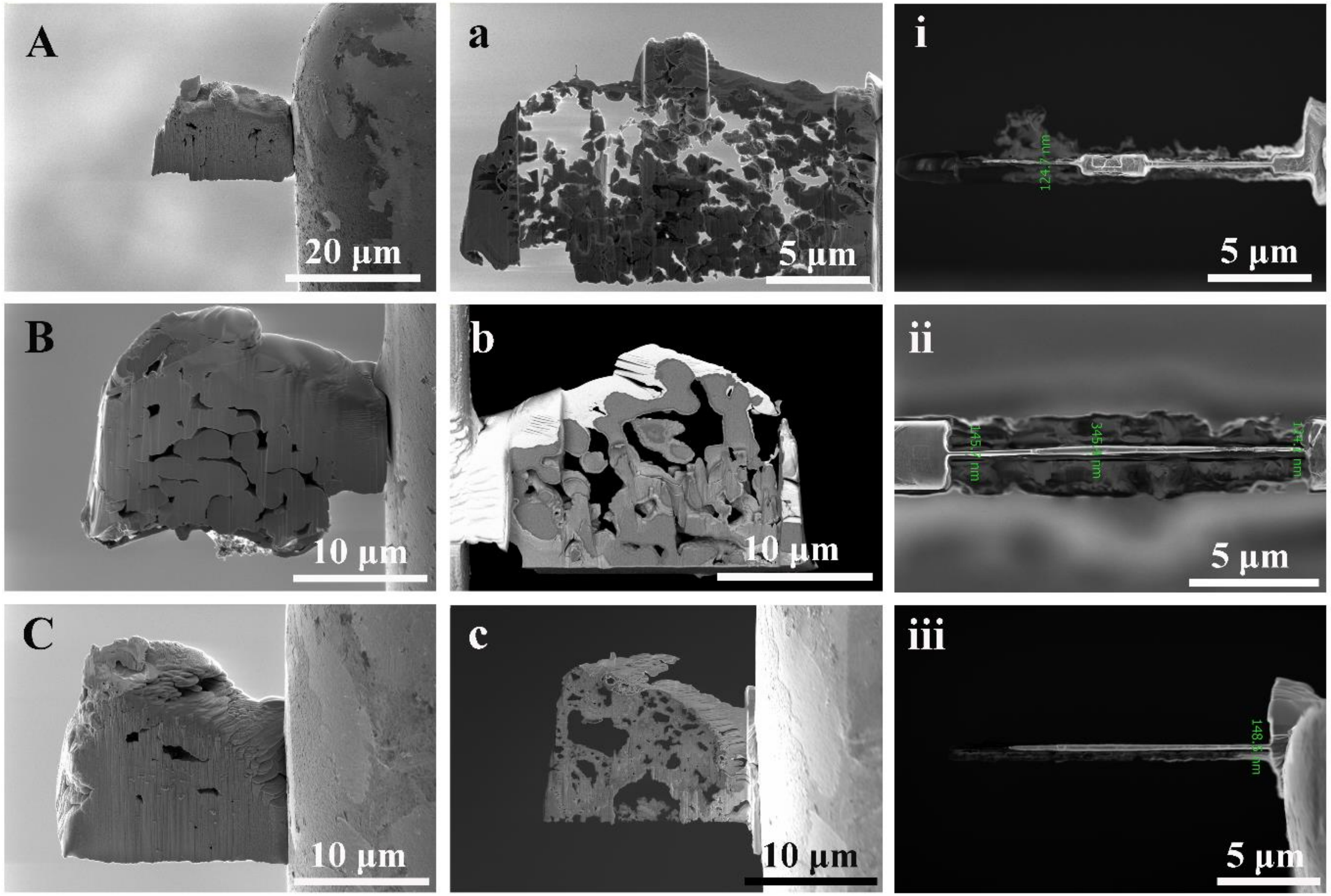
CaO 400C

CaO 600C

Sol-gel CaO 600C

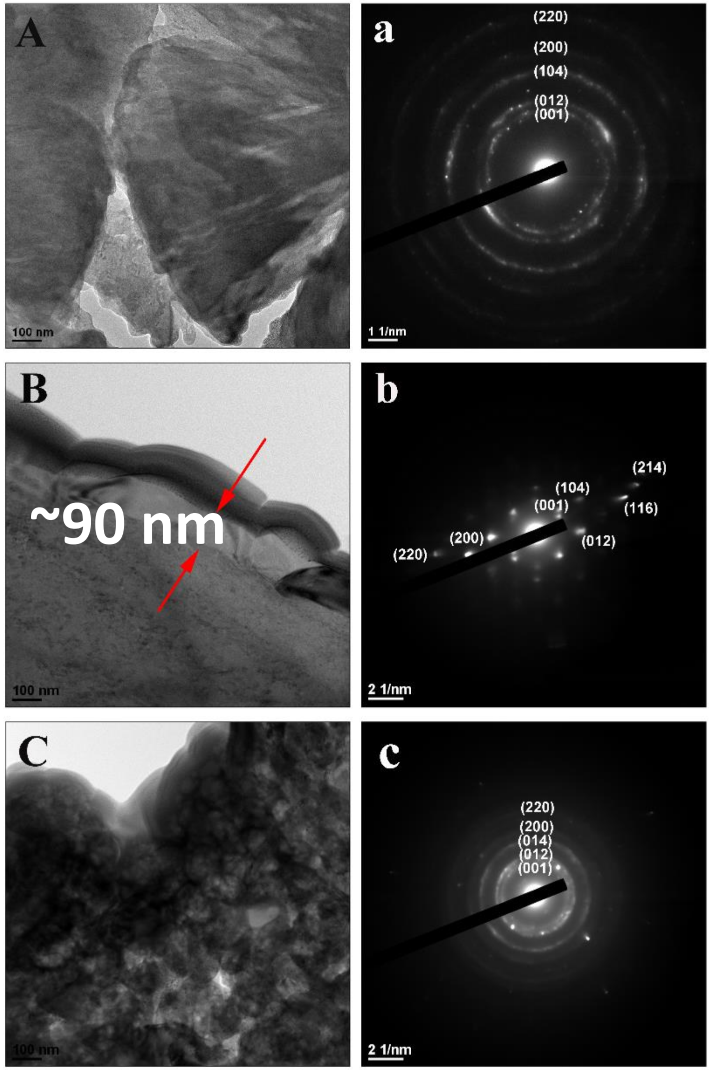


# FIB-TEM images and selected-area electron diffraction pattern of the cross-section product layer

CaO 400 ˚C ⇨

CaO 600 ˚C ⇨

Sol-gel CaO 600 ˚C ⇨



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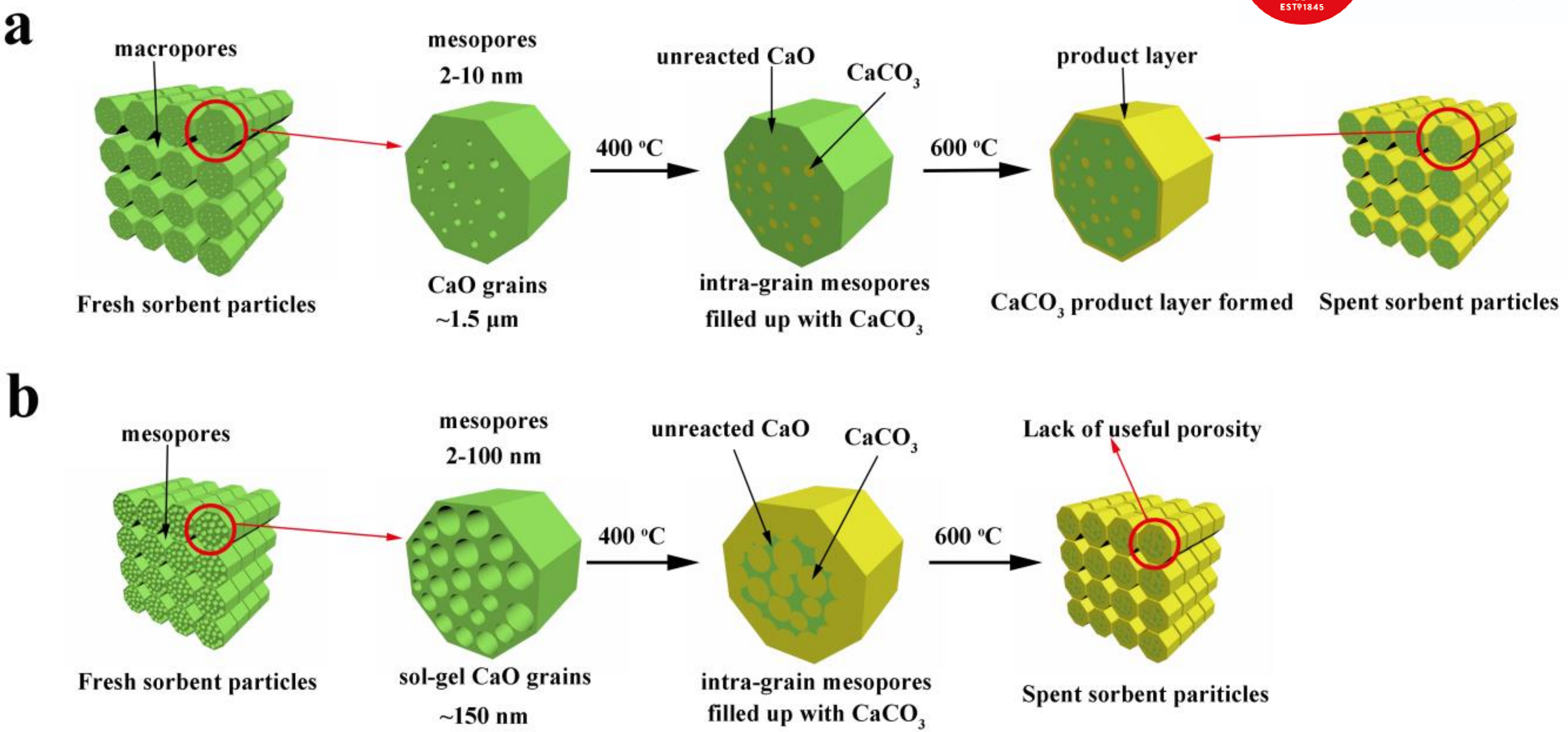

# Conclusions

- Pore structure of CaO is an important parameter for carbon capture
- A layer around 90 nm of $CaCO_3$ seems to be crucial for commercial CaO to capture $CO_2$
- Develop nano-scale CaO material with sufficient local space is suggested

# Acknowledgement


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- Dr Chris Palette (Aston University)
- Prof Ben Anthony (Cranfield University)

Thank you for your attention!