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Fundamental studies of carbon capture using CaO-based materials

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Abstract: Detailed understanding of the mechanisms of the fast stage during CaO carbonation is important to the design of novel efficient CaO materials. This work systematically studies the formation of CaCO₃ product layer on the outside surface of CaO grains during the fast reaction stage for carbon capture using two types of CaO adsorbents. The carbonation at 400 °C filled the small pores in the commercial CaO grains and no distinct product layer of CaCO₃ was observed. However, a distinct layer of CaCO₃ with a thickness around 90 nm was observed on the outside surface of the commercial CaO grains after the carbonation at 600 °C because the internal pores in the CaO grain had been filled and a layer of CaCO₃ product was deposited on the outside surface of the CaO grain. For sol-gel CaO, the carbonation reaction is limited by the availability of useful porosity for the growth of CaCO₃ product (confinement effect), instead of by the diffusion of ions in the critical layer of the CaCO₃ product. No surface product layer was observed. Therefore, fabricating nano-CaO having dimensions less than the critical thickness of the CaCO₃ layer (~90 nm) is of potentially great significance if it can be done cheaply and in bulk.

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24 **1. Introduction**

25 Greenhouse gas especially CO₂ emissions are responsible for climate change and the reduction of
26 greenhouse gas is important to the sustainable development of modern society.¹ It has been reported
27 by the Intergovernmental Panel on Climate Change (IPCC) that the global risks of climate change
28 are increasingly clear for agriculture, human health, ecosystems, and water supplies. The IPCC
29 concluded in 2014 that the world was ill-prepared for such risks.² Subsequently, the Parties to the
30 United Nations Framework Convention on Climate Change (UNFCCC) reached a landmark
31 agreement (the Paris Agreement) to accelerate actions and increase investments towards a
32 sustainable and low-carbon future.³ Carbon capture and utilisation (CCU) have been attracting
33 increasing attention.^{4, 5} CO₂ absorption using amine solution is commercially available. However, as
34 noted by Haszeldine et al.⁶ and Sadiq et al.,⁷ an estimated 30% of power plant output is required for
35 the regeneration of sorbents for carbon capture from post-combustion flue gas, because heating
36 water in the amine sorbent causes large energy losses. On the other hand, using solid sorbents to
37 capture CO₂ is attractive, with the following advantages: (1) the lower heat capacity of solids
38 significantly reduces the sensible energy required for sorbent regeneration; (2) corrosion problems
39 caused by the use of amine solutions (the current standard carbon capture method) are avoided;⁸ (3)
40 heat released during the exothermic carbon capture reaction at a high operating temperature
41 (comparable to gas turbine exhaust temperature)⁹ can be extracted by steam for power generation
42 enabling a highly efficient steam cycle. CaO, as one of the high-temperature CO₂ sorbents, has been
43 investigated extensively because of its high reactivity for CO₂ capture and high theoretical uptake
44 capacity of 17.8 mmol g⁻¹, as well as the extensive availability of CaO precursors possessing a
45 low-cost nature.¹⁰⁻¹⁴ One 1 MWth long-term pilot testing facility and a 1.7 MWth CaL pilot were
46 constructed in Technische Universität Darmstadt and La Pereda power plant, respectively.^{15, 16} It

was found that the semi-industrial CaL plants achieved an outstanding CO₂ capture efficiency (>90%) with a good operation stability (1200 h). In addition, a 1.9 MWth pilot plant constructed at 2013 in Taiwan confirmed that the CaL process is a promising technology for CO₂ capture.¹⁷

However, one of the main limitations of CaO derived from natural precursors is the sorbent deactivation during the regeneration process due to the sintering of CaO particles at high regeneration temperature.¹⁸⁻²⁰ This behaviour can be explained by considering the dramatic volume change between CaO and CaO to CaCO₃; for example an increase from 16.7 to 36.9 cm³ mol⁻¹ for CaO to CaCO₃. Furthermore, there are two stages in the carbonation reaction of CaO: an initially fast reaction stage and a subsequently slow reaction stage.²¹⁻²³ It is attributed that the reduction of carbonation rate in the slow stage was caused by the CO₂ diffusion through the formed CaCO₃ product.²² In the carbonation process, the ratio of reaction rates between the fast and slow reaction stages was around 100.²⁴ This value is in good consistency with the ratio of diffusion coefficients for CaO (0.3 cm² s⁻¹) and CaCO₃ (0.003 cm² s⁻¹).^{22, 25} Therefore, Barker suggested that there was a critical CaCO₃ product layer at which the carbonation reaction rate was determined by the CO₂ diffusion.²² During the fast reaction stage, CaCO₃ grew on the surface of CaO grains and then collapsed to form a continuous layer on the outside surface of the unreacted adsorbent. Thereafter, the fast reaction stage during the CaO carbonation suddenly finished.²⁶ Thus, the initially fast stage and the subsequently slow stage were controlled by the kinetic reaction and CO₂ diffusion through the CaCO₃ product layer, respectively.^{27, 28}

To better understand the fast stage during the CaO carbonation, which is particularly essential for practical applications due to the short reaction time, the critical thickness of the CaCO₃ product layer has been extensively studied. Barker²² demonstrated a “critical carbonate layer thickness” of 22 nm at which the carbonation reaction rate started to be controlled by CO₂ diffusion limitation.

70 However, the estimating equation adopted in that research was confounded by the uncertainties in
71 the carbonation model. A better understanding of pore model coupled with a carbonation pattern
72 across CaO particles was required in this model. In order to eliminate the influences of the
73 unquantifiable and complex morphology in natural materials, the long-duration carbonation reaction
74 on non-porous CaO particles was carried out by Mess et al.²⁹ It was found that the CaCO₃ product
75 layer was homogeneous and exhibited a thickness up to 2 µm under very severe carbonation
76 conditions (850 °C and 1.2 MPa of CO₂ for 2000 min). Subsequently, Alvarez and Abanades³⁰
77 refined the model proposed by Barker²² and suggested that before the maximum product thickness
78 was reached, the small pores in the sorbent were completely filled. In their proposed model, a
79 CaCO₃ layer was generated on the outside surface of CaO grains in the carbonation reaction and an
80 average value of 49 nm (standard deviation is around 19%) was determined.

81 However, the critical thickness of the CaCO₃ layer has only been estimated by means of
82 computer-aided modeling.^{22, 26, 29, 30} There has been no direct observation and measurement of the
83 critical thickness of CaCO₃ product layer formed in the CaO carbonation reaction. Thus, a detailed
84 experimental study is highly desirable for the design of novel CaO adsorbents and the
85 understanding of mechanisms of CaO carbonation.

86 In addition, most of the CaO carbonation work in the open literature was carried out at temperatures
87 higher than 500 °C. Only limited information on low-temperature carbonation of CaO at around 400
88 °C has been reported due to the relatively low reaction rate and low capacity of carbon capture.^{31, 32}

89 We have found that there are two stages of fast CaO carbonation maximising the reaction rate at 400
90 and 600 °C, respectively. Normally, one stage of the fast carbonation reaction was reported in other
91 work for non-isothermal CaO carbonation when the temperature was increased from room
92 temperature to 900 °C.³³ However, the presence of the carbonation gap between 400 and 600 °C has

93 not been clearly understood.

94 Furthermore, a potentially novel intensified process combining CO₂ capture and utilisation at
95 around 400 °C could be very interesting. For example, Duyar et al.³⁴ reported that using a
96 dual-functional catalyst for CO₂ capture at 320 °C, followed by the introduction of H₂ at the same
97 reaction temperature, resulted in the regeneration of sorbent and the production of methane. In this
98 scenario, the regeneration of sorbents and the conversion of captured CO₂ were processed without
99 an energy-intensive thermal-swing process. Therefore, it is of interest to understand the formation
100 of the CaCO₃ layer during CaO carbonation at key reaction temperatures of 400 °C and 600 °C. In
101 this work, two types of CaO adsorbents possessing different porosities were studied in relation to
102 the critical thickness of CaCO₃ product layer.

103

104 **2. Experimental section**

105 **2.1 Adsorbent preparation**

106 A standard sol-gel process proposed by Santos et al.³⁵ was used to synthesise a CaO adsorbent.
107 Predetermined amounts of calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, Sigma-Aldrich, 99.99%)
108 and citric acid monohydrate (C₆H₈O₇·H₂O, Sigma-Aldrich, 99.99%) acting as chelation agent, were
109 added to the distilled water at room temperature (water and citric acid to metal ion molar ratios
110 were 40:1 and 1:1, respectively). The mixture was continuously stirred at 80 °C to form a
111 translucent pale-yellow sol with good dispersion. After drying overnight at 130 °C of the prepared
112 sol, the translucent pale-yellow sol turned into a low-density foam. The obtained foam was then
113 calcined in a muffle furnace at 850 °C for 5 h with a heating rate of 2 °C min⁻¹. This synthesized
114 sample was designated as sol-gel CaO. A commercial CaO (Sigma-Aldrich, 99.99%) was used as
115 the reference adsorbent after dried overnight at 130 °C.

116 2.2 Carbonation/calcination tests

117 The carbon capture performance of adsorbents was conducted in both a fixed-bed reactor (as shown
118 in Fig. 1) and a thermogravimetric analyser (TGA, SDT Q600). In the case of the fixed-bed test,
119 500 mg of adsorbent was loaded into the sample tube (6.35 mm in diameter). Both the carbonation
120 and calcination processes were performed with a temperature-swing process with a heating rate of
121 10 °C min⁻¹ under 15% CO₂ balanced with N₂. The total flow rate of gases was controlled at 100
122 mL min⁻¹. The reacted CaO samples produced at both 400 °C and 600 °C in the fixed-bed reactor
123 were denoted as sol-gel FB-400 and sol-gel FB-600 for the sol-gel CaO, and FB-400 and FB-600
124 for the commercial CaO, respectively. After calcination, the sample was denoted as FB-des. The
125 same carbonation/calcination test was repeated over 3 cycles.

126 During the TGA test, around 15 mg of adsorbent was placed in an alumina crucible and heated to
127 800 °C with a heating rate of 20 °C min⁻¹ under the N₂ atmosphere (100 mL min⁻¹). When the
128 temperature decreased to room temperature, further increasing the temperature to 400 °C, 15% CO₂
129 was used to carbonate the sample for 10 h and then increase the temperature to 600 °C for 30 min.

130 The carbonation conversion was calculated as follows:³⁶

$$131 \quad X(\%) = \frac{m_t - m_0}{m_0} \cdot \frac{M_{\text{CaO}}}{M_{\text{CO}_2}} \cdot 100\% \quad (1)$$

132 where X is the carbonation conversion, m₀ is the mass of the sample after calcination, m_t is the mass
133 of the sample after carbonation for t minutes, and M_{CaO} and M_{CO₂} are the mole masses of CaO and
134 CO₂, respectively.

135 2.3 Characterisation of adsorbents

136 Powder X-ray diffraction (XRD) was performed on a PANalytical empyrean series 2 diffractometer
137 with Cu Kα radiation. Data were analysed by X'pert Highscore plus software. N₂
138 adsorption-desorption isotherms were collected using an ASAP 2000 analyser at -196 °C. The

139 Brunauer-Emmett-Teller (BET) surface area was calculated using the adsorption branch data at the
140 relative pressure (P/P_0) from 0.06 to 0.2, and the micropore volume (V_{micro}) was calculated by the
141 t-plot method.³⁷ The pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH)
142 method using nitrogen desorption branch data.

143 The surface morphology and microstructure of samples were characterised using scanning electron
144 microscopy (SEM, a Stereoscan 360) and transmission electron microscopy (TEM, JEOL 2010),
145 respectively. For TEM analysis of bulky solid samples, the samples were ground, dispersed with
146 acetone, and then deposited on a Cu grid covered with a perforated carbon membrane.

147 A Nanolab Dualbeam focused ion beam (FIB)-SEM coupled with an energy-dispersive X-ray
148 spectroscopy (EDX) and TEM coupled with selected area electron diffraction patterns, were used to
149 characterise and examine the critical thickness of the product layer deposited on the carbonated
150 adsorbents. For FIB-SEM analysis, the samples were cut using a focused ion beam to produce small
151 cross-section samples, which were attached to TEM grids using a platinum binder. After that, the
152 grids with the cross-section samples were analysed using TEM.

153 The crystalline phase change during the carbonation process for CaO and sol-gel CaO was detected
154 by the in-situ XRD. The Bruker D8 Advance XRD equipped with an Anton-Paar XRK-900
155 high-pressure XRD cell and a Cu $k\alpha$ source (0.154 nm) was conducted to collect the XRD patterns.
156 Sample activation was conducted at 800 °C in pure N₂ (1 bar, 50 mL min⁻¹) for 60 min, with a
157 heating rate of 10 °C min⁻¹ before cooling to 400 °C for data collection. The sample was pre-treated
158 with 15% CO₂ balanced with N₂ for 60 min and XRD patterns were continuously collected with the
159 scanning ranging from 22.5° to 40° with a step size of 0.1° and dwell time of 1 s (15 min scans
160 yielding 4 patterns to observe the phase changes).

161

162 3. Results and discussion

163 3.1 Characterisations of adsorbents

164 N₂ adsorption-desorption isotherms and pore size distributions were conducted to determine the
165 structure of the CaO materials (Fig. 2). The textural properties of different CaO adsorbents are
166 summarised in Table 1. The BET surface area (38.51 m² g⁻¹) and total pore volume (0.1527 cm³ g⁻¹)
167 of the sol-gel CaO are much higher than those of the commercial CaO (20.96 m² g⁻¹ and 0.0314 cm³
168 g⁻¹, respectively) due to the presence of micro-scale agglomerates generated by the voids between
169 the nano-scale grains,³⁵ which favor CO₂ carbonation performance.^{38, 39} The BJH pore size
170 distribution (Fig. 2b) indicates the formation of abundant mesopores and macropores ranging from
171 2 to 100 nm in the sol-gel CaO. The morphologies of the commercial CaO and the sol-gel CaO are
172 displayed in Fig. 3a and b, respectively. The commercial CaO possesses a compact structure with a
173 smooth surface and the diameter of CaO grains ranges from 1.5 to 2 μm (Fig. S1a). Compared to
174 the commercial CaO, the sol-gel CaO exhibits a much more fluffy and porous structure. In addition,
175 the diameter of the sol-gel CaO grains ranges from 120 nm to 180 nm as shown in Fig. S1b. Pores
176 less than 10 nm are observed in the commercial CaO as shown in Fig. 3g in agreement with the
177 distribution of small pores ranging from 2 nm to 10 nm in Fig. 2b. However, mesopores composed
178 of nano-sized grains are observed only in the sol-gel CaO, which is consistent with the BJH size
179 distribution (Fig. 2b).

180 3.2 Carbon capture testing

181 The carbonation of CaO at 400 and 600 °C was observed using a fixed-bed reactor. As shown in Fig.
182 4a and b, both the commercial CaO and the sol-gel CaO exhibited a dramatic CaO conversion at
183 400 °C. However, a further increase in temperature resulted in a sudden reduction of carbonation
184 rate at around 500 °C for both samples. The carbonation rate of the CaO increased again when the

185 temperature reached 600 °C. However, as shown in Table 2, the CO₂ uptake, from the 1st cycle to
186 the 2nd cycle, declined dramatically at a carbonation temperature of around 400 °C for both the
187 commercial CaO and the sol-gel CaO, while only a slight decrease of CO₂ uptake is observed after
188 carbonation at 600 °C. Compared to the 2nd cycle performance of CO₂ capture, the 3rd cycle carbon
189 capture exhibited slightly decreased carbonation rates at both 400 °C and 600 °C. It is noted that all
190 characterizations of materials are from 1st cycle carbon capture. It is suggested that with the increase
191 of carbonation/calcination cycles, less effect was observed on the carbon capture performance at the
192 second carbonation stage at around 600 °C. A more detailed understanding of mechanisms in
193 relation to the increase of carbonation/calcination cycles is suggested for future.

194 In order to eliminate the influence of moisture and other impurities inside the sorbent, both the
195 commercial CaO and the sol-gel CaO samples were heated to 800 °C under N₂ atmosphere; then the
196 samples were cooled to 400 °C for the CO₂ capture stage. Fig. S2 shows that the weight of the CaO
197 sample was increased initially due to the carbonation reaction and then showed relative stability at
198 400 °C, indicating that carbonation of CaO was almost completed at 400 °C. In addition, the sample
199 was held at 400 °C for 10 h prior to heating it to 600 °C for further carbonation. This is to ensure
200 that CaO carbonation at 600 °C was not due to incomplete carbonation at 400 °C. As shown in Fig.
201 S2, carbonation is clearly observed at 600 °C indicating the presence of a true two-stage fast
202 carbonation of CaO at around 400 and 600 °C, respectively.

203 A few studies have reported the existence of a reaction rate gap in the CaO carbonation when the
204 temperature ranges from 400 to 600 °C. Bhatia and Perlmutter⁴⁰ proposed that when the temperature
205 was lower than 515 °C, the CaO carbonation reaction as shown in Eq. (2) and (3) took place on the
206 pore surface and was governed by the diffusion of CO₂ molecules with an activation energy of 88.9
207 ± 3.7 kJ mol⁻¹. The ionic diffusion process is shown in Fig. S3a. This is consistent with the

208 observation of CaO carbonation at around 400 °C in this work. However, increasing the temperature
 209 of CaO carbonation to higher than 515 °C, the reaction was reported to take place at the interface
 210 between CaO and CaCO₃ as described in Eq. (4), where CO₃²⁻ is the diffusion species with an
 211 activation energy about 179.2 ± 7.0 kJ mol⁻¹ ⁴⁰ as shown in Fig. S3b.

212 T < 515 °C, carbonation occurs at the pore surface:

215 T > 515 °C, carbonation occurs at the CaO-CaCO₃ interface:

217 **3.3 Mechanisms of CaO carbonation**

218 XRD results for the CaO samples are shown in Fig. 5. For the fresh commercial CaO and sol-gel
 219 CaO samples, only one CaO phase is observed. After carbonation at 400 °C, the spent adsorbents
 220 exhibit a weak diffraction peak at 2θ = 29.4°, indicating the characteristic peak of CaCO₃ (1 0 4).⁴¹
 221 The XRD patterns for the commercial CaO and the sol-gel CaO after carbonation at 600 °C exhibit
 222 much stronger diffraction peaks at similar positions. This indicates that more CaCO₃ phases were
 223 generated at 600 °C compared with the reacted CaO sorbents obtained at 400 °C. The diffraction
 224 peaks of CaCO₃ disappear after increasing the carbonation temperature to 800 °C. This is attributed
 225 to the decomposition of CaCO₃ at 800 °C.

226 After carbonation of the commercial CaO and the sol-gel CaO at 400 and 600 °C, similar
 227 morphologies are observed for both FB-400 and FB-600 (Fig. 3c and e). From Fig. 3d and f, the
 228 mesopores in the sol-gel CaO appear to diminish after carbonation at 400 and 600 °C. Nevertheless,
 229 there are many attachments on the surface of the sol-gel CaO carbonated at 400 °C observed in the
 230 SEM images (Fig. 3d), showing that the mesopores between small grains are well connected.

231 However, the sol-gel CaO experienced a dramatic decrease of pores and the growth of grains after
232 carbonation at 600 °C due to the volume increase of the sorbent, as shown in Fig. 3f.

233 FIB-SEM coupled with EDX was used to measure the critical thickness of the CaCO₃ product layer
234 as shown in Fig. 6. It is noted that the top layer observed in the cross-section was coated with
235 indium which was used to protect the surface during the cutting of the CaO samples.⁴² As for the
236 commercial CaO, no product layer can be observed after carbonation at 400 °C as shown in Fig. 6a.

237 However, a uniform distribution of carbon element is shown in EDX mapping (Fig. S4) implying
238 that CaCO₃ was formed uniformly within the commercial CaO during carbonation at 400 °C. The
239 existence of CaCO₃ is also confirmed from the XRD analysis of FB-400 (Fig. 5a). The commercial
240 CaO sample has a bulk particle size around 3 mm with small grains (around 1.5 μm) containing
241 small pores ranging from 2 nm to 10 nm.^{43, 44} It appears that carbonation of the commercial CaO at
242 400 °C is dominated by the kinetic reaction between CaO and CO₂, and the small pores in the grains
243 were filled with the CaCO₃ formed. Although a layer of CaCO₃ is not observed on the FB-400
244 sample, EDX analysis (Fig. 7a and b) shows that the concentration of carbon in relation to CaCO₃
245 inside the small grains of the commercial CaO was around 5.44%, which is lower than the
246 concentration of carbon on the surface of the commercial CaO (6.16%) (FB-400). This indicates
247 that the outer layer of the CaO was concentrated with CaCO₃ in the fast carbonation stage at 400 °C.

248 A distinct layer is observed after the CaO sample was carbonated at 600 °C. It is suggested that after
249 the carbonation, the internal pores in the grain have been filled and a layer of product was formed
250 on the outside of the grain. It can be seen from Fig. S5 that the average thickness of the product
251 (CaCO₃) is around 90 nm. It is noted that the FB-600 sample was obtained when the maximum
252 carbonation rate was reached during carbonation at 600 °C in the fixed-bed reactor. In addition, the
253 distributions of oxygen and carbon elements show a gradual increase from the interior to the surface

254 of the CaO grains as shown in the EDX mapping of the FB-600 (Fig. 6f and g). By contrast, the
 255 weight percentage of calcium exhibits a decrease from the inner grains to the surface of the FB-600
 256 CaO. Similar results are observed in Fig. 7c and d. The weight percentage of carbon on the surface
 257 of the commercial CaO grains (5.96%) is twice as much as in the interior of the CaO grains (2.99%).
 258 This phenomenon suggests that the carbonation reaction happened on the interface between CaO
 259 and CaCO₃. CO₂ diffuses through the CaCO₃ layer as CO₃²⁻ ions.⁴⁰ Therefore, the concentration of
 260 carbon elements corresponding to CO₃²⁻ ions is higher on the surface of CaO grains after
 261 carbonation at 600 °C, compared to the carbon concentration inside the CaO grains.
 262 In this stage, CO₃²⁻ ions can decompose to produce CO₂ and O²⁻ as shown in Eq. (4). CO₂ molecule
 263 transfers to a neighboring, similarly vacated site, while CO₂ produced elsewhere moves to take its
 264 place and reform the CO₃²⁻. Therefore, the CO₂ molecule diffuses from site to site through the
 265 CaCO₃ product layer, until ultimately the carbonation reaction occurs at the interface between CaO
 266 and CaCO₃. The ionic diffusion process is shown in Fig. S3b. A higher activation energy, about
 267 $179.2 \pm 7.0 \text{ kJ mol}^{-1}$, is required for the decomposition of CO₃²⁻. This activation energy corresponds
 268 to a carbonation temperature around 600 °C, where the second-stage fast CaO carbonation occurred.
 269 The sudden change in activation energy between 500 and 600 °C could also be due to the phase
 270 change of CaCO₃ from aragonite to calcite.⁴⁵ The diffusion of ions within aragonite is much easier
 271 than calcite. The diffusion of ions (e.g., CO₃²⁻) is related to Tammann temperature (which is half the
 272 absolute melting point, and the temperature at which bulk diffusion starts to become significant),
 273 which is around 412 °C for aragonite and around 650 °C for calcite. In-situ XRD analysis of CaO
 274 carbonation at a temperature of 750 °C has been investigated and, to date, only calcite was reported
 275 ⁴⁶. However, at a lower carbonation temperature of 450 °C, aragonite-type CaCO₃ appears to be
 276 formed, according to in-situ XRD experimental tests.⁴⁷

277 In this work, the phase changes in the carbonation reaction at different temperatures were
278 investigated using an in-situ XRD equipment, as shown in Fig. 8. It is found that calcite was the
279 only phase of CaCO_3 observed with the increase of both the reaction time and temperature.
280 Therefore, the sudden change of CaO carbonation is unlikely due to the phase change of CaCO_3
281 from aragonite to calcite during the carbonation of CaO samples. However, a high-resolution
282 synchrotron XRD could be used to further confirm the absence of aragonite during CaO carbonation,
283 which might exist as an intermediate product.

284 In order to understand the influence of temperature on the critical thickness of the product layer
285 during the fast CaO carbonation, FIB-TEM coupled with selected-area electron diffraction patterns
286 were produced, as shown in Fig. 9. Even though no CaCO_3 product layer was observed in Fig. 9A,
287 (012) and (104) crystal phases of CaCO_3 were observed in the electron diffraction pattern (Fig. 9a)
288 which is in agreement with XRD results in Fig. 5a. In addition, (001) crystal phase (Ca(OH)_2) was
289 observed due to the reaction between the thin FIB-TEM sample (around 100 nm) and moisture in
290 the air. Three distinct layers and single-crystal characteristics after the carbonation at 600 °C are
291 shown in Fig. 9B and Fig. 9b, respectively. The outside layer was caused by the coating of indium
292 and platinum. The compact layer in the middle was the formed CaCO_3 product layer, with a
293 thickness around 90 nm. This phenomenon indicates that, as with commercial CaO, carbonation at
294 400 °C and 600 °C involves filling CaCO_3 in the small pores in the grains, and a product layer
295 deposited on the outside of the grains, respectively.

296 **3.4 Influence of porous structure**

297 Abundant mesopores, ranging from 2 to 100 nm, were generated by the lamellar structure in the
298 sol-gel CaO (Fig. 3b), which enhance the fast and kinetically-limited reaction stage. In addition,
299 large pore volume favors gas diffusion in the pore space of adsorbents.⁴⁸ Therefore, the sol-gel CaO

300 performed a higher carbon capture capacity compared to the commercial CaO in Table 2. No
301 obvious product layer was observed in the sol-gel CaO after carbonation at both 400 °C and 600 °C,
302 as shown in Fig. 6c and d. The distribution of carbon is consistent between the surface and the inner
303 grains of the sol-gel CaO grains (Fig. 7e and f). It appears that the carbonation of sol-gel CaO at
304 400 °C is similar to that of commercial CaO, involving the filling of small pores in the CaO grains
305 with the formed CaCO₃. However, the carbonation at 600 °C is retarded by the lack of useful
306 porosity (the confinement effect) which is required for the growth of CaCO₃ instead of the
307 formation of CaCO₃ product layer, as shown in Fig. 10b.⁴⁴ This is attributed to that local space is
308 required for the growth of particles from 16.7 to 36.9 cm³ mol⁻¹ for the conversion of CaO to
309 CaCO₃. The FIB-TEM image of sol-gel FB-600 as shown in Fig. 9C exhibits almost no porosity
310 which is good agreement with the FIB-SEM pictures in Fig. 6d. In addition, the crystal phases
311 (CaCO₃ and Ca(OH)₂) were observed in Fig. 9c, further indicating the formation of CaCO₃ in the
312 sol-gel FB-600. Therefore, fabricating nano-CaO having dimensions less than the critical thickness
313 of the CaCO₃ layer (~90 nm) is of potentially great significance if it can be done cheaply and in
314 bulk. For example, nanowire and nanofilm of the novel nano-CaO could be developed. However,
315 the resistance of sorbent sintering during the process of carbonation/calcination remains a
316 challenging topic. Furthermore, it is suggested to disperse CaO species into an inert support which
317 can provide a certain extent of porosity, prohibit CaO sintering and play an essential role in
318 restricting the growth of CaCO₃ layer.

319

320 4. Conclusions

321 The formation of CaCO₃ product layer on the outside surface of CaO grains during the fast reaction
322 stage for carbon capture using two types of CaO has been systematically studied. It was found that

for both the commercial CaO and the sol-gel CaO, two distinct stages of fast carbonation are observed at 400 and 600 °C. After carbonation at 600 °C for the commercial CaO, a layer of CaCO₃ with a thickness around 90 nm is observed. This is because the internal pores of the commercial CaO grains have been filled with CaCO₃ and a layer of the CaCO₃ product is deposited on the outside of the CaO grain. Here, the fast carbonation stage of the commercial CaO is terminated by the formation of the CaCO₃ layer. However, as with the synthesized sol-gel CaO, the carbonation reaction is retarded by the lack of useful porosity (space is required for the formation of CaCO₃ due to its larger molar volume than CaO), defined here as the confinement effect, instead of by the formation of a CaCO₃ product layer itself. Thus, a layer of CaCO₃ product on the sol-gel CaO cannot be observed after carbonation at 600 °C. This is attributed to the presence of abundant mesopores generated by the lamellar structure of the sol-gel CaO.

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335 **Conflicts of interest**

336 There are no conflicts to declare.

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402 **Fig. 1** Schematic diagram of the atmospheric carbonation/calcination reactor system (fixed bed).

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405 **Fig. 2** N_2 adsorption-desorption isotherms (a) and pore size distributions calculated from the BJH
406 desorption branch (b).

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Fig. 3 SEM images of a) CaO, b) sol-gel CaO, c) FB-400, d) sol-gel FB-400, e) FB-600, f) sol-gel FB-600 and TEM images of g) CaO, h) sol-gel CaO.

411

412 **Fig. 4** Cyclic CO₂ capture performance of a) CaO, b) sol-gel CaO, in a fixed-bed reactor (black line:

413 experimental curves; red dashed curve: peak I, carbonation at 400 °C, blue dashed curve: peak II,

414 carbonation at 600 °C).

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416 **Fig. 5** XRD patterns for CaO adsorbents obtained after reaching highest reaction rate at different

417 temperatures. a) CaO, b) sol-gel CaO.

Fig. 6 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.

Fig. 7 FIB-SEM images and carbon element percentage of a and b) FB-400, c and d) FB-600, and e and f) sol-gel FB-600.

Fig. 8 In-situ XRD patterns of CaO adsorbents at different temperatures. 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 (txy.z represents carbonation for xy.z min).

Fig. 9 FIB-TEM images and selected-area electron diffraction pattern of the cross-section product layer. A and a) FB-400, B and b) FB-600, C and c) sol-gel FB-600.

Fig. 10 Schematic illustration of the effect of temperature and structure on the CaCO₃ layer thickness during CaO carbonation reaction. a) CaO, b) sol-gel CaO.

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438

Table 1 Textural properties derived from different CaO adsorbents

Samples	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{ g}^{-1}$)	$S_{\text{micro}}^{\text{b}}$ ($\text{m}^2 \text{ g}^{-1}$)	$S_{\text{meso}}^{\text{c}}$ ($\text{m}^2 \text{ g}^{-1}$)	V_{p}^{d} ($\text{cm}^3 \text{ g}^{-1}$)	$V_{\text{micro}}^{\text{e}}$ ($\text{cm}^3 \text{ g}^{-1}$)	$V_{\text{meso}}^{\text{f}}$ ($\text{cm}^3 \text{ g}^{-1}$)
CaO	20.96	3.70	17.26	0.0314	0.0014	0.0331
sol-gel CaO	38.51	8.51	30.00	0.1527	0.0035	0.1511

439

^aBET surface areas

440

^bMicropore surface areas calculated by t-plot method

441

^cMesopore surface areas equal to S_{BET} minus S_{micro}

442

^dTotal pore volume measured at a relative pressure (P/P_0) of 0.99

443

^eThe t-plot micropore volume

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^fBJH adsorption cumulative volume

445

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Table 2 CO₂ uptake of a commercial CaO and a sol-gel CaO at different temperatures in a

447

fixed-bed reactor

CO ₂ uptake (mmol g^{-1})	1 st cycle		2 nd cycle		3 rd cycle	
	400 °C	600 °C	400 °C	600 °C	400 °C	600 °C
CaO	5.84	7.26	0.60	7.02	0.54	4.06
sol-gel CaO	8.50	6.16	0.76	5.12	0.74	4.20

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