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1 Alkali metal CO₂ sorbents and the resulting
2 metal carbonates: Potential for process
3 intensification of Sorption-Enhanced Steam
4 Reforming

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15

16 **ABSTRACT:** Sorption-enhanced steam reforming (SESR) is an energy and cost efficient
17 approach to produce hydrogen with high purity. SESR makes it economically feasible to
18 use a wide range of feedstocks for hydrogen production such as methane, ethanol and
19 biomass. Selection of catalysts and sorbents plays a vital role in SESR. This article
20 reviews the recent research aimed at process intensification by the integration of catalysis
21 and chemisorption functions into a single material. Alkali metal ceramic powders,
22 including Li_2ZrO_3 , Li_4SiO_4 and Na_2ZrO_3 display characteristics suitable for capturing
23 CO_2 at low concentrations ($< 15\% \text{CO}_2$) and high temperatures ($> 500 \text{ }^\circ\text{C}$), and thus are
24 applicable to pre-combustion technologies such as SESR, as well as post-combustion
25 capture of CO_2 from flue gases. This paper reviews the progress made in improving the
26 operational performance of alkali metal ceramics under conditions that simulate power
27 plant and SESR operation, by adopting new methods of sorbent synthesis and doping
28 with additional elements. The paper also discusses the role of carbonates formed after in-
29 situ CO_2 chemisorption during a steam reforming process in respect of catalysts for tar
30 cracking.

31 TOC



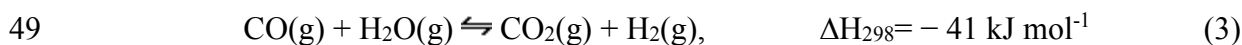
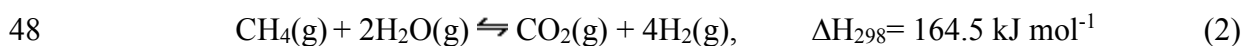
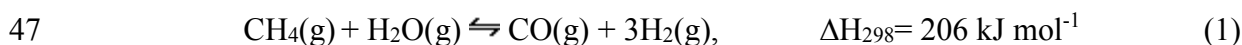
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33 **KEYWORDS:** Alkali metal ceramics, steam reforming, CO₂ sorbents, catalysts,
34 bifunctional materials

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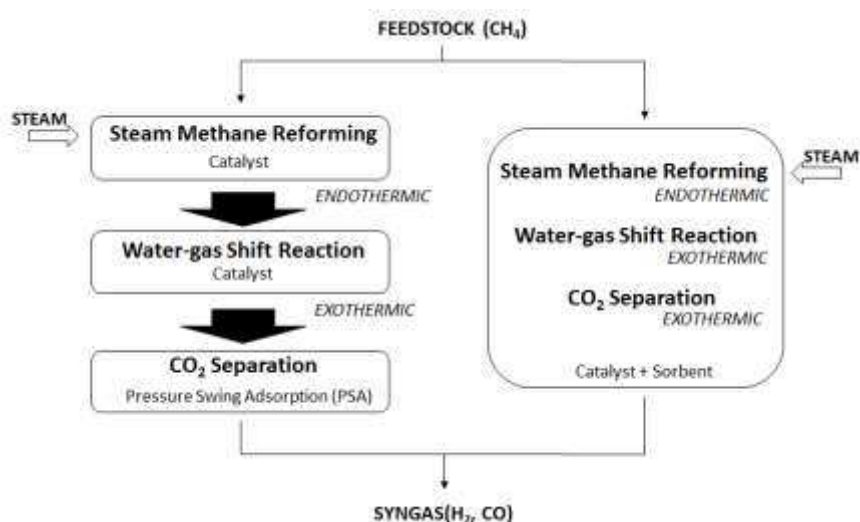
36 1. INTRODUCTION

37 Sorption-enhanced steam reforming (SESR) is a promising thermochemical approach
38 to producing hydrogen-rich fuel gases, utilizing steam as a gasifying agent, and is
39 applicable to multiple types of hydrocarbon feedstocks i.e. methane, ethanol and biomass
40 to generate hydrogen.^{1,2} Hydrogen is a green energy carrier with a calorific value (of 122
41 kJ g⁻¹), that is greater than other hydrocarbon fuels.³ SESR is a modification of the
42 conventional steam reforming method of hydrogen production, and involves less
43 intensive operating conditions than conventional steam methane reforming (SMR). In
44 conventional SMR, methane is reformed in the presence of a catalyst and steam to
45 produce syngas. The SMR process involves the following major reactions to produce
46 hydrogen (Eqns. 1-3):



50 The conventional SMR process requires two separate chambers for these reactions
51 because the endothermic methane reforming reactions, i.e. Eqns. (1) and (2), occur at
52 high temperatures (> 800 °C) and low pressures, while the exothermic water-gas shift
53 (WGS) reaction, Eqn. (3), occurs at lower temperatures (< 400 °C).⁴ Additionally, the

54 hydrogen stream has to be separated from CO₂ during the WGS reaction. By introducing
 55 a sorbent to capture CO₂ generated *in-situ* of the reforming reactions, the thermodynamic
 56 limits placed on the process are less restrictive (**Figure 1**). Thereby methane reforming,
 57 WGS and CO₂ removal (an exothermic reaction) can occur simultaneously in a single
 58 chamber.⁵ As such, SESR can be coupled with SMR to streamline a widely utilized
 59 industrial procedure for hydrogen production. At the same time, SESR also provides an
 60 opportunity to generate hydrogen from biomass feedstock; SESR is reported to produce
 61 H₂ with purity > 85%, almost doubling the amount of hydrogen reported from previous
 62 reactions.^{1, 6, 7}



63
 64 **Figure 1.** Simple schematic representations of SMR process (right) and SESR (left)
 65 utilizing methane to produce H₂ enriched syngas.
 66

67 The two vital materials that facilitate SESR are catalysts and sorbents. An appropriate
 68 catalyst for biomass-fueled SESR must be capable of catalyzing both tar-cracking and
 69 hydrocarbon reforming. Among the commonly used catalysts, Ni is widely regarded as

70 the most cost effective.⁸ Nano-sized Ni particles can be widely dispersed on supports,
71 leading to increased catalytic activity. For the purpose of *in-situ* CO₂ capture, a sorbent
72 must possess selectivity towards CO₂ in a stream of mixed gases, an ability to confine
73 and release CO₂ within itself at high temperatures (400 °C and above), and capacity to
74 maintain mechanical integrity under duress of cyclic CO₂ capture-and-release process.
75 Solid CO₂ sorbents have been proven to be the appropriate choice for high-temperature
76 SESR (>400 °C),⁹ and they have been widely researched for the removal of CO₂ from
77 flue gases.⁹⁻¹¹ This is an additional advantage of SESR because sequestration by the
78 sorbent can prevent CO₂ generated in-situ from being released into the atmosphere,
79 making the process net carbon negative when a carbon-neutral biomass is used as the
80 feedstock. Sorbents based on CaO are foremost among the solid sorbents that couple to
81 the reaction conditions of SESR.^{12, 13} These sorbents are cheap and show promising
82 chemisorption capacity and kinetics, 17.8 mmol-CO₂ g-sorbent⁻¹, at the moderate-to-high
83 temperatures required for SESR (450-750 °C), however a drawback lies in the tendency
84 of CaO to sinter during regeneration (up to 900 °C), resulting in gradual deactivation over
85 a multicycle process. Hydrotalcites (HTlcs) trap CO₂ in the temperature range of 200-500
86 °C and exhibit improved performance under steam saturated atmospheres, despite HTlcs
87 being limited by poor chemisorption capacity, < 1.0 mmol-CO₂ g-sorbent⁻¹, and slow
88 reaction kinetics.¹⁴ Magnesia, MgO is a naturally abundant resource, and active in
89 capturing CO₂ at low-to-moderate temperatures, i.e. 300-450 °C, have a CO₂
90 chemisorption capacity of < 3.4 mmol-CO₂ g-sorbent⁻¹, can be regenerated at 500 °C and
91 exhibits a positive influence of steam on its performance. But similar to CaO, MgO
92 sorbents deteriorate in a multi-cycle operation such as SESR.¹⁵ An ideal sorbent should

93 retain its performance over multiple operating cycles. In the past decade, a great deal of
94 effort has been devoted to improve the sintering-resistance of these sorbents.^{16, 17}

95 A recent research hotspot for SESR has been the development of a bifunctional
96 material (hybrid type) containing both active catalytic sites and chemisorption sites. The
97 most significant benefit of a bifunctional catalyst-sorbent is cost reduction as separate
98 catalyst and sorbent powders will no longer be needed. Theoretical studies conclude that
99 having catalyst and chemisorption sites closer will improve mass transfer as well as,
100 potentially maintain a relatively higher CO₂ partial pressure for chemisorption.¹⁸ In
101 principle, CO₂ molecules would have shorter distance to travel to chemisorption sites at
102 or beneath the surface of the sorbent, resulting in faster reaction kinetics and lower
103 residence times in the reactor.¹⁹

104 Alkali metal ceramics, which in the context of this review refers to binary-metal
105 oxides composed of at least a metal belonging to the alkali metal group of chemical
106 elements, have been widely researched as alternative sorbents to CaO, due to their ability
107 to trap CO₂ as alkali metal carbonates under a wide range of temperatures.²⁰ Examples
108 include Li₂ZrO₃, Li₄SiO₄ and Na₂ZrO₃. The carbonates can be decomposed at higher
109 temperatures making the materials suitable for multi-cycle operations that involve CO₂
110 capture and release, i.e. both post- and pre-combustion capture schemes. Furthermore,
111 alkali metal ceramics offer useful catalytic activity for steam reforming processes. Alkali
112 metal zirconates such as Na₂ZrO₃ are reported to be active in catalyzing CO conversion
113 to CO₂;²¹ and, their carbonated derivatives, i.e. Na₂CO₃ and K₂CO₃, formed after CO₂ is
114 chemisorbed, are common mineral components in biomass and have been investigated for
115 tar removal applications during biomass gasification.^{8, 22, 23} Alkali metal carbonates have

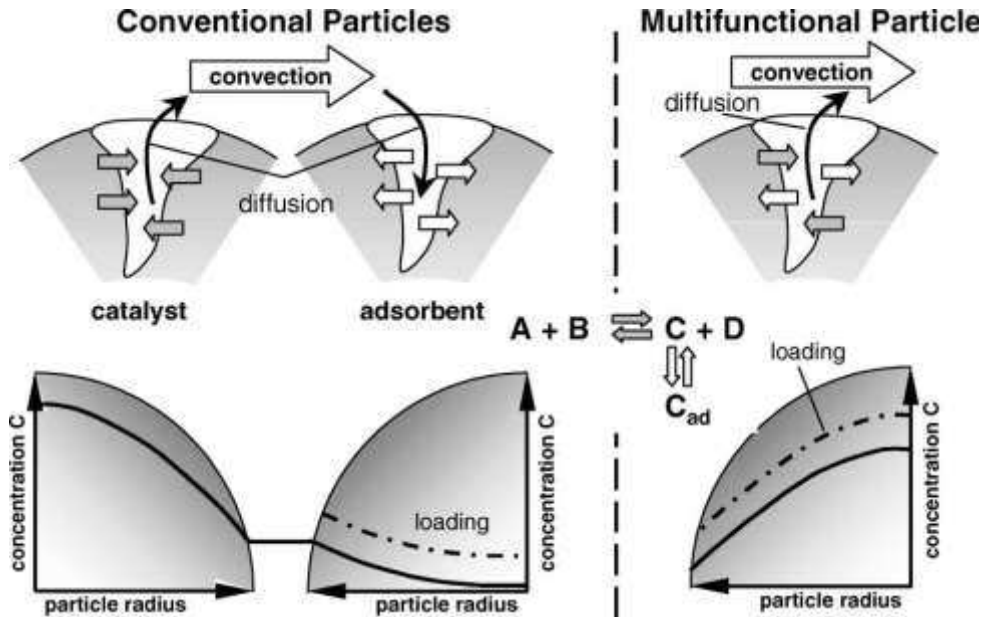
116 also been reported as catalysts in methane reforming, the WGS reaction,⁸ and
117 transesterification of soybean oil.²⁴ Therefore, alkali metal ceramics have potential to act
118 as a bifunctional catalyst-sorbent for SESR, even without grafting additional catalyzing
119 sites (such as inclusion of Ni nanoparticles).

120 After a brief review of a variety of recently developed bifunctional hybrid materials,
121 this article discusses in detail the potential of alkali metal ceramics as a standalone
122 bifunctional material in SESR, particularly with respect to the most widely researched
123 alkali-based sorbents Li_2ZrO_3 , Li_4SiO_4 and Na_2ZrO_3 . Modelling studies have suggested
124 these sorbents can be capable of producing up to 95 vol. % H_2 in SESR of methane and
125 ethanol and as such are discussed in this review.²⁵⁻²⁸ Research into the catalytic role of
126 alkali metal ceramics in SESR is also summarized. Finally, investigations of synthesis
127 methods, means of modifying the performance of the materials and the effects on CO_2
128 chemisorption are discussed.

129 **2. BIFUNCTIONAL CATALYST-SORBENT HYBRID MATERIALS**

130 Given the advantages of incorporating the WGS reaction and product stream
131 purification in a single chamber it is not surprising that the use of CO_2 sorbents (SESR)
132 have attracted so much recent interest.^{6, 29} Catalysts and sorbents need however to be
133 mixed before inserting in the reactor because it is extremely challenging to achieve
134 uniform mixing and avoid chemical inter-diffusion and loss of activity during operation.
135 As SESR produces a high-purity stream of hydrogen following Le Chatelier's principle,
136 any delay in removal of the product gas CO_2 is detrimental to the production of hydrogen.

137 A more direct removal of CO₂ is possible if catalyst and sorbent sites are intermixed in a
 138 single material (**Figure 2**).



139

140 **Figure 2.** Schematic comparison of the coupling of reaction and chemisorption and the
 141 resulting concentration profiles for conventional and multifunctional particles; the
 142 loading profile proceeds more directly in a multifunctional particle.¹⁹

143 The combined function materials used in SESR processes are usually termed
 144 bifunctional catalysts, bifunctional catalyst-sorbent materials or hybrid
 145 materials/composites. Satrio et al.³⁰ were the first to synthesize core-shell pellets, with
 146 sorbent (CaO) in the core surrounded by an alumina based shell incorporating a catalyst
 147 (Ni). The results showed that incorporated functionalities in core shell pellets catalyzed
 148 reactions of methane and propane in the presence of steam as well as removed CO₂
 149 produced *in-situ*, thus demonstrating an effective merging of the two functionalities for
 150 SESR. Study by Dewoolkar et al.³¹ displayed that performance of a hybrid Ni/CaO and

151 Ni/HTlc was superior to conventional solid mixing of catalyst and sorbent, for exhibiting
152 longer breakthrough time (35 and 15 min of hybrid Ni/CaO and Ni/Htcl over 10 and 5
153 min of conventional mixture of same materials, respectively) and better chemisorption
154 capacity (5.7 and 0.9 mol-CO₂ kg-sorbent⁻¹ of hybrid Ni/CaO and Ni/Htcl over 2 and 0.3
155 mol-CO₂ kg-sorbent⁻¹ of conventional mixture of same materials, respectively).
156 Subsequent research has focused on CaO and HTlcs as sorbent candidates that mainly
157 incorporate Ni as a catalyst.

158 **CaO-based composites**

159 As mentioned earlier CaO is vulnerable to sintering and a loss in capture capacity at
160 high temperatures in cyclic SESR processes. The most common strategy to inhibit this
161 sintering and to improve durability is to use a refractory ceramic support to separate the
162 active CaO particles. Such a two phase structure can also be utilized for dispersing an
163 additional catalyst. Martavaltzi et al.³² synthesized CaO-Ca₁₂Al₁₄O₃₃ and dispersed Ni
164 particles over the Ca₁₂Al₁₄O₃₃ phase. Incorporating chemisorption and catalysis phases
165 into a single material reduces the overall complexity of the reaction scheme. Ni can serve
166 as an additional stabilizer for CaO although too high a Ni content (> 16 wt. %) can block
167 access of CO₂ to chemisorption sites. The hybrid material produced H₂ yield of 90%
168 converting 80% of methane. Chanburanasiri et al.³³ compared Ni dispersed on Al₂O₃ and
169 CaO as SESR materials. Although the activity of Ni/CaO is lower than Ni/Al₂O₃, both
170 materials performed similarly in pre-breakthrough period, producing hydrogen of > 80%
171 purity, but at post-breakthrough period Ni/Al₂O₃ produced 70% hydrogen stream while
172 Ni/CaO could produce 65% hydrogen stream. The results imply that CaO has promise as
173 an active support. The authors also suggest that the use of Ni/CaO as a bifunctional

174 material can reduce material costs. Nahil et al.³⁴ used Ni-Mg-Al-CaO for biomass
175 gasification. This material exhibited better process stability over 20 cycles CO₂
176 capture/release compared to CaO. The highest hydrogen yield was 20.2 mmol g⁻¹ of
177 biomass when 20 wt. % CaO was loaded onto Ni-Mg-Al. The presence of Ni and CaO
178 was found to affect hydrocarbon reforming and WGS reactions as catalyst and sorbent
179 respectively. Radfarnia and Iluita³⁵ investigated the optimal Ni loading for a bifunctional
180 Al stabilized Ni/CaO material and found out that material loaded with 25 wt.% CaO
181 exhibited the best performance for CO₂ chemisorption/desorption (9.3 mmol-CO₂ g-
182 sorbent⁻¹ after 25 cycles) and for SESR of methane (99.1% methane conversion and
183 96.1% hydrogen production). In another study by the same authors³⁶, they used a ZrO₂
184 based support to stabilize a Ni/CaO bifunctional material and learnt that 20.5 wt. % of
185 NiO yielded best results (average H₂ yield of 89%). High Ni content also had advantage
186 of accelerated gasification of deposited coke. Ashok et al.³⁷ synthesized Ni/CaO-Al₂O₃
187 from HTlc derived precursors for steam reforming of biomass and model tar compound.
188 The optimum combination of Ni-Ca-Al (8:62:30) captured 3.9 mmol-CO₂ g-sorbent⁻¹
189 after 10 cycles of chemisorption/desorption. The authors observed a synergy between
190 presence of Ni and CaO phase which resulted in nearly 70% of toluene conversion and a
191 carbon deposition rate of 2.5 mg-C g⁻¹ h⁻¹. Under the same compound, the biomass
192 conversion was recorded to be approximately 85% at 650 °C. Xu et al.³⁸ prepared
193 bifunctional materials in the form of extrudates to improve the materials' stability and the
194 most stable sorbent displayed 4 % loss in capacity after 50 cycles capturing 0.436 g-CO₂
195 g-sorbent⁻¹. As the use of a refractory support material is critical to the performance of
196 CaO as a sorbent, research effort has now focused on means for uniformly distributing a

197 catalyst within a supported structure, and its optimal loading³⁹. **Table 1** summarizes the
 198 performances and the operating conditions of the various materials discussed here.

199

200 **Table 1.** Synthesis method, conditions and performance of various bifunctional materials.

Material	Preparation Method	Feedstock	Conditions	SESR Cycles	H ₂ purity	Ref.
Ni/CaO-Al ₂ O ₃	Conical drum pelletizer	CO	600 °C, S/CO=3	N/A	H ₂ > 97 %	40
Ni/Ca-ex-HTlc	Co-precipitation method	Methane	550 °C, S/C=4,	10	H ₂ = 99 %	41
Ni/CaO-Al ₂ O ₃	Wet-mixing method	Methane	650 °C, S/C=4	10	H ₂ = 96.1%	35
Ni/CaO-Ca ₅ Al ₆ O ₁₄	Sol-gel method	Methane	750 °C, S/C=4	10	H ₂ > 95%	38
Ni/CaO-Zr	Wet-mixing method	Methane	650 °C, S/C=4	10	H ₂ = 91%	36
Ni/CaO-Ca ₁₂ Al ₁₄ O ₃₃	Soft-chemistry route	Methane	650 °C, S/C=3.4	45	H ₂ = 90%	32
Ni/CaO	Incipient wetness method	Methane	600 °C, S/C=3	N/A	H ₂ = 80%	33
Ni/CaO-Al ₂ O ₃	Co-precipitation method	Ethanol	500 °C, S/C=4	10	N/A	39
Ni/Mg-HTlc	Co-precipitation method	Ethanol	300 °C, S/C=5	25	H ₂ = 90%	42
Ni/Cu-HTlc	Co-precipitation method	Ethanol	300 °C, S/C=5	25	H ₂ = 90%	42
K-Ni/Cu-HTlc	Wet impregnation	Ethanol	500 °C, S/C=10	N/A	H ₂ =99.8%	43

201

202 **HTlcs-based composites**

203 HTlcs sorbents are a good fit for SESR of ethanol because the reforming reactions
204 can take place at an intermediate temperature range ($< 500\text{ }^{\circ}\text{C}$) that is not detrimental to
205 the integrity of HTlcs' structure. Ethanol reforming requires high steam-to-carbon (S/C)
206 molar ratios to reduce carbon deposition and this is an energy intensive process. HTlcs
207 are regenerated when excess steam is supplied to rebuild the hydroxide structure.
208 However, an increased S/C ratio will lower the partial pressure of CO_2 produced in the
209 reactor. Partial pressure of CO_2 plays an important role in the chemisorption of CO_2 and
210 its decrease will adversely affect the performance of the sorbent. It is assumed that HTlcs
211 capture CO_2 *via* multilayer chemisorption, where multiple molecules of CO_2 can occupy a
212 single site forming a complex. Synthetic HTlcs offer versatility in the interlayer spacing
213 by tailored substitution of anions and cations.³¹ The alkalinity of HTlcs is a positive
214 attribute for a CO_2 sorbent, enhancing hydrogen selectivity and reducing carbon
215 deposition.⁴² HTlcs are suitable supports for catalysts too. Wu et al.⁴⁴ conducted a
216 simulated study on Ni/HTlcs ($\text{Mg}^{2+}/\text{Al}^{3+}$ based HTlc) in SESR of ethanol under different
217 conditions to predict the performance of the materials. The optimum reaction conditions
218 were found to be a molar ratio of steam/ethanol = 10 and weight to active metal/molar
219 flow rate of ethanol = $0.25\text{ kg h}^{-1}\text{ mol}^{-1}$ at $500\text{ }^{\circ}\text{C}$. Under these conditions hydrogen
220 concentrations remained over 95% for first 500 s, reaching as high as 99%. Dewoolkar
221 and Vaidya⁴² prepared synthetic Ni/HTlcs by cationic modification for SESR of ethanol.
222 The metal components for cationic substitution were Mg, Ca, Cu and Zn with Cu and Mg
223 shown to be most suitable as they displayed prolonged stability (over 25 cycles), highest
224 chemisorption capacity (of $0.74\text{ mol-CO}_2\text{ kg-sorbent}^{-1}$ and $0.42\text{ mol-CO}_2\text{ kg-sorbent}^{-1}$ for
225 Cu and Mg based material, respectively), longest breakthrough time (25 min and 15 min

226 for Cu and Mg based material, respectively), and high hydrogen purity (95.1 mol % and
227 89.3 mol % for Cu and Mg based material, respectively) In a comparison between a
228 synthesized bifunctional material (Ni/HTlc) and a conventionally mixed Ni/Al₂O₃ with
229 HTlc,³¹ the bifunctional material delivered 90% CH₄ conversion, 96.6% H₂ purity at 400
230 °C, 0.9 mol-CO₂ kg-sorbent⁻¹ chemisorption, and 15 min breakthrough time in reactor.
231 The results from bifunctional material were better than the results produced by
232 conventional mixture of the phases which amounted to H₂ purity <80%, as well as lower
233 chemisorption capacity and breakthrough time (0.3 mol-CO₂ kg-sorbent⁻¹ and 5 min,
234 respectively). Cunha et al. explored Cu based bifunctional material⁴⁵ and K-promoted Ni-
235 Cu bifunctional material⁴³ for ethanol SESR and obtained results showing > 90% H₂
236 stream for Cu/Mg-Al and 99.8% H₂ stream for K-Ni-Cu/HTlc.

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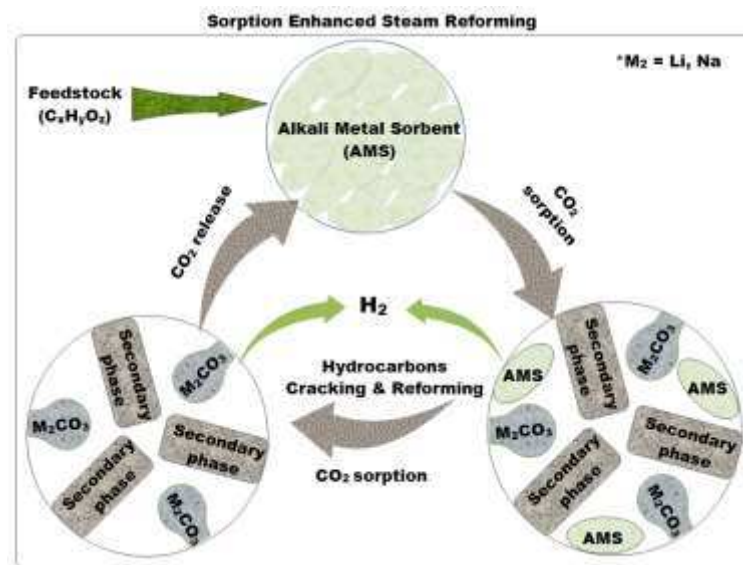
238 **3. ALKALI METAL CERAMICS: NON-HYBRID BIFUNCTIONAL**

239 **MATERIALS**

240 So far the choice of material has been limited to the hybrid-type materials and results
241 have shown an improvement over physical mixing of separate materials, a clear
242 demonstration of the merits of bifunctional materials. CaO-based composites are always
243 in need of an inert support to overcome poor mechanical durability. The support also
244 provides additional surface area to disperse catalyst, fulfilling a dual role. But even with
245 the addition of support, CaO based materials are prone to losing performance over time.
246 HTlcs-based materials are a good match for SESR of ethanol but they are limited by
247 rapid deterioration at high temperatures (> 500 °C) ruling them out as materials for SESR
248 of methane or biomass. Alkali metal ceramics are attractive as next-generation

249 compounds for bifunctional materials at temperatures > 500 °C because they exhibit
250 mechanical stability, CO₂ selectivity and recyclability in these conditions Unlike CaO-
251 based sorbents, alkali metal ceramics do not require additional refractory support for
252 mechanical stability in high-temperature scenarios. Furthermore, bringing catalyst and
253 sorbent sites closer will improve the kinetics of ceramics, which remain a frailty in the
254 otherwise attractive profile of the materials. More importantly, the alkali carbonate
255 products produced on CO₂ chemisorption can provide an intrinsic catalyst role, making
256 the ceramics exempt from further engineering to introducing additional catalysts.

257 **Figure 3** illustrates a hypothetical route of progress in bifunctional alkali metal
258 catalyst/sorbent during SESR. At the start, alkali metal sorbents absorb CO₂ generated by
259 degradation of feedstock as a function of high-temperatures. The catalytic alkali metal
260 carbonate sites are yielded as a result of CO₂ capture along with secondary phases which
261 may be metal oxides or derivative phases of alkali metal ceramics depending upon the
262 sorbents. The freshly formed catalyst functions to crack and reform the hydrocarbons
263 producing more CO₂ and the desired H₂, initiating simultaneous chemisorption and
264 reforming. The process continues until all the sorbent sites on the material have been
265 turned into catalyst sites and chemisorption cannot take place any longer. The ability of
266 alkali metal ceramics to release CO₂ makes the process cyclic and alkali metal carbonates
267 show good ability for tar cracking and degradation of biomass as discussed in Section 5.
268 Multiple pathways to synthesize alkali metal ceramics offer versatility in production and
269 control over morphology which will be valuable in developing bifunctional material
270 performance.



271

272 **Figure 3.** A hypothetical progression of alkali metal bifunctional catalyst/sorbent. The
 273 material starts as sorbent (top) and attains catalytic functionality after chemisorbing CO₂
 274 (bottom right), which makes it capable of chemisorption and reforming simultaneously.

275 The material becomes a catalyst after all chemisorption sites are filled (bottom left).

276 Alkali metal zirconates (Li₂ZrO₃, Li₆Zr₂O₇, Li₈ZrO₆ and Na₂ZrO₃) fit well with the
 277 requirements of a solid sorbent candidate and Li₂ZrO₃, in particular, has been extensively
 278 studied for this purpose.^{25-28, 46-54} Zirconates of other alkali metals have not been
 279 identified as CO₂ acceptors, but Duan⁵⁵ carried out a first-principle density functional
 280 theory study of K₂ZrO₃ as a CO₂ sorbent to suggest that K₂ZrO₃ requires too high a
 281 temperature (> 1000 °C) to regenerate economically. Li₂ZrO₃ and Na₂ZrO₃ display
 282 excellent selectivity towards CO₂ in a gas mixture, which makes them applicable to
 283 carbon capture from a flue gas stream where CO₂ concentrations can be less than 15%.
 284 Higher Li/Zr molar ratios lead to the formation of Li₆Zr₂O₇ and Li₈ZrO₆, respectively.⁵⁶
 285 ⁵⁷Li₆Zr₂O₇ captures over four times more CO₂ than Li₂ZrO₃ in the temperature range of

286 450-600 °C, owing to the greater Li content. However, after the lithium at the surface is
287 reacted, the kinetics of chemisorption slow. $\text{Li}_6\text{Zr}_2\text{O}_7$ requires CO_2 desorption
288 temperatures of over 800 °C and gradually loses its chemisorption potency during multi-
289 cycle operation due to sintering and sublimation of Li_2O .⁵⁷ Li_8ZrO_6 is not a widely
290 studied material owing to its difficult synthesis procedure.⁵⁸ Li_8ZrO_6 exhibits low uptakes
291 of CO_2 at temperatures lower than 700 °C capturing 7 mmol- CO_2 g-sorbent⁻¹ in 2 hours.⁵⁷
292 But upon reaching the melting point of Li_2CO_3 (710 °C or above) the chemisorption rate
293 significantly increases, and the sorbent can capture up to 12.2 mmol- CO_2 g-sorbent⁻¹
294 (53.98 wt. %) under 30 min.^{59, 60} Similar to the case of $\text{Li}_6\text{Zr}_2\text{O}_7$, the performance of
295 Li_8ZrO_6 declines over multiple chemisorption/desorption cycles due to sublimation of
296 Li_2O .

297 Alkali metal silicates (Li_4SiO_4 , Li_8SiO_8 , Li_2SiO_3 and Na_2SiO_3) are another widely
298 explored set of CO_2 sorbents. Among them Li_4SiO_4 is the promising alkali metal silicate
299 sorbent possessing the ability to trap CO_2 in the range of 450-650 °C and having a high
300 CO_2 holding capacity (up to 36.7 wt. % or 8.34 mmol- CO_2 g-sorbent⁻¹). Li_4SiO_4 has
301 exhibited fast chemisorption kinetics, good mechanical stability under multiple cycles,
302 and a low regeneration temperature range of 750-800 °C.^{20, 61} The chemisorption
303 performance of Li_4SiO_4 falls between Li_2ZrO_3 and Na_2ZrO_3 , but Li_4SiO_4 can be
304 synthesized from cheaper silicate precursors and it shares the same high temperature
305 performance qualities that make alkali metal zirconates desirable CO_2 sorbents.⁶² It has
306 been noted that prior to utilization of Li_4SiO_4 in industrial applications for CO_2 capture,
307 the flue gas must be desulfurized as Li_4SiO_4 can irreversibly react with SO_2 to form
308 Li_2SO_4 .⁶³ Li_8SiO_6 is a recently reported sorbent, formed as a result of high Li/Si ratio.⁶⁴

309 Li_8SiO_6 may produce different secondary phases while reacting with CO_2 depending upon
310 its quantity. However it requires a desorption temperature of $830\text{ }^\circ\text{C}$, which will make the
311 material vulnerable to Li_2O sublimation.⁶⁵ Alkali metal metasilicates (Li_2SiO_3 and
312 Na_2SiO_3) can capture a minute amount of CO_2 ($> 0.1\text{ mmol-CO}_2\text{ g-sorbent}^{-1}$) with only
313 superficial reaction at relatively low temperature of $130\text{ }^\circ\text{C}$ or below.^{66,67} Study of
314 Na_2SiO_3 showed that the packed structure of sorbent makes it unfavorable for CO_2
315 diffusion⁶⁷

316 Apart from the above mentioned zirconates and silicates, researchers have looked into
317 other alkali metal compounds. Lithium aluminate (Li_5AlO_4) is a lightweight polymorphic
318 ceramic possessing a very high ability to capture CO_2 at $19.8\text{ mmol-CO}_2\text{ g-sorbent}^{-1}$ (87.5
319 $\text{wt.}\%$).²⁰ Along with promising chemisorption capacity, Li_5AlO_4 has also displayed good
320 kinetics of chemisorption, however under multicycle operation, chemisorption capacity
321 of the lithium aluminates decayed.⁶⁸ Lithium cuprate (Li_2CuO_2) is another promising
322 lightweight compound that has exhibited an ability to capture CO_2 at a wider range of
323 temperatures than other alkali metal ceramics ($120\text{-}690\text{ }^\circ\text{C}$) and can remain an effective
324 CO_2 sorbent at low partial pressures of CO_2 .^{69, 70} Li_2CuO_2 is yet to be investigated under a
325 multicycle CO_2 capture and release process. Alkali metal titanates (Li_4TiO_4 and Na_2TiO_3)
326 can also capture CO_2 under a wide range of temperatures, $250\text{-}800\text{ }^\circ\text{C}$ but regenerate
327 poorly.^{71, 72} Lithium ferrite was tested and found to have insufficient capture capacity for
328 practical use as a CO_2 sorbent.⁷³

329 To summarize, alkali metal ceramics possess a number of compounds that can
330 actively trap CO_2 over a wide range of temperatures (**Table 2**). Li_5AlO_4 , and Li_2CuO_2
331 have shown promising results but they are in need of further studies with regards to their

332 regeneration and stability in a prolonged multi-cycle process. Li_2ZrO_3 , Li_4SiO_4 and
 333 Na_2ZrO_3 are the three sorbents that have been most scrutinized and display promising
 334 performance indicators for a CO_2 sorbent.

335

336 **Table 2.** Characteristic performance of alkali metal materials.

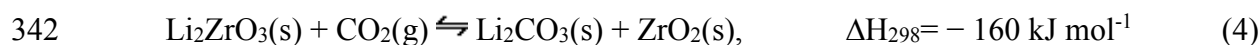
Material	Chemisorption Temperature (°C)	Regeneration Temperature (°C)	Max. CO_2 chemisorption (mmol g-sorbent ⁻¹)	Notes
Li_4SiO_4	450-650	750-850	8.34	Qualified sorbent for bifunctional material
Li_2ZrO_3	400-600	600-800	6.52	Durable sorbent with weak kinetics
Li_2CuO_2	120-690	700-840	9.13	Promising sorbent. Needs further research with regards to durability.
Li_5AlO_4	250-800	750	19.88	High chemisorption capacity, decent kinetics, lightweight material, Weak durability
LiFeO_2	350-500	600-700	5.27	Weak kinetics
Li_4TiO_4	250-800	> 1000	9.54	High desorption temperature
Li_8SiO_8	300-700	830	16.7	High desorption temperature makes the material vulnerable to Li_2O sublimation
Na_2ZrO_3	500-700	800	5.4	Qualified sorbent for bifunctional material
Na_2SiO_3	30-130	--	8.2	Only Superficial reaction registered.
Na_2TiO_3	250-780	700-800	7.04	Poor regeneration.

337

338 4. SYNTHESIS OF ALKALI METAL CERAMIC SORBENTS

339 Li_2ZrO_3

340 Li_2ZrO_3 was reported as having the ability to capture CO_2 at temperatures of 450-550
 341 °C by Nakagawa and Ohashi (Eqn. 4).²⁰

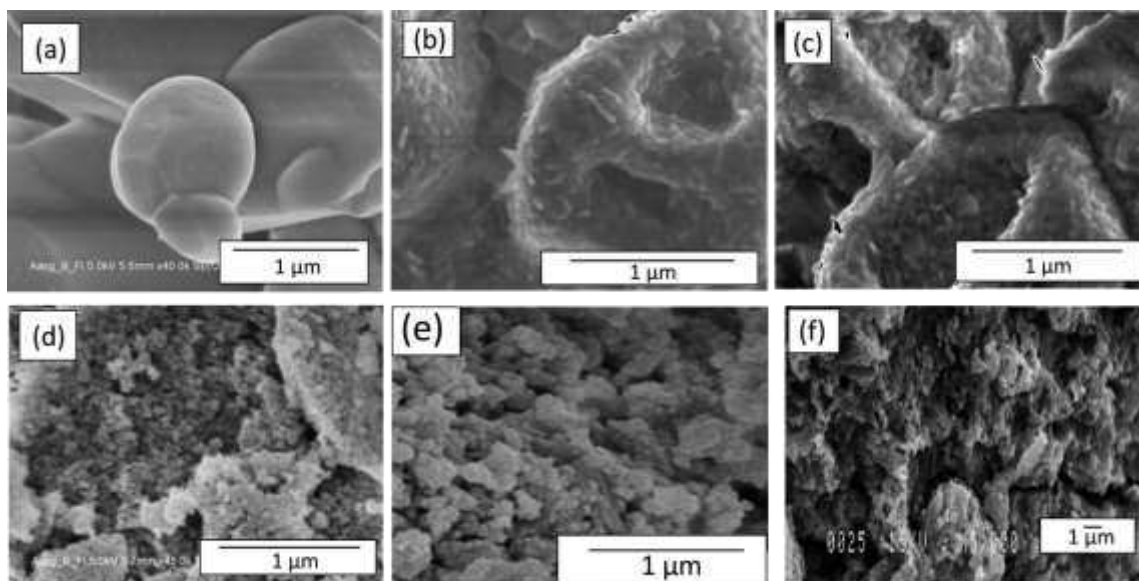


343 Li_2ZrO_3 has a theoretical maximum CO_2 chemisorption capacity of 6.5 mmol- CO_2 g-
344 sorbent⁻¹ (28.7 wt. %). It captures CO_2 in the temperature range of 450-650 °C and
345 regenerates at a relatively low temperature of 700 °C. After trapping 1 mol of CO_2 , the
346 volume of the material increases to 134%.^{46, 48} Generally, Li_2ZrO_3 is found in two phases:
347 tetragonal (t- Li_2ZrO_3) and monoclinic (m- Li_2ZrO_3). t- Li_2ZrO_3 displays better stability,
348 faster kinetics, and higher chemisorption capacity than m- Li_2ZrO_3 .⁴⁸ The performance of
349 Li_2ZrO_3 is highly dependent on the structure of the synthesized material where reduced
350 particle size, less particle agglomeration and phase purity result in increased CO_2 capture
351 efficiency, higher chemisorption rates, increased capacity and better cycle stability.
352 Compared to solid-state methods, soft-chemistry approaches can produce purer and
353 smaller sized t- Li_2ZrO_3 powder at a low synthesis temperature of 600 °C with improved
354 performance.⁷⁴ Studies suggested that at a calcination temperature of 400 °C, the
355 formation of Li_2ZrO_3 was incomplete as ZrO_2 was present alongside Li_2CO_3 , whereas at
356 calcination temperature of 800 °C the m- Li_2ZrO_3 was present with larger sized
357 particles.^{49, 74, 75} Soft-chemistry methods also bring forth increased CO_2 capture
358 efficiency, higher chemisorption rates, increased capacity and better cycle stability into
359 the materials.^{74, 76, 77}

360 Ensuing research has explored synthesis pathways to produce powdered t- Li_2ZrO_3
361 possessing smaller particle size and minimal agglomeration.^{74, 76, 78} Xiao et al.⁷⁶ reported
362 different preparation methods of the same nominal powder composition produced
363 different particle properties, leading to varied CO_2 chemisorption performances. The
364 authors also suggested that soft-chemistry methods produce heterogeneous ion

365 distributions resulting in uneven spatial dispersal of Li and Zr species which leads to
366 reduced CO₂ capture performance. Radfarnia et al.⁷⁸ used sonication to improve particle
367 stability during multi-cycle chemisorption/desorption. In a study by Kang et al.,⁷⁹
368 synthesis of Li₂ZrO₃ with Li₆Zr₂O₇ phases was recorded following a biomimetic solution
369 route using metal containing complexes of polymeric precursors. Khokhani et al.⁸⁰
370 synthesized Na doped Li₂ZrO₃ by citrate based sol-gel processing, using CTAB as a
371 surfactant and the product again showed high chemisorption capacity of 4.5 mmol-CO₂
372 g-sorbent⁻¹ under 20 min at 650 °C and stable cyclic ability over 5 cycles. The
373 hydrothermal route has also been explored to synthesize t-Li₂ZrO₃ nanotubes with
374 enhanced CO₂ chemisorption properties over Li₂ZrO₃ nanoparticles.^{58,81} **Figure 4** shows
375 SEM images of Li₂ZrO₃ particles synthesized by different methods.

376



377

378 **Figure 4.** SEM images of Li₂ZrO₃ samples prepared by different methods: (a) solid
379 state reaction,⁸² (b) soft-chemistry method with spray drying,⁷⁴ (c) soft-chemistry method
380 with freeze drying,⁷⁵ (d) co-precipitation method⁸² (e) sol-gel method⁷⁶ and (f) surfactant

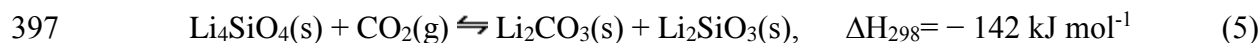
381 template with sonication assistance method.⁷⁸ Soft-chemistry, sol-gel method and co-
382 precipitation method give fine control over morphology yielding smaller particle size and
383 greater surface area which are of vital importance in helping sorbent capture CO₂ to their
384 fullest potential.

385

386 High CO₂ concentrations have proven to be beneficial for chemisorption in Li₂ZrO₃,
387 while partial pressures <0.3 bar slow down the diffusion of ions and hinder the
388 chemisorption.⁷⁸ Halabi et al.⁸³ studied Li₂ZrO₃ for chemisorption-enhanced auto-thermal
389 steam reforming of methane. Li₂ZrO₃ converted 99.5% of the initial methane and yielded
390 hydrogen of 99.5% purity at a temperature as low as 500 °C and pressure as low as 4.47
391 bar. The slow kinetics of chemisorption were attributed to a high concentration of
392 impurities (CO₂ and CO) in the gas effluent before the breakthrough into the transient
393 chemisorption-enhanced regime.

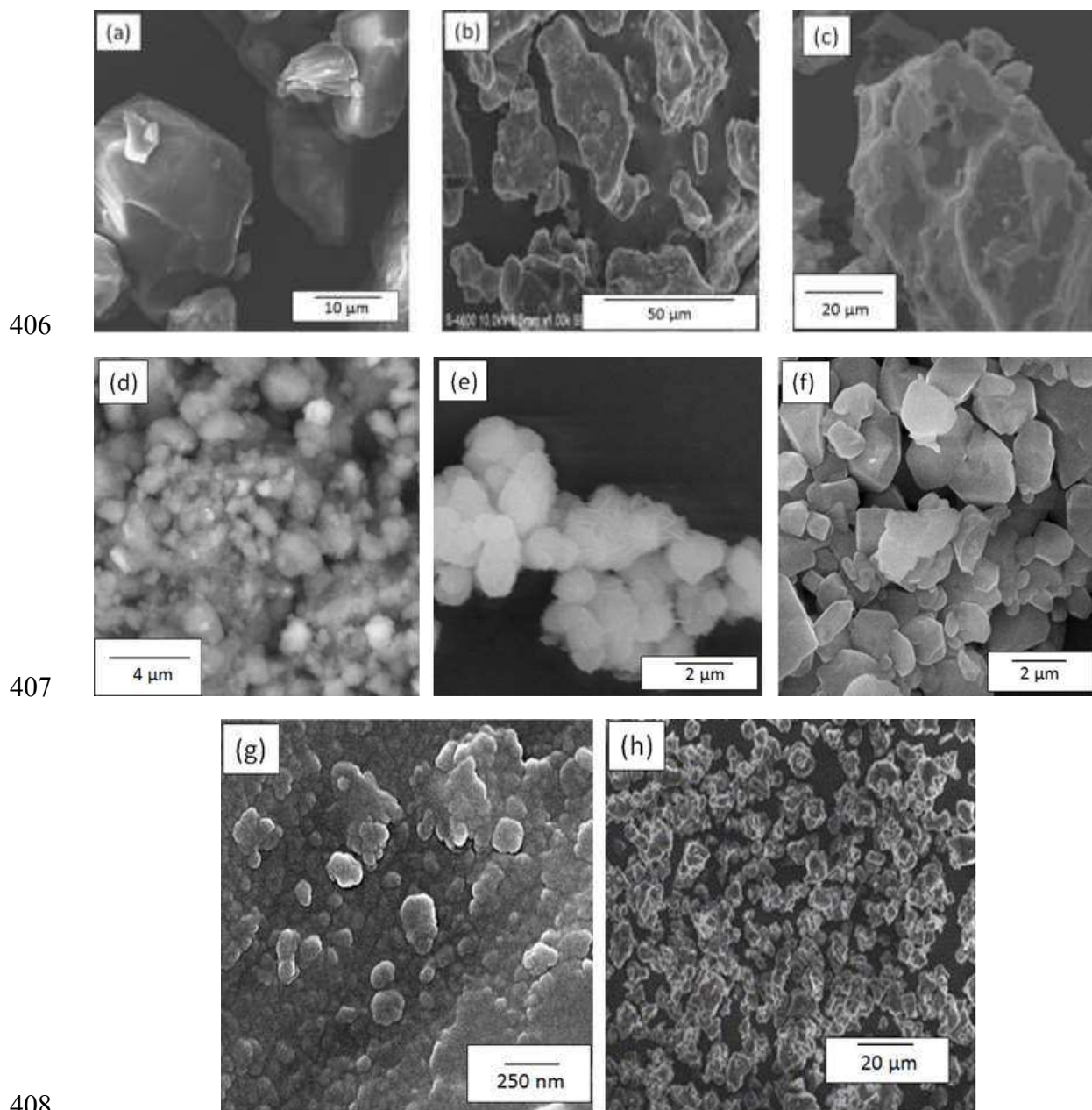
394 **Li₄SiO₄**

395 Li₄SiO₄ is a promising alkali metal ceramic sorbent and its reported fast
396 chemisorption kinetics have been subject to wide research interest (Eqn. 6).^{61,66}



398 Li₄SiO₄ can trap CO₂ up to 30 times faster than Li₂ZrO₃ at 500 °C (20 % CO₂
399 concentration) i.e. > 50 mg-CO₂ g-sorbent⁻¹. In the same experiment Li₄SiO₄ was able to
400 capture > 5.6 mmol-CO₂ g-sorbent⁻¹ in a CO₂ concentration of 2% in 50 min.⁴⁹ A
401 secondary phase of Li₂SiO₃ improves the kinetics of Li₄SiO₄, enhancing the diffusivity
402 Li⁺ and O²⁻ ions even at room temperature.⁸⁴ Similar to Li₂ZrO₃ particle size is a very

403 important factor in the performance of the material,⁸⁵ as fine grain size results in higher
404 surface area where Li atoms can reside. **Figure 5** summarizes different routes to
405 synthesize Li_4SiO_4 and how they affect particle morphology.



409 **Figure 5.** SEM images of Li_4SiO_4 samples prepared by different methods: (a) solid state
410 reaction,⁸⁵ (b) solid state reaction (rice ash husk sample),⁸⁶ (c) solid state reaction sample

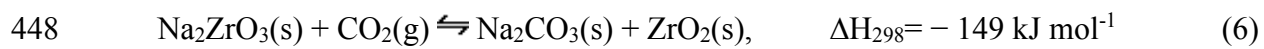
411 before ball-milling,⁸⁷ (d) solid state reaction sample after ball-milling,⁸⁷ (e) precipitation
412 method,⁸⁵ (f) sol-gel method,⁸⁵ (g) water-based sol-gel method,⁸⁸ and (h) impregnated
413 suspension method.⁸⁹ Li_4SiO_4 particle sizes are generally found to be larger than its
414 zirconates counterpart. Sol-gel method offers a desirable mesoporous structure.

415 Silicates are generally cheaper and of lower density than zirconates and one of the
416 benefits of Li_4SiO_4 is that it can be produced from waste and existing minerals. Li_4SiO_4
417 has been synthesized from fly-ash, rice husk and diatomite, and the products have
418 exhibited desirable chemisorption properties due to the high surface area and pore
419 volume of the precursors.^{86, 90-93} Wang et al.⁸⁶ used rice husk ash as a silica precursor for
420 Li_4SiO_4 synthesis. The synthesized sample displayed superior uptake performance over
421 15 cycles because the presence of impurity metals in the rice husk ash caused improved
422 reaction kinetics with CO_2 in comparison with pure Li_4SiO_4 . Olivares-Marin et al.⁹²
423 developed Li_4SiO_4 samples using fly-ash collected from power plants. The authors added
424 K_2CO_3 to the samples in varying ratios and results indicated 600 °C and 40 mol % K_2CO_3
425 to be optimum capture conditions under which samples were able to trap 101 mg- CO_2 g-
426 sorbent⁻¹ within 15 minutes. Yang et al.⁹⁴ synthesized Li_4SiO_4 using SiO_2 colloidal
427 solutions and organic lithium precursors *via* impregnated suspension method. At the end
428 of 40 cycles of CO_2 capture and release, the performed chemisorption capacity of
429 sorbents increased from 3.2 to 5.8 mmol- CO_2 g-sorbent⁻¹. The authors attributed this
430 improvement to the micron-sized pores which were produced during CO_2 released.
431 Consequently, the sorbents had an increased area of contact to chemisorb CO_2 . Wang et
432 al.⁹⁵ employed carbon coating with sol-gel method to restrict particle growth and create a
433 more porous structure during calcination. The material produced by sol-gel method is

434 required to undergo calcination to obtain Li_4SiO_4 phase, like any other synthesis method.
435 However, at high temperatures, the material is susceptible to undesired particle growth,
436 as well as, morphology deterioration. Carbon coating can act as an *in-situ* barrier for
437 particle growth and release of gases during carbonization of organic compounds
438 contribute in creating a porous structure. The resulting material was able to chemisorb 7.4
439 $\text{mmol-CO}_2 \text{ g-sorbent}^{-1}$ (32.8 wt. %) with improved chemisorption kinetics and better
440 stability over 20 cycles. In another study by Wang et al.⁹⁶ the authors used gluconic acid-
441 based carbon coating to acquired Li_4SiO_4 . With addition of glucoinc acid carbon coating,
442 the sorbent nanoparticles were formed in a hollow spherical shape with small grain size.
443 The results of CO_2 chemisorption test displayed that the sorbent was able to maintain it
444 chemisorption capacity of approximately of $7.7 \text{ mmol-CO}_2 \text{ g-sorbent}^{-1}$ for 10 cycles.

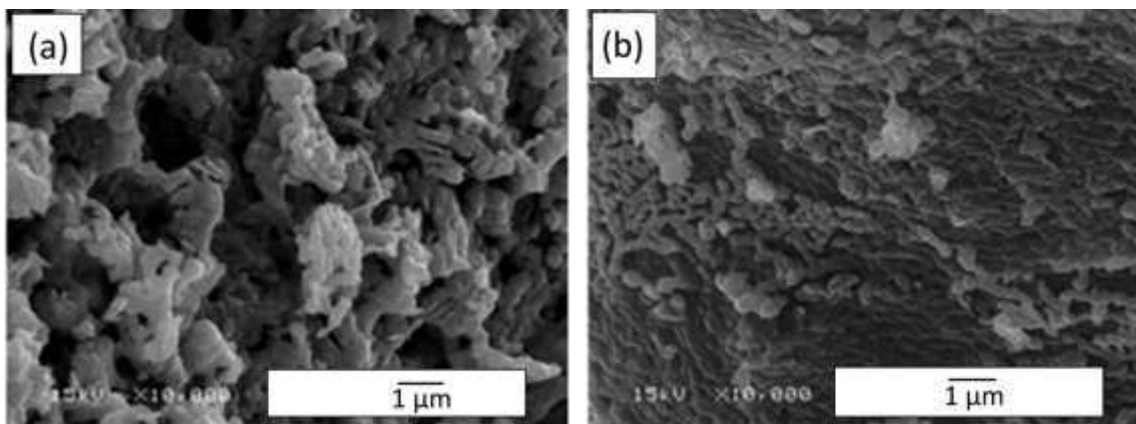
445 **Na_2ZrO_3**

446 In comparison to Li_2ZrO_3 and Li_4SiO_4 , Na_2ZrO_3 is a more capable CO_2 sorbent having
447 the fastest chemisorption kinetics among three (Eqn. 5).^{46, 97}



449 Na_2ZrO_3 has a theoretical maximum CO_2 uptake capacity of $5.4 \text{ mmol-CO}_2 \text{ g-sorbent}^{-1}$
450 (23.8 wt. %), lower than both Li_2ZrO_3 and Li_4SiO_4 . Na_2ZrO_3 can capture CO_2 over a
451 wide range of temperature, from room temperature to $700 \text{ }^\circ\text{C}$ and releases it at
452 temperature of $800 \text{ }^\circ\text{C}$ and above. Na_2ZrO_3 has a distinct layered structure where sodium
453 atoms are located among $(\text{ZrO}_3)^{2-}$ layers, favoring swift Na^+ ion diffusion during the bulk
454 reaction phase.^{51, 98} Na_2ZrO_3 is found in two phases, namely, monoclinic and hexagonal.
455 The monoclinic phase is more reactive towards CO_2 than the hexagonal phase, owing to

456 its higher surface reactivity, stability during multi-cycle chemisorption, and effective
457 performance at low CO₂ partial pressure.⁵⁰ Soft-chemistry methods provide a purer phase
458 of Na₂ZrO₃ when the heat treatment of the sample is done *via* a two-step calcination
459 process (**Figure 6**). The selection of Na and Zr precursor compounds also has a vital
460 effect on the final morphology of the product.⁹⁹ Zhao et al.^{50, 100} selected a soft-chemistry
461 route and utilized sodium citrate and zirconoxy nitrate as sources of Na and Zr,
462 respectively. The precursors formed NaNO₃ which has a low melting point (308 °C) and
463 that promotes diffusion of Na⁺ ions throughout ZrO₂. In contrast, when zirconoxy
464 chloride and sodium acetate were used as precursors, Na₂CO₃ was formed within a
465 zirconia complex. Na₂CO₃ has a high melting point (851 °C) and subsequently does not
466 support diffusion of Na⁺ ions as readily, ultimately hindering the formation of Na₂ZrO₃.



467
468 **Figure 6.** Na₂ZrO₃ samples prepared by soft-chemistry method⁵⁰ with (a) two-step
469 calcination, and (b) one-step calcination. As it can be seen from SEM images above two-
470 step approach produces a porous structure which can aid in diffusion of CO₂.

471

472 The CO₂ trapped at lower temperatures gets released at 800 °C however, the
473 desorption kinetics of Na₂ZrO₃ are slower than Li₂ZrO₃.⁵⁵ The representative synthesis

474 methods of different alkali metal ceramics and the resulting phases produced are
 475 presented in **Table 3**. There is clear evidence of increased surface area after improvement
 476 in synthesis routes.^{78, 101}

477

478 **Table 3.** Various synthesis methods for producing alkali metal zirconates and the effects
 479 on final composition.

Material	Method	Precursors	Phase	Particle size	Specific surface area (m ² g ⁻¹)	Refs.
Li ₂ ZrO ₃	Solid state reaction	Zirconyl nitrate, lithium acetate	m-Li ₂ ZrO ₃	–	1	101
Li ₂ ZrO ₃	Soft-Chemistry route	Zirconyl nitrate, lithium Acetate	t- Li ₂ ZrO ₃	13 nm	5	75
Li ₂ ZrO ₃	Soft-chemistry route	Zirconyl nitrate, lithium acetate	t- Li ₂ ZrO ₃	14 nm	2	102
Na-Li ₂ ZrO ₃	Sol-gel	Lithium carbonate, zirconium oxychloride, CTAB, citric acid, sodium carbonate	m-Li ₂ ZrO ₃	12 nm	–	80
Li ₂ ZrO ₃	Citrate sol-gel	Zirconium(IV) oxynitrate hydrate, Lithium Nitrate , Citrate Acid, Urea	t- Li ₂ ZrO ₃	17 nm	–	76
Li ₂ ZrO ₃	Surfactant-template/ultrasound assisted method	Zirconoxy nitrate, lithium acetate (CTAB as templates)	t- Li ₂ ZrO ₃	20 nm	12	78
Li ₂ ZrO ₃	Nanotube arrays	Zirconium foils, Lithium hydroxide	t- Li ₂ ZrO ₃	–	57.9	58
Li ₂ ZrO ₃	Liquid co-precipitation	Zirconium oxynitrate, lithium nitrate	t- Li ₂ ZrO ₃	5 nm	–	82
Li ₄ SiO ₄	Solid state reaction	Lithium carbonate, silicon dioxide	–	36 μm	–	85
Li ₄ SiO ₄	Solid state reaction	Lithium carbonate, Si - Rice ash husk	–	16 μm	6.2	86

Li_4SiO_4	Solid state reaction	(water rinsed) Lithium carbonate, Si - Rice ash husk (acid rinsed)	–	45 μm	4.6	86
Li_4SiO_4	Mechanical milling technique	Lithium hydroxide, silicon dioxide	–	1 – 3 μm	4.9	87
Li_4SiO_4	Precipitation method	Lithium acetate, tetraethyl orthosilicate	–	3 μm	–	85
Li_4SiO_4	Sol-gel method	Lithium hydroxide, Silicon dioxide	–	100 nm	–	88
Li_4SiO_4	Sol-gel method with carbon coating	Citric acid, lithium hydroxide, silicon dioxide	–	–	12.9	95
Li_4SiO_4	Impregnated suspension method	Lithium nitrate, silicon dioxide	–	–	> 1	89
Li_4SiO_4	Impregnated suspension method	Lithium lactate, silicon dioxide	–	1-6 nm	2.09	94
Li_4SiO_4	Impregnated suspension method	Lithium acetate dehydrate, silicon dioxide	–	1-6 nm	1.65	94
Na_2ZrO_3	Solid state reaction	Sodium carbonate, zirconium oxide	m- Na_2ZrO_3	150~400 nm	3.6	53
K- Na_2ZrO_3	Solid state reaction	Sodium carbonate, zirconium oxide, potassium carbonate	m- Na_2ZrO_3	500~800 nm	1.1	103
Na_2ZrO_3	Soft-chemistry route	Sodium Citrate, Zirconium(IV) oxynitrate hydrate	m- Na_2ZrO_3	30 nm	4	50

480 5. USE OF ALKALI METALS IN CATALYSIS

481 The evidence of catalytic activity of Na_2ZrO_3 was reported by Alcantar-Vazquez et
482 al.,²¹ where CO was catalytically oxidized into CO_2 and chemisorbed at $T \geq 200$ °C with
483 the processes apparently taking place simultaneously. Li_2CuO_2 ¹⁰⁴, NaCoO_2 ¹⁰⁵ and
484 Li_2ZrO_3 ¹⁰⁶ were also reported to perform catalytic CO oxidation to CO_2 and subsequent
485 chemisorption of CO_2 . The CO- CO_2 conversion in Li_2CuO_2 and NaCoO_2 follows a

486 double reaction Mars-van Krevelen mechanism.^{104, 105} A study on CO oxidation ability
487 of Li_2ZrO_3 and Na_2ZrO_3 reported that Na_2ZrO_3 performed better as a CO Oxidation
488 catalyst than Li_2ZrO_3 , achieving 100% CO conversion while Li_2ZrO_3 was able to only
489 convert 35% CO under similar experimental conditions (CO conversion isotherm were
490 conducted at temperature range of 30-850 °C with 5 vol.% CO and 5 vol.% O_2). Results
491 showed that a lower concentration of O_2 (3 vol.%) is unable to achieve full CO
492 conversion, which implies that in case of Na_2ZrO_3 the presence of oxygen for CO
493 conversion is necessary. As a contrast, CO conversion with NaCoO_2 was thought to be
494 aided by oxygen present in the structure of the NaCoO_2 . Furthermore, a comparison
495 between typical $\text{Na}_2\text{ZrO}_3\text{-CO}_2$ chemisorption process and $\text{Na}_2\text{ZrO}_3\text{-CO-O}_2$ chemisorption
496 system shows that the former system displays better chemisorption performance than
497 latter. $\text{Na}_2\text{ZrO}_3\text{-CO-O}_2$ system cannot completely chemisorb CO_2 that is produced by
498 catalysis due to low CO_2 concentration and kinetics of CO oxidation.¹⁰⁶ Mendoza-Nieto
499 et al.¹⁰⁷ reported that carbonated Na_2ZrO_3 having $\text{Na}_2\text{CO}_3\text{-ZrO}_2$ phase can reform
500 methane through dry reforming process to produce syngas ($\text{H}_2 + \text{CO}$). Role of carbonated
501 Na_2ZrO_3 is to supply CO_2 via desorption at high temperatures (> 750 °C) to initiate dry
502 reforming of methane and it may act as a catalyst for the reforming process.

503 Alkali metal carbonates have shown capacity of catalysis in CO_2 gasification and are
504 able to decrease the activation energies of CO_2 gasification. Their capacity of catalysis is
505 listed from weak to strong in the following order: $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$.¹⁰⁸ Alkali carbonates
506 have also exhibited catalysis activity on the steam gasification of bitumen coke. Alkali
507 metal carbonates Na_2CO_3 and K_2CO_3 along with KCl , CaCO_3 , CaO and MgO were tested
508 for steam gasification under temperature range of 600-800 °C. The carbonates displayed

509 the best results achieving near complete conversions for Na_2CO_3 , 95.6% and K_2CO_3 ,
510 99.3%. The carbonates were effective because they were mobile on the coke material. In
511 the resulting product stream, little trace of CO was found which suggested that carbonate
512 catalyst strongly promoted WGS reaction.¹⁰⁹ Alkali metal carbonates are able to catalyze
513 Boudouard reaction on coal char and graphite, although with different kinetic parameters
514 for each material.¹¹⁰ A study on catalytic effect on Li, Na and K carbonates on graphite in
515 the presence of water vapor showed that catalyzed reaction increased in the temperature
516 ranges of melting points carbonates.¹¹¹ Binary and ternary eutectic carbonate catalysts
517 have exhibited more catalytic activity than a single alkali carbonate could on coal char
518 samples. Similarly ternary eutectic carbonate catalyst is more reactive than a binary
519 eutectic carbonate catalyst. The lowered melting points of eutectic salts were believed to
520 be reason behind increased reactivity, as they enhanced the mobility of the catalyst
521 composite on the coal chars.^{112, 113}

522 Alkali metals are shown to be effective in tar removal during gasification of biomass.
523 Na and K carbonates within biomass show little or no carbon deactivation and slight
524 particle agglomeration. The method of catalyst addition to feedstock through dry mixing
525 or impregnation does not lend itself to recovery of the primary catalyst and does associate
526 with a high yield of ash content.⁸ Mudge, et al.²² have also shown potassium carbonate to
527 be an effective catalyst for conversion of wood into syngas.

528 Potassium and sodium are present in biomass and their presence significantly
529 influences the degradation temperature, degradation rate and the yield of products during
530 pyrolysis.²³ Smets, et al.¹¹⁴ used Na_2CO_3 as a primary catalyst along with $\gamma\text{-Al}_2\text{O}_3$ and
531 hexagonal zeolite surface modified to contain 5 angstrom pores (HZSM-5) as secondary

532 catalysts for slow pyrolysis of rapeseed cake. During pyrolysis, Na_2CO_3 converted fatty
533 acids into aliphatic hydrocarbons and reduced the organic compounds by 27.19 wt. %.
534 Na_2CO_3 ranked second among the three catalysts (highest yield was acquired with the use
535 of HZSM-5; 44.9 wt. %), however the product produced by Na_2CO_3 had the highest
536 calorific value of 36.8 MJ kg^{-1} . The presence of K_2CO_3 in the biochar for hydrothermal
537 gasification increases the gasification rate and hydrogen yield.¹¹⁵

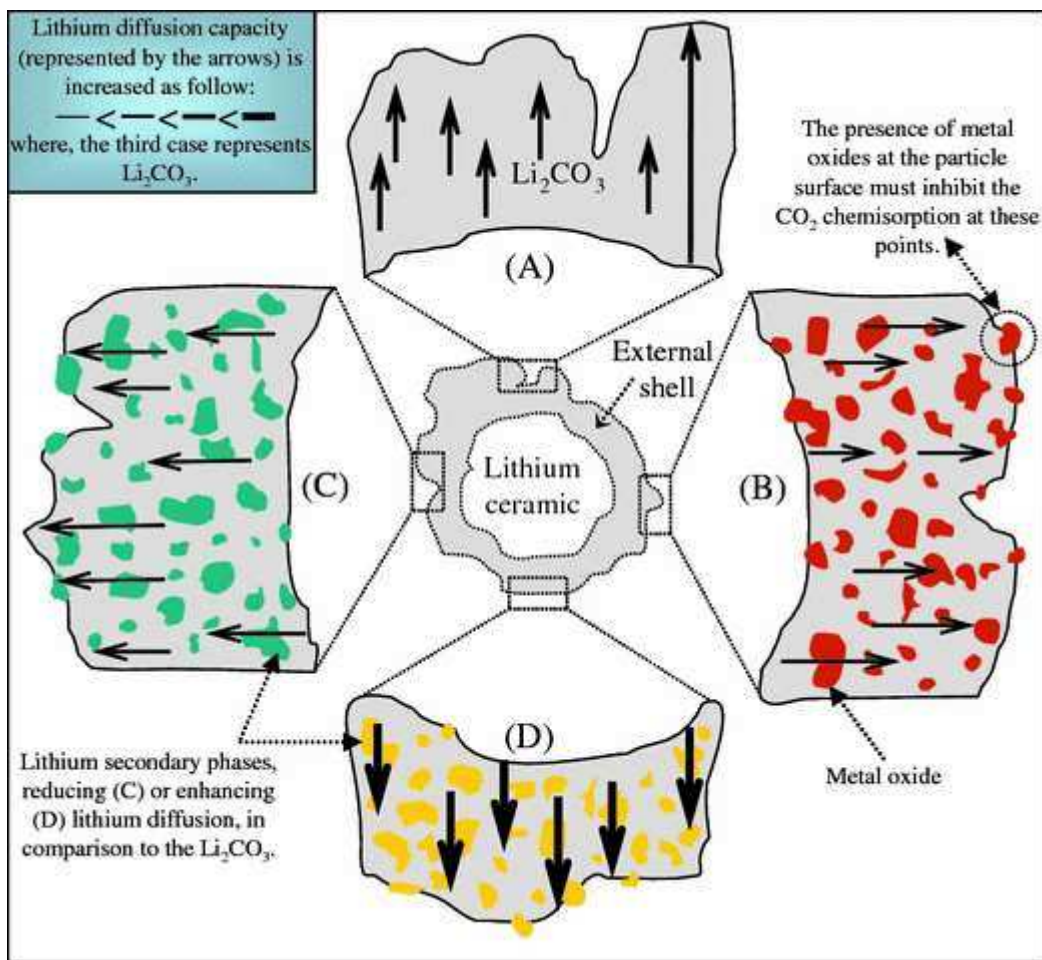
538 Alkali carbonates are also active in decomposition of alcohols and carboxylic acids,
539 and can catalyze the water-gas shift reaction in the presence of steam at $600 \text{ }^\circ\text{C}$ during
540 biomass gasification. However, under the same conditions, simple chains of
541 hydrocarbons remain unaffected, as do aldehydes and ketones. K_2CO_3 performed better
542 than Na_2CO_3 during catalytic reforming of methane at temperatures higher than $800 \text{ }^\circ\text{C}$.⁸
543 Alkali metal carbonates are also reported to be effective at converting condensed carbon
544 liquids into gases.¹¹⁶⁻¹¹⁸ Na_2ZrO_3 was used as a catalyst for transesterification of soybean
545 oil to produce biodiesel and the results displayed a 98.3% Fatty Acids Methyl Esters
546 (FAME) conversion rate.²⁴ These separate studies also indicate that the alkali metal
547 carbonates can efficiently be used for diverse catalytic chemical transformations.

548 **6. CHEMISORPTION OF CO_2 BY VARIOUS ALKALI METAL CERAMICS**

549 Interactions between alkali metal ceramics and CO_2 over the course of chemisorption
550 process have been extensively studied and consequently the mechanism of CO_2
551 chemisorption over alkali metal ceramics is well understood.^{119, 120} The basic nature of
552 alkali metal ceramics makes it possible for the chemisorption of CO_2 , which is acidic, to
553 occur on the material. CO_2 chemisorption can be distinguished into two steps. First is a

554 superficial reaction phase, where alkali metal available on the surface of the material
555 reacts with CO₂. Superficial reaction can occur at different temperatures for different
556 alkali compounds, i.e. Li₂ZrO₃ captures CO₂ above 400 °C, while Na₂ZrO₃ begins
557 superficial chemisorption at over 100 °C. The result is formation of alkali carbonate shell
558 along with unreacted metal oxide or secondary alkali metal phase.

559 Second is bulk diffusion phase which is initiated by diffusion of Li/Na and oxygen
560 atoms from the unreacted core to the surface to continue the chemisorption. The majority
561 of chemisorption taking place occurs via the bulk diffusion phase and diffusion of atoms
562 in this process is the rate limiting step of the reaction. Formation of Li/Na carbonate at
563 the surface of the sorbent cause vacancy formation which is filled by diffusion of Li/Na
564 and oxygen atoms from the interior of the material to the surface. Research has shown
565 that manufacturing vacancies causes improvement in the CO₂ chemisorption rates at low
566 temperatures.^{20, 121} Ortiz-Landeros et al.¹¹⁹ analyzed the effects of the presence of metal-
567 oxides and secondary lithium phases during chemisorption in lithium ceramics. Li₂CO₃
568 can exist along with a metal oxide phase (ZrO₂) or with a secondary lithium phase
569 (Li₂SiO₃) after chemisorption according to eqns. (4) and (5), respectively. The metal
570 oxide phase (ZrO₂) limits the chemisorption process by acting as a barrier for the
571 diffusion. On the other hand, the behavior of secondary lithium phase (Li₂SiO₃) in
572 diffusion process depends upon its lithium diffusion coefficient. If the lithium diffusion
573 coefficient is higher than Li₂CO₃'s, the CO₂ diffusion will be enhanced. A secondary
574 lithium phase with much lower diffusion coefficient than Li₂CO₃ can pose hindrance for
575 CO₂ diffusion (**Figure 7**).



576

577 **Figure. 7** The effects of metal-oxides secondary lithium phases during chemisorption
 578 process. (A) Lithium diffusion controlled by Li_2CO_3 only, (B) lithium diffusion being
 579 limited by metal oxide phase, (C) lithium diffusion being reduced by secondary lithium
 580 phase, having lesser lithium diffusion coefficient than Li_2CO_3 and (D) lithium diffusion
 581 being enhanced by secondary lithium phase having higher lithium diffusion coefficient
 582 than Li_2CO_3 ¹¹⁹

583 At the temperature range of room temperature to 300 °C, Na_2ZrO_3 is able to
 584 chemisorb CO_2 via superficial reaction. However, the capacity and rate of chemisorption
 585 is not uniform across the temperature range. The sorbent can capture 3.8 mmol- CO_2 g-
 586 sorbent in 5 hrs. at 150 °C, while at 250 °C the sorbent was able to capture 0.9 mmol- CO_2

587 g-sorbent. This phenomenon can be attributed to thermal shock due to rapid heating,
 588 which causes sintering that reduces the surface area⁵¹ or another possibility is desorption
 589 of CO₂ is activated and an equilibrium is reached between CO₂ chemisorption-desorption
 590 which results in lowered chemisorption.⁹⁸ A study by Martinez-dlCruz and Pfeiffer⁵³
 591 revealed that the sintering effect does exist however it is not caused by sintering of the
 592 ceramic itself but due to changes in textural properties of the external Na₂CO₃-ZrO₂ shell
 593 Na₂ZrO₃ possess higher kinetics of chemisorption than its lithium based counterparts.
 594 Not only does Na have higher reactivity towards CO₂, but Na₂ZrO₃ has a lamellar
 595 structure which enables better diffusion kinetics.¹²² The time required for desorption is
 596 dependent upon temperature; higher temperatures leads to faster desorption kinetics.⁷⁴
 597 Li₄SiO₄ displays superior regeneration ability than Li and Na zirconates, having faster
 598 desorption kinetics than Li₂ZrO₃ and lower regeneration temperature than Na₂ZrO₃.^{55, 97}
 599 Temperature also influences the equilibrium partial pressure of CO₂ for
 600 chemisorption/desorption. At low CO₂ concentrations, effective removal of CO₂ will be
 601 favorable under low temperatures.⁸² **Tables 4** summarizes the CO₂ capture performance
 602 under different operating conditions.

603

604 **Table 4.** Multi-cycle CO₂ chemisorption performance of alkali metal ceramics under
 605 varying conditions.

Material	Cycles	Chemisorption conditions	First cycle chemisorption (mmol-CO ₂ g-sorbent ⁻¹)	Last cycle chemisorption (mmol-CO ₂ g-sorbent ⁻¹)	Desorption conditions	Ref.
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Li ₂ ZrO ₃	3	550 °C, 100% CO ₂ , 200 ml min ⁻¹ , 20 min	5.9	5.9	690 °C, 100% N ₂ , 200 ml min ⁻¹ , 10 min	82
Li ₂ ZrO ₃	3	550 °C, 100% CO ₂ , 0.5 bar, 40 ml min ⁻¹ , 60 min	5.9 within 20 min	5.9	700 °C, 100% N ₂ , 40 ml min ⁻¹ , 60 min	76
K-Li ₂ ZrO ₃	4	550 °C, 0.25 bar, 40 ml min ⁻¹ , 60 min	5.1	5.1	675 °C, 100% N ₂ , 40 ml min ⁻¹ , 50 min	123
Li ₆ Zr ₂ O ₇	3	800 °C, 100% CO ₂ , 100 ml min ⁻¹ , 60 min	2.7	2	900 °C, 100% N ₂ , 100 ml min ⁻¹ , 60 min	57
Li ₈ ZrO ₆	4	800 °C, 100% CO ₂ , 100 ml min ⁻¹ , 30 min	7.9	5.3	900 °C, 100% N ₂ , 100 ml min ⁻¹ , 60 min	57
Li ₄ SiO ₄	5	700 °C, 100% CO ₂ , 60 min	7.9	7.9	850 °C, 100% N ₂ , 30 min	66
Li ₄ SiO ₄	50	600 °C, 20 % CO ₂ , 300 ml min ⁻¹ , 60 min	6.3	4.5	800 °C, 100 % N ₂ , 300 ml min ⁻¹ , 60 min	124
Li ₄ SiO ₄	5	650 °C, 100% CO ₂ , 60 min	5	5.7	750 °C, 100 % He, 30 min	121
Li ₄ SiO ₄	40	550 °C, 15% CO ₂ , 30 min	3.2	5.8	750 °C, 100 % N ₂ , 10 min	94
Li ₄ SiO ₄	20	680 °C, 100% CO ₂ , 15 min	7.4	7.4	800 °C, 100% N ₂ , 10 min	95
Li ₄ SiO ₄	10	665 °C, 100% CO ₂ , 30 min	7.7	7.6	800 °C, 100% N ₂ , 20 min	96
LiSiO ₄	15	650 °C, 100 % CO ₂ , 1 L min ⁻¹ , 15 min	5.5	5.0	800 °C, 100 % N ₂ , 1 L min ⁻¹ , 10 min	86
Li ₄ SiO ₄ - Diatomite	16	700 °C, 50% CO ₂ , 20 min	7.7	6.2	700 °C, 100% N ₂ , 30 min	90
Li ₄ SiO ₄ - Diatomite	10	700 °C, 50% CO ₂ , 20 min	7.8	7.3	700 °C, 100% N ₂ , 30 min	91
LiSiO ₄ – Rice Husk Ash	15	680 °C, 100 % CO ₂ , 1 L min ⁻¹ , 15 min	6.9	6.4	800 °C, 100 % N ₂ , 1 L min ⁻¹ , 10 min	93
LiSiO ₄ – Rice Husk Ash	15	650 °C, 100 % CO ₂ , 1 L min ⁻¹ , 15 min	7.7	7.5	800 °C, 100 % N ₂ , 1 L min ⁻¹ , 10 min	86
LiSiO ₄ – Rice Husk	15	650 °C, 100 % CO ₂ , 1 L min ⁻¹ , 15 min	7.7	7.5	800 °C, 100 % N ₂ , 1 L min ⁻¹ , 10	86

Ash					min	
Li _{3.7} Al _{0.1} SiO ₄	5	650 °C 100% CO ₂ , 60 min	5	3.1	750 °C, 100 % He, 30 min	121
Li ₄ SiO ₄ (2 % wt. Li ₂ ZrO ₃)	50	600 °C, 20 % CO ₂ , 300 ml min ⁻¹ , 60 min	6.3	4.8	800 °C, 100 % N ₂ , 300 ml min ⁻¹ , 60 min	124
Li ₄ SiO ₄ (5 % wt. Li ₂ ZrO ₃)	50	600 °C, 20 % CO ₂ , 300 ml min ⁻¹ , 60 min	6.3	5.8	800 °C, 100 % N ₂ , 300 ml min ⁻¹ , 60 min	124
Na ₂ ZrO ₃	20	500 °C , 100 %CO ₂ , 60 ml min ⁻¹ , 30 min	3.9	3.9	800 °C, 100% N ₂ , 60 ml min ⁻¹ , 30 min	54
Na ₂ ZrO ₃	20	550 °C , 100 %CO ₂ , 60 ml min ⁻¹ , 30 min	4.2	4.2	800 °C, 100% N ₂ , 60 ml min ⁻¹ , 30 min	54
Na ₂ ZrO ₃	20	600 °C , 100 %CO ₂ , 60 ml min ⁻¹ , 30 min	4.4	4.1	800 °C, 100% N ₂ , 60 ml min ⁻¹ , 30 min	54
Na ₂ ZrO ₃	20	700 °C , 100 %CO ₂ , 60 ml min ⁻¹ , 30 min	4.8	4.2	800 °C, 100% N ₂ , 60 ml min ⁻¹ , 30 min	54
Na ₂ ZrO ₃	20	800 °C , 100 %CO ₂ , 60 ml min ⁻¹ , 30 min	5	3.1	800 °C, 100% N ₂ , 60 ml min ⁻¹ , 30 min	54
K- Na ₂ ZrO ₃	8	400 °C	2	0.7	850 °C	103
Na ₂ (Zr _{1-x} Al _x)O ₃	20	550 °C, 60 ml min ⁻¹ , 30 min	4	4.3	800 °C, 100% N ₂	98

606

607 **Influence of steam on CO₂ absorption**

608 Na₂ZrO₃ has the ability to hold water. The reaction between CO₂ and water-laden
609 Na₂ZrO₃ produces sodium bicarbonate (NaHCO₃) along with ZrO₂. With the formation of
610 NaHCO₃, the ability of Na₂ZrO₃ to capture CO₂ increases two fold compared to dry
611 conditions (theoretical maximum of 10.8 mmol-CO₂ g-sorbent⁻¹). Santillan-Reyes et al.⁵²
612 reported 5.8 mmol-CO₂ g-sorbent⁻¹ or 35 wt. % of sorbent at the temperature of 60 °C
613 under water saturated conditions. A temperature of 60 °C is too low for the activation of

614 Na diffusion, therefore the increased activity can be attributed to the availability of water.
615 The maximum capacity of CO₂ chemisorption in m-Na₂ZrO₃ is reached in less than 30
616 seconds under the influence of 10% concentrations of steam, which is over three times
617 faster than that in dry conditions.¹²⁵ Li₂ZrO₃ also displays increased chemisorption
618 kinetics under wet conditions that are likely to be found in SMR, i.e. steam
619 concentrations > 20%.⁸²

620 Multiple studies have suggested that Li₂ZrO₃ and LiSiO₄ are capable of producing
621 over 87 vol. % H₂ in SESMR conditions and Na₂ZrO₃ led to production of 92.2 vol. % H₂
622 in SESR of ethanol.²⁵⁻²⁸ Steam might affect mobility of alkali ions as it lowers surface
623 free energy making them likely to move towards a surface and ease the reaction with
624 CO₂.¹⁰² Steam is also reported to enhance CO₂ diffusion through the layer of carbonate
625 formed over Li₂ZrO₃ and Li₄SiO₄.^{82, 120} However, it does cause a continuous deactivation,
626 diminishing the capacity of the acceptor due to phase segregation, sintering, and/or
627 vaporization of alkali metals after forming hydro-oxides in the presence of steam.
628 Capture kinetics, regeneration and stability of Li₂ZrO₃, K-doped Li₂ZrO₃, Na₂ZrO₃, and
629 Li₄SiO₄ under steam laden conditions were tested and the results showed that capture
630 kinetics were considerably improved with 10% steam concentrations.¹²⁵ Similarly, the
631 regeneration kinetics also showed improvement under the presence of steam except for
632 Li₄SiO₄ which did not display any significant change.

633 Potassium salts/oxides are hygroscopic and their addition to Li₂ZrO₃ will increase the
634 tendency to trap water in the modified sorbent. Martinez-dlCruz, et al.¹⁰¹ suggested that
635 K-Li₂ZrO₃ does not only trap water through chemisorption, but also through the reaction
636 between K-Li₂ZrO₃ and water, forming hydroxyl species. Prepared samples gained

637 weight due to hydroxylation and carbonation processes in the temperature range of 30-80
638 °C.

639 **Influence of partial pressure**

640 In operational conditions the partial pressure of CO₂ will rarely exceed 0.2 bar, which
641 makes chemisorption performance of sorbent in low partial pressure conditions a vital
642 parameter. The CO₂ in alkali metal sorbents is governed by its diffusion within the
643 sorbents and not all alkali metal sorbents are able to exhibit uniform performance at
644 different partial pressure of CO₂. Chemisorption of Li₂ZrO₃ is severely affected by the
645 low partial pressure, as reported by multiple studies.⁷⁶⁻⁷⁸ At low partial pressures mass
646 transfer limitations inhibit the CO₂ diffusion. In these conditions CO₂ will react with Li⁺
647 atoms available at the surface and form up a barrier of Li₂CO₃-ZrO₂ preventing CO₂
648 diffusion.⁸² Li₄SiO₄ presents a superior chemisorption performance than Li₂ZrO₃ at low
649 partial pressures (5.9 mmol-CO₂ g-sorbent⁻¹ at 0.2 bar within 30 min and 6.1 mmol-CO₂
650 g-sorbent⁻¹ at 0.02 bar within 50 min).¹²⁴ Unlike Li₂ZrO₃, Li₄SiO₄ has smaller grain sizes
651 which chemisorb CO₂ at a faster rate.⁴⁹ Due to its smaller grain size, the layer of Li₂CO₃-
652 ZrO₂ formed after chemisorption is much thinner and consequently a lesser obstruction
653 for CO₂ diffusion at low partial pressures. Na₂ZrO₃ has higher surface reactivity towards
654 CO₂, particularly its m-Na₂ZrO₃ phase, which enables it to retain its chemisorption
655 capacity at low partial ⁵⁰ The performance of alkali metal sorbents synthesized by at low
656 partial pressures as reported different authors is given in **Table 5**.

657

658 **Table 5.** Chemisorption performance of alkali metal sorbents under different CO₂ partial
 659 pressure conditions.

Material	Chemisorption Conditions	CO ₂ chemisorbed (mmol-CO ₂ g-sorbent ⁻¹)	Refs.
Li ₂ ZrO ₃	1.0 bar CO ₂ , 575 °C	5 within 20 min	78
Li ₂ ZrO ₃	0.75 bar CO ₂ , 575 °C	4.6 in 25 min	78
Li ₂ ZrO ₃	0.50 bar CO ₂ , 575 °C	1.1 in 25 min	78
Li ₂ ZrO ₃	0.25 bar CO ₂ , 575 °C	0.2 in 25 min	78
Li ₂ ZrO ₃	0.10 bar CO ₂ , 575 °C	0.1 in 25 min	78
Li ₄ SiO ₄	0.20 bar CO ₂ , 500 °C	5.9 in 30 min	124
Li ₄ SiO ₄	0.02 bar CO ₂ , 500 °C	6.1 in 50 min	124
Na ₂ ZrO ₃	0.1 bar CO ₂ , 575 °C	3.86 within 10 min	50
Na ₂ ZrO ₃	0.075 bar CO ₂ , 575 °C	3.6 in 40 min	50
Na ₂ ZrO ₃	0.050 bar CO ₂ , 575 °C	3.6 in 40 min	50
Na ₂ ZrO ₃	0.025 bar CO ₂ , 575 °C	3.6 in 40 min	50

660

661 7. ATTEMPTS TO IMPROVE THE INHERENT CO₂ CHEMISORPTION 662 CAPACITY OF ALKALI METAL CERAMICS

663 Effect of carbonate salts

664 During alkali metal ceramic carbonation, CO₂ diffusion through the solid carbonate
 665 outer shell occurs at temperatures below 600 °C. Addition of carbonate salts to form a
 666 molten carbonate shell at these temperatures will enhance diffusion of CO₂ and
 667 effectively increase the chemisorption range (**Table 6**).^{60, 75} Furthermore, alkali metal
 668 carbonate additions can form a molten salt ternary mixture which displayed a 2 mg g⁻¹
 669 min⁻¹ chemisorption rate at a low temperature of 450 °C.⁴⁹ It is reported that K-promoted

670 chemisorption improves kinetics in the diffusion of CO₂ through the bulk, but the surface
671 reaction chemisorption kinetics remain the same.⁹

672 Apart from CO₂ diffusion, molten carbonate eutectic phase mixtures change the
673 viscoelastic properties of the sorbent mixture i.e. materials display more liquid-like
674 characteristics. It is reported that molten carbonate phases require a heating rate of > 10
675 °C min⁻¹ to alter the viscoelastic properties and enhance the amount of molten carbonate
676 phase whereas a lower heating rate aids chemisorption and diffusion of CO₂ throughout
677 the sorbent. However, mass transfer at a heating rate of > 10 °C min⁻¹ limits CO₂
678 diffusion and, in this instance, formation of a molten phase prevails over diffusion of
679 CO₂.¹²⁶

680

681 **Table 6.** Composition and eutectic temperatures of binary and ternary eutectic mixtures
682 of carbonate salts studied by thermogravimetric analyzers.¹²⁷

Eutectic salt composition (mol %)	Melting point (°C)
K ₂ CO ₃ 38%, Li ₂ CO ₃ 62%	488
K ₂ CO ₃ 57.3%, Li ₂ CO ₃ 42.7%	498
Na ₂ CO ₃ 48%, Li ₂ CO ₃ 52%	500
KF 38%, Li ₂ CO ₃ 62%	N/A
K ₂ CO ₃ 57%, MgCO ₃ 43%	460
K ₂ CO ₃ 26.85%, Na ₂ CO ₃ 30.6%, Li ₂ CO ₃ 42.5%	393
K ₂ CO ₃ 16.4%, Na ₂ CO ₃ 26.4%, Li ₂ CO ₃ 57.1%	372
KCl 36.8%, NaCl 36.2%, Na ₂ CO ₃ 27 %	560
K ₂ CO ₃ 42%, NaF 32%, Na ₂ CO ₃ 26%	562
NaCl 31%, Na ₂ CO ₃ 54%, NaF 15%	575

683

684

685 **Influence of doping on CO₂ chemisorption**

686 The doping of Li₂ZrO₃ with K can change the melting point and create an eutectic
687 shell that becomes liquid at lower temperature, which significantly improves the CO₂
688 diffusion rate and provides better CO₂ chemisorption than a solid carbonate shell. K-
689 doped Li₂ZrO₃ shows faster kinetics of chemisorption in the presence of a molten eutectic
690 phase, the limiting step of the reaction becomes the diffusion of Li⁺ ions and O²⁻ ions in
691 place of CO₂ in the solid phase of an undoped Li₂ZrO₃.^{48, 60, 126-128} However, this addition
692 of potassium will adversely affect the equilibrium chemisorption capacity of the sample.
693 K_{0.2}Li₂Zr_{3.1} can theoretically capture 6.1 mmol-CO₂ g-sorbent⁻¹, but increasing K amount
694 to K_{0.6}Li₂Zr_{3.3} will lower the theoretical capture capacity to 5.5 mmol-CO₂ g-sorbent⁻¹.
695 K_{0.2}Li_{1.6}ZrO_{2.9} was found to be optimum ratio where the material captured 5.7 mmol-CO₂
696 g-sorbent⁻¹ in under 15 minutes.¹²³ Gauer and Heschel¹²¹ improved the performance of
697 Li₄SiO₄ by doping the material with Al and Fe and creating vacancies inside the structure
698 to facilitate improved chemisorption. Compared with K-doped Li₄SiO₄, which provides
699 good chemisorption at lower temperatures but requires higher temperatures to regenerate,
700 vacancy doped material, particularly Fe > Al, provides improved reactivity 500 °C. It
701 should also be noted that Li_{3.7}Al_{0.1}SiO₄ and Li_{3.7}Fe_{0.1}SiO₄ performed similarly in
702 chemisorption but desorption of Li_{3.7}Al_{0.1}SiO₄ was incomplete while Li_{3.7}Fe_{0.1}SiO₄
703 completed desorption at 750 °C. It is because Fe will form a weaker oxygen bond in
704 comparison with Al atoms, therefore O²⁻ ion diffusion is relatively unhindered by
705 Li_{3.7}Fe_{0.1}SiO₄ resulting in complete desorption. Seggiani et al.¹²⁹ tested Li₄SiO₄ silicates
706 samples doped with different carbonates at varying concentrations. The doped samples
707 performed better than pure Li₄SiO₄ however, the samples were subject to decay after the

708 first chemisorption/regeneration cycle due to sintering. The sample with 30% K_2CO_3 -
709 doped Li_4SiO_4 remained most stable after 25 cycles with only 4 wt. % loss of capture
710 capacity along with displaying best chemisorption performance in terms of kinetics and
711 chemisorption capacity of $3.4 \text{ mmol-CO}_2 \text{ g-sorbent}^{-1}$.

712 Addition of potassium to Na_2ZrO_3 also noticeably improves the chemisorption
713 kinetics of the material as a K-Na eutectic salt is formed. Again the low-temperature
714 molten carbonate phase enhances the diffusion of the CO_2 . However, thermal and cyclic
715 stability of the sorbent is affected due to potassium sublimation during high-temperature
716 desorption.¹⁰³ K-doped Na_2ZrO_3 favors chemisorption at much lower temperature (400
717 °C).¹⁰³

718 Dissolved aluminum in sodium zirconates produces $\text{Na}_2(\text{Zr}_{1-x}\text{Al}_x)\text{O}_3$ ($x \leq 0.3$).⁹⁸
719 Aluminum oxide addition gives improvements in CO_2 capture during the surface
720 chemisorption phase, and the $\text{Na}_2(\text{Zr}_{1-x}\text{Al}_x)\text{O}_3$ exhibits peak CO_2 capture at 600 °C (4
721 $\text{mmol-CO}_2 \text{ g-sorbent}^{-1}$; in contrast to Na_2ZrO_3 which displays its peak performance at 550
722 °C). 600 °C is the temperature at which the Na_2CO_3 outer shell densifies in Na_2ZrO_3
723 sorbents. Improved performance at 600 °C indicates that aluminum oxide addition
724 provides resistance to sintering and densification at 600 °C. These solid solutions have
725 good stable cycle stability.

726 Doping of Li into Na_2ZrO_3 is more favorable for chemisorption than doping with
727 K¹³⁰. Increasing Li as a dopant will lower regeneration temperature for Na_2ZrO_3 and
728 enhance the stability of the structure, whereas similar increments of K as a dopant will,
729 on the whole, increase the regeneration temperature and adversely affect the structure.

730 8. OUTLOOK

731 The concept of bifunctional catalyst-sorbent is a logical progression in the field of
732 SESR, on account of advantages offered such as reduced cost and improved mass transfer
733 over conventional sorbent and catalyst mixture. The research on bifunctional materials is
734 still in its infancy, but the inherent improvement in kinetics and stability, compared to
735 hybrid-type materials, brings forth alkali metal ceramics Li_2ZrO_3 , Li_4SiO_4 and Na_2ZrO_3
736 as bifunctional candidates. Their possible applications in this regard have not been
737 explored as yet in our knowledge. Alkali metal ceramics have been investigated as CO_2
738 sorbents in the context of post-combustion scenarios i.e. CO_2 capture from flue gas.
739 These sorbents have been extensively studied over past 15 years showing an improved
740 performance as their chemisorption mechanism is understood and refinements in their
741 synthesis methods have been reported. Furthermore, alkali metal carbonates, which are
742 formed as a result of CO_2 chemisorption by alkali metal sorbents, possess catalytic ability
743 pyrolysis and gasification with different hydrocarbon feedstocks and solid fuels. All of
744 this taken together clearly present a picture of a set of solid sorbents that, when utilized as
745 bifunctional material, benefit from improved kinetics and at the same time provide the
746 robustness under given operational conditions that are missing in CaO and HTICs based
747 materials.

748 In this context, alkali metal ceramics can be paired with conventional Ni catalyst to
749 provide absorptive support as well as a highly durable structure. The variance in effective
750 methods to synthesize alkali metal ceramics will be effective in controlling the
751 morphology of the material, providing a suitable porous structure to disperse the selected
752 catalyst upon. Likewise, the sturdiness of alkali metal ceramics eliminates the necessity

753 of using other metal refractory supports, resulting in a simplified synthesis process
754 consisting of only two materials, the catalyst and the sorbent. This is important because it
755 provides ease in manipulating the concentration profiles of catalyst and sorbent, and their
756 placements within the final material. Theoretical studies on bifunctional pellets have
757 assumed the presence of catalytic and sorbent sites within the material, their performance
758 under multi-cycle process, and the effects of variable distribution of said sites.

759 With alkali metal ceramics as bifunctional materials, it is possible to investigate the
760 validity of theoretical studies to identify the optimal makeup of a bifunctional material
761 under SESR conditions. According to the literature on catalytic abilities of alkali metal
762 carbonates, it is unlikely that a mixture of separate alkali metal zirconates/silicates and
763 carbonate phases can successfully fulfill the dual roles of catalyst and sorbent on its own.
764 However, the eventual formation of alkali metal carbonates in a bifunctional material as a
765 result of alkali metal ceramics carbonation adds an interesting dimension to their
766 potential future use in SESR. Alkali metal carbonates have been previously used as a
767 primary catalyst to breakdown larger hydrocarbon chains, and their presence as an
768 auxiliary catalyst should further increase the value of alkali metal ceramics as
769 bifunctional materials.

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776

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