

In situ XRD, Raman characterization and kinetic study of CO₂ capture by alkali carbonates-doped Na₄SiO₄

Dynamic thermal analyses

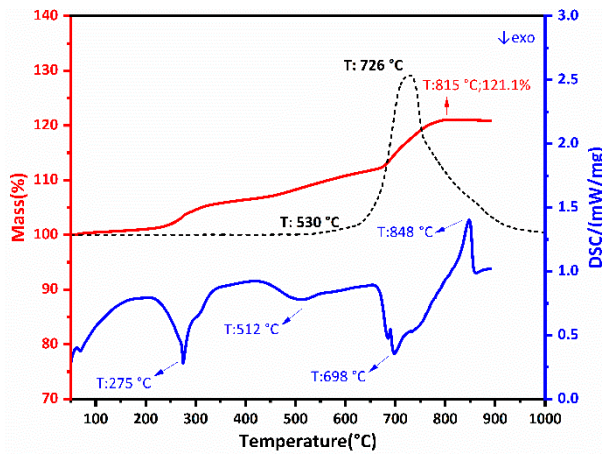


Figure S1. TG-DSC curves of P-Na at 50-900 °C with a heating rate of 10 °C·min⁻¹ in the 80%CO₂-20%N₂ atmosphere; Dashed line: TG curves of Li₄SiO₄(Wang et al., 2021).

The dynamic thermal analysis of P-Na exposed to an atmosphere of 80 % CO₂ is shown in Fig.S1. According to the TGA profile, CO₂ sorption consisted of three temperature regions: 50-300°C, 300-700 °C, and 700-815 °C. The CO₂ uptake started at 50 °C but occurred weakly, and the uptake rate increased at 275 °C when a clear DSC exothermic peak could be observed. At the temperature range from 300 to 700 °C, the CO₂ uptake capacity increased from 5 wt% to 12 wt %. A sharp weight gain can be observed from 700 to 815 °C, starting with the exothermic peak at 698 °C. The total CO₂ uptake capacity of Na₄SiO₄ from 50 to 815 °C was 21.1 wt% and the conversion of Na₄SiO₄ reached 88.3 %, which was comparable to the theoretical capacity of 23.9 wt%. According to the DSC plot, the desorption started at 848 °C with a clear endothermic peak. In previous studies(Liu et al., 2019), it was found that the solid products Na₂CO₃ and

Na_2SiO_3 would coat the surface of unreacted Na_4SiO_4 particles, hindering CO_2 diffusion and inhibiting the overall reaction. The endothermic peak at 848°C might be attributed to the volatilization of the product sodium carbonate because of melting, but according to the previous study (Liu et al., 2019), the TG curve showed a trend of weight loss without an exothermic peak being observed when the temperature was higher than 848°C , thereby it was considered that the exothermic peak was a superposition of the phase change of Na_2CO_3 and the decarbonization reaction.

As shown in Fig.S1, Li_4SiO_4 started to adsorb CO_2 at 530°C and rapidly desorbed at 726°C (Wang et al., 2021). In contrast, Na_4SiO_4 had slight CO_2 adsorption below 100°C and the weight gain became significant above 200°C . Na_4SiO_4 can achieve CO_2 capture in a wider temperature range and has the potential to be developed as a suitable CO_2 sorbent under improved kinetic conditions.

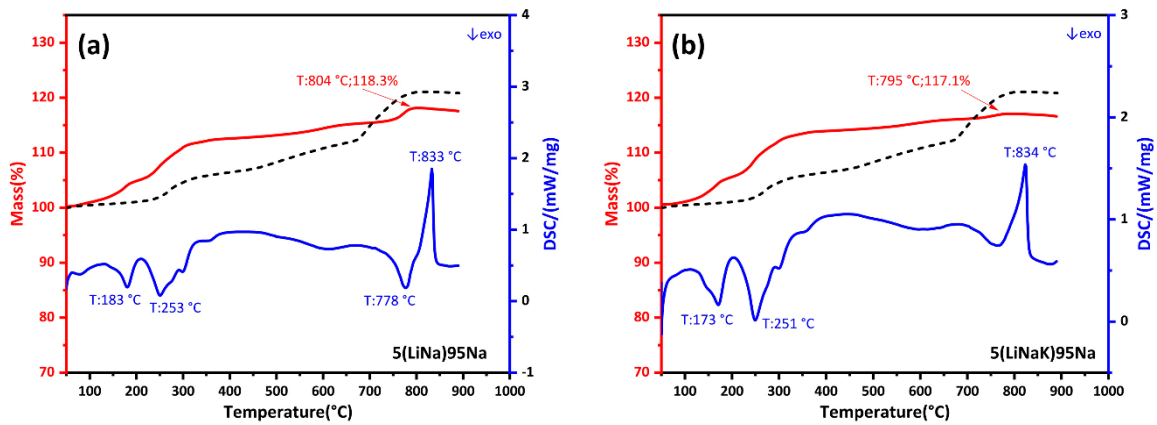


Figure S2. TG-DSC curves of 5(LiNa)95Na (a) and 5(LiNaK)95Na (b) at $50\text{--}900^\circ\text{C}$ with a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in the $80\%\text{CO}_2\text{--}20\%\text{N}_2$ atmosphere; Dashed line: TG curves of P-Na.

Carbonate doping is a facile method that has been widely adopted to improve the CO_2 capture performance of medium and high-temperature absorbers. In this study, the addition of alkali carbonates in the sorbent started from 5 mol%. The dynamic thermal analyses of 5mol% carbonates doped Na_4SiO_4 exposed to the atmosphere of 80 % CO_2 were shown in Fig. S2. For the sample of 5(LiNa)95Na shown in

Fig.S2(a), the weight gain experienced a significant increase from 50 to 300 °C, accompanied by two exothermic peaks at 183 °C and 253 °C in the DSC curve. At the temperature range from 300 to 700 °C, the CO₂ uptake rate decreased slightly. And the CO₂ uptake rate increased obviously at 700-800 °C with an exothermic peak at 778 °C. After that, the desorption took place and an endothermic peak could be found at 833 °C. Compared with the P-Na, the sample of 5(LiNa)95Na had a high CO₂ uptake rate below 700 °C especially at 50 to 300 °C, and the total CO₂ capacity was 18.3 wt% with a conversion of 78.5% for Na₄SiO₄.

In Fig.S2(b), the sample of 5(LiNaK)95Na also exhibited a higher adsorption rate but a lower capacity of 17.1 % with a conversion of 73.7 wt% for Na₄SiO₄. The addition of 5 mol% of carbonates had a minor effect on the desorption process, and the desorption temperature was only reduced by about 10 °C.

Compared with pure Na₄SiO₄, alkali carbonates acted as a promoter to accelerate the whole reaction effectively. When the temperature was below 500°C, the carbonates behaved like a solid phase and the apparent weight gain should be attributed to the contribution of pyrocarbonates that emerged from carbonate and CO₂(Liu et al., 2019). Pyrocarbonates could provide new reaction pathways, thus accelerating the overall chemisorption. When the temperature was above 500°C, the carbonates turned out to be melted. The doped carbonates served two functions: producing the intermediate product and forming the melt to reduce the diffusion resistance of CO₂.

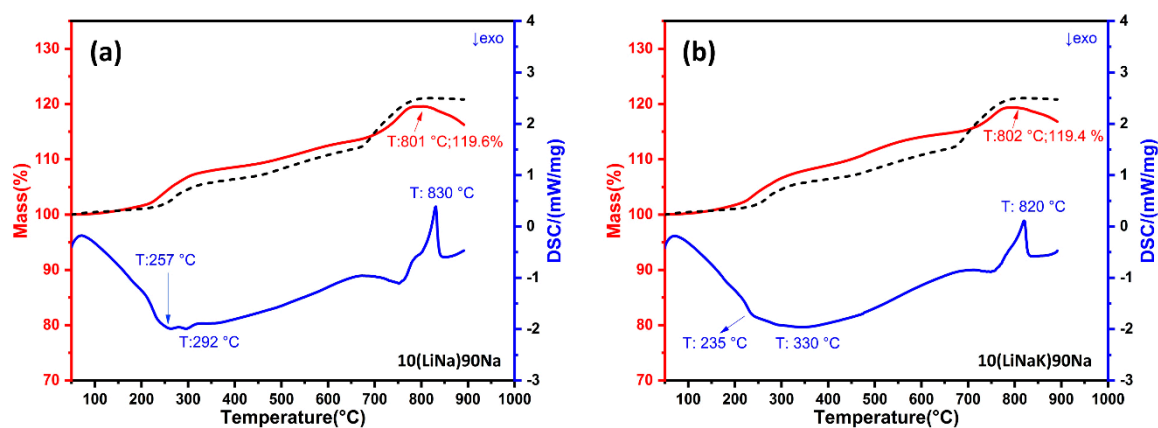


Figure S3. TG-DSC curves of 10(LiNa)90Na (a) and 10(LiNaK)90Na (b) at 50-900 °C with a heating rate of 10 °C·min⁻¹ in the 80%CO₂-20%N₂ atmosphere; Dashed line: TG curves of P-Na.

The dynamic thermal analyses of 10mol% carbonates doped Na₄SiO₄ exposed to an atmosphere of 80 % CO₂ were shown in Fig.S3. When the proportion of carbonates increased to 10 mol%, the weight gain involved two stages: 50-300°C, and 300-800 °C. For the result of 10(LiNa)90Na shown in Fig.S3(a), the rapid CO₂ uptake took place at 50-300 °C, accompanied by two exothermic peaks at 257 °C and 292 °C in the DSC curve. And the CO₂ uptake capacity reached up to 7 wt% at 300 °C, after which the CO₂ uptake rate decreased as the temperature increased. After 300°C, the adsorption capacity remains essentially constant until 800 °C, when desorption began and an endothermic peak occurred at 830 °C. The total CO₂ capacity of 10(LiNa)90Na from 50-800 °C was 19.6 wt% with a conversion of 86.4% for Na₄SiO₄. In Fig.S3(b), the sample of 10(LiNaK)90Na also showed a good CO₂ uptake performance but a lower capacity of 19.4 wt% with a conversion of 86.3% for Na₄SiO₄. The addition of 10 mol% of carbonates had little effect on the desorption process according to the endothermic peaks at 830 °C or 820 °C in the DSC plots, which were comparable to the endothermic peak at 848 °C for the P-Na.

Compared with pure Na₄SiO₄, alkali carbonates in doped sorbents acted as a promoter to accelerate the whole reaction effectively. Due to the doubling of the carbonate content, the promotion of carbonate was outstanding, especially below 300°C. The added alkali carbonates could not form the carbonate melt at low temperatures but could produce pyrocarbonates that enhanced the CO₂ uptake rate compared to P-Na.

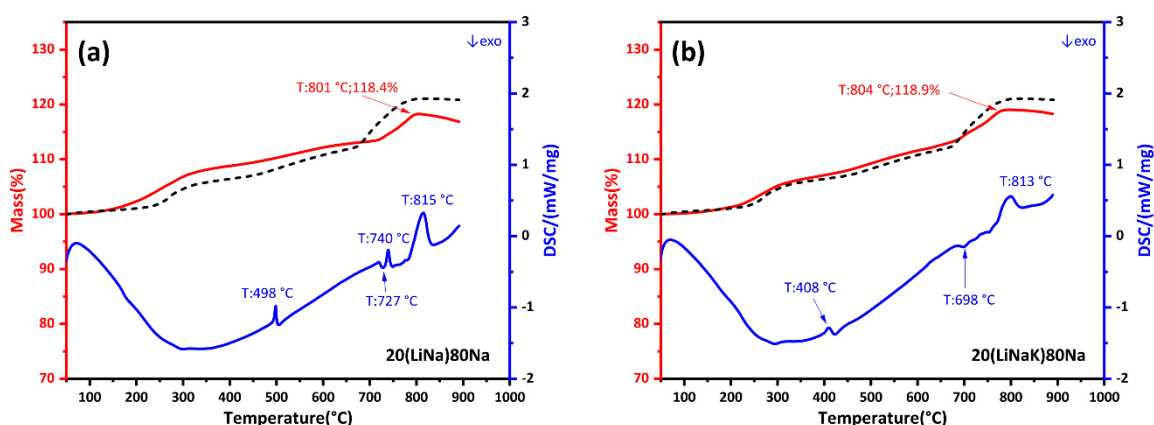


Figure S4. TG-DSC curves of 20(LiNa)80Na (a) and 20(LiNaK)80Na (b) at 50-900 °C with a heating rate of 10 °C·min⁻¹ in the 80%CO₂-20%N₂ atmosphere; Dashed line: TG curves of P-Na.

The dynamic thermal analyses of 20 mol% carbonates doped Na₄SiO₄ exposed to an atmosphere of 80 % CO₂ are shown in Fig.S4. The CO₂ adsorption was included in three stages: 50-300°C, 300-700 °C, and 700-800 °C. For the results of 20(LiNa)80Na shown in Fig.S4(a), the CO₂ uptake rate was only slightly greater than that of P-Na, and no exothermic peaks could be detected in the DSC curve. At the temperature range from 300 to 700 °C, the CO₂ uptake rate decreased slightly although the CO₂ capacity was marginally higher than that of P-Na. In this temperature range, no exothermic peak was detected and only an endotherm peak at 498 °C was attributed to the melting of added carbonates. When the temperature reached 727 °C, an exothermic peak was found which corresponded to a sudden weight gain. The total CO₂ uptake capacity of 20(LiNa)80Na at 50-800 °C was 18.4% with a conversion of 86.4% for Na₄SiO₄, and the desorption occurred at 801 °C followed by an endotherm peak at 815 °C. The results of 20(LiNaK)80Na were shown in Fig.S4(b), it has a similar CO₂ uptake performance to that of 20(LiNa)80Na. The endotherm peak at 408 °C was attributed to the melting of added ternary carbonates. The total CO₂ uptake capacity of 20(LiNaK)80Na was 18.9 wt% with a conversion of 90.4% for Na₄SiO₄.

For the samples of 20 mol% alkali carbonates doped Na₄SiO₄, the promotion was not obvious

compared to that of samples with minor alkali carbonates, but the conversion of Na_4SiO_4 increased. The alkali carbonates in sorbents acted as a binder to hold the free CO_2 in place to form pyrocarbonate. However, when there were excessive carbonates in the samples, the newly formed pyrocarbonates could not be transferred to Na_4SiO_4 in time and experienced serious retention. In this case, the doped carbonates could not exhibit a facilitative effect and cause a poor adsorption performance. Furthermore, the massive carbonate melts would cover the surface of Na_4SiO_4 and aggravate the resistance of CO_2 diffusion to Na_4SiO_4 when the temperature was above the melting points of carbonate mixtures.

It should be noted that the weight loss becomes more pronounced in the desorption process, as the proportion of carbonates in the sorbents increases. These results were consistent with the *in situ* XRD results.

This indicated that the liquid phase facilitated the CO_2 desorption.

Table S1. Weight gain and conversion of different samples at different temperatures

Samples	Temperature (°C)	Experimental Weight gain (%)	Theoretical weight gain (%)	Conversion(%)
P-Na	200	4.82	23.91	20.18
	250	6.21	23.91	25.99
	300	7.86	23.91	32.89
	500	11.33	23.91	47.38
	550	11.97	23.91	50.05
	600	13.79	23.91	57.68
5(LiNa)95Na	200	8.41	23.31	36.06
	250	9.76	23.31	41.86
	300	11.07	23.31	47.49
	500	14.21	23.31	60.94
	550	15.27	23.31	65.52
	600	16.36	23.31	70.18
5(LiNaK)95Na	200	8.51	23.21	36.66
	250	9.80	23.21	42.22
	300	11.12	23.21	47.92
	500	14.20	23.21	61.18
	550	14.81	23.21	63.83
	600	16.40	23.21	70.65
10(LiNa)90Na	200	10.87	22.68	47.94

	250	12.10	22.68	53.37
	300	13.29	22.68	58.58
	500	14.66	22.68	64.65
	550	15.27	22.68	67.35
	600	16.71	22.68	73.66
	200	10.93	22.47	48.64
	250	12.23	22.47	54.42
10(LiNa)K90Na	300	13.35	22.47	59.43
	500	14.00	22.47	62.31
	550	14.28	22.47	63.57
	600	15.70	22.47	69.87
	200	7.26	21.31	34.08
	250	8.67	21.31	40.67
20(LiNa)80Na	300	10.03	21.31	47.07
	500	12.80	21.31	60.06
	550	13.52	21.31	63.45
	600	15.58	21.31	73.13
	200	7.03	20.9	33.64
	250	8.33	20.9	39.84
20(LiNaK)80Na	300	9.71	20.90	46.47
	500	12.56	20.90	60.11
	550	13.27	20.90	63.48
	600	15.31	20.90	73.24
