

## A Pinch of Sodium: Rapid CO<sub>2</sub> Uptake with MgO-based CO<sub>2</sub> sorbents upon promotion with Na<sub>2</sub>CO<sub>3</sub> seeds

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There is an urgent need to develop and engineer functional materials that can capture and release CO<sub>2</sub> on demand. Solid oxide materials such as MgO and CaO constitute a promising family of materials for CO<sub>2</sub> capture, utilization, and storage, considering their favorable thermodynamics, high theoretical CO<sub>2</sub> uptake capacities and earth-abundance. However, despite favorable carbonation thermodynamics, MgO suffers from a limited CO<sub>2</sub> uptake due to very slow carbonation kinetics. The carbonation kinetics can be enhanced by adding an alkali metal nitrate promoter such as NaNO<sub>3</sub>, which dissolves surface carbonates in the form of [Mg<sup>2+</sup>...CO<sub>3</sub><sup>2-</sup>] ion pairs and thereby facilitates MgCO<sub>3</sub> crystallization.<sup>1,2</sup> Moreover, it was found that the addition of Na<sub>2</sub>CO<sub>3</sub> seeds to NaNO<sub>3</sub>-promoted MgO further increases the CO<sub>2</sub> uptake rate by a factor of 10.<sup>3</sup> We investigated the promotional effect of Na<sub>2</sub>CO<sub>3</sub> via in situ synchrotron-based X-ray powder diffraction (XRD) with a high time resolution (1 s) complemented by electron microscopy characterization. We demonstrate that Na<sub>2</sub>CO<sub>3</sub> rapidly transforms into Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> in the presence of MgO, CO<sub>2</sub>, and NaNO<sub>3</sub>. The Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> phase acts as an effective nucleation seed that boosts MgCO<sub>3</sub> growth. Our In-situ XRD measurements prove that MgCO<sub>3</sub> nucleates onto the Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> seeds while TEM imaging of the Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>-MgCO<sub>3</sub> interphase reveals that the Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> seeds promote MgO dissolution and thereby facilitate MgCO<sub>3</sub> growth. Taken together, the insights obtained here will help the development of more effective MgO-based CO<sub>2</sub> sorbents.

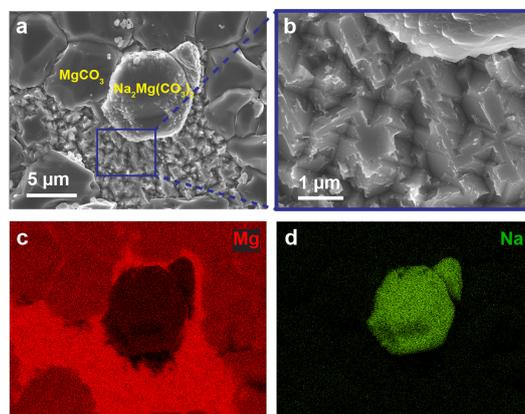


Figure 1. SEM-EDX analysis of a carbonated NaNO<sub>3</sub>/Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>-promoted MgO(100) single crystal. (a) SEM image of a Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> crystals surrounded by MgCO<sub>3</sub> crystals. (b) zoom focusing on the etching pits formed in the MgO(100) surface. (c) Corresponding Mg and (d) Na elemental maps.

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[2] Alexander H. Bork, Margarita Rekhtina, Elena Willinger, Pedro Castro-Fernández, Jakub Drnec, Paula M. Abdala, and Christoph R. Müller, *PNAS*, **2021**, 118, e2103971118

[3] Anh Tuan Vu, Keon Ho, Seongmin Jin, Chang Ha Lee, *Chem. Eng. J.* **2016**, 291, 161-173.