



	Experiment title: Alkali metal nitrate (MNO ₃ , M= K, Li) promoted MgO for CO ₂ capture: time resolved in situ studies on MgO and MgCO ₃ formation	Experiment number: EV-337
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Report:

The experiment led to the following publications:

- 1- Effect of molten sodium nitrate on the decomposition pathways of hydrated magnesium hydroxycarbonate to magnesium oxide probed by in situ total scattering†¹**

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Abstract

The effect of NaNO₃ and its physical state on the thermal decomposition pathways of hydrated magnesium hydroxycarbonate (hydromagnesite, HM) towards MgO was examined by in situ total scattering. Pair distribution function (PDF) analysis of these data allowed us to probe the structural evolution of pristine and NaNO₃-promoted HM. A multivariate curve resolution alternating least squares (MCR-ALS) analysis identified the intermediate phases and their evolution upon the decomposition of both precursors to MgO. The total scattering results are discussed in relation with thermogravimetric measurements coupled with off-gas analysis. MgO is obtained from pristine HM (N₂, 10 °C min⁻¹) through an amorphous magnesium carbonate intermediate (AMC), formed after the partial removal of water of crystallization from HM. The decomposition continues via a gradual release of water (due to dehydration and dehydroxylation) and, in the last step, via decarbonation, leading to crystalline MgO. The presence of molten NaNO₃ alters the decomposition pathways of HM, proceeding now through AMC and crystalline MgCO₃. These results demonstrate that molten NaNO₃ facilitates the release of water (from both water of crystallization and through dehydroxylation) and decarbonation, and promotes the crystallization of MgCO₃ and MgO in comparison to pristine HM. MgO formed from the pristine HM precursor shows a smaller average crystallite size than NaNO₃-promoted HM and preserves the initial nano-plate-like morphology of HM. NaNO₃-promoted HM was decomposed to MgO that is characterized by a larger average crystallite size and irregular morphology. Additionally, in situ SEM allowed visualization of the morphological evolution of HM promoted with NaNO₃ at a micrometre scale.

2- Deciphering the structural dynamics in molten salt-promoted MgO-based CO₂ sorbents and their role in the CO₂ uptake²

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The development of effective CO₂ sorbents is vital to achieving net-zero CO₂ emission targets. MgO promoted with molten salts is an emerging class of CO₂ sorbents. However, the structural features that govern their performance remain elusive. Using in situ time-resolved powder x-ray diffraction, we follow the structural dynamics of a model NaNO₃-promoted, MgO-based CO₂ sorbent. During the first few cycles of CO₂ capture and release, the sorbent deactivates owing to an increase in the sizes of the MgO crystallites, reducing in turn the abundance of available nucleation points, i.e., MgO surface defects, for MgCO₃ growth. After the third cycle, the sorbent shows a continuous reactivation, which is linked to the in situ formation of Na₂Mg(CO₃)₂

crystallites that act effectively as seeds for MgCO_3 nucleation and growth. $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ forms due to the partial decomposition of NaNO_3 during regeneration at $T \geq 450^\circ\text{C}$ followed by carbonation in CO_2 .

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1. Rekhtina, M.; Dal Pozzo, A.; Stoian, D.; Armutlulu, A.; Donat, F.; Blanco, M. V.; Wang, Z. J.; Willinger, M. G.; Fedorov, A.; Abdala, P. M.; Müller, C. R., Effect of molten sodium nitrate on the decomposition pathways of hydrated magnesium hydroxycarbonate to magnesium oxide probed by in situ total scattering. *Nanoscale* **2020**, *12* (31), 16462-16473.
2. Rekhtina, M.; Krödel, M.; Wu, Y.-H.; Kierzkowska, A.; Donat, F.; Abdala, P. M.; Müller, C. R., Deciphering the structural dynamics in molten salt-promoted MgO-based CO_2 sorbents and their role in the CO_2 uptake. *Science Advances* **2023**, *9* (26), eadg5690.