



Peering into buried interfaces with X-rays and electrons to unveil MgCO₃ formation during CO₂ capture in molten salt-promoted MgO

Alexander H. Bork^{a,1}, Margarita Rekhtina^{a,1}, Elena Willinger^{a,2}, Pedro Castro-Fernández^a, Jakub Drnec^b, Paula M. Abdala^{a,2}, and Christoph R. Müller^{a,2}

^aLaboratory of Energy Science and Engineering, Department of Mechanical and Process Engineering, Eidgenössische Technische Hochschule (ETH) Zürich, 8092 Zürich, Switzerland; and ^bEuropean Synchrotron Radiation Facility, 38000 Grenoble, France

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The addition of molten alkali metal salts drastically accelerates the kinetics of CO₂ capture by MgO through the formation of MgCO₃. However, the growth mechanism, the nature of MgCO₃ formation, and the exact role of the molten alkali metal salts on the CO₂ capture process remain elusive, holding back the development of more-effective MgO-based CO₂ sorbents. Here, we unveil the growth mechanism of MgCO₃ under practically relevant conditions using a well-defined, yet representative, model system that is a MgO(100) single crystal coated with NaNO₃. The model system is interrogated by in situ X-ray reflectometry coupled with grazing incidence X-ray diffraction, scanning electron microscopy, and high-resolution transmission electron microscopy. When bare MgO(100) is exposed to a flow of CO₂, a noncrystalline surface carbonate layer of ca. 7-Å thickness forms. In contrast, when MgO(100) is coated with NaNO₃, MgCO₃ crystals nucleate and grow. These crystals have a preferential orientation with respect to the MgO(100) substrate, and form at the interface between MgO(100) and the molten NaNO₃. MgCO₃ grows epitaxially with respect to MgO(100), and the lattice mismatch between MgCO₃ and MgO is relaxed through lattice misfit dislocations. Pyramid-shaped pits on the surface of MgO, in proximity to and below the MgCO₃ crystals, point to the etching of surface MgO, providing dissolved [Mg²⁺...O²⁻] ionic pairs for MgCO₃ growth. Our studies highlight the importance of combining X-rays and electron microscopy techniques to provide atomic to micrometer scale insight into the changes occurring at complex interfaces under reactive conditions.

CO₂ | carbonate | interfaces | X-rays | microscopy

Global concerns about the rising level of greenhouse gas emissions and the associated climate change require the development of efficient processes to remove CO₂ selectively from large point sources or directly from the atmosphere. Such processes are termed carbon dioxide capture and storage (CCS) (1) and can be implemented on the industrial scale in different configurations such as precombustion, postcombustion, or oxy-combustion CCS (2, 3). A large variety of both liquid and solid sorbent materials have been explored for CCS, with solid CO₂ sorbents being particularly interesting owing to their ability to capture large quantities of CO₂ from point sources with, compared to amines, favorable efficiency and cost penalty estimates (4). Yet, the development of inexpensive solid sorbents that capture CO₂ with fast rates, possess a high CO₂ capacity, and operate with high stability over many CO₂ capture and regeneration cycles remains a key challenge. To advance the current state of sorbent design in a rational fashion, an improvement of our current understanding of the interplay between a sorbent's structural features and its CO₂ capture characteristics is required.

Magnesium oxide (MgO) is an attractive solid CO₂ sorbent, in particular for precombustion CCS applications, that stands out owing to its high theoretical CO₂ uptake of 1.09 g_{CO₂}·g_{MgO}⁻¹ (24.8 mmol·CO₂·g_{MgO}⁻¹) and relatively low temperature for regeneration, as compared to other solid sorbents (e.g., CaO, Li₄SiO₄, and Li₂ZrO₃). Despite its high theoretical CO₂ capacity, bare MgO displays very

sluggish carbonation kinetics, yielding an experimental CO₂ uptake of only 0.02 g_{CO₂}·g_{MgO}⁻¹ after 1 h of exposure to CO₂ (5, 6). The low practically obtained CO₂ uptake compared to the high theoretical value has been attributed to the high lattice enthalpy of MgO reducing the kinetics of its reaction with CO₂ appreciably and to the formation of a monodentate carbonate layer on the surface of MgO, which acts as a CO₂-impermeable barrier hampering the further conversion of unreacted MgO (7–9). Encouragingly, the slow uptake of MgO can be accelerated appreciably through an engineering solution, that is, the addition of alkali metal salts (AMS; e.g., NaNO₃, KNO₃, LiNO₃, and their eutectic mixtures) which are molten at operating conditions (10–14). By optimizing the loading of AMS (ca. 20 wt. % AMS), the CO₂ uptake of MgO can be increased by a factor of 15 (0.31 g_{CO₂}·g_{sorbent}⁻¹) compared to unpromoted MgO at identical carbonation durations (13). The kinetics and stability of AMS-promoted MgO can be improved even further when adding alkali earth carbonates such as SrCO₃ or CaCO₃, which have been hypothesized to act as nucleation seeds or to lead to the formation of double carbonate phases that form with faster kinetics. For such systems, CO₂ uptakes of up to 0.65 g_{CO₂}·g_{sorbent}⁻¹ after 50 carbonation and calcination cycles have been reported (15–17).

Significance

The grand challenge of reducing CO₂ emissions requires the development of cost-effective CO₂ sorbents. Based on the theoretically obtainable weight-normalized CO₂ uptake, MgO-based materials promoted with molten salts are attractive sorbents when compared to amines or metal organic frameworks. However, there is very little understanding of the processes that occur at the atomic-to-micro scale during CO₂ capture conditions, hampering the advancement of such sorbents. Combining X-ray and electron-based characterization techniques, we observe that MgCO₃ crystals form via nucleation and growth at the interface between MgO and the molten salt and are oriented with respect to the MgO(100) surface. Hence, more-effective MgO-based sorbents will require maximizing the interfacial area and the number of nucleation sites at the interface.

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¹A.H.B. and M.R. contributed equally to this work.

²To whom correspondence may be addressed. Email: elenawi@ethz.ch, abdalap@ethz.ch, or muelchri@ethz.ch.

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Owing to the impressive effect of molten AMS on the CO₂ uptake of bare MgO, the elucidation of the underlying promoting mechanism(s) has been the aim of a series of studies that have led to the postulation of a number of working hypotheses (12, 13, 16, 18–22). For example, combining thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and powder X-ray diffraction (XRD), it has been proposed that the addition of AMS promotes the CO₂ uptake of MgO through the following two effects. Firstly, it has been argued that AMS prevent the formation of a CO₂-impermeable monodentate carbonate layer on the surface of MgO, and they dissolve CO₂ that reacts with oxide ions (O²⁻) in the nitrate (23), leading to the formation of reactive carbonate ions (CO₃²⁻) that subsequently react with Mg²⁺ to form MgCO₃ (13). A second hypothesis, based on TGA and density functional theory (DFT) calculations, has argued that the promoting role of the AMS is mainly due to the molten salt's ability to lower the energy barrier associated with the high lattice enthalpy of MgO by dissolving the solid metal oxide (12, 18). The dissolution of MgO in the molten promoter yields solvated [Mg²⁺...O²⁻] ionic pairs that have weaker bonds compared to the strong ionic bonds in bulk MgO (12). The DFT calculations showed that the rate-controlling step for the reaction between CO₂ and MgO is the activation of the MgO ionic bond; the energy barrier to form [Mg²⁺...O²⁻] ionic pairs in the molten NaNO₃ is 5.33 eV, compared to 7.07 eV without NaNO₃ (12). The dissolved ionic pair reacts with CO₂ that is adsorbed on the MgO surface, that is, at the triple phase boundary (TPB) between MgO, CO₂, and the molten phases, to form [Mg²⁺...CO₃²⁻] ionic pairs. Upon reaching saturation, the [Mg²⁺...CO₃²⁻] ionic pairs precipitate as a crystalline MgCO₃ phase. It is further argued that the carbonate may precipitate away from the original dissolution site so as to not prohibit further reaction. Following this argument, the reaction would, in theory, continue until MgO is completely converted. However, in practice, MgO conversion stops at ~70%, which has been argued to arise from a reducing TPB length. A recent in situ total scattering study points to a more multifaceted role of the AMS promoter in the MgO–CO₂ system, as the AMS do not affect only the nucleation of MgCO₃ but also the microstructure and growth of the MgCO₃ formed (20).

Turning to the kinetics of CO₂ absorption, TGA-based studies of NaNO₃-promoted MgO powders have shown that the formation of MgCO₃ is characterized by a nucleation and growth process (16). The characteristic sigmoidal kinetic curve of MgO conversion suggests that the carbonate formation is “autocatalytic”; that is, once a stable nucleation seed is formed, the growth rate is accelerated. This interpretation was corroborated by experimental evidence that showed that the induction period, that is, the time required for the first stable nuclei to form, can be shortened by the inclusion of “inert” SrCO₃ seeds, which act as nucleation sites for MgCO₃ (16). Although there is a general agreement on the nucleation- and growth-based mechanism for the formation of MgCO₃, there are competing hypotheses on the nature of magnesium carbonate formation, that is, where it forms (at the interface AMS/MgO, at the TPB, or inside the AMS), its growth habit, and its morphology. According to an in situ TEM study of MgO nanoparticles that were physically mixed with a eutectic mixture of AMS, MgCO₃ nucleates favorably at the TPB (24, 25). Nonetheless, a different study suggests that the TPB is not a necessary condition for the absorption to take place, as carbonates (MgCO₃) were detected on the surface of a MgO(100) single crystal that was covered completely by NaNO₃ and treated under CO₂ (330 °C), as revealed by ex situ FTIR after the removal of NaNO₃ (16). Jo et al. (16) proposed that MgCO₃ is formed inside the molten promoter through nucleation and growth steps.

Hence, despite extensive efforts, the mechanisms behind the promoting role of AMS on MgO-based CO₂ sorbents have not been unveiled yet. Atomic-level insight into the promoting effect of AMS would allow unlocking of the full potential of MgO-based

CO₂ sorbents and design materials that approach (repeatedly) full conversion over a large number of CO₂ capture and regeneration cycles. To obtain such atomic-level insight, well-defined model systems and interrogation of them with detailed (in situ) characterization techniques are required. In this study, we utilize a single-crystal MgO(100) surface [the most stable and abundant MgO facet (21, 26, 27)] coated with NaNO₃ and probe, in detail, its structural dynamics under CO₂ capture conditions. Synchrotron-based, in situ X-ray reflectometry (XRR) and grazing incidence XRD (GIXRD) unravel the changes occurring at the surface of MgO under CO₂ capture condition (allowing study of the buried interface between the NaNO₃ promoter and MgO). We complemented the in situ X-ray-based characterizations by (ex situ) scanning electron microscopy (SEM) to characterize, in detail, the morphology of the MgCO₃ product formed (after carbonation and after removing the NaNO₃ promoter). Our studies evidence the formation of a noncrystalline carbonate layer on bare MgO(100) under CO₂ capture conditions. In contrast, MgO(100) coated with NaNO₃ exhibited an island-type growth of MgCO₃, as opposed to a homogeneous surface layer growth. MgCO₃ grows in a highly oriented fashion with a sectored-plate habit growth at the interface between NaNO₃/MgO(100), following a nucleation and growth mechanism. High-resolution TEM (HRTEM) provided atomic-level insight into the MgCO₃/MgO interface, evidencing an epitaxial arrangement between MgCO₃ and MgO whereby the lattice mismatch between MgCO₃ and MgO is relaxed through lattice misfit dislocations.

Results and Discussion

Changes at the Surface of MgO under CO₂ Capture Conditions Probed by In Situ XRR-GIXRD. To gain atomic-scale insight into the morphological and structural changes at the surface of MgO(100) and at the interface between MgO(100) and molten NaNO₃ under CO₂ capture conditions, we employed in situ high-energy (70 KeV) XRR and GIXRD. XRR probes the morphology of surfaces and interfaces at the atomic scale, even in the absence of long-range order, providing information about the average electronic density profile (scattering length density) as a function of probing depth (28). GIXRD provides complementary information on the crystalline phases close to the surface of the material. The consecutive acquisition of both in situ XRR and GIXRD data was carried out using a quartz dome cell connected to a gas control system. A schematic of the setup is shown in Fig. 1A and *SI Appendix, Fig. S2*. The grazing incident geometry and the high photon flux of the synchrotron radiation source enhanced the surface sensitivity, while the high photon energy was beneficial to penetrate the sample environment. The setup allowed us to acquire consecutive XRR and GIXRD data under relevant CO₂ capture conditions on bare MgO(100) and NaNO₃-coated MgO(100) (Fig. 1A and *SI Appendix, Figs. S2 and S3*). First, the samples were pretreated in situ in He at 450 °C for ca. 15 min to remove adsorbed water, hydroxides, and carbonates adsorbed onto the surface (29–31) and were subsequently cooled down to 330 °C in He. The collected XRR data on bare MgO(100) and NaNO₃-coated MgO(100) at 330 °C under He flow are referred to as MgO(100)_{-He} and NaNO₃-MgO(100)_{-He}, respectively. The He pretreatment was followed by exposing the samples to a CO₂ flow (10 mL·min⁻¹) for ca. 90 min (MgO(100)_{-CO2} and NaNO₃-MgO(100)_{-CO2}, respectively). GIXRD patterns were collected consecutively after the respective XRR measurements (*SI Appendix, Fig. S3*).

The experimental and fitted XRR curves, plotting the intensity of the reflected X-rays as a function of the scattering vector Q_z normal to the surface (where $Q_z = 4\pi/\lambda \cdot \sin\alpha$, and α is the incident angle), are presented in Fig. 1B. A typical XRR curve includes the following features: 1) a total reflection region below the critical angle which is determined by the difference in the electron densities of the gas phase and the surface of MgO and 2) a reflectivity region above the critical angle, described by a combination of a

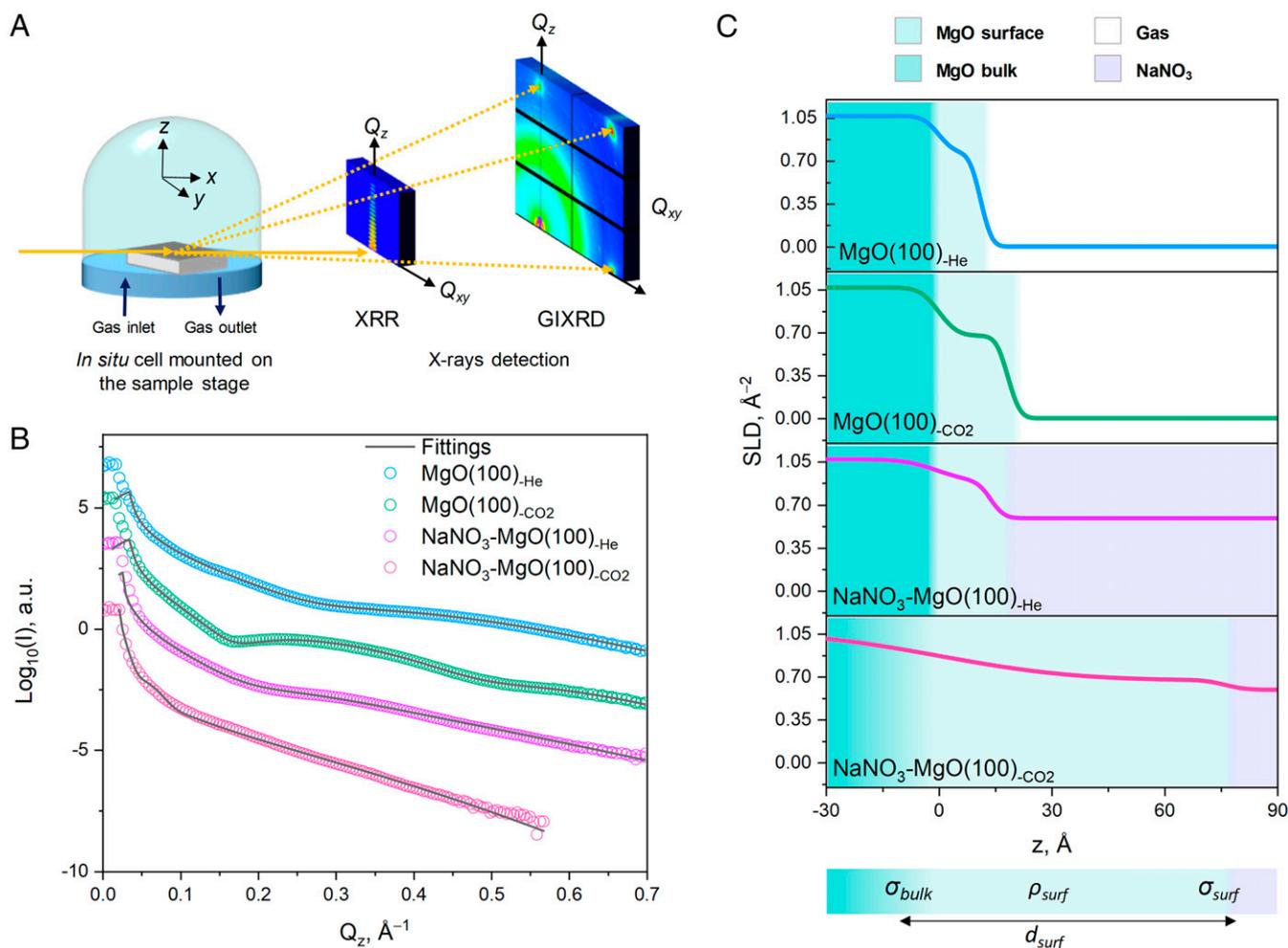


Fig. 1. (A) Schematic illustration of the in situ XRR-GIXRD setup. (B) Experimental (open circles) and fitted (gray lines) XRR curves for MgO(100)_{He}, MgO(100)_{CO₂}, NaNO₃-MgO(100)_{He}, and NaNO₃-MgO(100)_{CO₂}. The curves are offset vertically by two orders of magnitude for clarity. The XRR data are modeled via a layered structure model consisting of following components: 1) bulk MgO substrate, 2) a surface layer with a lower electronic density (slab due to surface hydroxide and carbonate species and surface imperfections) and 3) slab of a molten NaNO₃ phase for the NaNO₃-MgO(100) system. A misfit in the region below the critical angle is ascribed to the finite length and nonzero curvature of the crystal (65). (C) The scattering length density (SLD), i.e., electron density profiles obtained from the modeling; the colors represent the “bulk MgO” substrate, the surface layer, the gas phase, and the NaNO₃ coat, with their corresponding thickness, *d*, density, *ρ*, and roughness, *σ*. The fitted parameters were σ_{bulk} , σ_{surf} , d_{surf} , and ρ_{surf} , where the subscripts “bulk” and “surf” refer to the bulk MgO substrate and the surface layer, respectively. The fixed parameters are $\rho_{bulk-MgO} = 3.57 \text{ g/cm}^3$, $\rho_{NaNO_3} = 1.9 \text{ g/cm}^3$, $d_{bulk} = \infty$, $d_{gas} = \infty$, and $d_{NaNO_3} = \infty$ (SI Appendix, Table S1).

rapid decay in the reflected intensity (Fresnel reflectivity curve) and the oscillation (Kiessig) fringes (32, 33). The Fresnel curve and the Kiessig fringes are related to the morphology and electronic density of the surface layer(s) (SI Appendix, Fig. S4). Modeling of the XRR data allows determination of the electronic density profiles normal to the surface (Fig. 1C), yielding, in turn, the average thickness, density, and roughness of the layer(s) close to the surface of a material. The fitting results are provided in SI Appendix, Table S1 and the fitting parameters are illustrated in the schematic in Fig. 1C and SI Appendix, Fig. S6.

The experimental XRR curve of MgO(100)_{untreated} (SI Appendix, Fig. S7) exhibits Kiessig fringes in the range of 0.1 \AA^{-1} to 0.4 \AA^{-1} . These fringes can be attributed to both the presence of imperfect terminations at both the surface and subsurface of the crystal (34) and adsorbed species (such as water, hydroxyl, and carbonates due to exposure of the crystal to ambient conditions prior to the experiment; SI Appendix, Fig. S5) (21, 35). The presence of a defective surface is in line with previous studies (using ultraviolet diffuse reflectance and scanning tunneling microscopy) that have described the MgO(100) surface as composed of terraces of different heights,

separated by defects such as steps and kinks (36–40). MgO(100)_{He} exhibits a subtle Kiessig fringe at *ca.* 0.3 \AA^{-1} to 0.7 \AA^{-1} (Fig. 1B). Comparing MgO(100)_{He} to the untreated sample MgO(100)_{untreated}, we observed that pretreatment leads to a decrease in the fringe periodicity and its amplitude that translates to a decrease of the thickness of the surface layer as can be seen from the electronic density profile (Fig. 1B and SI Appendix, Fig. S7). This indicates that the adsorbed surface groups have been (partially) removed after the thermal treatment in He. However, the complete removal of all of the surface species would require higher temperatures; thus residual hydroxyl and carbonates species remain on MgO(100)_{He} (21). This is in line with in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results, showing that carbonates and hydroxyl groups (adsorbed onto the surface of untreated MgO) are partially removed after a treatment in an inert atmosphere at 450 °C (SI Appendix, Fig. S5). Thus, the surface of MgO(100)_{He} can be considered as an imperfect MgO surface containing also residual adsorbed hydroxyl and carbonates species. Accordingly, to fit the XRR data, we have used a model composed of 1) a semiinfinite substrate representing the bulk MgO and 2) a slab to model the

surface layer, referred to as “bulk MgO” and “surface layer,” respectively (Fig. 1B and *SI Appendix, Table S1*). The thickness of the surface layer in MgO(100)_{-He} was found to be *ca.* $d_{\text{surf}} = 11 \text{ \AA}$. The roughness of the surface layer (σ_{surf}), defined as the root-mean-square elevation of the surface contour (41), was determined to be 2.4 \AA , while the roughness of the interface between the bulk and surface MgO layers equals 3.3 \AA . The density of the surface layer in MgO(100)_{-He} was determined to be 2.6 g/cm^3 , that is, 75% of the bulk density of MgO. Overall, the decrease in thickness of the surface layer, d_{surf} , and decrease in interface roughness, σ_{bulk} , after 15 min of treatment in He at $450 \text{ }^\circ\text{C}$ is very likely due to the decomposition of surface species and a temperature-induced smoothening of the surface. Smoothening of a MgO(100) surface has been observed previously after thermal treatment using atomic force microscopy (35).

A noticeable change in the XRR curve can be observed for MgO(100)_{-CO₂} as compared to MgO(100)_{-He}. The XRR of MgO(100)_{-CO₂} shows a pronounced well-defined fringe between *ca.* 0.2 and 0.5 \AA^{-1} , indicating a thicker surface layer that is ascribed to the formation of carbonates on the surface. The calculated electronic density profile (Fig. 1C) shows an increase in the thickness of the surface layer by *ca.* 7 \AA ($d_{\text{surf}} = 18 \text{ \AA}$, $\sigma_{\text{surf}} = 2.5 \text{ \AA}$, and $\sigma_{\text{bulk}} = 4.0 \text{ \AA}$ MgO(100)_{-CO₂}; *SI Appendix, Table S1*) and a decrease in the density of the surface layer of MgO(100)_{-CO₂} to 2.3 g/cm^3 when compared to MgO(100)_{-He}. Previous combined DRIFTS and DFT studies have shown that CO₂ is adsorbed preferentially as a monodentate carbonate species at surface defects of MgO(100), such as undercoordinated O²⁻_{4C} steps and O²⁻_{3C} kinks (21, 30, 42). In line with these studies, in situ DRIFTS analysis on a MgO powder (*SI Appendix, Fig. S5*) confirms that a partially cleaned MgO surface (by thermal treatment in an inert atmosphere) shows the formation of carbonates and bicarbonates (the latter formed through the reaction of CO₂ with surface hydroxyls) after exposure to a CO₂ flow at $330 \text{ }^\circ\text{C}$, indicating that the increase in the thickness of the surface layer can be attributed to adsorbed carbonates. The XRR results are consistent with the observation that the GIXRD pattern of MgO(100)_{-CO₂} (*SI Appendix, Figs. S8 and S10*) shows no crystalline MgCO₃, indicating that the formation of carbonates on bare MgO(100) is largely limited to the surface, in line with previous studies (18, 21).

Turning to the NaNO₃-promoted material, to model the XRR data of NaNO₃-MgO(100)_{-He}, we use an additional infinitely thick slab to account for the molten NaNO₃, yielding a model that consists now of 1) “bulk MgO,” 2) “surface layer,” and 3) “molten NaNO₃” (Fig. 1C). The model yields a thickness of 14 \AA for the surface layer at the NaNO₃/MgO interface, with a density of 2.9 g/cm^3 (*ca.* 80% of the bulk density of MgO). We observe that the thickness and average electronic density of the surface layer of NaNO₃-MgO(100)_{-He} are comparable to MgO(100)_{-He} within the experimental error. Here, the modeled thicknesses are 11 and 14 \AA and the densities are 2.6 and 2.9 g/cm^3 , for MgO(100)_{-He} and NaNO₃-MgO(100)_{-He}, respectively (*SI Appendix, Table S1*). Based on these observations, we assume that, under identical (inert) pretreatment conditions, the presence of NaNO₃ does not lead to significant differences in the amount of remaining hydroxide and/or carbonate species on the respective surfaces. Interestingly, the roughness of the “bulk MgO,” σ_{bulk} , increases to *ca.* 7.3 \AA in comparison to 3.3 \AA for MgO(100)_{-He}. We interpret this roughening of the MgO(100) surface by the dissolution of surface MgO [Mg²⁺ and O²⁻] into the molten NaNO₃ (12, 18). Thus, our XRR measurements provide in situ evidence of the modification of the MgO(100) surface (partial dissolution of [Mg²⁺ . . . O²⁻] ionic pairs) by molten salts.

XRR data of the NaNO₃-promoted sample, after its exposure to CO₂ (NaNO₃-MgO(100)_{-CO₂}), show a more rapid intensity decrease with Q_z when compared to NaNO₃-MgO(100)_{-He}. In addition, we cannot observe any Kiessig fringes. These results indicate that a significant roughening of the surface must have occurred (Fig. 1C). Fitting with the three-layer model yielded a significant

increase in σ_{bulk} (the roughness of the interface between the bulk MgO and surface layer) to 29 \AA (*SI Appendix, Table S1*) which is approximately 4 and 7 times higher than that in NaNO₃-MgO(100)_{-He} and MgO(100)_{-CO₂}, respectively. It should be noticed that the “surface layer” in NaNO₃-MgO(100)_{-CO₂} is associated with the formation of MgCO₃. Hence, changes in σ_{bulk} represent an average roughness of the MgCO₃/MgO interface, while the thickness of the surface layer reflects the average thickness of the MgCO₃ product. This observation has two important implications. First, the MgCO₃ product is not formed as a homogenous, flat layer on the surface of MgO(100), in agreement with electron microscopy studies (*vide infra*). Second, the (structural) transformation of the MgO surface layer (i.e., the MgO/NaNO₃ interface), as quantified by its total roughness, is at least 4 times more pronounced when the NaNO₃-promoted sample is exposed to CO₂ compared to the surface restructuring arising purely due to the presence of NaNO₃. It should be noticed that XRR provides averaged information of the changes occurring at the MgO/NaNO₃ interface; the exact morphology (size and shape) of the MgCO₃ product will be assessed by electron microscopy (*vide infra*) that provides local information of the surface morphology.

To probe, in more detail, the formation of crystalline phases at the surface of the promoted material, we employ in situ GIXRD. In GIXRD data, a single crystal appears as dots, while a polycrystalline material with randomly oriented crystallites would reveal itself in the form of Debye-Scherrer rings with a homogeneous distribution of intensities along the azimuthal angle relative to the incident X-ray beam angle, φ . The crystal orientation is characterized by the distribution of intensities along φ (43, 44). The two-dimensional (2D) pattern of NaNO₃-MgO(100)_{-He} (*SI Appendix, Fig. S9*) shows single crystalline Bragg reflections (bright spots) due to the (200), (020), and (220) planes of MgO, indicative of the single crystal nature of the MgO(100) substrate (space group *Fm-3m*; Inorganic Crystal Structure Database (ICSD): 9863); we could not observe rings, due to polycrystalline MgO. Since NaNO₃ is molten under the experimental, in situ conditions employed, no Bragg reflections due to the NaNO₃ phase are present in the GIXRD patterns, yet an amorphous halo due to diffuse scattering of molten NaNO₃ is observed at *ca.* 1.5 \AA^{-1} . The corresponding GIXRD 2D pattern of NaNO₃-MgO(100)_{-CO₂} (Fig. 2A) reveals reflections due to crystalline MgCO₃ (space group *R-3c*; ICSD: 40117). The MgCO₃ reflections appear as spotty diffraction rings, revealing a preferred distribution of intensities at certain values of φ , highlighting that the MgCO₃ product consists of crystals with a marked preferred orientation (more insight into the orientation and size of the MgCO₃ crystals is gained by electron microscopy, *vide infra*). To analyze the distribution of the orientations of the crystallites formed, we plot the intensities of the MgCO₃(104) and MgCO₃(006) reflections as a function of φ (Fig. 2C). This analysis shows that a large proportion of the MgCO₃(104) and MgCO₃(006) reflections are preferably oriented at *ca.* $\varphi = 10^\circ, 45^\circ, \text{ and } 90^\circ$. Thus, these in situ GIXRD experiments reveal the formation of well-defined crystalline domains with a marked orientation along the [200], [220], and [020] directions of the MgO(100) substrate during product growth (Fig. 2A). The growth of MgCO₃ was analyzed with atom-scale resolution by HRTEM and will be discussed in more detail further below.

To probe the vertical location of the MgCO₃ product with respect to the NaNO₃/MgO interface, we collected GIXRD while varying the position of the sample in the z direction with respect to the incident beam (Fig. 1A). This scan was performed between *ca.* $30 \text{ }\mu\text{m}$ above and *ca.* $10 \text{ }\mu\text{m}$ below the NaNO₃/MgO interface, with a step size of $2 \text{ }\mu\text{m}$, providing information on the spatial distribution of the crystalline phases (*SI Appendix, Fig. S11*). *SI Appendix, Fig. S12* plots the integrated intensities of the MgCO₃(104) and MgO(220) reflections as a function of the z position with regard to the NaNO₃/MgO interface. The position of the NaNO₃/MgO interface was determined as the maximum of the derivative of the

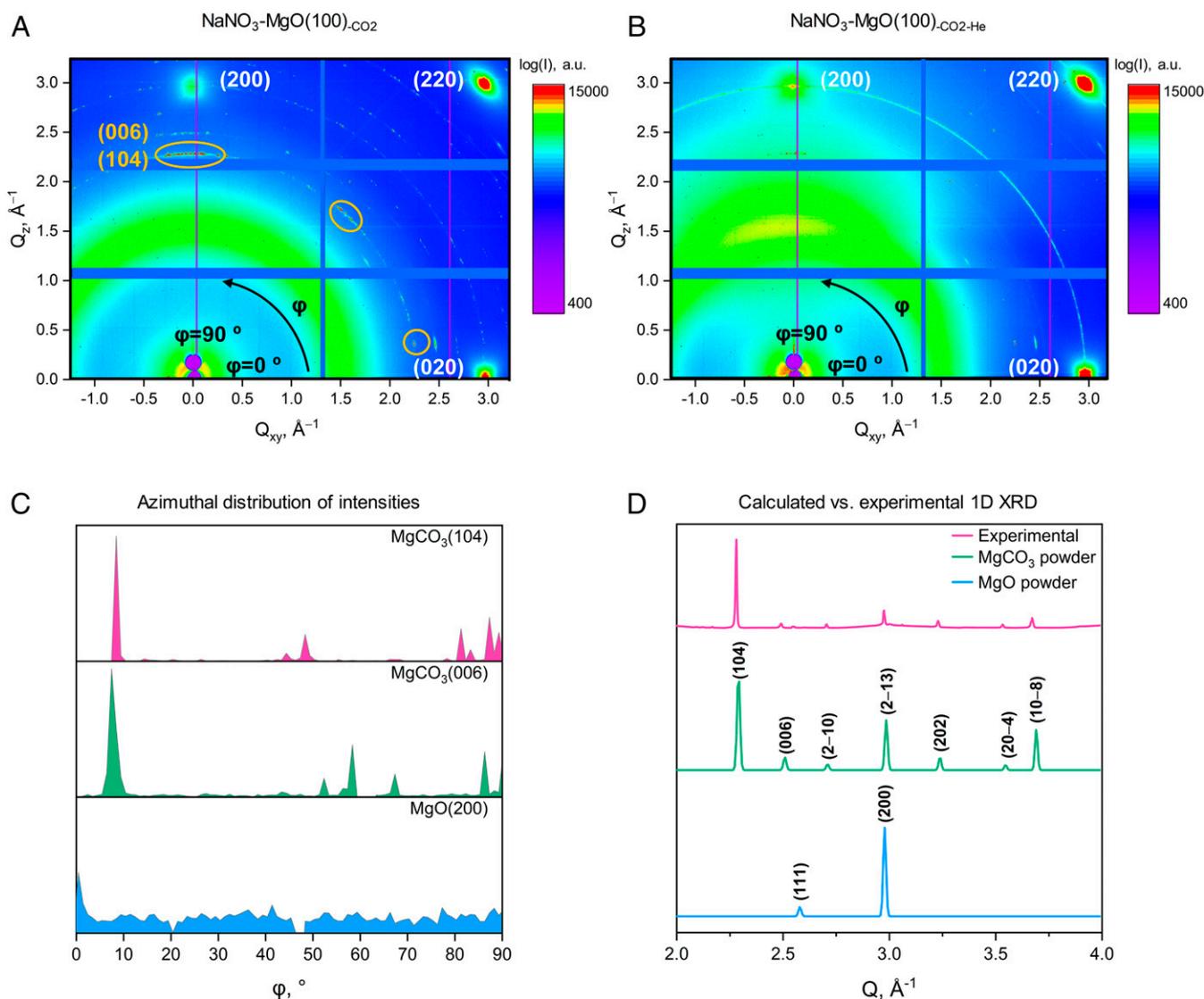


Fig. 2. The 2D GIXRD patterns of (A) $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$ and (B) $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2\text{-He}$. (C) Intensity of $\text{MgCO}_3(104)$ and $\text{MgCO}_3(006)$ reflections as a function of the azimuthal angle φ in $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$ and the $\text{MgO}(200)$ reflection in $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2\text{-He}$. (D) Azimuthally integrated GIXRD pattern of $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$ (background subtracted) and simulated powder XRD ($Q = 4\pi\sin(\theta)/\lambda$) patterns of MgCO_3 (ICSD: 40117) and MgO (ICSD: 9863).

$\text{MgO}(220)$ intensity vs. the sample position (*SI Appendix, Fig. S13*). The fact that the maximum intensity of the MgCO_3 reflection is observed close to the position of the NaNO_3/MgO interface suggests that MgCO_3 grows in the vicinity of the MgO surface, as opposed to a precipitation inside the NaNO_3 melt (12, 16). This analysis provided average and microscale information on the location of the formed MgCO_3 , yet more detailed insight, that is, with higher spatial resolution, into the MgCO_3/MgO interface was obtained by HRTEM (*vide infra*).

After carbonation, the sorbent regeneration step, that is, the decomposition of MgCO_3 back to MgO , was probed by treating $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$ at 450°C in He for *ca.* 15 min ($\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2\text{-He}$). After the regeneration step, the MgCO_3 reflections largely disappeared, with only a very weak $\text{MgCO}_3(104)$ reflection remaining (Fig. 2B). We observe the appearance of polycrystalline Debye-Scherrer rings due to MgO , indicating the formation of randomly orientated MgO crystallites after the decomposition of (oriented) MgCO_3 . This observation is confirmed further by the analysis of the azimuthal distribution of the $\text{MgO}(200)$ intensity (Fig. 2C). The intensity of MgO is distributed relatively homogeneously, that is, without a clear preferential orientation along

φ , indicating a random orientation of the MgO crystallites that are formed via the decomposition of MgCO_3 (in Fig. 2C, the high-intensity spot of the $\text{MgO}(100)$ single crystal substrate is found at *ca.* $\varphi = 0^\circ$).

In summary, in situ XRR shows that, under a CO_2 flow, a surface layer with a lower density and thickness of *ca.* 7 \AA forms on bare $\text{MgO}(100)$ due to CO_2 sorption; this takes place without appreciable changes in the surface roughness. The surface roughness of MgO changes when coated with NaNO_3 (330°C in He), but even more drastically when exposed to CO_2 (330°C), due to the formation of highly oriented MgCO_3 crystallites at the NaNO_3/MgO interface, as opposed to a precipitation with random orientation inside the molten salt (a growth at the TPB cannot, however, be excluded, due to the high mobility of the molten salt). Indeed, the surface roughness of NaNO_3 -promoted $\text{MgO}(100)$ is *ca.* 4 times higher under a CO_2 flow compared to He flow. In the following, we apply electron microscopy (SEM and HRTEM) to provide further insight into 1) the morphology of the MgCO_3 crystals formed, 2) MgO surface alterations, and 3) the atomic arrangement at the MgCO_3/MgO interface. Since MgCO_3 crystals do not form on bare MgO , electron microscopy is only applied to the $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$ system.

Morphology of the MgCO₃ Crystals Formed on MgO. To describe the morphology of the MgCO₃ product formed during carbonation, we turned to SEM. Pretreatment and carbonation conditions similar to those used in the in situ XRR-GIXRD experiment (NaNO₃-MgO(100)-CO₂) have been used for the as-prepared NaNO₃-MgO(100). In addition, a rinsing step in water was necessary to remove the NaNO₃ layer and to reveal the MgCO₃ product underneath. Prior to morphological analysis, Raman microspectroscopy mapping was used to unequivocally identify the MgCO₃ product on the MgO(100) surface (*SI Appendix, Fig. S6*).

The growth habit of the formed magnesium carbonate on NaNO₃-MgO(100)_{CO₂-RW} (the subscript RW refers to a rinse in water) as visualized by SEM is shown in Fig. 3 and *SI Appendix, Fig. S14*. Planar views of the MgCO₃ are displayed in Fig. 3A and B, and a cross-section, obtained by a focused ion beam (FIB) cut, is shown in Fig. 3C. SEM demonstrates that, on NaNO₃-MgO(100)_{CO₂-RW}, MgCO₃ grew as individual 2D crystals, or “2D islands,” on the surface of MgO with a diameter in the range of 10 μm to 50 μm and a thickness between 0.2 and 2 μm. The observed 2D island-type morphology is in line with in situ GIXRD data which revealed that carbonation of NaNO₃-MgO(100) leads to the formation of crystallites of MgCO₃ with a marked preferred orientation. The individual MgCO₃ islands, exemplified in the images shown in Fig. 3A and B, have a growth habit that can be described as a “sectored plate” showing characteristic straight dendrites with triangular tips branching radially from the center of the crystal (45–47). Side branches have grown from the primary branches and coalesced with the MgCO₃ product from neighboring branches. At some locations of the surface of NaNO₃-MgO(100)_{CO₂-RW}, islands of MgCO₃ grow separated by up to 200 μm, while, in other locations, the islands have grown closer to each other and merged to form larger clusters as observed in *SI Appendix, Fig. S15*.

Two-dimensional island-type growth with a sectored-plate morphology has been observed previously when precipitating MgCO₃ (48), CaCO₃ (49), ice crystals (45), and ice analog crystals (Na₂SiF₆) (46) from supersaturated solutions. The growth habits of ice crystals and ice analog crystals have been characterized and mapped in great detail with respect to the level of supersaturation and temperature (46–49). Ice analog crystals such as sodium fluosilicate (Na₂SiF₆) grow in an aqueous solution (crystal growth induced by

evaporation), whereby the growth habit depends strongly on the rate of evaporation (i.e., supersaturation level). For lower levels of supersaturation, a compact sectored-plate morphology is obtained, while, for higher levels of supersaturation, a less compact sectored-plate morphology occurs that can turn into stellar dendrites (46). Variations in the growth habit (difference in the length of the primary dendrites compared to the side branches), as observed also in the MgCO₃ crystals shown in Fig. 3A and B, may thus be a result of local heterogeneities in the level of supersaturation of MgCO₃ (i.e., [Mg²⁺...CO₃²⁻] ionic pairs). Generally, crystals can form from a supersaturated solution through either homogenous or heterogeneous nucleation (50). Here, the surface of MgO provides heterogeneous nucleation sites (characterized by a lower energy barrier of nucleation in comparison to homogeneous nucleation) (51). It is likely that the MgCO₃ nuclei are formed at defect sites on the MgO surface, where it is energetically more favorable for ions to bind (52). Hence, one would expect a polycrystalline powder material containing a variety of exposed facets (yet with the dominant facet being MgO(100)), grain boundaries, and/or defects such as dislocations to have a higher density of potential nucleation sites. Such a nucleation and crystal growth-based mechanism would be described by a sigmoidal-shaped (S-shaped) kinetic curve (50, 53). Indeed, the carbonation of a powder sample of MgO promoted with NaNO₃ shows an S-shaped kinetic curve and can be initiated by nuclei seeding (13, 16, 18). The resemblance of nucleation and crystal growth is important because it confirms that the MgO(100) model surface coated with NaNO₃ is mechanistically representative for practically more relevant (and scalable) powder samples of MgO promoted with NaNO₃.

From the cross-section shown in Fig. 3C, it is clear that the carbonate crystal has grown both inward and outward from the original NaNO₃/MgO interface (the dashed yellow line represents the location of the nonreacted (i.e., as-received) MgO surface, that is, the NaNO₃/MgO interface). A SEM image of the as-received MgO(100) single crystal is shown in *SI Appendix, Fig. S17*. The 2D growth of the carbonate product has a crucial implication for the design of MgO-based sorbents. Considering that MgCO₃ appears to grow less than 2 μm in the direction perpendicular to the surface (z direction), it will be difficult to fully convert large (thick, >2 μm) MgO crystallites. Hence, this observation suggests that MgO-based CO₂ sorbents

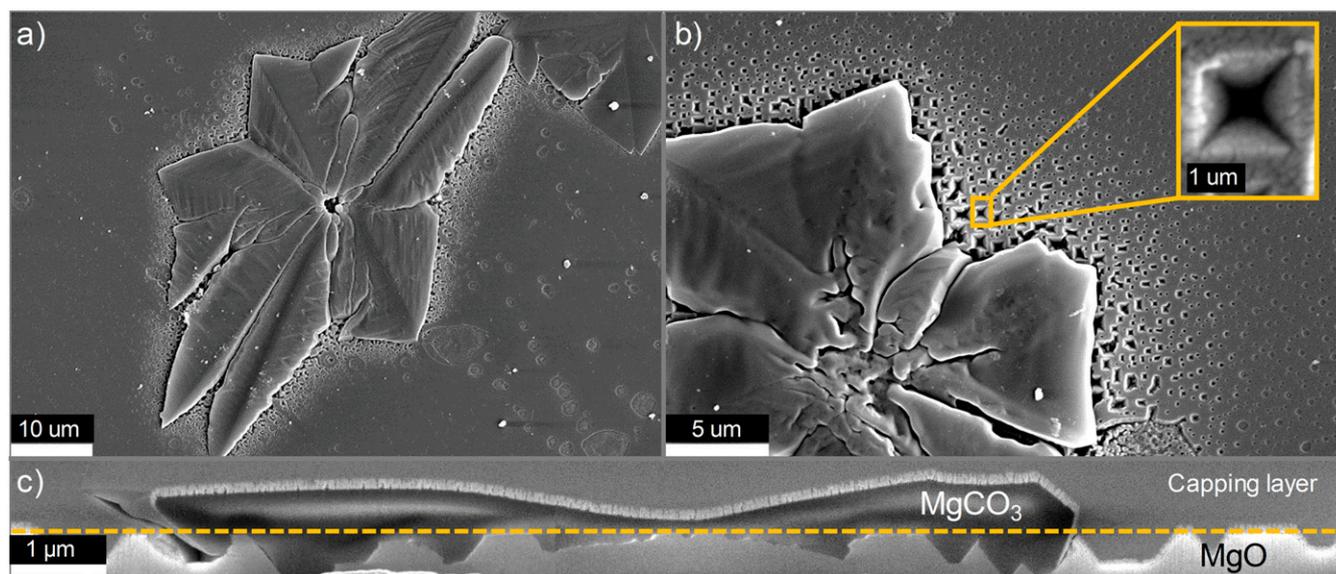


Fig. 3. SEM images of MgCO₃ formed on NaNO₃-MgO(100)_{CO₂-RW}: (A and B) images of two representative MgCO₃ features at different magnifications; *Inset* shows a pyramid-shaped dissolution pit on the MgO surface near the MgCO₃ product. (C) Cross-section of the MgCO₃ product formed on top of MgO. Dashed line highlights the location of the originally flat surface of the MgO(100) single crystal promoted with NaNO₃ before its reaction with CO₂.

should have a high MgO surface area that is in contact with NaNO₃, which can be achieved by small (i.e., submicrometric) MgO particles/crystallites being coated with alkali metal salt. Further, an excessive growth of the MgO crystallites/particles (over repeated CO₂ capture and regeneration cycles) may, in turn, lead to a deactivation of the sorbents (13, 54).

Etched MgO(100) Surface Surrounding the MgCO₃ Product. A very interesting structural feature in Fig. 3 are micrometer-sized pyramidal pits surrounding the magnesium carbonate crystals in NaNO₃-MgO(100)-CO₂-RW. Firstly, the pits are approximately square-shaped inverse pyramids with the square bases being co-oriented and parallel to the [100] direction of MgO(100). Secondly, there is a gradient in the size of the pits, with larger pits (>1 μm) being close to the MgCO₃ crystals and a decreasing pit size with increasing distance from the MgCO₃ crystal; we do not observe any pits at distances larger than 5 μm to 10 μm away from the MgCO₃ crystal. The pits are also present in the MgO substrate below the MgCO₃/MgO interface, as can be seen in the cross-section view (Fig. 3C). Moreover, a high-angle annular dark-field (ADF) scanning transmission electron microscope (HAADF-STEM) image of the MgCO₃/MgO(100) interface reveals a Z-contrast (atomic number) gradient in the interface region below the MgCO₃ crystal (*SI Appendix, Fig. S20*). The contrast gradient reflects a MgO depletion layer, which is due to the transport of MgO species toward the growing carbonate crystal. Similarly, the gradient of the pyramid size around the carbonate crystal can be considered as a MgO depletion layer along the MgO surface. As the diffusion length of the MgO species toward the MgCO₃ crystal increases, the pit sizes decrease. Therefore, the largest etching pits are observed in the vicinity of the carbonate, and there is a gradual decrease in their size with increasing distance from the carbonates. Hence, we can interpret this observation as a 2D hemispherical region of MgO depletion around the MgCO₃ product, since it is observed both in the growth plane of the carbonate on the MgO surface and under the 2D carbonate crystals.

Next, we may consider why the depletion of MgO near the surface followed by diffusion would lead to such crystallographically ordered defects (i.e., pyramidal pits). The observed pyramidal shaped pits are analogous to the etching pits observed on single crystalline MgO surfaces that are formed through acid treatment (52, 55, 56). The dissolution of MgO and the etching of pits are initiated preferentially at surface defects (e.g., edge dislocations) and are energetically favored to proceed along the [111] direction of the MgO(100) substrate, forming the characteristic pyramidal shape (52). Moreover, it is well known that diffusion is favored along dislocations, which may accelerate the etching process near the carbonate product (57, 58).

Our samples were rinsed in deionized water (neutral pH) for 1 min to remove the NaNO₃ coat, allowing for an SEM analysis of the otherwise buried MgCO₃ product. It should be noted that previous studies showed that the formation of the pits required a treatment with an aqueous acid solution (pH = 5.7) for 72 h (52); hence, the pits cannot form during the rinsing step with deionized water. Additionally, a control experiment using NaNO₃-coated MgO(100) treated at 420 °C for 1 h and 330 °C for 5 h in N₂ followed by rinsing with deionized water (NaNO₃-MgO(100))_{N₂-RW} confirmed the absence of etched pits when the sample was not exposed to a CO₂ flow (*SI Appendix, Fig. S16*). Therefore, based on the similar shape of the etched pyramids in our materials to a material derived via acid etching, we can infer that the observed pits are due to the dissolution of MgO in the presence of both NaNO₃ and CO₂ and are presumably initiated at the vicinity of surface defects (52).

Overall, the SEM analysis complements our in situ XRR and GIXRD results providing insight into the 2D growth of MgCO₃ islands, and the etching of the MgO surface when both NaNO₃ and CO₂ are present (*SI Appendix, Fig. S16*). This suggests that the interaction of CO₂ and NaNO₃ leads to a faster rate of MgO

dissolution when compared to NaNO₃-promoted MgO in an inert gas environment. When the dissolution of MgO (and its reaction with CO₂) yields a critical level of supersaturation, magnesium carbonate will crystallize. Lastly, as soon as MgCO₃ is formed, it promotes the further etching of MgO species, which diffuse toward the growing carbonate and provide building blocks for further, increased MgCO₃ growth. It is also important to recall that MgCO₃ does not nucleate and grow in the absence of a NaNO₃ promoter. Therefore, the modification of the MgO(100) surface by molten salts and the enhanced dissolution of MgO under CO₂ likely accelerates the nucleation and growth of MgCO₃. In other words, the carbonation reaction is autocatalytic (i.e., the reaction product catalyzes further reaction), and, for such reactions, the product concentration is given by a sigmoidal kinetic behavior as has been observed for powder samples of alkali metal salt-promoted MgO (16). We remark that NaNO₃ is mobile on the surface of MgO(100) under the operating conditions, preventing the provision of a definitive answer to the question whether nucleation is most favorable in the TPB (i.e., the portion of the NaNO₃/MgO interface in contact with CO₂) or at the “buried” NaNO₃/MgO interface. However, the 2D hemispherical shape of the MgO depletion layer around the 2D MgCO₃ islands points toward a rapid growth of MgCO₃ at the buried NaNO₃/MgO interface, as it is unlikely that an expanding TPB exists at the perimeter of a growing 2D MgCO₃ crystal. Since both NaNO₃ and CO₂ are necessary to facilitate a fast dissolution of MgO, CO₂ must be dissolved (13, 59, 60) in the molten salt to reach the reaction interface.

Atomic Scale Insight into the MgCO₃/MgO Interface by TEM. Having established that, under carbonation conditions, 1) a noncrystalline thin (*ca.* 7 Å) surface layer of carbonates forms on bare MgO(100) and 2) MgO(100) coated with NaNO₃ leads to the formation of crystallites of MgCO₃ with a marked preferred orientation at the interface between NaNO₃/MgO, we examine the atomic arrangement at the interface between MgO and the formed MgCO₃ crystals by TEM-based techniques.

Spatially resolved electron energy loss spectroscopy (EELS) was utilized to obtain high-resolution information on the electronic structure of the oxygen and carbon atoms, allowing us also to map the phases with high resolution at the interface of NaNO₃/MgO(100) in NaNO₃-MgO(100))_{CO₂-RW}. Similar to the SEM characterization, our TEM analysis focuses on NaNO₃-MgO(100))_{CO₂-RW} to gain atomic-scale insight into the formed MgCO₃. Fig. 4 shows a HAADF-STEM image of the MgCO₃/MgO(100) interface and the simultaneously recorded STEM-EELS data (acquired in the range of 250 eV to 400 eV for C K edge and 520 eV to 620 eV for O K edge). Elemental maps were obtained by background subtraction and the EELS spectrum peak integration using energy windows as shown in Fig. 4 F and G. From top to bottom, the layers are identified by their electronic structure as amorphous carbon (protection layer of amorphous carbon used for TEM lamella preparation), MgCO₃, and MgO. In addition, a clear MgCO₃/MgO phase separation is observed, with some overlap between the magnesium carbonate and the oxide phases (marked with arrows on Fig. 44) due to the inclined interface.

To gain insight into the atomic arrangement at the MgCO₃/MgO interface, we performed TEM analysis of a FIB cut lamella. Fig. 5A shows a selected area electron diffraction (SAED) pattern taken from the cross-section of a TEM lamella that was cut parallel to the (100) plane of the MgO support. Two sets of single crystalline diffraction spots can be observed and one set each assigned to the [100]-zone axis of MgO and the [310]-zone axis of MgCO₃. Both diffraction patterns are co-oriented along the [001] directions, indicating an epitaxial growth of the MgCO₃(001) plane onto the MgO(001) plane. This is in a good agreement with our in situ GIXRD analysis of the sample. More details on the local structure at the interface between MgO and MgCO₃ are provided by HRTEM (Fig. 5B, viewed along the MgO[100]-zone axis), showing a nearly

coherent interface between the two phases. The diffuse contrast in some regions can be explained by an overlap of the two lattices. An analysis of a further TEM lamella that was cut parallel to the MgO(110) plane provides a further confirmation of the epitaxial growth of MgCO₃ onto the MgO support (SI Appendix, Fig. S21).

Due to the different crystal structures of the film and the substrate (rhombohedral MgCO₃ vs. cubic MgO) and a large lattice mismatch (MgCO₃ $d_{006} = 2.5$ Å; ICSD: 40117; MgO $d_{002} = 2.1$ Å; ICSD: 9863), one would expect a severely strained MgCO₃ film with a compressive strain in the direction perpendicular to the interface. From the HRTEM micrograph in Fig. 5C, a strain map is obtained by performing a geometric phase analysis (GPA) (61) along the [001] direction. Indeed, in Fig. 5D, compressive strains are observed in the MgCO₃ phase at the interface region, but with a strain value below 1% (the regions outside the MgCO₃ crystal were not analyzed in the GPA map and correspond to noise). The obtained strain value is considerably lower than the expected value of 15% based on the large lattice mismatch. A possible stress relaxation mechanism in an epitaxial layer that has a large lattice mismatch with a substrate involves the incorporation of misfit dislocations into the interface between the epitaxial layer and substrate (62). Fig. 5E shows a bright-field (BF)-STEM image of a cross-section oriented along the MgO [100] direction. In contrast to the interface of the same orientation shown above (Fig. 5B, showing the interface viewed along the MgO[100]-zone axis), we can observe the edge-on interface of the MgCO₃(006) and the MgO(002) planes in Fig. 5E. Fourier filtering of the BF-STEM image using lattice fringes corresponding to the MgCO₃(006) and the MgO(002) planes reveals a regular arrangement of misfit dislocations in the MgCO₃/MgO interface (Fig. 5F). An interface of this type is characteristic for

the so-called domain-matching epitaxy, where m lattice parameters in the epilayer match with n lattice parameters in the substrate. The dimension of the domain is the length of the distance over which lattice matching is achieved repeatedly (63). As the lattice constant of MgCO₃ ($d_{006} = 2.5$ Å) is larger than that of MgO ($d_{002} = 2.1$ Å), the extra half-planes of the misfit dislocations appear in the MgO substrate. In the region shown, there are two domains of five MgCO₃ planes matching six MgO planes, alternating with one domain of six MgCO₃ planes matching seven MgO planes (Fig. 5F). In addition, due to an inclined interface with respect to the direction of the electron beam, the overlap of the two structures gives rise to a Moiré pattern (see red arrows in Fig. 5F). The rotation of the Moiré pattern reflects the angular mismatch between the two lattices.

Collectively, our TEM data reveal an epitaxial growth of the MgCO₃ crystal with respect to the MgO substrate in agreement with the preferred orientation observed in our in situ GIXRD analysis. Due to the relatively large mismatch in the lattice constants of MgCO₃ and the MgO support, the strained interface is relaxed through the incorporation of lattice misfit dislocations. This type of interface is called domain-matching epitaxy, where m lattice parameters in the epilayer match with n lattice parameters in the substrate. The domain size is the regularly repeating distance over which lattice matching is maintained.

Conclusions

In conclusion, we have reported on the morphological and structural changes occurring at the surface and interfaces of a model CO₂ sorbent, that is, MgO(100) coated with a NaNO₃ promoter under relevant CO₂ capture conditions as obtained by in situ XRR-GIXRD and ex situ SEM and TEM. Our findings provide important puzzle pieces for the elucidation of the role of AMS for the

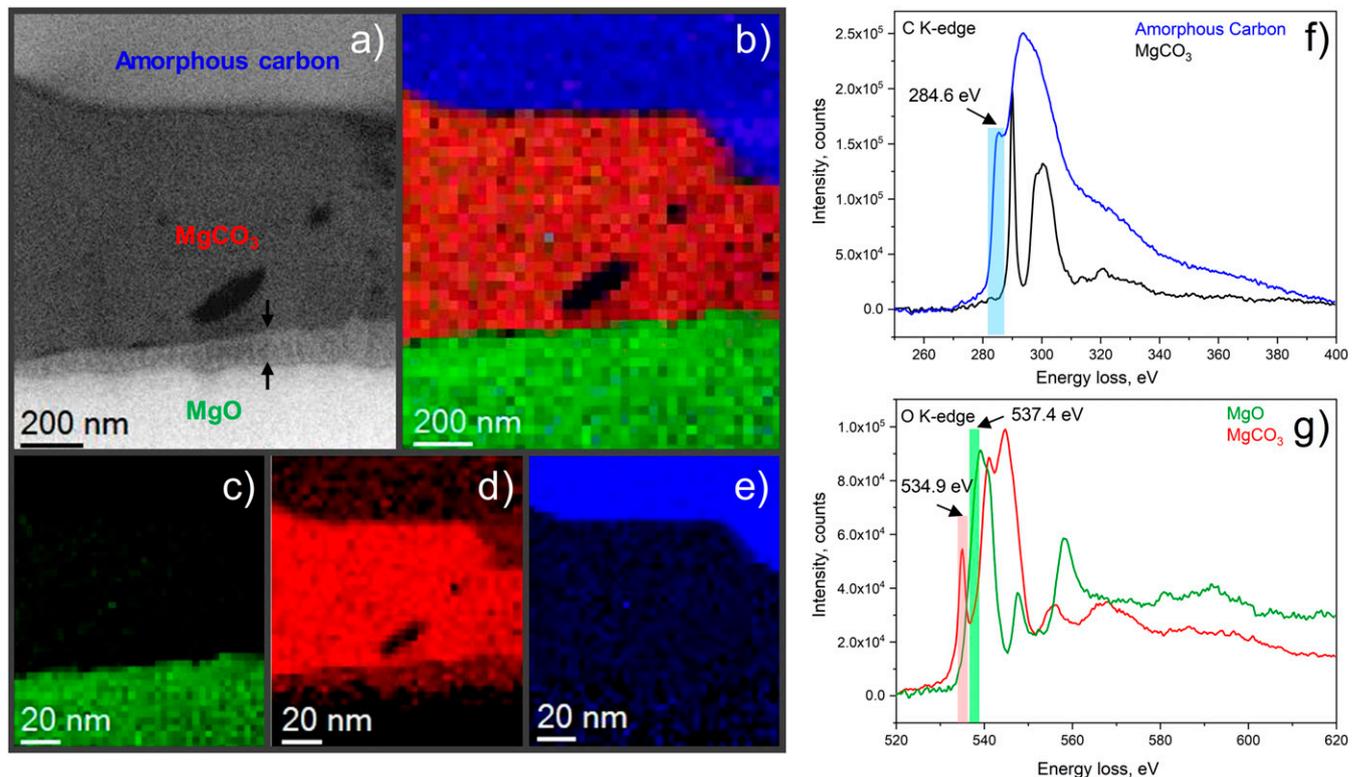


Fig. 4. EELS mapping of the MgCO₃/MgO interface oriented along the MgO[100] direction: (A) HAADF-STEM image (the arrows show an overlapping region of MgCO₃/MgO layers due to the inclined interface); (B) overview STEM-EELS elemental maps of the interface. Individual STEM-EELS elemental maps of (C) O K edge of MgO, (D) O K edge of MgCO₃, and (E) C K edge of amorphous carbon (protection layer used for TEM lamella preparation); (F and G) corresponding EELS spectra with marked energy windows used for elemental maps.

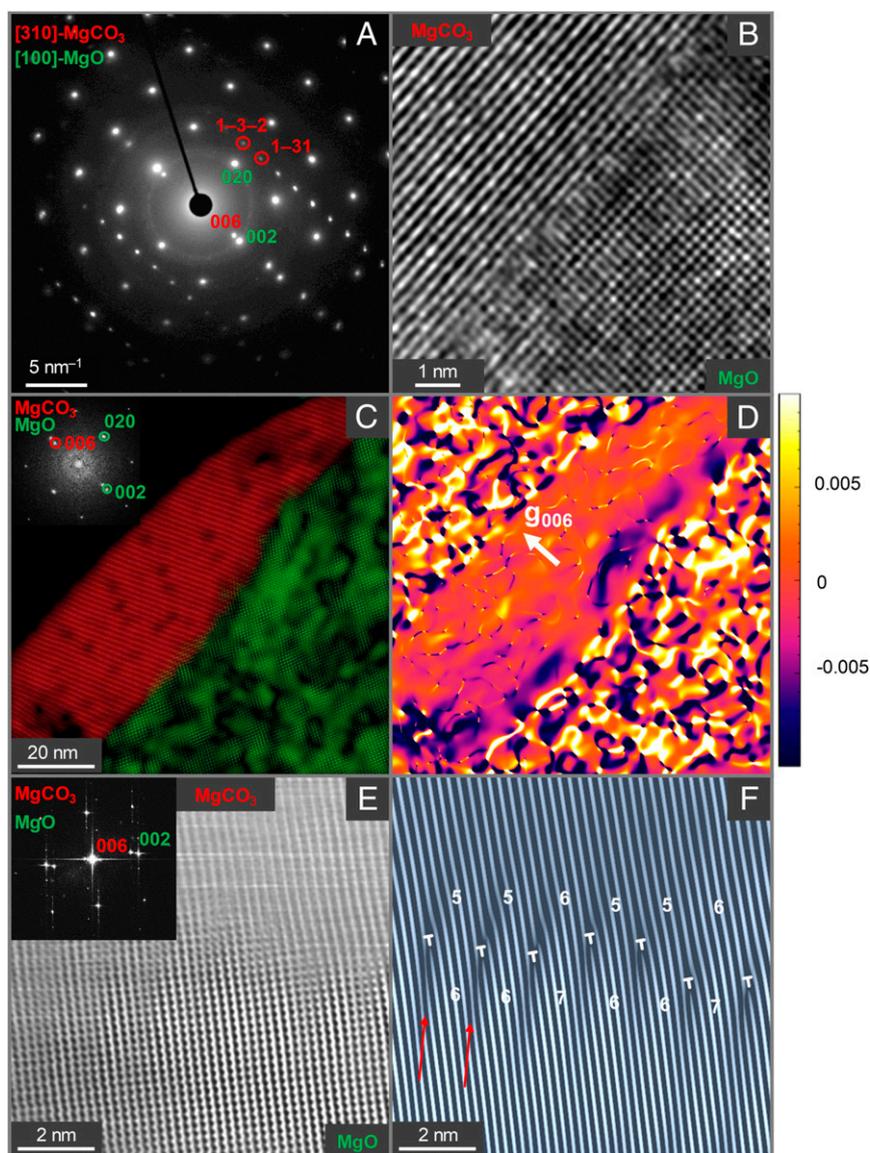


Fig. 5. Structure of the MgCO_3/MgO interface and geometrical phase analysis: (A) SAED pattern of the TEM lamella oriented along the $\text{MgO}[100]$ direction; (B) HRTEM micrograph of the interface viewed along the $\text{MgO}[100]$ zone axis. (C) The inverse FFT pattern obtained by applying a mask to the $\text{MgCO}_3(006)$ and the $\text{MgO}(002)$ reflections in the corresponding fast Fourier transform pattern (*Inset*). (D) HRTEM-GPA strain analysis map of the (006) strain component of the MgCO_3 film. (E) A bright-field STEM image of the edge-on interface viewed along the $\text{MgO}[100]$ zone axis (corresponding FFT pattern is shown as an *Inset*); (F) inverse Fourier-filtered image showing misfit dislocations in the $\text{MgCO}_3(006)$ and the $\text{MgO}(002)$ plane system; the Moiré patterns are highlighted by red arrows.

rapid CO_2 uptake of MgO . Under practically relevant CO_2 capture conditions, we have observed a roughening of the MgO surface and the formation of MgCO_3 crystallites that grow with a preferred orientation on the surface of $\text{MgO}(100)$. This work provides in situ evidence that MgCO_3 grows favorably at the interface MgO/NaNO_3 , a finding that will influence the design and rational advancement of more-effective MgO -based CO_2 sorbents. When treated under inert conditions (at 330°C), the surface roughness of NaNO_3 -promoted MgO increases by *ca.* 4 Å compared to a pristine $\text{MgO}(100)$ crystal, possibly due to MgO dissolution into the melt. The surface roughness increases drastically when the coated sample is also exposed to CO_2 . Morphological analyses of the MgCO_3 crystals formed by SEM revealed a 2D MgCO_3 islands-type growth with a sectored-plate morphology, whereby the thickness of the MgCO_3 product is less than 2 μm . The morphology agrees well with a heterogeneous nucleation mechanism followed by crystal growth on the MgO surface.

An interesting finding of this work is the observation of pyramidal-shaped micrometer-sized pits that are typically observed after an acidic etching of MgO . The fact that the dissolution of surface MgO into the (molten) NaNO_3 promoter is significantly enhanced in a CO_2 atmosphere is presumably due to its acidic nature. HRTEM analysis provides key insight into the atomic arrangement of the MgCO_3/MgO interface, revealing an epitaxial growth of a carbonate layer. Due to the lattice mismatch between the magnesium carbonate and the oxide crystals, the carbonate film relaxes through the incorporation of lattice misfit dislocations.

The fundamental knowledge obtained in this work provides guidelines for the design of more-effective MgO -based sorbents by maximizing the AMS/MgO interface area and the density of nucleation sites for the carbonation reaction. This study encourages further research aiming at understanding how to control and enhance the number of nucleation sites at the interface of AMS/MgO .

through, for example, seeding and/or defect engineering. An additional aim is to answer the question whether nucleation occurs most favorably at the AMS/MgO interface or the TPB and whether an optimum thickness of the AMS promoter exists to ensure a sufficient coverage for rapid MgO dissolution and to reduce the diffusion length of CO₂ and [Mg²⁺...CO₃²⁻] ionic pairs to the reaction interface.

Materials and Methods

In Situ XRR and GIXRD. In situ XRR combined with GIXRD experiments were performed at ID31 of the European Synchrotron Radiation Facility (ESRF). The two materials studied are 1) pristine MgO(100) single crystal and 2) MgO(100) single crystal coated with NaNO₃. Both pristine MgO(100) and NaNO₃-coated MgO(100) were studied in situ during He treatment and CO₂ uptake conditions. First, the samples were pretreated at 450 °C (10 °C·min⁻¹, 10 mL·min⁻¹) in He for 15 min to reproduce pretreatment conditions that are used typically for the regeneration of NaNO₃-promoted MgO sorbents and to allow a comparison with other works in the literature (12, 18, 54) while at the same time preventing the decomposition of NaNO₃ (64). Subsequently, the samples were cooled down to 330 °C under He flow and held at this temperature for 15 min. Next, the gas feed was switched to CO₂ (10 mL·min⁻¹) for 90 min, while acquiring XRR followed by GIXRD. Further details about the experimental setup, conditions, and data acquisition scheme can be found in *SI Appendix*, *Figs. S2 and S3*.

Ex Situ Characterization of the MgCO₃ Product on MgO(100) Promoted with NaNO₃. Samples for ex situ analysis were prepared in a similar manner as for in situ analysis and tested in a TGA to imitate the conditions during in situ analysis. The as-prepared NaNO₃-coated MgO(100) single crystal was pre-treated first for 1 h at 420 °C in 80 mL·min⁻¹ N₂ to remove surface species. Carbonation was then carried out for 5 h at 330 °C in 80 mL·min⁻¹ CO₂ to induce a large degree of carbonation. The heating and cooling rates were

10 °C·min⁻¹. Throughout the program, a purge flow of N₂ 25 mL·min⁻¹ was used in the TGA.

Raman spectra were collected with a Thermo Scientific Instrument equipped with a 455-nm laser using a spot size of 1.8 μm and 0.6 μm for a magnification of 10× and 100×, respectively. The spectra were acquired in the range of 100 cm⁻¹ to 3,500 cm⁻¹ with a spectral resolution of 0.96 cm⁻¹.

Cross-sections for SEM were prepared by FIB milling and collected with a Field Electron and Ion (FEI) Scios Dual Beam microscope. TEM lamellas were prepared on the FIB-SEM Helios NanoLab 600i. The FIB cut was parallel to the [100] direction of the single crystalline MgO support.

The microscale and atomic-scale structure of the samples was probed by analytical electron microscopy using a double Cs-corrected (TEM and STEM) JEOL JEM-ARM300F Grand ARM STEM that was operated at 300 kV. The microscope is equipped with the Dual Energy Dispersive Spectroscopy system (two large area silicon drift detectors with 100 mm² active area; total solid angle: 1.6 sr) and the Gatan Imaging Filter (GIF) Quantum ER EELS. Before recording the micrographs, the TEM lamella was aligned along the [100]-zone axis of the MgO support. ADF STEM images were recorded with a semi-convergence angle of 18 mrad and 55- to 177-mrad collection semiangles.

Data Availability. All study data are included in the article and *SI Appendix*.

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