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Peering into buried interfaces with X-rays and electrons to unveil MgCO_3 formation during CO_2 capture in molten salt promoted MgO

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Abstract

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 remains 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 non-crystalline 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 the proximity 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.

Significance Statement

The grand challenge of reducing CO₂ emissions requires the development of efficient and cost-effective CO₂-sorbents. While bare MgO is almost inactive for CO₂ capture, when promoted with molten alkali salts, high rates of CO₂ capture through the formation of MgCO₃ are obtained. However, there is very little understanding of the processes that occur at the atomic-to-micro scale and that determine the CO₂-capture properties of MgO-based sorbents. Unveiling the interfacial phenomena that lead to the formation and growth of MgCO₃ provides the fundamental understanding required to advance this technologically promising class of CO₂-sorbents. Our multi-technique approach demonstrates how the interrogation of buried interfaces are highly relevant for CO₂ capture.

Main Text

Introduction

Global concerns about the rising level of greenhouse gas emissions and the associated climate change requires 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 pre-combustion, post-combustion or oxy-combustion CCS (2–4). 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 (5). 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 sorbents' structural features and its CO₂ capture characteristics are required.

Magnesium oxide (MgO) is an attractive solid CO₂ sorbent, in particular for pre-combustion 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 a 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 a CO₂ uptake of only 0.02 g_{CO2} g_{MgO}⁻¹ after 1 hour of exposure to CO₂ (6, 7). 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 (8–10). Encouragingly, the slow uptake of MgO can be accelerated appreciably through an engineering solution, i.e. the addition of alkali metal salts (AMS, e.g. NaNO₃, KNO₃, LiNO₃ and their eutectic mixtures) which are molten at operating conditions (11–15). 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 bare MgO (14). 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 (16–18).

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 (13, 14, 17, 19–23). For example, combining thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and X-ray powder 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 (24) leading to the formation of reactive carbonate ions (CO₃²⁻) that subsequently react with Mg²⁺ to form MgCO₃ (14). 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 (13, 19). 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 (13). 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 (13). The dissolved ionic pair reacts with CO₂ that is adsorbed on the MgO surface, i.e. 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 as to not prohibit the further reaction. Following this argument, the reaction would in theory continue until MgO is completely converted. However, in practice MgO conversion stops at approximately 70 %, which has been argued to arise from a reducing triple phase boundary length. A recent in situ total scattering study points to a more multi-faceted role of the AMS promoter in the MgO-CO₂ system, as the AMS do not only affect the nucleation of MgCO₃, but also the microstructure and growth of the MgCO₃ formed (21).

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 (17). The characteristic sigmoidal kinetic curve of MgO conversion suggests that the carbonate formation is “auto-catalytic”, i.e. 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, i.e. 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 (17). 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, i.e. where it forms (at the interface AMS/MgO, at the TPB or inside the AMS), its growth habit and morphology. According to an in situ TEM study of MgO nanoparticles that were physically mixed with an eutectic mixture of alkali metal salts, MgCO₃ nucleates favorably at the TPB (25, 26). 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 FT-IR after the removal of NaNO₃ (17). Jo *et al.* (17) proposed that MgCO₃ is formed inside the molten promoter through nucleation and growth steps.

Hence, in spite of 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 alkali metal salts would allow to unlock 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 interrogating 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 (22, 27, 28)) coated with NaNO₃ and probe in detail its structural dynamics under CO₂ capture conditions. Synchrotron-based, in situ X-ray reflectometry (XRR) and grazing incident diffraction (GIXRD) unravel the changes occurring at the surface of MgO under CO₂ capture condition (without the need to remove the promoter). 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. Our studies evidence the formation of a non-crystalline 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 sectorial plate habit growth at the interface between NaNO₃/MgO(100), following a nucleation and growth mechanism. High resolution transmission electron microscopy (HRTEM) provided atomic level insight into the MgCO₃/MgO interface,

evidencing an epitaxial arrangement between MgCO_3 and MgO whereby the lattice mismatch between MgCO_3 and MgO is relaxed through lattice misfit dislocations.

Results and Discussion

Changes at the surface of MgO under CO_2 capture conditions probed by in situ XRR-GIXRD

To gain atomic scale insight into the morphological and structural changes at the surface of $\text{MgO}(100)$ and at the interface between $\text{MgO}(100)$ and molten NaNO_3 under CO_2 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, SLD) as function of probing depth (29). GIXRD provides complementary information of 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 Figures 1a and 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 CO_2 capture conditions on bare $\text{MgO}(100)$ and NaNO_3 -coated $\text{MgO}(100)$ (Figures 1a, S2 and S3). First, the samples were pre-treated in situ in He at 450 °C for ca. 15 min to remove adsorbed water, hydroxides and carbonates adsorbed onto the surface (30–32) and subsequently cooled down to 330 °C in He. The collected XRR data on bare $\text{MgO}(100)$ and NaNO_3 -coated $\text{MgO}(100)$ at 330 °C under He flow are referred to as $\text{MgO}(100)\text{-He}$ and $\text{NaNO}_3\text{-MgO}(100)\text{-He}$, respectively. The He pre-treatment was followed by exposing the samples to a CO_2 flow (10 ml min^{-1}) for ca. 90 min ($\text{MgO}(100)\text{-CO}_2$ and $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$, respectively). GIXRD patterns were collected consecutively after the respective XRR measurements (Figure 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 Figure 1b. A typical XRR curve includes the following features: (i) 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 ; (ii) a reflectivity region above the critical angle, described by a combination of a rapid decay in the reflected intensity (Fresnel reflectivity curve) and the oscillation (Kiessig) fringes (33, 34). The Fresnel curve and the Kiessig fringes are related to the morphology and electronic density of the surface layer(s) (Figure S4). Modelling of the XRR data allows to determine the electronic density profiles normal to the surface (Figure 1c), yielding in turn the average thickness, density, and roughness of the layer(s) close to the surface of a material (Table S1).

The experimental XRR curve of $\text{MgO}(100)\text{-untreated}$ (Figure S6) exhibits Kiessig fringes in the range of $0.1\text{--}0.4 \text{ \AA}^{-1}$. These fringes can be attributed to both the presence of both imperfect terminations at the surface and subsurface of the crystal (35) and adsorbed species (such as water, hydroxyl and carbonates due to exposure of the crystal to ambient conditions prior to the experiment; Figures S5) (22, 36). The presence of a defective surface is in line with previous studies (using UV diffuse reflectance and scanning tunneling microscopy) that have described the $\text{MgO}(100)$ surface as composed of terraces of different heights, separated by defects such as steps and kinks (37–41). $\text{MgO}(100)\text{-He}$ exhibits a subtle Kiessig fringe at ca. $0.3\text{--}0.7 \text{ \AA}^{-1}$ (Figure 1b). Comparing $\text{MgO}(100)\text{-He}$ to the untreated sample $\text{MgO}(100)\text{-untreated}$, we observed that pre-treatment 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 (Figures 1b and S6). 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 $\text{MgO}(100)\text{-He}$ (22). This is in line with in situ 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 (Figure 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 i) a semi-infinite substrate representing the bulk MgO and ii) a slab to model the surface layer, referred to as “bulk MgO” and “surface layer” respectively (Figure 1b, 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 (42) was determined as 2.4 Å, while the roughness of the interface between the bulk and surface MgO layers equals to 3.3 Å. The density of the surface layer in MgO(100)-He was determined as 2.6 g/cm³, that is 75% of the bulk density of MgO.

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. 0.2–0.5 Å⁻¹, indicating a thicker surface layer that is ascribed to the formation of carbonates on the surface. The calculated electronic density profile (Figure 1c) shows an increase in the thickness of the surface layer by ca. 7 Å ($d_{\text{surf}} = 18 \text{ \AA}$, $\sigma_{\text{surf}} = 2.5 \text{ \AA}$ and $\sigma_{\text{bulk}} = 4.0 \text{ \AA}$ MgO(100)-CO₂, Table S1) and a decrease in the density of the surface layer of MgO(100)-CO₂ to 2.3 g/cm³ when compared to MgO(100)-He. Previous combined DRIFTS and density functional theory (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 (22, 31, 43). In line with these studies, in situ DRIFTS analysis on a MgO powder (Figure 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°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 (Figure S7, S9) 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 (19)-(22).

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: i) “bulk MgO”, ii) “surface layer” and iii) “molten NaNO₃” (Figure 1c). The model yields a thickness of 14 Å for the surface layer at the NaNO₃/MgO interface with a density of 2.9 g/cm³ (ca. 80% of the bulk density of MgO). Interestingly, the roughness of the bulk MgO increases to ca. 7.3 Å in comparison to 3.3 Å 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 (19, 44). Thus, our XRR measurements provide new 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 (Figure 1c). Fitting with the three layer model yielded a significant increase in the roughness of the interface between the bulk MgO and surface layer to 29 Å (Table S1) which is approx. 4 and 7 times higher than that in NaNO₃-MgO(100)-He and MgO(100)-CO₂, respectively. 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 MgCO_3 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 (45, 46). The 2D pattern of $\text{NaNO}_3\text{-MgO}(100)\text{-He}$ (Figure S8) 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 $Fm\bar{3}m$, ICSD: 9863); we could not observe rings due to polycrystalline MgO. Since NaNO_3 is molten under the experimental, in situ conditions employed, no Bragg reflections due to the NaNO_3 phase are present in the GIXRD patterns, yet an amorphous halo due to diffuse scattering of molten NaNO_3 is observed at ca. $1.5 \text{ \AA}^{-1}$. The corresponding GIXRD 2D pattern of $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$ (Figure 2a) reveals reflections due to crystalline MgCO_3 (space group $R\bar{3}c$, ICSD: 40117). The MgCO_3 reflections appear as spotty diffraction rings, revealing a preferred distribution of intensities at certain values of φ , highlighting that the MgCO_3 product consists of crystals with a marked preferred orientation (more insight into the orientation and size of the MgCO_3 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 $\text{MgCO}_3(104)$ and $\text{MgCO}_3(006)$ reflections as a function of φ (Figure 2c). This analysis shows that a large proportion of the $\text{MgCO}_3(104)$ and $\text{MgCO}_3(006)$ reflections are preferably oriented at ca. $\varphi = 10^\circ$, 45° and 90° . 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 (Figure 2a). The growth of MgCO_3 was analyzed with atom-scale resolution by HRTEM and will be discussed in more detail further below.

To probe the vertical location of the MgCO_3 product with respect to the NaNO_3/MgO interface, we collected GIXRD while varying the position of the sample in the z-direction with respect to the incident beam (see Figure 1a). This scan was performed between ca. $30 \mu\text{m}$ above and ca. $10 \mu\text{m}$ below the NaNO_3/MgO interface, with a step size of $2 \mu\text{m}$, providing information of the spatial distribution of the crystalline phases (Figure S10). Figure S11 plots the integrated intensities of the $\text{MgCO}_3(104)$ and $\text{MgO}(220)$ reflections as a function of the z-position with regards to the NaNO_3/MgO interface. The position of the NaNO_3/MgO interface was determined as the maximum of the derivative of the $\text{MgO}(220)$ intensity vs. the sample position (Figure S12). 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 vicinity of the MgO surface, as opposed to a precipitation inside the NaNO_3 melt (13, 17). This analysis provided average and microscale information on the location of the formed MgCO_3 , yet more detailed insight, i.e. with higher spatial resolution, into the MgCO_3/MgO interface was obtained by HRTEM (vide infra).

After carbonation, the sorbent regeneration step, i.e. 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 have largely disappeared, with only a very weak $\text{MgCO}_3(104)$ reflection remaining (Figure 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 (Figure 2c). The intensity of MgO is distributed relatively homogeneously, i.e., 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 Figure 2c the high intensity spot of the MgO(100) single crystal substrate is found at ca. $\varphi = 0^\circ$).

In summary, in situ XRR show that under a CO_2 flow a surface layer with a lower density and thickness of ca. $7 \text{ \AA}$ forms on bare 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 NaNO₃ (330 °C in He), but even more drastically when exposed to CO₂ (330 °C) due to the formation of highly oriented MgCO₃ crystallites at the NaNO₃/MgO interface, as opposed to a precipitation with random orientation inside the molten salt (a growth at the TPB can, however, not be excluded due to the high mobility of the molten salt). Indeed, the surface roughness of NaNO₃-promoted MgO(100) is ca. 4 times higher under a CO₂ flow compared to He flow. In the following, we apply electron microscopy (SEM and HRTEM) to provide further insight into (i) the morphology of the MgCO₃ crystals formed, (ii) MgO surface alterations and (iii) the atomic arrangement at the MgCO₃/MgO interface.

Morphology of the MgCO₃ Crystals Formed on MgO

To describe the morphology of the MgCO₃ product formed during carbonation, we turned to scanning electron microscopy (SEM). Pre-treatment and carbonation conditions similar to those ones 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 micro-spectroscopy mapping was used to unequivocally identify the MgCO₃ product on the MgO(100) surface (Supporting Information 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 Figure 3 and Figure S13. Planar views of the MgCO₃ are displayed in Figure 3a, b, and a cross section, obtained by a FIB cut, is shown in Figure 3c. SEM demonstrates that on NaNO₃-MgO(100)_{CO₂-RW} MgCO₃ grew as individual two-dimensional crystals, or “2D-islands”, on the surface of MgO with a diameter in the range of 10–50 µm and a thickness between 0.2 µm to 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 Figures 3a, 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 (47–49). Side branches have grown from the primary branches and coalesced with the MgCO₃ product from neighboring branches. In some cases, the islands have grown closer to each other and merged to form larger clusters as observed in Figure S14.

Two-dimensional island-type growth with a sectored plate morphology has been observed previously when precipitating MgCO₃ (50), CaCO₃ (51), ice crystals (47) and ice analogue crystals (Na₂SiF₆) (48) from supersaturated solutions. The growth habits of ice crystals and ice analogue crystals have been characterized and mapped in great detail with respect to the level of supersaturation and temperature (48–51). Ice analogue crystals such as sodium fluoroarsenate (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 (48). 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 Figure 3a and 3b, 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 (52). Here, the surface of MgO provides heterogeneous nucleation sites (characterized by a lower energy barrier of nucleation in comparison to homogeneous nucleation) (53). 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 (54). Such a nucleation and crystal growth based mechanism would be described by a sigmoidal-shaped (S-shaped) kinetic curve (52, 55). Indeed, the carbonation of a powder sample of MgO promoted with NaNO₃, shows a S-shaped kinetic curve and can be initiated by nuclei seeding (14, 17, 19). This

resemblance is important because it confirms that the MgO(100) model surface coated with NaNO₃ is representative for practically more relevant (and scalable) powder samples of MgO promoted with NaNO₃.

From the cross section shown in Figure 3c, it is clear that the carbonate crystal has grown both inwards and outwards from the original NaNO₃/MgO interface (the dashed yellow line represents the location of the original (non-reacted) MgO surface, i.e. NaNO₃/MgO interface). The two-dimensional growth of the carbonate product has a crucial implication on 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 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 has to be limited (14, 56).

Etched MgO(100) Surface Surrounding the MgCO₃ Product

A very interesting structural feature in Figure 3 are micron 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-orientated 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 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 (Figure 3c). Moreover, a high-angle annular dark-field 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 (Figure S18). The contrast gradient reflects a MgO depletion layer, which is due to the transport of MgO species towards 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 towards 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 (54, 57, 58). The dissolution of MgO and the etching of pits are initiated preferentially at surface defects (e.g. edge dislocations) and is energetically favored to proceed along the [111] direction of the MgO(100) substrate forming the characteristic pyramidal shape (54). Moreover, it is well known that diffusion is favored along dislocations which may accelerate the etching process near the carbonate product (59, 60).

Our samples were rinsed in deionized water (neutral pH) for 1 minute 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 at least 72 hours; 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 hours 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 (Figure S15). 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 (54).

Overall, the scanning electron microscopy analysis complements our in situ XRR and GIXRD results providing new insight into the two dimensional growth of MgCO₃ islands, and the etching of the MgO surface when both NaNO₃ and CO₂ are present (Figure S15). 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 towards the growing carbonate and provide building blocks for further, increased MgCO₃ growth. In other words, the carbonation reaction is auto-catalytic (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 (17). 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 towards 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 (14, 61, 62) in the molten salt to reach the reaction interface.

Atomic Scale Insight into the MgCO₃/MgO interface by Transmission Electron Microscopy (TEM)

Spatially resolved electron energy loss spectroscopy (EELS) was utilized to obtain information on the electronic structure of the oxygen and carbon atoms, allowing us also to identify the MgO and MgCO₃ phases. Figure 4 shows a high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) image of the MgCO₃/MgO(100) interface and the simultaneously recorded STEM-EELS data (acquired in the range of 250–400 eV for C K-edge and 520–620 eV for O K-edge). Elemental maps were obtained by background subtraction and the EELS spectrum peak integration using energy windows as shown in Figures 4f,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 Figure 4a) due to the inclined interface.

To gain insight into the atomic arrangement at the MgCO₃/MgO interface, we performed transmission electron microscopy analysis of a FIB cut lamella. Figure 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 assigned to the [100]-zone axis of MgO and the [310]-zone axis of MgCO₃, respectively. 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 of the local structure at the interface between MgO and MgCO₃ is provided by HRTEM (Figure 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 (Figure S19).

Due to the different crystal structure 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 Figure 5c a strain map is obtained by performing a geometric phase analysis (GPA) (63) along the [001] direction. Indeed, in Figure 5d compressive strains are observed in the MgCO₃ phase at the interface region, however, 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 layer-substrate interface. Figure 5e shows a bright-field STEM image of a cross-section oriented along the MgO[100] direction. In contrast to the interface of the same orientation shown above (Figure 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 Figure 5e. Fourier filtering of the bright field (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 (Figure 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.(64) 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 5 MgCO₃ planes matching 6 MgO planes, alternating with one domain of 6 MgCO₃ planes matching 7 MgO planes (Figure 5f).

Collectively our TEM data reveals 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, i.e. 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 rapid CO₂ uptake of MgO. Under practically relevant CO₂ capture conditions we have observed a roughening of the MgO surface and the formation of MgCO₃ crystallites that grow with a preferred orientation on the surface of MgO(100). This is the first work that provides in situ evidence that MgCO₃ grows favorably at the interface MgO/NaNO₃ a finding that will influence the design and rational advancement of more effective MgO-based CO₂ sorbents. When treated under inert conditions (at 330 °C) the surface roughness of NaNO₃ promoted MgO increases by ca. 4 Å compared to a pristine MgO(100) crystal, possibly due to MgO dissolution into the melt. The surface roughness increases drastically when the coated sample is also exposed to CO₂. Morphological analyses of the MgCO₃ crystals formed by SEM revealed a two-dimensional MgCO₃ islands-type growth with a sectorized plate morphology, whereby the thickness of the MgCO₃ 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 micron-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 guideline for the design of more effective MgO based sorbents by maximizing the AMS/MgO interface area and the number 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 e.g. 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 triple phase boundary 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 CO_2 and $[\text{Mg}^{2+} \dots \text{CO}_3^{2-}]$ ionic pairs to the reaction interface.

Materials and Methods

In Situ X-ray Reflectometry (XRR) and Grazing Incident X-ray Diffraction (GIXRD)

In situ X-ray reflectometry (XRR) combined with grazing incidence X-ray diffraction (GIXRD) experiments were performed at ID31 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The two materials studied are: (i) pristine $\text{MgO}(100)$ single crystal and (ii) $\text{MgO}(100)$ single crystal coated with NaNO_3 . The MgO single crystals ($\text{MgO}(100)$ 10 mm x 10 mm x 0.5 mm; Sigma-Aldrich, $\geq 99.9\%$) were cut into pieces of ca. 3 mm x 4 mm x 0.5 mm; while sodium nitrate (NaNO_3 , Sigma-Aldrich, $\geq 99.5\%$) was used as purchased.

The incident X-rays with an energy of 70.0 keV ($\lambda = 0.1771 \text{ \AA}$) were micro-focused to yield a beam size of $\sim 10 \text{ }\mu\text{m}$ in the vertical direction (normal to the surface of the crystal) and $\sim 40 \text{ }\mu\text{m}$ in the horizontal direction. The XRR data were acquired using a CdTe MAXIPIX with 256×256 pixels ($55 \times 55 \text{ }\mu\text{m}^2$ pixel size). The data collection time was ca. 15 min/scan. The fittings of the XRR data were performed using the GenX software (65). The GIXRD data were collected with a Pilatus3 X CdTe 2M detector (the data acquisition time was 1s/scan). The incidence angle was set to 0.2° . A CeO_2 powder diffraction standard (National Institute of Standards and Technology, NIST) was used to determine the azimuthal integration parameters. The integration of the diffraction data was carried out using the Dioptas software (66). The intensity of the Bragg reflections of MgCO_3 and MgO were extracted as a function of the azimuthal angle relative to the incident X-ray beam (ϕ), corrected for the beam polarization effect and background subtracted. The Albula software was additionally used for the visualization of the 2D GIXRD patterns (67).

A quartz dome-type in situ cell (ESRF instrumental pool) allowed for the acquisition of in situ GIXRD and XRR data under relevant CO_2 capture conditions, i.e. allowing gas flow and control of temperature between room temperature and 450°C (Figure S2).

Both pristine $\text{MgO}(100)$ and NaNO_3 -coated $\text{MgO}(100)$ were studied in situ during He treatment and CO_2 uptake conditions. First, the samples were pre-treated at 450°C ($10^\circ\text{C min}^{-1}$, 10 ml min^{-1}) in He for 15 min to remove species adsorbed onto the surface. 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 CO_2 (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 Figure S2, S3.

Ex situ Characterization of the MgCO_3 Product on $\text{MgO}(100)$ Promoted with NaNO_3

Samples for ex situ analysis were prepared in a similar manner as for in situ analysis and tested in a thermogravimetric analyzer (TGA) to imitate the conditions during in situ analysis. The as-prepared NaNO_3 -coated $\text{MgO}(100)$ single crystal was pre-treated first for 1 h at 420 °C in 80 mL min^{-1} N_2 to remove surface species. Carbonation was then carried out for 5 h at 330 °C in 80 mL min^{-1} CO_2 to induce a large degree of carbonation. The heating and cooling rates were 10 °C min^{-1} . Throughout the program, a purge flow of N_2 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 10x and 100x, respectively. The spectra were acquired in the range of 100 – 3500 cm^{-1} with a spectral resolution of 0.96 cm^{-1} .

Diffuse reflectance infrared spectroscopy (DRIFTS) experiments were carried out in a Nicolet, 6700 FT-IR spectrometer coupled with a Harrick Praying Mantis cell. DRIFT experiments were performed on a self-supporting pellet of MgO powder. The MgO powder was produced from a metallic Mg foil via a methoxide route.⁽⁶⁸⁾ The solution of magnesium methoxide (methanol-toluene mixture) was slowly hydrolyzed, and then dried at room temperature (RT) over the course of one week in a fumehood. Afterwards, the $\text{Mg}(\text{OH})_2$ powder was collected and subjected to a second drying step at 120 °C for 12 hours. Subsequently, the powder was calcined in synthetic air (100 mL min^{-1}) at 500 °C for 5 hours (heating rate of 1 °C min^{-1}). The obtained MgO powder was pressed into a self-supporting pellet for in situ DRIFTS experiments. The DRIFTS experiments were executed as follows: the sample was pre-treated at 450 °C in a flow of pure N_2 (30 mL min^{-1}) for 30 min; afterwards cooled down to 330 °C and exposed to a flow of pure CO_2 (30 mL min^{-1}) for 60 min. The FT-IR signal of a KBr pellet collected at 300 °C under N_2 and CO_2 was applied as spectral background.

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

The micro- and atomic scale structure of the samples was probed by analytical electron microscopy using a double Cs corrected (TEM&STEM) JEOL JEM-ARM300F Grand ARM scanning transmission electron microscope that was operated at 300 kV. The microscope is equipped with the Dual Energy Dispersive Spectroscopy (EDS) system (two large area silicon drift detectors (SDD) with 100 mm² active area; total solid angle: 1.6 sr) and the GIF Quantum ER electron energy loss spectrometer (EELS). Before recording the micrographs, the TEM lamella was aligned along the [100] zone axis of the MgO support. Annular dark-field (ADF) scanning transmission electron microscopy (STEM) images were recorded with a semi-convergence angle of 18 mrad and 55–177 mrad collection semi-angles. Inverse Fourier filtering was applied for denoising the HRTEM micrographs and to highlight the specific atomic rows in the bright-field STEM image. The geometric phase analysis has been performed using the Strain ++ software (63).

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Figures and Tables

Figure 1. a) Schematic illustration of the in situ XRR-GIXRD setup. b) Experimental (open circles) and fitted (grey lines) XRR curves for $\text{MgO}(100)_{\text{-He}}$, $\text{MgO}(100)_{\text{-CO}_2}$, $\text{NaNO}_3\text{-MgO}(100)_{\text{-He}}$, and $\text{NaNO}_3\text{-MgO}(100)_{\text{-CO}_2}$. The curves are offset vertically by two orders of magnitude for clarity. The XRR data are modelled via a layered structure model consisting of following components: (i) bulk MgO substrate, (ii) a surface layer with a lower electronic density (slab due to surface hydroxide and carbonate species and surface imperfections) and (iii) slab of a molten NaNO_3 phase for the $\text{NaNO}_3\text{-MgO}(100)$ system. A misfit in the region below the critical angle is ascribed to the finite length and non-zero curvature of the crystal (69). c) The electron density profiles obtained from the modelling; the colors represent the different layers of the models, including their roughness (indicated by the color gradient).

Figure 2. 2D GIXRD patterns of a) $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$, 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 ($Q = 4\pi \cdot \sin(\theta)/\lambda$) patterns of MgCO_3 (ICSD: 40117) and MgO (ICSD: 9863).

Figure 3. SEM images of MgCO_3 formed on $\text{NaNO}_3\text{-MgO(100)-CO}_2\text{-RW}$ (RW: rinsed in water to remove the NaNO_3 coat): a)–b) images of two representative MgCO_3 features at different magnifications; inset shows a pyramid-shaped dissolution pit on the MgO surface near the MgCO_3 product. c) Cross section of the MgCO_3 product formed on top of MgO . Dashed line highlights the location of the originally flat surface of the MgO(100) single crystal promoted with NaNO_3 before its reaction with CO_2 .

Figure 4. EELS mapping of the MgCO_3/MgO interface oriented along the $\text{MgO}[100]$ direction: a) HAADF-STEM image; 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 MgCO_3 e) C K-edge of amorphous carbon (protection layer used for TEM lamella preparation); f–g) corresponding EELS spectra with marked energy windows used for elemental maps.

Figure 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 FFT 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.

Supplementary Information

Supplementary Information Text

In situ DRIFTS. To obtain additional information about the nature of the chemical transformations at the surface of pristine MgO, we turned to diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). This technique is used to characterize the chemical species at the surface of powders or rough solid materials (the roughness of the sample is essential to insure that light scatters diffusely at the surface, making DRIFTS studies on MgO(100) single crystal unfeasible). Therefore, we have applied in situ DRIFTS to investigate the nature of the surface groups on MgO using a MgO powder to provide complementary information to the XRR results of a MgO(100) single crystal. It is important to note that although the surface sites of a single crystal may differ from those of powders (e.g. due to the presence of grain boundaries and facets other than (100)), we can qualitatively identify the type of surface species typically adsorbed on MgO surfaces and their evolution upon treatment (in N₂ flow followed by CO₂ flow).

The recorded DRIFTS spectra are shown in Figure S5. The spectra obtained on MgO pellets (previously exposed to ambient conditions) reveal the presence of surface hydroxyls/water (3800–3200 cm⁻¹) and carbonate species (1750–1250 cm⁻¹, Figure S5a, b) in line with previous observations (1). In the OH region (Figure S5a), thermal pretreatment under N₂ to 450 °C reduces the intensity of the broad band around 3625 cm⁻¹ and leads to the emergence of a sharper band at 3740 cm⁻¹, confirming a partial surface dehydroxylation leaving behind only strongly-bonded isolated hydroxyls (2). On the other hand, in the carbonate range (Figure S5b), heating under N₂ induces a red shift of the peaks at temperatures above 350 °C as well as a loss of intensity for all peaks. At 450 °C remaining bands at 1528 and 1403 cm⁻¹ indicate the presence of monodentate carbonate species (3). Subsequently, the sample is cooled down to 330 °C under N₂ flow, stabilized at this temperature and exposed to a CO₂ flow for 60 min (Figure S5c). Exposure to CO₂ leads to an increase in the intensity of bands due to surface carbonate species. The appearance of new features at ca. 1654 and 1558 cm⁻¹ are attributed to the $\nu(\text{OCO})$ vibrational mode of adsorbed bicarbonate species formed through the reaction of CO₂ with surface hydroxyls (1654 cm⁻¹) and bidentate species (1558 cm⁻¹). A subtle peak at ca. 1218 cm⁻¹ can be ascribed to the $\delta(\text{COH})$ vibrational mode of bicarbonates (3–5).

To summarize, the results of in situ DRIFTS provided the following information. i) The surface of MgO(100)-_{untreated} contains surface carbonates and hydroxyl groups likely due to its exposure to the atmosphere. ii) Heat treatment under N₂ leads to a partial surface dehydroxylation, a red shift of the carbonate bands and a reduction of their intensities. iii) Flowing CO₂ over the sample at 330 °C resulted in the emergence of bands owing to carbonate and bicarbonate species.

Raman micro-spectroscopy mapping for identification of NaNO₃ and MgCO₃. Raman micro spectroscopy was used to identify NaNO₃ and MgCO₃ on the surface of NaNO₃-MgO(100)-CO₂, Figure S13. A rinsing step was necessary to allow the Raman laser to probe MgCO₃, which was buried underneath NaNO₃ (Figure S13a and b). The spectrum acquired for the sample before the water rinse (NaNO₃-MgO(100)-CO₂) has Raman bands at 186 cm⁻¹, 724 cm⁻¹, 1067 cm⁻¹ and 1385 cm⁻¹ which are characteristic for the NO₃⁻ ion in NaNO₃ (6–8), Figure S13c). The Raman band at 1067 cm⁻¹ is due to symmetric stretching vibrations, while those at 186 cm⁻¹, 724 cm⁻¹ and 1385

cm^{-1} are due to asymmetric stretching vibrations of the NO_3^- ion (7, 9). No Raman bands that are characteristic for MgCO_3 were detected in the non-rinsed sample. After the water rinsing step ($\text{NaNO}_3\text{-MgO(100)-CO}_2\text{-RW}$), optical microscopy revealed the presence of 10–50 micron sized plate-like features on the MgO(100) surface as illustrated in the top view in Figure S13b). A representative spectrum collected on one of these features (Figure S13c)) shows peaks at 328 cm^{-1} , 740 cm^{-1} and 1094 cm^{-1} (the most intense one) which are assigned to the CO_3^{2-} ion in MgCO_3 (10, 11). The peak at the low wavenumber is attributed to lattice vibration modes, while the 740 cm^{-1} and 1094 cm^{-1} modes are ascribed to bending and symmetric stretching vibrations of the CO_3^{2-} ion, respectively (10, 11). The Raman mapping of the MgCO_3 signal (using the band at 1094 cm^{-1}) on the MgO(100) surface (Figure S13d)) demonstrates that the observed plate-like features correspond to the MgCO_3 product. Thus, our Raman mapping confirmed the presence of MgCO_3 crystallites grown on the MgO(100) surface, in line with in situ GIXRD.

Control experiments of MgO(100) treated in CO_2 and $\text{NaNO}_3\text{-MgO(100)}$ treated in N_2 (330°C).

To further understand the observed changes on the surface of $\text{NaNO}_3\text{-MgO(100)-CO}_2\text{-RW}$ as described in the main manuscript (Figure 3), we carried out a series of control experiments. We prepared the following two materials: (i) $\text{NaNO}_3\text{-MgO(100)-N}_2\text{-RW}$ and (ii) MgO(100)-CO_2 and studied them by ex situ SEM. The materials were pre-treated at 420°C for 1 h in N_2 , then cooled down to 330°C and treated in N_2 ($\text{NaNO}_3\text{-MgO(100)-N}_2\text{-RW}$) or CO_2 (MgO(100)-CO_2) for 5 h. $\text{NaNO}_3\text{-MgO(100)-N}_2\text{-RW}$ was rinsed with water (RW) to remove the NaNO_3 coating before the SEM studies. Figure S15 compares the morphology of the surface of $\text{NaNO}_3\text{-MgO(100)-CO}_2\text{-RW}$ with the one of $\text{NaNO}_3\text{-MgO(100)-N}_2\text{-RW}$ and MgO(100)-CO_2 . The SEM (top-view) images are shown with lower and higher magnification in the top (Figure S15 a, d and g) and middle panels (Figure S15 b, e and h), respectively. The corresponding cross-sections acquired by FIB cuts are shown in the bottom panels (Figure S15 c, f and i).

The SEM images of $\text{NaNO}_3\text{-MgO(100)-N}_2\text{-RW}$ in Figure S15 d-e show the absence of etched pits in contrast to the etched pits observed in $\text{NaNO}_3\text{-MgO(100)-CO}_2\text{-RW}$. We observe some bright features on the surface of $\text{NaNO}_3\text{-MgO(100)-N}_2\text{-RW}$ (with a diameter of ca. 10 to 20 μm , Figure S15 f) and less than ca. 0.1 μm thick in the z-direction as seen in Figure S15 f. The EDS analysis of such features is shown in Figure S16 and exhibit signals due to Mg, O and traces of Na. The Na trace is attributed to residual NaNO_3 that was not completely removed during the rinsing step in water.

The surface of MgO(100)-CO_2 Figure S15 g-h, exhibits neither etched pits nor detectable changes in its surface morphology by SEM. On the entire surface of MgO(100) , we observed rare instances (approximately 10 instances on the entire area of $5\text{ mm} \times 5\text{ mm}$) of dark features in the backscatter image (two examples are shown in Figure S15 g). The thickness of these features in the z-direction is approximately 0.2 μm based on the assessment of the cross section shown in Figure S15 i. EDS analysis shows characteristic lines due to Mg, O, and C (Figure S17). Raman spectroscopy of this feature showed no bands characteristic for magnesium carbonate, which indicates that this feature does not correspond to MgCO_3 (in line with XRD) or that it is too thin for detection.

Overall, our control experiments show that etched pits only occur for $\text{NaNO}_3\text{-MgO(100)-CO}_2\text{-RW}$, while they are absent in $\text{NaNO}_3\text{-MgO(100)-N}_2\text{-RW}$ and MgO(100)-CO_2 . Secondly, substantial morphological changes (specifically the formation of sectorial plate MgCO_3 islands) are only observed on the surface of $\text{NaNO}_3\text{-MgO(100)-CO}_2\text{-RW}$. These observations of the local surface

changes are in qualitative agreement with in situ XRR that provides averaged information of a material's surface (see also Figure S1).

Supplementary Information Figures

Fig. S1. Schematic illustrating our use of in situ X-ray and ex situ electron microscopy techniques to provide micron to atomic scale insight into the formation and growth of MgCO_3 during CO_2 capture at the $\text{NaNO}_3/\text{MgO}(100)$ interface.

a) *Cell – side view*

b) *Cell – top view*

c) *Clamp*

Fig. S2. The experimental set-up used to acquire XRR-GIXRD data (ESRF instrumentation pool): a) overall view of the in situ cell mounted on the samples stage; b) detailed view of the top view of the cell with a MgO(100) single crystal mounted; c) clamp used to hold the crystal in place.

The quartz dome cell was provided with a heating element and the temperature of the cell was controlled via a thermocouple that was placed next to the heater, at a distance of ca. 5 mm (sidewise) to the sample, see Figure S2. The in situ cell was mounted on a stepping motor stage, providing a precise control of the sample position. The sample was fixed to the heating element with a metallic clamp. The sample was scanned vertically (z direction), with varying height using a step size of 2 μm .

Fig. S3. Experimental protocol and XRR – GIXRD data acquisition.

Fig. S4. The experimental XRR curve of $\text{MgO}(100)\text{-CO}_2$ with highlights of the features observed in a typical XRR curve.

Fig. S5. a) The DRIFTS spectra of a MgO pellet collected upon heating from 150 °C to 450 °C and stabilization for 30 min in N₂ with zoomed in areas corresponding to a) hydroxides b) carbonates; c) carbonate region after cooling down to 330 °C in N₂ and subsequent exposure to CO₂ for 60 min.

Fig. S6. a) Experimental (open circles) and the fitted (grey line) XRR curves of MgO(100)-untreated (collected for the pristine MgO(100) crystal prior to thermal treatment) and MgO(100)-He samples; a two-layer model was used in the fittings; b) comparison of electron density profiles of the MgO(100)-untreated and MgO(100)-He samples.

Fig. S7. 2D GIXRD pattern of MgO(100)-CO₂.

Fig. S8. 2D GIXRD pattern of $\text{NaNO}_3\text{-MgO}(100)\text{-He}$.

Fig. S9. Azimuthally integrated GIXRD patterns of $\text{MgO}(100)\text{-CO}_2$, $\text{NaNO}_3\text{-MgO}(100)\text{-He}$, $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$ and $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2\text{-He}$ samples; in the Q region of MgCO_3 (104) reflection.

Fig. S10. The distribution of intensities of the phases vs. z position of $\text{NaNO}_3\text{-MgO(100)-CO}_2$. Surface plot highlights the evolution of MgO (220) (white) and MgCO_3 (104) (black) reflections as a function of z-position of the sample.

Fig. S11. Normalized intensities of MgO(220) and MgCO₃(104) reflections of NaNO₃-MgO(100)-CO₂ as function of the probing depth (the horizontal grey line marks the position of the NaNO₃/MgO interface).

Fig. S12. Derivative of the MgO (220) intensity vs. the z position in $\text{NaNO}_3\text{-MgO}(100)\text{-CO}_2$; and fitting of the derivative with a Gaussian peak (FWHM = 14 μm , position of the peak center = 0 μm).

Fig. S13. Sample before and after removal of NaNO₃ for ex situ analysis of MgCO₃. a) Illustration of the sample before (NaNO₃-MgO(100)-CO₂) and after rinsing it with H₂O (NaNO₃-MgO(100)-CO₂-RW) to remove NaNO₃, exposing the formed MgCO₃ product b) Optical image of a MgCO₃ feature, indicating also with a white box the area used for Raman mapping and with a white spot the location of the Raman spectrum. c) Raman spectrum acquired in "Spot 1" compared to a reference powder sample of MgCO₃ and the Raman spectrum of NaNO₃. d) Raman map compiled from the measured intensity at 1094 cm⁻¹ (20 x 20 pixels and 1 μm spacing).

Fig. S14. Scanning electron microscopy images of MgCO_3 crystals grown on the surface of NaNO_3 - $\text{MgO}(100)\text{-CO}_2\text{-RW}$ a) –d) shows different areas.

Fig. S15. Scanning electron microscopy images of the $\text{MgO}(100)$ surface treated under different conditions. a)–c): $\text{NaNO}_3\text{-MgO}(100)_{\text{-CO}_2\text{-RW}}$, RW refers to rinse in water, d)–f) $\text{NaNO}_3\text{-MgO}(100)_{\text{-N}_2\text{-RW}}$ g)–i) $\text{MgO}(100)_{\text{CO}_2}$. Yellow box in g)–i) indicate rough estimate of thickness of features. The materials were first pre-treated at 420°C for 1 h in N_2 , followed by a treatment in N_2 or CO_2 at 330°C for 5h.

Fig. S16. EDS of features appearing on $\text{NaNO}_3\text{-MgO}(100)\text{-N}_2\text{-RW}$. a) SEM image using the SE detector with red circles highlighting the locations of the acquired EDS spectra. b) and c) show traces of Na, while the bare surface in d) does not show traces of Na.

Fig. S17. EDS of a feature appearing on MgO(100)-CO₂. a) Backscatter detector image shows a feature with a darker contrast indicative of a lower average atomic number. Red circles illustrate the locations of the acquired EDS spectra. Spectra b) and c) taken on the feature show a relatively higher intensity of carbon when compared to d) i.e. the bare MgO surface.

Fig. S18. HAADF STEM micrograph showing the MgCO₃/MgO cross-section view. The darker Z-contrast of the MgO substrate in close proximity of the interface reveals a depletion layer of MgO.

Fig. S19. Structure of the interface: a) HRTEM micrograph of the interface viewed along the $[110]$ MgO zone axis; b–d) FFT patterns and Fourier-filtered HRTEM images from areas of the MgCO_3 (b–c) and MgO regions (d–e), respectively.

Table S1. Fitting results of XRR presented in Figure 1 b and 1c (ρ_{surf} , d_{surf} , σ_{surf} – density, average thickness and roughness of “surface layer”; σ_{bulk} – roughness of “bulk MgO layer”)

Material	ρ_{surf}, g/cm³	d_{surf}, Å	σ_{surf}, Å	σ_{bulk}, Å	$2\theta_{off}$, °
MgO(100)-untreated	2.3(2)	35(3)	4.3(2)	9(3)	0
MgO(100)-He	2.6(1)	11(1)	2.4(1)	3.3(3)	0.003(3)
MgO(100)-CO ₂	2.3(1)	18(1)	2.5(1)	4.0(3)	0.003(3)
NaNO ₃ -MgO(100)-He	2.9(1)	14(1)	2.8(1)	7.3(1)	0
NaNO ₃ -MgO(100)-CO ₂	2.2(1)	80(5)	4.4(1)	29(3)	0

* $\rho_{bulk-MgO}$ =3.57 g/cm³

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