

Probing the Local Structure of Na in NaNO₃-Promoted, MgO-Based CO₂ Sorbents via X-ray Absorption Spectroscopy

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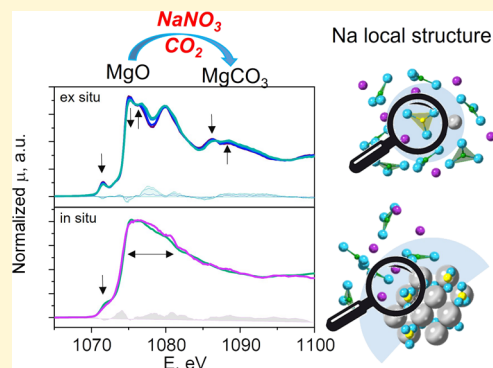


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ABSTRACT: This work provides insight into the local structure of Na in MgO-based CO₂ sorbents that are promoted with NaNO₃. To this end, we use X-ray absorption spectroscopy (XAS) at the Na K-edge to interrogate the local structure of Na during the CO₂ capture (MgO + CO₂ ↔ MgCO₃). The analysis of Na K-edge XAS data shows that the local environment of Na is altered upon MgO carbonation when compared to that of NaNO₃ in the as-prepared sorbent. We attribute the changes observed in the carbonated sorbent to an alteration in the local structure of Na at the NaNO₃/MgCO₃ interfaces and/or in the vicinity of [Mg²⁺...CO₃²⁻] ionic pairs that are trapped in the cooled NaNO₃ melt. The changes observed are reversible, i.e., the local environment of NaNO₃ was restored after a regeneration treatment to decompose MgCO₃ to MgO. The ex situ Na K-edge XAS experiments were complemented by ex situ magic-angle spinning ²³Na nuclear magnetic resonance (MAS ²³Na NMR), Mg K-edge XAS and X-ray powder diffraction (XRD). These additional experiments support our interpretation of the Na K-edge XAS data. Furthermore, we develop in situ Na (and Mg) K-edge XAS experiments during the carbonation of the sorbent (NaNO₃ is molten under the conditions of the in situ experiments). These in situ Na K-edge XANES spectra of molten NaNO₃ open new opportunities to investigate the atomic scale structure of CO₂ sorbents modified with Na-based molten salts by using XAS.



1. INTRODUCTION

The rising concentration of CO₂ in the atmosphere resulting largely from the combustion of fossil fuels is the major cause of global warming.^{1,2} In this context, the development and deployment of technologies for CO₂ capture and storage (CCS) is key to limit the global temperature increase below the 2 °C target.^{3,4} Yet, postcombustion and precombustion CCS techniques rely on the availability of efficient and cost-effective CO₂ sorbents.⁵ The most mature CCS technology that is applied on a large scale to capture CO₂ from natural gas is amine scrubbing. However, amine scrubbing has some drawbacks, such as the production of toxic components and a large energy penalty due to the high water content in the solvent. Hence, as a more cost-effective alternative, solid CO₂ sorbents based on metal oxides have been proposed. In this context, MgO-based CO₂ sorbents (via MgO + CO₂ ↔ MgCO₃, ΔH_{300K} = -106.05 kJ mol⁻¹)⁶ offer several advantages such as intermediate temperature operation (250–450 °C),⁷ natural abundance,⁸ environmentally benign nature,⁹ and a high theoretical CO₂ capacity (1.09 g_{CO₂}/g_{MgO}).^{10,11} However, due to the slow carbonation kinetics of pristine MgO, the addition of promoters such as molten alkali metal salts (AMSs, typically alkali metal nitrates) is required to ensure practically relevant CO₂ uptakes.^{12–16}

There have been a series of studies that have explored the role and functioning of promoters on the CO₂ uptake of MgO-based CO₂ absorbents.^{11,14–22} It has been proposed that MgO dissolves in the molten AMS promoter as [Mg²⁺...O²⁻] ionic pairs.^{14–16,22} Zhang et al. hypothesized that CO₂ is adsorbed at the triple phase boundary (TPB) between solid MgO, liquid AMS, and gaseous CO₂.¹⁶ The adsorbed CO₂ then reacts with [Mg²⁺...O²⁻] ionic pairs to form [Mg²⁺...CO₃²⁻] ionic pairs at the TPB.¹⁶ However, Jo et al. disproved the critical role of TPBs based on a control experiment using a MgO wafer that was completely covered with NaNO₃ (avoiding the presence of any TPB) and that was subjected to a carbonation treatment.²² The analysis of the treated wafer (after washing out the NaNO₃ coating) by Fourier-transform infrared spectroscopy (FT-IR) revealed carbonate formation despite the absence of any TPB.²² Hence, an alternative mechanism was proposed in which gaseous CO₂ dissolves in the molten salt²³ and reacts with O²⁻

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ions present in the molten salt (O^{2-} are formed either from the dissociation of the nitrate group via $\text{NO}_3^- \rightarrow \text{NO}_2^+ + \text{O}^{2-}$ ^{14,21} or from MgO dissolution)²² producing CO_3^{2-} ions.²⁴ Upon reaching supersaturation of $[\text{Mg}^{2+} \cdots \text{CO}_3^{2-}]$ ionic pairs in the melt, the precipitation of crystalline MgCO_3 takes place.¹¹ Further, it was found that MgCO_3 grows at the interface between MgO and NaNO_3 according to grazing incident diffraction and electron microscopy studies on a model $\text{MgO}(100)$ single crystal coated with molten NaNO_3 .¹⁷ More recently, using density functional theory (DFT) calculations and ¹⁸O labeling experiments, it was hypothesized that the carbonation mechanism of NaNO_3 -promoted MgO involves the rapid formation of surface carbonates followed by their dissolution, yielding $[\text{Mg}^{2+} \cdots \text{CO}_3^{2-}]$ ion pairs dissolved in the AMS melt, and oxygen of NO_3^- groups do not participate in carbonation reaction.²⁰

Despite the new insights gained into the mechanism of CO_2 uptake in alkali metal-promoted MgO, there is still little understanding of the local structure of the molten salt promoter under realistic carbonation conditions. This lack of knowledge is because the promoter is molten under reaction conditions, and only a few experimental techniques can probe the local structure of the molten salt under reactive conditions. Previous related studies have investigated the structure of (bare) molten alkaline nitrates via X-ray total scattering in combination with molecular dynamics simulations.^{18,25,26} However, due to the presence of multiple phases in the CO_2 sorbents under reaction conditions (i.e., MgO, MgCO_3 , and the molten nitrate), X-ray total scattering studies are not well-suited to study the local structure of molten promoters such as NaNO_3 under CO_2 capture conditions. In view of these challenges, element-selective techniques such as X-ray absorption spectroscopy (XAS) are highly suitable to probe the local structure around a specific element (such as Na) in multiphase systems. Yet, Na K-edge XAS studies under realistic CO_2 capture conditions face considerable experimental challenges because the X-ray absorption edge of Na is in the soft/tender X-ray region (0.2 to ~ 2 keV, Na K-edge 1.08 keV). Soft/tender X-rays are poorly transmitted through matter (i.e., through air or reaction cells), hence experiments must be performed under vacuum.^{27,28} Studies that apply Na K-edge XAS on CO_2 capture materials are scarce,^{29,30} and experimental developments are required to exploit the full potential of this technique in the field of CO_2 sorbents.

In this work, we explore Na K-edge XAS to probe the local environment of Na in NaNO_3 -promoted, MgO-based CO_2 sorbents. First, we investigate ex situ Na K-edge XAS data at room temperature to (indirectly) probe changes in the Na environment during CO_2 uptake conditions (i.e., during MgO carbonation). These experiments were complemented by ex situ structural characterization techniques including Mg K-edge XAS analysis, X-ray powder diffraction (XRD), and magic-angle spinning nuclear magnetic resonance (MAS ²³Na NMR). Next, an experimental setup that allows the collection of in situ XAS data at the Na and Mg K-edges under carbonation conditions was designed and constructed, allowing the acquisition of XAS data of NaNO_3 -promoted MgO for the first time. Both ex situ and in situ analysis reveal changes in the local structure around Na upon carbonation. We attribute the changes observed (both in situ and ex situ) to a restructuring (both in a liquid and in a solid state) at the $\text{NaNO}_3/\text{MgCO}_3$ interfaces and possibly in the vicinity of $[\text{Mg}^{2+} \cdots \text{CO}_3^{2-}]$ ionic pairs dissolved in the NaNO_3 .

2. EXPERIMENTAL SECTION

2.1. Materials. **2.1.1. Sorbent Synthesis.** The CO_2 sorbent $\text{MgO}-10\text{NaNO}_3$ was prepared from hydromagnesite $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Acros Organics, extra pure) and NaNO_3 (Sigma-Aldrich, $\geq 99.5\%$) by a wet mixing procedure described elsewhere (here the “10” in the sorbent name definition refers to the moles of Na per 100 mol of Mg in the sorbent).¹¹

2.1.2. Carbonation Treatment. The preparation of carbonated samples for ex situ structural analysis (vide infra) was carried out in a TGA DSC 3+ instrument (Mettler Toledo). Here, approximately ~ 100 mg of a sample was placed in a crucible and pretreated in N_2 (1 bar, 80 mL min^{-1}) for 30 min at 450 °C to yield a material that is referred to as the as-prepared sample ($\text{MgO}-10\text{NaNO}_3$ -as-prep). Next, the as-prepared sample was cooled down to 315 °C and subjected to a carbonation treatment in CO_2 (1 bar, 80 mL min^{-1}) for 5, 25, and 55 min to yield samples with varying degrees of carbonation being referred to as $\text{MgO}-10\text{NaNO}_3$ -carb5, $\text{MgO}-10\text{NaNO}_3$ -carb25, and $\text{MgO}-10\text{NaNO}_3$ -carb55, respectively. The respective regenerated material was produced by treating the $\text{MgO}-10\text{NaNO}_3$ -carb55 sample for 15 min at 450 °C in N_2 (1 bar, 80 mL min^{-1}); the regenerated sample is referred to as sample $\text{MgO}-10\text{NaNO}_3$ -regen (Figure S1).

2.1.3. Reference Samples. To assist the structural analysis, the following compounds were used as references: NaNO_3 (Sigma-Aldrich, $\geq 99.5\%$), NaNO_2 (Sigma-Aldrich, $\geq 97.0\%$), $\gamma\text{-Na}_2\text{CO}_3$ (Acros Organics, $\geq 99.5\%$), synthetic $\text{Na}_2\text{Mg}(\text{CO}_3)_2$, MgO, and MgCO_3 . $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ was prepared via a solid chemistry route in which hydromagnesite was thoroughly mixed with Na_2CO_3 in an agate mortar. The obtained powder was pelletized and treated at 350 °C in CO_2 for 10 h in a TGA DSC 3+ (Mettler Toledo) instrument. The treatment was repeated three times until XRD analysis showed that all of Na_2CO_3 was converted to $\text{Na}_2\text{Mg}(\text{CO}_3)_2$, with excess MgO (Section S2 of Supporting Information, Figure S2a). MgCO_3 was obtained from hydromagnesite via a wet chemistry route using a suspension of hydromagnesite in monoethylene glycol/water solution, which was refluxed at 150 °C in a continuous CO_2 flow (Figure S2b).³¹ The MgO reference was produced by calcination of hydromagnesite at 450 °C in air for 4 h. The crystalline phase composition of all references was confirmed by XRD.

2.2. Ex Situ Structural Analysis. **2.2.1. X-ray Powder Diffraction.** The crystalline phase composition of the CO_2 sorbent was studied by XRD. The diffractometer (Panalytical Empyrean) was equipped with a Bragg–Brentano HD mirror and operated at 45 kV and 40 mA by using $\text{CuK}\alpha_{1,2}$ radiation. Each sample was scanned in the 2θ range of 5–90°, the step size was 0.016°, and the scan time per step was 0.68 s. Rietveld refinements were performed using the FullProf software,³² using crystal structures previously reported and available in the Inorganic Crystal Structure Database (ICSD) database (MgO 9863, MgCO_3 40,117, NaNO_3 15,332, and $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ 100,482, more details are given in the Section S2 of Supporting Information).

2.2.2. X-ray Absorption Spectroscopy. XAS measurements at the Na and Mg K-edges were carried out at the undulator beamline PHOENIX II (X07MB) at the Swiss Light Source (SLS, PSI, Villigen, Switzerland). Ex situ data were collected using both fluorescence (1-element Si-drift diode detector SDD, Ketek, Germany) and total electron yield (TEY) signals. The powders were supported on a copper plate by using metallic indium for fixation. The current of the incident beam (I_0) was measured as the total electron yield signal using 0.5 μm thin polyester foil coated with metallic Ni (50 nm). The energy calibration was carried out using NaCl (1075.6 eV at the inflection point).²⁹ Both ex situ and in situ data were processed using the software Athena as part of the Demeter software package.³³

2.2.3. X-ray Absorption Near Edge Structure Simulation. Theoretical XANES data were simulated using the finite difference method implemented in the FDMNES code.^{34,35} The crystal structure of NaNO_3 (ICSD: 15332) with space group $R\bar{3}c$ was used. Full potential calculations were performed in either 8.5 Å (for manual O atomic position variation) or 9 Å (for machine learning (ML) type algorithm) radius around the absorbing Na atom. The structure-spectrum relationships were obtained in PyFitIt code³⁶ based on a data

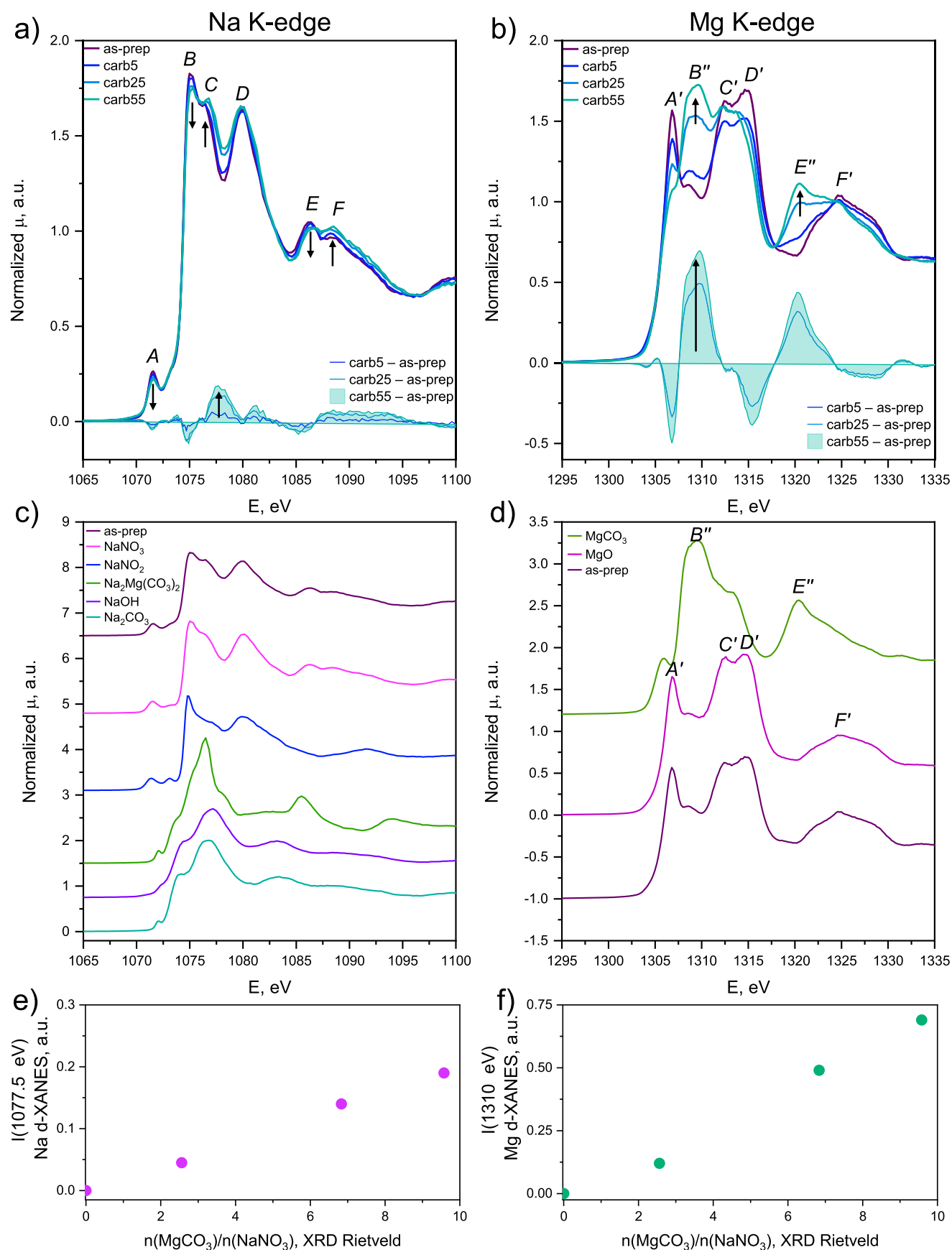


Figure 1. Ex situ XANES spectra for MgO–10NaNO₃_as-prep, MgO–10NaNO₃_carb5, MgO–10NaNO₃_carb25, and MgO–10NaNO₃_carb55 at the (a) Na K-edge and (b) Mg K-edge. XANES spectra of reference materials at the (c) Na K-edge and (d) Mg K-edge (stacked vertically for clarity).

Figure 1. continued

The intensity of the feature at (e) 1077.5 eV (Na K-edge XANES) and (f) 1310 eV (Mg K-edge XANES) in the difference spectra as a function of the ratio between MgCO_3 and NaNO_3 in the material, as determined by Rietveld analysis.

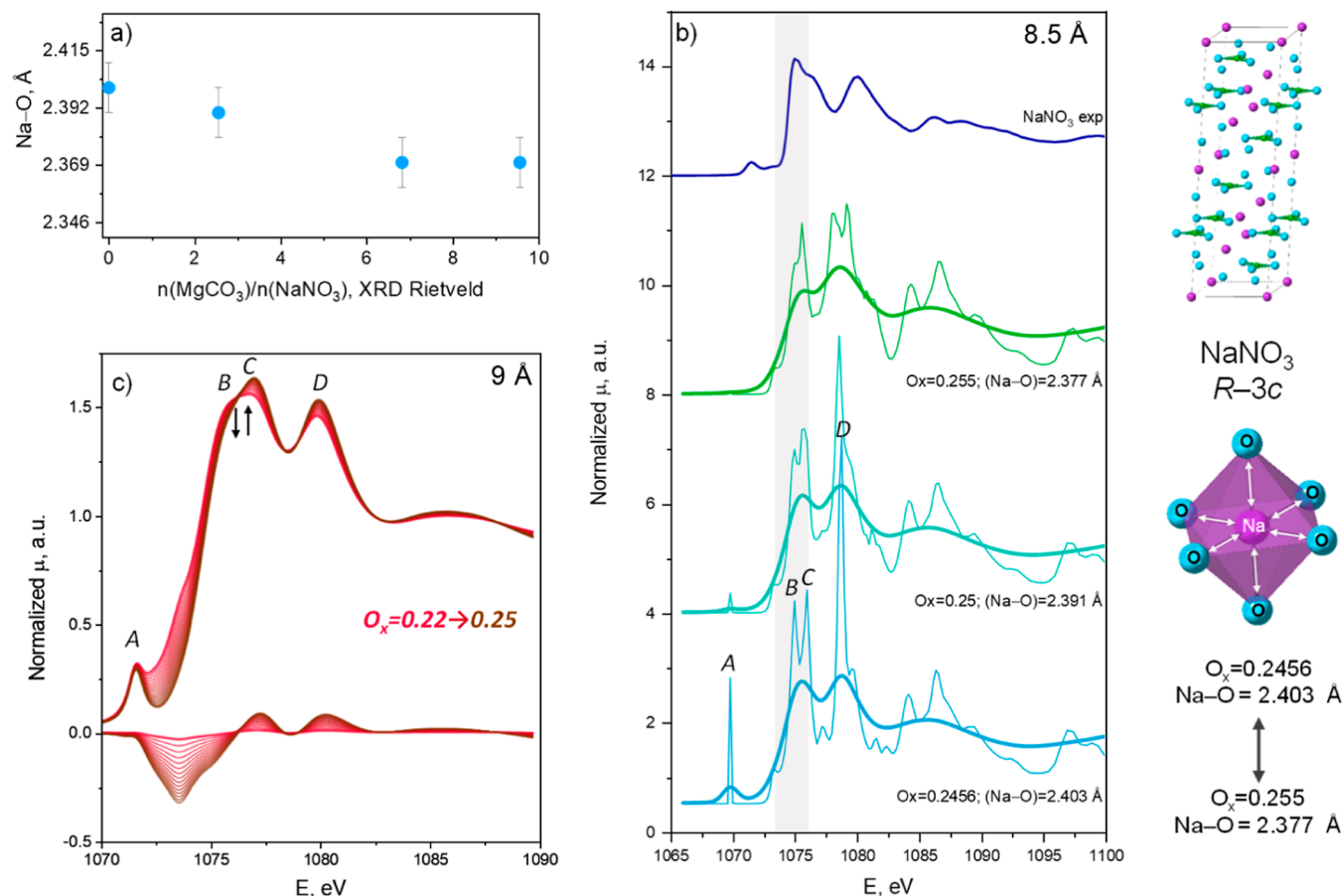


Figure 2. (a) Na–O interatomic distance obtained from EXAFS fitting vs a ratio between MgCO_3 and NaNO_3 in the samples, as determined by Rietveld refinement, (b) FDMNES simulation of the NaNO_3 Na K-edge XANES spectrum with varying O_x position (crystal structure based on ICSD: 15332), including the NaNO_3 crystal structure and the local NaO_6 octahedron, with the arrows pointing to the variation in Na–O distance upon variation of O_x position, (c) simulated Na K-edge XANES spectra of NaNO_3 with varying O_x (Na–O distance) using a ML type algorithm.

set of spectra for systematically varied structural parameters. More details about the simulations can be found in [Supporting Information](#).

2.2.4. Magic-Angle Spinning Nuclear ^{23}Na Magnetic Resonance. MAS ^{23}Na NMR spectra were obtained on a Bruker Avance, 700 MHz, operating at a ^{23}Na Larmor frequency of 158.74 MHz. The measurements were performed at room temperature using a triple-resonance 3.2 mm Bruker probe, at a magic angle spinning (MAS) rate of 20 kHz, with a $2.5 \mu\text{s} \pi/2$ pulse. The calibration of the chemical shift position was performed by using NaCl.

2.2.5. Scanning Transmission Electron Microscopy and Energy Dispersive X-ray. Scanning transmission electron microscopy and energy dispersive X-ray mapping were acquired using an FEI Talos F200X. The operation voltage of the instrument was set to 200 kV in STEM mode.

2.3. In Situ XANES at the Na and Mg K-Edges. To collect in situ Na and Mg XAS data during carbonation, we designed and constructed a dedicated cell ([Figures 3c and S5](#)). The cell allowed us to control the temperature (25–400 °C) and the gas flow (up to 0.4 bar of N_2 or CO_2) ([Figure 3d](#)) and was placed in a vacuum chamber at a pressure of approximately 2.5×10^{-4} mbar. In such experiments, the sample $\text{MgO}-10\text{NaNO}_3$ was pressed into a pellet (diameter of 9 mm and thickness of ca. 1 mm) and clamped onto a sample holder. The cell was equipped with two Si_3N_4 windows (Silson Ltd.) of 500 nm thickness: one window to allow for the transmission of the incoming beam onto

the sample and the second window to allow for the collection of the fluorescence signal from the sample using a single-element Si-drift diode detector (Manufacturer Ketek, Germany). The cell contains two windows made of Si_3N_4 of 500 nm thickness mounted perpendicular to each other (further details in [Figure S5](#)). The windows were glued using a high temperature epoxy, which was applied to the window holder. One window allowed the penetration of the incoming X-ray beam into the cell and its interaction with the sample. The other window allowed the detection of X-rays in fluorescence mode (using a 1-element Si-drift diode detector). Using separate windows for the incoming and outgoing beam allows mounting the windows further away from the hot sample and hence keeping the windows at temperatures that are compatible with the epoxy resin glue. Furthermore, a flow of gaseous nitrogen was used to cool the frame, which holds the window to minimize the heating of the windows ([Figure S5](#)). The sample was pressed into a cylindrical pellet of 9 mm in diameter and about 1 mm thickness and mounted in the heated sample holder in the cell. The sample holder for the pelletized sample was placed in a 45° angle with respect to each of the two windows ([Figures 3c and S5](#)). The cell was mounted inside the vacuum chamber of the end-station of the PHOENIX II beamline.

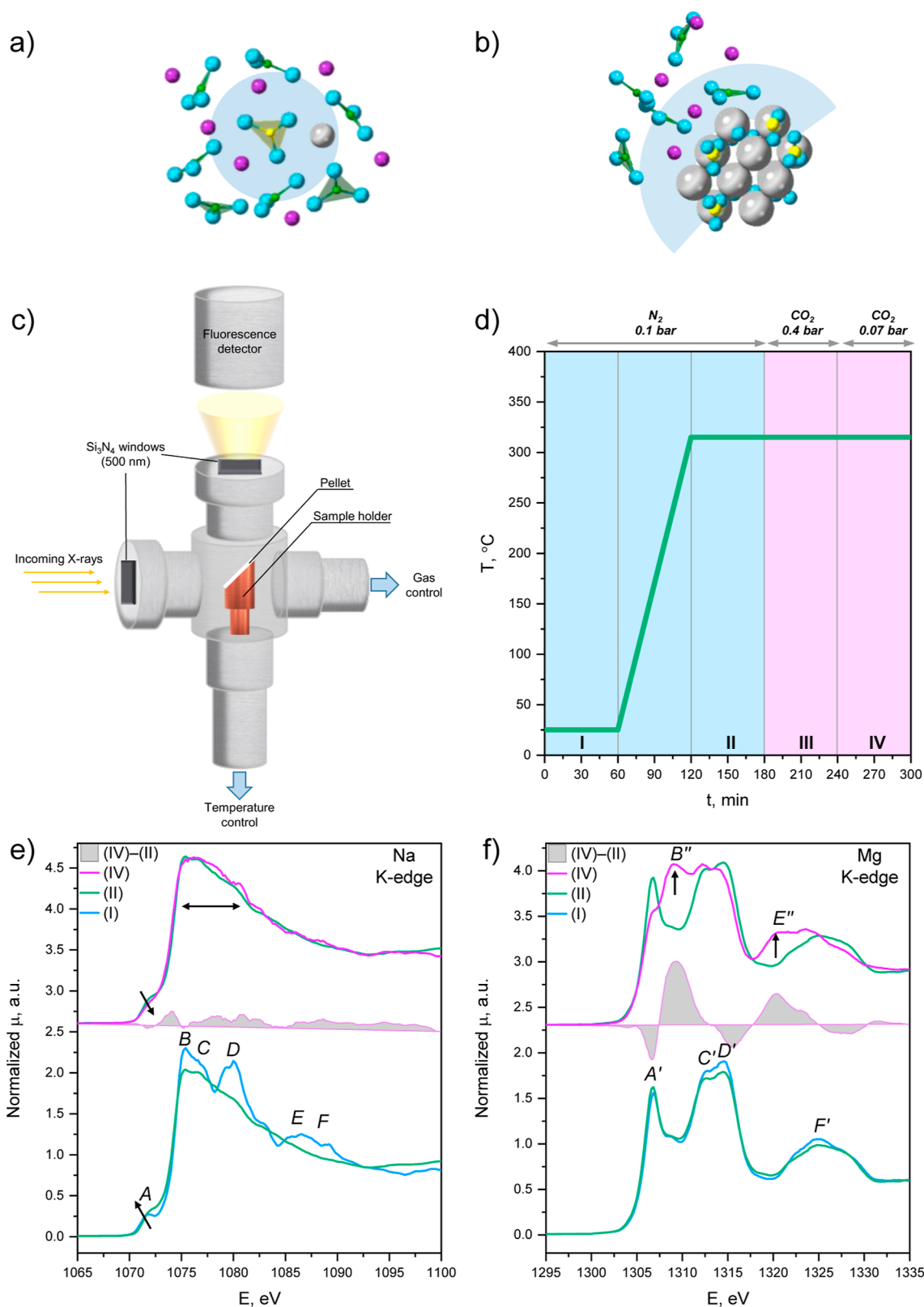


Figure 3. (a) Illustrations of the restructuring of molten NaNO₃ during carbonation due to (a) dissolved [Mg²⁺...CO₃²⁻] ionic pairs and the (b) NaNO₃/MgCO₃ interface. Color legend: blue—oxygen, purple—sodium, green—nitrogen, gray—magnesium, and yellow—carbon. (c) Schematics of the reaction cell used for collecting in situ XAS at the Na and Mg K-edges. (d) Experimental protocol for data acquisition; I—25 °C, N₂, 0.1 bar; II—315 °C, N₂, 0.1 bar; III—315 °C, CO₂, 0.4 bar; IV—315 °C, CO₂, 0.07 bar. XANES spectra at the (e) Na K-edge and (f) Mg K-edge.

3. RESULTS AND DISCUSSION

3.1. Ex Situ Structural Characterization of the As-Prepared, Carbonated, and Regenerated CO₂ Sorbents.

3.1.1. Crystalline Phase Composition. At room temperature the as-prepared MgO–10NaNO₃ as-prep CO₂ sorbent (pre-treated at 450 °C, N₂, 80 mL min⁻¹ for 30 min) contained two crystalline phases: MgO (*Fm* $\bar{3}$ *m*, 83 wt %) and NaNO₃ (*R* $\bar{3}$ *c*, 17 wt %) according to Rietveld refinements of XRD data (Section S2 in Supporting Information). The carbonated samples (at 315 °C, CO₂, 80 mL min⁻¹ for 5, 25, or 55 min) contained MgCO₃ (*R* $\bar{3}$ *c*), MgO (*Fm* $\bar{3}$ *m*), and NaNO₃ (*R* $\bar{3}$ *c*) in the following concentrations [MgCO₃, MgO, and NaNO₃]: [33, 54, and 13 wt %], [61, 30, and 9 wt %], and [76, 16, and 8 wt %] in MgO–10NaNO₃_carb5, MgO–10NaNO₃_carb25, and MgO–10NaNO₃_carb55, respectively. After carbonation for 55 min, a regeneration step was performed (450 °C, N₂, 80 mL min⁻¹ for 15 min), that restored the initial composition of the sorbent (within errors) in MgO–10NaNO₃_regen CO₂ sorbent: MgO (81 wt %) and NaNO₃ (19 wt %).

3.1.2. Local Structure. While XRD analysis provided information about the crystalline bulk average structure, the local structure of the as-prepared, carbonated, and regenerated CO₂ sorbents was characterized by ex situ XANES at the Na and Mg K-edges, which was further complemented by MAS ²³Na NMR. The XANES spectra at the Na and Mg K-edges for the as-prepared and the carbonated materials are presented in Figure 1a,b, respectively. All of the features, i.e., labeled as A' (1306.9 eV), C' (1312.5), D' (1314.7 eV) and F' (1324.8 eV), that were present in the acquired Mg K-edge spectrum of MgO–10NaNO₃_as-prep were well-described by the MgO reference (the absorption edge corresponds to the transition of the 1s electron to unoccupied states, with single and multiple photoscattering by neighboring atoms in the nearest and outermost coordination shells contributing to the features above the edge).^{37,38} During carbonation the intensity of the new features B'' (1309.3 eV) and E'' (1320.4 eV) due to MgCO₃ grew, indicative of an increasing fraction of MgCO₃ with increasing carbonation time.^{39,40} The emergence and growth of features B'' and E'' were also clearly observed in the difference spectra (i.e., the difference between the spectra of a MgO–10NaNO₃_carbX and that of the MgO–10NaNO₃_as-prep sorbents) and were in line with the XRD results. To confirm that the Mg K-edge spectra of the carbonated samples could be described by two phases only, i.e., MgO and MgCO₃, we performed a linear combination fitting (LCF) analysis of the Mg K-edge XANES spectra. The spectra of the carbonated materials were well-described by a LCF of the two references MgCO₃ and MgO (Figure S7) and yielded values of molar fractions [MgCO₃: (MgCO₃ + MgO)] = 0.13, 0.45, and 0.61 in MgO–10NaNO₃_carb5, MgO–10NaNO₃_carb25, and MgO–10NaNO₃_carb55, respectively, that were in good agreement with XRD and TGA measurements (see comparison in Figure S8). In the regenerated sorbent, MgO–10NaNO₃_regen, the features due to MgO were fully restored, which was in line with the complete decomposition of MgCO₃ into MgO after regeneration (Figure S9b).

The Na K-edge XANES spectrum of the MgO–10NaNO₃_as-prep sorbent, Figure 1a, showed identical features as the spectrum of the reference NaNO₃ (Figure 1c). The spectrum showed characteristic features of NaNO₃ above the edge, i.e., B (1075.3 eV), C (1076.9 eV), D (1079.8 eV), E (1086.3 eV), and F (1088.4 eV).⁴¹ In addition, both spectra

(NaNO₃ and MgO–10NaNO₃_as-prep) exhibit pre-edge feature A (1071.8 eV).

Interestingly, the Na K-edge XANES spectra of the carbonated samples differed from those of the as-prepared material. With increasing carbonation time, the intensity of the pre-edge features A, B, and E decreased, while the intensity of features C and F increased. In addition, with increasing carbonation time, features C and D became visibly broader. The described changes in the features become clearer in the difference spectra (Figure 1a). When plotting the intensity of the features C (Na K-edge at ca. 1077.5 eV) and B'' (Mg K-edge at ca. 1310 eV) in the difference spectra against the MgCO₃ content (determined by Rietveld refinement), we can infer that the changes observed in the Na K-edge XANES spectra upon carbonation scaled with the quantity of MgCO₃ formed (Figure 1e,f). The XANES spectrum of the regenerated sample revealed that the NaNO₃ environment of the as-prepared sample was largely restored. Notably, the intensity of feature B increased (which was slightly higher than that in the as-prepared sample), while features A, C, E, and F were largely restored to the initial positions and intensities, indicating that the changes that occurred upon carbonation were mostly reversible (Figure S9a).

One hypothesis to explain the changes observed in the Na K-edge XANES spectra upon carbonation could be the decomposition of NaNO₃, e.g., into NaNO₂ or Na₂O which would transform further under carbonation conditions (CO₂, 315 °C) to sodium-containing carbonates Na₂CO₃ and/or Na₂Mg(CO₃)₂, as previously observed.⁴² However, according to Rekhina et al., the decomposition of NaNO₃ does not take place below 450 °C. Also, Na₂CO₃ and Na₂Mg(CO₃)₂ could only be formed over repeated carbonation and regeneration (*T* ≥ 450 °C) cycles through the partial decomposition of NaNO₃ and the carbonation of the decomposition products, as previously observed by Rekhina et al.⁴² Since the carbonation temperature was considerably below the decomposition temperature (315 °C), NaNO₃ decomposition is not expected. In addition, we compared the XANES spectra of the carbonated sorbent with the most likely NaNO₃ decomposition products (under ambient or CO₂ capture conditions), i.e., Na₂CO₃, Na₂Mg(CO₃)₂, NaOH, and NaNO₂ (Figure 1c). Our analysis showed that none of these potential decomposition products explain feature C (1076.9 eV) in the carbonated samples. This is illustrated in Figure S10, which demonstrates that the Na K-edge XANES spectrum of MgO–10NaNO₃_carb55 was not well-described by a linear combination of the potential decomposition products. Note that neither Na₂CO₃, Na₂Mg(CO₃)₂, nor NaOH phases were detected by XRD (nor MAS ²³Na NMR, vide infra). Furthermore, the decomposition of NaNO₃ is an irreversible process; if there was NaNO₃ decomposition to occur, the initial spectrum should not be recovered in the regenerated material, which is, however the case (Figure S9a). Therefore, we discarded the hypothesis that changes in the Na K-edge XANES spectra of MgO–10NaNO₃ upon carbonation were due to the formation of either Na₂CO₃, Na₂Mg(CO₃)₂, NaNO₂, or NaOH. Since the cell parameters of MgCO₃ [e.g., *a* = 4.6408(4) Å and *c* = 15.065(1) Å for MgO–10NaNO₃_carb55] did not show an appreciable change with respect to the cell parameters of MgCO₃ reference [*a* = 4.64261(5) Å and *c* = 15.0604(2) Å], we also discarded the incorporation of Na⁺ in the MgCO₃ crystal structure (Section S2 of Supporting Information).

Instead, we hypothesize that the changes revealed by Na K-edge XANES upon carbonation were due to changes in the Na

local structure in the vicinity of MgCO_3 , i.e., at the $\text{NaNO}_3/\text{MgCO}_3$ interfaces and due to the dissolution of $[\text{Mg}^{2+}\cdots\text{CO}_3^{2-}]$ ion pairs in the NaNO_3 melt (vide infra). Even though these XANES data did not probe directly the interfaces of our materials (yielding a sum of surface, interfaces, and bulk Na sites), if a change of the Na local structure occurred at $\text{MgCO}_3/\text{NaNO}_3$ interfaces, we would expect that the spectral changes increase with increasing $\text{MgCO}_3/\text{NaNO}_3$ ratios as observed for our data (Figure 1b,e,f). In this context, it is worth noting that STEM–EDX mapping showed that Na (NaNO_3) was well distributed throughout the CO_2 sorbent (i.e., Na and Mg EDX signals overlap spatially), yet also some sub-micrometer-sized particles were observed (Figure S11).

Na K-edge XANES experiments were complemented by MAS ^{23}Na NMR (Figure S12). The MAS ^{23}Na NMR spectrum of the as-prepared sorbent showed a single peak with a chemical shift of -15.4 ppm (Figure S12a), in line with the MAS ^{23}Na NMR signature of the reference NaNO_3 (Figure S12c). After carbonation, a second peak developed in the MAS ^{23}Na NMR spectra, with a chemical shift located at around -11 ppm (Figure S12a). This peak could not be ascribed to the $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ or Na_2CO_3 references (Figure S12c), in line with XANES and XRD analyses (vide supra). Further, MAS ^{23}Na NMR also confirmed that the spectrum of $\text{MgO}-10\text{NaNO}_3_{\text{regen}}$ was similar to the spectrum of $\text{MgO}-10\text{NaNO}_3_{\text{as-prep}}$ (Figure S12b), i.e., further confirming that changes in the local environment of Na were reversible and related to the presence of MgCO_3 in the sample. Therefore, MAS ^{23}Na NMR data provides important additional (qualitative) evidence that the local environment around Na changes upon carbonation, while regeneration restores the initial NaNO_3 environment, confirming the results of the XAS analysis.

Extended X-ray absorption fine structure (EXAFS) analysis at the Na K-edge provided further insight into the change in the local environment of Na after carbonation. The Fourier transformed (FT) EXAFS data (not corrected for phase shift) exhibited a peak due to the Na–O coordination that was centered at ca. 1.9 Å and peaks due to Na–N and Na–Na coordination at ca. 3.5 and 4.7 Å, respectively (Figure S13). Due to the limited k range of the data ($k_{\text{max}} = 6.8$ Å $^{-1}$ limited by the Mg K-edge energy), only the first coordination shell was fitted. The results of the fitting showed a shortening of the Na–O interatomic distance with increased degree of carbonation, i.e., $\text{Na}-\text{O}_{\text{as-prep}} = 2.40(1)$ Å and $\text{Na}-\text{O}_{\text{carb55}} = 2.37(1)$ Å (Figure 2a) and an increase back after regeneration, i.e., $\text{Na}-\text{O}_{\text{regen}} = 2.39(1)$ Å (Table S5). Fitting of the EXAFS data also yielded higher Debye–Waller factors (σ^2) in the carbonated samples, which might indicate a higher degree of structural disorder in Na–O coordination upon carbonation. However, it should be noted that the errors in the σ^2 fitted are high.⁴³ Similar trends were obtained for the Na–O distances (and σ^2) when fitting in R -space (FT) or in k -space as shown in Figure 2a (i.e., using the back FT in the range between 1.2 and 2.6 Å, Figure S16) confirming the reproducibility of the fittings (Tables S5 and S6). To summarize, EXAFS analysis also indicated that the local structure around Na underwent changes upon carbonation, in line with Na K-edge XANES and MAS ^{23}Na NMR data.

Next, we turn to a theoretical analysis of the Na K-edge XANES spectra. The ab initio simulations of XANES was carried out in FDMNES code (more details are given in Section S8 of Supporting Information).³⁴ The nonstructural parameters of the calculation were obtained by reproducing the spectrum of NaNO_3 reference (Figure S19c). Next, to explain the spectral

variation observed in the carbonated materials, we attempted to establish the dependency of XANES upon the Na–O distance, based on the changes obtained in the EXAFS analysis. Starting from the crystal structure of NaNO_3 , the atomic position x of the oxygen atom (referred to as O_x herein for convenience, Table S7, Figures 2b and S3) was varied. An increase in O_x from 0.2456 ($\text{Na}-\text{O} = 2.403$ Å) to 0.25 ($\text{Na}-\text{O} = 2.391$ Å) (Table S8) led to clear changes in the XANES spectra, viz., an intensification of feature C and a decrease in the intensity of feature B (Figure 2b). A further increase of the O_x position to 0.255 ($\text{Na}-\text{O} = 2.377$ Å) resulted in further intensification of feature C and lowering of feature B. Additionally, we employed a machine learning (ML) type algorithm trained on the theoretical spectra of NaNO_3 with systematic variation of O_x coordinate range $[0.146-0.346]$ and cell parameters a $[4.97-5.17]$ and c $[16.7-16.9]$, which allowed prediction of XANES spectra for any combination of these parameters (Figure 2c, more details in Section S8 of Supporting Information). These results also showed how the shortening of the Na–O distance resulted in spectral changes resembling the ones observed in carbonated samples (Figure 1a). The Rietveld analysis of the XRD data did not reveal a similar trend of an O_x increase in the carbonated samples (Tables S3 and S4). Since XRD analysis relies solely on coherent X-ray scattering, it does not probe changes in the local structure that are related to imperfections in the material. Thus, the combined XAS and XRD analyses support the conclusion that the observed changes in the Na environment were not due to changes in the crystal (average) structure of NaNO_3 . Instead, these analyses indicated the occurrence of changes in the local structure of disordered regions upon carbonation (e.g., at the interfaces between NaNO_3 and MgCO_3).

To summarize, the combined analysis of Na K-edge XANES, EXAFS, MAS ^{23}Na NMR, STEM–EDX, and XRD data revealed that the local environment around Na was altered by the presence of carbonate species ($\text{MgCO}_3/[\text{Mg}^{2+}\cdots\text{CO}_3^{2-}]$ ionic pairs). Although we currently lack a detailed atomic-scale model, the correlation between the magnitude of the changes in the XANES spectra and the $\text{NaNO}_3/\text{MgCO}_3$ ratio suggests that the observed changes in the Na environment are related to the $\text{NaNO}_3/\text{MgCO}_3$ interfaces and due to the dissolution of $[\text{Mg}^{2+}\cdots\text{CO}_3^{2-}]$ ionic pairs in the molten salt.²⁰ This hypothesis can be rationalized in light of previous studies showing that MgCO_3 nucleates and grows at the buried interface between solid MgO and molten NaNO_3 via the dissolution of $[\text{Mg}^{2+}\cdots\text{CO}_3^{2-}]$ ion pairs in the melt $[\text{Na}\cdots\text{NO}_3^-]$. Thus, it is likely that as MgCO_3 crystallites form, NaNO_3 remains in intimate contact with MgCO_3 due to the formation of a NaNO_3 solvation shell around MgCO_3 . We propose that such dissolution (solvation) modifies the Na local structure in the melt and such structural modifications remain when the material is cooled (as NaNO_3 dispersed at the MgCO_3 surface and/or trapped within MgCO_3 as inclusions), as schematized in Figure 3a,b. This interpretation is in line with recent studies that proposed that the mechanism of CO_2 uptake in NaNO_3 -promoted MgO proceeds through the dissolution of $[\text{Mg}^{2+}\cdots\text{CO}_3^{2-}]$ ionic pairs in the NaNO_3 melt (these pairs precipitate upon supersaturation yielding crystalline MgCO_3).²⁰

3.2. In Situ Na and Mg K-Edge XANES. Lastly, we probed the local structure around Na and changes thereof during carbonation in the sorbent $\text{MgO}-10\text{NaNO}_3$ under operating conditions using in situ XANES. Such XANES measurements were performed using a custom-made cell to allow the collection of soft XAS data at high temperature (maximum tested

temperature of 400 °C) and under a gas flow of N₂ or CO₂. A schematic of the cell is given in Figure 3c, and its details are described in the Experimental Section.

In situ Na and Mg K-edge XANES spectra were collected within a single experiment in a consecutive fashion (Figure 3e,f). The spectra collected at room temperature (I, Figure 3e,f) agreed with the ex situ data reported in Figure 1a,b, albeit having a lower signal-to-noise ratio, confirming the well-functioning of the in situ set up. When heating to 315 °C in N₂ (II, Figure 3e,f), the Mg K-edge XANES spectrum did not undergo significant changes with respect to the spectrum acquired at room temperature. This was expected as MgO remains in its crystalline form under these conditions. The possible dissolution of [Mg²⁺...O²⁻] ionic pairs into the melt was not identified in these experiments very likely because their concentration is below the sensitivity of our measurements, which is dominated by the crystalline MgO signal. In the Na K-edge XANES spectrum of MgO–10NaNO₃ collected at 315 °C in N₂, the features became broader and less intense compared to the spectrum acquired at room temperature due to the increasing thermal and structural disorder attributed to the melting of NaNO₃. Despite the broader features, the Na K-edge XANES spectrum of the molten salt maintained some similarities to its crystalline state. Specifically, the pre-edge feature A remained present in the spectrum of the molten state, while its intensity slightly increased with respect to that of solid NaNO₃, possibly due to a higher degree of structural distortion around Na or a slight decrease in the average coordination number.^{44–46} Furthermore, features B–D were also clearly observed in molten NaNO₃, yet the relative intensity of these features differed from those in crystalline NaNO₃ suggesting a remaining local ordering of the NO₃⁻ ions around Na⁺ ions in molten NaNO₃. Features E and F disappeared, which was related to the loss of medium and long-range order around the Na⁺ ion.⁴⁷ When we compared the experimental XANES spectrum of molten NaNO₃ with our simulations of the NaNO₃ spectra when varying the cluster size (Figures S19 and S21), we could estimate the size of the local ordering. The experimental spectrum of molten NaNO₃ showed some resemblance (based on the overall spectral shape) to the simulated Na K-edge XANES spectrum of NaNO₃ using CS = 4.1 Å (using a CS of 4.1 Å in the simulation includes the first and second Na–O coordination shell, the first Na–N and the first Na–Na coordination shell, Figures S19 and S21). The simulated Na K-edge spectrum of NaNO₃ reproduced features A–C and the low intensity feature D of the experimental spectrum. However, the experimental spectrum showed broader features due to the high degree of disorder of NaNO₃ in the molten state. Although our simplified analysis does not consider the dynamics of the local Na structures, these observations are qualitatively in line with previous total scattering and molecular dynamics simulations studies of molten NaNO₃ structures, which show that the most intense interatomic correlations of molten NaNO₃ are below ca. 8 Å (i.e., local ordering), while there is no medium and long-range order.^{18,25,48} These studies have shown that the first Na–O distance in molten NaNO₃ is positioned at 2.5–2.7 Å compared with ca. 2.4 Å in crystalline NaNO₃,^{18,25,48} and a coordination number of 5.6 was reported, compared to 6 in crystalline NaNO₃.²⁵

Next, the sorbent was exposed to 0.4 bar of CO₂ to carbonate the sample (III in Figure 3d) for about 60 min. During XANES spectra collection, the partial pressure of CO₂ was reduced to 0.07 bar (IV), i.e., to reduce the absorption of soft X-rays due to

CO₂ in the area between the sample and the windows. Importantly, the appearance of the features B' (1309.3 eV) and E' (1320.4 eV) in the Mg K-edge XANES spectrum (Figure 3f) confirmed the formation of MgCO₃, in line with ex situ measurements (vide supra). Interestingly, the in situ experiments also showed some changes, albeit being small, in the Na K-edge XANES spectrum during carbonation (Figure 3e). Specifically, the spectrum broadened with respect to the spectrum prior to carbonation, and the intensity of the pre-edge feature decreased. These changes can be visualized better in the difference spectrum highlighted in gray in Figure 3e and are qualitatively in agreement with the observed changes in the ex situ Na K-edge XANES measurements when comparing the as-prepared and carbonated samples (Figure S22). However, due to the higher degree of disorder in the molten phase, the changes were less resolved and subtler than shown by the ex situ data. Nevertheless, it is possible that the changes observed in the in situ Na K-edge XANES spectrum upon carbonation were due to changes in the local environment/structure around Na due to the presence of [Mg²⁺...CO₃²⁻] pairs dissolved in the NaNO₃ melt and/or due to a solvation shell around MgCO₃ (as shown schematically in Figure 3a,b).^{49–51} More experiments and modeling studies are required to further test this hypothesis. However, we believe that the present study provides an innovative experimental approach and important data pointing toward the validity of the CO₂ uptake mechanism in NaNO₃-promoted MgO as proposed by Landuyt et al.²⁰

4. CONCLUSIONS

Ex situ analysis of XAS at the Na K-edge and MAS ²³Na NMR data of a NaNO₃-promoted MgO-based sorbent showed that the local structure around Na changed upon CO₂ capture, i.e., upon formation of MgCO₃. Quantitative EXAFS analysis revealed that the average Na–O distance decreased with increasing MgCO₃ content, i.e., increasing amount of CO₂ captured. Furthermore, the observed changes in the Na K-edge XANES spectra during carbonation scaled with the amount of MgCO₃ formed, in line with the MAS ²³Na NMR results. We rationalize our experimental observation of a change in the local structure of Na during carbonation as being due to the formation of NaNO₃/MgCO₃ interfaces and/or of the trapping of [Mg²⁺...CO₃²⁻] ionic pairs in the NaNO₃ melt after cooling. Such local structures differ from the local structure of Na in bulk NaNO₃. Moreover, the Na local structure of NaNO₃ was restored in the regenerated material (i.e., after MgCO₃ decomposed to MgO), further confirming that the observed changes were reversible and related to the presence of MgCO₃. Furthermore, using a customized reaction cell, we carried out in situ XAS measurements at the Na and Mg K-edges under operating conditions (i.e., during carbonation). Na K-edge XANES spectra of NaNO₃-promoted MgO-based sorbents whereby NaNO₃ was molten under in situ conditions are reported here for the first time. These in situ experiments also suggested changes in the Na K-edge XANES spectra, albeit the changes being smaller than the changes observed in the ex situ data when the sorbent was exposed to CO₂. The in situ formation of MgCO₃ was confirmed by Mg K-edge XANES data collected sequentially with the Na XANES data.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c02077>.

Thermogravimetric analysis (TGA), X-ray powder diffraction (XRD) data, Rietveld refinements, experimental set up to acquire in situ X-ray absorption spectroscopy (XAS) data at the Na and Mg K-edges, scanning transmission electron microscopy and energy dispersive X-ray (STEM-EDX), ab initio simulations of XANES spectra, fitting of the extended X-ray absorption fine structure (EXAFS), and magic-angle spinning ^{23}Na nuclear magnetic resonance (MAS ^{23}Na NMR) (PDF)

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Notes

The authors declare no competing financial interest.

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