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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.8b01845 • Publication Date (Web): 19 Mar 2018

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Carbon Capture by Metal Oxides: Unleashing the Potential of the (111) Facet

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ABSTRACT: Solid metal oxides for carbon capture exhibit reduced adsorption capacity following high temperature exposure, due to surface area reduction by sintering. Furthermore, only low coordinate corner/edge sites on the thermodynamically stable (100) facet display favourable binding towards CO₂, providing inherently low capacity. The (111) facet however, exhibits a high concentration of low coordinate sites. In this work, MgO(111) nanosheets displayed high capacity for CO₂, as well as a $\approx 65\%$ increase in capacity despite a $\approx 30\%$ reduction in surface area following sintering ($0.77 \text{ mmol g}^{-1} @ 227 \text{ m}^2 \text{ g}^{-1}$ vs $1.28 \text{ mmol g}^{-1} @ 154 \text{ m}^2 \text{ g}^{-1}$). These results, unique to MgO(111) suggest intrinsic differences in the effects of sintering on basic site retention. Spectroscopic and computational investigations provided a new structure-activity insight; the importance of high temperature activation to unleash the capacity of the polar (111) facet of MgO. In summary, we present the first example of a faceted sorbent for carbon capture and challenge the assumption that sintering is necessarily a negative process; here we leverage high temperature conditions for facet-dependent surface activation.

1. Introduction

Carbon capture, utilisation and storage (CCUS) is a portfolio of processes to combat anthropogenic climate change.¹ Capture is most economically viable for slowing CO₂ release at point sources, *e.g.* combustion power generation plants. Direct air capture is increasingly discussed,²⁻⁴ to immediately reduce atmospheric CO₂ concentration. CCUS allows the continued use of fossil fuels, or results in net negative carbon emissions, when in combination with bioenergy.^{5,6} Utilisation refers to the subsequent use of CO₂ in the synthesis of chemicals or enhanced oil recovery, in order to add value.^{7,8} Storage is generally the disposal of captured CO₂ in geological formations.⁹

Regardless of the fate of CO₂, it remains the case that capture is the most costly stage of CCUS,¹⁰ due to the immense volumes to be handled. Cyclic absorption-desorption of CO₂ using aqueous amines is inefficient and expensive, generating significant interest in developing new “task-specific” materials as replacements.¹¹⁻¹³ Solid adsorption-desorption cycles, “looping” processes, offer many advantages over amine scrubbing. They can be distinguished chiefly by their role: the supply of O₂ from air for combustion (providing inherent carbon capture);¹⁴ *in-situ* CO₂ sorption during H₂ production;¹⁵ and the removal of CO₂ from flue gases.¹⁶ Solid oxide adsorbents used in these processes, *e.g.* CaO or MgO, experience particularly

harsh environments. They are fluidised, handled at high temperature, and repeatedly cycled between oxidation/reduction or carbonation/calcination reactors. Sintering dramatically reduces sorbent performance, acutely evident in high temperature CO₂ adsorbents,¹⁷ leading to creative synthetic efforts in producing sintering-resistant materials.¹⁸⁻²⁰

For any adsorbent, the initial gas-solid reaction/interaction must occur at the surface. Using the carbonation of CaO in calcium looping as a pertinent example, carbonates first form at the surface, subsequently migrating to the bulk.²¹ The capacity of sorbents proposed for low temperature carbon capture is entirely limited to surface interaction, resulting in a race to produce ever increasing surface areas - exemplified by metal-organic frameworks (MOFs).^{22,23} This approach is likely to fail for solid oxides such as CaO or MgO due to sintering over large numbers of high temperature cycles. Increased surface area has been shown to enhance capacity, only in a limited number of cycles.²⁴⁻²⁶ Considered far less often for CO₂ adsorbents, if at all, is the synthetic control and subsequent utilisation of exposed “favourable” crystalline facets. This is surprising considering entire fields (*e.g.* catalysis) have developed largely by controlling this aspect of solids.²⁷⁻³⁰

In an attempt to bridge this concept with carbon capture, we considered that prominent high temperature

adsorbents include isometric crystals of the rock-salt structure (space group $Fm\bar{3}m$), more specifically group 2 alkaline earth metal oxides, *e.g.* MgO. In this structure, Mg and O atoms occupy octahedral geometry, forming independent face-centred cubic lattices, which merge together to produce an alternating cation/anion pattern propagating in three dimensions. The thermodynamically favoured (100) facet can easily be envisioned as an atomic checkerboard pattern. The (111) facet can be visualised as alternating polar layers of cation and anion (Figure 1a), with surface termination dependant on the environment. In O-rich conditions the facet will be oxygen terminated.³¹ The polar (111) facet has been shown to be stable at the nano-scale^{32,33} or when hydroxylated.³⁴⁻³⁶ *Ab initio* calculations have shown that hydroxylated (111) surfaces are more stable than clean (100) surfaces,³⁷ with experimental and theoretical investigation providing a hydroxylated surface energy hierarchy of $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$.³⁸

Returning to carbon capture, CO₂ adsorption on metal oxides is largely facilitated by low-coordination O²⁻ sites;³⁹⁻⁴² the acidic CO₂ molecule reacts with a basic O²⁻ site. On predominant MgO (100) facets, CO₂ adsorption will not occur,^{42,43} instead favouring corner and edge sites. DFT calculations have shown that the (111) facet of CaO is responsible for carbonate nucleation.⁴⁴ Synthesis methods,^{30,45-47} and examples of catalytic application are present in the literature for (111) metal oxides.^{34,48,49} Considering favourable surface chemistry, we postulated that a (111) faceted adsorbent would be promising for carbon capture. Such a sorbent should possess: 1) enhanced reactivity towards CO₂ (increased basicity of the polar O²⁻ sites); 2) enhanced capacity for CO₂ (doubled population of exposed O²⁻ compared to a (100) facet) and 3) unique CO₂ adsorption phenomena related to the (111) facet following high temperature treatment (removal of the stabilising hydroxylated surface layer to expose O²⁻).

Herein, we show that at sintering conditions found in practical application (800°C), MgO(111) nanosheets experience a $\approx 30\%$ reduction in surface area due to sintering, yet provide a $\approx 65\%$ increase in CO₂ capacity (0.77 mmol g⁻¹ @ 227 m² g⁻¹ vs 1.28 mmol g⁻¹ @ 154 m² g⁻¹). We compare MgO(111) nanosheets with commercial MgO, conventionally prepared nanoparticle MgO (nano-MgO), and MgO(111) treated at 800°C to unambiguously attribute the enhanced capacity to the presence of the cleaned (111) facet. Furthermore, we show experimentally and theoretically that the high temperature treatment removes specific surface hydroxyl groups, providing insight into a new structure-activity relationship leading to enhanced capacity. The article is structured in three parts: 1) the impact of high temperature treatment on the physical properties of MgO(111); 2) the subsequent paradoxical effect on CO₂ adsorption capacity and 3) the surface chemistry changes facilitating the enhanced capacity. Throughout, MgO(111) refers to the as prepared sample pre-treated at 400°C (below the temperature of calcination during synthesis) and MgO(111) 800°C refers to the as prepared sample pre-treated at 800°C.

2. Results

2.1 Adsorbent Characterisation

MgO(111) and MgO(111) 800°C were identified as periclase MgO in the Inorganic Crystal Structure Database (ICSD PDF 01-071-1176) (Figure 1b). Sharpening of the MgO(111) 800°C diffractogram indicated crystallite size growth (Scherrer average crystallite size increase from 5.3 to 8.5 nm). Bright-field transmission electron microscopy (BF-TEM) showed that MgO(111) was composed of plate-like nanosheets within a size range of 5 – 25 nm (Figure 1c). After treatment at 800°C *in-vacuo* for 2 h, morphology remained consistent, with growth of nanosheet size range to 15 – 30 nm (Figure 1c).

Scanning TEM (STEM) imaging and energy dispersive spectroscopy (EDS) further showed that both morphology and compositional homogeneity remained consistent after heat treatment (Figure S1). Nitrogen adsorption-desorption confirmed the morphology observation, with H₃ hysteresis loops present in all Type IV isotherms, indicative of

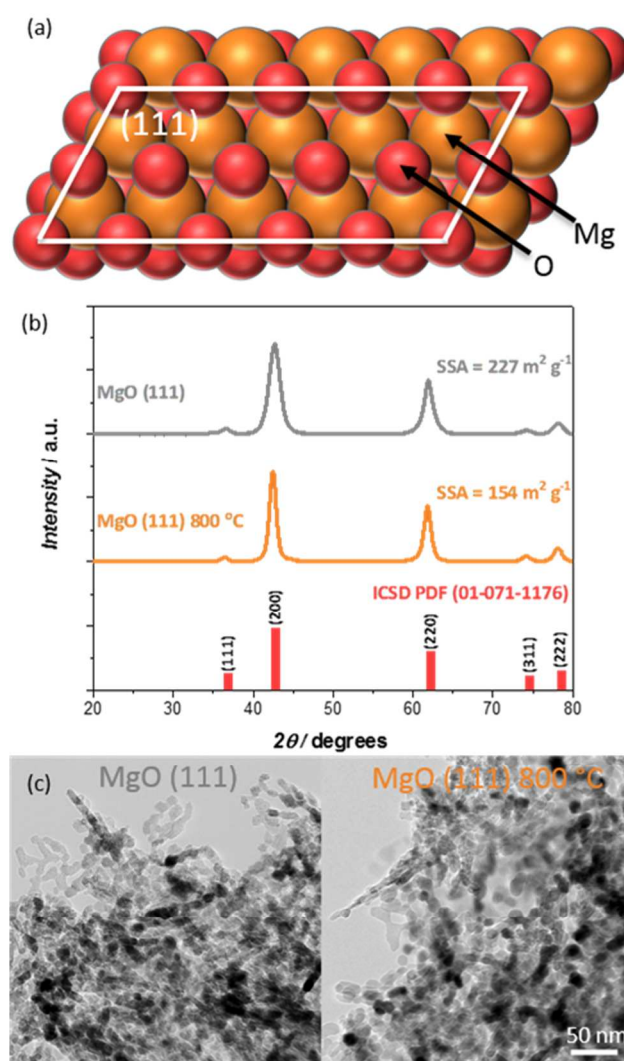


Figure 1. Structure and morphology of MgO(111) nanosheets. (a) Top view configuration of a 6x3 O-terminated MgO(111) surface; (b) phase identification by XRD for MgO(111) and MgO(111) 800°C with specific

surface area inset; (c) BF-TEM images of MgO(111) and MgO(111) 800°C.

aggregates of plate-like crystallites with intraparticle mesoporosity (Figure S2a).⁵⁰ The major effect of treatment at 800°C was a $\approx 30\%$ reduction in surface area from 227 to 154 $\text{m}^2 \text{g}^{-1}$, with little impact on the mesoporous pore size distribution (Figure 1b and S2). Taken together, the diffraction, microscopy, and N_2 adsorption-desorption clearly evidenced a degree of sintering in MgO(111) after treatment at 800°C.

2.2 Sintering and CO_2 Adsorption Capacity

It is generally recognised that sintering of an adsorbent material results in reduction of adsorption capacity, in terms of saturated gas uptake. Examples include linear correlations between H_2 gravimetric density and surface area of carbon aerogels,⁵¹ as well as CO_2 uptake and surface area of MOFs and carbons.^{52,53} One would therefore expect a significant reduction in the CO_2 capacity of the sintered MgO 800°C nanosheets, considering the $\approx 30\%$ reduction in surface area from 227 to 154 $\text{m}^2 \text{g}^{-1}$ (Figure S2a). However, a $\approx 65\%$ increase in CO_2 adsorption capacity was observed (Figure 2), from 0.77 to 1.28 mmol g^{-1} , indicating increased utility of the surface capacity of MgO. It is prudent to point out that carbonate formation on MgO is largely limited to the surface, particularly at low temperature ($T_{\text{ads}} = 35^\circ\text{C}$).^{54,55} Commercial MgO (SSA = 7 $\text{m}^2 \text{g}^{-1}$) and conventionally prepared nano-MgO (SSA = 84 $\text{m}^2 \text{g}^{-1}$) (Figure S2b) were compared with MgO(111), to investigate the link between increased capacity and presence of the (111) facet (Figure S3c and d). MgO(111) 800°C gave the highest adsorption capacity of all samples (Figure S3b), two orders of magnitude higher than commercial MgO. A simple explanation of increased physisorption to explain the increased capacity of MgO(111) after sintering is not possible due to the reduction in surface area. The full set of isotherms for all samples are provided, including adsorption at elevated temperature ($T_{\text{ads}} = 35 - 400^\circ\text{C}$) (Figure S3).

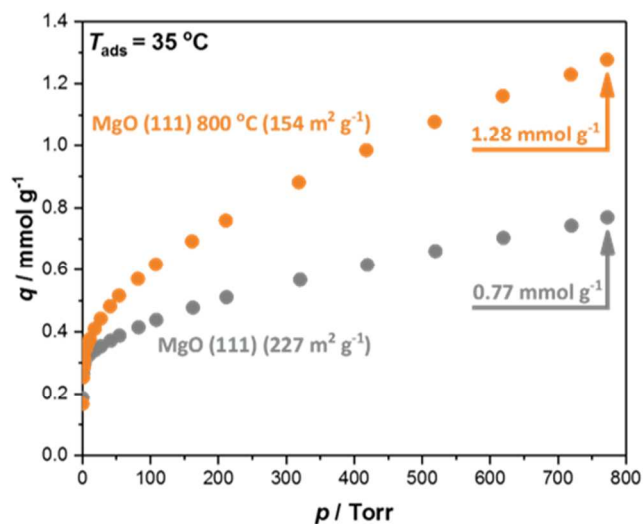


Figure 2. CO_2 adsorption isotherms ($T_{\text{ads}} = 35^\circ\text{C}$) on MgO(111) and MgO(111) 800°C with specific surface areas inset. Lower surface area conversely provides higher CO_2 uptake.

2.3 Surface Chemistry and Structure-Activity Relationship

Considering the paradoxical impact of sintering MgO(111) on CO_2 adsorption capacity, the surface chemistry of MgO(111) was investigated before and after sintering. Diffuse-reflectance infrared spectroscopy (DRIFTS) evidenced two “free” surface hydroxyl vibrational modes at 3760 and 3723 cm^{-1} amongst a range of hydrogen-bonded hydroxyl groups (ca. 3650 – 3300 cm^{-1}) (Figure 3a).^{56,57} Following treatment at 800°C *in-vacuo* for 2 h, a slight reduction in intensity of the band at 3760 was apparent, with the mode at 3723 cm^{-1} significantly reduced in intensity. Surface dehydration of the O-terminated (111) surface would leave behind the necessary low-coordinate O^{2-} sites required for CO_2 adsorption, as well as Mg^{2+} exposed by O vacancies.

Density functional theory (DFT) calculations were performed to elucidate the nature of the experimentally observed peaks at 3760 and 3723 cm^{-1} . A range of adsorbates were investigated, water and H (of the OH group), on O- and Mg-terminated MgO(111) surfaces, with a selection of surface coverage variations (Figure S4). A 100% H-covered O-terminated surface gave a calculated OH stretch mode frequency of 3764 cm^{-1} , sufficiently close to the experimental value so as to confirm the 3760 cm^{-1} band belonged to an OH stretching mode on such a surface (Figure 3a). A 100% H-covered, O-terminated surface has been shown computationally and experimentally to be extremely stable.^{58,59} Other simulated (111) surfaces (Figure S4a-d), as well as a small selection of MgO (110) and MgO (100) surfaces (not shown), could not be assigned to the remaining 3723 cm^{-1} band as a result of large frequency mismatch. These large differences were due to significant structural modifications such as the presence of water, or bonding to Mg^{2+} sites in place of O^{2-} sites. However, modifying the 100% H-covered O-terminated surface to remove every second row of OH groups, *i.e.* 50% H-covered, O-terminated surface (Figure S4e), gave a frequency band between 3733 and 3725 cm^{-1} . This indicated that the 3723 cm^{-1} band was likely due to portions of the O-terminated surface not 100% covered with hydrogen (Figure 3a). Sintering at 800°C removed hydrogen to reveal O^{2-} sites suitable for CO_2 adsorption, likely *via* condensation which would also reveal subsurface Mg^{2+} . Considered together with the DFT calculations (Figure S4), the major surface activation was the removal of hydroxyl groups from a partially covered (111) surface (3723 cm^{-1}). This would be logical considering the stability of the fully hydroxylated O-terminated surface.^{58,59} A more intricate dependence of the OH stretch mode frequency on H-coverage may well exist, with alternative explanations including hydrogen bonding of the 3760 cm^{-1} hydroxyl and lower index defects and edge planes.⁶⁰ The loss of the 3723 cm^{-1} peak indicated that it was strongly involved in changes to the surface upon sintering.

Further evidence for the creation of new basic O^{2-} sites on the (111) surface after treatment at 800°C was provided by temperature programmed desorption of CO_2 (CO_2 -

TPD) (Figure 3b). Briefly, MgO(111) was treated in flowing

He

at

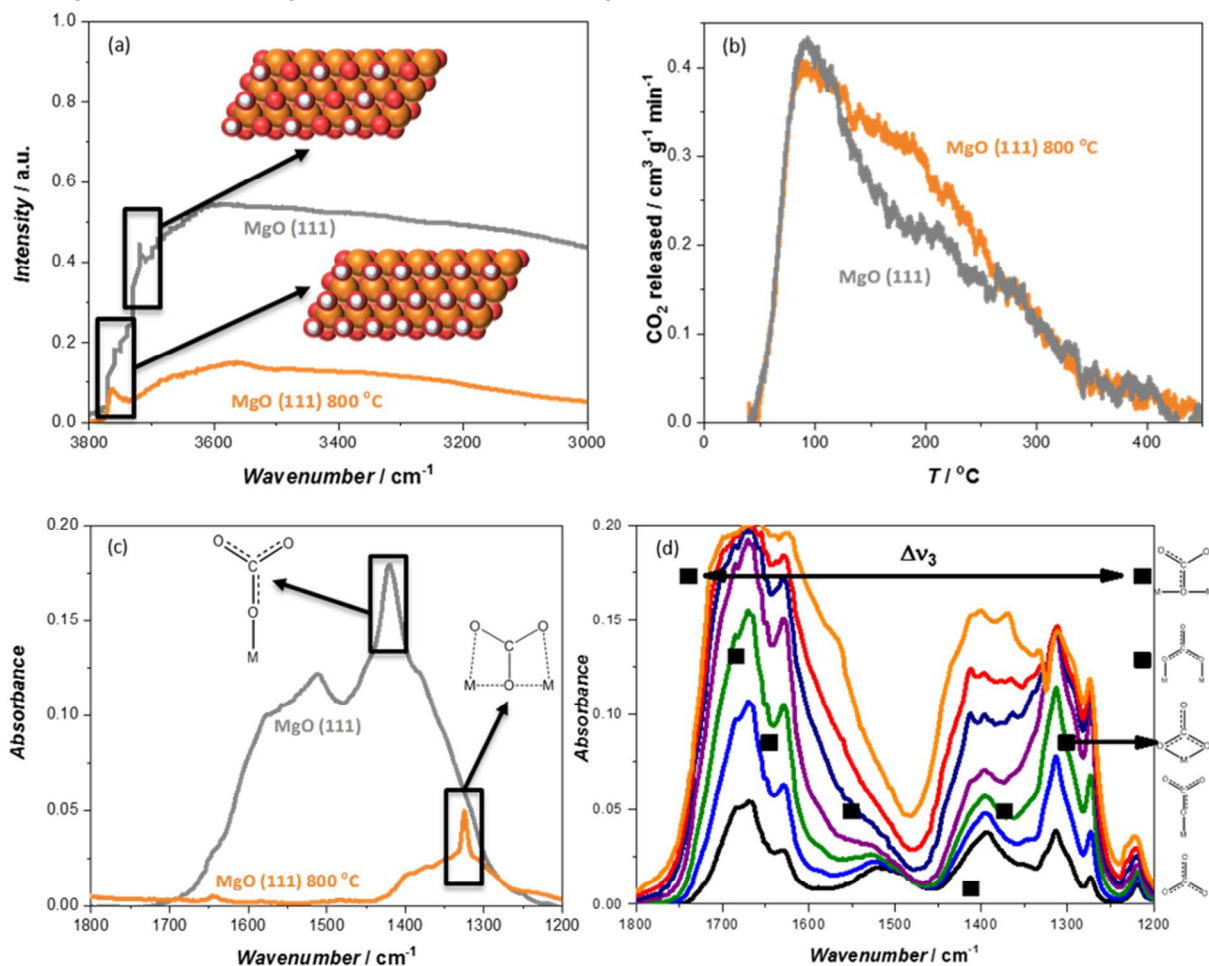


Figure 3. Surface chemistry investigation of MgO(111). (a) DRIFTS spectra of MgO(111) and MgO(111) 800°C evidencing surface hydroxyl removal, DFT simulated surfaces inset used to calculate hydroxyl stretch frequencies (Figure S4); (b) CO₂-TPD of MgO(111) and MgO(111) 800°C evidencing creation of new intermediate basicity sites due to surface hydroxyl removal; (c) *in-situ* transmission FTIR spectra of MgO(111) and MgO(111) 800°C of residual carbonates following thermal pre-treatment; (d) *in-situ* transmission FTIR spectra of MgO(111) 800°C following exposure of increasing pressures of CO₂, band growth in the 1800 – 1200 cm⁻¹ region evidencing formation of a variety of carbonates. Right hand axis displays different carbonate structures assignable on the basis of asymmetric stretching mode (ν_3) splitting.

400 and 800°C for 2 h before exposure to CO₂ and subsequent temperature programmed desorption. During temperature ramping from 50 to 400°C, CO₂ was evolved in a similar manner for both 400 and 800°C treated samples (Figure 3b). Weak ($T_d < 120^\circ\text{C}$) and strong ($T_d > 275^\circ\text{C}$) basic site densities were similar after both treatments (Table S1). In the intermediate strength range ($T_d = 120 - 275^\circ\text{C}$) a $\approx 30\%$ increase was observed after treatment at 800°C, due to the removal of hydroxyl functionality evidenced previously (Figure 3a). MgO(111) will present a large population of intermediate basicity sites, due to the unique structure;⁶¹ treating at high temperature increases this population further. Hydroxyl functionality on MgO powders has previously been shown to be stable to 500°C.^{56,57} Therefore, sintering at 800°C explores a new temperature region and results in the removal of further hydroxyl functionality, creating further sites for CO₂ adsorption. After sintering, the total number of basic sites increased from 357 to 415 $\mu\text{mol g}^{-1}$ assuming a stoichiometry of one basic site per CO₂ molecule. As will be shown later, this assumption gives a relative indication of basic site density, with any true evaluation dependant on car-

bonate coordination – far from trivial on MgO(111) (Figure 3d). Total CO₂ uptake closely matched that of the equilibrated isotherm at the CO₂ partial pressure used during TPD dosing (ca. 65 Torr).

Regarding the presence and formation of carbonates on the MgO(111) surface, significant differences following 2 h treatment at 400 and 800°C *in-vacuo* were observed by *in-situ* transmission FTIR spectroscopy (Figure 3c and d). Absorption bands due to carbonate species were observed in the 1800 – 1200 cm⁻¹ region following both treatments, yet the intensity decrease in the carbonate region was more pronounced following 800°C treatment (Figure 3c). A simple argument for increased capacity would be that removal of more carbonate species at 800°C provides additional capacity for CO₂. However, as surface area was reduced by $\approx 30\%$ yet capacity increased by $\approx 65\%$, a further explanation is required i.e. the aforementioned creation of O²⁻ and Mg²⁺ sites following sintering (Figure 3a). After treatment at 400°C, a prominent feature at 1420 cm⁻¹ indicated the presence of monodentate carbonates on the (111) surface.⁶² A maximum at 1512 cm⁻¹ and

weaker features/shoulders at 1650, 1590, and 1380 cm^{-1} indicated that a range of carbonate species remained on the surface.⁶³ These features were further evidence of the presence of the (111) surface contributing to CO_2 adsorption, as on well-defined (100) facets, absorption in the 1600 – 1350 cm^{-1} range was not observed.⁶⁴ Following treatment at 800°C, a uniquely sharp feature at 1325 cm^{-1} and a weak feature at 1645 cm^{-1} were assigned as tridentate carbonate species on the (111) surface facilitated by surface defects, either O^{2-} vacancies to expose subsurface Mg^{2+} , or at edges.⁶² Weak absorption at 1580 and 1400 – 1300 cm^{-1} indicated the presence of bidentate and monodentate carbonates.⁶³ Upon exposure of CO_2 to $\text{MgO}(111)$ after treatment at 800°C, a range of carbonate species were formed, identifiable on the basis of the splitting of the ν_3 asymmetric stretching mode (Figure 3d).⁶³ A variety of monodentate and bidentate carbonate species were identified, as well as bicarbonates formed in the presence of remaining surface hydroxyl groups as we have observed previously in related systems.^{65,66} In agreement with decreasing CO_2 capacity at increased temperature observed in CO_2 adsorption isotherms (Figure S3), an absorption maximum at 2345 cm^{-1} indicative of physisorbed CO_2 was present throughout (not shown). The complexity of carbonate speciation highlights the convoluted nature of the CO_2 -TPD basic site quantification, *i.e.* assuming a stoichiometry of one binding site per CO_2 molecule is incorrect.

2.3 Impact of the (111) Facet in Carbon Capture Processes

Clearly, the expected impact of surface area reduction on surface adsorption capacity is more complex than a simple linear relationship. The presence of the (111) facet overcame the significant reduction in surface area, facilitated by the removal of specific hydroxyl groups from the surface; wider impacts of these findings are briefly discussed. Firstly, in calcium looping, rehydration is a common strategy to enhance sorbent utility.¹⁶ Steam hydration of CaO (as opposed to hydration of CaCO_3) is favoured for regenerating spent sorbent.⁶⁷ Current interpretations of the positive impact of hydration involve the creation of new surface area and porosity, through rupturing of CaO particles upon hydration due to the larger specific volume of $\text{Ca}(\text{OH})_2$. Consider that hydration stabilises the (111) facet of rock salt oxides,^{34–36} and that this hydrated sorbent enters a high temperature carbonating reactor. Taken with our findings, we suggest that faceting plays a unique role in enabling the formation and retention of highly active CO_2 adsorption sites during hydration, despite overall loss of surface area. Furthermore, it is worth noting that so-called “double salt” carbon capture sorbents (a metal oxide with molten salt on the surface),^{68–70} and dual phase molten salt-ceramic membranes, [68] may inadvertently experience similar faceting effects to those noted here. Strong electrostatic interactions between molten salt ions and solid metal oxide surfaces significantly lower the surface energy of polar facets.⁴⁵ As a result, polar faceting in these sorbents and devices may well occur, contributing to interfacial phenomena.

3. Conclusions

An approach routinely applied in catalysis – synthetic control over crystalline facets – produced a sorbent for carbon capture with high capacity. This activity was due to the preferential exposure of the polar (111) facet and the surface exposed after thermal treatment. $\text{MgO}(111)$ nanosheets displayed a $\approx 65\%$ increase in CO_2 adsorption capacity following sintering at 800°C. This was unexpected as the treatment also resulted in a $\approx 30\%$ reduction in surface area. Further interrogation through spectroscopy and theory demonstrated that removal of hydroxyl functionality from the (111) facet exposes and retains low coordinate O^{2-} and Mg^{2+} sites, facilitating enhanced capacity.

Of consideration for all carbon capture processes, is the cost of sorbent manufacture. Although our synthesised (111) sorbent shows promising capacity, we suggest that the most important practical conclusion is that the addition of steam in looping cycles to stabilise the (111) facet and subsequent high temperature activation may well enhance capacity in existing affordable adsorbents. To be clear, we wish to highlight that control of specific facets through activation procedures easily integrated with existing pilot-scale carbon capture processes (e.g. calcium looping) is of primary significance.

In summary, we challenge the assumption that sintering is necessarily a negative process in high temperature “looping” cycles for CO_2 adsorption; the high temperature conditions can be leveraged for facet-dependent surface activation. In this case, we have shown that the presence of specific facets can be more important than the total surface area lost during sintering. We provide the first example of a faceted sorbent (of specified morphology) for carbon capture and give insight into new structure-activity relationships in materials relevant for environmental processes.

4. Materials and Methods

4.1 Adsorbent Synthesis

$\text{MgO}(111)$ nanosheets were prepared following a modified aero-gel methodology.⁴⁶ Magnesium belt (Mg) (Sigma-Aldrich, 99.5%) was roughened with sandpaper and cleaned with acetone (Pharmco-Aaper, 99.5%). The roughened magnesium was cut into small portions and dissolved in anhydrous methanol (Avantor, 99.9%) under nitrogen (Praxair, > 99.5%). Once dissolved, 4-methoxybenzyl alcohol (BZ) (Sigma-Aldrich, 98%) was added (molar ratio 2:1, Mg:BZ) and stirred for 5 h. Water in methanol was added (molar ratio 2:1, $\text{H}_2\text{O}:\text{Mg}$, 30.0 mL MeOH) dropwise with stirring. After 12 h of stirring the mixture was transferred to an autoclave, purged and then pressurised to 10 bar with argon (Praxair, > 99.998%). The mixture was heated at 265°C for 15 h, followed by venting of the supercritical solvent. The collected powder was calcined at 500°C in air for 6 h. Commercial MgO (Sigma-Aldrich, 98%) and conventionally prepared nano- MgO (NanoScale Corporation, NanoActive $\text{MgO} \geq 95\%$) were used as received.

4.2 Adsorbent Characterisation

Surface area and porosity analyses were conducted using a Micromeritics Tristar with N₂ as adsorbate. Powdered samples were treated at 200°C for 3 h in flowing N₂. Adsorption-desorption was performed at -196°C, with the Brunauer-Emmett-Teller (BET) method applied to determine surface area and the Barrett-Joyner-Halenda (BJH) method used to determine pore volume and pore size distribution.

X-ray diffraction (XRD) data were collected with an Empyrean diffractometer (PANalytical, NL) using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$). Powdered samples (*ca.* 0.2 g) were supported in aluminium holders after loose packing. Patterns were collected from 10 - 80° 2 θ with a step size of 0.026° and a total collection time of 20 minutes. Scherrer crystallite size analysis was performed on the (200) MgO periclase peak.

Transmission electron microscopy characterisation was conducted using an FEI Co. Talos F200X with a FEI X-FEG high brightness electron source operating at an accelerating voltage of 200 kV. Samples were prepared as an ultrasonic suspension in ethanol spread on a carbon coated copper grid. Bright-field (BF-TEM), scanning (STEM) and energy dispersive spectroscopy (EDS) modes were utilised.

4.3 CO₂ Adsorption

CO₂ adsorption isotherms were measured with a Micromeritics ASAP 2020C. Powdered samples were loaded into a quartz tube, surrounded by loosely packed plugs of quartz wool. Manual and automatic leak checks were conducted upon sample loading and immediately before adsorption isotherm collection respectively. CO₂ (BOC, 99.8%) was connected to the apparatus through a moisture trap (Alltech Hydro-Purge) filled with freshly conditioned adsorbent (Molecular Sieve 3A, Fischer Scientific). Sequenced experiments were run to obtain isotherms at 35, 100, 200, 300 and 400°C with initial and intermittent 400 and 800°C high temperature treatments (*i.e.* below and above the calcination temperature of synthesised sorbents).

4.4 Surface Chemistry and Structure-Activity Relationship

Diffuse reflectance infrared spectroscopy (DRIFTS) was conducted using a Thermo Nicolet 4700 IR spectrometer fitted with a liquid nitrogen cooled detector and DRIFTS accessory. KBr under vacuum ($< 3 \times 10^{-2}$ Torr) at room temperature was used as a background for all spectra. MgO(111) was heated to 400°C, held for 15 minutes, then heated to 800°C and held for 2 h. All ramp rates were 10°C min⁻¹. The sample was then cooled to room temperature before spectral acquisition. The complete procedure was under vacuum. Spectra were collected as an accumulation of 120 scans over a range of 4000 - 600 cm⁻¹ at a resolution of 4 cm⁻¹.

CO₂ temperature-programmed desorption (CO₂-TPD) was performed in a Micromeritics AutoChem II 2920 chemisorption instrument. Samples were treated *in situ*

with a 10°C min⁻¹ ramp under flowing He (UHP, 99.999%) to a final temperature of 400 or 800°C and held for 2 h before being cooled to 40°C under flowing He. The samples were dosed with a 10% CO₂/He blend for 1.5 h, and purged with He for 1 h to remove physisorbed CO₂. The thermal desorption of chemisorbed CO₂ was then performed in flowing He at a ramp rate of 10°C min⁻¹ to a final temperature of 800°C while the evolved CO₂ was quantified by changes in downstream thermal conductivity. Blank He-TPD experiments were performed on both samples to remove baseline differences between pretreatment temperatures due to desorbing water. All flow rates were 50 mL min⁻¹. Sample basicities are reported on a dry sample mass basis with an assumed stoichiometry of one basic site per CO₂ molecule (the appropriateness of which is discussed in the manuscript).

In-situ Fourier Transform Infrared Spectroscopy (FTIR) was performed using a PerkinElmer Spectrum 100 spectrometer. Powdered samples (*ca.* 20 mg) were pressed (Specac 15.011 Manual Hydraulic Press) at 1 - 3 tons into self-supporting discs of 13 mm diameter. Sample discs were suspended in a custom-made quartz holder and loaded into a high vacuum glass line apparatus, fitted with a high temperature furnace ($T_{\text{max}} = 1000^\circ\text{C}$). Sample discs were treated at 400 or 800°C under high vacuum ($< 3.75 \times 10^{-6}$ Torr) for 2 h. A 23 % CO₂ mixture (balance N₂) was used to fill a glass bulb which was attached to the vacuum apparatus. Following high temperature treatment, samples were cooled to room temperature under high vacuum before exposure to increasing pressures of CO₂. Spectra were collected as an accumulation of 25 scans over a range of 4000 - 1000 cm⁻¹ at a resolution of 4 cm⁻¹ with automated atmospheric background subtraction. Experimental spectra were subtracted from the initial spectrum collected immediately following pretreatment. In this way, changes to spectral features are only related to differences in the sample following CO₂ exposure.

DFT calculations were performed using the generalised gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhof^{72,73} functional and the plane-waves code VASP.^{74,75} Adsorbates on the surface were relaxed via conjugate-gradient in the presence of dipole corrections using a plane-wave cut-off of 500 eV, a 6 \times 3 surface cell, and Monkhorst-Pack *k*-point grid of 3 \times 3 \times 1 for sampling the Brillouin zone. Once residual forces on all ions had decreased below 0.005 eV/ \AA , relaxations were stopped and frequency calculations were performed. Several adsorbates, water and H (of the OH group), on both O- and Mg-terminated (111) surfaces were tested.

ASSOCIATED CONTENT

Supporting Information. Synthesis procedure, experimental methods, computational methods, transmission microscopy images, N₂ adsorption-desorption isotherms and pore size distributions, additional CO₂ adsorption isotherms and density functional theory model surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the Engineering and Physical Sciences Research Council (EPSRC) via a Doctoral Training Grant for G.A.M. (EP/K0502960/1) and a Doctoral Prize Fellowship (EP/M50791X/1). Dedicated to the memory of Kenneth J. Klabunde.

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