

Article

Preparation of Porous $\text{CaCO}_3 \cdot \text{MgO}$ Powder from Dolomite via Na_3PO_4 -Assisted Calcination

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Abstract

Structural stability and pore control of the resulting products remain challenging during dolomite calcination due to the complex crystal structure of dolomite, limiting the quality and performance of the final products. This paper systematically investigated how calcination parameters governed the structure of Na_3PO_4 -bearing dolomite derivatives in low temperature regions. The results revealed that controlled calcination of dolomite enabled the synthesis of hierarchically porous partially decomposed dolomite (PDD), consisting of a porous Mg-calcite framework and MgO nanospheres anchored to the pore networks. Magnesium retention in Mg-calcite was governed by temperature-time interplay, balancing kinetic trapping and thermodynamic expulsion. MgO coarsening followed temperature-dependent pathways. At 550 °C, low temperature enabled controlled MgO growth (59–73 nm), while 650 °C triggered sintering-dominated fusion (160 nm). At ≤ 550 °C, nano-MgO dispersion stabilized mesopores, whereas ≥ 600 °C MgO coarsening accelerated meso-macro pore transformation, culminating in sintering-induced collapse. Correspondingly, specific surface area underwent a gradual decline at lower temperatures, in contrast to the rapid decline at 650 °C. By revealing how thermal processing governs phase evolution and microstructure, this work identifies the key conditions for optimization of the microstructure and Mg content of PDD composites.

Keywords: porous materials; partially decomposed dolomite; MgO coarsening; Mg-calcite; hierarchy evolution

1. Introduction

The philosophical assertion that “nothing exists but atoms and voids” finds a modern analog in materials science, where the interplay between solid matrices and engineered voids defines the functionality of porous materials [1]. These materials, characterized by interconnected or isolated voids within their atomic or molecular frameworks, derive their high surface area, tunable permeability, and reduced density from the deliberate incorporation of empty spaces [2,3]. These voids are not passive structural features but active sites enabling applications ranging from molecular adsorption and catalytic activity to energy storage and biomedical engineering [4–7].

The synthesis of porous materials relies on methodologies that balance structural integrity with controlled porosity, leveraging both top-down and bottom-up approaches to tailor void architecture at multiple length scales. Templating relies on sacrificial scaffolds,



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such as colloidal crystals or surfactant micelles, to imprint ordered pore networks [5,8]. Sol-gel processing exploits hydrolysis and condensation reactions to form gel matrices [9,10]. Foaming introduces gas phases into polymers, ceramics, or metals to create voids [11]. Dealloying selectively dissolves components from an alloy to produce nanoporous metals [12]. Additive manufacturing enables geometric precision in porosity design [13]. Beyond these methods, phase separation emerges as a uniquely advantageous strategy due to its intrinsic simplicity, scalability, and versatility [14]. By leveraging thermodynamic incompatibilities in multicomponent systems, this method induces spontaneous segregation into distinct phases. Subsequent selective removal of one phase generates interconnected, homogeneous voids with narrow size distributions, bypassing the need for external templates, complex post-processing, or energy-intensive steps [14]. The self-assembly-driven nature of phase separation ensures precise control over pore size, geometry, and connectivity across multiple length scales, while its compatibility with bulk processing and diverse material classes (e.g., ceramics, polymers, composites) positions it as a cost-effective, industrially viable route for fabricating tailored porous architectures [15–17].

A paradigmatic example of phase separation is carbonate decomposition, where thermal treatment liberates gaseous byproducts, leaving behind porous residues [18,19]. Dolomite ($\text{CaMg}(\text{CO}_3)_2$), a double carbonate mineral with a rhombohedral crystal structure, has emerged as a promising precursor for synthesizing porous materials through controlled thermal decomposition [20]. Dolomite adopts a rhombohedral carbonate framework featuring alternating layers of Ca^{2+} and Mg^{2+} cations interspersed with carbonate anion sheets perpendicular to the *c*-axis [21]. The distinct decomposition temperatures of MgCO_3 and CaCO_3 , governed by differences in cation-oxygen bond strengths, enable sequential phase transitions theoretically [22]. When heated, the weaker MgCO_3 dissociates preferentially, releasing CO_2 and forming half-calcined dolomite (HCD, $\text{CaCO}_3 \cdot \text{MgO}$) [23]. This initial decarbonation generates a network of micropores as CO_2 escapes the lattice, while the retained CaCO_3 framework stabilizes the structure. Subsequent selective removal of the MgO phase [24], creating interconnected pores within the residual CaCO_3 matrix, yields porous calcite. If calcination continues to 800–1000 °C, the remaining CaCO_3 decomposes into porous CaO and CO_2 [23]. These materials hold significant potential for applications in environmental remediation, catalysis, and biomedicine, owing to their high surface area, tunable reactivity, and biocompatibility [25–28].

However, engineering controlled porosity in dolomite-derived materials remains fundamentally constrained by its crystallographic complexity and the challenges of managing decomposition kinetics [23]. During conventional calcination in air, dolomite undergoes rapid, full decomposition to CaO and MgO , accompanied by CO_2 release. This abrupt phase transition may induce significant mechanical stress due to the molar volume difference between dolomite and its decomposition products (CaO/MgO), leading to particle fracturing and pore collapse [29]. The coarsening of MgO crystallites at elevated temperatures (>700 °C) further reduces surface area and pore connectivity [30]. MgO crystallites grow from ~39 nm at 700 °C to ~109 nm at 1000 °C [31]. As a result, calcined dolomite after full decomposition typically retains only a modest BET area of 8–16 m²/g and pore volume of 0.016–0.048 cm³/g, a roughly sevenfold gain over the raw mineral [32,33]. However, no relevant data on HCD has been reported in recent work.

The application of elevated CO_2 partial pressure during dolomite calcination thermodynamically suppresses CaCO_3 decomposition, shifting its breakdown to higher temperatures (up to 950 °C) while maintaining half-decomposition within its original range (750–800 °C) [34]. This selective stabilization isolates the half-calcination step, enabling the targeted synthesis of the HCD. However, the high temperatures exacerbate MgO crystallite coarsening (>700 °C), as enhanced atomic diffusion promotes sintering and grain

growth. Simultaneously, cyclic carbonation-decarbonation processes where CaO intermittently reacts with CO₂ to re-form CaCO₃ and subsequently decomposes induce repeated volumetric expansion and contraction. These mechanical stresses might destabilize the pore architecture, leading to crack propagation, pore collapse, and irreversible densification [35]. The combined effects of MgO coarsening and cyclic degradation progressively encapsulate MgO domains, isolating them from reactive interfaces and diminishing the material's porosity, surface area, and functional utility. Thus, while high CO₂ partial pressure enables phase-selective HCD synthesis, it inadvertently amplifies structural instability, underscoring the need for strategies that decouple temperature-dependent coarsening from decomposition kinetics to preserve pore integrity.

Our prior research demonstrated that the incorporation of specific inorganic salts into dolomite significantly alters its thermal decomposition behavior [36,37]. By modifying the reaction pathway, these additives reduce the half-decomposition temperature to 400–650 °C, which is substantially lower than conventional calcination regimes, while accelerating the decomposition rate by several times [36]. The lower calcination temperature and shorter processing time can effectively suppress MgO sintering and prevent further decomposition of the residual calcite phase, thereby preserving the material's structural integrity. Crucially, this method may be helpful to retain the nascent porous architecture formed during CO₂ release, which is typically compromised at higher temperatures. However, while these salt-mediated modifications demonstrate significant potential for structural preservation, critical gaps persist in understanding how to actively engineer the porous architecture during calcination.

This study addresses this gap by systematically investigating how calcination parameters (temperature, duration) govern the pore structure of Na₃PO₄-bearing dolomite derivatives. We first establish a structural model for partially decomposed dolomite (PDD), then quantify how temperature and duration regulate MgO coarsening, pore evolution, and Mg incorporation dynamics to derive condition-property relationships. This mechanistic understanding enables the rational design of PDD and high-magnesian calcite with tailored porosity and composition, resolving a key barrier to industrial translation of low-temperature dolomite calcination technologies. Our findings provide both fundamental insights into non-equilibrium decomposition processes and practical guidelines for scaling porous mineral synthesis.

2. Materials and Methods

2.1. Materials

Natural dolomite was sourced from Hebei, China. The dolomite had a purity of 98.45% and a nearly ideal stoichiometric formula of CaMg(CO₃)₂ according to the ethylenediaminetetraacetic acid titration (EDTA) analysis. Because natural dolomite may deviate from the ideal CaMg(CO₃)₂ stoichiometry due to cation substitution, the measured Ca/Mg ratio was used to more accurately describe its partial decomposition behavior. The chemical composition of dolomite analyzed by X-ray fluorescence (XRF) is summarized in Table 1. Magnesium chloride hexahydrate (MgCl₂·6H₂O, 98% pure) was purchased from Kermel Co., Ltd. (Tianjin, China). The trisodium phosphate dodecahydrate (Na₃PO₄·12H₂O) was purchased from Kermel Co., Ltd. (Tianjin, China).

Table 1. Compositions of dolomite by XRF analysis.

Composition	CaO	MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	P ₂ O ₅	SO ₃	K ₂ O	Ignite Loss
Content (wt.%)	30.16	22.5	0.682	0.078	0.078	0.042	0.015	0.011	0.008	46.40

2.2. Preparation of Samples

The dolomite particles (1–2 mm) were crushed and ground together with Na_3PO_4 in a planetary ball mill for 30 min to pass through a 200-mesh sieve. The $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ was dehydrated at 105 °C for 2 h and 220 °C for another 2 h prior to use. The addition of Na_3PO_4 was 1.0 wt.% of dolomite. Because the Na_3PO_4 -bearing dolomite presents a notable decomposition rate above 550 °C, and calcite begins to decompose at a temperature above 650 °C [36], the PDD particles were prepared by calcination of Na_3PO_4 -bearing dolomite at 550–650 °C for various calcination time in a tubular furnace (SKGL-1200C, Shanghai Jvjing Precision Instrument Manufacturing Co., Ltd., Shanghai, China) with a diameter of 80 mm. The N_2 gas with a purity of 99.9% was used as purge gas with a flow rate of 100 mL/min. The samples were placed in an alumina crucible with dimensions of 100 mm × 40 mm × 40 mm (length × width × height). The temperature was increased from the room temperature to the targeted temperature with a rate of 10 °C/min, and the alumina crucible with samples was inserted into the furnace after the targeted temperature was reached. After calcination, the samples were taken out from the furnace, and cooled immediately in air. The PDD hereafter was named as “T-t” where T denotes the calcination temperature and t denotes the calcination time. In comparison, the dolomite particles without Na_3PO_4 were calcined at 650 °C for 25 min in the same furnace (650-25-C). In addition, the half-calcined dolomite (HCD) was prepared by the calcination of natural dolomite (40 g) at 750 °C for 1 h in the tubular furnace. Both ends of the tubular furnace were closed. CO_2 partial pressure during dolomite calcination thermodynamically suppresses Ca-CO_3 decomposition. The mass and calcination parameters of each sample are listed in Table 2.

Table 2. The mass and calcination parameters of samples.

Code	Mass (g)	Calcination Temperature (°C)	Calcination Time (min)	Mass Loss (wt.%)
550-90	10	550	90	20.81
550-150	20	550	150	22.86
550-330	40	550	330	22.97
550-720	80	550	720	23.04
550-1260	120	550	1260	23.22
600-55	20	600	55	21.74
600-70	30	600	70	22.39
600-110	40	600	110	22.92
600-220	80	600	220	23.11
600-440	120	600	440	23.07
650-15	10	650	15	21.78
650-25	10	650	25	22.67
650-25-C	10	650	25	0.83
650-40	20	650	40	23.05
650-50	40	650	50	23.12
650-75	80	650	75	23.22
650-130	120	650	130	23.21
650-240	120	650	240	23.38

Porous Mg-calcite particles were prepared by removing MgO nanospheres from the PDD particles. The MgO nanospheres were transferred to alcohol-leachable magnesium chloride gels. Firstly, the MgCl_2 solution with a concentration of 18.5 wt.% was prepared by dissolving $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ into deionized water. 4 g PDD particles were added into 100 g MgCl_2 solution in a 250 mL conical flask, and the flask was placed on the HY-5 oscillator (Nanfang Instrument Co., Ltd., Changzhou, China) and shaken with a constant speed of

170 r/min. After 48 h, the slurries were poured out into a 500 mL beaker and 200 mL alcohol was added to dilute the slurries. After 2 min of ultrasonic treatment, the diluted slurries were passed through a 200-mesh sieve. The left products were transferred into the beaker and 100 mL alcohol was added to ultrasonic-wash the particles to remove the excessive MgCl_2 and the gels in the pore volumes. The product may be washed several times until the conductivity of the filtrate falls below $2 \mu\text{S}\cdot\text{cm}^{-1}$. The particles were then dried in an oven at 200°C before further analysis.

2.3. Characterization of Samples

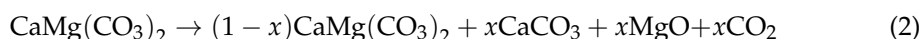
XRD tests were performed with Rigaku SmartLab 9kW using a $\text{Cu K}\alpha$ as radiation source ($\lambda = 1.5406 \text{ \AA}$) operated at 45 kV and 200 mA. Prior to characterization, the particles were ground and sieved through a 325-mesh sieve ($<45 \mu\text{m}$). The XRD patterns of pure calcite, dolomite, 650-25-C, PDD, HCD, and Mg-calcite particles were collected from 5° to 60° with a step size of 0.01° and 0.6 s per step. The phase identification was performed using MID Jade 6 software with the Inorganic Crystal Structure Database (ICSD). For presentation purposes, the XRD patterns were smoothed using Jade software's built-in Savitzky–Golay smoothing filter (parabolic, 5-point window, one pass). Smoothing was applied only to improve visual appearance; all peak positions, d -spacing values, and Mg contents were determined from the raw, unsmoothed data using identical peak-fitting procedures. The inclusion of Mg in the Mg-calcite lattice (X_{Mg}) was calculated by the shift in the (202) diffraction peak [38], as Equation (1).

$$X_{\text{Mg}} = \frac{d_{(202)\text{C}} - d_{(202)\text{D}}}{d_{(202)\text{C}} - d_{(202)\text{M}}} \times 100\% \quad (1)$$

where $d_{(202)\text{C}}$ is the d -spacing of calcite (0.2095 nm), $d_{(202)\text{M}}$ is the d -spacing of magnesite (0.1939 nm), and $d_{(202)\text{D}}$ is the d -spacing of magnesian calcite determined by XRD analysis.

For compositional analysis of PDD, thermogravimetric analysis (TGA) was performed for each calcined sample. TGA measurements were conducted using a Mettler Toledo TGA 2 (SF) system (Mettler Toledo, Shanghai, China) equipped with a high-sensitivity balance (0.1 mg) and a minimum baseline dynamic drift of $<10 \text{ mg}$. Each TGA run was performed with a fixed sample mass of $20 \pm 2 \text{ mg}$. The surrounding furnace was actively water-cooled, providing an effective heat sink and favoring precise temperature regulation. Temperature was monitored with a thermocouple positioned directly beneath and near the sample. A low nitrogen purge gas flow rate (20 mL/min) was applied to facilitate CO_2 removal. The temperature was increased from 35°C to 950°C with a heating rate of 10°C/min .

It is assumed that the partial decomposition of dolomite decomposes as Equation (2), with a conversion rate of x :



Therefore, as indicated by Equation (2), the calcined samples were composed of un-decomposed dolomite, calcite, and periclase. The mass loss (W) of PDD should be caused by the decomposition of calcite and un-decomposed dolomite (or Mg-calcite), and therefore W can be expressed by Equation (3):

$$W = \frac{m_{\text{C}} \times 0.44 + m_{\text{D}} \times 0.4772}{m_{\text{T}}} = \frac{100x \times 0.44 + (1-x) \times 184.3 \times 0.4772}{184.3/0.9845 \times 1.01 - 44x} \quad (3)$$

where m_{C} is the mass of calcium carbonate, m_{D} is the mass of un-decomposed dolomite in PDD, and m_{T} is the total mass of PDD. The coefficients of 100 and 184.3 are the molar mass of calcite and dolomite, and the coefficients of 0.44 and 0.4772 are the theoretical mass loss

of calcite and dolomite after calcination. The coefficient of 0.9845 is the measured purity of dolomite by EDTA test. The coefficient of 1.01 is given to the addition of 1 wt.% of Na_3PO_4 . Therefore, the conversion rate x can be solved using the mass losses of PDD samples at 35–950 °C, as Equation (4):

$$x = \frac{189.07W - 87.95}{44W - 43.95} \quad (4)$$

The mass fractions of calcite (w_C), dolomite (w_D), and periclase (w_P) can be calculated accordingly:

$$w_C = \frac{100x}{189.07 - 44x} \quad (5)$$

$$w_D = \frac{184.3 \times (1 - x)}{189.07 - 44x} \quad (6)$$

$$w_P = \frac{40.3x}{189.07 - 44x} \quad (7)$$

Nitrogen physisorption measurements were performed on an ASAP 2460 Surface Area and Porosimetry System (Micromeritics) at 77 K. The samples (ca. 1.0 g) were outgassed at 473 K for 24 h before the measurements. The surface areas were derived from the adsorption branch based on the Brunauer–Emmett–Teller (BET) equation in the relative pressure (P/P_0) range of 0.05–0.30. The pore size distributions were calculated using the desorption branch based on the Barrett–Joyner–Halenda (BJH) method.

The morphology of PDD, HCD, and porous Mg-calcite particles was observed using the Scanning Electron Microscope JSM-5900 (JEOL, Ltd., Changsha, China) at an accelerating voltage of 15 kV and a working distance of 10 mm. Prior to imaging, samples were sputter-coated with gold for 60 s. The size of MgO nanospheres was analyzed using the ImageJ 1.54 software, and 150 nanospheres were taken for size distribution analysis. All particle-size analysis was performed using ImageJ following standard image-analysis practice. SEM micrographs were acquired at 30,000 $\times$ with a calibrated scale bar. The pixel-to-micron calibration was set using the scale bar. Images were converted to 8-bit and thresholded using the Triangle method. Particles were outlined manually using the Freehand selection tool. For TEM analysis, PDD particles were dispersed in ethanol by ultrasonic treatment for 5 min. A drop of the suspension was placed on a carbon-coated copper grid (200 mesh) and vacuum-dried. TEM images were acquired on a JEOL JEM-2100F microscope (JEOL, Ltd., Changsha, China) operated at an accelerating voltage of 200 kV. Ca, Mg, C and O elemental mappings were obtained by energy-dispersive X-ray spectroscopy (EDS) in STEM mode using the same microscope. It should be stated that the reported XRD, SEM, and N_2 adsorption data are single-run results.

3. Results and Discussions

3.1. Basic Structure of PDD

To understand the basic structure of PDD, the Na_3PO_4 -bearing dolomite particles were calcined at 650 °C for 25 min and the products were collected for analysis. Figure 1 shows the XRD patterns of the Na_3PO_4 -bearing dolomite, pure calcite, HCD, control sample (650-25-C), and PDD (650-25) particles. The $(104)_C$ and $(202)_C$ peaks are ascribed to the calcite (ICSD #98-001-6710), and the $(104)_D$ and $(002)_P$ peaks are relevant to dolomite (ICSD #98-017-1522) and periclase (ICSD #98-015-9374), respectively.

The XRD patterns reveal that after calcination, the $(104)_D$ diffraction peak of Na_3PO_4 -bearing dolomite disappears while the diffraction peaks related to periclase $(200)_P$ and calcite $(104)_C$ occur. This suggests that only the half-decomposition of dolomite occurred during the calcination, forming the PDD products consisting of calcite and periclase. The control sample 650-25-C exhibits the same diffraction peaks as the un-calcined dolomite,

indicating that the 650-25-C did not decompose at 650 °C, which is consistent with the very small mass loss of 650-25-C during the calcination. The result suggests that without the effect of Na_3PO_4 , dolomite particles are thermally stable at a temperature below 650 °C.

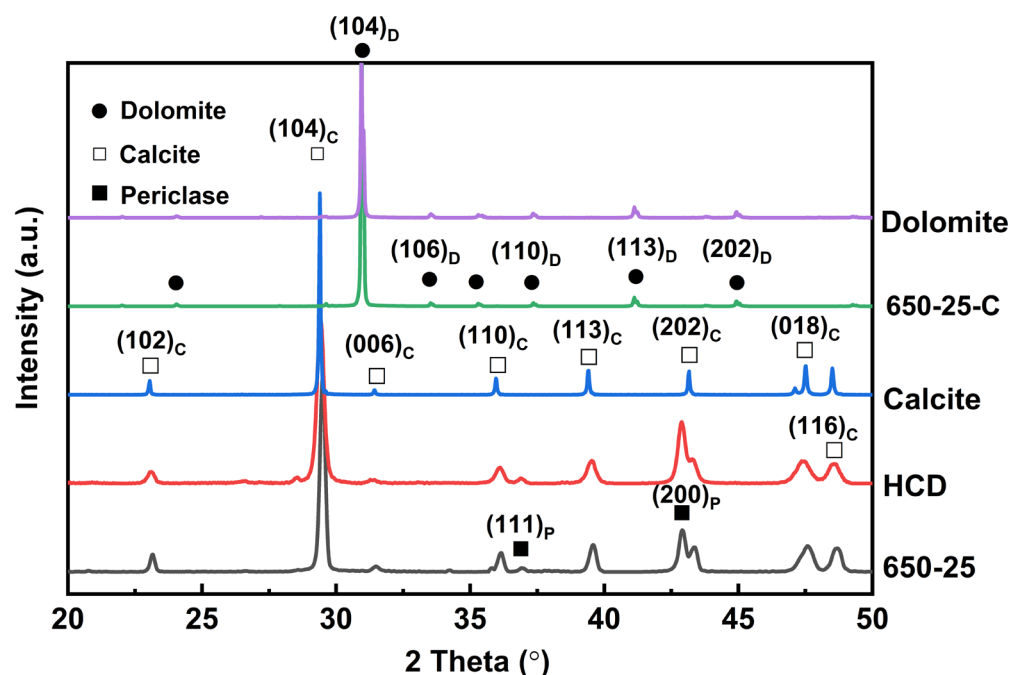


Figure 1. XRD patterns of natural dolomite, pure calcite, control sample (650-25-C), HCD, and PDD (650-25).

The $(104)_C$ and $(202)_C$ peaks of pure calcite are at $2\theta = 29.390^\circ$ and $2\theta = 43.179^\circ$, respectively. However, the $(104)_C$ and $(202)_C$ peaks of calcite in the 650-25 shift to higher angles (29.504° and 43.408° , respectively). This demonstrates the calcite in the PDD has smaller d -spacing values than the pure calcite, which may be caused by the incorporation of smaller Mg ions into the calcite lattice ($0.72 \text{ \AA}$ of Mg^{2+} as compared to $1.00 \text{ \AA}$ of Ca^{2+} in sixfold coordination) [39]. In addition, significant broadening of diffraction peaks of the calcite in the 650-25 is observed in Figure 1, a phenomenon typically associated with lattice defects [40]. Therefore, more precisely, the Mg-calcite rather than pure calcite was formed in the 650-25. The reduction in d values can be described as a linear relationship with Mg substitution between 2 and 16 mol% in calcite [39]. Accordingly, the Mg content in the Mg-calcite can be calculated from the shift in the d_{202} value [38], yielding a value of 8.39 mol%. Studies have demonstrated that the Mg substitution leads to inhomogeneous lattice distortions that would hinder dislocation motion and thus increase the hardness of calcite. The calcite plates containing 4.5–13 mol% Mg in the sea urchin tooth show ca. 40% increase in hardness in comparison with that of pure calcite [41]. This finding suggests that the 650-25 may offer mechanical-reinforcement potential, which should be evaluated by direct hardness and strength measurements. In contrast, the diffraction peaks of the calcite in HCD have the same positions as those of pure calcite, indicating that it contains no Mg ions in the crystal lattice. This is consistent with previous studies that reported no Mg-calcite solid solution formed in the decomposition of dolomite in an atmosphere of CO_2 (g) in the temperature range between 998 and 1193 K [42].

Figure 2a reveals the surface morphology of a 650-25 particle via scanning electron microscopy (SEM).

It can be seen that the 65-25 particle displays a hierarchical porous architecture decorated with nanoscale spherical particulates having a diameter of 30–100 nm. Cross-sectional

analysis (Figure 2b), obtained through fracturing of the epoxy-embedded 650-25, confirms the three-dimensional percolation of nanospheres across both external surfaces and internal pore walls. The spatially invariant distribution of these nanostructures, observed across multiple fracture planes, substantiates their uniform dispersion within the matrix. Nevertheless, the HCD (Figure 2c) exhibits a substantially non-porous structure, which may be a consequence of extensive condensed phase diffusion, a process that would probably close the intra-particle pores [43]. The control sample 650-25-C (Figure 2d) shows a very smooth surface, and no nanoparticles or pores can be observed. This is because the 650-25-C did not decompose at 650 °C, and consequently, the 650-25-C fully preserves the original shape of natural dolomite.

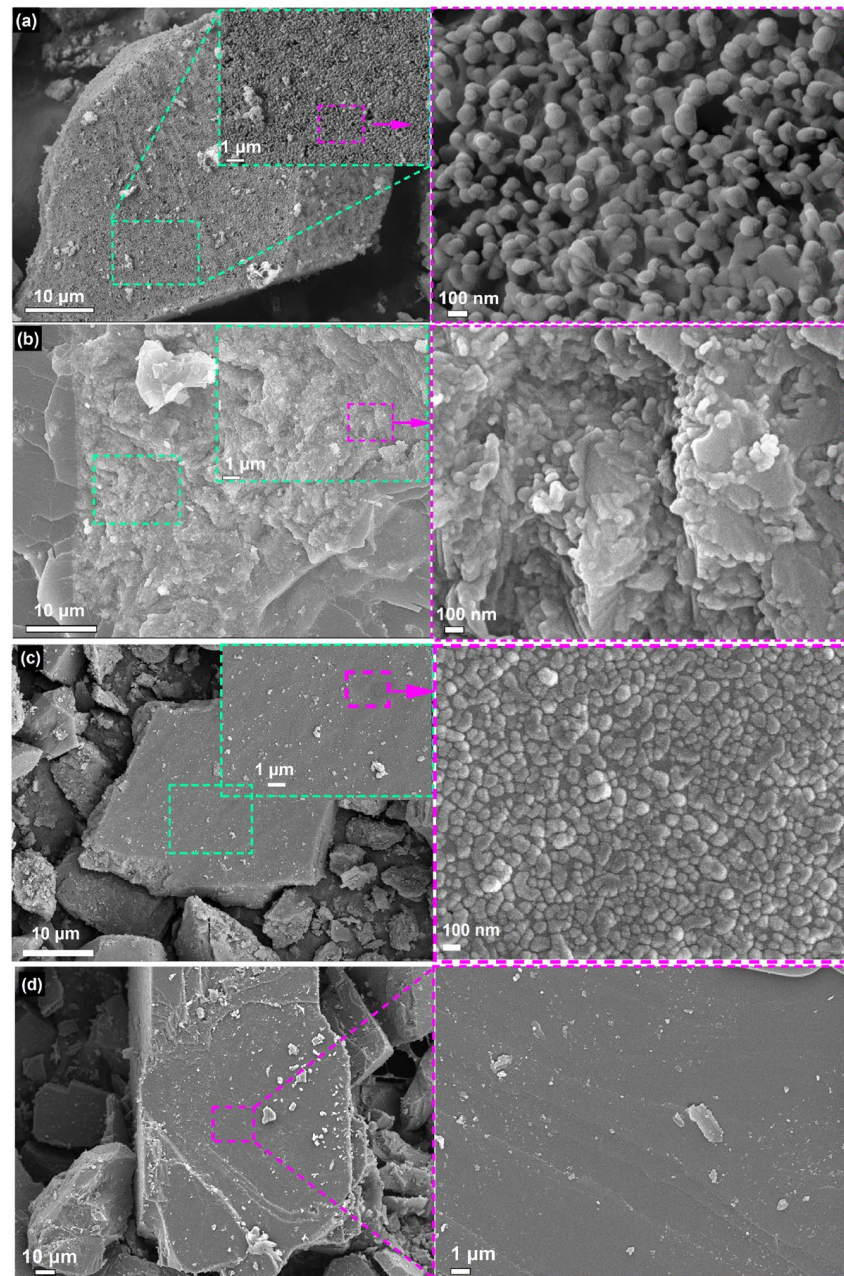


Figure 2. SEM images of (a) the surface and (b) the fracturing surface of PDD 650-25, (c) the surface of HCD, and (d) the surface of control sample 650-25-C.

Figure 3 presents transmission electron microscopy (TEM) characterization of the PDD 650-25 particle, confirming cross-scale structural fidelity with observations in Figure 2.

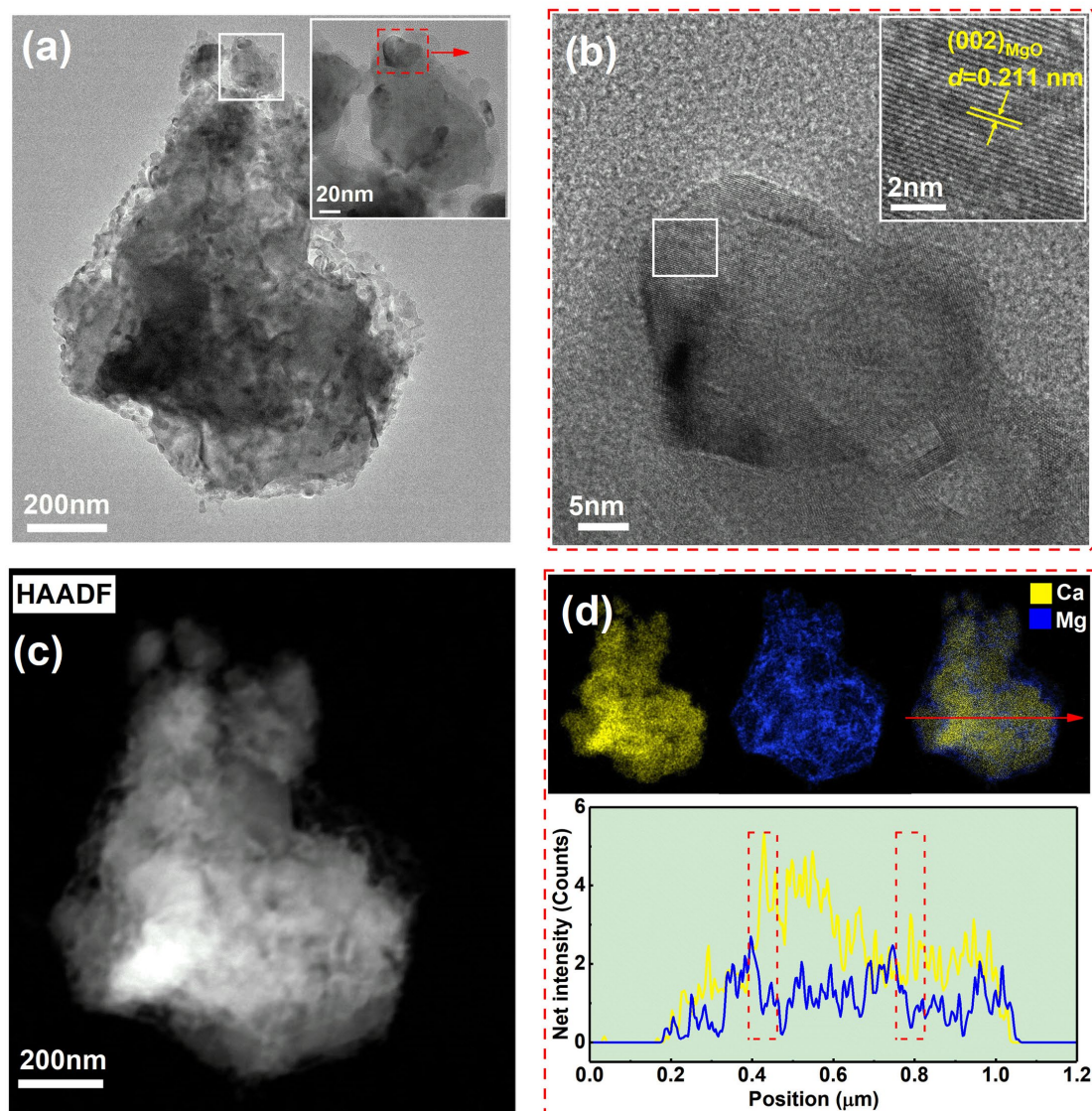


Figure 3. TEM images of PDD particle: (a) TEM image at $\times 46,000$ magnification and at $\times 190,000$ magnification (inset), (b) TEM image of selected area A at $\times 1,050,000$ magnification and HRTEM image (inset), (c) TEM image in HAADF mode, and (d) elemental mapping of Ca, Mg, overlapping maps, and the line scan element distribution map (below).

High-resolution TEM (HRTEM) analysis (inset) reveals nanocrystallites exhibiting lattice fringes with a mean interplanar spacing of 0.211 nm, consistent with the (200) crystallographic plane of periclase MgO (JCPDS 45-0946; theoretical $d_{200} = 0.2064$ nm). The small difference may reflect lattice strain or measurement uncertainty. Elemental mapping shows Mg-enriched surface domains with Ca and Mg remaining spatially correlated at grain boundaries. These observations indicate that MgO nanoparticles are closely associated with the CaCO_3 matrix, but they do not provide crystallographic orientation relationships and therefore cannot establish a topotactic transformation pathway as demonstrated in the previous literature [29]. Nevertheless, these observations are consistent with a decomposition pathway involving localized cation redistribution.

To elucidate the structural evolution of Mg-calcite during the partial-decomposition of dolomite, the removal of MgO nanospheres was achieved through their transformation into removable amorphous magnesium oxychloride gels, enabling detailed characterization of the residual Mg-calcite framework (see Supplementary Materials for details), as shown in Figure 4.

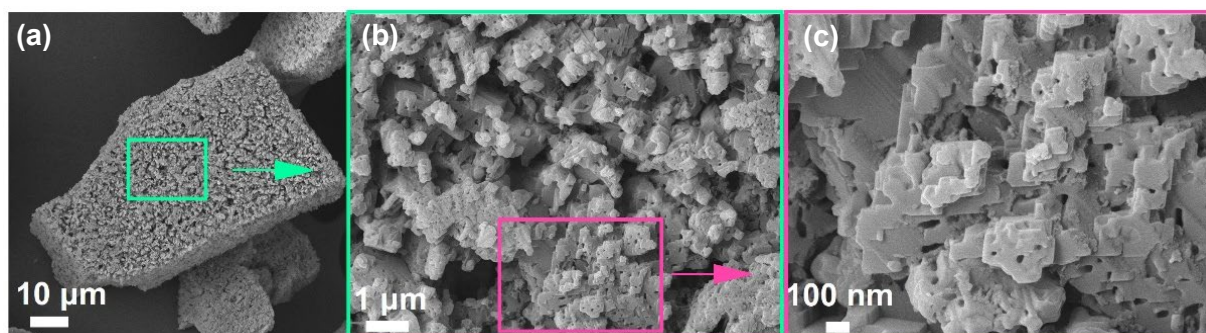


Figure 4. SEM images of Mg-calcite after MgO removal (a) at $\times 1000$ magnification, (b) at $\times 10,000$ magnification, and (c) $\times 30,000$ magnification.

Scanning electron microscopy shows that Mg-calcite inherits the external shape of the original dolomite but develops a porous structure. The pores exist at two scales: macropores around $1\ \mu\text{m}$ and interconnected nanopores below $100\ \text{nm}$. These pores may be associated with the local stress caused by the transformation from dolomite to Mg-calcite where the molar volume decreases from $64.3\ \text{cm}^3/\text{mol}$ (dolomite) to $36.9\ \text{cm}^3/\text{mol}$ (calcite) [29]. To comprehensively characterize the nanoporous architecture of the PDD particle, nitrogen physisorption analysis was performed (Figure 5), yielding adsorption–desorption isotherms that exhibit a Type V sorption profile with a pronounced H3 hysteresis loop in accordance with IUPAC classification [44]. The H3 hysteresis is characteristic of mesoporous materials dominated by slit-shaped pores formed through the aggregation of plate-like particles or non-rigid pore networks [44]. Barrett-Joyner-Halenda (BJH) pore size distributions indicate combined meso- and macroporosity, with peaks at $\sim 40\ \text{nm}$ and $\sim 70\ \text{nm}$. The BJH model is reliable primarily for mesopores and cannot quantitatively characterize macropores, and the $\sim 70\ \text{nm}$ feature is therefore reported as a qualitative indication of larger pores. The isothermal of HCD shows the typical characteristics of the IUPAC-type III sorption isotherm obtained with a nonporous or macro-porous absorbent [44]. The results are echoed by the pore size distribution curves. No mesopores but only some macropores are found in the HCD.

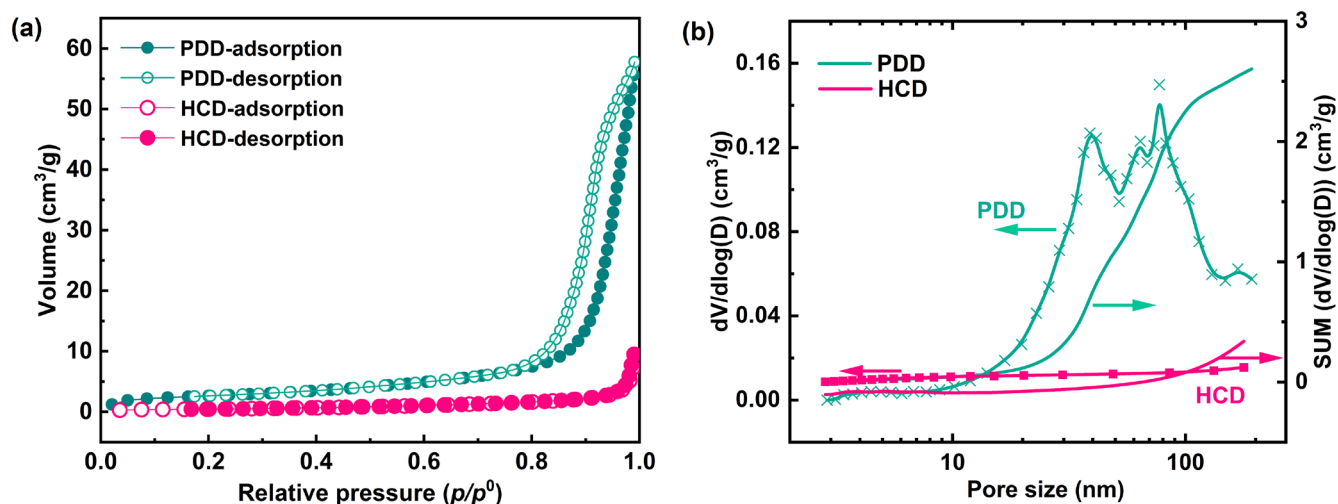


Figure 5. (a) Nitrogen adsorption–desorption isotherms of PDD and HCD particle, and (b) pore size distribution of PDD and HCD particle.

Based on the evidence presented, the PDD 650-25 architecture comprises two essential components, as shown in Figure 6: (1) a hierarchically porous Mg-calcite framework retain-

ing dolomite's original morphology, and (2) periclase nanospheres anchored to internal and external surfaces.

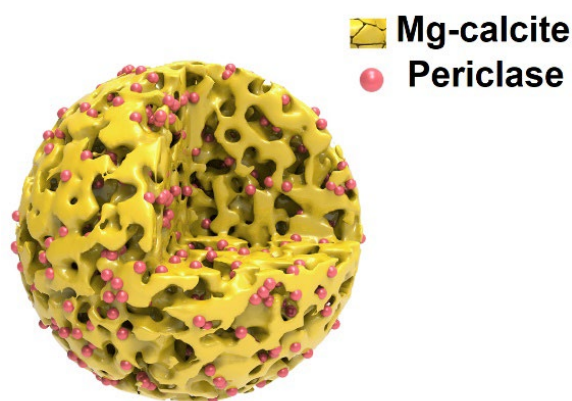


Figure 6. Structure model of PDD 650-25 particle.

3.2. Compositional and Structure Evolution of PDD

3.2.1. Composition Analysis of PDD

Figure 7 presents the XRD patterns of PDD. The diffraction peak $(104)_D$ of dolomite are observed in the samples calcined at 550 °C, even after very long calcination time. This indicates that the Na_3PO_4 -bearing dolomite cannot achieve full half-decomposition at 550 °C. At a temperature higher than 600 °C, only the samples subjected to very short calcination times (600-55 and 650-15) show noticeable dolomite diffraction peaks. With the extension of calcination time, only the diffraction peaks of calcite and periclase are observed. No diffraction peaks associated with CaO are found in the XRD patterns of all samples, suggesting that the calcite in the PDD samples did not decompose in the investigated temperature and calcination time ranges. Therefore, the Na_3PO_4 -bearing dolomite experienced only partial decomposition in the investigated conditions.

Quantitation results by TGA as Equations (2)–(7) is presented in Table 3. As the treatment time and temperature increase, the periclase and calcite contents slightly rise. Meanwhile, the dolomite content drops from 5.05% (650-25) to 0% (650-240). The impurity content remains relatively stable at around 2.88–3.28%. However, the overall compositions across the different samples do not vary drastically, especially for the main phases (periclase and calcite). The low residual dolomite values (mostly under 5%) suggest it is almost half-decomposed. It should be noted that from the table alone, assuming that all the undecomposed phase is strictly “dolomite” may not be entirely correct. It is highly possible that what is being detected as undecomposed dolomite is actually Mg-calcite ($\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$). TGA might not perfectly distinguish between these phases, leading to misclassification.

In Figure 7, the diffraction peaks of calcite shift to higher angles, indicating that the Mg-calcite rather than pure calcite was formed in all samples. The Mg content in the Mg-calcite lattice was quantified using the $(202)_C$ diffraction peak shift. The experimental data reveal a pronounced temperature-time coupling effect governing magnesium retention within the Mg-calcite lattice during dolomite calcination. At a relatively mild temperature of 550 °C, the magnesium content initially reaches 7.11 mol% after 90 min, then gradually declines to 5.83 mol% by 150 min and remains remarkably stable at this level through 720 min, suggesting a moderate but sustainable incorporation capacity. In contrast, calcination at 600 °C enables higher initial Mg^{2+} incorporation, peaking at 11.0 mol% at 55 min, followed by a steady decline to 4.55 mol% by 440 min. The trend becomes even more pronounced at 650 °C. The magnesium content reaches only 8.39 mol% at 25 min, which is lower than the peak value at 600 °C but then decreases rapidly to 3.39 mol% within 130 min. Data from

experiments above 600 °C demonstrate that high-magnesium calcite is thermodynamically unstable and can only persist transiently under extremely brief calcination durations.

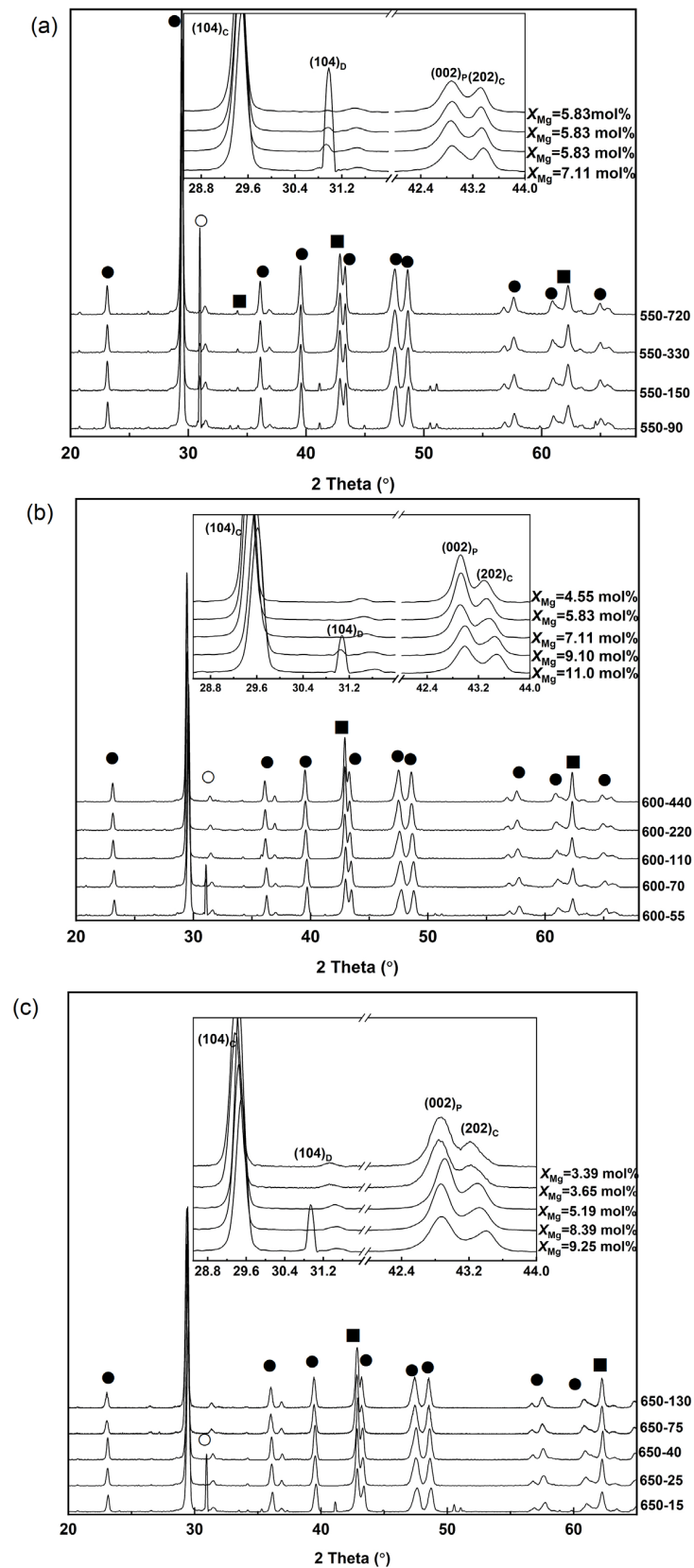


Figure 7. Mg content in the Mg-calcite lattice under (a) 550 °C, (b) 600 °C, and (c) 650 °C for different calcination time. The open circles, solid circles, and solid squares represent the diffraction peaks of dolomite, Mg-calcite, and periclase, respectively.

Table 3. The compositions of samples by TGA tests.

Code	Periclase	Calcite	Dolomite	Impurities *
550-150	26.67	66.19	4.05	3.09
550-330	26.89	66.72	3.3	3.09
550-720	27.18	67.45	2.27	3.1
550-1260	27.66	68.63	0.59	3.12
600-55	26.64	66.1	4.38	2.88
600-110	26.76	66.4	3.95	2.89
600-220	27.12	67.3	2.68	2.9
600-440	27.68	68.69	0.72	2.91
650-25	26.44	65.62	5.05	2.89
650-75	27.06	67.15	2.9	2.89
650-130	27.33	67.81	1.96	2.9
650-240	27.96	68.76	0	3.28

Note: * Impurities includes the original impurities in the dolomite and the Na_3PO_4 .

The observed magnesium retention dynamics may stem from atomic-scale processes governing dolomite decomposition and subsequent Mg^{2+} migration. During the phase transition, liberated Mg^{2+} ions initially occupy interstitial positions within the evolving calcite matrix before diffusing toward CaCO_3/MgO interfaces [45]. At 550 °C, sluggish phase transition kinetics prolong the decomposition period, allowing gradual Mg^{2+} redistribution that can establish a low-equilibrium concentration through balanced Mg^{2+} release from dolomite and outward diffusion. This kinetic pseudo-equilibrium may mask the inherent thermodynamic instability of magnesian calcite [38]. Conversely, high-temperature calcination (>600 °C) accelerates the phase transition, which may lead to rapid trapping of Mg^{2+} in metastable lattice sites. This may be a kinetic artifact enabled by incomplete ion mobilization during fast structural reorganization. However, this metastable configuration may become progressively destabilized with prolonged heating, as enhanced thermal energy reactivates diffusion pathways, systematically expelling Mg^{2+} to achieve thermodynamic equilibrium.

3.2.2. MgO Nanospheres Coarsening

During high-temperature calcination, MgO nanoparticles are prone to coarsening, which directly impacts the final porous structure and surface properties [30]. To enable controlled synthesis, this study investigates the size evolution of nano-sized MgO particles in the PDD particle under varying calcination conditions using scanning electron microscopy (SEM). Figure 8 displays SEM images of the PDD particles obtained under distinct calcination parameters. To quantitatively analyze the coarsening behavior of MgO during calcination, the size distribution of MgO particles in the SEM images was statistically evaluated using the image analysis software ImageJ 1.54, and the results are summarized in Figure 9, where d represents the mean particle diameter, and σ denotes the standard deviation of the size distribution.

Experimental observations reveal a multi-stage evolution of MgO morphology during dolomite decomposition. At 550 °C, initial stages (≤ 330 min) exhibit poorly defined aggregates, transitioning to sharp-boundary nanoparticles by 720 min, and ultimately forming monodisperse spherical crystals after 1260 min. This progression coincides with structural reorganization of the dolomite matrix, where localized collapse generates porous domains that expose Mg-calcite frameworks. Quantitative analysis (Figure 9) underscores temperature-dependent coarsening kinetics: at 550 °C, MgO diameters increase linearly from 59.02 nm (at 330 min) to 73.39 nm (at 720 min). This transition occurs more rapidly at higher temperatures. At 600 °C, spherical MgO particles appear after 220 min, while

at 650 °C, they form in just 25 min (a nearly ninefold increase in rate). These trends challenge classical models that attribute MgO coarsening solely to high-temperature sintering (>700 °C) [30] and highlight the critical role of calcination duration and additive-mediated pathways.

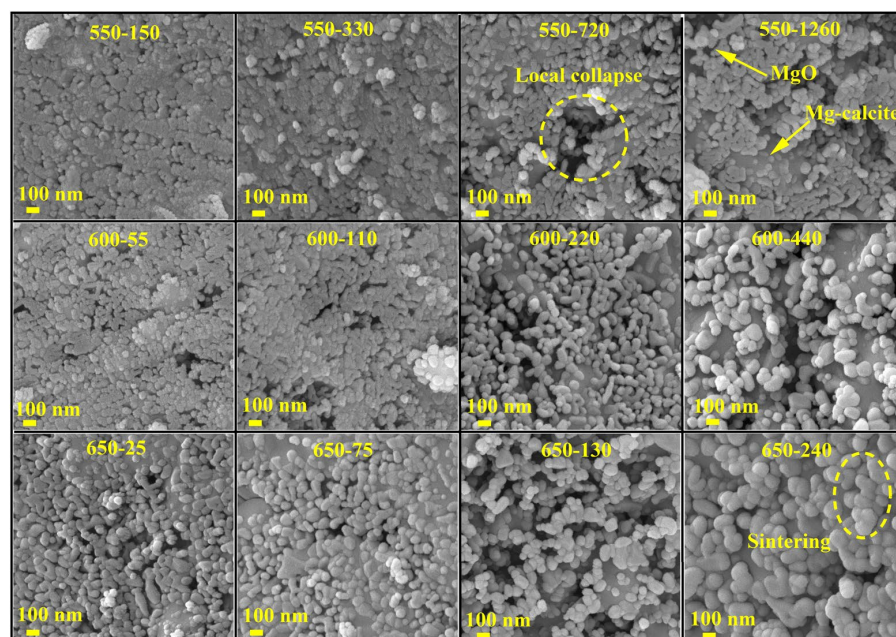


Figure 8. SEM images of PDD particles at $\times 30,000$ magnification.

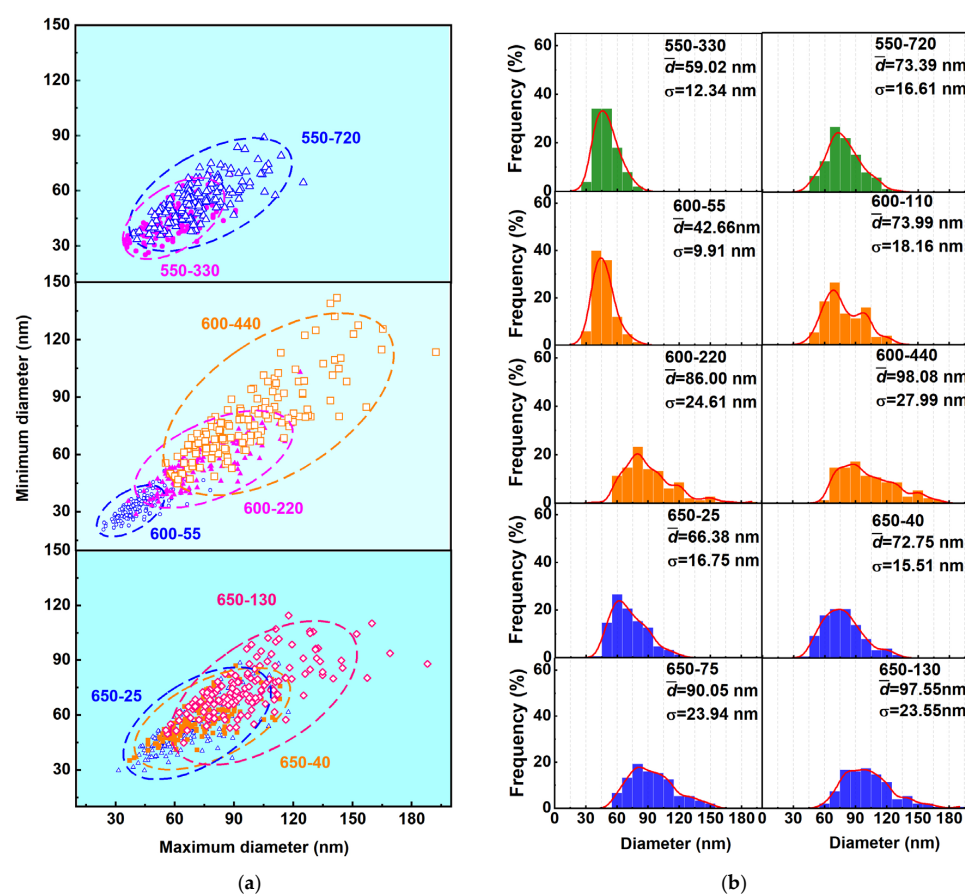


Figure 9. (a) The minimum and the maximum diameter of MgO nanospheres, and (b) size distribution of MgO nanospheres in the PDD particles.

However, prolonged calcination above 650 °C induces a mechanistic transition to sintering, wherein surface diffusion mediates particle fusion and pore elimination. This shift is exemplified by the 650-240 sample, where MgO aggregates grow to 160.90 nm via interparticle neck formation, accompanied by reduced intergranular porosity, a hallmark of sintering-dominated coarsening. The interplay between temperature and time emerges as a critical factor in dictating coarsening pathways.

The results demonstrate that, at a temperature below 650 °C, gradual particle growth without sintering fusion occurs. In contrast, 650 °C triggers a biphasic regime: initial rapid growth via temperature-promoted coarsening kinetics (66.38 nm in 25 min) is abruptly superseded by sintering beyond 130 min, leading to uncontrolled coarsening. This duality underscores the necessity of precise temporal control at elevated temperatures to mitigate undesirable particle fusion. These insights establish an empirical insight for optimizing MgO nanostructures by modulating calcination parameters.

3.2.3. Structure Evolution of Mg-Calcite Matrix

Pore Structure of Mg-Calcite

When heated, the residual Mg-calcite framework undergoes significant morphological and textural changes, as revealed by SEM imaging (Figure 10) and nitrogen adsorption analysis (Figure 11). These transformations may be driven by a molar volume difference between the parent dolomite and the evolving Mg-calcite, which may generate localized internal stresses. These stresses might induce contraction and pore nucleation, with pores acting as both stress-relief pathways and primary channels for CO₂ escape during decarbonation. The magnitude of stress is modulated by the density and size of MgO nuclei at the MgO/CaCO₃ interface, as well as pre-existing structural defects introduced during mechanical pre-treatment [29].

SEM observations reveal the morphological evolution of the Mg-calcite matrix. At 550 °C, particles retain the original dolomite morphology with sharp edges and a uniform mesoporous texture (2–50 nm), which persists even after prolonged calcination up to 1260 min (Figure 10a–d). At 600 °C, structural reorganization accelerates; within 440 min, the surface texture becomes coarser, and slit-like mesopores transform into larger pores (Figure 10e–h). By 650 °C, structural changes intensify. Sporadic macropores appear within 40 min (Figure 10i), and extending calcination to 240 min induces irregular micron-sized pores via crack propagation and partial fusion (Figure 10l).

Nitrogen adsorption analysis (Figure 11) corroborates a temperature-dependent pore evolution from mesoporous to hierarchical (meso-macroporous) and ultimately macroporous networks. At 550 °C, the pore size distribution remains concentrated in the mesopore range (<50 nm), maintaining structural stability regardless of duration. At 600 °C (e.g., 600–440), the distribution shifts toward larger diameters (>50 nm), indicating mesopore-to-macropore transformation. At 650 °C for 240 min, overall pore volume decreases significantly due to sintering. The text suggests that these transformations may be driven by localized internal stresses arising from the molar volume difference between parent dolomite and evolving Mg-calcite, potentially modulated by the density and size of MgO nuclei at the reaction interface [29]. However, direct evidence for this stress-driven mechanism is not provided in the current data.

3.2.4. Specific Surface Area

Specific surface area (SSA), a pivotal parameter governing the reactivity and adsorption capacity of porous materials, plays a critical role in applications such as catalysis, CO₂ capture, and cement hydration. In PDD, SSA directly influences the accessibility of nano-MgO particles to reactive environments, modulating interfacial interactions with solutions

and impacting macroscopic properties like cement rheology and hardening kinetics. This study quantifies SSA variations in PDD (Figure 12) derived from dolomite calcination using the multipoint Brunauer–Emmett–Teller (BET) method.

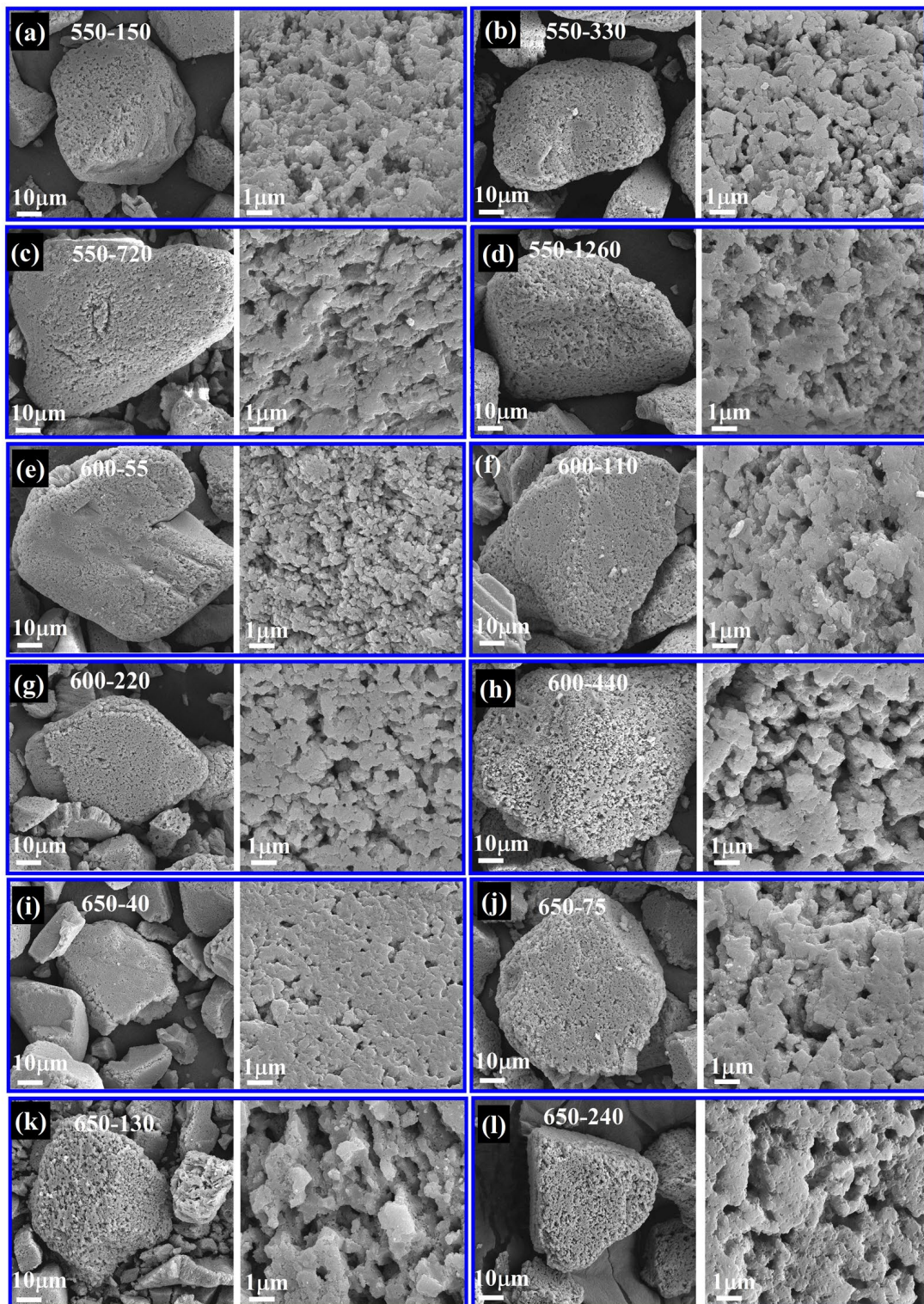


Figure 10. SEM images of the Mg-calcite matrix under different calcination conditions. For each sample, the left micrograph was acquired at $\times 1000$, and the right micrograph is the corresponding $\times 10,000$ magnification showing the structural details: (a) 550-150, (b) 550-330, (c) 550-720, (d) 550-1260, (e) 600-55, (f) 600-110, (g) 600-220, (h) 600-440, (i) 650-40, (j) 650-75, (k) 650-130, and (l) 650-240.

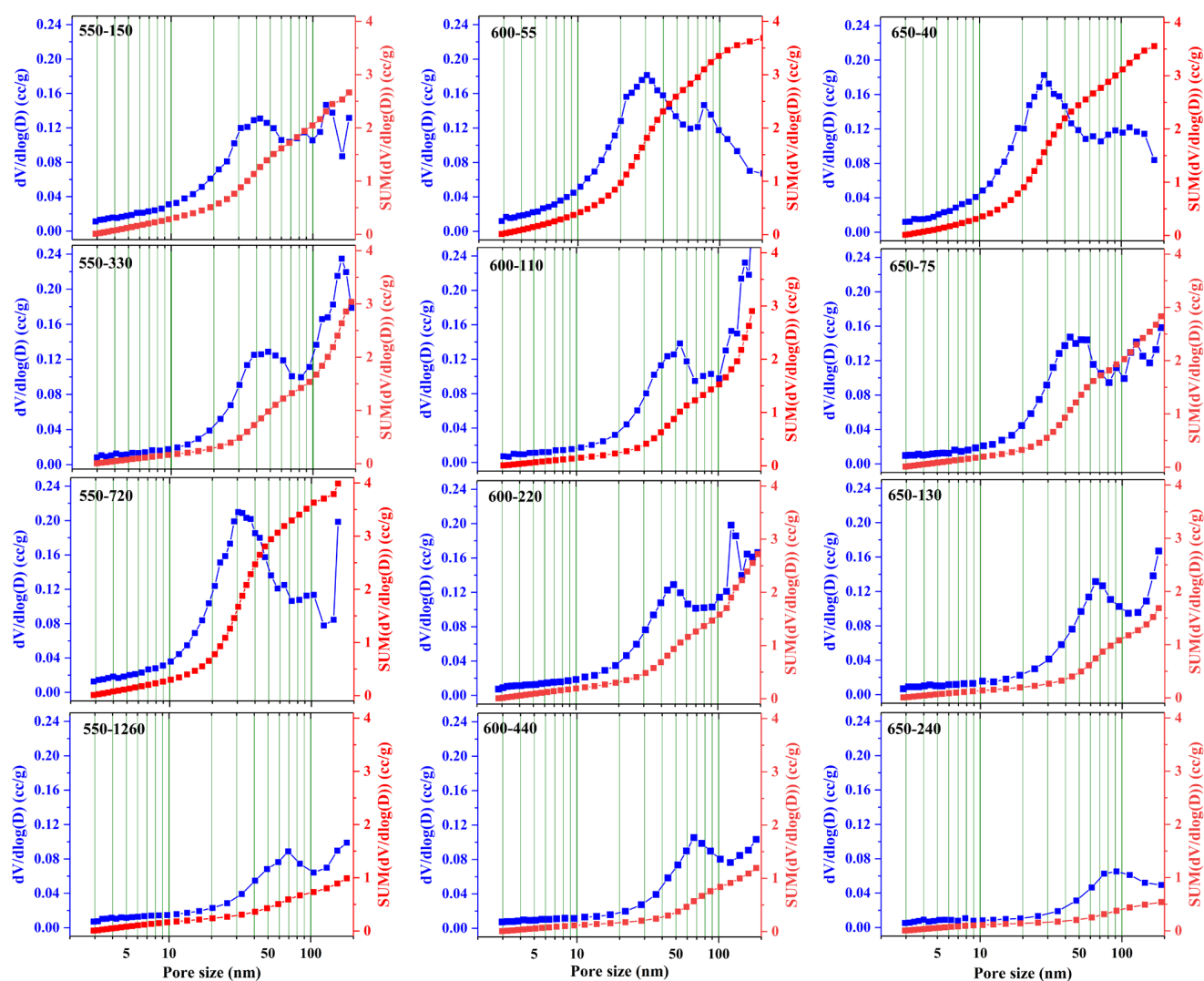


Figure 11. Pore size distribution of Mg-calcite matrix under different calcination conditions.

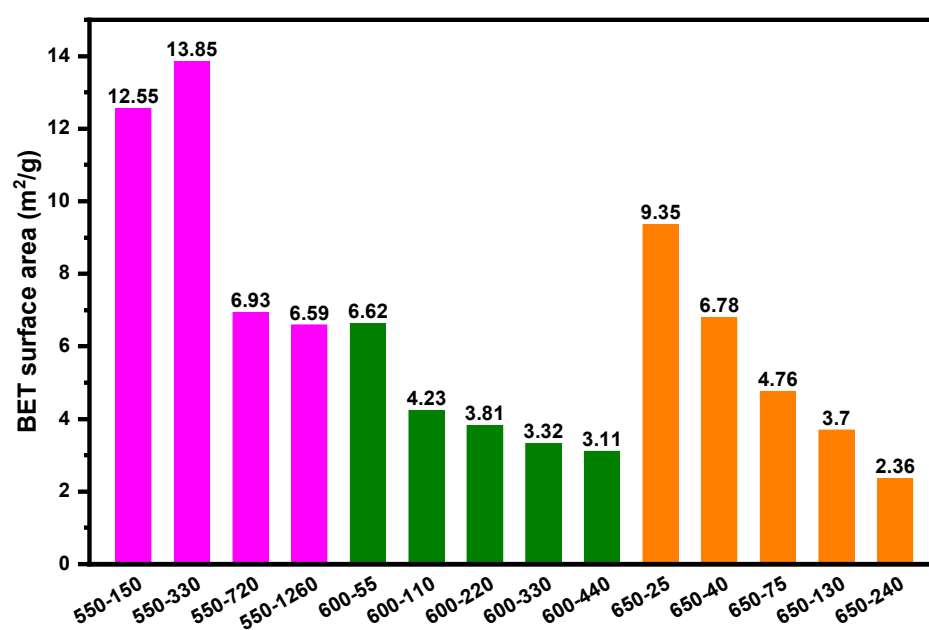


Figure 12. BET surface area of PDD under different calcination conditions.

The results reveal pronounced SSA dependence on calcination temperature and duration, with values ranging from 2.36 m²/g to 13.85 m²/g. At constant temperatures, SSA declines progressively with extended calcination time, exhibiting faster degradation rates at elevated temperatures. For instance, at 550 °C, SSA peaks at 13.85 m²/g (550-330 sample) but diminishes to 6.93 m²/g after 720 min, stabilizing near 6.59 m²/g by 1260 min. A similar trend is observed at 600 °C, where SSA decreases from 6.62 m²/g to 3.11 m²/g after 440 min, indicating a plateau effect once pore structures reach metastable configurations.

The decline in SSA may correlate with microstructural evolution driven by MgO coarsening and pore reorganization, as evidenced by SEM and pore size distribution analyses (Figures 9–11). Below 650 °C, coarsening-mediated MgO growth preserves residual mesoporosity, which may allow gradual SSA decline without catastrophic structural failure. Above this threshold, sintering may be capable of overcoming energy barriers for particle fusion, inducing irreversible pore collapse and surface area loss. The irreversible SSA reduction at elevated temperatures underscores the necessity of precise calcination control to balance reactivity and stability.

4. Future Work

Although the present study provides a systematic sample-series investigation of the thermal evolution of the studied carbonate system, the mechanistic understanding remains incomplete and the structure–property relationships are still largely qualitative. More in-depth mechanistic and quantitative studies are therefore required to clarify the atomic-scale pathways of Mg incorporation, phase transformation, and MgO formation, and to quantify the effects of thermal treatment on phase fractions, Mg substitution level, lattice distortion, crystallite size/strain, pore structure, and surface chemistry. The PDD produced in this study may serve as a promising functional material. The Mg-calcite phase, with its distorted lattice and Mg substitution, could contribute to enhanced mechanical properties, while the coexistence of periclase and the developed pore structure may offer advantages for adsorption, catalysis, and environmental applications [46,47]. The low-temperature formation of MgO also suggests potential use in energy-efficient magnesia-based materials [48]. Future work should therefore focus on evaluating these application-oriented properties, such as mechanical hardness, thermal stability, adsorption and catalytic performance, and biocompatibility, and on comparing them with those of conventionally derived dolomite materials.

5. Conclusions

This study systematically investigates the microstructural evolution of partially decomposed Na₃PO₄-bearing dolomite (PDD), establishing calcination parameters as key modulators of porosity and phase dynamics in derived composites. Key findings are summarized below:

- (1) Controlled calcination of Na₃PO₄-bearing dolomite produces hierarchically porous PDD composites. The products consist of a Mg-calcite framework that retains the original dolomite morphology, with MgO nanospheres anchored on internal and external surfaces.
- (2) The Mg content in Mg-calcite depends on calcination conditions. At 550 °C, the Mg content is approximately 5.83 mol%, whereas calcination at 600–650 °C leads to a transient Mg content of up to 11 mol%. However, prolonged calcination time reduces Mg retention.
- (3) The MgO nanostructure evolves with temperature and duration. At 550 °C, calcination allows controlled growth, whereas at 650 °C, coarsening and sintering become dominant.

- (4) The Mg-calcite morphology and pore structure are strongly affected by calcination conditions. At 550 °C, the Mg-calcite matrix can maintain a stable mesoporous structure within a long period, while prolonged heating at higher temperatures leads to a rapid transition from mesopores to macropores.
- (5) The specific surface area (SSA) decreases gradually at lower temperatures but drops sharply at 650 °C (from 9.35 to 2.36 m²/g).

Conclusions are valid only under the studied calcination conditions, based mainly on qualitative analysis with limited sampling and no statistical modeling. Despite these limitations, by linking thermal processing to phase transformations and microstructural evolution, this study establishes empirical relationships between processing conditions and structure within the investigated temperature-time window.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jmmp10100441/s1>, Figure S1: Photos of slurries (with a solid/liquid mass ratio of 1/25) after certain time. The slurries using the MgCl₂ solution with a concentration > 23.61 wt.% become “cream-like” pastes. Other slurries remain flowable after 48 h. Figure S2. The XRD patterns of PDD after MgCl₂-leaching for (a) different time and (b) in solutions with different concentrations. The results demonstrate that the MgO nanospheres can be almost removed from the PDD in the MgCl₂ solutions with a solution concentration > 18.55 wt.% for 48 h. Figure S3. TG/DTG curve of Mg-calcite after MgCl₂-leaching. The sample losses 43% mass in the temperature range of 600–850 °C due to carbonate decomposition. The content of calcite can be calculated as 97.7%, which confirms that the dolomite is partially decomposed.

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