

Article

Sol–Gel Engineering of Nanostructured MgFe_2O_4 Ferrite: Tunable Microstructure for Thermochemical Energy Conversion Applications

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Abstract

This study investigates the synthesis–structure relationships governing sol–gel-derived nanostructured MgFe_2O_4 ferrite powders for high-temperature thermochemical energy conversion applications. The effects of key processing parameters, including propylene oxide (PO) concentration, gel aging time, calcination temperature, and calcination duration, were systematically examined to tune the phase composition, specific surface area (SSA), pore volume, crystallite size, and nanoparticle morphology of MgFe_2O_4 . Increasing the PO concentration from 5 to 20 mL shortened the gelation time from 585 to 323 s and increased the SSA from 5.30 to 17.88 m^2/g , while the pore volume increased from 0.0074 to 0.0210 cm^3/g . In contrast, gel aging time between 24 and 120 h produced negligible changes in SSA, pore volume, and crystallite size, indicating that extended aging is not required for microstructural control. Calcination temperature strongly influenced the nanostructure: increasing the temperature from 600 to 1000 $^\circ\text{C}$ decreased SSA and pore volume while increasing crystallite size from 21.33 to 48.76 nm. Longer calcination times produced a similar but less pronounced effect, decreasing SSA from 18.83 to 14.89 m^2/g and increasing crystallite size from 17.55 to 30.12 nm. Overall, phase-pure MgFe_2O_4 with favorable textural properties was obtained using 20 mL of PO, 24 h of aging, and calcination in the 700–800 $^\circ\text{C}$ range. Under the identified synthesis conditions, namely 20 mL of PO, 24 h of aging, and calcination in the range of 700–800 $^\circ\text{C}$ for 2 h, phase-pure MgFe_2O_4 nanoparticles with particle sizes of approximately 10–50 nm were obtained. These results establish a processing–microstructure framework for engineering MgFe_2O_4 nanomaterials with tunable textural properties for solar thermochemical redox cycles and related high-temperature energy applications.



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1. Introduction

Developing sustainable pathways for converting CO_2 and H_2O into syngas is essential for mitigating the adverse impacts of CO_2 emissions while meeting rising global energy demand [1,2]. Among the various emerging approaches, solar-driven thermochemical conversion of H_2O (water splitting, WS) and CO_2 (carbon dioxide splitting, CDS) into syngas has garnered significant attention, as the resulting syngas serves as a critical

precursor for synthesizing liquid transportation fuels [3,4]. This process operates as a two-step redox cycle in which the thermochemical reactions are facilitated by the reversible oxidation–reduction behavior of metal oxides (MOs) [5].

Solar thermochemical cycles (STCs) employ both volatile and non-volatile metal oxides (MOs). Among volatile MOs, ZnO has been widely studied: its thermochemical reduction was demonstrated in a pilot-scale solar reactor [6,7], and its WS–CDS cycle efficiency was estimated thermodynamically [8]. SnO₂ shows similar redox behavior, with hydrolysis being demonstrated experimentally [9] and solar-to-fuel energy conversion efficiencies approaching ~50% under optimized TR and WS conditions.

Non-volatile ceria-based STCs have been extensively explored since their first experimental validation in 2006 [10], enabling H₂, syngas, and methane production. Numerous dopants have been incorporated to enhance ceria's reduction and re-oxidation performance, redox capacity, and solar-to-fuel energy conversion efficiency [11,12]. In the category of non-volatile MOs, perovskite oxides have also emerged as promising redox materials, with optimized La_xSr_{1-x}MnO_{3-δ} compositions exhibiting high O₂ release and CO production, and further improvements were achieved through A- and B-site substitutions [13]. DFT studies have additionally guided the design of Ca–Ce–M–O (M = 3d metals) perovskites by evaluating vacancy formation energetics and stability [14].

As another category in the non-volatile MOs, ferrites have also been utilized for STC operation. Bhosale reported a thermodynamic solar-to-fuel energy conversion efficiency of approximately 35% for the Ni-ferrite-based WS cycle [15]. Researchers also investigated the redox reactivity of Ni-ferrite and Co-ferrite toward WS and CDS and concluded that Co-ferrite exhibited a higher fuel production capacity than Ni-ferrite [16–18].

More recently, Mg-based ferrites have emerged as promising redox materials for WS and CDS applications because they combine favorable oxygen exchange characteristics, good thermal stability, low material cost, and the use of earth-abundant elements. Compared with ceria-based materials, Mg-ferrites can provide competitive redox performance while operating at relatively lower oxidation temperatures and utilizing less expensive constituent elements. The WS ability of the redox pair MgFe₂O₄/MgO was investigated [19], showing that this system generated higher H₂ yields at lower temperatures than ceria. In CDS applications, Mg–Fe–O ferrites demonstrated enhanced thermal stability and increased CO production activity [20]. In our recent study, several Mg_xFe_{3-x}O₄ compositions (x = 0.2–1.0) were synthesized via the sol–gel route and evaluated over ten CDS redox cycles [21]. The results confirmed that among all tested compositions, MgFe₂O₄ exhibited the highest CO yield during CDS. These findings collectively indicate that MgFe₂O₄ possesses a favorable combination of redox activity, thermal robustness, and practical scalability for thermochemical energy conversion applications.

Within the broader family of spinel oxides, NiFe₂O₄ and CoFe₂O₄ have also attracted considerable interest because of their favorable catalytic and redox properties and have demonstrated promising performance in thermochemical fuel production and related applications [16–18]. Furthermore, Boussafel et al. [22] reported the green synthesis of NiFe₂O₄, CoFe₂O₄, and Ni_{0.5}Co_{0.5}Fe₂O₄ spinel via a sol–gel auto combustion route, highlighting the versatility of ferrite spinel for advanced functional applications. In contrast, MgAl₂O₄ is recognized for its excellent thermal and structural stability; however, its redox activity is limited because aluminum does not participate in reversible oxygen exchange reactions [23]. Compared with these spinel materials, MgFe₂O₄ offers an attractive balance of redox activity, thermal robustness, low material cost, and earth-abundant constituent elements, making it particularly suitable for large-scale thermochemical energy conversion applications.

One of the key factors governing STC cycles is their physical properties, including phase/chemical composition, specific surface area (SSA), pore volume, crystallite size, and microstructural morphology. It is well established that MOs exhibiting stable phase composition, high SSA and pore volume, small crystallite size, and nanoparticulate morphology generally enable higher fuel yields during WS/CDS cycles [24]. These physical characteristics are equally important for other redox-driven applications such as thermochemical energy storage, methane reforming, and related high-temperature processes.

In this study, the term “nanostructured” denotes MgFe_2O_4 materials characterized by nanoscale crystallite and particle dimensions, high surface area, and porous microstructures produced via sol–gel processing. These features differentiate them from conventional ferrites synthesized by traditional solid-state methods, which generally possess larger particle sizes, lower surface areas, and limited pore accessibility. For thermochemical redox applications, nanoscale crystallites and particles offer advantages by increasing the density of accessible surface reaction sites, reducing oxygen diffusion distances within the oxide lattice, and facilitating more efficient gas–solid interactions. Therefore, precise control of nanoscale structural features is essential to enhance redox kinetics and optimize the utilization of the active material during thermochemical cycling.

From a nanotechnology perspective, controlling the microstructure of ferrite-based oxides is essential because redox activity, oxygen transport, and thermal stability are strongly influenced by particle size, crystallite growth, pore architecture, and accessible surface area. Sol–gel synthesis offers a flexible route for producing compositionally homogeneous nanostructured oxides, as gelation chemistry and subsequent thermal treatment can be adjusted to tailor phase formation, pore volume, and crystallite size. Therefore, establishing clear processing–structure relationships is important not only for improving thermochemical redox performance but also for advancing the broader design of functional oxide nanomaterials for high-temperature energy applications.

In this study, we examined the effects of key sol–gel synthesis parameters—including the concentration of the gelation agent (propylene oxide, PO), gel aging time, and calcination temperature and duration—on the physical properties of MgFe_2O_4 (Mg-ferrite). The objective was to identify the optimal synthesis conditions that yield phase-pure and compositionally stable Mg-ferrite with high SSA and pore volume, reduced crystallite size, and well-defined nanoparticle morphology. Achieving these favorable attributes is expected to significantly enhance the suitability of Mg-ferrite for solar-driven thermochemical applications.

In our previous work [21], various $\text{Mg}_x\text{Fe}_{3-x}\text{O}_4$ compositions were synthesized and evaluated for thermochemical CO_2 splitting, where MgFe_2O_4 exhibited superior redox performance under multi-cycle operation. However, that study primarily focused on compositional effects and redox reactivity without systematically investigating how sol–gel processing parameters influence microstructural evolution. The present study addresses this gap by conducting a detailed parametric analysis of propylene oxide concentration, aging duration, calcination temperature, and calcination time to establish synthesis–structure relationships critical for the microstructural engineering of MgFe_2O_4 .

Although MgFe_2O_4 has been synthesized using various methods and assessed for thermochemical redox applications, systematic studies examining the influence of individual sol–gel processing parameters on phase formation, crystallite growth, surface area, and pore evolution are limited. The present study establishes quantitative relationships between processing conditions and the resulting MgFe_2O_4 structure by comprehensively evaluating PO concentration, aging duration, calcination temperature, and calcination time. This methodology offers practical guidance for optimizing the microstructure of MgFe_2O_4 in thermochemical energy conversion applications.

2. Experimental

2.1. Precursors and Chemicals

Magnesium ferrite was synthesized via a sol–gel route employing magnesium and iron nitrate salts as metal precursors, ethanol (95%) as the solvent, and propylene oxide (99%) as the gelation agent. All reagents were procured from Sigma-Aldrich, USA and used without any further purification.

2.2. Sol–Gel Synthesis

Magnesium and iron nitrate salts were dissolved in ethanol at a stoichiometric ratio of Mg:Fe = 1:2. After that, the mixture was sonicated until a clear, uniform solution was produced. The gelation ingredient, propylene oxide (PO), was then added dropwise to create a stable gel. The as-synthesized gel was allowed to mature at room temperature for a predetermined duration, followed by aging and drying on a temperature-controlled hot plate at 100 °C for 2 h. The dried gel was subsequently calcined in air using a muffle furnace at selected temperatures and hold times. Figure 1 provides a schematic overview of the sol–gel synthesis route employed for MgFe₂O₄ preparation, while the detailed experimental procedure is described in Section 2.2.

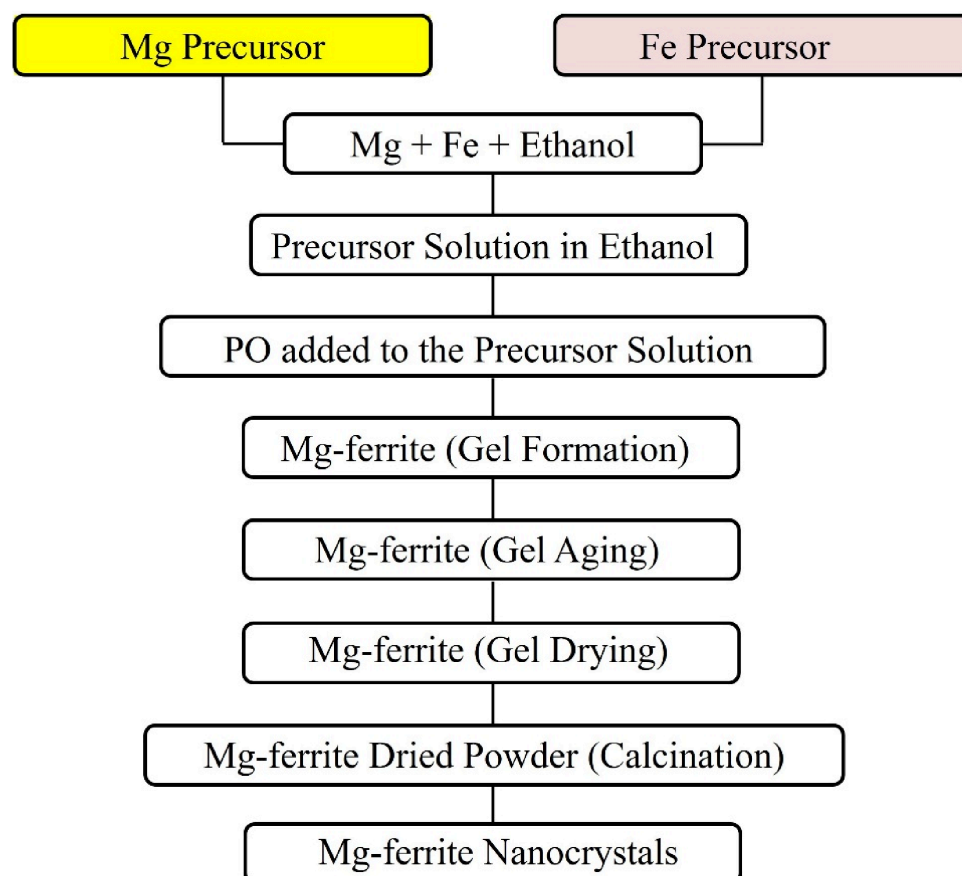


Figure 1. Schematic overview of the sol–gel synthesis route used for MgFe₂O₄ preparation.

2.3. Characterization

A thorough characterization procedure was performed on the calcined Mg-ferrite powder. In the first step, a Panalytical XPert MPD/DY636 powder X-ray diffractometer (PXRD) was used to analyze the phase composition. The Mg-ferrite powder was scanned

for 2θ between 20° and 70° , with a 5 s recording duration. The average crystallite size was estimated using the Scherrer equation, applied to the most intense diffraction peak.

$$\text{crystallite size} = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

K = Dimensionless shape factor (value close to unity, typical value of 0.9);

λ = X-ray wavelength;

β = Line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening (radians);

θ = Bragg angle.

Instrumental broadening corrections were not applied; therefore, the reported crystallite sizes should be considered approximate values and are primarily intended for comparative analysis among samples synthesized under different conditions.

The specific surface area (SSA) and cumulative pore volume (PV) of the Mg-ferrite material were measured using a BET surface area analyzer, an ASAP 2420 analyzer from Micromeritics. The BET-derived specific surface area (SSA) and pore volume values are presented to illustrate relative trends among samples rather than to provide precise measurements of pore architecture.

Additionally, a scanning electron microscope integrated with energy-dispersive X-ray spectroscopy (SEM/EDS, Nova Nano 450, FEI) and transmission electron microscopes (TEM, Tecnai G2 S Twin FEG, FEI) were used to examine the particle morphology of the ACRM particles. EDS was employed to verify the approximate elemental composition and magnesium stoichiometry of the synthesized samples. Due to the semi-quantitative nature of this technique, the reported compositions represent approximate values rather than precise chemical formulas.

3. Results and Discussion

3.1. Influence of PO Concentration

In sol-gel synthesis, precursor molecules undergo sequential hydrolysis and polycondensation reactions that ultimately lead to the formation of an extended inorganic network. The incorporation of a proton-scavenging agent such as PO accelerates these reactions by consuming protons generated during hydrolysis. This promotes rapid chain termination and network solidification, effectively “freezing” the growing molecular structure and significantly reducing the gelation time. The accelerated gelation induced by PO influences the development of the gel network. Rapid network formation limits structural collapse during drying, which preserves a greater fraction of the porous framework. As a result, samples prepared with higher PO concentrations demonstrate increased surface area and pore volume after calcination. These findings indicate that PO impacts both gelation kinetics and the evolution of the final textural properties of MgFe_2O_4 .

The influence of PO concentration on the physical properties of the sol-gel derived Mg-ferrite was first examined. For each synthesis batch, 10 g of Mg and Fe nitrate precursors (maintaining a Mg:Fe molar ratio of 1:2) was dissolved in 20 mL of ethanol to form a homogeneous precursor solution. Subsequently, varying volumes of PO were introduced to evaluate the effect of PO concentration on the resulting Mg-ferrite properties.

The influence of PO concentration on the gelation time of Mg-ferrite is illustrated in Figure 2. The results indicate a clear inverse relationship between PO content and gelation time. At a PO volume of 5 mL, the gelation time was approximately 585 s. Increasing the PO concentration to 10 mL reduced the gel time to 469 s, while a further increase to 20 mL resulted in a markedly shorter gel time of 323 s. However, beyond 20 mL, additional PO did not produce a meaningful reduction in gelation time, suggest-

ing that the proton-scavenging and chain-termination effects of PO approach saturation at higher concentrations. Although the inverse relationship between PO concentration and gelation time is anticipated due to the role of PO as a proton scavenger during sol–gel processing, quantifying this behavior is essential for defining the practical synthesis window for MgFe_2O_4 . The findings demonstrate that the positive effect of PO on gelation kinetics diminishes at higher concentrations, with approximately 20 mL being identified as an optimal PO level beyond which further increases yield minimal processing advantages.

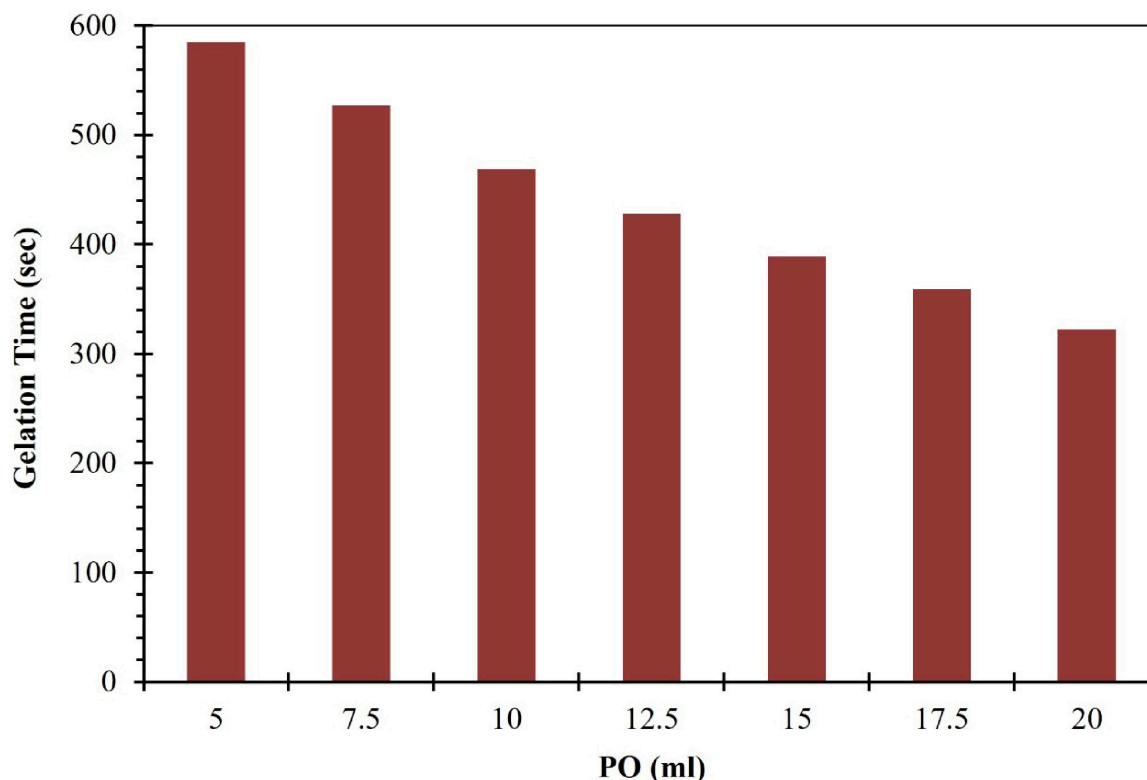


Figure 2. Variation in the gelation time as a function of rise in PO amount (sol–gel synthesis of Mg-ferrite) at 25 °C.

Following the addition of varying PO volumes, the gels were aged, dried, and subsequently calcined in air at 800 °C for 2 h. The calcined powder was characterized to determine the effect of PO on Mg-ferrite phase purity and chemical composition. As presented in Figure 3 and Table 1, neither the crystallographic phase nor the elemental stoichiometry exhibited any measurable dependence on PO content. EDS analysis confirmed stable chemical compositions of $\text{Mg}_{1.01}\text{Fe}_{2.00}\text{O}_{4.01}$, $\text{Mg}_{1.00}\text{Fe}_{2.00}\text{O}_{4.00}$, $\text{Mg}_{1.00}\text{Fe}_{2.01}\text{O}_{4.02}$, and $\text{Mg}_{1.00}\text{Fe}_{2.00}\text{O}_{4.00}$ for samples synthesized using 5, 10, 15, and 20 mL of PO, respectively. These results demonstrate that although PO strongly influences gelation kinetics and subsequently affects textural properties such as SSA and pore volume, it does not alter the phase formation or compositional integrity of the calcined MgFe_2O_4 powders. This observation is important because modifications in gelation chemistry can potentially affect nucleation and phase evolution during sol–gel processing. The PXRD results confirm that the investigated PO concentrations provide microstructural tuning without compromising phase purity.

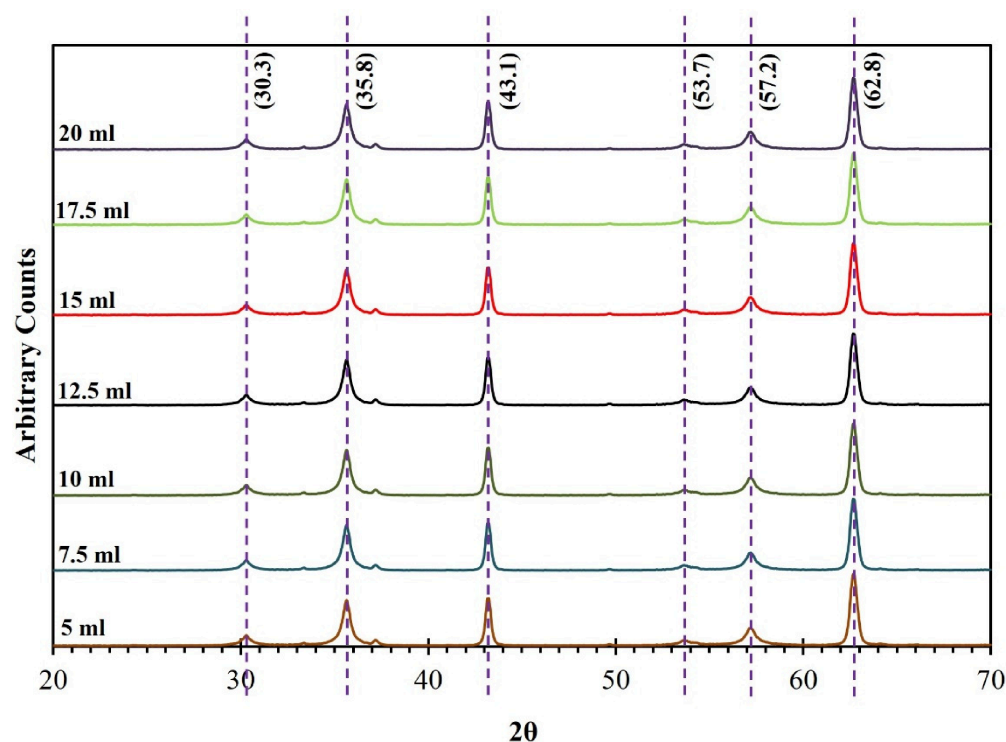


Figure 3. Influence of concentration of PO on phase composition of sol-gel-derived Mg-ferrite (calcination temperature = 800 °C and calcination time = 2 h). The vertical dotted lines indicate the experimentally observed positions of the characteristic MgFe₂O₄ diffraction peaks and are included as visual guides for comparison among samples.

Table 1. Influence of the concentration of PO on the chemical composition of sol-gel-synthesized Mg-ferrite (EDS characterization).

PO (mL)	Mg:Fe Molar Ratio (As-Prepared)	Mg:Fe Molar Ratio (After Calcination)	Chemical Composition (EDS Analysis)
5.0	1:2	1.01:2.00	Mg _{1.01} Fe _{2.00} O _{4.01}
7.5	1:2	1.01:2.00	Mg _{1.01} Fe _{2.00} O _{4.01}
10.0	1:2	1.00:2.00	Mg _{1.00} Fe _{2.00} O _{4.00}
12.5	1:2	1.01:2.00	Mg _{1.01} Fe _{2.00} O _{4.01}
15.0	1:2	1.00:2.01	Mg _{1.00} Fe _{2.01} O _{4.02}
17.5	1:2	1.01:2.00	Mg _{1.01} Fe _{2.00} O _{4.01}
20.0	1:2	1.00:2.00	Mg _{1.00} Fe _{2.00} O _{4.00}

The effect of PO concentration on the SSA of Mg-ferrite was also examined. The corresponding variations in pore volume and SSA with increasing PO content are presented in Figure 4a. The pore volume values reported in this study were obtained from nitrogen adsorption–desorption measurements and are expressed in units of cm³/g. As shown, the SSA of Mg-ferrite increased consistently with rising PO concentration. For example, increasing the PO volume from 5 to 20 mL resulted in an overall SSA enhancement of 12.58 m²/g. A major portion of this increase occurred between 5 and 15 mL of PO, yielding an improvement of 11.81 m²/g. However, further increasing the PO concentration from 15 to 20 mL produced only a marginal rise of 0.41 m²/g, indicating that the SSA approached a saturation limit at higher PO levels.

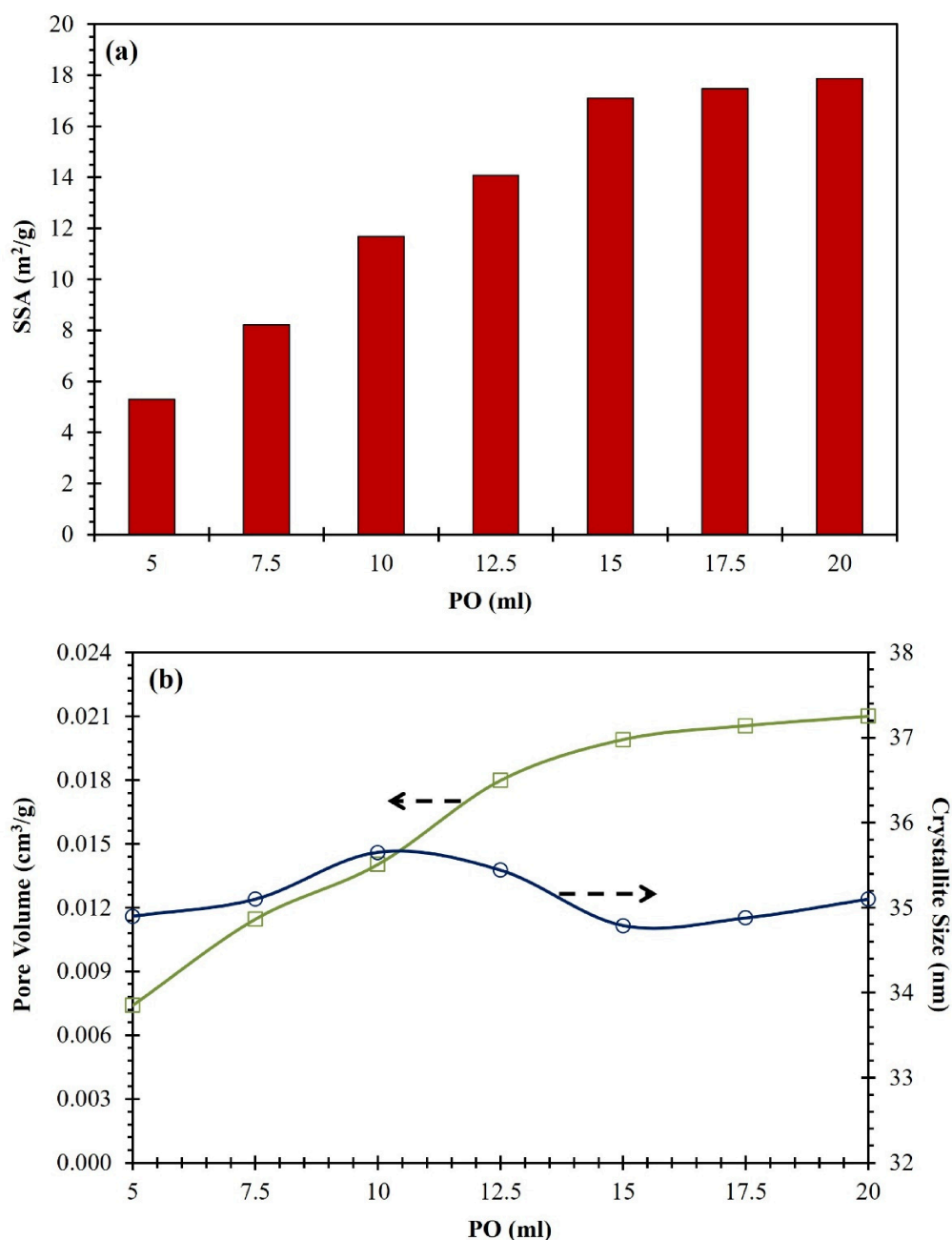


Figure 4. Influence of concentration of PO on (a) SSA and (b) pore volume and crystallite size of sol-gel-derived Mg-ferrite (calcination temperature = 800 °C and calcination time = 2 h).

The pore volume of Mg-ferrite also increased with rising PO concentration (Figure 4b). From a thermochemical redox perspective, increased pore volume is advantageous as it improves the accessibility of reactive gas species to the oxide surface and facilitates gas transport within the material. A more open pore structure reduces mass transfer limitations during oxidation and reduction steps, thereby increasing the utilization of active redox sites. Therefore, the observed increase in pore volume with higher PO concentration may enhance gas–solid interactions and promote more efficient oxygen exchange during thermochemical cycling.

The pore volume was 0.0074 cm^3/g at a PO concentration of 5 mL. The pore volume increased by 0.0136 cm^3/g as the PO content increased from 5 to 20 mL. Consistent with the trend observed for SSA, a substantial portion of this increase occurred between 5 and 15 mL of PO, yielding an improvement of 0.0125 cm^3/g , whereas the subsequent

increase from 15 to 20 mL resulted in only a minor change of $0.0011 \text{ cm}^3/\text{g}$. Overall, increasing PO concentration had a significant impact on pore volume and SSA, but it had no discernible effect on the Mg-ferrite's crystallite size. As the PO concentration was raised from 5 to 20 mL, Figure 4b demonstrated that the crystallite size of Mg-ferrite stayed nearly constant, ranging from 34.8 to 35.6 nm. This showed that while PO content had an impact on the textural characteristics (pore volume and SSA), it had no discernible effect on crystallite size.

3.2. Influence of Aging of the Gels

Aging the as-prepared gels was an essential step in the sol-gel synthesis as it enhanced the mechanical strength, molecular network connectivity, and uniformity of the final product. To evaluate the influence of aging duration, Mg-ferrite gels synthesized using 20 mL of PO were aged at room temperature for periods ranging from 24 to 120 h. Following aging, the gels were dried and subsequently calcined in air at 800°C for 2 h. The resulting Mg-ferrite powders were characterized, and as summarized in Table 2, the physical properties of Mg-ferrite remained unchanged across the examined aging durations, indicating that aging the gels for 24 to 120 h did not produce any measurable impact on these properties.

Table 2. Influence of the gel aging time on the physical properties of sol-gel-derived Mg-ferrite (PXRD, EDS, and BET characterization).

Aging Time (h)	Chemical Composition (EDS Analysis)	SSA (m^2/g)	Pore Volume (cm^3/g)	Crystallite Size (nm)
24	$\text{Mg}_{1.00}\text{Fe}_{2.00}\text{O}_{4.00}$	17.95	0.0221	34.4
48	$\text{Mg}_{1.01}\text{Fe}_{2.00}\text{O}_{4.01}$	16.89	0.0219	35.4
72	$\text{Mg}_{1.00}\text{Fe}_{2.00}\text{O}_{4.00}$	16.99	0.0230	34.8
96	$\text{Mg}_{1.00}\text{Fe}_{2.01}\text{O}_{4.02}$	17.23	0.0225	35.0
120	$\text{Mg}_{1.01}\text{Fe}_{2.00}\text{O}_{4.01}$	17.44	0.0215	34.1

The limited influence of aging duration observed in this study indicates that the primary hydrolysis, condensation, and gel network formation reactions are largely completed during the initial PO-assisted gelation stage. Since PO rapidly scavenges protons and accelerates network formation, the resulting gel structure is likely to attain a relatively stable state soon after gelation. Under these conditions, extending the aging period from 24 to 120 h does not induce substantial changes in phase composition, crystallite growth, or overall textural properties. Although no measurable differences were detected in SSA, pore volume, or crystallite size, more subtle changes in pore connectivity, nanoscale defects, or local structural ordering cannot be entirely excluded and may require advanced characterization techniques for further assessment.

Although extended aging did not significantly influence the measured physical properties, the aging step remains a critical component of the sol-gel process. During aging, residual condensation reactions may persist, further strengthening and stabilizing the gel network. Additionally, aging facilitates structural homogenization and the redistribution of solvent species within the gel. In this system, these processes primarily occur during the initial stages of aging and therefore do not result in measurable differences in the properties of the final calcined MgFe_2O_4 powders when the aging time exceeds 24 h.

The present conclusion is based on PXRD, EDS, and BET measurements, which primarily characterize phase composition, crystallinity, SSA, and cumulative pore volume. However, these techniques may not fully resolve subtle changes in nanopore architecture, pore connectivity, or defect structure. Previous studies using advanced characterization methods such as positron annihilation spectroscopy (PAS) have shown that spinel ox-

ides can undergo complex nanoporous transformations during thermal processing and aging [25]. Thus, the results indicate that aging had no measurable effect on the evaluated physical properties, although the possibility of finer-scale pore structure evolution cannot be entirely excluded.

3.3. Influence of Calcination Temperature

The influence of calcination temperature on the physical properties of sol-gel-synthesized Mg-ferrite was investigated through a systematic series of experiments. After preparation with 20 mL of PO, the Mg-ferrite gel was aged for 24 h, dried at 100 °C, and subsequently calcined at various temperatures in air for 2 h. The phase purity and chemical composition of the resulting calcined powders were assessed using PXRD and EDS. As shown in Figure 5 and Table 3, the produced Mg-ferrite maintained a consistent phase and chemical composition corresponding to nominally phase-pure MgFe_2O_4 across all calcination temperatures examined, with the exception of the sample calcined at 600 °C, which exhibited deviations from the expected phase assemblage. The powder obtained after calcination at 600 °C showed a mixed phase comprising both Mg-ferrite and residual hematite ($\alpha\text{-Fe}_2\text{O}_3$), indicating that this temperature was not sufficient for the complete formation of phase-pure MgFe_2O_4 . The presence of $\alpha\text{-Fe}_2\text{O}_3$ suggests incomplete reaction between the precursor species at this temperature. Increasing the calcination temperature to 700 °C eliminated the secondary phase reflections and resulted in the formation of phase-pure MgFe_2O_4 .

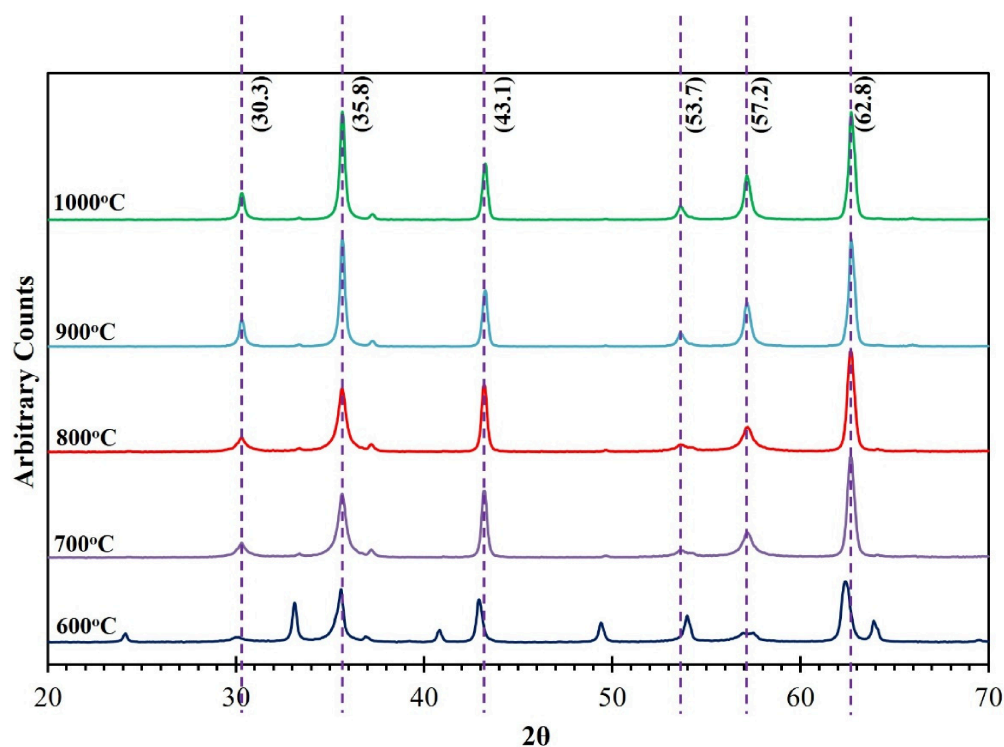


Figure 5. Influence of calcination temperature on the phase composition of sol-gel-derived Mg-ferrite (PO concentration = 20 mL and calcination hold time = 2 h). The vertical dotted lines indicate the experimentally observed positions of the characteristic MgFe_2O_4 diffraction peaks and are included as visual guides for comparison among samples.

As the calcination temperature increased, it was found that the Mg-ferrite PXRD peaks became sharper. This finding suggests that Mg-ferrite has a higher crystallinity at higher calcination temperatures. As the calcination temperature increased from 600 to 1000 °C, the crystallite size of Mg-ferrite increased dramatically (Figure 6). According to

the findings, the powder's crystallite size after calcination at 600 °C was 21.3 nm, and when the calcination temperature climbed to 1000 °C, it increased by 27.4 nm.

Table 3. Influence of the calcination temperature on the chemical composition of sol–gel-synthesized Mg-ferrite (EDS characterization).

Calcination Temperature (°C)	Mg:Fe Molar Ratio (As-Prepared)	Mg:Fe Molar Ratio (After Calcination)	Chemical Composition (EDS Analysis)
700	1:2	1.01:2.00	Mg _{1.01} Fe _{2.00} O _{4.01}
800	1:2	1.00:1.99	Mg _{1.00} Fe _{1.99} O _{3.99}
900	1:2	1.01:2.00	Mg _{1.01} Fe _{2.00} O _{4.01}
1000	1:2	1.00:2.01	Mg _{1.00} Fe _{2.01} O _{4.02}

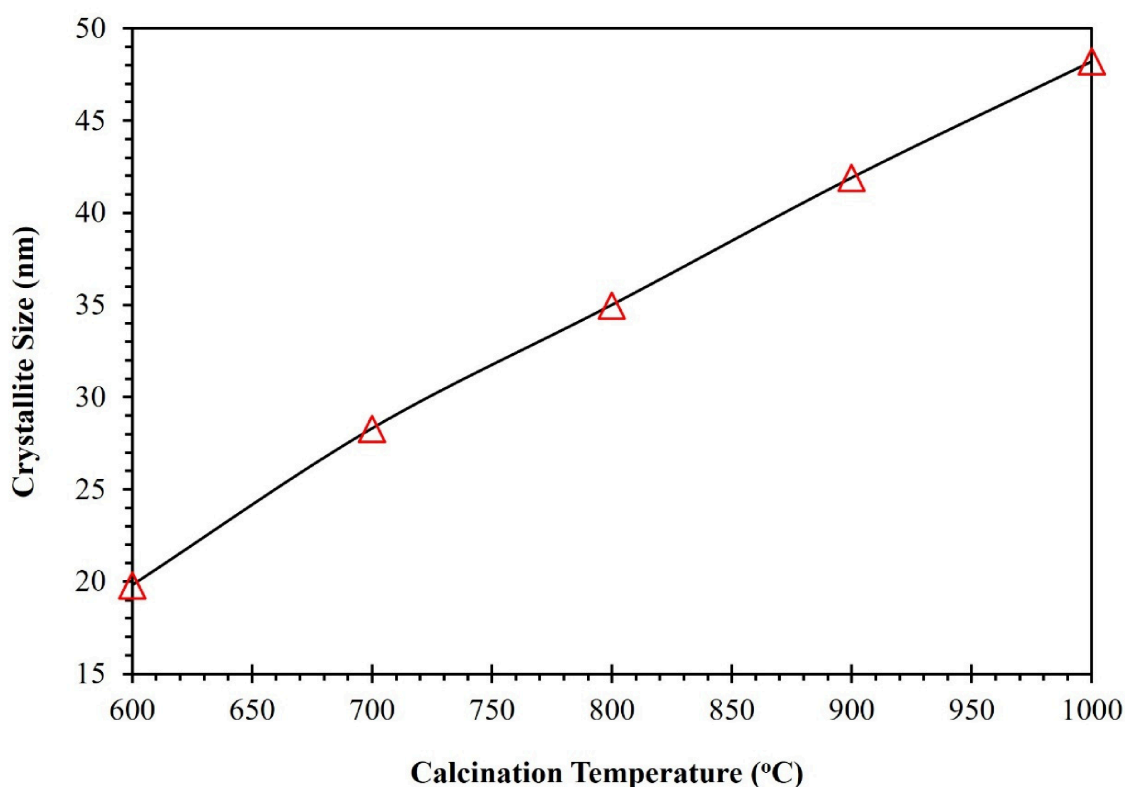


Figure 6. Influence of calcination temperature on the crystallite size of sol–gel-derived Mg-ferrite (PO concentration = 20 mL and calcination hold time = 2 h).

The BET results, presented in Figure 7a,b, showed that both SSA and pore volume decreased markedly with increasing calcination temperature. Specifically, the SSA dropped from 38.91 to 9.98 m²/g as the calcination temperature increased from 600 to 1000 °C. The reductions in SSA across successive temperature intervals were as follows: 600 to 700 °C (14.71 m²/g), 700 to 800 °C (6.27 m²/g), 800 to 900 °C (5.68 m²/g), and 900 to 1000 °C (2.27 m²/g). A similar trend was observed for pore volume, which decreased from 0.0701 to 0.0113 cm³/g over the same temperature range. The corresponding reductions in pore volume with increasing calcination temperature were as follows: from 600 to 700 °C, the pore volume decreased by 0.0355 cm³/g; from 700 to 800 °C, by 0.0124 cm³/g; from 800 to 900 °C, by 0.0069 cm³/g; and from 900 to 1000 °C, by 0.0040 cm³/g.

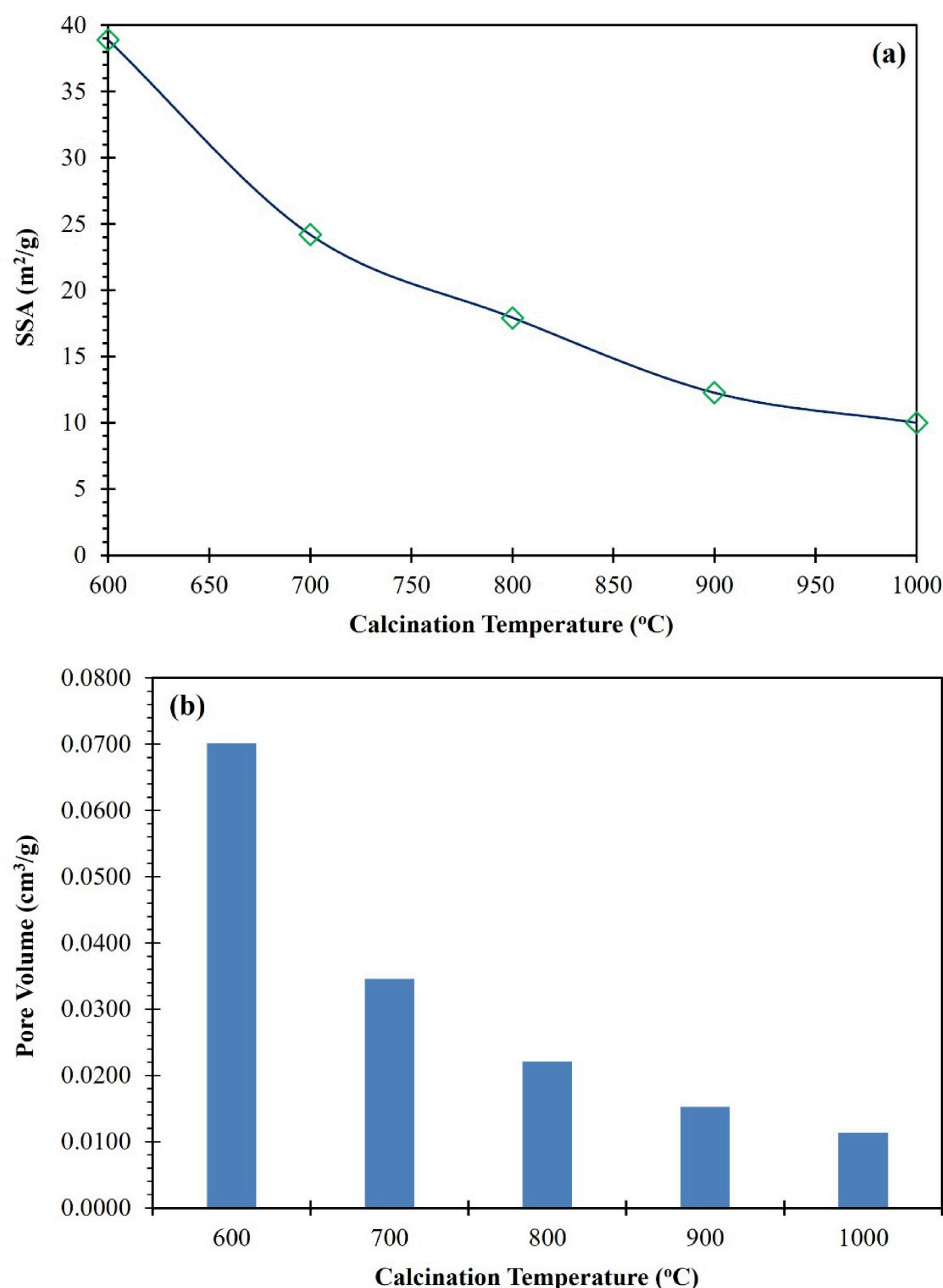


Figure 7. Influence of calcination temperature on the (a) SSA and (b) pore volume of sol-gel-derived Mg-ferrite (PO concentration = 20 mL and calcination hold time = 2 h).

A reduction in pore volume with increasing calcination temperature indicates progressive pore collapse and densification due to thermal sintering. Similar behavior has been reported in ferrite systems, where elevated temperatures promote densification, grain growth, and reduction of porosity through enhanced atomic diffusion and particle coarsening [26]. In thermochemical redox materials, these structural changes can impede gas diffusion and reduce the accessibility of internal reaction sites. Consequently, maintaining pore volume while achieving phase purity is essential for preserving favorable gas transport properties and maximizing the performance of redox-active MgFe_2O_4 during repeated high-temperature cycles.

Although pore volume provides useful information regarding the accessibility of the porous framework, it represents only one aspect of pore architecture. Characteristics such as pore size distribution, pore connectivity, and hierarchical organization may also influence gas transport and oxygen exchange behavior. Consequently, the BET-derived

parameters reported herein should be interpreted as indicators of overall textural evolution rather than a complete description of the pore structure. Furthermore, BET/BJH analyses provide indirect information regarding pore characteristics and cannot fully resolve complex nanoscale pore architectures or connectivity effects that may develop during synthesis and thermal treatment.

Although phase-pure MgFe_2O_4 was obtained at both 700 and 800 °C, the sample calcined at 700 °C exhibited a higher SSA, greater pore volume, and smaller crystallite size. Therefore, from a microstructural perspective, 700 °C appears to provide more favorable textural characteristics, while temperatures above 800 °C promote progressive crystallite growth and loss of SSA through thermal sintering.

3.4. Influence of Calcination Time

The effect of calcination time (t) was also systematically examined, similar to the evaluation performed for calcination temperature. Mg-ferrite gel was prepared with the same procedure as was done for investigating the influence of calcination temperature. The as-prepared gel was calcined at 800 °C for hold times ranging from 1 to 5 h. As indicated by the PXRD results and the EDS data presented in Table 4, variations in calcination time did not influence the phase or chemical composition. The PXRD data further showed that the crystallite size increased by 6.4 nm as the dwell time was raised from 1 to 3 h (Figure 8). Extending the calcination duration from 3 to 5 h produced an additional increase of 6.1 nm, following the same trend.

Table 4. Influence of the calcination time on the chemical composition of sol–gel-synthesized Mg-ferrite (EDS characterization).

Calcination Time (h)	Mg:Fe Molar Ratio (As-Prepared)	Mg:Fe Molar Ratio (After Calcination)	Chemical Composition (EDS Analysis)
1	1:2	1.00:2.00	$\text{Mg}_{1.00}\text{Fe}_{2.00}\text{O}_{4.00}$
2	1:2	1.01:2.00	$\text{Mg}_{1.01}\text{Fe}_{2.00}\text{O}_{4.01}$
3	1:2	1.00:1.99	$\text{Mg}_{1.00}\text{Fe}_{1.99}\text{O}_{3.99}$
4	1:2	1.00:1.99	$\text{Mg}_{1.00}\text{Fe}_{1.99}\text{O}_{3.99}$
5	1:2	1.00:2.00	$\text{Mg}_{1.00}\text{Fe}_{2.00}\text{O}_{4.00}$

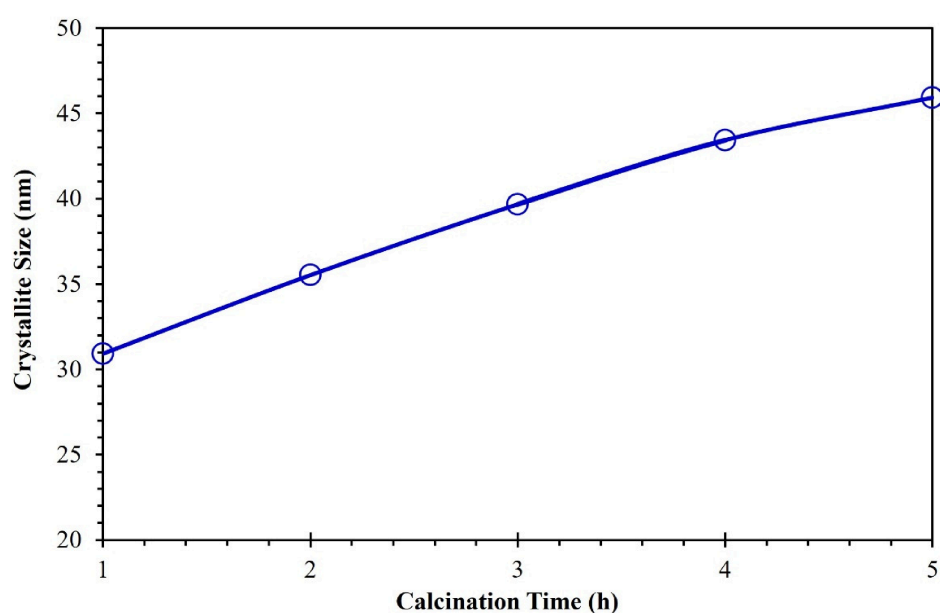


Figure 8. Influence of calcination time on crystallite size of sol–gel-derived Mg-ferrite (PO concentration = 20 mL and calcination temperature = 800 °C).

Figure 9a,b illustrate the variations in SSA and pore volume of Mg-ferrite as the calcination duration was extended from 1 to 5 h. Both properties decreased progressively with longer dwell times. For example, increasing the calcination time from 1 to 3 h resulted in reductions of $2.09 \text{ m}^2/\text{g}$ in SSA and $0.003 \text{ cm}^3/\text{g}$ in pore volume. Similarly, extending the calcination duration from 3 to 5 h led to further decreases of $3.76 \text{ m}^2/\text{g}$ in SSA and $0.005 \text{ cm}^3/\text{g}$ in pore volume. It was inferred that the reductions in SSA and pore volume with increasing calcination duration were caused by the progressive collapse of the porous structural framework of the Mg-ferrite as thermal exposure intensified.

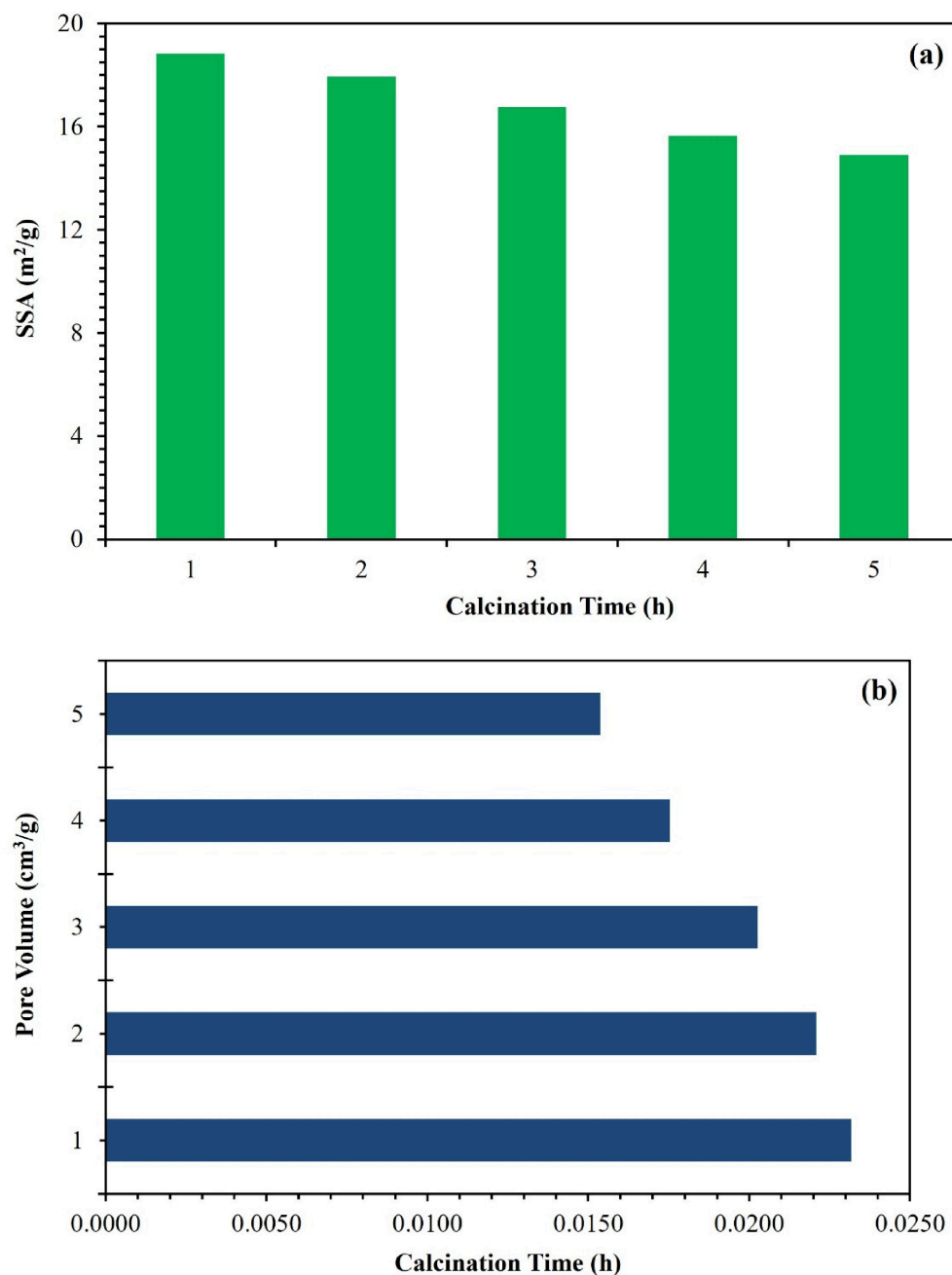


Figure 9. Influence of calcination time on the (a) SSA and (b) pore volume of sol-gel derived Mg-ferrite (PO concentration = 20 mL and calcination temperature = 800°C).

It was concluded that phase-pure MgFe_2O_4 with favorable textural properties and relatively small crystallite sizes can be obtained using 20 mL of PO, 24 h of aging, and calcination temperatures in the range of 700–800 °C. Within this range, the 700 °C sample exhibited the highest SSA and smallest crystallite size among the phase-pure materials investigated. Furthermore, SEM and TEM analyses of Mg-ferrite prepared using the optimized sol–gel synthesis conditions were conducted to validate the nanoparticle morphology (Figure 10a,b). The resulting micrographs confirmed that the typical Mg-ferrite particle size ranged from approximately 10 to 50 nm. While SEM and TEM characterization were limited to the representative phase-pure MgFe_2O_4 sample, the observed trends in crystallite size, SSA, and pore volume as a function of calcination temperature provide indirect evidence of microstructural evolution. Future work will include temperature-dependent electron microscopy studies to further elucidate morphology development and microstructural changes during calcination.

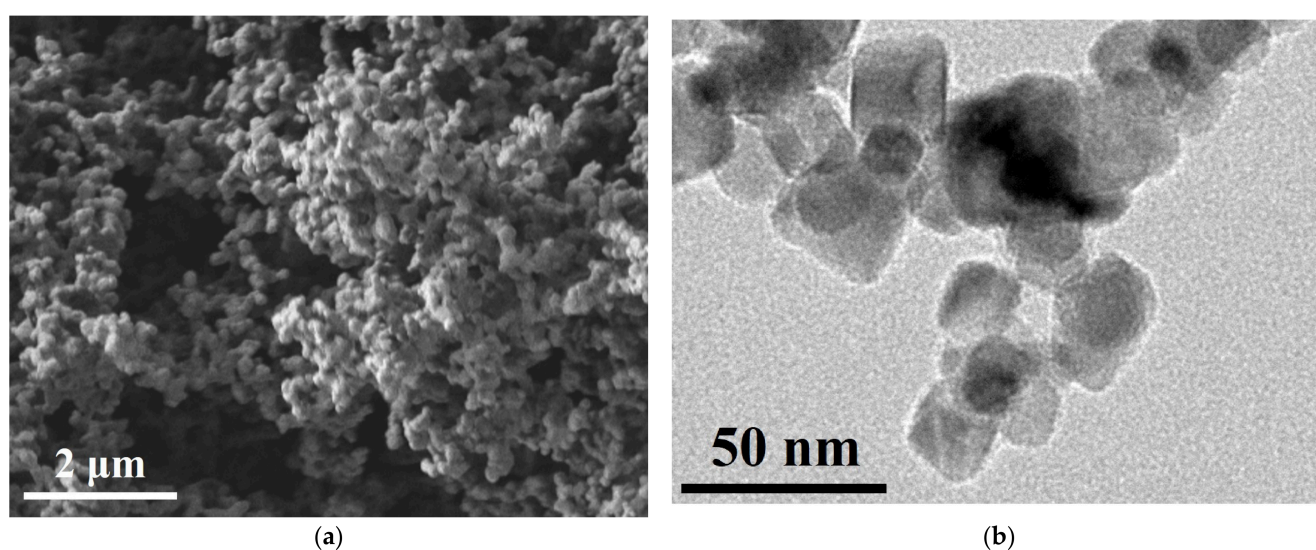


Figure 10. Structural characterization of sol–gel-derived Mg-ferrite: (a) SEM and (b) TEM images.

Ferrite-based thermochemical redox reactions involve oxygen vacancy formation and annihilation within the spinel lattice. These processes are intrinsically linked to crystallite size, pore architecture, and phase stability. Although the redox capability of MgFe_2O_4 has been previously demonstrated under severe thermochemical cycling conditions, a systematic understanding of how processing parameters govern these structural attributes was lacking. The present study addresses this gap by establishing a reproducible synthesis–structure framework.

3.5. Multi-Cycle High-Temperature Redox Stability of MgFe_2O_4

The thermochemical redox performance of sol–gel-synthesized MgFe_2O_4 has been previously evaluated in detail by our group [21]. In that study, MgFe_2O_4 (denoted as MF10) was subjected to multiple thermochemical CO_2 splitting cycles using a high-temperature thermogravimetric analyzer (TGA) under thermal reduction at 1400 °C and re-oxidation at 1000 °C. MF10 demonstrated stable multi-cycle redox activity, releasing an average of 58.7 $\mu\text{mol O}_2/\text{g}\cdot\text{cycle}$ and producing 79.6 $\mu\text{mol CO}/\text{g}\cdot\text{cycle}$ over nine consecutive cycles. The CO/O_2 molar ratio was in the range of 1.3–1.4, with O_2 recovery between 65 and 70%, confirming sustained redox capability and structural robustness under severe thermal conditions (Figure 11).

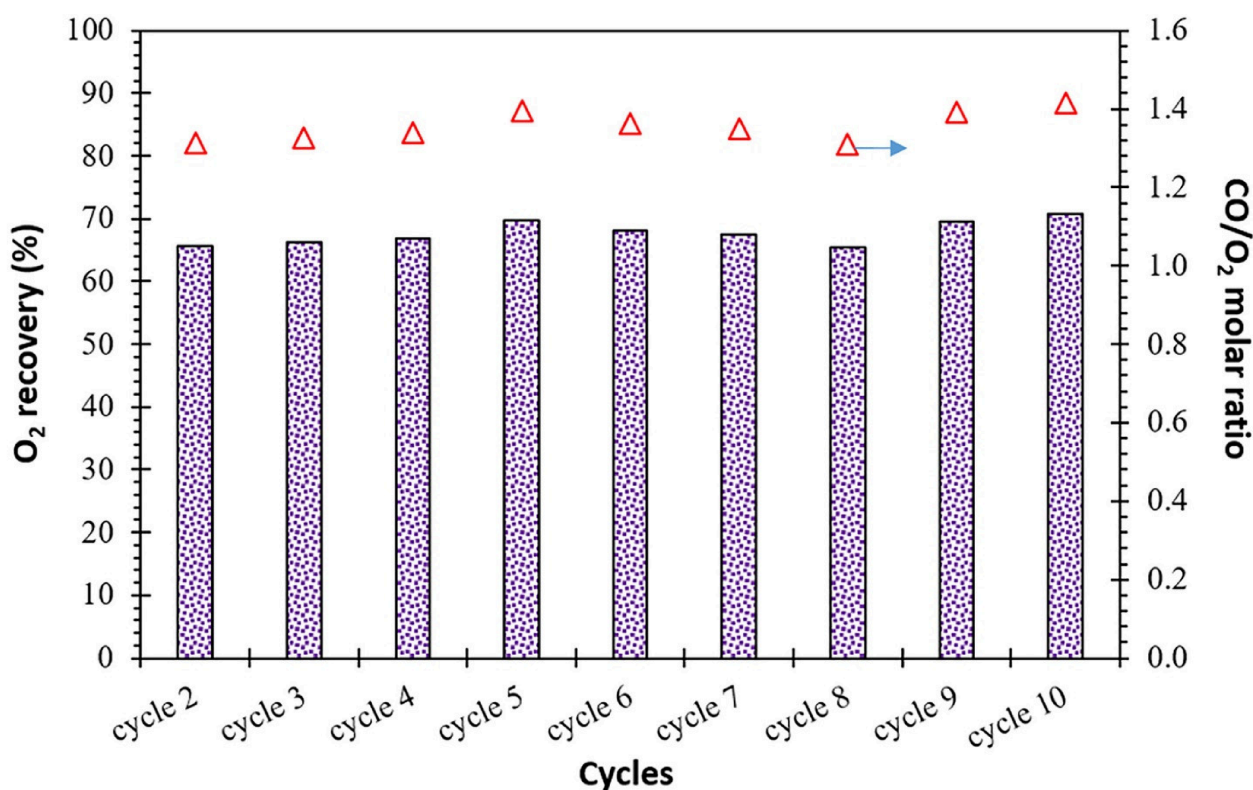


Figure 11. Multi-cycle thermochemical redox performance of MgFe_2O_4 (MF10) showing O_2 recovery and CO/O_2 molar ratio over nine cycles. Reproduced from Takalkar and Bhosale [21].

The present study does not seek to re-evaluate redox performance. Rather, it provides a systematic parametric investigation of the sol–gel processing variables that control phase formation, crystallite growth, and pore development in MgFe_2O_4 . While the earlier study validated thermochemical stability, it did not examine how gelation chemistry, aging duration, and calcination conditions govern the resulting microstructure. The quantitative analysis presented herein establishes the synthesis window required to reproducibly obtain phase-pure MgFe_2O_4 with controlled crystallinity and pore volume. This processing–structure framework is essential for ensuring consistent material preparation in future redox investigations and scale-up efforts.

4. Summary and Conclusions

This work systematically evaluated how sol–gel processing parameters control the structural and textural evolution of nanostructured MgFe_2O_4 ferrite powders. The results demonstrate that PO concentration plays a key role in regulating gelation behavior and microstructural development. Increasing PO from 5 to 20 mL shortened the gelation time by 262 s and increased SSA and pore volume by $12.58 \text{ m}^2/\text{g}$ and $0.0136 \text{ cm}^3/\text{g}$, respectively, without significantly affecting phase composition or crystallite size. In contrast, gel aging time had minimal influence on the measured properties, confirming that aging beyond 24 h is not necessary for obtaining stable MgFe_2O_4 powders.

Calcination temperature was the most influential parameter controlling the final nanostructure. Increasing the calcination temperature from 600 to 1000 °C decreased SSA from 38.91 to $9.98 \text{ m}^2/\text{g}$ and reduced pore volume from 0.0701 to $0.0113 \text{ cm}^3/\text{g}$, while crystallite size increased by 27.43 nm. Calcination duration produced a similar but less severe effect, with SSA decreasing by $5.85 \text{ m}^2/\text{g}$ and crystallite size increasing by 12.57 nm as the calcination time increased from 1 to 5 h. These trends indicate that thermal treatment

must be carefully controlled to balance the phase purity, crystallinity, and preservation of surface area and pore volume.

Overall, phase-pure MgFe_2O_4 nanoparticles with favorable textural properties were obtained using 20 mL of PO, 24 h of aging, and calcination temperatures between 700 and 800 °C. Among the phase-pure samples investigated, calcination at 700 °C yielded the highest SSA and smallest crystallite size, while higher temperatures promoted crystallite growth and reduced pore volume due to thermal sintering. The findings establish a practical processing–microstructure framework for preparing MgFe_2O_4 nanomaterials with tunable properties. Since the thermochemical redox stability of MgFe_2O_4 has already been demonstrated under multi-cycle CO_2 splitting conditions, the present study provides the missing synthesis-level understanding needed to reproducibly engineer MgFe_2O_4 for solar thermochemical WS/CDS cycles, thermochemical energy storage, and related high-temperature nanotechnology-enabled energy applications.

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