Microwave-assisted synthesis of $Co_{0.4}Ni_{0.6}Al_2O_4$ - Evaluating the effect of practical parameters on material properties

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ABSTRACT

In this study, microwave-assisted combustion synthesis (MACS) was used to prepare $Co_{0.4}Ni_{0.6}Al_2O_4$ spinel powders from respective metal nitrate salts and urea fuel using a domestic microwave oven. The study systematically varied the fuel-to-oxidizer (F/O) molar ratio and microwave output power to determine their influence on combustion behavior, phase formation, crystallinity, yield and morphology. Results show that the fuel content strongly controls combustion intensity and homogeneity, and a molar ratio Al^{3+}:urea = 1:6 (F/O = 1.8) produced the most uniform, dark-blue spinel with sharper X-ray diffraction (XRD) peaks and fewer secondary phases compared with both fuel-rich and fuel-poor conditions. Furthermore, microwave power critically affected ignition, conversion and phase purity. The insufficient power (770 W) failed to trigger self-propagating combustion, while excessive power (1100 W) induced local overheating and more secondary phases (α-Al_2O_3 and NiO). The optimal condition identified in this work was 990 W at Al^{3+}:urea = 1:6, which provided the highest mass conversion (91%) and well-crystallized $Co_{0.4}Ni_{0.6}Al_2O_4$ with porous morphology characteristic of combustion synthesis. The study demonstrates that control of F/O ratio and microwave power in MACS enables rapid, energy-efficient synthesis of Co–Ni aluminate spinels.

Keywords: Spinel aluminates; Microwave combustion; Urea.

1. INTRODUCTION

Spinel aluminates with the general formula MAl_2O_4 (M = Co, Ni, Mg, Mn, etc.) are technologically important materials because of their high thermal stability, mechanical strength, chemical resistance, and tunable optical and magnetic properties, making them suitable for pigments, catalysts, ceramics, magnetic devices, and optoelectronic applications [1-5] Among them, cobalt aluminate ($CoAl_2O_4$) is a well-known thermoresistant blue pigment and catalytic material due to its stability under high temperature and harsh chemical conditions, combined with unique optical absorption characteristics [1, 2, 6, 7]. Partial substitution of cobalt with nickel can significantly alter the cation distribution between tetrahedral and octahedral sites in the spinel lattice, which in turn modifies crystallinity, colorimetric parameters, magnetic response, and optical band gap [1, 8, 9].

Conventional synthesis techniques for spinel aluminates, including solid-state reactions, sol–gel, co-precipitation, and hydrothermal methods, often require high calcination temperatures (> 1200 °C) and long processing times, leading to coarse particles with non-uniform size distribution [1, 7, 10-12]. In contrast, combustion synthesis has emerged as an energy-efficient method for producing nanoscale spinel powders by exothermic redox reactions between metal nitrates (oxidizers) and organic fuels (e.g., urea, glycine, starch), resulting in rapid temperature rise, gas evolution, and short reaction times [4, 5, 13]. Microwave-assisted combustion synthesis (MACS) combines the advantages of combustion chemistry with volumetric and uniform microwave heating, leading to faster ignition, shorter synthesis times, reduced energy consumption, and improved control over particle size and morphology compared to conventional furnace heating [2, 3, 13]. This approach has been successfully used to synthesize various spinel aluminates such as $Mn_xCo_{1-x}Al_2O_4$ [2], $Co_xMg_{1-x}Al_2O_4$ [4], and related ferrite spinels [14]. Reports consistently show that key processing variables—particularly microwave output power and the fuel-to-oxidizer (F/O) molar ratio—have a strong influence on the combustion temperature, ignition time, degree of crystallinity, and particle agglomeration [3, 4, 6, 9]. The F/O ratio directly affects the reaction exothermicity, gaseous byproduct formation, and phase evolution, as described in propellant chemistry [5, 6, 9]. Similarly, microwave power determines the rate of volumetric heating and can alter the phase composition and crystallite size in spinel aluminates [3, 4, 6].

In this work, the key novelty lies in the systematic, dual-parameter control of both F/O ratio and microwave power for the synthesis of $Co_{0.4}Ni_{0.6}Al_2O_4$ spinel using a domestic microwave. Particularly, a two-stage experimental strategy was employed to independently tune chemical energy release and microwave energy input, enabling clear evaluation of their coupled effects on combustion behavior, phase formation, and structural quality. The findings contribute to understanding how process conditions in MACS can be optimized to tailor the purity and structural properties of Co–Ni spinel aluminates.

2. EXPERIMENT

2.1. Materials

In this work, all the chemicals were of analytical grade obtained from Xilong, China and were used as received without further purification. Nitrate salts were used, including $Co(NO_3)_2$, $Ni(NO_3)_2$ and $Al(NO_3)_3$, whereas urea acts as the fuel for the combustion process.

2.2. Experimental

2.2.1. Synthesizing spinel aluminates

Initially, a mixture of nitrate salts, including $Co(NO_3)_2$ (0.8 mmol; 233 mg), $Ni(NO_3)_2$ (1.2 mmol; 349 mg) and $Al(NO_3)_3$ (4.0 mmol; 1500 mg), was uniformly stirred in 20 mL of double-distilled water. Urea was then added to the mixture with different molar ratios of Al^{3+}:urea, and the solution was continuously stirred at room temperature. The homogeneous solution was subsequently transferred into a porcelain crucible and subjected to microwave irradiation at a frequency of 2.45 GHz for 5 minutes using a domestic microwave oven with the maximum power of 1100 W. During irradiation, the solution was heated and water evaporated; upon reaching the point of self-ignition, a combustion reaction occurred, producing a brief flame accompanied by the evolution of gaseous byproducts and yielding a porous blue solid. The obtained solid was washed three times with ethanol to remove impurities, dried at 80 °C for 2 hours, and finally ground into a fine blue powder.

In the first stage, four samples, namely F1-80, F2-80, F3-80 and F4-80, were prepared, with respect to molar ratios of Al^{3+}:urea of 1:9, 1:6, 1:10/3 and 1:5/3 with a microwave power of 880 W (80% of the maximum power). In the second stage, based on practical and analytical results, the molar ratio of Al^{3+}:urea of 1:6 was fixed, and the three other microwave power values, 770, 990 and 1100 W were surveyed. These samples were named F2-70, F2-90 and F2-100.

2.2.2. Characterizations

For morphological analysis, a TESCAN Mira 4 FESEM (Switzerland) was employed, operating at an accelerating voltage of 10 kV. Fourier Transform Infrared (FTIR) spectra ranging from 500 to 4000 cm^{-1} were obtained using the Platinum ATR Alpha II spectrometer (Bruker, Germany). The crystal structures of the synthesized samples were analyzed using X-ray diffraction (XRD, Bruker D2 Phaser) with Cu Kα radiation ($\lambda = 1.5406$ Å).

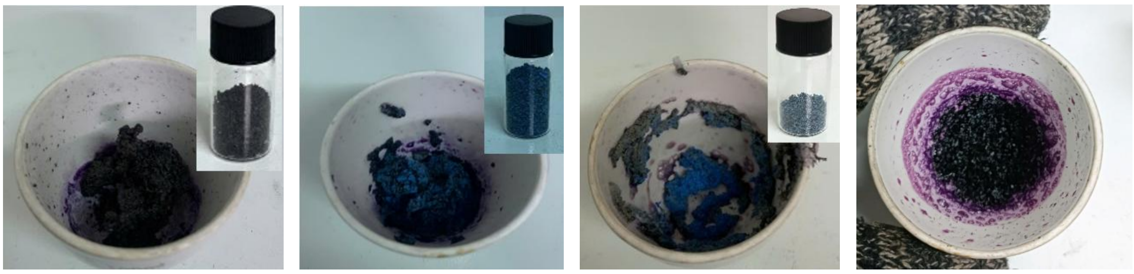
3. RESULTS AND DISCUSSION

3.1. Effect of fuel content on spinel aluminate synthesis

The formation of $Co_{0.4}Ni_{0.6}Al_2O_4$ spinel through stoichiometric redox reaction (F/O = 1) between metal nitrates and urea can be illustrated by the following theoretical equation.

$$0.6Ni(NO_3)_2 + 0.4Co(NO_3)_2 + 2Al(NO_3)_3 + 20/3CO(NH_2)_2$$
$$\rightarrow Co_{0.4}Ni_{0.6}Al_2O_4 + 40/3H_2O + 20/3CO_2(g) + 32/3N_2 \quad (1)$$

The equation (1) applies to F3-80, whereas other F/O ratios, 2.7, 1.8 and 0.5, are referred to F1-80, F2-80 and F4-80, respectively. Visual observations (figure 1) indicate that the F/O ratio plays a decisive role in governing the combustion intensity and purity of the obtained products under identical microwave power conditions (880 W). As for F1-80, the excessive amount of urea led to incomplete oxidation of the organic components during combustion. The surplus fuel favored localized overheating and carbonization, resulting in the formation of a black solid (figure 1a). In contrast, F2-80 exhibited the most balanced combustion, yielding a uniform, dark blue product with high purity (figure 1b), implying that the F/O ratio of 1.8 favors self-sustained and complete combustion. As for F3-80, further reduction of urea produced a dark-blue powder with visible grey impurities surrounding (figure 1c) and a low yield (22.1% vs. 64.5% for F2-80), due to insufficient thermal energy and incomplete reaction. These results indicate that experimental validation is necessary, as equation (1) cannot reliably predict the optimal F/O ratio for all conditions. Finally, F4-80 with the lowest urea concentration provided insufficient fuel, resulting in unreacted nitrates (purple sites) on the crucible wall and the black residue at the bottom (figure 1d). This result reflects partial self-ignition and an incomplete transformation of the precursors.



(a) *(b)* *(c)* *(d)*

Figure 1. *Digital images of (a) F1-80, (b) F2-80, (c) F3-80 and (d) F4-80 samples after combustion process. The insets are respective samples after drying.*

Structural analysis further confirmed the phrase components of F2-80 and F3-80. In figure 2, the XRD patterns of both F2-80 and F3-80 show characteristic peaks of spinel structure at 31.20°, 36.74°, 44.65°, 55.59°, 59.30° and 65.25°, which are attributed to (220), (311), (400), (422), (511) and (440) planes, respectively. These peaks match JCPDS No. 44-0160 of $CoAl_2O_4$, confirming the formation of the spinel phase. Using the Scherrer formula [9], crystallite sizes according to plane (311) of F2-80 and F3-80 are 10.26 and 8.87 nm. Besides, the weak peaks at 43.06° and 77.42° represent (200) and (222) planes of residual NiO, respectively [15]. Despite much lower intensities compared to the spinel phase, these peaks suggest inhomogeneous combustion at some localized reaction zones, which likely led to incomplete incorporation of Ni^{2+} ions into the spinel lattice. In comparison, a clear difference in crystallinity and phase purity can be observed between F2-80 and F3-80. The diffraction peaks of F2-80 are sharper and more intense, suggesting better crystallinity and a more complete formation of the spinel lattice. In other words, the higher urea content used in F2-80 enabled more uniform, self-sustained combustion. Overall, the F/O = 1.8 is more optimal (compared to F/O = 1) to generate more adequate heat, promoting complete decomposition of nitrate precursors and solid-state diffusion among Co^{2+}, Ni^{2+}, and Al^{3+} ions. Thus, the urea content critically determines the combustion efficiency and homogeneity, which in turn control the phase evolution and crystallinity of the resulting spinel oxide.

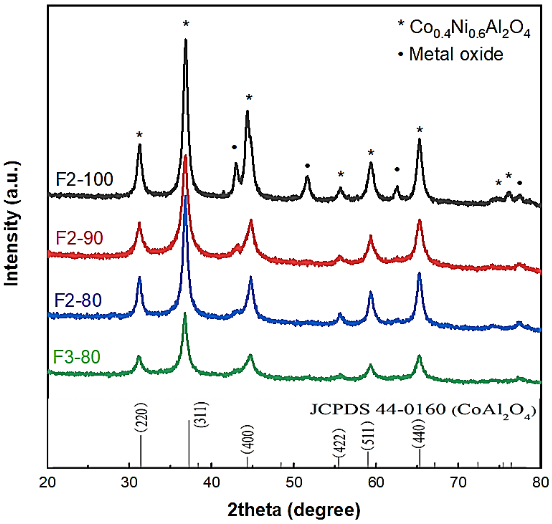


Figure 2. XRD patterns of spinel samples.

3.2. Impact of microwave power on spinel aluminate synthesis

The experimental outcomes clearly demonstrate that the applied microwave power governs both the initiation of the reaction and the quality of the resulting oxide product. At 770 W (sample F2-70), the energy input was insufficient to reach the self-ignition temperature. As a result, only slow evaporation and partial decomposition of metal nitrates occurred, and no visible flame or porous structure was observed (figure 3c). When the power was increased to 880 W (F2-80) and 990 W (F2-90), microwave energy triggered a rapid and uniform ignition after 3:42 and 3:20 (minute:second), respectively. The brief but intense flame, releasing gases such as CO_2, N_2, and H_2O, formed a highly porous solid structure. The sufficient temperature enabled the complete decomposition of nitrates and organic residues, yielding a dark blue product (figure 3b). The reaction of both F2-80 and F2-90 remained well controlled, suggesting that the power of 880-990 W lies within the optimal operational window. In contrast, at 1100 W (F2-100), the excessive microwave power tended to cause more rapid heating and localized "hot spots" that destabilized the reaction front. These harsh conditions favored undesirable side reactions, possibly the formation of secondary oxide or carbonaceous phases, thereby reducing the purity of the final product (black-blue solid in figure 3a).

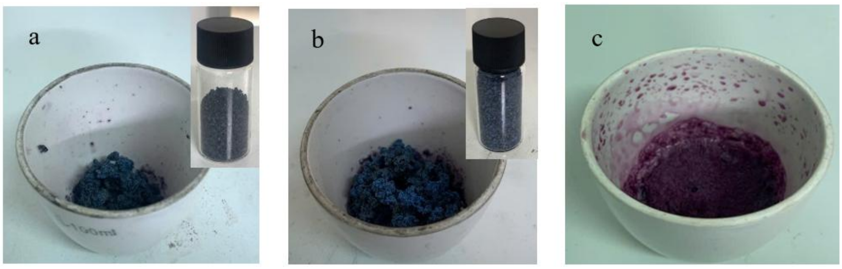


Figure 3. *Digital images of (a) F2-100, (b) F2-90 and (c) F2-70 samples after combustion process.*

The XRD analysis (figure 2) supports the above observations, revealing a clear correlation between microwave power and the structural quality of $Co_{0.4}Ni_{0.6}Al_2O_4$. XRD pattern of F2-90 is identical to that of F2-80, exhibiting characteristic peaks indexed to the (220), (311), (400), (422), (511), and (440) planes, confirming a well-crystallized spinel structure with the crystallite size according to plane (311) of 7.49 nm. This similarity indicates that increasing the microwave power from 880 to 990 W did not alter the phase composition but rather influenced the reaction completeness and yield. Specifically, the higher yield obtained for F2-90 (90.8%) compared to F2-80 (64.5%) suggests that the slightly higher energy input facilitated more efficient precursor decomposition and mass conversion. Besides spinel phase with the crystallite size of 10.21 nm according to plane (311), the XRD pattern of F2-100 reveals additional peaks corresponding to the (024) plane of α-Al_2O_3 at 51.64° and the (220) plane of NiO at 62.54° [15], indicating that excessive microwave power (1100 W) promoted local overheating and incomplete cation incorporation into the spinel lattice. These secondary phases are likely a consequence of the inhomogeneous thermal distribution and rapid temperature rise, which can interrupt the solid-state diffusion necessary for homogeneous spinel formation. Overall, considering both the structural purity and reaction efficiency, the sample synthesized at 990 W (F2-90) can be regarded as the optimal condition, achieving a high-yield, $Co_{0.4}Ni_{0.6}Al_2O_4$ spinel phase. The following analytical results further confirm this statement.

3.3. Elemental components and morphology

The FTIR spectra of spinel samples are demonstrated in figure 4. Accordingly, it was found that the metal–oxygen (M–O) stretching vibrations appeared within the range of 550–700 cm^{-1}, corresponding to the characteristic vibrations of M–O, Al–O, and M–O–Al bonds (where M represents Ni or Co) [2], except F3-80 with an unclear band. A weak band around 1654 cm^{-1} was observed for all samples and can be attributed to the bending mode of H–O–H vibrations. Furthermore, the characteristic peaks at 665 cm^{-1} and 591 cm^{-1} in F2-100, F2-90 and F2-80 confirmed the formation of a cubic spinel aluminate phase in the samples. Hardly any band correlating to organic groups was recorded, implying the complete removal of organic residuals.

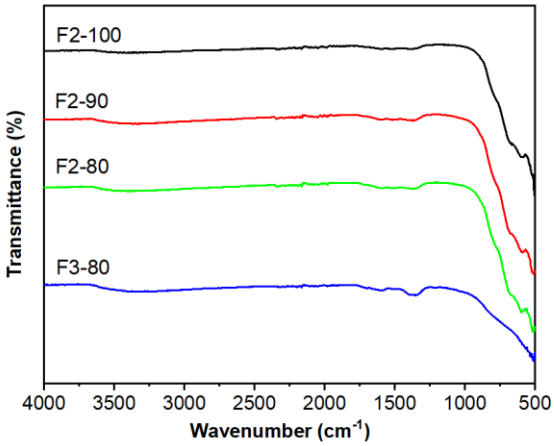


Figure 4. FTIR analysis of RH samples.

Table 1. *Atomic and weight percentages of elements.*

Element	Atomic %			Weight %		
	F2-80	**F2-90**	**Theory**	**F2-80**	**F2-90**	**Theory**
Oxygen (O)	53.99	54.48	57.14	32.60	33.48	36.21
Aluminum (Al)	28.88	29.69	28.57	29.41	30.77	30.54
Nickel (Ni)	11.41	10.43	8.57	25.27	23.51	19.92
Cobalt (Co)	5.72	5.41	5.71	12.73	12.24	13.34

According to the EDX spectrum, Al, Co, Ni and O are major elements in F2-80 and F2-90 samples (figure 5). Detailed elemental composition by atomic % and weight % is given in table 1. Both samples present atomic and weight percentages close to the theoretical values of

$Co_{0.4}Ni_{0.6}Al_2O_4$, but figures of F2-90 seem to achieve smaller errors. The FESEM images of the F2-80 and F2-90 samples (figure 5), captured at different magnifications, display crucial microstructural characteristics that correlate well with the synthesis conditions and resultant material properties. At high magnification (10,000x), the surface morphology reveals a relatively smooth yet porous topology, featuring numerous sub-micron to micron-sized voids distributed across the matrix. These pores likely result from the rapid gas evolution and exothermic nature of the microwave-assisted combustion synthesis process, reflecting localized volume expansion and partial compaction during formation. Meanwhile, the lower magnification view (1,000x) exhibits a heterogeneous, layered structure with apparent ridges, valleys, and significant interlayer cracks and voids.

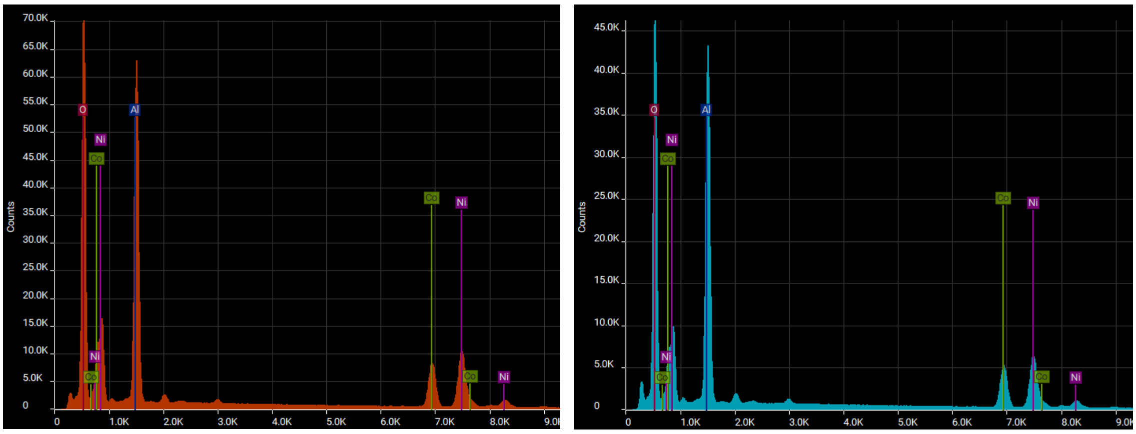
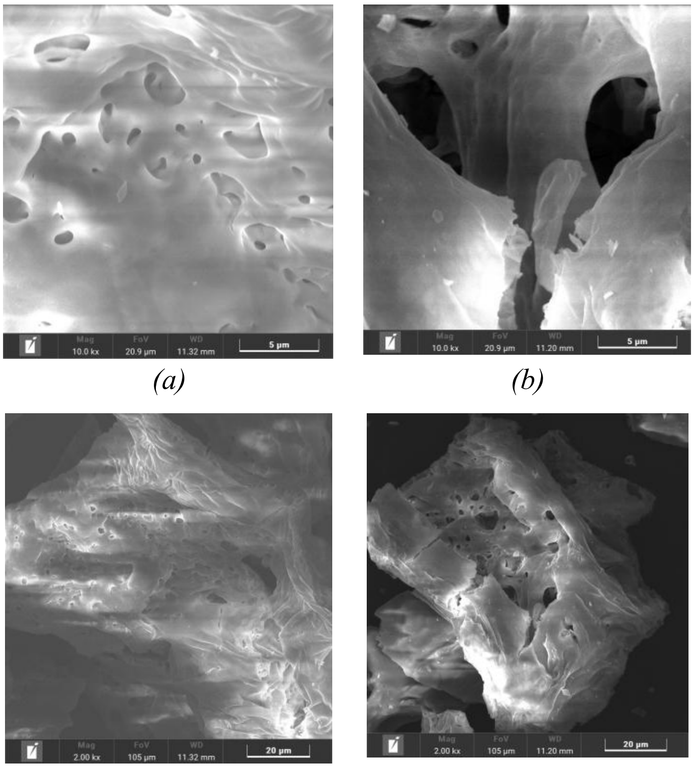


Figure 5. *EDX spectrum of F2-80 (left) and F2-90 (right).*



(a) *(b)*

(c) *(d)*

Figure 6. *FESEM images of spinel samples: F2-80 (a, c) and F2-90 (b, d).*

4. CONCLUSIONS

In conclusion, $Co_{0.4}Ni_{0.6}Al_2O_4$ spinel powders were successfully prepared by MACS using metal nitrates and urea as reactants. Results demonstrated that this method offers a rapid, energy-efficient, and controllable route for producing homogeneous spinel phases. Both the F/O ratio and the microwave output power play crucial roles in determining the combustion behavior, phase purity, and microstructure of the final product. An optimal Al^{3+}:urea ratio of 1:6 (F/O = 1.8) combined with a microwave power of 990 W yielded the most desirable results, producing a well-crystallized Co–Ni aluminate spinel with minimal secondary phases and a characteristic porous morphology. At lower microwave power (770 W), incomplete combustion was observed, while higher power levels (1100 W) led to localized overheating and secondary phase formation. The characterization results from XRD, FTIR, FESEM, and EDX confirmed the successful formation of the desired cubic spinel structure with uniform elemental distribution and high mass conversion (90.8%). These findings highlight that precise control of reaction parameters in MACS enables fine-tuning of phase composition and microstructure, making this approach a promising method for the efficient preparation of Co–Ni aluminate spinels for potential applications.

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TÓM TẮT

Tổng hợp $Co_{0.4}Ni_{0.6}Al_2O_4$ với nguồn vi sóng – Đánh giá ảnh hưởng của các thông số thực nghiệm đến tính chất vật liệu

Trong nghiên cứu này, phương pháp tổng hợp cháy hỗ trợ vi sóng (MACS) được sử dụng để tổng hợp bột spinel $Co_{0.4}Ni_{0.6}Al_2O_4$ từ các muối nitrat kim loại tương ứng và nhiên liệu urea bằng lò vi sóng gia dụng. Nghiên cứu đã khảo sát có hệ thống ảnh hưởng của tỷ lệ mol nhiên liệu/oxy hóa (F/O) và công suất vi sóng đến đặc tính cháy, sự hình thành pha, độ kết tinh, hiệu suất và hình thái sản phẩm. Kết quả cho thấy hàm lượng nhiên liệu có ảnh hưởng mạnh đến cường độ và tính đồng nhất của phản ứng cháy; tỷ lệ mol Al^{3+}:urea = 1:6 (F/O = 1.8) cho sản phẩm spinel màu xanh đậm, đồng nhất, với các đỉnh nhiễu xạ tia X (XRD) sắc nét hơn và ít pha thứ cấp hơn so với các điều kiện thừa hoặc thiếu nhiên liệu. Ngoài ra, công suất vi sóng có ảnh hưởng đáng kể đến quá trình bốc cháy, mức độ chuyển hóa và độ tinh khiết pha. Công suất thấp (770 W) không đủ để kích hoạt phản ứng cháy tự lan truyền, trong khi công suất quá cao (1100 W) gây ra hiện tượng quá nhiệt cục bộ và hình thành nhiều pha thứ cấp hơn (α-Al_2O_3 và NiO). Điều kiện tối ưu được xác định trong nghiên cứu là 990 W với tỷ lệ Al^{3+}:urea = 1:6, cho hiệu suất chuyển hóa khối cao nhất (91%) và sản phẩm $Co_{0.4}Ni_{0.6}Al_2O_4$ kết tinh tốt với hình thái xốp đặc trưng của quá trình tổng hợp cháy. Nghiên cứu này chứng minh rằng việc kiểm soát tỷ lệ F/O và công suất vi sóng trong MACS cho phép tổng hợp nhanh, hiệu quả năng lượng các Co–Ni spinel aluminat.

Từ khoá: Spinel aluminate; Đốt cháy vi sóng; Urea.