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Research Article

Microwave and Microwave Assisted Solvothermal Synthesis of Vanadium (V)-Benzene-1,3,5-Trycarboxylate Coordination Compound: Effect Microwave on Structural and Microstructural Evolution

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ABSTRACT

Abstract
V-BTC compounds were successfully synthesis using conventional solvothermal, direct microwave synthesis and microwave assisted solvothermal synthesis. The effect of microwave power on structure, morphology and crystallinity was investigated. The P-XRD revealed the direct microwave synthesis at 300W and 450W power resulting dominantly amorf structure, while the conventional solvothermal at 160^{o}C/48h and microwave assisted solvothermal produced the crystalline peak of XRD pattern. Proven by le-bail refinement methods, the crystal structures show agreement with polyoxovanate coordination structure of $[(C_2H_8N)_{12}[(V_5O_9Cl)_6(C_9H_3O_6)_8]$ which crystallized in $Fm\bar{3}m$ cubic crystal. SEM analysis revealed the differences in crystallinity and morphological evolution with increasing the microwave power. V-BTC solvothermal shows granular morphology with irregular shape, rough surface, porous and agglomerate particles, while microwave integration approach resulting more compact particles, higher crystallinity, and the growth of elongated plat-like morphology at 450W. Microwave-assisted synthesis produced smaller particles and narrowed the particle-size distribution compared with conventional solvothermal synthesis, demonstrating that microwave irradiation can influence the nucleation and crystal growth process of V-BTC compounds

Keywords: V-BTC, V-MOF, Microwave-Solvothermal Synthesis

Abstrak
Senyawa V-BTC berhasil disintesis menggunakan metode solvotermal konvensional, sintesis microwave langsung, dan sintesis solvotermal berbantuan microwave. Penelitian ini mempelajari pengaruh daya microwave terhadap perubahan struktur, morfologi, dan kristalinitas produk sintesis. Hasil P-XRD menunjukkan bahwa sintesis *microwave* langsung pada daya 300 W dan 450 W menghasilkan struktur yang dominan amorf, sedangkan metode solvotermal konvensional pada 160 °C selama 48 jam dan metode solvotermal kombinasi microwave menghasilkan puncak-puncak kristalin pada pola XRD. Berdasarkan hasil

refinement data P-XRD dengan metode Le Bail, struktur kristal menunjukkan kesesuaian dengan struktur koordinasi polioksovanadat dari senyawa $[(C_2H_8N)_{12}[(V_5O_9Cl)_6(C_9H_3O_6)_8]$, yang mengkristal dalam sistem kristal kubik $Fm\bar{3}m$. Analisis SEM menunjukkan adanya perbedaan kristalinitas dan evolusi morfologi seiring peningkatan daya *microwave*. V-BTC hasil sintesis solvotermal menunjukkan morfologi granular dengan bentuk tidak beraturan, permukaan kasar, berpori, dan partikel yang teraglomerasi, sedangkan pendekatan integrasi *microwave* menghasilkan partikel yang lebih kompak, kristalinitas yang lebih tinggi, serta pertumbuhan morfologi menyerupai pelat memanjang pada daya 450 W. Sintesis microwave-solvothermal menghasilkan partikel yang lebih kecil dan distribusi ukuran partikel yang lebih sempit dibandingkan dengan sintesis solvotermal konvensional, sehingga menunjukkan bahwa iradiasi *microwave* dapat memengaruhi proses nukleasi dan pertumbuhan kristal senyawa V-BTC

Kata Kunci: V-BTC, V-MOF, Sintesis *Microwave-Solvothermal*

1. Introduction

Metal Organic Frameworks (MOFs) is a class of crystalline porous material constructed from metal ion or metal node linked with organic ligand through continuous network of coordination bond. MOFs have drawn significant attention for various application due to the unique properties of ordered structure, tailored stability, porosity, and chemical functionality for catalysis, environmental remediation, energy harvesting and biomedical application. Distinctive combination between metal ion and ligand as organic linker has allow the diverse designs of specific structure, properties and function. Vanadium based MOF (V-MOF) has unique redox properties compared to divalent based metal MOF. Vanadium is a common transition metal with a $3d^3 4s^2$ outer electron structure [1]. It has many valence electrons that drive multiple oxidation state of Vanadium ions i.e +2, +3, +4 and +5**.** Stable forms of vanadium typically exhibit +4 (vanadyl) and +5 (vanadate) oxidation states [2].

Multiple oxidation state of vanadium ($V^{2+}V^{3+}/V^{4+}/V^{5+}$) can act as electron reservoir and undergo redox cycle. This characteristic enabling vanadium to assist oxygen transfer in selective redox catalytic reaction, CO_2 fixation, electrochemical energy conversion and energy storage [3]. In addition to energy conversion field, vanadium thio carboxylate MOF reported to exhibit superior performance in photooxidative desulfurization reaction for reducing sulfur contaminant in liquid fossil fuel addressing health and environment concern [1]. Linking trivalent, tetravalent and pentavalent vanadium metal nodes with polytopic ligand such as carboxylate compound can produce various polymeric compounds with diverse topologies. Polycarboxylic ligand of Benzene 1,4 dicarboxylic acid ligand, also known as H_2BDC or terephthalic acid reported forming MOF with topological structure of MIL 47(V), MIL refers to Material Institute of Lavoisier). MIL 47(V) has large pore, surface area, open structure produced from infinite chain of interconnecting terephthalic acid group with VO_6 corner-sharing [3].

Unlike the dicarboxylic BDC ligand, H_3BTC (benzene-1,3,5-tricarboxylic acid), also known as trimesic acid, contains three carboxylic groups that can coordinate with vanadium nodes, thereby modifying the self-assembly mechanism of vanadium-based MOFs. These three coordination sites act as effective bridging linkers, promoting the formation of multidimensional coordination structures and 3-D metal–organic frameworks. In the presence of H_3BTC, oxo-cantered vanadium trimer interconnected with three carboxylic sites to form super tetrahedra in MIL-100(V) framework with hierarchical mesoporous cages. In this oxo vanadium trimer node, MIL 100(V) has general formula $[V_3O(OOCR)_6L_3]^{n+}$ (*L* = terminal ligand such Cl, Br or H_2O). In aqueous media, Vanadium(III) ion from VCl_3 precursor assemble a typical MIL 100(V) structure with formula $[V_3O(H_2O)_2Cl\cdot[C_9H_3O_6]_2.3H_2O$ [4] [5].

In addition to ligand selection, the metal precursor and synthesis conditions strongly influence the structure and composition of V-MOF products. With H_3BTC as the ligand, V_2O_5 can produce a MIL-100(V)-type topology [6]. In contrast, vanadium oxychloride ($VOCl_3$) tends to form a dark green MOF with the general formula $[(V_5O_9Cl)_6(BTC)_8]^{12-}$, a cubic crystal with *space group* $Fm\bar{3}m$ in which vanadium is present in the mixed tetravalent and pentavalent oxidation state [7]. In the structure of the $[(V_5O_9Cl)_6(BTC)_8]^{12-}$ complex, each V^{5+} cationic unit coordinates with oxygen atoms from the carboxylate groups of BTC^{3-} ligands and one chloride ion. Each BTC^{3-} ligand acts as a six-connected linker, connecting six vanadium atoms through a bidentate coordination mode. Meanwhile, each vanadium building unit binds to four carboxylate groups from different BTC^{3-} ligands. Six vanadium building units further combine with eight BTC^{3-} ligands, resulting in a polyoxovanadate (POV)-based metal–organic framework.

In general, V-BTC based MOFs successfully synthesized via several conventional methods namely reflux methods, hydrothermal/solvothermal method, employing various solvents i.e water [5], ethanol [8], DMF [6] and combination of DMF-methanol solvent [7]. These hydrothermal/solvothermal synthesis of V-BTC MOFs typically require elevated temperature and prolonged time synthesis (200-220 for 72 h) thus facing a challenge in energy consumption, synthesis cost and reproducibility. In addition to these methods, wave-based assisted synthesis such sonochemical and microwave assisted synthesis offer a rapid processing and enhance reproducibility. Microwave radiation constitutes a region of the electromagnetic spectrum characterized by frequencies of approximately 0.3–300 GHz and corresponding wavelengths of 1–1000 mm, positioned between the infrared and radio-frequency regions [9]. Microwave Assisted synthesis (MAS) is based on the direct interaction of microwave electromagnetic radiation (typically 2.4GHz) with reaction medium. Unlike conventional heating, MAS generates heat within material through dipolar polarization. Polar molecule such as H_2O, ethanol

or DMF rotate continuously when absorbing the microwave energy, resulting heat to accelerate reaction within the medium.

Microwave-assisted synthesis of V-MOFs has previously been reported using 2,6-naphthalenedicarboxylic acid (H_2ndc) as the ligand and VCl_3 as the precursor. In aqueous media, the synthesis produced [V(OH)ndc]n at 180 °C for 10 min [10]. Another study reported the formation of [V(O)(2,6-ndc)]n at 190 °C for 30 min [11]. In addition, V^{III}(OH)(ndc)·H_2O was synthesized at 190 °C and 100 W for 30 min [12]. These studies demonstrate that microwave-assisted synthesis can produce different vanadium-based coordination structures under different reaction conditions. In comparison, MIL-100(V), a vanadium(III) trimesate framework based on the H_3BTC linker, has been synthesized under hydrothermal conditions at 220 °C for 72 h and crystallizes in the cubic Fd-3m space group [4]. Although V-BTC compounds have been reported using conventional hydrothermal or solvothermal methods, studies systematically investigating the effect of microwave irradiation on the structural and microstructural evolution of V-BTC compounds remain limited. Therefore, the novelty of this work lies in the systematic comparison of conventional solvothermal, direct microwave, and microwave-assisted solvothermal synthesis of V-BTC compounds. The effect of microwave power on crystallinity, crystallite size, morphology, and particle-size distribution was investigated to clarify its role in the formation and crystal growth of V-BTC compounds.

2. Materials and Method

2.1. Materials

All chemicals were used as received without further purification. The reagents employed in this research included vanadium(V) oxytrichloride ($VOCl_3$, density 1.84 g/mL, Sigma-Aldrich 99% assay), benzene-1,3,5-tricarboxylic acid (H_3BTC, Sigma-Aldrich), dimethylformamide (DMF, Supelco), distilled water (H_2O, Panadia Laboratory), and methanol (CH_3OH, Panadia Laboratory).

2.2. Methods

2.2.1 Microwave Synthesis Method of V-BTC

$VOCl_3$ (0.30 mL, 3.15 mmol) and H_3BTC (0.0756 g, 0.36 mmol) were dissolved in 7.5 mL of a DMF/methanol mixture (4:1, *v/v*). The mixture was stirred for 30 min at room temperature and subsequently transferred into a teflon-lined microwave reactor. The reaction was irradiated at 180, 300, or 450 W for 15 min. After irradiation, the reactor was allowed to cool to room temperature. The resulting solid was collected by filtration, washed successively with DMF and methanol, and dried at 65°C for 1 h to remove residual solvent. The dried products were cooled to room temperature, weighed, and subjected to further characterization.

2.2.2 Solvothermal Synthesis Method of V-BTC

$VOCl_3$ (0.30 mL, 3.15 mmol) and H_3BTC (0.0756 g, 0.36 mmol) were dissolved in 7.5 mL of DMF/methanol (4:1, *v/v*) and stirred for 30 min at room temperature. The resulting solution was transferred into a teflon-lined autoclave and heated at 160°C for 48 h. After cooling to room temperature, the resulting solid was collected by filtration, washed with DMF and methanol, and dried at 65 °C for 1 h. The dried product was weighed and characterized.

2.2.3 Microwave Assisted Solvothermal Synthesis Method of V-BTC

The precursor solution was prepared using $VOCl_3$ (0.30 mL, 3.15 mmol) and H_3BTC (0.0756 g, 0.36 mmol) in 7.5 mL of DMF/methanol (4:1, *v/v*) and stirred for 30 min at room temperature. The solution was transferred into a Teflon-lined autoclave and subjected to microwave irradiation at 300 or 450 W for 15 min, followed by heating at 160°C for 48 h. After cooling, the solid product was collected by filtration, washed with DMF and methanol, dried at 65°C for 1 h, and weighed prior to characterization.

2.3. Characterization of V-BTC Compound

2.3.1 Structural Characterization using Powder X-Ray Diffraction (P-XRD)

All obtained samples were analyzed using a *P*-XRD instrument with *X*-ray irradiation from a Ni-filtered Cu K*α* radiation source (40 kV, 30 mA, *λ* = 1.5406 Å). The diffraction patterns were recorded over a 2*θ* range of 5–50° at room temperature. The XRD data were refined using the Rietica program with the Le Bail method. The crystallite size of the synthesized V-BTC products was determined from peak broadening using the Debye–Scherrer equation as shown in Equation 1, with *D* is the crystallite size (nm), *λ* is the radiation wavelength, K is the shape factor constant (0.9), and *β* is the full width at half maximum (FWHM, in radians).

$$D = \frac{\mathrm{K}\alpha}{\mathrm{B}\,\mathrm{Cos}\,\theta} \qquad (1)$$

2.3.2 Microstructural Characterization using Scanning electron Microscope (SEM)

SEM analysis was performed to investigate the morphology, particle size distribution, and elemental composition of the synthesized products. The synthesized samples were analyzed using an SEM-EDX instrument at magnifications of 1000 and 5000×. The SEM characterization data were processed using *ImageJ* software to evaluate the morphology, particle size, and particle size distribution, as well as to determine the coefficient of determination (*R*-square/COD) for the V-BTC surface.

3. Result and Discussion

3.1. Synthesis Products of V-BTC Compounds

The synthesized products were evaluated based on their physical appearance, color changes, and product mass, as presented in **Table 1** and **Figure 1.** The observed differences in color and product formation indicate that the synthesis conditions affected the formation of the V-BTC products. As shown in **Table 1**, direct microwave synthesis exhibited a strong dependence of product formation on microwave power. No precipitate was obtained at 100 W, while 180 W produced only a small amount of product. Increasing the microwave power to 300 and 450 W substantially increased the product mass, whereas 600 W resulted in a black, burnt product. These results indicate that an intermediate microwave power range of 300–450 W provide favorable energy window for product formation, while excessive microwave power may promote undesirable thermal effects or decomposition.

Table 1. Mass of V-BTC products obtained by microwave, microwave-solvothermal, and conventional solvothermal synthesis

Code	Synthesis Method	Synthesis Condition	Product	Product Mass	% Relative to Conventional solvothermal
MW 100	*microwave*	100W, 15 min	No precipitate, green coloured filtrate	-	-
MW 180	*microwave*	180W, 15 min	Olive green powder	0,022 g	3.8%
MW 300	*microwave*	300W, 15 min	Dark Greenish Brown Powder	0,2154 g	37.6%
MW 450	*microwave*	450W, 15 min	Greenish Black powder	0,4315 g	75.4%
MW 600	*microwave*	600W, 15 min	Black (burnt product)	-	-
MW 300-Solvo	*microwave*-solvothermal	300W, 15min, *T*= 160°C , *t*= 48 h	Greenish-Black crystal and powder	0,3463 g	60.5%
MW 450-Solvo	*microwave*-solvothermal	450W, 15 min, *T*= 160°C, *t*= 48 h	Greenish-Black powder	0,4008 g	70%
Solvo 160°C	solvothermal	*T*= 160°C, *t*= 48 h	Greenish-Black crystal and powder	0,5726 g	100%

The microwave irradiation time used in this study was 15 min. This duration is consistent with previous studies on microwave-assisted synthesis of vanadium-based materials. Phoempoon and Sikong reported the

microwave-assisted preparation of VO_2 nanoparticles using microwave powers ranging from 180 to 600 W for 15 min before calcination [13]. Furthermore, $Na_3V_2(PO_4)_3$ was rapidly synthesized using microwave irradiation within 15 min [14]. These studies demonstrate that a microwave irradiation time of approximately 15 min has been applied to the synthesis of vanadium-based materials. In addition, vanadium-based coordination compounds of [V(OH)*ndc*]*n* and $V^{III}(OH)(ndc)\cdot H_2O$ were synthesized using microwave irradiation within 30 minutes [11] [12]. Therefore, the 15 min irradiation period used in the present study is within the range reported for related microwave-assisted synthesis of vanadium-based materials and typically more efficient than irradiation time of Vanadium-ndc based coordination materials.

The effect of microwave irradiation on product formation was further evaluated by comparing the direct microwave and microwave-assisted solvothermal products. When microwave pretreatment at 300 W was introduced before the solvothermal process, the relative product mass increased from 37.6% for direct microwave synthesis to 60.5% for microwave-assisted solvothermal synthesis. This increase suggests that microwave pretreatment may facilitate precursor activation and initial nucleation, which can subsequently proceed during the solvothermal treatment. At 450 W, however, the relative product mass obtained by direct microwave synthesis (75.4%) was slightly higher than that obtained by the microwave-assisted solvothermal method (70.0%). This difference may be associated with variations in precursor conversion or product evolution including product dissolution or reorganization during the subsequent solvothermal treatment. Further evidence from XRD and SEM analyses is therefore required to clarify the effects of microwave power on phase formation and microstructural evolution.

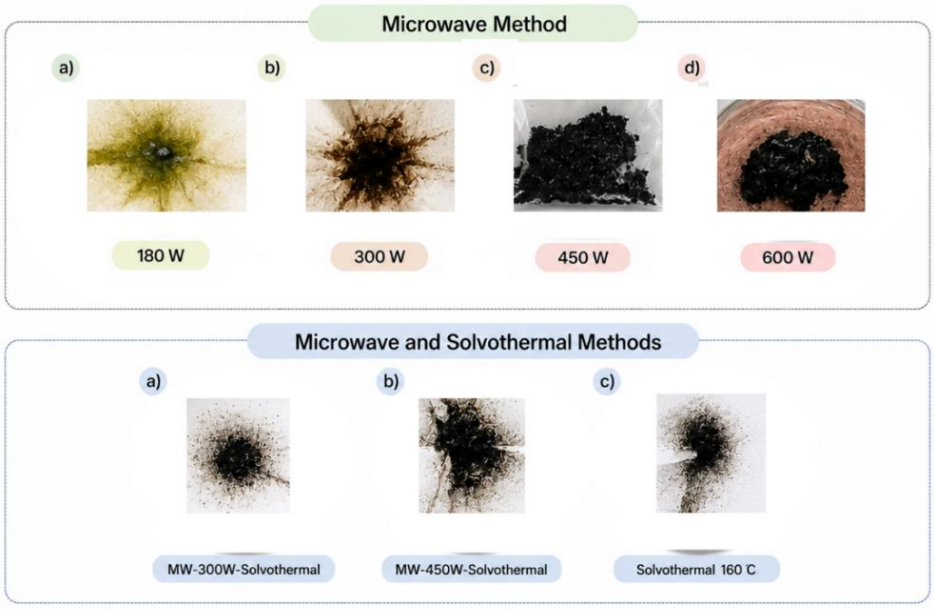


Figure 1. Visual synthesis products of Vanadium-BTC compound

3.2 Structural Properties of V-BTC Compound

Powder *X*-ray diffraction (P-XRD) analysis was conducted to determine the structural characteristics of the synthesized V-BTC compounds. This characterization was used to evaluate structural differences arising from the applied synthesis methods and variations in microwave power, particularly in terms of phase formation, crystallinity, and crystallite size. The XRD patterns of the synthesized V-BTC products are presented in **Figure 2**. The diffraction patterns were compared with those of the starting materials, vanadium oxytrichloride ($VOCl_3$; ICDD 01-085-0353) and H_3BTC (ICDD 00-045-1880). The products prepared by direct microwave, conventional solvothermal, and microwave-assisted solvothermal methods exhibited diffraction profiles different from those of the starting materials, indicating the formation of new crystalline phases during the synthesis process. The products obtained by direct microwave synthesis at 300 and 450 W exhibited predominantly broad diffraction

features, indicating low crystallinity or an amorphous character. Weak diffraction features were observed at 2θ = 7.67 and 25.86° for the 300 W product and at 2θ = 11.20 and 20.60° for the 450 W product. The broad diffraction features were associated with small crystallite sizes of approximately 1.90 and 3.86 nm for the 300 and 450 W products, respectively, as calculated using the Debye–Scherrer equation. In contrast, the products obtained by conventional solvothermal and microwave-assisted solvothermal synthesis exhibited more distinct crystalline diffraction peaks.

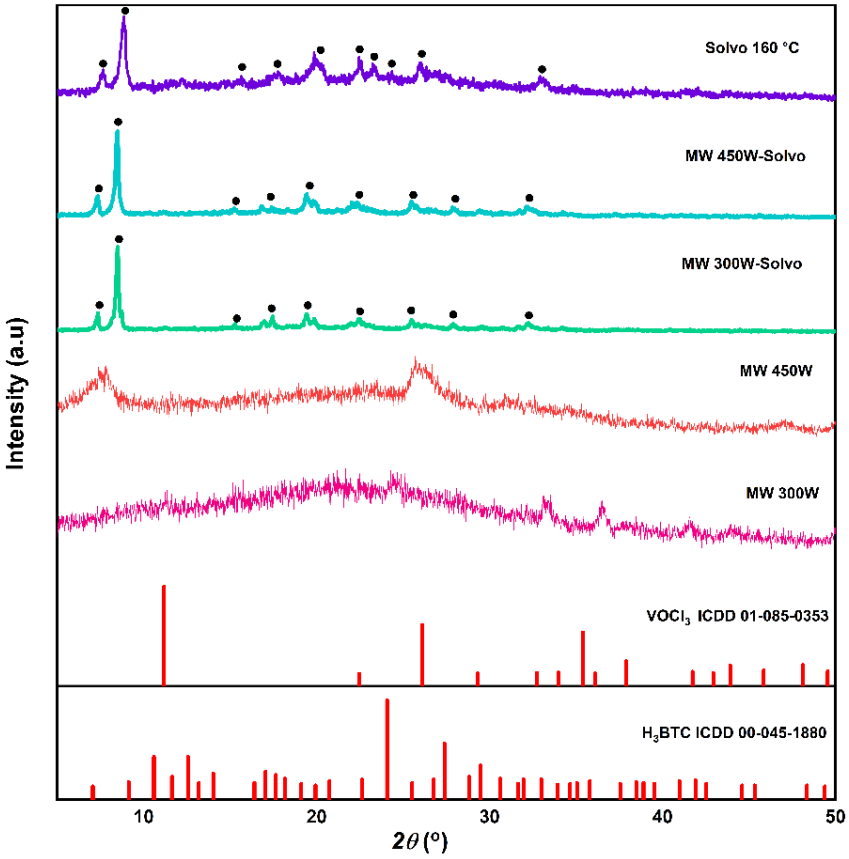


Figure 2. XRD pattern of synthesis products of Vanadium-BTC compound

The XRD pattern of the product obtained by the conventional solvothermal method exhibited crystalline peaks at 2θ = 7.66, 8.86, 19.86, 20.04, 22.58, 25.96, and 26.02°, with the most intense reflection observed at 2θ = 8.86°. Similar diffraction features were observed for the products synthesized using the microwave-assisted solvothermal method. However, the microwave-assisted solvothermal products exhibited sharper and more resolved diffraction peaks, indicating higher crystallinity than the conventional solvothermal product. The crystallite sizes calculated using the Debye–Scherrer equation were approximately 42.14 and 47.96 nm for the MW-300W and MW-450W microwave-assisted solvothermal products, respectively, whereas the conventional solvothermal product exhibited a smaller crystallite size of approximately 23.57 nm. Overall, the crystalline products exhibited similar major diffraction features, suggesting that the different synthesis methods produced related crystalline phases, while microwave-assisted solvothermal treatment resulted in higher peak resolution and larger apparent crystallite sizes. To further evaluate the possible phase identity, the experimental diffraction patterns were compared with the reported MIL-100(V) structure and reference vanadium oxide phases.

MIL-100(V) is a vanadium(III) trimesate structure that crystallizes in the cubic $Fd\bar{3}m$ space group with a lattice parameter of a = 73.0286(2) Å [4]. Synchrotron PXRD pattern reported for MIL-100(V) confirmed its isostructural character with MIL-100(Cr), MIL-100(Fe), and MIL-100(Al) associated with CCDC 640536 [15]. The reported MIL-100(V) by Lieb et al. [4] exhibits strong intensity of approximately 6 low-angle reflections around 3–12° with dominant fingerprint intensity at 2θ = 9.26°. These low-angle fingerprints are mainly due to the exceptionally large lattice parameter (~73 Å). The diffraction reflections occur at lower 2θ for Synchrotron

PXRD (λ = 1.29175 Å), and will shift to higher 2θ for XRD with Cu-$K\alpha$ radiation (λ = 1.5406 Å). In the present study, the synthesized V-BTC products did not exhibit a series characteristic of low-angle reflections in the 2θ = 3-12° region and only exhibited 2 low-angle reflections at 2θ = 7.66° and 8.86° with the most intense reflection at 8.86°, lower than 9.26° reflection from Synchrotron PXRD pattern. The overall positions of the experimental diffraction peaks did not show correspondence with the reported MIL-100(V) diffraction pattern. Therefore, based on the differences of the characteristic low-angle reflection and the lack of overall peak-position correspondence, the experimental XRD data do not support assignment of the synthesized products as the typical MIL-100(V) structure or topology.

Further phase comparison was performed using HighScore Plus by matching the experimental diffraction patterns with reference patterns of orthorhombic V_2O_3 (black solid), V_3O_5 (grayish black solid), VO_2 (dark green solid), V_2O_5 (brown solid), and monoclinic V_6O_{13} (PDF No. 43-1050). No clear correspondence was observed between the experimental diffraction peaks and the characteristic reflections of these vanadium oxide phases. Thus, the synthesized products could not be clearly assigned to the investigated vanadium oxide phases. These results suggest that the synthesized materials may represent another V-BTC coordination structure rather than the typical MIL-100(V) topology or the investigated vanadium oxide phases. To further evaluate the structural characteristics of the crystalline products, Le Bail refinement was performed using the Rietica program. The crystallographic reference for $[(C_2H_8N)_{12}[(V_5O_9Cl)_6(C_9H_3O_6)_8]$ was selected because the reported structure was obtained using a similar precursor system and synthesis conditions involving $VOCl_3$, H_3BTC, and a DMF/methanol solvent mixture [7].

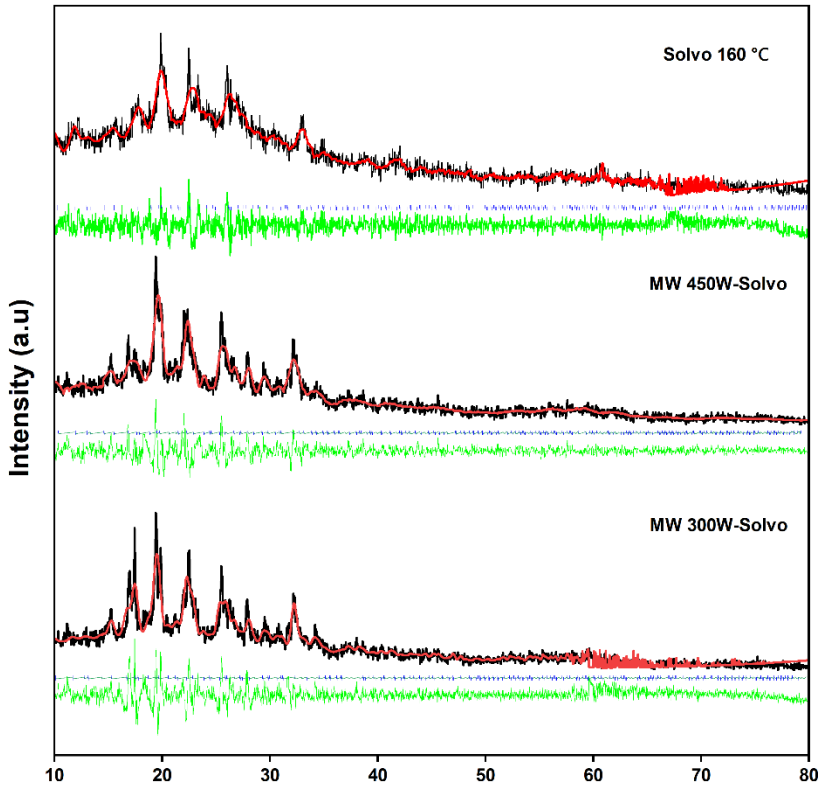


Figure 3. Le-Bail refinement plot of V-BTC coordination compound

The Le Bail method was applied to evaluate the agreement between the experimental diffraction profiles and the selected crystallographic reference and to obtain the corresponding crystallographic parameters. The refinement results are presented in **Table 2** and **Figure 3**. The three crystalline V-BTC products showed reasonable agreement with the selected reference structure, as indicated by the R_p (profile residual) and R_{wp} (weighted profile residual) values. In the refinement plots, the calculated diffraction pattern is represented by the red line and was generated from the crystallographic data, whereas the observed diffraction pattern is represented by the black dashed line corresponding to the experimental XRD data. The blue marks indicate the

expected peak positions of the reference structure, while the green line represents the difference between the observed and calculated diffraction profiles.

Based on the R_p and R_{wp} values, the MW-300W-solvothermal, MW-450W-solvothermal, and conventional solvothermal products exhibited R_p values of 10.71, 13.83, and 12.23%, respectively, while their corresponding R_{wp} values were 11.17, 18.93, and 14.98%. Lower R_p and R_{wp} values generally indicate higher agreement between the experimental and calculated diffraction profiles. The conventional solvothermal product exhibited the lowest R_p value (10.71%), whereas the MW-300W-solvothermal product exhibited the lowest R_{wp} value (11.17%). The differences in R_p and R_{wp} among the samples may be associated with differences in crystallinity, crystallite size, lattice parameters, and the thermal history resulting from the different microwave treatments.

Table 2. Crystallographic refinement data of V-BTC complexes

Parameter	H_3BTC (ICDD 00-045-1880)	Reference $[(C_2H_8N)_{12}[(V_5O_9Cl)_6(C_9H_3O_6)_8]$	Solvo 160 °C	MV 300W-Solvo	MW 450W-Solvo
Crystal system	Monoclinic	Cubic	Cubic	Cubic	Cubic
Space group	*C2/c*	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$	$Fm\bar{3}m$
a	26,9100	29.7184	29.099178	29.419453	29.992815
b	16,6200	29.7184	29.099178	29.419453	29.992815
c	26,2300	29.7184	29.099178	29.419453	29.992815
Z	48,00	4	4	4	4
R_p (%)		12.53	10.71	13.83	12.23
R_{wp} (%)		18.63	11.17	18.93	14.98

The microwave-assisted samples underwent an additional microwave pretreatment before the solvothermal process, which may have altered the heating profile, precursor activation, nucleation rate, and subsequent crystal growth compared with the conventional solvothermal treatment. Differences in the precursor-to-ligand ratio and solvent conditions may also contribute to variations in the crystallization process and diffraction profiles. In the present synthesis, $VOCl_3$ and H_3BTC were introduced into a DMF/methanol solvent mixture, while microwave irradiation was applied at different powers before the solvothermal treatment. Variations in microwave power can modify the heating rate and thermal history of the reaction mixture, potentially affecting precursor coordination, nucleation, and crystal growth. Consequently, differences in crystallinity, crystallite size, and lattice parameters can produce variations between the observed and calculated diffraction profiles and, therefore, contribute to the differences in R_p and R_{wp} values among the synthesized products.

*3.3 Microstructural Properties of V-*BTC Compound *from SEM-EDX Analysis*

The products synthesized using the direct microwave method did not produce a substantial amount of product and tended to result in an amorphous structure, as revealed by XRD analysis. Therefore, microstructural analysis was focused on the effect of microwave integration (300W and 450W) on conventional solvothermal method. SEM images at 1000 and 5000 magnifications in **Figure 4** revealed the noticeable effect of microwave irradiation at initial stage of synthesis. In **Figure 4a**, theses aggregate compose V-BTC solvothermal shows irregular granular shape with rough, porous and heterogeneous surface texture. The individual primary particles are difficult to distinguish since they appear to have undergo substantial agglomeration revealing the smaller crystallite size determined from XRD pattern. At low magnification, V-BTC solvothermal consist of numerous irregular aggregates, while at the highest magnification reveals that these aggregates composed of many small, irregular primary particles that combined into hierarchical clusters. Further investigation performed by processing the image using *Image-J* software in applying band pass filter mode in Fast Fourier Transform (FFT) to reduce noise and shading/background correction, resulting that the cluster particles appear with clear porosity and textured surface at 5000 magnifications.

In comparison, V-BTC produced from MW-300W-solvothermal (**Figure 4b**) appear to have more consolidated particle forming more compact aggregates with irregular shape. The higher magnification image shows numerous compact irregulars to polyhedral particles, with relatively well-defined boundaries. The surface texture is still rough but relatively dense compared to V-BTC solvothermal indicating better crystal growth and greater densification. While the microwave irradiation increased to 450W (**Figure 4c**), a heterogeneous morphology comprising irregular granular particles, larger plate-like aggregate, and partially faceted structure are observed at low magnification. At higher magnification, it reveals elongated and plat-like or lath-like structure. Several structures show relatively flat faces and elongated dimension, appearing as stacked plates. Platelet-like fragment has relatively smooth external surface, whereas others remain highly rough and porous-looking. It is indicating heterogeneous particle growth and particle-particle coalescence during synthesis. The evolution of particles from conventional solvothermal to integration of microwave irradiation reveals a substantial alignment with XRD results in term of crystallinity enhancement. Microwave pre-treatment may enhance nucleation lead to more organized crystal growth during the solvothermal treatment, resulted in higher crystallinity.

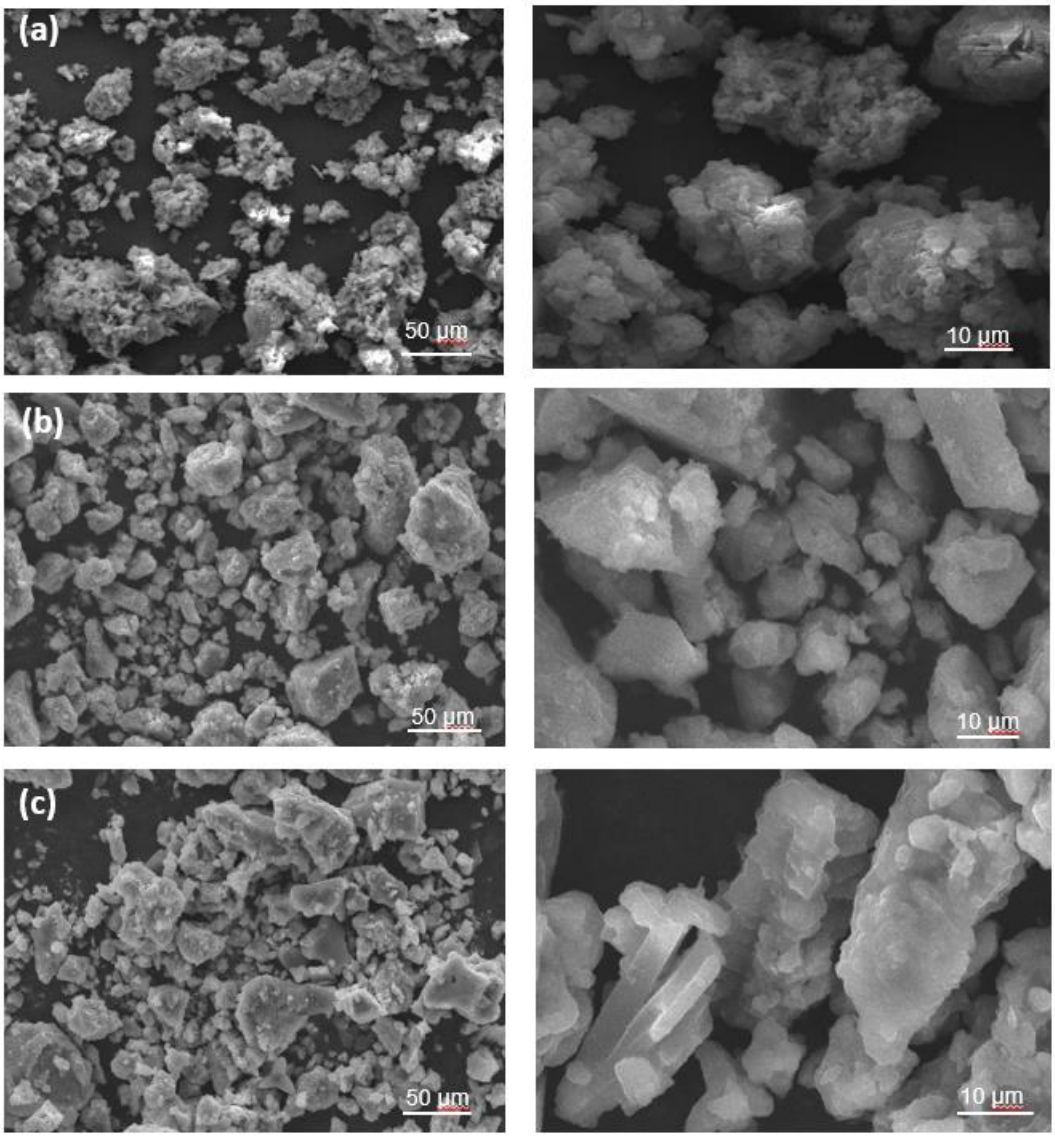


Figure 4. SEM micrographs of V-BTC coordination compound at 1000 and 5000× magnifications for (a) solvothermal, (b) MW-300W-solvothermal, and (c) MW-450W-solvothermal.

The particle diameter distribution of the V-BTC compounds were evaluated using ImageJ software, as presented in **Figure 5** and summarized in **Table 3**. The analysis was conducted using SEM micrographs recorded at 1000 magnification. Reliability of particle-size measurement determined from the coefficient of determination, expressed as *R*-square (COD), was used to assess the reliability of the particle-size fitting results. The *R*-square value close to one indicates better agreement between the measured data and the fitting model, suggesting a more reliable particle-size analysis. In general, the results show that the average particle diameter and particle size distribution range are relatively broad indicating agglomeration. V-BTC solvothermal average particle and particle size distribution range were generally larger than V-BTC MW-300W-Solvothermal and MW-450W-Solvothermal indicating that microwave power influenced particle growth during synthesis.

Furthermore, as shown in **Table 3**, increasing the microwave power from 300 to 450 W resulted in a further reduction in both the average particle diameter and particle-size distribution range. This behavior can be attributed to the enhanced heating rate and rapid volumetric energy transfer associated with microwave irradiation. This energy accelerates precursor activation and promote rapid nucleation. The formation of a greater number of nuclei increases the nucleation density and limits the amount of precursor available for growth of individual particles, thereby suppressing particle grain growth. The narrower size distribution at higher microwave power may further indicate a more rapid and synchronized nucleation process. Nevertheless, the broad distributions observed in all samples suggest that aggregation and subsequent particle growth remain significant during the 160°C for 48 h in solvothermal stage.

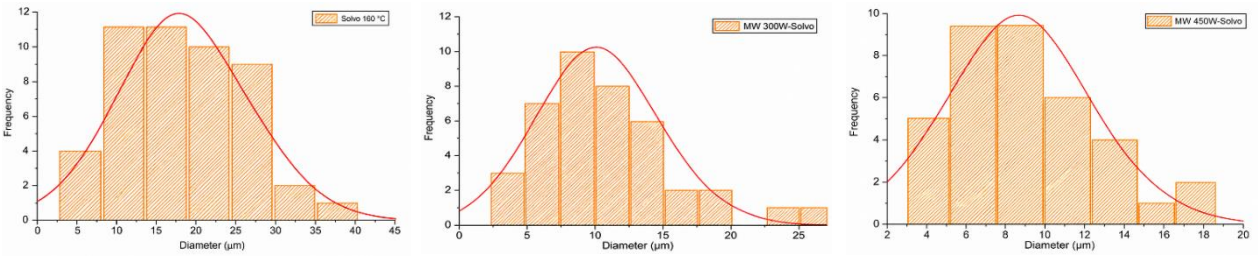


Figure 5. Image-J plot of micrograph SEM for V-BTC solvothermal, MW-300W-solvothermal and MW-450W-solvothermal collected from 1000 magnification image.

Tabel 3. Particle size distribution analysis of V-BTC

Code	Range of Particle Size (μm)	Average Diameter Particles (μm)	*R-Square* (COD)
MW 450W-Solvo	5.06–16.29	8.28 ± 0.26	0.96764
MW 300W-Solvo	4.95–24.22	9.60 ± 0.21	0.97064
Solvo 160°C	8.23–36.66	18.85 ± 1.14	0.90948

The nucleation stage acceleration is highly relevant with crystallization principle in the synthesis Cu-BTC crystals by microwave acceleration [16]**.** Microwave treatment generated a large population of nuclei and strongly accelerated the nucleation stage, although it also accelerated the crystal growth stage [9]. Increasing absorbed power reportedly produced a narrower size distribution of MIL 53(Al) [17], Even though the reported median particle size of MIL 53(Al) changed but the size distribution became substantially narrower at higher power, consistent with the research finding in this work. In principle, microwave irradiation not only contributes to shortening conventional synthesis methods but also plays a significant role in controlling the nucleation stage of crystal growth [18].

4. Conclusion

Microwave-assisted solvothermal synthesis significantly influenced the structure, morphology and particle size of V-BTC compound. The solvothermally synthesized V-BTC showed a crystalline structure with a larger

average particle diameter and a broader particle-size distribution than the microwave-assisted solvothermal samples. Introducing and increasing microwave power induced the formation of smaller average particle sizes and narrower particle-size distributions. This finding indicating that microwave pretreatment significantly influenced nucleation stage by enhancing the nuclei production at initial synthesis, followed by limited subsequent particle growth and agglomeration during the solvothermal process. These finding demonstrate the potential of microwave assisted synthesis for controlling the morphological characteristics of V-BTC Materials.

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