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# Optimizing Solvent Conditions for Reduced-Time Solvothermal Synthesis of Ti-MIL-125

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***Abstract*** – Titanium(IV)-based metal-organic frameworks (MOFs), particularly the highly porous and photo-catalytically active Ti-MIL-125 structure, exhibit significant potential for diverse applications. Conventional solvothermal methodologies often require prolonged synthesis times resulting with a wider particle size range, which poses a limitation for implementation in two-phase microfluidic systems allowing for production of monodispersed smaller particles. This study investigates the influence of different solvent systems on the nucleation and crystallization kinetics of Ti-MIL-125 to achieve reduced synthesis times. While n-methyl-2-pyrrolidone (NMP) as a solvent allowed for temperature-dependent crystallization with optimal results at 220 °C, it did not facilitate substantial time reduction. Incorporation of glycerol to elevate the solution boiling point and allow for use of higher synthesis temperatures without the solvent evaporating, resulted in a deceleration of nucleation kinetics, attributed to the augmented viscosity of the synthesis medium. A ternary solvent mixture of NMP, n,n-dimethylformamide (DMF), and methanol significantly accelerated the synthesis, achieving well-crystalline Ti-MIL-125 at a lower temperature of 162 °C and a reduced residence time of 4 hours. These findings highlight the critical role of solvent selection and its impact on diffusion and precursor assembly, providing valuable insights for optimizing Ti-MIL-125 synthesis, particularly for production in droplet-based microfluidic platforms.

***Keywords*:** Metal organic framework (MOF), solvothermal synthesis, Ti-MIL-125, solvent.

## 1. Introduction

Titanium (Ti) based metal organic framework (MOF) crystals provide ultra-high porosity and surface area-to-volume ratio [1] and advanced photocatalytic properties [2]. They offer promising applications in areas, such as catalysis [3, 4], chemical sensing [5, 6], energy storage [7, 8], cancer therapy [9], drug delivery [10, 11], water purification [12], and $CO_2$ capture [13]. Conventionally, crystalline particles with MOF structures are synthesized via solvothermal or hydrothermal methods [14]. The critical synthesis parameters that affect the successful nucleation and growth of MOF crystals are the composition of the precursor solution, including the type of metal salt, solvent, and organic linker, as well as their concentrations, synthesis temperature and duration. Homogeneous distribution of temperature, controlling the diffusion of molecules in the solvent, is a critical factor that affects the size and structure of the particles produced, as well as the yield. Droplet-based microfluidic systems offer a compelling alternative synthetic platform, leveraging micro-scale droplets as discrete capsules that act as reactors [15]. This approach facilitates enhanced heat and mass transfer rates and efficient mixing within confined volumes, thereby promoting a more homogeneous synthesis environment compared to bulk methods [16]. While such systems hold potential for yielding higher quality MOF products, their operation under atmospheric pressure necessitates the employment of high-boiling-point solvents to achieve typical solvothermal conditions. In addition, prolonged residence times within microfluidic channels can increase the risk of particle aggregation or precipitation, potentially leading to clogging of the channel and, thus, limiting the practical synthesis duration.

The selection of an appropriate solvent is a critical factor governing the formation and resultant properties of MOF structures [17]. Solvent media determines the rate of diffusion and pore volume in the crystal architectures that form [18]. Successful synthesis of desired structures is contingent upon specific solvent characteristics, such as its capacity to solubilize precursors, including metal salts and organic linkers, and its boiling point. N,n-dimethylformamide (DMF) is extensively utilized in MOF synthesis due to its effectiveness in dissolving a wide range of precursors. DMF is an amide with significant

dipole moment making it highly polar. Its hydrogen atoms are strongly bonded to oxygen or nitrogen and cannot be donated making it aprotic. It is a powerful solvent, but its relatively modest boiling temperature of ca. 155 ºC imposes limitations on its utility for solvothermal syntheses requiring elevated temperatures under atmospheric pressure. The solvothermal synthesis of Ti-MIL-125 MOF structures presents greater synthetic challenges compared to other metal-based MOFs due to the reactive nature of the titanium (IV) precursor. Consequently, meticulous optimization of synthesis parameters, particularly the solvent system involving cosolvents, is imperative. Typically, Ti-MIL-125 synthesis employs titanium(IV) isopropoxide as the cation source and terephthalic acid ($H_2BDC$) as the organic linker. Titanium alkoxides exhibit pronounced sensitivity to water and can result in undesired formation of titanium dioxide ($TiO_2$) or other solid phases through rapid hydrolysis and condensation reactions. The incorporation of a polar protic alcohol, such as methanol, as a cosolvent, modulates the reaction kinetics. Methanol likely interacts with the titanium salt, potentially via transesterification by exchanging isopropoxide for methoxide groups [19], thereby attenuating the rates of hydrolysis and condensation and slowing down the overall reaction kinetics. Decelerating the formation kinetics of the Ti-oxo secondary building units or clusters facilitates controlled nucleation and growth, allowing sufficient time for diffusion of molecules and structural ordering. This often results in Ti-MIL-125 particles with enhanced crystallinity, phase purity, and potentially improved morphology with larger crystal sizes. Studies indicate that the precise ratio of methanol within the DMF co-solvent system critically influences the nucleation of MIL-125 crystals. Supporting this approach, Dan-Hardi et al. [20] successfully employed a mixed solvent system comprising DMF and methanol at a volumetric ratio of 9:1 for Ti-MIL-125 synthesis. Given the inherent challenges associated with the synthesis of this MOF, Dan-Hardi's formulation has been widely adopted without modification in conventional solvothermal batch syntheses conducted in pressurized autoclaves [21-24]. These syntheses typically employ temperatures ranging from 150 ºC and 220 ºC and durations spanning 15 hours to 3 days. For continuous and uninterrupted production in microfluidic systems, synthesis durations should ideally be limited to a few hours, necessitating the optimization of current synthesis parameters.

The nucleation of Ti-MIL-125 requires substantial activation energy to facilitate the formation of robust molecular bonds, a process that can be effectively promoted at elevated temperatures. Nucleation is a diffusion-controlled process, and its kinetics depend strongly on the temperature. Assuming a sufficient thermodynamic driving force, higher temperatures enhance molecular diffusion rates, thereby accelerating the nucleation process. Consequently, conducting solvothermal synthesis at higher temperatures is a viable strategy to reduce the synthesis times required for microfluidic applications. This can be achieved through the utilization of high-boiling point solvents or solvent mixtures. Glycerol, a polar protic solvent with a boiling point of ca. 290 ºC, and 1-methyl-2-pyrrolidone (NMP), a polar aprotic solvent with a boiling point of ca. 202 ºC, represent promising alternative solvents for high-temperature microfluidic synthesis.

This study focused on the optimization of solvothermal synthesis parameters for Ti-MIL-125, with specific objectives of elucidating the influence of the solvent system on particle formation and achieving a reduction in the time required for potential implementation in droplet-based two-phase microfluidic systems. Glycerol and NMP were investigated as alternative solvents to the conventional DMF and methanol cosolvent system.

## 2. Materials and Methods

### 2.1. Materials

All chemicals used in the experiments were purchased commercially in analytical grades from Sigma Aldrich, St. Louis, Missouri, USA. The precursor solution constitutes of a single solvent or mixture of solvents, including n,n-dimethylformamide $(CH_3)_2NC(O)H$ (DMF, 99.8%), glycerol $CH_2OH\text{-}CHOH\text{-}CH_2OH$ (Gly, 100%), methanol $CH_3OH$ (M, 100%), and 1-methyl-2-pyrrolidone $C_5H_9NO$ (NMP, 99%), the organic ligand terephthalic acid $C_8H_6O_4$ ($H_2BDC$), and the metal salt titanium isopropoxide $Ti\{OCH(CH_3)_2\}$.

### 2.2. Preparation of Precursor Solution

Synthesis of Ti(IV)-based-MOF MIL-125 was conducted using a notation to name each recipe, denoted by the final molar ratio in the order of metal salt, organic ligand, solvents, temperature (°C), and synthesis time (h). The specific molar

ratios and synthesis parameters used are listed in Table 1. For the preparation of a precursor solution with a 1:3.5:155 metal salt:ligand:NMP molar ratio, 99.2 μL of metal salt was introduced to 5 mL of solvent and 0.195 g organic ligand. To prepare precursor solutions with metal salt:ligand:NMP:Glycerol molar ratios of 1:3.5:155:61 and 1:3.5:108:61, 1.5 mL glycerol was added to 5mL and 3.5 mL of NMP, respectively, maintaining a total solvent volume of 5mL for all synthesis, unless otherwise specified. The mixtures were homogenized via sonication in an ultrasonic bath for 10 minutes. Immediately following preparation, the precursor solution was transferred to an autoclave. The sealed autoclave was placed in an oven adjusted to the synthesis temperature. Upon completion of the predetermined synthesis time, the resultant particulate matter was recovered by centrifugation at 5000 rpm for 5 minutes and washed at least three times with the primary solvent. Particles were soaked in methanol overnight and washed with methanol at least two times and dried at 80 °C overnight. The as-synthesized MIL-125 particles were calcined at 200 °C.

Table 1: Solvothermal synthesis conditions for the macroscale batch system with molar ratios of precursors.

| $Ti(OiPr)_4$ | $H_2BDC$ | Solvent | Temperature, °C | Residence Time, h | Particle | MOF |
|---|---|---|---|---|---|---|
| 1 | 3.5 | 155NMP | 180 | 2 | Yes | Yes |
| 1 | 3.5 | 155NMP | 180 | 4 | Yes | No |
| 1 | 3.5 | 155NMP | 200 | 2 | Yes | No |
| 1 | 3.5 | 155NMP | 200 | 4 | Yes | Yes |
| 1 | 3.5 | 155NMP | 220 | 2 | Yes | Yes |
| 1 | 3.5 | 155NMP | 220 | 4 | Yes | Yes |
| 1 | 3.5 | 155NMP | 230 | 2 | Yes | No |
| 1 | 3.5 | 155NMP:61Gly | 230 | 2 | Yes | No |
| 1 | 3.5 | 108NMP:61Gly | 230 | 4 | Yes | No |
| 1 | 3.5 | 139NMP:37MeOH | 190 | 2 | Yes | No |
| 1 | 3.5 | 139NMP:37MeOH | 190 | 4 | Yes | Yes |
| 1 | 3.5 | 106DMF:54NMP:37MeOH | 162 | 2 | Yes | No |
| 1 | 3.5 | 106DMF:54NMP:37MeOH | 162 | 4 | Yes | Yes |

Crystalline structure of Ti-MIL-125 particles was characterized by powder x-ray diffraction (PXRD, Rigaku-Ultima IV, scan 1°/minute rate between 5°-50°).

## 3. Results and Discussion

The synthesis of Ti-MIL-125 crystals was investigated under various solvent and temperature conditions and the resulting crystalline phases were analysed using XRD results presented in Figures 1, 2, and 3. The bottommost pattern in these figures represents the simulated XRD of Ti-MIL-125, characterized by its specific peak positions and intensities, which serve as a benchmark for assessing the synthesized materials.

### 3.1 Effect of Temperature and NMP as Solvent

Initial experiments using NMP (boiling point 202 °C) as the primary solvent revealed a strong dependence of the nucleation rate on the reaction temperature (Figure 1). Preliminary studies using Dan-Hardi et al.'s [20] recipe with DMF and methanol at a 9:1 volume ratio had shown that the residence time could only be reduced to 8 hours at elevated temperatures. Higher temperatures generally promote faster nucleation in crystallization processes due to increased kinetic energy of the reacting species, leading to a higher frequency of successful collisions and faster formation of critical nuclei. Synthesis with NMP at l80 °C did not result in crystallisation before 4 hours even though nucleation might have started at 2 hours based on observation of the development of crystallographic planes in Figure 1. The best results with NMP were obtained at 220 °C, suggesting an optimal temperature range for Ti-MIL-125 formation in this solvent. Attempts to further reduce the residence time to 2 hours by increasing the temperature to 220 °C with NMP were unsuccessful and exceeding this temperature by heating up to 230 °C led to the absence of the desired crystal phase. This indicates that while higher

temperatures initially accelerate nucleation, exceeding an optimal point might lead to the decomposition of precursors or the formation of undesired phases.

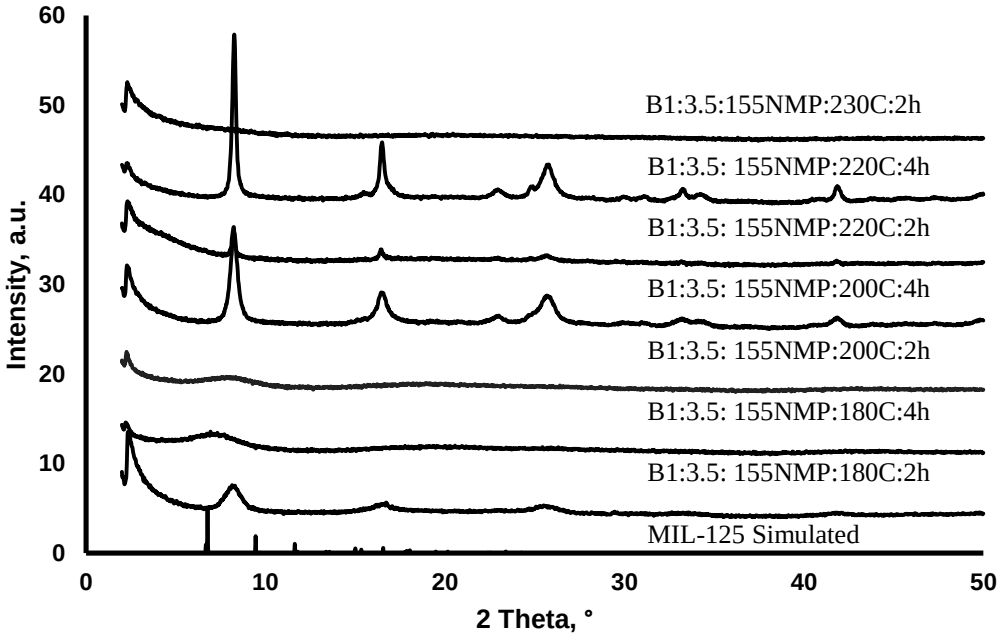


Fig. 1: XRD patterns illustrating the effect of synthesis temperature (180-230 °C) and residence time (2h and 4h) on the formation of Ti-MIL-125 in NMP solvent, compared against the simulated pattern.

### 3.2 Incorporation of Glycerol

To manipulate the boiling point of the reaction mixture and potentially influence the crystallization process, glycerol (boiling point 290 °C) was added to the NMP-based precursor solution (Figure 2). The results indicate that the addition of glycerol decelerated nucleation. Glycerol is a highly viscous solvent due to its multiple hydroxyl groups, which can form extensive hydrogen bonding networks. This increased viscosity likely hindered the diffusion of the precursor molecules in the solution, thus reducing the rate at which they could encounter each other and form the critical nuclei required for crystal growth. The slower diffusion rates, therefore, explain the observed deceleration of nucleation.

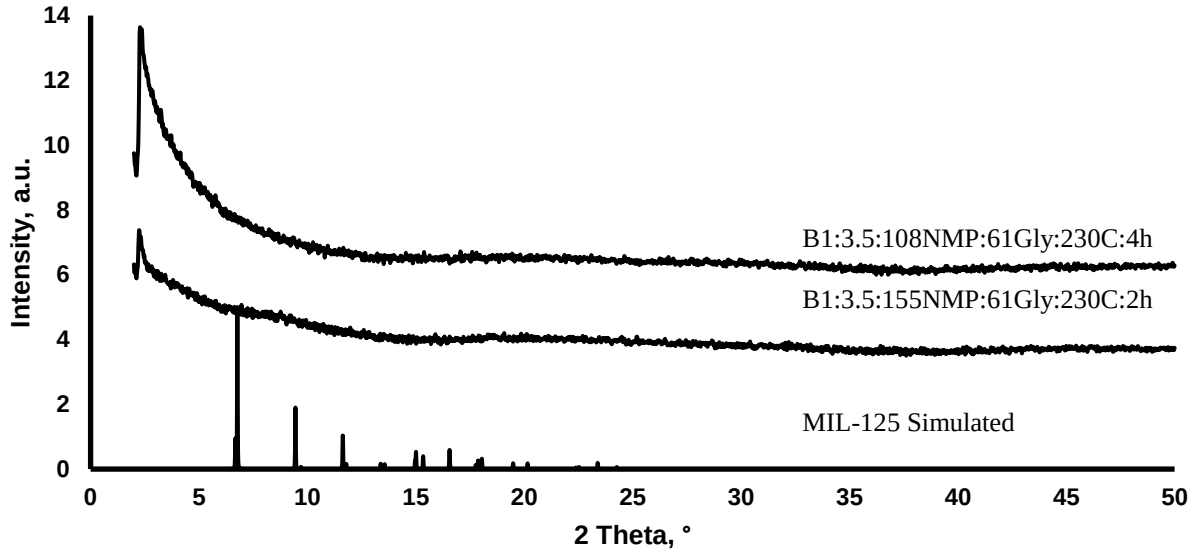


Fig. 2: XRD patterns illustrating the effect of addition of glycerol on the formation of Ti-MIL-125 in NMP solvent at 2 h and 4 h, compared against the simulated pattern.

### 3.3 Synergistic Effect of Solvent Mixture (NMP, DMF, and Methanol)

The most promising results were obtained when a mixture of NMP, DMF, and methanol was employed as the solvent system (Figure 3). This solvent combination led to a significant reduction in residence time to 4 hours, even at a reduced temperature of 162 °C. Ti-MIL-125 crystal peaks are observed to start to develop at the end of 2 hours. This acceleration of nucleation in the presence of DMF and methanol, compared to the glycerol-containing system, highlights the importance of solvent properties beyond just the boiling point. DMF is a polar aprotic solvent with a moderately high boiling point (153 °C) and a strong coordinating ability due to its nitrogen and oxygen atoms. This coordinating ability could influence the formation of the Ti-O-C bonds characteristic of the MIL-125 structure by effectively solvating the metal precursor and organic linker, potentially facilitating their assembly into the desired framework. The fact that DMF allowed for a shorter residence time compared to the initial NMP experiments (where formation started after 4 hours in Figure 1, implying a longer overall synthesis time) suggests that DMF might provide a more favourable environment for the initial nucleation.

Methanol is a polar protic solvent with a low boiling point (65 °C) and low viscosity. Its presence in the mixture likely enhances diffusion and mass transfer and the solubility of certain precursors. The combination of methanol's ability to facilitate diffusion, DMF's coordinating ability to promote precursor assembly, and NMP's role in allowing for higher synthesis temperatures as a high-boiling-point solvent, appears to create a synergistic effect that significantly accelerates the nucleation and crystallization of Ti-MIL-125. The fact that similar XRD patterns to the simulated peaks were obtained under these conditions suggests the formation of a highly crystalline and pure MIL-125 phase in a significantly shorter crystallisation time and at a lower temperature compared to using NMP alone or with glycerol.

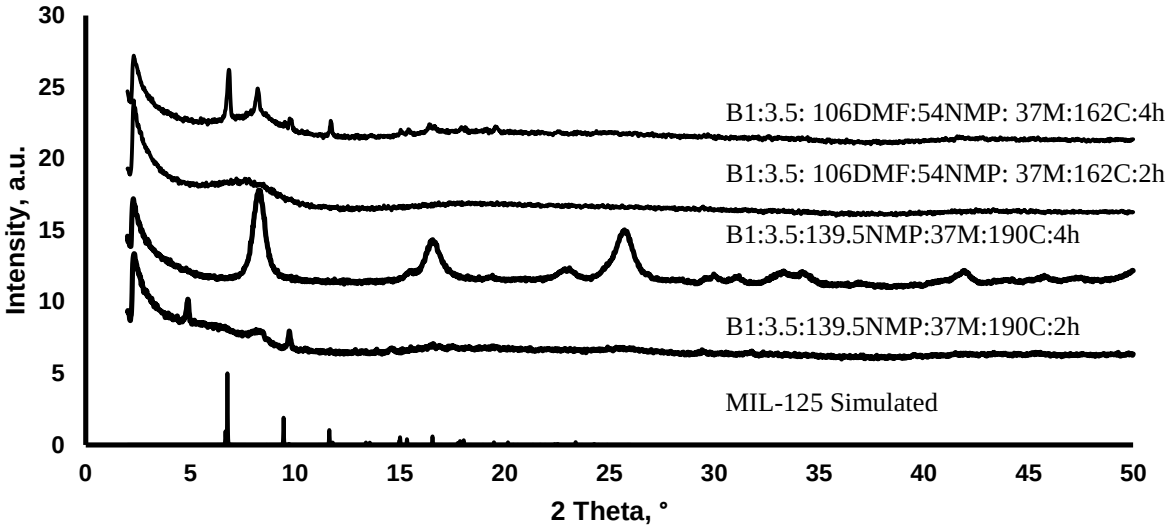


Fig. 3: XRD patterns of Ti-MIL-125 synthesized using different solvent mixtures of NMP, DMF, and methanol (M) at varying temperatures and residence times, compared to the simulated XRD pattern of Ti-MIL-125.

## 4. Conclusions

The study demonstrates the significant impact of solvent properties on the nucleation and crystallization kinetics of Ti-MIL-125. The choice of the solvent is found to be an important parameter to adjust synthesis temperature. In conventional MOF synthesis procedures, DMF and methanol are used as the solvents. Using this solvent system imposes restrictions at atmospheric pressure to use synthesis temperatures less than 155 °C due to the boiling point of DMF. NMP was used to extend the synthesis temperature up to 202 °C by its boiling point. It was concluded that nucleation was accelerated with increasing temperature and diffusion rates. While higher temperatures can initially accelerate nucleation, the choice of solvent and solvent mixtures plays a crucial role in optimizing the synthesis process. DMF appears to facilitate faster nucleation compared to NMP alone. The addition of a high-viscosity solvent like glycerol decelerates nucleation due to hindered diffusion. A ternary solvent mixture of NMP, DMF, and methanol exhibits a synergistic effect, leading to a substantial reduction in residence time by enhanced nucleation and the formation of highly crystalline Ti-MIL-125 at lower temperatures. These findings provide valuable insights into controlling the synthesis of MOF materials by carefully selecting and tuning the solvent environment and adopting optimum solvothermal synthesis conditions for faster microfluidic production of high-quality MIL-125 nanoparticles in picolitre droplets.

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