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Article

Response Optimization for the Preparation of MIL-100(Fe)@COF Materials Using Design of Experiments

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Abstract

Three different optimization studies were conducted for the synthesis of MIL-100(Fe) and MIL-100(Fe)@COF using design of experiments. In the first study, the optimal concentration of precursors was determined using a mixture design method, and a modified molar ratio of 0.4155:0.2664:0.3182 was found to yield the highest crystallinity. In the second study, a central composite design was used to optimize the main factors of synthesis temperature and time with a synthesis temperature of 161 °C and a synthesis time of 12 hours. In the third study, a screening design method was used to determine the effect of five precursors on the formation of MIL-100(Fe)@COF, and the presence of characteristic peaks at 1552, 1483, and 1354 cm^{-1} was found to be important for the existence of the COF structure. MIL-100(Fe)@COF synthesized with a modified molar ratio of 0.4831:0.4169:0.1 was predicted to exhibit optimal conditions.

Keywords: *MIL-100(Fe), COF material, Response optimization*

1. Introduction

Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are two classes of materials that have gained increasing attention in recent years due to their unique properties and potential applications in various fields [1]. MOFs are made up of metal ions or clusters connected by organic ligands to form a three-dimensional framework with large surface area and pore volume [2-5]. COFs, on the other hand, are composed of organic molecules that are linked together by covalent bonds to create a crystalline structure with well-defined pores [6-7]. Both MOFs and COFs have shown promise in applications such as gas storage and separation, catalysis, sensing, and drug delivery [8-14]. In this era of sustainable development, MOFs and COFs are also being explored for their potential to mitigate environmental issues such as carbon capture and water purification.

MIL-100(Fe) is a metal-organic framework (MOF) composed of iron (Fe) ions coordinated with organic ligands, specifically 1,3,5-benzenetricarboxylic acid (BTC) [15-17]. MIL-100(Fe) is one of the most well-studied MOFs and has shown promise in applications such as gas adsorption, water purification, and sensing. The unique properties of MIL-100(Fe) arise from its porous structure, which allows for high surface area and tunable pore sizes. The Fe(III) ions within the MOF can also act as active sites for catalytic reactions. The material can be synthesized using various methods, including solvothermal and hydrothermal synthesis. MIL-100(Fe) has been extensively studied for its potential in various applications. It has shown excellent performance in gas adsorption, such as carbon dioxide, hydrogen, and methane. The material has also been used for the removal of toxic heavy metal ions from water and as a catalyst for organic reactions. The unique properties of MIL-100(Fe) make it a promising material for future research in various fields, and it has the potential to contribute significantly to the development of new technologies.

Design of experiments (DOE) is a statistical method used in research and industrial settings to systematically plan, conduct, analyze, and interpret experiments. The goal of DOE is to obtain the maximum amount of information from the minimum number of experiments while minimizing the impact of extraneous variables on the results [18-21]. DOE allows researchers to determine the most important factors affecting a process or product, and to optimize those factors to achieve the desired outcomes. DOE involves selecting and manipulating specific variables, known as factors, and observing their effects on a response variable of interest. The factors can be either categorical or continuous, and their levels are defined prior to the experiment. The response variable can also be either categorical or continuous, depending on the nature of the experiment. DOE can be used in a wide range of fields, including engineering, manufacturing, pharmaceuticals, agriculture, and social sciences. It can be applied to various types of experiments, such as screening experiments, factorial experiments, and re-

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sponse surface experiments. In this study, different experimental design methods were used sequentially to optimize the MIL-100(Fe)@COF synthesis process. First, the optimization of the synthesis of MIL-100(Fe) were determined by mixture design and response surface method. Then, the optimization of MIL-100(Fe)@COF was confirmed by the mixture design of the three factors selected through the screening process.

2. Experiments

Trimesic acid, iron(III) nitrate nonahydrate, distilled water, ethylenediamine, melamine (MEL), terephthaldehyde (TPA), and dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich, and ethanol was purchased from Samjeon Chemical. All the chemicals were used without additional purification.

2.1. MIL-100(Fe) synthesis

Trimesic acid and iron(III) nitrate nonahydrate were added in distilled water, and stirred for 10 minutes. The amount of reagent was adjusted according to the concentration ratio determined by mixture design method. Then, the mixture was transferred to an autoclave and reacted under various conditions of temperature and time. Then MIL-100(Fe) was obtained from mixture solution by separating through filtration, washed with distilled water and ethanol, and dried at 80 °C.

2.2. NH_2_MIL-100(Fe) synthesis

MIL-100(Fe), ethylenediamine, and ethanol were put into a round bottom flask. Reflux reaction was performed at 80° C for 12 hours while mixing with a heated magnetic stirrer. Then, the resulting mixture was filtered to obtain NH_2_MIL-100(Fe) after washed with ethanol, and dried at 80 °C.

2.3. MIL-100(Fe)@COF synthesis

NH_2_MIL-100(Fe), melamine, terephthaldegyde, dimethylsulfoxide, and distilled water were stirred for 10 minutes. The amount of reagent was adjusted according to the concentration ratio determined by the design methods. After transferring the mixture to an autoclave, the reaction was performed in an oven at 180° C for 12 hours. The final product after the reaction was washed with ethanol after filtration and dry at room temperature to obtain MIL-100(Fe)@COF material.

2.4. Characterization

The powder XRD patterns of the catalysts were recorded using X-ray diffractometer (Shimadzu XRD-6000) operated at 40 kV and 30 mA using Cu Kα (λ = 0.15418 nm) radiation to determine the crystal structure and crystallinity. Fourier transform infrared (FT-IR) spectra were measured with an infrared spectrometer (iS50) from Thermo Fisher Scientific in the range of 4000~400 cm^{-1} by mixing the sample with KBr to form a pellet. All statistical assessments were performed using the Minitab 21 software.

3. Result and discussion

3.1. Optimization of precursor concentration for MIL-100(Fe) synthesis

The mixture design method was used to determine the optimal concentration of precursors for the synthesis of MIL-100(Fe). This method is a kind of response surface design used to evaluate products that consist of multiple components or ingredients. It is widely used in industrial development, including the preparation of mixtures and formulations. The result of this method is a function of the relative proportions of each component in the mixture. Three precursors, iron(III) nitrate nonahydrate ($FeNO_3$), trimesic acid (TMA) and distilled water (H_2O) were used to optimize their composition for the synthesis of MIL-100(Fe). In this study, extreme vertex design, a mixed design approach methodology that introduces additional constraints into the design, was employed. Lower and upper component ratio limits are no longer restricted to 0 to 1. Moreover, the ratio ranges for each component were not the same. The following proportion ranges were used in the design: $FeNO_3$ + TMA + H_2O = 1, 0.2 $\leq$ $FeNO_3$ $\leq$ 0.6, 0.1 $\leq$ TMA $\leq$ 0.5, and 0.1 $\leq$ H_2O $\leq$ 0.5. These values were based on the molarity of the material. Thirteen experimental conditions were designed and synthesis was performed accordingly. Statistical analysis was conducted using the crystallinity of the synthesized samples. Figure 1 shows the mixture contour plot of crystallinity of MIL-100(Fe) samples synthesized with different modified mole fractions of precursors. The plot reveals a optimum section clearly. A response optimization tool was used to determine the optimal molar ratio of the three precursors for the synthesis of MIL-100(Fe). This tool helps assess how different experimental settings affect the predicted responses of the saved model. According to Figure 2, MIL-100(Fe) synthesized using a modified molar ratio of 0.4155:0.2664:0.3182 was predicted to have the highest crystallinity.

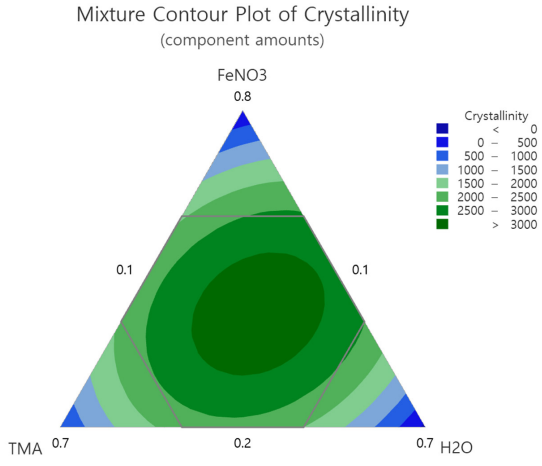

Figure 1. Mixture contour plot for crystallinity of MIL-100 synthesized with various modified mol faction of precursors.

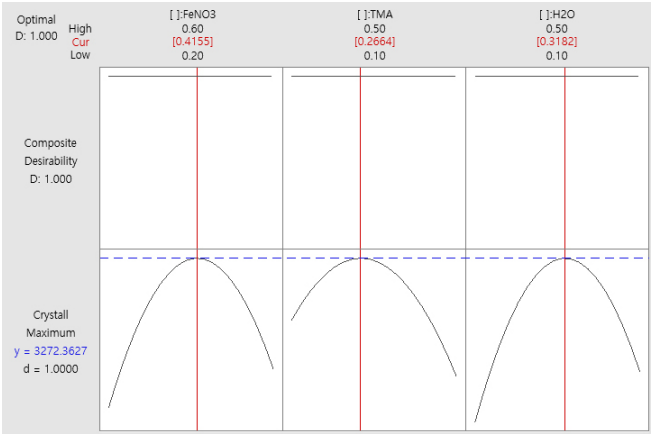

Figure 2. Response optimization plot for crystallinity of MIL-100 synthesized with various modified mol faction of precursors.

3.2. Optimization of synthesis condition of MIL-100(Fe)

Response Surface Methodology (RSM) was implemented to achieve statistical optimization. RSM is a collection of advanced design of experiments (DOE) techniques that enable a more complete understanding and optimization of responses. This approach is commonly used to refine a model after using factorial design to identify important factors. RSM relies on quadratic regression models to facilitate mapping of response surface regions, identify optimal levels of variables, and select operating conditions necessary to meet specifications. Central Composite Design (CCD), a variant of the RSM method, was specifically employed in this study. CCD has the ability to fit full quadratic models containing information gleaned from well-designed factorial experiments. Therefore, incorporating the center and axial points into a previously conducted factorial design is very effective for modeling curved response variables. We designed the experiment using the CCD method and optimized the main factors synthesis temperature and time. The design factors and levels are shown in Table 1. Thirteen experimental conditions were designed with temperature and time as variables. MIL-100(Fe) samples were synthesized according to the designed synthesis conditions under constant precursor composition optimized.

Statistical analysis was performed to investigate the importance of input factors and their interaction with output responses. First, Pareto charts were obtained to compare the importance of factors, as shown in Figure 3. Relative importance was observed on Pareto charts to compare relative importance and statistical significance between main factors and interactions. Factors above the baseline shown at 2.365 in the chart were considered potentially significant factors. Therefore, all factors except AB (interaction between temperature and time) as terms in the table were the key synthesis conditions for determining the crystallinity of MIL-100(Fe). Figure 4 illustrates the crystallinity of MIL-100(Fe) synthesized with varying temperature and time, as represented by contour and surface plots. The contour plot exhibits a 2D view in which the contour lines connect points with equivalent response values. As such, the crystallinity of MIL-100(Fe) could be predicted according to the synthesis temperature and time. In the contour map, a relatively wide range of optimum conditions were presented for

Table 1. Factor and Level for Central Composition Design

Factor	Level				
	$-\alpha$	-1	0	+1	$+\alpha$
Temp. (°C)	115	130	160	190	205
Time (h)	6	8	12	16	18

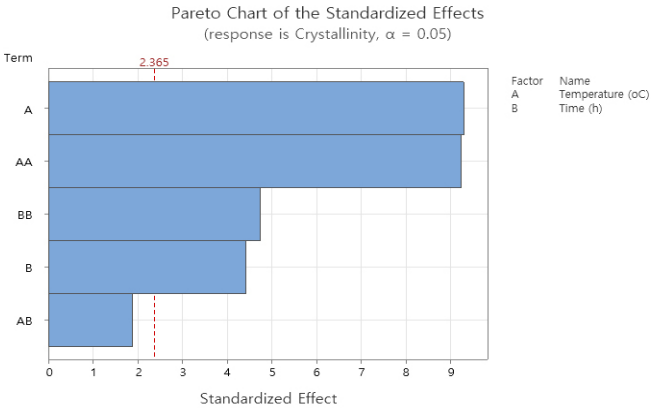

Figure 3. Pareto chart for the effects of synthesis conditions of MIL-100 on crystallinity designed by central composition design.

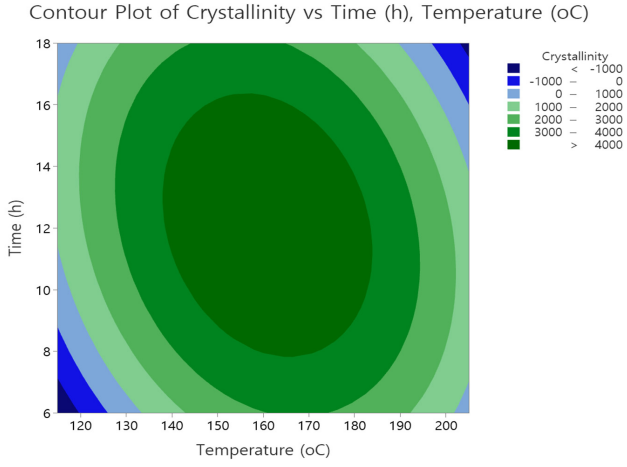

Figure 4. Contour plot for crystallinity of MIL-100 synthesized with various synthesis conditions designed by central composition design.

the synthesis temperature and time in the range of 145~180 °C and 8~16 h. Optimal values of the synthesis temperature and synthesis time to achieve the maximum crystallinity of MIL-100(Fe) were derived using a response optimizer. As shown in Figure 5, it was predicted that MIL-100(Fe) with maximum crystallinity could be synthesized under the conditions of a synthesis temperature of 161 °C and a synthesis time of 12 h.

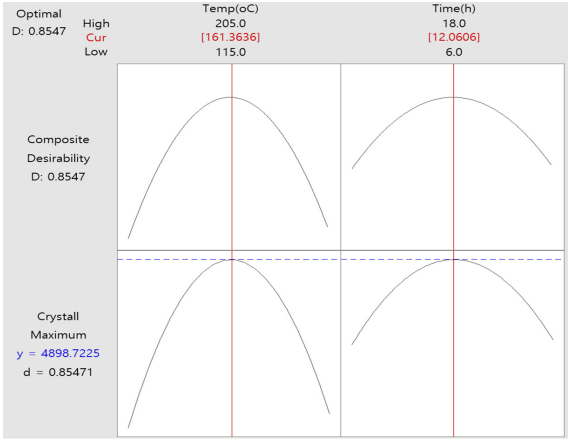

Figure 5. Response optimization plot for crystallinity of MIL-100 synthesized with various synthesis conditions designed by central composition design.

3.3. Optimization of precursor concentration for MIL-100(Fe)@COF synthesis

Figure 6 illustrates the FT-IR spectra of MIL-100(Fe) and M100C (MIL-100(Fe)@COF). The FT-IR spectrum of M100C exhibits distinct stretching vibrations at 1552, 1483, and 1354 cm^{-1} attributed to the C=N, C=C, and C－N bonds, respectively, indicating the occurrence of a condensation reaction and tautomerization. These peaks are considered crucial in confirming the presence of the COF structure. To investigate the effect of five precursors on the formation of M100C, a screening design method was utilized. Using three variables and five factors, 13 experimental conditions were derived from the design method. After synthesizing 13 samples according to these conditions, the size of the peak corresponding to C=N in the FT-IR spectrum was analyzed using statistical methods, and the main effect plot for M100C synthesized with different precursors is presented in Figure 7. The results indicated that TPA, DMSO, and DIW had a significant impact on the formation of M100C.

To obtain more accurate optimal conditions, a mixture design method, similar to the optimization of MIL-100(Fe), was utilized to analyze the three precursors. Thirteen conditions were designed and synthesized accordingly, followed by statistical analysis based on FT-IR analysis.. Figure 8 shows a cox response trace plot showing the effect of changing each mixture component while keeping everything else in constant proportion. Trace curves are reference blends and vertices. Plots can identify the most influential components and plot them in contour or surface plots. Indeed, the effects of DMSO and DIW on the FT-IR peaks were clearly observed in the plots. This trend was in good agreement with the above. Additionally, the presence of optimal compositions was detected for all three components. Optimal molar ratios of the three precursors for MIL-100(Fe)@COF synthesis were determined by a response optimization tool showing how different experimental settings affect the predicted response of the preserved model . As shown in Figure 9, MIL-100(Fe)@COF synthesized with a modified molar ratio of 0.4831:0.4169:0.1 was predicted to exhibit optimal conditions.

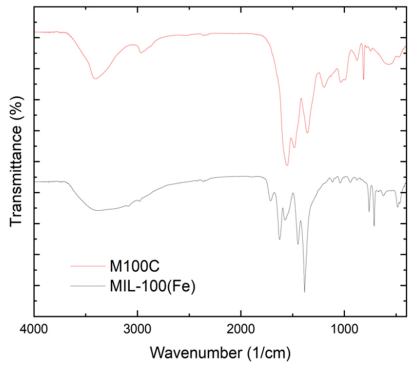

Figure 6. FT-IR spectra of MIL-100 and MIL-100(Fe)@COF materials.

Figure 7. Main effect plot for FT-IR peak of MIL-100(Fe)@COF synthesized with different precursors.

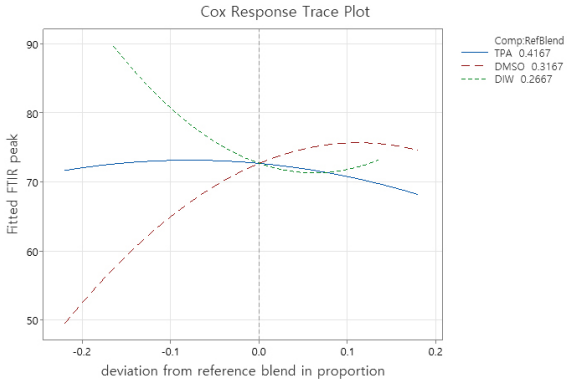

Figure 8. Cox response trace plot of FT-IR peak of MIL-100 (Fe)@COF based on precursor composition.

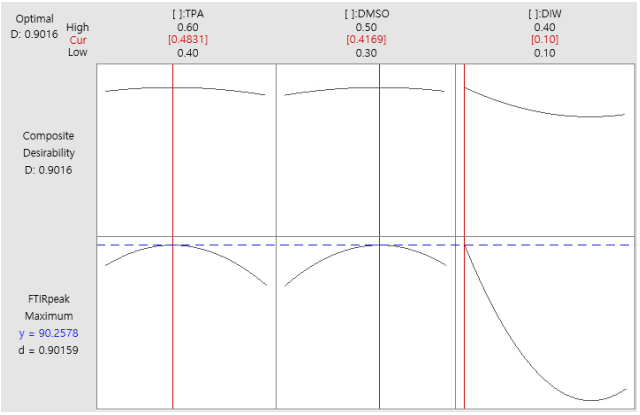

Figure 9. Response optimization plot for FT-IR peak of MIL-100 (Fe)@COF synthesized with various modified mol faction of precursors.

4. Conclusion

In conclusion, this study successfully optimized the synthesis conditions of MIL-100(Fe) and MIL-100(Fe)@COF using response surface methodology. The mixture design method was employed to determine the optimal concentration of precursors for the synthesis of MIL-100(Fe), and statistical analysis was performed using the crystallinity of the synthesized samples. Response surface methodology was implemented to optimize the main factors synthesis temperature and time for the synthesis of MIL-100(Fe). Central composite design was employed, and statistical analysis was performed to investigate the importance of input factors and their interaction with output responses. Moreover, a screening design method was used to determine the effect of five precursors on the formation of MIL-100(Fe)@COF. The results of this study provide insights into the synthesis of MIL-100(Fe) and MIL-100(Fe)@COF and can contribute to the development of more efficient and effective methods for synthesizing these materials.

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