

Spray-Drying Synthesis of Metal–Organic Frameworks
and Their Hybridization with Nanoparticles for Catalytic
Applications

Yuko Mitsuka

2026

Division of Chemistry

Graduate School of Science

Kyoto University

Contents

Chapter 1 General Introduction

1-1.	Catalysts for Alternative Energy Resources.....	1
1-2.	Metal Nanoparticles as Catalysts	2
1-3.	Catalyst Use of Porous Materials.....	3
1-4.	Spray Pyrolysis and Spray drying.....	5
1-5.	Metal Nanoparticle–MOF Hybridization via Spray Reaction Method	7
1-6.	Catalysts for Synthesizing Methanol from CO ₂	8
1-7.	Composition of This Dissertation.....	9
1-8.	References.....	10

Chapter 2 Synthesis of Metal-Organic Framework by Spray Pyrolysis and Spray-Drying Method

2-1.	Introduction	14
2-2.	Experimental	18
2-3.	Result and Discussion	25
2-4.	Conclusion	40
2-5.	References.....	41

Chapter 3 One-Step Synthetic Method for Metal/MOF Composites via Microwave Irradiation

3-1.	Introduction	43
3-2.	Experimental	45
3-3.	Result and Discussion	46
3-4.	Conclusion	49
3-5.	References	50

Chapter 4 Hybridization of Nanoparticle Catalysts with MOFs via a Spray-Based Synthetic Approach and Evaluation of Their Catalytic Performance

4-1.	Introduction	51
4-2.	Experimental	54
4-3.	Result and Discussion	63
4-4.	Conclusion	86
4-5.	References	87

Chapter 5

General Conclusion.....	92
--------------------------------	-----------

Acknowledgements.....	95
------------------------------	-----------

Chapter 1

General Introduction

1-1. Catalysts for Alternative Energy Resources

A catalyst is a substance that significantly increases the rate of a chemical reaction while remaining chemically unchanged before and after the reaction. One of the most notable historical examples is the development of an iron-based catalyst that can synthesize ammonia from nitrogen and hydrogen. This led to the Haber–Bosch process being established for the large-scale production of ammonia¹⁻². This innovation enabled the mass production of nitrogen fertilizers, dramatically increasing agricultural yields and alleviating global food shortages³. Since then, catalysts have played a vital role in developing energy supply systems based on fossil fuels, as well as in the growth of the chemical industry. They are indispensable for producing a wide range of energy-related and chemical products, including plastics, synthetic fibers, detergents, pharmaceuticals and fuels such as gasoline.

In the context of energy conversion, most catalysts used in industry are solid-state materials. The performance and functionality of these catalysts are governed by four key factors: (1) the catalytically active component; (2) the support material; (3) the presence of co-catalysts;

and (4) the method of catalyst preparation⁴. A comprehensive understanding of these factors is essential for elucidating the structure–function relationships in practical catalytic systems, as well as for the rational design of next-generation catalysts.

1-2. Metal Nanoparticles as Catalysts

As discussed in the previous section, the catalytic performance of a material is largely determined by its catalytically active components. In recent years, metal nanoparticles (NPs) have emerged as promising catalysts due to their high surface-to-volume ratio and unique surface properties, which can significantly enhance their reactivity. Moreover, metal NPs often exhibit different physical and chemical characteristics compared to their bulk counterparts, such as quantum size effects and enhanced catalytic activity. NPs in the size range of 1–100 nm have attracted significant attention from both fundamental research and industrial applications⁵⁻⁷. From an industrial standpoint, for example, silver NPs have been investigated as a potential replacement for traditional lead-based solders, offering an environmentally friendly alternative⁸⁻¹⁰. In the field of multilayer ceramic capacitors (MLCCs), copper NPs are being developed as a substitute for nickel NPs, due to copper's lower cost and comparable performance¹¹⁻¹². A variety of synthetic methods have been developed for the preparation of metal NPs. These include

hydrazine reduction¹²⁻¹⁴, borohydride reduction¹⁵⁻¹⁷, the polyol method¹⁸, organic acid reduction (e.g., using citric acid or ascorbic acid)¹⁹⁻²⁰, laser ablation²¹, and microwave (MW)-assisted reduction techniques²²⁻²⁴. Each method offers distinct advantages in terms of particle size control, dispersion stability, and scalability.

To further enhance the catalytic activity and stability of metal NPs, they are commonly dispersed on support materials with a high surface area, such as metal oxides (e.g. TiO₂, Al₂O₃) or carbon-based materials (e.g. activated carbon, carbon nanotubes). These supports prevent nanoparticle aggregation and contribute to improved electron transfer and thermal stability during catalytic reactions.

1-3. Catalyst Use of Porous Materials

In the previous chapter, it was emphasized that the nature of support plays a critical role in fully expressing the catalytic properties of NPs. To date, a wide variety of supports, including oxides and carbon-based materials, have been extensively investigated²⁵⁻²⁷. More recently, metal-organic frameworks (MOFs) have garnered considerable attention as promising catalyst support. MOFs are crystalline microporous materials constructed by the coordination of metal ions or clusters with organic ligands²⁸⁻³¹. In contrast to conventional porous materials such as zeolites,

MOFs offer highly tunable pore structures in terms of size, shape, and chemical environment, enabling the rational design of supports tailored to specific catalytic systems.

Hybrid materials composed of metal NPs and MOFs have emerged as a new class of functional materials, attracting significant interest for applications in gas storage, magnetism, optics, and catalysis due to the synergistic interactions between their constituents^{32–37}. For instance, Liyu Chen et al. reported palladium NPs embedded within UiO-67 MOFs as catalysts for selective olefin hydrogenation. They demonstrated that methyl cyclopentane could be hydrogenated selectively depending on the size and geometry of the interstitial voids in Zr-based MOF supports, highlighting the molecular sieving effect inherent to UiO-67³⁸.

Thus far, most design strategies for nanoparticle/MOF hybrid catalysts have focused primarily on exploiting the complementary physical and chemical properties of each component. In contrast, relatively little attention has been paid to hybrid systems in which electronic interactions between the metal NPs and the MOF support play a significant role^{39–40}. Given that catalytic performance—such as activity and selectivity—is often governed by the electronic structure of the active metal species, the ability to fine-tune the electronic properties of metal NPs through controlled modification of the MOF support is of importance for the advancement of next-generation hybrid catalysts.

1-4. Spray Pyrolysis and Spray Drying

As illustrated in the schematic diagram (Figure 1), the spray reaction method involves the formation of fine droplets (typically several to several tens of micrometers in diameter) by atomizing a solution or suspension containing precursor components of the target material. These droplets are introduced into a high-temperature atmosphere, where the solvent rapidly evaporates and the solutes undergo thermal decomposition or chemical reactions, leading to the instantaneous formation of particles at the droplet surface. Subsequently, the residual solvent inside the droplet evaporates, and shell-like particles with a hollow structure are formed upon continued heating, finally producing solid particles. This process enables the synthesis of monodisperse particles that retain the composition of the starting solution.

Spray pyrolysis and spray drying techniques can be applied to synthesize a wide range of materials, including metals, oxides, non-oxides, and their composites. The resulting fine particles typically exhibit the following characteristics: a dense, spherical morphology; narrow particle size distribution; high compositional homogeneity; high purity; excellent dispersibility; and low tendency to agglomerate. These features are attributable to the unique particle formation mechanism inherent to spray pyrolysis, wherein particles are derived directly from homogeneous solution droplets. In particular, the method is well-suited for the synthesis of multicomponent

systems, making it especially attractive for applications such as the preparation of precursor powders for oxide superconductors^{41–45}.

Despite its advantages, the application of spray pyrolysis and spray drying to the synthesis of MOFs remains limited. To date, only a few studies have been reported, notably the work by Mospoch et al. in 2013, in addition to the present study⁴⁶. Nevertheless, these methods hold great promise for industrial-scale MOF production. Its relatively low processing temperatures, compatibility with general-purpose equipment (with appropriate feed system design), and high versatility suggest that it can accommodate the synthesis of various MOF structures. Furthermore, spray pyrolysis and spray drying are a continuous flow process with excellent scalability and productivity, offering a cost-effective route for large-scale MOF fabrication.

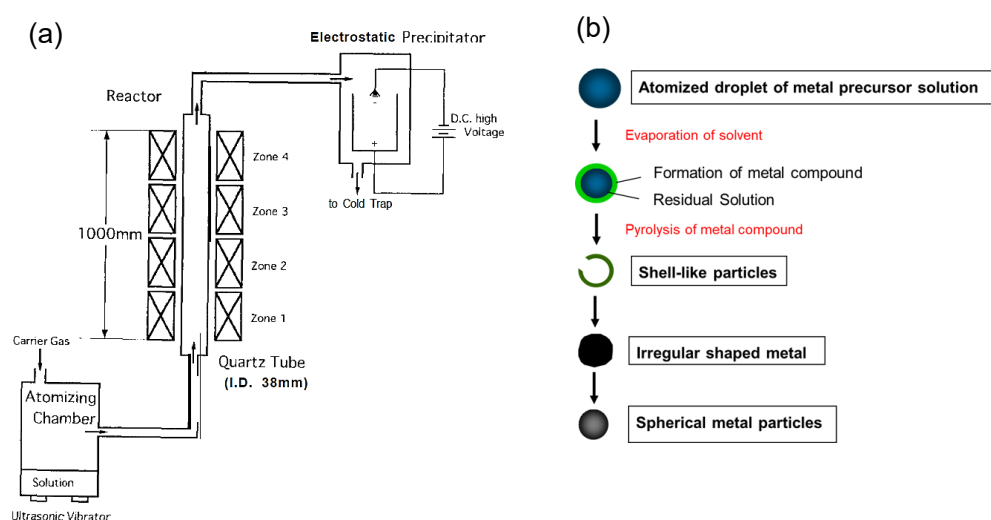


Figure 1. (a) Schematic diagram of the spray pyrolysis apparatus⁴⁴ and (b) the formation mechanism of particles.

1-5. Metal Nanoparticle–MOF Hybridization via Spray Reaction

Method

We propose the utilization of the spray reaction method for the rapid synthesis of metal–MOF hybrid catalysts. Conventionally, the formation of MOFs via coordination chemistry is considered to require a certain residence time to achieve complete complexation. In contrast, the spray process, characterized by its extremely short reaction time, offers a unique pathway for synthesizing hybrid catalysts in a single step.

This rapid synthesis strategy is particularly advantageous for accessing metastable or kinetically favored MOF structures—such as amorphous or low-crystallinity MOFs—that are often difficult to obtain through conventional solvothermal or diffusion-based methods. Moreover, if catalytically active metal NPs can be effectively incorporated or immobilized within the MOF cavities during the spray process, the resulting hybrid materials are expected to exhibit significantly enhanced catalytic performance due to the high dispersion of NPs and the potential for synergistic interactions between the metal and the MOF matrix.

1-6. Catalysts for Methanol Synthesis from CO₂

For the effective utilization of carbon dioxide, among the various CO₂ conversion pathways, the hydrogenation of CO₂ to methanol has attracted significant attention due to its potential for producing not only an important alternative transportation fuel but also a versatile chemical feedstock. Methanol can also serve as a precursor to produce dimethyl ether and other value-added chemicals. Previous studies have reported, for instance, that Cu NPs supported on ZrO₂ exhibit catalytic activity for CO₂ hydrogenation^{47–48}. In this context, replacing conventional oxide supports such as ZrO₂ with Zr-based MOFs is considered advantageous, owing to the tunable porosity and potential for synergistic interactions between the MOF framework and the active metal sites. Furthermore, we propose that the use of the spray reaction method to synthesize MOF-based hybrid catalysts offers a promising route to achieve both high catalytic performance and scalable production. This approach enables the convenient and continuous fabrication of such materials, which could contribute significantly to industrial applications.

1-7. Composition of This Dissertation

The objective of this dissertation is to demonstrate that Cu NPs and Cu–ZnO nano catalysts covered with MOFs can be successfully synthesized using a spray-drying technique. In Chapter 2, we show synthesis of MOFs by spray pyrolysis and spray-drying methods. In Chapter 3, we investigate the potential for synthesizing nanoparticle–MOF composites using microwave-assisted synthesis methods. Subsequently, in Chapter 4, we discuss the synthesis of Cu NPs and amorphous $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6]$ (***amUiO-66***, where BDC = 1,4-benzenedicarboxylate), as well as Cu–ZnO nanocomposites and ***amUiO-66*** hybrid materials. The structural and compositional characteristics of the resulting materials are analyzed using high-resolution transmission electron microscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDX), powder X-ray diffraction (PXRD), and extended X-ray absorption fine structure (EXAFS) spectroscopy.

Furthermore, the catalytic performance of these hybrid materials in the hydrogenation of CO_2 to methanol is investigated. To elucidate the origin of the observed catalytic activity, in situ Fourier-transform infrared (FTIR) spectroscopy is employed to obtain mechanistic insights into the interactions between the active metal sites and the MOF framework at the catalyst–substrate interface.

1-8. References

1. F. Haber, *Z. Für Elektrochem. Angew. Phys. Chem.*, **1914**, 20, 597-604.
2. F. Haber, Nobel Lecture **1920**
3. Report of the federal trade commission on the fertilizer industry January 9, **1950**
4. M. Haruta, Energy Conversion and Catalysts, Japan Society of Energy and Resources Vol.10
No.4 **1989**
5. J. D. Aiken, R. G. Finke, *J. Mol. Catal. Chem.*, **1999**, 145, 1-44.
6. J. D. Aiken, Y. Lin, R.G. Finke, *J. Mol. Catal. A: Chem.* **1996**, 114 29-51.
7. B. R. Cuenya, *Thin Solid Films.*, **2010**, 518, 3127-3150.
8. E. Asada, *US patent*, US4051074A, **1977**
9. K. Vanheusden, *US patent*, US20100269634A1 **2010**
10. M. H. Labranche, *PCT patent*, WO2012091901A1 **2012**
11. Murata Manufacturing Co., Ltd.: Ceramic capacitors – Basics and Application. Ohmsha, (2003
in Japanese).
12. T. Yonezawa, S. Takeoka, H. Kishi, K. Ida, M. Tomonari, *Nanotechnology*, **2008**, 19, 145706
13. S. Kawasaki, *JP patent*, JP2008050650A **2008**
14. Y. Kaneshiro, *PCT patent*, WO2013047332A1 **2013**

15. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.*, **1994**, 801-802.
16. T. Yonezawa, H. Genda, K. Koumoto, *Chem. Lett.*, **2003**, 32, 194-195
17. H. Hirai, H. Wakabayashi, M. Komiyama, *Bull. Chem. Soc. Jpn.*, **1986**, 59, 367-372
18. M. Yamauchi, H. Kobayashi, H. Kitagawa, *ChemPhysChem*, **2009**, 10, 2566-2576
19. X. C. Jiang, C. Y. Chen, W. M. Chen, A. B. Yu, *Langmuir* **2010**, 26(6), 4400-4408
20. W. Doi, *PCT Patent*, WO2013008505A1 **2013**
21. F. Mafune, J. Kohno, Y. Takeda, T. Kondow, H. Sawabe, *J. Phys. Chem. B*, **2000**, 35, 8331-8337
22. Y. Wada *Kakyoushi* **2006**, 54(10), 552
23. Y. Wada, H. Kuramoto, T. Sakata, H. Mori, T. Sumida, T. Kitamura, S. Yanagida, *Chem. Lett.*, **1999**, 28, 607-608
24. M. N. Nadagouda, T. F. Speth, R. S. Varma, *Acc. Chem. Res.*, **2011**, 44, 469-478
25. S. J. Tauster, *Acc. Chem. Res.*, **1987**, 20, 389-394
26. D. Kubička, N. Kumar, T. Venäläinen, H. Karhu, I. Kubičková, H. Österholm, D. Y. Murzin, *J. Phys. Chem. B*, **2006**, 110, 4937-4946.

27. S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, *Coord. Chem. Rev.*, **2016**, *312*, 99-148
28. S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem. Int. Ed.* **2004**, *43*, 2334-2375
29. O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim *Nature*. **2003**, *423*, 705-714.
30. J. R. Long, O. M. Yaghi, *Chem. Soc. Review*, **2009**, *38*, 1213-1214
31. G. Ferey, C. Serre, *Chem. Soc. Review*. **2009**, *38*, 1380-1399
32. G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, K. Kato, M. Takata, T. Yamamoto, S. Toh, S. Matsumura, H. Kitagawa, *Nat. Mater.*, **2014**, *13*, 802-806
33. P. Falcaro, F. Normandin, M. Takahashi, P. Scopece, H. Amenitsch, S. Costacurta, C. M. Doherty, J. S. Laird, M. D. H. Lay, F. Lisi, A. J. Hill, D. Buso, *Adv. Mater.*, **2011**, *23*, 3901-3906
34. Y. Zhao, N. Kornienko, Z. Liu, C. Zhu, S. Asahina, T-R. Kuo, W. Bao, C. Xie, A. Hexemer, O. Terasaki, P. Yang, O. M. Yaghi, *J. Am. Chem. Soc.*, **2015**, *137*, 2199-2202
35. J. Jiang, Y. Zhao, O. M. Yaghi, *Nano Lett.*, **2016**, *138*, 3255-3265
36. G. Li, S. Zhao, Y. Zhang, Z. Tang, *Adv. Mater.*, **2018**, *30*, 1800702
37. B. An, J. Zhang, K. Cheng, P. Ji, C. Wang, W. Lin, *J. Am. Chem. Soc.*, **2017**, *139*, 3834-3840
38. L. Chen, H. Chen, R. Luque, Y. Li, *Chem. Sci.*, **2014**, *5*, 3708-3714

39. B. Rungtaweeworant, J. Baek, J. R. Araujo, B. S. Archanjo, K. M. Choi, O. M. Yaghi, G. A. Somorjai, *Nano Lett.*, **2016**, *16*, 7645-7649

40. S. Yoshimasu, M. Sadakiyo, A. Staykov, K. Kato, M. Yamauchi, *Chem. Comn.*, **2017**, *53*, 6720-6723

41. A. Kato, A. Takayama, Y. Morimitsu, *Nippon Kagaku Kaishi (The Chemical Society of Japan)*, **1985**, *12*, 2342

42. K. A. Moore, J. CesaranoIII, D. M. Smith, T. T. Kodas, *J. Am. Ceram. Soc.*, **1992**, *75*, 213-215

43. T. Fukui, T. Oobuchi, Y. Ikuhara, S. Ohara, K. Kodaera, *J. Am. Ceram. Soc.*, **1997**, *80*, 261-263

44. K. Nagashima, Kyushu University Doctoral Degree Thesis **1990**

45. N. Yamada, Kyushu University Doctoral Degree Thesis **1993**

46. A. C. Sanchez, I. Imaz, M. C. Sarabia, D. Maspoeh. *Nature Chem.*, **2013**, *5*, 203-211

47. S. Tada, S. Satokawa, *Kagakukougaku Kaishi (The Society of Chemical Engineers, Japan)* , **2018**, *12*, 705

48. S. Tada, A. Katagiri, K. Kiyota, T. Honma, H. Kamei, A. Nariyuki, S. Uchida, S. Sato *J. Phys., Chem. C*, **2018**, *122*, 5430-5442

Chapter 2

Synthesis of Metal-Organic Framework by Spray pyrolysis and Spray-Drying Method

2-1. Introduction

Spray methods, such as spray pyrolysis and spray drying are techniques in which a slurry is atomized into fine droplets and introduced into a stream of hot air. This process increases the surface area between the liquid and air, facilitating rapid moisture evaporation and producing dry powders or granules. By directly converting slurries into powders, the spray methods can reduce sequential steps such as filtration, dewatering, drying, pulverization, and classification, thereby streamlining the production process. Although the drying time varies depending on apparatus size and the properties of the liquid, the droplets are typically micrometer-scale sizes, and drying is completed within several tens of seconds. This fast-drying process is advantageous for efficient MOF synthesis. Furthermore, spray drying of precursor solutions or suspensions often produces porous, spherical particles composed of aggregated primary particles. Such structures are beneficial for fabricating composite catalysts that integrate MOFs with functional NPs.

MOFs — also known as porous coordination polymers (PCPs) — have garnered

considerable interest owing to their crystalline nature, tunable pore sizes and surface functionalities (e.g., hydrophobicity/hydrophilicity, acidity/basicity), and structural diversity. These features make MOFs attractive candidates for applications in gas storage⁴⁹⁻⁵¹, gas separation⁵², and ion conduction⁵³. The properties of MOFs can be tailored by rationally selecting metal centers and organic ligands. Despite their potential, conventional synthesis methods such as hydrothermal, MW-assisted⁵⁴, and mechanochemical techniques⁵⁵⁻⁵⁶ still pose challenges for rapid and scalable MOF production. Recently, spray-drying has emerged as a low-cost, rapid, and scalable synthesis method for MOFs. It also enables control over particle size and morphology by tuning solvent and heating conditions. However, to date, spray-drying has primarily been applied to MOFs with a single type of ligand.

In this study, we report the synthesis of HKUST-1 ($[\text{Cu}_3(\text{BTC})_2]$; BTC = 1,3,5-benzene tricarboxylic acid) by spray pyrolysis as well as the synthesis of ZIF-8: $[\text{Zn}(\text{MeIM})_2]$ (MeIM = 2-methylimidazolate), UiO-66 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6$; BDC = 1,4-benzenedicarboxylate) and CID-1 ($[\text{Zn}_2(\text{ip})_2(\text{bpy})_2]$; ip = isophthalate, bpy = 4,4'-bipyridine) using a seed-mediated spray-drying technique. Notably, this represents the first successful preparation of a MOF composed of two distinct ligands via this method.

In typical spray methods, such as spray pyrolysis and spray drying, precursors dissolved

in a solvent are atomized and carried through a heated zone by a gas stream. Solvent vaporization initiates the self-assembly of MOFs, and the products are collected as dry powders (Figure 2a). In our approach, we particularly focus on forming MOF "seeds" before the precursor enters the heated zone (Figure 2b). These seeds are expected to act as nucleation centers, accelerating crystal growth compared to systems using direct precursor injections without seeding. For the synthesis of MOFs, we controlled operational conditions, including the precursor solution feed rate and gas flow rate, and conducted the process within the temperature range in which the MOF ligands do not thermally decompose (Table 1).

As the first demonstration of this seed-mediated spray-drying technique, we selected UiO-66 due to its outstanding thermal stability (above 673 K), and its resistance to water and chemicals—properties that make it highly suitable for catalytic applications⁵⁷ and CO₂ capture⁵⁸. Although many MOFs are conventionally synthesized using organic solvents, their industrial production remains costly and resource intensive. To address this, we investigated the feasibility of synthesizing MOFs from aqueous solutions. Replacing organic solvents with water significantly reduces production costs and capital investment required for large-scale manufacturing. However, the poor water affinity of many MOF ligands has historically impeded aqueous-phase synthesis. To date, ZIF-8 remains one of the few MOFs that can be successfully synthesized in water.

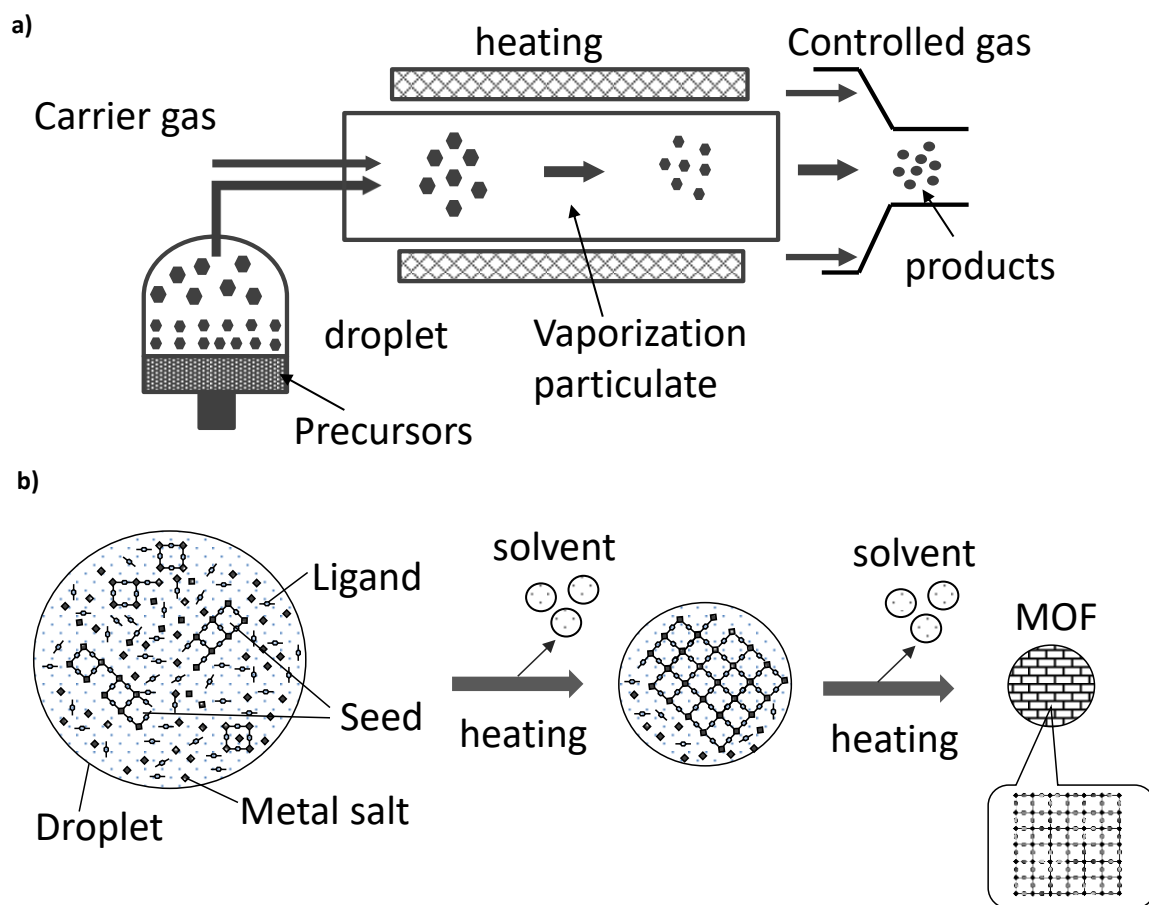
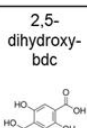
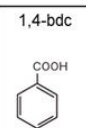
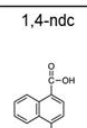
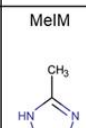
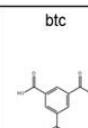
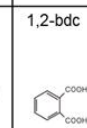
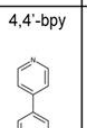
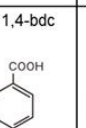
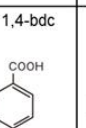


Figure 2. a) Schematic illustration of a typical spray pyrolysis and spray-drying system. b) Schematic illustration of the MOF formation process by the seed-mediated spray-drying method

Table 1. Various MOFs and the decomposition temperatures of their constituent ligands.

MOF									
Metal	Zn	Al	Al	Zn	Cu	Zn		Zn	Zr
Ligand	2,5-dihydroxy-bdc 	1,4-bdc 	1,4-ndc 	MeIM 	btc 	1,2-bdc 	4,4'-bpy 	1,4-bdc 	1,4-bdc 
Decomposition temp. of the ligand determined by TG in N ₂	250 ~	250 ~	450 ~	120 ~	250 ~	250 ~	150 ~	250 ~	250 ~

2-2. Experimental

Synthesis of samples

Synthesis of $[\text{Cu}_3(\text{BTC})_2]$; (BTC = 1,3,5-benzene tricarboxylic acid) : HKUST-1

Spray Pyrolysis

All chemicals were used as received from commercial suppliers (FUJIFILM-Wako) without further purification. Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 1.45 g, 6.0 mmol) and 1,3,5-benzenetricarboxylic acid (H_3BTC , 0.84 g, 4.0mmol) were dissolved in 40 mL of N, N-dimethylformamide (DMF). This solution was then introduced into a spray pyrolysis equipment. Pure air was employed as the carrier gas with a flow rate of 2 L/min. The feed solution was delivered at a rate of 10 mL/min through a conical nebulizer. The inlet temperature of the furnace was maintained at 500 °C. Upon passage through the heating zone, a dark blue powder was immediately collected. The resulting product is referred to as **HKUST-1-S**.

Hydrothermal Method

For comparison, HKUST-1 was also synthesized by a conventional hydrothermal method. All chemicals were used as received from commercial suppliers (FUJIFILM-Wako) without further purification. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.875 g, 3.6 mmol) were dissolved in de-ionized water (12ml) and

mixed with H₃BTC (0.42 g, 2.0 mmol) dissolved in ethanol (12ml) at room temperature. The mixture was filled in a Teflon liner and sealed and heated at 180 °C for 12 hours under static conditions. After cooling to room temperature in air, the resulting blue crystalline product was collected by filtration, thoroughly washed with ethanol and water, and dried at room temperature. This hydrothermal synthesis method follows previous reports and the resulting product is referred to as **HKUST-1-H**⁵⁹.

Synthesis of [Zn(MeIM)₂] ; (MeIM = 2-methylimidazolate) : ZIF-8

Seed-Mediated Spray-Drying Method

Zinc acetate dihydrate (0.878 g, 4mmol FUJIFILM-Wako) and 2-methylimidazole (0.657g, 8mmol TCI) were dissolved in 100 mL of de-ionized water and stirred for approximately 60 minutes. This solution was then introduced into a spray dryer. Spray drying was performed using a Mini Spray Dryer B-290 (BÜCHI) equipped with a two-fluid nozzle using nitrogen gas as the carrier. Pure air was employed as the carrier gas with a flow rate of 250 mL/min. The feed solution was delivered at a rate of 5 mL/min through a fluid nozzle with an orifice diameter of 0.4 mm. The inlet temperature of the drying chamber was maintained at 200 °C. Upon passage through

the heating zone, a white powder was immediately collected in the spray dryer's product chamber.

The resulting material was subsequently dried at 100 °C for 2 hours to ensure complete removal of residual moisture. The resulting product is referred to as **ZIF-8-S**.

Hydrothermal Method

For comparison, ZIF-8 was also synthesized via a conventional hydrothermal method. Zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.42 g, 2mmol FUJIFILM-Wako) and 2-methylimidazole (0.32 g 4mmol TCI) were dissolved in 40 mL of N, N-dimethylformamide (DMF FUJIFILM-Wako) in a 100 mL screw-cap vial. The solution was heated in a programmable oven at a rate of 5 °C/min to 140 °C and maintained at this temperature for 24 hours. Subsequently, the vial was cooled to room temperature at a rate of 0.4 °C/min. After decanting the mother liquor, chloroform was added to the reaction mixture. Colorless polyhedral crystals were collected from the upper layer, washed with DMF, and air-dried for 10 minutes. The typical yield was approximately 0.05 g. The resulting product is referred to as **ZIF-8-H**.

Synthesis of $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_6]$; (BDC = 1,4-benzenedicarboxylate) : UiO-66

Seed-Mediated Spray-Drying Method

In the seed-mediated spray-drying synthesis of UiO-66, 1,4-benzenedicarboxylic acid (H_2BDC 0.38 g, 2.29mmol FUJIFILM-Wako) and zirconium acetylacetonate $[\text{Zr}(\text{acac})_4]$, (1.07 g 2.19mmol, Aldrich) were separately dissolved in N, N-dimethylformamide (DMF, 200 mL, FUJIFILM-Wako). The two solutions were mixed and stirred at 80–90 °C for 2 hours to produce UiO-66 seed crystals in solution. This seed solution was then subjected to spray drying to obtain the **UiO-66-S** sample. Spray drying was performed using a Mini Spray Dryer B-290 (BÜCHI) equipped with a two-fluid nozzle (orifice diameter: 0.4 mm), using nitrogen gas as the carrier. The feed rate was set to 5 mL/min, the gas flow rate to 300 mL/min, and the inlet temperature to 220 °C. Upon passing through the heating zone, the solution yielded a white powder that was immediately collected in the cyclone separator. The obtained material was further dried under vacuum at 150 °C for 2 hours to remove residual DMF and byproducts such as acetic acid.

Hydrothermal Method

For comparison, UiO-66 was also synthesized by a conventional hydrothermal method. All chemicals were used as received from commercial suppliers (FUJIFILM-Wako) without further

purification. Zirconium chloride (ZrCl_4 , 0.053 g, 0.227 mmol) and 1,4-benzenedicarboxylic acid (H_2BDC , 0.034 g, 0.227 mmol) were dissolved in N, N-dimethylformamide (DMF, 20mL) at room temperature. The mixture was sealed and heated at 120 °C for 24 hours under static conditions. After cooling to room temperature in air, the resulting solid product was collected by filtration, thoroughly washed with methanol and water, and dried at room temperature. This hydrothermal synthesis method follows previous reports and the resulting product is referred to as **UiO-66-H**⁶⁰⁻⁶¹.

Synthesis of $[\text{Zn}_2(\text{ip})_2(\text{bpy})_2]$; (ip = isophthalate, bpy = 4,4'-bipyridine): CID-1

Seed-Mediated Spray-Drying Method

All chemicals were used as received from commercial suppliers (FUJIFILM-Wako) without further purification. To synthesize CID-1 via a seed-mediated spray-drying method, a mixture of zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1.19 g, 4.55mmol), isophthalic acid (H_2ip , 0.664 g, 4mmol Wako), and 4,4'-bipyridine (bpy, 0.624 g, 4mmol) was dissolved in N, N-dimethylformamide (DMF) and stirred at 50–60 °C for 30 minutes to form seed crystals. The resulting seed solution was then introduced into a spray dryer equipped with a two-fluid nozzle

(orifice diameter: 0.4 mm), using nitrogen gas as the carrier. The spray-drying parameters were set to a feed rate of 5 mL/min, gas flow rate of 300 mL/min, and an inlet temperature of 220 °C. After passing through the heating zone, a white powder was immediately collected in the cyclone collector. The collected powder was further dried under vacuum at 150 °C for 2 hours to remove residual DMF, and the resulting material was denoted as **CID-1-S**.

Hydrothermal Method

All chemicals were used as received from commercial suppliers (FUJIFILM-Wako) without further purification. For comparison, CID-1 was also synthesized via a conventional hydrothermal method. A solution of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.97 g, 10 mmol) in N, N-dimethylformamide (DMF) 10ml was mixed with a separate 10ml DMF solution containing isophthalic acid (H_2ip , 1.66 g, 10 mmol) and 4,4'-bipyridine (bpy, 1.56 g, 10 mmol). The combined solution was left to stand undisturbed at 393 K for several days. The resulting white precipitate was collected by filtration, washed successively with DMF, water, and ethanol, and dried under vacuum at 403 K. This product is referred to as **CID-1-H**⁶².

Experimental Procedure

Scanning Electron Microscopy (SEM)

For SEM observation, the samples were dispersed in ethanol and dropped onto carbon tape mounted on an aluminum sample holder. After drying, SEM images were acquired using a Hitachi SU8020 scanning electron microscope operated at an acceleration voltage of 5 kV.

Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR measurements were performed using a JASCO FT/IR-4200 spectrometer to identify functional groups present in the samples.

Powder X-ray Diffraction (PXRD)

PXRD patterns of UiO-66 samples were recorded using a Rigaku SmartLab automated multipurpose X-ray diffractometer. CID-1 samples were analyzed using a Bruker D8 ADVANCE diffractometer.

Nitrogen Sorption Isotherms

N₂ sorption isotherms were measured at 77 K using a BELSORP-mini instrument (Microtrac BEL Corp.) based on volumetric adsorption techniques. Prior to measurement, the

samples were activated under vacuum at 423 K for 15 hours.

2-3. Result and Discussion

From SEM images of HKUST-1 samples, **HKUST-1-H** exhibited well-defined crystals with a diameter of several micrometers (Figure 3a), while the **HKUST-1-S** obtained by the spray method based on spray pyrolysis exhibited a spherical hollow morphology (Figure 3b). The XRD patterns of the samples synthesized by the spray pyrolysis and hydrothermal methods were compared. As shown in Figure 4, the PXRD results indicate that the **HKUST-1-S** sample has the same crystal structure as that synthesized by the hydrothermal method (**HKUST-1-H**).

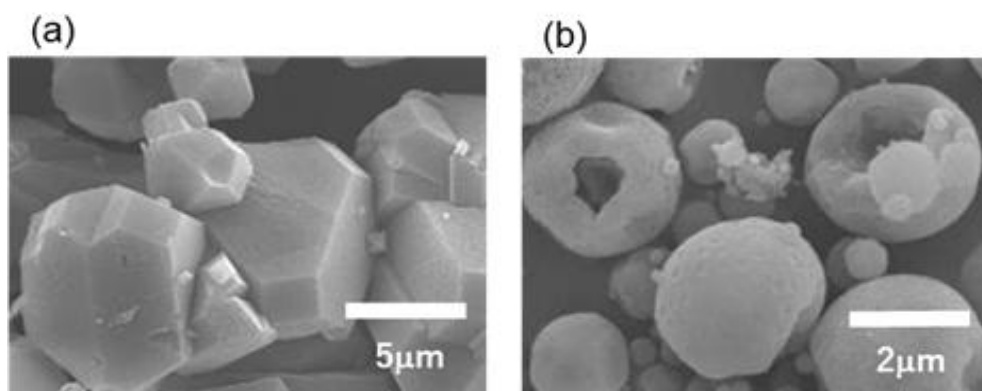


Figure 3. SEM images of (a) **HKUST-1-H** and (b) **HKUST-1-S**.

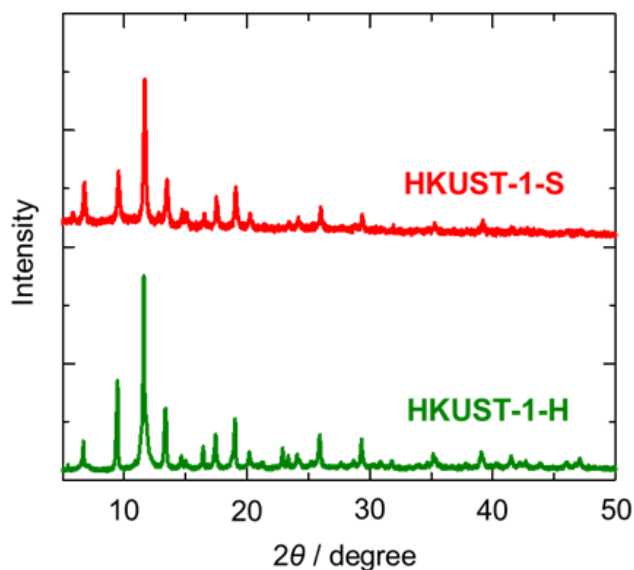


Figure 4. XRD patterns of **HKUST-1-H** and **HKUST-1-S**.

CO₂ adsorption/desorption isotherms were measured at 195 K for the **HKUST-1-S** and **HKUST-1-H** samples (Figure 5). Prior to the measurements, each sample was activated at 150 °C for 12 h under vacuum. The **HKUST-1-H** sample exhibited type I isotherms, which originate from its microporosity. However, the total adsorbed volume of **HKUST-1-S** was much lower than that of **HKUST-1-H**. Considering that a hollow morphology, which corresponds to the initial stage of particle formation (Figure 1b), was observed for **HKUST-1-S** from the SEM image (Figure 3b), the MOF formation was likely incomplete, resulting in a significantly lower adsorption capacity.

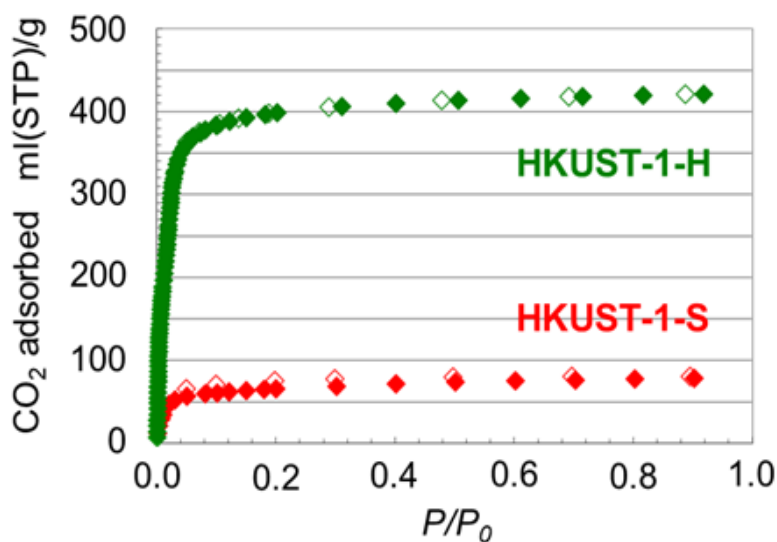


Figure 5. CO₂ adsorption/desorption isotherms were measured at 195 K for the **HKUST-1-S** and **HKUST-1-H** samples

Then, we discuss the origin of the incomplete formation of HKUST-1 using a LaMer diagram, which describes the time evolution of particle formation as a function of concentration (Figure 6). The LaMer diagram indicates that concentration during the nucleation stage is a critically important factor governing particle growth. In the spray pyrolysis synthesis of HKUST-1 in this study, the heating time is considered to be too short to ensure sufficient nucleation, leading to the formation of incomplete HKUST-1 with a low CO₂ adsorption capacity. On the basis of this hypothesis, we propose that introducing a solution containing pre-formed MOF nuclei can promote crystal growth. Accordingly, the synthesis protocol was changed from spray pyrolysis to

a seed-mediated spray method, in which the ligand and metal salt were preheated and stirred to form seed crystals for sufficient MOF crystal growth.

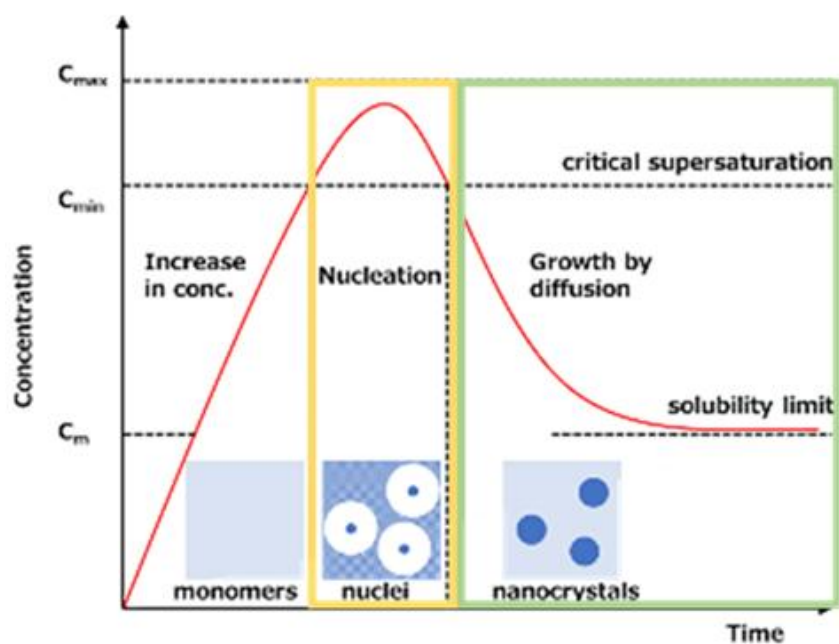


Figure 6. La Mer diagram for the generation of atoms, nucleation, and subsequent growth of colloidal systems (V. K. LaMer, R. H. Dinegat *J. Am. Chem. Soc.* **1950**, *72* 4857).

SEM image revealed that the **ZIF-8-S** sample obtained via the seed-mediated spray drying method exhibited a spherical morphology with a diameter of several micrometers. A high-magnification SEM image further indicated that **ZIF-8-S** was composed of agglomerated NPs with diameters of less than 100 nm (Figure 7).

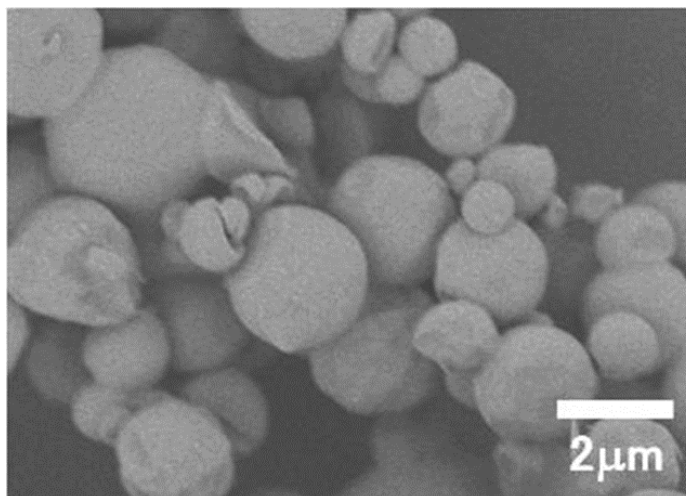


Figure 7. SEM image of **ZIF-8-S**

The XRD patterns of the samples synthesized by spray drying and hydrothermal methods were compared. As shown in Figure 8, the PXRD results showed that the **ZIF-8-S** sample had the same crystal structure as that synthesized by the hydrothermal method (**ZIF-8-H**).

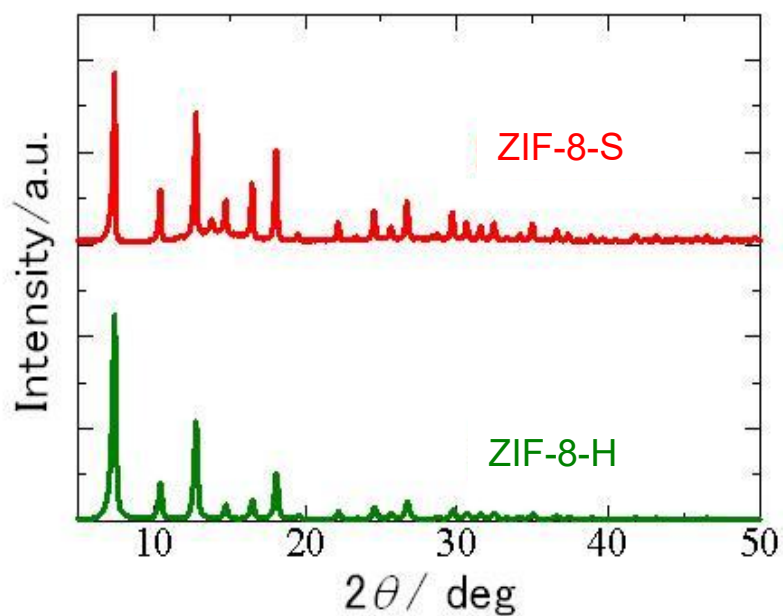


Figure 8. PXRD patterns of **ZIF-8-S** and **ZIF-8-H**

IR spectra confirmed that the absorption bands of **ZIF-8-S** were identical to those of **ZIF-8-H** (Figure 9). N₂ adsorption/desorption isotherms were measured at 77 K for the **ZIF-8-S** and **ZIF-8-H** samples (Figure 10). Prior to measurement, each sample was activated at 150 °C for 12 hours under vacuum. Both samples exhibited type I isotherms, which originate from microporosity. The slight decrease in the total adsorbed volume observed for **ZIF-8-S** suggests a partial loss of microporosity.

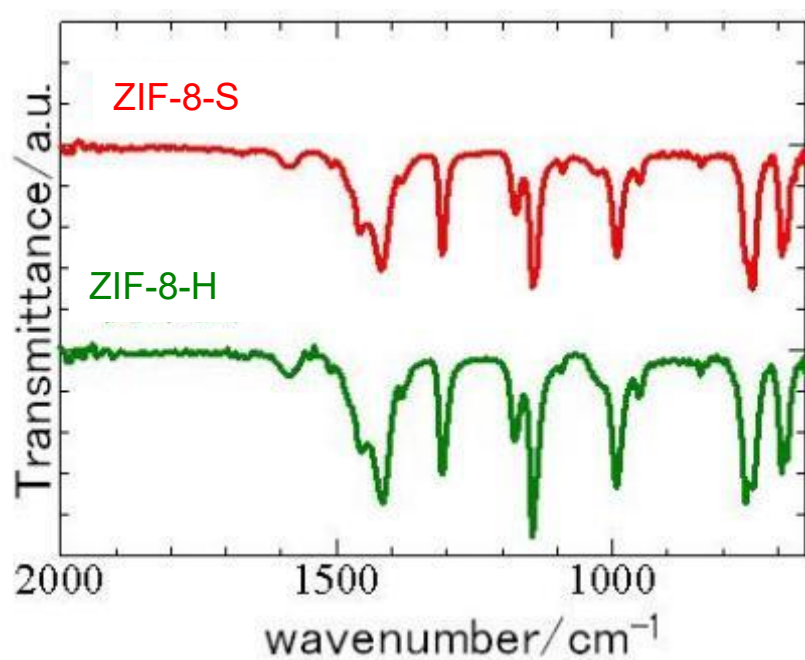


Figure 9. IR spectra of **ZIF-8-S** and **ZIF-8-H**

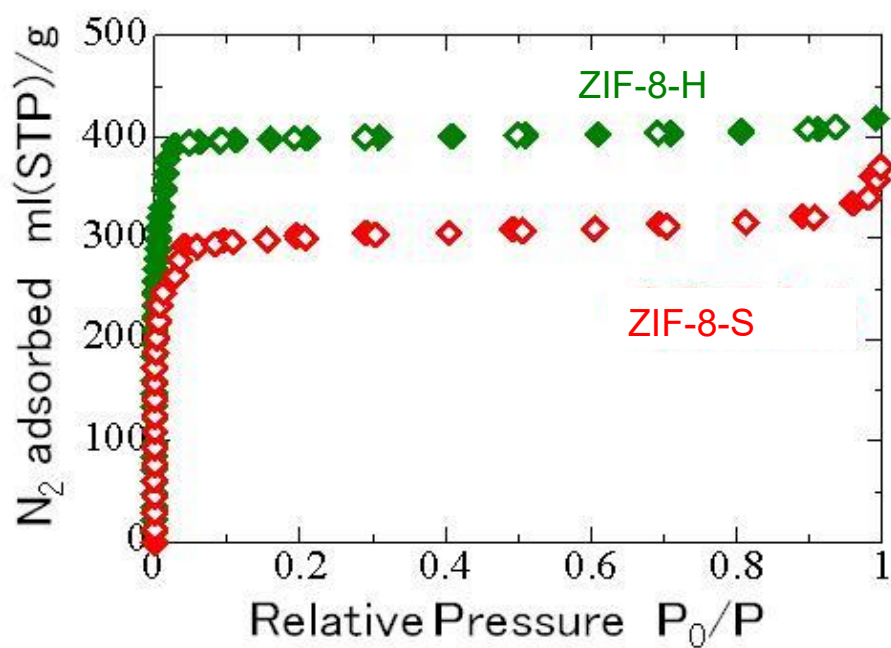


Figure 10. N_2 adsorption/desorption isotherms of **ZIF-8-S** and **ZIF-8-H**

SEM image revealed that the **UiO-66-S** sample obtained by the seed-mediated spray-drying method had a spherical morphology with a diameter of several micrometers. High-magnification SEM images further indicated that **UiO-66-S** consisted of agglomerates composed of primary particles less than 100 nm in diameter (Figure 11).

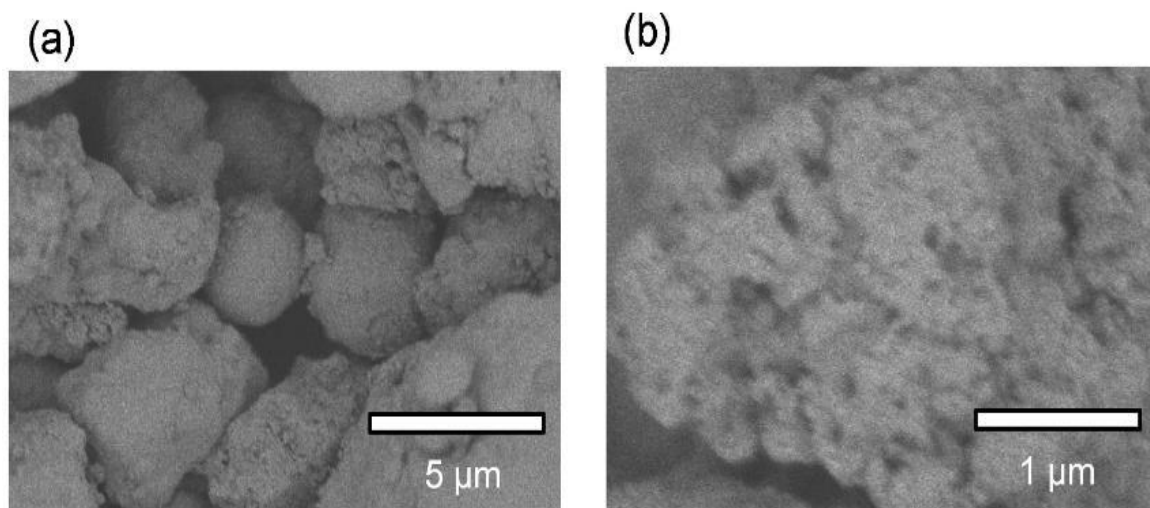


Figure 11(a)(b). SEM image of **UiO-66-S**

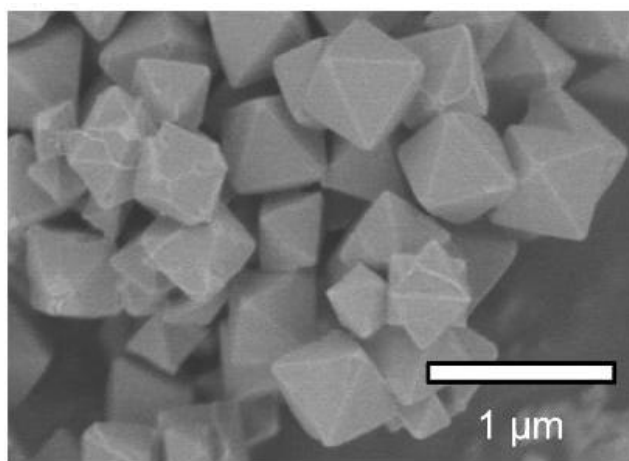


Figure 12. SEM image of **UiO-66-H**

In contrast, **UiO-66-H** exhibited well-defined octahedral crystals with an average size of approximately 500 nm (Figure 12).

The PXRD patterns of samples synthesized using spray-drying and hydrothermal methods showed that the crystal structure of the **UiO-66-S** sample was the same as that of the **UiO-66-H** sample. However, the diffraction peaks of **UiO-66-S** were relatively broad and weak compared to those of **UiO-66-H**, indicating lower crystallinity and/or a smaller crystallite size (Figure 13).

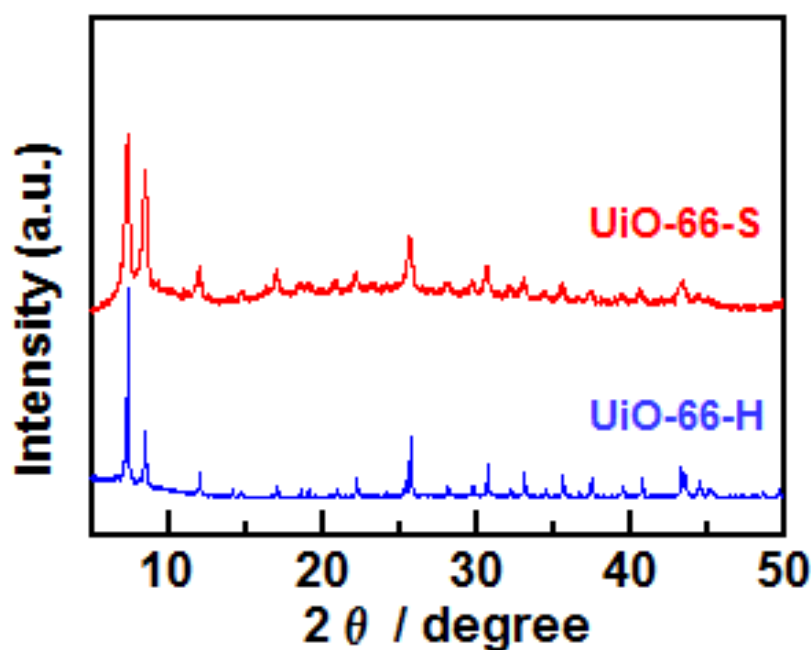


Figure 13. PXRD patterns of **UiO-66-S** and **UiO-66-H**

IR spectra confirmed that the absorption bands of **UiO-66-S** were identical to those of **UiO-66-H** (Figure 14). N_2 adsorption/desorption isotherms were measured at 77 K for both **UiO-66-S** and **UiO-66-H** samples (Figure 15). Prior to the measurements, each sample was activated at 150 °C for 12 hours under vacuum. Both samples exhibited typical type-I isotherms,

characteristic of microporous materials. A slight decrease in the total adsorbed volume observed for **UiO-66-S** suggests partial loss of microporosity, which is consistent with the PXRD results.

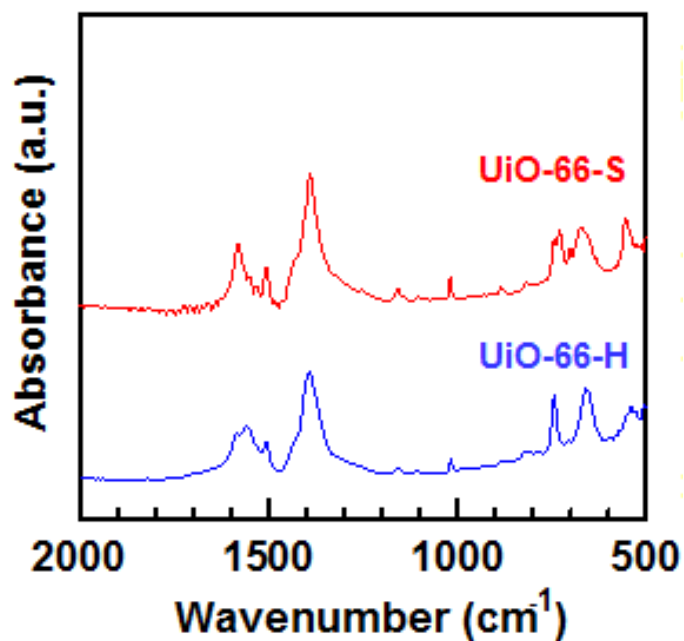


Figure 14. IR spectra of **UiO-66-S** and **UiO-66-H**

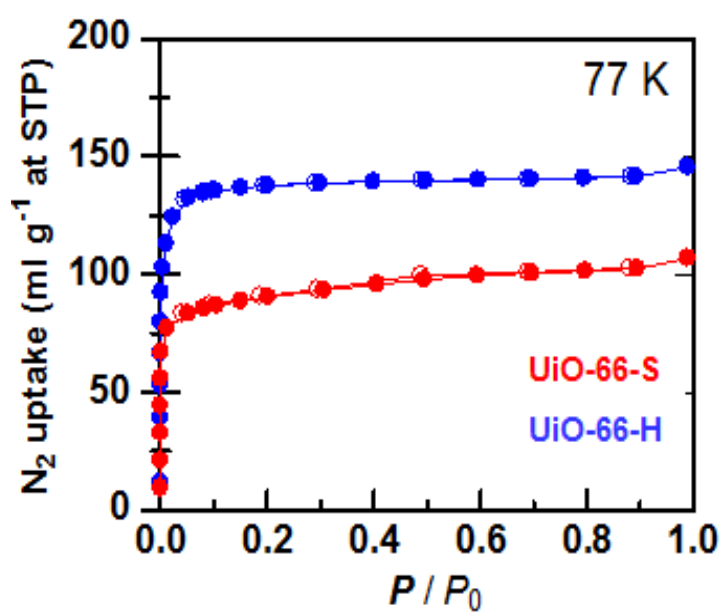
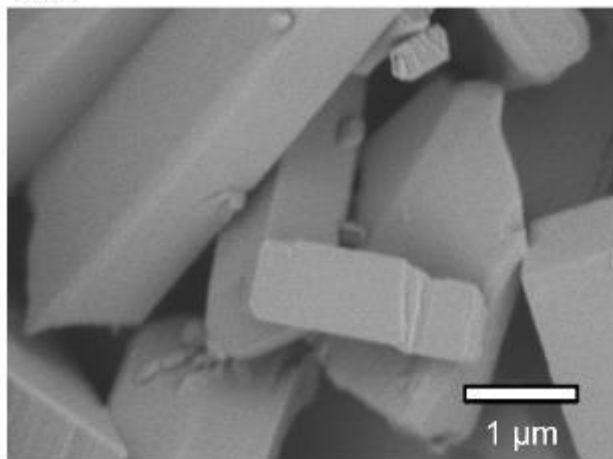


Figure 15. N₂ adsorption/desorption isotherms of **UiO-66-S** and **UiO-66-H**

To further validate the role of seed formation, we conducted a control experiment using a typical spray-drying procedure without the introduction of seed crystals. The atomized precursors were injected directly into the heating zone without prior seed formation, resulting in an amorphous product. This clearly demonstrates that seed particles play a crucial role in promoting the crystallization of MOFs during spray drying. It is worth noting that while ZrCl_4 is commonly used as a zirconium precursor for the synthesis of UiO-66, the chloride ions can corrode stainless-steel components of the spray dryer. In this study, we employed $\text{Zr}(\text{acac})_4$ as the metal precursor, which avoids corrosion issues and offers significant advantages in terms of handling safety and scalability for mass production.

To date, the spray-drying method has mainly been applied to the synthesis of MOFs containing a single type of organic ligand. In this study, we extended the approach to a flexible coordination polymer composed of two different organic ligands. As a proof of concept, we selected CID-1, a pillared-layer-type MOF, for demonstration. In a typical spray-drying synthesis of **CID-1-S**, the resulting sample did not exhibit a well-defined spherical morphology (Figure 16b). Compared to the SEM image of **CID-1-H** synthesized by the hydrothermal method (Figure 16a), the **CID-1-S** sample displayed a non-uniform size distribution, with particles ranging from the micrometer to the nanometer scale observed.

(a)



(b)

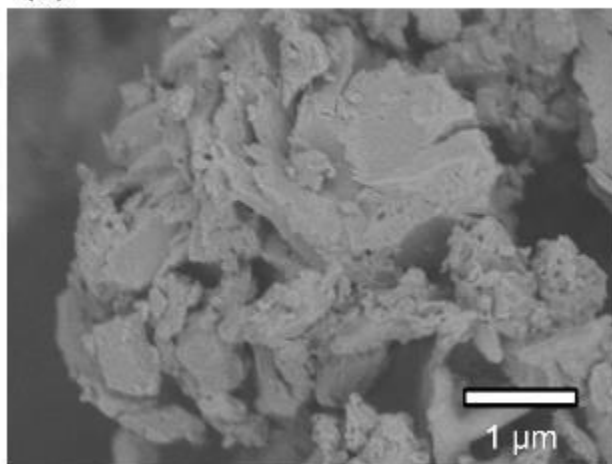


Figure 16. SEM images of (a) **CID-1-H** and (b) **CID-1-S**

The structure of CID-1 NPs has been reported to differ from that of the bulk⁶³⁻⁶⁴. The XRD pattern of **CID-1-S** in this study was also not fully consistent with that of **CID-1-H** (Figure 17).

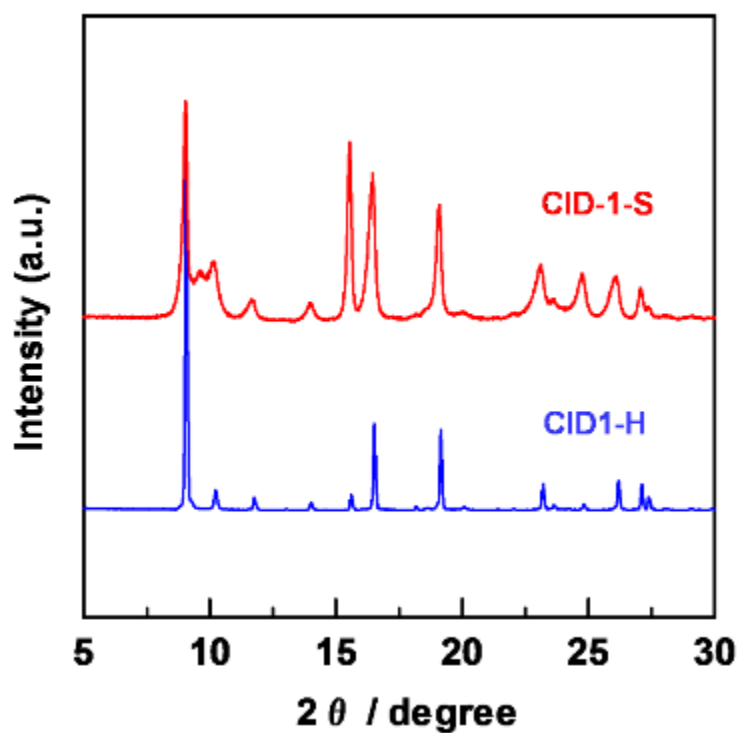


Figure 17. PXRD patterns of **CID-1-S** and **CID-1-H**

We then performed a LeBail analysis of the XRD pattern of **CID-1-S**. This was reproduced by summing the fitting curves derived from the CID-1 bulk and nanoparticle components (Figure 18, Table 2).

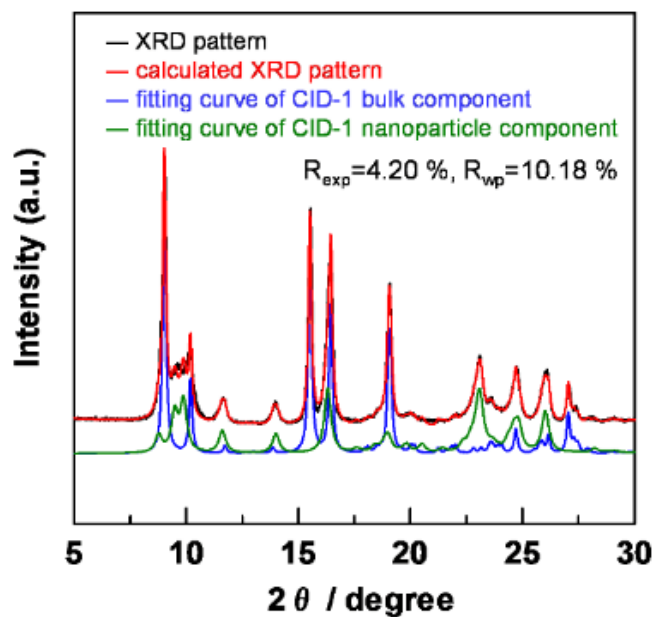


Figure 18. LeBail analysis of the XRD pattern of **CID-1-S**

Table 2. Cell parameters of **CID-1-S** with bulk and nanocrystal components

Component	<i>a</i> /Å	<i>b</i> /Å	<i>c</i> /Å	<i>α</i> /°	<i>β</i> /°	<i>γ</i> /°
CID-1 bulk	9.173(1)	10.0815(6)	10.177(2)	78.50(1)	72.526(9)	79.25(1)
CID-1 nanoparticle	9.525(2)	10.443(2)	9.962(3)	77.10(3)	71.62(2)	78.25(2)

The IR spectrum confirmed that CID-1 was successfully synthesized via the spray-drying method (Figure 19).

To evaluate the porosity of the material, the CO₂ adsorption isotherm of **CID-1-S** was measured at 195 K and compared with that of **CID-1-H**. Prior to measurement, each sample was

activated at 150 °C for 12 hours. **CID-1-S** exhibited a typical Type-I adsorption behavior, indicative of microporosity, similar to that observed for **CID-1-H** (Figure 20).

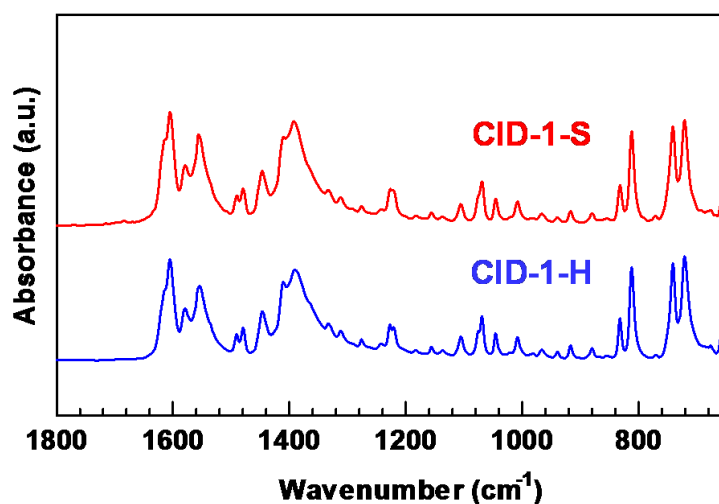


Figure 19. IR spectra of **CID-1-S** and **CID-1-H**

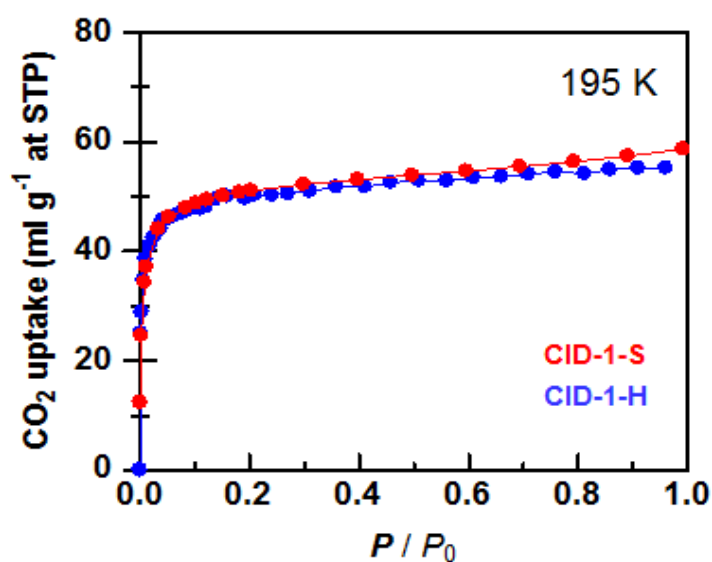


Figure 20. CO₂ adsorption/desorption isotherms of **CID-1-S** and **CID-1-H**

The total volume of CO₂ adsorbed was comparable between the two samples. These results demonstrate that the spray-drying technique can be successfully extended to the synthesis

of MOFs consisting of two or more types of ligands.

2-4. Conclusion

In this study, we successfully synthesized UiO-66 and ZIF-8 via the spray-drying method by their seed crystals. A comparative experiment without the seed demonstrated that seed formation plays a critical role in promoting the growth of the MOF during the spray-drying process. This finding provides valuable insight into the formation mechanism of MOFs synthesized through this method. Furthermore, we achieved the first successful synthesis of CID-1 — the MOF composed of two different organic ligands — using the spray-drying technique. This represents a significant advancement, as previous applications of spray drying have been limited to MOFs with a single ligand type. The successful fabrication of CID-1 indicates the potential of this method to expand the structural diversity of MOFs accessible via scalable synthesis. Importantly, the spray-drying process employed in this study utilized an aqueous solvent system, which is advantageous for practical applications due to its environmental compatibility and cost-effectiveness. This work thus presents a new synthetic strategy for the facile and scalable production of MOFs and is expected to contribute to the broader application and industrialization of MOF materials.

2-5. References

49. M. Eddaoudi, H. Li, T. M. Reineke, M. Fehr, O. M. Yaghi, *Science*. **2002**, 295, 469-472.
50. N. L. Rosi, J. Eckert, M. Eddaoudi, D.T. Vodak, J. Kim, M. O’Keeffe, O. M. Yaghi, *Science*. **2003**, 300, 1127-1129.
51. H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. Choi, A. O. Yazaydin, R.Q. Snurr, M. O’Keeffe, J. Kim, K. Kaneko, O. M. Yaghi, *Science*. **2010**, 329, 424-428
52. J. R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Review* **2009**, 38, 1477-1504
53. M. Sadakiyo T. Yamada, H. Kitagawa, *J. Am. Chem. Soc.* **2009**, 131, 9906-9907
54. Y.-K. Seo, J.-S. Chang, Y. K. Hwang, G.H. Young, S. H. Jung, *Micropor. Mesopor. Mat.* **2009**, 119, 331-339.
55. D. Braga, S. L. Giaffreda, F. Grepiomi, M. R. Chierotti, R. Gobetto, *Dalton Trans.*, **2006**, 1249-1269
56. M. Klimakow, P. Klobes, A. Thünemann, K. Rademann, F. Emmerling, *Chem. Mater.* **2010**, 22, 5216-5221
57. M. Kandiah, M.H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, K. P. Lillerud, *Chem. Mater.* **2010**, 22, 6632-6640
58. C. H. Lau, R. Babarao, M. R. Hill, *Chem. Commun.* **2013**, 49, 3634

59. K.Schlichte, T.Kratzke, S.Kaskel, *Micropor. Mesopor. Mater.* **2004**, *73*, 81.
60. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, K. P. Lillerud, S. Bordiga, C. Candles, *J. Am. Chem. Soc.* **2008**, *130*, 13850.
61. M. J. Katz, J. E. Mondloch, R. K. Totten, J. K. Park, S. T. Nguyen, J. T. Hupp, O. K. Farha, *Chem. Commun.* **2013**, *49*, 9449.
62. S. Horike, D. Tanaka, S. Kitagawa, *Chem. Commun.* **2007**, *32*, 3395-3397.
63. Y. Hijikata, D. Tanaka, B. Giese, S. Kitagawa, *Chem. Commun.* **2011**, *47*, 7632-7634.
64. Y Mitsuka, *JP patent*, 5795195B2, **2015**

Chapter 3

One-Step Synthetic Method for Metal/MOF Composites via Microwave Irradiation

3-1. Introduction

Significant advances have been made over the past few decades in the design and synthesis of composite materials comprising metal NPs and MOFs. There are two main synthetic strategies for these composites: (i) post-synthetic hybridization, in which metal NPs are deposited onto pre-formed MOFs (Figure 21a)⁶⁵⁻⁷⁰, and (ii) MOF growth on pre-synthesized metal NPs (Figure 21b). While both methods have been extensively explored and have produced a variety of functional materials, they typically require multi-step procedures involving complex operations, hindering their scalability and cost-effectiveness. To overcome these challenges, developing one-pot synthetic approaches for metal/MOF hybrids is of significant interest. In this section, we present a one-step synthesis method for metal NPs/MOF composites using MW irradiation, offering a rapid and energy-efficient technique for directly fabricating these hybrid structures (Figure 21c)⁷¹.

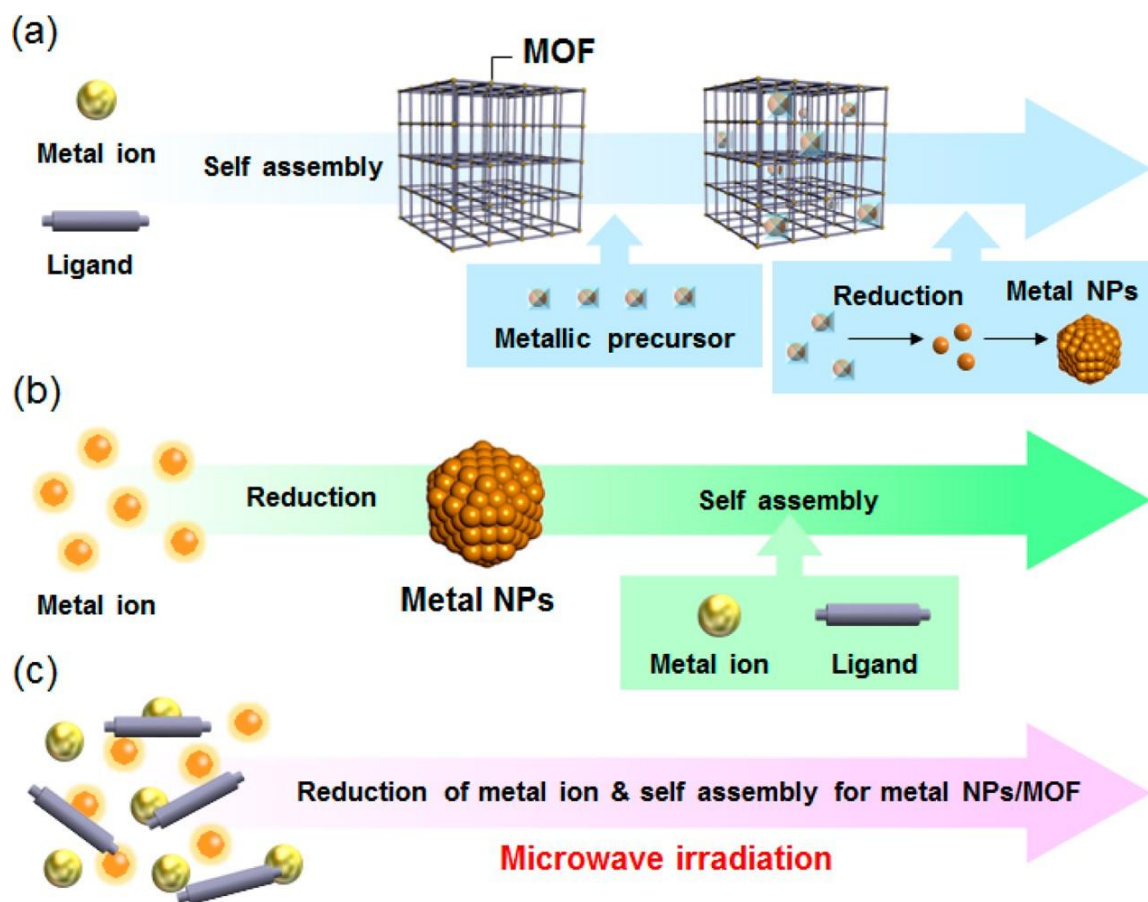


Figure 21. Synthesis images of metal/MOF nanomaterials

3-2. Experimental

Synthesis of samples

Chemicals

All reagents were purchased from commercial suppliers (FUJIFILM Wako Pure Chemical Corporation, Sigma-Aldrich) and used without further purification. Specifically, zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole, and N,N-dimethylformamide (DMF) were obtained from FUJIFILM Wako, and palladium acetylacetonate [$\text{Pd}(\text{acac})_2$] was obtained from Sigma-Aldrich.

Synthesis of Pd/ZIF-8-MW

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.59 g, 2 mmol), 2-methylimidazole (0.33 g, 4 mmol), and $\text{Pd}(\text{acac})_2$ (0.05 g, 0.16 mmol) was dispersed in N,N-dimethylformamide (DMF 10 mL). The resulting solution was subjected to MW irradiation at 180 °C for 1 h using a Biotage Initiator+ microwave reactor. After completion of the reaction, the precipitate was collected by filtration, washed thoroughly with ethanol, and dried under vacuum.

3-3. Result and Discussion

The XRD analysis revealed that the ZIF-8 sample synthesized using MW irradiation (**ZIF-8-MW**) exhibited a similar diffraction pattern to the commercially available ZIF-8 (Basolite Z1200), as shown in Figure 22a. Furthermore, the XRD pattern of the Pd-containing sample (**Pd/ZIF-8-MW**), prepared using the same synthetic procedure as **ZIF-8-MW** except for the addition of Pd(acac)₂, showed diffraction peaks corresponding to ZIF-8 and metallic Pd. These results demonstrate the successful formation of hybrid material.

IR spectroscopy confirmed that the characteristic absorption bands of ZIF-8 were preserved in both **ZIF-8-MW** and **Pd/ZIF-8-MW** (Figure 22b). Notably, the IR spectrum of **Pd/ZIF-8-MW** showed that the Pd NPs were incorporated directly into the ZIF-8 framework without the use of additional capping agents.

Nitrogen adsorption–desorption isotherms were measured at 77 K for ZIF-8, **ZIF-8-MW**, and **Pd/ZIF-8-MW** (see Figure 22c). Prior to measurement, each sample was activated at 150 °C for 12 hours under vacuum. Both **ZIF-8-MW** and **Pd/ZIF-8-MW** exhibited type I isotherms, which are indicative of microporous structures. The slight reduction in adsorption capacity observed for **Pd/ZIF-8-MW** suggests the presence of Pd NPs within the framework.

The composite structure of **Pd/ZIF-8-MW** was further examined using bright-field STEM. As shown in Figure 23a, the Pd NPs were found to be located around the ZIF-8 particles. The average size of the Pd NPs was estimated to be 14.5 ± 3.1 nm. STEM images (Figures 23b–d) clearly demonstrated that the Pd NPs are uniformly distributed around the ZIF-8 matrix. This MW-assisted technique is anticipated to serve as a powerful and versatile platform for the one-pot synthesis of a wide range of metal nanoparticle/MOF composites in future applications.

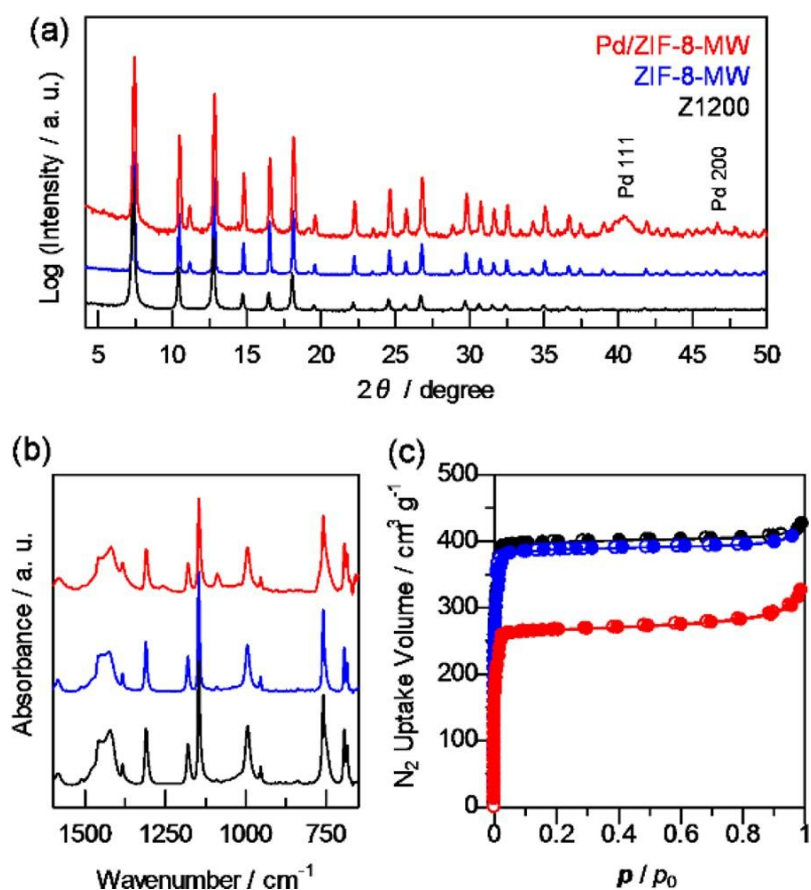


Figure 22. (a) PXRD patterns of **Pd/ZIF-8-MW**, **ZIF-8-MW** and Basolite Z1200 (b) IR spectra of **Pd/ZIF-8-MW**, **ZIF-8-MW** and Basolite Z1200 (c) N_2 adsorption/desorption isotherms of **Pd/ZIF-8-MW**, **ZIF-8-MW** and Basolite Z1200

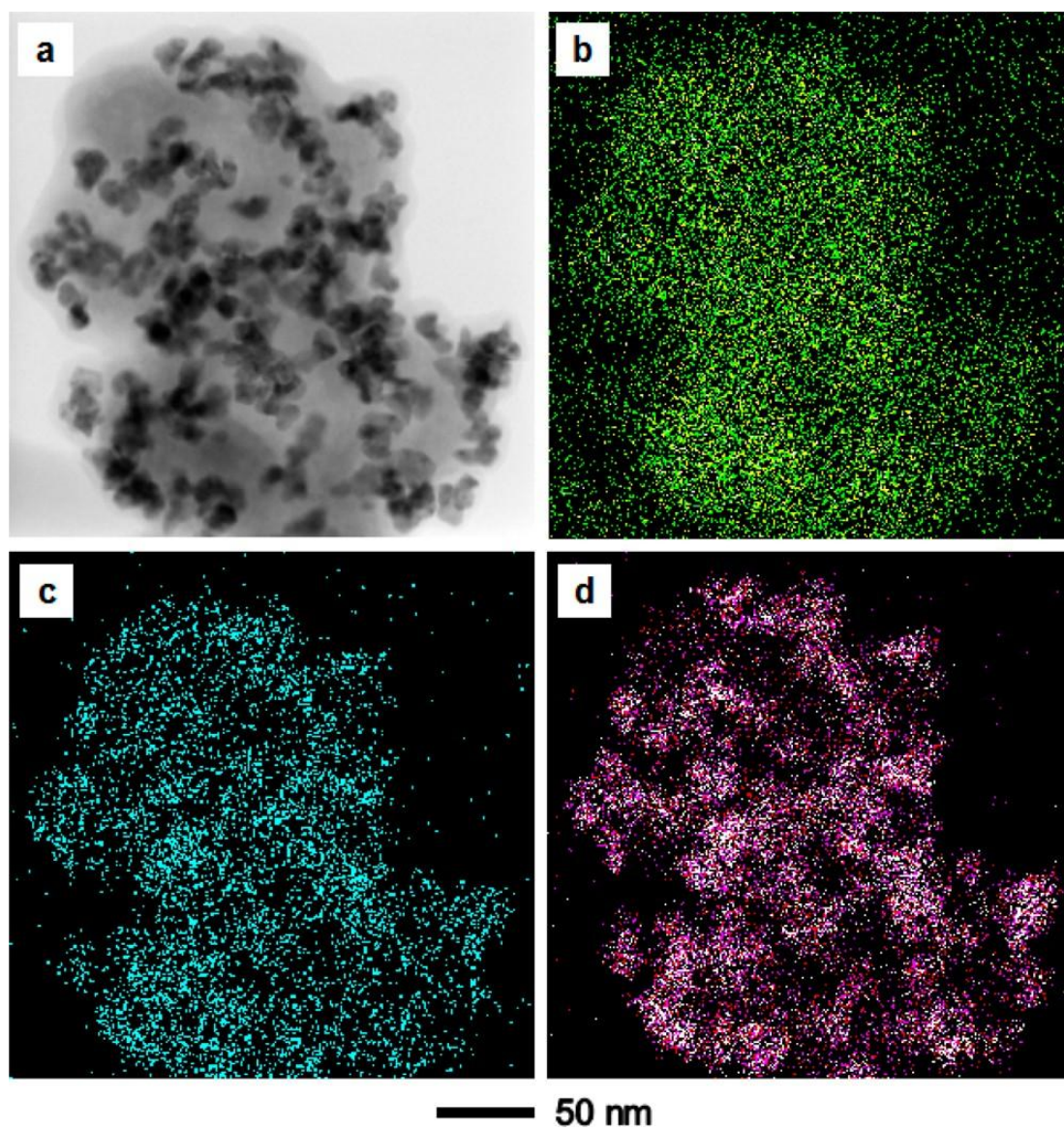


Figure 23. (a) HAADF-STEM image and (b–d) EDX mappings of **Pd/ZIF-8-MW** (b) C element, (c) Zn element, (d) Pd element

3-4. Conclusion

MW-assisted synthesis represents a novel and efficient approach for the preparation of nanoparticle–MOF composite materials, enabling uniform dispersion of NPs within the MOF matrix. However, the nature of the interactions between NPs and MOFs, as well as the fundamental origins and mechanisms underlying their hybridization under MW irradiation, remain unclear. Future systematic investigations aimed at elucidating these hybridization mechanisms are expected to facilitate the rational design of both NPs and MOFs, thereby promoting the development of a wide range of functional hybrid materials with enhanced properties.

3-5. References

65. S. Hermes, F. Schröder, R. Chelmoski, C. Wöll, R. A. Fisher, *Angew. Chem. Int. Ed.* **2005**, *44*, 6237-6241.
66. C. Zlotea, R. Campesi, F. Cuevas, E. Leroy, P. Dibandjo, C. Volkringer, T. Loiseau, G. Ferey, M. Latroche, *J. Am. Chem. Soc.* **2010**, *132*, 2991-2997.
67. J. Hermannsdörfer, R. Kempe, *Chem. Eur. J.* **2011**, *17*, 8071-8077.
68. M. Meilikhov, K. Tusenko, R. A. Fischer, *Eur. J. Inorg. Chem.* **2010**, 3701-3714.
69. T. Ishida, M. Nagaoka, T. Akita, M. Haruta, *Chem. Eur. J.* **2008**, *14*, 8456-8460.
70. Y. E. Cheon, M. P. Suh, *Angew. Chem. Int. Ed.* **2009**, *48*, 2899-2903.
71. H. Kobayashi, Y. Mitsuka, H. Kitagawa, *Inorg. Chem.* **2016**, *55*, 7301-7303.

Chapter 4

Hybridization of Nanoparticle Catalysts with MOFs via a Spray-Based Synthetic Approach and Evaluation of Their Catalytic Performance

4-1. Introduction

Crystalline metal–organic frameworks (**cryMOFs**), composed of metal ions or clusters coordinated with organic linkers, have been extensively investigated due to their high surface areas and versatile functionalities, including gas storage, molecular separation, charge transport, and heterogeneous catalysis^{28-31, 72}. In recent years, there has been a growing interest in the design of composite materials that comprise MOFs and metal NPs. These materials have demonstrated superior performance in gas adsorption^{67, 73-74}, catalytic reactions⁷⁵⁻⁷⁹ and optical applications⁸⁰. In particular, the rational integration of NPs into MOF matrices has proven effective in enhancing catalytic activity through synergistic interactions, such as the molecular sieving effect arising from the well-defined porous framework of MOFs and the inhibition of nanoparticle aggregation by spatial confinement⁸¹⁻⁸².

In contrast to crystalline MOFs, amorphous MOFs (**amMOFs**) have emerged as a novel class of materials, characterized by the preservation of metal–ligand coordination without long-range crystallographic order.⁸³⁻⁸⁵ The disordered and defect-rich nature of **amMOFs** contributes

to their distinct properties, such as improved electrical conductivity^{86–87} and enhanced optical responses^{88–89}, which often surpass those of their crystalline analogues. Moreover, the intrinsic porosity of *am*MOFs enables controlled molecular release^{90–91}, a feature not typically observed in *cry*MOFs. Despite these promising attributes, the utilization of *am*MOFs as supports for metal nanoparticle-based catalysts remains underexplored, and reports on such hybrid systems are limited^{92–93}.

This chapter presents a novel synthetic strategy for fabricating metal NP/*am*MOF composites. Furthermore, the effect of framework amorphization on catalytic performance is systematically evaluated through gas-phase CO₂ hydrogenation to methanol. This transformation represents a key reaction pathway for converting anthropogenic CO₂ emissions—particularly from fossil fuel combustion—into value-added chemical products, and holds promise for future carbon recycling technologies.

For the *am*MOF component in the composite material, [Zr₆O₄(OH)₄(BDC)₆] (UiO-66, BDC = 1,4-benzenedicarboxylate) was selected. This compound is constructed from hexanuclear Zr⁴⁺ oxy/hydroxy clusters interconnected in a three-dimensional network via terephthalate ligands⁹⁴. Recently, composites of Cu NPs and *cry*UiO-66 have been shown to demonstrate outstanding catalytic activity for CO₂ hydrogenation to methanol^{95–97}. In the case of crystalline MOF-based

composites, several preparation techniques such as solid-state grinding^{98–99}, wet impregnation^{100–101}, vapor-phase infiltration^{102–104}, and encapsulation methods^{105–109} have already been well established. On the other hand, synthetic approaches for fabricating amorphous MOF composites remain relatively underexplored and are still in development. To address this gap, we focused on employing a spray-drying technique for the synthesis of **amMOF** composites^{46,110}. This method offers advantages such as scalability, cost-effectiveness, and the potential for rapid formation of amorphous MOF structures due to the quick solidification process during solvent evaporation. As a first demonstration, we prepared **amUiO-66**, comprising Cu NPs dispersed in amorphous UiO-66, and **Cu–ZnO/amUiO-66**, consisting of Cu–ZnO nanocomposites embedded in **amUiO-66** (Figure 24). Owing to the disordered nature of the UiO-66 matrix, these materials exhibited significantly improved catalytic performance in the gas-phase hydrogenation of CO₂ to methanol, compared to **Cu/cryUiO-66** and conventional **Cu–ZnO/γ-Al₂O₃** catalysts, which are commonly used for this reaction.

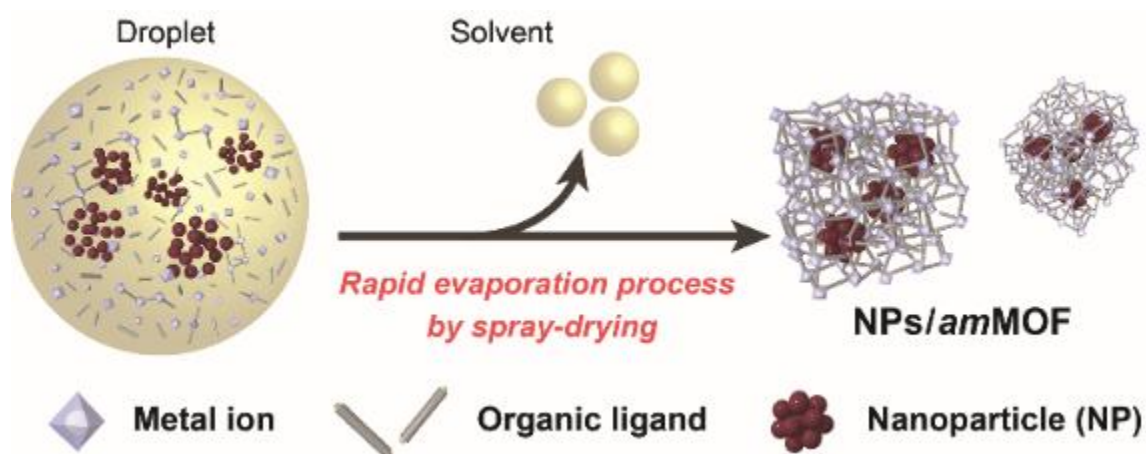


Figure 24. **Cu/amUiO-66** and **Cu–ZnO/amUiO-66** synthesized by the spray-drying method for highly enhanced catalytic activity of CO₂ hydrogenation for methanol synthesis

4-2. Experimental

Preparation of samples

Chemicals

All reagents were purchased from commercial sources (FUJIFILM Wako Pure Chemical Corporation, Sigma-Aldrich) and were used without further purification. Specifically, copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), benzene-1,4-dicarboxylic acid (H_2BDC) and N, N-dimethylformamide (DMF) were purchased from

FUJIFILM Wako Pure Chemical Corporation, Japan. Zirconium acetylacetonate $\text{Zr}(\text{acac})_4$ and copper acetylacetonate $\text{Cu}(\text{acac})_2$ were purchased from Sigma-Aldrich. $\gamma\text{-Al}_2\text{O}_3$ (AKP-G15) was purchased from Sumitomo Chemical Company Ltd.

Synthesis of CuO–ZnO nanocomposites.

An aqueous solution containing 25 g/L of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was prepared. The mixed solution was then sprayed into a tube furnace maintained at 1000 °C. As the droplets passed through the heating zone, solvent evaporation and thermal decomposition occurred, resulting in the formation of a CuO–ZnO nanocomposite powder, which was subsequently collected.

Synthesis of Cu/*am*UiO-66.

$\text{Zr}(\text{acac})_4$ (487 mg, 1.0 mmol) and H_2BDC (166 mg, 1.0 mmol) were dissolved in DMF (50 mL), and the mixture was heated to 80 °C and stirred for 2 h. Subsequently, $\text{Cu}(\text{acac})_2$ (104 mg, 0.4 mmol) dissolved in DMF (100 mL) was added dropwise to the $\text{Zr}(\text{acac})_4\text{-H}_2\text{BDC}$ solution. The resulting solution was introduced into a spray dryer (Mini Spray Dryer B-290) to synthesize Cu/*am*UiO-66. The spray-drying conditions were set as follows: feed rate of 5 mL/min,

carrier gas flow rate of 300 mL/min, and inlet temperature of 220 °C. The resulting powder was immediately collected, washed with ethanol, and dried under vacuum at 150 °C for 2 h to remove residual DMF. Finally, the material was heated at 250 °C under a flow of 4% H₂/N₂ to reduce CuO to Cu in **Cu/*am*UiO-66**.

Synthesis of Cu–ZnO/ γ -Al₂O₃.

γ -Al₂O₃ (1.22 g, 12 mmol) was dispersed in DMF (100 mL). A slurry was prepared by adding the pre-synthesized CuO–ZnO nanocomposite (0.2 g) to the γ -Al₂O₃ dispersion. The mixture was then spray-dried under the same conditions as used for **Cu/*am*UiO-66** synthesis. The resulting powder was collected, washed with ethanol, and dried under vacuum at 150 °C for 2 h to remove residual DMF. Finally, the powder was heated at 250 °C under a flow of 4% H₂/N₂ to reduce CuO to Cu in the **Cu–ZnO/ γ -Al₂O₃** composite.

Synthesis of Cu–ZnO/*am*UiO-66.

Zr(acac)₄ (487 mg, 1.0 mmol) and H₂BDC (166 mg, 1.0 mmol) were dissolved in DMF (50 mL), and the mixture was heated to 80 °C and stirred for 2 h. Then, CuO–ZnO nanocomposites (0.1 g) dispersed in DMF (100 mL) were added dropwise to the solution. The mixture was spray-

dried under the same conditions as those for **Cu/*am*UiO-66** synthesis. The resulting powder was immediately collected, washed with ethanol, and dried under vacuum at 150 °C for 2 h to remove residual DMF. Finally, the material was heated at 250 °C under a flow of 4% H₂/N₂ to reduce CuO to Cu in **Cu–ZnO/*am*UiO-66**.

Synthesis of Cu/ZrO₂.

Cu/ZrO₂ was synthesized via thermal decomposition of copper acetylacetonate (Cu(acac)₂) in the presence of ZrO₂. In a typical procedure, ZrO₂ (1 g, 8.11mmol) and Cu(acac)₂ (0.824 g, 3.14mmol) were dispersed in acetone (100 mL), and the suspension was stirred at room temperature for 12 h. After impregnation, the solid was collected by centrifugation and subsequently dried. The resulting composite was then heated at 350 °C under vacuum for 1 h to obtain **Cu/ZrO₂**.

Experimental Procedure

ICP–AES Analysis

Inductively coupled plasma atomic emission spectroscopy (ICP–AES) was carried out using a Shimadzu ICPS-7500 spectrometer. For sample preparation, accurately weighed samples were dissolved in a 3:7 (v/v) mixture of HNO₃ and HCl, followed by heating in a MW reactor at 180 °C for 1 h.

N₂ Sorption isotherm.

N₂ sorption isotherms of *cry*UiO-66, Cu/*am*UiO-66, Cu–ZnO/*am*UiO-66 and Cu–ZnO/ γ -Al₂O₃ were measured at 77 K using a BELSORP-mini instrument (BEL Japan, Inc.) via a volumetric method. Prior to measurement, the samples were degassed under vacuum at 423 K for 15 h to ensure complete activation.

EXAFS measurements.

EXAFS spectra were collected at the BL14B2 beam line, SPring-8 in the transmission mode under ambient conditions, using a Si (311) double crystal monochromator. The data were

processed with IFEFFIT. Fourier transformation was k^3 -weighted in the k range from 3.0 to 16.0 $\text{\AA}^{-1}$ for the Zr K -edge, from 3.0 to 12.0 $\text{\AA}^{-1}$ for the Cu K -edge and from 3.0 to 14.0 $\text{\AA}^{-1}$ for the Zn K -edge. Before the measurements, the sample was treated at 340 °C under H_2 gas for 10

h. The following equation was used for curve fitting the EXAFS spectra:

$$\chi(k) = S_0^2 \sum \frac{N_j f_j(k) \exp[-2k^2 \sigma_j^2]}{k r_j^2} \sin[2k_j r_j + \delta(k)],$$

where r is distance from the target to a neighboring atom, S_0 is amplitude reduction factor, N is the coordination number of the neighboring atom, and σ^2 is Debye–Waller factor. The photoelectron wavenumber k is given as $k = \sqrt{2m(E - E_0)/\hbar^2}$, $f(k)$ is the scattering amplitude, and $\delta(k)$ is the phase shift.

High-Resolution STEM and STEM-EDX Mapping.

High-resolution scanning STEM images and EDX elemental mapping were obtained using a JEOL JEM-ARM200F instrument operated at an accelerating voltage of 200 kV.

In Situ FT-IR Measurements.

In situ FT-IR spectroscopy of CO or NO adsorption was conducted to evaluate the

adsorption states on the catalyst surface. A self-supporting disk ($\sim 20 \text{ mg cm}^{-2}$) was placed in an IR cell equipped with CaF_2 windows. The sample was pretreated under H_2 at 340°C for 1 h, followed by exposure to 0.3% CO/He or 0.15% NO/He for 20 min at 50°C . Afterward, the system was purged with He at the same temperature for 20 min. Spectra were recorded at 0.5 min intervals using a Nicolet Nexus 670 FT-IR spectrometer with 64 scans accumulated at a resolution of 4 cm^{-1} .

Catalytic Tests.

Catalytic performance was evaluated in a fixed-bed flow reactor (Microtrac BEL) connected to a gas chromatograph (Shimadzu GC-2014). A catalyst amount of 0.3 g was loaded into the reactor. The reaction was conducted at 220°C and 2 atm using a gas mixture of CO_2 (20 sccm), H_2 (100 sccm), and He (20 sccm). Prior to the reaction, the catalyst was pretreated under the same gas mixture for 10 h. Methanol production was quantified using flame ionization gas chromatography.

PXRD.

PXRD patterns were collected using a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation to investigate the structure of the samples. Synchrotron powder XRD measurements were performed at the Super Photon Ring (SPring-8) BL02B2 beam line. The synchrotron XRD patterns of the samples sealed in a glass capillary were measured with wavelengths of 0.7998 Å

FT-IR Spectroscopy.

Ex situ FT-IR spectra were recorded using a Thermo Nicolet NEXUS 670 FT-IR spectrometer to characterize the functional groups present in the samples.

Cross-Sectional STEM and STEM-EDX Mapping.

For cross-sectional analysis, powder samples were embedded in epoxy resin containing Al_2O_3 fillers. Lamellae were prepared using the focused ion beam (FIB) lift-out technique with a Hitachi High Technologies MI400L system. STEM and STEM-EDX mapping images were acquired with a JEOL JEM-ARM200F instrument operated at 200 kV.

X-ray Photoelectron Spectroscopy (XPS) Measurements.

XPS was performed using a Shimadzu ESCA-3400 system with a monochromatic Mg K α source (1253.6 eV) operated at 200 W under a vacuum of 1×10^{-6} Pa. Spectra were collected with a pass energy of 150 eV and a scan step of 0.05 eV. A Shirley-type background was subtracted, and all binding energies were referenced to the C 1s peak at 284.8 eV. Prior to measurement, the samples were treated under H₂ at 340 °C for 10 h.

Scanning Electron Microscopy (SEM).

SEM images were acquired using a Hitachi High Technologies SU8020 microscope operated at an accelerating voltage of 1.0 kV.

4-3. Result and Discussion

ICP-OES analyses indicated that the Cu contents in **Cu/cryUiO-66** and **Cu/amUiO-66** were 14 wt% and 12 wt%, respectively, while the Cu–ZnO loadings in **Cu–ZnO/amUiO-66** and **Cu–ZnO/ γ -Al₂O₃** were 40 wt% and 37 wt%, respectively (Table 3).

Table 3. Composition information on the composites of **Cu/cryUiO-66**, **Cu/amUiO-66**, **Cu–ZnO/amUiO-66** and **Cu–ZnO/ γ -Al₂O₃**

Samples	Atomic ratio of Cu and ZnO	Wt% of Cu or Cu–ZnO
Cu/cryUiO-66		14 ⁹⁷
Cu/amUiO-66		12
Cu–ZnO/amUiO-66	0.56:0.44	40
Cu–ZnO/γ-Al₂O₃	0.56:0.44	37

The atomic ratio between Cu and ZnO was calculated to be 0.56:0.44 for both **Cu–ZnO/amUiO-66** and **Cu–ZnO/ γ -Al₂O₃**. Pore size distribution measurements revealed that **Cu/cryUiO-66** exhibited two distinct pore diameters of 7.4 Å and 9.4 Å, corresponding to the octahedral and tetrahedral cavities inherent to the crystalline UiO-66 framework. In contrast, **Cu/amUiO-66** and **Cu–ZnO/amUiO-66** showed a broader distribution, with pore sizes predominantly in the range of 11–13 Å.

SEM observations showed that **Cu/cryUiO-66** primarily consisted of octahedral crystals with an average diameter of approximately 0.5 μm . Meanwhile, **Cu/amUiO-66** and **Cu-ZnO/amUiO-66** were composed of small spherical particles with diameters ranging from 0.1 to 5 μm (Figures 25–27).

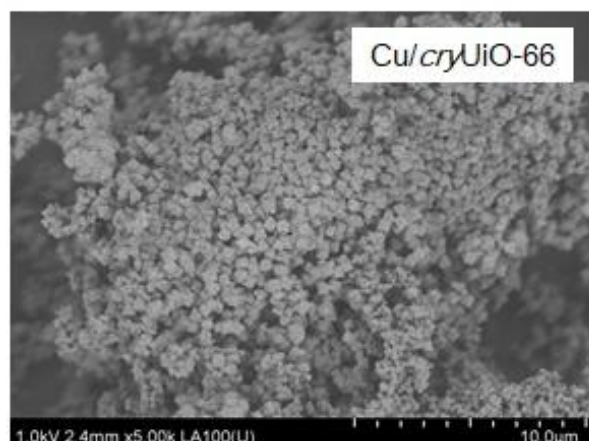


Figure 25. SEM image of **Cu/cryUiO-66**

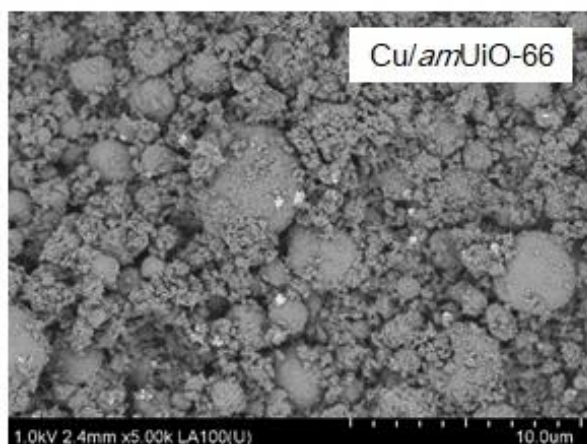


Figure 26. SEM image of **Cu/amUiO-66**

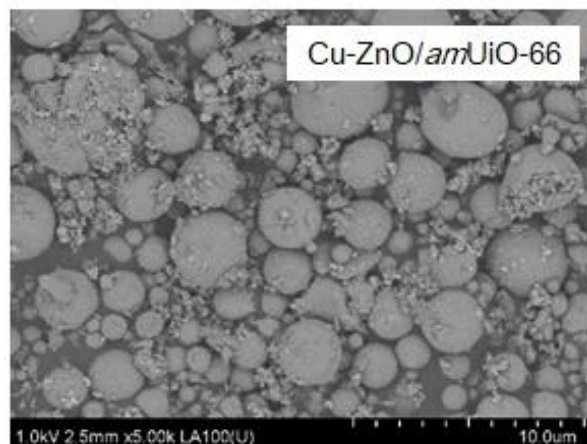


Figure 27. SEM image of **Cu-ZnO/amUiO-66**

Figure 28 shows the synchrotron XRD patterns of **Cu/cryUiO-66**, **Cu/amUiO-66**, **Cu-ZnO/amUiO-66**, and **Cu-ZnO/ γ -Al₂O₃**. In each pattern, characteristic diffraction peaks corresponding to the crystalline phases of Cu and/or ZnO were clearly identified. Based on Le Bail fitting analysis, the estimated crystallite sizes of Cu NPs were approximately 25 nm for **Cu/amUiO-66**, 60 nm for **Cu-ZnO/amUiO-66**, and 40 nm for **Cu-ZnO/ γ -Al₂O₃**. Similarly, the ZnO crystallite sizes were determined to be 53 nm and 55 nm for **Cu-ZnO/amUiO-66** and **Cu-ZnO/ γ -Al₂O₃**, respectively (Table 4). In the case of **Cu/amUiO-66**, in addition to the diffraction peaks associated with Cu NPs, a broad diffraction peak centered around $2\theta \approx 3^\circ$ was observed, which was also present in the pattern of **Cu-ZnO/amUiO-66**. This broad feature is attributed to the amorphous nature of the UiO-66 framework, reflecting the absence of long-range periodic order resulting from structural amorphization.

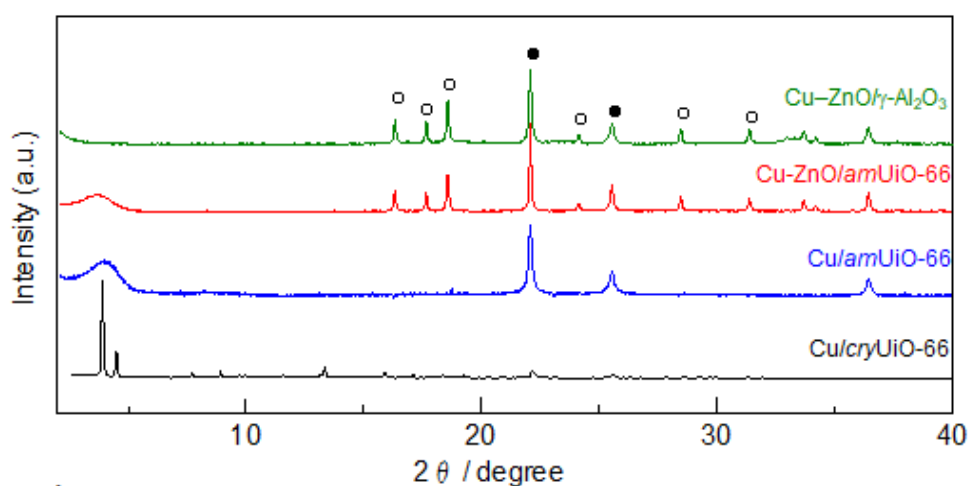


Figure 28. Synchrotron PXRD patterns of **Cu-ZnO/ γ -Al₂O₃**, **Cu/amUiO-66**, **Cu/amUiO-66** and **Cu/cryUiO-66**. Black and white circles show the diffraction peaks of Cu and ZnO, respectively.

Table 4. Nanoparticle information on the composites of **Cu/cryUiO-66**, **Cu/amUiO-66**, **Cu-ZnO/amUiO-66** and **Cu-ZnO/ γ -Al₂O₃**

Samples	Size of Cu (nm)	Crystal size of ZnO(nm)
Cu/cryUiO-66	$13.1 \pm 3.9^{*97}$	
Cu/amUiO-66	$25.2 \pm 0.1^*$	
Cu-ZnO/amUiO-66	$60.1 \pm 0.3^{**}$	53.2 ± 0.3
Cu-ZnO/γ-Al₂O₃	$40.3 \pm 1.0^{**}$	55.3 ± 1.4

* The value shows the Cu NP mean diameter

** The value shows the Cu NP crystal size

Figure 29 shows the N₂ adsorption isotherms of **Cu/amUiO-66** and **Cu-ZnO/amUiO-66** measured at 77 K. In contrast to the **Cu/cryUiO-66** sample, which exhibits a typical type I isotherm characteristic of microporous materials, both **Cu/amUiO-66** and **Cu-ZnO/amUiO-66** showed markedly reduced N₂ uptake and BET surface area (Table 5), indicating a significant loss of microporosity. This observation also supports the presence of an amorphous UiO-66 phase possessing low structural order. Although it has been previously demonstrated that crystalline UiO-66 can be obtained via spray-drying,¹¹⁰ the incorporation of Cu NPs or Cu-ZnO nanocomposites appears to interfere with the regular crystallization process. This interference

likely suppresses the formation of a well-ordered framework, leading instead to the generation of amorphous UiO-66 in both **Cu/amUiO-66** and **Cu-ZnO/amUiO-66**.

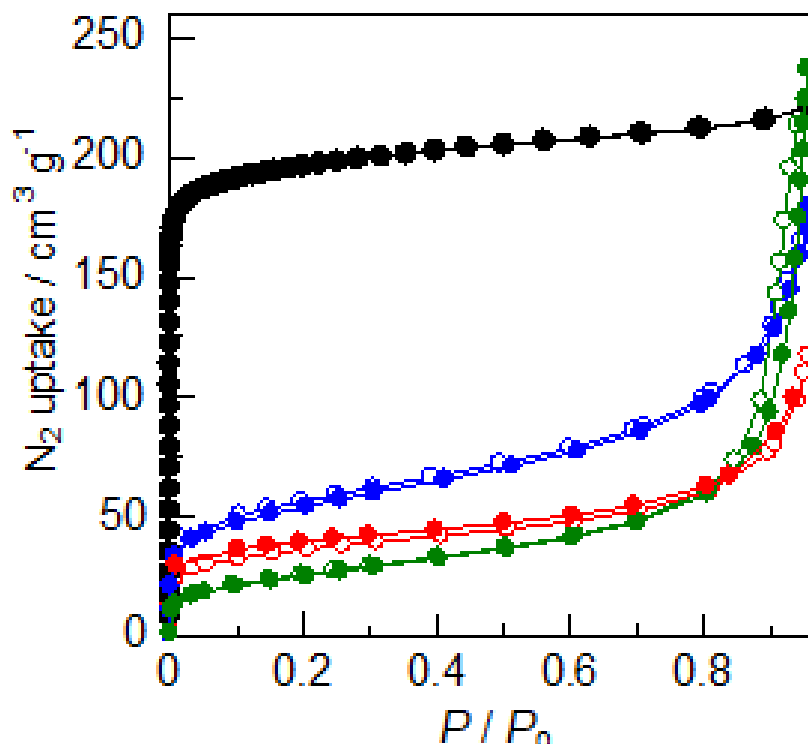


Figure 29. N₂ adsorption/desorption isotherms of **Cu/cryUiO-66** (black), **Cu/amUiO-66** (blue), **Cu-ZnO/amUiO-66** (red) and **Cu-ZnO/γ-Al₂O₃** (green)

Table 5. BET surface area and pore volume of **Cu/cryUiO-66**, **Cu/amUiO-66**, **Cu-ZnO/amUiO-66** and **Cu-ZnO/γ-Al₂O₃**.

Samples	BET surface area (m ² /g)	Pore volume (cm ³ /g)
Cu/cryUiO-66	707.0 ⁹⁷	0.343
Cu/amUiO-66	190.0	0.278
Cu-ZnO/amUiO-66	128.8	0.181
Cu-ZnO/γ-Al₂O₃	91.8	0.367

The FT-IR spectra of the amorphous UiO-66 phases in **Cu/amUiO-66** and **Cu-ZnO/amUiO-66** exhibited an additional absorption band near 1650 cm^{-1} , which was absent in the FT-IR spectrum of **Cu/cryUiO-66** (Figure 30). This spectral feature is attributed to the partial dissociation of coordination bonds between the Zr_6 metal cluster and the benzene-1,4-dicarboxylate linker, which contributes to the structural amorphization of UiO-66.¹¹¹

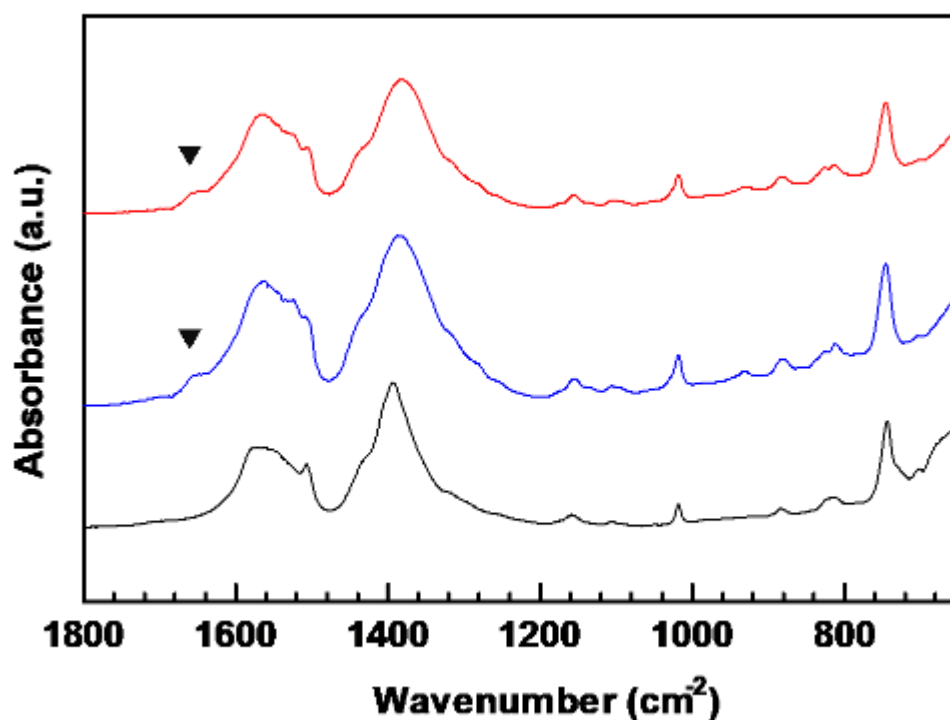


Figure 30. FT-IR spectra of **Cu/cryUiO-66** (black), **Cu/amUiO-66** (blue) and **Cu-ZnO/amUiO-66** (red).

In order to gain further insight into the local coordination environments within **Cu/amUiO-66**

and **Cu-ZnO/amUiO-66**, EXAFS analysis was conducted at the Zr K-edge (Figure 31).

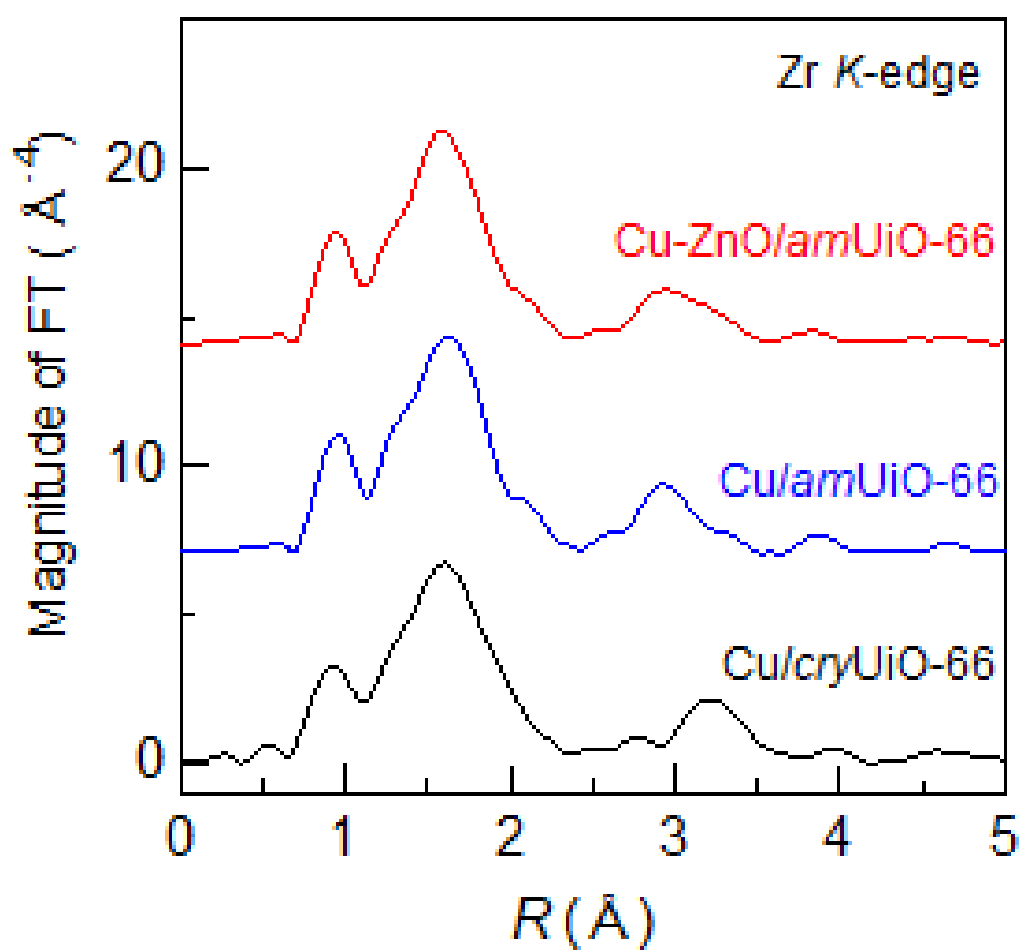


Figure 31. Zr K -edge EXAFS spectra in R space showing the magnitude of the Fourier transform.

In the EXAFS spectrum of **Cu/cryUiO-66**, two distinct peaks were observed at approximately 1.7 Å and 3.2 Å, corresponding to Zr–O and Zr–Zr bonds, respectively. These are characteristic of the $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ cluster structure with hydroxyl groups. In contrast, the spectra of **Cu/amUiO-66** and **Cu–ZnO/amUiO-66** displayed a Zr–Zr peak at 2.9 Å, indicative of the $\text{Zr}_6\text{O}_6(\text{CO}_2)_{12}$ unit, a dehydroxylated variant of the Zr_6 cluster. Both samples also showed a Zr–O peak near 1.7 Å, similar to that of **Cu/cryUiO-66**. These results suggest that **Cu/amUiO-66** and **Cu–ZnO/amUiO-66** largely retain the structural framework of the Zr_6 clusters found in **cryUiO-66**.

Table 6. Parameters refined by fitting the EXAFS spectrum for Zr–O shell of **Cu/cryUiO-66**, **Cu/amUiO-66** and **Cu–ZnO/amUiO-66**.

Samples	N	r (Å)	σ^2 (Å ²)	E_0 (eV)	R -factor
Cu/cryUiO-66	8.1 ± 1.1	2.114(19)	0.0052(25)	1.3 ± 2.0	0.0114
		2.252(21)	0.0051(27)		
Cu/amUiO-66	7.1 ± 1.1	2.107(24)	0.0044(33)	2.6 ± 2.2	0.0133
		2.267(28)	0.0050(42)		
Cu–ZnO/amUiO-66	7.2 ± 1.0	2.103(21)	0.0044(28)	1.5 ± 2.1	0.0132
		2.263(24)	0.0049(34)		

The coordination number of Zr–O bonds estimated from Zr-K edge EXAFS was slightly reduced in the amorphous samples: 7.1 ± 1.1 for **Cu/*am*UiO-66** and 7.2 ± 1.0 for **Cu–ZnO/*am*UiO-66**, compared to 8.1 ± 1.1 for **Cu/*cry*UiO-66** (Table 6). The amplitude reduction factor S_0^2 was determined empirically as 1.16(17), and fitting was performed in the radial distance range of 1.3–2.4 Å. Taken together with the FT-IR analysis (Figure 30), these findings support the partial dissociation of coordination bonds between the Zr_6 clusters and the BDC ligands in **Cu/*am*UiO-66** and **Cu–ZnO/*am*UiO-66**, resulting in the formation of bare Zr sites.

To elucidate the composite structures of **Cu/*am*UiO-66** and **Cu–ZnO/*am*UiO-66**, HAADF-STEM combined with EDX elemental mapping was conducted on their constituent elements. Figure 32 presents the HAADF-STEM images and corresponding EDX elemental overlay maps for **Cu/*am*UiO-66**, **Cu/*cry*UiO-66** and **Cu–ZnO/*am*UiO-66**. In **Cu/*am*UiO-66**, the Zr element originating from the amorphous UiO-66 was found to surround the Cu NPs (Figure 32a,b), in a manner similar to that observed in the **Cu/*cry*UiO-66** (Figure 32c,d)⁹⁷.

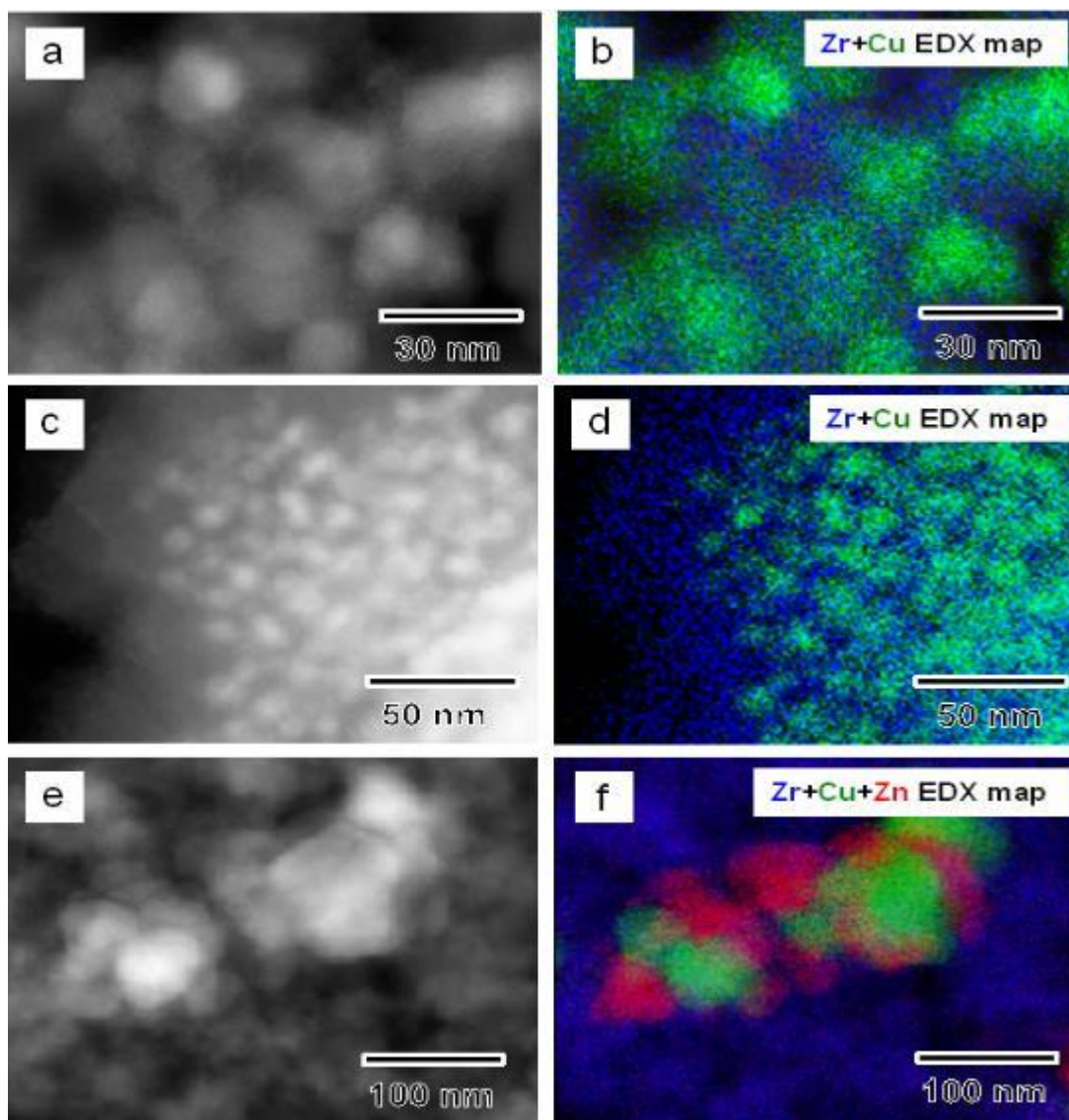


Figure 32. HAADF images and STEM-EDX maps of (a), (b) for $\text{Cu}/\text{amUiO-66}$, (c), (d) for $\text{Cu}/\text{cryUiO-66}$ and (e), (f) $\text{Cu-ZnO}/\text{amUiO-66}$ (green, Cu; blue, Zr; red, Zn)

The EDX elemental overlay maps of **Cu–ZnO/*am*UiO-66** indicate that Cu and ZnO NPs are not separately dispersed but are positioned in close proximity to each other, forming a nanocomposite structure (Figure 32e, f). A similar composite structure was also observed in **Cu–ZnO/ γ -Al₂O₃** (Figure 33). These Cu–ZnO nanocomposites are embedded within the amorphous UiO-66 matrix.

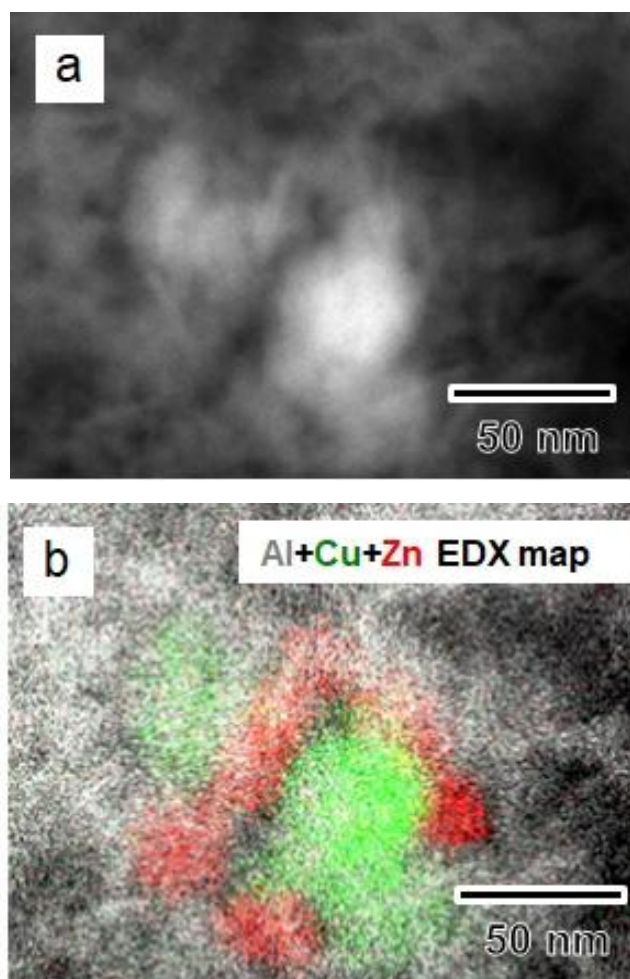


Figure 33. (a) HAADF images and (b) STEM-EDX maps of **Cu–ZnO/ γ -Al₂O₃** (green, Cu; gray, Al; red, Zn).

Moreover, low-magnification STEM-EDX mapping confirms a uniform distribution of the Cu–ZnO composites across the surface of *am*UiO-66 (Figure 34). Cross-sectional STEM-EDX analysis further reveals that the Cu–ZnO nanocomposites are encapsulated by the *am*UiO-66 framework (Figure 35).

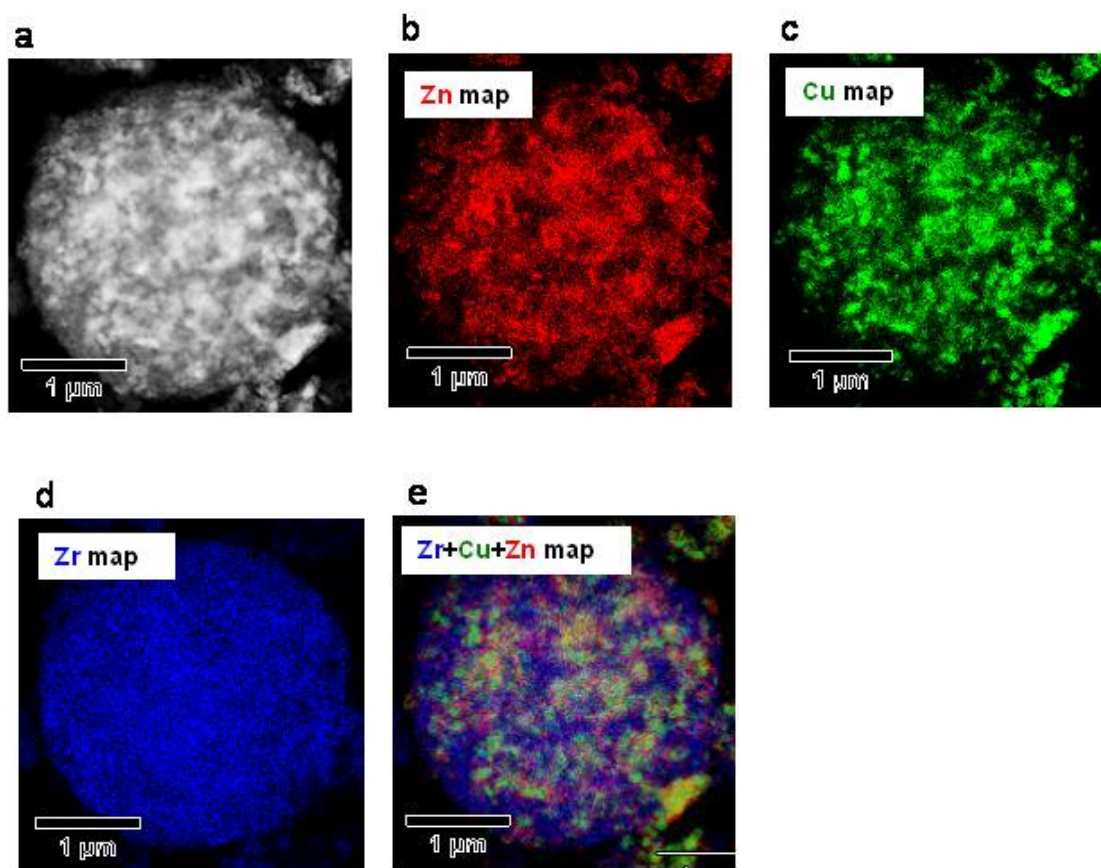


Figure 34. (a) HAADF image, (b) Zn-*K*, (c) Cu-*K* and (d) Zr-*L* STEM-EDX maps of **Cu–ZnO/*am*UiO-66**. (e) Reconstructed overlay image of the maps shown in panels b–d.

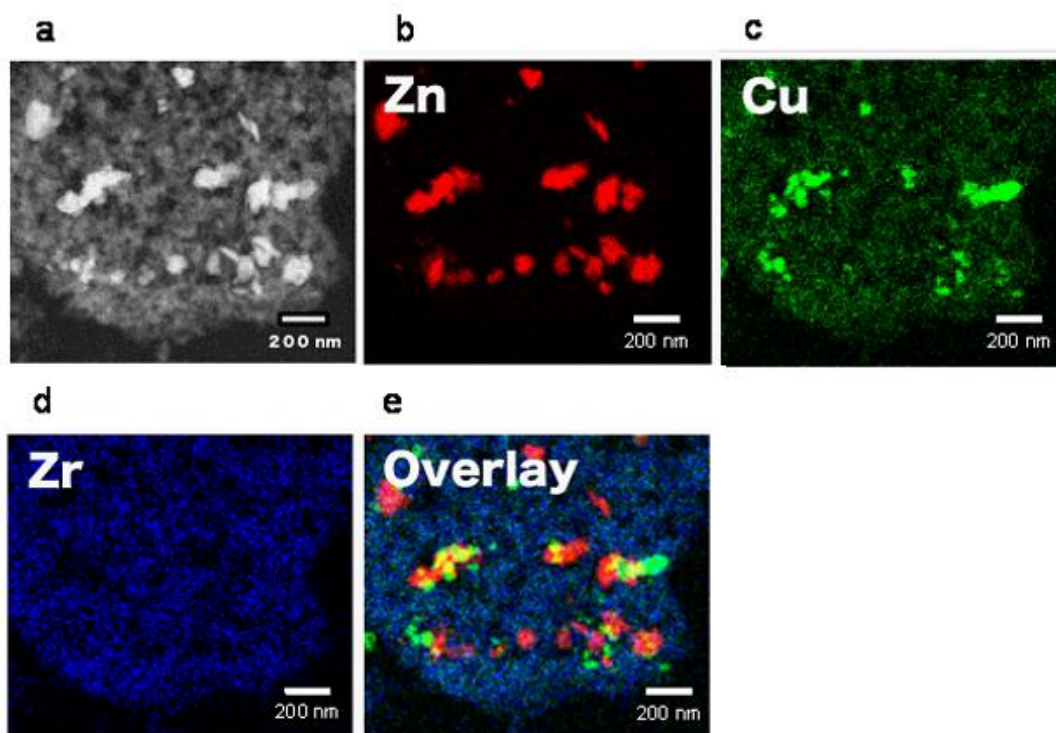


Figure 35. (a) Cross-sectional HAADF image, (b) Zn-K, (c) Cu-K and (d) Zr-L STEM-EDX maps of **Cu-ZnO/amUiO-66**. (e) Reconstructed overlay image of the maps shown in panels b–d.

The catalytic performance of **Cu/amUiO-66** and **Cu-ZnO/amUiO-66** for CO₂ hydrogenation to methanol was examined using a fixed-bed flow reactor. The reaction was conducted under a gas flow of 20 sccm CO₂, 100 sccm H₂, and 20 sccm He at 2 atm and 220 °C. In our previous study, we demonstrated that **Cu/cryUiO-66**⁹⁷ shows a significantly higher CO₂

hydrogenation activity ($128 \mu\text{mol/g}_{\text{Cu}} \cdot \text{h}$) compared to that of **Cu/ZrO₂** ($18 \mu\text{mol/g}_{\text{Cu}} \cdot \text{h}$) (Figures 36–38). Figure 39 shows the amount of methanol synthesized from CO₂ and H₂ by **Cu/cryUiO-66**⁹⁷, **Cu/amUiO-66**, **Cu–ZnO/ γ -Al₂O₃** and **Cu–ZnO/amUiO-66** catalysts, respectively.

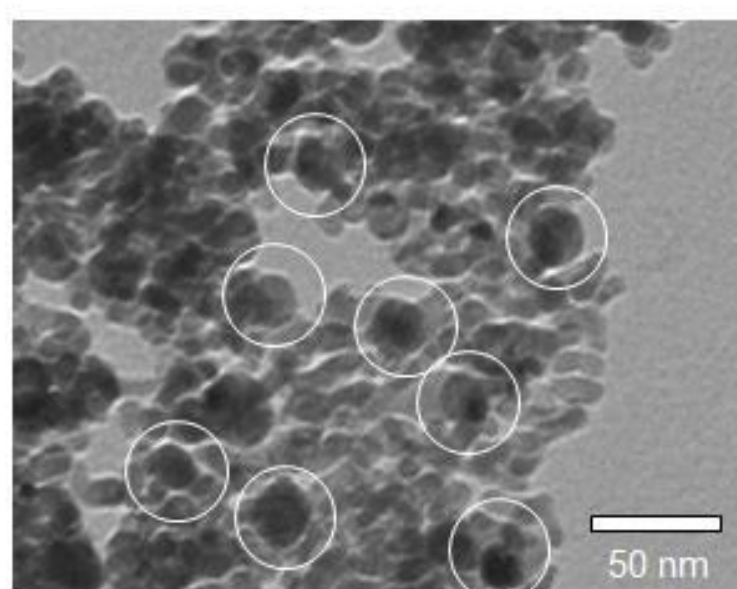


Figure 36. TEM image of **Cu/ZrO₂**. White circles show Cu NPs.

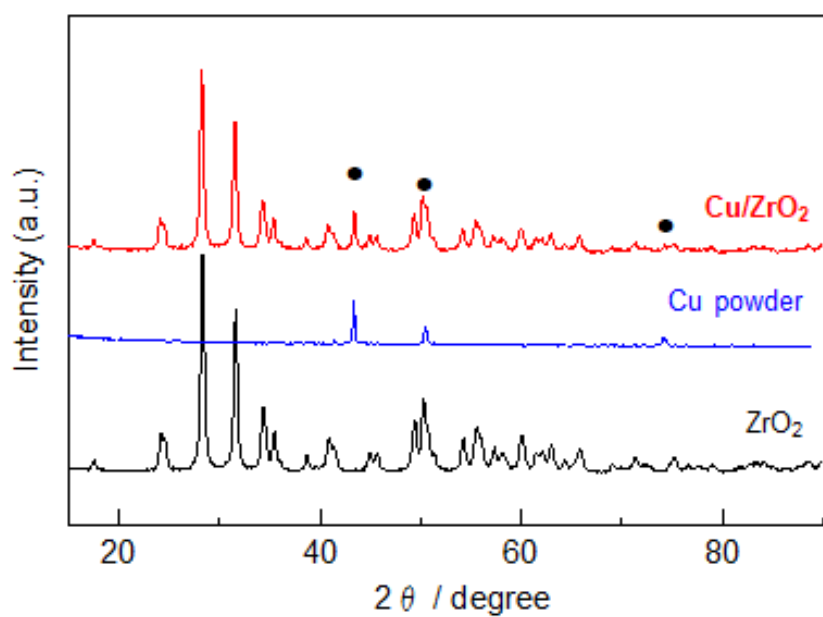


Figure 37. XRD pattern of **Cu/ZrO₂**. Black circles show the diffraction peaks of Cu.

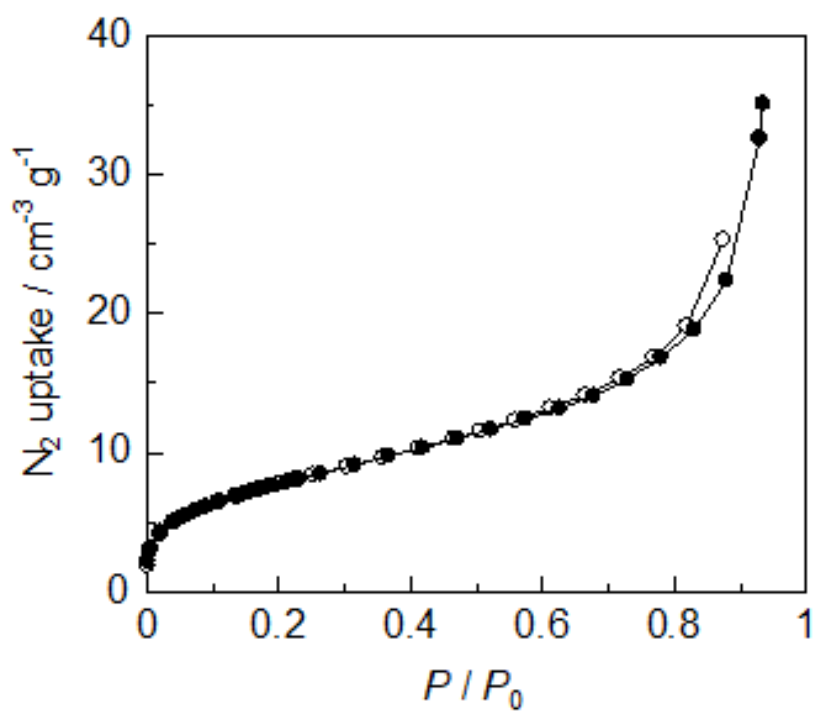


Figure 38. N₂ sorption isotherms at 77 K with adsorption represented by closed circles and desorption by open circles (P/P_0 , relative pressure) for **Cu/ZrO₂**.

As shown in Figure 39, **Cu/*am*UiO-66** exhibited a catalytic activity of 442.8 $\mu\text{mol/gCu}\cdot\text{h}$, which is more than three times higher than that of **Cu/*cry*UiO-66**.

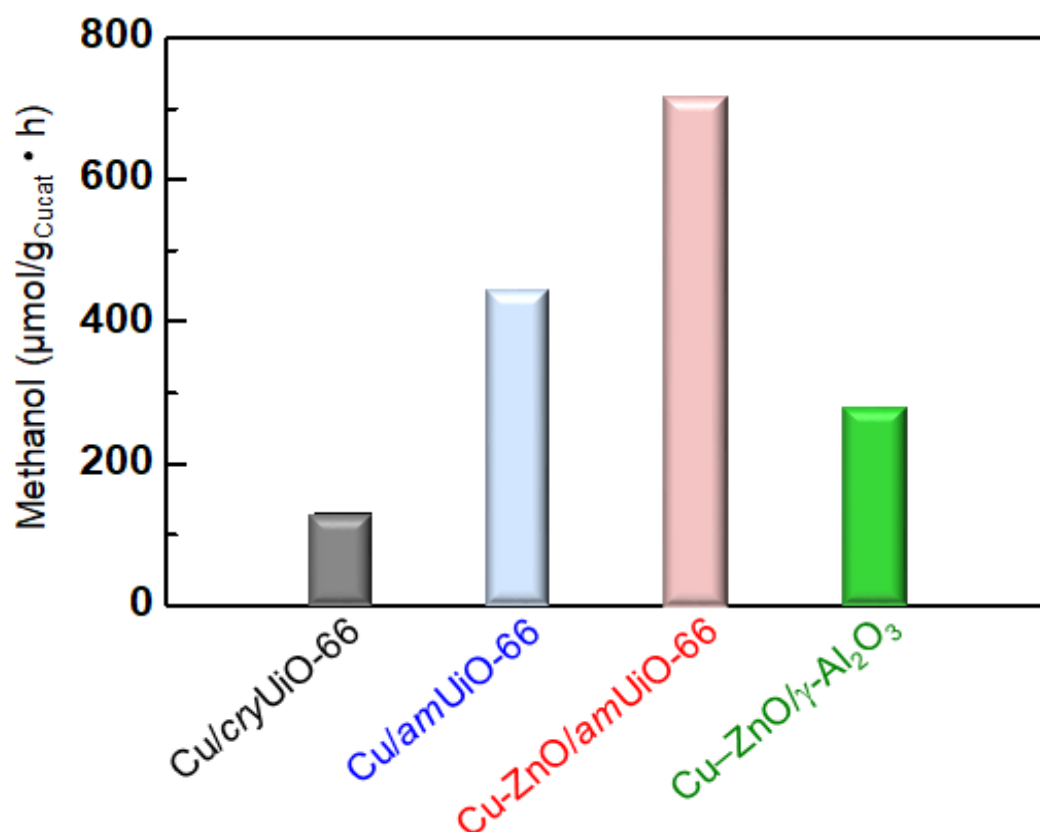


Figure 39. The amount of methanol synthesized from CO₂ and H₂ by **Cu/*cry*UiO-66**, **Cu/*am*UiO-66**, **Cu-ZnO/ γ -Al₂O₃** and **Cu-ZnO/*am*UiO-66** catalysts.

Moreover, the catalytic activity of **Cu/*am*UiO-66** was significantly higher than that of **Cu-ZnO/ γ -Al₂O₃** (271.4 $\mu\text{mol/gCu}\cdot\text{h}$). Typically, catalysts with larger Brunauer–Emmett–Teller (BET) surface areas allow reactant molecules to access the active sites more easily, thus enhancing catalytic performance. Interestingly, despite its notably higher catalytic activity,

Cu/amUiO-66 had a considerably smaller BET surface area ($190 \text{ m}^2/\text{g}$) than **Cu/cryUiO-66** ($707 \text{ m}^2/\text{g}$). Furthermore, the average size of the Cu NPs in **Cu/amUiO-66** ($25.2 \pm 0.1 \text{ nm}$) was larger than that observed in **Cu/cryUiO-66** ($13.1 \pm 3.9 \text{ nm}$). These observations imply that the reduced crystallinity of UiO-66 in **Cu/amUiO-66** may be a critical factor contributing to the enhanced CO_2 hydrogenation activity.

In the case of **Cu-ZnO/amUiO-66**, the methanol production rate reached $710.5 \mu\text{mol}/\text{gCu}\cdot\text{h}$, approximately 2.5 times higher than that of the benchmark catalyst **Cu-ZnO/ γ - Al_2O_3** ($271.4 \mu\text{mol}/\text{gCu}\cdot\text{h}$). The catalytic performance of both **Cu/amUiO-66** and **Cu-ZnO/amUiO-66** remained stable even after five consecutive reaction cycles (Figure 40), demonstrating their high durability and sustained activity.

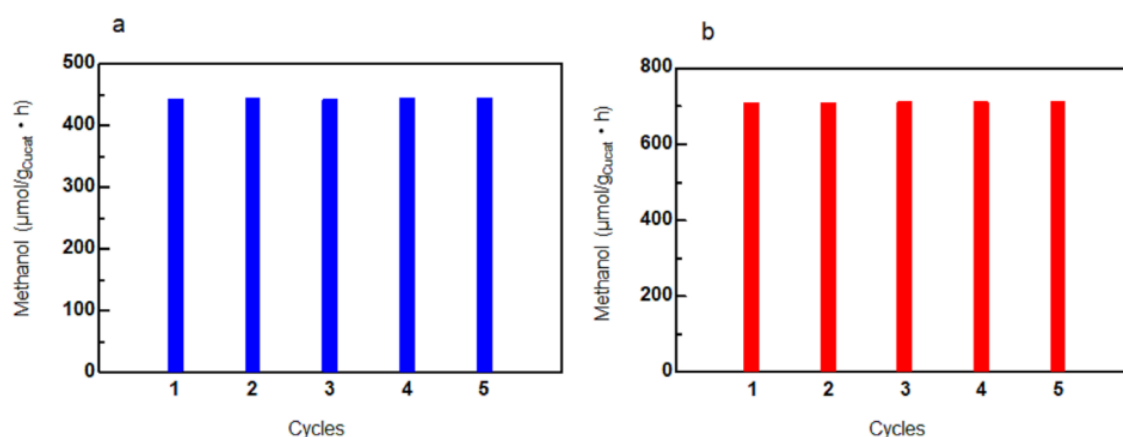


Figure 40. The recyclability tests of (a) **Cu/amUiO-66** and (b) **Cu-ZnO/amUiO-66**.

Cu species are known to play a crucial role in facilitating the hydrogenation of CO₂ to methanol.^{112–114} To gain insight into the surface characteristics of the Cu NPs in our composite catalysts, we conducted in situ FTIR spectroscopy and XPS. FT-IR, especially with adsorbed probe molecules such as CO or NO, is widely used to analyze the surface conditions of metallic catalysts.

In this study, we performed in situ FT-IR experiments using CO adsorption to investigate the surface states of Cu NPs in both **Cu/cryUiO-66** and **Cu/amUiO-66**. As Cu NPs are believed to be the primary active sites in CO₂ hydrogenation, it is essential to understand their surface characteristics. During the measurements, the samples were exposed to a 0.3% CO in He gas stream at 50 °C for 20 minutes, followed by purging with pure He at the same temperature for 30 seconds. IR spectra were collected every 30 seconds throughout the procedure (Figure 41).

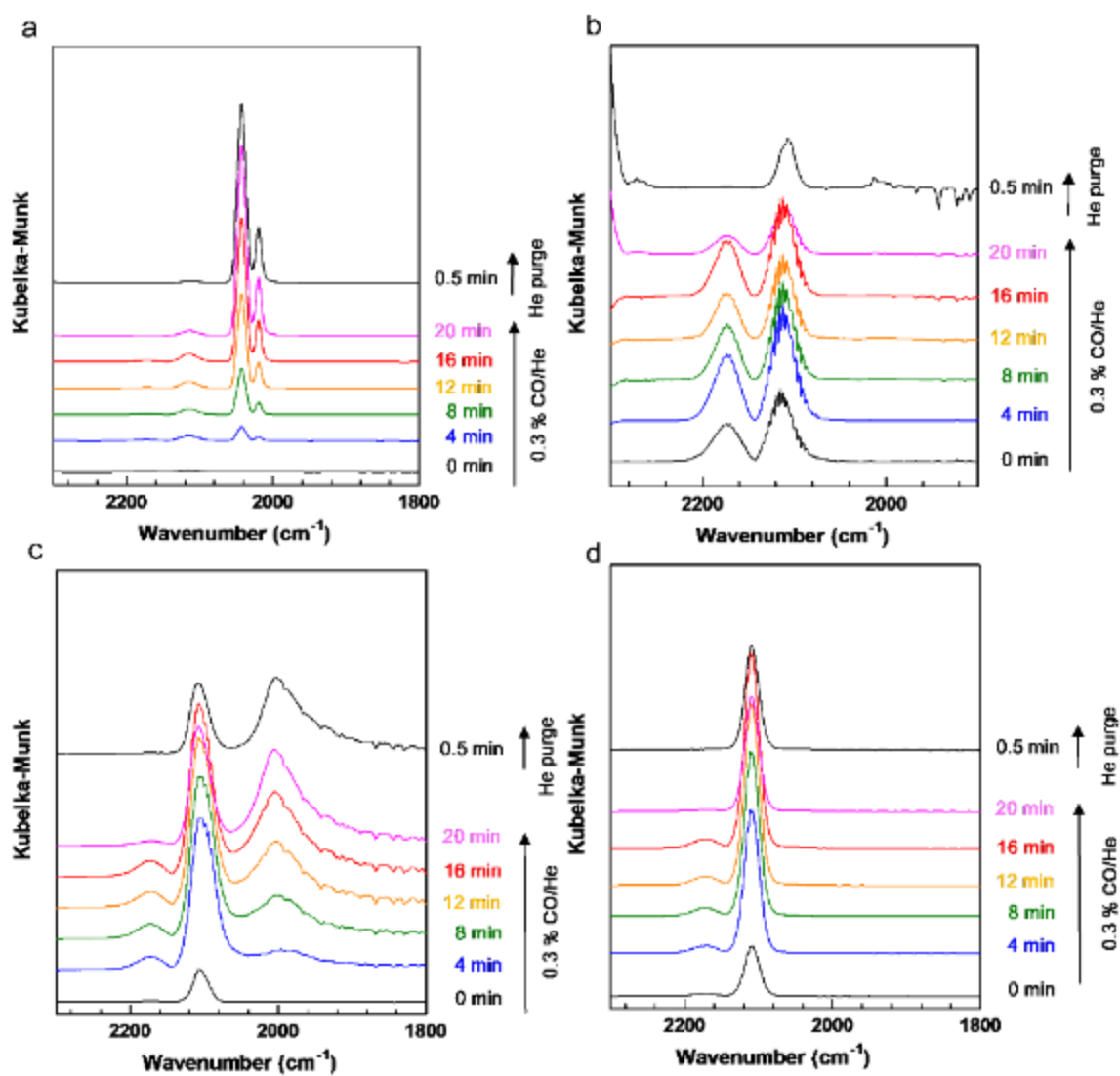


Figure 41. (a) In situ CO IR spectra of (a) **Cu/cryUiO-66**, (b) **Cu/amUiO-66**, (c) **Cu-ZnO/ γ -Al₂O₃** and (d) **Cu-ZnO/amUiO-66**.

Figure 42 shows the in situ IR spectra of CO adsorbed on Cu NPs in **Cu/cryUiO-66** and **Cu/amUiO-66**, collected under a He atmosphere following 20 minutes of exposure to a 0.3% CO/He gas stream. In the case of **Cu/amUiO-66**, a distinct absorption band appeared at 2107 cm^{-1} , which can be attributed to CO molecules bound to metallic copper (Cu^0 -CO species) ¹¹⁵.

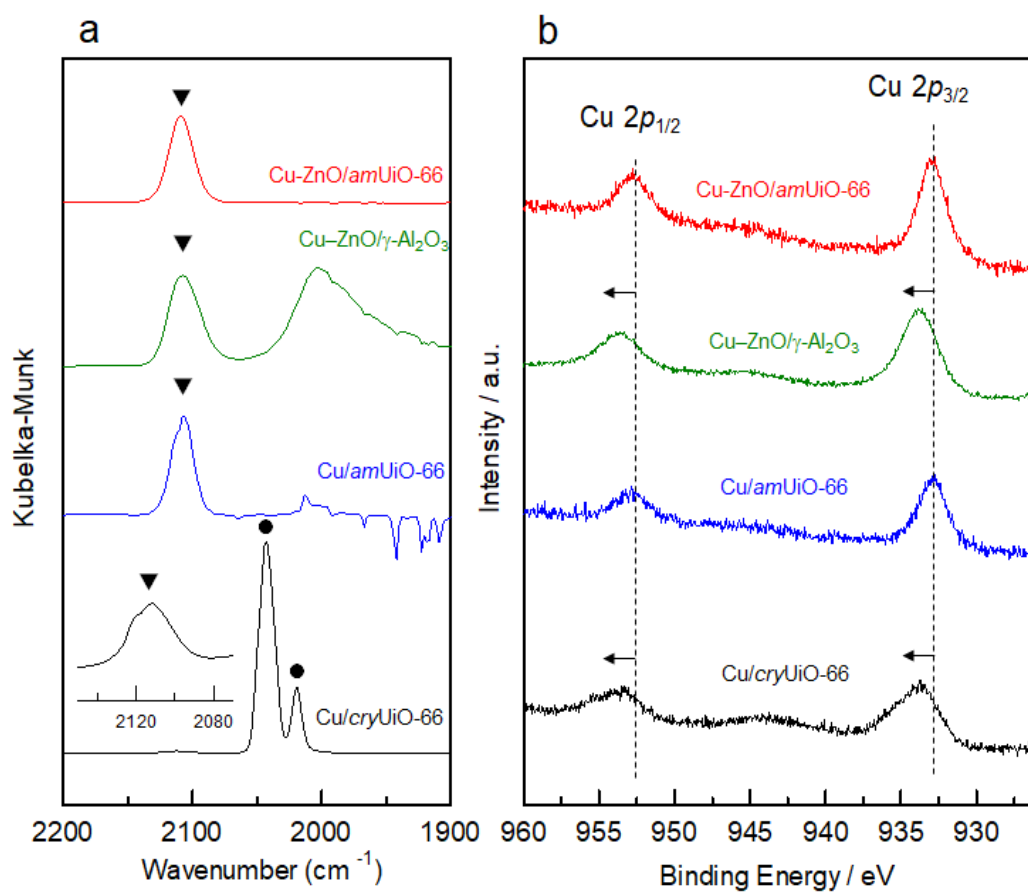


Figure 42. (a) In situ IR spectra under He after exposure to flow of 0.3% CO/He for 20 min and (b) XPS spectra for **Cu/cryUiO-66**, **Cu/amUiO-66**, **Cu-ZnO/ γ -Al₂O₃** and **Cu-ZnO/amUiO-66**.

For **Cu/cryUiO-66**, in addition to the minor Cu⁰–CO species, two distinct absorption bands were observed at 2043 and 2019 cm⁻¹. These are attributed to CO molecules adsorbed on low-coordinated copper sites, such as geminal Cu⁰(CO)₂ complexes and linearly bound carbonyl species¹¹⁶. These spectral features imply that the Cu NPs in **Cu/amUiO-66** exhibit a more uniform surface environment compared to those in **Cu/cryUiO-66**. In the Cu–ZnO systems, the IR spectrum of **Cu–ZnO/amUiO-66** closely resembled that of **Cu/amUiO-66**. In contrast, **Cu–ZnO/γ-Al₂O₃** displayed a broad absorption band centered around 2000 cm⁻¹, which can be associated with CO adsorption on coordinatively unsaturated and/or bridging Cu sites, in addition to the Cu⁰–CO species. This indicates that **Cu–ZnO/γ-Al₂O₃** possesses a more heterogeneous Cu surface structure than **Cu–ZnO/amUiO-66**, despite both being synthesized via the same spray-drying method. Thus, the combination of UiO-66 and spray-drying appears to promote the formation of Cu NPs with a more uniform surface composition.

To further elucidate the surface characteristics of Cu NPs, we conducted XPS. The results showed that Cu NPs in **Cu/cryUiO-66** and **Cu–ZnO/γ-Al₂O₃** were partially oxidized, while those in **Cu/amUiO-66** and **Cu–ZnO/amUiO-66** retained their metallic Cu(0) state (Figure 42b).

The in situ FT-IR spectra recorded under NO gas atmosphere also supported the observation that Cu NPs in **Cu/*am*UiO-66** and **Cu-ZnO/*am*UiO-66** exhibit higher stability in their metallic Cu(0) state compared to those in **Cu/*cry*UiO-66** and **Cu-ZnO/ γ -Al₂O₃** (Figures 43 and 44)¹¹⁷.

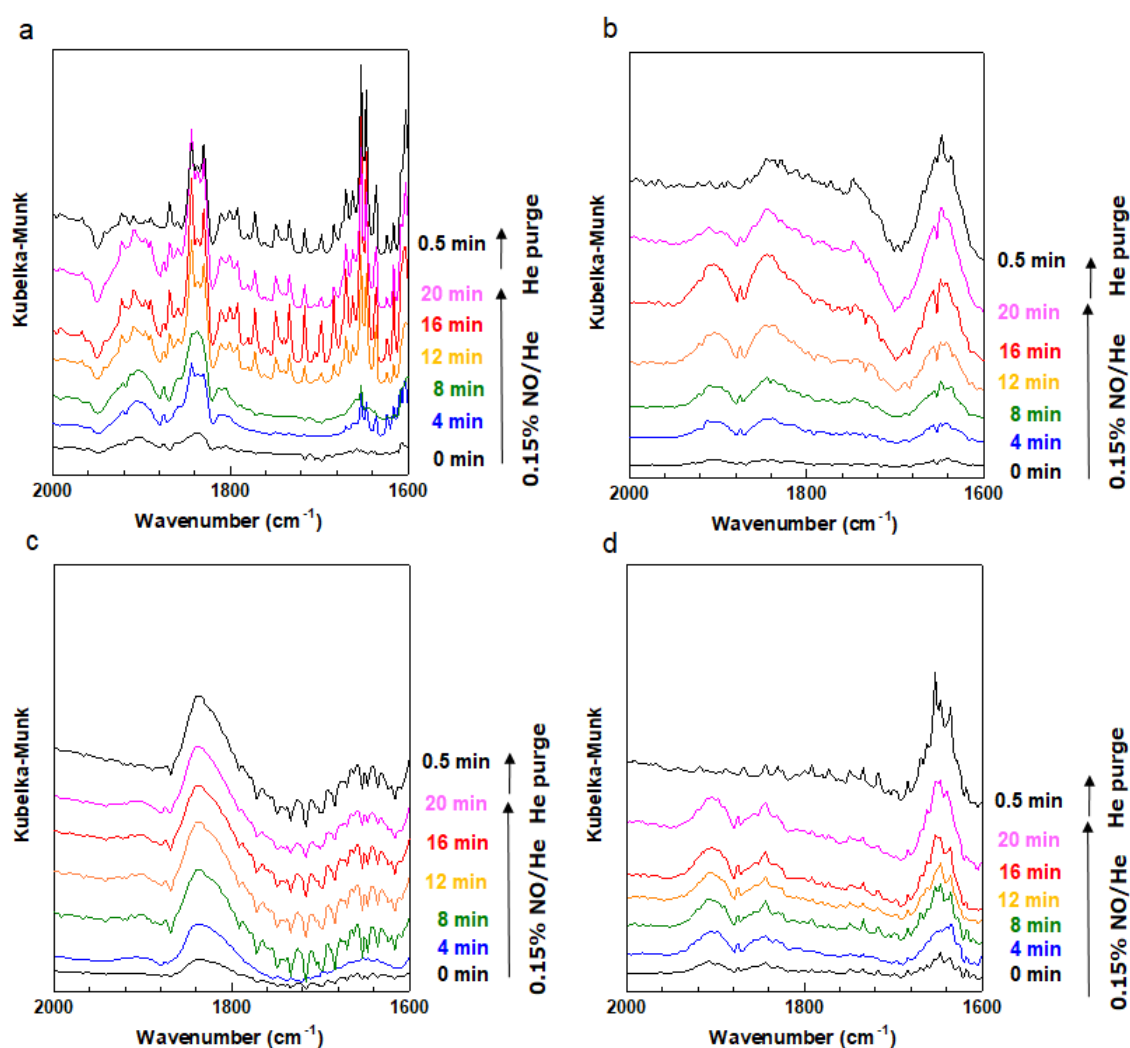


Figure 43. (a) In situ NO IR spectra of (a) **Cu/*cry*UiO-66**, (b) **Cu/*am*UiO-66**, (c) **Cu-ZnO/ γ -Al₂O₃** and (d) **Cu-ZnO/*am*UiO-66**.

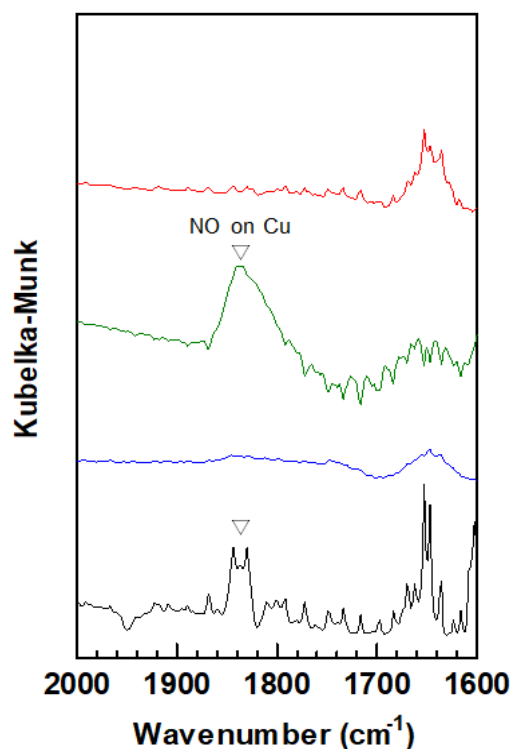


Figure 44. In situ IR spectra of **Cu/cryUiO-66** (black), **Cu/amUiO-66** (blue), **Cu-ZnO/γ-Al₂O₃** (green) and **Cu-ZnO/amUiO-66** (red) under He after exposure to flow of 0.15% NO/He for 20 min.

Based on the in situ FT-IR and XPS analyses, the Cu NPs in **Cu/amUiO-66** and **Cu-ZnO/amUiO-66** possess relatively uniform surface characteristics and exhibit greater stability in their metallic (Cu⁰) state due to fewer surface defects, compared to those in **Cu/cryUiO-66** and **Cu-ZnO/γ-Al₂O₃**. This stability is likely facilitated by the amorphous UiO-66 (**amUiO-66**) framework, which contains a higher density of unsaturated Zr sites, resulting from a reduced number of terephthalate linkers compared to **cryUiO-66**. In addition to the stabilization of Cu⁰

species, the **amUiO-66** matrix itself is expected to contribute to the activation of hydrogen by promoting its dissociation and subsequent spillover to Zr sites, thereby enhancing the catalytic efficiency for CO₂ hydrogenation to methanol on **Cu/amUiO-66** and **Cu-ZnO/amUiO-66**.

4-4. Conclusion

We developed Cu NP and Cu-ZnO nanocomposite catalysts supported on amorphous UiO-66 via a spray-drying technique. This represents the first reported example of combining metal NPs with an amorphous MOF for catalytic applications in gas-phase reactions. Structural characterization through XRD, EXAFS, and STEM-EDX elemental mapping confirmed the uniform dispersion of Cu or Cu-ZnO species within the amUiO-66 framework. The catalyst **Cu/amUiO-66** demonstrated CO₂-to-methanol hydrogenation activity three times greater than its crystalline analogue, **Cu/cryUiO-66**, highlighting the beneficial impact of the amorphous support structure. Moreover, the **Cu-ZnO/amUiO-66** catalyst exhibited even higher methanol productivity, outperforming **Cu/amUiO-66** by a factor of 1.5 and the conventional **Cu-ZnO/ γ -Al₂O₃** catalyst by a factor of 2.5. These findings indicate that the spray-drying approach offers a promising route to design advanced metal NP/ **amMOF** catalysts with superior catalytic properties.

4-5. References

72. P. Ramaswamy, N. E. Wong, G. K. Shimizu, *Chem. Soc. Rev.* **2014**, *43*, 5913-5932.
73. C. Zlotea, R. Campesi, F. Cuevas, E. Leroy, P. Dibandjo, C. Volkringer, T. Loiseau, G. Ferey, M. Latroche, *J. Am. Chem. Soc.* **2010**, *132*, 2991-2997.
74. G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, K. Kato, M. Tanaka, T. Yamamoto, S. Matsumura, H. Kitagawa, *Nat. Mater.* **2014**, *13*, 802-806
75. J.-D. Xiao, Q. Shang, Y. Xiong, H. Zhang, H.-L. Jiang, *Angew. Chem. Int. Ed.* **2016**, *55*, 9389-9393.
76. K. M. Choi, K. Na, G. A. Somorjai, O. M. Yaghi, *J. Am. Chem. Soc.* **2017**, *139*, 356-362
77. Q. Yang, Q. Xu, H.-L. Jiang, *Chem. Soc. Rev.* **2017**, *46*, 4774-4839.
78. J. D. Xiao, L. Han, J. Luo, S.-H. Yu, H.-L. Jiang, *Angew. Chem. Int. Ed.* **2018**, *57*, 1103-1107
79. N. Ogiwara, H. Kobayashi, Y. Yakushigawa, Y. Nishiyama, K. Sugimoto, M. Maesato, J. M. Taylor, H. Kitagawa, *Angew. Chem. Int. Ed.* **2019**, *58*, 11731-11736.
80. G. Lu, S. Li, Z. Xuan, O. K. Farha, J. T. Hupp, C. A. Mirkin, *Nat. Chem.* **2012**, *4*, 310-316
81. M. Zhao, C.-W. Kuo, Y.-Z. Huang, B.-C. Hu, H. Zhang, H.-L. Jiang, *Nature* **2016**, *539*, 76-80.
82. G. Li, S. Zhao, Y. Zhang, Z. Tang, *Adv. Mater.* **2018**, *30*, e1800702
83. T. D. Bennett, S. Cao, J. C. Tan, W. I. F. David, S. Hull, A. K. Kingston, P. Casati, P. J. Saines, A.

- K. Harrington, A. K. Cheetham, *J. Am. Chem. Soc.* **2011**, *133*, 14546-14549.
84. T. D. Bennett, A. K. Cheetham, *Acc. Chem. Res.* **2014**, *47*, 1555-1563.
85. A. D. Katsenis, A. Puškarić, V. Štrukil, C. Mottillo, P. A. Julien, K. Uzarevic, H. Uhirova, J. L. Do, S. A. Kimber, P. J. Fabbiani, T. Friscic, *Nat. Commun.* **2015**, *6*, 6662.
86. S. Tominaka, H. Hamoudi, S. Mei, T. D. Bennett, A. K. Cheetham, M. D. Allendorf, *Chem. Sci.* **2015**, *6*, 1465-1473.
87. W. Chen, Y. Huang, C. Li, J. Chen, H.-L. Jiang, H. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 5195-5199.
88. D. Umeyama, S. Horike, R. Babarao, M. R. Hill, S. Kitagawa, *Chem. Commun.* **2015**, *51*, 12728-12731.
89. A. Qiao, T. D. Bennett, H. Tao, A. J. Kraffer, M. N. Mortensen, Y. Yue, *Sci. Adv.* **2018**, *4*, eaao682
90. K. W. Chapman, G. J. Halder, P. J. Chupas, *J. Am. Chem. Soc.* **2011**, *133*, 18583-18585
91. C. Orellana-Tavra, E.F. Baxter, T. Tian, T. D. Bennett, N. K. H. Slater, A. K. Cheetham, D. Fairen-Jimenez, *Chem. Commun.* **2015**, *51*, 1387-1390.
92. B. Li, H. C. Zeng, *Chem. Mater.* **2019**, *31*, 5320-5330.
93. C. Liu, B. Li, H. C. Zeng, *Angew. Chem. Int. Ed.* **2020**, *59*, 3630-3638.
94. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, K. P. Lillerud, S. Bordiga, S. Svelle, *J. Am. Chem.*

- Soc.* **2008**, *130*, 13850-13851.
95. B. Rungtaweeworant, J. Baek, J. R. Araujo, B. S. Archanjo, K. M. Choi, O. M. Yaghi, G. A. Somorjai, *Nano Lett.* **2016**, *16*, 7645-7649.
96. B. An, Z. Li, Y. Song, J. Zhang, K. Cheng, C. Wang, W. Lin, *J. Am. Chem. Soc.* **2017**, *139*, 3834-3840.
97. H. Kobayashi, Y. Mitsuka, H. Kitagawa, *Chem. Sci.* **2019**, *10*, 3289-3294.
98. T. Ishida, M. Nagaoka, T. Akita, M. Haruta, *Chem. Eur. J.* **2008**, *14*, 8456-8460.
99. H.-L. Jiang, B. Liu, T. Akita, M. Haruta, H. Sakurai, Q. Xu, *J. Am. Chem. Soc.* **2009**, *131*, 11302-11303.
100. M. Sabo, A. Henschel, M. Fröba, M. Kondo, S. Kaskel, *J. Mater. Chem.* **2007**, *17*, 3827-3832.
101. R. J. T. Houk, B.W. Jacobs, J. P. Gabaldon, M. T. Luk, S. T. Pereira, J. S. Wheeler, V. Stavila, A. A. Talin, M. D. Allendorf, *Nano Lett.* **2009**, *9*, 3413-3418.
102. Q. L. Zhu, J. Li, Q. Xu, *J. Am. Chem. Soc.* **2013**, *135*, 10210-10213.
103. S. Hermes, M.-K. Schröter, R. Schmid, R. A. Fischer, *Angew. Chem. Int. Ed.* **2005**, *44*, 6237-6241.
104. M. Müller, S. Hermes, K. Kähler, M. W. E. VandenBerg, M. Muhler, R. A. Fisher, *Chem. Mater.* **2008**, *20*, 4576-4586.

105. W. Lim, K.M. Choi, S. B. Choi, J. H. Choi, K. Choi, *Angew. Chem. Int. Ed.* **2012**, *51*, 9814-9817.
106. P. Hu, X. Cao, B. Stahl, S. Li, S. Wu, C. Cheng, M. Shao, X. Wang, J. Jiang, H. Zhang, *J. Am. Chem. Soc.* **2014**, *136*, 10561-10564.
107. C. Rösler, D. Esken, C. Kirchberg, K. Hierl, I. S. Correu, M.W. E. VandenBerg, M. Muhler, R. A. Fisher, *Chem. Eur. J.* **2017**, *23*, 3583-3590.
108. H. Noh, C.-W. Kung, T. Islamoglu, A. W. Peters, Y. Liao, S. J. Garibay, X. Zhang, M. R. DeStefano, J. T. Hupp, O. K. Farha, *Chem. Mater.* **2018**, *30*, 2193-2197.
109. N. Ogiwara, G. V. Burgess, C. Richardson, H. Kitagawa, *Nano Lett.* **2020**, *20*, 426-432.
110. Y. Mitsuka, H. Kobayashi, H. Kitagawa, *Chem. Lett.* **2016**, *45*, 1313-1315
111. T. D. Bennett, J.-C. Tan, Y. Yue, E. Baxter, O. V. Magdysyuk, A. -V. Barthel, W. Chen, S. Ahlet, P. K. Cauligi, M. G. hanifa, M. Casati, P. J. Saines, A. K. Harrington, A. I. Dugulan, C. W. Ashling, A. K. Chakravaty, S. Li, T. J. Vickers, P. A. Chater, A. K. Cheetham, *Phys. Chem. Chem. Phys.* **2016**, *18*, 2192-2201.
112. M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, R. Kniep, J. K. Nørskov, R. Schlögl, *Science* **2012**, *336*, 893-897.
113. J. Zhong, H. C. Yang, H. C. Zeng, *Chem. Soc. Rev.* **2020**, *49* 1385-1413.
114. W. Wang, Z. Qu, L. Song, Q. Fu, *J. Energ. Chem.* **2020**, *40*, 22-30.

115. A. Dandekar, M. A. Vannice, *J. Catal.* **1998**, *178*, 621-639.
116. K. Hadjiivanov, T. Venkov, H. Knözinger, *Catal. Lett.* **2001**, *75*, 55-59.
117. T. Venkov, M. Dimitrov, K. Hadjiivanov, *J. Mol. Catal. A Chem.* **2006**, *243* 8-21.

Chapter 5

General Conclusion

This doctoral dissertation explores the development of new strategies for synthesizing hybrid materials comprising metallic NPs and MOFs, with a particular focus on their catalytic applications. The study not only explores the synthesis techniques, but also the structural characterization and catalytic performance of these hybrid materials.

Chapter 1 introduces the importance of catalysts in sustainable energy conversion. Conventional catalytic systems, such as metal NPs supported on metal oxides, zeolites or carbon-based materials, are reviewed briefly to provide a foundation. MOFs are then proposed as a promising alternative due to their high surface area, tunable porosity and flexible composition. Spray drying is selected as a promising approach for fabricating MOF-based composites with embedded NPs. This chapter discusses the potential of this technique to enable the efficient, scalable synthesis of well-dispersed nanocomposites. The chapter concludes by outlining the rationale behind using these hybrid materials in CO₂ hydrogenation reactions to produce methanol.

Chapter 2 explores the feasibility of synthesizing MOFs via spray drying. First, the fundamental principles of spray drying are introduced, followed by the design of a process to

synthesize MOF particles by optimizing reaction parameters. The resulting MOF powders are characterized using SEM, XRD, FTIR and nitrogen adsorption isotherms (BET analysis). This confirms the successful formation of MOFs via this method. Furthermore, the scope of MOF synthesis is expanded by using two different organic linkers, thereby demonstrating the spray-drying technique's versatility.

Chapter 3 presents a MW-assisted, one-pot synthesis approach for fabricating nanoparticle–MOF composites. This method enables the rapid complexation of pre-formed metal NPs with MOF precursors under controlled conditions. The structural and morphological properties of the resulting composites are verified using SEM, XRD, FT-IR and BET analyses, demonstrating the efficiency with which MW-assisted synthesis can produce NP–MOF hybrids.

Chapter 4 describes the fabrication of nanoparticle–MOF composites using the spray-drying method. A precursor solution containing MOF components and pre-synthesized NP is spray dried, then reduced, resulting in the successful integration of metal NPs within the MOF matrix. Structural characterization via SEM, XRD, FTIR and nitrogen adsorption measurements confirm the formation of the composite material. Catalytic testing reveals that the spray-dried composites exhibit 2.5 times higher activity for CO₂ hydrogenation to methanol than conventional catalysts supported on metal oxides, demonstrating superior dispersion and

accessibility of active sites.

In summary, this dissertation establishes a comprehensive methodology for designing and fabricating metal NP/MOF hybrid catalysts through scalable, efficient techniques such as spray drying and MW-assisted synthesis. The findings offer new insights into the structural control and functional enhancement of MOF-based catalytic materials, which show great potential for future applications in sustainable energy and green chemistry.

Acknowledgement

This thesis summarizes the author's work in collaboration with Kyoto University and Shoei Chemical Inc., under the supervision of Professor Hiroshi Kitagawa (Division of Chemistry, Graduate School of Science, Kyoto University), from September 2009 to March 2014.

Firstly, the author would like to express their sincere gratitude to Prof. Kitagawa. His enthusiastic guidance and valuable advice were essential to this research and significantly broadened the author's worldview. The author had the opportunity to conduct research under Prof. Kitagawa's guidance while participating in an industry-academia joint development project under the NEDO Project, supported by the Ministry of Economy, Trade and Industry. Throughout the project, the author engaged in fruitful discussions and received constant support, which taught the author a great deal about the role of a scientific researcher and the qualities of an organizational leader.

The author was also deeply impressed by the high standard of the Kitagawa Laboratory. It is an ideal environment for researchers, and the state-of-the-art equipment, analytical instruments, and simulation software were truly inspiring.

The author would like to express their sincere gratitude to Associate Professor Hirokazu Kobayashi for his invaluable support, insightful discussions and helpful guidance. Without Prof.

Kobayashi's support, the author could not have completed this research. The author is also very grateful for his continued support and research advice since leaving the project.

The author would also like to thank Professor Susumu Kitagawa, the deputy project leader of the NEDO project, and Professor Satoshi Horike, the theme leader. They taught the author about MOFs from the ground up, and their hard-working attitude sparked an interest in unknown areas of science.

Additionally, the author would like to thank Dr. Yasutaka Inubushi (Kuraray Co., Ltd.), Dr. Keisuke Kishida (Showa Denko K.K.), Ms. Yasuko Mitooka (Toyobo Co., Ltd.) and Dr. Lifan Yang, all of whom participated in the intensive research of the NEDO Project. Studying alongside members of academia and other companies for about eighteen months was an invaluable experience.

The author would also like to thank Ms. Saeka Fujiwara of the Kitagawa Laboratory, who measured many of the author's samples, and Professor Naoki Ogiwara for discussing the measurement data. Furthermore, the author would also like to thank Professor Masaaki Haneda of the Nagoya Institute of Technology for the in-situ FT-IR measurements and discussions. Special thanks are also due to Dr. Kazuro Nagashima (Senior Fellow) and Dr. Hidenori Ieda (Director of R&D) of Shoei Chemical Inc., for their valuable assistance in preparing this paper.

Special thanks are also due to Mr. Yuji Akimoto, Executive Director of Shoei Chemical Inc., for recommending our participation in the NEDO project. The author would also like to thank all the members of Shoei Chemical Inc. for their valuable contributions to this research. Finally, I would like to express their sincere gratitude to everyone who has supported and encouraged me, especially my parents.

Yuko Mitsuka

January 2026