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In Situ Thermal Solvent-Free Synthesis of Zeolitic Imidazolate Frameworks with High Crystallinity and Porosity for Effective Adsorption and Catalytic Applications

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Moreover, the beneficial chemical and physical properties of the synthesized material exhibited potential application for adsorption and catalysis. Overall, the IST method approach is a novel ZIF synthesis procedure generating high porous crystalline ZIFs. The IST is a green strategy avoiding solvent, activation, or posttreatment to remove unreacted residual, side-product, and guest molecules from the product. Additionally, the single-step IST process showed scalability for large-scale material synthesis.

1. INTRODUCTION

Highly crystalline and porous materials known as metalorganic frameworks (MOFs) having coordination between metal clusters/ions and organic ligands are still receiving increasing interest.¹ The flexibility in structures and intrinsic properties of MOFs, such as high specific surface area, tunable pore size, pore volume, etc., result in a high potential for the adsorption, separation, and beyond in advanced applications such as optical sensors and energy storage.²⁻⁵ Within the MOFs, metal ions tetrahedrally coordinated with organic imidazole-based linkers to construct a framework named zeolitic-imidazole frameworks (ZIFs), a subclass of MOFs.⁶ The organic linkers based on imidazole (IM), 1-methylimidazole (MIM), 2-methylimidazole (2-MIM), 1-ethylimidazole (EIM), and 2-nitroimidazole (NIM)) are mainly applied to construct ZIFs. Regarding the metal ions, mainly Zn, Co, Fe, and Mn are used to construct ZIFs. The ZIF structure, containing multiple coordination of metal ions and organic imidazole ligands, provides unique properties over other materials, such as zeolites, metal oxides, activated carbons, and so on. Among the ZIF structures, the 2-methylimidazole linker used for ZIFs (ZIF-8 (Zn), ZIF-67(Co), and bimetallic Zn/Co-ZIF) revealed a unique arrangement with interesting physical, chemical, mechanical, and thermal properties. Their structures disclose the most exposed development for synthesis, functionalization/modification, composite, and application over other ZIFs and MOFs. Several published experimental and review articles confirm the outstanding properties of these materials.⁷⁻¹¹ Due to their fascinating properties, these ZIFs were applied in a number of applications, such as adsorption, storage, and selective separation. Further, these enthralling properties, in which different metal species and functionalized imidazole ligand are combined to provide suitable heterogeneous catalysts and advance application in the field of chemical sensor and electrochemistry.^{7,9,12}

Various methods are developed to synthesize MOFs/ZIFs for numerous applications in a wide range of different fields. Typically, in the conventional route to synthesize MOFs or ZIFs, the metal ion and ligand precursor are dissolved in an organic solvent before heating under certain conditions (solvothermal method). The process could be carried out in long space-time, usually from several hours up to a week. Organic solvents such as DMF, DEF, THF, or alcohol, etc., are commonly used to synthesize MOFs/ZIFs due to their high

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✓ Scalable large production

ability to dissolve the precursors and support in crystal formation. Using water as a solvent, a green method was developed at room temperature, generating nanocrystal products and a high production yield compared to the solvothermal synthesis.^{13–15} However, only a limited number of precursors (metal and ligand) display solubility in water, resulting in only a few achievements for the synthesis of MOFs/ZIFs. Improvements in the green approach were obtained using advanced synthesis techniques such as microwave, mechanochemical, spray drying, electrochemistry, etc.^{16,17} The microwave-assisted method is developed for fast crystallization MOFs synthesis. Still, a unique instrument with a complicated operation is required. Nonconventional methods such as electrochemical deposition, nucleation agent seeding, etc., have been developed to synthesize ZIFs. Despite the currently available methods to synthesize these materials, there are still several drawbacks, e.g., high energy, utilization of expensive or harmful precursors and organic solvents, prolonged reaction time, excess of ligand (ligand/metal > 1), use of additives (acid/base), or application of a complex instrument, and so on. During the conventional method, the synthesis and subsequent post-treatment produce various wastes resulting in a nonenvironmentally friendly synthesis of the materials. Additionally, the presence of a solvent, salt residue, or side-products requires further processing as posttreatment (purification or activation) before introducing the MOF material in an application. The activation (posttreatment) is required to access all material's functionalities before using it in an application. All these reasons limit the synthesis and exploitation of ZIFs in new applications. Moreover, no practical information for the synthesis on a large scale is available. The reported different methods to synthesize the materials resulted in ZIFs with specific structures and properties. The obtained properties can be correlated with the desired applications.¹⁸⁻²⁰ Therefore, exploiting a new synthetic method with comparable facile and green procedures is of ongoing interest and challenge in the development of MOFs/ZIFs.

Herein, the development of a new method based on a facile and straightforward one-pot synthesis route to synthesize ZIFs (ZIF-8, ZIF-67, and ZnCo-ZIF) through the in situ thermal treatment (IST) method is reported. High porous crystalline materials were obtained in a short synthesis time under solvent- and additive-free conditions in this approach. The assynthesized materials were demonstrated to be isostructural and exhibited identical properties (i.e., porosity, surface area, and thermal stability) compared with traditional synthesized ZIFs. Moreover, no post-treatment or activation process of the synthesized material was required. Finally, the obtained ZIFs applying the straightforward and effective cost IST method demonstrated advantages for chemical and physical properties. These advantages were exemplified by adsorption and catalysis application. Moreover, the novel IST synthesis method for ZIFs provides the potential for industrial application. All arguments mentioned above are advantageous compared with the traditional or earlier reported synthesis methods.

2. EXPERIMENTAL SECTION

2.1. Materials and Synthesis. All reagents were used as received from Aladdin Ltd., including cobalt(II) acetylacetonate (97%), zinc acetylacetonate hydrate (97%), 2-methylimidazole (98%), and epichlorohydrin (analytical grade grad). In a typical synthesis of ZIF-67, the cobalt(II) acetylacetonate (1 mmol, 257 mg) and 2-

methylimidazole (3 mmol, 246 mg) were mixed and ground in a mortar about 5 min under ambient atmosphere. Cobalt(II) acetylacetonate was replaced by zinc acetylacetonate hydrate (1 mmol, 263 mg) to synthesize ZIF-8. For the synthesis of Zn/Co-ZIF, both metal precursors (50:50 ratio of cobalt(II) acetylacetonate/zinc acetylacetonate) were mixed. Then the obtained solid mixture was placed in an alumina boat $(30 \times 60 \times 15 \text{ mm}^3)$ before transferring into the quartz tube (OD: 60 mm, length: 1000 mm) inside the muffle furnace (TL 1200, Nanjing Bo Yun Tong Instrument Technology Co. Ltd). An Ar or N₂ (100 cm³·min⁻¹) stream was flown in the system. The temperature program was set in two steps; from room temperature to 100 °C within 30 min, increased to 200 °C (5 $^{\circ}$ C·min⁻¹), and then the temperature was kept constant for 1 h. Finally, the product was collected after cooling and used in further applications or characterization. The yield of the products was measured using eq 1.

synthesis yield (%) =
$$\frac{\text{average weight of product}}{\text{theoretical product}} \times 100$$
 (1)

2.2. Characterization. The X-ray diffraction (XRD) was performed using a Bruker D8 Advance diffractometer at 40 kV and 45 Ma with Cu K α radiation source (λ = 1.54056 Å at 40 kV and 45 Ma) and a scanning rate of $2^{\circ}/\text{min}^{-1}$. The field-emission scanning electron microscopy (FE-SEM, Zeiss Ultra Plus) was applied to determine the materials' size and morphology. The gas adsorptiondesorption measurement was carried out with an ASAP 2020 Analyzer (Micrometrics Instruments) using N2, CO2, and CH4 gases of 99.999% purity. In addition, samples were activated under a dynamic vacuum at 200 °C for 3 h before the adsorption measurement. The porosity and surface area were analyzed by the Brunauer-Emmett-Teller (BET) and Langmuir methods. The linearized BET and Langmuir equations were fitted in the range of $0.003 < P/P_0 < 0.05$. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 FT-IR spectrometer with KBr pellets in the wavelength range of 4000–400 cm⁻¹. Thermogravimetric analysis was carried out on a TGA from Netzsch (STA449c/3/G) Instrument with a heating rate of 10 °C·min⁻¹ under a nitrogen atmosphere. The acidity and basicity measurements were carried out on the Auto Chem II 2920 instrument equipped with a thermal conductivity detector (TCD) (Micromeritics). NH₃ and CO₂ were used probe gas for temperatureprogrammed desorption tests for acidity (NH₃-TPD) and basicity (CO₂-TPD) analysis, respectively. ¹H NMR spectra were recorded on a Bruker Avance III 500 spectrometer in CDCl₃ with 1,3,5,-trioxane as the internal reference, and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker Avance 500 (126 MHz) spectrometer.

2.3. Catalytic Reaction. The addition of CO_2 into epichlorohydrin was performed using the synthesized material (ZIF-67_1:3) and compared with the conventionally synthesized ZIF-67 in methanol at room temperature (ZIF-67-RT). The synthesized catalysts (50 mg) and substrates (9.2 mmol) were charged in a high-pressure glass tube (15 mL) with a magnetic stir bar. The reactor's atmosphere was exchanged with CO_2 (99.9% purities) before pressurizing to 1.5 bar of CO_2 . The reactor was immersed in a preheated oil bath at 90 °C under stirring conditions (400 rpm) for 24 h. The reactor was cooled to room temperature, and 1,3,5-trimethoxybenzene as an internal standard (3 mmol) and CDCl₃ (1 mL) were added. The reaction mixture was analyzed via ¹H NMR using CDCl₃ as a solvent. In the recyclability experiments, the catalyst was recovered by centrifugation, washed three times with methanol, and dried at 120 °C under vacuum for 12 h for the next reuse.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. Among zeolitic imidazole frameworks, ZIFs based on the 2-methylimidazole linker (ZIF-8, ZIF-67, and bimetallic ZnCo-ZIF) have been mainly synthesized and applied in a broad field of applications.^{7,21-23} In particular, ZIF-67 and its derivatives show outstanding characteristics and performances in various

applications, such as gas adsorption, molecular separation, electrochemistry, catalysis, and so on.^{9,24–27} Consequently, the in situ thermal (IST) synthesis concept was first adopted for the synthesis of ZIF-67. The chemical transformation of a mixture of precursors, cobalt(II) acetylacetonate, and 2-MIM, was investigated via weight changes in thermogravimetric analyses (TGA). The weight change in the mixture of solid precursors as a function of temperature under a nitrogen atmosphere was measured and is shown in Figure 1. The TGA



Figure 1. TGA profiles of physically mixed precursors and the assynthesized ZIF-67_1:3.

profile indicates two weight loss temperatures at 197 °C (78% weight change) and 560 °C (9% weight change) of the physically mixed precursor sample. Interestingly, the chemical reaction between the two precursors could occur at a weightloss temperature of ≈ 197 °C since this temperature is not related to the decomposition/evaporation temperature of the precursors (mp of 2-MIM: 144 °C; mp of cobalt(II) acetylacetonate: 165 °C; bp of 2-MIM: 267 °C). Moreover, the second weight loss temperature (\approx 560 °C) was related to the degradation temperature of ZIF-67.²⁸ To gain more insight into the chemical transformation, the sample of physically mixed precursors was investigated by temperature-programmed X-ray diffraction. Different crystal patterns were observed at a variance of temperatures, as depicted in Figure 2. The observed diffraction patterns changed at a treatment temperature of 150 °C and higher. The original pattern of the mixed precursors disappeared and was replaced by a new diffraction pattern. This result reveals the crystal formation initiation between the 2-MIM and cobalt ions in solvent-free conditions under thermal treatment. In particular, the generated peaks can be attributed to a mixed-phase of 2D (ZIF-L) and 3D structures of ZIF-67 (Figure S1). With the increase of the temperature in the range of 150-300 °C, new crystal structures further develop and grow. Moreover, an increasing crystal intensity is observed with increasing temperature. The diffraction pattern and peak position transform sharper and become similar to ZIF-67 (3D) after thermal treatment at 150 °C. This result indicates the occurrence of an intermediate phase on the route to ZIF-67. This outcome of the crystal transformation showed the minimum temperature required for the IST method to synthesize ZIF-67. In addition, one should be aware that the

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Figure 2. Temperature-programmed XRD patterns measured under a nitrogen flow, 1:4 mole ratio of cobalt(II) acetylacetonate/ 2-methylimidazole.

temperature was continuously increasing during the temperature-programmed X-ray diffraction analysis. Keeping the temperature constant (above 150 $^{\circ}$ C) could influence the crystallization process.

In an effort to rationally synthesize and optimize the properties of the synthesized materials, the ratio of precursors (metal/ligand), synthesis temperature, metal precursor, and time were adjusted. The mixtures of the precursors of cobalt(II) acetylacetonate and 2-methylimidazole were heated in a tubular furnace under an inert atmosphere (Ar or N_2). A high crystallinity and porosity combined with a large surface area are typical characteristic properties of ZIFs. Therefore, the optimization of synthetic parameters could be verified based on the crystalline pattern (XRD), surface area (BET), and porosity properties of the synthesized materials. During the synthesis, the mole ratio between metal ions and linkers is crucial in the crystal/framework of ZIFs formation.^{29,30} The cobalt ion bridging with four organic linkers (2-methylimidazole) is a theoretical structure of ZIF-67. Therefore, the mole ratio of metal-to-linker was initially investigated to gain insight into the influence on the crystal formation and properties of the synthesized materials by the IST method. Here, we employed different mole ratios (M/L) of cobalt(II) acetylacetonate/2-methylimidazole (1:1, 1:3, 1:4, 1:6, and 1:8) followed by an in situ thermal treatment at 200 °C for 1 h under an argon atmosphere (100 cm³·min⁻¹). The solid crystalline products obtained from different mole ratios after thermal treatment were then characterized by powder X-ray diffraction, as shown in Figure 3a. The observed XRD patterns reveal a crystal transformation in all ratios after the in situ thermal treatment (200 °C) compared with the physically mixed precursor (no thermal treatment). Moreover, the isocrystalline pattern was obtained starting from the mole ratio 1:3 and higher. The lowest ratio (ZIF- $67_{1:1}$) exhibited a different XRD pattern. The difference could be explained by the shortage of ligand during the synthesis that might limit the bridging framework compared to the theoretical ratio. The deficiency of the ligand was indicated by the color difference compared with the materials having higher ratios (deep purple to navy blue).



Figure 3. XRD patterns (a) and nitrogen isotherms (b) of ZIF materials obtained using the IST method.

Table 1. Opti	mum Conditions	Using the IST	' Method to Sy	nthesize ZIF	s Based on t	the Surface	Area and	Porosity	Properties
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					surface area			
sample	ratio (M/L)	time ^{b} (h)	temperature (°C)	product ^c (% yield)	BET	Langmuir	pore size ^c (nm)	pore volume ^{c} (cm ³ ·g ⁻¹)
ZIF-67	1:1	1.0	200	83	285	308	1.177	0.113
	1:3	0.5	200	84	1664	1773	1.243	0.549
		1.0		88	1610	1722	1.247	0.546
		1.5		87	1644	1623	1.244	0.525
		2.0		81	1618	1736	1.242	0.555
		1.0	300	81	1716	1849	1.252	0.618
	1:4	1.0	200	85	1624	1754	1.242	0.577
	1:6			85	1625	1766	1.239	0.591
	1:8			89	1609	1714	1.241	0.567
	2:6			90	1682	1783	1.241	0.574
	4:12			92	1633	1764	1.239	0.565
ZIF-67 ^d	1:8	24	room temp.	37	1888	1996	1.260	0.681
ZIF-8	1:3	1.0	200	86	1889	2010	1.273	0.675
ZIF-8 ^d	1:8	24	room temp.	42	1821	1913	1.294	0.66
ZnCo-ZIF	1:3	1.0	200	85	1682	1789	1.261	0.597
ZnCo-ZIF ^d	1:8	24	room temp.	40	1864	1998	1.268	0.62

^{*a*}Held at a certain temperature. ^{*b*}Product yield calculated from the average product weight obtained from two syntheses with theoretical molecular weight (MW) of ZIFs (ZIF-8 = 227 mol/g, ZIF-67 = 221 mol/g, ZnCo-ZIF = 224 mol/g) = $\frac{\text{average weight of product}}{\text{mole of metal precusor × MW of ZIFs}} \times 100$. ^{*c*}The Horvath–Kawazoe method. ^{*d*}ZIF synthesis was carried out at room temperature in methanol as reported in ref 15.

The porosity and surface area of the synthesized materials prepared with different mole ratios were further determined. The nitrogen isotherm type I for all of the ratios but with a different adsorption amount was observed (Figure 3b). In addition, the nitrogen isotherm type I could define the microporous structure of all synthesized materials. Interestingly, the hysteresis in the N2 isotherm was found for the lowest ratio (ZIF-67_1:1) and disappeared using a larger ligand ratio (Figure S2-S6). This presence of a hysteresis possibly indicates the ligand shortage (2-MIM) during the construction of the framework combined with a large metal residual in the product (ZIF-67_1:1). Hence, a low ligand ratio, lower than the theoretical M/L ratio 1:4 for ZIF-67, probably results in the incomplete construction of ZIF-67. The cobalt residual or unreacted species participated in product weight and decreased the surface area.³⁰ Also, the gas released

during the decomposition from precursor or chemical reaction during IST treatment suggests the formation of the hysteresis in the N_2 -isotherm. The amount of adsorbed nitrogen at -196°C was used to calculate the surface area and porosity of the materials. The Brunauer-Emmett-Teller method and Langmuir surface area of the synthesized materials revealed a varying degree of the surface area, as summarized in Table 1. The surface area increased according to the higher ligand mole ratio reaching a plateau after a 1:3 ratio. Simultaneously, the porosity properties (pore size and pore volume) exhibited a similar trend as the surface area (Table 1). This observation could imply that the ligand excess (M/L > 1:3) is unnecessary for the synthesis of ZIF-67 via the IST method as indicated by the slightly different porosity properties (surface area and porosity). It is worth mentioning that this is the first study, compared with other methods, describing the lowest possible

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Figure 4. SEM images of the materials with different mole ratios (M/L): 1:1 (a), 1:3 (b), 1:6 (c), and 1:8 (d) obtained by in situ thermal method at 200 $^{\circ}$ C for 1 h and 100 cm³/min argon.

metal-to-linker ratio to synthesize ZIFs.^{15,16} Interestingly, the lower mole ratio (M/L: 1:3) of the current investigation resulted in an isostructural material, with identical chemical properties as the ZIF structure using an M/L ratio of 1:4.¹⁶ The advantages of these cost-effective synthesized materials using the IST method were investigated; see the Applications section.

A pink to red-colored solid was first observed after grinding cobalt(II) acetylacetonate (red) and 2-methylimidazole (white) in mortar for 5 min. The melting point apparatus (M-565, Büchi) was used to monitor the changes in physical properties during the ramping temperature applied in the IST method (Figure S9). The pink to red-colored precursor mixture gradually transforms into a purple-colored solid after heating the sample to 250 °C (10 °C·min⁻¹) under an inert atmosphere (N_2 or Ar). The purple-colored product was characterized using powder X-ray diffraction, revealing the crystalline nature of the product. The same synthesis performed in the presence of oxygen (air atmosphere) resulted in a black solid of which the diffraction pattern did not match with that of crystalline ZIF-67. Here, the oxidation of ligand precursors occurs during the heat treatment in an air atmosphere. These results provided the significance of the atmosphere during the IST method. Interestingly, the initial precursor mixture volume subsided and turned to liquid-like (\approx 150 °C) before the sample was wholly transformed into the purple-colored product at 220 °C. This observation indicates that melting of the ligand precursor was the initial step before the chemical reaction (crystal formation) occurred. The observation of the physical transformation with temperature using the melting point apparatus supports the temperatureprogrammed X-ray diffraction results (Figure 2). Scanning electron microscope analysis (SEM) was applied to obtain morphologic information of the synthesized materials with

different mole ratios (M/L). A plate-like shape with a rough surface was detected for the product synthesized with a 1:1 mole ratio (Figure 4a). The corresponding diffraction pattern matched with the ZIF-67 pattern but was different regarding the peak intensity than the simulated ZIF-67 structure. For the M/L ratio higher than 1:3, the regular rhombic dodecahedral morphology was obtained (Figures 4b-d), although random particle sizes from 50 nm up to 500 nm were seen for materials with a ratio of 1:3 to 1:8. Additionally, SEM images disclosed a crystal-like agglomeration into large particles. Generally, in the conventional method (solvothermal synthesis) of ZIF-67 synthesis, the crystal formation starts from the nucleus and grows homogeneously to obtain crystals with a rhombic dodecahedral shape. However, the absence of solvent during the IST system could result in nonuniform geometries of the material. Nonetheless, the solvent- and additive-free ZIFs synthesis generating a nonuniform particle size distribution was reported in previous research.^{31,32}

The effect of the synthetic parameters applied in the IST method was investigated based on ZIF-67. These parameters include temperature, preparation time, and the metal precursor for the optimal synthesis condition. According to temperatureprogrammed XRD, three different synthesis temperatures (150, 200, and 300 $^{\circ}$ C) were applied, with a precursor mole ratio of 1:3 (M/L) and 1 h of synthesis time under an argon flow of 100 $\text{cm}^3 \cdot \text{min}^{-1}$. As expected, there was no crystal transformation observed at 150°C, which was in good agreement with the obtained TGA result (Figure 1). The temperature of 150 °C, which is just above the melting point of 2-MIM (145 °C) but lower than the melting point of cobalt(II) acetylacetonate (175 °C), might just not be enough to initiate the transformation since no crystal phase changes were observed at 150 °C. In comparison, the XRD analysis at 200 and 300°C revealed crystal transformation. Moreover, the

observed crystalline patterns of both temperatures matched perfectly with the crystalline pattern of ZIF-67 (Figure S7a). Also, slightly different yields were obtained at different temperatures: at 300 °C, 81% yield; and at 200 °C, 88% vield. The porosity (pore size and pore volume) and surface area properties of the material synthesized at 300 °C was slightly higher than the material obtained at 200 °C (Table 1 and Figure S7b). Also, thermal stability up to 500 °C was demonstrated for the obtained product similar to the reported ZIF-67 (Figures 1 and S10). At a synthesis temperature of 300 °C, the crystal formation could be completed at a lower temperature, and then the phase remains stable at the reaction condition of 300°C. The temperature experiments demonstrate that a temperature treatment at 200 °C was sufficient and efficient to generate ZIFs via the IST method. Therefore, a temperature treatment at 200 °C was applied to investigate other synthesis parameters since excellent material properties were obtained at 200 °C. Besides, a higher temperature treatment might generate byproducts (oxide, etc.) that can be trapped in the pores of the material and can hardly be removed later on.³¹ The kinetic experiments for the crystallization using the IST method were investigated for reaction times of 0.5, 1, 2, and 3 h at 200 °C and 1:3 (M/L). No difference in the XRD pattern, surface area, and porosity properties on varying the synthesis time could be observed (Figure S8). However, a slight decrease in the product yield was noticed with a longer synthesis time (Table 1). Although a 30 min synthesis time yields a material with similar characteristic properties as the materials obtained after longer synthesis times, unreacted precursor residues or byproducts remained in the sample as observed from the weight change after activation of the sample for surface area analysis. For a synthesis time of 1 h or longer, no weight change after activation was found, which was supported by TGA analysis (Figure S10). Consequently, the optimal synthesis time of 1 h using the IST method was selected for further investigations.

To verify the metal precursor, a series of commercial precursors based on cobalt(II) (acetate, nitrate, chloride, and acetylacetonate) were investigated applying the fixed conditions of 1:3 mole ratio (M/L) and 200 °C for 1 h. Unfortunately, a jellylike plate or film was found after heat treatment of nitrate or chloride precursor with 2-MIM. In contrast, a black solidlike film remained in the synthesized holder after heat treatment of cobalt(II) acetate and 2-MIM. The cobalt(II) acetylacetonate was the only metal precursor that generated ZIF-67 via the IST method. Remarkably, cobalt(II) oxide as a precursor was previously reported for the thermochemical synthesis of ZIF-67 under solvent-free conditions.³¹ However, the cobalt oxide in the synthesized product decreased the porosity and surface properties, which was a disadvantage of the advanced thermochemical method. Interestingly, herein, no impurities or residues (precursor, metal oxide, byproduct, etc.) were present in the synthesized materials. Moreover, high crystallinity and porosity were obtained in the synthesized ZIFs using the IST method, providing similar material properties compared to the materials synthesized traditionally (Table 1). The obtained results illustrate that the use of different metal sources significantly affects the ZIF-67 formation. Hence, the resulting characteristic properties of the crystal structure, surface area, and porosity of the synthesized ZIF-67 using cobalt(II) acetylacetonate indicated that optimized synthesis conditions were used (1:3 mole ratio (M/L) at 200 °C for 1 h). Moreover, the

obtained material properties were comparable with the reported properties of ZIF-67 obtained via the conventional method.

The primary material characteristics obtained via XRD and BET confirmed that no impurities were present inside the material obtained via the IST method. Thermogravimetric analysis (TGA) was used to determine the impurities and the thermal stability of the synthesized ZIF-67. The mass change or percentage weight change of the as-synthesized ZIF-67 was monitored as a function of temperature. The verification of decomposition or phase transfer was calculated from the weight change cure derivative at different temperatures (DTG), as shown in Figure S10. The TGA profile reveals that thermal events occur up to 500°C before degradation is initiated (69% weight change at 560 °C). The analyzed material gradually degrades with increasing temperature and eventually converts into carbon and cobalt species (>650°C). It needs to be mentioned that the TGA analysis was directly performed on the as-synthesized ZIFs from the IST method without pretreatment or post-activation. However, a small weight change appears (\approx 4.5% weight change) at 350°C, which could be assigned to imperfect coordination (defect structure) since that temperature is higher than the boiling point of 2-MIM.^{19,33} At 550 °C, a significant weight loss due to structural degradation of ZIF-67 obtained from the IST method was observed. Based on the TGA analysis, the thermal stability of ZIF-67 up to 450 °C was established. Considering the absence of distinct weight change at temperatures lower than 300 °C, no precursor residues, byproducts, or guest molecules were present in the material. Additionally, moisture desorption from the surface or pores of the material was absent and hence, did not participate in the degradation process.³ The TGA results were further supported since no weight change after degassing the material for surface area analysis was observed. The ZIF-67 obtained via the IST method indicated a similar thermal behavior as the ZIF-67 synthesized via the conventional method.35

Although the free-solvent synthesis of MOF/ZIFs was approached via mechanochemistry,^{36,37} the addition of solvent or a catalyst salt in small amounts was required to accelerate the construction of the coordination framework.³⁸ This method has an advantage for the large-scale production of MOFs. Nevertheless, the activation or post-treatment is needed to remove the residual reactants or byproducts after synthesis, which is problematic in the typical sizeable synthetic scale. In general, for porous materials, the activation process is mainly required to eliminate impurities such as solvent, moisture, etc., from the pores of the materials. This process fully opens the pore space of the porous material before being used in the desired applications (adsorption, catalyst, etc.). Alike for MOFs or ZIFs, activation due to the presence of certain guest molecules during the synthesis or storage (solvent, residual, moisture, etc.) is required. Mostly, the activation of MOFs is executed via a thermal process. However, during the thermal activation, the structure might change (flexibility property) due to the heat effect exerted on the organic compound in the framework. This structure change can result in different material properties after the activation process.^{39,40} The IST method demonstrated that there was no need for an activation process, which is an attractive advantage. Also, during the porosity analysis, the samples were degassed (activation) as a standard method for surface area and porosity analysis. Interestingly, no weight difference between the fresh



Figure 5. Characterization of ZIFs obtained via the in situ thermal method: (a) powder X-ray diffraction patterns, (b) nitrogen adsorption isotherms, and SEM analysis of (c) ZIF-8 and (d) bimetal ZnCo-ZIF. Synthesis conditions: M/L mole ratio 1:4, 200 °C for 1 h, argon flow: 100 cm³/min.

and activated ZIFs prepared via the IST method could be observed, suggesting the absence of organic residuals, water, guest molecules, etc. Although a direct synthesis of ZIFs from solid precursors under solvent-free has been reported, ^{31,41-45} a post-treatment to remove the residue and byproduct during the crystal formation is still required. Additionally, this route displayed several other drawbacks, including a significant excess of 2-MIM, long reaction time, the presence of unreacted precursor or byproduct in the final product, etc.

To the best of our knowledge, the direct synthesis of ZIFs without the need for activation and obtaining pure porous material have never been reported. The IST method differentiates itself from solvent-free methods such as sonochemical, mechanochemical, etc. Based on the characterization results, the IST method directly provides an "activated" product beneficial in both synthesis and the desired application. Next, the scalability of the IST method was the subsequent investigation. The optimal synthesis parameters of 200 °C for 1 h under a flow of 100 cm³·min⁻¹ argon atmosphere were applied on larger amounts of precursors with a constant mole ratio of cobalt(II) acetylacetonate/2-MIM (1:3). Two samples with M/L = 2:6 and 4:12 were applied to synthesize ZIF-67 (denoted as ZIF-67 2:6 and ZIF-67 4:12). The metal/ligand ratio (M/L) was kept constant, but the amounts were increased, e.g., ZIF-67_1:3 means 1 mol of M and 3 mols of L, while for ZIF-67_2:6, we used 2 mols of M and 6 mols of L; the same reasoning for the sample ZIF-67 4:12. The powder X-ray diffraction spectra of the obtained high crystalline materials matched well with the ZIF-67

structure as the characteristic product (Figure S13). Nevertheless, the porosity and surface area decreased when upscaling with ratios of 2:6 and 4:12, respectively, as shown in Figure S14a. Also, white crystals of 2-MIM were observed in the sample after degassing the material for porosity and surface area analysis. The impurities in the as-synthesized materials (mole ratio of 2:4 and 4:12) were apparent from the weight change of TGA results. A weight loss of 1.8% wt was observed at 205°C for ZIF-67 2:6 and a larger weight loss of 3.4 wt % for ZIF-67 4:12 (Figures S11 and S12). In addition, the temperature at the beginning of the weight loss was in between the melting point and boiling point of 2-MIM. To remove the remaining 2-MIM, the synthesized materials (ZIF-67 2:6 and ZIF-67_4:12) were immersed in methanol overnight and dried before surface analysis. The high porosities and surface area similar to the sample with a ratio of 1:3 was obtained for the upscaled samples (Figure S14b). To avoid the presence of the remaining 2-MIM for the upscaled strategy, a prolonged synthesis time of 2 h for ZIF-67_4:12 was used. The materials obtained using the extended reaction time possess a high crystallinity and porosity as proved in the material characterization (Figures S15 and S16), and importantly, no remaining 2-MIM could be detected. This experiment shows that the IST method is a genuinely solvent-free process and up-scalable producing ZIFs with high crystalline and porosity properties.

Next, the facile and cost-effective IST method was applied for the synthesis of ZIF-8 and bimetallic ZnCo-ZIF. The powder XRD patterns exhibit sharp peaks due to the high crystallinity of the sodalite-type structure (SOD) and matched

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excellently with the simulated spectra of ZIF-8 and ZnCo-ZIF (Figure 5a). No additional peaks were observed in the materials. Furthermore, the porosity and surface area further confirmed the quality of the synthesized materials. The materials revealed high adsorptions and large surface areas with a typical type-I isotherm confirming their microporosity (Table 1 and Figure 5b). Also, the characteristic vibrations present in ZIF materials were observed via FTIR analysis (Figure S17). These results confirmed that the IST method produced the topological crystal structure and properties similar to the reported conventional synthesis method.

3.2. Synthesis Mechanism. A mechanism for the in situ thermal synthesis of ZIFs was proposed based on the experimental results. Thermal X-ray diffraction revealed the generation of a new crystal phase at a temperature above 150 °C. Interestingly, this temperature was situated between the melting point and boiling point of 2-MIM (mp \approx 145 °C, bp \approx 267 °C). Also, the synthesis temperature at 200 °C was the optimal temperature for synthesizing the materials via the IST method. At 200 °C, 2-MIM is molten and can act as an organic linker, forming the framework and simultaneously as solvent. Since only metal and ligand precursors are present in the reaction mixture, the competition between template-assisted and solvent interactions, as in conventional preparations, is absent. Once metal acetylacetonate dissolves in molten 2-MIM, acetylacetonate is being substituted by 2-MIM due to the stronger donation ability of the nitrogen in 2-MIM, eq 2.

$$M(C_{5}H_{7}O_{2})_{2} + 2 - MIM$$

$$\rightarrow M(2 - MIM)_{2} + 2(C_{5}H_{8}O_{2})\uparrow$$
(2)

with M = Co or Zn and 2-MIM: 2-methylimidazole.

Any remaining 2-MIM could be removed during the thermal process due to its lower boiling point. It is commonly accepted that ZIFs have thermal stability up to 500 °C under an inert atmosphere.^{15,16} Highly pure ZIFs were directly obtained after the in situ thermal synthesis without post-treatment or activation process. Therefore, the crystal formation of ZIFs, based on 2-MIM, via the IST method could be similar to the ionothermal method. At the applied reaction temperature, 2-MIM melts and exhibits multiple roles in the crystal formation of ZIFs, including the following:

- 1. Acting as a solvent to transport reactants.
- 2. Employed as directing-agent (ligand) for coordinating with metal ions.
- 3. Used as a hydrophilic agent which influences the asformed framework structure.

3.3. Applications. Nowadays, MOFs/ZIFs are exploited for multiple applications with special attention for their advantageous properties, economics, and environmentally friendly preparation. The potential of ZIFs prepared via the IST method was examined for gas adsorption (CO_2 , CH_4) and heterogeneous catalysis (CO_2 addition into epoxide). Considering the high porosity of the synthesized ZIFs combined with the exposure of the incorporated basic sites from imidazole, the adsorption isotherms of the synthesized ZIFs for CO_2 and CH_4 were examined; see Figure S19. The gas adsorption was performed on ZIFs obtained via the IST method and compared with ZIFs synthesized via the room temperature method, as shown in Figure 6. The CO_2 and CH_4 adsorption capacities revealed that ZIFs obtained via the IST method are competitive with the ZIFs prepared via the room temperature



Figure 6. CO_2 (blue column) and CH_4 (orange column) adsorption at 273 K and pressure up to 800 kPa of ZIFs obtained via the IST method compared with ZIFs prepared via the room temperature method (RT).¹⁵

method. The variance in the surface area might cause a slight difference in the total adsorption amount of CO₂ and CH₄. Furthermore, the high CO₂ selectivity over CH₄ could be of interest for selective CO₂/CH₄ separation applications, such as pre- and postcombustion processes, natural gas production, or biogas upgrading.^{3,46,47}

Acid sites (metal sites) and basic sites (imidazole sites) present on ZIFs are the active species for several catalytic reactions. Recently, the fast crystallization rate of growing MOFs resulting in uncoordinated sites (defect structure) was reported to enhance the catalytic performance.¹⁹ Interestingly, shortening of the crystallization time under solvent-free conditions as applied in the IST method could increase the number of uncoordinated sites compared with the traditional synthesis method. Increasing the number of defect structures could promote catalytic performance in different applications. Considering the high ability for CO₂ adsorption on ZIFs prepared via the IST method, this could be an excellent property to be used in the catalytic conversion of CO₂. The efficient catalytic CO₂ cycloaddition into epoxide to afford cyclic carbonate by ZIF-67 was described earlier in several reports.^{26,48-51} Due to the functionalities in the ZIF-67 structure, acidic sites from cobalt and basic sites from the Ndonor of 2-methylimidazole are reported to promote the CO₂ cycloaddition.²⁶ The catalyst ZIF-67 exhibited an efficient catalytic performance under moderate reaction conditions with excellent selectivity in the absence of solvent and a cocatalyst. Moreover, the high thermal and chemical stability during the catalytic reaction was evidenced by the recyclability of ZIF-67 as a heterogeneous catalyst.⁴⁹ Hence, ZIF-67 prepared via the IST method was applied for the CO₂ cycloaddition into epoxide to synthesize cyclic carbonates. Until now, the most general ZIF-67 synthesis method is the room temperature method using organic solvents or even water.¹⁵ The catalytic performance of ZIF-67 synthesized via IST was compared with that of ZIF-67 synthesized via the room temperature method (ZIF-67-RT). The catalytic performance of the ZIFs toward the CO₂ cycloaddition with epichlorohydrin was evaluated under mild conditions (90 °C, 1.5 bar of CO₂ pressure, 24 h, and solvent- and cocatalyst-free). The catalytic performance revealed an excellent and higher conversion of ZIF-67 than ZIF-67-RT under the same reaction conditions (Figure 7a). The chemical characterization, e.g., acidity and basicity of the materials, was characterized by temperature-programmed desorption (TPD) using NH_3 and CO_2 as probe gas,

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Figure 7. Comparison of catalytic performance and recyclability (a) and NH3-TPD desorption profiles (b) of ZIF-67 synthesized via IST (ZIF-67) and via the room temperature method (ZIF-67-RT).

respectively. The NH₃-TPD results revealed that ZIF-67 via IST (ZIF-67, 0.319 mmol) provided a larger number of acid sites than ZIF-67-RT (0.126 mmol), as shown in Figure 7b. The higher cobalt content of ZIF-67 via IST could expose more acid sites than ZIF-67-RT, which is supported by the NH₃-TPD results. However, the basic characteristic properties $(CO_2$ -TPD) were found to be opposite to the NH₃-TPD results of those catalysts. The slightly lower basicity of ZIF-67 could be the result of a lower 2-MIM content in the structure compared with ZIF-67-RT (ICP and elemental analysis, Table S2). Nevertheless, the higher acidity exploited by ZIF-67 compared with ZIF-67-RT demonstrated an excellent catalytic activity. The acid sites are required for the initial reaction, the ring-opening of the epoxide.²⁶ Furthermore, the robustness of the heterogeneous catalyst was evidenced by the recyclability of the catalyst. The catalyst could be recycled at least four times with a negligible decrease in performance. Also, the spent catalyst XRD analysis determined the structural integrity of the spent catalyst compared to the fresh catalyst.

4. CONCLUSIONS

An efficient, straightforward route, the in situ thermal (IST) method, was proposed to synthesize high porous zeolitic imidazole frameworks (ZIF-67, ZIF-8, ZnCo-ZIF) without solvent or additives. The ligand (2-MIM) using IST acted in a bifunctional manner, forming coordination frameworks with ionized metals and as a solvent for the reaction at the same time. The thermal procedure delivered a crystalline framework and removed the residual 2-MIM and byproducts, if any, during the formation of the materials (free of post-treatment or activation procedure). Under these conditions, an effective synthesis strategy provided in a relatively short reaction time (1 h), a highly crystalline material. Furthermore, the IST method demonstrated to deliver a high yield, is a low-cost method with good reproducibility, avoiding the difficulty in the removal of guest molecules. The synthesized ZIFs via IST were applied for gas adsorption $(CO_2 \text{ and } CH_4)$ and as a catalyst in CO₂ fixation. The unique characteristic of the ZIFs obtained via the IST method showed advantages in the chemical properties enhancing the catalyst performance.

The thermochemical method (IST) is exciting in synthesizing porous ZIFs. In an ideal scenario, the IST is an unsophisticated procedure without solvent, toxic reagents, and a short synthesis time to produce high yield and pure porous materials. Moreover, this strategy indicates a greener way to synthesize metal—organic frameworks.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.1c00648.

Material synthesis; material characterization: XRD spectra, BET analysis, TGA analysis, TPD-analysis, CO_2 and CH_4 adsorption, FTIR spectra; catalyst performance; NMR spectra, XRD and SEM analysis of fresh and spent catalyst (PDF)

Synthesis progress (Video) (MP4)

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Notes

The authors declare no competing financial interest.

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