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## Mechanically fabricated Metal–organic framework/resin composite nanoparticles for efficient basic catalysis

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### **1** | INTRODUCTION

Metal–organic frameworks (MOFs) are promising porous materials for diverse applications due to their adjustable of apertures and versatile framework functionalities,<sup>[1-6]</sup> which lead to potential applications in gas separation and storage, sensing, and catalysis.<sup>[7–13]</sup> Among them, zeolitic imidazole frameworks (ZIFs) represent a series of MOFs composed by the coordination interaction of metal ions with the nitrogen atoms from imidazole or its derivatives.<sup>[14,15]</sup> Although ZIFs take advantages of ordered crystalline pores and high stability as zeolites,<sup>[14,16]</sup> the deliberate combination of ZIFs and

Zeolitic imidazolate framework-8 (ZIF-8) was successfully composited with an anionic basic resin 201  $\times$  7 (717-resin) to provide a novel ZIF-8/717-resin composite. Its catalytic activity toward the Knoevenagel condensation reaction was evaluated. Results showed that ZIF-8/717-resin composite could efficiently catalyze this reaction, affording the corresponding products in good to excellent yields. Good functional group tolerance, mild reaction conditions, good stability and reusability of the catalyst are the major features of present protocol.

#### KEYWORDS

composite, Knoevenagel condensation, mechanical fabrication, metal-organic frameworks, synergistic catalysis

particular materials gives rise to multifunctional composites adopting favorable properties that superior to the original individual components.<sup>[17,18]</sup>

ZIF-8, bearing a zeolitic sodality (SOD) topology, is one of the most classic ZIFs materials.<sup>[14]</sup> Owing to its unique cages with a pore diameter of 1.16 nm and an aperture of 0.34 nm, ZIF-8 is readily to accommodate multiple nanoparticles within cages for heterogeneous catalysis. ZIF-8 itself has both nitrogen basic sites and Zn<sup>II</sup> Lewis acidic sites and has been extensively used to construct versatile nanoparticle composites with metal or metal oxides, silica, organic polymers, quantum dots (QDs) and graphene toward diversiform structures for 2 of 9 WILEY-Organometallic-Chemistry

desired properties.<sup>[19]</sup> Through compositing with proper species, the active sites on ZIF-8 enable the activation of substrates to facilitate different type organic transformations such as the Knoevenagel condensation,<sup>[20-22]</sup> CO<sub>2</sub> cycloaddition of epoxides,<sup>[23,24]</sup> conjugate-addition reaction,<sup>[25]</sup> and so on.

The Knoevenagel condensation is one of the most useful organic reactions, which has been widely utilized for the synthesis of valuable  $\alpha$ , $\beta$ -unsaturated carbonyl compounds..<sup>[26–28]</sup> Conventionally, this reaction is catalyzed in the presence of either an acid or a base catalyst following a S<sub>N</sub>1 path of nucleophilic addition–elimination. Recently, the utilization of heterogeneous catalysts have received increasing attention. For example, supported amines catalysts have been successfully developed and employed in the Knoevenagel condensation.<sup>[29–31]</sup> These catalysts not only exhibited good activities but also could be readily recovered and reused after simple filtration.

Recently, MOFs especially ZIFs catalysts have also been found as efficient catalysts for the Knoevenagel condensation.<sup>[21,22,32-34]</sup> Phan and co-workers<sup>[22]</sup> reported that pristine ZIF-8 could efficiently promote the condensation of benzaldehyde and malononitrile at room temperature, albeit in an environment unfriendly solvent (toluene). Whereas methanol turned out to be an ineffective solvent due to the hydrophobility of the ZIF-8 catalyst. ZIF-8 nanoparticles has also been reported as an efficient and reusable catalyst for the Knoevenagel synthesis of cyanoacrylates and 3-cyanocoumarins.<sup>[33]</sup> The introduction of hydroxy groups to the substrates led to reasonable yields of cyanoacrylates in the polar ethanol solvent. Recently, a bimetallic Zn@ZIF-67 catalyst performed excellent catalytic activities for the Knoevenagel condensation between p-Br-benzaldehyde and malononitrile.<sup>[32]</sup> Although leading to a quantitative conversion, MeOH sovent was observed to be less reactive than toluene and DMSO. Obviously, heterogeneous catalyzed Knoevenagel reactions are very sensitive to the solvent polarities, and further studies need to be carried out to elucidate the effect of solvents and modify the ZIF-8 catalyst by changing its hydrophobility.

In another aspect, ion-exchange resins, most of them known as hydrophilic for they having hydrophilic groups, have been extensively employed as catalysts or support due to their good stability, high adsorption capacity, cost-economy, facile recoverability and rapid kinetics.<sup>[35,36]</sup> Recent literature showed that MOF could be composited with ion-exchange resins.<sup>[37]</sup> Such composites are more stable with enhanced catalytic activity in some cases. For example, the classic MOF-5 was introduced to strengthen a cycloaliphatic epoxy resin.<sup>[37]</sup> A Fe-MOF namely MIL-53 (Fe) was modified by ionic resins to improve its photocatalytic performance.<sup>[38]</sup> Very recently, a ZIF-8 modified macroporous D101-resin was prepared with few ZIF-8 particles in the macropores of the resin and used for selective solid-phase extraction.<sup>[39]</sup> However, to the best of our knowledge, the composition of ZIFs with crosslinking resins has not been documented so far. Notably, since anion-exchange resins have amine groups, they are typical catalysts for heterogeneous base-catalyzed model reactions including Knoevenagel condensation.<sup>[40–42]</sup> We anticipated that the combination of ZIF-8 with an anion-exchange basic resin may afford a bifunctional catalyst, which may serve as an efficient heterogeneous catalyst for Knoevenagel reactions. Moreover, the hydrophobility of ZIF-8 can be adjusted by introduction of a hydrophilic resin, which may enhance its catalytic activity in polar solvents.

Herein, we report the mechanical synthesis of a novel composite from ZIF-8 and an anionic  $201 \times 7$  resin (717-resin) containing basic divinylbenzene-styrene copolymer trimethylammonio groups and hydroxyl ions (Figure S1). Multiple characterizations clearly showed that the 717-resin was successfully composited with ZIF-8. The catalytic activity of ZIF-8/717-resin was also evaluated using Knoevenagel condensation reaction as the model reaction. High activity was observed under mild reaction conditions. Moreover, the ZIF-8/717-resin catalyst could be easily isolated from the reaction mixture by simple filtration and reused without significant loss in its activity.

#### 2 | EXPERIMENTAL

#### 2.1 | Synthesis of ZIF-8

The synthesis procedure was proceeded according to our previous reports.<sup>[43]</sup> Briefly, zinc nitrate hexahydrate [Zn  $(NO_3)_2 \cdot 6H_2O$  (2.76 g, 9.30 mmol)] was dissolved in 18 ml deionized water with sonication. 2-Methylimidazole (6.60 g, 80.38 mmol) was dissolved in 120 ml deionized water with sonication. Then the two solutions were mixed in a 250 ml round-bottom flask under mechanical stirring at room temperature for 6 hr. The obtained product was collected by centrifugation and washed with deionized water and methanol for three times. Finally, the obtained product was vacuum-dried at 80 °C for 24 hr.

# 2.2 | Synthesis of ZIF-8/717-resin composites

717-Resin spheres (hydroxide or chloride-type) were successively washed with methanol, followed by vacuumdrying at 50 °C before the synthesis of ZIF-8/717-resin. ZIF-8 (100 mg) and 717-resin were mixed in a mortar and grinded into powder in different mass ratios (1:1 and 1:2). During grinding, the appropriate amount of dichloromethane (DCM) was added to the mixture to enable the mixing homogeneity. The mixed powder was suspended in 15 ml DCM and stirred at room temperature for 7 days. After completion of the reaction, the solid was collected by rotary evaporation to remove DCM solvent. The solid was subsequently refluxed in tetrahydrofuran (THF) overnight and the filtered solid was washed with ethanol. Finally, the obtained product was dried at 80 °C in vacuum for 4 hr. The yields of ZIF-8/717-resin composites are 92% and 87% on the basis of the ZIF-8 moiety for the ZIF-8 and hydroxide-type 717-resin mass ratios of 1:1 and 1:2, respectively.

#### 2.3 | Catalytic studies

Catalytic activity of ZIF-8/717-resin for the Knoevenagel reaction was carried out using benzaldehyde and malononitrile as the model substrates. Initially, ZIF-8/ 717-resin was added to a methanol solution (8 ml) of benzaldehyde under magnetically stirring for 5 min. A solution of malononitrile in methanol was then added, and the resulting mixture was further stirred at room temperature for 6 hr. Aliquots of the reaction mixture were withdrawn at different time intervals to monitor the reaction conversion. Before the GC-MS examination, aliquots were quenched by acetone and filtered through a short silica gel pad. After the reaction, the ZIF-8/717resin catalyst was separated from the reaction mixture by simple centrifugation, washed by methanol and DCM several times, dried under vacuum at 80 °C for 6 hr, and reused if necessary.

#### **3** | RESULTS AND DISCUSSION

The as-synthesized ZIF-8/717-resin was then characterized using a variety of techniques. Firstly, the powder Xray diffraction (PXRD) diagrams (Figure 1) verify the highly crystalline feature of the ZIF-8/717-resin as its parent ZIF-8 materials. In this work, mechanical stirring of ZIF-8 and 717-resin in DCM leads to a well composited ZIF-8/717-resin, which is significantly different from the morphology of the pristine and crushed 717-resin (Figure 2a and 2b). The scanning electron microscope (SEM) micrograph (Figure 2c) shows that the crystal size of composites in irregular profile are ranging from 100 to 300 nm with somewhat aggregation, which is significantly different with the as-synthesized ZIF-8 nanoparticles that in well-shaped cubic crystals.<sup>[43]</sup> As expected, the transmission electron microscope (TEM) observation clearly reveals that the small aggregations reside on bigger crystalline composites (Figure 2d). To further confirm



FIGURE 1 PXRD diagrams of ZIF-8 and ZIF-8/717-resin

the composition of 717-resin and ZIF-8, Energydispersive X-ray spectroscopy (EDS) was conducted on the chloride-type ZIF-8/717-resin samples. EDS mapping indicates the successful composition of ZIF-8 and 717resin by the observation of well-dispersed chlorine (Figure 2e and 2f). Different ratios of the starting ZIF-8 and 717-resin lead to different weight percentages of ZIF-8 in ZIF-8/717-resin (ca. 68%/59% for ZIF-8/717resin = 1:1/1:2 according to EDS element analysis (Table S1 and Figure S2). On the contrary, a previously reported D101-resin @ZIF-8 was prepared using in-situ generation of ZIF-8 particles within the pores of the D101-resin, resulting in a relatively low loading amount of ZIF-8 (0.43 wt % of Zn<sup>2+</sup>).<sup>[39]</sup> Increasing the ratio of starting 717-resin cannot effectively enhance the percentage of 717-resin in the composite product. So the ZIF-8/ 717-resin = 1:1 composite sample was chosen for the further investigation.

Furthermore, the loading ratio of 717-resin in ZIF-8/ 717-resin = 1:1 sample is confirmed to be around 32 wt% of the composite based on thermogravimetric (TG) analysis. TG curve (Figure 3a) of ZIF-8/717-resin shows little weight loss from room temperature to 200 °C, demonstrating the release of water for 717-resin during composition. Due to the presence of ZIF-8, the thermal stability of the composite at 200-400 °C was significantly improved in comparison with 717-resin. It is also found a sharp weight loss step at the temperature range of 400 to 700 °C, representing the thermal decomposition of the ZIF-8/717-resin at this temperature range. The satisfactory thermal stability ensures the applicability of ZIF-8/717-resin in a wide temperature range. Fourier transform Infrared (FT-IR) spectra of ZIF-8/717-resin exhibited a combination feature of ZIF-8 and 717-resin (Figure 3b). The similar characteristic bands for ZIF-8



**FIGURE 2** (a) Photos of the pristine 717-resin and ZIF-8/717-resin. (b) A SEM image of the crushed 717-resin. (c) and (d) SEM and TEM images of the as-synthesized ZIF-8/717-resin. (e) and (f) A SEM image and the EDS mapping of the ZIF-8/717-resin tablet

and ZIF-8/717-resin samples within the ranges of 1300–1500 cm<sup>-1</sup> and 1100–1200 cm<sup>-1</sup> could be assigned to the stretching and the plane vibration of the imidazole skeleton, respectively.<sup>[32]</sup> In comparison with respective spectra of ZIF-8 and 717-resin, the absence of absorption bands at approximately 2300 cm<sup>-1</sup> of ZIF-8/717-resin may due to the effective composition, which has also been found in a composite that is ZIF-8 coatings on a polyimide substrate.<sup>[44]</sup>

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In addition, the nitrogen-sorption isotherm measurements (Figure 4) were carried out to compare the porosity of original ZIF-8 nanoparticles and ZIF-8/717-resin composites. Both of the two kinds of nanoparticles reveals reversible type I isotherms that indicates excellent N<sub>2</sub> uptake at relatively low pressures ( $P/P_0 < 0.1$ ), featuring typical microporous materials. By using the adsorption data points in the range of  $P/P_0 = 0.01-0.10$ , The surface areas of 1774 m<sup>2</sup>/g (Langmuir model) and 1108 m<sup>2</sup>/g [Brunauer–Emmett–Teller (BET) model] for ZIF-8 nanoparticles were obtained with a micropore volume of 0.523 cm<sup>3</sup>/g. The corresponding values are lower than the reported ones of pristine ZIF-8<sup>[45]</sup> and fastformed ZIF-8 nanoparticles,<sup>[33]</sup> which may be due to the lower quality of the crystalline products. For the ZIF-8/



FIGURE 3 (a) TG curves of the ZIF-8/717-resin. (b) FT-IR spectra of the ZIF-8/717-resin



FIGURE 4 N<sub>2</sub> adsorption/desorption isotherms (a) and the pore size distributions (b) of ZIF-8 and ZIF-8/717-resin nanocrystals

717-resin composite, the Langmuir and BET surface area are 1083 and 728 m<sup>2</sup>/g, respectively, and the values are lower than that of ZIF-8 nanoparticles, which is attributed to the successful composition of 717-resin (*ca.* 32%). Therefore, the crystallization of ZIF-8 components has strong tendency to form microspores without 717resin blocking during the composition. The total pore volume of micropores for ZIF-8/717-resin is about 0.358 cm<sup>3</sup>/g, and the stacking mesopores and macropores are not detected in this case, which is different with the aggregates of ZIF-8 nanocrystals.<sup>[46]</sup>

Due to fully exposing of large external surfaces, fast mass transfer within ZIFs heterogeneous catalysts is easily accessed even by large molecules. As a prototypical ZIF material, ZIF-8 has been verified as an efficient heterogeneous catalyst for the C-C bond formation reaction.<sup>[22]</sup> But its hydrophobility influence the catalytic activity in polar solvents, such as methanol, ethanol and water. Our strategy of the composition is based on the

combination of ZIF-8 that adopts unsaturated Lewis acidic sites and 717-resin that possesses strong basic sites, which may have strong affinity to various substrates with good tolerance to different sizes and substituents. So the catalytic activity of ZIF-8/717-resin catalyst was firstly assessed in the Knoevenagel condensation of benzalde-hyde (**1a**) and malononitrile (**2**) to form benzylidene malononitrile (**3a**) as the target product (Scheme 1).

The initial reaction was carried out using 5 mol % (based on Zn) ZIF-8/717-resin catalyst (40 mg) relative to benzaldehyde in methanol at room temperature. A moderate yield (64%) of desired product **3a** was obtained after 2 hr (Table 1, entry 1). As the reaction time increased, the reaction conversion rate increased, and the yield reached up to 97% after 6 hr (Table 1, entry 4).

Taking the aforementioned results into account, we decided to investigate the effect of catalyst concentration on the reaction yield. The catalyst concentration, with respect to zinc content in the ZIF-8/717-resin, was





TABLE 1 Optimization	of reaction	conditions <sup>a</sup>
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Entry	1a/2 (molar ratio)	Cat. (mg)	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	1/2	40	methanol	2	64
2	1/2	40	methanol	4	86
3	1/2	40	methanol	5	94
4	1/2	40	methanol	6	97
5	1/2	20	methanol	6	77
6	1/2	30	methanol	6	94
7	1/2	40	ethanol	6	89
8	1/2	40	dichloromethane	6	73
9	1/2	40	DMF	6	94
10	1/2	40	toluene	6	90
11	1/2	40	acetonitrile	6	39
12	1/2	40	dioxane	6	30
13	1/2	40	ethyl acetate	6	19
14	1/2	40 <sup>c</sup>	methanol	6	32
15	1/2	40 <sup>d</sup>	methanol	6	51
16	1/1	40	methanol	6	70
17	1/3	40	methanol	6	97
18	1/4	40	methanol	6	93
19	1/2	40 <sup>e</sup>	methanol	6	95
20	1/2	$40^{\mathrm{f}}$	methanol	6	85

<sup>a</sup>Reaction conditions: ZIF-8/717-resin catalyst (specific amounts) and **1a** (0.4 ml, 3.8 mmol) was dissolved in 8 ml solvent in a round-bottom flask under stirring for 5 min at room temperature. **2** (specific amount) was dissolved in 5 ml solvent. Then the solution was decanted into the flask and stirred for specific time.

<sup>b</sup>GC yields.

<sup>c</sup>ZIF-8 as the catalyst.

<sup>d</sup>717-resin as the catalyst.

 $e^{2}$ ZIF-8/717-resin = 1:2 sample as the catalyst.

<sup>f</sup>The ZIF-8:717-resin (1:1) mixture as the catalyst.

studied in the range of 20–40 mg. As expected, higher quantity of catalyst led to increased yields of product **3a** (Table 1, entries 4–6). The solvent also played an important role on this transformation. Conducting the reactions in other solvents such as ethanol, dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF) and toluene provided the desired product **3a** in good to excellent yield (73–94%, entries 7–10). However, much lower yields were obtained by preforming the reactions in acetonitrile, 1,4-dioxane or ethyl acetate (entries 11–13). Notably, the catalytic performance of ZIF-8/717-resin composite is much better than those of ZIF-8 or 717 resin (entry 14 and 15). Methanol was found to be more effective than toluene that used in the same Knoevenagel condensation according to previous reports.<sup>[22,44]</sup>

In addition, the molar ratios of two substrates significantly affected the yields (entries 16–18). Only slight increase in the yield was observed when increasing the substrate **2** to 3 equivalents (97% yield), while decreasing the substrate **2** to 1 equivalent led to a moderate yield (70%). Thus, the optimum reaction conditions were determined as following: aldehyde **1a** (3.8 mmol), **2** (2 equivalents), methanol as the solvent, room temperature, and 6 hr.

The scope and generality of the Knoevenagel condensation was then explored under the optimized reaction conditions (Table 2). In most cases, both malonitrile (2) and ethyl cyanoacetate (4) condensed with aromatic aldehydes smoothly to afford the corresponding products (5) in excellent yields. A series of functional groups including nitro, halogen, hydroxyl, methoxyl, methyl, and methylthio were well tolerated. Generally, benzaldehyde derivatives containing electron-withdrawing groups were more active than those with electron-donating groups since nucleophilic addition was the rate-determination step in such condensation reactions. Interestingly, the ZIF-8/ 717-resin catalyst exhibited high activity for benzaldehyde derivatives bearing either electron-withdrawing or electron-donating substituents, indicating the high catalytic activity of the bifunctional composite catalyst. The positions of the substituted groups have trivial influence on the yields of regioisomeric isomers (3b, 3c, 3i~3 k; **5b**, **5c**, **5i~5 k**). However, when the aryl aldehydes were replaced by aliphatic aldehydes, the yields dropped dramatically (3 l, 3 m, and 5 m). Especially for 5 l, several tries to obtain the pure products were failed. The reduced yields might be attributed to the presence of alkyl that weakens the conjugation effect, arisen from the original benzene ring and aldehyde carbonyl.

Another feature of heterogeneous catalysts is the facile separation and sustained reusability. Therefore, the recoverability and reusability was investigated using the model reaction listed in Table 1. After the reaction, the catalyst was separated by simple centrifugation and then washed with mixed solvents of anhydrous methanol and DCM to remove possible physisorbed reagents. The recovered catalyst was then dried under vacuum overnight. It was found that the ZIF-8/717-resin catalyst could be recovered and reused without a significant loss in its catalytic activity over five successive runs (Figure 5). Meanwhile, hotfiltration experiment was performed using the model reaction to testify the reaction a heterogeneous or homogeneous process. The reaction mixture was filtrated to remove the catalyst after one hour and the filtrate was kept stirring under the same condition. The completely termination of the reaction upon the removal of ZIF-8/717-resin was confirmed by GC and ICP analysis.

To evaluate the catalytic activities, some controlled experiments were performed (Table 1, entry 14, 15, 19

#### TABLE 2 Reaction scope



FIGURE 5 (a) PXRD patterns of reused ZIF-8/717-resin with a SEM image of the catalyst after 5 runs. (b) Recycling study

and 20). Results showed that when the reaction was performed in the presence of ZIF-8 or 717-resin, only 32% and 51% yields were obtained, respectively. For the ZIF-8:717-resin (1:1) mixture as the catalyst, the yield of the product is 85%, which is a little lower than that of ZIF-8/717-resin = 1:2 sample as the catalyst. On the contrary, nearly quantitative yield (97%, Table 1, entry 4) was obtained in the presence of the 1:1 ZIF-8/717-resin composite, indicating that the composite had synergistic catalytic effect.

In previous Knoevenagel condensation reaction that performed by using ZIF-8 or functionalized ZIF-8,<sup>[47]</sup>

methanol was found to be an ineffective solvent for the catalysis because of the hydrophobility of the ZIF-8 catalyst. In this work, the catalytic activity in methanol of ZIF-8 catalyst was significantly enhanced by compositing with hydrophilic 717-resin. As for the catalytic mechanism, the composite catalyst is an amphipathic catalyst that could form possible hydrogenbonding interactions to the polar methanol solvent. Additionally, both the basic catalytic centers of 717-resin and the acidic centers (Zn<sup>2+</sup>) of ZIF-8 promoted the nucleophilic addition–elimination S<sub>N</sub>1 path of the Knoevenagel condensation.

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#### 4 | CONCLUSION

In summary, a new type of ZIF-8/717-resin composite material was successfully prepared with highly crystalline and comparable loading amounts of both materials. The compositions of this composite were identified and quantified through a variety of methods especially EDS, IR, and TG analyses. The catalytic performance of ZIF-8/ 717-resin was probed using Knoevenagel reaction with an extended scope of benzaldehyde derivatives substrates in an eco-friendly alcohol solution instead of toluene. Highly conversions were achieved under the ambient without inert atmospheres, and the ZIF-8/717-resin catalyst could be easily reused without significant degradation in 5 runs in the catalytic activity.

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#### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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