

## From The Rational Design of Cobalt-zinc Bimetallic MOF to Catalytic Behavior in Knoevenagel Condensation Reaction

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### Abstract

In this study, a bimetallic Co-Zn metal-organic framework (Co-Zn-MOF) was synthesized through solvothermal conditions by using Co<sup>2+</sup> and Zn<sup>2+</sup> salts, DABCO and H<sub>2</sub>BDC as the rigid ligands (DABCO= 1,4-diazabicyclo (2.2.2) octane, H<sub>2</sub>BDC= Benzene-1,4-dicarboxylic acid). This bimetallic MOF was used as a catalyst for the Knoevenagel condensation reaction and exhibited enhanced catalytic activity compared to its parents' single metal MOFs derived from DABCO and H<sub>2</sub>BDC precursors (Co-MOF and Zn-MOF) at mild reaction conditions, which could be attributed to the synergistic effect between the metal ions.

**Keywords:** Metal-organic framework; Bimetal-MOF; Heterogeneous catalyst; Knoevenagel.

### Introduction

Nowadays, one of the essential formation reactions in synthetic organic chemistry for generating  $\alpha,\beta$ -unsaturated compounds that are produced via the C=C bond is the Knoevenagel condensation reaction. This reaction contains a nucleophilic addition reaction between carbonyl compounds and activated methylene groups with electron-withdrawing groups. The synthesis of heterocyclic compounds with biological importance and several fine chemical products, such as pharmaceuticals, polymers having a range of functional groups, cosmetic products, insecticides, and pesticides, frequently employs  $\alpha, \beta$ -unsaturated compounds. It is well known that this condensation reaction could be catalyzed by Lewis's acids or bases or bifunctional catalysts (1-3). The Lewis basic sites could support the generation of the C-C bond (4).

Crystalline metal-organic frameworks (MOFs) consist of metal ions/clusters and organic ligands that

form the structure of porous materials capable of supporting various applications. In many respects, MOFs are almost ideal for use as heterogeneous chemical catalysis (5-10). One of the most considerable advantages of MOFs lies in the diversity of structural adjustments by carefully selecting metal nodes and linkers. This feature offers flexibility in the design of high-potential structures (11). Multifunctional MOFs are one of the most promising materials studied as catalysts in various organic transformation reactions, such as the Knoevenagel reactions (12-14).

The introduction of second metal ions into the nodes of scaffolds could positively affect the properties of MOFs, for instance catalytic, electronic, and luminescence characteristics (15-16).

As mentioned before, since bimetallic MOFs present distinct benefits and increased synergistic performance of catalysis, some research has focused on synthesizing the bimetallic MOFs for catalytic reactions like Knoevenagel

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condensation. Hu et al. synthesized MIL-101(Al/Fe)-NH<sub>2</sub>(X) as a catalyst for tandem reaction, which exhibited increased catalytic activity compared to its parents' single metal (17). In addition, Yang et al. prepared bifunctional Ru/Uio-66 by post-synthesis method. Ru nanoparticles were embedded onto the scaffold of Uio-66 and used as a catalyst for the reduction of nitroarenes and tandem reaction (18). On the other hand, three bimetallic Zn@ZIF-67 were generated through room temperature synthesis by Zanon et al., which were used as heterogeneous catalysts for the Knoevenagel condensation reaction (19).

In this study, bimetallic Co-Zn-DABCO-BDC (Co-Zn-MOF) was prepared by a one-step solvothermal approach and employed as an efficient catalyst for Knoevenagel condensation reaction at room temperature. Furthermore, the advantage of having both metal ions (Co-Zn) in the framework to catalyze the Knoevenagel condensation was compared to its parents' single metal frameworks.

### Materials and Methods

All chemical reagents were purchased as analytical grades and used without further purification. The structural information of the sample was analyzed by a powder X-ray diffraction (XRD, HAOYUAN - DX2700BH) system equipped with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Thermogravimetric (TG) analysis was performed using an STA PT 1600 instrument under a nitrogen atmosphere. Fourier-transform infrared (FTIR, Equinox 55, Bruker) spectroscopy was carried out via the standard KBr method in the range of 500-4000 cm<sup>-1</sup>. EDX (Energy-Dispersive X-ray Spectroscopy) analysis was done with the TESCAN (Model VEGA 3 SEM) scanning electron microscope. The metal contents were specified by inductively coupled plasma (ICP, Perkin Elmer AAnalyst 100). The quantitative analysis of the catalytic reaction was determined via gas

chromatography (GC, HP Agilent 6890 N).

### Synthesis of (Co<sub>0.5</sub>Zn<sub>1.5</sub>(1,4-BDC)<sub>2</sub>(DABCO)) 4DMF.H<sub>2</sub>O (Co-Zn-MOF)

The bimetallic Co-Zn MOF was synthesized by solvothermal synthesis reaction. Generally, 0.42 mmol of each metal salts (Co (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and Zn (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) were dissolved in DMF (10 ml) followed by gradual addition of BDC (0.42 mmol) and DABCO (0.21 mmol) and stirred for 10 min. At that moment, the obtained solution was transferred to the 23 ml Teflon lined autoclave and heated at 120 °C for 48 h, and then cooled to room temperature. In conclusion, the solid material was washed with DMF and ethanol and then dried in a vacuum oven at 110 °C to remove the adsorbed and uncoordinated solvents. (yield: 81% based on DABCO).

### Synthesis of Co-MOF & Zn-MOF

The synthesis of parent's MOFs derived from DABCO and H<sub>2</sub>BDC precursors was accomplished through the solvothermal technique outlined in the published article (20-21).

### Catalytic studies

To evaluate the catalytic activity of Co-Zn-MOF in the Knoevenagel condensation (Figure 1), the reaction between benzaldehyde and malononitrile in the presence of a catalyst was selected as a model reaction. At first, 0.9 mmol (0.059 g) of malononitrile was added to the 10 ml test tube equipped with a magnet, then 1 ml of solvent and 1.1 mmol (0.11 ml) of benzaldehyde was added. Finally, a specific amount of catalyst was added to the mixture, stirring the solution at room temperature.

The as-prepared samples were diluted in toluene and then monitored with the help of GC.



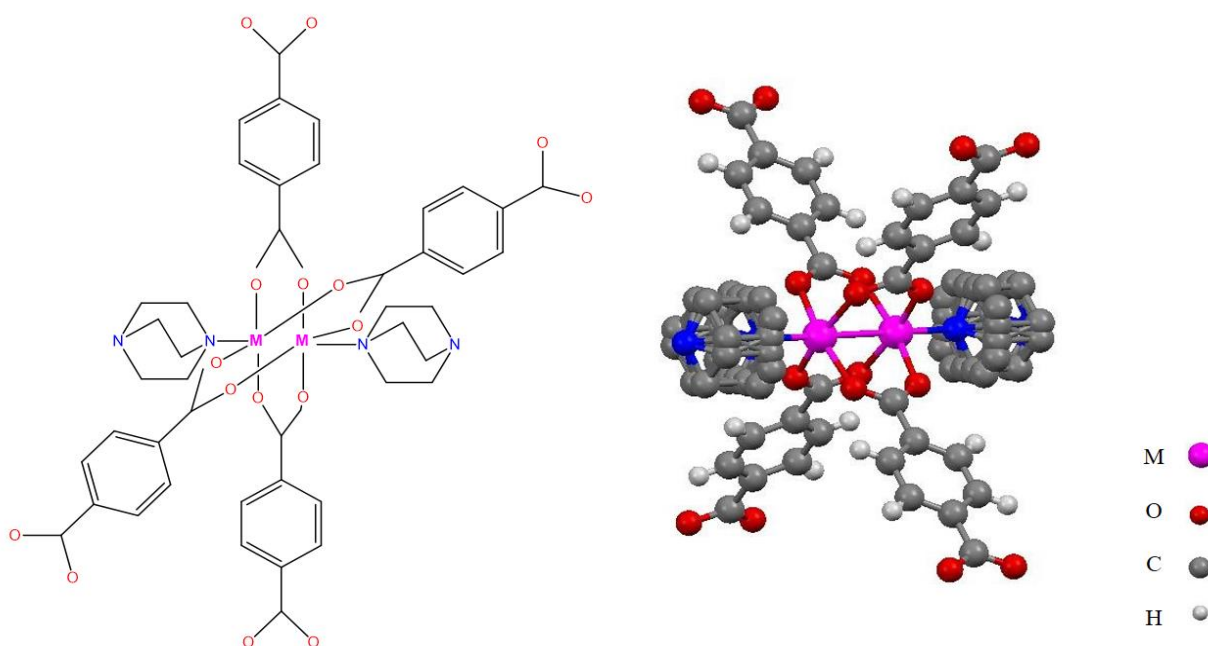
**Figure 1.** Knoevenagel condensation reaction catalyzed by Co-Zn-MOF.

## Results and Discussion

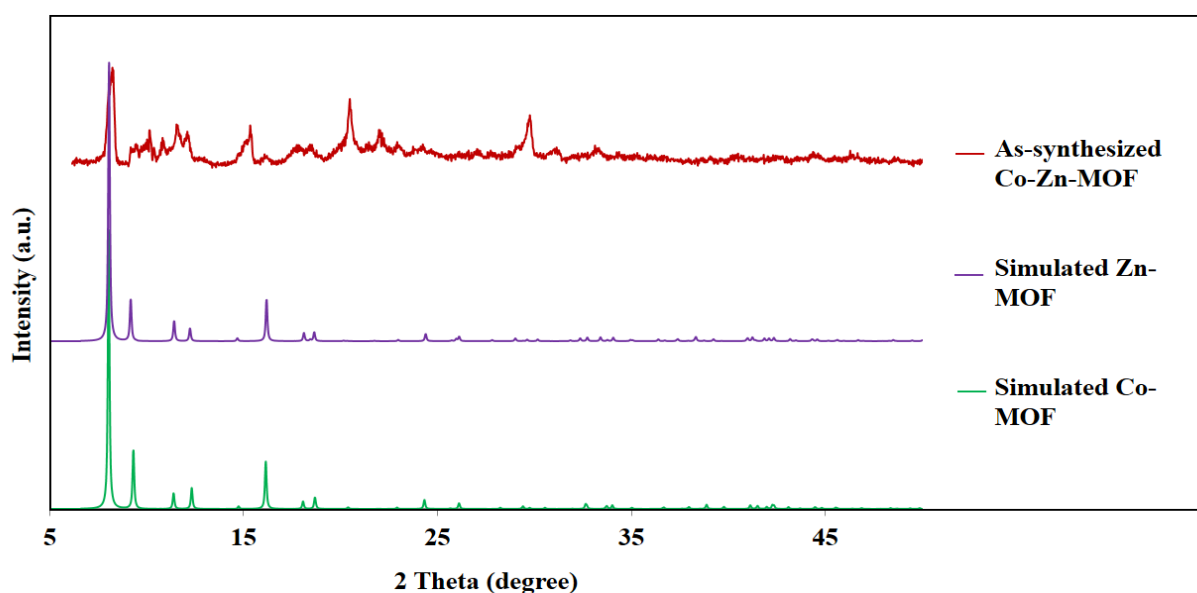
As mentioned before, synthesizing bimetallic MOFs is a newly interesting research field. Through this strategy efficient catalysts concluded from the induction of a second metal in the scaffold of MOF. The selected Co-MOF and Zn-MOF derived from DABCO and BDC are similar in terms of the crystal lattice structure. As a result, a similar structure with similar porosity for as-

synthesized Co-Zn-MOF could be expected (Scheme 1).

The crystalline phase stability and purity of Co-Zn-MOF were studied using powder X-ray diffraction (Figure 2). The prominent peaks for the as-synthesized Co-Zn-MOF are identical to two previously reported isostructural Co-MOF and Zn-MOF simulated patterns, confirmed the favorable formation of structure (20-21). However, some little shifts in the peaks and decreases in



**Scheme 1.** Crystal lattice structure assigned to as-synthesized Co-Zn-MOF.



**Figure 2.** The PXRD patterns of simulated Co-MOF, simulated Zn-MOF, and as-synthesized Co-Zn-MOF.

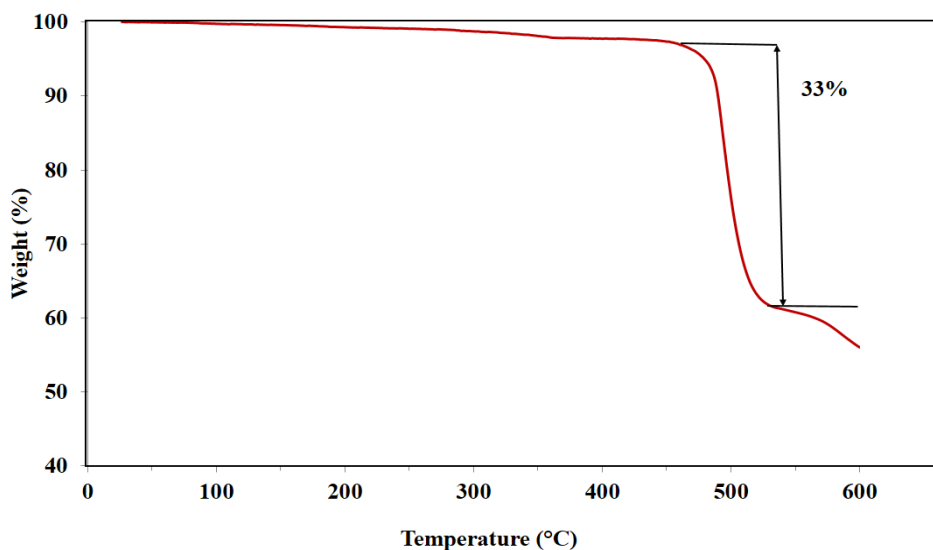


Figure 3. The TG curve for as-synthesized Co-Zn-MOF.

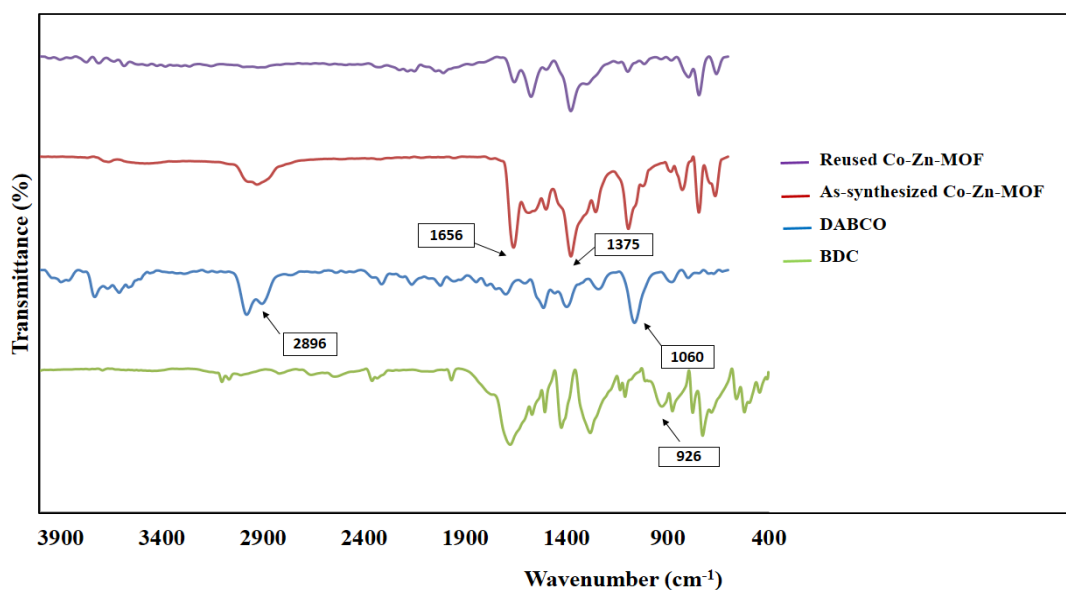


Figure 4. The FT-IR spectra of reused and as-synthesized Co-Zn-MOF, DABCO, and BDC ligand.

the crystallinity could be due to the induced of the second metal and small new peaks might be related to impurity.

The thermal stability of Co-Zn-MOF was determined by thermogravimetric (TG) analysis (Figure 3). The obtained TG curve indicated a slight release of the physically adsorbed water and organic solvents at temperatures below 400 °C. Moreover, a major weight loss of 33% was observed at about 480-530 °C, which could be attributed to the decomposition of organic linkers (DABCO and BDC). This strongly confirms the

excellent thermal stability of Co-Zn-MOF up to 480 °C.

The FT-IR spectra of Co-Zn-MOF, DABCO, and BDC ligand are depicted in Figure 4. The absence of OH bending vibrations of the carboxyl groups (COOH) at 926  $\text{cm}^{-1}$ , confirmed the attachment of BDC in the structure (22-23). Also, the notable bands at 1375 and 1656  $\text{cm}^{-1}$  in the as-synthesized Co-Zn-MOF were assigned to the symmetric and asymmetric stretching modes of the coordinated carboxylate ( $\text{COO}^-$ ) groups, respectively, which confirms the successful coordination

of metal ions to BDC ligand (24). Moreover, the stretching bands around 700-800  $\text{cm}^{-1}$  could be attributed to the M-O stretching vibrations (25-26). Besides this, the bands at 2896 and 1060  $\text{cm}^{-1}$  are related to  $\text{CH}_2$  symmetrical stretching vibrations and C-N stretching vibrations in DABCO, which exhibited a minor shift in as-synthesized Co-Zn-MOF (27-28).

EDX and Elemental mapping confirmed the existence of two metals in the framework. Based on the EDX results (Figure 5), the as-synthesized structure contains 5.18, and 16.67 wt% Co and Zn, respectively.

The acceptable uniform distribution of Co, Zn, C, O, and N was observed through elemental mapping. Also, it showed both metals are homogeneously distributed in the

framework (Figure 6). As mentioned earlier, the Knoevenagel condensation reaction has been widely employed as a test reaction for investigating the catalytic activity of heterogeneous catalysts. This reaction is fundamental condensation between an aldehyde (or ketone) and active methylene compounds, forming new C-C bonds (29).

In preliminary investigations, the effect of different solvents such as polar protic (ethanol, methanol, and isopropanol), polar aprotic (acetonitrile and chloroform), and non-polar (toluene) solvents were investigated, since the kind of solvent has a major influence on heterogeneous catalyzed reactions. In this regard, 30 mg of activated Co-Zn-MOF catalyst was added to the 1 ml

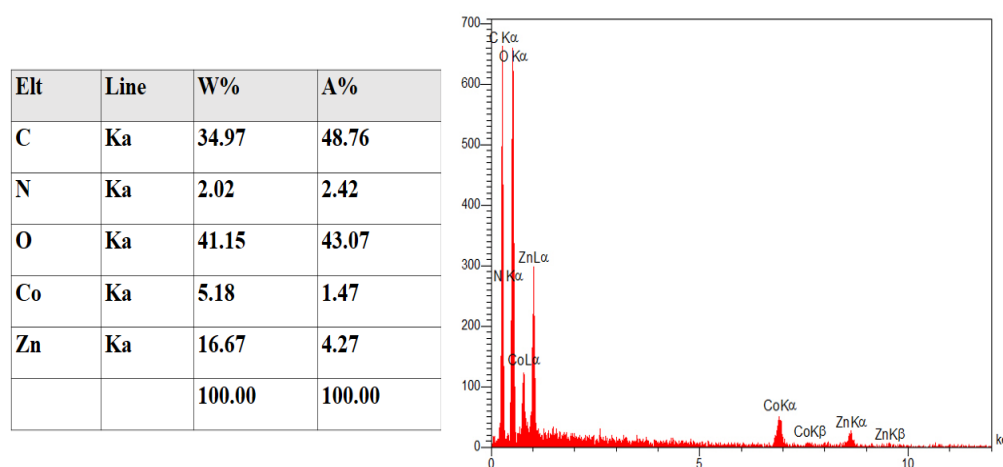


Figure 5. EDX results of as-synthesized Co-Zn-MOF.

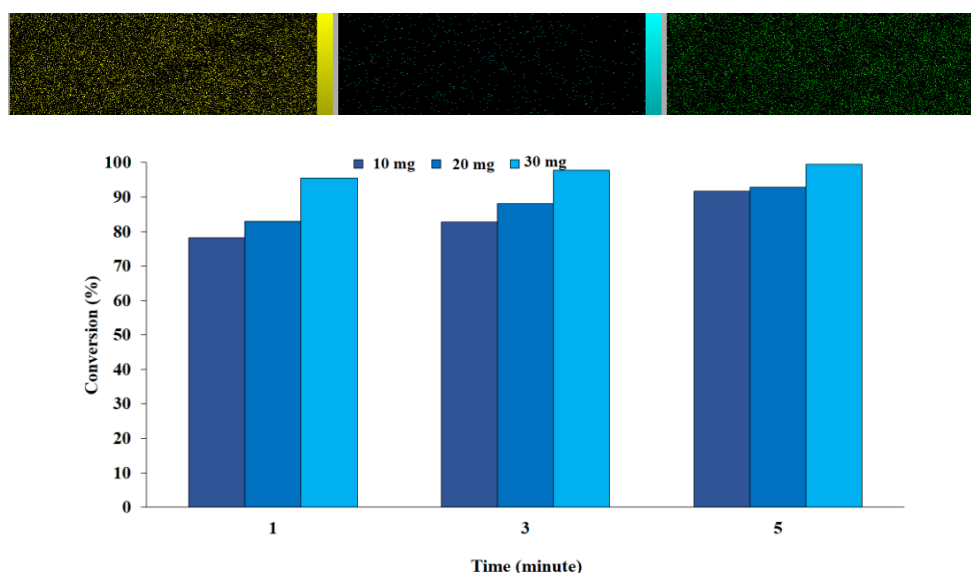
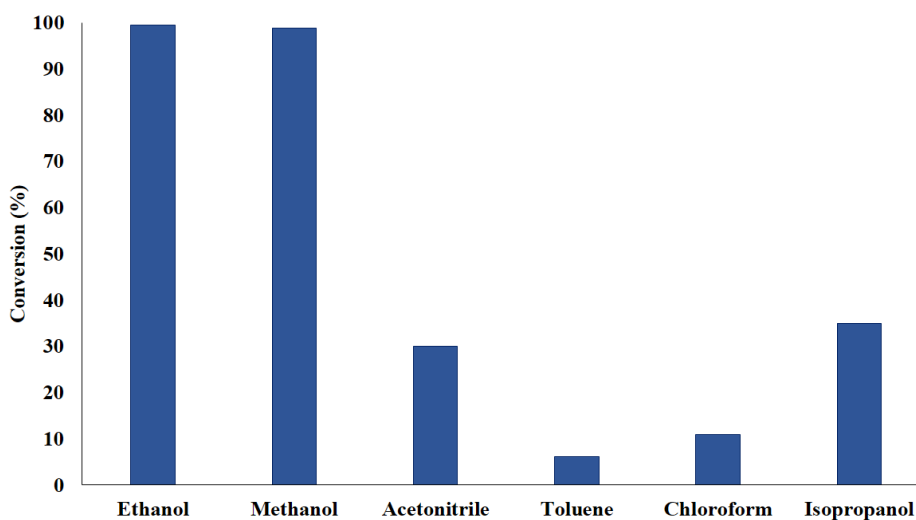


Figure 8. The effect of time and catalyst amount on Knoevenagel condensation in the presence of Co-Zn-MOF. (Reaction conditions: malononitrile (0.9 mmol), benzaldehyde (1.1 mmol), ethanol (1 ml), room temperature.)

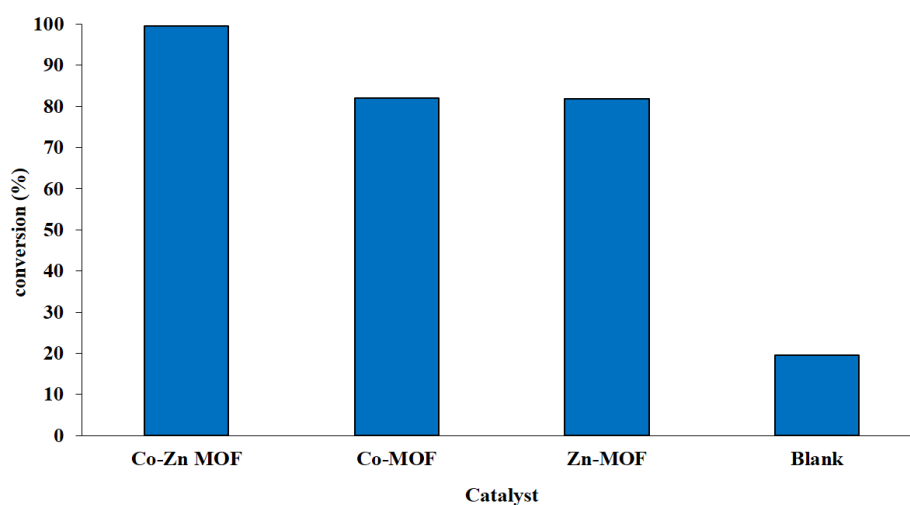


**Figure 7.** The effect of the solvent on Knoevenagel condensation in the presence of Co-Zn-MOF. (Reaction conditions: malononitrile (0.9 mmol), benzaldehyde (1.1 mmol), catalyst (30 mg), solvent (1 ml), 5 min, room temperature.)

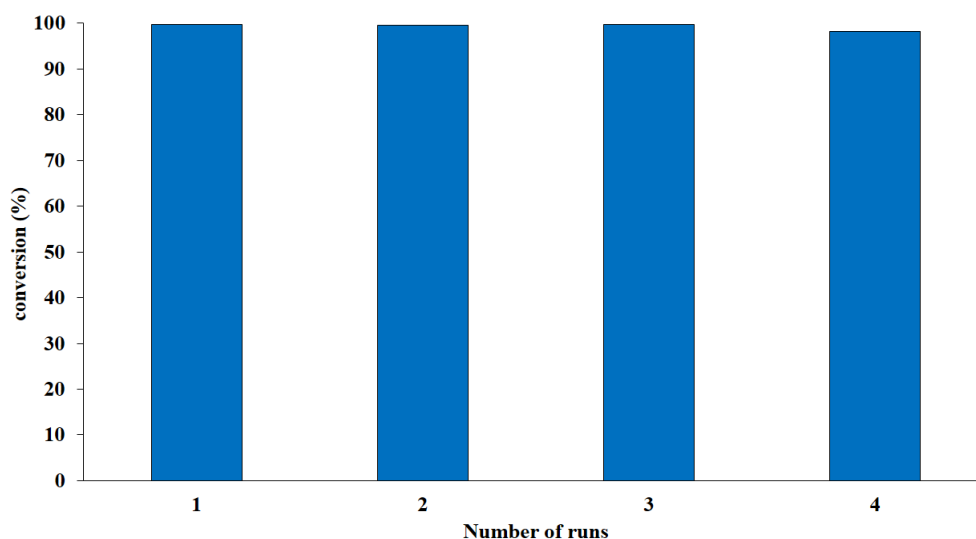
of the selected solvent containing benzaldehyde and malononitrile. Figure 7 depicts the results of Knoevenagel condensation in different solvents after 5 min. It could be concluded that polar solvents like ethanol and methanol are the most suitable reaction solvents. Ethanol gave a satisfying yield due to the better solubility of reactants and enhanced proton transfer efficiency, so it was chosen as the selected environmentally friendly solvent (30).

In the next step, the effect of the time and amount of catalyst were investigated simultaneously (Figure 8). The reaction conversion was continuously increased by increasing the amount of catalyst from 10 to 30 mg. Also, the positive effect on reaction progress was observed by prolonging the reaction time from 1 to 5 min. As regards, 30 mg of the catalyst and a reaction time of 5 min resulted in almost one hundred percent conversion, it was chosen as the optimized.

At last, the single metal MOFs, i.e., Co-MOF and Zn-MOF were utilized as catalysts in Knoevenagel condensation in optimized reaction conditions (Figure 9). As expected, the bimetallic MOF showed slightly better catalytic activity in comparison to its parents' single metal MOFs, which could be due to the synergy between  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  metal ions in Co-Zn-MOF structure. Besides this, the blank test was performed to study the reactivity of the substrates in test conditions, and only



**Figure 9.** The comparison of catalysts in Knoevenagel condensation reaction. (Reaction conditions: malononitrile (0.9 mmol), benzaldehyde (1.1 mmol), catalyst (30 mg), ethanol (1 ml), 5 min, room temperature.)



**Figure 10.** The Knoevenagel reaction in the presence of recycled Co-Zn-MOF.

19.5% conversion was obtained at 5 min. So, an efficient heterogeneous catalyst is highly needed for this type of organic transformation to achieve the maximum yield.

The significance of catalyst reusability in catalytic activity was demonstrated by employing the reused Co-Zn-MOF for the Knoevenagel condensation reaction in several runs. After four continuous catalytic runs, there was no noticeable decline in the catalyst's effectiveness. It was verified that both metals were present in the synthesized Co-Zn-MOF through EDX and ICP analysis. Also, the ICP analysis revealed that the catalyst remained

unaltered during the catalytic reaction, before and after the reaction.

Table 1 highlights the superior catalytic performance of the Co-Zn-MOF catalyst compared to other MOF-based catalysts. The conversion obtained in this research outperforms other research in several ways, including time, catalyst amount, and temperature. These findings imply that the as-prepared bimetallic Co-Zn MOF could be effectively used as a catalyst in the Knoevenagel condensation reaction.

**Table 1** .Comparison of the catalytic activity of Co-Zn-MOF with other MOF-based catalysts in Knoevenagel condensation reaction.

Entry	MOF-based catalyst	Benzaldehyde (mmol)	Malononitrile (mmol)	Amount of catalyst (mg)	Time (min)	Temp. (°C)	Conversion (%)	Ref.
1	Zn-MOF/COF	1	1.5	15	10	80-82	99	(31)
2	Fe <sub>3</sub> O <sub>4</sub> /cellulose/Co-MOF	1	1.5	15	10	20-25	94	(32)
3	[Cd(DDIH) <sub>2</sub> H <sub>2</sub> O] <sub>n</sub>	1	1.5	20	15	20-25	96	(33)
4	[Cd (BDC-OH)(DMF) <sub>2</sub> .DMF] <sub>n</sub>	1.1	0.9	15	10	20-25	<90	(34)
5	C <sub>38</sub> H <sub>37</sub> N <sub>7</sub> O <sub>6</sub> Zn	1	1.1	37	30	20-25	94.3	(35)
6	Co-Zn-MOF	1.1	0.9	10	5	20-25	91.8	This work
				30			99.6	work

### Conclusion

Briefly, a simple solvothermal method synthesized a bimetallic MOF (Co-Zn-MOF). The catalytic behavior of Co-Zn-MOF was examined toward the Knoevenagel condensation reaction between benzaldehyde and malononitrile and various variable factors were optimized. Ultimately, the catalytic behavior of as-synthesized bimetallic MOF was compared with its parents' single metal MOFs. Given the high conversion rate (nearly 100%) achieved in just 5 minutes using 30 mg of Co-Zn-MOF, it is evident that the incorporation of a second metal ion into the framework significantly enhances its catalytic activity in the Knoevenagel condensation reaction, as compared to its single metal MOF counterparts. Also, after exploring four continuous catalytic runs, there was no significant decrease in the catalyst's ability.

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