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### Efficient and recyclable novel Ni-based metal-organic framework nanostructure as catalyst for the cascade reaction of alcohol oxidation-Knoevenagel condensation

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Ghodsieh Bagherzade, Department of Chemistry, Faculty of Sciences, University of Birjand, PO Box 97175-615, Birjand, Iran. Email: bagherzadeh@birjand.ac.ir; gbagherzade@gmail.com A novel Ni-based metal-organic framework (Ni-MOF) with a Schiff base ligand as an organic linker,  $Ni_3(bdda)_2(OAc)_2 \cdot 6H_2O$  (H<sub>2</sub>bdda = 4,4'-[benzene-1,4diylbis(methylylidenenitrilo)]dibenzoic acid), synthesized and was characterized using powder X-ray powder diffraction, thermogravimetric analysis, Brunauer-Emmett-Teller measurements, inductively coupled plasma atomic emission spectroscopy, transmission electron microscopy, elemental analysis and Fourier transform infrared spectroscopy. The synthesized Ni-MOF exhibited a high catalytic activity in benzyl alcohol oxidation using tert-butyl hydroperoxide under solvent-free conditions. Also, the efficiency of the catalyst was investigated in the cascade reaction of oxidation-Knoevanagel condensation under mild conditions. The Ni-MOF catalyst could be recovered and reused four times without significant reduction in its catalytic activity.

### KEYWORDS

alcohol oxidation, cascade reaction, Knoevenagel, metal-organic framework

### **1** | INTRODUCTION

Nowadays, due to increasing environmental concerns, the design of uncomplicated and practical chemical syntheses of drugs and useful chemicals is very important. Therefore, researchers have focused on the design of synthetic systems that satisfy economic and ecological criteria for providing the goals of green chemistry.<sup>[1–4]</sup> One-pot cascade reactions are strategies aligned with green chemistry that reduce production wastes and energy consumption by the implementation of several consecutive reactions.<sup>[5-7]</sup> The use of new catalytic systems is a possible way for the effective progress of cascade reactions. For this purpose, a wide diversity of catalysts has been proposed to date. Nevertheless, many of these reports are based on homogeneous catalysts that are associated with some problems such as difficult separation from the reaction medium.<sup>[8,9]</sup> Also, effective heterogeneous catalysts for cascade reactions have been reported.<sup>[10,11]</sup> The reported heterogeneous

systems require the incorporation of noble-metal centres, high temperature and soluble base as an additive for achieving high yields of products in a reasonable time.<sup>[10-12]</sup> Therefore, the development of exceedingly efficient heterogeneous catalysts that can operate without additives (e.g. base) under mild conditions should be the subject of research for one-pot cascade reactions.

In the past decade, metal–organic frameworks (MOFs), constructed from metal clusters or ions and organic linkers through covalent bonds, have attracted great attention because of their adjustable highly porous structures and large specific surface areas that make them suitable for various applications in catalysis,<sup>[13]</sup> gas storage,<sup>[14,15]</sup> adsorption<sup>[16]</sup> and biomedicine.<sup>[17]</sup> In fact, MOFs as heterogeneous catalysts possess the useful combined features of both homogeneous and heterogeneous catalysts.<sup>[18,19]</sup> Also, the large surface area and pore size of MOFs allow the easy accessibility of organic substrates to transition metal ions inside the crystal structure.

Because of the highly dispersed metal ions in the crystal structure of MOFs, they can interact with organic substrates and can be active sites for catalysing organic reactions,<sup>[13,20,21]</sup> for example in carbon-carbon<sup>[22-25]</sup> carbon-nitrogen<sup>[26,27]</sup> bond and formation and oxidation<sup>[28-30]</sup> transformations. Anyway, a variety of MOFs with the controllable particle size and morphology can be achieved by replacing the many organic coordinated ligands with different metal cations of diverse oxidation states and coordination geometries.<sup>[31]</sup> Actually, the synthesis of MOFs can be propounded as a construction game in that, by selecting appropriate components and their compatibility, MOFs can be synthesized with favourable and appropriate structural and chemical properties for particular applications.

Also, the scaling down of MOFs has provided the same rich variety of compositions, structures and properties of bulk types with the advantages of nanomaterials. These compounds are a new class of materials known as nanoscale MOFs (NMOFs). It should be noted that the chemical properties, reactivity and catalytic activities of nanomaterials can be affected not only by their chemical composition but also by their morphological properties such as size, shape and surface properties. Notwithstanding an increasing interest in developing new synthesis routes to produce MOF nanoparticles, types of NMOFs are still quite rare.

Literature survey reveals only a few examples of MOFs that catalyse alcohol oxidation reactions<sup>[28–30]</sup> and cascade reactions.<sup>[32–35]</sup> Despite highly efficient and stable catalytic activity, some of the reported systems are associated with problems such as high cost and cumbersome synthesis process for the catalyst. Therefore, numerous challenges and opportunities still remain in this domain.

As a continuation of our work with the synthesis of NMOFs,<sup>[36]</sup> we report herein the fabrication of a novel Ni-MOF nanostructure (UoB-2) with the Schiff base 4,4'-[benzene-1,4-diylbis(methylylidenenitrilo)]dibenzoic acid (H<sub>2</sub>bdda) as an organic linker under ultrasound irradiation. Notably, UoB-2 is demonstrated as a highly active heterogeneous catalyst to promote benzyl alcohol oxidation and as well as the cascade reaction of oxidation–Knoevenagel condensation under mild conditions. Moreover, the catalyst could be easily recovered and reused for a number of times without significant loss in activity.

### 2 | EXPERIMENTAL

Terephthalaldehyde (CAS no. 623–27-8; 99% purity), 4aminobenzoic acid (CAS no. 150–13-0;  $\geq$ 99% purity) and all solvents and reagents were obtained from SigmaAldrich. All chemicals were used without any further purification. The progress of the reactions and the purity of the products were determined by TLC on silica-gel Polygram SILG/UV254 plates. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet system 800 beam splitter KBr SCAL = 800 in the range 400-4000 cm<sup>-1</sup>. The FT-IR spectrometer used a room temperature detector. NMR spectra were recorded in DMSO-d<sub>6</sub> using a Bruker Advance DPX-400 and 250 instrument using tetramethylsilane as internal standard. The powder X-ray diffraction pattern of UoB-2 was obtained with an X'Pert Pro MPD diffractometer with a Cu K $\alpha$  ( $\lambda$  = 1.54060 Å) radiation source between  $2\theta$  = 2° and 50.0°. Transmission electron microscopy (TEM) images were obtained using a Philips CM120 microscope. Thermogravimetric analysis (TGA) of nanopowders was carried out using a Shimadzu Thermoanalyzer between 30 and 710 °C with a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. Elemental analysis was performed with a PerkinElmer CHNS-O elemental analyser for determining the C, H and N contents. Inductively coupled plasma (ICP) atomic emission spectroscopy was conducted with an OPTIMA 7300DV. The Brunauer-Emmett-Teller (BET) surface area and pore size of UoB-2 were measured utilizing N2 adsorption-desorption isotherms at 77 K with a Belsorp Mini II instrument. The UoB-2 nanostructures were degassed at 300 °C for 12 h under conditions of dynamic vacuum before BET analysis. The specific surface areas for N<sub>2</sub> were calculated using the BET model over a relative pressure  $(P/P_0)$  range of 0.001-0.1. Total pore volumes were calculated from the uptake at a relative pressure of 0.95. Pore size distributions were calculated from the adsorption isotherms using the density functional theory method.

# 2.1 | Preparation of Schiff Base ligand (H<sub>2</sub>bdda)

To a solution of terephthaldehyde (1 mmol, 268 mg) in EtOH was added gradually a solution of 4-aminobenzoic acid (2 mmol, 137 mg) in EtOH (10 ml) at room temperature under magnetic stirring. The reaction mixture was maintained under the same conditions for 60 min. After that, the yellow crystalline precipitate of H<sub>2</sub>bdda was filtered, washed with EtOH three times and then dried in an oven under vacuum. The structural assignments of the synthesized Schiff base were based on FT-IR, CHN, <sup>1</sup>H NMR and <sup>13</sup>C NMR data. Anal. Calcd for H<sub>2</sub>bdda (C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>) (%): C, 70.96; H, 4.33; N, 7.23; found: C, 70.30; H, 4.46; N, 7.23. FT-IR (KBr pellet, selected bands,  $\nu$ , cm<sup>-1</sup>): 1681 s, 1623 w, 1585 s, 1422 m, 1288 m, 1265 m. <sup>1</sup>HNMR (DMSO,  $\delta$ , ppm): 6.555 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.8 Hz, Ar), 7.400 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, Ar),

7.626 (d, 2H,  ${}^{3}J_{HH} = 8.4$  Hz, Ar), 8.025 (d, 2H,  ${}^{3}J_{HH} = 8.4$  Hz, Ar), 8.080 (d, 1H,  ${}^{3}J_{HH} = 8.4$  Hz, Ar), 8.132 (s, 2H, CH=N), 8.188 (d, 1H,  ${}^{3}J_{HH} = 8$  Hz, Ar), 8.776 (d, 1H,  ${}^{3}J_{HH} = 8$  Hz, Ar), 8.950 (d, 1H,  ${}^{3}J_{HH} = 8$  Hz, Ar), 12.521 (b, COOH).

### 2.2 | Preparation of Ni-MOF (UoB-2)

At first,  $H_2$ bdda (1 mmol, 0.372 g) was sonicated in NaOH (10%, 1 ml)–deionized water (20 ml) to obtain a yellow and a clear solution. For a period of 15 min, a solution of nickel acetate (2 mmol, 0.353 g) in deionized water (10 ml) was added dropwise to the solution of  $H_2$ bdda at room temperature under ultrasonic irradiation. The reaction mixture remained in the sonicator under the same conditions for 30 min. The resulting light-green crystalline material was isolated by centrifugation and washed with water. Finally, Ni<sub>3</sub>(bdda)<sub>2</sub>(OAc)<sub>2</sub>·6H<sub>2</sub>O (UoB-2) was obtained after drying for 5 h at 100 °C.

### 2.3 | General procedure for benzyl alcohol oxidation

A mixture of benzyl alcohol (2 mmol), *tert*-butyl hydroperoxide (TBHP; 2 mmol) and UoB-2 (2 mol%) was stirred at 65 °C for an appropriate time in solvent-free conditions to afford the corresponding aldehyde. After cooling the reaction mixture to room temperature, UoB-2 was separated by centrifuging followed by washing several times with EtOAc. It was then dried and reused for the next run.

## 2.4 | General procedure for benzyl alcohol oxidation-Knoevenogel reaction

A mixture of benzyl alcohol (2 mmol), TBHP (2 mmol) and UoB-2 (2 mol%) was stirred at 65 °C for an appropriate time under solvent-free conditions. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. Then, an ethanolic solution (1 ml) of malononitrile (1 mmol) was added to the mixture and stirred for an additional appropriate time at room temperature to afford the corresponding products. At the end of the reaction, UoB-2 was recovered by centrifugation, then washed several times with EtOAc, dried and reused for the next run under the same reaction conditions. After evaporation of the solvent under vacuum, the crude product was exposed to silica gel plate chromatography eluted with *n*-hexane–EtOAc (3:1) to afford pure product. Applied VILEY-Organometallic 3 of 11 Chemistry

### 3 | RESULTS AND DISCUSSION

## 3.1 | Synthesis and characterization of UoB-2 nanostructure

As shown in Scheme 1, the Schiff base ligand was prepared by the condensation of terephthaldehyde and 4aminobenzoic acid in EtOH at room temperature, which was then used as an appropriate organic linker for the novel MOF. The Ni-MOF nanostructure was synthesized by the combination of H<sub>2</sub>abdda with Ni(OAc)<sub>2</sub> in water at room temperature under ultrasonic irradiation. Elemental CHN and ICP analyses suggested a molecular formula of Ni<sub>3</sub>(bdda)<sub>2</sub>(OAc)<sub>2</sub>·6H<sub>2</sub>O (calcd (%): C, 50.46; N 4.83; H, 3.89; Ni, 15.04), which reasonably agrees with the real amounts (%) of C (50.64), N (4.83), H (3.89) and Ni (14.04).

TGA was performed at a heating rate of  $10 \text{ °C min}^{-1}$  in nitrogen atmosphere over a range of 20-700 °C for investigation of the thermal behaviour of UoB-2 (Figure 1). The recorded curve showed the following two marked and well-separated weight loss steps: a first weight loss of 9.19% (calcd: 9.46%) from 45 to 250 °C, which can be ascribed to removal of water molecules, then followed by







FIGURE 1 TGA curve of UoB-2 catalyst



**FIGURE 2** FTIR spectra of (a) ligand and (b) UoB-2

another weight loss of 41.83% at 420 °C, which can be related to the decomposition of the organic parts.

The FT-IR spectra of UoB-2 nanostructure and Schiff base ligand are shown in Figure 2. A comparison of these FT-IR spectra displayed clearly a significant spectral shift of the carboxylate group that confirmed the coordination of Schiff base ligand to metal. In the spectrum of UoB-2, the strong and broad band at 3450 cm<sup>-1</sup> was attributed to the stretching vibrations of coordinated water molecules. Also, the band at 1697 cm<sup>-1</sup> established the presence of a coordinated acetate ligand. There were two strong bands at 1594 and 1396 cm<sup>-1</sup> due to the asymmetric and symmetric vibrations of the COO groups. It should be noted that the values of  $\Delta \nu (\Delta \nu = \nu_{as}(COO) - \nu_{as}(COO))$  $v_{\rm s}({\rm COO})$ ) for metal carboxylates are a powerful tool for classifying coordination modes.<sup>[37]</sup> According to this, the carboxylate group binds in a monodentate fashion if  $\Delta \nu$ (COO) of the complex is much greater than that of the ligand; a bidentate coordination is present if  $\Delta \nu$ (COO) is significantly less than that of the ligand; and bridging can be considered when close to the ionic values. Therefore, the observed  $\Delta \nu$  values for Ni-MOF nanostructure indicated a bridging coordination mode for the carboxylate groups.

The details of the nanostructure of the synthesized UoB-2 were determined from TEM images as shown in Figure 3. The TEM images indicated clearly that UoB-2 nanostructure consisted of roughly spherical particles with uniform morphology. Also, the TEM images revealed no amorphous component in the synthesized nanostructure.

In order to investigate the surface area, pore volume and pore structure of UoB-2, standard N<sub>2</sub> adsorption– desorption measurements were carried out at 77 K, as shown in Figure 4. It can be seen that UoB-2 featured a type IV isotherm which is typical for mesoporous materials.<sup>[38]</sup> The BET surface area was found to be 118 m<sup>2</sup> g<sup>-1</sup>. The total pore volume was estimated as 0.28 cm<sup>3</sup> g<sup>-1</sup> at relative pressure  $P/P_0 = 0.95$  single point. The mesopore size distribution curve, calculated from Barrett–Joyner–Halenda analysis, displayed an average pore diameter distribution at 9.44 nm (Figure 4, inset).

Despite the very best efforts, the size of the crystallites was too small for single-crystal structure determination.



FIGURE 3 TEM images of UoB-2 nanostructure



**FIGURE 4** Adsorption-desorption isotherm (inset showing the pore width) of UoB-2

Therefore the further investigation of the structure of UoB-2 was not possible. However, the powder X-ray diffraction pattern of this material is shown in Figure 5,



**FIGURE 5** X-ray diffraction patterns of (a) UoB-2 and (b) IRMOF-74-IV

which indicated the presence of a crystalline structure. Also, the pattern of UoB-2 was very similar to the simulated pattern reported for IRMOF-74-IV,<sup>[39]</sup> confirming the formation of isostructural MOF.

### 3.2 | Oxidation of benzyl alcohol

One of the most important chemical transformations in industrial and modern chemistry is the selective catalytic oxidation of alcohols to the corresponding carbonyl compounds, so there is considerable interest in the development of environmentally benign, high-performance and safe heterogeneous catalysts for alcohol oxidation.

To evaluate the catalytic activity of UoB-2, the selective oxidation of benzyl alcohol was chosen as a model reaction for optimization of reaction conditions. As a preliminary experiment, the model reaction under neat conditions did not proceed in the absence of the catalyst. Therefore, the use of an effective catalyst for the promotion of benzyl alcohol oxidation is essential. The effect of solvent was investigated using solvents such as water, EtOH, EtOAc and CH<sub>3</sub>CN and also under solvent-free conditions. As shown in Figure 6, the solventless condition is ideal for this selective oxidation. In the absence of any solvent, the influence of temperature on the catalytic performance was also examined for this reaction system (Figure 7). The conversion to benzaldehyde was significantly increased with increasing reaction temperature from room temperature to 65 °C, but using higher temperature decreased in the selectivity of the reaction. In the screening of various catalyst amounts, the presence of 2 mol% UoB-2 was sufficient for excellent conversion (Figure 8). A similar reaction was performed in the presence of Ni(OAc)<sub>2</sub>,



**FIGURE 6** Screening of solvent for oxidation reaction with molar ratio of benzyl alcohol:TBHP = 1:2 and UoB-2 (2 mol%), 65 °C



**FIGURE 7** Screening of temperature for oxidation reaction with molar ratio of benzyl alcohol:TBHP = 1:2 and UoB-2 (2 mol%), solvent free, 75 min



**FIGURE 8** Screening of catalyst amount for the oxidation reaction with molar ratio of benzyl alcohol:TBHP = 1:2, solvent free, 65  $^{\circ}$ C, 75 min

and the reaction proceeded only 30% after 75 min. The oxidation of benzyl alcohol with UoB-2 was examined in solvent-free conditions at 65 °C for determining the amount of oxidant (Figure 9). The model reaction was also studied in the presence of different oxidants with 2 mol% of the catalyst at 65 °C under solvent-free conditions (Figure 10). The results of this study suggested that TBHP gave the highest conversion of benzaldehyde.

One of the special properties of MOFs is the stability of the framework under reaction conditions, which leads to a decrease of the percentage of metal leaching into the organic solution and preservation of the heterogeneous nature of the system. In order to evaluate the



**FIGURE 9** Screening of TBHP amount for the oxidation reaction with molar ratio of benzyl alcohol:TBHP = 1:X and UoB-2 (2 mol%), solvent free, 65 °C, 75 min



**FIGURE 10** Screening of different oxidants for the oxidation reaction of benzyl alcohol:oxidant = 1:2 and UoB-2 (2 mol%), solvent free, 65 °C, 75 min

heterogeneous nature of UoB-2, the hot leaching test was carried out for benzyl alcohol oxidation in EtOAc as solvent at 65 °C. For this experiment, the catalyst was separated after 50% of the reaction time and the remaining solution was stirred in the absence of UoB-2 for an additional 6 h. The result indicated that no further increase in either the conversion or selectivity occurred in the absence of the catalyst. For further confirmation, ICP analysis of the remaining solution exhibited a negligible amount of Ni in the reaction mixture. This finding established that UoB-2 is a typical heterogeneous catalyst (Figure 11).

The reusability of a heterogeneous catalyst is very significant, particularly in industrial and chemical applications. Accordingly, the recyclability and reusability of UoB-2 were investigated in the oxidation of benzyl



**FIGURE 11** Hot leaching test for benzyl alcohol oxidation reaction using UoB-2 under optimized conditions

alcohol with TBHP under the optimized reaction conditions. After each run, the catalyst was separated easily from the ethanolic reaction solution by centrifuging. Then, the catalyst was washed with EtOH, dried for 1 h at 100 °C and used for the next run under the same reaction conditions. The stability of UoB-2, as well as the ease of recovery, permitted the catalyst to be recovered and reused effectively for at least four runs without significant loss of its activity (Figure 12). A comparison of the FT-IR spectra of used UoB-2 and fresh catalyst indicated that the structure of the catalyst remained substantially unchanged after four runs.

To explore the scope of this method, the oxidation reaction of a series of substituted benzyl alcohols was studied under optimal reaction conditions (Table 1). The results indicated clearly that the oxidation of different benzyl alcohols regardless of the types and position of the substituted functional groups proceeded with excellent conversion and reasonable selectivity in the presence of UoB-2.



FIGURE 12 Recycling potential of UoB-2

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 $^a\mathrm{Reaction}$  conditions: alcohol (1 mmol), TBHP (2 mmol), UoB-2 (2 mol%) at 65 °C and solvent-free.

<sup>b</sup>Isolated yield.

### 3.3 | Benzyl alcohol oxidation-Knoevenagel reaction

Knoevenagel condensation is one of the most well-known carbon-carbon bond coupling reactions which has been widely utilized for the preparation of a range of substituted olefins, coumarin derivatives,<sup>[40]</sup> cosmetics,<sup>[41]</sup> perfumes<sup>[42]</sup> and pharmaceutical chemicals.<sup>[43]</sup> Therefore, the catalytic behaviour of UoB-2, in addition to oxidation alcohols, was investigated in Knoevenagel of condensation. To a solution of benzaldehyde (1 mmol) in EtOH, malononitrile (1 mmol) was added and stirred in the presence of 3 mol% UoB-2. After 30 min, the reaction was completed and afforded the desired product. From this observation combined with the obtained results

**TABLE 2** One-pot oxidation-Knoevenagel cascade reaction withvarious substrates catalysed by UoB-2<sup>a</sup>



<sup>a</sup>Reaction conditions. First step: various substituted benzyl alcohols (1 mmol), TBHP (2 mmol), UoB-2 (2 mol%), 65 °C; second step: active methylene compound (1 mmol), EtOH (1 ml), room temperature.

<sup>b</sup>Time of Knoevenagel reaction.

<sup>c</sup>Isolated yield.

of the oxidation reaction, it could be concluded that the Ni-MOF nanostructure could be a bifunctional catalyst. In other words, UoB-2 could catalyse benzyl alcohol oxidation and the following Knoevenagel reaction in a successive manner.



FIGURE 13 Hot leaching test for benzyl alcohol oxidation– Knoevenagel reaction using on UoB-2



**FIGURE 14** FT-IR spectra of (a) fresh UoB-2, (b) after four recycles in alcohol oxidation and (c) after four recycles in cascade reaction. Right: TEM image of UoB-2 after four catalytic runs in cascade reaction

For this investigation, benzyl alcohol in the presence of UoB-2 was stirred with TBHP at 65 °C. After completion of the reaction, the mixture was allowed to cool to room temperature. Then, an ethanolic solution of malononitrile was added to the system and was stirred again for 30 min at room temperature to afford benzylidene malononitrile with excellent yield.

In order to extend the generality of this method, the efficiency of UoB-2 for a selective oxidation– Knoevenagl reaction of various benzyl alcohols was examined under the same conditions. The results are presented in Table 2, confirming the effectiveness of UoB-2 in simplifying oxidation–Knoevenagl reaction to afford corresponding substituted benzylidene malononitriles based on a cascade reaction. Also, this heterogeneous catalytic system was effective for both activated and deactivated benzyl with alcohols malononitrile. In addition to malononitrile, ethyl cyanoacetate as the active methylene compound was examined in oxidation-Knoevenagl reaction. The results the examination demonstrated that the desired products were obtained in good yields (Table 2, entries 11-13). It should be noted that the condensation reaction between carbonyl compound and ethyl cyanoacetate was somewhat slow compared to the reaction with malononitrile because malononitrile is more reactive than ethyl cyanoacetate.

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After the confirmation that UoB-2 nanoparticles were active for the given cascade reaction, the recyclability of the catalyst was investigated. Ni-MOF nanoparticles can be easily recovered and reused for the promotion of the cascade reaction. As shown in Figure 12, the activity of



SCHEME 2 Proposed mechanism for Knoevenagel condensation using UoB-2 nanocatalyst

TABLE 3 Comparison of catalytic activity in oxidation-Knoevenagel reaction with previously reported catalysts

					Yield (%)		
Entry	Catalyst	Catalyst amount	Conditions	Time (h)	Benzaldehyde	Benzylidene malononitrile	Ref.
1	Zr-MOF-NH <sub>2</sub>	100 mg	<i>p</i> -xylene/O <sub>2</sub> /UV irradiation	48	2	91	[48]
2	Zn-MOF-NH <sub>2</sub>	100 mg	<i>p</i> -xylene/O <sub>2</sub> /UV irradiation	48	28	7	[48]
3	Ti-MOF-NH <sub>2</sub>	100 mg	<i>p</i> -xylene/O <sub>2</sub> /UV irradiation	48	51	32	[48]
4	NH <sub>2</sub> -MIL-101(Fe)	20 mg	Trifluorotoluene/O <sub>2</sub> /UV irradiation	40	5	72	[49]
5	NH <sub>2</sub> -UiO-66(Zr)	20 mg	CH <sub>3</sub> CN/O <sub>2</sub> /70 °C	40	29	4.6	[49]
6	NH <sub>2</sub> -MIL-125(Ti)	20 mg	CH <sub>3</sub> CN/O <sub>2</sub> /70 °C	40	39	3.3	[49]
7	Cu <sub>3</sub> TATAT-3 <sup>a</sup>	8 mol%	CH <sub>3</sub> CN/O <sub>2</sub> /75 °C	12	0	95	[50]
8	Au@cu(II)-MOF	3 mol%	Toluene-MeOH/O <sub>2</sub> /110 °C	22	98	99	[51]
9	UoB-2	2 mol%	Solvent-free/EtOH/TBHP	1.5	95	94	This work

 ${}^{a}H_{6}TATAT = 5,5',5''-(1,3,5-triazine-2,4,6-triyl)tris(azanediyl)triisophthalate.$ 

the catalyst was not changed significantly after the fourth catalytic run. In order to gain insight into the heterogeneous nature of UoB-2, a hot leaching experiment was carried out. For this, after 50% of the reaction time of benzyl alcohol with malononitrile, the mixture was centrifuged to remove the solid catalyst. The reaction was continued in the absence of UoB-2 for an additional 4 h. As indicated in Figure 13, no further increase in the conversion was detected, confirming the catalysis was heterogeneous in nature. In addition, the FT-IR spectrum and TEM image of the reused UoB-2 illustrated the retention of its structural integrity (Figure 14). According to the obtained results from the hot leaching test, FT-IR spectrum and TEM, the minor loss of the activity of UoB-2 in the given cascade reaction is probably owing to the loss of solid during the separation process.

As the results show, the title methodology is economical and industrially important by reason of its being a one-pot cascade reaction under solvent-free conditions and in ethanol as a safe reaction medium. Also, UoB-2 has potential industrially because of its reusability as an active catalyst. Therefore, it is expected that this method is readily scalable. For testing the potential practicality, under а semi-scaled-up procedure (10.0 mmol) benzylidene malononitrile was obtained in 78% yield in the one-pot cascade reaction of benzyl alcohol with malononitrile in the presence of UoB-2 within 90 min.

According to the fact that Knoevenagel condensation is classically catalysed under basic conditions,<sup>[44–47]</sup> a proposed plausible mechanism is presented for the reaction of various aldehydes with malononitrile in Scheme 2. In this context, the C=N groups of the Schiff base ligand can act as highly reactive base sites. Actually, a Brønsted proton of the active methylene group of malononitrile, which is acidic because of the presence of two strong electron-withdrawing groups, is abstracted by the nitrogen of imine. The generated stable anion is subjected to nucleophilic attack on the carbonyl carbon atom of the substituted aromatic aldehyde. Finally, UoB-2 comes back to the initial structure after two cycles of protonation and deprotonation, and the product is released from the surface of the catalyst.

To demonstrate the efficiency of the present system, the obtained results of the reaction of benzyl alcohol with malononitrile were compared to show how well the present protocol holds up with respect to existing solid catalysts. The results of this comparison are summarized in Table 3, which demonstrate that the present protocol is superior to some of the previously reported procedures not only in terms of catalyst loading but also in terms of reaction time and yield.

### 4 | CONCLUSIONS

We carried out the synthesis and characterization of a novel Ni-MOF nanostructure (UoB-2) using a new Schiff base ligand (H<sub>2</sub>bdda) obtained under ultrasound conditions. UoB-2 exhibited high catalytic performance for benzyl alcohol oxidation and Knoevenagel condensation as a cascade reaction. This heterogeneous catalyst was used in both reaction steps leading to high yield under ambient conditions, being environmentally benign. UoB-2 can be recovered and reused for four runs without a significant loss in its activity. Most significantly, the ability of catalyst for performing the one-pot cascade reaction, with a decrease in production wastes and energy consumption, should be advantageous, and it could be a potential catalyst for applications in chemical industry.

### ACKNOWLEDGEMENT

The authors are grateful to the University of Birjand for financial support.

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How to cite this article: Aryanejad S, Bagherzade G, Farrokhi A. Efficient and recyclable novel Ni-based metal–organic framework nanostructure as catalyst for the cascade reaction of alcohol oxidation–Knoevenagel condensation. *Appl Organometal Chem.* 2017;e3995. <u>https://doi.org/</u> 10.1002/aoc.3995