Ultrasonic Synthesis and Characterization of 2D and 3D Metal–Organic Frameworks and Their Application in the Oxidative Amidation Reaction

Sepideh Bagheri, Farzane Pazoki, and Akbar Heydari

ABSTRACT: Ultrasound irradiation as an environmentally friendly and inexpensive method successfully applied for the synthesis of two-dimensional (2D) and three-dimensional (3D) metal–organic frameworks (MOFs). Sonochemically synthesized AM-Co1 and AM-Co2 powder has been employed as a green heterogeneous catalyst for the oxidative amidation reaction. The results show that AM-Co1 with a two-dimensional (2D) structure can act as an excellent catalyst for this reaction under ultrasonic irradiation compared to AM-Co2 with a three-dimensional (3D) structure. According to green principles, we used water as a green solvent and air as an oxidant for the oxidative amidation reaction. A wide variety of aldehydes and amines have been used for the synthesis of amides in good to excellent yields (75−90%). Also, the MOF catalyst could be recovered and reused several times without loss of activity.

1. INTRODUCTION

Nowadays, environmental issues have pursued many scientific researchers to find new methods for improving reaction conditions. Several goals have been adopted by the community to eliminate hazardous materials, which have a negative impact on the environment and human health. Hence, green chemistry has become a necessity to achieve more effective, harmless, and economical products. Green chemistry is classified into 12 principles, two of which are related to solvent and catalysis approaches. Due to the hazardous nature of traditional solvents, green solvents were produced from renewable compounds, which biodegrade to a nontoxic material. Indeed, green catalysts could be used in small quantities for repeating a reaction. Accordingly, many types of green catalysts including enzymes and heterogeneous catalysts have emerged to mitigate the detrimental effects of the chemical process on the environment. Thus, applying green catalysts and green solvents simultaneously leads to the most promising method for boosting the reaction conditions.

Like other porous compounds, metal–organic frameworks (MOFs) by chemical functionality groups hold great potential for many applications such as heterogeneous catalysts because of their chemical stability, large surface area, high thermal stability, and high porosity. In this regard, several methods have emerged to synthesize MOFs, such as solvothermal, slow diffusion, mechanochemical, electrochemical, grinding, microwave, and ultrasonic-assisted methods. Among them, the ultrasonic-assisted technique is one of the suitable methods for the direct synthesis of MOFs due to its energy efficiency, low cost, and mild and environmentally friendly nature.
compounds has attracted the interest of chemists for many years. In this regard, we synthesized sonochemically MOFs AM-Co (2D and 3D) by $N,N'$-(1,4-phenylene) disisonicotinamide (bpfb) and $N,N'$-bis(4-pyridinyl)-terephthalamide (bpta) linkers, respectively, to enhance the catalytic efficiency of MOFs (Figure 1). The two-dimensional layers were connected by linear bpfb ligands, and we realized that AM-Co1 is a more efficient catalyst for oxidative amidation because of its surface area and more accessible open metal sides than AM-Co2. AM-Co1 has been employed as a green heterogeneous catalyst for direct one-pot oxidative amidation of aldehyde in water. This atom-economical, cost-effective, and green method under ultrasound irradiation can be used as the most favorable replacement for the synthesis of amides.

2. RESULTS AND DISCUSSION

2.1. Sonochemical Synthesis of AM-Co1 and AM-Co2.

The MOF AM-Co1 with the formula [Co(oba)(bpfb)].$(N,N,N''$dimethylformamide (DMF))$_2$ (H$_2$oba:4,4'-oxydibenzoic acid; bpfb:$N,N'$(1,4-phenylene)disisonicotinamide) was sonochemically synthesized by mixing Co(NO$_3$)$_2$·6H$_2$O, the H$_2$oba ligand, and the bpfb amide-based pillaring ligand. The asymmetric unit for this MOF consists of a N donor ligand (bpfb ligand) and one oba ligand. Also, the coordination geometry around Co(II) confirms the disordered octahedral via the six coordination sites by the occupation of four oxygen atoms of the carboxylate groups of three different oba ligands with different coordination modes and two pyridyl nitrogen atoms of the bpfb ligand. Thus, two-dimensional AM-Co1 (2D) sheets were connected through the linear bpfb ligands (Figure 2).

The 3D framework structure of AM-Co2 contains the position of the bpta ligands between the two Co-oba. The structure of AM-Co2 was made of a binuclear Co$_2$ unit (Co1 and Co2) under sonication conditions. The coordination geometry around Co1–Co2 is octahedral with six coordination sites by the occupation of four oxygen atoms of the carboxylate groups of three different oba ligands and one pyridyl nitrogen atom from the bpta ligand (Figure 3).

The powder X-ray diffraction (PXRD) patterns of AM-Co1 and AM-Co2 were compared to the simulated XRD pattern of single-crystal data (Figure 4). These data reveal that the sonochemically synthesized MOFs are structurally identical with or almost similar to those of the simulated pattern form the single-crystal data. There is a good agreement in most of the peaks in the PXRD pattern, for example, with $2\theta$ of values of 7.20, 13.10, 17.60, 18.60, 18.70, 20, 25.00, and 26.00° for AM-Co1 and 7.20, 7.25, 7.30, 14.00, 15.20, 15.25, 18.70, 20.50, 22.20, 24.20, 28.00, and 33.30° for AM-Co2. The small displacement can be due to the different preparation methods.

Figure 1. $N,N'$-(1,4-phenylene)disisonicotinamide (bpfb) and $N,N'$-bis(4-pyridinyl)-terephthalamide (bpta) linkers.

Figure 2. Coordination environment around Co in AM-Co1: representation of the surface of pores along the axis (a–d).
The topology of the AM-Co1 structure showed that the nets are the sql/Shubnikov tetragonal plane net in the valence-bonded MOFs, with standard and cluster representations. Also, the net is uninodal and 4-connected with the point symbol \( \{4^4 \cdot 6^2\} \). The topology of the AM-Co2 structure demonstrated that the structure consists of a 3D framework with \( V_2Ti_5ScO_2N_2C_2 \). The point symbol for the net is uninodal and 6-connected with the point symbol \( \{4^4 \cdot 6^{10} \cdot 8\} \).

The IR spectra of sonochemically synthesized AM-Co1 and AM-Co2 indicate the symmetric \( \nu_{\text{sym}}(\text{COO}) \) and asymmetric \( \nu_{\text{as}}(\text{COO}) \) vibrations of the carboxylate group around 1400 and 1600 cm\(^{-1}\), respectively, which reveal the presence of 4,4\('\)-oxybis(benzoic acid) inside the framework (Figure 5). Also, the characteristic peaks for amide groups appearing at 900, 1100 cm\(^{-1}\), and 3400–3500 cm\(^{-1}\) are also related to the N–H bonds of amide, which confirm the presence of amide groups inside the MOFs.

Scanning electron microscopy (SEM) analysis was performed to characterize the morphology, size, and structure of sonochemically synthesized AM-Co1 and AM-Co2 (Figures 6 and 7). It reveals that ultrasound irradiation results in a smaller particle size than the solvothermal synthesis method (Figure 8). Also, there are no other phases present except the blocks of the produced MOF. Thus, we may conclude that our sonochemically synthesized MOFs were almost free from unreacted chemicals. Furthermore, the SEM images lead to the conclusion that there is no difference in the shape of MOFs before and after the reaction.

The MOFs were investigated using thermogravimetric analysis (TGA) (Figure 9). The TGA curves of AM-Co1 and AM-Co2 confirm that a first weight loss at 195 and 205 °C is related to the loss of DMF molecules from the framework.\(^{20}\) A second weight loss at 400 °C was related to the decomposition of the AM-Co1 and AM-Co2 framework. The final residual weights confirm the cobalt oxide of AM-Co1 and AM-Co2.

The Brunauer–Emmett–Teller (BET) measurement revealed that AM-Co1 (2D) is nonporous toward \( \text{N}_2 \) and AM-Co2 (3D) is porous toward \( \text{N}_2 \) at 77 K and can adsorb \( \text{N}_2 \). The BET surface area of AM-Co1 (2D) is nonporous toward \( \text{N}_2 \), these nanosheets exhibited higher catalytic activity than AM-Co 2. The enhanced catalytic activity may result mainly from the abundant active sites in the 2D structure (Table 1).

### 2.2. Catalytic Performance

The catalytic activity of the synthesized AM-Co1 (2D) and AM-Co2 (3D) has been investigated by different aldehydes derivatives. When benzaldehyde with aniline was used, there was no considerable difference between the catalytic activities of AM-Co1 and AM-Co2 (Table 2, entry 1). But in the case of larger functional groups of benzaldehydes and anilines, AM-Co1, with two-dimensional...
sheets, demonstrated better catalytic activity and also reached a maximum product yield (80%) after 120 min, while AM-Co2, because of its 3D structure, reached only (68%) product yield after 120 min (Table 2, entry 2). This significant difference could be related to their different structures. In other words, the fully exfoliated single layers of AM-Co1 will make every active site on its surface available to different small and large derivatives of benzaldehydes and anilines without diffusion limitations, whereas AM-Co2, due to its 3D structure and diffusion limitations, shows weaker catalytic activity toward larger functional groups. The accessibility in AM-Co1 can increase the catalytic activity with respect to AM-Co2 for the oxidative amidation reaction. In addition, to optimize the conditions, the reaction was carried out by utilization of solvents (H2O and acetonitrile), catalyst, and various temperatures to achieve excellent yield (Table 1, entry 7). The results indicate that using H2O as a green solvent is more effective to reach the maximum yield compare to acetonitrile, which is a toxic solvent. To improve the activity, we increased the temperature from room temperature to 80 °C, which gives the best result for oxidative amidation (Table 1, entry 7). Subsequently, we realized that 0.04 g of AM-Co1 (2D) was enough for this work, which gives the desired product in the range of 80−90% yields for corresponding amides.

Actually, the optimal reaction conditions for the oxidative amidation involves benzaldehyde (1.0 mmol), amine (1.0 mmol), and under air in an ultrasound bath at 80 °C for 120 min.

With the optimized conditions for oxidative amidation reactions, products are synthesized via AM-Co1 (2D) with excellent yields, and the results are summarized in Table 3. The table shows that the reaction of 4-methoxybenzaldehyde with aniline gave a moderate yield due to the electron donor of functional groups.

Recyclability and reusability tests of AM-Co1 were performed for the oxidative amidation of benzaldehydes (Figure 11). After the reaction, AM-Co1 was filtered off, washed with excess MeOH, and dried under vacuum at room temperature. Then, the recovered MOF was reused efficiently five times without a significant loss in catalytic activity. The yield of benzamide decreased (40%) when the reaction was carried out with

Figure 6. SEM images of AM-Co1 synthesized by sonochemical method: (a, b) before and (c, d) after reaction.
decreased air saturation. In this respect, when the reaction solution was saturated by air again, the yield of benzamide increased to 55%. This result confirms that using air has a positive impact on this reaction.

The mechanism of sonochemically oxidative amidation catalyzed by AM-Co1 is not clear. However, a suitable mechanism for this reaction is shown in Figure 12. Ultrasound irradiation through capitation induced can support several homogeneous and heterogeneous catalysts. We also used air as an oxidant in this reaction. The results confirm that air played a significant role in this reaction. Hence, it led to the conclusion that both AM-Co1 and air contribute to the progress of the oxidative amidation of aldehydes. We think that the reaction may be performed by a radical coupling, as shown in Figure 12. First, an oxygen radical was produced by cobalt. Then, the oxygen radical reacted with benzaldehyde and amine to produce radicals of amine and aldehyde simultaneously, and their subsequent coupling afforded the product amide.
3. CONCLUSIONS

Powder of AM-Co1 and AM-Co2 MOFs was synthesized in an effective and conventional ultrasonic-assisted synthetic approach, of which AM-Co1 exhibited high catalytic activity in the oxidative amidation reaction with respect to AM-Co2. This excellent catalytic activity of AM-Co1 as a suitable heterogeneous catalyst for the oxidative amidation reaction is related to the fully exfoliated single layers of 2D MOFs that offer a large surface and open metal sides. Furthermore, in this work, we have developed a simple and environmentally friendly method by applying ultrasound conditions for the synthesis of MOFs and also shown that the reactive progress factors of ultrasound irradiation via reducing reaction times and preparing corre-

Table 1. Optimization of Reaction Conditions

| entry | amount of catalyst (g) | conditions | d yield |
|-------|------------------------|------------|--------|
| 1     | AM-Co1 (0.05)          | H₂O, RT    | 80     |
| 2     | AM-Co1 (0.04)          | acetonitrile, reflux | 80 |
| 3     | AM-Co1 (0.05)          | reflux, H₂O, 80 °C | 80 |
| 4     | AM-Co1 (0.05)          | bath ultrasonic, H₂O, RT | 30 |
| 5     | AM-Co1 (0.04)          | bath ultrasonic, H₂O, 50 °C | 50 |
| 6     | AM-Co1 (0.04)          | bath ultrasonic, H₂O, 80 °C | 85 |
| 7     | AM-Co1 (0.03)          | bath ultrasonic, H₂O, 80 °C | 70 |
| 8     | AM-Co1 (0.02)          | bath ultrasonic, H₂O, 80 °C | 60 |
| 9     | AM-Co1 (0.05)          | bath ultrasonic, H₂O, RT | 20 |
| 10    | AM-Co2 (0.05)          | bath ultrasonic, H₂O, 50 °C | 30 |
| 11    | AM-Co2 (0.05)          | bath ultrasonic, H₂O, 80 °C | 75 |
| 12    | AM-Co2 (0.03)          | bath ultrasonic, H₂O, 80 °C | 55 |
| 13    | AM-Co2 (0.02)          | bath ultrasonic, H₂O, 80 °C | 40 |
| 14    | AM-Co2 (0.04)          | reflux, H₂O, 80 °C | 60 |
| 15    | AM-Co2 (0.04)          | bath ultrasonic, H₂O, 80 °C | 55 |

Best yield in bold. “Reaction conditions: Benzaldehyde (1.0 mmol), aniline (1.0 mmol), various solvents (3.0 mL), and under air for 120 min. “Reaction conditions: Benzaldehyde (1.0 mmol), aniline (1.0 mmol), various solvents (3.0 mL), and under air for 6 h. “Reaction conditions: Benzaldehyde (1.0 mmol), aniline (1.0 mmol), various solvents (3.0 mL), and in the absence of air. “Isolated yield.

Table 2. Effects of Reactant Size on the Catalytic Activity of AM-Co1 and AM-Co2 in Oxidative Amidation of Aldehydes

| entry | amount of catalyst (g) | conditions | d yield |
|-------|------------------------|------------|--------|
| 1     | AM-Co1 (0.05)          | H₂O, RT    | 80     |
| 2     | AM-Co1 (0.04)          | acetonitrile, reflux | 80 |
| 3     | AM-Co1 (0.05)          | reflux, H₂O, 80 °C | 80 |
| 4     | AM-Co1 (0.05)          | bath ultrasonic, H₂O, RT | 30 |
| 5     | AM-Co1 (0.04)          | bath ultrasonic, H₂O, 50 °C | 50 |
| 6     | AM-Co1 (0.04)          | bath ultrasonic, H₂O, 80 °C | 85 |
| 7     | AM-Co1 (0.03)          | bath ultrasonic, H₂O, 80 °C | 70 |
| 8     | AM-Co1 (0.02)          | bath ultrasonic, H₂O, 80 °C | 60 |
| 9     | AM-Co1 (0.05)          | bath ultrasonic, H₂O, RT | 20 |
| 10    | AM-Co2 (0.05)          | bath ultrasonic, H₂O, 50 °C | 30 |
| 11    | AM-Co2 (0.05)          | bath ultrasonic, H₂O, 80 °C | 75 |
| 12    | AM-Co2 (0.03)          | bath ultrasonic, H₂O, 80 °C | 55 |
| 13    | AM-Co2 (0.02)          | bath ultrasonic, H₂O, 80 °C | 40 |
| 14    | AM-Co2 (0.04)          | reflux, H₂O, 80 °C | 60 |
| 15    | AM-Co2 (0.04)          | bath ultrasonic, H₂O, 80 °C | 55 |

“Isolated yield.

Table 3. Preparation of Various Amide Compounds with Benzaldehyde

| reaction | product | yield |
|----------|---------|-------|
| Benzaldehyde (1.0 mmol), aniline (1.0 mmol), various solvents (3.0 mL), and under air for 120 min in an ultrasound bath. Isolated yield.

Figure 10. Nitrogen adsorption−desorption of AM-Co1 and AM-Co2.

Figure 11. Reusability of AM-Co1 in the oxidative amidation of benzaldehydes.
sponding amides are beneficial to the oxidative amidation of benzaldehydes.

4. EXPERIMENTAL SECTION

4.1. Materials and Instrumentation. All commercial materials were purchased from Merck or Fluka. The samples were characterized by a scanning electron microscope (SEM) ZEISS SIGMA VP (Germany) with gold coating. The X-ray diffraction (XRD) pattern of the sample was obtained from a Philips X’Pert 1710 diffractometer. 1H NMR (300 MHz) spectra were achieved on a Bruker DRX-500 Advance spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu FT-IR-8400S spectrometer. A Micromeritics ASAP 2030 surface area analyzer was used to measure the N2 adsorption isotherm at 77 K.

4.2. Preparation of MOFs. The solvothermal method has been reported for the synthesis of AM-Co-1 and AM-Co2 crystals previously. Here, ultrasonic irradiation was carried out for the synthesis of AM-Co1 and AM-Co2 by dissolving 0.298 g of Co(NO3)2·6H2O (1 mmol), 0.258 g of 4,4′-oxybis(benzoic acid) (1 mmol), 0.318 g of synthesized amide ligands bpfb (1 mmol), and 0.368 g of bpta in 15 mL of N,N″-dimethylformamide (DMF) sequentially. The mixture was located in a high-density ultrasonic probe and sonicated for 1 h at room temperature with a power output of 18 W. After filtering and washing with DMF, the resulting precipitates were dried in air.

4.3. General Procedure for the Oxidative Amidation of Benzaldehydes with Amines Under Ultrasonic Conditions. A mixture of benzaldehyde derivatives (1.0 mmol), amine derivatives (1.0 mmol), and 0.04 g of AM-Co1 as catalyst was added to water under air atmosphere as an oxidant, and the reaction mixture was dispersed under ultrasonic conditions at 80 °C for 120 min. Thin-layer chromatography (TLC) was done to monitor and determine the end point of reaction. After the reaction completed, the catalyst was removed by centrifugation and the product was decanted by diluting the residue with water. Finally, chromatography on silica gel was applied for the isolation of products.

ASSOCIATED CONTENT

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01773.

1H NMR, 13C NMR, and mass spectra of products (PDF)

AUTHOR INFORMATION

Corresponding Author
Akbar Heydari — Department of Chemical, Faculty of Sciences, Tarbiat Modares University, Tehran 14115-4838, Iran; orcid.org/0000-0003-2399-1401; Email: Heydar_A@modares.ac.ir

Authors
Sepideh Bagheri — Department of Chemical, Faculty of Sciences, Tarbiat Modares University, Tehran 14115-4838, Iran; orcid.org/0000-0003-3661-6838
Farzane Pazoki — Department of Chemical, Faculty of Sciences, Tarbiat Modares University, Tehran 14115-4838, Iran; orcid.org/0000-0001-8616-5591

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01773

Notes
The authors declare no competing financial interest.

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