Synthesis of Metal–Organic Frameworks MIL-101(Cr)-NH₂ Containing Phosphorous Acid Functional Groups: Application for the Synthesis of N-Amino-2-pyridone and Pyrano [2,3-c]pyrazole Derivatives via a Cooperative Vinylogous Anomeric-Based Oxidation

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ABSTRACT: In the current paper, we successfully developed and used metal–organic frameworks (MOFs) based on MIL-101(Cr)-NH₂ with phosphorus acid functional groups MIL-101(Cr)-N(CH₂PO₃H₂)₂. The synthesized metal–organic frameworks (MOFs) as a multi-functional heterogeneous and nanoporous catalyst were used for the synthesis of N-amino-2-pyridone and pyrano [2,3-c]pyrazole derivatives via reaction of ethyl cyanoacetate or ethyl acetoacetate, hydrazine hydrate, malononitrile, and various aldehydes. The final step of the reaction mechanism was preceded by a cooperative vinylogous anomeric-based oxidation. Recycle and reusability of the described catalyst MIL-101(Cr)-N(CH₂PO₃H₂)₂ were also investigated.

1. INTRODUCTION

Metal–organic frameworks (MOFs) have been considered as a new category of nanoporous material. They have been used for various purposes such as storage and separation of gas, catalysts, and heavy-metal adsorption. Metal–organic frameworks (MOFs) based on the type of their ligands and functional groups on their surface exhibit different properties. Their functional groups may be initially present in the organic ligand structures or after synthesizing MOFs to create functional groups within the structure. Metal–organic frameworks (MOFs) exhibit a unique catalytic role in the preparation of hydrogen and methane gas and the synthesis of a wide range of chemical and pharmaceutical compounds. These compounds have shown a unique catalytic power due to their nanosize and porous structures with various functional groups. Developing Cr-based metal–organic frameworks (MOFs) is envisaged to achieve the goals such as: higher surface area, enhanced adsorption, water, and thermal stability in the course of reaction processes.

Phosphorous acid and its derivatives are used as reagents, absorbents, catalysts for the preparation of food additives, precursor for the synthesis of phosphate fertilizers, and in pharmaceutical industries due to their nontoxicity as pH regulators. The design and synthesis of catalysts with phosphorous acid moieties are an attractive research proposal due to their biocompatibility. Recently, we have reported glycoluril, MIL-100(Cr)/En, and mesoporous SBA-15 with phosphorous acid tags. Design, synthesis, and use of metal–organic frameworks (MOFs) with phosphorous acid arms due to their properties of recovery, reuse, and high efficiency are suitable catalysts in the chemical processes.

Heterocyclic moieties have been used as important building blocks within a wide range of medicinal and biologically active molecules. Two of the most important subclasses of heterocyclic chemistry are oxygen- and nitrogen-containing rings, which can be found in the skeletal structures of various types of biologically active and pharmaceutical compounds (Scheme 1). Among oxygen and nitrogen heterocycles, the N-amino-2-pyridones and pyrano [2,3-c]pyrazoles have been shown to have anticancer, anticoagulant, anticonvulsant, antimicrobial, anti-HIV, antimalarial, antitumor, antibacterial, antifungal, and antitumor properties.

In spite of large usage of N-amino-2-pyridones and pyrano [2,3-c]pyrazoles, only a few procedures have been developed for their synthesis, using piperidine, ZnO, sodium L-ascorbate, and nano-M₆Zr(PO₄)₆ as catalysts. Therefore, the develop-
ment of new methodologies for the preparation of N-amino-2-pyridones and pyrano [2,3-c]pyrazoles is in great demand.

In the continuation of our previous investigation on the applications of catalysts with phosphorous acid functional groups, we have decided to design and synthesize a novel MIL-101(Cr)-N(CH2PO3H2)2 with phosphorous acidic arms as nanoporous MOFs and heterogeneous catalyst for the one-pot synthesis of pyrano [2,3-c]pyrazoles and N-amino-2-pyridones. The desired compounds were produced through the condensation of ethyl cyanoacetate or ethyl acetoacetate, hydrazine hydrate, malononitrile, and various aldehydes via a cooperative vinylogous anomeric-based oxidation mechanism and under solvent-free conditions (Scheme 2).

2. RESULTS AND DISCUSSION

In this paper, we reported a clean method for the preparation of MIL-101(Cr)-N(CH2PO3H2)2 as a metal–organic framework (MOFs) by the one-pot reaction of MIL-101(Cr)-NH2, formaldehyde, phosphorous acid, and p-toluenesulfonic acid (p-TSA) under refluxing EtOH. This catalyst was fully characterized by Fourier transform infrared (FT-IR), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), elemental mapping analysis, the scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric (TG), derivative thermal gravimetric (DTG), differential thermal analysis (DTA), and nitrogen adsorption–desorption isotherm Brunauer–Emmett–Teller (BET). Also, MIL-101(Cr)-N(CH2PO3H2)2 was tested for the synthesis of N-amino-2-pyridone and pyrano [2,3-c]pyrazole derivatives.

The FT-IR spectrum of MIL-101(Cr)-NH2 and MIL-101(Cr)-N(CH2PO3H2)2 is compared in Figure 1. The broad peak at 2600–3500 cm⁻¹ was related to the OH of PO3H2 groups. Also, the absorption bands observed at 1021 and 1081 cm⁻¹ are related to the P–O bond stretching and that at 1146 cm⁻¹ is related to P=O.26 Furthermore, peaks of Cr–O of octahedral CrO6 appeared at 1391 cm⁻¹ respectively27 (Figure 1). The FT-IR spectrum difference between MIL-101(Cr)-NH2 and MIL-101(Cr)-N(CH2PO3H2)2 confirmed the structure of the catalyst.

The presenting elements can be seen in the structure and morphology of MIL-101(Cr)-N(CH2PO3H2)2, using energy-dispersive X-ray spectroscopy (EDX), elemental mapping analysis, and scanning electron microscopy (SEM). Through energy-dispersive X-ray spectroscopy (EDX) and elemental mapping analysis, chrome, carbon, nitrogen, oxygen, and phosphor were confirmed in the structure of MIL-101(Cr)-N(CH2PO3H2)2 (Figure 2).

MIL-101(Cr)-NH2 and MIL-101(Cr)-N(CH2PO3H2)2 structures were calculated in the range of 2–80° using XRD as shown in Figure 3. The XRD patterns of our synthesized MIL-
101(Cr)-NH$_2$ matched well with those reported in the literature,
confirming the formation of MIL-101(Cr)-NH$_2$. The main Bragg reflection around $2\theta = 10$ confirmed the successful synthesis of MIL-101(Cr)-NH$_2$ as the MOF structure. The pattern of the phosphonic acid grafted MOF materials exhibits a very similar profile to the pattern of the as-synthesized MIL-101(Cr)-NH$_2$ and is composed of main diffraction peaks of the MOF, confirming that the structures of MIL-101(Cr)-NH$_2$ remained intact with no apparent loss of crystallinity but with some slight decrease in peak intensities along with an increase in phosphonic acid contents due to the partial filling by the grafting guest molecules.

The shape, morphology, and elements of MIL-101(Cr)-NH$_2$ and MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ were studied using SEM analysis. SEM images of MOFs catalyst reveal that the particles are cauliflower and the particle size is within the range of the nanoscales 13.77 and 30.55 (Figures 4 and 5). Figure 6 also shows the results of transmission electron microscopy (TEM) images of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$. Morphology and topology of MOF catalysts were confirmed to be quasi-cube structure. The particles of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ were observed to of nano size (approximately 30−40 nm) with proper dispersion.

Thermal gravimetric (TG) analysis and differential thermal analysis (DTA) of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ are shown in Figure 7. Two declining stages were observed for MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ in the TG pattern. The amount of weight loss is estimated to be 5−7%, which can be attributed to the decreases in solvent (organic and water). The results show that the catalyst can be used up to 220 °C, which can be related to the departure of PO$_3$H$_2$ arms and decomposition of the structure of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ (Figure 7).

Nitrogen adsorption−desorption isotherms of MIL-101(Cr)-NH$_2$ and MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ were measured and the results are presented in Figure 8a,c. Observation of hysteresis loops for both of them means that the prepared catalysts are mesoporous. The obtained BET surface areas of MIL-101(Cr)-NH$_2$ and MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ are 1708 and 528 m$^2$ g$^{-1}$, respectively. Their total pore volumes are 1.46 and 0.38 cm$^3$ g$^{-1}$, respectively. The Barrett−Joyner−Halenda (BJH) pore size distribution data are presented in Figure 8b,d, showing that most of the pores for both samples are smaller than 10 nm. After the structure of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ was approved, it was used as a MOFs catalyst for the synthesis of N-amino-2-pyridones and pyrano[2,3-c]pyrazoles. To synthe-

Figure 4. SEM images of MIL-101(Cr)-NH$_2$.

Figure 5. SEM images of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$.

Figure 6. TEM of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$.

Figure 7. TG analysis, DTG analysis, and DTA of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$. 
zeN-amino-2-pyridones, the four-part reaction between ethyl cyanoacetate (1 mmol, 0.113 g), hydrazine hydrate (1.2 mmol, 0.060 g), malononitrile (1.1 mmol, 0.072 g) and benzaldehyde (1 mmol, 0.106 g) under refluxing solvents such as: water, ethanol, acetonitrile, n-hexane solvents and solvent-free in the presence a catalytic amount of MIL-101(Cr)-N(CH2PO3H2)2, was tested, the results of which are shown in Table 1. The results are summarized in Table 1. The results show that refluxing water is best of choice for producing N-amino-2-pyridones (Table 1, entry 1). Increasing the amount of catalyst did not show any increase in efficiency (Table 1, entry 9). By decreasing the amounts of catalysts, a decrease in efficiency was observed (Table 1, entries 7 and 8). Reducing the temperature has increased the reaction time and reduced the efficiency of the product (Table 1, entries 10–13).

After optimization of the reaction conditions for the synthesis of N-amino-2-pyridones, a wide range of aromatic aldehydes, including electron withdrawal, electron release and heterocyclic rings have been synthesized (Table 2). Then, to investigate the effect of the functional group, ethyl acetoacetate replaced ethyl cyanoacetate, and it was observed that the product of pyrano [2,3-c]pyrazoles was synthesized by changing the cyano group to the carbonyl group. Under optimal conditions for N-amino-2-pyridones, a wide range of pyrano [2,3-c]pyrazoles were also synthesized (Table 3). The results reveal that the described catalyst can produce N-amino-2-pyridones and pyrano [2,3-c]pyrazoles derivatives in short reaction time and high efficiency.

Alabugin has recently comprehensively reviewed the stereo-electronic effects as a bridge between structure and reactivity.41–43 On the basis of Alabugin’s concept, we have recently introduced a new term “vinyllogous anomeric-based oxidation”.44–48 Vinylogous anomic effect has been approved by Katritzky.49 In the cooperative vinylogous anomic-based oxidation mechanism, through a multicomponent reaction strategy, starting materials interact with each other to yield a suitable intermediate. The vinylogous anomic effect is the major driving force of oxidation and/or aromatization of intermediate for preparing the desired product. For example, in the case of 2-amino-4,6-diphenylnicotinonitrile a cooperative vinylogous anomic-based oxidation mechanism occurs at the related intermediate (Scheme 3).50 A wide range of aromatized molecules through the described mechanism have been reported.51

The anomic effect can lead to bond weakening in a wide range of organic reactions. For example, recently we have suggested that in the Cannizzaro reaction after the addition of hydroxide (OH−) to the carbonyl group of aldehydes which did not have α-hydrogen (Scheme 4), both the lone pairs of electrons of oxygen atoms within the tetrahedral carbon shared their electrons in the antibonding orbital of the C−H bond (nN→σ* C−H) and weakened it. The resulting labile hydride acts as a powerful nucleophile that attacks the second molecule of aldehyde. Finally, this reaction produced equal amounts of corresponding alcohol and acid.52

On the basis of the above-mentioned background, a rational mechanism for the synthesis of N-amino-2-pyridones based on a cooperative vinylogous anomic-based oxidation for the final step is suggested in Scheme 5. At first, the carbonyl group of aldehyde is activated by the acidic group of MIL-101(Cr)-N(CH2PO3H2)2. Malononitrile reacts with the carbonyl group of aldehyde to afford an intermediate I by removing one molecule of H2O. Then, compound (A) attacks intermediate I as a Michael acceptor to give intermediate II. Further, intermediate II with intramolecular cyclocondensation reacts to give III. Finally, intermediate III was derived via a cooperative vinylogous anomic-based oxidation (−H2) to give the desired product (Scheme 5). It should be noted that the target reaction was also carried out under argon and nitrogen atmospheres to make sure that the final desired product was not produced via an aerobic oxidation pathway. The reaction was performed successfully under the air atmosphere. Thus, our evidence shows that the target reaction was preceded via a cooperative vinylogous anomic-based oxidation mechanism.

To evaluate the performance of MIL-101(Cr)-N-(CH2PO3H2)2 as a catalyst for the preparation of N-amino-2-pyridones, we have used various organic and inorganic acid...
catalysts for the condensation reaction between 4-nitro benzaldehyde (1 mmol, 0.151 g), ethyl cyanoacetate (1 mmol, 0.113 g), hydrazine hydrate (1.2 mmol, 0.060 g), and malononitrile (1.1 mmol, 0.072 g) (Table 3). As indicated in Table 3, MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ is the best catalyst for the synthesis of N-amino-2-pyridone derivatives (Table 4).

According to the results in Figure 9, MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ can be separated by centrifugation and reused without significantly reducing its catalytic activity. For this purpose, recyclability of the catalyst was tested in the reaction between 4-nitro benzaldehyde (1 mmol, 0.151 g), ethyl cyanoacetate (1 mmol, 0.113 g), hydrazine hydrate (1.2 mmol, 0.060 g), and malononitrile (1.1 mmol, 0.072 g) as a model reaction under the above-mentioned optimized reaction conditions. Therefore, MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ can be reused up to six runs without noticeable changes in the catalytic activity.
3. CONCLUSIONS

After the preparation of metal–organic framework MIL-101(Cr)-NH2 with phosphorous acid functional groups, its structure was approved. The presented MIL-101(Cr)-N(CH2PO3H2)2 was successfully applied for producing a wide range of pyrano [2,3-c]pyrazole and N-amino-2-pyridone derivatives via cooperative vinylogous anomeric-based oxidation mechanism. Short reaction times, clean profile of reaction, easy...

Table 3. Synthesis of Pyrano [2,3-c]pyrazoles Using MIL-101(Cr)-N(CH2PO3H2)2

| Entry | Product | Time (min) | Yield (%) | M. p (°C) Found (Lit. °C) |
|-------|---------|------------|-----------|--------------------------|
| 1     | ![Image](image1.png) | 25 | 90 | 243-245 (243-246) |
| 2     | ![Image](image2.png) | 22 | 89 | 195-196 (196-198) |
| 3     | ![Image](image3.png) | 25 | 91 | 210-212 (210-213) |
| 4     | ![Image](image4.png) | 20 | 90 | 232-235(231-235) |
| 5     | ![Image](image5.png) | 15 | 93 | 251-253(250-252) |
| 6     | ![Image](image6.png) | 20 | 91 | 213-215(214-216) |
| 7     | ![Image](image7.png) | 25 | 76 | 168-170(168-170) |

Scheme 3. Cooperative Vinylogous Anomeric-Based Oxidation Leads to the Production of 2-Amino-4,6-diphenylnicotinonitrile

Scheme 4. Anomeric-Based Oxidation Leads to Hydride Transfer in the Mechanism of Cannizzaro Reaction

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work-up, recyclability, and reusability of catalyst are advantages of the presented methodology.

4. EXPERIMENTAL SECTION

4.1. General Procedure for the Preparation of MIL-101(Cr)-NH$_2$. MIL-101(Cr)-NH$_2$ was synthesized according to our previously reported experimental procedure.$^{28,29}$ A mixture of Cr(NO$_3$)$_3$·9(H$_2$O) (2 mmol, 0.8 g), 2-aminoterephthalic acid (2 mmol, 0.362 g), and sodium hydroxide (5 mmol, 0.2 g) was dispersed and then stirred in 20 mL of water for 10 min. The resulting solution was heated in a Teflon-lined autoclave at 150 °C for 12 h. After cooling the reaction mixture to room temperature, the green solid was collected, washed with dimethylformamide (DMF), and then further purified by solvothermal treatment in ethanol at 100 °C for 24 h. Finally, the desired product was dried at 80 °C in a vacuum oven.

4.2. General Procedure for the Preparation of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$. In a 50 mL round-bottom flask, MIL-101(Cr)-NH$_2$ (1 g), formaldehyde (0.33 mL, 9 mmol), phosphorus acid (0.665 mL, 9 mmol), p-TSA (10 mol %, 0.017 g), and ethanol (25 mL) were refluxed for 8 h. Then, it was washed three times with ethanol and dried in a vacuum oven at 70 °C to obtain MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ (1.7 g) (Scheme 6). The amount of phosphorus is 4.56% of the MOFs component of MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$.

4.3. General Procedure for the Synthesis of Pyrano[2,3-c]pyrazole and N-Amino-2-pyridone Derivatives (10a–10t) Using MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$. In a four-component reaction in water reflux conditions, including ethyl cyanoacetate or ethyl acetoacetate (1 mmol), hydrazine hydrate (1.2 mmol, 0.060 g), malononitrile (1.1 mmol, 0.072 g), aldehyde (1 mmol), and MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ (10 mg) were stirred in a 25 mL round-bottom flask (time for any case has been presented in Tables 2 and 3). Thin-layer chromatography (TLC) technique was used to assess the reaction progress. After the reaction was completed, the solvent was evaporated and then 2 mL of ethylene glycol was added to the reaction mixture. The catalyst was removed from the
reaction using centrifugation at 1000 rpm. The product was purified using 96% ethanol (Scheme 2).

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02133.

Table 4. Evaluation of Various Catalysts for the Synthesis of N-Amino-2-pyridones in Comparison with MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ in Ethanol under Reflux Conditions

| entry | catalyst | amount of catalyst (mol %) | time (min) | yield (%) |
|-------|----------|---------------------------|------------|-----------|
| 1     | MIL-101(Cr)-N(CH$_2$PO$_3$H$_2$)$_2$ | 5 mg | 20 | 92 |
| 2     | MIL-101(Cr-NH$_2$) | 5 mg | 60 | 24 |
| 3     | [Py-SO$_3$H]Cl$^{13}$ | 10 | 35 | 82 |
| 4     | Fe$_3$O$_4$@SiO$_2$@Pr-NH$_2$ | 5 mg | 60 | 25 |
| 5     | SSA$^{15}$ | 10 | 25 | 85 |
| 6     | TrBr | 15 | 60 | 65 |
| 7     | p-TSA | 10 | 45 | 65 |
| 8     | nano-SB-[PSIM]Cl$_{16}$ | 10 | 35 | 78 |
| 9     | TrCl | 10 | 45 | 72 |
| 10    | GTBSA$_{27}$ | 10 | 30 | 85 |
| 11    | [Fe$_3$O$_4$@SiO$_2$@Pr-NH$_2$]Cl$_{28}$ | 10 mg | 35 | 82 |
| 12    | FeCl$_3$ | 10 | 50 | 75 |
| 13    | Al(HSO$_4$)$_3$ | 10 | 45 | 75 |
| 14    | H$_2$[p(W$_3$O$_10$)$_4$]·xH$_2$O | 15 | 60 | 75 |
| 15    | Fe$_3$O$_4$ | 10 mg | 55 | 68 |
| 16    | trichloroisocyanuric acid | 10 | 55 | 70 |
| 17    | Br$_2$N | 20 | 60 | trace |
| 18    | Na$_2$SO$_3$ | 10 | 60 | 35 |
| 19    | H$_2$PO$_3$ | 10 | 20 | 75 |
| 20    | H$_2$PO$_3$ + MIL-101(Cr)-NH$_2$ | 5 + 5 | 20 | 90 |

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FT-IR; $^1$H NMR; and $^{13}$C NMR spectroscopy details (PDF)

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Notes

The authors declare no competing financial interest.

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