Original Article

Bimetal-organic frameworks (Cu_x–Cr_{100–x}–MOF) as a stable and efficient catalyst for synthesis of 3, 4-dihydropyrimidin-2-one and 14-phenyl-14H-dibenzo [a, j] xanthene

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ABSTRACT

Successful three-dimensional bimetallic metal organic frameworks with different Cu/Cr ratios have been prepared under solvothermal conditions using chromium nitrate and copper nitrate as a bimetal and 1, 4 benzene dicarboxylic acid as an organic linker. Numerous techniques were used to characterize the resulting samples such as XRD, BET, SEM, TEM, SEM-EDS and FT-IR measurements. Combination of Cu and Cr in the same framework will cause some deformation in the structure and decrease in the surface area and pore size distribution. This decrease may be due to the incorporated copper have higher atomic weight than chromium ion. The acidic properties can be measured by non-aqueous titration. The catalytic performance of bimetallic MOFs was confirmed through the synthesis of 3, 4-dihydropyrimidin-2-one and 14-Phenyl-14H-dibenzo [a, j] xanthene. Pure Cu-BDC and Cr-MIL-101 possesses a relatively lower surface acidity as well as lower catalytic activity. It surprising that, the combination between copper and chromium in the same framework can significantly enhance the acidity and catalytic activity of the as-synthesized catalysts which may be due to the synergetic effect.

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1. Introduction

Over the past two decades, metal-organic frameworks (MOFs) have generated enormous scientific interest as a new class of materials due to their inherent high specific surface areas, exceptional porosity, diverse functionality, uniform but tunable cavities, high crystallinity and high modularity [1] that make them show potential in a broad spectrum of applications such as catalysis [2], gas storage [3], dye adsorption [4], smart sensors [5], separation [6] and drug delivery [7]. Their structures contain extended co-ordination networks of metal centers as nodes connected by organic ligands as linkers which provides huge structural and chemical diversity. These exclusive properties of metal organic frameworks offer a countless chance to generate specific required active sites...
and makes MOFs exceptional applicants for a variety of applications [8–10].

Multivariate (MTV-MOFs) or mixed-component (MC-MOFs) metal organic frameworks represent the incorporation of several metal ions [11,12] or multiple organic functionalities [13,14] within one structure resulting in materials with a higher catalytic activity. Basically, some original studies have previously revealed that the mixed-metal MOFs had superior properties over parent MOFs and in some cases, can even induce new functionalities, due to the insertion of the second metal ions in the same frameworks. One of the representative examples is the fruitful synthesis of multivariate metal organic frameworks (MTV-MOFs), described by Omar Yaghi, in which up to eight different organic linkers were combined into one single framework [15].

Kozachuk et al. [16] in 2012 showed the successful synthesis of a series of frameworks with the empirical formula Cu$^{II}_{1-x}$Zn$^{II}_{x}$(bdc)(dapc))$_{2}$, with the metal ratios of 5:95, 25:75, 50:50, 75:25, 95:5 (Cu: Zn). The mixed-metal frameworks were shown to be isoreticular to the parent frameworks. Also, Wang et al. [17] reported the synthesis of a series of MOFs with the empirical formula Mn$^{II}_{1-x}$Fe$^{III}_{x}$(cmcpp)(H)$\times$(H$_{2}$O) (cmcpp = carboxymethylpyridinium-4-carboxylate) using the metal ratios 1:1, 2:3 and 1:4 (Mn:Fe). Magnetic studies on these materials showed that the resultant behavior was a combination of the ferromagnetic behavior of the Fe(II) centers and the antiferromagnetic behavior of the Mn(II) centers and as the Fe(II) content increased there was a gradual evolution from antiferromagnetic to ferromagnetic behavior.

The Biginelli reaction is a multiple-component chemical reaction that gives 3,4-dihydropyrimidin-2(1H)-ones (DHPMs) that have potential applications in pharmaceutical industries such as calcium channel blockers [18], antihypertensive agents [19], antibacterial [20], antiviral [21], anti-inflammatory [22] and antitumor agents [23,24]. This reaction act as one of the most important reactions for producing compounds with diverse medicinal application which includes one-pot condensation of benzaldehyde, ethyl acetocetate and urea under acidic conditions and this reaction can be catalyzed by Bronsted acids and/or by Lewis acids [25].

Xanthenes and Benzo-xanthenes derivatives have a numerous therapeutic and pharmaceutical properties such as anti-inflammatory [26], antiviral [27], antibacterial and antifungal activities [28]. Furthermore, these heterocyclic derivatives are used as leuco-dyes in laser technology [29], as antagonists of the paralyzing action of zoxazolamine [30], as sensitizers in photodynamic therapy [31] and in fluorescent materials for visualization of biomolecules [32]. The reported procedures for the synthesis of 14-phenyl-14H-dibenzo [a, j] xanthenes involve mixing of β-naphthol and benzaldehyde in the existence of an acidic catalyst like; sulfamic acid supported on MIL-101 [33], silica sulfuric acid [34], boric acid [35] and heteropoly acid supported MCM-41 [36].

In the present study, we have synthesized mixed component metal organic frameworks (Cu$^{II}_{x}$Cr$^{III}_{1-x}$-MOF) for synthesis of 3,4-dihydropyrimidin-2(1H)-ones and 14-phenyl-14H-dibenzo [a, j] xanthenes. Copper and Chromium have been selected due to their readily available, environmentally benign, non-toxic and inexpensive. Structural characterization of the as-synthesized catalysts was identified by numerous techniques such as XRD, fourier transform-IR, TEM, SEM, SEM-EDS and non-aqueous titration with n-butylamine. Cu$_{x}$Cr$_{100-x}$-MOF enhanced the catalytic performance by a synergetic effect and reinforced the frameworks to preserve the stability in the recycle experiments. Remarkably, Cu$_{90}$-Cr$_{10}$-MOF exhibits higher catalytic activity with percent yield 94% in the synthesis of 3,4-dihydropyrimidin-2(1H)-ones and 93% in the synthesis of 14-phenyl-14H-dibenzo [a, j] xanthenes.

2. Experimental

2.1. Materials

Copper(II) nitrate trihydrate (Cu(NO$_{3}$)$_{2}$$\cdot$3H$_{2}$O, 98.5%) and Chromium nitrate (Cr(NO$_{3}$)$_{3}$.9H$_{2}$O, 98.5%) were purchased from Sigma-Aldrich chemical reagent co., terephthalic acid or benzene 1, 4-dicarboxylic acid (C$_{6}$H$_{8}$O$_{4}$, 99%) were purchased from Alfa Aesar. N, N-dimethyleformamide ((DMF ≥ 99.5%) and ethanol (≥ 99.5%) were commercially purchased from Alfa Aesar and used without further purification.

2.2. Synthesis of Cu$_{x}$Cr$_{100-x}$-MOF

Bimetallic Cu$_{x}$Cr$_{100-x}$-MOF was synthesized through a hydrothermal method according to the reported approach with slightly modified procedure [16]. The mixed-metal MOFs were synthesized by changing ratio copper and chromium precursors ratio. The reaction mixture with molar composition of (x Cu(NO$_{3}$)$_{2}$·3H$_{2}$O; (100-x) Cr(NO$_{3}$)$_{3}$·6H$_{2}$O : H$_{2}$bdc (332 mg) were dissolved in 30 ml DMF and 10 ml deionized water for each synthesis. Then the reaction mixture was poured into a Teflon lined stainless steel autoclave and heated at 120 °C for 48 h. After that the mixture was left to cooling, greenish Blue crystals (depending on the amount of chromium and copper) were collected and washed by DMF. Then the as-synthesized samples were washed again with excess hot ethanol (70 °C) for 4 h to remove unreacted terephthalic acid trapped within the pores and then dried at 100 °C overnight.

2.3. Catalyst characterization

X-ray powder diffraction (XRD) measurements of Cu$_{x}$Cr$_{100-x}$-MOF samples were recorded by Shimadzu Lab XRD 6100 diffractometer with Cu Ka radiation at wavelength equal 1.5418 Å. The scanning was obtained at 2θ between 4° and 70° with a step size 0.02 and a step time of 2 s. Surface area measurements were carried out with N$_{2}$ adsorption–desorption isotherms at –196 °C on BELSORP-mini II analyzer. All samples were outgassed at 150 °C for 12 h before adsorption measurements. The structure and morphology of the as-synthesized samples were measured by scanning electron microscopy (SEM, JEOL-JSM-6010LV) equipped with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, JEOL-JEM-2100Plus). The surface composition and functional groups of the samples were investigated by Fourier transform infrared (FTIR) spectra which operated at room temperature in the wavenumber range of 400–4000 cm$^{-1}$ using Bruker VERTEX 70 FTIR spectrometer. Non-aqueous potentiometric titration
was used to determine the total acidity, total number of acid sites and acid strength of the prepared samples [37] in which 0.1 gram of activated samples were suspended in 10 mL acetonitrile for 2 h then titrated with 0.05 N of n-butylamine in acetonitrile and electrode potential was measured by Orion 420 digital model.

2.4. Catalytic studies

2.4.1. Synthesis of 3,4-dihydropyrimidin-2(1H)-ones
In a typical experiment, 3,4-dihydropyrimidin-2(1H)-ones were prepared by mixing benzaldehyde (1 mmol) and ethyl acetoacetate (1 mmol) in existence of 0.05 g of Cu\textsubscript{x}-Cr\textsubscript{100-x}-MOF catalyst under solvent free conditions. This reaction mixture was heated at 100 °C for the required time (monitored by TLC). After the reaction was completed, 10 mL of ethanol was added and the reaction was cooled to room temperature then transferred into a crushed ice. After that the product was separated by simple filtration, washed by cold water and then recrystallized from ethanol to afford the pure product which was identified by melting point and FTIR spectra.

2.4.2. Synthesis of 14-phenyl-14H-dibenzo [a, j] xanthene
In a general procedure, 1 mmol of benzaldehyde and 2 mmol of β-naphthal was mixed together with 50 mg of Cu\textsubscript{x}-Cr\textsubscript{100-x}-MOF catalyst under free solvent conditions and then was heated at 120 °C until the reaction was completed (monitored by TLC). After that, the product was dissolved in chloroform and filtered to remove the catalyst, which was then washed with hot ethanol. After that, the clear solution (filtrate) was poured into a cold water to obtain crude 14-phenyl-14H-dibenzo [a, j] xanthene that settled down, filtered and dried at 90 °C and then recrystallized in hot ethanol. The crude product was identified by melting point and FTIR spectra.

3. Results and discussion

3.1. X-ray diffraction pattern (XRD)

Powder X-ray diffraction (XRD) pattern was performed to confirm the crystallinity of the as-synthesized Cu\textsubscript{x}-Cr\textsubscript{100-x}-MOFs samples as shown in Fig. 1. All XRD patterns of Cu\textsubscript{x}-Cr\textsubscript{100-x}-MOFs show a series of diffraction peaks at 2θ equal 9.1, 10.3, 17.6, 19.1 24.8° that agreed with XRD patterns of Pure Cr-MIL-101 [33] on the other hand, there are other different peaks at 2θ equal 9.1, 12.1, 17.6, 25.6° that agreed with XRD patterns of Pure Cu-BDC. XRD pattern of these samples indicate that highly crystalline product was obtained. The differences in characteristic diffraction peaks position were due to the combination between two different metals, but the peaks still remained sharp [38]. The intensity of the peaks was decreased in Cu\textsubscript{50}-Cr\textsubscript{50}-MOF which means that crystallinity of these samples was slightly decreased and this is may be due to the presence of high content of copper inside the framework of as-synthesized MOFs [39].

![Fig. 1 - X-ray diffraction pattern of (A) pure Cr-MIL101, (B) Cu\textsubscript{25}-Cr\textsubscript{75}-MOF, (C) Cu\textsubscript{50}-Cr\textsubscript{50}-MOF, (D) Cu\textsubscript{90}-Cr\textsubscript{10}-MOF and (E) pure Cu-BDC.](image1)

![Fig. 2 - N\textsubscript{2} adsorption desorption isotherms at \textasciitilde 196 °C for (a) pure Cr-MIL101, (b) Cu\textsubscript{10}-Cr\textsubscript{90}-MOF, (c) Cu\textsubscript{25}-Cr\textsubscript{75}-MOF, (d) Cu\textsubscript{50}-Cr\textsubscript{50}-MOF, (e) Cu\textsubscript{75}-Cr\textsubscript{25}-MOF, (f) Cu\textsubscript{90}-Cr\textsubscript{10}-MOF and (g) pure Cu-BDC.](image2)

3.2. BET measurements

Nitrogen adsorption isotherms for as synthesized catalysts were measured at \textasciitilde 196 °C to study porosity and surface area of these samples as shown in Fig. 2. Cr-MIL-101 displayed a type-II N\textsubscript{2} adsorption isotherm with pore volume (1.645 cm\textsuperscript{3} g\textsuperscript{-1}) and high Brunauer-Emmett-Teller (BET) surface area (2989 m\textsuperscript{2} g\textsuperscript{-1}) as shown in our previous work [33]. As well as, Cu-BDC and Cu\textsubscript{x}-Cr\textsubscript{100-x}-MOF displayed an intermediate mode between type-II and type IV (Fig. 2). BET surface area of Cu-BDC are 726 m\textsuperscript{2} g\textsuperscript{-1} and its total specific micropore volume are 0.317 cm\textsuperscript{3} g\textsuperscript{-1} which are in agreement with earlier reports [40]. As expected, when the Cu and Cr ions are existing together in the same framework to yield isoreticular Cu\textsubscript{x}-Cr\textsubscript{100-x}-MOF, the same general tendency in S\textsubscript{BET} and pore volume was observed as shown in Table 1. This decrease in S\textsubscript{BET} and pore volume are obviously suggested that the insertion of copper cation has positively replaced chromium cation in the framework of Cr-MIL-101 rather than exist in the pores.
Since the atomic weight of copper cation (63.546 g mol\(^{-1}\)) is larger than that of chromium (51.996 g mol\(^{-1}\)), the decrease in \(S_{\text{BET}}\) is may be due to the larger size of Cu\(^{2+}\) compared to Cr\(^{3+}\) [41,42]. This decrease in the \(S_{\text{BET}}\) and pore volume is due to the incorporation of copper cation as a larger atom in the framework of Cu\(_x\)-Cr\(_{100-x}\)-MOF.

### 3.3. **SEM, TEM images and EDS analysis**

The morphology of as synthesized single and bimetallic MOFs was investigated by scanning electron microscopy (SEM) and its images were presented in Fig. 3. Cr-MIL-101 crystal exhibit octahedral morphology while Cu-BDC has a cubic morphology which are identical of the previously reported literature [33,43]. On the other hand, Cu\(_x\)-Cr\(_{100-x}\)-MOF samples reveal the presence of irregular and similar octahedral structure with some defects depending on the percentage of copper metal inside the framework. Cu\(_{100}\)-Cr\(_0\)-MOF has no definite shape but mixed with some crystals which means that it doesn’t has high crystallinity as observed in XRD patterns.

TEM images for pure MIL-101, Cu-BDC and Cu\(_x\)-Cr\(_{100-x}\)-MOF samples were displayed in Fig. 4 which are well-consistent with the observed SEM images in terms of dimensionality and morphologies. As shown in TEM images, Cr-MIL-101 depict octahedral morphology with typical particle size approximately equal 0.48 \(\mu\)m [33]. While Cu-BDC has a smaller size which equal 0.35 \(\mu\)m with cubic morphology [43]. The as synthesized Cu\(_x\)-Cr\(_{100-x}\)-MOF samples show that octahedral morphologies were preserved until Cu\(_{50}\)-Cr\(_{50}\)-MOF then the morphology were nearly distorted which may be due to the high content of copper inside the framework as confirmed by SEM images and XRD pattern. Fig. 4 also indicate that the crystal size decrease by increasing the copper content until reached 102 nm in case of Cu\(_{50}\)-Cr\(_{50}\)-MOF.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) were used to investigate the elemental, chemical composition and the purity of the as-synthesized MOFs which are shown in Fig. 5. SEM-EDS figures show the diffraction peaks of Cu, Cr, O, C and N elements corresponding to single and bimetallic MOFs. Fig. 5 and Table 1 show that the experimental atomic ratio of Cu and Cr elements is very close to the theoretical one of different Cu\(_x\)-Cr\(_{100-x}\)-MOF samples and confirm that the mixed-metal MOFs were successfully synthesized.

### 3.4. **FT-IR spectra**

The Fourier transform infrared (FT-IR) spectra in Fig. 6 reflects the characteristic bands of the as-synthesized Cu\(_x\)-Cr\(_{100-x}\)-MOF. Peak appears at 1119 cm\(^{-1}\) may be related to the C–O stretching vibration [44]. Additionally, the resulting peak at wavelength equals 1401 cm\(^{-1}\) was related to symmetric stretching modes of coordinated carboxylic acid. The weak and narrow bands at 1006 and 749 cm\(^{-1}\) can be related to \(\gamma(C=O), \delta(C–H)\) vibration of aromatic rings [45]. The broad peak in the spectral range of 3000–3700 cm\(^{-1}\) was related to crystalline water or acidic OH of carboxylic groups while the strong peak at 1638 cm\(^{-1}\) was attributed to the vibration of (C=O) group. The weak peak at 671 cm\(^{-1}\) was most likely because of outplane and inplane bending modes of carboxylic (COO\(^{-}\)) groups [33]. The absence of strong absorption band near 1710 or 1714 cm\(^{-1}\) indicates that all carboxylic groups of the terephthalic ligand are deprotonated [46,47]. The band with medium strength at 582 cm\(^{-1}\) was due to metal–oxygen (M–O) vibrations, that confirms the formation of the desired metal organic framework [48].

### 3.5. **Surface acidity studies by non-aqueous titration**

The surface acidities of the as synthesized MOFs were determined through non-aqueous titration. This technique gives overall measurement of the acidity of the prepared solids but it does not allow to differentiate between Brønsted and Lewis acid sites. The potential corresponding to the initial point of the titration \((E_i \text{ mV})\) of the non-aqueous suspension allows the solids to be classified to its acid strength which can be categorized according to the following scale: \(E_i < 100 \text{ mV} \) (very weak sites), \(100 < E_i < 0 \text{ mV} \) (weak sites), \(0 < E_i < 100 \text{ mV} \) (strong sites) and \(E_i > 100 \text{ mV} \) (very strong sites) [49]. Also, the total number of acid sites can be calculated from the point where the plateau is reached (mmole amine per g) in the potentiometric titration curves as shown in the following relation:

\[
\text{Total number of acid sites/g} = \frac{\text{steady point of plateau + (equiv./g) \times Avogadro’s number}}{100}
\]

Fig. 7 indicates that by increasing the amount of copper cation inside the frameworks, acid strength of as-synthesized catalysts increased and created strong acid sites on the surfaces. Cu-BDC showed a maximum acid strength of \(E_i = 99 \text{ mV}\) [50] while Cr-MIL-101 showed a maximum acid strength.

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**Table 1 – The physicochemical properties of single and bimetallic MOFs catalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m(^2) g(^{-1}))</th>
<th>(V_{\text{pore}}) (cm(^3) g(^{-1}))</th>
<th>SEM-EDS (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-MIL-101</td>
<td>2989</td>
<td>1.645</td>
<td></td>
</tr>
<tr>
<td>Cu(<em>{10})-Cr(</em>{90})-MOF</td>
<td>2137</td>
<td>1.345</td>
<td></td>
</tr>
<tr>
<td>Cu(<em>{35})-Cr(</em>{65})-MOF</td>
<td>1725</td>
<td>1.058</td>
<td></td>
</tr>
<tr>
<td>Cu(<em>{35})-Cr(</em>{65})-MOF</td>
<td>1394</td>
<td>0.978</td>
<td></td>
</tr>
<tr>
<td>Cu(<em>{35})-Cr(</em>{65})-MOF</td>
<td>1090</td>
<td>0.758</td>
<td></td>
</tr>
<tr>
<td>Cu(<em>{35})-Cr(</em>{65})-MOF</td>
<td>926</td>
<td>0.578</td>
<td></td>
</tr>
<tr>
<td>Cu-BDC</td>
<td>726</td>
<td>0.317</td>
<td></td>
</tr>
</tbody>
</table>

**Note:**

- **C O N Cr Cu**
- **Theoretical percentage:**
  - Cu\(_{10}\)-Cr\(_{90}\)
  - Cu\(_{11.1}\)-Cr\(_{88.9}\)
  - Cu\(_{11.7}\)-Cr\(_{84.7}\)
  - Cu\(_{11.8}\)-Cr\(_{84.5}\)
  - Cu\(_{12}\)-Cr\(_{85}\)
  - Cu\(_{47.4}\)-Cr\(_{52.6}\)
  - Cu\(_{50}\)-Cr\(_{50}\)
  - Cu\(_{50}\)-Cr\(_{50}\)
  - Cu\(_{75}\)-Cr\(_{25}\)
  - Cu\(_{90}\)-Cr\(_{10}\)
  - Cu\(_{80}\)-Cr\(_{20}\)
  - Cu\(_{100}\)-Cr\(_0\)
  - Cu\(_{100}\)-Cr\(_0\)

**References:**

[41,42,33,43,44,45,46,47,48,49].
Table 2 – Acidic properties and percentage yield of 3,4-dihydropyrimidin-2(1H)-ones and 14-phenyl-14H-dibenzo [a, j] xanthenes over the as-synthesized samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial potential (Ei)</th>
<th>No. of acid sites in mequiv. g⁻¹ (×10¹⁹)</th>
<th>3,4-dihydropyrimidin-2(1H)-ones</th>
<th>14-phenyl-14H-dibenzo [a, j] xanthenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-MIL-101 [33]</td>
<td>+148.2</td>
<td>2.031</td>
<td>22.4</td>
<td>38.2</td>
</tr>
<tr>
<td>Cu₁₀₀·Cr₀₀–MOF</td>
<td>+138.4</td>
<td>2.568</td>
<td>73.1</td>
<td>67.8</td>
</tr>
<tr>
<td>Cu₁₂₅·Cr₇₅–MOF</td>
<td>+214.8</td>
<td>2.899</td>
<td>79.2</td>
<td>75.5</td>
</tr>
<tr>
<td>Cu₇₅·Cr₂₅–MOF</td>
<td>+254.6</td>
<td>3.375</td>
<td>87.5</td>
<td>82.4</td>
</tr>
<tr>
<td>Cu₂₅·Cr₇₅–MOF</td>
<td>+284.2</td>
<td>3.892</td>
<td>89.3</td>
<td>90.1</td>
</tr>
<tr>
<td>Cu₉₀·Cr₁₀–MOF</td>
<td>+318.6</td>
<td>4.047</td>
<td>93.3</td>
<td>94.1</td>
</tr>
<tr>
<td>Cu-BDC</td>
<td>+99.2</td>
<td>1.872</td>
<td>71.0</td>
<td>65.0</td>
</tr>
</tbody>
</table>

of E_i = +148 mv as shown in our previous work [33]; However, combination between copper and chromium in the same framework to produce the desired Cu_x·Cr_{100−x}–MOF was accompanied by a progressive increase in acidic strength until reached to E_i = +319 mv for Cu₉₀·Cr₁₀–MOF sample as shown in Table 2. As well as, the total number of acid sites were varied by the same trend as shown in Table 2. These results indicate that mixing copper and chromium to form various mixed...
metal MOFs with different metal contents will enhance the acidic properties of these MOFs. These enhancements may be due to synergetic effect between cupper and chromium metals which leads to increase porosity, active sites and open metal sites.

3.6. Catalytic studies

3.6.1. Synthesis of 3,4-dihydropyrimidin-2(1H)-ones

3, 4-dihydropyrimidin-2(1H)-ones was synthesized under solvent-free condition by reacting benzaldehyde, ethyl acetoacetate and urea in the existence of different amount of Cu\textsubscript{x}-Cr\textsubscript{100-x}–MOF catalysts without using any solvents. A background reaction was examined in absence of supported catalysts and no product was produced. In this reaction, we have efficaciously used solid acid catalysts as substitutional to classical methods for preparation of the desired dihydropyrimidinones, which characterized by its melting point (m.p = 195 °C) and FT-IR spectroscopy. The percent yields of the products (%) were calculated as the quantity of experimental dihydropyrimidinones (g) divided into quantity of theoretical dihydropyrimidinones (g) *100.

3.6.1.1. Effect of reaction molar ratio. The effect of reaction molar ratio in the synthesis of 3, 4-dihydropyrimidin-2(1H)-ones was carried out by varying the ratio of substrate (benzaldehyde: urea: ethyl acetoacetate) from 1:1:1 into 1:1.5:1 into 1:2:1 into 1:2.5:1 using 0.05 g of Cu\textsubscript{50}-Cr\textsubscript{50}–MOF catalyst at 100 °C for 30 min. The results indicate that percentage yield of 3, 4-dihydropyrimidin-2(1H)-ones was increased from 60.2% to 87.2% then decreased again by increasing the urea content to 75.5% and 71.1% with increase the molar ratio 1:1:1.
into 1:1.5:1 into 1:2:1 into 1:2.5:1, respectively as shown in Fig. 8A so, the molar ratio of 1:1.5:1 produce the highest percentage yield which act as the optimum condition for 3, 4-dihydropyrimidin-2(1H)-ones synthesis.

3.6.1.2. Effect of the reaction temperature, reaction time and catalyst weight. The reaction temperature was varied from 80 °C to 120 °C to observe the change in the percentage yield. We found that the percentage yield of product was very little at lower temperature. The highest product yield was observed at 100 °C by using 0.05 g of Cu50-Cr50-MOF catalyst then there was no significant increase in the percentage yield above 100 °C as shown in Fig. 9A so, we choose the temperature 100 °C as the optimum condition for synthesis of the desired dihydropyrimidinones.

The Biginelli reaction has been examined at different intervals of times at 100 °C over Cu50-Cr50-MOF catalyst. The percentage yield of 3, 4-dihydropyrimidin-2(1H)-ones raises with the rise in reaction time from 10 min to 30 min, which reached saturation and there was no significant elevation in the percentage yield of the product after 30 min.

The catalytic activity of Cu50-Cr50-MOF catalyst has been examined by changing the catalyst weight 0.02 into 0.05 into 0.07 into 0.1 using the reactant molar ratio (benzaldehyde: urea: ethyl acetoacetate) of 1:1.5:1 for 30 min. The results reveal that percent yield of the desired dihydropyrimidinones increase from 54.2 to 87.2% then to 89.4 and 90.1 with increas-

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**Fig. 5** – EDS analysis for single and bimetallic MOFs.
Fig. 6 – FT-IR spectra for (A) pure Cr-MIL101, (B) Cu\textsubscript{100}–Cr\textsubscript{50}–MOF, (C) Cu\textsubscript{25}–Cr\textsubscript{75}–MOF, (D) Cu\textsubscript{50}–Cr\textsubscript{50}–MOF, (E) Cu\textsubscript{75}–Cr\textsubscript{25}–MOF, (F) Cu\textsubscript{90}–Cr\textsubscript{10}–MOF and (G) pure Cu-BDC.

Fig. 7 – Potentiometric titration curves of (A) pure Cr-MIL101, (B) Cu\textsubscript{100}–Cr\textsubscript{50}–MOF, (C) Cu\textsubscript{25}–Cr\textsubscript{75}–MOF, (D) Cu\textsubscript{50}–Cr\textsubscript{50}–MOF, (E) Cu\textsubscript{90}–Cr\textsubscript{10}–MOF, (F) pure Cu-BDC catalysts.

ing the catalyst weight from 0.02 into 0.05 into 0.07 into 0.1, respectively. These results reveal that the higher yield was achieved at 0.05 g of catalyst and there was no significant elevation in the percentage yield after 0.05 gram of the catalyst.

3.6.1.3. Effect of catalyst. The catalyst samples were tested to find the most appropriate catalyst for synthesis 3, 4-dihydropyrimidin-2(1H)-ones. The reaction was carried out at 100 °C using the reactant molar ratio (benzaldehyde: urea: ethyl acetoacetate) of 1:1.5:1 for 30 min. The results clearly show that the copper ions in the framework of the MOF enhanced the catalytic activities as shown in Fig. 10A and Table 2. From this figure, we found that the best catalyst was Cu\textsubscript{90}–Cr\textsubscript{50}–MOF for synthesis of 3, 4-dihydropyrimidin-2(1H)-ones which has highest acidity and highest total number of acid sites.

In order to assess the efficiency of catalysts, the obtained results from the reaction of ethyl acetoacetate, urea and benzaldehyde have been compared with those of the previously reported catalysts such as FeCl\textsubscript{3} immobilized in Al-MCM-41 [51], InBr\textsubscript{3} [52], Halogenated Amberlyst-15 resins [53] and ZrOCl\textsubscript{2}/mont K10 [54]. It was found that Cu\textsubscript{x}–Cr\textsubscript{100–x}–MOF catalysts is a fairly good reagent with respect to reaction time, amount of catalyst, reaction temperature and product yield.

3.6.1.4. Reusability of the catalyst. To check the reusability of the catalyst, Cu\textsubscript{90}–Cr\textsubscript{50}–MOF catalyst was separated by simple filtration, washing with ethanol and dimethylformamide and drying in an oven at 120 °C before every reuse in successive reactions. The percentage yield of the product was found between 87% and 80% as shown in Fig. 11A. It was obvious that the activity of the catalyst had no significant decrease even after three runs. The results showed that Cu\textsubscript{90}–Cr\textsubscript{50}–MOF could be reused at least three times without significant decrease in the catalytic activity as proved in the leaching test revealed in Fig. 12.

3.6.2. Synthesis of 14-phenyl-14H-dibenzo [a, j] xanthene Synthesis of 14-phenyl-14H-dibenzo [a, j] xanthene was performed by mixing a stoichiometric amount of β-naphthol (2 mmol) and benzaldehyde (1 mmol) with calculated amount of catalyst under free solvent conditions.

3.6.2.1. Effect of molar ratio. Initially the liquid phase condensation of benzaldehyde and β-naphthol was performed at 120 °C and 90 min using Cu\textsubscript{90}–Cr\textsubscript{50}–MOF with varying ratio of substrate (benzaldehyde: β-naphthol) from 1:1 to 1:4 as shown in Fig. 8B. It was observed that the percentage yield of 14-phenyl-14H-dibenzo [a, j] xanthene increases from 60% to 82%
3.6.2.2. Effect of the reaction temperature and reaction time.

The reaction was applied over Cu_{50}-Cr_{50}-MOF catalyst using reactant molar ratio (benzaldehyde: β-naphthol, 1:2) at 80, 100, 120 and 140 °C. Product yield of the desired xanthenes was raised from 63.7% to 82.4% as reaction temperature varied from 80 °C to 120 °C. At 140 °C, the percentage yield was slightly increased to 83.7% as shown in Fig. 9B. From this figure, we carry out the catalytic reaction at temperature equal 120 °C.

Reaction time was considered over 0.05 gram of Cu_{50}-Cr_{50}-MOF catalyst at 120 °C for 2 h using benzaldehyde: β-naphthol mole ratio 1:2 under solvent free conditions. As predictable, a gradual increase in the percentage yield of 14-phenyl-14H-dibenzo [a, j] xanthene as reaction period increased. Percentage yield of the desired xanthene becomes nearly constant after 90 min and after this time there are no change in the percentage yield. This suggests that the optimum reaction time was 90 min.

3.6.2.3. Effect of catalyst.

The reaction between benzaldehyde and β-naphthol was carried out over different Cu_{x}-Cr_{150-x}-MOF to examine their catalytic activity individually. The reaction was performed at 120 °C using the reactant molar ratio (benzaldehyde: β-naphthol) 1:2 for...
90 min. All the catalysts were compared based on the product yield which have the following order in the activity: Cu_{100-x}-Cr-MOF > Cu_{75}-Cr_{25}-MOF > Cu_{50}-Cr_{50}-MOF > Cu_{25}-Cr_{75}-MOF > Cu_{10}-Cr_{90}-MOF > Cu-BDC > Cr-MIL-101, as shown in Table 2 and Fig. 10B. From this figure, the formation of 14-phenyl-14H-dibenzo[a,j]xanthene increases gradually with increasing the copper content till reaches the maximum (94.1%) in Cu_{90}-Cr_{10}-MOF catalysts. As it clear from Fig. 10B, the prominent efficient catalyst was Cu_{80}-Cr_{10}-MOF for synthesis of the desired xanthene which has highest acidity and highest total number of acid site.

By comparing the results of our work with other literature such as sulfamic acid supported on MIL-101 [33], silica sulfuric acid [34], heteropoly acid supported MCM-41 [35] and boric acid [36]. We found that mixed metal organic frameworks (Cu_{x}-Cr_{100-x}-MOF) act as efficient catalyst with regard to the obtained reaction time and percentage yield.

3.6.2.4. Reusability of the catalyst. Catalyst reusability was carried out using Cu_{50}-Cr_{50}-MOF sample. After performing the reaction over fresh catalyst, the catalyst was separated by simple filtration and washed with toluene to check the complete elimination of any remaining material on the surface and then the catalyst was dried at 120°C for 2 h to reuse in subsequent reactions as shown in Fig. 11B.

4. Conclusions

In summary, we have demonstrated the successful synthesis of Cu_{x}-Cr_{100-x}-MOF through solvothermal method and characterized by numerous techniques. We confirmed that the combination of two metals into the same organic framework led to superior catalytic performance when compared with pure Cr-MIL-101 and Cu-BDC. Structural characterization proved a successful synthesis of bimetallic Cu_{x}-Cr_{100-x}-MOF. XRD patterns of Cu_{x}-Cr_{100-x}-MOF agreed with those of the parent Cu-BDC and Cr-MIL-101, which confirmed that the topology was retained and the results indicate that highly crystalline product was obtained. The decrease in S_BET and pore volume with increase the copper content was due to the replacement of chromium ions by copper cation as a larger atom in the framework of Cu_{x}-Cr_{100-x}-MOF. SEM-EDS shows that the experimental atomic ratio of Cu and Cr elements is very close to the theoretical one of different Cu_{x}-Cr_{100-x}-MOF samples and confirm that the mixed MOFs were successfully synthesized. It was surprising that mixing copper and chromium metal to form various mixed MOFs with different metal content, enhanced the acidic properties and catalytic activity of these MOFs which may be due to the synergetic effect.

Conflicts of interest

The authors have declared no conflicts of interest.

References
