

Cobalt –Metal Organic Frameworks (Co-MOFs) Nanocatalyst: An Efficient Catalyst for the Preparation of 3, 4-Dihydropyrimidinone

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Abstract: Cobalt-metal organic frameworks (Co-MOFs) nanocatalyst was prepared by solvothermal method. Properties of Co-MOFs nanocatalyst were investigated by XRD, FT-IR, and TEM techniques. The surface acidity of the prepared Co-MOF sample was measured by potentiometric titration. The catalytic activity of Co-MOFs nanocatalyst was tested by the Biginelli reaction (3, 4-dihydropyrimidinone). The Co-MOFs nanocatalyst was reused for several times (four times) with good yield from 3, 4-dihydropyrimidinone.

Keywords: Co-MOFs, metal organic frameworks, nanocatalyst, catalytic activity

1. Introduction

MOFs and MILs materials are a well-known class of porous materials^[1]. Among them, Zn-, Cu-, Cr-, Mg-, Fe-MOFs and other MOFs materials contain more than a metal. MOFs and MILs are novel materials with large number of uniformly sized nanoporous (microporous or mesoporous)^[2]. Various uses of MOFs materials have been studied such as separation^[3], catalysis^[4,5], gas adsorption^[6-8], electronic^[9,10], magnetic^[11,12] and optical properties^[13,14]. MOFs as new materials can be designed for several different aspects, such as framework topology, pore size, inner surface properties, surface area, and the number of metals in MOFs. MOFs catalysts have been proposed as selective and active

nanocatalysts for a wide range of chemical reactions. MOFs materials are prepared by using metal salt (chloride, nitrate or acetate) with organic compound as ligand (linker). These catalysts represent a class of porous nanomaterials, in which metal-containing nodes are connected by multi-dentate organic molecules (ligand)^[15,16]. Here, we demonstrated a simple methodology for solvothermal preparation of Co-MOFs nanocatalyst.

2. Materials and Methods

2.1. Materials

Terephthalic acid, dimethylformamide (DMF), cobalt nitrate hexahydrate, triethylamine, ethanol, chloroform, distilled H₂O, dimethyl sulfoxide (DMSO), benzaldehyde, ethyl acetoacetate, urea, n-butylamine, and acetonitrile were purchased from Alfa-Aeser.

2.2. Preparation of Co-MOF Nanocatalyst

Co-MOFs nanocatalyst was synthesized by mixing Co(NO₃)₂·6H₂O with terephthalic acid (1:1 molar ratio M:L) in 40 ml DMF under stirring, adding 2.2 ml of triethylamine dropwise with stirring. The mixture of metal and ligand is stirred for 2 hrs, then transferred into the autoclave at 120°C for 4 hrs. The purple precipitate was formed. The solid Co-MOFs sample was filtered by centrifuges (4000 rpm), washed with DMF, and immersed in 50mL of chloroform for overnight. Finally, the precipitate was filtered and dried at 60°C in vacuum oven for 6 hrs^[17-21].

2.3. Characterization of the Prepared Co-MOFs Nanocatalyst

XRD pattern of the prepared Co-MOFs nanocatalyst was performed using PW 150 (Philips) using Ni-filtered and Cu K α radiation ($\lambda=0.1541\text{nm}$) in the 2θ ranges of 3-70 (wide angle). The X-ray instrument was operated at 45 mA and 40 kV, under room temperature. FT-IR spectra of Co-MOFs nanocatalyst was scanned in potassium bromide (KBr) pellets and recorded with Nicolit Managa-IR 550 spectrometer with a 4 cm⁻¹ resolution, in the range from 400cm⁻¹ to 4000cm⁻¹. TEM images of the prepared Co-MOFs nanocatalyst were carried out by using jeol-jem-2100 TEM operating at 120 KV. The TEM specimen was prepared in an alcohol (isopropanol suspension) and dropped onto a carbon-coated grid and dried at ambient temperature.

3. Results and Discussion

3.1. Surface Acidity (Non-aqueous titration)

Non-aqueous titration was used to investigate the acidity of Co-MOFs surfaces, using an orion 420 digital a model with a double junction electrode. Based on non-aqueous titration, the initial

electrode potential(E_i) indicates to the maximum acid strength of the acid sites. Non-aqueous titration is related to the acidity of solid heterocatalysts as shown in Figure 1, and Table 1. Pizzio et al^[22,23] proposed this method to estimate the number and strength of acid sites on hetero-solid nanocatalysts. According to pizzio, E_i denotes to the strength of acid sites on surfaces of the solid catalyts, where the acidic strength of heterocatalysts a classified as the following^[24, 25]: $E_i < -100$ mV (very weak acidic sites), $-100 < E_i < 0$ mV (weak acidic sites), $0 < E_i < 100$ mV (strong acidic sites), and $E_i > 100$ mV (very strong acidic sites). The potentiometric titration results confirmed that E_i of Co-MOFs nanocatalyst was 141.4 mV (more than 100 mV); this means that Co-MOFs nanocatalyst contains very strong acid sites.

Total acid sites/g= (mequiv/g)*N/1000, where N is the Avogadro's number.

Table 1: Total number of acid sites of Co-MOF catalyst

Samples	E_i (Mv)	No. of acid sites* 10^{-20}
Co-MOF	141.4	2.34

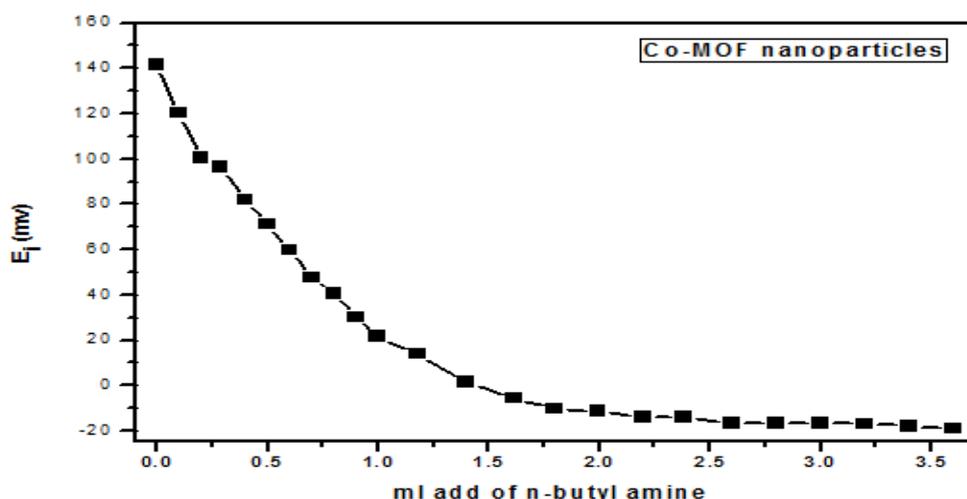


Figure 1. Potentiometric titration curve for Co-MOF nanocatalyst

3.2. XRD of Co-MOFs Nanocatalyst

To investigate the crystal structure of Co-MOFs nanocatalyst, we used XRD pattern. From Figure 2, the results show all the peaks of Co-MOFs nanocatalyst at 2-theta: 9.28, 10.55, 12.57, 15.34, 17.61, 20.19, 21.76, 23.34, 25.45, 27.94, 29.85, 34.35, 36.03 and 33.67, which indicate that the Co-MOFs nanocatalyst was formed with well crystalline^[26-28]. The XRD shows two main peaks at 2 theta-scale = 9.29 and 20.19 which are correspond to the standard pattern^[29]. The crystallite size of the prepared nanocatalyst was 21.6-161.1 nm.

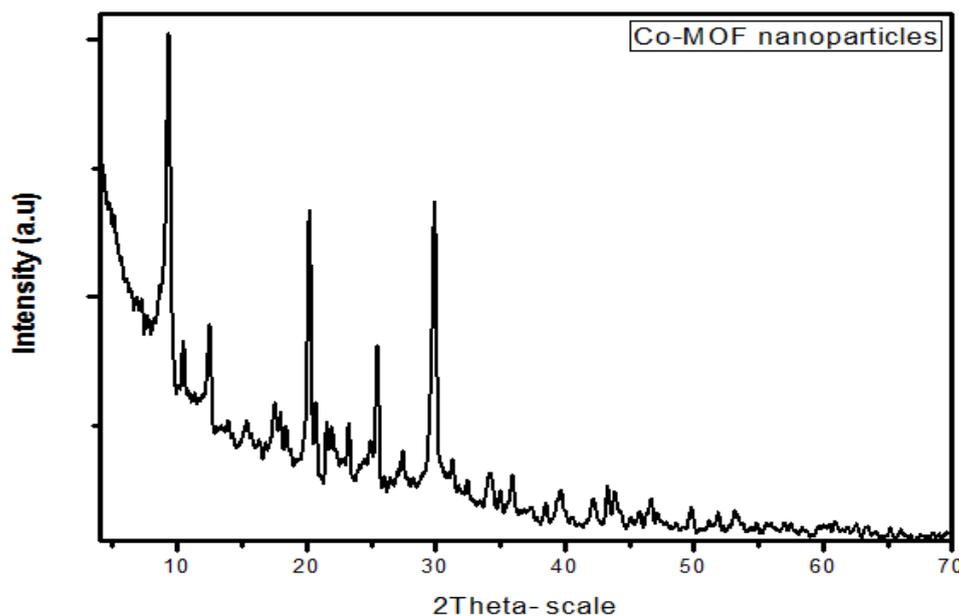


Figure 2. XRD of Co-MOF nanocatalyst

3.3. FT-IR Spectroscopy of Co-MOF Nanocatalyst

The prepared Co-MOFs nanocatalyst was characterized by Fourier-Transform infrared (FT-IR) spectrum, at room temperature which used to confirm the presence of BDC and solvent molecules in this compounds (to confirm formation of the Co-MOFs sample) as in Figure 3. The peaks at (1663 cm^{-1} and 1579 cm^{-1}) and (1478 cm^{-1} and 1384 cm^{-1}) indicate the asymmetric and symmetric of carboxylate groups, respectively^[30-32]. Additionally, the absence of strong absorption band near $1710\text{--}1714\text{ cm}^{-1}$ indicates that all carboxyl groups of the terephthalic ligand are deprotonated^[32-34]. The broad and medium intensity at $3420\text{--}3432\text{ cm}^{-1}$ produced from to the OH stretching vibrations of the coordinated water molecules (presence of bound water or free water in Co-MOF nanocatalyst)^[32,34]. Generally, most of the bands in the region from about $1600\text{--}1605$ to $700\text{--}800\text{ cm}^{-1}$ are due to the stretching of the aromatic ring. The weak bands at $1065\text{--}1083$ and $750\text{--}782\text{ cm}^{-1}$ can be attributed to $\gamma(\text{C-H})$, $\delta(\text{C-H})$ vibration of aromatic rings, respectively^[35]. The band with medium strength at $538\text{--}557\text{ cm}^{-1}$ is due to M-O vibrations, which proves that the metal organic framework indeed has been formed^[36]. The absorptions of the CH_2 groups of the aliphatic chains of triethylamine are observed at $2932\text{--}2981$ and 2811 cm^{-1} which are attributed to the asymmetric and symmetric stretching vibrations and deformation vibrations^[33]. Additionally, the peak appear at $1105\text{--}1111\text{ cm}^{-1}$ is related to the C-O stretching vibration^[33,34].

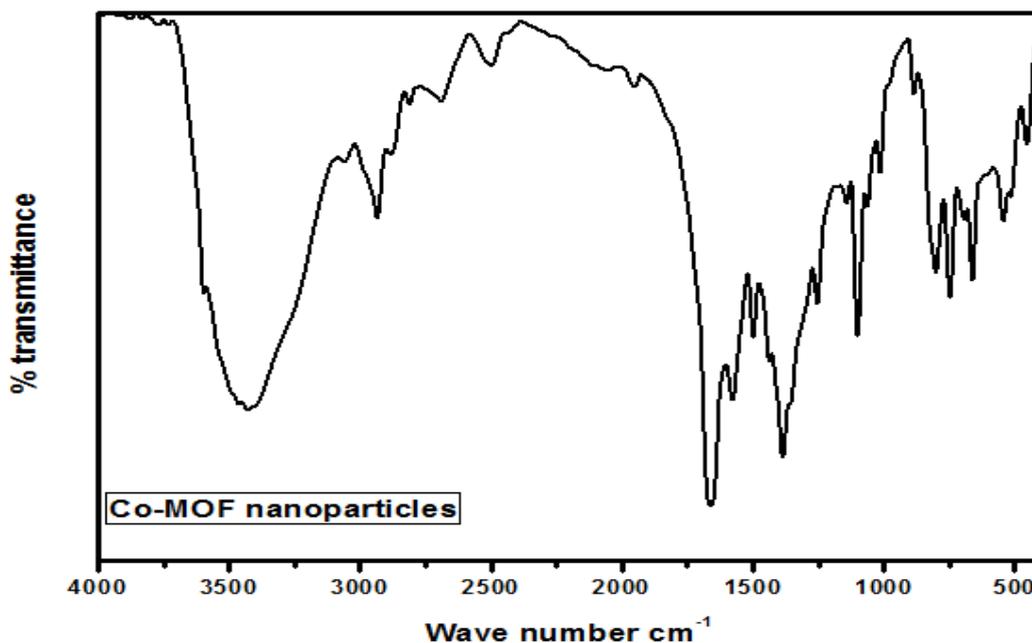


Figure 3. FT-IR of Co-MOF nanocatalyst

3.4. Transmission Electron Microscopy (TEM) of Co-MOFs Nanocatalyst

TEM images of structure of Co-MOFs nanocatalyst is presented in Figure 4. The results show presence of irregular and similar octahedral nanoparticles with crystalline size 28.8-132.7 nm, which prove the formation of Co-MOFs nanoparticles with well crystalline. These results appeared well-defined uniform polyhedron cobalt-metal organic framework nanocrystals, which are in accordance with XRD results. The TEM and XRD results confirm that Co-MOFs nanocatalyst was formed with high degree of crystallinity.

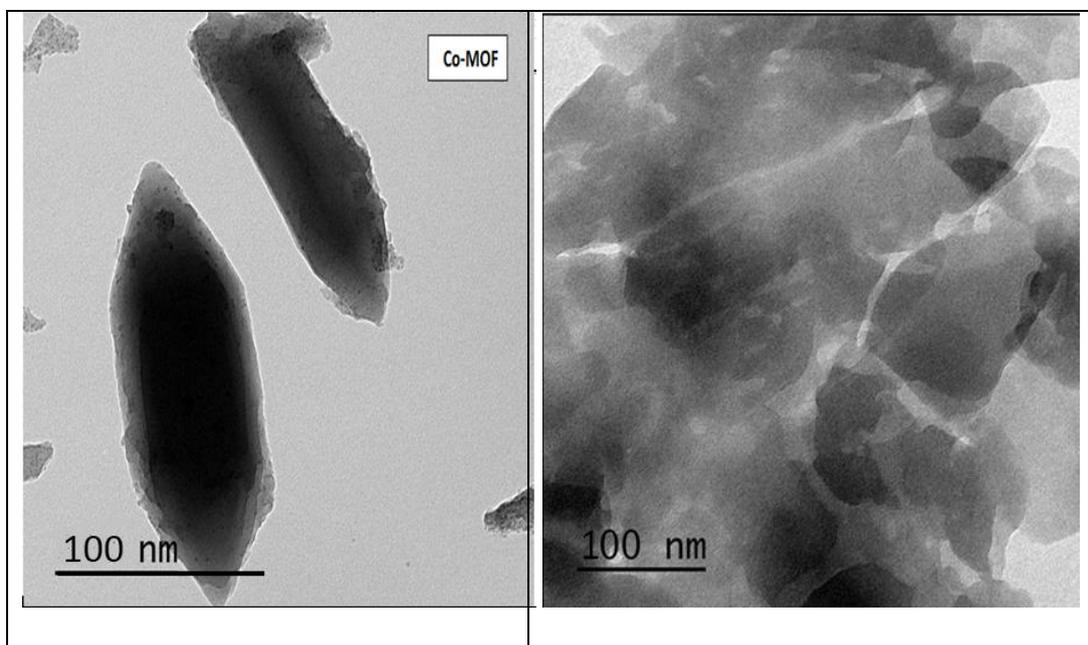


Figure 4. TEM images of Co-MOF nanocatalyst

3.5. Catalytic activity of Co-MOF Nanocatalyst

3.5.1. Catalytic activity for synthesis of 3, 4-dihydropyrimidinone (Biginelli reaction)

3,4-dihydropyrimidinone is known to expose a vast range of biological activities such as antiviral, antibacterial, antitumor, anticancer and anti-inflammatory properties^[37-40]. The Biginelli reaction (3,4-dihydropyrimidinone) needs long reaction time (20-30 hours) and usually suffers from low yield of products^[41,42]. The first study for synthesis of 3,4 dihydropyrimidinone (Biginelli reaction) was in 1893, under strongly acidic conditions which suffer from poor yield of 3,4 dihydropyrimidinone and long reaction time^[37-42], by different catalysts such as LiClO_4 and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ^[43,44]. Recently, Lewis acid catalyzed Biginelli reaction (3,4 dihydropyrimidinone) have been extensively reported in the literature, like ZrCl_4 , CuCl_2 , $\text{Cu}(\text{OTf})_2$, $\text{Bi}(\text{OTf})_3$, ZrOCl_2 , $\text{Mn}(\text{OAc})_3$, FeCl_3 , $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})$, InBr_3 , InCl_3 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, CdCl_2 , $\text{La}(\text{OTf})_3$ and zeolites^[42, 41-59], but these methods led to low and moderate yields of 3,4 dihydropyrimidinone^[37-42]. To overcome these problems, we prepared acid solid Co-MOFs nanocatalyst for synthesis of 3,4 dihydropyrimidinone with relative high yield and short reaction time.

We studied catalytic activity of Co-MOFs nanocatalyst to synthesize 3,4-dihydropyrimidinone at 80°C by using 1:1:2 molar ratio (benzaldehyde: ethyl-acetoacetate: urea in ethanol), in the presence of a catalytic amount of Co-MOFs nanocatalyst (0.03g). The progress of the reaction was monitored by TLC. After finishing the reaction, the Co-MOFs nanocatalyst was filtered off, washed and dried. The combined organic layers were also washed and dried. The solvent was evaporated under reduced pressure and the pure product was obtained without any further purification. Figure 5, shows FT-IR of 3,4-dihydropyrimidinone compound.

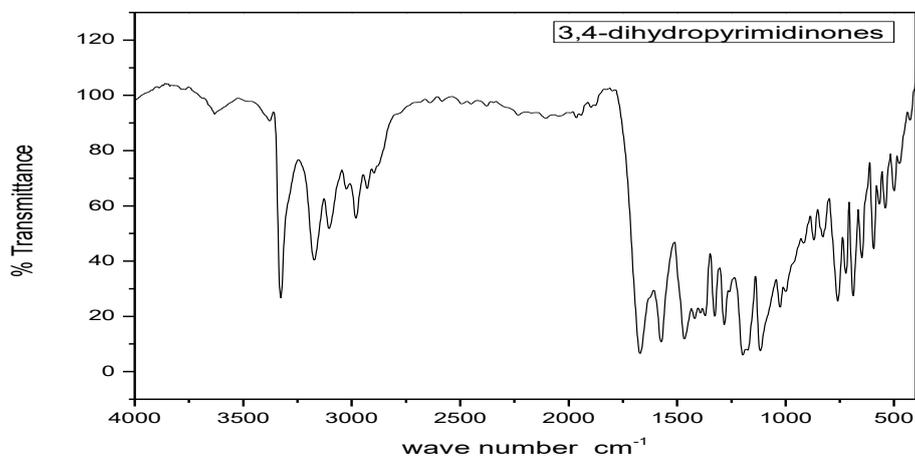


Figure 5. FT-IR analysis of 3,4- dihydropyrimidinone compound

3.5.2. Effect of reaction time on synthesis of 3,4-dihydrobyrimidonene

Effect of reaction time on the 3, 4-dihydropyrimidonene synthesis by Co-MOFs nanocatalyst is given in Figure 6. The reaction was carried out by using 0.03g of Co-MOFs nanocatalyst under other similar conditions. We studied the effect of reaction time duration 5 hrs. The results show that the % yield of 3, 4-dihydropyrimidonene increases with reaction time from 0.5 to 4 hrs, thereafter no notable increase in % yield of 3,4-dihydropyrimidonene. The % yield of 3, 4-dihydropyrimidonene was 23.06, 41.02, 50.89, 58.09, 71.09 and 71.12%, after 0.5, 1, 2, 3, 4 and 5 hrs, respectively. The results indicate that the highest yield of 3, 4-dihydropyrimidonene by Co-MOFs nanocatalyst was 71.09% after 4 hrs.

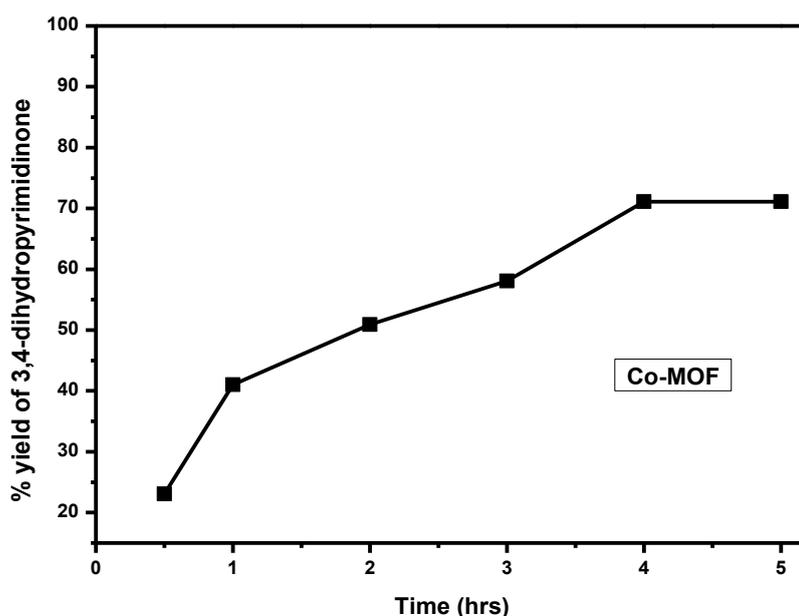


Figure 6. Effect of reaction time on synthesis of 3,4-dihydropyrimidonens by Co-MOF nanocatalyst

3.5.3. Effect of molar-ratio on synthesis of 3, 4-dihydropyrimidinone by Co-MOFs nanocatalyst

The catalytic activity of Co-MOFs nanocatalyst increases with increasing the molar-ratio from 1:1:1, 1:1:1.5 into 1:1:2 (benzaldehyde : ethyl acetoacetate : urea.) and decreases with 1:1:3 molar ratio, where the % yield of 3,4-dihydropyrimidinones was 45.00, 61.09, 71.09, 64.34% with 1:1:1, 1:1:1.5, 1:1:2 and 1:1:3 molar ratio, respectively. Figure 7, shows that 1:1:2 molar ratio gives the highest % yield of 3, 4-dihydropyrimidinone compound. The decrease in the catalytic activity of Co-MOFs nanocatalyst at molar ratio 1:1:3 may be explained on the basis that the increasing of the amount of urea hinders the chemical reaction by blocking the acidic sites on Co-MOFs nanocatalyst, as a result of saturating of the active sites on surface of Co-MOFs nanocatalyst with urea molecules.

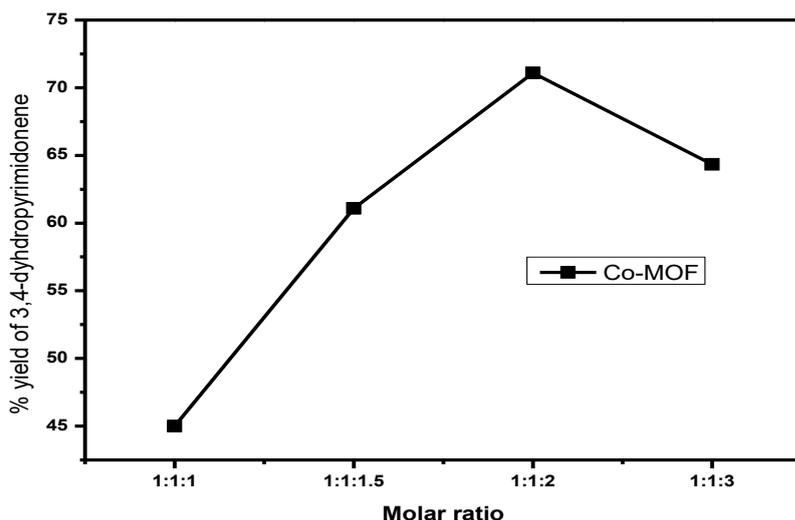


Figure 7. Effect of molar ratio on the formation of 3,4-dihydropyrimidinone

3.5.4. Effect of reusability (recyclability) study of Co-MOFs catalyst

We also studied, reusability of the prepared Co-MOFs nanocatalyst with keeping the reactant molar ratio of benzaldehyde: ethylacetoacetate: urea 1:1:2, for several time (four times) by 0.03 g of Co-MOF nanocatalyst. Results of reusing of weight of Co-MOFs nanocatalyst are shown in Figure 8. The results indicate that the catalytic activity of Co-MOFs nanocatalyst slightly decreases with increasing the number of reusing, where % yield of 3,4-dihydropyrimidinone was 71.09, 50.12, 45.023, and 32.87% for one, two, three and four times, respectively, maybe due to the gradual loss of the weight of Co-MOFs nanocatalyst during filtration and washing, for four consecutive times, where the Co-MOFs nanocatalyst weight decreased about 30%.

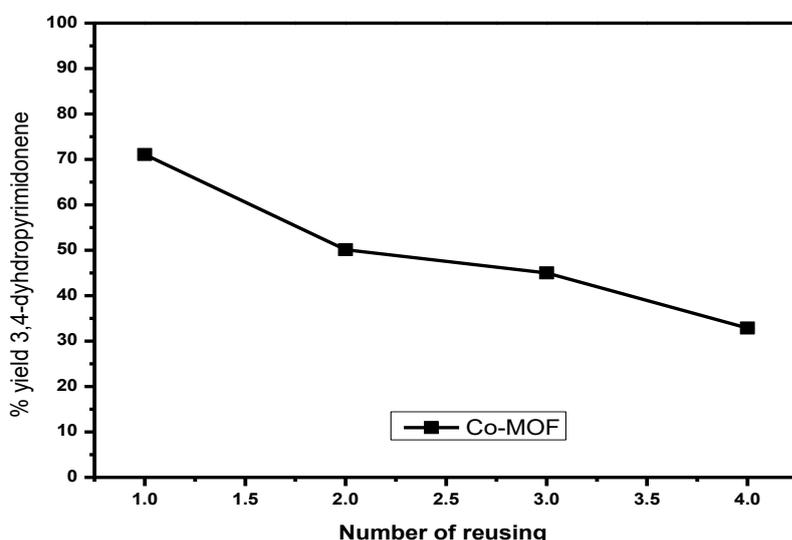


Figure 8. Effect of recyclability study of Co-MOF nanocatalyst

3.5.5. Effect of weight of Co-MOFs nanocatalyst

We used different weights 0.01, 0.03, 0.05, and 0.07g from Co-MOFs nanocatalyst to study effect of the catalyst weight on formation of 3,4-dihydropyrimidinone compound. Figure 9, shows that the catalytic activity of Co-MOFs nanocatalyst increases with increase of the weight of Co-MOFs nanocatalyst, where the % yield of 3,4-dihydropyrimidinone was 43.09, 71.09, 72.12, and 75.92%, for 0.01, 0.03, 0.05 and 0.07g of Co-MOFs nanocatalyst, respectively. The increase in the weight of the Co-MOFs nanocatalyst, leads to increase of the surface area and active sites, so the catalytic activity of Co-MOF nanocatalyst increases.

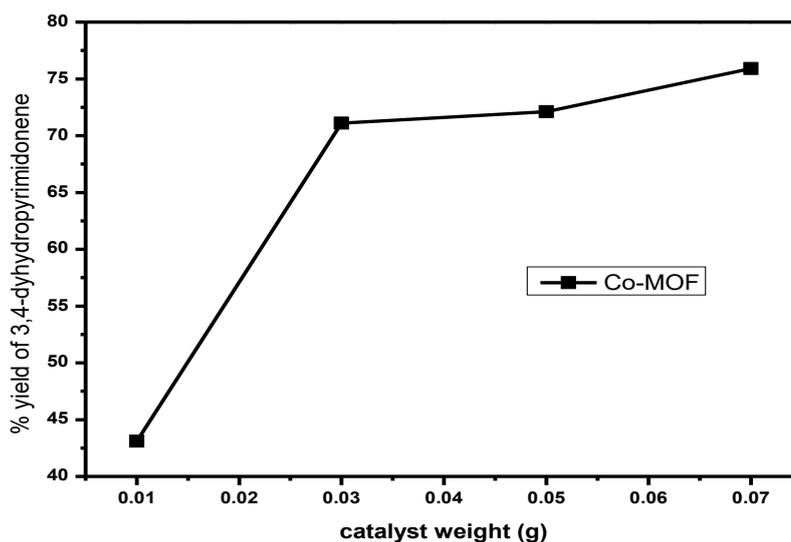


Figure 9. Effect of weight of Co-MOF nanocatalyst

4. Conclusion

Co-MOFs nanocatalyst was prepared by solvothermal method. The XRD, TEM, and FT-IR results proved that Co-MOFs nanocatalyst was formed with well crystalline (the crystallite size was 21.6-161.1). The non-aqueous titration showed that Co-MOFs nanocatalyst has high acidity with very strong acid sites. The catalytic activity of Co-MOFs nanocatalyst was tested by the Biginelli reaction and was relatively high. The optimum conditions have been found that the molar ratio is 1:1:2 (benzaldehyde: ethyl acetoacetate: urea) and reaction time is 4 hrs.

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