



Synthesis, characterization and Catalytic activities of sulfuric acid loaded on Copper metal organic frameworks (Cu-BDC)

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Abstract

A series of sulfate loaded on Cu-BDC ($\text{SO}_4^{2-}/\text{Cu-BDC}$) catalysts with different sulfate content (15-85 wt. %) of SO_4^{2-} were prepared by wet impregnation technique in aqueous solution for one day. The total surface acidity was measured by non-aqueous titration of n-butyl amine in acetonitrile. While both Brønsted and Lewis acid sites were determined by FT-IR spectrum of pyridine adsorbed on the catalysts. FT-IR spectrum of pyridine adsorbed on the catalysts showed the presence of both Brønsted and Lewis acid sites that increased with increasing sulfate content. The strong acidic character of prepared samples was examined by using them as catalysts for the synthesis of 7-hydroxy-4-methyl coumarin via solvent free pechmann reaction condensation. The catalytic activity well associated with Brønsted acid sites of these catalysts. The catalyst was reused for three times with excellent yield from 7-hydroxy-4-methyl coumarin.

Keywords: sulfuric acid, Cu-BDC, impregnation, surface acidity, coumarin.

Introduction

Much interest has been devoted to studies of sulfate groups loaded on mesoporous silica (S-Cu-BDC) as a super acid due to its significant catalytic activity in many reactions, such as estrification, isomerization, alkylation, acylation and etherification. Replacement of homogeneous liquid acids by heterogeneous solid super acids as catalysts in the chemical industry is expected to bring about an ease of separation from the reaction mixture, which allows continuous operation, as well as regeneration and reutilization of the catalyst. Furthermore, the heterogeneous solid catalysts can offer other advantages, such as no corrosion of the reaction and no environmental problem for disposal of used catalyst (1,2)

It has been shown that the catalytic activity of sulfated copper metal organic frameworks is largely due to its acid properties. Some authors have reported that the catalyst contains both Brønsted and Lewis acid sites which are responsible for this activity such as hydrogenation (3), estrification (4, 5), as well as epoxidations reactions (6). The absence of functional groups and selective sites in most

stable metal organic frameworks led to the weakness of the use of MOFs in applications such as catalysis. In the ability to functionalize MOFs with various active sites including heteropoly acids, mineral acids, or metal nanoparticles have been loaded into different MOFs through different methods (7-11)

Coumarin and its derivatives are one of the most important compounds of natural products due to its usage as anticoagulants (12), additives in food and cosmetics (13), and in the preparation of insecticides, optical brighteners (14), and dispersed fluorescent and laser dyes (15). Coumarin has been synthesized by several methods including the von Pechmann reactions (16) Conventionally, the Pechmann reaction is carried out in presence of concentrated sulfuric acid catalyst (17-18) phosphorous pentoxide (19) and trifluoroacetic acid (20). These acids are corrosive and required in excess amount. To avoid such problems, there have been efforts to find environmentally benign alternative and heterogeneously catalyzed synthetic routes. This can be achieved by the development of

solid acid catalysts that are stable, regenerable and active at moderate temperatures.

In the present work, sulfate loaded on Cu-BDC ($\text{SO}_4^{2-}/\text{Cu-BDC}$) prepared firstly by hydrothermal method then modified by SO_4^{2-} introduced in Cu-BDC by impregnation technique in aqueous solution for one day. The effect of sulfate contents on the surface acidity of $\text{SO}_4^{2-}/\text{Cu-BDC}$ catalysts will be characterized by potentiometric titration of n-butylamine in acetonitrile and by pyridine adsorption. The catalytic activity of the resultant sulfated Cu-BDC composite was studied by carrying out resorcinol and ethyl acetoacetate in free pechmann condensation reaction, which give high yield from 7-hydroxy-4-methyl coumarin.

1. Experimental

1.1 synthesis of the catalyst

1.1.1 Synthesis of Cu-BDC

Cu-BDC was prepared through hydrothermal methods. A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.053 mg), 1,4-benzene dicarboxylic acid (TPA) (740 mg) and DMF (87 mL) were sonicated until a suspension of blue-colored was formed, Then the suspension was transferred into a teflon-lined autoclave bomb and placed in an oven for 36 hr. at 110°C . After cooling, the suspension was centrifuged to isolate the blue powder of Cu-BDC and the resulting product was soaked in N, N-dimethylformamide for one day to remove unreacted terephthalic acid encapsulated inside the pores and the solid product washed with DMF and hot ethanol, filtered off and finally dried in an oven at 150°C for 5 h ⁽²¹⁾

1.1.2 Synthesis of Sulphate loaded on Cu-BDC: -

$\text{SO}_4^{2-}/\text{Cu-BDC}$ ($\text{SO}_4^{2-}\text{-Cu-BDC}$) were prepared by direct impregnation of the as-synthesized Cu-BDC with the desired amount of sulfuric acid (1M) and left for one day. After that the product was filtered, washed, dried at 80°C over night.

1.2 Surface Acidity Measurement

1.2.1 Potentiometric Titration

The total acidity of the solid samples was measured by non-aqueous Potentiometric titration ⁽²²⁻²³⁾. The activated catalyst (0.1 g) was suspended in 10 ml acetonitrile. Then, the suspension was titrated with 0.01N n-butyl

amine in acetonitrile. The electrode potential variation was measured with an Orion 420 digital model using a double junction electrode.

1.2.2 Pyridine adsorption

Lewis and Brønsted acid sites presented on the surface were determined with FT-IR spectra of adsorbed pyridine. The samples were placed under high vacuum oven with 100 ml beaker containing pyridine for one week, after that the samples were conducted using FT-IR spectrophotometer; by mixing 0.02 g of the sample with 0.1 g KBr in 30 mm diameter self supporting discs were used.

1.3 catalytic activity

The synthesis of 7-hydroxy-4-methyl coumarin was carried out by using a mixture of resorcinol (1.1g, 10 mmol) and ethyl acetoacetate (2.5ml, 20 mmol) in 50 ml round flask and refluxed in oil bath for 2 hrs at 120°C in the presence of 0.1g catalyst. The resultant mixture was filtered and pouring into 50 ml beaker containing crushed ice. The product was characterized by melting point ($185\text{-}186^\circ\text{C}$) and IR spectroscopy. The yield of coumarin derivatives was obtained as follow:

Yield (Wt%)

$$= \frac{\text{obtained weight of product}}{\text{theoretical weight of product}} \times 100$$

2. Results and discussion

2.1 Surface acidity measurements

2.1.1 Non-aqueous titration

Non-aqueous titration technique was used to investigate the surface acidity characters including the acidic strength and the total number of acid sites. According to this technique the initial electrode potential (E_i) be taken as the acid strength of the surface sites and the range where the plateau is reached indicate the total number of acid sites. Non aqueous titration carried out by n-butyl amine ($\text{pK}_a = 10.73$), which is a basic molecule suitable for titrating the medium and strong acid sites on the surface of the catalyst ⁽²⁴⁻²⁵⁾ The value for the electrode potential in this method is related to the surface acidity of the catalyst as shown in Fig. 1.

From table 1 and Fig. 2, the total acidity of $\text{SO}_4^{2-}/\text{Cu-BDC}$ catalysts increases with the rise of sulfate content to reaches maximum at 50 wt. % SO_4^{2-} . The increase in surface acidity may be due to strong interaction between sulfate and Cu-BDC surface ^(26, 27). As the

coverage of Cu-BDC surface increases by sulfate, the number and strength of acid sites will increase. The sample with content more than 50 wt% above surface saturation coverage

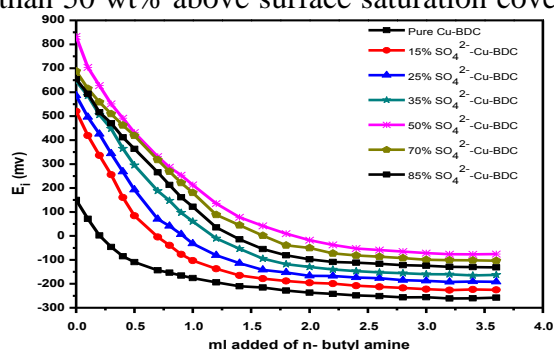


Fig. 1: Potentiometric titration of n-butylamine in acetonitrile for (a) Pure Cu-BDC, (b) 15%, (c) 25%, (d) 35%, (e) 50%, (f) 70% and (g) 85% SO_4^{2-} /Cu-BDC.

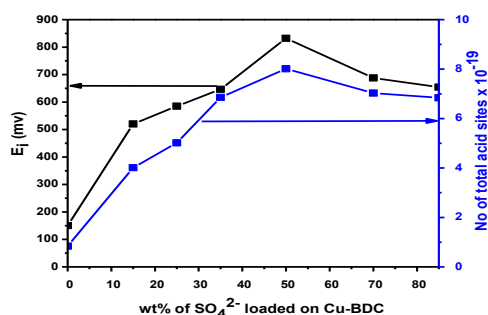


Fig. 2: Effect of weight % of sulfate of SO_4^{2-} /Cu-BDC on initial potential and total number of acid sites.

2.1.2 FT-IR pyridine adsorption

Adsorption of pyridine as a base on the surface of solid acids is one of the most frequently applied methods for characterization of surface acidity to investigate both Brønsted and Lewis acid sites. FT-IR pyridine adsorption spectra in region $1400 - 1700 \text{ cm}^{-1}$ of catalyst with different sulfate content are shown in Fig. 3. All the samples show typical bands of adsorbed pyridine at around 1449 cm^{-1} and 1600 cm^{-1} on Lewis acid sites and 1535 cm^{-1} , 1632 cm^{-1} on Brønsted acid sites, in addition, the band at 1492 cm^{-1} indicates the formation of the adjacent Lewis and Brønsted acid sites together (28). The percentage of Lewis-Brønsted acid sites can be calculated by using the integrated areas or the relative intensity of the characteristic bands of pyridine adsorbed on Lewis and/or Brønsted acid sites. In this study the percentage of Lewis and Brønsted acid sites

shows loss of acidity and acid strength probably due to agglomeration of sulfate on the surface.

were calculated by the following equations (29, 30).

$$\% \text{Bronsted} = \frac{A_B}{A_B + A_L} \times 100 \quad \&$$

$$\% \text{Lewis} = \frac{A_L}{A_B + A_L} \times 100$$

Where A_B is the integrated area of the peak at 1535 cm^{-1} , 1632 cm^{-1} , attributed to the pyridinium cation adsorbed on the Brønsted acid site and A_L is the intensity at 1444 cm^{-1} or 1606 cm^{-1} of the pyridine molecule coordinated to the Lewis acid site.

It was found that with the increase in sulfate content, the number of Lewis acid sites increased, but also induced a large amount of strong Brønsted acidic sites on the surface of Cu-BDC. The acidity of both Brønsted and Lewis were increased reached a maximum at 50 wt. % SO_4^{2-} / Cu-BDC. The increase in Lewis acidity by sulfate may be due to the presence of surface sulfur complex which has a covalent S=O bond, that act as electron-withdrawing species followed by the inductive effect. Thus, the inductive effect of S=O makes the Lewis acid strength of copper stronger (31).

The Brønsted acid sites, Lewis acid sites and Brønsted/Lewis acid sites ratio were shown in Table 1, which indicates that Brønsted and Lewis acid sites increased with the increase of the inserted amount of sulfate up to 50 wt. % then decreased.

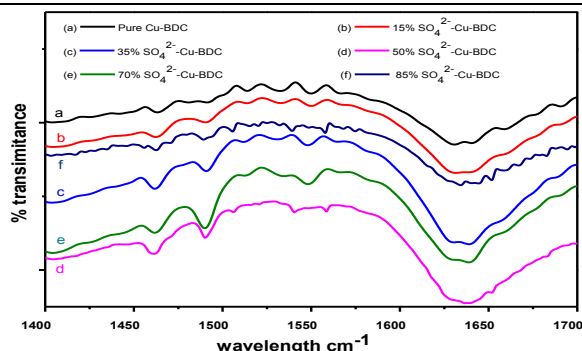


Fig. 3: Pyridine adsorbed FT-IR spectra of (a) Pure Cu-BDC, (b) 15%, (c) 35%, (d) 50%, (e) 70% and (f) 85% $\text{SO}_4^{2-}/\text{Cu-BDC}$.

Table 1: Effect of sulfate content on the acidic properties and catalytic activity of $\text{SO}_4^{2-}/\text{Cu-BDC}$ catalysts.

Samples	E_i (mv)	No. of acid sites/g $\times 10^{-19}$	B/L	Coumarin yield
Pure Cu-BDC	150.1	0.8424	0.3124	Traces
15 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$	520.1	4.0124	2.4737	57.5
25 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$	585.2	5.0142	---	69.4
35 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$	646.5	6.8541	2.7616	88.2
50 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$	832.1	8.0136	3.0202	96.8
70 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$	687.6	7.0324	2.8401	89.2
85 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$	654.2	6.8412	2.6124	85.2

2.2 catalytic activity (synthesis of 7-hydroxy-4-methyl coumarin)

Condensation reaction between resorcinol and ethyl acetoacetate (EAA) was carried out using 0.1g of SO_4^{2-} supported catalyst (2% - 45%) for synthesis of 7-hydroxy-4-methyl coumarin. A background reaction was examined in absence of SO_4^{2-} and no product was observed. Here we have successfully used solid acid catalysts as alternative to conventional methods for synthesis of 7-hydroxy-4-methyl coumarin, which characterized by its melting point (m.p = 185°C).

2.2.1 Effect of molar ratio

Generally, Pechmann condensation of resorcinol and EAA for synthesis 7-hydroxy-4-methyl coumarin was performed at 120°C for 2hrs using 50 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$ with varying ratio of substrate (resorcinol : EAA) as shown in Fig. 4. This graph show that, within the increase in molar ratio of resorcinol: ethyl acetoacetate from 1:1 to 1:2, the percentage yield increased from 75.7% to 96.8% with 100% selectivity, respectively. A further increase in molar ratio to 1:3, the percentage yield of 7-hydroxy-4-methyl coumarin decreased to 69.2%. From these results, the

molar ratio 1:2 was found to be optimum for solvent free synthesis of 7-hydroxy-4-methyl coumarin. The decrease in catalytic activity may be explained on the basis of the fact that the increase in the ethyl acetoacetate concentration hinders the reaction by blocking the active sites on the catalyst surface (32, 33).

2.2.2 Effect of weight percentage of sulfate on catalytic activity

In Table 1 and Fig. 5, the percentage yield of 7-hydroxy-4-methyl coumarin increases gradually with increasing the amount of sulfate loaded on Cu-BDC till reach the maximum at 50 wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$ then decreased again. This is due to the surface acidity of sulfate increase both the intensity and number of acid sites "Brønsted acid sites". This results show that the catalytic activity and Brønsted to Lewis acid sites ratio increases with increase in SO_4^{2-} loading up to 50 Wt. % $\text{SO}_4^{2-}/\text{Cu-BDC}$, then decrease with further increase in SO_4^{2-} content as shown in Fig. 6.

Several studies have been carried out to study the effect of solid acid catalysts on coumarin synthesis, however, with different observations. For example, Ahmed *et al.* (34) have reported the yield of the same derivative using $\text{H}_3\text{PW}_{12}\text{O}_{40}$ supported on nanoparticles tin oxide (78%) and Romanelli *et al.* (35) also found similar yield of the same derivative using heteropoly acid catalyst (87%). From these studies, it seems that the efficiency of the catalyst may be depend upon the amount and the strength of the acid sites on the catalysts used and seems to be responsible for the variation in the yield of 7-hydroxy 4-methyl coumarin

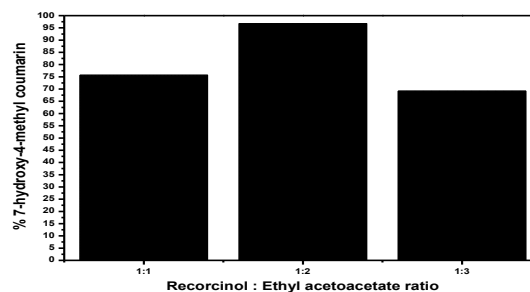


Fig. 4: Effect of molar ratio on the yield % 7-hydroxy-4-methylcoumarin over 50% $\text{SO}_4^{2-}/\text{Cu-BDC}$ catalyst.

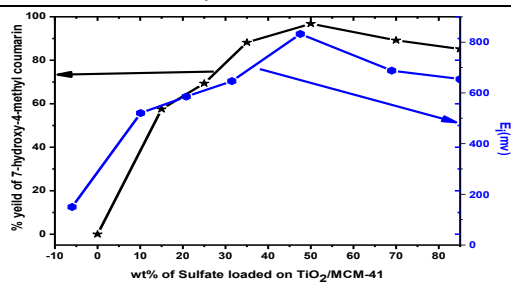


Fig. 5: Effect of sulfate content (wt %) on acid strength (E_i) and yield % of 7-hydroxy-4-methyl coumarin.

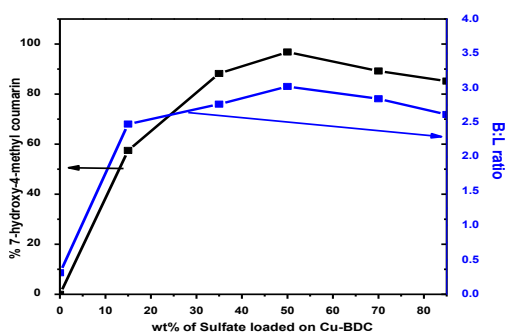


Fig. 6: Effect of sulfate content (wt %) on (B/L) ratio and yield % of 7-hydroxy-4-methyl coumarin.

2.2.3 Reusability of catalyst

Reusability of the catalyst is an important aspect of any industrial process. For this purpose, reusability of the catalyst 50 wt. %SO₄²⁻/Cu-BDC is tested by carrying out repeated runs of the reaction at 120°C, keeping the reactants molar ratio (resorcinol: ethyl acetoacetate) at 1:2. In order to regenerate the catalyst after each 4h reaction, it was separated by filtration, washed with distilled water several times, dried for 2 h. Fig. 11 shows the excellent reusability with little activity loss from the fresh run, which may be due to the decrease in SO₄²⁻ content in solid acid catalyst as a partial leaching of the SO₄²⁻.

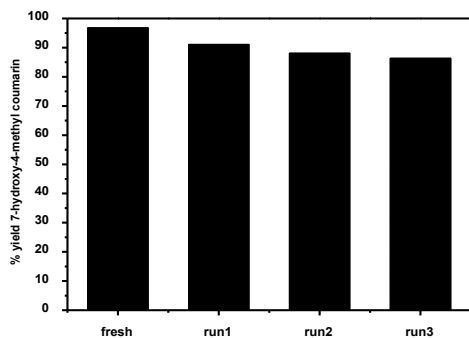


Fig. 11: Effect of reuse of the 50 wt. %SO₄²⁻/Cu-BDC catalyst on Yield% of 7-hydroxy-4-methyl coumarin.

3. Conclusions

The results presented in this work provided a detailed description of the changes in the acidic features of sulfate modified Copper metal organic frameworks (Cu-BDC), which was characterized by Potentiometric titration with n-butyl amine and FTIR of adsorbed pyridine. The acidity of catalysts increases with the increase in sulfate content up to 50 wt. %SO₄²⁻/Cu-BDC. The correlation between catalytic activity and surface acidity holds for synthesis of 7-hydroxy-4-methyl coumarin. The optimum conditions have been found, that the molar ratio of resorcinol: ethyl acetoacetate is 1:2, temperature 120°C and reaction time is 2 hrs. Catalyst activity indicates that the activity for synthesis of 7-hydroxy-4-methyl coumarin is related to the availability of Brønsted acid sites which in turn depends of the SO₄²⁻ content, which means we can use these catalysts in green chemistry.

4. References

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