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Research Article

Melamine-terephthalaldehyde supported Copper tetrabenzenecarboxylic acid As An Efficient Heterogeneous Acidic Catalyst (COF-MOF) for the One-pot Preparation of 1,8-Dioxooctahydroxanthenes

Zahra Baymaninezhad[1], Haman Tavakkoli[1*], Seyyed Jafar Saghanezhad[2], Elham Tahanpesar[1]

[1]Department of Chemistry, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran.
[2]ACECR-Production Technology Research Institute, Ahvaz, Iran.

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✉: H. Tavakkoli
htavakkoli59@gmail.com

ABSTRACT

In this research article, we report the preparation of from melamine-terephthalaldehyde supported Copper-1,2,4,5-tetrabenzenecarboxylic acid (COF-MOF) as a porous acidic catalyst for the one-pot preparation of 1,8-Dioxooctahydroxanthenes. As a new methodology, this strategy offers several advantages including green reaction conditions, high yield of the products, short reaction time, facile work-up, and recyclability of the catalyst.

Keywords: Nanoporous, Melamine; Terephthalaldehyde; Copper; 1,2,4,5-tetrabenzenecarboxylic acid.

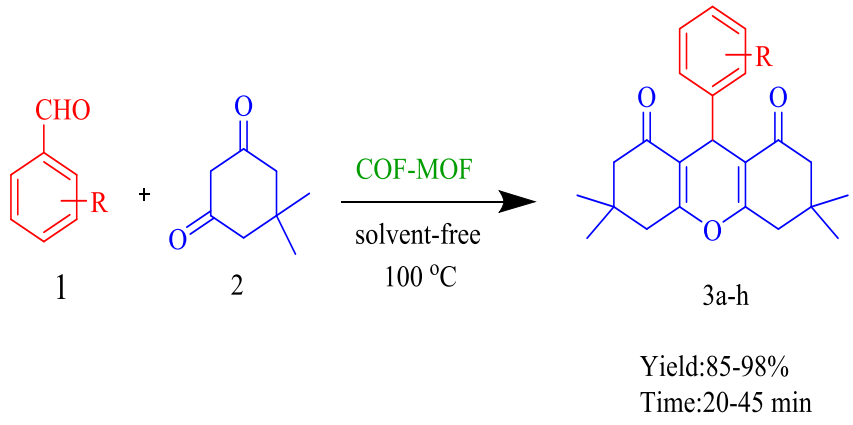
1. Introduction

Covalent organic frameworks (COFs) have been utilized as novel catalysts in various reactions. Quite recently, the synergistic effect of combining the covalent organic frameworks and metal-organic frameworks (MOF) have been explored. In this case, selection of various structures of both MOF and COF lead to novel hybrid materials with multiple diversity in structure and properties [1-5].

Multi-Component Reactions (MCR) are one-pot reactions in which the product is prepared with simple mixing of starting materials. By applying MCR methodology, several heterocyclic compounds have been prepared recently [6, 7].

On the other hand, Xanthenes, are an important group of biologically active heterocycles and have attracted special attention due to their many roles such as application in the paint industry, laser technology, and therapeutic and biological properties. Therefore, the development of easy synthesis methods for the preparation of these heterocycles is of great importance. Numerous methods have been reported for the synthesis of 1,8-dioxo-octahydroxanthenes which involves the one-pot condensation of aldehydes and dimedone in the presence of chloride[8] [nPr_2NH_2][HSO_4][9] Sc^{3+}-mont-morillonite[10] sulfonated starch nanoparticles[11] tetrapropylammonium bromide (TPAB) [12].

In this regard, along with our previous effort to prepare novel catalysts for organic reactions [13-18], herein we report COF-MOF as a novel efficient porous catalyst for the one-pot preparation of 2-Aryl Substituted 2,3-Dihydroquinazoline-4(1H)-one derivatives and 2,3-diphenyl-2,3-dihydroquinazolin-4(1H)-one derivatives via the three-component reaction of isatoic anhydride, aromatic aldehydes and aniline/ammonium acetate under solvent-free conditions.



Scheme 1. One-pot preparation of 1,8-dioxooctahydroxanthenes (3a-h) in the presence of COF-MOF under solvent-free conditions via the condensation reaction of aromatic aldehydes (1) and dimedone (2).

2. Experimental

General

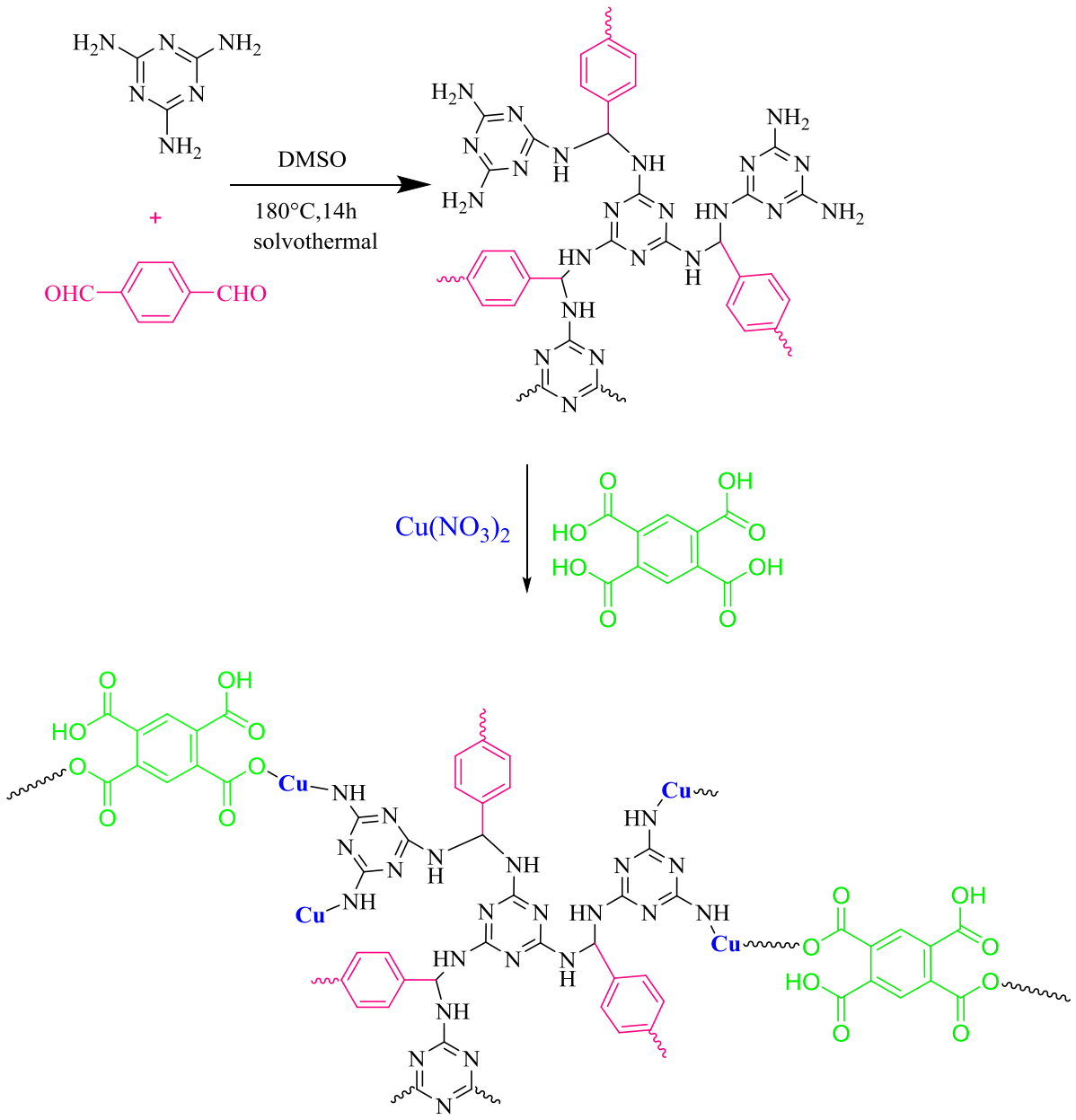
Chemicals were purchased from Merck and Fluka Chemical Companies Merck and used without further purification. The catalyst (COF-MOF) was prepared according to our previous report [19].

General procedure for synthesis of 1,8-Dioxooctahydroxanthenes catalyzed by COF-MOF under solvent free conditions

A mixture of various aldehydes (1 mmol), dimedone (2 mmol) in the presence of COF-MOF (0.02 g) as an acid catalyst in a solvent-free test tube on an oil bath at 100 °C for It was mixed well(in Table2). Reaction progress was evaluated with TLC. After completion of the reaction as observed by TLC, hot ethanol was added to the reaction mixture and the heterogeneous catalyst was filtered, then the product was crystallized with ethanol and water with a yield of 85 to 98% (Scheme 1).

3. Results and discussion

COF-MOF was easily prepared in two steps, by reaction of melamine (MA) with terephthalaldehyde (TA) and subsequent addition of copper (II) nitrate and 1,2,4,5-tetrabenzenecarboxylic acid and refluxing the mixture (Scheme 2).



Scheme 2. Synthesis of COF-MOF

In order to evaluate the activity of this catalyst in the one-pot preparation of 1,8-Dioxooctahydroxanthenes, the reaction of benzaldehyde (1 mmol), dimedone (2 mmol) and different amounts of the catalyst at different temperatures was assessed. It was surprising that the reaction conducted very easily under solvent-free conditions with the molar ratio of 1 mmol of benzaldehyde, 2 mmol of dimedone and 0.02 g of COF-MOF (Table 1).

Table 1: Optimization of conditions for the condensation reaction of benzaldehyde (1 mmol), Dimedone (2 mmol) under solvent-free conditions

Entry	MOF-COF (g)	Temperature (°C)	Time (min)	Yield (%)
1	-	80	60	-
2	0.005	80	60	65
3	0.01	90	30	75
4	0.02	90	25	82
5	0.02	100	25	98

Table 2. Synthesis of Substituted 1,8-dioxo-octahydro-xanthenes catalyzed by COF-MOF under solvent-free conditions

Entry	**R**	**Time (min)**	**Yeild (%)**
1	H	25	98
2	4-Me	30	95
3	4-OH	45	85
4	2-Cl	35	96
5	4-Br	20	95
6	4-CN	25	91
7	3-Me	40	94
8	4-Cl	20	93

After successful preparation of the target product, it was decided that a library of these products be prepared. Fortunately, the products were prepared in short reaction time and high yield (Table 2).

To verify the preparation of the stated products, the structure of 4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)benzonitrile was confirmed via ^{1}HNMR and ^{13}CNMR spectroscopy (Figs 1 and 2).

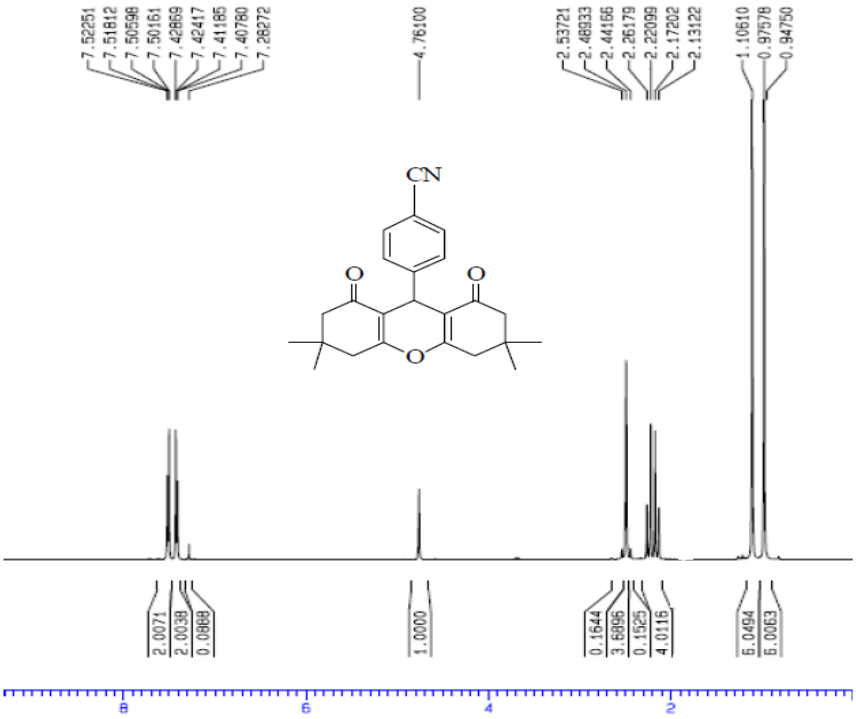


Fig. 1. [1]HNMR of 4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)benzonitrile

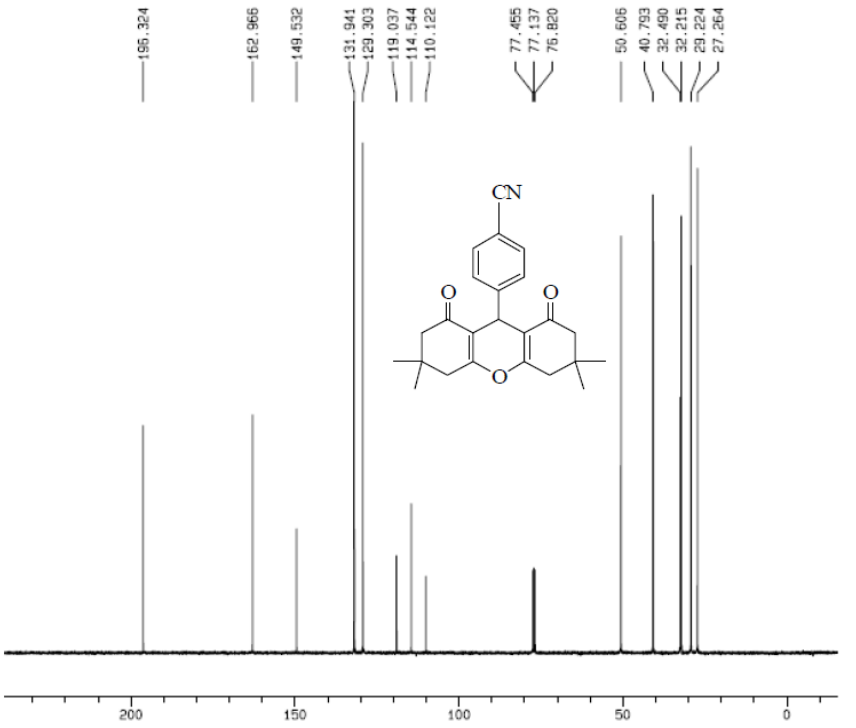


Fig. 2. [13]CNMR of 4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl)benzonitrile

The reusability of the catalyst was also evaluated in accordance with green chemistry principles. After preparation of the product, the catalyst was recycled and reused for five other cycles. The results showed the great potential of the catalyst with slight decrease in its activity.

Conclusion

In conclusion, we have utilized a new porous catalyst (COF-MOF) for the one-pot preparation of 1,8-Dioxooctahydroxanthene derivatives. This methodology offers several advantages including solvent-free and eco-friendly conditions high yield of the products, short reaction time, simple work-up procedure, and ease of recyclability of the catalyst. Accordingly, this catalyst can be considered as an efficient catalyst for other multi-component reactions or organic transformations.

Acknowledgements

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