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Preparation of New and Efficient Sandwich Polyoxometalate Nanocatalyst for the One-Pot Synthesis of 4*H*-Pyran Derivatives †

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Abstract

In this research, a sandwich-type polyoxometalate (Cu) was conveniently prepared and characterized by different methods. Characterization of the obtained nanomaterial was performed using Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS) and elemental mapping as well as X-ray diffraction analysis (XRD) methods. This nanomaterial can effectively facilitate the synthesis of 4*H*-pyran derivatives, as a heterogeneous nanocatalyst, in a one-pot reaction through multi-component reactions (MCRs) strategy. This heteropolyonion-based nanocatalyst possessed suitable acidic and basic active sites, enabling it to serve as a multifunctional catalyst. The $Cu_6W_{18}O_{70}$ nanocatalyst demonstrated high product yields and short reaction times. Furthermore, the heterogeneous catalyst exhibited remarkable reusability, maintaining its catalytic activity for at least five cycles without significant loss of its efficiency.

Keywords: Polyoxometalate; 4*H*-Pyran; One-Pot synthesis; MCRs; Heterogeneous catalyst; Nanocatalyst

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1. Introduction

Cluster science to grow rapidly, with metal clusters garnering attention due to their unique properties and structures. At present, numerous reports have detailed the synthesis of metallic nanoclusters (NCs) with single-crystal structure and metal-metal bond types, further assisting the understanding of the formation mechanism, as well as the possible catalytic and optical behaviors. These clusters have some particular metal atoms in a metallic core surrounded by the ligands that stabilize them and avoid, during their synthesis, any possible excessive aggregation impinging directly on the cluster size, structures, and chemical/physical properties [1,2].

Recent studies on Cu-based clusters indicate promising applications. For example, a scalable synthesis method for stable Cu cluster catalysts has shown high selectivity in hydrogenation reactions [3]. on the other research, Cu clusters confined in hollow mesoporous carbon spheres for CO_2 electroreduction achieved an 88.7% selectivity for C_2 products at −1.0 V vs. RHE, with the confinement effect enhancing C-C bond coupling. These

advancements highlight the versatility and potential of Cu-based clusters in fields like radiation detection, electrochemical reactions and especially the catalyst [4].

Polyoxometalates (POMs) are a fascinating class of inorganic compounds that have garnered significant attention in the fields of chemistry, materials science, and catalysis due to their unique structural properties and versatile applications [5,6]. Polyoxometalates are anionic clusters composed of metal-oxygen units, denoted as MOx (where M represents metals such as W, Mo, V, Nb, Ta, and x ranges from 4 to 7). These units are interconnected through different ways, resulting in the formation of intricate three-dimensional frameworks. A specific category of these compounds, known as heteropolyanions, have MOx units that are centralized around a heteroatom, which plays a crucial role in influencing the compound's properties. Among the various types of heteropolyanions, poly Sandwich oxometalates, characterized by the general formula $[[7]_n^-$ (where X can be P, Si, Ga, etc.), exhibit distinctive attributes such as adjustable acidity, exceptional selectivity, and thermal stability. These characteristics render them highly promising for exploring catalytic applications across a range of chemical reactions, garnering significant interest in recent research endeavors [8–10].

Multicomponent reactions (MCRs) are efficient one-pot processes that integrates three or more reactants to yield intricate products. These reactions provide notable benefits in terms of synthetic efficiency, such as enhanced atom economy, reduced waste generation, and improved overall yields. MCRs have found extensive application in the fields of drug discovery and development, especially in the production of anticancer agents and active pharmaceutical compounds [7,11–20].

Contemporary research on 4*H*-pyran multi-component reactions has focused on the development of green synthesis methods utilizing efficient catalysts. The synthesis of these derivatives typically involves Knoevenagel condensation, Michael addition, and intramolecular cyclocondensation steps. Recent advancements have emphasized the development of sustainable catalysts and environmentally friendly protocols for the multicomponent synthesis of various pyran-containing heterocycles, including bicyclic, tricyclic, polycyclic, and spirocyclic systems [7,21–26].

In this study, $Cu_6W_{18}O_{70}$ will serve as a heterogeneous and effective catalyst for the multicomponent synthesis of 4*H*-pyrans. The reaction is done through present of dimedone, malonitrile, and an aldehyde as reactants. The characterization of this newly synthesized heterogeneous compound will be conducted using various techniques. the catalytic performance of this nanocomposite will be evaluated in the one-pot multicomponent synthesis of 4*H*-pyrans.

2. Materials and Methods

2.1. Materials:

Ethanoic acid (CH_3COOH), Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$, 99%), Copper (II) nitrate nonahydrate (Cu $(NO_3)_2.9H_2O$, 99%), Dimedone, Malononitrile and different aromatic aldehydes were purchased from prominent international chemical com-panies include SIGMA-Aldrich & Merck.

2.2. Methods:

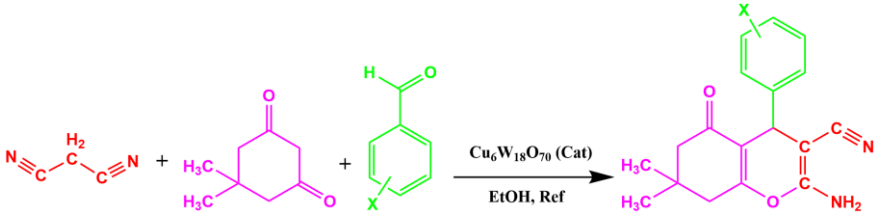
2.2.1. General Procedure for the Preparation of $Cu_6W_{18}O_{70}$ Nanocatalyst

A sandwich-type Cu-polyoxometalate cluster was prepared using the sol-gel method, as previously reported. Briefly, $Na_2WO_4{\cdot}2H_2O$ was dissolved in 15 mL distilled water and heated to 75 °C until a homogeneous solution was obtained. Subsequently, 5 mL of distilled water containing $Cu(NO_3)2{\cdot}H_2O$ was introduced into the solution and the pH was adjusted to around 3–4 using acetic acid under magnetic stirring. Following

magnetic stirring for 60 min, the solution was cooled to room temperature to induce green-blue precipitate. The precipitate was isolated by filtration, washed, and dried at 80 °C for three hours.

2.2.2. General Procedure for the synthesis of 4H-pyran derivatives:

To synthesis the 4*H*-Pyran derivatives, dimedone (1 mmol), malononitrile (1 mmol), and a benzaldehyde derivative (1 mmol) as reactants of this MCRs were mixed to a 10 mL round-bottom flask. nanocatalyst (10 mg), and 2.5 mL of EtOH as solvent were also added to this mixture and the reaction was proceeded under magnetic stirring and reflux at 60 °C. The reaction progress was monitored via TLC, and within less than 15 min, a lemon-colored precipitate formed. Upon completion of the reaction, the catalyst was separated and washed for reuse and also product was purified by crystallization in EtOH. Scheme 1.



Scheme 1. Synthesis of 4*H*-pyran through one-pot three component condensation of aromatic aldehydes via $Cu_6W_{18}O_{70}$ nanocatalyst.

3. Results and Discussion

In this section, some of spectrometric and microscopic analyses, such as FTIR and FESEM, were conducted to characterize the catalyst (Figure 1). The bands observed below 1000 cm^{-1} indicate specific molecular vibrations within the anion. these are ascribed to the Cu-O_a, W-O_b-W, W-O_c-W and W=O_d, respectively. (O_a: central oxygen, O_b/O_c: bridging oxygen, O_d: terminal oxygen). Also, the peak about 3400 is related to OH in this structure.

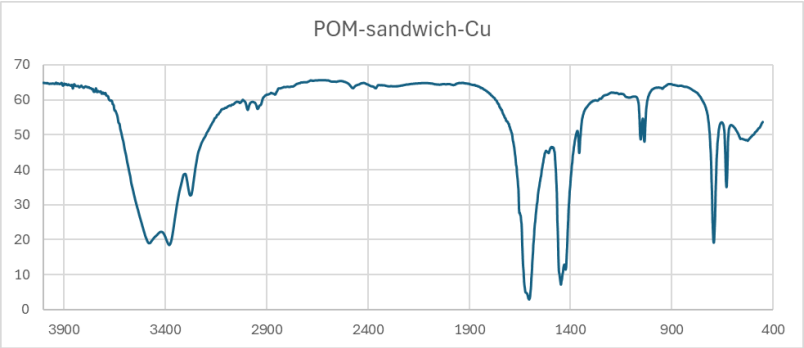


Figure 1. FT-IR spectrum of POM nanocatalyst.

Addition, for more information on available elements, we can see XRD analysis. X-ray diffraction (XRD) is a powerful analytical technique for identifying and characterizing crystalline materials [27]. It provides information on lattice constants, phases, grain size, and crystal defects [28].

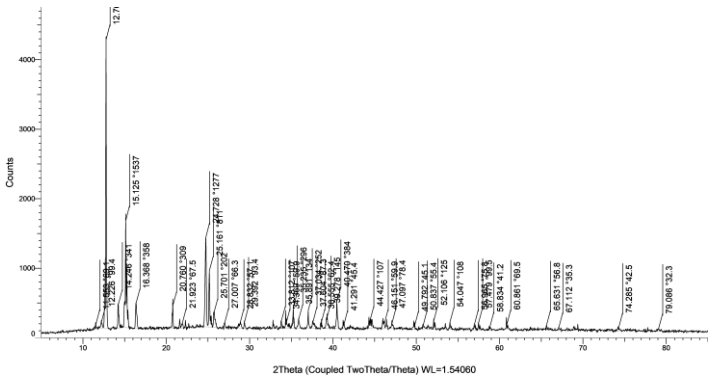
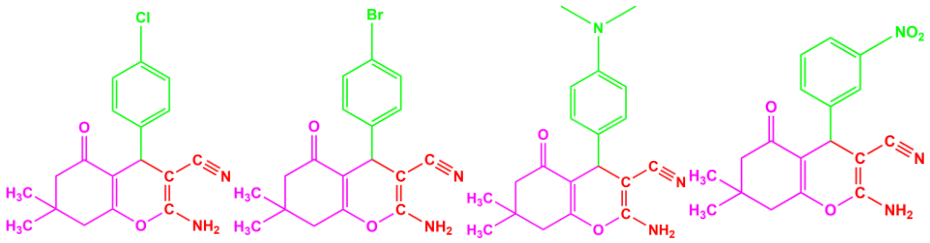


Figure 2. X-ray diffraction (XRD) spectra of $Cu_6W_{18}O_{70}$.

In this MCR reaction, the synthesis of 4 derivatives of 4*H*-Pyran's products was selected as a model reaction. Various derivatives of aldehydes were utilized, and multiple conditions were evaluated. The optimal result was achieved using 10 mg of catalyst in ethanol as a solvent under reflux conditions, with a reaction time of 15 min. The results indicated that the yields of the desired derivatives were obtained in the presence of 10 mg of catalyst within 10–15 min. It is noteworthy that the aforementioned derivatives exhibited significantly lower yields (40%) and extended reaction times (>1 h) in the absence of a catalyst. An additional advantage of this nanocatalyst is its facile separation and recyclability from the reaction mixture. This catalyst was reused in a minimum of five experiments without substantial loss in its catalytic activity.



Scheme 2. Some of 4*H*-pyran derivatives (**a**–**d**) synthesis catalyzed by POM nanocatalyst.

The following data were obtained fron H-NMR analysis for 2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile: m.p 208–210; ^{1}H NMR (500 MHz, DMSO-d6) δ 7.39–7.30 (m, 2H), 7.21–7.12 (m, 2H), 7.07 (s, 2H), 4.19 (s, 1H), 3.37–3.28 (m, 2H), 2.50 (d, J = 17.1 Hz, 4H), 2.25 (d, J = 16.1 Hz, 1H), 2.10 (d, J = 16.1 Hz, 1H), 1.03 (s,3H), 0.94 (s, 3H).

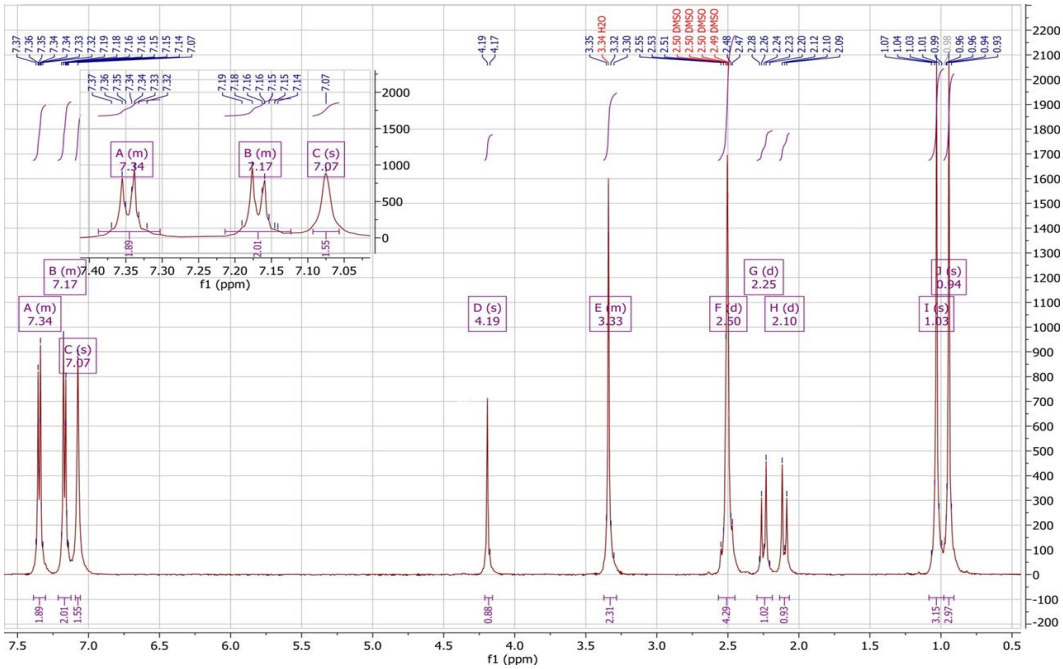


Figure 3. ¹H-NMR analysis for 2-Amino-4-(4-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile.

On the other hands, melting points of mention derivatives were measured and compared in Table 1.

Table 1. Comparison of the melting point of mentioned derivatives with relevant references.

Derivatives	m.p (This Work)	m.p (Ref)
a	209–210	208–210 [29]
b	198–200	197–199 [29]
c	210–211	210–212 [30]
d	210–213	209–211 [31]

4. Conclusions

In this paper, we studied $Cu_6W_{18}O_{70}$ as a useful nanocatalyst in the multi-component reaction for the synthesis of 4*H*-pyran derivatives. the nanocatalyst has advantages such as easy separation, good recovery, high product yield and maintenance of the catalytic activity up to several cycles. also, the low need for catalyst and solvent and on the other hands, are use of solvent non-toxic are other benefits of this catalyst in reactions.

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Conflicts of Interest:

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