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Catalytic application of a novel nano-catalyst of CuO/MnO_2 for the synthesis of propargylamine derivatives

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ABSTRACT

In the present research, an efficient process for the synthesis of propargylamine derivatives catalyzed by a novel nanocomposite of CuO/MnO_2 is reported. CuO/MnO_2 nano-catalyst was synthesized by the co-precipitation process and characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction(XRD), ICP-OES and BET surface area analysis. A broad range of aromatic aldehydes was reacted with amines and phenylacetylene to produce the corresponding propargylamines. The CuO/MnO_2 nano-catalyst is recyclable up to 7 repeated runs and it can be easily recovered by simple filtration. The present method affords additional advantages such as straightforward procedure, ease of workup, clean method and moderately short reaction times.

***Keywords**: CuO/MnO₂ nano-catalyst, Propargylamine derivatives, Amine, Phenylacetylene, Aldehyde.*

1. Introduction

Nowadays, the synthesis of various organic compounds using multicomponent reactions (MCRs), has received much attention. Due to the benefits of these reactions such as selectivity, high atom economy and flexibility, multicomponent reactions have been a large synthetic tool to the synthesis of complex structures from simple precursors via a one-pot process [1]. Among these, the multicomponent reaction of aldehydes, amines, and alkynes for the synthesis of propargylamine derivatives has received major consideration in recent years [2]. Propargylamines are used as intermediates in the synthesis of many biologically active compounds, drugs, and natural molecules [3-4]. A variety of the catalysts have been used for the multicomponent synthesis of these useful compounds, that among them, copper-based catalysts have shown good performance in this regard [5-16].

Comparing with other catalysts, supported-copper catalysts like copper-based nanoparticles can catalyze the synthesis of propargylamines and considered to be the most important catalysts due to their good performance, stability, and selectivity.

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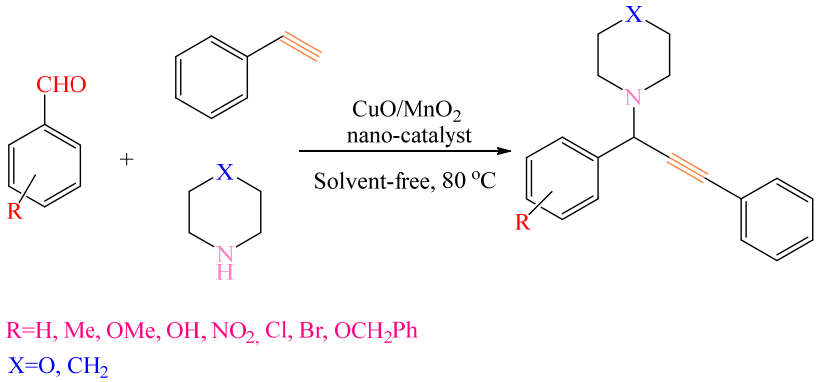
The interaction between used support and copper nanoparticles also plays the key function in the modification of catalytic properties. Good interaction increases the distribution of copper nanoparticles, and the adhesion of copper species, which increases the catalytic activity and stability of the catalyst.

CuO/MnO_2 catalysts with porous structure have been supposed to be ideal catalysts with great potential to be exploited in various catalysis reactions [17]. Some progress of the catalytic application in the presence of different kinds of CuO/MnO_2 catalysts was studied [18-21]. According to our information, CuO/MnO_2 nano-catalyst has not used as a catalyst in organic synthesis reactions, especially for the synthesis of propargylamines. Therefore, in continuation of our studies on the synthesis and use of new nano-catalysts in the organic reactions [22-26], here, we report the preparation of an efficient kind of CuO/MnO_2 nano-catalyst for the solvent-free synthesis of propargylamine derivatives (Scheme 1).

2. Experimental

All the chemicals used in this research were purchased from Merck or Fluka companies. The synthesized products were identified using spectroscopic data, physical properties, and comparison with the reported in the literature.



Scheme 1. Synthesis of propargylamine derivatives catalyzed by CuO/MnO_2 nano-catalyst.

Yields related to the pure compounds prepared. The morphology of the CuO/MnO_2 nano-catalyst was investigated by scanning electron microscopy (SEM) method by a MIRA3TESCAN device, set with an EDS analytical system to study the existence of different components of the nano-catalyst. The XRD study was done using an X-ray diffractometer, Cu-Kα monochromatized radiation source and a nickel filter (PANalytical X'Pert Pro) to explore the structure and crystallinity of the catalyst. Scherrer equation was used to determine the average crystallite size of the particles. The BET surface area was tested by the N_2 adsorption-desorption method. The investigation was carried out using an automated gas adsorption analyzer (Belsorp-mini II Microtrace Bell).

2.1. Preparation of the catalyst

The CuO/MnO_2 nano-catalyst was prepared *via* a co-precipitation procedure by the addition of maleic acid (0.05 M) drop-wise into a mixture of $Cu(SO_4).5H_2O$ (0.02 M), and $KMnO_4$ (0.2 M), solutions under vigorous stirring. The obtained suspension was kept 24 h at room temperature, then filtered and washed with warm deionized water. The precipitates were dried overnight at 100 °C, followed by calcination at 400 °C for 4 h to get the CuO/MnO_2 nano-catalyst.

2.2. General procedure

A mixture of phenylacetylene (1.5 mmol), amine (1 mmol), aromatic aldehyde (1 mmol) and Cu/MnO_2 nano-catalyst (0.05 g) in an oil bath (80 °C), was stirred. The progress of reactions was checked by thin-layer chromatography (TLC). After reaction completion, hot chloroform was added, the catalyst was separated and then washed with hot chloroform (2×5 mL), as well as dried for the following reaction run. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to give the pure corresponding propargylamines. The spectral and analytical information for the newly synthesized compound is as follows:

Table 3, entry 18:

Oil. ^{1}HNMR ($CDCl_3$, 400 MHz): δ= 2.55 (br 4H), 3.66 (br, 4H), 4.67 (s, 1H), 5.00 (s, 2H), 6.89 (d, 2H), 6.91-7.45 (m, 10H), 7.45 (d, 2H) ppm. ^{13}CNMR ($CDCl_3$, 100 MHz): δ= 61.44, 67.17, 70.05, 85.29, 88.30, 114.48, 122.99, 127.52, 128.02, 128.25, 128.32, 128.62, 129.78, 131.81, 136.96, 158.44 ppm. Elem. Anal. Found= C, 81.54 %; H, 6.63 %; N, 3.71 %. Calc= $C_{26}H_{25}NO_2$: C, 81.43 %; H, 6.57 %; N, 3.65 %.

3. Results and Discussion

The XRD pattern of the CuO/MnO_2 nano-catalyst shown in Fig. 1. As explained in different studies [27-29], manganese dioxide as a polymorph material can be prepared as amorphous, α, β, γ and δ-MnO_2 in various synthetic conditions. The peaks characteristic of the XRD pattern of the synthesized CuO/MnO_2 are very close to the XRD pattern of the α-MnO_2 reported by Xing Kang Huang *et al.* [30]. The diffraction peaks centered at 2θ= 12.98, 2θ= 18.28, 2θ= 28.93,2θ= 37.68, 2θ= 41.23, 2θ= 42.18, 2θ= 49.93, 2θ= 56.33, 2θ= 60.23, 2θ= 65.58 and 2θ= 69.68 can be attributed to the (110), (200), (310), (211),(420), (301), (411), (600), (521), (002) and (541) crystalline planes of MnO_2 crystals, respectively [31]. The diffraction peaks with low intensities centered at about 2θ= 36.58, 2θ= 47.86 and 2θ= 63.42 may be attributed to the (111), (202) and (113) planes of CuO structure, respectively [32]. This description can be correct because the percentage of CuO (10%) in the nano-catalyst structure is lower compared to the catalyst support. However, the XRD pattern of the synthesized nano-catalyst may be proof to demonstrate the presence of MnO_2 as a major component, and CuO as an active catalytic ingredient of the produced nano-catalyst.

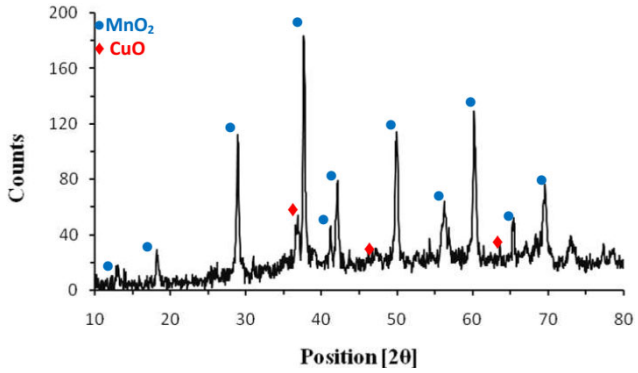


Fig. 1. The XRD pattern of CuO/MnO_2nanocatalyst.

The N_2-adsorption/desorption isotherm and pores size distribution of the CuO/MnO_2 nano-catalyst shown in Fig. 2(a) and Fig. 2(b), respectively. As seen, the isotherm of the synthesized nano-catalyst displays a considerable hysteresis loop between p/p_0=0.4-1.0. According to the IUPAC isotherm classification, the obtained N_2-adsorption/desorption could be categorized as type IV [33]. As seen in Fig. 2(b), the pore size distribution of CuO/MnO_2 nano-catalyst is significantly widened as the pore volumes decreased. However, the range of the pore size varied between mesoporous to macro-porous structures (Table 1).

The adsorption/desorption isotherm and pore size distribution of the pure MnO_2 were also shown in Fig. 3. The specific surface area and porosity of the synthesized MnO_2 support and the nano-catalyst were obtained by Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. It was observed that the specific surface area of the MnO_2 support decreases with the deposition of the CuO nano-catalyst. The results are shown in Table 1, which are approximately in agreement with the data, as previously reported [34].

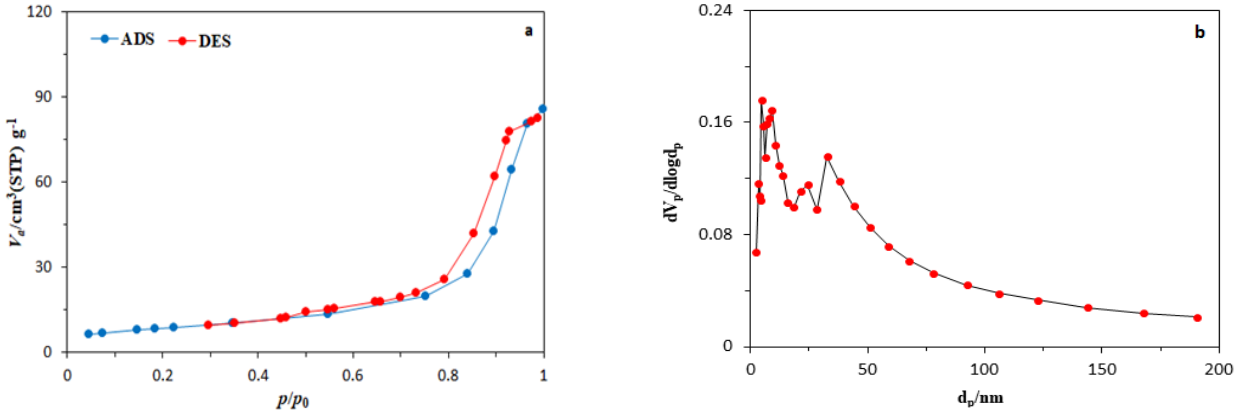


Fig. 2. The N_2-adsorption/desorption (a) and pore width distribution (b) of the CuO/MnO_2 nano-catalyst.

Table 1. Structural parameters of the CuO/MnO_2 nano-catalyst.

Catalyst	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	D_p (nm)
CuO/MnO_2	30	0.1303	4.76
MnO_2	98	0.1967	21.3

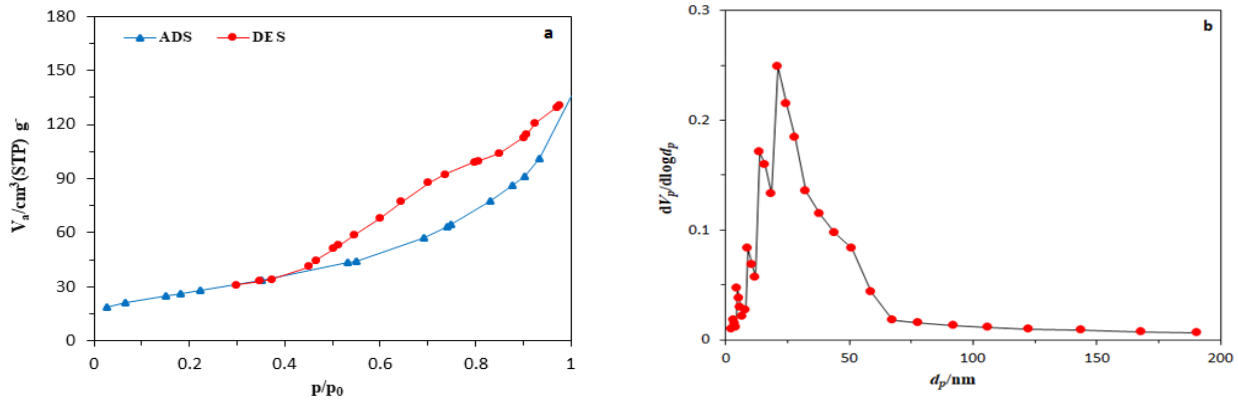


Fig. 3. The N_2-adsorption/desorption (a) and pore width distribution (b) of the MnO_2.

The SEM image with different magnifications and the EDS of the synthesized CuO/MnO_2 nano-catalyst were shown in Fig. 4 (a and b) and Fig. 4 (c), respectively. As seen, the CuO/MnO_2 nanospheres had diameters less than 25 nm and were smaller than the MnO_2 crystals with diameters of 200 and 400 nm reported by Ling *et al*. [35], and Wang *et al.* [36], respectively. However, the aggregation of the CuO/MnO_2 nano-catalyst also appeared in the SEM images. The EDS results demonstrated in Fig. 4 (c) represented the characteristic x-ray wavelengths of the Mn, K and Cu elements and indicated the successful synthesis of the CuO/ MnO_2. The EDS analysis showed the Cu content of about 10% $ww^{-1,}$ which agrees with the results obtained by ICP-OES (9.74% w w^{-1}).

After the characterization of the CuO/MnO_2 nano-catalyst, its catalytic activity in the synthesis of propargylamines was investigated. To this purpose, the reaction between phenylacetylene, morpholine and 4-chlorobenzaldehyde was selected as a model reaction and studied to find the optimal reaction conditions. The reaction was checked in various solvents such as water, ethanol, acetonitrile, toluene and under solvent-free conditions. Moreover, the reaction was investigated in the presence of different amounts of catalysts at various temperatures. The results showed that no product was obtained at room temperature and in different solvents by changing catalyst amounts. Finally, the results of optimization showed that under solvent-free conditions 80 °C and using 0.05 g of CuO/MnO_2 nano-catalyst, the desired product was synthesized at the highest yields and in the shortest time. Also, optimizing the amounts of initial materials showed that 4-chlorobenzaldehyde (1 mmol), morpholine (1 mmol) and phenylacetylene (1.5 mmol) would produce the best results (Table 2). Therefore, all reactions were studied in the presence of 0.05 g CuO/MnO_2 nano-catalyst under solvent-free conditions at 80 °C.

To synthesis propargylamine derivatives, the reaction of various aldehydes, including electron-donating and electron-withdrawing groups with phenylacetylene, piperidine, or morpholine, were studied under optimal reaction conditions (Table 3). In all reactions, the desired products were synthesized easily and with excellent efficiency. The type of group on the aromatic ring did not affect the efficiency of the reaction, but in the presence of electron-withdrawing groups, times of reactions were reduced (Table 3).

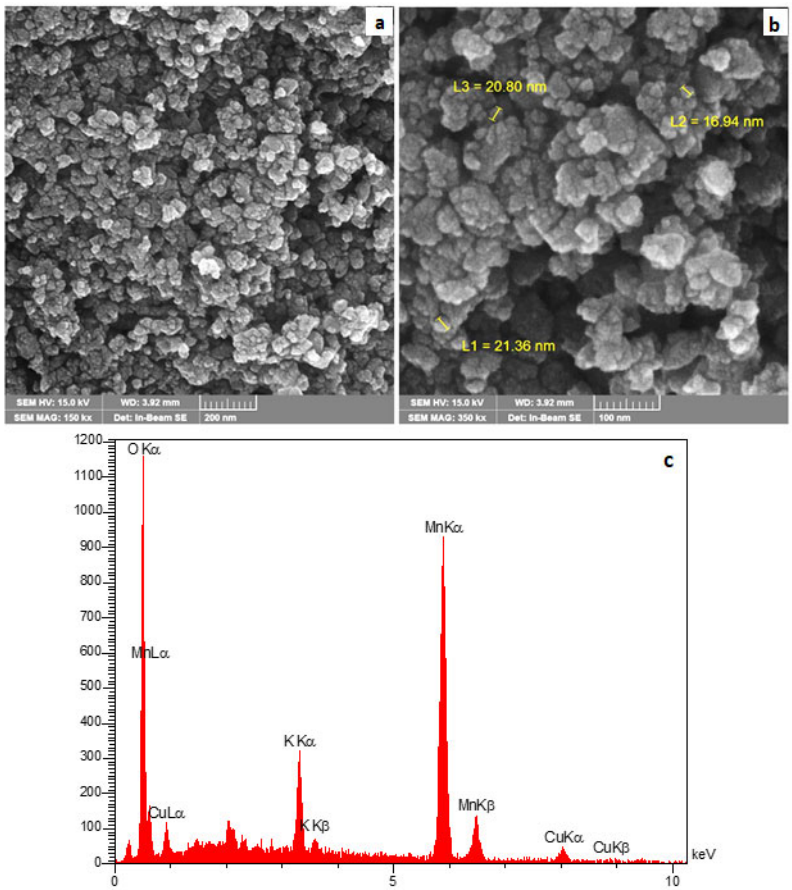


Fig. 4. SEM micrographs (a, b) and EDS analysis results (c) of CuO/MnO_2nanocatalyst.

Table 2. Optimization of the reaction conditions.[a]

Entry	Solvent	Condition	Catalyst	Time (h)	Yield (%)[b]
1	Toluene	r.t.	0.05 g	6	-
2	Toluene	reflux	0.05 g	5	30
3	CH_3CN	r.t.	0.05 g	6	Trace
4	CH_3CN	reflux	-	6	-
5	CH_3CN	reflux	0.05 g	5	50
6	CH_3CN	reflux	0.07 g	5	60
7	EtOH	r.t.	0.05 g	6	-
8	EtOH	reflux	0.05 g	5	Trace
9	H_2O	r.t.	0.05 g	6	-
10	H_2O	reflux	0.05 g	5	Trace
11	MeOH	r.t.	0.05 g	6	-
12	MeOH	reflux	0.05 g	5	Trace
13	DMSO	r.t.	0.05 g	6	Trace
14	DMSO	reflux	0.05 g	5	40
15	DMSO	reflux	0.07 g	5	50
16	Solvent-free	60 ºC	0.05 g	3	50
17	Solvent-free	60 ºC	0.07 g	3	50
18	Solvent-free	80 ºC	0.05 g	2	91
19	Solvent-free	80 ºC	0.03 g	3	75
20	Solvent-free	80 ºC	0.07 g	2	90
21	Solvent-free	100 ºC	0.05 g	2	91
21	Solvent-free	100 ºC	-	6	-

[a]Reaction conditions: 4-chlorobenzaldehyde (1 mmol), morpholine (1mmol), phenylacetylene (1.5 mmol).
[a]Isolated yield.

In these processes, like morpholine, piperidine also reacts well with aldehydes and phenylacetylene and similar product prepared in excellent yields. Also, from the reaction of 4-benzyloxybenzaldehye, morpholine and phenylacetylene, a new compound was synthesized from the reaction of in high yield, which was identified with spectroscopic data and physical properties (Table 3, entry 18). More studies were carried out to determine the catalyst recyclability. The solvent-free synthesis of the corresponding propargylamine was carried out 7 times in the subsequent runs, with only a small decrease in the yield of products (The yields ranged from 91 to 89%). After reaction completion, the catalyst washed with hot chloroform, dried, and kept for continual reaction run.

4. Conclusions

In summary, in this research, we have reported the preparation and identification of a novel nanocomposite of CuO/MnO_2 as an efficient catalyst for catalyzing the multicomponent synthesis of propargylamines under solvent-free conditions in high yields. The CuO/MnO_2 nano-catalyst was easily separated from the reaction mixture with simple filtration and displayed an excellent act on the synthesis of propargylamines. The catalyst is also recyclable up to seven times and has an excellent stability during the reactions.

Acknowledgments

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Table 3. Synthesis of propargylamines catalyzed by CuO/MnO_2 nano-catalyst.[a]

Entry	R	Amine	Time (h)	Yield (%)[b]
1	H	piperidine	2	91
2	3-NO_2	piperidine	2	92
3	4-NO_2	piperidine	1.5	93
4	4-Br	piperidine	2	91
5	4-Cl	piperidine	2	91
6	2-Cl	piperidine	3	89
7	4-OMe	piperidine	3	88
8	4-OH	piperidine	3	89
9	2-OH	piperidine	3.5	87
10	H	morpholine	2.5	90
11	4-Cl	morpholine	2.5	93
12	2-Cl	morpholine	3	91
13	4-NO_2	morpholine	2	93
14	3-NO_2	morpholine	3	90
15	4-OH	morpholine	3	87
16	2-OH	morpholine	4	86
17	4-OMe	morpholine	3	88
18	4-OCH_2Ph	morpholine	4	89[c]

[a]Reaction conditions: Aldehyde (1 mmol), Amine (1 mmol), phenylacetylene (1.5 mmol), CuO/MnO_2 nanocatalyst (0.05 g), under solvent-free condition. Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature [9, 10, 14].
[b]Isolated pure products.
[c]New compound.

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