Received: 30 May 2018 | Revised: 10 September 2018 | Accepted: 11 September 2018
DOI: 10.1002/aoc.4625

FULL PAPER

WILEY Applied Organometallic Chemistry

Solvent-free synthesis of propargylamines catalyzed by an efficient recyclable ZnO-supported CuO/Al_2O_3 nanocatalyst

Zohreh Sotoudehnia | Jalal Albadi | Ahmad Reza Momeni

Department of Chemistry, Faculty of Science, Shahrekord University, Shahrekord, Iran

Correspondence
Jalal Albadi, Department of Chemistry, Faculty of Science, Shahrekord University, Shahrekord, Iran.
Email: jalal.albadi@gmail.com; albadi@sku.ac.ir

Funding information
Shahrekord University

An efficient nanocatalyst of ZnO-supported CuO/Al_2O_3 ($CuO/ZnO/Al_2O_3$ nanocatalyst) was prepared by the co-precipitation method and characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray powder diffraction and Brunauer–Emmett–Teller surface area analysis. $CuO/ZnO/Al_2O_3$ nanocatalyst proved to be a very efficient catalyst on the synthesis of propargylamines under solvent-free conditions in high yields. Moreover, the catalyst can be recyclable without reducing catalytic activity up to five times.

KEYWORDS
aldehyde, $CuO/ZnO/Al_2O_3$ nanocatalyst, phenylacetylene, propargylamines, solvent-free conditions

1 | INTRODUCTION

Propargylamines have attracted a lot of attention due to their medicinal and biological properties, such as antiparkinson,[1] anti-Alzheimer,[2] anti-apoptotic[3] and bovine plasma amine oxidase inhibitors.[4] Propargylamine derivatives are useful synthetic intermediates in organic synthesis, and are also significant structural elements in natural products and therapeutic drug molecules, as well as for the synthesis of polyfunctional amino derivatives.[5,6] Due to the importance of propargylamines, various catalytic procedures have been reported for the synthesis of these compounds. According to previous reports, various metal-based catalysts, including Ag, Fe, Li, Ni, Pd, In and Au, have been reported for the synthesis of propargylamines.[7–16] In this view, copper and zinc catalysts are the most important for the synthesis of propargylamine derivatives, and good results have been achieved in the presence of these catalysts.[17–28]

In previous researches, the use of hybrid metal oxide catalysts has attracted a lot of attention both in industry and in organic chemistry. To increase the performance and reducibility of copper-based catalysts, most studies have focused on using a suitable promoter and synthesis procedure.[29] Among these catalysts, $Cu/ZnO/Al_2O_3$(CZA), as the commercial catalyst that contains high loading of Cu and ZnO as well as a relatively lower amount of Al_2O_3, has been used most widely in steam reforming of methanol reaction.[30] Various factors, such as synthesis procedure and appropriate promoters, can competently effect the physicochemical and catalytic properties of these catalysts. ZnO is identified as an operative promoter for the improvement of reducibility and distribution of copper particles that can effect the spreading and redox properties of the copper species as well as being responsible for better metal support interaction.[31] Moreover, Al_2O_3 as a constitution promoter has a good effect on the CuO/ZnO catalysts reactivity, and was added to the CuO/ZnO catalysts to increase the surface area, mechanical resistance and thermal stability.[32] On the other hand, in recent years, increasing attention has been focused on the catalytic application of nanocatalysts. Catalytic systems using nanocatalysts, such as hybrid metal oxide catalysts, have resulted in various important advantages, such as good properties, high stability, dispersity of the particles, superior activity and catalyst recyclability.

Based on the literature, the catalytic application of ZnO-supported CuO/Al_2O_3 ($CuO/ZnO/Al_2O_3$ nanocatalyst) has not been studied on organic synthesis reactions, particularly for the synthesis of propargylamines. In previous researches, we have reported the catalytic activity of various nanocatalysts on the organic synthesis reactions.[33–36] In an extension of our research, herein, we wish to report the preparation and characterization of an efficient recyclable kind of ZnO-supported CuO/Al_2O_3 nanocatalyst ($Cu/ZnO/Al_2O_3$ nanocatalyst) as well as its catalytic activity on the synthesis of propargylamines under solvent-free conditions (Scheme 1).

2 | EXPERIMENTAL

2.1 | General

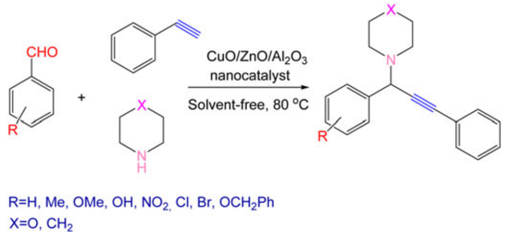
Chemicals were purchased from Merck and Fluka. The nanocatalyst was prepared by the co-precipitation method, and characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD) and Brunauer–Emmett–Teller (BET) surface area study. All obtained products were characterized by comparison of their physical and spectroscopic properties with those reported in the literature. NMR spectra were recorded on a Bruker Advance 400 MHz. Yields refer to isolated pure products.

2.2 | Catalyst preparation

The catalyst was prepared through a co-precipitation process, by adding Na_2CO_3 solution (0.5 M) drop-wise into a mixture of Cu $(NO_3)_2{\cdot}3H_2O$ (0.03 M), Zn $(NO_3)_3{\cdot}6H_2O$ (0.03 M) and aluminum nitrate (0.03 M) solutions under strong stirring. The obtained suspension was aged at pH 8.5 for 15 min at 50°C, then filtered and washed with warm deionized water. The precipitates were dried for 12 h at 100°C, followed by calcination at 300°C for 3 h to obtain the $CuO/ZnO/Al_2O_3$ nanocatalyst.

2.3 | Catalyst characterization

The morphology of the nanocatalyst was studied using SEM by a JEOL JSM-6500F device, equipped with an EDS analytical system to study the existence of different components of the catalyst. The XRD study was performed using an X-ray diffractometer, Cu-Kα monochromatized radiation source and a nickel filter (Panalytical X'Pert-Pro), in order to explore the structure and crystallinity of the catalyst. The Scherrer equation was used to determine the average crystallite size of the sample. The BET surface area was tested by N_2 adsorption–desorption method. The investigation was carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). The sample was purged with nitrogen gas for 3 h at 300ºC by a VacPrep 061 degas system (Micrometrics).



SCHEME 1 Synthesis of propargylamines catalyzed by $Cu/ZnO/Al_2O_3$ nanocatalyst

2.4 | General procedure

In a round-bottom flask, a heterogeneous mixture of aldehydes (1 mmol), amine (1 mmol) and phenylacetylene (1.2 mmol) $Cu/ZnO/Al_2O_3$ nanocatalyst (0.05 g) was stirred at 80°C for the appropriate times (mentioned in Table 3) under solvent-free conditions. The improvement of the reaction was monitored by thin-layer chromatography (TLC). After reaction completion, the reaction mixture was allowed to cool at room temperature. Then hot chloroform was added and the catalyst was separated. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to obtain the pure corresponding propargylamines. The spectral and analytical data for the new prepared compound are as follows:

Table 3, entry 9: Oil; ^1H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.34–1.54 (m, 6H), 2.47 (br, 4H), 4.68 (s, 1H), 4.96 (s, 2H), 6.87 (d, 2H), 7.21–7.43 (m, 10H), 7.45 (d, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 24.48, 26.13, 50.58, 61.78, 70.05, 86.28, 87.76, 114.36, 127.57, 128.01, 128.11, 128.33, 128.64, 129.81, 131.85, 137.09, 158.31. Elem. Anal. Found: C, 85.09%; H, 7.19% N, 3.73% (calcd for $C_{27}H_{27}NO$: C, 85.00%; H, 7.13%; N, 3.67%).

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization results

Figure 1 represents the SEM images of the $Cu/ZnO/Al_2O_3$ nanocatalyst with different magnifications. An aggregation of the Al_2O_3 and CuO nanoparticles was observed on the surface of ZnO support. The sizes of these nanoaggregates with different shapes are less than 20 nm. As a quantitative proof, the EDS (Figure 1d) analysis has been performed, and presented the content of ZnO support greater than 75% by weight.

The XRD pattern of the $CuO/ZnO/Al_2O_3$ nanocatalyst was shown in Figure 2. The peaks centered at about $2\theta = 31.9$, $2\theta = 34.76$, $2\theta = 56.84$, $2\theta = 69.18$ corresponded to the 100, 002, 110 and 200 crystalline planes of ZnO support, respectively.[37] The peaks observed at $2\theta = 36.58$, $2\theta = 47.86$ and $2\theta = 63.32$ may be related to 111, 202 and 113 planes of CuO, respectively.[38] It is valuable to

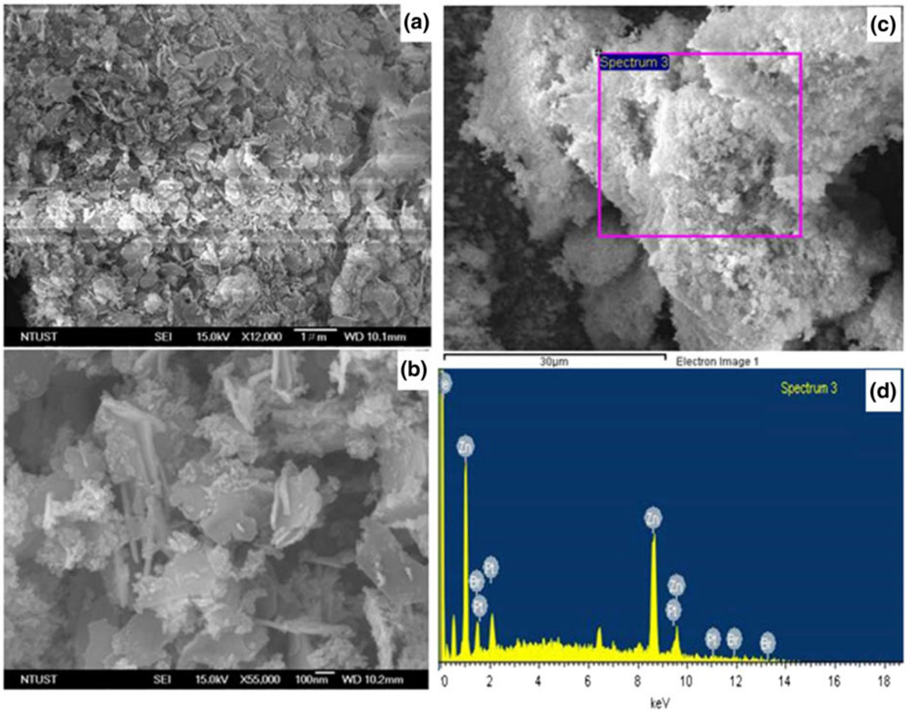


FIGURE 1 Scanning electron microscopy (SEM) micrographs and energy-dispersive X-ray spectroscopy (EDS) analysis results of the CuO/ZnO/Al_2O_3 nanocatalyst

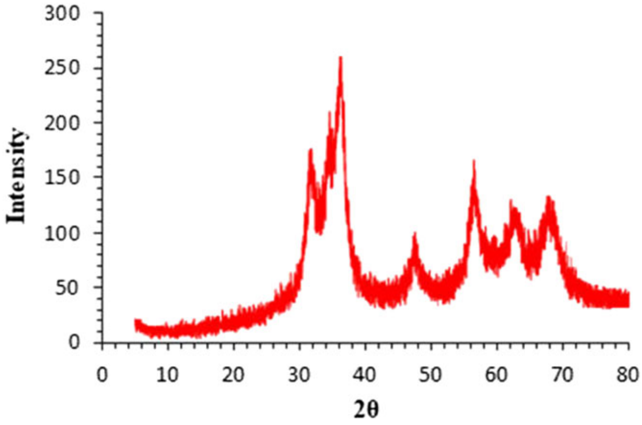


FIGURE 2 The X-ray powder diffraction (XRD) of the CuO/ZnO/Al_2O_3 nanocatalyst

note that the peaks related to different phases of Al_2O_3 as α, δ, θ and γ, δ, θ appeared at about $2\theta = 36.58$ and $2\theta = 47.86$.[33] This XRD interpretation can be stated, because the percentages of Al_2O_3 (10% w/w) and CuO (5% w/w) in the target nanocatalyst are nearly close. As seen, the CuO/ZnO/Al_2O_3 nanocatalyst was synthesized by co-precipitation of three metal oxide phases, so that the peak overlapping is inevitable, and subsequently influences the detailed interpretation of the given XRD pattern. However, the XRD data indicated the presence of three metal oxide crystals in the composite nanocatalyst.

The N_2 adsorption–desorption isotherms of the ZnO support and CuO/ZnO/Al_2O_3 nanocatalyst are presented in Figure 3. As can be seen, thin hysteresis loops between $p/p0 = 0.3–0.8$ and $p/p0 = 0.3–0.85$ appeared in the isotherms of the support and nanocatalyst, respectively. According to the IUPAC recommendation, these N_2-isotherms, type III, can be attributed to the metal oxides with a non-porous structure.[38,39] As represented in Figure 3a, the capacity of the nanocatalyst for adsorption of the inert N_2 is greater than that of the support in the relative pressure range below 0.8.

The BET and Barrett–Joyner–Halenda methods were employed to evaluate the specific surface area ($m^2\ g^{-1}$) and porosity of the support and nanocatalyst, respectively. The pattern of pore width distribution and structural characteristics of the support and catalyst were shown in Figure 3b and Table 1, respectively. As seen from Figure 3b, a wide pore size distribution for both the ZnO support and the ZnO-supported nanocatalyst CuO-Al_2O_3 with a maximum are at about 30 and 24 nm, respectively. It is obvious from Figure 3b that the pore sizes of support and nanocatalyst are in the range of mesoporous and macroporous structures. Thus, this observation indicates the formation of the non-porous structure of metal oxides that co-precipitate together.[38] The low pore size, high surface area and total pore volume of the CuO/ZnO/Al_2O_3 nanocatalyst with respect

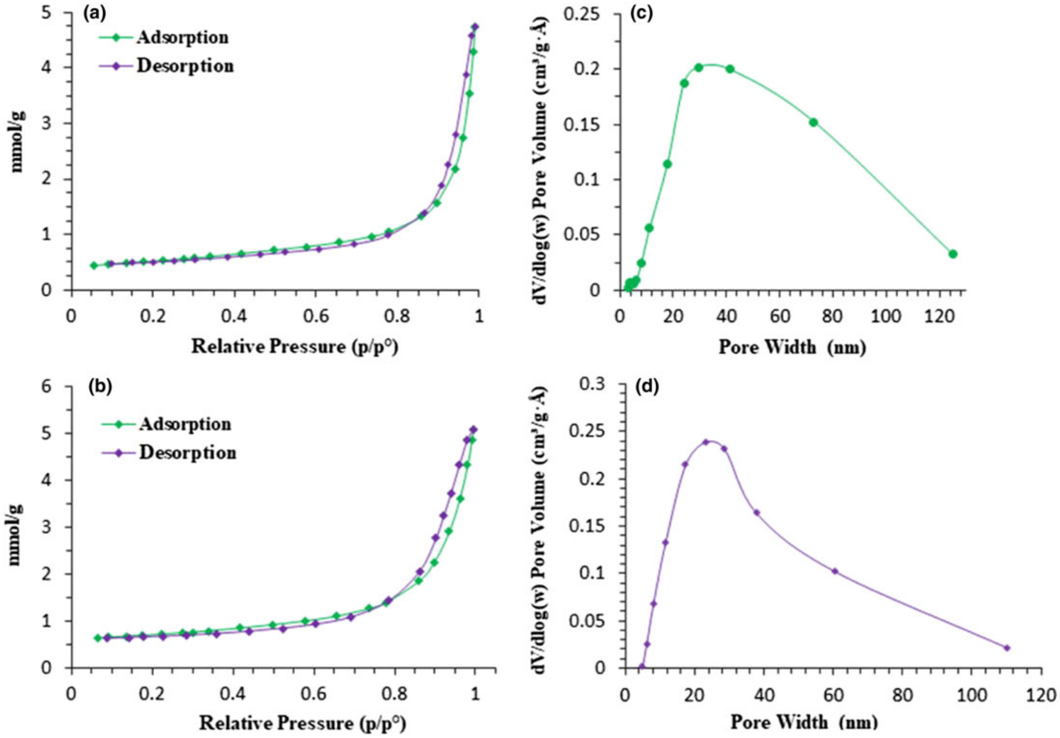


FIGURE 3 (a, b) The N_2 adsorption/desorption of ZnO support and $CuO/ZnO/Al_2O_3$ nanocatalyst, (c, d) pore width distribution of the ZnO and $CuO/ZnO/Al_2O_3$ nanocatalyst

TABLE 1 Structural parameters of the support and the nanocatalyst

Catalyst	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Average pore width (nm)
ZnO	38.93	0.161	22.62
$CuO/ZnO/Al_2O_3$	50.22	0.173	17.64

BET, Brunauer-Emmett-Teller.

to the ZnO support may be due to the incorporation of the Al_2O_3 phases in the nanocatalyst.[39]

3.2 | Catalytic activity

According to reports on the use of copper and zinc catalysts on the synthesis of propargylamines, we decided to prepare and use a hybrid catalyst of these metals. After preparation and characterization of $CuO/ZnO/Al_2O_3$ nanocatalyst, we considered the optimal conditions for the synthesis of propargylamines. For this purpose, initially, reaction of 4-bromobenzaldehyde, piperidine and phenylacetylene was selected as a pattern reaction and various parameters were studied on the process of this reaction. Parameters such as solvent, temperature, catalyst and raw materials amounts were studied. Various solvents such as water, ethanol, acetonitrile, toluene, as well as solvent-free conditions were carefully studied. The reaction was also checked at different temperatures. The results showed that 80°C is appropriate for the reaction, and increasing temperature does not affect the speed of the reaction and yield of the desired product. It was found that in the absence of the catalyst the reaction failed to form the corresponding product even after 18 h. Therefore, the effect of the catalyst amount on the reaction was also examined. Moreover, the reaction was also investigated in the presence of various amounts of raw materials. The outcomes indicated that the best results were achieved from the reaction of 4-nitrobenzaldehyde, piperidine and phenylacetylene (with 1:1:1.2 mol ratios), in the presence of $CuO/ZnO/Al_2O_3$ nanocatalyst (0.05 g), under solvent-free conditions at 80°C (Table 2). Increasing the amount of catalyst did not have a particular effect on the yield of product and reaction time. Moreover, the obtained results in water and ethanol as solvent resulted in the corresponding

TABLE 2 Optimization of the reaction conditions

Entry	Solvent	Condition	Catalyst (g)	Time (h)	Yield (%)[a]
1	CH_3CN	reflux	0.05	4	Trace
2	Toluene	reflux	0.05	2	60
2	EtOH	reflux	0.05	4	Trace
3	H_2O	reflux	0.05	4	Trace
4	Solvent-free	80°C	0.05	1.5	90
5	Solvent-free	100°C	0.05	1.5	90

[a] Isolated yields. Reaction conditions: 4-bromobenzaldehyde (1 mmol), piperidine (1 mmol) and phenylacetylene (1.5 mmol).

product in lower yield. It is obvious that the catalytic activity of the $CuO/ZnO/Al_2O_3$ nanocatalyst is limited by the solvation, so that the product yields were increased in solvent-free medium. In water and ethanol as solvent, there can be nucleophilic competition with amine. It also interferes with the presence of protons in the formation of copper salt with phenylacetylene. In acetonitrile, a by-product was detected. There may be an interaction between the catalyst and acetonitrile, and then it has been nucleophilic attacked by amine. Thus, all of the reactions were performed in the presence of $CuO/ZnO/Al_2O_3$ nanocatalyst (0.05 g), under solvent-free conditions at 80°C.

After optimization, we explored the possibility of $CuO/ZnO/Al_2O_3$ nanocatalyst on the synthesis of different propargylamines under optimized conditions. The results are shown in Table 3.

As shown in Table 3, various aromatic aldehydes carrying both electron-donating or -withdrawing substituents, secondary amines and phenylacetylene gave high yields of products with good performance. Aromatic aldehydes possessing electron-donating substituents such as OH, OMe or Me groups afforded the desired products in high yields. Moreover, a new product was synthesized from 4-benzyloxybenzaldehyde, piperidine and phenylacetylene in good yield, and characterized by physical properties and spectroscopic data (Table 3, entry 9).

Excellent yields of propargylamines were found while aromatic aldehydes containing electron-withdrawing groups such as NO_2, Cl or Br were employed as the substrates (Table 3). Also, in these reactions, both piperidine and morpholine responded well and showed good results. Moreover, the duration of the reactions in this procedure is low and the desired products were obtained at short reaction times.

The model reaction was checked with individual salts (ZnO, CuO and Al_2O_3) and with their combinations. The results revealed that in the presence of CuO and ZnO, prepared products were obtained in much lower yields and high reaction times. Moreover, excess amounts of the catalyst need to be used for reaction completion. In the presence of Al_2O_3, no product was obtained. Also, in the presence of their combinations, corresponding products were synthesized in lower yields and longer times than $CuO/ZnO/Al_2O_3$ nanocatalyst (Table 4).

TABLE 3 Synthesis of propargylamines catalyzed by $CuO/ZnO/Al_2O_3$ nanocatalyst

Entry	R	Amine	Time (h)	Yield (%)[a]
1	H	piperidine	1.5	94
2	4-Br	piperidine	1.5	93
3	4-Cl	piperidine	2	94
4	2-Cl	piperidine	2.5	91
5	4-NO_2	piperidine	1.5	92
6	3-NO_2	piperidine	2	93
7	4-OH	piperidine	2	89
8	2-OH	piperidine	2	86
9	4-OCH_2Ph	piperidine	2	88[b]
10	4-OMe	piperidine	2	90
11	4-Cl	morpholine	2	89
12	2-Cl	morpholine	2.5	92
13	4-NO_2	morpholine	1.5	93
14	3-NO_2	morpholine	2	92
15	4-OH	morpholine	2.5	87
16	4-OMe	morpholine	2	91

[a] Isolated pure products.

[b] New compound. Reaction conditions: aldehyde (1 mmol), amine (1 mmol), phenylacetylene (1.5 mmol), $CuO/ZnO/Al_2O_3$ 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.[12,21,25]

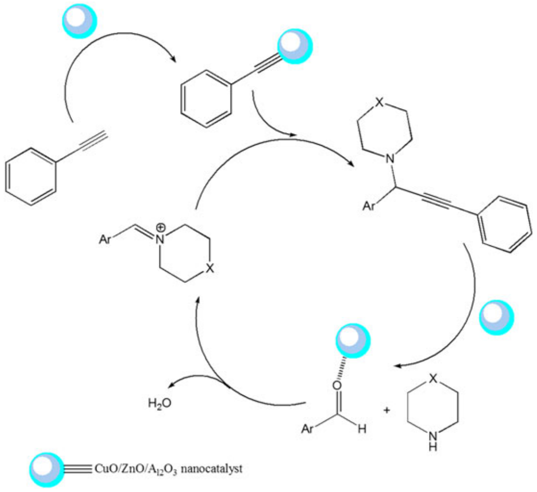
A probable mechanism of the synthesis of propargylamines catalyzed by $CuO/ZnO/Al_2O_3$ nanocatalyst is shown in Scheme 2. At first, $CuO/ZnO/Al_2O_3$ nanocatalyst activated the C-H bond of phenylacetylene to afford the desired acetylidine complex. Also, nucleophilic attack of amine to the activated aldehyde (by $CuO/ZnO/Al_2O_3$ nanocatalyst), followed

TABLE 4 Comparision study between $CuO/ZnO/Al_2O_3$ nanocatalyst ZnO, CuO, Al_2O_3, and with their combinations for the synthesis of propargylamines

Entry	Catalyst	Catalyst amount (g)	Time (h)	Yield (%)[a]
1	CuO	0.05	5	30
2	ZnO	0.05	5	25
2	Al_2O_3	0.05	5	–
3	Combinations[b]	0.05	4	50

[a] Isolated yields.

[b] Combination of CuO, ZnO and Al_2O_3, Reaction conditions: 4-bromobenzaldehyde (1 mmol), piperidine (1 mmol) and phenylacetylene (1.5 mmol), under solvent-free condition.



SCHEME 2 The proposed mechanism for the synthesis of propargylamines catalyzed by $CuO/ZnO/Al_2O_3$ nanocatalyst

by H_2O removal, provides iminium ion. Then, the acetylidine complex was added to iminium ion to give the corresponding propargylamine.

The reusability of the $Cu/ZnO/Al_2O_3$ nanocatalyst was also studied in the reaction between 4-bromobenzaldehyde, piperidine and phenylacetylene under optimized conditions (Table 5). After the reaction completion, which was monitored by TLC, the catalyst was separated by filtration and washed with hot chloroform. Then, it was dried and stored for the following reaction run. This process was carried out seven times without significant loss of activity. These results prove the convenient recyclability of the $Cu/ZnO/Al_2O_3$ nanocatalyst, and consequently confirm its potential role on the organic synthesis reactions (Table 5).

The XRD pattern of the recycled catalyst after being used seven consecutive times was compared with the XRD pattern of the catalyst before the reaction for the

TABLE 5 Recyclability study of $CuO/ZnO/Al_2O_3$ nanocatalyst

Run	1	2	3	4	5	6	7
Time (h)	1.5	1.5	1.5	2	2	2.5	3
Yield (%)[a]	93	93	93	92	90	90	89

[a] Isolated pure products.

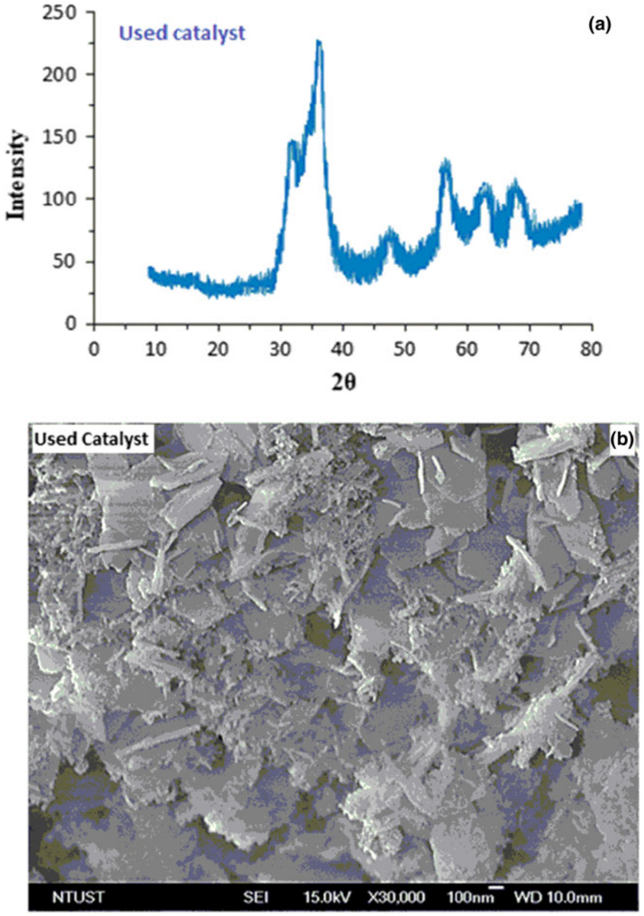


FIGURE 4 The X-ray powder diffraction (XRD) pattern (a) and scanning electron microscopy (SEM) image (b) of the recycled $CuO/ZnO/Al_2O_3$ nanocatalyst

TABLE 6 Comparison study between $CuO/ZnO/Al_2O_3$ nanocatalyst with some other catalysts used for the synthesis of propargylamines

Entry	Catalyst	Condition	Time (h)	Yield (%)[a]	Reference
1	Ag-NPs@mmt	toluene/100°C	2	95	[7]
2	CuSBA-15(42) catalys	toluene/100°C	6	80	[19]
3	Cu salen	solvent-free/80°C	2.5	95	[20]
4	Cu@MOF-5-C	toluene/100°C	6	96	[21]
5	zinc titanate nanopowder	water/100°C	5	93	[25]
6	$Cu/ZnO/Al_2O_3$ nanocatalyst	solvent-free/80°C	1.5	94	This research

[a] Isolated yield.

synthesis of product 1. As seen from Figure 4a, the intensity of some peaks was reduced but the crystal structure of the catalyst remained. Comparison of the SEM image of the used catalyst (Figure 4b) with fresh catalyst showed more agglomeration of the catalyst particles in the used catalyst.

In order to show the quality of the present method, Table 6 compares the results of the synthesis of propargylamine by reaction of benzaldehyde, piperidine and phenylacetylene catalyzed by $Cu/ZnO/Al_2O_3$ nanocatalyst with some of the reported methods in the literature. In contrast with other reported catalysts, $Cu/ZnO/Al_2O_3$ nanocatalyst accelerates the reaction very effectively in less time and gives the corresponding products in high yields under solvent-free conditions. The catalyst can be recovered simply by filtration and can be reused for seven runs without significantly diminishing its activity. Moreover, the reaction in the presence of some other catalysts has been reported in organic toxic solvents and required longer reaction times (Table 6).

4 | CONCLUSION

In conclusion, we have reported the preparation and characterization of an efficient recyclable nanocatalyst of ZnO-supported CuO/Al_2O_3 as well as its application on the synthesis of propargylamines. All reactions were carried out under solvent-free conditions and corresponding products were obtained in high yields. $Cu/ZnO/Al_2O_3$ nanocatalyst showed excellent performance, recyclability and stability on the synthesis of propargylamines. It was simply separated from the reaction mixture and catalyzed reactions up to seven times.

ACKNOWLEDGMENTS

The authors are grateful to the research council of Shahrekord University for the support of this research.

ORCID

Jalal Albadi http://orcid.org/0000-0002-9914-9133

REFERENCES

[1] J. J. Chen, D. M. Swope, *J. Clin. Pharmacol.* **2005**, *45*, 878.

[2] I. Bolea, A. Gella, M. Unzeta, *J. Neural. Transm.* **2013**, *120*, 893.

[3] W. Maruyama, T. Yamamoto, K. Kitani, M. C. Carrillo, M. Youdim, M. Naoi, *Mech. Ageing Dev.* **2000**, *116*, 181.

[4] H. B. Jeon, L. M. Sayre, *Biochem. Biophys. Res. Commun.* **2003**, *304*, 788.

[5] V. A. Peshkov, O. P. Pereshivko, E. V. Van der Eycken, *Chem. Soc. Rev.* **2012**, *41*, 3790.

[6] K. Layek, R. Chakravarti, M. LakshmiKantam, H. Maheswaran, A. Viru, *Green Chem.* **2011**, *13*, 2878.

[7] S. J. Borah, D. K. Das, *Catal. Lett.* **2016**, *146*, 656.

[8] B. Sreedhar, A. S. Kumar, P. S. Reddy, *Tetrahedron Lett.* **2010**, *51*, 1891.

[9] S. D. Dindulkar, B. Kwan, K. T. Lim, Y. T. Jeong, *J. Chem. Soc.* **2013**, *125*, 101.

[10] J. Safaei-Ghomi1, S. H. Nazemzadeh, *Catal. Lett.* **2017**, *147*, 1696.

[11] D. A. Kotadia, S. S. Soni, *Appl. Catal. A: Gen.* **2014**, *488*, 231.

[12] R. Manikandan, P. Anitha, P. Viswanathamurthi, J. G. Malecki, *Polyhedron* **2016**, *119*, 300.

[13] M. Rahman, A. K. Bagdi, A. Majee, A. Hajra, *Tetrahedron Lett.* **2011**, *52*, 4437.

[14] V. Kar-Yan Lo, K. Ka-Yan Kung, M.-K. Wong, C.-M. Che, *J. Organomet. Chem.* **2009**, *694*, 583.

[15] A. Feiz, A. Bazgir, *Catal. Commun.* **2016**, *73*, 88.

[16] R. Magg, A. Bello, C. Oro, G. Sartori, L. Soldi, *Tetrahedron* **2008**, *64*, 1435.

[17] M. Mirabedini, E. Motamedi, M. Z. Kassaee, *Chin. Chem. Lett.* **2015**, *26*, 1085.

[18] J. Safaei-Ghomi, S. H. Nazemzadeh, H. Shahbazi-Alav, *Res. Chem. Intermed.* **2017**, *43*, 7375.

[19] M. Srinivas, P. Srinivasu, S. K. Bhargava, M. L. Kantam, *Catal. Today* **2013**, *208*, 66.

[20] M. Tajbaksh, M. Farhang, H. R. Mardani, R. Hosseinzadeh, Y. Sarrafi, *Chin. J. Catal.* **2013**, *34*, 2217.

[21] S. Cheng, N. Shang, C. Feng, S. Gao, C. Wang, Z. Wang, *Catal. Commun.* **2017**, *89*, 91.

[22] M. Mominul Islam, A. S. Roy, S. Manirul Islam, *Catal. Lett.* **2016**, *146*, 1128.

[23] E. Ramu, R. Varala, N. Sreelatha, S. R. Adapa, *Tetrahedron Lett.* **2007**, *48*, 7184.

[24] K. V. V. Satyanarayana, P. Atchuta Ramaiah, Y. L. N. Murty, M. Ravi Chandra, S. V. N. Pammi, *Catal. Commun.* **2012**, *25*, 50.

[25] C. Mukhopadhyay, S. Rana, *Catal. Commun.* **2009**, *11*, 285.

[26] B. Kodicherla, P. C. Perumgani, M. R. Mandapati, *Appl. Organomet. Chem.* **2014**, *28*, 756.

[27] Q. Zhang, J.-X. Che, W.-X. Gao, J.-C. Ding, H.-Y. Wu, *Appl. Organomet. Chem.* **2010**, *24*, 809.

[28] M. M. Khakzad Siuki, M. Bakavoli, H. Eshghi, *Appl. Organomet. Chem.* **2018**, 32.

[29] J.-P. Shen, C. Song, *Catal. Today* **2002**, *77*, 89.

[30] K. M. Eblagon, P. H. Concepción, H. Silva, A. Mendes, *Appl. Catal. B: Environ.* **2014**, *154*, 316.

[31] F. Ahmadi, M. Haghighi, H. Ajamein, *J. Mol. Catal. B: Chem.* **2016**, *421*, 196.

[32] P. H. Matter, D. J. Braden, U. S. Ozkan, *J. Catal.* **2004**, *223*, 340.

[33] J. Albadi, A. Alihosseinzadeh, M. Jalali, A. Mansournezhad, *Appl. Organomet. Chem.* **2018**, 32.

[34] J. Albadi, M. Jalali, A. R. Momeni, *Res. Chem. Intermed.* **2018**, *44*, 2395.

[35] J. Albadi, A. Alihosseinzadeh, A. Razeghi, *Catal. Commun.* **2014**, *49*, 1.

[36] J. Albadi, A. Alihosseinzadeh, A. Mansournezhad, *Synth. Commun.* **2015**, *45*, 877.

[37] J. Chauhan, N. Shrivastav, A. Dugaya, D. Pandey, *J. Nanomed. Nanotechnol.* **2017**, *8*, 429.

[38] C.-L. Chiang, K.-S. Lin, *Int. J. Hydrogen. Energ.* **2017**, *42*, 23 526.

[39] M. Jalali, A. Aliakbar, *Int. J. Environ. Anal. Chem.* **2015**, *96*, 542.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Sotoudehnia Z, Albadi J, Momeni AR. Solvent-free synthesis of propargylamines catalyzed by an efficient recyclable ZnO-supported CuO/Al_2O_3 nanocatalyst. *Appl Organometal Chem*. 2018;e4625. https://doi.org/10.1002/aoc.4625