Journal of Applied Chemical Research, 10, 1, 29-34 (2016)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Nanocatalyst of ZnO Supported Copper Oxide Catalyzed Chemoselective Synthesis of 1,1-diacetates

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(Received 11 Jun. 2015; Final version received 07 Nov. 2015)

Abstract

In this research, a metal oxide nanocatalyst of ZnO supported copper oxide is reported as a highly efficient recyclable catalyst for the chemoselective synthesis of 1,1-diacetates. The catalyst was synthesized by co-precipitation method and characterized by XRD, BET specific surface area, ESEM, EDS and TEM analysis. A wide range of aldehydes, including aromatic and aliphatic aldehydes were converted into the corresponding 1,1-diacetates. The experimental procedure with CuO-ZnO nanocatalyst is quite straightforward. The catalyst can be recovered by simple filtration and recycled up to 6 consecutive runs without any losing of its efficiency.

Keywords: *CuO-ZnO nanocatalyst, Acetic anhydride, 1,1-diacetate, Chemoselective, Aldehyde.*

Introduction

Among the various procedures available for the protection of carbonyl groups, acetylation has attracted attention of many organic chemists. This considerable attention can be attributed to the stability of the produced 1,1-diacetates against the neutral and basic medium and easy conversion into parent aldehydes. Furthermore, these compounds are useful starting materials and intermediates in organic synthesis [1-2]. Generally, the formation of 1,1-diacetates is carried out by reaction of aldehydes with acetic anhydride in the presence of a suitable catalyst [3-18]. Recently, improvement of nanocatalyst has emerged as an abundant field for research and innovation. Nanocatalysts have appeared as a competitive substitute to usual catalysts because the nanoparticles possess a high surface-to-volume ratio, which enhances their activity and selectivity.

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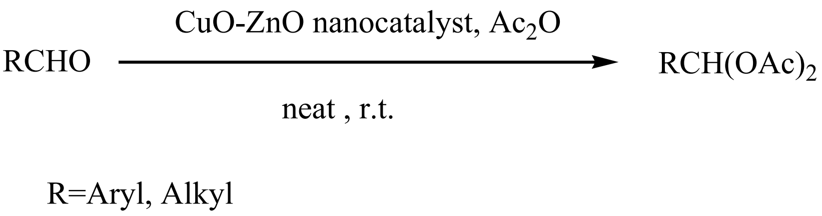
In particular, nanostructure metal oxides have proved to be important to chemists in the laboratory and industry. Nanostructure metal oxides have shown good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier work-up and recyclability [19]. Recently, we have reported the preparation and characterization of $CuO-CeO_2$ nanocomposite and Au/CuO-ZnO nanostructure as well as their catalytic applications in organic synthesis [20-26]. In continuation of our research program to prepare of nanostructure catalysts, herein we wish to report the applicability of novel metal oxide of CuO-ZnO nanocatalyst as an efficient heterogeneous and recyclable catalyst for the chemoselective synthesis of 1,1-diacetates from aldehydes under solvent-free conditions (Scheme 1).



$$RCHO \xrightarrow[\text{neat , r.t.}]{\text{CuO-ZnO nanocatalyst, } Ac_2O} RCH(OAc)_2$$

R=Aryl, Alkyl

Scheme 1. Chemoselective synthesis of 1,1-diacetates catalyzed by CuO-ZnO nanocatalyst.

Experimental

Material and methods

Chemicals were purchased from Merck chemical companies. All products were characterized by comparison of their spectroscopic data (^{1}H NMR, IR) and physical properties with those reported in the literature. Yields refer to isolated pure products.

Preparation of catalyst

The 20 wt% CuO supported on ZnO catalyst was prepared via a co-precipitation method, by adding 0.5 M $Na_2CO_3.H_2O$ solution drop-wise into a mixture of 0.03 M $Cu(NO_3)_2.3H_2O$ and $Zn(NO_3)_3.6H_2O$ solutions under continuous mixing. The obtained suspension was kept at pH=8.5 for 15 min at 65°C, then filtered and washed with warm deionized water. The precipitates were dried 12h at 100°C followed by calcination at 300°C for 3h. In addition, a batch of ZnO support was prepared under this condition for the supplementary tests. The prepared catalyst is entitled as 20CuO/ZnO, where 20 is the amount of CuO weight percent in the catalyst.

Catalyst characterization

The Bruker AXS D8 advanced diffractometer carries out the X-ray diffraction (XRD) analysis to determination of structural properties of the catalyst. The sample was scanned over the range of $2\theta=10-80°$ at a rate of 0.05°/s using Cu Kα radiation (λ = 1.5406 ˚A). The specific surface area of samples determined by nitrogen adsorption-desorption using BET method. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). Prior to BET tests, the samples were degassed under vacuum at 150°C for 2 h. The morphology of the catalyst was investigated comprehensively by field emission scanning electron microscopy (SEM), and high resolution transmission electron microscopy (HRTEM) techniques using a HITACHI S-4160 instrument, as well as JEOL JEM-2100 (200 kV) microscope equipped with an EDS analytical system.

General procedure

A mixture of aldehyde (1 mmol), acetic anhydride (1.2 mmol) and CuO-ZnO nanocatalyst (0.05 g) was stirred under solvent-free conditions at room temperature. After reaction completion (monitored by TLC), the mixture reaction was diluted with acetone and catalyst was recovered by filtration to be reused subsequently. The filtrate was washed with 5% solution of $NaHCO_3$, then with water and dried over $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel afforded the pure product.

Results and discussion

The CuO-ZnO nanocatalyst was prepared by a co-precipitation method. BET surface area, XRD, SEM (Figure 1), TEM (Figure 2), and EDS analysis, were used to characterize the catalyst [27-28].

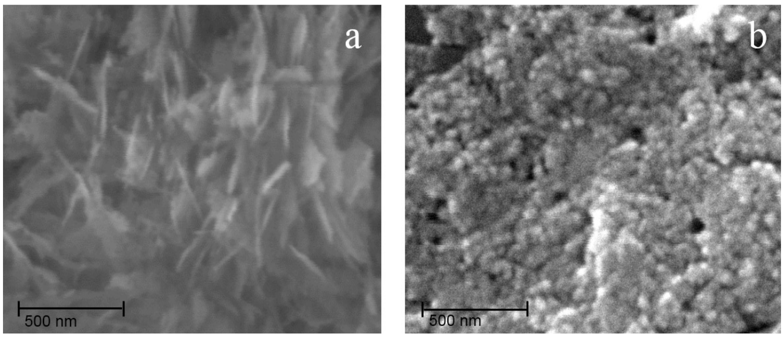


Figure 1. SEM micrographs of (a) ZnO, and (b) CuO-ZnO samples.

Figure 1 displays the SEM analysis of ZnO support and CuO-ZnO nanocatalyst. The ZnO micrograph (Figure 1a) exhibits an aggregation of nano-slit-like particles. However, the morphology of the catalyst after Cu loading is changed drastically. As can be seen, incorporation of Cu into the ZnO support has a significant effect on the morphology of the catalyst. The CuO-ZnO sample exhibits an agglomerate of nanoparticles with a particle size of about 38 nm in diameter.

Figure 2a shows TEM image and the CuO particle size distribution of CuO-ZnO nanocatalyst. More than 200 particles are measured in order to obtain particle size distribution. CuO nanoparticles are highly dispersed on the catalyst surface. Figure 4a-inset picture exhibits the CuO nanoparticle size distribution, by an average CuO particle size of about 4.4 nm. The HRTEM image of CuO-ZnO are shown in Figure 2b.

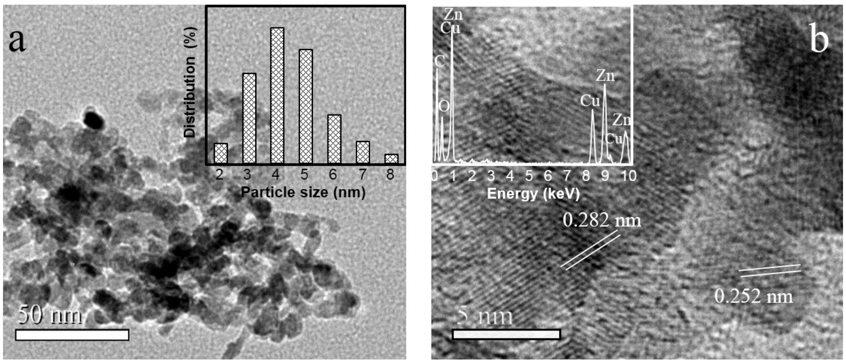


Figure 2. TEM (a), and HRTEM image of CuO-ZnO nanocatalyst (b).

In order to optimize the reaction conditions, the reaction of benzaldehyde and acetic anhydride was selected as the model and its behavior was studied under a variety of conditions. It was found that the best results were achieved by carrying out the reaction of benzaldehyde and acetic anhydride (with 1: 1.2 mol ratios) in the presence of 0.05 g of CuO-ZnO nanocatalyst under solvent-free conditions at room temperature. After optimization of reaction conditions, the reaction of various aromatic aldehydes, including electron-donating and electron-withdrawing groups, were explored (Table 1).

As in Table 1, all substrates were efficiently converted to their corresponding acylals in good to high yields during the short reaction times. The experimental procedure is very simple and the catalyst can be recovered easily by filtration. Moreover, this procedure is environmentally friendly as it does not use any toxic auxiliary or solvent. The versatility of this method is well demonstrated with the fact that both aromatic (Table 1, entries 1-12) and aliphatic (Table 1, entries 13-14) aldehydes afforded their corresponding products in good to high yields. Because of the stability of ketones under the mentioned reaction conditions (Table 2, entries 15-16), the reported method can be used for the chemoselective synthesis of 1,1-diacetates from aldehydes in the presence of ketones (Table 1, entry 17). The activity of the recovered catalyst was also examined under the optimized conditions and it was found that the desired product was obtained in high yields after 1-6 runs (Table 2).

Table 1. Chemoselective synthesis of 1,1-diacetates catalyzed by CuO-ZnO nanocatalyst.

Entry	Aldehyde	Time (min)	Yield (%) [a]	M.p (ºC) [b]	
				Found	Reported
1	C_6H_5CHO	20	93	44-45	44-46[11]
2	2-ClC_6H_4CHO	17	90	50-52	51-52[11]
3	2,4-$Cl_2C_6H_3CHO$	20	91	89-100	89-90[11]
4	4-ClC_6H_4CHO	15	92	82-84	81-82[11]
5	3-$O_2NC_6H_4CHO$	15	90	65-67	65-67[11]
6	4-$O_2NC_6H_4CHO$	10	94	124-125	124-126[11]
7	2-$O_2NC_6H_4CHO$	20	92	90-92	90-91[9]
8	4-BrC_6H_4CHO	20	90	92-94	93-95[11]
9	4-$MeOC_6H_4CHO$	30	90	64-66	65-66[11]
10	4-MeC_6H_3CHO	22	92	81-82	80-82[11]
11	4-HOC_6H_4CHO	45	89	90-92	90-92[11]
12	4-CNC_6H_4CHO	20	91	100-102	100-101[11]
13	$PhCH_2CH_2CHO$	20	80	Oil	Oil[9]
14	$CH_3(CH_2)_4CHO$	30	90	Oil	Oil[9]
15	PhCOPh	60	-	-	-
16	PhCOMe	60	-	-	-
17	C_6H_5CHO + PhCOMe	20	90 -	44-45 -	44-46[11] -

[a] Ioslated pure products. [b] Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature [9,11].

Table 2. Recyclability study of CuO-ZnO nanocatalyst.

Run	1	2	3	4	5	6
Time(min)	20	20	22	25	25	30
Yield (%)[a]	93	92	92	90	90	88

[a] Ioslated pure products.

Conclusion

In conclusion, in this research, we have reported the preparation of novel metal oxide nanocatalyst of CuO-ZnO as an efficient and recyclable catalyst and its catalytic activation for the chemoselsective synthesis of 1,1-diacetates under solvent-free conditions. The catalyst easy to handle and can be recovered 6 runs simply by filtration. Moreover, heterogeneous reaction conditions, high yields of products, short reaction times, ease of work-up and clean procedure will make this procedure useful. We are exploring more applications of CuO-ZnO nanocatalyst for the other types of organic reactions in our laboratory.

Acknowledgements

We are thankful to the Behbahan Khatam Alanbia University of Technology for their partial supports of this work.

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