

Article

Efficient approach for the chemoselective acetylation of alcohols catalyzed by a novel metal oxide nanocatalyst CuO-ZnO



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1. Introduction

Methods for the protection of hydroxyl groups play a significant role in multistep organic syntheses because of the ease with which these transformations can be affected as well as the mild conditions required for the subsequent removal of the corresponding protecting groups [1]. The acetylation of hydroxyl groups is used in a variety of different applications, including organic synthesis and pharmaceutical chemistry, as well as numerous other industrial applications [2]. Although many useful procedures have been reported for the acetylation of hydroxyl groups [3-16], only a few procedures have been reported for the selective acetylation of alcohols in the presence of other functional groups such as phenols and amines. There is therefore still an urgent need for the development of new catalysts capable of affecting the chemoselective acetylation of hydroxyl groups in the presence of other reactive groups under mild conditions.

ABSTRACT

A new method has been developed for the chemoselective acetylation of alcohols with acetic anhydride in the presence of phenols using a novel, recyclable CuO-ZnO nanocatalyst. The catalyst was synthesized using the co-precipitation method and characterized by N₂ adsorption-desorption, X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy dispersion scanning analyses. Furthermore, this catalyst could be recycled up to six times without significant loss in its activity.

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During the course of the last decade, nanocatalysts have emerged as a sustainable and competitive alternative to conventional catalysts. Nanoparticles possess a high surface-to-volume ratio, which enhances their activity and selectivity, while at the same time maintaining the intrinsic features of a heterogeneous catalyst [17]. In particular, the number of practical applications of nano metal oxides as catalysts in organic synthesis has increased considerably during the last 5 years because of the high catalytic activity resulting from their high surface area [18-20]. Nano metal oxides are effective alternatives to conventional solid heterogeneous catalysts, and can be readily synthesized from commercially available materials. Catalysts of this type have proven to be useful to chemists working in both academic and industrial research laboratories because they provide good activation of adsorbed compounds, enhanced reaction rates, high selectivity, facile work-up and good recyclability characteristics, as well as providing eco-friendly reaction

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ROH
$$\xrightarrow{\text{CuO-ZnO nanocatalyst}}$$
 ROAc $\xrightarrow{\text{Ac}_2\text{O}, \text{CH}_2\text{Cl}_2, \text{r.t.}}$

Scheme 1. Chemoselective acetylation of alcohols catalyzed by a CuO-ZnO nanocatalyst.

conditions [21–23]. Because of their attractive properties, nano metal oxides have been used extensively as solid catalysts in a variety of organic reactions.

We previously reported the preparation of several nanocatalysts and an evaluation of their catalytic activity towards a wide variety of organic reactions [24–29]. In continuation of our research in this area, we herein wish to report the preparation of a CuO-ZnO nanocatalyst, and its application for the chemoselective acetylation of alcohols with acetic anhydride at room temperature (Scheme 1).

2. Experimental

2.1. Preparation of catalyst

All of the chemicals used in this study were purchased from Merck (Germany). The catalyst was prepared using a co-precipitation method. Briefly, a Na₂CO₃·H₂O solution (0.5 mol/L) was added to a mixture of 0.03 mol/L Cu(NO₃)₂·3H₂O and Zn(NO₃)₃·6H₂O in water in a drop-wise manner with continuous stirring, and the resulting suspension was held at pH = 8.5 for 15 min at 65 °C. The mixture was then filtered and the filter-cake washed with warm deionized water. The precipitate was subsequently collected and dried at 100 °C for 12 h followed by calcination at 300 °C for 3 h. A batch of the ZnO support was also prepared under these conditions for supplementary tests. The resulting catalyst was named 20CuO/ZnO, where the 20 refers to the weight percentage of CuO in the catalyst.

2.2. Characterization

Products were characterized by a comparison of their spectroscopic data (e.g., NMR and IR) and physical properties with those reported in the literature for the authentic compounds. The IR spectra were recorded on a PerkinElmer 781 spectrophotometer (USA). All of the NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer (Germany). Yields refer to isolated pure products. X-ray diffraction (XRD) analyses were conducted on a Bruker AXS D8 advanced diffractometer to determine the structural properties of the catalyst. Samples for XRD analysis were scanned at 2θ values in the range of 10° – 80° at a rate of 0.05° /s using Cu K_{α} radiation ($\lambda = 1.5406$ Å). The specific surface area of the samples was determined by N2 adsorption-desorption experiments using the BET method. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics, USA). Prior to the tests, samples of the catalyst were degassed under vacuum at 150 °C for 2 h. The morphological characteristics of the catalyst were investigated comprehensively by field emission scanning electron

microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) techniques using a HITACHI S-4160 instrument (Japan) and a JEOL JEM-2100 (200 kV) microscope equipped with an energy dispersion scanning (EDS) analytical system (Japan). A GBC 906AA flame atomic absorption spectrophotometer (Australia) was used to determine the Cu contents of the catalysts.

2.3. General procedure for the acetylation of alcohols

A heterogenous mixture of alcohol (1 mmol), acetic anhydride (1.2 mmol) and the 20CuO-ZnO nanocatalyst (0.05 g) in CH₂Cl₂ (10 mL) was stirred at room temperature. Upon completion of the reaction, as determined by TLC, the mixture was filtered to recover the catalyst. The catalyst was washed with CH₂Cl₂ (5 mL) and then dried at $X \circ C$ for Y h before being used in consecutive runs. The combined organic layers were washed sequentially with 5% (w/v) NaHCO₃ solution and water and then dried over MgSO₄. The solvent was then removed in vacuo to give the crude product as a residue, which was purified by column chromatography over silica gel to afford the pure desired products in high yield.

3. Results and discussion

The catalyst was characterized by XRD, N_2 adsorption-desorption, SEM, TEM, and EDS analyses.

Figure 1 shows the XRD patterns of the pure ZnO and 20CuO-ZnO samples. Several peaks in the XRD patterns were attributed to ZnO over a wide range of 2θ values, including those at 31.7°, 34.3°, 36.3°, 47.3°, 56.4°, 62.8°, 66.2°, 67.8°, 69.0°, 72.5°, and 76.9°, which were characteristics of the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes of ZnO (JCPDS 89-1397). 20CuO-ZnO catalyst revealed diffraction peaks at 2θ = 35.5°, 35.6°, 38.7°, and 38.92°, which were attributed to the (002), (11**1**), (111) and (200) planes of cubic CuO, respectively (JCPDS 05-0661).

The peaks intensities for the ZnO crystals in the 20CuO-ZnO catalyst were lower and broader than those of the ZnO support. This result indicated that the ZnO crystals were less crystalline and smaller in size following the addition of CuO, which could be attributed to the incorporation of CuO into the structure of



Fig. 1. XRD patterns of ZnO (1) and 20CuO-ZnO (2) nanocatalyst.

Table 1

Structural properties of the ZnO and 20CuO/ZnO samples prepared in the current study.

Commis	Crystal s	Crystal size * (nm)		Pore volume	Pore size
Sample	D_{CuO}	$D_{\rm Zn0}$	(m^2/g)	(cm ³ /g)	(nm)
ZnO	_	23	53	0.13	22.6
20CuO/ZnO	8	12	89	0.32	17.9
* Calculated her VDD					

* Calculated by XRD.

ZnO. As shown in Table 1, the ZnO crystals were about 23 and 12 nm in size for the ZnO support and 20CuO-ZnO catalyst, respectively. Furthermore, the average size of the CuO crystals in the catalyst was calculated to be 8 nm using the Scherrer equation. The structural properties of the ZnO and 20CuO/ZnO samples prepared in the current study are presented in Table 1.

The surface area of the ZnO support was determined to be 53 m²/g, which increased to 89 m²/g following the loading of 20 wt% CuO onto the support. As shown in Table 1, the pore volume of the 20CuO-ZnO catalyst increased compared with ZnO following the incorporation of CuO, whereas its pore size decreased. The N₂ adsorption-desorption isomers for the ZnO support and 20CuO-ZnO catalyst are shown in Fig. 2(a). Based on the IUPAC classification, the isotherms for these materials can be categorized as type IV with borderline type II characteristics and a type H3 hysteresis loop, indicating the presence of mesopores with a pore size distribution continuing into the macropore domain (Fig. 2(b)) [30]. Furthermore, type H3 hysteresis are usually only observed on solids containing aggregates or agglomerates of particles, which can lead to slit-shaped pores that are non-uniform in size and shape.

Figure 3 shows the SEM images of the ZnO support and 20CuO-ZnO catalyst. The ZnO micrograph showed that slit-like nanoparticles were aggregating on the surface of the ZnO support. Notably, SEM analysis of the 20CuO-ZnO material revealed that the incorporation of CuO into the ZnO support had a significant effect on the morphology of the catalyst, and the micrograph of the 20CuO-ZnO sample revealed the presence of nanoparticles agglomerates on the surface of the material with an average diameter of about 38 nm.

Figure 4(a) shows a TEM image and the CuO particle size distribution of the 20CuO-ZnO nanocatalyst. More than 200 particles were measured to obtain an accurate particle size



Fig. 3. SEM micrographs of the ZnO (a,b) and 20CuO-ZnO (c,d) samples.

distribution. The CuO nanoparticles were found to be highly dispersed on the catalyst surface. The inset in Fig. 4(a) shows the particle size distribution of the CuO nanoparticles, where the average CuO particle size was determined to be about 4.4 nm. HRTEM image of the 20CuO-ZnO catalyst is shown in Fig. 4(b). The reflections with *d*-spacing values of 0.282 and 0.252 nm correspond to the ZnO (100) and CuO (111) lattice planes, respectively. The EDS results were found to be in good agreement with the nominal Cu loadings from the preparation process.

The reaction of benzyl alcohol with acetic anhydride was selected as a model reaction and conducted under a variety of different conditions in the presence of the 20CuO-ZnO nanocatalyst to determine the optimal conditions for this transformation. The performances of various CuO-ZnO nanocatalysts containing different amounts of CuO (i.e., 5, 10, and 20 wt%) were evaluated for the acetylation of alcohols. The results revealed that the activity of the catalyst increased as the CuO content increased, and that the 20Cu-ZnO catalyst gave the highest yield of 92% over the shortest reaction time (15 min). Optimization experiments revealed that the best results were obtained in the presence of 0.05 g of the 20CuO-ZnO nanocata-



Fig. 2. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of the ZnO and 20CuO-ZnO samples.



Fig. 4. TEM (a) and HRTEM (b) images of the 20CuO-ZnO nanocatalyst.

lyst at room temperature, when the relative molar ratio of the substrate to acetic anhydride was 1:1.2. With the optimized conditions in hand for the acetylation of alcohols, we proceeded to screen a wide range of different alcohols, including benzylic, primary, secondary, and tertiary alcohols. The results of these reactions revealed that all of the alcohols tested were converted to the corresponding acetates in excellent yields under the optimized conditions (Table 2). Benzylic alcohols bearing electron-donating groups were found to be the most reactive of all of the substrates tested and were converted to the corresponding acetates in the shortest reaction times. Furthermore, the reaction proceeded at a slower rate for aromatic substrates bearing an electron-withdrawing group (Table 2, entries 2–7).

The results of these experiments revealed that cyclic and linear alcohols were converted to the corresponding products in suitably high yields (Table 2, entries 14-25). Notably, the tertiary alcohol 1-adamantanol was also successfully acetylated in high yield to give the corresponding acetylated material (Table 2, entry 24). The acetylation of phenols with acetic anhydride was also investigated using the 20CuO-ZnO catalyst. The results revealed that phenols did not react under the optimized reaction conditions (Table 1, entries 26-28). The selectivity of the catalytic system was evaluated using a mixture of alcohols and phenols. For this purpose, an equimolar mixture of benzyl alcohol and phenol was reacted with acetic anhydride in the presence of the 20CuO-ZnO catalyst. The results of this reaction revealed that it proceeded with absolute chemoselectivity towards the benzyl alcohol (Table 1, entry 29). This method could therefore be useful for the chemoselective acetylation of alcohols in the presence of phenols. A plausible mechanism of the reaction is shown in Scheme 2.

The recyclability of a true heterogeneous catalyst is an important performance characteristic. The reaction of benzyl alcohol with acetic anhydride was selected as a model to investigate the recyclability of the 20CuO-ZnO catalyst (Table 3). The results revealed that the catalyst could be reused up to six times without significant loss in its activity.

To highlight the efficiency of this new method, we compared the results obtained with our new 20CuO-ZnO nanocatalyst for the chemoselective acetylation of benzyl alcohol with the results reported for the same reaction using a wide range of different catalysts (Table 4).

Compared with several other catalysts reported for this

Table 2

Chemoselective acetylation of alcohols in the presence of the 20CuO-ZnO nanocatalyst.

Entwo	Substrate	Draduat	Time	Isolated
Entry	Substrate	Product	(min)	yield (%)
1	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CH ₂ OAc	15	92
2	3-NO ₂ C ₆ H ₄ CH ₂ OH	3-NO ₂ C ₆ H ₄ CH ₂ OAc	45	89
3	4-NO ₂ C ₆ H ₄ CH ₂ OH	4-NO ₂ C ₆ H ₄ CH ₂ OAc	60	88
4	2-ClC ₆ H ₄ CH ₂ OH	2-ClC ₆ H ₄ CH ₂ OAc	25	89
5	4-ClC ₆ H ₄ CH ₂ OH	4-ClC ₆ H ₄ CH ₂ OAc	20	92
6	2,4-Cl ₂ C ₆ H ₃ CH ₂ OH	2,4-Cl ₂ C ₆ H ₃ CH ₂ OAc	20	92
7	4-BrC ₆ H ₄ CH ₂ OH	4-BrC ₆ H ₄ CH ₂ OAc	25	88
8	2-MeOC ₆ H ₄ CH ₂ OH	2-MeOC ₆ H ₄ CH ₂ OAc	18	90
9	3-MeOC ₆ H ₄ CH ₂ OH	3-MeOC ₆ H ₄ CH ₂ OAc	15	92
10	4-MeOC ₆ H ₄ CH ₂ OH	4-MeOC ₆ H ₄ CH ₂ OAc	12	93
11	4-Me ₃ C ₆ H ₄ CH ₂ OH	4-Me ₃ C ₆ H ₄ CH ₂ OAc	15	90
12	3-HOC ₆ H ₄ CH ₂ OH	3-HOC ₆ H ₄ CH ₂ OAc	15	93
13	4-HOC ₆ H ₄ CH ₂ OH	4-HOC ₆ H ₄ CH ₂ OAc	10	93
14	C ₆ H ₅ CH ₂ CH ₂ OH	C ₆ H ₅ CH ₂ CH ₂ OAc	20	91
15	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OH	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OAc	20	89
16	C ₆ H ₅ CH(OH)CH ₃	C ₆ H ₅ CH(OAc)CH ₃	30	89
17	CH ₃ CH(OH)CH ₃	CH ₃ CH(OAc)CH ₃	32	90
18	CH ₃ CH ₂ CH ₂ CH ₂ OH	CH ₃ CH ₂ CH ₂ CH ₂ OAc	30	89
	OH	OAc		
19			35	88
20			30	97
20			30	07
	, i	\sim		
21	ОН	OAc	60	86
22		OAc	25	90
22	On	OAc	30	90
23	A-J		50	50
24	\square	\square	70	00
24	ИЛОН	OAc	70	88
25			60	89
	но́	AcO		
26	C ₆ H ₅ OH	C ₆ H ₅ OAc	120	0
27	4-BrC ₆ H ₄ OH	4-BrC ₆ H ₄ OAc	120	0
28	4-MeOC ₆ H ₄ OH	4-MeOC ₆ H ₄ OAc	120	0
29	C6H5CH2OH+C6H5OH	C6H5CH2OAc	15	91

Reaction conditions: alcohol 1 mmol, acetic anhydride 1.2 mmol, catalyst 0.05 g, room temperature, solvent CH_2Cl_2 .



Scheme 2. Proposed mechanism for the acetylation of alcohols in the presence of a CuO-ZnO nanocatalyst.

Table 3

Recyclability study for the 20CuO-ZnO nanocatalyst.

Run	1	2	3	4	5	6
Time (min)	15	15	18	20	22	25
Isolated yield (%)	92	90	90	89	88	87
-						

Reaction conditions: see Table 2.

transformation, the 20CuO-ZnO nanocatalyst promoted the reaction effectively to give the desired product in high yield over a short reaction time. This catalyst is inexpensive and easy to handle, and the acetylation of hydroxyl groups using this catalyst only required a low loading of the catalyst and a small excess of Ac₂O. Furthermore, the results of this study show that this catalyst could be used to achieve the chemoselective protection of alcohols in the presence of phenols. Notably, the catalyst could also be readily recovered by filtration and reused up to six times without any discernible decrease in the yield of the products.

4. Conclusions

We have developed a new, simple, and efficient procedure for the chemoselective acetylation of alcohols with Ac₂O at room temperature using a novel recyclable CuO-ZnO nanocatalyst. This newly developed catalyst could be recycled at least six times without any discernible loss in its activity. Furthermore, the ease of work-up and environmentally friendly nature of this procedure make it a useful and important addition to the currently available methods. Further work towards exploring the application of CuO-ZnO nanocatalysts to other functional group transformations is currently underway in our laboratory.

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Table 4

Comparison of the efficiency of the 20CuO-ZnO nanocatalyst with several other catalysts for the chemoselective acetylation of benzyl alcohol.

Entry	Catalyst	Acylation agent	Time (min)	Isolated yield (%)	Ref.
1	Cu-BDC	Ac ₂ O (2 mmol)	1440	87	[5]
2	ZnAl ₂ O ₄ nanoparticles	Ac ₂ O (10 mmol)	18	90	[11]
3	ZnO	RCOCl (12 mmol)	35	93	[6]
4	Nano ZnO	CH₃COOH (5 ml)	180	81	[16]
5	20CuO-ZnO nanocatalyst	Ac ₂ 0 (1.2 mmol)	15	92	this work

Graphical Abstract Graphical Abstract Chin. J. Catal., 2015, 36: 308–313 doi: 10.1016/S1872-2067(14)60259-X Efficient approach for the chemoselective acetylation of alcohols catalyzed by a novel metal oxide nanocatalyst CuO-ZnO Jalal Albadi *, Amir Alihoseinzadeh, Mehdi Mardani Behbahan Khatam Alanbia University of Technology, Iran; University of Tehran, Iran CuO-ZnO nanocatalyst ROAc Ac₂O, CH₂Cl₂, r.t. A new CuO-ZnO nanocatalyst has been developed as an efficient recyclable catalyst for the chemoselective acetylation of alcohols.

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