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Chemoselective Synthesis of Pentaerythritol Diacetals Catalyzed by CuO-CeO$_2$ Nanocomposite under Solvent-free Conditions

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Abstract

CuO-CeO$_2$ nanocomposite is reported as a green recyclable catalyst for the chemoselective synthesis of pentaerythritol diacetals from aromatic aldehydes under solvent-free conditions. The catalyst was synthesized by co-precipitation method and characterized by XRD, BET specific surface area, FESEM and EDS analysis. This procedure provides some advantages such as simple work-up, clean procedure, short reaction times and high yields of the products.

Key words: *CuO-CeO$_2$ nanocomposite, Nanocatalyst, Pentaerythritol diacetals, Aromatic aldehyde, Chemoselective.*

Introduction

Pentaerythritol diacetals are a series of useful organic compounds. They have been used as plasticizers and vulcanizer, active physiologically substance, and potential protective groups for aldehydes and ketones. Also, these compounds are important in synthetic carbohydrate and steroid chemistry [1-3]. Therefore, synthesis of pentaerythritol diacetals has been well investigated. Various catalysts such as strong protic acids and Lewis acids have been employed for the synthesis of these compounds [4-13]. However these methods are not entirely satisfactory and suffer from one or more of following disadvantages such as using toxic solvent, corrosive acid, long reaction times, low yields, tedious work-up, effluent pollution and non-recyclable catalysts. Therefore, there is a demand for the developing an efficient and convenient catalytic method for the reaction using inexpensive and non-polluting

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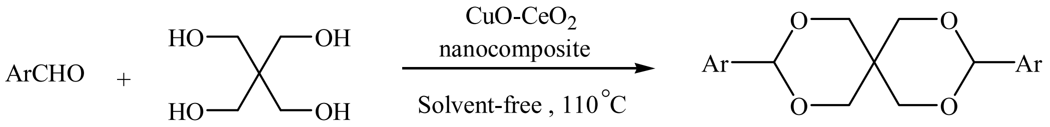
reagent. In recent years, nanocrystalline oxides have proved to be useful to chemists in the laboratory and in industry due to the good activation of adsorbed compounds, reaction rate enhancement, selectivity, easier work-up, recyclability of the catalyst and the eco-friendly reaction conditions [14-18]. Also, the practical applications of nanocomposite metal oxides have increased in organic synthesis due to their high catalytic activity resulting from their high surface area [19-20]. Recently, we have reported the preparation $CuO-CeO_2$ nanocomposite and its catalytic activity for the synthesis of xanthenes derivatives [21]. This catalyst is safe, easy to handle and environmentally benign. In continuation of these studies and our studies on the synthesis of pentaerythritol diacetals [22], herein, we wish to report the applicability of $CuO-CeO_2$ nanocomposite as a green recyclable catalyst for the chemoselective synthesis of pentaerythritol diacetals from aromatic aldehydes under solvent-free conditions (Scheme 1).



Scheme 1. Synthesis of pentaerythritol diacetals catalyzed by $CuO-CeO_2$ nanocomposite.

Experimental

Material and methods

Chemicals were purchased from Merck and Fluka 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. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. The NMR spectra were recorded on a Bruker Advance 500 MHz. Melting points were recorded on a Bransted Electro thermal 9100BZ melting point apparatus. Yields refer to isolated pure products.

Catalyst preparation

$CuO-CeO_2$ nanocomposite was prepared by co-precipitation method using aqueous solution of cerium and copper nitrates and drop-wise KOH as precipitant agent under vigorous mixing while temperature and *p*H was fixed at unique values. Then acquired sample was filtered, washed and calcined to obtain final catalyst for using in the synthesis of pentaerythritol diacetals.

Catalyst characterization

The catalyst structure characterization was performed by X-ray Powder diffraction (XRD), using a Bruker AXS D8 advanced diffractometer equipment with CuKα radiation (λ=1.5406A°). The Debye-Scherrer equation is used to determine average crystallite size of nanoparticles. Emission scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) carried out by a Hitachi S4160 instrument to see the morphology, evaluation of cluster size and metal composition of the catalyst. BET specific surface area was estimated from the N2 adsorption/desorption isotherms, measured at 77 °K using a Quantachrome CHEMBET-3000 instrument. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer

General procedure

A mixture of aldehyde (2 mmol), pentaerythritol (1 mmol) $CuO-CeO_2$ nanocomposite (0.07 g) was heated in an oil bath (100 ºC) for the appropriate time (Table 1). The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled and ethylacetate (10ml), was added and the catalyst was recovered by filtration to be reused subsequently. The catalyst washed with ethyl acetate, dried and stored for another consecutive reaction run. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol afforded the pure products in good to high yields. The spectral data for the selected compounds are as follow:

Table 1, entry 5: IR (KBr) ν_{max}/cm^{-1}: 3100, 2950, 1560, 1520, 1480, 1355, 1205, 1085. ^1H NMR ($CDCl_3$, 500 MHz), δ (ppm): 3.664 (d, 1H,), 3.793-3.867 (dd, 1H,), 3.844 (d,1H,), 4.754 (d, 1H,), 7.506 (t, 1H,), 7.635 (t, 1H, Ar), 7.862 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 32.50, 71.57, 71.05, 102.19, 125.94, 128.37, 129.16, 137.85, 164.82.

Table 1, entry 6: IR (KBr) ν_{max}/cm^{-1}: 3110, 2950, 1570, 1525, 1480, 1350, 1200, 1080. ^1H NMR ($CDCl_3$, 250 MHz), δ (ppm): 3.66 (d, 1H, *J*= 11.5), 3.84-3.90 (m, 2H), 4.88 (d, 1H, *J*=11.25 Hz), 5.418 (s, 1H), 7.20-7.53 (3, 4HAr). ^{13}C NMR ($CDCl_3$, 75 MHz), δ (ppm): 32.51, 71.61, 71.06, 102.29, 126.04, 128.38, 129.15, 137.87, 164.86.

Table 1, entry 8: IR (KBr) ν_{max}/cm^{-1}: 3000, 2900, 1600, 1580, 1200, 1180, 1080. ^1H NMR ($CDCl_3$, 500 MHz), δ (ppm): 3.30 (d, 2H, *J*= 11.65), 3.803-3.832 (dd, 4H, $2CH_2$, J_2=2.92 Hz), 4.794 (d, 2H, CH_2, J=11.41 Hz), 5.411 (s, 2H, 2CH), 7.351 (d, 4H, J= 8.4 Hz, Ar), 7.501 (d, 4H, J= 8.38 Hz, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 32.30, 71.34, 102.51, 126.15, 129.16, 138.99, 164.11.

Table 1, entry 10: IR (KBr) ν_{max}/cm^{-1}: 3000, 2900, 1560, 1480, 1200, 1080. ^1H NMR ($CDCl_3$, 250 MHz), δ (ppm): 2.36 (s, 6H, 2CH3), 3.63 (d, 2H, $2CH_2$,), 3.81-3.87 (dd, 4H, $2CH_2$), 4.85 (d, 2H, $2CH_2$,), 5.44(s ,2H, 2CH), 7.21 (d, 4H, Ar), 7.37 (d, 4H, Ar). ^{13}C NMR (CDCl3, 75 MHz), δ (ppm): 12.30, 31.30, 71.04, 102.13, 125.92, 129, 138.90, 163.81.

Results and discussion

The catalyst was synthesized by co-precipitation method. The structure of catalyst characterization was performed by XRD, BET specific surface area, ESEM (Figure 1), and EDS analysis [21].

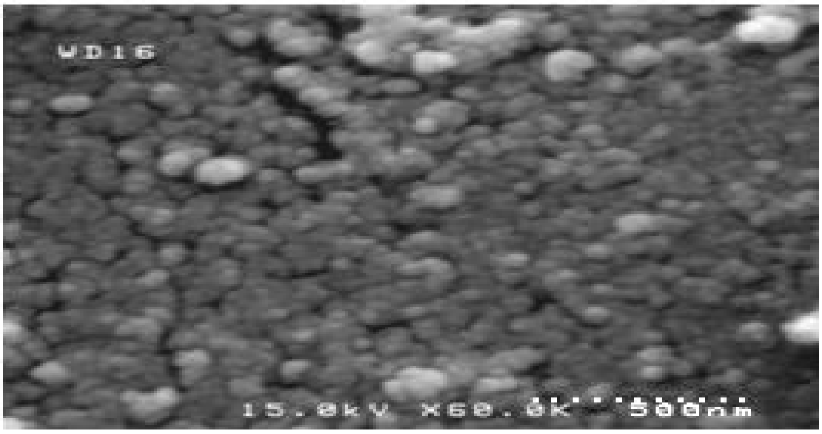
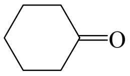


Figure 1. ESEM image of the CuO–CeO$_2$ nanocomposite catalyst.

The reaction was optimized using benzaldehde and pentaerythritol as a model reaction. The best results were obtained with 1 mmole of benzaldehde and 2 mmol of pentaerythritol in the presence of 0.07 g of CuO-CeO2 nanocomposite at 100 °C under solvent-free conditions. In order to generalize the optimize conditions, a wide range of various aromatic aldehydes were successfully reacted to afford the desired products. As shown in Table 1, aromatic aldehydes containing electron-withdrawing groups (entries 4-8) accelerate the reaction, compared to the electron-donating groups (entries 9-13). It is noteworthy that aliphatic aldehydes and ketones did not undergo the reaction under the same conditions. For instance, when an equimolar mixture of benzaldehyde and cyclohexanone was allowed to react with pentaerythritol in the presence of CuO-CeO2 nanocomposite, only pentaerythritol diacetals of benzaldehyde was obtained and cyclohexanone was recovered (Table 1). Therefore our procedure can be used for the chemoselective synthesis of pentaerythritol diacetals from the aromatic aldehydes in the presence of ketones or aliphatic aldehdes (Table 1, entry 16, 17). The activity of the recovered catalyst was also studied under the optimized conditions.

Table 1. CuO-CeO$_2$ nanocomposite catalyzed chemoselective synthesis of pentaerythritol diacetals.

Entry	Substrate	Time (min)	Yield (%)[a]	M.p .(°C)[b]	
				Reported	Found
1	PhCHO	20	95	153-154	152-154
2	2-ClPhCHO	20	93	140-141	141-142
3	3-ClPhCHO	25	92	120-122	121-123
4	4-ClPhCHO	20	93	198-200	197-199
5	2-NO$_2$PhCHO	20	93	163-165	163-165
6	3-NO$_2$PhCHO	20	92	183-185	184-186
7	4-NO$_2$PhCHO	12	94	226-228	226-228
8	4-BrPhCHO	20	89	221-223	222-224
9	3-MePhCHO	35	91	189-191	190-191
10	4-MePhCHO	40	91	209-211	210-212
11	4-MeOPhCHO	60	88	180-182	180-182
12	4-HOPhCHO	80	88	109-111	109-110
13	4-Me$_2$NPhCHO	60	88	223-224	223-224
14		60	0 [c]	---	111-113
15	Ph$_2$CO	60	0 [c]	---	163-164
16	PhCHO + Ph$_2$CO	30	100 [d] + 0 [d]	153-154	152-154
17	PhCHO + MeCHO	30	100 [d] + 0 [d]	153-154	152-154

[a]Ioslated yield. [b] Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature [22]. [c]Starting material recovered intact. [d]Conversion.

To investigate these properties, the reaction of benzaldehyde with pentaerythritol was selected as a model (Table 2). The results showed that the catalyst could be easily recovered from the reaction mixture by simple filtration. After reaction completion, it was washed with ethylacetate, dried and stored for another consecutive reaction run. This process repeated for 5 runs and no appreciable yield decrease was observed.

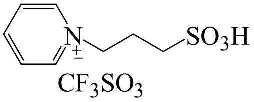
Table 2. Recyclability study of $CuO\text{-}CeO_2$ nanocomposite.

Run	1	2	3	4	5
Tim (min)	20	20	25	30	40
Yield (%)[a]	95	94	93	93	90

[a] Ioslated yield.

In order to show the efficiency of this method, Table 3 compares the results from the synthesis of pentaerythritol diacetals from benzaldehyde in the presence of $CuO\text{-}CeO_2$ nanocomposite and some of other catalysts. In comparison with previously reported methods, our new catalyst promotes the reaction very effectively, gives the desired product in very short times and products gave in good to high yields. Very low amount of the catalyst is needed. This catalyst is safe, easy to handle and its preparation is simple. It can be recovered simply by filtration and can be recycled in the next runs without significant decrease in its activity. Moreover, our procedure is environmentally friendly as it does not use any toxic auxiliary or solvent.

Table 3. Comparison of the efficiency of $CuO\text{-}CeO_2$ nanocomposite in the synthesis of pentaerythritol diacetal from benzaldehyde, with other reported methods.

Entry	**Reagent**	**Conditions**	**Time (min)**	**Yield (%)**[a]	**Reference**
1	$H_3PW_{12}O_4$	Toluene/reflux	120	92	11
2		100 °C	90	91	13
3	NH_2SO_3H	Toluene/110 °C	240	96	9
4	$H_3PW_{12}O_4$ suported on MCM-41	Toluene/reflux	120	92	12
5	$FeSO_4$	Benzene/reflux	90	97	10
6	$P_4VPy\text{-}CuI$	Solvent-free/110 °C	25	95	23
7	$CuO\text{-}CeO_2$ nanocomposite	Solvent-free/100 °C	20	95	This work

[a] Ioslated yield.

Conclusion

In conclusion, we have developed a new, green and highly efficient procedure for the chempselective synthesis of pentaerythritol diacetals catalyzed by $CuO\text{-}CeO_2$ nanocomposite under solvent-free conditions. This catalyst can promote the yields and reaction times over 5 runs without significant loss of its activity. Moreover, heterogeneous reaction conditions, high yields of products, short reaction times, ease of work-up and clean procedure, will make this procedure a useful addition to the available methods

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