



Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Adv. Synth. Catal. 10.1002/adsc.201901133

Link to VoR: http://dx.doi.org/10.1002/adsc.201901133

10.1002/adsc.201901133

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Copper-Impregnated Magnesium-Lanthanum Mixed Oxide: A Reusable Heterogeneous Catalyst for Allylation of Aldehydes and Ketones

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201#######.((Please delete if not appropriate))

Abstract: Copper-impregnated magnesium-lanthanum mixed oxide [Cu(II)/Mg-La] was used as catalyst in synthesis of homoallylic alcohols from aldehydes and ketones using allyltributylstannane as the allylating source. The present protocol provides a great application potential for the synthesis of corresponding allyl alcohols with excellent yields and selectivity. The catalyst exhibits broad functional group compatibility with a variety of substituted aldehydes and ketones to furnish the desired products in high yields under heterogeneous conditions.

Importantly, the heterogeneous catalyst could be recovered from the reaction mixture by centrifugation and used up to three cycles.

Keywords: aldehydes; ketones; allylation; copper, magnesium-lanthanum mixed oxide; homoallylic alcohols: heterogeneous catalysis; reusability.

Introduction

Allylation of carbonyl compounds is an important synthetic organic transformation since in this reaction, a new carbon-carbon bond is formed along with the introduction of hydroxyl functionality.^[1] Moreover, the double bond of the allylic moiety can further undergo a number of synthetically useful transformations such as hydrogenation, ozonolysis, hydroboration, cycloaddition, epoxidation, dihydroxylation, hydroformylation, hydration, etc.^[2] The general practice for the preparation of homoallylic alcohols involves nucleophilic addition of an allylic metal reagent to carbonyl compounds.^[3-7] However, the Barbier reaction^[8] is an alternative method for the synthesis of homoallylic alcohols, the reaction of a carbonyl compound with an organic halide in the presence of magnesium metal. Different transition metal catalyzed Barbier reactions in aqueous medium are well documented in the literature.^[9-18] From nonperspective, heterogeneous catalytic aqueous process has advantages over homogeneous in view of its ease of handling, simple work-up and recoverability.^[19] Now a days most of these methods are used even on an industrial scale as the methods offer good yield and selectivity. The main disadvantage of the homogeneous catalysis is contamination of the metal in the product, which is unacceptable e.g. in pharmaceutical syntheses. This induces a considerable research effort to develop new heterogeneous catalytic systems. Unfortunately, in these reactions, the use of zero-valent metals causes metal oxide or hydroxide precipitation on the surface of the metal which leads to termination or increased duration of the reaction. Furthermore, some zero-valent metals are too reactive and

significant amount of by-products such as pinacol are produced. Roy et al. reported the first example of carbonyl allylation in heterogeneous media involving SnO and catalytic Cu₂O^[20] while Kantam and co-workers had reported the Cu-exchanged fluorapatite catalyst for the allylation of aldehydes with allyltributylstannane or allyltrimethylsilane.^[21] Recently, magnesium-lanthanum mixed oxide (Mg-La mixed oxide) has found extensive applications as a heterogeneous catalyst for various organic transformations. Figueras and co-workers examined the direct condensation of alcohols^[22] and Michael addition reactions^[23] over highly basic Mg-La mixed oxide catalyst. The catalytic activity of the Mg-La mixed oxide was demonstrated in the condensation of aldehydes and imines with ethyl diazoacetate using water as a solvent.^[24] Different transition-metals impregnated Mg-La mixed oxide catalysts have also been developed and used as effective heterogeneous catalysts in various organic transformations.^[25] In search for a suitable heterogeneous catalyst for allylation of carbonyl compounds, we envisaged that copper impregnated magnesium-lanthanide mixed oxide, Cu(II)/Mg-La could exhibit interesting catalytic activities.

Herein, we disclose efficient allylation of aldehydes and ketones enabled by Cu(II)/Mg-La mixed oxide catalyst without the need of expensive ancillary ligands or additives, demonstrating the versatility of the reaction (**Scheme 1**) with the following advantages: high yields, shorter reaction time, low costs, and simplicity in process. The fresh and used Cu(II)/Mg-La mixed oxide catalysts were characterized by XPS and XRD analysis and a plausible reaction mechanism is discussed.



Scheme 1. Allylation of aldehydes and ketones using Cu(II)/Mg-La mixed oxide catalyst.

Results and Discussion

Characterization

The Mg-La mixed oxide was synthesized by coprecipitation of magnesium and lanthanum nitrate as described in the literature.^[25a] Cu(II)/Mg-La mixed oxide was prepared by impregnation method. The BET surface area was measured by N_2 adsorption at 77 K and revealed values of 35.9 m²g⁻¹ for Mg-La mixed oxide and 29.0 m²g⁻¹ for Cu-loaded Mg-La mixed oxide. Copper content of the catalyst was determined by ICP-OES analysis and found to be 6.1 wt%.

The X-ray photoelectron spectroscopic analysis (XPS) of freshly prepared Cu(II)/Mg-La catalyst was carried out to evaluate the oxidation state of copper on Cu(II)/Mg-La catalyst (**Fig. 1**). The binding energies of Cu(II)/Mg-La were observed at 934.48 and 954.69 eV that correspond to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ binding energy peaks due to copper in +2 oxidation state.



Fig. 1: XPS of A) fresh and B) used Cu(II)/Mg-La catalyst.

XRD patterns of the fresh and used Cu(II)/Mg-La mixed oxide catalysts revealed the presence of both $La_2O_2(CO_3)_2$ and CuO phases (Fig. 2).



Fig. 2: XRD of (A) fresh and (B) used Cu(II)/Mg-La catalyst.

Diffraction peaks at 2θ = 13.1, 22.8, 29.5° are attributed to the lanthanum oxide carbonate phase^[25h] and that at 2θ = 32.48, 35.5, 38.7, 46.2, 48.8, 53.5, 58.3, 61.5, 66.2, 68.2° are due to copper in oxide form.^[25i]

Optimization of reaction conditions:

Optimization of reaction conditions was performed using 4-nitrobenzaldehyde as a model substrate. 20 mg of Cu(II)/Mg-La mixed oxide catalyst (6.1 wt% mmol of 4-nitrobenzaldehyde Cu). 1 and allyltributyltin (1.2 mmol). Initially, the effects of different solvents on the product yields were examined. The reaction was performed in different solvents such as dichloromethane (DCM), THF, methanol, acetonitrile, toluene, water, DMSO and DMF (Table 1). In DCM solvent, the yield of the desired product, 1-(4-nitrophenyl)but-3-en-1-ol was low (Table 1, entry 1), polar solvents such as THF, methanol, acetonitrile, DMSO and DMF furnished moderate to good yields of the product (Table 1, entries 2, 3, 4, 8 and 9). In an effort to further improve the yield, the reaction was carried out at 65°C in acetonitrile. Gratifyingly, the product was obtained in excellent yields of 94% with shorter reaction duration (Table 1, entry 5). Moreover, moderate product yields were obtained using water as a solvent (Table 1, entry 7).

Table 1. Screening of reaction parameters.^[a]

СНО			I	
	SnBu ₃	Cu(II)/Mg-La, 1.9 mol % of Cu		
	/ ~	Solvent	-	
NO ₂				NO ₂
1a	2a			3b
Entry	Solvent	Temp (°C)	Time (h)	Yield (%) ^[b]
1	DCM	40	24	20
2	THF	65	24	82
3	Methanol	60	24	68
4	Acetonitrile	RT	24	48
5	Acetonitrile	65	05	94
6	Toluene	100	24	85
7	Water	100	24	60
8	DMSO	80	24	65
9	DMF	100	24	70

^[a]Reaction conditions: 4-Nitrobenzaldehyde (1 mmol), allyltributylstannane (1.2 mmol), Cu(II)/Mg-La (20 mg, 1.9 mmol% of Cu), solvent (3 mL). ^[b]Isolated yields. The structure of the product was confirmed by ¹H NMR and Mass spectroscopic analysis (detailed characterization of the products are provided in supporting information).

A variety of commercially available copper salts such as CuI, Cu₂O, CuCl, CuCl₂.2H₂O, CuO, Cu(acac)₂.H₂O and Cu-bronze were screened in allylation reaction using acetonitrile as a solvent at 65 °C to compare the catalytic activity with Cu(II)/Mg-La mixed oxide catalyst (Table 2, entries 1, 2, 3, 4, 5, 6 and 7). Though moderate to good yields of the desired products were obtained, a longer reaction duration was needed (24 to 30 hours). The activity of synthesized catalysts such as $Cu(II)/Al_2O_3$, $Cu(0)/Al_2O_3$, $Cu(II)/Fe_3O_4$, Cu(0)/Fe₃O₄ were also compared in this reaction (Table 2, entries 8, 9, 10, 11) and moderate to good yields of the desired product were observed.





^[a]Reaction conditions: 4-Nitrobenzaldehyde (1 mmol), allyltributylstannane (1.2 mmol), catalyst, acetonitrile (3 mL) at 65 °C. ^[b]Isolated yields.

Significantly, lower yield of the product was obtained when only Mg-La mixed oxide was used as a catalyst (Table 2, entry 12) while Cu(II)/Mg–La furnished excellent yields with short reaction time (Table 2, entry 13). It is important to note that

in the absence of any catalyst, the reaction failed to produce any product (Table 2, entry 14).

The activities of different allylating reagents were also tested and the results are summarized in (Table 3). It can be seen from table 3, the rate of the reaction is highly dependent on the choice of the allylating agent. Both tetraallyltin and allyl tributylstannane afforded excellent yields in short period of time (Table 3, entry 1& 2). However, allylsilanes such as allyltrimethylsilane and tetraallylsilane furnished low yields of the product (Table 3, entries 3 and 4). Allyltributylstannane was further used in the allylation reaction taking into account the lower price and safety aspect of the reagent.





Entry	Allylating reagent	Time (h)	Yield (%) ^[b]
1	Sn (3	92
2	Bu ₃ Sn	5	94
3	Me ₃ Si	24	40
4	Si (24	NR

^[a]Reaction conditions: 4-Nitrobenzaldehyde (1 mmol), allylating reagent (1.2 mmol), Cu(II)/Mg-La (20 mg, 1.9 mmol% of Cu), acetonitrile (3 mL) at 65 °C. ^[b]Isolated yields. NR= No reaction.

Next, the catalytic activity of Cu(II)/Mg-La mixed oxide was tested in the allylation of different structurally divergent aldehydes possessing a wide range of functional groups to understand the scope and the generality of the developed process. The results are summarized in Table 4. Simple benzaldehyde produced the corresponding product in good yields (Table 4, entry **3a**). Nitro substituted benzaldehydes furnished the desired product in excellent yields without reduction of the nitro group (Table 4, entries **3b-d**).

Table 4: Study of substrate scope in the allylation of aldehydes catalyzed by Cu(II)/Mg-La mixed oxide.^[a]





^[a]Reaction conditions: Aldehyde (1 mmol), allyltributylstannane (1.2 mmol), 1.9 mmol% of Cu, acetonitrile (3 mL) at 65 °C. ^[b]Isolated yields.

Remarkably, other functional groups such as cyano and methoxy were well tolerated and the corresponding allylic alcohols were obtained in satisfactory yields (Table 4, entries **3e–i**).

Fluro-, chloroand bromosubstituted benzaldehydes smoothly underwent the allylation reaction furnishing good yields of the product (Table 4, entries **3j-m**). Importantly, in these reactions, no dehalogenated homoallylic products were observed. In general, electron-donating group products (Table 4, entry **3n**) on the aromatic ring furnished lower yields of desired products compared to electron-withdrawing groups. However, allylation was slow with bulky substrates such as 1naphthaldehyde and 2-naphthaldehyde when compared with other aromatic aldehydes (Table 4, entries 30-p).

Among the various aldehydes tested, hetero aldehydes such as 2-pyridine aromatic carboxaldehyde, 3-pyridine carboxaldehyde and 4pyridine carboxaldehyde produced good yields (Table 4, entries **3q-s**). Notably, in the allylation of β-unsaturated aldehydes such as α, cinnamaldehyde good yield of the desired product was obtained (Table 4, entry 3t). Significantly, more challenging aliphatic aldehydes such as hexanaldehyde gave satisfactory yields (Table 4, entry 3u).

Encouraged by the results obtained from Table 4, we planned to examine the catalytic activity of Cu(II)/Mg-La mixed oxide in the allylation of more challenging and difficult carbonyl substrates ketones.

Initially, we performed the reaction of simple acetophenone ketone. such as with allyl tributylstannane (Table 5, entry 5a). Remarkably, a moderate yield of the desired tertiary homoallylic alcohol was obtained using Cu(II)/Mg-La (20 mg, 1.9 mmol % of Cu) as catalyst, allyl tributylstannane as allylating reagent and acetonitrile as solvent at 65 °C. Moreover, chloro-, hydroxyland bromosubstituted nitro-, acetophenones (5b-d)provided the corresponding desired products in moderate to good yields (Table 5). The allylation reaction was also attempted using alkyl ketones, but it failed to furnish the desired allylic product.

Table 5: Study of substrate scope in the allylation of ketones catalyzed by Cu(II)/Mg-La mixed oxide.^[a]



Spurred with the success of allylation of aldehydes and ketones with allyltributylstannane, a gram-scale synthesis of 1-(4-nitrophenyl)but-3-en-1-ol was carried out under the standard reaction conditions. Pleasingly, homoallyl alcohol **3b** was obtained in satisfactory yield of 82 % when the reaction was carried out at 20.0 mmol scale (**Scheme 2**).



Scheme 2. Allylation of 4-nitrobenzaldehyde in gram-scale reactions.

Recyclability of the catalyst

The recyclability of the catalyst was examined using 4-nitrobenzaldehyde with allyl tributylstannane at 65 °C in acetonitrile and the results are shown in Fig. 3. The activity graph illustrates that the catalyst can be used for four consecutive cycles. The observed decrease in the conversion (%) from the cycles could be due to the clogging of some of the catalytic active sites with organic reagents during the course of the reaction and not due to leaching of active metal from the support (see Experimetal Section). In the recyclability studies, catalyst was recovered by centrifugation and washed with distilled water, airdried and reused directly for the next cycle without any further purification. The ICP-OES analysis showed that the Cu content in the fresh and in the 3rd cycle are 6.1% and 5.6 wt%, respectively.



Fig. 3: Recyclability test over Cu(II)/Mg-La catalyst.

Plausible reaction mechanism

In order to get insight into the mechanism of the allylation reaction catalyzed by Cu(II)/Mg-La, we first investigated the role of tin species in the allylation of aldehydes. In a controlled experiment, Cu(II)/Mg-La mixed oxide and allyltributylstannane were refluxed in acetonitrile. The solid material was filtered off, washed with THF and vacuum dried to get surface transient organometallic (STO) intermediate. Interestingly, on heating STO intermediate with 4-nitrobenzaldehyde in acetonitrile yielded the corresponding homoallylic alcohol. But, our efforts to isolate the intermediate along with aldehydes failed. At this juncture, we speculate that the plausible mechanism of allylation may be undergoing formation of copper (IV) species from the oxidation of Cu(II)/Mg-La mixed oxide by allyltributylstannane. However, we are not sure whether the active catalytic species is copper (IV) or not. In the recent reports, Kar and coworkers have postulated Cu (IV) as a possible intermediate in oxidation catalysis.^[26] The authors claim is based on the series of experimental characterization including electrochemistry, UV/Vis/NIR, EPR, XANES measurements, and DFT calculations which indicates the existence of +IVoxidation state of Cu.^[25c] It is indeed true that the observation of the oxidation state + IV is very rare in copper chemistry.

To investigate the oxidative addition step, the mixture of copper(II)/magnesium-lanthanum mixed oxide and allyltributylstannane was refluxed in acetonitrile and solid material was filtered off, washed with acetonitrile and vaccume dried. The trapped intermediate was subjected to TGA-DTA-MS analysis (**Fig. 4**). The observed m/z values of the evolved gas fragments are 26, 41 and 43 a.m.u. corresponding to C_2H_2 , C_3H_5 , and C_3H_7 , respectively. The m/z value corresponding to allyl tributylstannane was not detected, which suggests that the mass fragmentation occurred during pyrolysis of intermediate.



Fig. 4: TGA-DTA-MS thermogram of STO.

Further, the reaction of trapped intermediate with 4nitrobenzaldehyde yielded the corresponding desired homoallylic alcohol. At this stage, we assume that the reaction path may follow the Cu(II) to Cu (IV) oxidation state. Further investigation in this direction is in progress.

Supporting Information

Characterization of all compounds with ¹H and ¹³C NMR spectra are available in the Supporting Information.

Conclusion

We have developed a simple and efficient method for the allylation of aldehydes and ketones using copper(II)/magnesium-lanthanum mixed oxide as heterogeneous and reusable catalyst. The catalyst preparation involves simple synthetic steps and can be scaled-up to a large scale. The simple allylation methodology, easy recovery, and reusable catalytic systems are expected to contribute to the development of benign allylation processes for a variety of aldehydes and ketones.

Experimental Section

Preparation of catalyst

The Mg-La mixed oxide was obtained by coprecipitation of magnesium nitrate [Mg(NO₃)₂·6H₂O] and lanthanum nitrate [La(NO₃)₃·6H₂O] (0.39 mol and 0.13 mol respectively, in 0.5 L water for an atomic ratio Mg/La=3) at a constant pH 10.0 using a mixture of KOH (1 mol) and K₂CO₃ (0.26 mol) in 0.52 L of distilled water. The gel was washed until the pH reached neutral followed by oven dried at 120 °C subsequently calcined in static air at 650 $^{\circ}$ C/5 h at a ramping rate of 10 $^{\circ}$ C min⁻¹. The copper impregnated Mg-La mixed oxide catalyst was synthesized by an impregnation method. Mg-La mixed oxide (1.5 g) was suspended in 150 mL of aqueous Cu(NO₃)₂·3H₂O (0.362 g, 1.5 mmol) solution and stirred at 25 °C for 12 h under a nitrogen atmosphere. The solid was filtered, washed with distilled water, dried at 100 °C and calcined at 250 °C for 5 h to obtain the grey colored powder Cu (II)/Mg-La catalyst.

Typical procedure for the allylation of 4nitrobenzaldehyde with allyltributylstannane

A mixture of 4-nitrobenzaldehyde (1 mmol), allyl tributylstannane (1.2 mmol) and Cu (II)/Mg-La (20 mg) in 3 mL of acetonitrile was stirred at 65 °C for 5 h. The reaction was monitored by TLC (n-hexane-ethyl acetate, 9:1). After completion of the reaction as determined by TLC, the reaction mixture was cooled to room temperature, centrifuged to separate the solid catalyst and the catalyst was washed 3 times with ethyl acetate (3x10mL). The combined organic layer was treated with saturated aqueous solution of NH₄Cl. Next, distilled water was added and the organic layer was separated. The aqueous layer was back extracted with ethyl acetate (15 mL). The combined organic layer was dried on anhydrous Na₂SO_{4.} The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel with hexane and ethyl acetate (9:1) to produce the corresponding homoallylic products.

Recyclability experiments

The following experiment was conducted to investigate the heterogeneous nature of Cu(II)/Mg-La catalyst. In a mixture of 4-nitrobenzaldehyde (1 mmol, 151mg) and allyltributylstannane (1.2 mmol, 0.37 mL), Cu (II)/Mg-La (20 mg) in 3 mL of acetonitrile was added and stirred at 65 °C for 3 h. After 3 h, the catalyst was separated from the hot reaction mixture by centrifugation and analysed the product by GC (only 50% conversion was observed). The same reaction mixture (in absence of catalyst) was continued at 65 °C and no increase in the product conversion was observed even after 5 h. Inductively coupled plasma optical emission spectroscopic (ICP-OES) analysis of the reaction mixture demonstrated that the negligible amount of copper metal (0.062 ppm) was leached into the solution, thus suggesting that the present reaction proceeds heterogeneously.

Acknowledgements

The authors wish to thank the CSIR and industry sponsored project SSP-0670 for financial support and thanks to AcSIR for all academic activities. S.L thanks DST, govt. of India for financial support (WOS-A/CS-1103/2015G). The authors are grateful to the Director, CSIR-IICT for providing the necessary infrastructure. (Manuscript Communication number: IICT/Pubs./2019/26)

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FULL PAPER

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