


Reusable Copper-Aluminum Hydrotalcite/*rac*-BINOL System for Room Temperature Selective Aerobic Oxidation of Alcohols

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Abstract: An efficient catalyst system consisting of copper-aluminum hydrotalcite/*rac*-BINOL ligand has been developed for the oxidation of alcohols using air as a green oxidant at room temperature. Various alcohols could be transformed into their corresponding aldehydes or ketones in good to excellent yields using the set of optimal conditions. This composite

catalytic system can also be recovered and reused for several cycles without a significant loss of catalytic activity.

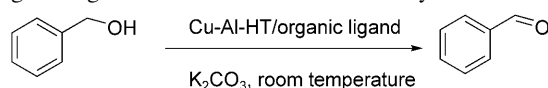
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Introduction

The selective oxidation of alcohols under mild reaction conditions has been a challenge for many years and is of significance for the synthetic organic community because the oxidized product, aldehydes or ketones, have wide applications in the total synthesis of natural products and fine chemicals.^[1] Although several inorganic oxidants have been developed to effect this transformation,^[2] there are considerable drawbacks associated with these oxidizing agents such as their utility in stoichiometric amounts and production of environmentally hazardous/toxic by-products. The use of molecular oxygen/air as the primary oxidant has remarkable advantages, including abundance, low cost, and the by-products are benign. Over the last few years, many transition metal salts (Cu, Co, V, Pd, Ru, Rh, and Mo) alone or in combination with a co-oxidant have been extensively studied for the aerobic oxidation of alcohols.^[3] However, their high cost, non-recovery, use of expensive co-oxidants and high temperature are considered as major drawbacks. On the other hand hydroxyapatite-bound RuHAP, PdHAP, as well as Ru/Al₂O₃, AuCeO₂, Au-Pd/TiO₂ and Cu/MgAl-HT are good reusable catalysts for the aerobic oxidation of alcohols, but they work only at high temperatures.^[4] The use of heterogeneous/reusable catalysts in the aerobic oxidation of alcohols at room temperature is an important protocol from an industrial point of view as it offers several ad-

vantages over the present conventional methods. One of the important advantages is that alcohols with low boiling can be used. However, the examples of these room temperature reactions are very limited.^[5] Therefore, the development of reusable catalysts for the aerobic oxidation of alcohols at room temperature, is an attractive and challenging subject in the organic synthesis.

Layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTLCs) have recently received much attention in view of their potential usefulness as adsorbents, anion exchangers and catalysts.^[6] These materials are represented by general formulae, [M(II)_{1-x}M(III)_x(OH)₂]ⁿ⁺A_{n-x/n}^{y-}·yH₂O where M(II) and M(III) are divalent and trivalent metal ions, respectively. The activity of this inorganic compound can be easily tuned up by the set of heteroelements M(II)/M(III) and changing their ratio for brucite sheets and or by incorporating different anions in the interlayer of brucite from a wide range of multiple options.^[7] The interesting characteristic of this material is that it preferentially retains the organic ligand through ionic interaction and/or anionic exchange ability (surface hydroxy groups) at surface sites and makes them unique organic-inorganic hybrid materials.^[8] We have recently reported Cu-Al hydrotalcite/(*S*)- and (*R*)-BINAP combination as an efficient reusable catalyst for asymmetric reduction of ketones using PMHS as a reducing agent at room temperature.^[9] In continuation of our interest in exploring the

Table 1. Screening of catalysts and organic ligands for the oxidation of benzyl alcohol at room temperature.^[a]

Entry	Catalyst	Ligand	Time [h]	Isolated yield [%]
1	Cu-Al-HTA	<i>rac</i> -BINOL	10	99
2	Cu-Al-HTB	<i>rac</i> -BINOL	10	99,99 ^[b]
3	Cu-Al-HTC	<i>rac</i> -BINOL	17	98
4	Cu-Al-HTB	<i>rac</i> -BINAP	27	12
5	Cu-Al-HTB	<i>rac</i> -BINAM	27	26
6	Cu-Al-HTB	Cyclohexane-1,2-diol	27	41
7		Cyclohexane-1,3-diol	27	28
8		Cyclohexane-1,4-diol	27	n.r
9	Cu-Al-HTB	Cyclohexane-1,2-diamine	42	31
10		Cyclohexane-1,3-diamine	42	12
11		Cyclohexane-1,4-diamine	42	n.r.

^[a] Reaction conditions: alcohol (1 mmol), Cu-Al-HT/*rac*-BINOL (50 mg), K₂CO₃ (1.2 mmol), stirred for the appropriate time under air.

^[b] Isolated yield after 5th cycle. n.r = no reaction.

application of Cu-Al-HT in combination with other organic ligands in various organic transformations, herein we report the selective oxidation of alcohols at room temperature catalyzed by a recyclable catalytic system consisting of copper-aluminum hydrotalcite and *rac*-BINOL using air as a green oxidant. We believe that the employment of a chelating ligand has provided the major driving force behind the evaluation of active metal catalysts which, in turn, activate the molecular oxygen in the oxidation process.

Results and Discussion

Cu-Al hydrotalcite with varying ratios of Cu:Al (Cu-Al-HTA, Cu:Al 3:1; Cu-Al-HTB, Cu:Al 2.5:1; Cu-Al-HTC, Cu:Al 2:1) were used in combination with various organic ligands to obtain the best catalytic system for the oxidation of benzyl alcohol and the results are summarized in Table 1. Various bases were also screened for this reaction; the best result was obtained with K₂CO₃ as a base. Eventually, the catalytic system consisting of Cu-Al-HTB, *rac*-BINOL and K₂CO₃ as a base was chosen for the oxidation of various primary, secondary, aliphatic open chain and cyclic alcohols using air as an oxidant at room temperature (Table 1, entry 2). Although the Cu-Al-HTA catalyst also performed well in combination with *rac*-BINOL, the yield of oxidized product was decreased in successive recycle studies.

The present methodology provides an eco-friendly, simple and efficient catalytic system for the conversion of alcohols to aldehydes with good to excellent yields.

To test the electronic influence of substituents on the phenyl ring, various electron-withdrawing and

electron-donating groups at various positions were tested (Table 2, entries 2–9). Among the substitutions at various position, *ortho*-substituted benzyl alcohols afforded comparatively high yields of the corresponding oxidized products in relatively shorter reaction times (Table 2, entries 3, 5, 7 and 8) when compared to the corresponding *para*-substitution, this may be

Table 2. Aerobic oxidation of primary alcohols.^[a]

Entry	Alcohol	Time [h]	Isolated yield [%]
1	R ¹ = H, R ² = H	10	99,99 ^[b]
2	R ¹ = 4-Cl, R ² = H	18	65 ^[c]
3	R ¹ = 2-Cl, R ² = 6-Cl	12	76 ^[c]
4	R ¹ = 4-NO ₂ , R ² = H	12	65 ^[c]
5	R ¹ = 2-NO ₂ , R ² = H	10	69 ^[c]
6	R ¹ = 4-OH, R ² = H	12	75 ^[c]
7	R ¹ = 2-OH, R ² = H	10	79
8	R ¹ = 2-OCH ₃ , R ² = 5-OCH ₃	8	99 ^[c]
9	R ¹ = 3-OH, R ² = 4-OCH ₃	10	79 ^[c]
10	CH ₃ (CH ₂) ₆ CH ₂ OH	16	65
11	CH ₃ (CH ₂) ₇ CH ₂ OH	18	71
12	CH ₃ (CH ₂) ₁₀ CH ₂ OH	18	60

^[a] Reaction conditions: alcohol (1 mmol), Cu-Al-HT/*rac*-BINOL (50 mg), K₂CO₃ (1.2 mmol) under air.

^[b] Yield after fifth cycle.

^[c] 2 mL of toluene were used as a solvent.

due to the chelation of *ortho*-substituted groups to copper thereby providing an activating effect. However, the oxidation of aliphatic primary alcohols afforded the corresponding carbonyl derivatives in good to moderate yields (Table 2, entries 10–12) under the same reaction conditions. Overall, the presence of substitution (electron-donating or electron-withdrawing groups) on the phenyl ring does not seem to show much appreciable effect on the yield of oxidation products.

Next, we tested the catalytic activity in the oxidation of secondary and *N*-heterocyclic alcohols (Table 3, entries 1–11). Among the secondary alcohols tested, the less reactive alicyclic alcohols were oxidized to the corresponding ketones with good to excellent yields (Table 3, entries 1–7). Thus, cyclohexanol which is known to be a less reactive substrate for oxidation by precious metals such as Pd and Ru under molecular oxygen, gave high yields of cyclohexanone under our experimental conditions (Table 3, entry 1). Cyclohexanols with electron-donating group(s) at the 3, 4 and 5 positions showed higher reactivity than the unsubstituted cyclohexanol (Table 3, entry 1 vs. 2–4) and no aldol product is formed which

is usually observed under high temperature reaction conditions. Cyclopentanol also undergoes the oxidation at room temperature but afforded a moderate yield of the oxidized product. However, by using conventional heating (100 °C), the yield of cyclopentanone was increased along with the formation of aldol product (99:1) (Table 3, entry 7). It is important to note that the oxidation of 1-phenylethanol to acetophenone requires pure molecular oxygen to avoid the poisoning of reaction due to the presence of CO₂ whereas using our catalytic system, the oxidation could be achieved in the presence of air with 85% yield (Table 3, entry 9).^[10] In the case of *N*-heterocyclic benzylic alcohols, (pyridin-3-yl)methanol and 1-(pyridin-3-yl)ethanol (Table 3, entries 10 and 11) were oxidized to the corresponding aldehydes and ketones but the reaction times were longer. The yield of oxidized product was further increased when the reaction was attempted at elevated temperature.

The Cu-Al-HT/*rac*-BINOL catalytic system can also be used for selective oxidation. When an equimolar mixture of 2,5-dimethoxybenzyl alcohol and 1-phenylethanol was used for the oxidation, 2,5-dimethoxybenzyl alcohol was completely oxidized to the corresponding aldehyde and only 10% of acetophenone was isolated (Table 4, entry 1). Similarly, when an equimolar mixture of 2,5-dimethoxybenzyl alcohol and 1-octanol was subjected to oxidation, 2,5-dime-

Table 3. Aerobic oxidation of secondary and *N*-heterocyclic alcohols.^[a]

Entry	Alcohol	Time [h]	Isolated yield [%]
1	R ¹ = H, R ² = H	20	81
2	R ¹ = 3-CH ₃ , R ² = 5-CH ₃	10	99
3	R ¹ = 3-CH ₃ , R ² = H	18	87
4	R ¹ = 4-CH ₃ , R ² = H	15	92
5		10	99
6		12	99
7		24, 7 ^[b]	63, 99 ^[b]
8		7	99 ^[c]
9		10	85
10		48, 7 ^[b]	31, 75 ^[b]
11		32, 7 ^[b]	54, 86 ^[b,c]

^[a] Reaction conditions: alcohol (1 mmol), Cu-Al-HT/*rac*-BINOL (50 mg), K₂CO₃ (1.2 mmol), under air.

^[b] Reaction performed at 100 °C.

^[c] 2 mL of toluene were used as a solvent.

Table 4. Selective oxidation of primary alcohols.^[a]

Entry	Alcohol	Product	Time [h]	Yield [%]
1			8	99
2			16	99
3			12	99
			12	11

^[a] Reaction conditions: alcohols (1 mmol), Cu-Al-HT/*rac*-BINOL (50 mg), K₂CO₃ (1.2 mmol), stirred under air.

thoxybenzyl alcohol was selectively oxidized to the corresponding aldehyde and only a trace amount of octanal was observed in 16 h (Table 4, entry 2). A mixture of benzyl alcohol and 4-hydroxybenzyl alcohol used for the oxidation afforded selectively benzaldehyde in high yield (Table 4, entry 3) over 4-hydroxybenzaldehyde. The reactivity trend clearly shows that primary benzyl alcohols are more reactive than substituted benzyl alcohols, secondary benzyl alcohols (Table 4, entry 1) and aliphatic alcohols (Table 4, entry 2).

Furthermore, the catalytic system can be reused for several cycles without loss of its activity (Table 2, entry 1). The true heterogeneity of the catalyst was examined when the reaction was discontinued after 50% conversion and the reaction was continued with the filtrate (solid catalyst was removed by filtration) for the next 7 h, no oxidation reaction was observed, which indicates that the active catalytic species was not leached out from the solid catalyst.

The catalyst was well characterized by XRD, TPR and XPS, FT-IR and TGA-MS for the BINOL fragments (see Supporting Information). From the XPS study, it is observed that the increment in the area percentage of O 1s of hydroxide of Cu-Al-HT/*rac*-BINOL clearly demonstrates the interaction of *rac*-BINOL with Cu-Al-HT which was further confirmed through FT-IR and TGA-mass spectroscopic analysis. XRD and TPR analyses show no change in the active phases indicating that the interaction takes place largely at the surface of Cu-Al-HT. The plausible mechanism of oxidation may be through the formation of an alkoxide by interaction of the alcohol with the Brønsted OH group (basic sites) of the brucite layer originally present in the Cu-Al-HT. We believe that *rac*-BINOL ligated copper plays an important role in activating the molecular oxygen to form a peroxide which in turn is responsible for the formation of the carbonyl product through hydride transfer from the alkoxides. Copper is known for a biomimetic functional model of copper enzyme galactose oxidase^[11] and other oxidation reactions through activation of molecular oxygen/hydrogen peroxide.^[12] Aluminum is well documented both in Oppenauer oxidation and Meerwein-Ponndorf-Verley (MPV) reduction, as well as in the recently reported MPV reduction by Ni-Al HT and Mg-Al-HT.^[13]

Conclusions

In conclusion, we have developed an efficient and reusable copper-aluminum hydrotalcite/*rac*-BINOL catalyst system for the oxidation of benzylic, secondary and heterocyclic alcohols to the corresponding oxidized products under oxidant- and additive-free conditions.

Experimental Section

Preparation of the Catalyst Cu-Al-HTB/*rac*-BINOL

0.1 g of Cu-Al-HTB was taken in a 50-mL, round-bottomed flask and 50 mg (0.2 mol%) of *racemic* BINOL were added, to this 25 mL of CH₃CN were added and the mixture was stirred under aerobic conditions for 24 h. The mixture was then filtered and washed several times with doubly deionized water and finally with CH₃CN, the catalyst was then oven-dried at 65 °C overnight to obtain the Cu-Al-HT/*rac*-BINOL two component catalytic system as a blue powder.

General Procedure for the Oxidation Reaction

Benzyl alcohol (1.0 mmol), Cu-Al-HT/*rac*-BINOL (50 mg), and K₂CO₃ (1.2 mmol) were taken in a 50-mL, round-bottomed flask equipped with a teflon-coated magnetic stirring bead and stirred for an appropriate time. The progress of the reaction was monitored by TLC and on completion of the reaction, the reaction mixture was centrifuged to separate the catalyst, the solid residue was washed with EtOAc (1 × 5 mL) to make the catalyst free from organic matter, the reaction mixture was diluted with water (20 mL), and then extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to yield the crude product. It was then purified by flash chromatography over silica gel (60–120 mesh) column using hexane/ethyl acetate (80:20) v/v as an eluent to afford the pure product. The products were characterized by ¹H NMR, ¹³C NMR and mass spectrometric analysis.

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