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Short Communication

Clean borrowing hydrogen methodology using hydrotalcite supported copper catalyst

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ABSTRACT

The catalytic activity of Mg–Al hydrotalcite supported copper catalyst was investigated for clean C–C and C–N bond forming reactions using alcohols as alkylating agent via borrowing hydrogen methodology. The catalyst showed excellent conversion of ketone and amine substrates (71–99%) to alkylated products with high selectivity in alkylation reactions.

1. Introduction

In recent years, borrowing hydrogen/hydrogen auto transfer methodology for C–C and C–N bond formation (e.g., C-alkylation of carbonyls and N-alkylation of amines) using alcohols as alkylating agent (avoiding the use of traditional mutagenic halide reagents) has received much attraction as extremely atom efficient and greener process [1–8]. The C-alkylation of carbonyls and N-alkylation of amines are considered to be very important reaction in synthetic organic chemistry [9,10]. The borrowing hydrogen methodology (Scheme 1) involves the activation of an alcohol (**I**) by removal of hydrogen (H_2) to a carbonyl (**II**) for reaction with a nucleophile (carbanions of carbonyls/amines) to an unsaturated product (**III**), followed by hydrogenation using H_2 generated in dehydrogenation step to finally α-alkylated carbonyl or N-alkylated amine product (**IV**) [1–8]. A suitable catalyst is required for activation of the alcohols and to transfer hydrogen for reduction step. Several catalytic systems were developed to activate the alcohols for C- and N-alkylation reactions via borrowing hydrogen [11–32]. In spite of atom efficient feature of borrowing hydrogen method; this strategy could not offer 100% greener and industrially viable process for C- and N-alkylation reactions. The major constraints are the use of precious noble metal based catalyst along with ligands, metal salts or bases in high quantity as promoter, use of volatile and hazardous solvents under reflux condition, requirement of hydrogen acceptor in some cases, etc. The reported heterogeneous catalysts could also not show viability of this method due to very high temperature operation, side products formation and use of precious metals like Pd, excess amount of base as promoter, hydrogen acceptor, solvents, etc. [33–36]. The use of additives (base, salts, hydrogen acceptor, etc.) reduces the atom efficiency of the process. Williams stated that the development of more reactive catalysts, avoiding the use of noble metals, will be a welcome addition in this area [5]. Beller et al. mentioned that the development of less expensive bio-relevant metals such as iron or copper based catalyst will be one of the important goals to be achieved in this field [8]. Therefore, it is of great importance to develop an efficient, cheap and eco-friendly catalyst for activation of alcohols for borrowing hydrogen to have economically viable and environmentally more benign synthetic route for C–C and C–N coupling.

The copper catalysts, being less expensive metal based catalysts, have attracted much attention in heterogeneous catalysis, especially in alcohols activation [37–44]. The synergistic effect between the basicity of support and the hydrogen spillover of copper nanoparticle were reported to provide high activity in alcohols dehydrogenation and hydrogen transfer [42]. Recently we reported that the copper on Mg–Al hydrotalcite (Cu-HT) showed multifunctional activity in alcohol transformations [44]. It was of interest to combine the basic property of hydrotalcite with the catalytic property of copper to develop a supported copper catalyst for borrowing hydrogen. To the best of our knowledge, it is the first report of clean borrowing hydrogen methodology for activation of alcohols at comparatively low temperature with high selectivity using a purely heterogeneous catalyst.

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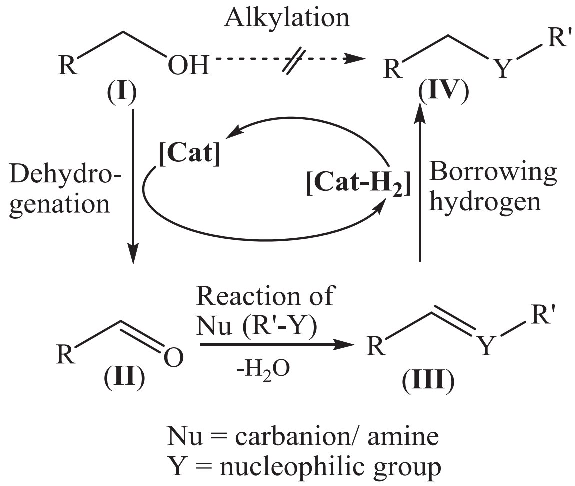
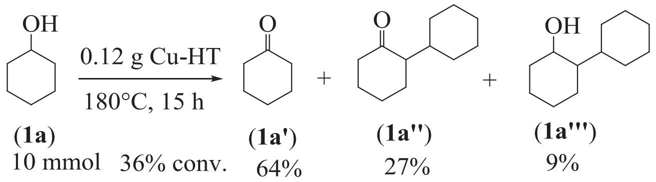


Scheme 1. Borrowing hydrogen methodology for C – C/C – N bond formation using alcohols.



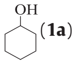
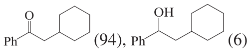
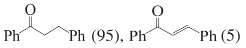
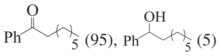
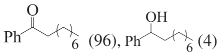
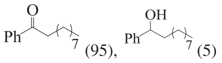
Scheme 2. Cu-HT catalyzed cyclohexanol (**1a**) activation via borrowing hydrogen.

2. Experimental

2.1. General

All the chemicals used were of synthetic grade having purity >99% and were used without any further purification. The Mg–Al hydrotalcite (HT) sample with Mg/Al molar ratio of 2.0 was synthesized by co-precipitation method at constant pH [45]. The HT supported copper (Cu-HT) catalyst was prepared by wet impregnation of HT (4 g) with aqueous solution of copper acetate (0.025 M, 40 mL) under stirring for 24 h at room temperature, followed by filtration of solid and washing with distilled water (4×50 ml) and then drying at 70 °C for 12 h [44]. The Cu-HT was calcined at 520 °C for 4 h to obtain copper containing mixed oxides of MgO and Al_2O_3 (Cu-AHT). The catalysts were characterized by XRD, FT-IR, ICP, N_2 adsorption–desorption analysis, TGA, NH_3 & CO_2-TPD and H_2-TPR, and the details of catalyst characteristics have already been reported in our previous paper [44].

Table 1
C-alkylation of acetophenone (**2a**) with alcohols (**1**).

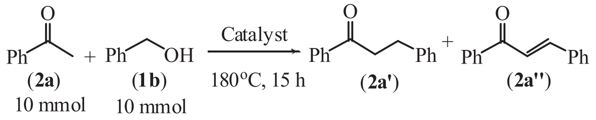
Entry	1	Conv. (%)	Product (%)
1		71	
2		99	
3		84	
4		94	
5		90	

2.2. General procedure for C-alkylation of ketones and N-alkylation of amines using supported copper catalysts

A mixture of ketone/amine and alcohol in required molar ratio along with the catalyst was taken in a 50 mL reaction tube of reaction station at desired temperature under stirring for required reaction time. Afterwards the reaction mixture was cooled and diluted with dichloromethane (5 mL). The catalyst was filtered to recover it from the liquid phase. The reaction mixture was analyzed by gas chromatography (Agilent 5975) having a HP-5 (60 m) capillary column with a programmed oven temperature from 50 to 280 °C, a 0.5 cm^3/min flow rate of N_2 as carrier gas and FID detector. The conversion of substrate (ketone/amine) was calculated on the basis of its weight percent. The products formed in the reactions were characterized by GC–MS analysis. The values in parenthesis given in all tables are selectivity.

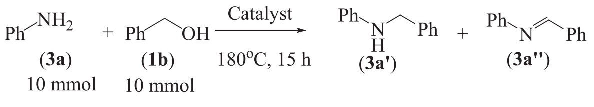
3. Results and discussion

The Cu-HT and Cu-AHT catalysts possess finely dispersed copper species (3.0 and 3.5 wt.% copper, respectively) and multifunctional sites (acidic–basic sites and good surface reducibility) [44]. During the



Catalyst	Conv. (wt.%) of 2a	Selec. (wt.%) of 2a'	Selec. (wt.%) of 2a''
Cu-HT	80	60	40
Cu-AHT	30	5	95

Scheme 3a. C-alkylation of acetophenone (**2a**) using benzyl alcohol (**1b**) over supported copper catalysts.



Catalyst	Conv. (wt.%) of 3a	Selec. (wt.%) of 3a'	Selec. (wt.%) of 3a''
Cu-HT	99	60	40
Cu-AHT	48	13	87

Scheme 3b. N-alkylation of aniline (**3a**) using benzyl alcohol (**1b**) over supported copper catalysts.