Physico-chemical and catalytic properties of Mg–Al hydrotalcite and Mg–Al mixed oxide supported copper catalysts

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The Mg–Al hydrotalcite (HT) and Mg–Al mixed oxide supported copper catalysts containing 3–3.5 wt.% copper in finely dispersed form were synthesized and characterized. The effect of support nature on physico-chemical and catalytic properties of supported copper species were studied. The loading of copper on the supports was observed to be influencing the surface acidic, basic and reducibility properties, and catalytic behavior in dehydrogenation of benzyl alcohol. The high basicity and intercalated copper ions in Mg–Al hydrotalcite supported copper sample showed multifunctional activity in catalytic transformations of alcohols (primary, secondary and aromatic alcohols).

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1. Introduction
Catalytic transformations of alcohols like dehydrogenation, lactonization of diols, oxidative esterification, amination, α-alkylation of carbonyls, etc. are industrially important organic reactions to synthesize various pharmaceuticals, polymers, perfumery chemicals and fine chemicals. Copper catalysts, less expensive metal based catalysts, have attracted much attention in heterogeneous catalysis, especially in catalytic transformation of alcohols [1–8]. Copper is always used with an additive and/or in the supported form in order to have fine dispersion of copper species and to avoid the sintering of copper at high temperature. The activated carbon, silica, zinc oxide, zirconia, alumina, chromia, MgO, mixed oxide systems (ZnO/SiO₂, ZnO/Al₂O₃, Cr₂O₃/MgO), different hydrotalcites (LDH’s: layered double hydroxides) and their corresponding mixed oxides have been widely used as support for copper [5,9–19]. It has been reported by many researchers that the nature of support and promoters, the preparation method and copper content influence the activity of copper catalysts. In supported copper catalysts, chromia were used as a structural promoter as it enhances the BET surface area and also inhibits the sintering of copper particles [20]. In addition, use of alkalis such as barium oxide or sodium oxide and lanthanum oxide further improves the catalytic activity by improving the stability of copper in the catalyst.

The introduction of copper in the framework of silica possesses significant catalytic activity towards dehydrogenation of alcohols [19]. It is therefore of interest to combine the desirable properties of mesoporous silica (porosity and morphological characteristic such as high surface area and narrow pore size distribution) with the beneficial effects of Cu to have enhanced activity in dehydrogenation reactions. However, it has been noticed that the silica and some of the support materials like alumina, zinc oxide, zirconia, etc. exhibit significant amount of surface acidity in the copper based catalysts [3,4,14,18,21–25]. The surface acidity was found to be responsible for side reactions like dehydration during the dehydrogenation of alcohols, which lowered the selectivity of the carbonyl product. The basic supports such as MgO and its mixed oxides (e.g. Cr₂O₃/MgO), different hydrotalcites and their derived mixed oxides have received great attention in recent years as an appropriate support for copper [5–8,17,26–28]. The copper nanoparticles supported on these basic supports were reported to be highly active for catalytic transformation of alcohols (dehydrogenation, lactonization of diols, coupled dehydrogenation–hydrogenation, transfer dehydrogenation, etc.) due to the synergistic effect between the basicity of the support and the fast hydrogen spill over of Cu nanoparticles [1,6–8,27]. Similarly, the H₂ reduced Cu/MgO and Cu–Cr₂O₃/MgO systems have been reported to be highly active catalysts for alcohol dehydrogenation, transfer dehydrogenation and coupled dehydrogenation–hydrogenation reactions [5,7,17,18,26].

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The LDH’s consist of positively charged metallic hydroxide layers, where the positive charges are balanced by anions (CO$_3^{2-}$, NO$_3^-$, Cl\textsuperscript{−}, OH\textsuperscript{−}, etc.) located in the interlayer spaces. The thermal decompositions of LDH’s results to mixed oxides exhibiting a homogeneously dispersed elements, high specific surface area and basic properties. The LDH’s and their mixed oxides containing reducible cation (e.g. copper ions) after reduction in flow of H$_2$ produce well dispersed metal particles in strong interaction with the support [1,6–8,27,28]. The hydrotalcite supported copper nanoparticle catalysts have been reported as an efficient heterogeneously catalyst for oxidant-free dehydrogenation of alcohols and lactonization of diols [6,27]. Similarly, copper nanoparticles supported on MgO also showed significant activity for primary alcohol (1-octanol) dehydrogenation in presence of styrene as hydrogen acceptor [7,8]. The H$_2$ reduced Al–Cu–Mg mixed oxides derived from hydrotalcite (HT) type materials with different Cu:Mg:Al ratios showed high activity for dehydrogenation of 2-octanol [28]. However, the reported catalysts possess high copper content and were used in the reduced form (after thermal treatment in flow of H$_2$) to have dehydrogenation activity in the catalyst. The most of the copper based catalysts were found to be active for dehydrogenation of benzylic and secondary alcohols, and very less activity was observed for primary alcohols dehydrogenation.

The multifunctional solid catalysts (possessing various surface catalytic sites such as acid, base and redox) are very important in heterogeneous catalysis to develop greener and sustainable chemical processes. The LDH’s and their mixed oxides possessing metals (as redox sites), basic/acid–base sites have been reported to be potential multifunctional catalysts for multistep synthesis in single pot [31,32a–32n]. The multifunctional catalysts can bring about direct transformation of multi step reactions in one pot giving environmental friendly, economic and efficient fine-chemical syntheses process. Furthermore, the processes involving use of alcohols as starting substrate are of great interest to have an economic and environmentally friendly route for synthesis of valuable chemicals of commercial interest. Several copper based dehydrogenation catalysts have already been developed for conversion of alcohols to carbonyl products [9–19]. A copper based multifunctional catalyst (containing metal and acid–base sites), which can catalyze the dehydrogenation of alcohols to carboxyls followed by various catalytic reactions of carboxyls (such as transfer hydrogenation or reduction and hydrogen auto transfer reaction), can be promising heterogeneous catalyst to carry out multistep synthesis in single pot. The present work was aimed to develop a multifunctional supported copper catalyst showing activity in alcohol dehydrogenation and transfer dehydrogenation/hydrogen auto transfer reactions. The support nature (acidity/basicity) was observed to be influencing the physico-chemical and catalytic properties of supported copper species. The multifunctional catalytic activity of the Mg–Al hydrotalcite supported copper catalyst showing activity in dehydrogenation, transfer dehydrogenation/hydrogen auto transfer reaction was demonstrated with different types of alcohols (primary, secondary and aromatic). The catalyst showed significant activity for conversion of primary alcohol (n-octanol).

2. Experimental

2.1. Materials

All the chemicals used were of synthetic grade having purity above 99%. The Cu(CH$_3$COO)$_2$, Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, NaOH and Na$_2$CO$_3$ were obtained from s.d. fine chemicals Ltd., India. The alcohols (benzyl alcohol, p-nitro benzyl alcohol, cyclohexanol, n-octanol, furfuryl alcohol and cinnamyl alcohol) and copper oxide (CuO) were purchased from Merck India Ltd. The alcohols (purity 99.8%) were used without any further purification.

2.2. Synthesis of Mg–Al hydrotalcite and Mg–Al mixed oxide samples

The Mg–Al hydrotalcite sample with Mg/Al molar ratio of 2.0 was synthesized by co-precipitation method at constant pH [26]. An aqueous solution (called A) of Mg(NO$_3$)$_2$·6H$_2$O (0.22 mol) and Al(NO$_3$)$_3$·9H$_2$O (0.11 mol) was prepared in 200 mL. double distilled deionized water. The solution A was added drop wise into a second solution (B) containing mixture of NaOH (0.72 mol) and Na$_2$CO$_3$ (0.21 mol) in 200 mL double distilled deionized water, in around 2 h under vigorous stirring at room temperature. The content was then aged at 70 °C for 14 h. After 14 h, the precipitate formed was filtered and washed thoroughly with hot distilled water until pH of the filtrate was 7. The washed precipitate was then dried in an oven at 80 °C for 14 h, which gives Mg–Al hydrotalcite (HT). The HT sample was calcined at 520 °C for 4 h to obtain Mg–Al mixed oxides (AHT).

2.3. Synthesis of supported copper samples

The copper was loaded on the synthesized hydrotalcite by wet impregnation of hydrotalcite (4 g) with aqueous solution of copper acetate (0.025 M, 40 mL) under stirring for 24 h at room temperature. The copper impregnated hydrotalcite was washed with distilled water (4 × 50 mL) to remove free copper and acetate ions and then dried at 70 °C for 12 h. The HT supported copper sample was named as Cu-HT. The Cu-HT sample was calcined at 520 °C for 4 h to obtain copper containing mixed oxide of MgO and Al$_2$O$_3$ (Cu-AHT).

2.4. Characterization of supported copper samples

2.4.1. Physico-chemical properties

The copper content in the copper containing samples was estimated by Inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin Elmer Instrument, Optima 200 DV). The sample (100 mg) was dissolved in 40% HF solution (15–20 drops) followed by addition of 5 wt.% boric acid solution making up to 100 mL in volumetric flask, which was analyzed by ICP. The BET (Brunauer–Emmett–Teller) surface area (S$_{BET}$) of the samples, degassed at 110 °C for 2 h under vacuum, was determined from N$_2$ adsorption data (by using BET equation) measured at 77 K using Quantachrome NOVA 1000e surface area analyzer. The particles surface area of the samples was analyzed by measuring zeta potential of the samples using Zetasizer (Malvern) by dispersing the samples in iso-propanol.

The crystalline phase in the synthesized samples were characterized by Powder X-ray diffraction (XRD) using (Philips X’pert, using Cu Kα radiation: λ= 1.5405 A, in 20 range of 10–80°). The samples were analyzed by Fourier transform infrared (FT-IR) spectroscopy (IRPremistige-21, Shimadzu) using a Diffuse Reflectance Scanning disc technique, mixing the sample with dried KBr, in the wavelength range of 400–4000 cm$^{-1}$. Thermo gravimetric analysis (TGA) of hydrotalcite samples were carried out using Mettler thermal analyzer, TGA/DSC 1 SF/752, by heating the sample in the range of 50–800 °C with a heating rate of 10 °C min$^{-1}$ under nitrogen flow (50 mL min$^{-1}$).

Temperature programmed desorption of CO$_2$ (CO$_2$ TPD) and NH$_3$ (NH$_3$ TPD) and H$_2$ temperature programmed reduction (H$_2$ TPR) for the samples were carried out using Micromeritics, USA, taking 50 mg of sample. The sample was heated at 100 °C for 1 h under helium flow (30 mL h$^{-1}$) as carrier gas. For CO$_2$ and NH$_3$ TPD analysis, the CO$_2$/NH$_3$ was adsorbed on the samples at 50 °C by exposing to a flow of helium mixed CO$_2$/NH$_3$ gas (10%, 20 mL h$^{-1}$).
for 1 h. The desorption of CO₂/NH₃ was performed by heating the sample up to the final temperature of 800 °C (12 °C min⁻¹) and was measured by gas chromatography with thermal conductivity detector (TCD). Temperature programmed reduction (H₂ TPR) analysis was carried out by passing a mixture of hydrogen and argon (10%, 30 mL h⁻¹) through sample bed. The temperature was increased linearly at a ramp of 10 °C min⁻¹ from room temperature to 800 °C. The change in the H₂ concentration was monitored by gas chromatography with TCD.

2.4.2. Catalytic activity of supported copper samples

The catalytic activity of the synthesized supported copper samples was evaluated by using dehydrogenation of benzyl alcohol in liquid phase as model reaction (Scheme 1). The benzyl alcohol (1.1 g) along with the catalyst (0.1 g) were taken in the reaction tubes (10 mL) of reaction station (12 Place Heated Carousel Reaction Station, RR99030, Radleys Discovery Technologies, UK). Initially, the reaction was carried out at 180 °C under stirring for required reaction time to evaluate the catalytic activity of the synthesized samples and then in the temperature range of 140–200 °C to study the temperature effect on activity of the catalyst. The reaction kinetics was studied by carrying out the reaction with the sample, showing best catalytic activity, at optimized reaction condition from 4 h to 15 h. After the reaction, the reaction mixture was filtered to separate the spent catalyst. The reaction mixture was analyzed by gas chromatography (Sigma Instruments, India) having a HP-5 (30 m) capillary column with a programmed oven temperature from 50 to 200 °C, a 0.5 cm² min⁻¹ flow rate of N₂ as carrier gas and FID detector. The conversion of alcohol was calculated on the basis of its weight percent as given below:

\[
\text{Conversion of alcohol} = \frac{\text{Initial wt. \% of alcohol} - \text{final wt. \% of alcohol}}{\text{Initial wt. \% of alcohol}} \times 100
\]

The products formed in the reactions were characterized by GC–MS analysis and the data were matched with those reported in the literature. GC–MS analysis was carried out using gas chromatograph mass spectrometer (Agilent 5975 GC/MSD with 7890A GC system) having HP-5 capillary column of 60 m length and 250 μm diameter with a programmed oven temperature from 50 to 280 °C, at 1 mL min⁻¹ flow rate of He as carrier gas and ion source at 230 °C.

The supported copper sample, showing best activity in benzyl alcohol conversion in terms of highest selectivity towards dehydrogenation and transfer hydrogenation reactions, was also employed with various alcoholic substrates like p-nitrobenzyl alcohol (deactivated aromatic alcohol), cyclohexanol (cyclic alcohol), n-octanol (primary alcohol), furfuryl alcohol (heteroaromatic alcohol), cinnamyl alcohol (unsaturated alcohol).

3. Results and discussion

3.1. Physico-chemical properties of supported copper samples

From the elemental analysis of supported copper samples by ICP (Table 1), the copper content in hydrotalcites and mixed oxide samples (Cu-HT and Cu-AHT) was found to be 3.0 and 3.5 wt.% respectively. The BET surface area ($S_{BET}$) of HT and AHT was 76 and 195 m²/g respectively (Table 1), which slightly decreased in the supported copper samples (72 and 192 m²/g for Cu-HT and Cu-AHT samples, respectively) indicating the fine dispersion of copper species in the samples.

Zeta potential of the samples was measured to examine the surface charge of the particles. The particles of AHT support were observed to be negatively charged (−1.9 mV), whereas the surface charge on HT particles was positive (+30 mV) (Table 1). There was no significant change in zeta potential of Cu-HT as compared to HT, which may be due to intercalation of copper ions in the interlayer space of HT. The surface charge in Cu-AHT was +30 mV, which could be attributed to presence of copper species on the surface of mixed oxides.

The XRD patterns (Fig. 1) of the supported copper samples (Cu-HT and Cu-AHT) did not show any diffraction peaks corresponding to crystallites of copper species, which indicates that the copper species are highly dispersed on the surface of the supports and they are too less (3.0–3.5 wt.%) as well as small to be detected. The XRD patterns of HT and Cu-HT samples (Fig. 1) showed sharp, intense and symmetric diffraction peaks in 2θ range of 10–25° and broad asymmetric diffraction peaks in 2θ range of 30–50°, which are characteristics of highly crystalline layered structure of hydrotalcite [31]. The XRD patterns of HT and Cu-HT samples were similar showing hydrotalcite phase in both the samples and no
structural change in hydrotalcite after loading of copper ions. The d-spacing for the planes (0 0 3) in both the samples was 7.486 Å indicating the presence of CO$_3^{2-}$ anions in interlayer space. The calcination of hydrotalcite samples (HT and Cu-HT) at 520 °C resulted to Mg–Al mixed oxide [Mg(Al)O] phase showing characteristic broad peaks in XRD of both calcined hydrotalcite samples (Fig. 1).

The infrared spectrum of HT (Fig. 2) shows the characteristic absorption bands of hydrotalcite [34,35a–35f]. A broad band at 3420 cm$^{-1}$ (due to the interlayer water molecules and structural hydroxyl groups in the brucite-like layer), a weak peak at 1640 cm$^{-1}$ (interlayer H$_2$O bending vibration), a shoulder near 3000 cm$^{-1}$ (due to interaction of interlayer H$_2$O and carbonate ions) and a strong peak at 1359 cm$^{-1}$ (the vibration of carbonate ions) are the major bands in IR spectrum of HT [35b–35d]. The sharp intense band at 1359 cm$^{-1}$ with a shoulder at 1559 cm$^{-1}$ are v$_3$ asymmetric stretching of interlayer carbonate, which are splitting of the v$_3$ band (in to 1359 cm$^{-1}$ and 1559 cm$^{-1}$) due to lowering of local symmetry of carbonate in the interlayer [32]. A very weak shoulder at 1058 cm$^{-1}$ can be ascribed to the v$_1$ mode of carbonate, which is IR inactive in the D$_3h$ symmetry of free carbonate and also arises due to lowering of local symmetry of carbonate in the interlayer of HT [35e,35f]. The band at 877 cm$^{-1}$ as a weak shoulder can be assigned to out-of-plane deformation in the v$_4$ mode of carbonate and that at 679 cm$^{-1}$ corresponds to in-plane bending (v$_2$ mode) of carbonate [35a]. The bands at 788 and 550 cm$^{-1}$ can be assigned to translation modes of hydroxyl ions associated with trivalent aluminum and that at 940 cm$^{-1}$ is the corresponding deformation modes. The band at 450 cm$^{-1}$ can be assigned to Al–O bonds vibrations of octahedrally coordinated aluminum [35a]. A major spectral change was noticed in the FTIR spectrum of Cu-HT sample (Fig. 2) showing a more intense the shoulder v$_3$ band at 1559 cm$^{-1}$ as compared to HT. It may be due to interaction of intercalated copper ions with carbonate ions lowering the local symmetry of carbonate. It indicates that intercalated copper ions in interlayer space of HT are associated with interlayer CO$_3^{2-}$ ions. The copper ions are dispersed in interlayer of HT, which do not show much effect on the structural and textural properties of HT. The FTIR spectrum of calcined hydrotalcite sample (AHT) (Fig. 2) shows reduced intensity of the bands at 3100–3776 cm$^{-1}$, ~3000 cm$^{-1}$, 1634 cm$^{-1}$ and 1370 cm$^{-1}$ indicating the removal of interlayer water molecules and CO$_3^{2-}$ anions. The FTIR spectrum of Cu-AHT sample resembles the FTIR spectrum of AHT.

The thermogravimetric (TGA–DTG) profiles (Fig. 3a and b) of as synthesized HT and HT supported copper samples (Cu-HT) showed two-step thermal decomposition on heating the samples from 50 °C to 800 °C. The decomposition below 250 °C was due to removal of physisorbed water and interlayer water molecules and the decomposition in the range of 270–500 °C was attributed to loss of hydroxyls of brucite layer and interlayer anions like CO$_3^{2-}$ and OH$^-$ ions as CO$_2$ and H$_2$O. However, the second step decomposition profile (270–500 °C) in HT sample showed a shoulder in DTG curve at ~340 °C indicating decomposition of interlayer anions in two steps. The intercalation of copper ions in HT significantly changed the second step decomposition profile (300–500 °C) showing the decomposition of interlayer anions in single steps in Cu-HT sample. The change in thermal decomposition profile of interlayer anions in Cu-HT may be attributed to the interaction of copper ions with interlayer anions (CO$_3^{2-}$ and OH$^-$ ions). The total loss in mass was slightly higher for Cu-HT sample (48.80 wt.%) than that in HT (47.23 wt.%). The Cu-HT sample gave ~1.57 wt.% excess loss in mass as compared to HT during thermal decomposition. This increase in loss for Cu-HT sample may be associated with the hydroxylation of brucite layer or copper intercalation with water (solvent medium) during the synthesis. The 1.57 wt.% loss accounts for 0.92 mmol HO$^-$ in 1 g of Cu-HT sample, which will be equivalent to 0.47 mmol Cu$^{2+}$ in 1 g of Cu-HT sample (0.92 mmol HO$^-$/g = 0.47 mmol Cu$^{2+}$). From ICP analysis of Cu-HT sample, the copper content in the sample was found to be 3.0 wt.%, which accounts for 0.47 mmol copper/g Cu-HT sample. This indicates that intercalation of one copper ion in interlayer of hydrotalcite is accomplished with inclusion of two hydroxyl ions in hydrotalcite. The positive charges of brucite layer are balanced by interlayer anions (carbonate and hydroxyl ions). The association of one copper ion with interlayer anion (either with one carbonate ion or with two hydroxyl ions) will leave two unbalanced positive charges on the brucite layer. To balance these positive charges of brucite layer, two hydroxyl ions might be added in the interlayer. These two hydroxyl ions can be generated from the reaction of two acetate ions (from copper acetate molecules) with two water molecules giving two molecules of acetic acid. The TGA graph of Cu-HT sample shows increased loss in mass in first (~0.59 wt.%) and second (~0.97 wt.%) steps as compared to HT sample. The extra loss in first step may be dehydroxylation of hydroxyl ions associated with copper ions whereas the extra loss in mass in second step can be attributed to dehydroxylation of added hydroxyl ions, which are associated with brucite layer. Thus TGA results indicate that intercalated copper ions can be associated with one carbonate or two hydroxyl ions in interlayer structure.

As the maximum thermal decay of Cu-HT sample took place till 500 °C, the Cu-HT sample was calcined at 520 °C to get its mixed oxide sample (Cu-AHT).

The acidic and basic properties of the samples (amount of acidic and basic sites and their strength) were determined by NH$_3$ and CO$_2$ TPD analysis respectively. The amount of NH$_3$ and CO$_2$ evolved during the TPD study were calculated by integrating the area under the desorption peaks, which are correlated with the total amount of acidic and basic sites in the materials, respectively [34]. The acidic sites can be classified as weak (150–250 °C), medium (250–350 °C) and strong (350–450 °C) on the basis of the desorption temperature [35]. In CO$_2$ TPD, the low temperature desorption peak corresponds to CO$_2$ adsorbed on the weak basic sites (OH groups) while the peak in intermediate temperature range and at high temperature represent CO$_2$ adsorptions on the medium strength (O$^2-$ ions) and strong strength basic (O$^{2-}$ ions) sites, respectively [36]. The amount of acidic and basic sites along with their strength in the samples is reported in Tables 2 and 3, respectively. The NH$_3$ TPD profiles of HT, Cu-HT, AHT and Cu-AHT samples (Fig. 4a and b) indicate the broad distribution of acidic sites strength; however, presence of copper in the sample and calcination slightly affects the distribution of sites showing the

![Fig. 2. FTIR spectra of HT, Cu-HT, AHT and Cu-AHT samples.](image-url)
slight shifting of the desorption peaks towards lower temperature. The HT and Cu-HT samples contain medium to strong strength acidic sites with predominantly stronger sites (desorption maxima at \( \sim 420 \) °C). The AHT and Cu-AHT samples possess weak, medium and stronger acid sites indicating the formation of some weak acid sites in the sample on calcination (Table 2). The total amount of acidic sites in Cu-HT sample was observed to be slightly higher (0.72 mmol NH\(_3\)/g) than HT sample (0.57 mmol NH\(_3\)/g), but much lesser than Cu-AHT (6.91 mmol NH\(_3\)/g) and AHT (6.16 mmol NH\(_3\)/g) samples. It indicates that the loading of copper do not show much effect on the number of acidic sites in the copper containing samples (i.e. Cu-HT and Cu-AHT) in comparison of their corresponding support material. However, the calcination of as-synthesized samples significantly increases the amount of acidic sites in calcined (AHT and Cu-AHT) samples as compared to as-synthesized (HT and Cu-HT) samples. Similar observation was also reported by Romero et al. [34]. The source of acidity in hydrotalcite and derived mixed oxide is aluminum ions, which generate strong Lewis acidity [37].

The CO\(_2\) TPD profile of HT (Fig. 5a) is showing a broad peak with maxima centered at \( \sim 168 \) °C revealing the presence of medium strength basic sites (site density: 0.66 mmol CO\(_2\)/g) in the HT sample. The CO\(_2\)-TPD pattern of Cu-HT reveals the presence of significantly high basicity in Cu-HT sample as compared to HT (Fig. 5a), which may be originated due to association of copper ions.

![Graph](image-url)

**Fig. 3.** TGA–DTG profiles of (a) HT and (b) Cu-HT samples.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Acid sites (mmol NH(_3)/g)</th>
<th>Total acid sites (mmol NH(_3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>420</td>
<td>0.57</td>
<td>0.57</td>
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<tr>
<td>Cu-HT</td>
<td>418</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>AHT</td>
<td>133</td>
<td>0.15</td>
<td>6.16</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>386</td>
<td>5.72</td>
<td></td>
</tr>
<tr>
<td>Cu-AHT</td>
<td>109</td>
<td>0.39</td>
<td>6.91</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>6.52</td>
<td></td>
</tr>
</tbody>
</table>
with interlayer carbonate and hydroxyl ions as well as hydroxyl-
ation of brucite layers. Two types of basic sites were observed in Cu-HT sample, which desorb maximum carbon dioxide from 100 to 200 °C and 220 to 500 °C showing the presence of medium strength (site density: 5.44 mmol CO$_2$/g) and strong strength (site density: 7.32 mmol CO$_2$/g) basic sites respectively (Fig. 5a). The calcination of Cu-HT reduced the basicity in Cu-AHT showing presence of lesser basic site density (4.56 mmol CO$_2$/g) with broad distribution of site strength (weak, medium and strong sites) in the Cu-AHT sample (Fig. 5b). The predominant peak representing stronger sites in the Cu-AHT sample was observed to be slightly shifted to higher temperature in comparison of the Cu-HT sample. In calcined HT sample (i.e. AHT), the basicity was observed to be significantly increased (total basic site density: 5.21 mmol CO$_2$/g) as compared to HT. Di Cosimo et al., reported that calcination of as-synthesized hydrotalcite gives a well-dispersed mixture of Mg and Al mixed oxides having strong Lewis (isolated O$^{2-}$ anions) and weaker Brønsted (OH$^-$ groups) basic sites [36]. They observed that the numbers of stronger Lewis (O$^{2-}$) sites are higher as compared to weaker Brønsted (OH$^-$) sites in calcined hydrotalcite. It has also been reported that the calcined hydrotalcite is strong basic catalyst compared to as-synthesized hydrotalcite, both in terms of basic strength and number of basic sites [38]. It indicates that the presence of copper in mixed oxide might be reducing the amount of surface basic sites in Cu-AHT. Thus, it can be assured from TPD study that the acidity of the as-synthesized Cu-HT sample was much lower than the basicity whereas the acidity of Cu-AHT was higher than basicity. Presence of copper enhanced the basicity in as-synthesized sample as compared to HT, whereas in calcined sample presence of copper showed decreased basicity.

The H$_2$ TPR profile of Cu-HT sample indicates reducibility of the copper species in the temperature range of 175–280 °C in two steps showing two maxima at 210 °C and at 240 °C for maximum

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Amount of basic sites (mmol CO$_2$/g)</th>
<th>Total amount of basic sites (mmol CO$_2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>168</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>Cu-HT</td>
<td>218</td>
<td>5.44</td>
<td>12.76</td>
</tr>
<tr>
<td></td>
<td>376</td>
<td>7.32</td>
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</tr>
<tr>
<td>AHT</td>
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</tr>
<tr>
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<td>218</td>
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<td>357</td>
<td>3.98</td>
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</tr>
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</table>

Fig. 4. NH$_3$-TPD profiles of (a) HT, Cu-HT and (b) AHT, Cu-AHT samples.

Fig. 5. CO$_2$-TPD profiles of (a) HT, Cu-HT and (b) AHT, Cu-AHT samples.
hydrogen consumption, which may be attributed to reduction of 
\( \text{Cu}^{2+} \) to \( \text{Cu}^+ \) and \( \text{Cu}^+ \) to \( \text{Cu}^0 \) respectively [18]. The two broad peaks at high temperature ranging from 300 °C to 560 °C may be attributed to reduction of copper ions strongly associated with support (HT). The Cu-AHT sample shows a single and sharp peak at 310 °C for reduction of copper species in \( \text{H}_2 \) TPR profile, which also reveals reduction of copper in single step (\( \text{CuO} \) to \( \text{Cu}^0 \)) [17]. The peak maximum at higher temperature in Cu-AHT sample as compared to Cu-HT sample indicates stronger interaction of copper with basic mixed oxide support (\( \text{MgO}–\text{Al}_2\text{O}_3 \)) than Cu-HT. Agrell et al. [39] stated the shifting in the reduction temperature peak in the TPR patterns of \( \text{CuO}–\text{ZnO}–\text{Al}_2\text{O}_3 \) catalysts due to the presence of larger \( \text{CuO} \) crystallites and/or possibly to a strong copper-support interaction.

3.2. Catalytic activity of supported copper samples in dehydrogenation of benzyl alcohol

The catalytic activity of Cu-HT and Cu-AHT samples was evaluated for catalytic transformation of alcohol using dehydrogenation of benzyl alcohol as model reaction. Usually the copper catalysts are reduced in flow of \( \text{H}_2 \) gas before testing the catalytic performance in dehydrogenation reactions [5–8,17,18,26,27], however, in the present study the samples were used as such without reducing the copper species. For comparison, the catalytic activity of respective supports (without copper) and commercial copper oxide was also examined for dehydrogenation of benzyl alcohol.

The support materials without copper (HT and AHT) were found to be inactive in dehydrogenation reaction as they did not show any conversion of benzyl alcohol (Table 4). The commercial copper oxide gave 96% conversion of benzyl alcohol with 25% selectivity towards benzaldehyde along with formation of benzyl benzoate (51%), toluene (2%), benzoic acid (13%) and di-benzyl ether (9%). The basic supports (hydrotalcite and its derived mixed oxide) have been reported to be suitable support for copper to promote its catalytic activity for dehydrogenation reactions [5–8,17,18,26,28].

To avoid the by-products formation (or acid catalyzed reactions) during alcohol dehydrogenation, the use of basic supports like Mg-Al hydrotalcite and its mixed oxides derived form could be best alternative to enhance the selectivity towards dehydrogenation reaction. The Cu-HT gave 94% conversion with 28% selectivity towards benzaldehyde along with formation of toluene (22%) and benzyl benzoate (49%). The copper containing hydrotalcite derived mixed oxide sample (Cu-AHT) gave highest selectivity of benzaldehyde (67%), but conversion was very less (17%) as compared to other samples. In addition, the benzyl benzoate was also formed in significant amount (27%). The high conversion of benzyl alcohol with Cu-HT may be attributed to high basicity and low temperature reducibility of copper species as compared to Cu-AHT [Fig. 6]. The acidic/metal sites are the adsorption sites for alcohols and the basic sites extract a proton from alcoholic hydroxyl group, forming metal-alcoholate species on the catalyst surface [1]. The β-hydride elimination with the help of metal ion/Lewis acid sites results to the carbonyl product. The low temperature reducibility of copper species in Cu-HT as compared to Cu-AHT can facilitate the abstraction of β-hydride ion from the alcohol during dehydrogenation.

With copper oxide, significant amount of benzoic acid was formed during dehydrogenation, which indicates that benzyl benzoate might be formed by acid catalyzed esterification of benzyl alcohol of benzoic acid, formed by over oxidation of benzaldehyde. As benzoic acid was not observed to be formed with the supported copper catalysts (Cu-HT and Cu-AHT), it seems that benzyl benzoate formation may be via oxidative esterification of benzaldehyde with benzyl alcohol and not by esterification of benzoic acid (formed by over oxidation of benzaldehyde) with benzyl alcohol. It indicates that the supported copper catalysts possess significant activity for oxidative esterification, which is a very important catalytic reaction in organic synthesis to produce esters from aldehydes and alcohols [40].

In Cu-HT catalyzed dehydrogenation of benzyl alcohol, significant amount of toluene (22%) was formed. The formation of toluene (in very less amount 2–3%) with CuO and Cu-AHT catalysts) can be possible by transfer hydrogenation of benzaldehyde with two molecules of hydrogen giving a water molecule. A similar reaction mechanism has been reported for hydrogenation of furfural in the coupling process of dehydrogenation of 1,4-butadiol and hydrogenation of furfural catalyzed by Cu-Zn–Al catalyst [41]. The basic sites of HT extract a proton from the alcoholic hydroxyl group, forming metal-alcoholate species on catalyst surface followed by β-hydride elimination with the help of metal ion/Lewis acid sites, giving the carbonyl product. The
protons and hydride ions removed from alcohol will remain adsorbed on basic and metal/Lewis acid sites, respectively and the catalytic cycle would be completed after the reaction of proton and hydride species to H2 or with a hydrogen acceptor (O2 or unsaturated molecules; here benzaldehyde). The protons and hydride ions (2H+ and 2H−) generated in dehydrogenation of benzyl alcohol can be utilized in catalytic reduction of benzaldehyde to toluene. This type of reaction, in which hydrogen (as protons and hydride ions adsorbed on the sites) produced during catalytic dehydrogenation reaction, is transferred to some other unsaturated molecules for catalytic hydrogenation/reduction reaction are generally known as transfer hydrogenation reactions and have great scope in coupling of dehydrogenation–hydrogenation reactions in single pot [5,7,18,41]. It clearly indicates the potential of Cu-HT catalyst in transfer hydrogenation reactions to combine dehydrogenation with transfer hydrogenation reactions to carry out single pot synthesis of dehydrogenated (unsaturated) and hydrogenated products. The catalysis results clearly indicate that Cu-HT has higher catalytic activity for dehydrogenation reaction as compared to Cu–AHT supported catalyst as Cu-HT gave highest conversion of benzyl alcohol and highest selectivity towards dehydrogenation and transfer hydrogenation. The high basicity with significant amount of acidity and low temperature reducibility of copper species in Cu-HT may be the required features to show multifunctional catalytic properties. From catalytic evaluation of the supported copper catalysts, it was found that the Cu-HT catalyst possesses multifunctional catalytic property and it could be an efficient catalyst for transformations of alcohols. However, the further optimization of catalyst characteristics can improve the activity in terms of desired product selectivity (towards transfer hydrogenation reaction).

The effect of reaction temperature on the catalytic performance of Cu-HT sample in terms of conversion of alcohol and selectivity towards dehydrogenation and transfer hydrogenation reaction was studied (Fig. 7). All the conversions and selectivity data reported in Fig. 7 are within ±2% precision. At lower temperature (<160 °C), the conversion of alcohol was less, however, selectivity of benzaldehyde was high (73–99%). At high temperature (>160 °C), benzaldehyde selectivity was reduced due to formation of toluene and benzyl benzoate. With temperature conversion of alcohol increases from 160 °C to 190 °C and then slightly decreases at 200 °C indicating that the optimum temperature for highest conversion is 190 °C. The selectivity of toluene increases from 160 °C to 180 °C and remains steady up to 200 °C, whereas the selectivity for benzyl benzoate gradually increased from 160 °C to 190 °C and then remains almost constant up to 200 °C. The formation of toluene and benzyl benzoate in significant amount above 160 °C indicates that catalyst is active for transfer hydrogenation and oxidative esterification of alcohol above 160 °C.

As 190 °C reaction temperature is optimum temperature giving highest conversion and steady selectivity for benzaldehyde, toluene and benzyl benzoate, the kinetics of the reaction was studied at 190 °C to know the product distribution with reaction progress from 4 h to 15 h. The kinetics graph (Fig. 8) shows that benzyl alcohol conversion gradually increases till 15 h indicating no deactivation of catalyst. The highest selectivity for toluene was achieved at 4 h and it remained unchanged throughout the reaction period, which indicates that the nature of the sites responsible for toluene formation (transfer hydrogenation) may be changed or those sites may be deactivated. The selectivity of benzaldehyde gradually decreased with time on expense of benzyl benzoate formation.

3.3. Catalytic activity of HT supported copper catalyst in catalytic transformation of different alcohols

The Cu-HT showed significant activity in conversion of different alcohols to dehydrogenation and transfer hydrogenation/hydrogen auto transfer products (Table 5); however the conversion of alcohols and selectivity of the products varied, which were observed to be dependent on the nature of alcohol. The benzyl alcohol (1) being a reactive alcohol (having benzylic group) showed highest reactivity for conversion of benzyl alcohol (95%) to benzaldehyde (1a; 11%), toluene (1b; 22%) and benzyl benzoate (1c; 67%). The toluene (1b) and benzyl benzoate (1c) are formed in transfer hydrogenation of benzaldehyde and oxidative esterification of benzaldehyde with benzyl alcohol (Scheme 2). The p-nitrobenzyl alcohol selectively resulted to p-nitrobenzaldehyde (51% conversion) showing that the electron withdrawing −NO2 group deactivate the benzylic group for dehydrogenation reaction as well as retard the other reactions.

Cyclohexanol, a cyclic secondary alcohol gave 34% conversion with 68% selectivity of cyclohexanone (3a). The other products formed during the reaction of cyclohexanol were bi-cyclohexyl 2-one (3b; 24%) and 2-cyclohexyl cyclohexanone (3c; 7%). The bi-cyclohexyl 2-one (3b) is possible to be formed by a consecutive two step reaction; the first step base catalyzed self aldol condensation of two molecules of cyclohexanone (3a) to an α,β-unsaturated...
carbonyl (ND: not detected in reaction mixture) followed by C−C bond hydrogenation with adsorbed H2 on the basic and metal sites (as H+ and H−) produced in dehydrogenation of cyclohexanol (Scheme 2). The overall reaction results to α-alkylated carbonyl product (α-cyclohexyl cyclohexanone), therefore, the reaction is called as α-alkylation of carbonyl. The 2-cyclohexyl cyclohexanone (3c) might be formed by hydrogenation of C=O bond of bicyclohexyl 2-one (3b) with adsorbed H2. The reactions involving production of hydrogen in dehydrogenation step and its utilization in consecutive reactions for hydrogenation of unsaturated bonds (C=C/C=O bonds) are known as hydrogen auto transfer (borrowing hydrogen) reactions. This type of reactions using a multifunctional catalyst is promising for single pot multi-step synthesis involving dehydrogenation, aldol condensation, dehydration and hydrogenation.

The Cu-HT showed significant activity with a primary alcohol (n-octanol) giving 60% conversion of n-octanol to n-octanal (4a, 13%), 2-hexyl decanal (4b, 15%), n-octyl octanoate (4c: 30%), dioctyl ether (11%) and others (31%). The 2-hexyl decanal (4b) and n-octyl octanoate (4c) are products of α-alkylation of n-octanol (obtained from n-octanol) and oxidative esterification of n-octanol with n-octanol respectively (Scheme 2).

The formation of bi-cyclohexyl 2-one (3b) and 2-hexyl decanal (4b) from cyclohexanone (obtained from cyclohexanol) and n-octanal (obtained from n-octanol) reveals that Cu-HT may have good scope in α-alkylation of carbonyls. The one-pot synthesis of methyl iso-butyl ketone (MIBK) from acetone and 2-methyl-3-phenyl-propanal (MPPAL) from benzaldehyde and propanal are examples of this type of reaction (α-alkylation of carbonyls), which is of great industrial interest. The classical industrial

### Table 5

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Conversion (wt.%)</th>
<th>Products (wt.% selectivity) formed in</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3OH</td>
<td>95</td>
<td>CH(O) (1a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH3 (1b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O=O (1c)</td>
</tr>
<tr>
<td>CH3OH</td>
<td>51</td>
<td>CH(O) (2a)</td>
</tr>
<tr>
<td>NO2</td>
<td></td>
<td>NO2 (2b)</td>
</tr>
<tr>
<td>OH</td>
<td>34</td>
<td>O (3a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(3b)</td>
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<td></td>
<td></td>
<td>(3c)</td>
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<tr>
<td></td>
<td>60</td>
<td>CHO (4a)</td>
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<tr>
<td></td>
<td></td>
<td>CHO (4b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O (4c)</td>
</tr>
<tr>
<td>CH3OH</td>
<td>59</td>
<td>CH(O) (5a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH3 (5b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6a)</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>CHO (6b)</td>
</tr>
</tbody>
</table>

- a Reaction condition: 1.1 g alcohol substrate, 0.1 g catalyst, 190 °C, 15 h.
- b 11% di-octyl ether and 31% others.
- c 16% di-furfuryl ether and 19.5% others.
- d At 140 °C.
- e 21% others.
process for their preparation involves the base (NaOH) catalyzed aldol condensation of acetone (for MIBK) or benzaldehyde and propanal (for MPPAL) followed by dehydration (base catalyzed) to an α,β-unsaturated carbonyl intermediate (mesityl oxide and 2-methyl cinnamaldehyde respectively), in which the C=C bond is finally hydrogenated to MIBK or MPPAL generating large amount of waste. Several bi-functional acid/metal catalysts and multifunctional base/acid/metal catalysts were used to have a more eco-friendly process based on heterogeneous catalysis [32a–32n]. However, Ni, Pd, Pt and Cu supported on basic supports were found more efficient as multifunctional base/acid/metal catalysts [32a,32c,32e,32g,32j–32m]. It is to be noted that H₂ is supplied from external source for hydrogenation reaction. It clearly indicates that the synthesized Cu-HT catalyst can be used as multifunctional catalyst in α-alkylation of carbonyls using alcohol as source of carbonyl as well as alkylating agent.

Furfuryl alcohol (5) conversion was 59% and it gave 60.5% furfural (5a; dehydrogenation product), 4% 2-methyl furan (5b; transfer hydrogenation product of furfural), 16% di-furfuryl ether (product of etherification of furfuryl alcohol) and 19.5% others. It was noticed that the benzylic (except p-nitrobenzyl alcohol and furfuryl alcohol) and primary alcohols (n-octanol, cinnamyl alcohol) showed remarkable reactivity towards oxidative esterification giving respective esters (benzyl benzoate from benzyl alcohol, n-octyl octanoate from n-octanol and cinnamyl cinnamate from cinnamyl alcohol).

3.4. Regeneration and reusability of spent catalyst

To regenerate the spent Cu-HT catalyst, the spent catalyst obtained after filtration from the benzyl alcohol reaction mixture, was washed with acetone by adding in 4 mL acetone and stirred for 30 min. The washed catalyst was filtered and dried at 80 °C for 12 h. The regenerated catalyst was used in next reaction cycles (for benzyl alcohol reaction) to evaluate the reusability of the catalyst. The regenerated catalyst showed almost similar catalytic activity in next three consecutive reaction cycles without showing much reduction in conversion and selectivity. The fresh Cu-HT catalyst is greenish powder and turns to brown color during the reaction, which may be due to reduction of copper species (Fig. 9).

When the spent catalyst (brown color) is washed with acetone, the color of the catalyst turns to its original color indicating the complete regeneration of catalyst. It shows that by washing catalyst could be easily regenerated. The adsorption of alcohol or intermediates on copper sites might be reducing the copper
species and on washing with acetone, the adsorbed species might be desorbed from the copper sites.

4. Conclusions

The Mg–Al hydrotalcite and derived mixed oxides supported copper catalysts were synthesized and characterized. The supported copper catalysts were found to be active for dehydrogenation reaction. The nature of support material has strong influence on catalytic performance of copper catalyst in catalytic transformation of alcohols. The HT supported copper was found to be highly active catalyst towards the benzylic alcohol dehydrogenation and in transfer hydrogenation/hydrogen auto transfer reactions. The high basicity and intercalated copper ions in Mg–Al hydrotalcite supported copper sample showed multifunctional activity in various catalytic transformations of alcohols.

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