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

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ABSTRACT

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).

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/SiO_2, ZnO/Al_2O_3, Cr_2O_3/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. Cr_2O_3/MgO), different hydrotalcites and their derived mixed oxides have received great attention in recent years as an appropriate support for copper [5–8,17,18,26–28]. 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 H_2 reduced Cu/MgO and Cu–Cr_2O_3/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^-, OH^-, 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 heterogeneous 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 environmental 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 carbonyls followed by various catalytic reactions of carbonyls (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 $Cu(CH_3COO)_2$, $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH and Na_2CO_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 $Mg(NO_3)_2{\cdot}6H_2O$ (0.22 mol) and $Al(NO_3)_3{\cdot}9H_2O$ (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_2CO_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_2O_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 charge 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: $\lambda = 1.5405$ Å, in 2θ range of 10–80°). The samples were analyzed by Fourier transform infrared (FT-IR) spectroscopy (IRPrestige-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})