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Study on the catalytic properties of silica supported copper catalysts

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Abstract

The mesoporous silica (MS) supported copper catalysts containing 2 wt. % copper in finely dispersed form were synthesized and characterized. A comparative study on the effect of calcination temperature and reduction of the supported metal on catalytic property of supported copper species was carried out. The loading of copper on the supports provides good reducibility and catalytic activity for dehydrogenation of benzyl alcohol. The acidity and copper ions in mesoporous silica supported copper sample showed good activity in catalytic transformations of benzyl alcohol.

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1. Introduction

Catalytic transformations of alcohols like dehydrogenation, oxidative esterification, amination, 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 [1-5]. 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, and Cr₂O₃/MgO), different hydrotalcites (LDH's: layered double hydroxides) and their corresponding mixed oxides have been widely used as support for copper [5, 6-9]. 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 has been used as a structural promoter as it enhances the BET surface area and also inhibits the sintering of copper particles [10]. The introduction of copper in the framework of silica possesses significant catalytic activity towards dehydrogenation of alcohols [11]. 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, 7, 8, 12-17]. 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 multifunctional catalysts

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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.

In the present work, we studied the influence of silica support on physico-chemical and catalytic properties of supported copper species for dehydrogenation of benzyl alcohol.

2. Experimental

2.1. Materials

All the chemicals used were of synthetic grade having purity above 99%. HCl, $\text{Cu}(\text{CH}_3\text{COO})_2$, and cetyl trimethyl ammonium bromide (CTAB) were obtained from s.d fine chemicals Ltd. India. Tetraethyl orthosilicate (TEOS, Molar Mass = 208 g, synthetic grade, purity >99 %) was purchased from Aldrich Chemicals, India. The benzyl alcohol (GR, purity 99.8%) was purchased from Merck India. Ltd and used without any further purification.

2.2. Synthesis of mesoporous silica

Mesoporous silica was prepared by template assisted sol-gel method reported in literature [17]. During the synthesis, HCl (2.2 mol) and TEOS (1.0 mol) were mixed in distilled water (700 mol) at room temperature and then the surfactant CTAB (0.1 mol) was added to obtain a homogeneous solution. After dissolution, the reaction was then continued at room temperatures under vigorous stirring for 4 h. Thereafter, the reaction mixture was then heated to 100°C and maintained at this temperature for 1 h. The resultant precipitate was filtered and dried at 70°C overnight. The mesoporous silica thus formed is calcined at 600°C for 4 h. The final yield of mesoporous silica after calcination was 25 %.

2.3. Synthesis of supported copper samples

The copper was loaded on the support (mesoporous silica) by wet impregnation of silica (4 g) with aqueous solution of copper acetate (0.025 M, 40 mL) under stirring for 24 h at room temperature. The copper impregnated silica with distilled water (4 X 50 ml) to remove free copper and acetate ions and then dried at 70°C for 12 h. The copper impregnated silica was calcined at 600°C for 4 h to get silica supported copper sample (Cu-MS).

Table 1. Catalyst samples prepared and their preparation method are summarized below

Sample	Preparation parameters (calcinations temperature of silica, precursor concentration, reduction, final calcinations temperature)
Cu-SiO (600/ 400)	600°C, 10 wt.% copper acetate solution, 400°C
Cu-SiO (600/ 600)	600°C, 10 wt.% copper acetate solution, 600°C
Cu-SiO (800/ 400)	800°C, 10 wt.% copper acetate solution, 400°C
Cu-SiO (800/ 600)	800°C, 10 wt.% copper acetate solution, 600°C
RCu-SiO (600/ 400)	600°C, 10 wt.% copper acetate solution, reduction, 400°C
RCu-SiO (600/ 600)	600°C, 10 wt.% copper acetate solution, reduction, 600°C
RCu-SiO (800/ 400)	800°C, 10 wt.% copper acetate solution, reduction, 400°C
RCu-SiO (800/ 600)	800°C, 10 wt.% copper acetate solution, reduction, 600°C

2.4. Characterization of supported copper samples

The copper content in the copper containing samples was estimated by Inductive Couple Plasma-OES (Perkin Elmer Instrument USA, Optima 200 DV). The BET surface area (S_{BET}) of the samples, was determined from N_2 adsorption data (by using BET equation) measured at 77K using Quantachrome NOVA 1000e USA surface area analyzer. The synthesized samples were characterized by Powder X-ray diffraction (XRD) using (Philips X'pert, Netherland, using $\text{CuK}\alpha$ radiation: $\lambda = 1.5405 \text{ \AA}$, in 2θ range of 10–80°). The operating voltage and the current were 40 kV and 35 mA. Thermo gravimetric

analysis (TGA) of the samples were carried out using Mettler thermal analyzer TGA/DSC 1 SF/752 USA, 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 CO₂ (CO₂-TPD) and NH₃ (NH₃-TPD) and H₂ temperature programmed reduction (H₂-TPR) for the samples were carried out using Micromeritics, USA, taking 50 mg of sample (heated at 100°C for 1 h), under helium flow (30 mL h⁻¹) as carrier gas. For CO₂-TPD and NH₃-TPD analysis, the adsorption of CO₂/ NH₃ on the samples was carried out at 50°C by exposing to a flow of helium mixed CO₂/ NH₃ gas (10%, 20 mL h⁻¹) for 1 h. The desorption of CO₂/ NH₃ was carried out by heating the sample up to the final temperature of 900°C (12°C min⁻¹) and was monitored by gas chromatography with thermal conductivity detector (TCD).

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

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 catalyst) were taken in the reaction tubes (10 ml) of reaction station (12 Place Heated Carousel Reaction Station, RR99030, Radleys Discovery Technologies, UK). The reaction was carried out at desired temperature under stirring for required reaction time. 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 meter) capillary column with a programmed oven temperature from 50 to 200°C, a 0.5 cm³/min flow rate of N₂ as carrier gas and FID detector. 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, USA) 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.

3. Results and discussion

3.1. Catalyst characterization

The EDAX and the ICP analysis revealed that copper loading was up to (1.8 wt. %) in the samples prepared by using copper acetate precursor. The XRD study in small angle range of mesoporous silica calcined at 600°C and 800°C showed that silica is a SBA type material. The XRD patterns (Fig 1) of supported copper catalysts (calcined at 400°C and 600°C) prepared without reduction of copper did not show any characteristic peaks of copper species, which may be due to presence of very small amount of copper species in dispersed form which is further supported by the fact that no sintering occurs at the calcination temperatures of final catalyst, to give bigger aggregates of copper species. No significant peak shifts were observed for various catalyst samples. There was no change observed in the structure of support material after loading copper.

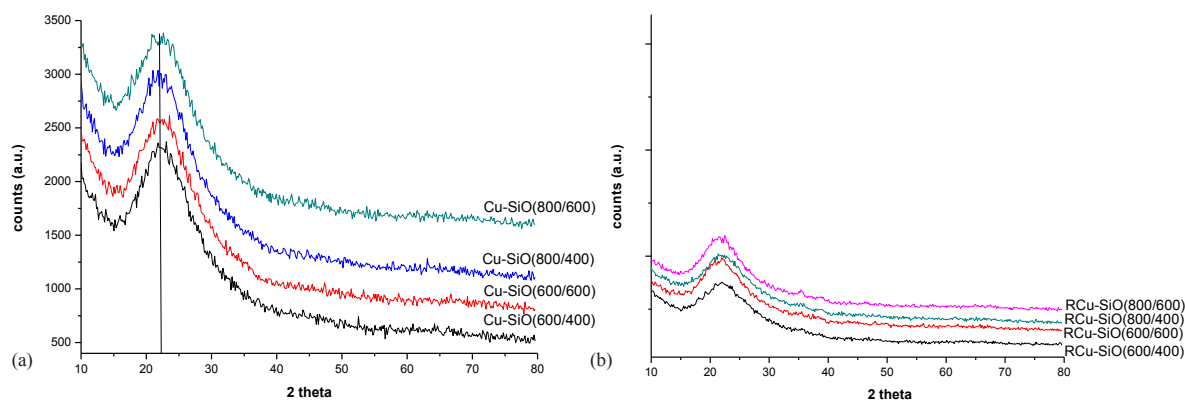


Fig 1. (a) XRD pattern of Cu-SiO₂ (b) reduced Cu-SiO₂ samples calcined at different temperature and CuO.

BET surface area, pore radius and pore volume of the mesoporous silica calcined at 600°C was 596 m²/g, 1.4 Å and 0.399 cc/g. It was observed that loading of copper followed by calcinations lowered the surface area, and pore volume of the supported materials.

Table 2. BET surface area (S_{BET}), pore size and pore volume of SiO₂ and Cu-SiO₂ samples calcined at different temperature.

Sample	S_{BET} (m ² /g)	Pore radius (Å)	Pore volume (cc/g)
Mesoporous silica calcined at 600°C	596	1.40	0.39
Cu-SiO(600/400)	343	1.32	0.29
Cu-SiO(600/600)	300	1.30	0.28
Cu-SiO(800/400)	258	1.35	0.31
Cu-SiO(800/600)	460	1.39	0.34

The thermogravimetric and differential scanning calorimetric (TGA-DSC) study of the silica supported copper sample (Cu-MS) revealed the high thermal stability of the material as it did not show any significant weight loss as well as heat change on heating from room temperature to 800°C. The NH₃-TPD (Fig 2a) profile of supported copper catalyst shows that loading of copper significantly enhanced the surface acidity of the catalyst as compared to mesoporous silica. The H₂-TPR (Fig 2b) results indicate that the supported copper has significant hydrogen consumption in the range of 150°C to 250°C showing good reducibility of the catalyst due to copper species. TPR study confirms that this catalyst should have potential activity in dehydrogenation reactions. The H₂-TPR profile (Fig 2b) of Cu-MS sample shows a single broad peak (centered at 198°C) in the range of 125°C to 250°C indicating the reducibility of copper species in one step (CuO to Cu⁰).

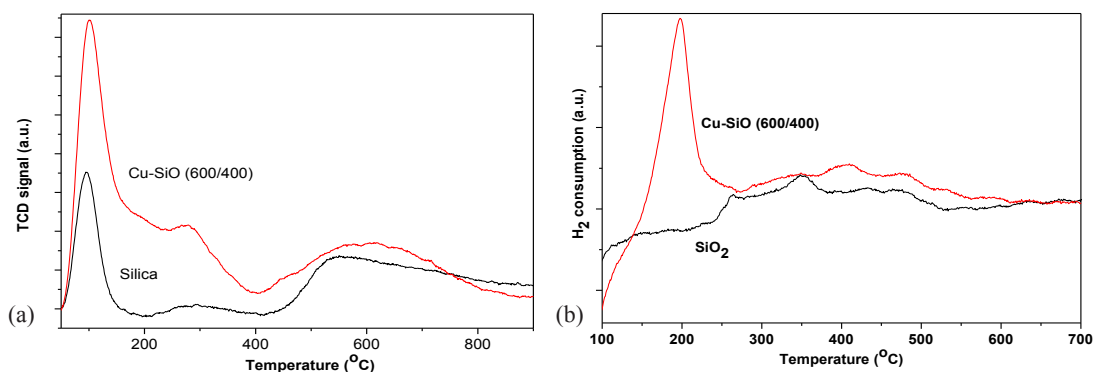


Fig 2. (a) NH₃-TPD (b) H₂-TPR of mesoporous silica and silica supported copper catalyst.

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

The catalytic activity of Cu-MS 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 H₂ gas before testing the catalytic performance in dehydrogenation reactions [5,8] however, in the present study the samples were used without reducing the copper species and also compared with samples which are reduced by sodium borohydride. All silica supported copper catalysts were found to be active for dehydrogenation reaction giving significant conversion (9% to 76%) of benzyl alcohol. The support materials without copper (MS) were found to be inactive in dehydrogenation reaction as they did not show any conversion of benzyl alcohol (Table 3). With Cu-MS, the maximum conversion of benzyl alcohol as well as selectivity for benzaldehyde was (71 % and 17 % respectively). The benzyl benzoate (20%), di-benzyl ether (22%) and

some by-products (41%) were also obtained in Cu-MS catalyzed dehydrogenation of benzyl alcohol. The di-benzyl ether and some of other by-products formed with Cu-MS are expected to be produced by acid catalyzed reactions of benzyl alcohol, which reduces the selectivity of benzaldehyde. As alcohols are highly reactive towards acids and the Cu-MS possesses significant amount of surface acidity (Fig. 2a), benzyl alcohol can undergo different acid catalyzed reactions like O-alkylation (etherification) of benzyl alcohol to di-benzyl ether, C-alkylation (Friedel-Craft alkylation) of benzyl alcohol with benzyl alcohol to benzylated derivatives of benzyl alcohol, etc.

The catalysts prepared by reduction of loaded copper ions with NaBH₄ followed by calcinations showed less conversion (9-16%) of benzyl alcohol to benzaldehyde with high selectivity (76-95%). Whereas, the calcinations without reduction of copper ions gave high conversion (38-76%) of benzyl alcohol, but the selectivity of benzaldehyde was significantly less (5-17%). It can be seen that the calcinations temperature of support (silica) and final calcinations of supported material also influenced the conversion and selectivity profile. To confirm the dehydrogenation is oxidative or not vapour phase reaction at fixed bed reactor were performed. The vapour phase dehydrogenation reaction at 300°C resulted selectively to benzaldehyde (100%), however conversion was less (~20%). There was no influence of the presence of oxygen on the dehydrogenation of benzyl alcohol in liquid or vapour phase reactions. As benzoic acid was not observed to be formed with the supported copper catalysts (Cu-MS,) therefore, 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 [18]. This type of reactions, 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 addition on unsaturated bonds are generally known as transfer dehydrogenation reactions and have great scope in coupling of dehydrogenation-hydrogenation reactions in single pot [5,8]. It clearly indicates the potential of the catalyst in transfer hydrogenation reactions to combine dehydrogenation with and hydrogenation reactions to carry out single pot synthesis of dehydrogenated (unsaturated) and hydrogenated products. From catalytic evaluation of the supported copper catalysts, it was found that the catalyst possesses multifunctional catalytic property and it could be an efficient catalyst for different transformations of alcohols. As 180°C reaction temperature is optimum temperature giving highest conversion and steady selectivity for benzaldehyde, toluene and benzyl benzoate, the reaction was studied at 180°C to know the product distribution with different catalysts. The reason of major by-products formation in liquid phase batch reaction with silica supported catalyst may be due to the surface acidity of the silica in presence of Cu metal, which catalyzes etherification of alcohols to ether and esterification of benzyl alcohol with benzoic acid formed by oxidation of benzaldehyde.

Table 3. Catalytic activity of different silica supported copper catalysts for dehydrogenation of benzyl alcohol in liquid phase

Sample	Conversion (wt. %)	Selectivity (%)			
		Benzaldehyde	Benzyl benzoate	Dibenzyl ether	Others
Cu-SiO ₂ (600/400)	63	16	52	24	8
Cu-SiO ₂ (600/600)	71	17	22	41	20
Cu-SiO ₂ (800/400)	38	17	44	39	0
Cu-SiO ₂ (800/600)	57	6	4	77	13
RCu-SiO ₂ (600/400)	16	76	19	5	0
RCu-SiO ₂ (600/600)	12	93	7	0	0
RCu-SiO ₂ (800/400)	9	89	11	0	0
RCu-SiO ₂ (800/600)	11	79	17	4	0

Reaction Conditions: 1.1 g benzyl alcohol, 0.15 g catalyst, 180C, 15 h.

Conclusions

The mesoporous silica supported copper catalysts were synthesized and characterized. All silica 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 surface acidity of the silica in presence of copper reduces the selectivity of dehydrogenation product. The silica supported copper catalysts prepared without reduction of copper as well as by reduction followed by calcinations at 400°C and 600°C did not show any characteristic peaks of copper species. The preparative parameters and reaction conditions have strong influence on catalytic performance of catalyst in dehydrogenation reaction

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