

Synthesis and Surface Characterization of Supported Copper based Catalysts

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Citation: Harisekhar M, Chary KVR, Vishwanathan V (2021) Synthesis and Surface Characterization of Supported Copper based Catalysts. *TechnoLock Arch Mater Sc* 1: 1-7

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ABSTRACT

A study was carried out to understand the structural and textural properties of SBA-15 supported copper catalysts. The Cu/SBA-15 catalysts were prepared by the incipient wetness method using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as precursor and the copper content was varied between 5 and 20 wt%. The catalysts were characterised by X-ray diffraction (XRD), Temperature programmed Reduction (TPR), Temperature programmed desorption (TPD) and N_2 adsorption and desorption measurements. XRD profile revealed that at a lower copper loading (<5 wt%), smaller crystallites of CuO were highly dispersed. TPD of NH_3 and CO_2 results showed a reverse trend in acidity and basicity of the catalysts with increasing copper content on the surface of SBA-15, respectively. The influence of catalyst functionalities such as metal dispersion, metal area and surface acidity and basicity were attempted to correlate against the catalytic activity in terms of conversion, selectivity, and stability through a test reaction viz., gas phase hydrogenolysis of glycerol under atmospheric pressure.

Keywords: Incipient Wetness; Characterisation; Desorption; Acidity; Basicity

Introduction

There are only few limited reports available on mesoporous silicious materials supported copper oxide catalysts [1,2]. Copper as a metal plays an important role due to its redox properties, polarizability, lower cost, and higher reduction potential among other transition metals [3]. Silica supported copper oxide catalysts are used in many industrial reactions such as hydrogenation, dehydrogenation, dehydration, hydrogenolysis and so on [4-7]. Highly dispersed amorphous copper oxide systems have been studied extensively due to their good activity.

Mesoporous silica materials have been used widely as catalytic supports due to the presence of two-dimensional hexagonal symmetry of their cylindrical pores and their high hydrothermal stability [8]. They have cylindrical pores with diameter ranging from 5 to 35 nm diameter and has a high surface area (880m²/g) [9,10]. It is a promising new support material for catalysts as its thick framework walls (31–64 Å) provide high hydrothermal stability that exceeds those of the thinner-walled MCM-41 materials. The present investigation deals with the synthesis and surface characterization of Cu/SBA-15 catalysts. The catalysts were characterized by XRD, TPR and by gas adsorption measurements to determine the Cu dispersion, metal area and the acid-base properties of the catalysts. The main aim of the presentation is to correlate the influence of catalyst functionalities against reaction activity in terms of conversion, selectivity, and stability by conducting a gas phase hydrogenolysis of glycerol as a model reaction.

Experimental

SBA-15 silica was prepared as per the reference [11,12] using block copolymer poly-ethylene glycol–block-polypropylene glycol–block-poly-ethylene glycol (P123, average molecular mass 5800) as a template. Two grams of P123 copolymer was dissolved in a mixture of 15g of water and 45g of 2M HCl under stirring followed by the addition of 0.2g of cetyltrimethylammonium bromide (CTMABr) and 5.9g of tetraethyl orthosilicate (TEOS). The resultant product, SBA-15 was kept at 100 °C for 24 h and washed with ethanol, and dried. A series of copper catalysts with Cu loadings varying from 5 to 20 wt% were prepared by incipient wetness method using Cu (NO₃)₂·3H₂O as precursor on as-synthesised SBA-15 support. The samples were dried at 80 °C for 16 h and subsequently calcined at 500 °C for 5 h in air.

The characterization of the catalysts was studied using various analytical techniques. X-ray diffraction (XRD) profiles were obtained with a Rigaku, Miniflex diffractometer, using nickel filtered Cu K α radiation ($\lambda=1.5406\text{\AA}$). Nitrogen adsorption-desorption isotherms were measured using Autosorb (Quanta chrome instruments) at 77 K. The surface areas and pore sizes were determined from BET and BJH methods, respectively. Temperature programmed reduction (TPR) was carried in hydrogen gas using Autochem 2910 (Micromeritics) instrument to calculate copper dispersion and reducibility. H₂ consumption and T_{max} positions were calculated using the GRAMS/32 software. Copper surface area, percentage dispersion and Cu crystallite size were calculated through N₂O decomposition. Temperature programmed desorption (TPD) experiments were conducted using NH₃ and CO₂ as adsorbate molecules to determine the surface acidity and basicity, respectively.

Gas phase hydrogenolysis of glycerol was used as a model reaction to study the performance of the catalysts in terms of activity and selectivity. The reaction was carried out in a fixed-bed glass reactor operating under atmospheric pressure. The reaction products were analysed on a GC–MS apparatus (HP 5973).

Results and Discussion

The low angle XRD profiles of Cu/SBA-15 catalysts showed a well-resolved diffraction peak at $2\theta = 0.8^\circ$ along with two other low intense peaks at $2\theta = 1.59^\circ$ and 1.80° (Figure 1). All the samples showed a mesoporous structure of SBA-15 with three well-resolved diffraction peaks at (100), (110) and (200) reflections. These peaks confirm that the synthesised SBA-15 is a mesoporous silicious structure and in agreement with reported literature [13]. Also, it confirms that no major changes were observed in the structure of SBA-15 even after the impregnation of copper oxide on its surface. The wide-angle XRD profiles of Cu/SBA-15 catalysts are shown in Figure 1. The broad diffraction peak appeared at $2\theta = 24^\circ$ corresponds to an amorphous silica phase [14,15]. There were no detectable diffraction peaks of crystalline CuO below appeared below 5 wt% copper loading. This suggest that small crystallites of CuO may be present in a highly dispersed state on the surface of SBA-15. However, at higher loadings of copper, the larger crystal-

lites of CuO were observed at $2\theta = 35.5^\circ, 38.7^\circ, 48.7^\circ, 58.3^\circ$ and 61.8° . The intensities of the peaks showed an increasing trend with the increase in copper loading. The presence of high intensity confirms the strong crystallinity of the catalysts [16,17].

The BJH pore size distribution of SBA-15 and Cu/SBA-15 catalysts are shown in Figure 2. The surface areas of the catalysts were measured by BET method using N₂ at 77 K. The results are shown in Table 1. The surface area of as-synthesised SBA-15 was 869 m²/g. With increasing copper loading, the surface area values decreased. This decrease is attributed to the blockage of pores of SBA-15 with CuO crystallites. Similarly, the pore volume of the catalysts decreased with copper content. Once again, this behaviour indicates the blockage of pores by the CuO crystallites. Figure 2 clearly shows the decrease in intensity of the peaks with increase in copper content on SBA-15.

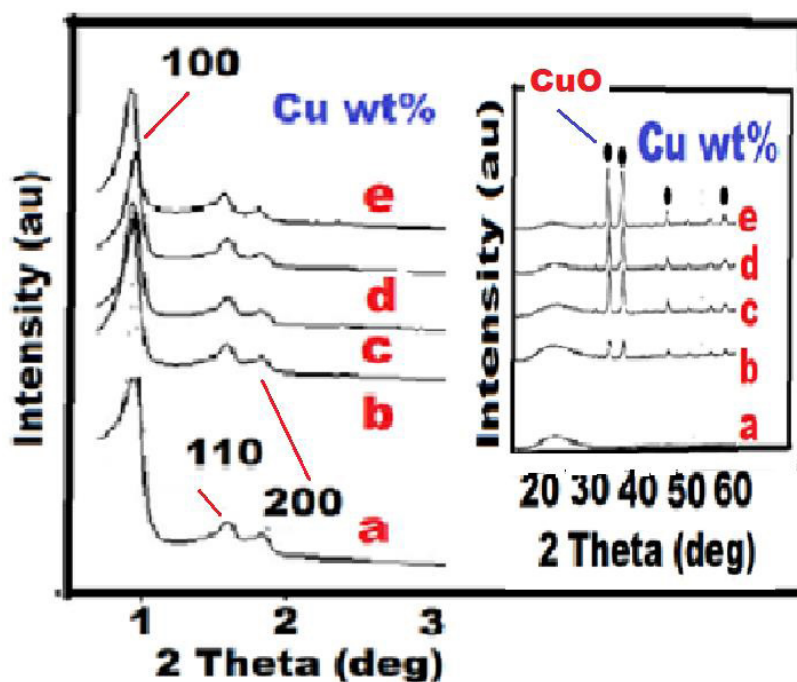


Figure 1: XRD profiles of low angle diffraction peaks of SBA-15 (a) and of Cu/SBA-15 catalysts with loading of Cu wt% 5 (b); 10 (c); 15 (d); and 20 (e). The corresponding wide angle diffraction peaks are shown in the inset

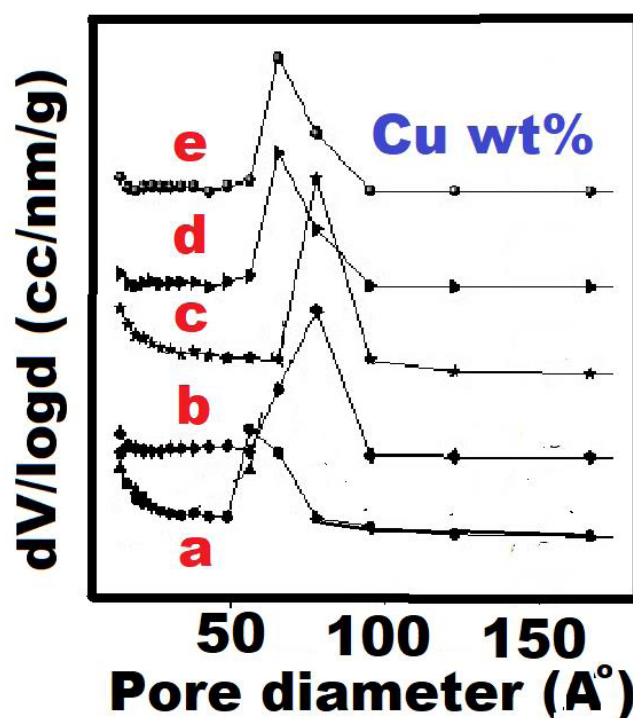


Figure 2: The pore size distribution of SBA-15 (a) and of Cu/SBA-15 catalysts with loading of Cu wt% 5 (b); 10 (c); 15 (d); and 20 (e)

The reducibility of copper oxide species on the catalysts were investigated by TPR experiments as shown in Figure 3. The reduction profile provides information on the reduction of metal crystallites on the surface and demonstrate the on-set of metal-support interaction in Cu/SBA-15 catalysts [18-20]. TPR profiles shows the presence of two different copper species. Two reduction peaks appeared around 230 °C and 353 °C with different H₂ consumption values. The reduction peak at 353 °C and at 230 °C are attributed to the reduction of bulk CuO crystallites and to the highly dispersed crystallites of CuO, respectively. Highly dispersed smaller crystallites of copper oxide are known to be easily reducible at lower temperature as compared to larger crystallites [14]. With increasing copper loading, the intensity of the second peak increased. This shows the formation of more number of larger crystallites of CuO on the surface of SBA-15 which were reduced. The broadening of the peak and the shifting of the maximum temperature (T_{max}) towards higher temperatures may be due to the increasing crystallinity of CuO phase with increasing Cu loading. This is agreement with the XRD results. The increase in H₂ consumption with the second peak at higher Cu loading further confirms the formation of larger CuO crystallites.

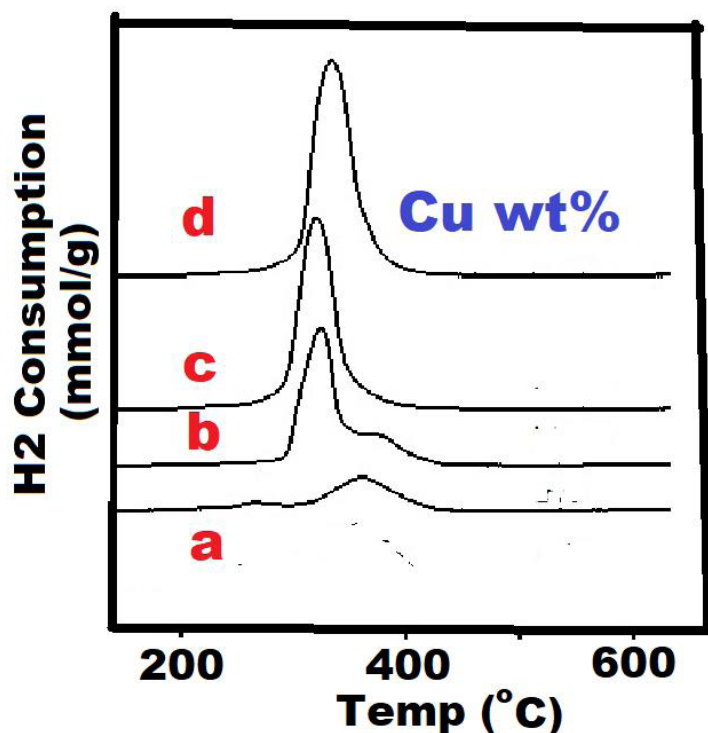


Figure 3: TPR profiles of Cu/SBA-15 catalysts with loading of Cu wt% 5 (a); 10 (b); 15 (c); and 20 (d)

Cu (wt%)	Surface Area (m ² /g)	Pore Volume (ml/g)	Pore Area (nm)	Metal Dispersion (%)	Metal Area (m ² /g.Cu)	Crystallite Size (Å)	Total Acidity (μmol/g)	Total Basicity (μmol/g)
0	869	0.93	5.7	-	-	-	985	1176
5	643	0.86	7.75	16.6	107.4	6.62	1112	1000
10	537	0.79	7.72	9.06	58.4	11.5	1265	999
15	500	0.75	6.61	8.68	56.1	12.0	1365	848
20	480	0.67	6.60	6.41	46.3	16.2	1480	807

Table 1: The physico-chemical properties of Cu/SBA-15 catalysts

The Temperature programmed desorption (TPD) of ammonia determines the acidity of catalysts and their strength distribution. TPD profiles of Cu/SBA-15 catalysts and the total acidity values are shown in Figure 4 and Table 1, respectively. Three desorption regions, one <180 °C, two between 180° and 450 °C, and three > 450 °C were observed. The desorption peaks below 180°C represent the weak acid sites on SBA-15 surface. While the 2nd and 3rd peaks represent the medium and strong acid sites on the surface of the catalysts, respectively [21-23]. The total acidity increased with copper loading suggest the formation of larger CuO crystallites at higher content of copper. Similarly, the basicity of the Cu/SBA-15 catalysts was studied by TPD with CO₂ as adsorbate. The

pure SBA-15 showed more basicity than the supported copper catalysts. Interestingly, one observes that with increase in copper loading, the total surface basicity decreases (Table 1). These findings of surface acidity and basicity are in agreement with some of the reported literature [24,25].

The Cu/SBA-15 catalysts were tested for the gas phase hydrogenolysis of glycerol to 1,2-propanediol at 220°C under atmospheric pressure. The as-synthesized SBA-15 showed very low glycerol conversion (10 %) as well as poor selectivity for propanediol (Figure 5). With increasing copper loading both conversion and selectivity went through a maximum at 5 wt% and decreased thereafter. This decrease may be due to the presence of larger crystallites of CuO on the surface. Among the catalysts tested under this model reaction, 5 wt% Cu/SBA-15 catalyst showed better conversion and selectivity. The high dispersion of smaller crystallites of CuO and surface basicity below 5 wt% may be responsible for the significant enhancement of conversion and selectivity. The effect of reaction time was also investigated under the same reaction conditions Figure 5 (Inset). The conversion and the selectivity were higher initially for the first 2 hours of the run. Thereafter, they gradually decreased to a level of 50% after 10 hours. This decrease in the hydrogenolysis activity may be due to severe coke deposition on the catalyst surface. Table 1 shows that the Cu metal atoms exposed, and the corresponding metal area increased with copper loading up to 5 wt% and thereafter decreased. This indicates that glycerol conversion may be directly correlated to the number of copper active sites as well as on the availability of the basic sites on the catalyst surface. In other words, both dispersion of copper and basic sites play an important role during the reaction.

Conclusion

SBA-15 supported copper catalysts were prepared by incipient wetness method. The surface properties of the catalysts were characterized by XRD technique and by gas adsorption measurements using N_2 , H_2 , CO_2 and NH_3 as adsorbates. The XRD results revealed the presence of higher dispersion of smaller crystallites of CuO present on the surface of the catalysts at lower copper loading. The metal area and metal dispersion were found to decrease with increase in copper content up to 5 wt% and thereafter decreased. The surface acidity and basicity of Cu/SBA-15 catalysts showed an inverse trend with increase in copper content. Gas phase hydrogenolysis of glycerol was studied as a model reaction to correlate the catalyst functionalities against the reaction activity. The reaction study suggested that the catalyst functionalities such as metal dispersion, metal area, crystallite size and acido-basic properties play an important role in the enhancement of catalytic performance in terms of conversion, selectivity, and stability.

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