

## Synthesis and Surface Characterization of Supported Copper Oxide Catalysts

Mitta Harisekhar<sup>1</sup>, Komandur V R Chary<sup>1</sup> and Venkataraman Vishwanathan<sup>2\*</sup>

<sup>1</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Chemical Technology, Hyderabad, India

<sup>2</sup>Department of Applied Sciences, Faculty of Engineering and Technology (FET), Botho University, Gaborone, Botswana

### \*Corresponding author

Venkataraman Vishwanathan, Department of Applied Sciences, Faculty of Engineering and Technology (FET), Botho University, Gaborone, Botswana

Submitted: 09 Sep 2021; Accepted: 13 Sep 2021; Published: 23 Sep 2021

**Citation:** Mitta Harisekhar, Komandur V R Chary and Venkataraman Vishwanathan (2021) Synthesis and Surface Characterization of Supported Copper Oxide Catalysts. *J App Mat Sci & Engg Res*, 5(2), 21-25.

### 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  $\text{N}_2$  adsorption and desorption measurements. XRD profile revealed that at a lower copper loading (<5 wt%), smaller crystallites of  $\text{CuO}$  were highly dispersed. TPD of  $\text{NH}_3$  and  $\text{CO}_2$  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 few limited reports on mesoporous silicious materials supported copper oxide catalysts available for industrial applications [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 used in many important 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 is extensively used as a catalytic support material, They have cylindrical pores with diameter ranging from 5 to 35 nm diameter and has a high surface area ( $880\text{m}^2/\text{g}$ ) [8-10]. The present investigation deals with the synthesis and surface characterization of Cu/SBA-15 catalysts. An attempt has been made to correlate the influence of catalyst functionalities against reaction activity in terms of conversion, selectivity, and stability by using gas phase hydrogenolysis of glycerol as a test reaction.

### Experimental

SBA-15 silica was prepared as per the reference using block copolymer poly-ethylene glycol-block-polypropylene glycol-block-poly-ethylene glycol (P123, average molecular mass 5800)

as a template [11,12]. 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  $100^\circ\text{C}$  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  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  as precursor on as-synthesised SBA-15 support. The samples were dried at  $80^\circ\text{C}$  for 16 h and subsequently calcined at  $500^\circ\text{C}$  for 5 h in air.

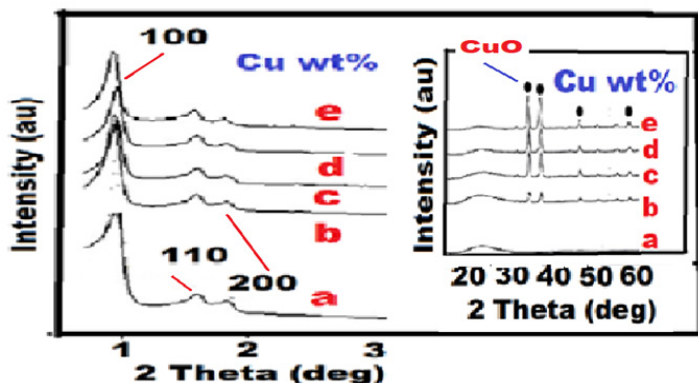
The characterization of the catalysts was studied using various analytical techniques. X-ray diffraction (XRD) profiles were obtained with a Rigaku, Miniflex diffractometer, using nickel filtered  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ). Nitrogen adsorption-desorption isotherms 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.  $\text{H}_2$  consumption and  $T_{\text{max}}$  positions were calculated using the GRAMS/32 software. Copper surface area, percentage dispersion and Cu crystallite size were calculated through  $\text{N}_2\text{O}$  decomposition. Temperature programmed desorption (TPD) experiments

were conducted using NH<sub>3</sub> and CO<sub>2</sub> 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  $2\theta = 0.80$  along with two other low intense peaks at  $2\theta = 1.590$  and  $1.80$  (Figure 1). All the

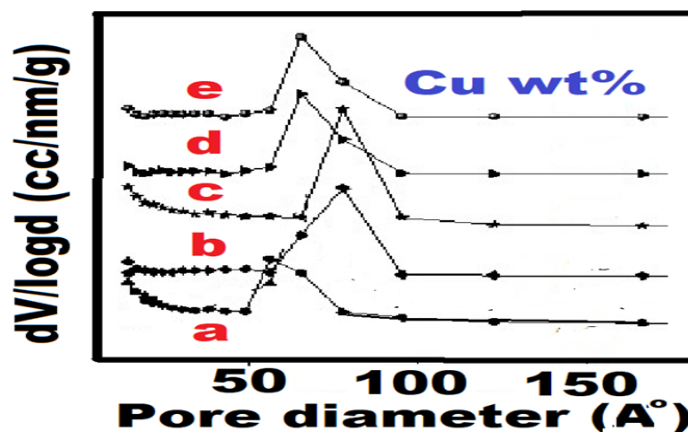


**Figure 1:** XRD profiles of low angle diffraction peaks of SBA-15 (a) and of Cu/SBA-15 catalysts with loading of Cu wt% 5 (b); 10 (c); 15 (d); and 20 (e). The corresponding wide angle diffraction peaks are shown in the inset.

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 (inset)**. 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 crystallites of CuO were observed at  $2\theta = 35.5^\circ, 38.7^\circ, 48.7^\circ, 58.3^\circ$  and  $61.8^\circ$ . 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.



**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 surface areas of the catalysts were measured by BET method using N<sub>2</sub> at 77 K. The results are shown in Table-1. The surface area of as-synthesised SBA-15 was 869 m<sup>2</sup>/g. With

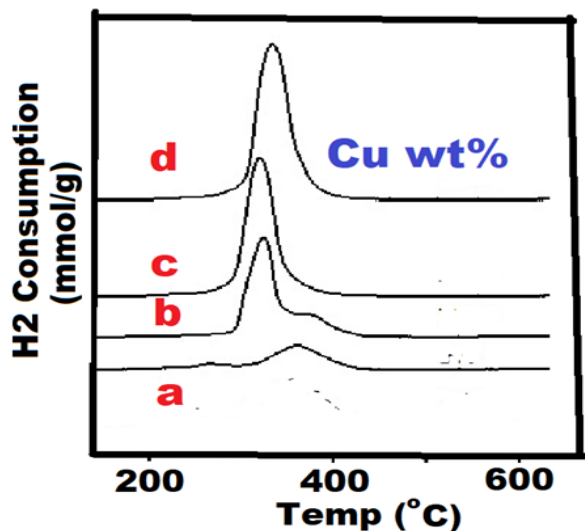
**Table 1: The physico-chemical properties of Cu/SBA-15 catalysts.**

Cu (wt%)	Surface Area (m <sup>2</sup> /g)	Pore Volume (ml/g)	Pore Area (nm)	Metal Dispersion (%)	Metal Dispersion (%)	Crystallite Size (Ao)	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

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 cop-

per content on SBA-15.

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

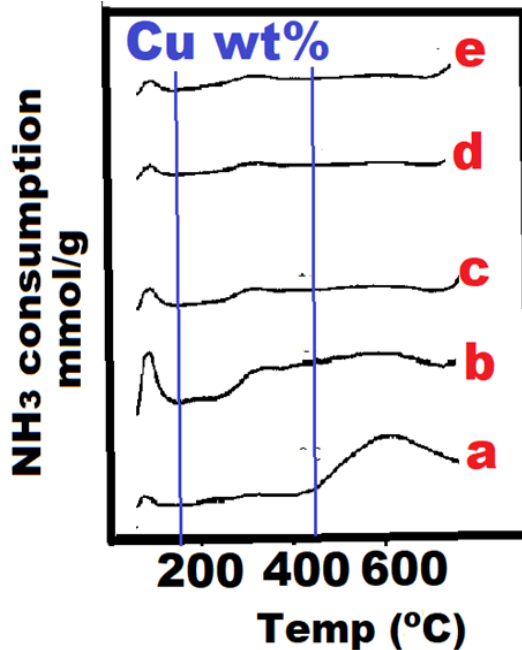


**Figure 3:** TPR profiles of Cu/SBA-15 catalysts with loading of Cu wt% 5 (a); 10 (b); 15 (c); and 20 (d).

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 H<sub>2</sub> 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 H<sub>2</sub> consumption with the second peak at higher Cu loading further confirms the formation of larger CuO crystallites.

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

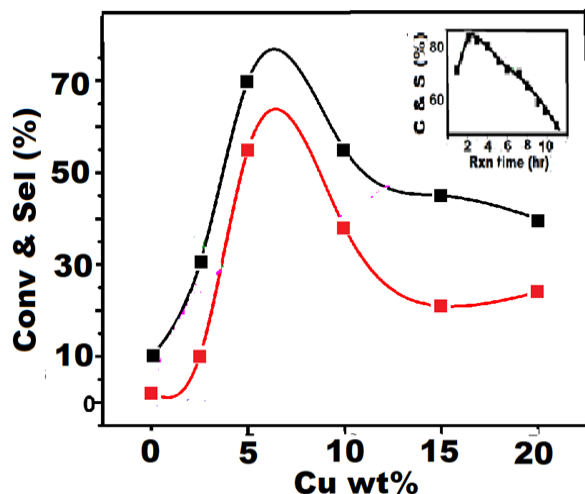
regions, one <180°C, two between 180° and 450°C, and three > 450°C were observed. The desorption peaks



**Figure 4:** TPD profiles of NH<sub>3</sub> of SBA-15 (a) and of Cu/SBA-15 catalysts with loading of Cu wt% 5 (b); 10 (c); 15 (d); and 20 (e).

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<sup>-</sup> catalysts was studied by TPD with CO<sub>2</sub> 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-propnediol at 220oC under atmospheric pressure. The as-synthesized SBA-15 showed very low glycerol conversion (10 %) as well as poor selectivity for propanediol (Figure 5). With



**Figure 5:** Gas phase hydrogenolysis reaction at 220°C under atmospheric pressure on 5 wt% Cu/SBA-15 catalyst showing conversion of glycerol (Black curve) and selectivity for propanediol (Red curve) and the reaction time (Inset).

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 plays 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.

## References

1. Dragoi B, Mazilu I, Chiriac A, Ciotonea C, Ungureanu A, et al. (2017) Highly dispersed copper (oxide) nanoparticles prepared on SBA-15 partially occluded with the P123 surfactant: toward the design of active hydrogenation catalysts. *Catal Sci Tech* 7: 5376-5385.
2. Cruz P, Pérez Y, del Hierro I, Fajardo M (2016) Copper, copper oxide nanoparticles and copper complexes supported on mesoporous SBA-15 as catalysts in the selective oxidation of benzyl alcohol in aqueous phase. *Micro Meso Mater* 220: 136-147.
3. Finocchio E, Rossetti I, Ramis G (2013) Redox properties of Co- and Cu-based catalysts for the steam reforming of ethanol. *Int J Hydrogen energy* 38: 3218-3225.
4. Ossipoff NJ, Cant NW (1994) The hydrogenation and oligomerization of propyne over an Ion-Exchanged copper on silica catalyst. *J Catal* 148: 125-133.
5. Saadi A, Rassoul Z, Bettahar MM (2000) Gas phase hydrogenation of benzaldehyde over supported copper catalysts. *J Mol Catal A: Chem* 144: 205-216.
6. Chary KVR, Sagar GV, Srikanth CS, Rao VV (2005) Characterization and Reactivity of Copper Oxide Catalysts Supported on  $TiO_2-ZrO_2$ . *J Phy Chem B* 109: 9437-9444.
7. Chary KVR, Sagar GV, Srikanth CS, Rao VV (2007) Characterization and catalytic functionalities of copper oxide catalysts supported on zirconia. *J Phy Chem B* 111: 541-550.
8. Shinde PS, Suryawanshi PS, Patil KK, Belekar VM, Sankpal SA, et al. (2021) A brief overview of recent progress in porous silica as catalyst supports. *J Composites Sci* 5: 75.
9. Friedrich H, Sietsma JRA, DeJongh PE, Verkley AJ, De Jong KP (2007) Nanopore- confined matter: Towards stable energy storage and catalytic materials. *J Am chem Soc* 129: 10249-10254.
10. Zhang Y, Lam FLY, Hu X, Yan Z, Sheng P (2007) Fabrication of copper nanowire encapsulated in the pore channels of SBA-15 by metal organic chemical vapor deposition. *J Phys Chem C* 111: 12536-12541.
11. Wang L, Qi T, Zhang Y, Chu J (2006) Morphosynthesis route to large-pore SBA-15 microspheres. *Micro Meso Mater* 91: 156-160.
12. Azimov F, Markova I, Stefanova V, Sharipov KH (2012) Synthesis and characterisation of SBA-15 and Ti-SBA-15 nanospheres materials for DME catalysts. *J Univ Chem Tech and Met* 47: 333-340.
13. Chun FZ, Wang YM, Cao Y, Zhuang TT, Huang W, et al. (2006) Solvent-free surface functionalized SBA-15 as a versatile trap of nitrosamines. *J Mater Chem* 16: 1520-1528.
14. Patel A, Rufford TE, Rudolph V, Zhu Z (2011) Selective catalytic reduction of NO by CO over CuO supported on SBA-15: Effect of CuO loading on the activity of catalysts. *Catal Today* 166: 188-193.
15. Szegedi A, Popova M, Lázár K, Klébert S, Drotár E (2013) Impact of silica structure of copper and iron-containing SBA-15 and SBA-16 materials on toluene oxidation. *Micro Meso Mater* 177: 99-104.



16. Liu CH, Lai NC, Lee JF, Chen CS, Yang CM (2014) SBA-15-supported highly dispersed copper catalysts: Vacuum-thermal preparation and catalytic studies in propylene partial oxidation to acrolein. *J Catal* 316: 231-239.
17. Chiriac A, Dragoi B, Ungureanu A, Ciotonea C, Mazilu I, et al. (2016) Facile synthesis of highly dispersed and thermally stable copper-based nanoparticles supported on SBA-15 occluded with P123 surfactant for catalytic applications. *J Catal* 339: 270-283.
18. Tu CH, Wang AQ, Zheng MY, Wang XD, Zhang T (2006) Factors influencing the catalytic activity of SBA-15-supported copper nanoparticles in CO oxidation. *Appl Catal A: Gen* 297: 40-47.
19. DV, Caballero JMR, González JS, Tost RM, Robles JMM, et al. (2014) Furfuryl alcohol from furfural hydrogenation over copper supported on SBA-15 silica catalysts. *J Mol Catal A: Chem* 383: 106-113.
20. Lee JC, Trim DL, Wainwright MS, Cant NW (1990) Metal-support effects in copper catalysts for the liquid phase hydrolysis of acrylonitrile. *Appl Catal* 60: 173-179.
21. Corma A, Abd Hamid SB, Iborra S, Vely A (2005) Lewis and Bronsted basic active sites on solid catalysts and their role in the synthesis of monoglycerides. *J Catal* 234: 340-347.
22. González J, Wang JA, Chen LF, Manríquez ME, Doming JM (2017) Structural defects, Lewis acidity, and catalysis properties of mesostructured WO<sub>3</sub>/SBA-15 nanocatalyst. *J Phy Chem C* 121: 23988-23999.
23. Khalaf A, El Madani EA, Mansour SE (2011) Surface properties of copper-modified tin oxide catalysts Hussein. *Global J Inorganic Chem* 2: 102-109.
24. De Sousa FF, Filho JM, Pinheiro GS, Barros NA, Souza HSA, et al. (2013) Metal oxides nanoparticles from complexes on SBA-15 for glycerol conversion. *Chem Engg J* 228: 442-448.
25. Li Y, Sabbaghi A, Huang J, Li KC, Tsui LS, et al. (2020) Aerobic oxidation of benzyl alcohol: Influence from catalysts basicity, acidity, and preparation methods. *Mol Catal* 485: 110789.

*Copyright:* ©2021 Venkataraman Vishwanathan, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.