



## **SYNTHESIS OF (111) CRYSTALLINE FACET DOMINATING CUPROUS OXIDE AND INVESTIGATION OF ITS CATALYTIC ACTIVITY**

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Cuprous oxide ( $\text{Cu}_2\text{O}$ ) is a semiconducting metal oxide. By adjusting synthesis conditions, specific crystalline facets of  $\text{Cu}_2\text{O}$  possessing different levels of catalytic activity can be synthesized. In this study,  $\text{Cu}_2\text{O}$  nanoparticles having (111) crystalline facet as the dominating facet were synthesized by a surfactant assisted hydrothermal method. Synthesized  $\text{Cu}_2\text{O}$  particles were characterized using FTIR, XRD, and SEM techniques. The X-ray diffraction patterns confirmed the presence  $\text{Cu}_2\text{O}$  with the dominating (111) facet. It was also found that the facets (110), (200), (220) and (311) were present but in small amounts. Additionally, the FTIR spectrum indicated a stretching vibration of Cu (I)-O at  $607\text{ cm}^{-1}$ . SEM images revealed the presence of rhombic dodecahedral structured particles. Synthesized  $\text{Cu}_2\text{O}$  particles were then finely ground with  $\text{K}_2\text{CO}_3$  and used as a heterogeneous catalyst and without a solvent for the reaction between benzylamine and bromobenzene. The reaction was carried out for 5h at  $120\text{ }^\circ\text{C}$ . The product mixture was analyzed using  $^1\text{H}$  NMR and it was found that the catalyst can selectively produce imine (73% selectivity to imine; NMR peaks at 8.5–8.6 ppm - protons of  $\text{sp}^2$  hybridized carbon bonded to the nitrogen atom in the imine, peaks at 4.8–4.9 ppm - protons attached to  $\text{sp}^3$  hybridized carbon in the imine). Yield of the products of reaction was quantified using by quantitative NMR analysis employing 9-Anthraldehyde as the internal standard. It has been reported in the literature that  $\text{Cu}_2\text{O}$  particles catalyze the coupling reaction between bromobenzene and benzylamine in the presence of polar solvents such as DMF or DMSO producing N-phenylbenzylamine as the major product. In contrast,  $\text{Cu}_2\text{O}$  particles with (111) as the dominating crystalline facet produced imine from benzylamine with fairly high selectivity.

Keywords:  $\text{Cu}_2\text{O}$ , cuprous oxide, Ullmann condensation, Imine, facet selective

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### **INTRODUCTION**

Cuprous oxide is a semiconducting metal oxide. Solid particles of cuprous oxide dominating different crystalline faces have been synthesized applying various synthetic methods. Electrochemical methods, methods using controlled conditions and methods using surfactants are some examples (Jayasingha et al., 2017; Kwon et al., 2015). It has been reported that by controlling the conditions of synthesis, particles with a particular crystalline facet as the dominating surface could be produced (Jayasingha et al., 2017). It has also been reported that different crystalline facets have different levels of catalytic activity. For example, (111) facet has a higher affinity for carbon dioxide compared to the other facets and acts as an efficient catalyst for the conversion of carbon dioxide into methanol (Bendavid & Carter, 2013). Synthesized copper oxide particles have also been used as a catalyst in organic reactions. One prominent example is the use of this material in the reaction of coupling aryl halides with aryl amines, known as the Ullmann reaction (Allen et al., 2013). High yields of coupling products have been obtained when copper oxide has been used as a heterogeneous catalyst in Ullmann reaction and in the presence of a solvent such as dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO) (Allen et al., 2013). In general the Ullman reaction requires the presence of a polar non aqueous solvent such as DMSO and a ligand to coordinate with  $\text{Cu}^+$  ions. This pose problems in product separation. Therefore, the application of a heterogeneous catalyst without solvents is desirable as that offers easy separation of products of the reaction.

The present investigation focusses on the synthesis of a solid catalyst and application of the same under solvent free conditions for the reaction between benzylamine and bromobenzene. Therefore,  $\text{Cu}_2\text{O}$  nanoparticles having (111) as the dominating plane were synthesized using a carefully optimized procedure. The synthesized catalyst was then used without a solvent for the reaction between bromobenzene and benzylamine. The product mixture was analyzed using  $^1\text{H}$ NMR, and quantitative NMR techniques. The catalyst was characterized using FTIR, XRD, and SEM techniques.

### **METHODOLOGY**

Initially, 0.4990 g of copper (II) acetate (Sisco, India) was dissolved in 50 mL of deionized water and mixed thoroughly. Then, 1.0235 g of disodium EDTA (S D Fine-Chem, India) and another 50 mL of deionized water were added to the solution, which was stirred continuously at 800 rpm for 15 minutes until a clear solution was obtained. Following this, 3.1552 g of CTAB (Sisco, India) was added and stirred thoroughly, and 0.8032 of NaOH pellets (Sisco, India) were added and stirred for an additional 15 minutes until the blue color appeared. Then 0.5725 g of L-ascorbic acid (Sisco, India) was added and continuously stirred until the solution turned reddish brown. After that, the solution was loaded into a Teflon-lined autoclave, sealed, and kept at 60 °C for two hours. After heat treatment, the solution was centrifuged at 3200 rpm for 20 minutes, and the precipitate was obtained. The precipitate was then washed with deionized water and ethanol, respectively. Then the precipitate was transferred to a porcelain crucible and oven-dried for 5 hours at 50 °C to obtain the final product.

A mixture containing 200 mg of synthesized  $\text{Cu}_2\text{O}$  catalyst and 100 mg of  $\text{K}_2\text{CO}_3$  (Merck, India) were thoroughly ground in a crucible. Then, 0.22 mL (~0.22 mmol) of benzylamine (Sisco, India) and 0.22 mL (~0.22 mmol) of bromobenzene (Aldrich, Germany) were measured in to an ignition tube and 200 mg of the catalyst &  $\text{K}_2\text{CO}_3$  mixture was added into it. The ignition tube was placed in a sand bath and



maintained 120 °C for 5 hours, alongside a control reaction mixture with the same components but without synthesized Cu<sub>2</sub>O particles.

The reaction mixture was then centrifuged at 3200 rpm for 20 minutes. The liquid layer was transferred to a test tube using a glass pipette. Subsequently, dichloromethane (DCM) and deionized water were added (4 mL each) to the liquid phase after the reaction, and shaken vigorously, and allowed to settle to facilitate layer separation. The resulting DCM layer was transferred to another test tube, and further extraction of the aqueous layer was performed using two 2.0 mL portions of DCM. The collected DCM layers were combined, treated with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and subjected to solvent evaporation using a rotary evaporator until a consistent volume was achieved. The same extraction process was applied to the control mixture.

## RESULTS AND DISCUSSION

### *Analysis of the products of the reaction*

Initially the products were separated using TLC and observed under UV light. The <sup>1</sup>HNMR spectrum that obtained (in the presence of small amount of DCM as the solvent) for the product mixture revealed the presence of the Ullmann coupling product of bromobenzene and benzylamine and imine produced by the direct oxidation of benzylamine (NMR peaks at 8.5–8.6 ppm - protons of sp<sup>2</sup> hybridized carbon bonded to the nitrogen atom in the imine, peaks at 4.8–4.9 ppm - protons attached to sp<sup>3</sup> hybridized carbon in the imine, peaks at 4.2–4.3 ppm - protons attached to the CH<sub>2</sub> group of N-phenylbenzylamine, peak at 3.8 ppm - sp<sup>3</sup> hybridized carbon of unreacted benzylamine).

The quantitative NMR analysis was conducted employing 9-Anthraldehyde (50 g/L) as the internal standard (IS). The quantification of the imine product yielded a value of ~0.08 mmol while for N-phenylbenzylamine, calculated value was ~0.06 mmol. Accordingly the solid Cu<sub>2</sub>O catalyst showed a high selectivity (73%) for imine and comparatively low selectivity (20%) for N-phenylbenzylamine. Under the condition applied approximately 90% conversion of benzylamine to the above two products was observed. Diagram below shows the possible reaction path leading to the formation of the imine.

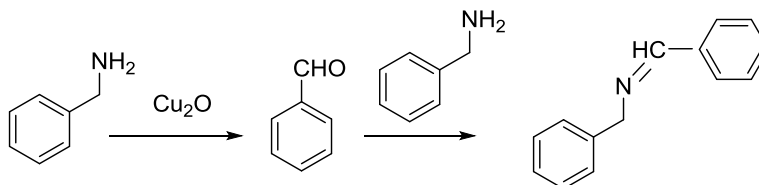


Figure 1: Formation of the imine

### *Characterization of the catalyst*

FTIR analysis of the synthesized solid catalyst showed a prominent peak at 607 cm<sup>-1</sup> corresponding to the stretching vibration of Cu(I)-O bonds (Figure 1). The XRD analysis of the catalyst showed characteristic peaks at 2θ values corresponding to crystallographic planes (110), (111), (200), (220), and (311) of Cu<sub>2</sub>O (Figure 2). It was observed that (111) is the dominating crystalline facet of the particles. The 2θ values agreed closely with standard data from JCPDS for Cu<sub>2</sub>O (JCPDS: 05-0667). Peak at 2θ = 38.1° exhibited the highest intensity, indicating that the dominating crystalline facet is the (111) plane. XRD analysis confirmed that no other phases of copper oxide (eg. CuO) were formed under the conditions applied for the synthesis. The SEM images of Cu<sub>2</sub>O particles revealed the presence of particles of the diameter ~500 nm and distinctive structures, primarily comprising of rhombic dodecahedra (Figure 3).

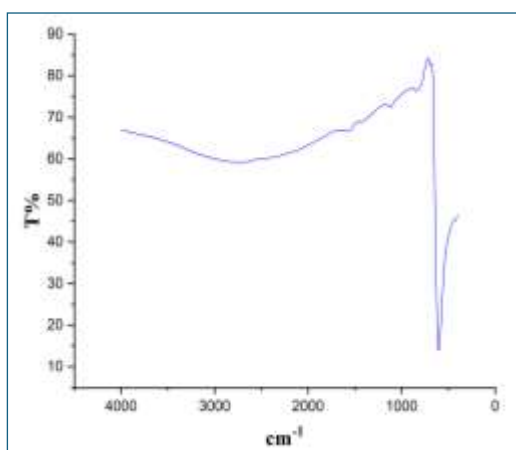


Figure 1. FTIR spectrum of synthesized  $\text{Cu}_2\text{O}$  nanoparticles

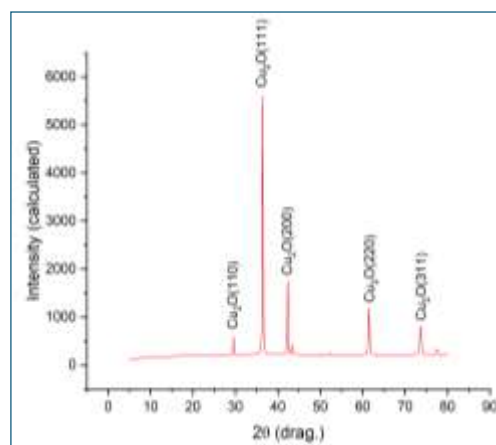


Figure 2. X-ray diffraction pattern of synthesized  $\text{Cu}_2\text{O}$  nanoparticles

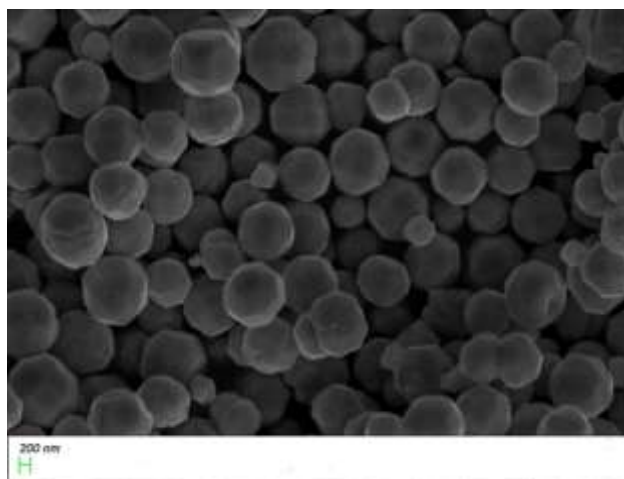


Figure 3. SEM images of synthesized  $\text{Cu}_2\text{O}$  nanoparticles

## CONCLUSIONS/RECOMMENDATIONS

Based on the findings of this study, it is possible to draw the conclusion that, as opposed to catalyzing the condensation of bromobenzene and benzylamine, the  $\text{Cu}_2\text{O}$  (111) surface catalyzes the oxidation of benzylamine generating the imine product under solvent-free reaction conditions. Due to simplicity of product separation, and considerable high activity, this catalyst is a candidate for further development as an oxidation catalyst for selective oxidation of benzyl amine to the imine. Imines are used in the synthesis of antibacterial, antimalarial and antifungal compounds.



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