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Green Synthesis of Copper Oxide Nanoparticles in Aqueous Medium as a Potential Efficient Catalyst for Catalysis Applications

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Abstract

In this research, we have developed a reliable green method for the synthesis of copper oxide nanoparticles as a potential efficient catalyst for several catalysis applications. In our experimental approach, microwave-assisted synthesis technique was used in order to perform chemical reduction of copper salt using hydrazine hydrate as a strong reducing agent. The prepared catalyst was characterized using various techniques showing the formation of well dispersed copper oxide nanoparticles. The synthesized Copper oxide catalyst shows many advantages including the use of environmentally benign solvent systems, green synthetic approach, and mild reaction conditions.

Keywords: nanoparticles, copper oxide, hydrazine hydrate, microwave heating, catalysis.

INTRODUCTION

Transition metal nanoparticles have been widely investigated as a potentially advanced pathway in catalysis field due to their distinctive properties. [1-3] The precise optimization through controlling the particle size is one of the key factors to obtain unique physical and chemical properties.[4-6] Recently, Copper based nanoparticles have a huge impact in the field of catalysis research as they have been tested in several major reactions such as Suzuki-Miyaura cross–coupling.[7, 8]

The previously mentioned research studies have revealed the high catalytic activity of metallic and bimetallic nanoparticles through using copper oxide as an ideal support in C-C cross-coupling reactions which are considered as one of the most relevant processes in Organic Synthesis. [9] The importance of those kinds of nanomaterials are not only because they are covering the research area of cross-coupling reactions which are widely used in several strategic industries like cosmetic, pharmacy, agriculture, and natural products; but also as they cover other potential applications in sensors, catalysis and energy conversion. [10, 11]

It is important to notice that there is also a main advantage of using copper oxide as a support as it significantly increase the surface area of the active ingredient of the used catalyst, hence causing a huge enhancement of the contact between reactants and catalyst to be nearly like that of the homogeneous catalysts. [12-15] This also led to some innovative ideas regarding the use of nano-catalysis for green chemistry development including the possibility of using the concept of microwave assisted synthesis combined with nano-catalysis.[7, 8, 16-23]

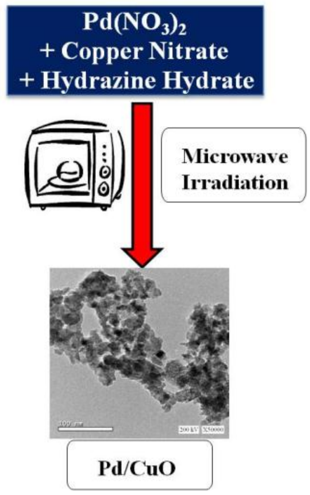
In this manuscript, we report on a green efficient method to prepare highly active copper oxide nanoparticles as a highly efficient catalyst for potential use in Suzuki cross–coupling.

EXPERIMENTAL

All chemicals were used as received without any purification. Absolute ethanol (99.9 %) and deionized water (D.I. H_2O) were used for all experiments. Palladium nitrate (10 wt. % in 10 wt. % HNO_3, 99.999%), copper (II) nitrate hemipentahydrate, hydrazine hydrate (80 %), bromobenzene, all other aryl halides, and potassium carbonate were obtained from Sigma Aldrich.

Synthesis of Copper Oxide Nanoparticles

366 mg of copper (II) nitrate hemipentahydrate $Cu(NO_3)_2.2.5H_2O$ was added to 50 mL deionized water, then sonicated for 1 hr. Then, the mixture was stirred for another 1 hr. After finishing the step of stirring; 400 µl hydrazine hydrate were added to the entire mixture. Then, it is heated using a microwave oven for 20 s, filtered, washed with deionized water and then ethanol, finally, dried in oven till constant weight of catalyst.



Catalyst Characterization

A JEOL JEM-1230 electron microscope was used for TEM images. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific ESCALAB. The X-ray diffraction patterns were measured at room temperature using an X'Pert PRO PAN analytical X-ray diffraction unit.

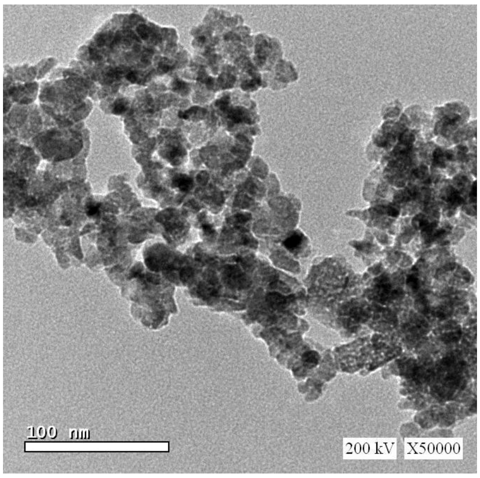


Figure 1: TEM – image of CuO nanoparticles

From the TEM images in **Figure 1**, the well dispersion of copper oxide nanoparticles of size (18 ± 2 nm) is obviously noticed. The TEM images here can be used as an evidence of the high catalytic activity which is probably due to the lack of negative effect of the agglomeration of the particles.

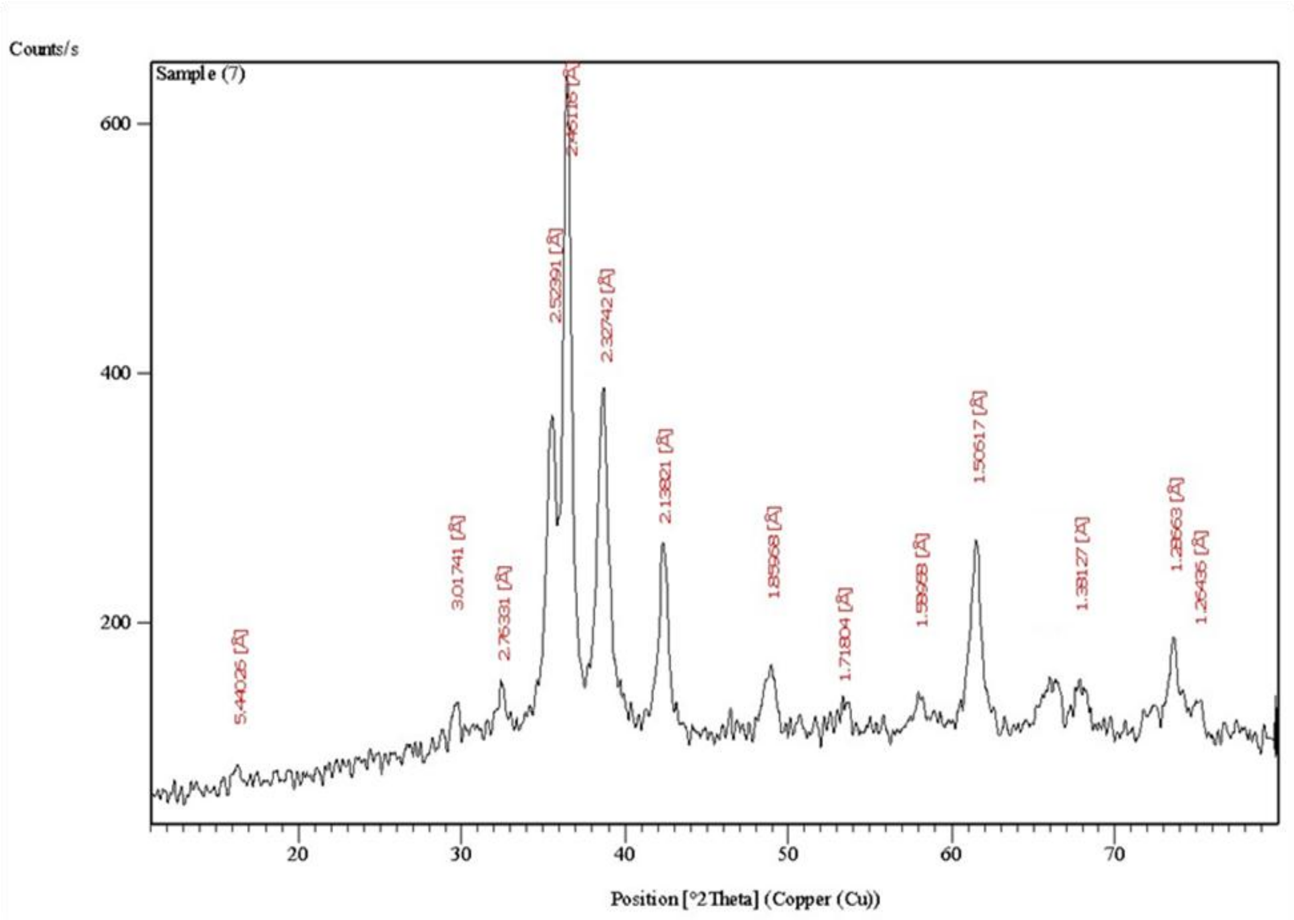


Figure 2: XRD pattern of CuO nanoparticles

Figure 2 displays the XRD diffraction pattern of copper oxide nanoparticles that were prepared by microwave method. Further characterization of the microwave synthesized copper oxide catalyst (CuO) was achieved by XRD pattern of catalyst sample as seen in Figure 2. XRD reflections of CuO match that of JCPDS no. 48-1548 corresponding to monoclinic structure.[24, 25] The diffraction peaks are ascribed to the (110), (111), (112), (202), (112), and (113) planed of copper oxide NPs as shown in figure 2.[26-28]

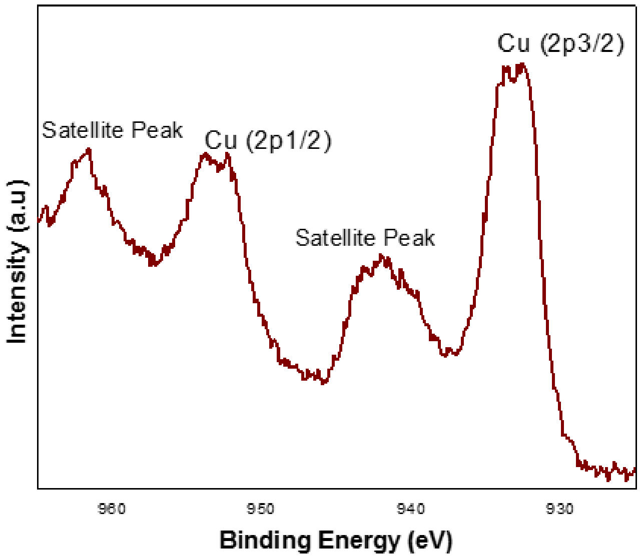


Figure 3: XPS (Cu2p) of CuO nanoparticles

The XPS technique is widely used as a more accurate and reliable technique for the chemical analysis of surface oxides than XRD.[29] In **Figure 3**, samples reveal the existence of copper oxide. The XPS show that the binding energy of Cu $2P^{3/2}$ was located at 933.1 eV and the binding energy of Cu $2P^{1/2}$ was located at 953.1 eV, showing that Copper was found as Cu^{2+}. There is also shake-up satellite peaks located at eV 941.9, 961.7 eV.[26-28]

CONCLUSIONS

In summary, we developed a simple and efficient synthetic protocol to highly active copper oxide nanoparticles as an efficient catalysts using microwave irradiation. The synthesis of the catalyst is based on the chemical reduction of the corresponding aqueous mixture of copper nitrate salts using hydrazine hydrate as reducing agent. The synthesized CuO catalyst was fully characterized using TEM, XRD, and XPS and was found to have 18 ± 2 nm as size range. Currently, our research group is working on the development of catalytic systems through using Palladium with one of the most promising transition metals which is copper due to its unique several advantages like abundant reserve, low cost, versatility, less harmful to the environment, and wide use in different applications in the field of catalysis.[24, 25]

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