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Copper Oxide Nanoparticles as a Highly 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.***

***Index Terms*—copper oxide, nanoparticles, catalysis.**

I. INTRODUCTION

Catalysis research based on transition metal nanoparticles have been extensively investigated as potentially advanced route in several catalysis field applications due to their promising properties. [1-3] The nanostructured materials play a vital role in the field of heterogeneous catalysis through its huge impact on several related applications especially in the few recent years.[4-8] The precise design of an overall particle size distribution through controlling particle size is one of the decisive key points to obtain new unique physical and chemical properties.[9-11] Recently, the palladium based nanoparticles have attracted a tremendous efforts in the field of catalysis research. Copper-based catalysts have been tested in some sorts of important reactions such as Suzuki-Miyaura cross–coupling.[12, 13]

Palladium has a unique ability to catalyze several chemical reactions under both homogeneous and heterogeneous reaction conditions.[14-17] Recently, research developments have been reported using both metallic and bimetallic nanoparticle catalysts for a variety of several chemical transformations.[18-21] The previously mentioned research studies have revealed superior catalytic activity for both metallic and bimetallic nanoparticles using copper oxide as an ideal support.[19, 22] The importance of this focused scientific research approach is due to the fact that C-C cross-coupling reactions are considered as one of the most relevant processes in Organic Synthesis. [22] The importance of those nanomaterials are not only covering the research area of cross-coupling reactions which are widely used in many such as cosmetic, pharmacy, agriculture, and natural products; but also covers other potential applications in sensors, catalysis and energy conversion. [20, 21]

The bimetallic Pd-based nanoparticles were designed using several other transition metals like Co, Ag, Pt, Au, Ni, and Cu.[25] We have recently developed a series of metal oxide supported palladium nanoparticles with high catalytic activity.[21-23]. Currently, we are working on the development of similar catalytic systems through using 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.[21-23] There is also a main advantage of using copper oxide as a support for palladium base catalysts which is preventing the potential agglomeration of palladium nanoparticles. The main advantage of using those types of nano-sized particles is that they largely 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. [31-34] 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.[12, 13, 21-24]

II. METHODOLOGY AND APPROACH TO THE PROBLEM

A. Principle

In this manuscript, we report on a green efficient method to prepare highly active copper oxide nanoparticles as a preliminary step towards preparing a highly efficient catalyst for Suzuki cross–coupling. The high performance of the catalyst including both catalytic activity and recyclability of the synthesized catalytic nanoparticles will be experimentally investigated in ligand–free Suzuki cross-coupling reaction using a series of substrates. The microwave assisted synthesis approach was used in catalyst preparation as a reliable, fast, and efficient synthetic technique.

B. Materials

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.

C. Method of preparation

200 mg of copper (II) nitrate hemipentahydrate $Cu(NO_3)_2.2.5H_2O$ was added to 100 mL deionized water, then sonicated for 1 hr. Then, the mixture was stirred for another 1.5 hr. After finishing the step of stirring; 200 µl hydrazine hydrate were added to the entire mixture. Then, it is heated using a microwave oven for 60 s, filtered, washed with deionized water and then ethanol, finally, dried in oven till constant weight of catalyst.

III. EXPERIMENTAL PROCEDURE

A. Characterization of the prepared catalyst

A JEOL JEM-1230 electron microscope was used for TEM images. GC–MS analyses were used to monitor the catalytic activity of the catalyst in selected reactions. 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.

IV. RESULTS AND DISCUSSION

From the TEM images in **Figure 1**, the well dispersion of copper oxide nanoparticles of size (20 ± 2 nm) is obviously noticed as in figure 1. The TEM images here can be used as an evidence of the high performance of the preparation technique used in the adopted synthetic approach.

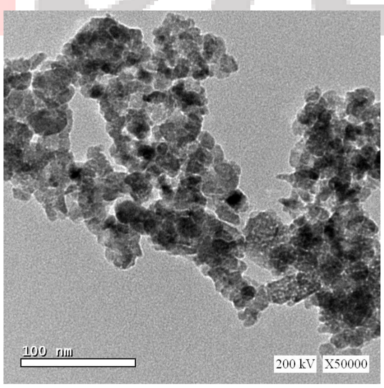

Figure 1 TEM – image of CuO nanoparticles

Figure 2 displays the XRD diffraction pattern of copper oxide nanoparticles that was 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. The XRD reflections of CuO match that of JCPDS no. 48-1548 corresponding to monoclinic structure.[21-24] The diffraction peaks are ascribed to the (110), (111), (112), (202), (112), and (113) planed of copper oxide NPs as shown in figure 2.[21-24]

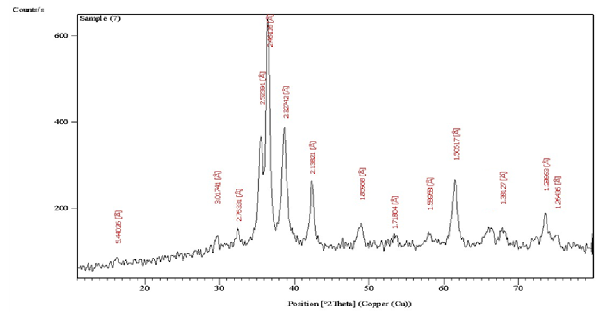

Figure 2 XRD pattern of CuO nanoparticles

The XPS technique is widely used as a more accurate and reliable technique for the chemical analysis of surface oxides than XRD.[24] In **Figure3,** 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.[21-24]

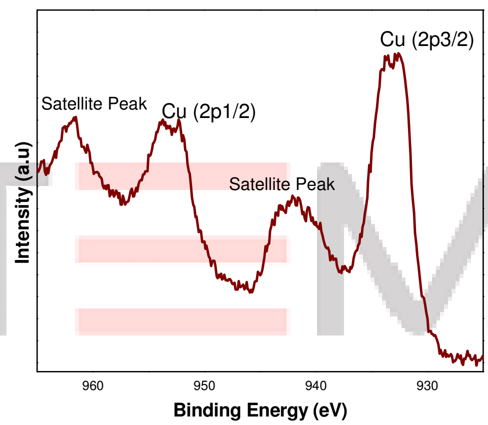

Figure 3 XPS (Cu2p) of CuO nanoparticles

V. CONCLUSION

In summary, we developed a simple and efficient synthetic protocol to prepare highly active copper oxide nanoparticles as a catalyst using microwave irradiation. The synthesis of the catalyst is based on the chemical reduction of the aqueous mixture of copper nitrate salt using hydrazine hydrate as an efficient reducing agent. The synthesized CuO catalyst was fully characterized and found to have 20 ± 2 nm as size range. In addition, its catalytic performance will be examined in our future research in catalyzing Suzuki cross–coupling reactions.

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