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Ceria-supported copper nanoparticles: A highly efficient and recyclable catalyst for *N*-arylation of indole

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ABSTRACT

Cu@CeO$_2$ catalytic nanomaterials have been synthesized by impregnation of ceria by copper acetate, followed by reduction and calcination under nitrogen. The components of these nanomaterials were characterized by means of XRD, XPS, N$_2$ adsorption/desorption, TGA, SEM, and TEM microscopy techniques. The XRD spectra of ceria and Cu@CeO$_2$_1 (3.4 wt% copper loading) revealed a slight shift of the position of the planes with a small increase of the crystal lattice parameters, which can be explained by an eventual insertion of Cu^0 in interstitial sites and/or a partial substitution of Ce^{4+} by Cu^{2+}. Cu@CeO$_2$ nanomaterials were found to be efficient catalysts for the *N*-arylation of indole with various aryl bromides to produce good yields of the desired products. The decrease in the catalytic activity of the catalyst during the reuse was probably due to oxidation of Cu^0 to Cu^{2+} and its poisoning of KBr that was formed *in situ*.

1. Introduction

Catalysis is widespread in the manufacturing industry and over 60% of manufactured products have undergone at least one catalytic cycle [1]. Although homogenous and heterogenous catalysis are the two main methods of catalysis currently developed, nanocatalysis is a third option that combines the advantages of both types of previously established catalysis and is being explored by both the academic and manufacturing industries [2]. A large portion of research regarding catalysis has often focused on the metal nanoparticles supported on nanostructured materials, specifically mesoporous non-siliceous oxides [3,4]. Indeed, ceria fits into this category. It is one of the most important functional rare earth oxides [5,6], and has attracted significant interest because of its wide applications in cutting-edge technology sectors like automotive three-way catalysts, solid oxide fuel cells, UV absorption ability, gas sensors, and antioxidant therapy [7–12]. All these uses are due to certain unique properties of ceria, particularly its: inherent chemical component, high oxygen capacity, and high oxygen mobility originating from storing/releasing O$_2$ due to the Ce^{4+}/Ce^{3+} redox couple. However, this oxide has been widely used as a catalyst or support-catalyst of several metal nanoparticles for various chemical transformations [13–16]. Thus, Cargnello et al. demonstrated that ceria as a support has a crucial role in the catalytic activity and the interaction between the metal nanoparticles (nickel, palladium, and platinum) and this oxide (support) is decisive for the CO oxidation [17]. In another work, Li et al. conducted a comparative study on several catalysts prepared by supporting gold on different materials, namely: CeO$_2$, TiO$_2$, Al$_2$O$_3$, activated carbon, and graphene [18]. This experimental and theoretical study demonstrated that the use of ceria as support has a synergistic effect and has boosted the catalytic activity of gold. These observations led Li et al. to conclude the presence of a strong interaction and an electronic exchange between metal and ceria in comparison with

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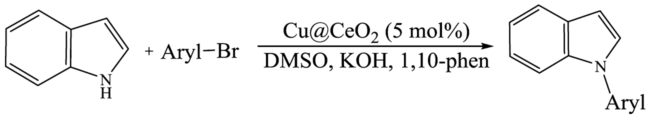

Scheme 1. *N*-arylation of indole with various substituted aryl bromide by a nanostructured catalyst (Cu@CeO_2).

the other oxides. The impregnation of ceria by copper nanoparticles or copper oxide, or vice versa (ceria-supported on copper nanoparticles), is widely studied for oxidation of CO [19,30], and organic volatile compounds [21,22], but especially for Water–Gas shift reaction [23–25]. However, it should be noted that the majority of studies revealed that there is a cooperative effect of ceria does not just have an inert support role, but also contributes to the catalytic activity of the system: metal@CeO_2. Given the central importance of copper nanoparticles in boosting the catalytic activity of ceria, or reciprocally, this catalyst has been studied by using theoretical tools to elucidate and corroborate experimental data [26–28].

Alternatively, *N*-aryl indoles have attracted a keen interest over the last few years due to their diverse biological activities that have already been revealed and exploited [29,30]. Historically, the synthesis of these *N*-substituted heterocyclic compounds has been carried out *via* the Ullmann coupling reactions. However, these reactions generally suffered from high temperatures and the use of stoichiometric amounts of copper reagents, which make their further applications limited [31,32]. To overcome these drawbacks, another class of catalysts was developed by Buchwald and Hartwig, who separately reported that the *N*-arylation of nitrogen containing heterocycles with aryl halides could be achieved in the presence of appropriate copper compounds and ligands under mild conditions [33–38]. However, these homogeneous systems pose significant issues related to product purification and toxic waste produce after separation of a copper catalyst. One of the most favorable ways to overcome these problems is the realization of the *N*-arylation reaction *via* heterogeneous catalysts [39–44]. Most of these systems are copper-based catalysts in various forms, including: (i) copper nanoparticles alone or supported [45–47], (ii) copper oxides [48–53], and (iii) supported copper (Cu^{1+} or Cu^{2+}) [54–59]. Relatedly, Hyeon et al. prepared CuO coated copper nanoparticles by thermal decomposition, using copper acetylacetonate. They then reported the use of this nanostructured material to catalyze the Ullmann amination coupling reaction of various aryl chlorides [60]. In another example, Choudary et al. designed a catalyst for *N*-arylation of imidazoles *via* the cation exchange of fluoroapatite and *tert*-butoxyapatite with copper [61]. In light of these facts, Choudary et al. discovered this reaction by using arylboronic acids and obviously a copper-exchanged fluorapatite-like catalyst [62]. Another kind of material to catalyze the *N*-arylation reaction has been developed recently; it comes from a nanostructured mixed oxide, based on iron and copper [63]. Zhang et al. synthesized and then tested a series of magnetic mixed oxides ($CuFe_2O_4$, $MgFe_2O_4$, $NiFe_2O_4$, $MnFe_2O_4$, $CoFe_2O_4$). These authors revealed that $CuFe_2O_4$ was the best of all the prepared oxides, with an excellent yield obtained [64]. It is in light of these studies that this work is situated. The objective of this study is the synthesis and characterization of ceria doped with copper nanoparticles, and then its use as a catalyst in the reaction of *N*-arylation of indole with bromo-aryl derivatives (Scheme 1).

2. Experimental

2.1. Materials and apparatus

All commercial reagents were purchased from Aldrich Chemical Company and were used without further purification. Thermogravimetric analysis (TGA) was conducted under air or nitrogen in a TA Instrument Q500 apparatus, with a 10 °C/min ramp between 25 and 1000 °C. Fourier transform infrared (FT-IR) spectra of samples in KBr pellets was measured on a Bruker Vector 22 spectrometer. X-ray diffraction patterns were obtained at room temperature on a Bruker AXS D-8 diffractometer using Cu-Kα radiation in Bragg–Brentano geometry (θ–2θ). TEM micrographs were obtained on a Tecnai G2 microscope at 120 kV. High-resolution transmission electron microscopy analysis was carried out on a Jeol 2100F microscope, equipped with a high-resolution pole piece, field emission gun and operating at 200 kV. The gas adsorption data was collected using a Micromeritics 3Flex Surface characterization analyzer, using N_2. Prior to N_2 sorption, all samples were degassed at 150 °C overnight. The specific surface areas were determined from the nitrogen adsorption/desorption isotherms (at −196 °C), using the BET (Brunauer–Emmett–Teller) method. Pore size distributions were calculated from the N_2 adsorption isotherms with the “classic theory model” of Barret, Joyney and Halenda (BJH) [65]. XPS studies were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al-Kα X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under 1.0×10^{-9} Torr vacuum. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 and 20 eV, respectively. The instrument work function was calibrated to give an Au 4f7/2 metallic gold binding energy of 83.95 eV. The spectrometer dispersion was adjusted to give a binding energy of 932.63 eV for metallic Cu 2p3/2. Samples were mounted in floating mode in order to avoid differential charging; charge neutralization was required for all samples. The electronic binding energy of C 1s (284.80 eV) was used as the internal standard. The data was analyzed with commercially available software, CasaXPS. The individual peaks were fitted by a Gaussian (70%)–Lorentzian (30%) (GL30) function after Shirley type background subtraction.

2.2. Preparation of the catalyst

2.2.1. Preparation of ceria

For preparation of ceria powder by the co-precipitation method, high purity (99.5%) ammonium cerium (IV) nitrate $(NH_4)_2Ce(NO_3)_6$ and ammonia (NH_4OH) were used. In a typical procedure, ammonia (25%) was added by the drop to an aqueous solution of ammonium cerium (IV) nitrate, which was prepared by solubilizing 1 g of cerium precursor in 100 mL of water. The ammonia was added until a basic pH (∼12) was reached. Thus, the reaction took place under vigorous stirring during 4 h, at 70 °C. The obtained light yellow precipitate was separated by centrifugation and washed with water several times. The obtained solid was dried overnight at 80 °C under vacuum and calcined for 3 h at 550 °C to lead to cerium oxide.

2.2.2. Preparation of Cu@CeO_2

The preparation of Cu@CeO_2 was performed by impregnating the ceria with copper acetate with a loading of 3.4 and 7 wt%, followed by the reduction of the Cu^{2+} to copper nanoparticles. The first step was to dissolve copper acetate (∼0.54 mmol) in 10 mL of diethylene glycol, where another aqueous solution of sodium dodecyl sulfate (0.1 M), was subsequently added. In the second step, 1 g of previously prepared ceria was added to the first mixture and stirred at 70 °C for 24 h. The pH of this mixture was adjusted to pH > 10 by adding NH_4OH. Then, hydrazine hydrate (80%, 1 mL) was added to reduce Cu^{2+} to copper nanoparticles. In the final step, the resulting powder was filtered and sequentially washed with ethanol and acetone, dried at 80 °C under vacuum, and finally calcined at 550 °C under nitrogen for 3 h. According to the measurement of copper content, the aforementioned procedure led to two catalysts: Cu@CeO_2_1 (3.4 wt%) and Cu@CeO_2_2 (7 wt%).