



C–N cross-coupling on supported copper catalysts: The effect of the support, oxidation state, base and solvent



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ARTICLE INFO

Article history:

Received 5 April 2016

Revised 10 June 2016

Accepted 19 June 2016

Keywords:

Heterogeneous catalysis

C–N cross coupling

Copper catalysts

Precipitation-deposition technique

Amination of bromobenzene

ABSTRACT

A series of supported copper catalysts at two different loadings (1 and 2 wt%) have been prepared by deposition precipitation on various supports including TiO₂, ZnO, Al₂O₃ and active carbon and submitted or not to reductive treatments to favor the increase in population of Cu(I). The samples have been characterized by textural measurements, electron microscopy and spectroscopic techniques including EPR and XPS, concluding the presence of dispersed copper oxides on the support with small particle size and contrasting prevalence of Cu(II) or Cu(I). The catalytic activity of all these catalysts for the C–N coupling of aniline and bromobenzene has been evaluated. A strong influence of the support, copper oxidation state, solvent, nature of the base was observed, the optimal conditions being the use of ZnO or TiO₂ as supports and toluene/dioxane as solvent and EtOK as base. *t*-C₅H₁₁OK as base in either THF or toluene give rise to the formation of *t*-C₅H₁₁ phenyl ether in some extent. The catalyst undergoes deactivation during the reaction, but about 88% of the activity of the fresh sample could be regained by dioxane washings before reuse. XPS indicates that the most likely origin of catalyst deactivation is adsorption on the copper catalyst surface of KBr and inorganic salts formed as byproducts during the reaction.

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1. Introduction

Cross-coupling is a very powerful strategy to generate aryl-carbon and aryl-heteroatom covalent bonds and may occur following different routes [1–15]. Among these, the formation of the C–N bonds elicited a large interest in the synthesis of compounds with pharmaceutical, cosmetic, agrochemical and optical devices [16–23] applications. Because of this it received a great industrial and academic importance in the past two decades [24]. Initiated by Migita et al. [25] using aminostannanes, the amination of aryl halides is mostly known as a Buchwald-Hartwig reaction [26–31].

Classical Buchwald-Hartwig reaction represents a palladium-mediated cross-coupling procedure [32,33] under homogeneous catalytic conditions, using strong bases, aprotic and/or polar and non-polar solvents and different ligands [34–39].

Along with the choice of the ligand, an important component of the C–N cross-coupling reaction is the nature of the base (e.g. carbonates, phosphates, alkaline hydroxides, alkoxides, inorganic flu-

oride or silylamide) that plays an important role on the evolution of the reaction, being involved in the deprotonation of the N-substrate. A suitable base affords considerable benefits in the functional group tolerance of Pd-catalyzed amination reactions. Classical solvents usually employed in the Buchwald-Hartwig amination reaction [40] are nonpolar and aprotic being thus able to dissolve all reactants with the exception of NaO-*t*-Bu (the traditional base of this reaction).

Although palladium [32,33] is the most widely used active metal of the Buchwald-Hartwig cross-coupling reactions, copper, nickel and iron have been also considered as alternatives because they are less expensive, and require cheaper bidentate ligands such as phenanthrolines, 1,3-diketones, imines, α -amino acids, salicylamides, diamines, lowering thus the overall synthesis procedure costs [41].

The literature already reported a broad variety of nucleophiles that were successfully used in homogeneous copper-mediated cross-coupling reactions to form C(aryl)–N bond: amines, anilines, amides, imides, ureas, carbamates, sulfonamides as well as aromatic heterocycles (imidazoles, pyrazoles, thiazoles, tetrazoles, benzimidazoles, indazoles) [42,43].

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Converting the C–N cross-coupling reaction from homogeneous to heterogeneous conditions is very attractive because of the multiple advantages offered by the heterogeneous catalysis: (a) easy of product separation, (b) use of a small amount of metal catalyst supported on large surface area materials, (c) possibility of recycling the catalyst, (d) minimal metal contamination of the product. To combine the advantages of homogeneous and heterogeneous catalysis, supported homogeneous complexes were designed allowing covalent immobilization in order to efficiently recover and reuse the catalyst, but strong basic conditions and mono/bidentate ligands were still required to generate a ligand-stabilized metal catalyst. In this scope a fiber-supported PdCl₂-triphenylphosphine catalyst was reported for the reaction of *p*-bromotoluene with piperazine in the presence of a strong base. The catalyst facilitated the desired amination, but side products were present, as in homogeneous conditions. Moreover the catalyst was unstable in the reaction conditions, releasing active components from the polymer support [44]. Anchoring a homogeneous copper (II) catalyst on an insoluble polymer (reported for the C–N cross-coupling reaction of primary amines with aryl iodides [45]) provided a more stable catalytic system, but the yield was small [46]. Chaudhari et al. [47] developed heterogenized copper complexes on solid supports in the presence of bidentate N-ligands and phosphotungstic acid (using encapsulation and tethering protocols) for the coupling of aryl amines with iodobenzene. The reaction was carried out using over stoichiometric quantities of strong bases, as well as 4–8% copper-containing catalysts, but the selectivity in diphenylamine was low, due to diffusion-limitation occurring into the zeolite supports. Lipshutz et al. [48,49] used a high content of nickel and copper oxide (10 wt%) on activated charcoal matrix (stabilized with bidentate ligands) for aromatic amination of activated aryl halides with secondary alkylamines or aniline where the metal leaching at the end of the reaction was considerable.

Several Cu(I)/Cu(II) 'ligand-free' catalytic systems have also been described with the aim to develop more attractive systems for industry. Park and co-workers [50] used catalytic amounts of acetylene-carbon-immobilized CuO-hollow nanospheres for N-arylation reactions of various N-containing heterocycles with aryl halides at high temperature, using very strong bases. However, even for a large content of the copper catalyst (5%), the efficiency for the N-arylation of aniline with iodobenzene was low. A dependence of the reaction rate on the morphology and size of the Cu(I)/(II) oxides was also reported [51,52]. Punniyamurthy and co-workers [53,54] exploited the high surface area and reactive morphology of the CuO nanoparticles for C–N, C–O, and C–S cross-coupling reactions showing that the catalytic properties of Cu(II) oxide were improved for the N-arylation of pyrazole with aryl halides by the presence of [Fe(acac)₂] as co-catalyst [55]. Correa and Bolm [56] also reported a ligand-free catalyst system for N-arylation of heterocycles using 10 mol% Cu₂O under argon atmosphere where the role of FeCl₃ was again emphasized [57]. DFT calculations also recommended Cu₂O as a suitable catalyst for this reaction [58].

Our interest is to convert C–N cross coupling into a truly heterogeneous process. Previous work in amination of bromobenzene using titania-supported gold catalysts [59] indicated that this reaction can occur indeed with very high selectivity, but only for moderate conversions. The base plays a very important role also under heterogeneous conditions. Based on this state of the art the aim of the present work was to investigate the catalytic activity of copper catalysts deposited on various supports (different Cu(I)/Cu(II) ratios on TiO₂, active carbon, alumina, or ZnO) in amination of an unactivated aryl bromide (bromobenzene), as reaction test.

2. Experimental

2.1. Catalysts synthesis

All starting materials were of analytical purity, and used as received without any further purification: Cu(NO₃)₂·3H₂O (Sigma–Aldrich) as copper precursor salt, NaOH (Sigma–Aldrich), hydrazine monohydrate solution (64–65%, in water) (Sigma–Aldrich) as reducing agent, and TiO₂ – Degussa P25 (Sigma–Aldrich), active carbon – NORIT A SUPRA EUR, alumina – Alfa Aesar/Johnson Matthey, ZnO – NanoTek, Alfa Aesar as supports.

The preparation of the heterogeneous copper catalysts was performed via a deposition–precipitation method (DP) onto the above commercial supports. Aqueous 1.57 mM Cu(NO₃)₂·3H₂O (for 1 wt% copper catalysts) and 3.21 mM Cu(NO₃)₂·3H₂O (for 2 wt% copper catalysts) solutions were adjusted at pH = 9–9.5 (with NaOH, added drop-wise) and then heated at 80 °C for 1 h in the presence of 1 g support. After that, the catalysts were washed with double distilled water till a conductivity of 10 μS, and dried at 110 °C under vacuum for 10 h. Following this procedure samples with 1 and 2 wt% Cu were obtained. Table S11 compiles the values of the nominal concentration of copper determined by ICP-OES compared to the deposited amount of copper.

Activation of the catalysts has been carried out following two different routes: (i) calcination at 300 °C with the purpose of generating supported CuO species (samples denoted as CuO/support); (ii) reduction under different reductive atmospheres in order to generate supported Cu₂O species. Thus, the reduction of the catalysts was carried out following two routes: (a) the treatment of the samples at 300 °C under a flow of N₂ (10 mL min⁻¹) (samples denoted as Cu₂O-N₂/support); and (b) the treatment of the samples under ambient temperature with a hydrazine monohydrate solution for 15 min under vigorous stirring. Then, the samples were dried for 12 h at 40 °C, for 6 h at 120 °C, under vacuum, and heated at 300 °C under an Ar flow (10 mL min⁻¹) (samples denoted as Cu₂O-N₂H₄/support).

For reference commercial anhydrous CuCl₂, and CuO and Cu₂O (all from Sigma–Aldrich, over 99.9% purity) were used as homogeneous and heterogeneous catalysts, respectively, without any additional treatment.

2.2. Catalysts characterization

The prepared catalysts were characterized using different techniques. Textural characteristics (surface area and pore diameter) were determined from the adsorption–desorption isotherms of nitrogen at –196 °C using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. DRUV–Vis spectra were collected under ambient conditions with a Specord 250 (Analytic Jena) equipment. The equipment is provided with a measuring device in the reflectance mode using Spectralon as reference material. The collected spectra were transformed using the Kubelka–Munk F(R) function. The final spectra were averaged from 400 scans at a resolution of 4 cm⁻¹. Raman spectra were collected with a Horiba Jobin Yvon – Labram HRUV–Visible–NIR (200–1600 nm) Raman spectra were recorded using a Raman Microscope Spectrometer, and a laser with the wavelength of 632 nm. The spectra were collected from 10 scans at a resolution of 2 cm⁻¹. Powder X-ray Diffraction patterns were collected at room temperature using a Shimadzu XRD-7000 apparatus and the Cu Kα monochromatic radiation λ = 1.5406 Å, 40 kV, 40 mA with a scanning rate of 0.1 2θ min⁻¹, in the 2θ range of 5–80. XPS spectra were recorded at room temperature using a SSX-100 spectrometer, Model 206 from Surface Science Instrument. The pressure in the analysis chamber during the analysis was 1.33 mPa. Monochromatized Al Kα radiation (hν = 1486.6 eV) generated by bombarding the Al anode

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