



On the homogeneity/heterogeneity of solid copper oxide precatalysts in the oxidative homocoupling of ethynylbenzene



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ABSTRACT

The heterogeneity of copper oxide supported on γ -Al₂O₃ (10CuO-Al₂O₃) and TiO₂ (10CuO-TiO₂) precatalysts is assessed in the oxidative homocoupling of ethynylbenzene in piperidine, with a focus on the effect of temperature, support, and solvent on copper leaching and catalyst reactivity. It is demonstrated that for this alkyne homocoupling reaction, elevated temperature is needed to solubilize copper and activate it, likely by production of soluble molecular copper-piperidine complexes. Once this activation occurred, the reaction can occur at room temperature, giving good yields of the desired product. Copper oxide is shown to interact differently on the two supports; CuO supported on TiO₂ is more dispersed and accessible than CuO supported on γ -Al₂O₃. Less copper leaches from 10CuO-TiO₂ than from 10CuO-Al₂O₃ at room temperature. Nevertheless, copper species that leach from 10CuO-TiO₂ are more active than the species leached from 10CuO-Al₂O₃, as some of the copper leached from alumina likely exists as fine, inactive CuO nanoparticles. Piperidine has multiple roles in this reaction: it acts as solvent, base, as well as an important ligand. The precatalyst 10CuO-TiO₂ is reused three times, with improved performance after each cycle. Nevertheless, it cannot be considered a recyclable catalyst, but rather a reusable solid precatalyst that produced new soluble active copper species in each cycle.

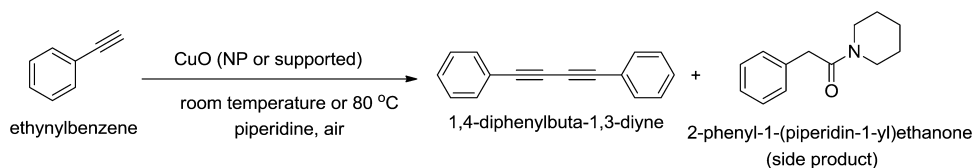
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1. Introduction

Copper oxide nanoparticles [1–3] and supported copper [4–8] catalysts are widely studied and used as heterogeneous catalysts (or perhaps precatalysts, as this work will detail) in a variety of homo- and cross-coupling reactions in organic synthesis. Heterogeneous catalysts are of course of interest because they are easy to separate from the reactants and products, recover, and potentially recycle, thus reducing waste. However, in many cases whereby solid palladium [9] and copper precatalysts were used in liquid phase coupling reactions, the nature of the active species remained ambiguous, with some authors asserting heterogeneous catalysis occurs at the solid Cu or Pd surface, while other studies demonstrating that metal species leached into solution could account for some or all of the catalytic turnover. Often claims of heterogeneity are supported with limited definitive data on the nature of the active species, with simple catalyst recyclability tests often used as a way to suggest the catalysts' heterogeneity [1–3]. Thus, in most cases, a rigorous assessment of catalyst heterogeneity is not completed.

Having worked extensively on the elucidation of the heterogeneity/homogeneity of supported Pd catalysts in Heck and Suzuki coupling reactions, we became interested in the heterogeneity/homogeneity question as it relates to supported copper oxide catalysts in liquid phase coupling reactions. This literature is substantially sparser than the related palladium literature, though there is an array of studies of catalyst leaching and heterogeneity in selected coupling reactions. For example, He and Cai [4] showed that their Amberlyst A-21 polymer-supported copper iodide catalyst, used for terminal alkyne homocoupling under solvent-free conditions, was recyclable with insignificant copper leaching from the support. On the other hand, Biffis et al. [5] showed that despite the observed high activity for Sonogashira coupling, an alumina supported CuO precatalyst significantly leached copper and the catalyst was not fully recoverable. Oishi et al. [6] claimed their TiO₂ supported Cu(OH)_x catalyst to be truly heterogeneous catalyst for the oxidative alkyne-alkyne homocoupling reaction, and supported their conclusions with hot filtration and recyclability tests. They also successfully synthesized supported copper hydroxide catalyst on manganese oxide-based octahedral molecular sieve OMS-2 (Cu(OH)_x/OMS-2) [10] and used it as a heterogeneous catalyst for terminal alkyne homocoupling. This catalyst was reused 13 times, with a total TON of 666. In another study, Ma et al. [7] showed that copper (I) leached significantly from a N,N,

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Scheme 1. Ethynylbenzene oxidative homocoupling reaction.

N,N'-tetraethylenetriamine (TEDETA)-modified SBA-15 silica support when used for the oxidative homocoupling of terminal alkynes without added free base, and that this leaching affected the recyclability of the catalyst. Previously [8], we studied the oxidative homocoupling of benzylamine using the CuO supported on mesoporous CeO₂ (CuO/CeO₂) and showed that the concentration of leached copper in the solution correlated with the rate of reaction. Thus, the literature contains an array of reports describing the heterogeneity of supported copper precatalysts in liquid phase coupling reactions with varied conclusions with regard to catalyst stability and heterogeneity.

In this work, the oxidative homocoupling of ethynylbenzene to form 1,4-diphenylbutadiyne was chosen as a test reaction to explore the catalytic activity and stability of three prototypical supported CuO catalysts, unsupported CuO nanoparticles, CuO/ γ -Al₂O₃, and CuO/TiO₂. Alumina supported copper catalysts have been used for a variety of different coupling reactions including Sonogashira couplings, oxidative coupling of 2-naphthols, S-arylation, and (3+2) Huisgen cycloadditions [5,11–14] among others. In most cases, the solid precatalyst was recovered and recycled, and often the catalyst was deemed to be recyclable with some loss of activity after each cycle [11,12]. The reasons behind those losses were often not explored [12,13], or attributed to site blocking effects associated with deposition of reactants or products on the catalyst surface [11]. Titania supported copper catalysts have also been used for various homo- [6] and cross-coupling reactions [15]. Yamaguchi et al. [15] reported a relation between the polarity of the solvent and copper leaching from the support in the 1,3-dipolar cycloaddition of organic azides to terminal alkynes, and that by choosing the right solvent, non-polar in that case, the catalysis was intrinsically heterogeneous, as supported by a hot filtration test.

For the oxidative homocoupling of terminal alkynes, catalysts based on copper [4,6,7,16–21] as well as other metals [22–26] have been used. Jia et al. [19] reported the use of copper acetate as a catalyst and air as the oxidant in DMSO solvent at 90 °C for the efficient oxidative homocoupling of terminal alkynes. Room temperature terminal alkyne homocoupling was reported by Li et al. [20] using CuI with *N*-bromosuccinimide and *N,N*-diisopropylethylamine (CuI/BS/DIPEA) as the catalytic system. An amine functionalized mesoporous silica SBA-15 supported copper iodide catalyst was also used and claimed to be recyclable, despite the fact that copper leached significantly from the support [7]. In another report, Adimurthy et al. [16] showed that the room temperature homocoupling reaction in acetonitrile as a solvent required base and ligand in addition to CuCl to achieve high product yields. He and Cai [4] employed an Amberlyst A-21 polymer-supported copper iodide catalyst under solvent-free conditions for room temperature terminal alkyne homocoupling. That catalyst was described as recyclable with some loss of activity after each cycle, with insignificant copper leaching. However, as a result of a filtration test, at least part of the catalytic activity could be ascribed to a homogeneous pathway. van Gelderen et al. [27] immobilized copper species on amine functionalized silica and used the catalyst in alkyne homocoupling reactions. They claimed their catalyst to be heterogeneous and used a hot filtration test to demonstrate that no active copper leached to the reaction mixture.

Another amine functionalized silica-supported copper catalyst was synthesized by Li et al. [28] and used for terminal alkyne homocoupling at room temperature. They reused the catalyst six times and claimed that the catalyst retained its mesoporous structure, but found that its catalytic activity decreased by 40% over the six cycles.

In the present study, the activity and stability of unsupported CuO nanoparticles, CuO/ γ -Al₂O₃, and CuO/TiO₂ are explored in oxidative homocoupling of ethynylbenzene to form 1,4-diphenylbutadiyne (DPBD), Scheme 1, at systematically varied reaction conditions, elucidating the nature of the reactive copper species. The results suggest that all these precatalysts are reservoirs for soluble molecular copper species, which act as the true catalyst in this reaction under the conditions employed.

2. Experimental

2.1. Catalyst preparation

2.1.1. CuO/Al₂O₃

γ -Alumina was synthesized as per a procedure previously reported that employed the surfactant P-123[®] to mediate the self-assembly of pseudoboehmite nanoparticles [29]. In a typical synthesis, 13.75 g of pseudoboehmite obtained from Sasol North America (Catapal B, 74.3% Al₂O₃) was peptized in a mixture of 0.9 mL nitric acid (Fischer Scientific, ~70%) and 200 mL distilled water. The suspension obtained was then sonicated for 90 min at room temperature followed by stirring at 60 °C for 17 h. The suspension was next cooled to room temperature and the peptized alumina thus obtained was added to a stirred surfactant solution comprising 15.30 g Pluronic P123[®] in 200 mL ethanol (200 proof). The resulting solution was further stirred for 24 h at room temperature followed by evaporation of the solvent at 60 °C. The obtained alumina composite was then dried at 75 °C for 24 h. The white sol-gel derived mesoporous γ -alumina was finally obtained by calcination of this composite at 700 °C for 4 h with a heating ramp of 1 °C/min and an intermediate holding step of 150 °C for 1 h for the removal of water and ethanol. To load the support with copper species, a solution of 193 mg of copper nitrate trihydrate, Cu(NO₃)₂·3H₂O (Sigma-Aldrich, purity >99%) in 0.60 mL of de-ionized water was added to 500 mg of the above synthesized γ -Al₂O₃, to yield a 10 wt% alumina-supported copper oxide catalyst. Then, the wet sample was heated to 120 °C at ramp of 3 °C/min in an air flow and dried at 120 °C for 3 h. Next, the temperature was increased to 500 °C at a ramp of 3 °C/min, and the catalyst was calcined in flowing air at 500 °C for 3 h. This catalyst is referred to as 10CuO-Al₂O₃.

2.1.2. CuO/TiO₂:

Commercial mesoporous anatase TiO₂ (*S*_{BET} = 127 m²/g and *V*_{pore} = 0.25 cm³/g) was also used as a support for CuO. A solution was prepared by dissolving 435 mg of copper nitrate trihydrate, Cu(NO₃)₂·3H₂O (Sigma-Aldrich, purity >99%), in 0.12 mL of de-ionized water. The total volume of this solution was 0.30 mL. To aid the distribution of copper in the pores of the mesoporous TiO₂, half of this solution was added to 1 g of commercial mesoporous TiO₂, dried at 75 °C, and then the other half was added, to yield

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