

Highly selective CuO NP catalyst for semi-hydrogenation of alkynes

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Introduction

The semi-hydrogenation of alkynes is of special relevance in fine chemistry industries since it is an efficient method for the production of alkenes [1]. A variety of palladium catalysts promoted by a second metal is available for the conversion of alkynes into alkenes [2]; for example, the Lindlar catalyst, comprised of a Pd catalyst partially poisoned with lead. Catalyst deactivation and the presence of toxic lead are the main drawbacks of this catalyst system. An innovative patent-protected manufacturing technology, called NanoSelect™, has been used to prepare highly active and selective Pd catalysts, which are lead-free Lindlar catalyst replacements in alkyne-to-cis-alkene hydrogenations [3]. In a recent study [4], we have shown that ligands grafted on the support surface (magnetite modified with -N, -S donor functional groups) cause important changes in the hydrogenation activity and selectivity of supported Pd nanoparticles. Pd catalysts are known to be unselective if not adequately poisoned [5]. Here we present our recent studies on the development of copper nanoparticle-based catalysts for selective hydrogenations, in the search for alternatives to the use of palladium.

Results e Discussion

We synthesized copper(I) oxide nanoparticles stabilized with polyvinyl alcohol (PVA) and supported them on a silica-coated magnetic support previously developed in our research group [6]. The catalyst was then calcined and characterized as CuO NPs by different techniques such as TEM, XRD, XAFS and XPS. The magnetic support was chosen to facilitate the catalyst separation and handling using a permanent magnet. The catalytic tests were performed on a glass reactor at constant pressure (6 atm H₂) and temperature (100°C). The H₂ gas consumption was followed during the hydrogenation reaction in order to indicate the end of the reaction. The catalyst was separated magnetically from the reaction medium and the organic phase was analyzed by GC. The selectivity was confirmed by FTIR and NMR analysis.

The results obtained in the catalytic studies are summarized in Table 1. The catalyst is highly selective for the conversion of alkynes to the semi-

hydrogenated product, leading to the formation of olefinic compounds. The hydrogenation of diphenylacetylene shows, in minor quantities, the total hydrogenated product. However, the selectivity to the olefinic compound is still high, and the analysis of the product by NMR shows only the presence of the *cis* isomer, (*z*)-diphenylethylene. These results are very promising, because copper catalysts are known to polymerize the hydrogenated substrate, and this was not observed here.

Table 1. Hydrogenation of alkynes using CuO NPs.

Substrate	Conv. (%)	Selectivity (%)		TOF ^a (h ⁻¹)
		-C=C-	-C-C-	
Propargyl alcohol	>99,9	100	-	51
3-butyn-1-ol	>99,9	100	-	110
diphenylacetylene	>99,9	89,9	10,1	50

Conditions: 0.1 mol % Cu; T=100°C; t=24h and 6 bar H₂. ^aTOF = mol substrate converted per mol of catalyst per h, at initial rates.

Conclusions

We have prepared a highly selective copper-based nanoparticle catalyst for the semi-hydrogenation of alkynes to the corresponding alkenes, and the high selectivity is maintained even after the reaction went to completion. The reaction rates still need improvement. Studies on the possibility to incorporate a second metal to enhance the activity of this catalyst are in progress.

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