

# Remarkable catalytic effect of piperazine-capped Au nanoparticles for selective hydrogenation of alkynes

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## Abstract

We report here a remarkable catalytic effect of piperazine-capped Au NPs for selective hydrogenations. Au NPs supported on silicon oxide were inactive for the hydrogenation of alkynes and become highly active and selective for the semihydrogenation of alkynes into alkenes with >99% conversion and ~100% selectivity, as a result of the addition of piperazine. The amine ligands act as activity and selectivity switchers by improving molecular hydrogen dissociation. The transformation can proceed smoothly using H<sub>2</sub> as the hydrogen source and under relatively mild conditions.

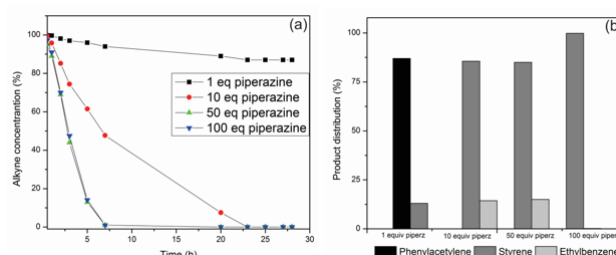
## Introduction

The semihydrogenation of alkynes is a very important and fundamental reaction in the manufacturing processes of bulk and fine chemicals for the preparation of alkenes. To date, lead-free environmentally benign semihydrogenation catalyst systems involving Ni, Pd, and Pt metals have been developed as alternatives to the Lindlar catalyst [Pd/CaCO<sub>3</sub> treated with Pb(OAc)<sub>2</sub>], nevertheless they usually exhibit low selectivity for alkenes.<sup>1</sup> Ligands containing -N, -S, and -O groups are added to Lindlar catalyst with the intention of inhibiting the alkene interaction with the catalyst surface. Catalyst deactivation and the presence of toxic lead are drawbacks of Lindlar catalyst system. The development of selective heterogeneous catalyst for this reaction would be highly desirable from the point of view of organic synthesis and industrial interest. Herein, we report a remarkable selectivity and catalytic activity of amine capped supported Au NPs for the hydrogenation of alkyne to the corresponding alkene.

## Results and Discussion

The synthesis of Au/SiO<sub>2</sub> followed a previously reported and highly reproducible method.<sup>2</sup> Characterizations with transmission electron microscopy (TEM) revealed that the Au NPs were highly dispersed on the silica support with an average diameter of 2.3±0.6 nm. The formation of the Au NPs could, also, be evidenced by SPR (surface plasma resonance) band at 525 nm observed in the UV-Vis spectra. The catalyst was also characterized by XPS and XRD. We next

investigated the catalytic activity of Au/SiO<sub>2</sub> in the semihydrogenation of alkyne in the presence of increasing amount of capping ligand (Figure 1). The limited hydride formation over the non-capped Au NPs hinder completely its activity in the hydrogenation reaction, but piperazine was able to act as an activity switcher by improving molecular hydrogen dissociation over ligand-capped Au nanoparticles. Owing to the preferential adsorption of the triple bond at the gold nanoparticles, high selectivity to the alkene product was achieved. Blank experiments show no conversion in the absence of hydrogen.



**Figure 1.** Hydrogenation of phenylacetylene catalyzed by Au NPs with increasing amounts of piperazine: a) alkyne concentration versus time; b) product distributions after 24 h. Reaction conditions: 1 mmol phenylacetylene, 0.01 mmol Au, 2 mL of ethanol at 100 °C, 6 bar H<sub>2</sub>.

## Conclusions

In summary, the catalytic performance of piperazine-capped Au/SiO<sub>2</sub> has been investigated for the semihydrogenation alkyne to alkene. High conversion of a range of terminal alkynes (up to ~100%) with excellent selectivity (~100%) for alkene products was achieved using ethanol at 100 °C and H<sub>2</sub> as hydrogen source. XPS results showed no change in the oxidation state of gold, but further characterization of the active species is in progress.

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<sup>1</sup>Fujitani, T.; Nakamura, I.; Akita, T.; Okumura, M.; Haruta, M. *Angew. Chemie - Int. Ed.* **2009**, *48*, 9515.

<sup>2</sup>Oliveira, R. L.; Kiyohara, P. K.; Rossi, L. M. *Green Chem.* **2010**, *12*, 144.