



Gold-catalyzed aerobic epoxidation of *trans*-stilbene in methylcyclohexane. Part I: Design of a reference catalyst

Kevin Guillois, Laurence Burel, Alain Tuel, Valérie Caps*

Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON, UMR 5256 CNRS – University of Lyon), 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

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ABSTRACT

The kinetics of the heterogeneous gold-catalyzed aerobic epoxidation of stilbene in the liquid phase has been shown to be hindered by diffusion limitations, due to the use of supports which are unsuitable to apolar reaction media. The choice of these supports is generally dictated by the ability of standard methods of preparation to stabilize highly dispersed gold nanoparticles on them. Hence, new methods need to be designed in order to produce catalytically active gold nanoparticles on hydrophobic supports in general and on passivated silicas in particular. By investigating Tsukuda's method to produce colloidal solutions of gold nanoparticles upon reduction of the triphenylphosphine gold chloride complex in solution, we found that direct reduction of AuPPh₃Cl in the presence of a commercially available silica support functionalized with dimethylsiloxane, Aerosil R972, leads, in a highly reproducible and potentially scalable way, to the best catalyst ever reported for this reaction.

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1. Introduction

The oxidative transformation of alkane and alkene into useful oxygenated intermediates, such as alcohols and epoxides, is a key-step in the synthesis of fine chemicals. Such reactions are typically achieved in the presence of a metal salt under pure oxygen pressure or using excess peracid, respectively. Given the hazardousness of the processes and of the compounds involved, there was a need for safer catalytic ways. In this respect, the development of microporous titanium silicalite-1 (TS-1) [1,2], which can efficiently catalyze the partial oxidation of certain alkanes and alkenes, using hydrogen peroxide as the oxygen source [3], was an improvement. However, the confinement of the active site in microporous cavities makes the process unsuitable to the oxidation of large substrate molecules [4], such as stilbene for example [5–7]. Furthermore, the process would be even greener if using air as the primary oxidant.

It recently appeared that supported gold nanoparticles (NP) could catalyze the aerobic epoxidation of larger alkenes [8,9] and especially the aerobic co-oxidation of stilbene and methylcyclohexane [10–13]. Apparent reaction rates can be improved using supports with non-oxygenated surfaces, such as graphite [14,15] or a hydrophobic Au/SiO₂ catalyst which exhibited enhanced wettability in the poorly polar reaction medium [16], or using

unsupported, soluble gold colloids [17]. This indicated that gold nanoparticles were the active sites and that the support affected apparent kinetics essentially via mass-transfer limitations. In order to use macro-kinetics in the liquid phase to study the mechanisms involved, it is essential to prepare a significant amount of catalyst which exhibits high affinity with the apolar solvent, e.g. using passivated silica supports. The current synthesis leading to the state-of-the-art catalyst actually relies on a sophisticated, multi-step protocol based on reaction between {Au[N(SiMe₃)₂]}₄ and an aerosil silica support partially dehydroxylated upon stringent vacuum treatments. Passivation of the silica surface is subsequently achieved upon degradation of the grafted complex. The main issue with this method is the synthesis of the {Au[N(SiMe₃)₂]}₄ precursor which suffers from very low yields (ca. 5%), preventing any upscale of the catalyst preparation.

To the best of our knowledge, there is, to date, no reported method to directly prepare gold nanoparticles on hydrophobic silicas. This is attributed to two factors. First, in many gold-catalyzed reactions, the support actually takes an active part in the mechanism, whether through surface hydroxyl groups or surface oxygen ions [18–22]. Second, when carried out in the liquid phase, reactions catalyzed by gold nanoparticles usually involve polar solvents and substrates in which supports bearing oxygen functions at the surface (oxides [23–27], activated carbons [28–31], ...) are properly dispersed. Until the discovery of gold-catalyzed alkane/alkene oxidations, there was thus no real incentive to prepare Au NP on hydrophobic supports. On the contrary, oxygenated surface groups actually proved useful in immobilizing gold. Hydroxyls have been shown to react with gold precursors in the deposition–precipitation

* Corresponding author. Present address: KAUST Catalysis Center (KCC), 4700 King Abdullah University of Science and Technology, Thuwal 23955 – 6900, Saudi Arabia. Tel.: +966 2 808 0304.

E-mail address: valerie.caps@kaust.edu.sa (V. Caps).