Effect of the titania morphology on the Au/TiO$_2$-catalyzed aerobic epoxidation of stilbene

Pascal Lignier$^a$, Massimiliano Comotti$^b$, Ferdi Schült$^b$, Jean-Luc Rousse$^a$, Valérie Caps$^a, *$

$^a$Institut de recherches sur la catalyse et l’environnement de Lyon (IRCELYON, CNRS-Université de Lyon), 2 avenue Albert Einstein, F-69626 Villeurbanne Cedex, France
$^b$Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim a.d. Ruhr, Germany

ABSTRACT

We use a colloidal deposition method to prepare gold nanoparticles with similar size distributions centered at 3 nm over various anatase titania supports. All UV100, PC500 and AK350 titanias are loaded with similar amount of gold (1.0 ± 0.2 wt.%) which is in similar electronic and optical environments, as shown by X-ray photoelectron spectroscopy (XPS) and UV–vis. This allows us to assess the effect of the titania crystallization, morphology and chemical composition on the catalytic properties of gold in the aerobic epoxidation of trans-stilbene. We find that Au/UV100 is more active than Au/PC500 and Au/AK350 but that selectivities are similar on all materials. Epoxide yields on the other hand critically depend on the support functionalization and surface composition. TG–DTA characterization of the bare titania powders reveals indeed that AK350, which leads to the least active catalyst, is slightly less hydroxylated than PC500 and UV100. This indicates that surface titanol groups might be involved in the epoxidation of trans-stilbene. The presence of boron oxide on Au/UV100 (XPS), due to reaction of UV100 with the NaBH$_4$ reductant during the synthesis, is also thought to promote the epoxide-forming mechanism. This chemical promotion effect appears to compensate for the specific and beneficial gold–P25 interaction. As a result, Au/UV100 is more efficient than the reference Au/P25 catalyst for this reaction.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Epoxidations of substituted alkenes are key-reactions of the fine chemical industry; the oxygenated products they provide are essential intermediates for the chemical syntheses of more sophisticated molecules. Although epoxidations of lower alkenes have been carried out since the 1980s over the well-known microporous titanium silicate TS-1 (Enichem) [1,2], the heterogeneous epoxidations of larger alkenes have relied on the synthesis of titanium-based structures with larger pores [3–5]. However, if stability of the porous catalyst is not the main issue, reactions involving the bulkiest olefins still suffer from diffusional limitations due to confinement of the active site within deep inorganic cavities. In addition, these materials usually require the use of organic oxidants (e.g. tert-butyl hydroperoxide), which are less environmentally friendly than the hydrogen peroxide associated with TS-1. This has its importance, considering that these hazardous oxidizing agents are used in stoichiometric amounts or even in excess, since epoxide yields on peroxides are quantitative [1]. One structure should be mentioned though, where the environment of the catalytic site is made more hydrophobic, just like in TS-1, in order to allow the use of H$_2$O$_2$ as oxidant [6,7]. However, the synthesis of these complex structures from expensive titanium precursors is not straightforward and probably difficult to scale-up.

When looking into cleaner, safer and simpler alternatives to these epoxidation processes of larger alkenes, we found that supported gold nanoparticles could epoxidize trans-stilbene in methycyclohexane using air as principal oxidant [8]. In particular, the Au/TiO$_2$ reference catalyst [9] from the World Gold Council (WGC) exhibited higher activity and selectivity than the reference Au/C-WGC [10]. However, the P25 support used is a low surface area titania that does not disperse well within the apolar reaction medium. Although it is accepted that P25 is the optimum support for gold in the oxidation of CO, we found that it might not be appropriate for oxidations in the liquid phase and that testing higher surface area titanias could be interesting.

In this paper, we make use of a colloidal deposition method developed by Comotti et al. [11] to prepare similar gold particle size distributions over various titania supports, including high surface area materials. The key-idea of this technique is the synthesis of a gold sol with a narrow size distribution before