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Stereoselective stilbene epoxidation over supported gold-based catalysts†

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The gold reference catalyst Au/TiO$_2$ exhibits high activity in the stereoselective epoxidation of *trans*-stilbene in methylcyclohexane in the presence of 5 mol% TBHP, by taking part in a chain reaction involving the activation of molecular oxygen by a radical produced from methylcyclohexane.

Epoxidation of lower alkenes, *i.e.* with kinetic diameters below 5.5 Å, such as 1-hexene, are usually carried out over the microporous titanium silicalite-1 (TS-1) using a stoichiometric amount of hydrogen peroxide as the oxidant.[1] Larger alkenes, such as cyclohexene or *cis*-stilbene can be epoxidised over Ti-MCM-41 with *tert*-butylhydroperoxide (TBHP) as the primary oxidant[2] while the epoxidations of 1-octene, vinylcyclohexene, limonene and monoterpenes have been reported using metal-substituted polyoxometalates (POM) and excess H_2O_2.[3] Cyclooctene and norbornene can be epoxidised by molecular oxygen over ruthenium-substituted POM catalysts.[4] In all cases, the mechanisms involved are non radical, which is held as the reason for the high yields of epoxides achieved.[3] Epoxidations with POM however require the use of environmentally unfriendly chlorinated solvents.[3] On the other hand, Hughes *et al.* reported in 2005 on the epoxidation of a few bulky alkenes (cyclohexene, cyclooctene, styrene, *cis*-stilbene) over Au/C in the presence of catalytic amounts of TBHP in air at atmospheric pressure.[5] In these reactions, low yields of epoxide were obtained and mechanistic considerations were limited to the description of TBHP as the "initiator of a chain reaction sustained by molecular oxygen" and the presence of an intermediate "allowing rotation about the C–C bond". Earlier on, it had been shown that gold complexes could catalyse the epoxidation of cyclohexene, using molecular oxygen as oxidant, but also in very low yields.[6]

Here, we report on the stereoselective epoxidation of *trans*-stilbene (tS) over the reference catalysts Au/TiO$_2$ (P25), Au/C and Au/Fe$_2$O$_3$ (all provided by the World Gold Council)[7] and one home-made Au/TiO$_2$-PC500. We propose a reaction mechanism involving free-radicals and we look into the ability of titania-supported gold to make it highly selective towards the epoxide.

First, unlike Ti-silicates- and POM- catalysed alkene epoxidations,[2] gold exhibits higher yield and selectivity towards epoxide in *low polarity solvents*. In fact, in the presence of excess TBHP (400 mol%), yields of *trans*-stilbene oxide are higher in methylcyclohexane (MCH) than in cyclohexane (CH), toluene (TOL) and acetonitrile (ACN), over Au/C as well as Au/TiO$_2$ (see ESI†), even with a poorer dispersion of the catalytic powder. The epoxide is formed as the primary product; by-products are essentially degradation products (see ESI†). Au/TiO$_2$ is more active and selective than Au/C (Fig. 1). Actually, while 19% of tS is converted (in 24 h) in the absence of a catalyst with 52% selectivity to the corresponding epoxide, adding just TiO$_2$-P25 increases the tS conversion to 31% with similar selectivity. TiO$_2$-PC500 brings the conversion to 48% with lower selectivity, which is probably due to the presence of sulfonated (*i.e.* acidic) surface functions on this high surface area titania. However, the conversions observed over very different gold-containing catalysts vary in a short range from 81 to 95%, indicating that the reaction is only slightly influenced by the nature of the support, unlike some gold-catalysed reactions in the gas phase, such as CO oxidation.[8] Selectivities vary in an equally short range from 51 to 75% with Au/TiO$_2$ > Au/TiO$_2$-PC500 ~ Au/Fe$_2$O$_3$ > Au/C, illustrating the superiority of titania as a support for epoxidation. Furthermore, Pt/C is more active and selective than Au/C and nearly as selective as Au/TiO$_2$, indicating that, in excess TBHP, the reaction is only slightly influenced by the nature of the metal.

However, when the TBHP/tS molar ratio is reduced to 0.05, Pt/C becomes completely inactive, converting 14% tS and yielding no epoxide, just like in the absence of a solid catalyst (Fig. 2). Adding TiO$_2$-PC500 increases tS conversion to 44%, but again without forming epoxide. On the other hand, TiO$_2$-P25 *decreases* tS conversion but *trans*-stilbene oxide is now formed with 63% selectivity. Over Au/TiO$_2$, the yield of epoxide reaches 53% in 24 h, showing a real effect of gold in this reaction. The differences in the catalytic behaviours of the gold reference materials are now more obvious, the order for activity/selectivity remaining the same (Au/TiO$_2$ > Au/Fe$_2$O$_3$ > Au/C).

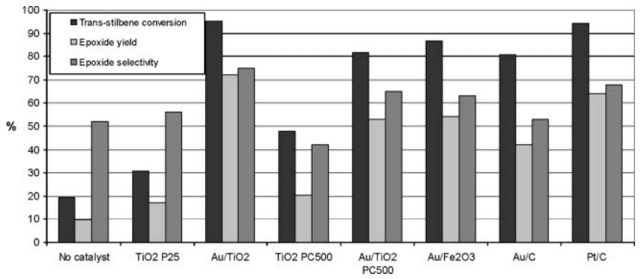

Fig. 1 tS (1 mmol), gold-based catalyst (Au: 10 μmol), MCH (20 mL), TBHP (4 mmol), 80 °C, 24 h.

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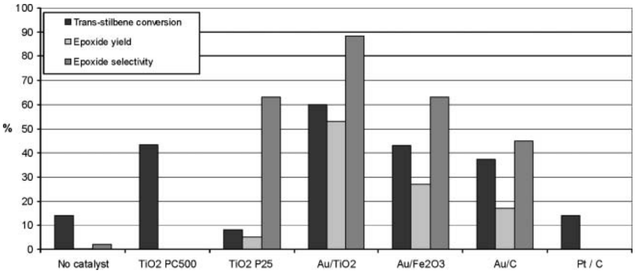
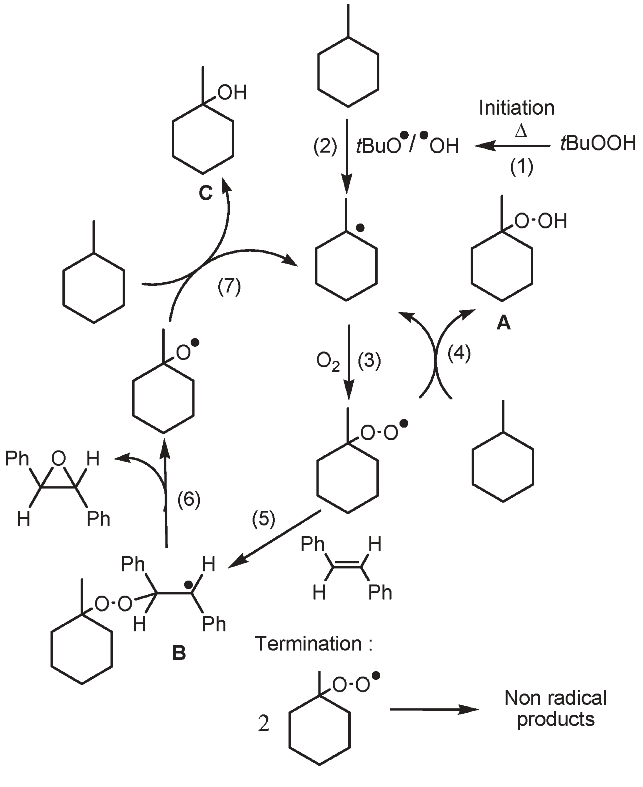


Fig. 2 tS (1 mmol), gold-based catalyst (Au: 10 μmol), MCH (20 mL), TBHP (0.05 mmol), 80 °C, 24 h.

The fact that 0.53 mmol tS are converted to *trans*-stilbene oxide over Au/TiO_2 with only 0.05 mmol TBHP shows that molecular oxygen from the air has been used during the process. This is confirmed by the experiment carried out under argon, in which less than 5% *trans*-stilbene oxide is yielded. The use of a radical scavenger (2,6-di-*tert*-butyl-4-methylphenol, 10 mol%) in the reaction mixture also results in less than 5% *trans*-stilbene oxide, which seems to indicate that oxygen is most probably activated *via* free-radical species. The critical solvent effects (acetonitrile and toluene yielding less than 5% *trans*-stilbene oxide; see ESI†) show that, unlike TBHP activation, oxygen activation is tightly related to the solvent nature, suggesting direct involvement of the solvent molecule in the reaction mechanism. It is possible indeed that a methylcyclohexane peroxy radical is produced *via* hydrogen abstraction from methylcyclohexane and that the epoxidation of *trans*-stilbene involves a cooxidation of MCH and tS (Scheme 1).



Scheme 1 Proposed mechanism for the epoxidation of *trans*-stilbene in methylcyclohexane, in the presence of TBHP (5 mol%) and a gold-based catalyst.

This free-radical mechanism is consistent with the model for the non-catalytic autoxidation of styrene.[9] The initiation step includes thermolysis of TBHP (1) and production of the methylcyclohexyl radical (2). The propagation step (3) would consist in production of the methylcyclohexyl peroxy radical. It can then add to tS (5) or, to a lesser extent,[10] carry out hydrogen abstraction from methylcyclohexane (4) to regenerate the methylcyclohexyl radical and form methylcyclohexyl hydroperoxide (compound **A**, identified by GC-MS). Addition to (as compared to hydrogen abstraction from) tS is favored since tS has no allylic hydrogen that could be abstracted.[9] Species **B** is consistent with the results obtained in the Au/C-catalysed oxidation of *cis*-stilbene, which yields exclusively *trans*-stilbene oxide. This implies the presence of an intermediate which allows rotation around the C–C bond. Addition can be followed by unimolecular decomposition (6) to form the epoxide and a methylcyclohexoxy radical. This species will then abstract the tertiary hydrogen from MCH (7) to produce methylcyclohexan-1-ol (compound **C**, identified by GC-MS) and regenerate the methylcyclohexyl radical. Termination probably occurs *via* recombination of the peroxo radicals.[11]

Of course, although $RO^{\bullet}$ are generally less active for addition than for abstraction,[12] addition of hydroxyl radicals to tS cannot be fully excluded,[13] especially in excess TBHP. Addition of *tert*-butoxy radicals would be slower.[14] $^{t}BuO^{\bullet}$ are more active for hydrogen abstraction.[15] It is interesting that H_2O_2 (4 mmol) leads, over Au/C, to 30% tS conversion *without formation of any epoxide*. This indicates that the conversion of *trans*-stilbene due to attack by the hydroxyl radical will lead exclusively to degradation products, which could explain the lower selectivities obtained in excess TBHP. Moreover, since 14% *trans*-stilbene is transformed while only 0.3% epoxide is produced in the absence of a catalyst (5 mol% TBHP), we believe that this attack of tS by $OH^{\bullet}$ is non-catalytic and guided only by the electrophilicity of the hydroxyl radical.[16]

The introduction of TiO_2-P25 brings selectivity to the reaction, while lowering the conversion (8%). It is possible that titania will trap these non-selective hydroxyl radicals and allow $^{t}BuO^{\bullet}$ to react with MCH, enabling the epoxide-forming reaction to proceed. The presence of gold on titania P25 further increases both conversion and selectivity. The actual role of gold is yet unclear but it seems that it could act in synergy with the titania support and maybe catalyse hydrogen abstraction from MCH by $^{t}BuO^{\bullet}$ (2) and/or formation of the peroxo radical (3). Its involvement in the propagation sequence is undoubted since the yield of epoxide produced after the catalyst has spent 6 h in the reaction medium before being removed remains at about 18%, instead of going up to 33% (24 h, Au/C, 0.4 mmol TBHP). It is also interesting that the produced epoxide is always in the *trans* form, whether from *trans*- or *cis*-stilbene, suggesting that selective unimolecular decomposition (6) has occurred. This is consistent with adsorption onto a solid surface, which creates sterical constraints, thereby decreasing both symmetry and accessibility of the molecule and forcing the reaction to proceed in a specific way. Furthermore, less than 0.04 ppm gold was detected (ICP-MS) in the reaction medium after removal of the catalyst, showing that less than 0.04% of supported gold have leached into the organic phase. On the other hand, 50 ppm of free gold was found inactive for the production of epoxide from *trans*-stilbene, indicating that the reaction is truly heterogenous.

XPS studies show two contributions for the Au $4f_{7/2}$ peak on the Au/TiO_2 and Au/C catalysts, both before and after reaction: the main contribution ($\sim$90%) is at a binding energy of 83.0 $\pm$ 0.1 eV for Au/TiO_2 and at a binding energy of 84.1 $\pm$ 0.1 eV for Au/C, corresponding to $Au^{\delta-}$ and Au^0 respectively. The presence of $Au^{\delta-}$ in titania-supported gold catalysts has already been explained by a charge transfer from the support to the gold particle.[8] The minor contribution ($\sim$10%) is at a binding energy of 85.5 $\pm$ 0.1 eV both for Au/TiO_2 and Au/C, before and after reaction, indicating the presence of Au^+, probably at the gold–support interface. It is interesting that this contribution is insignificantly increased after reaction, suggesting that gold has suffered negligible oxidation during the reaction. It is not clear which oxidation state of gold is actually active in this reaction. However, if we assume that active gold is involved in interactions with electrophilic peroxy radicals, we could suggest that $Au^{\delta-}$ is more active than Au^0 and Au^+, which would be consistent with the observation that Au/C is less active and selective than Au/TiO_2. Finally, a maximum reaction rate of 150 $mol_{tS}\ mol_{Au}{}^{-1}\ h^{-1}$ is obtained over Au/TiO_2 using 5 mol% TBHP and an optimized amount of the catalyst.

In conclusion, we have shown that, in methylcyclohexane, *trans*-stilbene can be epoxidized stereoselectively in the presence of Au/TiO_2 and 5 mol% TBHP. Both gold and titania seem to take part in the free-radical reaction mechanism sustained by molecular oxygen, possibly by trapping the unselective hydroxyl radicals, catalysing radical formation and stabilising the intermediate resulting from the addition of the methylcyclohexyl peroxy radical onto *trans*-stilbene.

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