

Electronic Supplementary Information (ESI)

Catalyst preparation, characterization and testing

Reference catalysts from the World Gold Council (WGC)

The 1.5%Au/TiO₂ (type A, lots no. Au-TiO₂ #02-05 and #02-06, sample Nos. 53 and 84), 1%Au/C (type D, sample No. 24) and 5%Au/Fe₂O₃ (type C, lot no. Au-Fe₂O₃ #02-04, sample no. 56) catalysts were purchased from the World Gold Council (WGC). Their preparation and characterization have been extensively described elsewhere [M. Azar, V. Caps, F. Morfin, J.-L. Rousset, A. Piednoir, J.-C. Bertolini and L. Piccolo, *J. Catal.* 2006, **239**, 307; W. B. Kim, G. J. Rodriguez-Rivera, S. T. Evans, T. Voithl, J. J. Einspahr, P. M. Voyles and J. A. Dumesic, *J. Catal.* 2005, **235**, 327.].

- Au/TiO₂ is prepared at AIST (Japan) following a deposition-precipitation protocol developed by M. Haruta and coworkers, from titania P25 (Degussa, 50 ± 15 m²g⁻¹, 75 ± 5 wt% anatase + 25±5 wt% rutile with mean particle diameters of 25 and 39 nm, respectively, as determined by XRD) and HAuCl₄·3H₂O. The powder catalyst contains 1.4±0.1 wt% of gold, as determined by inductively coupled plasma (ICP) chemical analysis. The average particle diameter of gold in the fresh catalyst is 3.7±1.5 nm, as analyzed by transmission electron microscopy.

- Au/Fe₂O₃ is prepared by co-precipitation at AIST (Japan). It contains 4.4wt% gold with average particle diameter 4.0±0.9 nm.

- Au/C is prepared at Milano University (Italy) by deposition of gold sols on high surface area carbon (X40S, 1200 m²g⁻¹). Gold content is 1.0wt% with average particle diameter 10.5 nm (TEM) / 6.7 nm (XRD).

Au/TiO₂-PC500 prepared in-house

It was prepared using a typical deposition-precipitation method from HAuCl₄·3H₂O (Alfa Aesar, 99.99%) and TiO₂ PC500 (Millenium Chemicals, 340 m²g⁻¹, 83.4wt% TiO₂, 100% anatase, 0.34wt% SO₃). The deposition-precipitation method consists in adjusting the pH (3) of a HAuCl₄·3H₂O solution in water (5×10⁻³ M) to 9, by adding a NaOH 0.2 M solution. The resulting solution is then added drop by drop to a stirred suspension of the support material (1 g) in water (50 mL). The pH of the resulting mixture is again adjusted to 9 before it is left to stir at 20°C for 18 h. The powder is recovered by filtration, washed with 1 L deionized water to ensure complete removal of chlorine ions (AgNO₃ test) and weakly adsorbed species and dried at 80°C in vacuum for 20 h, which ensures reduction of gold. This allows to minimize the Cl content in our materials (<100 ppm in all cases). It contains 1.6wt% gold with average particle diameter (in the fresh catalyst) 5.8±2.9 nm (TEM). The average crystallite size of pure anatase TiO₂-PC500 is 8 nm. Its characterization is being published.[V. Caps, Y. Wang, J. Gajecski, B. Jouguet, F. Morfin, A. Tuel and J.-L. Rousset, *Stud. Surf. Sci. Catal.* 2006, in press.]

Blank experiments

TiO₂ P25 was purchased from Degussa, 1%Pt/C from Aldrich.

Methods of characterization

- The gold contents of the catalysts were determined by in-house chemical analysis (ICP or ICP-MS).

- Thermogravimetric analysis (TGA) and differential temperature analysis (DTA) were performed on a Setaram Instrumentation SETSYS Evolution – 1200. Samples were heated in flowing air (50 ml/min) from 20 to 900°C at 10°/min. The data were collected and analyzed using the SETSOFT2000 software.

- X-ray Photoelectron Spectroscopy (XPS) experiments were carried out in a VG Scientific ESCALAB 200R spectrometer including a hemispherical analyzer and working at a pressure lower than 10⁻⁹ mbar. XPS measurements were performed using the AlK_α line of the dual anode and a pass energy of 50 eV. The instrument was calibrated with a silver sample (Ag 3d_{5/2} at 368.3 eV). The peaks were referenced to the C-(C,H) components of the C1s band at 284.6 eV.

- Transmission electron microscopy (TEM) was performed on a JEOL JEM 2010-F operating at 200 kV and equipped with a Pentafet-Link ISIS energy dispersive X-ray (EDX) spectrometer from Oxford Instruments allowing local elemental analysis with a spatial resolution of ~ 1 nm.

- X-ray diffraction (XRD) powder patterns were recorded between 3 and 80° (2θ) on a Bruker (Siemens) D 5005 diffractometer using CuK_{α2} radiation with steps of 0.02° and 10 s (or 1 s) per step.

Catalytic testing and products analysis

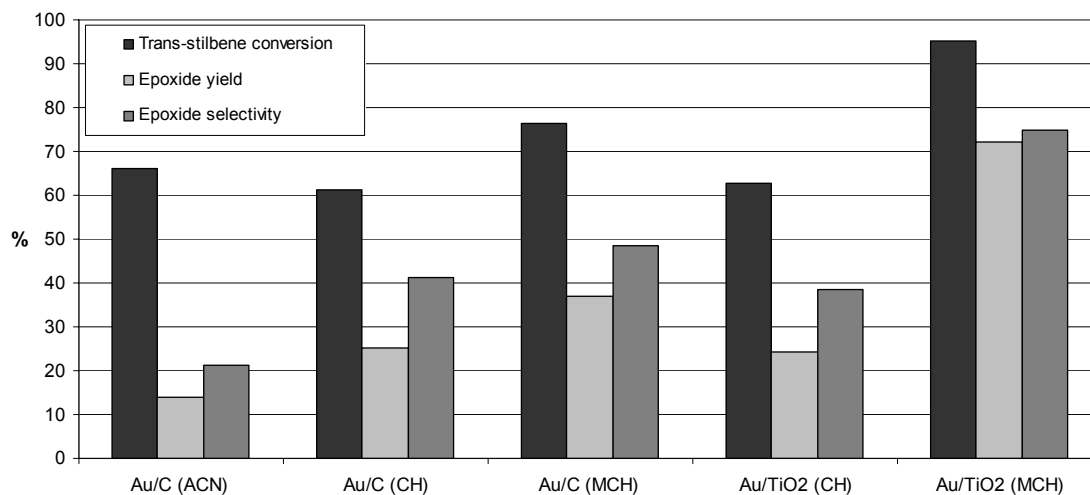
The catalytic tests were carried out with *tert*-butylhydroperoxide (TBHP, 70% in H₂O, Alfa Aesar), *trans*-stilbene (tS, 97%, Alfa Aesar), methycyclohexane (MCH, 99%, Sigma-Aldrich).

Catalytic tests were carried out in magnetically stirred (900 rpm) glass batch reactors containing substrate (tS, 1 mmol), gold-based catalyst (Au: 10 μmol), solvent (20 mL), oxidant (TBHP, 0.05 to 4 mmol) and held at 60°C or 80°C (depending on solvent) in air at atmospheric pressure for 24 h. The reaction products were identified and quantified by HPLC (Perkin Elmer Series 200 lc pump, autosampler and UV-vis detector set at 250 nm, reverse phase C-18 column Brownlee,

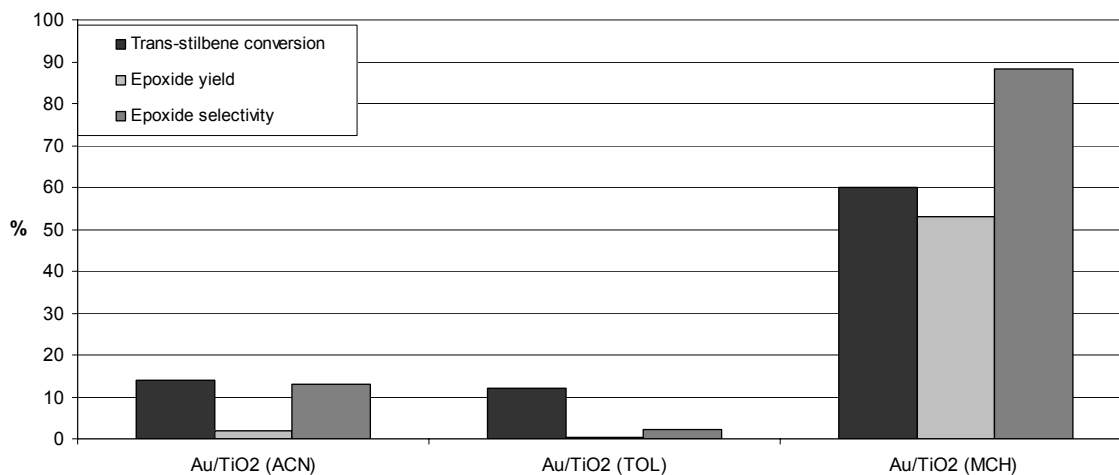
ValueLineSpheri-5 C18, 220×4.6 mm, acetonitrile/water as eluent at 1 cm³min⁻¹). Some reaction mixtures were also analyzed by GC-MS (Hewlett Packard 6890/5973 system; electron impact ionization at 70 eV, He carrier gas, 30 m × 0.25 mm VF5 - MS, 100% dimethylpolysiloxane capillary column).

Additional results

Solvent effect



Reaction conditions : *trans*-stilbene (1 mmol), TBHP (400mol%), supported catalyst (Au: 10 μmol), solvent (20 mL), 60°C (ACN, CH) or 80°C (MCH), 24 h.

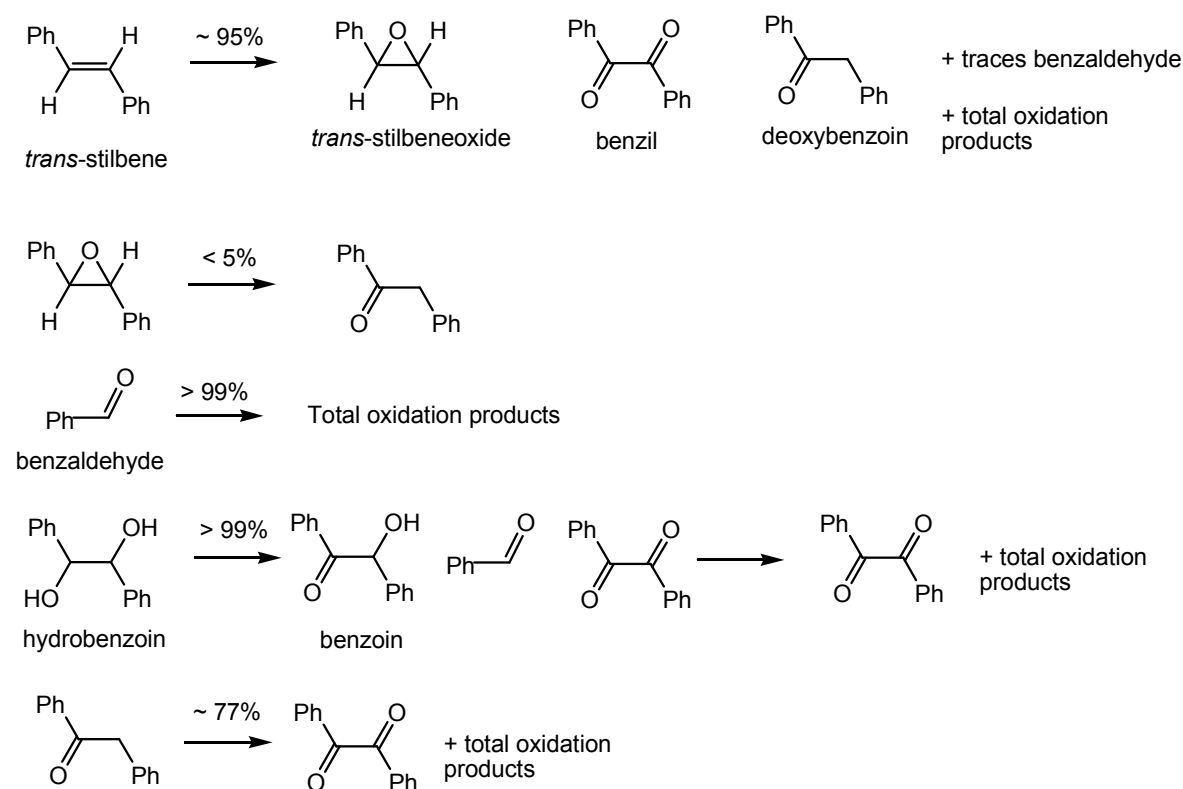


Reaction conditions : *trans*-stilbene (1 mmol), TBHP (5mol%), Au/TiO₂ (Au: 10 μmol), solvent (20 mL), 60°C (ACN) or 80°C (TOL, MCH), 24 h.

The yield of epoxide increases with decreasing polarity (dielectric constant) of the solvent whatever the amount of TBHP used. The rate of β-scission of the *tert*-butoxy radical also decreases with decreasing solvent polarity [Y. P. Tsentalovich, L. V. Kulik, N. P. Gritsan and A. V. Yurkovskaya, *J. Phys. Chem. A*, 1998, **102**, 7975], which indicates that the active (i.e. propagating) radical is indeed one produced from the solvent and not the methyl radical coming from the reaction of β-scission.

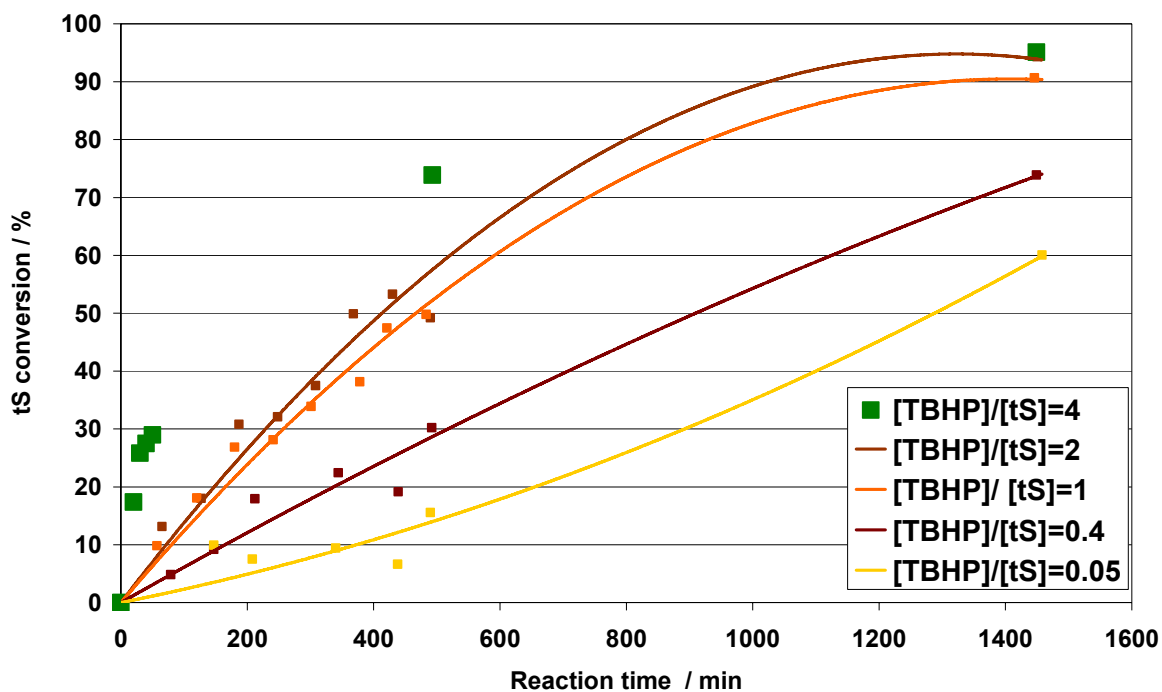
Identification and reactivity of (potential) by-products

In an attempt to determine by-products in the Au/TiO₂-catalyzed oxidation of tS with excess TBHP, we found that less than 2% of tS is converted to other HPLC-detectable products such as deoxybenzoin and benzil. *Trans*-stilbeneoxide is thus produced with 76% selectivity to tS but with more than 98% selectivity to C₁₄ partial oxidation products. Benzaldehyde is detected as a trace product (<0.1%) both with HPLC and GC-MS but nearly 20% of converted tS remains unaccounted for. We believe that this fraction is probably transformed into total oxidation products such as CO₂. Despite the presence of excess TBHP, by-products do not seem to come from over-oxidation of *trans*-stilbeneoxide. Indeed, when 1 mmol of the epoxide is let to react under the same conditions (MCH, TBHP 4 mmol, Au/TiO₂), less than 5% is converted after 24 h mainly to deoxybenzoin. On the other hand, under the same conditions, 1 mmol benzaldehyde is fully converted within 30 minutes to HPLC-undetectable products, illustrating the high oxidizability, i.e. susceptibility to autoxidation, of this compound [J. A. Howard, *Adv. Free-Radical Chem.* 1972, 4, 49.], and 1 mmol hydrobenzoin is fully converted over 30 minutes to benzil, benzoin and benzaldehyde. Benzoin and benzaldehyde will be fully transformed in the next 22 h, while benzil will be only partially converted, to HPLC-undetectable products. When 1 mmol deoxybenzoin is let to react under the same conditions, 47% is converted after 8 h and 77% is converted after 24 h to benzil (with 53 and 23% selectivity respectively) and HPLC-undetectable products.



Reaction conditions : substrate (1 mmol), TBHP (400mol%), Au/TiO₂ (Au: 10 μmol), MCH (20 mL), 80°C, 24 h.

Reactivity as a function of the TBHP/tS molar ratio



Reaction conditions: tS (1 mmol), Au/TiO₂ (Au: 10 μmol), MCH (20 mL), TBHP (0.05 to 4 mmol) 80°C, 24 h