

Gold and gold palladium catalysts for the selective epoxidation of cyclo-octene

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Introduction

Selective oxidation of hydrocarbons is of immense importance to the chemical industry. Invariably oxygen from the air is considered to be the oxidant of choice and represents the greenest choice. However, in many cases more active forms of oxygen have to be used, including non-green stoichiometric oxygen donors [1]. Propene can be efficiently epoxidised using hydrogen peroxide as an activated form of oxygen using the titanium silicalite TS-1 as catalyst [2]. Whilst hydrogen peroxide is considered to be a green oxidant, the use of oxygen in the form of air would be preferable. We have shown that graphite-supported gold nanoparticles could selectively epoxidise a range of alkenes using oxygen as oxidant if catalytic amounts of TBHP or H₂O₂ were added [3]. We showed that for the oxidation of cyclooctene using mild solvent-free conditions selectivities of over 80% to the epoxide could be achieved. We also showed that the peroxy initiator was not required to achieve selective oxidation but that lower selectivities to the epoxides were observed in their absence. In this presentation we extend our initial studies [3] to investigate graphite-supported gold palladium catalysts for the selective epoxidation of cyclooctene using oxygen together with catalytic amounts of a peroxy initiator.

Experimental

Catalysts (1 wt% total metal/carbon) were prepared using the following standard deposition precipitation method as detailed in [3]. AuPd/C catalysts were prepared in a similar manner using mixed solutions of HAuCl₄·3H₂O and PdCl₂. All reactions were performed in a stirred glass round bottom flask (50 ml) fitted with a reflux condenser and heated in an oil bath. Typically, the reactant (10 ml) was stirred at the 80 °C. Then the radical initiator (0.01 mmol) was added followed by the catalyst (0.12g) and the reactions were typically carried out for 24 hours. Analysis was carried out using a gas chromatography (Varian star 3400 CX) with DB-5 column and a flame ionization detector.

Results/Discussion

The effect of the addition of Pd to Au has been investigated and the results are shown in Table 1. It is apparent that this variable has a major effect on the observed activity with two minima in activity being observed with Au:Pd molar ratios of 1:4 and 4:1 and a distinct maximum at Au:Pd = 1:1. However, the monometallic Au and Pd catalysts showed marginally higher activity when compared with the bimetallic Au-Pd = 1:1 catalyst. The selectivity to the epoxide was unaffected by the Au:Pd molar ratio and was *ca.* 75-80% across the composition range (Table 1).

Table 1. Influence of AuPd ratio of catalysts with 1 wt. % total metal supported on graphite for *cis*-cyclooctene epoxidation.

Catalyst Composition (Au Molar %)	Conversion (%)	Epoxide Selectivity (%)
1	4.0	78.2
0.74	1.5	70.3
0.59	1.7	75.2
0.35	3.6	77.7
0.17	2.5	74.7
0.09	2.2	76.9
0	4.5	78.0

We have shown that gold and gold palladium nanoparticles supported on graphite are very effective catalysts for the epoxidation of cyclooctene using catalytic amounts of an added hydroperoxy species. The catalyst is effective under mild, solvent-free conditions using oxygen from air as the oxidant. Selectivities to the epoxide can be greater than 70%.

References.

1. R. A. Sheldon *Stud. Surf. Sci. Catal.*, **66** 33 (1991)
2. E. Klemm, E. Dietzsch, T. Schwarz, T. Kruppa, A. Lange de Oliveira, F. Becker, G. Markowz, S. Schirrmeister, R. Schütte, K. J. Caspary, F. Schüth and D. Hönicke, *Ind. Eng. Chem. Res.*, **47** 2086 (2008).
3. M.D. Hughes, Y.-J. Xu.; P. Jenkins, P. McMorn, P. Landon, D.I. Enache, A.F. Carley, G.A. Attard, G.J. Hutchings, F. King, E.H. Stitt, P. Johnston, K. Griffin and C.J. Kiely, *Nature*, **437** 1132 (2005).