

LETTERS

Tunable gold catalysts for selective hydrocarbon oxidation under mild conditions

Mathew D. Hughes¹, Yi-Jun Xu¹, Patrick Jenkins¹, Paul McMorn¹, Philip Landon¹, Dan I. Enache¹, Albert F. Carley¹, Gary A. Attard¹, Graham J. Hutchings¹, Frank King², E. Hugh Stitt², Peter Johnston³, Ken Griffin³ & Christopher J. Kiely⁴

Oxidation is an important method for the synthesis of chemical intermediates in the manufacture of high-tonnage commodities, high-value fine chemicals, agrochemicals and pharmaceuticals; but oxidations are often inefficient¹. The introduction of catalytic systems using oxygen from air is preferred for 'green' processing². Gold catalysis is now showing potential in selective redox processes³⁻⁶, particularly for alcohol oxidation⁷⁻¹⁰ and the direct synthesis of hydrogen peroxide^{11,12}. However, a major challenge that persists is the synthesis of an epoxide by the direct electrophilic addition of oxygen to an alkene¹³. Although ethene is epoxidized efficiently using molecular oxygen with silver catalysts in a large-scale industrial process¹⁴, this is unique because higher alkenes can only be effectively epoxidized using hydrogen peroxide¹⁵⁻¹⁷, hydroperoxides¹⁸ or stoichiometric oxygen donors. Here we show that nanocrystalline gold catalysts can provide tunable active catalysts for the oxidation of alkenes using air, with exceptionally high selectivity to partial oxidation products (~98%) and significant conversions. Our finding significantly extends the discovery by Haruta^{19,20} that nanocrystalline gold can epoxidize alkenes when hydrogen is used to activate the molecular oxygen; in our case, no sacrificial reductant is needed. We anticipate that our finding will initiate attempts to understand more fully the mechanism of oxygen activation at gold surfaces, which might lead to commercial exploitation of the high redox activity of gold nanocrystals.

Our initial experiments investigated the oxidation of cyclohexene using 1% Au/C with oxygen using polar solvents (for example, water) in a stirred autoclave reactor or a stirred non-pressurized glass reactor. Even under relatively mild conditions (60–80 °C, 4–24 h), only CO₂, formic acid and oxalic acid were formed with up to 100% cyclohexene conversion (Table 1), but no C₆ products were observed. Experiments involving the potential reaction of expected C₆ products with water as solvent under identical conditions indicated that had these been formed they would have been observed (conversions: cyclohexene oxide 5.6%, 2-cyclohexen-1-ol 0.2%, 2-cyclohexen-1-one 6.7%, *trans*-1,2-cyclohexanediol 0%, 1,6-hexanediol 23.0%). It is therefore clear that in polar solvents the oxidation of the alkene does not proceed via the epoxide. At this stage, we carried out a key experiment in the absence of solvent but in the presence of molecular oxygen, in a stirred autoclave reactor. In this case, 2-cyclohexen-1-one and 2-cyclohexen-1-ol were observed.





In view of these promising results, we investigated a range of apolar solvents and showed that with these media we could readily achieve selectivities for C₆ products in the range 60–80%, with yields of 10–30% (Table 1), provided that a small amount of an initiator was added at the start. In the absence of an initiator (either H₂O₂ or

t-butyl hydroperoxide, TBHP) no cyclohexene conversion was observed; however, we emphasize that only catalytic amounts of these initiators are required (Supplementary Table 1). In the absence of the gold catalyst, but in the presence of the catalytic amount of the radical initiator, again no conversion was observed, confirming that the nanocrystalline gold catalyst is necessary. The most significant finding with these solvents is that the C₆ product distribution is dependent on the solvent. The highest selectivity for cyclohexene oxide (50%) was observed with 1,2,3,5-tetramethylbenzene with 1% Au/C as catalyst (Table 1), and decreasing the Au loading decreased the yield of cyclohexene oxide (Table 2, Supplementary Table 1). Investigation of the reaction profile with reaction time (Supplementary Fig. 1) indicated this has to be carefully monitored to ensure the highest yields are achieved, as the epoxide is formed as a primary product and the other products are formed as a consequence of sequential oxidation. These findings suggest that the Au/C catalysts are tunable by careful selection of the reaction conditions. With toluene as solvent, 2-cyclohexen-1-ol and 2-cyclohexen-1-one were formed and no cyclohexene oxide was formed (Table 1). The use of *d*₅-deuteriotoluene did not lead to any discernable change in the rate of reaction, nor did we observe the incorporation of deuterium into the products. This indicates that the solvent is not involved intimately with the reaction, and the absence of a kinetic isotope effect indicates that the solvent was not acting as a sacrificial source of hydrogen in the rate-determining step, in contrast to the way in which sacrificial H₂ is required in previous studies for propene oxidation^{19,21}.

In a further set of experiments, styrene was used as substrate, using 1,2,4,5-tetramethylbenzene with 1% Au/C, and selectivities up to 97% were observed (Supplementary Table 1). To confirm the general applicability of this oxidation catalyst, experiments were conducted with *cis*-stilbene, and again selectivities for the epoxide of up to 90% were achieved (Supplementary Table 2). The observation of high selectivities for the *trans*-epoxide indicates that the two C–O bonds of the epoxide are formed sequentially with this substrate. Interestingly, we have also found recently that the same Au/C catalysts are effective for alkane oxidation; initial experiments indicate that cyclohexane can be oxidized at 70 °C to a mixture of cyclohexanone and cyclohexanol with a combined selectivity of near 100% at low conversion, and we are currently exploring these preliminary results in more detail²².

We have also investigated the modification of the Au/C catalysts using Bi. The addition of Bi is well known to affect the selectivity of supported Pt catalysts²³, but to date effective promoters have not been reported for Au catalysts. Addition of Bi markedly enhances the selectivity for C₆ oxidation products from cyclohexene (Table 2).

Table 1 | Effect of solvent on selective oxidation of cyclohexene using a 1% Au/carbon catalyst

Solvent	Conversion (%)	Product selectivity				E _{CO} C ₆ *	E _{CO} C ₆ †
							
Water	100‡	0	0	0	0	0	
Methanol	27.1§	0	0	0	0	0	
THF	5.8	0	0	0	0	0	
Hexane	26.1	Tr	Tr	Tr	0	0	
Toluene	29.1	Tr	35.1	25.1	0	60.2	
1,4-Dimethylbenzene	53.5	0	12	0	43.5	95.5	
1,2,3,5-Tetramethylbenzene	8	Tr	78.1	Tr	0	78.1	
1,2,3,5-TMB§	29.7	50.2	26.3	0	0	76.3	
1,2,4,5-TMB§/1,4-dimethylbenzene	23.1	26	42	9.1	0	77.1	
Quinoline	33.2	0	10.5	0	0	10.5	
1,4-Difluorobenzene	29.1	0	47.1	26.8	0	73.9	
Hexafluorobenzene	15.8	8.9	36.1	2.5	0	47.5	




Reaction conditions: 1% Au/C (0.22 g), C₆H₁₀ (0.032 mol), 80 °C, 24 h, solvent (20 ml). For apolar solvents, *t*-butyl hydroperoxide, TBHP (5 mol% based on C₆H₁₀) was added.
 * Total selectivity to C₆ partial oxidation products.
 † Total yield of C₆ partial oxidation products.
 ‡ Products exclusively CO₂, HCOOH and malic acid.
 § 1,6-Hexanediol.
 || 2-Tetramethylbenzene.

With the Bi-modified 0.5% Au/C catalyst, the selectivity for C₆ products was the highest observed (97.9%). The yields observed with these modified catalysts are higher than those previously reported for the oxidation of alkenes using molecular oxygen^{19,24}, where H₂ was used as a sacrificial reductant. The promotion effect was also observed with *p*-xylene as solvent (Table 2). X-ray photoelectron spectroscopic (XPS) analysis of the catalyst before and after reaction revealed a loss of Bi from the catalyst surface (Supplementary Fig. 2). The initial molar ratio of Bi:Au for the fresh sample was 0.40, which decreased to 0.25 after reaction. To rule out the possibility that the leached Bi was promoting a homogeneous reaction, the used catalyst was re-tested with a new reactant mixture—the conversion and selectivity observed were almost identical to those obtained during the initial experiment with the fresh Bi-modified Au/C catalyst (Table 2), and the Bi:Au ratio decreased further to 0.13. In both cases, the solution recovered from the catalytic reactor exhibited no catalytic activity, confirming that the Bi-modification was due to a heterogeneously catalysed reaction. Clearly, only relatively small amounts of Bi are required to enhance the selectivity of the gold catalyst. Furthermore, initial experiments using Sn, Sb and Pb as promoters (Supplementary

Table 3) show that some enhancement in activity can be observed with these dopants, and this indicates there is potential for the design of improved grid oxidation catalysts involving promoters.

We have used cyclic voltammetry to study the Bi-modified catalysts. Figure 1a shows the first voltammetric cycle of the Bi-modified 0.5% Au/C catalysts as a function of increasing bismuth coverage. The initial stages of bismuth adsorption give rise to a series of redox peaks between 0.1 and 0.6 V associated with an irreversibly adsorbed surface bismuth layer in contact with the gold surface. Such surface intermediates have already been reported for bismuth on platinum^{25,26}. The formation of the initial monolayer coverage is associated with a feature at -0.4–0.45 V (Fig. 1a). Once these states are filled, a multilayer bismuth stripping peak is observed on the positive potential sweep at 0.2 V which grows continuously with increasing bismuth loading. Figure 1b shows the cyclic voltammograms (CVs) of the modified catalyst before and after reaction. It is evident from these data that the Bi multilayer peak intensity is much reduced after the reaction, with some attenuation of the first bismuth monolayer states. This finding is in accordance with the XPS results measured pre- and post-reaction (Supplementary Fig. 2). Evidently only the adsorbed bismuth in the first monolayer is stable (and

Table 2 | Cyclohexene oxidation with molecular oxygen using unmodified and Bi-modified Au/C catalysts

Catalyst	Conversion (%)	Product selectivity			E _{CO} C ₆ *	E _{CO} C ₆ †
						
1.0% Au/C (10 ml Bi soln)	23.2	42.4	50.0	1.0	93.4	21.7
1.0% Au/C (5 ml Bi soln)	22.5	40.8	41.8	3.2	85.8	19.3
1.0% Au/C (unmodified)	29.7	50.2	26.3	Tr	76.5	22.7
0.5% Au/C (10 ml Bi soln)	24.2	49.6	44.2	4.1	97.9	23.7
0.5% Au/C (5 ml Bi soln)	19.5	48.6	41.7	3.7	94.0	18.3
0.5% Au/C (1 ml Bi soln)	20.4	41.2	42.2	4.4	87.8	17.9
0.5% Au/C (unmodified)	36.4	28.6	26.1	3.0	57.7	21.0
1.0% Au/C (unmodified)§	53.5	0	12.0	0	35.5	29.7
1.0% Au/C (10 ml Bi soln) first used	13.9	26.6	31.9	8.6	66.1	9.2
1.0% Au/C (10 ml Bi soln) re-used	18.7	21.4	34.2	7.0	62.6	11.7

* Total selectivity to C₆ partial oxidation products.
 † Total yield of C₆ partial oxidation products.
 ‡ Reaction conditions: 0.22 g catalyst, C₆H₁₀ (0.032 mol), 1,2,3,5-tetramethylbenzene (20 ml), TBHP (5 mol% based on C₆H₁₀), 80 °C, 24 h.
 § Reaction conditions: as 1 but with 1,4-dimethylbenzene as solvent instead of 1,2,3,5-tetramethylbenzene.
 || Solvent re-used with selectivity of 43.2%.

¹School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK. ²Johnson Matthey Catalysts, PO Box 1, Teeside TS23 1LR, UK. ³Johnson Matthey Catalysts, Orchard Road, Reydon, Herts SG8 5HE, UK. ⁴Center for Advanced Materials and Nanotechnology, Lehigh University, 5 East Packer Avenue, Bethlehem, Pennsylvania 18015, USA.

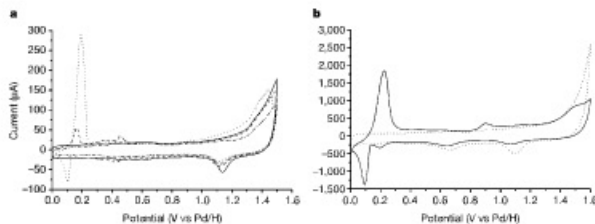


Figure 1 | Cyclic voltammograms of 0.5 wt% Au/carbon catalyst. **a**, Changes in voltammetric response as a function of irreversibly adsorbed Bi. The feature at 0.4–0.5 V is associated with Bi in the first monolayer. Multi-layers of Bi are associated with a stripping peak at 0.2 V. Bi loading (mmol): solid line, 0; dot-dashed, 0.3; dashed, 1.48; dotted, 5.92. **b**, Loss of

multi-layer Bi after reaction as demonstrated by the attenuation of the Bi stripping peak. The presence of the Bi monolayer feature suggests that some Bi remains on the catalyst. Solid line, before reaction; dotted line, after reaction.

active) under reaction conditions. However, in addition there are clearly some molecular fragments still strongly adsorbed on the surface, as indicated by the attenuation of the 'oxide' region between 1.0 and 1.6 V relative to the CV for the modified catalyst before reaction.

In a final set of experiments, we investigated the oxidation of *cis*-cyclooctene both in the presence (Supplementary Table 3) and absence (Table 3) of solvents. In particular, we wished to determine if the amount of radical initiator could be markedly reduced compared to our initial studies (Tables 1, 2 and Supplementary Tables 1, 2). We found that with *cis*-cyclooctene (Table 3) as substrate, high selectivities can be achieved even when the amount of TBHP is decreased to as low as 0.002 g per 10 ml substrate, representing a cyclooctene:TBHP molar ratio of 300 and a molar ratio of epoxide to peroxide of 32. With our non-optimized system, yields of 35 mol product per mol Au per h (1.9 mol per kg catalyst per h) can be achieved, which is higher than previous reports for propene epoxidation by Haruta and co-workers^{18,19}. We also found that, with careful tuning of catalyst and conditions, selective oxidation could be achieved without the need for the addition of solvent (Table 3), which is a major tenet of 'green' chemistry.

The high selectivity for the epoxide, particularly for cyclohexene and *cis*-cyclooctene, demonstrates that direct oxidation of the carbon = carbon double bond is occurring with this catalyst system. Commenting on the mechanism, we consider that HOOH and BuOOH act as initiators of a chain reaction, which is sustained by molecular oxygen. The observation of *trans*-stilbene oxide strongly suggests that for this substrate the two C–O bonds in the epoxide are not formed simultaneously; the formation of the *trans*-epoxide is evidence of a rotation about the C–C bond following the formation of the initial C–O bond. However, this behaviour may be restricted to

aromatic substrates, which may interact differently with the gold surface as compared with non-aromatic alkenes. Experiments at low conversion indicate that the epoxide is formed initially (Supplementary Fig. 1) and that the other reaction products observed represent the products of a sequential oxidation process that competes with non-selective oxidation. The active species and intermediates leading to the desired epoxide product, as well as the sequential products, are likely to be closely associated with the gold surface, and we consider that they do not involve very reactive O-centred radicals, as the preferred solvents contain benzylic C–H bonds and these are not attacked (as evident from the absence of deuterated products from the reaction in deuterated toluene). Such attack at the benzylic C–H would moreover be expected to lead to benzyl dimer formation, and the formation of selective oxidation products would be diminished because of inhibition of the chain process involving molecular oxygen; also, we see no dimeric products. The solvent does, however, influence the selectivity observed, possibly by controlling the rates of the consecutive oxidation steps as well as the formation of the active intermediates. The mediation of the solvent in the oxidation process could be via a weak interaction with the gold surface, particularly influencing the ease of electron transfer to, or from, the gold nanoparticle to establish the active chain carrier. Such a weak interaction has been observed with the C₆₀-mediated aggregation of gold nanoparticles by Brust et al.²³

At present, our results show the gold catalyst to have significant potential for selective epoxide formation rather than the competing allylic oxidation. This characteristic is promising, but we note that in order to have a practical impact at the commercial level, yields will need to be significantly improved (perhaps using continuous flow reactors) and the long-term stability and performance of the catalyst demonstrated. Work along these lines is now in progress.

Table 3 | *cis*-Cyclooctene oxidation with molecular oxygen in the absence of a solvent

Catalyst	TBHP (g)	Conv. (%)	Selectivity (%)				Σ _i C _i
1% Au/C	0.12	7.9	81.2	9.3	4.1	0.5	95.1
1% Au/C	0.02	7.1	79.2	6.8	3.0	0.5	89.5
1% Au/C	0.002	1.3	82.6	7.4	2.1	0.6	92.7
No catalyst	0.008	2.0	Trace	0.0	0.0	0.0	–
Graphite	0.008	2.3	Trace	0.0	0.0	0.0	–

Reaction conditions: 0.12 g catalyst, *cis*-cyclooctene (10 ml), 0.064 mol, 80 °C, 24 h. Conv., conversion.

METHODS

Preparation of supported gold catalysts. 1 wt% gold catalysts supported on carbon were prepared as follows. The carbon support (graphite, Johnson Matthey, 113.2 g) was stirred in deionized water (1 l) for 15 min. An aqueous solution of chloroauric acid (41.94% Au, Johnson Matthey, 2.38 g in 70 ml H₂O) was added slowly dropwise over a period of 30 min, after addition, the slurry was then refluxed for 40 min and following cooling, formaldehyde was added as reducing agent. The catalyst was recovered by filtration and washed until the washings contained no chloride. The catalyst was dried for 16 h at 106 °C. This method was also used to prepare 0.25 wt% Au/C and 0.5 wt% Au/C catalyst using smaller amounts of chloroauric acid. Analysis by transmission electron microscopy of the catalyst showed they all comprised Au nanocrystals with a broad size range (~3–50 nm), with a mean particle diameter of ~25 nm of multiply twinned nanocrystals (Supplementary Fig. 3), and the particle density varied with gold loading in the expected manner.

Catalyst testing. Reactions in a stirred autoclave reactor were carried out by suspending the catalyst (0.22 g) in a solution of alkene (0.012 mol) in solvent (20 ml) in a Parr autoclave (50 ml). The initiator was added as required. The autoclave was pressurized to the required pressure with oxygen (43 p.s.i.) and heated to the required temperature (50–80 °C). The reaction mixture was stirred (1,500 r.p.m.) for 4 h. Reactions in a stirred glass reactor were carried out using equal quantities of catalyst, alkene and solvent as above, but always in the presence of radical initiator (5 mol% alkene) in a 50 ml round-bottomed flask with reflux condenser connected. Experiments were carried out in an oil bath heated to 60–80 °C, with reaction mixtures stirred for 4–24 h.

Analysis of products in reactions using cyclohexene or *cis*-cyclooctene as substrate were carried out using a gas chromatograph (Varian Star 3400 CX) fitted with a DB-5 column and a flame ionization detector (FID). Samples were taken at the end of reactions; 200 µl of sample was added to 20 µl of standard (3-pentanone, 98%, Aldrich) and 0.5 µl of this sample was analysed. When styrene or *cis*-stilbene was used as substrate, analysis was carried out using high-pressure liquid chromatography with an ultraviolet detector. Reactant and product were separated using an APEX ODS 5 µm column (Jones Chromatography). The eluent was a 70:30 or 90:10 mixture of CH₂Cl₂:H₂O for styrene and *cis*-stilbene, respectively. Samples were taken at the end of the reactions; 20 µl of sample was diluted in 10 ml of standard solution (biphenyl in CH₂Cl₂, 1 mM solution) and 50 µl of this solution was analysed.

Preparation of Bi-doped catalyst. Bi(NO₃)₃ (0.0359 g) was dissolved in ultrapure water (50 ml) and stirred for 2 h. The required amount to obtain a particular surface concentration (referred to as 'ml Bi soln' in Table 2) was transferred to an evaporating basin containing AuCl₃ (1 g), and stirred for 3 h, after which the stirring was then stopped and the solution was allowed to evaporate overnight. The catalyst was washed with 20 ml of ultrapure water, which was filtered off under vacuum. The catalyst was finally washed with ultrapure water (3 × 20 ml) and dried (100 °C, 1 h).

XPS measurements. Spectra were recorded with an ESCALAB 220 spectrometer using an AlKα source and an analyser pass energy of 100 eV.

Cyclic voltammetry measurements. The electrochemical cell and cyclic voltammetry methods were carried out as reported previously¹¹.

Received 6 May; accepted 2 September 2005.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements We acknowledge the support of the Engineering and Physical Sciences Research Council (EPSRC) of the UK, Johnson Matthey plc (project ATHENA) and the European Union (project AURICAT). We also thank D. Bethell for discussions on the reaction mechanism.

Author Contributions M.D.H. and Y.-J. X. prepared and tested the catalysts under the supervision of P.L., D.J.E. and P.M. C.J.K. made the TEM measurements and A.F.C. the XPS measurements. P. Jenkins prepared the Bi-doped catalysts and made the CV measurements under the supervision of G.A.A. G.J.H. directed the research and wrote the paper. E.H.S., F.K., P. Johnson and K.G. provided discussions and advice on catalyst synthesis.

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