Solvent-free selective epoxidation of cyclooctene using supported gold catalysts

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Received 24th December 2008, Accepted 14th April 2009
First published as an Advance Article on the web 28th April 2009
DOI: 10.1039/b823286p

Oxidation is one of the major pathways for the synthesis of chemical intermediates. The epoxidation of alkenes by the electrophilic addition of oxygen to a carbon–carbon double bond remains one of the most significant challenges in oxidation. Of key importance is the use of oxygen as the oxidant, but in many cases more reactive, and less green, sources of oxygen are used. We report the solvent-free epoxidation of cyclooctene with air using supported gold catalysts with small amounts of a hydroperoxide. We identify the appropriate reaction conditions to maximize the selectivity of the epoxide. In the absence of a hydroperoxide initiator, using air at atmospheric pressure, no reaction is observed. Choice of the peroxide initiator is crucial and in the absence of a catalyst or a support the reaction of the alkene can be observed with di-*t*-butyl peroxide and *t*-butyl hydroperoxide (TBHP) only when high concentrations are used at high temperatures ≥ 80 °C, and TBHP was found to be the more selective to epoxide formation. In contrast, cumene hydroperoxide was highly reactive under all conditions evaluated. TBHP was selected for more detailed study. Use of graphite as a support was found to give the best combination of selectivity and conversion. In general the selectivity to the epoxide increased with reaction temperature from 60–80 °C and was highest at 80 °C. Other carbon supports, *e.g.* activated carbon, were found to be less effective. TiO_2- and SiO_2-supported Au catalysts were also selective for the epoxidation reaction and the general order of activity was: graphite > SiO_2 > TiO_2. The major by-product is the allylic alcohol and the reaction pathways to the epoxides and the allylic alcohol are discussed. Preparation of catalysts using a sol-immobilisation method significantly enhanced catalyst activity with retention of selectivity to the epoxide.

Introduction

The synthesis of chemical intermediates using selective oxidation includes reactions of major significance in the chemical processing 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 such as permanganate and chromates.[1] One of the greatest challenges in selective oxidation chemistry is the electrophilic addition of oxygen to an alkene to form an epoxide. For the simplest case, ethene, this is a reaction that can be carried out commercially on a very large scale and with very high specificity using oxygen with a supported silver catalyst.[2] However, even in this case non-green additives, *i.e.* chloro-compounds and NO_x have to be added to limit non-selective oxidation. At present, the epoxidation of higher alkenes with oxygen has not proved to be successful on a commercial basis, and remains the subject of great research interest. Propene can be efficiently epoxidised using hydrogen peroxide as an activated form of oxygen using the titanium silicalite TS-1 as catalyst.[3] Whilst hydrogen peroxide is considered to be a green oxidant, the use of oxygen in the form of air would be preferable.

Recently, Rossi *et al.*[4] have reviewed the key aspects concerning selective oxidation reactions, and, in particular, the recent advances that have been made using supported gold catalysts. Haruta *et al.* were the first to demonstrate the potential of supported gold catalysts for the epoxidation of propene with oxygen in the presence of H_2 as a sacrificial reductant that permits the activation of O_2 at relatively low temperatures.[5,6] Haruta *et al.* found that Au/TiO_2, prepared using deposition precipitation, was selective for propene epoxidation and the catalysis was associated with an intimate contact between hemispherical gold nano-crystals (2–5 nm in diameter) and the TiO_2 support. Initial selectivities were low but promising and improvements were made by using different titanium-containing supports including TS-1, Ti-zeolite β, Ti-MCM-41 and Ti-MCM-48.[7–20] A key issue that remains with this experimental approach is the selectivity based on H_2, which can be very low. Haruta *et al.* have tried to address the issue of poor H_2 utilisation and have shown that, using mesoporous titanosilicates as a support,[21] improved H_2 consumption was attained together

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with high propene oxide yields (93 g h^{-1} kg_{cat}^{-1} at 160 °C). Propene oxide selectivities of >90% were observed at propene conversions of *ca.* 7%, together with a hydrogen efficiency of 40%.[17] However, this H_2 efficiency is far lower that than currently achievable (*ca.* ≥95%) with indirect H_2O_2 synthesis[22] and so this approach cannot compete with the TS-1 catalysed epoxidation of propene using H_2O_2.[3]

Choudhary *et al.*,[23–27] and subsequently Yin *et al.*[28] have shown that gold nanoparticles supported on a range of oxides are active for the epoxidation of styrene using tertiary butylhydroperoxide (TBHP) in greater than stoichiometric amounts. Selectivities to styrene oxide of *ca.* 50% are readily achieved using this approach.

In our initial studies we showed that graphite-supported gold nanoparticles could selectively epoxidise a range of alkenes using oxygen as an oxidant if catalytic amounts of TBHP or H_2O_2 were added.[29] 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 addition we indicated that when the peroxy initiator was present in the absence of the catalyst, or in the presence of the graphite support some reactivity of the alkene was observed, but that it was not selective to the epoxide. This effect is presumably due to molecular oxygen being a di-radical in its ground state and so can participate in radical reactions without the need for activation at the catalyst surface. Subsequently, Caps *et al.*[30–32] have studied this experimental approach in detail for the oxidation of stilbene, for which they have proposed a radical mechanism. This mechanism is consistent with the initial observation that catalytic amounts of a peroxy species were required to observe selective epoxidation.[29] Deng and Friend[33] showed using model studies with a Au (111) surface that styrene could be directly epoxidised with oxygen giving 53% styrene oxide. Most recently, Lambert *et al.*[34] have shown that very small Au_{55} nanocrystals supported on carbon are active catalysts for styrene oxidation with oxygen but only minor selectivity to the epoxides was observed and the major product was benzaldehyde. In this paper we extend our initial studies[29] to determine the reaction conditions that are optimal for the selective epoxidation of cyclooctene using oxygen together with catalytic amounts of a peroxy initiator.

Experimental

Catalyst preparation

Unless otherwise stated, catalysts (1 wt% Au/support) were prepared using the following standard deposition precipitation method (denoted DP). A solution of $HAuCl_4.3H_2O$ (5 ml, 2 g in 100 ml distilled water) was diluted with water (45 ml). Aqueous sodium carbonate was added with stirring until pH = 10 was attained. This solution was then added, with continuous stirring, to a slurry of the support in water (4.95 g in water 50 ml). The mixture was stirred for 1 h at 20 °C, maintaining the pH at 10. The mixture was heated to 70 °C and formaldehyde was added as a reducing agent. The solid was recovered by filtration and washed with water (1 l) until the washings were found to be chloride free. The catalyst was dried (110 °C, 16 h) prior to use.

Two other preparation methods were also evaluated. For the impregnation method the support was suspended in distilled water (4.95 g in 100 ml) for 15 min. A solution of $HAuCl_4.3H_2O$ (5 ml, 2 g in 100 ml distilled water) was added to the slurry slowly dropwise over 30 min. The mixture was stirred under reflux for 30 min; after cooling, formaldehyde was added as a reducing agent. The solid was recovered by filtration and washed with water (1 l) until the washings were found to be chloride free. The catalyst was dried (110 °C, 16 h) prior to use.

For the sol-immobilization method an aqueous solution of $HAuCl_4.3H_2O$ was prepared. Polyvinylalcohol (PVA) (1 wt% solution, Aldrich, MW = 10 000, 80% hydrolyzed) was added (PVA/Au (by wt) = 0.65); a freshly prepared solution of $NaBH_4$ (0.1 M, Aldrich, $NaBH_4$/Au (mol/mol) = 5) was then added to form a dark-brown sol. After 30 min, the colloid that had been generated was immobilized by adding the support (acidified at pH 1 by sulfuric acid) with stirring. The amount of support material required was calculated so as to have a total final metal loading of 1 wt%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (1 l). The catalyst was dried (110 °C, 16 h) prior to use.

Catalyst testing and characterisation

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, *cis*-cyclooctene (10 ml) was stirred at the desired temperature. Then the radical initiator was added followed by the catalyst (0.12 g) and the reactions were typically carried out for 24 h. Analysis was carried out using a gas chromatography (Varian star 3400 CX) with DB-5 column and a flame ionization detector. As conversions were low and the reaction was carried out using solvent-free conditions, alkene conversion was determined on the basis of the concentrations of the observed products, and no CO_x was observed. Experiments were carried out in triplicate and the experimental variation was determined to be ≤ 1%, and mass balances were typically 100% within experimental error. Further experiments were conducted to determine the amount of cyclooctene hydroperoxides since these products are not detected by the standard gas chromatography analysis. Standard reactions (24 h and 72 h) using 1% Au/graphite prepared by deposition precipitation were carried out and after completion the reaction mixture was filtered and then divided into two aliquots; the first aliquot was stirred for 1 h with excess triphenylphosphine (PPh_3) in air at room temperature, the second aliquot was not treated with PPh_3. All samples were analysed by GC (FID, DB-wax column, Varian 3400). ^1H NMR spectroscopy (Bruker DPX 400 spectrometer) was used to confirm the presence of cyclooct-2-enyl hydroperoxide.

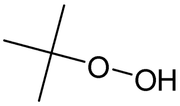
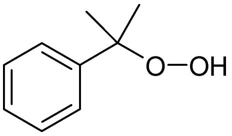
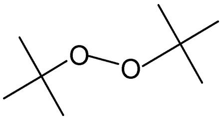
Samples for examination by transmission electron microscopy (TEM) were prepared by dispersing the catalyst powder in high purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon film supported by a lacey carbon TEM grid. Samples were then subjected to bright field diffraction contrast imaging experiments in order to determine particle size distributions. The instrument used for this analysis was a JEOL 2000FX TEM operating at 200 kV.

Results and discussion

Reaction in the absence of catalyst

Since we are seeking to oxidise cyclooctene with molecular oxygen it is important we determine the reactions that occur in the absence of catalyst. As we noted in our earlier research[29] we observed some non-selective conversion of cyclooctene in the absence of catalyst. Since molecular oxygen is a diradical in its ground state it can participate in radical reactions in the absence of a catalyst, especially in the presence of radical initiators. These non-catalysed reactions can often lead to lower selectivities being achieved and can, in the extreme cases, mask any catalytic reaction that may be occurring. Hence, we need to determine reaction conditions where no reaction occurs either in the absence of the catalyst or the undoped support. The reactivity of the supports will be considered alongside the data for the catalysts in subsequent sections. In the absence of a peroxy initiator and in the absence of a catalyst no reaction was observed over the temperature range we have studied in this paper. We then investigated the effect of the peroxy species. Three peroxy initiators were investigated at 80 °C with alkene/peroxy mol ratios between 74.6 and 748, and the results are shown in Table 1. Cumene hydroperoxide (CHP) is active at all the concentrations evaluated and gave the epoxide with *ca.* 64–70% selectivity. TBHP and di-*t*-butyl peroxide (DTBP) were inactive at the lowest concentration evaluated, but were active at higher concentrations, but TBHP was more selective. Of the peroxides examined, CHP has the lowest reported[35] activation energy for homolysis of the O–O bond (126 kJ mol^{-1} in benzene solvent) and is probably the most susceptible to radical-induced decomposition. DTBP is reported to have a shorter half-life at low concentrations, although it has a higher E_a = 162 kJ mol^{-1}. TBHP homolyses the least rapidly of the three (E_a = 134 kJ mol^{-1}). All three have 10 h half-lives at temperatures above that of the present experiments (TBHP 170 °C, CHP 135 °C, DTBP 125 °C), suggesting that, at least in part, the uncatalysed reaction may not require simple homolysis for initiation. TBHP was selected for more detailed evaluation (Table 2). At low concentrations of TBHP, even at 80 °C, no reaction is observed and consequently a concentration of 1.03×10^{-4} mol l^{-1} TBHP was selected as the standard concentration for the subsequent studies. At higher concentrations a trace of reaction was observed at 60 °C, but no epoxide was formed, and the reactivity and selectivity to the epoxides increased with reaction temperature and with increasing initial peroxide concentration.

Table 1 Reaction of cyclooctene using different peroxide initiators

Peroxy initiator/mol		Blank reaction[a]		1% Au/graphite[b]	
		Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
	0.1032×10^{-2}	0.68	66.8	8.5	78.7
	0.0516×10^{-2}	0.12	36.9	6.6	78.7
	0.0103×10^{-2}	0.02	0	4.0	78.2
	0.1032×10^{-2}	7.0	68.9	8.1	63.9
	0.0516×10^{-2}	3.92	69.8	5.8	73.2
	0.0103×10^{-2}	1.3	64.1	2.9	79.3
	0.1032×10^{-2}	0.91	36.9	0.53	3.9
	0.0516×10^{-2}	0.27	8.0	0.26	0
	0.0103×10^{-2}	0.04	0	0.04	0

[a] Reaction in the absence of catalyst: cyclooctene (10 ml, 0.077 mol), 80 °C, 24 h, atmospheric pressure. [b] Reaction using 1% Au/graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

Table 2 Effect of reaction of cyclooctene with TBHP in the absence of catalyst[a]

	60 °C		70 °C		80 °C	
TBHP/Mol × 10^{-2}	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
0.103	0.04	0	0.11	16.1	0.68	66.8
0.083	0.03	0	0.05	0	0.17	59.5
0.052	0.03	0	0.04	0	0.12	36.9
0.031	0.03	0	0.04	0	0.04	58.3
0.026	0.03	0	0.04	0	0.09	4.3
0.012	0	0	0.02	0	0.04	0
0.0103	0	0	0.02	0	0.04	0

[a] Reaction conditions: cyclooctene (10 ml, 0.077 mol), 24 h, atmospheric pressure.

Table 3 Reaction using graphite as a support

		Graphite[a]		1% Au/graphite[b]	
TBHP/mol × 10^{-2}	Temperature/°C	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
0.1032	60	0.40	58.4	1.9	68.3
0.0516		0.16	30.7	1.6	64.2
0.0103		0.01	0.01	0.6	63.9
0.1032	70	0.90	63.2	3.9	71.4
0.0516		0.36	64.5	2.6	72.3
0.0103		0.04	86.4	1.9	72.3
0.1032	80	4.46	74.2	8.5	78.7
0.0516		1.79	62.6	6.6	78.7
0.0103		0.1	42.6	4.0	78.2
0.1032	100	12.91	79.1	12.9	73.2
0.0516		9.91	78.8	11.1	76.1
0.0103		3.3	80.5	10.9	79.7
0.1032	120	16.41	77.1	13.4	71.4
0.0516		14.21	77.7	14.0	72.8
0.0103		13.88	77.3	14.6	73.6

[a] Reaction using graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure. [b] Reaction using 1% Au/graphite: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

Oxidation of cyclooctene using carbon-supported catalysts

Graphite. In our initial studies[29] we showed that 1 wt% Au/graphite was a very effective catalyst for the oxidation of cyclooctene at 80 °C. In addition, we showed that graphite also displayed some non-selective oxidation activity at this temperature. In view of this we now extend these studies to compare the catalytic and blank reactions to determine the optimal reaction conditions. We initially prepared the catalyst using an impregnation method coupled with a reduction step using formaldehyde. In this study we have used a modified technique designed by Prati and Rossi[36] to prepare the Au/graphite catalyst as they have shown the method to provide a robust recyclable catalyst for alcohol oxidation.

Our initial experiments were carried out to study the effect of different concentrations of TBHP using graphite and 1 wt% Au/graphite (Table 3). As noted by us previously,[29] the graphite support does show some catalytic activity, particularly at higher temperatures and higher concentrations of TBHP. Indeed at reaction temperatures ≥100 °C the support is as active as the gold catalyst (table 3) and shows the highest selectivity to the epoxide. However, at lower temperatures the 1 wt% Au/graphite is significantly more active and in the presence of gold the selectivity to the epoxides is greatly enhanced and, importantly, is independent of the TBHP concentration.

The effect of reaction time for the reactivity of 1 wt% Au/graphite is compared with the reactivity of the graphite support in Fig. 1 using the optimal conditions for epoxide formation that give a compromise between rate of reaction and selectivity (1.03×10^{-4} mol TBHP, 80 °C). Under these conditions the contribution to the reaction observed from the support or the non-catalysed reaction is minimized. The selectivity to the epoxide remains steady at *ca.* 80% throughout the reaction time and the major by-products are the allylic alcohol and cyclooctenone, which are formed throughout in approximately 2 : 1 molar ratio, which is consistent with our earlier study.[29] In addition traces of the dione are produced as we also observed in our earlier study.[29] Under these reaction conditions, after 24 h we observe a turnover frequency of 25 mol epoxide mol Au^{-1} h^{-1} which is comparable to that reported previously for the epoxidation of propene using Au/TiO_2 catalysts when H_2 is used as sacrificial reductant.[7–20] The turnover frequency for the TBHP is *ca.* 35. This is in contrast to earlier studies which used greater than stoichiometric amounts of TBHP which also gave lower epoxide selectivity.[23–28]

Activated carbon. We examined the reactivity of a range of different activated carbon supports manufactured from wood, coconut shell and coal. Activated carbons are widely used as supports and hence we contrasted their reactivity with that of graphite and the results are shown in Table 4 and 5. In general the activated carbons prepared from coal were the most selective for epoxide formation (Table 4). However, the addition of gold was not observed to enhance the catalytic activity under any conditions evaluated (Table 5) and in some cases the addition of gold led to a decreased activity (Table 4), although the presence of Au did lead to slightly higher epoxide selectivity. For the most active activated carbon support derived from wood (Aldrich G60) epoxidation of cyclooctene was observed at temperatures as low as 40 °C even with very low concentrations of TBHP. The heterogeneous nature of the functional groups present on the surface of the activated carbons provide a diverse set of sites that are capable of initiating the reaction with TBHP. Decoration of these sites by nanoparticles of gold can block this reactivity. Hence for the epoxidation of alkenes graphite is the preferred carbon support.

Oxidation of cyclooctene using oxide-supported catalysts

The use of TiO_2 and SiO_2 as supports has also been investigated and the results for the effect of reaction temperature and concentration of TBHP are shown in Tables 6 and 7. Both oxide supports, in the absence of gold, show very limited activity with low concentrations of TBHP. The TiO_2-supported gold catalysts display higher activity and epoxide selectivity than SiO_2-supported catalysts which is consistent with earlier

Table 4 Reaction using a range of activated carbon as a support

Carbon	Source	Conversion[a] (%)	Selectivity (%)
Aldrich G60	Wood	1.6	69.3
1 wt% Au/Aldrich G60	Wood	1.6	69.3
Norit Rox 0.8	Wood	0.1	59.4
1 wt% Au/Norit Rox 0.8	Wood	0.06	65.5
Norit GCN-3070	Coconut shell	0.01	—
1 wt%Au/Norit GCN-3070	Coconut shell	0.01	32.9
Norit PDKA 10 × 30	Coal	0.6	82.7
1 wt%Au/Norit PDKA 10 × 30	Coal	0.2	67.6

[a] Reaction conditions : cyclooctene (10 ml, 0.077 mol), catalyst/carbon (0.12 g), 80 °C, 24 h, atmospheric pressure, TBHP (0.1 mmol).

Table 5 Reaction using activated carbon as a support

		Activated carbon[a]		1% Au/activated carbon[b]	
TBHP/mol × 10^{-2}	Temperature/°C	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
0.0103	50	0.4	62.4	0.4	58.7
0.0516	60	1.7	63.6	1.9	63.4
0.0258		1.5	63.2	1.5	66.4
0.0103		1.2	66.9	0.8	58.8
0.0516	70	2.9	63.5	2.9	70.5

[a] Reaction using activated carbon: cyclooctene (10 ml, 0.077 mol), carbon (0.12 g), 80 °C, 24 h, atmospheric pressure. [b] Reaction using 1% Au/activated carbon: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

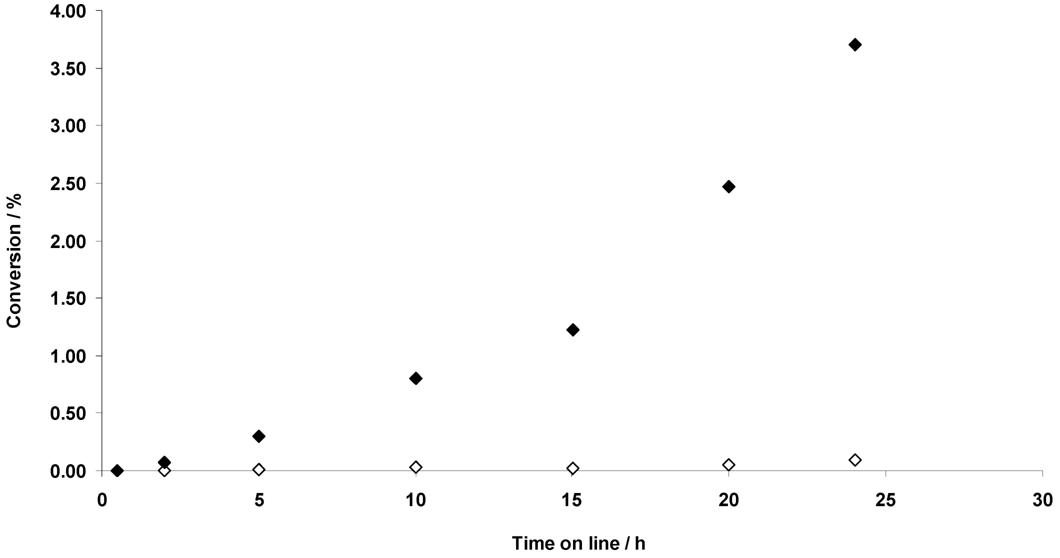


Fig. 1 Effect of reaction time for the conversion of cyclooctene using 1% Au/graphite (closed symbol) and graphite (open symbol). Reaction conditions: catalyst/graphite 0.12 g, cyclooctene (10 ml, 0.077 mol), TBHP 0.01 ml, temperature 80 °C, atmospheric pressure.

observations with propene epoxidation.[7–23] In a further set of experiments we investigated the use of Al_2O_3 as a support which under standard reaction conditions (cyclooctene (0.077 mol), catalyst/support (0.12 g), 80 °C, 24 h, TBHP (0.1 mmol)) gave no conversion for the support, and with 1 wt% Au only gave 0.5% conversion, and the epoxide selectivity was >90%. However, in general, the oxide supports are less effective than graphite as a support for the epoxidation of cyclooctene.

Effect of the preparation method

In a final set of experiments we prepared 1 wt% Au graphite-catalysts using three different preparation methods (Table 8). In our earlier studies we used a formaldehyde reduction method using an impregnation procedure (designated impregnation).[29] In this paper we have used a variant on this procedure in which the gold was deposited onto the support by precipitation with aqueous sodium carbonate prior to addition of the support[35] (designated DP). In addition, we have recently shown that a sol-immobilisation method[37] can be very effective for the preparation of active gold catalysts. We have now compared these three methods for the epoxidation of cyclooctene. The three 1 wt% Au/graphite catalysts have been characterized using transmission electron microscopy and the micrographs and particle size distributions are given in Fig. 2. The particle size

Table 6 Reaction of cyclooctene with TiO_2 and TiO_2-supported catalysts

		TiO_2[a]		1% Au/TiO_2[b]	
TBHP/mol $\times 10^{-2}$	Temperature/°C	Conversion	Selectivity	Conversion	Selectivity
0.1032	60	1.1	65.7	1.8	67.7
0.0516		0.8	71.2	1.3	69.1
0.0103		0.3	85.6	0.9	71.6
0.1032	70	1.7	78.7	3.8	73.4
0.0516		1	77.0	3.0	64.9
0.0103		0.13	75.2	2.0	75.4
0.1032	80	4.96	80.4	8.8	77.7
0.0516		2.29	83.1	6.3	79.0
0.0103		0.07	78.8	0.3	78.3

[a] Reaction using TiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure. [b] Reaction using 1% Au/TiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

Table 7 Reaction of cyclooctene with SiO_2 and SiO_2-supported catalysts

		SiO_2[a]		1% Au/SiO_2[b]	
TBHP/mol $\times 10^{-2}$	Temperature/°C	Conversion	Selectivity	Conversion	Selectivity
0.1032	60	0.4	64.5	0.9	64.8
0.0516		0.4	67.8	0.7	66.7
0.0103		0.1	0.1	0.4	67.8
0.1032	70	0.9	70.8	1.8	80.3
0.0516		0.3	74.5	1.3	81.1
0.0103		0.1	75.4	0.9	75.0
0.1032	80	4.5	74.5	6.0	80.2
0.0516		2.0	77.1	4.0	83.8
0.0103		0.1	0.1	2.7	79.7

[a] Reaction using SiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure. [b] Reaction using 1% Au/SiO_2: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

Table 8 Reaction of cyclooctene with graphite- and TiO_2-supported catalysts prepared using different methods

	1% Au/graphite[a]	
Preparation method	Conversion	Selectivity
Deposition precipitation	4.0	78.2
Sol-immobilization	7.7	81.5
Impregnation	4.2	71.3

[a] Reaction condition: cyclooctene (10 ml, 0.077 mol), catalyst (0.12 g), 80 °C, 24 h, atmospheric pressure.

distributions for the impregnation and deposition precipitation methods are very similar, with most Au nanoparticles being in the 10–30 nm size range. This is in agreement with the activity of these two catalysts (Table 8) which are also very similar. In contrast, the particle size distribution of the 1 wt% Au/graphite catalyst prepared using the sol-immobilisation method shows this comprises much smaller particles, with most particles being 2–3 nm in diameter. This catalyst is more active for the epoxidation of cyclooctene (Table 8). With the 1 wt% Au/graphite catalyst prepared by sol-immobilisation, using our standard reaction conditions (1.03×10^{-4} mol TBHP, 80 °C), after 24 h we observe a turnover frequency of 48 mol epoxide mol Au^{-1} h^{-1} which is higher than that reported previously for the epoxidation of propene[7–23] and the turnover frequency for the TBHP is enhanced to *ca.* 67. These results show that by careful investigation of catalyst design further significant improvements in selectivity can be expected.

Comments on the reaction mechanism

With respect to the peroxy initiators we have selected for study, TBHP is the only peroxide that shows strong enhancement in the presence of Au/graphite catalyst. CHP is susceptible to radical induced decomposition and its epoxidation performance is improved only slightly by the Au catalyst. DTBP shows no enhancement by the Au, suggesting that *t*-Bu-O radicals are not significant in the catalytic reaction pathway. We suggest that the uncatalysed epoxidation may not be a conventional radical chain reaction but seems to be a higher temperature analogue of epoxidation by peroxycarboxylic acids. In particular, we observe that the selectivity to epoxide increases with TBHP concentration in the uncatalysed reaction but is constant in the catalysed process. If the uncatalysed peroxide were generating a reactive free radical species capable in part of O-transfer to the alkene, its partitioning between the various pathways should be roughly independent of peroxide concentration. In particular, the competition between epoxidation and allylic oxidation should be independent of TBHP concentration. This is not observed (Table 3) and we consider this to suggest that there is a direct O-transfer between the hydroperoxide and the alkene at temperatures below that necessary for homolysis of the O–O linkage.

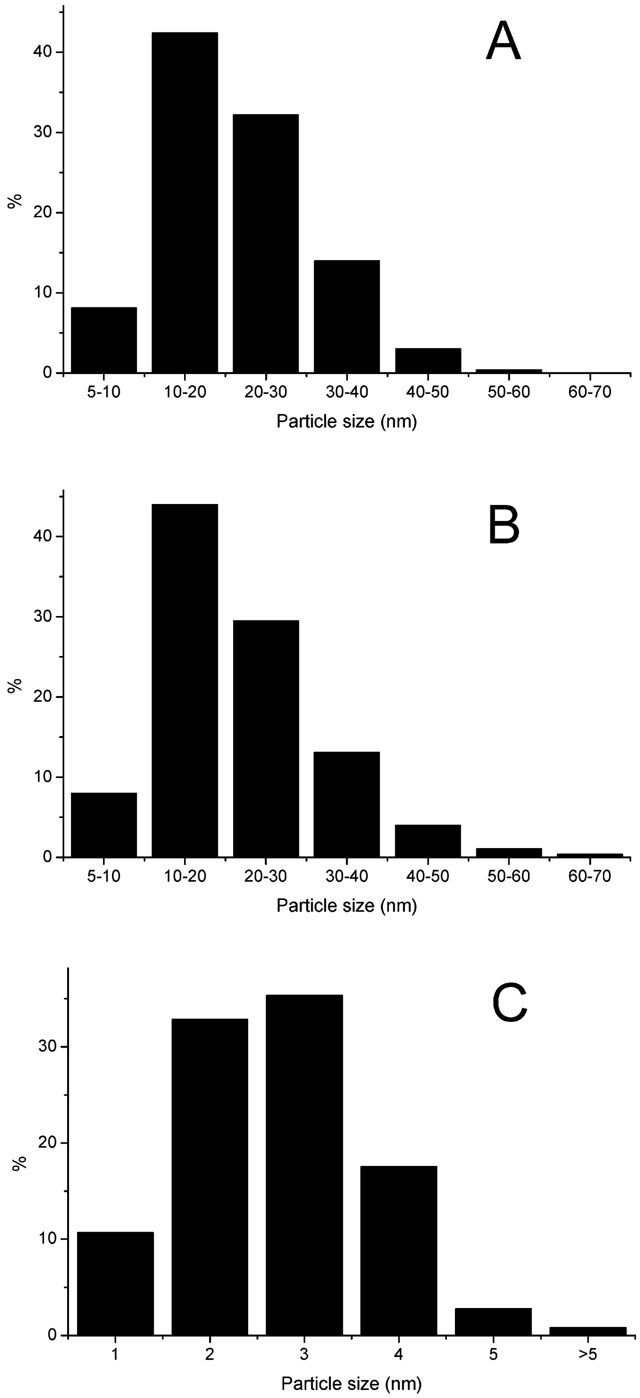


Fig. 2 Particle size distribution data, as determined from bright field TEM micrographs for the 1 wt% Au/graphite catalysts prepared by (A) impregnation, (B) deposition precipitation and (E) sol-immobilisation.

With Au, hydroperoxides seem necessary and that suggests to us that a surface O-species may be produced that is capable of O-transfer, either to an adsorbed alkene or an alkene in the liquid phase. With the Au-catalysed reaction we observe that the ratio between the epoxide and the byproducts remain constant as the conversion increases. This constant product ratio might come from parallel pathways but could equally arise by partitioning of an intermediate species on the catalyst surface that is partitioned between attacking cyclo-octene at its double bond or its two allylic positions. Abstraction of H from the allylic positions would allow formation of the allylic hydroperoxide, by incorporating O_2, which could either eliminate water to give the enone or get involved in the catalytic cycle, in the same role as TBHP, to produce more of the O-transfer species. After O-transfer to the alkene, the surface species would have to be reconstituted either directly from gaseous O_2 or indirectly *via* formation of the intermediate allylic hydroperoxide.

Analyses have been carried out looking specifically for the presence of cyclo-oct-2-enyl hydroperoxide in reaction mixtures generated under standard conditions using 1% Au/graphite as a catalyst. Samples for analysis taken from the reaction mixture were divided into two; one half was analysed directly and the other was treated with triphenylphosphine, which is expected to convert any hydroperoxides quantitatively into the corresponding alcohol and triphenylphosphine oxide. After phosphine treatment, the glc results should thus show an increased level of cyclo-oct-2-enol. The amount of the related cyclo-oct-2-enone, the likeliest major decomposition product of the hydroperoxide when injected into the gas chromatograph, should show a comparable decrease. Representative results are shown in Table 9, where it can be seen that there is indeed a small increase in the selectivity to the allylic alcohol and decrease in the enone selectivity, suggesting the presence of fairly low levels of the allylic hydroperoxide, as expected if it is formed and then consumed in epoxidation. The results in Table 9 show that the increase in the allylic alcohol selectivity is greater than the decrease in the enone selectivity, a situation for which we have as yet no satisfactory explanation. Direct confirmation of the presence of the hydroperoxide was obtained using ^{1}H NMR spectroscopy. Examination of the spectrum of product samples, taken after 24 and 72 h reaction and not treated with triphenylphosphine, showed two multiplets (dt) centred at δ4.63 and 4.93, the former arising from the proton on the allylic carbon atom bearing the hydroxyl group in authentic cyclo-oct-2-enol and the other assigned to the corresponding proton in the hydroperoxide. After phosphine treatment, the signal at δ4.93 had disappeared.

Although we have demonstrated the presence of the allylic hydroperoxide in the reaction mixtures, it seems unlikely that it

Table 9 Effect of the addition of triphenylphosphine (PPh_3) on allylic alcohol selectivity in cyclooctene epoxidation

		Selectivity Without PPh_3			Selectivity With PPh_3 in air			Selectivity With PPh_3 in N_2		
Reaction time/h	Conversion (%)	Epoxide	Alcohol	Ketone	Epoxide	Alcohol	Ketone	Epoxide	Alcohol	Ketone
24	4.9	74.3	8.3	6.4	71.4	13.0	4.2	71.0	13.0	4.2
72	20.3	77.3	5.4	5.4	75.6	7.3	4.8	76.6	7.0	4.7

Reaction conditions: cyclooctene (10 ml), TBHP (0.01 ml), 80 °C, 1% Au/graphite (0.12 g) atmospheric pressure.

can play a major role in catalysis of epoxidation, since it seems likely that its role will be to transfer only one of its O-atoms, leaving a molecule of the allylic alcohol. The very high epoxide selectivities attainable in these systems would seem to preclude a catalytic cycle involving the hydroperoxide. On the basis of the present data, we can only speculate about the detailed course of the reaction. We plan further experimental studies to test these mechanistic proposals.

Conclusions

We have shown that gold supported on graphite is a very promising catalyst for the epoxidation of cylcooctene 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 80% and we consider that with appropriate catalyst design further enhancements inactivity and selectivity can be expected.

Acknowledgements

This work formed part of an EPSRC funded project and we thank them for funding this research. We also thank King Abdul Aziz University (Saudi Arabia Government) for financial support. We thank a referee for helpful comments.

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