Partial oxidations with NO_2 catalyzed by large gold particles

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Large gold particles catalyze alkene epoxidation by NO_2 under mild conditions, oxygen adatoms being the likely active species.

In 1987 Haruta *et al.* reported the striking and unexpected discovery that small particles of Au deposited on semiconducting transition-metal oxides were active for the catalytic oxidation of CO.[1] Subsequently, they showed that very small Au particles supported on TiO_2 were effective catalysts for a much more demanding reaction—the epoxidation of propene by dioxygen (O_2).[2] Their key conclusion was that Au particle size is a critically important parameter in determining catalytic behaviour. Later fundamental work by Goodman *et al.* confirmed this conclusion and showed that the Au size threshold effect is associated with a metal–insulator transition[3] implying that the catalytic properties of nanoscopic Au (particles smaller than ~ 3.5 nm) are necessarily intrinsically different from those of larger Au particles and extended Au surfaces. These developments have stimulated much subsequent work focussed on the special properties of nanoscopic gold.

Against this background, the catalytic efficacy of extended Au surfaces and large Au particles has been somewhat overshadowed, even though from the 1970s, if not earlier, it has been known that Au catalysts are active for the partial oxidation of propene to acrolein[4] and for oxidative dehydrogenation reactions, such as the conversion of methanol to formaldehyde.[5,6] In both the above cases, *large* Au particles are used in conjunction with *dioxygen* as the oxidant. While extended Au surfaces and large Au particles are able to adsorb dioxygen species,[3,4,6–9] it is well established that they cannot dissociatively chemisorb dioxygen to yield oxygen adatoms. The implication is that O_a cannot be the active species in the above two reactions.

Lately, Hughes *et al.* reported styrene epoxidation with O_2 catalysed by carbon-supported Au nanoparticles (~ 25 nm)[10] although addition of a peroxy "initiator" was essential for the reaction to occur. Angelici *et al.* recently reported catalysis by unsupported Au powder (~ 1000 nm particles)[11,12] of the oxidative dehydrogenation by O_2 of a range of secondary amines to imines.[12] However, the reaction mechanisms that operate and the identity of the active oxidizing species are substantial issues that have been left almost entirely undiscussed.

Accordingly, we used "big" and "medium" gold (powder and ~ 16 nm supported particles, corresponding to the work of Angelici and Zhu[12] and Hughes *et al.*,[10] respectively) to investigate both styrene epoxidation and secondary amine oxydehydrogenation using O_2 and NO_2 as alternative oxygen donors. The reactions were run both separately and competitively and the logic behind these experiments is as follows. (i) Ultra-high vacuum single crystal studies show that when oxygen adatoms are deposited on extended Au surfaces, for example, by thermal dissociation of gaseous O_2 using hot filaments, they readily oxidize alkenes.[7,13,14] (ii) Large Au entities cannot supply O_a *via* dissociative chemisorption of O_2,[8] but NO_2 *can* deposit O_a on extended Au surfaces.[15] Therefore a comparison of the behaviour of styrene and secondary amines towards catalytic oxidation driven by O_2 *versus* NO_2 should provide mechanistic information concerning Au-catalyzed partial oxidation.

Au nanoparticles supported on carbon were prepared using a microemulsion technique.[16,17]† The support was chosen so as to eliminate any electronic interaction with the Au, in contrast with, for example, TiO_2.[18] High resolution transmission electron microscopy (HRTEM) showed the Au particle mean size to be 16.1 nm (Fig. 1).† The Au powder (Alfa Aesar, 99.96+% spherical APS 0.8–1.5 micron) had a surface area of 0.15–0.45 $m^2\ g^{-1}$. Reactions were carried out in a sealed glass reactor fitted with a water-cooled reflux head and the same general procedure was followed for each run: 500 mg of Au powder or 100 mg of supported Au catalyst (1 wt% Au/C) was suspended in toluene (Aldrich, $>99.9\%$) or DMF (Aldrich, $>99.9\%$) to which styrene (Aldrich, 99%) or amine (pyrrolidine, Fluka, $>95.5\%$ or 1,2,3,4-tetrahydroisoquinoline, Aldrich, 96%) was added. The reactor was sealed and thrice evacuated and flushed with O_2 (Messer, 99.995%) or NO_2 (BOC, 2% NO_2–He)—reactions took place at 100 °C, with stirring (1100 rpm), under 0.5 bar overpressure and run for 24 h. The resulting product mixtures were analysed by gas chromatography (Hewlett-Packard GC 5890 Series II, FID detector) using decane (99+% anhydrous, Aldrich) as an internal standard. Product identification and GC calibration were carried out using both GC-MS and standard solutions of each product identified. Conversion of styrene was calculated with reference to products formed. The amount of Au powder and supported Au catalyst used for each catalytic run was chosen so as the Au surface areas of the two types of catalyst were comparable.

Table 1 summarises the results obtained for the partial oxidation of styrene; the test conditions used were similar to those employed by Hughes *et al.*,[10] though in our case no peroxy "initiator" was added. As expected, when using O_2 alone, both Au powder and supported Au nanoparticles (~ 16 nm diameter) were catalytically inactive for styrene oxidation.[10] However, when NO_2 was used as the oxidant, *both Au powder and carbon supported 16 nm Au were found to be active towards epoxidation.* The supported nanoparticles

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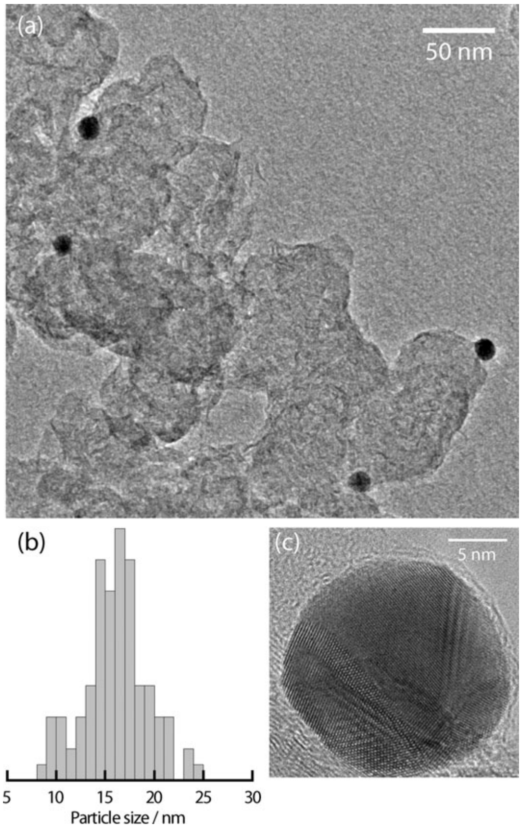


Fig. 1 (a) Representative post-reaction TEM image of 1 wt% Au/C prepared using a microemulsion method. (b) Full particle size distribution taken from a random count of 100 particles—bar height represents relative frequency, mean particle size 16.1 nm, standard deviation 3.22 nm. (c) TEM image of a single typical Au particle acquired at high magnification. Fringes associated with the Au lattice are clearly resolved.

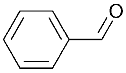
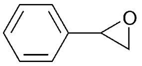
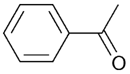
delivered conversions of 0.7% and 0.5% in toluene and DMF, respectively, with selectivity of 24% and 53% towards the epoxide. The corresponding figures for the Au powder were conversions of 1.0% and 0.5% in toluene and DMF, respectively, with epoxide selectivities of 39% and 50%. The calculated turnover number with respect to available surface Au atoms for both nanoparticles and powder was ~30. The other partial oxidation product was benzaldehyde, its relative yield being comparable to that reported by Hughes *et al.* for their peroxy-initiated system.[10] Control experiments confirmed that the carbon support was indeed catalytically inert.

Although the conversions we report are relatively low, their significance is high—and it should be borne in mind that the NO_2 partial pressure was only 2% that of the O_2. (In passing we note that our conversions are in the same order as those initially reported by Haruta *et al.* for the vapour phase epoxidation of propene catalyzed by very small Au particles.[2]) This observation is unprecedented in that it is the first example of alkene epoxidation catalyzed by large Au particles using NO_2 for oxygen delivery under conditions of turnover—and our results indicate that this system delivers particularly good selectivity towards the desired epoxide. Moreover, under these same conditions O_2 is ineffective. The implication is that at least some dissociation of NO_2 occurs on the Au surface, the resulting oxygen adatoms causing epoxidation.

To gain further insight into the nature of gold-catalyzed oxidations with NO_2, we examined a reaction that *does* occur when using O_2 in combination with large Au particles: the oxidation of secondary amines to imines, a class of reactions that has been known for many years.[6] Our observation that epoxidation with O_2 is not catalyzed by "medium" and "big" Au particles confirms that oxygen dissociation is precluded on the surfaces of such materials. This implies that some form of dioxygen is the active species in these oxydehydrogenation reactions.[8]

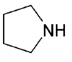
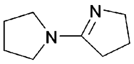
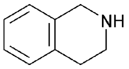
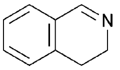
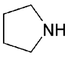
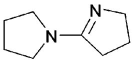
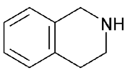
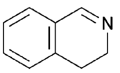
Table 2 summarises the results we obtained using Au powder and supported nanoparticles to catalyze the oxidative dehydrogenation of pyrrolidine and 1,2,3,4-tetrahydroisoquinoline using O_2 and NO_2. These two reactants, included in the studies of Angelici and Zhu,[12] were chosen because they provide examples of inter- and intramolecular oxydehydrogenation. The results confirm that Au powder is active towards oxidation of secondary amines to imines by dioxygen, as also are 16 nm supported Au particles. The conversions are comparable with those achieved in toluene by Angelici and Zhu.[12] Note also that in every case they are comparable for the two types of catalyst, reflecting the similar active Au metal

Table 1 Catalytic results of the partial oxidation of styrene using dioxygen (O_2) or nitrogen dioxide (NO_2) for supported Au nanoparticles (1 wt% Au/C) and powder Au catalysts[a]

					Selectivity (%)		
Catalyst	Oxidant	Reaction time/h	Au size/nm	Conversion (%)			
1 wt% Au/C	O_2	24	16.1	No reaction[b]	—	—	—
Au powder	O_2	24	~1000	No reaction[b]	—	—	—
1 wt% Au/C	NO_2	24	16.1	0.7[b]; 0.5[c]	76.5[b]; 47.4[c]	23.5[b]; 52.6[c]	0.0[b]; 0.0[c]
1 wt% Au/C	NO_2	48	16.1	1.5[b]; 1.0[c]	70.8; 45.1	22.3[b]; 54.9[c]	6.1[b]; 0.0[c]
Au powder	NO_2	24	~1000	1.0[b]; 0.5[c]	51.6[b]; 50.4[c]	39.1[b]; 49.6[c]	9.2[b]; 0.0[c]

[a] Reaction conditions: 100 mg of 1 wt% Au/C or 500 mg Au powder, styrene (6 mmol), solvent (10 mL), 100 °C, under 0.5 bar overpressure of gas. [b] Toluene as solvent. [c] DMF as solvent.

Table 2 Catalytic results of the oxidation of secondary amines to imines for supported Au nanoparticles (1 wt% Au/C) and Au powder catalysts using O_2 or NO_2[a]

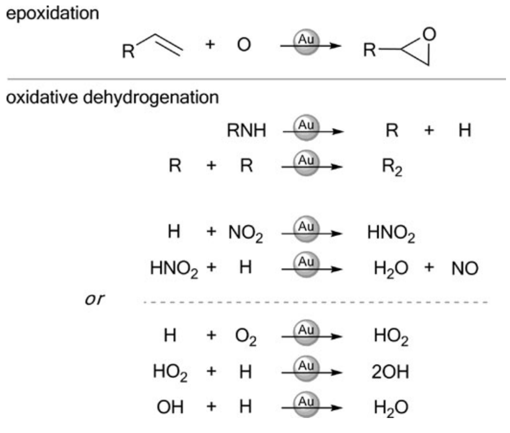
Catalyst	Oxid.	Substrate	Product	Conversion (%)
1 wt% Au/C	O_2			91.1[b]
Au powder	O_2			83.1[b]
1 wt% Au/C	O_2			19.6[b]; 30.8[c]
Au powder	O_2			23.1[b]; 24.7[c]
1 wt% Au/C	NO_2			98.9[b]
Au powder	NO_2			86.1[b]
1 wt% Au/C	NO_2			63.7[b]; 72.2[c]
Au powder	NO_2			75.8[b]; 63.2[c]

[a] Reaction conditions: 100 mg of 1 wt% Au/C or 500 mg Au powder, amine (0.1 mmol), solvent (5 mL), 100 °C, 24 h, under 0.5 bar overpressure of gas. [b] Toluene as solvent. [c] DMF as solvent.

surface areas, and confirming the inert nature of the support. Again, we show that there is no chemical difference between 1000 nm and 16 nm Au particles.

Table 2 also shows that NO_2 is an even more effective oxidant than O_2 in this reaction, especially when account is taken of the fact that the NO_2 partial pressure was ~50 times lower than the O_2 partial pressure. For example, the conversion of 1,2,3,4-tetrahydroisoquinoline catalyzed by Au powder increased from 23% to 76% when 1.5 bar O_2 was replaced by 0.03 bar NO_2. Use of DMF as solvent in place of toluene had no major effect on overall performance (Table 2).

The fact that both O_2 and NO_2 are effective oxidants for amine oxidative dehydrogenation whereas only NO_2 is effective for styrene epoxidation clearly demonstrates that the active oxygen-containing species is different in the two cases. Our findings may be rationalized in terms of the following surface mechanism. Note that H-abstraction from adsorbed organic molecules by gold surfaces has long been known.[5,6]



We also examined what happened when the two reactions were run competitively. Toluene solutions containing equimolar (0.1 mmol) quantities of alkene *and* secondary amine were reacted in the presence of both Au powder and supported Au nanoparticles. It was found that the two processes ran independently and did not perturb each other—conversions and selectivities were the same as when the reactions were run separately. This is consistent with the scheme proposed above.

In summary, we have demonstrated that Au in the form of both very large particles and 16 nm nanoparticles is an active epoxidation catalyst when NO_2 is used as the oxidant; under the same conditions O_2 is ineffective. This new route is of interest for application in a wide range of Au-catalyzed selective oxidation reactions both in the liquid phase, and in the gas phase. In contrast, both NO_2 and O_2 are effective for the Au-catalyzed oxydehydrogenation of secondary amines, with the former being significantly more active. The active oxygen-containing surface species must be different in these two different classes of reaction and we propose schemes that are consistent with observation: oxygen adatoms, deposited by NO_2, are responsible for alkene epoxidation whereas NO_2(a) (and O_2(a)) drive oxidative dehydrogenation of secondary amines by "cleaning off" H adatoms.

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Notes and references

† Supported 1 wt% Au/C catalysts were prepared using a microemulsion technique.[16,17] Au nanoparticles were prepared in water–oil microemulsions with *n*-heptane as the continuous oil domain. An aqueous solution of the Au precursor hydrogen tetrachloroaurate trihydrate (0.1 M $HAuCl_4$) was added to a mixture of the oil and 22.93 wt% surfactant, polyethylene glycol dodecyl ether (Brij 30, Fluka). The volume of aqueous solution added was calculated to result in a water-to-surfactant molar ratio of 8 ($n_w/n_s = 8$). The Au complexes were reduced by adding hydrazine (Au : N_2H_4, 1 : 8). The carbon support (C black, 50% compressed, >99.9%, Alfa Aesar, 75 $m^2\ g^{-1}$) was added to the particle suspension under vigorous stirring, after which acetone was added slowly to break the microemulsion and allow the particles to deposit on the support. The mixture was then stirred, filtered, and washed with acetone and absolute ethanol to remove the surfactant. The resulting catalyst was dried in air at 85 °C for 24 h. HRTEM studies were performed in a JEOL JEM-3011 electron microscope operating at 300 kV. Samples were ultrasonically dispersed in acetone prior to deposition on carbon-coated Cu grids.

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