

Direct propylene epoxidation on chemically reduced Au nanoparticles supported on titania†

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A highly selective titania supported propylene epoxidation catalyst was synthesized from chemically reduced, thiol capped, gold nanoparticles, and characterized by TEM and XPS.

When formed as particles of less than ~10 nm in dimension and supported on metal oxides, Au is an active catalyst with unusual, size-dependent activity and selectivity which has been demonstrated for CO oxidation and propylene epoxidation.^{1–6} Size and preparation route have been determined to be particularly important for propylene epoxidation. When prepared by deposition precipitation (DP) Au nanocluster catalysts are active for propylene epoxidation.^{7–9} However, clusters produced by this method cannot readily be applied to silica supports. Supported Au cluster catalysts prepared by direct impregnation from solutions containing Au³⁺ are not selective or active for propylene epoxidation.^{1,9}

Au nanoparticles can also be synthesized such that they are chemically reduced to metallic Au⁰ in solution before deposition on metal oxide supports. This preparation method of nanoparticles on metal oxides is different from DP in that (1) it starts with Au⁰ clusters in solution (which may have narrow-size distributions); and (2) the method relies on coordinating ligands in the precursor solution and on the oxide surface to prevent aggregation of the particles.^{10–11} In this communication, we report that well dispersed Au nanoparticles synthesized by chemical reduction and impregnated onto titania supports are selective for the synthesis of propylene oxide from propylene, oxygen, and hydrogen.



Gold nanoparticles were prepared using the method reported by Hutchison¹² with further modifications using dodecylthiol to produce thiol-capped Au nanoparticles.¹³ The thiol-capped Au particles were dissolved in toluene and mixed with titania (P25, DeGussa). The solvent was evaporated slowly and the sample was then calcined in air at 300 °C for 3 hours to remove the ligands. The Au content in the titania was measured to be approximately 5% (by mass) using energy dispersion X-ray spectroscopy (EDS, Princeton Gamma Tech) performed in an environmental scanning electron microscope (ESEM, Philips XL-30 ESEM-FEG).

The morphology of the Au nanoparticles supported on P25 before and after calcination at 300 °C is shown in Fig. 1. The images obtained by high resolution transmission electron microscopy (HRTEM, JEOL 2010FX) show that the Au particles are

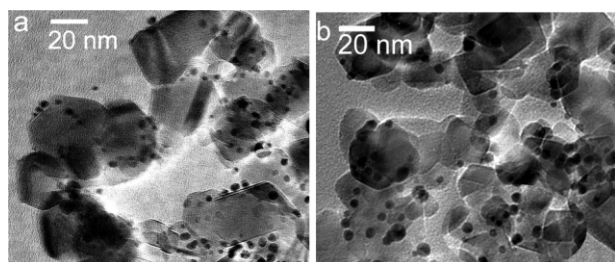


Fig. 1 TEM images of Au nanoparticles supported on titania before (a) and after (b) calcination at 300 °C.

† Electronic supplementary information (ESI) available: reactions for catalyst preparation. See <http://www.rsc.org/suppdata/cc/b4/b403213f/>

isolated and dispersed on the support before and after calcination. The supported nanoparticles have a narrow size distribution with only modest sintering at high temperature. The Au particles before and after calcination had an average size of 3.4 ± 0.6 nm and 4.6 ± 0.5 nm respectively, as measured by HRTEM.

X-ray Photoelectron Spectroscopy (XPS, Kratos Axis Ultra, Al-K α) was used to investigate the oxidation states of the Au on the support following synthesis and after propylene epoxidation reaction. Fig. 2a shows the Au 4f emission from nanoparticles supported on P25 before calcination. The two sharp peaks are consistent with the Au⁰ state (87.4 and 83.7 eV).^{14–16} After calcination (broken line – Fig. 2b), both peaks became broader and the two peaks shift positively by 0.1 eV. The broadening of the peaks and small shift is likely a manifestation of modest charging of Au nanoparticles during calcination. A simulated spectra using one chemical state of Au⁰ was in excellent agreement with the data (solid line – Fig. 2b). XPS spectra obtained from the Au nanocluster catalyst after reaction with propylene, hydrogen and oxygen also showed two sharp Au peaks consistent with Au⁰, Fig. 2c. The expected binding energy of Au⁺ is indicated in Fig. 2 for reference. Sulfur was observed by XPS before calcination (~2%); after calcination, however, no sulfur was detectable by XPS.

The reaction of propylene with oxygen and hydrogen on the Au/P25 catalyst was studied in a continuous flow packed bed reactor (diameter 0.6 cm, length 25 cm). The volume ratios of C₃H₆ : H₂ : O₂ were controlled to be 1 : 1 : 1 by mass flow controllers and the total flow rate was 360 ml h⁻¹. The pressure was atmospheric and the space velocity was 1.8 l (h-gcat)⁻¹. High purity gases were used (99.99%, Matheson Gas Products, Inc.). The catalyst was pre-reduced (or it was not active) in hydrogen (10% in argon) at 250 °C for 1 hour. We observed that the Au nanoparticle catalyst required “activation” in hydrogen before it was active for epoxidation. The propylene reaction was monitored by both mass spectroscopy (MS) and nuclear magnetic resonance spectroscopy (NMR). The differentially pumped MS was used to sample the output of the flow

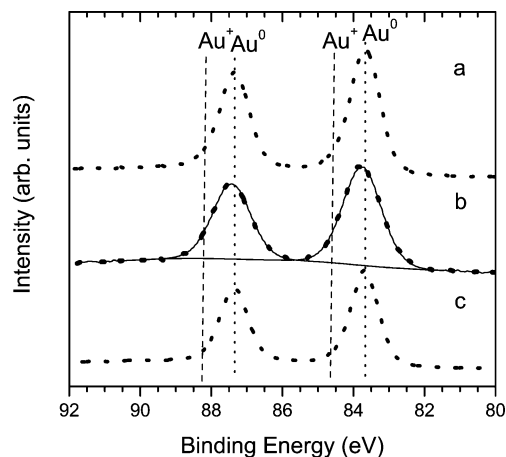


Fig. 2 XPS of Au nanoparticles supported on P25. (a) Before calcination, (b) after calcination (points are experimental data, solid line is simulation), (c) after reaction with propylene zero valence Au peaks are observed at binding energies of 87.3 eV and 83.7 eV (Au-4f_{1/2}).

reactor at atmospheric pressure. A cold trap with CDCl_3 was used for collecting all products for NMR analysis.

Fig. 3a shows the MS signal while the reactor is brought to temperature (70°C). Propylene oxide (mass 58) production was observed to increase slowly to a maximum over approximately 30 minutes then fall off over two hours. Even at temperatures as low as 25°C propylene oxide production was observable at high selectivity, Table 1.[‡]

¹H-NMR (Varian UNITY INOVA 400 MHz) of the products captured in the CDCl_3 solvent cold trap was used to assign ambiguous MS peaks, Fig. 3b. The mass 58 products at both 25°C and 70°C were confirmed to be propylene oxide (PO) by ¹H-NMR. The spectrum, obtained at room temperature, showed the characteristic resonances PO and the propylene reactant. No C_3H_8 was detected by NMR suggesting that under these conditions hydrogenation was not active on the Au/P25 catalyst. Since there was no NMR evidence of propane or acetaldehyde (both mass 44), the mass 44 signal observed to increase together with PO at 70°C and remained as a by-product was attributed to CO_2 .

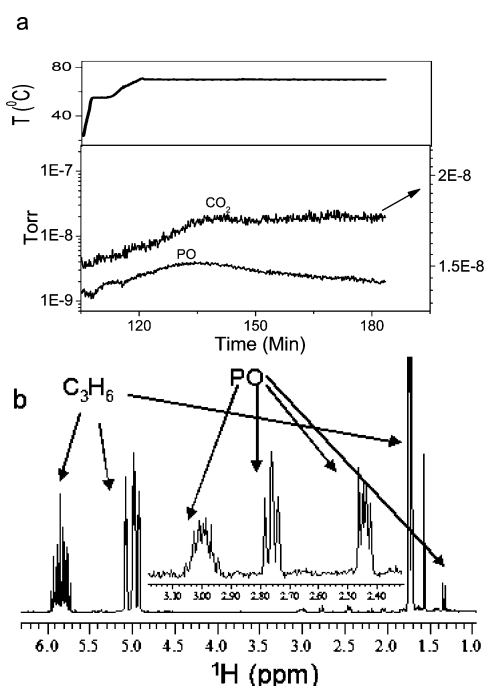


Fig. 3 (a) Mass trace of propylene epoxidation reaction at 70°C . Temperature is shown on the top. The gases are CO_2 and PO. (b) ¹H-NMR performed at room temperature of products of propylene epoxidation reaction run at 70°C .

Table 1 5% 4.6 ± 0.5 nm Au catalyst performance^a

$T/^\circ\text{C}$	Selectivity (PO)	Selectivity (CO_2)	Propylene conversion
25	99%	0	0.3%
70	83%	17%	0.6%

^a Reaction conditions: $\text{C}_3\text{H}_6 : \text{H}_2 : \text{O}_2 = 1 : 1 : 1$ (vol%).

The gradual deactivation of the catalyst after 1 hour at 70°C is observed in Fig. 3a with nearly constant CO_2 production. Regeneration in H_2 at 250°C restored the original activity consistent with hydrogenation and desorption of site filling decomposition or polymerization products retained on the catalyst surface. Previously, the deactivation of supported gold catalysts in propylene epoxidation observed on Au/P25 and Au/TS-1 was attributed to either polymerization of PO⁷⁻⁸ or decomposition of the PO product.¹⁷

Chemically reduced, thiol-capped, Au nanoparticles can be supported on metal oxides with a narrow size distribution. Au clusters, 4.6 nm in diameter deposited by this route on P25 titania are selective for propylene epoxidation and exhibit activity even at 25°C . Further investigations of propylene epoxidation together with the dependence on support material are underway for gold nanoparticles synthesized by this method.

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Notes and references

[‡] Conversion, X , and selectivity, S , are calculated from the partial pressures, P , determined by MS and NMR peak ratios. $X = (P_0 - P) * 100 / P_0 = ([P_{\text{CO}_2} / 3P_0] + [P_{\text{PO}} / P_0]) * 100$; $S_{\text{PO}} = [P_{\text{PO}} / P_0] * 100 / ([P_{\text{PO}} / P_0] + [P_{\text{CO}_2} / 3P_0])$; $S_{\text{CO}_2} = [P_{\text{CO}_2} / 3P_0] * 100 / ([P_{\text{PO}} / P_0] + [P_{\text{CO}_2} / 3P_0])$, where P_0 and P are the partial pressures at the reactor input and output of C_3H_6 . The ratio $P_{\text{CO}_2} / 3P_0$ is calculated from the MS partial pressures and P_{PO} / P_0 calculated from H-NMR.

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