Catalytic epoxidation of propene with H_2O-O_2 reactants on Au/TiO_2

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Au/TiO_2 catalysts form hydroperoxy species from H_2O-O_2 mixtures at near-ambient temperatures. These species can be used in the selective epoxidation of propene to propylene oxide.

Propylene oxide (PO) is a useful intermediate in the synthesis of polyurethane, organic intermediates and solvents (*e.g.* propylene glycol).[1] PO is currently produced by chlorohydrin or hydroperoxide processes,[2] which require toxic, corrosive, or explosive reagents, and form significant amounts of waste by-products. Hydrogen peroxide has been used as an oxidant to replace alkyl hydroperoxides in PO synthesis.[3]

Small Au clusters (<5 nm) dispersed on Ti-containing oxides, such as TiO_2 and TS-1, catalyze propene epoxidation via the *in situ* formation of hydroperoxy species (*OOH) from H_2-O_2 mixtures.[4-7] Mechanistic studies have suggested that hydroperoxy species form on Au clusters via H_2 reactions with O_2; these species then react with propene on adjacent Ti centers to form PO with high selectivity.[8,9] This process uses H_2 as a sacrificial reductant, which predominantly converts, however, to H_2O via unproductive side reactions, and leads to low H_2 utilization efficiencies (30-40%, defined as PO formed per H_2 consumed) and unfavorable economics.[2] H_2O_2 was recently detected during CO oxidation with aqueous systems and Au catalysts[10]; these molecules or their adsorbed precursors may therefore form also from O_2/H_2O mixtures. Our recent kinetic and isotopic data indicate that *OOH species formed from H_2O/O_2 account for the strong effect of H_2O on the rate of CO oxidation on Au catalysts.[11] We provide here evidence for the formation of *OOH species from H_2O and O_2 by detecting and reporting for the first time the formation of PO via propene reactions using H_2O/O_2 mixtures, which appear to act as precursors for peroxide species. H_2O/O_2 mixtures form PO with selectivities as high as 80% on Au/TiO_2 at near-ambient temperatures (300-350 K).

Au/TiO_2 (1.56 wt.% Au, 3.3 ± 0.7 nm mean cluster diameter) was prepared by deposition-precipitation and provided by the World Gold Council. Au/Al_2O_3 (0.61 wt.%, 3.5 ± 1.2 nm) was also prepared by deposition-precipitation methods.[12] $HAuCl_4·xH_2O$ (0.24 g, Aldrich, 99.999%) was dissolved in deionized H_2O (80 cm^3) at 353 K. The support (5 g, γ-Al_2O_3, Alcoa) was treated in air at 923 K for 5 h and suspended in deonized H_2O (120 cm^3) at 353 K. Au was deposited onto Al_2O_3 at 353 K and a pH of 7 (adjusted with 0.5 M NaOH) by mixing the two solutions with stirring for 1 h. Solids were filtered and washed twice with deionized water at ambient temperature and then once at slightly higher temperatures (323 K), and held in ambient air for 24 h. TiO_2 was obtained from Degussa (P25, anatase/rutile ~4). Propene (4 kPa, Praxair, UHP) epoxidation rates and selectivity were measured using O_2 (4 kPa, Praxair, UHP) at 350 K in the presence and absence of H_2 (4 kPa, 99.999%, Praxair) or H_2O (0-12 kPa) using a tubular flow reactor with plug-flow hydrodynamics (He was used as a balance). Au/TiO_2 was used as-received, while Au/Al_2O_3 was treated using protocols reported previously.[12] Reactant and product concentrations were measured by gas chromatography (Agilent 6890GC) using a Porapak Q packed-column (80–100 mesh, 1.82 m × 3.18 mm) and a HP-1 capillary column (50 m x 0.32 mm; 1.05 μm film) with thermal conductivity and flame ionization detection, respectively.

Figure 1 shows propylene oxide formation rates (metal-time yield, per Au atom) at 350 K as a function of time-on-stream on Au/TiO_2 when H_2-O_2 or H_2O-O_2 were used as the oxidant. Propene epoxidation rates and selectivities (~95%) and catalyst deactivation rates (0.76 h^{-1} first-order deactivation rate constant) in H_2-O_2 mixtures are similar to those previously reported (Supplementary Information†). Strongly-adsorbed PO-derived species have been claimed to cause this deactivation.[13] PO selectivities remained nearly unchanged as deactivation occurred and conversion decreased (Figure 2). These data, taken together with the intermediate selectivites observed as data are extrapolated to zero conversion, indicate that both PO and acetone form as primary products and that deactivation occurs by blocking of sites without concomitant changes in the relative rates of PO and acetone synthesis.
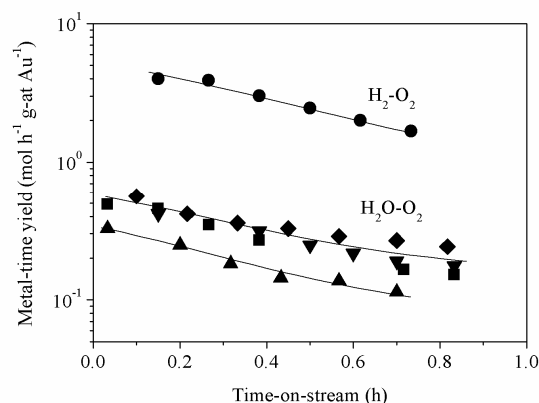

Fig. 1. Rate of propylene oxide formation (expressed as metal-time yield) from C_3H_6 (4 kPa) and O_2 (4 kPa) at 350 K from with Au/TiO_2 as a function of time-on-stream using H_2 or H_2O as co-reactants: 4 kPa H_2 (●); 1 kPa H_2O (▲), 2 kPa H_2O (■); 6 kPa H_2O (▼); 12 kPa H_2O (♦).

Figures 1 and 2 provide evidence for the previously unrecognized ability of Au/TiO_2 to catalyze propene epoxidation with O_2 and H_2O (instead of H_2) as co-reactant. The synthesis of PO during water electrolysis, probably via *in situ* generation of H_2O_2 or OOH species, has been reported.[14]

In contrast, catalytic epoxidation of propene or other substrates with H_2O-O_2 reactants have not been reported. PO synthesis rates with H_2O-O_2 reactants are significantly lower than with H_2-O_2, but the former avoid the significant loses of costly H_2 co-reactants via its unproductive pathways to form H_2O instead of OOH species (hydrogen efficiency ~29 %).

Both H_2O and O_2 are needed to form active hydroperoxy species required for PO synthesis. Neither C_3H_6-O_2 nor C_3H_6-H_2O reactants formed detectable products on Au/TiO_2 at 350 K. PO synthesis also requires the presence of both Au and Ti sites. We did not detect PO from C_3H_6-O_2-H_2 or C_3H_6-O_2-H_2O reactants on either TiO_2 or Au/Al_2O_3 catalysts. Au and Ti sites must reside in reasonable proximity, since PO was not detected when C_3H_6-O_2-H_2 or C_3H_6-O_2-H_2O reactants were contacted with a physical mixture Au/Al_2O_3 and TiO_2 (mass ratio 1:1, 0.125-0.250 mm aggregates).

The rate of PO formation (extrapolated to zero time-on-stream) increased slightly from 0.5 to 0.7 mol h^{-1} (g-at Au)$^{-1}$ when the H_2O partial pressure in equimolecular C_3H_6-O_2 mixtures (4 kPa) increased from 1 to 2 kPa (Figure 1); higher H_2O pressures (up to 12 kPa), however, did not influence reaction rates.

The PO synthesis rates reported here are inconsistent with the use of gaseous H_2O_2 reactants as intermediates and indicate that PO is formed instead from propene and adsorbed hydroperoxide species. H_2O_2 pressures in equilibrium with O_2/H_2O (4 kPa/12 kPa) are 7×10^{-18} kPa ($K_{eq} = 1.48 \times 10^{-19}$ kPa$^{-1/2}$; 350 K). At this pressure, the frequency of H_2O_2 collisons with Au clusters (Supplementary Information†) would be 5×10^{-6} mol h^{-1} (g-at Au)$^{-1}$, a value much lower than required to maintain the observed epoxidation rates (~0.7 mol h^{-1} (g-at Au)$^{-1}$), consistent with an inadequate supply of H_2O_2(g) as the reactive species and with PO synthesis via propene reactions with hydroperoxy surface species instead of H_2O_2. The involvement of bound hydroperoxy species requires, in turn, atomic proximity between the sites that form *OOH (Au) and those that consume it via reactions with propene (Ti), possibly at Au-TiO_2 interfaces, as proposed earlier [4] and consistent with the absence of epoxidation turnovers on physical mixtures of Au/Al_2O_3 and TiO_2.

Density functional theory (DFT) [15] suggests that OOH species can form from H_2O and O_2 on Au_8 clusters to form $[O_2 \cdot H_2O]$ complexes in which protons are shared between H_2O and O_2 to ultimately form adsorbed (HOO*) complexes. We propose that these species can act as effective oxidants in reactions of CO to CO_2 [11] and, in the present study, for propene epoxidation to PO.

C_3H_6-O_2-H_2O reactants form predominantly PO and acetone on Au/TiO_2 at 350 K. Figure 2 shows PO selectivities at various H_2O inlet pressures. PO selectivities increased slightly from 65 to 70% as H_2O pressure increased from 1 to 2 kPa, but then decreased markedly (70 to 20 %) at higher H_2O pressures (2-12 kPa). with a concurrent increase in acetone selectivity. The selectivities to PO and acetone depend only weakly on propene conversion, suggesting that both can form via primary pathways. The strong effects of H_2O pressure on PO selectivity and the slight increase in acetone selectivity with increasing conversion show, however, that secondary reactions of PO to form acetone are favored by H_2O. PO

synthesis rates, however, are independent of H_2O pressure above 2 kPa, while acetone synthesis rates increased monotonically with H_2O pressure.
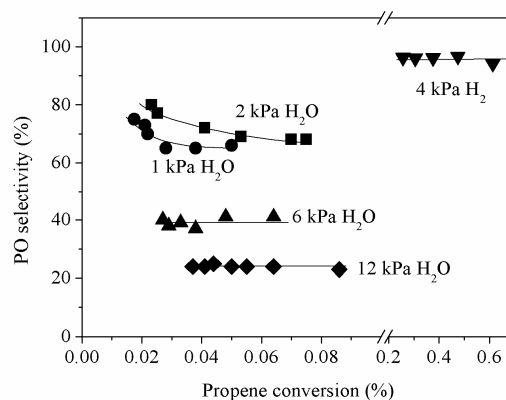

Fig. 2. Selectivity (carbon basis) to propylene oxide obtained with Au/TiO_2 at 350 K at different propene conversion levels changed by catalyst deactivation (4 kPa C_3H_6; 4 kPa O_2; 4 kPa H_2; 1-12 kPa H_2O).

The data in Figures 1 and 2, taken together, suggest that maximum PO yields are achieved at intermediate H_2O pressures. While rates are lower than with H_2 as co-reactants, the use of H_2O avoids the need for H_2 and its predominant loss via unproductive combustion side reactions.

In summary, we provide evidence here for the unprecedented ability of Au/TiO_2 catalysts to form hydroperoxy surface species from O_2/H_2O mixtures and for their involvement in oxidation reactions, such as selective conversion of propene to PO at near-ambient temperatures (350 K). These pathways provide an attractive strategy to replace H_2 by H_2O in propene epoxidation reactions. We expect that these hydroperoxy intermediates will prove useful for other epoxidation reaction upon more rigorous evaluation and optimization.

Notes and references

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† Electronic Supplementary Information (ESI) available: propene epoxidation with Au/TiO_2 catalysts and frequency of H_2O_2 collisions with Au clusters. See DOI: 10.1039/b000000x/

1. G.C. Bond, C. Louis and D.T. Thompson, *Catalysis by gold*; Imperial College Press: London, 2006.

2. T.A. Nijhuis, M. Makkee, J.A. Moulijn and B.M. Weckhuysen, *Ind. Eng. Chem. Res.*, 2006, **45**, 3447.

3. A. Tullo, *Chem. & Eng. News*, 2004, **82**, 15.

4. T. Hayashi, K. Tanaka and M. Haruta, *J. Catal.*, 1998, **178**, 566.

5. J.J. Bravo-Suarez, J. Lu, C.G. Dallos, T. Fujitani and S.T. Oyama, *J. Phys. Chem. C*, 2007, **111**, 17247.

6. T.A.R. Nijhuis, T. Visser and B.M. Weckhuysen, *Angew. Chem. Int. Ed.*, 2005, **44**, 1115.

7. G.J. Hutchings, *Chem. Commun.*, 2008, **10**, 1148.

8. D.G. Barton and S.G. Podkolzin, *J. Phys. Chem. B*, 2005, **109**, 2262.

9. B. Chowdhury, J.J. Bravo-Suarez, N. Nimura, J. Lu, K.K. Bando, S. Tsubota and M. Haruta, *J. Phys. Chem. B*, 2006, **110**, 22995.

10. W.C. Ketchie, M. Murayama and R.J. Davis, *Topics Catal.*, 2007, **44**, 307.

11. M. Ojeda, B.Z. Zhang and E. Iglesia, *in preparation*.

12. C.K. Costello, J. Guzman, J.H. Yang, Y.M. Wang, M.C. Kung, B.C. Gates and H.H. Kung, *J. Phys. Chem. B*, 2004, **108**, 12529.

13. J. Lu, X. Zhang, J.J. Bravo-Suarez, S. Tsubota, J. Gaudet and S.T. Oyama, *Catal. Today*, 2007, **123**, 189.

14. K. Otsuka, T. Ushiyama, I. Yamanaka and K. Ebitani, *J. Catal.*, 1995, **157**, 450.

15. A. Bongiorno and U. Landman, *Phys. Rev. Lett.*, 2005, **95**, 106102.