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$_2$O–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 Ti centers located within molecular distances to form PO with high selectivity.[8,9] This process uses H$_2$ as a sacrificial reductant, which predominantly converts, however, to H$_2$O *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$_2$O$_2$ 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$_2$O mixtures. Our recent kinetic and isotopic data indicate that *OOH species formed from H$_2$O/O$_2$ account for the strong effect of H$_2$O on the rate of CO oxidation on Au catalysts.[11] We provide here evidence for the formation of *OOH species from H$_2$O and O$_2$ by detecting and reporting for the first time the formation of PO *via* propene reactions using H$_2$O/O$_2$ mixtures, which appear to act as precursors for peroxide species. H$_2$O/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 determined by transmission electron microscopy) was prepared by deposition–precipitation and provided by the World Gold Council. Au/Al$_2$O$_3$ (0.61 wt%, 3.5 ± 1.2 nm) was also prepared by deposition–precipitation methods.[12] HAuCl$_4$·xH$_2$O (0.24 g, Aldrich, 99.999%) was dissolved in deionized H$_2$O (80 cm^3) at 353 K. The support (5 g, γ-Al$_2$O$_3$, Alcoa) was

treated in air at 923 K for 5 h and suspended in deionized H$_2$O (120 cm^3) at 353 K. Au was deposited onto Al$_2$O$_3$ 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$_2$O (0–12 kPa) using a tubular flow reactor with plug-flow hydrodynamics (He was used as balance). Au/TiO$_2$ was used as-received, while Au/Al$_2$O$_3$ 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 × 0.32 mm; 1.05 μm film) with thermal conductivity and flame ionization detection, respectively.

Fig. 1 shows PO 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$_2$O–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 (ESI†). Strongly-adsorbed PO-derived species have been claimed to cause this deactivation.[13] PO selectivities remained nearly unchanged as deactivation occurred and
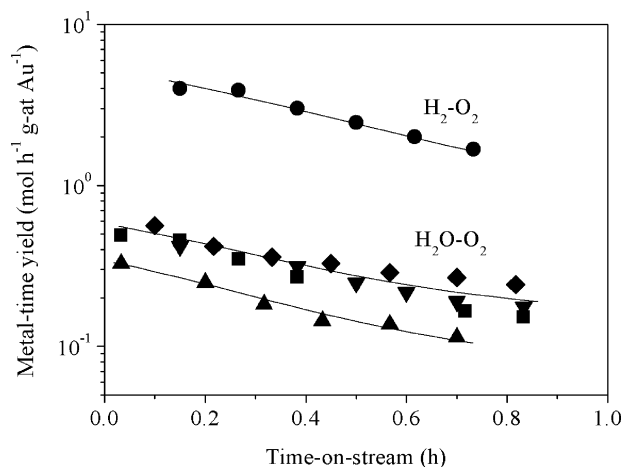
Fig. 1 Rate of propylene oxide formation (expressed as metal-time yield) from C$_3$H$_6$ (4 kPa) and O$_2$ (4 kPa) at 350 K from with Au/TiO$_2$ as a function of time-on-stream using H$_2$ or H$_2$O as co-reactants: 4 kPa H$_2$ (●); 1 kPa H$_2$O (▲); 2 kPa H$_2$O (■); 6 kPa H$_2$O (▼); 12 kPa H$_2$O (◆).

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† Electronic supplementary information (ESI) available: Products identification by gas chromatography, rate of propene epoxidation with Au/TiO$_2$ catalysts, proximity between Au and Ti centers, frequency of H$_2$O$_2$ collisions with Au clusters, and high-resolution TEM micrographs. See DOI: 10.1039/b813589d
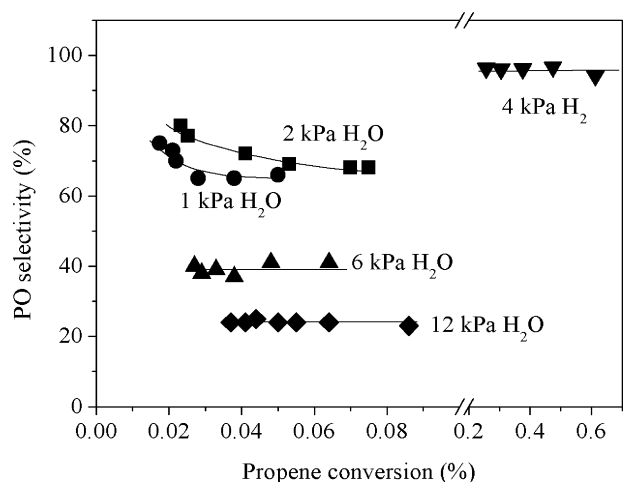
Fig. 2 Selectivity (carbon basis) to propylene oxide obtained with Au/TiO_2 at 350 K at different propene conversion levels changed by catalyst deactivation (4 kPa C_3H_6; 4 kPa O_2; 4 kPa H_2; 1–12 kPa H_2O).

conversion decreased (Fig. 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 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. We have carried out experiments for extended periods of time (ESI†), during which we carry out more than 10 epoxidation turnovers, calculated on the basis of surface Au atoms (from TEM cluster diameters). These turnover numbers represent a lower bound, because they assume that all exposed Au atoms act as active sites, irrespective of their location with respect to Ti centers. These data confirm that the propene epoxidation rates reported here with $H_2O–O_2$ co-reactants are catalytic on Au/TiO_2.

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 previously reported. PO synthesis rates with $H_2O–O_2$ reactants are significantly lower than with $H_2–O_2$, but the former avoid significant losses of costly H_2 co-reactant *via* its unproductive pathways to form H_2O instead of OOH species (hydrogen efficiency ~29%). $O_2–H_2O$ mixtures may form HOO* species *via* the microscopic reverse of elementary steps for H_2O_2 decomposition.[15,16] These steps can occur, in spite of their unfavorable thermodynamics, because of their kinetic coupling with propene epoxidation steps that scavenge HOO* intermediates to form PO. OH* groups formed in these steps must recombine to form H_2O* and O*, since H_2O is not consumed during reaction. O* is not predominantly removed *via* unselective scavenging with PO to form other products (*e.g.*, acetone, propanal, acrolein), because measured PO selectivities are >50% (Fig. 2). Thus, O* species must act as epoxidation reactants, desorb as O_2 ($2O* \rightarrow O_2 + 2*$), or form ozone molecules ($O* + O_2 \rightarrow O_3*$), which are then used in epoxidation turnovers.[17,18]

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). Water inhibits combustion during $C_3H_6–O_2$ reactions on Ag-based catalysts, but does not increase PO synthesis rates.[19–21] We find instead that the role of H_2O on Au/TiO_2 is to significantly increase PO synthesis rates. Propene combustion rates were undetectable on Au/TiO_2 with or without added H_2O.

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 (Fig. 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 collisions with Au clusters (ESI†) 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)[22] suggests that OOH species can form from H_2O and O_2 on Au_8 clusters to form [O_2·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. Fig. 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.

The data in Fig. 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-reactant, the use of H_2O avoids the need for H_2 and its predominant loss *via* unproductive combustion side reactions.

The presence of small Au clusters (<5 nm) is a key parameter for their catalytic reactivity in many reactions.[1] Recent studies have shown, however, that large Au clusters (~ 16 nm) are also active in alkene epoxidation with NO_2 as the oxidant.[23]

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 reactions upon more rigorous evaluation and optimization.

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