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Catalytic epoxidation of propene with H$_2$O-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).

$^3$ 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.

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-O$_2$ mixtures.

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.

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.

H$_2$O$_2$ was recently detected during CO oxidation with aqueous systems and Au catalysts; 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.

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) 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.

H$_2$O$_2$ (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 a balance). Au/TiO$_2$ was used as-received, while Au/Al$_2$O$_3$ was treated using protocols reported previously.

Reactant and product concentrations were measured by gas chromatography (Agilent 6890GC) using a Porapak Q packed-column (80–100 mesh, 1.82 m x 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$_2$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-O$_2$ mixtures are similar to those previously reported (Supplementary Information†).

Strongly-adsorbed PO-derived species have been claimed to cause this deactivation.

PO selectivities remained nearly unchanged as deactivation occurred and conversion decreased (Figure 2). These data, taken together with the intermediate selectivities 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$_3$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 (▲). Figures 1 and 2 provide evidence for the previously unrecognized ability of Au/TiO$_2$ to catalyze propene epoxidation with O$_2$ and H$_2$O (instead of H$_2$) as co-reactant. The synthesis of PO during water electrolysis, probably via in situ generation of H$_2$O$_2$ or OOH species, has been reported.
In contrast, catalytic epoxidation of propene or other substrates with H$_2$O-O$_2$ reactants have not been reported. PO synthesis rates with H$_2$O-O$_2$ reactants are significantly lower than with H$_2$-O$_2$, but the former avoid the significant losses of costly H$_2$ co-reactants via its unproductive pathways to form H$_2$O instead of OOH species (hydrogen efficiency ~29\%).

Both H$_2$O and O$_2$ are needed to form active hydroperoxy species required for PO synthesis. Neither C$_3$H$_6$O$_2$ nor C$_3$H$_6$- H$_2$O 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$_3$H$_6$-O$_2$-H$_2$ or C$_3$H$_6$-O$_2$-H$_2$O reactants on either TiO$_2$ or Au/Al$_2$O$_3$ catalysts. Au and Ti sites must reside in reasonable proximity, since PO was not detected when C$_3$H$_6$-O$_2$-H$_2$ or C$_3$H$_6$-O$_2$-H$_2$O reactants were contacted with a physical mixture Au/Al$_2$O$_3$ 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$_2$O partial pressure in equimolecular C$_3$H$_6$-O$_2$ mixtures (4 kPa) increased from 1 to 2 kPa (Figure 1); higher H$_2$O 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$_2$O$_2$ reactants as intermediates and indicate that PO is formed instead from propene and adsorbed hydroperoxide species. H$_2$O$_2$ pressures in equilibrium with O$_2$/H$_2$O (4 kPa/12 kPa) are 7x10$^{-19}$ kPa ($K_{eq} = 1.48x10^{-19}$ kPa$^{-1/2}$; 350 K). At this pressure, the frequency of H$_2$O$_2$ collisions with Au clusters (Supplementary Information) would be 5x10$^{-6}$ 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$_2$O$_2$ as the reactive species and with PO synthesis via propene reactions with hydroperoxy surface species instead of H$_2$O$_2$. The involvement of bound hydroperoxy species requires, in turn, atomic proximity between the sites that form OOOH (Au) and those that consume it via reactions with propene (Ti), possibly at Au-TiO$_2$ interfaces, as proposed earlier and consistent with the absence of epoxidation turnovers on physical mixtures of Au/Al$_2$O$_3$ and TiO$_2$.

Density functional theory (DFT) suggests that OOH species can form from H$_2$O and O$_2$ on Au$_6$ clusters to form [O$_2$-H$_2$O] complexes in which protons are shared between H$_2$O 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$_2$ and, in the present study, for propene epoxidation to PO. C$_3$H$_6$-O$_2$-H$_2$O reactants form predominantly PO and acetone on Au/TiO$_2$ at 350 K. Figure 2 shows PO selectivities at various H$_2$O$_2$ inlet pressures. PO selectivities increased slightly from 65 to 70% as H$_2$O$_2$ pressure increased from 1 to 2 kPa, but then decreased markedly (70 to 20%) at higher H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$. PO synthesis rates, however, are independent of H$_2$O$_2$ pressure above 2 kPa, while acetone synthesis rates increased monotonically with H$_2$O$_2$ pressure.

The data in Figures 1 and 2, taken together, suggest that maximum PO yields are achieved at intermediate H$_2$O$_2$ pressures. While rates are lower than with H$_2$ as co-reactants, the use of H$_2$O 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$_2$O 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$_2$O in propene epoxidation reactions. We expect that these hydroperoxy intermediates will prove useful for other epoxidation reaction upon more rigorous evaluation and optimization.

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Notes and references