

ENVIRONMENTAL CATALYSIS

A team of researchers is focusing on the mechanistic aspects of selective oxidation by transition metal-mediated catalysis.

Principal Investigators: Harold Kung, Mayfair Kung

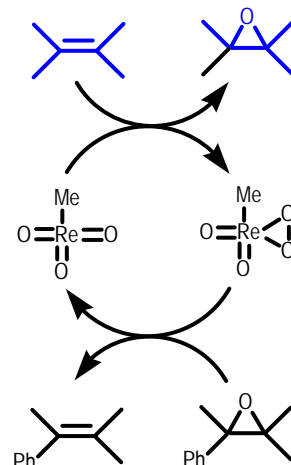
Collaborators: Sonbinh Nguyen (Department of Chemistry), Jeffrey Miller (BP Chemical)

Objective: Better understanding of the fundamental mechanistic chemistry of catalytic transformations should allow for objective designs of catalysts with enhanced specificities and activities that would be environmentally safer and more efficient. Recent work of the Kung group in this area includes investigation of direct oxidation of olefins to epoxides catalyzed by methyltrioxorhenium (MTO) and the study of CO oxidation over supported gold catalysts. At present, the syntheses of epoxides – chemical intermediates for a variety of applications – often involve the use of expensive oxidants or processes that are environmentally unfriendly. The preferred route of direct oxidation of olefins to epoxides using oxygen gas has only been realized successfully for ethylene and butadiene. Similarly, the origin of the remarkable activity of supported gold catalysts for low temperature CO oxidation is unclear and warrants further examination.

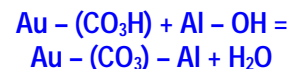
Approach: Mechanistic aspects of olefins epoxidation by MTO and CO oxidation by a supported gold catalyst are investigated by a variety of techniques including NMR spectroscopy, TEM, XANES and EXAFS, FTIR, isotope labeling and kinetics studies. The results are used to identify the nature of the catalytic active centers and the reaction mechanisms.

Results: The Kung group has shown that trans-epoxidation of 2,3-dimethyl-2-butene with styrene oxide is possible using MTO as a catalyst. Although not all side products have been identified, the initial analysis suggests that catalyst deactivation may be due to the formation of oligomers comprised of organics and MTO. Therefore, addition of chelating amines can provide a pathway to avoid oligomerization as well as to increase the efficiency of the deoxygenation reaction. In a study of CO oxidation over Au/ γ -Al₂O₃, the Kung group has demonstrated that passing either H₂O or H₂ over the catalyst can prevent its deactivation or reactivate it. The deuterium isotope effects of H₂O and H₂ suggest that deactivation stems from the formation of an inactive carbonate at the active site by deprotonation of the surface bicarbonate intermediate, whereas hydrogen regeneration of the catalyst proceeds by hydrogenolysis of the carbonate. Interestingly, calcined catalysts (air, 350 °C) are active without further treatment, while uncalcined Au/ γ -Al₂O₃ are not active unless activated in a flow of H₂ and H₂O at 100 °C. Circumstantial evidence provides support to the model of the active site recently put forward by the researchers, which involves an ensemble of metallic Au atoms and ionic Au⁺-OH⁻ species.

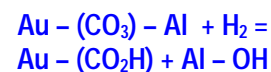
Publications: Costello CK, Kung MC, Oh H-S, Wang Y, Kung HH *Appl. Catal. A: Gen.* **2002**, 232:159; Costello, Yang JH, Law H-Y, Wang Y, Lin J-N, Marks LD, Kung MC, Kung HH, *Appl. Catal. A: Gen.* **2003**, 243: 15; Kung HH, Kung MC, Costello CK, *J. Catal.* **2003**, in press.



The trans-epoxidation reaction is a two-step process: oxygen transfer from an epoxide to the catalyst (bottom) and its subsequent incorporation into an alkene to form another epoxide (top).



Deactivation of the Au catalyst during CO oxidation results from the formation of an inactive carbonate at the active site by deprotonation of the surface bicarbonate intermediate.



Hydrogen regeneration of the gold catalyst proceeds by hydrogenolysis of the carbonate to a formate or hydroxycarbonyl and a hydroxyl.