Chemical Engineering Seminar  
Thursday, April 14, 2016  
12 – 12:50 PM  
Nitschke Seminar Room 1027  

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Deactivation of Au/TS-1 Catalysts during the Epoxidation of Propylene in the Presence of H₂/O₂  

ABSTRACT:  
Since the discovery of titania-supported gold catalysts for propylene epoxidation in the presence of both H₂ and O₂ [1], significant subsequent work has improved both the catalyst selectivity and rate while also providing a clearer understanding of mechanism [2-5]. Despite this success, to date no commercial implementation of this hydro-oxidation to propylene oxide (HOPO) process is imminent, and many recent PO expansions have opted for liquid-phase processes that utilize H₂O₂ as a raw material, circumventing the H₂/O₂ co-feed route [6]. Ultimately, the industrial viability of the HOPO process is a function of not only the PO space-time yield, but also generally poor hydrogen selectivity and catalyst longevity. The discussion of these later catalyst variables is limited in the literature, and this lecture will discuss these phenomena and the synthetic approaches taken to stem their effects.  

Deactivation studies conducted on Au/TS-1 demonstrated short-term gold sintering with time-on-stream. As the catalyst progressed in age, the TEM-determined growth rate of the particle size distribution mean slowed, eventually reaching a level of statistical noise. However, catalyst deactivation continued well beyond the time at which particle sintering was significantly reduced, and this was attributed to an increased contribution due to TS-1 deactivation. Evidence for TS-1 deactivation was supported by separate H₂O₂ and steam-treatment experiments of alkali-promoted TS-1 that showed irreversible support structure modifications. The deactivation mechanism of Au/TS-1 is distinctly different than that of Au supported on non-dispersed Ti-clusters, such as on TiO₂, where catalyst active site fouling with PO oligomers can and does occur. Au/TS-1 deactivation was slowed by
catalyst synthetic strategies using pre-sintered gold derived from cluster-based precursors, where the gold was purposefully located on the exterior of primary TS-1 crystallites. These cluster-derived catalysts demonstrated significant lifetime advantages relative to gold salt-derived catalysts by curbing sintering phenomena, while limiting, but not completely preventing, TS-1 degradation in the presence of required alkali-promoters. Long-term TS-1 deactivation was exacerbated at the higher pressures needed to make the process economically viable. These results detail the importance of studying catalyst deactivation phenomena under realistic pressures when a true estimate of catalyst lifetime for reaction engineering is required.


(Light refreshments served at 11:45)