Reaction kinetics of direct gas-phase propylene epoxidation on Au/TS-1 catalysts

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Propylene oxide (PO), is a key intermediate in the production of value-added products, such as polyurethanes and propylene glycol. Current industrially practiced methods of propylene epoxidation, including hydrochlorination, epoxidation by organic peroxides, and the Hydrogen Peroxide to Propylene Oxide (HPPO) process either produce PO unselectively, necessitating energy intensive separation processes, produce environmentally damaging byproducts, or require several sequential reaction vessels. A potential solution for these issues exists in the form of a single-step, highly selective gas phase reaction to produce PO. Industrial adoption of a process utilizing this technology has not occurred due to the failure of state-of-the-art Au/TS-1 catalysts, consisting of gold supported on titanium MFI, to meet economic targets for hydrogen use efficiency, selectivity to PO, and PO rate-per-mass, improvement on all of which has been hindered by a lack of understanding of how Au-TS-1 catalysts fundamentally operate. Therefore, the goal of this work has been to understand the active site requirements and reaction kinetics with the aim of lowering barriers to commercialization of this more environmentally benign process.

Once we had developed a general understanding of product inhibition, we applied this knowledge to the kinetics of propylene epoxidation over Au/TS-1 catalysts. We measured gas phase kinetics in a continuous stirred tank reactor (CSTR) free from temperature and concentration gradients. Apparent reaction orders measured at 473 K for H_2, O_2, and propylene for a series of Au-DP/TS-1 with varied Au and Ti contents were consistent with those reported previously. Co-feeding propylene oxide enabled measurement of the apparent reaction order in propylene oxide and the determination that relevant pressures of propylene oxide reversibly inhibit propylene epoxidation over Au-DP/TS-1, while co-feeding carbon dioxide and water had no effect on the propylene epoxidation rate. The measured reaction orders for propylene epoxidation, after corrected to account for propylene oxide inhibition, are consistent with a ‘simultaneous’ mechanism requiring two distinct, but adjacent, types of sites. Hydrogen oxidation rates are not inhibited by propylene oxide, suggesting that the sites required for hydrogen oxidation are distinct from those required for propylene epoxidation.

We then shifted focus to elucidate structural details of gold active sites and their interaction with Ti active sites. To determine whether the roles of extracrystalline and intracrystalline gold nanoparticles supported on titanosilicate-1 on direct propylene epoxidation are intrinsically different, the kinetics of direct propylene epoxidation were measured in a gas-phase continuous stirred tank reactor (CSTR) over

polyvinylpyrrolidone-coated gold nanoparticles (Au-PVP/TS-1) deposited on TS-1 supports. The PVP-coated gold nanoparticles were too large to fit into the micropores of TS-1, even after ligands were removed in situ by a series of pretreatments, as confirmed by both TEM and TGA-DSC. The activation energy and reaction orders for H_2, O_2, propylene, propylene oxide, carbon dioxide, and water for propylene epoxidation measured on Au-PVP/TS-1 catalysts were consistent with those reported for Au/TS-1 prepared via deposition-precipitation (Au-DP/TS-1). However, while the reaction orders for hydrogen oxidation on Au-PVP/TS-1 were similar to those measured on Au-DP/TS-1, a decrease in activation energy from approximately 30 kJ mol^{-1} for Au-DP/TS-1 to 4-5 kJ mol^{-1} for Au-PVP/TS-1 suggests there is a change in mechanism, rate-limiting step, and/or active site for hydrogen oxidation. Additionally, an active site model was developed which determines the number of Ti within an interaction range of the perimeter of extracrystalline Au nanoparticles (i.e., the number of Au-Ti active site pairs). Turnover frequencies estimated for this active site model for a dataset containing both Au-DP/TS-1 and Au-PVP/TS-1 were ~20x higher than any previous report (80 s^{-1} vs. 1-5 s^{-1} at 473 K) for catalytic oxidation on noble metals, suggesting that the simultaneous mechanism occurring over proximal Au-Ti sites alone is incapable of explaining the observed rate of propylene epoxidation and that short-range migration of hydrogen peroxide is necessary to account for the catalytic rate. The agreement of reaction orders, activation energy, and active site model for propylene epoxidation on both Au-DP/TS-1 and Au-PVP/TS-1 suggests a common mechanism for propylene epoxidation on both catalysts containing small intraporous gold clusters and catalysts with exclusively larger extracrystalline nanoparticles. Rates of hydrogen oxidation were found to vary proportionally to the amount of surface gold atoms. This is also consistent with the hypothesis that the observed decrease in hydrogen efficiency and PO site-time-yield per gold mass with increasing gold loading are driven primarily by the gold dispersion in Au/TS-1 catalysts.