Liquid- and vapor-phase hydrogenation of 1-epoxy-3-butene using self-assembled monolayer coated palladium and platinum catalysts

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Alkanethiol self-assembled monolayers (SAMs) have recently been shown to be effective catalyst modifiers for increasing the selectivity of the hydrogenation of 1-epoxy-3-butene (EpB) to 1-epoxybutane in the gas phase. In the results reported here, we demonstrate that SAM coatings can similarly be applied to other supported metals (Pt) and in liquid-phase reaction environments. Coating a Pt/Al2O3 catalyst with n-octadecanethiol resulted in a large improvement in selectivity during vapor-phase EpB hydrogenation, similar to that observed for supported Pd. The liquid phase hydrogenation of EpB using SAM-coated catalysts showed similar selectivity trends in some cases, but interactions of the solvent with the SAM were also important in controlling selectivity. In particular, using a heptane solvent, epoxybutane selectivity increased from 36% with an uncoated Pt/Al2O3 catalyst to 74% with a thiglycerol SAM-coated catalyst. SAM quality was shown to have a strong impact on the rate of reaction but little effect on selectivity. The results generally indicated that selectivity modification with thiol SAMs is extendable to other supported metals and a variety of reaction environments.

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1. Introduction

Methods for controlling the chemoselectivity of reactions are desirable for industrial catalysts because they reduce separations costs and increase productivity [1,2]. Recently, it was shown that the coating of a Pd/Al2O3 catalyst with alkanethiol self-assembled monolayers (SAMs) increased the selectivity for vapor-phase hydrogenation of 1-epoxy-3-butene (EpB) to 1-epoxybutane from <20% on an uncoated catalyst to >90% on a SAM-coated catalyst under equivalent conditions [3]. For this reaction, the deposition of SAMs on the Pd/Al2O3 surface increased the kinetic barrier to epoxide ring opening while the binding of the olefin functionality was not significantly changed [4]. A similar thiol SAM coating technique was also shown to increase the selectivity for the isomerization of allyl alcohols to the corresponding carbonyl compounds using a Pd nanoparticle catalyst [5]. SAM films produced from amines have been applied to catalysts for the selective hydrogenation of α,β-unsaturated aldehydes such as cinnamaldehyde and citral [6]. More generally, chiral catalyst modifiers such as cinchonidine have been used over platinum catalysts to steer enantioselectivity for the selective hydrogenation of ethyl pyruvate [7].

In previous work, the improved selectivity of EpB hydrogenation was largely attributed to the sulfur head group of the alkanethiol.

During deposition (Scheme 1), organic thiols adsorb dissociatively through cleavage of the S–H bond. Though the adsorbed monolayer is characterized by covalent bonds with the surface and has not been observed to form ion metal states, the S–metal attachment does exert a significant electronic effect on the metallic surface [3,4,8]. The thiols were found in surface science experiments to strongly suppress epoxide C–O scission while still permitting adsorption of the olefin function in a reactive pi-bound state [4].

Various “tail group” ligands were found to have little effect on selectivity; however, they played an important role in controlling activity, with longer alkyl tails being associated with higher rates. It is known that SAMs comprised of precursors with longer tail functions generally result in more ordered (e.g. “crystalline”) films as indicated by infrared spectroscopy measurements [3,8–10].

Compared to gas phase reactions, EpB hydrogenation in the liquid phase presents new possibilities for tail group effects on selectivity. For example, in some previous work, the solvent has been shown to play a significant role in catalytic hydrogenation reactions by affecting hydrogen solubility, thermodynamic interactions of the solvent and reactant, and the adsorbed structures of reagents, thus affecting the reaction pathways [11–13]. The hydrophobicity of the solvent, as measured by the dielectric constant, has also been shown to affect the enantioselectivity of 1-phenyl-1,2-propanedione hydrogenation [14]. However, not all hydrogenation reactions exhibit solvent effects. The hydrogenation of α,β-unsaturated aldehydes has been extensively studied in the liquid phase, where solvent composition was shown to have an