

## Adsorption and epoxide ring-opening of 1-epoxy-3-butene on Pt(111): Implications for selective catalysis of bifunctional molecules

Andrea Loh and J. Will Medlin\*  
University of Colorado, Boulder, CO 80309 (USA)  
\*will.medlin@colorado.edu

### Introduction

One current area of research interest is the design of catalysts that enable a reaction to be more selective towards the reaction of one functional group in a multifunctional molecule, thereby directing selectivity toward a particular product in a reaction. The design of more selective catalysts would have a broad impact, since multifunctional molecules are used in a variety of industries, including biorefining reactions to produce chemicals from biomass. One proposed method to improve selectivity is the use of bimetallic catalysts. However, not much is known as to why or how these trends in selectivity occur, and most information is indirect. Fundamental studies of the interaction of multifunctional molecules on metals are needed to better understand selectivity trends and potentially enable the design of more selective catalysts.

One reaction of interest is the hydrogenation of 1-epoxy-3-butene (EpB), a simple bifunctional molecule used in industrial processes. Hydrogenation of either the olefin or epoxide functions of the molecule lead to desired products; however, selectivity control is needed to reduce separations costs and prevent hydrogenation of both functions, which generates less valuable products. Monnier and coworkers have developed bimetallic catalysts, notably PtAg, that show promise for selective hydrogenation of the olefin function to produce 1-epoxybutane. Adsorption and reaction of EpB on Ag(110) has been studied previously. In this work, we have investigated adsorption and reaction of EpB on Pt(111) to characterize how the Pt component of bimetallic catalysts may function and suggest methods for rational design of improved catalysts.

### Materials and Methods

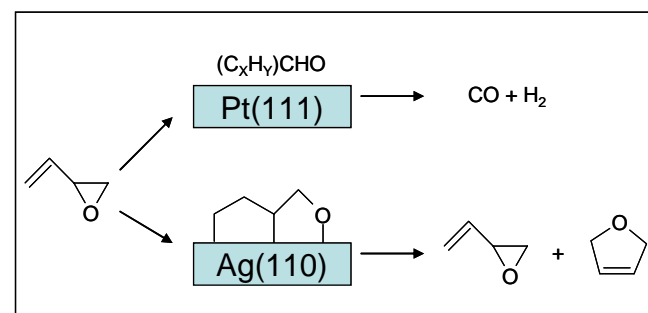
Two ultrahigh vacuum chambers were used in these experiments, both held at a base pressure below  $10^{-10}$  Torr. One chamber was equipped for high resolution electron energy loss spectroscopy (HREELS), the other for temperature programmed desorption (TPD). All experiments were performed by backfilling the chamber with 98% purity EpB (Sigma-Aldrich), using a Pt(111) single crystal as the substrate.

### Results and Discussion

Experiments have been performed with HREELS and TPD after adsorption of EpB on Pt(111) at various temperatures. EpB dosed on Pt(111) at temperatures below 150K adsorbs molecularly and desorbs from this state without reaction. This result is consistent with studies of EpB on Ag(110) and ethylene oxide on Pt(111) [1,2], in which the epoxide desorbs from a molecular state without reaction.

EpB adsorbed on the Pt surface at higher temperatures ( $> 220\text{K}$ ) undergoes epoxide ring-opening to form a stable surface intermediate. This result is consistent with studies of epoxides

on Ag(110), in which higher exposure temperatures are necessary to overcome the activation energy for epoxide ring-opening [1,3]. On Ag(110), the EpB ring-opening process resulted in isolation of a stable oxametallacycle intermediate. On Pt(111), however, HREELS results show that the ring-opened intermediate is characterized by a strong aldehyde C=O loss peak at  $1700\text{ cm}^{-1}$ , indicating that the structure may be similar to that of adsorbed crotonaldehyde. Comparison to vibrational spectra obtained after adsorption of crotonaldehyde on Pt(111) by our group and others [3] suggests a subtle difference in the structure of the EpB-derived aldehyde intermediate, likely due to irreversible loss of hydrogen from the  $\text{C}^1$  carbon. Upon heating, the EpB-derived intermediate undergoes decarbonylation to produce CO, hydrogen and surface carbon. The cumulative picture of EpB chemistry on the Pt(111) and Ag(110) surfaces is shown in Figure 1.



**Figure 1.** Ring-opening pathways of EpB on Pt(111) and Ag(110) observed after higher temperature exposures.

These results, along with results obtained from modeling studies conducted by our group, can be used to help explain trends seen in experiments with bimetallic catalysts. Monnier et al have studied the selectivity of EpB to 1-epoxybutane with different coverages of Ag on a Pt/SiO<sub>2</sub> catalyst and found that the selectivity of EpB to 1-epoxybutane increased by 22% when 1/4ML of Ag was deposited onto a Pt/SiO<sub>2</sub> catalyst. Our studies suggest that Ag interacts with the epoxide end of the molecule, suppressing aldehyde formation and allowing intact desorption of the epoxide function.

### Significance

Strategies for catalyst design to control selectivity are key for reactions of multifunctional molecules, including EpB. The results described here provide a foundation for identifying the types of surface interactions that may promote such selectivity.

### References

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