Reactions of Complex Epoxides on Silver Surfaces

Adrienne C. Lukaski and Mark A. Barteau*
Department of Chemical Engineering, University of Delaware, Newark, DE 19716
*barteau@udel.edu

Introduction

Direct oxidation processes, such as ethylene epoxidation to ethylene oxide (EO), have been extensively researched due to their commercial significance. Union Carbide first commercialized a process that converted ethylene directly to EO using oxygen and a supported Ag-catalyst in 1937 [1]. Despite almost seventy years of industrial practice, the reaction pathways of ethylene epoxidation were not well understood until recently [2-5]. The lack of a fundamental understanding of the epoxidation mechanism has limited the application of direct oxidation chemistry in synthesis of more complex epoxides, such as propylene oxide (PO).

Surface science and computational studies [2-6] identified an oxametallacycle (OME) species as the *active* intermediate in Ag-catalyzed epoxidation of both ethylene and 1,3-butadiene. This species controls selectivity through competitive ring-closure to form the epoxide and isomerization or decomposition. Linic and Barteau [2] isolated the first stable surface OME from EO on Ag(111) by activating the ring-opening process with adsorption at 250 K; the OME reformed EO near 300K during subsequent reaction plus small amounts of acetaldehyde. Oxametallacycles have also been synthesized from 2-iodo-ethanol on Ag(110) [7] and Ag(111) [4, 8], epoxybutene on Ag(110) [3] and Ag(111) , and styrene oxide (StO) on Ag(111) [5].

Surface science techniques and Density Functional Theory (DFT) are used in this study to probe the reactions of complex epoxides on Ag-surfaces. The initial part of this work explores the role of unsaturated substituents in the surface chemistry and structure of intermediates derived from epoxides and includes the recent study of StO on Ag(110). Subsequent discussion explores the effect of allylic hydrogen atoms through investigation of reactions of isoprene oxide (IO) on Ag-surfaces; the presence of allylic hydrogen and its facile abstraction by adsorbed oxygen species makes direct oxidation of propylene difficult.

Materials and Methods

Temperature-programmed desorption (TPD) and vibrational spectroscopy were used to probe surface reactions and identify active intermediates under UHV conditions. Geometric structures of intermediates on isolated Ag-clusters were optimized using the Amsterdam Density Functional software package with double-zeta basis sets and Becke88 and Perdew86 gradient approximations for the respective exchange and correlation energies; subsequent optimization of geometries on semi-infinite slabs (dacapo source code) verified the absence of artifacts induced through a terminated cluster model of the Ag-surfaces.

Results and Discussion

Styrene oxide undergoes activated ring-opening upon adsorption above 200K to form stable OME on both Ag(111) and (110); the unsaturated phenyl group interacts with the Ag-surface and stabilizes the OME relative to that derived from EO. Ring-closure and isomerization of the OME reforms the respective epoxide and aldehyde species near 505K on Ag(110). Similar to the StO-derived OME on Ag(111), DFT calculations predict that epoxide ring-opens at the carbon bound to the substituent group and adsorbs with the phenyl rings nearly parallel to the Ag(110) surface.

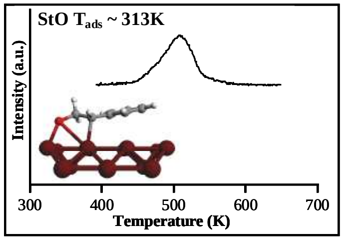

Figure 1. StO TPD and DFT-predicted OME.

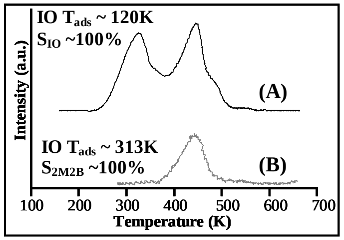

Figure 2. IO TPD A) 120K, B) 313K.

Adsorption of IO on Ag(110) at 120K forms an intermediate that reacts *solely* to reform the epoxide in two peaks at 320 and 460K; the product distribution in these two states is identical and corresponds to the gas-phase cracking pattern of IO. Adsorption of IO on Ag(110) at higher temperatures, however, leads to complete isomerization during TPD with desorption of 2-methyl-2-butenal (2M2B) a single peak at 460K. In agreement with the absence of other isomerization or decomposition products from TPD experiments, DFT calculations predict that IO ring-opens at the carbon bound to the substituent groups to form a linear OME; isomerization of this OME via hydrogen transfer forms 2M2B.

Significance

Identification of OME intermediates from complex epoxides with similar surface chemistry and structure to the active species in Ag-catalyzed epoxidation of ethylene suggests a common mechanism for olefin epoxidation. Through investigation of a variety of epoxides on Ag-surfaces, we hope to obtain a better understanding of the epoxidation pathways and facilitate the development of catalysts capable of oxidizing numerous olefins directly.

References

1. Weissermel, K. and Arpe, H.-J. in "Industrial Organic Chemistry" Weinheim, New York, 1993.
2. Linic, S., Barteau, M.A., *J. Am. Chem. Soc*, 124, 310 (2002).
3. Medlin, J.W., Barteau, M.A., Vohs, J.M., *J. Mol. Catal. A: Chemical*, 163, 129 (2000).
4. Linic, S., Medlin, J.W., Barteau, M.A., *Langmuir*, 18, 5197 (2002).
5. Enever, M., Linic, S., Uffalussy, K., Vohs, J.M., Barteau, M.A., *J. Phys. Chem. B*, 109, 2227 (2005).
6. Linic, S., Barteau, M.A., *J. Catal.*, 214, 200 (2003).
7. Jones, G.S., Mavrikakas, M., Barteau, M.A., Vohs, J.M., *J. Am. Chem. Soc*, 120, 3196 (1998).
8. Wu, G., Stacchiola, D., Kaltchev, M., Tysoe, W.T., *Surface Science*, 463, 81 (2000).