113c Mechanistic Investigation of Higher Olefin Epoxidation: Styrene Oxide and 1-Epoxy-3-Butene

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Introduction

Heterogeneous epoxidation represents an important class of chemical reactions due to the multiple uses of the epoxide products and their derivatives. Beyond the mature ethylene oxide (EO) industry and the recent development of the Eastman Chemical 1-epoxy-3-butene production process utilizing supported Ag catalysts, limited progress has been made in direct oxidation for the manufacture other epoxides. This is attributable in part to the absence of a detailed understanding of the reaction mechanisms in heterogeneous epoxidation processes.

This research utilizes surface science techniques and Density Functional Theory (DFT) to understand the interaction of higher olefin epoxides with Ag crystal surfaces. Through the elucidation of surface intermediate structures, reaction products, and kinetic parameters, information relevant to the development of epoxidation processes may be obtained in the form of reaction mechanisms leading to the desired product. Through correlation of theoretical predictions of vibrational spectra, binding energy spectra, and kinetic parameters with experimental data, relevant surface intermediates can be identified.

Through the study of the interaction of 1-Epoxy-3-Butene (EpB) and Styrene Oxide (StO) with the Ag(111) surface, the effect of different substituent groups on the surface chemistry and intermediate structure can be determined and compared with previous results obtained for EO on Ag(111) and EpB on Ag(110). In both these cases, oxametallacycle intermediates were formed. These species are characterized by the insertion of a surface metal atom into a C-O bond of the epoxide ring.

Experimental and Theoretical Methods

The experimental techniques of temperature-programmed desorption (TPD), high resolution electron energy-loss spectroscopy (HREELS), and high resolution x-ray photoelectron spectroscopy (HRXPS) were utilized to obtain kinetic data, product distributions, surface intermediate vibrational information, and C1s binding energy information respectively on the Ag(111) surface under UHV conditions.

Density Functional Theory (DFT) calculations were performed using the Amsterdam Density Functional (ADF) software package. The optimized theoretical surface intermediate structures were calculated using double-zeta basis sets on 10, 15 and 20 atom Ag clusters. ADF represents molecular orbitals as linear combinations of Slater-type atomic orbitals. Becke88 and Perdew86 gradient approximations were used to describe exchange and correlation energies respectively. A Koopman's Theorem approach was utilized to calculate theoretical C1s binding energies from DFT-generated intermediate structures.

Results and Discussion

For both StO and EpB on Ag(111), oxametallacycles were identified as the reactive intermediates on the crystal surface. TPD experiments showed that both epoxides give rise to more stable oxametallacycles than observed for EO. In the case of StO, the oxametallacycle was observed to reform styrene oxide along with phenylacetaldehyde at 485 K. These products combined with HREELS and HRXPS results indicate the preservation of the phenyl substituent and confirm theoretical predictions.

In the case of EpB, two separate desorption events were observed in TPD at approximately 300 K and 480 K. HREELS experiments and DFT suggest that these two events result from the presence of two separate intermediate structures co-existing on the Ag surface. A predominance of heterocyclic ring structures are observed in the 300 K peak, while the reformation of EpB dominates in the 480 K peak. These product distributions and DFT predictions of the similar stability of intermediates resembling the gas-phase products suggest the possibility of product selectivity control by different (cis and trans) oxametallacycle isomers.

Significance

The significance of this works lies in the identification of intermediates which may be relevant to industrial heterogeneous epoxidation processes. By confirmation of the oxametallacycle structure as the relevant intermediate in epoxidation processes and study of the effect of different substituents to the epoxide functional group, it may be possible to improve upon current industrial processes and develop methods for manufacturing other epoxides by direct oxidation methods.