

Investigating Catalyst Design Strategies for Selective Reaction of Cyclic C₄ Oxygenates from Biomass

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Introduction

The ability to design catalysts capable of high selectivity towards the conversion of a single functional group in a multifunctional molecule is a major objective for heterogeneous catalysis research.^{1,2} This need for high selectivity toward a single functional group is of growing importance in efforts to establish biorefining operations, where biomass-derived multifunctional carbohydrates are key “building block” intermediates that must be converted to commodity chemicals.³ The objective of this work is to identify methods to tailor surfaces to facilitate reaction of one functional group in a multifunctional molecule. This presentation focuses on studying structure-property relations for a series of unsaturated C₄ cyclic oxygenates and related species on catalytic metal surfaces. Possible catalyst design strategies for improving selectivity in reactions of these molecules are discussed.

Materials and Methods

High resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD) experiments were performed on Pt(111) and Pd(111) single-crystal surfaces under ultrahigh vacuum conditions. Experimental results were complemented by density functional theory (DFT) calculations employing Amsterdam Density Functional (ADF) and Vienna Ab-initio Simulation Package (VASP) software.

Two main types of multifunctional oxygenate species have been studied in detail. 1-Epoxy-3-butene (EpB) contains a 3-membered epoxide ring and an unsaturated olefin functionality. γ -Butyrolactone (GBL) and 2(5H)-furanone (25HF) each contain a five-membered lactone ring. In addition, 25HF contains a C=C bond within its lactone ring. Investigations were focused on developing a molecular-scale understanding of how these adsorbates adsorb and react on key metal surfaces for design of selective catalysts.

Results and Discussion

The detailed adsorption structures and reaction pathways have been mapped for EpB and a key isomer, 2-butenal, on both Pt(111) and Pd(111). On both surfaces, the EpB epoxide ring opens irreversibly at temperatures above ca. 220 K to form an aldehyde structure while the C=C functional group has a strong interaction with the surface. DFT calculations have been employed not only to identify adsorption structures, but also to suggest surface structures that may give rise to improved selectivity (figure 1).⁴ These studies have suggested the Ag/Pt surfaces orient the EpB adsorption structure to favor selective reduction of the olefin function. This hypothesis is consistent with recent studies on bimetallic supported Ag/Pt catalysts.⁵

Recent studies of the adsorption and thermal reaction of 25HF also indicate that the olefin group interacts strongly with a platinum or palladium metal surface, and therefore plays a role in determining how the molecule reacts. As in the decomposition of EpB, 25HF decomposes by ring-opening on both Pd(111) and Pt(111), though the reaction pathways on the two surfaces are clearly different, indicating likely differences in catalytic reaction chemistry. Implications for catalyst design in reactions of furanic compounds on transition metals will be discussed.

Significance

The ability to design catalysts to selectively react single functional groups in multifunctional molecules has widespread applications within the field of biorefining and beyond.

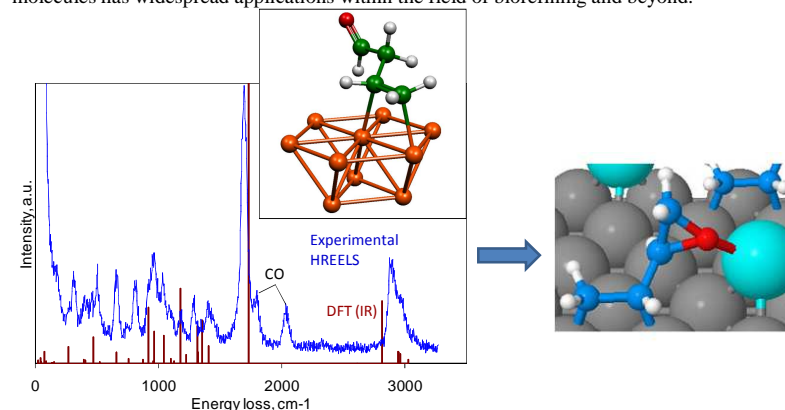


Figure 1. A combination of spectroscopic techniques and DFT calculations are used to understand reaction pathways of multifunctional molecules such as EpB (pictured) and 25HF. These studies on model surfaces are employed to identify surface structures that impart desired adsorbate-surface interactions.

References

1. Somorjai, G.A. and Yang, M.C. *Topics in Catalysis* 24, 61 (2003).
2. Mohr, C., Hofmeister, H., Radnik, J., and Claus, P. *J. Amer. Chem. Soc.* 125, 1905 (2003).
3. Davda, R.R., Shabaker, J.W., Huber, G.W., Cortright, R.D., and Dumesic, J.A. *Appl. Catal. B-Environ.* 56, 171 (2005).
4. Loh, A.S., Davis, S.W., and Medlin, J.W. *J. Amer. Chem. Soc.* 130, 5507 (2008).
5. Schaal, M., Pickerell, A., Williams, C., Monnier, J. *J. Catalysis* 254, 131 (2008).