Investigating catalyst design strategies for selective reaction of cyclic C4 oxygenates from Biomass

Clay Horiuchi and Dr. Will Medlin
Department of Chemical and Biological Engineering
University of Colorado at Boulder
Boulder, Colorado, USA

March 10, 2009
Biorefinery overview

Biochemical conversions (Fermentation)

Biomass → Carbohydrates → Commodity & fine chemicals

Lipids → High-cetane diesel

Thermochemical conversions (Reforming)

Biomass → Syn gas

Syn gas → FT liquids

Syn gas → Methanol

Methanol → MTG liquids

Tar removal

Carbohydrate “Building Blocks”
The goal of this project is to design catalysts that are highly selective for reactions of multifunctional molecules.

- Applications throughout heterogeneous catalysis and huge potential in biorefining.
Catalyst selectivity might be improved by using a bimetallic catalyst

- Degree of interaction between each functional group and the catalyst surface will determine reactivity
Must first develop molecular-level understanding of surface-adsorbate interactions on individual metals
This work focuses on surface studies of cyclic multifunctional probe molecules

- Multifunctional species:
  - 3-membered ring
    - 1-Epoxy-3-butene (EpB)
  - 5-membered rings
    - 2(5H)-Furanone (25HF)
    - γ-butyrolactone (GBL)

- Contain four carbons, multifunctional oxygenates
- Useful model molecules for complex biorefining “building blocks”
Surface science approaches used to develop molecular-level understanding

Methods for studies on single crystals

- High Resolution Electron Energy Loss Spectroscopy (HREELS)
- Temperature Programmed Desorption (TPD)
- Density functional theory (DFT)

Pt(111)  Pd(111)  Ag(110)
Use EpB to refine strategy for designing a selective catalyst

EpB = 3,4 epoxy-1-butene
crotonaldehyde = 2-buten-1-al
crotyl alcohol = 2-buten-1-ol
3-Bu-1-ol = 3-buten-1-ol

n-butanal = n-butyraldehyde
n-BuOH = n-butanol
BO = butylene oxide (epoxybutane)

Schaal et al, J Catalysis 254 (2008) 131
At low temperatures, EpB on Pt(111) adsorbs through olefin function. 

The diagram shows the energy loss spectra with markers for different intensities:

- **6.0 L**: (C=C) stretch
- **2.0 L**: Di-sigma bound (C-H) stretch
- **1.0 L**: Epoxide deformation

The graph, labeled as Loh, Davis, Medlin, JACS 130 (2008) 5507, illustrates the adsorption process with molecular structures indicating the bonding nature.
EpB undergoes irreversible ring-opening to form an aldehyde on Pt(111) by 230 K

C¹=O aldehyde
C¹-H aldehyde

Epoxide ring opens
Di-sigma bonded

Loh, Davis, Medlin, JACS 130 (2008) 5507
EpB / Pt(111) TPD: EpB decomposes by decarbonylation and dehydrogenation

Loh, Davis, Medlin, JACS 130 (2008) 5507
To summarize EpB results:

- On Pt(111):
  - Binds primarily through C=C
  - Ring opens irreversibly
  - Undergoes decarbonylation and dehydrogenation

- On Ag(110) (previous work):
  - Forms oxametallacycle intermediate
  - Ring opens reversibly
  - Can desorb as molecular EpB

Loh, Davis, Medlin, *JACS* 130 (2008) 5507
Selectivity to various products is a sensitive function of surface composition

- Supported bimetallic catalyst (Ag-Pt/SiO$_2$) improves selectivity

Now progress to more complicated probe molecule

- Start by studying the probe molecules on Pd(111) and Pt(111)
25HF reacts differently on Pt and Pd. 25HF ring opens and reactions proceed through unique intermediates. Adsorbed through olefin. 25HF reacts differently on Pt and Pd. 25HF ring opens and reactions proceed through unique intermediates. Adsorbed through olefin. Small dose does not saturate the surface. Large dose saturates and forms multilayers. Small dose does not saturate the surface. Large dose saturates and forms multilayers.
25HF TPD results show decarbonylation and dehydrogenation

[Diagram showing TPD results for Pd(111) and Pt(111) surfaces with peaks at m/e=2 (H₂), m/e=28 x 1/10 (CO and CO₂), m/e=44 (CO₂), m/e=4 (25HF), and m/e=55 x 3 (25HF).]
Reaction schemes for 25HF

- 25HF proceeds through distinct intermediates on Pd(111) and Pt(111)

Vinyl acetate
TPD results for GBL show decarbonylation and dehydrogenation

- Unlike 25HF, CO$_2$ is produced from both Pt and Pd
HREELS GBL on Pd(111)

- Different intermediate than 25HF
- Shift indicates decarbonylation to surface-bound CO
- Ring-opening reaction occurs at lower temperature for GBL
Surface science approaches facilitate an understanding of trends in adsorption and reaction of unsaturated cyclic oxygenates:

- Adsorption on Pd and Pt dominated by adsorption through olefin
- Activated ring-opening reactions dependent on structure of the ring

Combining observations from different surfaces allows design of catalysts for selective oxygenate conversions.
“Knowledge is in the end based on acknowledgement.” - Ludwig Wittgenstein

- Medlin group members
  - In particular:
    - Dr. Dylan Kershner
    - Steve Marshall
    - Meghana Rangan
    - Wenyu Zhang
    - Ben Israel

- Funding sources
  - NSF
  - U.S. Dept of Ed. GAANN
  - CU Graduate School
Results of surface science studies

Comparison of EpB intermediates

Adsorbed through olefin

Di-sigma bonded

Epoxide ring opens Aldehyde species forms

Intermediate decomposes via Decarbonylation and Dehydrogenation

Pt(111)

Pd(111)

Energy loss, cm$^{-1}$
DFT helps in assigning vibrational modes, suggests furanone adsorbed in tilted configuration through olefin.
Adsorption and reaction of EpB on Pd(111)

Epoxide ring deformation

C'\text{=}O aldehyde

C'\text{-H aldehyde}

EpB adsorbs through olefin group

Epoxide ring opens

Perhaps better to put in EpB/Pt b/c the di-sigma thing is more clear?

CH₂ twisting/rocking

CH₂ scissoring
TPD results for EpB on Pd(111) indicate decarbonylation and dehydrogenation reactions

- CO and H$_2$ are major products
- Small amounts of propylene (m/e=41)
- NO EpB re-forms
Summary of “design” cues for EpB and 25HF

- Low temperature adsorption on Pt and Pd occurs (primarily) through olefin function, suggesting potential for selective C=C hydrogenation.
- Irreversible ring-opening occurs by 200 K for EpB and by 300 K for 25HF on Pd and Pt.
- Ring-opening of epoxides on Ag surfaces has been observed to be...
At low temperature, 25HF on Pt111 adsorbs through olefin functionality.

Got rid of peak labels. Now identify major modes (C=O, C-H, etc). OK, sounds great.

This cartoon could be improved – C=O closer to parallel.
HREEL spectra show clear differences between ring-opened EpB on Pt vs. Pd (111)

Aldehyde formation and decarbonylation clearly observed on both surfaces....

... but intermediate on Pd(111) is likely to be more dehydrogenated

Loh, Davis, Medlin, JACS (2008)
TPD results for EpB on Pd(111)

- H₂ desorption becomes more activated at higher coverage (harder for C-H scission to occur as surface gets more crowded)
Compare EpB and Crotonaldehyde

Virtually identical on Pd(111).
Similar but not identical on Pt(111).
25HF multilayers on Pd and Pt
How HREELS works
Selection Rules

- Long-range dipole scattering and short-range impact scattering

- Dipole scattering:
  - ~3 nm
  - Electric field of moving electron interacts with scatterer; electron acts as a wave
  - Electrons are reflected specularly

- Impact scattering:
  - ~0.2 nm
  - Electron exchanges momentum with scatterer; electron acts as a particle
  - Electrons are reflected diffusely
EpB on Pd(111) adsorbs through olefin functional group

HREELS indicates EpB is bound preferentially through olefin group

Why don't I see a C=C at high coverage? And why is there a C=O stretch?
Illustration of HREELS vibrational modes and multilayer formation