Deoxygenation of Furfural on Pd-based Catalysts:
The Effect of Adsorption Orientation

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Introduction
Multifunctional oxygenates, molecules that possess multiple functional groups with at least one group containing oxygen, are prevalent as intermediates in the decomposition of biomass. In particular, aromatic oxygenates such as furfural and benzyl alcohol can be produced by acid-catalyzed dehydrations and partial pyrolysis [1, 2]. Compared to simpler petroleum feedstocks, relatively little is known about the metal-catalyzed reactivity of these complex compounds. One particular reaction of interest is hydrodeoxygenation where the oxygen content of the feed is reduced while preserving the number of carbon atoms in the molecule. This presents a challenge for the catalysis community because over highly active catalysts such as Pd, complete hydrogenation or decarbonylation pathways are favored.

This contribution focuses on experimental and computational investigations into the reaction mechanisms of deoxygenation and decarbonylation from multifunctional oxygenates and control of reaction selectivity via rational catalyst design [3, 4]. Temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) are used in conjunction with density functional theory (DFT) calculations to elucidate the adsorption and reaction pathways of these compounds on Pd catalysts.

Materials and Methods
Surface science experiments were performed by exposing molecules to the Pd(111) single crystal surface at 150 K through a direct dosing line facing the sample. TPD experiments were performed by increasing the temperature at a rate of 60 °C/min and desorption products were monitored by a mass spectrometer. HREELS experiments were conducted at a specular angle of 60° with respect to the surface normal using LK Technologies ELS5000.

DFT calculations were performed using the Vienna Ab-Initio Simulation Package (VASP). The exchange-correlation energy was calculated using the revised Perdew-Burke-Ernzerhof (rPBE) functional [5]. Van der Waals interactions were accounted for using Grimme’s DFT-D2 method [6]. The Brillouin zone was sampled using a 7x7x1 k-point grid and the plane-wave cutoff energy was 360 eV.

Gas-phase hydrogenation experiments were conducted using 5 wt% and 1 wt% Pd/Al2O3 in a tubular packed bed flow reactor at atmospheric pressure and constant furfural partial pressure. The hydrogen-to-reactant molar ratio was kept constant at 25:1.

Results and Discussion
HREELS experiments reveal that the orientation of adsorbates on surfaces can be influenced by the coverage of the adsorbates. At low coverage, aromatic oxygenates like benzyl alcohol adsorb with the ring parallel to the surface in a flat-lying structure. As coverage increases, some molecules adsorb through the hydroxyl oxygen with the ring extending into vacuum, more upright than the other proposed structure. These structures are investigated using DFT calculations, and reveal that for furfuryl alcohol, the flat-lying structure is much more energetically favorable compared to the upright structure, suggesting that the flat-lying structure will be formed if there are available surface sites. HREELS experiments are correlated with exposure-dependent TPD to examine the effect of coverage on product distribution. At low coverage, decarbonylation and complete decomposition dominates. However, as coverage increases, deoxygenation reaction begins to occur alongside decarbonylation. These reactions are summarized in Scheme 1.

The energetics of dehydrogenation and deoxygenation reactions are computed using DFT and reveal that the two structures have different propensities for reaction. From the flat structure, dehydrogenation is strongly preferred. From the upright structure, dehydrogenation is still preferred but deoxygenation becomes competitive. The products from TPD can be examined more closely by pre-exposing the Pd(111) surface to deuterium. This experiment reveals that methylfuran is produced by two mechanisms; a methylfuran peak at 385 K incorporates up to three deuterium atoms while the peak at 345 K incorporates none. We propose that methylfuran can be produced by bimolecular interaction between adsorbates.

Using the insight gained from surface science experiments, gas-phase hydrogenation of furfural is conducted using a variety of catalyst modifiers such as a co-flow of carbon monoxide, selectively deposited Au atoms, and alkane-thiolate self-assembled monolayers to improve selectivity on Pd catalysts. Because carbon monoxide forms a well-ordered pattern on Pd and reduces the number of contiguous surface sites, the flat-lying geometry should be more difficult to form than on the clean surface. This is evidenced by reduced selectivity to furan and increased selectivity to furfuryl alcohol and methylfuran.

Significance
This contribution makes progress towards understanding the surface-mediated mechanism of deoxygenation and catalyst design towards selective hydrodeoxygenation.

References