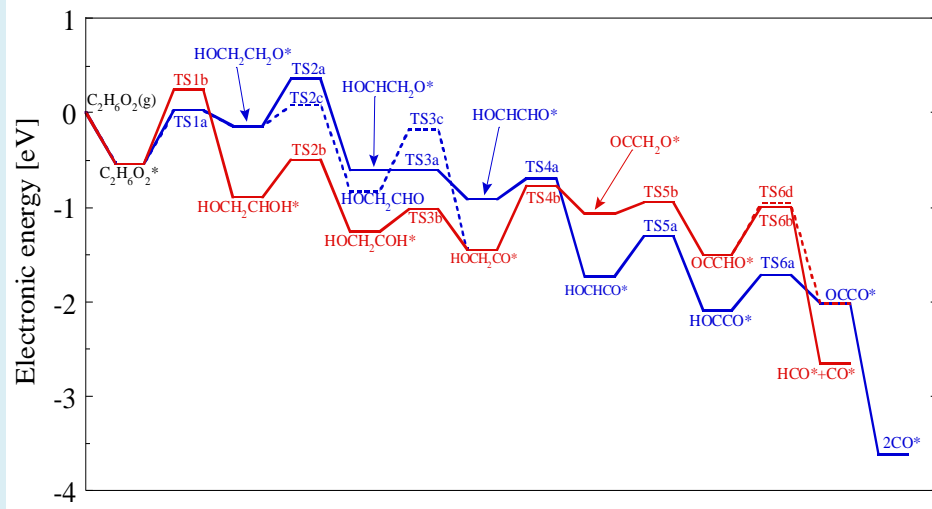


First-Principles Simulation and Model-Driven Isotopic Labeling Experiments Reveal Biomass Decomposition Pathways¹

Potential decomposition pathways of $C_2H_6O_2$ on Pt(111)

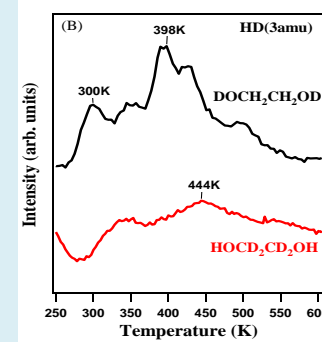
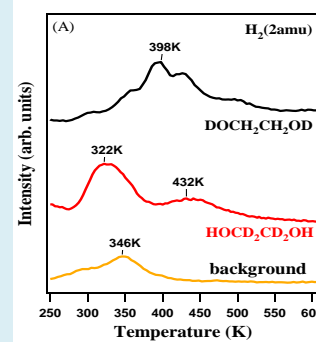


Initial O-H bond cleavage is favored energetically over initial C-H bond cleavage. Further, downstream C-C bond cleaving barriers are lower than initial dehydrogenation barriers

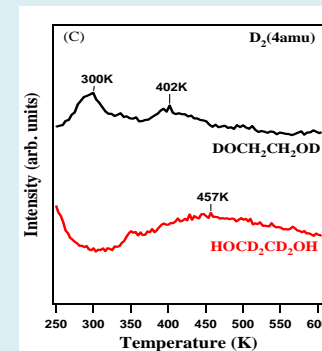
Key Findings:

- Density functional theory (DFT) calculations of ethylene glycol decomposition on Pt(111) and Ni/Pt(111) reveal key differences between decomposition of highly functionalized oxygenates compared to mono-alcohols and hydrocarbons
 - Very low C-C scission barriers exist for highly dehydrogenated $C_2H_XO_2$ surface intermediates
 - Highest barriers correspond to early O-H and C-H reactions
- Reaction pathway changes between Pt and more active Ni/Pt
 - Decomposition on Pt proceeds through initial O-H bond cleavage followed by scission of C-H and O-H bonds
 - Ethylene glycol decomposition on Ni-Pt-Pt shows formation of the 1,2-dioxyethylene (both O-H bonds break initially) (right)

Theory driven experimental confirmation



Temperature programmed desorption (TPD) of deuterated ethylene glycols confirms that reaction occurs through initial O-H bond cleavage, followed by C-H and O-H bond cleavage on Pt(111).



DFT comparison of pathways over Pt and Ni/Pt

