

Untangling Complexities of Selective Carbon-Oxygen Bond Activation using Multiscale Modeling and Quantum Theory Development

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Selective carbon-oxygen bond activation in C_{2+} molecules represents an essential part of the carbon-neutral, solar energy-based economy of the future. In biomass-mediated pathways, the initial CO_2 reduction and C-C coupling are carried out through biochemical photosynthesis in photoautotrophic organisms. The resulting chemicals and bioproducts are typically over-oxygenated. Subsequently, selective C-O bond scission in fatty acids, glucose, glycerol, and furans is conducted to remove some of the excess oxygen. Despite a plethora of proposed heterogeneous catalysts, the C-O activation mechanism and peculiarities of catalyst reactivity remain poorly understood.

In this thesis, we report the discovery of a radical-mediated C-O bond activation mechanism on the multifunctional Ru/RuO_x catalyst that enabled 2-methyl furan production from furfural with up to 76% yield at temperatures <200°C. To the best of our knowledge, this was the first evidence of a low-temperature radical *reduction* mechanism in heterogeneous catalysis. The breakthrough was made possible by extensive exploration of various catalytic site architectures and reaction mechanisms using density functional theory, together with microkinetic modeling that showed agreement with experiment in both ultrahigh vacuum and liquid phase, thus bridging the pressure gap.

Through collaborative experimental/computational work, we show the mechanism generality by identifying a wide range of reducible oxides that can catalyze the C-O bond scission on vacancies. Moreover, we find reactivity trends for saturated vs. unsaturated compounds to be fully consistent with computational predictions regarding the positive effect of conjugation on C-O bond scission rates.

We obtain computational evidence that a similar mechanism is at play on 3-4 nm PtCo nanocrystals, covered with a CoO_x monolayer, and is responsible for ultrahigh yields (99%) of 2,5-dimethylfuran from 5-(hydroxymethyl)furfural. The catalyst structure and the reaction mechanism are fully consistent with EXAFS, XANES, XRD, TEM, chemisorption, and reactivity data.

Advancements in mechanistic understanding were made possible by development of first principles microkinetic models, specifically designed to simulate experiments involving isotopically labeled species and to predict mass fragmentation patterns. Initial work led to the discovery of the ring-opening deuteration mechanism that shed light on the roles of substituent groups and of solvent on deuteration rates of furanics. The mechanism was in stark contrast to the commonly known Brønsted acid-catalyzed mechanism.

Over the course of our studies, we encountered challenges associated with reliable reaction rate predictions on metal oxide catalysts, revealing deficiencies of current quantum mechanical methods. To address them, we propose a non-empirical quantum-theoretical framework, aimed to describe electronic structure of such materials more accurately. Remarkably, the rigorous quantum theoretical basis of the method makes it applicable also to molecules and metals, demonstrating a consistently improved description of chemical bonding across the chemical compound space. The newly developed method holds promise to make first principles predictions in catalysis, especially metal oxide catalysis, more reliable and at minimal extra computational cost.