

Leveraging First-Principles Modeling for Deeper Insights into Biomass Processing

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Demand for sustainable products is increasing due to growing awareness of the environmental liabilities of petroleum-derived fuels and chemicals. This has driven investment in alternative, renewable chemicals from biomass. To enable production of these new chemicals, novel processes and catalysts must be developed to achieve efficient processes with high yields. However, designing catalysts and reactors for biomass presents new challenges in catalysis, including catalysis of highly oxygenated biomass feedstocks with diverse functional groups, and accounting for reactions in the condensed phase.

One such process is the “furans platform,” in which biomass-derived sugars are dehydrated to form furan derivatives, which can be modified to form a wide variety of useful fuels and chemicals. 5-hydroxymethylfurfural (HMF) is one of these furan derivatives, and can be produced from cellulose through isomerization of glucose to fructose, and dehydration of fructose to HMF. Major issues in HMF production include the high cost of fructose, as well as side reactions in dehydration. To address these concerns, we have leveraged electronic structure calculations to better understand (1) solvent effects relevant to HMF stability, (2) the active sites in catalysts for glucose isomerization, and (3) fructose ketalization reaction that boosts fructose yields from glucose via a new catalyst.

In the acid-catalyzed dehydration of fructose, the stability of the product HMF was found to be dramatically improved by the addition of certain organic co-solvents, but the fundamental reasons were not understood. To develop deeper fundamental understanding into these interactions and their effects on reaction chemistry, electronic structure calculations are integrated with IR spectroscopy and kinetic studies conducted by experimentalists in the Catalysis Center for Energy Innovation (CCEI). HMF stability and solvation are probed using IR spectroscopy, and an important descriptor of the observed solvent-induced frequency shifts is identified: the Guttmann Acceptor Number (AN), a measure of solvent Lewis acidity. Using a model that could accurately predict the solvent-induced frequency shifts, the underlying mechanisms behind the shifts are discovered and the origin of the stability of HMF in co-solvent mixtures is identified.

Glucose isomerization to fructose is a critical step in forming HMF, and the Sn-Beta zeolite is a useful heterogeneous Lewis acid catalyst for isomerization. However, Sn-Beta as-synthesized contains a distribution of active sites, and modifications of the zeolite, for example, with Na-exchange, affect these active sites and their chemistry. To better understand the complex heterogeneous Sn-Beta, three homogeneous analogues (Sn-silsesquioxanes) are synthesized and characterized by CCEI experimentalists to investigate how particular changes in the active site structure affect glucose isomerization to fructose and to mannose, a side product. In addition, reaction networks for glucose isomerization are computed using electronic structure methods. Integrating these experiments with theory leads to new understanding on the catalytic roles of the Sn-O-Si moiety, the acetylacetonate ligands, and the SiOH group, for these sugar chemistries.

To characterize the distribution of active sites in Sn-Beta, an exhaustive survey is performed to probe the relative stability of the possible open site geometries. The T1 and T9 sites are most thermodynamically favored, although substitution at the different T sites yielded fairly similar energies. More importantly, the relative positions of the SnOH and the SiOH in the open site are not adjacent, as reported in prior literature, but the SiOH is opposite the SnOH. This geometry creates unusual Brønsted acidity when strong bases, such as NH₃ and pyridine, are adsorbed, because the Sn can stabilize the SiOH oxygen, increasing the acidity of the proton. Characterizing the active site of Sn-Beta, as well as identifying the source of Brønsted acidity inferred by recent experiments, could assist future modeling efforts that utilize this active site geometry.

The highest glucose to fructose yield by Sn-Beta is 33%, but a new catalyst, Sn-SPP (Self-Pillared Pentasil zeolite with framework Sn sites) can achieve a record 65% yield. In ethanol solvent, Sn-SPP catalyzes a novel reaction: fructose ketalization to ethyl fructoside. When coupled with glucose isomerization to fructose, ketalization removes the fructose product *in situ*, permitting yields greater than the glucose/fructose equilibrium without ketalization (50%). However, many fundamental questions were unanswered by the experimental work, including how the structure of the active site enables this chemistry, why Sn-SPP performs ketalization while Sn-Beta does not, and why fructose ketalization is catalyzed but not glucose acetalization. These questions are answered using periodic DFT calculations. The most thermodynamically stable active site geometries indicate the active site of Sn-SPP is a “closed” Sn site with three adjacent silanol groups, while the active site of Sn-Beta is a hydrolyzed Sn site with a single, more distant silanol group. Identification of the most favorable ketalization mechanism reveals that the silanols in Sn-SPP facilitate ketalization through key H-bonding interactions at the transition state. However, the silanol in the Sn-Beta active site is not positioned to stabilize the TS, giving a larger barrier and indicating why Sn-Beta is not active for this chemistry. Analyzing glucose acetalization reveals differences in stability of the key oxonium intermediate at the respective transition states, indicating the reason for the remarkable selectivity of this process for fructose ketalization over glucose acetalization.

In summary, this dissertation contributes the first computational study on solvent-induced frequency shifts and their role in solvation and determination of liquid structure, which contributed to understanding of the enhanced stability of HMF by polar aprotic co-solvents. In addition, reaction mechanisms are presented for glucose isomerization on homogeneous Sn-silicate catalysts, and the role of catalyst structure on reactivity and selectivity. Key features of the Sn-Beta active site were identified, explaining the observed Brønsted acidity in Sn-Beta. The first computational study of ketalization and acetalization is also presented here, in the context of explaining the unique reactivity of the mesoporous Sn-SPP due to its unique active site.

Application of computational modeling will continue to improve fundamental understanding of biomass catalysis. Several next steps inspired by the current work are discussed, including pairing DFT with other spectroscopic techniques to characterize liquid structure, developing water-stable Sn-silsesquioxanes for Sn-Beta active site characterization, and leveraging fructose ketalization as protecting-group chemistry to improve yields in one-pot glucose to HMF reactors.