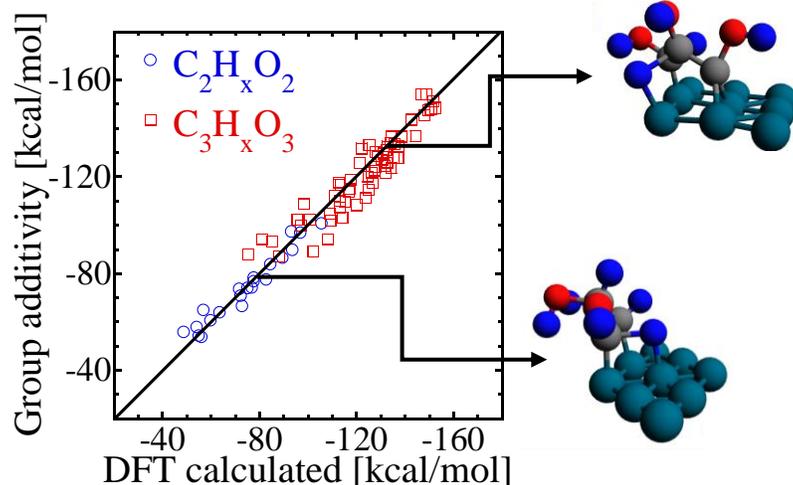




Computational Methods Predict Thermochemistry and Kinetics of Biomass Derivatives on Transition Metals

This research was conducted by the groups of Dion Vlachos, Jingguang Chen and Mark Barteau at the University of Delaware.

First-principle simulation of biomass processing is hindered by the sheer size of biomass derivatives and the associated computational cost of quantum calculations. Researchers at the University of Delaware developed a new framework for estimating thermochemistry of oxygenated species and rate constants on transition metals that drastically reduces the expense involved in kinetic modeling of biomass catalytic processing. This methodology allows for an inexpensive screening of a reaction mechanism that can be followed by refinement of sensitive mechanistic parameters via a limited number of (expensive) quantum calculations. The framework has been applied to ethylene glycol and glycerol decomposition chemistry on platinum to reveal interesting reactivity trends. It has been found that initial C-H bond scission reactions in the mechanism are rate controlling, whereas C-C bond cleavage is expected to be fast under typical thermal decomposition conditions. The heats of formation of oxygenate-surface intermediates calculated via group additivity are compared to those via density functional theory for ethylene glycol and glycerol decomposition intermediates in the figure. Very good agreement is seen. Part of this framework is described in a recent publication.^[1]



Parity graph comparing first-principle density functional theory (DFT) calculations to semi-empirical, excel-based group additivity values along with snapshots of structures of oxygenated species on Pt manifesting the multi-dentate nature of binding of these adsorbates.

RELEVANT PUBLICATION:

^[1] Saliccioli, M; Chen, Y.; Vlachos, D.G., “Density functional theory-derived group additivity and linear scaling methods for prediction of oxygenate stability on metal catalysts: Adsorption of open-ring alcohol and polyol dehydrogenation intermediates on Pt-based metals,” *Journal of Physical Chemistry C*, 114(47), (2010). [DOI: 10.1021/jp107836a]