Semi-empirical thermochemical property estimation for biomass derivatives on transition metal surfaces

Density functional theory (DFT) has become an essential tool in estimating thermochemistry and activation barriers in heterogeneous catalysis. For small molecules, we have been able to elucidate reaction mechanisms and parameterize kinetic models that reproduce experimental data with high accuracy[1]. A shift towards modeling larger biomass derivatives interacting with metal surfaces introduces new levels of complexity, including longer computational time, multiple adsorption conformations, and a greater number of intermediates and elementary steps due to multiple pathways encountered in this chemistry. For example, furfural, an important biomass derivative, can undergo hydrogenation, hydrogenolysis, decarbonylation, and even ring opening depending on the metal catalyst[2], making it impractical to compute all possible intermediates, conformations, and reaction barriers with DFT, even on a single metal surface.

In this work, we present a DFT-parameterized semi-empirical scheme capable of predicting thermochemical properties of furan-related intermediates on metal surfaces. This model extends prior group additivity for open-chain molucles[3] to account for furan ring corrections, such as ring deformation. The properties include the heat of formation, entropy, heat capacity, and the dispersion contribution to the heat of adsorption, estimated using dispersion-corrected DFT (D3) and statistical mechanics formulae. For the proposed model, the vibrational and rotational contributions of gas-phase-like groups are estimated using G4-level calculations. We find that the group additivity scheme developed for open-chain molecules is inaccurate for furanics. We report 17 new groups, involving heteroatom-nearest neighbor interactions and 4 new corrections that account for furan ring deformation and the level of ring hydrogenation. Furthermore, we extend the thermochemistry scheme so the thermochemistry estimation can be applied to multiple metal catalysts as a generalization of the linear scaling relations[4] introduced for small molecules. We demonstrate how to construct energy diagrams for various catalysts by combining these methods with linear free energy relations. Comparison of the pathways of furfural chemistry on a select number of metals will be shown.

References

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