

Interaction of Solvent, Reactive Species and Surface in Heterogeneous Catalysis: Experiments and Modeling

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Introduction

With the ongoing transition of the chemical industry towards renewable carbon resources, liquid processes are becoming increasingly relevant. Consequently, there is an increasing focus on processes involving solvents, adding a new facet to the choice of the solvent-reactant pairing, particularly in heterogeneous catalysis. This influence can be observed, for example, in the chemo- and stereo-selective hydrogenation of acetophenone, which serves as an industrially significant model compound for hydrogenation. However, despite the increase in degree of freedom in solvent and reactor design, the interaction of solvent, reactive species, and surface has rarely been explored. Therefore, the objective of this study is to develop a comprehensive model of solvent affected reaction kinetics based on kinetic measurements examining how solvent properties interact with catalytic performance in the hydrogenation of acetophenone. This model will serve as a starting point for an optimized reactor design, considering the choice of solvent and catalyst, and addressing the challenges posed by the transition to renewable resources. [1,2]

Laboratory set up for kinetic measurements

To address this, we present an advanced laboratory setup integrating a Berty-type reactor for precise kinetic measurements, coupled with Raman spectroscopy employing immersion optics. This setup enables real-time monitoring of reaction dynamics in multiphase systems, providing valuable insights into solvent effects under varying conditions. In pursuit of fundamental insights across a broad spectrum of influencing parameters, we aim to vary not only the reactive surface but also the solvent choice, temperature, and hydrogen pressure.

Kinetic modeling approach

In our kinetic modeling approach, we employ Transition State Theory (TST) and Free Linear Energy Relationships (LER) to elucidate underlying mechanisms and predict

reaction rates as a function of solvent properties. TST facilitates the identification of energy barriers at transition states along the reaction pathway, while LER establishes correlations between free energy changes and reaction kinetics constants. To comprehensively describe solvent parameters and their influence, solvatochromic parameters are employed. Typically, these parameters are determined using ambient temperature and pure substance data. However, to gain deeper insights into their behavior in reaction environments, we conduct measurements under comparable conditions [3,4,5].

Temperature and pressure dependence of solvatochromic parameter

Our preliminary findings highlight the temperature and pressure dependence of solvatochromic parameters, with a particular focus on Kamlet and Taft parameters [6]. These parameters are invaluable in indicating solvent behavior, especially in terms of solvatochromism. Figure 1 illustrates initial results of the concentration and temperature dependence of Kamlet and Taft parameters using acetophenone in ethanol as the model system. The color map represents an empirically fitted correlation, enabling the calculation of solvatochromic parameters based on temperature and pressure variations. These parameters are then integrated into the reaction kinetic model.

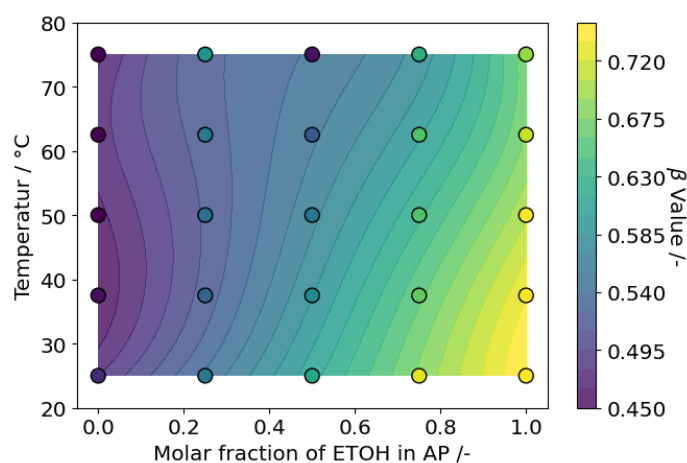


Figure 1: The dependence of the beta parameter on the solvent molar fraction and the temperature; Data points are measurement data; the color map is based on a first correlation. Adapted from [6]

References

- [1] Bertero et al. Applied Catalysis A: General 394, 2011
- [2] Yoshida et al. Green Chem., 17(3), 2015
- [3] Gengnan et al. Surf. Sci. Rep. 76(4), 2021
- [4] Pots et al. Chem. Soc. Rev. 50, 2021
- [5] Folic et al. AIChE Journal, 53(5), 2007
- [6] Zeppenfeld BA Thesis, TU Dortmund, REC, 2024