Reaction Kinetic Analysis of Solvent Effects in Heterogeneous Catalysis on the Example of the Hydrogenation of Acetophenone

Maximilian Gstettenbauer, Karl Steffen Wulle, Marion Börnhorst, Hannsjörg Freund

TU Dortmund University,

Institute of Reaction Engineering and Catalysis, Dortmund, Germany

Motivation

As the chemical industry transitions towards renewable carbon resources, liquid-phase processes such as the hydrogenation of biomass-based compounds using heterogeneous catalysts are becoming increasingly important. While solvent effects have been extensively studied in homogeneous catalysis, the critical influence of solvent-reactant interactions in heterogeneous catalysis and reactor design, where solvent polarity, hydrogen solubility, and adsorption phenomena govern both catalyst and reactor performance, remains largely unexplored. For integrating solvent and reactor design, a detailed consideration of solvent-reactant-surface interactions in reaction kinetic models is required. Therefore, the objective of this study is to develop a comprehensive kinetic model that captures solvent effects on reaction rates based on detailed kinetic measurements. This model links solvent properties to catalytic performance and serves as a foundation for improved multiphase catalytic reactor design. [1, 2]

Methodology and Reaction System

The heterogeneously catalyzed hydrogenation of acetophenone (AP) serves as a model reaction system (see Fig. 1 a), representing a chemo-selective hydrogenation allowing for a systematic study of the interplay between solvent properties and reaction and mass transport kinetics. [3]

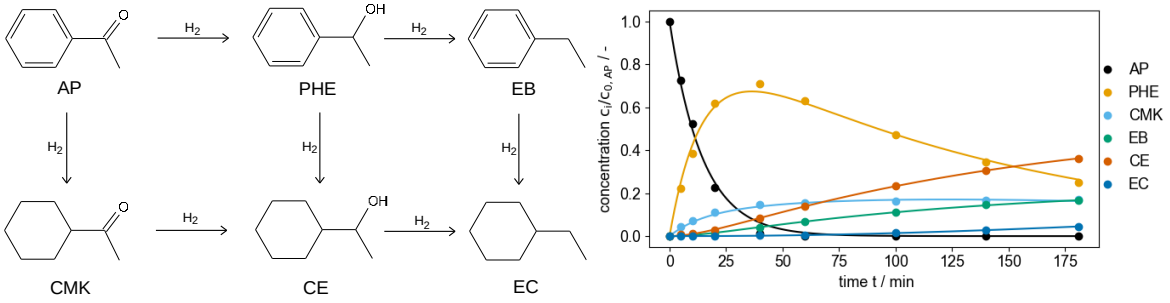

Figure 1: a) Reaction scheme for the hydrogenation of acetophenone (AP) consisting of parallel reactions to phenylethanol (PHE) and cyclohexyl-methyl-ketone (CMK), followed by consecutive reactions to cyclohexyl-ethanol (CE), ethylbenzene (EB) and ethyl-cyclohexane (EC) [4], and b) Reaction concentration profile normalized with the initial concentration of AP (0.64 mol L^{-1} in isopropanol, 10 bar, 80 °C, 0.08 mg mL^{-1} Rh).

An advanced laboratory setup was developed, combining a high-pressure reactor for precise kinetic measurements with in-situ Raman spectroscopy using immersion optics and complementary GC analysis. Batch reactor experiments were performed under systematic variation of fifteen different solvents, solvent mixtures, temperature, and hydrogen pressure. A commercial Rh/Al_2O_3 catalyst (Sigma Aldrich) was used.

Incorporation of Solvent Influence in Kinetic Model

The concentration profiles shown in Figures 1 and 2 reveal a pronounced solvent influence on the kinetic behavior and product selectivity, while water and polar protic solvents display the highest reaction rates. To describe and evaluate the solvent effects, a simplified pseudo-first-order power-law model was applied to compare apparent kinetic constants across various solvents.

The kinetic data were correlated with the hydrogen solubility and the Kamlet–Taft parameters (e.g., solvent polarity) to interpret these trends on a phenomenological level. To move beyond descriptor-based correlations, mechanistic kinetic models were subsequently explored to capture solvent influences on individual surface reaction steps. These models indicate that the dominant solvent effects arise from proton-transfer processes, potential transfer-hydrogenation pathways, and competitive adsorption at the catalyst surface. Incorporating these interactions is essential for a mechanistic understanding of solvent-mediated catalysis and constitutes a critical step toward predictive models for rational solvent selection in catalytic process design.

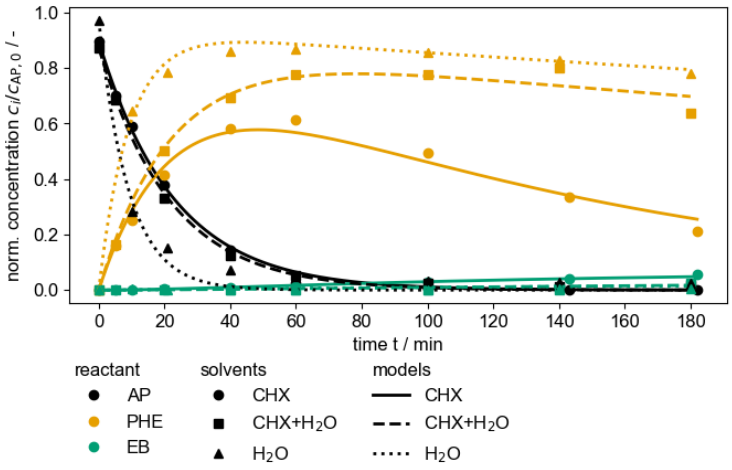

Figure 2: Reaction concentration profile normalized with the initial concentration of AP (0.64 mol L^{-1} in solvent, 10 bar, 80 °C, 0.08 mg mL^{-1} Rh) Solvents: water (H_2O), cyclohexane (CHX), and 7.5 wt% water in cyclohexane.

References

[1] Li, Yan, et al., Catal. Sci. Technol., 2018, 14, 3580–3589
[2] Potts, David S. et al., Chem. Soc. Rev., 2021, 22, 12308–12337
[3] Li, Jinlei, et al., ChemCatChem, 2024, 14
[4] Bertero, Nicolás M., et al., Appl. Catal. Gen., 2011, 1-2, 228–238