Solvent effects in the heterogeneously catalyzed hydrogenation of acetophenone investigated by Raman spectroscopy

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Introduction

With the chemical industry transitioning towards renewable carbon sources such as biomass, the demand for renewable resources continues to grow. As a result, liquid-phase reactions and processes are gaining increasing relevance in sustainable chemical production. Consequently, solvent selection will become a critical factor in heterogeneously catalyzed liquid phase reactions, influencing reaction rates, selectivity, and catalyst stability. These effects are particularly evident in the selective hydrogenation of acetophenone, a widely studied model compound in hydrogenation reactions (c.f. Figure 1).[1–3]

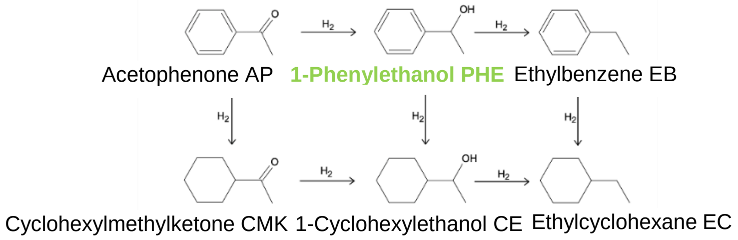

Figure 1: Reaction network of the hydrogenation of acetophenone.

Despite the increasing importance of solvents, the fundamental interactions between solvent, reactive species and solid catalyst surface have received limited attention in reaction engineering so far.[4] The objective of this study is to elucidate the solvent effects on reaction kinetics in heterogeneous catalysis on the example of acetophenone (AP) hydrogenation to provide a basis for the development of a comprehensive model of solvent affected reaction kinetics on the long-term.

Laboratory set-up for kinetic measurements

For kinetic measurements, an advanced reactor set-up was built, ensuring suitable reaction conditions. The reactor (Parr 4567) is equipped with a gas-injection stirrer for hydrogen supply. Concentration profiles of the main components are obtained by online Raman spectroscopy employing immersion optics (Endress+Hauser RNX2). Calibration is done via indirect hard modelling with the software Peaxact.[5] Additional gas chromatography measurements were conducted to validate the concentrations measured by the Raman spectroscopy. The experimental setup and procedure enable online monitoring of the hydrogenation of AP, providing valuable insights into the reaction kinetics under solvent variation.

Results

Focusing on solvent influences, a comprehensive parameter variation across all relevant variables would significantly exceed the scope and applicability of this work. To reduce the number of measurements, a suitable development point is determined. Therefore, in the first step, a sophisticated factorial design of experiments was carried out to investigate the influences of catalyst mass, temperature, and initial concentration. Figure 2 shows exemplary concentration profiles for the acetophenone hydrogenation for three different conditions.[6]

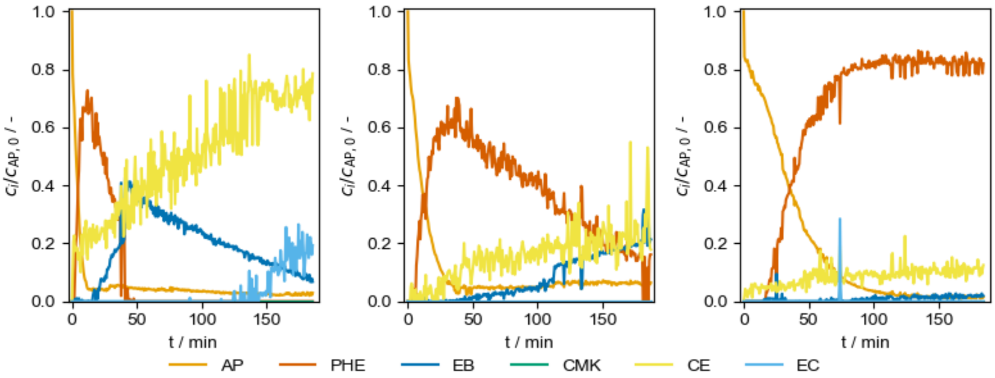

Figure 2: Concentration time profiles for the hydrogenation of acetophenone at 11 bar p_{H2} in isopropanol. Left: 0.64 $\frac{g}{mol}$ $c_{AP,0}$, 0.368 g m_{cat}, 100 °C; center: 0.64 $\frac{g}{mol}$ $c_{AP,0}$, 0.369 g m_{cat}, 80 °C; right: $1.28 \frac{g}{mol}$ $c_{AP,0}$, 0.333 g m_{cat}, $80°C$. Normalized to the initial concentration of acetophenone.

With increasing temperature, the initial rate of depletion of acetophenone rises according to the Arrhenius equation. A higher initial concentration of AP results in the suppression of the consecutive reaction of PHE, which we attribute to the strong adsorption of PHE on the catalytic surface.[6] First results from experiments with solvent variations indicate a change in the initial reaction rate of AP as well as in the maximum concentration of the intermediate PHE.[6] As an overall result of this work, valuable insights into solvent influence on heterogeneously catalyzed liquid phase reactions are obtained, which will contribute to improving the efficiency of liquid-phase processes of the future.

References

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