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A Kinetic Model for the Hydroformylation of 1-Octene in supercritical CO₂

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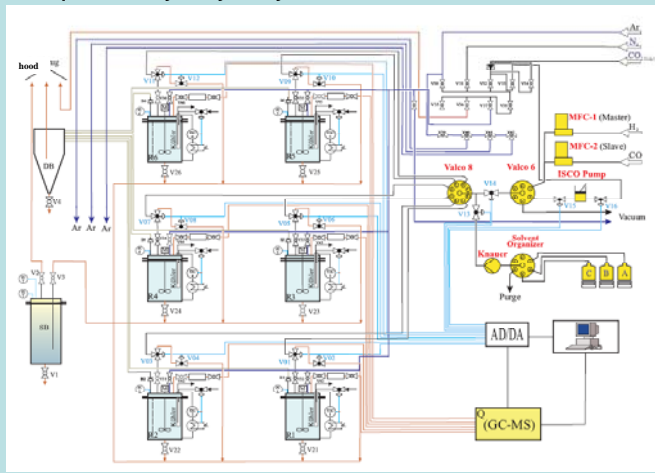
Introduction

The hydroformylation of olefins is one of the industrially most important homogeneously catalyzed reactions. Since early 90th, supercritical carbon dioxide (scCO₂) has been investigated as an alternative medium replacing conventional organic solvents in hydroformylation. The physical-chemical properties of scCO₂ are between those of liquids and gases. In catalysis applications, the tuneable solvent properties of scCO₂ can result in a variety of effects, such as affecting kinetic rates by both temperature and pressure, shifting equilibrium constants in favour of the desired products, and increasing selectivity and yields. One particular benefit of scCO₂ is that interface diffusion does not take place.

In this work we present our recent studies on Co₂(CO)₈ catalyzed hydroformylation of 1-octene in scCO₂.

Experimental

Experiments were carried out in a parallel six-reactor system allowing for faster exploration of process parameters up to 350 bar pressure. Automation of reactant dosing, experiments and data recording was performed using a programmable controller. Samples for kinetic analyses were quantitatively analyzed by GC.



Kinetics and Formal Kinetics

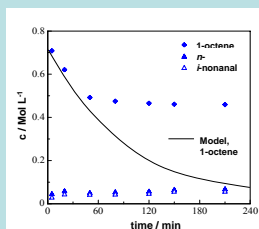
An activation enthalpy of 117 kJ mol⁻¹ for 1-octene hydroformylation was determined in the range between 90 and 150°C. Experiment series at various concentrations of each 1-octene, CO, H₂ and Co₂(CO)₈ were performed, with 1-octene conversion expressing the rate of hydroformylation. Initial reaction rates and concentrations were determined at 120°C.

The following equation (1) was used to describe the reaction rate.

$$-r_{\text{model}} = \frac{k \cdot C_{1\text{-octene}}^{0.56} \cdot C_{\text{H}_2}^{0.9} \cdot C_{\text{CO}}^{-1.68} \cdot C_{\text{Co}}^{0.88}}{(1 + K_{\text{CO}} \cdot C_{\text{CO}})^{-1.68} \cdot (1 + K_{1\text{-octene}} \cdot C_{1\text{-octene}})^{0.56}} \quad (1)$$

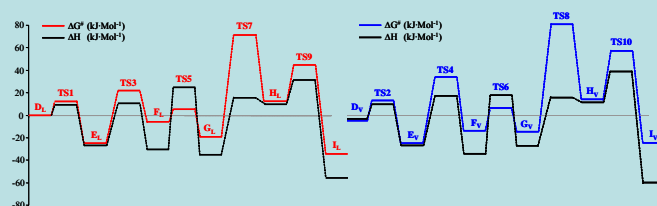
Constants in Eq. (1) were fitted to $k = 13$, $K_{\text{CO}} = 0.2$ and $K_{1\text{-octene}} = 0.3$.

As most of the variable influences studied are well expressed by this model, influence of low CO partial pressure (Fig. Right) is not described satisfyingly. Formal kinetics can also not describe regioselectivity.



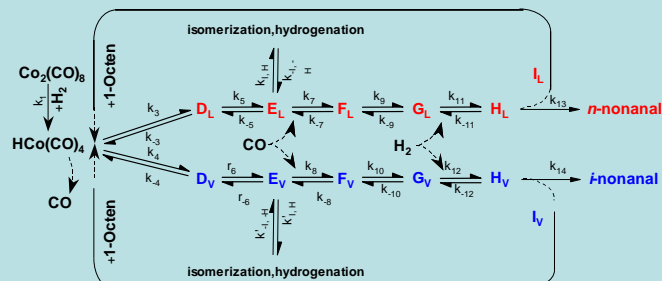
Microkinetics

Kinetic parameters for the formation of *n*- and *i*-nonanal from 1-octene were determined from the reaction mechanism established by DFT calculations.



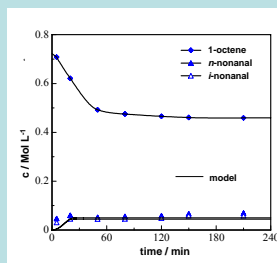
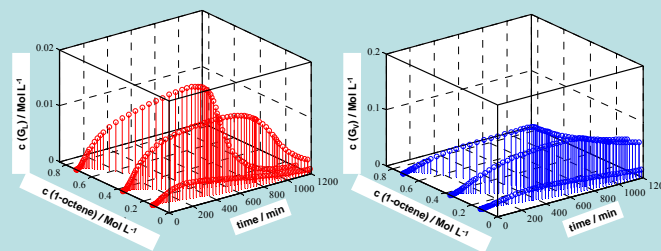
For both pathways oxidative addition of H₂ through transition states **TS7** (finally yielding the linear product) and **TS8** (yielding the branched product) is energetically the rate-limiting step.

From thermodynamical values calculated for all intermediates, the respective rate constants k_i and k_{-i} of the elementary reactions were determined.



The non-linear microkinetic model for the hydroformylation pathways was constructed using the SIMULINK toolbox integrated in Matlab®. Visualization of concentrations as function of reaction time took place by utilization of programmable S-function modules in SIMULINK.

Regioselectivity in aldehyde formation is explained from the difference in activation enthalpy through transition states **TS5** and **TS6**, respectively. The microkinetic model quantitatively describes the concentration profiles of the corresponding products in the catalytic cycle, (Co(CO)₃-CO-C₈H₁₇), **G_L** and **G_V** (here in dependence from initial 1-octene concentration), in a stirred tank-reactor.



In contrast to formal kinetics the microkinetic model is able to reproduce also the rate at a low CO partial pressure (Fig. Left) and to describe regioselectivity on a high level of accuracy.

Additionally it allows for the extrapolation outside the experimental range.