Effects of solvent and of catalyst on the acid-catalyzed esterification of levulinic acid via activity-based models

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This study focuses on understanding the kinetics and thermodynamics of the esterification of levulinic acid with ethanol. So far, thermodynamic models have been used to predict solvent influences on reaction rates and reaction yields. The idea of this work was to also consider the catalyst activity in the kinetic model. Accessing catalyst activity with the model ePC-SAFT allowed the first time to precisely predict the catalyst effects on reaction rates.

When considering the transition from a fossil-fuel based economy to a sustainable one, biomass valorization represents a promising strategy. Increasing the knowledge in the catalyst-kinetics-thermodynamics relation allows understanding and improving the efficiency of biomass conversion, e.g. into levulinic acid (LA) or ethyl levulinate (ELA). In general, ELA is synthesized via an acid-catalyzed esterification reaction of LA with an excess amount of ethanol (Eqs. 1 & 2).

$$\mathrm{LA} + \mathrm{EtOH} \rightleftharpoons \mathrm{ELA} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{H_2SO_4} + \mathrm{H_2O} \rightleftharpoons \mathrm{HSO_4^-} + \mathrm{H_3O^+} \qquad (2)$$

The solvent influences H_2SO_4 dissociation, reaction kinetics, catalyst activity and reaction equilibrium. We studied the influence of the green solvent GVL (γ-valerolactone) and of the H_2SO_4 concentration on reaction kinetics of (1) (see Figure 1).

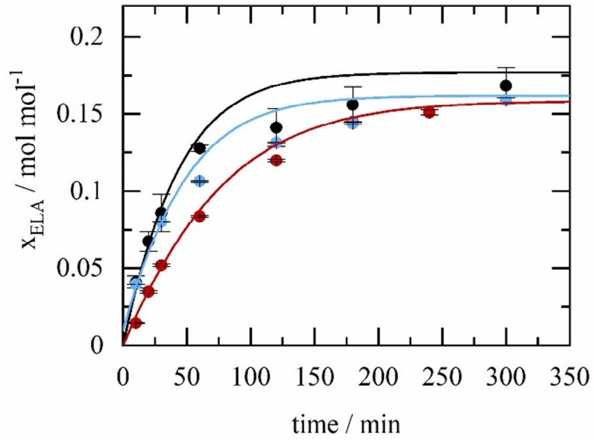

Figure 1: Ethyl levulinate mole fraction during the esterification reaction without cosolvent (black, "ref"), with GVL cosolvent (blue, "3"), with GVL cosolvent and reduced catalyst concentration (red, "4") at 333 K. Symbols: Exp. data, lines: ePC-SAFT predictions. Exact conditions: See publications.

The kinetics of LA esterification in the cosolvent-free system (black) appears to be the fastest, followed by the reaction under GVL addition. Decreased amount of catalyst reduces the reaction kinetics. This behavior has been confirmed by an ePC-SAFT prediction. For the latter, we developed an activity-based model to account for the catalyst interactions with the reaction components. The resulting equation describes the reaction rate r by

$$\frac{r}{a_{\mathrm{H_3O^+}}} = k_1 \cdot \gamma_{LA} x_{LA} \cdot \gamma_{EtOH}\, x_{EtOH} \cdot - \frac{k_1}{K_{th}} \cdot \gamma_{ELA} x_{ELA} \cdot \gamma_{H_2O} x_{H_2O}$$

where x, γ and K_{th} describe the mole fractions, the activity coefficients and the thermodynamic equilibrium constant, respectively. This approach incorporates the dissociation of H_2SO_4 in the reaction mixture, which we solved in order to predict proton activity (aH_3O^+) along the reaction coordinate using ePC-SAFT.

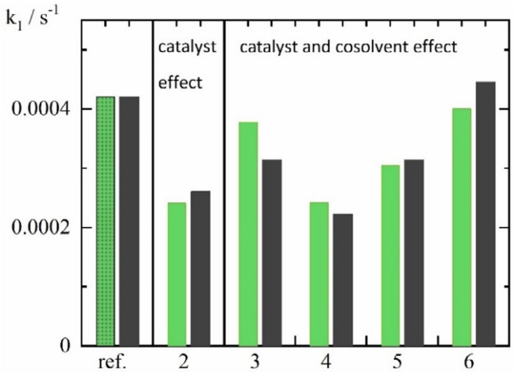

Figure 2: Rate constants k_1 for selected conditions at 333 K. Green: exp. data, Black: ePC-SAFT prediction using one experiment as reference (shaded, "ref"). Exact conditions: See publication.

Figure 2 compares experimental and predicted rate constants k_1 at various experimental conditions (see figure caption of Figure 1). The results show that the activity-based model is capable of predicting the catalyst effect on the reaction rate. Only one reference experimental k_1 ("ref.") was required to predict the influence of catalyst and cosolvent on the kinetics. This was possible at the different conditions (2-6) concerning the cosolvent or catalyst concentration. To conclude, we were able to predict kinetics in an arbitrarily chosen reaction environment concerning solvent, catalyst, and any concentration by combining proton activity, dissociation equilibria and reactant activities from ePC-SAFT into a reaction kinetics approach.

Publications:
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