Polyoxometalates and strongly non-ideal solvent mixtures (SNISMs) towards boosting acid-catalysed esterification reactions

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Abstract

The ester substance class provides a wide variety of applications. Esters are not only used as flavouring additives but fatty acid methyl esters (FAME) won by vegetable oils and methanol (from syngas) are also used as biodiesel, which makes them ideal products of biomass valorisation. Esterification reactions are limited by their thermodynamic equilibrium. Therefore, it is one of the goals of this research work to exceed equilibrium yields calculated by classical means using the assumption that concentration and activity of all reacting components are equal.

Process economics depend strongly on the solvent and on the solvent/catalyst combination. Finding sustainable non-toxic solvents that allow high activity of the catalyst even at low temperatures is a growing field of research. Because single-component solvents usually only allow optimization of one important parameter (activity of substrates, products, catalyst or phase behaviour) this research project explores **s**trongly **n**on-**i**deal **s**olvent **m**ixtures (SNISMs). The focus lies on acid-catalysed esterification reactions of short-chain alcohols and carboxylic acids like formic acid, acetic acid or lactic acid at temperatures between 298 K and 323 K. With the use of tailor-made SNISMs it is possible to tune the thermodynamic activity of the catalyst and of the reacting agents. Ideally the SNISM also allows separation and recycling of the catalyst to approach more sustainable processes. Our catalysts of choice are heteropoly acids (HPAs), which are inorganic metal-oxide clusters with high Brønsted acidity.[1] Thermodynamic modelling using ePC-SAFT advanced is used for the screening of suitable SNISMs and has successfully been applied to esterification reactions before without any catalyst.[2]

Reaction progress and kinetics were investigated using ^{1}H-NMR spectroscopy and Karl Fischer titration. Catalyst characterisation was performed with IR spectroscopy, thermogravimetric analysis and inductively coupled plasma optical emission spectroscopy for the pure catalyst and NMR spectroscopy (^{31}P and ^{29}Si) as well as Raman spectroscopy in (reaction) solution.

Equilibrium yields and kinetics will be discussed for different alcohol-acid combinations, HPAs (Keggin and Wells-Dawson types) and varying reaction parameters (T, molar ratio of starting materials, c_{cat}). Furthermore, this experimental data will be compared to predictions calculated using ePC-SAFT modelling. Phase behaviour of reaction solutions is investigated as well as the acidity of the HPA catalysts.

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References

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