



CAMURE-11 11th International Symposium on Catalysis in Multiphase Reactors

ISMR-10 10th International Symposium on Multifunctional Reactors

MILANO, ITALY - 21-24 March, 2021

Kinetics assessment of the homogeneously catalysed hydroformylation on a Rh-catalyst

Sébastien Siradze¹, Jeroen Poissonnier¹, Morten Frøseth², Richard Heyn², Joris Thybaut^{1*}

¹ Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Ghent, Belgium;

² SINTEF Industry, P.O.Box 124 Blindern, 0314 Oslo, Norway

*Corresponding author E-Mail: joris.thybaut@ugent.be

1. Introduction

Hydroformylation is a process used to convert olefins and syngas, i.e. a mixture of CO and H₂, to aldehydes containing one more carbon atom than the reactant olefin, and was discovered in 1938 by Otto Roelen [1]. It is the largest-scale application of homogeneous catalysis in the chemical industry. Ethylene hydroformylation in particular is useful to produce propanal, which can be readily converted to bulk chemicals such as propanol and propylene [2]. It is thus a more CO₂-neutral alternative to steam cracking for propylene production.

One of the major drawbacks related to hydroformylation is that it is catalysed homogeneously, leading to difficult catalyst separation/recycling and product stream contamination [3]. Although these issues could be circumvented by the use of a heterogeneous catalyst, it remains a challenge to develop such a catalyst with the same activity and selectivity as the widely-used homogeneous ones [4]. Strategies for the heterogenization of the catalyst typically mimic the common homogeneous ligand-modified Rh and Co catalysts structurally [3].

A better understanding of the kinetics and catalyst performance in ethylene hydroformylation will be acquired in this work via detailed kinetic model construction. An enhanced insight in the kinetics of the homogeneously catalysed hydroformylation and the reasons why it is able to achieve high activities and selectivities to aldehydes will provide guidelines for the heterogenization of the catalyst.

2. Procedures

The reaction mechanism of the homogeneously catalysed hydroformylation is described using the widely accepted Wilkinson mechanism [5]. Selective propanal formation is assumed, since propanal selectivities amounting to 100% have been experimentally observed and are reported in the literature at typical industrial conditions [6]. In other words, the formation of hydrogenation products such as ethane and propanol can be considered negligible. The Wilkinson mechanism using a ligand-modified Rh catalyst is illustrated in Figure 1.a. Seven reactions, i.e. five coordination reactions of five components (blue) and two reaction steps on the catalyst (orange), are included in the model.

The reactions are simulated accounting for their reversibility, leading to fourteen rate coefficients. To calculate these, the model employs 11 parameters, determined by theoretical calculations or *via* regression to experimental data. The activation energies of the coordinations are assumed to be zero, while those of the two reactions on the catalyst are set as adjustable parameters. The enthalpy changes for all reactions but one are also determined by regression, as they are linked through an energy balance. The remaining three adjustable parameters are the entropy changes of the two dissociative coordinations and one of the reactions on the catalysts, as the others are calculated using an energy balance or estimated using the Sackur-Tetrode equation.

The reaction rate equations are used to calculate the production of each component in the reactor. The mass balance of the components is expressed over a gas-liquid batch reactor, typically employed for kinetic data

acquisition for homogeneously catalysed hydroformylation, with the reactions occurring in the liquid phase. The gas phase originally consists of ethylene, CO, H₂ and argon as inert, which can all get dissolved into the liquid phase, initially only consisting of toluene. Gas-liquid equilibrium is assumed at all times during the reaction and is mathematically described using the PSRK equation of state. Simulations of the reactor content composition are performed by solving the reactor model equations using a differential equation solver [7].

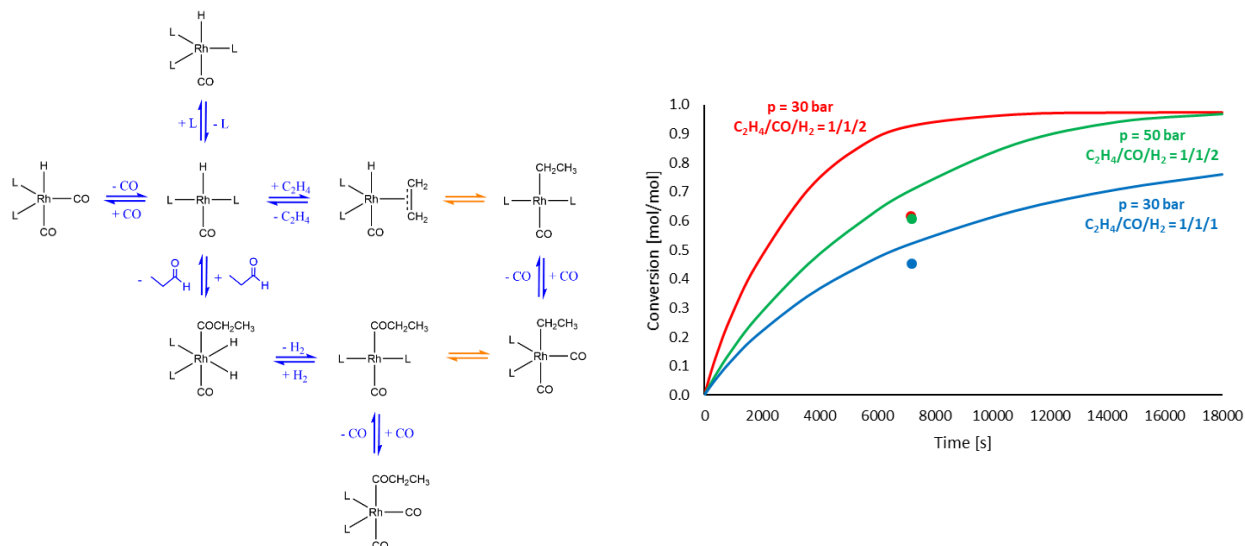


Figure 1. (a) Wilkinson mechanism for the homogeneously catalysed hydroformylation, with five coordinations of the ligand, CO, H₂, ethylene and propanal (blue) and two reactions on the catalyst: beta-hydride addition of ethylene and CO-insertion in ethyl (orange), (b) ethylene conversion as a function of the batch time for varying total pressure and reactant ratios at a temperature of 150 °C and a catalyst mass of 12 mg; the lines represent the model simulated values while the symbols represent the experimental measurements

3. Results and discussion

Figure 1.b shows the ethylene conversion in a gas/liquid batch reactor as a function of time for varying total pressure and reactant ratios while keeping the temperature and the catalyst mass fixed. It is observed that equilibrium conversion is reached at a later point at a higher total pressure, resulting from the larger amount of reacting feed. A positive effect of the pressure on the equilibrium conversion is also observed, as a result of the principle of Le Chatelier. Likewise, the decrease in conversion when the C₂H₄/CO/H₂ ratio changes from 1/1/2 to 1/1/1 (leading to more ethylene in the feed) is captured by the model. By varying the temperature in the simulations (not shown), a positive effect of the temperature on the reaction rate is observed. As hydroformylation is an exothermic reaction, the temperature is expected to have an unfavourable effect on the equilibrium conversion, which is also reflected by the model. A larger amount of data at different operating conditions in terms of batch time, catalyst mass, temperature and total pressure will feed the model. To conclude, the model is physically realistic and is able to correctly predict the observed experimental trends.

4. Conclusions

A kinetic model was developed for the homogeneously catalysed hydroformylation of ethylene in a gas-liquid batch reactor. The Wilkinson mechanism, a widely accepted mechanism for the considered reaction, was proposed for the model and the reaction steps were described using the law of mass action. The model-simulated product spectra are physically realistic and showcase the effect of varying the temperature, total pressure and reactant ratios on the ethylene conversion.

References

- [1] R. Franke, D. Selent, and A. Börner, *Chemical Reviews*, 112(11), 2012, pp. 5675-5732.
- [2] B.A. Rodriguez, W.J. Tenn, *Applied Catalysis A: General*, 421-422, 2012, pp. 161-166.
- [3] C. Li, et al., *Front. Chem. Sci. Eng.*, 12(1), 2018, pp. 113-123.
- [4] B. Cornils, et al., *Applied Homogeneous Catalysis with Organometallic Compounds*, 2017, pp. 1-22.
- [5] D. Evans, J.A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1968, pp. 3133-3142.
- [6] G. Kiss, et al., *Journal of Molecular Catalysis A: Chemical*, 138(2), 1999, pp. 155-176.
- [7] P.N. Brown, A.C. Hindmarsh, and L.R. Petzold, *SIAM J. Sci. Comp.*, 15(6), 1994, pp. 1467-1488.