## Microkinetic analysis of ethylene hydroformylation on a heterogeneous Rh-modified MOF catalyst

Sébastien Siradze<sup>1</sup>, Jeroen Poissonnier<sup>1</sup>, Silje F. Håkonsen<sup>2</sup>, Morten Frøseth<sup>2</sup>, Richard H. Heyn<sup>2</sup>, Joris W. Thybaut<sup>1</sup>

## <sup>1</sup>Laboratory for Chemical Technology, Ghent University, Ghent, Belgium <sup>2</sup>SINTEF, Oslo, Norway

As a generally homogeneously catalyzed process, hydroformylation still faces issues regarding catalyst separation and recycling. However, the development of heterogeneous catalysts with the same activity and aldehyde selectivity as the widely-used ligand-modified Rh or Co catalysts remains a challenge. One approach currently gaining attention is the heterogenization of the homogeneous catalyst through immobilization on a solid material, such as a MOF. We have previously developed a microkinetic model for the hydroformylation of ethylene on a homogeneous PPh<sub>3</sub>-modified Rh catalyst [1], based on Wilkinson's dissociative mechanism. The aim is now to verify whether the reaction mechanism on a heterogenized catalyst is similar as on a homogeneous catalyst, through the development of a microkinetic model for the heterogenized catalyst.

An experimental investigation of ethylene hydroformylation on a Rh-functionalized MOF catalyst is conducted in a fixed-bed reactor in order to investigate the effects of the reaction conditions (T = 100-120 °C,  $p_{tot}$  = 10-20 bar, F(C<sub>2</sub>H<sub>4</sub>) = 2.5-7.5 µmol/s, n(CO)/n(C<sub>2</sub>H<sub>4</sub>) = 1-2, n(H<sub>2</sub>)/n(C<sub>2</sub>H<sub>4</sub>) = 1-2) on the ethylene conversion and the propanal selectivity. The catalyst was synthesized starting from NU-1000 [2], a mesoporous MOF, which is first functionalized using 4-(diphenylphosphino)benzoic acid. This group then allows the homogeneous catalyst Rh(CO)H(PPh<sub>3</sub>)<sub>3</sub> to lose one of its PPh<sub>3</sub> ligands and get immobilized on the MOF. Propanal and ethane were observed as products, along with trace amounts of propanol.

To model the reactor, an ideal steady-state plug flow reactor is considered. For each gas phase component and intermediate, a mass balance equation is solved. The production and consumption of the components are modeled using Wilkinson's dissociative mechanism, as the catalyst is structurally very similar to the homogeneous ligand-modified Rh catalysts. The model has 10 parameters, comprising activation energies and reaction enthalpies of the considered elementary steps, which are estimated through regression to experimental data. The parameter values obtained for the homogeneous process [1] were used as initial guesses and the difference in their values can be considered to be a result



 $\begin{array}{l} \mbox{Figure 1: Simulated flow rates of propanal at $T=100 \ ^{\circ}C$ (blue), $110 \ ^{\circ}C$ (purple) and $120 \ ^{\circ}C$ red) as a function of inlet ethylene flow rate. $W_{cat}=0.046$ g, $p_{tot}=10$ bar, $n(N_2)/n(tot)=0.05$, $n(C_2H_4)/n(CO)/n(H_2)=1/1/2$ } \end{array}$ 

of the reaction taking place in the gas phase, as opposed to in a solvent, as in the homogeneous case. The simulation results are shown in Figure 1, which exhibit a realistic trend for the outlet flow rate of propanal as a function of the inlet flow rate of ethylene. The model is able to capture the negative effect of the temperature on the conversion to propanal.

[1] Siradze, S. et al. Kinetics assessment of the homogeneously catalyzed hydroformylation of ethylene on an Rh catalyst. I&EC Research. 60/46, p16665-16681 (2021)

[2] Wang, C. et al. Scalable synthesis and post-modification of a mesoporous metal-organic framework called NU-1000. Nat Protoc. 11, p149-162 (2016)

E-mail : sebastien.siradze@ugent.be