Ethylene Oligomerization on Bifunctional Heterogeneous Catalysts: Model Development and Catalyst Optimization

*K. Toch, J.W. Thybaut and G.B. Marin*   E-mail: Kenneth.Toch@UGent.be

Universiteit Gent, Laboratory for Chemical Technology Krijgslaan 281 (S5), 9000 Ghent, Belgium - http://www.lct.UGent.be

Introduction and Objective

- Valorization of natural gas and biogas by Oxidative Coupling of Methane, followed by Oligomerization to Liquids (*OCMOL*)[1]
- Detailed mechanistic insights lead to an '*in-silico*' optimization of both the catalyst and process conditions applied (Model Based Catalyst Design)[2]
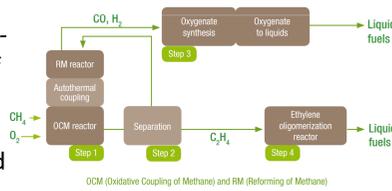
Experimental Study

1.8wt% Ni-SiO$_2$-Al$_2$O$_3$
  absence of acid catalysis
  → determination of **metal-ion kinetics**

4.89wt% Ni-Beta
  both metal-ion as acid catalysis
  → determination of **acid kinetics**

Operating conditions:
T: 443 – 523 K | p$^0_{C2}$: 1.0 – 3.5 Mpa | W$_{cat}$/F^0: 4.0 – 15.0
intrinsic kinetics regime (absence of transport limitations)

Modelling Approach: *SEMK*

Single-Event MicroKinetics:
- classification of elementary steps into reaction families (energetic/enthalpic considerations)
- accounting for symmetry effects (entropic consideration)
- pre-exponential factors calculated based on statistical thermodynamics
- activation energies/reaction enthalpies: determined by regression
  ✓ **catalyst descriptors**: catalyst properties
  ✓ **kinetic descriptors**: reaction family properties
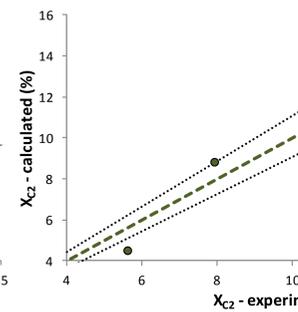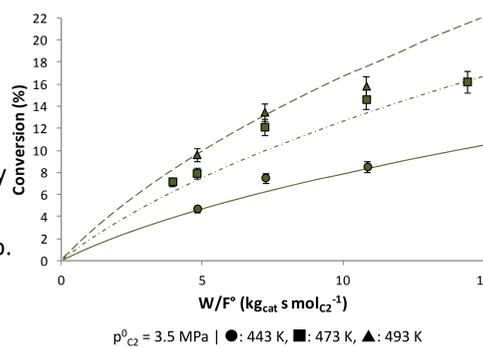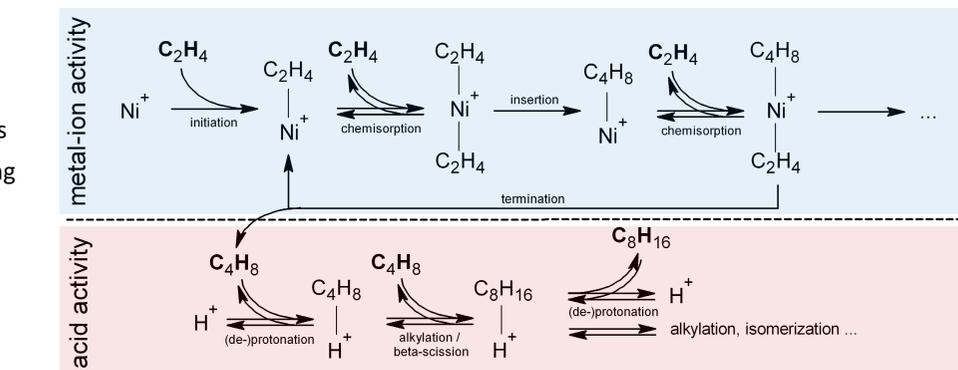
Metal-ion kinetics determination

- 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$ is highly selective towards dimerization (83-86%)
  → mainly production butenes
  → maximum up to C$_8$ detected
  → no odd carbon numbered components
- Product selectivities independent of operating conditions
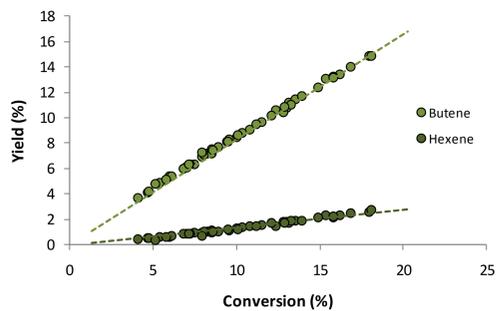
- Insertion/termination mechanism inspired by homogeneous polymerization kinetics
- Parameters estimates by regression to 51 exp. data points
  → significant parameter estimates
  → adequate model predictions

Acid kinetics determination

- 4.89wt% Ni-Beta is highly selective towards dimerization (>80%)
  → mainly production butenes
  → maximum up to C$_8$ detected
  → lower activity (≈60%) than 1.8wt% Ni-SiO$_2$-Al$_2$O$_3$
  but:
  → formation of odd carbon numbered components (C$_3$ and C$_5$)
- Alkylation of C$_4$ to C$_8$, with consecutive cracking to C$_3$ and C$_5$ components
  → selectivity towards C$_3$ and C$_5$: 0.5–2.0%

p$^0_{C2}$ = 3.5 MPa | ●: 443 K, ■: 473 K, ▲: 493 K

Catalyst descriptors	ΔH$_{phys(C2)}$	ΔΔH$_{phys(2C)}$	ΔH$_{chem(C2)}$	Kinetic descriptors	E$_{a,ins}$	E$_{a,ter}$
Est. value (kJ mol^{-1})	-7.2 ± 0.2	-12.3 ± 0.4	-49.9 ± 0.6	Est. value (kJ mol^{-1})	76.3 ± 0.6	67.8 ± 0.6

phys: physisorption, *chem*: chemisorption, *ins*: insertion, *ter*: termination

Catalyst descriptors	ΔH$_{phys(C2)}$	ΔΔH$_{phys(2C)}$	ΔH$_{chem(C2)}$	ΔH$_{pr}$	Kinetic descriptors	E$_{a,alk}$
Est. value (kJ mol^{-1})	-4.9 ± 1.7	-9.9 ± 2.6	-39.3 ± 0.7	-46.6 ± 18.9	Est. value (kJ mol^{-1})	65.1 ± 22.5

phys: physisorption, *chem*: chemisorptio, *pr*: protonation, *alk*: alkylation

'*In Silico*' Catalyst Development

- The SEMK model for ethylene oligomerization, including the kinetic descriptors, as 'engine' of the catalyst development tool
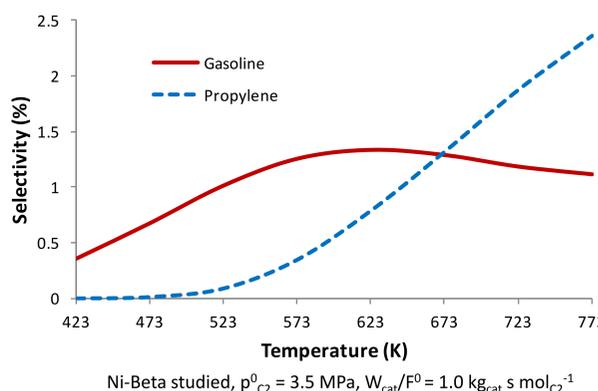- Adjustable parameters:
  → **catalyst descriptors**, c.q., catalyst properties
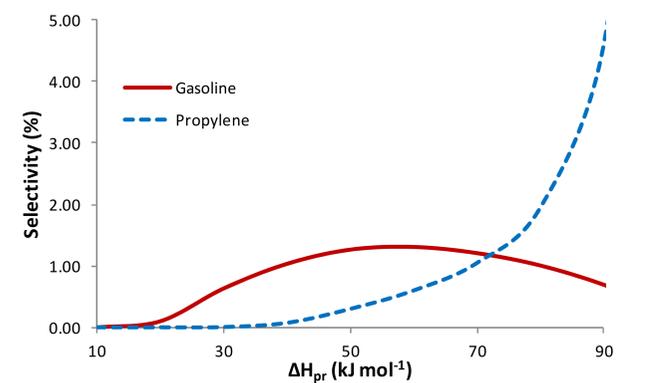 → reaction conditions
- Objective function defined on economic relevant base
  e.g., maximization of the yield of **gasoline** or **propylene**

$$\sum_{i=CN_{min}}^{CN_{max}} \sum_{j=BR_{min}}^{BR_{max}} Y_{C_{i,j}} \xrightarrow{\beta} Max$$

$$\underline{\beta} = \begin{cases} \Delta H_{phys(C_2)} \Delta\Delta H_{phys(2C)} \Delta H_{chem(C_2)} \Delta H_{pr} \\ T, p^0_{C_2}, W_{cat}/F^0 \end{cases}$$

Ni-Beta studied, p$^0_{C2}$ = 3.5 MPa, W$_{cat}$/F^0 = 1.0 kg$_{cat}$ s mol$_{C2}^{-1}$

- Low temperature: only metal-ion catalyzed reactions
- High temperature: increasing importance of cracking

modified Ni-Beta, T = 573 K, p$^0_{C2}$ = 3.5 MPa, W$_{cat}$/F^0 = 1.0 kg$_{cat}$ s mol$_{C2}^{-1}$

however:
- Simultaneous determination of catalyst properties and reaction conditions is a difficult optimization problem

Conclusions

- Ni-SiO$_2$-Al$_2$O$_3$ and Ni-Beta allowed to investigate resp. the metal-ion and acid catalyzed oligomerization kinetics in detail
- Ni-SiO$_2$-Al$_2$O$_3$ studied is more active than Ni-Beta
  → lower chemisorption enthalpy of ethylene
  → lower physisorption enthalpies of the olefins
- Catalyst descriptors were determined significant
- Optimal reaction conditions and catalyst properties determination using the tool is possible

Future Work

- Expand the experimental dataset on the Ni-Beta
  → increased insight in the effect of the reaction conditions on the catalyst's activity
  → input for the kinetic model
- Expand and refine the kinetic model
  → more significant determination of catalyst and kinetic descriptors
- Use the refined kinetic model as 'engine' for the catalyst development tool
  → determine a full set of optimal catalyst properties and reaction conditions for different, economic relevant, objective functions, e.g., maximized gasoline yield

[1] http://www.ocmol.eu
[2] J.W. Thybaut, I.R. Choudhury, J.F. Denayer, G.V. Baron, P.A. Jacobs, J.A. Martens and G.B. Marin, Top. Catal. (52) 1251 - 1260