

Hydroaminomethylation of a long-chain olefin: Influence of operating parameters

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Motivation

Investigation of:

- Rh-based homogeneous catalysis
- thermomorphic multiphase systems (TMS)
- tandem reactions
- **mechanistic reaction kinetics**
- hydroaminomethylation as amine synthesis

high reaction rates
catalyst recovery
less process steps
transferability
high atom-efficiency

Thermomorphic multiphase systems

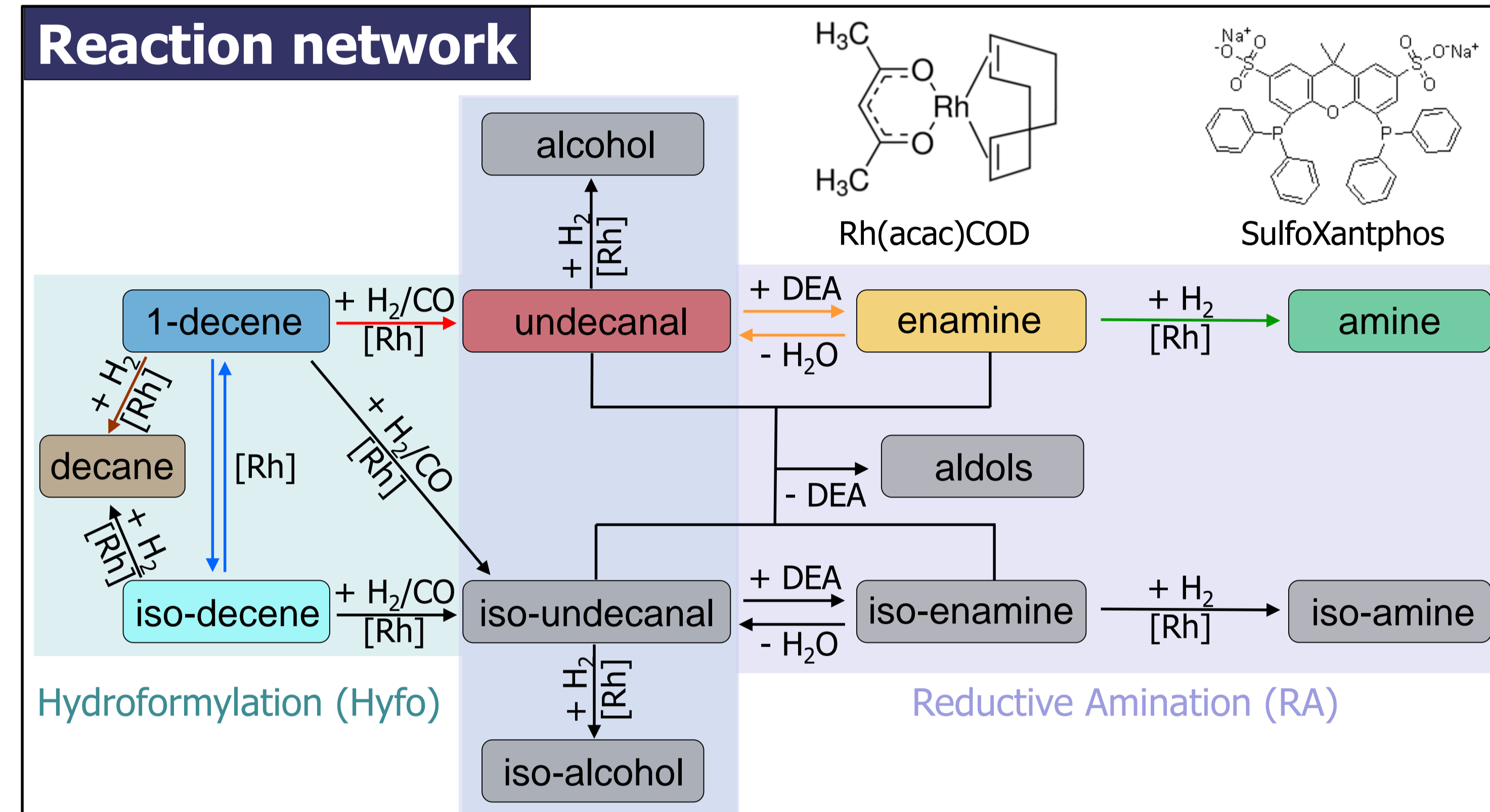
$W_{\text{methanol}}/W_{\text{n-dodecane}} = 50/50$

Room Temperature: Nonpolar solvent + Polar solvent

Reaction Temperature: Homogenous solution

No mass transport limitations (T ↑)

Separation Product/Catalyst (T ↓)



Reaction mechanism based kinetic models

model derivation → Christiansen mathematics to consider the distribution of the catalytic material within the catalytic cycles

model reduction → irreversible and rate-determining steps as well as most abundant catalyst containing species (macs) [6]

Hyfo, Hyd, 1-Dec, Iso, Hyd, En

catalyst pre-equilibrium

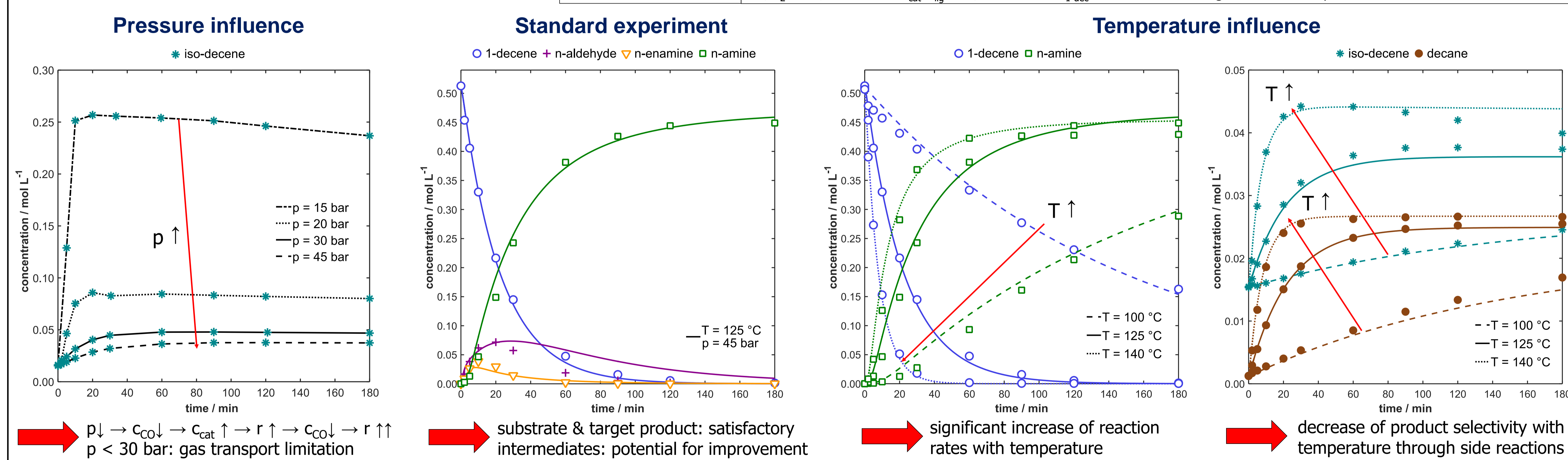
$$c_{\text{cat}} = \frac{c_{\text{cat,tot}}}{1 + K_{\text{cat}}^{\text{eq}} \cdot c_{\text{CO}}}$$

Results: experiments & simulations

symbols = experiments, colored lines = simulations

$P_{\text{tot}} = 45 \text{ bar}$, $x_{\text{cat}} = 0.08 \text{ mol\%}$, $n_{\text{DEA}}/n_{1\text{-dec}} = 8/7$, precatalyst: Rh(acac)(cod), TMS: $W_{\text{MeOH}}/W_{\text{Dodec}} = 50/50$, $T = 125 \text{ }^\circ\text{C}$

$\text{CO}/\text{H}_2 = 1/2$, $n_{\text{cat}}/n_{\text{lig}} = 1/3.5$, $W_{1\text{-dec}} = 10 \text{ wt\%}$, ligand: Sulfoxantphos



Hydroformylation subnetwork

Hydroformylation:

$$r_{\text{Hyfo}} = \frac{k_{\text{Hyfo}} \cdot c_{1\text{-Dec}} \cdot c_{\text{CO}} \cdot c_{\text{H}_2}}{1 + K_{\text{Hyfo}}^{\text{I}} \cdot c_{\text{H}_2} + K_{\text{Hyfo}}^{\text{II}} \cdot c_{\text{CO}} \cdot c_{\text{H}_2}} \cdot c_{\text{cat}}$$

Hydrogenation of 1-decene:

$$r_{\text{Hyd,1-Dec}} = \frac{k_{\text{Hyd,1-Dec}} \cdot c_{1\text{-Dec}} \cdot c_{\text{H}_2}}{1 + K_{\text{Hyd,1-Dec}} \cdot c_{\text{H}_2}} \cdot c_{\text{cat}}$$

Isomerization:

$$r_{\text{Iso}} = \frac{k_{\text{Iso}} \cdot (c_{1\text{-Dec}} - \frac{c_{\text{iso-Dec}}}{K_{\text{Iso}}^{\text{eq}}})}{1 + K_{\text{Iso}}^{\text{I}} \cdot c_{\text{iso-Dec}}} \cdot c_{\text{cat}}$$

Isomerization equilibrium:

$$K_{\text{Iso}}^{\text{eq}} = C_1 \cdot T^4 + C_2 \cdot T^3 + C_3 \cdot T^2 + C_4 \cdot T + C_5$$

parameter re-estimation for an existing mechanistic kinetic Hyfo model (transfer to HAM)

Reductive Amination subnetwork

Condensation:

$$r_{\text{Cond}} = k_{\text{Cond}} \cdot (c_{\text{Und}} \cdot c_{\text{DEA}} - \frac{c_{\text{En}} \cdot c_{\text{H}_2\text{O}}}{K_{\text{Cond}}})$$

Condensation equilibrium:

$$K_{\text{Cond}} = e^{-\frac{\Delta_R G}{RT}}$$

Hydrogenation of n-enamine:

$$r_{\text{Hyd,En}} = \frac{k_{\text{Hyd,En}} \cdot c_{\text{En}} \cdot c_{\text{H}_2}}{1 + K_{\text{Hyd,En}} \cdot c_{\text{H}_2}} \cdot c_{\text{cat}}$$

parameter estimation for a new mechanistic kinetic RA model [1-6]

Conclusion

- Transfer of the structure of a mechanistic kinetic model for the Hyfo to HAM conditions through reparameterization
- Derivation of a new kinetic mechanistic model for the enamine hydrogenation (RA) based on the postulated reaction mechanism
- Kinetic description of HAM successful due to coupling the Hyfo kinetics with a new mechanistic approach for the RA in the investigated parameter range

Outlook & Discussion

- Influence of higher CO concentrations on reaction kinetics?
- Potential of using the co-substrate DEA in excess
- Influence of higher H₂O amounts on condensation reaction (equilibria)
- Consideration of neglected low abundant side components

References

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