

MicroKinetic Engine (μ KE): Exploiting Transient Strategies for Top-Down Kinetic Modelling

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Highlights

- μ KE performs microkinetic analysis of complex reaction networks.
- No pseudo-state approximation is assumed for surface intermediates.
- Quasi-equilibrated reactions are recognized and treated separately.
- Transient calculations allow smooth approach to steady-state solution.

1. Introduction

Top-down kinetic modelling presents a strategy to simulate a chemical reaction by gradually increasing the complexity of the considered mechanism, the ultimate aim being to quantify it in terms of the relevant elementary steps. The MicroKinetic Engine (μ KE), a user-friendly software tool developed within the Laboratory for Chemical Technology at Ghent University [1], enables easy (micro)kinetic model construction and assessment. The current version of the software allows simulation of steady-state situations and regression to steady-state experimental intrinsic kinetic data [2,3]. In order to improve and accelerate the convergence to the steady-state solution, time has been implemented into μ KE as additional independent variable. Apart from guaranteeing efficient convergence towards steady-state solutions, information on reaction sequences in complex reaction networks can be obtained with transient kinetic data analysis [4].

2. Methods

μ KE has been previously developed for allowing kinetic modeling of (complex) catalytic reaction networks. [1] Component mass balances have now been expressed in transient terms for continuous stirred-tank (CSTR) and plug flow reactor (PFR). No pseudo-steady state approximation was made for (surface) intermediates; therefore, sets of ordinary differential (ODEs) and partial/ordinary differential equations (PDE/ODEs) were obtained for CSTR and PFR, respectively. Quasi-equilibrated reactions were identified and the number of differential equations was reduced accordingly. The method of lines in combination with backward differentiation formulas was used for PDE/ODEs integration. Both Rosenbrock and Levenberg–Marquardt method [5, 6] were employed during the nonlinear parameter regression against the experimental data obtained at steady-state.

3. Results and discussion

To solve a set of algebraic equations (AEs) describing a steady state situation, good initial guesses have to be provided. This proved to be very challenging, particularly for complex reaction networks. By implementing the transient term in component mass balances, AEs are transformed into ODEs, where the initial conditions (at $t = 0$) are known, thus facilitating the approach to a steady-state solution. By increasing the complexity of the kinetic model, i.e., by following the top-down kinetic modelling approach, the transient feature becomes more important for numerical reasons. This is being elaborated for two case studies, namely benzene hydrogenation in CSTR and methane steam reforming in PFR. Table 1 shows the first two steps adopted in top-down kinetic modelling for the case of benzene hydrogenation, with the aim of implementing the Single-Event MicroKinetic (SEMK) model in the last instance [7].

Table 1. Kinetic and adsorption parameters obtained for the initial models tested in reaction mechanism elucidation for benzene hydrogenation in CSTR. No. exp. = 43, $T = 423\text{--}428$ K, $P = 1\text{--}3$ MPa, $V_R = 2$ ml. At $t < 0$ s, only inert gas is present in the reactor.

Global reaction step	Dissociative adsorption of H ₂ and global surface reaction step	
$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$	$H_2 + 2^* \leftrightarrow 2H^*$	quasi-equilibrated reaction
	$C_6H_6 + ^* \leftrightarrow C_6H_6^*$	quasi-equilibrated reaction
	$C_6H_6^* + 6H^* \rightarrow C_6H_{12} + 7^*$	
$k_{Tm} = 8.5 \text{ m}^3 \text{ mol}^{-3} \text{ h}^{-1}$	$K_{H_2, Tm} = 3.636E-09 \text{ Pa}^{-1}$	$\Delta H_{H_2} = -59600.0 \text{ J mol}^{-1}$ [6]
$E_a = 28706.7 \text{ J mol}^{-1}$	$K_{B, Tm} = 6.40E-06 \text{ Pa}^{-1}$	$\Delta H_B = -64500.0 \text{ J mol}^{-1}$ [6]
	$k_{Tm} = 3.09E05 \text{ Pa h}^{-1}$	$E_a = 65415.3 \text{ J mol}^{-1}$

With the transient kinetic approach, the number of integration steps required to achieve the steady state was up to two times lower compared to the number of iterations required to reach the steady-state solution directly from a set of algebraic equations. Increasing the number of surface species in the reaction network requires additional initial solution guesses for AEs, rendering the transient modelling effective and invaluable method for the networks with increased complexity.

4. Conclusions

Determining reaction kinetics in terms of elementary steps typically is a challenging task when done for complex reaction networks with different time-scales of different reactions. Where methods aiming at directly solving steady state situations may fail or require extensive iterations prior to convergence, the μ KE nowadays allows a user-friendly assessment of the reaction network via a transient solution strategy. Being demonstrated for a relatively simple reaction network representing benzene hydrogenation, the benefits of the methodology will be more pronounced for more complex models such as the Single-Event MicroKinetic one.

References

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Keywords

Microkinetic modelling; regression; transient simulations