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Single-Event MicroKinetics: Catalyst design for complex reaction networks

J.W. Thybaut *, G.B. Marin

Ghent University, Laboratory for Chemical Technology, Technologiepark 914, Ghent B-9052 Belgium

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ABSTRACT

Microkinetic modeling provides unprecedented insight in chemical kinetics and reaction mechanisms. In particular for reactions in complex mixtures that pertain to a limited number of reaction families, the Single-Event MicroKinetic (SEMK) methodology has been developed. Kinetic descriptors determined from dedicated model component experimentation can be employed for the full-fledged simulation of industrial feed conversion. The SEMK methodology constitutes a versatile tool for quantifying the contributions of competing reaction pathways to the overall feed conversion. Apart from kinetic descriptors, the SEMK model also comprises catalyst descriptors that allow quantifying the effect of the catalyst properties on the chemical kinetics and, hence, rational design toward novel and innovative catalysts. It is reviewed how a 10% increase in hydroisomerization yields could be achieved after having unequivocally identified the responsible elementary steps for feed losses through cracking. Moreover, 2 novel examples illustrate how, upon implementation of the SEMK model in an adequate reactor model, industrial reactor operation can be efficiently simulated and the rate-determining phenomena in the overall feed conversion can be determined.

1. Introduction

Kinetic modeling allows acquiring unique insights in a chemical reaction mechanism. It establishes a mathematical relationship between proposed reaction mechanisms and experimental data and, hence, forms a bridge between theory and practice [1,2]. Based on a qualitative interpretation of experimental data as well as of ab initio calculations, hypotheses can be formulated with respect to the mechanism of the investigated reaction that can be verified by model regression [3]. Of course, this is a necessary but not sufficient condition for the correctness of the proposed mechanism. Complementary characterization techniques such as Temporal Analysis of Products (TAP), Steady State Isotopic Transient Kinetic Analysis (SSITKA), and physico-chemical characterization should be used for this purpose.

Reaction kinetics modeling is an elegant manner to bridge the gap between theory and practice. It requires making compromises between the physical significance of the phenomena that are accounted for on the one hand, and on the other hand, their relevance in the simulation of an acquired data set as well as in the extrapolation toward alternative operating conditions [1–3]. Generally stated, the more explicitly a kinetic model accounts for the individual reactions which are occurring, the better it is in describing the simulated process. On the other hand, complex kinetic models may include steps that do not significantly contribute to the overall reaction and, hence, for which the corresponding parameters are difficult to determine in a statistically significant manner. The advantages of complex models include, e.g., the feed invariance of the kinetic parameters and a high accuracy over an extended range of operating conditions [4]. Less explicit models consider rate-determining steps as independent of the operating conditions or group various components into a single pool of components, a so-called lump, the properties of which are an average over the components included in that lump [5].

Whether a global kinetic model or a model based on elementary steps is required, largely depends on the objectives that are pursued. Straightforward power law models, expressing the rate in terms of a global rate coefficient and reactant concentrations elevated to a component specific "power," in this case the partial reaction order, may suffice for monitoring reactor behavior around a stable operating point or for a screening of a first generation catalyst library [6]. Despite the global character of power law models, especially the partial reaction orders may already provide some details about the underlying reaction mechanism, e.g., with respect to adsorption saturation, competitive adsorption, etc. [3]. If, on the other hand, a detailed understanding of the investigated reaction mechanism is pursued to be exploited in advanced reactor and/or catalyst design, all elementary steps have to be accounted for without further simplifying assumptions concerning rate-determining or quasi-equilibrated steps. In that case, the so-called microkinetic

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* Corresponding author. Address: Ghent University, Laboratory for Chemical Technology, Technologiepark 914, Ghent B-9052, Belgium.

E-mail address: Joris.Thybaut@UGent.be (J.W. Thybaut).

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Nomenclature

B	Boolean matrix for molecule representation
C	concentration (mol kg^{-1})
h	Planck's constant (6.626 10^{-34} m^2 kg s^{-1})
H	enthalpy (J mol^{-1})
I	identity matrix
K_{deh}	dehydrogenation equilibrium coefficient (Pa)
$\tilde{K}_{isom}$	single-event isomerization equilibrium coefficient (–)
K_L	Langmuir physisorption coefficient (Pa^{-1})
$\tilde{K}_{prot}$	single-event protonation equilibrium coefficient (kg mol^{-1})
k	rate coefficient (mol kg^{-1} s^{-1})
$\tilde{k}$	single-event rate coefficient (mol kg^{-1} s^{-1})
k_B	Boltzmann constant (1.381 10^{-23} m^2 kg s^{-2} K^{-1})
LC	lumping coefficient (Pa)
m	type of carbenium ion
n	number of chiral carbon atoms (–)
$n_{classes}$	number of structural classes
n_e	number of single events (–)
p	partial pressure (Pa)
P	Boolean matrix for β neighbor indication
r	reaction rate (mol kg^{-1} s^{-1})
R	universal gas constant (J mol^{-1} K^{-1})
s	secondary carbenium ion
S	entropy (J mol^{-1} K^{-1})
$\tilde{S}$	single-event entropy (J mol^{-1} K^{-1})
t	tertiary carbenium ion
T	temperature (K)
y	molar fraction (–)

Symbols

#	number
σ	global symmetry number (–)

Superscripts

0	standard conditions
$\neq$	activation

Subscripts

$\neq$	transition state
ext	external
g,h	lump indexes
glob	global
i,j,k,q,r	component indices for reactant alkanes, alkenes, and carbenium ions and product alkanes and carbenium ions
int	internal
isom	isomerization
O	alkene
R^+	carbenium ion
sat	saturation
t	Brønsted acid sites

models are obtained [2]. Models of the Langmuir–Hinshelwood/Hougen–Watson (LHHW) type, i.e., models that account for the occurring elementary steps, but that assume a rate-determining step and quasi-equilibration of the other steps [7], are situated in between power law and microkinetic models. They particularly account for adsorption effects in catalytic reactions but, in their conventional version, cannot account for variations in rate-determining step as a function of the operating conditions.

A specific feature to be considered, on top of the degree of detail accounted for in the model, is the feed complexity [4,8–10]. Particularly when constructing microkinetic models, the number of elementary steps to be accounted for increases dramatically with the number of feed components. However, recognizing that the considered chemical transformations pertain to reactive moieties, rather than to individual molecules, it becomes possible to classify the huge number of elementary steps into a limited number of reaction families, hence, also requiring a limited number of kinetic parameters. Within a reaction family, Polanyi relationships may be used for relating the rate coefficients to each other or symmetry effects may be eliminated to obtain a unique rate coefficient per reaction family, such as in the Single-Event MicroKinetic (SEMK) methodology [10,11].

Having an adequate kinetic model at hand provides several advantages. It does not only support the operation of industrial-scale processes, but also forms a sound basis for the rational design of innovative and enhanced process schemes. A more recent trend is to include catalyst descriptors into kinetic models and exploit these for catalyst design. Where, traditionally, catalyst design used to be a trial and error procedure involving synthesis and performance testing activities [12–16] and high-throughput technologies have been implemented to enhance discovery rates, fundamental kinetic modeling complemented by "in silico" design are more and more coming forward to provide "smarter" feedback from the catalyst performance testing to the synthesis [17–20]. The construction of fundamental kinetic models is not straightforward, however, especially when novel reactions are being investigated. Hence, complementary feedback from performance testing to synthesis, as in the more traditional approach, may still be helpful. Additionally, e.g., via sequential design techniques, kinetic modeling may indicate what further performance testing could be performed without the need of synthesizing a new catalyst generation.

New challenges in microkinetic modeling of complex mixtures are opened up by societal evolutions. The global society as we know it today is *heavily supported by energy and chemicals*. The corresponding needs are satisfied to a large extent by products that are derived from fossil resources in general and crude oil in particular [21]. The crude oil production, however, is expected to peak in the near future, and hence, *alternative resources need to be explored* [22]. Fossil resources originate from *biomass* that was generated eons ago and covered by layers of mud, silt, and sand that formed into sedimentary rock. Geologic heat and the pressure of the overlying rock turned the biomass into hydrocarbon-rich material, known today as coal, oil, or gas. In order to evolve to a sustainable society, we need to speed up, i.e., catalyze, this transformation of biomass into hydrocarbons and chemicals by several orders of magnitude. Rational catalyst design based on a microkinetic understanding of the chemical transformations brings this objective within reach. Because of the chemical complexity of the biomass involved, methodologies such as Single-Event MicroKinetics are ideally suited to address this challenge.

In the present work, the history of the Single-Event MicroKinetic (SEMK) methodology as a technique to describe the kinetics in complex mixtures is sketched as well as its evolution toward the present-day applications that are concentrated on catalyst and reactor design. A brief review is made of an example in rational hydroisomerization and hydrocracking catalyst design [23], prior to addressing the novel industrial reactor simulations for