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An integrated approach to modelling of chemical transformations in chemical reactors

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Abstract
An integrated approach to the modelling of chemical reactors, particularly catalytic ones is presented. The modelling approach starts from quantum-chemical calculations, mechanistic hypothesis, derivation of kinetic expressions in order to achieve an appropriate kinetic model. The model parameters are determined by regression analysis and the complex behaviour of fixed bed reactors, including catalyst deactivation is described in an adequate manner. A general flowsheet for the procedure is proposed.

Keywords: kinetics, reactor, modelling, quantum chemistry

1. Introduction

Mathematical modelling of chemical reactors is one of the most demanding tasks in chemical engineering because of the interaction of several simultaneous phenomena, such as chemical kinetics, mass and heat transfer as well as fluid dynamics. In recent years, a lot of attention has been paid on detailed modelling and calculation of fluid dynamics (CFD). However, the crucial point in the description of a chemical reactor is the chemical transformation itself. In addition, a majority of industrially operating chemical reactors involve the presence of two or three phases, which emphasizes the role of interfacial mass and heat transfer. For heterogeneously catalysed processes, the modelling of intraparticle mass and heat transfer is included. The tendency in chemical reaction engineering research is nowadays to move more from bulk chemicals to fine and specialty chemicals. Thus the system cannot be described by few reactions, but a complex reaction network appears. The kinetics of the incorporated reactions is usually experimentally measurable, but the development of rate equations requires a deep-going insight on the reaction mechanism. The general chemical intuition can give inspiration to mechanistic considerations, but more rigorous calculations provided by quantum chemistry are needed to confirm/reject the kinetic hypotheses.

In the current paper, we present an integrated approach to the modelling of chemical reactors. The goal is to achieve as good but as simple as possible model. The integrated modelling approach was applied on several catalytic systems, such as three-phase hydrogenation of aldehydes and ketones as well as hydrocarbon transformations (i.e.

skeletal isomerizations of alkenes) over mesoporous and microporous catalysts. The characteristic feature of the systems considered is that a simplistic, rough modelling approach discarding the detailed reaction mechanisms leads to inappropriate rate equations, which are not able to describe the progress of the reactions and the development of the product selectivities correctly.

2. Case study

Skeletal isomerization of linear alkanes to branched counterparts has attracted attention to a large extent, since increasing the degree of branching of alkanes can boost the octane quality of a gasoline fraction. The application of branched hydrocarbons is an environmentally more acceptable alternative compared with other techniques, such as blending with aromatics or oxygenates (Ertl et al 1997, Guillaume et al 2003, Houžvičk et al. 1997, Nieminen et al. 2004, Ouno 2003). Kinetics of *n*-butane isomerization over bifunctional Pt-H-Mordenite was studied in a catalytic fixed-bed reactor by varying reactant partial pressure and temperature. The main products were isobutane, propane and pentanes. The state of adsorbed species inside the catalyst pores (channels) was investigated by quantum-chemical calculations, which suggested that alkoxy species are formed inside the channels – an example of the calculations is displayed in Fig. 1. The reaction rate showed complex dependence on the reactant partial pressure. Three kinetic models were developed based on the current understanding of the reaction mechanisms including hydrogenation and dehydrogenation steps on the metal sites, skeletal isomerization on the acid sites and deactivation due to the coke formation. Model **A** enabled monomolecular isobutane formation path, model **B** bimolecular and model **C** both reaction paths.

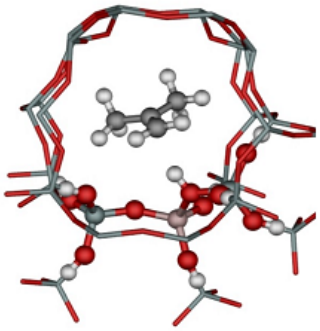


Fig.1 1-butene in the zeolite channel according to quantum chemistry.

A kinetic model based on the experimental results was developed. Only the reactions proposed in the literature to produce the main products, propane, isobutane and pentanes, were taken into account while other reaction paths, such as hydrogenolysis and monomolecular butane cracking were omitted. The reason for this is that the amount of by-products is minor and neglecting them keeps the model reasonably simple containing less estimated parameters while still being able to capture the main kinetic features of the reaction. The pentanes, isopentane and *n*-pentane, were lumped together,

because both of them are (hydrogenated) cracking products of $C_8^= \rightarrow C_3^= + C_5^=$. The reaction network on the catalytic sites is displayed in table 1..

Table 1 Reaction network on the catalytic sites

	$N^{(1)}$	$N^{(2)}$	$N^{(3)}$	$N^{(4)}$	$N^{(5)}$	
1. $n-C_{4,o}^{*H^+} \leftrightarrow iso-C_{4,o}^{*H^+}$	1	0	0	0	0	(1)
2. $2n-C_{4,o}^{*H^+} \rightarrow C_{8,o}^{*H^+} + {}^{*H^+}$	0	1	1	1	1	(2)
3. $C_{8,o}^{*H^+} + {}^{*H^+} \rightarrow C_{5,o}^{*H^+} + C_{3,o}^{*H^+}$	0	0	0	1	1	(3)
4. $C_{5,o}^{*H^+} + n-C_{4,o}^{*H^+} \rightarrow 3C_{3,o} + 2\,{}^{*H^+}$	0	0	0	0	1	(4)
5. $C_{8,o}^{*H^+} + {}^{*H^+} \rightarrow 2iso-C_{4,o}^{*H^+}$	0	1	0	0	0	(5)
6. $C_{8,o}^{*H^+} + {}^{*H^+} \rightarrow iso-C_{4,o}^{*H^+} + n-C_{4,o}^{*H^+}$	0	0	1	0	0	(6)
A. $C_{3,o} + {}^{*H^+} \;\Xi\; C_{3,o}^{*H^+}$	0	0	0	-1	-1	(7)
B. $n-C_{4,o} + {}^{*H^+} \;\Xi\; n-C_{4,o}^{*H^+}$	1	2	1	2	3	(8)
C. $iso-C_{4,o} + {}^{*H^+} \;\Xi\; iso-C_{4,o}^{*H^+}$	-1	-2	-1	0	0	(9)
D. $C_{5,o} + {}^{*H^+} \;\Xi\; C_{5,o}^{*H^+}$	0	0	0	-1	0	10

On the right hand side of the equations (1)-(10) above, the stoichiometric numbers (N) the of steps along independent routes are presented. Model **A** corresponds to monomolecular isobutane formation and included route $N^{(1)}$ as the sole path to isobutane. Routes $N^{(4)}$ and $N^{(5)}$ describe byproduct formation. In model **B** isobutane is formed bimolecularly ($N^{(3)}$) and the monomolecular path for isobutane formation is neglected. The valid routes are $N^{(3)}$-$N^{(5)}$. Model **C** includes routes $N^{(1)}$, $N^{(3)}$-$N^{(5)}$. Thus, in model **C** isobutane can be formed either monomolecularly or bimolecularly. The rate equations of Langmuir-Hinshelwood type were derived using the assumption that rate-limiting steps are the surface reactions on the catalyst

$$r_1 = \frac{k_1\left(K_{C_4^=,H^+}\, p_{C_4^=} - K_{i-C_4^=,H^+}\, p_{i-C_4^=} K_1^{-1}\right)}{\sum} \qquad r_2 = \frac{k_2 K_{C_4^=,H^+}^2\, p_{C_4^=}^2}{\sum^2} \qquad (1)$$

$$r_3 = \frac{k_3 \theta'_{C_8^=,H^+}}{\sum^2} \qquad r_4 = \frac{k_4 K_{C_5^=,H^+}\, p_{C_5^=} K_{C_4^=,H^+}\, p_{C_4^=}}{\sum^2} \qquad r_6 = \frac{k_6 \theta'_{C_8^=,H^+}}{\sum^2} \qquad (2)$$

$$\text{where } \sum = 1 + \sum_{\substack{i,olefin \\ i \neq C_8^=}} K_{i,H^+} p_i + \theta'_{C_8^=,H^+} \quad \text{and} \quad \theta'_{C_8^=,H^+} = \frac{\theta_{C_8^=,H^+}}{\theta_V} \tag{3}$$

The rate constants and their temperature dependencies were modelled with the Arrhenius equation, modified in order to improve simultaneous estimation of pre-exponential factor and activation energy.

Since catalyst deactivation is a profound feature, it was included in a general way in the model. The rate of the reactions are given by equation below, where $r_{0,i}$ is the initial reaction rate for reaction *i*, and *a* denotes the relative activity:

$$r_i = r_{0,i}\, a \tag{4}$$

where the activity factor is calculated from

$$a = \left[\frac{1}{1 + (\alpha - 1) k' c_{P,0}^{\alpha - 1} t} \right]^{\frac{\beta}{\alpha - 1}} \quad \alpha \neq 1 \tag{5}$$

$$a = \exp\left(- \beta k' c_{P,0}^{\alpha - 1} t \right) \quad \alpha = 1 \tag{6}$$

Reaction and deactivation were assumed to be uniform throughout the reactor bed and the catalyst particles. The component mass balance is written as (p=partial pressure).

$$\frac{dp_j}{d\tau} = m_{cat} r_j a \quad j = C_3, C_4, i-C_4, C_5 \tag{7}$$

where τ is the space time of the fixed bed.

The overall generation rates of alkanes are determined by the isomerization of olefins on acid sites giving generation rates

$r_{C_3} = r_3 + 3r_4$ (propane)

$r_{i-C_4} = r_1 + r_6$ (isobutane)

$r_{C_4} = -r_1 - 2r_3 - r_4 - r_6$ (*n*-butane)

$r_{C_5} = r_3 - r_4$ (pentane)

$r_{H_2} = r_{C_{LH}} = r_{C_3^=} = r_{C_4^=} = \ldots = 0$

The reactor model equations were solved numerically by a stiff ODE-solver during the parameter estimation which was carried out by a Levenberg-Marquardt algorithm implemented in the software Modest (Haario 2001).

Examples of the fit of the model to the experimental data are provided by Figs 2-3. The figures reveal that the description of the conversion alone – including the catalyst deactivation – is not enough, but a detailed analysis of the product distribution is needed, as revealed by the selectivity analysis (Fig. 3). The detailed kinetic modeling

enables us to judge, which mechanism is prevailing under specified conditions (pressure, temperature). The model, which enabled bimolecular reaction path for isobutane formation, had a good fit on the selectivity to isobutane at high reactant pressures but was incapable to predict the increase in selectivity to isobutane with decreasing *n*-butane pressures. At the same time, the above mentioned tendency was very well predicted by the models enabling monomolecular mechanism for isobutane formation. The kinetic modelling also supported the proposal that excess of propane compared to pentanes is due to consecutive codimerization of formed $C_5^=$ with $C_4^=$ to $C_9^=$ followed by cracking to three $C_3^=$ species.

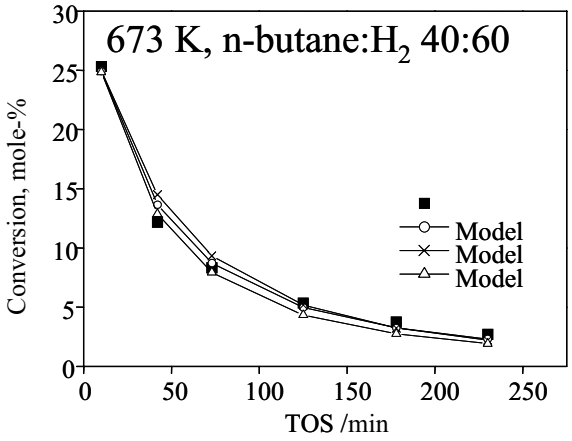


Figure 2. Examples of conversion as a function of time on stream at 673 K by the kinetic models compared to the experimental values.

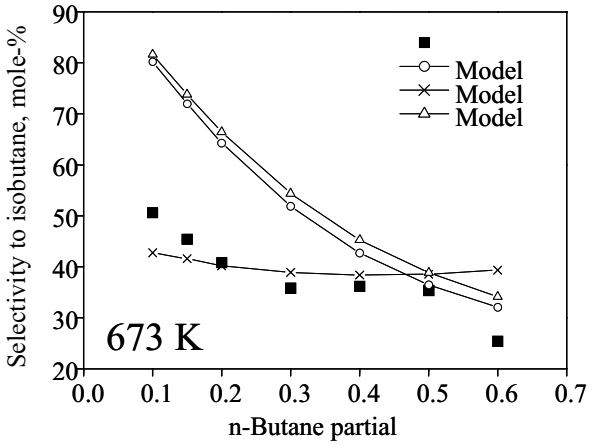
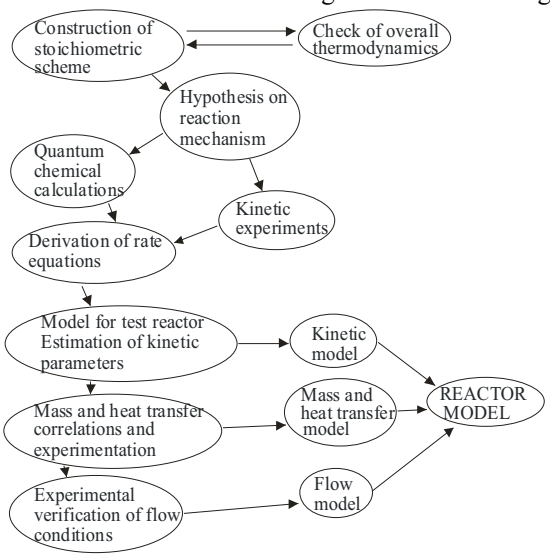


Figure 3. Selectivity to isobutane at TOS = 10 min as a function of n-butane partial pressure at 673 K by the kinetic models compared to the experimental values.

3. Conclusions

The approach applied is briefly summarized in the flowsheet sketched below. Successful modelling of catalytic reactors requires a strongly integrated approach. Due to the progress of applied quantum chemistry it is possible to get ideas and inspiration for mechanistic hypothesis, which are brought to kinetic equations including catalyst deactivation. Furthermore, models for heat and mass transfer as well as flow models are incorporated. Efficient and robust numerical algorithms are used to solve the kinetic and reactor models. The approach should not have a single missing link, since the final goal is a reliable design tool for chemical reactors integrated to surrounding process units.



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