Identification of kinetic models of heterogeneously catalyzed reactions

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Abstract

Three case studies present different aspects of the identification of kinetic models in heterogeneous catalysis. The demonstrations are based on the real examples of laboratory catalytic hydrogenation experiments. The common target of all the studies is to demonstrate the possibilities of maximizing the reliability of parameter estimates for the limited experimental sets of data. The topics of the case studies include the comparison of Langmuir–Hinshelwood (LH) and non-stationary kinetic models, a discussion concerning the effects of invalid assumptions for catalyst surface coverage, and issues related to the design of experiments. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

A wide range of diverse mathematical models of varying degrees of complexity and detail-level can be employed to describe the kinetic behavior of a heterogeneously catalyzed reaction [1]. Simultaneously, the present standard of computers has enabled the application of previously unfeasible regression techniques and more detailed mathematical models to become a common practice. These new approaches can alter the validity of many empirical rules and the adequacy of the established approaches. This article intends to demonstrate several interesting situations occurring in the data handling, using several model studies based on a practical background.

Langmuir–Hinshelwood (LH) models, describing the kinetics of heterogeneously catalyzed reactions, can be regarded as “standard”. Their ideas have not changed since the work of Hougen and Watson. A simple, heterogeneously catalyzed reaction is considered as a series of three consecutive steps—adsorption, surface reaction, and desorption—the one of which is substantially slower than the others. The slow step, usually the chemical reaction of adsorbed molecules on the catalyst’s surface, is described by a kinetic equation in accordance with its far-from-equilibrium assumption. Other steps are assumed to be near equilibrium and thus equilibrium equations are used for them. The typical rate equation is given by

$$r = \frac{K_{CA}}{1 + \sum_{i} K_{ci}}$$

(1)

where $k$ is the rate constant, $r$ the reaction rate, $K$ the formal adsorption coefficient, $c$ the concentration of reaction species in the fluid phase, $A$ the educt, and the sum in the denominator is performed through all components of the reaction mixture.
The validity of the pseudo-stationary state is usually reasonably accomplished for a single reaction. However, the probability of significant deviations from the pseudo-stationary assumptions is much greater for more complex reaction systems where multiple reaction steps compete for the same type of catalyst active sites and the interactions of different reaction steps are significant. The validity of the pseudo-stationary state can be assessed by comparing the reaction rates of all reaction steps. It is essential to point out that the comparison of rate constants is inadequate if the dynamic reaction systems (e.g. batch reactors) are concerned. The comparison of reaction step rates (varying with the reaction mixture composition) within the entire experimental range is absolutely necessary to determine whether a particular reaction step is faster than the others.

2. Pseudo-stationary state or non-stationary kinetics?

Reaction systems of several components almost consistently contain a few steps, the rates of which are of the same magnitude. Therefore, the usage of non-stationary models for such reaction systems can be beneficial [2]. These models use kinetic equations for the surface reactions as well as for the adsorption/desorption processes, so that the models contain the total component balances as well as balances on the catalysis’s surface. The balances for the i-th component are given by

\[ \frac{dC_i}{dt} = \sum_j \nu_{ij} k_j \theta_j \gamma \]  \\
\[ \frac{d\theta_i}{dt} = \frac{1}{\gamma} \left[ k_i (c_i - \theta_i \gamma) \theta_i - k'_i \theta_i + \sum_j \nu_{ij} k_j \theta_j \gamma \right] \]  \\
\[ \gamma = \frac{wq}{V \sum_i C_{0i}} \]

where \( t \) is the time, \( \nu \) the stoichiometric coefficient, \( \theta \) the fractions of catalyst’s active sites covered by species in subscripts, \( \gamma \) the catalyst to substrate ratio expressed in terms of moles of active sites per mole of substrate (see Eq. (2c)), \( k \) and \( k' \) are the rate constants of the particular component adsorption and desorption, respectively, \( V \) the total fluid phase volume, \( q \) the moles of active sites per gram of catalyst, \( w \) the weight of catalyst used and \( C_0 \) the initial concentration. Subscripts \( i \) and \( j \) denote reaction components and chemical reactions, respectively, and \( \gamma \) represents vacant active sites.

Experimental hydrogenation of butynedioic acid dimethylester [3] on platinum catalyst is one of a series of examples, where attempts to use the single rate-controlling step assumption fail. The reaction
Fig. 1. Reaction scheme of butynedioic acid dimethylester hydrogenation on Pt catalyst \( (A = \text{butynedioic acid dimethylester},\ B = \text{butenedioic acid dimethylester (trans- and cis-isomer does not form significantly)}, C = \text{butanedioic acid dimethylester})\).

Fig. 2. Reaction scheme of toluene hydrogenation \( (A = \text{toluene},\ B = \text{methylcyclohexene}, C = \text{methylcyclohexane})\).

A formal LH model (Eq. (3)) can be designed, as well as the detailed model concerning the aspects of non-stationary kinetics (Eq. (4)).

\[
\begin{align*}
\frac{dA}{dt} &= -k_1 A + k_2 B + k_3 C \\
\frac{dB}{dt} &= k_1 A - k_2 B \\
\frac{dC}{dt} &= k_2 B
\end{align*}
\]

\[
\begin{align*}
\frac{dA}{dt} &= -k_1 A Y + k_2 B Y + k_3 C Y \\
\frac{dB}{dt} &= k_1 A Y - k_2 B Y \\
\frac{dC}{dt} &= k_2 B Y
\end{align*}
\]

Hydrogen concentration in the fluid phase could be assumed constant, due to its constant pressure, solvent, and sufficient mixing. Therefore, its concentration was included into the rate constants of hydrogenation reactions.

The regression analysis of experimental data was performed for both the kinetic models. The comparisons of experimental data with the simulated ones are provided in Figs. 3 and 4. The comparison of the two figures or the values of objective function attained...
by both the models, allows making the conclusion that the LH model is not able to describe the kinetics of the reaction system satisfactorily. The sum of residual squares yielded by the regression using the LH model, was by more than one order of magnitude higher than the one attained for the non-stationary kinetic model. The optimal parameter estimates for the non-stationary kinetic model are given in Table 1, where their 95% confidence limits were used rather than more common confidence limits. They characterize the real confidence region instead of an approximate elliptical confidence region assumed by confidence interval computation. All computations involved were performed using the ERA software [5].

Table 1

<table>
<thead>
<tr>
<th>Parameter (min⁻¹)</th>
<th>Value</th>
<th>95% confidence limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
<td>3.1</td>
<td>1.6 to 1.4 × 10⁻⁹</td>
</tr>
<tr>
<td>k₂</td>
<td>9.7</td>
<td>1.5 to (max)</td>
</tr>
<tr>
<td>kₐ</td>
<td>5.8 × 10⁻⁹</td>
<td>3.5 × 10⁻⁹ to 1.3</td>
</tr>
<tr>
<td>k₇</td>
<td>3.3 × 10⁻¹</td>
<td>2.2 × 10⁻¹ to 6.1 × 10⁻¹</td>
</tr>
<tr>
<td>k₈</td>
<td>1.6 × 10⁻¹</td>
<td>1.9 × 10⁻² to (max)</td>
</tr>
<tr>
<td>k₉</td>
<td>7.7 × 10⁻²</td>
<td>4.9 × 10⁻² to 2.4 × 10⁻²</td>
</tr>
</tbody>
</table>

* 9 = 2.49 × 10⁻⁹.

Fig. 5. Modified reaction scheme of butynedioic acid dimethylester hydrogenation on Pt catalyst (A = butynedioic acid dimethylester, B = butenedioic acid dimethylester, C = butanedioic acid dimethylester).

The inability of the LH model to describe the reaction mixture behavior can be fully ascribed to the fact that the reaction system cannot fulfill the assumption of a single rate-controlling step. It is especially true for the reaction step B → C, where all the three reactions (B adsorption, B desorption, and surface B hydrogenation) occur in a non-stationary state. Part of the intermediate product B formed by the first surface reaction leaves the catalyst’s surface, but its amount is less than that at equilibrium. Its remainder is further hydrogenated to the final product before it can leave the surface. In terms of LH kinetics, this process can only be described by introducing the third (virtual) reaction into the reaction system (Fig. 5). The reaction r₂ in the scheme corresponds to the portion of the real A → B reaction product, which achieves the equilibrium with the fluid phase, while reaction r₃ corresponds to the formation of an intermediate product subject to further reaction without leaving the surface.

The LH model is able to describe the kinetics of the system similarly to the non-stationary kinetic description after the modification, but it is no further mechanistic because A → C reaction is purely theoretical. On the other hand, the non-stationary kinetic model is much closer to reality. Last, but not the least, the understanding of the reaction kinetics arises directly from the results of general non-stationary kinetic model applications. This is a great advantage compared to the LH model, which had to be set up empirically to provide the desired results.

More detailed attention should be paid to the method of interpretation of the non-stationary kinetic model. Fig. 6 shows the course of the catalyst’s surface coverage by reaction components in time. Disregarding the peaks in the very beginning of some profiles, which are present due to relatively low substrate/catalyst ratio, the profile of the intermediate product B maintains its low but relatively steady level, although the component A concentration in the fluid phase drops quickly. The concentration of the intermediate product in the fluid phase also does not reach excessive values. This means that the consequent hy-
dissociation of the intermediate product is fast enough to prevent adsorption–desorption equilibrium, which is in strict contradiction to the original LH model presumption. Despite this, it is unfeasible to choose other rate-controlling step for the LH model, because the rate of the second reaction is governed by at least three steps—the formation of the intermediate product, its adsorption, and desorption of the final product. Evidence of this can be seen in the upper confidence limits in Table 1. Rate constants of these reactions are relatively reliably estimated, and their values are quite comparable.

3. “Strong” catalyst–sorbate interaction

The application of the LH models frequently tends to adopt further simplifications in addition to that of the rate-controlling step. The assumption of the negligible vacant/occupied active sites ratio can be introduced as an example. Its aim is to eliminate one regression parameter and to decrease correlations among the remaining parameters significantly by neglecting the fraction of vacant sites and expressing reaction components adsorptivities only on a relative basis. It allows achieving more accurate and reliable parameter estimates, although there is a risk of the model losing its mechanistic character due to the simplifications.

The LH model of kinetics of toluene hydrogenation over the ruthenium catalyst [6] was designed in accordance with the scheme in Fig. 2. The experimental arrangement was similar to that described in the previous section. Rate equations for the first basic LH model for the reactor mass balance are given by

\[ r_1 = k_1 \frac{K_{AA}C_A}{1 + K_{AA}C_A + K_{BB}C_B + K_{CC}C_C} \]  

\[ r_2 = k_2 \frac{K_{AA}C_A + K_{BB}C_B + K_{CC}C_C}{K_{BB}} \]  

\[ r_3 = k_3 \frac{K_{AA}C_A + K_{BB}C_B + K_{CC}C_C}{K_{BB}} \]  

The comparison of experimental data with that simulated by the mathematical model is presented in Fig. 7. An interesting conclusion can be drawn about the results of regression analysis of this model (Table 2). Lower confidence limits for all adsorption

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>95% confidence limits to (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 ) (min(^{-1}))</td>
<td>( 3.9 \times 10^{-2} )</td>
<td>( 2.0 \times 10^{-2} )</td>
</tr>
<tr>
<td>( k_2 ) (min(^{-1}))</td>
<td>( 1.6 \times 10^{-2} )</td>
<td>( 6.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>( k_3 ) (min(^{-1}))</td>
<td>( 5.7 \times 10^{-2} )</td>
<td>( 8.0 \times 10^{-3} )</td>
</tr>
<tr>
<td>( K_A )</td>
<td>1.8</td>
<td>~0</td>
</tr>
<tr>
<td>( K_B )</td>
<td>1.3</td>
<td>~0</td>
</tr>
<tr>
<td>( K_C )</td>
<td>1.8</td>
<td>0</td>
</tr>
</tbody>
</table>

\( S = 1.59 \times 10^{-2} \).
coefficients are equal to ($K_A$) or approaching zero ($K_A$ and $K_B$). It can be explained by relatively weak sorption of reaction components on the catalyst's surface (equilibrium constants of adsorption $K_A$--$K_C$ are low), so that the term $K_{ACA} + K_{ACB} + K_{CPC}$ in the Eq. (5) denominators is almost negligible. Hence, the model's rate equations approximate equations.

$$r_1 = k_1^c c_A$$  \hspace{1cm} (6a)
$$r_2 = k_2^c c_B$$  \hspace{1cm} (6b)
$$r_3 = k_3^c c_B$$  \hspace{1cm} (6c)

where $k_i^c$ parameters represent the products of rate constants and adsorption coefficients from model [5]. A model using the set of rate Eq. (6) provides a description as accurate as the former one, but the reliability of its parameter estimates is significantly better (see Tables 3 and 4).

The assumption of negligible vacant/occupied active sites ratio will be made formally in order to demonstrate the problems associated with its application. It is difficult to justify its validity though, due to the results discussed above. The set of rate equations (Eqs. (7a)-(7c)) shows the result of the negligible vacant/occupied active sites ratio assumption.

$$r_1 = k_1 r_{ACA}^c / (K_A + r_{ACA}^c)$$  \hspace{1cm} (7a)
$$r_2 = k_2 r_{ACA}^c / (K_A + r_{ACA}^c)$$  \hspace{1cm} (7b)
$$r_3 = k_3 r_{ACA}^c / (K_A + r_{ACA}^c)$$  \hspace{1cm} (7c)

where $K$ are the relative adsorption coefficients given by $K_i = K_i^c / K_{ref}$. An adsorption coefficient of an arbitrary reaction component can be chosen for reference purpose. The best approach is to choose the one, which decreases covariances among other parameters as much as possible. It was discovered empirically that it is usually the component acting as the educt in most elementary reaction steps. All the three adsorption coefficients were tested as reference ones for the purpose of this study. The choice of $K_A$ was found to be optimal.

The comparison of the experimental data and those simulated by a model using Eq. (7) is virtually indistinguishable from the comparison presented in Fig. 7. It is in accordance with the very similar values of the objective function for the models with relative and absolute adsorption coefficients. All parameters of the model with relative coefficients (Eq. (7)) are significant and thus, the model cannot be simplified any further. The same applies for the model with absolute coefficients (Eq. (6)), except for the fact that it needs two parameters less and hence the reliability of its parameters is much higher. However, significant differences can be found between the interpretations of parameter estimates for both models.

Fig.8 shows the time-dependent profiles of the catalyst active sites fractions occupied by reaction components computed by the model with relative adsorption coefficients. These fractions are large in severe contrast to the results of the model, less restricted by simplification with absolute adsorption coefficients, which indicates a low degree of catalyst surface coverage.

The study clearly demonstrated the drawbacks of formal and/or insufficiently considered applications of simplified LH models with relative adsorption coefficients on modelling reaction systems with limited validity of assumption of high surface coverage of the
catalyst. This application was proved to lead to gratuitously inaccurate and unlike parameter estimates. However, the consequences of the drawbacks above are not necessarily apparent from the results of regression analysis. It should be the sufficient reason to avoid the application of the negligible vacant/occupied active sites ratio simplifying assumption, without having proved its validity.

4. Pre-experimental design

The reliability of kinetic parameter estimates is known to be strongly dependent on the applied design of kinetic experiments. In practice, it is generally reduced to the “more experiments = greater reliability” rule and modest effect of the experimental points within the time-scale is also admitted. Despite the unquestionable validity of that rule, the effect of increasing the number of experiments diminishes with the number of already available experiments. This fact makes the effect of additional experiments marginal, beyond certain limits. The exact value of those limits depends mostly on the variance of measured concentration and the concentration profiles complexity. It can be stated to vary between 10 and 15 for the typical properties of reaction systems, provided that the points are optimally distributed along the time-scale. Thus, if greater reliability of the parameter estimates is to be achieved by the experiment, additional independent variables should be taken into account for the design of experiments in order to accomplish the appointed goal.

The following example concerning the hydrogenation of butylenedioic acid dimethylester on palladium catalyst is intended to demonstrate the validity of the above statements. A simplifed reaction mechanism described by the reaction scheme identical to that in Fig. 1 was used for the design of the mathematical model. LH rate equations were used for simplicity.

\[
\begin{align*}
    r_1 &= \frac{k_1 K_A c_A}{1 + K_A c_A + K_B c_B} \quad \text{(8a)} \\
    r_2 &= \frac{k_2 K_B c_B}{1 + K_A c_A + K_B c_B} \quad \text{(8b)}
\end{align*}
\]

The experiments were carried out in an isothermal batch reactor. Two designs of experiments were used to fulfill the purpose of this demonstration. Time was the natural independent variable for both experiments. In the second one, the initial concentrations of reaction species were used as additional independent variables. The detailed structure of both designs is shown in Figs. 9 and 10. The designs consist of 20 experimental points. The experimental error can also be assumed to be identical for both experiments. As all the points in the first design were measured using identical initial concentrations of reaction components, the

![Fig. 8. Profiles of catalyst surface coverage by reaction components for toluene hydrogenation calculated by LH model with relative adsorption coefficients.](image)
Fig. 10. Experimental and simulated data for the variable initial composition design (butynedioic acid dimethylester (C), butene-dioic acid dimethylester (L), butanedioic acid dimethylester (Δ)). Empty and closed symbols represent different experimental series.

The results of regression analysis performed with the same model for experimental data from both experiments are summarized in the Table 5. The overall reliability of parameter estimates is characterized by the overall variance coefficient $Q$, given by

$$Q = \sum_{k} \frac{p_{k}^{+} - p_{k}^{-}}{p_{k}}$$

(9)

where the $p_{k}^{+}$ and $p_{k}^{-}$ symbols represent lower and upper 95% confidence limits for regression parameters.

Comparing the overall variance criterion values for both experimental designs, the superiority of the design with varied initial concentrations is clearly apparent. In order to justify the statement concerning the marginal effect of experimental point increase above a certain limit, the regression analysis was also performed for the set of data from the first design, where each second point was removed. The overall variance coefficient $Q = 0.978$ was obtained. The comparison of this value with that for a full set ($Q = 0.936$) shows that cutting the data set size in half does not affect the parameter estimates reliability nearly as severely as could be deduced from the experiments number reduction. From the other point of view, it is possible to state that simple doubling of the number of experimental points brought about only 5% more reliable parameter estimates. On the other hand, the identical increase of the number of parameters leads to nearly 30% more reliable parameter estimates, if two different initial compositions of reaction mixture are used.

5. Conclusions

The advantages of the non-stationary kinetics upon the standard LH models in reaction systems without the assumption of a single rate-controlling step were demonstrated. The non-stationary kinetic model consistent with the real reaction network was successful even in the case, where the LH model failed. It was also shown that non-stationary kinetic models need not be much more difficult to implement and handle compared to the LH models.

The application of LH models with the assumption of total catalyst surface coverage and relative adsorption coefficients was found to be questionable. It can improve the reliability of parameter estimates, but the models lose their semi-mechanistic character to some extent, as well as the interpretability of parameters.

The significant effect of the design of experiments on the parameter estimates reliability was also proved.
It was found that the simple addition of more experimental points brings about only a marginal effect on the reliability beyond a certain limit, unless the variability of initial conditions is included into the design of the experiments.

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References