

Microkinetic modeling as a tool in catalyst discovery

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We propose a new approach for catalyst development that combines different scientific disciplines: experimental design, surface science, reaction kinetics and simulations with the objective of accelerating catalyst development. In this paper we present a study of the possibilities of using small data sets in microkinetic modeling, and studies of the required precision of temperature measurement.

KEY WORDS: catalysis; microkinetic modeling; catalyst development.

1. Introduction

Macro-kinetic modeling is using simple models based on power law kinetics or empirical Hougen-Watson kinetic expressions with experimental observations, i.e. gas composition, temperature, and pressure [1]. Macro-kinetic modeling is very useful and widely used in chemical reactor design, quality control in catalyst production, catalyst selection, and studying of catalyst deactivation [2]. The models used in macro-kinetic calculations are very flexible functions for fitting of kinetic data. However, the flexibility that makes them so useful when used as empirical expressions makes them virtually useless for deduction of mechanistic information. The models do not describe elementary reactions at the microscopic level and different models can fit the same data well [3]. More detailed studies of reaction kinetics can be done by microkinetic modeling, where a reaction mechanism and the molecular properties of reactants and intermediates are used in simulations of the reaction at the macroscopic level. Verification of microkinetic models is based on more detailed surface science measurement techniques. Some successful kinetic models, for example the reaction mechanism for ammonia synthesis [4], helped to understand the reaction at the microscopic level [5] and allowed faster catalyst development [6]. Unfortunately many important reactions remain uninvestigated because of lack of detailed experimental data.

The purposes of this paper are: (a) to present a proposal for catalyst development, combining microkinetic modeling with a traditional experimental approach, (b) to investigate if small experimental data sets can be used in microkinetic modeling, and (c) to study the influence of systematic temperature errors, random temperature errors and outliers.

2. Proposal for catalyst development

Traditionally catalysts have been discovered, developed and optimized by trial and error. Recently the initial search for catalyst candidates has been speeded up by combinatorial methods and parallel screening [7]. The search for a catalyst candidate, using the combinatorial method, is based on testing small amounts of samples of many different compositions. This method has the advantage of checking many compositions, but the small amounts of catalyst limit products concentrations. This might lead to false candidates, i.e. materials that look promising in the screening, but suffer from product inhibition, poor selectivity, or rapid decay at higher product concentrations and high conversions.

Parallel screening facilitates catalyst testing in a multi-tube reactor under more accurate and realistic conditions than in miniaturized combinatorial techniques [8]. However, testing many catalysts under the same conditions may miss good catalysts that would operate better under different conditions.

There are two major complications in the development of new catalysts:

- (1) When a catalyst candidate is identified by parallel screening, the laborious and slow optimization remains.
- (2) Even if mechanistic information would be helpful in an early stage in the catalyst development, kinetic data are generally not analyzed in details at this stage.

In order to accelerate development of catalysts, an algorithm for catalysts discovery is proposed.

Figure 1 presents the scheme of the approach; the thicker arrows illustrate the information flow in the traditional approach. In the new approach information will flow along all the arrows: Exploration of a new catalyst starts with the proposal of a series of reaction mechanisms. Microkinetic models are derived for each mechanism [9,10] and data from other sources such as

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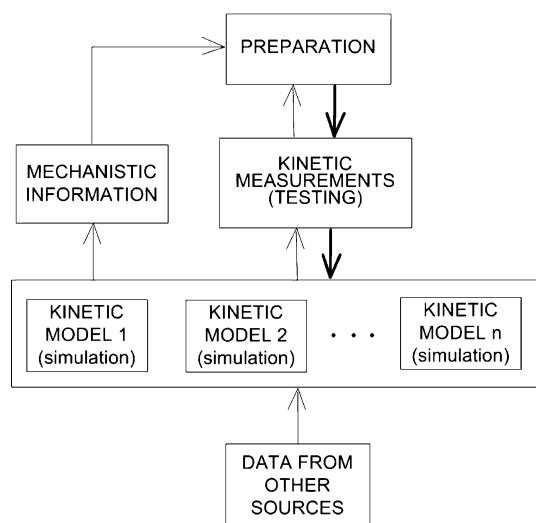


Figure 1. The scheme of the method for catalyst development.

spectroscopy, isotopic labeling and density functional theory (DFT) calculations are incorporated. Afterwards a small library of catalysts is tested at a limited number of reaction conditions. After each measurement, all available information is analyzed, and a new measurement is proposed in order to rapidly uncover the properties of the catalyst. When different metals are used as a catalyst for the same reaction, it is generally observed that the reaction rate can be correlated with the position of the metal in the periodic table [6]. After several catalysts have been explored, the observed relation between catalyst composition, structure and activity is used as a source of inspiration for new preparations.

3. Microkinetic modeling

An important part of the proposed approach for catalyst development is the analysis of small data sets. In order to investigate if it is possible to determine different reaction mechanisms with very limited numbers of measurements, 8 calculated observations are fitted into 11 different microkinetic models.

3.1. Calculated observations

The experimental points, called observations, are calculated in an integral plug flow reactor for the

hypothetical reaction $A_2 + 2B = 2AB$ with reaction mechanism 2, see Table 1, and step 1 as the rate limiting step [10].

The parameters used in the calculation are: the pre-exponential factor $A = 1 \times 10^{11} \text{ s}^{-1}$ and the activation enthalpy of the rate limiting step $H^\ddagger = 80 \text{ kJ}/(\text{mol K})$. Thermodynamic parameters, entropy and enthalpy, describing the properties of the gases and intermediates are presented in Table 2.

The microkinetic models are derived from the reaction mechanism using a number of simplifying assumptions, i.e. a Langmuir-Hinshelwood mechanism proceeding on a surface of identical and non-interacting adsorption sites [9]. Evidently this is a simplification; however, it does have some advantages. First, data from other sources, such as spectroscopic and thermodynamic data for intermediates, are easily incorporated in the model. Secondly, interpretations based on a simplified, physical models, are much more reliable than interpretations based on more flexible expressions with no physical basis. Figure 2 presents the 8 ideal observations that have been used in the simulations.

In order to simulate real data, the following errors were added to the observations: (1) a systematic temperature error from 1 to 6 K, (2) a random error simulated with Gaussian distribution with a standard deviation from 1 to 6 K, (3) ideal temperature measurements with one outlier [11].

3.2. Microkinetic models

The simple reaction $A_2 + 2B = 2AB$ can have a very simple, or very complicated reaction mechanism [10,12]. On the basis of three different reaction mechanisms, see Table 1, 11 models were used in the calculation. They are named 1a, 1b, 2a, 2b, 2c etc., where 1, 2, 3 is the reaction mechanisms and a, b, c is the rate limiting step. For example model 3b is using reaction mechanism 3 with step 2 as the rate limiting step. The thermodynamic parameters for the gases are shown in Table 2 and were used in all simulations. The parameters fitted to the calculated data from figure 2 are the activation enthalpy and the preexponential factor of the rate limiting step and enthalpies of the intermediates.

Table 1
Reaction mechanisms for reaction $A_2 + 2B = AB$ [10]

Reaction mechanism 1	Reaction mechanism 2	Reaction mechanism 3
Step 1: $A_2 + 2^* = 2A^*$ Step 2: $A^* + B = AB + ^*$	Step 1: $A_2 + 2^* = 2A^*$ Step 2: $B + ^* = B^*$ Step 3: $A^* + B^* = AB^* + ^*$ Step 4: $AB^* = AB + ^*$	Step 1: $A_2 + ^* = A_2^*$ Step 2: $A_2^* + ^* = 2A^*$ Step 3: $B + ^* = B^*$ Step 4: $A^* + B^* = AB^* + ^*$ Step 5: $AB^* = AB + ^*$

Table 2
Thermodynamic parameters of species [10]

Species	S_i [J/(mol K)]	H_i [J/mol]
A_2	210	6,000
A_2^*	160	-5,000
A^*	30	-42,000
B	250	63,000
B^*	195	25,000
AB^*	275	-80,000
AB	210	-30,000

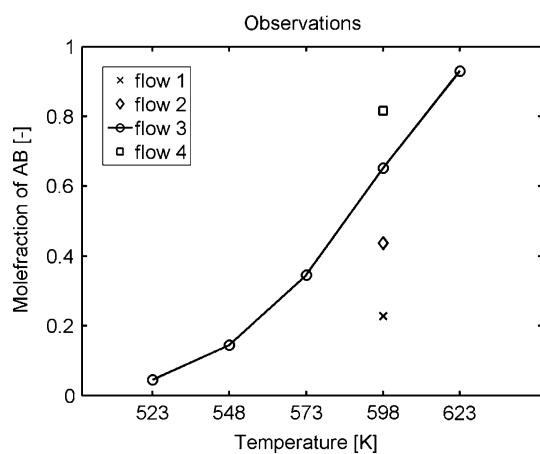


Figure 2. Calculated observations.

4. Results

Table 3 presents the result of a simulation where the ideal observations from figure 2 have been fitted into the 11 kinetic models. The lower the value of the sum of squares, the better fit of the data to the model. The sum of squares equal to 10^{-2} means that the average variation of calculated molefraction is equal to 25% of the observed value. For a sum of squares equal to 10^{-4} the variation is 10%, and for 10^{-6} less than 1%. The table shows that model 2a, which has been used for generating the observations, gives the best fit. Model 3b has obtained the second best fit, almost as good as the fit of model 2a. This happens because models 2a and 3b are different mechanisms that are having the same kinetics; they have the same rate limiting step with the difference that adsorption of A_2 occurs in two steps in model 3b.

Figures 3–5 present the results of studies of required precision of temperature measurement. Figure 3 shows fitting of the data with a systematic error. We present 9 models; 2 models that performed the worst are off scale. It can be seen that model 2a, that was used for generating the data, has been found to be the best when no temperature variation was applied, $\Delta T = 0$. At a small variation of the temperature, model 3b appears to be the best. Even 6 K of systematic error allows distinguishing models 2a and 3b from all other models.

Table 3
Fit of kinetic models to the ideal data

Model	Sum of squares
1a	$1.0 \cdot 10^{-2}$
1b	$1.6 \cdot 10^{-2}$
2a	$4.4 \cdot 10^{-6}$
2b	$3.4 \cdot 10^{-4}$
2c	$1.8 \cdot 10^{-3}$
2d	$4.2 \cdot 10^{-2}$
3a	$2.8 \cdot 10^{-4}$
3b	$7.3 \cdot 10^{-6}$
3c	$4.2 \cdot 10^{-4}$
3d	$1.8 \cdot 10^{-3}$
3e	$4.4 \cdot 10^{-2}$

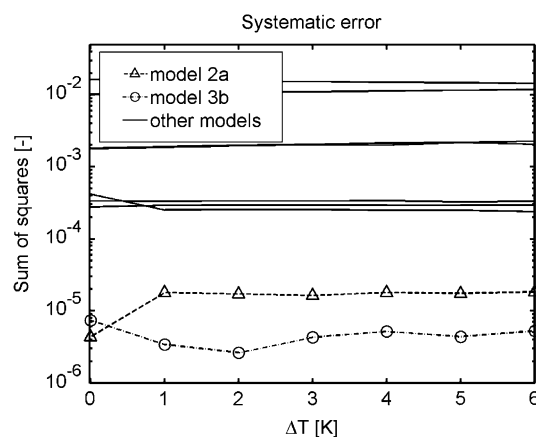


Figure 3. Results of simulations with systematic error of temperature measurement.

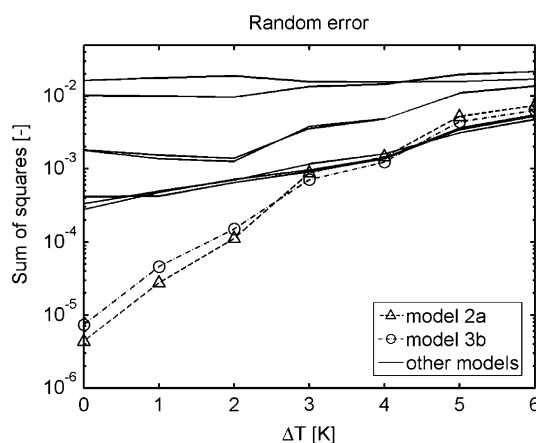


Figure 4. Results of simulations with random error of temperature measurement.

Figure 4 presents fitting of the data with a random temperature measurement error. 9 models are presented; 2 models that performed the worst are off scale. A random error in the temperature measurement with a standard deviation equal to 3 K makes it difficult to

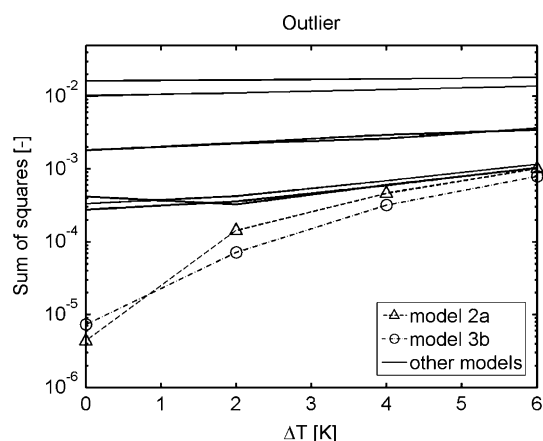


Figure 5. Results of simulations with one outlier.

discriminate models 2a and 3b from the others, but 6 models can be eliminated.

In practice, depending on the temperature controller, fluctuations of temperature in a microreactor can be from 0.5 to 2 K. Is it then reasonable to use small data sets in microkinetic calculations? Yes, because even if we are not able to find the right reaction mechanism with 8 observations, it is possible to eliminate many false reaction mechanisms, which can be very helpful in planning of the next experiments.

Figure 5 shows the fit of ideal data with one outlier; 9 best models are presented. The data can not be fitted to model 2a, when the temperature of the outlier is about 4 K away from the expected value.

5. Conclusions

A new approach for catalyst development, combining experimental design, reaction kinetics and surface science, has been presented. The method suggests detailed analysis of initial kinetic measurements by the use of microkinetic modeling. In order to study possibilities of using small experimental data sets in microkinetic calculations, 8 ideal calculated observations and observations with (a) systematic error, (b) random error and (c) one outlier have been fitted to 11 kinetic models.

The simulations show that the ideal observations were perfectly fitted to model 2a and 3b. Model 2a has been used to calculate the data points and model 3b is almost identical to model 2a. This supports the idea that small kinetic datasets can be used to deduce mechanistic details provided the fitting functions are chosen with care.

In the studies of measurement errors we have found that systematic errors do not influence the calculations. Even if the systematic error is equal to 6 K, the correct model had the second best fit. A random error of measurement equal to 2 K still allows us to find the correct model for the small data set. The presence of outliers in the measurements is very detrimental: a 2 K error on one of the measurements makes it difficult to find the right model. This shows that small data sets can be used in microkinetic calculations, but precision of the measurements is very important.

In order to minimize the effect of measurement error, we would like to include the outlier detection in our future simulations and study the change of the random error with repetition of the measurements.

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