

Microkinetic Assessment of Propane Selective Oxidation to Acrylic Acid

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Abstract

This work describes and uses an advanced (micro)kinetic modeling tool, which allows researchers with little programming skills to both implement and assess advanced microkinetic models. The propane selective oxidation to acrylic acid is used as the model reaction.

Introduction

Microkinetic modeling is gaining more and more attention during the last years as an efficient way to bridge the gap between surface science and applied catalysis. The overall behavior of catalytic materials is assessed through a microkinetic description based on elementary steps [1]. The understanding of the reaction mechanisms and the control of selectivity in catalysis by oxides, such as the challenging 1-step propane selective oxidation [2], requires an integrated effort between theory, modeling, surface characterization and reactivity testing.

Microkinetic modeling, i.e. including all possible elementary steps and without assuming the existence of rate-determining steps, provides in principle better insight in the importance of the different reaction pathways and can possibly relate the latter to specific catalytic properties [3]. However, the drawback of this kind of models is their complexity requiring more time to capture and analyze the results as well as to build the network in the first place. The large number of parameters is another challenge. It may be dealt with, to some extent, by calculating model parameters based on transition-state theory [4]. Nevertheless, the fundamental nature of a microkinetic model makes it more robust when extrapolating to a wider range of conditions. Moreover, the rate coefficients used can be related to catalyst properties and, hence, could unveil important information, e.g. about how different composition or synthesis procedures might affect reaction selectivity or yield [5].

This kind of kinetic model can be easily incorporated in workflows that use computational tools to treat data acquired, for instance, from High-Throughput Experimentation (HTE) by conducting, e.g. kinetic modeling and reactor simulation. For that, an interactive user environment is necessary, enabling experts as well as non-experts to construct and deploy their analytic applications with minimum programming effort. Designed correctly, such systems increase productivity, while enabling scientists to concentrate on the scientific aspects of experimental research. Therefore, the prime goal lies in speeding up the whole discovery and optimization process, but minimizing the costs and human efforts needed in the experimental

workflow. This goal is only to be achieved by adequate software tools at every single stage of the experimentation process [6].

For this task, a software tool – microKinetic Engine (μ KE) – was developed that automatically translates any reaction network into a mathematical model. The corresponding differential and algebraic equations are solved using appropriate mathematical routines and the statistical analysis of the regression of experimental data follows. This is the core engine of the tool that can be implemented into any existing application supporting a Graphical User Interface (GUI). Combined with such a high end software application in, e.g., an MS Windows environment, the user friendliness is significantly enhanced. The tool can handle any amount of data, an unlimited number of elementary steps and components and can treat homogeneous as well as heterogeneous reactions. Furthermore, stochastic algorithms, such as genetic algorithms, can be used for the optimization of objective functions, in addition to deterministic algorithms.

The μ KE is used for solving a set of differential algebraic equations and for optimizing kinetic parameters through regression with propane selective oxidation to acrylic acid over propene and acrolein as model reaction [7].

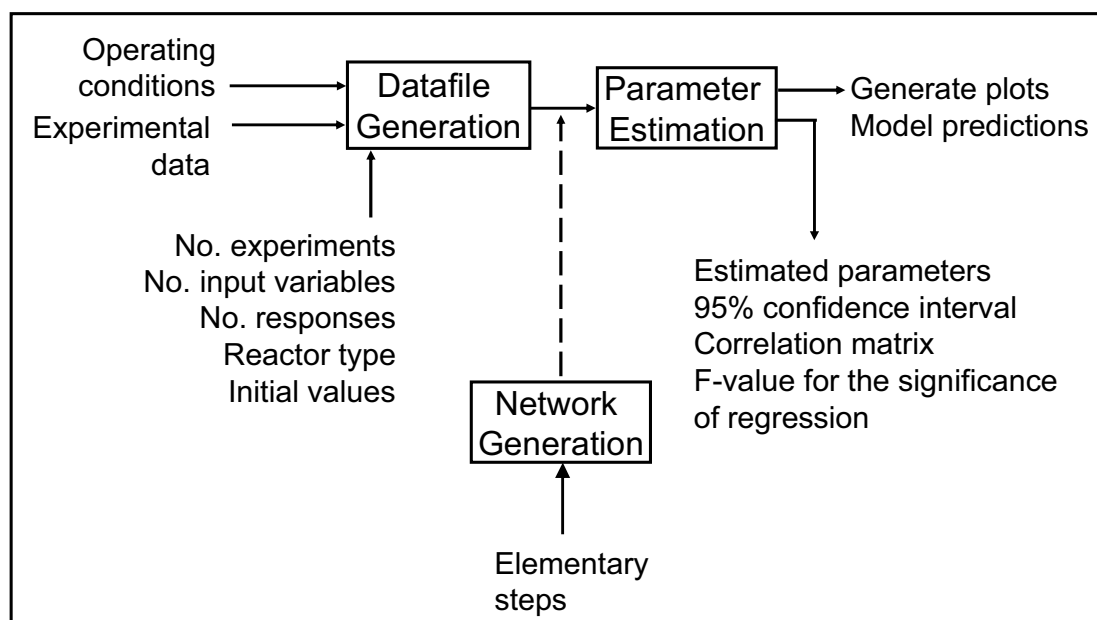


Figure 1. Schematic diagram of the microkinetic engine (μ KE)

Software tool: Microkinetic Engine (μ KE)

A general scheme of a kinetic modeling workflow is presented in Figure 1. The necessary input information, such as the number of experiments, initial parameter guesses, operating conditions, experimental results, etc, need to be gathered in an input file. When all requested input information is available, a FORTRAN executable is called that is responsible

for conducting the parameter estimation, resulting in the model calculations accompanied by appropriate plots. Finally, a statistical analysis of the results and a sensitivity analysis take place, giving information about the quality of the fit, the correlation between the parameters, the significance of the regression and the dependence of the responses to each parameter. Before introducing the Graphical User Interface (GUI) in the next section, some parts of the tool will be discussed more thoroughly.

Reaction Network

In the part of the input data file where the reaction network is constructed, the number of reactions and the list of components are given first. More advanced features are also implemented such as the ability to distinguish between observable species and reaction intermediates and to work on a catalytic reaction. In the latter case, the intermediates refer to any surface species either being involved in an adsorption or in a surface reaction while the observables correspond to the components being measured experimentally. The latter are the so-called responses for which the experimentally observed outlet flow rates and also the values for the applied weights are provided. A maximum of three reactants and three products can be involved in an elementary step. Examples of possible reaction steps in the reaction network are:

$A \rightarrow B$	homogeneous reaction, 1 reactant and 1 product
$A + B \rightarrow C + D$	homogeneous reaction, 2 reactants and 2 products
$A + B + C \rightarrow D + E + F$	homogeneous reaction, 3 reactants and 3 products
$A + * \rightarrow A^*$	heterogeneous reaction, adsorption of species A on the catalytic surface
$A^* + B^* \rightarrow D^* + E^*$	heterogeneous surface reaction, the species are adsorbed on the catalytic surface, and react on the surface
$A^* + B \rightarrow D^*$	Eley-Rideal type of reaction, B comes from the gas-phase and reacts with adsorbed A
$A^* + B^\# \rightarrow D^* + E^\#$	heterogeneous reaction between adsorbed species on different active sites (bifunctional catalysts)

When a catalytic reaction is modeled, the active site * or # is always included as one more species of the network. The sequence of elementary steps that constitute the network can be subjected to changes any time. An extension will consist of including homogeneous and heterogeneous reactions together by distinguishing between intermediates in the gas phase and intermediates on the surface.

Mathematical Model and Parameter Estimation

For a plug flow reactor, the following differential equations have to be integrated for each gas phase i component:

$$\frac{dF_i}{dW} = R_i \tag{1}$$

F_i : molar flow rate of component i [mol s⁻¹]

W : catalyst mass [kg]

R_i : net production rate of component i [mol kg⁻¹·s⁻¹]

The net rate of formation of species i is obtained by the summation of the rates of the elementary steps in which i is produced minus the rates of the elementary steps in which i is consumed:

$$R_i = \sum_j k_j C_{\text{observable}}^n C_{\text{intermediate}}^m \quad (2)$$

k_j : rate coefficient of elementary step j

$C_{\text{observable}}$: concentration of the observable [mol kg^{-1}]

$C_{\text{intermediate}}$: concentration of the intermediate [mol kg^{-1}]

n, m : reaction orders

The pseudo-steady state approximation is made for the intermediates. Consequently, the net production rate of the intermediates is zero.

$$R_{\text{intermediate}} = 0 \quad (3)$$

The mass balance of the catalyst active sites is given by:

$$C_{\text{tot}} = C_* + \sum C_{\text{intermediate}} \quad (4)$$

That leads to a set of differential and algebraic equations that is solved using the subroutine DASPK [8].

The objective function defined as the residual sum of squares of the molar flow rates of the components and minimized with respect to the unknown parameters k_j is given below:

$$S(k_j) = \sum_{p=1}^q \sum_{j=1}^l w_p (F_{j,p} - \hat{F}_{j,p})^2 \xrightarrow{k_j} \min \quad (5)$$

Where q equals the number of responses, l equals the number of experiments, \hat{F} represents the experimental flow rates and w_p are the weights for each response.

Non isothermal data can be dealt within the software tool through reparameterized Arrhenius expressions [9]. Reparameterization is performed in order to reduce the correlation between pre-exponential factor and activation energy.

The microkinetic engine serves as an independent tool since its executable can be attached to any existing code written in any programming language. Two deterministic optimization techniques are used: Rosenbrock is the first optimization subroutine called to find the good direction in the parameter space without leading to divergence and then the more sophisticated Levenberg-Marquardt method (ODRPACK 2.01 [8]) continues to estimate the final values for the parameters. In order to overcome issues related to deterministic parameter estimation routines, such as getting trapped in a local minimum, the engine was coupled with a stochastic optimization routine. To enhance the user friendliness of the tool a graphical user interface has been developed. Both items are further discussed in the following sections.

Genetic Algorithms

The set of equations that has to be solved in models incorporating chemical kinetics is generally highly non-linear and the mathematical problem is usually numerically stiff [9]. In addition, the large number of parameters included in microkinetic models leads to non-convex objective functions. The conventional “hill-climbing” algorithms, such as Rosenbrock, are prone to ending up in local optima, while the common gradient-based optimization routines such as Levenberg-Marquardt can identify a local optimum mainly around the initial guess [10]. In such cases, evolutionary algorithms such as genetic algorithms (GA) are preferred, which: a) do not use initial values for the parameters but ranges, b) are resistant to early convergence in local optima and c) appropriate for large-scale optimization problems.

Genetic algorithms combine survival of the fittest among string structures with a random information exchange to form a search algorithm. They are stochastic search procedures in which a population of randomly generated solutions is progressively modified using genetic operators – selection, crossover and mutation – in order to single out the individuals with the “genetic information” that leads to the best performance and improve the population’s fitness as measured by their effectiveness in predicting the experimental data [11].

Therefore, in the case of large parameter spaces, genetic algorithms could serve well in finding initial guesses, since many different possibilities are investigated and refined simultaneously [12]. Nevertheless, binary GA encoding does not give the exact value of the global minimum but instead provides a limited area with a high probability to find an overall minimum. Once this region is determined after the GA run, it is necessary to implement a local minimization strategy so as to refine the search and reach the global optimum as desired.

The major drawback of the genetic algorithms is that there is no rigorous mathematical proof that they will converge to the global optimum. Moreover, their performance is strongly influenced by the GA control parameters which need tuning [11]. The genetic algorithms incorporated in the microkinetic engine as a separate subroutine is a micro-genetic one, which uses a smaller population size and for that performs faster than typical GA [13]. The GA routine is called before the deterministic optimization algorithms and uses the same objective function.

Graphical User Interface

The disadvantage of such an advanced, mathematically oriented FORTRAN code is that it cannot be handled by users that are not familiar with, no to say expert in, programming. Hence, a graphical user interface is essential for providing the user friendliness required to address dissemination and manageability. An in-house Windows application was developed using Visual Basic .NET. The forms on the main window are arranged in a tab-like structure where the components are displayed in separate tabs on the upper part of the window.

The purpose of the application is to provide the user the ability to easily create the input file required for the FORTRAN executable. The “Import Data” tab includes all the necessary information that should be provided in the beginning to construct the input file such as the number of input/output variables, the selection of running in simulation or estimation mode, the reactor type used and the type of reaction, i.e. catalytic or not.

The “Generate Network” tab (Figure 2) represents the original part of this software. It gathers both the reaction network and the components. To that purpose, a data grid linked to a MS Access database is used. There are two ways of adding or deleting components: the combo box in the upper part of the window can be used or the user can write directly inside the cells of the data grid. Whatever method is applied, the “UpdateDB” button should be pushed afterwards to update the database. The checkbox serves in distinguishing between the intermediates and the observables.

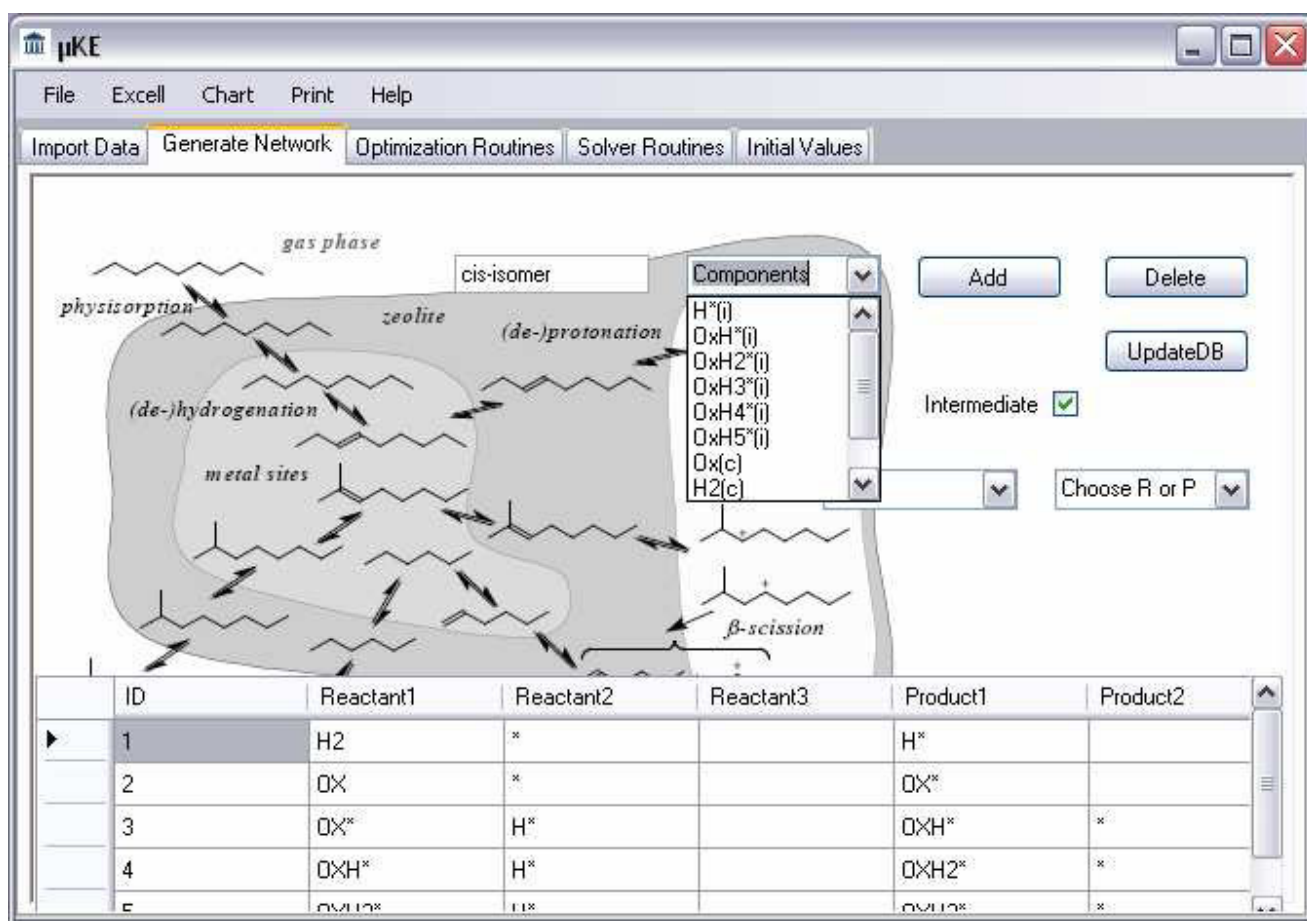


Figure 2. In-house Windows application, “generate network” tab

The tabs named “Optimization Routines and Solver Routines” include the control parameters for Rosenbrock and Levenberg-Marquardt algorithms as well as for the solvers. Default values are available that have proven to perform well in common regression problems.

The last tab serves in providing the initial guesses and the upper/lower limits for the parameters.

Summarizing, this Windows application is a flexible tool, which in conjunction with the core engine comprises a robust, user-friendly tool for treating high-throughput data. In the future, more features could be added such as MS Excel sheets and figures.

Propane Selective Oxidation to Acrylic Acid

The last 2 decades, there has been a major interest for the selective oxidation of light alkanes into the more valuable alkenes [1], [14], which could be further oxidized to aldehydes, acids, etc. The ongoing use of natural gas, where methane, ethane and propane are abundant, together with the increasing need for various commercially important polymers lead researchers and industry to pursue 1-step direct processes for that conversion. The economical gain could be enormous as i.e., components like propane are much cheaper than propylene. The successful manufacture of maleic anhydride from n-butane by selective oxidation – back in the 80s – was considered as an encouraging indication of what could follow in the future. In this work, we focus on the microkinetic modeling of the 1-step propane selective oxidation to acrylic acid, which is favorable compared to the 2-step process that is currently being used.

Experimental Data

Experimental data were obtained at two temperature levels, i.e., 350°C and 380°C and four space times, i.e., 3.75, 7.5, 10 and 12.5 kg×s×mol⁻¹. The propane partial pressure was 5kPa and the molar oxygen to propane ratio amounted around 2. A MoV_{0.3}Te_{0.17}Nb_{0.1}O_x catalyst was used which is known to give among the highest acrylic acid selectivities and yields.

Network Construction

To build the microkinetic model used in this work, Wong et al.'s [7] proposed network for selective propylene oxidation was used, utilizing only the route to acrylic acid and adding few more steps for propane conversion to propylene. Because of the limited number of experimental data considered, the elementary steps were classified into slow and fast steps. In order to be able to tune the selectivity, a second rate coefficient for the slow steps in the formation of acrolein was used. Hence, three kinetic coefficients are to be determined.

Results-Discussion

The propane conversion, acrylic acid yield and selectivity are qualitatively if not quantitatively described by the model, as can be seen in Figures 3–5. The reverse surface elementary reactions, i.e., from propene to propane (steps 6-8), acrolein to propene (steps 15-17) and acrylic acid to acrolein (steps 23-25) were found to occur only at low rates at the operating conditions used (Table 1). Two among the three steps considered for catalyst re-oxidation and water formation are in quasi-equilibrium. The estimates for the rate coefficients

are reported in Table 2. The calculated t-values for the individual significance of the parameter estimates are around 10, which is sufficiently higher than the tabulated value of 2. Also the F-value for the global significance of the regression is sufficiently high, i.e., between 500 and 1000. The 1st rate coefficient controls the propane conversion while the second describes the potentially fast and, hence, quasi-equilibrated elementary steps. The third one is specific for acrolein production and, as a consequence, is responsible for changes in the acrylic acid selectivity and yield, vide Table 2.

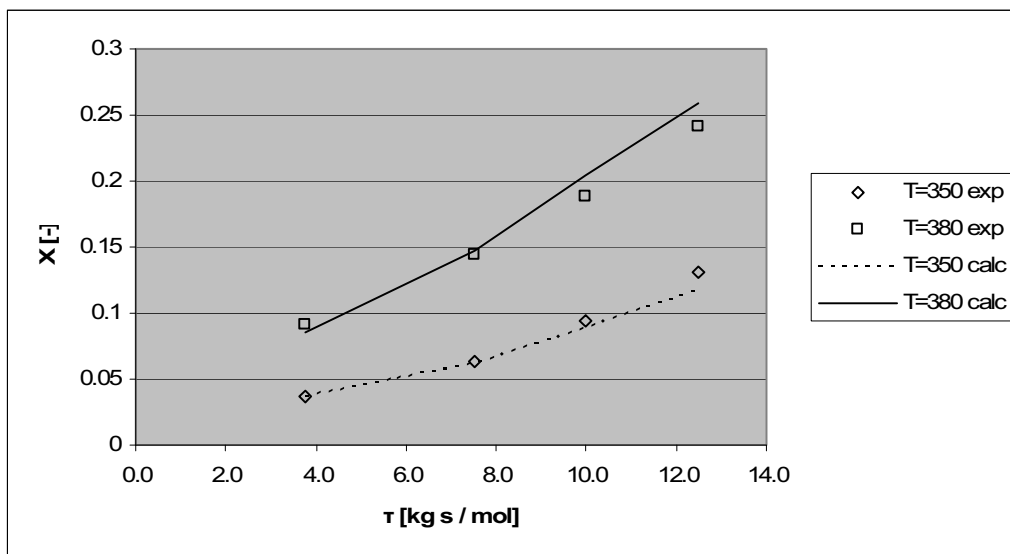


Figure 3. Experimental and calculated conversion of propane versus space time at 350 and 380°C

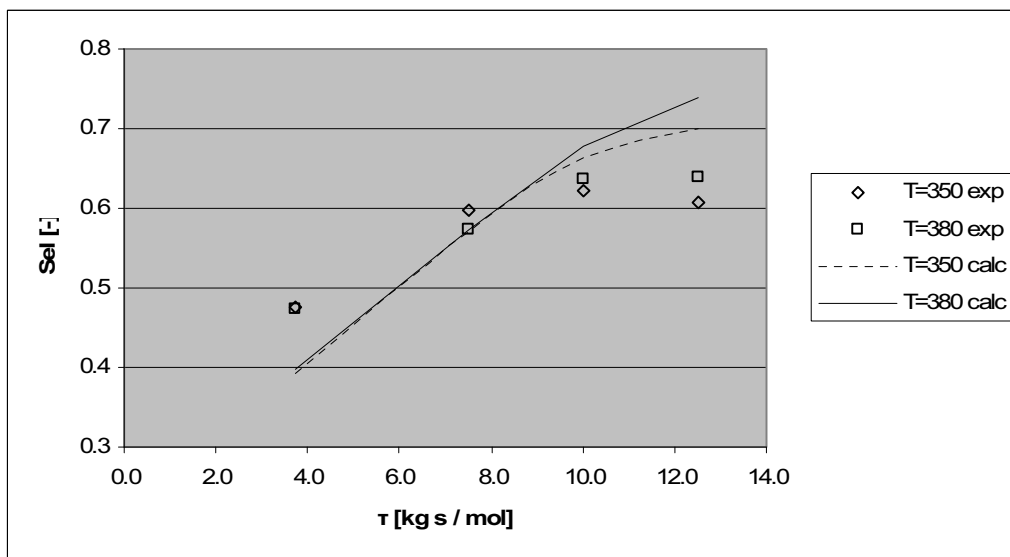


Figure 4. Experimental and calculated selectivity of acrylic acid versus space time at 350 and 380°C

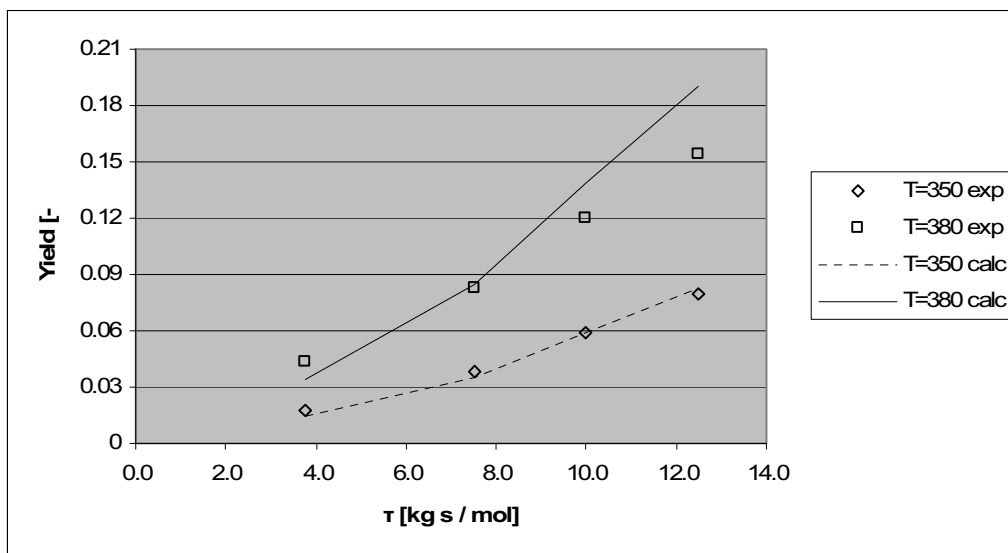


Figure 5. Experimental and calculated yield of acrylic acid versus space time at 350 and 380°C

Table 1. Elementary steps and correspondingly assigned rate coefficients and calculated reaction rates at 350, 380°C

Step	Reactant1	Reactant2	Product1	Product2	Coeff.	Rate (350°C)	Rate (380°C)
1	CH3CH2CH3	*O	*(OH)CH2CH2CH3		1	3.3E-02	2.0E-02
2	*(OH)CH2CH2CH3	*O	*OCH2CH2CH3	*OH	2	3.3E-02	1.9E-02
3	*OCH2CH2CH3	*O	*CH2(O)CHCH3	*OH	2	3.3E-02	1.9E-02
4	*CH2(O)CHCH3	*	*CH2CHCH3	*O	2	3.8E-02	2.3E-02
5	*CH2CHCH3		CH3CHCH2	*	1	3.3E-02	2.1E-02
6	*(OH)CH2CH2CH3		CH3CH2CH3	*O	1	5.5E-07	6.7E-05
7	*OCH2CH2CH3	*OH	*(OH)CH2CH2CH3	*O	1	8.0E-08	9.8E-06
8	*CH2(O)CHCH3	*OH	*OCH2CH2CH3	*O	1	2.4E-08	3.5E-06
9	*CH2CHCH3	*O	*CH2(O)CHCH3	*	1	5.0E-03	3.5E-03
10	CH3CHCH2	*	*CH2CHCH3		1	2.2E-06	1.9E-03
11	CH3CHCH2	*O	*(OH)CH2CHCH2		3	3.3E-02	2.0E-02
12	*(OH)CH2CHCH2	*O	*OCH2CHCH2	*OH	2	3.3E-02	2.0E-02
13	*OCH2CHCH2	*O	*OCHCHCH2	*OH	2	3.3E-02	2.0E-02
14	*OCHCHCH2		CH2CHCHO	*	3	2.5E-02	2.2E-03
15	*(OH)CH2CHCH2		CH3CHCH2	*O	1	5.5E-07	6.8E-05
16	*OCH2CHCH2	*OH	*(OH)CH2CHCH2	*O	1	8.0E-08	1.0E-05
17	*OCHCHCH2	*OH	*OCH2CHCH2	*O	1	6.4E-08	9.2E-06
18	CH2CHCHO	*	*OCHCHCH2		1	1.9E-02	6.7E-04
19	*OCHCHCH2	*O	*C(O)CHCH2	*OH	2	2.7E-02	1.8E-02
20	*C(O)CHCH2	*O	*OC(O)CHCH2	*	2	2.7E-02	1.8E-02
21	*OC(O)CHCH2	*OH	*OC(OH)CHCH2	*O	2	2.7E-02	1.8E-02
22	*OC(OH)CHCH2		CH2CHCOOH	*	2	6.4E-02	2.5E-02
23	*C(O)CHCH2	*OH	*OCHCHCH2	*O	1	6.4E-08	9.3E-06
24	*OC(O)CHCH2	*	*C(O)CHCH2	*O	1	2.6E-07	3.9E-05
25	*OC(OH)CHCH2	*O	*OC(O)CHCH2	*OH	1	2.4E-08	2.3E-06
26	CH2CHCOOH	*	*OC(OH)CHCH2		1	3.8E-02	6.7E-03
27	O2	*	*O	*O	2	5.8E+04	1.3E+02
28	*OH	*OH	*O	*H2O	2	5.4E+04	1.0E+02
29	*H2O		H2O	*	1	9.0E-01	3.5E-01
30	*O	*O	O2	*	2	5.8E+04	1.3E+02
31	*O	*H2O	*OH	*OH	2	5.4E+04	1.0E+02
32	H2O	*	*H2O		1	8.3E-01	3.1E-01

Table 2. Estimates for the three rate coefficients at 350 and 380°C

Coeff.	$T = 350^{\circ}\text{C}$	$T = 380^{\circ}\text{C}$
k1	2.71E+00	6.64E+00
k2	4.77E+03	2.34E+04
k3	9.63E+01	8.03E+01

Conclusions

The microKinetic Engine is a valuable tool in assessing high-throughput generated data. The automatic generation of the kinetic equations from the specified reaction network significantly reduces the time required by the researcher. Estimates for fundamental kinetic parameters can be compared for a series of catalysts allowing correlating catalyst composition and synthesis procedure with the behavior at relevant operating conditions. This not only leads to a fundamental understanding of the observed phenomena but also provides a means for further catalyst design and development.

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