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# Transient kinetic analysis of multipath reactions: An educational module using the IPython software package

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ABSTRACT

A large number of industrial catalytic reactions proceeds via multiple pathways. A transient response method has been successfully utilized for the analysis of kinetics and mechanism of multipath reactions. In this paper, we describe an educational module for teaching kinetics of complex heterogeneously-catalyzed reactions based on the software package for simulation of transient responses in a tubular packed-bed reactor. The module includes the reactor model description, derivation and verification of kinetic equations, analysis of steady-state kinetics, numerical simulation of transient responses, and visualization and analysis of results utilizing the developed IPython notebooks. The use of the module helps students to acquire theoretical knowledge as well as the practical and analytical skills related to the kinetic analysis of multipath reactions.



## 1. Introduction

The catalytic reactions lay at the core of industrially important chemical processes. Due to the existence of different types of active sites on the catalyst surface, these reactions frequently proceed through numerous paths and could include more than hundreds of intermediate reactions before producing the desired products. For example, the Fischer–Tropsch synthesis, the process vital in the preparation of chemicals and fuels from gas, coal or biomass, is a complex multipath catalytic reaction that converts the mixture of carbon monoxide and hydrogen into long-chain hydrocarbons (Maitlis and de Klerk, 2013). Azadi et al. (2015) proposed a Fischer–Tropsch reaction mechanism with 128 elementary reactions on a Co/$\gamma$-$Al_2O_3$ catalyst.

Although multi-pathway reactions are widely utilized in industry, the kinetic analysis of multi-pathway reactions remains a challenging task. The successful analysis requires one to discriminate each reaction path, identify the surface active species contributing to the reaction path and classify the elementary steps belonging to the path (Kobayashi et al., 1995). The analysis frequently becomes complicated because contribution of the particular reaction route into overall reaction rate varies depending on the working range of reactant concentrations. Thus, commonly utilized steady-state kinetic analysis will not be able to provide enough information to elucidate the detailed mechanism of multi-pathway reactions. To further enhance understanding of the mechanism and kinetics of catalytic reactions, the transient methods have been developed.

The transient method allows to discriminate reaction pathways and estimate kinetics of elementary steps by analyzing the temporal response of product concentration to the variation of inlet composition. The step response technique (Kobayashi and Kobayashi, 1974; Bennett, 1999), pulse response procedure (Redekop et al., 2014), transient analysis with a tapered element oscillating microbalance (Berger et al., 2008) etc. were successfully applied to the analysis of

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complex reactions. Recently, Metkar et al. (2011) carried out the transient experiments to demonstrate the mechanism of selective catalytic reduction of NO with $NH_3$ on commercial Fe-zeolite monolith catalyst. Pinaeva et al. (2014) studied water gas shift and partial oxidation of $CH_4$ over nanocrystalline $CeO_2$–$ZrO_2$(–$La_2O_3$) and Pt/$CeO_2$–$ZrO_2$(–$La_2O_3$) catalyst using the step response method. González and Schaub (2015) performed the step-change experiments to investigate the activity of iron-based catalyst in the Fischer–Tropsch synthesis with $H_2/CO_2$.

Chemical reaction engineering course is a fundamental subject for the advanced training of chemical engineers. The kinetic analysis of complex chemical reactions, which includes the multi-pathways catalytic reactions, is an essential section in that class. Recent utilization of computer-aided educational modules significantly impacted the chemical engineering pedagogical field (Cartaxo et al., 2014; Hernández et al., 2014). Several programs have been developed both commercially (CHEMSIMUL, Kirkegaard and Ejegbakke, 2000; Chemical-Workbench, Deminsky et al., 2003; CHEMKIN, Coltrin et al., 2001) and individually by instructors (Tenua, Wachsstock, 2015) to help students with the basic understanding of the chemical kinetics modeling. However, the skills obtained from using these modules are not easily translated to practical experience because derivations of reaction kinetic equations are programmed to be done automatically and a student has no real exposure to the actual problem solving process. Furthermore, the experimental setup for transient analysis of catalytic reaction requires fairly complicated and expensive equipment to be implemented in the student laboratory course. Therefore, there is a need to develop an alternative tool, such as an educational software to help students learn the theoretical background of transient response method while acquiring the practical skills in applying the following method for industrially important reactions.

The educational software should ideally be based on the open-source resources, be easy to learn and modify, and have an extensive capability to visualize the results of simulation. The IPython system (Pérez and Granger, 2007) is well suited for the development of educational software. It uses the Python language, which is an open-source, straightforward and at the same time a powerful programming language. The IPython notebook web-based interface allows to mix the model explanation, computer code, simulation results and plots in a single file. Thus, it provides an ideal environment for students to learn the theory, construct their own kinetic model, input the model equations into the computer code by modifying the existent ones, conduct the simulation transient experiments and analyze the obtained results. Moreover, IPython notebook also offers an easy way for the instructor to monitor students' performance as the derived kinetic model, computer code, simulation parameters and results are all present in the same place.

In this paper, the educational template software was created with the aim to introduce students to the transient response method for the analysis of complex multi-pathway catalytic reactions. The notebooks contain tutorials to assist students in their learning. Using examples, a student can derive model equations himself, and by doing so broaden his knowledge on this subject. Students can use the software code as a template for his/her project. The software also includes notebooks with graphical user interface (GUI) to study the steady-state kinetics as well as to simulate the transient responses of multipath reactions. The software is available from the author on request.

## 2. Materials and methods

### 2.1. Mathematical model

The stoichiometric equation for heterogeneous catalytic reaction is given as (Yablonsky et al., 1991; Murzin and Salmi, 2005)

$$\mathbf{\Gamma}\,\mathbf{a} + \sum_{w=1}^{W} \mathbf{\Gamma}_{\mathrm{int},w} \quad \mathbf{a}_{\mathrm{int},w} = 0, \tag{1}$$

where $\mathbf{\Gamma}$ is the stoichiometric matrix for the gas-phase reacting components, $\mathbf{\Gamma}_{\mathrm{int,w}}$ is the stoichiometric matrix for the surface intermediates attached to the active sites of $w$ type, $\mathbf{a}$ is the vector-column of the gas-phase components, $\mathbf{a}_{\mathrm{int,w}}$ is the vector-column of intermediates and $W$ is the number of active site types. The dimensions of the stoichiometric matrices $\mathbf{\Gamma}$ and $\mathbf{\Gamma}_{\mathrm{int,w}}$ are $S \times N$ and $S \times N_{\mathrm{int,w}}$, respectively, where $S$ is the number of elementary reactions, $N$ is the number of gas-phase reacting species and $N_{\mathrm{int,w}}$ is the number of intermediates fixed on the $w$th type of active sites.

The reaction rates of the gas-phase components, $\mathbf{r}$, and surface intermediates, $\mathbf{r}_{\mathrm{int}}$, are calculated as

$$\mathbf{r} = \mathbf{\Gamma}^T\,\mathbf{R} \tag{2}$$

and

$$\mathbf{r}_{\mathrm{int}} = \mathbf{\Gamma}_{\mathrm{int}}^T\,\mathbf{R}, \tag{3}$$

where $\mathbf{\Gamma}^T$ and $\mathbf{\Gamma}_{\mathrm{int}}^T$ are the transposed stoichiometric matrices of gas-phase reacting components and surface intermediates, respectively, and $\mathbf{R}$ is the vector-column of reaction rate for elementary steps.

The reaction rate for elementary step $s$, $R_s$, is defined as

$$R_s = k_s^+ \prod_{i=1}^{N} c_i^{\Gamma_s^i\left(\mathrm{sign}\left(\Gamma_s^i\right)-1\right)/2} \prod_{w=1}^{W} \prod_{j=1}^{N_{\mathrm{int},w}} c_{\mathrm{int},j}^{\Gamma_{\mathrm{int},w_s}^j\left(\mathrm{sign}\left(\Gamma_{\mathrm{int},w_s}^j\right)-1\right)/2} - k_s^- \prod_{i=1}^{N} c_i^{\Gamma_s^i\left(\mathrm{sign}\left(\Gamma_s^i\right)+1\right)/2} \prod_{w=1}^{W} \prod_{j=1}^{N_{\mathrm{int},w}} c_{\mathrm{int},j}^{\Gamma_{\mathrm{int},w_s}^j\left(\mathrm{sign}\left(\Gamma_{\mathrm{int},w_s}^j\right)+1\right)/2}, \tag{4}$$

where $c_i$ is the concentration of $i$ gas-phase component and $c_{\mathrm{int},j}$ is the concentration of $j$ surface intermediate.

The overall reactions for all paths can be written as

$$\boldsymbol{\nu}^T\,\mathbf{\Gamma}\,\mathbf{a} = 0, \tag{5}$$

where $\boldsymbol{\nu}$ denotes the $S \times P$ matrix for stoichiometric numbers of $s$ reaction in $p$ path and $P$ is the number of basic paths. The stoichiometric numbers should satisfy the equation

$$\nu^T\,\mathbf{\Gamma}_{\mathrm{int}} = 0 \tag{6}$$

This equation ensures the absence of intermediate species in the overall equation for each path.

The following assumptions are made for the modeling of the laboratory scale fixed-bed reactor.