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Modeling of cyclohexene hydrogenation and dehydrogenation reactions in a continuous-flow microreactor

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Abstract

Microreactors provide opportunities for improving process efficiency and control in chemical/biochemical kinetic studies. Advantages of microreactors, as compared to normal scale reactors, include high surface to volume ratio, improved heat and mass transfer properties, small size, negligible chemical waste, and increased safety.

In this study, we use a stochastic compartmental modeling approach to model a continuous-flow microreactor with chemical reaction. The stochastic model developed is general, simple, and can be easily solved analytically. We apply the model to cyclohexene hydrogenation and dehydrogenation reactions. Model parameters were estimated by fitting the model to experimental data on cyclohexene conversion. From these estimates, it was possible to characterize the residence time distribution of the microreactor, to estimate the reaction kinetic parameters, and to predict cyclohexene conversion.

Keywords: Stochastic modeling; Microreactor; Cyclohexene hydrogenation and dehydrogenation

1. Introduction

Microreactors and microreaction technology play a significant role in chemical and biochemical kinetic investigations. Miniaturization of a chemical process will increase process safety, efficiency, and productivity. Microreactors have the following advantages in comparison to normal scale reactors: high surface to volume ratio, improved heat and mass transfer properties, small size, negligible chemical waste, and increased safety. The high surface-to-volume ratio of a microreactor improves heat transfer, making it suitable for the study of exothermic reactions [1,2].

Several chemical reactions have been explored utilizing microreactors. One such reaction is cyclohexene hydrogenation and dehydrogenation. The reaction of cyclohexene (C_6H_{10}) and hydrogen on a platinum catalyst, Pt (1 1 1), has been investigated by a number of groups using a variety of surface analytical techniques [3–7]. Studies of this reaction scheme at the microscale were conducted by several authors [8–12]. This reaction system is a useful prototype model for similar systems ubiquitous in the chemical process and petroleum refining industries such as hydrotreating for aromatics reduction, desulfurization, and denitrogenation [13], reforming for aromatics reduction and dehydrocyclization [14,15], and fuel processing of liquid hydrocarbons for the generation of hydrogen feed for fuel cells [16]. Previous results on Pt (1 1 1) catalyst revealed that cyclohexene underwent selective dehydrogenation to form benzene [6,17]. Thus, cyclohexene can react selectively to give two products, cyclohexane (C_6H_{12}) or benzene (C_6H_6). The hydrogenation reaction:

$$C_6H_{10} + H_2 \xrightarrow{k_1} C_6H_{12} \tag{1}$$

gives cyclohexane and is favored at low temperatures. On the other hand, the dehydrogenation reaction:

$$C_6H_{10} \xrightarrow{k_2} C_6H_6 + 2H_2 \tag{2}$$

produces benzene and is favored at high temperatures.

Of interest in this research is to model the microreaction process. This involves modeling of flow and reaction in a continuous-flow microreactor. A model that can simulate the

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behavior of a process is essential for predicting process performance. Also, it plays an important role in process optimization.

In this study, we developed a stochastic model of a continuous-flow microreactor that comined both the residence time with chemical reaction properties of the system. We applied the model to experimental data on cyclohexene conversion in order to estimate model parameters and characterize the residence time distribution in the microreactor as well as to predict the probability of conversion of cyclohexene to cyclohexane or benzene.

2. Residence time distribution

A microreactor usually consists of a rectangular micro-channel, with lateral and vertical dimensions in micrometers. The residence time distribution (RTD) in a microreactor is a measure of its efficiency with regard to conversion in a microreaction process. A simple, yet realistic first approach to modeling the residence time distribution is to divide the reactor in the flow direction into n arbitrary compartments of equal size where each compartment is perfectly mixed as in a continuous stirred tank reactor (CSTR). Using cyclohexene hydrogenation or dehydrogenation reaction, consider a cyclohexene molecule, which enters the reactor in compartment 1 and exits from compartment n. Because of the ideal mixing in a compartment, the probability that a molecule in compartment $j-1$ exits to compartment j ($j = 2, 3, \ldots, n+1$, where $n+1$ is the exit stream) during the infinitesimal time interval $(t, t+\Delta t)$ can be assumed to equal $\lambda\Delta t$, where λ is the exit or transition intensity. As such, it can be readily seen that the residence time distribution in any compartment is exponential with probability density function (pdf) $\lambda e^{-\lambda t}$. Considering that a molecule enters compartment 1 and exits compartment n, the time it takes the molecule to exit the reactor is the sum of n independent exponential random variables which is given by the Gamma distribution [18]:

$$\frac{\lambda\, e^{-\lambda t}(\lambda t)^{n-1}}{\Gamma(n)} \qquad (3)$$

The Gamma distribution Eq. (3) can be used to characterize the residence time distribution of a chemical reactor by running experiments where the input is either pulse or continuous feed. In this research, continuous feed cyclohexene hydrogenation experiments were run, and the partial pressure of cyclohexene (pp) in the exit stream was measured. The ratio pp/pp$_{\text{base}}$ at time T is an estimate of the probability that a cyclohexene molecule, entering the reactor at time, τ exits the reactor by time $T-\tau$, where pp$_{\text{base}}$ is the partial pressure of the reactant (cyclohexene) in the exit stream at equilibrium. This probability is given by:

$$\int_0^T \frac{\lambda\, e^{-\lambda(T-\tau)}(\lambda(T-\tau))^{n-1}}{\Gamma(n)}\, d\tau \qquad (4)$$

Fitting the model to the experimental observations (pp/pp$_{\text{base}}$) over time, one can estimate λ and n for a given continuous-flow microreactor.

3. Chemical kinetics

The hydrogenation (Eq. (1)) and dehydrogenation (Eq. (2)) reactions in which cyclohexene reacts to produce cyclohexane or benzene are considered. When a reaction occurs, it is assumed that in the infinitesimal time interval $(t, t+\Delta t)$ the probability that a cyclohexene molecule in compartment $j-1$ reacts is $\mu\Delta t$ (a reasonable assumption in that, with a microreactor, one can safely ignore the mass transfer effect when considering the catalytic reaction occurring on the walls of the reactor). On the other hand, the probability that the cyclohexene molecule exits to compartment j in an infinitesimal time interval $(t, t+\Delta t)$ is $\lambda\Delta t$. It is known [19,20] that for a bimolecular reaction $A + B \rightarrow C$, μ is equivalent to $k_1 N_B$, where N_B is the number of B molecules and k_1 is the reaction rate constant. On the other hand, $\mu = k_2$ (reaction rate constant) for a monomolecular reaction, $A \rightarrow C$. However, for hydrogenation and dehydrogenation reactions, such as the cyclohexene reactions in Eqs. (1) and (2), it has been observed in the literature [21,22] that the reaction can be described by a Langmuir-Hinshelwood model, implying that the reaction order may vary from zero to first-order.

Under continuous feed, the probability (P) that a cyclohexene molecule (C_6H_{10}) entering the reactor at time τ exits by time T ($T \geq \tau$) is given by:

$$\begin{aligned} P &= \text{Probability}[C_6H_{10} \text{ exits at time} T, \\ &\quad \text{given that} C_6H_{10} \text{ did not react by time} T] \\ &\quad \times \text{Probability}[C_6H_{10} \text{ did not react by time} T] \\ &= \int_0^T e^{-\mu(T-\tau)} \frac{\lambda\, e^{-\lambda(T-\tau)}(\lambda(T-\tau))^{n-1}}{\Gamma(n)}\, d\tau. \end{aligned} \qquad (5)$$

In Eq. (5), $e^{-\mu(T-\tau)}$ is the probability (C_6H_{10} did not react by time T).

The probability of exiting the reactor by time T can be evaluated by integrating Eq. (5) to give:

$$\begin{aligned} &\left[-\frac{\lambda^n T^{n-1}}{\Gamma(n)(\lambda+\mu)} - \frac{\lambda^n T^{n-2}}{\Gamma(n-1)(\lambda+\mu)^2} - \cdots \right. \\ &\quad \left. - \frac{\lambda^n T}{(\lambda+\mu)^{n-1}}\right] e^{-(\lambda+\mu)T} + (1 - e^{-(\lambda+\mu)T}) \frac{\lambda^n}{(\lambda+\mu)^n}, \\ &n = 2, 3, \ldots \end{aligned} \qquad (6)$$

For $n = 1$:

$$P = \frac{\lambda}{\lambda+\mu}[1 - e^{-(\lambda+\mu)T}] \qquad (7)$$

As T approaches infinity, Eq. (6) reduces to:

$$\frac{\lambda^n}{(\lambda+\mu)^n} \qquad (8)$$

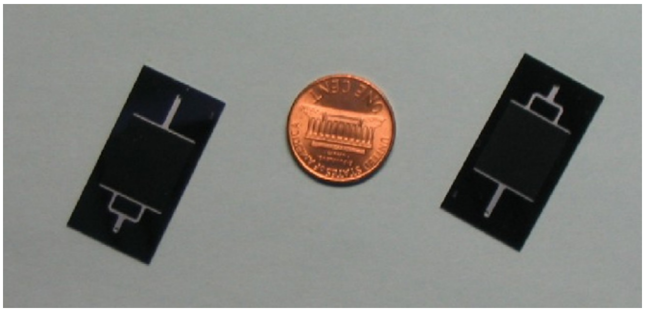

Fig. 1. Microreactor scale.

4. Microreactor experiment

In this study, a microreactor made from a double-sided polished, silicon orientation wafer (4 in. in diameter, and 500 μm thick) was used (Fig. 1). The microreactor is 1.6 cm × 3.1 cm in size, with 1.2 cm × 1.34 cm for the micro channels. It is composed of an inlet-via (a hole through the wafer) to allow gas to flow into the microreactor, inlet channel, a manifold region to distribute gases throughout the micro channels, reaction zone, outlet channel, and an outlet-via to allow gas to exit the reactor. The reaction zone is made of 599, 5 μm wide and 100 μm in height, waved channels coated with a catalyst on the bottom and side walls of the channels.

The reactant gas flows through the inlet-via into the microreactor and into the inlet channels. After entering the inlet channel, the chemical species mix in the manifold area and then flow into the reaction zone, which is composed of 599 microchannels. Once the reaction is complete, the effluent of the microreactor moves out of the reactor through the outlet channel and outlet-via. Then, the effluent is sent to a mass spectrometer for chemical information analysis. The microreactor effluents were continuously sampled and monitored for composition using a Stanford Research Systems mass spectrometer (QMS 200) having its own PC for acquisition and control.

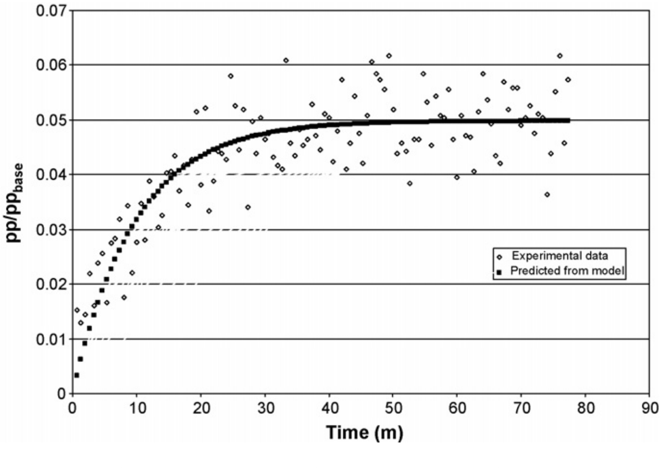

Fig. 2. Plot of the observed conversion rate (pp/pp$_{base}$), for the cyclohexene dehydrogenation reaction, and predicted value by fitting the experimental data to the model in Eq. (4). The operating condition was 186.67 °C with flow rates of 0.28 and 0.82 sccm (standard cubic cm per minute) for H_2 and Ar, respectively.

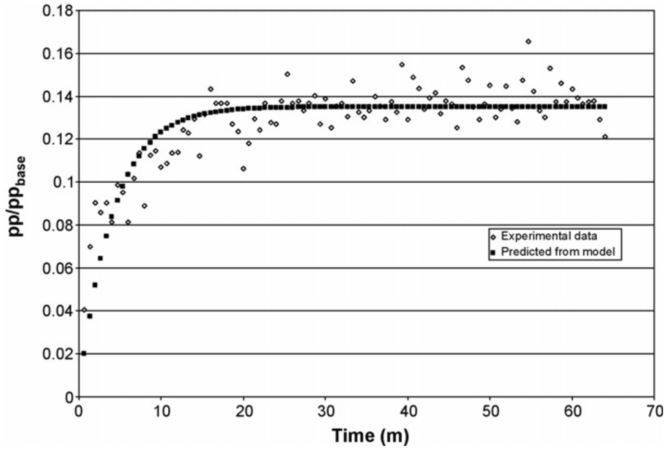

Fig. 3. Plot of the observed pp/pp$_{base}$, for the cyclohexene hydrogenation reaction, and predicted value by fitting the experimental data to the model in Eq. (4). The operating condition was 102 °C with a flow rate of 0.55 sccm for each of H_2 and Ar.

For the cyclohexene hydrogenation experiments, hydrogen flow was initiated at room temperature for at least 1 h as a method of pre-treatment of the Pt catalyst. The cyclohexene fed to the microreactor was controlled using argon carrier gas bubbled through a column of liquid cyclohexene. Pure hydrogen was the other reactant gas. Platinum (Pt) was used as the catalyst, and sputtering deposition was the method used for a uniform Pt coating inside the microchannels of the microreactor.

5. Model fitting to data and estimates of the reaction parameters

For characterizing the microreactor with regard to its residence time distribution, we fitted the above model (Eq. (6), using least squares) to cyclohexene pp/pp$_{base}$ data over time in the exit stream by specifying different n values ($n = 1, 2, 3, \ldots$). Note that the probability (P) of exiting the microreactor in Eq. (6) is estimated as pp/pp$_{base}$. The sum of squares error (sum of squares of deviations between observed and expected) increased with an increase in n. The best fit was for $n = 1$ which gave the smallest sum of squares error (SSE). For the sake of space, we present only two figures showing the fit of the model to the data when $n = 1$. These figures are representative of the fit of the model to other experimental data. It is seen from Figs. 2 and 3 that the model gave good fit to the data for $n = 1$. Since the

Table 1
Estimates of the reaction rate μ for cyclohexene hydrogenation and dehydrogenation reactions at different temperatures, $n = 1$

Temperature (°C)	μ (l/min)
Cyclohexene hydrogenation	
102.5	0.2096
56.4	0.0793
Cyclohexene dehydrogenation	
186.7	0.0966
353.3	0.1104

best fit was for $n = 1$, this implies that the microreactor flow is well mixed and can be classified as a CSTR microreactor with an exponential residence time distribution.

Table 1 presents estimates of the reaction rate μ from fitting the model for $n = 1$ to the cyclohexene hydrogenation and dehydrogenation data at different temperatures.

It is seen from these estimates that the sensitivity of the hydrogenation reaction to temperature was higher than that observed for dehydrogenation. Equilibrium calculations confirmed that the reactions were kinetically limited.

Relating the above reaction rates at different temperatures to the Arrhenius equation, one has:

$$\mu_1 = k_0\,\mathrm{e}^{-E_\mathrm{a}/RT_1}, \qquad \mu_2 = k_0\,\mathrm{e}^{-E_\mathrm{a}/RT_2}. \tag{9}$$

From Eq. (9), one can estimate the activation energy of the reaction. This is given as:

$$E_\mathrm{a} = \frac{\ln(\mu_1/\mu_2)}{-(1/RT_1) + (1/RT_2)} \tag{10}$$

Substituting the values from Table 1 into Eq. (9) and taking R as 8.314 J/mol K, the activation energy is calculated to be 21,694.52 J/mol for the hydrogenation reaction and 429.5 J/mol for the dehydrogenation reaction.

6. Conclusions

It is well known that gas flow in a microreactor is stochastic when considered at the molecular level. Hence, in this study, a stochastic compartmental model, coupling residence time and reaction kinetic, was developed to simulate the dynamics of a reaction process in a continuous-flow microreactor. The model was applied to data on the conversion of cyclohexene to cylcohexane (hydrogenation reaction) or to benzene (dehydrogenation reaction). The model gave best fit to the cyclohexene conversion data when the microreactor was considered as one compartment or a CSTR. This model may be thought of as a discretized diffusion process. It is simple, general, and can be easily solved analytically. Also, this modeling approach can be readily extended to include adsorption and desorption of reactants and products on the catalyst surface allowing one to assess their relative importance.

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References

[1] W. Ehrfeld, V. Hessel, L. Lowe, Microreactors: New Technology for Modern Chemistry, Wiley–VCH, Weinheim, Germany, 2000, p. 210.
[2] K.F. Jensen, Technical Digest of the 2000 Solid-state Sensor and Actuator Workshop, Hilton Head Isl., SC, 2000, pp. 105–110.
[3] E. Segal, R.J. Madon, M.J. Boudart, J. Catal. 52 (1978) 45.
[4] S.M. Davis, G.A. Somoriai, J. Catal. 65 (1980) 78.
[5] C. Xu, B.E. Koel, Surf. Sci. 304 (1994) 249.
[6] J.G. Chen, B. Fruhberger, Surf. Sci. 367 (1996) 102.
[7] K. Su, K.Y. Kung, J. Lahtinen, Y.R. Shen, G.A. Somorjai, J. Mol. Catal. A: Chem. 141 (1999) 9.
[8] J.T. Roberts, R.J. Madix, Surf. Sci. 226 (1990) 71.
[9] S. Hassan, A. Sadek, A. Salwa, Catalysts in Petroleum Refining and Petrochemical Industries, 1995, p. 407, ISSN: 0167-2991.
[10] D.E. Hunka, D.P. Land, in: Proceedings of the 214th ACS National Meeting, Book of Abstracts, Las Vegas, NV, September 7–11, 1997.
[11] H. Surangalikar, X. Ouyang, R.S. Besser, Chem. Eng. J. 93 (2003) 217.
[12] X. Ouyang, R.S. Besser, Catal. Today 84 (2003) 33.
[13] H.F. Rase, Handbook of Commercial Catalysts: Heterogeneous Catalysts, CRC Press, Boca Raton, 2000, p. 105.
[14] J.H. Gary, G.E. Handwerk, Petroleum Refining, Technology and Economics, Marcel-Dekker, New York, 2001, p. 175.
[15] K. Weissermel, H.J. Arpe, Industrial Organic Chemistry, Wiley–VCH, Weinheim, 1997, p. 314.
[16] G. Sandestede, in: B. Cornils, W.A. Herrmann, R. Schlogl, C.-H. Wong (Eds.), Catalysis from A to Z, A Concise Encyclopedia, Wiley–VCH, Weinheim, 2000, p. 228.
[17] F.C. Henn, A.L. Diaz, M.E. Bussell, M.B. Hugenschmidt, M.E. Domagala, C.T. Campbell, J. Phys. Chem. 96 (1992) 5965.
[18] C.L. Chiang, An Introduction to Stochastic Processes and Their Applications, Krieger, New York, 1980, p. 62.
[19] J.R. Too, L.T. Fan, R. Nassar, Comp. Chem. Eng. 7 (1983) 1.
[20] S.T. Chou, L.T. Fan, R. Nassar, Chem. Eng. Sci. 43 (1988) 2807.
[21] G. Padmavathi, K.K. Chaudhuri, D. Rajeshwer, R.G. Sreenivasa, K.R. Krishnamurthy, P.C. Trivedi, K.K. Hathi, N. Subramanyam, Chem. Eng. Sci. 60 (2005) 4119.
[22] N.S. Chang, A. Salvador, M.T. Holtzapple, R.R. Davison, Chem. Eng. Sci. 55 (2000) 5721.