DEVELOPING A SIMPLE BUT EFFECTIVE KINETICS MODEL FOR METHANOL-TO-OLEFINS (MTO) REACTION

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ABSTRACT

Methanol to olefin (MTO) reaction is regarded as an important bridge between traditional coal and modern petrochemical industry. Its importance poses significant challenges at the same time in terms of complexity. Many works have been made to effectively represent the mechanism and expand its application. A new kinetic model is proposed for the methanol-to-olefins (MTO) reaction in this paper. The MTO reaction kinetics is investigated by way of a lumped kinetic model based on certain assumptions. The kinetic parameters were determined by using some experimental data treated by genetic algorithm. In the proposed model, the deactivation constant a is the only intrinsic parameter required to represent the effect of catalyst deactivation on the conversion and product yields. This approach is shown to be effective for modeling complex deactivation kinetics in MTO. The proposed model gives a reasonable representation of the experimental data.

Keywords: Methanol-to-olefins, modeling, kinetics deactivation, Light olefins

NONMENCLATURE

Parameters	
y_i	molar yield of lump i
R_i	formation rate of lump i
C_i	concentration of lump i (mol L^{-1})

θ_w	water effect parameter
K_w	resistance constant
X_w	molar fraction of water
k_i	rate constant of formation of lump i
k_{i0}	pre-exponential factor (L g$_{cat}$$^{-1}$ min^{-1})
T	Temperature (K)
Ea_i	activation energy of step i
R	universal gas constant
w_{ij}	weighting factor
y_{ij}^{cal}	Calculated yield through the model
y_{ij}^{exp}	Measured yield from experiment
t	Time on stream (h)
τ	contact time (g h mol^{-1})
τ_0	Initial contact time (g h mol^{-1})
a	deactivation constant (g h^{-1})
R_D	deactivation rate (g h^{-1})
X	conversion
R^2	coefficient of determination

1. INTRODUCTION

The catalytic conversion of methanol to olefins (MTO) is an important route for olefin production. Oil reserves are continuously declining, so it is necessary to establish an alternative to classical olefin production routes. Light olefins such as ethylene, propylene, and butene are basic sources of essential chemical intermediates. In the early 2000s, the MTO process was

commercially demonstrated by the Dalian Institute of Chemical Physics (DICP) in China [1].

Kinetic models are the most economical tools to gain insight into the overall MTO reaction. Especially, the lumped kinetic model reduces the chemical complexity by grouping the components into lumps based on their similar properties and simplifying the reaction pathway between these lumps. Thus, it has advantages of less computation load for parameter estimations and simple application to reactor design [2].

It is imperative to understand deactivation behavior as well as the reaction kinetics for a catalytic process. Especially, MTO reactions over SAPO-34 catalyst are accompanied by fast deactivation due to pore blockage and mass transfer limitation ascribed to coke deposition on the catalyst.

This study establishes a new lumped kinetic model that takes into account 9 reaction steps for the production of 7 lumps in the MTO process over SAPO-34. We demonstrate that the deactivation behavior of the SAPO-34 catalyst can be described using a single parameter. The validity of this model is conformed by comparing the results with experiment data.

2. MATHEMATICAL MODEL

2.1 Reaction kinetics

A simplified kinetic scheme of MTO reaction is proposed and illustrated in Fig. 1. In this scheme, methanol and dimethyl ether (DME) rapidly reach equilibrium over the catalyst surface and are regarded as a single lump denoted as MDOH. All hydrocarbons formed over SAPO-34 catalyst were identified as the primary product of MDOH. The formation steps of higher olefins from lower olefins by methylation were taken into account. And all the reaction rate expressions of individual steps are assumed to be first-order in MDOH or lower olefin concentrations.

The kinetic model can be described by:

$$\frac{dy_i}{d(W/F_{MeOH}^0)} = R_i \tag{1}$$

$$R_{CH_4} = k_1\theta_w C_{MDOH} \tag{2}$$

$$R_{C_2H_4} = k_2\theta_w C_{MDOH} - k_8\theta_w C_{C_2H_4} \tag{3}$$

$$R_{C_3H_6} = k_3\theta_w C_{MDOH} + k_8\theta_w C_{C_2H_4} - k_9\theta_w C_{C_3H_6} \tag{4}$$
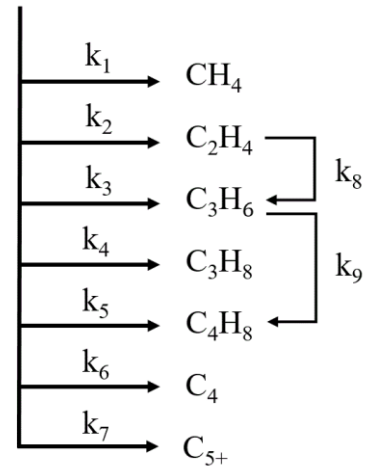
$$R_{C_3H_8} = k_4\theta_w C_{MDOH} \tag{5}$$

Fig. 1. Proposed kinetic scheme for the MTO reaction.

$$R_{C_4H_8} = k_5\theta_w C_{MDOH} + k_9\theta_w C_{C_3H_6} \tag{6}$$

$$R_{C4} = k_6\theta_w C_{MDOH} \tag{7}$$

$$R_{C5+} = k_7\theta_w C_{MDOH} \tag{8}$$

$$R_{MDOH} = -\sum_{i=1}^{7} R_i \tag{9}$$

$$R_{H_2O} = \sum_{i=1}^{7} R_i \tag{10}$$

The water in the reaction medium attenuates the deactivation but also plays the role of an inert gas that inhibits the production of the hydrocarbons. This effect has been taken into account by incorporating the term θ_w in the kinetic equations.

$$\theta_w = \frac{1}{1 + K_w X_w} \tag{11}$$

To express the kinetic rate constant k_i and the temperature relationship, a reparameterized Arrhenius equation was used.

$$k_i = k_{i0} \exp\left(-\frac{Ea_i}{R}\left(\frac{1}{T} - \frac{1}{723.15}\right)\right) \tag{12}$$

Optimization was conducted in Matlab R2017b using a genetic algorithm to estimate the kinetic parameters by minimizing the error objective function in Eq (13).

$$EOF = \sum_{i=1}^{n} \sum_{j=1}^{m} w_{ij}\left(y_{ij}^{exp} - y_{ij}^{cal}\right)^2 \tag{13}$$

2.2 Deactivation kinetics

To derive the expression of the deactivation kinetics for the MTO reaction, the concept proposed by Janssens [3] was combined with the proposed reaction kinetic model. The key point of the concept is that the catalyst deactivation in the MTO process is regarded as a loss of the effective amount of active catalyst with the assumption that the rate of reduction is proportional to the conversion. Thus, the deactivation rate (the change in the effective contact time with time on stream) is represented as follows:

$$R_D = \frac{d\tau}{dt} = -aX \tag{14}$$

The rate expression for MDOH can be represented based on the lumped kinetic model in Eq (1) and Eq (9) :

$$\frac{dy_{MDOH}}{d\tau} = -\left(\sum_1^7 k_i\right)\theta_w C_{MDOH} = -K'\theta_w C^0_{MeOH} y_{MDOH} \tag{15}$$

If we introduce the conversion X , Eq (16) can be rewritten as:

$$\frac{dX}{d\tau} = K(1-X) \tag{16}$$

Where $K = K'\theta_w C^0_{MeOH}$, Using the chain rule, the expression for the conversion with time on stream becomes:

$$\frac{dX}{dt} = \frac{dX}{d\tau}\frac{d\tau}{dt} = -aXK(1-X) \tag{17}$$

The expression of product distributions as a function of time on stream can be represented in the same way:

$$\frac{dy_i}{dt} = \frac{dy_i}{d\tau}\frac{d\tau}{dt} = -aXR_i \tag{18}$$

The analytical solution of Eq (17) is obtained using initial condition $t=0$ at $X=X_0$:

$$\ln\left(\frac{X}{1-X}\frac{1-X_0}{X_0}\right) = -aKt \tag{19}$$

From the introduction of $X_0 = 1-\exp(K\tau_0)$, which is the analytical solution of Eq (16), and the rearrangement of Eq (19), the catalyst lifetime to conversion X can be described by:

$$t = \frac{\ln(\exp(K\tau_0)-1) - \ln\left(\frac{X}{1-X}\right)}{Ka} \tag{20}$$
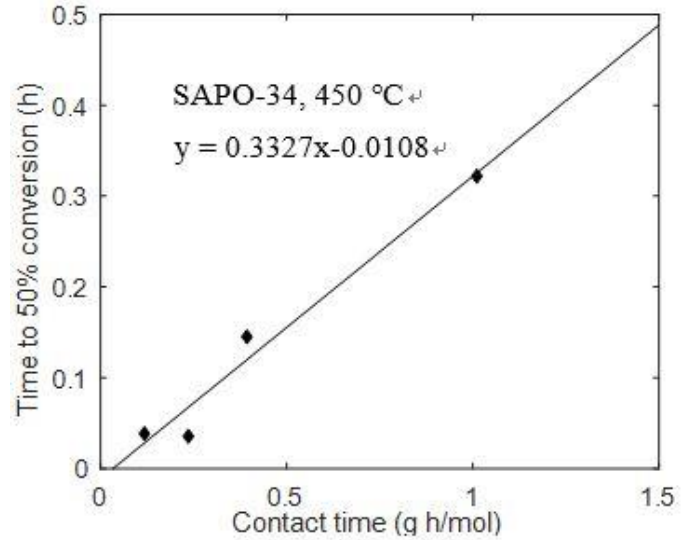

Fig. 2. Measured catalyst lifetime to reach 50% conversion as a function of the contact times for SAPO-34.

Then, the catalyst lifetime to 50% conversion is found to be:

$$t_{0.5} = \frac{\ln(\exp(K\tau_0)-1)}{Ka} \approx \frac{\tau_0}{a} \tag{21}$$

Because $\exp(K\tau_0)$ is much larger than 1 in most cases, it is possible to approximate it as in Eq (21).

This indicates that the catalyst lifetime to 50% conversion and the initial contact time τ_0 are linearly related with a slope of 1/a. Using this linear correlation, the deactivation constant can be calculated easily. Fig. 2 illustrates the experimental catalyst lifetime to 50% conversion obtained for SAPO-34. The deactivation constant derived from the reciprocal of the slope of this line is 3.005 g mol^{-1}. This was manually adjusted to 2.5 g mol^{-1} in consideration of experimental error to match the overall behavior of the measured data. The main point is that the deactivation constant a , which is independent of the activity of acid sites, is an intrinsic value that can characterize the deactivation behavior of a specific catalyst.

3. RESULTS AND DISCUSSION

To evaluate the validity of the kinetic model, parity plots are presented. Fig. 3 (a, b) are parity plots for reaction kinetic model and deactivation kinetic model, respectively. The almost symmetrical distribution of data points on both sides of the parity plot's diagonal was obtained in both models.
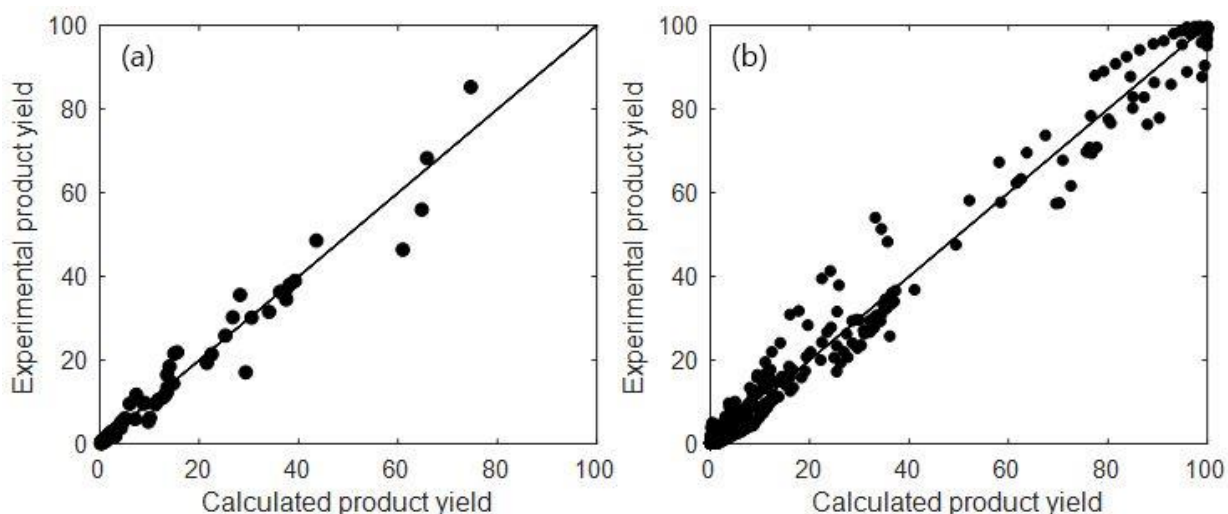
Fig. 3. Comparison between the experimental data and the results of (a) reaction kinetic model and (b) deactivation kinetic model.

Kinetics	MDOH	CH_4	C_2H_4	C_3H_6	C_3H_8	C_4H_8	C_4	C_{5+}
Reaction	0.91	0.63	0.87	0.90	0.90	0.93	0.86	0.90
Deactivation	0.93	0.48	0.94	0.94	0.76	0.82	0.87	0.90

Table 2. R^2 for each lumps

The accuracy of the proposed models can be checked by the coefficient of determination R^2, which ranges from 0 to 1. A value closer to 1 indicates goodness of the fit. The R^2 values for each lump are listed in Table 2, and most of them are larger than 0.8. The largest error occurred for methane due to the inaccuracy of measurements caused by the low mole fraction of methane in the reactor outlet.

4. CONCLUSION

This paper addressed the chemical kinetics for MTO reaction over SAPO-34 catalyst in a fixed bed reactor. The proposed model has good capability to predict the performance of a catalytic fixed bed reactor. It can be used for process-condition analysis of the production capacity of olefins. It has been confirmed that the concept of deactivation being considered as a decrease of active catalyst can also be further expanded to MTO reactions over SAPO-34. This model provides satisfactory information on the overall deactivation behavior during MTO reaction over SAPO-34, despite its overwhelming simplicity compared to existing complex deactivation models.

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