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A KINETIC STUDY OF METHANOL TO OLEFINS (MTO) PROCESS IN FLUIDIZED BED REACTOR

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ABSTRACT

A kinetic study of methanol to olefins (MTO) process has been carried out for industrial DMTO catalyst in a $\Phi 19\text{mm} \times 350\text{mm}$ fluidized bed reactor. The industrial DMTO catalyst is an improved SAPO-34 catalyst. The temperature of the experiments is in the range of 573K to 763K. A lumped kinetic model, including catalyst deactivation, is proposed based on the hydrocarbon pool mechanism. The lumped kinetic model, incorporated with a simple dynamic fluidized bed two-phase model, can predict the experimental data well.

INTRODUCTION

The petrochemical processes such as naphtha steam cracking and fluid catalytic cracking are conventional ways for light olefins (ethylene and propylene) production. Recent drastic fluctuation of oil price in the market, as well as the increasing demands for light olefins, has stimulated the development of alternative routines for light olefins production. Methanol transformation to olefins (MTO) has been considered as a promising approach since the methanol feedstock can be easily obtained from coal and natural gas. The study in recent decades accelerates the development and application of the MTO process. Dalian Institute of Chemical Physics (DICP) is amongst the pioneers in the commercialization of MTO process. The world's first commercial MTO unit (1.8 Mt/a methanol feed) was successfully started up in 2010 in North China by use of DICP's MTO (DMTO) technology. The unit is now running at full load with the selectivity of ethylene and propylene exceeding 80%.

Although the MTO process has been commercialized, extensive studies are still undergoing to further increase the selectivity to light olefins (Chen *et al* (1)) and prolong catalyst life time (Alvaro-Munoz *et al* (2)). Kinetic modeling of the MTO process, however, remains high priority for the optimal design of the reactor. In the open literature, various kinetic models have been developed for MTO process, which can be grouped into two types: detailed models (Mihail *et al* (3), Park and Froment (4)(5)) and lumped models (Schipper and Krambeck (6), Bos *et al* (7), Gayubo *et al* (8)). As a powerful tool in the reactor design, lumped models have attracted widely

attention because of their simplicity and reliability. Unfortunately, most of the lumped models were established based on laboratory synthesized MTO catalyst, which has different activity due to the variation of synthesis procedures and can be hardly applied in industrial reactor design.

MTO reaction is normally conditioned by a fast deactivation of catalyst, which leads to a significant change of olefins selectivity and methanol conversion with time on stream. Therefore in the lumped kinetic model the catalyst deactivation should be included. Most of the deactivation models (Chen *et al* (9), Hu *et al* (10)) were based on plug flow reactor, which cannot reflect the effect of coke distribution on the product selectivity since there is a spatially inhomogeneous distribution of coke along the catalyst bed

In this work, a lumped kinetic model for the MTO reaction, which includes the deactivation of catalyst, is presented based on the experimental data obtained from a micro-scale fluidized bed. Industrial DMTO (improved SAPO-34) catalyst was used for the kinetic study, and this catalyst has been successfully employed in the commercial DMTO fluidized bed reactor. On the basis of the simple hydrodynamics of two phase theory, in which the reaction was assumed to take place in both emulsion and bubble phase, the MTO process in the micro-scale fluidized bed reactor has been simulated. The results were compared with the experimental data.

EXPERIMENT

In this study, a micro-scale fluidized bed reactor operating at atmospheric pressure was used. The diagram of the reaction equipment is given in Figure 1. The fluidized bed reactor has an inner diameter of 0.019 m. Industrial DMTO (improved SAPO-34) catalyst was used in the experiments, which has a mean particle size of $d_p=83 \mu\text{m}$. Before each run, the catalyst was pre-treated in nitrogen flow (180 ml/min) at 450°C for 1 h and then the temperature was adjusted according to the desired reaction conditions. Aqueous methanol solution was fed by a piston pump and passed to a pre-heater. The vaporized reactant from the pre-heater then entered the reactor through a gas distributor and contacted with catalyst. The effluent gas was analyzed on line using Agilent 7890A gas chromatography equipped with a FID detector and a PoraPLOT Q-HT capillary column (25m×0.53mm×0.02mm). The coke content of the deactivated catalyst with different residence time was measured by thermogravimetric analysis.

LUMPED FLUIDIZED BED KINETIC MODEL

Kinetic model

The reaction network for methanol transformation to hydrocarbons can be reasonably represented by Figure 2, where methanol and dimethyl ether (DME) are lumped as oxygenate, the other five lumps are ethylene, propylene, sum C4 (butenes and

butanes), sum C5 (rest of hydrocarbons) and coke. It has to be argued that the compositions of product gas from MTO reaction are far more complicated. However, ethylene, propylene, and sum C4 (butenes and butanes) are expected to be the major products in practice. Coke, on the other hand, has a significant influence on the selectivity of these products. Therefore, reaction network shown in Figure 2, though simplified, fit for industrial application. The formation of hydrocarbon and coke was found to be first order in methanol composition, and the kinetic model is expressed as follows:

$$r_i = k_i C_{MeOH} \varphi_i \quad i = 1 - 4 \quad (1)$$

Coke leads to the deactivation of catalyst because they are restrained in the SAPO-34 cages. Their concentration evolves with time on stream according to

$$\frac{dC_c}{dt} = k_5 C_{MeOH} \varphi_5 \quad i = 5 \quad (2)$$

Here k_i is the initial rate constant for hydrocarbon formation and $k_5 = k_d$ for coke formation, φ_i is the deactivation function. A deactivation function different from the literature (Froment and Bischoff (13)) was proposed in this work,

$$\varphi_i = \frac{A}{1 + B \exp(D \times (C_c - E))} \exp(-\alpha_i C_c) \quad i = 1 - 4 \quad (3)$$

Note that A , B , D and E are constants for all the four steps, while C_c being the weight percent of coke on the catalyst. Selective deactivation was found in MTO reaction, that is, different α_i values for different reaction steps. The effect of coke content on product selectivity can be taken into account by introducing different values for the empirical constants α_i . For the coke formation deactivation, an exponential deactivation function was adopted.

$$\varphi_i = \exp(-\alpha_i C_c) \quad i = 5 \quad (4)$$

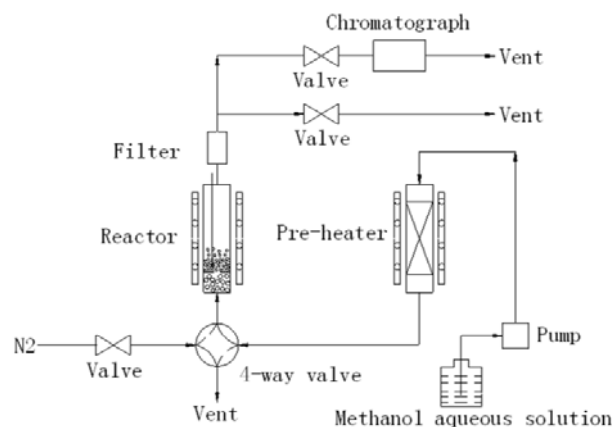


Figure 1. Diagram of the reaction equipment

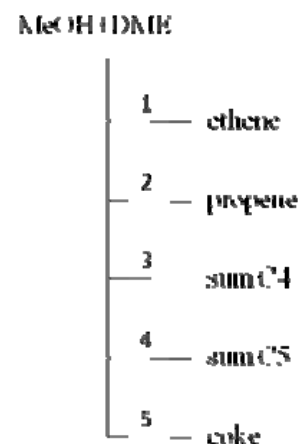


Figure 2. Reaction network for MTO reaction

Fluidized-bed model

The fluidized bed reactor was operated in the bubbling fluidization regime, with a superficial gas velocity of 0.093-0.105 m/s. And the hydrodynamics of the fluidized bed was characterized with a dynamic two phase model proposed by Mostoufi *et al* (14), in which the reactions were considered taking place in both bubble and emulsion phase. The following assumptions were made: (1) the fluidized bed consists of two phase, i.e. the bubble phase and emulsion phase; (2) all bubbles in the fluidized bed have the same size; (3) the gas only flows in axial direction, and no dispersion in the radial direction; (4) the mass transfer mainly takes place between the bubble and emulsion phase; (5) the coke is uniformly distributed in the fluidized bed. As the purpose is just to check the effectiveness of our lumped kinetic model, these assumptions, despite simplifying the problems, are reasonable in describing the hydrodynamics of the fluidized bed. In the two phase model, the mass balance can be written as:

$$\text{Emulsion phase: } \frac{dC_{i,e}}{dz} = \frac{R_{i,e}(1-\varepsilon_e)\rho_s(1-\delta) + K_{be}\delta(C_{i,b} - C_{i,e})}{u_e(1-\delta)} \quad (5)$$

$$\text{Bubble phase: } \frac{dC_{i,b}}{dz} = \frac{R_{i,b}(1-\varepsilon_b)\rho_s - K_{be}(C_{i,b} - C_{i,e})}{u_b} \quad (6)$$

The hydrodynamic correlations used for the dynamic two phase model can be found in Mostoufi *et al* (14).

The kinetic parameters have been estimated by use of the nonlinear least-squares method based on Levenberg-Marquardt algorithm. The objective function is given in Equation (7),

$$OF = \sum_{i=1}^n \sum_{j=1}^m (X_{i,j} - X_{i(\text{calc}),j})^2 \quad (7)$$

where $X_{i,j}$ are the measured data of the mass fraction corresponding to component i at time on stream j , and $X_{i(\text{calc}),j}$ are the calculated data.

RESULTS

Effect of reaction temperature

Temperature plays a significant role in the MTO reaction. There exists a pronounced induction period at 300°C (Figure 3), in which catalyst activity increases before maximum conversion is reached and then declines, this is consistent with the hydrocarbon pool mechanism. Further raising the reaction temperature, methanol can be completely converted at the beginning of the reaction; the same trend has been reported by other researchers (Bleken *et al* (11), Wei *et al* (12)). As can be

seen, the catalyst has the longest life time at 425°C, but deactivates fastest at 490°C. The effect of reaction temperature on ethylene selectivity is shown in Figure 4, it shows that ethylene selectivity first follows the similar trend with temperature, with higher value at higher temperature, and then falls sharply after reaching a plateau. An explanation might be the increasing cracking rate of long chain olefins at higher temperature.

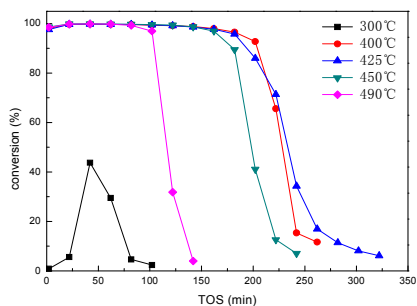


Figure 3. Conversion of methanol at WHSV=1.5 gg⁻¹h⁻¹ and water to methanol ratio, Xw0=1.5.

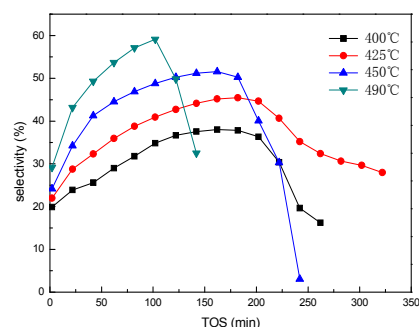


Figure 4. Ethene selectivity at WHSV=1.5gg⁻¹h⁻¹ and water to methanol ratio, Xw0=1.5

Effect of coke content

Coke is of pronounced importance in MTO reaction. From Figure 5 it can be seen that ethylene increases with the coke content when coke is ranging from 1 wt% to 6.5 wt%, then decreases swiftly together with methanol conversion. The rapid decreasing of ethylene may be due to the dominating role of product shape selectivity. The compositions of sum C4 and sum C5 decrease from the beginning, meanwhile a maximum value for methane is observed when the catalyst starts to deactivate.

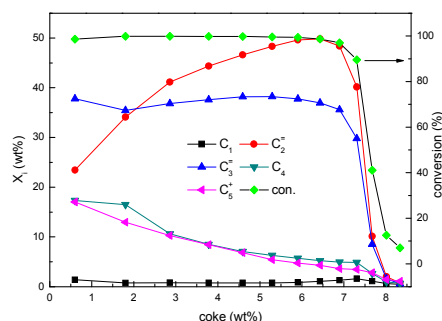


Figure 5. Methanol conversion and product distribution versus coke content at 450°C, WHSV=1.5/h and Xw0=1.5

Modeling results

Preliminary studies show that the parameters A , B and D are not sensitive to the operating conditions, and therefore they are fixed as constant 1.0, 9.0 and 2.3, respectively. For parameter E , it is actually the threshold coke content where a sharp decrease in methanol conversion and olefins selectivity appear. It has been found that when E exceeds 7.0 a tempestuously change of methanol conversion and product distribution will be expected. Therefore, In this work, E is simply set as 7.0.

Table 1 list the calculated reaction rate constants and deactivation rate constants. Note that the calculation of deactivation constants α_i follows the aforementioned discussion. The kinetic constants were tested for Arrhenius's law, as shown in Figure 6. The temperature dependence can be well demonstrated.

Table 1. Reaction rate constants, deactivation rate constants

T(°C)	k_1	k_2	k_3	k_4	k_d
400	0.0367	0.0455	0.0151	0.0108	0.60
425	0.0617	0.0555	0.0176	0.0134	0.74
450	0.0901	0.0672	0.0206	0.0184	0.98
490	0.1707	0.0989	0.0273	0.0267	2.28
α_i	0.012	0.085	0.20	0.23	0.25

Figure 7 plots the mass fraction of product obtained by both modeling prediction and experimental data. The modeling prediction results match the experimental data very well. This indicates that the proposed lumped model is reasonable and reliable for predicting main products in MTO process. A further work to simulate large fluidized bed reactor is undergoing.

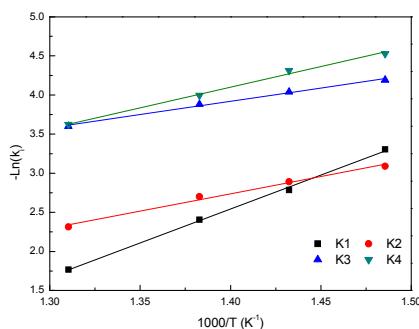


Figure 6. Arrhenius plot for reaction rate constants.

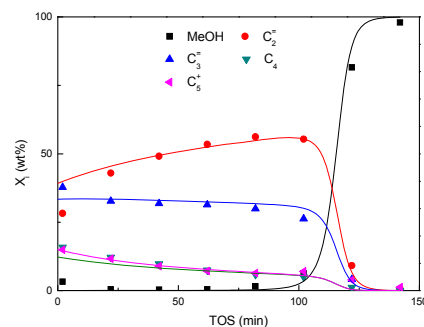


Figure 7. Comparison between measured (symbols) and predicted (lines) products distribution at 490°C.

CONCLUSION

A lumped MTO kinetic model, including catalyst deactivation, was developed for the industrial DMTO catalyst. The model consists of 5 reactions and includes 4 main components plus coke, where all the reactions are considered first order in methanol. A deactivation function was proposed to quantify the effect of coke content in the fluidized bed. A simple dynamic two phase model was used to account for the hydrodynamics, in which the reactions were assumed to take place in both bubble phase and emulsion phase. The lumped kinetic model, incorporated with this simple two-phase model, can predict the experimental data in the micro-scale fluidized bed very well. A further work to simulate large fluidized bed reactor is undergoing.

ACKNOWLEDGMENT

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NOTATION

A, B, D=constant	scheme, L/(gcat min)
C_C =weight percent of coke on the catalyst, g/100gCat	k_d =deactivation rate constant, L/(mol min)
C_{MeOH} =methanol concentration, mol/L	u_0 =superficial gas velocity m/s
C_i =mean concentration of component i, mol/L	u_b =bubble velocity, m/s
D=molar diffusion coefficient	u_{br} =bubble rise velocity, m/s
d_b =bubble diameter, m	u_e =emulsion velocity, m/s
d_p =particle diameter, m	u_{mf} =minimum fluidization velocity, m/s
E=critical coke content	r_i =reaction rate for formation of component i, mol/(gcat h)
g=acceleration due to gravity, m/s ²	t=time, min
K_{bc} =bubble to cloud mass transfer coefficient, s ⁻¹	T=temperature, °C
K_{ce} =cloud to emulsion mass transfer coefficient, s ⁻¹	WHSV =weight hour space velocity g/(gcat h)
K_{be} =bubble to emulsion mass transfer coefficient, s ⁻¹	X_{w0} =weight fraction of water in the feed
k_i =kinetic constant of step i in the kinetic	Z=reactor height, m
	α_i = empirical deactivation constant
	δ =bubble fraction

ε_e =average emulsion voidage

ε_b =average bubble voidage

μ =gas viscosity, kg/(m s)

ρ_s =catalyst density, kg/m³

ρ_g =gas density, kg/m³

φ_i =deactivation function for component i

Subscripts

b=bubble

e=emulsion

mf=minimum fluidization

s=solid

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