



Comparative study of MTO kinetics over SAPO-34 catalyst in fixed and fluidized bed reactors



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HIGHLIGHTS

- MTO kinetics in fluidized bed reactor and fixed bed reactor was experimentally studied.
- Coke deposition profile leads to different performances in fixed bed and fluidized bed reactor.
- Olefin conversion is responsible for the changes of selectivity in fixed bed reactor.
- A modeling approach was developed to unify fixed and fluidized bed reactor for MTO process.

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ABSTRACT

In this work, a comparative study on methanol to olefins (MTO) kinetics in fixed and fluidized bed reactors was conducted. Based on the analysis of experimental observations, a modeling approach that can be used to simulate both reactor configurations was proposed. The coke deposition was shown responsible for the difference of product selectivities for these two reactor configurations. In a fluidized bed reactor, the distribution of the coke deposition is spatially uniform, and evolves with time on stream. However, the coke deposition shows a distribution along the bed height in a fixed bed reactor, and olefins conversions were taken into consideration to account for the selectivity changes with time on stream. With the proposed model, we established a linkage between fixed bed reactors and fluidized bed reactors through coke deposition. By use of this model, it is possible to predict the performance of MTO reaction over SAPO-34 catalyst in fluidized bed reactor with experimental data obtained in fixed bed reactor, or vice versa.

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1. Introduction

Light olefins are basic materials in chemical industries and are widely used to make polyethylene, polypropylene and other important products. Traditionally, light olefins are produced by steam cracking units and fluid catalytic cracking units, where the main feedstock is crude oil. Methanol to olefins (MTO) process provides an alternative approach to produce light olefins from non-oil resources such as coal and natural gas. The Dalian Institute of Chemical Physics (DICP) has recently commercialized a methanol to olefins (DMTO) process [1]. In the DMTO process, the fluidized bed reactor-regenerator configuration is used due to the rapid mixing of solids, uniform temperature distribution in the bed, and easy

controlling of the catalyst circulation [2]. However, the transportation of catalyst between the reactor and regeneration causes the mixing of catalyst with different ages in the reactor.

In MTO process, the age of catalyst can have significant effects on the reactions. For example, the amount of coke deposited on the catalyst dominates the catalyst activity and product selectivity [1,3,4], and transformation of light olefins to paraffin and aromatics can easily occur over fresh catalyst [5]. The role of catalyst age in MTO reaction therefore is very important, and the kinetic modeling of coke formation is necessary for revealing the effect of coke content on the product distribution of MTO reaction, and optimizing the design and operation of MTO reactor. In laboratory, the fixed bed reactors are commonly used for catalyst evaluation and kinetics study due to its simple construction and low catalyst loading. In a fixed bed reactor, however, the catalyst usually shows an age distribution along the bed. In other words, the catalyst in a

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fixed bed reactor can have a spatial age distribution. Haw and Marcus [6] depicted the time-evolution of coke distribution in the fixed bed reactor during an MTO experiment over SAPO-34 catalyst as “cigar burn”. Luo et al. [7] further developed the “cigar-burn” model, and suggested that the fixed bed reactor filled with SAPO-34 catalyst could be divided into three zones: deactivation section, methanol conversion section and olefins conversion section. Kaarsholm et al. [8] investigated the coking evolution of ZSM-5 catalyst along a fixed bed reactor and found a similar pattern. This is quite different to a fluidized bed reactor. In a batch fluidized bed reactor, the catalyst is well mixed and the age distribution is almost uniform in space, and thus only the variation with time needs to be considered [9]. The different aging behavior of catalyst in fixed bed reactor and fluidized bed reactor has been noticed in previous studies for MTO processes [10,5,11,12]. However, a quantitative mathematical model is lacked to link the fixed bed reactor and fluidized bed reactor. Such a model is apparently useful to transfer experimental data in fixed bed reactor to fluidized bed and vice versa.

Considered that the MTO reaction has a relatively long residence time, the classic chemical reaction engineering models might be more suitable for predicting time-dependent behaviors of reactors based on experimental results. Aguayo et al. [10] proposed a kinetic model for both fixed and fluidized bed reactors in the MTG process, in which different deactivation kinetic constants were used to account for the differences in deactivation in both reactors. Müller et al. [12] compared the performance of MTO reaction over ZSM-5 catalyst in plug-flow (PFR) and fully back-mixed reactors (CSTR), and also found that catalyst lifetime in a CSTR is drastically longer. They explained the phenomenon as higher local methanol concentrations in the PFR induced more oxygen-containing carbon deposits. In early contributions by Weekman and co-workers [13,14], they related fixed, moving and fluid-bed reactors based on the principles of reaction kinetics for FCC process. They presented the model in terms of the extent of reaction and catalyst decay. By use of this model and constants obtained from the moving-bed experiments, they showed that the fixed bed experimental results could be predicted. They also showed that the maximum gasoline yield is the same for all three kinds of reactors. Inspired by Weekman’s work, it is our purpose in this research to develop a model approach that can link the coking behavior in both fixed bed reactor and fluidized bed reactor, and thus transfer kinetic data obtained in fixed bed reactor to fluidized bed reactor and vice versa.

In this paper, we first established a model approach to correlate both the fixed bed reactor and fluidized bed reactor with a focus on coke formation. The kinetic parameters for methanol conversion, light olefins formation and coke deposition are derived with experimental results from a batch fluidized bed reactor. The evolution of coke deposition with time on stream is related to the concentration of the feed, space velocity and density of the catalyst bed. With the obtained coke deposition profile in a fixed bed reactor, the methanol conversion and light olefins product distribution could be calculated. Then the results are compared with experimental results to validate the model.

2. Model approach

2.1. Reactor model

From the viewpoint of modeling, the evolution of species j , regardless of reactor configuration, could be described based on mass conservation equation [15]:

$$\frac{\partial \rho_j}{\partial t} + \nabla \cdot (\rho_j \mathbf{u}) + \nabla \cdot \mathbf{J}_j = \mathbf{R}_j \quad (1)$$

where ρ_j represents the density of species ($\text{kg}\cdot\text{m}^{-3}$), t is the time on stream (s), \mathbf{u} is the mass-average velocity vector ($\text{m}\cdot\text{s}^{-1}$), \mathbf{J}_j is the molar flux vector for species j with respect to the mass average velocity ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), and \mathbf{R}_j is the reaction rate of species ($\text{kg}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$).

A batch fluidized bed reactor could be considered as an ideal mixed flow reactor, thus a simple model is adequate to describe the hydrodynamics in the fluidized bed reactor, and the diffusion term in Eq. (1) could be eliminated. In a mixed flow reactor, we may assume that the density of species in the reactor is the same as that in the outlet flow, so the following simplified continuity equation for a continuous, completely mixed reactor could be obtained:

$$\frac{d\rho_j}{dt} = k_f(\rho_j^{\text{in}} - \rho_j) + \mathbf{R}_j \quad (2)$$

where, ρ_j^{in} and ρ_j represent the inlet and outlet flow density of species j respectively, and k_f is the ratio of volume flow rate of the feed to gas phase volume (s).

For a fixed bed reactor, a plug flow model is usually used to model the hydrodynamics. On the other hand, in terms of concentration profile, a plug flow reactor can be treated as the connection of a number of mixed flow reactors in series [2]. Thus, it is reasonable to use a series of completely mixed reactors to model a fixed bed reactor. For the i th reactor, the continuity equation could be written in a similar form as Eq. (2):

$$\frac{d\rho_{ij}}{dt} = k_f(\rho_{i-1,j} - \rho_{ij}) + \mathbf{R}_{ij} \quad (3)$$

where $\rho_{i-1,j}$ represents the density of species j in the $(i-1)$ th reactor, which is regarded as the inlet feed of the i th reactor, and ρ_{ij} and \mathbf{R}_{ij} represent the density and reaction rate of species j in the i th reactor respectively. It should be noted that the reaction rate in the current work is defined on the basis of time on stream, so that both the evolution of gas phase composition and the coke deposition with time on stream could be calculated.

2.2. Kinetic model

2.2.1. Coke deposition model

The coke deposition on SAPO-34 catalyst has a significant impact on methanol conversion and product selectivity in MTO process, and the main difference for a fixed bed reactor and fluidized bed reactor can be explained by the different distribution of coke [11]. For this reason, the coke deposition model is of great importance in establishing a kinetic model. Chen et al. [16] modified the conventional model of Froment et al. [15] to account for the effect of space velocity on coke formation. In their model, coking rate was related to the conversion of oxygenates and the reactant to catalyst ratio. Their results indicated that coking rate varies with the feed and space velocity. By comparing experimental results from two reactor configurations, we found that the coke content shows a certain deviation. Our analysis suggests that the catalyst bed density may also have an influence on the coking rate. Therefore, the coking rate is defined as a function of the feed concentration, the space velocity and the density of the catalyst bed in this study, and the resulting equation is as following:

$$\frac{dc_c}{dt} = k \cdot \rho_{\text{in}}^m \cdot WHSV^n \cdot \alpha \cdot (c_c^{\text{max}} - c_c) \quad (4)$$

where c_c is the coke content, i.e. the weight percentage of the coke deposited on the catalyst, and c_c^{max} is the maximum coke content. k is the kinetic parameter for coke formation, which is estimated from experimental data. The parameters m and n describe the effect of inlet methanol density ρ_{in} and weight hourly space velocity

(WHSV) on coke formation, and α describes the effect of density of the catalyst bed. The initial condition is

$$c_c|_{t=t_0} = c_c^0 \quad (5)$$

and when $t_0 = 0$, $c_c^0 = 0$.

In a batch fluidized bed reactor, the coking formation could be obtained by integration, and the relationship between coke content and time on stream is

$$c_c = c_c^{\max} \left[1 - \left(1 - \frac{c_c^0}{c_c^{\max}} \right) e^{-k \rho_{\text{in}}^m \text{WHSV}^n \alpha (t-t_0)} \right] \quad (6)$$

As a fixed bed reactor can be considered as the connection of several completely mixed reactors in series as described previously, the coke content in a certain reactor could also be derived:

$$c_c = c_c^{\max} \left[1 - \left(1 - \frac{c_c^0}{c_c^{\max}} \right) e^{-k \int_{t_0}^t \rho_{\text{in}}^m (N \cdot \text{WHSV})^n \alpha dt} \right] \quad (7)$$

where N is the number of reactors. The parameters in Eqs. (6) and (7) could be estimated from experimental data for different reactors.

2.2.2. Reaction network

In the published kinetic models, products of the MTO reaction are usually assumed to be formed directly from methanol or over sequential reactions [17–20,11]. However, recent studies suggest that products of the MTO reaction are formed via a “dual-cycle” mechanism [21,22]. Our initial work indicates that taking the “dual-cycle” mechanism into consideration can better describe the kinetics of MTO reaction. In this work, we assume that methanol conversion occurs simultaneously via an olefins-based cycle and an aromatics-based cycle, which are represented by two virtual lumps and designated with S and R respectively. S and R are further assumed to be protonated active site of the catalyst and protonated aromatics species trapped inside the catalyst, and the summation of their quantities is constant. S and R are quantified as mass fraction per mass unit of catalyst, denoted by $c_c^{\max} - c_c$ and c_c , where c_c^{\max} is the maximum coke content. The reaction network is given in Fig. 1, where minor products are not considered herein. In the current work, only the relevant results of the kinetic model are given, and the detailed description will be documented in another publication.

From the above assumptions, the methanol conversion and product formation rate can be written as following:

$$R_{\text{MeOH}} = -\frac{W_{\text{Cat}}}{V_g} [k_{s,1}(c_c^{\max} - c_c) + k_{c,1}c_c] \rho_{\text{MeOH}} \phi \quad (8)$$

$$R_{C_2} = \frac{W_{\text{Cat}}}{V_g} \{ [k_{s,2}(c_c^{\max} - c_c) + k_{c,2}c_c] \rho_{\text{MeOH}} \phi + k_{c,5}c_c \rho_{C_4} \phi - k_{5,S}(c_c^{\max} - c_c) \rho_{C_2} \phi \} \quad (9)$$

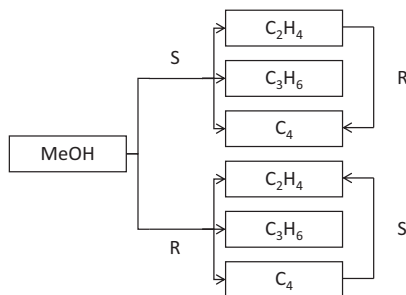


Fig. 1. Simplified kinetic scheme for the MTO reaction.

$$R_{C_3} = \frac{W_{\text{Cat}}}{V_g} [k_{s,3}(c_c^{\max} - c_c) + k_{c,3}c_c] \rho_{\text{MeOH}} \phi \quad (10)$$

$$R_{C_4} = \frac{W_{\text{Cat}}}{V_g} \{ [k_{s,4}(c_c^{\max} - c_c) + k_{c,4}c_c] \rho_{\text{MeOH}} \phi - k_{c,5}c_c \rho_{C_4} \phi + k_{5,S}(c_c^{\max} - c_c) \rho_{C_2} \phi \} \quad (11)$$

In Eqs. (8)–(11), $k_{s,i}$ and $k_{c,i}$ are kinetic constants. The parameter ϕ is the deactivation function, which is defined by the following equation:

$$\frac{d\phi}{dc_c} = -k_d \phi \left(\frac{c_c^{\max} - c_c}{c_c^{\max} - c_c^{\text{cri}}} \right)^{-(p+1)} \quad (12)$$

Integrate Eq. (12), and after simplification, the following correlation can be obtained:

$$\phi = \frac{\exp \left(-k_d \frac{c_c^{\max} - c_c^{\text{cri}}}{c_c^{\max} - c_c} \right)^p}{\exp \left(-k_d \frac{c_c^{\max} - c_c^{\text{cri}}}{c_c^{\max}} \right)^p} \quad (13)$$

where k_d is a constant, c_c^{cri} is the critical coke content, p is a parameter related to operation conditions. The correlation can depict the deactivation of MTO process over SAPO-34 catalyst pretty well. When c_c is smaller than c_c^{cri} , ϕ tends to be 1, which means the catalyst is fully active; when c_c is comparable with c_c^{cri} , ϕ drops significantly, and the catalyst begins deactivation; when c_c is larger than c_c^{cri} , ϕ tends to be 0, which means the catalyst is deactivated. By adjusting c_c^{cri} and p , various deactivation profiles can be represented with this correlation.

By use of this kinetic model together with reactor models discussed above, both fixed bed and fluidized bed reactors can be simulated, and the results can be compared with experimental data.

2.3. Experiments

The experimental data was obtained with an automatic reaction equipment, and the experimental procedure was similar as described previously [11]. The fixed bed reactor has an inner diameter of 0.004 m and the fluidized bed reactor has an inner diameter of 0.019 m and a height of 0.35 m. In both experimental operation, weight hourly space velocity was altered by loading different amount of catalyst while keeping the same methanol flow rate. Aqueous methanol solution was fed by a piston pump. The liquid flow passed through a vaporizer before entering the reactor with or without nitrogen altering the partial pressure of methanol or guarantee well vaporization of liquid feed. The reactor was first heated to 500 °C and maintained for 1 h while keeping the catalyst in nitrogen flow, and then the reaction temperature was adjusted to 450 °C. The industrial DMTO catalyst used in the experiments is SAPO-34 zeolite catalyst. Typical properties of the catalyst could be found in open literature [1]. On-line analysis of the products was performed with an Agilent 7890A gas chromatography equipped with a FID detector and a PorapLOT Q-HT capillary column (25 m × 0.53 mm × 0.02 mm). The coke content of the deactivated catalyst discharged at different time on stream was determined offline by thermogravimetric analysis.

3. Results and discussion

3.1. Comparison between fixed and fluidized bed reactors

The MTO reaction over DMTO catalyst was performed in both fixed and fluidized bed reactor under similar operation conditions. As an example, Fig. 2 shows the evolution of methanol conversion and product selectivity with time on stream in the fixed and flu-

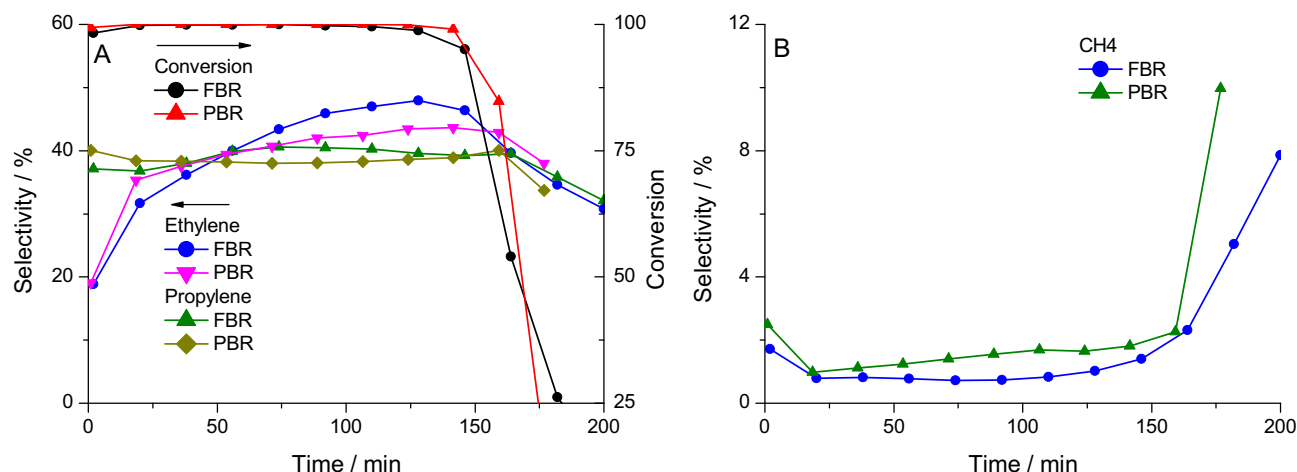


Fig. 2. Evolution of conversion and product selectivity with time on stream in fixed and fluidized bed reactor. FBR: Fluidized Bed Reactor; PBR: Fixed Bed Reactor. Temperature: 450 °C; WHSV = 2.10 $\text{g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$; $X_{\text{w}0} = 0.25$ (g of water) (g of methanol)⁻¹.

idized bed reactor. As shown in Fig. 2(A), methanol conversion, as a function of time on stream, shows similar trend in two different reactors, which suggests that catalyst lifetime may not change with different reactor configurations. At the initial time on stream, the selectivity to ethylene and propylene in the fixed bed reactor is larger than that in the fluidized bed reactor. But after about 50 min, the selectivity to ethylene and propylene in fluidized bed reactor becomes higher. Haw and Marcus [6] suggested that the performance of an MTO fixed bed reactor might not be representative due to the spatial distribution of coke. Kaarsholm et al. [8] observed three distinct zones in the MTO fixed bed reactor with phosphorous modified ZSM-5 catalyst. As the coke formation over SAPO-34 catalyst is faster than that over ZSM-5 catalyst, the spatial distribution of coke in our experiments would be more pronounced. In a fluidized bed reactor, coke deposition on the catalyst is relatively uniform [9]. It has been found that the MTO reaction is dominated by product shape selectivity [4], and there exists an optimal coke content which gives the highest selectivity to light olefins. In a fixed bed reactor, product selectivity is averaged over different coke contents. At initial time on stream, only a small fraction of catalyst is involved in the methanol conversion, and this part of catalyst gains coke rapidly and the selectivity to light olefins increases fast at this stage. While in a fluidized bed reactor, the catalyst in the whole bed takes part in the reaction, and thus the coke formation as well as the increase of selectivity to light olefins changes slowly.

As shown in Fig. 2(B), selectivity to methane is relatively high at initial time on stream and decreases rapidly afterwards. However, during the steady conversion period, selectivity to methane increases in the fixed bed reactor and keeps constant in the fluidized bed reactor. Sun et al. [23] suggested that initial redox reactions of methanol can eventually lead to the formation of coke and methane, which can explain the high initial selectivity to methane. The increase of selectivity to methane in the fixed bed reactor might be due to the deactivated catalyst.

To further investigate the effect of non-uniform coke deposition on the methanol conversion and product selectivity, MTO reaction in a confined fluidized bed reactor was performed. The experiments were carried out in a fluidized bed reactor and quartz wool was placed at different height of the reactor to obtain confined fluidized bed or fixed bed reactor. In a confined fluidized bed reactor, the quartz wool was placed above the catalyst bed so that the expansion of catalyst bed was restricted. In a fixed bed reactor,

the catalyst bed was compressed by the quartz wool and the catalyst could not fluidize at all. As shown in Fig. 3, the results demonstrate that when fluidization of catalyst is confined, the methanol conversion profile keeps the same. However, in a confined fluidized bed reactor, selectivity to ethylene lies between that of a fixed bed reactor and a fluidized bed reactor. This result suggests that the variation in selectivity to ethylene in different reactor configurations is due to the different coke deposition patterns. Comparing the results in Figs. 2 and 3, it should also be noted that under different operation conditions, the catalyst lifetime for fixed and fluidized bed reactors are still the same. Since the deactivation of MTO reaction over SAPO-34 is dominated by coke deposition, the results suggest that the effect of operation conditions, such as the fraction of water in the feed and space velocity, on the coking behavior in both reactors is similar.

Methanol conversion and product selectivity along the catalyst bed in a fixed bed reactor was obtained by carrying out experiments with different amount of catalysts while keeping other operating conditions identical. The results are shown in Figs. 4 and 5. In

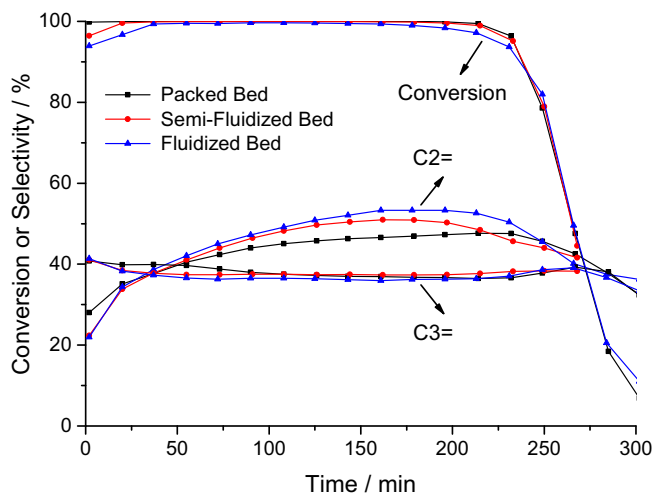


Fig. 3. Evolution of conversion and product selectivity with time on stream in fixed bed, restricted fluidized bed and fluidized bed reactor. Temperature: 450 °C; WHSV = 1.68 $\text{g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$; $X_{\text{w}0} = 1.50$ (g of water) (g of methanol)⁻¹.

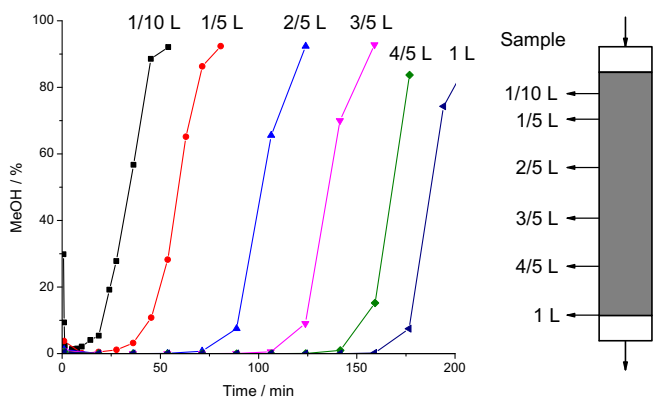


Fig. 4. Time evolution of methanol conversion along the catalyst bed in a fixed bed reactor and the corresponding sampling position. Left: Methanol conversion; Right: Sampling position. Temperature: 450 °C; $X_{w0} = 0.25$ (g of water) (g of methanol)⁻¹.

Fig. 4, the lines on the left side demonstrate the time evolution of methanol conversion at different height of the catalyst bed. The column on the right side shows the sampling position. The results suggest that methanol is fully converted with only a small amount of catalyst, and this amount of catalyst deactivates rapidly, which leads to the front of reaction zone moves along the reactor.

Fig. 5 shows the time evolution of selectivity to ethylene, propylene, and C₄ along the fixed bed reactor. The selectivities along the reactor suggest that, even if the methanol is completely consumed, the light olefins may still be transformed over the catalyst. As can be seen, the selectivities to ethylene and propylene decrease while that to higher olefins increases along the catalyst bed. As time on stream proceeds, the selectivity to ethylene increases and that to the butylene decreases, this can be attributed to shape selectivity by coke deposition.

As shown in Fig. 6, when the ratio of water to methanol in the feed is elevated, the deviation of selectivity to different products along the reactor almost vanishes. The increase rate of ethylene and decrease rate of butylene with time on stream are also attenuated. The results suggest that water may prohibit olefins conversions. Then we further investigated the effect of water on olefins conversions, and the results are shown in Fig. 7. When molar ratio of water to ethylene is increased to 2:1, ethylene conversion is strongly suppressed. Propylene conversion can also be attenuated by water. These results can explain elimination of the deviation of selectivity to different products along the reactor. Fig. 7 also depicts that higher water content can prompt the catalyst lifetime in ethylene transformation, which suggests that coke deposition

might be attenuated. In reality, the coke deposition due to olefins conversions in a fixed bed reactor may contribute to product selectivity as the front of reaction zone moves along the reactor. Therefore, with reduced coke deposition by olefins, the change of product selectivity with time on stream is attenuated.

3.2. Schematic fixed bed reactor model

As depicted by Haw and Marcus [6], the fixed bed reactor proceeds as a “cigar-burn” process. Luo et al. [7] further suggested that the fixed bed reactor with SAPO-34 catalyst could be divided into three zones: deactivation section, methanol conversion section and olefins conversion section. Based on these results, a schematic fixed bed reactor model with three zones is shown in Fig. 8. However, the roles of these sections in the MTO process still needs further investigation.

In the deactivation section, very little methanol is converted and the main product is methane. This result is in accordance with experimental observations in either fixed bed reactor or fluidized bed reactor after the whole catalyst bed deactivates. The length of the deactivation zone increases in fixed bed reactor as the reaction proceeds, so more methane is produced with time on stream. The methanol conversion section is the main reaction zone. Fast autocatalytic reactions occur in this section and most methanol are consumed. In the olefins conversion section, there exists olefins conversion reactions, which produces a small amount of coke. Considered the quite small amount of methanol consumed in the deactivation section, it is reasonable to assume that methanol is only consumed in the methanol conversion section. Further study of the methanol conversion section suggests that a non-uniform distribution of coke might exist. If no olefins conversions occur in the fixed bed reactor, the methanol conversion section should start with deactivated catalyst and end with fresh catalyst, thus the product is an averaged result of the catalyst in this section. As the front of methanol conversion section moves along the reactor, the reaction product should keep constant. In a previous work, the fixed bed reactor was evaluated with COMSOL Multiphysics software with embedded models [11], and secondary reactions were not considered. The results clearly show that the methanol conversion section is almost the same in the whole reaction period. As the methanol conversion section contains just a small amount of catalyst, the time needed to establish this zone is negligible. Based on this, we can understand that MTO reaction and coke deposition in a fixed bed reactor mainly occur gradually from the top of the catalyst bed to the bottom with the evolution of time, and can be regarded as a spatial evolution rather than a time evolution, which is different to a fluidized bed reactor where methanol conversion

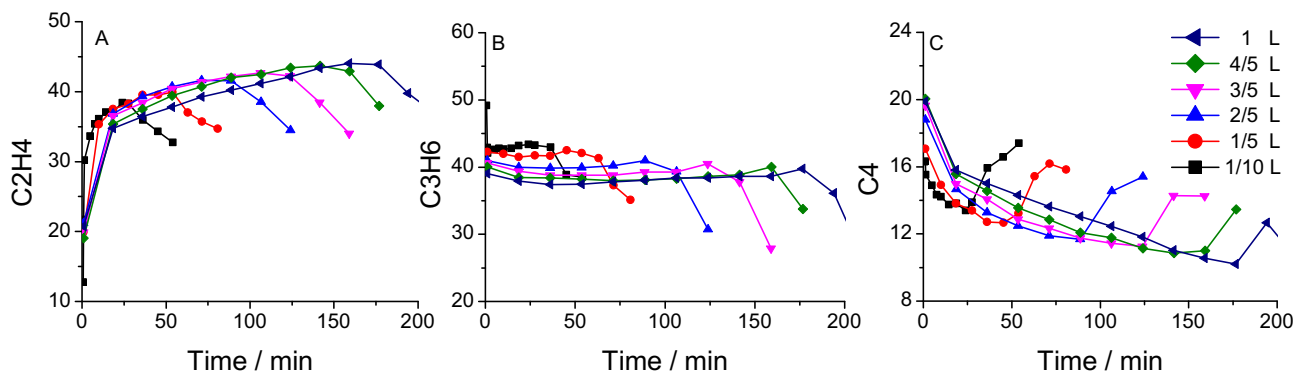


Fig. 5. Time evolution of product selectivity along the catalyst bed in a fixed bed reactor. Temperature: 450 °C; $X_{w0} = 0.25$ (g of water) (g of methanol)⁻¹.

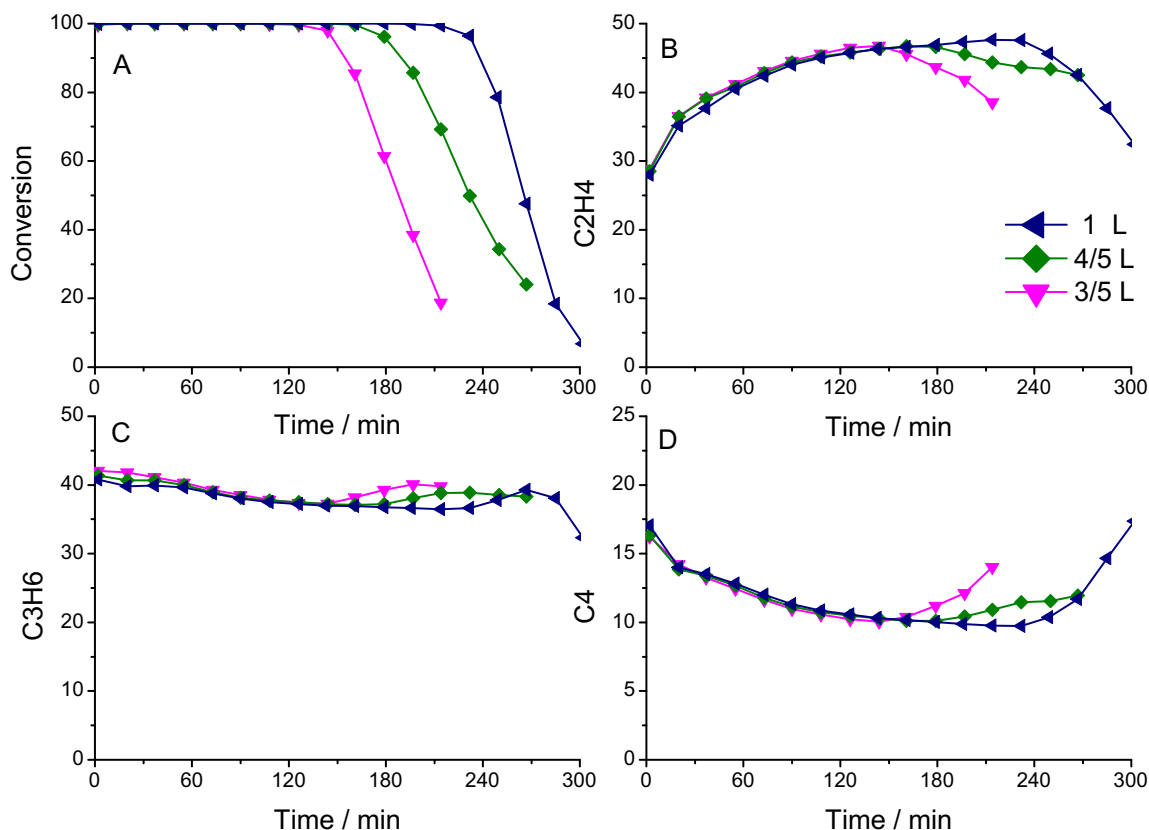


Fig. 6. Time evolution of methanol conversion and product selectivity along the catalyst bed in a fixed bed reactor with elevated water content in the reaction feed. Temperature: 450 °C; $X_{w0} = 1.50$ (g of water) (g of methanol)⁻¹.

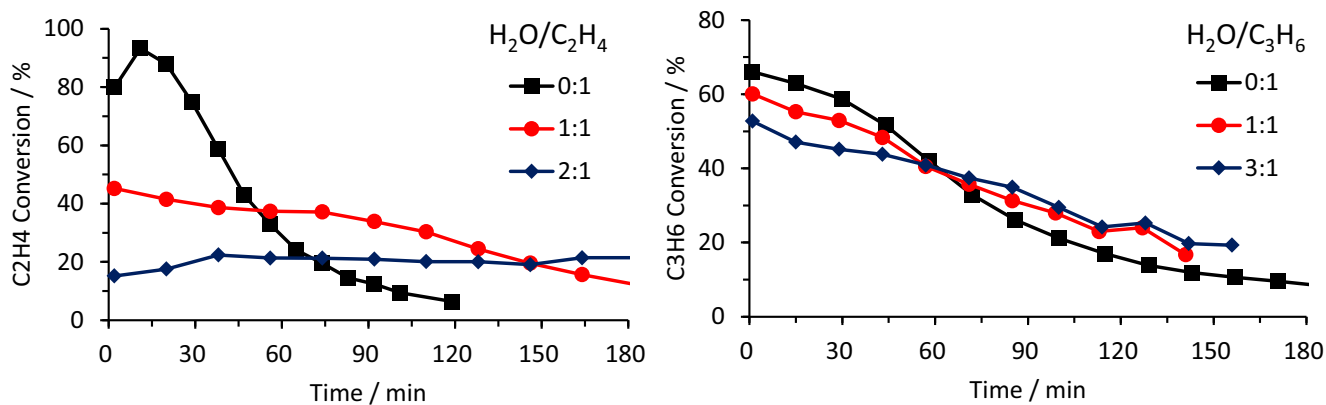


Fig. 7. Effect of water on ethylene and propylene conversion.

and coke deposition are uniform in the reactor and only evolve with time.

In a fixed bed reactor, coke deposition by olefins conversions was actually observed in the olefins conversion section. Thus, the methanol conversion section in fact ends with pre-coked catalyst and the selectivity to light olefins may increase due to the coke deposition. In this sense, the methanol conversion section moves along the reactor with time on stream, and the feed might contact with catalyst that contains more coke. Pre-coke experiments were performed with n-butylene as reaction feed before exposing the catalyst to methanol, and the results showed enhanced selectivity to ethylene in MTO reaction, which is in accordance with other researchers's observations [24]. The effect of olefins conversions

on methanol conversion can be well represented by considering the coke deposition due to olefins conversion.

3.3. Model evaluation

Since a spatially non-uniform aging of catalyst along the fixed bed reactor is observed, the coke distribution rather than the averaged coke content should be determined to account for the effect of coke on product selectivity. However, the distribution of coke content in fixed bed reactor is hard to measure. For this reason, coke content was determined with a fluidized bed reactor, and the results were used to estimate parameters in the coke deposition model. The parameter c_c^{\max} in Eq. (6) is determined in the experi-

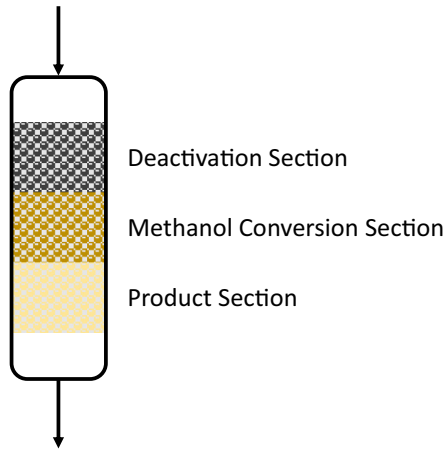


Fig. 8. A schematic fixed bed reactor model.

ment and its value is 0.11. Parameters m and n represent the relative influence of inlet methanol density and WHSV on coke formation, and we obtain $m = 0.6$ and $n = 0.7$ by best fitting all the experimental data. The parameter k is estimated to be 0.28. For the batch fluidized bed reactor, parameter α is set to 1, which is the ratio of catalyst bed density to the batch fluidized bed reactor for other reactor configurations. α is found to be 1.5 for the fixed

bed reactor. As shown in Fig. 9, this model can predict the influence of temperature (A), space velocity (B), water content (C) and methanol partial pressure (D) pretty well. The deviation between experimental and calculated results are within the range of experimental error.

Kinetic constants in the kinetic model is estimated with fluidized bed experimental data. The detailed kinetic model will be the scope of another work, and thus only the relevant kinetic parameters are given in Table 1. The parameter k_d in Eq. (13) is estimated to be 3.8, and different values of c_c^{crit} are adopted for methanol conversion (0.087) and olefins conversion (0.092). The parameter p has a great influence on the deactivation curve. The larger the p , the more sharp the deactivation curve. Since the slopes of the deactivation curve for methanol conversion under different WHSVs are not the same, the parameter p is set as a function of the WHSV. Based on our experimental work, we obtained that p is equal to 0.9 for WHSV of $4.2 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ or higher; $p = 1.3$ for WHSV of $2.8 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$; $p = 1.8$ for WHSV of $2.1 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ and $p = 2$ for WHSV of $1.7 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ or lower. Compared to methanol conversion, the deactivation of olefins conversions is more rapid, thus p is set to 5 for olefins conversions.

Fig. 10 shows the comparison of the evolution of the experimental and calculated product composition (water free basis) for different space velocities. The lines correspond to the values calculated using the kinetic model and the points refer to the experi-

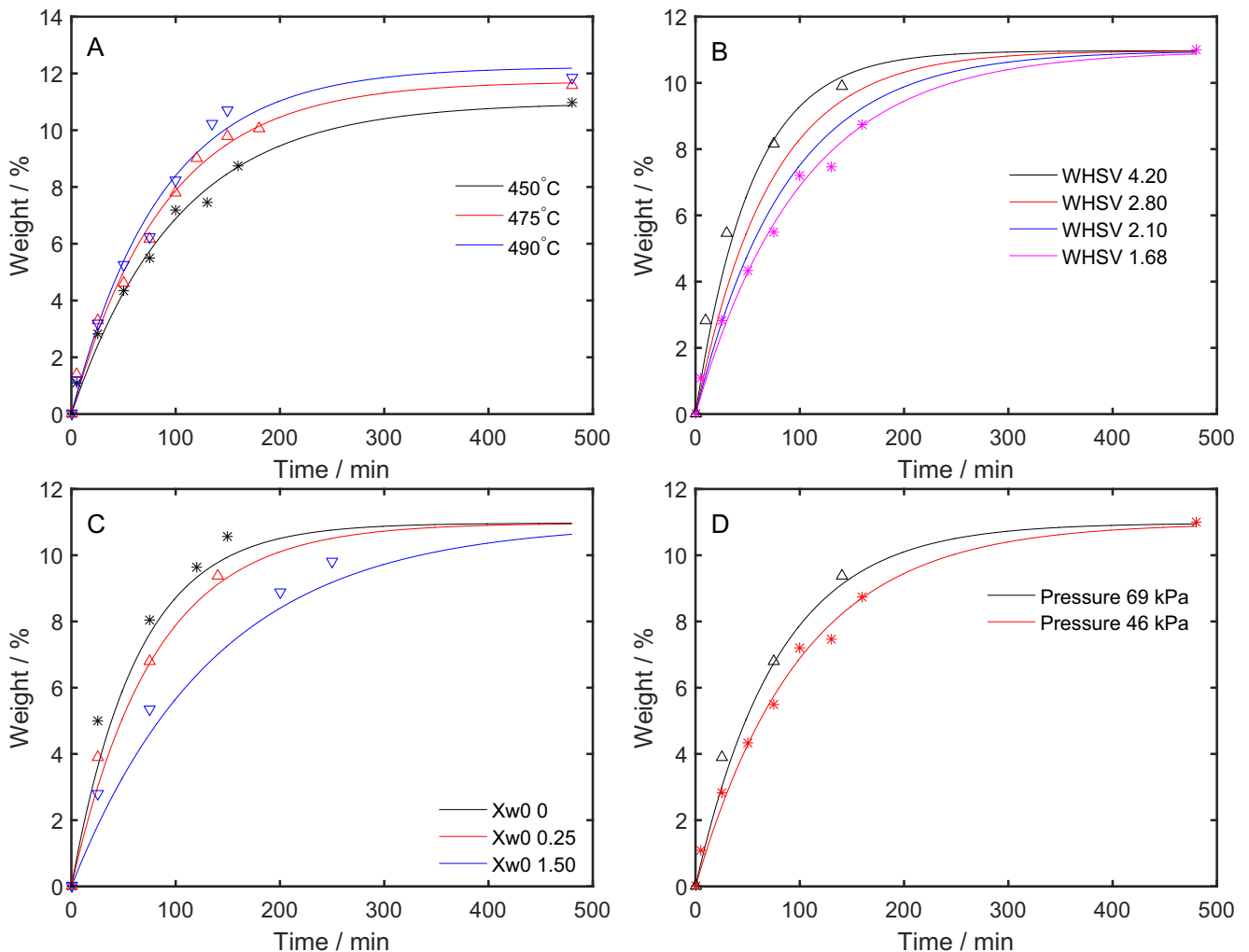


Fig. 9. Coke content versus time on stream for different temperature, WHSV, water content and methanol partial pressure. Dots: Experimental result; Line: Calculated result.

Table 1
Kinetic parameters.

i	1	2	3	4	5
$k_{s,i}$	169	0	69	37	6
$k_{c,i}$	2034	823	823	274	3

Unit: $\text{m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$.

mental results. The fact that the model is feasible for a relatively large range of space velocities, from 1.68 to $8.40 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, suggests that it might be further extrapolated to a higher space velocity, which is quite important for the simulation of fixed bed reactors.

Since the parameters for the coke deposition model and the kinetic model are independent of the reactor configurations, a fixed

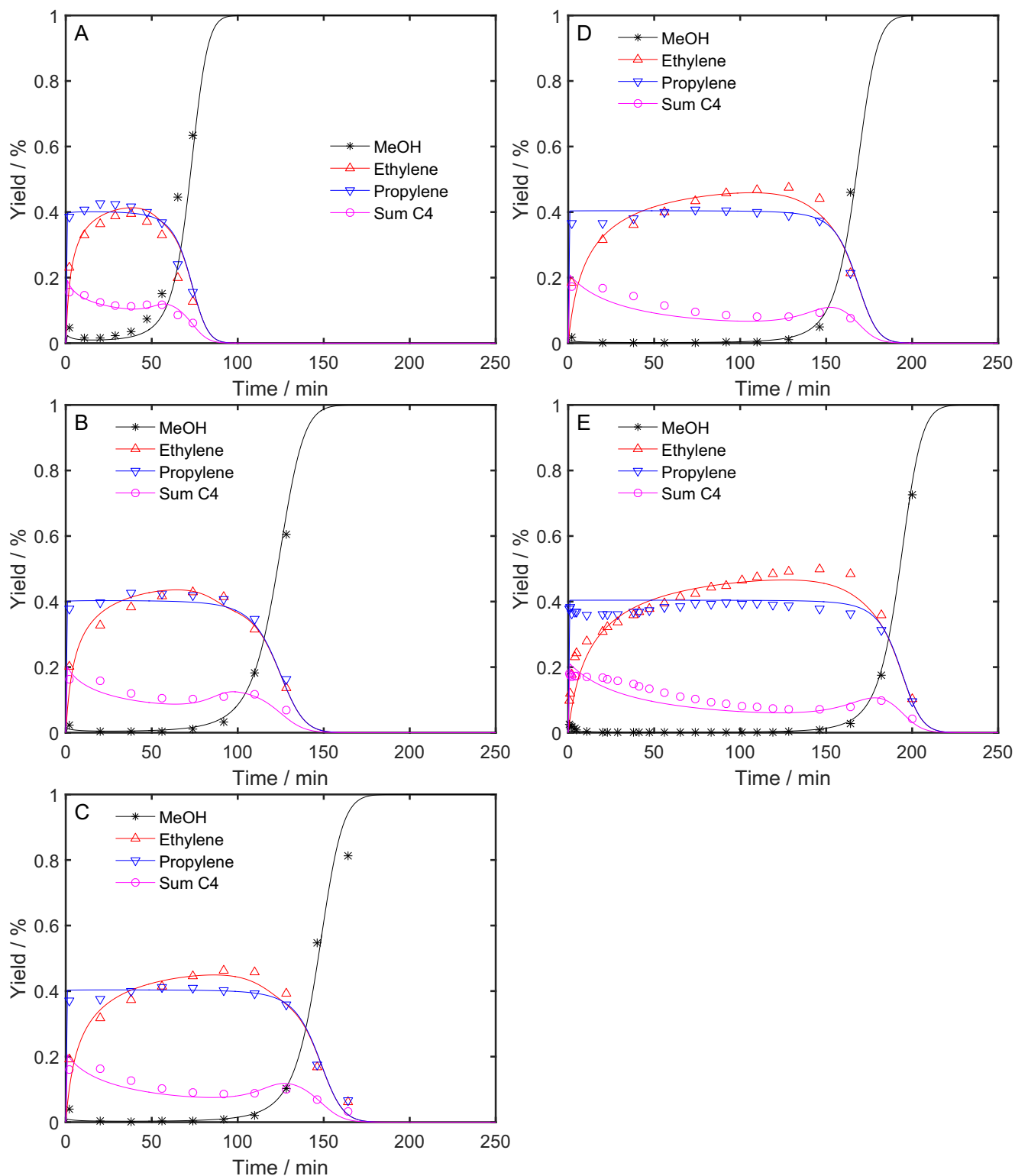


Fig. 10. Time evolution of methanol and light olefins in fluidized bed reactor at different space velocities. Dots: Experimental result; Line: Calculation result. WHSV: (A) 8.40; (B) 4.20; (C) 2.80; (D) 2.10; (E) 1.68. Unit: $\text{g}_{\text{MeOH}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$.

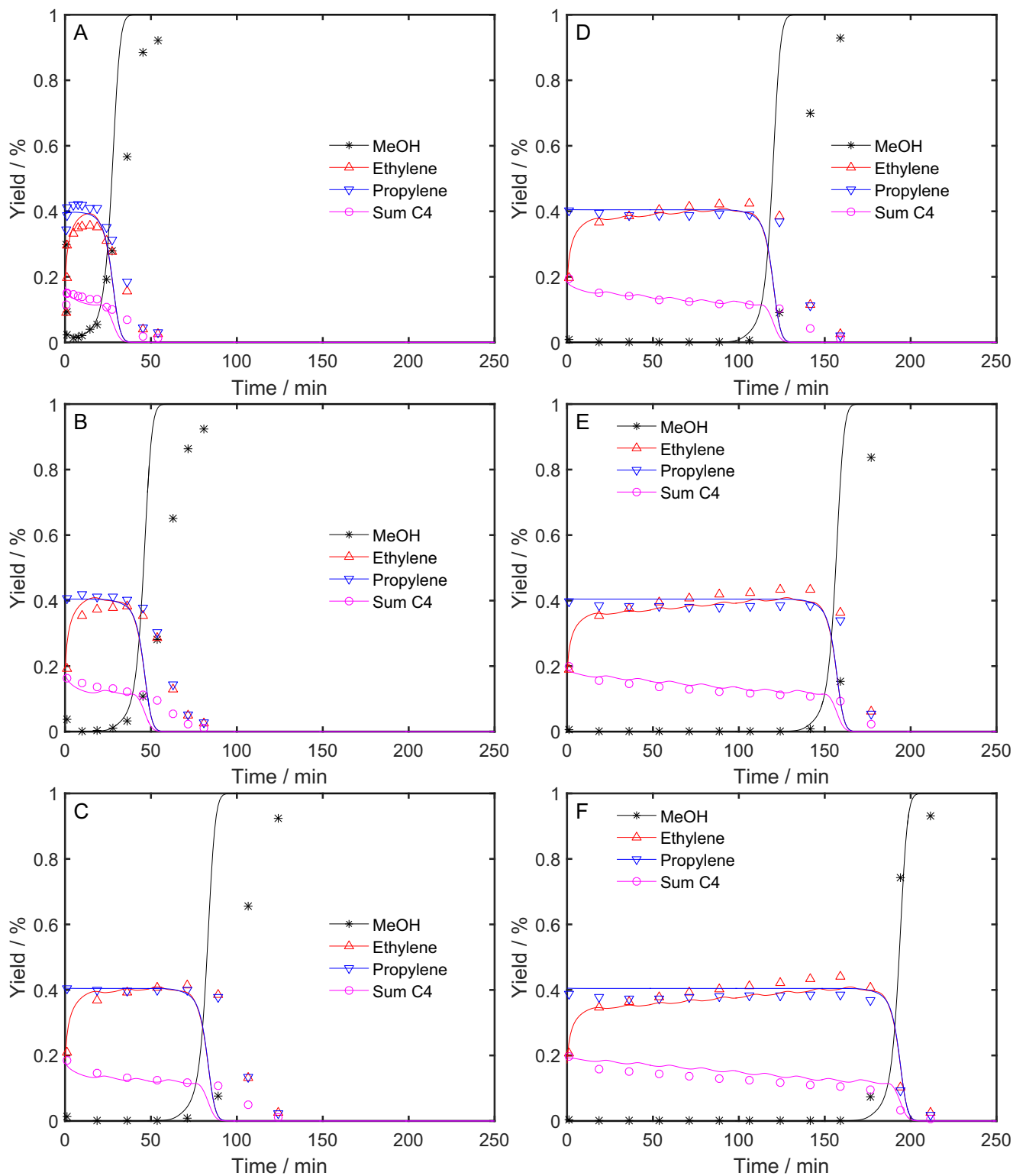


Fig. 11. Time evolution of methanol and light olefins along the catalyst bed in a fixed bed reactor. Lines: Calculated result. Dots: Experimental result. Sampling position: (A) 1/10 L; (B) 1/5 L; (C) 2/5 L; (D) 3/5 L; (E) 4/5 L; (F) 1 L.

bed reactor can also be simulated with these results. Fig. 11 shows the time evolution of methanol and light olefins along the catalyst bed in a fixed bed reactor for both experimental and calculation data. Note that a fluctuation for the light olefins is observed in the simulation result, which is caused by the transition from one reactor to the next reactor in Eq. (3). The fluctuations might be

eliminated by dividing the fixed bed reactor to a higher number of completely mixed reactors, namely a higher N in Eq. (3), which means extrapolating the kinetic model to a much higher space velocity. However, the errors caused by the extrapolation might become too significant. Except for the fluctuations, the results are quite consistent, which indicate that the model could be used to

predict fixed bed results with experimental data from fluidized bed reactor.

From the above discussions, we showed that the model can be used to simulate a fixed bed reactor based on the parameters derived from experiments in a fluidized bed reactor. In this way, the performance of fixed bed reactors can be estimated with experiments conducted over fluidized bed reactors. It should also be noted that the other way around is also possible in current model. Given the coke distribution profile, the kinetic parameters can be obtained with experimental results from fixed bed reactors. Preliminary results of further extending the current model to circulating fluidized bed reactors are also in agreement with experimental results, where the circulating fluidized bed reactors are considered as multiple CSTRs.

4. Conclusion

A quantitative mathematical model for both the fixed bed reactor and fluidized bed reactor was proposed, where coke formation was considered to be the dominant reason that affects methanol conversion in different reactor configurations. In a batch fluidized bed reactor, the coke deposition could be considered as spatially uniform, and only evolves with time on stream. Whereas the catalyst in a fixed bed reactor gains coke sequentially and the reactor has a spatial coke deposition distribution. Olefins conversion also has an impact on the methanol conversion in a fixed bed reactor. On the one hand, olefins conversion tailors the overall product selectivity, and on the other hand olefins conversion deposits coke on the catalyst. Thus when the front of methanol conversion section moves, it comes across the pre-coked catalyst. As a consequence, the product in the methanol conversion section also changes.

To validate the model, the parameters of the kinetic model were first obtained from experimental data in a fluidized bed reactor, and then applied to predict the MTO reaction in a fixed bed reactor. The predicted results show good agreement with the experimental data in fixed bed reactor. This indicates that the model could be used to estimate fixed bed reactor performance with experimental data obtained from a fluidized bed reactor. This can also be done in other way around suppose that coke deposition profile along the fixed bed reactor are known. It is shown that our model can provide a generic tool unifying the fixed bed and fluidized bed reactor for MTO process. In fact the model approach can also be extended to other processes without difficulty.

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