

Kinetic Study of Methanol to Propylene Process on High Silica H-ZSM5 Catalyst

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Abstract

A series of experiments were carried out by mixture of methanol and water as feed of the methanol to propylene (MTP) process in temperature range of 623-823 K. The H-ZSM5 catalyst with the Si/Al ratio of 200 was applied for carrying out the experiments. A novel lumped kinetic scheme was proposed for methanol to propylene (MTP) process. The reactor was mathematically modeled by assumptions of being isothermal, fixed bed, plug flow and the hybrid genetic algorithm was applied for estimating the kinetic parameters. The temperature dependency of the kinetic parameters was determined, using the modified Arrhenius relation. A good agreement was observed between the experimental and the calculated data. Effect of temperature on propylene and ethylene selectivity was investigated. It was found that the propylene selectivity increases with temperature until 773.15 K, but after that it decreases.

Keywords: *Kinetic Study, Methanol to Propylene Process, Lumped Mechanism, Hybrid Genetic Algorithm, High silica H-ZSM5 Nano Catalyst*

1. Introduction

Since propylene is an essential feedstock for production of vast types of polypropylene plastics and these types of plastics are applied widely in many aspects of people's lives, it plays an important role in gas conversion industries nowadays. Obviously the demand for propylene and its derivatives is increasing fast [1]. Old methods of propylene production, such as steam cracking and fluid catalytic cracking (FCC) of crude oil consume enormous amounts of petroleum resources [2]. In these methods propylene is

produced as a byproduct and the rate of propylene production is low. These old methods could not afford the future growing demand for propylene. In recent years, the conversion of methanol to propylene (MTP) process has been launched as a new technology for propylene production generated from the methanol to olefins (MTO) process [3]. The feed of the MTP process consists of methanol which is mostly synthesized from synthesis gas (mixture of CO and H₂). The synthesis gas is obtained from steam reforming of natural gas or

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gasification of coal. Furthermore, large amounts of methanol can also be produced by biomass [4, 5]. The economical aspect of the MTP process is that, by using this process, the need for crude oil will be removed. Because of plentiful amounts of natural gas and coal resources to produce the synthesis gas and also renewable resources of biomass, the MTP process can be considered as a novel process for production of propylene [6].

Kinetic models are essential for reactor design, modeling and optimization of processes. They are implemented in mathematical models of various reactors for estimation of product selectivity, product distribution and determination of the dimensions of the reactor. These models form the quantitative basis for comparison of different reactor types and selecting the optimum type of the reactor to maximize the most valuable product in a particular process [7]. The kinetic models are categorized into two main groups: (a) lumped models in which the detailed chemical species are summarized in larger groups and represent the reality of process, (b) detailed model that takes into account single event reaction steps which consist of molecules, ions and unstable intermediates. Because of the complexity of type (b) models, for design purposes type (a) is applied in most cases [8]. Due to the complexity of the reaction network of the methanol conversion into light olefins, most of the kinetic models in

MTO/MTP processes are lumped models. A brief review of kinetic models that have been proposed for MTO/MTP processes is given here.

The reaction path for methanol conversion to hydrocarbons has been expected to involve sets of steps which are shown in Fig. 1 [9].

The initial reversible step of dimethyl ether (DME) formation has been proven to be rapid and mainly at equilibrium under the conditions of hydrocarbon formation [9-11]. Chang and Silvestri [12] proposed a mechanism involving carbenoid intermediates. Chen and Reagan [13], who observed evidence of autocatalytic behavior of methanol conversion over ZSM5 zeolites, supported the mechanism of Chang and Silvestri [12]. Ono and Mori [14] demonstrated the selectivity behavior of C₂-C₅ olefins during the initial stages of the reaction. Chang [9] modified the model of Chen and Reagan [13]. The model proposed by Chang [9] was based on the reactivity of carbene species, which was generated via α -elimination of water. Bos *et al.* [7] developed a kinetic model for the MTO process based on the SAPO-34 molecular sieve. The final scheme consisted of 12 reactions involving 6 product lumps plus coke. The other kinetic model on the SAPO-34 was proposed by Gayubo *et al.* [15]. The kinetic parameters of this model were obtained by experiments that were carried out in a fixed bed isothermal reactor.

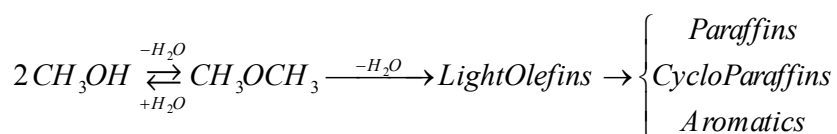


Figure 1. Reaction scheme proposed by Chang [9].

Another lumped kinetic model for the MTO/MTP processes, known as "Hydrocarbon pool" has been introduced [16-21]. This kinetic model mainly contains a central complex chemical species. Nuclear magnetic resonance (NMR) studies demonstrated that the complex molecules form initially in the later stages of the process undergo cracking to produce the light olefins [22, 23].

In all of the above works, the MTO process has been emphasized. The objective of the MTO process is to increase the selectivity of ethylene, while in the MTP process only propylene is valuable and attempts are focused on increasing propylene selectivity. Few researches exist in the kinetic study of the MTP process. For instance, Mei *et al.* [24] developed a simple lumped model for the MTP (Fig. 2).

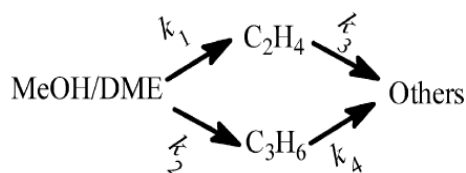


Figure 2. The reaction pathway for the MTP process proposed by Mei *et al.* [24].

Wu *et al.* [25] proposed a kinetic model for the MTP process over a high silica H-ZSM5 catalyst. The kinetic model included a cycle methylation from C_4^+ through C_5^+ to C_6^+ and further to C_7^+ . The β -scission of C_6^+ and C_7^+ causes propylene production. Guo *et al.* [26] applied the reaction mechanism suggested by Wu *et al.* [25] and carried out some experiments using the monolithic and packed bed reactors for estimation of the kinetic parameters in the MTP process. More

recently, Hadi *et al.* [27] suggested a kinetic model for the MTP process on Mn/H-ZSM5 based on the theory of the hydrocarbon pool and the conjugate methylation/cracking reactions using a fixed bed reactor. This kinetic model consists of 17 reactions and 14 chemical species in which initially methanol dehydrates to form higher olefins. The higher olefins undergo the methylation reactions. Hexene and heptene crack to form light olefins: ethylene and propylene.

There exist some single event kinetic models for the MTO process. Mihail *et al.* [28] developed a complex model for the MTO process on a modified synthetic mordenite catalyst. The model contained individual steps up to 53 reactions and about 37 chemical species including radicals and molecules. Park and Froment [29-30] developed a detailed kinetic model based on elementary steps of carbenium ion chemistry in which ethylene and propylene were the main products. H-ZSM5 catalyst with Si/Al ratio of 200 was applied and activation energies for each elementary step were obtained through the Evans-Polanyi relationship.

In the present work due to kinetic study, the activity of the high silica H-ZSM5 catalyst on selectivity of propylene was examined at several WHSV (Weight Hourly Space Velocity) and reaction temperatures. A lumped kinetic model with 10 reactions was proposed for the MTP process. The kinetic parameters were estimated by modeling of a fixed bed, plug flow reactor using hybrid genetic algorithm. The model of the reactor was derived by solving mass conservation on each chemical species, consequently a heterogeneous model in which the reaction

was assumed to occur in the solid catalytic bed was obtained.

2. Experimental

2-1. Catalyst preparation

The starting material for preparation of catalyst was Na-ZSM5 with a Si/Al ratio of 200 (JCPDS. 44-0003), BET surface area of 400 (m²/g) and pore volume of 0.16 (cm³/g) which was supplied by ZEOCHEM[®] (Switzerland). The samples in the NH₄-form were prepared by ion-exchange with NH₄Cl (Merck[®], Germany) solution (1M) at 50°C for 24 h. The H-ZSM5 zeolites were obtained through calcination of the NH₄-zeolites in air at 500°C for 5 h.

2-2. Catalyst characterization

X-ray diffraction pattern of the catalyst was taken in order to characterize the phases and crystallinities of the H-ZSM5 zeolite. The prepared catalyst was analyzed at room temperature by X-ray diffraction using a Siemens[®] D500 X-ray diffractometer with monochromatic Cu-K α radiation (wavelength $\lambda = 0.154$ nm at the range of 2θ from 4° to 70° and at the scanning rate of 2°/min). The surface morphology of the sample was determined by scanning electron microscopy (SEM) recorded on a Vega TESCAN[®] microscope. In order to provide evidence about nanostructure of the zeolite, transmission electron microscopy (TEM) image of the catalyst was taken with a Philips[®] CM 200 FEG instrument.

2-3. Set up and catalyst test

A fixed bed plug flow reactor was applied to test the catalyst activity. The reactor was a pyrex tube with 900 mm length and 9 mm in diameter. The catalyst powder was placed

over a plug of quartz wool and inserted into the reactor. The length of the bed was 100 mm in the reactor. The reactor was placed in an electrical furnace controlled by a proportional-integral-derivative controller (PID), (Fig. 3). Feed of the process (the mixture of methanol and water) was passed through the preheater, mixed by carrier gas (N₂) and fed to the reactor bed. In order to delay the catalyst deactivation, and also to increase the selectivity of propylene, the feed consisted of 20 mol% of methanol and 80 mol% of water. The experiments were carried out at 350, 375, 400, 425, 450, 500 and 550°C. The required pressure for the reaction was supplied by N₂ inert gas. The inlet pressure of the reactor was 1.5bar. Because of the large porosity of the quartz wool, the pressure drop in the reactor was negligible. The product was condensed and analyzed by Shimadzu[®] 2010 plus model gas chromatograph.

The GC analyzer (Shimadzu 2010 plus model) was equipped with a HP-PLOT Al₂O₃S, Agilent capillary column (length: 50m and internal diameter: 0.53mm) and Flame Ionization Detector (FID). Helium was applied as the carrier gas of the GC analyzer.

2-4. Modeling of the reactor

The model of the reactor was obtained by mass conservation equations on each chemical species. The result is a heterogeneous model in which the reaction was assumed to occur in the solid catalytic bed. In this model, the space time of the feed (W/F_{Oxy}) is considered as independent variable and the weight fractions (ω_i) of chemical species are considered as dependent ones.

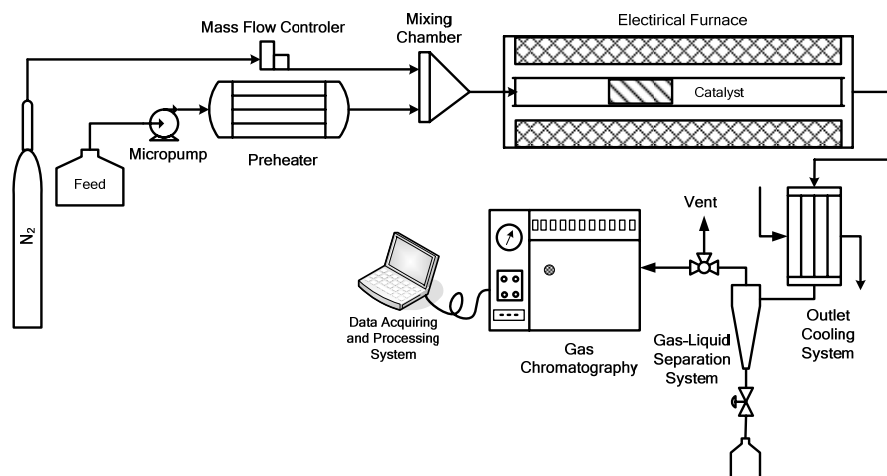


Figure 3. Experimental set up for the MTP process.

$$\frac{d\omega_i}{d(W/F_{oxy.})} = \sum_{j=1}^n r_j \quad i = 1, 2, \dots, \text{number of components} \quad (1)$$

Where ω_i indicates the weight fraction of chemical species ($g_i \cdot g_{total}^{-1}$), $W/F_{oxy.}$ is the space time of the feed ($g_{catalyst} \cdot h \cdot g_{oxy.}^{-1}$). The term r_j indicates the rate of j^{th} reaction. All reactions were assumed elementary and pseudo first order reactions.

$$r_j = k_j \prod_{i=1}^m \omega_i \quad j = 1, 2, \dots, \text{number of reactions} \quad (2)$$

3. Results and discussion

3-1. Catalyst characterization

The XRD pattern of the catalyst which represents the phases and crystallinities of the H-ZSM5 (Si/Al=200) is shown in Fig. 4. This pattern represents distinct broad diffraction peaks in 8-10 and 20-25 in 2θ ranges [31]. The XRD pattern indicates no remarkable damage of the ZSM-5 (JCPDS.44-0003) structure.

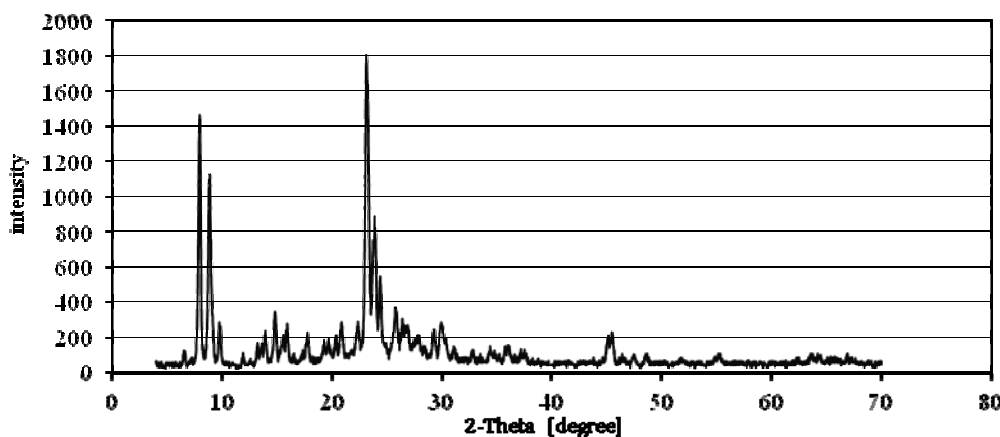


Figure 4. XRD pattern of the H-ZSM5 catalyst with Si/Al=200.

SEM image shows the surface morphology and crystallite size of the H-ZSM5 catalyst with Si/Al=200. According to the SEM image, distribution of the particles size seems to be rather uniform and the external surface of the H-ZSM5 zeolites seems clear and smooth. TEM image confirms the nanostructure of H-ZSM5 (Fig. 6).

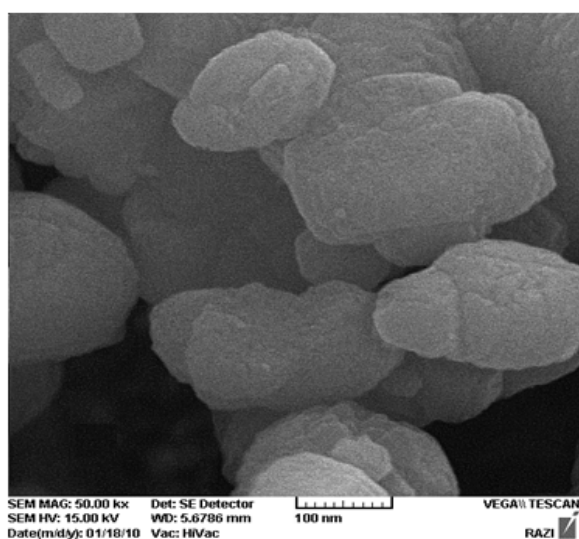


Figure 5. SEM image of the H-ZSM5 catalyst.

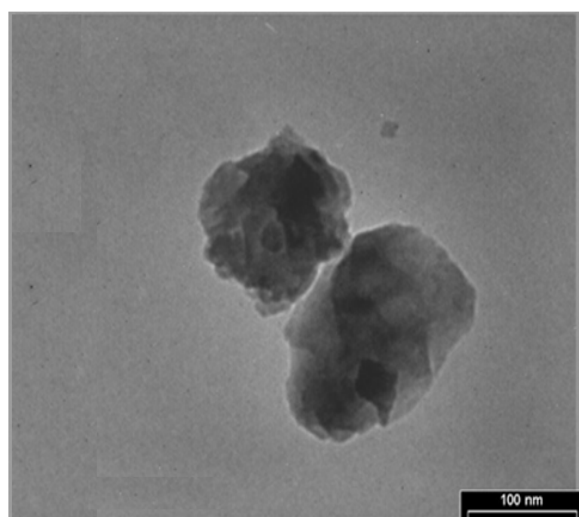


Figure 6. TEM image of the H-ZSM5 catalyst.

3-2. Kinetic study

A lumped kinetic model was proposed based on the following simplification assumptions:

Methanol is at equilibrium with dimethyl ether (DME). So the equilibrium mixture of methanol and DME can be assumed as a chemical species named 'Oxygenate' [13, 14, 15, 24]. Iso-butane and n-butane are the structural isomers of butanes and summation was considered for these products which are mentioned as ' C_4H_{10} ' chemical species. The different isomers of butene such as: Trans-2-butene, Cis-2-butene, Iso-butene and 1-butene were gathered together as ' C_4H_8 ' chemical species. Also, the different isomers of pentene such as trans-2-pentene, 1-pentene, Cis-2-pentene were counted as ' C_5H_{10} ' chemical species. The rest of the hydrocarbons, for example, pentanes, Aromatics (benzene, toluene, xylenes) and other heavier hydrocarbons were listed as ' C_5+ ' chemical species [7, 15].

Because the feed was enriched with water; the formation of coke was low. Existence of water provided a way to increase the selectivity to light olefins by decreasing the selectivity of aromatics [14]. The reaction scheme, which contains 10 reactions and 9 chemical species, is outlined in Fig. 7. It was supposed that oxygenate was directly converted to light olefins such as ethylene and propylene. Light olefins tend to generate the higher olefins such as butenes and pentenes [25]. Some paraffins such as methane, ethane, propane, butanes and pentanes were formed directly via oxygenate [18]. The final reaction step led to the formation of higher hydrocarbons. For example, pentenes tend to form heavier hydrocarbons such as higher paraffins and aromatics which were shown as ' C_5+ ' chemical species in reaction scheme (Fig. 7).

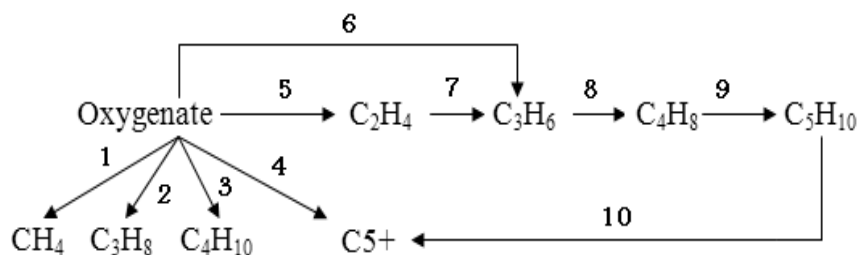


Figure 7. Proposed scheme of reaction.

3-3. Kinetic modeling

According to the equation 2, the rates of reactions are elementary and pseudo first order and by considering the reaction pathway of Fig. 7, the equations shown in Table 1 can be driven for reaction rates. The method for estimation of the kinetic parameters consisted of solving the mass conservation equations for each chemical species mentioned in the kinetic scheme. For parameter estimation, the rates of reactions were considered as a power law relation. By using equation 1, the relations which are shown in Table 1 can be written for each chemical species. The differential equations corresponding to the mass conservation equations of chemical species were solved by ode15s function in MATLAB[®]. The kinetic parameters were estimated using hybrid genetic algorithm (GA) in MATLAB[®] optimization Toolbox. The objective function which was applied to minimize the deviation between the experimental and the calculated weight fraction of chemical species was according to the equation 3.

$$of = \sum_{i=1}^m \sum_{j=1}^p (\omega_{i,j} - \omega_{i,j}(calc.))^2 / mp \quad (3)$$

Where $\omega_{i,j}(\text{calc.})$ are the values of the calculated weight fraction that were obtained by solving the mass conservation equations for component i in the experimental point j that correspond to a specified value of space time, $\omega_{i,j}$ are the values of the experimental weight fraction that were obtained for seven different temperatures with different space time of feed. To reduce the calculation of the kinetic parameters, reparametrization was carried out for estimation of the pre exponential factor (k_0) and the activation energy (E). The reparametrized relationship between the kinetic parameters and temperature is according to the modified Arrhenius equation:

$$k_i = k_{oi} \exp\left[\frac{-E}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \quad (4)$$

Thus the kinetic parameters for each reaction involved in the reaction scheme are optimized at a reference temperature, $T_m=708.86$ K. The optimal parameters which were applied in GA running were as follows: population size=100; generation=200; crossover fraction=0.5; crossover function: crossover arithmetic. The other parameters in GA were held on their default values. The

hybrid function (fminsearch) existing in the MATLAB[®] optimization Toolbox was applied to optimize the kinetic parameters end of GA run. The average corresponding value of the objective function, equation 3, was 4.392×10^{-5} . The respective spans for the 95% confidence intervals of each of the estimated parameters have been calculated by regression analysis using GA. According to the equation 4, the values of the pre exponential factor and the activation energy of each reaction with their 95% confidence intervals are reported in Table 1.

From the values of the kinetic parameters, it is concluded that the formation of propylene takes place mainly from the chemical species of oxygenates and a lesser value from

ethylene. At T_m the kinetic parameters corresponding to the formation of propylene from oxygenates and from ethylene are: $k_6=2.345 \text{ h}^{-1}$ and $k_7=1.256 \text{ h}^{-1}$, respectively. Low reaction rate of steps 1, 2 and 4 which refer to formation of paraffins such as methane, propane and chemical species of C5+ is also notable. Their kinetic parameters at T_m are $k_1=0.08 \text{ h}^{-1}$, $k_2=0.291 \text{ h}^{-1}$ and $k_4=0.454 \text{ h}^{-1}$. The greatest value for activation energy (E) belongs to the 5th reaction and demonstrates that the formation of ethylene is sharply dependent on temperature. The calculated correlation coefficient between E and k_0 values is 0.084 which shows there is no significant correlation between these parameters.

Table 1. The reaction rates and the mass conservation equations for each chemical species.

Mass conservation equations for chemical species	Reaction rate	Kinetic parameters according to equation 4
$\frac{d\omega_{oxy, cnac}}{d(w / F_{oxy.})} = -(r_2 + r_2 + r_2 + r_4 + r_6 + r_8)$	$r_2 = k_2\omega_{oxy, cnac}$	$k_2 = 0.038(\pm 0.005)_{exp} \left[\frac{02953(\pm 36)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_2M_4}}{d(w / F_{oxy.})} = r_2$	$r_2 = k_2\omega_{oxy, cnac}$	$k_2 = 0.291(\pm 0.014)_{exp} \left[\frac{-4537(\pm 55)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_2M_6}}{d(w / F_{oxy.})} = r_2$	$r_2 = k_2\omega_{oxy, cnac}$	$k_2 = 0.971(\pm 0.009)_{exp} \left[\frac{01461(\pm 48)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_4M_{10}}}{d(w / F_{oxy.})} = r_2$	$r_4 = k_4\omega_{oxy, cnac}$	$k_4 = 0.454(\pm 0.012)_{exp} \left[\frac{-3665(\pm 37)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_2+}}{d(w / F_{oxy.})} = r_2 + r_{20}$	$r_5 = k_5\omega_{oxy, cnac}$	$k_5 = 2.039(\pm 0.053)_{exp} \left[\frac{-6039(\pm 94)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_2M_6}}{d(w / F_{oxy.})} = r_5 - r_7$	$r_6 = k_6\omega_{oxy, cnac}$	$k_6 = 2.356(\pm 0.047)_{exp} \left[\frac{-1950(\pm 28)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_2M_6}}{d(w / F_{oxy.})} = r_6 + r_7 - r_8$	$r_7 = k_7\omega_{C_2, M_4}$	$k_7 = 1.256(\pm 0.002)_{exp} \left[\frac{03297(\pm 48)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_4M_6}}{d(w / F_{oxy.})} = r_5 - r_0$	$r_8 = k_8\omega_{C_2, M_6}$	$k_8 = 2.555(\pm 0.060)_{exp} \left[\frac{-1483(\pm 38)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
$\frac{d\omega_{C_2M_{10}}}{d(w / F_{oxy.})} = r_0 - r_{20}$	$r_9 = k_9\omega_{C_4, M_8}$	$k_9 = 3.432(\pm 0.058)_{exp} \left[\frac{-4637(\pm 123)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$
	$r_{10} = k_{10}\omega_{C_2, M_{10}}$	$k_{10} = 0.777(\pm 0.004)_{exp} \left[\frac{-5353(\pm 79)}{R} \left(\frac{1}{T} - \frac{1}{708.86} \right) \right]$

Fig. 8 represents the main product distribution versus space time of the feed at seven temperatures. The experimental and calculated values were shown by points and lines respectively. A good agreement is observed between the experimental and the calculated data obtained from kinetic model.

Effect of temperature on the propylene mole fraction is shown in Fig. 9. The mole fraction of propylene increases when the temperature increases to 773.15 K but decreases at higher than this temperature. The propylene mole fraction is higher than ethylene in all temperatures except at 623.15K.

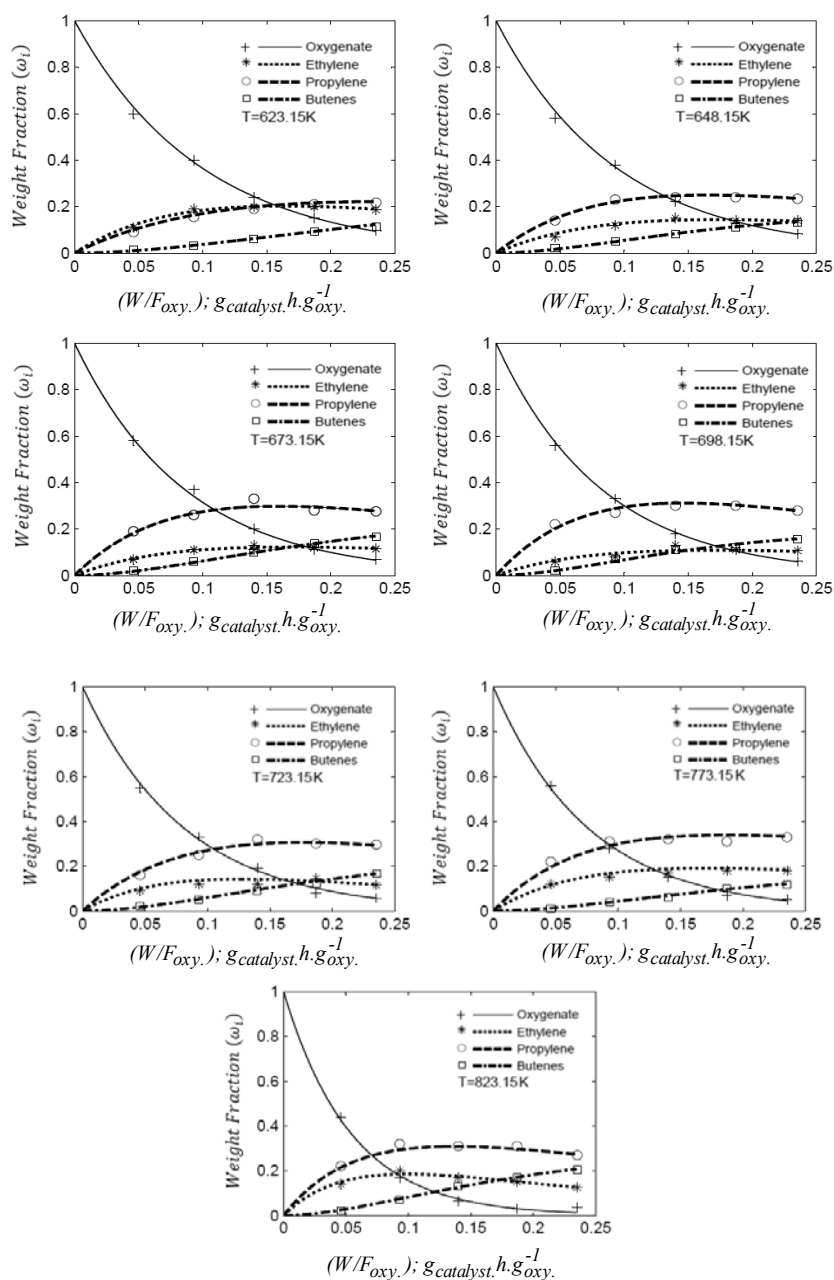


Figure 8. Weight fraction of each olefin and oxygenate versus space time of feed for different values of reaction temperatures. Points: experimental results. Lines: calculated with the kinetic model.

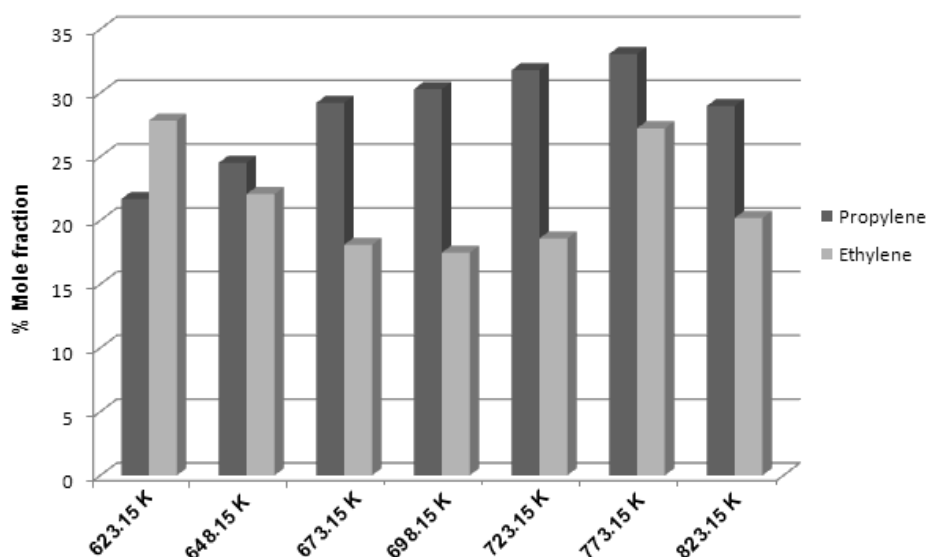


Figure 9. Effect of temperature on mole fractions of propylene and ethylene.

4. Conclusions

- A new lumped kinetic model was proposed for methanol to propylene process on high silica HZSM-5 (Si/Al=200) catalyst. The kinetic parameters were estimated successfully using hybrid genetic algorithm.
- A good agreement was observed between experimental and calculated profiles of the species. The mole fraction of propylene is increased gradually with increasing of temperature but it decreases higher than 773.15 K.

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