

Development of a Reaction Scheme for Methanol to Propylene Process Using Zeolite Nano Catalyst

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ABSTRACT

A series of experiments at three different temperatures were carried out by means of mixture of methanol and water as feed of methanol to propylene process. The weight hourly space velocities (WHSV) for methanol were 3, 4 and 6 h⁻¹. With the usage of mole fractions of the main products such as methane, ethane, ethylene, propylene, propane, four and five carbonated hydrocarbons that were obtained from gas chromatograph (GC) analysis, a reaction scheme was developed for methanol to propylene process. The behavior of isothermal, fixed bed and plug flow reactor was mathematically modeled and the genetic algorithm was used for estimating kinetic parameters.

NOMENCLATURE

ω_i : weight fraction of the *i* th chemical species,

E: activation energy, J/mol

k_j : kinetic parameter for the *j* th chemical reaction, hr⁻¹

k_0 : preexponential factor of the kinetic parameters, hr⁻¹

m: number of chemical species

n: number of reactions

R: universal constant of gases, J.mol⁻¹.K⁻¹

r_j : reaction rate, gr_f.gr⁻¹.hr⁻¹

T: reaction temperature, K

T_m: reference temperature

W/F_{MeOH}: Space time, hr

INTRODUCTION

Old methods of propylene production, such as steam cracking and catalytic cracking of crude oil are applying enormous amounts of petroleum resources. In recent years, the conversion of methanol to propylene (MTP) process was proposed as a new method for propylene production. Methanol is synthesized from synthesis gas. Synthesis gas is the mixture of CO and H₂ that are obtained from natural gas or coal. Since there are a lot of natural gas resources in world, in the future the MTP process can

be considered as an economic process for producing of strategic material, propylene.

A lot of reaction schemes were developed, since the discovery of the methanol to light olefin (MTO) reactions. Mihail (1983) developed a detailed reaction scheme containing 53 reactions and 37 chemical species on the mordenite zeolite with Si/Al=20 [1]. Bos et al (1995) expanded another reaction scheme on the molecular sieve SAPO-34. This lumped mechanism contained 12 reactions and 6 chemical species [2]. The next reaction scheme on SAPO-34 was proposed by Gaybo et al (2000). The kinetic parameters of this model were obtained by experiments that were done in a fixed bed isothermal reactor [3]. Park and Froment (2001) developed a detailed reaction scheme for MTO process on ZSM-5 in a plug flow reactor. For parameter estimation the hybrid genetic algorithm was used [4], [5]. In all projects that were mentioned, the MTO process has been emphasized. The object of MTO process is increasing the selectivity of light olefins such as ethylene, propylene and butylenes. While in the MTP process the valuable product is only propylene. In this work a lumped reaction scheme was developed on the basis of experiments that were carried out on HZSM-5 modified zeolite catalyst with Si/Al=200. By modeling of a fixed bed plug flow reactor, the kinetic parameters were obtained with using of genetic algorithm.

EXPERIMENTAL

Catalyst preparation

For the preparation of modified HZSM-5 zeolite catalyst, Na-ZSM5 nano structure was used as the basis of catalyst. The ratio of Si/Al in these types of zeolites was 200. Then one molar solution of ammonium chloride was prepared, in order to have ion exchange between Na-ZSM5 and NH₄Cl. This solution was stirred, so the action of ion exchange

was carried out and protonated form of zeolite was obtained. The solution was dried and then it was calcinated.

Set up

As can be seen in Figure1 feed is pumped to the reactor. A fixed bed plug flow reactor is used for doing experiments. By using a furnace, the reactor acts as an isothermal reactor. The products are analyzed by 2010 plus Shimadzu gas chromatography (GC). The GC analyzer was equipped with a HP-PLOT Al_2O_3/S , Agilent capillary column (length: 50m and internal diameter: 0.53mm). Helium was used as the carrier gas and Flame Ionization Detector (FID) was applied.

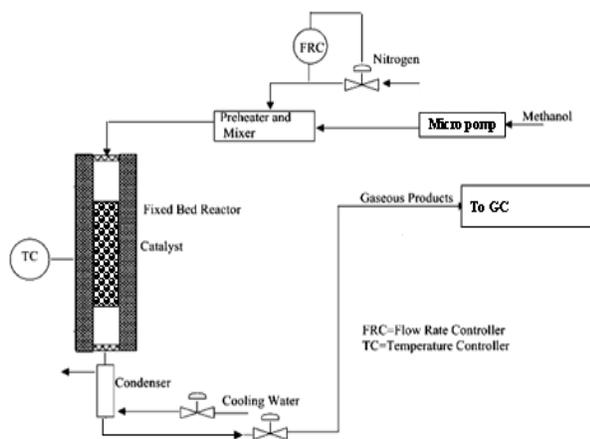


Figure1. The experimental set up of the process

In order to have some evidence about nanostructure of zeolite, transmission electron microscopy (TEM) images of the catalyst were taken with a Philips CM 200 FEG instrument [6].

All experiments were carried out at WHSV=3, 4 and 6 (hr^{-1}) and three different temperatures: 350°C, 450°C, 550 °C. On the basis of results that were obtained from GC analysis and some logical assumptions, a lumped reaction scheme was proposed.

The simplification assumptions are as follows:

- Methanol is at equilibrium with dimethyl ether (DME). So we can assume methanol and DME as a chemical species named 'Oxygenate' [7].
- Iso-butane and n-butane are the structural isomers of butanes, so we did summation for these products and mentioned them 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.

- Rest of hydrocarbons for example pentanes, benzene, toluene, xylenes (Aromatics) and other heavier hydrocarbons plus coke were stated as ' C_5+ ' chemical species.

The proposed lumped reaction scheme is shown in Figure2.

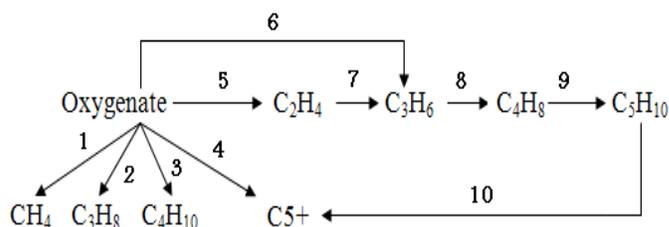


Figure2. Proposed reaction scheme

We have adopted the pseudo heterogeneous model in which the reactions were assumed to occur in gas phase [3]. Referring to this model, the weight fractions of the chemical species are given by:

$$d\omega_i / d(W/F_{MeOH}) = \sum_{i=1}^n r_j \quad (1)$$

Where ω_i indicates the weight fraction of chemical species in $gr_i \cdot gr_{total}^{-1}$, W/F_{MeOH} is the space time of the feed in $gr_{catalyst} \cdot hr \cdot gr_{MeOH}^{-1}$. The term of r_j indicates the rate of j th reaction. All reactions are assumed pseudo first order and elementary reactions.

$$r_j = k_j \prod_{i=1}^m \omega_i \quad (2)$$

Where k_j is the kinetic parameter of j th reaction.

RESULTS AND DISCUSSION

Equations 1 and 2 were solved together in a computer program and then in order to estimate the kinetic parameters, the computer program was connected to the genetic algorithm, so the parameters were obtained for three temperatures. 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 kinetic parameters and temperature is:

$$k_i = k_{0i} \exp(-(E/R)(1/T - 1/T_m)) \quad (3)$$

where T_m is the arithmetic average value of the temperatures. Figure4 shows the weight fractions of

chemical species versus space time at three temperatures that the experiments were carried out. Figure 3 demonstrate a good agreement between experimental and calculated data obtained from kinetic scheme. So the performance of the genetic algorithm in parameter estimation is evaluated well.

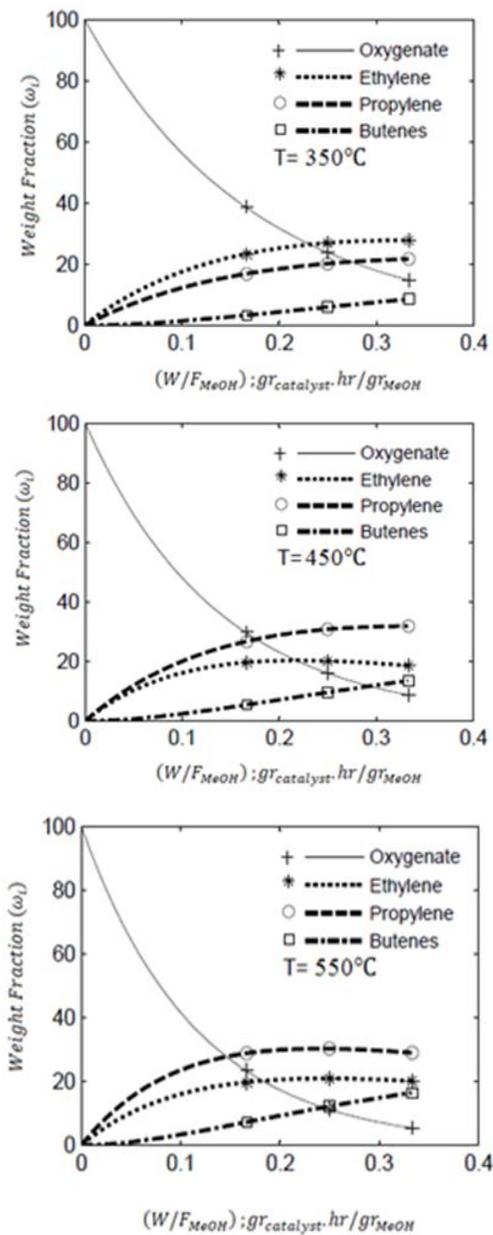


Figure 3. Weight fraction of each olefin and oxygenate versus space time for $T=350^{\circ}\text{C}$, $T=450^{\circ}\text{C}$ and $T=550^{\circ}\text{C}$. Points: experimental results. Lines: calculated with the kinetic model

CONCLUSIONS

A lumped reaction scheme was proposed for MTP reaction. The reactor was modeled and all kinetic parameters were estimated via genetic algorithm. The activation energy and the pre exponential factor of

each reaction were calculated based on a reparametrized relationship. Results taken experimentally were compared with calculated results and a good agreement between experimental and calculated results was observed.

KEYWORDS

Reaction Scheme, Kinetic Modeling, Methanol to Propylene Process, Genetic Algorithm, Nano Catalyst

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