



Kinetic modeling formulation of the methanol to olefin process: Parameter estimation



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ABSTRACT

Detailed kinetic models at the elementary step level were developed for the methanol to olefins (MTO) process over SAPO-34 catalyst. Starting from believable mechanisms, forming primary products was modeled rigorously by the Hougen–Watson formalism. Discrimination of kinetic equations and calculation of the parameters of best fit were performed by solving the mass conservation equations of the main products of the kinetic scheme. For rate constants, preexponential factors and apparent activation energies were then calculated according to the Arrhenius equation. For thermodynamic constants, the difference between apparent activation energies of forward and reverse reaction was considered. The kinetic model fits well the experimental data, which is obtained in a fixed bed reactor. The results showed that rising space-time is favorable for olefin yields while an optimum temperature might produce the maximum olefin.

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1. Introduction

Rising availability of natural gas has caused continued interest in new roads to main petrochemical chemicals such as ethylene and propylene. The catalytic conversion of methanol to olefin (MTO) is a promising alternative to current process, i.e. steam cracking [1–3]. Different studies approved that small pore silicoaluminophosphate molecular sieve; SAPO34 is a good catalyst in converting methanol to olefin (MTO). It gives high selectivity (>80%) to light olefins with almost 100% methanol conversion. These properties are due to the mild acidity and effective pore openings of SAPO-34 because of adsorbing only straight chain molecules such as primary alcohols, linear paraffins, and olefins. Branched isomers, aromatics, and diffusion of larger molecules such as aromatics are largely restricted [4–7].

The importance of this process for petrochemical industry justifies the interests of modeling development. Many studies concerns the effect of operating conditions, catalyst synthesis, and modifications on the olefin yields, however, detailed mechanistic and kinetic studies of this process is required. Kinetic study is one of the most important aspects of catalytic processes that models and simulates the reactor, predicts the products distribution and finally optimizes the operating conditions for industrial applications [8,9].

The proposed kinetic schemes are classified according to description of each step or individual reaction [10], or simplified lumped model of main products [11,12].

Because of complexity and incomplete chemical analysis, the kinetic modeling of this process is often based on reaction schemes consisting of a few reactions among pseudo-components or among “lumps” of species. These lumps sometimes defined more precisely by physical properties, like boiling range, than by chemical characteristics [13]. Several kinetic models for methanol to olefin process are available for light olefins production [14,15]. Park and Froment [10,11] developed the detailed kinetic models at the elementary step level for the methanol to olefin (MTO) process over HZSM-5 catalyst with a Si/Al ratio of 200. Starting from possible mechanisms, forming primary products was modeled rigorously by the Hougen–Watson formalism. Carbenium ion mechanisms expressed forming higher olefins. They used a computer algorithm to generate the reaction network. The estimation was performed with the genetic algorithm, followed by the Levenberg–Marquardt routine, but in combination with sequential quadratic programming to account for the physico-chemical constraints. Gayubo et al. [16] proposed a kinetic model for the individual olefin formation (ethylene, propylene, and C₄⁺ olefins) from methanol over a SAPO-18 catalyst in a wide range of operating conditions. The kinetic model considered three steps that change with time on stream: initiation period (where active intermediate compounds were formed), olefin production, and deactivation. Different kinetic schemes for forming each individual olefin were tested. Models considered interconversion between

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olefins did not provide significant improvement over the models that quantified formation of individual olefin only by direct reaction of oxygenates (methanol/DME) with intermediate compounds. Aguayo et al. [17] showed a kinetic model of seven lumps which quantified the product distribution (oxygenates, *n*-butane, C₂–C₄ olefins, C₂–C₄ paraffins (without *n*-butane), C₅–C₁₀ fraction, methane) in the transformation of methanol into hydrocarbons at high temperature (400–550 °C) on a HZSM-5 zeolite with high acidic strength and agglomerated with bentonite and alumina. The kinetic model fitted well the experimental data which was obtained in a fixed bed reactor, from small values of space time in which the formation of hydrocarbons is incipient, to a space time of 2.4 (g of catalyst) h (mol CH₂)⁻¹ for a complete conversion of methanol. Najafabadi et al. [18] proposed a new kinetic model for methanol to olefin process over SAPO-34 catalyst based on data which was obtained from a micro catalytic reactor using suitable reaction network. Comparing the experimental and predicted data showed the predicted values from the presented model were well fitted to the experimental data.

Most of the proposed kinetic models suited to the results of silicoaluminate or the lump models. However, detailed kinetic model are required to predict the behavior of SAPO-34 catalyst with a reaction mechanism. Enough detail of chemical steps is necessary for a model to be of real use. Only then, the product distribution, which is an important feature of complex commercial processes, might be reliably predicted.

In the present work, the process is written with elementary steps, without lumping, neither of components nor of steps. The friendly kinetic model that is proposed for the MTO process on SAPO-34 is to quantify the individual evolution of each olefin (ethylene, propylene, and butenes) with space-time at different temperatures. The interest for the individual quantification of olefin is relevant for a suitable adjustment of process conditions to evolve demand.

2. MTO reaction network

For methanol to olefin process over SAPO-34 catalyst, a reaction mechanism was developed in this paper. The reaction network, which is shown in Table 1, describes the methanol to olefin process. Generally, more reaction a model includes, more kinetic parameters need to be estimated and, therefore, more experimental data is required. The proposed MTO process consists of the following categories of reactions for main products: (1) the dehydration of methanol to dimethyl ether (DME), (2) ethylene formation, (3) propylene formation and (4) other products.

A reaction scheme for DME formation in terms of elementary steps is displayed. Methanol is quickly dehydrated to form dimethyl ether and water through a mechanism with the methoxy ion as an intermediate. Methanol is adsorbed through hydrogen to the bridging hydroxyl on the Brønsted sites. The protonation is fast on strong acidic sites and is considered to reach equilibrium.

Many mechanisms considered the possible reactions for ethylene formation [19–21]. In this paper, we suggested the association of the methoxy species (R₁⁺) with a conjugate basic site, bs, led to ethylene based upon a surface-bonded oxonium methylide, represented by OM which is proposed by Hutchings and Hunter [21]. This pathway was approved because the basic strength of the SAPO-34 catalyst may be sufficient to form the oxonium methylide by proton abstraction from the methoxy species.

Deprotonation of highly unstable carbenium ions such as the propylcarbenium ion (R₃⁺) and the butylcarbenium ion (R₄⁺) generates propylene and butene. These ions are formed from

Table 1

Elementary steps describing the products formation of the MTO process and related rate and equilibrium parameters.

DME formation	
MeOH + H ⁺ ↔ MeOH ₂ ⁺	$K_{\text{MeOH}_2^+} = \frac{C_{\text{MeOH}_2^+}}{C_{\text{H}^+} P_{\text{MeOH}}}$
MeOH ₂ ⁺ ↔ R ₁ ⁺ + H ₂ O	$K_{R_1^+} = \frac{C_{R_1^+} P_{\text{H}_2\text{O}}}{C_{\text{MeOH}_2^+}}$
R ₁ ⁺ + MeOH ↔ DMO ⁺	$r_{\text{DMO}^+} = k_{\text{sr,DMO}^+}^* \left(C_{R_1^+} P_{\text{MeOH}} - \frac{C_{\text{DMO}^+}}{K_{\text{sr,DMO}^+}} \right)$
DMO ⁺ ↔ DME + H ⁺	$K_{\text{DMO}^+} = \frac{C_{\text{DMO}^+}}{P_{\text{DME}} C_{\text{H}^+}}$
Ethylene formation	
MeOH + H ⁺ ↔ MeOH ₂ ⁺	$K_{\text{MeOH}_2^+}$
MeOH ₂ ⁺ ↔ R ₁ ⁺ + H ₂ O	$K_{R_1^+}$
DME + H ⁺ ↔ DMO ⁺	K_{DMO^+}
R ₁ ⁺ + bs ↔ OM + H ⁺	$K_{\text{OM}} = \frac{C_{\text{OM}} C_{\text{H}^+}}{C_{R_1^+} C_{\text{bs}}}$
OM + DMO ⁺ R ₂ ⁺ + MeOH + bs	$r_{R_2^+} = k_{\text{sr,R}_2^+}^* C_{\text{OM}} + C_{\text{DMO}^+}$
R ₂ ⁺ ↔ O ₂ + H ⁺	$K_{R_2^+} = \frac{C_{R_2^+}}{P_{\text{O}_2} C_{\text{H}^+}}$
Propylene formation	
O ₂ + H ⁺ ↔ R ₂ ⁺	$K_{R_2^+}$
DME + H ⁺ ↔ DMO ⁺	K_{DMO^+}
R ₂ ⁺ + DMO ⁺ → R ₃ ⁺ + MeOH ₂ ⁺	$r_{R_3^+} = k_{\text{sr,R}_3^+}^* C_{R_2^+} C_{\text{DMO}^+}$
R ₃ ⁺ ↔ O ₃ + H ⁺	$K_{R_3^+} = \frac{C_{R_3^+}}{P_{\text{O}_3} C_{\text{H}^+}}$
MeOH ₂ ⁺ ↔ MeOH + H ⁺	$K_{\text{MeOH}_2^+}$
Butene formation	
O ₃ + H ⁺ ↔ R ₃ ⁺	$K_{R_3^+}$
DME + H ⁺ ↔ DMO ⁺	K_{DMO^+}
R ₃ ⁺ + DMO ⁺ → R ₄ ⁺ + MeOH ₂ ⁺	$r_{R_4^+} = k_{\text{sr,R}_4^+}^* C_{R_3^+} C_{\text{DMO}^+}$
R ₄ ⁺ ↔ O ₄ + H ⁺	$K_{R_4^+} = \frac{C_{R_4^+}}{P_{\text{O}_4} C_{\text{H}^+}}$
MeOH ₂ ⁺ ↔ MeOH + H ⁺	$K_{\text{MeOH}_2^+}$
Methane formation	
MeOH + H ⁺ ↔ MeOH ₂ ⁺	$K_{\text{MeOH}_2^+}$
MeOH ₂ ⁺ ↔ R ₁ ⁺ + H ₂ O	$K_{R_1^+}$
R ₁ ⁺ + MeOH → CH ₄ + HCHO + H ⁺	$r_{\text{CH}_4} = k_{\text{sr,CH}_4}^* C_{R_1^+} P_{\text{MeOH}}$

reaction of a carbenium ion and DMO⁺. Ethylene and propylene are intermediates in the kinetic scheme that take part as reactants in the autocatalytic step of the “hydrocarbon pool” mechanism to form more olefins and heavy products by methylation, oligomerization, cyclization, and aromatization and paraffins by the mechanisms of oligomerization-cracking.

In the elementary reaction steps, the structure of the reactant olefin and stability differences between reactant and product cations, as the major driving force for the reaction, should be considered. Methane is a byproduct of oxygenate decomposition and involves donating methanol to the surface methoxy.

For the elementary steps, which are involved in forming the primary products, five independent rate equations are necessary: (1) formation of the dimethyloxonium ion on acidic site, $r_{\text{DMO}^+} = f(x, \beta)$; (2) its consumption to form the ethylcarbenium ion on basic site, $r_{R_2^+} = f(x, \beta)$; (3) the production of highly active propylcarbenium ion on acidic site, $r_{R_3^+} = f(x, \beta)$; (4) the surface reaction of propylcarbenium and dimethyloxonium ions to form butylcarbenium ion, $r_{R_4^+} = f(x, \beta)$; and (5) formation of methane, $r_{\text{CH}_4} = f(x, \beta)$. In these equations, *x* represents the vector of partial pressures and *β* the parameter vector.

A larger number of reaction schemes can be written for the MTO process, for example, considering some other products and type of adsorption, nondissociated or dissociative. In this paper, formation of higher olefins is ignored because of simplicity and low yield. Furthermore, surface reaction was chosen as rate-determining step (r.d.s).

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