On the Kinetic of LPDME Process over Bi-Functional Catalyst in N-Hexadecane

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Received: December 29, 2011 / Accepted: October 17, 2012 / Published: January 25, 2013.

Abstract: The intrinsic kinetics of the three phase dimethyl ether (DME) synthesis from syngas over a bi-functional catalyst has been investigated in an agitated slurry reactor at 20-50 bar, 200-240 °C and H2/CO feed ratio from 1 to 2. The bi-functional catalyst was prepared by physical mixing of CuO/ZnO/Al2O3 as methanol synthesis catalyst and H-ZSM-5 as methanol dehydration catalyst. The three reaction including methanol synthesis from CO and H2, methanol dehydration to dimethyl ether (DME) and water-gas shift reaction were chosen as the independent reactions. A kinetic model for the combined methanol + DME synthesis based on a methanol synthesis model proposed by Graaf and a methanol dehydration model by Bercic and Levec have been fitted our experimental data. Coefficients in the equations follow the Arrhenius and Van’t Hoff relation. The calculated apparent activation energy of the methanol synthesis reaction and methanol dehydration reaction are 86.1 and 71.37 kJ/mol, respectively. Furthermore, slurry liquid (Hexadecane) affects the activity of the catalyst via interaction between liquid and adsorbed surface species and competitive adsorption of a solvent onto the catalyst carrier will reduce the reaction rate insignificantly.

Key words: Dimethyl ether, syngas, bi-functional catalyst, slurry reactor, kinetics model.

1. Introduction

Synthesis of new liquid fuel or other chemicals from coal or natural gas is becoming a hot research topic in many countries in recent years. Among those products, dimethyl ether (DME) is not only a clean fuel substituting for car and liquid petroleum gas (LPG) but also an excellent propellant and refrigerant. It is an important feedstock for the preparation of light alkenes too [1, 2].

At present, DME is commercially prepared by dehydration of methanol using acidic porous catalysts such as zeolites, silica-alumina, alumina, etc. Recently, an original technique named STD (synthesis gas to dimethyl ether) process was developed for the direct synthesis of DME from synthesis gas in a single reactor on bi-functional catalysts. The most common bi-functional catalysts reported in the literature for STD process are the physical mixture of the methanol synthesis catalyst and the solid acid catalyst. Among the solid acids used for methanol dehydration, H-ZSM-5 and γ-Al2O3 are the two catalysts that have been studied intensively both for academic and commercial purposes. Haldor-Topsoe has developed a bi-functional catalyst by the addition of H-ZSM-5 to the traditional CuO/ZnO/Al2O3 methanol synthesis catalyst. The main reactions in the STD process can be shown as follows [3]:

Methanol synthesis: \[ \text{CO} + 2\text{H}_2 \leftrightarrow \text{MeOH} -90.4 \text{ kJ/mol} \] (1)

Methanol dehydration: \[ 2\text{MeOH} \leftrightarrow \text{DME} +\text{H}_2\text{O} -41.0 \text{ kJ/mol} \] (2)

Water gas shift: \[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 +\text{H}_2 -23.0 \text{ kJ/mol} \] (3)

\[ 3\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{CO}_2 -258.312 \text{ kJ/mol} \] (4)

The research of direct DME synthesis is focused on
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the catalyst and the process at present, but in order to provide basic data for designing the reactor for plant or industry, the kinetics study of direct DME synthesis from syngas is necessary. Most of the kinetic studies reported in the literature were performed in fixed bed reactors because of their simplicity. However, better and more reliable kinetic data are available from tests made in slurry stirred tank reactors because of good temperature control that enables experiments at near isothermal conditions regardless of reaction heats and rates. Small catalyst particles can be used to eliminate intraparticle mass transfer effects. Slurry stirred tank reactors have come to common use for methanol and dimethyl ether synthesis studies [2, 4].

In comparison with the numerous studies which have been published for the gas-phase dimethyl ether synthesis from syngas [1, 2, 5], relatively few investigations have been published concerning the liquid-phase process [6, 7]. Although the mechanism of gas-phase catalytic hydrogenation of CO₂ and CO, accompanied by the water gas shift reaction (WGSR), and methanol dehydration has been reasonably well established, few reliable kinetic models can be found in the open literature.

The present study, investigates the steady state kinetics of single step DME synthesis on a CuO-ZnO-Al₂O₃/H-ZSM-5 catalyst in the slurry reactor. Moreover, the influences of different process parameters, such as pressure, temperature, H₂/CO ratio in feed gas are simulated by proposed kinetic models.

2. Experiments

2.1 Catalyst

Bi-functional catalyst (BFC) was prepared by admixing of the two catalysts, commercial methanol synthesis catalyst (manufactured by KMT Co.) and methanol dehydration catalyst (supplied by Süd-Chemie Co., sample No. 304 H/06), namely H-ZSM-5. Two commercial catalysts were finely milled and sieved to sizes less than 90 μm, and well mixed at mass ratio 3:1. This mass ratio obtained in our previous study [8]. Then the mixture was molded under pressure into tablets, which were then crushed and sieved to 90-120 mesh size particles in order to avoid pore diffusional limitations. The description in detail about characterization test of catalyst such as TPR, XRD, XRF and BET could be found elsewhere [8].

2.2 Experimental Set-up and Catalytic Tests

A schematic view of the laboratory scale setup is shown elsewhere [8]. In brief the reactants CO, H₂, and nitrogen as the internal standard were fed through a set of mass flow controllers and blended in a mixer. The mixture was preheated to the reaction temperature before entering into the reactor. The STD reaction was carried out in a 1 L mechanically agitated slurry reactor, in which 10.5 g of catalyst was suspended in 350 g of pure liquid paraffin (C₁₆H₃₄).

Before each kinetic test, the catalysts had been reduced with pure hydrogen at the normal pressure according the following heating program: heated from room temperature to 250 °C with heating rate 1°C/min and was kept for 6 h at this temperature. Then the catalysts were cooled to room temperature at the presence of hydrogen flow. After this pre-treatment, the feed (H₂: CO: N₂) was introduced into the slurry reactor. A small portion of the reactor effluent was sent to gas chromatograph (GC) for on line analysis. Varian CP-3800 gas chromatograph equipped with two packed columns: HaySep Q (80-100 mesh, 2m X 1/8” X 2.0 mm, SS), Chrompack Molecular Sieve 13X (80-100 mesh, 2m X 1/8” X 2.0 mm, SS) for separating CO₂, H₂, N₂, CO & MeOH, DME, CH₄ respectively and detecting by a thermal conductivity detector. Analysis of water content in exit stream showed that H₂O content was so small that it could not be detected. Then it was assumed that water-gas shift reaction in LPDME process is in equilibrium, because Cu-based methanol synthesis catalyst is really a good catalyst for water-gas shift reaction. Similar assumption was made bye other researchers [6, 9].
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The water partial pressure is calculated by following equation:

$$P_w = \frac{P_{CO_2}P_{H_2}}{P_{CO}K_{P,WGS}}$$

(5)

where $P_{H_2O}$, $P_{CO_2}$, $P_{H_2}$ and $P_{CO}$ are partial pressure (bar) of $H_2O$, $CO_2$, $H_2$ and $CO$ respectively; and $K_{P,WGS}$ is the equilibrium constant of water gas shift reaction.

2.3 Experimental Condition

The kinetic experiments were always carried out under steady-state condition. This state was achieved within 20 h from start up. Mass and heat transfer limitations were negligible during the experimental conditions chosen. At a 3 wt% slurry (corresponding to 10.5 g of catalyst per 350 g of solvent) in a mechanically agitated slurry reactor, the gas solid mass transfer dose not limit the overall rate. Also, in preliminary experiment it was checked for the intraparticle mass transfer limitation: above 1500 rpm of impeller speed, no mass transfer resistances were found. To assure that gas-liquid mass transfer limitations were absent, the experimental was carried out at 1,600 rpm.

In order to carry out kinetic modeling, a broad range of experimental conditions have been carried out under following reaction conditions: 200-240 °C, 20-50 bar, $H_2/CO$ molar ratio from 1:1 to 2:1 and space velocity of 1,100 mL/(gr-cat.hr) which is sufficiently far from equilibrium conditions. A subsequent paper on the subject of the effect of feed composition and space velocity on direct synthesis of dimethyl ether from syngas will be presented in the near future [8]. For each experiment the carbon balances over the reactor were calculated. The deviations were very small, usually less than 3%.

3. Simulation and Parameter Estimation

In three-phase dimethyl ether synthesis the overall kinetics are determined by the following steps:

- Mass-transfer from gas-phase to gas-liquid interface.
- Bulk liquid transport.
- Mass-transfer from liquid bulk to liquid-solid interface.
- Reaction and diffusion in the porous catalyst.

The reactants undergo Steps 1, 2, 3 and 4 in order to reach the catalyst where reaction and diffusion take place (Step 5). In practice, not all transport resistances are important. In this study experiments were designed such that all mass transfer resistances (including intra-particle diffusion limitations) were negligible. In the LPDME process, the real driving force for reactants should be the reactant concentration in liquid. But because of absence of mass transfer resistance, it may be assumed that the gas phase and the liquid phase to be in thermodynamic equilibrium. Then it would be logical to base the kinetic rate expression on partial fugacities [8]. However, preferred to in engineering calculations (e.g., material balances) it is use concentrations instead of fugacities. Therefore the gas-liquid solubilities of all components in direct synthesis of dimethyl ether from syngas in the slurry liquid (paraffin) are needed. The concentrations of reactants and products in the liquid phase were calculated by means of the Henry's law. The temperature dependence of the constant was accounted for by the exponential relation, $H = aexp(b/RT)$.

In the temperature range of interest in this study (210-260 °C) and for hexadecane as the solvent the Henry coefficients $a$ and $b$ for $CO$, $CO_2$, $H_2$, methanol and water were taken from Graaf, et al. [10] and for dimethyl ether from Song, et al. [11].

Several kinetic models for methanol synthesis and methanol dehydration in literature, from the screening result by other researcher, the model for methanol synthesis proposed by Graaf, et al., [12, 13] based on duel-site Langmuir-Hinselwood mechanism (on site 1 $CO$ and $CO_2$ adsorb competitively, while on site 2 $H_2$ and $H_2O$ adsorb competitively), and the
dehydration model proposed by Bercic, et al., [14] based on reaction of dissociatively adsorbed methanol, were selected for analysis and simulation of the STD process. The kinetic rate equations for methanol synthesis and dehydration were Eqs. (6) and (7):

\[
r_{\text{CO}_2 \text{hydrogenation}} : r_{M-2D} = \frac{k_i K_{f COH}^{\frac{2}{n} - C_{\text{COH}}}}{\left[1 + k_i K_{COH}^C + K_{C} + K_{D} C_{\text{D}} / K_{i \text{out}}^D \right]} \tag{6}
\]
\[
r_{\text{MeOH dehydration}} : r_D = \frac{k_i K_{f H}^2 (C_{\alpha}^2 - C_{\beta} C_{\alpha} / K_{i \text{out}}^H)}{\left(1 + 2(K_{C} C_{\alpha})^{1/2} + K_{C} C_{\alpha} \right)} \tag{7}
\]

where \( r_{\text{CO}_2 \text{hydrogenation}} \) is methanol equivalent productivity, the sum of methanol productivity and two time of DME productivity (\( r_M + 2D \)), and \( r_{\text{MeOH dehydration}} \) is DME productivity (\( r_D \)). The equilibrium constant for the three reaction (\( K_i \)) given by Wang et al. [15]:

\[
\log K_{f COH} = 13.814 + \frac{3478.7}{T} - 9.2833 \log T + 3.1475 \times 10^{-3} T - 4.2613 \times 10^{-7} T^2 \tag{8}
\]
\[
\log K_{f H} = \frac{2167}{T} - 0.5194 \log T + 1.037 \times 10^{-3} T - 2.33 \times 10^{-7} T^2 - 1.2777 \tag{9}
\]
\[
\ln K_{f COH} = 4.019 + 3.707 \log T - 2.783 \times 10^{-3} T + 3.8 \times 10^{-7} T^2 - 6.561 \times 10^{1} T^2 - 26.64 \tag{10}
\]

The simulation of dimethyl ether synthesis reaction was based on CSTR model. Because the reactor was back mixed, so the rate of formation or disappearance for the various spies could be calculated directly from the inlet and outlet composition and flow rate. So the experimental methanol equivalent productivity and DME productivity was calculated by the following equations:

\[
r_{M+2D} = \frac{F_{out} \times (y_{\text{MeOH}} + 2y_{\text{DME}})}{W} \tag{11}
\]
\[
r_D = \frac{F_{out} \times y_{\text{DME}}}{W} \tag{12}
\]

With knowing that nitrogen was not participate in any reactions of STD process, the outlet flow rate obtained from \( N_2 \) balance:

\[
F_{in} \times y_{N_2,in} = F_{out} \times y_{N_2,out} \tag{13}
\]

Parameter estimation was based on the minimization of the following objective function:

\[
OF = \sum_{i=1}^{N} w_i \left( \frac{r_i^{\text{EXP}} - r_i^{\text{CAL}}}{r_i^{\text{EXP}}} \right)^2 \tag{14}
\]

Where \( N \) is the total number of experiments and \( w_i \) stands for the weight factor for response \( i \). The latter was set proportional to \( 1/r_i^{\text{EXP}} \), because relative experimental errors are approximately the same for all experimental points over whole range of experimental conditions. Minimization of this objective function made use of simplex method [16].

3. Results and Discussion

3.1 Kinetic Parameters

Three sets of kinetic parameters were obtained for three different temperatures. To establish the kinetic parameters as a function of temperature, the following equation was used:

\[
k_i(T) = A_i \exp(-B_i / RT) \tag{15}
\]

where \( k_i \) denotes a model parameter, \( A_i \) is the pre-exponential factor, and \( B_i \) is the activation energy for a rate constant or heat of adsorption for adsorption equilibrium constant and then \( B_i < 0 \). By following the previously described methodology, the parameters of the proposed kinetics model, with a 95% confidence interval, are given by the following equations.

For methanol synthesis:

\[
k_1 = 47691 \exp\left(\frac{-86099.78}{RT}\right) \tag{16}
\]
\[
K_{CO} = 2 \times 10^{-4} \exp\left(\frac{35343.645}{RT}\right) \tag{17}
\]
\[
K_{COH} = 4 \times 10^{-7} \exp\left(\frac{36912.18}{RT}\right) \tag{18}
\]
\[
K_{H_2O} / K_{H_2}^{0.5} = 2 \times 10^{-11} \exp\left(\frac{9850.27}{RT}\right) \tag{19}
\]

For methanol dehydration:

\[
k_2 = 874575 \exp\left(\frac{-71375.65}{RT}\right) \tag{20}
\]
\[
K_M = 3 \times 10^{-4} \exp\left(\frac{16495.81}{RT}\right) \tag{21}
\]
\[
K_M = 6 \times 10^{-7} \exp\left(\frac{31796.89}{RT}\right) \tag{22}
\]
The Arrhenius plots for the rate constants are presented in Fig. 2 as a function of temperature, whereas the Van’t Hoff relationships for equilibrium constants are shown in Figs. 3 and 4 as a function of temperature. Symbols represent the experimental results and lines model predictions. The good linearity confirms the validity of Eq. (15). Parity plots of the observed and calculated reaction rates for methanol synthesis and dehydration are presented in Fig. 5 and 6. Note that a majority of rate data lies in ± 15% region. These figures clearly show the excellent agreement between model calculations and experimental in whole range of operating conditions. According to these kinetic modeling results, the apparent activation energies for the direct DME synthesis from syngas on CuO-ZnO-Al2O3/H-ZSM-5 in slurry phase are derived from the slope of the straight lines of Arrhenius plot through linear fitting. Activation energy estimates of 86.1 and 71.37 kJ/mol are found for the methanol synthesis and dehydration reactions, respectively. In comparison to gas phase process [7], paraffin solvent reduced the activation energy. This indicates that the solvent increases the rate of the rate determining step [17]. It can be seen that the influence of the temperature differs between the two- and three-phase systems. From a literature review concerning the influence of a liquid-phase on the heterogeneous reaction kinetics in general, we conclude:

Competitive adsorption of a liquid on active catalytic sites will reduce the reaction rates [17].

The liquid can interact with weakly adsorbed surface species and can either increase or decrease the reaction rate in comparison with the vapor phase reaction [17].

The adsorption enthalpies for the CO, CO2, methanol and water, evaluated from Figs. 3 and 4, are lower than to the corresponding components in gas-phase process [7]. Lower values found in this work maybe attributed to the presence of the liquid-phase.
4. Conclusions

A kinetic model for the LPDME process over a CuO-ZnO-Al₂O₃/H-ZSM-5 catalyst based on a methanol synthesis model proposed by Graaf et al and a dehydration model by Bercic and Levec was found to agree well with experimental results over a wide range of experimental conditions. The kinetic parameters were determined as function of the temperature between 200 and 240 °C. The performance of the syngas-to DME reaction system was determined by kinetics model. The calculated apparent activation energy of methanol synthesis reaction and methanol dehydration reaction are 86.1 and 71.37 kJ/mol, respectively. Slurry reactors were introduced to provide a good solution for temperature control and to avoid pore diffusion by using a liquid and very fine catalyst particles. Furthermore, slurry liquid (Hexadecane) affects the activity of the catalyst via interaction between liquid and adsorbed surface species and competitive adsorption of a solvent onto the catalyst carrier will reduce the reaction rate insignificantly.

References


