

# A Comparative Study on the Thermodynamics of Dimethyl Ether Synthesis from CO Hydrogenation and CO<sub>2</sub> Hydrogenation

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The effects of temperature, pressure, and the initial composition of feed gas on the synthesis of dimethyl ether from CO hydrogenation and from CO<sub>2</sub> hydrogenation are investigated in a wide range of reaction conditions. By the detailed contrast between the dimethyl ether synthesis process from CO hydrogenation and that from CO<sub>2</sub> hydrogenation, it is seen that the former holds an advantage over the latter because of outstanding synergic effects. On the basis of the observation of the transition processes by adding CO<sub>2</sub> into the CO hydrogenation system through two different ways, it has been found that there are two kinds of critical states in which the equilibrium conversions of CO and CO<sub>2</sub> reach zero. After many critical states in the whole triangle region composed of the feed concentrations of CO, CO<sub>2</sub>, and H<sub>2</sub> are obtained, the dimethyl ether synthesis process is divided into three parts: CO hydrogenation, CO<sub>2</sub> hydrogenation, and parallel hydrogenation of CO and CO<sub>2</sub>.

## 1. Introduction

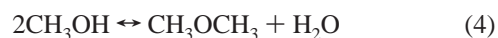
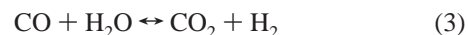
Dimethyl ether (DME) has been known as an ultraclean fuel which can be used in diesel engines, households, power generation, and for other purposes.<sup>1,2</sup> Due to the huge market potential, the research on dimethyl ether synthesis<sup>3,4</sup> and its utilization<sup>5,6</sup> have been attracting more and more interests. Nowadays, DME is produced mainly from syngas containing CO and H<sub>2</sub> through methanol (MeOH) synthesis and methanol dehydration, known as the two-step process. When the two processes take place simultaneously within one reactor using a composite catalyst, namely, the one-step process, a higher once-through conversion can be obtained due to the synergic effect.<sup>7,8</sup> Although most researchers believe that the dimethyl ether synthesis process is controlled by the kinetics<sup>9,10</sup> rather than by thermodynamics, a comprehensive thermodynamic analysis on this process is essential for understanding of its intrinsic characteristics. There is much literature reporting the thermodynamic behavior of dimethyl ether synthesis either from CO hydrogenation<sup>11–13</sup> or from CO<sub>2</sub> hydrogenation,<sup>14–16</sup> however, few papers which cover the two processes simultaneously and make a comprehensive thermodynamic comparison between them are found.<sup>17</sup>

In this paper, the effects of a wide range of temperature, pressure, and the initial composition of the feed gas on the dimethyl ether synthesis from CO hydrogenation and CO<sub>2</sub> hydrogenation are investigated. Although the equilibrium conversion of the feed gas for DME synthesis is very high,<sup>18</sup> it is needed to recycle the unconverted syngas in the industrial process to obtain higher overall conversion. Thus, the recycled gas containing a higher level of CO<sub>2</sub> and unconverted syngas is mixed with the fresh syngas and fed into the synthesis reactor. In this case, the real reaction conditions, especially the composition of the feed gas, are significantly different from the fresh syngas. The role that CO<sub>2</sub> plays in the reaction process cannot be ignored. In this paper, the intrinsic relation between CO hydrogenation and CO<sub>2</sub> hydrogenation were studied by adding different amount of

CO<sub>2</sub> into the system of dimethyl ether synthesis from CO hydrogenation.

## 2. Theoretical Analysis

**2.1. The Definition of Different Reaction Systems and Corresponding Parameters.** For whichever of three synthesis approaches of dimethyl ether, CO hydrogenation, CO hydrogenation, or parallel hydrogenation of CO and CO<sub>2</sub>, there are always four reactions involved in the dimethyl ether synthesis process:



By phase law, the number of independent reactions in the dimethyl ether synthesis process is three. Therefore, by selecting any one of the following three reaction systems, 1 + 2 + 4, 1 + 3 + 4, or 2 + 3 + 4, the same effluent composition can be obtained on thermodynamics. In this paper, the 1 + 3 + 4 system is used for the thermodynamic calculation of the dimethyl ether synthesis.

The conversion, selectivity, yield, and effluence composition at the equilibrium state, respectively, are given as the following formulas:

$$\frac{F_{0y_{\text{CO}_x^0}} - Fy_{\text{CO}_x}}{Fy_{\text{CO}_x}} \quad (\text{CO}_x \text{ as reactant}) \quad (5)$$

$$S_i = \frac{n(Fy_i)}{F_{0y_{\text{CO}_x^0}} - Fy_{\text{CO}_x}} \quad (\text{CO}_x \text{ as reactant, } n \text{ is number of carbon atoms in product } i) \quad (6)$$

$$Yd_i = C_{\text{CO}_x} S_i \quad (\text{CO}_x \text{ as reactant, } i = \text{product}) \quad (7)$$

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For the conversions of the methanol dehydration reaction and the water/gas shift reaction,

$$C_{\text{MeOH}} = \frac{2y_{\text{DME}}}{y_{\text{MeOH}} + 2y_{\text{DME}}} \quad (8)$$

$$C_{\text{H}_2\text{O}} = \frac{y_{\text{CO}_2}}{y_{\text{H}_2\text{O}} + y_{\text{CO}_2}} \quad (9)$$

Because the above formulas cover the different hydrogenation processes, the definition of  $\text{CO}_x$  as reactant or product changes with the hydrogenation reaction. The exact state is as follows: when dimethyl ether synthesis from  $\text{CO} + \text{H}_2$  proceeds,  $\text{CO}_2$  is considered as the product. When synthesis from  $\text{CO}_2 + \text{H}_2$  results,  $\text{CO}$  is considered as the product, and when the parallel hydrogenation processes result, both  $\text{CO}$  and  $\text{CO}_2$  are considered as the reactants, rather than products.

**2.2 Calculation of the Fugacity Coefficients.** The Soave–Redlich–Kwong (SRK) equation of state<sup>19</sup> is adopted to calculate the fugacity coefficients of all compositions in the dimethyl ether synthesis and methanol synthesis.

The SRK equation of state is

$$P = \frac{R_g T}{V - b} - \frac{a}{V(V - b)} \quad (10)$$

The fugacity coefficients can be calculated from another expression as

$$\ln \varphi_i = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{B} \left( 2 \frac{a_i^{0.5}}{a^{0.5}} - \frac{b_i}{b} \right) \ln \left( 1 + \frac{B}{Z} \right) \quad (11)$$

where

$$A = \frac{a_i P}{R_g^2 T^2}$$

$$B = \frac{b_i P}{R_g T}$$

$$Z = \frac{PV}{R_g T}$$

The parameters in this equation were evaluated using the original mixing rules with interaction coefficients

$$a = \sum_i \sum_j (y_i y_j a_{ij}) \quad a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij}) \quad b = \sum_i y_i b_i$$

Due to a lack of experimental data, all  $k_{ij}$  are set equal to 0; however, considering the presence of a typical quantum gas, hydrogen, the coefficient  $\alpha_{\text{H}_2}$  should be corrected using the formula<sup>20</sup>

$$\alpha_{\text{H}_2} = 1.202 \exp(-0.30288T/T_c) \quad (12)$$

**2.3. Equilibrium Constants of the Corresponding Reactions.** There is a relation between the equilibrium constant calculated as fugacity and that as pressure.

$$K_f = K_\varphi K_p \quad (13)$$

**Table 1. Equilibrium Constants of Four Reactions Obtained by Equilibrium Calculator and Regression Coefficients**

$T/K$ and $M, N$	$K_{p,1}, \text{bar}^{-2}$	$K_{p,2}, \text{bar}^{-2}$	$K_{p,3}$	$K_{p,4}$
473	$2.25 \times 10^{-2}$	$9.92 \times 10^{-5}$	227.000	5.145
498	$6.63 \times 10^{-3}$	$4.89 \times 10^{-5}$	135.516	4.456
523	$2.11 \times 10^{-3}$	$2.45 \times 10^{-5}$	86.102	3.959
548	$7.44 \times 10^{-4}$	$1.30 \times 10^{-5}$	57.017	3.555
573	$2.88 \times 10^{-4}$	$7.35 \times 10^{-6}$	39.140	3.231
M	$1.79 \times 10^{59}$	$2.97 \times 10^{32}$	$6.76 \times 10^{26}$	$1.486 \times 10^7$
N	-22.772	-13.634	-9.153	-2.417
R <sup>2</sup>	0.9995	0.9997	0.9989	0.9974

On the basis of eqs 11 and 13, the  $K_f$ , equilibrium constants as fugacity, are dependent on the temperature, pressure, and composition at the equilibrium state. However, in view of the trouble in the iterative calculation,  $K_p$  commonly takes the place of  $K_f$ .<sup>21</sup> Although there are many types of expressions for the  $K_p$  of reactions 1–4,<sup>22,23</sup> considering the consistency of the equilibrium constants, all of them are obtained by Equilibrium Calculator, a noncommercial software program by Dr. Yamazaki. The results of the calculation and the regression coefficients of the power function ( $K_p = mT^n$ ) are shown in Table 1.

**2.4. Calculation of Thermodynamic Equilibrium.** The flow velocity ratio of input to output in the system can be calculated by the characteristic of the reaction system,

$$R = F_0/F = 1 + 2y_{\text{MeOH}} + 4y_{\text{DME}} \quad (14)$$

Dimethyl ether, methanol, and carbon dioxide are considered as the three independent components in the effluent; the others can be got by the balance equations of C, H, and O.

While the DME synthesis process arrives at equilibrium, the three reactions arrive at the equilibrium state simultaneously:

$$K_{f,1} = \frac{f_{\text{MeOH}}}{f_{\text{CO}} f_{\text{H}_2}} \quad (15)$$

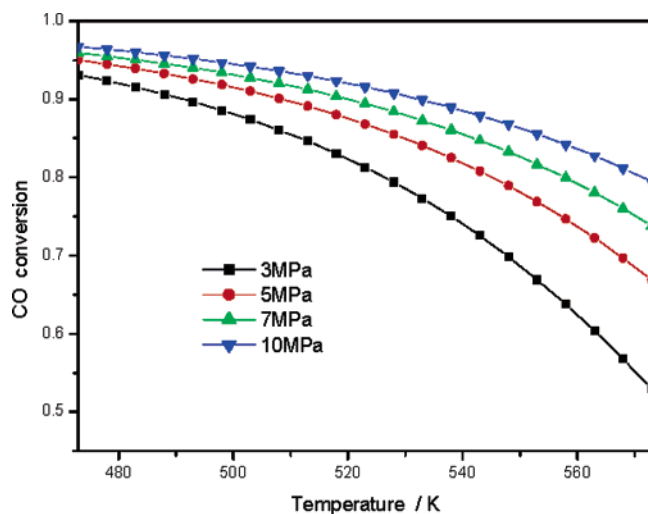
$$K_{f,3} = \frac{f_{\text{CO}} f_{\text{H}_2\text{O}}}{f_{\text{CO}_2} f_{\text{H}_2}} \quad (16)$$

$$K_{f,4} = \frac{f_{\text{DME}} f_{\text{H}_2\text{O}}}{f_{\text{MeOH}}^2} \quad (17)$$

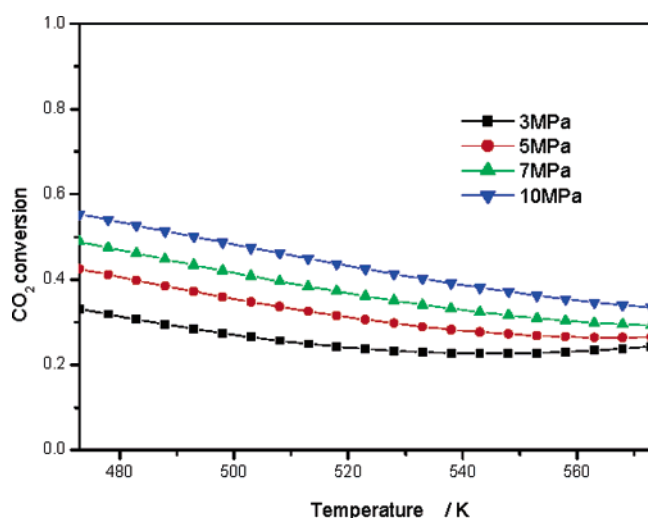
Gauss–Newton arithmetic is introduced to solve the above nonlinear equation group, and the original values of three independent components ranging from 0 to 1 are given randomly by Rand function in the MATLAB program. The error is less than  $10^{-6}$ . After the three solutions are obtained, the conversion, selectivity, and yield at the equilibrium state are resolved by the combination of eqs 5, 6, and 7 with the balanced equations of the three elements.

### 3. Results and Discussion

**3.1. Influences of Temperature and Pressure on Dimethyl Ether Synthesis.** The influences of temperature and pressure on dimethyl ether synthesis both from  $\text{CO}$  hydrogenation and from  $\text{CO}_2$  hydrogenation were investigated at 3–10 MPa and 473–573 K. In the two hydrogenation processes, the  $1\text{CO}/1\text{H}_2$  feed was used for the former and the  $1\text{CO}_2/3\text{H}_2$  feed was employed for the latter. The equilibrium conversions of carbon



**Figure 1.** Influences of temperature and pressure on equilibrium conversion; initial  $\text{CO}/\text{H}_2 = 1:1$ .

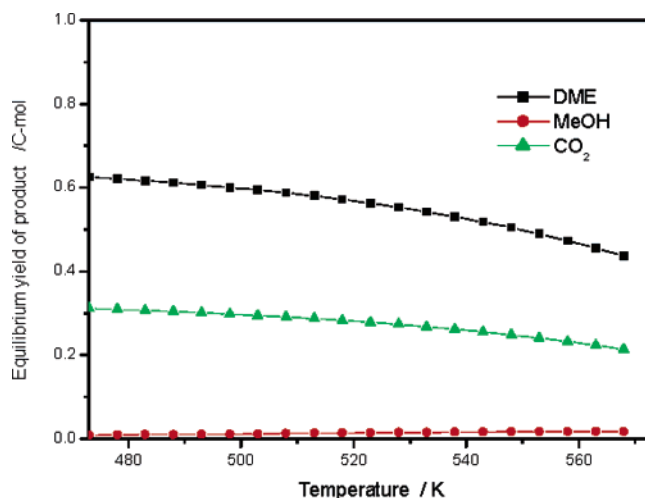


**Figure 2.** Influences of temperature and pressure on equilibrium conversion; initial  $\text{CO}_2/\text{H}_2 = 1:3$ .

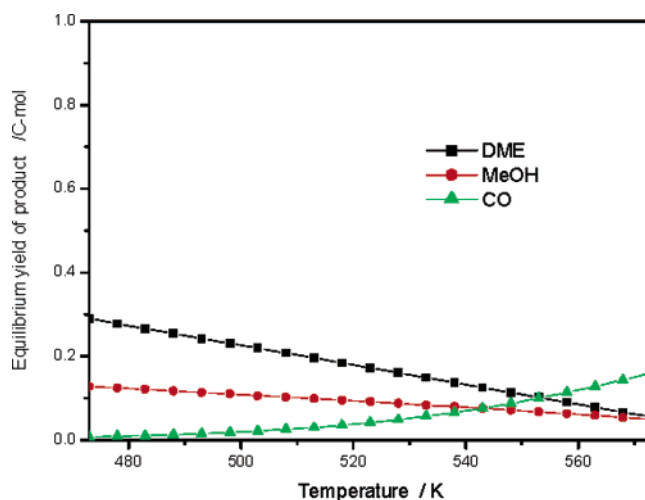
oxides and yields in the two processes are demonstrated in Figures 1–4, respectively.

It is found from Figures 1 and 2 that for the CO hydrogenation process, the equilibrium conversion of CO declines gradually with an increase in temperature because all of the involved reactions—methanol synthesis reactions from CO hydrogenation, the water/gas shift reaction, and the methanol dehydration reaction—are exothermic reactions. For the  $\text{CO}_2$  hydrogenation process, however, the equilibrium conversion of  $\text{CO}_2$  shows different changes at different pressure when the temperature increases. As a general understanding, dimethyl ether synthesis processes from  $\text{CO}_2$  hydrogenation consists of three reactions:  $\text{CO}_2$  hydrogenation to methanol, methanol dehydration to DME, and reversed water/gas shift reaction. Because the last one is an endothermic reaction which prefers high temperature, resulting in high  $\text{CO}_2$  conversion at low pressure. When the pressure increases to a certain degree (7 MPa and 10 MPa in Figure 2), the first reaction,  $\text{CO}_2$  hydrogenation to methanol, is controlled by the high pressure because it is a molar decreasing reaction. The general temperature effect does not appear at the study range.

From Figures 1 and 2, it is confirmed that when the pressure increases, there is an improvement in equilibrium conversion for the two processes over the whole range of temperatures.



**Figure 3.** Effects of temperature on equilibrium yields; initial  $\text{CO}/\text{H}_2 = 1:1$ .



**Figure 4.** Effects of temperature on equilibrium yields; initial  $\text{CO}_2/\text{H}_2 = 1:3$ .

However, the difference between them lies that the elevated ranges with pressure are different in the different temperature regions. For CO hydrogenation, the equilibrium conversion promoted by pressure is enhanced with the increase in temperature. For the  $\text{CO}_2$  hydrogenating process, the results are just the opposite.

To explore this in further detail, the difference between the two processes at 5 MPa, the temperature-dependent equilibrium yields of oxygenates and carbon oxides in the dimethyl ether synthesis from both CO hydrogenation and  $\text{CO}_2$  hydrogenation are illustrated in Figures 3 and 4, respectively.

As can be seen from a comparison between Figures 3 and 4, CO hydrogenation proceeds at a higher equilibrium yield of DME than  $\text{CO}_2$  hydrogenation at the cost of the formation of excess  $\text{CO}_2$  over the whole temperature region. For the  $\text{CO}_2$  hydrogenation process, however, a small amount of CO is formed at low temperature, while the equilibrium yield of CO improves rapidly and even exceeds enormously the equilibrium yield of DME at high temperature with rising temperature. On the basis of the above facts, it can be concluded that provided that the excess  $\text{CO}_2$  can be separated inexpensively from the effluent, the CO hydrogenation suits the production of DME from the CO-rich syngas.<sup>24</sup> However, for the  $\text{CO}_2$  hydrogenating process, it is well suited for the production of the mixture of DME and methanol at low temperature because both of them merely occupy small portions of the effluent.<sup>25</sup>

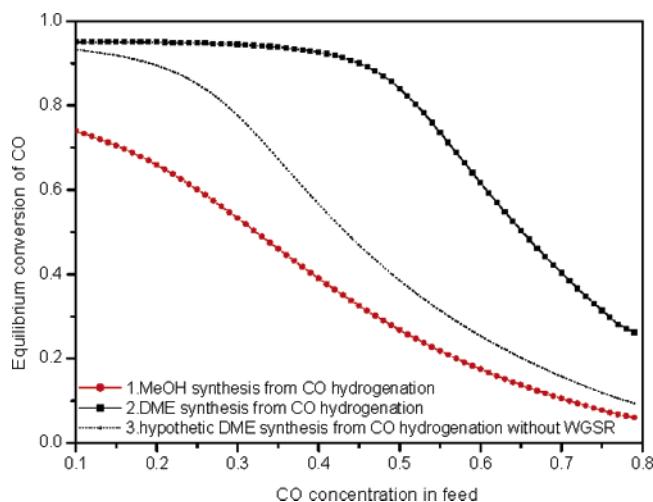


Figure 5. Dependence of the equilibrium conversion of CO on feed composition; 5 MPa, 533 K.

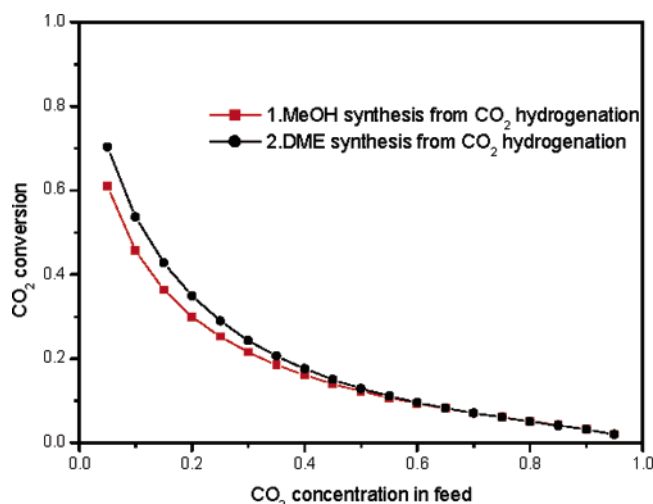


Figure 6. Dependence of the equilibrium conversion of CO<sub>2</sub> on feed composition; 5 MPa, 533 K.

**3.2. Influence of the Feed Gas Composition.** The effects of the feed gas composition on dimethyl ether synthesis both from CO hydrogenation and from CO<sub>2</sub> hydrogenation are investigated in a wide composition range at 5 MPa and 533 K. The effects of the feed composition on the synthesis processes of dimethyl ether and methanol both from CO hydrogenation and from CO<sub>2</sub> hydrogenation are demonstrated in Figures 5 and 6, respectively.

Figure 5 shows that the equilibrium conversion of CO in dimethyl ether synthesis from CO hydrogenation is higher than that in the methanol synthesis from CO hydrogenation in the whole region and that the gap between DME synthesis and MeOH synthesis reaches the maximum when the CO concentration in the feed reaches 0.50. It is underlined that the dashed line in Figure 5 represents the hypothesis state of the dimethyl ether synthesis from CO hydrogenation without the water/gas shift reaction. The contribution of the two reactions on the equilibrium conversion can be divided by this dashed line. For the CO<sub>2</sub> hydrogenation process, there is a little improvement in the equilibrium conversion of CO<sub>2</sub> in the dimethyl ether synthesis which promoted by the synergic effect between methanol formation and methanol dehydration.

Compared with the equilibrium conversion, the term of equilibrium yield of the desired product can better describe the advantage and disadvantage of the given process. Figures 7 and

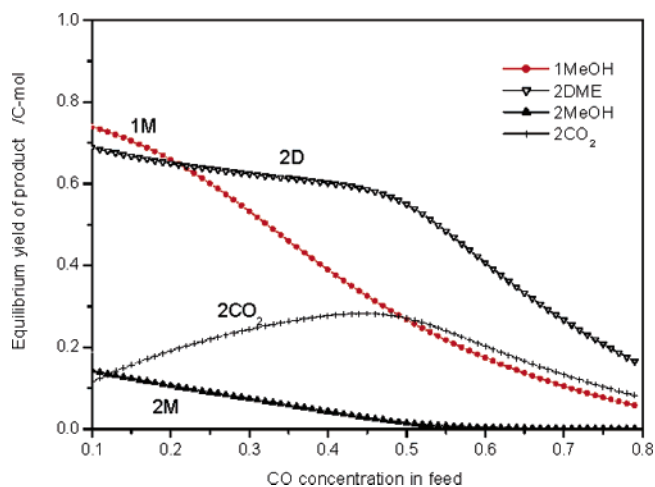


Figure 7. Effect of CO concentration in feed on equilibrium yields of oxygenates in DME synthesis and MeOH synthesis; 5 MPa, 533 K.

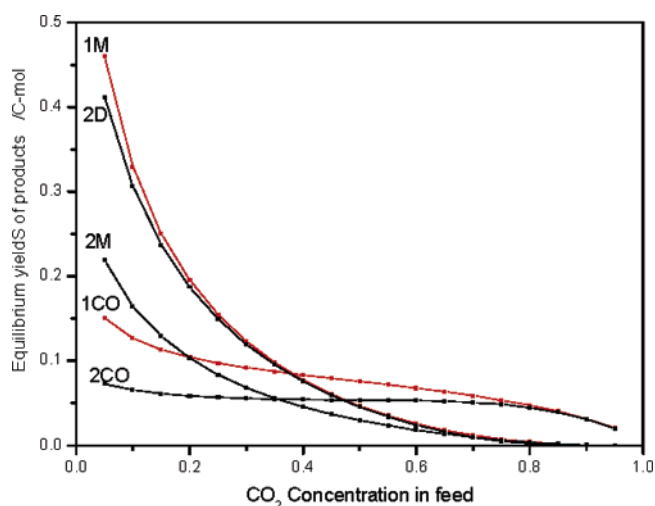


Figure 8. Effect of CO<sub>2</sub> concentration in feed on equilibrium yields of oxygenates in DME synthesis and MeOH synthesis; 5 MPa, 533 K.

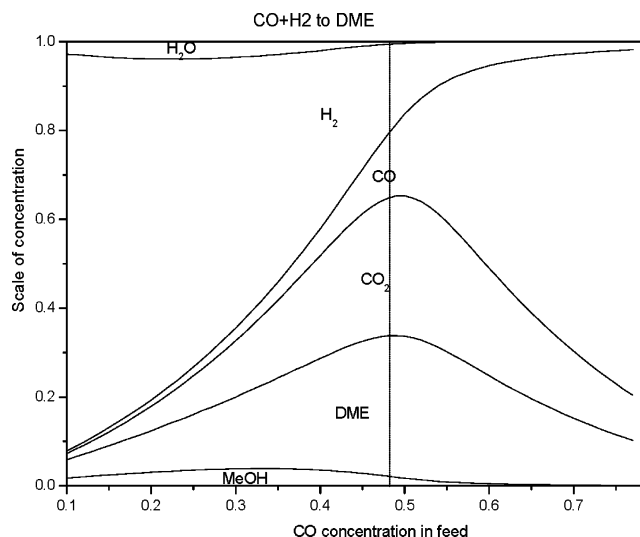
8 exhibit in detail the change of the equilibrium yields of oxygenates with the feed composition.

As can be seen, over the whole range, dimethyl ether synthesis from CO hydrogenation can obtain a much higher equilibrium yield of the desired product than methanol synthesis. However, the formation of excess CO<sub>2</sub> is disadvantageous for the high-efficiency utilization of the carbon atom in syngas. For the CO<sub>2</sub> hydrogenation process, the equilibrium yield of dimethyl ether approaches the equilibrium yield of methanol in the corresponding methanol synthesis. Based on the above analysis, it is believed that the dimethyl ether synthesis from CO<sub>2</sub> hydrogenation has no more advantage than the corresponding methanol synthesis.

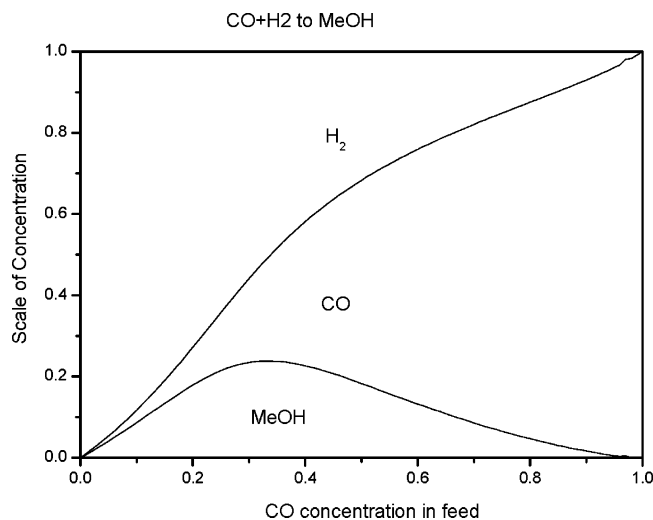
It is found from the two figures that the formation of a large amount of non-dimethyl ether composition is unfavorable for the purification and separation of the products. To go further into the disadvantages, it is essential to investigate the change of the equilibrium composition in a possibly wide range. The results both in dimethyl ether synthesis and in methanol synthesis from the two hydrogenation processes are demonstrated in Figures 9–12, respectively. In these figures, the distances between the two adjacent lines along the ordinates represent the concentration of a certain component in the effluent at the equilibrium state.

The advantages and disadvantages of the two hydrogenation processes can be observed distinctly from the comparison of

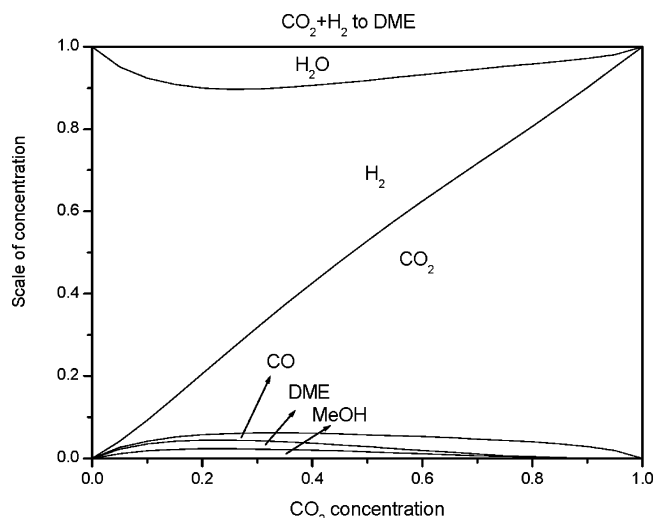




**Figure 9.** Effect of CO concentration in feed on the equilibrium composition in DME synthesis; 5 MPa, 533 K.

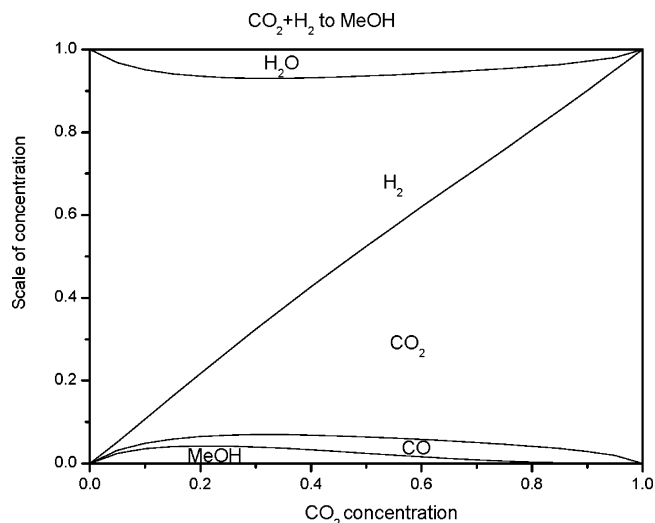


**Figure 10.** Effect of CO concentration in feed on the equilibrium composition in MeOH synthesis; 5 MPa, 533 K.



**Figure 11.** Effect of CO<sub>2</sub> concentration in feed on the equilibrium composition in DME synthesis; 5 MPa, 533 K.

the four figures of equilibrium composition. For dimethyl ether synthesis from CO hydrogenation, due to the synergic effects derived from methanol dehydration and the water/gas shift



**Figure 12.** Effect of CO<sub>2</sub> concentration in feed on the equilibrium composition in MeOH synthesis; 5 MPa, 533 K.

reaction, when the ratio of H<sub>2</sub> to CO is 1:1, the concentration of dimethyl ether in the effluent exceeds 0.3. However, for the CO<sub>2</sub> hydrogenation processes, the total concentration of dimethyl ether, methanol, and CO is not higher than 10%, while the water concentration in the effluent exceeds 0.1.<sup>26, 27</sup> This indicates that for dimethyl ether synthesis, the CO hydrogenation process has a great advantage over the CO<sub>2</sub> hydrogenation process. Because of the formation of excess carbon oxide and water, both of them have the problems of separation and purification.

**3.3. Division of the Different Hydrogenation on Thermodynamics.** In addition to CO and H<sub>2</sub>, the commercial syngas contains a certain content of CO<sub>2</sub>. For example, in the known Texaco and BGC-Lurgi syngas, the concentration of CO<sub>2</sub> approaches 13–16%.<sup>28</sup> To investigate the complex process in the coexistence of CO and CO<sub>2</sub> on thermodynamics, a gradual change from one hydrogenation process to the other can be realized by adding CO<sub>2</sub> into the CO hydrogenation process. There are two typical ways of adding CO<sub>2</sub>. One is by regulating the ratio of CO<sub>2</sub> to CO at a constant concentration of H<sub>2</sub>, namely, a replacement-type addition. The other is by adding CO<sub>2</sub> directly at a constant CO/H<sub>2</sub> ratio, namely, a dilution-type addition. The conversion profiles of dimethyl ether synthesis and methanol synthesis are demonstrated in Figures 13–16, respectively.

Figure 13 shows the transition process of DME synthesis from CO hydrogenation to CO<sub>2</sub> hydrogenation as the replacement-type process. The equilibrium conversion of CO undergoes a gradual change from positive to negative, while that of CO<sub>2</sub> comes through the reversed process with an increase in CO<sub>2</sub> concentration. It is worth noting that there are two critical points (designated as *a* and *b*) in the whole region, where the equilibrium conversions of carbon oxides are zero. At *a*, the equilibrium conversion of CO<sub>2</sub> is zero. In other words, the input of CO<sub>2</sub> equals the output of CO<sub>2</sub>, and the water/gas shift stops the thermodynamics. At *b*, the equilibrium conversion of CO arrives at zero, and CO can be considered an inert gas in the reaction.

The change of carbon oxide conversions with the addition of CO<sub>2</sub> to the methanol synthesis system from CO + H<sub>2</sub> as the replacement-type process is demonstrated in Figure 14. Different from the profile of CO<sub>2</sub> conversion in dimethyl ether synthesis, when CO<sub>2</sub> is added to the methanol synthesis system, CO<sub>2</sub> and CO participate simultaneously in the synthesis of methanol. With the rise of CO<sub>2</sub> concentration in the feed, CO conversion decreases gradually while the trend of CO<sub>2</sub> conversion is the

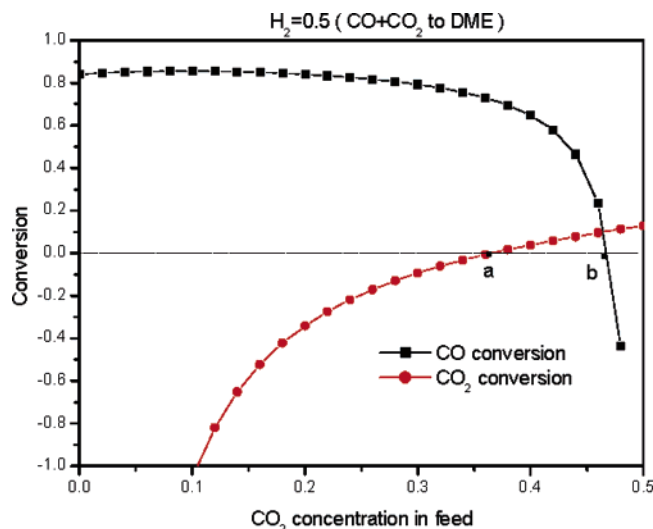


Figure 13. Transition of DME synthesis from CO hydrogenation to CO<sub>2</sub> hydrogenation at constant concentration of H<sub>2</sub>; 5 MPa, 533 K.

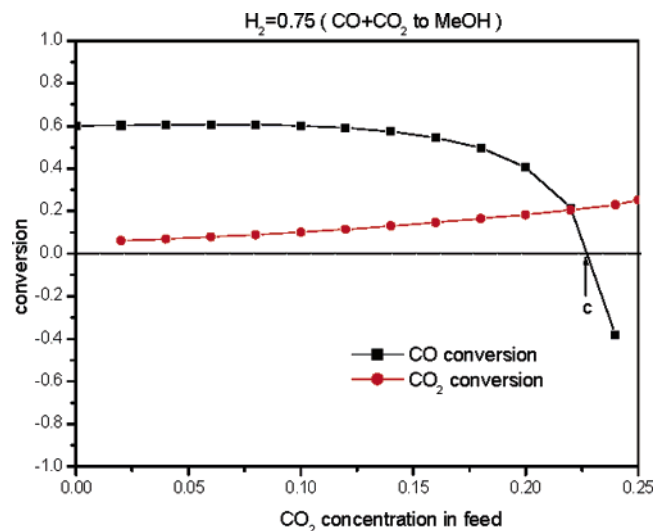


Figure 14. Transition of MeOH synthesis from CO hydrogenation to CO<sub>2</sub> hydrogenation at constant concentration of H<sub>2</sub>; 5 MPa, 533 K.

opposite. When the CO<sub>2</sub> concentration in the feed arrives at a certain value, *c*, the CO conversion goes to zero. This critical point is considered not only as the termination of the CO hydrogenation reaction but also as the start of the reversed water/gas shift reaction. When the CO<sub>2</sub> concentration in the feed exceeds *c*, CO will be formed through the reversed water/gas shift reaction.

The gradual change of carbon oxide conversions when CO<sub>2</sub> is added into the dimethyl synthesis system and the methanol synthesis system as the dilution-type process is demonstrated in Figures 15 and 16. The two profiles are similar to those as the replacement-type process. However, it can be found on the basis of a careful comparison that only when the CO<sub>2</sub> concentration in the feed arrives at a higher value CO<sub>2</sub> can be converted partly to dimethyl ether. Otherwise, CO<sub>2</sub> can be accumulated but not converted to any product. Therefore, the idea of reducing the emission of an excess of CO<sub>2</sub> derived from the dimethyl ether synthesis from CO + H<sub>2</sub> by means of recycling of the unconverted syngas containing CO<sub>2</sub> is impractical. The excess CO<sub>2</sub> must be separated from the system by some other means.<sup>24</sup>

Although by adding CO<sub>2</sub> into the system of methanol synthesis from CO + H<sub>2</sub> in the dilution-type process CO<sub>2</sub> can be converted to methanol, the equilibrium conversion of CO<sub>2</sub>

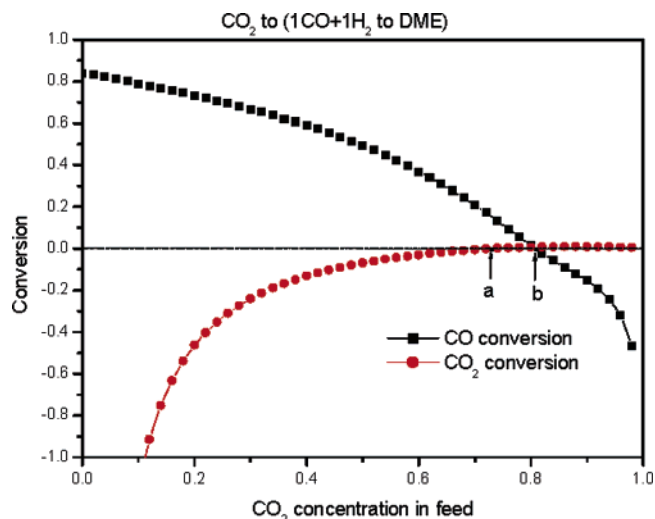


Figure 15. Transition of DME synthesis from CO hydrogenation to CO<sub>2</sub> hydrogenation at constant ratio of H<sub>2</sub> to CO; 5 MPa, 533 K.

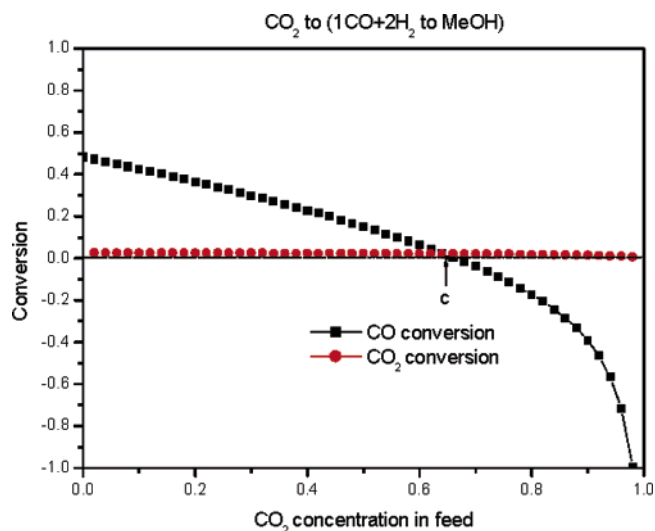


Figure 16. Transition of MeOH synthesis from CO hydrogenation to CO<sub>2</sub> hydrogenation at constant ratio of H<sub>2</sub> to CO; 5 MPa, 533 K.

is very low due to the relative lack of hydrogen in the system. Therefore, the excess CO<sub>2</sub> does not contribute to CO hydrogenation to methanol in a practical process. As the carbon resource, CO<sub>2</sub> should be reformed with natural gas, coal bed methane, coke oven gas, biosyngas, and other methane-containing gas feedstocks to produce synthesis gas with the proper H<sub>2</sub>/CO ratio instead of adding it to the CO hydrogenation system.<sup>29–31</sup>

It is also found from the two transition processes of CO hydrogenation to CO<sub>2</sub> hydrogenation that the profiles of carbon oxide conversions demonstrate the same rules of gradual change. In view of the presence of three points (*a*, *b*, *c* in Figures 13–16), those points can be searched by the dichotomy method, provided that the hydrogen concentration in the feed is given. Linking those points, it is possible to divide the scopes of different hydrogenation processes on the triangle region consisting of CO, CO<sub>2</sub>, and H<sub>2</sub>.

By the searching for and linking those points at the different feed concentrations of hydrogen at 10% intervals, the scopes of different hydrogenation processes both in dimethyl ether synthesis and in methanol synthesis are divided. The results of the two processes are given in Figure 17 and 18, respectively.

It is clear from the two figures that in dimethyl ether synthesis, the gradual change from CO hydrogenation to CO<sub>2</sub> hydrogenation

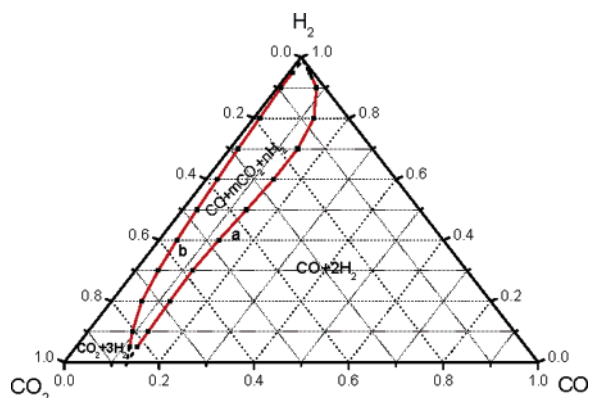


Figure 17. Division of  $\text{CO}_x$  hydrogenation in DME synthesis on thermodynamics; 5 MPa, 533 K.

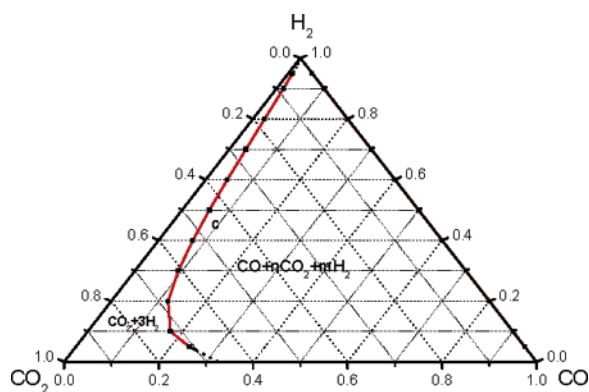


Figure 18. Division of  $\text{CO}_x$  hydrogenation in MeOH synthesis on thermodynamics; 5 MPa, 533 K.

tion covers three processes, the CO hydrogenating process, the parallel hydrogenation process of carbon oxides, and the  $\text{CO}_2$  hydrogenation process. However, for the methanol synthesis process, because it is impossible that the CO hydrogenation reaction and water/gas shift reaction take place simultaneously under the conditions of no  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the feed, the gradual change covers the last two of the three processes.

On the basis of the comparison between the two figures, it is found that because of the addition of the methanol dehydration reaction and the water/gas shift reaction, the CO hydrogenation process takes up the larger area in dimethyl ether synthesis. However, in methanol synthesis, the parallel hydrogenation of carbon oxide occupies a majority of the scope.

## Conclusions

1. Because the direction of the water/gas shift reaction in dimethyl ether synthesis from the CO hydrogenation process as well as in the  $\text{CO}_2$  hydrogenation process is reversed, the equilibrium conversion in the former declines much more rapidly with the temperature increases, whereas that in the latter decreases slowly, although it increases slightly at the low pressure and high temperature.

2. Although the dimethyl ether synthesis process from CO hydrogenation can obtain a higher equilibrium conversion and yield, the formation of  $\text{CO}_2$  is unfavorable from the point view of the efficiency of carbon utilization.

3. Dimethyl ether synthesis from  $\text{CO}_2$  hydrogenation has no advantage when compared to methanol synthesis. If CO and  $\text{H}_2\text{O}$  can be separated from the reaction system to obtain a higher driving force, the  $\text{CO}_2$  hydrogenation process is suitable to produce a mixture of DME and methanol at low temperature.

4. With an increase in  $\text{CO}_2$  concentration in the feed, dimethyl ether synthesis gradually shifts from CO hydrogenation to CO and  $\text{CO}_2$  hydrogenation. In the dimethyl ether synthesis, the gradual change from CO hydrogenation to  $\text{CO}_2$  hydrogenation covers in turn the three processes, CO hydrogenating process, the parallel hydrogenation process of carbon oxide, and  $\text{CO}_2$  hydrogenating process. However, in the methanol synthesis process, because it is impossible for CO hydrogenation and the water/gas shift reaction to take place simultaneously on thermodynamics under the conditions of no  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in the feed, a gradual change covers only CO +  $\text{CO}_2$  hydrogenation and  $\text{CO}_2$  hydrogenation.

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## Nomenclature

- $a$  = parameter in SRK equation
- $a_{ij}$  = parameter in SRK equation
- $A$  = defined constant by the corresponding equation
- $b$  = parameter in SRK equation
- $B$  = defined constant by the corresponding equation
- $C_i$  = equilibrium conversion of reactant  $i$
- $\text{CO}_x$  = carbon oxide, CO or  $\text{CO}_2$
- $f_i$  = fugacity of the  $i$ th component
- $F$  = flow velocity of effluent in equilibrium state
- $F_0$  = flow velocity of fresh syngas
- $k_{ij}$  = binary interaction coefficient for SRK
- $K_j$  = equilibrium constants of  $j$ th equilibrium equation
- $P$  = pressure, MPa
- $R$  = ratio of output to input
- $R^2$  = multiple correlation coefficient
- $S_i$  = equilibrium selectivity of product  $i$
- $T$  = absolute temperature, K
- $T_c$  = critical temperature, K
- $V$  = gas volume,  $\text{m}^3$
- $y_i$  = concentration of the  $i$ th component
- $Y_d$  = equilibrium yield of product
- $Z$  = compressibility factor
- $\varphi$  = fugacity coefficient
- $\omega$  = acentric factor

## Literature Cited

- (1) Galvita, V. V.; Semin, G. L.; Belyaev, V. D.; Yurieva, T. M.; Sobyatin, V. A. Production of hydrogen from dimethyl ether. *Appl. Catal., A* **2001**, *216*, 85–90.
- (2) Tartamella, T. L.; Lee, S. Development of specialty chemicals from dimethyl ether. *Fuel Process. Technol.* **1997**, *38* (4), 228.
- (3) Jia, G. X.; Ma, H. B.; Tan, Y. S.; Han, Y. Z. Effect of particle size on the hybrid catalyst activity for slurry phase dimethyl ether synthesis. *Ind. Eng. Chem. Res.* **2005**, *44*, 2011–2015.
- (4) DOE topical report. Liquid-phase dimethyl ether demonstration in the LaPorte Alternative Fuels Development Unit. Cooperative Agreement No. DE-FC22-92PC90543; January, 2001.
- (5) Cai, G. Y.; Liu, Z. M.; Shi, R. M.; He, C. Q.; Yang, L. X.; Sun, C. L.; Chang, Y. J. Light alkenes from syngas via dimethyl ether. *Appl. Catal., A* **1995**, *125*, 29–38.
- (6) Jiang, T.; Liu, C. J.; Rao, M. F.; Yao, C. D.; Fan, G. L. A novel synthesis of diesel fuel additives from dimethyl ether using dielectric barrier discharges. *Fuel Process. Technol.* **2001**, *73*, 143–152.
- (7) Sunggyu, L.; Makarand, R. G.; Conrad, J. K. A novel single-step dimethyl ether (DME) synthesis in a three-phase slurry reactor from co-rich syngas. *Chem. Eng. Sci.* **1992**, *47*, 3769–3776.

- (8) Wang, Z. L.; Diao, J.; Wang, J. F.; Jin, Y.; Peng, X. D. Study on synergy effect in dimethyl ether synthesis from syngas. *Chin. J. Chem. Eng.* **2001**, *9*, 412–416.
- (9) Peng, X. D.; Wang, A. W.; Toseland, B. A.; Tijim, P. J. A. Kinetics understanding of the chemical synergy under LPDME conditions—once-through applications. *Chem. Eng. Sci.* **1999**, *54*, 2787.
- (10) Ng, K. L.; Chadwick, D.; Toseland, B. A. Kinetics and modelling of dimethyl ether synthesis from synthesis gas. *Chem. Eng. Sci.* **1999**, *54*, 3587–3592.
- (11) Skrzypek, J.; Lachowska, M.; Grzesik, M.; Sloczynski, J.; Nowak, P. Thermodynamics and kinetics of kinetics of low-pressure methanol synthesis. *Chem. Eng. J. Biochem. Eng. J.* **1995**, *58*, 101–108.
- (12) Jia, G. X.; Ma, H. B.; Tan, Y. S.; Han, Y. Z. Synthesis of dimethyl ether from CO hydrogenation: a thermodynamic analysis of the influence of water gas shift reaction. *J. Nat. Gas Chem.* **2005**, *14*, 47–53.
- (13) Grzesik, M.; Ptaszek, A.; Skrzypek, J. Equilibrium conversion degree in direct synthesis of dimethyl ether from CO and H<sub>2</sub>. *Inz. Chem. Proc.* **2000**, *21*, 725–732.
- (14) Meshcheryakov, V. D. Thermodynamic equilibrium in the synthesis of dimethyl ether from synthesis gas. *Theor. Found. Chem. Eng.* **2000**, *34* (1), 85–89.
- (15) Shen, W.-J.; Jun, K.-W.; Choi, H.-S.; Lee, K.-W. Thermodynamic investigation of methanol and dimethyl ether synthesis from CO<sub>2</sub> hydrogenation. *Korean J. Chem. Eng.* **2000**, *17*, 210–216.
- (16) Kulawska, M.; Skrzypek, J.; Grzesik, M. The effect of process parameters on the equilibrium dimethyl ether yield in its direct synthesis from CO<sub>2</sub> and H<sub>2</sub>. *Przem. Chem.* **2000**, *79* (7), 231–233.
- (17) Grzesik, M.; Skrzypek, J. Chemical equilibria in direct synthesis of dimethyl ether. *Stud. Surf. Sci. Catal.* **1999**, *122*, 411–414.
- (18) Wang, Z. L.; Wang, J. F.; Diao, J.; Jin, Y. The synergy effect of process coupling for dimethyl ether synthesis in slurry reactors. *Chem. Eng. Technol.* **2001**, *24*, 507–511.
- (19) Soave, G. Equilibrium constants from a modified Redlich–Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.
- (20) Cybulski, A. Liquid-phase methanol synthesis: catalyst, mechanism, kinetics, chemical equilibria, vapor–liquid equilibria, and modeling—a review. *Catal. Rev.-Sci. Eng.* **1994**, *36*, 557–613.
- (21) Graaf, G. H.; Stamhuis, E. J.; Beenackers, A. A. C. M. Kinetics of low-pressure methanol synthesis. *Chem. Eng. Sci.* **1988**, *43*, 3185–3195.
- (22) Jean, B.; Claude, N. Kinetics of methanol dehydration on dealuminated H-mordenite: model with acid and basic active centres. *Appl. Catal.* **1991**, *69*, 139–148.
- (23) Graaf, G. H.; Sijtsema, P. J. M. J.; Stamhui, E. J.; Joosten, G. E. H. Chemical equilibria in methanol synthesis. *Chem. Eng. Sci.* **1986**, *41*, 2883–2890.
- (24) Peng, X. D.; Barry, W. D.; Tsun-Chiu, R. T.; Bharat, L. B. Separation process for one-step production of dimethyl ether from synthesis gas. U.S. Patent 6,458,856, 2002.
- (25) Jun, K. W.; Rao, K. S. R.; Jung, M. H.; Lee, K.-W. The CO<sub>2</sub> hydrogenation toward the mixture of methanol and dimethyl ether: investigation of hybrid catalysts. *Bull. Korean Chem. Soc.* **1998**, *19*, 466–470.
- (26) Kim, H. J.; Jung, H.; Lee, K. Y. Effect of water on liquid-phase DME synthesis from syngas over hybrid catalysts composed of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> and g-Al<sub>2</sub>O<sub>3</sub>. *Korean J. Chem. Eng.* **2001**, *18*, 838–841.
- (27) Ana, G. G.; Andres, T. A.; Angel, L. M.; Martin, O.; Javier, B. Role of water in the kinetic modeling of catalyst deactivation in the MTG process. *AIChE J.* **2002**, *48*, 1561–1571.
- (28) Peng, X. D.; Toseland, B. A.; Wang, A. W.; Parris, G. E. *Progress in Development of LPDME Process: Kinetics and Catalysts*; Presented at the fall meeting of the Proceedings Coal Liquefaction & Solid Fuels Contractors Review Conference, Pittsburgh, PA, September, 1997.
- (29) Meyer, S. Production of hydrogen and methanol from natural gas with reduced CO<sub>2</sub> emission. *Int. J. Hydrogen Energy* **1998**, *23* (6), 419–425.
- (30) Pan, W. Tri-reforming and combined reforming of methanol for producing syngas with desired H<sub>2</sub>/CO ratios. Ph.D. Dissertation, The Pennsylvania State University, 2002.
- (31) Ptaszek, A. Modelling of direct synthesis of dimethyl ether. Ph.D. Dissertation, Polish Academy of Sciences, 2004.

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