

Thermodynamic Investigation of Methanol and Dimethyl Ether Synthesis from CO₂ Hydrogenation

Wen-Jie Shen, Ki-Won Jun[†], Ho-Suk Choi* and Kyu-Wan Lee

Chemical Technology Division, Korea Research Institute of Chemical Technology,
P.O. Box 107, Yusong, Taejeon 305-600, Korea

*Chemical Engineering Department, Chungnam National University, Taejeon 305-764, Korea

(Received 11 October 1999 • accepted 10 January 2000)

Abstract—The thermodynamics involved in the catalytic hydrogenation of CO₂ have been examined extensively. By assuming that methanol and dimethyl ether (DME) are the main products, two reaction systems each consisting of two parallel reactions were analyzed and compared in terms of the equilibrium yield and selectivity of the useful products, methanol and DME. The calculation results demonstrated that the production of DME allows much higher oxygenate yield and selectivity than that of methanol.

Key words: Carbon Dioxide Hydrogenation, Dimethyl Ether Synthesis, Equilibrium Conversion, Methanol Synthesis, Reverse Water Gas Shift Reaction, Thermodynamic Calculation

INTRODUCTION

Carbon dioxide hydrogenation to methanol has received much attention in recent years due to the increase in the recycle of emitted CO₂ [Saito, 1998; Lee and Lee, 1995; Lee et al., 1996]. During the methanol synthesis from CO₂ hydrogenation, the reverse water-gas-shift (RWGS) reaction takes place as well. The two major reactions are given by the stoichiometric relationships:



Thermodynamically the methanol synthesis from CO₂ hydrogenation is less favored compared to that from CO ($\Delta G = 9.96$ vs 5.06 kcal/mol at 500 K), and it has smaller heat of reaction ($\Delta H = -13.9$ vs -23.4 kcal/mol at 500 K) [Amenomiya, 1987; Lee et al., 1998]. A comparative study showed that the hydrogenation of CO₂ to methanol on Cu/ZnO catalysts is faster and begins at low temperature [Amenomiya, 1987; Tagawa et al., 1985]. A few authors such as Skrzypek et al. [1990] examined the equilibrium conversion of CO₂ to methanol and carbon monoxide. However, their selected feed gas composition and reaction variables are somewhat different from those reported in literature and thus make it inconvenient to compare with the experimental data.

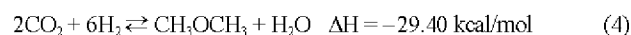
Since methanol formation from the hydrogenation of CO₂ is thermodynamically restricted within very low conversion under operating conditions of interest, alternative ways such as the production of dimethyl ether (DME) from CO₂/H₂ have been suggested [Dubois et al., 1992]. Furthermore, the production of DME may provide opportunity for a new CO₂ utilization technology because DME has a great deal of potential use as a new CO₂ utilization technology because DME has a great deal of potential use as a clean alternative fuel for diesel engines [Fleisch et

al., 1997].

DME can be formed in situ from the dehydration of methanol by addition of a solid acid catalyst in the methanol synthesis (3).



The combination of reaction (1) and (3) gives overall reaction (4),



Though the improvement of yield over the mixture of a methanol synthesis catalyst and a solid acid has been reported [Dubois et al., 1992; Jun et al., 1998, 1999], no detailed analysis of thermodynamics considering all the reactions involved in the DME synthesis from H₂/CO₂ has been reported.

In this paper, detailed results of thermodynamic calculation are presented in terms of the equilibrium conversions of CO₂ and concentrations of components in both the reaction system consisted of reactions (1) and (2) for methanol synthesis and the reaction system consisted of reactions (4) and (2) for DME synthesis. Two assumed production processes are also compared in terms of their yield and selectivity of oxygenates which are the most useful products in CO₂ hydrogenation.

THERMODYNAMIC CALCULATION

First, it is necessary to define the equilibrium yields of methanol and CO formed via reaction (1) and (2), respectively:

$$Y_{\text{CH}_3\text{OH}}^{\text{eq}} = 100 \times (N_{\text{CH}_3\text{OH}}^{\text{eq}} - N_{\text{CH}_3\text{OH}}^0) / N_T^0$$
$$Y_{\text{CO}}^{\text{eq}} = 100 \times (N_{\text{CO}}^{\text{eq}} - N_{\text{CO}}^0) / N_T^0$$

where all computations start at $N_{\text{CH}_3\text{OH}}^0 = 0$, and yields defined here refer to an initial total carbon number N_T^0 including CO₂ and CO in the feed mixture. This approach involves the fact that reaction (2) may change its direction in the mixture which contains even a small quantity of CO at the initial stage. Under such con-

[†]To whom correspondence should be addressed.

E-mail: kwjun@pado.kRICT.re.kr

ditions, CO₂ becomes a reactant of reaction (1) and a product in reaction (2). Hence the CO equilibrium constant becomes a negative value, which means that some CO are converted into CO₂ and further hydrogenated to methanol.

The following expressions for the mole fraction of each component can then be easily obtained:

$$\begin{aligned}x_{\text{CO}_2}^{eq} &= (x_{\text{CO}_2}^0 - x_1^{eq} - x_2^{eq}) / (1 - 2x_1^{eq}) \\x_{\text{CO}}^{eq} &= (x_{\text{CO}}^0 + x_2^{eq}) / (1 - 2x_1^{eq}) \\x_{\text{CH}_3\text{OH}}^{eq} &= x_1^{eq} / (1 - 2x_1^{eq}) \\x_{\text{H}_2}^{eq} &= (x_{\text{H}_2}^0 - 3x_1^{eq} - x_2^{eq}) / (1 - 2x_1^{eq}) \\x_{\text{H}_2\text{O}}^{eq} &= (x_1^{eq} + x_2^{eq}) / (1 - 2x_1^{eq})\end{aligned}$$

where x_1^{eq} is the molar concentration of CO₂ converted to methanol, and x_2^{eq} are the molar concentration of CO₂ shifted to CO. Since the methanol synthesis from CO₂ hydrogenation is a reaction in which total moles of components are decreasing as the reaction proceeds, it is natural to have a contraction factor of $(1 - 2x_1^{eq})$ in the denominators.

The equilibrium conversions x_1^{eq} and x_2^{eq} are obtained from the numerical solutions of a non-linear system of two algebraic equations as follows:

$$\begin{aligned}K_{P1} &= P_{\text{H}_2\text{O}} P_{\text{CH}_3\text{OH}} / (P_{\text{CO}_2} P_{\text{H}_2}^3) \\&= x_1^{eq} (x_1^{eq} + x_2^{eq})^3 / (x_{\text{CO}_2}^0 - x_1^{eq} - x_2^{eq}) (x_{\text{H}_2}^0 - 3x_1^{eq} - x_2^{eq})^3 P^2 \\K_{P2} &= P_{\text{H}_2\text{O}} P_{\text{CO}} / (P_{\text{CO}_2} P_{\text{H}_2}) \\&= (x_{\text{CO}}^0 + x_2^{eq}) (x_1^{eq} + x_2^{eq}) / (x_{\text{CO}_2}^0 - x_1^{eq} - x_2^{eq}) (x_{\text{H}_2}^0 - 3x_1^{eq} - x_2^{eq})\end{aligned}$$

where $K_{P1} = K_{a1}/K_{\phi 1}$, $K_{\phi 1} = \phi_{\text{CH}_3\text{OH}} \phi_{\text{H}_2\text{O}} / (\phi_{\text{CO}_2} \phi_{\text{H}_2}^3)$
 $K_{P2} = K_{a2}/K_{\phi 2}$, $K_{\phi 2} = \phi_{\text{CO}} \phi_{\text{H}_2\text{O}} / (\phi_{\text{CO}_2} \phi_{\text{H}_2})$

The values of the equilibrium constants for reactions (1) and (2), K_{a1} and K_{a2} , are calculated from well-known thermodynamic relations [Chinchen et al., 1988] and expressed in the following forms:

$$\begin{aligned}K_{a1} &= K_{a2} \exp[22.225 + (9143.6/T) \\&\quad - 7.492 \ln T + 4.076 \times 10^{-3} T - 7.161 \times 10^{-8} T^2]\end{aligned}$$

where K_{a1} is in atm⁻², and

$$\begin{aligned}K_{a2} &= \exp[13.148 - 5693/T - 1.077 \ln T \\&\quad - 5.44 \times 10^{-4} T + 1.125 \times 10^{-7} T^2 + (49170/T^3)]\end{aligned}$$

The K_a is a function of temperature only, while the K_{ϕ} is a function of both temperature and pressure. This P, T dependence of K_{ϕ} is taken from Klier [1982] in the following form,

$$\begin{aligned}K_{\phi 1} &= (1 - A_1 P)(1 - A_2 P) \\K_{\phi 2} &= 1/(1 - A_2 P)\end{aligned}$$

where $A_1 = 1.95 \times 10^{-4} \exp(1703/T)$ and
 $A_2 = 4.24 \times 10^{-4} \exp(1107/T)$.

It should be noted that K_{a1} and $K_{\phi 1}$ here were obtained as a product of the corresponding constants for methanol synthesis from CO and the RWGS reaction, the combination of which yields methanol synthesis from CO₂.

For the DME synthesis by CO₂ hydrogenation, the same treatment as above can be applied by considering the reaction system of DME synthesis containing reactions (4) and (2). The equilibrium constants for reaction (4) are obtained by combining reactions (1) and (3), i.e., $K_{a4} = K_{a1}^2 \times K_{a3}$ and K_{a3} is suggested by Diep

and Wainwright [1987],

$$K_{a3} = \exp[2835.2/T + 1.675 \ln T - 2.39 \times 10^{-4} T - 0.21 \times 10^{-6} T^2 - 13.360]$$

The fugacity correction factor K_{ϕ} is calculated by using the Soave-Redlich-Kwong equation of state [Soave, 1972] and expressed in an empirical form as the following:

$$\begin{aligned}K_{\phi 3} &= \phi_{\text{DME}} \phi_{\text{H}_2\text{O}} / \phi_{\text{CH}_3\text{OH}}^2 = 1/(1 - A_3 P), \\A_3 &= 6.592 \times 10^{-6} \exp(3067.48/T)\end{aligned}$$

and thus $K_{P3} = K_{a3}/K_{\phi 3}$.

RESULTS AND DISCUSSION

1. Methanol Synthesis from CO₂ Hydrogenation

1-1. Temperature and Pressure

Table 1 presents calculated methanol yield and CO yield depending on temperature and pressure for the feed gas of H₂/CO₂ of 3.0 (molar ratio) which is the typical feed composition as well as the exact stoichiometric requirement. It is shown that both temperature and pressure have a considerable effect on the equilibrium yields. The equilibrium conversion of CO₂ to methanol increases distinctively with increasing pressure and decreases strongly as the temperature increases. Within a temperature range of 473 K to 543 K, the decrease in methanol yield is almost linear at pressures of 3.0-9.0 MPa. On the other hand, the equilibrium yield of

Table 1. Effect of temperature on CH₃OH and CO yields at equilibrium for different pressures (H₂/CO₂ = 3.0)

Temp. (K)	Methanol yield (C-mol%)					
	1 MPa	2 MPa	3 MPa	5 MPa	7 MPa	9 MPa
473	8.92	19.48	27.91	40.94	51.13	59.93
483	6.79	16.43	24.48	37.14	47.18	55.80
493	5.01	13.55	21.15	33.43	43.28	51.77
503	3.68	10.89	17.95	29.80	39.45	47.80
513	2.64	8.51	14.91	26.22	35.66	43.87
523	1.88	6.53	12.10	22.73	31.90	39.96
533	1.34	4.91	9.60	19.34	28.18	36.08
543	0.95	3.64	7.45	16.14	24.53	32.21
553	0.68	2.68	5.69	13.19	20.98	28.38
563	0.49	1.97	4.30	10.57	17.61	24.61
573	0.36	1.45	3.22	8.32	14.51	20.98
Temp. (K)	CO yield (C-mol%)					
	1 MPa	2 MPa	3 MPa	5 MPa	7 MPa	9 MPa
473	6.71	3.79	2.50	1.36	0.86	0.57
483	8.56	5.29	3.58	2.00	1.29	0.88
493	10.41	7.05	4.97	2.88	1.90	1.32
503	12.30	9.10	6.70	4.05	2.72	1.94
513	14.03	11.27	8.75	5.55	3.81	2.77
523	15.74	13.42	10.97	7.39	5.22	3.86
533	17.36	15.58	13.37	9.55	6.98	5.27
543	18.92	17.55	15.70	11.97	9.08	7.02
553	20.44	19.48	18.02	14.52	11.50	9.14
563	21.94	21.30	20.18	17.18	14.13	11.58
573	23.43	23.02	22.19	19.73	16.92	14.30

CO via the RWGS reaction increases with temperature greatly and decreases with increasing pressure. Because of this opposite temperature and pressure dependence of the two accompanying reactions, the relative selectivity between methanol and carbon monoxide would decrease greatly with increasing temperature and increase with increasing pressure.

1-2. H_2/CO_2 Ratio

The effect of the initial CO_2 concentrations was examined with an H_2/CO_2 ratio ranging from 1/2 to 5/1. The computation results are presented in Tables 2 and 3. It can be seen that the effect of the initial H_2/CO_2 ratio is quite considerable. A significant increase in equilibrium yield of methanol is observed with decreasing initial CO_2 concentration in the feed. In the case of equilibrium yield of CO, it decreases with the increase in H_2/CO_2 ratios. However, at high pressure the CO equilibrium yield is slightly declining with the increase of H_2/CO_2 ratio. Furthermore, the opposite pressure dependence between CH_3OH and CO yields is clearly observed for all the feed compositions.

1-3. $CO/(CO+CO_2)$ Ratio

The effect of initial $CO/(CO_2+CO)$ ratio is examined by keeping the hydrogen mole fraction to be 0.75 and the whole mole fraction of CO_2+CO to be 0.25. The computation results are presented in Tables 4 and 5. It is seen that with the partial replacement of CO_2 by CO, the equilibrium yield of CO practically becomes negative, i.e., the forward WGS reaction takes place:



When the reactants contain no CO and consist only of CO_2 and H_2 , the equilibrium yield of carbon monoxide has always a positive value, which means that CO is an inevitable product formed through the RWGS reaction in the absence of CO in the feed mixture.

From Tables 4 and 5 it can be seen that the equilibrium yield of methanol is increasing with the increase of CO concentration,

Table 2. Effect of the initial H_2/CO_2 ratio on CH_3OH and CO yields at equilibrium for different pressures ($T = 523$ K)

H_2/CO_2	Methanol yield (C-mol%)					
	1 MPa	2 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0.5	0.13	0.52	1.14	2.63	4.28	5.81
1	0.47	1.77	3.52	7.32	10.84	13.96
2	1.24	4.34	8.27	16.02	22.80	28.69
3	1.90	6.57	12.10	22.70	31.92	39.97
4	2.50	8.49	15.35	28.37	39.55	49.22
5	3.02	10.14	18.10	33.04	45.68	56.48

H_2/CO_2	CO yield (C-mol%)					
	1 MPa	2 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0.5	6.81	6.66	6.36	5.62	4.86	4.22
1	9.60	8.96	8.08	6.40	5.10	4.16
2	13.27	11.71	9.90	7.01	5.17	3.98
3	15.74	13.42	10.97	7.39	5.22	3.86
4	17.80	14.84	11.91	7.71	5.27	3.77
5	19.53	16.03	12.68	7.98	5.31	3.68

Table 3. Effect of the initial H_2/CO_2 ratio on CH_3OH and CO yields at equilibrium for different temperatures ($P = 3$ MPa)

H_2/CO_2	Methanol yield (C-mol%)		
	483 K	523 K	563 K
0.5	3.43	1.14	0.29
1	8.52	3.52	1.06
2	17.56	8.27	2.85
3	24.45	12.10	4.29
4	30.29	15.35	5.60
5	35.12	18.10	6.72

H_2/CO_2	CO yield (C-mol%)		
	483 K	523 K	563 K
0.5	3.17	6.36	9.18
1	3.32	8.08	12.80
2	3.45	9.90	17.25
3	3.58	10.97	20.18
4	3.71	11.91	22.54
5	3.82	12.68	24.50

Table 4. Effect of the initial $CO/(CO + CO_2)$ ratio on CH_3OH and CO yields at equilibrium for different temperatures ($P = 3$ MPa)

$CO/(CO + CO_2)$	Methanol yield (C-mol%)					
	463 K	483 K	503 K	523 K	543 K	563 K
0	31.49	24.45	17.98	12.14	7.49	4.29
0.04	33.11	26.06	19.34	13.16	8.13	4.68
0.12	36.58	29.47	22.38	15.47	9.63	5.53
0.3	45.38	38.34	30.40	21.66	13.64	7.80
0.4	50.91	43.97	35.49	25.58	16.19	9.24
0.6	63.40	56.55	46.65	34.08	21.72	12.42
0.8	77.76	70.38	58.44	42.19	27.55	15.82

$CO/(CO + CO_2)$	CO yield (C-mol%)					
	463 K	483 K	503 K	523 K	543 K	563 K
0	1.69	3.58	6.70	10.97	15.70	20.18
0.04	-2.24	-0.23	3.15	7.81	12.92	17.66
0.12	-10.08	-7.80	-3.86	1.63	7.59	12.94
0.3	-27.67	-24.62	-19.12	-11.36	-3.13	3.76
0.4	-37.38	-33.81	-27.26	-18.05	-8.41	-0.56
0.6	-56.63	-51.72	-42.76	-30.42	-17.81	-7.91
0.8	-75.47	-68.77	-57.09	-40.85	-26.04	-14.02

and the equilibrium yield of CO is constantly decreasing. Moreover, the methanol equilibrium yield is always higher than that without CO in the feed, while the equilibrium yield of CO shows the opposite trend. Therefore, the presence of CO in the synthesis gas is highly advantageous in direct methanol synthesis from CO_2 . A large increase in the equilibrium yield of methanol is observed, while the CO yield greatly decreases with increasing initial CO concentration because reaction (2) proceeds in the reverse direction. Owing to this change in the direction of the course of reaction (2), the advantageous and considerable increase in the

Table 5. Effect of the initial CO/(CO + CO₂) ratio on CH₃OH and CO yields at equilibrium for different pressures (T = 523 K)

CO/(CO + CO ₂)	Methanol yield (C-mol%)				
	1 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0	1.90	12.14	22.70	31.92	39.97
0.12	2.66	15.47	27.11	36.52	44.56
0.3	4.16	21.66	34.80	44.32	52.08
0.4	5.13	25.58	39.62	49.12	56.63
0.6	7.19	34.08	50.28	59.79	66.62
0.8	8.78	42.19	61.88	71.81	78.00

CO/(CO + CO ₂)	CO yield (C-mol%)				
	1 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0	15.74	10.97	7.39	5.22	3.86
0.12	9.44	1.63	-3.45	-6.20	-7.84
0.3	2.54	-11.36	-19.29	-23.18	-25.33
0.4	-0.33	-18.05	-27.85	-32.51	-35.00
0.6	-4.85	-30.42	-44.32	-50.82	-54.17
0.8	-7.87	-40.85	-59.72	-68.42	-72.95

equilibrium yield of methanol from the main reaction [reaction (1)] is achieved.

2. DME Synthesis from CO₂ Hydrogenation

2-1. Temperature and Pressure

Table 6 presents calculated methanol yield and CO yield depending on temperature and pressure for the DME synthesis from CO₂ hydrogenation, in which two parallel reactions are also co-existent-one is the DME synthesis [reaction (4)] and the other is the RWGS reaction [reaction (2)]. It is seen that there is a considerable improvement in CO₂ conversion to oxygenates and a great decrease in CO formation through the RWGS reaction as compared to the methanol synthesis (compare with Table 1). Both temperature and pressure have a critical influence on the equilibrium yields of DME and CO. Within the whole temperature range investigated, the DME equilibrium yields decrease almost linearly at the pressure range of 2.0-9.0 MPa. On the contrary, the equilibrium yields of CO increase with temperature and decrease with pressure. Within the temperature range of 503 to 573 K, this temperature and pressure dependence becomes more significant than that at low temperature regions.

2-2. H₂/CO₂ Ratio

Tables 7 and 8 show the computation results for the effect of the initial CO₂ concentration in the feed gas with an H₂/CO₂ ratio in the range of 1/2 to 5/1. The effect of the initial H₂/CO₂ ratio on DME and CO yields is also quite considerable. A significant increase in equilibrium yield of DME is observed with decreasing initial CO₂ concentration in the feed. It can be further revealed that for any feed composition, the equilibrium DME yield is always increasing with pressure and decreasing with temperature. The equilibrium yield of CO becomes a little complicated. At low temperature (below 523 K at 5 MPa) it decreases with the increase in H₂/CO₂ ratios and increases with H₂/CO₂ ratio at temperature above 523 K. Similarly, the CO equilibrium yield increases with H₂/CO₂ ratio at 523 K in the pressure range below

Table 6. Effect of temperature on DME and CO yields at equilibrium for different pressures (H₂/CO₂ = 3.0)

Temp. (K)	DME yield (C-mol%)					
	1 MPa	2 MPa	3 MPa	5 MPa	7 MPa	9 MPa
473	17.67	30.87	40.08	52.87	61.91	69.42
483	14.54	27.21	36.24	49.01	58.21	65.73
493	11.51	23.69	32.48	45.18	54.45	61.89
503	8.60	20.26	28.80	41.40	50.70	58.24
513	5.91	16.89	25.28	37.65	46.95	54.54
523	3.63	13.58	21.68	33.94	43.21	50.83
533	1.88	10.37	18.24	30.25	39.48	47.10
543	0.87	7.36	14.72	26.57	35.74	43.36
553	0.46	4.77	11.36	22.87	31.98	39.59
563	0.22	2.67	8.16	19.15	28.18	35.79
573	0.10	1.39	5.41	15.45	24.34	31.92

Temp. (K)	CO yield (C-mol%)					
	1 MPa	2 MPa	3 MPa	5 MPa	7 MPa	9 MPa
473	3.03	1.42	0.88	0.47	0.30	0.20
483	4.44	2.12	1.33	0.71	0.45	0.31
493	6.30	3.11	1.97	1.07	0.69	0.48
503	8.62	4.46	2.86	1.57	1.02	0.72
513	11.29	6.24	4.07	2.26	1.49	1.06
523	14.05	8.50	5.68	3.21	2.13	1.53
533	16.65	11.22	7.74	4.47	3.00	2.17
543	18.82	14.26	10.29	6.12	4.15	3.03
553	20.48	17.37	13.28	8.21	5.65	4.17
563	22.08	20.33	16.57	10.78	7.57	5.64
573	23.57	22.81	19.88	13.83	9.94	7.52

Table 7. Effect of the initial H₂/CO₂ ratio on DME and CO yields at equilibrium for different temperatures (P = 5 MPa)

H ₂ /CO ₂	DME yield (C-mol%)				
	463 K	483 K	523 K	543 K	563 K
0.5	9.94	8.38	4.77	2.79	1.06
1	20.93	18.06	11.89	8.53	5.10
2	41.14	35.57	24.43	18.79	13.04
3	56.75	49.01	33.94	26.57	19.15
4	69.03	59.88	41.88	33.11	24.32
5	77.60	68.03	48.26	38.45	28.59

H ₂ /CO ₂	CO yield (C-mol%)				
	463 K	483 K	523 K	543 K	563 K
0.5	0.51	1.06	3.72	6.05	8.66
1	0.42	0.90	3.34	6.04	9.67
2	0.35	0.78	3.25	6.02	10.32
3	0.30	0.71	3.21	6.12	10.78
4	0.26	0.66	3.20	6.23	11.20
5	0.23	0.62	3.19	6.34	11.57

5 MPa and then it declines with increasing H₂/CO₂ ratio in the feed. The dependence of CO yield on initial feed composition indicates that the RWGS reaction is more sensitive to reaction

Table 8. Effect of the initial H_2/CO_2 ratio on DME and CO yields at equilibrium for different pressures ($T = 523$ K)

H_2/CO_2	DME yield (C-mol%)				
	1 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0.5	0.06	2.19	4.77	6.73	8.27
1	0.52	6.91	11.89	15.52	18.40
2	2.04	15.34	24.43	31.22	36.74
3	3.63	21.72	33.94	43.21	50.83
4	5.01	27.12	41.88	53.04	62.13
5	6.21	31.59	48.26	60.63	70.44

H_2/CO_2	CO yield (C-mol%)				
	1 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0.5	6.85	5.28	3.72	2.84	2.30
1	9.46	5.38	3.43	2.51	1.97
2	12.36	5.49	3.25	2.25	1.69
3	14.05	5.68	3.21	2.13	1.53
4	15.46	5.87	3.20	2.04	1.40
5	16.65	6.06	3.19	1.96	1.29

condition. The direction of the reaction of the RWGS may be forward or backward depending on the initial feed composition, temperature, and pressure.

2-3. $CO/(CO+CO_2)$ Ratio

The effect of initial $CO/(CO_2+CO)$ ratio is investigated by keeping the hydrogen mole fraction to be constant (0.75) and replacing CO_2 by CO in the initial feed gas. The computation results are presented in Tables 9 and 10. It is seen that with the partial replacement of CO_2 by CO, the equilibrium yield of CO practically becomes negative, implying that the RWGS reaction takes place backwards.

From Tables 9 and 10 it can be revealed that with the increase of CO mole fraction in the feed gas the equilibrium yield of DME is increasing linearly and the equilibrium yield of CO is constantly decreasing, and under most conditions the added CO is converted

Table 9. Effect of the initial $CO/(CO + CO_2)$ ratio on DME and CO yields at equilibrium for different temperatures ($P = 5$ MPa)

$CO/(CO + CO_2)$	DME yield (C-mol%)				
	463 K	503 K	523 K	543 K	563 K
0	56.75	41.40	33.95	26.57	19.14
0.04	58.18	42.98	35.58	28.22	20.73
0.1	60.33	45.37	38.07	30.75	23.20
0.4	71.03	57.60	50.98	44.20	36.82

$CO/(CO + CO_2)$	CO yield (C-mol%)				
	463 K	503 K	523 K	543 K	563 K
0	0.30	1.57	3.21	6.11	10.79
0.04	-3.70	-2.44	-0.80	2.14	6.90
0.1	-9.71	-8.46	-6.81	-3.84	1.04
0.4	-39.75	-38.57	-36.97	-33.96	-28.76

Table 10. Effect of the initial $CO/(CO + CO_2)$ ratio on DME and CO yields at equilibrium for different pressures ($T = 523$ K)

$CO/(CO + CO_2)$	DME yield (C-mol%)				
	1 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0	3.63	21.73	33.95	43.22	50.84
0.04	4.60	23.41	35.58	44.78	52.33
0.1	6.34	26.01	38.07	47.13	54.56
0.4	19.04	40.03	50.98	59.15	65.83

$CO/(CO + CO_2)$	CO yield (C-mol%)				
	1 MPa	3 MPa	5 MPa	7 MPa	9 MPa
0	14.05	5.67	3.21	2.13	1.53
0.04	10.98	1.72	-0.80	-1.89	-2.49
0.1	6.28	-4.21	-6.81	-7.91	-8.52
0.4	-19.32	-34.16	-36.97	-38.09	-38.68

into DME via CO_2 as an intermediate. Moreover, the DME equilibrium yield is always higher than those without CO in the feed, while the equilibrium yield of CO shows the opposite. Therefore, the presence of CO in the synthesis gas is highly advantageous in DME synthesis from CO_2 . A highly remarkable increase in the equilibrium yield of DME can be achieved by adding CO in the feed while the CO yield is greatly decreased and causes the reaction (2) proceed in the reverse direction. Because of this change in the direction of the RWGS reaction a considerable improvement in the equilibrium yield of DME from the main reaction [reaction (4)] is obvious.

Detailed data of the computations also showed a strong dependence of the DME concentration in the liquid products (DME + water) on the initial composition. If there is no CO in the feed, the mole fraction of DME in the liquid products does not exceed 0.25. A considerable increase in the DME concentration is achieved as the initial CO concentration is increased. Moreover, there is always a characteristic maximum against temperature for the synthesis gas containing CO as the case of methanol synthesis.

3. Comparison between Methanol Synthesis and DME Synthesis

Fig. 1 compares the oxygenates and CO equilibrium yields as a function of temperature ranging from 423 K to 573 K for a pressure of 3 MPa between methanol synthesis and DME synthesis. It is worth noting that the CO_2 equilibrium conversion to DME is always considerably higher than that of CH_3OH , while the CO equilibrium yield accompanied with DME formation is significantly lower than that accompanied with CH_3OH production. This result demonstrates that the formation of DME does improve the CO_2 conversion to methanol by depressing the CO formation. All these facts agree with the experimental results presented elsewhere [Dubois et al., 1992; Jun et al., 1999].

Due to the increase in oxygenate formation and decrease in CO production, the relative selectivity between oxygenates and CO increases rapidly with decreasing temperature for the case of DME synthesis as shown in Fig. 2. It can be further observed that the relative selectivity in both cases increases greatly with decreasing temperature below 523 K. Within the temperature range

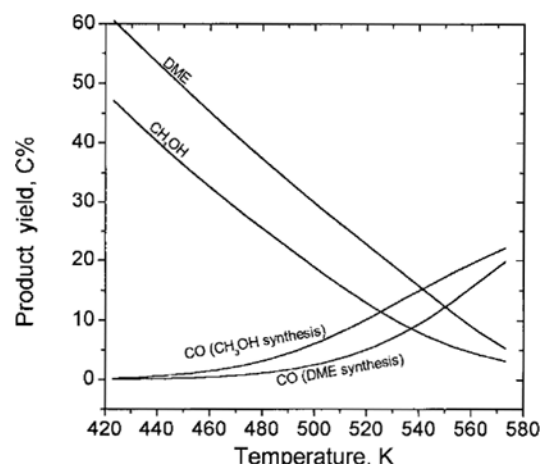


Fig. 1. Comparison of product yields at equilibrium between methanol and DME synthesis ($P = 3$ MPa, $H_2/CO_2 = 3.0$).

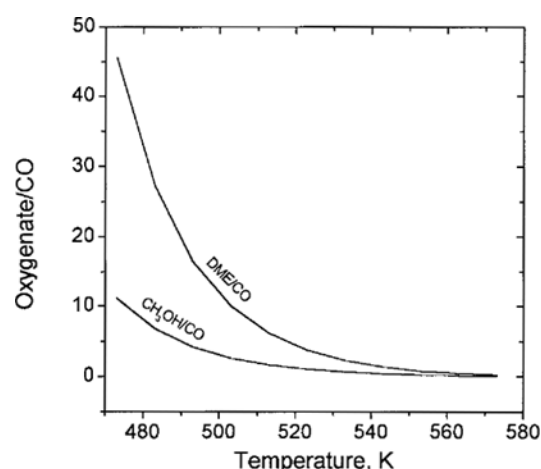


Fig. 2. Comparison of the relative selectivity at equilibrium between methanol and DME synthesis ($P = 3$ MPa, $H_2/CO_2 = 3.0$).

of 523 to 573 K the temperature dependence of relative selectivity becomes less remarkable. This implies that CO₂ hydrogenation to either CH₃OH or DME should be operated at low temperature in order to achieve higher selectivity to oxygenates by depressing the formation of carbon monoxide.

Figs. 3 and 4 further compare the effect of the initial feed composition on the product yield. Fig. 3 shows that both the methanol and DME yields increase with the increase in the initial H_2/CO_2 ratio, i.e., the decrease in CO₂ mole fraction in the feed. Whereas the CO yield from DME production is declining slightly against H_2/CO_2 ratio, and the CO yield from methanol formation increases slightly with increasing H_2/CO_2 ratio in the feed. It can be further revealed that the initial H_2/CO_2 ratio shows strong influence on the DME yield than that on the CH₃OH yield. Meanwhile, the corresponding CO yield in DME synthesis is always lower than that of methanol synthesis. As mentioned before, the addition of carbon monoxide to H_2/CO_2 mixture can significantly improve the equilibrium conversion of CO₂ to DME and methanol, respectively, as shown in Fig. 4. Both the DME and the methanol yield increase almost linearly with increasing the initial $CO/(CO_2 +$

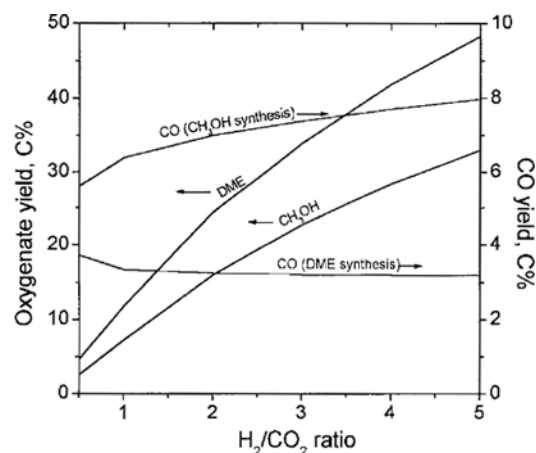


Fig. 3. Comparison of equilibrium yields as functions of the initial H_2/CO_2 ratio between methanol and DME synthesis ($P = 3$ MPa, $T = 523$ K).

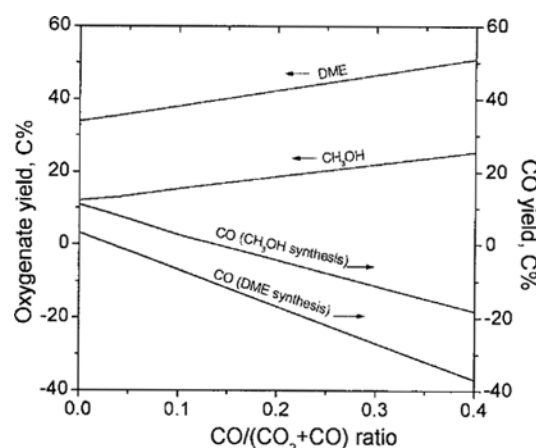


Fig. 4. Comparison of equilibrium yields as functions of the initial $CO/(CO_2 + CO)$ ratio between methanol and DME synthesis ($P = 3$ MPa, $T = 523$ K).

CO) ratio in the feed, while the corresponding CO yields are declining sharply against H_2/CO_2 ratio for both cases.

CONCLUSION

The thermodynamic equilibria involved in the catalytic hydrogenation of CO₂ to produce methanol and DME, respectively, were examined by investigating the effects of temperature, pressure and the initial feed composition on the equilibrium conversion of carbon dioxide and yields of the main products. From the comparison of two reaction systems, it has been demonstrated that the production of DME allows much higher oxygenate yield and selectivity than that of methanol in the equilibrium.

REFERENCES

- Amenomiya, Y., "Methanol Synthesis from CO₂ + H₂: Copper-based Binary and Ternary Catalysts," *Appl. Catal.*, **30**, 57 (1987).
- Chinchen, G. C., Denny, P. J., Jennings, J. R., Spencer, M. S. and Waugh, K. C., "Synthesis of Methanol: part 1. Catalysts and Kine-

- tics," *Appl. Catal.*, **36**, 1 (1988).
- Diep, B. T. and Wainwright, M. S., "Thermodynamic Equilibrium Constants for the Methanol-Dimethyl-Water System," *J. Chem. Eng. Data*, **32**, 330 (1987).
- Dubois, J. L., Sayama, K. and Arakawa, H., "Conversion of CO₂ to Dimethylether and Methanol over Hybrid Catalysts," *Chem. Lett.*, 1115 (1992).
- Fleisch, T. H., Basu, A., Gradassi, M. J. and Masin, J. G., "Dimethyl Ether: A Fuel for the 21st Century," *Stud. Surf. Sci. Catal.*, **107**, 117 (1997).
- Jun, K.-W., Rama Rao, K. S., Jung, M.-H. and Lee, K.-W., "The CO₂ Hydrogenation Toward the Mixture of Methanol and Dimethyl Ether: Investigation of Hybrid Catalysts," *Bull. Korean Chem. Soc.*, **19**, 466 (1998).
- Jun, K.-W., Shen, W.-J. and Lee, K.-W., "Concurrent Production of Methanol and Dimethyl Ether from Carbon Dioxide Hydrogenation: Investigation of Reaction Conditions," *Bull. Korean Chem. Soc.*, **20**, 993 (1999).
- Klier, K., Chatikavanij, V., Herman, R. G. and Simmons, G. W., "Catalytic Synthesis of Methanol from CO/H₂: 4 the Effects of Carbon Dioxide," *J. Catal.*, **74**, 343 (1982).
- Lee, E. K., Kim, S. B. and Hahn, H. S., "Two-stage Strategy to Improve Methanol Yield in Carbon Dioxide Hydrogenation," *HWAHAK KONGHAK*, **36**, 821 (1998).
- Lee, H. J., Park, J. W. and Hahn, H. S., "Methanol Synthesis by the Hydrogenation of Carbon Dioxide," *HWAHAK KONGHAK*, **34**, 716 (1996).
- Lee, K. H. and Lee, J. S., "Effects of Catalyst Composition on Methanol Synthesis from CO₂/H₂," *Korean J. Chem. Eng.*, **12**, 460 (1995).
- Saito, M., "R&D Activities in Japan on Methanol Synthesis from CO₂ and H₂," *Catal. Surv. Jpn.*, **2**, 175 (1998).
- Skrzypek, J., Lachowska, M. and Serafin, D., "Methanol Synthesis from CO₂: Dependence of Equilibrium Conversions and Exit Equilibrium Concentrations of Components on the Main Process Variables," *Chem. Engng. Sci.*, **45**, 89 (1990).
- Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Engng. Sci.*, **27**, 1197 (1972).
- Tagawa, T., Pleizier, G. and Amenomiya, Y., "Methanol Synthesis from CO₂+H₂," *Appl. Catal.*, **18**, 285 (1985).