Thermodynamic Investigation of Methanol and Dimethyl Ether Synthesis from CO_2 Hydrogenation

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Abstract−The thermodynamics involved in the catalytic hydrogenation of CO_2 have been examined extensively. By assuming that methanol and dimethyl ether (DME) are the main products, two reaction systems each consisting of two pararell 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 CO_2 [Saito, 1998; Lee and Lee, 1995; Lee et al., 1996]. During the methanol synthesis from CO_2 hydrogenation, the reverse water-gas-shift (RWGS) reaction takes place as well. The two major reactions are given by the stoichiometric relationships:

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad (1)$$
$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (2)$$

Thermodynamically the methanol synthesis from CO_2 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 CO_2 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 CO_2 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 CO_2 is thermodynamically restricted within very low conversion under operating conditions of interest, alternative ways such as the production of dimethyl ether (DME) from CO_2/H_2 have been suggested [Dubois et al., 1992]. Futhermore, the production of DME may provide opportunity for a new CO_2 utilization technology because DME has a great deal of potential use as a new CO_2 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).

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad \Delta H = -5.60 \text{ kcal/mol} \qquad (3)$$
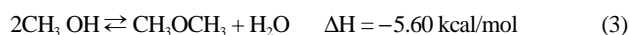
The combination of reaction (1) and (3) gives overall reaction (4),

$$2CO_2 + 6H_2 \rightleftarrows CH_3OCH_3 + H_2O \quad \Delta H = -29.40 \text{ kcal/mol} \qquad (4)$$

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 H_2/CO_2 has been reported.

In this paper, detailed results of thermodynamic calculation are presented in terms of the equilibrium conversions of CO_2 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 CO_2 hydrogenation.

THERMODYNAMIC CALCULATION

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

$$Y_{CH_3OH}^{eq} = 100 \times (N_{CH_3OH}^{eq} - N_{CH_3OH}^0)/N_T^0$$
$$Y_{CO}^{eq} = 100 \times (N_{CO}^{eq} - N_{CO}^0)/N_T^0$$

where all computations start at $N_{CH_3OH}^0 = 0$, and yields defined here refer to an initial total carbon number N_T^0 including CO_2 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-

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ditions, CO_2 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 CO_2 and further hydrogenated to methanol.

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

$$x_{CO_2}^{eq} = (x_{CO_2}^0 - x_1^{eq} - x_2^{eq})/(1 - 2x_1^{eq})$$
$$x_{CO}^{eq} = (x_{CO}^0 + x_2^{eq})/(1 - 2x_1^{eq})$$
$$x_{CH_3OH}^{eq} = x_1^{eq}/(1 - 2x_1^{eq})$$
$$x_{H_2}^{eq} = (x_{H_2}^0 - 3x_1^{eq} - x_2^{eq})/(1 - 2x_1^{eq})$$
$$x_{H_2O}^{eq} = (x_1^{eq} + x_2^{eq})/(1 - 2x_1^{eq})$$

where x_1^{eq} is the molar concentration of CO_2 converted to methanol, and x_2^{eq} are the molar concentration of CO_2 shifted to CO. Since the methanol synthesis from CO_2 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:

$$K_{P1} = P_{H_2O}P_{CH_3OH}/(P_{CO_2}P_{H_2}^3)$$
$$= x_1^{eq}(x_1^{eq} + x_2^{eq})(1 - 2x_1^{eq})^2/(x_{CO_2}^0 - x_1^{eq} - x_2^{eq})(x_{H_2}^0 - 3x_1^{eq} - x_2^{eq})^3 P^2$$
$$K_{P2} = P_{H_2O}P_{CO}/(P_{CO_2}P_{H_2})$$
$$= (x_{CO}^0 + x_2^{eq})(x_1^{eq} + x_2^{eq})/(x_{CO_2}^0 - x_1^{eq} - x_2^{eq})(x_{H_2}^0 - 3x_1^{eq} - x_2^{eq})$$

where $K_{P1} = K_{a1}/K_{\varphi1}$, $K_{\varphi1} = \varphi_{CH_3OH}\varphi_{H_2O}/\varphi_{CO_2}\varphi_{H_2}^3$,
$K_{P2} = K_{a2}/K_{\varphi1}$, $K_{\varphi2} = \varphi_{CO}\varphi_{H_2O}/\varphi_{CO_2}\varphi_{H_2}$

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:

$$K_{a1} = K_{a2}\exp[22.225 + (9143.6/T)$$
$$-7.492\ln T + 4.076\times10^{-3}T - 7.161\times10^{-8}T^2]$$

where K_{a1} is in atm^{-2}, and

$$K_{a2} = \exp[13.148 - 5693/T - 1.077\ln T$$
$$-5.44\times10^{-4}T + 1.125\times10^{-7}T^2 + (49170/T^2)]$$

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,

$$K_{\varphi1} = (1 - A_1P)(1 - A_2P)$$
$$K_{\varphi2} = 1/(1 - A_2P)$$

where $A_1 = 1.95\times10^{-4}\exp(1703/T)$ and
$A_2 = 4.24\times10^{-4}\exp(1107/T)$.

It should be noted that K_{a1} and $K_{\varphi1}$ 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 CO_2.

For the DME synthesis by CO_2 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],

$$K_{a3} = \exp[2835.2/T + 1.675\ln T - 2.39\times10^{-4}T - 0.21\times10^{-6}T^2 - 13.360]$$

The fugacity correction factor $K_{\varphi3}$ is calculated by using the Soave-Redlich-Kwong equation of state [Soave, 1972] and expressed in a empirical form as the following:

$$K_{\varphi3} = \varphi_{DME}\varphi_{H_2O}/\varphi_{CH_3OH}^2 = 1/(1 - A_3P),$$
$$A_3 = 6.592\times10^{-6}\exp(3067.48/T)$$

and thus $K_{p3} = K_{a3}/K_{\varphi3}$.

RESULTS AND DISCUSSION

1. Methanol Synthesis from CO_2 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 H_2/CO_2 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 CO_2 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 CH_3OH and CO yields at equilibrium for different pressures ($H_2/CO_2 = 3.0$)

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:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (2a)$$

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 $CO/(CO + CO_2)$ ratio on CH_3OH 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 CO_2 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 CO_2 hydrogenation, in which two parallel reactions are also coexistent-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 CO_2 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. H_2/CO_2 Ratio

Tables 7 and 8 show the computation results for the effect of the initial CO_2 concentration in the feed gas with an H_2/CO_2 ratio in the range of 1/2 to 5/1. The effect of the initial H_2/CO_2 ratio on DME and CO yields is also quite considerable. A significant increase in equilibrium yield of DME is observed with decreasing initial CO_2 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 H_2/CO_2 ratios and increases with H_2/CO_2 ratio at temperature above 523 K. Similarly, the CO equilibrium yield increases with H_2/CO_2 ratio at 523 K in the pressure range below

Table 6. Effect of temperature on DME and CO yields at equilibrium for different pressures ($H_2/CO_2 = 3.0$)

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 H_2/CO_2 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 H_2/CO_2 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 H₂/CO₂ 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+CO₂) Ratio

The effect of initial CO/(CO₂+CO) ratio is investigated by keeping the hydrogen mole fraction to be constant (0.75) and replacing CO₂ 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 CO₂ 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 + CO₂) 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 + CO₂) 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 CO₂ 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 CO₂. 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 CO₂ equilibrium conversion to DME is always considerably higher than that of CH₃OH, while the CO equilibrium yield accompanied with DME formation is significantly lower than that accompanied with CH₃OH production. This result demonstrates that the formation of DME does improve the CO₂ 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
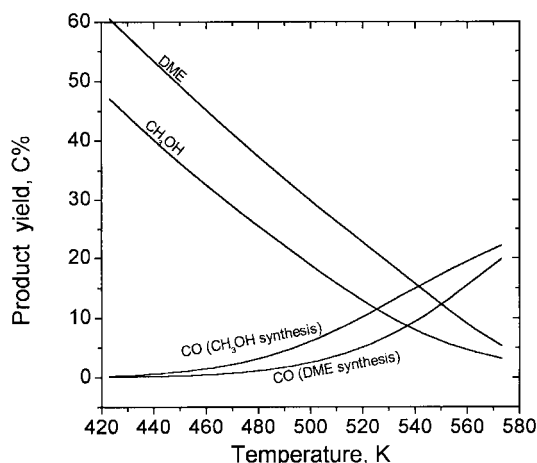
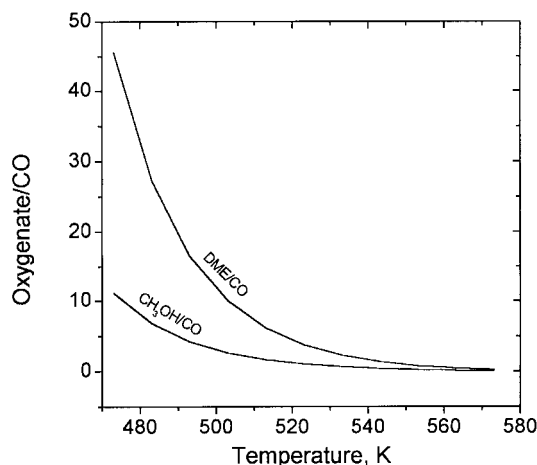Fig. 1. Comparison of product yields at equilibrium between methanol and DME synthesis (P = 3 MPa, H_2/CO_2 = 3.0).

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

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).

of 523 to 573 K the temperature dependence of relative selectivity becomes less remarkable. This implies that CO_2 hydrogenation to either CH_3OH 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 CO_2 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 CH_3OH 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 CO_2 to DME and methanol, respectively, as shown in Fig. 4. Both the DME and the methanol yield increase almost linearly with increasing the initial $CO/(CO_2+$
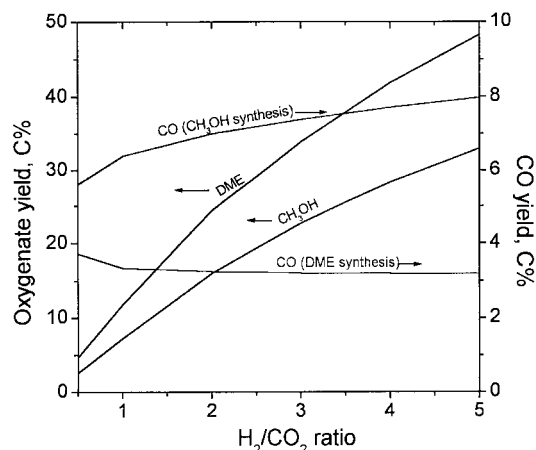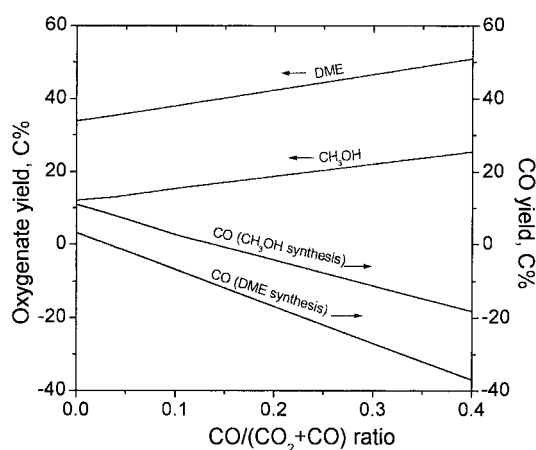
CO) ratio in the feed, while the corresponding CO yields are declining sharply against H_2/CO_2 ratio for both cases.

CONCLUSION

The thermodynamic equilibriums involved in the catalytic hydrogenation of CO_2 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.

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