

# Thermodynamic analysis on the CO<sub>2</sub> conversion processes of methane dry reforming for hydrogen production and CO<sub>2</sub> hydrogenation to dimethyl ether

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**Abstract.** Based on the principle of Gibbs free energy minimization, the thermodynamic analysis on the CO<sub>2</sub> conversion processes of dry reforming of methane for H<sub>2</sub> and CO<sub>2</sub> hydrogenation to dimethyl ether was carried out. The composition of the reaction system was determined on the basis of reaction mechanism. The effects of reaction temperature, pressure and raw material composition on the equilibrium conversion and the selectivity of products were analyzed. The results show that high temperature, low pressure, CO<sub>2</sub>/CH<sub>4</sub> molar ratio of 1.0-1.5 and appropriate amount of oxygen are beneficial to the dry reforming of methane. For CO<sub>2</sub> hydrogenation to dimethyl ether, low temperature, high pressure, the appropriate H<sub>2</sub>/CO<sub>2</sub> and the proper CO addition in feed are favorable. The calculated results are compared with the relevant studies, indicating that industrial catalytic technology needs further improvement.

## 1. Introduction

The excessive use of fossil fuels leads to the increase of greenhouse gases, and carbon dioxide conversion and utilization is one of the current problems to be solved. In the CO<sub>2</sub> conversion technologies, biogas reforming for hydrogen production and carbon dioxide hydrogenation are two effective methods. Hydrogen production by dry reforming of methane can provide hydrogen source for CO<sub>2</sub> hydrogenation.

Biogas is a renewable and important secondary energy friendly to the environment, which is a gas mixture rich in CH<sub>4</sub> (50-70 vol.%) and CO<sub>2</sub> (25-40 vol.%) produced by digestion or fermentation of organic matter under anaerobic conditions. CH<sub>4</sub> and CO<sub>2</sub> are the main greenhouse gases that cause global warming, but they are also valuable resources. Hydrogen production by dry reforming of biogas is an effective way for simultaneous utilization of CH<sub>4</sub> and conversion of CO<sub>2</sub>. The process of biogas reforming is essentially methane reforming. Dry Reforming of Methane (DRM) was proposed at the Tenth International catalytic conference in 1992. But as early as 1928, Fisher and Tropsch have studied the process. CO<sub>2</sub> reforming of methane to syngas has made some progress[1-5], but due to the coke deactivation and sintering of catalyst, there is still a gap between laboratory technology and industrial application. Thermodynamic analysis is needed to explore the optimal reaction conditions to reduce carbon deposition, which can be used as reference for practical application.

CO<sub>2</sub> hydrogenation is an effective method to convert CO<sub>2</sub>, which can produce a variety of products, such as carbon monoxide, carboxylic acid, aldehydes, alcohols and hydrocarbons [6]. Dimethyl ether



(DME) is a new car fuel with the good performances of easy storage and transportation and clean and friendly environment. The process of CO/CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH (MeOH) is currently relatively mature technology in the industry [7]. However, the synthesis of methanol by CO<sub>2</sub> hydrogenation is thermodynamically limited and the methanol yield is low. The resulting methanol is further dehydrated to produce DME, which can break the thermodynamic equilibrium of methanol synthesis and inhibit the side reaction. CO<sub>2</sub>/CO hydrogenation catalysts and CO hydrogenation thermodynamic analysis have been mainly researched [6-9], however there are less researches on thermodynamics of CO<sub>2</sub> hydrogenation for DME.

Based on the purpose of conversion and utilization of CO<sub>2</sub>, a thermodynamic analysis of the important dry reforming of methane and the hydrogenation of carbon dioxide to dimethyl ether was carried out and the influences of reaction conditions on the equilibrium product were investigated. The calculated results were compared with the relevant experimental and numerical results. The thermodynamic analysis results of hydrogen production and hydrogenation are expected.

## 2. Calculation Principles and Methods

### 2.1. Reaction mechanism analysis

In the process of dry reforming of methane for H<sub>2</sub> and the process of CO<sub>2</sub> hydrogenation to two methyl ether, the main reaction equations involved in two reaction systems are shown in Table 1.

**Table 1** The main reaction equations involved in the reaction system

Reaction system	Reaction Equation	$\Delta H_{298\text{ K}}$ (kJ·mol <sup>-1</sup> )	Reaction explanation	No.
Dry reforming of methane for H <sub>2</sub>	CH <sub>4</sub> + CO <sub>2</sub> ↔ 2CO + 2H <sub>2</sub>	260.5	CO <sub>2</sub> reforming of methane	(1)
	CO <sub>2</sub> + H <sub>2</sub> ↔ CO + H <sub>2</sub> O	41.0	RWGS	(2)
	CH <sub>4</sub> + H <sub>2</sub> O ↔ CO + 3H <sub>2</sub>	206.0	Steam reforming of methane	(3)
	CH <sub>4</sub> + 2H <sub>2</sub> O ↔ CO <sub>2</sub> + 4H <sub>2</sub>	165	Steam reforming of methane	(4)
	CH <sub>4</sub> + 2O <sub>2</sub> ↔ CO <sub>2</sub> + 2H <sub>2</sub> O	-802	Combustion of methane	(5)
	CH <sub>4</sub> + 0.5O <sub>2</sub> ↔ CO + 2H <sub>2</sub>	-36	Partial oxidation of methane	(6)
	CH <sub>4</sub> ↔ C + 2H <sub>2</sub>	75.0	Decomposition of methane	(7)
	2CO ↔ CO <sub>2</sub> + C	-172.5	Disproportionation reaction	(8)
	CO + H <sub>2</sub> ↔ H <sub>2</sub> O + C	-131.5	CO reduction	(9)
CO <sub>2</sub> hydrogenation to DME	2CO <sub>2</sub> + 6H <sub>2</sub> ↔ CH <sub>3</sub> OCH <sub>3</sub> + 3H <sub>2</sub> O	-122.2	Overall reaction	(10)
	CO <sub>2</sub> + H <sub>2</sub> ↔ CO + H <sub>2</sub> O	41.0	RWGS	(2)
	CO <sub>2</sub> + 3H <sub>2</sub> ↔ CH <sub>3</sub> OH + H <sub>2</sub> O	-49.4	CO <sub>2</sub> hydrogenation to MeOH	(11)
	2CH <sub>3</sub> OH ↔ CH <sub>3</sub> OCH <sub>3</sub> + H <sub>2</sub> O	-23.4	MeOH dehydration	(12)
	3CO + 3H <sub>2</sub> ↔ CH <sub>3</sub> OCH <sub>3</sub> + CO <sub>2</sub>	-256.6	CO hydrogenation to DME	(13)

**2.1.1. Dry reforming of methane for H<sub>2</sub>.** In methane reforming reaction, the main reactions might be methane reforming reaction (1, 3, 4, 6), reverse water gas shift reaction (RWGS) (2) and carbon deposition reaction (7-9). In the case of steam, steam reforming of methane (SRM) occurs. If oxygen is added to the reaction, methane oxidation (5, 6) will occur. Carbon deposition reactions (7-9) may occur in the reaction system. The increase of temperature is favorable to the positive reaction of the main reaction, and the side reaction has a great influence on the products. Syngas with H<sub>2</sub>/CO < 1.0 is suitable for synthesis of dimethyl ether.

**2.1.2 CO<sub>2</sub> hydrogenation to DME.** In the CO<sub>2</sub> hydrogenation to DME, there are three main reactions related: methanol synthesis from CO<sub>2</sub> hydrogenation (11), RWGS (2) and the methanol dehydration reaction (12). The overall reaction was equation (10). Methanol synthesis reaction (12) is limited by chemical equilibrium and needs to be completed under higher pressure. The H<sub>2</sub>O produced by RWGS (2) causes the methanol dehydration reaction (11) to be inhibited positively, and then affects the

overall reaction of the dimethyl ether synthesis (10). In addition, the reaction of CO hydrogenation to dimethyl ether (13) also occurs in the reaction system.

## 2.2. Calculation Methods and Parameters

The method of Gibbs free energy minimization is used to analyze the equilibrium composition of the reforming systems. In this analysis, RGibbs reactor model was used by Aspen Plus software. The reaction system is complex and there are many kinds of products. According to the analysis of reaction mechanism, only the products corresponding to the main reactions are considered. (1) For dry reforming of methane for H<sub>2</sub>, the selected substances in system are CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, CO, H<sub>2</sub>O and C<sub>(s)</sub>, which belong to the coexistence of gas and solid phase. (2) For the reaction system of CO<sub>2</sub> hydrogenation to DME, CO<sub>2</sub>, H<sub>2</sub>, CO, H<sub>2</sub>O, CH<sub>3</sub>OH(MeOH) and CH<sub>3</sub>OCH<sub>3</sub>(DME) were determined and other substances are not considered. In thermodynamic analysis, the Peng-Robinson equation of state is chosen due to the existence of nonideal gas in the system. The effects of reaction conditions on conversion of raw material and the selectivity of products were mainly discussed in this analysis.

The raw material conversion and the product selectivity were defined as follows, respectively.

$$X(i_c) = [(F_{i(C),in} - F_{i(C),out}) / F_{i(C),in}] \times 100\% \quad (14) \quad X(H_2) = [(F_{H_2,in} - F_{H_2,out}) / F_{H_2,in}] \times 100\% \quad (15)$$

$$S_{i(C)} = [\lambda F_{i(C),out} / (F_{i(C),in} - F_{i(C),out})] \times 100\% \quad (16) \quad S_{H_2O} = [2F_{H_2O} / (F_{H,in} - F_{H,out})] \times 100\% \quad (17)$$

In which,  $X(i_c)$  and  $X(H_2)$  are the conversion of carbonaceous material (CH<sub>4</sub>, CO<sub>2</sub>, CO) and H<sub>2</sub>, respectively.  $F_i$  is the molar flow rate of species  $i$  and the subscripts of in and out indicate the state of being in and out, respectively.  $S_i$  is the selectivity of carbonaceous substances, in which  $\lambda$  is the number of carbon atoms in species  $i$ .  $S_{H_2O}$  is the selectivity of H<sub>2</sub>O calculated according to the amount of transformed hydrogen.

## 3. Results and discussion

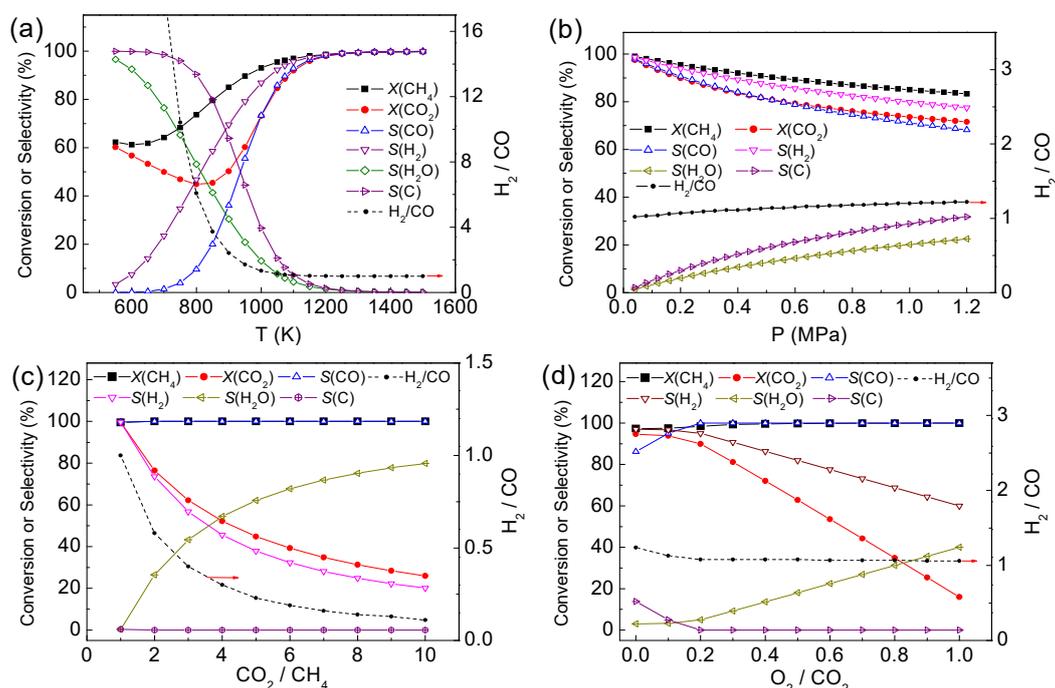
### 3.1. Dry reforming of methane for H<sub>2</sub>

The thermodynamic analysis of dry reforming of methane was carried out under the conditions of reaction temperature (550-1500 K), pressure (0.04-1.2 MPa), CO<sub>2</sub>/CH<sub>4</sub> molar ratio (1.0-10) and O<sub>2</sub>/CO<sub>2</sub> molar ratio (0-1.0) in the feed. The influences of reaction conditions on the equilibrium system of DRM are shown in Figure 1.

As shown in Figure 1(a), the conversion of CH<sub>4</sub> and CO<sub>2</sub> and the selectivity of CO and H<sub>2</sub> increase with the increase of temperature, indicating that the increase of temperature is beneficial to hydrogen production, but when the temperature reaches about 1200 K, the increase of temperature has little effect on the conversion of raw material and H<sub>2</sub> selectivity. The molar ratio of H<sub>2</sub>/CO changed from 1.33 to 1.0 above 1000 K. High temperature is beneficial to reduce carbon deposition, and 950-1200 K can be considered as a better reaction temperature range. High temperature is beneficial to hydrogen production [3,4], mainly because the reforming reaction (1) is endothermic reaction, and the water content decreases with the increase of temperature, which is due to the hydrogen production from methane steam reforming at high temperature.

From Figure 1(b), the conversion of CH<sub>4</sub> and CO<sub>2</sub>, the selectivity of CO and H<sub>2</sub> decrease with the increase of pressure, which is mainly due to the main reforming reaction (1) positive direction is the increasing number of moles, indicating low pressure is beneficial to the reforming reaction and atmospheric pressure is suitable for reforming [4]. The molar ratio of H<sub>2</sub>/CO was 1.0-1.19 in the condition of changing the pressure reaction.

As shown in Figure 1(c), with the increase of CO<sub>2</sub>/CH<sub>4</sub> value, CH<sub>4</sub> conversion of is higher and almost 100% conversion is achieved, while CO<sub>2</sub> conversion is a decreasing trend, indicating that CO<sub>2</sub> is excessive. There is a high conversion of raw material in the range of CO<sub>2</sub>/CH<sub>4</sub>=1.0-1.5. The molar ratio of H<sub>2</sub>/CO decreases with the increase of CO<sub>2</sub>/CH<sub>4</sub>. Syngas with H<sub>2</sub>/CO molar ratio close to 1.0 can be obtained at low CO<sub>2</sub>/CH<sub>4</sub> molar ratio.



**Figure 1.** Influences of reaction conditions on the equilibrium system of DRM.

Reaction conditions: (a) 0.1 MPa,  $\text{CO}_2/\text{CH}_4=1.0$ ; (b) 1123 K,  $\text{CO}_2/\text{CH}_4=1.0$ ;

(c) 1123 K, 0.1 MPa; (d) 1123 K, 0.1 MPa,  $\text{CO}_2/\text{CH}_4=1.2$ .

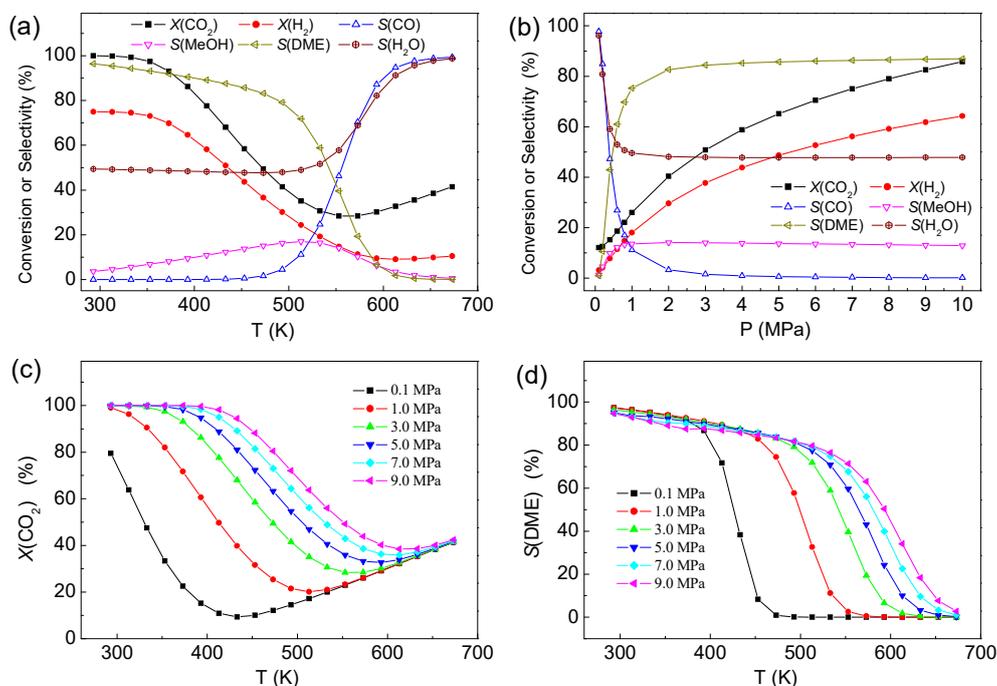
From Figure 1(d), with the increase of oxygen content in feed,  $\text{CH}_4$  conversion and CO selectivity increase, while  $\text{H}_2$  selectivity and  $\text{CO}_2$  conversion rate decreased. This is mainly because the reaction between  $\text{CH}_4$  and  $\text{O}_2$  occupies a dominant position. At the same time,  $\text{CO}_2$  conversion is obviously inhibited, which is because  $\text{O}_2$  reacts with part of CO in the syngas to form  $\text{CO}_2$ . The addition of oxygen in raw materials is beneficial to reduce carbon deposition. The  $\text{H}_2/\text{CO}$  molar ratio decreases slightly with the addition of oxygen in feed, but it is close to 1.0. The addition of oxygen has no significant effect on the composition of syngas. The suitable amount of oxygen was  $\text{O}_2/\text{CO}_2$  of 0.1-0.2.

### 3.2. $\text{CO}_2$ hydrogenation to DME

The effects of reaction conditions on the equilibrium material conversion and the product selectivity of  $\text{CO}_2$  hydrogenation to dimethyl ether were analyzed at temperature of 293-673 K, pressure of 0.1-10 MPa,  $\text{H}_2/\text{CO}_2$  molar ratio of 1-20 and adding water and CO to the feed.

**3.2.1. Effects of temperature and pressure.** Figure 2 shows the effects of temperature and pressure on the equilibrium products of  $\text{CO}_2$  hydrogenation to DME. From Figure 2(a), with the gradual increasing of reaction temperature, the equilibrium conversion of  $\text{CO}_2$  firstly decreases and then slightly increases, DME selectivity decrease, CO selectivity increase, and  $\text{CH}_3\text{OH}$  selectivity firstly increased and then reduce. The main reasons for these trends are that the reaction (10) of  $\text{CO}_2$  hydrogenation to dimethyl ether is the exothermic reaction and RWGS (2) is the endothermic reaction. The reactions (11,12) dominate at low temperature and so  $\text{CO}_2$  conversion decreases with increasing temperature. However, When the temperature rises to a certain range, RWGS has a high reaction rate, which affects CO selectivity and dominates  $\text{CO}_2$  conversion at high temperature [6]. Although  $\text{CH}_3\text{OH}$  selectivity increases and then decreases with increasing temperature, the amount of methanol is not dominant throughout the process. As shown in Figure 2(b-d), high pressure can improve the conversion of  $\text{CO}_2$  and  $\text{H}_2$ , DME selectivity and  $\text{CH}_3\text{OH}$  selectivity, while the CO selectivity is not improved. From the overall reaction (10), it can be seen that the reaction system is the reaction of decreasing molar number, which indicates that the increasing of pressure is beneficial to the direction of the product. Based on

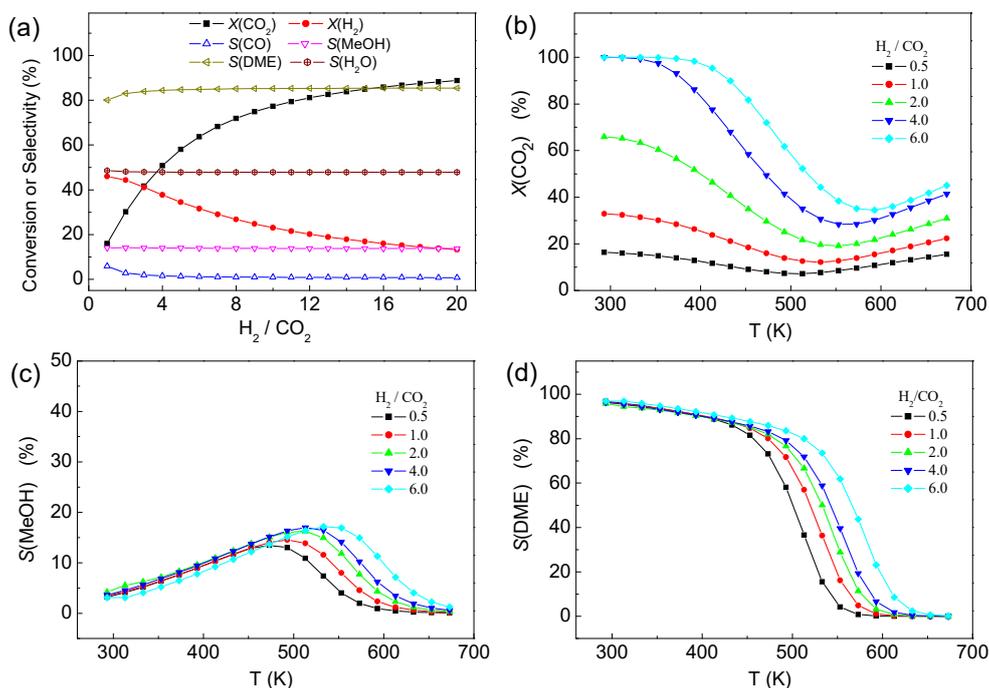
the above analysis and economic considerations, it is recommended that a typical CO<sub>2</sub> hydrogenation to DME process requires a lower temperature (< 600 K) and a higher pressure (2.0-6.0 MPa). This conclusion is close to the conclusion of the relevant study [6]. The synthesis of dimethyl ether is not suitable for high temperature conditions, which also requires that industrial catalysts must have good low temperature activity [7].



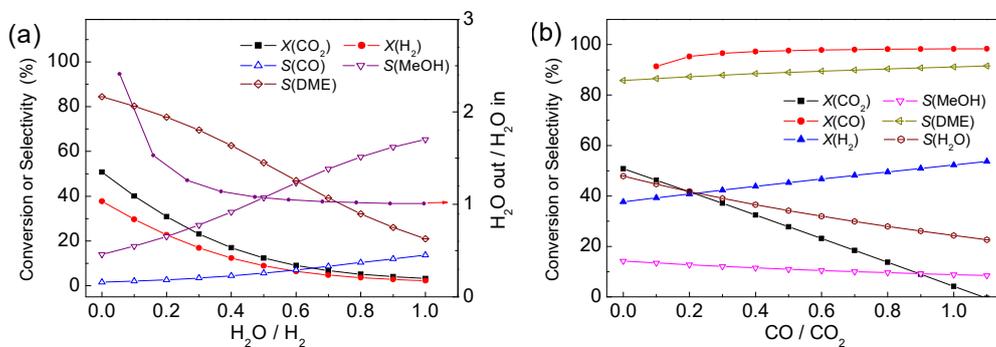
**Figure 2.** Effects of temperature and pressure on the equilibrium products of CO<sub>2</sub> hydrogenation to DME. (a, b)  $X$  or  $S_i$ ; (c)  $X(\text{CO}_2)$ ; (d)  $S(\text{DME})$ . Reaction conditions: (a) 3.0 MPa,  $\text{H}_2/\text{CO}_2=4$ ; (b) 473 K,  $\text{H}_2/\text{CO}_2=4$ ; (c-d)  $\text{H}_2/\text{CO}_2=4$ .

**3.2.2. Effect of  $\text{H}_2/\text{CO}_2$  molar ratio.** Figure 3 shows effect of  $\text{H}_2/\text{CO}_2$  molar ratio on equilibrium products of CO<sub>2</sub> hydrogenation to DME. From Figure 3, with the increase of  $\text{H}_2/\text{CO}_2$ , CO<sub>2</sub> conversion and the selectivity of dimethyl ether increase, the selectivity of CO decreases slightly. The selectivity of methanol does not change with  $\text{H}_2/\text{CO}_2$ . The results indicates that increasing the  $\text{H}_2/\text{CO}_2$  molar ratio is favorable for the hydrogenation reaction. However, when the hydrogen /carbon ratio is increased to 5.0, the selectivity of dimethyl ether increases slowly with the  $\text{H}_2/\text{CO}_2$  ratio. In order to save H<sub>2</sub> and obtain high CO<sub>2</sub> conversion and high DME selectivity, a reaction condition of less than 550 K and  $\text{H}_2/\text{CO}_2$  of 3.0-6.0 can be selected. The results of the  $\text{H}_2/\text{CO}_2$  molar ratio show that the actual hydrogen /carbon ratio in industrial production should be appropriately increased [10].

**3.2.3. Effect of H<sub>2</sub>O or CO addition in raw material.** There are more than H<sub>2</sub>, CO, CO<sub>2</sub> and H<sub>2</sub>O, DME, CH<sub>3</sub>OH of six product components in the actual reaction process because a portion of the gas, after separation of the product from the feed, is recycled to the reactor for reuse. Therefore, the feed gas also contains some of the recycled CO, water vapor and inert components in addition to H<sub>2</sub> and CO<sub>2</sub>, these components have an impact on the chemical balance. Figure 4 presents effect of H<sub>2</sub>O or CO addition of raw material on equilibrium products of CO<sub>2</sub> hydrogenation to DME.



**Figure 3** Effect of  $H_2/CO_2$  molar ratio on equilibrium products of  $CO_2$  hydrogenation to DME. (a)  $X$  or  $S_i$ ; (b)  $X(CO_2)$ ; (c)  $S(MeOH)$ ; (d)  $S(DME)$ . Reaction conditions: (a) 473 K, 3.0 MPa; (b-d) 3.0 MPa.



**Figure 4.** Effect of  $H_2O$  or  $CO$  addition of raw material on equilibrium products of  $CO_2$  hydrogenation to DME. Reaction conditions: 473 K, 3.0 MPa,  $H_2/CO_2=4.0$ .

From Figure 4(a),  $CO_2$  conversion and the selectivity of dimethyl ether decrease as the amount of  $H_2O$  in the feed increases, but  $CO$  selectivity and methanol selectivity increase. This is mainly because that the addition of water make the reverse transformations of reactions (2,10-12) occur. In order to obtain higher product selectivity, it is necessary to remove the generated water in time during the whole reaction. The rich water environment may also make it easier to grow  $Cu$  and  $ZnO$  grains in the copper-based methanol synthesis catalyst and destroy the acidic center of the methanol dehydration catalyst, causing the deactivation of the catalyst and thereby reducing the stability of synthesis catalyst.

Figure 4(b) show effects of  $CO$  addition on the equilibrium products. It can be seen that  $H_2$  conversion increases with the increasing of  $CO$  addition ratio. when  $CO$  is added in feed, water vapor shift reaction may occur. In addition, there may be a competitive reaction between  $CO$  hydrogenation and  $CO_2$  hydrogenation to methanol [9]. The addition of  $CO$  will improve the equilibrium yield of dimethyl ether. This is because increasing the  $CO$  content is equivalent to removing part of the water,

leading to a methanol synthesis reaction in the positive direction, which will slightly reduce the equilibrium yield of CH<sub>3</sub>OH and H<sub>2</sub>O. When the amount of CO in raw material is greater than the amount of CO<sub>2</sub>, the reaction process becomes the CO hydrogenation, and the CO hydrogenation to dimethyl ether is easier to react than the CO<sub>2</sub> hydrogenation to dimethyl ether.

### 3.3. Results comparison

This thermodynamic calculation results are compared with the relevant experimental results, listing Table 2. The results in Table 2 show that the conclusions of this study are consistent with the relevant research conclusions. It can be seen that the raw material conversion and the selectivity of target product in experimental tests are lower than those under thermodynamic optimization conditions, which indicates that the catalysts should be further improved to improve the performance of the catalysts for hydrogen production or hydrogenation reaction.

**Table 2.** Comparison of this calculation results with related research results.

Reaction type and conditions	Main research results	References
(1) Dry reforming of methane for H <sub>2</sub>		
0.5 wt.%Rh/MgO catalyst, 20.0 mg <sub>cat</sub> , T=1023 K, CH <sub>4</sub> /CO <sub>2</sub> =1.0, F=20 mL·min <sup>-1</sup> , Space velocity = 60 000 mL·h <sup>-1</sup> ·g <sup>-1</sup> .	X(CH <sub>4</sub> ) = 80.3 %, X(CO <sub>2</sub> ) = 85.8 %, H <sub>2</sub> /CO=0.92, CO yield = 83.1 %, H <sub>2</sub> yield =76.5 %,	[2]
10 wt.%Ni/Al <sub>2</sub> O <sub>3</sub> catalyst, T=1073K, 30 h.	X(CH <sub>4</sub> ) = 63.0 %, X(CO <sub>2</sub> ) = 69.0 %	[11]
Gibbs free energy minimization. T= 573-1473 K, P=0.1-2.5 MPa, CO <sub>2</sub> /CH <sub>4</sub> = 0.5-3.0. Syngas, C <sub>2</sub> , MeOH, DME and coke were considered.	Thermodynamic optimal conditions: temperature of 1073K, feed ratio of CO <sub>2</sub> :CH <sub>4</sub> :O <sub>2</sub> = 1:1:0.1, and atmospheric pressure.	[3]
Gibbs free energy minimization. T= 823-1473 K, P= 0.05-5 MPa, CH <sub>4</sub> /CO <sub>2</sub> = 0.5-2.0.	The optimum operating conditions for carbon free regime were T > 1273 K, CH <sub>4</sub> /CO <sub>2</sub> mole ratio of 1.0 and pressure of 0.1 MPa.	[4]
Gibbs free energy minimization. T= 550-1500 K, P= 0.04-1.2 MPa, CO <sub>2</sub> /CH <sub>4</sub> = 1.0-10, adding oxygen in raw materials. CH <sub>4</sub> , CO <sub>2</sub> , H <sub>2</sub> , CO, H <sub>2</sub> O and C(S) in the reaction system were considered.	The optimal conditions obtained: T= 950-1200 K, atmospheric pressure, CO <sub>2</sub> /CH <sub>4</sub> =1.0-1.5 and the proper oxygen addition (O <sub>2</sub> /CO <sub>2</sub> =0.1-0.2). At this condition, CO <sub>2</sub> conversion and the selectivity of H <sub>2</sub> and CO are higher than 90 %, H <sub>2</sub> /CO ratio was maintained near 1.0.	This study
(2) CO <sub>2</sub> /CO hydrogenation to DME		
CO <sub>2</sub> hydrogenation to DME: Cu-ZnO-ZrO <sub>2</sub> /HZSM-5 catalyst, T=513 K, P=3.0 MPa, GHSV = 9000 ML·g <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> .	The results show a superior DME productivity (4.4 mmol·kg <sub>cat</sub> <sup>-1</sup> ·s <sup>-1</sup> ) using the bifunctional catalyst prepared by physical mixing.	[5]
CO <sub>2</sub> /CO hydrogenation to DME: The method of equilibrium constants. T= 473-573 K, P= 3-10 MP, the initial CO <sub>2</sub> concentration in feed = 0-1.0.	If CO and H <sub>2</sub> O can be separated from the reaction system, the CO <sub>2</sub> hydrogenation process is suitable to produce a mixture of DME and methanol at low temperature.	[9]
DME synthesis from syngas. Thermodynamics: T=473-2673 K, P=2.0-5.0 MPa, H <sub>2</sub> /CO=1.0-2.0 Experiment: CuO/ZnO/Al <sub>2</sub> O <sub>3</sub> + H-ZSM-5 catalyst.	Theoretical model calculations are in good accordance with experimental values. High temperature, low pressure and high H <sub>2</sub> /CO ratio are favorable for CO hydrogenation to DME.	[12]
CO <sub>2</sub> hydrogenation to DME: Gibbs free energy minimization. T= 293-673 K, P= 0.1-10 MPa, H <sub>2</sub> /CO <sub>2</sub> =1-20. Adding a certain amount of water or CO to the raw material.	The optimization conditions obtained: T < 550 K, P=2.0-6.0 MPa, H <sub>2</sub> /CO <sub>2</sub> =3.0-6.0. The proper CO addition is in favour of the CO <sub>2</sub> hydrogenation to DME.	This study

## 4. Conclusions

In this paper, the thermodynamic analysis on methane dry reforming for H<sub>2</sub> and CO<sub>2</sub> hydrogenation to dimethyl ether was simulated. The effects of reaction temperature, pressure, feed molar ratio and the addition of third component in raw material on the equilibrium products were analyzed. The results of this study are compared with the relevant research results. The main conclusions obtained under the analysis conditions are as follows:

- (1) For the process of CO<sub>2</sub> reforming of methane, high temperature, low pressure and appropriate

feedstock ratio are beneficial to reforming hydrogen production. Thermodynamic optimization conditions are obtained: temperature range of 950-1200 K, atmospheric pressure,  $\text{CO}_2/\text{CH}_4$  of 1.0-1.5, and the suitable  $\text{O}_2/\text{CO}_2$  amount of 0.1-0.2. At the optimum condition, conversions and the selectivity of  $\text{H}_2$  and  $\text{CO}$  are higher than 90 %, the  $\text{H}_2/\text{CO}$  molar ratio was maintained near 1.0, and water formation and carbon deposition are minimal.

(2) For the process of  $\text{CO}_2$  hydrogenation to DME, low temperature and high pressure are beneficial to the  $\text{CO}_2$  hydrogenation. Thermodynamic optimization conditions with high raw material conversion and high DME selectivity were obtained: temperature below 550 K, higher pressure of 2.0-6.0 MPa and  $\text{H}_2/\text{CO}_2$  ratio of 3.0-6.0. The addition of  $\text{CO}$  is in favour of the  $\text{CO}_2$  hydrogenation to DME, while adding water is unfavorable to the reaction and it is necessary to remove the generated water in time.

(3) Compared the thermodynamic calculation results with the relevant research results, it can be seen that the conclusions of this study are consistent with the relevant research conclusions and the catalytic technology should be further developed to improve the performance of catalysts.

### Acknowledgements

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### Nomenclature

DRM— Dry ( $\text{CO}_2$ ) reforming of methane;  
 SRM— Steam reforming of methane;  
 RWGS— Reverse water gas shift reaction;  
 DME— Dimethyl ether;  
 MeOH— methanol;  
 $\Delta H_{298\text{ K}}$ — standard enthalpy change ( $\text{kJ}\cdot\text{mol}^{-1}$ );  
 T— Temperature (K);  
 P— Pressure (MPa);  
 X— Conversion;

$F, F_{i(C)}, F_{i,in}, F_{i,out}$ —molar flow rate ( $\text{mol}\cdot\text{s}^{-1}$ ). Subscripts of  $i, i(C), in$  and  $out$  are the  $i$ th species, carbonaceous species, feed, product, respectively.

$S_{i(C)}, S_{\text{H}_2\text{O}}$ —Selectivity of the carbonaceous product,  $\text{H}_2\text{O}$ , respectively.

$\lambda$ —The number of carbon atoms in the  $i$ th species in products;

$\text{CO}_2/\text{CH}_4, \text{H}_2/\text{CO}, \text{H}_2/\text{CO}_2, \text{O}_2/\text{CO}_2, \text{H}_2\text{O}/\text{H}_2, \text{CO}/\text{CO}_2$ —The mole ratio of the corresponding symbols respectively.

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