

Thermodynamic analysis on the CO₂ conversion processes of methane dry reforming for hydrogen production and CO₂ hydrogenation to dimethyl ether

Xinyi He¹, Liping Liu^{2*}

¹ School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

² School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, China

*The corresponding author's e-mail: zhenglip@163.com, tjuhexinyi@163.com (He).

Abstract. Based on the principle of Gibbs free energy minimization, the thermodynamic analysis on the CO₂ conversion processes of dry reforming of methane for H₂ and CO₂ 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, CO₂/CH₄ molar ratio of 1.0-1.5 and appropriate amount of oxygen are beneficial to the dry reforming of methane. For CO₂ hydrogenation to dimethyl ether, low temperature, high pressure, the appropriate H₂/CO₂ 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 CO₂ 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 CO₂ hydrogenation.

Biogas is a renewable and important secondary energy friendly to the environment, which is a gas mixture rich in CH₄ (50-70 vol.%) and CO₂ (25-40 vol.%) produced by digestion or fermentation of organic matter under anaerobic conditions. CH₄ and CO₂ 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 CH₄ and conversion of CO₂. 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. CO₂ 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.

CO₂ hydrogenation is an effective method to convert CO₂, 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/CO₂ hydrogenation to CH₃OH (MeOH) is currently relatively mature technology in the industry [7]. However, the synthesis of methanol by CO₂ 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. CO₂/CO hydrogenation catalysts and CO hydrogenation thermodynamic analysis have been mainly researched [6-9], however there are less researches on thermodynamics of CO₂ hydrogenation for DME.

Based on the purpose of conversion and utilization of CO₂, 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 H₂ and the process of CO₂ 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 ⁻¹)	Reaction explanation	No.
Dry reforming of methane for H ₂	CH ₄ + CO ₂ ↔ 2CO + 2H ₂	260.5	CO ₂ reforming of methane	(1)
	CO ₂ + H ₂ ↔ CO + H ₂ O	41.0	RWGS	(2)
	CH ₄ + H ₂ O ↔ CO + 3H ₂	206.0	Steam reforming of methane	(3)
	CH ₄ + 2H ₂ O ↔ CO ₂ + 4H ₂	165	Steam reforming of methane	(4)
	CH ₄ + 2O ₂ ↔ CO ₂ + 2H ₂ O	-802	Combustion of methane	(5)
	CH ₄ + 0.5O ₂ ↔ CO + 2H ₂	-36	Partial oxidation of methane	(6)
	CH ₄ ↔ C + 2H ₂	75.0	Decomposition of methane	(7)
	2CO ↔ CO ₂ + C	-172.5	Disproportionation reaction	(8)
	CO + H ₂ ↔ H ₂ O + C	-131.5	CO reduction	(9)
CO ₂ hydrogenation to DME	2CO ₂ + 6H ₂ ↔ CH ₃ OCH ₃ + 3H ₂ O	-122.2	Overall reaction	(10)
	CO ₂ + H ₂ ↔ CO + H ₂ O	41.0	RWGS	(2)
	CO ₂ + 3H ₂ ↔ CH ₃ OH + H ₂ O	-49.4	CO ₂ hydrogenation to MeOH	(11)
	2CH ₃ OH ↔ CH ₃ OCH ₃ + H ₂ O	-23.4	MeOH dehydration	(12)
	3CO + 3H ₂ ↔ CH ₃ OCH ₃ + CO ₂	-256.6	CO hydrogenation to DME	(13)

2.1.1. Dry reforming of methane for H₂. 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 H₂/CO<1.0 is suitable for synthesis of dimethyl ether.

2.1.2 CO₂ hydrogenation to DME. In the CO₂ hydrogenation to DME, there are three main reactions related: methanol synthesis from CO₂ 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 H₂O 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 Gibbs 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 H₂, the selected substances in system are CH₄, CO₂, H₂, CO, H₂O and C_(s), which belong to the coexistence of gas and solid phase. (2) For the reaction system of CO₂ hydrogenation to DME, CO₂, H₂, CO, H₂O, CH₃OH(MeOH) and CH₃OCH₃(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 (CH₄, CO₂, CO) and H₂, 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 λ is the number of carbon atoms in species i . S_{H_2O} is the selectivity of H₂O calculated according to the amount of transformed hydrogen.

3. Results and discussion

3.1. Dry reforming of methane for H₂

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), CO₂/CH₄ molar ratio (1.0-10) and O₂/CO₂ 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 CH₄ and CO₂ and the selectivity of CO and H₂ 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 H₂ selectivity. The molar ratio of H₂/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 CH₄ and CO₂, the selectivity of CO and H₂ 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 H₂/CO was 1.0-1.19 in the condition of changing the pressure reaction.

As shown in Figure 1(c), with the increase of CO₂/CH₄ value, CH₄ conversion of is higher and almost 100% conversion is achieved, while CO₂ conversion is a decreasing trend, indicating that CO₂ is excessive. There is a high conversion of raw material in the range of CO₂/CH₄=1.0-1.5. The molar ratio of H₂/CO decreases with the increase of CO₂/CH₄. Syngas with H₂/CO molar ratio close to 1.0 can be obtained at low CO₂/CH₄ molar ratio.

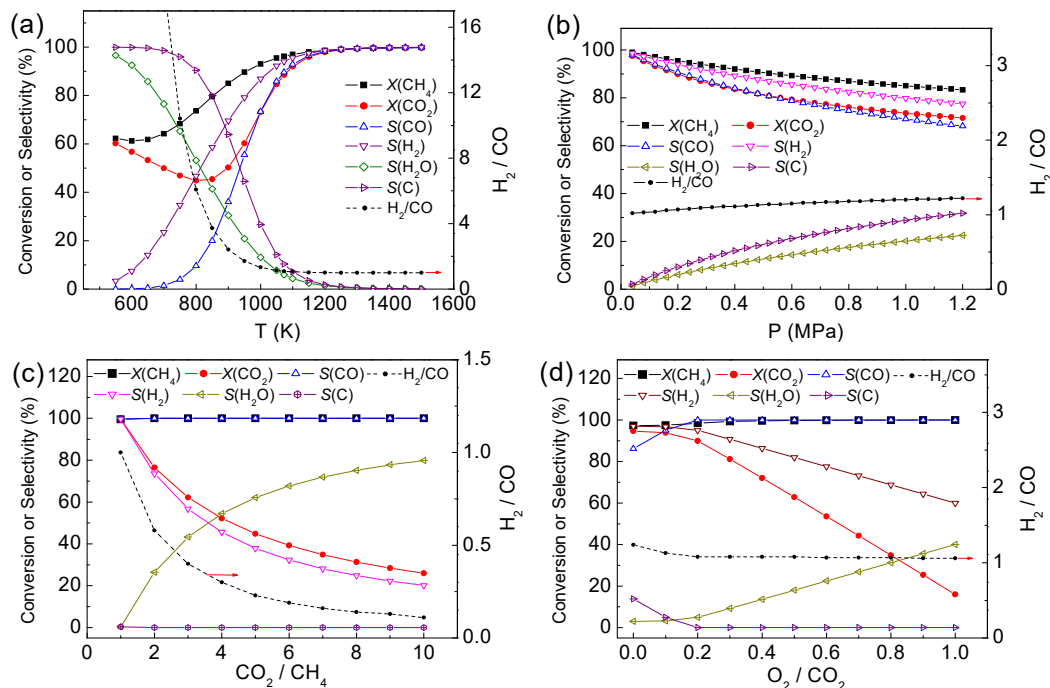


Figure 1. Influences of reaction conditions on the equilibrium system of DRM.

Reaction conditions: (a) 0.1 MPa, $CO_2/CH_4=1.0$; (b) 1123 K, $CO_2/CH_4=1.0$;

(c) 1123 K, 0.1 MPa; (d) 1123 K, 0.1 MPa, $CO_2/CH_4=1.2$.

From Figure 1(d), with the increase of oxygen content in feed, CH_4 conversion and CO selectivity increase, while H_2 selectivity and CO_2 conversion rate decreased. This is mainly because the reaction between CH_4 and O_2 occupies a dominant position. At the same time, CO_2 conversion is obviously inhibited, which is because O_2 reacts with part of CO in the syngas to form CO_2 . The addition of oxygen in raw materials is beneficial to reduce carbon deposition. The H_2/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 O_2/CO_2 of 0.1-0.2.

3.2. CO_2 hydrogenation to DME

The effects of reaction conditions on the equilibrium material conversion and the product selectivity of CO_2 hydrogenation to dimethyl ether were analyzed at temperature of 293-673 K, pressure of 0.1-10 MPa, H_2/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 CO_2 hydrogenation to DME. From Figure 2(a), with the gradual increasing of reaction temperature, the equilibrium conversion of CO_2 firstly decreases and then slightly increases, DME selectivity decrease, CO selectivity increase, and CH_3OH selectivity firstly increased and then reduce. The main reasons for these trends are that the reaction (10) of 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 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 CO_2 conversion at high temperature [6]. Although CH_3OH 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 CO_2 and H_2 , DME selectivity and CH_3OH 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 CO₂ 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].

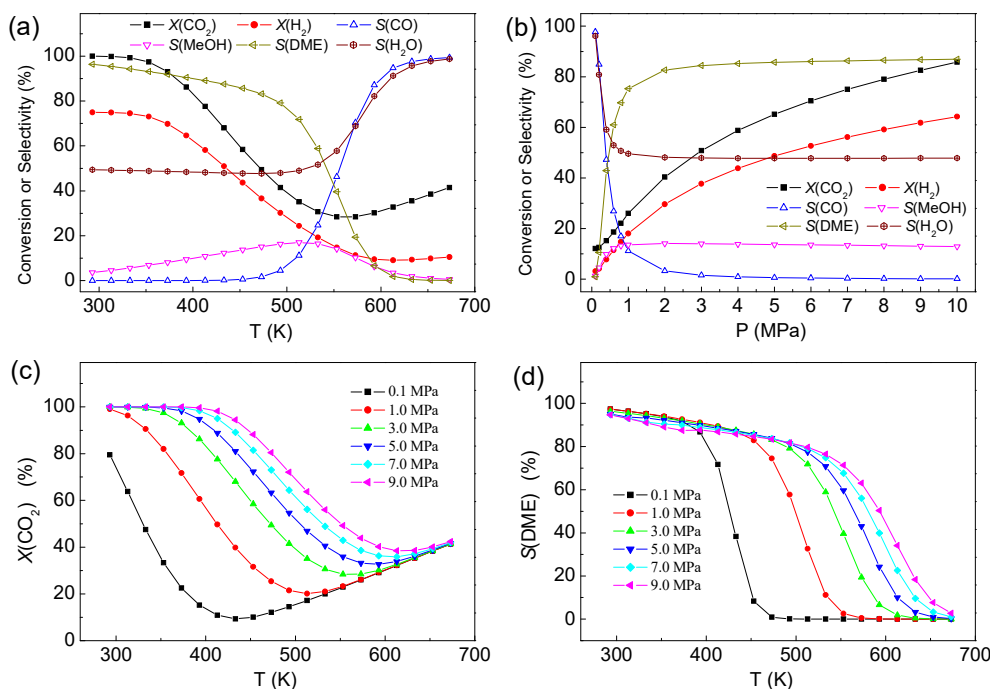


Figure 2. Effects of temperature and pressure on the equilibrium products of CO₂ hydrogenation to DME.

(a, b) X or S ; (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 H_2/CO_2 molar ratio. Figure 3 shows effect of H_2/CO_2 molar ratio on equilibrium products of CO₂ hydrogenation to DME. From Figure 3, with the increase of H_2/CO_2 , CO₂ conversion and the selectivity of dimethyl ether increase, the selectivity of CO decreases slightly. The selectivity of methanol does not change with H_2/CO_2 . The results indicates that increasing the H_2/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 H_2/CO_2 ratio. In order to save H₂ and obtain high CO₂ conversion and high DME selectivity, a reaction condition of less than 550 K and H_2/CO_2 of 3.0-6.0 can be selected. The results of the H_2/CO_2 molar ratio show that the actual hydrogen /carbon ratio in industrial production should be appropriately increased [10].

3.2.3. Effect of H₂O or CO addition in raw material. There are more than H₂, CO, CO₂ and H₂O, DME, CH₃OH 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 H₂ and CO₂, these components have an impact on the chemical balance. Figure 4 presents effect of H₂O or CO addition of raw material on equilibrium products of CO₂ hydrogenation to DME.

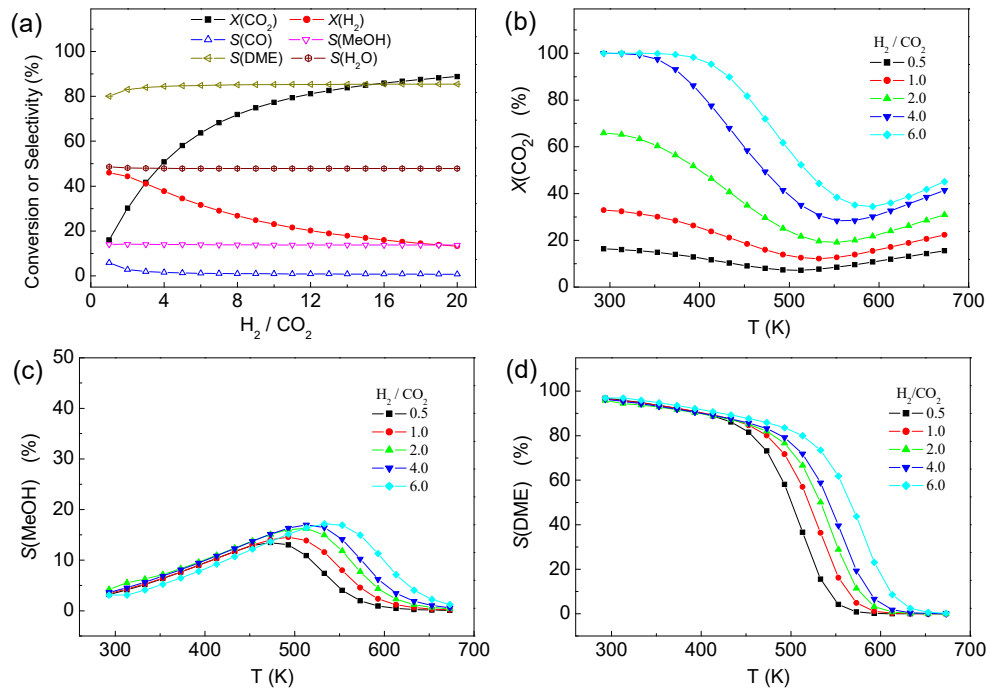


Figure 3 Effect of H_2/CO_2 molar ratio on equilibrium products of CO_2 hydrogenation to DME. (a) X or S ; (b) $X(CO_2)$; (c) $S(MeOH)$; (d) $S(DME)$. Reaction conditions: (a) 473 K, 3.0 MPa; (b-d) 3.0 MPa.

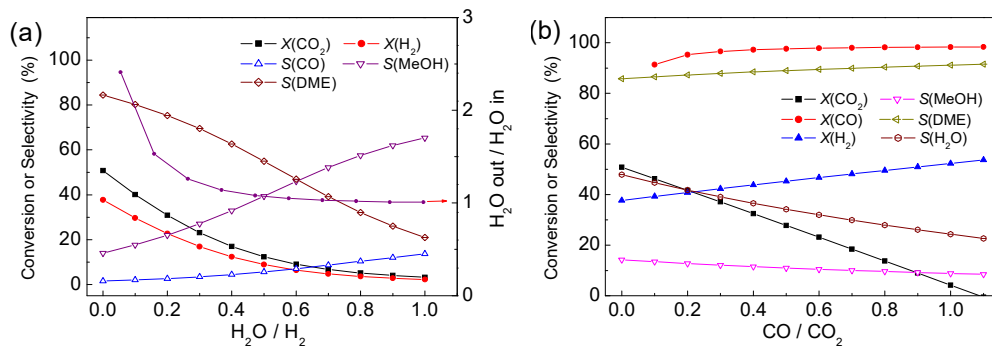


Figure 4. Effect of H_2O or CO addition of raw material on equilibrium products of CO_2 hydrogenation to DME. Reaction conditions: 473 K, 3.0 MPa, $H_2/CO_2=4.0$.

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_3OH and H_2O . When the amount of CO in raw material is greater than the amount of CO_2 , the reaction process becomes the CO hydrogenation, and the CO hydrogenation to dimethyl ether is easier to react than the CO_2 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_2		
0.5 wt.%Rh/MgO catalyst, 20.0 mg _{cat} , T=1023 K, $\text{CH}_4/\text{CO}_2=1.0$, $F=20 \text{ mL}\cdot\text{min}^{-1}$, Space velocity = 60 000 $\text{mL}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.	$X(\text{CH}_4) = 80.3 \%$, $X(\text{CO}_2) = 85.8 \%$, $\text{H}_2/\text{CO}=0.92$, CO yield = 83.1 %, H_2 yield =76.5 %,	[2]
10 wt.%Ni/ Al_2O_3 catalyst, T=1073K, 30 h.	$X(\text{CH}_4) = 63.0 \%$, $X(\text{CO}_2) = 69.0 \%$	[11]
Gibbs free energy minimization. T= 573-1473 K, P=0.1-2.5 MPa, $\text{CO}_2/\text{CH}_4 = 0.5$ -3.0. Syngas, C_2 , MeOH, DME and coke were considered.	Thermodynamic optimal conditions: temperature of 1073K, feed ratio of $\text{CO}_2:\text{CH}_4:\text{O}_2 = 1:1:0.1$, and atmospheric pressure.	[3]
Gibbs free energy minimization. T= 823-1473 K, P= 0.05-5 MPa, $\text{CH}_4/\text{CO}_2 = 0.5$ -2.0.	The optimum operating conditions for carbon free regime were T > 1273 K, CH_4/CO_2 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, $\text{CO}_2/\text{CH}_4 = 1.0$ -10, adding oxygen in raw materials. CH_4 , CO_2 , H_2 , CO, H_2O and C(S) in the reaction system were considered.	The optimal conditions obtained: T= 950-1200 K, atmospheric pressure, $\text{CO}_2/\text{CH}_4=1.0$ -1.5 and the proper oxygen addition ($\text{O}_2/\text{CO}_2=0.1$ -0.2). At this condition, CO_2 conversion and the selectivity of H_2 and CO are higher than 90 %, H_2/CO ratio was maintained near 1.0.	This study
(2) CO_2 /CO hydrogenation to DME		
CO_2 hydrogenation to DME: Cu-ZnO-ZrO ₂ /HZSM-5 catalyst, T=513 K, P=3.0 MPa, GHSV = 9000 $\text{ML}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$.	The results show a superior DME productivity (4.4 $\text{mmol}\cdot\text{kg}_{\text{cat}}^{-1}\cdot\text{s}^{-1}$) using the bifunctional catalyst prepared by physical mixing.	[5]
CO_2 /CO hydrogenation to DME: The method of equilibrium constants. T= 473-573 K, P= 3-10 MP, the initial CO_2 concentration in feed = 0-1.0.	If CO and H_2O can be separated from the reaction system, the CO_2 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, $\text{H}_2/\text{CO}=1.0$ -2.0 Experiment: CuO/ZnO/ Al_2O_3 + H-ZSM-5 catalyst.	Theoretical model calculations are in good accordance with experimental values. High temperature, low pressure and high H_2/CO ratio are favorable for CO hydrogenation to DME.	[12]
CO_2 hydrogenation to DME: Gibbs free energy minimization. T= 293-673 K, P= 0.1-10 MPa, $\text{H}_2/\text{CO}_2=1$ -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, $\text{H}_2/\text{CO}_2=3.0$ -6.0. The proper CO addition is in favour of the CO_2 hydrogenation to DME.	This study

4. Conclusions

In this paper, the thermodynamic analysis on methane dry reforming for H_2 and CO_2 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_2 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, CO_2/CH_4 of 1.0-1.5, and the suitable O_2/CO_2 amount of 0.1-0.2. At the optimum condition, conversions and the selectivity of H_2 and CO are higher than 90 %, the H_2/CO molar ratio was maintained near 1.0, and water formation and carbon deposition are minimal.

(2) For the process of CO_2 hydrogenation to DME, low temperature and high pressure are beneficial to the 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 H_2/CO_2 ratio of 3.0-6.0. The addition of CO is in favour of the 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

Financial supports from Key Research Projects of Higher Education in Henan province of China (15A480010) and the horizontal research project (20150100) are gratefully acknowledged.

Nomenclature

DRM— Dry (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, H_2O , respectively.

λ —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.

References

- [1] Safariamin M, Lucette H Tidahy, Abiaad E, Siffert S, & Aboukaïs A. 2009, *Comptes rendus - Chimie*, 12(6), 748-753.
- [2] Wang H Y, Ruckenstein E. 2000, *Applied Catalysis A General*, 204(1), 143-152.
- [3] Li Y, Jin B, & Xiao R. 2007, *Korean J. Chem. Eng.*, 24(4), 688-692.
- [4] Nikoo M K, & Amin N A S. 2011, *Fuel Process. Technol.*, 92(3), 678-691.
- [5] Cao P, Adegbite S, & Wu T. 2017, *Energy Procedia*, 105, 1864-1869.
- [6] Jia C, Gao J, Dai Y, Zhang J, & Yang Y. 2016, *Journal of Energy Chemistry*, 25(6), 1027-1037.
- [7] Matej Huš, Venkata D.B.C. Dasireddy, Neja Strah Štefančič, & Blaž Likozar. 2017, *Applied Catalysis B:environmental*, 207, 267-278.
- [8] Wang Z, Wang J, Ren F, Han M, & Jin Y. 2004, *Tsinghua Sci. Technol.*, 9(2), 168-176.
- [9] Guangxin Jia, Yisheng Tan, Yizhuo Han. 2006, *Ind. Eng. Chem. Res.*, 45(3), 1152-1159.
- [10] Botta G, Solimeo M, Leone P, & Aravind P V. 2015, *Fuel Cells*, 15(5), 669-681.
- [11] Hao Z, Zhu Q, Jiang Z, Hou B, & Li H. 2009, *Fuel Process. Technol.*, 90(1), 113-121.
- [12] Moradi G R, Ahmadvpour J, Yaripour F, & Wang J. 2011, *Can. J. Chem. Eng.*, 89(1), 108-115.