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

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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 | ΔΗ²⁹⁸ K (kJ·mol⁻¹) | Reaction explanation | No. |
|-----------------|-------------------|--------------------|----------------------|-----|
| Dry reforming of methane for H₂ | CH₄ + CO₂ ↔ 2CO + 2H₂ | 260.5 | CO₂ reforming of methane | (1) |
| | CO₂ + H₂ ↔ CO + H₂O | 41.0 | RWGS | (2) |
| | CH₄ + H₂O ↔ CO + 3H₂ | 206.0 | Steam reforming of methane | (3) |
| | CH₄ + 2H₂O ↔ CO₂ + 4H₂ | 165 | Steam reforming of methane | (4) |
| | CH₄ + 2O₂ ↔ CO₂ + 2H₂O | -802 | Combustion of methane | (5) |
| | CH₄ + 0.5O₂ ↔ CO + 2H₂ | -36 | Partial oxidation of methane | (6) |
| | CH₄ ↔ C + 2H₂ | 75.0 | Decomposition of methane | (7) |
| | 2CO ↔ CO₂ + C | -172.5 | Disproportionation reaction | (8) |
| | CO + H₂ ↔ H₂O + C | -131.5 | CO reduction | (9) |
| CO₂ hydrogenation to DME | 2CO₂ + 6H₂ ↔ CH₃OCH₃ + 3H₂O | -122.2 | Overall reaction | (10) |
| | CO₂ + H₂ ↔ CO + H₂O | 41.0 | RWGS | (2) |
| | CO₂ + 3H₂ ↔ CH₃OH + H₂O | -49.4 | CO₂ hydrogenation to MeOH | (11) |
| | 2CH₃OH ↔ CH₃OCH₃ + H₂O | -23.4 | MeOH dehydration | (12) |
| | 3CO + 3H₂ ↔ CH₃OCH₃ + CO₂ | -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.

\[
X_{(iC)} = \frac{(F_{(iC),in} - F_{(iC),out})}{F_{(iC),in}} \times 100\% \tag{14}
\]

\[
X_{(H2)} = \frac{(F_{H2,in} - F_{H2,out})}{F_{H2,in}} \times 100\% \tag{15}
\]

\[
S_{(iC)} = \frac{\lambda F_{(iC),in}}{(F_{(iC),in} - F_{(iC),out})} \times 100\% \tag{16}
\]

\[
S_{H2O} = \frac{2 F_{H2O}}{(F_{H2,in} - F_{H2,out})} \times 100\% \tag{17}
\]

In which, \(X_{(iC)}\) and \(X_{(H2)}\) 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. \(S_{(iC)}\) is the selectivity of carbonaceous substances, in which \(\lambda\) is the number of carbon atoms in species i. \(S_{H2O}\) 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.
From Figure 1(d), with the increase of oxygen content in feed, CH4 conversion and CO selectivity increase, while H2 selectivity and CO2 conversion rate decreased. This is mainly because the reaction between CH4 and O2 occupies a dominant position. At the same time, CO2 conversion is obviously inhibited, which is because O2 reacts with part of CO in the syngas to form CO2. The addition of oxygen in raw materials is beneficial to reduce carbon deposition. The H2/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 O2/CO2 of 0.1-0.2.

3.2. CO2 hydrogenation to DME
The effects of reaction conditions on the equilibrium material conversion and the product selectivity of CO2 hydrogenation to dimethyl ether were analyzed at temperature of 293-673 K, pressure of 0.1-10 MPa, H2/CO2 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 CO2 hydrogenation to DME. From Figure 2(a), with the gradual increasing of reaction temperature, the equilibrium conversion of CO2 firstly decreases and then slightly increases, DME selectivity decrease, CO selectivity increase, and CH3OH selectivity firstly increased and then reduce. The main reasons for these trends are that the reaction (10) of CO2 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 CO2 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 CO2 conversion at high temperature [6]. Although CH3OH 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 CO2 and H2, DME selectivity and CH3OH 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](image_url)

**Figure 2.** Effects of temperature and pressure on the equilibrium products of CO₂ hydrogenation to DME. (a, b) X or Si; (c) X(CO₂); (d) S(DME). Reaction conditions: (a) 3.0 MPa, H₂/CO₂=4; (b) 473 K, H₂/CO₂=4; (c-d) H₂/CO₂=4.

### 3.2.2. Effect of H₂/CO₂ molar ratio.

Figure 3 shows effect of H₂/CO₂ molar ratio on equilibrium products of CO₂ hydrogenation to DME. From Figure 3, with the increase of H₂/CO₂, CO₂ conversion and the selectivity of dimethyl ether increase, the selectivity of CO decreases slightly. The selectivity of methanol does not change with H₂/CO₂. The results indicates that increasing the H₂/CO₂ 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 H₂/CO₂ ratio. In order to save H₂ and obtain high CO₂ conversion and high DME selectivity, a reaction condition of less than 550 K and H₂/CO₂ of 3.0-6.0 can be selected. The results of the H₂/CO₂ 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 Si; (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$_2$O 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$_2$O 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 CH₃OH and H₂O. When the amount of CO in raw material is greater than the amount of CO₂, the reaction process becomes the CO hydrogenation, and the CO hydrogenation to dimethyl ether is easier to react than the CO₂ 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.

| Reaction type and conditions | Main research results | References |
|------------------------------|-----------------------|------------|
| (1) Dry reforming of methane for H₂ | \( X(\text{CH}_4) = 80.3\% \), \( X(\text{CO}_2) = 85.8\% \), \( H_2/CO=0.92 \), CO yield = 83.1\%, \( H_2 \) yield = 76.5\% | [2] |
| 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, \( \text{C}_2 \), MeOH, DME and coke were considered. | Thermodynamic optimal conditions: temperature of 1073K, feed ratio of \( \text{CO}_2/\text{CH}_4 = 1:1:0.1 \), and atmospheric pressure. | [3] |
| Gibbs free energy minimization, T= 823-1473 K, P=0.05-5 MPa, \( \text{CO}_2/\text{CH}_4 = 0.5-2.0 \). | The optimal operating conditions for carbon free regime were \( T > 1273 \) K, \( \text{CH}_4/\text{CO}_2 \) mole ratio of 1.0 and pressure of 0.1 MPa. | This study |
| CO₂ hydrogenation to DME: \( \text{Cu-ZnO-ZrO}_2 / HZSM-5 \) catalyst, T=513 K, P=3.0 MPa, GHSH = 9000 \( \text{NL·g}_{\text{cat}}^{-1} \cdot \text{h}^{-1} \). The results show a superior DME productivity (4.4 \( \text{nmol·kg}_{\text{cat}}^{-1} \cdot \text{s}^{-1} \)) using the bifunctional catalyst prepared by physical mixing. | [5] |
| CO₂/CO hydrogenation to DME: The method of equilibrium constants, T= 473-573 K, P=3-10 MP, the initial \( \text{CO}_2 \) concentration in feed = 0-1.0. If CO and \( \text{H}_2\text{O} \) can be separated from the reaction system, the CO₂ 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, \( H_2/CO=1.0-2.0 \). Experiment: \( \text{CuO/ZnO/Al}_2\text{O}_3 + H-ZSM-5 \) 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] |
| CO₂ hydrogenation to DME: Gibbs free energy minimization, T= 293-673 K, P=0.1-10 MPa, \( H_2/CO=3.0-6.0 \). 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, \( H_2/CO=3.0-6.0 \). The proper CO addition is in favour of the CO₂ hydrogenation to DME. | [This study] |

### 4. Conclusions

In this paper, the thermodynamic analysis on methane dry reforming for \( \text{H}_2 \) and \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 been 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.

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Nomenclature

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

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

$S_{i(C)}$, $S_{i(H_2O)}$—Selectivity of the carbonaceous product, H$_2$O, respectively.

$\lambda$—The number of carbon atoms in the ith species in products.

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

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