



# CO<sub>2</sub> Hydrogenation for Ethanol Production: A Thermodynamic Analysis

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**Abstract:** The thermodynamics of CO<sub>2</sub> hydrogenation to ethanol synthesis was analyzed by using the principle of Gibbs free energy minimization. According to the reaction mechanism, the product components of the reaction system were determined. The effects of reaction temperature, pressure and the molar ratio of hydrogen to carbon on the equilibrium products were investigated. The results show that methane has a high selectivity in equilibrium products. In order to analyze the influence of reaction conditions on the target product of ethanol, the thermodynamics of CO<sub>2</sub> hydrogenation was studied in methane free products. Since the process of CO<sub>2</sub> hydrogenation is accompanied by the CO hydrogenation reaction (FT synthesis), the CO hydrogenation process was also analyzed and compared with CO<sub>2</sub> hydrogenation. The results show that the CO hydrogenation has more advantages than the CO<sub>2</sub> hydrogenation, and that low temperature and high pressure can improve CO<sub>2</sub>/CO conversion and the selectivity of ethanol. The suitable H<sub>2</sub>/CO<sub>2</sub> molar ratio in the CO<sub>2</sub> hydrogenation is 3.0-5.0, while the suitable H<sub>2</sub>/CO molar ratio in the CO hydrogenation is 0.5-2.0. The comparison of the simulation results with the related experimental results shows that the hydrogenation catalyst needs to be developed continuously to improve the conversion of raw materials and the selectivity to the target product.

**Keywords:** Thermodynamics, CO<sub>2</sub> Hydrogenation, CO Hydrogenation, Ethanol, Methanol, Dimethyl Ether

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## 1. Introduction

The conversion of carbon dioxide into chemicals and fuels is an important way to reduce climate change and ocean acidification because CO<sub>2</sub> is an important greenhouse gas. In the process of CO<sub>2</sub> resource utilization, CO<sub>2</sub> catalytic hydrogenation is an important field of current C1 chemistry [1, 2]. CO<sub>2</sub> hydrogenation can produce a variety of products such as carbon monoxide, carboxylic acids, aldehydes, alcohols, and hydrocarbons [3-5]. The hydrogenation of CO<sub>2</sub> to methane technology is more mature. CO<sub>2</sub> hydrogenation to methanol, ethanol and dimethyl ether fuel is a promising technology. Methanol synthesis by CO<sub>2</sub> hydrogenation is an effective way to transform CO<sub>2</sub> in industry [6-10]. According to the reaction mechanism, the produced methanol can be further dehydrated to produce dimethyl ether, which can break the thermodynamic equilibrium of methanol synthesis and inhibit the side reaction through the produced water [11-14].

Ethanol is a kind of high quality power fuel, and the

development of fuel ethanol technology is one of the measures to reduce environmental pollution. At present, the methods of ethanol production are mainly crop fermentation and ethylene hydration method. The fermentation method uses corn and other grain crops as raw materials, which will be subject to food security and rising food prices. For the ethylene hydration method, a large amount of sulfuric acid is produced during ethylene hydration, which can corrode the equipment. Therefore, the development of CO<sub>2</sub>/CO hydrogenation to ethanol is of great significance.

The study of catalytic hydrogenation of CO<sub>2</sub> to low alcohols is focused on the development of catalysts and thermodynamic studies. Rh based catalysts were used for CO<sub>2</sub> hydrogenation and CO catalytic hydrogenation to ethanol [15-20]. There are few thermodynamic researches on the synthesis of ethanol by CO<sub>2</sub> hydrogenation. An experimental and thermodynamic study for CO<sub>2</sub> conversion to methane and CO using Cu-K/Al<sub>2</sub>O<sub>3</sub> catalyst has been

reported [21]. Jia et al [22] carried out the thermodynamics analysis and experimental validation for complicated systems in CO<sub>2</sub> hydrogenation process. The thermodynamic research on CO<sub>2</sub> hydrogenation to low alcohols is based on some reactions of the same type products, considering methanol, ethanol, propanol and C<sub>4</sub> alcohols in the products. However, the actual CO<sub>2</sub> hydrogenation process is complex and produces various products simultaneously. To analyze the real CO<sub>2</sub> hydrogenation process, the suitable hydrogenation process and reaction product components were selected based on the reaction mechanism. The thermodynamic analysis of the influence of reaction conditions on the equilibrium product system was carried out and compared with the experimental results.

## 2. Calculation Principles and Methods

### 2.1. Reaction Mechanism Analysis

CO<sub>2</sub> hydrogenation to ethanol passes through the intermediate substance CO (CO<sub>2</sub> + H<sub>2</sub> ↔ CO + H<sub>2</sub>O) and then continues to be hydrogenated by CO to ethanol. Kusama et al [23] studied the reaction mechanism of CO<sub>2</sub> hydrogenation to ethanol on Rh-Fe/SiO<sub>2</sub> catalyst, as shown in Figure 1.

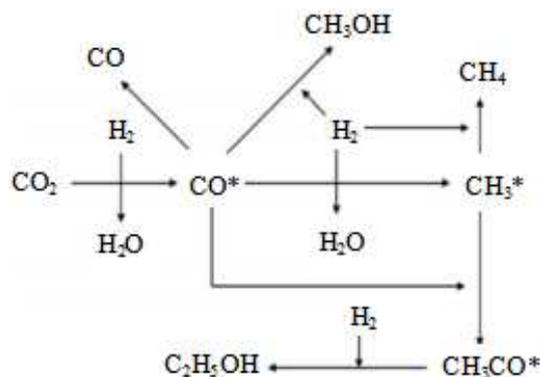


Figure 1. A possible reaction network of CO<sub>2</sub> hydrogenation [23].

Figure 1 presents a schematic diagram of the reaction network of the formation of CH<sub>4</sub>, CO, and ethanol during the hydrogenation of CO<sub>2</sub>. In the first step, CO<sub>2</sub> is adsorbed on the catalyst surface by the reverse water gas shift reaction. The adsorbed CO\* undergoes successive insertions of H to form an adsorbed CH<sub>3</sub>\* (methyl) and an adsorbed CH<sub>3</sub>CO\* (acyl) groups. The hydrogenation of CH<sub>3</sub>\* produces CH<sub>4</sub> and the acyl group hydrogenation leads to ethanol [15]. The main reactions occurring in the CO<sub>2</sub> hydrogenation system are shown in Table 1.

Table 1. The main reactions in the CO<sub>2</sub> hydrogenation system.

| No.  | Reaction Equation   | $\Delta G_{298\text{ K}}$<br>(KJ/mol) | $\Delta H_{298\text{ K}}$<br>(KJ/mol) | $K_{298\text{ K}}$    |
|------|---|---------------------------------------|---------------------------------------|-----------------------|
| (1)  | CO <sub>2</sub> + H <sub>2</sub> ↔ CO + H <sub>2</sub> O  | 28.6                                  | 41.1                                  | 9.67×10 <sup>-6</sup> |
| (2)  | CO + 3H <sub>2</sub> ↔ CH <sub>4</sub> + H <sub>2</sub> O   | -141.9                                | -206.0                                |                       |
| (3)  | CO <sub>2</sub> + 4H <sub>2</sub> ↔ CH <sub>4</sub> + 2H <sub>2</sub> O   | -113.5                                | -165.0                                | 7.79×10 <sup>19</sup> |
| (4)  | CO + 2H <sub>2</sub> ↔ CH <sub>3</sub> OH   |                                       | -90.4                                 |                       |
| (5)  | CO <sub>2</sub> + 3H <sub>2</sub> ↔ CH <sub>3</sub> OH + H <sub>2</sub> O                                       | 3.5                                   | -49.3                                 | 2.45×10 <sup>-1</sup> |
| (6)  | 2CH <sub>3</sub> OH ↔ CH <sub>3</sub> OCH <sub>3</sub> + H <sub>2</sub> O                                       |                                       | -24.52                                |                       |
| (7)  | CH <sub>3</sub> OCH <sub>3</sub> + CO ↔ CH <sub>3</sub> COOCH <sub>3</sub>                                      |                                       |                                       |                       |
| (8)  | CH <sub>3</sub> COOCH <sub>3</sub> + 2H <sub>2</sub> ↔ C <sub>2</sub> H <sub>5</sub> OH + CH <sub>3</sub> OH    |                                       |                                       |                       |
| (9)  | CH <sub>3</sub> OH + CO + 2H <sub>2</sub> ↔ C <sub>2</sub> H <sub>5</sub> OH + H <sub>2</sub> O                 | -97.0                                 | -165.1                                |                       |
| (10) | 2CH <sub>4</sub> + H <sub>2</sub> O ↔ C <sub>2</sub> H <sub>5</sub> OH + 2H <sub>2</sub>                        |                                       |                                       |                       |
| (11) | C <sub>2</sub> H <sub>5</sub> OH → CH <sub>3</sub> CHO + H <sub>2</sub> ↔ CH <sub>4</sub> + CO + H <sub>2</sub> |                                       |                                       |                       |
| (12) | 2CO + 4H <sub>2</sub> ↔ C <sub>2</sub> H <sub>5</sub> OH + H <sub>2</sub> O                                     | -221.1                                | -253.6                                |                       |
| (13) | 2CO <sub>2</sub> + 6H <sub>2</sub> ↔ C <sub>2</sub> H <sub>5</sub> OH + 3H <sub>2</sub> O                       | -32.4                                 | -86.7                                 | 4.70×10 <sup>5</sup>  |
| (14) | C <sub>2</sub> H <sub>5</sub> OH + 3H <sub>2</sub> O ↔ CH <sub>3</sub> COOH + 2H <sub>2</sub>                   |                                       |                                       |                       |
| (15) | 2CO <sub>2</sub> + 7H <sub>2</sub> ↔ C <sub>2</sub> H <sub>6</sub> + 4H <sub>2</sub> O                          | -78.7                                 | -132.1                                | 6.26×10 <sup>13</sup> |
| (16) | 3CO <sub>2</sub> + 10H <sub>2</sub> ↔ C <sub>3</sub> H <sub>8</sub> + 6H <sub>2</sub> O                         | -70.9                                 | -125.0                                | 2.64×10 <sup>12</sup> |
| (17) | CH <sub>4</sub> ↔ C + 2H <sub>2</sub>   |                                       | 74.9                                  |                       |
| (18) | 2CO ↔ CO <sub>2</sub> + C   |                                       | -172.5                                |                       |

F-T synthesis yields alkanes (C<sub>n</sub>H<sub>2n+2</sub>), olefins (C<sub>n</sub>H<sub>2n</sub>), alcohols (C<sub>n</sub>H<sub>2n+1</sub>OH), aldehydes (C<sub>n</sub>H<sub>2n+1</sub>COH) and carbon deposits (equation 18, 19). In the process of CO<sub>2</sub>/CO hydrogenation, methanation is easy to occur. Too high methane is not conducive to the synthesis of ethanol. In order to discuss the influence of reaction conditions on the target product system, the synthesis processes of CO<sub>2</sub> hydrogenation in the products containing methane and in the absence of methane were studied.

Since the process of CO<sub>2</sub> hydrogenation to ethanol is usually accompanied by the processes of CO hydrogenation and the hydrogenation of CO and dimethyl ether (DME) to ethanol synthesis, the following calculations were determined.

(a) CO<sub>2</sub>/(CO+DME) hydrogenation to ethanol products containing methane; (b) CO<sub>2</sub>/CO hydrogenation to ethanol products in the absence of methane.

### 2.2. Calculation Methods and Parameters

The Gibbs free energy minimization method is widely used to analyze the equilibrium composition of complex reaction systems. RGibbs reactor model was used by Aspen Plus software in this analysis. In thermodynamic analysis, it is assumed that all the equilibrium components are gas and do not take into account the influence of carbon deposition, implying that the reactions (17, 18) are not considered in Table 1. Considering the existence of nonideal gas in the

system, the Peng-Robinson equation of state is chosen.

In this simulation, the raw material conversion rate and the product selectivity were defined as follows, respectively.

$$X(\text{CO}_x) = [(F_{\text{CO}_x,\text{in}} - F_{\text{CO}_x,\text{out}}) / F_{\text{CO}_x,\text{in}}] \times 100\% \quad (1)$$

$$X(\text{H}_2) = [(F_{\text{H}_2,\text{in}} - F_{\text{H}_2,\text{out}}) / F_{\text{H}_2,\text{in}}] \times 100\% \quad (2)$$

$$S_i = [\lambda F_{i,\text{out}} / (F_{C,\text{in}} - F_{C,\text{out}})] \times 100\% \quad (3)$$

$$S_{\text{H}_2\text{O}} = [2F_{\text{H}_2\text{O}} / (F_{\text{H}_2,\text{in}} - F_{\text{H}_2,\text{out}})] \times 100\% \quad (4)$$

Among which,  $X(\text{CO}_x)$  and  $X(\text{H}_2)$  are the conversion rates of 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 respectively indicate the state of being in and out.  $S_i$  is the selectivity of carbonaceous substances, in which  $\lambda$  is the number of carbon atoms in species  $i$ .  $S_{\text{H}_2\text{O}}$  is the selectivity of H<sub>2</sub>O calculated according to transformed H<sub>2</sub>.

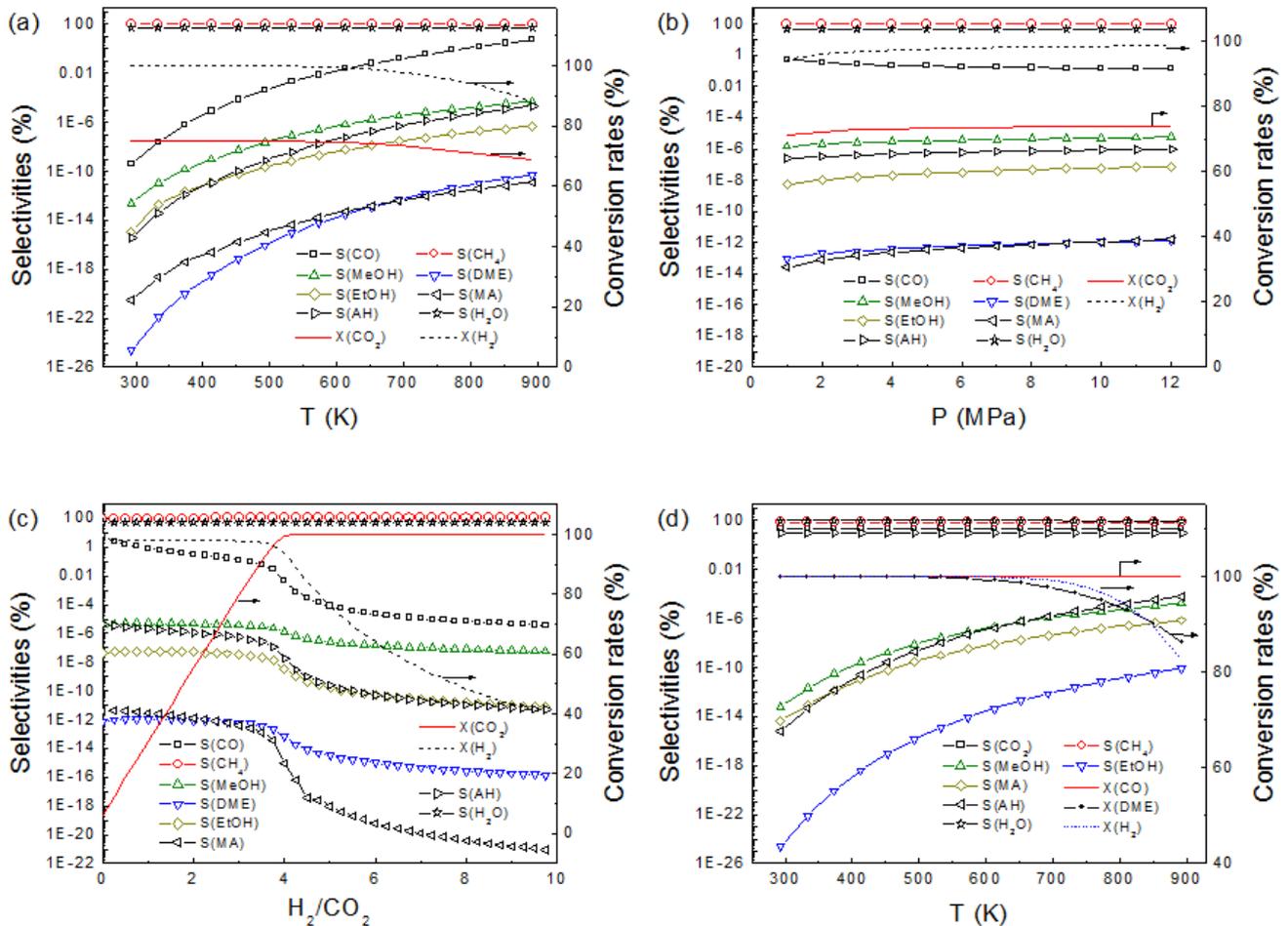
The equilibrium product yield can be defined by the equation of  $Y_i = X(\text{CO}_x) \cdot S_i$ , indicating that  $Y_i$  can be determined by the rate of raw material conversion and the selectivity of the product [24]. Therefore, the effects of reaction conditions on the conversion of raw materials and the selectivity of products were discussed.

### 3. Results and Discussion

#### 3.1. CO<sub>2</sub>/(CO+DME) Hydrogenation to Ethanol Products Containing Methane

For the processes of CO<sub>2</sub> hydrogenation and CO+DME hydrogenation to synthesize ethanol, according to the reaction mechanism in Figure 1 and the equation (1-13) in Table 1, the determined components and their codes of the reaction system were respectively as follows: CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, CH<sub>3</sub>OH (MeOH), CH<sub>3</sub>OCH<sub>3</sub> (DME), C<sub>2</sub>H<sub>5</sub>OH (EtOH), CH<sub>3</sub>COOCH<sub>3</sub> (MA), CH<sub>3</sub>CHO (AH) and CH<sub>4</sub>.

Figure 2 shows the effects of reaction conditions on CO<sub>2</sub>/(CO+DME) hydrogenated products containing methane. As can be seen from Figure 2, for CO<sub>2</sub> hydrogenation and CO+DME hydrogenation, the amount of CH<sub>4</sub> in the equilibrium composition is relatively large. Under the reaction conditions, the selectivity of CH<sub>4</sub> is close to 100%, while the amount of other products is relatively low, which suggests that the reaction is largely thermodynamically beneficial to methanation [25]. For the reaction (3) of (CO<sub>2</sub> + 4H<sub>2</sub> ↔ CH<sub>4</sub> + 2H<sub>2</sub>O), the reaction is exothermic and the equilibrium constant is in the order of 10<sup>19</sup> in standard condition. At other temperatures, the equation (3) also has high reaction equilibrium constants.



**Figure 2.** Effects of reaction conditions on CO<sub>2</sub>/(CO+DME) hydrogenated products containing methane. (a, b, c) CO<sub>2</sub> hydrogenation; (d) CO+DME hydrogenation. Reaction conditions: (a) 6.0 MPa, H<sub>2</sub>/CO<sub>2</sub> = 3.0; (b) 693 K, H<sub>2</sub>/CO<sub>2</sub> = 3.0; (c) 693 K, 7.0 MPa; (d) 6.0 MPa, H<sub>2</sub>:CO:DME = 2:1:1.

As shown in Figure 2(a), for CO<sub>2</sub> hydrogenation, with the increase of the reaction temperature, the equilibrium conversion rate of carbon dioxide and hydrogen decreases, and the selectivity of CO increases. The amount of other oxygenated compounds is very low, but their selectivities increase with increasing reaction temperature, and the selectivity of methanol is slightly higher than that of ethanol. The amount of other oxygenated compounds is small, but their selectivity increases with reaction temperature.

As shown in Figure 2(b), increasing the reaction pressure can increase the conversion rate of raw materials and the selectivity of products. It is shown that the total reaction is a reaction of reduced pressure, which can also be seen from several major reactions (3, 5, 13) in Table 1. Increasing the pressure is beneficial to hydrogenation. However, the reaction pressure will affect the equipment investment, production cost and safety, so the working pressure should be properly chosen.

As illustrated in Figure 2(c), feed composition influences its conversion rate and the product selectivity. In the CO<sub>2</sub> hydrogenation process, the CO<sub>2</sub> conversion rate increases with the increase of H<sub>2</sub>/CO<sub>2</sub>. After H<sub>2</sub>/CO<sub>2</sub> to 4.0, the conversion rate of CO<sub>2</sub> can reach 100%, and the H<sub>2</sub> conversion rate and CO selectivity decrease obviously due to hydrogen excess. In H<sub>2</sub>/CO<sub>2</sub> range of 0-10, the selectivity of methane is close to 100%, the selectivity of H<sub>2</sub>O is also high, and the selectivity of other products is very low. The appropriate H<sub>2</sub>/CO<sub>2</sub> ratio is 3.0-5.0.

As shown in Figure 2(d), in the CO+DME hydrogenation process, the conversion rate of CO is close to 100%, but the conversion of DME and H<sub>2</sub> decrease with the increase of temperature. Under the reaction conditions, the selectivities of methane, water and CO<sub>2</sub> are high and the selectivity of other

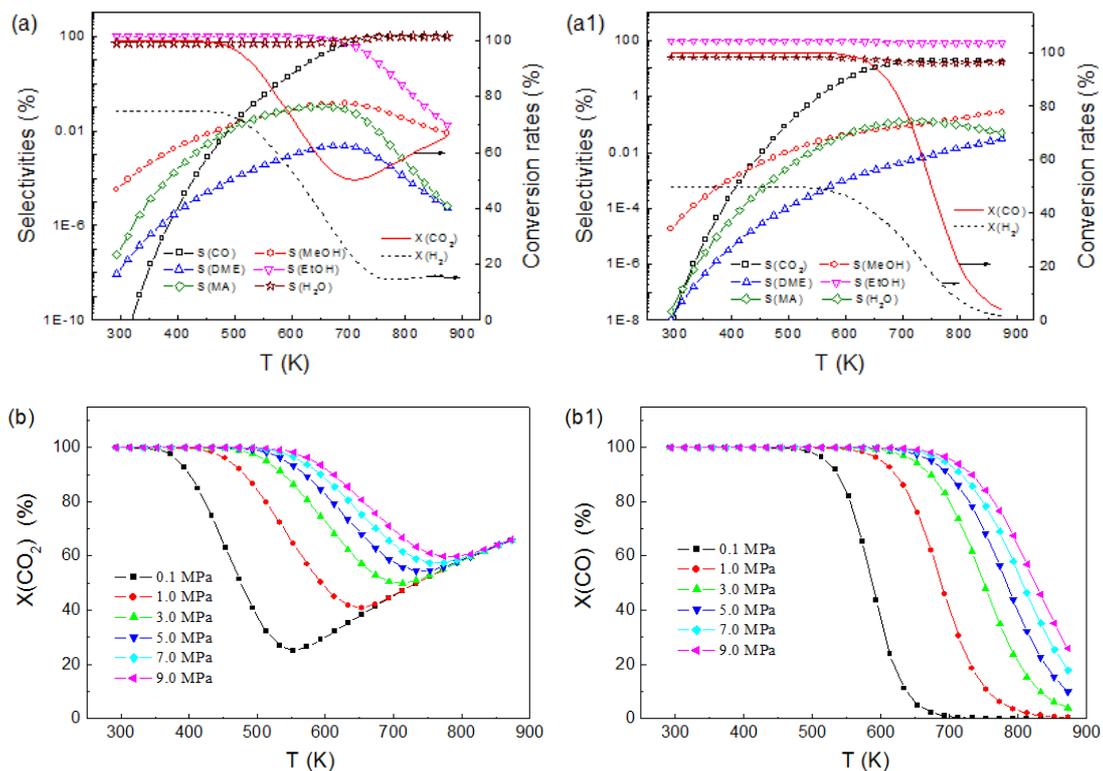
substances is very low, but they also show a tendency to increase with the increase of the reaction temperature. The effects of pressure and the molar ratio of hydrogen to carbon on the equilibrium product of CO+DME hydrogenation are similar to that of CO<sub>2</sub> hydrogenation (Figures omitted). The results of Figure 2(a, d) show that the hydrogenation of CO<sub>2</sub> and CO+DME hydrogenation are exothermic reactions, and the water gas shift and its reverse reactions are dominant in the reaction. To improve the conversion rate of raw materials, the reaction should be carried out at low temperature.

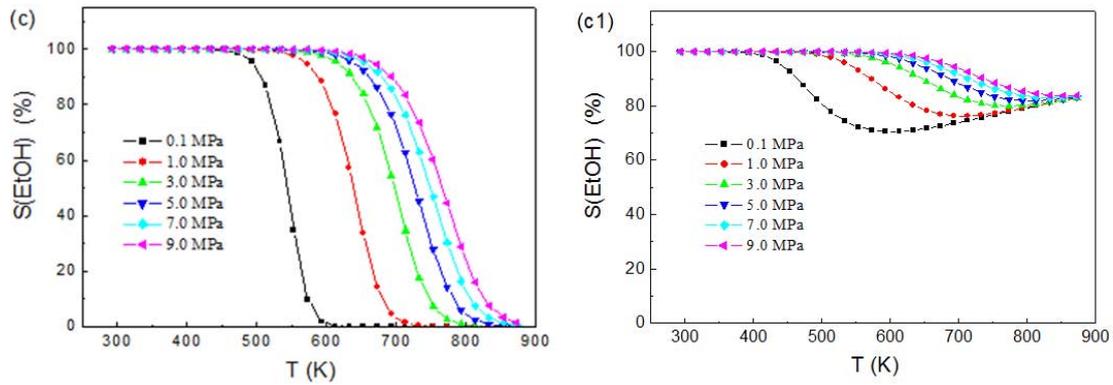
### 3.2. CO<sub>2</sub>/CO Hydrogenated Products in the Absence of Methane

In order to analyze the influence of reaction conditions on the target products of CO<sub>2</sub> hydrogenation and CO hydrogenation in detail, the thermodynamic analysis of the processes of CO<sub>2</sub> hydrogenation and CO hydrogenation to ethanol was carried out without considering methane in products. According to the reaction mechanism of Figure 1 and the reaction (4-9) and (12, 13) in Table 1, the material compositions of the reaction system were selected: CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, CH<sub>3</sub>OH (MeOH), CH<sub>3</sub>OCH<sub>3</sub> (DME), C<sub>2</sub>H<sub>5</sub>OH (EtOH) and CH<sub>3</sub>COOCH<sub>3</sub> (MA). The calculated conditions are as follows: the reaction temperature is 293-873 K, the reaction pressure is 0.1-9.0 MPa, and the molar ratio of H/C is 0.5-10.

#### 3.2.1. Effects of Temperature and Pressure

The effects of reaction temperature and pressure on the synthesis equilibrium products in the absence of methane by CO<sub>2</sub>/CO hydrogenation are shown in Figure 3.





**Figure 3.** Effects of temperature and pressure on the synthesis equilibrium products in the absence of methane by CO<sub>2</sub> hydrogenation (a, b, c) and CO hydrogenation (a1, b1, c1). Reaction condition: (a) 3.0 MPa, H<sub>2</sub>/CO<sub>2</sub>=4.0; (a1) 3.0 MPa, H<sub>2</sub>/CO=4.0; (b, c) H<sub>2</sub>/CO<sub>2</sub>=4.0; (b1, c1) H<sub>2</sub>/CO=4.0.

As shown in Figure 3(a, b, c), for CO<sub>2</sub> hydrogenation, the equilibrium transformation of CO<sub>2</sub> decreases first and then increases with the increase of the reaction temperature. At a certain temperature, increasing the pressure is beneficial to increase the conversion rate of CO<sub>2</sub>. In Figure 3(a), the conversion of hydrogen decreased from 75% to a minimum value of 15% at about 750 K, and then slightly increased. The selectivity of CO increases with the increase of temperature. As shown in Figure 3(a, c), the selectivity of ethanol is close to 100% at low temperature. The selectivity of ethanol decreases with the increase of temperature. Increasing the pressure is beneficial to the temperature range of high ethanol selectivity. The selectivity of ethanol is higher than that of methanol in thermodynamics [22], which can be explained by the equilibrium constant of ethanol synthesis from CO<sub>2</sub> hydrogenation in Table 1 above the corresponding value of methanol synthesis. The selectivities of CH<sub>3</sub>OH, CH<sub>3</sub>OCH<sub>3</sub> and CH<sub>3</sub>COOCH<sub>3</sub> are low, and their selectivities increases first and then decreases with the increase of temperature.

The main reasons for the above trend is that the synthesis of methanol, ethanol and dimethyl ether are all exothermic reactions and the reverse water gas shift reaction (RWGS) is an endothermic reaction. The hydrogenation reaction is dominant at low temperature and the reverse water gas shift reaction is not dominant, showing the conversion rate of CO<sub>2</sub> decrease with the increase of temperature. When the temperature rises to a certain extent, the reaction rate of

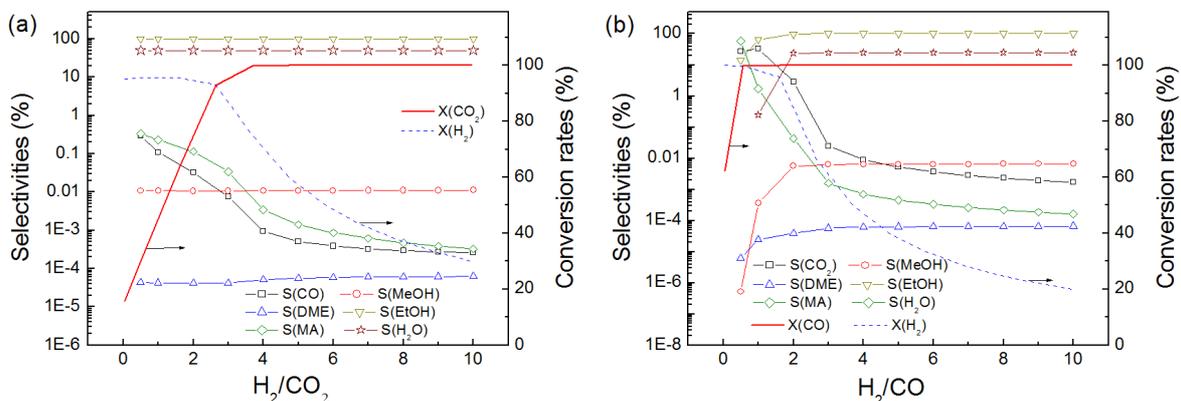
reverse water gas shift will be higher than that of hydrogenation reaction, the CO<sub>2</sub> conversion rate is increased with the increase of temperature [22]. Therefore, according to this thermodynamic result, CO<sub>2</sub> hydrogenation synthesis is not suitable for under high temperature conditions, and this requires that industrial hydrogenation catalyst must have good low temperature activity.

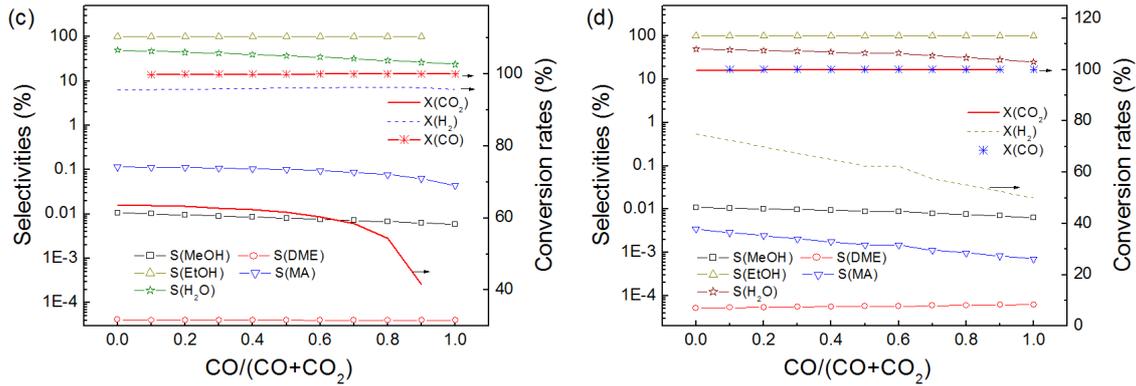
As shown in Figure 3(a1, b1, c1), the reaction rule of CO hydrogenation is slightly different from that of CO<sub>2</sub> hydrogenation. In Figure 4(a1), the CO conversion rate is close to 100% at low temperature. When the temperature is above 650 K, the conversion rate of CO decreases rapidly with the increase of temperature, and the conversion rate of hydrogen shows a similar trend. The selectivities of ethanol and water decrease slightly with the increase of temperature. The reason for this phenomenon is that the main reaction is controlled by water vapor shift reaction at high temperature.

As illustrated in Figure 3(b1, c1), Increasing the pressure is beneficial to increase the conversion rate of CO and the selectivity of ethanol. However, when the pressure is higher than 5.0 MPa, the increase of the pressure can not significantly increase the conversion of CO and the selectivity of ethanol.

### 3.2.2. Effect of Raw Material Composition

The effect of raw material composition on the synthesis of ethanol balanced products in the absence of methane by CO<sub>2</sub>/CO hydrogenation is shown in Figure 4.





**Figure 4.** Effect of raw material composition on the synthesis equilibrium products in the absence of methane by  $\text{CO}_2$  hydrogenation (a),  $\text{CO}$  hydrogenation (b) and  $(\text{CO}_2+\text{CO})$  hydrogenation (c, d). Reaction condition: 5.0 MPa, 473 K, in addition, (c)  $\text{H}_2/(\text{CO}+\text{CO}_2)=2.0$ , (d)  $\text{H}_2/(\text{CO}+\text{CO}_2)=4.0$ .

As shown in Figure 4(a, b), the material composition has a great influence on the  $\text{CO}_2/\text{CO}$  hydrogenation process. Under the reaction conditions of 5.0 MPa and 473 K, the conversion rate of  $\text{CO}_2$  increases with the change of  $\text{H}_2/\text{CO}_2$  from 0 to 4.0, and when  $\text{H}_2/\text{CO}_2$  is above 4.0, the conversion rate of  $\text{CO}_2$  almost reach 100% in thermodynamics.  $\text{CO}$  hydrogenation also showed a similar pattern.

As illustrated in Figure 4(c), under a certain condition of hydrogen to carbon ratio, both  $\text{CO}$  and  $\text{H}_2$  have high conversion rates with the increase of  $\text{CO}$  content in carbon source. However, the conversion rate of  $\text{CO}_2$  decreases with

the increase of  $\text{CO}$  content in the raw material, which shows that  $\text{CO}$  is easier to convert than  $\text{CO}_2$ .

As shown in Figure 4(d), in the case of hydrogen to carbon ratio of 4.0, due to the relatively sufficient hydrogen content,  $\text{CO}$  and  $\text{CO}_2$  have high conversion rates with the increase of  $\text{CO}$  content, that is, they are basically transformed in thermodynamics. But the conversion rate of  $\text{H}_2$  is low, which is mainly due to the occurrence of water gas shift reaction. The amount of  $\text{CO}_2$  is completely transformed, but the  $\text{H}_2$  conversion rate decreases due to the excess hydrogen.

**Table 2.** Comparison of  $\text{CO}_2/\text{CO}$  hydrogenation calculation results with experimental results.

| Experimental results            |   |   |  |   | Calculation results  |                          |  |  |  |
|---------------------------------|---|---|--|---|--|--------------------------|--|--|--|
| References                      | Catalyst  | Reaction conditions   | Conversion rates (%)   | Selectivities (%)   | Calculation conditions   | Conversion rates (%)     | Selectivities (%)  |  |  |
| (1) $\text{CO}_2$ hydrogenation |   |   |  |   |  |                          |  |  |  |
| [15]                            | 2%Rh<br>-2.5%Fe/TiO <sub>2</sub>                | 543 K, 1.0 MPa,<br>$\text{H}_2/\text{CO}_2=1.0$ ,<br>0.15 g <sub>cat</sub> ,<br>WHSV<br>=8000 cm <sup>3</sup> /(g <sub>cat</sub> h) | X(CO <sub>2</sub> ) 6.48   | CH <sub>4</sub> 58.7<br>C <sub>2</sub> H <sub>6</sub> +C <sub>3</sub> H <sub>8</sub> +C <sub>4</sub> H <sub>10</sub> 5.88<br>AH, CO 0.44, 29.3<br>MeOH, EtOH 1.28, 4.37 | 533 K,<br>1.0 MPa,<br>$\text{H}_2/\text{CO}_2=3.0$                           | X(CO <sub>2</sub> ) 74.6 | CH <sub>4</sub> 100  |  |  |
| [15]                            | 2%Rh/TiO <sub>2</sub>                           | 543 K, 2.0 MPa,<br>$\text{H}_2/\text{CO}_2=1.0$ ,<br>0.15 g <sub>cat</sub> ,<br>WHSV<br>=8000 cm <sup>3</sup> /(g <sub>cat</sub> h) | X(CO <sub>2</sub> ) 19.2   | CH <sub>4</sub> 93.3<br>C <sub>2</sub> H <sub>6</sub> +C <sub>3</sub> H <sub>8</sub> +C <sub>4</sub> H <sub>10</sub> 5.18<br>AH, CO 0, 4.16<br>MeOH, EtOH 0, 0          | 533 K,<br>3.0 MPa,<br>$\text{H}_2/\text{CO}_2=3.0$                           | X(CO <sub>2</sub> ) 74.8 | CH <sub>4</sub> 100  |  |  |
| [16]                            | 5 wt%Rh<br>-Co-Na<br>(1:1:0.5)/SiO <sub>2</sub> | 533 K, 5.0 MPa,<br>$\text{H}_2/\text{CO}_2=3.0$ ,<br>Flow rate<br>=100cm <sup>3</sup> /min  | X(CO <sub>2</sub> ) 19.8   | CH <sub>4</sub> 36.7<br>C <sub>2</sub> H <sub>6</sub> +C <sub>3</sub> H <sub>8</sub> 14.2<br>MeOH, EtOH 2.0, 8.7<br>CO 27.1   | 533 K,<br>5.0 MPa,<br>$\text{H}_2/\text{CO}_2=4.0$<br>(CH <sub>4</sub> free) | X(CO <sub>2</sub> ) 96.4 | MeOH 0.03<br>EtOH 99.9<br>MA 0.02<br>CO 0.05<br>DME 0              |  |  |
| [16]                            | 5 wt% Rh-Co<br>(1:1)/SiO <sub>2</sub>           | 533 K, 5.0 MPa,<br>$\text{H}_2/\text{CO}_2=3.0$ ,<br>Flow rate<br>=100 cm <sup>3</sup> /min   | X(CO <sub>2</sub> ) 25.2   | CH <sub>4</sub> 73.0<br>C <sub>2</sub> H <sub>6</sub> +C <sub>3</sub> H <sub>8</sub> 2.5<br>MeOH, EtOH 13.4, 1.2<br>CO 9.8  | 533 K,<br>6.0 MPa,<br>$\text{H}_2/\text{CO}_2=3.0$                           | X(CO <sub>2</sub> ) 74.9 | CH <sub>4</sub> 100<br>CO 0.002                                    |  |  |
| [17]                            | Rh <sub>10</sub> Se/TiO <sub>2</sub>            | 523 K,<br>0.047 MPa,<br>$\text{H}_2/\text{CO}_2=2.0$  |  | EtOH 83.0   | 533 K,<br>0.1 MPa,<br>$\text{H}_2/\text{CO}_2=4.0$<br>(CH <sub>4</sub> free) | X(CO <sub>2</sub> ) 27.0 | MeOH 0.024<br>EtOH 66.6<br>MA 0.03<br>DME 0<br>CO 33.3             |  |  |
| (2) $\text{CO}$ hydrogenation   |   |   |  |   |  |                          |  |  |  |
| [18]                            | RMLF/CNTs                                       | 593 K,<br>3.0 MPa,<br>$\text{H}_2/\text{CO}=2.0$  | X(CO) 5.16   | CH <sub>4</sub> 14.6<br>C <sub>2+</sub> hydrocarbons 12.5<br>C <sub>2+</sub> oxygenates 52.4<br>MeOH, CO <sub>2</sub> 1.5, 19.0   | 573 K,<br>3.0 MPa,<br>$\text{H}_2/\text{CO}=3.0$                             | X(CO) 74.6               | CH <sub>4</sub> 99.99<br>CO 0.01                                   |  |  |
| [19]                            | 2%Rh<br>-2%Ce/SiO <sub>2</sub>                  | 453 K, 0.1 MPa,<br>$\text{H}_2/\text{CO}=1.2$ ,<br>0.2 g <sub>cat</sub> , 8 h<br>30 cm <sup>3</sup> /min,                           | Activity<br>(μmol/<br>(g·h))<br>CO<br>amount<br>converte<br>d=20.9 | CH <sub>4</sub> 30.8<br>MeOH 12.0<br>EtOH 16.6<br>AH 8.7<br>C <sub>2</sub> oxygenates 25.3  | 543 K,<br>0.1 MPa,<br>$\text{H}_2/\text{CO}_2=1.0$<br>(CH <sub>4</sub> free) | X(CO) 91.85              | MeOH 0.01<br>EtOH 74.5<br>MA 0.04<br>DME 0<br>CO <sub>2</sub> 25.5 |  |  |

By comparing CO<sub>2</sub> hydrogenation with CO hydrogenation, it can be concluded that CO hydrogenation has advantages over CO<sub>2</sub> hydrogenation [24]. CO hydrogenation have high conversion rate and wider temperature range with higher ethanol selectivity. The thermodynamic optimization conditions are as follows. For the CO hydrogenation reaction, the temperature is below 650 K, the pressure is 1.0-5.0 MPa, and the H<sub>2</sub>/CO molar ratio is 0.5-2.0. For the CO<sub>2</sub> hydrogenation, the temperature is below 500 K, the pressure is 1.0-5.0 MPa, and the H<sub>2</sub>/CO<sub>2</sub> molar ratio is 3.0-5.0.

### 3.3. Results Comparison

Table 2 gives the comparison of the results of this calculation with the experimental results. As shown in Table 2, for the establishment of products in hydrogenation reaction system, the results obtained in this study are basically in agreement with the experimental results of catalytic hydrogenation [15-19]. It can be seen that CO<sub>2</sub> and CO hydrogenation have a higher thermodynamic conversion than that of the catalytic experimental reaction under close reaction conditions. The selectivity of the product is closely related to the performance of the catalyst, and the actual hydrogenation reaction is more complicated. At the same time, it is concluded that the performance of CO<sub>2</sub> hydrogenation catalyst needs further improvement to improve the conversion of CO<sub>2</sub>/CO and the selectivity of catalyst to the target product.

## 4. Conclusions

In this paper, according to the reaction mechanism, the thermodynamics of ethanol production by CO<sub>2</sub> hydrogenation was simulated. Since the process of CO<sub>2</sub> hydrogenation contain the processes of CO hydrogenation and CO+DME hydrogenation, different hydrogenation processes are discussed in this paper, in which CO<sub>2</sub> hydrogenation synthesis processes in the products containing methane and in methane free products were emphatically analyzed.

The influences of reaction temperature, pressure and composition of raw material, such as H<sub>2</sub>/CO<sub>2</sub> molar ratio, on reaction equilibrium system were analyzed. The change rules of material equilibrium conversion rate and product selectivity with reaction conditions were obtained. The main conclusions of this paper are as follows.

(1) For the CO<sub>2</sub> hydrogenation to ethanol synthesis containing methane, with the increase of the reaction temperature, the equilibrium conversion rate of carbon dioxide and hydrogen decrease, and the selectivity of CO increase. Under the reaction conditions, the selectivity of CH<sub>4</sub> is close to 100%, and water has higher selectivity, while other oxygenated hydrocarbons are little, suggesting that methanation is thermodynamically easy to occur.

(2) For the CO+DME hydrogenation to ethanol synthesis containing methane, the reaction law similar to that of CO<sub>2</sub> hydrogenation was obtained. The conversions of H<sub>2</sub> and dimethyl ether decrease with the increase of the reaction temperature. Under the reaction conditions, CO has a

conversion rate of 100%, methane has nearly 100% selectivity and the other substances are similar to that of CO<sub>2</sub> hydrogenation.

(3) For the CO<sub>2</sub> hydrogenation to ethanol products in the absence of methane, the equilibrium transformation of CO<sub>2</sub> decreases first and then increases with the increase of the reaction temperature. The selectivity of ethanol is close to 100% at low temperature and then decreases with the increase of temperature. The selectivity of ethanol is higher than that of methanol and Increasing the pressure is beneficial to improve the temperature range with high ethanol selectivity.

(4) The comparison of CO hydrogenation with CO<sub>2</sub> hydrogenation in methane free products, the results show that CO hydrogenation has advantages over CO<sub>2</sub> hydrogenation. CO hydrogenation has a wide range of temperature with a high conversion rate and a high selectivity for ethanol. The thermodynamic optimization conditions are as follows. For the CO<sub>2</sub> hydrogenation reaction, the temperature is below 500 K, the pressure is 1.0-5.0 MPa, and the H<sub>2</sub>/CO<sub>2</sub> molar ratio is 3.0-5.0. For the CO hydrogenation reaction, the temperature is below 650 K, the pressure is 1.0-5.0 MPa, and the H<sub>2</sub>/CO molar ratio is 0.5-2.0.

(5) The thermodynamic results were compared with the experimental results, which indicating that the hydrogenation catalysts need to be improved to increase the conversion of the raw materials and the selectivity of the target product.

(6) The reaction system of CO<sub>2</sub> hydrogenation is complex and produces many kinds of products. Carbon deposition is easy to occur at low temperature, which can lead to deactivation of catalyst. Based on the more accurate catalyst reaction mechanism and considering carbon deposition in the product system, the thermodynamic analysis and kinetic study should be further developed.

## Nomenclature

|                                 |   |
|---------------------------------|---|
| MeOH                            | methanol  |
| DME                             | dimethyl ether  |
| EtOH                            | ethanol   |
| AH                              | acetaldehyde  |
| H <sub>2</sub> /CO <sub>2</sub> | the molar ratio of H <sub>2</sub> /CO <sub>2</sub>                |
| RWGS                            | reverse water gas shift reaction                                  |
| $F_{i,in}$                      | molar flow rate of the <i>i</i> th species in feed (mol/s)        |
| $F_{i,out}$                     | molar flow rate of the <i>i</i> th species in products (mol/s)    |
| $F_C$                           | molar flow rate of carbon (mol/s)                                 |
| $\Delta G_{298 K}$              | standard Gibbs free energy change (kJ/mol)                        |
| $\Delta H_{298 K}$              | standard enthalpy change (kJ/mol)                                 |
| $K_{298 K}$                     | standard equilibrium constant                                     |
| $P$                             | pressure (MPa)  |
| $S$                             | selectivity of the product  |
| $T$                             | temperature (K)   |
| $X$                             | conversion rate   |
| $X(H_2)$                        | H <sub>2</sub> conversion rate                                    |
| $Y_i$                           | equilibrium yield of product                                      |
| $\lambda$                       | the number of carbon atoms in the <i>i</i> th species in products |

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