

# Thermodynamic Analysis of CO<sub>2</sub> Hydrogenation to Higher Alcohols (C<sub>2–4</sub>OH): Effects of Isomers and Methane

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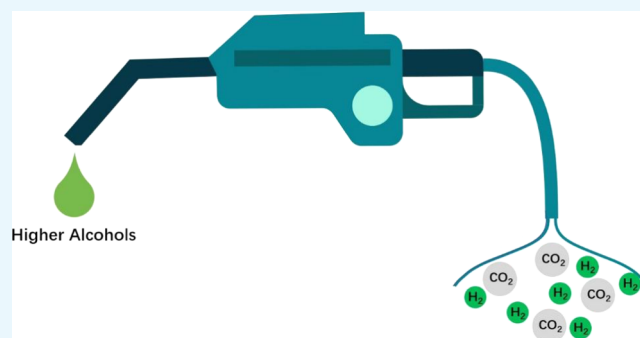


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**ABSTRACT:** Synthesis of higher alcohols (C<sub>2–4</sub>OH) by CO<sub>2</sub> hydrogenation presents a promising way to convert CO<sub>2</sub> into value-added fuels and chemicals. Understanding the thermodynamics of CO<sub>2</sub> hydrogenation is of great importance to tailor the reaction network toward synthesis of higher alcohols; however, the thermodynamic effects of various alcohol isomers and methane in the reaction system have not yet been fully understood. Thus, we used Aspen Plus to perform thermodynamic analysis of CO<sub>2</sub> hydrogenation to higher alcohols, studying the effects of alcohol isomers and methane. Thermodynamically, methane is the most favorable product in a reaction system containing CO, CO<sub>2</sub>, and H<sub>2</sub>, as well as C<sub>1–4</sub> alkanes, alkenes, and alcohols. The thermodynamic favorability of alcohol isomers varies significantly. The presence of methane generally deteriorates the formation of higher alcohols. However, low temperature, high pressure, high H<sub>2</sub>/CO<sub>2</sub> ratio, and formation of alcohols with a longer carbon chain can reduce the effects of methane. Our current study, therefore, provides new insights for enhancing the synthesis of higher alcohols by CO<sub>2</sub> hydrogenation.



## 1. INTRODUCTION

CO<sub>2</sub> is one of the most important greenhouse gases resulting in global warming, and its emission keeps increasing in recent years.<sup>1,2</sup> It is mainly produced by the combustion of fossil resources, and the CO<sub>2</sub> emitted from fossil fuels and industrial processes takes up 0.65 of the global greenhouse gas emission.<sup>3</sup> Thus, reducing CO<sub>2</sub> emission as well as capturing/utilizing CO<sub>2</sub> from the atmosphere/industrial waste gas is indispensable to mitigate global warming and enable societal sustainability.<sup>4,5</sup> Carbon capture and utilization (CCU) technology, which captures CO<sub>2</sub> and turns it into fuels and chemicals, plays a key role in reducing the CO<sub>2</sub> concentration in the atmosphere and mitigating climate change.<sup>6</sup> Moreover, since fossil fuel is the most important CO<sub>2</sub> source, capturing the CO<sub>2</sub> emitted from the combustion of fossil fuels and again turning it back into fuels contributes largely to a carbon-neutral circular economy.<sup>7,8</sup>

Converting CO<sub>2</sub> to fuels such as methane, higher hydrocarbons, methanol, and higher alcohols (C<sub>2–4</sub>OH) has attracted considerable interest in recent years.<sup>9–13</sup> Among them, higher alcohols possessing a high volumetric energy density, a relatively high octane/cetane number, and low vapor pressure are promising alternatives for gasoline and diesel.<sup>14,15</sup> Ethanol, 1-propanol, 2-propanol, 1-butanol, and isobutanol have been reported as alternative fuels in a gasoline/diesel engine.<sup>16–26</sup> The higher alcohols can be blended with

gasoline/diesel or can be used alone, and their content varies from below 0.05 to 1. Depending on the nature of the higher alcohol and its content, the engine can be used directly or after modifications. Notably, the ethanol–gasoline blend has been widely used all over the world. When the content of ethanol is lower than 0.05, no adjustment to the gasoline engines is required; however, modifications are necessary as the ethanol content is higher than 0.05.<sup>18</sup> In addition, ED95, a bioethanol fuel for heavy diesel vehicles provided by SEKAB, containing ethanol (0.95) and an ignition improver (0.05), has been successfully used in modified diesel engines.<sup>16,17</sup>

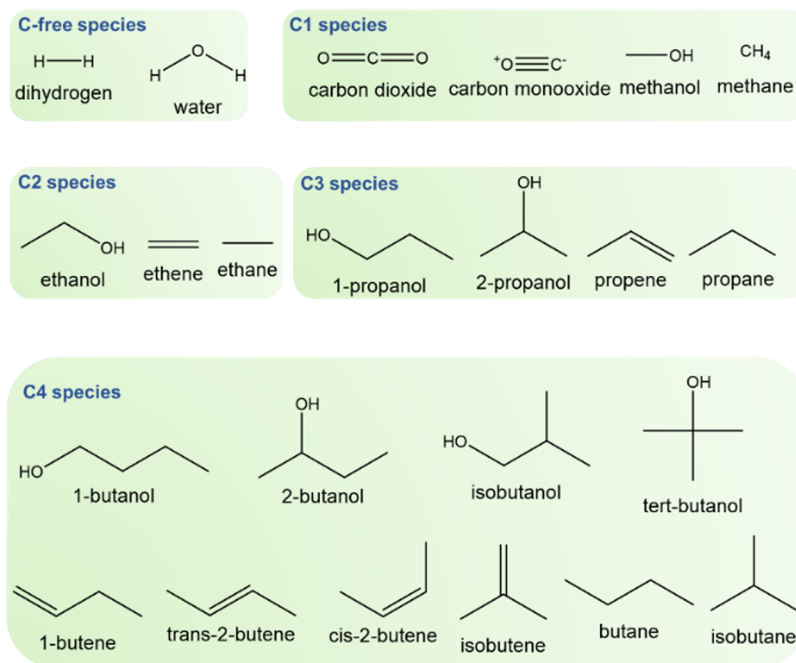
Even though hydrogenation of CO<sub>2</sub> to higher alcohols has been extensively studied for years focusing on thermodynamic analysis as well as the design and development of highly active catalysts,<sup>10,11,13,27,28</sup> its commercial application is still absent due to the low selectivity to higher alcohols. Generally, the hydrogenation of CO<sub>2</sub> in the gas phase possesses a low selectivity to higher alcohols with ethanol as the main higher alcohol.<sup>29</sup> Furthermore, C<sub>3</sub> and C<sub>4</sub> alcohols, which could be

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**Figure 1.** Species reported in the hydrogenation of  $\text{CO}_2$  to higher alcohols.

better alternative fuels due to their higher energy density, present a minor product. Enhancing the formation of  $\text{C}_3$  and  $\text{C}_4$  alcohols has drawn great attention;<sup>30,31</sup> however, most of the existing thermodynamic analysis includes only  $\text{C}_1$  and  $\text{C}_2$  species.<sup>32–36</sup> Some studies concern the formation of  $\text{C}_3$  and  $\text{C}_4$  alcohols,<sup>37,38</sup> but various isomers, which may possess different properties as an alternative fuel, are not included. Moreover,  $\text{CH}_4$  is the most thermodynamically favorable product, and its presence renders the formation of alcohols thermodynamically very unfavorable. Thus, the thermodynamic analysis for the synthesis of higher alcohols generally excludes methane.<sup>37,38</sup> However, a comparable amount of  $\text{CH}_4$  is usually present in practical higher alcohol synthesis from  $\text{CO}_2$  hydrogenation and may influence the formation of higher alcohols thermodynamically, leaving room for further investigation.<sup>39–41</sup>

Herein, we analyzed the thermodynamics of the synthesis of higher alcohols from  $\text{CO}_2$  hydrogenation using an RGibbs model in Aspen Plus. Various isomers of  $\text{C}_{1-4}$  alkanes, alkenes, and alcohols were included to analyze their effects. Moreover, the effects of a certain amount of  $\text{CH}_4$  in the reaction system were also investigated. We found that methane is the most thermodynamically favorable product. Alcohol isomers such as 1/2-propanol and 1/2-iso/tert-butanol possess various thermodynamic favorability. Methane generally exerts negative impacts on higher alcohol formation, which can be reduced by lowering the reaction temperature, increasing the pressure and  $\text{H}_2/\text{CO}_2$  ratio, and forming alcohols with a longer carbon chain. Our study sheds light on the impacts of alcohol isomers and methane on  $\text{CO}_2$  hydrogenation to higher alcohols.

## 2. METHODOLOGY

Aspen Plus V11 was used to perform the simulation, and an RGibbs model was used to simulate the simultaneous phase and chemical equilibrium of the  $\text{CO}_2$  hydrogenation system. In principle, at constant temperature and pressure, the Gibbs free energy of a system is minimized when reaching equilibrium. The RGibbs model develops a general expression for the Gibbs

energy of the system in terms of the number of moles of all species (i.e., reactants, products, and inert species) present in all phases. Furthermore, the minimum total Gibbs energy of the system can be obtained by varying the number of moles of each species in each phase subjected to the stoichiometric constraints.<sup>42</sup> The PSRK property method (see the [Supporting Information](#)), which is based on the predictive Soave–Redlich–Kwong equation-of-state model, was employed for the simulation. Concerning the complexity as well as the high pressure of the reaction system, we used the PSRK method because it enables the prediction of the binary interactions at any pressure.<sup>43</sup>

We consider the hydrogenation of  $\text{CO}_2$  in a fixed bed reactor in which a solvent is absent. The hydrogenation of  $\text{CO}_2$  leads to the formation of various products depending on the catalyst and the reaction conditions (i.e., temperature, pressure, and  $\text{H}_2/\text{CO}_2$  ratio). In previous studies of  $\text{CO}/\text{CO}_2$  hydrogenation to higher alcohols, various products have been observed (Figure 1).<sup>44,45</sup> In this study, we included all or some of these species for thermodynamic analysis. To the best of our knowledge, it is the first time that isomers for  $\text{C}_3$  and  $\text{C}_4$  species were considered in simulating the synthesis of higher alcohols from  $\text{CO}_2$  hydrogenation.

First, we included all of the products listed in Figure 1 and used the RGibbs model to simulate the hydrogenation of  $\text{CO}_2$  ( $\text{H}_2/\text{CO}_2 = 4$ ) at temperatures from 50 to 600 °C and pressures of 2, 50, and 100 bar. Then, we studied the chemical equilibrium constant of the  $\text{CO}_2$  hydrogenation reactions with a REquil model, which determines the equilibrium constants of reactions from the Gibbs free energy.<sup>46</sup> The effects of temperature were studied by performing sensitivity analysis in a temperature range of 50–600 °C with a step of 1 °C. After that, we studied the thermodynamic favorability of the  $\text{CO}_2$  hydrogenation reactions as well as investigated the effects of the temperature, pressure, and  $\text{H}_2/\text{CO}_2$  ratio. Typically, all of the possible products were included in the simulation using the RGibbs model. The thermodynamic favorability was then

ranked according to the selectivity of the products. Notably, the products with a selectivity lower than 0.05 were excluded when ranking and were added to a new simulation to achieve an obvious difference in selectivity. Finally, we studied the effects of CH<sub>4</sub> on the thermodynamics of CO<sub>2</sub> hydrogenation. Generally, when CH<sub>4</sub> is incorporated in the simulation, no alcohol can be obtained. Thus, to study the effects of CH<sub>4</sub> on thermodynamics, we defined a certain amount of CO<sub>2</sub> (0.1, 0.2, and 0.3) converting to CH<sub>4</sub>, and treated it as an inert gas in an RGibbs reactor. Different CO<sub>2</sub> hydrogenation systems, i.e., C<sub>2</sub> (products: CO, CH<sub>4</sub>, H<sub>2</sub>O, and C<sub>1–2</sub> alcohols), C<sub>3</sub> (products: CO, CH<sub>4</sub>, H<sub>2</sub>O, and C<sub>1–3</sub> alcohols), and C<sub>4</sub> (products: CO, CH<sub>4</sub>, H<sub>2</sub>O, and C<sub>1–4</sub> alcohols) systems, were investigated. The CO<sub>2</sub> conversion and product selectivity were calculated according to eqs 1–3. When studying the effects of CH<sub>4</sub>, it is excluded for selectivity calculation (eq 3)

$$\text{CO}_2 \text{ conversion} = \frac{n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}}}{n_{\text{CO}_2,\text{in}}} \quad (1)$$

$$\text{selectivity to product } i = \frac{j_i n_{i,\text{in}} - j_i n_{i,\text{out}}}{n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}}} \quad (2)$$

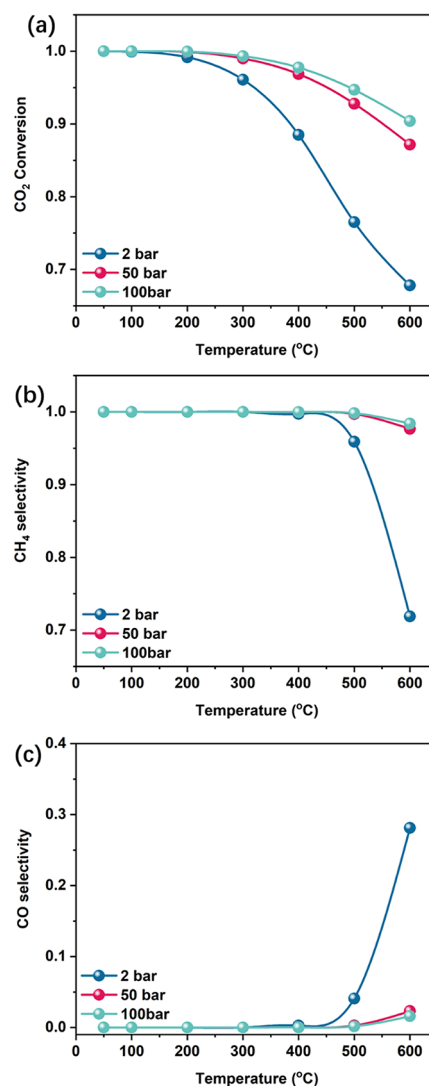
methane free selectivity to product *i*

$$= \frac{j_i n_{i,\text{in}} - j_i n_{i,\text{out}}}{n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}} - n_{\text{CH}_4,\text{out}}} \quad (3)$$

where  $n_{i,\text{in}}$  and  $n_{i,\text{out}}$  are the mole flow rate of species *i* at the inlet and outlet, respectively, and  $j_i$  is the number of carbon atoms in the molecular species *i*.

### 3. RESULTS AND DISCUSSION

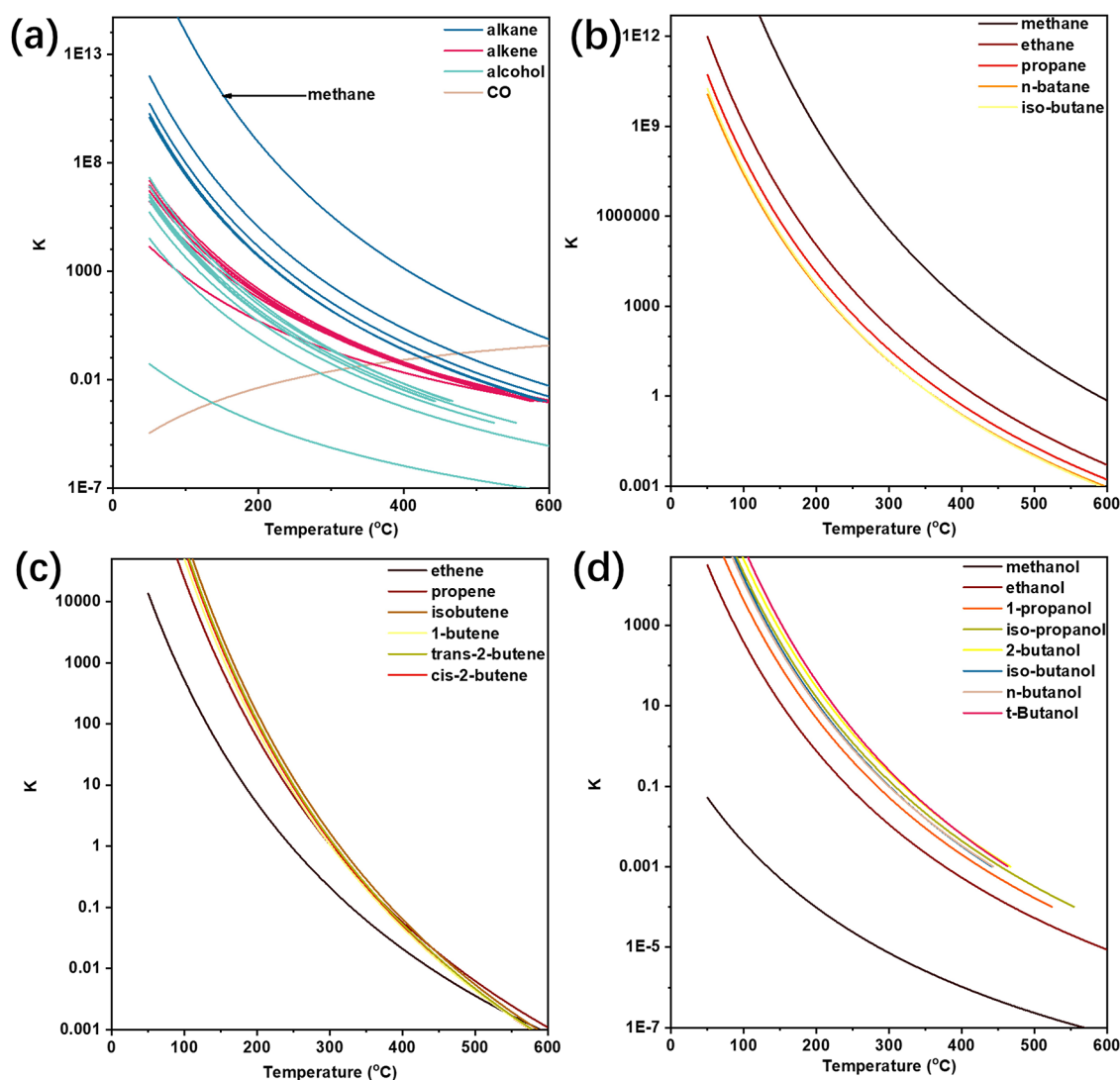
**3.1. Thermodynamic Analysis of CO<sub>2</sub> Hydrogenation to C<sub>1–4</sub> Products.** We used the RGibbs model in Aspen Plus to simulate the spontaneous phase and chemical equilibrium of CO<sub>2</sub> hydrogenation with the PSRK method. All of the species in Figure 1 were incorporated into the simulation, and we performed the simulation in a temperature range of 50–600 °C and a pressure of 2, 50, and 100 bar with a H<sub>2</sub>/CO<sub>2</sub> ratio of 4 in the feed. Figure 2 presents the CO<sub>2</sub> conversion, CH<sub>4</sub> selectivity, and CO selectivity as a function of temperature. The CO<sub>2</sub> conversion decreases with increasing temperature and decreasing pressure. As the temperature increases from 50 to 600 °C, a much more significant decrease in CO<sub>2</sub> conversion was observed at 2 bar (0.322) than at 50 (0.128) and 100 bar (0.096). Under the investigated conditions, CH<sub>4</sub> is always the major product; however, its selectivity decreases from 1 to 0.719 (2 bar), 0.977 (50 bar), and 0.984 (100 bar) when the temperature increases from 50 to 600 °C. In contrast, the CO selectivity increases with increasing temperature. Miguel et al. and Swapnesh et al. observed a similar trend in CO<sub>2</sub> conversion and product selectivity when performing thermodynamic analysis.<sup>34,47</sup> They ascribed the reason to the exothermic nature of CO<sub>2</sub> methanation and endothermic nature of reverse water gas shift (RWGS) reactions, as well as the reduction in the mole of the species during CO<sub>2</sub> methanation. However, catalytic results over nickel-based catalysts by Gac et al. show that CO<sub>2</sub> conversion is only limited by thermodynamics when the temperature exceeds 350 °C. Below this temperature, CO<sub>2</sub> conversion increases with increasing temperature.<sup>48</sup> Notably, the total selectivity to (CH<sub>4</sub> + CO) reaches 1 in all cases we investigated, indicating that



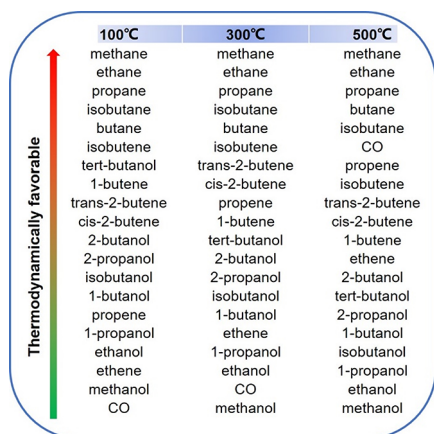
**Figure 2.** CO<sub>2</sub> conversion (a), CH<sub>4</sub> selectivity (b), and CO selectivity (c) as a function of temperature at 2, 50, and 100 bar, respectively; H<sub>2</sub>/CO<sub>2</sub> = 4.

alcohols are not thermodynamically favored under such conditions. Thus, it is indispensable to impose a kinetic barrier to inhibit the formation of CH<sub>4</sub>, enabling the formation of alcohols.

To further illustrate the observed trends, we performed a sensitivity analysis to study the effects of temperature on the equilibrium constant (*K*) of a series of CO<sub>2</sub> hydrogenation reactions (Reaction R1–R20) using the REquil model. Figure 3 presents *K* of the CO<sub>2</sub> hydrogenation reactions as a function of temperature. We found that *K*<sub>CH<sub>4</sub></sub> (Reaction R3) is much higher than that of the other reactions, consistent with CH<sub>4</sub> as the predominant product under the investigated conditions. Except that *K*<sub>CO</sub> (Reaction R1, RWGS) increases with increasing temperature, *K* of other reactions decreases as temperature increases. This explains the increasing CO selectivity with increasing temperature. In addition, we observed that *K* of different types of reactions ranked in order of *K*<sub>alkane</sub> > *K*<sub>alkene</sub> > *K*<sub>alcohol</sub>, again supporting the indispensability to impose a kinetic barrier inhibiting the formation of alkane and alkene as well as favoring the formation of alcohols. Furthermore, we observed that *K*<sub>alkane</sub>

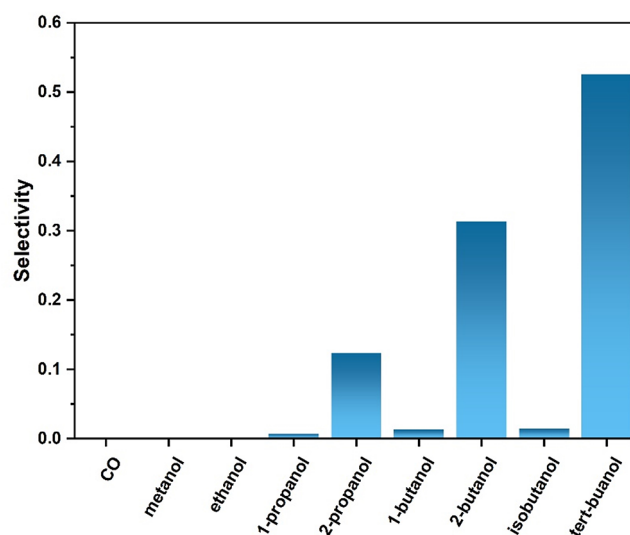


**Figure 3.** Equilibrium constant of various  $\text{CO}_2$  hydrogenation reactions (a), which are specified in (b)–(d), alkane formation reactions (b), alkene formation reactions (c), and alcohol formation reactions (d) as a function of temperature.



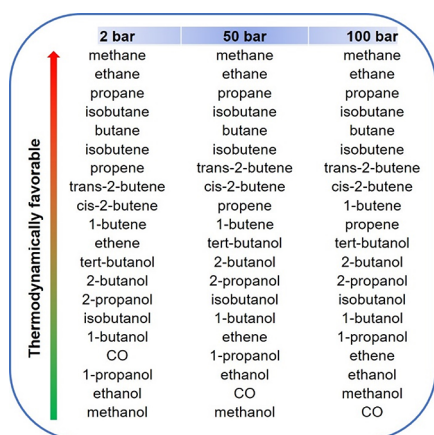
**Figure 4.** Effects of temperature on the thermodynamic favorability of various products in  $\text{CO}_2$  hydrogenation; 50 bar and  $\text{H}_2/\text{CO}_2 = 4$ .

decreases with an increasing number of carbon atoms in the molecule of the product, while  $K_{\text{alkene}}$  and  $K_{\text{alcohol}}$  show an opposite trend. These trends are in line with the thermodynamic analysis results by Jia et al.<sup>37</sup> Also, we observed a

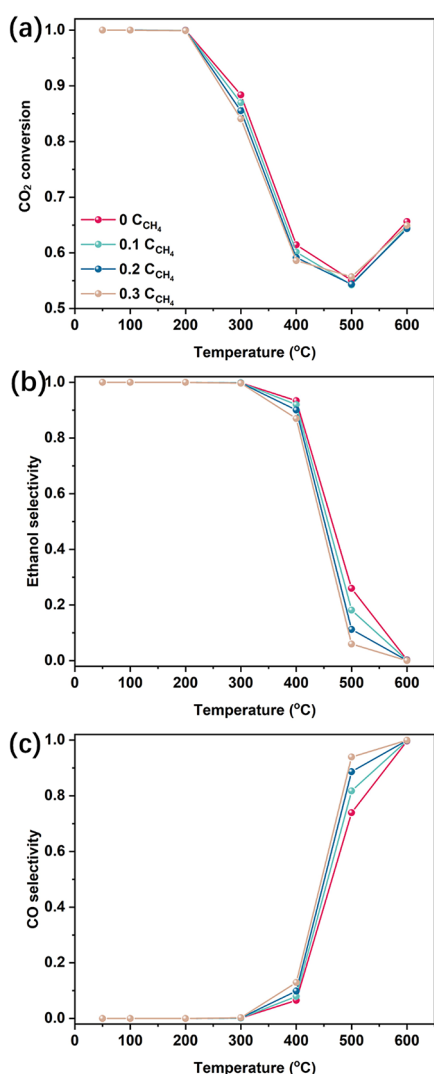


**Figure 5.** Product selectivity when hydrocarbons are not included in the simulation; 300 °C, 50 bar, and  $\text{H}_2/\text{CO}_2 = 4$ .





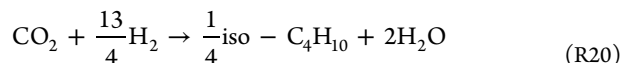
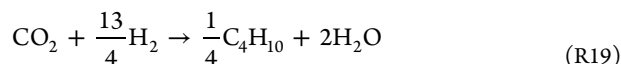
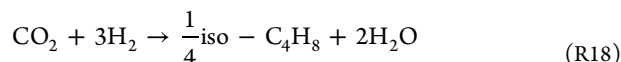
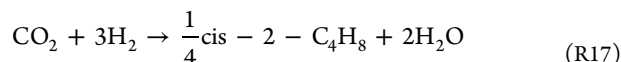
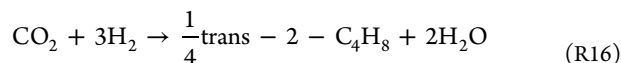
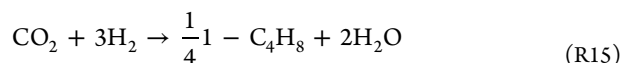
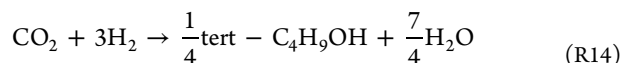
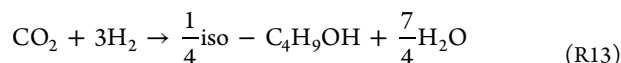
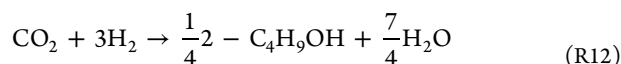
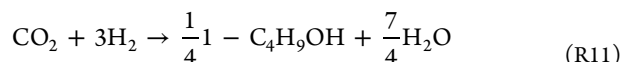
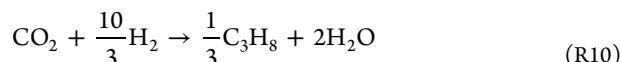
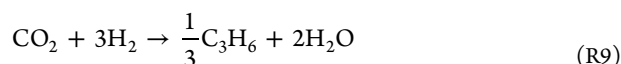
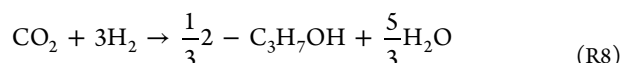
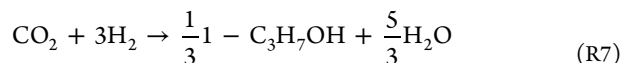
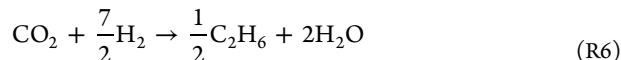
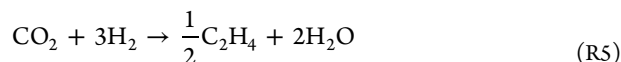
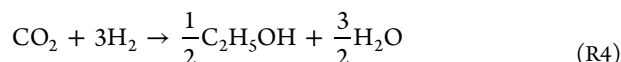
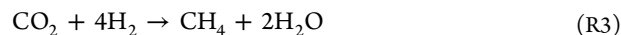
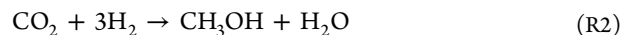
**Figure 6.** Effects of reaction pressure on the thermodynamics of CO<sub>2</sub> hydrogenation; 300 °C and H<sub>2</sub>/CO<sub>2</sub> = 4.



**Figure 7.** CO<sub>2</sub> conversion (a), ethanol selectivity (b), and CO selectivity (c) as a function of temperature with C<sub>CH4</sub> = 0, 0.1, 0.2, and 0.3. The products include CO, CH<sub>4</sub>, methanol, and ethanol; 50–600 °C, 50 bar, and H<sub>2</sub>/CO<sub>2</sub> = 4.

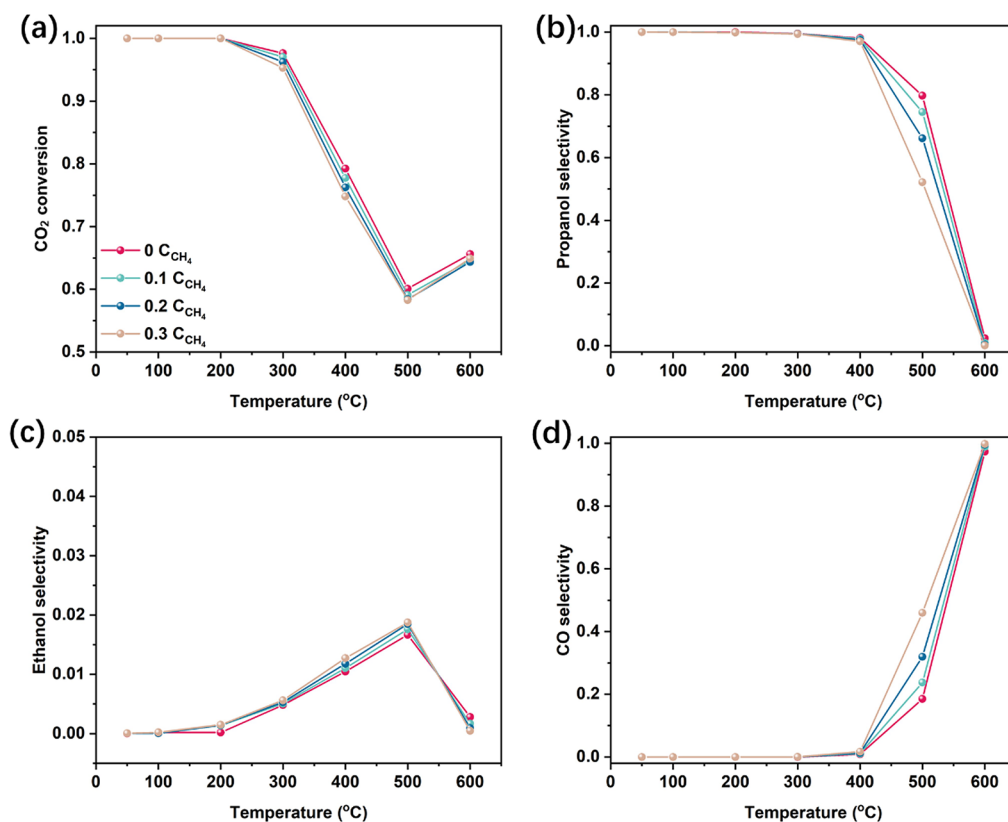
difference in the  $K$  of the formation of different isomers. We will discuss the thermodynamic favorability of all of the species

including different isomers under various conditions in the next paragraphs.

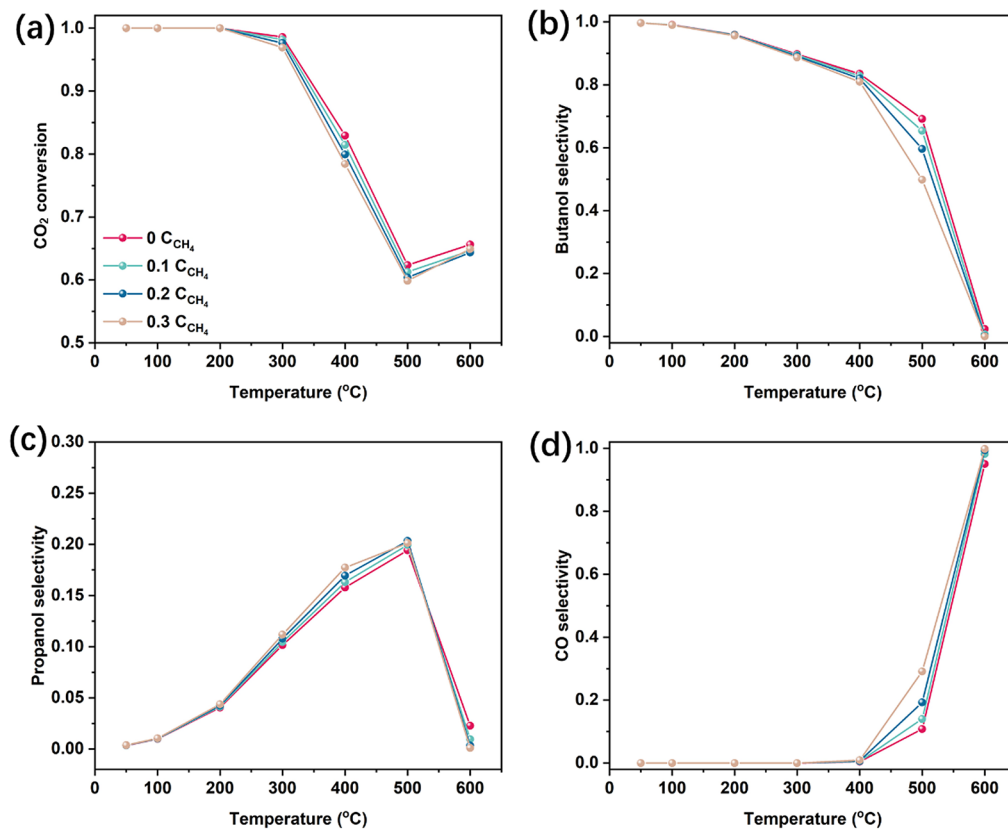


### 3.2. Effects of Isomers on the Thermodynamics of CO<sub>2</sub> Hydrogenation.

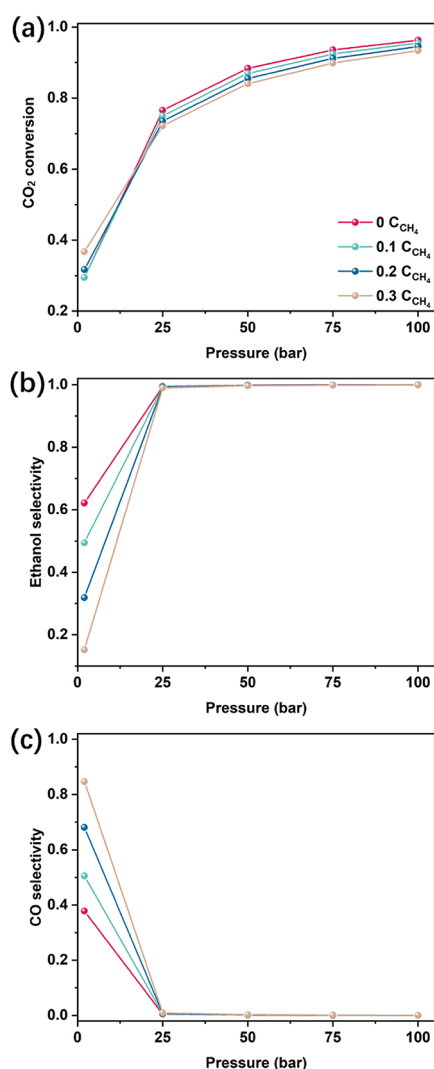
We further studied the thermodynamic favorability of the products under various conditions (i.e., various temperatures, pressures, and H<sub>2</sub>/CO<sub>2</sub> ratios) using the selectivity obtained by the RGibbs model. Under typical conditions for the synthesis of higher alcohols from CO<sub>2</sub> hydrogenation (i.e., 300 °C, 50 bar, H<sub>2</sub>/CO<sub>2</sub> = 4), alkanes are the most thermodynamically favorable products with an order methane > ethane > propane > (iso)butane (Figure 4,



**Figure 8.** CO<sub>2</sub> conversion (a), propanol selectivity (b), ethanol selectivity (c), and CO selectivity (d) as a function of temperature with  $C_{CH_4}$  = 0, 0.1, 0.2, and 0.3. The products include CO, CH<sub>4</sub>, methanol, ethanol, and propanol; 50–600 °C, 50 bar, and H<sub>2</sub>/CO<sub>2</sub> = 4.

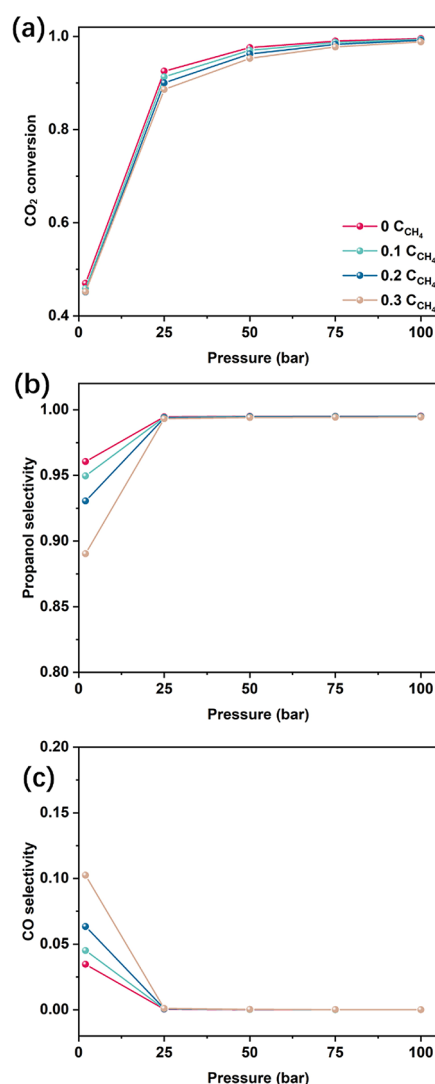


**Figure 9.** CO<sub>2</sub> conversion (a), butanol selectivity (b), propanol selectivity (c), and CO selectivity (d) as a function of temperature with  $C_{CH_4}$  = 0, 0.1, 0.2, and 0.3. The products include CO, CH<sub>4</sub>, methanol, ethanol, propanol, and butanol; 50–600 °C, 50 bar, and H<sub>2</sub>/CO<sub>2</sub> = 4.



**Figure 10.** CO<sub>2</sub> conversion (a), ethanol selectivity (b), and CO selectivity (c) as a function of pressure with C<sub>CH<sub>4</sub></sub> = 0, 0.1, 0.2, and 0.3. The products include CO, CH<sub>4</sub>, methanol, and ethanol; 300 °C, 2–100 bar, and H<sub>2</sub>/CO<sub>2</sub> = 4.

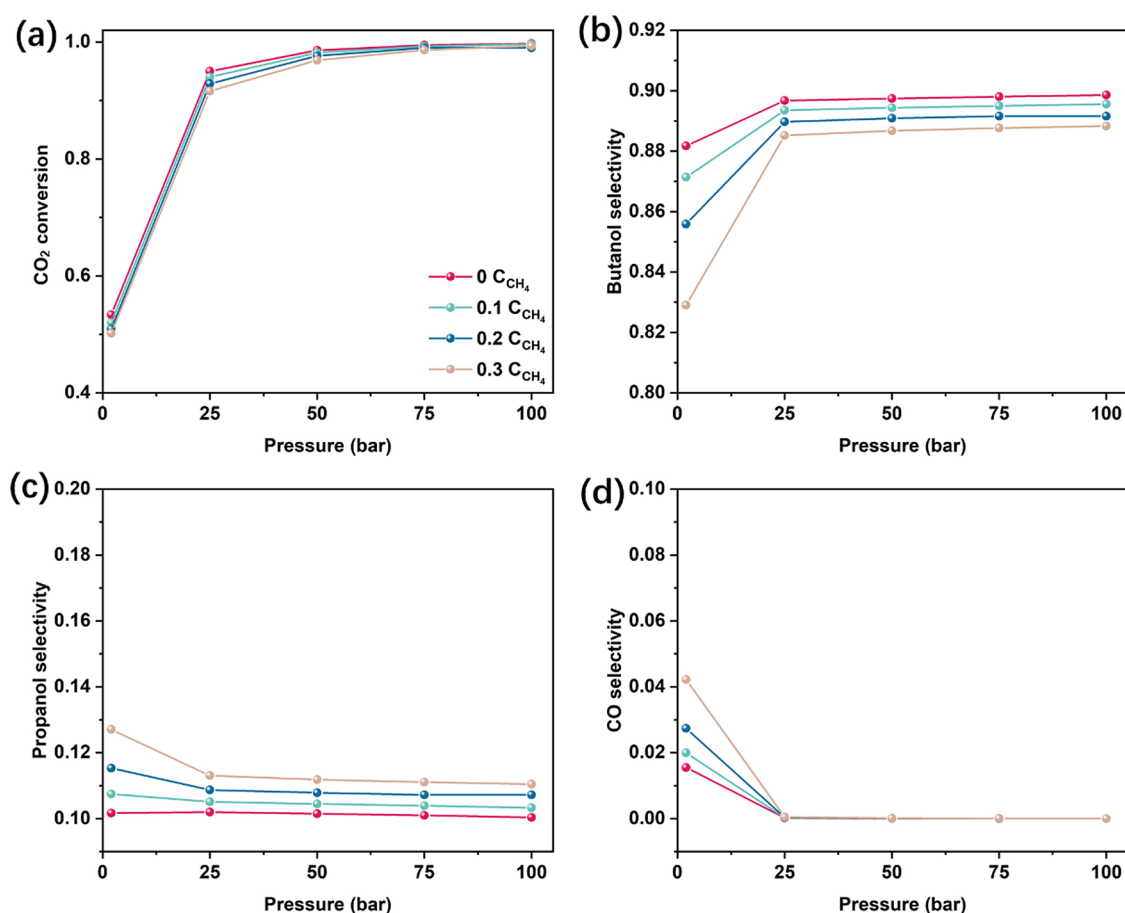
middle column). This phenomenon also applies to all of the conditions we studied. It is consistent with the order of  $K_{\text{alkane}}$  we obtained as well as the thermodynamic analysis of Jia et al.<sup>37</sup> Moreover, Dorner et al. found such a trend when performing CO<sub>2</sub> hydrogenation with a Co–Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>49</sup> Except for ethene, alkenes are more favorable than alcohols. The favorability of alkenes and alcohols generally increases with a longer carbon chain; however, propene and 2-propanol are exceptions. Even though long-chain alkenes and alcohols are favored thermodynamically, they are generally difficult to form in CO<sub>2</sub> hydrogenation due to the high kinetic barrier for carbon chain propagation.<sup>27</sup> The favorability of C<sub>3</sub> and C<sub>4</sub> alcohol isomers differ obviously. Figure 5 presents the product selectivity when hydrocarbons are not included in the simulation. Obviously, 2-propanol is more favorable than 1-propanol, while tert-butanol and 2-butanol are more favorable than the other isomers. However, Qian et al. found that 1-butanol and isobutanol are more favorable when performing CO<sub>2</sub> hydrogenation in a 1,3-dimethyl-2-imidazolidinone solvent with a Rh-based catalyst.<sup>50</sup> Such a divergence may be ascribed to the difference in the reaction conditions and the



**Figure 11.** CO<sub>2</sub> conversion (a), propanol selectivity (b), and CO selectivity (c) as a function of pressure with C<sub>CH<sub>4</sub></sub> = 0, 0.1, 0.2, and 0.3. The products include CO, CH<sub>4</sub>, methanol, ethanol, and propanol; 300 °C, 2–100 bar, and H<sub>2</sub>/CO<sub>2</sub> = 4.

influence of the catalyst. The favorability of isomers has not yet been well studied experimentally. CO presents an unfavored product under such conditions.

Next, the effects of temperature in the range of 100–500 °C (50 bar, H<sub>2</sub>/CO<sub>2</sub> = 4) are studied. Interestingly, isobutane is more favorable than butane at 100 °C; however, at 300 and 500 °C, butane is more favorable. This is consistent with the experimental results of Li et al. They synthesized isobutane by hydrogenation of CO/CO<sub>2</sub> over a CuZnZrAl/Pd-β catalyst and found that the isobutane/butane ratio decreases with increasing temperature.<sup>51</sup> Moreover, as the temperature increases, the favorability of alcohols decreases, while that of alkenes and CO increases. Alcohols become the least favorable product at 500 °C, while the favorability of CO and propene increases significantly. Liu et al. studied the hydrogenation of CO<sub>2</sub> over GaN and found a significant increase in CO and hydrocarbon selectivity as the temperature increases from 300 to 450 °C,<sup>52</sup> while Ren et al. observed a similar trend from 230 to 310 °C over a modified Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>53</sup> However, over a K/Cu–Zn–Fe catalyst, the CO selectivity decreases first and then increases as the temperature increases from 200



**Figure 12.**  $CO_2$  conversion (a), butanol selectivity (b), propanol selectivity (c), and CO selectivity (d) as a function of pressure with  $C_{CH_4}$  = 0, 0.1, 0.2, and 0.3. The products include CO,  $CH_4$ , methanol, ethanol, propanol, and butanol; 300 °C, 2–100 bar, and  $H_2/CO_2$  = 4.

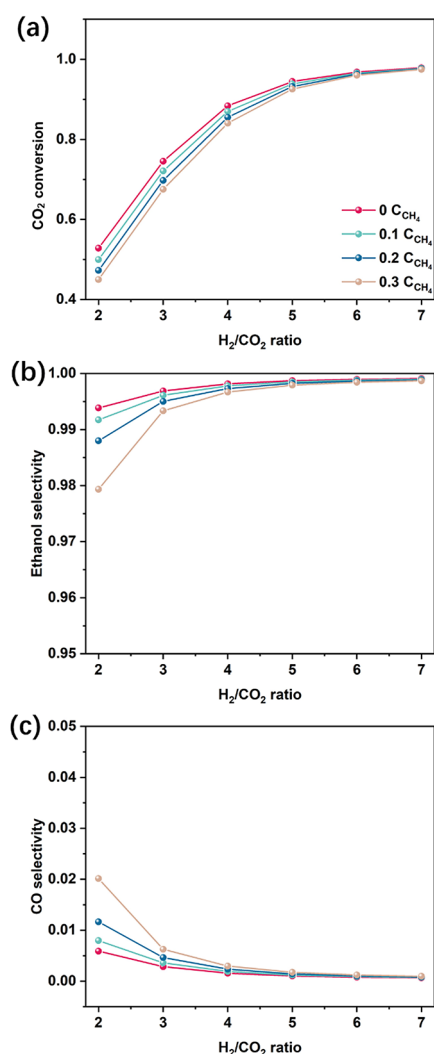
to 350 °C, while the selectivity to ethanol increases first and then decreases.<sup>54</sup> The kinetic barrier seems to be the key factor leading to such divergence with thermodynamic analysis. Notably, tert-butanol is more favorable than most of the alkenes at 100 °C, indicating that it is a promising product when the kinetic barrier is optimized.

We further studied the effects of pressure (2, 50, and 100 bar) at 300 °C and  $H_2/CO_2$  = 4. As shown in Figure 6, propene, ethene, and CO become less favorable with increasing pressure, while the formation of alcohols becomes more favorable. Cai et al. observed decreasing ethene selectivity in  $CO_2$  hydrogenation over a  $Au_8Pd_1$  catalyst with increasing pressure from 1 to 2 MPa.<sup>55</sup> The decreasing CO selectivity with increasing pressure was observed in the range of 0.1–3.2 MPa over various catalysts.<sup>53,56,57</sup> Kusama et al. found that the selectivity to ethanol increases with increasing pressure from 0.1 to 5 MPa in  $CO_2$  hydrogenation over a Rh/SiO<sub>2</sub> catalyst.<sup>58</sup> Such a phenomenon can be explained by the mole change of the corresponding reactions. Since the mole number of reactants equals that of products in the RWGS reaction, it is not sensitive to pressure. The other hydrogenation reaction possesses a larger reactant mole number than the product mole number, pushing the reactions to the right side. These together result in the lowest CO favorability at 100 bar. Since the mole change in propene and ethene formation is less significant compared with the other reactions (except RWGS), they become less favorable with increasing pressure.

In addition, we have also investigated the effects of the  $H_2/CO_2$  ratio in the range of 1–7 (300 °C, 50 bar). The  $H_2/CO_2$  ratio shows no influence on the order of the product favorability, which is identical to that obtained at 300 °C, 50 bar, and  $H_2/CO_2$  = 4 (middle column in Figure 4). This is not the case in practical catalytic  $CO_2$  hydrogenation. During  $CO_2$  hydrogenation over a Rh/SiO<sub>2</sub> catalyst, Kusama et al. observed a significant influence on ethanol and CO selectivity as well as an obvious increase in methane selectivity as the  $H_2/CO_2$  ratio increases from 0.6 to 9.<sup>58</sup> Nieskens et al. observed a decrease in CO selectivity as well as an increase in alcohol and alkane selectivity when the  $H_2/CO_2$  ratio increases from 1 to 3.<sup>59</sup> We ascribed such divergences to the influence of kinetic factors.

**3.3. Effects of Methane on the Thermodynamics of  $CO_2$  Hydrogenation.** **3.3.1. Effects of Methane at Various Temperatures.** We further used an RGibbs reactor to investigate the influence of  $CH_4$  on the thermodynamics of  $CO_2$  hydrogenation. We investigated the cases where 10 mol % ( $C_{CH_4}$  = 0.1), 20 mol % ( $C_{CH_4}$  = 0.2), 30 mol % ( $C_{CH_4}$  = 0.3), and 40 mol % ( $C_{CH_4}$  = 0.4) of  $CO_2$  was converted to methane, which is assumed as an inert component in the reactor. Figure 7 presents the effects of  $CH_4$  in a  $CO_2$  hydrogenation system with CO,  $CH_4$ , methanol, and ethanol as the products ( $C_2$  system, 50–600 °C, 50 bar,  $H_2/CO_2$  = 4). For all of the systems with various  $C_{CH_4}$ ,  $CO_2$  conversion remains unchanged from 50 to 200 °C and then decreases until 500 °C and finally increases at 600 °C. The selectivity (methane free, the same below) to ethanol remains constant (1) until

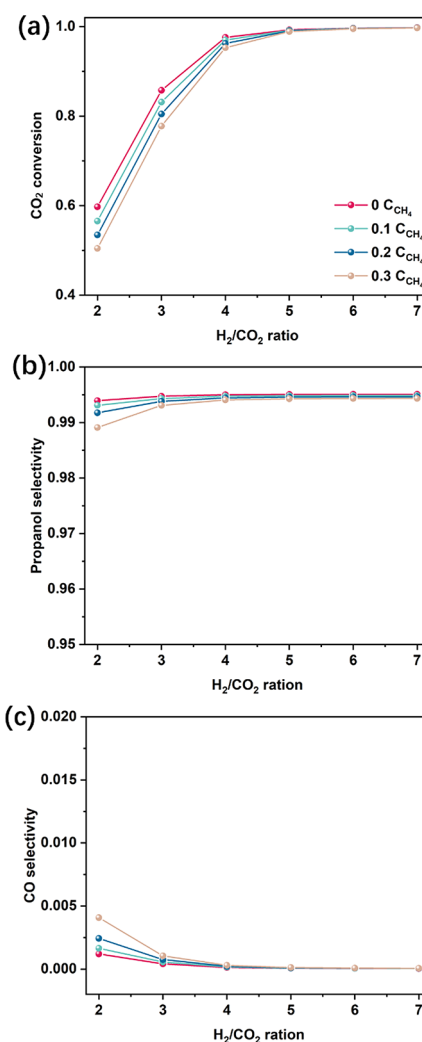




**Figure 13.**  $\text{CO}_2$  conversion (a), ethanol selectivity (b), and CO selectivity (c) as a function of  $\text{H}_2/\text{CO}_2$  ratio with  $\text{C}_{\text{CH}_4}$  = 0, 0.1, 0.2, and 0.3. The products include CO,  $\text{CH}_4$ , methanol, and ethanol; 300 °C, 50 bar, and  $\text{H}_2/\text{CO}_2$  = 2–7.

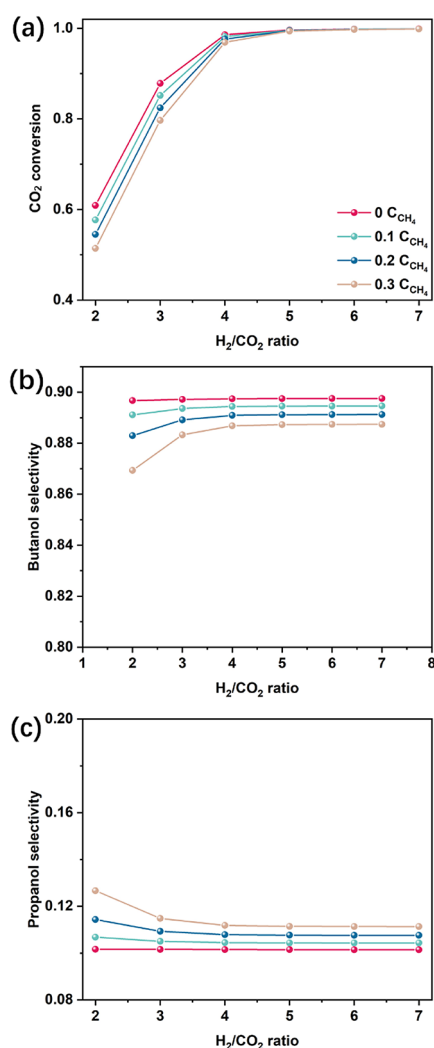
300 °C and then decreases quickly to  $\sim 0$  at 600 °C, while CO selectivity presents an opposite trend. At a low temperature,  $K_{\text{ethanol}}$  is much bigger than  $K_{\text{RWGS}}$ .  $K_{\text{ethanol}}$  decreases, while  $K_{\text{RWGS}}$  increases with increasing temperature, and at a temperature higher than 280 °C,  $K_{\text{RWGS}}$  is larger. Thus, as the temperature increases, the predominant product shifts from ethanol to CO. In addition, no obvious formation of methanol was observed since  $K_{\text{methanol}}$  is much smaller than  $K_{\text{ethanol}}$  in the whole temperature range investigated.

At a temperature lower than 200 °C, the  $\text{CO}_2$  conversion is almost the same regardless of  $\text{C}_{\text{CH}_4}$ . However, at a temperature of 300 °C, which is a typical temperature for the synthesis of higher alcohols,  $\text{CO}_2$  conversion decreases from 0.883 to 0.841 as  $\text{C}_{\text{CH}_4}$  increases from 0 to 0.3. However, the difference in  $\text{CO}_2$  conversion becomes smaller as the temperature further increases. A difference in ethanol selectivity was observed at a higher temperature of 400 °C, and the selectivity to ethanol decreases with increasing  $\text{C}_{\text{CH}_4}$ . Furthermore, the difference becomes more obvious at 500 °C. However, ethanol selectivity decreases to 0 at 600 °C regardless of  $\text{C}_{\text{CH}_4}$ . The selectivity to CO possesses an opposite trend.



**Figure 14.**  $\text{CO}_2$  conversion (a), propanol selectivity (b), and CO selectivity (c) as a function of  $\text{H}_2/\text{CO}_2$  ratio with  $\text{C}_{\text{CH}_4}$  = 0, 0.1, 0.2, and 0.3. The products include CO,  $\text{CH}_4$ , methanol, ethanol, and propanol; 300 °C, 50 bar, and  $\text{H}_2/\text{CO}_2$  = 2–7.

We further included  $\text{C}_3$  and  $\text{C}_4$  alcohols for simulation. After incorporating  $\text{C}_3$  ( $\text{C}_3$  system, Figure 8) and  $\text{C}_4$  ( $\text{C}_4$  system Figure 9) alcohols, the  $\text{CO}_2$  conversion shows a similar trend to that of the  $\text{C}_2$  system, and the  $\text{CO}_2$  conversion of different systems in the range of 300–500 °C ranks in the order of  $\text{C}_4 > \text{C}_3 > \text{C}_2$  due to higher thermodynamic favorability of butanols and propanols under such conditions. However, the influence of  $\text{C}_{\text{CH}_4}$  on  $\text{CO}_2$  conversion at 300 °C becomes less significant in  $\text{C}_3$  (decrease by 0.023) and  $\text{C}_4$  (decrease by 0.017) systems compared to the  $\text{C}_2$  (decrease by 0.043) system. The largest difference in  $\text{CO}_2$  conversion was observed at 400 °C for  $\text{C}_3$  (decrease by 0.044) and  $\text{C}_4$  (decrease by 0.045) systems, and it decreases with further increasing temperature. In the  $\text{C}_3$  and  $\text{C}_4$  systems, the selectivity for the highest alcohol decreases, while CO selectivity increases with increasing temperature, and different from the  $\text{C}_2$  system, the influence of  $\text{C}_{\text{CH}_4}$  on product selectivity is not obvious at 400 °C. The main difference in the product selectivity was observed at 500 °C. The selectivity to the highest alcohol in the system decreases with increasing  $\text{C}_{\text{CH}_4}$  by 0.276 and 0.193 for  $\text{C}_3$  and  $\text{C}_4$  systems, respectively, while it is 0.200 for the  $\text{C}_2$  system. The selectivity to CO possesses an opposite trend. The second highest alcohol in  $\text{C}_3$



**Figure 15.**  $CO_2$  conversion (a), butanol selectivity (b), and propanol selectivity (c) as a function of  $H_2/CO_2$  ratio with  $C_{CH_4} = 0, 0.1, 0.2$ , and  $0.3$ . The products include  $CO$ ,  $CH_4$ , methanol, ethanol, propanol, and butanol;  $300\text{ }^\circ\text{C}$ ,  $50\text{ bar}$ , and  $H_2/CO_2 = 2\text{--}7$ .

and  $C_4$  systems, ethanol and propanol, both possess a volcano shape trend against temperature; however, the selectivity to ethanol in the  $C_3$  system is below  $0.020$ , while propanol selectivity in the  $C_4$  system can be as high as  $0.200$ . At low temperatures ( $\leq 500\text{ }^\circ\text{C}$ ), the increasing  $C_{CH_4}$  leads to higher selectivity for ethanol (in the  $C_3$  system) and propanol (in the  $C_4$  system), but at  $600\text{ }^\circ\text{C}$ , an opposite trend occurs. Thus, in the typical temperature range ( $200\text{--}400\text{ }^\circ\text{C}$ ) for the synthesis of higher alcohols, the formation of methane deteriorates the synthesis of higher alcohols thermodynamically; however, in the case that  $C_3$  or  $C_4$  alcohol forms as the main product, the effects of methane can be reduced.

**3.3.2. Effects of Methane under Various Pressures.** Figure 10 illustrates the effects of  $C_{CH_4}$  on the  $CO_2$  hydrogenation in the  $C_2$  system ( $300\text{ }^\circ\text{C}$ ,  $2\text{--}100\text{ bar}$ ,  $H_2/CO_2 = 4$ ).  $CO_2$  conversion increases with increasing pressure because thermodynamically, ethanol formation is favored at high pressure. Interestingly, at  $2\text{ bar}$ , the  $CO_2$  conversion is higher with increasing  $C_{CH_4}$ , but when the pressure is higher than  $25\text{ bar}$ ,  $C_{CH_4}$  shows an opposite effect. The selectivity to ethanol increases with increasing pressure, and at pressures higher than  $25\text{ bar}$ , the selectivity to ethanol reaches  $1$ . The influence of

$C_{CH_4}$  on product selectivity was only observed at  $2\text{ bar}$ , and the ethanol selectivity decreases from  $0.622$  to  $0.153$  when  $C_{CH_4}$  increases from  $0$  to  $0.3$ . In addition, the selectivity to  $CO$  possesses an opposite trend.

In the  $C_3$  (Figure 11) and  $C_4$  (Figure 12) systems, the  $CO_2$  conversion–pressure correlation shows a similar trend to that in the  $C_2$  system with a  $CO_2$  conversion order of  $C_4 > C_3 > C_2$  because alcohols with a longer carbon chain are more thermodynamically favorable under such conditions. In  $C_3$  and  $C_4$  systems, the influence on  $CO_2$  conversion and product selectivity is similar to that in the  $C_2$  system but slighter. With increasing  $C_{CH_4}$ , the selectivity to the highest alcohols in  $C_3$  and  $C_4$  systems, propanol and butanol, at  $2\text{ bar}$  decreases by  $0.071$  and  $0.053$ , which are much smaller than that in the  $C_2$  system ( $0.459$ ), respectively. Specifically, a difference in butanol selectivity at pressures higher than  $25\text{ bar}$  was observed in the  $C_4$  system, with decreasing butanol selectivity at higher  $C_{CH_4}$ . Furthermore, a comparable amount of propanol formed in the  $C_4$  system, and its selectivity increases with increasing  $C_{CH_4}$ . Even though a low pressure such as  $2\text{ bar}$  is not a typical pressure for the synthesis of alcohol from  $CO_2$  hydrogenation, synthesizing methanol and higher alcohols under near atmospheric pressure has drawn great attention recently.<sup>60–63</sup> To increase the thermodynamic favorability of higher alcohols at lower pressures, one should restrain the formation of methane as well as promote the formation of alcohols with a longer carbon chain.

**3.3.3. Effects of Methane under Various  $H_2/CO_2$  Ratios.** Moreover, the effects of  $C_{CH_4}$  on  $CO_2$  hydrogenation with various  $H_2/CO_2$  ratios from  $2$  to  $7$  are also investigated. Figure 13 presents the  $CO_2$  conversion, ethanol selectivity, and  $CO$  selectivity as a function of the  $H_2/CO_2$  ratio with  $C_{CH_4} = 0, 0.1, 0.2$ , and  $0.3$  in the  $C_2$  system. The  $CO_2$  conversion increases with increasing  $H_2/CO_2$  ratio because of the shift of the chemical equilibrium to the right side due to an increasing  $H_2$  concentration. Moreover, the  $CO_2$  conversion decreases with increasing  $C_{CH_4}$  at low  $H_2/CO_2$  ratios; however, this effect is eliminated at a high  $H_2/CO_2$  ratio such as  $7$ . The selectivity to ethanol increases with increasing  $H_2/CO_2$  ratio and decreases with increasing  $C_{CH_4}$ ; however, their influence is inconspicuous (in the range of  $0.979\text{--}1$ ). At a  $H_2/CO_2$  ratio of  $2$ , the ethanol selectivity increases slightly from  $0.979$  to  $0.994$  as  $C_{CH_4}$  increases from  $0$  to  $0.3$ , while the selectivity to  $CO$  shows an opposite trend to ethanol.

In  $C_3$  and  $C_4$  systems, the  $CO_2$  conversion shows the same trend as that in the  $C_2$  system (Figures 14 and 15). The selectivity to the highest alcohols, propanol in the  $C_3$  system and butanol in the  $C_4$  system, possesses a similar trend to ethanol in the  $C_2$  system. However, at high  $H_2/CO_2$  ratios, the decrease of butanol selectivity in the  $C_4$  systems due to increasing  $C_{CH_4}$  can still be observed. Moreover, in the  $C_4$  system, a comparable amount of propanol was observed showing an opposite trend to butanol, decreasing with increasing  $H_2/CO_2$  ratio and decreasing  $C_{CH_4}$ . Under a low  $H_2/CO_2$  ratio, the formation of methane deteriorates higher alcohol formation thermodynamically. This effect can be reduced significantly in the  $C_2$  and  $C_3$  systems by increasing the ratio of  $H_2/CO_2$ , while its elimination is difficult in the  $C_4$  system.

## 4. CONCLUSIONS

Synthesis of higher alcohols from  $CO_2$  hydrogenation offers an important way for  $CO_2$  utilization. We performed a

thermodynamic analysis of CO<sub>2</sub> hydrogenation to higher alcohols using Aspen Plus. The thermodynamic effects of various alcohol isomers and methane are illustrated. Under typical reaction conditions for the synthesis of higher alcohols from CO<sub>2</sub> hydrogenation, methane is the most thermodynamically favorable product in a reaction system containing CO, CO<sub>2</sub>, and H<sub>2</sub>, as well as C<sub>1–4</sub> alkanes, alkenes, and alcohols. Alcohol isomers possess significantly different thermodynamic favorability. 2-Propanol is more thermodynamically favorable than 1-propanol, while tert/2-butanol is more favorable than 1/isobutanol. Generally, the presence of methane leads to a decreasing CO<sub>2</sub> conversion and selectivity to higher alcohols (methane free). Lowering the temperature, increasing the pressure and the H<sub>2</sub>/CO<sub>2</sub> ratio, and forming alcohols with a longer carbon chain can reduce the negative effects of methane. These results provide new insights for enhancing the synthesis of higher alcohols by CO<sub>2</sub> hydrogenation.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c00502>.

Introduction to the Predictive Soave–Redlich–Kwong (PSRK) method (PDF)

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### Notes

The authors declare no competing financial interest.

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