

Thermodynamic Analysis of CO₂ Hydrogenation to Higher Alcohols (C_{2–4}OH): Effects of Isomers and Methane

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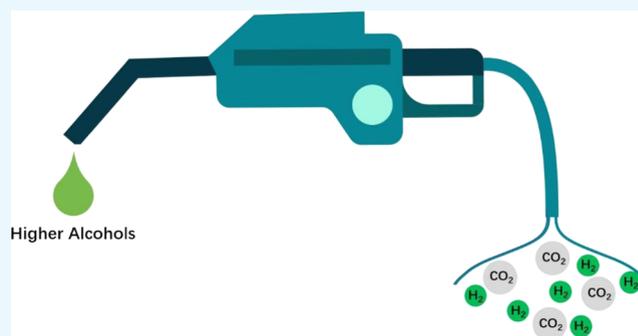


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ABSTRACT: Synthesis of higher alcohols (C_{2–4}OH) by CO₂ hydrogenation presents a promising way to convert CO₂ into value-added fuels and chemicals. Understanding the thermodynamics of CO₂ hydrogenation is of great importance to tailor the reaction 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 CO₂ 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, CO₂, and H₂, as well as C_{1–4} 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 H₂/CO₂ 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 CO₂ hydrogenation.



1. INTRODUCTION

CO₂ is one of the most important greenhouse gases resulting in global warming, and its emission keeps increasing in recent years.^{1,2} It is mainly produced by the combustion of fossil resources, and the CO₂ emitted from fossil fuels and industrial processes takes up 0.65 of the global greenhouse gas emission.³ Thus, reducing CO₂ emission as well as capturing/utilizing CO₂ from the atmosphere/industrial waste gas is indispensable to mitigate global warming and enable societal sustainability.^{4,5} Carbon capture and utilization (CCU) technology, which captures CO₂ and turns it into fuels and chemicals, plays a key role in reducing the CO₂ concentration in the atmosphere and mitigating climate change.⁶ Moreover, since fossil fuel is the most important CO₂ source, capturing the CO₂ emitted from the combustion of fossil fuels and again turning it back into fuels contributes largely to a carbon-neutral circular economy.^{7,8}

Converting CO₂ to fuels such as methane, higher hydrocarbons, methanol, and higher alcohols (C_{2–4}OH) has attracted considerable interest in recent years.^{9–13} 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.^{14,15} Ethanol, 1-propanol, 2-propanol, 1-butanol, and isobutanol have been reported as alternative fuels in a gasoline/diesel engine.^{16–26} 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 0.05.¹⁸ 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.^{16,17}

Even though hydrogenation of CO₂ to higher alcohols has been extensively studied for years focusing on thermodynamic analysis as well as the design and development of highly active catalysts,^{10,11,13,27,28} its commercial application is still absent due to the low selectivity to higher alcohols. Generally, the hydrogenation of CO₂ in the gas phase possesses a low selectivity to higher alcohols with ethanol as the main higher alcohol.²⁹ Furthermore, C₃ and C₄ alcohols, which could be

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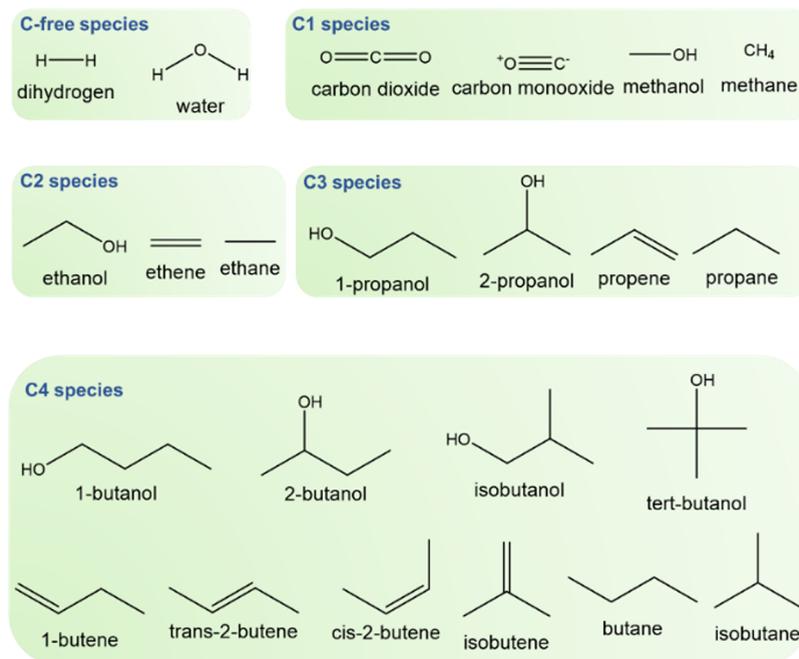


Figure 1. Species reported in the hydrogenation of CO₂ to higher alcohols.

better alternative fuels due to their higher energy density, present a minor product. Enhancing the formation of C₃ and C₄ alcohols has drawn great attention;^{30,31} however, most of the existing thermodynamic analysis includes only C₁ and C₂ species.^{32–36} Some studies concern the formation of C₃ and C₄ alcohols,^{37,38} but various isomers, which may possess different properties as an alternative fuel, are not included. Moreover, CH₄ 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.^{37,38} However, a comparable amount of CH₄ is usually present in practical higher alcohol synthesis from CO₂ hydrogenation and may influence the formation of higher alcohols thermodynamically, leaving room for further investigation.^{39–41}

Herein, we analyzed the thermodynamics of the synthesis of higher alcohols from CO₂ hydrogenation using an RGibbs model in Aspen Plus. Various isomers of C_{1–4} alkanes, alkenes, and alcohols were included to analyze their effects. Moreover, the effects of a certain amount of CH₄ 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 H₂/CO₂ ratio, and forming alcohols with a longer carbon chain. Our study sheds light on the impacts of alcohol isomers and methane on CO₂ 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 CO₂ 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.⁴² 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.⁴³

We consider the hydrogenation of CO₂ in a fixed bed reactor in which a solvent is absent. The hydrogenation of CO₂ leads to the formation of various products depending on the catalyst and the reaction conditions (i.e., temperature, pressure, and H₂/CO₂ ratio). In previous studies of CO/CO₂ hydrogenation to higher alcohols, various products have been observed ([Figure 1](#)).^{44,45} 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 of C₃ and C₄ species were considered in simulating the synthesis of higher alcohols from CO₂ hydrogenation.

First, we included all of the products listed in [Figure 1](#) and used the RGibbs model to simulate the hydrogenation of CO₂ (H₂/CO₂ = 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 CO₂ hydrogenation reactions with a REquil model, which determines the equilibrium constants of reactions from the Gibbs free energy.⁴⁶ 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 CO₂ hydrogenation reactions as well as investigated the effects of the temperature, pressure, and H₂/CO₂ 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 CH₄ on the thermodynamics of CO₂ hydrogenation. Generally, when CH₄ is incorporated in the simulation, no alcohol can be obtained. Thus, to study the effects of CH₄ on thermodynamics, we defined a certain amount of CO₂ (0.1, 0.2, and 0.3) converting to CH₄, and treated it as an inert gas in an RGibbs reactor. Different CO₂ hydrogenation systems, i.e., C₂ (products: CO, CH₄, H₂O, and C_{1–2} alcohols), C₃ (products: CO, CH₄, H₂O, and C_{1–3} alcohols), and C₄ (products: CO, CH₄, H₂O, and C_{1–4} alcohols) systems, were investigated. The CO₂ conversion and product selectivity were calculated according to eqs 1–3. When studying the effects of CH₄, it is excluded for selectivity calculation (eq 3)

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

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

$$\begin{aligned} &\text{methane free selectivity to product } i \\ &= \frac{j_i n_{i,\text{in}} - j_i n_{i,\text{out}}}{n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}} - n_{\text{CH}_4,\text{out}}} \quad (3) \end{aligned}$$

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 CO₂ Hydrogenation to C_{1–4} Products. We used the RGibbs model in Aspen Plus to simulate the spontaneous phase and chemical equilibrium of CO₂ 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 H₂/CO₂ ratio of 4 in the feed. Figure 2 presents the CO₂ conversion, CH₄ selectivity, and CO selectivity as a function of temperature. The CO₂ conversion decreases with increasing temperature and decreasing pressure. As the temperature increases from 50 to 600 °C, a much more significant decrease in CO₂ conversion was observed at 2 bar (0.322) than at 50 (0.128) and 100 bar (0.096). Under the investigated conditions, CH₄ 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 CO₂ conversion and product selectivity when performing thermodynamic analysis.^{34,47} They ascribed the reason to the exothermic nature of CO₂ methanation and endothermic nature of reverse water gas shift (RWGS) reactions, as well as the reduction in the mole of the species during CO₂ methanation. However, catalytic results over nickel-based catalysts by Gac et al. show that CO₂ conversion is only limited by thermodynamics when the temperature exceeds 350 °C. Below this temperature, CO₂ conversion increases with increasing temperature.⁴⁸ Notably, the total selectivity to (CH₄ + CO) reaches 1 in all cases we investigated, indicating that

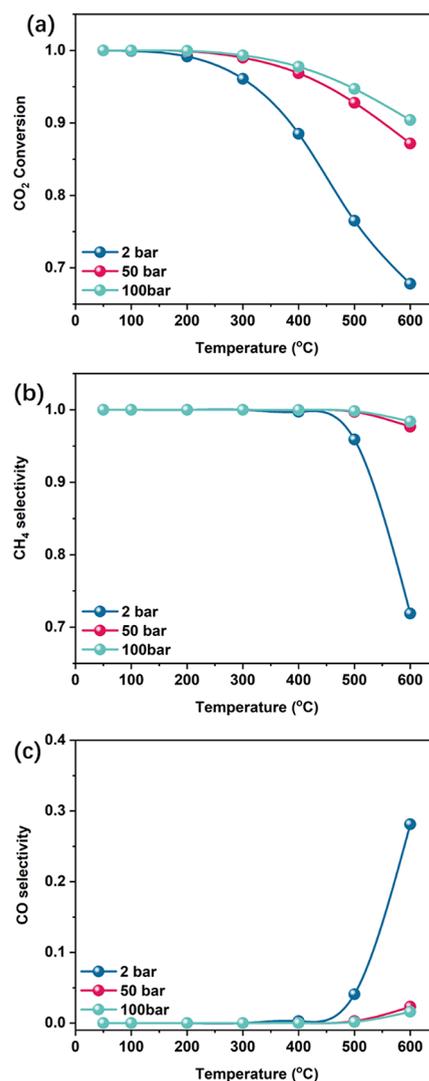


Figure 2. CO₂ conversion (a), CH₄ selectivity (b), and CO selectivity (c) as a function of temperature at 2, 50, and 100 bar, respectively; H₂/CO₂ = 4.

alcohols are not thermodynamically favored under such conditions. Thus, it is indispensable to impose a kinetic barrier to inhibit the formation of CH₄, 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 CO₂ hydrogenation reactions (Reaction R1–R20) using the REquil model. Figure 3 presents K of the CO₂ hydrogenation reactions as a function of temperature. We found that K_{CH_4} (Reaction R3) is much higher than that of the other reactions, consistent with CH₄ as the predominant product under the investigated conditions. Except that K_{CO} (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 $K_{\text{alkane}} > K_{\text{alkene}} > K_{\text{alcohol}}$ 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_{alkane}

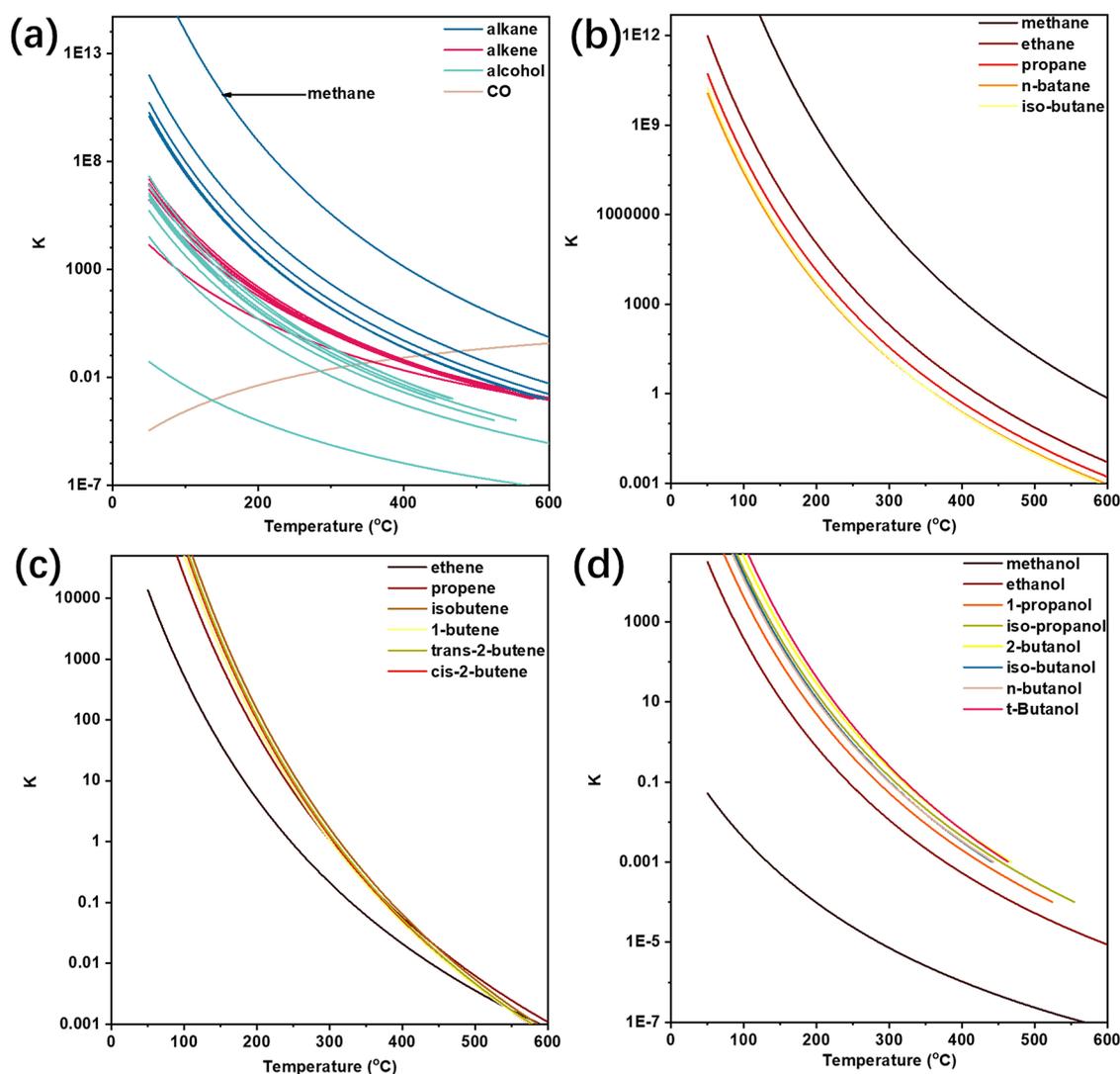


Figure 3. Equilibrium constant of various CO_2 hydrogenation reactions (a), which are specified in (b)–(d), alkane formation reactions (b), alkene formation reactions (c), and alcohol formation reactions (d) as a function of temperature.

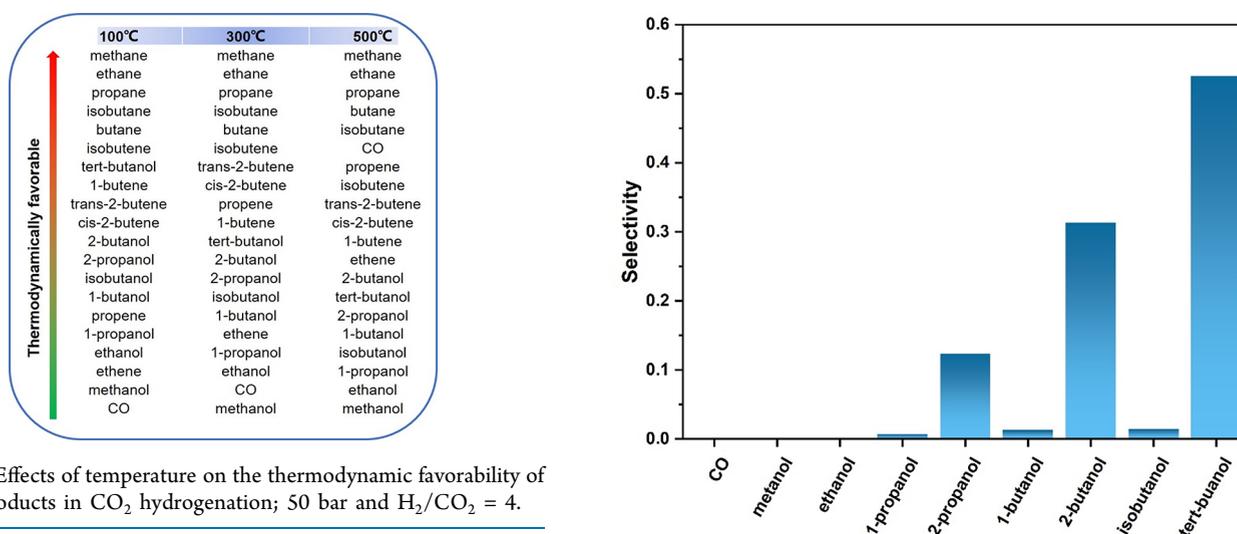


Figure 4. Effects of temperature on the thermodynamic favorability of various products in CO_2 hydrogenation; 50 bar and $\text{H}_2/\text{CO}_2 = 4$.

Figure 5. Product selectivity when hydrocarbons are not included in the simulation; 300 °C, 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_{alkene} and K_{alcohol} show an opposite trend. These trends are in line with the thermodynamic analysis results by Jia et al.³⁷ Also, we observed a

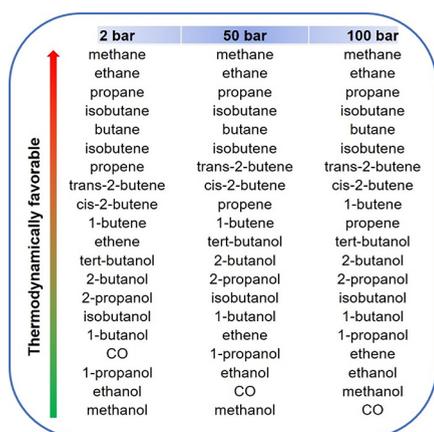


Figure 6. Effects of reaction pressure on the thermodynamics of CO₂ hydrogenation; 300 °C and H₂/CO₂ = 4.

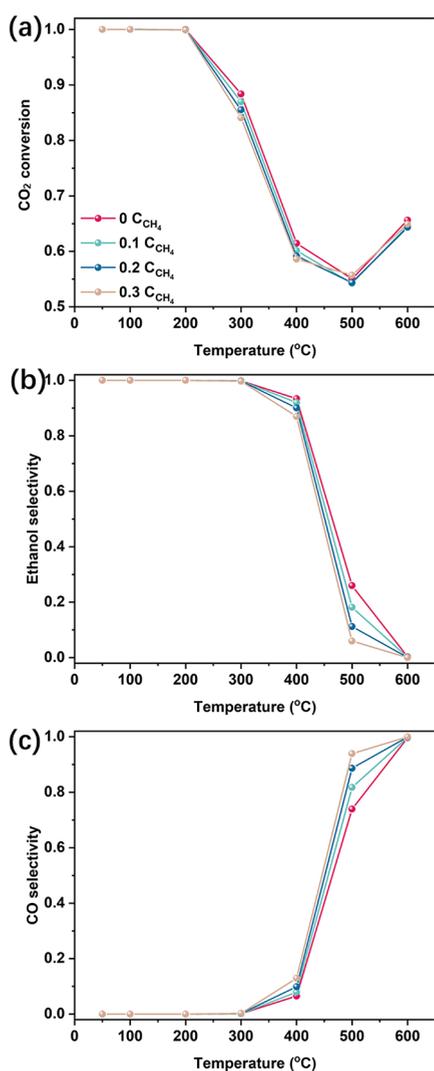
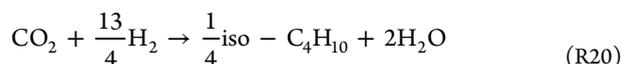
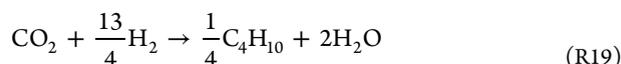
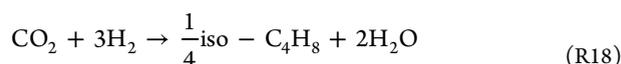
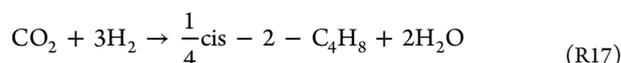
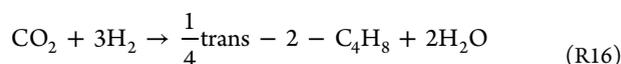
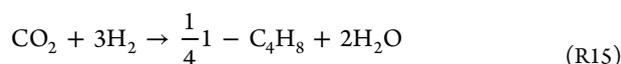
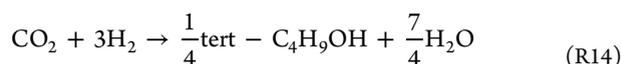
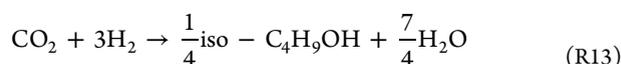
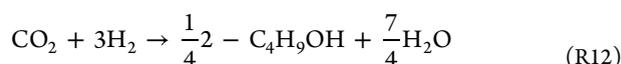
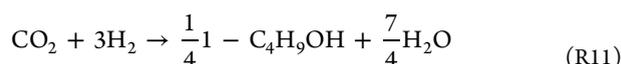
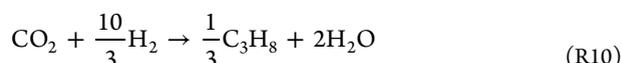
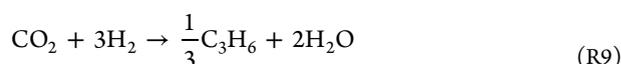
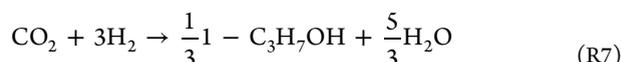
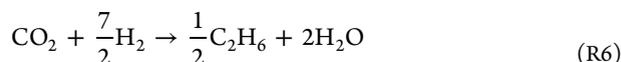
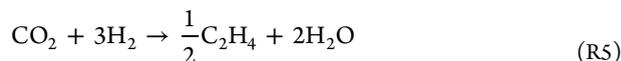
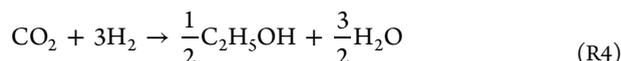
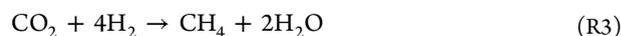
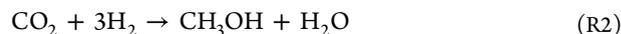


Figure 7. CO₂ conversion (a), ethanol selectivity (b), and CO selectivity (c) as a function of temperature with C_{CH₄} = 0, 0.1, 0.2, and 0.3. The products include CO, CH₄, methanol, and ethanol; 50–600 °C, 50 bar, and H₂/CO₂ = 4.

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 CO₂ Hydrogenation.

We further studied the thermodynamic favorability of the products under various conditions (i.e., various temperatures, pressures, and H₂/CO₂ ratios) using the selectivity obtained by the RGibbs model. Under typical conditions for the synthesis of higher alcohols from CO₂ hydrogenation (i.e., 300 °C, 50 bar, H₂/CO₂ = 4), alkanes are the most thermodynamically favorable products with an order methane > ethane > propane > (iso)butane (Figure 4,

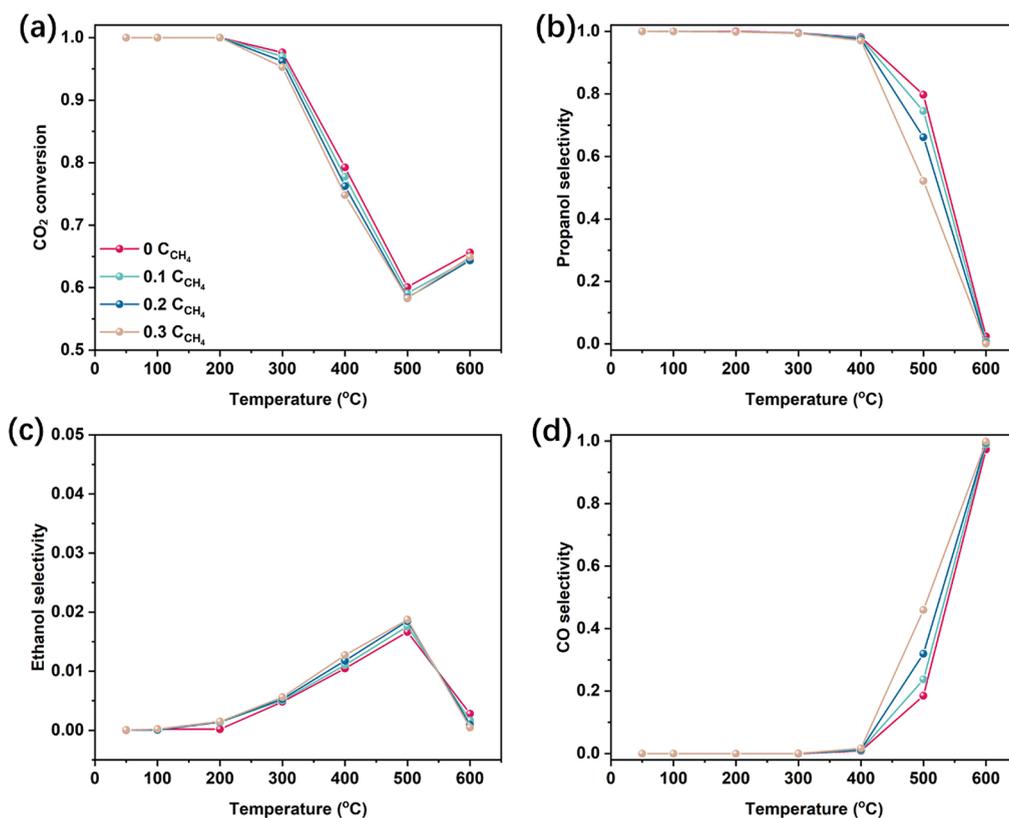


Figure 8. CO_2 conversion (a), propanol selectivity (b), ethanol selectivity (c), and CO selectivity (d) as a function of temperature with $C_{CH_4} = 0, 0.1, 0.2,$ and 0.3 . The products include CO, CH_4 , methanol, ethanol, and propanol; 50–600 °C, 50 bar, and $H_2/CO_2 = 4$.

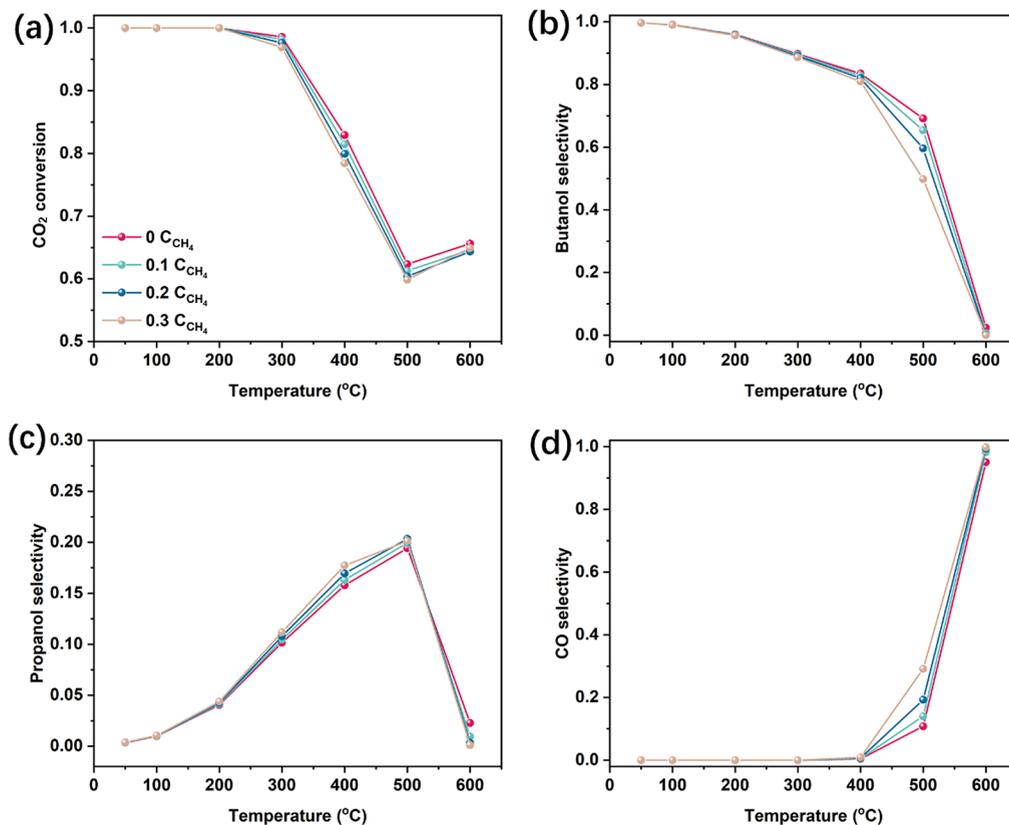


Figure 9. CO_2 conversion (a), butanol selectivity (b), propanol selectivity (c), and CO selectivity (d) as a function of temperature with $C_{CH_4} = 0, 0.1, 0.2,$ and 0.3 . The products include CO, CH_4 , methanol, ethanol, propanol, and butanol; 50–600 °C, 50 bar, and $H_2/CO_2 = 4$.

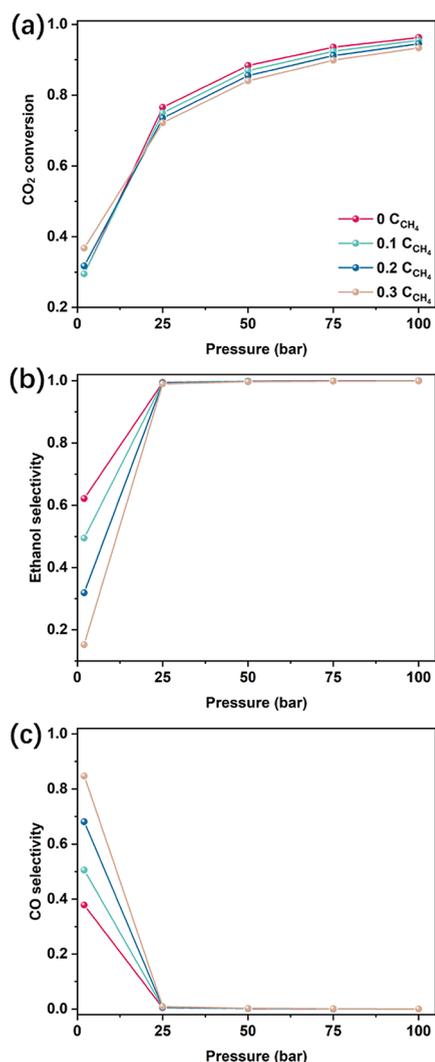


Figure 10. CO₂ conversion (a), ethanol selectivity (b), and CO selectivity (c) as a function of pressure with $C_{CH_4} = 0, 0.1, 0.2,$ and 0.3 . The products include CO, CH₄, methanol, and ethanol; 300 °C, 2–100 bar, and H₂/CO₂ = 4.

middle column). This phenomenon also applies to all of the conditions we studied. It is consistent with the order of K_{alkane} we obtained as well as the thermodynamic analysis of Jia et al.³⁷ Moreover, Dorner et al. found such a trend when performing CO₂ hydrogenation with a Co–Pt/Al₂O₃ catalyst.⁴⁹ 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 CO₂ hydrogenation due to the high kinetic barrier for carbon chain propagation.²⁷ The favorability of C₃ and C₄ 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 CO₂ hydrogenation in a 1,3-dimethyl-2-imidazolidinone solvent with a Rh-based catalyst.⁵⁰ Such a divergence may be ascribed to the difference in the reaction conditions and the

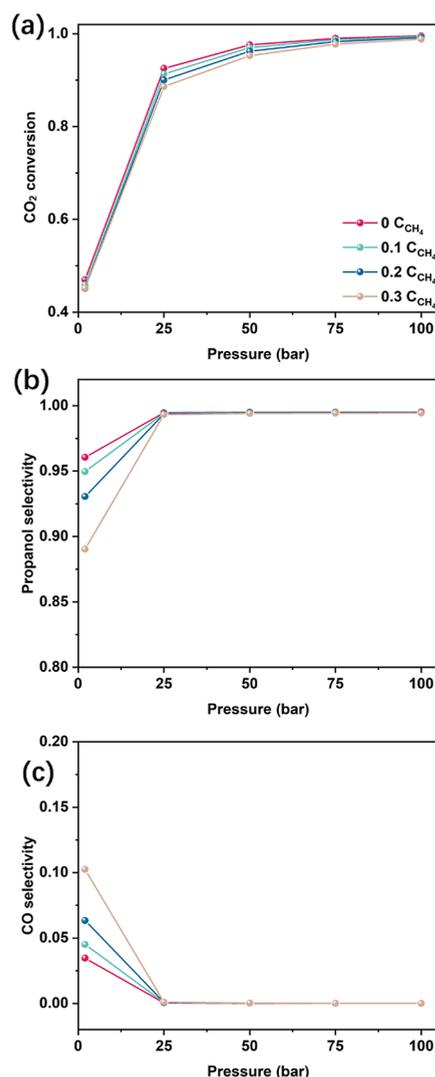


Figure 11. CO₂ conversion (a), propanol selectivity (b), and CO selectivity (c) as a function of pressure with $C_{CH_4} = 0, 0.1, 0.2,$ and 0.3 . The products include CO, CH₄, methanol, ethanol, and propanol; 300 °C, 2–100 bar, and H₂/CO₂ = 4.

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, H₂/CO₂ = 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/CO₂ over a CuZnZrAl/Pd- β catalyst and found that the isobutane/butane ratio decreases with increasing temperature.⁵¹ 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 CO₂ over GaN and found a significant increase in CO and hydrocarbon selectivity as the temperature increases from 300 to 450 °C,⁵² while Ren et al. observed a similar trend from 230 to 310 °C over a modified Cu/ γ -Al₂O₃ catalyst.⁵³ However, over a K/Cu–Zn–Fe catalyst, the CO selectivity decreases first and then increases as the temperature increases from 200

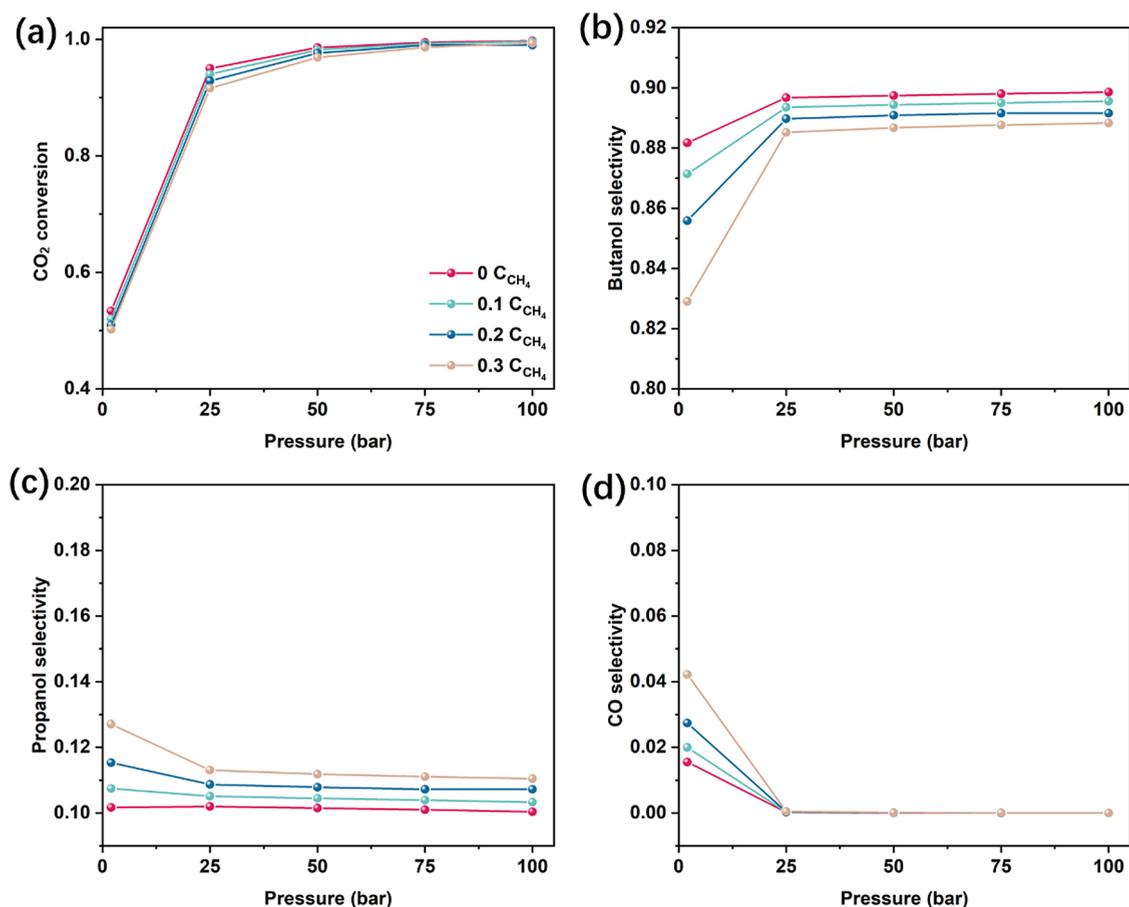


Figure 12. CO₂ conversion (a), butanol selectivity (b), propanol selectivity (c), and CO selectivity (d) as a function of pressure with $C_{\text{CH}_4} = 0, 0.1, 0.2,$ and 0.3 . The products include CO, CH₄, methanol, ethanol, propanol, and butanol; 300 °C, 2–100 bar, and H₂/CO₂ = 4.

to 350 °C, while the selectivity to ethanol increases first and then decreases.⁵⁴ 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 H₂/CO₂ = 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 CO₂ hydrogenation over a Au₈Pd₁ catalyst with increasing pressure from 1 to 2 MPa.⁵⁵ The decreasing CO selectivity with increasing pressure was observed in the range of 0.1–3.2 MPa over various catalysts.^{53,56,57} Kusama et al. found that the selectivity to ethanol increases with increasing pressure from 0.1 to 5 MPa in CO₂ hydrogenation over a Rh/SiO₂ catalyst.⁵⁸ 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 H₂/CO₂ ratio in the range of 1–7 (300 °C, 50 bar). The H₂/CO₂ ratio shows no influence on the order of the product favorability, which is identical to that obtained at 300 °C, 50 bar, and H₂/CO₂ = 4 (middle column in Figure 4). This is not the case in practical catalytic CO₂ hydrogenation. During CO₂ hydrogenation over a Rh/SiO₂ catalyst, Kusama et al. observed a significant influence on ethanol and CO selectivity as well as an obvious increase in methane selectivity as the H₂/CO₂ ratio increases from 0.6 to 9.⁵⁸ Nieskens et al. observed a decrease in CO selectivity as well as an increase in alcohol and alkane selectivity when the H₂/CO₂ ratio increases from 1 to 3.⁵⁹ We ascribed such divergences to the influence of kinetic factors.

3.3. Effects of Methane on the Thermodynamics of CO₂ Hydrogenation.

3.3.1. Effects of Methane at Various Temperatures. We further used an RGibbs reactor to investigate the influence of CH₄ on the thermodynamics of CO₂ hydrogenation. We investigated the cases where 10 mol % ($C_{\text{CH}_4} = 0.1$), 20 mol% ($C_{\text{CH}_4} = 0.2$), 30 mol % ($C_{\text{CH}_4} = 0.3$), and 40 mol % ($C_{\text{CH}_4} = 0.4$) of CO₂ was converted to methane, which is assumed as an inert component in the reactor. Figure 7 presents the effects of CH₄ in a CO₂ hydrogenation system with CO, CH₄, methanol, and ethanol as the products (C₂ system, 50–600 °C, 50 bar, H₂/CO₂ = 4). For all of the systems with various C_{CH_4} , CO₂ 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

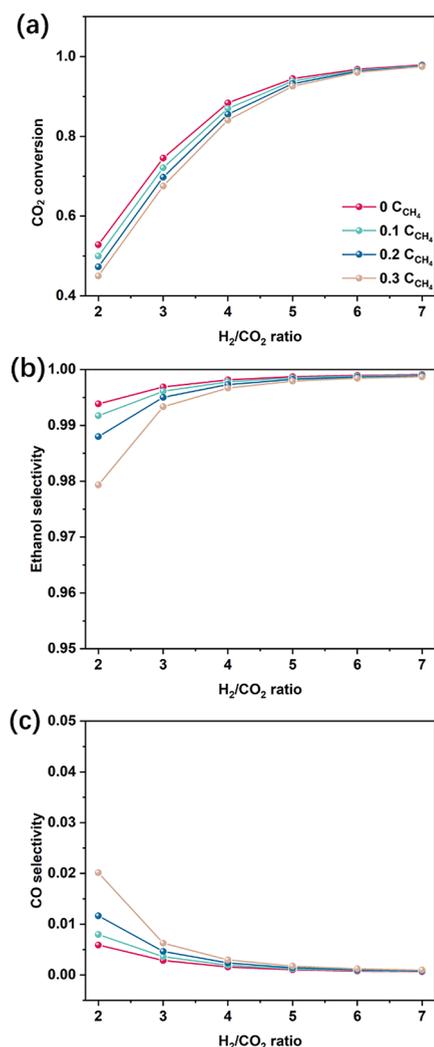


Figure 13. CO_2 conversion (a), ethanol selectivity (b), and CO selectivity (c) as a function of H_2/CO_2 ratio with $C_{CH_4} = 0, 0.1, 0.2,$ and 0.3 . The products include CO, CH_4 , methanol, and ethanol; $300\text{ }^\circ\text{C}$, 50 bar, and $H_2/CO_2 = 2\text{--}7$.

$300\text{ }^\circ\text{C}$ and then decreases quickly to ~ 0 at $600\text{ }^\circ\text{C}$, while CO selectivity presents an opposite trend. At a low temperature, K_{ethanol} is much bigger than K_{RWGS} . K_{ethanol} decreases, while K_{RWGS} increases with increasing temperature, and at a temperature higher than $280\text{ }^\circ\text{C}$, K_{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_{methanol} is much smaller than K_{ethanol} in the whole temperature range investigated.

At a temperature lower than $200\text{ }^\circ\text{C}$, the CO_2 conversion is almost the same regardless of C_{CH_4} . However, at a temperature of $300\text{ }^\circ\text{C}$, which is a typical temperature for the synthesis of higher alcohols, CO_2 conversion decreases from 0.883 to 0.841 as C_{CH_4} increases from 0 to 0.3. However, the difference in CO_2 conversion becomes smaller as the temperature further increases. A difference in ethanol selectivity was observed at a higher temperature of $400\text{ }^\circ\text{C}$, and the selectivity to ethanol decreases with increasing C_{CH_4} . Furthermore, the difference becomes more obvious at $500\text{ }^\circ\text{C}$. However, ethanol selectivity decreases to 0 at $600\text{ }^\circ\text{C}$ regardless of C_{CH_4} . The selectivity to CO possesses an opposite trend.

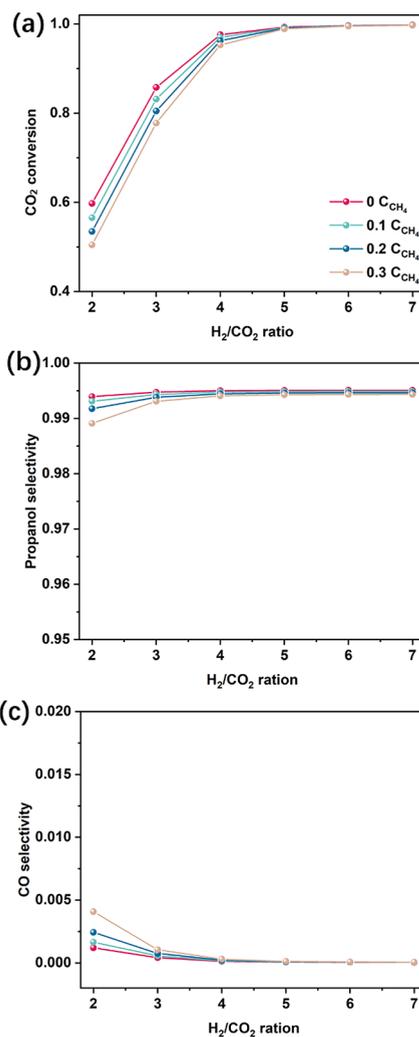


Figure 14. CO_2 conversion (a), propanol selectivity (b), and CO selectivity (c) as a function of H_2/CO_2 ratio with $C_{CH_4} = 0, 0.1, 0.2,$ and 0.3 . The products include CO, CH_4 , methanol, ethanol, and propanol; $300\text{ }^\circ\text{C}$, 50 bar, and $H_2/CO_2 = 2\text{--}7$.

We further included C_3 and C_4 alcohols for simulation. After incorporating C_3 (C_3 system, Figure 8) and C_4 (C_4 system Figure 9) alcohols, the CO_2 conversion shows a similar trend to that of the C_2 system, and the CO_2 conversion of different systems in the range of $300\text{--}500\text{ }^\circ\text{C}$ ranks in the order of $C_4 > C_3 > C_2$ due to higher thermodynamic favorability of butanols and propanols under such conditions. However, the influence of C_{CH_4} on CO_2 conversion at $300\text{ }^\circ\text{C}$ becomes less significant in C_3 (decrease by 0.023) and C_4 (decrease by 0.017) systems compared to the C_2 (decrease by 0.043) system. The largest difference in CO_2 conversion was observed at $400\text{ }^\circ\text{C}$ for C_3 (decrease by 0.044) and C_4 (decrease by 0.045) systems, and it decreases with further increasing temperature. In the C_3 and C_4 systems, the selectivity for the highest alcohol decreases, while CO selectivity increases with increasing temperature, and different from the C_2 system, the influence of C_{CH_4} on product selectivity is not obvious at $400\text{ }^\circ\text{C}$. The main difference in the product selectivity was observed at $500\text{ }^\circ\text{C}$. The selectivity to the highest alcohol in the system decreases with increasing C_{CH_4} by 0.276 and 0.193 for C_3 and C_4 systems, respectively, while it is 0.200 for the C_2 system. The selectivity to CO possesses an opposite trend. The second highest alcohol in C_3

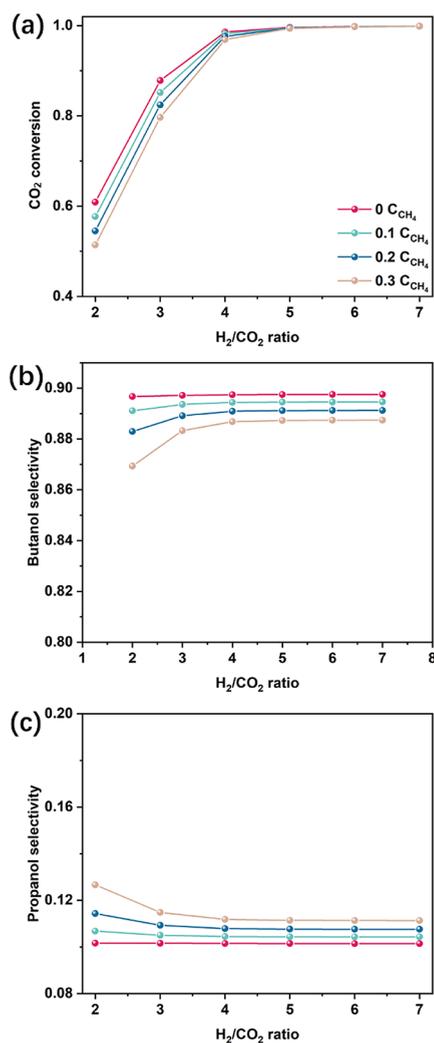


Figure 15. CO₂ conversion (a), butanol selectivity (b), and propanol selectivity (c) as a function of H₂/CO₂ ratio with C_{CH₄} = 0, 0.1, 0.2, and 0.3. The products include CO, CH₄, methanol, ethanol, propanol, and butanol; 300 °C, 50 bar, and H₂/CO₂ = 2–7.

and C₄ systems, ethanol and propanol, both possess a volcano shape trend against temperature; however, the selectivity to ethanol in the C₃ system is below 0.020, while propanol selectivity in the C₄ system can be as high as 0.200. At low temperatures (≤ 500 °C), the increasing C_{CH₄} leads to higher selectivity for ethanol (in the C₃ system) and propanol (in the C₄ system), but at 600 °C, an opposite trend occurs. Thus, in the typical temperature range (200–400 °C) for the synthesis of higher alcohols, the formation of methane deteriorates the synthesis of higher alcohols thermodynamically; however, in the case that C₃ or C₄ 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_{CH₄} on the CO₂ hydrogenation in the C₂ system (300 °C, 2–100 bar, H₂/CO₂ = 4). CO₂ conversion increases with increasing pressure because thermodynamically, ethanol formation is favored at high pressure. Interestingly, at 2 bar, the CO₂ conversion is higher with increasing C_{CH₄}, but when the pressure is higher than 25 bar, C_{CH₄} shows an opposite effect. The selectivity to ethanol increases with increasing pressure, and at pressures higher than 25 bar, the selectivity to ethanol reaches 1. The influence of

C_{CH₄} on product selectivity was only observed at 2 bar, and the ethanol selectivity decreases from 0.622 to 0.153 when C_{CH₄} increases from 0 to 0.3. In addition, the selectivity to CO possesses an opposite trend.

In the C₃ (Figure 11) and C₄ (Figure 12) systems, the CO₂ conversion–pressure correlation shows a similar trend to that in the C₂ system with a CO₂ conversion order of C₄ > C₃ > C₂ because alcohols with a longer carbon chain are more thermodynamically favorable under such conditions. In C₃ and C₄ systems, the influence on CO₂ conversion and product selectivity is similar to that in the C₂ system but slighter. With increasing C_{CH₄}, the selectivity to the highest alcohols in C₃ and C₄ systems, propanol and butanol, at 2 bar decreases by 0.071 and 0.053, which are much smaller than that in the C₂ system (0.459), respectively. Specifically, a difference in butanol selectivity at pressures higher than 25 bar was observed in the C₄ system, with decreasing butanol selectivity at higher C_{CH₄}. Furthermore, a comparable amount of propanol formed in the C₄ system, and its selectivity increases with increasing C_{CH₄}. Even though a low pressure such as 2 bar is not a typical pressure for the synthesis of alcohol from CO₂ hydrogenation, synthesizing methanol and higher alcohols under near atmospheric pressure has drawn great attention recently.^{60–63} To increase the thermodynamic favorability of higher alcohols at lower pressures, one should restrain the formation of methane as well as to promote the formation of alcohols with a longer carbon chain.

3.3.3. Effects of Methane under Various H₂/CO₂ Ratios.

Moreover, the effects of C_{CH₄} on CO₂ hydrogenation with various H₂/CO₂ ratios from 2 to 7 are also investigated. Figure 13 presents the CO₂ conversion, ethanol selectivity, and CO selectivity as a function of the H₂/CO₂ ratio with C_{CH₄} = 0, 0.1, 0.2, and 0.3 in the C₂ system. The CO₂ conversion increases with increasing H₂/CO₂ ratio because of the shift of the chemical equilibrium to the right side due to an increasing H₂ concentration. Moreover, the CO₂ conversion decreases with increasing C_{CH₄} at low H₂/CO₂ ratios; however, this effect is eliminated at a high H₂/CO₂ ratio such as 7. The selectivity to ethanol increases with increasing H₂/CO₂ ratio and decreases with increasing C_{CH₄}; however, their influence is inconspicuous (in the range of 0.979–1). At a H₂/CO₂ ratio of 2, the ethanol selectivity increases slightly from 0.979 to 0.994 as C_{CH₄} increases from 0 to 0.3, while the selectivity to CO shows an opposite trend to ethanol.

In C₃ and C₄ systems, the CO₂ conversion shows the same trend as that in the C₂ system (Figures 14 and 15). The selectivity to the highest alcohols, propanol in the C₃ system and butanol in the C₄ system, possesses a similar trend to ethanol in the C₂ system. However, at high H₂/CO₂ ratios, the decrease of butanol selectivity in the C₄ systems due to increasing C_{CH₄} can still be observed. Moreover, in the C₄ system, a comparable amount of propanol was observed showing an opposite trend to butanol, decreasing with increasing H₂/CO₂ ratio and decreasing C_{CH₄}. Under a low H₂/CO₂ ratio, the formation of methane deteriorates higher alcohol formation thermodynamically. This effect can be reduced significantly in the C₂ and C₃ systems by increasing the ratio of H₂/CO₂, while its elimination is difficult in the C₄ system.

4. CONCLUSIONS

Synthesis of higher alcohols from CO₂ hydrogenation offers an important way for CO₂ utilization. We performed a

thermodynamic analysis of CO₂ 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 CO₂ hydrogenation, methane is the most thermodynamically favorable product in a reaction system containing CO, CO₂, and H₂, as well as C_{1–4} 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 CO₂ conversion and selectivity to higher alcohols (methane free). Lowering the temperature, increasing the pressure and the H₂/CO₂ 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 CO₂ 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

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