

Thermodynamic and Mechanistic Analyses of Direct CO₂ Methylation with Toluene to *para*-Xylene

Yong Yang,* Zhuoyu Wen, Zixuan Zu, Dongliang Wang, Huairong Zhou, and Dongqiang Zhang*

Cite This: *ACS Omega* 2023, 8, 24042–24052

Read Online

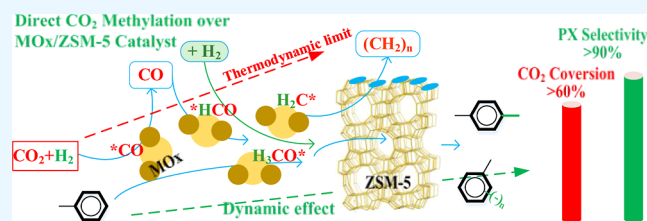
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Direct CO₂ methylation with toluene, as one of the CO₂ hydrogenation technologies, exhibits great potential for the CO₂ utilization to produce the valuable *para*-xylene (PX), but the tandem catalysis remains a challenge for low conversion and selectivity due to the competitive side reactions. The thermodynamic analyses and the comparison with two series of catalytic results of direct CO₂ methylation are conducted to investigate the product distribution and possible mechanism in adjusting the feasibility of higher conversion and selectivity. Based on the Gibbs energy minimization method, the optimal thermodynamic conditions for direct CO₂ methylation are 360–420 °C, 3 MPa with middle CO₂/C₇H₈ ratio (1:1 to 1:4) and high H₂ feed (CO₂/H₂ = 1:3 to 1:6). As a tandem process, the toluene feed would break the thermodynamic limit and has the higher potential of >60% CO₂ conversion than that of CO₂ hydrogenation without toluene. The direct CO₂ methylation route also has advantages over the methanol route with a good prospect for >90% PX selectivity in its isomers due to the dynamic effect of selective catalysis. These thermodynamic and mechanistic analyses would promote the optimal design of bifunctional catalysts for CO₂ conversion and product selectivity from the view of reaction pathways of the complex system.



1. INTRODUCTION

Extensive efforts have been made to develop efficient technologies for CO₂ capture and utilization (CCUS) to alleviate the environmental problems such as climate warming and ocean acidification caused by the greenhouse gas.^{1–3} Catalytic CO₂ utilization using hydrogen produced from renewable energy is one of the promising chemical processes that attracts widespread attention.^{4–6} Meanwhile, *para*-xylene (PX), as one of substantial value-added chemicals of benzene, toluene, and xylene (BTX), is widely used in the downstream polyester industry.^{7,8} Therefore, as one of the CO₂ hydrogenation technologies, selective methylation of toluene using CO₂ as the C1 source exhibits great potential to produce PX.^{9,10}

Generally, PX is produced using CO₂ as C1 feedstocks through two routes. One is the indirect methylation route including CO₂ hydrogenation to methanol^{11,12} and subsequent methanol methylation with toluene,^{7,13,14} where the metal oxide (MO_x) and modified zeolite are the catalysts for these two steps separately. The other one is the direct methylation route upon a bifunctional catalyst combining CO₂ hydrogenation and methylation as a tandem catalysis process.^{15–18} Similarly, syngas (CO + H₂), as another C1 feedstock, has also been introduced in the direct methylation route,^{19–22} while direct CO₂ methylation with benzene has also demonstrated to be more advantageous.^{23,24} For direct CO₂ methylation, Zuo and Yuan et al.⁹ concluded that the methoxy H₃CO* species formed on MO_x preferably migrate into the channel of zeolite for methylation with adsorbed toluene rather than desorb as methanol. Liu et al.¹⁶ believed that the intermediate-generated methanol is the

key species that consumed by benzene or toluene on the acid sites of zeolite. Due to the complex reaction pathways and various products of olefins, liquid fuel, and aromatics,^{17,18,25} the tandem catalysis is the poor selectivity due to thermodynamic barrier and competitive side reactions. Besides, these reported results are conducted under extreme conditions of the feed ratio.

The thermodynamic study can be effective in adjusting the feasibility of CO₂ hydrogenation to an aromatics system toward higher selectivity under different temperatures or reactant mole ratios.^{26–28} It is also useful in clarifying the catalyst's role and its effectiveness in the CO methanation system by comparing the thermodynamic and experimental results.²⁹ Recently, thermodynamic analyses have been introduced to check the limitations and optimal conditions for CO₂ hydrogenation to CH₄ or CH₃OH.^{30,31} However, no thermodynamic analysis has been found for direct CO₂ methylation, which would provide new insights for the direct CO₂ methylation on the view of complex reaction pathways.

In this study, we aim to investigate the product distribution and the thermodynamic trends for the direct CO₂ methylation system using the Gibbs free energy minimization method. Then,

Received: May 1, 2023

Accepted: June 6, 2023

Published: June 21, 2023



the possible mechanism is analyzed from the view of reaction pathways by comparing the thermodynamic distribution with the reported two series experimental results, which is supposed to provide further support for catalyst design and CO₂ methylation technology development.

2. MATERIALS AND METHODS

2.1. Thermodynamic Analysis Method. **2.1.1. Direct and Indirect CO₂ Methylation Reactions.** To clearly describe the whole methylation system, the reactions are classified as CO₂ to methanol, methanol methylation, direct CO₂ methylation, disproportionation and isomerization, and so on^{9,10,28} (listed in Table 1). PX, MX, and OX are the isomers of PX, *meta*-xylene,

Table 1. Direct and Indirect CO₂ Methylation Reactions for Thermodynamic Analysis

R _{NOX}	reactions	R _{NOX}	reactions
	CO ₂ to Methanol		Methanol Methylation
1	CO ₂ + 3H ₂ ⇌ CH ₃ OH + H ₂ O	6	CH ₃ OH + C ₇ H ₈ ⇌ PX + H ₂ O
2	CO ₂ + H ₂ ⇌ CO + H ₂ O	7	2CH ₃ OH ⇌ C ₂ H ₆ O + H ₂ O
3	CO ₂ + 3H ₂ ⇌ 1/2C ₂ H ₄ + 2H ₂ O	8	2CH ₃ OH ⇌ C ₂ H ₄ + 2H ₂ O
4	CO + 2H ₂ ⇌ CH ₃ OH	9	CH ₃ OH + C ₆ H ₆ ⇌ C ₇ H ₈ + H ₂ O
5	CO + 2H ₂ ⇌ 1/2C ₂ H ₄ + H ₂ O	10	CH ₃ OH + PX ⇌ C ₉ -TM + H ₂ O
		11	C ₇ H ₈ + C ₂ H ₄ ⇌ C ₉ -ET
	Aromatization Reaction		
12	CH ₃ OH ⇌ 1/7C ₇ H ₈ + 3/7H ₂ + H ₂ O	13	1/2C ₂ H ₄ ⇌ 1/7C ₇ H ₈ + 3/7H ₂
	Direct CO ₂ Methylation		Disproportionation and Isomerization
14	CO ₂ + 3H ₂ + C ₇ H ₈ ⇌ PX + 2H ₂ O	17	2C ₇ H ₈ ⇌ C ₆ H ₆ + PX
15	CO ₂ + 3H ₂ + C ₆ H ₆ ⇌ C ₇ H ₈ + 2H ₂ O	18	PX ⇌ MX
16	CO ₂ + 3H ₂ + PX ⇌ C ₉ -TM + 2H ₂ O	19	PX ⇌ OX

and *ortho*-xylene, respectively. The ethylene (C₂H₄, C₂) is considered as representative for olefins, while 1,2,4-trimethylbenzene (C₉-TM) and 4-ethyltoluene (C₉-ET) denote the heavy aromatics. Due to the high thermodynamic stability of CH₄ and alkanes, CO₂ or CO tends to form methane and the CO₂ conversions may be up to 90% with a nearly 100% selectivity for CH₄.^{29–32} Since we focus on the potential for direct CO₂ methylation and the CH₄ or alkanes are detected in extremely low content in experimental results, the reactions of CO₂ methanation and olefin hydrogenation are ignored.

2.1.2. Thermodynamic Calculation Method. The basic thermodynamic study is introduced to evaluate Gibbs energy (*G*), enthalpy (*H*), entropy (*S*), and equilibrium constant (*K*) for the reaction system. The *K* is used to determine the feasibility

and the extent for a certain reaction.³³ While the reactive *G*, *H*, and *S* are useful to elucidate whether the reaction is spontaneous or non-spontaneous, exothermic, or endothermic. These properties can be determined using eqs 1–4.^{34,35}

$$\ln \frac{K^0}{K} = \frac{\Delta H_r^0}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \quad (1)$$

$$K^0 = \exp(-\Delta G_r^0/RT) \quad (2)$$

$$\Delta H = \Delta G + T\Delta S \quad (3)$$

$$\Delta G_r^0 = \Delta H_r^0 - T\Delta S_r^0 \quad (4)$$

where ΔH_r^0 and ΔG_r^0 are the standard enthalpy and standard Gibbs free energy of reaction, K^0 and K are the corresponding equilibrium constants at reference temperature (T^0) and arbitrary temperature (T), respectively. ΔG and ΔS are Gibbs free energy and entropy, respectively. The subscripts 0 refer to the standard state of 298.15 K.

On the other hand, the Gibbs free energy minimization method is most suitable and sufficient to calculate the equilibrium composition. A system at a specific pressure and temperature moves simultaneously toward the state of minimum total Gibbs energy, which results into the chemical equilibrium position.^{36–38} The total Gibbs free energy of a system is measured by eq 5.

$$G^t = \sum_{i=1}^N n_i G_i^0 + RT \sum_{i=1}^N n_i \ln \frac{f_i}{f_i^0} \quad (5)$$

where G^t is total Gibbs free energy and G_i^0 is standard Gibbs free energy of species *i*. *R* is the molar gas constant, n_i is the moles of species *i*. f_i and f_i^0 are the fugacity and standard state fugacity, respectively.

2.2. Mechanistic Analysis and Evaluation Indicators.

The mechanistic analysis is conducted by the single reaction pathway analysis and the comparison between thermodynamic calculation and reported experimental results at the same conditions of temperature, pressure, and feed ratio.^{29,36} The comparison and difference is expected not only to explore the thermodynamic potential for the catalytic conversion but also to reflect the effect of the reaction path and catalytic kinetics in the direct CO₂ methylation with toluene. The reported catalytical performance of ZnZrO_x/HZSM-5 (ZZO-*n*ZS)⁹ and ZrCuO_x-ZS (ZrCuO-*n*ZS)¹⁰ is used to compare with the thermodynamic production distribution. These metal oxides were synthesized by a coprecipitation method and *n* means the repetition number for passivation of ZSM-5 zeolites, and the reaction conditions are listed in Table 2.^{9,10}

$$X_C = \frac{F_{in_CO_2} - F_{out_CO_2}}{F_{in_CO_2}} \times 100\% \quad (6)$$

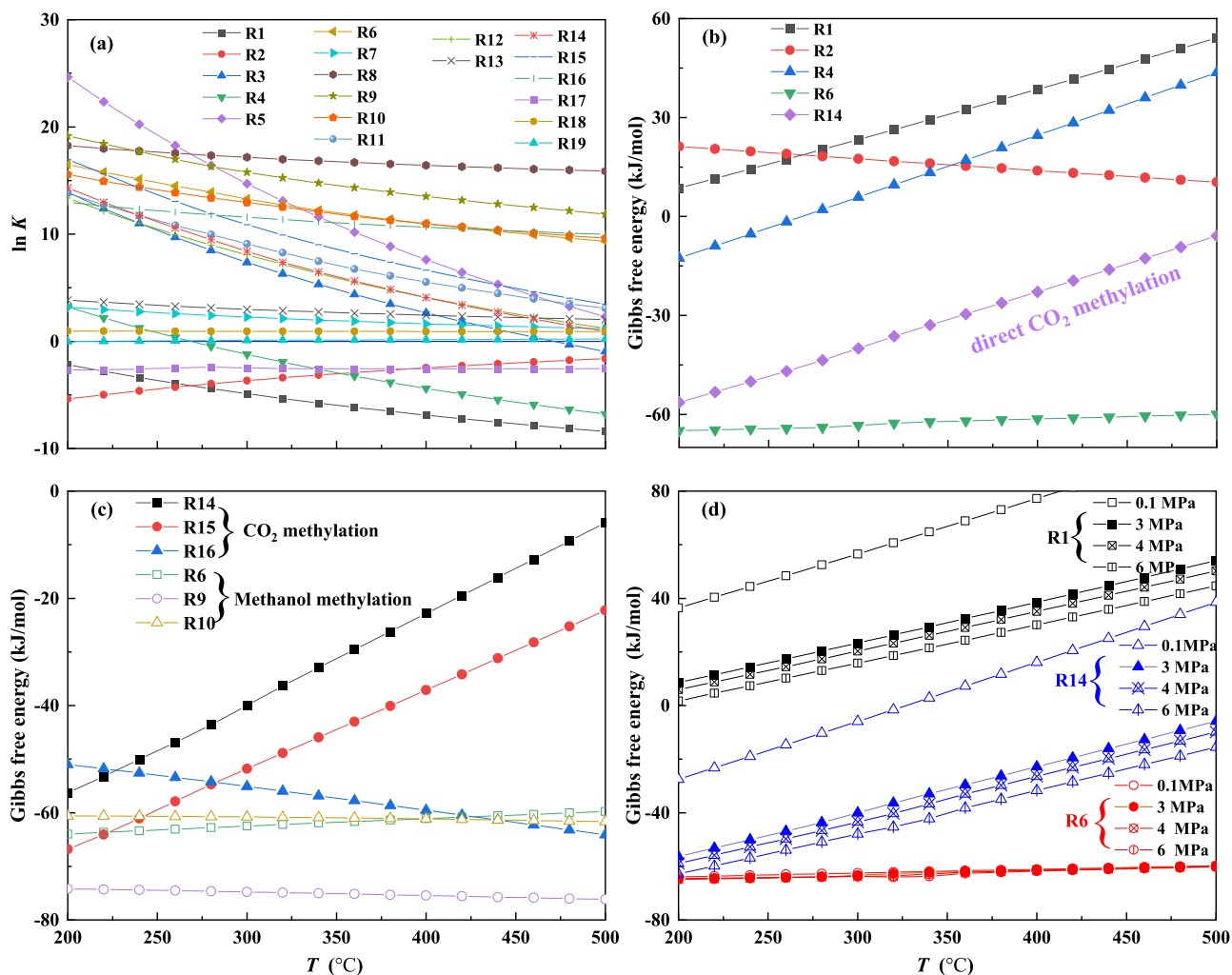
Table 2. Conditions for Catalytic Methylation Evaluation^a

catalyst		feed 1		feed 2		pressure MPa	temperature °C
name	mass	CO ₂ /H ₂ /N ₂	GHSV mL g ⁻¹ h ⁻¹	T/M	WHSV h ⁻¹		
ZnZrO- <i>n</i> ZS	200 mg + 800 mg quartz	24/72/4	12,000	1/—	1.0	3.0	360
<i>n</i> ZS		—/72/28		2/1	0.9	0.1/3.0	
ZrCuO- <i>n</i> ZS	0.364 g + 1.636 g quartz	1/3/1	12,000	1/—	1.0	3.0	360
<i>n</i> ZS		—/60/40		2.5/1			

^aThe conversion and selectivity are defined by the molar flow rate of feed (F_{in}) or outlet effluent (F_{out}) according to equations.

Table 3. Thermodynamic Data of Reactions in CO₂ Methylation at 25 °C and 0.1 MPa

reaction	description	ΔH_r^0 (kJ/mol)	ΔS_r^0 (J/mol)	ΔG_r^0 (kJ/mol)	$\ln(K^0)$	nature
R1	CO ₂ hydrogenation to CH ₃ OH	-49.42	-177.41	3.47	-1.40	exothermic
R2	reverse water-gas shift	41.11	41.86	28.63	-11.55	endothermic
R3	CO ₂ hydrogenation to olefins	-128.05	-118.92	-57.13	23.05	exothermic
R4	CO hydrogenation to CH ₃ OH	-90.53	-219.27	-25.15	10.15	exothermic
R5	CO hydrogenation to olefins	-210.26	-160.78	-114.39	46.15	exothermic
R6	CH ₃ OH methylation with toluene	-73.09	-20.17	-67.08	27.06	exothermic
R7	CH ₃ OH to dimethyl ether	-23.97	-24.36	-16.71	6.74	exothermic
R8	CH ₃ OH to olefins	-29.20	116.98	-64.08	25.85	exothermic
R9	CH ₃ OH methylation with benzene	-73.65	0.09	-73.67	29.72	exothermic
R10	CH ₃ OH methylation with PX	-62.17	-4.35	-60.88	24.56	exothermic
R11	toluene ethylation	-106.06	-141.50	-63.87	25.77	exothermic
R12	CH ₃ OH aromatization	-33.72	50.63	-48.82	19.69	exothermic
R13	olefins aromatization	-19.12	-7.86	-16.78	6.77	exothermic
R14	CO ₂ methylation with toluene	-122.52	-197.59	-63.61	25.66	exothermic
R15	CO ₂ methylation with benzene	-123.07	-177.32	-70.20	28.32	exothermic
R16	CO ₂ methylation with PX	-111.59	-181.76	-57.40	23.16	exothermic
R17	toluene disproportionation	0.55	-20.26	6.59	-2.66	endothermic
R18	xylene isomerization	-0.71	6.48	-2.64	1.06	exothermic
R19	xylene isomerization	1.05	1.51	0.60	-0.24	endothermic

Figure 1. Thermodynamic properties in the range of 200–500 °C under 3 MPa: (a) equilibrium constant at 3 MPa, (b) Gibbs free energy for two methylation routes, (c) CO₂ methylation vs methanol methylation, and (d) Gibbs free energy at different pressures.

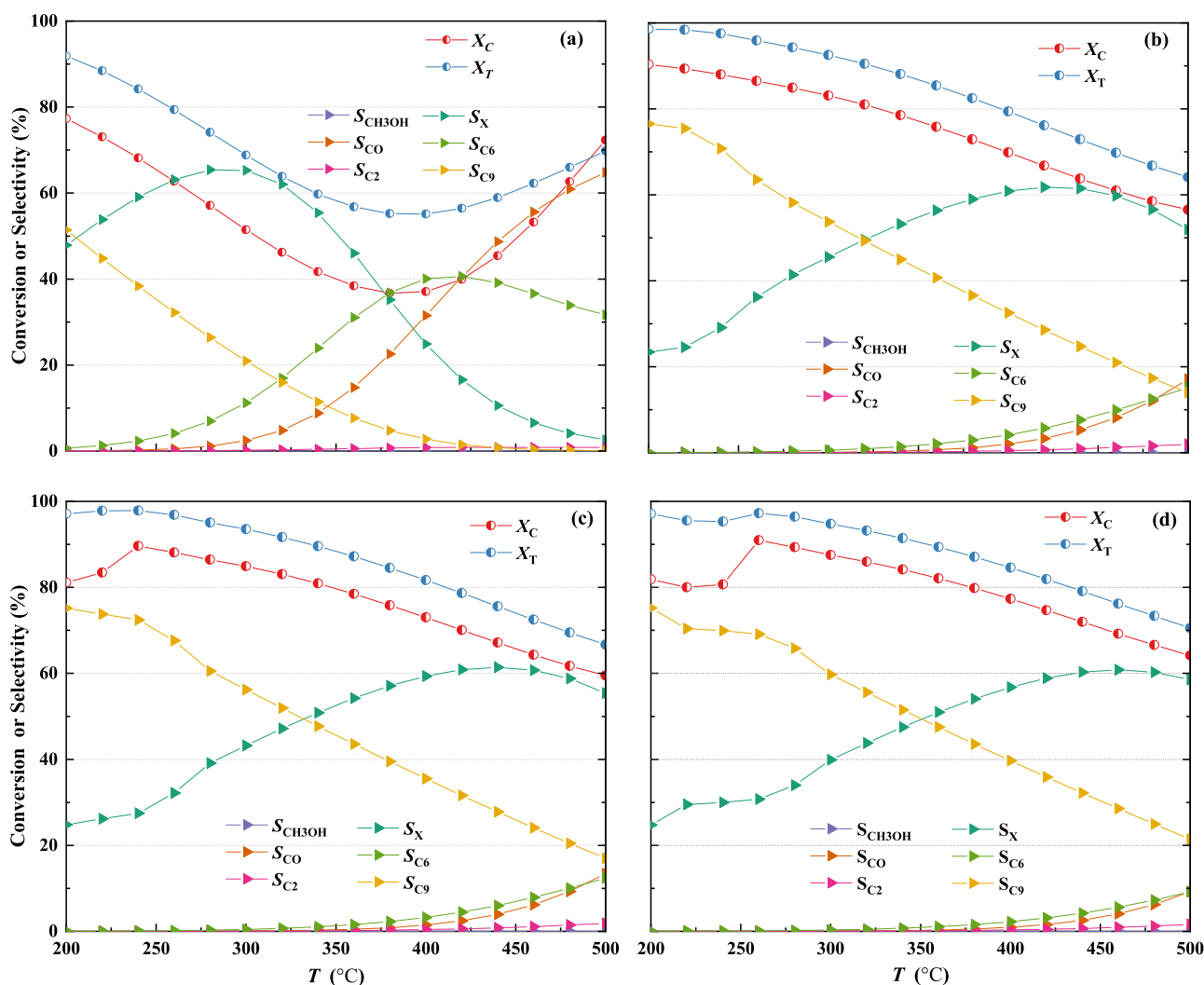


Figure 2. Effects of temperature and pressure on equilibrium distribution with the feedstock of $\text{CO}_2/\text{H}_2/\text{C}_7\text{H}_8 = 1:3:1$. (a) 0.1, (b) 3, (c) 4, and (d) 6 MPa.

$$X_T = \frac{F_{\text{in}_T} - F_{\text{out}_T}}{F_{\text{in}_T}} \times 100\% \quad (7)$$

$$S_i = \frac{F_{\text{out}_i}}{F_{\text{out}}} \times 100\% \quad (8)$$

where X_C and X_T indicate the conversion of CO_2 and toluene, S_i indicates the product distribution or selectivity excluding the H_2O and feed components. For simplicity, species i refers to the CO, methanol (CH_3OH), olefins (C2), benzene (C6), xylene (X, including PX and its isomers), and heavy aromatics (C₉₊), respectively.

3. RESULTS AND DISCUSSION

3.1. Equilibrium Constant and Feasibility of Reaction.

Table 3 systematically lists the enthalpy, entropy, Gibbs free energy, and equilibrium constants for the reactions listed in Table 1 at standard state. These calculated values are consistent with the literature results.^{26,27,29–31} Under the standard conditions, most reactions are spontaneous due to $\Delta G_r < 0$ except for the reactions of R1, R2, R17, and R19. The R1 is an exothermic process that is different from the other three non-spontaneous reactions. It is also worth noting that reactions of

R1, R18, and R19 are the thermodynamic equilibrium limit in the standard state with the $\ln(K^0)$ around ± 1 .

The equilibrium constants of all possible reactions are displayed in Figure 1a in the range of 200–500 °C at 3 MPa. It can be seen that CO_2 hydrogenation to CH_3OH or CO and toluene disproportionation are unfavorable reactions as numbered R1, R2, R4, and R17 with $\ln K < 0$, respectively. It is more infeasible for hydrogenation to CH_3OH of R1 and R4 with the increase in temperature. The xylene isomerization of R18 and R19 are in thermodynamic equilibrium and have little disturbance along with the temperature. Moreover, the olefin formation and deep methylation would be the main side reactions affecting the CO_2 methylation. The order of thermodynamic advantage is methanol methylation > CO_2 methylation > CO_2 to olefins.

The Gibbs free energy for two methylation routes are given in Figure 1b. The direct CO_2 methylation has huge thermodynamic advantages and breaks the thermodynamic limits for CO_2 hydrogenation to CH_3OH . However, this advantage decreases as the temperature increases. The comparison between CO_2 methylation and methanol methylation is presented in Figure 1c. CO_2 methylation has less advantageous due to the small negative values which also reduce significantly with the increase of

temperature. Figure 1d shows the results for indirect and direct methylation at different pressures, which shows that increasing pressure is helpful to the process of CO₂ to methanol or xylene but has no effect on the methanol methylation. The detailed trends of ΔH_r , ΔS_r , ΔG_r , and $\ln K$ for all reactions are shown in Figure S1 in the Supporting Information.

3.2. Equilibrium Product Distribution of CO₂ Methylation. To further confirm the thermodynamic advantage and the influence of multiple side reactions, the equilibrium product distributions are analyzed for different temperatures, pressures, and feed compositions on the basis of minimum total Gibbs energy.^{36,38}

3.2.1. Effect of Temperature and Pressure on Product Distribution. The equilibrium product distributions are illustrated in Figure 2 for four pressures during the range of 200–500 °C with the feed composition 1:3:1 of CO₂/H₂/C₇H₈. It can be noticed that, for an atmospheric pressure of 0.1 MPa in Figure 2a, both low and high temperatures contribute to the high conversion of CO₂ and toluene. Along with the increase of temperature, the CO and benzene selectivity increase gradually, while the yields of xylene and heavy aromatics decrease significantly. Since CO comes from R2 and benzene comes from R17 in Table 1, the high temperature is favorable for the reactions of reverse water gas shift and toluene disproportionation.

Once the pressure increases to 3–6 MPa (as shown in Figure 2b–d), the influence trend of the temperature is still similar but the selectivity is significantly reduced for low carbon number products of CO, C₂H₄, and benzene. While the peak values of xylene selectivity move to the range of 340–500 °C, the conversion of CO₂ and toluene are higher than that of atmospheric pressure. In other words, the higher pressure would lead to the higher conversion and xylene yield. When pressure increases from 3 to 6 MPa, both conversion and the S_{C9} increase a little bit more but the xylene selectivity decreases slightly. With 3 MPa for example, the both conversions are higher than 60% among the temperature range with a peak S_X of 61.77% at 420 °C. It can be noticed that two conversions are approximately proportional to each other and the intermediate methanol has near zero selectivity. The toluene feed would be helpful for the CO₂ and methanol methylation. Low temperature will help to inhibit the side reaction of CO and other side reaction of small-molecule products, excessive pressure will promote the poly-methylation reaction and reduce the xylene selectivity.

The equilibrium distribution for xylene isomers is analyzed separately in Figure 3 since the isomerization among the xylene isomers is thermodynamically equilibrium limited as mentioned in Table 3 and Figure 1a. The PX selectivity in its isomers varies less with pressure but relatively significantly with temperature. However, the variation is not significant. With 3 MPa, for example, S_{PX} reduces from 21.66 to 21.34% and S_{Ox} rises from 23.01 to 26.03% when temperature increases from 280 to 480 °C.

3.2.2. Effect of CO₂/C₇H₈ on Product Distribution. Figure 4 shows the effect of CO₂/toluene feed ratios on the equilibrium distribution for four temperatures with a fixed CO₂/H₂ of 1:3 at 3 MPa. At lower temperature (200 °C in Figure 4a), the higher CO₂/C₇H₈ ratio would result in a conversion close to 100% and a high heavy aromatics selectivity of >75%. Once the CO₂/C₇H₈ ratio reduces lower than 1:1, the CO₂ conversion drops dramatically, the S_X and S_{C6} increase significantly, and S_{C9} decreases sharply due to the toluene disproportionation as a

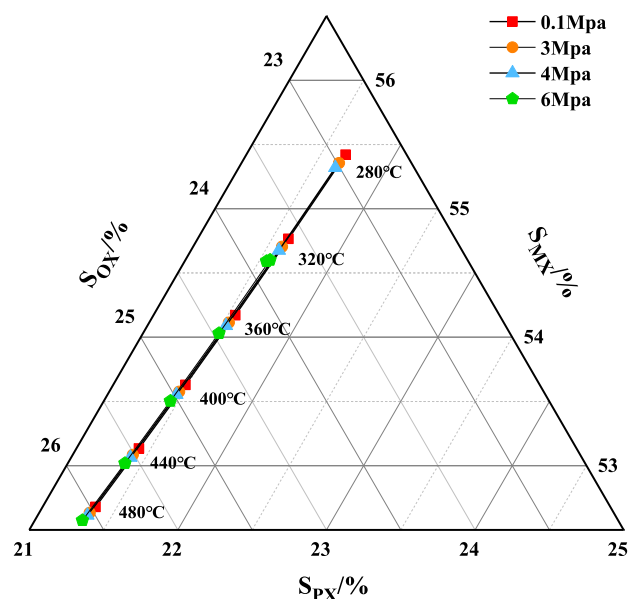


Figure 3. Equilibrium distribution for xylene isomers.

result of high toluene concentration. With the increase of temperature (Figure 4b–d), the CO₂ conversion decreases and the drop trend flattens out, the toluene conversion also goes down. The toluene conversion increases first and then decreases with the decrease of the CO₂/C₇H₈ ratio and reaches the peak around the ratio of 1:1 to 1:2. The peak of S_X shifts to the CO₂/C₇H₈ ratio of 1:4 to 1:8. It is noticed that a lot of CO, olefin, and benzene are formed at high temperature especially under a large CO₂/C₇H₈ ratio with low toluene conversion. Thus, with xylene or PX as target product, the CO₂/C₇H₈ ratio of 1:1 to 1:4 is helpful for direct CO₂ methylation to xylene as a compromise of conversion and product distribution. Besides, the pressure does not change the influence trend of CO₂/C₇H₈ ratio, but it has the lowest toluene conversion and xylene selectivity for atmospheric pressure of 0.1 MPa, while the higher pressure enhances the conversion but reduce the xylene selectivity for a pressure of 3–6 MPa (shown in Figure S2 in the Supporting Information).

3.2.3. Effect of CO₂/H₂ on Product Distribution. Figure 5 gives the effect of CO₂/hydrogen feed ratios (CO₂/H₂) on the equilibrium distribution for four temperatures with a fixed CO₂/C₇H₈ = 1:1 at 3 MPa. Similarly, both conversions decrease with the increase of temperature, while the xylene selectivity maintains high value for 360–420 °C. Along with the CO₂/H₂ going down from 4:1 to 1:6, both conversions increase visibly and the CO₂ conversion rises sharply when CO₂/H₂ is greater than 1:1. The high value of CO₂/H₂ favors the formation of CO and benzene, while high H₂ feed (CO₂/H₂ = 1:6) would be helpful to the olefin and methylation process.

3.3. Comparison between Thermodynamic Analysis and Experimental Results. To further explore the pathways of CO₂ methylation, the experimental results were introduced to be compared with the thermodynamic distribution both for CO₂ methylation and methanol methylation.

3.3.1. Direct CO₂ Methylation. The comparison for direct CO₂ methylation is shown in Figure 6. Three typical catalysts in Figure 6a were selected from Zuo's results⁹ according to the conditions in Table 2 (360 °C, 3 MPa, GHSV = 12,000 mL g⁻¹ h⁻¹ and WHSV = 1 h⁻¹). The 50% ZrZnO-2ZS had the highest conversions for CO₂ of 7% and for toluene of 25%, but has lowest methylation usages of 36.5% and middle PX selectivity of

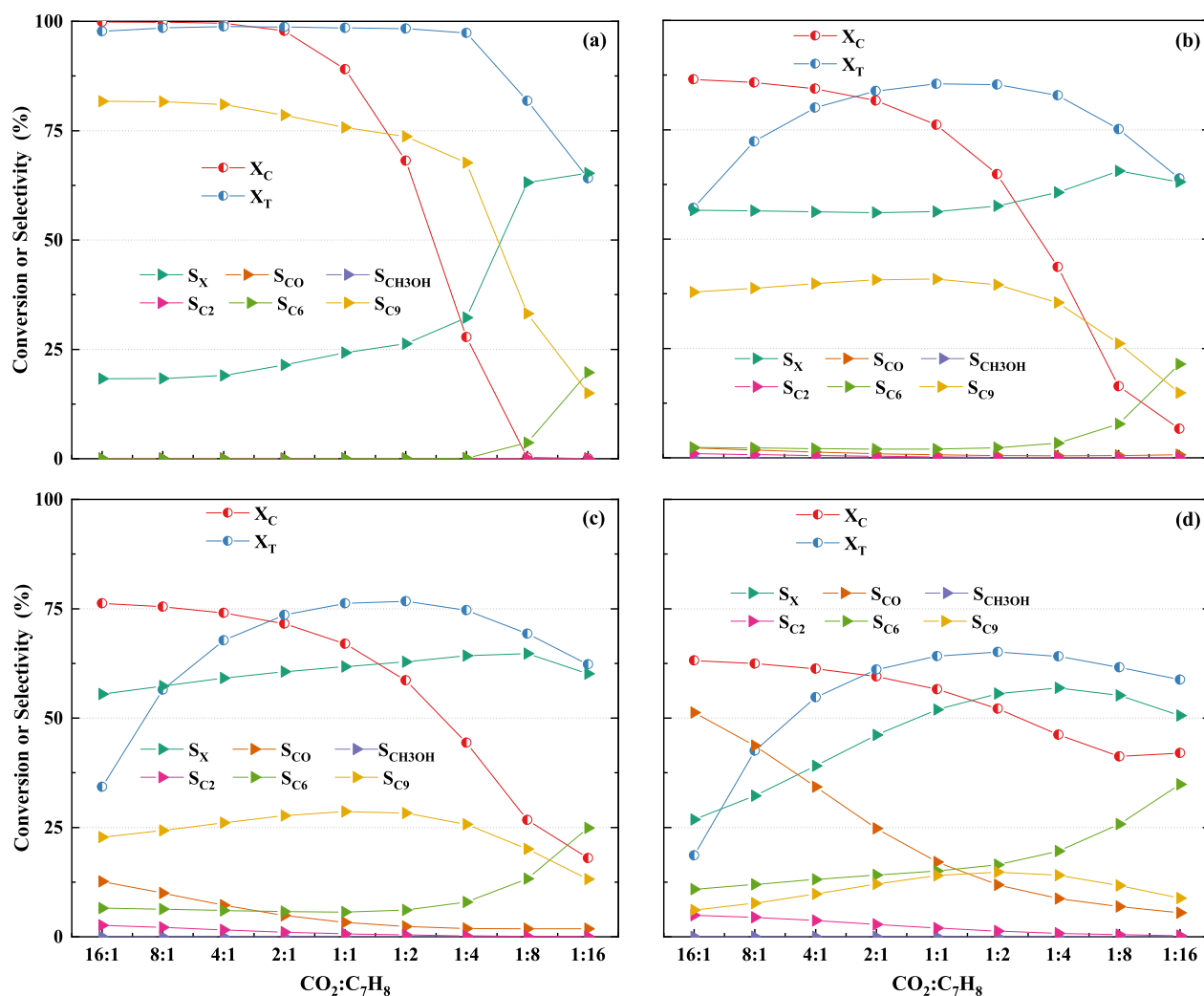


Figure 4. Effects of different molar ratios ($\text{CO}_2/\text{C}_7\text{H}_8$) on the equilibrium distribution with $\text{CO}_2/\text{H}_2 = 1:3$ at 3 MPa. (a) 200, (b) 360, (c) 420, and (d) 500 °C.

48% in xylenes. The 10% ZrZnO-2Z5 had the highest methylation usages of 93.1% for converted CO_2 to obtain 92.4% xylenes selectivity. However, the PX selectivity in xylenes in only 33% which is a little bit more than that of thermodynamic content. The 50% ZZO-4Z5 had the highest PX selectivity of 70.8% in xylenes with a modest feedstock conversion, resulting in a methylation usage of 85.6% and S_X of 80.96%. By compared under equal conditions, the thermodynamic obtained a very high conversion of 86.70% for CO_2 and nearly 100% for toluene. While for the products selectivity, the CO content is extremely low, 3.39%, but the C9 content is relatively high, 35.57%.

The $\text{ZrCuO}_{0.1}\text{-Zr}_{0.5}$ (50) and $\text{ZrCuO}_{0.1}\text{-Zr}_{0.5}$ (25) in Figure 6b were selected from Xiao's reports (360 °C, 3 MPa, GHSV = 12,000 $\text{mL g}^{-1} \text{h}^{-1}$ and WHSV = 1 h^{-1}),¹⁰ enhancing the conversions to 24.73 and 30.56% for CO_2 and 44.61 and 36.63% for toluene, respectively. However, these two catalysts have only 20.37 and 13.78% carbon usages for methylation. The thermodynamic value exhibits low CO content and high C_{9+} content under the equal experimental conditions.

It is worth noting that the two experimental systems both had a very large of feed ratio for CO_2 /toluene according to the conditions listed in Table 1, which are around 151:1 and 126:1 for ZnZrO-*n*Z5 and ZrCuO-Z5, respectively. The high ratio for CO_2 /toluene would favor aromatization and multi-methylation

reactions through thermodynamic minimization of Gibbs free energy, which may lead to the negative toluene conversion. Only when the aromatization is overlooked, it obtains nearly 100% toluene conversion in thermodynamics (in Figure 6). Despite the thermodynamic advantages of the methylation process, large amounts of CO and light hydrocarbons are still generated upon the bifunctional catalysts of 50% MO_x . When the MO_x amount and surface acid of Z5 are adjusted, the xylene yield, heavy aromatics yield, and PX selectivity in xylene would be significantly optimized at the expense of decreasing conversion.

3.3.2. Two Methylation Routes. To meaningfully understand the CO_2 methylation process, Zuo⁹ and Xiao¹⁰ et al. compared the results of two methylation routes after screening the effects of different parameters (temperature, pressure, carrier gas, and feed ratio) with a 13.2% toluene conversion. Similarly, the experimental and thermodynamic results for the two methylation routes are shown in Figure 7, where the selected catalysts have the max S_X . It can be noticed that CO_2 route produces a certain amount of CO, which even reach the maximum of 73.52% for the $\text{ZrCuO-Zr}_{0.5}$ (50). For the C1–C5 distribution, Cu has a catalytic advantage over Zn in CO_2 hydrogenation, and the methanol route has more activity may due to the surface acid and hydrogen atmosphere. For the aromatic products, the CO_2 route generates less benzene and C_{9+} but more xylene than the

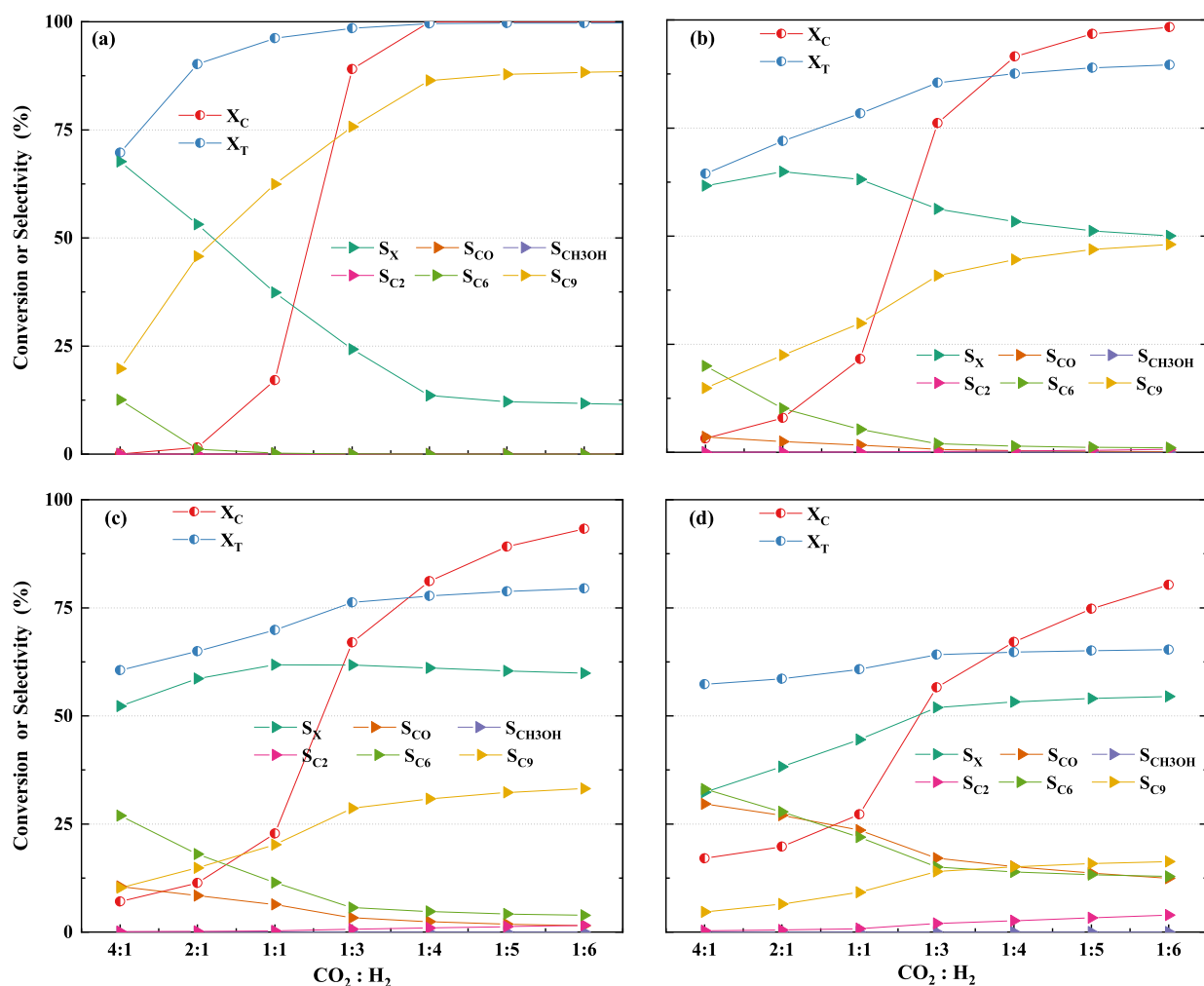


Figure 5. Effects of different molar ratios (CO_2/H_2) on the equilibrium distribution with $\text{CO}_2/\text{C}_7\text{H}_8 = 1:1$ at 3 MPa: (a) 200, (b) 360, (c) 420, and (d) 500 °C.

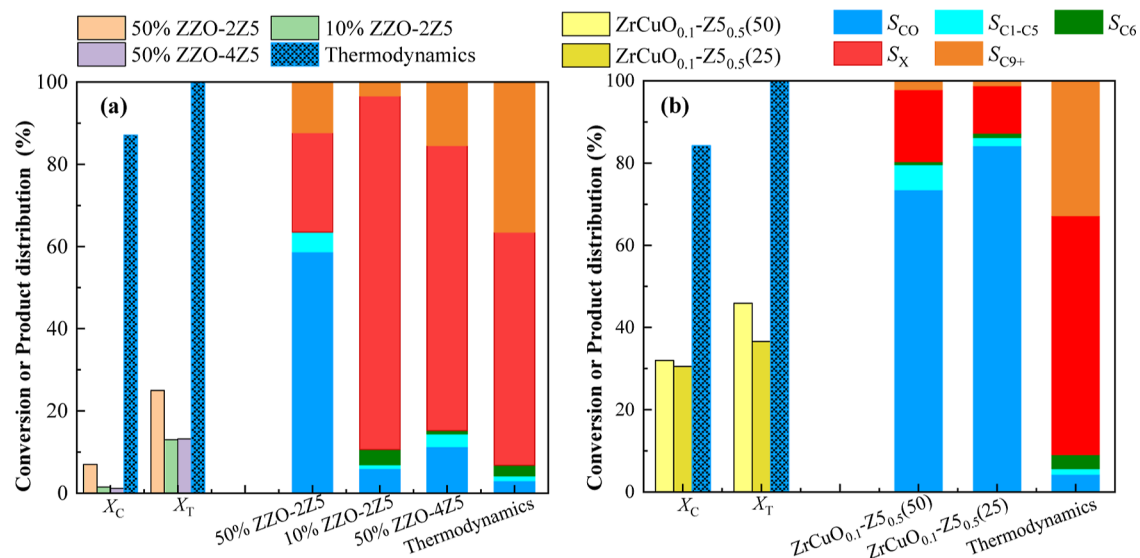


Figure 6. Comparison of experimental results and thermodynamic distribution for direct CO_2 methylation: (a) ZZO- n Z5 and (b) ZnCuO-Z5.

thermodynamic distribution, while the methanol route has the opposite distribution. Thus, the CO_2 route produces more CO due to the CO_2 activation of MO_x but more methylation

products due to the selective catalysis. Methanol route generates more light hydrocarbons and benzene due to the MTO or MTA side reactions.³⁷ It can be concluded that CO_2 replacing

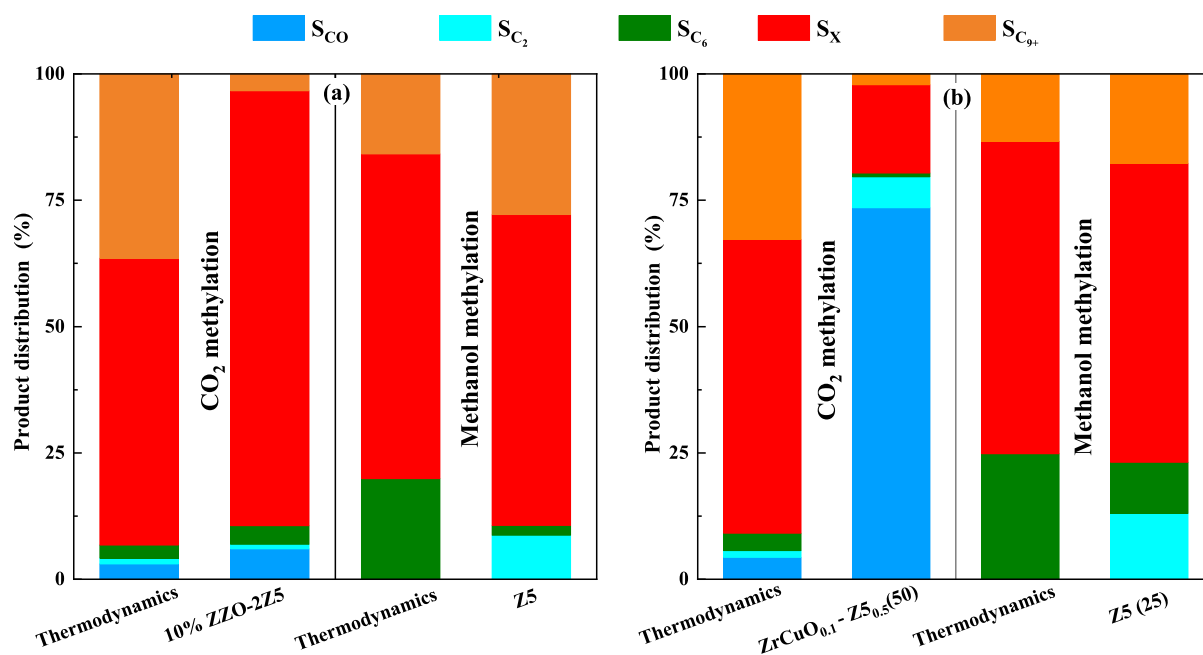


Figure 7. Comparison of experimental results and thermodynamic distribution for two methylation routes: (a) catalysts results of ZZO-Z5 and (b) catalysts results of ZnCuO-Z5.

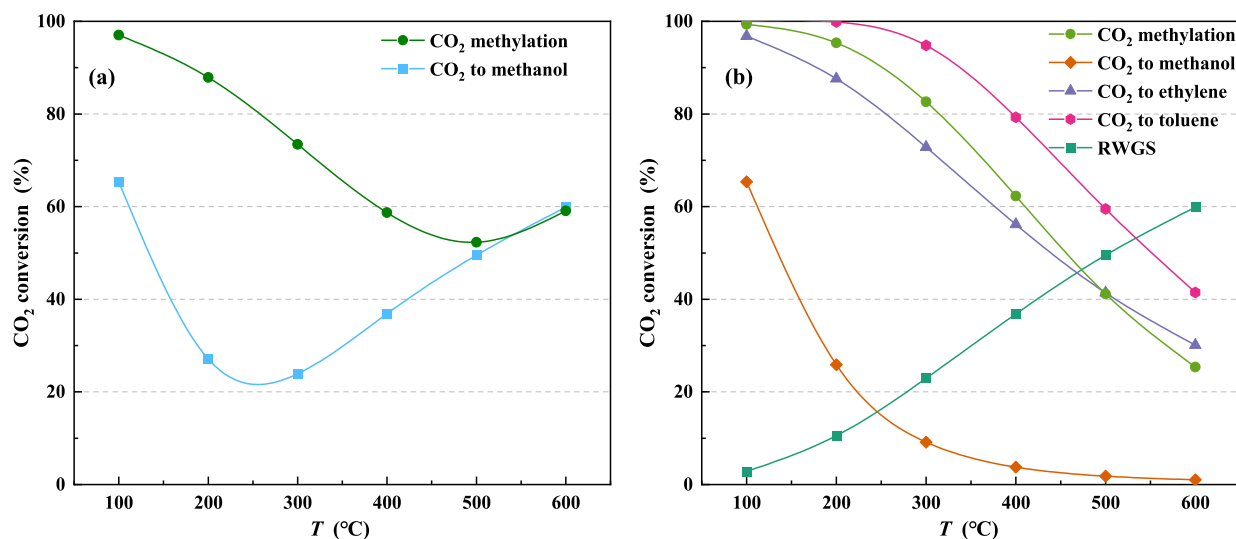


Figure 8. Thermodynamic equilibrium conversion for the main reactions with an initial feed of $\text{CO}_2/\text{H}_2/\text{N}_2/\text{C}_7\text{H}_8 = 10:30:10:1$ at 3.0 MPa. (a) Composite reaction system including R1–R3 and R6 and (b) single reactions.

methanol as C1 for toluene to PX process has a good prospect after further optimizing the activity and proportion for MO_x and selective catalysis for zeolite.

3.4. Conceptual Reaction Mechanism. The comparison has demonstrated that the direct CO_2 methylation with toluene would break the thermodynamic limit for CO_2 hydrogenation, and the temperature, pressure, feed composition, catalyst composition, and structure will all affect the methylation pathways. Actually, Zuo et al.⁹ has proposed a possible reaction mechanism and proven that the reactive methylation species of H_3CO^* entity is much easier obtained by the CO_2 hydrogenation route. The thermodynamic analysis of the main reactions separately is expected to supply more information for the CO_2 methylation mechanism from the view of reactive pathways.

The CO_2 conversions for different system are exhibited in Figure 8. As shown in Figure 8a, the CO_2 methylation pathway enhances the CO_2 conversion below 500 °C. Meanwhile, the single CO_2 hydrogenation pathways in Figure 8b have the following thermodynamic priorities: aromatization > methylation > CO_2 to olefins > CO_2 to methanol. The RWGS pathway gradually becomes competitive with the increase in temperature, especially above 500 °C. When the reaction temperature below 500 °C, it has the potential for CO_2 conversion higher than 60%.

Based on the thermodynamic analysis and the comparison with the experimental results, a possible reaction mechanism has been proposed over the bifunctional catalyst of MO_x and modified zeolite (shown in Figure 9). First, the CO_2 is activated on the MO_x in a hydrogen atmosphere so as to generate H_3CO^* and other intermediates. Second, the $^*\text{CO}$ intermediates forms CO or CO is activated to other intermediates. Then, the H_3CO^*

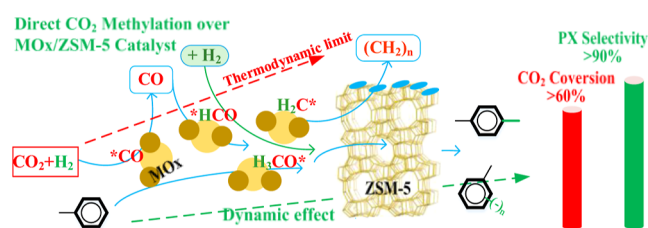


Figure 9. Possible reaction mechanism of direct CO₂ methylation over the MO_x/ZSM-5 bifunctional catalyst.

intermediate acts with the benzene ring to produce xylene and other methyl aromatics under the selective catalysis of modified zeolite. Meanwhile, the intermediates also would generate light hydrocarbons or lead to the aromatization reaction. For the CO₂ hydrogenation, the conversion is limited by the thermodynamic equilibrium. Once toluene is co-fed, the diffusion rate and catalytic kinetics would be the key issue that determine the catalytic performance and product distribution. As a thermodynamics potential, the direct CO₂ methylation would have a CO₂ conversion of >60% and a PX selectivity in xylene of >90% with the assistance of selective catalytic zeolite.

4. CONCLUSIONS

In summary, this study investigated the innovative route for direct CO₂ methylation with toluene to generate a high value product of PX. The thermodynamic analyses via the minimization method of Gibbs free energy have been introduced to consider the influence of temperature, pressure, and feed ratio, and the comparison with the experimental results have been used to inspect the possible mechanism of the CO₂ methylation from the view of reaction pathways of a complex system. The major findings are as follows:

- (1) The optimal conditions for direct CO₂ methylation are 360–420 °C, 3 MPa with middle CO₂/C₇H₈ ratio (1:1 to 1:4) and high H₂ feed (CO₂/H₂ = 1:3 to 1:6). The CO₂ conversion can get maximum 98.35% when toluene conversion is 89.52% and the xylene selectivity is 84.79% in CO₂-converted products under these conditions (360 °C, CO₂/H₂/C₇H₈ = 1:6:1).
- (2) The direct CO₂ methylation, as a tandem process, would break the thermodynamic limit and has the higher potential of >60% CO₂ conversion than that of CO₂ hydrogenation without toluene. The single CO₂ hydrogenation pathways below 500 °C have the following thermodynamic priorities: aromatization > methylation > CO₂ to olefins > CO₂ to methanol, and the RWGS pathway (CO₂ to CO) gradually become competitive with the increase in temperature.
- (3) Compared with the experimental results over bifunctional catalysts of MO_x/ZSM-5, the thermodynamic potential is large for CO₂ conversion. The direct CO₂ methylation route also has advantages over the methanol route in generating less benzene and C₉₊, but more xylene products. CO₂ replacing methanol as the C1 source for methylation to PX has a good prospect after further optimizing the activity and proportion of MO_x and selective catalysis of zeolite since the latter is determined by the catalytical dynamic effect.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c02999>.

Experimental catalyst and reaction conditions, conditions for catalytic methylation evaluation, thermodynamic properties in the range of 200–500 °C under 3 MPa, and effects of different pressures and molar ratios of CO₂:C₇H₈ on the equilibrium distribution (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Yong Yang – School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, China; Key Laboratory of Low Carbon Energy and Chemical Engineering of Gansu Province, Lanzhou, Gansu 730050, China; orcid.org/0000-0003-1588-6273; Email: yangy@lut.edu.cn

Dongqiang Zhang – School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, China; Key Laboratory of Low Carbon Energy and Chemical Engineering of Gansu Province, Lanzhou, Gansu 730050, China; Email: zhangdq@lut.edu.cn

Authors

Zhuoyu Wen – School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, China

Zixuan Zu – School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, China

Dongliang Wang – School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, China; Key Laboratory of Low Carbon Energy and Chemical Engineering of Gansu Province, Lanzhou, Gansu 730050, China

Huairong Zhou – School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, China; Key Laboratory of Low Carbon Energy and Chemical Engineering of Gansu Province, Lanzhou, Gansu 730050, China; orcid.org/0000-0002-2129-2968

Complete contact information is available at <https://pubs.acs.org/10.1021/acsomega.3c02999>

Author Contributions

CRedit authorship contribution statement: Yong Yang: conceptualization, formal analysis, and writing—review and editing. Zhuoyu Wen: investigation, data curation, formal analysis, and writing—original draft. Zixuan Zu: software, investigation, and formal analysis. Dongliang Wang: methodology and software. Huairong Zhou: software, investigation, and data curation. Dongqiang Zhang: supervision, funding acquisition, and data curation.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Joint Funds of National Natural Science Foundation of China (no. U22A20415), the Basic Research Innovation Group Project of Gansu Province (no. 22JRSRA219), and the Young Doctor Fund project of Education Department of Gansu Province (nos. 2021QB-041 and 2022QB-214).

REFERENCES

- (1) Tian, H.; He, H.; Jiao, J.; Zha, F.; Guo, X.; Tang, X.; Chang, Y. Tandem catalysts composed of different morphology HZSM-5 and metal oxides for CO₂ hydrogenation to aromatics. *Fuel* **2022**, *314*, 123119.
- (2) Kamkeng, A. D. N.; Wang, M.; Hu, J.; Du, W.; Qian, F. Transformation technologies for CO₂ utilisation: Current status, challenges and future prospects. *Chem. Eng. J.* **2021**, *409*, 128138.
- (3) Saravanan, A.; Senthil kumar, P.; Vo, D.-V. N.; Jeevanantham, S.; Bhuvaneswari, V.; Anantha Narayanan, V.; Yaashikaa, P. R.; Swetha, S.; Reshma, B. A comprehensive review on different approaches for CO₂ utilization and conversion pathways. *Chem. Eng. Sci.* **2021**, *236*, 116515.
- (4) Chen, J.; Wang, X.; Wu, D.; Zhang, J.; Ma, Q.; Gao, X.; Lai, X.; Xia, H.; Fan, S.; Zhao, T.-S. Hydrogenation of CO₂ to light olefins on CuZnZr@(Zn-)SAPO-34 catalysts: Strategy for product distribution. *Fuel* **2019**, *239*, 44–52.
- (5) Baak, J. A.; Pozarlik, A. K.; Arentsen, M. J.; Brem, G. Techno-economic study of a zero-emission methanol based energy storage system. *Energy Convers. Manage.* **2019**, *182*, 530–545.
- (6) Wang, D.; Xie, Z.; Porosoff, M. D.; Chen, J. G. Recent advances in carbon dioxide hydrogenation to produce olefins and aromatics. *Chem* **2021**, *7*, 2277–2311.
- (7) Zhou, J.; Liu, Z.; Wang, Y.; Kong, D.; Xie, Z. Shape selective catalysis in methylation of toluene: Development, challenges and perspectives. *Front. Chem. Sci. Eng.* **2017**, *12*, 103–112.
- (8) Chakinala, N.; Chakinala, A. G. Process Design Strategies To Produce p-Xylene via Toluene Methylation: A Review. *Ind. Eng. Chem. Res.* **2021**, *60*, 5331–5351.
- (9) Zuo, J.; Chen, W.; Liu, J.; Duan, X.; Ye, L.; Yuan, Y. Selective methylation of toluene using CO₂ and H₂ to para-xylene. *Sci. Adv.* **2020**, *6*, 5433.
- (10) Xiao, Z.; Huang, H.; Cao, C.; Xu, J.; Yang, Z. Designing a bifunctional ZrCuOx/HZSM-5 catalyst for selective methylation of toluene with carbon dioxide to para-xylene. *Fuel* **2022**, *319*, 123848.
- (11) Jiang, X.; Nie, X.; Guo, X.; Song, C.; Chen, J. G. Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chem. Rev.* **2020**, *120*, 7984–8034.
- (12) Sharma, P.; Sebastian, J.; Ghosh, S.; Creaser, D.; Olsson, L. Recent advances in hydrogenation of CO₂ into hydrocarbons via methanol intermediate over heterogeneous catalysts. *Catal. Sci. Technol.* **2021**, *11*, 1665–1697.
- (13) Wang, D.; Zhang, J.; Dong, P.; Li, G.; Fan, X.; Yang, Y. Novel Short Process for p-Xylene Production Based on the Selectivity Intensification of Toluene Methylation with Methanol. *ACS Omega* **2022**, *7*, 1211–1222.
- (14) Li, G.; Wu, C.; Ji, D.; Dong, P.; Zhang, Y.; Yang, Y. Acidity and catalyst performance of two shape-selective HZSM-5 catalysts for alkylation of toluene with methanol. *React. Kinet., Mech. Catal.* **2020**, *129*, 963–974.
- (15) Ting, K. W.; Kamakura, H.; Poly, S. S.; Toyao, T.; Hakim Siddiki, S. M. A.; Maeno, Z.; Matsushita, K.; Shimizu, K. i. Catalytic Methylation of Aromatic Hydrocarbons using CO₂/H₂ over Re/TiO₂ and H-MOR Catalysts. *ChemCatChem* **2020**, *12*, 2215–2220.
- (16) Liu, X.; Pan, Y.; Zhang, P.; Wang, Y.; Xu, G.; Su, Z.; Zhu, X.; Yang, F. Alkylation of benzene with carbon dioxide to low-carbon aromatic hydrocarbons over bifunctional Zn-Ti/HZSM-5 catalyst. *Front. Chem. Sci. Eng.* **2021**, *16*, 384–396.
- (17) Miao, D.; Pan, X.; Jiao, F.; Ji, Y.; Hou, G.; Xu, L.; Bao, X. Selective synthesis of para-xylene and light olefins from CO₂/H₂ in the presence of toluene. *Catal. Sci. Technol.* **2021**, *11*, 4521–4528.
- (18) Ting, K. W.; Kamakura, H.; Poly, S. S.; Takao, M.; Siddiki, S. M. A. H.; Maeno, Z.; Matsushita, K.; Shimizu, K.-i.; Toyao, T. Catalytic Methylation of m-Xylene, Toluene, and Benzene Using CO₂ and H₂ over TiO₂-Supported Re and Zeolite Catalysts: Machine-Learning-Assisted Catalyst Optimization. *ACS Catal.* **2021**, *11*, 5829–5838.
- (19) Bai, Y. B.; Yang, F.; Liu, X. Y.; Liu, C. X.; Zhu, X. D. Performance of Bifunctional ZnZr/ZSM-5 Catalysts in the Alkylation of Benzene with Syngas. *Catal. Lett.* **2018**, *148*, 3618–3627.
- (20) Lee, S.; Kim, D.; Lee, J.; Choi, Y.; Suh, Y.-W.; Lee, C.; Kim, T. J.; Lee, S. J.; Lee, J. K. An in situ methylation of toluene using syngas over bifunctional mixture of Cr₂O₃/ZnO and HZSM-5. *Appl. Catal., A* **2013**, *466*, 90–97.
- (21) Yang, X.; Su, X.; Chen, D.; Zhang, T.; Huang, Y. Direct conversion of syngas to aromatics: A review of recent studies. *Chin. J. Catal.* **2020**, *41*, 561–573.
- (22) Wen, D.; Zuo, J.; Han, X.; Liu, J.; Ye, L.; Yuan, Y. Synthesis of durenene by methylation of 1,2,4-trimethylbenzene with syngas over bifunctional CuZnZrOx–HZSM-5 catalysts. *Catal. Sci. Technol.* **2022**, *12*, 2555–2565.
- (23) Zhao, Y.; Cheng, J.; Zhang, P.; Liu, X.; Zhuang, J.; Yu, Y.; Zhao, Q.; Wang, Y.; Zhu, X.; Yang, F. Examination of key factors determining the catalytic performance of Zn-Ga/HZSM-5 bifunctional catalysts and establishment of reaction network in alkylation of benzene with carbon dioxide. *Appl. Catal., A* **2022**, *643*, 118785.
- (24) Bian, G.; Niu, P.; Jia, L.; Guo, H.; Li, D. Alkylation of benzene using CO₂ and H₂ over ZnZrOx/ZSM-5: the effect of Y doping. *New J. Chem.* **2023**, *47*, 609–617.
- (25) Wang, T.; Yang, C.; Gao, P.; Zhou, S.; Li, S.; Wang, H.; Sun, Y. ZnZrOx integrated with chain-like nanocrystal HZSM-5 as efficient catalysts for aromatics synthesis from CO₂ hydrogenation. *Appl. Catal., B* **2021**, *286*, 119929.
- (26) Zhang, X.; Zhang, A.; Jiang, X.; Zhu, J.; Liu, J.; Li, J.; Zhang, G.; Song, C.; Guo, X. Utilization of CO₂ for aromatics production over ZnO/ZrO₂-ZSM-5 tandem catalyst. *J. CO₂ Util.* **2019**, *29*, 140–145.
- (27) Saeed Baamran, K.; Tahir, M. Thermodynamic investigation and experimental analysis on phenol steam reforming towards enhanced H₂ production over structured Ni/ZnTiO₃ nanocatalyst. *Energy Convers. Manage.* **2019**, *180*, 796–810.
- (28) Nezam, I.; Zhou, W.; Gusmão, G. S.; Realf, M. J.; Wang, Y.; Medford, A. J.; Jones, C. W. Direct aromatization of CO₂ via combined CO₂ hydrogenation and zeolite-based acid catalysis. *J. CO₂ Util.* **2021**, *45*, 101405.
- (29) Hussain, I.; Jalil, A. A.; Mamat, C. R.; Siang, T. J.; Rahman, A. F. A.; Azami, M. S.; Adnan, R. H. New insights on the effect of the H₂/CO ratio for enhancement of CO methanation over metal-free fibrous silica ZSM-5: Thermodynamic and mechanistic studies. *Energy Convers. Manage.* **2019**, *199*, 112056.
- (30) Miguel, C. V.; Soria, M. A.; Mendes, A.; Madeira, L. M. Direct CO₂ hydrogenation to methane or methanol from post-combustion exhaust streams – A thermodynamic study. *J. Nat. Gas Sci. Eng.* **2015**, *22*, 1–8.
- (31) Ateka, A.; Pérez-Urriarte, P.; Gamero, M.; Ereña, J.; Aguayo, A. T.; Bilbao, J. A comparative thermodynamic study on the CO₂ conversion in the synthesis of methanol and of DME. *Energy* **2017**, *120*, 796–804.
- (32) Sahebdehfar, S.; Takht Ravanchi, M. Carbon dioxide utilization for methane production: A thermodynamic analysis. *J. Pet. Sci. Eng.* **2015**, *134*, 14–22.
- (33) Zhang, D.; Yang, M.; Feng, X. Aromatics production from methanol and pentane: Conceptual process design, comparative energy and techno-economic analysis. *Comput. Chem. Eng.* **2019**, *126*, 178–188.
- (34) Abdel Karim Aramouni, N.; Zeaiter, J.; Kwapinski, W.; Ahmad, M. N. Thermodynamic analysis of methane dry reforming: Effect of the catalyst particle size on carbon formation. *Energy Convers. Manage.* **2017**, *150*, 614–622.
- (35) Nikoo, M. K.; Amin, N. A. S. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. *Fuel Process. Technol.* **2011**, *92*, 678–691.
- (36) Bello, T. O.; Bresciani, A. E.; Nascimento, C. A. O.; Alves, R. M. B. Thermodynamic analysis of carbon dioxide hydrogenation to formic acid and methanol. *Chem. Eng. Sci.* **2021**, *242*, 116731.
- (37) Kattel, S.; Yan, B.; Yang, Y.; Chen, J. G.; Liu, P. Optimizing Binding Energies of Key Intermediates for CO₂ Hydrogenation to Methanol over Oxide-Supported Copper. *J. Am. Chem. Soc.* **2016**, *138*, 12440–12450.
- (38) Ouda, M.; Mantei, F. K.; Elmehlawy, M.; White, R. J.; Klein, H.; Fateen, S. E. K. Describing oxymethylene ether synthesis based on the

application of non-stoichiometric Gibbs minimisation. *React. Chem. Eng.* **2018**, *3*, 277–292.