Coupling Conversion of CO₂ and *n*-Butane Over Modified ZSM-5: Incorporation of the Carbon from CO₂ into Hydrocarbon Products

Kuo Yang, Jinzhe Li, Changcheng Wei, Zhongkui Zhao,* and Zhongmin Liu*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The coupling reaction of CO_2 and n-butane was conducted over different metal-modified (Mn, Zr, Ni, Ti, Zn) ZSM-5 catalysts. A high CO_2 conversion of 26.5% and n-butane conversion of 100% with the aromatics selectivity of 69.1% was achieved at a CO_2 to n-butane ratio of 0.95 over Zn/ZSM-5. CO_2 addition promoted BTX & olefin selectivity, while it inhibited alkane & A_{9+} formation. A detailed analysis showed that 13% of the carbon atoms from CO_2 were incorporated in the generation of aromatic hydrocarbons. Oxygenated intermediates, such as aliphatic alcohol, aliphatic ketones, and substituted cyclopentenones, were detected sequentially with the increase of the reaction temperature. In addition, reverse Boudouard reaction, water gas shift reaction, and dry reforming also participated in the formation of CO over Zn/ZSM-5. Based on these findings and the detailed characterization results, a plausible mechanism of direct and indirect incorporation of carbon from CO_2 into aromatics was proposed for the coupling reaction.

Coupling reaction of n-butane and CO_2 over Zn/ZSM-5

KEYWORDS: *n-butane, CO₂ utilization, coupling reaction, metal-modified, zeolite*
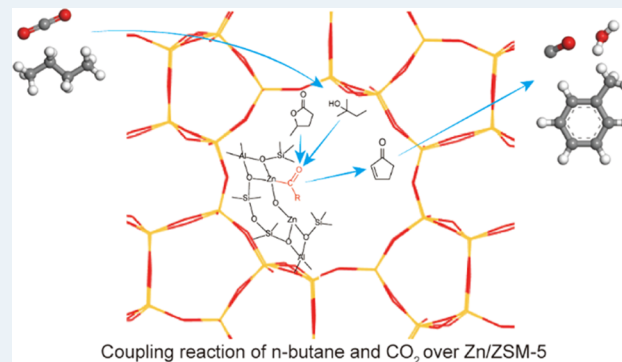
1. INTRODUCTION

CO_2 utilization has attracted extensive attention worldwide in recent years.[1] The major obstacle for CO_2 utilization arises from its thermodynamic stability and low reactivity, which needs significant energy and "talented" catalysts to achieve the conversion into high-value chemicals.[2] A tremendous amount of research has been done on the conversion of CO_2 to valuable chemicals.[3]

One of the promising routes for CO_2 utilization is oxidative dehydrogenation (CO_2-ODH) of alkanes with CO_2 to olefins and aromatic products.[1,4,5] In this case, CO_2 acts as a soft oxidant, which can consume not only H_2 to shift the reaction equilibrium, but also the coke via the reverse Boudouard reaction ($CO_2 + C \rightarrow 2CO$) to enhance the catalyst stability.[4] However, in most of the previous reports, CO_2 was solely converted into CO and the C atom in CO_2 was not converted into hydrocarbon products.

In our latest research, H-ZSM-5 was found to be an effective catalyst for the coupling conversion of CO_2/CO and alkanes,[6−8] where CO_2/CO was used as a hydrogen-deficient substance to balance the excess hydrogen of straight-chain alkanes to achieve high aromatic selectivity, and it has been verified that the carbon atom in CO_2/CO can be incorporated into aromatic products via oxygenate intermediates. The catalytic performance of H-ZSM-5 zeolite in alkane conversion has been extensively explored and is attributed to its unique channel size (0.55 nm) and acidic properties;[9,10] the modification of ZSM-5 with different metal cations, such as $Zn^{11−13}$ and $Ga,^{14−16}$ has also been carried out to improve the dehydrogenation properties. Therefore, modifications of H-ZSM-5 by metal cations are also expected to improve its performances in the coupling reaction of CO_2 and alkanes.

Herein, we systematically studied the coupling reaction of CO_2 and *n*-butane over different metal-modified (Mn, Zr, Ni, Ti, Zn) ZSM-5 zeolites. Among them, Zn/ZSM-5 showed the best catalytic performance for CO_2 conversion and aromatics' selectivity. *In situ* characterizations and isotope labeling experiments further revealed that the carbon atoms in CO_2 could be partly incorporated into the aromatics over Zn/ZSM-5, and a plausible reaction mechanism was proposed.

2. EXPERIMENTAL SECTION

2.1. Catalyst and Catalyst Characterization. H-ZSM-5 zeolites with different Si/Al ratios were purchased from NanKai University Catalyst Co., Ltd. $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and butyl titanate were supplied by Tianjin Damao Chemical Reagent Factory. $Zr(NO_3)_4 \cdot 5H_2O$ and

$Mn(NO_3)_2 \cdot 4H_2O$ were obtained from Sanen Chemical Technology (Shanghai) Co., Ltd. and Shanghai Aladdin Biochemical Technology Co., Ltd., respectively. *N*-butane/CO_2 mixture (*n*-butane, 2.5%; CO_2, 92.5%; Ar, 5%), *n*-butane/He mixture (*n*-butane, 2.5%; helium, 97.5%), CO_2 (CO_2, 95.0%; Ar, 5.0%), and helium (>99.999%) were purchased from Dalian Special Gas Co., Ltd.

The X-ray diffraction (XRD) patterns of the zeolites were identified using a PANalytical X' Pert Pro diffractometer with Cu Kα radiation. The silicon to aluminum ratio of H-ZSM-5 zeolites was measured by XRF using a PANalytical AXIOS spectrometer. The surface area and pore volume of the H-ZSM-5 zeolites were determined by nitrogen adsorption and desorption analysis recorded at 77 K on a Micromeritics ASAP-2020 analyzer after the sample was degassed at 350 °C under vacuum for 4 h. The total surface area was calculated via the Brunauer-Emmett-Teller (BET) equation, and the total pore volume was measured by the N_2 adsorption amount at $P/P_0 = 0.97$. Micropore surface area, external surface area, and micropore volume were determined by the *t*-plot method.

The total acid amount of zeolite was measured by temperature-programed desorption (TPD) experiments using ammonia as the probe molecule, which was performed on a Micromeritics AutoChem 2920 equipped with a thermal conductivity detector (TCD). After 0.2 g of zeolite was loaded into a quartz tube and pretreated at 650 °C in helium gas for 30 min, it was cooled to 100 °C and saturated with NH_3. Subsequently, the sample was pretreated with helium gas to remove the physically adsorbed ammonia. After that, the desorbed NH_3 was recorded from 100 to 650 °C at a heating rate of 10 °C/min in helium gas. The XRF, N_2 adsorption–desorption, and NH_3-TPD results of H-ZSM-5 are depicted in the Supporting Information Table S1.

The metal-modified catalysts were prepared by incipient wetness impregnation. Typically, a certain amount of metallic salt was dissolved in deionized water and then the zeolite sample was added into the solution. After impregnation, the samples were placed in the atmosphere statically for 2 h, dried overnight at 120 °C, and then calcined at 550 °C for 4 h. The obtained samples were denoted as *x*%M/ZSM-5-*y* (*x*, M, and *y* represent the metal content, metal name, and Si/Al ratio of ZSM-5, respectively). All of the catalysts were tableted, crushed, and sieved to 40–60 mesh for reaction evaluations.

2.2. Catalytic Testing. In brief, the exact weight of the prepared catalyst was loaded into a quartz tube fixed-bed reactor (6 mm i.d.) enclosed in a stainless steel reactor. The catalyst bed was held between two quartz wool plugs, and the upstream dead volume was packed with silica granules. Prior to the reaction evaluation, the catalyst bed was heated in flowing helium (40 mL/min) at 550 °C for 1 h and adjusted to the reaction temperature. After that, the n-butane and CO_2 mixture (*n*-butane, 2.5%; CO_2, 92.5%; Ar, 5%) controlled by s Seven Star mass flowmeter was introduced into the catalyst bed. The catalytic reactions were performed at 400–550 °C under 0.1–2.5 MPa. The contact time was changed by adjusting the catalyst weight (0.05–0.4 g), while maintaining other reaction conditions.

All of the effluent products were analyzed by an online gas chromatograph (Agilent 7890A) equipped with a HP-1 capillary column (100 m × 250 μm × 0.5 μm) connected to a flame ionization detector (FID) and applied to analyze the hydrocarbon products' distribution. A TDX-01 packed column (2 m × 1/8 m) connected to a thermal conductivity detector

(TCD) was applied to analyze the CO_2 conversion and CO selectivity.

$$X_{CO_2} = \frac{CO_{2_{inlet}} - CO_{2_{outlet}}}{CO_{2_{inlet}}} \times 100\%$$

$$Sel_{CO} = \frac{CO_{outlet}}{CO_{2_{inlet}} - CO_{2_{outlet}}} \times 100\%$$

where $CO_{2_{inlet}}$, $CO_{2_{outlet}}$, and CO_{outlet} represent the moles of CO_2 at the inlet and outlet, and CO at the outlet, respectively, and were analyzed by GC using Ar as an internal standard. CO_2 (X_{CO_2}) conversion and CO selectivity (Sel_{CO}) were calculated based on the above equation.

$$X_{butane} = \frac{butane_{inlet} - butane_{outlet}}{butane_{inlet}} \times 100\%$$

N-butane conversion (X_{butane}) was calculated using the above formula. Butane$_{inlet}$ and butane$_{outlet}$ represent the carbon mole fractions of *n*-butane in the inlet and outlet, respectively.

The carbon selectivity of C_nH_m ($Sel_{C_nH_m}$) in the hydrocarbons was calculated as follows

$$Sel_{C_nH_m} = \frac{C_nH_{m_{outlet}}}{\sum_1^n C_nH_{m_{outlet}}} \times 100\%$$

where $C_nH_{m_{outlet}}$ represents the carbon mole fraction of product C_nH_m at the outlet. $\sum_1^n C_nH_{m_{outlet}}$ represents the sum of the carbon mole fractions of all of the hydrocarbon products (not including feedstock) at the outlet.

2.3. In Situ DRIFT Spectroscopy Study. *In situ* DRIFT spectra were recorded using a Bruker Tensor 27 FTIR spectrometer equipped with a diffuse reflectance attachment and MCT detector. Generally, zeolite powder was loaded into the diffuse reflectance infrared cell with a ZnSe window; then, the infrared cell was heated to 500 °C for 1 h under a 30 mL/min (at STP) N_2 stream and cooled to 50 °C. The stream of CO_2 (or He) with *n*-butane was introduced into the infrared cell at 10 mL/min. The *in situ* DRIFT spectra recorded with 32 scans at a resolution of 4 cm^{-1} were collected as the temperature increased from 100 to 300 °C at a constant rate of 10 °C/min. The IR difference spectra were obtained by subtracting the spectra of the Zn/ZSM-5 zeolite framework from the collected spectra at the corresponding temperatures.

2.4. Isotope Tracing Experiments. The experiments were conducted with $^{13}CO_2$ and ^{12}C n-butane as the reactants using the same apparatus. N-butane mixture (*n*-butane, 2.5%; He, 97.5%) with 5 mL/min and $^{13}CO_2$ (or $^{12}CO_2$ using in contrast experiment) with 5 mL/min were introduced into the reactor. The reaction was performed at 220 and 500 °C under 0.5 MPa. The gas-phase products were collected by CH_2Cl_2 absorption and analyzed by gas chromatography-mass spectrometry (GC-MS) to determine the isotopic distribution. The catalyst was removed from the reactor after 40 min on stream and then quenched by liquid nitrogen. The retained species over the spent Zn/ZSM-5 were analyzed and identified via GC-MS by dissolving 0.1 g of the spent catalysts in 20% hydrofluoric solution and extracting the organic phase using 0.4 mL of CH_2Cl_2.[17,18] The organic species were analyzed using the GC-MS.

3. RESULTS AND DISCUSSION

3.1. Effects of Composition on the Catalytic Performance of the Metal-Modified ZSM-5 Under Atmospheric
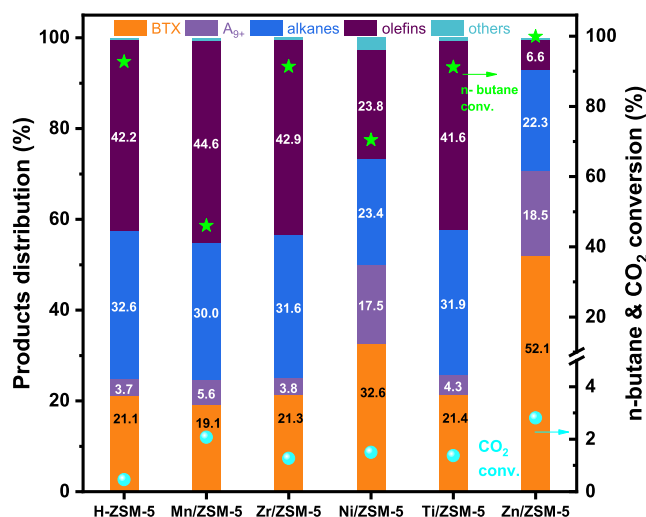

Figure 1. Catalytic performance of the co-feeding of CO_2 and n-butane over metal-modified ZSM-5. Reaction conditions: 0.2 g of the catalyst (ZSM-5 Si/Al = 17), T = 550 °C, P = 1 bar, CO_2/n-butane/Ar = 37/1/2, total flow = 10 mL/min at standard temperature and pressure (STP), TOS = 1.5 h. Others are mainly composed of C_{4+} alkanes. A_{9+} aromatics are composed of ethylbenzene and aromatics with more than 8 carbon atoms.

Pressure. Co-feeding of CO_2 and n-butane over different metal-modified ZSM-5 was performed and compared with that over H-ZSM-5. As shown in Figure 1, Mn, Zr, and Ti modification promoted CO_2 conversion, but had limited effects on product selectivity. With the introduction of Ni and Zn, the selectivity of aromatics was significantly improved (50.1% for Ni/ZSM-5 and 70.6% for Zn/ZSM-5). Assuming that n-butane was completely converted to methane and aromatics, the theoretical maximum of the aromatic selectivity was calculated to be 56.3% (Table S2). The aromatic selectivity (70.6%) over Zn/ZSM-5 was much higher than the theoretical maximum; thus, further investigations were conducted over Zn/ZSM-5.

In consideration of the importance of Si/Al ratio for the catalyst performance, ZSM-5 with different Si/Al ratios was used to prepare Zn-modified catalysts and the catalytic results are shown in Figure 2a,b. As the Si/Al ratio increased from 17 to 222, the CO_2 and n-butane conversion decreased gradually; meanwhile, BTX and A_{9+} selectivity also decreased. This indicates that Brønsted acid sites contribute to the conversion of n-butane and CO_2 and promote the generation of aromatics.

Table 1 shows the CO selectivity of the co-feeding reaction over Zn/ZSM-5 with different Si/Al ratios. On the catalysts with Si/Al ratio lower than 131, CO selectivities are higher than 100%, which indicates that the molar number of the CO generated is larger than that of the CO_2 converted. According to the literature, CO can be generated by reverse water gas shift reaction, reverse Boudouard reaction, and dry reforming reaction.[19,20] On the basis of element balance, the latter two reactions will produce more CO. Although CO_2 conversion was lower than 1% over Zn/ZSM-5 (Si/Al = 222), CO selectivity was 76.5%.

The influence of Zn content on the co-feeding reaction was further investigated (Figure 2c,d). The XRD patterns of ZSM-5 with different Zn contents are shown in Figure S1. The main characteristic peaks of the catalysts were consistent with those of H-ZSM-5, indicating that the metal-modified zeolites still retain the MFI topological structure. The intensity of the peaks was decreased with the increase of Zn content; this indicates that the crystallinity of the catalyst decreases gradually. The CO_2 and n-butane conversion increased sharply with the increase of Zn content (Figure 2c). As the Zn content increased to 10%, CO_2 conversion was 8% and n-butane conversion was 100%. Aromatics' selectivity increased and olefin selectivity decreased significantly with the introduction of Zn. BTX selectivity gradually decreased with the increase of Zn content (Figure 2d). These results suggest that Zn could promote the aromatization during the co-feeding reaction. As shown in Table 2, CO selectivities were higher than 100%.

3.2. Effects of Reaction Conditions on the Catalytic Performance of Zn/ZSM-5 under Atmospheric Pressure.

The effect of reaction temperature is shown in Figure 3a,b. Aromatics' selectivity first increased and then decreased when the temperature increased from 450 to 600 °C, and a maximum of about 70% was observed at 550 °C, while alkane selectivity increased almost linearly and olefin selectivity decreased gradually. As shown in Figure 3b, BTX selectivity showed a maximum at 500 °C, while A_{9+} selectivity increased gradually with the increasing temperature, indicating that high temperature promotes the light aromatics' transformation to the heavy aromatics over the Zn/ZSM-5 catalyst. As shown in Table 3, CO selectivity increased with increasing temperature, which indicates that the reforming reaction is benefited.

The effects of the contact time on the co-feeding reaction are shown in Figure 3c,d. Prolonging the contact time could significantly increase the aromatics' and alkane selectivity (Figure 3c). In contrast, the olefin selectivity decreased sharply, which indicates that olefins tend to form aromatics through hydrogen transfer reactions over Zn/ZSM-5 with the increase of contact time.[21,22] A longer contact time was beneficial for the CO_2 and n-butane conversion (Figure 3d). As shown in Table 4, CO selectivity increased with increasing contact time. These results indicate that longer contact time results in the transformation of light aromatics to the heavy aromatics and also benefits the reforming reaction.

3.3. Comparison of n-Butane Conversion under CO_2 or He over Zn/ZSM-5 at 0.5 MPa. Based on the above investigations of the reaction conditions and catalyst composition under atmospheric pressure, we found that CO selectivity was higher than 100% in most cases. This indicates that the carbon atom of CO_2 was not incorporated into hydrocarbon products and almost all of the converted CO_2 was transformed into CO. In order to promote the incorporation of CO_2 into the hydrocarbons, experiments were conducted under higher pressure (0.5 MPa). In addition, to minimize the formation of CO, the contact time was shortened by reducing the catalyst load (0.05 g) to eliminate the reforming reaction and reverse Boudouard reaction of CO_2. The catalytic performances of Zn/ZSM-5 were compared in CO_2 atmosphere and He atmosphere (Figure 4). Introduction of CO_2 into n-butane conversion dramatically promoted olefin selectivity and decreased alkane selectivity, demonstrating that the CO_2 participated in the conversion of n-butane; O takes away H from alkanes to generate more unsaturated alkenes. When the temperature was above 500 °C, the
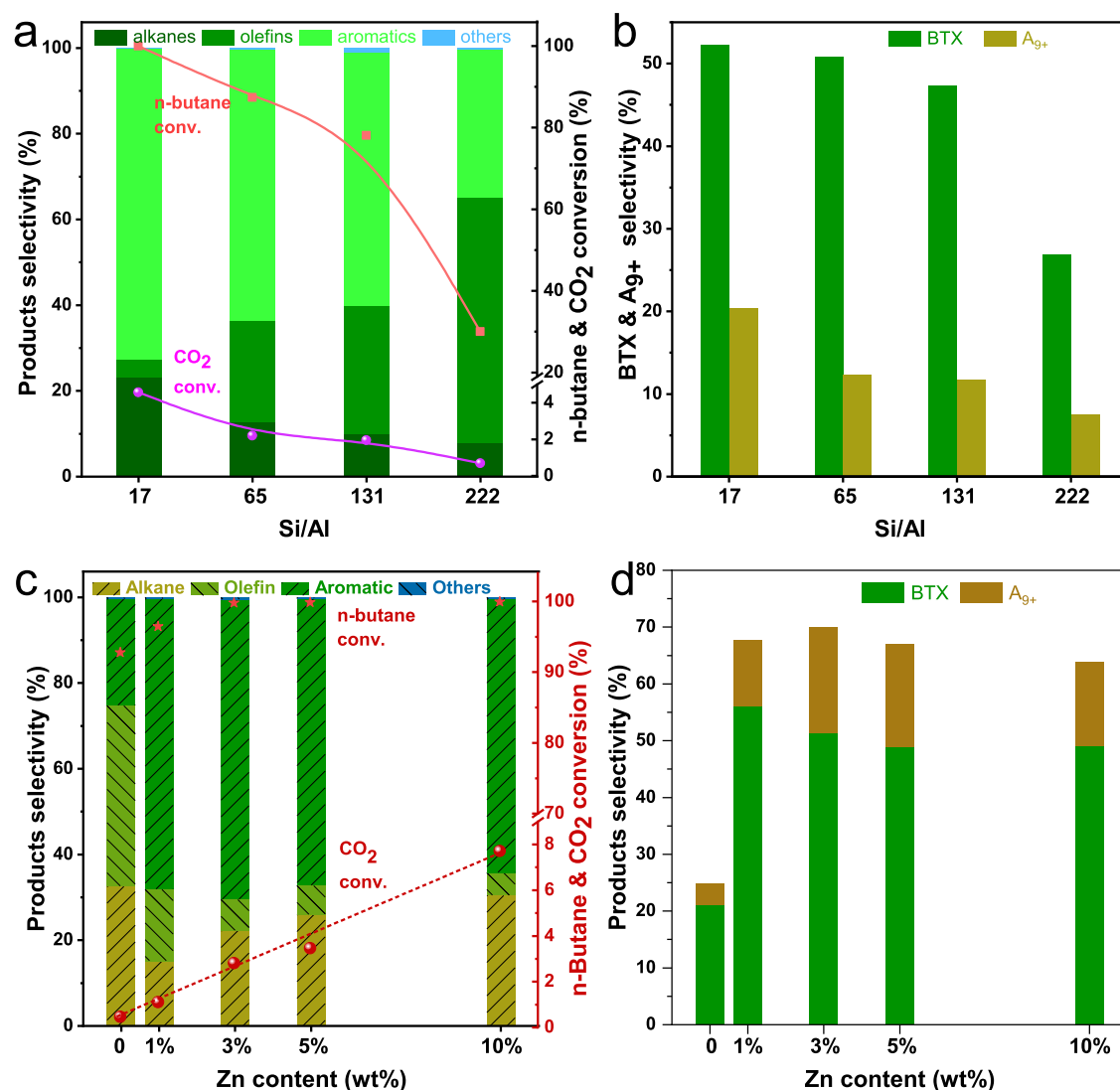
Figure 2. Effect of catalyst composition on the catalytic performance of co-feeding of CO_2 and *n*-butane. (a, b) Effect of Si/Al ratio (17, 65, 131, 222) on the catalytic performance of 3%Zn/ZSM-5. (c, d) Effects of Zn content (0−10%) on the catalytic performance of Zn/ZSM-5 (Si/Al = 17). Reaction conditions: 0.2 g of catalyst, $T = 550°C$, $P = 1$ bar, CO_2/*n*-butane/Ar = 37/1/2, total flow = 10ml/min, TOS = 2.2 h.

Table 1. CO Selectivity during the Co-Feeding Reaction over 3%Zn/ZSM-5 with Different Si/Al Ratios

Zn/ZSM-5	Si/Al = 17	Si/Al = 65	Si/Al = 131	Si/Al = 222
CO selectivity (%)	139.3	118.5	114.4	76.5

Table 2. Effects of the Zn Content on the CO Selectivity during the Co-Feeding Reaction

Zn content (%)	0	1	3	5	10
CO selectivity (%)		146.9	139.3	136.9	127.2

aromatics' selectivity increased significantly by CO_2 co-feeding. A relatively high CO_2 conversion was also obtained (2.1% at 500 °C and 4.5% at 550 °C). Moreover, as shown in Figure 4e,f, CO_2 addition was beneficial for the light aromatics (BTX). Table 5 shows the CO selectivity at different reaction temperatures. It can be seen that CO selectivity was lower than 80%, which demonstrates that the part of the carbon atoms in CO_2 are incorporated into the hydrocarbon products, especially into aromatics at higher reaction temperatures. Furthermore, introduction of CO_2 hinders the further

evolution of BTX to heavy aromatics. With the increase in temperature, aromatics' selectivity increased, while alkane selectivity increased in He atmosphere. In contrast, aromatics' selectivity increased while alkane selectivity gradually decreased in CO_2 atmosphere. This indicates that the introduction of CO_2 partially changes the reaction route, and there is a coupling effect during the reaction.

3.4. Effect of CO_2 Partial Pressure on *n*-Butane Conversion over Zn/ZSM-5. The catalytic performance of Zn/ZSM-5 at different CO_2 partial pressures is shown in Figure 5. It can be seen that the aromatics' selectivity increased with CO_2 partial pressure, while the alkane selectivity decreased (Figure 5a), which is consistent with the results in Section 3.3. If the aromatics were formed via hydrogen transfer reaction, a large amount of light alkanes would be produced simultaneously.[21,22] On the basis of low CO selectivity (<100%), aromatics' selectivity increased while alkane selectivity decreased with the increase of CO_2 conversion. These results indicate that CO_2 is incorporated in the generation of aromatics and the hydrogen transfer route is partially changed.
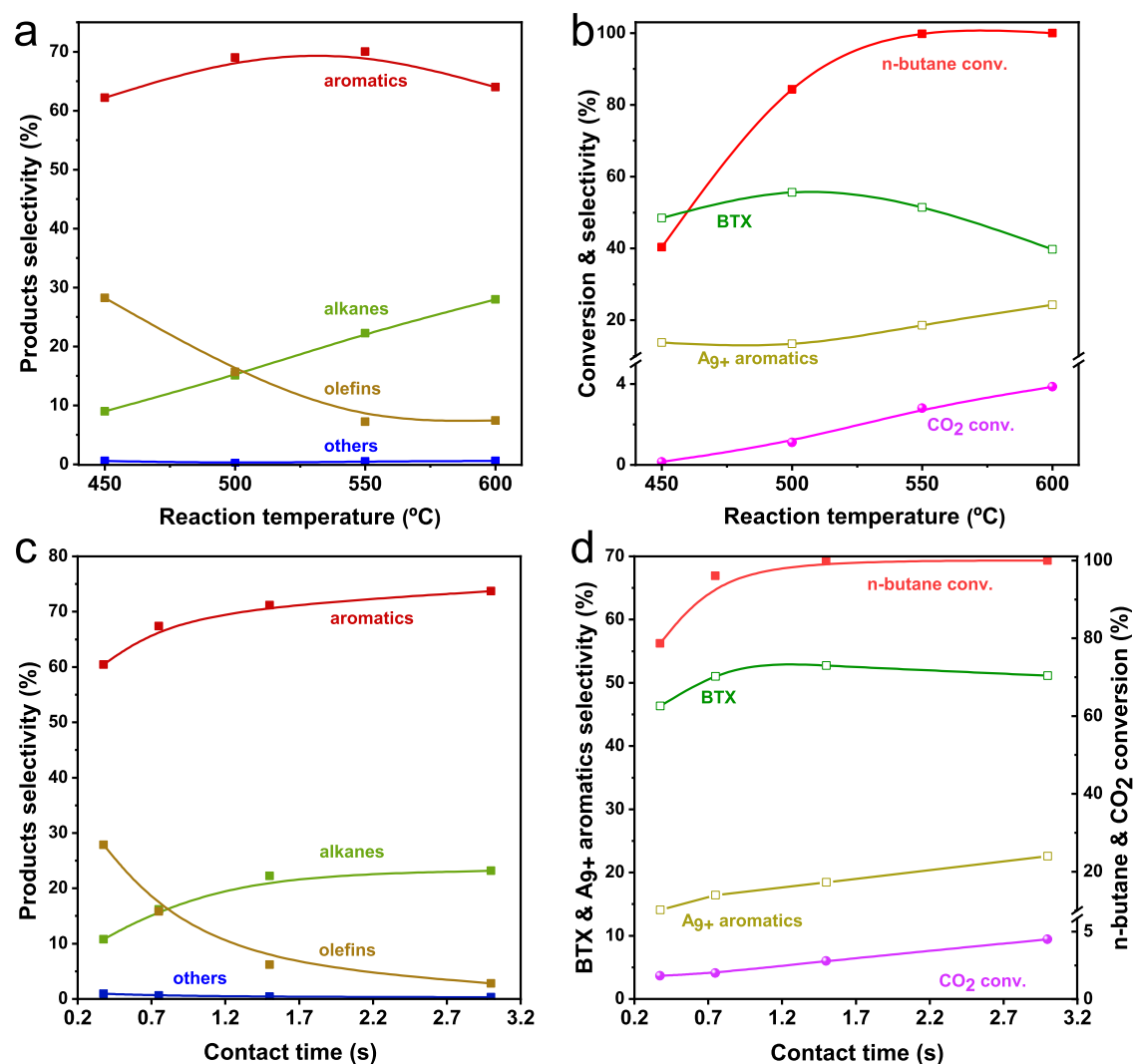
Figure 3. Effects of reaction conditions on the catalytic performance of the co-feeding reaction of CO_2 and n-butane over Zn/ZSM-5. (a, b) Effects of reaction temperature on the catalytic performance. (a) Products' selectivity, (b) conversion and BTX & A_{9+} aromatic selectivity. Reaction conditions: 0.2 g of 3%Zn/ZSM-5 (Si/Al = 17), T = 450−600 °C, P = 1 bar, CO_2/n-butane/Ar = 37/1/2, total flow = 10 mL/min, TOS = 2.2 h. (c, d) Effects of contact time on the catalytic performance. (c) Products' selectivity, (d) conversion and BTX & A_{9+} aromatic selectivity. Reaction conditions: 0.05−0.4 g of 3%Zn/ZSM-5 (Si/Al = 17), T = 550 °C, P = 1 bar, CO_2/n-butane/Ar = 37/1/2, total flow = 10 mL/min, TOS = 2.2 h.

Table 3. CO Selectivity during the Co-Feeding Reaction Over 3%Zn/ZSM-5 at Different Reaction Temperatures

temperature (°C)	450	500	550	600
CO selectivity (%)		132.3	139.3	166.3

Table 4. Effects of the Contact Time on the CO Selectivity during the Co-Feeding Reaction

contact time (s)	0.375	0.75	1.5	3.0
CO selectivity (%)	112.6	117.6	139.3	127.2

With the increase of CO_2 partial pressure, the CO selectivity decreased from 86 to 54% (Figure 5b). This means that part of the carbon atoms of the converted CO_2 (increased from 14 to 46%) were incorporated into the hydrocarbon products. Although the CO_2 conversion decreased with the increase of CO_2 partial pressure, the molar ratio of converted CO_2 to the converted n-butane significantly increased. Combining the converted molar ratio of CO_2/n-butane and the CO selectivity,

it can be deduced that a higher CO_2 partial pressure is favorable to the transformation of CO_2 into hydrocarbons.

3.5. Coupling Reaction at Low CO_2/*n*-Butane Ratio under 2.5 MPa. To investigate the coupling reaction under the conditions closed to practical applications, the coupling reaction was conducted over Zn/ZSM-5 with a low ratio of CO_2 to *n*-butane (Figure 6a,b). When the ratio of CO_2 to *n*-butane was 4.75, the conversion of CO_2 and n-butane was 12.3 and ∼100%, respectively, and the aromatics selectivity was 66.8%. The CO selectivity of 83.4% means that about 17% of the carbon atoms in the converted CO_2 were incorporated into hydrocarbon products. As the ratio of CO_2/*n*-butane was further declined, the CO_2 conversion increased significantly. A high CO_2 conversion of 26.5% and aromatics selectivity of 69.1% was achieved with the ratio of 0.95. At this ratio, about 13% of the carbon atoms of the converted CO_2 were transformed into hydrocarbon products (CO selectivity was 86.8%). As the main product in alkanes, CH_4 selectivity gradually increased with the increase of CO_2 partial pressure (Figure 6b). BTX selectivity increased while that of A_{9+}
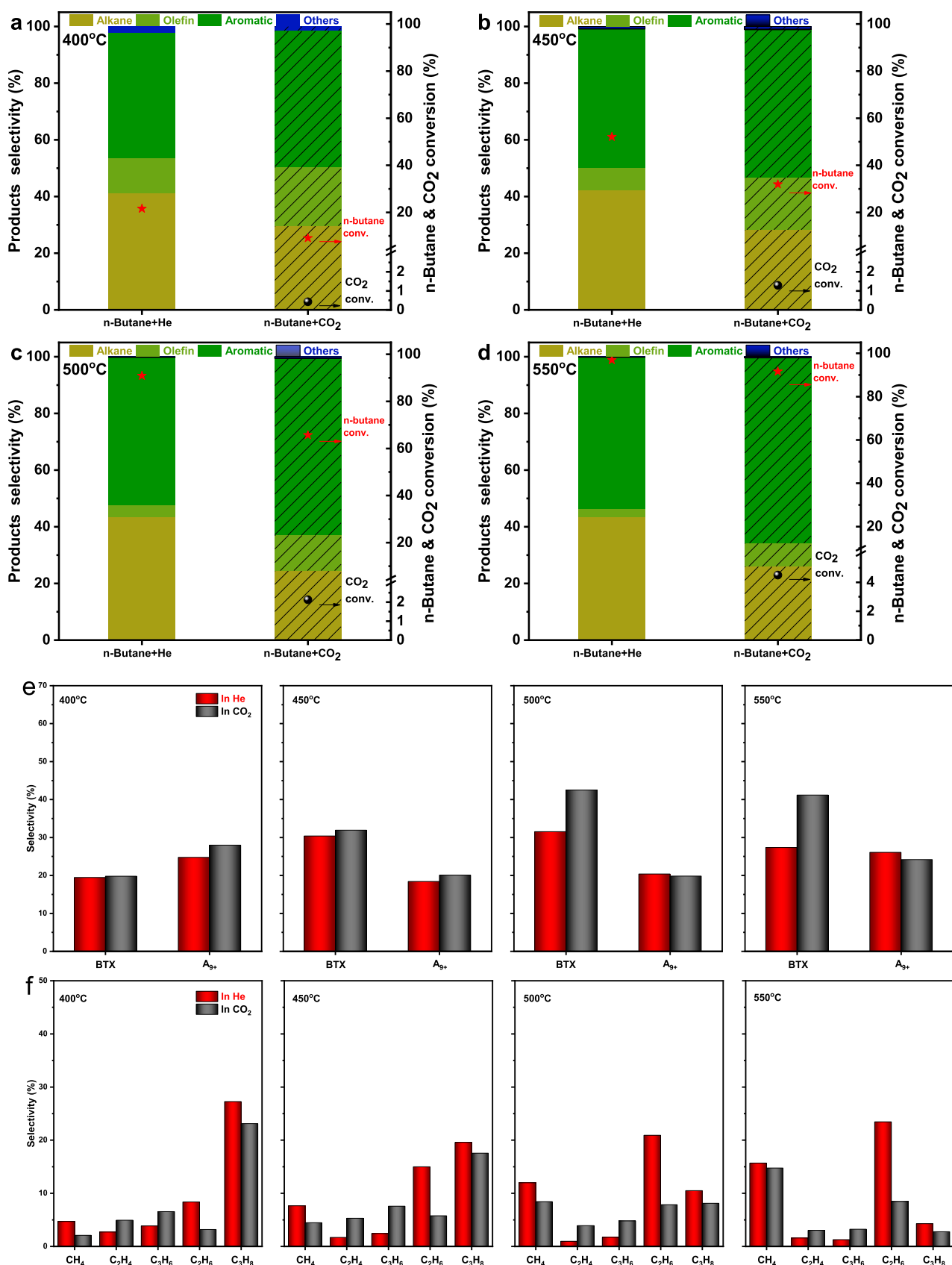
Figure 4. Catalytic performance for the conversion of n-butane in the presence of He or CO_2 over Zn/ZSM-5. (a−d) Conversion and selectivity, (e, f) BTX and A_{9+} aromatic selectivity; CH_4, C_2H_6, C_3H_8 selectivity; C_2H_4, C_3H_6 selectivity. Reaction conditions: 0.05 g of 5%Zn/ZSM-5 (Si/Al = 17), T = 400−550 °C, P = 0.5 MPa, CO_2/n-butane/Ar = 37/1/2, He/n-butane/Ar = 37/1/2, total flow = 10 mL/min, TOS = 2.1 h.

Table 5. Effects of Temperature on the CO Selectivity during the Coupling Reaction

temperature (°C)	400	450	500	550
CO selectivity (%)	12.1	30.7	79.0	80.4

aromatics decreased with the increase of CO_2 partial pressure. Based on the high CO_2 conversion, the coupling reaction provides a potential route for utilization of CO_2 as chemical feedstock.

3.6. GC-MS Analysis of the Retained Species over the Spent Zn/ZSM-5. The retained species were analyzed and identified by the method described in Section 2.4 (C_2Cl_6 as internal standard).[17,18] The FID signals of GC-MS in Figure 7 indicate the presence of oxygenates and aromatics between 400 to 550 °C under CO_2 atmosphere (Figure 7a,b). In contrast, no oxygenates were detected in the retained species under the He atmosphere (Figure S2). The detailed MS spectra of the oxygenated compounds are given in Figure S3 and the standard spectra of the corresponding substances were obtained from the NIST Standard Reference Database. These oxygenated species include methyl-substituted cyclopentenones (ketones with one ring), methyl-substituted indanones (ketones with two rings), fluorenone and phenalenone (ketones with three rings), benzanthrone (ketones with four rings), and phenol (methyl-substituted phenol and phenanthrenol).

Cyclopentenones and methyl-substituted cyclopentenones (CPOs) were detected with strong peak intensities at a lower temperature (400 °C), which decreased dramatically as the temperature increased (such as 2-cyclopenten-1-one, methyl-2-cyclopenten-1-one, dimethyl-2-cyclopenten-1-one, and tri-methyl-2-cyclopenten-1-one). Meanwhile, the peak intensities of aromatics, especially heavy aromatics such as naphthalene, fluorene, and other polycyclic aromatic hydrocarbons, increased significantly. These results indicate that the CPOs can be converted to aromatics at high temperatures over Zn/ZSM-5. However, these CPOs were not detected in the gas-phase products by online GC, indicating that the CPOs can strongly adsorb on the Brønsted acid sites as the active species undergo further transformation during the coupling reaction.[7]

At high temperatures (above 500 °C), some oxygenated polycyclic aromatics containing carbonyl groups were observed. In consideration of the facile generation of phenyl carbonium ions by the aromatic species, direct carbonylation of CO to produce heavy aromatics might occur, which is also a possible pathway for the formation of heavy aromatics. However, the partial pressure of the generated CO in our reaction system is relatively low, indicating that this route might not be prominent.

To further investigate the formation and transformation of aromatic compounds during the coupling reaction over Zn/ZSM-5, reactions at low temperatures from 150 to 350 °C were conducted. As shown in Figure 7c, multiple oxygenated compounds were detected at low temperatures from 150 to 250 °C, and 2-methyl-2-butanol was predominant. As the temperature increased to 350 °C, 2-methyl-2-butanol disappeared, while the cyclopentenones and methyl-substituted cyclopentenones were detected in large amounts. In addition, tremendous amounts of aromatics were detected at 350 °C, which indicates that these aliphatic alcohols might be the initial intermediates, which are further converted to the cyclopentenones and eventually to aromatics. It is worth noting that a trace of γ-valerolactone was detected (retention time 13.4 min) and reached its maximum at 220 °C, gradually decreasing with the increasing temperature. The investigation of γ-valerolactone is discussed in the following section.

3.7. Formation Pathway of Valerolactone. In the previous work of our research group, the formation of γ-valerolactone as an intermediate during the coupling reaction of CO_2 and n-butane over H-ZSM-5 was reported.[8] During the short contact time experiments described above, it was challenging to detect the γ-valerolactone over the spent Zn/ZSM-5 catalysts. To gain further insight into this crucial intermediate, we investigated the coupling reaction under a longer contact time by increasing the reaction pressure and the catalyst loading to enhance the generation of γ-valerolactone. As shown in Figure 8, γ-valerolactone was detected significantly at 220 °C under both 0.5 and 2.5 MPa. In the case of prolonged contact time, γ-valerolactone was found to be the primary oxygenated compound instead of aliphatic alcohol and aliphatic ketone, which indicates these alcohol and
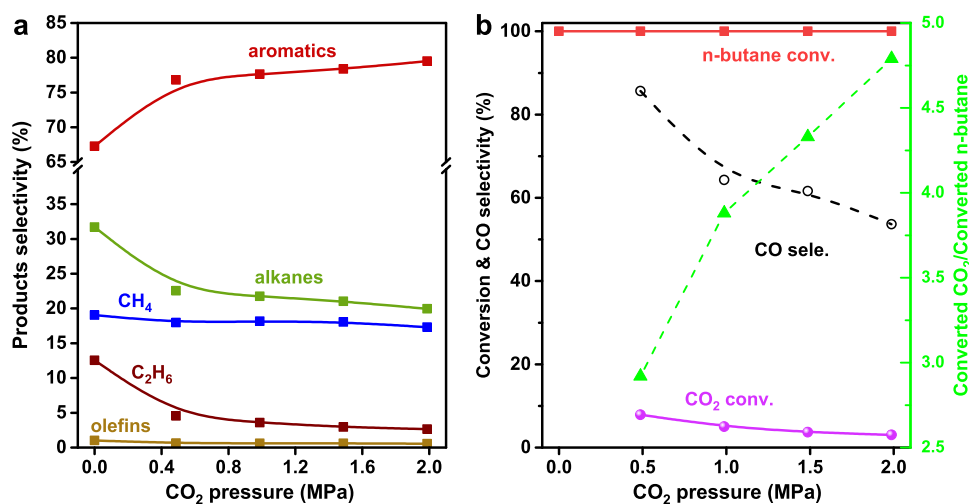

Figure 5. Effects of the CO_2 partial pressure on the conversion of n-butane over Zn/ZSM-5. (a) Products' selectivity, (b) conversion, CO selectivity, the molar ratio of converted CO_2 to converted n-butane. Reaction conditions: 0.2 g of 3%Zn/ZSM-5 (Si/Al = 17), T = 550 °C, $P_{n\text{-butane}}$ = 13 kPa, P_{CO_2+Ar} = 0−1987 kPa, total flow = 10−40 mL/min at STP, contact time = 3.6 s, TOS = 1.5 h.
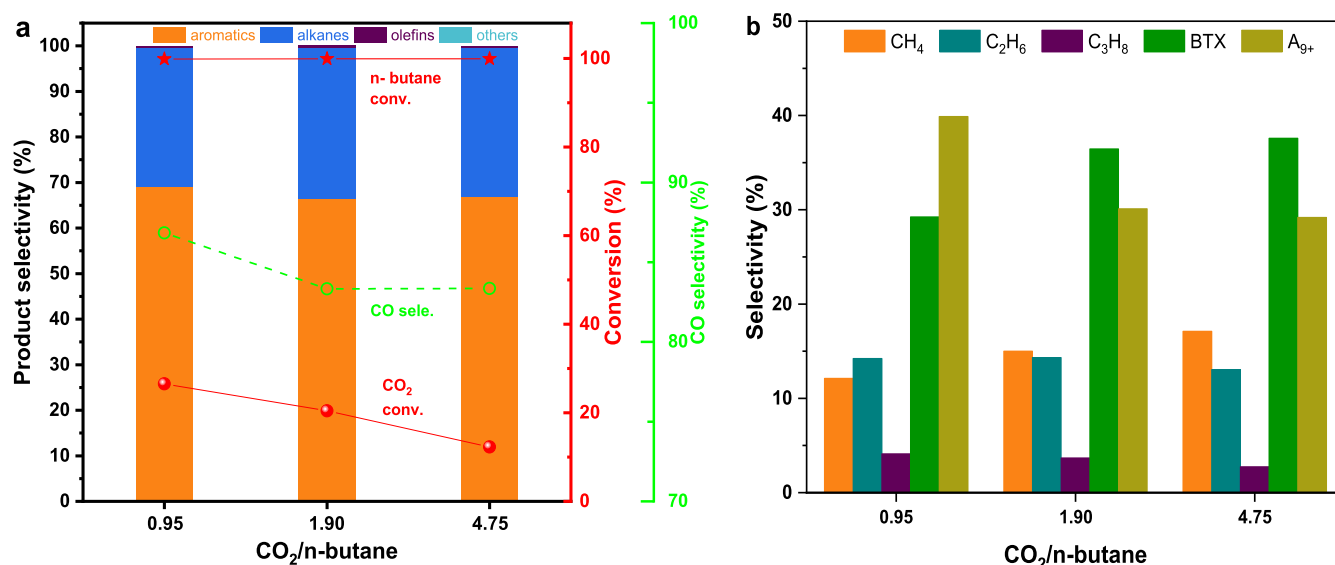
Figure 6. Catalytic performance of the coupling reaction at a low ratio of CO_2 to n-butane over Zn/ZSM-5. (a) Conversion and product & CO selectivity. (b) CH_4, C_2H_6, C_3H_8, BTX, and A_{9+} selectivity. Reaction conditions: 1.2 g of 5%Zn/ZSM-5(Si/Al = 17), T = 550°C, P = 2.5 MPa, $P_{CO_2}/P_{n\text{-butane}}/P_{Ar}$ = 1.9/2/0.1, 1.9/1/0.1, 1.9/0.4/0.1, total flow = 30 mL/min at STP, TOS = 2.1 h.

ketone species might act as precursors for lactones or belong to different reaction pathways. The γ-valerolactone disappeared as the temperature increased to 300 °C and large amounts of cyclopentenones and heavy aromatics were detected instead. This indicates that the γ-valerolactone further converts to cyclopentenones at high temperature and eventually generates aromatic hydrocarbons, with part of the carbon atoms from CO_2 being directly incorporated into the aromatic hydrocarbons.[8]

The oxygenated compounds detected over the spent catalysts during the low-temperature reaction were mainly composed of aliphatic alcohol and aliphatic ketone. Considering that the interaction of CO_2 with the alcohol compound produces alkyl carbonate intermediates, which are further cyclized to form lactone species,[8,23] co-reactions of 2-methyl-2-butanol with CO_2 were performed over Zn/ZSM-5 at different temperatures (ranging from 200 to 300 °C). As shown in Figure 9, multiple alcohol species and γ-valerolactone were detected at 200°C but almost disappeared at 300°C. Instead, a significant amount of aromatic hydrocarbons was generated. This indicates the possibility of a transformation route from the alcohol species to lactone and ultimately to the aromatic hydrocarbons during the coupling reaction over Zn/ZSM-5.

3.8. In Situ DRIFT Analysis of the Coupling Reaction of CO_2 and n-Butane over Zn/ZSM-5. *In situ* DRIFT characterizations were conducted at different temperatures (the full range of wavenumbers from 4000 to 700 cm^{-1} is given in Figure S4). As shown in Figure 10a,b, the bands observed at 3800−3600 cm^{-1} can be attributed to Si-OH, Al-OH, and the bridging hydroxyl Si(OH)Al.[24] The bands at 3495, 2960, and 2870 cm^{-1} were attributed to the interactions of bridging hydroxyl groups with the n-butane and physically adsorbed n-butane.[24,25] These bands exhibited a decrease with the increase of temperature, indicating a reduction in the physical adsorption of n-butane. Meanwhile, the bands at 2925 cm^{-1} (attributed to the vibrations of C−H[26]) increased with the increase of temperature, indicating that the adsorbed n-butane was transformed into carbenium ions.[12]

It is worth noting that a new band at 1678 cm^{-1}, attributed to the C═O stretching vibrations of acyl species,[27,28] appeared at 230°C. The intensity increased and then decreased with the increase of temperature. This indicates that there is a pathway for the interaction of CO with carbonium ions to generate acyl species during the coupling reaction.[6,7] The band at around 1661 cm^{-1} could be attributed to the stretching vibration of C═C, indicating the generation of alkenes.[29] More interestingly, the bands at 1757 and 1694 cm^{-1} were attributed to the C═O stretching vibrations of lactone and unsaturated ketone,[30,31] respectively, which is consistent with the findings from GC-MS analysis. The intensity of the band at 1757 cm^{-1} gradually increased as the temperature increased from 100 to 250°C but subsequently decreased. In contrast, the appearance of a band at 1694 cm^{-1} at 250 °C indicates that the lactones could convert to unsaturated ketones. The bands observed at 1604 and 1511 cm^{-1} were attributed to aromatic carbenium ions and the cyclic coke precursor, respectively,[29] demonstrating the generation of aromatic hydrocarbons and carbon deposition during the reaction. The intensity of the band at 1462 cm^{-1}, which is attributed to the CH deformation vibration of ether, decreased with the increase of temperature. Meanwhile, the bands at 1496 and 1386 cm^{-1} showed an increase in intensity. These two bands were attributed to COO^- groups,[27] indicating that hydrogenation of CO_2 into formate species is feasible during the coupling reaction.[32] Therefore, the formate species might act as intermediates for incorporating a small amount of CO_2 directly into the products.

3.9. ^{13}C Isotope Tracing Experiments for the Coupling Reaction of CO_2 and n-Butane Over Zn/ZSM-5. ^{13}C isotope tracing experiments were performed at 220 and 500 °C under 0.5 MPa. The ^{13}C distributions of the observed oxygenated intermediates and representative products (shown in Figure 11) were calculated by comparing the MS spectra of the reaction of n-butane with $^{13}CO_2$ and $^{12}CO_2$, respectively. The detailed MS spectra are shown in Figures S5 and S6. Most of the oxygenated intermediates observed contained at least one ^{13}C atom, and the MS spectra with ^{13}C
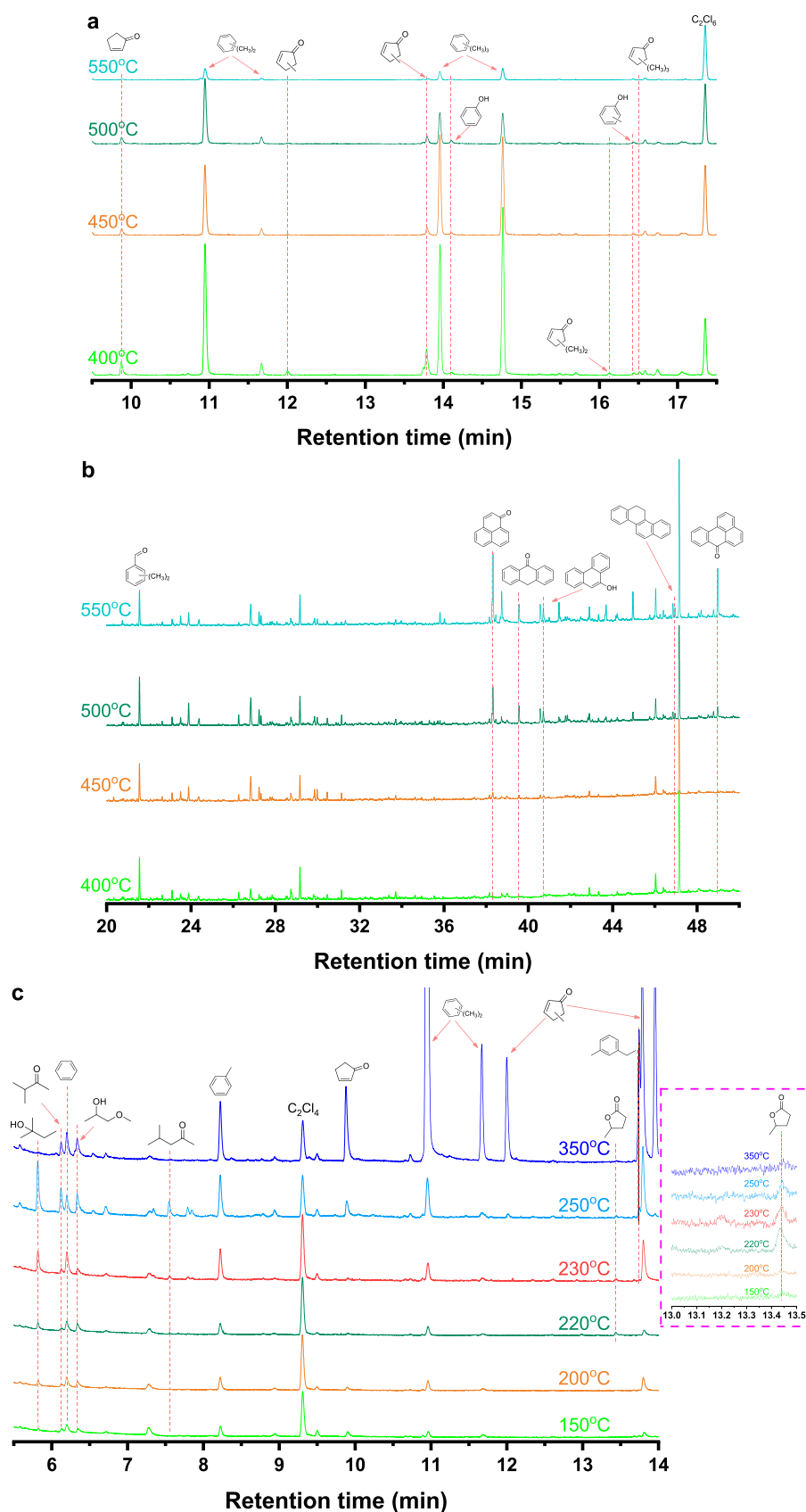
Figure 7. GC-MS results for the retained species over the spent Zn/ZSM-5 catalysts during the coupling reaction of CO_2 and n-butane at different temperatures. FID signals of GC-MS with retention times (a) from 9.5 to 17.5 min, (b) from 20 to 50 min (a, b under high temperature, 400−550 °C), (c) from 5.5 to 14 min (c under low temperature, 150−350 °C). Reaction conditions: 0.05 g of 5%Zn/ZSM-5 (Si/Al = 17), P = 0.5 MPa, CO_2/n-butane/Ar = 37/1/2, total flow = 10 mL/min, TOS = 2.2 h.
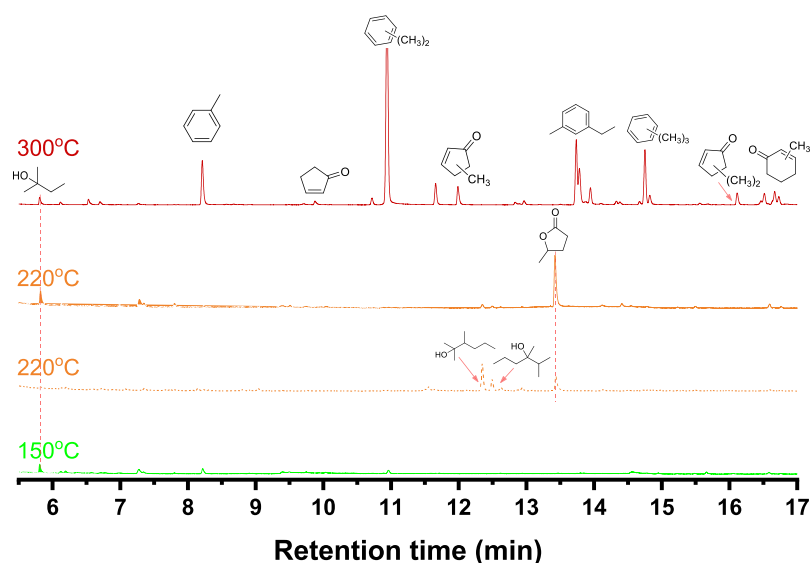
Figure 8. GC-MS results for the retained species over the spent Zn/ZSM-5 catalysts under a long contact time. Reaction conditions: 0.4 g of 5% Zn/ZSM-5 (Si/Al = 17), P = 2.5 MPa (solid line) and 0.5 MPa (dashed line), CO_2/n-butane/Ar = 37/1/2, total flow = 10 mL/min, TOS = 3 h.
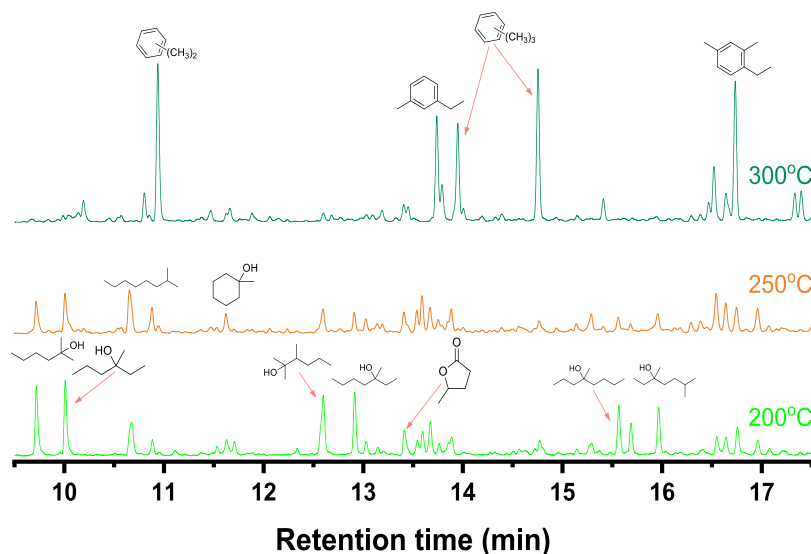

Figure 9. Co-reaction of 2-methyl-2-butanol with CO_2 over Zn/ZSM-5. Reaction conditions: 0.05 g of 5%Zn/ZSM-5 (Si/Al = 17), P = 1 bar, T = 200−300 °C, carrier gas (CO_2) = 10 mL/min, WHSV = 16 h^{-1}, TOS = 1 h.

labeling shifted systematically in comparison to the unlabeled spectra. Around 10 to 30% of the aromatics contained a single ^{13}C atom, whereas only a small proportion of cyclo-olefins contained one ^{13}C atom (<2%). This observation suggests that the incorporated ^{13}C atom was located within the aromatic ring, implying that partial aromatics might be generated from the oxygenated intermediates rather than through hydrogen transfer reactions of olefins. These results clearly reveal that the carbon atom in CO_2 was incorporated into the oxygenated intermediates and subsequently transformed into BTX products, resulting in an increase in BTX selectivity.

3.10. Reaction Mechanism Proposed for the Coupling Reaction of CO_2 and n-Butane Over Zn/ZSM-5. Based on the above results and discussion, a plausible mechanism of coupling reaction was proposed (shown in Figure 12). Firstly, n-butane is absorbed on Brønsted acid sites or $[Zn\text{-}O\text{-}Zn]^{2+}$[33] over Zn/ZSM-5 and might form carbenium

ions or short-chain hydrocarbon species. Then, CO_2 is incorporated into the reaction via two routes.

Indirect route: CO, which is formed by reverse Boudouard reaction or dry reforming of CO_2, adsorbs and inserts into the carbonium ions to generate the acyl group. Meanwhile, partial CO interacts with H_2 to generate alcohol species, which are easily further transformed to hydrocarbons. The acyl groups interact with olefins to generate the oxygenated intermediates (methyl-substituted cyclopentenones) by cyclization and Friedel−Crafts acylation of olefins.[34] Finally, these cyclopentenone species will further transform to aromatic hydrocarbons.

Direct route: The alkyl carbonate intermediate is generated through the insertion of CO_2 into carbonium ions,[8,35] and then further cyclized to form the γ-valerolactone. After that, the γ-valerolactone intermediate is isomerized to generate pentenoic acid. The acyl cations are formed by dehydration of pentenoic acid or dehydroxylation of carboxylic acid groups (generated
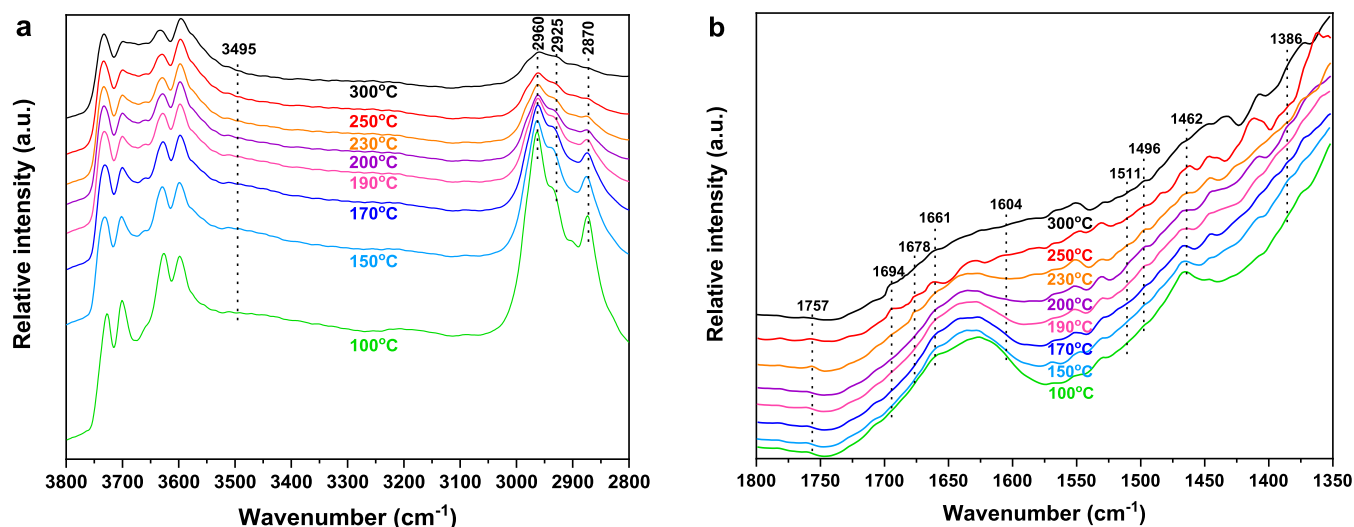
Figure 10. In situ DRIFT spectra recorded during the coupling reaction of n-butane and CO_2 over Zn/ZSM-5 at different temperatures. Range of wavenumber: (a) 3800−2800 cm^{-1}, (b) 1800−1350 cm^{-1}.

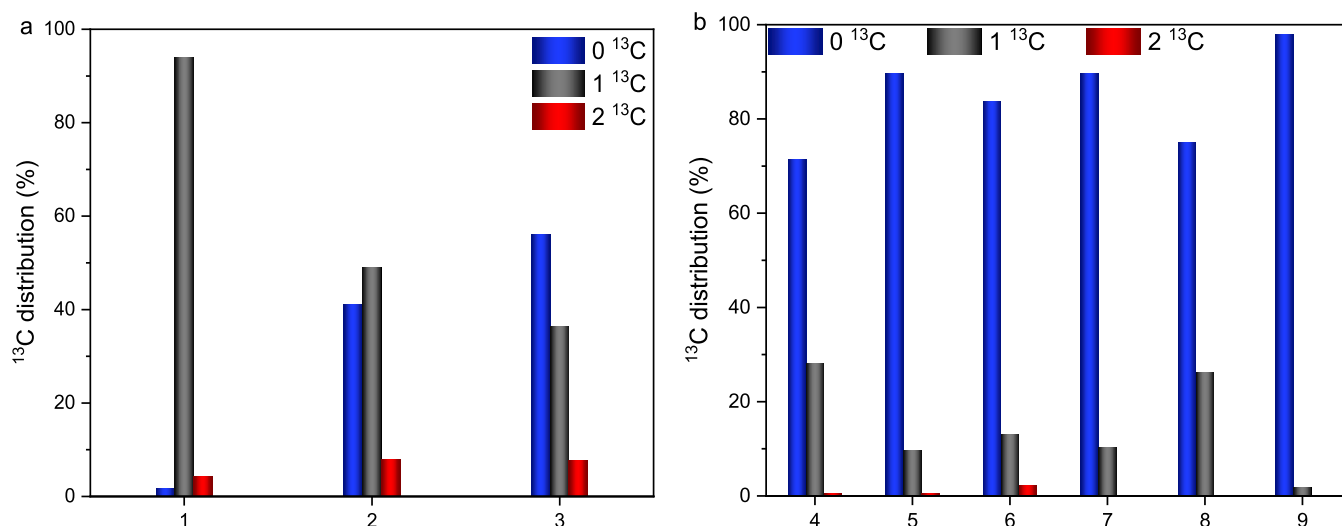**Figure 11.** ^{13}C distributions of the (a) oxygenated intermediates over the spent Zn/ZSM-5 and (b) representative products in the effluent during the coupling reaction of *n*-butane with $^{13}CO_2$. (1) γ-Valerolactone, (2) 2-cyclopenten-1-one, (3) 2-methyl-2-butanol, (4) phenol, (5) benzene, (6) methylbenzene, (7) dimethylbenzene, (8) ethylbenzene, (9) 1,3,5,7-cyclooctatetraene. Reaction conditions: 0.4 g of 5%Zn/ZSM-5 (Si/Al = 17), T = 220 and 500 °C, $P_{n\text{-butane}}$ = 6 kPa, P_{He} = 244 kPa, P_{CO_2} = 250 kPa, total flow = 10 mL/min at STP. The catalyst was removed after the reaction for 40 min and then quenched by liquid nitrogen. Gas-phase products were collected by CH_2Cl_2.

from the interaction of CO_2 with H_2), which further transform to cyclopentenones by cyclization.[8,35]

4. CONCLUSIONS

The coupling reaction of CO_2 and *n*-butane was systematically investigated over metal-modified ZSM-5. CO_2 addition led to a significant increase in the selectivity of aromatics and olefin, and a decrease in the selectivity of alkanes. Aromatic selectivity was favored by prolonging the contact time. A high CO_2 conversion of 26.5% and *n*-butane conversion of 100% with the aromatics selectivity of 69.1% was achieved at the CO_2 to *n*-butane ratio of 0.95. About 13% of the carbon atoms of the converted CO_2 was transformed into hydrocarbon products corresponding to the CO selectivity of 86.8%. This aromatic selectivity is much higher than the theoretical value for the conversion of sole *n*-butane (56.3%). The results of GC-MS analysis, *in situ* DRIFT characterization, and ^{13}C isotope

tracing experiments demonstrate that the coupling reaction of n-butane with CO_2 might proceed by the direct or indirect route. Indirect route: CO (formed by reverse Boudouard reaction or dry reforming of CO_2) inserts into the carbonium ions to generate acyl groups, and then oxygenated intermediates (methyl-substituted cyclopentenones) are generated by the interaction of the acyl groups with olefins (cyclization and Friedel−Crafts acylation of olefins), which are finally transformed to aromatics. Direct route: CO_2 directly inserts into alkene or carbonium ions to generate the lactone. The lactone intermediate is isomerized to generate pentenoic acid, followed by dehydration to form acyl cations, which are further transformed to cyclopentenones by cyclization.
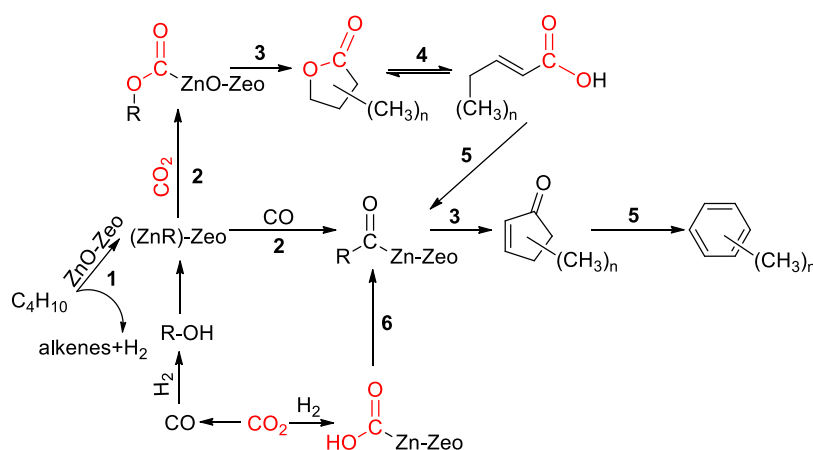
Figure 12. Proposed mechanism for the coupling reaction of CO_2 with *n*-butane over Zn/ZSM-5. 1. Cracking, 2. carbonylation, 3. cyclization, 4. isomerization, 5. dehydration, 6. dehydroxylation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c02158.

> It includes additional data regarding catalyst characterization, GC-MS results for the retained species over spent Zn/ZSM-5 catalysts during co-feeding of He and *n*-butane, theoretical values of aromatic selectivity based on ideal reaction equations, *in situ* DRIFT spectra during the coupling reaction, and MS spectra contrast (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Zhongkui Zhao − *State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*; Email: zkzhao@dlut.edu.cn

Zhongmin Liu − *National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 Liaoning, China; University of Chinese Academy of Sciences, Beijing 100049, China;* ● orcid.org/0000-0002-7999-2940; Email: liuzm@dicp.ac.cn

Authors

Kuo Yang − *State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China; National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 Liaoning, China*

Jinzhe Li − *National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023 Liaoning, China*

Changcheng Wei − *National Engineering Research Center of Lower-Carbon Catalysis Technology, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023*

Liaoning, China; University of Chinese Academy of Sciences, Beijing 100049, China

Complete contact information is available at:
https://pubs.acs.org/10.1021/acscatal.3c02158

Author Contributions

K.Y. conceived and performed the experiments, collected and analyzed the data, and wrote the manuscript. J.L. analyzed the data and revised the manuscript. C.W. carried out the reaction under atmospheric pressure. Z.Z. analyzed the data and discussion. Z.L. supervised the study, designed the experiments, and revised the manuscript. All authors discussed the results and commented on the manuscript at all stages.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Ansari, M. B.; Park, S. E. Carbon dioxide utilization as a soft oxidant and promoter in catalysis. *Energy Environ. Sci.* **2012**, *5*, 9419−9437.

(2) Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of carbon dioxide. *Chem. Rev.* **2007**, *107*, 2365−2387.

(3) Aresta, M.; Dibenedetto, A.; Quaranta, E. State of the art and perspectives in catalytic processes for CO2 conversion into chemicals and fuels: The distinctive contribution of chemical catalysis and biotechnology. *J. Catal.* **2016**, *343*, 2−45.

(4) Gomez, E.; Nie, X. W.; Lee, J. H.; Xie, Z. H.; Chen, J. G. G. Tandem Reactions of CO2 Reduction and Ethane Aromatization. *J. Am. Chem. Soc.* **2019**, *141*, 17771−17782.

(5) Chang, J. S.; Vislovskiy, V. P.; Park, M. S.; Hong, D. Y.; Yoo, J. S.; Park, S. E. Utilization of carbon dioxide as soft oxidant in the dehydrogenation of ethylbenzene over supported vanadium-antimony oxide catalystst. *Green Chem.* **2003**, *5*, 587−590.

(6) Wei, C.; Li, J.; Yang, K.; Yu, Q.; Zeng, S.; Liu, Z. Aromatization mechanism of coupling reaction of light alkanes with CO over acidic zeolites: Cyclopentenones as key intermediates. *Chem. Catal.* **2021**, *1*, 1273−1290.

(7) Wei, C. C.; Yu, Q. J.; Li, J. Z.; Liu, Z. M. Coupling Conversion of n-Hexane and CO over an HZSM-5 Zeolite: Tuning the H/C Balance and Achieving High Aromatic Selectivity. *ACS Catal.* **2020**, *10*, 4171−4180.

(8) Wei, C.; Zhang, W.; Yang, K.; Bai, X.; Xu, S.; Li, J.; Liu, Z. An efficient way to use CO2 as chemical feedstock by coupling with alkanes. *Chin. J. Catal.* **2023**, *47*, 138−149.

(9) Saito, H.; Inagaki, S.; Kojima, K.; Han, Q.; Yabe, T.; Ogo, S.; Kubota, Y.; Sekine, Y. Preferential dealumination of Zn/H-ZSM-5 and its high and stable activity for ethane dehydroaromatization. *Appl. Catal., A* **2018**, *549*, 76−81.

(10) Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. Crystal-Structure and Structure-Related Properties of Zsm-5. *J. Phys. Chem. A* **1981**, *85*, 2238−2243.

(11) Liu, J. X.; He, N.; Zhou, W.; Shu, M.; Lin, L.; Wang, J. L.; Si, R.; Xiong, G.; Xin, Q.; Guo, H. C. Operando dual beam FTIR spectroscopy unravels the promotional effect of Zn on HZSM-5 in iso-butane aromatization. *Catal.: Sci. Technol.* **2019**, *9*, 1609−1620.

(12) Liu, J. X.; He, N.; Zhou, W.; Lin, L.; Liu, G. D.; Liu, C. Y.; Wang, J. L.; Xin, Q.; Xiong, G.; Guo, H. C. Isobutane aromatization over a complete Lewis acid Zn/HZSM-5 zeolite catalyst: performance and mechanism. *Catal.: Sci. Technol.* **2018**, *8*, 4018−4029.

(13) Tamiyakul, S.; Sooknoi, T.; Lobban, L. L.; Jongpatiwut, S. Generation of reductive Zn species over Zn/HZSM-5 catalysts for n-pentane aromatization. *Appl. Catal., A* **2016**, *525*, 190−196.

(14) Xin, M. D.; Xing, E. H.; Gao, X. Z.; Wang, Y. R.; Ouyang, Y.; Xu, G. T.; Luo, Y. B.; Shu, X. T. Ga Substitution during Modification of ZSM-5 and Its Influences on Catalytic Aromatization Performance. *Ind. Eng. Chem. Res.* **2019**, *58*, 6970−6981.

(15) Samanta, A.; Bai, X. W.; Robinson, B.; Chen, H.; Hu, J. L. Conversion of Light Alkane to Value-Added Chemicals over ZSM-5/Metal Promoted Catalysts. *Ind. Eng. Chem. Res.* **2017**, *56*, 11006−11012.

(16) Wannapakdee, W.; Suttipat, D.; Dugkhuntod, P.; Yutthalekha, T.; Thivasasith, A.; Kidkhunthod, P.; Nokbin, S.; Pengpanich, S.; Limtrakul, J.; Wattanakit, C. Aromatization of C-5 hydrocarbons over Ga-modified hierarchical HZSM-5 nanosheets. *Fuel* **2019**, *236*, 1243−1253.

(17) Guisnet, M.; Magnoux, P. Coking and Deactivation of Zeolites - Influence of the Pore Structure. *Appl. Catal.* **1989**, *54*, 1−27.

(18) Guisnet, M.; Costa, L.; Ribeiro, F. R. Prevention of zeolite deactivation by coking. *J. Mol. Catal. A: Chem.* **2009**, *305*, 69−83.

(19) Li, X. D.; Yan, B. H.; Yao, S. Y.; Kattel, S.; Chen, J. G. G.; Wang, T. F. Oxidative dehydrogenation and dry reforming of n-butane with CO2 over NiFe bimetallic catalysts. *Appl. Catal., B* **2018**, *231*, 213−223.

(20) Ihm, S. K.; Park, Y. K.; Lee, S. W. Effects of CO2 addition on the aromatization of propane over metal-loaded ZSM-5 catalysts. *Appl. Organomet. Chem.* **2000**, *14*, 778−782.

(21) Sun, X. Y.; Mueller, S.; Liu, Y.; Shi, H.; Haller, G. L.; Sanchez-Sanchez, M.; van Veen, A. C.; Lercher, J. A. On reaction pathways in the conversion of methanol to hydrocarbons on HZSM-5. *J. Catal.* **2014**, *317*, 185−197.

(22) Chen, Z. Y.; Ni, Y. M.; Zhi, Y. C.; Wen, F. L.; Zhou, Z. Q.; Wei, Y. X.; Zhu, W. L.; Liu, Z. M. Coupling of Methanol and Carbon Monoxide over H-ZSM-5 to Form Aromatics. *Angew. Chem., Int. Ed.* **2018**, *57*, 12549−12553.

(23) Jung, K. T.; Bell, A. T. An in Situ Infrared Study of Dimethyl Carbonate Synthesis from Carbon Dioxide and Methanol over Zirconia. *J. Catal.* **2001**, *204*, 339−347.

(24) Zhu, N.; Wang, Y.; Cheng, D. G.; Chen, F. Q.; Zhan, X. L. Experimental evidence for the enhanced cracking activity of n-heptane over steamed ZSM-5/mordenite composite zeolites. *Appl. Catal., A* **2009**, *362*, 26−33.

(25) van Bokhoven, J. A.; Tromp, M.; Koningsberger, D. C.; Miller, J. T.; Pieterse, J. A. Z.; Lercher, J. A.; Williams, B. A.; Kung, H. H. An explanation for the enhanced activity for light alkane conversion in mildly steam dealuminated mordenite: The dominant role of adsorption. *J. Catal.* **2001**, *202*, 129−140.

(26) Hernandez, E. D.; Jentoft, F. C. Spectroscopic Signatures Reveal Cyclopentenyl Cation Contributions in Methanol-to-Olefins Catalysis. *ACS Catal.* **2020**, *10*, 5764−5782.

(27) Blasco, T.; Boronat, M.; Concepcion, P.; Corma, A.; Law, D.; Vidal-Moya, J. A. Carbonylation of methanol on metal-acid zeolites: Evidence for a mechanism involving a multisite active center. *Angew. Chem., Int. Ed.* **2007**, *46*, 3938−3941.

(28) Luzgin, M. V.; Thomas, K.; van Gestel, J.; Gilson, J. P.; Stepanov, A. G. Propane carbonylation on sulfated zirconia catalyst as studied by C-13 MAS NMR and FTIR spectroscopy. *J. Catal.* **2004**, *223*, 290−295.

(29) Wei, Y. X.; Zhang, D. Z.; Liu, Z. M.; Su, B. L. Highly efficient catalytic conversion of chloromethane to light olefins over HSAPO-34 as studied by catalytic testing and in situ FTIR. *J. Catal.* **2006**, *238*, 46−57.

(30) Zhou, J. Y.; Lu, G. D.; Wu, S. H. A New Approach for the Synthesis of Alpha-Methylene-Gamma-Butyrolactones from Alpha-Bromomethylacrylic Acids (or Esters). *Synth. Commun.* **1992**, *22*, 481−487.

(31) Lievens, C.; Mourant, D.; He, M.; Gunawan, R.; Li, X.; Li, C. Z. An FT-IR spectroscopic study of carbonyl functionalities in bio-oils. *Fuel* **2011**, *90*, 3417−3423.

(32) Álvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A. V.; Wezendonk, T. A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO2 Hydrogenation Processes. *Chem. Rev.* **2017**, *117*, 9804−9838.

(33) El-Malki, E. M.; van Santen, R. A.; Sachtler, W. M. H. Introduction of Zn, Ga, and Fe into HZSM-5 cavities by sublimation: Identification of acid sites. *J. Phys. Chem. B* **1999**, *103*, 4611−4622.

(34) Luzgin, M. V.; Romannikov, V. N.; Stepanov, A. G.; Zamaraev, K. I. Interaction of olefins with carbon monoxide on zeolite H-ZSM-5. NMR observation of the friedel-crafts acylation of alkenes at ambient temperature. *J. Am. Chem. Soc.* **1996**, *118*, 10890−10891.

(35) Behr, A.; Henze, G. Use of carbon dioxide in chemical syntheses via a lactone intermediate. *Green Chem.* **2011**, *13*, 25−39.