



Cite this: DOI: 10.1039/d3cy01550e

## Highly efficient production of aromatics from C<sub>2</sub>H<sub>5</sub>Cl coupling with CO over H-zeolites†

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Value-added utilization of C<sub>2</sub>H<sub>6</sub> as an important component of natural gas and petrochemical by-products has attracted much attention. Aromatic synthesis from C<sub>2</sub>H<sub>6</sub> is a crucial direction but remains a significant challenge due to its high stability. Chloroethane (C<sub>2</sub>H<sub>5</sub>Cl) is an essential derivative of C<sub>2</sub>H<sub>6</sub>, which effectively solves the C–H bond activation of C<sub>2</sub>H<sub>6</sub>. Herein, we report a pathway for the synthesis of aromatics *via* the coupling of CO and C<sub>2</sub>H<sub>5</sub>Cl over H-ZSM-5. Up to 76% aromatics selectivity is achieved *via* the coupling strategy whereas it is only 40% with the traditional methods. The introduction of CO not only facilitates the conversion of C<sub>2</sub>H<sub>5</sub>Cl, but also enhances the selectivity to aromatics over H-ZSM-5. Cyclopentenone species are detected and proved to be the key intermediate leading to a markedly improved aromatics selectivity. The <sup>13</sup>C isotope tracing experiment reveals that CO participates in the formation of cyclopentenone species and aromatics. Furthermore, C<sub>2</sub>H<sub>4</sub> formed from C<sub>2</sub>H<sub>5</sub>Cl has been observed to undergo carbonylation processes over H-ZSM-5. This work further expands the coupling reaction system between small molecule compounds and CO, providing an insight for natural gas conversion on H-zeolites.

Received 8th November 2023,  
Accepted 5th January 2024

DOI: 10.1039/d3cy01550e

rsc.li/catalysis

### Introduction

Aromatics are crucial raw materials in the chemical industries and widely employed in the production of fuels, plastics, pharmaceuticals, *etc.*<sup>1,2</sup> Currently, aromatics are mainly produced *via* the catalytic reforming of naphtha.<sup>3</sup> It is necessary to explore sustainable non-petroleum routes for producing aromatics due to the depletion of petroleum resources. As an environmentally sustainable energy source, natural gas can be transformed into bulk chemicals such as aromatics.<sup>4,5</sup> C<sub>2</sub>H<sub>6</sub> is one of the principal components of natural gas and by-product of the petrochemical industry and the transformation of C<sub>2</sub>H<sub>6</sub> into aromatics is an essential direction. Dehydro-aromatization of C<sub>2</sub>H<sub>6</sub> over zeolite catalysts is regarded as a primary route for C<sub>2</sub>H<sub>6</sub> conversion.<sup>1,6</sup> To improve the catalytic performance, metals, such as Zn and Pt, have been introduced into zeolites for activating C<sub>2</sub>H<sub>6</sub>.<sup>1,7–10</sup> Unfortunately, the conversion of C<sub>2</sub>H<sub>6</sub> remains low at high temperature (773–873 K) resulting from the high C–H bond energy of C<sub>2</sub>H<sub>6</sub> (413.8 kJ mol<sup>-1</sup>).<sup>7,8,11</sup>

Additionally, the significant difference in the H/C ratios between C<sub>2</sub>H<sub>6</sub> and aromatics acts as a limiting factor for achieving high aromatic selectivity.<sup>12</sup> Consequently, it is crucial to explore new pathways for the efficient production of aromatics from C<sub>2</sub>H<sub>6</sub>.

Recently, the coupling between small molecular hydrocarbons and CO catalyzed by acidic zeolites is an appealing strategy for enhancing aromatics selectivity.<sup>12–14</sup> Specifically, Chen *et al.* reported that introducing CO into methanol could improve aromatics selectivity from 40% to *ca.* 80%.<sup>15</sup> Furthermore, a coupling strategy was employed to investigate the conversion of C<sub>4</sub>–C<sub>6</sub> alkanes to aromatics, and 85% aromatics selectivity was obtained over H-ZSM-5.<sup>12,16</sup> Apparently, the presence of CO can significantly tune the H/C ratio between reactants and products, enhancing the selectivity towards aromatics. Nevertheless, the coupling strategy of C<sub>1</sub>–C<sub>3</sub> alkanes with CO over acidic zeolites remains challenging due to their inertness.<sup>14</sup> Therefore, it is challenging to exploit a novel and alternative coupling pathway for the conversion of C<sub>2</sub>H<sub>6</sub> to aromatics with high selectivity.

Halogen-mediated conversion of hydrocarbons is an efficient and significant pathway for utilizing alkanes.<sup>17</sup> Currently, significant progress has been made in the selective transformation of CH<sub>4</sub> into value-added chemicals, such as aromatics and acetic acid using CH<sub>3</sub>Cl with CO.<sup>18</sup> Moreover, C<sub>2</sub>H<sub>5</sub>Cl can be also produced from C<sub>2</sub>H<sub>6</sub> *via* a halogenation

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3cy01550e>

reaction with high selectivity.<sup>19,20</sup> These findings shed light on transforming C<sub>2</sub>H<sub>6</sub> into high-valued chemicals. Unfortunately, research on direct transformation of C<sub>2</sub>H<sub>5</sub>Cl is still in its infancy.<sup>21</sup> In this study, we first reported a process for C<sub>2</sub>H<sub>6</sub> conversion *via* the coupling of C<sub>2</sub>H<sub>5</sub>Cl and CO to produce aromatics over acidic zeolite catalysts, which up to 77% aromatics selectivity was achieved over H-ZSM-5 at 673 K and 5.0 MPa. Using *in situ* FTIR and <sup>13</sup>C isotope tracing, C<sub>2</sub>H<sub>4</sub> and methyl cyclopentenone are proven to be the key intermediates for the formation of aromatics. The aromatization mechanism is proposed. This work has extensive implications for producing other high-valued chemicals from low carbon (C<sub>1</sub>–C<sub>3</sub>) alkanes.

## Experimental procedures

### Catalyst information

Micro-sized H-ZSM-5 was purchased from Nankai University Catalyst Company. The samples were named H-ZSM-5<sub>X</sub> and X represents the ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

### Catalyst characterization

The crystallinity of zeolites was characterized with PANalytical X'Pert PRO X-ray powder diffraction equipment using a Cu-Kα (λ = 0.151 nm) radiation source operated at 40 kV and 40 mA. The bulk composition of zeolites was determined using Philips Magix-601 X-ray fluorescence apparatus. The surface morphology images of zeolites were obtained using a Hitachi SU8020 scanning electron microscope.

The textural properties of zeolites with different topologies were obtained by N<sub>2</sub> adsorption and desorption at 77 K. The acidity of zeolites was measured on a Micromeritics Auto Chem 2920 equipped with a TCD. 0.15 g zeolite sample was loaded into a U-shaped quartz tube and pre-treated at 823 K for 30 min in helium. Then, the sample is cooled to 423 K and saturated with NH<sub>3</sub>. After removing physically adsorbed NH<sub>3</sub> in helium, desorption was performed from 423 K to 923 K at a heating rate of 10 K min<sup>-1</sup> in helium.

The *in situ* DRIFT spectra were obtained on a Bruker Tensor 27 instrument equipped with a diffuse reflectance attachment and MCT detector under reaction conditions. Firstly, 50 mg of H-ZSM-5<sub>36</sub> was placed in the diffuse reflectance infrared cell. And then the sample was calcined in an argon (Ar) stream at 723 K for 2 h. Afterwards, the catalyst was cooled down to reaction temperature in the Ar stream and the spectrum of the sample was recorded as the background. The stream of mixed gas 1 (0.5% C<sub>2</sub>H<sub>5</sub>Cl, 54.5% CO, 45% Ar), mixed gas 2 (0.5% C<sub>2</sub>H<sub>5</sub>Cl, 99.5% Ar), mixed gas 3 (13% C<sub>2</sub>H<sub>4</sub>, 87% CO) and mixed gas 4 (13% C<sub>2</sub>H<sub>4</sub>, 87% Ar) at 40 mL min<sup>-1</sup> was introduced into the cell at 1.0 MPa. The spectra were scanned continuously to observe surface species. The reaction was quenched by liquid nitrogen and the catalysts were collected to analyze the organic

species. The zeolites were dissolved in 20% HF solution and extracted using CH<sub>2</sub>Cl<sub>2</sub>, which were analyzed *via* GC-MS (Agilent 7890/5975C).

The <sup>13</sup>C NMR spectra of the products and coke were collected on a Bruker Avance III HD 700 MHz spectrometer equipped with a 9.40 T wide-bore magnet. 0.5 g H-ZSM-5<sub>36</sub> was loaded into a reactor. The catalyst was first pre-treated at 723 K for 3 h with an Ar flow (flow rate, 40 mL min<sup>-1</sup>) and the temperature was cooled down to 573 K. The mixed gas (CO/C<sub>2</sub>H<sub>5</sub>Cl = 100) was introduced into the reactor in the presence of <sup>13</sup>CO or <sup>12</sup>CO. The products were collected using CH<sub>2</sub>Cl<sub>2</sub> for 1 h and analyzed by GC-MS (Agilent 7890/5975C). Moreover, the reaction was quenched with liquid nitrogen. The catalysts were collected and analyzed following the above step by GC-MS and <sup>13</sup>C liquid-state NMR. The resonance frequencies were set up at 176.0 MHz for <sup>13</sup>C. Approximately 0.15 mL of CDCl<sub>3</sub> was dissolved in 0.5 mL samples in a 10 mm NMR tube. <sup>13</sup>C NMR spectra were recorded using high-power proton decoupling. Fixed scans were collected with a π/2 pulse of 12.6 μs and a 2 s recycling delay.

### Catalyst test

The conversion of C<sub>2</sub>H<sub>5</sub>Cl was performed in a high-pressure fixed-bed flow reactor (inside diameter = 7 mm) made of stainless steel. Typically, a suitable amount of the catalyst (20–40 mesh) mixed with quartz sand (20–40 mesh) was loaded into the reactor. Prior to the reaction, the catalyst was first pre-treated at 723 K for 3 h with an Ar flow (flow rate, 40 mL min<sup>-1</sup>) to remove water in the zeolite and reactor. Subsequently, the temperature cools down to 673 K. The reactants which contain C<sub>2</sub>H<sub>5</sub>Cl and CO were introduced into the reactor at fixed pressure. In doing so, the results of catalyst evaluation were discussed using the data at equilibrium. Products were analyzed using an online gas chromatograph (Agilent 7890B), which was equipped with a flame ionization detector (FID). The PLOT-Q capillary column and HP-5 capillary column were connected with the FID to separate and analyze the products. The C<sub>2</sub>H<sub>5</sub>Cl conversion and product selectivity were calculated on a molar carbon basis.

$$\text{Conv C}_2\text{H}_5\text{Cl} = \frac{\sum_1^n n\text{C}_n\text{H}_m - \text{C}_2\text{H}_5\text{Cl}_{\text{outlet}}}{\sum_1^n n\text{C}_n\text{H}_m} \times 100\%$$

$$\text{Sel product } X = \frac{\text{products } X_{\text{outlet}}}{\sum_1^n n\text{C}_n\text{H}_m - \text{C}_2\text{H}_5\text{Cl}_{\text{outlet}}} \times 100\%$$

$n\text{C}_n\text{H}_m\text{O}_{\text{outlet}}$ : carbon atoms of  $\text{C}_n\text{H}_m\text{O}_{\text{outlet}}$  at the outlet.

$\text{C}_2\text{H}_5\text{Cl}_{\text{outlet}}$ : carbon atoms of  $\text{C}_2\text{H}_5\text{Cl}_{\text{outlet}}$  at the outlet.

Product  $X_{\text{outlet}}$ : carbon atoms of product  $X_{\text{outlet}}$  at the outlet.

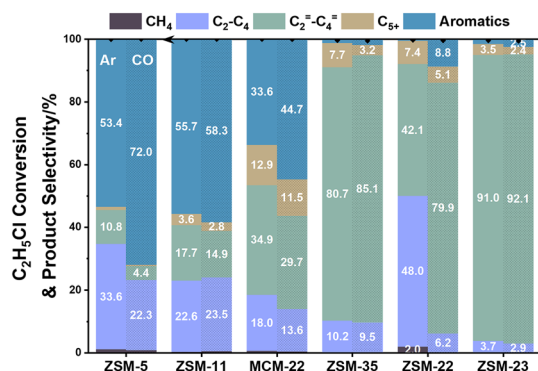


Fig. 1 Catalytic performance in the conversion of  $C_2H_5Cl$  over zeolites with different topologies under an Ar or CO atmosphere. Reaction conditions: 673 K,  $P(CO + Ar \text{ or } Ar) = 1990.47 \text{ kPa}$ ,  $P(C_2H_5Cl) = 9.53 \text{ kPa}$ ,  $WHSV = 0.1 \text{ g}_{C_2H_5Cl} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ .

## Results and discussion

### Effect of zeolite topology on the reaction of $C_2H_5Cl$ to aromatics

Zeolites with different 10-membered ring channels are employed as catalysts for the  $C_2H_5Cl$  to aromatics reaction, and their physical-chemical properties are provided in Table S1 and Fig. S1–S4.† Fig. 1 illustrates the catalytic performance of the conversion of  $C_2H_5Cl$  to aromatics under an Ar or CO atmosphere at 673 K, 2.0 MPa and  $0.1 \text{ g}_{C_2H_5Cl} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ . Obviously, aromatics selectivities over H-ZSM-5 (53.4%), H-ZSM-11 (55.7%), and H-MCM-22 (33.6%) are higher than those over H-ZSM-35 (1.2%), H-ZSM-22 (0.5%), and H-ZSM-23 (1.5%) under an Ar atmosphere. Additionally, as shown in Fig. S5,† the oxygen-containing species content in ZSM-5 (3D) is higher than that in ZSM-11 (3D). A similar phenomenon is also observed in MCM-22 (2D) and ZSM-35 (2D), as well as ZSM-22 (1D) and ZSM-23 (1D). This finding offers preliminary indications that the topological structure of zeolites may have a significant impact on the reaction performance of the CO-

coupled  $C_2H_5Cl$  to produce aromatics. These results indicate that zeolites with higher dimensional structures and multiple 10-membered ring channels are advantageous for aromatics formation. Surprisingly, aromatics selectivity is improved after introducing CO over the different zeolites as well. Note that up to 72.0% aromatics selectivity can be achieved over H-ZSM-5 ( $SiO_2/Al_2O_3 = 36$ ), while the selectivity to alkane decreases to 22.3%. These observations indicate that the introduction of CO changes the traditional reaction networks of  $C_2H_5Cl$ .

Furthermore, H-ZSM-5 zeolites with different  $SiO_2/Al_2O_3$  ratios and good crystallinity (Fig. S6†) are evaluated in the coupling reaction of CO and  $C_2H_5Cl$  at 673 K and 2.0 MPa (Fig. S7†). Aromatics selectivity increases from 29.6% to 72.0% as the  $SiO_2/Al_2O_3$  ratio reduces from 222 to 36, revealing that a low  $SiO_2/Al_2O_3$  ratio is favourable for the formation of aromatics. Thus, H-ZSM-5 with a  $SiO_2/Al_2O_3$  ratio of 36 (H-ZSM-5<sub>36</sub>) will be used for subsequent experiments. Based on the above, it can be concluded that enhancing aromatics selectivity is feasible through the coupling of  $C_2H_5Cl$  with CO catalyzed by H-ZSM-5<sub>36</sub>.

### Effect of reaction conditions on the coupling reaction of $C_2H_5Cl$ and CO over ZSM-5<sub>36</sub>

The effect of reaction conditions on the formation of aromatics has been investigated. Fig. 2a shows the influence of the temperature on the coupling reaction of  $C_2H_5Cl$  and CO over H-ZSM-5. The selectivity to aromatics shows a significant increase from 0% to 72.0% as the temperature is increased from 473 K to 673 K. However, as the temperature is further increased from 673 K to 723 K, the selectivity slightly declines to 71.1%. Furthermore, the conversion of  $C_2H_5Cl$  increases from 18.6% to 40.1% at 523 K once Ar is substituted with CO (Fig. S8†). These suggest that an appropriate reaction temperature is beneficial for the generation of aromatics, and the presence of CO significantly

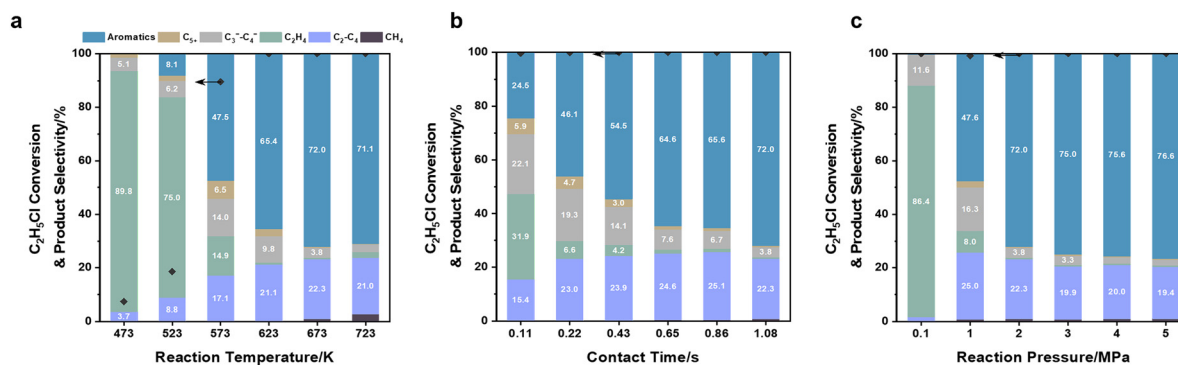


Fig. 2 Effects of reaction conditions on the coupling reaction of  $C_2H_5Cl$  and CO. (a) The  $C_2H_5Cl$  conversion and product selectivity at different reaction temperatures over H-ZSM-5<sub>36</sub>. (b) The  $C_2H_5Cl$  conversion and product selectivity at different contact times over H-ZSM-5<sub>36</sub>. (c) The  $C_2H_5Cl$  conversion and product selectivity at different reaction pressures over H-ZSM-5<sub>36</sub>. Reaction conditions: a: 473–723 K,  $P = 2.0 \text{ MPa}$ ,  $P(CO) = 1130 \text{ kPa}$ ,  $P(C_2H_5Cl) = 9.53 \text{ kPa}$ ,  $WHSV = 0.1 \text{ g}_{C_2H_5Cl} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ , Ar as balance gas. b: 673 K,  $P = 2.0 \text{ MPa}$ ,  $P(CO) = 1130 \text{ kPa}$ ,  $P(C_2H_5Cl) = 9.53 \text{ kPa}$ ,  $WHSV = 1-0.1 \text{ g}_{C_2H_5Cl} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ , Ar as balance gas. c: 673 K,  $P = 1.0-5.0 \text{ MPa}$ ,  $P(CO) = 570-2820 \text{ kPa}$ ,  $P(C_2H_5Cl) = 4.79-23.9 \text{ kPa}$ ,  $WHSV = 0.1 \text{ g}_{C_2H_5Cl} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ , Ar as balance gas.

enhances the conversion of  $C_2H_5Cl$ . Notably, a dramatic decline of  $C_2H_4$  selectivity (89.8% to 0.63%) is observed with an increase in aromatics selectivity. Similar phenomena can be observed when the reaction contact time and reaction pressure change. As shown in Fig. 2b, aromatics selectivity increases monotonically whereas the selectivity to olefins and alkanes decreases gradually with the contact time. About 24.5% aromatics selectivity and 54.0% olefins selectivity can be obtained when the contact time is 0.11 s. Prolonging the contact time, aromatics selectivity of over 72% is achieved. Simultaneously, the selectivity to  $C_2H_4$  is reduced to about 0.62% in the products. Fig. 2c depicts the effect of reaction pressure on the  $C_2H_5Cl$  conversion and product selectivity.  $C_2H_4$  selectivity decreases obviously from 86.4% to 0.47% with an increase of aromatics selectivity from 46.6% to 76.6% when the reaction pressure is increased from 0.1 MPa to 5.0 MPa. Moreover, the changes in selectivity to  $CH_4$  and  $C_2-C_4$  alkanes are subtle. All these indicate that olefins especially  $C_2H_4$  might be important intermediates in the coupling reaction of CO and  $C_2H_5Cl$ , and the hydrogen transfer reaction is distinctly suppressed.

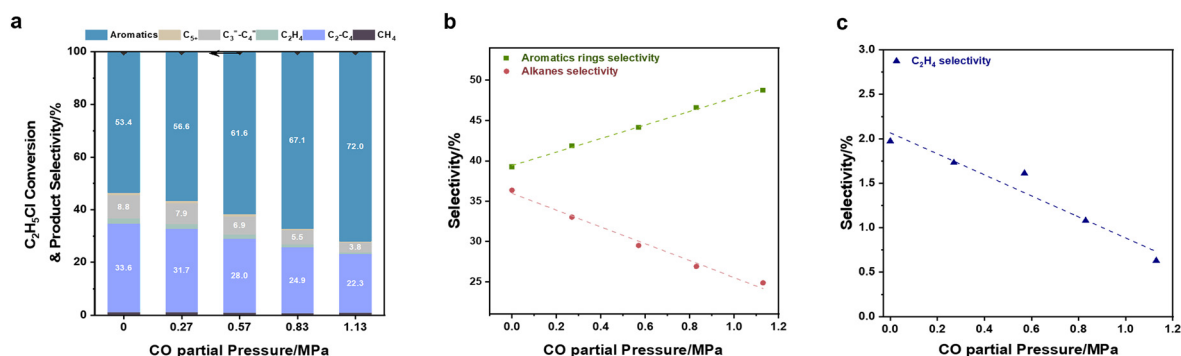
### Discussion on the influence of CO partial pressure on the coupling reaction performance of $C_2H_5Cl$ and CO

Fig. 3 reveals the effect of CO partial pressure under the same reaction conditions. It is evident that with the increase in CO partial pressure from 0 to 1.13 MPa, the aromatics selectivity increased from 53.4% to 72.0%. This indicates that elevating the proportion of CO in the reaction system is favourable to produce aromatics (Fig. 3a). Interestingly, the selectivity to aromatic rings increases linearly while the selectivity to alkanes linearly decreases with increasing CO partial pressure (Fig. 3b). Furthermore, there is a linear decrease in the selectivity to  $C_2H_4$  with the increase in CO partial pressure (Fig. 3c), in which the opposite results appear when adjusting the partial pressure of  $C_2H_5Cl$  (Fig. S9†). These observations suggest that the introduction of CO changes the pathway of aromatics formation and there may be further consumption

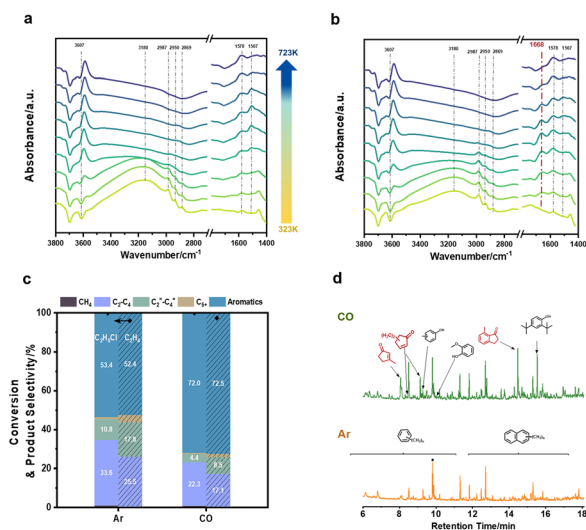
of  $C_2H_4$  in the system, inconsistent with the traditional aromatization mechanism. Moreover, the retained species on the spent H-ZSM-5<sub>36</sub> catalyst under an Ar or CO atmosphere, respectively, are analyzed by GC-MS (Fig. S10†). Notably, abundant oxygenated species are captured when co-feeding  $C_2H_5Cl$  with CO. These results conclusively show that, in contrast to the hydrogen transfer mechanism, CO actively participates in the conversion of  $C_2H_5Cl$  and plays a key role in the heightened selectivity of aromatics. In addition, the reaction system exhibits good reaction stability on ZSM-5 (Fig. S11†).

### Tracking the coupling reaction process of $C_2H_5Cl$ and CO by *in situ* infrared and $C_2H_4$ probe experiments

To further clarify the role of CO in the coupling reaction of  $C_2H_5Cl$  and CO, *in situ* DRIFTS is conducted using temperature programming. Fig. 4a shows the evolution of surface species on H-ZSM-5<sub>36</sub> under an Ar atmosphere. Evidently, the negative peak at  $3607\text{ cm}^{-1}$  is observed, which is attributed to the adsorption of  $C_2H_5Cl$  on the Brønsted acidic sites. Moreover, a broad peak at  $3180\text{ cm}^{-1}$  appears at temperatures below 450 K, assigned to the physical adsorption of  $C_2H_5Cl$ . The C–H vibration peaks ( $2987$ ,  $2950$ , and  $2869\text{ cm}^{-1}$ ) formed by  $C_2H_5Cl$  decrease gradually until they disappear with increasing temperature.<sup>22,23</sup> Aromatic carbonium ions and cyclic coke precursors are detected at peaks  $1578$  and  $1507\text{ cm}^{-1}$ , respectively.<sup>16</sup> These results are consistent with the traditional hydrogen transfer mechanism. Remarkably, a clear peak at  $1668\text{ cm}^{-1}$  is observed after introducing CO, as shown in Fig. 4b, which corresponds to the C=O vibration of the acyl species.<sup>24</sup> The appearance of a new peak indicates that CO participates in the conversion of  $C_2H_5Cl$ . Additionally, the intensity of the peak at  $1668\text{ cm}^{-1}$  exhibits a characteristic volcano-shaped pattern with increasing temperature. Therefore, it has been preliminarily demonstrated that CO generates oxygenated species through the formation of acyl intermediates with  $C_2H_5Cl$ .



**Fig. 3** Effect of CO partial pressure on the coupling reaction of  $C_2H_5Cl$  and CO. (a) The  $C_2H_5Cl$  conversion and product selectivity at different contact times. (b) The aromatic ring selectivity and alkane selectivity with different CO partial pressures. (c) The  $C_2H_4$  selectivity and alkane selectivity with different CO partial pressures. Reaction conditions: a–c: 673 K,  $P = 2.0\text{ MPa}$ ,  $P(\text{CO}) = 0\text{--}1130\text{ kPa}$ ,  $P(\text{C}_2\text{H}_5\text{Cl}) = 9.53\text{ kPa}$ ,  $\text{WHSV} = 0.1\text{ g}_{\text{C}_2\text{H}_5\text{Cl}}\text{ g}_{\text{cat}}^{-1}\text{ h}^{-1}$ , Ar as balance gas.



**Fig. 4** Characterization of the mechanism for the formation of cyclopentenone species. (a) Temperature-programmed *in situ* DRIFT characterization of the C<sub>2</sub>H<sub>5</sub>Cl to aromatics reaction under an Ar atmosphere. (b) Temperature-programmed *in situ* DRIFT characterization of the C<sub>2</sub>H<sub>5</sub>Cl to aromatics reaction under a CO atmosphere. (c) C<sub>2</sub>H<sub>4</sub> probe experiment: comparison of product distribution from C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>5</sub>Cl feeds under an Ar or CO atmosphere over H-ZSM-5<sub>36</sub>. (d) C<sub>2</sub>H<sub>4</sub> probe experiment: GC-MS of organic materials retained in spent H-ZSM-5<sub>36</sub> in the conversion of C<sub>2</sub>H<sub>4</sub> under an Ar or CO atmosphere. Reaction conditions: a:  $P(\text{Ar})/P(\text{C}_2\text{H}_5\text{Cl}) = 109$ , 323–723 K,  $P = 0.1$  MPa. b:  $P(\text{CO})/P(\text{C}_2\text{H}_5\text{Cl}) = 109$ , 323–723 K,  $P = 0.1$  MPa, Ar as balance gas. c:  $P(\text{CO} + \text{Ar or Ar}) = 1990.47$  kPa,  $P(\text{C}_2\text{H}_4 \text{ or } \text{C}_2\text{H}_5\text{Cl}) = 9.53$  kPa,  $\text{WHSV} = 0.1 \text{ g}_{\text{C}_2\text{H}_5\text{Cl or C}_2\text{H}_4} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ , Ar as balance gas. d:  $P(\text{CO} + \text{Ar or Ar}) = 1990.47$  kPa,  $P(\text{C}_2\text{H}_4) = 9.53$  kPa,  $\text{WHSV} = 0.1 \text{ g}_{\text{C}_2\text{H}_5\text{Cl or C}_2\text{H}_4} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ , Ar as balance gas.

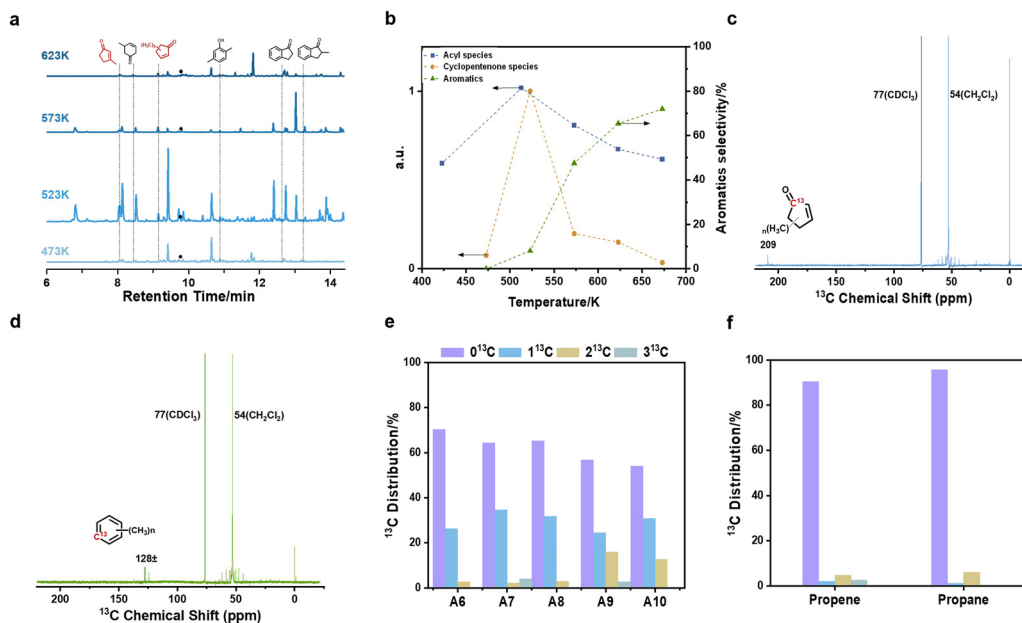
It has been demonstrated that C<sub>2</sub>H<sub>4</sub> plays an important role in the formation of aromatics under the experimental reaction conditions, indicating the presence of a significant pathway for C<sub>2</sub>H<sub>4</sub> to aromatics in the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO. Subsequent probe experiments were conducted using C<sub>2</sub>H<sub>4</sub> as the feedstock under an Ar or CO atmosphere to explore this speculation (Fig. 4c). It can be observed that the introduction of CO into the reaction system leads to a significant increase in aromatics selectivity, reaching 72.5%. Specifically, the selectivity for aromatic rings is approximately 48.1% (Table S2†). These are identical with the results of the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO. The retained species in the spent catalysts are also analyzed using GC-MS, as shown in Fig. 4d. The oxygenated species can be observed under a CO atmosphere, suggesting that CO participates in the reaction as well. More importantly, *in situ* DRIFT characterization of the temperature-programmed C<sub>2</sub>H<sub>4</sub> feed under a CO atmosphere was performed for exploring this pathway (Fig. S12†). The peak at 1668 cm<sup>-1</sup> is also observed in the CO atmosphere and this observation aligns with the trend shown in Fig. 4b. Building upon the prior contributions of researchers such as Alexander G. Stepanov, they employed solid-state nuclear magnetic resonance (NMR) technology to monitor the reactions of various olefins and alkanes with HZSM5 in the presence of CO. This allowed

them to track the corresponding acid generation and identify the associated acyl species. These findings further corroborate the assignment of this peak to acyl species.<sup>24–26</sup> These observations indicate that C<sub>2</sub>H<sub>4</sub>, generated from C<sub>2</sub>H<sub>5</sub>Cl, can also react with CO to form acyl species, thereby enhancing the selectivity towards aromatics over H-ZSM-5<sub>36</sub>. This phenomenon is significant because the reaction of olefins with CO is commonly thought to require metal catalysis *via* the hydroformylation pathway.<sup>27–29</sup>

### Identifying key intermediate species

Generally, capturing intermediate products at low conversion rates to explore reaction mechanisms is a reasonable pathway.<sup>30</sup> Therefore, the retained species in spent catalysts at different reaction temperatures have been captured and analyzed using GC-MS to investigate the aromatization mechanism during the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO (Fig. 5a). As the temperature increases from 473 K to 523 K, the C<sub>2</sub>H<sub>5</sub>Cl conversion rate increased from 7.4% to 18.6%. The content of cyclopentenone species, such as methyl-2-cyclopentene-1-one (MCPO) and dimethyl-2-cyclopentene-1-one (DMCPO), increases gradually. However, with increasing temperature to 623 K, C<sub>2</sub>H<sub>5</sub>Cl undergoes complete conversion. The content of these compounds gradually decreases, which are similar with the change trend of acyl species. Fig. 5b displays the normalized relative contents of acyl species and cyclopentenone species in the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO, which are obtained from *in situ* DRIFT results and GC-MS analysis of the coke formed on the spent catalysts at different temperatures. The relative contents of acyl species and cyclopentenone species increase firstly and then decrease with increasing reaction temperature. In the temperature range of 523 K to 573 K, a simultaneous rapid increase in the selectivity towards aromatics is observed as the relative content of cyclopentenone species sharply decreases. These findings suggest a potential new pathway for aromatics formation, where acyl species are converted to cyclopentenone species, and then transformed into aromatics. To explore the relationship between the acyl species and cyclopentenone species, propionic anhydride is employed as a probe molecule under CO and Ar atmospheres, respectively (Fig. S13a†). Obviously, the product selectivity is similar to that of the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO under the CO atmosphere. Furthermore, the presence of cyclopentenone species is identified by GC-MS analysis (Fig. S13b†). These above results confirm that the acyl species can be transformed into cyclopentenone species.

Furthermore, <sup>13</sup>C isotope labelling experiments are employed to further clarify the reaction mechanism. Fig. 5c shows a signal at about 209 ppm, which corresponds to the carbon atom in the <sup>13</sup>C=O of the cyclopentenone species. These results provide explicit evidence that the carbonyl group of cyclopentenone species originates from CO. Moreover, the signal at 128 ppm is assigned to the carbon



**Fig. 5** Characterization of the mechanism for the formation of aromatics from cyclopentenone species. (a) GC-MS of organic materials retained in spent H-ZSM-5<sub>36</sub> at different temperatures. (b) The normalized relative content of acyl species/cyclopentenone species/aromatics at different temperatures over H-ZSM-5<sub>36</sub>. (c) <sup>13</sup>C liquid-state NMR spectra of the retained species in the presence of <sup>13</sup>CO during the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO over H-ZSM-5<sub>36</sub>. (d) <sup>13</sup>C liquid-state NMR spectra of the products in the presence of <sup>13</sup>CO during the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO over H-ZSM-5<sub>36</sub>. (e) <sup>13</sup>C distribution in liquid products of the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and <sup>13</sup>CO. (f) <sup>13</sup>C distribution in propylene and propane collected from the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and <sup>13</sup>CO. Reaction conditions: a: 473–673 K, P(CO) = 1130 kPa, P(C<sub>2</sub>H<sub>5</sub>Cl) = 9.53 kPa, WHSV = 0.1 g<sub>C<sub>2</sub>H<sub>5</sub>Cl</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, Ar as balance gas; b–f, 573 K, P = 1.0 MPa, CO/C<sub>2</sub>H<sub>5</sub>Cl = 100, WHSV = 0.04 g<sub>C<sub>2</sub>H<sub>5</sub>Cl</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, Ar as balance gas.

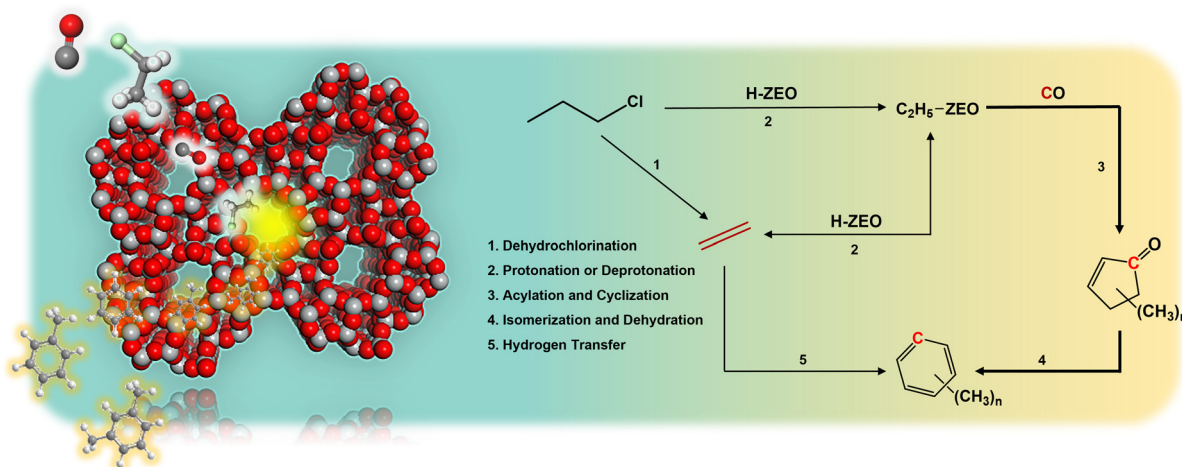
atom in the aromatic ring (Fig. 5d), revealing that CO is involved in the formation of the aromatic ring.<sup>26</sup> More importantly, these above results directly demonstrate that cyclopentenone species are the key intermediates for the generation of aromatics.

Fig. 5e and f show the distribution of <sup>13</sup>C atoms in the products collected using CH<sub>2</sub>Cl<sub>2</sub>. Essentially, there is only one CO involved in the formation of the aromatic ring, and one cyclopentenone species contains only one <sup>13</sup>C. The amount of <sup>13</sup>C incorporated into propene and propane is significantly lower than that incorporated into aromatics.

This reveals that the partial aromatics were generated with the participation of CO. Combining with the results mentioned above, a reasonable inference is proposed: the cyclopentenone species are key intermediates in the formation of aromatics in the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO.

### Proposing the reaction mechanism

Based on the above discussion, we proposed the reaction pathway for enhancing aromatics selectivity in the coupling



**Fig. 6** The proposed mechanism in the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO over H-ZSM-5.

reaction of C<sub>2</sub>H<sub>5</sub>Cl with CO in Fig. 6: 1) C<sub>2</sub>H<sub>5</sub>Cl is converted to C<sub>2</sub>H<sub>4</sub> through dehydrochlorination. 2) C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>4</sub> (converted from C<sub>2</sub>H<sub>5</sub>Cl) adsorb on the active sites of the H-ZSM-5 catalyst to form ethoxy groups. 3) The remaining ethoxy groups are inserted into CO to form acyl species. 4) The acyl species are converted to cyclopentenone species. 5) The cyclopentenone species are transformed into aromatics. Moreover, the hydrogen transfer process of olefins to aromatics is also inevitable due to the high activity of C<sub>2</sub>H<sub>4</sub> in the coupling reaction of C<sub>2</sub>H<sub>5</sub>Cl and CO.

## Conclusions

In conclusion, we report a strategy for the highly efficient generation of aromatics based on C<sub>2</sub>H<sub>6</sub> conversion *via* the coupling of C<sub>2</sub>H<sub>5</sub>Cl and CO over H-ZSM-5. Up to 77% selectivity to aromatics is achieved over H-ZSM-5<sub>36</sub> under the reaction conditions of 673 K and 5.0 MPa. Combined with *in situ* DRIFTS and <sup>13</sup>C isotope labelling experiment, CO has been demonstrated to participate in the formation of aromatics. By tracing the transformation pathway of C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>4</sub> in the reaction system, it is confirmed that C<sub>2</sub>H<sub>4</sub> could be effectively carbonylated at the H-zeolites even without the use of transition metal modification. This work would be beneficial for expanding the coupling reaction system between small molecule compounds and CO, providing fresh insights for natural gas conversion on H-zeolites.

## Author contributions

Conceptualization: W. L. Z., H. C. L., and B. L.; investigation: B. L., X. D. F., H. C. L., Z. Y. C., M. G. X., and L. L. Y.; validation: B. L. and H. C. L.; writing – original draft: B. L.; visualization: B. L. and H. C. L.; writing – review & editing: W. L. Z. and H. C. L.; supervision: W. L. Z. and H. C. L.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21972141, 21991094 and 21991090), the “Transformational Technologies for Clean Energy and Demonstration”, Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA21030100), the Dalian High Level Talent Innovation Support Program (2017RD07), and the National Special Support Program for High Level Talents (SQ2019A2TST0016).

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