Coupling of Methanol and Carbon Monoxide over H-ZSM-5 to Form Aromatics

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Abstract: *The conversion of methanol into aromatics over unmodified H-ZSM-5 zeolite is generally not high because the hydrogen transfer reaction results in alkane formation. Now circa 80 % aromatics selectivity for the coupling reaction of methanol and carbon monoxide over H-ZSM-5 is reported. Carbonyl compounds and methyl-2-cyclopenten-1-ones (MCPOs), which were detected in the products and catalysts, respectively, are considered as intermediates. The latter species can be synthesized from the former species and olefins.* ^{13}C *isotope tracing and* ^{13}C *liquid-state NMR results confirmed that the carbon atoms of CO molecules were incorporated into MCPOs and aromatic rings. A new aromatization mechanism that involves the formation of the above intermediates and co-occurs with a dramatically decreased hydrogen transfer reaction is proposed. A portion of the carbons in CO molecules are incorporated into aromatic, which is of great significance for industrial applications.*

$\mathbf{A}$romatics, especially benzene, toluene, and xylene (BTX), are important bulk chemicals that are primarily produced from petroleum by catalytic reforming or cracking.[1] Obtaining aromatics from non-petroleum resources, such as coal, natural gas, or biomass, is very important because of the increase in market demand for such products and the depletion of petroleum resources. Methanol can be derived from these alternative resources via syngas chemistry, and aromatics can be readily synthesized from methanol by a methanol-to-aromatics (MTA) reaction.[2] Generally, acidic ZSM-5 zeolites are selected as MTA catalysts owing to their unique topology and three-dimensional micropore systems. However, acidic H-form ZSM-5 zeolite (H-ZSM-5) without metal modifications usually has low aromatics selectivity because of the corresponding formation of alkanes

via hydrogen transfer.[3] Although modifications with metals such as Zn,[2a,c,e] Ga,[2d] and Ag[2b] increase aromatics formation by enhancing the dehydrogenation of alkanes via catalysis by these metal species,[4] some methanol decomposition and the formation of unrecoverable catalyst structure owing to metal evaporation, segregation, and aggregation are inevitable.[2a,5]

Recently, Cheng et al. reported that aromatization could be enhanced by CO over the bifunctional $ZnZrO_x$/H-ZSM-5 catalysts in the conversion of syngas or intermediate methanol because CO plays a role in the removal of H species and subsequent formation of methanol. As a result, it can be deduced that $ZnZrO_x$ is indispensable to the catalysis mechanism.[6]

In the presence of CO, H-zeolites catalyze methanol carbonylation to form methyl acetate (MeOAc) and acetic acid (HOAc) through the Koch reaction.[7] It has been proposed that the formation of the first carbon–carbon bond occurs through methanol carbonylation during the methanol to olefin reaction.[8]

Herein we report an aromatics selectivity of 80 % along with 65 % BTX for the coupling reaction of methanol and CO (CMTA) over H-ZSM-5 zeolite. A new aromatization mechanism in which the hydrogen transfer reaction is sharply decreased is proposed.

The CMTA and MTA reactions were performed at 673 K under 4.0 MPa over Z-25 (H-ZSM-5 with the SiO_2/Al_2O_3 ratio = 25). The results are shown in Figure 1a, an approximate 40 % initial aromatics selectivity with a 53 % C_2–C_4 paraffin selectivity was obtained under N_2, which agree with the typical hydrogen transfer mechanism.[3] Interestingly, the initial aromatics selectivity was dramatically increased to 80 % along with 65 % BTX when methanol was coupled with CO, while the CH_4 and C_2–C_4 paraffin selectivity was only 3 % and 20 %, respectively (Figure 1b). The detailed selectivity of aromatics is shown in the Supporting Information, Figure S1. As presented in the Supporting Information, Figure S2, increasing the reaction temperatures of the CMTA reaction was advantageous to aromatics generation because C_2–C_4 paraffin formation was suppressed; however a much higher temperature (723 K) led to lower aromatics selectivity owing to sharp increases in CH_4.

H-ZSM-5 zeolites with SiO_2/Al_2O_3 ratios ranging from 25 to 175 were employed to study the effect of acidity on aromatization in the CMTA reaction. The XRD, N_2 absorption–desorption, and NH_3-TPD results are depicted in the Supporting Information, Figure S3, Table S1, and Figure S4, respectively. A lower SiO_2/Al_2O_3 ratio results in more acidic sites.[9] As seen in Figure 2, the aromatics selectivity increased

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📄 Supporting information (including experimental details, catalyst
ⓘ characterization, enlarged part of GC-MS chromatograms) and the
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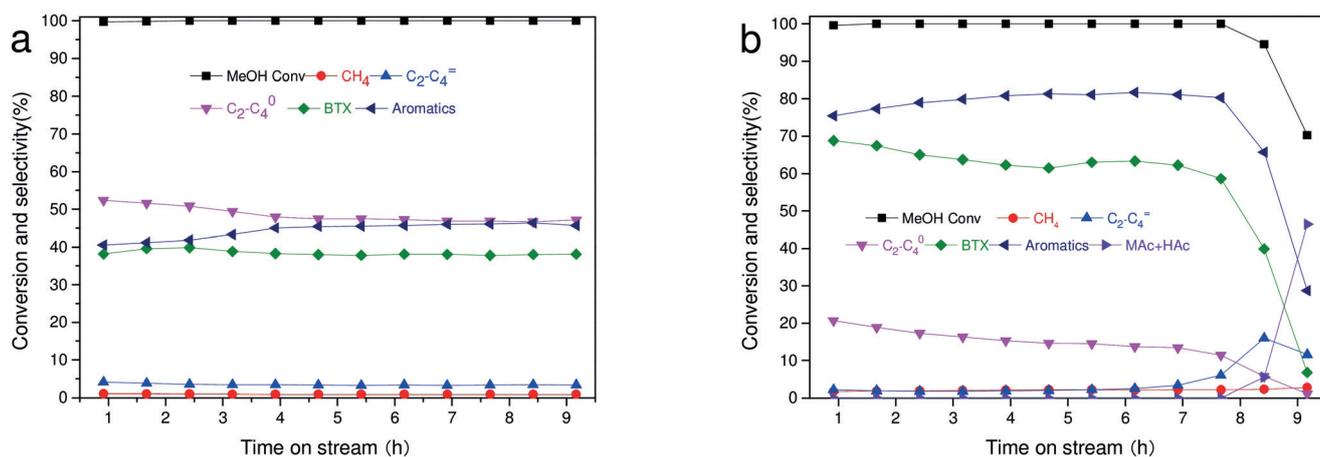   be found under:
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Figure 1. a) MTA and b) CMTA performance over Z-25. Reaction conditions: $T = 673$ K; WHSV $= 0.15$ g g^{-1} h^{-1}; N$_2$ or CO/CH$_3$OH $= 113$; $P = 4$ MPa.
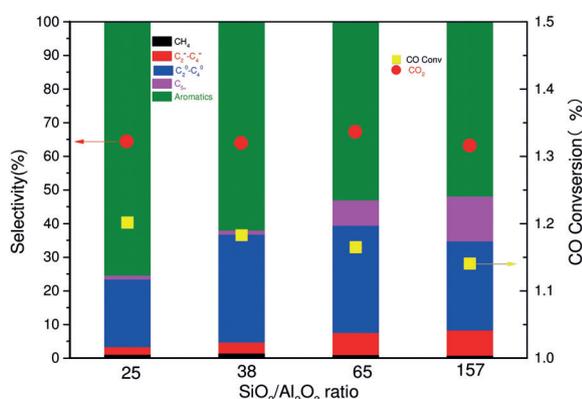

Figure 2. Effect of SiO$_2$/Al$_2$O$_3$ ratio of H-ZSM-5 on CMTA performance. Reaction conditions: $T = 673$ K; WHSV $= 0.5$ g g^{-1} h^{-1}; CO/CH$_3$OH $= 20$; $P = 5$ MPa time on stream $= 4$ h; PS:C$_{5+}$ excludes aromatics.

as the SiO$_2$/Al$_2$O$_3$ ratio decreased (or the number of acidic sites increased). Notably, 1.1–1.2 % CO was converted, whereas approximately 65 % CO$_2$ selectivity from CO was obtained. As shown in the Supporting Information, Table S2, an almost equivalent CO$_2$ amount were detected when co-fed CO-MeOH over H-ZSM-5 and CO-H$_2$O over quartz sand; therefore we consider that CO$_2$ was primarily derived from the water-gas-shift reaction (CO + H$_2$O $\rightleftharpoons$ CO$_2$ + H$_2$, H$_2$O was formed through the MTH reaction) caused by the materials (such as Fe, Ni, and Cr) of the stainless steel tubular reactor. Therefore, approximately 35 % of the carbon atoms in the consumed CO are incorporated into the hydrocarbon products. At a CO/MeOH ratio $= 20$, the hydrocarbons yield will increase ca. 8 % compared to the yield from methanol conversion, which is of great significance to industrial applications. Considering that the nanostructure of H-ZSM-5 is beneficial to prevent coke formation,[2c,f,10] we chose a nanosized H-ZSM-5 with a SiO$_2$/Al$_2$O$_3$ ratio $= 41$ to study the catalytic stability of the CMTA reaction. As shown in the Supporting Information, Figure S5, the aromatics selectivity

remained at approximately 70 % as methanol was completely converted into products in 100 h on stream.

The enhanced aromatization in the CMTA reaction could not be explained by the dehydrogenation of alkanes[4] or the synthesis of methanol[11] owing to the absence of metal species. We also confirmed that propane was slightly converted into products over Z-25 at 673 K and 4 MPa in the presence of CO. CO was inactive when fed alone or syngas (H$_2$: CO $= 2$:1) over Z-25 at 673 K and 4 MPa.

In the presence of CO, carbonyl compounds including MeOAc and HOAc were also detected at the beginning of deactivation at 673 K (Figure 1b). When the reaction temperature dropped to 493 K, methanol conversion remained at 11 % with a 91 % selectivity for MeOAc and HOAc (Supporting Information, Figure S6a). The other products were C$_2$H$_4$ and C$_4$H$_8$. When the temperature rose to 523 K, the selectivity for MeOAc and HOAc reached 92.4 % with circa 40 % methanol conversion in the beginning, which then rapidly dropped to a very low value with the generation of hydrocarbons and complete methanol conversion. Upon catalyst deactivation, the aromatics selectivity decreased and the carbonyl compounds appeared again (Supporting Information, Figure S6b). It is widely accepted that the MTH reaction is an autocatalytic reaction, and critical levels of species such as polymethylbenzenes in the hydrocarbon pool are necessary to initiate autocatalytic reactions.[12] Thus we propose that carbonyl compounds could be transformed into species in the hydrocarbon pool to initiate the autocatalytic MTH reaction, which can explain the decrease in carbonyl compounds with the increase in methanol conversion. Overall, we suppose that carbonyl compounds take part in the formation of aromatics.

To clarify the effect of the carbonyl compounds, methanol was co-fed with MeOAc over Z-25 under N$_2$ at 0.1 MPa. As listed in the Supporting Information, Table S3, increasing the MeOAc concentration enhanced the selectivity for aromatics. The selectivity for aromatics increased with increasing CO partial pressure (shown in the Supporting Information, Figure S7), which agrees with previous works showing that the

carbonylation rates increase linearly with the CO partial pressure.[7b,c] This relationship suggests that carbonylation could have a close relationship with aromatization. We also investigated the intermediates formed at a reaction temperature as high as 673 K by shortening the contact time. It is obvious from the Supporting Information, Figure S8 that the carbonyl compounds were detected when the contact time was less than 0.15 s, and that prolonging the contact time decreased the selectivity for HOAc, MeOAc, and olefins and increased that for aromatics. These results indicate that the carbonyl compounds act as intermediates to form aromatics.

To illustrate the evolution from carbonyl intermediates to aromatics, the reactions at 523 K were quenched by liquid nitrogen and active species were extracted and analyzed by GC-MS following Guisnet's method.[13] The results are shown in Figure 3, and the catalytic performance is shown in the
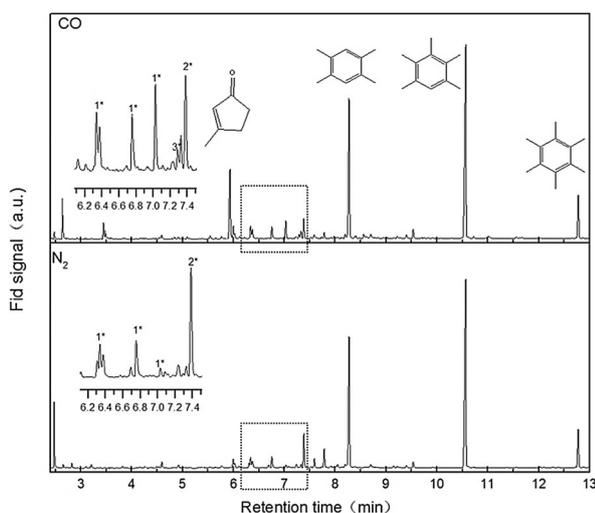

Figure 3. GC-MS chromatograms of organic materials retained in catalysts. Reaction conditions: $T = 523$ K; WSHV $= 0.15$ g g^{-1} h^{-1}; N$_2$ or CO/CH$_3$OH $= 113$; $P = 4$ MPa. The catalysts were removed at 120 min during the methanol conversion in (N$_2$ (bottom) and CO (top)). The enlarged region of retention time from 6.2 to 7.4 min are shown in the inset, where dimethyl-2-cyclopenten-1-one species are labeled 1*, trimethyl-2-cyclopenten-1-one is labeled 2* while 3-methyl-2-cyclo-hexen-1-one is labeled 3*.

Supporting Information, Figures S9 and S6b. The primary organics retained in the catalyst after the MTA reaction under N$_2$ were polymethylbenzenes, and we observed a few methyl-2-cyclopenten-1-ones (MCPOs), which have been detected in the conventional MTH reaction.[14] Interestingly, the introduction of CO in the reaction strikingly enhanced the amount of MCPOs. Thus we propose that MCPOs act as intermediates during the conversion of carbonyl compounds into aromatics. From the catalysis results in Figure 1 and the Supporting Information, Figure S8, it can also be found that the selectivity of aromatics increased with decreasing selectivity for olefins and carbonyl compounds. Therefore, MCPOs may be generated by the reaction of low olefins and carbonyl compounds.

To identify the product from the reaction of olefins with carbonyl compounds, excess acetic anhydride was absorbed

onto the ZSM-5 catalyst, which was then sealed together with C$_3$H$_6$ (5% C$_3$H$_6$, 95% N$_2$) or N$_2$. The products formed at 523 K were analyzed by Guisnet's method. As shown in the Supporting Information, Figure S10, MCPOs were hardly detected when acetic anhydride alone was converted over the ZSM-5 catalyst. However, a sharp increase in MCPOs occurred after the addition of propene, indicating that MCPOs formed from olefins and carbonyl compounds.

To further confirm that CO participates in forming aromatics, ^{13}C isotope tracing was utilized to examine the reactions, and the catalytic performance is shown in Figure S11. The MS spectra of products in the presence of ^{12}CO or ^{13}CO are displayed in the Supporting Information, Figure S12. The ^{13}C distribution in the products can be calculated on the basis of the ^{12}C distribution. As determined from Figure 4a, the amount of ^{13}C incorporated into benzene and toluene was significantly higher than that incorporated into propene and propane, which is crucial evidence supporting the involvement of CO in the formation of aromatic rings. Moreover, this result indicates that the principal mechanism of aromatization in the coupling reaction of methanol with CO is not conventional olefin dehydrogenation because the amount of ^{13}C incorporated into aromatics, olefins, and
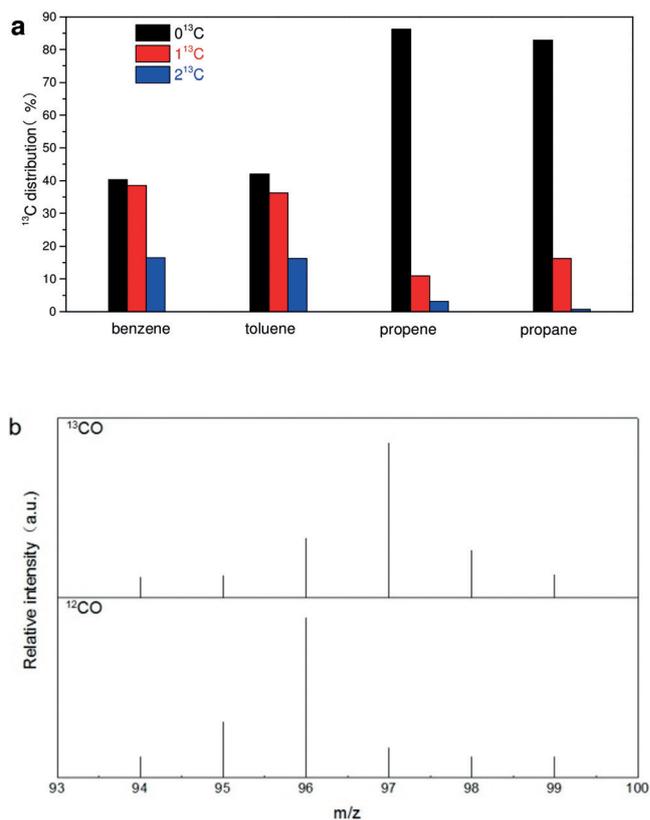

Figure 4. The results of the ^{13}CO isotope tracing method. a) ^{13}C distribution in products of coupling reaction of methanol and ^{13}CO. Reaction conditions: $T = 673$ K; WHSV $= 0.15$ g g^{-1} h^{-1}; CO/CH$_3$OH $= 28$; $P = 1$ MPa. b) MS spectra of 3-methyl-2-cyclopenten-1-one in ^{12}CO (bottom) and ^{13}CO (top) during the coupling reaction of methanol and CO. Reaction conditions: $T = 523$ K; WHSV $= 0.15$ g g^{-1} h^{-1}; CO/CH$_3$OH $= 28$; $P = 1$ MPa. The catalysts were removed at 120 min during the reaction.

paraffin differed greatly. The ^{13}C in olefins and paraffin could have derived from the ^{13}C polymethylbenzenes, as it is widely accepted that hydrocarbon pool species could produce light olefins.[15] Because benzene containing one ^{13}C atom was predominant, we consider that one CO molecule took part in forming an aromatic ring and that olefins containing a ^{13}C atom from aromatics led to the inclusion of more than one ^{13}C atom in aromatics. We also analyzed the ^{13}C incorporation into MCPOs intermediates. As shown in Figure 4b and the Supporting Information, Figure S13, the mass of the base peak of MCPOs increased by 1 when ^{12}CO switched to ^{13}CO, indicating that only one CO molecule was involved in the formation of one MCPO intermediate. Considering that only one CO molecule takes part in the formation of aromatics, we believe that MCPOs act as the intermediates to form aromatics.

The products of $^{13}CO/CH_3OH$ feeds and used catalysts were analyzed by ^{13}C liquid-state NMR spectroscopy. The ^{13}C NMR spectra of the liquid products collected from the $^{13}CO/CH_3OH$ feed are shown in the Supporting Information, Figure S14. The signal at 128 ppm was assigned to the C atom of the aromatics ring.[16] Signals of methyl groups were not observed in the ^{13}C NMR spectra. These results prove that the ^{13}C atoms of ^{13}CO are indeed introduced into the aromatic rings. The used ZSM-5 catalyst was extracted by CH_2Cl_2 following Guisnet's method, and the resultant liquid solution was analyzed through ^{13}C liquid-state NMR spectroscopy (Supporting Information, Figure S15). The signal at 209 ppm was assigned to keto C while the signals corresponding to the other C atoms in MCPOs (2-cyclopenten-1-one was used as stand reference) were not observed, which indicates that the keto C in MCPOs comes from CO.

Because CO participates in the formation of aromatics via carbonyl compounds and MCPO intermediates, we propose a new mechanism of aromatization, as shown in Figure 5; the reaction formulas are shown in the Supporting Information, Scheme S1. First, carbonyl compounds such as HOAc and MeOAc are produced by a Koch-type carbonylation reaction, which has been repeatedly confirmed by our results and past studies.[7] Our work demonstrates that carbonyl compounds react with olefins to generate MCPOs. As MCPOs have been reported to easily transform into aromatic compounds,[14] we propose MCPOs with 5-MR were transformed into aromatics with 6-MR by dehydrolysis. Since the isotope tracing results indicate that a portion of aromatics do not contain carbon from CO, the conventional aromatization mechanism of olefin hydrogen transfer co-occurs with the new mechanism.

In summary, 80 % aromatics selectivity and 65 % BTX selectivity are achieved in the coupling conversion of methanol and CO over the H-ZSM-5 catalyst. A new aromatization mechanism that includes the formation of carbonyl compounds and MCPO intermediates and that co-occurs with a drastically decreased hydrogen transfer reaction is proposed. A portion of the carbons in CO molecules are incorporated into aromatics, which is of great significance for industrial applications.
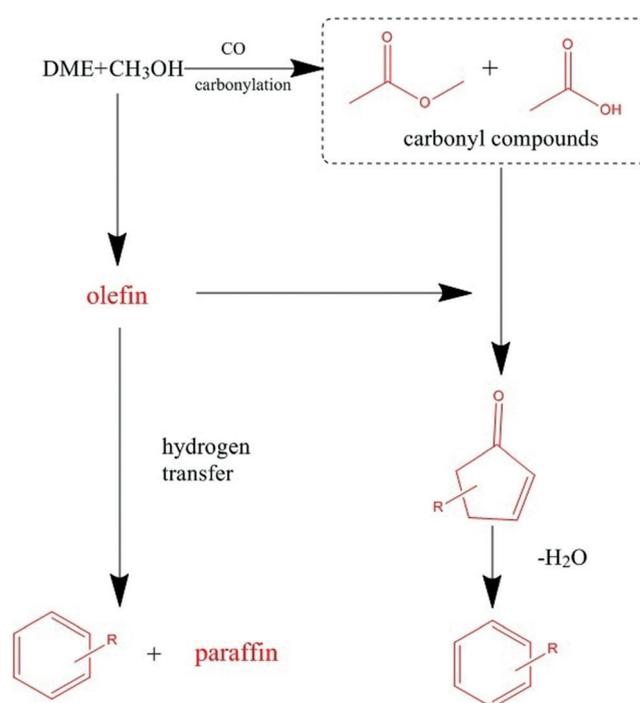

Figure 5. Proposed mechanism for aromatics formation on CMTA over H-ZSM-5. The reaction products and immediate indicated in red have been experimentally detected in this work.

Conflict of interest

The authors declare no conflict of interest.

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