

H-ZSM-5-Catalyzed Hydroacylation Involved in the Coupling of Methanol and Formaldehyde to Aromatics

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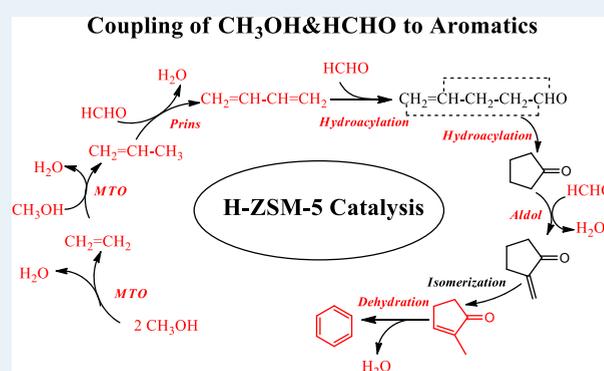
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Supporting Information

ABSTRACT: The selectivity of aromatics in methanol conversion over H-ZSM-5 zeolite is generally unsatisfactory because of the hydrogen transfer reaction which causes the simultaneous formation of alkanes. Here, we report an approximately 70% aromatics selectivity with lower olefins as primary byproducts in the coupling reaction of methanol and formaldehyde over H-ZSM-5 at 723 K and ambient pressure. Hydroacylation reactions catalyzed by H-ZSM-5 zeolite have been first discovered and confirmed during the coupling reaction. Besides Prins and aldol reactions, hydroacylation reactions also participate in the formation of aromatics. Moreover, the coupling mechanism including dienes and methyl-2-cyclopenten-1-ones intermediates is also proposed. This coupling reaction has the potential to be used in various applications.

KEYWORDS: methanol, formaldehyde, aromatics, hydroacylation, H-ZSM-5



1. INTRODUCTION

Methanol (MeOH) conversion chemistry can be applied to prepare various petrochemical products from nonpetrochemical resources including coal, natural gas, and biomass. The gradual depletion of petroleum resources has brought extensive attention to methanol chemistry for nearly four decades.^{1–5} Aromatics, which are important petrochemical and primarily produced by catalytic reforming and cracking, can also be synthesized via methanol-to-aromatics (MTA) reaction.^{6–9}

Acidic ZSM-5 zeolites are often used as catalysts for MTA reactions because of their special MFI topology and three-dimensional ten-membered ring micropore systems. However, the selectivity of aromatics over pure H-ZSM-5 generally is not high because the alkanes are correspondingly formed via hydrogen transfer (HT) reaction.⁴ Further enhancement of aromatics can be achieved via modification of H-ZSM-5 by some metals such as Zn, Ga, and so forth,^{7–12} as these metals can catalyze the dehydrogenation of alkanes and cycloalkanes to aromatics. However, as a result of loss and agglomeration of metal species for metal-modified ZSM-5 zeolites,^{13–15} it is still challenging to maintain their structural stability and catalytic performance after repeated regeneration. Recently, we reported that highly selective aromatics could be obtained by the coupling reaction of methanol and CO over H-ZSM-5 via methyl-2-cyclopenten-1-ones (MCPOs) intermediates.¹⁶ Although there is sufficient evidence that MCPOs are related to form aromatic rings, the formation pathways of MCPOs are

not well understood. Some interesting findings from Lercher or Bhan et al. indicated that introduction of formaldehyde (HCHO) to methanol could help to increase aromatics over H-ZSM-5 because HCHO could readily react with alkenes by Prins reaction into dienes and finally to aromatics.^{17–19} However, the primary products are alkenes and the selectivity of aromatics (less than 20%) is still unsatisfactory. Considering that both CO and HCHO are hydrogen-deficient carbonyl-containing C₁ compounds, their mechanisms for promoting aromatization may have something in common. Furthermore, improving the selectivity of aromatics in the conversion of MeOH and HCHO would be promising to applications because the HCHO promoting effect can occur at ambient pressure.

Here, we first report an H-ZSM-5 zeolite-catalyzed hydroacylation reaction, which participates in the coupling MeOH and HCHO to aromatics. Previously, hydroacylation could only be catalyzed by metals such as Rh, in which C=C double bonds of alkenes are inserted into the formyl C–H bonds of aldehydes formally.^{20–23} About 70% aromatics selectivity along with lower olefins as primary byproducts is obtained. Moreover, the coupling mechanism is also proposed.

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2. EXPERIMENTAL SECTION

2.1. Catalyst Information. The nanosized and microsized H-ZSM-5 zeolites were commercially supplied, which are the same as those in our recent work.¹⁶ The microsized H-ZSM-5 was used only in Figure 1d.

2.2. Catalytic Tests. The reactions were carried out in a typical fixed bed stainless steel reactor with 8 mm inner diameter. Methanol, DMM, or a mixture of methanol and formalin were fed using a high-pressure constant flow pump. All products were heated to the gas phase and analyzed online by two tandem gas chromatographs. One was Agilent 7890B GC equipped with an FID detector connecting a HP-PLOT/Q capillary column and a TCD detector connecting a TDX-1 column. The other one was Agilent 7890A GC equipped with an FID detector connecting an FFAP capillary column and a TCD detector connecting a Paropak Q column. The TDX-1 column was applied to separate CO, CH₄, and CO₂; meanwhile, the Paropak Q column was utilized to separate CH₄ and HCHO. CH₄ was used as a reference bridge between TCD and FID. Conversion and product selectivity were based on the carbon atom number.

2.3. GC–MS Analysis for the Collected Effluents and the Organic Species Retained in Spent Catalysts. All of the gas chromatography–mass spectrometry (GC–MS) analyses were conducted on an Agilent 7890B GC–MS instrument. The effluents were collected by 0.5 L gas sampling bags. The species in the effluents were separated by a HP-PLOT/Q capillary column during GC–MS analysis. The spent catalysts were first dissolved in HF solution (20 wt %), followed by neutralization with NaOH solution (5 wt %). Then, the soluble organic species were extracted by CH₂Cl₂ which contains 10 ppm of C₂Cl₆ as the internal standard. The soluble organic species were separated by a HP-5 capillary column during GC–MS analysis.

2.4. TGA–MS Analysis for the Spent Catalyst. The spent catalyst sample for the thermogravimetric and MS analysis (TGA–MS) was prepared under reaction conditions: 0.6 g H-ZSM-5, $T = 573$ K, $P = 0.1$ MPa, He flow = 50 mL min⁻¹, DMM feed rate = 0.26 mmol C min⁻¹. The catalysts were cooled and removed after 40 min before TGA–MS at 673 K under N₂. TGA–MS analysis was conducted on a SDT-Q600 instrument collected with an OmniStar 300 mass spectrometer. About 20 mg of the spent catalyst was heated to 673 K in 100 mL min⁻¹ N₂ at a ramping rate of 10 K min⁻¹.

3. RESULTS AND DISCUSSION

3.1. Catalytic Performance. Conversion of various C₁ feedstocks over the H-ZSM-5 zeolite (the molar ratio of SiO₂/Al₂O₃ = 40 with a nanosized structure) catalyst was investigated at 723 K and 0.1 MPa. As shown in Figure 1a, the selectivity of aromatics is up to 35% with about 29% C_{2–4} olefins and 25% C_{2–4} paraffins in MeOH conversion, which is a typical result of HT reaction. Interestingly, the aromatics are greatly improved after adding formalin to methanol (MeOH/HCHO/H₂O = 2/1/2.7). The selectivity of aromatics reaches 66.5% with 17.7% C_{2–4} olefins. The molar ratio of C_{2–4} olefins/C_{2–4} paraffins (O/P) can arrive at 4.0, which is much higher than that in MeOH conversion. It indicates that the HT reaction is greatly suppressed after introducing HCHO. Compared with MeOH conversion, MeOH and HCHO conversion yields more CH₄ (3.9%) and CO (3.9%), which may be related to easier decomposition of HCHO.

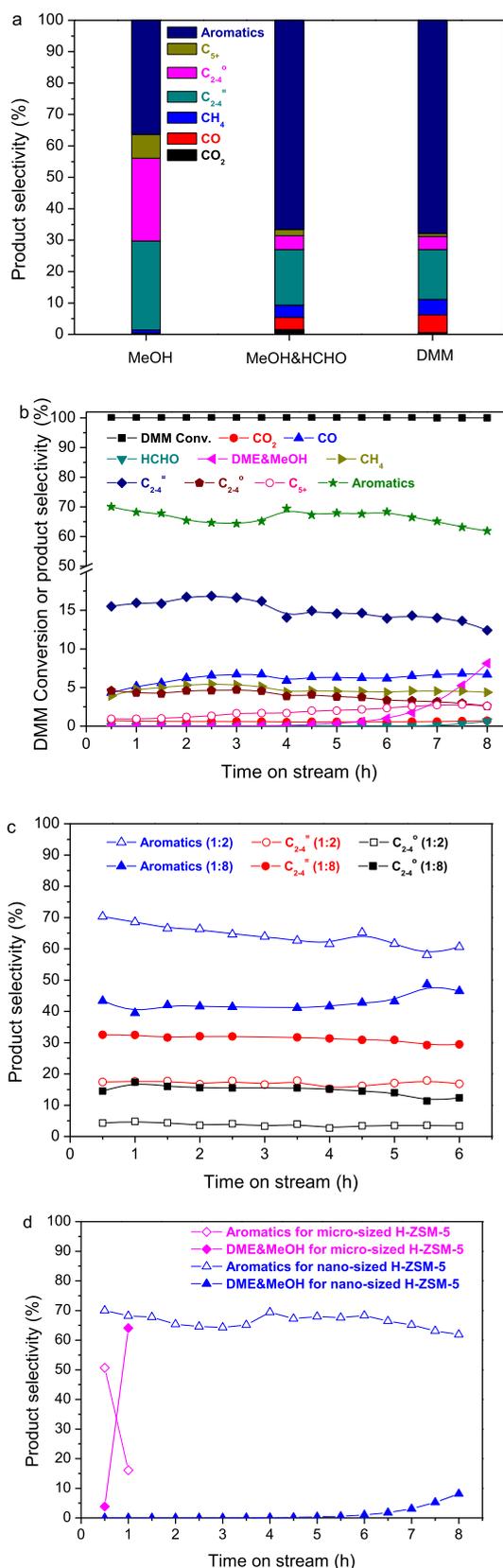


Figure 1. Catalytic results for conversion of various C₁ feedstocks over H-ZSM-5. (a) Comparison for the conversion of MeOH, MeOH and HCHO (a mixture of MeOH and formalin), and DMM; 0.6 g H-ZSM-5, $P = 0.1$ MPa, $T = 723$ K, He flow = 50 mL min⁻¹, feed rate = 0.26 mmol C min⁻¹, MeOH/HCHO/H₂O (molar ratio) = 2/1/2.7; catalytic data were collected at 1.5 h on stream, and the feedstocks

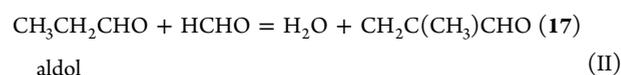
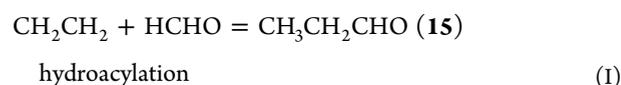
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were completely converted. (b) DMM conversion; 0.6 g H-ZSM-5, $P = 0.1$ MPa, $T = 723$ K, He flow = 50 mL min^{-1} , feed rate = $0.26 \text{ mmol C min}^{-1}$. Note that the retained species including cokes in the spent H-ZSM-5 was about 2.6 wt % of the reacted DMM by TGA analysis. (c) Effect of the HCHO/CH₃OH molar ratio on the conversion of MeOH and HCHO; 0.6 g H-ZSM-5, $P = 0.1$ MPa, $T = 723$ K, He flow = 50 mL min^{-1} , feed rate = $0.26 \text{ mmol C min}^{-1}$; (d) comparison for DMM conversion over microsized and nanosized H-ZSM-5; 0.6 g H-ZSM-5, $P = 0.1$ MPa, $T = 723$ K, He flow = 50 mL min^{-1} , feed rate = $0.26 \text{ mmol C min}^{-1}$. C_{2–4} refers to C₂–C₄ alkanes. C_{2–4}⁺ refers to C₂–C₄ alkenes. C₅₊ excludes aromatics.

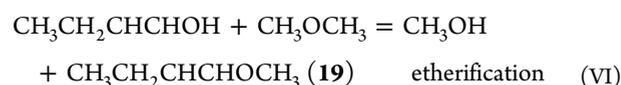
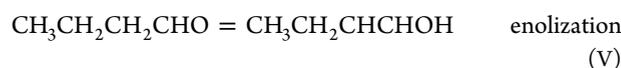
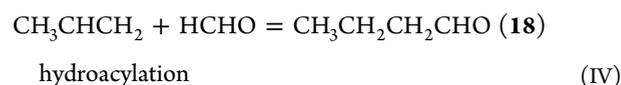
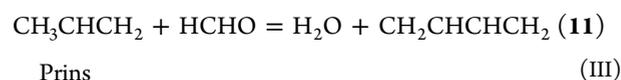
Considering that DMM can be synthesized by the reaction ($2\text{CH}_3\text{OH} + \text{HCHO} = \text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{H}_2\text{O}$), conversion of pure DMM over H-ZSM-5 is also compared. It is obvious that DMM conversion also yields a high selectivity of aromatics and its product distribution is similar to MeOH and HCHO conversion. That is to say, H₂O in the system has little influence on aromatization promoted by HCHO. As shown in Figure 1b, the aromatics slightly decrease from 70.0% at the initial stage to 61.9% at 8 h on stream; DME, MeOH, and HCHO gradually appear after 6 h during DMM conversion. The fraction of aromatics in hydrocarbons (around 73%) is stable during DMM conversion (Figure S1). The catalytic stability of DMM conversion is lower than MeOH conversion (Figure S2). Notably, the ratio of ethylene in C_{2–4} olefins (56.4%) for DMM conversion is much higher than that (34.4%) for MeOH conversion (Figure S3). It is generally accepted that the aromatic cycle and olefin cycle mechanisms coexist in the methanol-to-hydrocarbon reaction. The former preferentially produces aromatics and ethylene, while the latter primarily yields propylene and higher olefins.^{4,24,25} Obviously, the aromatic cycle is predominant for DMM conversion. The conversion of DMM or MeOH favors the formation of aromatics with 8–9 carbon atoms. (Figure S3). As presented in Figures 1c and S2, introducing a small amount of HCHO to MeOH (HCHO/CH₃OH = 1/8) cannot substantially enhance aromatization, but the O/P ratio is essentially increased. Increasing the ratio of HCHO/CH₃OH to 1/2 can result in a significant drop in olefins but a corresponding increase in aromatics, which demonstrates that the formation of aromatics is related to the reaction of olefins and HCHO. Notably, some previous works have studied the conversion of MeOH and HCHO or DMM over H-ZSM-5, or even found that HCHO can promote the formation of aromatics,^{17–19,26} but they have not achieved about 70% selectivity of aromatics. For example, Arora and Bhan reported that aromatics could increase to 17.1% after co-feeding a little HCHO (CH₃OH/HCHO = 30),¹⁸ Lercher et al. found that the addition of 5 C % HCHO to CH₃OH could increase the aromatics selectivity to 12.2%.¹⁹ We speculate that these studies may be primarily concerned with the mechanisms of olefin formation and the addition of HCHO is not enough, resulting in a low selectivity of aromatics. The behaviors of DMM conversion over two H-ZSM-5 zeolites with similar SiO₂/Al₂O₃ ratios but different physical structures (Table S1 and Figure S4) were investigated. In comparison with nanosized H-ZSM-5, the selectivity of aromatics for microsized H-ZSM-5 decreases very fast (Figure 1d). It demonstrates that nanostructures help to resist rapid deactivation caused by HCHO. This result also may explain why the aromatics were not observed as the main product in

DMM conversion over H-ZSM-5 zeolites in the previous study.²⁶ As shown in Figure S5, DMM is completely converted to DME, methyl formate (MF), CO, and MeOH at 423 K. This process should include DMM disproportionation ($2\text{CH}_3\text{OCH}_2\text{OCH}_3 = 2\text{CH}_3\text{OCH}_3 + \text{HCOOCH}_3$) and MF decomposition ($\text{HCOOCH}_3 = \text{CH}_3\text{OH} + \text{CO}$) reactions.^{27,28} Aromatics can be extensively generated at 573 K.

3.2. H-ZSM-5 Catalyzed Hydroacylation. The role of HCHO in promoting aromatization may be related to some corresponding intermediates. However, they could be so active that it is difficult to observe when HCHO is completely converted. Therefore, the catalytic behaviors of the almost inactive H-ZSM-5 zeolite catalyst were explored. As shown in Figures 2a and S6, over deactivated H-ZSM-5, DMM is primarily decomposed to DME and HCHO; only a small amount of which is continuously converted to hydrocarbons. Interestingly, at the same time, a trace of aldehydes such as acetaldehyde (8), 2-propenal (14), propanal (15), and methacrolein (17) have appeared in the effluent. Their structures are confirmed by the detailed mass spectrum in Figures 2b and S7. In general, it is hard to directly synthesize higher aldehydes from HCHO. As far as we know, only hydroacylation reactions, in which multiple C–C bonds of alkenes or alkynes can be inserted into the formyl C–H bonds of aldehydes formally, could achieve this goal.^{20–23} However, it has been found that only a few metal (such as Rh) complexes can catalyze hydroacylation reactions until now. Our findings mentioned above suggest that H-ZSM-5 zeolite might also catalyze hydroacylation. It can be found from Figure 2a that the amount of propanal (15) or methacrolein (17) was obviously increased after cofeeding ethylene during DMM conversion. In other words, ethylene is undoubtedly involved in their synthesis. According to conservation of mass, they should be generated by reactions I and II, which definitely prove that H-ZSM-5 zeolite can catalyze hydroacylation.



The increase in butanal (18) and 2-ethylacrolein (22) (Figures 2c and S7) after cofeeding propylene further proves that hydroacylation can take place over H-ZSM-5 zeolite. In addition, the formation of 1,3-butadiene (11) and some unsaturated ethers (19–21) could be described by the following reactions



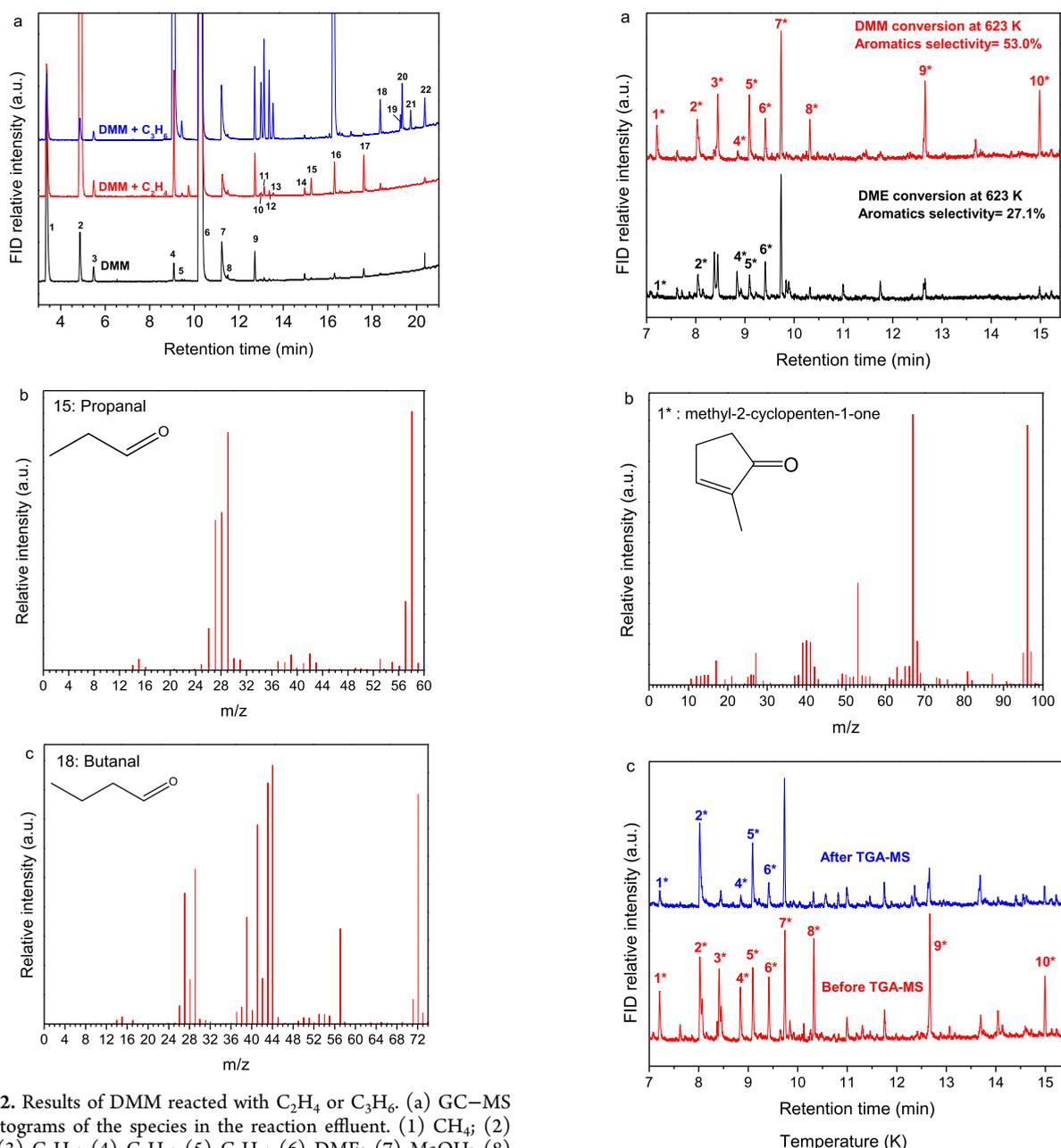


Figure 2. Results of DMM reacted with C_2H_4 or C_3H_6 . (a) GC–MS chromatograms of the species in the reaction effluent. (1) CH_4 ; (2) C_2H_4 ; (3) C_2H_6 ; (4) C_3H_8 ; (5) C_3H_6 ; (6) DME; (7) MeOH; (8) acetaldehyde; (9) MF; (10, 12 or 13) butenes; (11) 1,3-butadiene; (14) 2-propenal; (15) propanal; (16) DMM; (17) methacrolein; (18) butanal; (19,21) 1-methoxy-1-butene; (20) 4-methoxy-1-butene; (22) 2-ethylacrolein. The species were separated by a PLOT-Q capillary column. The effluent of DMM conversion was collected after about 2.0 h on stream under conditions: 0.2 g H-ZSM-5, $T = 723$ K, $P = 0.1$ MPa, He flow = 50 mL min^{-1} , feed rate of DMM = 0.76 mmol C min^{-1} . Then, 50 mL min^{-1} C_2H_4 (5% molar content)/ N_2 was fed instead of He and the effluent for DMM + C_2H_4 conversion was collected. Finally, 50 mL min^{-1} C_3H_6 (5% molar content)/ N_2 was fed instead of He and the effluent for DMM + C_3H_6 conversion was collected. (b) Mass spectrum of species 15. (c) Mass spectrum of species 18.

3.3. Characterization of the Intermediates. The soluble organic species retained in spent catalysts were studied. As shown in Figure 3a, the selectivity of aromatics in DMM conversion is 25.9% higher than DME conversion at 623 K. After reacted for 30 min on stream, the catalysts were quickly cooled to room temperature. According to Guisnet's and

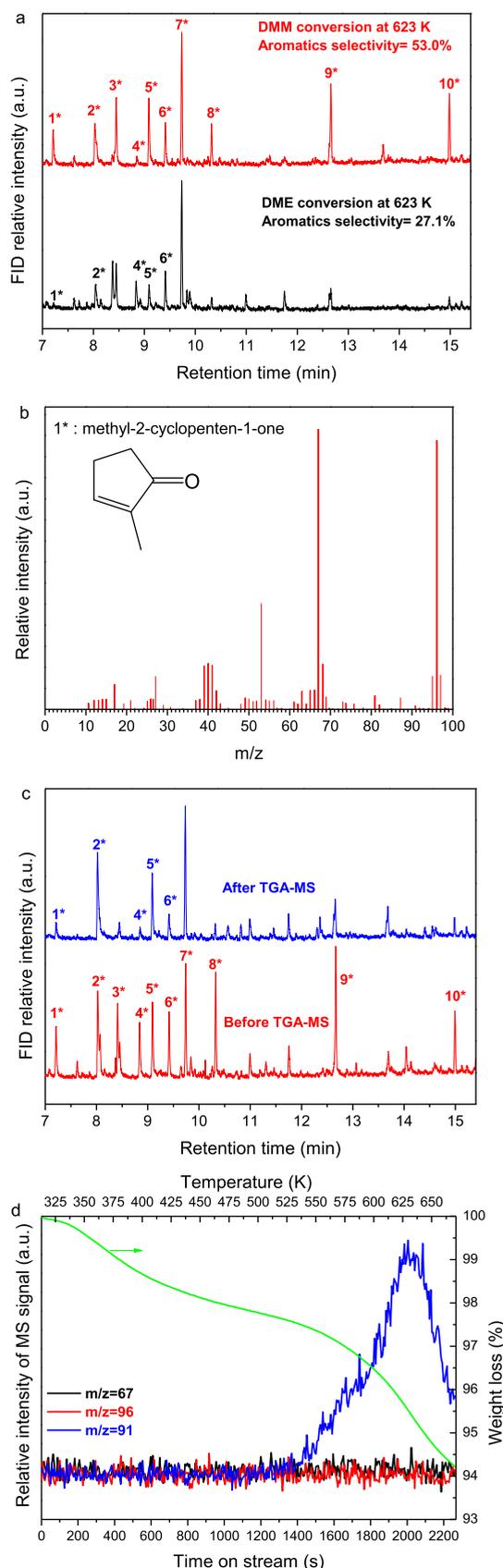


Figure 3. Characterization of the organic species retained in spent catalysts. (a) Comparison for the retained organic species after DMM and DME conversion. The spent catalysts were prepared under conditions: 0.2 g H-ZSM-5, $T = 623$ K, $P = 0.1$ MPa, mixed gas (0.5% molar content of DMM or 0.75% molar content of DME in Ar) flow

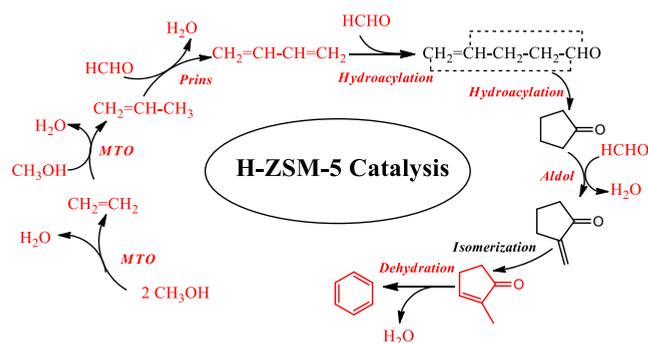
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= 50 mL min⁻¹. The catalysts were cooled and removed at 30 min, then dissolved in HF, extracted with CH₂Cl₂, and analyzed by GC–MS. The species were separated by an HP-5 capillary column. C₂Cl₆ is used as the internal standard. (b) Mass spectrum of species 1*. (c) Comparison of the retained organic species before and after TGA–MS. The spent catalyst before TGA–MS was prepared under conditions: 0.6 g H-ZSM-5, *T* = 573 K, *P* = 0.1 MPa, He flow = 50 mL min⁻¹, DMM feed rate = 0.26 mmol C min⁻¹. The catalysts were removed after 40 min before TGA–MS at 673 K under N₂. (d) Results of TGA–MS. 1*: or 2*: methyl-2-cyclopenten-1-one; 3*: trimethyl-benzene; 4* or 5*: dimethyl-2-cyclopenten-1-one; 6*: trimethyl-2-cyclopenten-1-one; 7*: C₂Cl₆; 8*: tetramethyl-benzene; 9*: pentamethyl-benzene; 10*: hexamethyl-benzene.

Magnoux method,²⁹ the spent catalysts were dissolved in HF and the organic materials retained were extracted with CH₂Cl₂ and analyzed by GC–MS. MCPOs species in the spent H-ZSM-5 catalyst after DMM conversion are obviously more than DME conversion. The similar results can also be obtained when they are converted at 673 K (Figure S8). The structures of MCPOs are confirmed by the detailed mass spectrum in Figures 3b and S9. In our recent work, MCPOs have been identified as important intermediates to form aromatics in the coupling reaction of MeOH and CO.¹⁶ Therefore, we infer that HCHO could be beneficial for the synthesis of MCPO intermediates, resulting in promoting aromatization. The formation of MCPOs during DME conversion may be also related to HCHO because HCHO can be formed on Lewis acid sites of H-ZSM-5 via HT of MeOH.¹⁷ The spent H-ZSM-5 for DMM conversion at 573 K was analyzed by the TGA–MS method at 673 K under N₂. As shown in Figure 3c, the content of MCPOs is obviously decreased after analysis. From about 573 to 673 K, a large weight loss occurs; meanwhile, a peak for the MS signal of *m/z* = 91 appears (Figure 3d), which can be attributed to the formation of light aromatics such as toluene and xylenes. However, there is no corresponding peak at *m/z* = 67 or 96, which can be assigned to MCPOs because of their relatively high abundance (Figure 3b). It suggests that the reduced MCPOs have possibly been converted to aromatics during TGA–MS analysis.

3.4. Proposed Mechanism. According to all of the findings mentioned above and previous literatures, we proposed a mechanism for the coupling MeOH and HCHO to aromatics over H-ZSM-5. As shown in Scheme 1, alkenes such as ethylene and propylene can be first synthesized by methanol-to-olefins reaction,⁴ and then transformed to dienes

Scheme 1. Proposed Mechanism for the Coupling MeOH and HCHO to Aromatics over H-ZSM-5



(e.g., 1,3-butadiene) in the presence of HCHO via Prins condensation.¹⁹ As presented in Figure S10, 1,3-butadiene gradually increases with aromatics decreasing, suggesting that dienes should be involved in the synthesis of aromatics. Unsaturated aldehydes can be obtained by intermolecular hydroacylation between dienes and HCHO, and then converted to cyclopentanone and its derivatives by intramolecular hydroacylation, which have been realized over Rhodium complex catalysts.²¹ MCPOs could be continuously produced by the aldol condensation³⁰ of cyclopentanones and HCHO and subsequent isomerization. Our recent calculation results indicated that the extracyclic double bond of cyclopentene species can be converted to an internal double bond,³¹ suggesting that the isomerization is possible. MCPOs finally are dehydrated to form aromatics, which has been discussed in Figure 3a–d and our recent work.¹⁶ Notably, the species in red have been detected in the spent catalyst and effluent; meanwhile, the reactions in red have been proved by our findings or reported by previous literatures.

4. CONCLUSIONS

In summary, hydroacylation reactions catalyzed by H-ZSM-5 zeolite have been first discovered and confirmed. About 70% aromatics selectivity along with lower olefins as primary byproducts is achieved in the coupling reaction of methanol and formaldehyde over H-ZSM-5 at 723 K and ambient pressure. Besides Prins and aldol reactions, the hydroacylation reaction also participates in the coupling reaction. Moreover, the coupling mechanism including dienes and MCPOs intermediates is also proposed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b03474.

Supporting characterization data and spectra, and supporting catalytic data (PDF)

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Author Contributions

Y.N. designed and performed the experiments, analyzed the data, and wrote the manuscript. W.Z. and 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.

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