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Formaldehyde intermediate participating in the conversion of methanol to aromatics over zinc modified H-ZSM-5

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ABSTRACT

Metal-modified H-ZSM-5 has a high selectivity of aromatics in methanol to aromatics (MTA) reaction, which is often attributed to the metal promoting the aromatization of intermediate olefins. However, the effect of methanol dehydrogenation on aromatics formation over these catalysts is rarely studied. Here, we report that HCHO, which is formed by methanol dehydrogenation over Zn/H-ZSM-5 prepared by Zn impregnation, can participate in the synthesis of aromatics. Methanol conversion can produce more aromatics than olefins (propylene or ethylene) conversion over Zn/H-ZSM-5, indicating the conventional MTA pathway including methanol-to-olefins and olefins-to-aromatics is not complete. Moreover, an MTA mechanism including the conventional pathway and the methanol and HCHO coupling pathway is systematically proposed.

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1. Introduction

Aromatics are important bulk chemicals, which are extensively applied in not only the production of synthetic polymer materials including fibers, rubbers and plastics, but also the manufacture of fine chemical commodity such as surfactants and dyes [1,2]. At present, almost all the aromatics come from petroleum resources through catalytic reforming of naphtha and stream cracking [3]. Increasing demand for aromatics and decreasing oil reserves make it necessary to find non-petroleum routes to produce aromatics [4]. In the past 50 years, the methanol-to-aromatics (MTA) reaction is widely considered to have great potential to solve this problem [5–7], because methanol can be derived from non-petroleum carbon resources such as coal, natural gas, biomass and even CO_2 [8–11].

Acid ZSM-5 zeolite is recognized as the most suitable MTA catalyst because of its unique three-dimensional ten-membered ring microporous structures. Modifying ZSM-5 zeolites by some metals such as Zn, Ga, Ag, Mo, etc. is usually required because the aromatics selectivity over pure H-ZSM-5 catalysts is not high [12–15]. Because aromatics are generally regarded as the products of subsequent conversion of olefins, the conventional MTA pathway consists of methanol-to-olefins (MTO) and olefins-to-aromatics (OTA) reactions [16–18]. In OTA reaction, olefins need to be cyclized to cycloalkanes and then dehydrogenated to aromatics [2]. At the same time, the side reaction of olefins hydrogenation to alkanes is inevitable. These hydrogenation and dehydrogenation reactions together are called hydrogen transfer (HT) reactions [19]. It is well accepted that the function of metals is to improve aromatics in OTA reaction via enhancing the dehydrogenation of cycloalkanes and alkanes [2,7,20]. Some previous literatures reported that metal modified zeolites could also catalyze the dehydrogenation of methanol to formaldehyde (HCHO) [21]. Moreover, cofeeding HCHO to methanol has been proved to be beneficial for the aromatization in our recent work [22]. Until now, there has been no research concerning the function of methanol dehydrogenation to HCHO in MTA reaction over metal modified zeolites.

Here, we report that HCHO, which is formed by methanol dehydrogenation over Zn modified H-ZSM-5 zeolite catalyst, can participate in the synthesis of aromatics. Moreover, an MTA mechanism including the conventional pathway and the methanol and HCHO coupling pathway is systematically proposed. Compared with our recent research on the coupling of methanol and formaldehyde

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to produce aromatics [22], the HCHO in this study does not need to be added, but is generated *in situ* by methanol dehydrogenation.

2. Experimental

2.1. Catalyst preparation

H-ZSM-5 zeolite with SiO_2/Al_2O_3 molar ratio = 40 (by X-ray fluorescence analysis, XRF) was identical to the catalyst in our recent work [22]. Zn modified H-ZSM-5 zeolite catalyst was prepared by a typical impregnation method, which was exactly the same as that in our previous work [6]. In brief, an aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ was mixed with H-ZSM-5 zeolite. After impregnated at room temperature for 18 h, the sample was dried at 373 K overnight, and then calcined at 823 K for 4 h. The resultant product was named as Zn/H-ZSM-5 catalyst. Zn weight content of Zn/H-ZSM-5 was about 2% by XRF.

2.2. Catalytic tests

The equipment for catalytic tests, which mainly includes a fixed-bed reactor and two online tandem gas chromatographs (GC), was also identical to that in our recent paper [22]. Methanol was fed by a high-pressure constant flow pump. Gases such as a standard mixed gas of C_2H_4 and N_2 (molar ratio = 5:95), a standard mixed gas of C_3H_6 and N_2 (molar ratio = 5:95), and He were introduced by gas mass flow meters. One GC was equipped with two columns: a HP-PLOT/Q capillary column to FID detector and a TDX-1 column to TCD detector. The other GC was also equipped with two columns: an FFAP capillary column to FID detector and a Paropak Q column to TCD detector. The product methane (CH_4) was acted as a calculating bridge between the signals of TCD and FID. All the catalytic results such as selectivity and distribution were based on the number of carbon atoms. Dimethyl ether (DME) was treated as reactant in methanol conversion. Distribution of products was selected to conveniently compare the conversion of methanol and olefins.

2.3. Characterization method

A PANalytical X'Pert PRO X-ray diffractometer with Cu Kα radiation was used to test the XRD profiles. A Philips Magix-601 XRF spectrometer was utilized to analyze the element content. A Micromeritics AutoChem II 2920 equipped with a TCD detector was used to test NH_3-TPD profiles. The effluents after the reaction of methanol and propylene over inactive Zn/H-ZSM-5 were collected and analyzed on an Agilent 7890B GC–MS instrument equipped with a HP-PLOT/Q capillary column. The organic species retained in spent catalysts were extracted and analyzed on the above GC–MS equipped with a HP-5 capillary column. The specific procedures were similar to our recent work [22].

3. Results and discussion

Conversion of methanol, ethylene or propylene over H-ZSM-5 or Zn/H-ZSM-5 at 723 K and 0.1 MPa was investigated. The feed rates based on carbon numbers of the three reactants are equal. For comparison, the reaction results are expressed by the distribution (or percentage) of the components in the effluent. As shown in Fig. 1(a) and 1(b), in methanol conversion over H-ZSM-5, the non-aromatic and aromatic hydrocarbons are about 63 and 37%, respectively. The ratio of C_{2-4} alkenes/C_{2-4} alkanes ($C^{=}_{2-4}/C^{o}_{2-4}$) is 1.1 and the area of H_2 in GC is extremely low (Table S1), suggesting that almost all the hydrogen removed during aromatization is added to the olefins to form alkanes. This is a typical result of HT reaction restricting aromatization [11]. Interestingly, the product distribution for methanol conversion changed significantly after Zn impregnation. The aromatics and $C^{=}_{2-4}/C^{o}_{2-4}$ increase to nearly 73% and 7.3, respectively. Besides, H_2 is obviously generated (Table S1). That is to say, HT reaction is greatly suppressed over Zn/H-ZSM-5. HT reaction actually includes two reactions: dehydrogenation and hydrogenation, which could be simultaneously catalyzed by Brønsted (B) acids of zeolites. Because no excess H_2 is released, the hydrogenation and dehydrogenation abilities of B acids for H-ZSM-5 should be approximately equal. According to previous reports [4,7,12], for Zn/H-ZSM-5 prepared by impregnation, some Zn^{2+} exchanges with part of H^+ at the B acid sites, which balances the negative charge of the zeolite framework and reduces the amount of B acids. The remaining Zn species is dispersed in the form of oxides on the outer surface or micropores of the zeolite [23]. In view of this, the holistic behaviors of Zn/H-ZSM-5 should be determined by the hydrogenation and dehydrogenation abilities for Zn species and the remaining B acids. Since the two abilities for B acids are probably equal, and dehydrogenation products including aromatics and H_2 are predominant over Zn/H-ZSM-5, it could be inferred that the dehydrogenation ability of Zn species is much greater than its hydrogenation ability under such reaction conditions. This also explains the results that the aromatics and $C^{=}_{2-4}/C^{o}_{2-4}$ both increased in ethylene or propylene conversion after Zn modification (Fig. 1(a)). The findings and discussions above seem to be reasonable for conventional MTA pathway. If all the aromatics really come from the reactions of MTO and OTA reactions, from the perspective of chemical kinetics, it could be deduced that the aromatics from MTA should be no more than those from OTA. However, it can be noted that the synthesized aromatics over Zn/H-ZSM-5 follows this order: ethylene conversion < propylene conversion < methanol conversion. Even the amount of carbon atoms in the aromatic rings also follows it (Fig. 1(b)). According to the widely accepted hydrocarbon pool (HCP) mechanism for MTO reaction, the initial olefins are actually a mixture of ethylene and propylene [24,25]. It can be deduced that methanol conversion should also yield more aromatics than these mixed olefins conversion. It means that besides conversional MTA pathway, there may be another pathway to generate aromatics.

The change of catalytic performances with the time on stream for methanol conversion at 723 K over Zn/H-ZSM-5 is shown in Fig. 2(a) and (b). The selectivity of aromatics reaches above 70% in the initial 2.5 h. After that, the aromatics decline rapidly, whereas CO, CO_2 and H_2 all increase quickly. According to the previous studies, the latter three products could be formed by methanol decomposition ($CH_3OH = CO + 2H_2$) and water shift gas reaction ($CO + H_2O = CO_2 + H_2$), respectively [23]. It can be found from Fig. S1(a) and (b) that the stability of Zn/H-ZSM-5 in propylene or ethylene conversion is better than that in methanol conversion. It is worth noting that HCHO, the product of methanol dehydrogenation ($CH_3OH = HCHO + H_2$), starts to appear at 10.5 h on stream, and then continues to grow, even reaches 30.7% at 18.5 h on stream. HCHO is deemed to be an intermediate product for methanol decomposition to CO [23]. Our recent research found that the coupling of methanol and HCHO could get about 70% aromatics with $C^{=}_{2-4}$ as the main byproducts over H-ZSM-5 [22], which is exactly similar to the results of methanol conversion over Zn/H-ZSM-5. It suggests that HCHO could act as an intermediate to form aromatics in MTA reaction over Zn/H-ZSM-5. Moreover, before the appearance of HCHO, as the aromatization ability decreased, the trace (below 0.2%) product 1, 3-butadiene gradually increased, which is also an important feature that HCHO is involved in aromatization. Next, this will be explained in detail.

If HCHO is indeed an aromatization intermediate here, the proposed mechanism for the coupling of methanol and HCHO to aromatics should also be effective. This coupling mechanism is

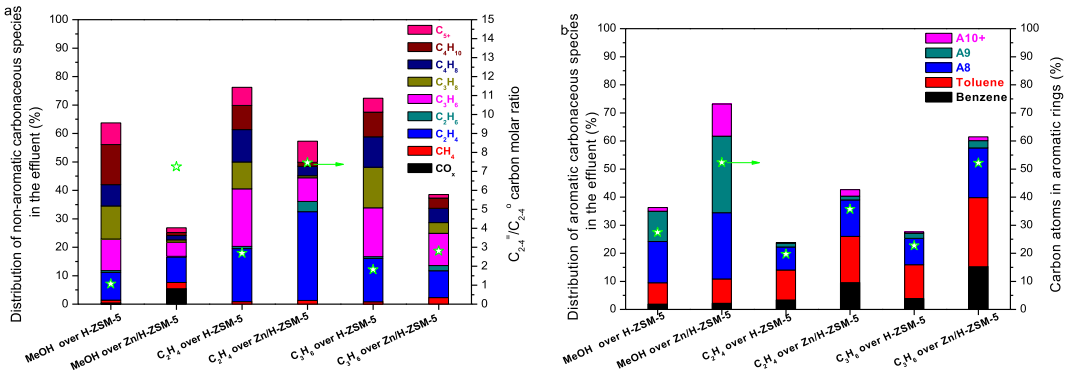


Fig. 1. The catalytic performances of methanol, ethylene or propylene conversion over H-ZSM-5 or Zn/H-ZSM-5. (a) The distribution of non-aromatic species; (b) The distribution of aromatic hydrocarbons. Reaction conditions: catalyst mass = 0.6 g, P = 0.1 MPa, T = 723 K, GHSV (carrier gas and reactant) is about 6×10^3 mL $g^{-1}h^{-1}$, reactant feed rate (based on carbon atoms) = 0.017 mol C h^{-1}. Catalytic data were collected at 1.5 h on stream.

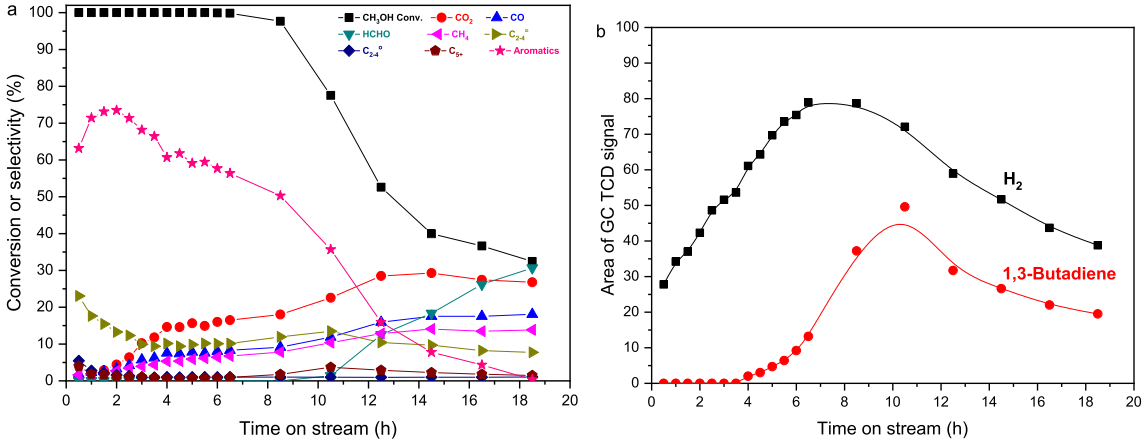


Fig. 2. Catalytic results for the methanol conversion over Zn/H-ZSM-5. (a) Conversion or selectivity versus time on stream; (b) H_2 and 1, 3-butadiene GC signals versus time on stream. Reaction conditions: catalyst mass = 0.6 g, P = 0.1 MPa, T = 723 K, feed rate = 0.017 mol C h^{-1}, carrier gas = 50 mL min^{-1}.

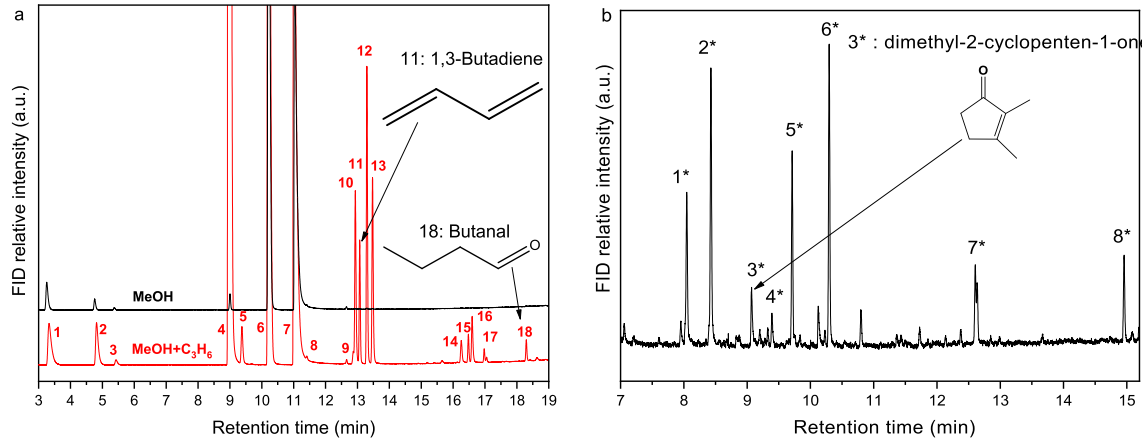
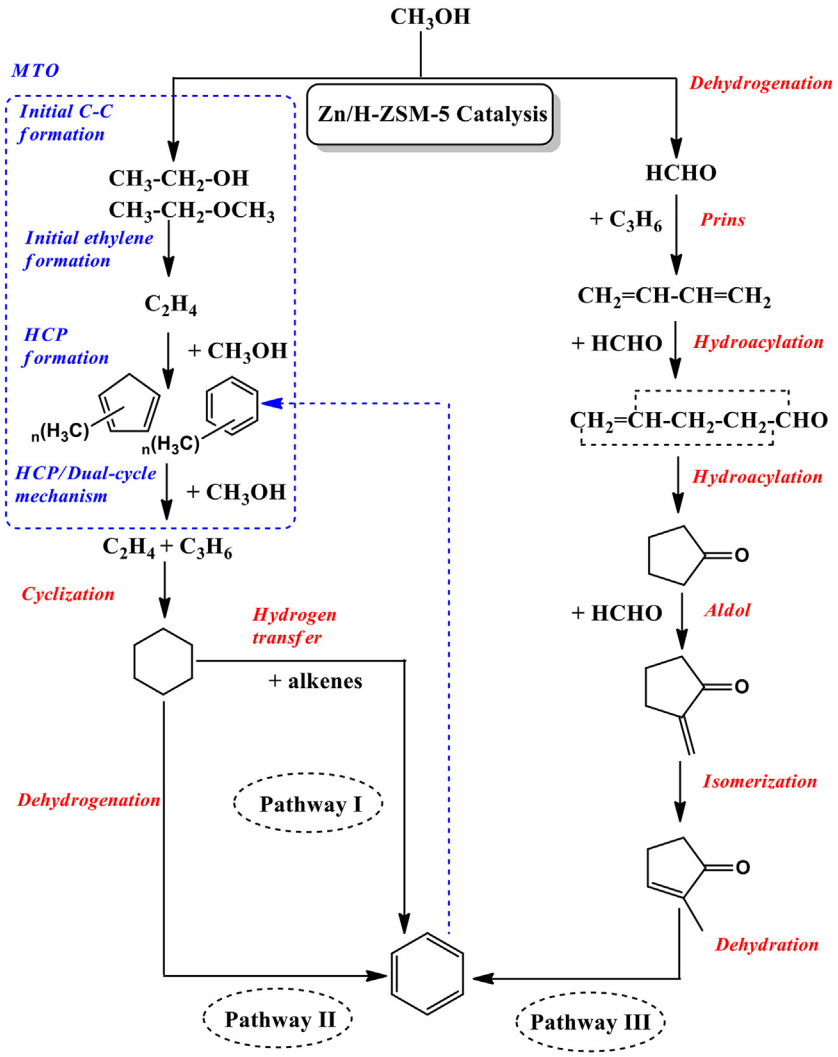


Fig. 3. Results of GC–MS analysis for the collected effluent and retained species. (a) GC–MS chromatograms of the collected effluent. Methanol conversion under conditions: 0.2 g nearly deactivated Zn/H-ZSM-5, T = 723 K, P = 0.1 MPa, He carrier gas = 50 mL min^{-1}, feed rate = 0.017 mol C h^{-1}. Methanol and propylene conversion under the similar conditions except 5% C_3H_6/N_2 mixed gas instead of He. 1: CH_4; 2: C_2H_4; 3: C_2H_6; 4: C_3H_6; 5: C_3H_8; 6: DME; 7: MeOH; 8: Acetaldehyde; 9: Methyl formate; 10, 12 or 13: Butenes; 11: 1,3-Butadiene; 14,15 or 16: Pentenes; 17: Pentadiene; 18: Butanal. (b) GC–MS chromatograms of the organics retained in spent Zn/H-ZSM-5. 1*, 2*: trimethyl-benzene; 3*: dimethyl-2-cyclopenten-1-one; 4*: trimethyl-2-cyclopenten-1-one; 5*: C_2Cl_6; 6*: tetramethyl-benzene; 7*: pentamethyl-benzene; 8*: hexamethyl-benzene. Reaction conditions: catalyst mass = 0.2 g, P = 0.1 MPa, T = 673 K, He carrier gas = 50 mL min^{-1}, methanol feed rate = 0.01 mol C h^{-1}. The catalyst was removed after 30 min on stream.



Scheme 1. Proposed mechanism for methanol conversion to aromatics over Zn/H-ZSM-5.

characterized by the involvement of hydroacylation and prins reactions [22]. In order to verify it, methanol conversion over an almost inactive Zn/H-ZSM-5 was investigated. The results of GC–MS analysis for the collected effluents are shown in Fig. 3(a) and Fig.S2(a) and (b). It can be noted that after cofeeding with propylene, 1, 3-butadiene (**11**) and butanal (**18**) apparently emerged. The following three reactions can describe their formation.

(I) CH_3OH = HCHO + H_2 Dehydrogenation

(II) CH_3CHCH_2+HCHO=CH_3CH_2 CH_2CHO **(18)** Hydroacylation

(III) CH_3CHCH_2+HCHO= H_2O+ $CH_2CHCHCH_2$ **(11)** Prins

Therefore, we confirm that a considerable part of the aromatics is obtained through the process of the dehydrogenation of methanol to HCHO and the coupling of methanol and HCHO. Furthermore, in accordance with the method of M. Guisnet [26], the retained species in the used Zn/H-ZSM-5 after methanol conversion were analyzed. It can be found from Fig. 3(b) and Fig. S2(c) that some methyl-2-cyclopenten-1-ones (MCPOs) are retained in the spent catalyst. MCPOs, which would be derived from olefins and HCHO according to the coupling mechanism, can be dehydrated to aromatics [11,22].

The XRD patterns of H-ZSM-5 and Zn/H-ZSM-5 in Fig. S3 show that the intensities of the peaks became slightly lower after Zn impregnation. Diffraction peaks of ZnO crystallites cannot be observed for Zn/H-ZSM-5, suggesting they are extremely tiny and highly dispersed in the zeolites [12]. It has been proved in our latest paper that the tiny structure of ZnO is good for suppressing the hydrogenation of olefins [27]. The NH_3-TPD profiles of H-ZSM-5 and Zn/H-ZSM-5 in Fig. S4 show that the amount of acid obviously decreased after impregnating Zn. This could be mainly caused by the exchange of Zn^{2+} with the H^+ of B acids [4,7,12]. The reduction of B acid is beneficial to inhibit HT reaction.

Based on the results in this work and previous literatures [2,6,7,16–18,22], the mechanism of MTA over Zn/H-ZSM-5 is proposed, which contains three concurrent pathways. As illuminated in Scheme 1, pathway I primarily includes MTO, cyclization and HT reactions, which features low aromatics, $C_{2-4}^{=}/C_{2-4}^{o}$ and H_2. Actually, the MTO reaction is very complicated, which usually includes the first C–C bond formation, the HCP generation and the automatic catalytic process based on the HCP and the double-cycle mechanisms [18,24,25,28–30]. It should be noted that the cyclization products may be C_5 and C_6 cycloalkanes or cycloalkenes [2,16], and are only represented by cyclohexane here. Pathway I is predominant during the transformation of methanol, ethylene, or propylene over H-ZSM-5. Compared with pathway I, pathway II strengthens the dehydrogenation of cycloalkanes and weakens the HT reaction, which works in ethylene or propylene conversion over Zn/H-ZSM-5. Pathway III is a combination of methanol dehydrogenation to HCHO and coupling of methanol and HCHO to aro-

matics. The coupling process is mainly composed of some reactions such as prins, hydroacylation, aldol, which has been systematically explained in our recent work [22]. Besides, these reactions do not necessarily happen exactly in the order we proposed. For example, 1, 3-butadiene may also be synthesized by aldol condensation of acetaldehyde [31,32]. Moreover, the aromatics produced by these three pathways can also serve as hydrocarbon pools when they have not diffused out of the micropores of the zeolite.

4. Conclusions

In summary, methanol conversion can produce more aromatics than olefins (propylene or ethylene) conversion over Zn/H-ZSM-5, indicating the conventional MTA pathway including MTO and OTA is not complete. A considerable part of the aromatics is obtained through methanol dehydrogenation to HCHO and then methanol and HCHO coupling. Moreover, an MTA mechanism including the conventional MTA pathway and the coupling pathway is also systematically proposed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2020.05.063.

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