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Aromatization of ethylene – main intermediate for MDA?

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Abstract: Methane dehydroaromatization (MDA) over Mo/HZSM-5 has been hypothesized in literature to proceed via a two-step mechanism: methane is first converted to ethylene on the molybdenum (Mo) functionality and then ethylene is oligomerized, cyclized and dehydrogenated on the Brønsted acid sites (BAS) of the HZSM-5 support. This hypothesis is tested by studying the conversion of ethylene at the same conditions as used for MDA, namely 700 °C, atmospheric pressure, and by co-feeding experiments with H₂ and CH₄. Our results suggest that ethylene is not the main intermediate for MDA, because the aromatic selectivities obtained from methane conversion are higher than selectivities measured during ethylene conversion. Furthermore, carbonaceous deposits formed during MDA have a lower density, are more hydrogenated and more active than the ones formed during ethylene aromatization (EDA). Similarly as for MDA, an activation period in which Mo carburizes to its active phase and an induction period, in which aromatics formation rates increase to their maximum are observed for ethylene conversion. The induction period, which was explained by the buildup of a hydrocarbon pool (HCP) is much faster with methane than with ethylene. This period, is attributed to a slow buildup of hydrocarbons, strongly adsorbed on Mo sites, because it is only observed with catalysts containing Mo. Hydrogen co-feeding with ethylene leads to the formation of more reactive coke species and a significantly prolonged lifetime of the catalyst, but not to a faster buildup of the HCP.

Introduction

Aromatics, such as benzene, toluene and xylene (BTX) are in demand, because they enhance the octane number of fuels and are used as feedstock for the fine-chemicals industry, commodity goods, plastics and medicine. Alternative ways to obtain BTX are desired, because the current source for BTX, naphtha crackers, are revamped to gas crackers.^[1] This is the case especially in the United States due to the availability of cheap shale gas.^[2] There is also great interest in the direct conversion of methane to aromatics, because of the high availability of cheap methane.^[2] For the methane dehydroaromatization (MDA) over the

Mo/HZSM-5 catalyst, a two-step mechanism has been proposed. Methane first converts to C₂ hydrocarbons on the Mo site of the catalyst, which then get further dehydrogenated and aromatized on the Brønsted acid sites (BASs) of the zeolite support. Both ethylene and acetylene have been proposed as likely intermediates for this mechanism.^[3] Mériaudeau *et al.* investigated whether ethylene or acetylene is a more likely intermediate, comparing their reactivity at MDA conditions of 700 °C and atmospheric pressure with methane conversion.^[4] They found that acetylene led to higher benzene formation rates, likely due to its higher reactivity.

While methane cannot be activated directly on BASs, ethylene is easily activated on the BASs of the zeolite even at temperatures as low as 200 °C^[5], but aromatics are formed at higher temperatures.^[6] At these high temperatures, however, coking becomes significant leading to a fast drop-off in activity. This can be mitigated to some extent by introducing a metal like Ga to the zeolite. This not only decreases overall acidity because the metal cation replaces the acidic proton to anchor to the zeolite framework, it also enhances aromatics selectivity through dehydrogenation of paraffins, as observed for Ga, Ag and Mo.^[4b, 7]

Another studied phenomenon is the delay in the onset of aromatics production. For the MDA catalyst Mo/HZSM-5, it is well known that there is one delay associated with the carburization of Mo to its active phase called 'activation period' and a second delay due to the so-called 'induction period'.^[8] The induction period has recently been associated with the buildup of a hydrocarbon pool (HCP) analogous to what is observed for the methanol to olefins process (MTO).^[9] For the HCP, C₂ hydrocarbon species have also been speculated to serve as the intermediate, which react on the BAS to build up the HCP.

The present authors have recently found that the carburization of Mo is achieved also with a treatment in carbon monoxide, which creates a catalyst immediately active but without containing aromatic deposits that usually form during activation in methane.^[10] This allows for the clear separation of the activation, the induction period and the formation of deactivating coke species, which usually overlap in time.

In this study, we study ethylene as a possible intermediate by comparing the catalytic behavior and selectivities of ethylene aromatization (EDA) with the characteristics of MDA. Next to comparing MDA and EDA, in this study the effect of co-feeding methane and hydrogen and the role of Mo are investigated. The coke formed during ethylene conversion with different co-feeds and over different catalysts is characterized and compared with the coke formed during MDA.

We test whether Mo mainly acts in activating the C-H bond in methane or if it can also aide aromatization. We also investigate the proposed mechanism for the hydrocarbon pool (HCP) formation and the possible role of ethylene as

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a precursor for this process occurring during the induction period of the catalyst. Finally, the activation of Mo/HZSM-5 in ethylene, methane, in an ethylene/H₂ mixture and in CO are compared to separately study the activation and induction period and to prevent coke formation during the activation period.

1. Comparison of aromatics selectivity

The conversion of methane is around ~10 mol% at the applied conditions and would lead to an ethylene concentration of ~5 mol%. Therefore, EDA is performed feeding 5 mol% of ethylene diluted in N₂ to the bare zeolite (HZ) and compared to feeding 95 mol% methane in N₂ to Mo/HZSM-5, **MoHZ** (Figure 1). It was found that these conditions lead to similar rates of aromatics formation (Figure S1a). The selectivities observed in these two cases, however, develop differently with time on stream (TOS) (Figure 1). While benzene selectivity is similar in the beginning of the reaction, it drops much faster during ethylene feeding over HZ. In addition, the naphthalene selectivity is much lower for ethylene feeding. While benzene selectivity decreases, ethylene conversion stays high (Figure S1b) indicating a high coking rate for ethylene feeding over HZ (Figure S2). This leads to a full deactivation after about 300 min TOS, whereas the **MoHZ** catalyst under MDA conditions is still active. Coke selectivities, shown in Figure S2, increase up to 50 mol% for EDA, while they stay below 10 mol% for MDA. Thus, coke amounts formed are much higher during ethylene conversion on HZ as well, and the coke species formed are denser (Table S3).

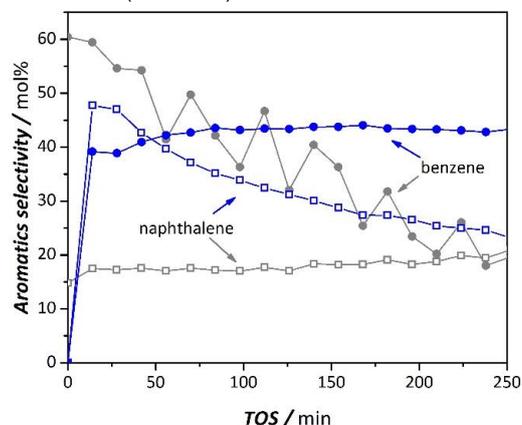


Figure 1. Comparison of selectivity to aromatics when feeding 15 ml/min 95 mol%CH₄/5 mol%N₂ to **MoHZ** (blue symbols) or feeding 5 mol%C₂H₄/95 mol%N₂ to HZ (grey symbols).

2. Characterization of carbonaceous deposits

The more reactive nature of carbonaceous deposited during MDA is demonstrated by thermogravimetric analysis (TGA) in Figure 2.

For EDA on the bare HZ, only one coke oxidation peak is observed at high temperature (~650 °C), which is associated with diffusion-limited combustion of coke deposited in the

micropores of the zeolite.^[11] When Mo is present on the catalyst, two peaks are observed in the DTGA for both MDA and EDA. The peak at lower temperature is associated with the Mo, while the high temperature peak is associated with coke in the micropores.^[11] Both types of coke oxidize at lower temperatures after MDA than after ethylene feeding over **MoHZ** as well as over HZ. In addition, the coking rate is higher during ethylene aromatization resulting in more coke deposits formed for the same contact time (Error! Reference source not found. 5), which also leads to higher pore filling as determined by N₂ adsorption measurements (Table S3).

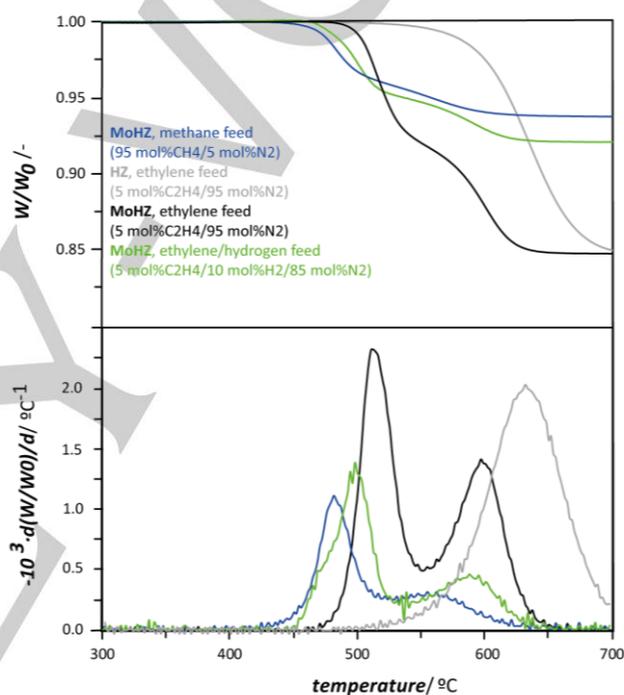


Figure 2. TGA (top) and DTGA (bottom) profiles after reaction, feeding 15 ml/min 95 mol%CH₄/5 mol%N₂ to **MoHZ**, 5 mol%C₂H₄/95 mol%N₂ to HZ and **MoHZ** and 5 mol%C₂H₄/10 mol%H₂/85 mol%N₂ to **MoHZ**. TGA was performed in air with a heating rate of 10 °C/min. Total catalyst weight (m_{cat}) was the same for all experiments, 500 mg. Coke amounts can be calculated by $(1-w/w_0) \cdot m_{cat}$.

Although virtually no differences are observed in the ¹³C NMR spectra taken on the spent catalysts (Figure S4), the density of the carbonaceous deposit formed from ethylene is higher than from methane, as determined by N₂ adsorption measurements (Table S3) in line with a lower reactivity. To analyze whether this is due to a lower H/C ratio in the feed for EDA, a co-feeding experiment with H₂ is performed with H₂ in an amount resembling that when 10 mol% methane is fully converted. The resulting coke has a lower density and oxidizes at a lower temperature.

During H₂ co-feeding, the profiles of aromatic yields look almost identical as during an experiment solely with ethylene feed up to 200 min on stream, but with co-feeding the benzene yield stays stable for the duration of the experiment and does not drop as in

EDA (**Figure 3**). In addition, the final coke amount deposited is lower, especially the more refractory coke (**Figure 2** and **Table S2**). The oxidation of the Mo-associated coke formed during the co-feeding experiment shifts to lower temperatures and thus becomes more similar to the species observed after MDA, while the coke species associated with BAS stay the same as during EDA (**Figure 2**). Thus, the higher H/C ratio of methane leads to the formation of less coke which is slightly more hydrogenated and reactive. Also the ratio of the reactive and refractory coke is higher.

In conclusion, the lower density and higher reactivity of carbonaceous deposits formed after MDA over **MoHZ** is mostly attributed to the formation of more hydrogenated coke species. Deactivation is faster with ethylene than with methane due to a higher selectivity to carbonaceous deposits, indicated as coke.

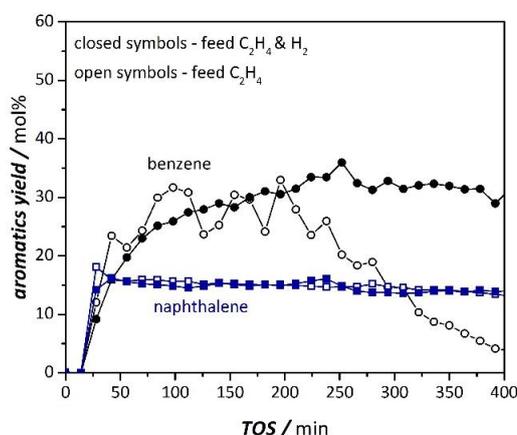


Figure 3. Yield to aromatics when feeding 15 ml/min 5 mol% C_2H_4 /95 mol% N_2 or 5 mol% C_2H_4 /10 mol% H_2 /85 mol% N_2 to **MoHZ** (closed symbols).

3. Thermodynamic considerations

Comparison of thermodynamic predictions with the experimental observations are used to determine whether the aromatization of the two reactions is under thermodynamic or under kinetic control. At the reaction conditions applied, naphthalene and benzene (predicted selectivities 54 mol% and 41 mol%) are the most stable products for MDA, while methane also becomes a preferred product for ethylene conversion (naphthalene: 56 mol%, methane: 33 mol%, benzene: 11 mol%). Thermodynamically, much lower benzene selectivity is predicted during ethylene conversion (**Figure S6**). However, in the initial phase of the reaction, benzene selectivity is much higher while naphthalene and methane selectivities (**Figure S6**) are much lower than what is predicted by thermodynamics. At the same time, experimentally observed selectivities are very close to thermodynamic predictions for MDA over **MoHZ**. It has to be noted that if coke was considered in the thermodynamic calculations it would be the sole predicted product. Due to the shape-selectivity of the zeolite and kinetics however the next most preferred products naphthalene and benzene are formed. It appears that benzene formation from ethylene is kinetically favored over formation of the bigger molecule naphthalene as

benzene selectivity exceeds thermodynamic predictions. In contrast, for MDA the product distribution resembles what is found by thermodynamic considerations.

4. The function of Mo in ethylene aromatization

The question arises whether aromatization can be achieved on Mo as it was observed earlier that the Mo functionality cannot be separated from the BAS of the bifunctional Mo/HZSM-5 catalyst. In addition, it was demonstrated that Mo supported on silicalite-1, which has the same topology as ZSM-5 but lacks the BAS, was able to produce aromatics during MDA.^[12] After introducing Mo to the zeolite, the acid site density and overall acidity is lowered as Mo cations replace some of the acidic protons of the zeolite. This is clear from Py-IR measurements (**Figure S9**), where the vibrations for pyridine adsorbed on BAS are less intense for **MoHZ** than for **HZ**. Further, the conversion of ethylene over a bare zeolite catalyst with a higher Si/Al ratio (**HZ-40**, Si/Al = 40) than **HZ** and thus lower acidity is compared with **MoHZ**. After introduction of Mo **HZ** has the same Brønsted acidity as **HZ-40** as is shown by Py-IR (**Figure S9**). Nevertheless, aromatic yields observed over **MoHZ** are much higher than over **HZ-40** (**Figure 4**). Since coke selectivities are lower over **MoHZ**, it is concluded that Mo does not only speed up the activation of ethylene but also plays an important role in the aromatization of ethylene likely during the dehydrogenation step.

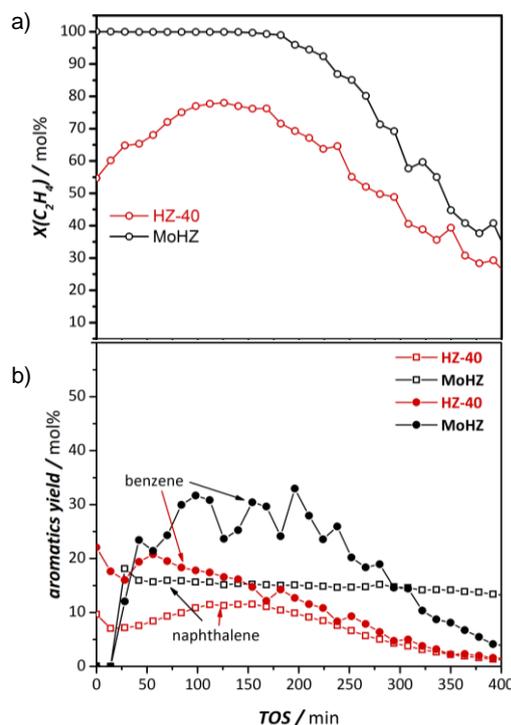


Figure 4. a) Ethylene conversion and b) yield to benzene and naphthalene with time on stream when feeding 15 ml/min of 5 mol% C_2H_4 /95 mol% N_2 to either **MoHZ** (black) or **HZ-40** (red).

5. Activation and induction period

Aromatics are instantaneously formed over **HZ** and **HZ-40**, while over **MoHZ** there is a delay in the formation. The delay in the onset of aromatics production and the slow increase in aromatics production to its maximum is only observed when Mo is present on the catalyst. A similar behavior was observed for methane aromatization^[8] and was coined 'activation period' for the delay and 'induction period' for the increase afterwards.^[9a] For MDA, it was found that Mo carburizes before being active to convert methane to aromatics. To test if Mo carbide is also the active phase in EDA, a CO pretreatment was applied to **MoHZ** prior to contact with ethylene (**Figure 5a**). This pretreatment effectively eliminated the delay in the onset of aromatics formation and the CO formation, due to Mo oxide reduction, during this period (**Figure S10**). The increase of aromatic yields to their maximum, however, remained. The two phases can thus be clearly assigned to the activation of Mo through carburization and the buildup of hydrocarbons inside the pores of the zeolite, respectively.^[9a]

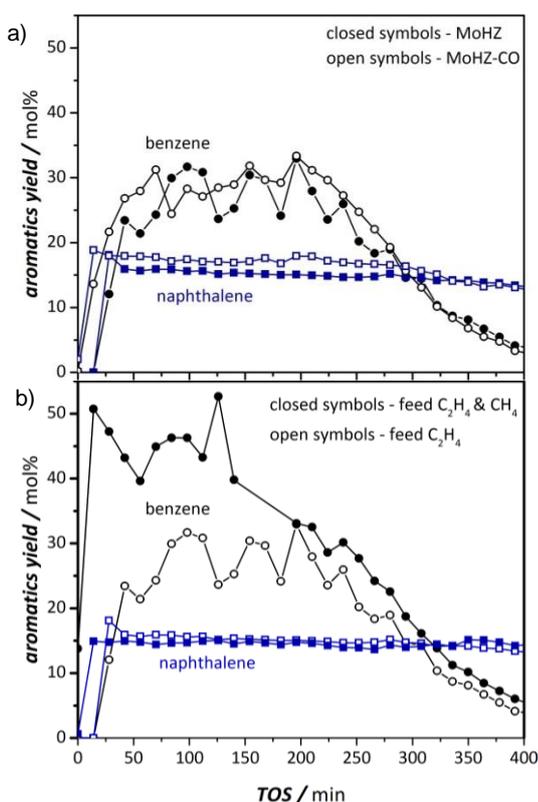


Figure 5. a) Yield to benzene and naphthalene when feeding 15 ml/min 5 mol% C₂H₄/95 mol% N₂ to **MoHZ** with (*open symbols*) and without a CO pretreatment (*closed symbols*). For the CO-treatment a 30 ml/min flow of 2.5 mol% CO/97.5 mol% He is passed over the catalyst while heating to 780 °C with 10 °C/min and keeping it at this temperature for 30 min before cooling to the reaction temperature of 700 °C. b) Yield to benzene and naphthalene when feeding 15 ml/min 5 mol% C₂H₄/95 mol% N₂ (*open symbols*) or 15 ml/min of 5 mol% C₂H₄/90 mol% CH₄/5 mol% N₂ (*closed symbols*) to **MoHZ**.

Both the activation and the induction period are much shorter during MDA. To investigate this further, a co-feeding experiment was performed where the inert N₂ was partially replaced by CH₄ (Error! Reference source not found. **5b**). Benzene forms after less than 14 min (14 min being the time resolution of the GC measurement) during MDA. CO is produced until benzene is observed (**Figure S11**), demonstrating the carburization of Mo oxide to Mo (oxy-)carbide. During EDA and co-feeding experiments, CO evolution is observed for almost 28 min, thus carburization takes at least twice as long with ethylene than with methane.

The faster activation period observed can be explained by the higher carburization activity of methane, leading to about 6 mol% initial methane conversion during this period in the co-feeding experiment (**Figure S12**). We discuss possible explanations for the shortened induction period. One could be that methane is just much faster to react than ethylene thus leading to the buildup of a critical level of hydrocarbon filling of the pores and thus a faster evolution of products from the pores. This option seems unlikely because of the low methane conversion (0-2 mol%, **Figure S12**) observed. An alternative explanation is that the aromatics formed from methane are more hydrogenated because of a higher H/C ratio in CH₄ than in C₂H₄ and thus more reactive than the ones forming from ethylene. This is however refuted by the fact that when co-feeding H₂ with ethylene in a mixture leading to the same H/C ratio as during MDA, the induction period remains the same as during pure EDA. Instead it could be that the aromatics formed initially strongly interact with Mo and are only freed once a certain pore filling and chain length is achieved. Methane could act to destabilize the strong interaction of the aromatics with Mo and effectively free them from the pores.

That these species strongly interact with the catalyst is demonstrated by a flushing experiment. The catalyst was flushed with He at the reaction temperature of 700 °C after feeding ethylene until the induction period was completed and the benzene yield fully developed, at 100 min on stream. The evolution of all products immediately stops once the flow is switched from ethylene to pure He (Error! Reference source not found. **6** and **Figure S13**). Only naphthalene continues evolving for another 100 min. This is expected, because the naphthalene yield is limited by a sublimation equilibrium in the downstream flow lines from the reactor to the GC which are kept at 150 °C. Higher line tracing temperatures were not used, to avoid ethylene reacting in the lines.^[5] The fact that the benzene yield immediately achieves the same level as prior to flushing and does not experience an induction period indicates that the HCP species are retained on the catalyst.

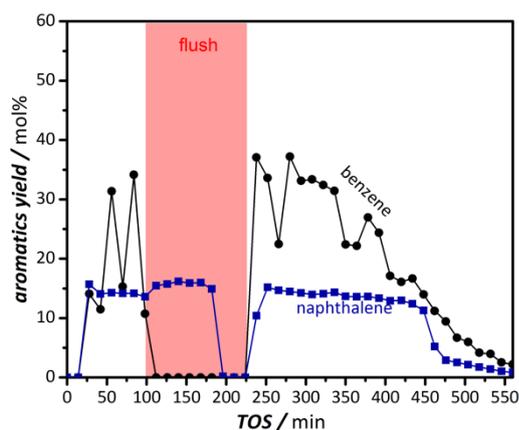


Figure 6. Observed yield to benzene and naphthalene when the reactor is flushed with a 15 ml/min He flow for 130 min after 100 min on stream feeding 15 ml/min 5 mol% C_2H_4 /95 mol% N_2 to **MoHZ**.

Since 100 mol% conversion of ethylene is achieved under the applied conditions it can be assumed that the concentration of ethylene throughout MDA at any given point is rather low, if ethylene were to be the main intermediate. Our experiments with 5 mol% of ethylene in the flow are however representative, because the two-step mechanism dictates that any product has to be formed from the intermediate ethylene. And thus the ethylene flow is chosen so that similar aromatics formation rates are achieved (Figure S1a).

The presented results cast doubt on the proposal of ethylene as the main intermediate of MDA. Firstly, because benzene and naphthalene selectivities are quite different when feeding ethylene or methane at levels encountered in MDA even when co-feeding H_2 . Secondly, thermodynamic limits are reached during MDA, while EDA seems to be commanded by kinetics. Thirdly, the carbonaceous deposits and the HCP species formed during EDA are much less reactive than the ones forming during MDA. This is evident from the longer induction period encountered with ethylene feeding and the higher oxidation temperature during TGA. This cannot solely be attributed to a higher H/C ratio in the feed for CH_4 , as co-feeding H_2/C_2H_4 does not shorten the induction period and the TGA profile of coke deposited during this experiment does not fully resemble the TGA profile measured on a catalyst after MDA.

The higher coking rate observed during EDA compared to MDA has implications for an industrial process aiming at aromatics. It has been proposed to split up MDA in two steps.^[13] In a first reactor methane would be coupled to produce ethylene, which would then be aromatized in a second reactor. However, as more and less reactive coke is formed during ethylene feeding, it is more recommended to form aromatics directly from methane in one step. When ethylene aromatization with a high selectivity to BTX is desired, co-feeding methane and or hydrogen should be beneficial enhancing aromatics selectivity and prolonging the lifetime of the catalyst.

Conclusions

The two-step mechanism as proposed earlier for MDA does not cover the full picture, ethylene likely not being the main intermediate of the reaction.

The hydrocarbon pool (HCP) forming during MDA is made up by less dense and more hydrogenated species than the ones forming from ethylene.

The carbonaceous deposits formed from methane are more reactive than the ones formed from ethylene. Co-feeding hydrogen with ethylene leads to reactive and hydrogenated coke species and prolongs the lifetime of the catalyst.

Mo has to be carburized first before being active for ethylene aromatization. This carburization can be achieved by CO, similarly to what has been observed for MDA. Furthermore, methane is a better carburizing agent than ethylene.

Experimental Section

Catalyst synthesis: Catalytic tests are performed on the H-form the commercial HZSM-5 zeolites with Si/Al = 24 (PQCorporation, CBV 5020E) denoted **HZ** and on another commercial catalyst with Si/Al = 40 (Zeolyst, CBV 8014) denoted **HZ-40**. Mo is introduced to **HZ** through IWI by dissolving appropriate amounts of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$, AHM) in a volume of water needed to fill the pores of the zeolite powder (400 μ l/g). The AHM solution is introduced to the zeolite dried at 120 $^{\circ}C$ for 10 h und mixing. The impregnated samples are dried overnight at 80 $^{\circ}C$ and calcined in static air at 550 $^{\circ}C$ for 5 h using a heating rate of 2 $^{\circ}C$ /min. Samples are prepared with a Mo/Al ratio of 0.6, which is equivalent to 3.4 wt% and are denoted as **MoHZ**.

Thermogravimetric analysis (TGA) is performed on a Mettler Toledo TGA/SDTA851e using 10 to 20 mg of sample under flowing 100 ml/min of air at a heating rate of 10 $^{\circ}C$ /min up to 800 $^{\circ}C$. The amount of coke formed during the reaction is calculated from the weight loss between 300 $^{\circ}C$ and 800 $^{\circ}C$ of the catalyst after 7 h of reaction.

Catalytic testing is performed in a quartz reactor tube with an inner diameter of 6 mm, using 500 mg catalyst pelletized and sieved to 212 to 355 μ m. A reaction temperature of 700 $^{\circ}C$ is applied in all tests and the reactor is brought to reaction temperature under a 15 ml/min flow of He with a heating rate of 10 $^{\circ}C$ /min. The flow is switched to the reaction mixture once the final temperature is reached and the first GC injection is done after the catalyst is already subjected to the reactant flow for 5 min. A weight hourly space velocity (WHSV) of 1.21 h^{-1} (based only on methane flow) is used when feeding methane corresponding to 15 ml/min STP flow of 95 mol% CH_4 /5 mol% N_2 . For experiments with ethylene as a reactant, a 15 ml/min flow of 5 mol% C_2H_4 /95 mol% N_2 is used, as this would be the flow of C_2H_4 corresponding to 10 mol% conversion of CH_4 entirely to ethylene. In addition, co-feeding experiments are performed with either methane or hydrogen where 15 ml/min flows of 5 mol% C_2H_4 /90 mol% CH_4 /5 mol% N_2 or 5 mol% C_2H_4 /10 mol% H_2 /85 mol% N_2 are used. For all experiments with ethylene and/or methane, N_2 serves as the internal standard.

Reactant conversion is calculated according to **Equation 1**, where $A_{i,in}$ ($i = C_2H_4, CH_4$ or N_2), the integrated peak area from the GC analysis is determined from three initial GC calibration injections, measured while sending the reaction mixture through the bypass. Product analysis is achieved on an Interscience Trace GC with one TCD and two FIDs.

Product yields are calculated according to **Equation 2**, where F_i [mol/h] denotes the molar flow of molecule n , x the number of carbons and y the number of hydrogens in a product molecule, while $\#C_{reactant}$ denotes the number of carbons in the reactant molecule. The integral selectivity to each gaseous product i over the whole time on stream (TOS) is obtained using **Equation 3**, where the number of the GC injection is denoted by j . Integral coke selectivity over the whole TOS calculated with **Equation 4**.

$$X_{reactant} = \frac{\left(\frac{A_{reactant,in}}{A_{N_2,in}}\right) - \left(\frac{A_{reactant,out}}{A_{N_2,out}}\right)}{\frac{A_{reactant,in}}{A_{N_2,in}}} * 100\%, \text{ reactant} = C_2H_4 \text{ or } CH_4$$

Equation 1

$$Y_i [\text{mol}\%] = \frac{F_{C_xH_y,out}}{F_{reactant,in} * \#C_{reactant}} * x * 100\%, \quad i = \text{product}, C_xH_y$$

Equation 2

$$\sum_{TOS} S_i [\text{mol}\%] = \frac{\sum_j Y_i}{\sum_j X_{reactant}} * 100\%, \quad j = \text{GC injection\#}$$

Equation 3

$$\sum_{TOS} S_{coke} [\text{mol}\%] = \sum_j X_{reactant} - \sum_i \sum_{TOS} S_i$$

Equation 4

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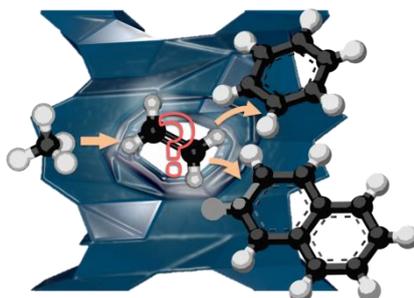
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Keywords: methane dehydroaromatization • ethylene aromatization • HZSM-5 • molybdenum • coking

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Does it all revolve around ethylene?
According to our study this is very unlikely. In contrast to what had been hypothesized, the formation of aromatics from methane does not proceed solely via the formation of ethylene in a first step. Likely other intermediates and aromatics can directly form on Mo, while intermediate alkenes get aromatized on Brønsted acid sites in the zeolite pores of the catalyst.



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Aromatization of ethylene – main intermediate for MDA