



Effect of Si/Al ratio of ZSM-5 support on structure and activity of Mo species in methane dehydroaromatization

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ABSTRACT

The effect of the Si/Al ratio of the ZSM-5 support on the structure and activity of Mo/HZSM-5 catalysts in methane dehydroaromatization (MDA) was studied. ZSM-5 (with Si/Al = 15, 25, and 40) supported Mo oxide catalysts (MoO_x/ZSM-5) with 3 and 10 wt% Mo loading were prepared by incipient wetness impregnation followed by calcination in air at 500 °C. The as-prepared catalysts were activated by temperature programmed reduction in hydrogen in order to maximize Mo dispersion. To understand the structure-activity relationship, the fresh and spent samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), N₂ adsorption isotherms, Scanning Transmission Electron Microscopy with Energy Dispersive X-Ray Spectroscopy (STEM-EDS), X-ray absorption spectroscopy (EXAFS and XANES), thermogravimetric analysis (TGA), and Raman spectroscopy. The results show that the Si/Al ratio does not influence the local structure around the Mo centers. It does however affect the number of available Brønsted acid sites in the support and the amount of Mo species entering the zeolite channels. A lower Si/Al ratio and higher Mo loading resulted in a higher Mo occupation within the zeolite channels. The higher channel occupation directly correlated with higher benzene selectivity and yield, as well as a lower catalyst deactivation rate.

1. Introduction

Methane dehydroaromatization (MDA) is a reaction that directly converts methane to benzene and hydrogen ($6\text{CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9\text{H}_2$). It poses an effective solution for efficient utilization of natural gas (NG), as more shale gas reserves are being discovered, making methane a more available resource. Methane is also obtained as an undesirable by-product or as a component of an off-gas from a range of petrochemical processes. Around 3.5% of the global NG production from these crude oil facilities, where NG is a byproduct, is flared due to a lack of small-scale technology capable of converting NG into useful products on-site [1]. This is a waste of a potentially valuable resource as well as an additional source of greenhouse gas emissions. Hence, conversion of methane into value added products via direct conversion methods such as MDA draws significant interest. A challenge with conversion of methane is its high stability, requiring high temperatures to activate the C–H bonds. Thermodynamic calculations have shown that the equilibrium conversion of methane in MDA is only around 14% at 700 °C [2]. Without the presence of an oxidant this high temperature also favors

coke formation which causes a rapid catalyst deactivation.

Different metals such as W [3–6], Re [7–9], Fe [10,11], and Cr [12] on a wide array of different supports such as HZSM-8, HZSM-11, HMCM-22, HMCM-41, HMCM-36, HMCM-49, NU-87, ITQ-2, ITQ-13, TNU-9, FSM-16, Al₂O₃, SiO₂, and sulfated hafnia have been tested for MDA [13–15]. HZSM-5 and HMCM-22 supported Mo catalysts have proven to be the best among those studied in terms of methane conversion and benzene selectivity. The most common agreement is that Mo/zeolites act as bifunctional catalysts for MDA, having two different active sites consisting of Mo species responsible for activating methane, and Brønsted acid sites responsible for oligomerization and aromatization [14,16–21]. Molybdenum oxide species supported on zeolites are converted into molybdenum carbide at the reaction temperature (typically 700 °C). The carbide formation occurs during an induction period when no aromatics are formed. It is thus deduced that it is the molybdenum carbide phase which is the active phase for the conversion of methane into C₂H_x and C₃H_x intermediates, which are subsequently oligomerized into benzene on the Brønsted acid sites (BAS) of the zeolite support. Comparing the performance of Mo

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catalysts using ZSM-5 with different Si/Al ratios Tessonier et al. [22] found that catalysts with lower Si/Al ratio present an overall better performance (higher benzene yield and stability). They proposed that the reason behind the better performance at lower Si/Al ratio is not the contribution of a higher number of BAS, but the higher dispersion of Mo species and formation of monomeric Mo oxide (MoO_2^{2+}) species at lower Si/Al ratio. They speculated that at higher Si/Al ratios the Mo oxide species anchor to the zeolite in the form of dimeric oxides ($(\text{Mo}_2\text{O}_5)^{2+}$) and thus the difference in catalyst activity could be due to a different nature of the active sites. Recently Zhao et al. [23] have drawn similar conclusions based on the Pyr-IR, XPS, H_2 -TPR, and UV-Raman spectroscopy characterization results of Mo/ZSM-5 catalysts with different Si/Al ratios ranging from 16 to 136. Other groups have concurred that BAS are not essential for MDA: Solymosy et al. [24] reported MDA on $\text{MoO}_3/\text{SiO}_2$ although with lower methane conversion and benzene selectivity, whereas, Guo et al. [25] obtained high benzene yield over Fe@SiO_2 at 1000 °C. None of these catalysts contained BAS which, according to a bifunctional mechanism, would be responsible for oligomerization of the intermediate C_2 molecules. Recently Kosinov et al. [26] and Agote-Aran et al. [17] reported that Mo/Silicate-1 shows some MDA activity. These groups suggest that the ability to form benzene is an intrinsic property of Mo carbide species when they are located within a confined space, however, as the benzene yield and catalyst stability were both very low in these studies compared to catalysts containing BAS, further experimentation would be required to determine the role of the BAS in the reaction mechanism.

According to the literature, a low Mo loading (typically 2–3 wt%) is required for high methane conversion and benzene selectivity. It has been shown that higher Mo loading reduces catalytic performance by mainly causing structural damage to the zeolite support by dealumination, and by pore blocking due to sintering. However, in our previous studies [27,28] we were able to overcome fast deactivation in catalysts with high Mo loading (10 wt%) by changing the activation conditions. A controlled activation of the catalyst under reducing conditions prevents structural damage of the zeolite, sintering of the Mo species, and allows higher dispersion of Mo at high Mo loading, resulting in higher selectivity to benzene. Most published work on the effect of Si/Al ratio targets catalysts that have been pretreated in He or CH_4 . In the work presented here we study the effect of Si/Al ratio (i.e. the acid site concentration) on the structure and activity of Mo/HZSM-5 catalysts prepared following the protocol of reduction in H_2 with a slow temperature ramp [27,28] prior to submitting the catalysts to MDA reaction conditions. Our goal was to investigate if the Si/Al ratio of HZSM-5 influences the dispersion and distribution of Mo species, their local structure around Mo centers (Mo coordination and cluster size), the nature of active sites and the MDA performance when the catalysts undergo a controlled reduction before MDA as a function of the Mo loading. For this, two groups of catalysts with low (3 wt%) and high (10 wt%) Mo loading were prepared using a HZSM-5 support with different Si/Al atomic ratios ranging from 15 to 40.

2. Results and discussion

2.1. Structural characterization of the as-prepared and reduced catalysts before reaction

2.1.1. X-ray diffraction (XRD)

XRD patterns of the parent HZSM-5 supports and of the fresh as-prepared catalysts with Si/Al ratio of 15, 25 and 40 are shown in Fig. 1. The characteristic peaks for the HZSM-5 support are present in all the catalysts, revealing that after impregnating with Mo and calcining at high temperature (5 h at 500 °C) the zeolite support retains its crystalline structure. The absence of discernable diffraction peaks due to MoO_3 in the catalysts for 3 wt% Mo loading suggests that Mo oxides are highly dispersed for all the Si/Al ratios at the low Mo loading. At 10 wt % Mo loading a peak at $2\theta = 27.3^\circ$, characteristic of the (0 2 1) plane of

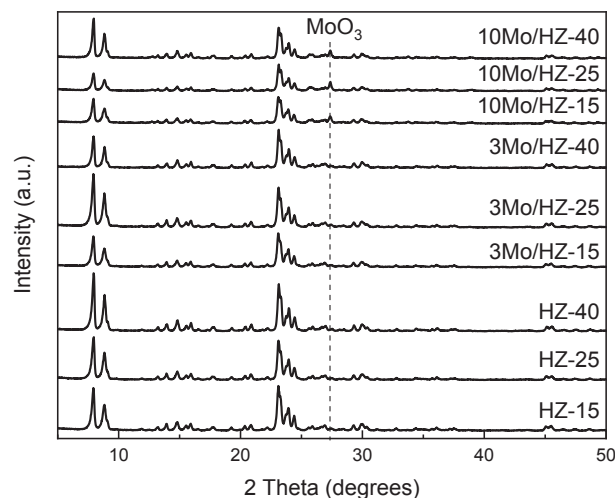


Fig. 1. X-ray diffraction patterns of fresh calcined catalysts. The position of the (0 2 1) peak of MoO_3 is indicated by the dashed line.

MoO_3 (JCPDS File No. 04-012-8070) appears for the catalysts regardless of the Si/Al ratio, suggesting presence of crystalline species which are larger than the diameter of the zeolite channel (~ 0.55 nm) and must therefore be located on the external surface of the zeolite. The size of these detected MoO_3 crystals are calculated using the Scherrer equation and are presented in Table S1. The crystal sizes range from ~ 15 to 39 nm and are clearly too large to fit inside the zeolite channels. No other phases, e.g. $\text{Al}_2(\text{MoO}_4)_3$, were detectable for any of the catalysts. Thus, we surmise that there is not a significant extraction of framework Al from the zeolite to form crystalline $\text{Al}_2(\text{MoO}_4)_3$ species during the catalyst synthesis. The XRD patterns of the reduced catalysts are shown in Fig. S1, where a peak corresponding to metallic Mo is observed for the 10 wt% Mo catalysts, indicating a reduction of the Mo oxide precursors before they are exposed to reaction conditions.

2.1.2. Textural properties

Textural properties of the reduced catalysts, obtained from N_2 adsorption isotherms, are summarized in Table 1 (Table S1, which includes the BET surface areas and micropore volumes obtained for the as-prepared catalysts, indicates that there are no significant variations in the textural properties of the catalysts after undergoing reduction in hydrogen). For each Si/Al ratio the surface area and micropore volume is higher for 3 wt% Mo loading compared to 10 wt% loading, suggesting that more Mo species occupy the space inside the channels at 10 wt% Mo. Since the three different bare zeolites present slightly different BET surface areas, the changes in surface area and micropore volume observed upon addition of Mo have been normalized for each zeolite by calculating the % drop in each of these properties before and after addition of Mo (Table 1). This allows us to compare the textural properties of the catalysts at fixed Mo loading and varying Si/Al ratios. The numbers show that the drop in micropore volume follows no clear trend with the change in Si/Al ratio when the Mo loading is low (3 wt %). At 10 wt% Mo loading, the drop in micropore volume is higher at Si/Al = 15 suggesting that the higher number of BAS which potentially serve as anchoring sites for Mo promote more available Mo species to enter the zeolite channels at higher loadings [17].

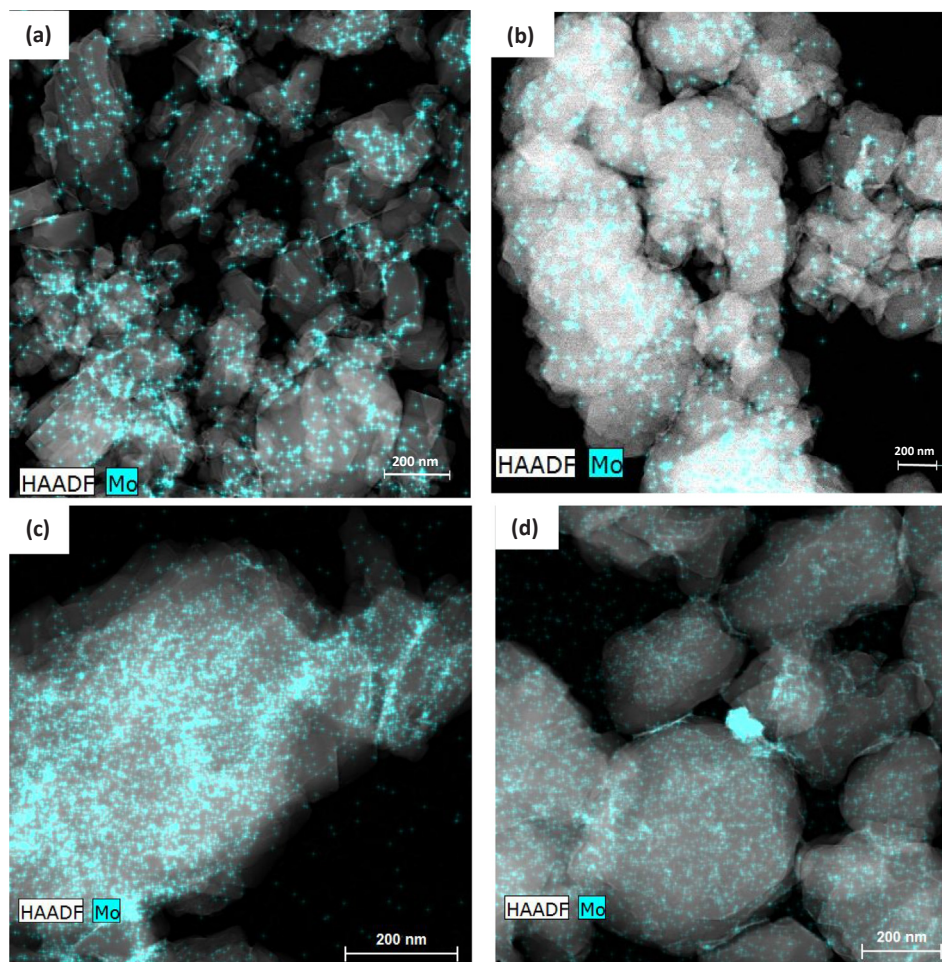
2.1.3. Scanning Transmission Electron Microscopy with energy dispersive X-ray spectroscopy (STEM-EDS) imaging with elemental mapping to probe dispersion of Mo species

To visualize the dispersion of Mo species in the active catalysts we performed *ex-situ* STEM-EDS analysis after treating the samples in H_2 flow. The STEM-EDS images of 3Mo/HZ-15, 3Mo/HZ-40, 10Mo/HZ-15, and 10Mo/HZ-40 and the corresponding elemental maps of Mo for

Table 1

Textural properties of blank HZSM-5 and reduced samples.

Sample	BET area (m ² /g)	Micropore volume (cm ³ /g)	% Decrease in BET area with respect to parent HZSM-5	% Decrease in micropore volume with respect to parent HZSM-5
HZ-15 (HZSM-5 with Si/Al = 15)	435	0.132		
HZ-25 (HZSM-5 with Si/Al = 25)	458	0.142		
HZ-40 (HZSM-5 with Si/Al = 40)	464	0.145		
3Mo/HZ-15	390	0.119	10	10
3Mo/HZ-25	416	0.129	9	9
3Mo/HZ-40	422	0.124	9	14
10Mo/HZ-15	345	0.098	21	26
10Mo/HZ-25	360	0.117	21	18
10Mo/HZ-40	386	0.119	17	18

**Fig. 2.** TEM-EDS of reduced samples: (a) 3Mo/HZ-15, (b) 3Mo/HZ-40, (c) 10Mo/HZ-15, (d) 10Mo/HZ-40.**Table 2**

Surface atomic concentrations determined from XPS.

Sample	Mo/(Si + Al) (XPS)	^a [Mo/(Si + Al)] × 10 ⁶ (bulk)
3Mo/HZ-15	0.018	3.47
3Mo/HZ-25	0.015	3.39
3Mo/HZ-40	0.034	3.34
10Mo/HZ-15	0.089	11.58
10Mo/HZ-25	0.090	11.29
10Mo/HZ-40	0.222	11.13

^a [Mo/(Si + Al)] × 10⁶ calculated from nominal Mo wt% and Si/Al ratios of HZSM-5

these samples are shown in Fig. 2. 10Mo/HZ-15 clearly presents a higher density of Mo compared to 3Mo/HZ-15, as would be expected due to its higher Mo loading. At higher Si/Al = 40, 10Mo/HZ shows more heterogeneity in the distribution of the species, with sporadically large Mo clusters (size approx. 50–70 nm) detected along the dispersed Mo species (Fig. 2 (d)). One would anticipate that due to lower number of anchoring sites for precursor Mo oxide species in 10Mo/HZ-40 compared to 10Mo/HZ-15, there would be higher chances of forming larger agglomerates of Mo particles on the zeolite external surface that would significantly reduce the accessibility to the active sites inside the channels. The Si/Al ratio does not appear to have any measurable influence on the Mo distribution at 3 wt% Mo, but at 10 wt% Mo, the high Si/Al ratio cannot stabilize a high dispersion and larger Mo agglomerates, which must be on the external surface of the zeolite, are observed.

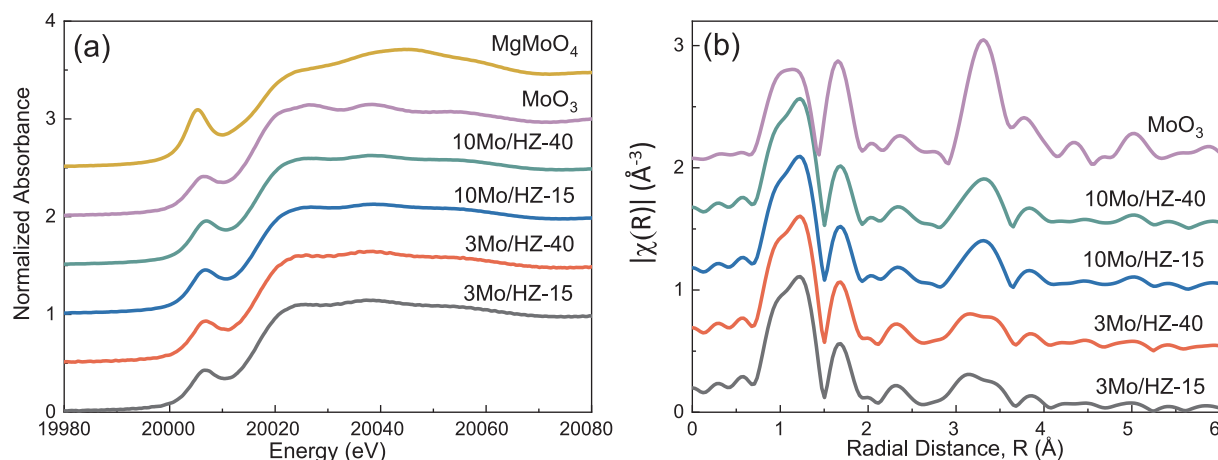


Fig. 3. (a) Mo K-edge XANES and the (b) k^2 -weighted magnitude of the Fourier Transform EXAFS spectra characterizing the as-prepared catalysts at room temperature in flowing helium. Spectra and transforms are stacked for ease of viewing.

2.1.4. X-ray photoelectron spectroscopy (XPS)

The Mo/(Si + Al) atomic ratios of the reduced catalysts were measured by XPS and are shown in Table 2 (the Mo 3d XPS spectra of the samples are represented in Fig. S2). The nominal bulk value of the Mo/(Si + Al) ratios calculated from Mo wt% and Si/Al ratios of HZSM-5 are also included in the table. All the reduced samples were taken out of the reactor and were exposed to air before the XPS measurements. Since XPS probes the outer few nm of the catalyst surface, comparing the Mo/(Si + Al) values gives an estimate of the relative amount of Mo that remains on the external surface of the zeolite versus the amount that migrates inside the channels. The XPS results in Table 2 show that while for the lower Si/Al ratios (15 and 25) the Mo/(Si + Al) does not vary significantly, at the higher Si/Al ratio of 40 the Mo/(Si + Al) is larger, suggesting that more Mo remains on the outer surface when there are a lower the number of BAS. The 10Mo/HZ-40 sample shows the highest ratio, which is in agreement with the TEM-EDS images showing large agglomerates of Mo external to the zeolite.

2.1.5. Local structure of Mo species in the as-prepared and reduced and carburized catalysts by X-ray absorption measurements

Figs. 3 and 4 show the Mo K-edge X-ray absorption near edge spectra (XANES) and magnitude of the Fourier Transform extended X-ray absorption fine structure (EXAFS) spectra of Mo/HZSM-5 catalysts with Si/Al = 15 and 40 in two different conditions respectively: the fresh as-prepared catalysts at room temperature, and the activated catalysts quenched after undergoing reduction and followed by

exposure to methane flow for two hours at 700 °C.

The XANES of the as-prepared catalysts is similar at a fixed Mo loading but the XANES of the 3 and 10 wt% Mo catalysts are different from each other (Fig. 3 (a)). This indicates that major factor determining in the local structure of the Mo is the loading rather than the Si/Al ratio of ZSM-5. The Mo K-edge XANES of all the catalyst samples display a pre-edge peak at around 20006.6 eV visible on the rising edge of the main $1s \rightarrow 5p$ transition. This peak is assigned to the dipole-forbidden $1s \rightarrow 4d$ electronic transition providing information regarding the average local structure and geometry of the Mo species that are present [29–34]. If the intensity of this peak is compared to that of MgMoO_4 (tetrahedral environment around Mo) with that of MoO_3 (distorted octahedral environment around the Mo) in Fig. 3 (a), then it can be seen that the intensity (and peak position) aligns better with that of MoO_3 than MgMoO_4 , indicating that the local structure of the Mo is octahedral, not tetrahedral, in all of the catalysts. When comparing the magnitude of the Fourier-transform of the EXAFS data for each catalyst to that of MoO_3 (Fig. 3 (b)), then those of the 10 wt% Mo catalysts closely resemble that of MoO_3 compared to the 3 wt% Mo samples. The presence of the peak in the Fourier transform in the 3–4 Å range corresponds to the Mo–O–Mo scattering, indicating that there is longer range scattering present in the 10% sample compared to the 3%, indicating the presence of small agglomerates of MoO_3 species. This is in agreement with the XRD results.

The Mo K-edge XANES of the quenched catalysts (Fig. 4 (a)) are drastically different to those of the as-prepared catalysts. All of the

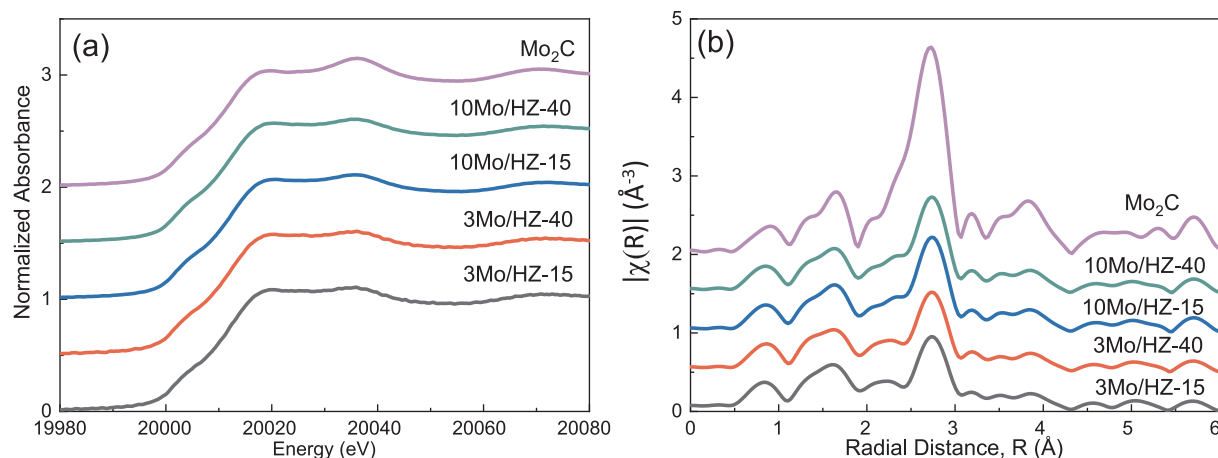


Fig. 4. (a) Mo K-edge XANES and (b) k^2 -weighted magnitude of the Fourier Transform EXAFS spectra of reduced and carburized catalysts ((2 h of methane flow on reduced samples at 700 °C)) at room temperature.

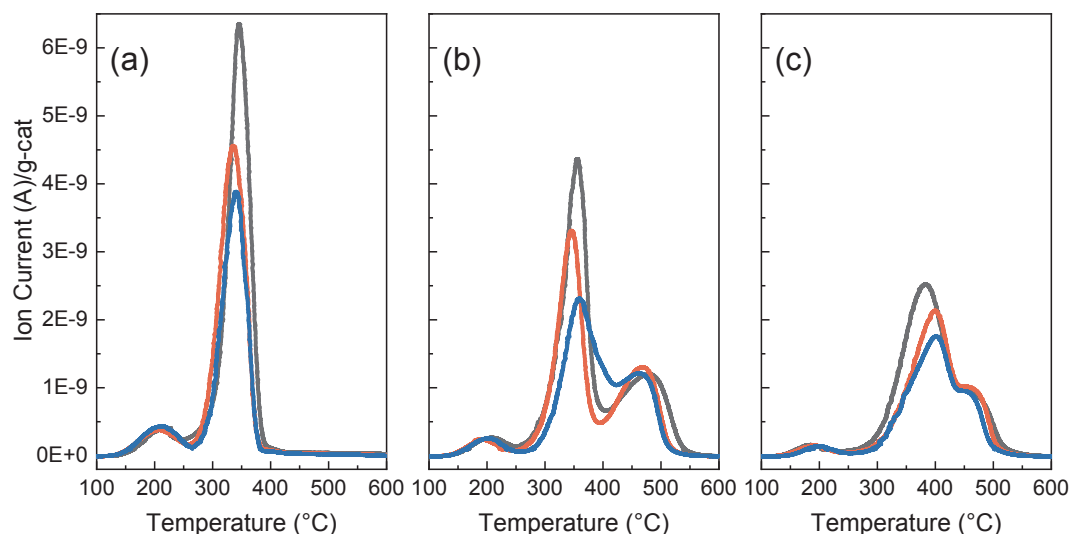


Fig. 5. Mass spectrometer signals for propylene ($m/z = 41$) recorded during IPA TPD of (a) blank zeolites, (b) reduced 3Mo/HZSM-5, and (c) reduced 10Mo/HZSM-5. Black lines: Si/Al = 15, red lines: Si/Al = 25, blue lines Si/Al = 40. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spectra characterizing the 3 and 10 wt% Mo catalysts now resemble that of Mo_2C , indicating that the Mo is fully carbided. The Mo EXAFS data of the activated samples, shown in Fig. 4 (b), further support the conclusion that the Mo is present as a Mo_2C phase in all of the spent catalysts. There are no features that differentiate the magnitude of the Fourier transform of the EXAFS for the Si/Al = 15 samples from those of the Si/Al = 40 catalysts, implying that the Si/Al ratio is not a major factor in determining the local structure of the Mo.

2.1.6. Measurement of the acidity of the catalysts by isopropylamine temperature programmed desorption (IPA-TPD)

The amount of Brønsted acid sites in the blank zeolites and in the reduced Mo catalysts were determined by temperature-programmed desorption of isopropylamine (IPA-TPD) method. IPA reacts with the Brønsted sites (Si-OH-Al) in a very narrow temperature range in TPD via a reaction similar to Hoffman elimination reaction and produces propylene and ammonia [35]. Fig. 5 shows the propylene signals for all the samples recorded during TPD, while the IPA and ammonia signals are shown in Figs. S2 and S3. As observed from Fig. 5 (a), the blank zeolites have two propylene peaks centered at ~ 200 °C and ~ 350 °C. The peaks centered at 350 °C are assigned to propylene produced from the reaction between adsorbed IPA and BAS [35–38], whereas, the peaks centered at 200 °C are assigned to propylene obtained from weakly adsorbed IPA on silanol groups [39]. Fig. 5 (b) and (c) show that the reduced and the as-prepared catalysts present additional peaks centered at ~ 450 °C. Previous studies have shown that this additional peak also appears in the IPA-TPD profiles of Ga/zeolite samples [40–42] suggesting the formation of new acid sites (Metal-OH) that can only decompose IPA at high temperatures (> 450 °C). The relative amount of BAS between the samples were determined from the areas of the peaks centered at ~ 350 °C after peak deconvolution and are shown in Table 3. The results indicate that the number of BAS sites

decreases with increasing Si/Al ratio and also with increasing Mo loading. It is important to note that there are free BAS in all the samples, even in the sample with the highest Si/Al ratio and the highest Mo loading (10Mo/HZ-40).

2.2. Catalytic results

Methane conversion and benzene yield for 3Mo/HZSM-5 and 10Mo/HZSM-5 catalysts with different Si/Al ratios are represented with time on stream (TOS) in Fig. 6. As observed from Fig. 6 (a) and (b) all the catalysts exhibit high initial methane conversion, but there is a sharp decline in conversion during the first hour of reaction. The high initial conversion is due to reaction of methane with completely and partially reduced Mo species to form Mo carbide/oxy-carbide during the reaction induction period [26,28,32,33,43].

The data show that for each Mo loading, the methane conversion and benzene yield (Fig. 6c–d) show a similar trend and are higher for the catalysts presenting higher number of BAS, i.e. decreasing Si/Al ratio. This is in agreement with previous work [44–46] and has been explained based on the fact that zeolites with lower Si/Al ratio provide a higher number of strong anchoring sites inside the channels, thus promoting more anchoring of Mo oxides within the zeolite channels, which are the species that act as precursors for the active sites for aromatization. Our structural characterization data are in agreement with the catalytic behavior since the XPS data indicate that there is a higher degree of displacement of Mo from the external zeolite surface into the channels at the lower Si/Al ratios (15 and 25). The IPA-TPD data (see Fig. 5) indicate that upon addition of Mo, the intensity of the low temperature peak, corresponding to the BAS, drops, corroborating that Mo interacts with these acid sites.

Fig. 7 shows the selectivity of the main reaction products (selectivity to other minor products are shown in Fig. S5). Analysis of the product distribution in Fig. 7 indicates that at a fixed Mo loading, whether 3 wt% or 10 wt% Mo, the selectivity to benzene increases as Si/Al ratio decreases, while the selectivity to ethylene and coke follow the opposite trend. This is in alignment with the idea that the Mo species within the channels are responsible for converting CH_4 to benzene, and the greater their number, the higher the benzene yield. The Mo species that are not inside the channels, but rather on the external surface of the zeolite, can still activate CH_4 , however they lead to decomposition and formation of coke due to the lack of shape/size selectivity at that location. With respect to ethylene, the most

Table 3
IPA TPD Results for blank Zeolites and reduced samples.

Mo content (wt%)	BAS relative to HZSM-5		
	Si/Al = 15	Si/Al = 25	Si/Al = 40
0	100	82	65
3	85	61	56
10	75	56	48

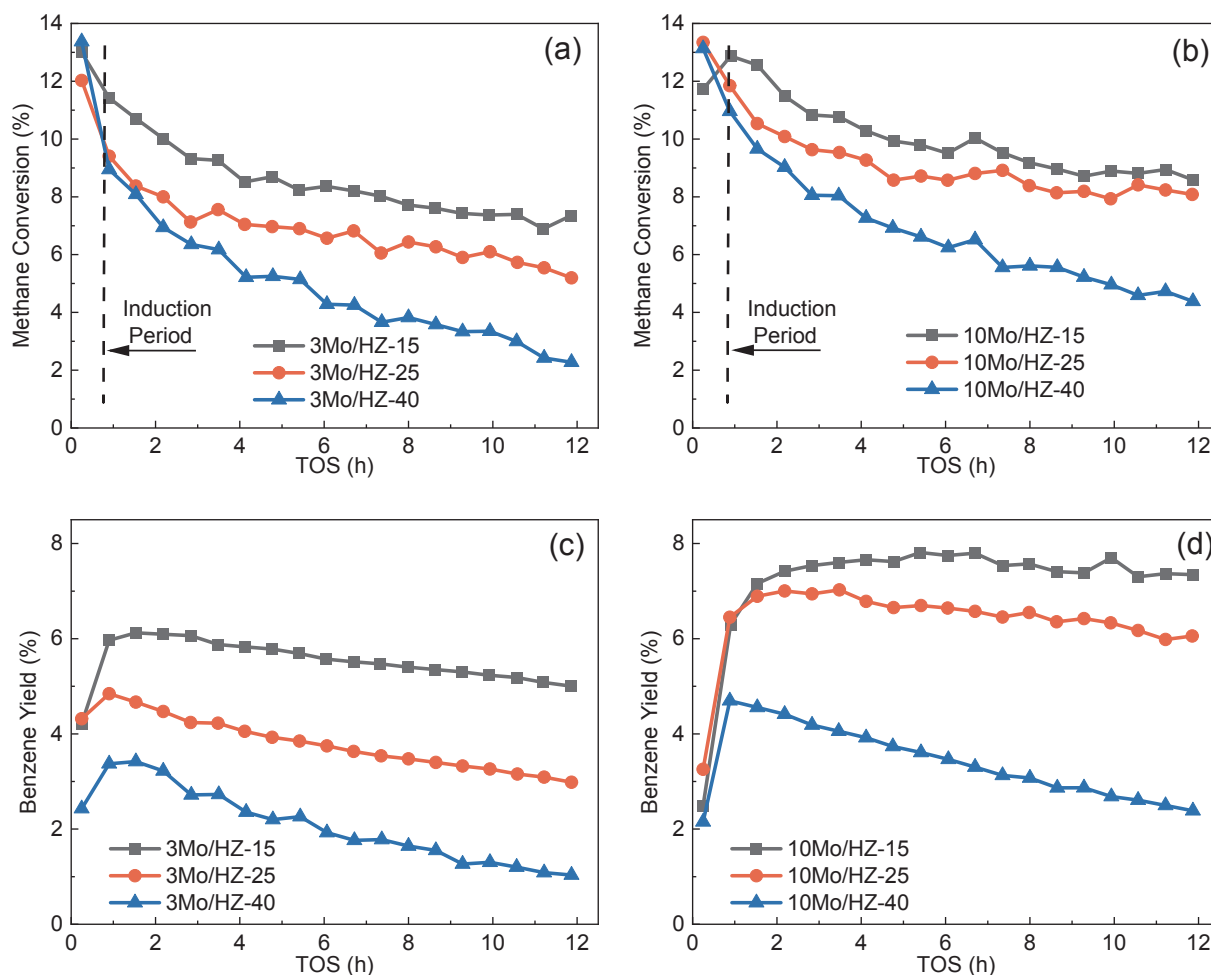


Fig. 6. Methane conversion against TOS for (a) 3Mo and (b) 10 Mo catalysts using ZSM-5 with different Si/Al ratios; benzene yield against TOS for (c) 3Mo and (d) 10 Mo catalysts using ZSM-5 with different Si/Al ratios. (Reactions were performed with 500 mg of as-prepared catalysts, with space velocity of 1550 ml/h.gcat in 9% N_2/CH_4 at 700 °C.)

commonly accepted reaction pathway implies that ethylene is formed on the Mo carbide sites and that it is oligomerized on the BAS to form benzene. Based on this mechanism, a low availability of BAS (high Si/Al ratio) would result in the formation of more ethylene and less benzene. The catalytic results obtained here corroborate this reaction mechanism. Su et al. [47] and Tessonier et al. [22] showed that there is no correlation between the number of BAS and the benzene yield, and that a small number of BAS are sufficient to perform the oligomerization step. However, recently there have been several groups that claim that the Mo/zeolite catalysts are monofunctional since they found that benzene formation is observed on a Silicate-1 supported Mo catalyst (the siliceous version of ZSM-5 with no Al in the framework, Si/Al = ∞ , i.e. no BAS are present) [17,26], and proposed that BAS are not required at all for MDA. This claim, while possible, requires further experimental confirmation, especially since it is known that HZSM-5 zeolite support itself is capable of oligomerizing ethylene to form benzene, in other words, the BAS are active in ethylene oligomerization. We assert that while Mo carbide may have the intrinsic property to aromatize CH_4 to form benzene, the presence of BAS can contribute to the enhancement of benzene yield.

When comparing the catalysts with different loadings, we find that the 10 wt% Mo catalysts present higher CH_4 conversion and benzene selectivity and yield compared to the lower loading 3 wt% Mo catalysts at each Si/Al ratio. The higher benzene selectivity can be explained based on the fact that at higher Mo loading there is a larger population of active Mo species inside the zeolite channels. This is corroborated by

the structural characterization results that show a higher drop in micropore volume and a bigger drop in the number of BAS at 10 wt% loading compared to 3 wt% loading.

One of the main differences observed in the catalytic behavior at different Si/Al ratios is the rate of deactivation. To quantify the deactivation, the first order deactivation constants, k_d , for all the catalysts were calculated from the slopes of the semilogarithmic plots of the rate of formation of benzene as a function of TOS (shown in Fig. 8) from the moment that the rate of formation of benzene begins to drop. The k_d values are summarized in Table 4. For each fixed loading, the deactivation rate constant increases with Si/Al ratio, showing that higher zeolite acidity enhances catalytic stability. Moreover, the deactivation rates are overall lower for the catalysts with higher Mo loading.

2.3. Characterization of the spent catalysts

To find possible causes for catalyst deactivation, we analyzed the role that the catalyst structure plays on the catalytic stability, by determining the BET surface areas, quantifying the coke produced (by thermogravimetric analysis (TGA)), and analyzing the nature of the coke deposits (by differential thermogravimetric analysis (DTGA) and Raman spectroscopy) in the spent catalysts.

2.3.1. BET surface areas

Table 5 shows the BET surface areas of the spent catalysts and the % drop in surface area between fresh and spent catalysts. There is a clear

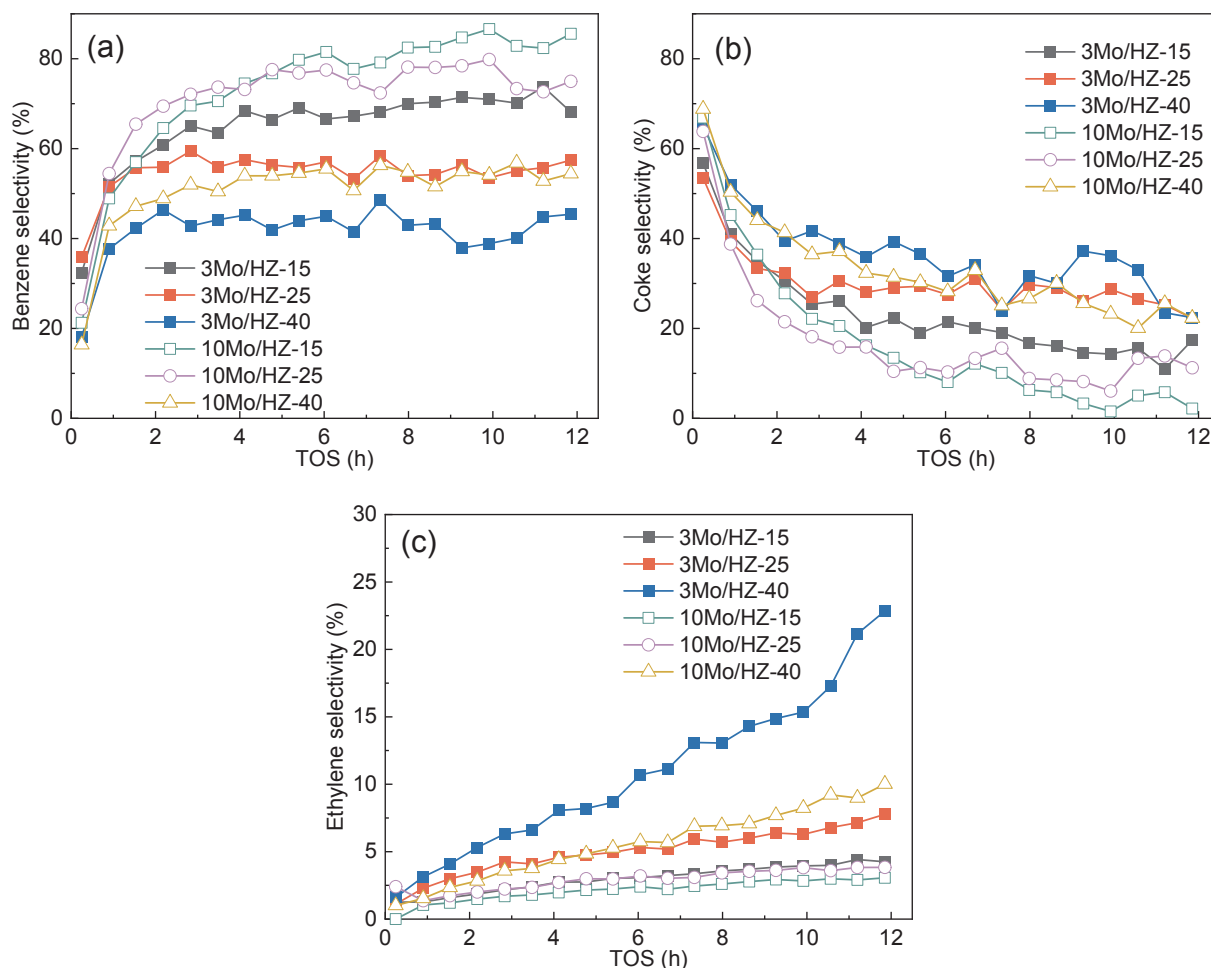


Fig. 7. Selectivity to (a) benzene, (b) coke, and (c) ethylene against TOS for all the catalysts. (Reactions were performed with 500 mg of as-prepared catalysts, with space velocity of 1550 ml/h-gcat in 9% N_2/CH_4 at 700 °C.)

trend in the % drop in surface area and the catalyst stability, with the most stable catalysts showing smaller drops in surface area, and consequently lower channel blocking, and thus higher accessibility of the active sites within the channels to the CH_4 reactant. It is known that Mo is capable of extracting Al from the zeolite framework, resulting in formation of $Al_2(MoO_4)_3$ species that are inactive in MDA [48] and can cause a collapse of the zeolite framework with consequent drop in

surface area. In our previous work we found that $Al_2(MoO_4)_3$ is formed at high Mo loadings (> 6 Mo wt%) [27] and that when the catalyst precursors are pretreated in H_2 , the fraction of aluminum molybdate formed decreases. We also observed that under these conditions no structural collapse occurred. ^{27}Al MAS-NMR measurements of the 10 wt % Mo catalysts in the current work (see Fig. S6) indicate that extraction of framework Al is not playing a major role in the catalytic performance

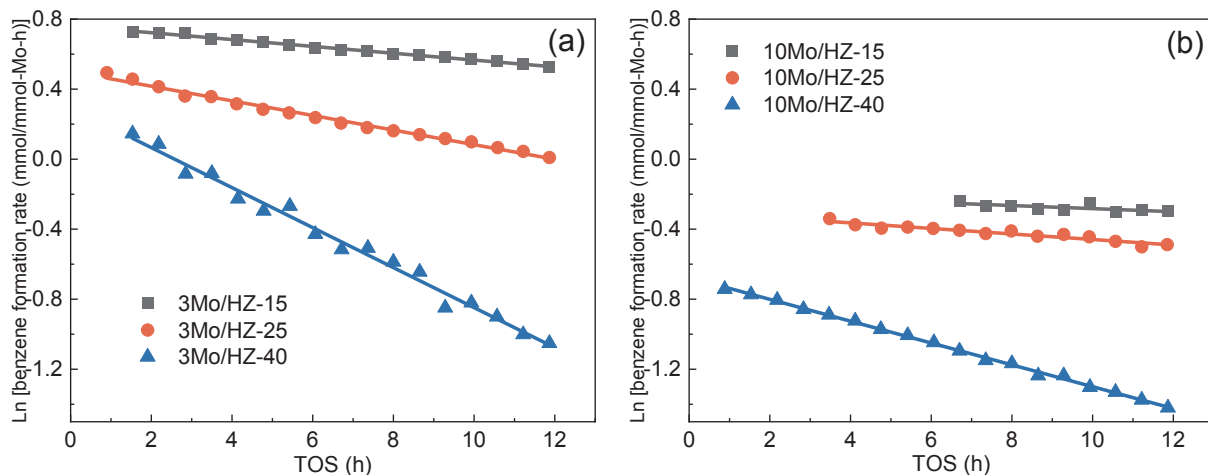


Fig. 8. Semilogarithmic plots for the rate of formation of benzene with TOS for (a) 3Mo catalysts and (b) 10Mo catalysts. (Reactions were performed with 500 mg of as-prepared catalysts, with space velocity of 1550 ml/h-gcat in 9% N_2/CH_4 at 700 °C.)

Table 4
First order deactivation rate constant, k_D .

Sample	k_D (h^{-1})
3Mo/HZ-15	0.02
3Mo/HZ-25	0.04
3Mo/HZ-40	0.11
10Mo/HZ-15	0.01
10Mo/HZ-25	0.02
10Mo/HZ-40	0.06

of the high loading Mo catalysts.

2.3.2. TGA

To investigate whether the formation of carbon deposits was responsible for the drop in surface area, TGA of the spent samples was performed.

The TGA profiles of the spent catalysts are shown in Fig. 9 and the corresponding amount of carbon deposits calculated from these profiles are presented in Table 6. The weight loss in the TGA profiles from room temperature to 200 °C is due to the desorption of adsorbed moisture by the samples, and the slight weight increase until 450 °C is due to the reaction between Mo carbide and air that results in the formation of Mo oxide, which has a higher molecular weight compared to the Mo carbide [27,49,50]. The final weight loss that starts around 450 °C is attributed to the burning-off of the coke which is deposited during reaction. The amount of coke measured in the spent catalysts for a fixed Mo loading increases as the acidity decreases (or Si/Al ratio increases), which is in line with the higher coke selectivity (Fig. 7) and lower catalyst stability obtained at higher Si/Al values (Table 4). This result is similar to the findings of Zhao et al. within the same Si/Al range [23]. For a fixed Si/Al ratio, the amount of coke deposited decreases at higher Mo loading, also in line with the lower coke selectivity and higher catalyst stability observed with our activity data.

The TGA results suggest that there is a direct correlation between the catalysts' deactivation and the amount of coke deposited in reaction. Considering that the Mo sites responsible for aromatization are within the channels, and knowing that the catalysts with high Si/Al values present fewer Mo species within the channels, this offers an explanation of why the selectivity to coke is higher in the samples with a lower BAS population; the higher the amount of non-confined Mo species they possess, the greater the conversion of CH₄ to ethylene and further polymerization to coke [22].

To analyze the nature of the coke formed in reaction we represented the derivatives of the TGA curves (DTGA) as shown in Fig. 10. Two peaks are observed in all the DTGA profiles – a low temperature peak (LTP) and a high temperature peak (HTP). In the literature, the LTPs have been assigned to carbon that is in close proximity to Mo species, while the HTPs have been assigned to polyaromatic carbon, formed as a result of condensation of aromatic molecules on the BAS [17,20,26,27,50]. These two different types of coke have also been referred to as “soft coke” (LTP) and “hard coke” (HTP). The LTP and HTP are at ~470 and ~580 °C, respectively, for 3 wt% Mo loading, while at 10 wt% Mo, the LTPs are shifted to a slightly lower

temperature, at ~450 °C and the HTPs consist of broader peaks covering a range from ~500–550 °C.

The shift to lower temperature of the LTPs for the 10 wt% Mo catalysts can be explained as a result of the higher content of Mo species on the external surface (as shown by the presence of large MoO₃ crystals in the XRD patterns, as well as the higher Mo/(Si + Al) ratios measured by XPS) at higher Mo loading, which can lead to the formation of more carbon deposits on the external surface of the zeolite that are easier to burn off than carbon associated to Mo species located within the channels. In the case of the HTPs, at a fixed Mo loading their contribution increases with increasing Si/Al ratio, which seems to contradict this peak's assignment to carbon associated to BAS [17,20,26,27,50]. Our IPA-TPD results indicate that the number of residual ZSM-5 BAS after Mo incorporation decreases with increasing Si/Al ratio in both 3 and 10 wt% Mo samples. The trend observed with the HTPs in our samples is in line with observations from the Beale group [17] that reported that even when the support consisted of silicalite (i.e. absence of BAS), a HTP was detected in the DTGA profiles. They concluded that the LTP was due to carbon in close proximity to Mo species, as it has been reported previously that Mo is capable of catalyzing combustion of carbon [17,51–53] and therefore the LTP is formed due to burning of any carbon species that are in proximity to the Mo species. In line with this interpretation, we observe that in our samples, as the Si/Al ratio increases, the Mo aggregates present in the external surface are larger, which we have also observed through our XPS data for both 3 and 10 wt% Mo samples and TEM-EDS imaging for 10 wt% Mo samples. The larger aggregates result in less contact between Mo species and the deposited carbon, thus the contribution of the HTP increases with Si/Al ratio. This can also explain why the relative contribution of the HTP is higher for the 3 wt% Mo samples, as smaller quantities of Mo will result in less contact between Mo and the carbon that is formed. When contrasting the trends observed with the DTGA profiles with the deactivation rate constants (Table 4), it is clear that there is a correlation between the degree of contribution of the HTP and the stability, indicating that the “hard coke” contributes mostly to the catalyst deactivation and that more of it is formed when fewer acid sites are present.

2.3.3. Raman spectroscopy

The nature of the carbon deposits on the spent samples was investigated further by Raman spectroscopy of the spent samples. As observed in the Raman spectra in Fig. 11, two Raman bands are detected in all spent samples: the band appearing at ~1600 cm⁻¹ is denoted as G (graphitic) band [17,54] and is assigned to in-plane bond stretching vibration of pairs of sp² hybridized carbon atoms that represents ideal graphitic lattice vibration. The band around 1360 cm⁻¹ is denoted as D1 (disordered) and is assigned to in-plane breathing vibration of sp² bonded carbon [17,54]. This band is thought to arise from disorder in the graphite structure. To quantify the degree of order in the deposited carbon, the ratio of intensities of D1 and G bands (I(D1)/I(G)) [17,55,56] were calculated for each sample and are presented in Table 7. For the 3 wt% samples, no significant differences are observed between the degree of disorder and the Si/Al ratios of 15 and 25, however, at Si/Al = 40, the degree of disorder increases. A similar

Table 5
Textural properties of spent samples.

Sample	BET area (m ² /g)	Micropore volume (cm ³ /g)	% Decrease in BET area with respect to reduced sample	% Decrease in micropore volume with respect to reduced sample
3Mo/HZ-15	325	0.092	17	23
3Mo/HZ-25	275	0.079	34	38
3Mo/HZ-40	225	0.067	47	46
10Mo/HZ-15	278	0.083	19	15
10Mo/HZ-25	285	0.088	21	25
10Mo/HZ-40	230	0.068	40	43

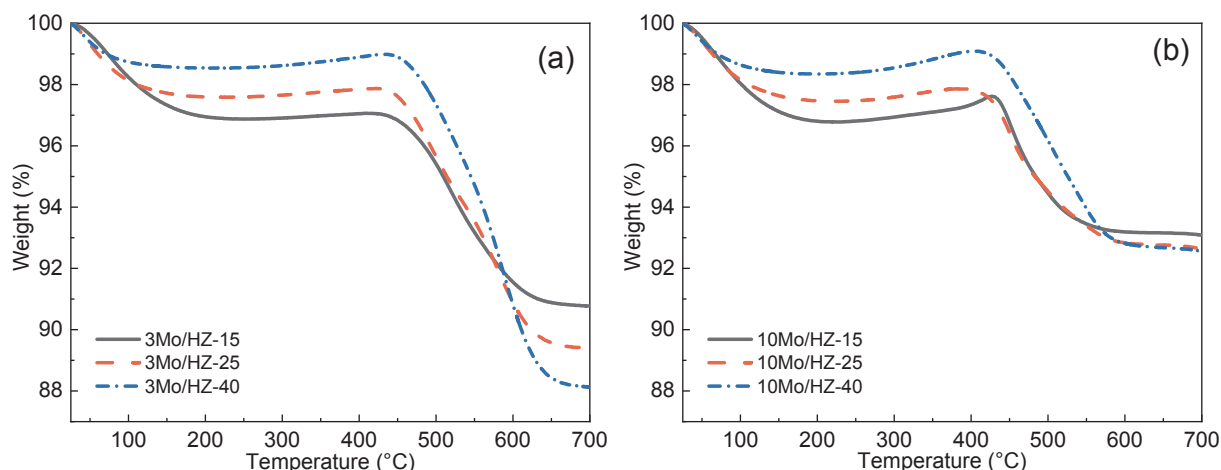


Fig. 9. TGA profiles of spent (a) 3 wt% Mo and (b) 10 wt% Mo catalysts.

Table 6

Carbon burn off data calculated from TGA profiles of spent catalysts.

Mo content (wt%)	Deposited carbon (mg/g-cat)		
	Si/Al = 15	Si/Al = 25	Si/Al = 40
3	69	95	124
10	49	56	71

effect is observed for the 10 wt% Mo catalysts although at the higher Mo loading the differences are much smaller. The effect of Mo loading at a fixed Si/Al is clearer: I(D1)/I(G) is significantly higher in catalysts with 10 wt% Mo loading compared to catalysts with 3 wt% Mo loading. Hence, the structural disorder in the carbon deposits is higher at high Si/Al ratio and high Mo loading, coinciding with the trends observed by Zhao et al. [23] when studying zeolites with Si/Al ratios within the same range, and by the Beale group [17], where they found that the carbon in spent catalysts is more amorphous for a Mo/silicalite catalyst with no BAS, compared to Mo/ZSM-5. Considering that for the catalysts with higher Si/Al ratio and/or higher Mo loading more Mo species remain on the external surface of zeolite, it is possible that the carbon associated to these external Mo species possesses more defects and is responsible for the higher contribution of the D1 bands.

3. Conclusions

The activation conditions employed with Mo/HZSM-5 catalysts can

affect their performance in methane dehydroaromatization, and in our past work we demonstrated that a slow, temperature controlled reduction in H_2 of the as-prepared zeolite-supported Mo oxide precursors can lead to more stable catalysts with higher dispersion of the active Mo carbide species. Here, the effect of the Si/Al ratio of the ZSM-5 support was studied for Mo/HZSM-5 catalysts with low (3 wt%) and high (10 wt%) Mo content when undergoing the controlled reduction pretreatment. It was found that both the Si/Al ratio and the Mo loading affect the amount of Mo species entering the zeolite channels. A lower Si/Al ratio and higher Mo loading resulted in a higher Mo occupation within the zeolite channels. The higher channel occupation directly correlated with higher benzene selectivity and yield, as well as a lower catalyst deactivation rate. While temperature controlled H_2 pretreatment can improve the dispersion of the Mo species in the catalysts, even after 12 h of reaction, the Si/Al ratio has a stronger effect on catalyst stability and low Si/Al ratios are required to maintain benzene yield over longer periods of time. X-Ray absorption measurements of the supported Mo oxide precursors and of the catalysts after reduction in H_2 and exposure to CH_4 at reaction temperature showed that the Si/Al ratio does not affect the local structure around the Mo centers at least in the range that we studied. The deactivation of the catalysts over time was due to coke deposition and seems to be directly related to the formation of amorphous carbon deposits.

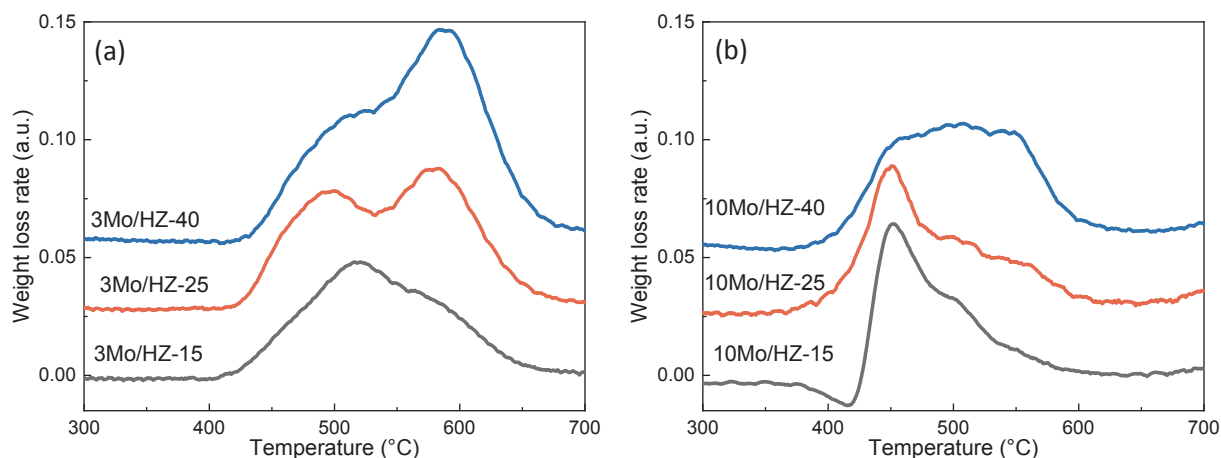


Fig. 10. DTGA profiles of spent (a) 3 wt% Mo and (b) 10 wt% Mo catalysts.

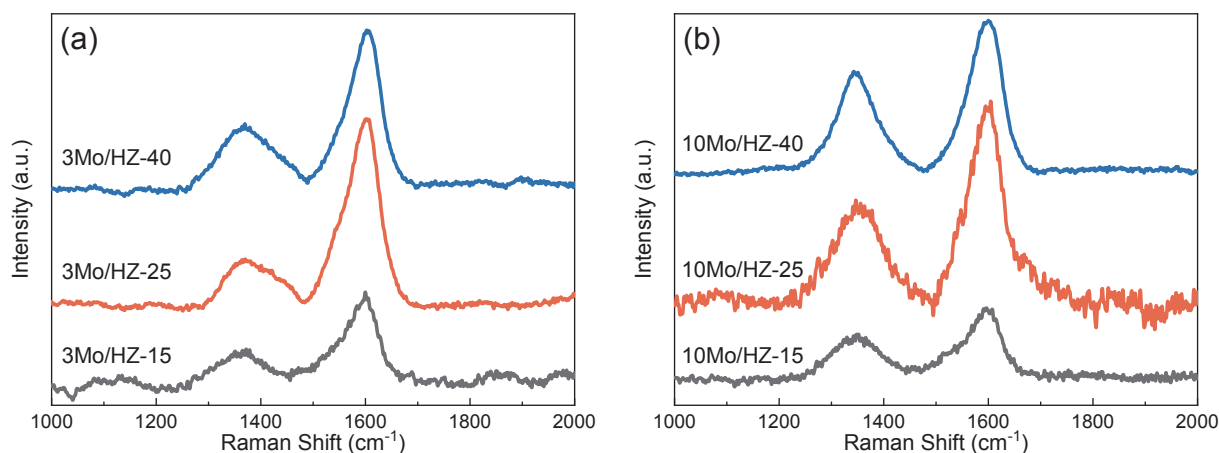


Fig. 11. Raman spectra for spent (a) 3 wt% Mo and (b) 10 wt% Mo catalysts.

Table 7

Ratio of the intensities of amorphous carbon and graphitic carbon obtained from Raman spectra of the spent samples.

Mo content (wt%)	I(D)/I(G)		
	Si/Al = 15	Si/Al = 25	Si/Al = 40
3	0.28	0.24	0.38
10	0.6	0.51	0.66

4. Experimental

4.1. Catalysts preparation

NH₄ZSM-5 with Si/Al = 15, 25, and 40 (Zeolyst International) were first converted into HZSM-5 by calcining them at 500 °C for 6 h. HZSM-5 supported Mo catalysts were prepared by incipient wetness impregnation using an aqueous solution of ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, Sigma Aldrich). The nominal Mo loading in the samples were 3 and 10 wt%. The impregnated samples were then dried overnight at room temperature followed by calcination in static air at 500 °C for 5 h. The powder catalysts obtained were pelletized, crushed and sieved to 60–120 mesh particles. The base HZSM-5 zeolite with a given Si/Al ratio is designated HZ-X, where X is the Si/Al ratio. The catalysts with added Mo are then designated YMo/HZ-X where Y is the wt% loading of Mo.

4.2. Catalysts characterization

The samples that were characterized fell into three categories: as-prepared (oxide) catalysts, reduced (activated) catalysts, and spent catalysts. The reduction procedure of the as-prepared samples consisted in heating the sieved samples from room temperature (RT) to 700 °C in a flow of pure H₂ (6000 ml/h-gcat) at a ramp rate of 5 °C/min. After maintaining the H₂ flow for 10 min at 700 °C the reduced catalysts were quenched to RT and then were taken out of the reactor for characterization with different techniques.

XRD patterns of the fresh as-prepared and reduced catalysts were recorded at room temperature on a Rigaku Ultima III PXRD diffractometer using Cu Kα radiation. The instrument was operated at 20 KV and 44 mA, and the samples were scanned at a rate of 0.5°/min. The Scherrer equation (with $K = 0.94$) was used to calculate the crystal sizes for MoO₃ and metallic Mo:

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

where

B is the full width at half maximum

K is the crystal shape factor

λ is the wavelength of X-rays (0.15406 nm for the Cu target)

L is the crystal size (nm)

θ is the Bragg's angle

Textural properties of the reduced catalysts were measured by N₂ physisorption at liquid N₂ temperature with a Quantachrome Autosorb iQ instrument. Prior to the measurement, the samples were outgassed at 350 °C for 5 h to remove any adsorbed moisture.

The morphology of the reduced catalysts was studied by Scanning Transmission Electron Microscopy (STEM), using FEI Talos F200X equipment (Thermo Fisher Scientific, Waltham, MA, USA) that combined outstanding high-resolution TEM and STEM with a HAADF imaging with industry-leading energy dispersive X-ray spectroscopy (EDS) signal detection, and chemical characterization with compositional mapping. The samples were suspended in isopropyl alcohol and dropped onto a perforated carbon film grid.

The Brønsted acidity of the reduced catalysts was measured by temperature-programmed desorption of isopropylamine (IPA-TPD) using a Quantachrome Autosorb iQ instrument which is connected to a PrismaPlus mass spectrometer (MS). In each measurement 100 mg of sample was loaded in a U-shaped flow reactor (having provision for septum injection) and was pretreated in a 40 ml/min of helium flow at 300 °C for 1 h. The sample was then cooled down to 100 °C in the same helium flow and consecutive pulses of IPA (5 μL/pulse) was injected onto the sample until saturation, as observed by a constant MS signal for IPA. Physically adsorbed IPA was removed by flushing the catalyst bed with helium for 2.5 h. IPA TPD was performed by heating the sample from 100 °C to 600 °C at a heating rate of 10 °C in a helium flow (40 ml/min). The evolution of IPA ($m/z = 44$), propylene ($m/z = 41$), and ammonia ($m/z = 16$ and 17) was continuously monitored by the MS during the temperature ramp.

X-ray absorption spectra of the as-prepared and the spent catalysts were recorded at the Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 9–3 using a cryogenically cooled double crystal Si (2 2 0) monochromator. The storage ring was operated at 3 GeV with a ring current of 500 mA in top-off mode. The beam spot on the sample was 0.5 mm × 0.5 mm. The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded at the Mo K-edge (20000.0 eV) in transmission geometry mode using nitrogen-filled ion chambers. A spectrum of Mo foil was simultaneously acquired and used for energy calibration. Spectra were acquired at room temperature with the catalysts powder inside a quartz reactor tube (3 mm i.d.). The data were processed using Athena [57].

X-Ray Photoelectron spectra (XPS) of the reduced catalysts were collected using a Physical Electronics PHI 5700 spectrometer with non-

monochromatic Mg K α radiation (300 W, 15 kV, 1253.6 eV) for the analysis of the core level signals of C 1s, O 1s, Si 2p, Al 2p and Mo 3d and with a multi-channel detector. Binding energy (BE) values were referenced to the C 1s peak (284.8 eV) from the adventitious contamination layer. The spectrometer energy scale was calibrated using Cu 2p $_{3/2}$, Ag 3d $_{5/2}$, and Au 4f $_{7/2}$ photoelectron lines at 932.7, 368.3, and 84.0 eV, respectively. The PHI ACCESS ESCA-V6.0 F software package and Multipak v8.2b were used for acquisition and data analysis, respectively. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss-Lorentz curves, in order to determine the binding energy of the different element core levels more accurately. The error in BE was estimated to be ca. 0.1 eV. MoO $_3$ (Sigma Aldrich, 99.97% purity), MgMoO $_4$ (Alfa Aesar, 99.9% purity), and Mo $_2$ C (Sigma Aldrich, 99.5% purity) were mixed with cellulose (used as binder) and pressed into wafers. These materials were used as standards in the structural analysis of the Mo/ZSM-5 samples.

For ^{27}Al MAS NMR the as-prepared and the reduced catalysts were packed into standard wall 3.2 mm pencil rotors (Agilent Technologies, Santa Clara, CA and Loveland, CO) to a standard volume of 22 μL . ^{27}Al spectra were recorded on an Agilent DD2 600 MHz spectrometer equipped with a BALUN 3.2 mm probe at a spinning rate of 15 kHz. The magnetic field was 14.1 T corresponding to a ^{27}Al resonance frequency of 156.37 MHz. ^{27}Al signal of an aqueous 1 M Al(NO $_3$) $_3$ solution was used as a universal chemical shift reference. The sample temperature setpoint was 10 $^\circ\text{C}$, corresponding to a sample temperature of 16 ± 2 $^\circ\text{C}$. The spectra were acquired with a $\pi/12$ excitation pulse (1.2 μs).

The carbon deposit on the spent samples was determined by thermogravimetric analysis (TGA) using a Mettler TGA/SDTA851e instrument. In each experiment a blank alumina crucible was first heated in a mixture of air (50 ml/min, reactive gas) and N $_2$ (20 ml/min, protective gas) flow from 25 $^\circ\text{C}$ to 700 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}/\text{min}$. The crucible was then loaded with approximately 10 mg of sample and was heated with the same profile as the blank run. The weight loss profile of the spent sample due to the burning of coke by air was obtained by subtracting the blank run from the sample run.

Raman spectroscopy was used to determine the types of coke deposited on the spent samples. The spectra were acquired with a Senterra dispersive Raman microscope spectrometer (Bruker Optics). The samples were excited by a 532 nm laser source (2 mW power). The spectra acquisition consisted in two 60 s accumulation.

4.3. Catalytic evaluation

Methane dehydroaromatization reactions on the reduced Mo/HZSM-5 catalysts (YMo/HZ-X, where Y denotes Mo wt% and X denotes Si/Al ratio) were carried out in a fixed-bed quartz reactor (8 mm i.d.) at 700 $^\circ\text{C}$ and atmospheric pressure. Approximately 500 mg of sieved calcined catalyst (60–120 mesh) was loaded into the reactor tube and the catalyst bed was supported by two quartz wools. The catalyst was heated from room temperature to 700 $^\circ\text{C}$ with a ramp of 5 $^\circ\text{C}/\text{min}$ in 50 ml/min of H $_2$ flow and the flow was maintained for 10 min after reaching to 700 $^\circ\text{C}$. A mixture of 9% N $_2$ /CH $_4$ was then introduced into the reactor through a mass flow controller at a space velocity of 1550 ml/h.gcat. N $_2$ was used as an internal standard to calculate methane conversion and benzene selectivity. The formulas for calculating conversion and selectivity are provided in the SI. The product gases leaving the reactor were analyzed by an on-line gas chromatograph (Shimadzu GC-2014) that was equipped with a Mol sieve 5 $\text{\AA}$ column to separate H $_2$, N $_2$, CH $_4$ and CO, a Haysep-T column to separate C $_2$ and CO $_2$, and a Haysep-N and a Capillary column to separate C $_3$ and higher hydrocarbons. C $_3$ and higher hydrocarbons were detected by an FID detector and all the other gases were detected by a TCD detector. The line from the reactor outlet to the GC was maintained at 160 $^\circ\text{C}$ to avoid any condensation of heavy hydrocarbons.

CRedit authorship contribution statement

Mustafizur Rahman: . : Conceptualization, Validation, Investigation, Writing - original draft. **Antonia Infantes-Molina:** Investigation, Writing - review & editing. **Adam S. Hoffman:** Investigation, Formal analysis, Writing - review & editing. **Simon R. Bare:** Investigation, Formal analysis, Writing - review & editing. **Kayla L. Emerson:** Investigation. **Sheima J. Khatib:** Conceptualization, Supervision, Visualization, Writing - review & editing.

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.fuel.2020.118290>.

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