Non-oxidative methane dehydroaromatization reaction over highly active α - MoC_{1-x} ZSM-5 derived from pretreatment

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Abstract. The catalytic active-phase of reduced Mo species plays a vital role in non-oxidative methane dehydroaromatization (MDA) reaction. Pretreatment effect of one of the gases containing N_2 , H_2 and (90 vol%) $\text{CH}_4 + \text{H}_2$ over 15% Mo-loaded HZSM-5 catalyst has been investigated in the present work. Various spectroscopic investigations viz., XRD, TPR, TPO, XPS, etc., show that the pretreatment of 15% Mo-HZSM-5 catalyst with (90 vol%) $\text{CH}_4 + \text{H}_2$ gas stream exclusively leads to the formation of $\text{MoO}_x\text{C}_y\text{H}_z$ which acts as precursor moieties for the formation of highly active metastable *fcc* (α - MoC_{1-x}) and MoO_xC_y phases during the induction period. Comparatively, H_2 and N_2 -pretreated catalysts showed major formation of *hcp* (β - Mo_2C) species that are found to be a less-active phase in MDA reaction. The active *fcc* (α - MoC_{1-x}) phases are immune to inert coking and assist primary ethylene products formed on carbonized Mo associated Brønsted acid sites to travel in the zeolite channels which is further aromatized over Brønsted acid sites deep inside the channels. XPS analysis of the catalyst shows that α - MoC_{1-x} and β - Mo_2C are major catalytic phases that are covered with graphitic carbon and amorphous carbon present on the surface. The active phases α - MoC_{1-x} and MoO_xC_y , associated with Brønsted acid sites along with the vacant Brønsted acid sites in catalyst pretreated with (90 vol%) $\text{CH}_4 + \text{H}_2$ mixture are responsible for high activity in methane conversion ($\sim 13\%$), excellent aromatic selectivity (38%), and high stability of the catalyst.

Keywords. Molybdenum oxycarbide; dehydroaromatization; Mo_2C ; α - MoC_{1-x} .

1. Introduction

There is a continuous increase in the demand for energy and an ever-increasing dependence on petroleum since liquid petroleum is the main energy resource for various industries as well as a transportation fuel. Over 86.7 million barrels of petroleum are processed every day in refineries around the world to meet the demand for liquid transportation fuels such as gasoline, diesel and jet fuel. The declining crude oil reserves have shifted focus towards natural gas as an alternative fuel source. Methane is a very abundant fuel resource as its reserves are spread around the world. Researchers have explored a number of strategies ranging from fundamental science to advanced engineering technology for conversion of methane to useful chemicals.¹ In

this regard, non-oxidative methane dehydroaromatization (MDA) over Mo/HZSM-5 catalyst is a promising approach for production of higher hydrocarbons mainly benzene, toluene, xylene and naphthalene along with hydrogen.² Considerable efforts have been made to understand the mechanism of methane activation and active sites formed over Mo-modified catalyst. It is believed that, Mo_2C species, which are highly dispersed on the external surface of the HZSM-5, act as active sites and are responsible for the initial methane activation.^{3–7} During the period of calcination at 500–700 °C in air stream, molybdenum species replaces the Brønsted acid sites with 1:1 stoichiometry and exists in the channels of the H-ZSM-5 zeolite.^{8–11} However, there is no unanimous agreement about the precise active molybdenum species in MDA reaction among the sci-

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entific community. Moreover, its location depends on several factors, viz., method of catalyst preparation and amount of metal loading as well temperature, duration and gas phase composition involved in the calcination process.^{12–14} Conversion of externally located molybdenum oxide to molybdenum carbide on the external zeolite surface and its transformation to MoO_xC_y inside the zeolite channels is a widely accepted phenomenon in MDA reaction. It has also been investigated that the Mo species in the channels are more effective in the activation of methane and less susceptible to the formation of carbonaceous deposits.^{12–14} When reduced with methane, MoO₃, not associated with the Brønsted acid sites are converted to Mo carbide species whereas, MoC_xO_y species which are formed are associated with the Brønsted acid sites.^{12–14} Various attempts have been made to enhance the activity, aromatic selectivity and stability of the Mo-HZSM-5 catalyst.^{15–31} Addition of promoters,^{15–17} creating secondary mesopores or preparing hierarchical pore structures in microporous catalysts HZSM-5,^{18,19} co-feeding of CO, CO₂, H₂O and H₂ for *in situ* catalyst-regeneration^{20–22} and pretreatment by different gas streams, (H₂, C₂H₄, C₃H₈, H₂O or CO₂) are chiefly the studied areas.^{23–31} Among these, pretreatment studies are one of the favorite areas in MDA reaction. Pretreatment of the catalyst with different gas streams or hydrocarbon/H₂ mixture substantially alters the topotactic nature of the active carbide species as well the catalyst performance. Periodic pulsing of oxygen into the methane feed³⁰ and cyclic CH₄-H₂ feed in switch mode ensuring reduced coking behavior³¹ are quite recent studies in MDA reaction. Nevertheless, the inherent thermodynamic limitation and rapid catalyst deactivation are still subject to investigation. Bouchy *et al.*,²⁴ have claimed the presence of two active phases, more active metastable *fcc* (α -MoC_{1-x}) and thermodynamically stable *hcp* (β -Mo₂C) as the key species involved. Hence, the reactions carried over the catalyst with chief active phases, metastable *fcc* α -MoC_{1-x}, will be an ideal way to overcome these limitations.

In this work, we report the exclusive formation of metastable *fcc* (α -MoC_{1-x}) over Mo-HZSM-5 zeolite catalyst by pretreating it with (90 vol%) CH₄ + H₂ mixture at 550 °C for 4 h. Comparatively, pretreatment with H₂ and N₂ was also done to get more insight into the active species formation. The catalysts were systematically studied and catalytic performances were evaluated in MDA reaction. The formation of active metastable α -MoC_{1-x} species and coke deposition on the spent catalyst were identified by using XRD, TG-DTA, XPS and TPO methods. Catalyst pretreated with (90 vol%) CH₄ + H₂ mixture at 550 °C for 4 h shows higher con-

version (~13%) aromatic selectivity (38%) compared to the catalyst pretreated with H₂ and N₂.

2. Experimental

2.1 Catalyst preparation

The Mo-supported catalyst was synthesized by impregnation of ammoniumheptamolybdenate (AHM) (Rankem) on zeolite (Zeolite-CBV3024E, Surface area = 400 m²/g). Prior to impregnation, NH₄-ZSM-5 catalyst was converted to H-ZSM-5 by calcination in air at 550 °C for 6 h. In a typical procedure, required amount of AHM was dissolved in the double distilled water and then mixed with activated H-ZSM-5. The resultant slurry was homogenized under stirring at 80 °C for 1 h and excess water was removed by Buchi rotary vacuum evaporator. This catalyst was further dried at 120 °C for 12 h and then calcined for 4 h at 550 °C. Resulting catalyst was finely ground, pelletized, broken and sieved to 20–60 mesh size.

2.2 Catalyst activation by pretreatment

Pretreatment of the activated catalyst was achieved by flushing different gas streams at the desired temperature and about 4 h. Thus these are hereafter named as 15% Mo-HZSM-5-C (N₂ pretreated catalyst at 300 °C for 4 h), 15% Mo-HZSM-5-B (H₂ pretreated at 350 °C for 4 h) and 15% Mo-HZSM-5-A (90 vol% CH₄/H₂ pretreated at 550 °C for 4 h). The catalytic performance of this pretreated catalyst was evaluated for MDA reaction in fixed bed reactor at 700 °C, 1 atm. and GHSV=1200 mL/h_{cat}.

2.3 Catalytic evaluation and product analysis

The activity testing of catalyst was carried out in a fixed bed tubular continuous flow reactor of 6 mm I.D., 8 mm O.D. and 450 mm length made of quartz. The catalyst was plugged in between ceramic wool, above and below the catalyst, SiC beads were placed to minimize the gas phase reactions.³² This reactor was placed in the isothermal region of the electrically heated tubular furnace. The plug flow conditions of the reactor were maintained by keeping L/dp > 50 and D/dp > 10 where L is catalyst bed length, dp is the diameter of the catalyst particle and D is the diameter of the reactor, respectively.³³ The feed rates were controlled by mass flow controllers (MKS Instruments, USA type 246). The reactant gas stream was passed over the catalyst at a required temperature and the outlet product mixture was directly sent to Gas Chromatography (GC) connected to Flame Ionization Detector (FID) and thermal conductivity detector (TCD). Higher hydrocarbons were detected in the Nucon gas chromatograph with Supel-Q Plot column (Supelco, 30 m × 0.53 mm) which is connected to FID. H₂, N₂, CO, CH₄ and CO₂ gases were detected in the GC-TCD connected with Carbosieve (2 m × 52 mm) column. Prior to the gas analysis, gas chromatograph was calibrated with the standards of known samples and response factors

for FID and TCD were calculated as described in the literature.³⁴ The standard mixture of 90% CH₄ and 10% N₂ as an internal standard was used for the total gas outlet of the reactor. Here, 90% stands for vol%, keeping methane partial Pressure = 0.9 bar while Nitrogen partial Pressure = 0.1 bar, with a total pressure of 1 bar. Methane conversion, selectivity of hydrocarbons and coke formation was calculated based on carbon mass balance as reported in detail.³⁵

2.4 Catalyst characterization

Powder X-ray diffraction (XRD) patterns for phase analysis and crystallinity verification were recorded using a Rigaku Miniflex X-ray diffractometer with CuK α radiation (λ = 1.54 Å), operated at 20 mA and 40 kV. Powder diffractograms were recorded over a range of 2θ values from 5–80° at a scanning rate of 4°/min. The textural properties of the catalysts were determined by nitrogen adsorption-desorption analysis at –196 °C using an automatic micropore physisorption analyzer (Micrometrics ASAP 2020, USA). Prior to the analysis, samples were degassed at 250 °C for 12 h under 0.133 Pascal pressure. The H₂-Temperature programmed reduction (TPR) measurements were recorded, using the Micrometrics Auto Chem II 2920 chemisorption analyzer. The calcined samples (0.1 g) were loaded in a U shaped quartz reactor placed inside the furnace. Prior to the analysis, the sample was degassed at 200 °C for 1 h under helium flow (40 mL/min) and cool down to the room temperature. The furnace temperature was raised from room temperature to 900 °C at a heating rate of 10 °C/min with a 10% H₂/Ar gas flow of 50 mL/min. H₂ consumption was measured using a thermal conductivity detector (TCD) and the total H₂ consumption was obtained from the integrated peak area of the reduction profiles relative to the calibration curve.

The NH₃-TPD studies were conducted using Micromeritics Auto Chem II 2920 chemisorption analyzer. The samples were first degassed for 1 h at 200 °C under the flow of helium (40 mL/min) to desorb the moisture and impurities present. Subsequently, at 100 °C, 10 vol% NH₃- He gas mixture (20 mL/min) was passed into the reactor for 1 h to ensure complete chemisorption of ammonia. The physisorbed ammonia present over the sample was removed by flushing the He (50 mL/min) for 1 h. Samples were consequently heated up to 800 °C with a heating rate of 10 °C/min and amount of ammonia desorbed was monitored using a TCD detector. The quantity of NH₃ adsorbed was calculated from

the pulse calibration data collected using the same gas mixture.

Temperature-Programmed Surface Reactions (TPSR) of methane were carried out in the same tubular flow reactor. Prior to the reaction catalyst was activated to 300 °C in He gas flow at the rate of 10 °C/min and for 2 h. The effect of pretreatment and MDA reactions were evaluated under similar conditions used in the experimental reaction. Product gases from the reactor were analyzed by HIDEN MAS soft quadruple mass spectrometer connected to the outlet of the reactor. Products of reaction m/e of 2(H₂), 16(CH₄), 18(H₂O), 27(C₂H₄), 28(CO), 44(CO₂), 78(C₆H₆) and 91(C₇H₈) were recorded in the MID mode.

X-ray photon spectroscopy (XPS) for surface characterization of working catalyst was conducted over a SPECS PHOIBOS HAS 3500 spectrometer equipped with a single channel detector coupled with MgK α radiation (1253.6 eV). The spectra were obtained using samples prepared in the form of pressed wafers mounted on the sample holder. The charging effect of the sample was corrected by referring to the Si 2p_{3/2} peak of SiO₂ (103.4 eV)^{7,36} and the C1s peak of contaminant carbon binding energy (BE) = 284.6 eV³⁷, respectively.

3. Results and discussion

3.1 Catalytic activity testing of pretreated samples

The pretreatment of the catalyst leads to the formation of different active species which play a key role in methane dehydroaromatization.²⁶ Catalysts pretreated with various gas streams and their resulting activity in methane dehydroaromatization is listed in Table 1. 15% Mo-HZSM-5-A shows high conversion (13%), high aromatic selectivity (38%) and less coke deposition (54%) as compared to 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C. Methane conversion falls down to 10.5% and 5.6% in case of 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C respectively.

The latter two catalysts suffer more coke formation (64% and 69% coke selectivity) which leads to blockage of zeolite pore opening and hence less aromatic selectivity (29% and 14%). The results show that less coking in 15% Mo-HZSM-5-A is responsible for its high activity.

Table 1. Methane conversion and product selectivity over different pretreated catalyst at 700 °C, 1 atm and GHSV = 1200 mL/h.g_{cat}.

Catalyst	Methane conversion (%)	Selectivity (%)					
		C ₂ -C ₃	Benzene	T+X	Naphthalene	CO	Coke
15% Mo-HZSM-5-C	5.6	15.0	14.0	0.50	0.15	1.2	69
15% Mo-HZSM-5-B	10.5	3.4	29	2.0	0.5	1.3	64
15% Mo-HZSM-5-A	13.0	7.5	34.5	2.5	1.0	0.5	54

Figure 1. Methane conversion and product selectivity with time on stream. (a) 15% Mo-HZSM-5 A catalyst; (b) 15% Mo-HZSM-5-B (c) 15% Mo-HZSM-5-C.

3.1a Methane conversion with time on stream: The effects of catalyst pre-reduction with a different gas stream on methane conversion with time-on-stream (TOS) are shown in Figure 1. The methane conversion (~13%) and benzene selectivity (~32%) over 15% Mo-HZSM-5-A catalyst was nearly constant for 15 h as shown in Figure 1a.

The coke selectivity increased from 50 to 60% and the C₂-C₃ hydrocarbon selectivity increases from 5 to 8% for this catalyst. On the other hand, selectivity to the other aromatic compounds (Toluene, Xylene and Naphthalene) was found to be negligible over other two catalysts, 15%Mo-HZSM-5-B and 15% Mo-HZSM-5-C also. The performance of 15% Mo-HZSM-5-B catalyst (Figure 1(b)) shows lower activity than the 15% Mo-HZSM-5-A. The conversion of methane on this catalyst decreases from 11.2 to 7% and simultaneously, benzene selectivity also decreases from 26 to 20%. The coke selectivity on this catalyst increased from 60 to 69% and C₂-C₃ hydrocarbon selectivity from 2 to 9.6%,

possibly due to the increased cracking reaction. The 15% Mo-HZSM-5-C catalyst (Figure 1(c)) shows poor conversion than the other two catalysts, and after 11 h of TOS, the catalytic activity was lost. The conversion rapidly decreases from 6.2 to 1.5%. Benzene selectivity goes to maximum 15% and then drops to 6%. The selectivity towards C₂-C₃ hydrocarbon increases from 10 to 25%. The results are analogues to earlier reported trends,³⁸ where the simultaneous ethylene selectivity increased when the conversion of methane and benzene decreases with time-on-stream. This is attributed to deactivation of the Brønsted acid sites, which are responsible for oligomerization or cyclization of reaction intermediates.

3.2 XRD analysis

The XRD patterns of various samples *viz.*, pure ZSM-5, Mo impregnated, pretreated and spent catalyst are illustrated in Figure 2. The diffraction pattern reveals

Figure 2. XRD patterns : (a) Pure HZSM-5; (b) 15% Mo-HZSM-5; (c) 15% Mo-HZSM-5-A; and spent catalysts of, (d) 15% Mo-HZSM-5-A after 50 min; (e) 15% Mo-HZSM-5-A after 3 h; (f) 15% Mo-HZSM-5-B after 3 h; (g) 15% Mo-HZSM-5-C after 3 h.

the formation of MoO_3 species ($2\theta = 27.8, 28.5, 30.3, 35.1, 34.2, 39.1, 49.8$ and 53.7°) which are availed from impregnation of AHM over the ZSM-5 followed by calcination at 550°C .

The relative crystallinity of Mo-loaded catalyst decreases to 78% (Table 2) compared to pure ZSM-5, which manifests that MoO_3 species are highly dispersed on ZSM-5 surface and in its channels. It is noteworthy to mention that AHM ions do not exchange directly onto HZSM-5 during the impregnation, rather MoO_3 species are formed first in aerial atmosphere at $227\text{--}377^\circ\text{C}$ on the external surface of ZSM-5, and further diffused into zeolite channels.^{39,40} The XRD patterns of the catalyst pretreated with H_2 and N_2 are shown in Figures 2f and 2g, respectively. The formation of $\beta\text{-Mo}_2\text{C}$ phase ($34.3, 37.9$, and 39.4°) after the reaction run of 3 h is consistent with reports in the literature.²⁴ The MoO_3 species in 15% Mo-HZSM-5-A (Figure 2(a)) are converted to monoclinic MoO_2 ($2\theta = 26.1, 37.1, 49.6, 53.7, 60.4, 67.0^\circ$) phases with traces of face-centered cubic (fcc) $\text{MoO}_x\text{C}_y\text{H}_z$ ($2\theta = 43.8, 49.8^\circ$).^{41,42} During the carburization in methane stream these phases are converted into $\alpha\text{-MoC}_{1-x}$ ($36.9, 41.2, 62.5, 74.5^\circ$) with trace amount of MoO_xC_y ($2\theta = 38.4, 45.6, 64.0, 64.4$ and 65.6°).^{24,43}

Earlier reports have claimed that the insertion of carbon by catalyst pretreating with n-butane/hydrogen gas mixture at 350°C for 24 h was necessary for

the synthesis of highly active metastable face-centered cubic (fcc) structure $\alpha\text{-MoC}_{1-x}$ over $\text{MoO}_3\text{-HZSM-5}$. However, the present study suggests that highly active metastable face-centered cubic (fcc) structure $\alpha\text{-MoC}_{1-x}$ over $\text{MoO}_3\text{-HZSM-5}$ can be achieved by pre-treating the catalyst with (90%) CH_4/H_2 at 550°C for 4 h only.

3.3 Crystallinity and BET surface area analysis of the catalyst

Textural properties of the parental catalyst and 15% Mo-HZSM-5 catalyst with successive treatments are summarized in Table 2. The BET surface area of the 15% Mo-HZSM-5 as calcined catalyst decreased, which may be attributed to the deposition of MoO_3 over the zeolite. The decrease in the external surface area and micropore area of 15% Mo-HZSM-5 catalyst indicates the MoO_3 has migrated into zeolite channel during the calcination as discussed in section 3.2. BET surface area and crystallinity of the catalyst further decreased after pretreatment with CH_4/H_2 , possibly, due to increase in migration of Mo species into the zeolite channels. After 3 h reaction time, the BET surface area of the different catalysts further decreases due to coke deposition over the MoO_3 surface and zeolite channel. The external surface area of the spent catalyst is higher than the parental Mo loaded catalyst. This confirms that the Mo species

Table 2. Crystallinity and BET surface area measurements of the different catalysts.

S. No	Catalyst	Relative crystallinity (%)	Surface Area (m ² /g)		Pore Volume (cm ³ /g)		Total acidity (mmol/g _{cat})
			BET	External	Micro pore	Meso pore	
1.	H-ZSM-5	100	363.5	124.2	239.1	0.125	0.135
2.	15% Mo-HZSM-5	78.6	260.5	78.0	182.3	0.088	0.094
3	15% Mo-HZSM-5-A	54.0	200.0	58.0	142.0	0.062	0.11
4.	15% Mo-HZSM-5-A [#]	62.0	250.0	136.0	114.0	0.050	0.15
5.	15% Mo-HZSM-5-B [#]	56.0	240.0	132.4	107.6	0.053	0.087
6.	15% Mo-HZSM-5-C [#]	56.5	232.0	137.0	95.0	0.047	0.073

spent catalysts after 3 h TOS

on the external surface migrated during carburization, thus, the micropore area was decreased.

3.4 H₂-temperature programmed reduction of Mo-HZSM-5

The deconvoluted H₂-TPR profile of 15% Mo-HZSM-5 (Figure S1 in Supplementary Information) have shown a two-stage reduction of MoO₃ to MoO₂ followed by its conversion into pure metallic Mo.^{44–47} Consumption of hydrogen (fitted peaks) over this catalyst was observed at 518 °C, 620 °C, 678 °C and 758 °C. The observed trend suggests that there are two kinds of Mo⁺⁶ species located on Mo-HZSM-5 catalyst: (i) Mo located on the external surface, and (ii) Mo present in the zeolite channels. Mo species present over the surface is easy to be reduced than the Mo existing in zeolite channels.¹³ The reduction temperature 518 °C is attributed to the conversion of surface deposited MoO₃ to MoO₂ and hydrogen consumption peak at 678 °C is assigned to further reduction of MoO₂ to Mo.^{46,48} The TPR peak at 620 °C corresponds to reduction of MoO₃ present in zeolite channels to MoO₂ and the reduction peak at 758 °C is ascribed to reduction of Mo⁴⁺ species associated with Brønsted acid sites to MoO_x and subsequent reduction of MoO₂ species to metallic Mo respectively.^{49,50} However, H₂ consumption at 678 °C was only 54% to that of the corresponding peak at 518 °C, which indicates that the total amount of Mo⁴⁺ species are not reduced into metallic Mo. Hence, at this stage, simultaneous existence of Mo⁴⁺ and metallic Mo species were evident. The observation matches well with XRD profile in Figure 2.

3.5 NH₃-temperature programmed desorption studies

The NH₃-TPD profiles of various samples and spent catalyst with different modes of activation are shown in Figure 3. The NH₃ desorption peak at low temperature (193 °C) corresponds to the weak acidic sites (Lewis) while desorption peak at high temperature (392 °C) is attributed to the presence of strong Brønsted acid sites.^{51–54} The Gaussian curve fitted, deconvoluted profile illustrates that pure HZSM-5 (Figure 3a) is associated with high amount of NH₃ adsorbed (0.84 m.mol/g_{cat}) owing to the presence of strong acidity. Mo loading and pretreatment leads to shifting in desorption profile (Figure 3b–3f) towards lower temperature.

This is attributed to a decrease in acidity of Mo-HZSM-5 (0.62 m.mol/g_{cat}) and pretreated catalyst (0.53 mmol/g_{cat}). 15% MoO₃, impregnated on HZSM-5 (Figure 3b) shows a new peak at 196–213 °C with

Figure 3. NH_3 -TPD profiles of, (a) pure HZSM-5, (b) 15% Mo-HZSM-5, (c) 15% Mo-HZSM-5-A, (d) 15% Mo-HZSM-5-A after 3 h, (e) 15% Mo-HZSM-5-B after 3 h, and (f) 15% Mo-HZSM-5-C after 3 h.

medium acid strength. The disappearance of the high-temperature peak after Mo loading owes to a decrease in strong acidic sites and migration of MoO_2 into the zeolite channels and their interaction with OH groups of the HZSM-5 zeolite.^{52,55–59} The deconvoluted TPD profiles of the 15% Mo-HZSM-5-A (0.53 mmol/g_{cat.}) depicts further decrease in acidity, and desorption temperature of NH_3 was shifted to lower temperatures. This is possibly due to the migration of Mo species into zeolite channels and the coordination of MoO_x with the Brønsted acid sites, which results in suppression of acid sites during the pretreatment. Interestingly, the NH_3 uptake on the pretreated catalyst after reaction 3 h reaction run had decreased (Figures 3d–3f). This may be due to the coke deposition on strong Brønsted acid sites in the catalyst, which is more for the catalyst pretreated with H_2 and N_2 compared to the $\text{CH}_4 + \text{H}_2$ mixture. At the same time, in 15% Mo-HZSM-5-A (Figure 3d) the acidity of weak acid sites and medium acid sites was increased. This is attributed to the formation of catalytically active sites (most probably MoC_{1-x}) due to the interaction of methane stream with the Mo located on the external surface and the Mo exchanged with Brønsted acid site in the zeolite channels. It also suggests that all three types of acid sites have interacted with the feed during the reaction. Increase in area under the Lewis acid sites

after pretreatment owes to the transformation of surface MoO_3 to Mo_2C species.⁶⁰

These observations are in good agreement with quantitative acidity profile of the spent catalyst (Table 2) where the total acidity of the 15% Mo-HZSM-5-A (0.68 mmol/g_{cat.}) spent catalyst was higher than the 15% Mo-HZSM-5-B (0.44 mmol/g_{cat.}) and 15% Mo-HZSM-5-C (0.43 mmol/g_{cat.}) catalyst. Furthermore, the micropore area and total acidity of spent catalysts together confirm that coke deposition on the 15% Mo-HZSM-5-A was less as compared to 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C. Hence, the overall TPD studies suggest that pretreatment of the catalyst with $\text{CH}_4 + \text{H}_2$ mixture leads to the formation of more number of catalytically active sites (MoC_{1-x}), prevents coking, and helps in preserving high acidity and long catalyst lifetime (> 15 h).

3.6 Temperature programmed surface reactions (TPSR) of MDA

3.6a CH_4 -temperature programmed surface reaction (TPSR) studies on N_2 pretreated catalyst: The TPSR of methane over 15% Mo-HZSM-5-C (Figure 4a), depicts the reduction of molybdenum species present on the zeolite surface and in its channels. TPSR profiles of methane shows that consumptions of methane appeared to be started at 500 °C and up to 700 °C, formation of double stage CO_2 , CO and H_2O was evident owing to the two-stage reduction of MoO_3 .⁶¹

In the first stage, MoO_3 is reduced to MoO_2 below 700 °C, where, the consumption of methane is low and in second stage MoO_2 is further reduced to Mo_2C as shown in equations (1–3).^{60,62} This can be clearly justified by second stage reduction of MoO_2 accompanied by relatively high consumption of methane and evaluation of H_2 and CO as shown in the Figure 4(a). Hence, the formation of Mo_2C phases is expected to occur during the induction period i.e., after 25 min of TOS where the formation of benzene takes place. The formation of β - Mo_2C phases was also observed in the XRD profile of this catalyst after 3 h TOS. Consumption of methane during the reduction period was higher due to high amount of methane dissociation on the MoO_3 that convert it into active species. After the completion of induction period (25 min), methane consumption decreases and the formation of ethylene, benzene and xylene was observed. This shows that the formation of carburized Mo species is essential for methane conversion to aromatics.

Figure 4. TPSR of CH₄ over (a) 15% Mo-HZSM-5-C, and (b) 15% Mo-HZSM-5-B.

3.6b CH₄-TPSR studies on H₂ pretreated catalyst:

The TPSR profiles of 15% Mo-HZSM-5-B Figure 4(b) illustrates that consumption of methane started from 650 °C and there is no observation of two-stage product formation. This shows that during the pretreatment period with H₂ at 350 °C, MoO₃ was reduced to form MoO₂.^{24,43} As the temperature rises to 700 °C, methane consumption increases and formation of CO₂, CO, H₂ and water is observed. This is due to reduction of MoO₂ species with methane to form molybdenum carbide species. This shows that methane activation takes place over the Mo₂C sites as reported in literature.¹¹ The induction period (38 min) on this catalyst was increased possibly due to agglomeration of Mo and their migration into the zeolite channels.

3.6c CH₄-TPSR studies on 90% CH₄/H₂ pretreated catalyst: The TPSR profiles of 15% Mo-HZSM-5-A (Figure 5a) shows that hydrogen consumption starts at 300 °C, increases up to 550 °C and simultaneously methane consumption is increased with temperature.

The reduction of MoO₃ in methane stream is more readily facilitated than in the H₂ atmosphere as described in equations 1 and 2.

Thus, the first stage of evolution of CO₂ and H₂O as well as consumption of hydrogen, corresponds to reduction of surface deposited MoO₃ to MoO₂ facilitated by CH₄ and H₂ mixture. The second stage evolution of CO₂, H₂O, CO and H₂ after 500 °C is due to the reduction of MoO₃ which are located inside the zeolite channels to MoO₂ and MoO_xC_y species as described in eq. 3. Consumption of methane and desorption of trace amounts of CO reveals the formation of molybdenum hydroxycarbide (MoO_xC_yH_z) phase which was also detected in XRD analysis (Figure 2c), and NH₃-TPD of the pretreated catalyst (Figure 3c), where the acidity of the Brønsted acid sites are reduced due to increase in carbonization of Mo exchanged Brønsted acid sites present in the zeolite channels. The TPSR profiles of 15% Mo-HZSM-5-A catalyst during the reaction run (Figure 5b) show that consumption of methane gradually increases up to 625 °C and is accompanied by simultaneous formation of H₂, H₂O, CO and CO₂ and ethylene with further rise in temperature up to 700 °C. This is ascribed to the reduction of MoO₂ species formed

Figure 5. TPSR of CH₄ over 15% Mo-HZSM-5-A.

during the pretreatment to form the molybdenum carbide species. Consumption of methane at induction period (40 min) of the catalyst was higher than the other catalyst. The methane consumption started immediately after pretreatment and maximum consumption was reached at (625 °C). On the other hand, in the case of 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C the methane consumption started after reaching the reaction temperature (700 °C). This shows that pretreatment of catalyst favors formation of highly active catalytic phase, which can activate the methane at lower temperature. In addition, ethylene formation occurs in three steps. This suggests that methane is activated on the three active phases, which are dependent on the location of their sites. Surface located MoO₂ are readily reduced in the methane stream to form Mo₂C (as we can see on the catalyst B and C), whereas, the MoO₂ located in the zeolite channels are very hard to reduce. They are partially reduced to form the MoO_xC_y or MoO_xC_yH_z. These sites are highly active and more stable than the Mo₂C. Hence, we interpret that the first two humps are due to carbonization of MoO₂ located in zeolite channels. The TPSR profiles of ethylene, hydrogen and water also follow the same trend. This indicates that partially carburized Mo species (MoO_xC_y/MoO_xC_yH_z) formed during the pretreatment may recombine the methane fragmented species to form the ethylene. The

intermediate ethylene formation is assisted by Mo associated Brønsted acid sites followed by aromatization on the Brønsted acid sites.⁶⁰ We believe that MoO_xC_y or MoO_xC_yH_z sites which are facilitated by the pretreatment at 550 °C with 90% CH₄/H₂ are responsible for the formation of ethylene where the free Brønsted sites are very less as shown in Figure 3(c). Thus, the catalytically inactive [Mo₂O₅²⁺] species in the zeolite channels are reduced by methane to form the active centres for C-H bond activation and initial C-C bond formation along with an acid site for oligomerization and cyclization. Hence, benzene is formed later when ethylene aromatizes on vacant Brønsted acid sites, deep inside the zeolite channels.

3.7 Thermogravimetric analysis (TGA) of the coked 15% Mo-HZSM-5 catalyst

The TG-DTG/DTA profiles of the various catalyst after 3 h run are shown in the Figure 6. The endothermic weight loss (4–5%) from 70–250 °C is ascribed to moisture desorption and weight gain from 300 to 450 °C accompanied by endothermal process corresponds to burning of coke associated with molybdenum oxide.

The increase in weight loss is due to burning of coke on the Mo₂C to form the MoO₃.⁶² The catalyst pretreated with CH₄ + H₂ at 550 °C (Figure 6a) shows

Figure 6. TG-TGA/DTA profiles of, (a) 15% Mo-HZSM-5-A; (b) 15% Mo-HZSM-5-A after 3 h; (c) 15% Mo-HZSM-5-B after 3 h; (d) 15% Mo-HZSM-5-C after 3 h.

negligible formation of carbon deposits. This is due to the fact that consumption of methane is accompanied by reduction of MoO_3 species and these temperatures do not favor the formation of coke. The consumption of methane and formation of CO_2 , CO and H_2O during the pretreatment with $\text{CH}_4 + \text{H}_2$ (as discussed in TPSR) ensures that MoO_3 species forms MoO_xC_y .⁴¹ The DTA curve profile of 15% Mo-HZSM-5-A shows the small variation in peaks with endothermic weight increase (0.4 mg). This is attributed to the combustion of chemically associated coke with MoO_3 . The DTA profile of this catalyst shows that the combustion of Mo_2C to MoO_3 is highly endothermic due to several reaction steps involved and the activation energy of this step is found to be twice that of the combustion of other coke.^{63,64} The order of formation of coke associated with Mo_2C is as follows: 15% Mo-HZSM-5-A (0.98 mg) < 15% Mo-HZSM-5-C (1.04 mg) < 15% Mo-HZSM-5-B (1.4 mg). This shows that the catalyst pretreated with H_2 retains a high amount of Mo on the surface of the catalyst. The exothermic weight loss at high temperature (450–600 °C) is ascribed to burning of aromatic or polycondensed coke deposited over the surface of the

catalyst during the reaction. Again, the order of the coke deposition on high temperature follows the same trend: (15% Mo-HZSM-5-A (0.48 mg) < 15% Mo-HZSM-5-C (0.52 mg) < 15% Mo-HZSM-5-B (0.96 mg)). Since coking forms continuously fashion over molybdenum carbide as well as on Brønsted acid sites, it leads to the formation of multilayer coke with varied characteristics.⁶⁵ The three exothermic combustion humps at (436 °C, 468 °C, 506 °C) for 15% Mo-HZSM-5-A after 3 h run can be attributed to combustion of coke deposited on the molybdenum associated with Brønsted acid site followed by vacant Brønsted acid sites deep inside the zeolite channels. In 15% Mo-HZSM-5-B, only two exothermic peaks (452 °C and 521 °C) were identified. This signifies the decrease in Brønsted acid sites associated with molybdenum species. The DTA profile peaks (467 °C and 533 °C) of 15% Mo-HZSM-5-C are shifted to high temperatures. From TG-DTG profiles of the catalysts, we notice that there are three distinct weight losses at 760, 800 and 920 °C. The decomposition of the MoO_3 takes place at around 750 °C.⁴¹ The amount of weight loss (3%) at 760 °C is nearly same as the weight gained after the combustion of the Mo_2C to form MoO_3 .

Figure 7. TPO profile of, (a) 15% Mo-HZSM-5-A; (b) 15% Mo-HZSM-5-A after 3 h; (c) 15% Mo-HZSM-5-B after 3 h; (d) 15% Mo-HZSM-5-C after 3 h.

Hence, we can attribute this weight loss to decomposition of MoO_3 on the external surface. As discussed in the section 3.2, four kinds of Mo is deposited on the HZSM-5. Two kinds of Mo species exist mainly on the external surface of the HZSM-5 zeolite and third kind of Mo species is located in the zeolite channels. The small weight loss (3–4%) at 800 °C is due to square pyramidal coordinated Mo^{5+} and the steep change in weight loss (7%) at 920 °C on TG curve is due to decomposition of MoO_3 in the zeolite channels.

3.8 Temperature programmed oxidation (TPO) analysis of coked catalyst

TPO profile of the coke formed over various catalysts is shown in Figure 7. Burning of coke deposits associated with MoO_x , preferably Mo_2C and Mo oxycarbides occurs at lower temperature while coke deposited on vacant acid sites occurs at higher temperatures (> 527 °C).^{63–67} The low-temperature combustion peaks observed at 434, 445 and 460 °C (Figures 7a–7c) are due to oxidation of external molybdenum carbide and coke

deposited over there in 15% Mo-HZSM-5-A and 15% Mo-HZSM-5-B.⁶⁷ During induction period, externally located MoO_3 are converted to Mo_2C and Mo located in the channels are partially converted to MoO_xC_y and $\text{MoO}_x\text{C}_y^{n+}$.⁵⁶ The TPO peak at 487 °C, 511 °C, and 507 °C on these two catalysts is due to burning of coke associated with Mo-exchanged Brønsted acid sites inside zeolite channels. The methane activated on Mo_2C or Brønsted acid site-associated molybdenum carbide is further adsorbed on Mo species to form the coke.⁶⁸ Since pretreatment by $\text{CH}_4 + \text{H}_2$ mixture exclusively forms $\alpha\text{-MoC}_{1-x}$ and MoO_xC_y phases, which are less susceptible to coking during reaction, we assume that most of the coke in 15% Mo-HZSM-5-A is formed over these active sites and it is soft, reactive and reversible in nature. Consequently, coke selectivity for 15% Mo-HZSM-5-A was also less compared to H_2 and N_2 pretreated samples as shown in Figure 1.

The TPO peaks at the high temperature (>560 °C) are attributed to cokes generated from aromatics on the Brønsted acid site. Thus, the TPO peak at 543 °C, 568 °C and 585 °C is due to the polycondensed coke present

Figure 8. XPS spectra in Mo 3d region (left) and in C 1s region (right) of (a) 15% Mo-HZSM-5; (b) after 3 h (TOS) of catalyst 15% Mo-HZSM-5-A; (c) 15% Mo-HZSM-5-B; (d) 15% Mo-HZSM-5-C.

over the zeolite channels.⁶⁷ It is noteworthy to mention that coke formed on the Mo species are reactive and reversible but the coke formed on vacant Brønsted acid sites are irreversible and inert.^{67,68} The corresponding formation of H₂O peak (Figures 7a–7c) over 15% Mo-HZSM-5-A and 15% Mo-HZSM-5-B shows that there are two kinds of aromatics present in the catalyst. The low-temperature peaks 490 °C and 475 °C are due to the oxidation of polycondensed aromatics with high H/C, and the peaks at 557 °C and 530 °C are due to the oxidation of polycondensed aromatics with hydrogen deficient H/C, respectively.

The fourth kind of coke present on the N₂ pretreated catalyst (Figure 7d) is inert aromatic coke deposited on the Brønsted acid sites, quite similar to the coke formed on the pure HZSM-5 at 587 °C with the absence of water formation. The micropore surface area and mesopore volumes of the catalyst 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C was less as compared to 15% Mo-HZSM-5-A, due to polyaromatic hydrocarbon (PAH) coke formed on the zeolite channels as shown in Table 2. These PAH hard cokes formed on the external zeolite surface and inside its cavity leads to micropore blockage that results in the decrease in accessibility

to Brønsted acid site and restricts the primary products formed to aromatize further.⁶⁹ The severe pore blocking at catalyst pore entrance, due to hard cokes of polyaromatics leads to the increased selectivity of C₂–C₃ hydrocarbons over 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C (Figure 1) which supports very well with the experimental results. Conclusively, TPO analysis illustrates that catalytically active α -MoC_{1-x} phase over 15% Mo-HZSM-5-A is more immune to coke formation than β -Mo₂C phase over 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C. Moreover, most of the coke in 15% Mo-HZSM-5-A formed is soft in nature with low-temperature burn-off and less aromatic origin which makes the catalyst highly efficient and stable in MDA reaction.

3.9 XPS Characterization of coked 15% Mo-HZSM-5

The chemical state of Mo and C in fresh 15% Mo/HZSM-5 and catalyst after various pretreatments followed by reaction runs are presented in Figure 8. The XPS peaks of 15% Mo-HZSM-5 catalyst (Figure 8a) in Mo 3d region exhibits doublet peaks at 232.5 eV (Mo (3d_{5/2}))

and 235.7 eV (Mo ($3d_{3/2}$)) which are assigned to the formation of MoO_3 on the surface of the catalyst.^{50,70}

Presence of such Mo^{+6} species as orthorhombic MoO_3 is quite obvious, as its formation was also observed in the XRD characterization (Figure 2b). The analogous C1s XPS spectra for this catalyst has shown peaks at 284.6 eV, which is attributed to adventitious or graphite-like carbon present on the surface as well as in the zeolite channels of the catalyst.^{7,70,71} The two major doublet peaks at 228.7 (Mo ($3d_{5/2}$)) and 232.5 eV (Mo ($3d_{3/2}$)) in Mo 3d XPS spectra of 15% Mo/HZSM-5-B and 15% Mo/HZSM-5-C (Figures 8c and 8d) catalysts after MDA reaction for 3 h is attributed to the formation of $\beta\text{-Mo}_2\text{C}$.^{3,7,72–74} The analogous C 1s XPS profile of these two catalysts exhibited peaks at 282.8 eV and 284.6 eV which are attributed to carbidic carbon and graphitic carbon/coke, respectively.^{3,7,70–74} Since during induction period and methane carburization in MDA reaction, Mo species follow the order ($\text{MoO}_3 \rightarrow \text{MoO}_2 \rightarrow \beta\text{-Mo}_2\text{C}$) over zeolite surface hence, we assign these carbidic/graphitic carbon/coke associated with $\beta\text{-Mo}_2\text{C}$ deposited on the surface of the catalyst. This justification is well in agreement with the $\beta\text{-Mo}_2\text{C}$ phase formation evident in XRD profile (Figure 2) of catalysts pretreated with N_2 and H_2 . Weckhuysen *et al.*,⁷ employed angle-resolved XPS technique and reported that peak at 284.6 eV corresponds to adventitious or graphitic C and is mainly present in the zeolite channel. Our investigations suggest that adventitious or graphitic cokes are first formed on the surface of zeolite, and during the course of reaction they are profusely formed at the pore entrance of catalyst preventing the primary ethylene products to reach to active sites and aromatize further. During the course of the reaction, their concentration increases inside channels, leading to a continuous drop in benzene selectivity and increase in coke selectivity, as evident in Figures 1b and 1c. However, the Mo 3d XPS peak over the 15% Mo/HZSM-5-A (Figure 8b) is shifted to 225.0 eV, Mo ($3d_{5/2}$) and 228.2 eV, Mo ($3d_{3/2}$) which are lower than the Mo_2C peak. This peak shift towards lower binding energy suggests that less molybdenum coordinated carbon atom is probably present in ($\alpha\text{-MoC}_{1-x}$). The $\alpha\text{-MoC}_{1-x}$ phases were also observed in the XRD analysis as shown in Figure 2c, hence we suggest that this peak is due to the formation of $\alpha\text{-MoC}_{1-x}$.⁷ The C 1s peak at 285.6 eV in 15% Mo-HZSM-5-A is due to the formation of aromatic-aliphatic coke present in the catalyst.^{7,36,37,75} The combined comparative findings from TG/DTA, TPO and XPS conclude that concentration of inert coke types with high temperature burn-off is more pronounced in H_2 and N_2 pretreated catalyst compared to 15% Mo/HZSM-5-A. Crystallinity and BET

surface area of the 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C are lower than the 15% Mo/HZSM-5-A and the micropore surface area of the catalyst A is higher than the other two catalysts. This gives the strong evidence that decrease in micropore surface area is due to the formation of coke deposited inside the zeolite channels.

4. Conclusions

The effect of pretreatment strongly influences the methane conversion and product selectivity in non-oxidative MDA reaction. The pretreatment of the $\text{MoO}_3/\text{HZSM-5}$ catalyst with $\text{CH}_4 + \text{H}_2$ at 550 °C for 4 h leads to the formation of monoclinic MoO_2 and partially carbonized $\text{MoO}_x\text{H}_y\text{C}_z$ sites. These sites act as precursors and are prerequisites for the formation of highly active metastable *fcc* ($\alpha\text{-MoC}_{1-x}$) phases co-existing with MoC_xO_y in MDA reaction. Pretreatment of catalyst increases the exchangeability of MoO_x species with Brønsted acid sites. The activation of methane and primary product (ethylene) formation take place on the $\alpha\text{-MoC}_{1-x}$ or MoO_xC_y active sites followed by aromatization over Brønsted acid sites. H_2 and N_2 pretreated catalysts showed the major formation of *hcp* $\beta\text{-Mo}_2\text{C}$ species which is found to be a less active phase in MDA reaction. The catalytically active $\alpha\text{-MoC}_{1-x}$ phase over 15% Mo-HZSM-5-A is more immune to coke formation than $\beta\text{-Mo}_2\text{C}$ phase over 15% Mo-HZSM-5-B and 15% Mo-HZSM-5-C. Molybdenum associated coke formed on the zeolite surface were burnt-off endothermally at lower temperature. Molybdenum associated coke with Brønsted acid sites and coke formed on the vacant Brønsted acid sites are burnt-off at higher temperature due to their location in the zeolite channels. Hydrogen-poor coke, which is formed on the Brønsted acid sites, leads to catalyst deactivation. Catalyst containing $\alpha\text{-MoC}_{1-x}$ and molybdenum oxycarbide species associated with vacant Brønsted acid sites play a major role in high conversion, product selectivity and catalyst stability in the MDA reaction.

Supplementary Information (SI)

Figure S1 as Supplementary Information is available at www.ias.ac.in/chemsci.

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