Genesis of methane activation sites in Mo-exchanged H–ZSM-5 catalysts

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Dedicated to the late Werner O. Haag in appreciation of his outstanding contributions to heterogeneous catalysis and zeolite science

Abstract

Exchanged (MoO₂)₇²⁻ dimers form during treatment in air of MoO₃/H–ZSM-5 (Si/Al = 14.3) physical mixtures at 773–973 K. The amount of water desorbed during exchange and the number of residual protons (measured by D₂–OH exchange) showed that each Mo⁶⁺ replaces 1.1 (± 0.1) protons in H–ZSM-5 (for Mo/Al < 0.37). ²⁷Al NMR, X-ray absorption, and Raman spectra confirmed the proposed (MoO₂)₇²⁻ structure and its location at zeolite exchange sites. When the Mo content exceeds that required to form a MoO₃ bilayer on the external zeolite surface (Mo/Al > 0.5), MoOₓ sublimes or forms Al₂(MoO₄)₃ by extracting framework Al. Al₂(MoO₄)₃ domains reduce slowly and lead to low CH₄ reaction rates. The rate of hydrocarbon synthesis from CH₄ at 930–973 K increased as exchanged MoOₓ dimers reduce and carburize during CH₄ reactions. About 2.5 O atoms per Mo (± 0.1) are removed as CO, CO₂, and H₂O during activation, suggesting that all but the zeolite framework oxygen atoms are removed during activation. Reduction and carburization rates depend on Mo content and on the rate of removal of CO, CO₂, and H₂O, which inhibit reduction/carburization steps.

Hydrocarbons were not detected during the initial removal of about one O per Mo, but ethylene, benzene, naphthalene, and H₂ formation rates increased as larger amounts of O were removed during CH₄ reactions. CH₄ reactions require initial activation of CH₄ on MoOₓ, but with the retention of C-atoms to form MoCₓ. These MoCₓ then activate C–H bonds and desorb the hydrocarbons formed, which then oligomerize and cyclize via rapid bifunctional pathways on H⁺ and MoCₓ sites within constrained ZSM-5 channels. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Mo carburization; Mo/H–ZSM-5; Mo structure; Pyrolysis

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1. Introduction

Cation-exchanged H-ZSM-5 materials are widely used as catalysts for the activation of light alkanes [1–3]. Steric constraints imposed by zeolite channels limit chain growth and prevent the formation of large aromatics, which can lead to deactivation and to loss of selectivity during alkane conversion reactions. Recently, Mo/H-ZSM-5 has been shown to convert CH₄ to equilibrium benzene yields at 973 K, without significant yields of products larger than naphthalene [4–6]. Mo/H-ZSM-5 catalysts have been prepared by slurry or incipient wetness impregnation of H-ZSM-5 with aqueous ammonium heptamolybdate [AHM; (NH₄)₆Mo₇O₂₄·4H₂O], followed by treatment in air at high temperatures (723–973 K) [4–7]. Large hydrated molybdate ions, however, do not exchange directly onto H-ZSM-5 during aqueous exchange or impregnation [8]. Infrared spectroscopy and differential thermal analysis [9] suggested that AHM decomposes in air between 500 and 630 K to form MoO₃ crystallites on external zeolite surfaces [10,11]. At about 773 K, MoO₃ infrared bands disappear as MoO₃ crystallites desperse on external ZSM-5 surfaces, and ultimately migrate and exchange within zeolite channels [9]. As isolated MoO₃ species migrate into ZSM-5 channels via vapor or surface diffusion, they anchor at cation exchange sites by replacing protons in H-ZSM-5. Dealumination and loss of ZSM-5 crystallinity occur concurrently with this exchange process and they lead to the loss of acidic protons. MoO₃ species within zeolite channels are precursors to the active sites required for non-oxidative CH₄ aromatization. MoO₃/H-ZSM-5 catalysts show very low initial CH₄ aromatization rates at 973 K, but the reduction and carburization of highly dispersed MoO₃ species into molybdenum carbide lead to the initial conversion of CH₄ to CO₂ H₂, and H₂O, and to significantly higher CH₄ aromatization rates after 0.2–1.0 h on stream [5,6]. MoC₃ species convert CH₄ into ethane and ethylene, which then react to form C₆H₆ aromatics on acid sites via rapid oligomerization, cracking, and cyclization reactions. These reactions also benefit from the hydrogen removal function provided by MoC₃ sites via pathways similar to those reported on Ga- and Zn-exchanged H-ZSM-5 [12]. Previous CH₄ activation studies on MoO₃/H-ZSM-5 used chromatographic methods in order to measure the initial rate increase and the concurrent reduction and carburization after initial contact of MoO₃/H-ZSM-5 precursors with CH₄. The time resolution of such methods was, however, very low (0.5 h) because of the time required for chromatographic analyses [5,6,13]. These studies showed that H₂O, CO₂, and CO are the predominant gas-phase products until reduction-carburization processes are complete; thereafter, benzene, naphthalene, and ethylene become the most abundant products during steady-state catalysis. The lack of detailed measurements of the extent and rate of reduction and carburization during this initial carburization process has led to conflicting proposals about the structure and the stoichiometry of the Mo active sites required for C–H bond activation. X-ray photoelectron spectroscopy suggested that Mo₃C species exist in activated catalysts [6]. MoO₃/C₃H₈ species were proposed based on CH₄ reaction rates on partially oxidized Mo₃C/H-ZSM-5 catalysts [14]. In this study, MoO₃/H-ZSM-5 was prepared by solid-state exchange methods using physical mixtures of MoO₃ and H-ZSM-5. This synthesis method eliminates the evolution of large amounts of N₂, NH₃, and H₂O during subsequent air treatment [9] and it allows accurate measurements of the nature and rate of MoO₃ exchange from the water evolved from condensation reactions of OH groups. Our study addresses the synthesis of MoO₃/H-ZSM-5 from mixtures of MoO₃ and H-ZSM-5, and the structure and density of Mo and acid sites in both catalyst precursors and active catalysts. We also report here detailed measurements of the rate of oxygen removal and of the rate and selectivity of CH₄ conversion during the activation of MoO₃/H-ZSM-5 precursors with a wide range of Mo content (MoO₃/Al₂O₃=0–0.68).

2. Experimental

NH₄[ZSM-5 was prepared by sequential aqueous exchange of Na/ZSM-5 (Zeochem, Si/Al=...
The effect of thermal treatment in air on the structure and catalytic properties of MoO$_3$/H-ZSM-5 samples was examined using MoO$_3$/H-ZSM-5 mixtures (0.3 g, 0.8 wt% Mo; Mo/Al = 0.87) dried at 623 K for 24 h in 20% O$_2$/Ar (100 cm$^3$/min). Samples were heated at 0.16 K s$^{-1}$ to 973 K and H$_2$O evolution rates were measured by mass spectrometry (Leybold Inficon, TPH-TS200) with a time resolution of 2 s using CH$_4$ measured by mass spectrometry (Leybold Inficon, 0.16 K s$^{-1}$). The number of H atoms remaining as OH groups with the displacement of Al cations was reported in detail previously [1]. Al NMR procedure was reported in detail previously [13]. Tetrahedral Al in the ZSM-5 framework has a chemical shift of 56 ppm [relative to dilute Al(NO$_3$)$_3$ solutions], octahedral extra-framework Al species in ZSM-5 and Al$_2$O$_3$ show no chemical shift and Al$_2$(MoO$_4$)$_3$ (octahedral Al, tetrahedral Mo centers) shows an NMR line at -13 ppm [15].

The rate of carburization of MoO$_3$/H-ZSM-5 samples was measured at 950 K after treating exchanged MoO$_3$/H-ZSM-5 samples at 950 K in 20% O$_2$, He (100 cm$^3$/min, Matheson, >99.99% purity) for 0.5 h. The samples were flushed with He (100 cm$^3$/min), then exposed to reactants (CH$_4$/Ar = 1:1, 100 cm$^3$/min, Praxair Inc., 99.995% purity). Argon was used as an internal standard in order to calculate the rates of CH$_4$ conversion and of CO$_2$, H$_2$, H$_2$O, and hydrogen carbonation, and the amount of carbon left on the catalyst and in the transfer lines. The effluent was sampled into a mass spectrometer (Leybold-inficon) through a differentially pumped chamber and a capillary leak tube in order to avoid mass discrimination. Accurate measurements of multiple species with overlapping mass fragmentation patterns required deconvolution of the mass spectra using fragmentation patterns and calibrated response factors for each product, as described in detail elsewhere [16].

3. Results and discussion

3.1. Structure and density of MoO$_3$ species formed from MoO$_3$/H-ZSM-5 physical mixtures

CH$_4$ reaction rates on Mo/H-ZSM-5 samples prepared by solid-state reactions of MoO$_3$/H-ZSM-5 physical mixtures [13] and on samples prepared by impregnation of H-ZSM-5 with aqueous AHM [6] were very similar [13]. During treatment in air at high temperatures (~973 K), MoO$_3$ species in both samples spread on external zeolite surfaces and then migrated into zeolite channels and replaced H$^+$ present at cation exchange sites [13].

H$_2$O evolution was detected between 673 and 973 K during temperature-programmed oxidation (TPO) of MoO$_3$/H-ZSM-5 mixtures, even after physisorbed water was completely removed by drying samples at 623 K for 24 h (Fig 1). Below 740 K, the rate and amount of H$_2$O evolved did not depend on Mo content (Fig 2), suggesting that it arises from the condensation of neighboring OH groups with the displacement of Al cations from their crystallographic positions in the ZSM-5 framework [17]. Between 740 and 840 K, H$_2$O desorption rates increase with increasing Mo content (Fig 2). This desorption feature reflects...
Elemental analysis of samples after treatment in air showed that samples containing more than 2 wt% Mo lost some MoO$_x$ due to sublimation (Table 1). In the rest of this paper, initial Mo concentrations will be used when discussing treatments of the starting physical mixtures; Mo concentrations in the final MoO$_x$/H–ZSM-5 samples will be used in describing all characterization and catalytic studies after synthesis. Initial and final Mo contents for each sample are shown in Table 1.

The initial H$_2$O desorption rates (between 740 and 840 K) were very similar on MoO$_3$/H–ZSM-5 mixtures containing 4 and 8 wt% Mo (Figs. 1 and 2). At higher temperatures, however, the curve for the 8 wt% Mo sample diverges from those for samples with 1–4 wt% Mo (Fig. 1). Elemental analysis after treatment in air at 973 K for 0.5 h showed that about 19.3% of the Mo in the mixture sublimed and formed small MoO$_3$ crystallites on the reactor walls just outside the heated zone (Table 1). X-ray diffraction and N$_2$ physisorption results showed significant loss of zeolite crystallinity and micropore volume on the sample with the highest Mo content [13]. $^{27}$Al NMR spectroscopy showed that this sample contained only Al$_2$(MoO$_4$)$_3$ domains after treatment. Samples with less Mo (1–4 wt%), however, did not show any NMR lines characteristic of Al$_2$(MoO$_4$)$_3$ [13]. The unusual H$_2$O evolution profile for the sample with the highest Mo content (Fig. 1) reflects the extraction of Al from crystallographic framework positions in ZSM-5 to form stable Al$_2$(MoO$_4$)$_3$ domains with the concomitant collapse of zeolite channels. These structural changes occur above 840 K and they lead to the unusual H$_2$O evolution curves on mixtures with high Mo content (Figs. 1 and 2). The formation of Al$_2$(MoO$_4$)$_3$ domains and the loss of zeolite crystallinity was previously reported on MoO$_3$/H–ZSM-5 samples with 3–15 wt% Mo prepared by aqueous methods and treated in air at 773–973 K [15]. Mixtures with Mo contents below about 5 wt% form MoO$_3$ monolayers on external zeolite surfaces (~25 m$^2$ g$^{-1}$), which gradually migrate within zeolite channels to form anchored (MoO)$_n$ species [13]. Excess MoO$_3$ remains as

![Fig. 1](image1.png)

**Fig. 1** H$_2$O desorption between 623 and 973 K from MoO$_3$/H–ZSM-5 mixtures with varying Mo initial concentration (0.3 g, 100 cm$^3$/min, 20% O$_2$–Ar, heat at 0.16 K s$^{-1}$, hold at 973 K for 0.5 h).

![Fig. 2](image2.png)

**Fig. 2** H$_2$O desorption rate during TPO of MoO$_3$/H–ZSM-5 mixtures at 740 and 840 K (from Fig. 1) Mo/Al ratios are as prepared. Mo concentrations after TPO are shown in Table 1.

the replacement of H$^+$ species by Mo-oxo cations and the anchoring of MoO$_3$ species via condensation reactions [13].
Table 1
Mo content of MoO$_3$/H–ZSM-5 mixtures before and after air treatment to 973 K (0.5 h), and micropore volume (from N$_2$ physisorption at 77 K) of treated samples

<table>
<thead>
<tr>
<th>Mo in mixture (wt%)</th>
<th>Mo/Al ratio$^a$</th>
<th>Mo content after preparation (wt%)</th>
<th>Mo/Al ratio after preparation</th>
<th>Micropore volume (cm$^3$/g ZSM-5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.128</td>
</tr>
<tr>
<td>1</td>
<td>0.11</td>
<td>1.07</td>
<td>0.11</td>
<td>0.119</td>
</tr>
<tr>
<td>2</td>
<td>0.21</td>
<td>2.00</td>
<td>0.20</td>
<td>0.120</td>
</tr>
<tr>
<td>4</td>
<td>0.42</td>
<td>3.60</td>
<td>0.37</td>
<td>0.107</td>
</tr>
<tr>
<td>8</td>
<td>0.87</td>
<td>6.34</td>
<td>0.68</td>
<td>0.059</td>
</tr>
</tbody>
</table>

$^a$ Mo/Al ratio calculated from wt% Mo and Si/Al ratio (14.3) of H-ZSM-5.

decreased as the Mo content increased, even for samples with low Mo content (1–4 wt%: Fig. 3). Water evolution from pure H ZSM-5 at 673–973 K reflects the condensation of next-nearest neighbor hydroxyl groups at Al sites to form Al–O–Al species that cannot remain in the tetrahedral symmetry required by the zeolite framework. The loss of Brønsted acid sites occurs concurrently with the local disruption of the zeolite structure, which distorts Al centers from their pure tetrahedral symmetry and causes, at even higher temperatures, the nucleation of Al$_2$O$_3$ domains with octahedral Al centers. These hydroxyl condensation events also occur in MoO$_3$/H–ZSM-5 mixtures during treatment in air. Therefore, we have estimated the framework Al centers (Al$_F$) remaining in MoO$_3$/H–ZSM-5 samples by subtracting the number of Al atoms extracted from the framework (from the H$_2$O evolved from H–ZSM-5) from the total number of Al atoms in the sample (Si/Al = 14.3). This corrected Al$_F$ content is used in reporting hydroxyl densities as H/Al$_F$ (Table 2).

The exchange of D$_2$O with H–ZSM-5 after aqueous exchange of H$^+$ by Zn$^{2+}$ cations [12].

small crystallites, which sublime as MoO$_3$ oligomers or melt. Either process leads to their migration within zeolite channels where they provide nucleation sites for the formation of thermodynamically stable, but catalytically inactive, Al$_2$MoO$_7$$_3$ domains.

The intensity of $^{27}$Al NMR lines corresponding to Al centers at tetrahedral framework positions and containing O–H groups ($\delta = 56$ ppm)

![Fig. 3. Number of acids sites (H) or framework Al (Al$_F$) remaining per total Al for series of Mo/H–ZSM-5 samples after TPO and TPR treatment to 973 K (0.5 h) measured by $^{27}$Al NMR, D$_2$O–H, and H$_2$O–D. Reported Mo/Al ratios are after air treatment to 973 K, 0.5 h.](image)
OH groups decreased linearly with increasing Mo content, suggesting that each MoO\(_x\) species replaces a single H\(^+\) in physical mixtures with 1–4 wt% Mo. These data also suggest that the nature of exchanged Mo species is similar in all samples with 1–4 wt% Mo (Mo/Al=0–0.42). Fig. 5 shows the number of OH/Al replaced by MoO\(_3\) during exchange (from H\(_2\)O desorption) and the number of remaining OH/Al remaining after exchange (from D\(_2\) exchange) as a function of the Mo/Al ratio in the samples. The sum of the remaining OH groups and those removed is very similar in all samples and about equal to the number of OH groups remaining after treatment in air on pure H-ZSM-5. The materials prepared by exchange from physical mixtures of MoO\(_3\) and H-ZSM-5 show a single type of MoO\(_x\) species, something that is rarely achieved in the synthesis of heterogeneous catalysts.

The amount of water evolved between 673 and 973 K during treatment of MoO\(_3\)/H-ZSM-5 mixtures in air shows that each MoO\(_x\) replaces O–H groups with a stoichiometry of 1±0.2 H/Mo for mixtures containing 1–4 wt% Mo (Table 2; Figs. 3 and 4).

### Table 2

<table>
<thead>
<tr>
<th>Mo content after TPO (wt%)</th>
<th>Mo/Al ratio</th>
<th>H(_2)O desorption</th>
<th>Residual H content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H/Al(^a)</td>
<td>H/Al(^b)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.029</td>
<td>0.060</td>
</tr>
<tr>
<td>1.0</td>
<td>0.11</td>
<td>0.347</td>
<td>0.118</td>
</tr>
<tr>
<td>2.0</td>
<td>0.20</td>
<td>0.474</td>
<td>0.245</td>
</tr>
<tr>
<td>3.6</td>
<td>0.37</td>
<td>0.686</td>
<td>0.457</td>
</tr>
<tr>
<td>6.3</td>
<td>0.68</td>
<td>0.665</td>
<td>0.436</td>
</tr>
</tbody>
</table>

\(^a\) From integrated area of H\(_2\)O desorption above 623 K (Fig. 1).

\(^b\) Subtract value in column to the left from that for H-ZSM-5 (0 wt% Mo).

\(^c\) Divide value in column to the left by Mo/Al ratio.
These data, the requirement for charge balance, 
\(^{27}\text{Al}\) NMR [13] and X-ray absorption [18] results previously reported show that MoO\(_x\) species exist at exchange sites as isolated (MoO\(_x\)\(^{3}\))\(^{2-}\) ditectrahedra containing framework oxygen atoms associated with two Al sites. In contrast, samples prepared from mixtures initially containing 8 wt% Mo (6.24 wt% after exchange) give a replacement stoichiometry of H/Mo ratio of 0.64, in agreement with the value expected for the formation of \(\text{Al(MoO}_3\text{)}_2\) domains (H/Mo = 0.67).

3.2. Activation of MoO\(_x\)/H–ZSM-5 precursors during CH\(_4\) reactions

(MoO\(_x\)\(^{3}\))\(^{2-}\) dimers formed during synthesis do not catalyze CH\(_4\) conversion to hydrocarbons, but they form active Mo–C centers by using CH\(_4\) to reduce and carburize MoO\(_x\) species at 950–1000 K [13], as also reported by others [6,14]. Mass spectrometric analysis with matrix deconvolution of complex overlapping spectra was used in order to measure the evolution of reaction products and the kinetics of reduction and carburization of MoO\(_x\) precursors during the initial contact with CH\(_4\). The time resolution of the data was about 2 s. A deconvolution matrix was developed from the mass spectra of each product detected by gas chromatography. Response factors were obtained by matching the product yields obtained by mass spectrometry with quantitative analyses by gas chromatography using flame ionization and thermal conductivity detection [16].

Reactant (CH\(_4\)) and product (H\(_2\), H\(_2\)O, CO, CO\(_2\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_6\), C\(_3\)H\(_8\), benzene, toluene, naphthalene) concentrations were measured on MoO\(_x\)/H–ZSM-5 (0.5 g) prepared from mixtures with 1–8 wt% Mo using a 50% CH\(_4\)/Ar mixture (100 cm\(^3\)/min) at 950 K. Typical results are shown in Fig. 6 for one of the MoO\(_x\)/H–ZSM-5 samples (3.6 wt% Mo); the trends on the other samples were similar. In all MoO\(_x\)/H–ZSM-5 samples, CO\(_2\) and H\(_2\)O formed as the predominant initial products. These products form via reactions of CH\(_4\) with O-atoms in MoO\(_x\) precursors. As O-atoms in MoO\(_x\) are depleted by reduction, CO and H\(_2\) become the predominant gas-phase products. Hydrocarbons ultimately become the cata-lytic products of CH\(_4\) reactions as oxygen removal rates decrease; C\(_2\), C\(_3\), and aromatics (benzene, toluene and naphthalene) were detected in the gas phase as CO and H\(_2\) formation rates decreased. As isolated molybdenum carbide species are formed, catalytic CH\(_4\) conversion begins, producing C\(_2\)H\(_4\) products. C\(_2\)H\(_4\) is then rapidly converted to aromatics on acid sites in H–ZSM-5.

The total amount of oxygen removed as CO\(_2\), CO\(_2\), and H\(_2\)O reflects the extent of reduction of (MoO\(_x\)\(^{3}\))\(^{2-}\) dimers. The oxygen removal rate and they form active Mo–C centers by using CH\(_4\) to reduce and carburize MoO\(_x\) species at 950–1000 K [13], as also reported by others [6,14]. Mass spectrometric analysis with matrix deconvolution of complex overlapping spectra was used in order to measure the evolution of reaction products and the kinetics of reduction and carburization of MoO\(_x\) precursors during the initial contact with CH\(_4\). The time resolution of the data was about 2 s. A deconvolution matrix was developed from the mass spectra of each product detected by gas chromatography. Response factors were obtained by matching the product yields obtained by mass spectrometry with quantitative analyses by gas chromatography using flame ionization and thermal conductivity detection [16].

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Fig. 6. Desorption rates of products during start-up period of CH$_4$ activations (0.5 g, 3.6 wt% Mo/H-ZSM-5, 950 K, 100 cm$^3$/min 1:1 CH$_4$/Ar).

Fig. 7. Total desorption rates of all oxygen-containing compounds (top, mol O/atom Mo-s) and the cumulative oxygen removed (O$_{\text{rem}}$/Mo, bottom) versus time during the start-up period of CH$_4$ activation (0.5 g, 950 K, 100 cm$^3$/min 1:1 CH$_4$/Ar).

Sample with the highest Mo content (6.3 wt%), which contains predominantly Al$_2$(MoO$_4$)$_3$ domains. Yet, the amount of oxygen removed (O$_{\text{rem}}$/Mo $\approx$ 2.5) is similar to that on samples containing exchanged Mo dimers, instead of that expected from the complete reduction of Mo$^{VI}$ to Mo$^0$ in Al$_2$(MoO$_4$)$_3$ domains. These results suggest that such domains retain some Mo--O--Al bonds during reduction and carburization in CH$_4$ at 973 K. Bulk Al$_2$(MoO$_4$)$_3$ is difficult to reduce in H$_2$ or CH$_4$ atmospheres below 1000-1200 K [19]. Dispersed Al$_2$(MoO$_4$)$_3$ species in H-ZSM-5, however, reduce and carbure during the initial stages of CH$_4$ conversion reactions, albeit much more slowly than (MoO$_2$)$_2^+$ species. Bulk Al$_2$(MoO$_4$)$_3$ appears to lack the C--H bond activation sites required to initiate reduction/carbure reactions in CH$_4$ atmospheres. This suggests that coor-
Table 3 shows CH₄ conversion rates and product selectivities on all Mo/H–ZSM-5 samples used in this study. The similar CH₄ conversions observed on MoOₓ/H–ZSM-5 samples with 1.1–3.6 wt% Mo reflect the near-equilibrium conditions achieved at the reactor exit on all samples. As a result, apparent CH₄ conversion rates (per Mo) decrease with increasing Mo content. The lower CH₄ conversions reached on the sample with the highest Mo content (6.3 wt%) appear to reflect the formation of poorly dispersed Mo₅O₁₇ species present in the 6.3 wt% Mo/H–ZSM-5 sample.

Table 3

<table>
<thead>
<tr>
<th>Catalyst (wt% Mo)</th>
<th>1.1</th>
<th>2.0</th>
<th>3.6</th>
<th>6.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ conversion (%)</td>
<td>10.7</td>
<td>13.2</td>
<td>11.1</td>
<td>3.4</td>
</tr>
<tr>
<td>CH₄ conversion rate (10⁻² CH₄/Mo-s)</td>
<td>6.12</td>
<td>3.66</td>
<td>1.60</td>
<td>0.22</td>
</tr>
<tr>
<td>Selectivity (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₄</td>
<td>8.2</td>
<td>7.6</td>
<td>8.2</td>
<td>10.2</td>
</tr>
<tr>
<td>C₆–C₁₀ aromatics</td>
<td>87.6</td>
<td>88.8</td>
<td>88.9</td>
<td>84.7</td>
</tr>
<tr>
<td>C₂H₄/aromatics ratio</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The rapid removal of C₂H₄ (via aromatization) removes thermodynamic and kinetic constraints that would otherwise limit CH₄ conversion to about 3.8% at 950 K. The similar trends observed when conversion is varied by varying reactor residence time or the number of active sites (via deactivation) show that deactivation removes active sites from the catalyst without any changes in the catalytic properties of the remaining active sites.

Fig. 8 shows product selectivities on 4 wt% Mo/H–ZSM-5 at 950 K as a function of conversion. CH₄ conversion varied by changing the reactor residence time and by allowing the catalyst to deactivate during CH₄ reactions. These selectivity-conversion curves demonstrate that CH₄ reacts sequentially to form C₂H₄ as initial reactive products, C₂H₆ as a secondary product, and naphthalene as the kinetic end point (except for its slow reduction and carburization of Al₂(MoO₄)₃ species present in the reaction time).

The accompanying steric constraints limit chain growth to naphthalene and larger molecules.
3.3. Evolution of CH₄ conversion rates during reduction and carburization

The effect of the amount of oxygen removed on CH₄ conversion and product formation rates is shown in Fig. 9 for the 1 wt% MoOₓ/H–ZSM-5 sample and in Figs. 10 and 11 for all MoOₓ/H–ZSM-5 catalysts. The rate of methane conversion increases markedly with the initial removal of oxygen from the catalyst, but the predominant products are H₂ (Fig. 9), CO (Fig. 9), CO₂, and H₂O. After removal of about one O atom per Mo, the rate of reduction/carburization decreases and the rate of formation of hydrocarbons begins to increase until it reaches maximum ethylene and benzene formation rates as the amount of oxygen removed (O/Mo) reaches 1.5–1.9. This behavior suggests that the reduction proceeds in two steps. The first step involves the reduction of Mo⁶⁺ to Mo⁴⁺ with the formation of sites that activate methane but which do not desorb hydrocarbon fragments, but instead retain C atoms from CH₄ and release H atoms as H₂. The second reduction step is slower and it leads directly to the formation of sites active for methane conversion, but these sites form sequentially along the catalyst bed, because of the inhibition of reduction/carburization processes by the oxygen-containing products of this reaction. Maximum rates of formation of benzene and ethylene are achieved before complete reduction/carburization takes place because deactivation has decreased the conversion rates by the time the entire bed has been carburized and the last remaining oxygen atoms have been removed. An alternate explanation is that sites that activate C–H bonds and allow the removal of adsorbed hydrocarbons before complete dehydrogenation to carbon require the presence of some residual O-atoms in MoCₓ species. Such species, however, appear to reduce further and they cannot be maintained during CH₄ conversion reactions.

The removal of only 2.5 O/Mo suggests that either Mo⁺ [specifically (MoCₓHₓ)⁺] species remain anchored at one Al site or that Mo⁰ species during reduction. Mo⁰–O bonds have been detected in radial distribution functions derived...
increase initially without a concomitant increase in the rate of formation of hydrocarbon products (Fig. 10). CO\textsubscript{x} and H\textsubscript{2}O also form initially as MoO\textsubscript{x}/H–ZSM-5 samples reduce and carburize during contact with CH\textsubscript{4} at 973 K. Samples with 1.1 and 2.0 wt% Mo start to form hydrocarbons after the removal of about one oxygen atom per Mo (Fig. 11). Samples with higher Mo content appear to require a greater extent of reduction before hydrocarbons can be formed at significant rates. Maximum rates are obtained at intermediate times on stream for all samples because side reactions leading to carbon formation deactivate MoC\textsubscript{x} sites formed during the initial induction period. Deactivation influences the rate of benzene formation more strongly than the rate of ethylene formation because of the sequential nature of the reaction pathways illustrated by the data in Fig. 8. In effect, deactivation decreases CH\textsubscript{4} conversion levels and the effective reactive residence time of molecules within the catalyst bed. As a result, it moves the product distribution towards the initial products of the reaction sequence.

The effect of space velocity (defined as moles CH\textsubscript{4} fed per g-atom Mo-s) is shown in Fig. 12 for the 3.6 wt% Mo/H–ZSM-5 sample. As the space velocity increases from 0.16 s\textsuperscript{-1} to 0.65 s\textsuperscript{-1}, the initial reduction/carburization rate increases (Fig. 12) and it approaches the rates measured on a sample with lower Mo content at the higher value of the space velocity (1.07 wt% Mo; 0.61 s\textsuperscript{-1}). These data are consistent with the explanation that reduction rates are inhibited by the products of reduction/carburization steps, as discussed previously. Interestingly, the sample with 3.6 wt% Mo activates more slowly than that with 1.07 wt% Mo, even when the space velocity is maintained at similar values (0.65 versus 0.61 s\textsuperscript{-1}). This reflects diffusional restrictions within zeolite crystallites (~1–2 m diameter), which cause gradients in the concentration of H\textsubscript{2}O and CO\textsubscript{2} within crystals as MoO\textsubscript{x} precursors reduce and carburize. The higher MoO\textsubscript{x} content in the 3.6 wt% sample leads to more severe intraparticle gradients and to a stronger inhibitory effect of products, even when reactor residence times are similar. A qualitative assessment of the severity of intraparticle gradients using the Weisz–Prater criterion [22] supports this conclusion.
Increasing the space velocity also influences ethylene (Fig. 12) and benzene (Fig. 12) formation rates. The delay initially observed on the 3.6 wt% Mo/H-ZSM-5 samples is markedly shortened when the space velocity is increased from 0.16 to 0.65 s\(^{-1}\) and formation rates approach those measured on the 1.07 wt% Mo samples at similar space velocity (0.61 s\(^{-1}\)). The remaining differences between the two samples at similar space velocities reflect the diffusional restrictions discussed in the previous paragraph.

3.4. Stoichiometry and properties of active Mo species during CH\(_4\) conversion

In this section, the carbon and hydrogen contents of MoC\(_x\) species and of strongly bound carbonaceous deposits on Brønsted sites within zeolite channels are reported from measurements of the amounts of carbon removed during treatments in H\(_2\) and air after CH\(_4\) reactions at 950 K for 2 h. The initial CH\(_4\) reaction rates on deactivated MoO\(_x\)/H-ZSM-5 catalysts can be restored by a treatment in pure H\(_2\) at reaction temperatures (950 K), without the recurrence of an activation period [14]. This method restores near-equilibrium methane conversions, without requiring the complex temperature cycling involved in O\(_2\) regeneration procedures used to remove carbon deposits and restore MoO\(_x\) species [6]. Product selectivities at a given CH\(_4\) conversion were identical on fresh and H\(_2\)-regenerated catalysts. After extensive deactivation (~700 h on stream), initial rates could not be restored by H\(_2\) at 950 K, but treatment in a 20% O\(_2\)-Ar mixture as the temperature is raised from 300 to 950 K at 0.16 K s\(^{-1}\) removed all carbon deposits and restored both the initial CH\(_4\) conversion rates and selectivities and the activation period. Thus, it appears that long-term deactivation arises from carbon deposits and not from irreversible structural changes in ZSM-5 or MoC\(_x\) sites. H\(_2\) removes carbon species responsible for the initial deactivation, but oxidation reactions are required in order to remove more refractory forms of carbon that form slowly during CH\(_4\) conversion.

The amount of carbon removed during H\(_2\) treatment (predominantly as CH\(_2\)) is much smaller than that removed during subsequent treatment in 20%
Table 4 was calculated from the sum of the CH$_4$ formed during H$_2$ treatment and the CO$_x$ formed during temperature-programmed treatments in H$_2$ (TPR) and 20% O$_2$–He (TPO) (0.5 g, 100 cm$^3$/min, 0.16 K s$^{-1}$, carburized for 2 h in 1:1 CH$_4$/Ar; TPR: 5% H$_2$–Ar, TPO: 20% O$_2$–He).

<table>
<thead>
<tr>
<th>Carbon removed (C/Mo ratio)</th>
<th>(Mo wt%)</th>
<th>Mo/Al</th>
<th>0.106</th>
<th>0.217</th>
<th>0.388</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPR CH$_4$ produced</td>
<td>1.70</td>
<td>1.31</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPO CO$_2$</td>
<td>17.0</td>
<td>6.34</td>
<td>2.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPO CO$_2$</td>
<td>25.3</td>
<td>10.7</td>
<td>5.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPO H$_2$O</td>
<td>5.35</td>
<td>2.58</td>
<td>1.42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TPO Total</td>
<td>42.3</td>
<td>17.0</td>
<td>8.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>44.0</td>
<td>18.3</td>
<td>9.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ C/Mo is the ratio of carbon atoms per Mo atom.

Fig. 13. TPO of MoC$_x$/H-ZSM-5 after carburization in CH$_4$–Ar at 950 K; 2 h (1–4 wt% Mo, 0.16 K s$^{-1}$, 100 cm$^3$/min 20% O$_2$–Ar) (after (1) 2 h carburization 100 cm$^3$/min 50% CH$_4$/Ar, 950 K; (2) 0.5 h reduction, 100 cm$^3$/min 20% H$_2$–Ar, 950 K; (3) 2 h carburization 100 cm$^3$/min 50% CH$_4$/Ar, 950 K; (4) TPR 973 K, 0.16 K s$^{-1}$, 100 cm$^3$/min 5% H$_2$–Ar).

O$_2$–Ar. (Table 4). The latter removes all carbon species (Fig. 13) and restores fully initial CH$_4$ reaction rates, including the initial activation process. Two distinct desorption features were observed for all products (CO, CO$_2$, and H$_2$O). The area under the peak at ~723 K decreases with increasing Mo content, whereas that of the peak at higher temperatures (~823 K) increases as acid site concentration increases. The total amount of carbon desorbed was calculated from the sum of the CH$_4$ formed during H$_2$ treatment and the CO$_2$ formed during oxidation (Table 4). MoC$_x$/H-ZSM-5 samples contain two types of sites: MoC$_x$ species at exchange sites and residual acid sites (H$^+$). Both types of sites are likely to contain carbon and hydrogen during CH$_4$ reactions at 950 K.

If MoC$_x$ and H$^+$ sites contain carbonaceous Mo (Mo wt% 1.1 2.0 3.6), the carbon balance is given by

\[
\frac{\text{C}}{\text{Mo}} = \frac{M\text{H}^+}{\text{Al}} + \frac{N\text{Mo}}{\text{Al}},
\]

where $M$ carbon atoms reside at acid sites and $N$ carbons at MoC$_x$ sites. The number of acid sites remaining in these catalysts after treatment at 973 K can be estimated from D$_2$–OH and $^2$H NMR results (see Fig. 3). Dividing both sides of Eq. (1) by the Mo/Al ratio gives:

\[
\frac{\text{C}}{\text{Mo}} = \frac{M\text{H}^+}{\text{Mo}} + N.
\]

Fig. 14 shows the total C/Mo ratio obtained in
the samples of this study as a function of the Brønsted acid site density from D$_2$−OH and $^{27}$Al NMR results (see Fig. 3). The linear relation shown in Fig. 14 suggests that Brønsted acid sites contain about 9.3 carbon atoms per Brønsted acid site. The y-intercept corresponds to 4.8 carbon atoms per Mo. The Brønsted acid site density measurements in Fig. 14 have an uncertainty of about ±0.05 [13], which translates to a range of 8.5–11.5 carbon atoms per H$^+$ and 4.0–6.8 carbon atoms per Mo. Weckhuysen et al. [23] reported the deposition of 10 carbon atoms per Mo on a 2 wt% Mo/H-ZSM-5 (Si/Al=25) after CH$_4$ reaction at 973 K for 13 h, but the study did not address the relative amounts associated with acid and Mo sites. Their results (filled square in Fig. 14) are well within the range of those obtained in this study. A similar analysis of the amount of hydrogen removed as H$_2$O during treatment in O$_2$/Ar led to values of about two hydrogen atoms per acid site and also about two hydrogen atoms per Mo. These values, however, may not reflect the actual hydrogen content during CH$_4$ reactions, because the intervening H$_2$ treatment may have altered the hydrogen content of these carbonaceous deposits.

This analysis suggests that surface carbons formed during CH$_4$ aromatization consist of species with nominal C$_{10}$H$_{21}$ stoichiometry on acid sites and with nominal C$_5$H$_2$ stoichiometry on Mo sites. The amount of carbon removed during TPR is proportional to the Mo concentration (Table 4), suggesting that the removal of only one or two C-atoms per Mo restores catalytic activity after H$_2$ regeneration by removing excess carbon from the MoC$_x$ sites required for C–H bond activation in CH$_4$. Guisnet et al. [24] have detected the presence of multi-ring aromatic carbocations (C$_{11}$–C$_{25}$) on acid sites in H-ferrierite by dissolving the zeolite after n-butene isomerization reactions at 673 K and extracting aromatic species with methyl chloride. These results, our measured C/H$^+$ ratio of about 10, and the size constraints of ZSM-5 channels (0.55–0.57 nm), suggest that acid sites in Mo/H-ZSM-5 are covered during CH$_4$ reactions at 950 K with highly unsaturated aromatic carbocations with an average stoichiometry corresponding to dehydrogenated naphthalene or methyl-naphthalene species. These ‘living carbocations’ are alkylated by alkenes formed from methane and lead to the formation of observed products via β-scission reactions, as also proposed for methanol conversion to hydrocarbons on H-ZSM-5 [25–27].

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References