Methane Conversion to Aromatics on Mo/H-ZSM5: Structure of Molybdenum Species in Working Catalysts

Weiping Ding,† Senzi Li, George D Meitzner,‡ and Enrique Iglesia*

Materials Sciences Division, E. O. Lawrence Berkeley National Laboratory, and Department of Chemical Engineering, University of California at Berkeley, Berkeley, California 94720

Received: August 24, 2000; In Final Form: October 27, 2000

The structure and density of Mo species in Mo/H−ZSM5 during catalytic CH4 reactions was investigated using in-situ X-ray absorption spectroscopy (XAS), temperature-programmed oxidation after reaction, and the isotopic exchange of CH4 with OH groups in H−ZSM5 before and after CH4 reactions. These methods reveal that CH4 reactions cause exchanged Mo2O4+ dimers, formed from physical mixtures of MoO3 and H−ZSM5, to reduce and carburize to form small (0.6−1 nm) MoC clusters with the concurrent regeneration of the bridging OH groups that were initially replaced by Mo oxo dimers during exchange. In this manner, catalytically inactive Mo oxo species activate in contact with CH4 to form the two sites required for the conversion of CH4 to aromatics: MoC for C−H bond activation and initial C−C bond formation and acid sites for oligomerization and cyclization of C2 hydrocarbons to form stable aromatics. These MoC clusters resist agglomeration during methane reactions at 950 K for >10 h. The Brönsted acid sites formed during carburization and oligomerization of MoC species ultimately become covered with hydrogen-deficient reaction intermediates (H/C ~ 0.2) or unreactive deposits. The highly dispersed nature of the MoC clusters was confirmed by detailed simulations of the XAS radial structure function and by the low temperatures required for the complete oxidation of these MoC species compared with bulk Mo2C. Initial CH4 reactions with MoO3 precursors are stoichiometric and lead first to the removal of oxygen as CO, CO2, and H2O and to the introduction of carbide carbons into the reduced structures. As carbide carbon passivates the surface, C−H bond activation reactions become catalytic by the coupling of this activation step with the removal of the resulting CH4 species to form C2 hydrocarbons, which desorb to re-form the MoC clusters for C−H bond activation steps.

Introduction

The activation of CH4 and its conversion to higher hydrocarbons remains an important challenge posing significant thermodynamic and kinetic hurdles.1−4 The catalytic conversion of methane to aromatics via non-oxidative routes has attracted significant attention since the initial report of the selective formation of benzene at near equilibrium concentrations on Mo/H−ZSM5 [5]. Subsequently, many catalysts consisting of transition metal ions, such as Mo, W, V, Fe, and Cr, exchanged into or loaded onto various zeolites (H−ZSM5, H−ZSM11, H−ZSM8, H-beta, H−MCM41, HY, and H-mordenite) have been examined for this reaction.6−8 Mo/H−ZSM5 remains the most attractive catalyst and several synthetic routes and zeolite sources have led to similar catalytic performance, in most cases because such materials achieve near equilibrium methane conversions with high selectivity to benzene.

The detailed mechanism of the initial C−C bond formation and of the structure of the active Mo species during catalysis remain unclear. Xu et al. speculated that heterolytic splitting of C−H bonds in CH4 on acid sites and molybdenum carbene-like complexes are involved.9 These molybdenum carbene complexes then dimerized to form ethylene as the first product. These authors have also suggested that the active centers consist of partially reduced molybdenum oxide species MoO3−x.10 Lin et al. proposed that the activation of methane to form CH3 free radicals requires the synergistic involvement of MoO and Brönsted acid sites and that the CH3 free radicals then dimerize in the gas phase to form ethane as the first product.11 These early mechanistic proposals have remained speculative and lack direct experimental support. Lunsford et al., using X-ray photoelectron spectroscopy, showed that Mo2C is present in Mo/H−ZSM5 catalysts after CH4 reactions. They detected carbide carbon on Mo/H−ZSM5 and showed that MoO3 species reduce to almost zero valency during reaction;12 they also suggested that molybdenum carbide clusters within zeolite channels are involved in rate-determining C−H bond activation steps to form ethylene and H2 as products. Solymosi et al.13−16 explored the catalytic behavior of unsupported and supported Mo species; they concluded that Mo2C provides the active sites for ethylene formation, and that acid sites catalyze its subsequent conversion to benzene. More recently, Lunsford et al. proposed a critical role of carbonaceous deposits in the reaction chemistry; they found that the preformation of Mo2C without excess carbon did not eliminate the initial activation period observed with Mo(VI) precursors during methane reactions.17

Previously, we have shown that MoO3 species migrate into zeolite channels and exchange with OH groups in H−ZSM5 to form (Mo2O4)2+ dimers, anchored at two cation exchange sites (Scheme 1), when MoO3/H−ZSM5 physical mixtures are heated in dry air.18−21 These results confirmed the highly dispersed and unreduced nature of catalyst precursors. In these studies,
we also measured the amount of oxygen removed during methane reactions and confirmed the reduction and carburization of these materials using in situ X-ray absorption spectroscopy.\textsuperscript{18–21}

Here, we describe our additional recent results dealing with the reduction, carburization, and migration of Mo species during CH\textsubscript{4} reactions. Our approach includes in-situ X-ray absorption spectroscopy,\textsuperscript{18} 

\begin{itemize}
  \item methane conversion and the rate of evolution of products.
  \item The amount of H\textsubscript{2} evolved was more than two times larger than the quantity of CO formed; this shows that some carbon was retained by the catalyst as carbidic carbon, carbon-containing reactive intermediates, or deactivating deposits. Mo(VI) species were reduced to lower valent molybdenum species during the induction period of time, and then reduced further and converted to MoC\textsubscript{x}.
\end{itemize}

\textbf{Experimental Methods}

Mo/H−ZSM5 (4 wt % Mo) was prepared from physical mixtures of H−ZSM5 (Zeolyst International, Si/Al=15) and bulk MoO\textsubscript{3} powder (Johnson Matthey Electronics, 99.95%). Powder mixtures were ground in an agate mortar for 0.5 h, pressed into lose pellets, and crushed to 35 − 60 mesh before thermal treatment. These mixtures were then treated as follows before isothermal transient reduction or reaction (ITR), isotopic D\textsubscript{2} exchange with OH groups, and temperature-programmed oxidation (TPO) studies:

(a) MoO\textsubscript{3}/H−ZSM5 physical mixtures (0.2 g) were placed in a quartz cell.

(b) Samples were heated in 100 cm\textsuperscript{3}/min 20\% O\textsubscript{2}/He (Airgas, ultrahigh purity grade) at 10 K/min to 973 K and held for 0.5 h; this procedure leads to the quantitative exchange of MoO\textsubscript{3}, predominantly as Mo oxo dimers (Mo\textsubscript{2}O\textsubscript{5})\textsuperscript{2+},\textsuperscript{18–21}

(c) Samples were cooled in He (100 cm\textsuperscript{3}/min, Airgas, ultrahigh purity) to 950 K.

(d) The flow was switched to CH\textsubscript{4}/Ar/He (1:1:3; 100 cm\textsuperscript{3}/min) and maintained for various periods of time. The concentration of unreacted CH\textsubscript{4} and of reaction products was monitored by mass spectrometry (Leybold-Inficon Transector 1.0). Ar was used as an internal standard in order to calculate CH\textsubscript{4} conversion and the rate of evolution of products.

(e) Samples were then treated in 100 cm\textsuperscript{3}/min H\textsubscript{2}/He (40\%, Matheson, high purity grade) at 950 K for 2 h [hydrocarbons (CH\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}) were no longer detected after 0.5 h] followed by He treatment for 1 h at 950 K. This procedure was used to attempt to desorb any reaction intermediates present on the surface of the catalyst during CH\textsubscript{4} reactions.

(f) Samples were cooled to room temperature in 100 cm\textsuperscript{3}/min He.

(g) The flow was switched to 60 cm\textsuperscript{3}/min D\textsubscript{2}/He (5\%, Matheson), and deuterium exchange with protium present in the sample was measured by increasing the temperature to 973 K at 10 K/min.

(h) The carrier gas was switched from D\textsubscript{2}/He to H\textsubscript{2}/He (10\%) at 973 K for 10 min (D is re-exchanged back to H so that H\textsubscript{2}O can be measured during subsequent TPO).

(i) Samples were cooled to room temperature in 100 cm\textsuperscript{3}/min He.

(j) The flow was switched to 100 cm\textsuperscript{3}/min O\textsubscript{2}/He (40\%) in order to carry out the temperature-programmed oxidation of carbonaceous deposits to CO\textsubscript{2} and H\textsubscript{2}O by increasing the sample temperature to 973 K at 10 K/min.

X-ray absorption spectroscopic (XAS) measurements were carried out at beamline BL2−3 in the Stanford Synchrotron Radiation Laboratory (SSRL). A Si (220) double crystal monochromator was used to obtain a monochromatic X-ray beam. The in-situ XAS cell has been described previously.\textsuperscript{22} A physical mixture of H−ZSM5 and MoO\textsubscript{3} containing 4wt % Mo (24 mg; particles < 60 mesh) was placed within a quartz tube of 2 mm diameter and wall thickness < 0.1 mm. The samples were heated in flowing 20\% O\textsubscript{2}/He (2 cm\textsuperscript{3}/min) to 973 K at 10 K/min, held for 0.5 h, and then cooled to room temperature in He before XAS data were collected after the exchange process. Then, the samples were heated in He to 955 K and He was switched to CH\textsubscript{4}/Ar (1 cm\textsuperscript{3}/min) for various periods of time. XAS data were collected on reduced-carburized samples at room temperature in flowing He.

XAS measurements were also carried out for a MoC\textsubscript{x} sample synthesized within the XAS cell. MoO\textsubscript{3} (3 mg) diluted with graphite (4 mg) was placed in the cell and heated in a 20\% CH\textsubscript{4}/H\textsubscript{2} (2 cm\textsuperscript{3}/min) to 1023 K at 10 K/min and held at this temperature for 0.5 h. This procedure leads to the formation of crystalline β-Mo\textsubscript{3}C.\textsuperscript{23}

EXAFS (Extended X-ray Absorption Fine Structure) data were analyzed using WinXas97\textsuperscript{24} (version 1.2) and FEFF8.0.\textsuperscript{25} The code ATOMS\textsuperscript{26} was used to provide coordination numbers and interatomic distances from compounds with known structures (Mo, MoO\textsubscript{3}, MoO\textsubscript{2}, Mo\textsubscript{2}C) for use in the cluster simulations. The k\textsuperscript{2}-weighted EXAFS was Fourier transformed in the range 0.3 − 1.5 nm\textsuperscript{−1} and fitted in R-space to 0.8 nm, using a MoC\textsubscript{2} cluster of radius 0.4 nm as a starting model. A multishell fitting was used to determine interatomic distances (R), coordination numbers (CN), and energy shifts (ΔE\textsubscript{0}).

\textbf{Results and Discussion}

Figure 1 shows methane conversion and product formation rates at 950 K during the initial exposure of exchanged Mo/H−ZSM5 samples to methane (step (d) in methods section). Accurate determinations of the concentrations of species in the complex product mixture were achieved using frequent calibrations of the mass fragmentation patterns of individual compounds and matrix deconvolution methods that account for overlapping mass fragments arising from the complex product mixture.\textsuperscript{27}

After an induction period of about 150 s, methane conversion rates increased sharply and subsequently decreased with reaction time. This appears to reflect the autocatalytic nature of the reduction of Mo(VI) species, which catalyze the activation of C−H bonds in CH\textsubscript{4} with increasing efficiency as reduction proceeds.\textsuperscript{28} During this induction period, the conversion of methane leads predominately to CO\textsubscript{2}, H\textsubscript{2}O, and CO, without the concurrent formation of hydrocarbons. This reflects the partial removal of oxygen from the Mo(VI) oxo dimers in the starting material. As the reduction proceeded, the rate of methane conversion increased and CO and H\textsubscript{2} became the predominant products and matrix deconvolution methods that account for overlapping mass fragments arising from the complex product mixture.\textsuperscript{27}

Figure 2 shows the evolution of oxygen-containing products during reduction and carburization of pure MoO\textsubscript{3} using a 20\% CH\textsubscript{4}/H\textsubscript{2} mixture at conditions that lead to the formation of β-Mo\textsubscript{3}C.\textsuperscript{23} Figure 2 also shows the subsequent reoxidation in 20\% O\textsubscript{2}/He mixtures (100 cm\textsuperscript{3}/min) of the Mo\textsubscript{C}. The reaction of MoO\textsubscript{3} with CH\textsubscript{4}/H\textsubscript{2} takes place in two stages as reported by
Lee et al., 23,28 but the reoxidation of the Mo\(_2\)C occurs as a single fast process with the sharp evolution of CO at 725 K.

Figure 3 shows the rate of HD formation during isotopic exchange of D\(_2\) with H-atoms after catalysts were used for methane reactions for various periods of time (step (g)) at 950 K. Exchangeable hydrogen species in these samples include OH groups (zeolitic bridged OH groups, silanols, or OH groups at extraframework Al) and hydrogen-containing carbonaceous deposits or intermediates, such as polynuclear aromatics. Maximum HD evolution rates were observed at \(\sim 780\) K and \(\sim 610\) K for H\(\sim\)ZSM5 and MoO\(_3\)/H\(\sim\)ZSM5, respectively. MoO\(_x\) species exchanged onto ZSM5 catalyze rate-determining D\(_2\) dissociation steps during isotopic exchange more effectively than sites available in H\(\sim\)ZSM5. The reduction and carburization of these MoO\(_x\) species during initial contact with CH\(_4\) at 950 K leads to even lower HD evolution peak temperatures; these temperatures decreased to 475 K after CH\(_4\) reaction for 200 s (curve c in Figure 3), suggesting that the MoC\(_x\) sites formed during contact of MoO\(_x\) species with CH\(_4\) at 950 K are more active for D\(_2\) activation than the MoO\(_x\) precursors initially present after exchange. The higher activity of MoC\(_x\) for D\(_2\) dissociation compared with MoO\(_x\) parallels a similar trend in the catalytic behavior for hydrocarbon reactions as bulk MoO\(_3\) converts to bulk Mo\(_2\)C. Lee et al. have reported high catalytic activity of Mo\(_2\)C loaded on \(\gamma\)-Al\(_2\)O\(_3\) for hydrogenolysis of \(n\)-butane at 510 K. 30,31 Turnover rates for hydrogenolysis reactions on Mo\(_2\)C were high, only slightly lower than that on Ru and Os and much higher than on MoO\(_3\).

After CH\(_4\) reactions for \(\sim 800\) s, D\(_2\) exchange occurs with the formation of a single HD peak at low temperatures (\(\sim 475\) K). This appears to reflect the near complete reduction and carburization of MoO\(_x\) species in the MoO\(_x\)/H\(\sim\)ZSM5 precursor and the formation of uniform Mo\(\sim\)C species. These data are in agreement with the isothermal transient data shown in Figure 1, which showed that the evolution of CO\(_2\) and H\(_2\)O during methane reactions is almost complete after about 800 s. At shorter CH\(_4\) reaction times, the HD evolution peak at \(\sim 475\) K is more complex, apparently because incomplete conversion to Mo carbides leads to a wide range of MoO\(_x\)C\(_y\) stoichiometries and to a broad distribution of D\(_2\) dissociation sites.

Longer CH\(_4\) reaction times lead to the accumulation of carbon deposits and to an increase in the amount of HD evolved (shown in parentheses in Figure 3) with increasing reaction time. Thus, it appears that the surface density of OH groups or of hydrogen-
containing adsorbed species increases with increasing exposure to CH₄ at 950 K. It seems reasonable to assume that OH groups account for the initial observed increase in the amount of exchangeable hydrogen atoms during methane reactions, but clearly some of the H atoms must also be present within hydrogen-containing hydrocarbon species. These conclusions are supported by the results of temperature-programmed oxidation of the reduced-carburized samples after various CH₄ reaction times (shown in Figures 4 and 5). Short methane reaction times lead to low concentrations of carbon deposits, which contain small amounts of hydrogen. The H/C ratio for carbon deposits is basically a constant 0.2, as measured by TPO for methane reactions longer than 0.3 h (cf. Figure 7). For example, the hydrogen contained in carbon deposits accounts for only ~30% of the hydrogen atoms under curve e in Figure 3. An increase in the number of OH groups would require that exchanged Mo species leave cation exchange sites during reduction and carburization. Methane appears to convert the isolated MoOₓ dimers initially present after exchange to well-dispersed MoCₓ clusters. Even if such clusters retained a positive charge in the presence of alkyl adsorbed species, the multiatomic nature of the clusters would mean that fewer exchange sites are occupied by Mo species. Therefore, acidic OH groups must form during methane reactions. In this manner, methane reactions form the two sites required for the bifunctional conversion of methane to aromatics from noncatalytic but reactive MoOₓ dimers in H-ZSM5 differ significantly from those in bulk Mo₂C crystallites. The formation of transition metal carbides and the reoxidation of carbides appear to be controlled by the diffusion of oxygen in or out of the bulk crystallites. As a result, we infer that the small size of the MoCₓ clusters in Mo/H-ZSM5 provides a much shorter diffusion path for the reoxidation of the carbide structure.

Figure 3. HD evolution during D-H exchange on 4 wt % Mo/H-ZSM5 reduced and carburized by methane. (a) H-ZSM5; (b) fresh Mo/H-ZSM5 calcined at 973 K for 0.5 h; (c) Mo/H-ZSM5 reacted with methane at 950 K for 200 s; (d) 450 s; (e) 800 s; (f) 1200 s; (g) 0.5 h; (h) 1 h; and (i) 15 h (These methane reaction times do not include the induction time.). The figures in parentheses are the molar amount of HD under peak 1 or peak 1 + peak 2 (μmol/g).

Figure 4. COₓ evolution detected in TPO on 4 wt % Mo/H-ZSM5 after methane reaction and D-H exchange. (10 K/min, 100 cm³/min 40% O₂/He). The letters have the same meaning as in Figure 3. Figures in parentheses are amounts of COₓ under corresponding peaks (μmol/g).
the TPO experiments. The H/C ratio after CH$_4$ reactions at 950 K and H$_2$ and He treatments also at 950 K decreased from a value greater than 3 at short reaction times to a constant value of 0.2 for times longer than 0.3 h. The high initial (H/C) values at short reaction times are atypical of unreactive carbonaceous deposits, which tend to be very hydrogen deficient. One possible mechanism for this apparently high H/C ratio is that small MoC$_x$ clusters initially formed during CH$_4$ reactions oxidize during TPO and that the resulting MoO$_x$ clusters re-exchange with acidic OH groups to form H$_2$O via pathways identical to those responsible for the initial anchoring of (Mo$_2$O$_5$)$_2^{2+}$ dimers during their synthesis from MoO$_3$/H$_2$ZSM5 mixtures. This plausible explanation for the high (H/C) ratio evident during TPO would also imply that these OH groups were re-formed during CH$_4$ reactions by carburization of these Mo oxo dimers and removal from exchange sites. At longer reaction times, these acid sites may become covered by cationic C$_x$H$_y$ species, which would compensate the negative charge in the bridging Si–O–Al sites in ZSM5 and act as precursor or spectator species in the observed formation of higher hydrocarbons.

Near-edge X-ray absorption spectra for Mo/H–ZSM5 samples treated at various conditions are shown in Figure 8. The Mo–K absorption edges shift to lower energies during CH$_4$ reaction at 950 K ($\Delta E \approx 5$ eV) and the preedge feature corresponding to Mo(VI) disappears, consistent with the reduction of Mo(VI) centers. The $k^2$-weighted experimental and simulated molybdenum radial distribution functions are shown in Figure 9 for Mo/H–ZSM5 after reaction with methane for various periods of time. The corresponding results for MoC$_3$ prepared by carburization of bulk MoO$_3$ are also shown in this Figure 9.
Before examining the structure of MoC species formed during CH₄ reactions on MoO₃/H-ZSM5 precursors, the structure of the bulk Mo₂C prepared from MoO₃ in the XAS cell was examined and compared with previous reports (Table 1). The structure compares well with that reported by Epicier et al. Mo in bulk Mo₂C has three carbon neighbors at a distance of about 0.21 nm and twelve Mo neighbors at distances from 0.290 to 0.301 nm. For the Mo/H-ZSM5 samples reduced and carburized during CH₄ reactions, the Mo K-EXAFS fine structure was fitted using shells between 0.08 and 0.368 nm from the Mo absorber. The structure of Mo₂C (Table 1) was used as the starting point in the structural determination and the structure was refined in order to improve agreement with the experimental radial structure functions. The Mo–C and Mo–Mo coordination numbers, interatomic distances, the Mo–Mo Debye–Waller factors, and energy shifts were allowed to vary in order to describe the experimental results. The Mo–C Debye–Waller factor was held at zero because a strong correlation between the Mo–C coordination number and the corresponding Debye–Waller factor prevented convergence using physically reasonable structural parameters. Although the Mo site in bulk Mo₂C is described by three Mo–C and seven Mo–Mo distances, within what could be broadly regarded as the first two coordination shells, these collapsed into single Mo–C and Mo–Mo distances when the same model was used to fit the EXAFS from the carburized Mo/H–ZSM5 samples.

The analysis results, listed in Table 2, show one Mo–C and one Mo–Mo shell are sufficient to describe the radial structure function of the Mo–C species present during CH₄ reactions on Mo/H-ZSM5 catalysts.

The simulated and the experimental radial distribution functions are shown in Figure 9. Mo–C and Mo–Mo interatomic distances were 0.210 and 0.297 nm, respectively. These are similar to those in Mo₂C bulk, implying that the local structures of Mo atoms in Mo₂C and in MoCₓ/H–ZSM-5 are very similar. Even after CH₄ reacts for 1.3 h, the Mo–Mo coordination number is close to 3 (Table 2), instead of the value of 12

**TABLE 1: Mo₂C Structure Parameters Obtained by Analysis of Mo–K–EXAFS**

<table>
<thead>
<tr>
<th>shells</th>
<th>coordination number</th>
<th>distance (Å)</th>
<th>2α²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ref (30)</td>
<td>ref (30)</td>
<td></td>
</tr>
<tr>
<td>Mo–C (1)</td>
<td>1</td>
<td>2.091</td>
<td>5.4e-5</td>
</tr>
<tr>
<td>Mo–C (2)</td>
<td>1</td>
<td>2.114</td>
<td>6.1e-5</td>
</tr>
<tr>
<td>Mo–C (3)</td>
<td>1</td>
<td>2.118</td>
<td>7.3e-5</td>
</tr>
<tr>
<td>Mo–Mo (4)</td>
<td>1</td>
<td>2.898</td>
<td>4.5e-5</td>
</tr>
<tr>
<td>Mo–Mo (5)</td>
<td>1</td>
<td>2.900</td>
<td>6.4e-5</td>
</tr>
<tr>
<td>Mo–Mo (6)</td>
<td>2</td>
<td>2.936</td>
<td>4.5e-5</td>
</tr>
<tr>
<td>Mo–Mo (7)</td>
<td>1</td>
<td>2.975</td>
<td>3.4e-5</td>
</tr>
<tr>
<td>Mo–Mo (8)</td>
<td>1</td>
<td>2.977</td>
<td>7.9e-5</td>
</tr>
<tr>
<td>Mo–Mo (9)</td>
<td>4</td>
<td>3.009</td>
<td>7.9e-5</td>
</tr>
<tr>
<td>Mo–Mo (10)</td>
<td>2</td>
<td>3.013</td>
<td>3.4e-5</td>
</tr>
</tbody>
</table>

α²: Debye–Waller factor.
expected for large MoC crystallites, suggesting that isolated Mo precursors form very small Mo₂C clusters during the initial stages of reduction and carburation. The Mo—Mo coordination numbers increased slightly with increasing reaction time, consistent with the subsequent gradual growth of these initial MoC clusters during CH₄ reactions. Using an analogy with previously reported effects of cluster size on coordination number for metal particles, the parameters listed in Table 2, we estimate MoC clusters to be ~0.6 nm diameter and to contain ~10 molybdenum atoms. Perhaps coincidentally, this cluster size is similar to the diameter of the channels in ZSM₅ (0.55 × 0.57 nm) within which these MoC clusters are likely to reside.

At longer CH₄ reaction times, the size of the MoC clusters may exceed the channel diameter. Then, clusters must reside at channel intersections, crystalline defects, or external surfaces. Metal clusters have been shown to migrate readily to external zeolite crystal surfaces at high temperatures. For example, it was reported that Co metal clusters confined within Y zeolite migrate to form large crystallites at external zeolite surfaces at ~473 K. In contrast, MoC clusters within ZSM₅ channels remain small and unusually resistant to migration and external agglomeration at even higher temperatures. MoC nanoclusters smaller than ~1 nm in size are evident during CH₄ reactions at 950 K for several hours. The high melting point and low vapor pressure of molybdenum carbides, the high initial dispersion of the MoO₃ precursors, and the possible complexation of MoC clusters by framework oxygens may contribute to the remarkable structural stability of these MoC/H—ZSM₅ materials.

These data lead to the pathways for reduction of (Mo₂O₅)₂⁺ dimers to form MoC clusters shown schematically in Scheme 2. The oligomerization of isolated Mo dimers into small clusters releases the monomers from exchange sites with the concurrent regeneration of the acidic OH groups, initially replaced by Mo₂O₅⁺ dimers during the synthesis from physical mixtures of MoO₃ and H—ZSM₅. The aggregation of molybdenum to form carbide clusters releases most of acid sites required for aromatization reactions of intermediates.

This mechanistic suggestion, in turn, leads us to a description of the initial stages of the reduction and carburation of the precursor MoO₃ dimers. C—H bonds in CH₄ are activated slowly until O-atoms start to be removed as CO and H₂O after the initial C—H bond activation step. As oxygen atoms continue to be removed, C—H bond activation becomes more facile and carbidic carbon is gradually deposited. The strong bond between carbidic carbon and molybdenum causes the aggregation of molybdenum to form Mo—C clusters. The depositing of carbidic carbon passivates the surface against further carbon deposition, but still allows the catalytic activation of C—H bonds. The catalytic ability of MoC sites in activation of C—H bonds in alkanes has been widely reported, in the context of hydrogenation and dehydrogenation reactions.

One important and challenging question remaining in this mechanistic proposal is the nature of the intermediates involved in the formation of C—C bonds from CH₄ fragments formed by C—H bond activation in CH₄. We have attempted to probe this quenching of the CH₄ reaction and attempting the deuteration of any CH₄ present using D₂.

Figure 10 shows the rates of desorption of species with masses 17, 18, and 19 amu during deuterogenation experiments as a function of temperature during reactions of D₂ with H-species present in Mo/H—ZSM₅ after CH₄ reactions. The mass fragments detected correspond to the parent ions for CH₃D, CH₂D₂, and CHD₃, respectively. The various profiles shown in Figure 10 correspond to samples treated by procedures (a) to (f) (see Methods section), but without the H₂ treatment of step (e) for curves d ~ f in Figure 10. This last step was avoided in an attempt to preserve, to the extent possible, the density and type of methane-derived intermediates present during reaction. These data were obtained after methane reactions were carried out for a period of time (1 h) sufficient to ensure the complete reduction and carburation of the MoO₃ precursors. The results obtained on the same catalyst, but after a H₂ treatment using the procedure described in step (e), are also given in the Figure 10 for comparison. An accurate measurement of the concentration of the various methane isotopomers is difficult because of significant kinetic isotopic effects in the fragmentation of CH₄—D₄ isotopomers and because of the strong overlap among the mass.

![Scheme 2](image-url)
spectra from the various isomers. Qualitatively, these data reflect, however, the relative surface concentrations of CHx fragments formed from methane during steady-state catalysis. CHx appears to be the most abundant surface fragment present during methane reactions, whereas CH3 fragments are less abundant but react with D2 at a lower temperature. CH fragments are lowest in abundance. The temperature required for the reactive desorption of CH3 to form CH3D is ~450 K, which is lower than for the reaction of CH2 to form CH2D2. This mainly reflects the different desorption strength of CH3 and CH2 and not necessarily the relative kinetic importance of these two possible intermediates during methane reactions.

Solymosi et al. have detected the presence and conversion to adsorbed CH2x of CH3 formed from CH4I on the surface of Mo5C grown on Mo (111) using TPD and EELS (electronic energy loss spectroscopy). They observed the desorption of CH4 at ~300 K and C2H4 at ~520 K after adsorption of CH4 at 100 or 300 K. Their results suggest that CH3 and CH2 species adsorbed on Mo5C are stable. It is reasonable to expect stronger interactions of CH2x fragments with nanoclusters of molybdenum carbides than with bulk carbide surfaces because of higher coordinative unsaturation of Mo centers in such small clusters. As a result, it is likely that these CH2x fragments condense on the surface of Mo–C clusters to form C2H4 or C2H6 molecules, which can oligomerize and cyclize to form aromatics on θ-Bronsted acid sites aided by the presence of Mo5C species that desorb hydrogen as H2 during methane reactions.

Conclusions

The reduction and carburization of (Mo5O12)2+ species during CH4 reactions cause the formation of MoC5 clusters (0.6–1 nm diameter) and the concurrent regeneration of the bridging OH groups initially displaced by the Mo oxo dimers during catalyst synthesis. In this manner, Mo5O12 species initially exchanged but catalytically inactive convert into the two catalytic functions required for CH4 conversion: MoC5 for C=H bond activation and C2 formation and θ-Bronsted acid sites for the formation of aromatics from C2. These MoC5 clusters contain ~10 Mo atoms and they resist agglomeration for extended times (~10 h) during methane reactions at 950 K. C=H bond activation on these clusters lead to the formation of CH3 species that condense to give the initial C2 products of methane conversion reactions.

Acknowledgment. This work has been supported by the Division of Fossil Energy of the U.S. Department of Energy (Contract No. DE-AC03-76SF00098) under the technical supervision of Dr. Daniel Driscoll. The authors gratefully acknowledge the Stanford Synchrotron Radiation Laboratory for all the measurements of X-ray absorption spectroscopy included in this paper. W.D. thanks Nanjing University for his leave of absence to work at the University of California at Berkeley.

References and Notes


(23) Buynax97 is an XAS data analysis program for PCs running MS Windows by Thorsten Ressler (e-mail: t_reessler@compuserve.com; webpage: http://ourworld.compuserve.com/homepages/t_reessler).


(26) The code ATOMS is written by Bruce Ravel (e-mail: ravel@u.washington.edu) to calculate coordination numbers and interatomic distances from compounds with known structures and all input for FEFF8.0.


