Isolated molybdate species supported on silica are reported to have the highest specific activity and selectivity for the direct oxidation of methane to formaldehyde. The present investigation was undertaken to understand the elementary redox processes involved in the formation of formaldehyde over such species. A MoO$_x$/SiO$_2$ catalyst was prepared with a Mo loading of 0.44 Mo/nm$^2$. On the basis of evidence from extended X-ray absorption fine structure (EXAFS) and Raman spectroscopy, the Mo atoms in this catalyst are present as isolated, pentacoordinated molybdate species containing a single Mo=O bond. Isotopic labeling experiments in combination with in-situ Raman spectroscopy were used to examine the reducibility of the dispersed molybdate species and the exchange of O atoms between the gas phase and the catalyst. It was established that treatment of MoO$_x$/SiO$_2$ at 873 K under pure methane reduces the dispersed molybdate species to only a limited extent and results mainly in the deposition of amorphous carbon. During CH$_4$ oxidation to formaldehyde, the catalyst undergoes only a very small degree of reduction and typically only $\sim$50–500 ppm of Mo$^{VI}$ is reduced to Mo$^{IV}$. Reactions carried out using CH$_4$ and $^{18}$O$_2$ show that there is extensive scrambling of O atoms between the species in the gas phase and the catalyst. Additional experiments revealed that H$_2$O formed in the reaction is the principal species responsible for the exchange of O atoms between the gas phase and the SiO$_2$ support. Low concentrations of H$_2$O were observed to enhance the activity of MoO$_x$/SiO$_2$ for CH$_4$ oxidation to formaldehyde. A mechanism for the oxidation of CH$_4$ over MoO$_x$/SiO$_2$ was formulated in light of the observations made here and is discussed in the light of previous studies. It is proposed that peroxides are produced by the reaction of O$_2$ with a small concentration of reduced molybdate species and that the reaction of CH$_4$ with these peroxide species leads to the formation of formaldehyde. The proposed mechanism also accounts for the positive effects of low concentrations of H$_2$O on the rate of formaldehyde formation.

Introduction

The direct oxidation of methane to formaldehyde in a single step is a potentially attractive process for upgrading natural gas to a more valuable chemical feedstock. Such a process could in principle become competitive with the indirect conversion of methane to formaldehyde, which involves three separate steps—steam reforming of methane to produce synthesis gas, conversion of synthesis gas to methanol, and partial oxidation of methanol to formaldehyde. While highly dispersed MoO$_3$ and VO$_x$ supported on SiO$_2$ are known to be active for the direct oxidation of methane to formaldehyde, the highest single-pass yields of formaldehyde are typically on the order of 2–5%.$^{1–5}$ As a result, there is considerable interest in understanding the elementary processes involved in the formation and loss of formaldehyde, so that this knowledge might be used to prepare more highly selective catalysts.

The reaction mechanism for the conversion of methane to formaldehyde over SiO$_2$-supported MoO$_3$ has been investigated by a number of authors, and several schemes have been proposed to explain the kinetics of methane oxidation to formaldehyde and spectroscopic observations of the catalyst.$^{1,6–10}$ A common feature in these schemes is the involvement of multiple Mo centers in one or more of the elementary steps involved in transforming methane to formaldehyde. While effective in describing the observed reaction kinetics, the inclusion of such elementary steps fails to explain why the highest specific activity for MoO$_x$/SiO$_2$ occurs at Mo surface concentrations of $<$1 Mo/nm$^2$, for which virtually all of the Mo is present as isolated molybdate species.$^{11–20}$ Since gas-phase free-radical reactions are insignificant during methane oxidation over MoO$_x$/SiO$_2$, it is not clear how multiple isolated molybdate centers are able to participate in the oxidation of methane and the reduction of molecular oxygen. Observations made during experiments involving 18-labeled oxygen and during experiments in which H$_2$O is added to the feed give rise to further questions regarding the reaction mechanism. Isotopic labeling experiments have revealed that oxygen from the SiO$_2$ support is incorporated extensively into the oxygenated products of methane oxidation formed over SiO$_2$-supported MoO$_3$ and VO$_x$.$^{22,23}$ suggesting that labile SiO$_2$ oxygen may be involved in the oxidation of CH$_4$. Both a positive and a negative influence of H$_2$O on the rate of CH$_4$ oxidation has been reported for oxidation of CH$_4$ by O$_2$. $^{10,24–26}$ but a mechanism has not been proposed to explain the chemical effect of H$_2$O on the reaction.

The aim of the present work was to understand the elementary processes involved in the oxidation of CH$_4$ over a MoO$_x$/SiO$_2$ catalyst in which the Mo is present solely as isolated molybdate species. X-ray absorption spectroscopy (XAS) and O$_2$ titration were used to determine the oxidation state of Mo after reduction.
Experimental Section

Sample Preparation. Silica gel (Silicycle R10070B-00, 60 Å pore diameter) was washed in 9 M HNO₃ at 333 K, rinsed thoroughly with deionized water, and calcined in flowing air for 3 h at 973 K in order to remove alkaline earth impurities. This treatment reduced the silica surface area from 500 m²/g to 460 m²/g, as measured by five-point analysis of the BET adsorption isotherm. MoO₃/SiO₂ was prepared by impregnation with an aqueous solution of ammonium heptamolybdate (AHM) tetrahydrate (Aldrich, 99.98% pure). AHM (0.067 g) was suspended in 2.1 g of deionized water (150% of the pore-filling amount) for each gram of silica gel to be impregnated. The expected Mo loading was thus 3.5 wt % elemental Mo. The suspension was immersed in a bath heated at 333 K and stirred until the solvent was evaporated. The resulting solid was oven dried at 383 K overnight and calcined under flowing air at 873 K for 3 h. The surface area of the calcined catalyst was 426 m²/g. The Mo weight fraction determined by elemental analysis for 100 mg were used for treatment in pure CH₄ or H₂ and of 1000 ppm O₂/He (Praxair certified standard) was used to generate pulses containing 17.4 nmol O₂. Pulses were injected until the detected area was constant for at least 3 min for the TCD or 20 min for the MS. Gas flow rates were maintained at 30 cm³(STP)/min during treatment under CH₄ and H₂ and at 60 cm³(STP)/min during treatment under CH₄/O₂ mixtures. During treatment under CH₄/O₂ mixtures, the reactor effluent was monitored with the mass spectrometer, to ensure that oxygen conversion was incomplete. Oxygen conversion was at most ~70%. Four-way switching valves (Swagelok 40 series) were used to switch between gas flows. Square pulses of O₂/He were introduced at room temperature into the He stream using a six-way crossover valve (Swagelok 40 series). A 0.421 cm³ sample loop was used to set the pulse size. For CH₄ and H₂-treated samples, 10.3% O₂/He (Matheson certified standard) was used to generate pulses containing 1.79 μmol O₂. For samples treated in CH₄/O₂ mixtures, 1000 ppm O₂/He (Praxair certified standard) was used to generate pulses containing 17.4 nmol O₂. Pulses were injected into the He stream at 2 min intervals for CH₄- and H₂-treated samples or at 40 s intervals for samples treated in CH₄/O₂. Pulses were injected until the detected area was constant for at least three consecutive pulses. The oxygen uptake was calculated from the following equation

\[ n_{O}^{\text{sample}} = 2 \times n_{O_{2}}^{\text{loop}} \left( N \times A_{i} - \sum_{i=1}^{N} A_{i} \right) / A_{i} \]

where \( n_{O}^{\text{sample}} \) is the moles of O adsorbed by the sample, \( n_{O_{2}}^{\text{loop}} \) is the moles of O₂ contained in a full pulse, \( N \) is the total number
of pulses injected, \( A_i \) is the detected area of the \( i \)th pulse, and \( A_f \) is the area of the final pulse, corresponding to a full pulse. Chemisorption of \( \text{O}_2 \) by the \( \text{H}_2 \)-reduced empty reactor was small but measurable (<0.5 \( \mu \text{mol} \) O), and this amount was subtracted from the amount adsorbed by \( \text{H}_2 \)-reduced \( \text{MoO}_x/\text{SiO}_2 \) samples, which was on the order of 36 \( \mu \text{mol} \) O. No \( \text{O}_2 \) chemisorption was measurable for \( \text{H}_2 \)-reduced \( \text{SiO}_2 \), and no \( \text{O}_2 \) chemisorption was measurable for the empty reactor or for bare \( \text{SiO}_2 \) treated in pure \( \text{CH}_4 \) or \( \text{CH}_4/\text{O}_2 \) mixtures.

Characterization of \( \text{MoO}_x/\text{SiO}_2 \) by Raman Spectroscopy. A heated quartz microreactor containing a rotating sample holder was used for the acquisition of in-situ Raman spectra. A detailed description of this apparatus has been presented previously.\(^{26,27}\) Sample masses were typically 31 mg. \( \text{He} \) (Praxair UHP), \( \text{CH}_4 \) (Matheson research grade), 10.3\% \( \text{O}_2/\text{He} \) (Matheson certified standard), and 20\% \( ^{18}\text{O}_2/\text{He} \) (Isotec, >99\% \( ^{18}\text{O} \) isotopic purity) were metered into the cell using Porter 201 mass flow controllers. The mass flow controllers were calibrated at multiple points with a soap bubble meter. Flow setpoints were applied manually using a Porter PCIM-4 control unit. \( ^{18}\text{O}_2 \) was introduced into the \( \text{He} \) stream by directing the flow through a 15 mL gas-washing bottle (LabGlass ML-1490-710) filled with \( ^{18}\text{O} \) (Isotec/Sigma-Aldrich, >95\% \( ^{18}\text{O} \) isotopic purity) at room temperature and with 1 mm glass beads (Cole-Parmer 36270-50) to raise the liquid level. All tubing and valves located downstream of the gas-washing bottle were maintained at \( \sim 333 \) K to prevent condensation. Total gas flow rates were 20 or 31 cm\(^3\) (STP)/min. The heated volume of the Raman cell was estimated to be 15 cm\(^3\). Four-way crossover valves (Swagelok 40 series) were used to switch between gas flows.

Deconvolution of the Raman spectra of \( \text{SiO}_2 \) and \( \text{MoO}_x/\text{SiO}_2 \) was carried out using the procedure described in ref 28. Only the essential aspects of the procedure are summarized here. The spectra of \( \text{MoO}_x/\text{SiO}_2 \) were fit by summing the Lorentzian components for each of the Raman-active \( \text{SiO}_2 \) and \( \text{MoO}_x \) features including the \( \text{SiO}_2 \) \( D_2 \) feature and the \( Mo=O \) stretching vibration, observed at 614 and 988 cm\(^{-1}\), respectively, for \(^{16}\text{O}_2 \)-calcined \( \text{MoO}_x/\text{SiO}_2 \).\(^{13,32,33}\) During \(^{18}\text{O} \) exchange, the \( Mo=^{16}\text{O} \) band at 988 cm\(^{-1}\) decreased in intensity and a separate \( Mo=^{18}\text{O} \) band appeared at 938 cm\(^{-1}\), which increased in intensity. The fraction of the molybdenyl occupied by \(^{16}\text{O} \) was calculated from the fraction of the total \( Mo=O \) area in the 938 cm\(^{-1}\) peak

\[
\frac{A_{938}}{A_{938} + A_{988}}
\]

The \( D_2 \) feature of \( \text{SiO}_2 \) has been attributed to either cyclic \( (\text{Si}--\text{O}--\text{Si})_3 \) moieties\(^{32,34,35}\) or homopolar \( \text{Si}--\text{Si} \) and \( \text{O}--\text{O} \) bonds at the \( \text{SiO}_2 \) surface.\(^{36,37}\) This band is well-resolved and is red shifted by 33 cm\(^{-1}\) as the \(^{18}\text{O} \) in the feature is replaced with \(^{16}\text{O} \). Therefore, the position of the \( D_2 \) band is a useful measure of the isotopic composition of the oxygen of the \( \text{SiO}_2 \) surface. It was assumed that the position of the \( D_2 \) peak is linearly proportional to the fraction of \(^{16}\text{O}\)-labeled oxygen incorporated into the structure responsible for the band. Therefore, the fraction of \(^{16}\text{O} \) in the feature was calculated as the accomplished change in the peak position

\[
\frac{\mu_{D_2}^{18} - \mu_{D_2}^{16}}{\mu_{D_2}^{18} - \mu_{D_2}^{16}}
\]

\( \mu_{D_2} \) is the peak position of the \( D_2 \) feature, and \( \mu_{D_2}^{16} \) and \( \mu_{D_2}^{18} \) are the peak positions of the \( D_2 \) feature with pure \(^{16}\text{O} \) and pure \(^{18}\text{O} \), respectively.

**Analysis of Gas-Phase Composition during Isotope Exchange Experiments.** Isotopic exchange experiments were carried out to determine the rate at which gas-phase \( ^{16}\text{O}_2 \) exchanges \( ^{18}\text{O} \) atoms in the catalyst and the rate at which \(^{18}\text{O} \) is incorporated into the catalyst during \( \text{CH}_4 \) oxidation by \(^{18}\text{O}_2 \). These experiments were carried out in the Raman cell. The isotopic composition of the effluent from the Raman cell was monitored with an MKS Minilab mass spectrometer. Data were gathered in analogue mode using 16 points per mass, sweeping from \( m/e = 1 \) to 50. An accuracy setting of 5 was used (2\% samples per data point), allowing the collection of 1 mass spectrum every 41 s. Peak maxima were used for quantification of partial pressures. Response factors were determined relative to \( \text{He} \) for all of the fragments of \( \text{CH}_4, \text{CH}_2\text{O}, \text{CO}, \text{CO}_2, \text{H}_2, \text{O}_2, \) and \( \text{H}_2\text{O} \) by mult-point calibration, and the appropriate corrections were made to the fragmentation patterns of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) to account for the natural abundance of \(^{16}\text{O} \). It was assumed that the response factors for \(^{18}\text{O} \)-containing fragments were identical to those of the corresponding \(^{16}\text{O} \)-containing fragments. \( \text{CH}_4 \) produced fragments from \( m/e = 26 \) to \( m/e = 30 \) from fragment combination that interfered with the peaks of \( \text{CH}_2\text{O} \) and \( \text{CO} \) that were second order with respect to \( \text{CH}_4 \) partial pressure. The apparent linear response factors of these fragments were determined from a single-point calibration at the molar fraction of \( \text{CH}_4 \) employed in the feed in this study (40\%). The relative response factors at \( m/e = 2, 12-16, 18, 20, 27-36, \) and 44-49 for the oxygen isotopomers of each of the components were assembled into a matrix. The Moore–Penrose inverse of this matrix was applied to each vector of reaction intensities of the listed mass fragments to yield each composition vector including all of the oxygen isotopes.

**Measurement of Catalytic Activity.** Catalytic activity was measured using the flow reactor described previously.\(^1\) An amount of 196 mg of 0.44 Mo/\( \text{nm}^2 \) \( \text{MoO}_x/\text{SiO}_2 \) was supported on quartz wool in a quartz tube (6 mm ID) and was heated to 873 K at 10 K/min in flowing air prior to the introduction of reactants. \( \text{CH}_4 \) (Matheson research grade), \( \text{O}_2 \) (Matheson UHP), and \( \text{He} \) (Praxair UHP) were metered into the flow manifold by Porter 201 mass flow controllers. \( \text{H}_2\text{O} \) was introduced into the \( \text{He} \) stream by directing the flow through a 15 mL gas-washing bottle (LabGlass ML-1490–710) filled with deionized \( \text{H}_2\text{O} \). The gas-washing bottle was immersed in a bath. The \( \text{H}_2\text{O} \) feed fraction was varied by adjusting the temperature of the bath, which was controlled by a Thermo Electron Neslab RTE-9 recirculating heater/chiller. An HP 6890 N gas chromatograph equipped with a heated 250 \( \mu \)L sampling loop was used to measure the composition of both the reactor feed and the reactor effluent. A 30 foot long, 1/8 in. diameter column packed with Hayesep DB 80/100 mesh was used to separate all components. The column temperature was held at 278 K for 7 min, ramped at 45 K/min to 423 K, and held at 423 K for 15 min. Eluted components were detected with a thermal conductivity detector.

**Results and Discussion**

**Catalyst Structure.** We have recently described the structural characterization of the \( \text{MoO}_x/\text{SiO}_2 \) sample utilized in this work by Raman spectroscopy and XAS.\(^{28}\) The magnitude of the \( k^3 \)-weighted Fourier transform of the \( \chi(k) \) EXAFS spectrum of the sample contained no backscattering peaks in the range from 2.5 to 4.0 Å characteristic of Mo—Mo backscattering, demonstrating that the MoO\(_x\) are isolated from each other on the \( \text{SiO}_2 \) surface. The edge energy of the calcined \( \text{MoO}_x/\text{SiO}_2 \) was consistent with assignment of the oxidation state as Mo\(^{VI}\). The area of the pre-edge feature in the XANES region was similar.
MoCH$_4$, the edge energy was 7.8 eV, a shift of only
in intensity to that of (NH$_4$)$_2$Mo$_6$O$_{18}$, which contains octahedrally coordinated and tetrahedrally coordinated Mo in a 1:1 ratio.

Such a pre-edge feature is expected for pentacoordinate MoO$_5$. The Raman spectrum exhibits only a single Mo=O stretch, or two Mo=O stretches upon partial replacement of Mo=O with Mo=O, indicating that the supported MoO$_5$ has only a single terminal oxo group. The SiO$_2$-supported MoO$_5$ species are therefore isolated, pentacoordinated, MoVIO, moieties containing a single terminal oxo (Mo=O) function. This assignment is in agreement with previous studies.

Reducibility of MoO$_5$/SiO$_2$. The reducibility of MoO$_5$/SiO$_2$ by CH$_4$ and by the products of CH$_4$ oxidation was investigated by in-situ XAS. Mo K-edge XANES spectra of MoO$_5$/SiO$_2$ taken during catalyst reduction with CH$_4$, CH$_2$O, CO, and H$_2$ at 873 K are shown in Figure 1 for reference. XANES spectra of fully oxidized MoO$_5$/SiO$_2$ taken in flowing O$_2$/He at 873 K and in a vacuum at 77 K are also shown. Edge energies were determined for each of the samples relative to Mo foil. This was done by aligning the rising slopes of the spectra in the region of 20 010–20 020 eV. The edge energy relative to Mo foil (20 000 eV) and the integrated intensity of the pre-edge feature are listed in Table 1 for each sample. The edge energy observed under flowing He following calcination was identical, and only a slight reduction in spectral intensity is observed for reduction in H$_2$.

In-situ EXAFS data of MoO$_5$/SiO$_2$ gathered during exposure to flowing reductants at 873 K yielded results that were qualitatively similar to those obtained from XANES data. The magnitude of the Fourier transform of the $k^3$-weighted scattering function, $\chi(k)$, is presented in Figure 2 for MoO$_5$/SiO$_2$. The spectrum of calcined MoO$_5$/SiO$_2$ recorded under vacuum at 77 K is shown for comparison to the spectrum gathered in-situ under flowing 10% O$_2$/He at 873 K. The spectra are qualitatively identical, and only a slight reduction in spectral intensity is observed at 873 K relative to the intensity observed at 77 K.

While an effort was made to fit the EXAFS spectra using standard techniques, it was not possible to determine a unique set of EXAFS parameters because of strong correlations between these parameters arising from both overlap of the oxygen scatterers at low $R$ values with contributions from atomic EXAFS and the uncertainty in the Debye–Waller factors of the oxygen shells of MoO$_5$/SiO$_2$. These difficulties are likely responsible for the conflicting findings reported previously for MoO$_5$/SiO$_2$. Nevertheless, the EXAFS data could still be used in a qualitative manner in order to assess the extent of...
molybdate reduction. Under 10% O₂/He, oxygen backscattering peaks were observed in the Fourier transformed χ(κ) spectrum at 0.75, 1.20, and 1.60 Å. Under pure CH₄ and 4% CO/He, these peaks retained their shape but were decreased in intensity by ~15%. Under 1% CH₂O/He, the intensity of the peaks was reduced by ~35% and the peaks at 0.75 and 1.20 Å became poorly resolved. Under H₂, the peak intensity was ~50% of the observed intensity under 10% O₂/He. These results demonstrate a successively decreasing amount of oxygen coordinated to Mo during the reduction of MoOₓ/SiO₂ which follows the order CH₄ ≈ CH₂O < CH₃O < H₂, consistent with the levels of reduction observed by XANES.

The reoxidation of MoOₓ/SiO₂ reduced in pure H₂ and CH₄ was investigated by pulsed chemisorption of O₂, and the results are shown in Figure 3. The pulsed chemisorption spectrum of MoOₓ/SiO₂ treated in 90% CH₄/10% O₂ is also shown in Figure 3 and will be discussed later. After reduction in pure H₂ at 873 K, MoOₓ/SiO₂ takes up 1 O per Mo during titration with O₂ and therefore Mo⁴⁺ is the stable form of H₂-reduced MoOₓ/SiO₂, as noted above. The character of the titration curve following CH₄ reduction differs from that observed following H₂ reduction. After H₂ reduction, the chemisorption of O₂ by the reduced surface was very rapid. Each pulse of O₂ was almost entirely adsorbed by the catalyst until the catalyst approached saturation (~1 O per Mo), after which the breakthrough of O₂ occurred rapidly, and all of the O₂ in each pulse passed through the oxygen-saturated catalyst bed. By contrast, the consumption of O₂ by the CH₄-reduced catalyst was slow. CH₄-reduced MoOₓ/SiO₂ did not take up entire O₂ pulses but consumed part of each pulse for many pulses. There was no sharp breakthrough of O₂ to indicate that the surface had been saturated with oxygen. After 45 pulses, the sample had consumed 0.55 O per Mo and was still consuming O slowly with each pulse.

In-situ Raman spectroscopy was used to characterize the MoOₓ/SiO₂ in its fully oxidized state and after reduction in pure CH₄. The Raman bands of SiO₂ and of SiO₂-supported MoOₓ are identified in Figure 4 based on previously published work for MoO₃/SiO₂ under flowing air at 920 K. The SiO₂ features ω₁, D₁, D₂, ω₃, ω₄(LO), ω₅(LO), and ω₆(LO) were observed at 450, 500, 614, 810, 975, 1051, and 1179 cm⁻¹, respectively. The Mo=O bending and stretching modes δₑ(Mo=O) and νₑ(Mo=O) were observed at 369 and 988 cm⁻¹, respectively.

Figure 5 shows the Raman spectra of MoOₓ/SiO₂ recorded at 920 K in air, in a mixture of 90% CH₄/10% O₂, and in pure CH₄. The Raman spectrum of MoO₃/SiO₂ recorded during CH₄ oxidation is indistinguishable from that observed under flowing air, in agreement with a previous report. However, none of the Raman bands of MoO₃/SiO₂ are observed during treatment under pure CH₄ at 920 K. Instead, an intense fluorescent background centered at about 1450 cm⁻¹ is observed together with two peaks at 1390 and 1560 cm⁻¹, which are attributable to amorphous carbon. The deposition of carbon is consistent with the observation that the catalyst changes color from white to dark gray upon reduction in CH₄. The carbonaceous deposit is removed by exposure to flowing air for several minutes, after which the amorphous carbon peaks and intense fluorescent background disappear, and the Raman spectrum of MoO₃/SiO₂ is restored, as is shown in Figure 5. Hence, CH₄ reduction of MoO₃/SiO₂ deposits amorphous carbon on the surface, and during O₂ chemisorption by CH₄-reduced MoO₃/SiO₂, O₂ reacts.
Selective Oxidation of Methane over MoO$_x$/SiO$_2$

### TABLE 2: Amount of O Adsorbed during O$_2$ Pulse Chemisorption by MoO$_x$/SiO$_2$ Treated at 873 K under CH$_4$/O$_2$ Mixtures of Varying CH$_4$ and O$_2$ Concentration

<table>
<thead>
<tr>
<th>CH$_4$ Feed Fraction (%)</th>
<th>O$_2$ Feed Fraction (%)</th>
<th>O adsorbed (nmol O/g cat)</th>
<th>(O/10$^6$ Mo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>10</td>
<td>0</td>
<td>0 (53$^a$)</td>
</tr>
<tr>
<td>43</td>
<td>10</td>
<td>34</td>
<td>110</td>
</tr>
<tr>
<td>67</td>
<td>10</td>
<td>57</td>
<td>180</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>110</td>
<td>340</td>
</tr>
<tr>
<td>90</td>
<td>6.7</td>
<td>180</td>
<td>580</td>
</tr>
</tbody>
</table>

$^a$ Determined from the extrapolation of data obtained at higher CH$_4$ feed fractions.

with the amorphous carbon, rather than with reduced Mo centers. On the basis of the XAS results, it appears that CH$_4$ reduction of MoO$_x$/SiO$_2$ reduces the surface by much less than 2 e$^-$ per Mo, and therefore, amorphous carbon is deposited onto MoO$_x$ sites that remain nearly fully oxidized. The small amount of reduction observed by XAS during exposure to CH$_4$ may result from reduction of MoO$_x$ by H$_2$ produced during carbon deposition. Apparently, H$_2$ reduction of the MoO$_x$ does not proceed once the MoO$_x$ are carburized, since the level of reduction was stabilized at $\approx$2 e$^-$ per Mo. Carbon deposition was not observed during CH$_4$ oxidation, as can be seen by comparison of the Raman spectra presented in Figure 5. This indicates that carbon deposition is much slower than carbon removal by O$_2$, so that during steady-state CH$_4$ oxidation carbon deposits do not accumulate on the catalyst.

The low level of reducibility of MoO$_x$ by CH$_4$ implies that CH$_4$ oxidation over MoO$_x$/SiO$_2$ cannot proceed according to a Mars–van Krevelen mechanism in which stable surface O$^-$ anions are removed by CH$_4$ to yield products. For such a mechanism to produce CH$_2$O and H$_2$O, the surface would have to be reduced by 4 e$^-$ per CH$_4$ converted, namely

$$\text{CH}_4 + 2\text{O}^{2-} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + 4\text{e}^-$$

Since the MoO$_x$ are isolated on SiO$_2$, such a mechanism would result in the reduction of MoVI to MoIV. If, instead, a mechanism involving the removal of O$^{2-}$ anions from two MoO$_x$ sites was postulated, as has been done in the formulation of microkinetic models for CH$_4$ oxidation over MoO$_x$/SiO$_2$, then it would be expected that the reduction of MoVI to MoIV would be observed under CH$_4$. Since the average reduction of Mo observed by XAS under CH$_4$ at 873 K is $\approx$2 e$^-$ per Mo, it is inferred that CH$_4$ is incapable of reducing MoO$_x$/SiO$_2$ by removing O$^{2-}$ anions.

O$_2$ chemisorption was performed on MoO$_x$/SiO$_2$ after the catalyst was treated under CH$_4$/O$_2$ mixtures at 873 K in order to gauge the level of catalyst reduction during steady-state CH$_4$ oxidation. The O$_2$-pulsed titration curve obtained after treatment of MoO$_x$/SiO$_2$ under 90% CH$_4$/10% O$_2$ is shown in Figure 5 for comparison to those obtained after H$_2$ and CH$_4$ treatment. The character of the O$_2$ pulsed titration curves obtained after treatment under CH$_4$/O$_2$ mixtures was similar to that obtained after treatment under H$_2$; the sample adsorbed O$_2$ rapidly until it was saturated, after which adsorption ceased. The level of reduction observed during CH$_4$ oxidation was very small, and pulses containing only 17.4 nmol O$_2$ were utilized to titrate the reduced sites of $\approx$500 mg of MoO$_x$/SiO$_2$ after exposure to CH$_4$ oxidation conditions. The amounts of reduced sites titrated after treatments at 873 K under feeds of various CH$_4$/O$_2$ compositions are summarized in Table 2 as the number of O atoms adsorbed per Mo atom. As the CH$_4$ feed fraction was increased, the level of reduction of the surface increased. O$_2$ adsorption was measurable for CH$_4$ feed fractions $\geq$43%. After treatment under 90% CH$_4$/10% O$_2$, 340 O atoms were adsorbed per million Mo atoms. The level of reduction could also be increased by decreasing the O$_2$ feed fraction. After treatment under 90% CH$_4$/6.7% O$_2$, 580 O atoms were adsorbed per million Mo atoms. When a mixture of 20% CH$_4$/10% O$_2$ was used, no measurable adsorption of O$_2$ was observed. The amount of adsorption expected based on extrapolation of data gathered under CH$_4$/O$_2$ mixtures containing 43–90% CH$_4$ was 53 O atoms per million Mo atoms, which was near the detection limit of the technique. This is in good agreement with the previously reported amount of O$_2$ adsorption following treatment of MoO$_x$/SiO$_2$ with a loading of 2.67 wt % Mo at 873 K under 20% CH$_4$/10% O$_2$, which was reported as 13 nmol O/g of catalyst or 48 O atoms per million Mo atoms.$^{48}$

**Isotopic Exchange of Oxygen during CH$_4$ Oxidation by $^{18}$O$_2$.** Previous studies of CH$_4$ oxidation over SiO$_2$-supported oxides have determined that a large amount of the $^{18}$O of SiO$_2$ is incorporated into the reaction products when a CH$_4$/$^{18}$O$_2$ mixture is used as the feed and reaction products are analyzed by mass spectrometry.$^{22,23}$ We have observed a similar phenomenon when a H$_2$/$^{18}$O$_2$ mixture is reacted over MoO$_x$/SiO$_2$. Moreover, in-situ Raman spectroscopy revealed that $^{18}$O is incorporated into the exposed surface of SiO$_2$. These studies revealed that the isotopic compositions of Mo=O species and H$_2$O were in quasi-equilibrium and that H$_2$O exchanged O atoms rapidly with the SiO$_2$ support. A similar approach was used in the present study in order to investigate the distribution of O isotopes between the products and the catalyst when CH$_4$ was oxidized by $^{18}$O$_2$ over MoO$_x$/SiO$_2$.

The Raman spectrum of MoO$_x$/SiO$_2$ is shown in Figure 6 after calcination at 920 K and after 8 and 78 min of exposure to a mixture containing 40% CH$_4$/6% 18O$_2$/54% He. Open circles are the fit composed of the Lorentzian components shown on the abscissa. The total gas flow rate was 20 cm$^3$(STP)/min; the catalyst mass was 31.0 mg.
indicating that 79\% of the 16O in the D2 feature had been replaced by 18O.

Figure 7 shows the isotopic compositions of the surface Mo=O and SiO2 D2 features as functions of time during exposure of the catalyst to a mixture of 40\% CH4/6\% 18O2/54\% He at 920 K. The isotopic compositions of the oxygen-containing products are also shown in this figure. The isotopic compositions of H2O and CO2 are identical to that of the Mo=O feature at all times. We have recently shown that the exchange of oxygen between H2O and Mo=O occurs very rapidly,\textsuperscript{28} and previous work has demonstrated the rapid exchange of oxygen between CO and MoOx/\textsubscript{SiO2}.\textsuperscript{22} The 16O fraction of the D2 feature of SiO2 decreases with time on stream but is significantly greater than that of the Mo=O feature at all times, indicating that 16O is exchanged more slowly with the SiO2 surface than with the supported MoO\textsubscript{x} species. The 16O fractions of CH3O and CO are slightly greater than that of the Mo=O feature for reaction times >20 min but are less than that of the D2 feature of SiO2. The 16O fraction of CH3O approaches 20\% after 80 min of reaction, whereas that of Mo=O is <10\%. This is probably the result of direct oxygen exchange between CH3O and the SiO2 surface, which is enriched in 18O relative to the MoO\textsubscript{x}, at any time on stream. CO is formed via decomposition of CH3O over MoOx/\textsubscript{SiO2},\textsuperscript{1,2} and it has been shown previously that CO does not exchange oxygen at a significant rate with MoOx/\textsubscript{SiO2}.\textsuperscript{22} As a consequence, the isotopic compositions of CH3O and CO are expected to be identical, which is what was observed.

The amount of 16O incorporated into oxygenated products was estimated by integration of the molar flow rates of 16O-containing products over the duration of an experiment. Because the reaction rates for exchange of oxygen between the products and the surfaces of the in-situ Raman cell were unknown, there was some uncertainty in the estimate but the amount of exchangeable oxygen was estimated as 22–30 \textsuperscript{16}O atoms per Mo atom. This is much more oxygen than the 5 \textsuperscript{16}O atoms coordinated to the supported MoO\textsubscript{x} moieties and is about equal to the amount of oxygen on the surface of MoOx/\textsubscript{SiO2}.\textsuperscript{28} Hence, in addition to the oxygen associated with the supported MoO\textsubscript{x} moieties, all of the oxygen present on the surface of the SiO2 support can be incorporated into the reaction products during CH4 oxidation.

An effort was made to ascertain whether oxygen from the SiO2 surface is incorporated into the reaction products as a direct consequence of the oxidation of CH4 or as the result of the secondary exchange of oxygen between H2O (or other oxygen-containing products) and the SiO2 surface. To this end, a comparison was made between the kinetics of oxygen exchange between the gas phase and the D2 feature of SiO2 observed during CH4 oxidation by 18O2 over MoOx/\textsubscript{SiO2} and the kinetics observed during exposure of MoOx/\textsubscript{SiO2} to H2\textsuperscript{18}O. Assuming the gas phase in the Raman cell is completely backmixed, the rate of exchange of oxygen between the oxygen of a surface feature j and gaseous H2O is given by

\[ r_j = \frac{d\theta_j}{dt} = k_p H_2 O \eta (\theta_j - \eta) - \theta_j (1 - \eta) \]

where \( r_j \) is the (negative) rate of 16O accumulation in the surface feature j in mol min\textsuperscript{-1}, \( n_j \) is the total number of moles of oxygen in the surface feature j, \( \theta_j \) is the fraction of the oxygen in surface feature j that is 16-labeled, \( k_p \) is the rate constant for oxygen exchange in units of (atm min\textsuperscript{-1}), \( p_{H_2O} \) is the partial pressure of H2O, \( \eta \) is the fraction of oxygen in H2O that is 16-labeled, and t is time.

To isolate the kinetics of oxygen exchange with the D2 feature of SiO2, the rate of depletion of 16O from the D2 feature, \(-d\theta_D/dt\), can be plotted parametrically against the kinetic group \( p_{H_2O}/(\theta_D - \eta) \) to yield the oxygen exchange rate constant \( k_D \). Such a plot is shown in Figure 8 for oxygen exchange with the SiO2 D2 feature occurring during exposure of MoOx/\textsubscript{SiO2} to H2\textsuperscript{18}O and during the reaction of 40\% CH4/6\% 18O2. While the data are quite noisy due to experimental error, it is clear that the rates of depletion of 16O from the D2 feature are comparable for the two processes. Linear regression of the data in Figure 8 gives values of \( k_D \), equal to 1.9 and 2.0 (atm min\textsuperscript{-1}) for exposure of the catalyst to H2\textsuperscript{18}O and for CH4 oxidation by 18O2, respectively. The similarity in the values of \( k_D \) for the two processes indicates that the incorporation of 16O into the products of CH4 oxidation occurs after these products are formed rather than during the process of their formation. If the opposite were true, then the rate of oxygen exchange would have been greater during the reaction of CH4 with 18O2 than during the exposure of the catalyst to H2\textsuperscript{18}O. This view is supported by the observation that the rate of exchange between H2\textsuperscript{18}O and the D2 feature of SiO2 was \( \sim 0.5 \mu\text{mol min}^{-1} \), whereas the rate of oxygen consumption to produce products was \( \sim 20 \mu\text{mol min}^{-1} \). Therefore, during CH4 oxidation by 18O2, the 16O of the SiO2 surface is exchanged into the gas phase primarily by direct
exchange with H$_2^{18}$O produced by the reaction. A small amount of direct exchange between CH$_2$O and the surface oxygen of SiO$_2$ probably also occurs, as evidenced by the slight enrichment in the $^{16}$O fraction of CH$_2$O and CO relative to the $^{16}$O fraction of Mo=O shown in Figure 7. Since the oxygen of the SiO$_2$ support is not involved in the redox cycles that convert CH$_4$ to oxygenated products, the redox processes that convert CH$_4$ to products involve only the O atoms present in the isolated MoO$_3$ species.

Effect of H$_2$O Addition on the Rate of CH$_4$ Oxidation. The addition of H$_2$O to the feed during CH$_4$ oxidation over MoO$_3$/SiO$_2$ yields useful information regarding the reaction mechanism. The activity for methane conversion and the product distribution are tabulated in Table 3 vs feed fractions of CH$_4$ and H$_2$O at 873 K with the O$_2$ feed fraction fixed at 10% and the contact time fixed at 0.15 s. With no H$_2$O in the feed, the rate of CH$_4$ consumption increased from 0.44 to 1.2 $\mu$mol/(cm$^3$ cat s) as the feed fraction of CH$_4$ was increased from 20 to 78%. This indicates that the kinetics of CH$_4$ oxidation are less than first order with respect to CH$_4$, as we have recently reported.$^1$ As the H$_2$O feed fraction was increased from 0 to 1.0% with the CH$_4$ feed fraction fixed at 20% and the contact time fixed at 0.15 s, the rate of CH$_4$ consumption increased from 0.44 to 0.77 $\mu$mol/(cm$^3$ cat s). This large increase in CH$_4$ conversion was accompanied by slight decreases in CH$_2$O selectivity from 48 to 41% and in CO$_2$ selectivity from 14 to 10% and a slight increase in CO selectivity from 38 to 48%. Increasing the feed fraction of H$_2$O to 2.0% did not further enhance the rate of CH$_4$ oxidation or affect the product distribution. A similar trend has been reported for CH$_4$ oxidation by N$_2$O over MoO$_3$/SiO$_2$.$^{10}$ When the feed fraction of CH$_4$ was increased from 20 to 78%, the mole fraction of H$_2$O in the reactor effluent increased from $\sim$0.9 to 2.3%, so it might be expected that the addition of H$_2$O to the 78% CH$_4$ feed would not enhance the CH$_4$ conversion. However, the addition of 2.0% H$_2$O to the 78% CH$_4$ feed did result in a large enhancement in the rate of CH$_4$ consumption from 1.2 to 2.0 $\mu$mol/(cm$^3$ cat s).

Summary of Observations and Discussion of Mechanism of CH$_4$ Oxidation. The XAS and in-situ Raman observations reported here indicate that isolated molybdate species supported on SiO$_2$ cannot be reduced significantly by CH$_4$ at 873 K. On the other hand, significant reduction of molybdate species occurs if H$_2$ is the reducing agent and a moderate degree of reduction is observed with CH$_3$O. In the latter case, H$_2$ produced via CH$_2$O decomposition is believed to be the actual reducing agent, since CO, the other decomposition product, is ineffective for the reduction of isolated molybdate species. Oxygen titration experiments indicate that only $\sim$50–500 ppm of the molybdate species is reduced from Mo$^{VI}$ to Mo$^{IV}$ during steady-state CH$_4$ oxidation at 873 K. These findings suggest that the oxygen atoms involved in the oxidation of CH$_4$ to CH$_2$O are not those coordinated with the stable molybdate species but, rather, are present in metastable structures formed via the reaction of gas-phase O$_2$ with the molybdate species. This deduction is in agreement with that drawn from the previously reported observation that a pulse of CH$_4$ without O$_2$ is converted to CH$_2$O over MoO$_3$/SiO$_2$ to a much smaller extent than a pulse of CH$_4$ including O$_2$.$^{28}$

A mechanism that is consistent with the findings of the present work and with the findings of previous studies is shown in Scheme 1. The first step in the reaction network is a two-electron reduction of the isolated molybdate species by H$_2$, which is present in small concentration under steady-state conditions as a product of CH$_2$O decomposition.$^{1,49,50}$ The Mo$^{IV}$ cations associated with the reduced molybdate species are then oxidized by O$_2$ to form peroxide species. The reaction of the molybdenum peroxide species with CH$_4$ produces CH$_2$O and H$_2$O. Alternatively, the peroxide can react with H$_2$ to regenerate the stable Mo$^{VI}$-containing molybdate species. The dissociative adsorption of CH$_4$ on the peroxide species is taken to be reversible and quasi-equilibrated. The rate-limiting step, leading to CH$_2$O and H$_2$O, is the abstraction of a proton from the methoxide species formed via CH$_4$ adsorption. The H$_2$ shown as the reducing agent for the oxidized molybdate species is envisioned to originate from the decomposition of CH$_2$O formed as the principal reaction product during steady-state CH$_4$ oxidation.$^1$

Scheme 2 is an extension of Scheme 1, which is written with the aim of explaining the increase in the rate of methane oxidation with increasing H$_2$O partial pressure. Water is shown to hydrolyze Mo=O–Si bonds reversibly, and this reaction may be at quasi-equilibrium under reaction conditions, as suggested by isotopic labeling studies.$^{28}$ With increasing concentration in the gas phase, the concentration of surface hydroxide groups

### TABLE 3: Steady-State Activity and Selectivity of MoO$_3$/SiO$_2$ at 873 K vs CH$_4$ and H$_2$O Feed Fractions

<table>
<thead>
<tr>
<th>CH$_4$ feed fraction (%)</th>
<th>H$_2$O feed fraction (%)</th>
<th>CH$_4$ conversion (%)</th>
<th>CH$_4$ consumption rate ($\mu$mol CH$_4$/cm$^3$ cat $\times$ s)</th>
<th>CH$_3$O (%)</th>
<th>CO (%)</th>
<th>CO$_2$ (%)</th>
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<td>5.0</td>
<td>0.77</td>
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<td>48</td>
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<tr>
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<td>2.0</td>
<td>3.3</td>
<td>2.0</td>
<td>40</td>
<td>52</td>
<td>8</td>
</tr>
</tbody>
</table>

* Feed includes 10% O$_2$, balance He. Total gas flow rate, 30 cm$^3$ (STP)/min; catalyst mass, 196 mg; pressure, 2 psig; contact time, 0.15 s.
SCHEME 2. Proposed Mechanism of CH₄ Oxidation at Isolated, SiO₂-supported MoO₃ Sites, Including Parallel Pathways Enabled by the Presence of H₂O

The pathways outside of the dashed envelope are active when H₂O is present in the gas phase.

would increase, thereby enhancing their availability for reaction with the methoxide species produced during the activation of methane. It should be noted that excessive addition of H₂O to the feed would be detrimental, since complete hydrolysis of all Mo—O—Si bonds can lead to the removal of Mo from the support as volatile MoO₃(OH)₂. This phenomenon has been observed in our laboratory for MoO₃/SiO₂ catalysts with Mo loadings ranging from 0.2 to 9.3 Mo/nm².51

The large number of surface species and reaction pathways associated with the mechanism shown in Scheme 2 precludes quantitative fitting of the scheme to the observed kinetics. Nevertheless, this reaction mechanism is consistent with the observation of a lower than first-order rise in the rate of CH₄ oxidation with increasing CH₄ partial pressure. Since the reaction of methoxide species with hydroxyl species is thought to be rate limiting, the surface concentration of methoxide species will increase with increasing CH₄ partial pressure, thereby shifting the equilibrium for the reversible adsorption of CH₄ to the right

\[ \text{CH}_4 + \text{Mo(OSi≡≡)}_d \text{(O)}_2 \rightleftharpoons \text{Mo(OSi≡≡)}_d \text{(OCH₃)} \text{(OH)} \]

The increased surface concentration of methoxide drives the rate of the reverse reaction (methane desorption), so that the increase in methoxide concentration with respect to CH₄ is less than linear. Hence, the observed rate of CH₄ oxidation is less than first order with respect to CH₄ partial pressure. Unfortunately, the rates of reaction of the surface peroxide and surface methoxide are apparently too rapid to allow their concentrations to be quantified or even to allow their observation by in-situ Raman spectroscopy.

Scheme 1 is consistent with prior observations made in the literature. As noted above, it has been reported that a pulse of CH₄ without O₂ reacts over isolated Si-supported molybdate species to a much smaller extent than does a pulse of CH₄ including O₂.45 The authors of this study attribute the difference in reactivity for the two cases to a metastable form of surface oxygen that is incompletely reduced, such as, for example, the Mo-bound peroxide species shown in Schemes 1 and 2. Such an active form of surface oxygen is also consistent with surface potential measurements of MoO₃/SiO₂ made previously during CH₄ oxidation. By measuring the change in surface potential under varying partial pressures of CH₄ and O₂, it was determined that the form of oxygen that is active for CH₄ oxidation is reduced by one electron per O atom.52 The Mo-bound peroxide proposed in Schemes 1 and 2 is representative of such a species.

Previously published schemes for CH₄ oxidation, including ours, have attempted to explain the kinetics for CH₄ oxidation over MoO₃/SiO₂ by mechanisms in which multiple oxide anions react with CH₄ to yield CH₂O, H₂O, and a reduced catalyst.1,9,10 While such mechanisms do describe CH₄ oxidation kinetics successfully,1,9 they predict a much greater level of molybdate reduction (10–20%) than is observed experimentally.1 The inability of CH₄ to reduce MoO₃/SiO₂ significantly, as observed here by XAS, is perhaps the strongest evidence that such mechanisms are incorrect physically. Such mechanisms have also relied on the participation of multiple Mo-containing sites, which is inconsistent with the fact that the highest specific activity for methane oxidation is observed for MoO₃/SiO₂ catalysts in which Mo is present as the sole isolated molybdate species. Such mechanisms are inconsistent, as well, with the findings that the active form of surface oxygen is short-lived48 and reduced by one electron per O atom.52 Hence, we believe that the mechanism shown in Schemes 1 and 2 is more likely to be physically correct than previously published mechanisms.

Some precedent does exist for the existence of Mo peroxides and for their activity for the oxidation of organic molecules. Peroxide-ligated Mo complexes have been observed by Raman spectroscopy both in solution and in crystalline solids53,54 and are known to catalyze the oxidations of alcohols, amines, and sulfides at low temperatures.55 Furthermore, metal peroxide species have been implicated as the active surface species responsible for the oxidation of CH₄ to CH₂O over Fe₀.₅ Al₀.₅ PO₄ and have been observed by in-situ IR spectroscopy at 623 K.56 Efforts undertaken in the course of the present study to observe peroxide species on MoO₃/SiO₂ by Raman spectroscopy under similar conditions were not successful, probably because of the much lower concentration of active metal in MoO₃/SiO₂ as compared to Fe₀.₅ Al₀.₅ PO₄. Nevertheless, the indirect evidence for peroxide species presented above support the conclusion that the formation of such species is an essential step in the oxidation of methane to formaldehyde.

Conclusions

MoO₃/SiO₂ prepared with a Mo loading of 0.44 Mo/nm² consists of isolated, pentacoordinated species containing a single Mo==O bond. These species are readily reduced by H₂ to molybdate species containing Mo⁴⁺ cations, but CH₄ and CO are not effective reducing agents for this process. During steady-state oxidation of CH₄ to CH₂O, only ~50–500 ppm of Mo⁴⁺ in the catalyst is reduced to Mo⁴⁺. On the basis of these observations, it is proposed that the active species for methane oxidation is a peroxide species formed by the reaction of O₂ with the low concentration of reduced molybdate species present on the catalyst surface. As shown in Schemes 1 and 2, the...
activation of methane is envisioned to be reversible and at quasi-equilibrium. In this scheme, the rate-limiting step for the formation of CH₂O and H₂O is taken to be proton abstraction from methoxide groups formed by the dissociative adsorption of CH₄ by surface peroxide groups. Isotopic tracer experiments show that H₂O rapidly exchanges O atoms with the dispersed molybdate species and with the silica support. However, the oxygen of the silica support does not participate directly in the catalytic cycles that oxidize CH₄. The addition of low concentrations of H₂O to the feed enhances the rate of methane oxidation, and this phenomenon is ascribed to an enhancement in the concentration of surface hydroxide groups on the catalyst surface (see Scheme 2).

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References and Notes