Photo-oxidation of Methanol Using MoO$_3$/TiO$_2$: Catalyst Structure and Reaction Selectivity

Y. C. Liu,* G. L. Griffin,* S. S. Chan,† and I. E. Wachs†

*Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455; and †Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

Received July 11, 1984; revised February 5, 1985

Laser Raman spectra, UV-visible spectra, and photo-catalytic activity measurements are described which show that supported MoO$_3$/TiO$_2$ catalysts prepared by impregnation possess a layer of surface molybdate species coordinated to the titania support. The saturation coverage of this surface molybdate monolayer corresponds to a surface density of ca. 4 x 10$^{-15}$ Mo atoms per cm$^2$ of TiO$_2$. The properties of this surface monolayer are markedly different from bulk MoO$_3$, as reflected in different vibrational frequencies for the surface molybdate species and for bulk MoO$_3$, and in the higher photo-catalytic activity of the surface molybdate relative to bulk MoO$_3$. The photo-efficiency of the TiO$_2$ catalyst containing the surface molybdate monolayer is about one-fifth of the photo-efficiency of pure TiO$_2$, but the selectivity for suppressing secondary oxidation reactions is significantly greater. The major photo-assisted oxidation product on TiO$_2$ is methyl formate, independent of methanol conversion. In contrast, the molybdate monolayer catalyst has nearly 100% selectivity for dimethoxymethane (the reversible condensation product of CH$_3$O + 2 CH$_2$OH) at low conversions. For both catalysts the selectivity of the primary oxidation step appears to be insensitive to the mode of excitation (i.e., thermal vs photo-assisted). Photo-induced changes in selectivity at a given conversion are due primarily to differences in adsorbate coverage at the different operating temperatures required to give equal conversion for dark vs light reactions.

INTRODUCTION

Surface morphology has a major effect on the activity and selectivity of heterogeneous catalysts, especially for multicomponent catalysts such as those used for partial oxidation reactions. A variety of surface morphologies may be encountered with these catalysts, ranging from the homogeneous limit in which the surface composition reflects the composition of a bulk-phase alloy, to the completely segregated limit in which each component exists as crystallites of its own phase. Understanding the structure and chemical behavior of such multicomponent surfaces is a major challenge in the area of partial oxidation catalysis, and in catalysis in general.

Recently our group at Minnesota has become interested in supported MoO$_3$/TiO$_2$ as a possible catalyst for selective photo-oxidation reactions. TiO$_2$ is well known as a photo-catalyst for the partial oxidation of alkanes, alkenes, and alcohols (1-5), but it has relatively poor selectivity for thermally catalyzed reactions (6, 7). In contrast, MoO$_3$ is selective for a number of partial oxidation reactions (8-10), but shows little intrinsic photo-activity (see below). Therefore we decided to investigate whether a properly prepared MoO$_3$/TiO$_2$ catalyst might combine the desired photo-activity and selectivity of the separate components.

A second reason for studying the MoO$_3$/TiO$_2$ system is to determine whether Mo forms a surface molybdate monolayer on TiO$_2$ (11-13). The existence of a surface
molybdate layer is already well documented for Mo supported on Al₂O₃ (14). For the case of MoO₃/TiO₂, a similar monolayer structure may be responsible for the improved thermal selectivity reported for partial oxidation of olefins and alcohols on these catalysts. Non-photo-assisted reactions that have been studied include the oxidation of toluene (12), butadiene (15, 16), isobutene (16), 2-propanol and CO (11), methanol (6), and ethanol (13), and NO reduction using NH₃ (17, 18).

The reaction we have chosen to study is the partial oxidation of CH₃OH. Alcohol oxidation is of general interest as a synthetic reaction, while methanol oxidation provides a simple enough example so that most of the intermediate products can be monitored. If the mechanism is written as a simple series reaction

\[ \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} \rightarrow \text{HCOOCH}_3 \rightarrow \text{CO} \rightarrow \text{CO}_2 \]  

\[ (1) \]

then the goal of our photooxidation research is to determine if it is possible to photo-excite the primary oxidation step (i.e., CH₃OH \rightarrow CH₂O) at low enough temperatures to suppress the rates of subsequent oxidation steps.

Our presentation of results and their subsequent discussion will be divided into two parts. In the results section we first describe the physical characterization of a series of MoO₃/TiO₂ catalysts with different Mo loadings. We then present the results of a series of activity and selectivity measurements for selected catalyst compositions, comparing light and dark reactions. Similarly in the discussion section we deal first with the surface morphology of the catalysts, and then with the probable reaction mechanism for CH₃OH oxidation.

**EXPERIMENTAL**

Catalysts were prepared by impregnating TiO₂ (Degussa P-25) with aqueous solutions containing different concentrations of (NH₄)₆Mo₇O₂₄. The TiO₂ support had a surface area of ca. 50 m²/g, and contained 60% anatase and 40% rutile as determined by X-ray diffraction. The impregnated pastes (ca. 0.5 mℓ solution per gram TiO₂) were dried in air at 393 K overnight, calcined at 773 K for 4 h, and then ground to a fine powder.

X-Ray diffraction patterns were obtained with a Philips diffractometer using CuKα radiation and a diffracted beam monochromator. The diffraction measurements revealed that the anatase : rutile ratio of the TiO₂ support was not altered by the calcination treatment. Surface areas were determined using a standard BET apparatus with N₂ as the adsorbing gas. An average value of 47 ± 2 m²/g was obtained for all of the catalyst compositions studied up to 13.5 wt%, indicating that the TiO₂ support was stable at these calcination temperatures.

Raman spectra were obtained using a multichannel laser Raman spectrometer (19, 20). An Ar⁺ ion laser (Spectra Physics, Model 165) was tuned to the 514.5-nm line for excitation. The laser power at the sample location was set at 40 mW. The Raman spectrometer was a triple monochromator (Instruments SA, Model DL203) that was coupled to a cooled intensified photodiode array detector and an optical multichannel analyzer (Princeton Applied Research, Model OMA 2). The spectral resolution was 6 cm⁻¹.

UV-Visible absorbance spectra were obtained using a Cary 17-D spectrometer. Spectra were obtained in the direct transmission mode, using thin layers of catalyst resuspended from acetone onto NaCl windows.

The photoreactor used in these experiments is shown in Fig. 1. It consists of an aluminum body and a Suprasil window mounted with Teflon gaskets, and can be operated at atmospheric pressure and temperatures up to 473 K. The thin-layer design minimizes residence time, allows good temperature control, and provides a well-defined flow field for the reactant gas, at the expense of operating as an integral reactor at high conversions.
The light source was a 100-W medium-pressure Hg arc lamp, with principle spectral output lines at 365, 545, 580, 435, and 405 nm, according to manufacturer’s data. No attempt was made to calibrate the absolute intensity of the lamp; the relative intensity was controlled by changing the distance between the lamp and the photoreactor.

The catalyst samples were coated onto the illuminated surface of the photoreactor by deposition from a resuspended aqueous slurry. The amount of catalyst used was 100 mg, spread over 20 cm². Photo-activity measurements were obtained using a reactant mixture of 4% CH₃OH/22% O₂/74% He. Product analysis was performed using a gas chromatograph (Porapak T column, 4 ft. × § in., He carrier flow 20 cm³/min) with a flame ionization detector. The reactant residence time in the photoreactor was fixed at 0.2 min for all measurements reported here. The observed partial oxidation products included CH₂O, dimethoxy-methane (DMM = (CH₃O)₂CH₂), methyl formate (MF = HCOOCH₃), and dimethyl ether (DME = (CH₃)₂O). We did not attempt to measure the yields of CO and/or CO₂ at high CH₃OH conversions; their sum could be estimated by applying a carbon balance over the remaining products.

The laser Raman spectra, X-ray diffraction patterns, and surface areas were obtained at Exxon. The catalyst preparation, UV–visible spectra, and catalytic activity measurements were performed at Minnesota.

RESULTS

I. Physical Characterization

The catalyst compositions studied in this work are listed in Table I. Weight percentage loadings are calculated as (grams MoO₃)/(grams MoO₃ + grams TiO₂), based on concentration and quantity of solution used during the impregnation step. For reference we also list the effective surface concentration of Mo atoms per square centimeter of TiO₂ for each loading, based on the average measured BET surface area of 47 m²/g.

X-Ray diffraction. Diffraction patterns were obtained for samples containing 0.8 to 13.5 wt% MoO₃. Crystalline MoO₃ was detected only in the XRD patterns of the 7.5 and 13.5 wt% loadings. The absence of bulk-phase MoO₃ in the XRD patterns for the 0.8, 1.8, and 4.0 wt% loadings implies that for these samples the molybdenum oxide is present in either a noncrystalline state or as small crystallites of less than 4 nm in diameter. Additional information

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Catalyst Compositions Studied in This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% loading</td>
<td>(MoO₃)/(MoO₃ + TiO₂)</td>
</tr>
<tr>
<td>0.3</td>
<td>2.8 x 10¹³</td>
</tr>
<tr>
<td>0.8</td>
<td>7.0 x 10¹³</td>
</tr>
<tr>
<td>1.9</td>
<td>1.6 x 10¹⁴</td>
</tr>
<tr>
<td>4.0</td>
<td>3.6 x 10¹⁴</td>
</tr>
<tr>
<td>7.5</td>
<td>6.8 x 10¹⁴</td>
</tr>
<tr>
<td>13.5</td>
<td>1.3 x 10¹⁵</td>
</tr>
<tr>
<td>44.0</td>
<td>6.5 x 10¹⁵</td>
</tr>
<tr>
<td>66.0</td>
<td>1.7 x 10¹⁶</td>
</tr>
</tbody>
</table>
about the state of molybdenum oxide at these low loadings is provided by other spectroscopic results presented below.

**Laser Raman spectra.** In Fig. 2 we show the laser Raman spectra over the frequency range from 750 to 1200 cm\(^{-1}\) for the five catalyst compositions mentioned above, and for unpromoted TiO\(_2\). The sharp vibrational bands at 821 and 997 cm\(^{-1}\) seen for the 7.5 and 13.5 wt% MoO\(_3\)/TiO\(_2\) catalysts are characteristic of bulk MoO\(_3\) (21). The anatase phase of the TiO\(_2\) support possesses a weak second-order feature at 794 cm\(^{-1}\) (22). The 0.8, 1.8, and 4.0 wt% catalysts, however, exhibit a broad Raman band between 900 and 1000 cm\(^{-1}\). The peak of the broad Raman band shifts from 940 to 97 cm\(^{-1}\) as the molybdenum oxide loading increases. The position, shape, and loading-dependent shift of this band preclude its assignment to either crystalline MoO\(_3\) or TiO\(_2\). Instead, we associate the band with a surface molybdate species coordinated to the TiO\(_2\) support.

The Raman spectra of the 7.5 and 13.5 wt% catalysts also exhibit the broad band at 967 cm\(^{-1}\) assigned to the surface molybdate phase, in addition to the sharp bands at 821 and 998 cm\(^{-1}\) assigned to MoO\(_3\) crystallites. However, the features of the broad Raman band of the surface molybdate phase remain constant for the 4.0, 7.5, and 13.5 wt% samples. This suggests that the coverage of the surface molybdate species reaches a saturation limit at a catalyst loading of about 4 wt% MoO\(_3\)/TiO\(_2\).

**UV-Visible spectra.** In Fig. 3 we show the UV-visible spectra over the wavelength range 350–600 nm for all of the catalyst compositions listed in Table 1, and for pure TiO\(_2\) and pure MoO\(_3\). Pure TiO\(_2\) shows an absorption edge at 420 nm, corresponding to the bulk TiO\(_2\) band gap of 3.1 eV (23). As the Mo loading increases to 4.0 wt% MoO\(_3\)/TiO\(_2\), corresponding to the range of loadings over which the surface molybdate Raman band became fully developed, the sharpness of the TiO\(_2\) absorption edge degrades progressively. For the 4.0 wt% loading, the absorption edge is no longer directly apparent. Instead, the absorbance decreases continuously over the region 400 to 500 nm, suggesting a broadened distribu-
tion of absorption transitions over this energy range.

For loadings greater than 4.0 wt% MoO$_3$/TiO$_2$, the absorption spectrum from 400 to 500 nm remains essentially unchanged. This provides further evidence that the surface molybdate monolayer is completed at a loading of approximately 4.0 wt% MoO$_3$/TiO$_2$. A structureless increase in the baseline absorbance above 500 nm is observed, which we attribute to absorbance by MoO$_3$ crystallites. The spectrum of bulk MoO$_3$ is shown at the top of the figure. It shows a poorly defined absorption edge at 405 nm corresponding to the bulk MoO$_3$ band gap of 2.9 eV (23), and a slowly rising structureless absorbance above 450 nm.

Additional evidence for the assignment of the absorbance slope between 400 and 500 nm is given in Fig. 4, in which we compare the UV-visible spectra for pure TiO$_2$, pure Mo$_3$, the 4.0 wt% MoO$_3$/TiO$_2$ catalyst, and an 8.0% MoO$_3$/Al$_2$O$_3$ catalyst. The latter sample was prepared from Degussa Alon-C (surface area 100 m$^2$/g), using the same impregnation procedure as above. Previous laser Raman studies have shown that a surface molybdate monolayer is present on γ-Al$_2$O$_3$ at this loading (21).

The absorbance in the region 400–500 nm is essentially constant for the 8 wt% MoO$_3$/Al$_2$O$_3$ catalyst, in contrast to the monotonic decrease seen for the 4.0 wt% MoO$_3$/TiO$_2$ catalyst. Since both catalysts contain about a monolayer of surface molybdate species, this suggests that the absorption transitions in this region are not intrinsic to surface molybdate species on all supports. Instead, we suggest that the absorbance in the region 400–500 nm may be due to sub-band gap transitions in the near-surface region of the TiO$_2$ support that are induced by the presence of the surface molybdate monolayer.

II. Kinetic Characterization

Two kinds of kinetic experiments were performed to probe the reaction characteristics of these catalysts. In the first set we measured the photo-conversion and major product yields for catalysts with different molybdena loadings, using a fixed reactor temperature (403 K) and light source distance (11 cm). In the second set (see below) we examined product yields as a function of conversion for selected catalyst compositions.

Catalyst loading studies. Figure 5 shows the photo-conversion of CH$_3$OH as a function of molybdena loading. Loadings are expressed as Mo atom concentration per square centimeter of TiO$_2$ surface area (cf. Table 1), using a logarithmic concentration axis to clearly display the entire range that was studied. Photo-conversion (vertical axis) is defined as the difference between the fractional conversion of CH$_3$OH measured with the light on and off. At 403 K, the dark conversion was negligible on TiO$_2$ and reached a maximum value of 6% for the 13.5 wt% loading.
The highest conversions are obtained with low Mo loadings. This behavior is consistent with the high photo-efficiency expected for TiO₂. The photoconversion drops steadily as the Mo loading is increased, and there is no measurable photo-conversion for bulk MoO₃. We note, however, that most of the decrease in photo-conversion occurs over the range of loadings where the Raman and UV-visible data showed that the surface molybdate layer was being completed. This suggests that sites on the uncovered TiO₂ and the surface molybdate layer are kinetically distinguishable. The two types of site have different specific photo-efficiencies, with the surface molybdate layer sites being the less efficient type.

Further evidence that the surface molybdate layer becomes complete over the range of loadings up to approximately 4.0 wt% MoO₃/TiO₂ is seen in the major product yields for each loading. Figure 6 shows the relative photo-assisted yield of methyl formate (MF) observed for each catalyst loading, as measured directly from the difference between the GC peak areas recorded with the light on and off. Methyl formate is the major product observed for catalysts with low Mo loadings, and for pure TiO₂ (see below). The photo-yield of MF decreases for higher loadings, with most of the decrease again occurring over the range where the surface molybdate layer is being completed.

Figure 7 shows the photo-yield of dimethoxymethane (DMM) observed for each loading. At 403 K, DMM rather than CH₂O is observed as the primary oxidation product (see below). The dependence on catalyst loading is markedly different from that seen for MF. The DMM yield is small for catalysts with low Mo loadings, and increases to a maximum near the loading where the surface molybdate layer is complete. This shows that DMM is the favored photo-product at sites on the surface molybdate layer. At higher loadings the DMM photo-yield decreases, and the yield drops to zero for pure MoO₃. This suggests that for loadings above monolayer coverage, the surface molybdate sites become partially blocked by MoO₃ crystallites which are themselves photo-inert.

Yield vs conversion studies. Two methods were used to vary the conversion, in order to separate thermally induced effects from photo-assisted effects. In the first method, we varied the conversion of the photo-controlled reaction by changing the distance between the light source and the photoreactor. In the second method we varied the conversion of the dark reaction by changing the reactor temperature. To achieve comparable conversions in the two sets of experiments, it was necessary to perform the thermal reactions in a separate tubular reactor that could be operated above 473 K.
In Fig. 8 we show the yields of all measurable intermediate products for the dark reaction on TiO$_2$. Here the yield is defined as the exit concentration of each product, divided by the inlet concentration of CH$_3$OH. The yields are plotted as a function of CH$_3$OH conversion, so that a tangent to the curve through the data points for each product has a slope equal to the instantaneous selectivity for that product. The temperature needed to achieve each indicated conversion is shown along the top axis.

For TiO$_2$, the dark reaction does not become measurable until 440 K. At this temperature, the only observed products are dimethyl ether (DME) and methyl formate (MF). Neither CH$_2$O nor DMM are observed, indicating that secondary oxidation occurs rapidly. The MF yield passes through a maximum at a CH$_3$OH conversion of only 10%, indicating that MF oxidation to CO or CO$_2$ is also fast relative to the primary oxidation rate.

For comparison, Fig. 9 shows the photo-yields as a function of conversion for illuminated TiO$_2$ at 403 K. The distance between the light source and the sample needed to achieve each conversion is listed along the top axis of the figure. We see that comparable conversions are obtained at substantially lower temperatures, and that MF is still the major product. However, the MF yield does not pass through a maximum, and there are significant yields of CH$_2$O and DMM. Thus the secondary oxidation steps have been significantly suppressed by operating at lower temperature. Also, there is no measurable photo-yield of DME.

The corresponding results for the surface molybdate catalysts are shown in Figs. 10–12. Figure 10 shows the product yields for the dark reaction on the 4.0 wt% MoO$_3$/TiO$_2$ catalyst. It should be remembered that this loading corresponds approximately to a complete monolayer of the surface molybdate species. Reaction occurs at much lower temperatures than on TiO$_2$, and both DMM and CH$_2$O products are seen in addition to MF and DME. The DMM yield passes through a maximum because its formation from CH$_2$O and two CH$_3$OH molecules becomes unfavorable at higher temperatures. The maximum in the CH$_2$O yield is attributed to the onset of secondary oxidation at higher temperatures.

Since the results in Fig. 8 showed that TiO$_2$ is very active for the thermally controlled oxidation of CH$_3$OH, it seems possible
that the decay of the CH$_2$O yield at high conversions seen for the 4.0 wt% MoO$_3$/TiO$_2$ catalyst might be due to oxidation at exposed TiO$_2$ sites not completely covered by the surface molybdate layer. To test this possibility, we also examined the 13.5 wt% MoO$_3$/TiO$_2$ catalyst in detail. At this loading the surface molybdate monolayer should be complete, although at the expense of having MoO$_3$ crystallites present.

The yields for the dark reaction on the 13.5 wt% MoO$_3$/TiO$_2$ catalyst are shown in Fig. 11. The CH$_2$O yield increases monotonically for conversions up to 90%. This supports the idea that exposed TiO$_2$ is responsible for some of the MF formation seen with the 4.0 wt% catalyst. However, significant amounts of MF are still produced on the 13.5 wt% catalyst, indicating that MF is also produced at molybdenum sites. At present we cannot determine whether this MF production occurs preferentially at the sites on the surface molybdate layer or on the MoO$_3$ crystallites.

In Fig. 12 we show the yields for the light reaction on the 13.5 wt% MoO$_3$/TiO$_2$ catalyst at 403 K. The highest photo-assisted conversion that could be achieved is 16%, compared to the 63% conversion that could be obtained with pure TiO$_2$. The DMM and MF selectivities are both similar to those seen for the thermal reaction at low conversion, which suggests that the relative rates of the first and second oxidation steps are independent of whether the reaction is thermally or photochemically controlled. The major difference is that CH$_2$O is not detected in the photo-controlled reaction, indicating again that condensation to produce DMM is strongly favored at the lower temperature. Also, DME is absent as a photo-product.

The yield vs conversion curves for the photo-controlled reaction on the 4.0 wt% MoO$_3$/TiO$_2$ catalyst are nearly identical to those in Fig. 12. This confirms that the MoO$_3$ crystallites present at the higher loading are photo-inert. It also suggests that
the exposed TiO\textsubscript{2} sites in the 4.0 wt% catalyst comprise a small enough fraction of the total surface that their presence does not contribute significantly to the photo-behavior of the catalyst.

**DISCUSSION**

*Catalyst morphology.* The spectroscopic and kinetic results for the different Mo loadings (cf. Figs. 2–7) provide convincing evidence that a surface molybdate monolayer is formed in the MoO\textsubscript{3}/TiO\textsubscript{2} system. All of the measurements show a transition in behavior at approximately 4.0 wt% MoO\textsubscript{3}/TiO\textsubscript{2} loading. As shown in Table 1, this loading corresponds to a surface concentration of $3.6 \times 10^{14}$ Mo atom/cm\textsuperscript{2} of TiO\textsubscript{2}. We estimate the relative uncertainty of this number to be ±10%. Thus the saturation coverage of the surface molybdate layer on TiO\textsubscript{2} is comparable to the value for molybdena on Al\textsubscript{2}O\textsubscript{3} reported by Weller ($4 \times 10^{14}$ cm\textsuperscript{-2}) (24). This similarity suggests that the packing of the surface molybdate may be insensitive to the structure of the underlying support. We note further that the (001) anatase and (110) rutile crystal planes have surface unit cell densities of 7.0 and $5.4 \times 10^{14}$ cm\textsuperscript{-2}, respectively (25); these are the principal crystal planes expected in an anatase–rutile mixture (26, 27). Thus we conclude that the surface molybdate layer contains less than one Mo atom per surface unit cell of TiO\textsubscript{2}, and may have a stoichiometry as low as one Mo atom per every two surface cells.

The laser Raman spectroscopy results are particularly helpful in demonstrating the molybdena morphology due to the sensitivity of this technique for both small MoO\textsubscript{3} crystallites and noncrystalline molybdena species (21). Thus we can confidently conclude that MoO\textsubscript{3} crystallites are not present in these catalysts until the molybdena loading exceeds approximately 4.0 wt%, and that in catalysts with lower loadings the molybdena is present only as a noncrystalline surface molybdate layer.

Additional information about the surface molybdate layer is provided by the coverage dependence of the Raman band 940–970 cm\textsuperscript{-1}. The large width of this band indicates that it is due to transitions within a distribution of vibrational states, rather than a single discrete transition. The coverage dependence of the molybdate Raman band suggests that the local environment of the surface molybdate species is changing with coverage. This suggests that the Mo atoms in the partially completed monolayer are randomly distributed over the TiO\textsubscript{2} surface rather than being present in saturated islands of a surface molybdate phase. Recent in situ studies have shown that shifts in Raman bands may be associated with changes in the average number of adsorbed H\textsubscript{2}O molecules coordinated to the molybdate species, and that this number is a function of the molybdate coverage (28).

*Reaction mechanism.* A reaction pathway which can account for our observed kinetic results is given in Scheme 1. For clarity, surface OH species are omitted from this representation.

The first step (r1) is assumed to be the dissociative adsorption of CH\textsubscript{3}OH. Spectroscopic evidence for the CH\textsubscript{3}OH intermediate has been observed on both MoO\textsubscript{3} (29) and TiO\textsubscript{2} (30), and the analogous C\textsubscript{2}H\textsubscript{5}OH intermediate has been reported on MoO\textsubscript{3} supported on SiO\textsubscript{2} (31).

The CH\textsubscript{3}O\textsubscript{(a)} intermediate can then react via either an oxidative or nonoxidative channel. In the nonoxidative channel, it reacts with a neighboring CH\textsubscript{3}O\textsubscript{(a)} group or...
physically adsorbed CH$_3$OH molecule to produce the condensation product DME (r2). The reaction occurs thermally on both TiO$_2$ and the surface molybdate catalysts, but it cannot be photo-excited on either catalyst.

The oxidative channel involves H-atom abstraction from CH$_3$O$_{(a)}$ to produce a transient adsorbed CH$_2$O$_{(a)}$ intermediate (r3). This has been shown to be the rate-limiting step on MoO$_3$ and Fe$_2$O$_3$-MoO$_3$ methanol oxidation catalysts (8). Our results show that this step can be photo-excited on both TiO$_2$ and the surface molybdate catalyst. The mechanism of the photo-excited reaction probably involves hole capture at a surface O$^-$- anion to produce a surface O$^-$ species, which then abstracts an H atom from a neighboring CH$_3$O$_{(a)}$ group (32).

The CH$_2$O$_{(a)}$ intermediate can then react via one of three channels: desorption, condensation, or further oxidation. Desorption (r4) is the major thermal reaction on the 13.5 wt% catalyst above 450 K (cf. Fig. 11). Desorption also occurs with about 33% selectivity on TiO$_2$ under photo-controlled conditions (cf. Fig. 9).

The condensation reaction results in the formation of DMM (r5). This is the major reaction on the molybdate catalysts at low conversion (cf. Figs. 10–12), and occurs with about 10% selectivity on TiO$_2$ under photo-controlled conditions (cf. Fig. 9). The reaction is favored by low temperatures, as indicated by the simultaneous decrease in DMM yield and increase in CH$_2$O yield as temperature is increased for the thermally controlled reaction (cf. Figs. 11). We note that the sum of the DMM and CH$_2$O yields is nearly linear with respect to conversion through the low-temperature region, which indicates that both products originate from the same CH$_2$O$_{(a)}$ intermediate. The condensation mechanism is probably analogous to that for acetal formation (33), with nucleophilic attack by the O atoms of two neighboring CH$_2$O$_{(a)}$ or CH$_3$OH species onto the C atom of the CH$_2$O$_{(a)}$ intermediate.

The oxidation channel involves the immediate conversion of the CH$_2$O$_{(a)}$ intermediate into an adsorbed formate species (r6). This reaction has already been shown to occur on ZnO surfaces (34). Evidence that it occurs on TiO$_2$ under photo-controlled conditions is seen in the yield plot for MF (cf. Fig. 9), which is linear with respect to conversion of CH$_2$OH. The absence of positive curvature indicates that MF is a primary oxidation product under these conditions. This in turn indicates that the rate of the oxidation step (r6) is first order in CH$_2$O$_{(a)}$ concentration, and that the subsequent reaction to produce MF (r7) is fast. The mechanism for the oxidative channel probably involves nucleophilic attack at the C atom in the CH$_2$O$_{(a)}$ intermediate by a neighboring O$^-$ surface anion.

We note that these results do not eliminate the possibility that MF is also produced via CH$_2$O disproportionation at higher conversions.

The final steps in Scheme 1 involve the decomposition of the formate intermediate. Again, three channels are available: condensation to produce MF (r7), direct decomposition to produce CO (r8), and oxidative decomposition to yield CO$_2$ (r9). We cannot comment on the selectivity ratio r8/r9, since the product concentrations of CO and CO$_2$ were not measured in this work. However, a carbon balance on the products indicates that hydrogen-containing species make up all of the product spectrum below 450 K. Thus, the ratio (r7)/(r8 + r9) is large at low temperature. This confirms one of the initial goals of this study, namely the use of photoexcitation to activate the primary oxidation step at low enough temperature to suppress the formation of higher oxidation products. Additional work is planned to determine conditions for optimizing this effect.

**SUMMARY**

(1) Molybdena supported on TiO$_2$ is present as a surface molybdate monolayer
at loadings less than $4 \times 10^{14}$ cations/cm$^2$. At higher loadings the additional molybdena is present as MoO$_3$ crystallites.

(2) In the oxidation of CH$_3$OH on both TiO$_2$ and the surface molybdate catalysts, the primary oxidation step is H-atom abstraction from an adsorbed CH$_3$O$_3$($\alpha$) species.

(3) On TiO$_2$, the resulting CH$_2$O$_3$($\alpha$) intermediate is primarily converted to HCOO$_3$($\alpha$), leading to the desorption of MF as the major photo-oxidation product.

(4) On molybdena/TiO$_2$ at 403 K, the CH$_2$O$_3$($\alpha$) intermediate condenses with neighboring CH$_3$O$_3$($\alpha$) groups to produce DMM as the major photo-oxidation product.

(5) Desorption of CH$_2$O does occur as the primary product at higher temperatures on the molybdena/TiO$_2$ catalysts, and under photo-controlled conditions from a minority fraction of the TiO$_2$ surface sites.

(6) The formation of CO and CO$_2$ on TiO$_2$ catalysts is significantly reduced by operating under photo-controlled reaction conditions.

(7) For CH$_3$OH oxidation, the selectivity of the primary oxidation step is insensitive to excitation mechanism. However, overall selectivity is strongly influenced by the reaction temperature and its effect on surface coverages during reaction following the primary oxidation step.

ACKNOWLEDGMENT

This work was supported by the Petroleum Research Fund, administered by the American Chemical Society, under Grant PRF-AC 14072-AC5.

REFERENCES