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True and Spectator Intermediates in Catalysis: The Case of Ethanol Oxidation on Molybdenum Oxide As Observed by in Situ Laser Raman Spectroscopy

S. T. Oyama* and W. Zhang

Contribution from the Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0211

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Abstract: A high-throughput laser Raman spectrometer is used to detect adsorbed ethoxide species during the catalytic oxidation of ethanol over supported molybdenum oxide at atmospheric pressure. Two different species are observed, a true reaction intermediate and a relatively inert spectator on the surface. Steady-state and dynamic experiments indicate that the reactive species is associated with Mo═O terminal bonds on the surface, while the spectator is associated with Mo−O−Mo bridging bonds. Deuterium isotopic substitution experiments indicate that the active intermediate is formed in an equilibrated adsorption step, and decomposes by a rate-determining α-C−H bond-breaking step to form acetaldehyde.

Introduction

Most studies of heterogeneous catalysts are carried out by analyzing the products of reaction and by measuring catalyst properties in the absence of reaction. The need to observe catalysts in their working state to derive mechanistic information was pointed out nearly 40 years ago.[1] Since then, considerable progress has been made in the study of catalytic processes by different *in situ* techniques.[2] However, in only a few cases have adsorbed intermediates been observed and proven to be true reaction intermediates. Examples of these are N atoms formed in the course of the low-pressure decomposition of NH_3 on tungsten[3] and molybdenum[4] as studied by Auger electron spectroscopy, NH_4^+ species in the NH_3 and NO reaction on vanadia−titania catalysts as measured by Fourier transform infrared spectroscopy,[5,6] N atoms in the CO and NO reaction on rhodium as detected by surface-enhanced Raman spectroscopy (SERS),[7] CO in CO oxidation on platinum as observed by photoemission electron microscopy,[8,9] and ethyl and propyl species in ethylene and propylene hydrogenation on Pt(111) as observed by sum frequency generation spectroscopy.[10,11] The present study provides a detailed description of the mechanism of ethanol oxidation on supported molybdenum oxide studied by *in situ* laser Raman spectroscopy and kinetic isotope effect measurements.

A considerable challenge in the application of *in situ* techniques is that even if a surface species is observed, it is not guaranteed to be directly involved in the reaction pathway.[12] In order to prove that an observed species is a true intermediate, dynamic measurements are needed that relate its concentration under working conditions to the reaction mechanism. There are a number of cases in which the observed species is simply an inert spectator on the surface, with only an incidental role in the catalytic mechanism. Examples of these are formate ions in the decomposition of formic acid on alumina[13] or long-chain alkyl groups on the surface of Ru[14,15] or Ni[16] in the course of CO hydrogenation. In these studies, the actual intermediates are protonated formate groups and CH_y species, respectively, but they are not detectable spectroscopically because their concentrations are too low. The present investigation is the first in which both a spectator and an actual reaction intermediate are simultaneously observed. The system comprises ethanol oxidation on silica-supported molybdenum oxide at atmospheric pressure and a temperature range of 375−498 K.

Experimental Section

In this study an advanced laser Raman spectrometer with high light-throughput is used to detect reaction intermediates. Details of the instrument are presented elsewhere.[17] Briefly, the instrument utilizes a highly efficient holographic interference filter (Kaiser Optics, supernotch) to remove the Rayleigh line, which allows the use of a short (0.5 m) single-stage monochromator, rather than a three-stage spectrometer, as has been the norm. Other studies have employed Raman spectroscopy to study working catalysts, but have concentrated on the state of the catalyst itself,[18−21] or adsorption.[22,23] Except for the SERS study cited above, low sensitivities have not allowed dynamic experiments to monitor true reaction intermediates.

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* To whom correspondence should be addressed.

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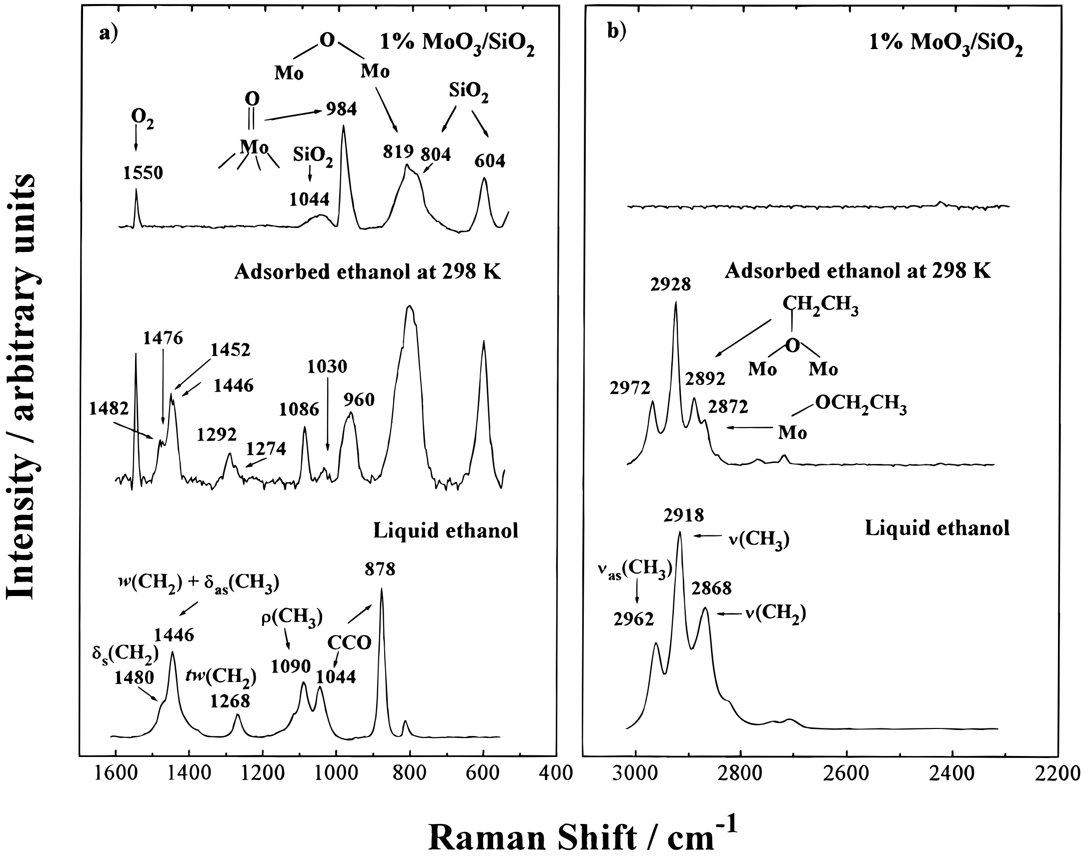

Figure 1. Reference laser Raman spectra in the low- (a) and high- (b) wavenumber regions. Spectra of 1% MoO$_3$/SiO$_2$ in pure oxygen (top), 1.6% ethanol in oxygen adsorbed on 1% MoO$_3$/SiO$_2$ (center), and liquid ethanol (bottom). The spectra were taken at room temperature while rotating the wafer at 800 rpm, using 100 mW at the sample with 120 scans for 7200 s.

The catalyst employed in these studies is a 1% MoO$_3$/SiO$_2$ sample prepared by incipient-wetness impregnation and used in the form of a pressed wafer. Its oxygen chemisorption uptake is 29 μmol g^{-1} and its BET surface area is 83 m^2 g^{-1}.[24] The wafer is held in a controlled atmosphere cell and is rotated at 600−1000 rpm to avoid sample degradation. The cell is connected to a flow manifold and to a gas chromatograph (SRI Model 8610) for analyzing reactants and products. The combined reactivity and spectroscopic measurements were carried out with a mixture of ethanol and oxygen at atmospheric pressure at a total flow rate of 270 μmol s^{-1} (400 cm^3 min^{-1}). The ethanol partial pressure was varied from 0.1 to 0.55 kPa. The oxygen chemisorption value is important because it is the basis for calculating turnover rates. As will be discussed, it gives consistent results with coverages determined independently in transient desorption experiments.

Results and Discussion

The top traces in Figure 1, parts a and b display the *in situ* laser Raman spectra of the 1% MoO$_3$/SiO$_2$ sample in the low- and high-wavenumber regions. Blank experiments show that the features at 604, 804, and 1044 cm^{-1} originate from the silica support, while that at 1550 cm^{-1} is due to gas-phase oxygen. Previous work has already established that the strong peak at 984 cm^{-1} is due to Mo═O terminal bonds, while the small feature at 819 cm^{-1} is associated with Mo−O−Mo bridging bonds.[24,25] The oxygen in the bridging bonds may be coordinated to more than 2 Mo atoms. The middle traces of Figure 1 show the spectra of adsorbed ethanol in the same regions. All of the peaks can be assigned with reference to the spectra of ethanol and recent *ab initio* theoretical work on adsorbed ethoxide species on molybdenum.[26] The assignments are indicated in the bottom traces for ethanol. The adsorbed species can be positively identified as an ethoxide moeity as shown by retention of all the CH$_2$ and CH$_3$ features and replacement of the skeletal CCO modes at 878 and 1044 cm^{-1} by a weak signal at 1030 cm^{-1}, as predicted in the *ab initio* calculations. A notable aspect of the ethoxide spectra is that all the peaks with CH$_2$ character, the symmetric deformation mode (δ_s) at 1476/1482 cm^{-1}, the wagging mode (ω) at 1446/1452 cm^{-1}, and the stretching mode (ν) at 2872/2892 cm^{-1}, are split. This strongly indicates that there are two different types of ethoxide groups on the surface. As will be seen, the ethoxide species with ν(CH$_2$) at 2872 cm^{-1} can be associated with Mo═O bonds, while that with ν(CH$_2$) at 2892 cm^{-1} can be associated with Mo−O−Mo groups. The vibrations with CH$_3$ character appear broadened, but unsplit, because the methyl group is distant from the bonding center at the surface. Adsorption of ethanol on the silica support itself is molecular, and two orders of magnitude smaller than on 1% MoO$_3$/SiO$_2$.

The intensity of the ν(CH$_2$) bands can be used to calculate coverage. The coverage is obtained by normalizing the integrated areas of the deconvoluted ν(CH$_2$) peaks at 2872 and 2892 cm^{-1} to those obtained at saturation conditions obtained at high pressures of ethanol and low temperatures (1.8 kPa and 298 K). All measurements are taken using the SiO$_2$ signal at 604 cm^{-1} as an internal standard.

Figure 2 shows a set of spectra taken at *in situ* reaction conditions that serve in the identification of the ethoxide species. The major product was acetaldehyde at these conditions. The measurements at each temperature are obtained after several hours, when rates have reached a steady state. The left panel

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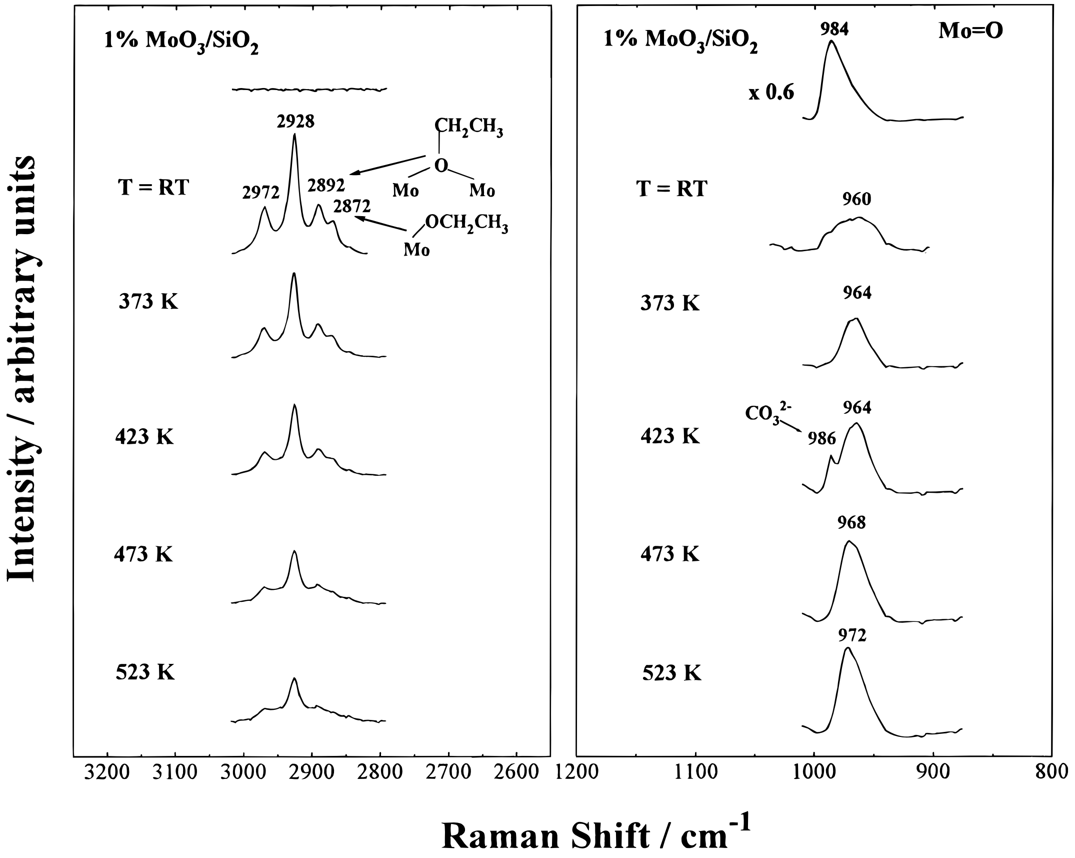

Figure 2. Laser Raman spectra taken at *in situ* steady-state reaction conditions at atmospheric pressure. Ethanol (1.6%) in pure oxygen was employed. The spectra were taken while rotating the wafer at 800 rpm using 100 mW at the sample with 120 scans for 7200 s.

shows the C−H stretch region, with the two peaks at 2872 and 2892 cm^{-1} clearly visible. The two peaks show a different response to temperature: the 2872 cm^{-1} feature disappears at 473 K, while the 2892-cm^{-1} peak persists up to 523 K. This confirms that there are two species. The right panel of Figure 2 focuses on the Mo=O bond. On the freshly oxidized sample, it appears at 984 cm^{-1} with high intensity, but with adsorption of ethanol at room temperature, it is significantly attenuated, and is shifted down to 960 cm^{-1}. This behavior of the Mo=O bond has been observed earlier by infrared spectroscopy.[27] With reaction commencing at 373 K, the Mo=O peak increases in intensity and shifts to higher wavenumber. By the time the temperature reaches 523 K, the peak has recovered to 972 cm^{-1}. The increase in the Mo=O bond peak intensity is directly related to the decrease in the concentration of the ethoxide with ν-(CH_2) at 2872 cm^{-1} and suggests that the two species are associated with the observed reaction. These results are quantitated in Figure 3, which plots the decrease in steady-state coverage, θ, with temperature and the concomittant increase in intensity of the Mo=O feature. Clearly, there is a direct relationship between the two quantities.

In contrast to the Mo=O functionality, after adsorption of ethanol at low temperature the Mo−O−Mo feature does not come back with increasing temperature until the sample is reoxidized at 773 K for 2 h in pure oxygen. Correspondingly, this suggest that the remaining ethoxide species, characterized by the band at 2872 cm^{-1}, is associated with the Mo−O−Mo sites and is relatively unreactive. Indeed, experiments at different partial pressures show that the coverage with this species is constant even though the rate changes, indicating that the species is not participating directly in the reaction. Thus, it is likely to be an unreactive spectator on the surface. More extensive work to be published elsewhere[28] shows that in samples supported on Al_2O_3 and TiO_2 only the 2872-cm^{-1} band is present, and the rest of the CH_2 peaks are unsplit. These supports are known to form atomically dispersed O=Mo terminal molybdenum oxide species, confirming that the 2892-cm^{-1} species is associated with the Mo−O−Mo sites present only on the SiO_2 support.

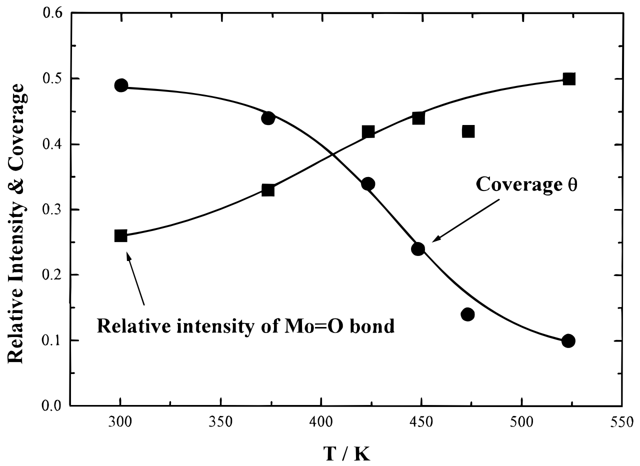

Figure 3. Total steady-state coverage versus intensity of the Mo=O signal at different temperatures. Conditions were the same as in Figure 2.

Further kinetic work using deuterium isotopic substitution on a 9% MoO_3/SiO_2 sample establishes the mechanism of the reaction. Three deuterated ethyl alcohols (Aldrich, C_2H_5OD, 99.5% D; CH_3CD_2OH, 98% D; and CD_3CH_2OH, 99% D) were

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Table 1. Isotopic Substitution Experiments

	v_H/v_D		
temp/K	C_2H_5OD	CD_3CH_2OH	CH_3CD_2OH
488	1.04		
508	1.06	1.33	2.20

used. The ratio of rates of ethanol and the deuterated molecule are reported in Table 1.

The ratio of C_2H_5OH to C_2H_5OD oxidation rates is just slightly larger than unity, suggesting the formation of an ethoxide species in an equilibrated step before the rate-determining step. The small positive deviation from unity is consistent with an equilibrium isotope effect. The ratio of C_2H_5OH to CH_3CD_2OH or CD_3CH_2OH rates is greater than unity suggesting that α- and β-hydride eliminations are rate determining for acetaldehyde or ethylene production. Importantly, the use of CH_3CD_2OH decreases the rate of acetaldehyde formation, but does not increase the rate of ethylene or diethyl ether production, suggesting that these species are formed on different sites.

A schematic sequence of steps that can account for the acetaldehyde formation is:

$$C_2H_5OH + M^* + O^* \overset{K_1}{\rightleftharpoons} M^*{-}OCH_2CH_3 + O^*{-}H$$

$$M^*{-}OCH_2CH_3 \xrightarrow{k_2} CH_3CHO + M^*{-}H$$

The asterisk represents surface species, which include metal sites, M*, and oxygen sites, O*. The key features of the mechanism are that ethanol adsorption leads to the equilibrated formation of an adsorbed ethoxide species, $C_2H_5OM^*$, which undergoes rate-determining α-H elimination to produce acetaldehyde. Not included, because they are not kinetically significant, are the reaction of the hydroxyl, HO*, and hydride, HM*, species to form water or the reoxidation of the site with molecular oxygen. The rate expression obtained with the above sequence shows a good fit with kinetic data obtained by variations of partial pressure.[29] The sequence above is similar to the one accepted for methanol oxidation on silica-supported molybdenum oxide. Isotope effect experiments like the ones reported here have established that methoxide formation is equilibrated and C−H bond-breaking is rate determining.[30,31]

The rate dependence on coverage presented as reaction isotherms is shown in Figure 4. The figure shows the expected behavior for a true intermediate: the steady-state rate increases with temperature, and the corresponding coverage increases with decreasing temperature. Furthermore, the rate increases linearly with coverage, just as predicted from the sequence above which gives $v = k_2\theta$. However, the data show one peculiarity, the isotherms do not extrapolate to zero coverage. This can be explained by the presence of the spectator species on the surface. The coverage of the spectator can be directly measured by integrating the area under the $\nu(CH_2)$ peak at 2892 cm^{-1}, and when this coverage is accounted for, the isotherms duly pass through the origin. The spectator coverage is $\theta_S = 0.16$ at 498 K, 0.24 at 473 K, and 0.36 at 448 K, and interestingly, it is larger than the actual reaction intermediate coverage. The coverage of the intermediate is about three times smaller.

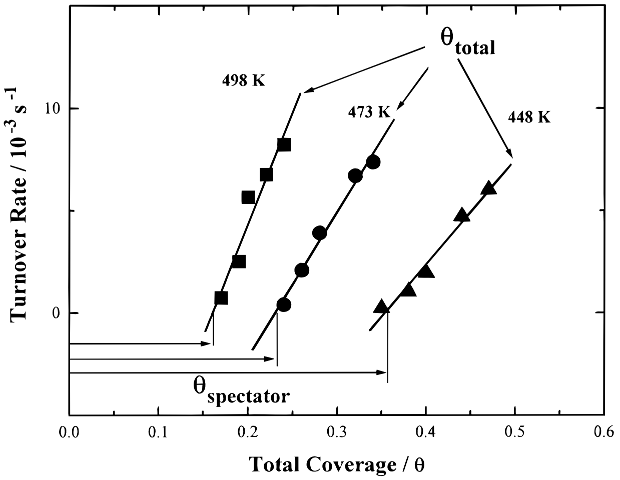

Figure 4. Reaction isotherms for ethanol oxidation. Turnover rates are based on oxygen chemisorption and coverages are measured by Raman spectroscopy.

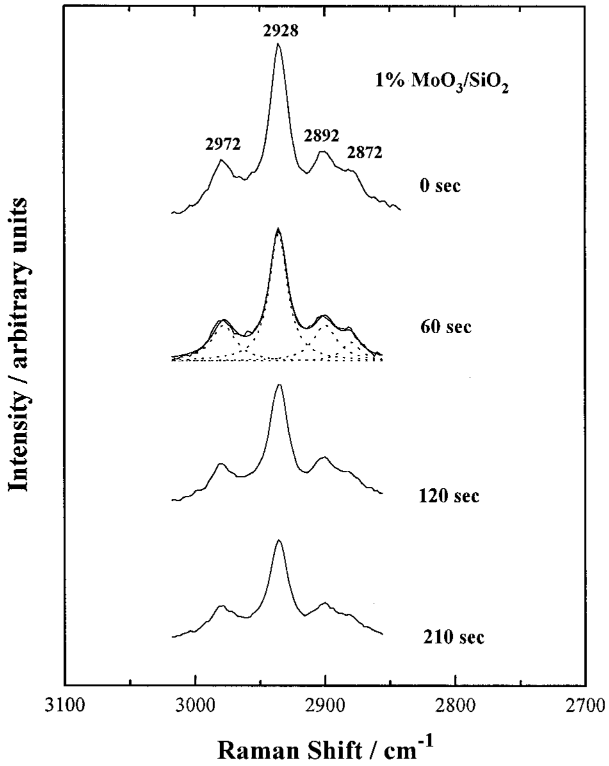

Figure 5. Transient experiment showing the $\nu(CH_2)$ region following interruption of the ethanol supply. The spectra were taken at 448 K using 100 mW at the sample and 1 scan of 30-s duration. The prior steady-state rate was obtained with 0.55% ethanol in oxygen at 448 K using a flow rate of 270 μmol s^{-1} (400 cm^3 min^{-1}).

From its steady-state behavior (Figure 4), the ethoxide species ($\nu(CH_2) = 2872$ cm^{-1}) has all the attributes of a reaction intermediate. However, the ultimate proof that it is a true intermediate lies is in its dynamic behavior.[12] The results of such a dynamic experiment are reported in Figures 5 and 6. Figure 5 shows transient Raman spectra taken after the reaction was suddenly interrupted by cutting off the ethanol supply. As shown in one of the traces, the peaks can be deconvoluted to yield coverages. Figure 6 shows these coverages as well as the transient acetaldehyde and ethanol production rates. The latter were obtained by repeating chromatographic injections at close intervals and by restarting the experiments several times. The important result is that the decline in product formation

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tracks well the decrease in coverage of the intermediate, establishing a direct relationship between the two quantities. The correspondence is not exact because of error in the data (~10%), but the order of magnitude of the time responses is similar. The spectator coverage remains relatively unperturbed in the course of the transient experiment. It was found in previous work[17] that the selectivity to ethylene or diethyl ether increased with molybdenum oxide loading and with higher temperatures. Thus, the spectator species ceases to be inert at the more severe conditions and is likely to be involved in the formation of ethylene. The steps in the reaction can be deduced to be as depicted below. In previous work it was shown that the mode of adsorbate bonding controls selectivity in oxidation reactions,[32] and this case provides another example.

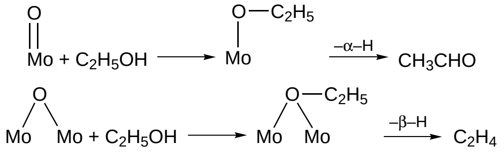

Figure 6 also shows the decline in ethanol production. Integration of the area under this curve together with that of the acetaldehyde gives the absolute coverage of ethoxide species present in the steady state. (The analysis corrected for the depletion of the gas-phase species in the reactor volume, as determined in a separate blank experiment.) The measured value was within experimental error of the coverage based on the Raman measurements and the oxygen uptake values.

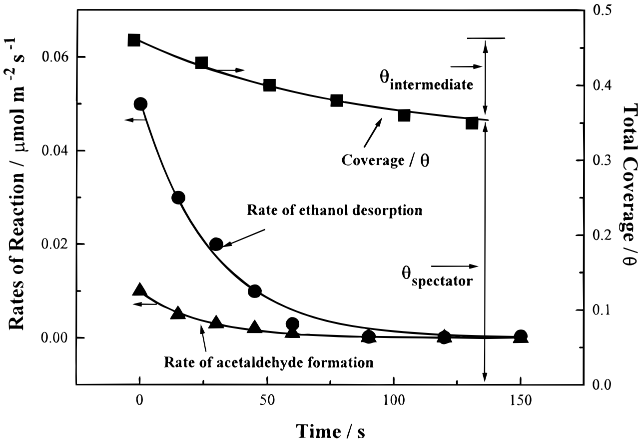

Figure 6. Transient experiment showing the evolution of coverage together with ethanol and acetaldehyde production following interruption of the ethanol supply. The ethanol signal has a substantial blank which has not yet been subtracted. Conditions were the same as in Figure 5. The measurements were carried out by repeating chromatographic injections at close intervals and by restarting the experiment several times from the same steady-state conditions.

Conclusions

The present studies have provided a detailed picture of the mechanism of ethanol oxidation on supported molybdenum oxide. The reaction takes place in two steps: the equilibrated adsorption of ethanol to form ethoxide species, and the rate-determining abstraction of an α-hydrogen from the ethoxide groups to form acetaldehyde. By combining steady-state and transient experiments with in situ laser Raman spectroscopic measurements it has been possible to identify two types of adsorbed species. Ethoxide species associated with Mo=O terminal bonds are true reaction intermediates, while ethoxide species associated with Mo−O−Mo bridging groups are relatively inert spectators. Our studies demonstrate that the mere observation of surface species during reaction is not sufficient to establish that they are involved in the actual reaction. To show that adsorbates are true reaction intermediates it is necessary to show that they respond in a dynamic manner to changes in reaction conditions.

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