Effect of Support in Ethanol Oxidation on Molybdenum Oxide

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The oxidation of ethanol on MoO3 supported on SiO2, Al2O3, and TiO2 was studied in a flow reactor at atmospheric pressure. The reactivity sequence followed the order $MoO_3/TiO_2 > MoO_3/Al_2O_3 > MoO_3/SiO_2$ and correlated with the reducibility of the surface molybdenum species. Ethanol oxidation produced mainly acetaldehyde, diethyl ether, and ethylene through ethoxide type intermediates adsorbed on different sites $(M=0, M_0-0-M_0, or M_0-0-M)$. Two types of ethoxide species were identified using laser Raman spectroscopy under in situ conditions and could be associated with the Mo=O and Mo-O-Mo sites. Although rates were strongly affected by the support, the rates did not depend substantially on the loading. This was due to a compensation between the equilibrated adsorption of ethanol and the rate-determining decomposition of the ethoxide intermediates. The activation energy did not vary with support, suggesting that activity was controlled by a term in the preexponential factor. The link to reducibility and the existence of a common ethoxide intermediate indicated that the controlling factor was likely to be the electronic partition function associated with the density of electron-accepting levels in the molybdate-support complex.

Introduction

In this paper, recently developed titration techniques for counting surface metal centers on oxide catalysts^{1,2} are used to determine accurate turnover rates of ethanol oxidation. This is coupled with in situ laser Raman spectroscopy (LRS) measurements at reaction conditions to identify reactive intermediates. The combination allows investigation of the nature of support effects and the overall mechanism of the ethanol oxidation reaction on MoO₃ supported on SiO₂, Al₂O₃, and TiO₂ and the roles of Mo-O-Mo and Mo=O bonds. it will be shown that electronic effects associated with the availability of empty states above the Fermi energy strongly influence the reactivity of the surface molybdenum species.

The main body of literature on alcohol oxidation over MoO₃containing catalysts is of studies of methanol oxidation to formaldehyde.³⁻²² These studies have covered the nature of adsorbed intermediates,³⁻⁹ the effect of structure,¹⁰⁻¹⁴ the measurement of kinetic isotope effects, 15,16 the identity of active sites (e.g., Mo=O or Mo-O-Mo), $^{3-14,16,19}$ the nuclearity of active centers (e.g., Mo monomer or Mo dimer),¹⁷⁻²¹ and the effect of supports.^{14,22} Among the various authors, there is general agreement that a methoxide type intermediate is responsible for the formation of formaldehyde³⁻⁹ and that the rate-determining step involves abstraction of a hydrogen atom from the adsorbed methoxy group.^{16,17} However, controversy about the effect of structure and support and the nature of the active sites still remains.

In the literature, fewer papers have dealt with ethanol oxidation than methanol oxidation over MoO3-containing catalysts.^{11,23-30} In analogy to methanol oxidation, Tatibouët et al.^{11,23} carried out ethanol oxidation over oriented MoO₃ crystallites prepared by sublimation. They showed the formation of acetaldehyde on basal planes (010) containing Mo=O bonds

and apical planes (001) + (101) containing both Mo=O and Mo-O-Mo bonds in the presence and absence of oxygen and suggested that Mo=O sites were responsible for acetaldehyde formation. A similar conclusion was reached by Iwasawa et al.24 and Ono et al.25,26 Iwasawa et al.24 used infrared (IR) spectroscopy to show that the Mo=O bond in MoO₃/SiO₂ reacted easily with adsorbed ethanol at 423 K and returned back to its original form after reoxidation at the same temperature. Ono et al.²⁵ suggested that the reactivity of MoO₃ highly dispersed on group IV oxide supports for ethanol oxidation was related to its surface structure. Crystalline MoO₃ gave a low reactivity, whereas surface polymolybdates gave a high reactivity. In the case of the polymolybdates, the Mo=O bond strength obtained using LRS and IR data depended on the support and followed the order of $SiO_2 > TiO_2 > ZrO_2$. The reactivity expressed as turnover rates for ethanol oxidation followed the reverse order $ZrO_2 > TiO_2 > SiO_2$. The turnover rates were calculated based on surface concentration of noncrystalline molybdenum oxide. In another study of ethanol oxidation on different MoO₃ loadings on TiO₂, Ono et al.²⁶ further related the reactivity in ethanol oxidation to the Mo=O bond strength measured by IR spectroscopy. A maximum rate of oxidation of ethanol obtained over a 10 wt % MoO₃/TiO₂ sample was attributed to a weakening of the Mo=O bond strength.

In addition to the role of the Mo=O bond, Iwasawa et al.^{27,28} proposed that Mo dimers were the active centers for ethanol oxidation to acetaldehyde over MoO₃/SiO₂ by demonstrating the high reactivity of SiO2-attached Mo dimer species prepared from organometallic precursors. This was supported by a reactivity study of ethanol oxidation over MoO₃/Al₂O₃ and MoO_3/TiO_2 prepared by the metal oxide vapor synthesis (MOVS) method.²⁹ In this study, Alyea et al. showed that these catalysts with the Mo dimer structure on the surfaces reached a conversion of 100% at 523 K and a selectivity of 100% to acetaldehyde. Although an ethoxide type intermediate for ethanol oxidation to acetaldehyde over supported MoO3 catalysts was suggested by Iwasawa et al.24 and Farneth et al.,30 the studies provided little kinetic data and only limited evidence

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TABLE 1: O₂ Chemisorption Data

sample	O_2 uptake/ μ mol g ⁻¹	$SA/m^2 g^{-1}$		
SiO ₂	8±1	89		
1% MoO ₃ /SiO ₂	29	61		
9% MoO ₃ /SiO ₂	59	73		
Al_2O_3		93		
5% MoO ₃ /Al ₂ O ₃	120	82		
15% MoO ₃ /Al ₂ O ₃	450			
TiO2		46		
1% MoO ₃ /TiO ₂	34	35		
9% MoO ₃ /TiO ₂	250	33		
MoO ₃	46	5.5		

from IR and temperature-programmed desorption (TPD) measurements. The roles of Mo–O–Mo and Mo–O–M (M = support) structures and details of the reaction steps of ethanol oxidation over supported MoO₃ catalysts have not been touched upon.

In this paper, the effect of structure is examined by varying the loading of molybdenum on the supports. It will be shown that catalyst structure does not have a strong influence on the rate, but this is due to a compensation between an adsorption equilibrium step and a subsequent rate-determining step. The overall rate is strongly affected by electronic factors associated with the metal oxide-support interaction.

Experimental Section

Catalyst Preparation and Characterization. Samples were prepared by impregnating silica (Cabosil L90, $S_g = 89 \text{ m}^2 \text{ g}^{-1}$), alumina (Degussa Aluminumoxid C, $S_g = 93 \text{ m}^2 \text{ g}^{-1}$), and titania (Degussa P25, $S_g = 46 \text{ m}^2 \text{ g}^{-1}$) with solutions of ammonium molybdate (Aldrich, 98%) in distilled water to incipient wetness. These materials and the pure supports were then dried at 393 K for 6 h and calcined at 773 K for 6 h. Sample preparation and characterization using oxygen chemisorption, BET, XRD, and LRS methods have been described in detail elsewhere.^{1,2} Surface area and oxygen uptake data for the samples used in the present study are summarized in Table 1. Two sets of samples were used: low loading (1% MoO₃/SiO₂, 5% MoO₃/Al₂O₃, and 1% MoO₃/TiO₂) and high loading (9% MoO₃/SiO₂, 15% MoO₃/Al₂O₃, and 9% MoO₃/TiO₂).

Steady-State Reactivity Studies. The reactor system used for the steady-state reaction study was a conventional flow reactor. Mass flow controllers (Brooks, Model 5850E) calibrated for each specific gas employed were used to obtain the desired composition and flow rate of the feed stream. A liquid mixture of ethanol and water was injected through an injection port with a syringe pump (Sage Model 341B). The feed stream was passed through a U-shaped quartz reactor (13 mm i.d.), and product analysis was performed by an on-line gas chromatograph (SRI Model 8610) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). A Carbosphere column (Alltech, 80/100 mesh) was used with the TCD to separate O₂, CO, CO₂, and H₂O, and a Porapak QS column (Alltech, 80/100 mesh) was used with the FID to separate C₂H₄, CH₃CHO, (C₂H₅)₂O, CH₃COOH, and CH₃-COOC₂H₅. Data processing was carried out by using Peaksimple II software. A six-way valve allowed switching between a calibration gas stream and the reaction feed without disconnecting the sample cell.

Gases used in this study were helium (Linde Ultra High Purity Grade, 99.999%) and oxygen (Linde Ultra High Purity Extra Dry Grade, 99.6%). They were passed through purifiers (Zeolite R3-11 for O_2 and Molsieve SA for He) during use. Ethyl alcohol (Pharmco, 99%) was used without further purification. The standard partial pressures of reactants in the reactivity study were $P_{C_2H_3OH} = 8$ kPa, $P_{O_2} = 8$ kPa, $P_{H_2O} = 4$ kPa, and $P_{He} = 81$ kPa. Typically, sample sizes loaded in the quartz reactor were 1 g, and the total flow rate for all experiments was 110 μ mol s⁻¹ or 160 cm³/min. Rates were expressed as turnover rates based on surface sites titrated by high-temperature oxygen chemisorption. Briefly, oxygen uptakes were measured by a pulse method on samples prereduced in hydrogen at moderate temperatures (600-640 K). The reduction was carried out at a temperature just below that at which bulk reduction occurred, and the method was independently calibrated by laser Raman spectroscopy at low loadings and by X-ray diffraction at high loadings.^{1,2}

Attention was paid to establish steady states and to ensure that the catalysts were stable during each experiment. Each sample was pretreated for 1 h with the O_2 , He, and H_2O mixture (without C_2H_5OH) at the highest temperature to be reached in the experiment. Steady-state reactivity data were taken at each desired temperature after maintaining conditions for at least 2 h. After each set of measurements, one initial point was repeated to verify catalyst stability. Carbon and oxygen balances closed to $100 \pm 5\%$ for most experiments, with just a few points, yielding $100 \pm 8\%$. Nevertheless, catalyst deactivation was observed due to molybdenum oxide sublimation, particularly in the low loading samples. Measurements were carried out for time periods for which catalysts were stable (10-30 h).

Raman Spectroscopy. Raman spectra were obtained using the 514 nm line of an Ar ion laser (Lexel, Model 95) with a power of 100 mW at the sample. The scattered light was filtered with a holographic super notch-plus filter (Kaser Optical) and directed into a single monochromator (Spex, Model 500M) equipped with a liquid nitrogen cooled CCD detector. A slit width of 50 μ m was used to achieve a resolution better than 5 cm⁻¹.

The spectra of supported molybdenum oxide catalysts and the adsorbed species were obtained in a cell that allowed *in situ* measurements. The samples (~0.3 g of powder) were pressed into thin wafers of 1 mm thickness and were spun at 600-1000 rpm to avoid local sample heating. The spectroscopic measurements were carried out while simultaneously running the catalytic reaction with 1.6 kPa of ethanol and 99.4 kPa of oxygen at a total flow rate of 110 μ mol s⁻¹. High oxygen partial pressure was chosen so as to keep a bright sample color. Acquisition time for each spectrum was typically 2 h in order to obtain a desired signal-to-noise ratio.

The 1% MoO_3/SiO_2 sample was chosen for study because with the 9% MoO_3/SiO_2 sample the features from adsorbed ethanol species were covered by the intense Raman bands of crystalline molybdenum oxide. Another reason for the use of the well-dispersed sample was that it could be used to study the role of the different surface groups (Mo=O, Mo-O-Mo) in activating ethanol.

Partial Pressure Effects. The partial pressure effect studies were performed under conditions away from the flammability limit (2-5% ethanol in oxygen).³¹ These studies were carried out by varying the concentration of one of the reactants while maintaining the total space velocity constant by adjusting the flow rate of He.

Results

Steady-State Reactivity Studies. Figure 1 shows the plots of conversion and selectivity versus temperature for low MoO₃ loading samples (1% MoO₃/SiO₂, 5% MoO₃/Al₂O₃, and 1% MoO₃/TiO₂). Figure 2 shows the same plots for high MoO₃ loading samples (9% MoO₃/SiO₂, 15% MoO₃/Al₂O₃, and 9% MoO₃/TiO₂) and pure MoO₃. During the reactions, the main



Figure 1. Conversion and selectivity for ethanol oxidation at different temperatures over the low loading sample.



Figure 2. Conversion and selectivity for ethanol oxidation at different temperatures over the high loading samples.

products were acetaldehyde, ethylene, diethyl ether, and CO_x at both loading levels. Blank experiments on the pure supports (dashed lines in Figure 1) showed that their activity was considerably lower than the supported samples with SiO₂ being the most inert. SiO₂ produced only a small amount of acetaldehyde at very high temperature (>570 K), whereas Al₂O₃ produced mainly diethyl ether in the whole temperature range (400-525 K) and CO_x at very high temperature, while TiO₂ produced mainly acetaldehyde in the whole range and CO_x at high temperature. Unsupported MoO3 produced mainly acetaldehyde and diethyl ether. Considerable amounts of acetic acid were formed by all samples at high Mo loading. Conversions and selectivities for all samples are summarized in Tables 2-4. Figures 3 and 4 present Arrhenius plots of total rates for the low loading and the high loading samples, respectively. Rates are reported as turnover rates based on surface Mo atoms titrated by oxygen chemisorption.^{1,2}

The reactivity of both sets (low and high loadings) of samples follows the same order, $TiO_2 > Al_2O_3 > SiO_2$. Apparent activation energies (E_{app}) cluster around 50–60 kJ mol⁻¹ for the low-loading samples and 90–100 kJ mol⁻¹ for the high loading samples (Table 5). The Arrhenius plot of pure MoO₃ is shown in Figure 4, while those for different MoO₃ loading samples on SiO₂ are shown in Figure 5. The plots are very close together and indicate a slight trend toward higher activity for the high loading samples. Apparent activation energies also increase with loading: 54 kJ mol^{-1} for 1% MoO₃/SiO₂, 66 kJ mol⁻¹ for 5% MoO₃/SiO₂, 92 kJ mol⁻¹ for 9% MoO₃/SiO₂, and 129 kJ mol⁻¹ for pure MoO₃. Selectivities to the main products versus support at a fixed conversion are plotted in Figures 6 and 7. The selectivity for the low loading samples is independent of support, whereas the selectivity for the high loading samples shows a strong dependence on support.

Raman Spectroscopy. Raman results are presented in Figures 8 and 9. The Raman spectra of SiO₂ and 1% MoO₃/SiO₂ were taken after calcining at 773 K under moisture-free conditions at room temperature in a flow of purified oxygen. The Raman bands at 604, 804, 974, and 1044 cm⁻¹ are due to amorphous silica,^{32,33} whereas the Raman band at 984 cm⁻¹ is due to Mo=O stretching in octahedrally coordinated monomeric molybdenum species.³³ The weak band at 819 cm⁻¹ due to Mo-O-Mo stretching indicates that trace amounts of crystalline molybdenum oxide are present on the surface.^{1,2,33} The band at 1550 cm⁻¹ is due to gas phase oxygen.^{34,35} This was confirmed by the disappearance of the band after switching from oxygen to helium.

All measurements reported below are carried out at steadystate reaction conditions, not temperature-programmed conditions. After introducing the reaction mixture ($P_{EtOH} = 1.6$ kPa, $P_{\rm O_2} = 99.4$ kPa) at room temperature, the intensity of the band at 984 cm⁻¹ drops dramatically, and its position is shifted to \sim 960 cm⁻¹ where it appears as a broad feature. At the same time, the Mo–O–Mo stretching feature at 819 cm^{-1} disappears. The drop in the intensity of the Mo=O stretching band is accompanied by a sample color change from white to blue. The intensity of the band increases gradually with increasing temperature while the reaction mixture is flowing through the cell. The sample color changes from blue back to white when the temperature reaches 523 K, while the peak position recovers to 972 cm^{-1} at this point. The band returns to its original form only by heating the sample in O_2 at 773 K for 2 h after cutting off the reaction mixture supply.

New features with peak positions at 1030, 1086, 1274, 1292, 1446, 1452, 2722, 2770, 2872, 2892, 2928, and 2972 cm⁻¹ appear with introduction of the reaction mixture at room temperature. The assignment of these features is summarized in Table 6. These features can be attributed to ethoxy groups adsorbed on two different type of sites. This will be covered in detail in the discussion section. The decrease of the intensity of these features with increasing temperature indicates the reaction of the two adsorbed species. Interestingly, one of the two types of ethoxy groups, characterized by the band at 2872 cm⁻¹, reacts faster than the other. It is almost invisible when the temperature reaches 458 K. In contrast, the ethoxy group characterized by the band at 2892 cm⁻¹ is still visible even when the temperature is raised to 523 K.

As the temperature reaches 423 K, three new bands appear at 656, 810, and 986 cm⁻¹, which correspond to vibration modes of carbonate.³⁶ These bands remain at 458 K, but disappear at 473 K and above. The formation of the carbonate species is probably due to the decomposition of the ethoxy groups at intermediate temperatures.

Partial Pressure Effects. The partial pressure effects for C_2H_5OH , O_2 , and H_2O on the three main products, acetaldehyde, ethylene and diethyl ether, are carried out on the 9% MoO₃/SiO₂ sample. Only the results for acetaldehyde formation are reported in this paper. A detailed kinetic analysis will be published elsewhere.³⁷

FABLE 2: Et	hanol Oxidation	on MoO ₃ /SiO ₂
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selectivity/%									
sample	temp/K	C_2H_4	CH ₃ CHO	$(C_2H_5)_2O$	CH ₃ COOH	CH ₃ COOC ₂ H ₅	CO _x	conv/%	$v_t^a/10^{-3} \text{ s}^{-1}$
1% MoO ₃ /SiO ₂	480		96	4				0.5	0.7
	532	2	92	3	2			1.9	2.7
	558	1	86	10	3			2.3	3.4
	575	3	81	14	2			2.4	3.5
	585	3	87	7	3			4.2	6.2
	662	9	78	1	4	4	4	24.3	35.5
9% MoO ₃ /SiO ₂	478	3	63	23	11			1.1	0.8
	490	2	69	7	27			4.7	3.4
	506	1	72	11	8			7.5	5.5
	533	2	77	10	3	6		20.7	15.0
	563	4	72	7	4	10	13	42.7	31.0

^{*a*} $v_{\rm t}$ is the turnover rate.

TABLE 3: Ethanol Oxidation on MoO₃/Al₂O₃

		selectivity/%							
sample	temp/K	C_2H_4	CH ₃ CHO	$(C_2H_5)_2O$	CH ₃ COOH	CH ₃ COOC ₂ H ₅	CO _x	conv/%	$v_{\rm t}/10^{-3}~{\rm s}^{-1}$
5% MoO ₃ /Al ₂ O ₃	448		92	8				1.9	0.7
	473		92	7		1		7.6	2.7
	498	1	82	15		2		27.7	9.9
	523	2	74	17		3	4	59.8	21.3
	548	5	64	22		3	6	79.8	28.5
15% MoO ₃ /Al ₂ O ₃	408		71		29			0.7	0.1
	423	2	77	7	14			3.1	0.3
	438	2	90	6	2			9.9	1.0
	453	3	82	10	3	2		17.7	1.7
	473	1	84	10	1	2	2	43.0	4.1

TABLE 4: Ethanol Oxidation on MoO₃/TiO₂





Figure 3. Arrhenius plots for ethanol oxidation over the low loading samples.

Discussion

Steady-State Reactivity Studies. The dispersion of MoO_3 on SiO₂, Al₂O₃, and TiO₂ has been studied using oxygen chemisorption, X-ray diffraction, and laser Raman spectroscopy in our previous papers.^{1,2} These studies indicated that, under *in situ* conditions, the highly dispersed phases on the low loading samples were isolated monomeric Mo(VI) species and small



Figure 4. Arrhenius plots for ethanol oxidation over the high loading samples.

crystallites of MoO_3 on the high loading samples. In order to correlate reactivity with surface structure, in the present study ethanol oxidation was carried out on both low and high loading samples.

Figures 3 and 4 show that the reactivity of ethanol oxidation over MoO₃ on the various supports follows the trend $TiO_2 >$ Al₂O₃ > SiO₂. Our previous results established that the molybdate-support interaction is of an acid-base nature, where

TABLE 5: Activation Energies



Figure 5. Arrhenius plots for ethanol oxidation over different MoO₃ loadings on SiO₂.



Figure 6. Selectivity dependence on support for ethanol oxidation over the low loading samples.



Figure 7. Selectivity dependence on support for ethanol oxidation over the high loading samples.

the strength of the interaction, with respect to the support, also follows the order $TiO_2 > Al_2O_3 > SiO_2$.² TPR³⁸ results on the low MoO₃ loading samples show that reducibility of surface molybdates on the various supports also follows the same sequence. Clearly, the reactivity for ethanol oxidation over



Figure 8. Raman spectra of adsorbed species at different reaction temperatures in the low wavenumber region.



Figure 9. Raman spectra of adsorbed species at different reaction temperatures in the high wavenumber region.

MoO₃ on SiO₂, Al₂O₃, and TiO₂ can be associated with the molybdate-support interaction and the reducibility of the surface molybdate. This finding is in good agreement with a theoretical study by Weber.³⁹ On the basis of a molecular orbital study of C-H bond breaking during the oxidative dehydrogenation of methanol catalyzed by metal oxide surfaces, he proposed that the more reducible supports such as TiO₂ and ZrO₂ produce more active catalysts than the refractory supports such as SiO₂ and Al₂O₃ for methanol oxidation, because the more reducible supports have a more accessible set of empty orbitals. This is discussed further at the end.

 TABLE 6:
 Assignment of Laser Raman Bands

frec	l ^a /cm ⁻¹		
liquid ethanol	adsorbed species	assign ^b	ref
430 w		δ(CCO)	46
878 vs		$\nu(CCO)$	45, 46
	1030 vw	$\nu(CCO)$	45
1044 m		$v_{\rm as}(\rm CCO)$	46
1090 m	1086 m	$\rho(CH_3)$	45, 46
1268 w	1274, 1292 w	$t(CH_2)$	45, 46
1446 s	1446, 1452 s	$\delta_{\rm s}({\rm CH}_2) + \delta_{\rm as}({\rm CH}_3)$	24, 45, 46
2868 s	2872, 2892 s	$\nu_{\rm s}({\rm CH}_2)$	24, 45, 46
2918 vs	2928 vs	$\nu_{\rm s}({\rm CH}_3)$	24, 45, 46
2962 vs	2972 vs	$v_{as}(CH_3)$	24, 45, 46

^{*a*} vs = very strong, s = strong, m = medium, w = weak, vw = very weak. ^{*b*} v = stretching, δ = in-plane deformation, t = twisting, ρ = rocking.

An interesting aspect of the ethanol oxidation reaction is the effect of structure probed by the reactivity dependence on dispersion. Figure 5 shows that there is only a small increase in reactivity with MoO₃ loading, indicating that ethanol oxidation is apparently not highly dependent on structure. This will be shown to be due to a compensation effect, with rate parameters changing considerably with particle size, actually making the reaction structure sensitive. The same conclusion can be drawn for ethanol oxidation over MoO₃ on Al₂O₃ and TiO_2 where the high loading samples have only slightly higher rates than the low loading samples (Figures 3 and 4). The slight increase of reactivity with Mo loading is consistent with the proposal of Allison and Goddard III et al.,¹⁹ that two neighboring Mo sites are responsible for the formation of formaldehyde in methanol oxidation. Iwasawa et al.^{27,28} also demonstrated the high reactivity of SiO₂-attached dioxo Mo dimer species for ethanol oxidation prepared from organometallic precursors. Mo dimers were also observed on Al₂O₃ and TiO₂.²⁹ A conversion of 100% in the temperature range 503-523 K and a selectivity of 100% to acetaldehyde in ethanol oxidation over the catalysts prepared by the metal oxide vapor synthesis (MOVS) method were reported by the same authors.

The finding here of an increase in reactivity with Mo loading is consistent with a gradual increase of neighboring molybdenum centers. The effect on the overall rate is small because of a compensation effect. This is indicated by the observation of an isokinetic temperature (Figure 5) for the SiO₂-supported samples and an increase in apparent activation energy with loading (Figures 3 and 4) for all samples. As will be discussed further, the compensation is due to the presence of an equilibrated step prior to the rate-determining step.

The role of adsorbate bonding has been extensively discussed in our previous papers.^{40,41} We suggested that the existence of two types of intermediates (M–O–R and M–R) is responsible for selectivity in partial oxidation of hydrocarbons. The M–O–R type intermediate, where the hydrocarbon is bonded through an oxygen atom, produces selective oxidation products, and the M–R type intermediate, where a direct metal–carbon bond exists, produces CO_x. In the case of ethanol oxidation, a simple intermediate, an adsorbed ethoxy group, is mainly responsible for the formation of the selective oxidation products. This is supported by the finding of ethoxy groups by the *in situ* laser Raman studies in the present study.

The plots of selectivity of various products versus support shown in Figures 6 and 7 indicate that the selectivity for the low loading samples is independent of support $SiO_2 \sim Al_2O_3$ $\sim TiO_2$, but the selectivity for the high loading samples has a strong dependence on support. The selectivity to diethyl ether on 9% MoO₃/TiO₂ increases by a factor of 2 in comparison to that on 1% MoO₃/TiO₂. This suggests that acetaldehyde, ethylene, and diethyl ether are produced through intermediates adsorbed on different sites.

The in situ Raman investigation of ethanol oxidation over 1% MoO₃/SiO₂ in the present study shows that there are at least two types of ethoxy groups present on the surface. These ethoxy groups can be associated with the Mo=O and Mo-O-Mo sites. Clearly, the diethyl ether formation in the present study is not due to Mo-O-Mo sites because an increase in selectivity to diethyl ether with increasing MoO_3 loading on SiO₂ and Al₂O₃ is not observed. A more plausible explanation for our results is that diethyl ether formation is associated with the Mo-O-M sites (M = Si, Al, and Ti). On the other hand, acetic acid formation occurs through Mo-O-Mo sites, since acetic acid is produced only on the high loading samples. It should be noted that, in all cases, the protons associated with the metaloxygen sites may be important in determining selectivity. However, our results suggest that neighboring Mo centers, as far as selectivity is concerned, play an important role in ethanol oxidation.

On the basis of IR and kinetic studies of ethanol oxidation over SiO₂-attached dioxo Mo monomer and dimer catalysts, Iwasawa *et al.*^{24,27,28} showed that these catalysts had a selectivity of 97% to acetaldehyde. They proposed that the Mo=O bond was the active site for acetaldehyde formation by showing that this species reacted reversibly with adsorbed ethanol at 423 K. Acetaldehyde was the only product formed at this temperature at steady state.

Ono et al.25 studied the activity of ethanol oxidation over different MoO₃ loadings on TiO₂ and found that acetaldehyde was the major product during reaction. They attributed the maximum reactivity of 10% MoO₃/TiO₂ to the weakening of the Mo=O bond. In a more recent study of ethanol oxidation over highly dispersed MoO₃ on group IV oxide supports, Ono et al.²⁶ reported that acetaldehyde was again the major product. They showed that reactivity reported by turnover rates followed the order $ZrO_2 > TiO_2 > SiO_2$, and the trend could be directly related to Mo=O bond strength as measured by IR and Raman spectroscopy: a weak Mo=O bond gave a high reactivity, and a strong Mo=O bond gave a low reactivity. By comparing the trend of reactivity of the low loading samples in the present study to the Raman results reported previously,^{1,2} we find no direct relation between Mo=O bond strength and reactivity. The same finding was also reported by Wachs's group recently.42

Raman Spectroscopy. In-depth studies of alcohol adsorption on metal oxides using vibrational spectroscopy were first conducted by Greener.43 He carried out an IR study of the adsorption of methanol and ethanol on aluminum oxide and reported the first spectroscopic evidence for the formation of surface methoxide from methanol and surface ethoxide from ethanol at 308 K. Since then, the surface ethoxide species have been reported on iron,44 vanadium oxide,32 molybdenum oxide,24 and molybdenum single crystals.⁴⁵ Only one study has dealt with the investigation of reaction intermediates in ethanol oxidation over supported molybdenum oxide catalysts. In this paper, Iwasawa et al.24 studied ethanol oxidation over silica supported molybdenum oxide catalysts prepared by organometallic processors using IR spectroscopy under in situ reaction conditions at 423 K. The IR features originated from adsorbed ethanol species at 1373, 1385, 1446, 2900, 2835, and 2982 cm⁻¹ were assigned to the ethoxide structure. A detailed study of ethoxide adsorbed on the Mo (110) surface by HREELS and *ab initio* calculations was reported by Uvdal *et al.* recently.⁴⁵ Due to the poor resolution of the spectrometer (\sim 70 cm⁻¹), the HREELS spectra of molybdenum ethoxide in the paper are not

useful for the assignment of the Raman features in the present study, but the *ab initio* calculations for the vibrational frequencies of the normal modes of molybdenum ethoxide in the same work are very helpful.

The major difference of the present study from the previous investigations is that the laser Raman measurements of the reaction intermediates in the present study were carried out at *in situ* continuous reaction conditions over a wide range of temperatures (300-523 K).

In the present study, the Raman bands developed from ethanol adsorption on 1% MoO₃/SiO₂ are at 1030, 1086, 1274 and 1292 (doublet), 1446 and 1452 (doublet), 2770, 2722, 2872 and 2892 (doublet), 2928, and 2972 cm^{-1} (Figures 8 and 9). Ethanol adsorption on SiO₂ did not show any significant Raman features. Even though the Raman bands at 1086, 1446, and 2872 cm^{-1} coincide with those of liquid ethanol,⁴⁶ all the bands from 1030 to 2972 cm⁻¹ can still be assigned to dissociatively adsorbed species because the most intense Raman band due to the CCO stretching mode at 878 cm⁻¹ from liquid ethanol does not show up. Instead, this mode appears at 1030 cm^{-1} as a weak and broad feature which is the characteristic evidence for the formation of an adsorbed species.⁴⁵ The bands at 1086, 1446, and 2872 cm^{-1} still remain visible even at 423 K, but are very unlikely to be due to molecularly adsorbed ethanol at such a high temperature. Rather, they belong to dissociatively adsorbed species.

Other than the bands at 1030, 1086, 1274, 1292, 2722, and 2770 cm^{-1} , the rest of the bands at 1446 and 1452, 2892, 2928, and 2972 cm⁻¹ are close to the IR bands reported for the ethoxide structure by Iwasawa et al.²⁴ In fact, Iwasawa, et al.²⁴ did not report any IR bands below 1300 cm⁻¹. The two bands at 2722 and 2770 cm^{-1} observed in the standard liquid ethanol and adsorbed ethanol spectra in Figure 9 are probably due to aldehyde impurities in the ethanol used in the present study.⁴⁷ In the ab initio study by Uvdal et al.45 calculations for molybdenum ethoxide did predict the existence of the CCO stretching mode at 1020 cm⁻¹, CH₃ rocking mode at 1091 cm⁻¹, and CH₂ twist mode at 1274 cm⁻¹, which are very close to the observed modes at 1030, 1086, 1274, and 1292 cm^{-1} . Based on the above discussion, the Raman bands at 1030, 1086, 1274 and 1293 (doublet), 1446 and 1452 (doublet), 2872 and 2892 (doublet), 2928, and 2972 $\rm cm^{-1}$ can be assigned to ethoxy groups adsorbed on molybdenum oxide.

The splitting of the Raman bands associated with CH_2 vibrations together with the broad CCO stretching mode at 1030 cm⁻¹ strongly suggests the presence of two types of ethoxy groups on molybdenum oxide. The formation of the two types of ethoxy groups can be related to the disappearance of the molybdenum oxide features at 984 and 819 cm⁻¹, which correspond to the Mo=O and Mo-O-Mo vibrations, respectively. Since this study does not provide information about the Mo-O-Si vibration modes, we cannot rule out the possibility that a third type of ethoxy group adsorbs on the Mo-O-Si sites and is not distinguishable from the above two ethoxy groups. Blank experiments rule out adsorption on SiO₂ itself.

According to the present study, the Mo=O bond is more reactive than the Mo-O-Mo bond. After introducing the reaction mixture at room temperature, both the Raman bands due to the Mo=O stretching mode at 984 cm⁻¹ and the Mo-O-Mo stretching mode at 819 cm⁻¹ disappear owing to the interaction with ethanol. A change of sample color from white to blue is observed at the same time, indicating reduction. With increasing temperature from 373 to 523 K while the reaction mixture is flowing through the Raman cell, the Mo=O is easily reoxidized as indicated by the increase in the intensity of this band and the peak position shift from 964 to 972 cm⁻¹. The decrease in the concentration of the ethoxy groups characterized by the 2872 cm^{-1} band in the same temperature range probably suggests that this type of ethoxy group is associated with the Mo=O sites. Furthermore, the selectivity at these conditions suggests that the ethoxide species associated with the Mo=O sites preferentially produces acetaldehyde. Although the Mo=O sites are associated with the ethoxide species, specifics of the bonding arrangement and the reaction pathways are uncertain.

In contrast to the Mo=O functionality, after reduction at room 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 suggests that the remaining ethoxy group characterized by the band at 2892 cm⁻¹ at 523 K is associated with the Mo-O-Mo sites and is relatively unreactive.

Kinetics. A detailed study of the partial pressure effect on 9% MoO₃/SiO₂ was performed at 523 K to provide further information about the mechanism of ethanol oxidation and will be reported in detail elsewhere.³⁷ The experimentally determined ethanol partial pressure dependence for acetaldehyde production was $v_{CH_3CHO} = (L)kP_{C_2H_5OH}^{0.86}$. A two-step sequence that is consistent with the obtained kinetics is

$$CH_{3}CH_{2}OH + S_{1} \xrightarrow{\kappa} S_{2}$$
$$S_{2} \xrightarrow{k} CH_{3}CHO + S_{3}CHO + S_{3}C$$

where S₁ represents empty sites and S₂ occupied sites (adsorbed ethoxide). The sequence incorporates the key finding from isotopic studies,³⁷ namely, equilibrated adsorption of ethanol to form an ethoxide species (step 1) and rate-determining decomposition of that species to acetaldehyde (step 2). Employing the Temkin theory of rates⁴⁷ on nonuniform surfaces, it is possible³⁷ to derive the following expression for the rate: $v_{CH_3CHO} = (L)k'P_{C_2H_5OH}^{0.86}$, which agrees with the experimental rate. The rate parameter, k', is a product of the rate constant for the second step and a function of equilibrium constants associated with the adsorption of ethanol, water, and oxygen. For the simplified sequence above it is just $k' = kK^{1-m}$, where m is the Brønsted transfer coefficient.⁴⁸

The overall apparent activation energy, E_{app} , is seen to be composed of two terms, $E_{app} = E + (1 - m)\Delta H$, where E is the activation energy of the rate-determining step and ΔH is the heat of adsorption of ethanol. Since adsorption processes are mostly exothermic, ΔH is a negative quantity which results in smaller apparent activation energies. This explains why the observed activation energies are substantially lower than the C-H bond dissociation energy of CH₃CH(OH)-(H) of 389 kJ mol^{-1} . Also, the increase in activation energies from 50-60 kJ mol⁻¹ for the low loading samples to 90-100 kJ mol⁻¹ for the high loading samples can be understood from a decrease in the heat of adsorption by 40 kJ mol⁻¹ in this range. Thus, as particle size increases, equilibrium ethanol adsorption becomes less exothermic and adsorbate coverages decrease. As will be explained subsequently, this offsets increases in the rate constant with particle size so that overall rates do not change appreciably with loading. This is the origin of the compensation.

Controlling Factor for Reactivity. An important conclusion to be derived from the present work is that electronic factors are important in alcohol oxidation. The relevant results are the following. First, the loading of molybdenum oxide does not have a major effect on the rate of oxidation. Instead, the identity of the support has a great influence on the rate, the order being $TiO_2 > Al_2O_3 > SiO_2$. However, interestingly, the activation

energy for the reaction at similar loadings does not vary significantly with support. Isotopic studies³⁷ indicate that the same mechanism is operating in all cases, namely, equilibrated formation of an ethoxide intermediate followed by rate-determining decomposition of the intermediate. The rate is given by a power-rate law expression that is consistent with those steps. The expression contains the total number of sites, (L), a rate parameter, k', and a function of concentration, f(C).

Exactly the same general observations have been made by others³⁻²² for the methanol oxidation reaction. In recent work on methanol oxidation on $V_2O_5^{49}$ and MoO_3 ,⁴² the 1–3 order of mangitude difference in rate with support was attributed to different numbers of active sites participating in the reaction. It is hard to believe that this would be the case on 1% loading samples used in those studies, which Raman spectroscopy showed to be molecularly dispersed. In the present study, the number of surface molybdenum atoms in the sample was carefully titrated by oxygen chemisorption^{1,2} and cannot account for the difference in rates. At most the error may be a factor of 2.

If the number of sites, (L), is not responsible for the difference, then the cause must lie elsewhere. Assuming that the equilibrium constants associated with adsorption shift in the same direction for the different supports, this points to the rate constant for the rate-determining step, k, as the cause for the difference. Moreover, since the activation energies, E, are close, the quantity responsible must be the preexponential factor, A, of the rate constant.

$$k = A \exp(-E/RT) \qquad A_{\text{TiO}_2} > A_{\text{Al}_2\text{O}_3} > A_{\text{SiO}_2}$$

According to transition state theory the preexponential factor can be expressed as a product of the universal frequency, kT/h, and the ratio of partition functions of the activation complex, Q^{\ddagger} , and the reactant, Q.

$$A = \frac{kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) = \frac{kT}{h} \frac{Q^{\ddagger}}{Q} \qquad Q^{\ddagger}_{\text{TiO}_{2}} > Q^{\ddagger}_{\text{Al}_{2}\text{O}_{3}} > Q^{\ddagger}_{\text{SiO}_{2}}$$

The overall partition function can be factored into translational, vibrational, rotational, and electronic partition functions. The first three contributions are generally small and should not differ very much for the same intermediate. The last, however, has no upper limit.

$$Q^{\ddagger} = q^{t}q^{v}q^{r}q^{e} \qquad q^{e}_{\operatorname{TiO}_{2}} > q^{e}_{\operatorname{Al}_{2}\operatorname{O}_{3}} > q^{e}_{\operatorname{SiO}_{2}}$$

The conclusion is that the origin of the difference in rates resides in the electronic partition function of the activated complex. This is precisely the conclusion of Weber³⁹ based on his molecular orbital calculation of methanol oxidation on molybdenum oxide that indicates that hydride transfer to a metal center is rate-determining. Morokuma's group had similar conclusions.⁵⁰ The way that this relates to the mechanism is as follows.

The rate-determining step remains the breaking of the C-H bond. Thus, the activation energy is constant for different supports. However, the probability that the system gets to the top of the barrier depends on the number of states available in the transition state to accept the electrons in the hydride transfer. The rate-determining step is taken to include both proton and electron transfer. Here, the surface oxide-support complex is involved, with the larger density of empty states, the higher the rate. This is depicted in Figure 10, which shows a number of equal-energy states for the activated complex, representing the electronic partition function. The density of empty states should track with the reducibility (electron-accepting character)



Figure 10. Energy diagram of transition state.

of the species, as has been observed.³⁸ The involvement of the density of empty states is also related to earlier suggestions that the conduction band of oxides acts as an electron sink.^{51,52} It is also consistent with the observed increase in rate as the molybdenum species forms dimers^{24,27–29} or larger ensembles, which are expected to have a larger number of empty electronic states. Of course, as discussed earlier, the increase in the preexponential factor is offset by the decrease in the heat of adsorption of ethanol in the equilibrated first step, so that a compensation in the rate is observed.

Conclusions

1. The reactivity of ethanol oxidation on supported molybdenum oxide at low and high loadings follows the order of TiO_2 > Al_2O_3 > SiO_2 . Activation energy is independent of support.

2. The product distribution for ethanol oxidation over these supports is similar, acetaldehyde is the main product followed by diethyl ether and ethylene, and they are produced through ethoxide type intermediates adsorbed on different sites.

3. The reaction to form acetaldehyde proceeds in two stages: a quasi-equilibrated adsorption of ethanol to form adsorbed ethoxide and a second rate-determining decomposition of ethoxide through an α -hydrogen abstraction. Compensation between the two steps causes the overall rate not to vary with loading, although the reaction remains a structure-sensitive reaction.

4. The differences in rates with support can be associated with the availability of empty electronic energy states in the metal oxide-support complex.

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