J. Phys. Chem. **1995,** *99,* 10911–10922

Catalytic Properties of Supported Molybdenum Oxide Catalysts: *In Situ* Raman and Methanol Oxidation Studies

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Received: January 3, 1995; In Final Form: March 28, 1995[⊗]

The oxidation of methanol was studied over supported molybdenum oxide catalysts as a function of the specific oxide support (TiO_2, ZrO_2, Nb_2O_5, and Al_2O_3) and molybdenum oxide loading (surface coverage). The surface molybdenum oxide species were selective for the production of formaldehyde, and the oxide support sites yielded dimethyl ether (alumina and niobia) and methyl formate (zirconia) or were relatively inactive (titania). The turnover frequency (TOF) for the selective oxidation of methanol to formaldehyde varied by a factor of 2–4 with surface molybdenum oxide coverage and a factor of approximately 10 with the specific oxide support at monolayer coverage. The molecular structures of the surface molybdenum oxide species (isolated, tetrahedral at low coverages and polymerized, octahedral/tetrahedral at high coverages) did not affect the reaction selectivity but did appear to influence the slight increase in TOF with surface coverage. The order of magnitude variation in TOF with the specific oxide support correlated with the reducibility of the support and suggests that the Mo–O–support bond is critical in controlling the TOF. *In situ* Raman studies during methanol oxidation revealed that the supported molybdenum oxide species were 100% dispersed up to monolayer coverage. The percent reduction of the surface molybdenum oxide species, reflected by the decrease in the Raman intensity of the Mo=O bond, during methanol oxidation was not a strong function of surface coverage and the specific oxide support. This suggests that the order of magnitude variation in the TOF with the specific oxide support is primarily related to the activity per site of the surface molybdenum oxide species rather than variation in the number of participating sites.

Introduction

Following the previous study[1] on the molecular structure of the surface molybdenum oxide species on different oxide supports, this paper presents the studies of the catalytic properties of the same catalyst systems for the methanol oxidation reaction. Oxidation reactions play an increasingly important role both in the production of materials needed and in the destruction of undesired products by total catalytic oxidation. Supported molybdenum oxide catalysts are among the most useful oxidative catalysts.[2] The evaluation of reactivity of oxidative catalysts can be performed by the methanol oxidation reaction which is a valuable probe for studyng the surface metal oxide redox sites.[3–7] During the partial oxidation of methanol, the methanol molecules are initially adsorbed on surface molybdenum sites as a methoxy (CH_3O) species.[3–8] The methoxy species subsequently react in various ways to form formaldehyde (FA, HCHO), methyl formate (MF, $HCOOCH_3$), dimethoxymethane (DMM, $CH_2[OCH_3]_2$), dimethyl ether (DME, CH_3OCH_3), and carbon oxides (COx, CO, and CO_2). The nature of the surface active sites determines the product distribution. Generally, surface acid sites produce the dehydration product DME, basic sites form carbon oxides, and redox sites produce FA, MF, and DMM.[3,8,9]

Bulk molybdate catalysts have been studied in detail for methanol oxidation reactions by Sleight *et al.*,[4–7] Tatibouët *et al.*,[8–10] and Chung *et al.*[11,12] The breaking of the C–H bond was found to be the rate-limiting step for the methanol oxidation over molybdate catalysts. The oxidative properties of supported molybdenum oxide catalysts have also been studied by many researchers, but most studies focused on the MoO_3/SiO_2 system.[13–17] Molybdenum oxides on TiO_2 and ZrO_2 were found to be the most active catalysts and possess higher selectivity for the oxidative dehydrogenation of methanol to formaldehyde.[18–22] Investigations of the oxidative properties of molybdenum oxides supported on Al_2O_3 and Nb_2O_5 are even rarer due to the high activity of the Al_2O_3 and Nb_2O_5 supports toward methanol dehydration reactions that dominate the catalytic activity of these catalysts.[23–25] The factors that influence the reactivity and selectivity of the supported molybdenum oxide catalysts and the relationships between the catalytic properties and the structure of the surface molybdenum oxide species present in such catalysts have not been extensively investigated.

The previous characterization studies using *in situ* Raman and XANES spectroscopies[1] revealed that the structure of the surface molybdenum oxide species on different oxide supports depends on both the specific oxide support and the surface molybdenum oxide coverage. Under dehydrated conditions, the surface molybdenum oxide species are primarily isolated, tetrahedrally coordinated at low loadings and tend toward polymerized, octahedrally coordinated at high loadings. At monolayer coverages, the structure of the surface molybdenum oxide species primarily possesses an octahedral coordination on TiO_2, but the structure is a mixture of tetrahedral and octahedral coordinations on Al_2O_3. The previous determinations of the structures of the dehydrated surface molybdenum oxide species on different oxide supports are summarized in Table 1 along with the corresponding Raman band positions of the terminal Mo=O bond. In the current study, the same catalyst systems were tested for their catalytic reactivity during methanol oxidation in order to gain information about the structure–reactivity relationships of the supported molybdenum oxide catalysts. In addition, *in situ* Raman spectra during methanol

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[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

0022-3654/95/2099-10911$09.00/0

TABLE 1: Structures of the Surface Mo Species at Low and Near Monolayer Coverage for Supported Molybdenum Oxide Catalyst[1]

	low coverage (1%)		monolayer coverage	
catalyst	Raman band of Mo=O (cm^{-1})	structure	Raman band of Mo=O (cm^{-1})	structure
MoO_3/TiO_2	993	Td	998	Oh, polymer
MoO_3/ZrO_2	980	(Td)	997	(Td + Oh, polymer)
MoO_3/Nb_2O_5	992	(Td)	996	(Oh, polymer)
MoO_3/Al_2O_3	990	Td, isolated	1006	Td + Oh, polymer

oxidation reaction were obtained to learn more about the nature of the surface molybdenum oxide species under reaction conditions.

Experimental Section

Catalyst Preparation. The supported molybdenum oxide catalysts were prepared by the incipient-wetness impregnation method with aqueous solutions of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) as described in detail in the previous study.[1] After impregnation, the samples were dried overnight under ambient conditions and further dried at 393 K in air overnight. The TiO_2 and ZrO_2 supported catalysts were finally calcined in dry air at 723 K for 2 h. The Nb_2O_5 and Al_2O_3 supported catalysts were calcined in dry air at 773 K for 2 h. The molybdenum oxide loading of the catalysts is given as the nominal weight percent of the MoO_3 in the samples.

Methanol Oxidation. The reactivity of supported molybdenum oxide catalysts was probed by the methanol oxidation reaction. The reactor system consisted of a digital flow rate controller (Brooks), a methanol reservoir, a condenser, a tube furnace (Lindberg), and an on-line gas chromatograph (HP 5840). The He and O_2 gaseous mixture, whose flow rate was adjusted by the mass flow rate controller, flowed through the methanol reservoir to the condenser maintained at 282.7 K. The methanol content in the flowing gas was obtained by calculating the partial pressure of methanol at this temperature. A 6.9/11.0/82.1 ratio of the $CH_3OH/O_2/He$ gaseous mixture was typically supplied to the reactor.

The catalysts were placed in the center of a 6 mm o.d. Pyrex microreactor of glass tubing supported by glass wool, placed in a vertical furnace, and preactivated under the flow of pure oxygen at 503 K for half an hour. The reaction was then run at the same temperature. The catalyst weight (1–50 mg) was adjusted to maintain less than 10% methanol conversion in order to avoid complications due to heat and mass transfer limitations. The reaction products were analyzed on line after steady state was reached (~10 min). The gas chromatograph was modified to operate with two thermal conductivity detectors (TCD) and one flame ionization detector (FID) and programmed to perform automatic data acquisition and analysis. A Porapak R column was used at 408 K for the separation of CO_2, HCHO, $HCOOCH_3$, $CH_2(OCH_3)_2$, and CH_3OCH_3, and a Carbosieve SII column operating at room temperature was used for the analysis of CO. The catalytic activities were obtained by integrating the peak areas of the products and calculated according to mole products per hour per gram of catalyst used. The selectivities are expressed in mole percent for each product and defined as the ratio between the yield of this product and that of the total methanol reacted. Careful control of the total conversion is important for the study of selectivity since methyl formate and dimethoxymethane are the secondary products of both formaldehyde and methanol and high conversion of methanol favors higher selectivity of methyl formate and dimethoxymethane.

The redox turnover frequency (TOF) was normalized per surface molybdenum site since the Raman measurements demonstrated that the molybdenum oxide in the supported catalysts was 100% exposed on the support surface below monolayer coverage. The TOFs of the catalysts above monolayer coverage were also calculated assuming complete exposure of molybdenum oxide sites in order to make comparisons, but most of the present study focuses on monolayer or submonolayer coverages where 100% exposure is present. The TOFs of the surface molybdenum oxide active sites had to be corrected for the support reactivity since certain products resulted from the supports. The Al_2O_3, TiO_2, and Nb_2O_5 supports were essentially inactive for redox product formation; thus, the TOF of these catalysts was calculated from the amount of redox products (formaldehyde, methyl formate, and dimethoxymethane) formed. However, the ZrO_2 support possesses some activity for the production of methyl formate, and the TOF of the MoO_3/ZrO_2 catalysts had to be corrected for the support reactivity.

***In Situ* Raman Spectroscopy.** The *in situ* Raman spectra of the supported molybdenum oxide catalysts were obtained with a laser Raman apparatus equipped with a flow-through sample cell. The 514.5 nm line of an Ar^+ laser (Spectra Physics, Model 171) was used as the excitation source. The laser power at the sample was ~50 mW. The scattered radiation from the sample was directed into a Spex Triplemate spectrometer (Model 1877) coupled to a Princeton Applied Research (Model 1463) OMA III optical multichannel photodiode array detector. The detector was cooled thermoelectrically to 238 K to decrease thermal noise. The Raman spectra were recorded using a computer and OMA III software. The spectral resolution and reproducibility were experimentally determined to be better than 4 cm^{-1}. The *in situ* cell was equipped with a spinning sample holder, rotated at a speed of ~2000 rpm, and a quartz reaction cell which allowed the flowing of gases and heating of the samples. A cylindrical furnace was used to heat the sample cell to a controlled temperature which was measured by an internal thermocouple. About 0.2 g of each supported molybdenum oxide catalyst was pressed into a thin wafer of about 1 mm thickness and held onto the sample holder. The spectra were measured after dehydration at 723–773 K for 30 min and then cooled to 503 K, which was the standard methanol oxidation reaction temperature. Different reaction temperatures were also used when studying the effect of temperature. The MoO_3/Al_2O_3 catalysts had to be calcined at 923 K for 2 h before the Raman measurements in order to eliminate fluorescence from the support. The *in situ* Raman spectra were obtained through the following procedure: the dehydrated Raman spectra before reaction were collected after heating the sample in a gaseous mixture of He/O_2, partial pressure ratio about 11/6, at 773 K (723 K for the TiO_2 and ZrO_2 supported catalysts) for 30 min and then cooled to 503 K. The Raman spectra during methanol oxidation were collected after passing the $CH_3OH/He/O_2$ gaseous mixture for at least 1 h. The CH_3OH partial pressure was controlled by maintaining the methanol reservoir at 273 K with a water–ice bath. After the methanol oxidation reaction, the samples were reoxidized by the He/O_2 gas at 503 K for 1 h, and the Ramn spectra were again collected. Raman spectra for some of the samples reoxidized at 773 K were also collected.

TABLE 2: Reactivity of MoO_3/TiO_2 Catalysts as a Function of MoO_3 Loading for Methanol Oxidation Reaction

				selectivity[b] (%)				
sample	density (Mo atoms/nm^2)	activity/(mmol/(g h))	TOF[a] (redox)(10^{-1} s^{-1})	FA	MF	DMM	DME	CO_x
MoO_3		10	0.2[c]	76	tr	6	16	2
TiO_2		2					91	9
0.5%MoO_3/TiO_2	0.4	20	1.3	77	tr	6	13	4
1% MoO_3/TiO_2	0.8	61	2.2	85	1	5	5	4
2% MoO_3/TiO_2	1.5	159	3.0	87	1	7	2	3
3% MoO_3/TiO_2	2.3	370	4.7	91	tr	5	3	1
5% MoO_3/TiO_2	3.8	786	5.8	85	3	4	6	2
6% MoO_3/TiO_2	4.6	942	5.7	85	tr	5	6	4
7% MoO_3/TiO_2	5.3	1082	5.7[e]	90	tr	2	6	2

[a] Redox TOF is based on the formation of FA + MF + DMM. [b] FA = formaldehyde (HCHO); MF = methyl formate ($HCOOCH_3$); DMM = dimethoxymethane ($CH_2(OCH_3)_2$); DME = dimethyl ether (CH_3OCH_3); CO_x = CO + CO_2. [c] Based on the exposed MoO_3 surface area. [d] Reaction temperature at 503 K, $CH_3OH/O_2/He$ = 6.9/11/82.1. [e] Apparent TOF since dispersion is not 100% due to presence of crystalline MoO_3 particles.

TABLE 3: Reactivity of MoO_3/ZrO_2 Catalysts as a Function of MoO_3 Loading for Methanol Oxidation Reaction

				selectivity (%)				
sample	density (Mo atoms/nm^2)	activity (mmol/(g h))	TOF[a] (redox) (10^{-1} s^{-1})	FA	MF	DMM	DME	COx
ZrO_2		20			86		tr	14
0.5% MoO_3/ZrO_2	0.5	21	*b*	4	51		3	42
1% MoO_3/ZrO_2	1.1	38	*b*	18	48	tr	4	30
2% MoO_3/ZrO_2	2.1	185	2.4	63	27	1	2	7
3% MoO_3/ZrO_2	3.2	612	6.1	74	18	1	2	5
5% MoO_3/ZrO_2	5.4	754	5.1[c]	82	12	2	3	1
7% MoO_3/ZrO_2	7.5	811	3.9[c]	83	11	1	3	2

[a] Redox TOF is based on the formation of FA + DMM. [b] Not calculated due to significant contribution from the ZrO_2 support. [c] Apparent TOF since dispersion is not 100% due to presence of crystalline MoO_3 particles.

During the methanol oxidation reaction, the intensities of Raman signals from the surface molybdenum oxide species decreased due to the reduction of the oxidized surface molybdenum oxide species. The reduction also produced a systematic decrease in the Raman signals of the catalysts due to the darker color of the samples. To correct for the different sample colors, the overall Raman spectra were normalized to the Raman band intensities of the oxide supports which were used as internal intensity standards. The decrease in the normalized terminal Mo=O Raman band intensity of the catalysts during methanol oxidation is assumed to quantitatively represent the percent reduction of the supported molybdenum oxide species. The errors associated with the experimental and calculation procedures should not exceed 50%.

Results

Catalytic Properties of Supported Molybdenum Oxide Catalysts for Methanol Oxidation. *MoO_3/TiO_2.* The reactivities and product selectivites of the MoO_3/TiO_2 catalysts as a function of molybdenum oxide loading during methanol oxidation at 503 K are listed in Table 2. Previous Raman characterization studies have demonstrated that monolayer coverage of the surface molybdenum oxide species on this TiO_2 corresponds to ~6–7% MoO_3/TiO_2.[1,26] The properties of the pure TiO_2 support and the bulk MoO_3 are included for references. Formaldehyde is the major reaction product formed on the bulk MoO_3 catalyst, and there is some activity toward formation of dimethyl ether and dimethoxymethane. Trace amounts of COx and methyl formate are also found. The turnover frequency (TOF) for bulk MoO_3 is $\sim 2.1 \times 10^{-2}$ s^{-1} based on the exposed surface area of the MoO_3 powder.[27] Bulk TiO_2 exhibits an extremely low activity toward methanol oxidation and produces mainly the dimethyl ether dehydration product as well as minor amounts of total oxidation products (COx). The specific activity of sample increases by 1 order of magnitude after only 0.5% molybdenum oxide is dispersed on the surface of the TiO_2 support, and the predominant product becomes formaldehyde (selectivity ~77%). The activity of the MoO_3/TiO_2 catalysts further increases ~50 times upon increasing the molybdenum oxide loading from 0.5% to 7% MoO_3, and there is also a slight increase in formaldehyde selectivity. Minor amounts of dimethoxymethane and methyl formate are also formed from the surface molybdenum oxide redox sites. The yield of FA + MF + DMM was used to calculate the redox turnover frequency (TOF) of the surface molybdenum oxide sites on TiO_2. The TOF increases about 4-fold as the molybdenum oxide loading increases. No further changes in the TOF and selectivity are observed in the vicinity of monolayer coverage (6–7% MoO_3/TiO_2). The methanol oxidation TOF of the surface molybdenum oxide species on TiO_2 at high surface coverages is more than 1 order of magnitude higher, as well as somewhat more selective to formaldehyde, than bulk MoO_3.

MoO_3/ZrO_2. The reactivities and selectivites of the MoO_3/ZrO_2 catalysts as a function of molybdenum oxide loading during methanol oxidation at 503 K are listed in Table 3 along with the pure ZrO_2 support for reference. Previous Raman characterization studies have demonstrated that monolayer coverage of the surface molybdenum oxide species on this ZrO_2 corresponds to ~4% MoO_3/ZrO_2.[1] The ZrO_2 support exhibits some methanol oxidation activity toward methyl formate, COx, and trace amounts of dimethyl ether. With increasing loadings of molybdenum oxide on ZrO_2, the main product formed by the surface molybdenum oxide sites is formaldehyde. A small amount of dimethoxymethane is also observed with the addition of molybdenum oxide to ZrO_2. The selectivity toward methyl formate significantly decreases as the molybdenum oxide loading increases, which suggests that the ZrO_2 surface is being covered by the surface molybdenum oxide species. The TOFs of the 0.5% and 1% MoO_3/ZrO_2 samples have not been calculated since the reactivity of these samples is close to that of the ZrO_2 support, and it is difficult to separate the contribution of the support from the activity of the surface molybdenum oxide species. Furthermore, the ZrO_2 support not only competes

TABLE 4: Reactivity of MoO_3/Nb_2O_5 Catalysts as a Function of MoO_3 Loading for Methanol Oxidation Reaction

				selectivity (%)				
sample	density (Mo atoms/nm^2)	activity (mmol/(g h))	TOF[a] (redox) (10^{-2} s^{-1})	FA	MF	DMM	DME	COx
Nb_2O_5		15.7					100	
0.5% MoO_3/Nb_2O_5	0.4	17.3	[b]	10		2	88	tr
1% MoO_3/Nb_2O_5	0.8	24.8	[b]	30	tr	1	68	tr
2% MoO_3/Nb_2O_5	1.5	66.3	8.8	65	tr	2	32	tr
3% MoO_3/Nb_2O_5	2.3	134.5	14.0	76	tr	2	22	tr
4% MoO_3/Nb_2O_5	3.0	124.0	9.4	72	tr	4	23	tr
5% MoO_3/Nb_2O_5	3.8	271.6	17.8	80	tr	2	18	tr
6% MoO_3/Nb_2O_5	4.6	351.7	19.2	80	tr	2	18	tr
7% MoO_3/Nb_2O_5	5.3	323.3	15.3[c]	80	tr	3	17	tr

[a] Redox TOF is based on the formation of FA + MF + DMM. [b] Not calculated due to the high activity of the Nb_2O_5 support. [c] Apparent TOF since dispersion is not 100% due to presence of crystalline MoO_3 particles.

TABLE 5: Reactivity of MoO_3/Al_2O_3 Catalysts as a Function of MoO_3 Loading for Methanol Oxidation Reaction

				selectivity (%)				
sample	density (Mo atoms/nm^2)	activity (mmol/g h)) (10^3)	TOF[a] (redox) (10^{-2} s^{-1})	FA	MF	DMM	DME	COx
Al_2O_3		3.7					100	
1% MoO_3/Al_2O_3	0.2	1.8					100	
6%MoO_3/Al_2O_3	1.4	3.0	[b]	0.5		tr	99.5	
12%MoO_3/Al_2O_3	2.8	1.4	[b]	4	tr	tr	96	
18%MoO_3/Al_2O_3	4.2	1.6	9.4	11	tr	tr	89	
20%MoO_3/Al_2O_3	4.6	2.6	11.1	21	tr	tr	79	

[a] Redox TOF is based on oxidation products (FA + MF + DMM) formed. [b] Not calculated due to the high activity of the Al_2O_3 support.

with the surface molybdenum oxide species for the methanol reactant but probably also functions together with surface molybdenum oxide species to form methyl formate since isolated Mo species are present for the low loading MoO_3/ZrO_2 catalysts.[1] Thus, the redox TOF for the surface molybdenum oxide sites was calculated from the yield of formaldehyde and dimethoxymethane and did not take into consideration the minor amounts of methyl formate produced from the combination of the ZrO_2 support and the surface molybdenum oxide species. At 2% MoO_3/ZrO_2 and higher Mo loadings, the reactivity and selectivity are both dominated by the surface molybdenum oxide species. The TOF varies from 2.4×10^{-1} to 6.1×10^{-1} s^{-1} for the 2% to 3% MoO_3/ZrO_2 samples. Above monolayer coverage (~4% MoO_3/ZrO_2), the TOF decreases because of the low exposure and specific activity of crystalline MoO_3 for methanol oxidation compared to the surface Mo species on ZrO_2.

MoO_3/Nb_2O_5. The reactivities and selectivities of the MoO_3/Nb_2O_5 catalysts as a function of molybdenum oxide loading during methanol oxidation at 503 K are listed in Table 4 along with the data for the Nb_2O_5 support for reference. Previous Raman characterization studies have demonstrated that monolayer coverage of the surface molybdenum oxide species on this Nb_2O_5 support corresponds to ~6% MoO_3/Nb_2O_5.[1] The acidity of the Nb_2O_5 surface exclusively produces dimethyl ether. The surface molybdenum oxide species form oxidation products of formaldehyde and small amounts of methyl formate and dimethoxymethane. The formaldehyde selectivity increases gradually, and the dimethyl ether selectivity decreases as the molybdenum oxide loading increases. The yields of FA + MF + DMM were used to calculate the redox TOF of the surface molybdenum oxide species on Nb_2O_5. The TOFs of the 0.5% and 1% MoO_3/Nb_2O_5 samples were not calculated since the activity of the Nb_2O_5 support is comparable to these catalysts, and the Nb_2O_5 is competing with the surface molybdenum oxide species for the methanol reactant. At 2% MoO_3/Nb_2O_5 and higher Mo loadings, the activity of the surface molybdenum oxide species becomes more pronounced and dominates the reactivity for the higher Mo loading catalysts. The TOF varies within $(0.9-1.9) \times 10^{-1}$ s^{-1}, as the molybdenum oxide loading increases from 2% to 6% of surface molybdenum oxide species. No further increase in activity is observed for the sample containing more than monolayer coverage of surface molybdenum oxide species (7% MoO_3/Nb_2O_5), and the apparent TOF decreases slightly due to the presence of crystalline MoO_3 particles.

MoO_3/Al_2O_3. The reactivities and selectivities of the MoO_3/Al_2O_3 catalysts as a function of molybdenum oxide coverage for methanol oxidation at 503 K are listed in Table 5 along with the Al_2O_3 support as reference. Previous Raman studies have demonstrated that monolayer coverage of the surface molybdenum oxide species on Al_2O_3 corresponds to ~20% MoO_3/Al_2O_3.[1] The Lewis acid sites of the Al_2O_3 support possess a very high activity for the dehydration of methanol to dimethyl ether. The formaldehyde partial oxidation product is only detected at molybdenum oxide loadings of 6% MoO_3 and above, and the selectivity to formaldehyde increases with increasing Mo loading. Only trace amounts of methyl formate and dimethoxymethane were detected above 6% MoO_3/Al_2O_3, and COx was not a reaction product. The dimethyl ether formed from the Al_2O_3 support decreases as molybdenum oxide loading increases, which indicates that the surface of the Al_2O_3 support has been covered by the deposition of surface molybdenum oxide species. As molybdenum oxide loading increases, the total activity remains essentially the same, which suggests that the dehydration of methanol on the Al_2O_3 surface is faster than than the partial oxidation of methanol over the surface molybdenum oxide sites. No TOF was calculated for the 6% and 12% MoO_3/Al_2O_3 samples since too much of the Al_2O_3 surface is exposed, and the activity of Al_2O_3 dominates the reactivity of these catalysts. The Al_2O_3 acidity is very competitive with the surface molybdenum oxide sites, and only ~21% selectivity toward formaldehyde formation was obtained at monolayer coverage (20% MoO_3/Al_2O_3). The amount of FA + MF + DMM produced was taken to represent the redox TOF of the surface molybdenum oxide sites of high loading catalysts, and a TOF of ~1.1×10^{-1} s^{-1} was obtained at monolayer coverage.

***In Situ* Raman Spectra of Supported Molybdenum Oxide Catalysts during Methanol Oxidation.** The Raman spectra of the dehydrated surface molybdenum oxide species possess bands in the 980–1006 cm^{-1} region, corresponding to the

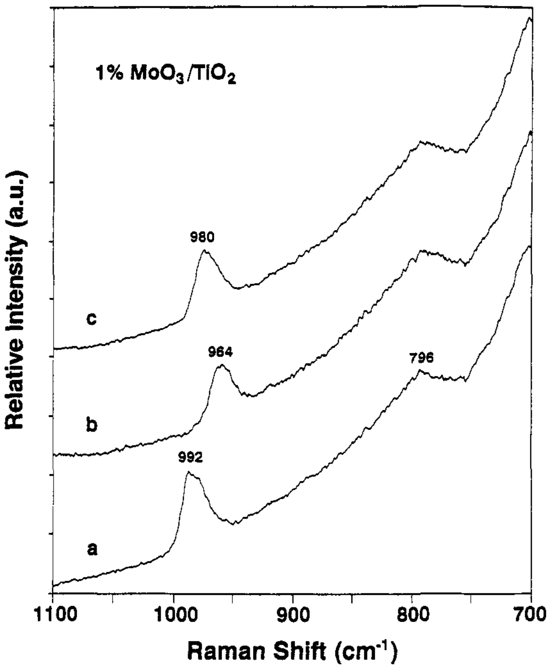

Figure 1. *In situ* Raman spectra of the 1% MoO_3/TiO_2 catalyst during methanol oxidation: (a) 503 K, He/O_2; (b) 503 K, $CH_3OH/He/O_2$; (c) 503 K, He/O_2 after reaction.

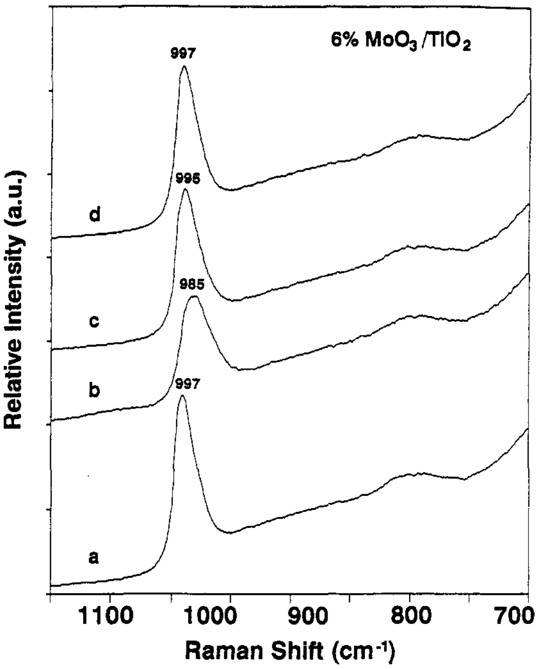

Figure 2. *In situ* Raman spectra of the 6% MoO_3/TiO_2 catalyst during methanol oxidation: (a) 503 K, He/O_2; (b) 503 K, $CH_3OH/He/O_2$; (c) 503 K, He/O_2 after reaction; (d) 773 K, He/O_2.

terminal Mo=O stretching mode. The high loading catalysts possess additional Raman bands in the ~860–910 cm^{-1} region which were assigned to the stretching mode of the Mo–O–Mo bridging bond.[1] The Raman band at ~1000 cm^{-1} of the Mo=O terminal stretching mode is usually sharp and relative strong, and the ~900 cm^{-1} Raman band of the Mo–O–Mo bond is usually very broad. The surface molybdenum oxide species become partially reduced during methanol oxidation, which is reflected in a decrease in the normalized intensity of the Mo=O Raman band. It was assumed that the reduction of the catalysts is quantitatively reflected by the decrease in the normalized Raman intensity of the terminal Mo=O bond. Furthermore, Raman is more sensitive to the Mo=O double bonds than the Mo–O–Mo bridging bonds, and the changes in the Raman intensity of the broad bridging bond were not substantial and may also be complicated by the overlap of the Raman band of the reduced surface molybdenum oxide species. (For example, see the Raman spectra below of the MoO_3/Al_2O_3 catalyst during methanol oxidations.) The vibrational modes of the bridging Mo–O–support bond are not Raman-active due to the slight ionic character of these bonds. Therefore, the decrease in the terminal Mo=O Raman band intensity of the catalysts during methanol oxidation is used to represent the percent reduction of the supported molybdenum oxide catalysts or the percent of surface molybdenum oxide species participating in the reaction.

MoO_3/TiO_2. The *in situ* Raman spectra of the 1% and 6% MoO_3/TiO_2 catalysts are presented in Figures 1 and 2, respectively. The Raman spectra before, during, and after methanol oxidation were all normalized according to the synchronous Raman intensity changes of the crystalline TiO_2 support bands at 640, 520, and 399 cm^{-1}. During methanol oxidation, the Raman band of the terminal Mo=O stretching mode of the surface molybdenum oxide species of the 1% MoO_3/TiO_2 catalyst at 992 cm^{-1} decreases in intensity and shifts to 964 cm^{-1}, and that of the 6% MoO_3/TiO_2 catalyst also decreases in intensity and shifts from 997 to ~985 cm^{-1}. There is also a slight broadening for this Raman band during methanol oxidation. The decrease in the Raman signal of the terminal Mo=O bond reflects a certain extent of reduction of the surface molybdenum oxide species, and the broadening and shifts to lower frequency are probably partially due to the presence of methoxy species during methanol oxidation[28,29] (see Discussion). The frequency shift of the terminal Mo=O Raman band for the low loading catalyst is more pronounced than that of the high loading catalyst. After the methanol flow is terminated and the samples are oxidized for 1 h with a He/O_2 gas at the reaction temperature (503 K), the catalysts are only partially reoxidized (~10% differences to their initial states; compare parts a–c of Figures 1 and 2). The catalysts are fully reoxidized to the original state after an oxidation treatment at 773 K (compare parts a and d of Figure 2), which suggests the reduction is the main cause of the Raman intensity decrease rather than reconstruction. The decrease in the Raman intensity of the terminal Mo=O bond of the surface molybdenum oxide species is ~23% under the methanol oxidation conditions. Unfortunately, no reduced surface molybdenum oxide species were identified in the Raman spectra.

The temperature dependence of the structure of the surface molybdenum oxide species during methanol oxidation was also studied by *in situ* Raman spectroscopy. Figure 3 shows the Raman spectra of the 6% MoO_3/TiO_2 catalyst in the oxidized state and during methanol oxidation at 503, 573, and 633 K. Increasing the temperature during methanol oxidation results in sharper Raman bands and a decrease in the shift of the Raman band when comparing the spectra before and during reaction. These changes reflect less methoxy adsorption on the catalyst surface with increasing reaction temperature.[28] However, the decreases in the intensities of the Raman bands associated with the terminal Mo=O bonds at all temperatures are ~25% of the fully oxidized surface Mo species and do not show a strong dependence upon reaction temperature over the range investigated (503–633 K).

MoO_3/ZrO_2. The *in situ* Raman spectra of the 1% and 4% MoO_3/ZrO_2 catalysts are presented in Figures 4 and 5, respectively. The spectra were normalized according to the Raman intensity changes of the crystalline ZrO_2 support bands at 554, 532, and 497 cm^{-1}. During methanol oxidation at 503 K, the

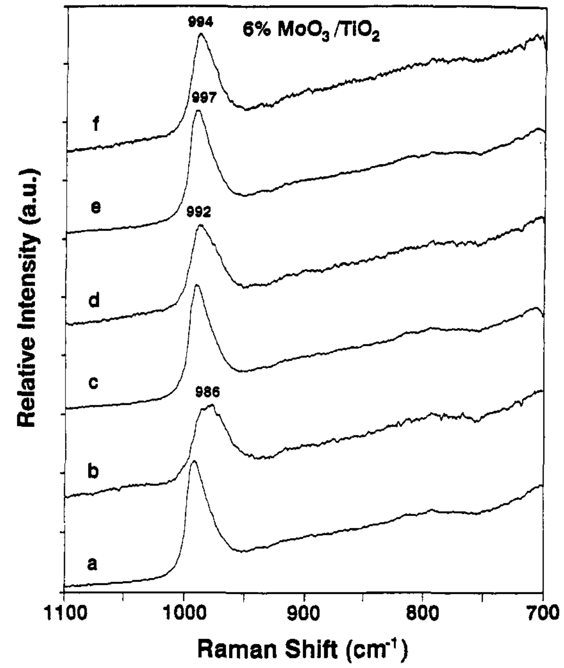

Figure 3. *In situ* Raman spectra of the 6% MoO_3/TiO_2 catalyst during methanol reaction at (a, b) 503 K, (c, d) 573 K, and (e, f) 633 K. Where (a), (c), and (e) are taken before reactions and (b), (d), and (f) are taken during the reactions.

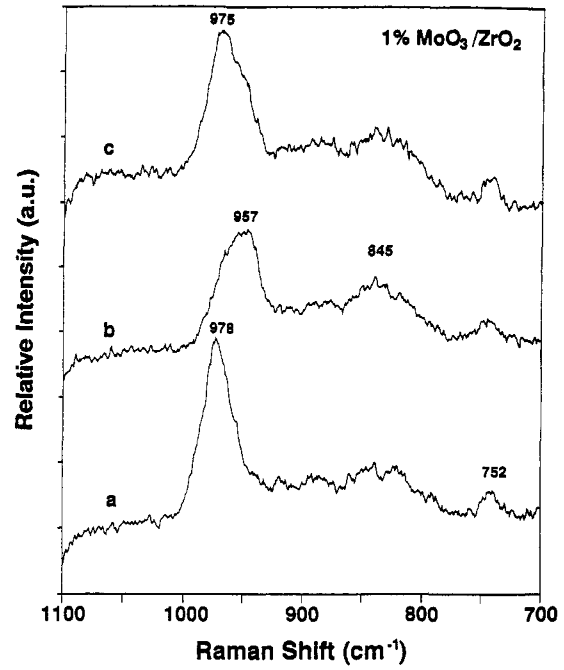

Figure 4. *In situ* Raman spectra of the 1% MoO_3/ZrO_2 catalyst during methanol oxidation: (a) 503 K, He/O_2; (b) 503 K, $CH_3OH/He/O_2$; (c) 503 K, He/O_2 after reaction.

Raman band of the terminal Mo=O stretching mode of the 1% MoO_3/ZrO_2 catalyst decreases in intensity and shifts from 978 to ~957 cm^{-1}, and that of the 4% MoO_3/ZrO_2 catalyst also decreases in intensity and shifts from 995 to ~983 cm^{-1}. A substantial broadening of the terminal Mo=O Raman band is also observed for both MoO_3/ZrO_2 catalysts. Similar to the MoO_3/TiO_2 catalysts, the shift of the terminal Mo=O Raman band of the low loading sample upon methanol oxidation is larger than that of the high loading sample. The Mo=O Raman bands of the samples during methanol oxidation decrease ~33% and 43% compared to the fully oxidized surface molybdenum oxide species for the 1% and 4% MoO_3/ZrO_2 catalysts, respectively. After reoxidation with He/O_2 at 503 K, the reduced surface molybdenum oxide species partially recover their initial Raman intensities (~70%) and shift back toward their initial positions. No Raman bands due to the reduced Mo species are observed. The influence of temperature on the Raman spectrum during methanol oxidation was also studied for the 3% MoO_3/ZrO_2 sample and is shown in Figure 6. The temperature dependence of the Raman spectra for the 3% MoO_3/ZrO_2 catalyst is similar to that of the MoO_3/TiO_2 catalyst (Figure 3). Increasing the methanol oxidation reaction temperature sharpened the Raman bands and decreased the shift of the band. However, the changes in the surface area of the Mo=O Raman

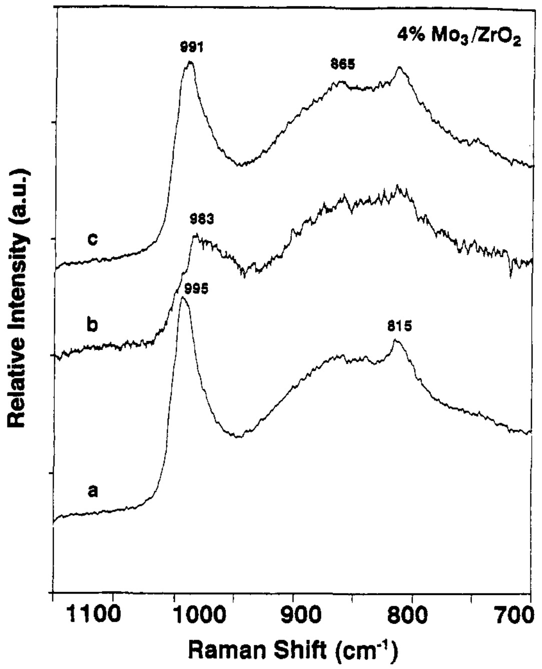

Figure 5. *In situ* Raman spectra of the 4% MoO_3/ZrO_2 catalyst during methanol oxidation: (a) 503 K, He/O_2; (b) 503 K, $CH_3OH/He/O_2$; (c) 503 K, He/O_2 after reaction.

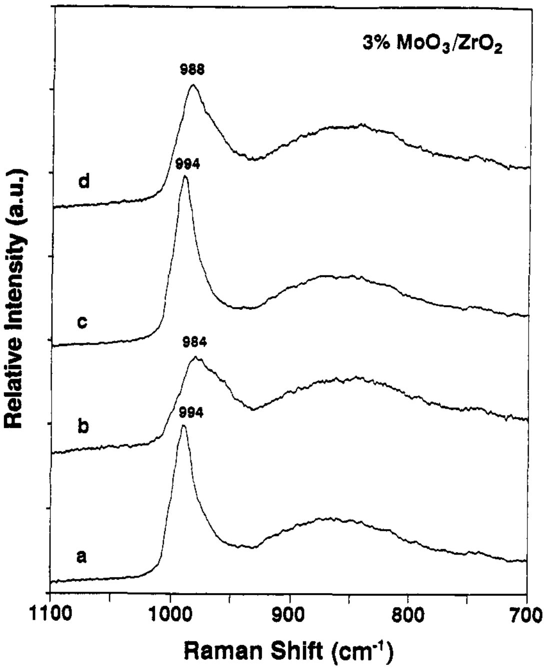

Figure 6. *In situ* Raman spectra of the 3% MoO_3/ZrO_2 catalyst during methanol reaction at (a, b) 573 K and (c, d) 633 K, where (a) and (c) are before reactions and (b) and (d) are during reactions.

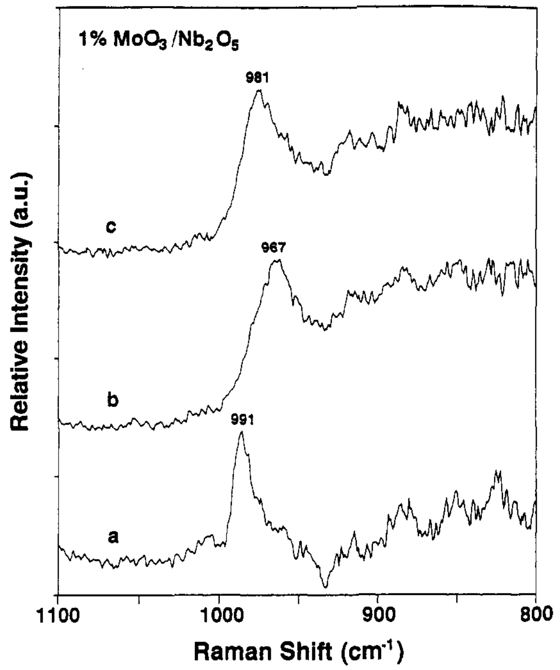

Figure 7. *In situ* Raman spectra of the 1% MoO_3/Nb_2O_5 catalyst during methanol oxidation: (a) 503 K, He/O_2; (b) 503 K, $CH_3OH/He/O_2$; (c) 503 K, He/O_2 after reaction.

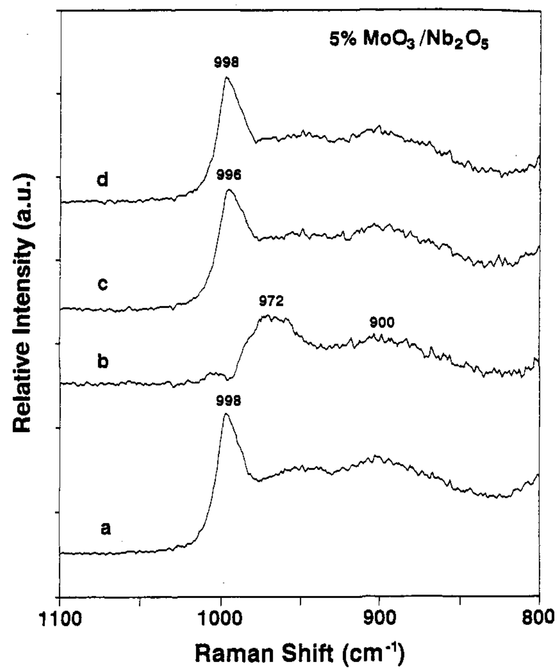

Figure 8. *In situ* Raman spectra of the 5% MoO_3/Nb_2O_5 catalyst during methanol oxidation: (a) 503 K, He/O_2; (b) 503 K, $CH_3OH/He/O_2$; (c) 503 K, He/O_2 after reaction; (d) 773 K, He/O_2.

bands during methanol oxidations do not strongly depend on reaction temperature. The decreases of the Mo=O Raman band upon changing temperature are ~38% of their initial Raman intensities.

MoO_3/Nb_2O_5. The *in situ* Raman spectra of the 1% and 5% MoO_3/Nb_2O_5 catalysts are presented in Figures 7 and 8, respectively, and were obtained by subtracting the background spectrum of the Nb_2O_5 support in order to enhance the surface molybdenum oxide signals. The normalization was made according to the Nb_2O_5 Raman band at ~220 cm^{-1}. During methanol oxidation a decrease in the intensity of the Raman band of the terminal Mo=O stretch mode occurs, and the band shifts from 991 to 967 cm^{-1} for the 1% MoO_3/Nb_2O_5 catalyst and from 998 to 972 cm^{-1} for the 5% MoO_3/Nb_2O_5 catalyst. The decrease in Mo=O Raman intensity of the surface molybdenum oxide species for 5% MoO_3/Nb_2O_5 during methanol oxidation is determined to be ~20% according to the terminal Mo=O Raman band intensity of the fully oxidized Mo species. Reoxidation of the catalysts by He/O_2 at the reaction temperature (503 K) recovers the intensity of the Raman bands of the original surface molybdenum oxide species (~90%), and at 773 K the reoxidation is complete (Figure 8d). Similar to the MoO_3/TiO_2 and MoO_3/ZrO_2 catalyst systems, the shifts to lower frequency during methanol oxidation is more pronounced for the lower loading catalyst.

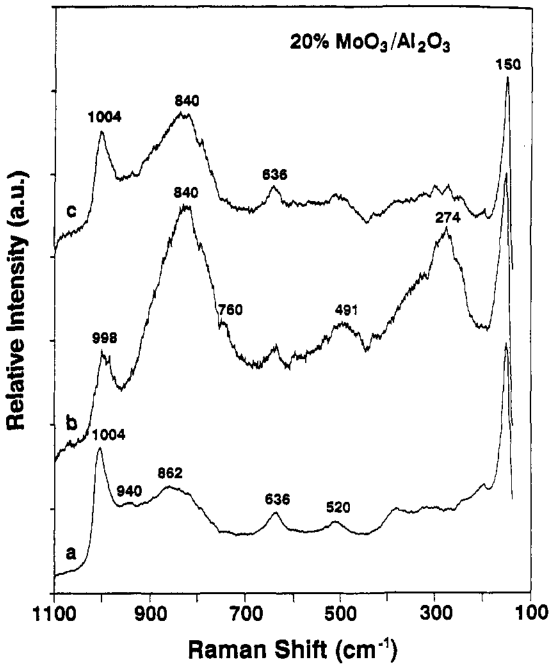

Figure 9. *In situ* Raman spectra of the 20% MoO_3/Al_2O_3 catalyst during methanol oxidation: (a) 503 K, He/O_2; (b) 503 K, $CH_3OH/He/O_2$; (c) 503 K, He/O_2 after reaction.

MoO_3/Al_2O_3. The *in situ* Raman spectra of the 20% MoO_3/Al_2O_3 catalysts are presented in Figure 9. The *in situ* Raman spectra of the lower loaded MoO_3/Al_2O_3 catalysts (1% and 6% sample) were not obtainable due to fluorescence of the samples during the methanol oxidation reaction conditions. The normalization of the *in situ* Raman signal for MoO_3/Al_2O_3 is difficult due to the lack of Raman bands from the Al_2O_3 support. Thus, the Raman spectra in Figure 9 were normalized by adding ~0.5% TiO_2 (anatase, 20 m^2/g) as an internal standard that employs to the TiO_2 Raman band at 636 cm^{-1}. The migration of the surface molybdenum oxide species to the surface of the TiO_2 support can be neglected since the relative surface area of the TiO_2 internal standard is small (relative surface areas of Al_2O_3/TiO_2 ~ 2000/1). Exposure of the 20% MoO_3/Al_2O_3 to the reaction mixture results in the major Raman band at 1004 cm^{-1}, due to the terminal Mo=O stretching mode, to decrease in intensity and slightly shift to 998 cm^{-1}. However, new Raman bands at ~840, ~760, 491, and 274 cm^{-1} simultaneously increase and dominate the spectrum during the methanol oxidation. The decrease in the Mo=O Raman intensity of the surface molybdenum oxide species is determined to be ~24% during methanol oxidation. Reoxidation with He/O_2 at the reaction temperature (503 K) recovers only ~70% the oxidative species (compare spectra c and a of Figure 7). Reoxidation at 773 K recovers all of the oxidized species (spectrum is not shown). The ~760, 491, and 274 cm^{-1} Raman bands were

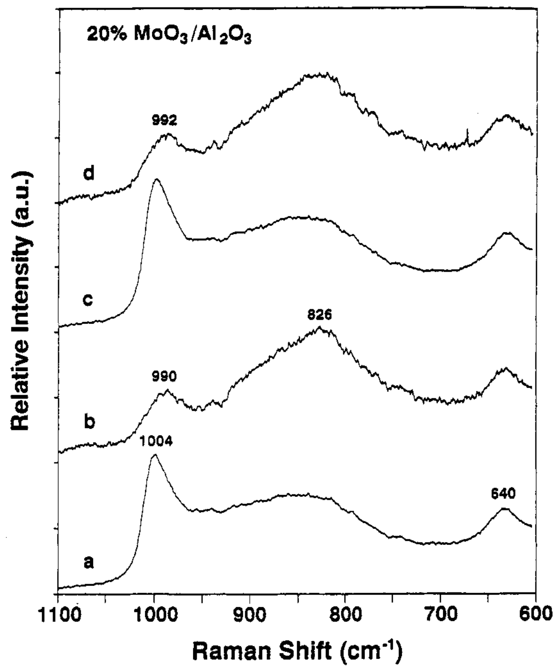

Figure 10. *In situ* Raman spectra of the 20% MoO_3/Al_2O_3 catalyst during methanol reaction at (a, b) 573 K and (c, d) 633 K, where (a) and (c) are before reactions and (b) and (d) are during reactions.

previously assigned to reduced surface molybdenum oxide species on Al_2O_3, but the ~840 cm^{-1} Raman band was previously assigned to the microcrystalline MoO_3 phase.[30] However, the current Raman spectra, after normalization with the internal TiO_2 standard, reveal that the 840 cm^{-1} band has actually increased in intensity and shifted position compared to the oxidized Mo species, and thus, it should be due to a reduced surface molybdenum oxide species. A similar trend was found for the temperature dependence of the 20% MoO_3/Al_2O_3 catalyst, shown in Figure 10, as that for the MoO_3/TiO_2 and the MoO_3/ZrO_2 catalysts. No strong dependence of the Mo=O Raman intensity upon reaction temperature is found. The 640 cm^{-1} band in Figure 10 is due to the TiO_2 anatase added as an internal standard for normalization of the Raman signals of the surface molybdenum oxide species. A shift of the Raman band at ~840 cm^{-1} to ~826 cm^{-1} is also observed upon increasing the reaction temperature. Note that the Raman spectra in Figures 9 and 10 are plotted in different cm^{-1} regions.

Reduction of Surface Molybdenum Oxide Species. The decreases in the normalized and integrated intensities of the terminal Mo=O Raman bands of the surface molybdenum oxide species during methanol oxidation are compared in Figure 11. The decrease in the Mo=O Raman band intensity of the surface molybdenum(VI) oxide species during methanol oxidation is approximately 20–24% on titania, niobia and alumina and slightly higher on zirconia, 33–43%. As previously discussed, it is assumed that the decrease in the normalized Mo=O Raman band intensity is proportional to the extent of reduction. Nevertheless, the decrease in the normalized Mo=O Raman band intensities is about the same for all catalysts. Therefore, the percent reduction of the surface molybdenum oxide species during methanol oxidation does not appear to be a strong function of surface coverage or the specific oxide support.

Discussion

Factors Influencing the Selectivity of the Supported Molybdenum Oxide Catalysts. The overall selectivity of the supported molybdenum oxide catalysts was determined by the reactivity properties of both the surface molybdenum oxide species and the specific oxide support. The surface molybdenum oxide species primarily were responsible for the formation of formaldehyde but could also yield small amounts of methyl formate (see MoO_3/TiO_2 data in Table 2) and dimethoxymethane (see MoO_3/ZrO_2 data in Table 3). The Lewis acid sites on the alumina and niobia supports were very active and resulted in significant amounts of dimethyl ether production (see data in Tables 4 and 5). In contrast, the Lewis acid sites on the titania support were not very active and resulted in only small amounts of dimethyl ether production. The small dimethyl ether production observed for the MoO_3/TiO_2 catalysts may even have originated from acid sites associated with the surface molybdenum oxide species rather than the titania support. The redox sites on the zirconia support possessed a modest activity and yielded methyl formate from pairs of either Zr–Zr sites or Zr–Mo sites. The competitive reactions between the surface molybdenum oxide species and the specific oxide support determined the final overall reaction selectivity. The relative contribution of these two reactive sites was a strong function of the surface molybdenum oxide coverage since the surface molybdenum oxide species covered the reactive oxide support sites at high surface coverages. The primary reaction product formed at monolayer coverage of the surface molybdenum oxide species on the different supports was formaldehyde with approximately 80% selectivity. However, the very active Lewis acid sites on the alumina support, and possibly even acid sites associated with the surface molybdenum oxide species on alumina,[31] were reponsible for the catalyst exhibiting a formaldehyde selectivity of 21% at monolayer coverage. The generally high selectivity of the supported molybdenum oxide catalysts toward formaldehyde production during methanol oxidation demonstrates that this is the primary redox product from the surface molybdenum oxide species.

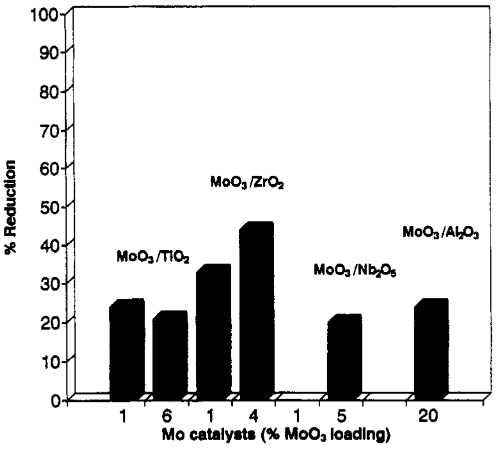

Figure 11. Percent reduction (decrease in the Raman Mo=O band intensity) for different oxide-supported molybdenum oxide catalysts during methanol oxidation at 503 K.

The selective production of formaldehyde during methanol oxidation over the supported molybdenum oxide catalysts does not appear to be dependent on the molecular structure of the surface molybdenum oxide species. The product selectivity for the 1% and 6% MoO_3/TiO_2 catalysts is essentially identical (see Table 2); however, these catalysts possess different surface molybdenum oxide structures.[1] The surface molybdenum oxide species primarily possess tetrahedral coordination for the 1% MoO_3/TiO_2 catalyst and octahedral coordination for the 6% MoO_3/TiO_2 catalyst, and the extent of polymerization of the surface molybdenum oxide species also increases with surface coverage (see Table 1). The zirconia-supported samples appear to possess both tetrahedral and octahedral coordinated surface molybdenum oxide species at monolayer coverage (see Table 1), and this catalyst also yields a comparable formaldehyde selectivity during methanol oxidation. Thus, the specific molecular structure of the surface molybdenum oxide species is not a critical parameter affecting the rate of selective oxidation of methanol to formaldehyde.

Factors Influencing the TOF of the Supported Molybdenum Oxide Catalysts. The redox TOFs of the supported molybdenum oxide catalysts increase by a factor of about 2–4 as the coverage of the surface molybdenum oxide species increases toward monolayer coverage (see Tables 2–4). The most extensive catalytic data exist for the MoO_3/TiO_2 system since the titania support was relatively inactive toward methanol oxidation at low surface molybdenum oxide coverages, and the TOF for this system increases approximately 4-fold with coverage. Comparison of the methanol oxidation reactivity data with the corresponding structural data for the surface molybdenum oxide species (see Table 1) suggests that this slight increase in reactivity may be related to structural differences of the surface molybdenum oxide species. The surface molybdenum oxide species on titania are predominantly isolated, tetrahedral species at low loadings and predominantly polymerized, octahedral species at high loadings. Similar structural and catalytic trends for the surface molybdenum oxide species are also observed for the other supported molybdenum oxide catalysts but are somewhat overshadowed by the contributions of the oxide supports at low surface coverages. Thus, it appears that polymerized, octahedral/tetrahedral surface molybdenum oxide species may be slightly more active, but a factor of 2–4, than isolated, tetrahedral surface molybdenum oxide species on oxide supports.

The redox TOFs of the supported molybdenum oxide catalysts at monolayer coverage increase by a factor of about 6 as the specific oxide support is changed (see Tables 2–5). Furthermore, the TOF for methanol oxidation over low coverage MoO_3/SiO_2 catalyst is a factor of 2 lower than for MoO_3/Al_2O_3, but only isolated surface molybdenum oxide species are present on silica.[27] The relative TOFs follow the pattern $Zr \sim Ti \gg Nb > Al > Si$. The current findings for the reactivity patterns of the supported molybdenum oxide catalysts have much in common with a similar series of studies on methanol oxidation over supported vanadium oxide catalysts.[3] The TOFs of the supported vanadium oxide catalysts were also found to vary with the specific oxide support: $Zr \sim Ti > Nb \gg Al \gg Si$. This trend in reactivity with the specific oxide support is the same for both the supported vanadium oxide and molybdenum oxide catalysts. However, the TOFs for the supported molybdenum oxide catalysts vary by approximately 1 order of magnitude, whereas the TOFs for the supported vanadium oxide catalysts vary by approximately 3 orders of magnitude. Furthermore, the trend in TOF for the supported vanadium oxide catalysts was found to inversely correlate with the reduction temperature during temperature-programmed reduction experiments: the more active catalysts reduce at lower temperature.[3] The same correlation is also found when the TOFs of the supported molybdenum oxide catalysts at monolayer coverage are compared with the reduction temperatures during temperature-programmed reduction experiments[26] (see Figure 12). The line drawn in Figure 12 is not a curve fitting and is meant to illustrate that the oxidation activity is inversely related to the T_{max} temperature of TPR. Thus, these correlations suggest that the oxide support acts as a very important ligand for the surface metal oxide species and that its reducibility is a critical parameter in the redox activity of the supported metal oxide catalysts. It has been proposed for the supported vanadium oxide catalysts that the reducibility of the bridging V–O–support bonds control the TOF during methanol oxidation,[3] and a similar conclusion appears to be valid for the supported molybdenum oxide catalysts. A molecular orbital study for the oxidative dehydrogenation of methanol over transition metal oxide surfaces by Weber[32] suggested that the bridging oxygens are more labile than the terminal oxygens, which is consistent with the current results.

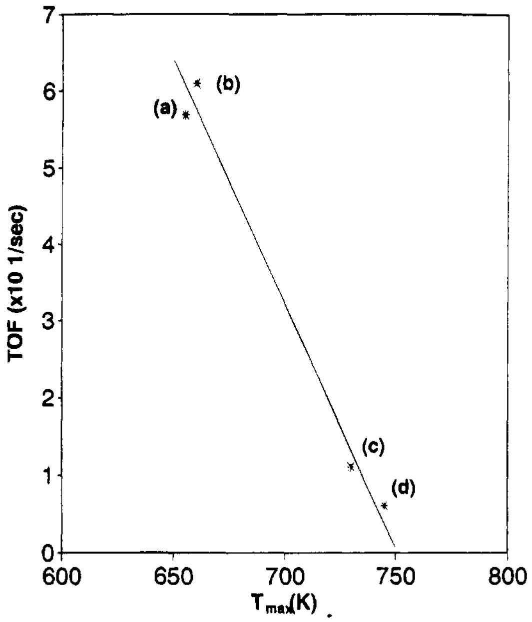

Figure 12. Plot of TOF versus the T_{max} temperature of TPR for the (a) MoO_3/TiO_2, (b) MoO_3/ZrO_2, (c) MoO_3/Al_2O_3, and (d) MoO_3/SiO_2 catalysts. T_{max} is from ref 26, and the TOF of MoO_3/SiO_2 is from ref 27.

Additional support for the above conclusion that the bridging Mo–O–support bond controls the TOF is provided by the current Raman data and literature data on methanol oxidation over various molybdenum oxide-containing catalysts. Comparison of the Raman data in Table 1 with the corresponding methanol oxidation TOFs (Tables 2–5) reveals that a correlation does not exist between the terminal Mo=O bond strength—higher frequencies correspond to shorter and stronger bonds[33]—and the methanol oxidation TOF. The Raman Mo=O band position of the fully oxidized surface molybdenum oxide species is essentially the same for the surface molybdenum oxide species on titania, zirconia, and niobia, but the TOF varies by a factor of 3. The Raman Mo=O band position difference is the greatest between the alumina and silica supports (approximately 20 cm^{-1}),[27] but these two systems are the least active catalysts. The surface molybdenum oxide species also possess the same structures on titania and niobia, but the TOF varies by a factor of 3. Similarly, the surface molybdenum oxide species are similar on zirconia and alumina, but the TOF varies by a factor of about 6. Thus, the change in the TOF of the surface molybdenum oxide species with the specific oxide support, about a factor of 10 when silica is included, appears to be related to a property of the support rather than the structure of the surface molybdenum oxide overlayer. Furthermore, methanol adsorption studies over the MoO_3 single crystal(010) basal plane, which possesses the surface containing the most saturated Mo=O bonds in the layered MoO_3 structure, found no chemisorption of methanol. It was, thus, hypothesized that methanol adsorption leading to reaction is favored by the coordinatively unsaturated Mo sites (the edge planes possessing Mo–O–Mo and Mo–OH bonds).[5,7,34] Eguchi *et al.*[35] observed with *in situ* IR during methanol oxidation over heteropolyanion Keggin units that the bridging Mo−O−Mo bond was reduced at low degrees of reduction of the heteropolyanions and that the terminal Mo═O oxygen was consumed only at high extent of reduction. Thus, there currently is no supporting evidence that the terminal Mo═O bond controls the TOF during methanol oxidation.

Matsuoka *et al.*[21] were the first to study the activity of a series of supported molybdenum oxide catalysts (Al_2O_3, TiO_2, ZrO_2, and CeO_2 supports) for methanol oxidation. The dependence of the TOF on the surface molybdenum oxide coverage and the specific oxide support was reported (see Figure 12 of ref 21). Their investigation found that the TOF increases with surface Mo coverage, and the activity sequence for the supports, $ZrO_2 > TiO_2 > Al_2O_3$, agrees with the current findings. However, the larger increase of the TOF with the surface Mo loading in the prior studies compared to the current investigation may have been caused by the extremely low activities of the oxide supports in the earlier studies. The overall TOFs of the monolayer catalysts reported by Matsuoka *et al.* were also much lower than our results, even after taking into account the lower reaction temperature and lower partial pressure of the methanol employed. Kim *et al.*[26] also studied methanol oxidation over different supported molybdenum oxide catalysts, under similar reaction conditions as Matsuoka's, and reported TOFs of the surface molybdenum oxide species which are very close to the current findings. Matsuoka *et al.* did not give an explanation for the TOF dependence, and a structure−reactivity relationship was not discussed since only the ambient structures of the surface molybdenum oxide species, rather than the structures under reaction conditions, were studied.

***In Situ* Raman Studies of Supported Molybdenum Oxide Catalysts.** Additional insights into the states of the surface molybdenum oxide species during the methanol oxidation reaction were provided by *in situ* Raman spectroscopy studies. The *in situ* Raman studies demonstrated that the surface molybdenum oxide species on ZrO_2, TiO_2, Nb_2O_5, and Al_2O_3 were stable during methanol oxidation and did not agglomerate into crystalline MoO_3 particles. Thus, the exposure of the surface molybdenum oxide species on these oxide supports remained 100% during methanol oxidation below monolayer surface coverage (see Figures 1−10). This is in contrast to methanol oxidation over MoO_3/SiO_2 where the surface molybdenum oxide species agglomerate into crystalline β-MoO_3 particles at high loadings.[27]

The *in situ* Raman studies also revealed that the surface molybdenum oxide species are influenced by the methanol oxidation reaction. The Mo═O Raman bands of the surface molybdenum oxides decrease in intensity, become broader, and are usually shifted to lower frequencies by $\sim$10 cm^{-1}. These changes are primarily attributed to the participation of the surface molybdenum oxide species in the methanol oxidation reaction as well as coordination by surface methoxy species (the reaction intermediate[5−7]). Shifting to lower frequency and broadening of the Mo═O Raman bands can also be caused by adsorbed moisture.[28] However, the low water partial pressures in the *in situ* cell during methanol oxidation and the elevated reaction temperatures, 503−633 K, should minimize the perturbation of adsorbed moisture upon the Raman Mo═O band. In fact, moisture does not perturb the Raman Mo═O band of MoO_3/SiO_2 because of the hydrophobic nature of the silica support, and this band also broadens and shifts to lower frequencies during methanol oxidation.[27] Thus, the changes in the shape and position of the Mo═O Raman bands are associated with the surface methoxy intermediates. The lifetime of the reactive methoxy intermediates on the surface Mo sites appears too short to be detected by normal Raman, and the stable methoxy species readily seen by Raman during methanol oxidation are located on exposed sites of the oxide support.[28,29] The Raman signal of these stable surface methoxy species decreases with metal oxide loading and becomes undetectable when monolayer metal oxide coverage is approached. Therefore, the presence of these stable surface methoxy species on the exposed sites of the oxide support affects the Raman Mo═O band of the surface molybdenum oxide as discussed above: the Mo═O Raman bands shift to lower frequencies and become broader. The decreases in the frequency shift and broadening of the Raman band with increasing surface molybdenum oxide coverage also indicated that the location of the surface methoxy species was on the exposed oxide support surface. The Mo═O Raman band features of the surface molybdenum oxide species during methanol oxidation were also sensitive to reaction temperature (see Figures 3, 6, and 10) and generally became sharper and shifted to higher frequencies as a consequence of reduction in the number of surface methoxy species with increasing reaction temperature.[28] However, the integrated and normalized intensities of the Mo═O Raman bands did not change significantly from 503 to 633 K, and the differences were within 15% for all temperatures. Thus, over the temperature range investigated, the percent reduction of the surface molybdenum oxide species was not significantly influenced by temperature.

The decrease in the normalized intensity of the Raman Mo═O band during methanol oxidation was taken as a reflection of reduction of the surface molybdenum(VI) oxide species to lower oxidation states. This assumption needs to be quantitatively confirmed with experiments such as *in situ* UV/vis diffuse reflectance spectroscopy which can measure the distribution of oxidation states under reaction conditions. The reduced surface molybdenum oxide species are apparently not Raman-active or give rise to weak signals on titania, zirconia, and niobia, but in the case of MoO_3/Al_2O_3 the reduced surface molybdenum oxide species are readily observable (see Figure 9). This observation is consistent with previous XPS measurements that demonstrated that surface molybdenum oxide species are more readily reduced in hydrogen on titania than on alumina.[36,37] For MoO_3/TiO_2, it was found that no MO(+6) species remained after reduction at 503 K.[37] However, for MoO_3/Al_2O_3, significant amounts of Mo(+6) remained even after a reduction treatment at 773 K.[36] The absence of observable Raman bands for the reduced surface molybdenum oxide species on zirconia, titania, and niobia may be a consequence of their lower oxidation states during methanol oxidation.

The *in situ* Raman studies during methanol oxidation also provide additional insights into the determine factors controlling the TOFs for methanol oxidation over the different supported molybdenum oxide catalysts. The *in situ* Raman studies reveal that the number of surface molybdenum oxide sites participating in the methanol oxidation reaction at steady state, reflected by the percent reduction of the normalized Mo═O Raman bands in Figure 11, is approximately the same for all the supported molybdenum oxide catalysts ($\sim$25%). As discussed above, the percent reduction of the surface molybdenum oxide species during methanol oxidation was also not significantly influenced by the reaction temperature. These observations reveal that only approximately one-quarter of the surface molybdenum oxide species simultaneously participate in the methanol oxidation reaction under steady state, even though the surface molybdenum oxide species are 100% dispersed up to monolayer coverage. All the surface molybdenum oxide species appear to participate in the methanol oxidation reaction since all the surface Mo═O Raman bands are reduced when only methanol (in helium gas) is passed over the catalysts. Details of the extent of participation would require *in situ* isotope experiments to be carried out. A similar situation was found for methanol oxidation over supported vanadium oxide catalysts where approximately 50% of the surface vanadia species were reduced under the same reaction conditions.[29] The *in situ* Raman studies also reveal that the differences in reactivity among the oxide supports are not generally related to different numbers of surface molybdenum oxide species participating in the methanol oxidation reaction. This suggests that the increase in reactivity with the specific oxide support, as well as reaction temperature, is associated with an increase in the specific reactivity of the surface molybdenum oxide active sites.

The constant number of surface molybdenum oxide sites participating on the different oxide supports during the methanol oxidation reaction, under the standard reaction conditions, has significant implications for the kinetics of this reaction. The kinetics of methanol oxidation to formaldehyde has been extensively investigated over many different types of catalysts (molybdenum oxide,[5-9,12,34] supported vanadia,[3] and metals[38]), and the same mechanism and activation energy were always found. The oxidation of methanol to formaldehyde proceeds via a surface methoxy intermediate, and the rate-determining step is the breaking of the C$-$H bond which typically requires about 85 kJ/mol. Furthermore, under the present standard conditions of methanol oxidation, the reaction was first-order in methanol concentration and zero-order in oxygen because of the excess oxygen employed. The constant activation energy for the methanol oxidation reaction, as well as the constant number of participating surface molybdenum oxide sites as discussed above, reveals that the order of magnitude difference observed in the TOF of the supported molybdenum oxide catalysts originates with the preexponential factor of the Arrhenius rate constant and is associated with an entropy term for the activated transition state complex. The increase in entropy of the transition state complex may be related to the more labile Mo$-$O$-$support bridging oxygen present for supported molybdenum oxide species on ZrO_2 and TiO_2 compared to Nb_2O_5, Al_2O_3, and SiO_2. The increase in TOF with molybdenum oxide surface coverage can be accounted by an increase in the density of electronic states which increases the entropy of the activated complex during the methanol oxidation reaction. The current findings are in agreement with the molecular orbital study of surface methoxy C$-$H bond breaking by metal oxide surfaces by Weber, which indicated that the electron delocalization to the support increases the activation entropy of the methanol oxidation reaction.[32] A similar conclusion was reached for the corresponding supported vanadia catalysts during methanol oxidation.[29]

Conclusions

The final overall selectivity during methanol oxidation over the supported molybdenum oxide catalysts was determined by the competitive reactions between the surface molybdenum oxide species and the specific oxide support. The surface molybdenum oxide redox sites selectively yielded formaldehyde, the Lewis acid sites on the alumina and niobia supports resulted in dimethyl ether production, the surface redox sites on zirconia formed methyl formate, and the titania surface sites were relatively inactive. At monolayer coverage of the surface molybdenum oxide species, formaldehyde selectivities of approximately 80% were achieved on titania, zirconia, and niobia. The high activity of the alumina support resulted in a maximum formaldehyde selectivity of only 21% at monolayer coverage. The molecular structure of the surface molybdenum oxide species (isolated, tetrahedral or polymerized, octahedral/tetrahedral) did not correlate with the selectivity of methanol oxidation to formaldehyde.

The redox TOFs of the supported molybdenum oxide catalysts increased by a factor of 2$-$4 with surface molybdenum oxide coverage. This suggests that polymerized, octahedral/tetrahedral surface molybdenum oxide species may be slightly more active than isolated, tetrahedral surface molybdenum oxide species. The redox TOFs of the supported molybdenum oxide catalysts increased by a factor of about 10 as the specific oxide support was changed: $Zr \sim Ti \gg Nb > Al > Si$. This suggests that the oxide support acts as an important ligand that controls the reactivity of the surface molybdenum oxide overlayer. It was proposed that the reducibility of the bridging Mo$-$O$-$support bond controls the TOF during methanol oxidation.

In situ Raman studies during methanol oxidation demonstrated that the dispersion of the surface molybdenum oxide species was 100% below monolayer coverage. The surface molybdenum oxide Mo=O Raman bands decreased in intensity, became broader, and shifted to lower frequencies during methanol oxidation. These changes were due to the adsorption of surface methoxy species on the catalysts and partial reduction of the surface molybdenum oxide species (reflected in the decreased normalized intensity of the Mo=O Raman bands). The percent reduction of the surface molybdenum oxide species during methanol oxidation was not found to be a strong function of surface coverage and the specific oxide support. This suggests that the order of magnitude variation in the TOF with the specific oxide support is primarily related to the specific reactivity of the bridging bond between the surface molybdenum oxide species and the oxide support. The results agree with Weber's proposal that the entropy of the activated complex is affected by the density of accessible electronic states associated with the support.[32]

Acknowledgment. The authors gratefully acknowledge the helpful discussions with Dr. R. S. Weber and Dr. G. Deo. Financial support by the National Science Foundation (Grant CTS 9006258) is also gratefully acknowledged.

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JP950017H