

Reactive and Inert Surface Species Observed during Methanol Oxidation over Silica-Supported Molybdenum Oxide

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The mechanism of methanol oxidation over highly dispersed 1% MoO₃/SiO₂ was studied using a combination of steady state and transient kinetic measurements together with in situ Fourier transform infrared (FTIR) observations of surface-adsorbed species. The main reactive intermediates were methoxide species formed on surface Mo centers. Deuterium substitution experiments showed that these species decomposed through a rate-determining C–H bond-breaking step to form the primary product of reaction, formaldehyde. The steady state data gave an apparent activation energy of 89 kJ/mol, while the oxidation rate of the surface intermediate gave an activation energy for the rate-determining step of 108 kJ/mol. The difference in these gives a heat of adsorption of –19 kJ/mol. Although the oxidation reaction occurred on the Mo centers, the methoxide species were found to migrate to the silica support by reversibly displacing mobile silica OH groups. Two kinds of methoxide species were distinguished, spectators and active intermediates. Only the active intermediates could be oxidized at temperatures lower than 300 °C, and these were the actual participants in the reaction. Quantitative FTIR measurements indicated that the number of methoxide species on the silica support was about six times larger than the number of Mo centers. Thus, the silica surface, which was otherwise inert, participated in a noninnocent manner, holding a substantial population of the reactive intermediates.

Introduction

The methanol oxidation reaction on oxide catalysts has been the subject of much work aimed at understanding the mechanism of the reaction. In a recent study, Burcham, Badlani, and Wachs¹ carried out a comprehensive comparison of the kinetics over a wide number of supported oxide catalysts. Using in situ infrared spectroscopy to monitor the surface intermediates, they concluded that methoxide species were involved in the reaction and that at differential conditions the kinetics were described by the general expression

$$r_t = k_{\text{rds}} K_{\text{ads}} P_{\text{CH}_3\text{OH}} \quad (1)$$

where r_t is the turnover rate, k_{rds} is the rate constant for the rate-determining step, and K_{ads} is the equilibrium constant for methanol adsorption. In this study, we have carried out an in-depth study of the fundamental surface steps involved in methanol oxidation on 1% MoO₃/SiO₂. Although our overall results are consistent with the general form of the proposed rate expression and with the finding that methoxide species are the key intermediate,¹ we have uncovered new phenomena that shed fresh light on how a catalyst–support system can function. What we find is that the support surface can act as a reservoir or storage medium for both unreactive spectator species, which are not involved in the chemical transformations, and for reactive intermediates, which are actual participants in the reaction. Using quantitative in situ infrared spectroscopy, we have measured

the storage capacity of the surface and have found it to be substantial, in this case six times the number of active sites actually carrying out the reaction. The findings here will require a re-assessment of the role of the support in many catalytic reactions.

The most frequently used supported metal oxide catalysts are vanadium and molybdenum oxide supported on silica, alumina, titania, and zirconia.^{2,3} Although strong dependence of activity on the type of support is well-documented, the effect of the support on the kinetic mechanism remains unclear. However, it is commonly presumed that the role of the support is only indirect, i.e., all of the active species (reactants, intermediates, and products) are located on the metal center.^{4–10} In such a case, the support can affect the rate of the reaction through its interaction with the metal but does not hold the active species. We suggest that such behavior of the support be called innocent. In contrast, if the support plays an active role in the reaction, for example, by holding reactive intermediates, we propose calling such behavior noninnocent. In this case, the support interacts directly with the active species. If the idea of the support as a storage medium for reaction intermediates is taken into account, then the reaction mechanism must be supplemented with additional steps, which describes the transport of reaction intermediates between the support and the active site. These steps do not necessarily change the formal kinetic expression, so they have been difficult to recognize in the past. However, they become observable at certain critical conditions, including an abrupt change in the concentration of reactant in the feed. The experiments carried out in this study allow a complete description of the reaction behavior over a wide range of conditions.

It is well-known that methanol adsorption on supported molybdenum oxide results in formation of physisorbed methanol

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and chemisorbed methoxide species (CH_3O^*).^{5,11–13} The symbol * here is used to denote adsorbed surface species. Because of weak adsorption, molecularly adsorbed methanol is observed only at low temperatures (less than approximately 100 °C). At higher temperatures (over 100 °C), methanol chemisorbs to form methoxide species and hydroxyl groups. Subsequent reaction of the hydroxyl groups and water desorption allows further adsorption of methanol and methoxide species formation, and the adsorption can proceed. Water vapor can also adsorb in competition with methoxy groups resulting in inhibition.¹⁴ Holstein and Machiels¹⁵ studied the inhibition of methanol oxidation over iron molybdenum oxide by water vapor at temperatures between 200 and 300 °C. They found that above 200 °C, water was only weakly physisorbed and there was no competitive adsorption between water and methoxy groups. However, they noted that at temperatures below 200 °C site blockage by water can be substantial.^{14–16}

Methoxide species formed from methanol adsorption are the intermediate species of methanol oxidation, and their oxidation produces the primary product of reaction, formaldehyde.⁵ The rate-determining step is generally agreed to be the cleavage of the C–H bond in the adsorbed methoxide species.^{5,17,18} In general, selectivity to HCHO decreases with increasing methanol conversion because of subsequent reactions of the formaldehyde. The main side products are methyl formate, CO, CO₂, and possibly dimethoxymethane and dimethyl ether.

When compared to silica-supported molybdenum oxide, the activity of plain silica (SiO₂) between 270 and 330 °C is very low and the main product is CO₂. This means that the selective oxidation properties of silica-supported molybdenum oxide catalysts are attributed to the molybdenum component.^{19–21} Water desorbs easily under vacuum from MoO₃/SiO₂, while methoxy groups are strongly held and remain adsorbed even at 600 °C. However, if oxygen is admitted above 300 °C, the CH₃O* groups disappear rapidly and surface OH groups recover.^{20,22}

Considerable attention has been given to understanding the identity of the active sites and the structure sensitivity of the reaction. The structure of supported molybdenum oxide has been studied by various spectroscopic techniques including laser Raman spectroscopy (LRS), ultraviolet–visible diffuse reflectance spectroscopy (UVDRS), X-ray diffraction, extended X-ray absorption fine structure (EXAFS), and near edge X-ray absorption fine structure (NEXAFS).^{4,19,23,24} These methods are increasingly complemented by ab initio quantum chemical calculations.³⁴ The results indicate that the loading amount and the structure of the support, surface hydration, and presence of impurities are important factors, which influence the structure of supported molybdenum oxide. The structures usually reported are tetrahedral (dioxo), octahedral (mono-oxo), dimer, and crystalline MoO₃, often coexisting together.^{4,19,23,25–27} In a study of molybdenum oxide supported on various metal oxides, Briand et al.⁵ reported that the strongest correlation of activity for methanol oxidation appeared to be with the nature of the support and not the structure of the Mo oxides. They concluded that the Mo–O support bond is critical in controlling the selective oxidation process.

Probably the most direct approach for understanding a catalytic mechanism is in situ observation of intermediate species during reaction.²⁸ Infrared and Raman spectroscopy are powerful techniques frequently employed to study the structure and behavior of surface intermediates.^{10,25,27,29} The methoxy intermediates adsorbed on supported metal oxides typically give strong signals and are well-suited for spectroscopic study.⁵

Morterra, Magnacca, and Bolis²⁶ observed methanol adsorption on two types of silica by IR spectroscopy. At low temperature, all of the methanol was adsorbed in an undissociated molecular form characterized by several bands in the C–H stretching region (bands of 3000, 2950, and 2845 cm^{–1}). At higher temperature, dissociation led to the formation of surface methoxy groups, characterized by shifted bands in the C–H stretching region at 3000, 2958, and 2858 cm^{–1}.²⁶

Although many studies presume that the methoxy groups are located on the active metal oxide,^{2,30–33} Jehng et al. reported in a Raman study of silica-supported metal oxide catalysts (M = V, Nb, Cr, Mo, W, Re) that M–O–CH₃ species were only found on a V₂O₅/SiO₂ catalyst. In contrast, the methoxy groups observed on the other catalysts were formed via reaction with surface silanol (Si–OH) groups.²⁰ Because the methoxy groups were essentially located on the support, the spectrum of adsorbed methanol on MoO₃/SiO₂ was very similar to that on SiO₂. Because of the stability of the Si–OCH₃ species in an O₂/He stream, they concluded that these were primarily spectator species that did not participate in the reaction.²⁰ In this study, we will show that the methoxide species observed on MoO₃/SiO₂ are indeed partly spectator species but mostly true active participants in the reaction. Observation of their reactivity is possible when methanol is removed from the gas phase and the methoxide species migrate from the silica to the molybdenum centers.

During methanol oxidation, the intensity of terminal M=O bonds decreased,²⁰ indicating that activation of methanol occurs on supported molybdenum oxide. Bañares, Hu, and Wachs²⁷ reported that there are two active sites in methanol oxidation over silica-supported molybdenum oxide catalysts: surface molybdenum sites and silanol groups. Surface molybdenum oxide interacts with methanol to form HCHO. It was suggested that this HCHO may desorb or interact with another methanol molecule attached to a silanol group and form methyl formate.²⁷ Although in our study we found the formation of formaldehyde on molybdenum oxide, we did not observe the formation of methyl formate species.

In this work, we focus on the kinetics of methanol oxidation on MoO₃/SiO₂ and use quantitative analysis of reactants, intermediates, and products to obtain considerable insight into the complex process of surface reaction. Our studies employ an IR spectrometer coupled to a reactor system to study the reaction pathway from gas phase methanol through surface methoxide species to formaldehyde. A notable finding from our work is the observation that the surface of the silica support, which by itself is inert in the reaction, actually plays an important role in the presence of molybdenum. The silica is able to hold both reactive participating species and inert spectators during the catalytic reaction and is thus a noninnocent support.

Experimental Section

Catalyst Preparation and Characterization. The preparation and characterization of the catalyst was described in detail in a previous paper.³⁴ Briefly, a 1 wt % molybdenum oxide supported on silica catalyst (MoO₃/SiO₂) was prepared by the impregnation of an aqueous solution of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Aldrich, >99.99%) on silica (Cabosil EH-5, 350 m² g^{–1}) using the incipient wetness technique. This was followed by drying at 120 °C for 6 h and calcination at 500 °C for 6 h.

The catalyst was characterized by surface area measurements and temperature programmed reduction (TPR). Oxygen chemi-

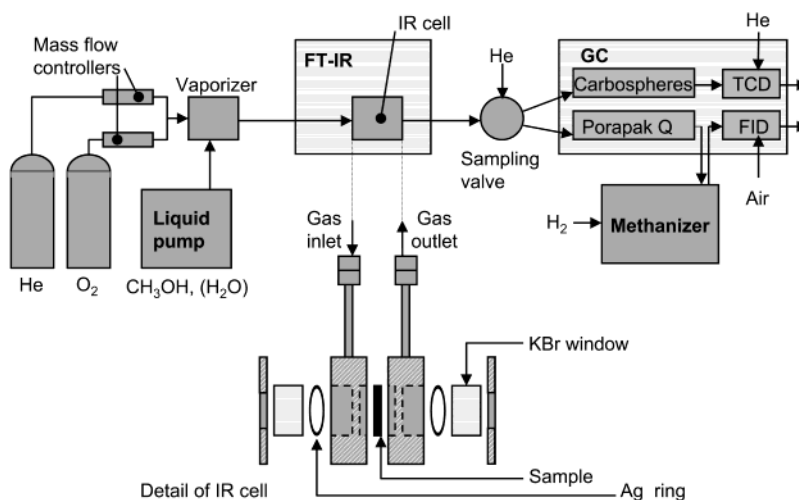


Figure 1. Experimental apparatus.

sorption (oxygen uptake) was taken at the point of initial reduction of the sample. The reduction temperature of the sample was 497 °C. The catalyst had a surface area of 337 m²/g and an O₂ uptake of 37 μmol/g.³⁴ Because the total amount of Mo in the catalysts was 70 μmol/g, assuming a Mo/O ratio of 1, this indicated complete dispersion. A full description of the structure of the catalyst was provided by LRS, NEXAFS, and EXAFS measurements supplemented by Hartree–Fock ab initio calculations at the 3-21G(d) level.³⁵ The combination of these techniques revealed that the molybdenum species in the MoO₃/SiO₂ catalyst were atomically dispersed and had tetrahedral geometry.

Kinetic and Infrared Spectroscopy Studies. Kinetic and spectroscopic measurements on the MoO₃/SiO₂ catalyst were made in a system combining a flow reactor and an infrared spectrometer. A schematic of the system is shown in Figure 1. The reactor consisted of a heatable, evacuable sample cell attached to a gas delivery system and a gas chromatograph (GC). The catalyst was in the form of a thin, self-supported wafer (20 mg) pressed at 3 MPa. Gases were delivered through electronic mass flow controllers, and liquid methanol was metered using a syringe pump attached to a tubular heated vaporizer. A ten-way sampling valve at the exit of the reactor cell allowed injection of samples into a GC (Shimadzu 14B) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A carboxphere column was used in conjunction with the TCD to separate CO, CO₂, and H₂O, and a Porapak Q column was used with the FID to resolve CH₃OH, HCHO, and CH₃OCHO (methyl formate). The formaldehyde was converted to CH₄ in a methanizer prior to analysis. Calibration curves were determined for each gas by the injection of standards at different concentrations. All gas lines connecting the vaporizer, IR reactor cell, and GC were heated to prevent water condensation and formaldehyde polymerization.

Reaction kinetic measurements were carried out between 150 and 350 °C. Results are reported as turnover frequency values (TOF) based on the total methanol conversion and the catalyst oxygen uptake. The TOF is defined as the number of moles of products formed per second per mole of molybdenum atoms exposed. TOF_{HCHO} values refer to the selective oxidation of methanol to formaldehyde.

Experimental conditions were chosen so as to give low conversions (<10%) and resulted in differential operation. Absence of internal diffusion limitations was checked using the Weisz–Prater criterion.³⁶ It was confirmed that at the highest temperature used (350 °C) the quantity R^2r/C_sD_e had a value

TABLE 1: Flow Conditions for Kinetic and Infrared Measurements

experiment	total flow (μmol s ⁻¹)	CH ₃ OH (%)	O ₂ (%)	H ₂ O (%)	He (%)
(a) steady state kinetics (dry)	67	8.5	15	0	76
(b) steady state kinetics (wet)	67	5.0	15	5.0	75
(c) IR steady state measurements	66	5.2	15	0	80
(d) IR methanol adsorption	66	5.0	0	0	95
(e) IR methoxy oxidation	67	0	15	0	85

of 0.37, where R = thickness of wafer (cm), r = volumetric rate (mol/cm³ s), C_s = methanol concentration (mol/cm³), and D_e = diffusivity of methanol (cm²/s), and satisfied the criterion, $R^2r/C_sD_e < 1$.

The gas mixture used for reaction consisted of a blend of methanol and oxygen diluted in helium, with or without water vapor. For the steady state kinetic measurements without water, the total feed flow rate was 94 cm³ (NTP) min⁻¹ (67 μmol/s) and the CH₃OH/O₂/He composition was set as reported in entry (a) of Table 1. For steady state measurements with water vapor, the total feed flow rate was 95 cm³ (NTP) min⁻¹ (67 μmol/s) with the CH₃OH/O₂/H₂O/He composition as shown in entry (b) of Table 1. Before each experiment, the catalyst (MoO₃/SiO₂) was pretreated for 10 h at the highest reaction temperature (350 °C) in a flow of 50% O₂ diluted with He. After the pretreatment, only Si–OH groups and framework vibrations of the support were observed in the IR spectra.

Blank runs with the empty cell (no catalyst) using the conditions in entry (a) of Table 1 resulted in no detectable conversion of methanol up to 350 °C, demonstrating that no gas phase reactions occurred. Also, kinetic measurements on the plain support (same weight as the catalyst, 20 mg) showed very low activity up to 350 °C (less than 3% of methanol conversion) and produced mainly CO and CO₂.

The same apparatus as described above (Figure 1) was used for the in situ studies of surface processes by transmission Fourier transform infrared (FTIR) spectroscopy. The catalyst was in the form of a self-supported wafer (20 mg of MoO₃/SiO₂ or SiO₂). The IR windows were made of KBr, with a diameter of 15 mm and a length of 15 mm. The FTIR spectra were recorded at a resolution of 4 cm⁻¹ using a rapid scan spectrometer (Jasco, model 620) equipped with a TGS (triglycine sulfate) detector, with the measurements from 32 scans usually averaged.

The gaseous mixture used for the steady state IR experiments consisted of methanol and oxygen diluted in He and was fed at

a total flow rate of $94 \text{ cm}^3 \text{ (NTP) min}^{-1}$ ($66 \mu\text{mol s}^{-1}$) at the composition reported in entry (c) of Table 1. The temperature was varied between room temperature and 350°C .

Transient IR measurements were carried out in two manners. In a first set of experiments, methanol was dosed onto the catalyst at conditions reported in entry (d) of Table 1. In a second set of experiments, adsorbed methoxy groups were oxidized in an oxygen stream using the conditions reported in entry (e) of Table 1.

Quantification of the number of methoxy groups adsorbed on $\text{MoO}_3/\text{SiO}_2$ was carried out by determination of the extinction coefficient of its band at 2857 cm^{-1} . This band was chosen because it had the least overlap with other bands and provided the best signal for quantification using Beer–Lambert's Law. The measurements were carried out with the IR cell attached to a closed circulation system, using a self-supporting wafer of the 1 wt % $\text{MoO}_3/\text{SiO}_2$ (0.07 g) pretreated at 400°C in 100% O_2 . Blank runs using the apparatus with no catalyst confirmed that adsorption of methanol on the inner walls of the system was negligible. The measurements were carried out in successive steps by adsorbing on the catalyst small amounts of methanol diluted in He (0.57–5.8 mol %). The adsorbed amount was measured manometrically (by pressure drop). Small amounts of methanol diluted in helium (0.57 and 5.8 vol. %) were quantitatively adsorbed on the catalyst at 250°C in steps, and FTIR spectra were taken.

The extinction coefficient ($E_{\text{CH}_3\text{O}}$) represents the slope of the integrated intensity ($A_{\text{CH}_3\text{O}}$) versus adsorbed molar amount ($n_{\text{CH}_3\text{O}}$) curve and is based on the assumption that one adsorbed methanol molecule forms one methoxy molecule. The estimated coefficient was standardized by the weight of the catalyst (W_{cat}) and by the area of the catalyst exposed to the IR beam ($S_{\text{beam}}/S_{\text{cat}}$), as measured by an iris attachment.

$$A_{\text{CH}_3\text{O}} = \frac{n_{\text{OCH}_3}}{W_{\text{cat}}} \cdot \frac{S_{\text{beam}}}{S_{\text{cat}}} \cdot E_{\text{OCH}_3} \quad (2)$$

The extinction coefficient was estimated as 46 ± 0.25 (intensity·g/mmol). The results show a high degree of linearity (linear regression coefficient $r^2 = 0.9992$), indicating that the assumptions above were reasonable. The variation of the coefficient with temperature in a reasonably small range is expected to be negligible. Using the obtained extinction coefficient, quantitation and comparison of actual amounts of surface species became possible.

Results and Discussion

Catalytic Activity. Methanol conversion and product selectivities at steady state conditions were determined in the temperature range of 150 – 350°C . Two different feed conditions were used. In one, the feed gas mixture was a blend of methanol and oxygen in helium (entry a) in Table 1, and in the other, a small amount of water vapor was used (entry b) in Table 1. Comparison of these two conditions allows the influence of moisture on the reaction to be determined.

The reaction with water in the feed produced formaldehyde, CO, CO_2 , and water. Conversion of methanol, selectivities, and TOFs at 250 , 300 , and 350°C is presented in Table 2. Conversion of methanol and TOF values increased with increasing temperature. Selectivities to side products (CO and CO_2) were relatively high, and the results were reminiscent of steam reforming. The selectivities to formaldehyde and CO_2 decreased with increasing reaction temperature, while the selectivity to CO increased.

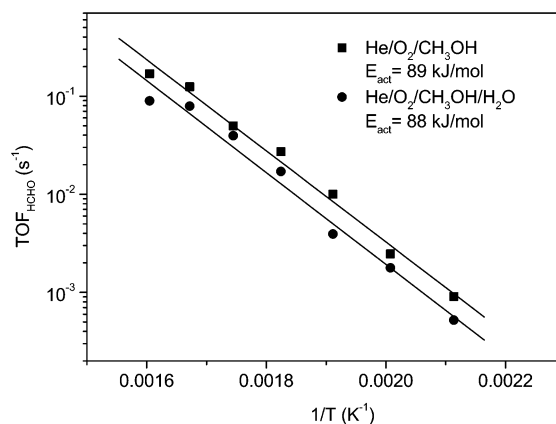


Figure 2. Arrhenius plots for selective TOF of methanol oxidation to formaldehyde over 1 wt % $\text{MoO}_3/\text{SiO}_2$ EH5. Plots for the reaction with and without additional water in the reaction gas mixture are shown, and corresponding activation energies are indicated.

TABLE 2: Methanol Oxidation for $\text{He}/\text{O}_2/\text{CH}_3\text{OH}/\text{H}_2\text{O}$ Reaction Mixture

temp ($^\circ\text{C}$)	conv. (%)	selectivity (%)			TOF (s^{-1})	TOF_{HCHO} (s^{-1})
		CO	CO_2	HCHO		
250	0.1	63	14	23	0.017	0.004
300	1.6	78	8	14	0.276	0.040
350	4.8	83	5	12	0.769	0.090

TABLE 3: Methanol Oxidation for $\text{He}/\text{O}_2/\text{CH}_3\text{OH}$ Reaction Mixture

temp ($^\circ\text{C}$)	conv. (%)	selectivity (%)			TOF (s^{-1})	TOF_{HCHO} (s^{-1})
		CO	CO_2	HCHO		
250	0.2	9	11	80	0.012	0.010
300	1.8	37	11	52	0.097	0.050
350	8.7	59	9	32	0.530	0.169

The reaction without additional water in the feed also produced formaldehyde, CO, CO_2 , and water. The conversion of methanol, selectivities, and TOFs at 250 , 300 , and 350°C is presented in Table 3. The trends for methanol conversion, TOF values, and selectivity values with increasing temperature were similar to the experiment with additional water. However, there were also some significant differences. The selectivity to formaldehyde was considerably higher for the reaction without water in the feed, while the overall TOF was lower for the run with additional water.

These results clearly demonstrate an inhibition effect by water on the production of formaldehyde. As will be discussed, the influence of water vapor on the steady state concentration of adsorbed methoxy groups is predicted by the proposed kinetic mechanism. As a result of the presence of water vapor, the selective oxidation of methanol is inhibited. This allows side reactions to occur that lead to the formation of CO and CO_2 . The rate of oxidation of methanol to formaldehyde can be expressed as

$$r = \frac{k'}{P_{\text{H}_2\text{O}}^n} \quad (3)$$

where k' is a proportionality constant and n = order.

The apparent activation energy for oxidation to formaldehyde is estimated from the Arrhenius plots of TOF_{HCHO} (Figure 2). The apparent activation energies are very similar for the reaction at dry and wet conditions. For the reaction without water in the

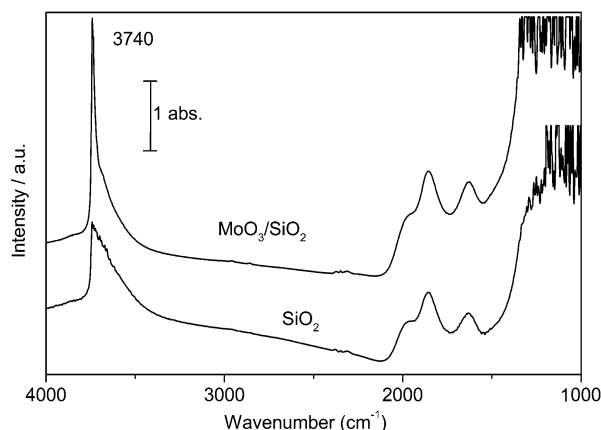


Figure 3. Background spectra of pretreated $\text{MoO}_3/\text{SiO}_2$ and SiO_2 at 250 °C. Given in units of absorbance.

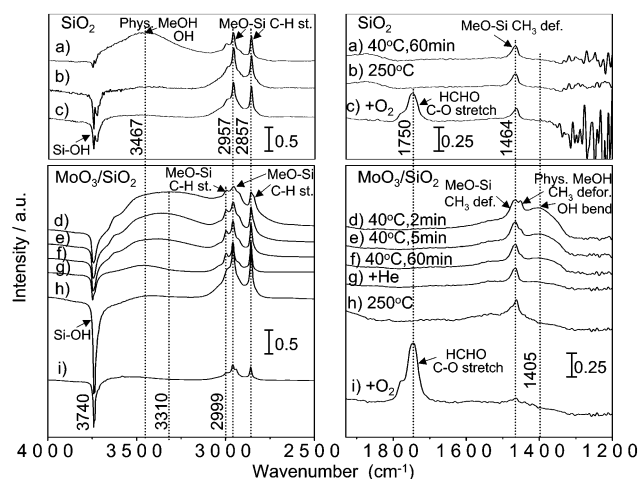


Figure 4. IR spectra of $\text{MoO}_3/\text{SiO}_2$ and SiO_2 : (a) methanol adsorption on SiO_2 for 60 min at 40 °C, (b) SiO_2 adsorbed by methoxide species at 250 °C (before O_2 flow), (c) oxidation of methoxide species on SiO_2 for 20 min at 250 °C (transient experiment), (d–f) time course of methanol adsorption on $\text{MoO}_3/\text{SiO}_2$ at 40 °C ((d) 2 min, (e) 5 min, and (f) 60 min), (g) $\text{MoO}_3/\text{SiO}_2$ adsorbed by methanol after He flow for 20 min at 40 °C, (h) $\text{MoO}_3/\text{SiO}_2$ fully adsorbed by methoxide species at 250 °C (before O_2 flow), and (i) oxidation of methoxide species on $\text{MoO}_3/\text{SiO}_2$ for 20 min at 250 °C (transient experiment).

feed, the activation energy is 88 kJ/mol and for that with water it is 89 kJ/mol. This suggests that a mechanism with the same rate-determining step applies irrespective of the presence of water.

FTIR Studies. Adsorption and surface reaction studies were carried out using in situ infrared spectroscopy. To determine the contribution of the support, measurements were carried out on both $\text{MoO}_3/\text{SiO}_2$ and the plain SiO_2 support. Before each experiment, the samples were pretreated at 350 °C in O_2/He flow until all surface impurities disappeared. Unfortunately, the support was highly absorbing in the region of framework vibrations ($<1250\text{ cm}^{-1}$) and no metal oxide vibrations were observed.

Typical background spectra of $\text{MoO}_3/\text{SiO}_2$ and SiO_2 at 250 °C are shown in Figure 3. Background spectra were taken of the samples with no surface-adsorbed species, and these were subtracted from subsequent spectra for clear observation of the signals of the surface species. On both $\text{MoO}_3/\text{SiO}_2$ and SiO_2 , a very intense band of isolated Si–OH groups was observed at 3740 cm^{-1} . This band had a low-frequency tail due to the presence of hydrogen-bonded OH groups. The shape of the Si–OH band was very much influenced by the temperature and

TABLE 4: Assignments of Bands

wavenumber (cm^{-1})	description	assignment	species
3740	intense	OH stretch	Si–OH
3467	very broad	OH stretch	$\text{CH}_3\text{OH}/\text{SiO}_2$
3310	very broad	OH stretch	$\text{CH}_3\text{OH}/\text{MoO}_3$
3037	broad	CH_3 d-stretch	CH_3OH
2999		CH_3 stretch	CH_3O
2957	very intense	CH_3 stretch	CH_3O
2857	very intense	CH_3 stretch	CH_3O
2840		CH_3 s-stretch	CH_3OH
1776		CO stretch	HCHO
1750		CO stretch	HCHO
1629		OH bend	H_2O
1465		CH_3 d-deform	CH_3O
1451	broad	CH_3 s-deform	CH_3OH
1405	broad	OH bend	CH_3OH

the duration of pretreatment. With treatment at high temperature and long times, the isolated OH band became sharper and more intense and the shoulder due to the hydrogen-bonded species diminished in intensity.

Methanol adsorption resulted in the consumption of OH groups on the silica surface and the formation of physisorbed methanol (molecularly adsorbed) and methoxide species (disociatively adsorbed). The FTIR spectra showing methanol adsorption and methoxide oxidation on SiO_2 and $\text{MoO}_3/\text{SiO}_2$ are presented in Figure 4. The methoxide species on silica were characterized by C–H stretching bands at 2999 and 2957 cm^{-1} and a combination mode involving the first overtone of bending at 2857 cm^{-1} . Molecular methanol on silica was identified by bands at 3467 and 1464 cm^{-1} . Methoxy groups on similar systems have been studied by many authors, and its bands have been previously assigned.^{5,10} The assignments are summarized in Table 4. The methoxide species are very stable in He up to approximately 300 °C, but in the presence of oxygen, they are readily oxidized and their concentration decreases.

Physisorbed methanol was only observable at low temperatures (under 100 °C) and was identified and distinguished from methoxide species by its OH stretching band. On SiO_2 , physisorbed methanol had a very broad OH band at around 3467 cm^{-1} (Figure 4a). The adsorption of CD_3OD resulted in a complete shift of the 3467 cm^{-1} band to 2620 cm^{-1} , indicating that the broad OH band belonged to CH_3OH and not to the hydrogen-bonded silanol groups. When the temperature was raised above 100 °C, the 3467 cm^{-1} band decreased and the methoxy bands increased (Figure 4b). This indicates that methoxy groups are formed from physisorbed methanol on SiO_2 .

On silica-supported molybdenum oxide, the main features were similar to those obtained with the SiO_2 support. Again, bands at 2999, 2957, 2857, and 1464 cm^{-1} were indicative of the presence of adsorbed methoxy groups. The exact correspondence of the vibrational frequencies to those measured on SiO_2 indicates that these species reside on the support.

However, there are differences. On silica-supported molybdenum oxide, two very broad bands were distinguished at 3467 and 3310 cm^{-1} . The band at 3310 cm^{-1} (spectra d–f in Figure 4) was not observed on SiO_2 and, therefore, was assigned to methanol molecularly adsorbed on supported molybdenum oxide. Because the OH band of this physisorbed methanol appears at a lower frequency than that of methanol on SiO_2 , the OH bond is surmised to weaken on supported molybdenum oxide. Indeed, this band is somewhat unstable and is only observed in the initial stages of adsorption. Later, during adsorption or upon raising the temperature, this band decreased in intensity and soon disappeared (spectra g,h in Figure 4), while the intensity of the accompanying methoxy bands increased.

This indicates that CH_3OH adsorbed on the molybdenum center is a precursor of the methoxide species on $\text{MoO}_3/\text{SiO}_2$. During methoxide species formation on $\text{MoO}_3/\text{SiO}_2$, the 3467 cm^{-1} band for methanol adsorbed on $\text{Si}-\text{OH}$ decreased as well, but this species is not likely to be the main contributor to methoxy group formation on the catalyst as its rate of formation on pure silica was low.

Another difference with the silica support is that bands at 1451 and 1405 cm^{-1} appeared only on $\text{MoO}_3/\text{SiO}_2$ and only at the very beginning of methanol adsorption at low temperature. During further adsorption and desorption, they quickly disappeared. Because of this behavior and the fact that they could only be seen when the concentration of methanol was very high, these bands are assigned to molecularly adsorbed methanol. The 1451 cm^{-1} band is assigned to a CH_3 deformation, and the 1405 cm^{-1} band is assigned to OH bending in physisorbed methanol. The 1464 cm^{-1} band is assigned to OH bending in physisorbed methanol. The 1464 cm^{-1} band was more stable than the 1451 cm^{-1} band. Moreover, during desorption in He, when surface methanol was converted into methoxide species, the 1464 cm^{-1} band increased in intensity. This behavior supports the assignment of the 1464 cm^{-1} band to the methoxy groups. Bands at 2920 and 2840 cm^{-1} behaved in exactly the same manner as the 1451 cm^{-1} band, suggesting that these also belong to physisorbed methanol. These bands are associated with C–H stretches in physisorbed methanol. Again, the assignment of the bands is tabulated in Table 4.

During oxidation of preadsorbed methoxy groups in the absence of methanol in the gas phase above $200\text{ }^\circ\text{C}$ (spectra c,i in Figure 4), two bands appeared at 1776 and 1750 cm^{-1} . As the methoxy groups were oxidized, these bands at first increased in intensity and then decreased. It is proposed that they are bands due to $\text{C}=\text{O}$ stretching in formaldehyde physisorbed on silica. On bare silica, methoxide species were oxidized very slowly below $300\text{ }^\circ\text{C}$, and correspondingly, only a small amount of formaldehyde was observed, while the reaction proceeded more rapidly on the silica-supported molybdenum oxide.

One particular surprising result is the qualitative similarity between the pretreated and the covered surfaces of SiO_2 and $\text{MoO}_3/\text{SiO}_2$. No separate bands assignable to methoxide species or formaldehyde residing on the molybdenum oxide could be distinguished. The methoxide species observed by FTIR were mostly located on the SiO_2 support. If present on Mo, the species would have to have IR bands that were less intense than on SiO_2 but with similar vibrational frequencies. Nevertheless, as will be discussed later, the molybdenum oxide species has a vital function: it acts like a porthole for the entrance and departure of adsorbed species to and from the SiO_2 surface.

Quantitative Analysis of FTIR Studies. *Amounts of Surface Species.* The quantitation of the surface species by IR absorption spectroscopy provides valuable information, but its accuracy must be assessed carefully. The absorption process generally follows the Beer–Lambert equation, which was originally proposed for homogeneous systems. The practical application for heterogeneous systems is complicated by various factors, of which the most important are the specific surface area, the thickness of the sample, the dehydration level, and the scattering properties of the adsorbent. As a result, the IR spectroscopic response to the amount of adsorbed species (i.e., adsorption coefficient) is largely nonlinear when affected by these factors. Morterra, Magnacca, and Bolis²⁶ extensively researched the use of molar absorption coefficients for methanol adsorption on silica. They concluded that the analytical data yields only information specific to a particular type of sample; therefore, the values of apparent absorption coefficient cannot be trans-

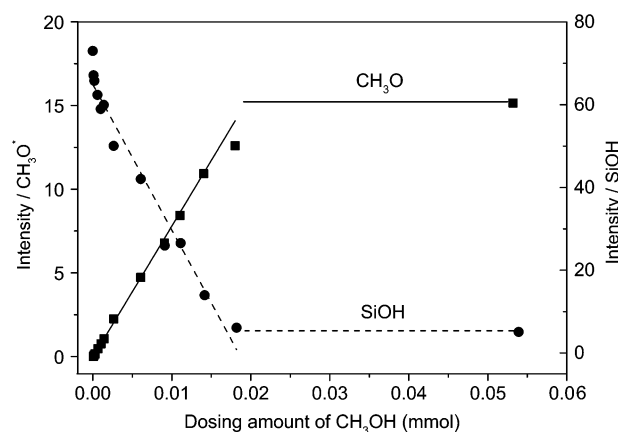


Figure 5. Estimation of extinction coefficient of methoxide on $\text{MoO}_3/\text{SiO}_2$: change in the intensity of 3740 cm^{-1} ($\text{Si}-\text{OH}$) and 2857 cm^{-1} (CH_3O^*) bands during methanol dosing. Intensity is given as the integrated intensity of the corresponding band.

ferred from one system to another. For the justifiable use of absorption coefficients for the quantification of the amount of surface methoxy groups, it is necessary to use samples of comparable scattering properties, surface area, and weight.²⁶ This was done, and the detailed procedures were described in the Experimental Section.

The integrated intensities of the key bands of silanol (3740 cm^{-1}) and methoxy (2857 cm^{-1}) groups are plotted vs the total amount of methanol introduced at $250\text{ }^\circ\text{C}$ (Figure 5). At this temperature, methanol adsorbs preferentially as methoxide species. The IR spectra showed that physisorbed methanol or formaldehyde were not present at these conditions even when the amount of methoxide species increased. The decrease in the silanol band and the increase in the methoxide band show a linear relation with respect to the amount of dosed methanol up to 0.02 mmol . Quantification of the silanol band was difficult, because it was partially overlapped by the broad hydrogen-bonded silanol band, and there is more error in these measurements. When the amount of introduced methanol increased, the amount of surface methoxide species reached saturation and the signal–concentration curve leveled off. This is because methanol introduced beyond the saturation point adsorbs as physisorbed methanol or remains in the gas phase. The formation of physisorbed methanol at this stage was also confirmed by the IR spectra.

At the saturation point, almost all of the SiOH groups are consumed by the methoxy groups, because CH_3O^* groups replace silanol $^*\text{OH}$ groups in a ratio of 1:1. Therefore, it is possible to estimate the number of silanol $^*\text{OH}$ groups by comparing the intensity of the 2857 cm^{-1} band (CH_3O^*) to the 3740 cm^{-1} band ($\text{Si}-\text{OH}$). The amount of surface methoxy groups at the saturation point is estimated to be 0.39 mmol/g , while the amount of silanol groups on the pretreated sample is 0.41 mmol/g .

The quantity of surface Mo atoms is calculated from the loading amount ($1\text{ wt } \%$) as 0.070 mmol Mo/g . The quantity of surface Mo atoms can be also calculated from the oxygen uptake value, which was measured as $37\text{ } \mu\text{mol/g}$. Presuming a stoichiometry of one oxygen atom per surface metal atom, the Mo amount is calculated as 0.074 mmol Mo/g , which is in good agreement with the previous value obtained from the loading amount. The metal dispersion for $\text{MoO}_3/\text{SiO}_2$ is, therefore, close to 100% and is consistent with results of our previous characterization study,³⁴ which indicated that the Mo is in the form of atomically dispersed tetrahedral species.

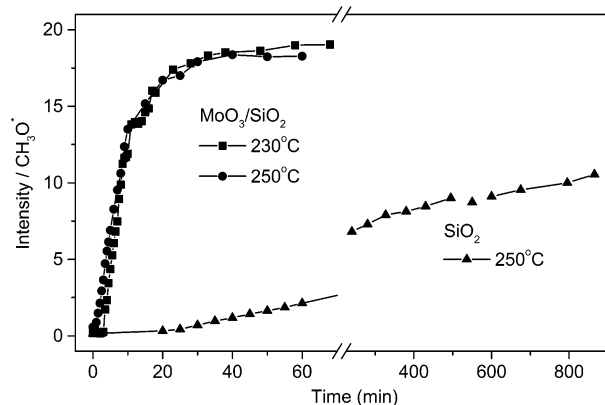


Figure 6. Time course of formation of methoxide species from methanol adsorption on $\text{MoO}_3/\text{SiO}_2$ and SiO_2 .

Comparison of the number of methoxy groups (0.39 mmol/g) and silanol groups (0.41 mmol/g) to the number of surface molybdenum atoms (0.070 mmol/g) clearly indicates that the methoxy groups are located on the silica support. At the saturation point, the ratio of methoxy groups to molybdenum atoms equals 5.6. Another way to support this interpretation is to consider the behavior of the OH stretching vibration band on silica. As the amount of adsorbed methoxide increases, the silica OH groups are consumed and the OH band proportionally decreases. This indicates that the methoxy groups are present on silica as $\text{Si}-\text{OCH}_3$. Thus, the methoxy groups are first formed on the molybdenum center and then undergo spillover onto the silica support.

Formation of Methoxy Groups. The time course of methoxide formation from methanol adsorption was measured at 230 and 250 °C. In this temperature range, no physisorbed methanol was observed. Although OH groups should have been formed as a result of methoxy group formation, in fact, silica OH groups were consumed. This can be explained by a rapid reaction of these OH groups to form water, which immediately desorbs. This explanation was confirmed by the absence of the band of the bending mode of water ($1650\text{--}1600\text{ cm}^{-1}$) in the spectrum and by GC analysis of the gas mixture leaving the IR cell. The water formation step has to occur in close association with the adsorption process, for otherwise the OH formed could migrate on to the SiO_2 support. How this might occur will be explained in the section describing the overall mechanistic steps.

The formation rate of methoxide on $\text{MoO}_3/\text{SiO}_2$ was initially rapid and then slowed as the surface reached saturation as shown in Figure 6. The formation rate was almost the same regardless of the temperature, which means that the activation energy is negligible (Figure 6). The formation rate of methoxide was significantly lower on bare silica at 250 °C (Figure 6). This indicates that the adsorption of methanol is significantly promoted by the presence of supported molybdenum oxide on the surface as noted earlier. This is one of the significant conclusions of this study and will be discussed further later on.

Methoxide Oxidation and Aldehyde Formation. Upon exposure to an O_2/He flow (entry e in Table 1), the preadsorbed methoxy groups were oxidized to form formaldehyde. The time sequence of the IR spectra during methoxy group oxidation at 250 °C is shown in Figure 7. The figure shows that OH groups are recovered (left spectra) and methoxy bands decrease (middle spectra), and this is accompanied by the appearance and growth of formaldehyde bands (right spectra).

The rates of oxidation of the methoxy groups for different temperatures are shown in Figure 8, where two distinguishable stages are observed. In the beginning stage, the oxidation rate

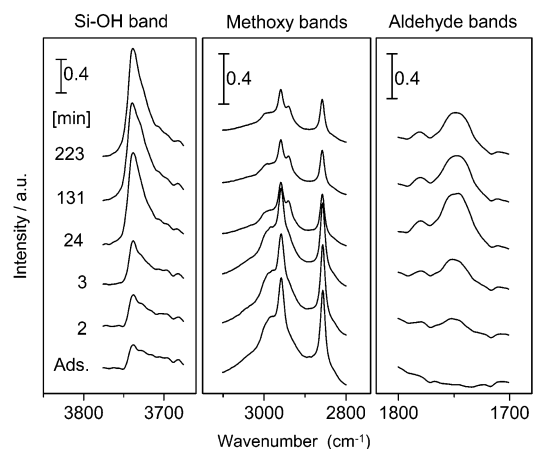


Figure 7. Spectra of $\text{MoO}_3/\text{SiO}_2$ during oxidation of preadsorbed methoxide species (transient experiment) at 250 °C; time from the beginning of oxidation is indicated.

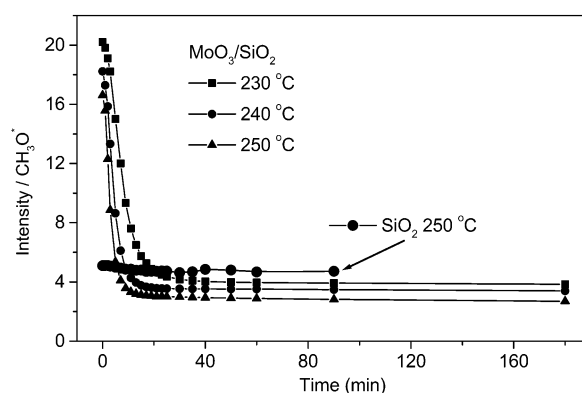


Figure 8. Quantification of methoxide species during oxidation on $\text{MoO}_3/\text{SiO}_2$ and SiO_2 at 230, 240, and 250 °C.

was rapid, while in the subsequent stage it was very slow. In this second stage, a certain quantity of methoxy groups remained on the surface. It is also shown in Figure 8 that only the second type of process (slow oxidation) occurs on plain silica. This type of dynamic behavior suggests that there are two types of methoxy groups on silica-supported molybdenum oxide. The highly reactive methoxide species are only observed when there is Mo on the surface and are probably present in the vicinity of the Mo centers. The less reactive methoxy groups persist for a prolonged period and are only spectators. The portion of the slowly oxidizing methoxy groups amounts to approximately 16–20% of the total amount for reaction at 230–250 °C. A simple calculation yields that the amounts of quickly disappearing methoxide species and slowly disappearing methoxide species are 4.5 and 1.1 species, respectively, per 1 molybdenum oxide species at 250 °C. The identification of these two types of species is probably the most significant finding of this study. The slowly reacting species can be considered as spectators on the support. The rapidly reacting species are active participants in the reaction but are not directly adsorbed on the Mo centers. They are formed on the Mo complexes, then undergo spillover to the silica surface, but can migrate back to the Mo centers to be oxidized. This is the first time such species have been identified and quantitated in a catalytic system.

An interesting result was obtained from the oxidation of methoxide species at partial coverage of the surface. By controlling the time of adsorption, a fresh $\text{MoO}_3/\text{SiO}_2$ surface was covered by methoxide species in an amount corresponding to the quantity of spectator methoxide species. It was found that these methoxide species remained stable in a flow of

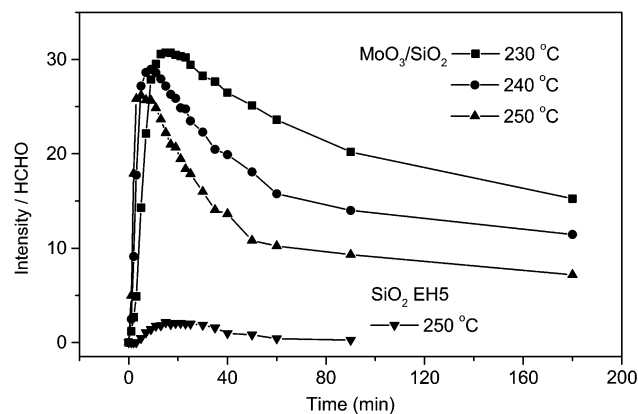


Figure 9. Quantification of aldehyde species formed during methoxide oxidation on $\text{MoO}_3/\text{SiO}_2$ and SiO_2 at 230, 240, and 250 °C.

oxygen, which indicates that the spectator methoxide species are formed first before the formation of active species. The rate of formation of methoxide species is faster in the beginning (Figure 6), which leads to the conclusion that spectator methoxide species are formed faster than the active methoxide species on $\text{MoO}_3/\text{SiO}_2$. The spectator species probably reside in a limited number of sites, possibly defect sites, which impart to them their particular stability.

As described in the section on the methoxide species, the presence of molybdenum oxide significantly accelerates their formation. At 250 °C, the surface of $\text{MoO}_3/\text{SiO}_2$ becomes fully saturated by methoxide species within 40 min. In comparison, the surface of SiO_2 at 250 °C is only occupied to an extent of 58% of the maximum amount even after 14 h and saturation is not reached. It is confirmed that at this point there is formed a small amount of active methoxide species; i.e., species that can be readily oxidized to formaldehyde in O_2 flow at 250 °C (spectra c in Figure 4). However, it must be noted that adsorption for 14 h in $\text{He}/\text{CH}_3\text{OH}$ flow is a rather extreme situation that is very different from the conditions of steady state reaction. In fact, under typical reaction conditions (steady state $\text{He}/\text{CH}_3\text{OH}/\text{O}_2$ flow), no active methoxide species are formed on SiO_2 ; that is, all of them are stable in oxygen flow at 250 °C. At that point, the coverage in the methoxide species is about 39%. Also, no active methoxide species are observed from adsorption of methanol on SiO_2 for a comparable time as on $\text{MoO}_3/\text{SiO}_2$ (40 min at 250 °C).

To determine the rate constant of methoxy group oxidation, methanol was adsorbed to the saturation point on pretreated $\text{MoO}_3/\text{SiO}_2$ and SiO_2 , and then, the methanol feed was stopped and switched to He to remove the gas phase methanol from the cell. The methoxy-covered surface was exposed to an O_2/He flow, and spectra were collected as a function of time. The entire procedure was repeated at 230, 235, 240, 245, and 250 °C. The methoxide species were oxidized to formaldehyde while the Si-OH groups were recovered. The time course of the integrated peak intensity of the formaldehyde band (1750 cm^{-1}) is shown in Figure 9. At first, the intensity of the formaldehyde peak increased, but after a certain time, it decreased. Assuming that the oxidation of the methoxide species is the rate-determining step, the process can be described as a first-order reaction:

$$r = -\frac{d(*\text{OCH}_3)}{dt} = k''(*\text{OCH}_3) \quad (4)$$

where $(*\text{OCH}_3)$ represents the concentration of adsorbed methoxide species.

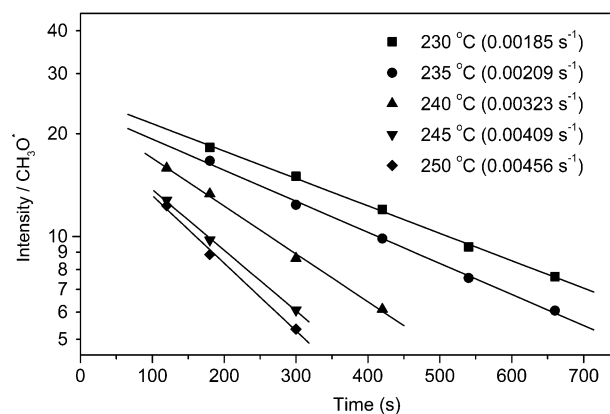


Figure 10. Estimation of rate constants of methoxide oxidation on $\text{MoO}_3/\text{SiO}_2$ at 230, 235, 240, 245, and 250 °C.

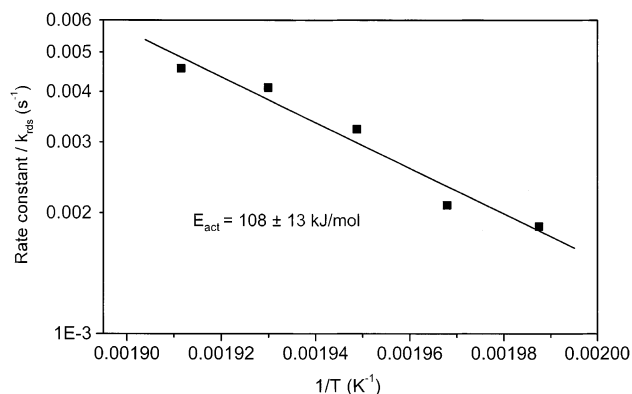


Figure 11. Arrhenius plot for rate constants of methoxide oxidation on $\text{MoO}_3/\text{SiO}_2$.

The rate constant (k'') then can be determined from the slope of a plot of $-\ln(*\text{OCH}_3)$ vs time (Figure 10). The activation energy is estimated from the variation of the rate constant with temperature (Figure 11). The rate constant is found to increase with reaction temperature from 0.00185 s^{-1} (230 °C) to 0.00456 s^{-1} (250 °C). Linear regression coefficients for these fits are in the range of 0.9976–0.9995. The temperature dependence of the reaction rate constant leads to the Arrhenius expression (Figure 11): $k = 3.35 \times 10^8 \exp(-E_{\text{act}}/RT)$ where $E_{\text{act}} = 108 \pm 13.1\text{ kJ/mol}$.

It was found that the formation of methoxide species led to a decrease in the signal from adsorbed formaldehyde. When the methanol flow was started, the surface aldehyde groups on the surface immediately disappeared, indicating that the methoxy groups were replacing the adsorbed formaldehyde species. During steady state experiments, because methanol is always present in the gas phase, adsorbed formaldehyde was not observable.

The oxidation rate of the methoxide species formed from deuterated methanol (CD_3O) was also studied. Deuterated methanol (CD_3OD) was adsorbed on freshly pretreated $\text{MoO}_3/\text{SiO}_2$ and SiO_2 and then exposed to an O_2/He flow while the spectra were collected as a function of time. The procedure was repeated at 230, 240, and 250 °C, and results analogous to the oxidation of preadsorbed CH_3O^* species were obtained. The CD_3O^* species were oxidized to deuterated formaldehyde (DCDO) while Si-OD species were recovered. Quantitation of the deuterated methoxide species was based on its 2080 cm^{-1} band. The extinction coefficient of the 2080 cm^{-1} band was not determined. However, it could be estimated based on the fact that the intensity of Si-OH/Si-OD groups in a fully saturated sample decreased to almost zero for both CH_3O^* and

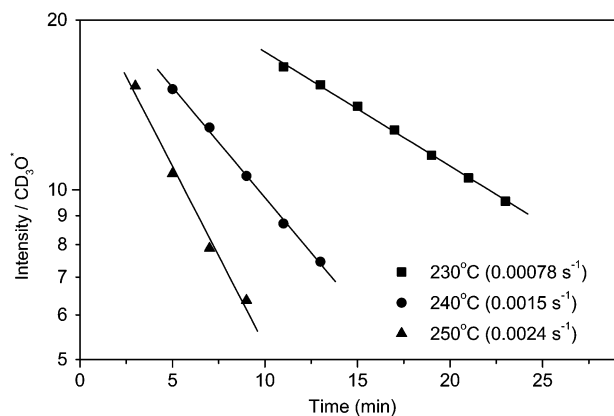


Figure 12. Estimation of rate constants of deuterated methoxide oxidation on MoO₃/SiO₂ at 230, 240, and 250 °C.

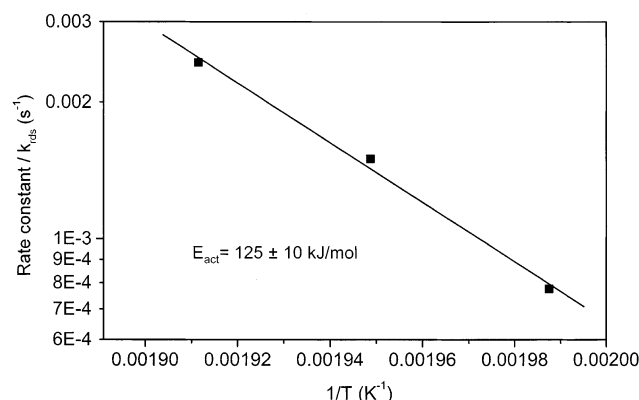


Figure 13. Arrhenius plot for rate constants of deuterated methoxide oxidation on MoO₃/SiO₂.

CD₃O* species. Therefore, at the saturation point, all OH groups were exchanged by methoxide species and the extinction coefficient for the 2080 cm⁻¹ band could be derived from the extinction coefficient for the 2857 cm⁻¹ band. The rate constant was found to increase with reaction temperature from 0.00078 s⁻¹ at 230 °C to 0.0024 s⁻¹ at 250 °C (Figure 12). The rate constant is given by $8.39 \times 10^9 \exp(-E_{\text{act}}/RT)$, where the activation energy is estimated as $E_{\text{act}} = 125 \pm 9.5$ kJ/mol (Figure 13).

Tatibouët and Lauron-Pernot³⁷ described transient isotopic experiments during methanol and deuterated methanol oxidation over an unsupported V₂O₅ catalyst. In a switch from CH₃OH to CD₃OD, the methanol species in the gas phase were replaced rapidly, whereas on the surface of the catalyst, the initially adsorbed species were still present. Because no isotopic effect was found by using CH₃OD instead of CH₃OH, it was concluded that the main isotopic effect comes from C–H bond breaking, and this reaction was proposed as the rate-determining step. This is in agreement with the results for the methoxy group oxidation over MoO₃/SiO₂ reported in this paper. The rate constants for normal and deuterated methoxide oxidation over MoO₃/SiO₂ are compared in Table 5. The kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) is found to decrease with temperature and confirms that the C–H cleavage is the rate-determining step during methanol oxidation.

Effect of Partial Pressure of Oxygen. The effect of the partial pressure of oxygen was studied on the MoO₃/SiO₂ catalyst. The surface was first saturated with methoxy groups at atmospheric pressure and 250 °C. Then, the methoxy groups were exposed to mixtures of O₂/He at partial pressures of oxygen varying from 6 to 30 kPa, and the decline of the methoxy groups concentration was used as before to find the rate of reaction. It was found

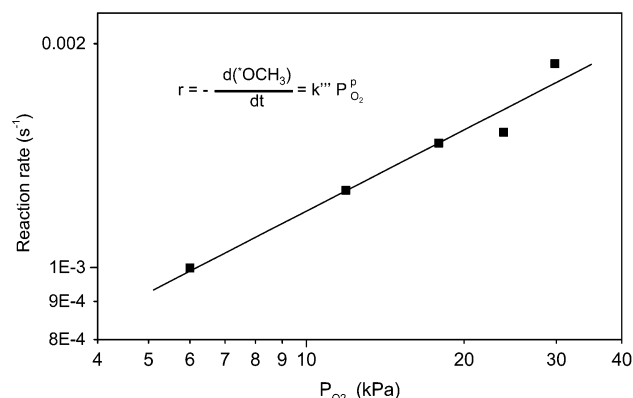


Figure 14. Plot of the reaction rate vs partial pressure of O₂ (MoO₃/SiO₂ at 250 °C).

TABLE 5: Comparison of the Rate Constants of CH₃O and CD₃O Oxidation on Kinetic Isotope Effect at Various Temperatures

temp (°C)	CH ₃ O oxidation	CD ₃ O oxidation	$k_{\text{H}}/k_{\text{D}}$
230	0.00185 s ⁻¹	0.00078 s ⁻¹	2.37
235	0.00209 s ⁻¹		
240	0.00323 s ⁻¹	0.0015 s ⁻¹	2.15
245	0.00409 s ⁻¹		
250	0.00456 s ⁻¹	0.0024 s ⁻¹	1.9
act energy	108 kJ/mol	124 kJ/mol	

that the rate was proportional to a fractional order in oxygen partial pressure. The plot of partial pressure of O₂ vs the rate (both in logarithmic scale) leads to the value of the exponent p from eq 5 (Figure 14). The value of p is estimated as 0.36.

$$r = -\frac{d(*\text{OCH}_3)}{dt} = k''' P_{\text{O}_2}^p \quad (5)$$

If no oxygen was present in the gas phase, the reaction stopped and the methoxide species was stable. These results are consistent with a rapid cleavage of molecular oxygen to form adsorbed atomic oxygen, which is proposed to be the active oxygen species in the reaction. These results rule out the direct reaction of molecular O₂ with the methoxide species.

Effect of Temperature. The effect of temperature on the amount of methoxide species during steady state adsorption was studied on the MoO₃/SiO₂ and SiO₂ catalysts. With increasing temperature, the equilibrium surface coverage of methoxide species decreased (ΔH_{ads} is negative). The coverage by methoxide species on the plain support at low temperature (150 °C) was significantly lower as compared to that on the supported molybdenum oxide. However, this difference became smaller with increasing temperature (Figure 15).

Effect of Partial Pressure of Methanol. The effect of the methanol concentration upon the steady state reaction rate at 250 °C and atmospheric pressure was investigated in a series of experiments where the partial pressure of methanol in He was varied from 1.0 to 9.1 kPa. The coverage of the surface by methoxy groups as given by the FTIR intensity increased with increasing partial pressure and leveled off as the surface reached the saturation point. A plot of the FTIR intensity vs the logarithm of the partial pressure of methanol in the gas phase is linear (Figure 16). Taking the coverage, $\theta_{*\text{OCH}_3}$, to be proportional to the intensity, the adsorption isotherm corresponds to the Temkin eq 6

$$\theta_{*\text{OCH}_3} = \text{const} \cdot \ln(P_{\text{CH}_3\text{OH}}) \quad (6)$$

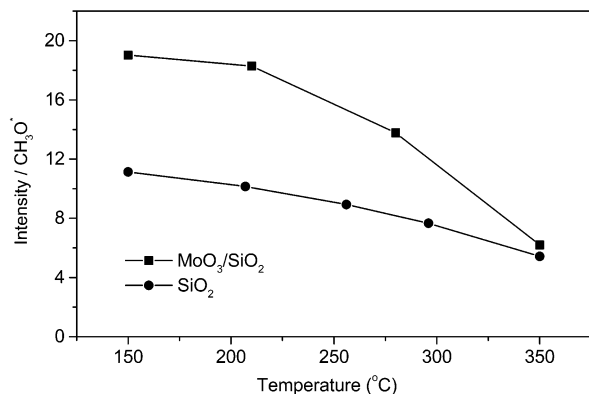


Figure 15. Steady state concentrations of methoxide species during methanol adsorption on $\text{MoO}_3/\text{SiO}_2$ and SiO_2 at various temperatures.

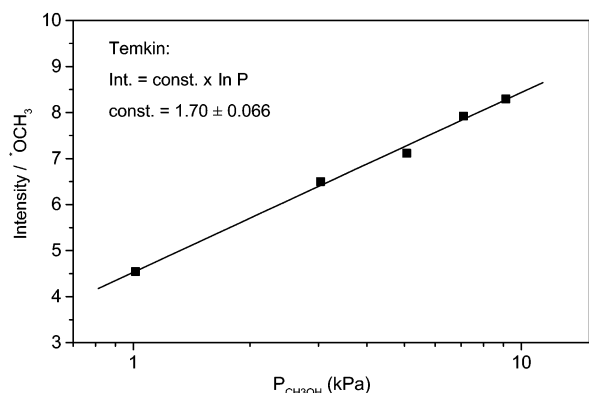


Figure 16. Steady state concentrations of methoxide species formed on the surface of $\text{MoO}_3/\text{SiO}_2$ at various methanol partial pressures; adsorption isotherm at 250 °C.

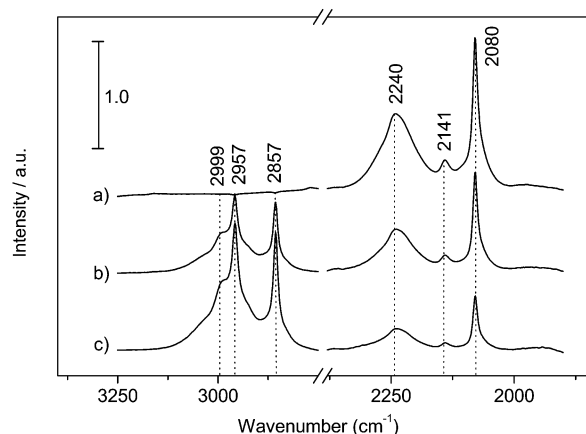


Figure 17. Spectra during methanol isotopic exchange on $\text{MoO}_3/\text{SiO}_2$. (a) Surface with deuterated methoxide species and (b,c) deuterated methoxide species (CD_3O^*) partially exchanged by methoxide species (CH_3O^*).

Isotopic Exchange of CH_3O and CD_3O . The nature of the occupation of the methoxy sites was investigated by the sequential and simultaneous adsorption of deuterium-labeled and -unlabeled methanol. In a first experiment, deuterated methanol (CD_3OD) was adsorbed on freshly pretreated $\text{MoO}_3/\text{SiO}_2$ to form CD_3O^* species. After it reached the saturation point, the feed was switched to unlabeled CH_3OH and the formation of CH_3O^* species was observed as a function of time. Figure 17 shows the $\text{MoO}_3/\text{SiO}_2$ at the point where its surface is saturated with deuterated methoxy groups (a) and then after flowing CH_3OH for 20 min (b) and 180 min (c). In spectra b and c, CD_3O^* is partially exchanged by CH_3O^* and the signatures of both

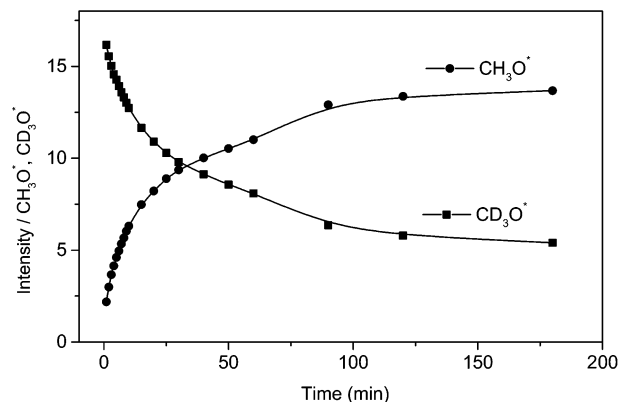


Figure 18. Methanol isotopic exchange experiment; adsorption of methanol on $\text{MoO}_3/\text{SiO}_2$ surface covered with deuterated methoxide species (230 °C).

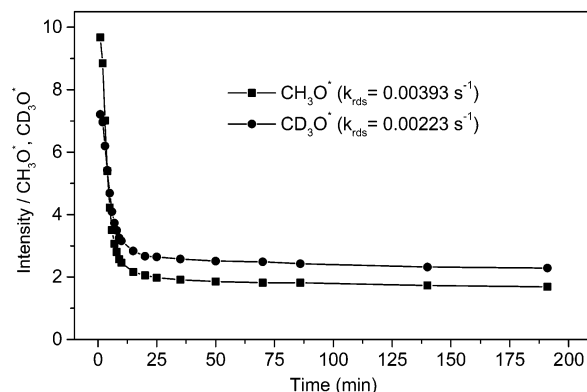


Figure 19. Isotopic exchange experiment; oxidation of CH_3O^* and CD_3O^* coadsorbed on $\text{MoO}_3/\text{SiO}_2$ (250 °C); oxidation rate constants are indicated.

species are seen. This procedure was repeated at 230, 240, and 250 °C. In the beginning, the CH_3O^* formation was rapid, but then with increasing saturation of the surface, it slowed (Figure 18). After 180 min, there were still substantial amounts of methoxy groups, which were not exchanged. The quantity was approximately the same as that of the spectator species observed before (1.1 methoxy groups per 1 Mo atom). The conclusion is that all active methoxy groups are exchanged, while the spectator species remain unperturbed. In the experimental temperature range (230–250 °C), the rate of exchange between species is nearly independent of temperature, so the activation energy is small.

To check the possibility of migration of methoxide species along the surface of $\text{MoO}_3/\text{SiO}_2$, a second experiment was conducted. The surface was saturated with normal methoxide species (CH_3O^*), and then, approximately half of the amount was replaced by deuterated species (CD_3O^*). After exposure to oxygen (at 250 °C), a decrease in CH_3O^* and CD_3O^* species was observed with time (Figure 19), indicating that both CH_3O^* and CD_3O^* are oxidized from the start. The oxidation rates were almost precisely the same as the rates of the individual CH_3O^* and CD_3O^* oxidations. These facts indicate that a homogeneous mixture of active methoxides is formed that freely intermingles and thus has mobility on the surface of the catalyst. If the active methoxide species did not migrate, CD_3O^* should have been oxidized first and then CH_3O^* , which did not happen.

Because the methoxide species are formed from the original hydroxyl species, it is likely that these are also very mobile on the surface. This accounts for the migration of the methoxide species from the Mo centers to the silica surface. The mobile

OH species on the SiO₂ support approach the Mo centers and undergo exchange with Mo–OCH₃ groups to form Si*–OCH₃ and Mo*OH species. The methoxide species then moves away on the silica surface. The mobility of the hydroxyl and methoxy groups occurs by hopping from site to site, likely without movement of the oxygen.

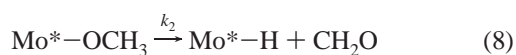
From the first experiment, it would be expected that the inactive spectator methoxide species do not migrate. This is likely to be the case. However, in the second experiment, it was found that the spectator species became a mixture of CH₃O* and CD₃O* species. The difference is that in the first experiment the surface was saturated at all times, so the mobility of species was limited and restricted to the reactive species. In the second experiment, the coverage was lower and exchange occurred between the two methoxide types.

Mechanism

The previous sections presented the results of various measurements carried out to probe the effects of temperature and of the partial pressures of water vapor, oxygen, and methanol on the rates of reaction and concentrations of adsorbed intermediates. The results give the following picture for the reaction. Methanol adsorbs as physisorbed methanol and methoxide species. Volatile physisorbed methanol is only observed at low temperatures and readily desorbs in a vacuum or helium flow. Methanol adsorbs dissociatively to form methoxy groups, and this occurs on Mo centers, as SiO₂ by itself is inactive. The methoxy groups go on to produce formaldehyde, which desorbs. There is no increase in hydroxide groups upon methanol adsorption, so any OH groups formed likely go on to produce water, which immediately desorbs.

Oyama and Zhang³⁸ proposed that ethoxy group formation occurs preferentially through a terminal Mo–oxygen bond (Mo=O). This was deduced from the decreased intensity of the corresponding Raman band during ethanol adsorption. The oxidation of the ethoxide species also occurs on the supported molybdenum oxide or in its vicinity and involves a C–H bond cleavage step, which is rate-determining. Because of the negligible activity of SiO₂, the activation of oxygen is also considered to take place on the supported molybdenum oxide. The formaldehyde that is formed interacts weakly with the surface and is only observable as a physisorbed species when methanol is absent from the gas phase. In the presence of methanol, it quickly desorbs. Further oxidation produces CO, CO₂, and water.

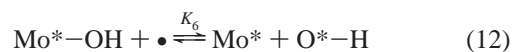
The results obtained can be rationalized in terms of a mechanism that describes the elementary steps of the reaction. The mechanism follows closely that proposed by Holstein and Machiels.¹⁵ Two types of sites are taken to be present on the molybdenum catalyst, sites associated with the molybdenum center itself, Mo*, and sites associated with an oxygen atom attached to the molybdenum, O*.



These four steps form the basic elements of the mechanism. Methanol is dissociatively adsorbed on a Mo center to form an

adsorbed methoxide species and an OH group. The methoxide species undergoes a rate-determining hydride elimination to produce formaldehyde. Subsequent steps are fast. First, the hydride combines with the OH group to release water, and then, molecular oxygen reoxidizes the reduced site. As discussed by Holstein and Machiels, the hydride is not important for the derivation of the kinetic expression. The hydrogen could just as well be placed on another oxygen atom, O*. However, work by ourselves³⁴ does indicate that the hydride is formed, and so, the step is written as depicted. From the results of the present study, it is not possible to determine whether the terminal (Mo=O) or the bridging (Mo–O–Si) bond is involved in the oxidation.

The steps above need to be supplemented by two other reactions. One describes the normal adsorption of water, which occurs analogously to step 1 for methanol adsorption. The other describes a mass balance between OH groups.



With these expressions, Holstein and Machiels derived the following rate expression:

$$r = k_2 \frac{K_1 K_4^{1/4} P_{\text{CH}_3\text{OH}} P_{\text{O}_2}^{1/4}}{(K_5 K_6)^{1/2} P_{\text{H}_2\text{O}}^{1/2}} \quad (13)$$

The oxygen partial pressure dependency is one-fourth rather than one-half because of an interplay with the adsorption of water (step 5), which consumes an adsorbed oxygen species, O*. In the absence of water, the equation becomes dependent on $(P_{\text{O}_2})^{1/2}$.¹⁵ Using a similar scheme, Zhang, Oyama, and Holstein³⁹ obtained an alternative expression, which takes into consideration the nonuniformity of the Mo sites:

$$r = kK \frac{P_{\text{CH}_3\text{OH}}^{1-m} P_{\text{O}_2}^{(1-m)/4}}{P_{\text{H}_2\text{O}}^{(1-m)/2}} \quad (14)$$

$$k = \frac{\pi}{\sin(\pi m)} \frac{\gamma}{\exp(\gamma f - 1)} k_2^0 \quad (15)$$

$$K = K_1^{1-m} K_4^{(1-m)/4} K_5^{(1-m)/2} \quad (16)$$

where m , γ , and f are parameters from nonuniform surface theory and k_2^0 is the rate constant of step 2 at zero coverage. This last treatment describes the main features of the mechanism well. The rate depends on the methanol pressure to an exponent somewhat less than 1, on oxygen to a small positive exponent, and on water to a small negative exponent. Furthermore, the rate of decomposition of the methoxide species is first-order in its concentration, in agreement with eq 4.

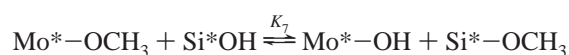
It can be seen that the leading terms in the two kinetic expressions (eqs 13 and 14) are essentially the product of the rate constant for the rate-determining step and a combination of equilibrium constants as described in eq 1. The combination of equilibrium constants represents the adsorption of methanol but modulated by the adsorption of oxygen and water, so it has a more complex meaning than given in eq 1. The expression gives rise to the following relation, where ΔH_{ads} is an effective heat of adsorption of methanol:

$$E_{\text{app}} = E_{\text{rds}} + \Delta H_{\text{ads}} \quad (17)$$

This was the approach taken by Burcham, Badlani, and Wachs,¹ who found ΔH_{ads} values of -28 kJ/mol for $\text{MoO}_3/\text{Al}_2\text{O}_3$ and -22 kJ/mol for $\text{MoO}_3/\text{TiO}_2$ and E_{rds} values of 99 kJ/mol for $\text{MoO}_3/\text{Al}_2\text{O}_3$ and 88 kJ/mol for $\text{MoO}_3/\text{TiO}_2$.

In the present work, the steady state reaction data give an apparent activation energy value of $E_{\text{app}} = 89$ kJ/mol, and the decomposition of the surface methoxy intermediate gives an activation energy for the rate-determining step of $E_{\text{rds}} = 108$ kJ/mol. From these values, it is possible to calculate a heat of adsorption of $\Delta H_{\text{ads}} = -19$ kJ/mol. Thus, the present results are in good agreement with those obtained earlier.

A critical difference between previous results and the findings of this study is the observation that the methoxide species that are formed on molybdenum migrate to silica and reversibly displace the silica OH groups. Thus, the following step needs to be added to the overall description:



As mentioned earlier, the surface species on the silica are mobile. Two kinds of methoxide species are distinguishable by their behavior: spectators and participants. Both are located on the silica support and are formed by spillover from the Mo center. Spectator methoxides are formed first (about 1.1 methoxides per Mo), and once they find their adsorption sites, they do not migrate. The participant methoxide species (about 5.5 methoxides per Mo) are mobile on the surface of the catalyst. Upon exposure to oxygen below 300 °C, the immobile spectators remain stable, while the active methoxy groups are readily oxidized to formaldehyde. There is a dynamic equilibrium between the participant methoxide species on the silica and the molybdenum. Thus, a methoxy group initially formed on Mo can spill over to the silica surface, exchange, and return to the Mo site to react. Reaction on the Mo is a slow step, which results in a reduced Mo center. Reoxidation by molecular oxygen must occur before another methanol from the gas phase can be adsorbed. A simplified scheme of the reaction mechanism is shown in Figure 20.

The process of migration of the methoxide species formed on the molybdenum center to the silica sites is an example of spillover. The inverse process of migration back to the molybdenum center is a case of the porthole effect,⁴⁰ except that in this case the methoxy group undergoes reaction at the metal oxide center not simple desorption. The porthole effect was first postulated by Taylor⁴¹ and invoked by Fujimoto and Toyoshi⁴² to explain the effect of metal particles in the dehydrogenation of pentane on carbon. The role of the metal particles was to allow desorption of hydrogen, which was formed on the carbon and otherwise stayed and blocked sites.

The oxidation reaction remains as described by reactions 1–6, and the equilibrium with the silica surface does not affect the kinetics or C–H isotope effect. This may explain why this equilibrium was never observed or reported. Although the equilibrium does not alter the kinetics, it does affect the interpretation of any quantitative adsorption data. Methanol adsorption has been suggested as a method of counting active sites,^{1,10,27} and the present study indicates that this is fraught with danger. Because the support equilibrium is silent with respect to the kinetics, this applies to any support besides silica.

From a more general perspective, the results of the present study have uncovered a new role for the support and a new type of surface entity. First, it has been shown that the surface

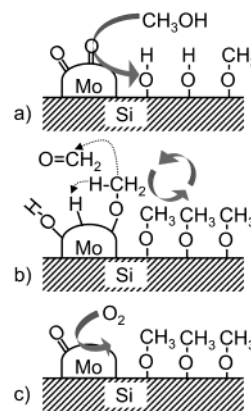


Figure 20. Scheme of the reaction mechanism. (a) Methanol adsorption, (b) methoxide species oxidation, and (c) oxygen activation.

can act as a reservoir for a large number of reactive species. In the steady state of the reaction, these species do not influence the kinetics, but at transient conditions, they play an important role. We have introduced the term noninnocent behavior for this action of the support. Second, this study also identifies a new classification of these surface species, which are denoted here as participatory species. Although their coverage is not related to the reaction rate, they are not simply spectators because they have the potential to react.

Conclusions

Kinetic data for methanol oxidation over $\text{MoO}_3/\text{SiO}_2$ are reported, and details on the reaction mechanism and the role of the support in the catalytic reaction have been clarified by a quantitative in situ FTIR method combined with product analysis by gas chromatography.

Molybdenum oxide is the active site in the silica-supported molybdenum oxide system and promotes methanol and oxygen activation, methoxide oxidation, and desorption of formaldehyde and water. Two kinds of methoxide species were observed, participants and spectators. Only the active participants could be oxidized at temperatures lower than 300 °C. The support (silica) was found for the first time to have a new role in a catalytic reaction, namely, as a storage place for both active and spectator reaction intermediates. Until now, it has been commonly presumed that the reaction occurred solely on supported molybdenum oxide and that all nonreactive species were found on silica. The findings of our studies will require a complete reexamination of the results of alcohol oxidation on supported oxides and possibly other reactions on supported systems.

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