

Direct Observation of Surface Intermediates Formed by Selective Oxidation of Alcohols on Silica-Supported Molybdenum Oxide

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The behavior of surface species, formed from the adsorption of methanol and isobutyl alcohol (2-methyl-1-propanol) on $\text{MoO}_3/\text{SiO}_2$, was studied in an oxygen-containing atmosphere by in situ Fourier transform infrared spectroscopy (FTIR). At 250 °C, methanol adsorption resulted in the formation of surface methoxide species ($\text{CH}_3\text{O}-$), whereas isobutyl alcohol adsorption resulted in surface isobutoxide species ($(\text{CH}_3)_2\text{CHCH}_2\text{O}-$). Kinetic studies indicated that the rate-determining step for the alcohol oxidation was the cleavage of the $\alpha\text{-C}-\text{H}$ bond in the alkoxide intermediates. Although the $\alpha\text{-C}$ is a primary carbon in the case of methanol (CH_3OH) and a secondary carbon in the case of isobutyl alcohol ($(\text{CH}_3)_2\text{CHCH}_2\text{OH}$), the activation energies for the rate-determining step were found to be similar. Theoretical molecular orbital calculations confirmed these experimental results by also predicting similar activation energies for both alkoxide species. During oxidation of the alkoxide species in the absence of alcohol in the gas phase, new bands were observed, which were assigned to the $\text{C}=\text{O}$ bands of adsorbed acyl species. In the case of these species, further reaction with oxygen produced CO_2 . The acyl species are therefore likely not to be intermediates that lead to aldehyde products in alcohol oxidation.

1. Introduction

In the past, numerous authors have studied the overall kinetics of selective alcohol oxidation by the quantitative analysis of the products and measurement of the apparent activation energy. Recently, there have been growing attempts to describe the mechanism in terms of detailed reactions, ideally as a set of elementary steps.^{1–3} One of the approaches for such a study is the in situ observation of the behavior of surface intermediates by spectroscopic techniques. Alcohol adsorption over supported metal oxide catalysts is known to result in the formation of surface alkoxide species,^{1–5} which are usually well observable by vibrational spectroscopy. For this kind of experiment, supported metal oxides are an ideal catalytic model because at low loadings the active metal oxide is highly dispersed over the surface of the support at less than a monolayer and the catalyst can serve as a structurally uniform two-dimensional system.

Because of the relative simplicity of interpretation of the spectra, methanol^{6–8} and 2-propanol (isopropyl alcohol)^{1–4} are used most frequently for the study of surface species by infrared (IR) spectroscopy. Methanol and 2-propanol undergo very similar surface processes. At temperatures lower than 100 °C, methanol and 2-propanol adsorb both dissociatively as surface alkoxides and associatively as physisorbed alcohols.⁹ At higher temperatures the scission of the $\text{O}-\text{H}$ bond of the physisorbed alcohol becomes predominant and in the presence of oxygen is followed by subsequent cleavage of the $\alpha\text{-C}-\text{H}$ bond resulting in the formation of the oxygenated reaction products.⁹

Ermini et al.¹⁰ studied adsorption of 2-propanol on $\gamma\text{-Al}_2\text{O}_3$ in an oxygen-containing atmosphere by Fourier transform infrared (FTIR) spectroscopy. After contact of the 2-propanol with the alumina surface below 150 °C, predominant bands typical of isopropoxide species were observed. At 150 °C these bands disappeared and a new band assigned to the $\text{C}=\text{O}$ bond stretching of adsorbed acetone was observed up to 200 °C. Above 150 °C a new set of bands, assigned to a mixture of carboxylate species (formate and acetate), began to appear and grow in intensity up to 300 °C. Above 300 °C bands due to bicarbonates appeared.

Busca et al.¹¹ studied 2-propanol and acetone oxidation on Mn_3O_4 using FTIR spectroscopy. Below 150 °C strong bands of isopropoxide groups were predominant in the spectra. Above 100 °C new bands, assigned to carboxylate species, grew until they started to disappear progressively above 200 °C, while bands due to surface carbonates appeared. A weak band present at temperatures up to 150 °C was assigned to the $\text{C}=\text{O}$ stretching mode of adsorbed acetone. In excess oxygen the isopropoxide species were transformed mainly to acetone by oxidative dehydrogenation, and the acetone was subsequently oxidized to CO_2 through the intermediacy of acetate and formate species. Similar results for oxidation of 2-propanol and acetone on Mn_3O_4 were reported by Baldi et al.¹² The predominant isopropoxide species, formed from 2-propanol adsorption, gradually disappeared as the temperature was raised to 250 °C. The spectrum of adsorbed acetone contained physisorbed acetone bands, which started to decrease in intensity near 150 °C and completely disappeared by 200 °C. Between 200 and 250 °C new bands corresponding to acetate species were observed together with bands due to carbonates.

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In this work, we investigated the formation and oxidation of alkoxy groups produced by the adsorption of methanol and 2-methyl-1-propanol (isobutyl alcohol) on a 1 wt % molybdenum oxide supported on silica catalyst ($\text{MoO}_3/\text{SiO}_2$). The resultant alkoxy groups were methoxy ($\text{CH}_3\text{O}-$) and isobutoxy ($(\text{CH}_3)_2\text{CHCH}_2\text{O}-$) groups, respectively. The spectra of the surface species during oxidation of the alkoxides were observed, and the similarities and differences in the kinetic properties of the different adsorbed species were determined.

2. Experimental Section

The catalyst (1 wt % $\text{MoO}_3/\text{SiO}_2$) was prepared using the incipient wetness technique, by the impregnation of silica (Cabosil EH-5, 350 m^2/g) with an aqueous solution of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Aldrich, >99.99% pure). The impregnation was followed by drying at 120 °C for 6 h and calcination at 500 °C for 6 h.¹ The surface area of the catalyst was measured as 337 m^2/g . By temperature-programmed reduction (TPR) the reduction temperature of the sample was found to be 497 °C, and the oxygen chemisorption (uptake) amount at the point of initial reduction was determined to be 37 $\mu\text{mol}/\text{g}$.¹ An amount of 20 mg of the catalyst was pressed at 3 MPa to form a thin self-supporting wafer, and this was placed inside a heatable IR cell with KBr windows. Pretreatment of the sample was performed by flowing 50% O_2 diluted with He at 350 °C for 10 h. After the pretreatment only Si-OH groups and framework vibrations of the support were observed in the IR spectra. The adsorption of methanol and isobutyl alcohol were carried out by dosing the catalyst in a stream containing 5 mol % of the alcohol in He. The FTIR spectra were recorded with a spectrometer (Jasco, model 620) at a resolution of 4 cm^{-1} with the measurements from 32 scans usually averaged. The spectrometer was equipped with a TGS (triglycine sulfate) detector. The IR cell was directly connected through a 10-way valve to a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

Theoretical molecular orbital calculations were used in this study to determine $\alpha\text{-C-H}$ bond energies, $E_{\alpha\text{-C-H}}$, and heats of reaction, ΔH_{rxn} . These calculations were run on a Sun 6500 high-performance computing system equipped with the Gaussian 98 program. Different theoretical methods were used in this study depending on the molecular species being investigated. For example, when performing calculations for methanol and isobutyl alcohol, the composite CBS-Q method was used. The CBS-Q¹³ level of theory is a complete basis set (CBS) method consisting of a series of calculations on the molecular system to determine very accurate total energies and can only be applied to molecules containing first and second row elements. Specifically, the CBS-Q method begins with an MP2 level geometry optimization and an HF level zero-point energy calculation. It then calculates an MP2 base energy with a higher basis set and corrects for the energy using a CBS extrapolation. Two higher level calculations are then performed to approximate higher order effects while the model corrects for spin contamination and size-consistency empirically.¹⁴ When doing calculations for molecules containing molybdenum, the B3LYP¹⁵⁻¹⁸ density functional theory (DFT) method was used. The B3LYP method is the Becke's three-parameter hybrid functional using the LYP correlation functional. Two basis sets were used in these DFT calculations. The LANL2DZ^{15,19-22} basis set was used for only Mo while the 6-31G(d)²³⁻²⁷ basis set was applied to all other atoms in the molecules. The LANL2DZ basis set uses the Los Alamos effective core potential (ECP) for the Mo atoms, which

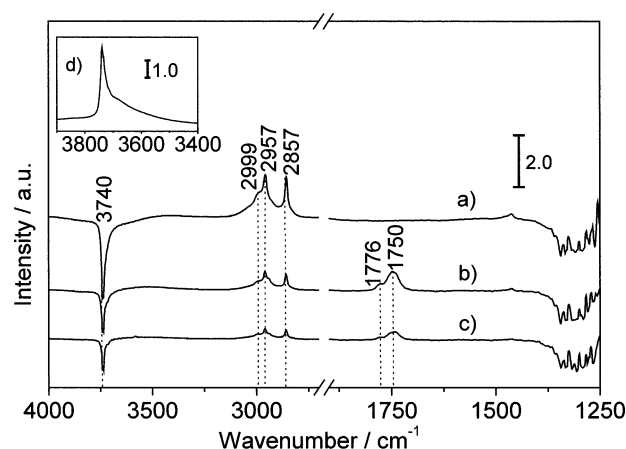
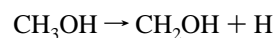


Figure 1. FTIR spectra of catalyst (a) fully saturated by methoxide species at 250 °C, (b) after 10 min of He/O_2 flow at 250 °C, and (c) after 180 min of He/O_2 flow at 250 °C. The inset (d) shows the FTIR spectrum of the Si-OH band of the pretreated $\text{MoO}_3/\text{SiO}_2$ at 250 °C.

treats electrons near the nucleus in an approximate way. The 6-31G(d) basis set is a split valence basis set that uses polarized d functions for heavy atoms.¹⁴

The net charge of all the molecules used in this study was set to zero. These species were then optimized, and their total energies were calculated making sure that true minima were found on the potential energy surface for each structure. The $\alpha\text{-C-H}$ bond energies were determined by calculating the total energies of the molecular species before and after scission of the $\alpha\text{-C-H}$ bond. For example, the following dissociation reaction was considered for methanol:



The $\alpha\text{-C-H}$ bond energy, $E_{\alpha\text{-C-H}}$, was then determined by

$$E_{\alpha\text{-C-H}} = E_{\text{CH}_2\text{OH}} + E_{\text{H}} - E_{\text{CH}_3\text{OH}}$$

The heats of reaction, ΔH_{rxn} , were determined by first calculating the total energy of each species involved in the reaction of interest. Then, the heat of reaction for a specific reaction was simply the sum of the energies for the product species minus the sum of the energies for the reactant species.

3. Results and Discussion

3.1. Identification of the Surface Species. The spectrum of the catalyst fully saturated in 5 mol % methanol/He at 250 °C is shown in Figure 1a. The bands at 2999, 2957, and 2857 cm^{-1} are characteristic of the C-H vibration modes of methoxy groups.³ The $\text{MoO}_3/\text{SiO}_2$ catalyst itself was characterized by an intense band at 3740 cm^{-1} , which was due to isolated Si-OH groups. The spectrum of a pretreated reference sample, displayed in Figure 1 as the inset d, has been subtracted to make the bands of the adsorbed species more clear, and therefore, the silanol OH band appears as a negative band. For this OH band alone a decrease in absolute intensity indicates an increase in concentration. Because the support was highly absorbing in the region of framework vibrations under 1250 cm^{-1} , the vibrations of molybdenum oxide (Mo=O and Mo-O modes) could not be observed. The adsorption of the alcohols also produced OH groups, which underwent a rapid reaction with silanol groups to form water. The produced water likely adsorbed immediately at this temperature, as indicated by the absence of the band for the bending mode of water (1650–

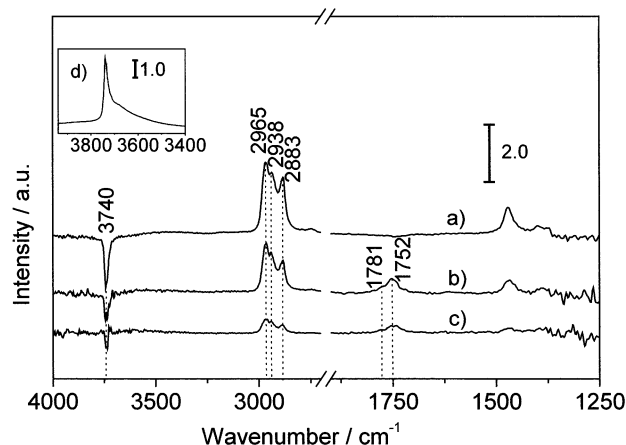


Figure 2. FTIR spectra of catalyst (a) fully saturated by isobutoxide species at 250 °C, (b) after 10 min of He/O₂ flow at 250 °C, and (c) after 180 min of He/O₂ flow at 250 °C. The inset (d) shows the FTIR spectrum of the Si-OH band of the pretreated MoO₃/SiO₂ at 250 °C.

1600 cm⁻¹) in the spectra as well as by the detection of water by GC analysis of the gas mixture leaving the IR cell.

The gas lines were swept clear of traces of methanol by flowing pure He. In helium flow, the methoxide species remained stable on the surface. After the flow was switched to O₂/He at the same temperature (250 °C), the methoxy group bands started to decrease in intensity as a result of oxidation. At the same time as this intensity decreased, the negative OH band decreased in magnitude (Figure 1b,c), indicating recovery of OH groups. During the methoxy group oxidation, new bands appeared at 1776 and 1750 cm⁻¹ (Figure 1b,c). These bands are indicative of the presence of another species formed during oxidation of the methoxide species. As will be discussed later, these species have an acyl structure.



As the amount of the methoxide species on the surface decreased, the intensity of the bands at 1776 and 1750 cm⁻¹ increased sharply at first and then slowly started to decrease, while GC analysis showed the presence of CO, CO₂, and water at the outlet from the IR cell. When the gas flow was switched to pure He, the bands at 1776 and 1750 cm⁻¹ were stable, and the gas-phase analysis did not indicate any reaction products. However, the bands at 1776 and 1750 cm⁻¹ disappeared immediately after methanol was added to the gas phase.

During steady-state methanol oxidation, that is, in O₂/CH₃OH/He gas flow, bands due to methoxy groups were present, but the bands at 1776 and 1750 cm⁻¹ were not observed. The GC analysis indicated the presence of products of the reaction, which were formaldehyde, CO, CO₂, and water.

Saturated adsorption of isobutyl alcohol at 250 °C resulted in species with bands at 2965, 2938, and 2883 cm⁻¹ (Figure 2a). These were assigned to the C-H vibration modes of adsorbed isobutoxide species, in analogy to the assignment of the bands in this region for the methoxide species formed from methanol adsorption. Again, as in the case of the methanol spectra, a reference spectrum of the fresh sample was subtracted resulting in a negative band at 3740 cm⁻¹ for the Si-OH groups. The spectrum of the silanol groups before isobutyl alcohol adsorption is also shown in the inset d.

The oxidation of isobutyl alcohol showed behavior very similar to the oxidation of methanol. When the flow was switched from isobutyl alcohol/He to O₂/He at 250 °C, the bands

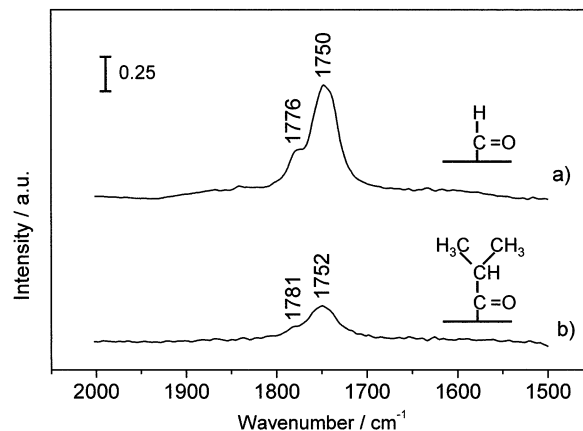


Figure 3. Acyl species formed from (a) oxidation of methoxide species and (b) oxidation of isobutoxide species on MoO₃/SiO₂ (all at 250 °C).

due to the adsorbed alkoxide species decreased with time and the band for OH recovered (became less negative). New bands appeared in the carbonyl stretching region at 1781 and 1752 cm⁻¹, indicating the presence of product species of isobutoxide oxidation (Figure 2b,c), which were again acyl species.

The observed bands of alkoxide species are not assigned to the true reaction intermediates themselves but to species which spilled over from the molybdenum site to the support and, in effect, became observable. We base this conclusion on our earlier study¹ of methanol adsorption on the same 1 wt % MoO₃/SiO₂ catalyst, which showed that the quantity of adsorbed methoxide species was 5–6 times greater than the number of Mo centers. The vibrational spectrum of the species was also identical to that obtained on the SiO₂ support, so it was deduced that the methoxide species resided mostly on SiO₂. Although the true reaction intermediates are not directly observed, it is presumed that their structure is similar to that of the spillover species. During steady-state reaction, these spillover species are in equilibrium with newly formed methoxide species on the Mo centers and do not affect the kinetics of the reaction. The spillover alkoxide species are stable in He flow up to 300 °C. When alcohol is absent in the gas phase, their stability causes an overoxidation in the presence of O₂, and acyl species are formed. However, when alcohol is added to the gas phase, the methoxide species can migrate to the Mo centers and form the aldehyde product. Evidently, the presence of alcohol in the gas phase is necessary for the formation of the aldehyde detected at the exit of the reactor.

In our previous work¹ isotopic labeling studies of the adsorbed methoxide species showed that the species had high mobility on the silica surface. Also, because the presence of Mo was needed for the oxidation reaction, it was concluded that the species could move back and forth between the Mo and the silica and were in equilibrium. The role of oxygen was not studied in depth in this work. The oxygen molecules are important in reoxidizing the Mo sites, and because these sites are mostly isolated on the surface, it could be that some oxygen transport occurs via surface diffusion. The silica is able to oxidize some of the alkoxides, albeit at a small rate, so this suggests that the silica is able to adsorb the oxygen.

The C=O stretching bands, which appeared during methoxide oxidation at 1776 and 1750 cm⁻¹ and during isobutoxide oxidation at 1781 and 1752 cm⁻¹, indicated the presence of oxidized species. They are compared in Figure 3. In both cases, doublets were observed and they behaved in the same manner so that the ratio of their intensities did not change. Such behavior indicates that both bands can be attributed to the same mode, a

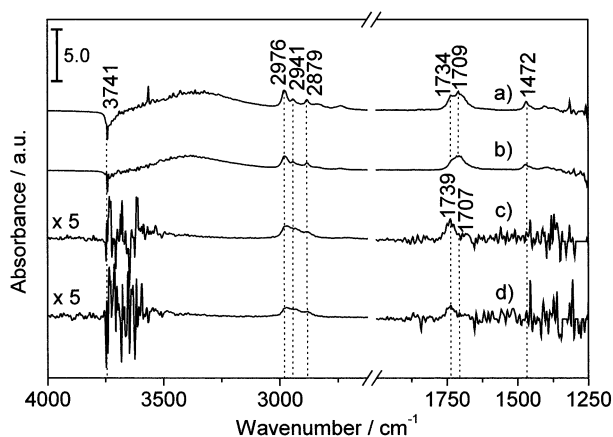


Figure 4. FTIR spectra of catalyst (a) after isobutyl alcohol adsorption at 35 °C, (b) after He flow at 35 °C, (c) after isobutyl alcohol adsorption at 250 °C, and (d) after He flow at 250 °C.

C=O stretching vibration, with the split likely caused by a Fermi resonance of the fundamental vibration with an overtone or combination of some other vibration such as C–H and/or C=O bending. The species, characterized by the two C=O stretching bands, interact strongly with the surface; in He flow they are stable up to 300 °C. In He/O₂ flow they oxidize, producing CO_x and H₂O. As mentioned earlier, the species are likely to be acyl species, and this will be discussed below.

To obtain insight on the nature of the adsorbed species with the C=O group, isobutyraldehyde (2-methyl-1-propanal, (CH₃)₂CHCHO) was adsorbed on the surface of the catalyst. The spectra of the physisorbed aldehyde were compared with the spectra of the sample after the oxidation of adsorbed isobutoxide species. After isobutyraldehyde adsorption at room temperature (35 °C) (Figure 4a), the silica hydroxy band at 3741 cm⁻¹ decreased, while new bands at 2976, 2941, 2879, and 1472 cm⁻¹ appeared. New C=O stretching vibrations also arose at 1734 and 1709 cm⁻¹. In He flow at 35 °C (Figure 4b), all the bands decreased slightly in intensity, while the silica hydroxy band partially recovered. For isobutyraldehyde adsorption at the reaction temperature (250 °C) (Figure 4c), the spectrum was similar to the one at 35 °C, only the bands were considerably weaker in intensity. Although the estimation of the exact position of bands is difficult because of their low intensity, the C=O stretching vibration bands appeared to be shifted to 1739 and 1707 cm⁻¹, respectively. At 250 °C in He flow all the bands again decreased in intensity, while the silica hydroxy band partially recovered (Figure 4d).

The C=O stretching vibration bands, located in the 1700–1750 cm⁻¹ region, are compared in Figure 5. Figure 5a shows the spectrum of the species obtained from oxidation of adsorbed isobutoxide species at 250 °C. Figure 5b shows the spectrum of physisorbed isobutyraldehyde at 25 °C, and Figure 5c shows that at 250 °C. The position of the bands of the physisorbed species is shifted about 45 cm⁻¹ to lower wavenumbers, indicating that the C=O bond is weaker. The likely explanation is that the C=O bond of the physisorbed species is interacting with the surface of the support. While adsorption of isobutyraldehyde resulted in the formation of physisorbed aldehyde, the oxidation of some of the alkoxide species formed the acyl species. Conversion of the physisorbed aldehyde to the acyl species on MoO₃/SiO₂ was not observed in the experimental range between 25 and 250 °C. This is an interesting result because very often adsorption of stable intermediate species is carried out to prove their involvement in reaction sequences. The finding here about isobutyraldehyde shows that this is not

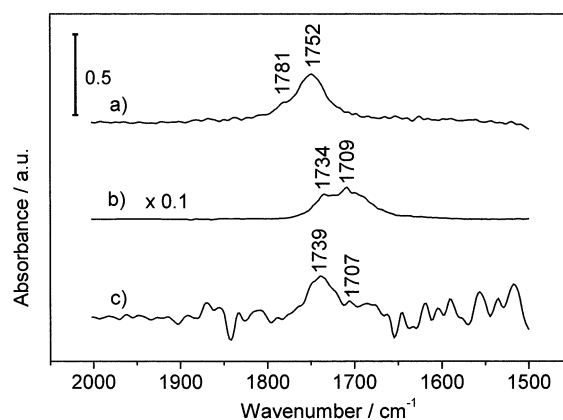


Figure 5. Stretching bands of C=O observed (a) during oxidation of isobutoxy groups, (b) during isobutanol adsorption at 35 °C, and (c) during isobutanol adsorption at 250 °C.

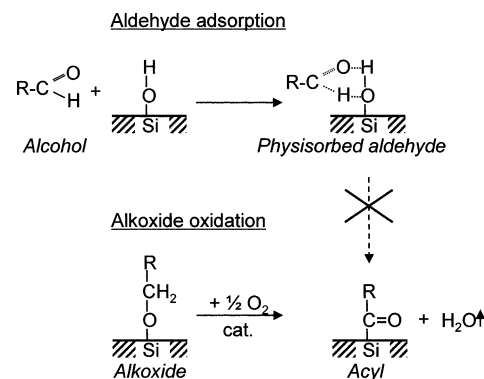


Figure 6. Surface reaction during aldehyde adsorption and alkoxide oxidation.

general. The scheme of the surface reactions is outlined in Figure 6. The lower frequency of the C=O bond in the physisorbed species is attributed to interactions with surface hydroxyl groups, which are present on the surface at the conditions of adsorption.

The acyl species are only formed in the absence of gas-phase alcohol. The oxidation route, which involves the acyl species, follows the sequence alcohol → alkoxide → acyl → CO₂ and occurs mostly on the SiO₂ surface. It represents a dead end, as the acyl species are too stable and only leave the surface as CO₂. Therefore, it is possible to conclude that continuous flow of alcohol and formation of alkoxide species is essential for the production of aldehyde products. This occurs by an α-hydride elimination from the alkoxy groups on the Mo centers. The reaction results in the formation of a free aldehyde, which is the main product of the reaction. As noted earlier, the alkoxy groups on the Mo centers are not directly observed but are presumed to be in equilibrium with the alkoxide species on the SiO₂ support.

3.2. Kinetics of the Surface Reaction. After switching the gas flow to the He/alcohol mixture, the formation rate of alkoxy groups on fresh MoO₃/SiO₂ was initially rapid and then slowed as the surface reached saturation. In comparison, the formation rate of alkoxides on bare silica was significantly lower; at 250 °C the surface was only occupied to an extent of 58% of the maximum amount even after 14 h, and saturation was not reached. Therefore, the presence of Mo centers is essential for the rapid formation of alkoxides.

The time course of the quantity of both alkoxy groups during oxidation is shown in the insets in Figure 7. The oxidation rate of both alkoxides was initially rapid, but after a certain time the rate slowed. However, the quantity of alkoxy groups did

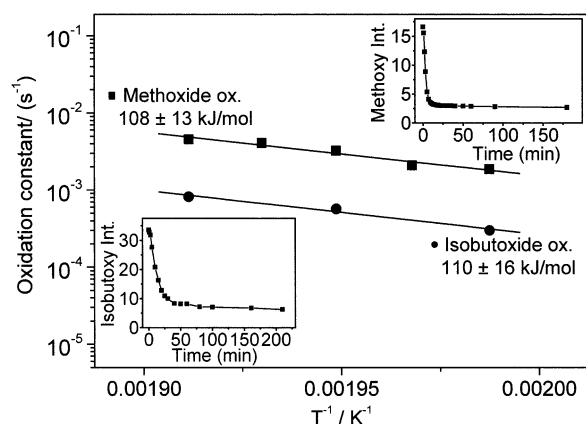


Figure 7. Arrhenius plots of the oxidation rate constant of surface methoxide species (upper trace) and isobutoxide species (lower trace) on $\text{MoO}_3/\text{SiO}_2$. In the insets the time courses of oxidation of methoxide and isobutoxide species are displayed (in units of integrated intensity vs time).

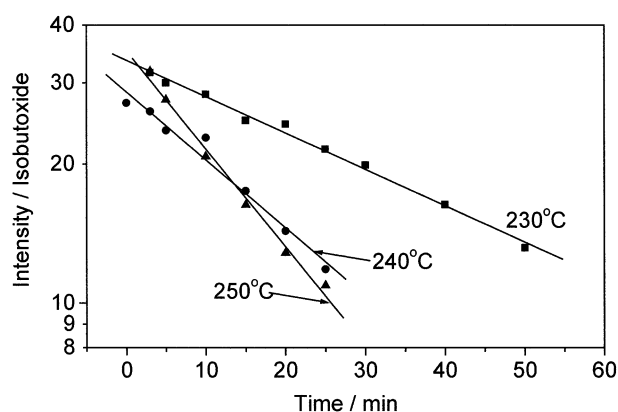


Figure 8. Plot of the intensity of the 2883 cm^{-1} band of isobutoxide vs the time of oxidation on $\text{MoO}_3/\text{SiO}_2$ at 230, 240, and 250 °C.

not drop to zero, indicating that a certain amount of the alkoxy groups remained intact on the surface (Figure 1c and Figure 2c). From this, two types of alkoxy groups are distinguishable: highly reactive species, which are mobile and move to and from the Mo centers, and inactive species, regarded as spectators. The spectator species are probably formed from the mobile participant species on a limited number of sites and are characterized by particular stability. At 250 °C, the amount of quickly disappearing species and slowly disappearing species was 80% and 20%, respectively, for both methoxide and isobutoxide species.

Results from kinetic analysis of the oxidation of the alkoxy species are shown in Figure 7. The quantification of the alkoxy species is based on the integrated intensities of the 2857 cm^{-1} band in the case of the methoxide species and of the 2883 cm^{-1} band in the case of the isobutoxide species. These bands had the least overlap with other bands and, therefore, were the most suitable for the quantitative analysis. For the estimation of the rate constants of the oxidation of the alkoxy species it was assumed that the reaction was a first-order process. This assumption was proven reasonable. Linearization of the first-order kinetic equation gave $\ln([*\text{OCH}_3]/[*\text{OCH}_3]_0) = -kt$, where $[*\text{OCH}_3]$ is the concentration of adsorbed alkoxy species, k is the reaction constant in units of s^{-1} ; the data fit the linear relation well (Figure 8). The alkoxy concentration can be directly related to the integrated area of the 2857 or 2883 cm^{-1} bands, respectively, through the extinction coefficient. Only the values from the kinetic region, before the curve levels

off, were used to avoid interference from diffusion. For methoxide oxidation, the rate constant was found to increase with reaction temperature from 0.00185 s^{-1} (230 °C) to 0.00456 s^{-1} (250 °C). The temperature dependence of the reaction rate constant leads to the Arrhenius expression $k = 2.96 \times 10^8 \exp(-E_{\text{act}}/RT)$ where $E_{\text{act}} = 108 \pm 13\text{ kJ/mol}$ (Figure 7, upper line). The rate constant for isobutoxide oxidation increased from 0.00030 s^{-1} (230 °C) to 0.00082 s^{-1} (250 °C), with the associated Arrhenius expression $k = 0.87 \times 10^8 \exp(-E_{\text{act}}/RT)$ where $E_{\text{act}} = 110 \pm 16\text{ kJ/mol}$ (Figure 7, lower line). For comparison, Burcham et al.³ found the activation energies for methanol oxidation to be 99 kJ/mol on $\text{MoO}_3/\text{Al}_2\text{O}_3$ and 88 kJ/mol on $\text{MoO}_3/\text{TiO}_2$.

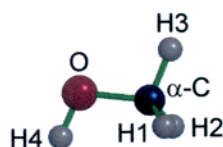
The rate-determining step of methanol oxidation is generally agreed to be cleavage of the C–H bond.^{4,28,29} Similarly, the rate-determining step for alcohols with higher number of carbons is the scission of the C–H bond on the α -carbon atom. The α -carbon is taken to be the one adjacent to the oxygen in the alkoxy group, as is a convention in heterogeneous catalysis. The scission of the α -C–H bond was proposed as the rate-determining step for 2-propanol oxidation⁹ and, in analogy, is expected to be so for the oxidation of isobutyl alcohol as well. In this work the activation energies of methoxide and isobutoxide oxidation were found to be strikingly similar, 108 and 110 kJ/mol, respectively.

The similarity in the activation energies was unexpected. Activation energies can be related to bond energies through the Polanyi relation,³⁰ and the α -C–H bond energies in the methoxide and isobutoxide species were expected to be different. Usually C–H bond strengths decrease in the order primary > secondary > tertiary, which reflects the increasing likeliness to undergo a reaction. As a result, the activation energy for the cleavage of the α -C–H bond should have been less in the case of isobutyl alcohol (secondary carbon) than in the case of methanol (primary carbon) but larger than in the case of 2-propanol (tertiary carbon). However, the experimental data presented here show similar activation energies for isobutoxy and methoxy group oxidation.

The energetics of the α -C–H bond in isobutyl alcohol were not found in the literature. To obtain insight into the activation energy results, theoretical calculations were used to determine the α -C–H bond energies; for methanol and isobutyl alcohol (2-methyl-1-propanol) the CBS-Q method was used, and for adsorbed methoxide and isobutoxide species the DFT method described in the Experimental Section was used. In a previous study the structure of molybdenum oxide supported on SiO_2 was found to be best fit by a model in which a molybdenum atom was linked to two support silicon atoms by bridging oxygen atoms.¹ In this work, the molybdenum atom was linked to a single silicon atom and methoxy and isobutoxy groups were then added to this structure to determine the geometries and total energies.

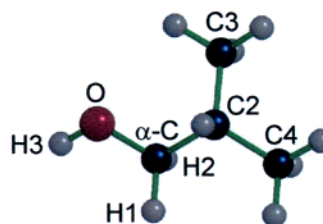
Figure 9 presents the geometries, structural parameters, total energies, and α -C–H bond energies for both methanol (Figure 9a) and isobutyl alcohol (Figure 9b). Structural parameters such as bond distances and bond angles that surround the α -C are similar for both methanol and isobutyl alcohol. Bond energies can be obtained by using the thermochemical equation described in the Experimental Section. In the α -C–H bond energy calculations, the total energy for a single hydrogen atom (-0.50 Hartree) was calculated using the CBS-Q method. For methanol, calculated total energies for CH_3OH (-115.53 Hartree), CH_2OH (-114.88 Hartree), and H were used to determine the α -C–H bond energy. For isobutyl alcohol, total energies for $(\text{CH}_3)_2$ -

a)



Methanol					
Bond Type	Distance nm	Bond (e.g.)	Bond Angle Type	Angle °	Bond (e.g.)
C-H	0.110	α C-H1	O-C-H	112.5	O- α C-H1
	0.110	α C-H2		112.5	O- α C-H2
	0.109	α C-H3		106.5	O- α C-H3
C-O	0.142	α C-O	C-O-H	107.8	α C-O-H4
O-H	0.096	O-H4	H-C-H	108.6	H1- α C-H2
				108.3	H1- α C-H3
				108.3	H2- α C-H3
Total Energy = -115.53 Hartree					
α -C-H Bond Energy = 402.03 kJ/mol					

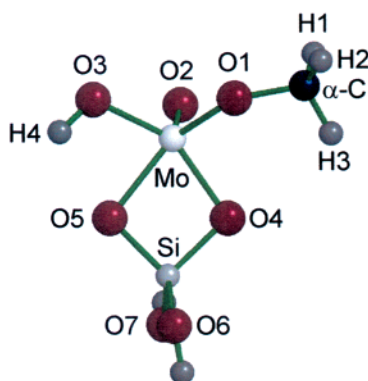
b)



Isobutanol					
Bond Type	Distance nm	Bond (e.g.)	Bond Angle Type	Angle °	Bond (e.g.)
C-H	0.110	α C-H1	O-C-H	111.0	O- α C-H1
	0.110	α C-H2		111.1	O- α C-H2
C-C	0.152	α C-C2	C-C-C	110.8	α C-C2-C3
	0.153	C2-C3		110.1	α C-C2-C4
	0.153	C2-C4		111.4	C3-C2-C4
C-O	0.142	α C-O	C-O-H	108.0	α C-O-H3
O-H	0.097	O-H3	H-C-H	107.5	H1- α C-H2
Total Energy = -233.22 Hartree					
α -C-H Bond Energy = 398.68 kJ/mol					

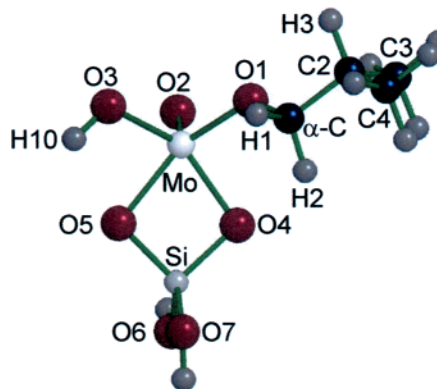
Figure 9. Geometry optimized structures, bond parameters, total energies, and α -C-H bond energies using the CBS-Q method: (a) methanol; (b) isobutyl alcohol.

a)



Adsorbed Methoxide (1 Silicon)					
Bond Type	Distance nm	Bond (e.g.)	Bond Angle Type	Angle °	Bond (e.g.)
C-H	0.110	α C-H1	O-C-H	110.4	O1- α C-H1
	0.109	α C-H2		107.8	O1- α C-H2
	0.110	α C-H3		108.8	O1- α C-H3
C-O	0.142	α C-O1	C-O-Mo	132.7	α C-O1-Mo
Mo-O	0.187	Mo-O1	O-Mo-O	109.1	O1-Mo-O2
	0.189	Mo-O3		99.4	O1-Mo-O3
	0.195	Mo-O4		104.5	O2-Mo-O3
				73.1	O4-Mo-O5
Mo=O	0.170	Mo-O2	Mo-O-Si	99.0	Mo-O4-Si
Si-O	0.168	Si-O4	O-Si-O	91.3	O4-Si-O5
	0.164	Si-O6		113.4	O4-Si-O6
				106.1	O6-Si-O7
Total Energy = -925.49 Hartree					
α -C-H Bond Energy = 291.34 kJ/mol					

b)



Adsorbed Isobutoxide (1 Silicon)					
Bond Type	Distance nm	Bond (e.g.)	Bond Angle Type	Angle °	Bond (e.g.)
C-H	0.110	α C-H1	O-C-H	108.0	O1- α C-H1
	0.110	α C-H2		107.3	O1- α C-H2
C-C	0.153	α C-C2	C-C-C	109.1	α C-C2-C3
	0.154	C2-C3		111.5	α C-C2-C4
	0.153	C2-C4		111.8	C3-C2-C4
C-O	0.143	α C-O1	C-O-Mo	132.0	α C-O1-Mo
Mo-O	0.187	Mo-O1	O-Mo-O	106.6	O1-Mo-O2
	0.191	Mo-O3		97.9	O1-Mo-O3
	0.196	Mo-O4		106.4	O2-Mo-O3
				73.5	O4-Mo-O5
Mo=O	0.170	Mo-O2	Mo-O-Si	98.3	Mo-O4-Si
Si-O	0.167	Si-O4	O-Si-O	91.4	O4-Si-O5
	0.164	Si-O6		113.3	O4-Si-O6
				106.0	O6-Si-O7
Total Energy = -1043.35 Hartree					
α -C-H Bond Energy = 261.28 kJ/mol					

Figure 10. Geometry optimized structures, bond parameters, total energies, and α -C-H bond energies using the B3LYP/LANL2DZ method on Mo atoms and the B3LYP/6-31G(d) method on all other atoms: (a) adsorbed methoxide; (b) adsorbed isobutoxide.

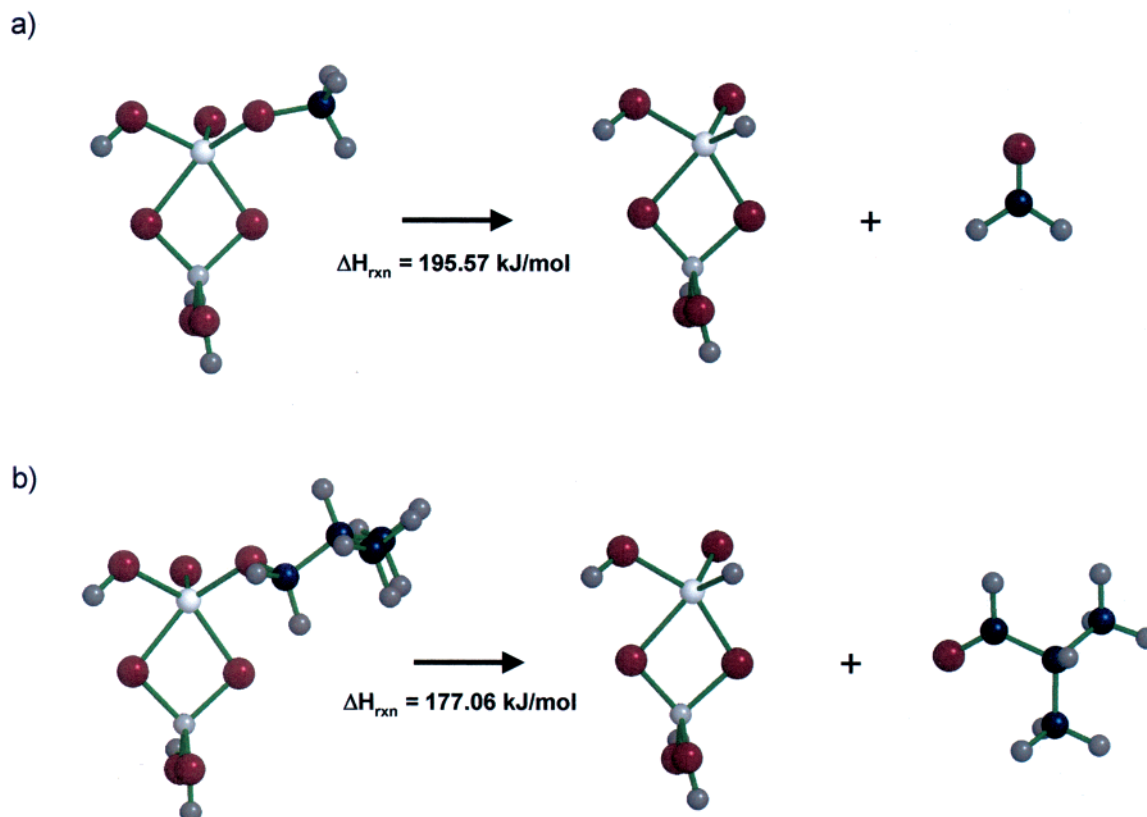


Figure 11. Hydride transfer reactions and corresponding theoretical heats of reaction: (a) methoxide oxidation; (b) isobutoxide oxidation.

CHCH_2OH (−233.22 Hartree), $(\text{CH}_3)_2\text{CHCHOH}$ (−232.57 Hartree), and H were employed. Using these total energies and the energy for a single hydrogen atom, the $\alpha\text{-C-H}$ bond energies for both compounds were found to be quite similar, 402.03 kJ/mol for methanol and 398.94 kJ/mol for isobutyl alcohol (1 Hartree = 2625.44 kJ/mol). These comparable $\alpha\text{-C-H}$ bond energies help explain why the activation energy for the cleavage of the $\alpha\text{-C-H}$ bond in methanol (primary carbon) and isobutyl alcohol (secondary carbon) were similar. However, it was recognized that the relevant C–H bonds were not those of the parent alcohols, but those in the adsorbed alkoxide species. For this reason further calculations were undertaken.

Figure 10 presents the geometries, structural parameters, total energies, and $\alpha\text{-C-H}$ bond energies for both methoxide (Figure 10a) and isobutoxide (Figure 10b) adsorbed on $\text{MoO}_3/\text{SiO}_2$. As expected, the structural parameters that surround the $\alpha\text{-C-H}$ were comparable for both the methoxide and isobutoxide species. For the methoxide, calculated total energies for Mo-OCH_3 (−925.49 Hartree), Mo-OCH_2 (−924.88 Hartree), and H were used to determine an $\alpha\text{-C-H}$ bond energy of 291.34 kJ/mol. Similarly, total energies for $\text{Mo-OCH}_2\text{CH}(\text{CH}_3)_2$ (−1043.35 Hartree), $\text{Mo-OCHCH}(\text{CH}_3)_2$ (−1042.76 Hartree), and H were used to determine an $\alpha\text{-C-H}$ bond energy of 261.28 kJ/mol for the adsorbed isobutoxide species. Thus, the $\alpha\text{-C-H}$ bond energy of the adsorbed methoxide is roughly 30 kJ/mol greater than that of the adsorbed isobutoxide species. Even though a difference of 30 kJ/mol in $\alpha\text{-C-H}$ bond energies initially seems significant, one must use the Polanyi relation to obtain activation energies to determine if these theoretical calculations do indeed support the experimental data.

The Polanyi relation for an endothermic reaction is

$$E_{\text{act}} = E_0 + (1 - \alpha)\Delta H_{\text{rxn}}$$

where E_{act} is the activation energy, ΔH_{rxn} is the heat of reaction, and E_0 and α are Polanyi parameters that change from one reaction family to the next.³⁰ Figure 11 shows the relevant reactions and their corresponding heats of reaction, ΔH_{rxn} , as the alkoxide species adsorbed on the catalyst surface react by transferring a hydride to molybdenum and releasing the corresponding aldehyde product. In the case of the methoxide species, the reaction to form formaldehyde has a heat of reaction of 195.57 kJ/mol (Figure 11a). For the isobutoxide species, the reaction to form butyraldehyde has a heat of reaction of 177.06 kJ/mol. Watson et al.³¹ performed an extensive study to determine Polanyi parameters (E_0 and α) from experimental data. In that study, E_0 values were determined for many different reaction families. For hydride transfer reactions similar to the ones dealt with here, an E_0 value of 54.4 kJ/mol was reported. It was also reported in the study of Watson et al. that a precise value of α could not be determined because of the lack of sensitivity in the optimization results. It is known that Polanyi α values fall in the range of 0.5 ± 0.25 . For an optimized α value of 0.71, theoretical activation energies for methoxide and isobutoxide oxidation are calculated to be 111.12 and 105.75 kJ/mol, respectively. These two activation energy values are very similar and therefore confirm the experimental activation energies for methoxide and isobutoxide oxidation of 108 ± 13 kJ/mol and 110 ± 16 kJ/mol, respectively.

Figure 12 shows the geometries, structural parameters, and total energies for the other species involved in the hydride transfer reactions mentioned previously. Figure 12a shows the molybdenum hydride on the monosilicon-supported catalyst, Figure 12b presents formaldehyde, and Figure 12c presents butyraldehyde.

The ratio of the preexponential factors of the Arrhenius expressions for the methoxide versus isobutoxide species is 3.40 ($2.96 \times 10^8/0.87 \times 10^8$), whereas the statistical factor for C–H

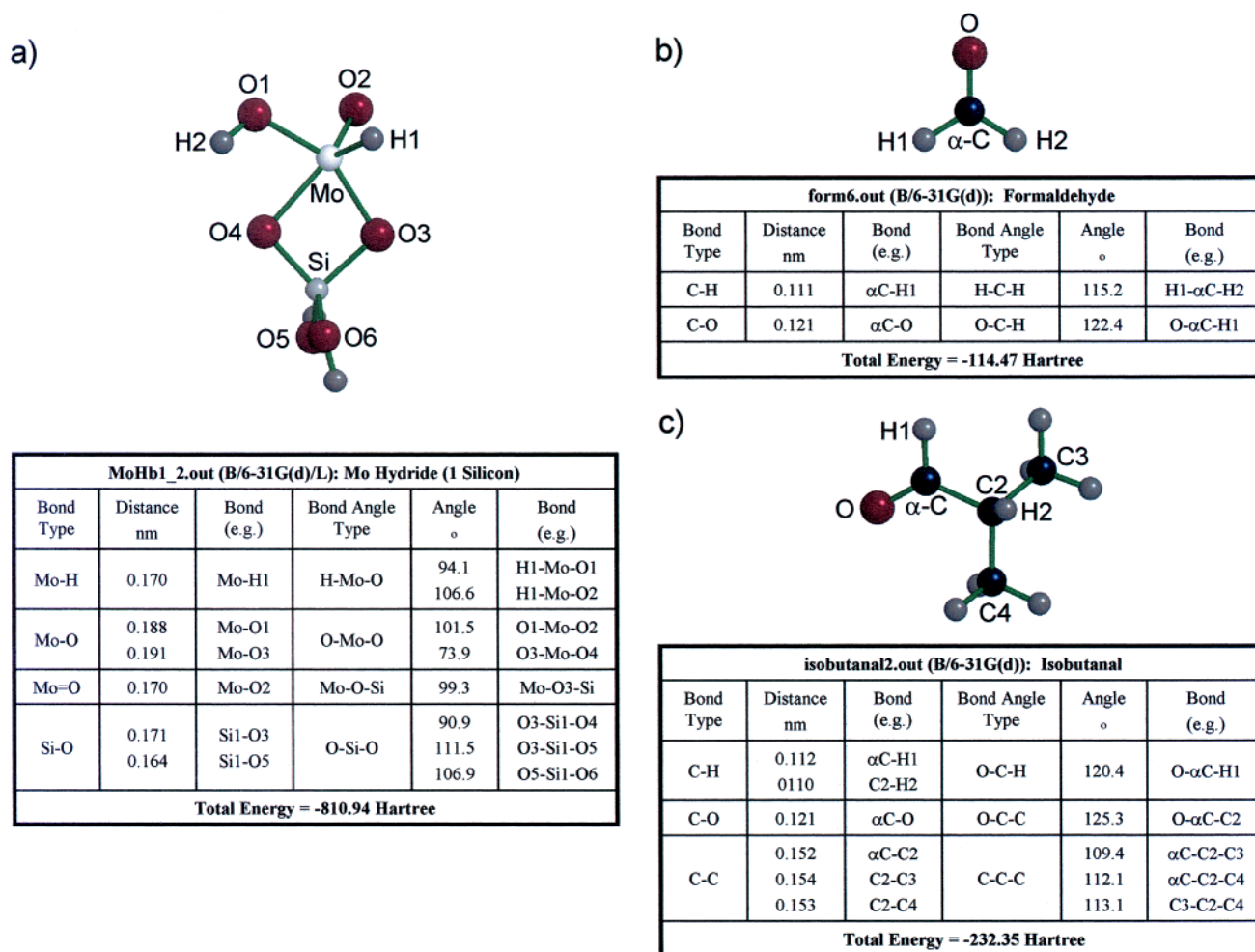


Figure 12. Geometry optimized structures, bond parameters, and total energies using the B3LYP/LANL2DZ method on Mo atoms and the B3LYP/6-31G(d) method on all other atoms: (a) molybdenum hydride; (b) formaldehyde; (c) butyraldehyde.

cleavage is only 1.5 (3/2). The preexponential factor is a product of statistical and steric components. The steric factor is certainly lower for the isobutoxide species than for the methoxide species and reduces the value of the preexponential factor.

In this study it was found that the silica surface was able to hold a number of adsorbed species that were related to the main oxidation reactions. Mobile alkoxide species constituted the majority of the surface species. These were participatory species. In the presence of gas-phase alcohol and O₂ these species migrated to the Mo centers and produced gas-phase aldehyde while regenerating surface hydroxyls, which were also mobile. The role of O₂ in the mechanism is to maintain the Mo centers in an oxidized form so that they can produce the aldehyde product. The surface hydroxyls readily recombined, producing water, which immediately desorbed. There was also a proportion (20%) of the alkoxide species that consisted of stable spectators and did not react. The ability of the silica surface to hold these adsorbed species was described in our previous paper as “noninnocent” behavior.¹

In the absence of gas-phase alcohol, but with O₂ present, the surface methoxide species produced acyl species. These acyl species were stable in He flow, but in the presence of O₂ they oxidized to CO_x and H₂O. In the presence of gas-phase alcohol they readily disappeared from the surface.

The oxidation of the alkoxide intermediates on the Mo centers occurred by α-C–H bond breaking and resulted in the formation of the gas-phase aldehyde products. Similar activation energies were found for the methoxide and isobutoxide intermediates,

which were explained using theoretical molecular orbital calculations together with the Polanyi relation.

4. Conclusions

The adsorption and oxidation of methanol and isobutyl alcohol on MoO₃/SiO₂ was studied by in-situ FTIR spectroscopy. The adsorption of methanol and isobutyl alcohol resulted in the formation of methoxide and isobutoxide species on the silica support, accompanied by the formation and desorption of water. The majority of these alkoxide species (80%) were mobile on the silica and could migrate to the Mo centers to be oxidized in an O₂/He flow to produce the corresponding aldehydes (formaldehyde and isobutyraldehyde). The remaining species (20%) were inert spectators. In the absence of gas-phase alcohol the participant species formed stable adsorbed acyl species, which were identified by C=O stretching bands at 1700–1800 cm⁻¹. These acyl species are considered to be a dead end in the oxidation process, producing only CO_x and H₂O.

Activation energies for C–H bond breaking in the adsorbed alkoxide species were close, 108 ± 13 kJ/mol for the methoxide species and 110 ± 16 kJ/mol for the isobutoxide species. The similarity was explained using theoretical molecular orbital calculations in conjunction with the Polanyi relation.

The similarity of the oxidation kinetics of both alkoxide species suggested that the reaction proceeded with the same rate-determining step, namely, the cleavage of the α-C–H bond. These results indicate that many of the essential features of the

mechanism of methanol oxidation on $\text{MoO}_3/\text{SiO}_2$ can be generalized to other alcohols. The ability of the silica surface to hold actual participants in the reaction categorized the silica as a noninnocent support.

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