

Promotion of Formaldehyde Production from Adsorbed Methoxy by Oxidation of Mo(110) with NO₂

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The reaction of methoxy (OCH₃) in the presence of NO₂ is studied on a thin-film oxide of Mo(110) for its relevance to the alkane-assisted reduction of NO_x. Temperature-programmed reaction indicates that oxygen deposited by NO₂ dissociation promotes formaldehyde evolution. This pathway is not observed in any appreciable amount for methoxy on the thin-film oxide of Mo(110), nor for the reaction of methoxy in the presence of NO or O₂. No new intermediates, in particular those containing C–N bonds, are detected after NO₂ is exposed to the surface containing methoxy. Furthermore, infrared spectra provide evidence that the presence of NO₂ does not significantly perturb the methoxy intermediate. These results indicate that surface oxidation rather than intermolecular complexation is the most likely mechanism by which NO₂ promotes the evolution of oxygenates. In addition, the presence of methoxy decreases the capacity of the Mo surface to reduce NO₂. No N₂ is produced, and molecular desorption predominates. There are also no NO_x species present after heating to 500 K when NO₂ reacts in the presence of methoxy, whereas monomeric NO and dinitrosyl are present when NO₂ reacts alone. These results are discussed in the context of CH₄-assisted NO_x reduction.

Introduction

Understanding alkane-assisted reduction of nitrogen oxides is key to further decreasing automotive NO_x emissions. While it is known that methane promotes NO_x reduction over Pd(110),¹ rare earth oxides,² and Li-promoted MgO,³ it remains unclear whether the hydrocarbon interacts directly with the NO_x species or whether it modifies the surface in a manner that favors reduction. Some suggest that alkyl radicals are the active species, scavenging oxygen deposited during NO_x reduction so as to avert catalyst deactivation. Others propose that NO_x species couple with alkanes to form intermediates containing a C–N bond that are subsequently reduced. Recently, studies of plasma-assisted NO_x reduction have shown that selective catalytic reduction occurs with a higher conversion rate if the NO and hydrocarbons are first converted to NO₂ and hydrocarbon radicals in a plasma created by an electrical discharge.⁴ There are several explanations for the increased efficiency of NO₂ reduction as compared to NO reduction. For instance, the surface-mediated reaction of NO₂ may activate the C–H bond of CH₄ to create methyl radicals.^{5,6} Alternatively, NO₂ may react with methyl radicals formed by another means to produce nitromethane.^{6–9} NO₂ could also couple with a species containing a C–N bond, such as nitromethane.⁵

In this study, we examine the reaction of NO₂ with adsorbed methoxy (OCH₃) on oxidized Mo(110) in order to address the general question of how NO₂ modifies the decomposition pathway of surface-bound intermediates. The thin-film oxide is comprised of oxygen in high coordination sites but not terminal sites. Methoxy was studied because it forms methyl radicals on oxidized Mo(110).¹⁰ Methoxy decomposes to methyl radicals and adsorbed oxygen on oxidized Mo(110) above 500

K under ultrahigh vacuum conditions.¹¹ There is also some decomposition to H₂. No oxygenates are detected.¹¹ It is important to note here that methoxy decomposition to methyl radicals on our Mo(110) thin-film oxide is an unusual result. Formaldehyde is the predominant product of methoxy decomposition over more highly oxidized films¹² and over MoO₃.¹³

The presence of NO₂ and intermediates formed on the methoxy-precovered thin-film oxide changes the product distribution in that formaldehyde is evolved. The yield of methyl radicals is concomitantly decreased by ~20%. No water is evolved from methoxy or from methoxy in the presence of NO₂. A small amount of H₂ is evolved from methoxy, irrespective of the presence or absence of NO₂. We attribute formaldehyde production to the deposition of surface oxygen during the reduction of NO₂. NO₂ readily deposits oxygen on oxidized Mo(110).¹⁴ Gaseous N₂ and NO are also produced from NO₂. On the methoxy-precovered surface, no N₂ forms but molecular NO₂ desorption increases. Insights regarding the interaction of NO₂ with oxidized Mo(110) and with oxygenates may also be applicable to reactions of NO₂ with C–N-bond-containing intermediates.

Experimental Section

All experiments were performed in a stainless steel ultrahigh vacuum chamber with a base pressure of $<1 \times 10^{-10}$ Torr, described previously.¹⁵ It is equipped with a quadrupole mass spectrometer (UTI model 100C), an Auger electron spectrometer, and low-energy electron diffraction optics (LEED). It is interfaced with a clean-air-purged Fourier transform infrared spectrometer (Thermo Nicolet Nexus 670).

The thin-film oxide was prepared by directed dosing of O₂ at 1200 K and subsequent heating to 1400 K ($dT/dt \sim 20$ K/s). The crystal was positioned ~3 mm away from the doser, and

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the oxygen dose was sufficient to cause the background pressure to rise by 1×10^{-9} Torr. The thin-film oxide is populated by subsurface oxygen and oxygen in high coordination sites. There is no terminal oxygen present on the surface.¹⁶

NO_2 was used as it was received from Specialty Gases. NO_2 was introduced to the chamber through a stainless steel manifold and doser. The crystal was biased at -90 V during dosing to prevent electrons from the ion gauge from inducing NO_2 reaction, as observed during dosing of nitromethane (CH_3NO_2).¹⁷ The manifold and doser were prepared so as to prevent NO_2 reaction with walls. Specifically, all conflat connections were made with gold-plated copper gaskets, and all stainless steel surfaces were heated to 100°C for ~ 2.5 h in the presence of NO_2 . Purity of the NO_2 dosed through the specially prepared manifold was confirmed by mass spectrometry of NO_2 condensed on the surface. A trap containing oxide ceramics (MgO pellets), installed before the turbo and mechanical pumps, was used to prevent contact between pumps and NO_2 .

Methanol (CH_3OH , 100.0%, Mallinckrodt) was stored over molecular sieves in a glass equilibration flask. The compound was purified each day through multiple freeze–pump–thaw cycles, and purity was confirmed by mass spectrometry. The methoxy (OCH_3) overlayer was created by dosing a small multilayer of methanol at 100 K and then heating to 500 K ($dT/dt \sim 10$ K/s). This procedure desorbs molecular methanol and water, leaving only methoxy on the surface.

Temperature-programmed reaction experiments were performed with the crystal biased at -90 V and positioned ~ 3 mm away from the aperture of the mass spectrometer shield. To reach temperatures of 800 K, radiative heating was used ($dT/dt \sim 10$ K/s). To reach temperatures of 1400 K, electron bombardment heating was used. The electron bombardment heating rate was nonlinear but reproducible ($dT/dt \sim 10$ K/s average).

Reflection absorption infrared spectroscopy experiments were performed with the crystal temperature at ~ 120 K and at a resolution of 4 cm^{-1} . Data and background collection entailed 500 scans. The liquid-nitrogen-cooled semiconductor photodiode MCT-A detector resided in a N_2 -purged, CO_2 - and water-free box.

Results

Temperature-Programmed Reaction. The presence of NO_2 qualitatively alters the product distribution of methoxy reaction on the thin-film oxide grown on Mo(110). The only carbon-containing product observed in the temperature-programmed reaction of methoxy on the thin-film oxide is methyl radical, in a peak at ~ 600 K (Figure 1). Methyl radical has been identified previously on the basis of the ($m/z = 15$):($m/z = 16$) ratio.¹⁶ Methoxy on Mo(110) has been characterized by infrared spectroscopy.¹⁸ In contrast, formaldehyde is detected at 575 K during temperature-programmed reaction experiments performed after adsorption of NO_2 at 110 K (saturation dose) on a surface containing methoxy (saturation coverage) (Figure 1). Concomitantly, the amount of methyl radical evolved decreases by $\sim 20\%$ and the peak temperature for methyl radical evolution increases to 625 K. Though formaldehyde has not been observed previously in our work with methoxy on the thin-film oxide, it is evolved from molybdenum oxides created under stronger oxidizing conditions¹² and for methane reaction on MoO_3 .¹⁹

No CH_2^{18}O ($m/z = 32$) is detected for the reaction of CH_3^{16}O in the presence of NO_2 on an ^{18}O -labeled thin-film oxide on Mo(110). Yields of CH_2^{18}O as low as $\sim 15\%$ of the actual

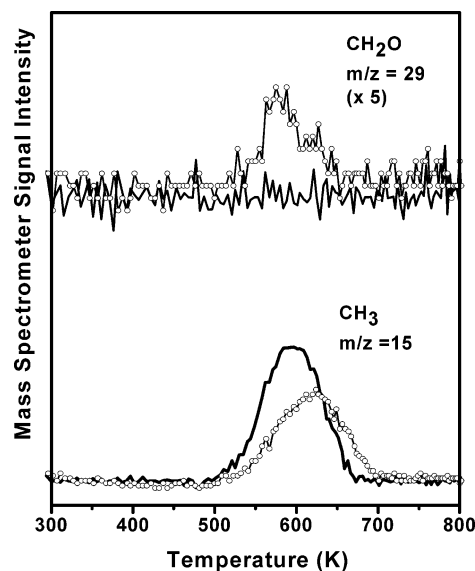


Figure 1. Temperature-programmed reaction data obtained after formation of a saturated layer of OCH_3 from methanol on a thin-film oxide formed on Mo(110): as prepared (solid line) and after exposure to NO_2 at 100 K (open circles).

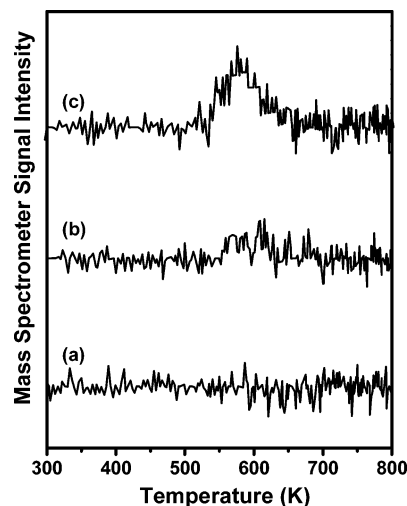


Figure 2. The formaldehyde trace (CH_2O , $m/z = 29$) obtained during temperature-programmed reaction of a saturation coverage of methoxy on the thin-film oxide that has been exposed to (a) O_2 , (b) NO , and (c) NO_2 . O_2 , NO , and NO_2 exposures were equal to saturation coverage.

CH_2^{16}O yield would be detectable, indicating that the lack of observed CH_2^{18}O is not likely due to signal-to-noise limitations.

No formaldehyde is detected from the reaction following coadsorption of O_2 with methoxy at 110 K (Figure 2). Only a trace amount of formaldehyde is observed following the coadsorption of NO with methoxy at 110 K. Hence, NO_2 is distinct in its ability to promote formaldehyde evolution. The amount of methyl radical evolved from the reaction of methoxy in the presence of NO and O_2 is essentially the same as the amount evolved from the as-prepared oxide. This provides further evidence that neither O_2 nor NO exerts significant control over the reaction pathway of methoxy.

A small amount of dihydrogen is also detected between 350 and 550 K from methoxy reaction, both in the presence and in the absence of NO_2 . NO_2 does not induce any detectable perturbation in the dihydrogen trace (data not shown). Whether or not NO_2 is present, no water is detected. However, it is important to note here that the possibility of water evolution cannot be ruled out due to the rising background of the $m/z =$

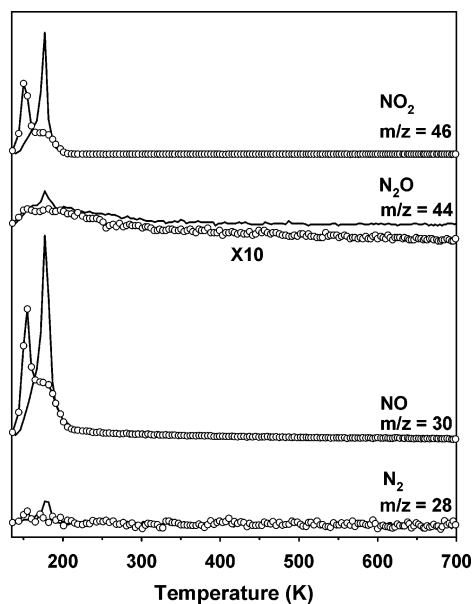


Figure 3. Nitrogen-containing species evolved during temperature-programmed reaction on a thin-film oxide formed on Mo(110) for NO₂ alone (solid line) and NO₂ exposed to the surface saturated with methoxy (open circles). The NO₂ coverage is approximately equal to saturation. The data are not corrected for fragmentation.

TABLE 1: Relative Yields^a of Products from NO₂ Reaction on a Thin-Film Oxide Formed on Mo(110) and on a Methoxy-Precovered Thin-Film Oxide Grown on Mo(110)

	N ₂	NO	N ₂ O	NO ₂ ^b
NO ₂ /thin-film oxide	0.13	0.57	0.04	0.27
NO ₂ /OCH ₃ /thin-film oxide	0.00	0.51	0.05	0.44

^a Yields are expressed as a fraction of total reaction on each surface. Traces are corrected for fragmentation from higher masses, but not for ionization efficiency differences. ^b NO₂ ~ saturation coverage.

18 trace. As such, it is possible that a small amount of hydrogen leaves the surface via water evolution but goes undetected.

The selectivity for reduction of NO₂ decreases in the presence of methoxy as the proportion of molecular desorption increases (Figure 3, Table 1), signifying a lower capacity for oxygen uptake when methoxy is present. The amount of NO and N₂O formed are essentially the same with and without methoxy; however, no N₂ is produced from NO₂ reduction in the presence of methoxy. Furthermore, the NO₂ dose required to saturate the first layer of NO₂ is lower in the presence of methoxy than on the as-prepared oxide.

Infrared Spectroscopy. No new intermediates are detected on the surface by infrared spectroscopy when NO₂ is exposed to oxidized Mo(110) covered with methoxy at 110 K (Figure 4, Table 2). All peaks are assigned to methoxy and species arising from NO₂ reaction. The assignments of species derived from NO₂-N₂O₄, monomeric NO, and terminal oxygen are based on previous detailed studies of NO₂ on this surface.²⁰ With the exception of the $\nu(\text{C}-\text{O})$, the methoxy bands do not shift significantly when exposed to NO₂ (Figure 4, Table 2). There are no measurable shifts in any peaks associated with NO₂ upon isotopic labeling. The peak at $\sim 980 \text{ cm}^{-1}$ is sensitive to isotopic labeling.

There is also no evidence for formation of new surface intermediates upon heating to 500 K, after the point of all NO_x desorption, and at the temperature immediately preceding formaldehyde evolution (Figure 5, Table 3). The C-H stretch bands and the overtone of the CH₃ deformation mode are the same whether or not NO₂ was present on the surface prior to

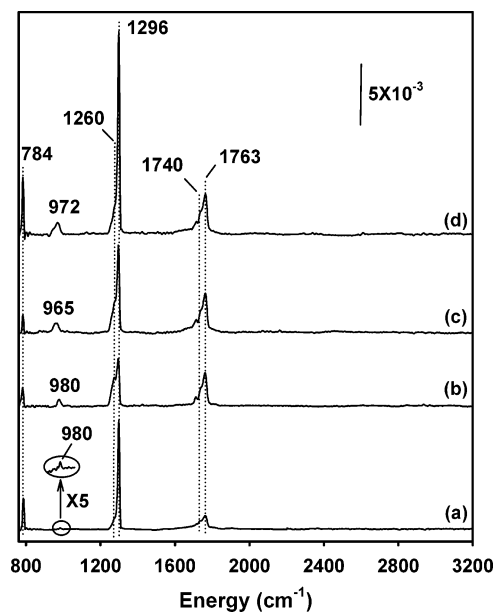


Figure 4. Infrared spectra of the region from 750 to 3200 cm⁻¹ obtained after adsorption of various species onto a thin-film oxide of Mo(110): (a) NO₂, (b) NO₂ exposed to a surface saturated with OCH₃, (c) NO₂ exposed to a surface saturated with OCH₃, and (d) NO₂ exposed to OCH₃ on an ¹⁸O-labeled thin-film oxide. All data collected for the surfaces as prepared at 100 K.

heating (Figure 5, Table 3). These bands are sensitive to molecular symmetry and to carbon coordination. No $\nu(\text{O}-\text{H})$ is detected. Furthermore, there are no detectable NO_x species present. However, there is a shoulder on the band in the $\nu(\text{C}-\text{O})$ region at 1020 cm⁻¹ when CH₃O exposed to NO₂ is heated to 500 K. Methoxy itself has a sharp, characteristic feature at 987 cm⁻¹. In the reaction of deuterated methanol (CD₃O) in the presence of NO₂, the sharp peak appears at 984 cm⁻¹, while the feature at 1020 cm⁻¹ remains in its original position (Figure 5). As such, the 987 cm⁻¹ peak is assigned primarily to the $\nu(\text{C}-\text{O})$ of methoxy, while the 1020 cm⁻¹ is assigned to Mo=O. On the ¹⁸O-labeled surface there is again a band at 987 cm⁻¹ (Figure 5). The shoulders of the peak now include both the band at 1020 cm⁻¹ and one at 955 cm⁻¹. Oxygen is labile on the Mo surface at 500 K,²¹ so it is expected that there will be terminal oxygen features corresponding to Mo=¹⁶O (from NO₂, $\sim 1020 \text{ cm}^{-1}$) and to Mo=¹⁸O (from displaced surface oxygen, 955 cm⁻¹). Since the sharp peak (987 cm⁻¹) is the same on the ¹⁶O and the ¹⁸O-labeled surfaces, it must be due primarily to the intact C-O bond of methoxy.

While the peak near 980 cm⁻¹ is assigned primarily to the $\nu(\text{C}-\text{O})$ of methoxy, its exact position is the result of a combination of the $\nu(\text{C}-\text{O})$ band of methoxy and the $\nu(\text{Mo}=\text{O})$. Importantly, the spectrum obtained after heating methoxy in the presence of NO₂ is reproduced by adding spectra produced by heating the pure components to 500 K (Figure 6). For example, the band from OCD₃ in the presence of NO₂ is at 984 cm⁻¹, which is downshifted from the $\nu(\text{C}-\text{O})$ of OCD₃ by only 3 cm⁻¹ (Figure 6). The position of the terminal oxygen stretch from NO₂ alone is 981 cm⁻¹, and the position of the $\nu(\text{C}-\text{O})$ from OCD₃ alone is 987 cm⁻¹. When these two spectra are added together mathematically, the 987 cm⁻¹ band shifts to 984 cm⁻¹ as observed in the spectrum of OCD₃ in the presence of NO₂.

The terminal oxygen species present after the reaction of OCH₃ in the presence of NO₂ are different from those present after the reaction of NO₂ alone (Figure 7). The reaction of NO₂ on the thin-film oxide deposits three types of terminal oxygen

TABLE 2: NO₂ on a Methoxy-Precovered Thin-Film Oxide As Prepared at 110 K^a

assignment	NO ₂ /OCH ₃ / thin-film oxide	NO ₂ /OCD ₃ / thin-film oxide	NO ₂ /OCH ₃ / ¹⁸ O-labeled thin-film oxide	NO ₂ on thin-film oxide of Mo(110) ^b	OCH ₃ / thin-film oxide ^b
δ(NO ₂)	784	965	972		996
δ _s (CH ₃)					1423
ν _s (CH)					2817
2δ _a (CH ₃)					2860
ν _a (CH)					2935
ν _s (NO ₂) of N ₂ O ₄ monolayer	1260	1260	1260	1260	
ν _s (NO ₂) of N ₂ O ₄ multilayer	1296	1296	1296	1296	
ν(NO) of monomeric NO	1740	1740	1740	1740	
ν _{as} (NO ₂) of N ₂ O ₄ multilayer	1763	1763	1763	1763	

^a All values in cm⁻¹. ^b Ref 20. ^c Refs 27,28.

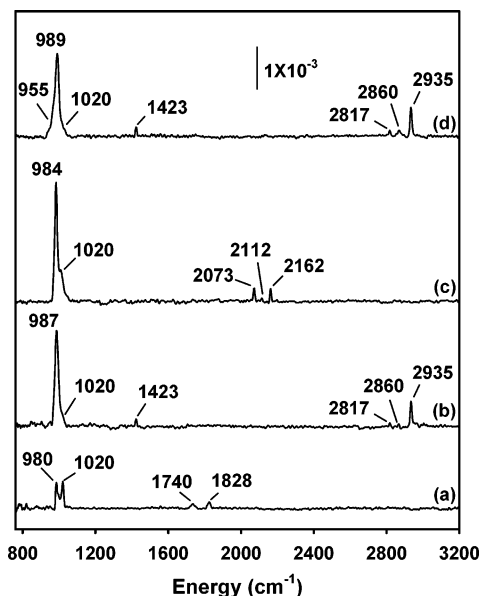


Figure 5. Infrared spectra showing the effect of heating various mixtures adsorbed on a thin-film oxide of Mo(110) to 500 K: (a) saturation coverage of NO₂, (b) NO₂ exposed to a surface saturated with OCH₃, (c) NO₂ exposed to a surface saturated with OCD₃, (d) NO₂ exposed to a saturated layer of OCH₃ on an ¹⁸O-labeled thin-film oxide. All spectra are taken after cooling to 110 K.

signified by peaks at 985, 999, and 1026 cm⁻¹. The most intense peak is at 985 cm⁻¹, which has been previously assigned to Mo=O adjacent to vacancies.²¹ After the reaction of OCH₃ in the presence of NO₂, peaks at 984, 999, and 1026 cm⁻¹ are again visible, but the intensity of the 984 cm⁻¹ peak is less than that of the 999 cm⁻¹ peak; this indicates that the majority of terminal oxygen now resides on terrace sites.²¹

Discussion

Coadsorption of NO₂ and methoxy on the thin-film oxide formed on Mo(110) changes the reaction path of both adsorbates such that reduction of NO₂ decreases while oxygenate formation from OCH₃ increases. Formaldehyde production occurs after the desorption of all NO₂; therefore, the change in oxygen distribution and the change in surface oxidation state are responsible for the reactivity change. Oxidation of the surface by NO₂ may favor formaldehyde evolution by reducing the number of available sites for methoxy to leave behind oxygen via C–O bond scission (and methyl radical evolution). It may also create an overall higher oxidation state for surface Mo atoms. This increased oxidation state likely favors formaldehyde evolution, a behavior characteristic of MoO₃¹³ rather than zerovalent Mo.¹¹ Indeed, previous studies showed that NO₂ could produce MoO₂ on Mo(110).²²

Importantly, formaldehyde is formed from dehydrogenation of methoxy with C–O bond retention. Given the lability of oxygen at the temperature of formaldehyde evolution,²¹ the absence of CH₂¹⁸O when methoxy reacts in the presence of NO₂ on the ¹⁸O-labeled thin-film oxide is strong evidence that formaldehyde is formed via a C–O bond retention mechanism rather than via methyl radical addition to surface oxygen. Further evidence for C–O bond retention is provided by comparing the formaldehyde yields from CH₃NO₂ and from OCH₃ in the presence of NO₂. The yield of CH₂O from a saturation coverage of CH₃NO₂ is ~20% less than the yield from OCH₃ reaction in the presence of NO₂, indicating that a large (and hence spectroscopically detectable) amount of nitromethane would have to be created to account for all the formaldehyde produced.²³

There is no infrared evidence for a stable O–H species formed from the hydrogen lost during the evolution of formaldehyde. Indeed, O–H is not usually observed on oxygen-modified Mo(110) beyond 500 K.²⁴ We believe that the hydrogen lost may be evolved as a small amount of water. However, detection of this water is difficult due to its small quantity and to the rising background of the water trace in our mass spectra.

The decrease in the yields of reduction products from NO₂ when it reacts in the presence of OCH₃ indicates that the surface has less capacity to accept oxygen, possibly due to site blocking by methoxy.²⁵ The proposed site-blocking effect is corroborated by the fact that the amount of terminal oxygen deposited from NO₂ reaction at 110 K in the presence of OCH₃ is ~10% less than that in the absence of methoxy. Furthermore, there are no NO-containing species present after heating to 500 K when NO₂ reacts in the presence of methoxy, whereas monomeric and dinitrosyl forms of NO are present when NO₂ reacts on the surface with no coadsorbed species. These observations are consistent with fewer coordination sites available for NO_x species when methoxy is present.

The terminal oxygen present after the reaction of NO₂ on the clean thin-film oxide resides primarily at sites adjacent to vacancies, indicating that reduction may occur preferentially at these sites. In the presence of methoxy, a certain proportion of those sites are blocked which may diminish complete reduction. This result is important in the context of the alkane-assisted reduction of NO_x in that it highlights the need for oxygenates to carry oxygen away from high coordination sites. In the absence of such a mechanism, full reduction occurs less readily.

Our results suggest that the selectivity for oxygenate formation in hydrocarbon oxidation is sensitive to the distribution of oxygen on the surface. A strong oxidizing agent, such as NO₂, may create an environment where partial oxidation occurs. These results show one mechanism by which NO₂ can perturb surface

TABLE 3: Vibrational Assignments for NO₂ on a Methoxy-Precovered Thin-Film Oxide^{a,b}

assignment	NO ₂ /OCH ₃ / thin-film oxide	NO ₂ /OCD ₃ / thin-film oxide	NO ₂ /OCH ₃ / ¹⁸ O-labeled thin-film oxide	OCD ₃ / thin-film oxide (this work) ^c
δ _s (NO ₂)	784	784		
ν(CO)	987	984	989	987
ν(Mo=O)	1020	1020	955, 1020	
δ _s (CH ₃)	1423	1423	1423	
ν _s (CH)	2817	2073	2817	2073
2δ _a (CH ₃)	2860	2112	2860	2112
ν _a (CH)	2935	2162	2935	2162

^a Surfaces are prepared at 100 K and subsequently heated to 500 K. ^b All frequencies in cm⁻¹. ^c Vibrational assignments for OCH₃/thin-film oxide are in Table 2.

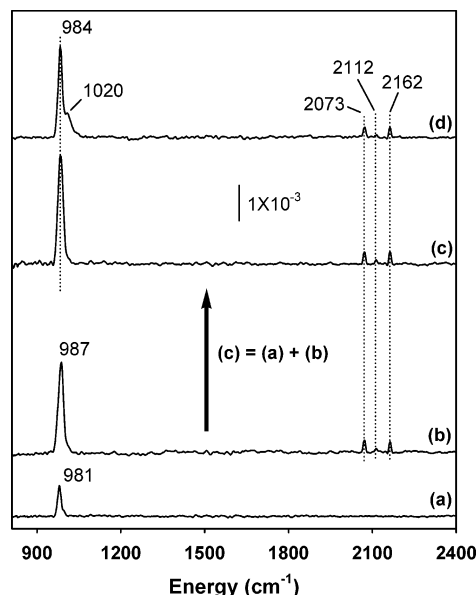


Figure 6. Infrared spectra of the ν(Mo=O) region obtained after (a) heating a low coverage of NO₂ to 500 K, (b) creating a saturated layer of CD₃O by heating CD₃OH to 500 K, (c) adding spectra (a) + (b), and (d) exposing NO₂ to a saturated layer of CD₃O at 100 K and subsequently heated to 500 K.

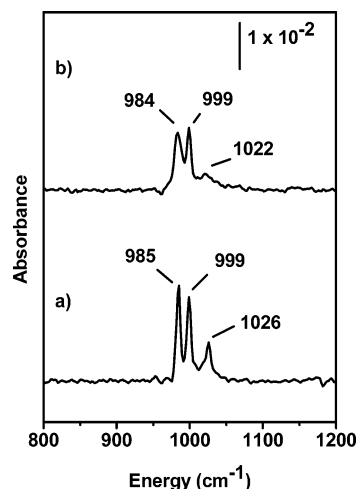


Figure 7. The ν(Mo=O) region obtained after heating to 800 K: (a) saturation coverage of NO₂, (b) a saturated layer of NO₂ exposed to the surface covered with CH₃O formed from CH₃OH.

reactions. Importantly, we find no evidence that NO₂ reacts directly or complexes with methoxy on the surface, as has been suggested by others.²⁶ This suggests that oxygen distribution and oxidation state, which are controlled by the species present during reaction, are most important in determining reaction selectivity. Of course, while this result is definitive for the ultrahigh vacuum conditions under which we have conducted

our study, we cannot completely rule out the possibility of direct reaction between NO₂ and hydrocarbons under high or even ambient pressures of NO₂.

Conclusions

The presence of methoxy decreases the amount of NO₂ reduction. Simultaneously, the presence of NO₂ changes the surface such that OCH₃ reaction leads to formaldehyde evolution. The complete reduction of NO₂ to N₂ is inhibited by blockage of high coordination site vacancies, underscoring the importance of such vacancies for complete reduction. Our results indicate that selectivity for hydrocarbon oxidation and NO_x reduction is sensitive to the distribution and total amount of oxygen present and that the nature of the oxidizing agent can play a pivotal role in determining the state of the surface.

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