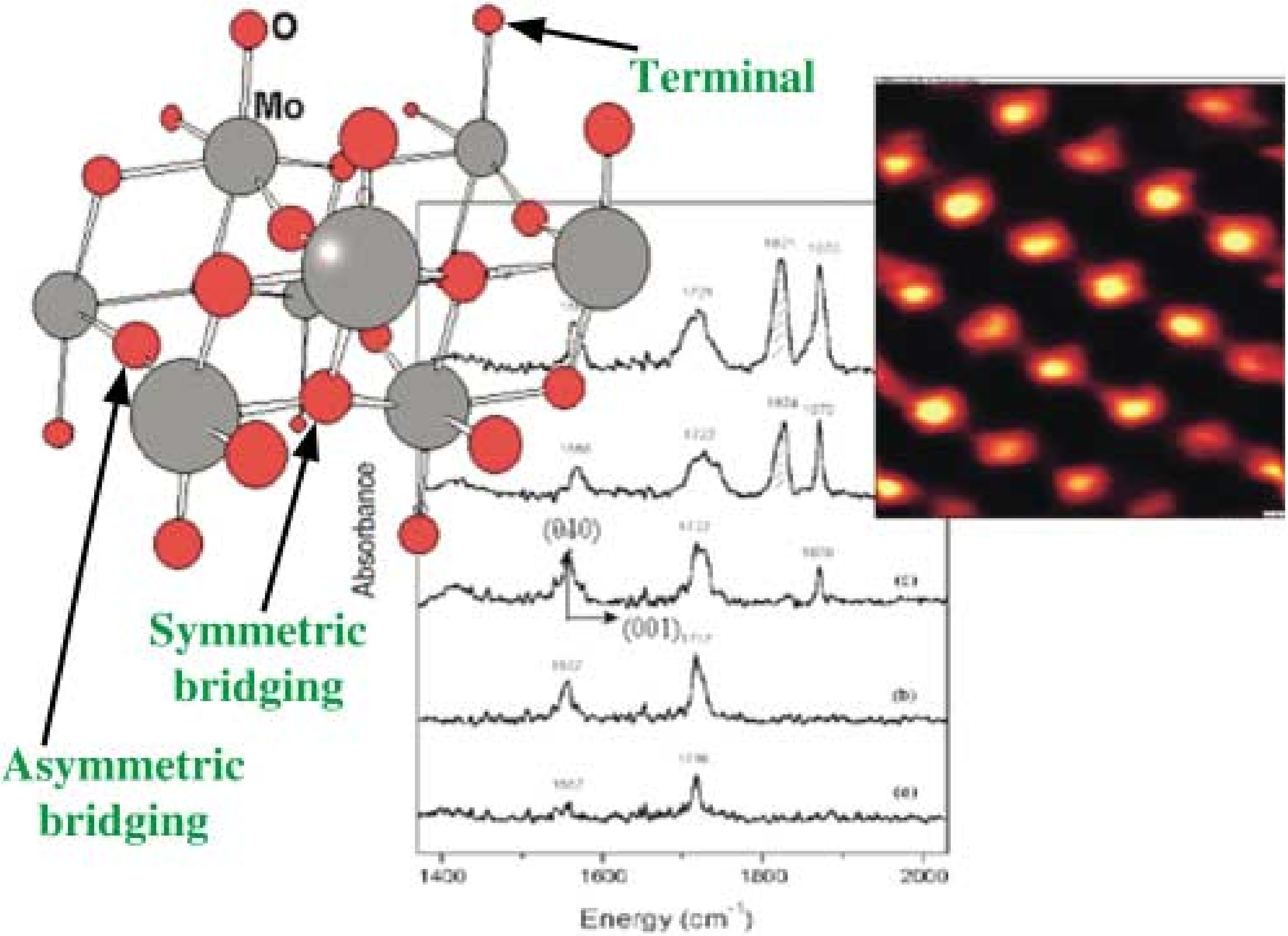

Molybdenum trioxide is a potential catalyst for the reduction of NO_x species that arise from combustion. Surface reactions contribute to elementary steps in the overall reduction, however, due to the complex nature of the catalyst, it is not possible to study specific elementary steps. By forming a thin film on a single crystal of the Mo(110) substrate to model one type of MoO_3 surface, reaction intermediates can be identified by, among other techniques, vibrational spectroscopy.

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Site-Selective Surface Reactions: Nitric Oxide Reduction on Mo(110)

Katherine Queeney[a] and Cynthia M. Friend*[a]

The catalytic reduction of NO_x compounds formed in combustion processes is a critical factor in maintaining a clean environment. The introduction of the "catalytic converter" has been extremely effective in reducing these pollutants in automobile exhaust over the last two decades. Nevertheless, new environmental regulations have necessitated the development of processes that operate over a wider range of conditions and that are more efficient, so that NO_x emissions can be reduced further. The need for new catalysts and processes has motivated a considerable number of studies of NO reduction using metal oxides as catalysts. In order to better understand the mechanisms for NO reduction on oxides, we have systematically studied the reactions of NO on thin-film oxides grown on Mo(110). By using a thin-film oxide, we are able to change the type of coordination sites that are available for NO binding and to use surface-sensitive spectroscopies to identify intermediates on the surface. We specifically explore the role of low-temperature NO coupling to a dinitrosyl species in our work and contrast this reaction to the higher temperature process, NO dissociation followed by nitrogen atom coupling.

KEYWORDS:

nitrogen oxides · heterogeneous catalysis · surface chemistry · vibrational spectroscopy

1. Introduction

The increasing emphasis on emissions control, spurred by concern for the global environment, has rendered certain catalytic processes among the most important global technologies. Of paramount importance in reaching the goals for improved emissions standards is improvement in heterogeneous catalysts for NO reduction in automotive exhausts and power plants. Such an improvement would take the form of catalysts that operate efficiently both at lower temperatures and over a wider range of reaction conditions than existing catalysts (for example, in fuel/air mixtures in the case of automobile exhaust). Recent work has focused on the use of metal-oxide based catalysts for NO reduction,[1–6] since some of these materials have shown promise for satisfying the above requirements at a relatively low cost.

The three-way catalyst currently used in catalytic converters for automobile exhaust contains rhodium, platinum, and palladium, in which rhodium the essential component for NO_x reduction. This system is less than optimal because of both the high cost of rhodium and the narrow window of operating conditions under which efficient NO reduction takes place.[7]

Several studies have shown that, upon addition of even small amounts of MoO_3 to Rh-,[8] Pt-,[9] and Pd-based catalysts,[10–12] the activity of those catalysts for NO reduction is improved. Specifically, the addition of MoO_3 reduced the proportion of NO detectable in the product stream relative to that achieved in the absence of MoO_3. Since NO is known to form dinitrosyl species (Figure 1) on MoO_3 and MoO_3-containing catalysts,[9, 13–16] the coupling of two intact NO molecules on a single catalytic site has been proposed[9] to favor N–N bond formation and NO reduction. While this model makes intuitive sense, it is important to note that there is no *direct* evidence from the aforementioned catalytic studies to link dinitrosyl formation to improved efficiency in NO reduction.

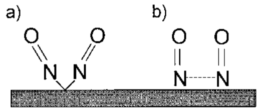

Figure 1. Schematic representation of NO coupling in a) surface dinitrosyl species and b) condensed-phase type NO dimers.

The possibility that direct N–N coupling leads to NO reduction frames a rather general question in NO surface reactions: Is it more favorable to form N–N bonds via a dissociative pathway—such as the reaction of adsorbed nitrogen atoms either with itself or with NO—or via the reaction of two intact NO molecules? In this Review, we illustrate how ultrahigh vacuum, single-crystal studies can be used to elucidate fundamental details about site selectivity in surface reactions. Specifically, we examine possible mechanisms for the low temperature reduction of NO on oxidized molybdenum to see how the presence of MoO_3 might enhance the NO-reduction activity of noble-metal catalysts.

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The reduction of NO induced by MoO_3 is an example of a complex system that is difficult to understand on a molecular level. Molybdenum trioxide is a layered material with a distorted perovskite lattice, which has three types of oxygen atom coordination: a twofold-coordinated asymmetric bridging oxygen, a threefold-coordinated symmetric bridging oxygen, and the singly coordinated terminal oxygen, $Mo{=}O$. Furthermore, oxygen vacancies, generally thought to be required for catalytic processes on oxides, are also typically present in catalysts that contain MoO_3. In addition to the structural complexity of MoO_3, the high pressures and temperatures used for actual catalytic reactions result in a complex mixture of gas-phase and adsorbed species, which make it virtually impossible to investigate individual elementary steps.

Cynthia Friend
is recognized for her research studying complex reactions occurring on solid surfaces. She joined the Harvard faculty in 1982 after receiving her Ph.D. in Physical Chemistry from the University of California, Berkeley, and doing postdoctoral research at Stanford University. She was promoted to Full Professor at Harvard University in 1989 and is now the Theodore William Richards Professor of Chemistry. In her current research, she studies the mechanisms of reactions important in semiconductor device fabrication and heterogeneous catalysis. Prof. Friend has received several honors recognizing her research, which include the 1991 Garvan Medal of the American Chemical Society, the 1991 Iota Sigma Pi Agnes Fay Morgan Research Award in Chemistry, the 1990 Distinguished Young Alumna Award, University of California, Davis, and a Union Carbide Innovation Recognition Award in 1988 – 89. She is also featured as a "host scientist" in the "Science in American Life" exhibit at the Smithsonian Institution.

Kate Queeney
received her B.A. in Chemistry from Williams College in 1992 and her Ph.D. from Harvard University in 1998. Her thesis work with Prof. Friend, including the studies described in this article, focused on the role of surface oxygen in a variety of catalytically-relevant reactions on Mo(110). After a postdoctoral period at Bell Labs, using surface infrared spectroscopy to investigate silicon passivation, she joined the chemistry department at Smith College as an assistant professor. Her current research centers on studies of surface chemistry at solid/liquid interfaces under ambient conditions.

The approach we have taken to studying the elementary steps important in processes on metal oxide surfaces, for example NO reduction, is to synthesize model systems using controlled oxidation of a metal surface. This approach, used by us and others,[17, 18] offers the additional advantage that electron-based surface spectroscopies can be applied to the investigation of these processes. By varying the conditions for Mo(110) oxidation, we are able to control not only the extent of Mo oxidation but also the structure of the surface oxide, since oxygen atoms occupy different coordination sites depending on the exact oxidation protocol followed.[19]

While the surface chemistry of a bulk oxide material, such as MoO_3, is, naturally, distinct from that of its component metal, our model system provides insight into how the geometric and electronic properties of different coordination sites affect specific elementary steps. Furthermore, the use of an oxidized single crystal allows us to regenerate the surface for a series of comparative studies. A link between the behavior of our model oxides and that of MoO_3 itself is provided by companion theoretical studies that probe the effect of specific oxygen vacancies in MoO_3 both on oxide electronic structure and on the resultant NO reduction chemistry. This information can then be used to guide thinking about the analogous steps in the related catalytic process.

Our work shows that dinitrosyl species do, in fact, form on both clean and oxidized Mo(110) under ultrahigh vacuum conditions. Furthermore, these intermediates lead to N–N bond formation and to the evolution of gas-phase reduction products. Surface vibrational spectroscopy not only demonstrates the existence of dinitrosyl species but also sheds light on the role of surface oxygen in the formation and reaction of these potential intermediates in selective catalytic reduction of NO. Our theoretical studies of dinitrosyl binding to MoO_3 provide a picture of the bonding interactions that are important in N–N coupling, as well as insight into the mechanism for their formation.

We have subsequently made use of our detailed understanding of NO chemistry on oxidized Mo(110) to investigate the reduction of adsorbed NO by alkyl species. Methane (CH_4) has shown promise as a reducing agent for NO over a variety of metal oxide catalysts,[1, 2, 4–6] to potentially offer a cheaper, safer, and more effective route than current technologies used for NO reduction in both automobile and stationary sources of NO_x emissions. Since the active alkyl species in these reactions are thought to be gas-phase methyl radicals ($^{\bullet}CH_3$), our studies focus on the elementary step of the $^{\bullet}CH_3$ reaction with adsorbed NO on a range of oxidized Mo(110) surfaces. We find that $^{\bullet}CH_3$ reacts preferentially with molecular NO species on oxidized Mo(110). At low temperature, there is a loss of NO_x species, which suggests that coupled NO species are also potentially important in the reduction of NO in the presence of hydrocarbons.

2. NO Reduction: Dissociation versus Dinitrosyl Formation

Pathways to selective catalytic reduction of NO can be divided into two general classes: dissociative and molecular. In the first class, the catalyst dissociates NO into its constituent N and O atoms, with surface-bound atomic N subsequently undergoing N—N bond formation; in the second case, NO binds as a molecular species and the catalyst induces N—N bond formation directly from this molecular precursor. Our studies of NO reduction on oxidized Mo(110) demonstrate that both pathways operate and that their relative importance depends on the number of vacant coordination sites that can accept the dissociation products, O_a and N_a. Molecular pathways can lead to the evolution of both N_2 and N_2O from the surface; in fact, both of these products are observed for a range of surface oxidation conditions on Mo(110). As with NO dissociation, the branching ratio for N_2 versus N_2O production also depends on the availability of vacant oxygen coordination sites. Taken together, our results indicate that molecular pathways may be more important for efficient NO reduction over oxide catalysts and that the electronic structure of the oxide catalyst is instrumental in accessing the molecular reduction pathway. These conclusions are based on a combination of experimental and theoretical studies, which are discussed below.

2.1. NO Reaction on Mo(110): The Dissociative Pathway

Dissociation of NO is known to occur on a variety of transition metal surfaces and ultimately leads to NO reduction to N_2 via recombination of nitrogen atoms. However, nitrogen atom recombination is often a very thermally active process on surfaces that are capable of NO dissociation, since the strong metal-nitrogen bond that promotes the production of N_a from NO_a leads to a high energy barrier for nitrogen atom diffusion. For example, N_2 is formed from the coupling of nitrogen atoms above 1000 K on Mo(110), at 805 K on Pd(100),[20] and at 770 K on Rh(100).[21] Another limitation of the dissociative pathway for N_2 formation is its requirement for open coordination sites to accommodate nitrogen and oxygen atoms—four sites for a completely dissociative pathway versus two sites for reaction of two intact NO molecules.

The reaction of NO on Mo(110) allows direct comparison of dissociative versus nondissociative NO reduction, since both reaction pathways are accessable on this surface. Nitric oxide dissociates even at 100 K on clean Mo(110), which subsequently leads to nitrogen atom recombination and N_2 evolution at $\approx$1200 K. The amount of NO dissociation on clean Mo(110) is self-limiting and is at least in part related to the availability of open coordination sites for the dissociation products, N_a and O_a, as discussed below. It is also possible that the dissociation products change the electronic properties of the surface, which thereby helps inhibit dissociation by altering the extent of intramolecular bond weakening in adsorbed NO. The existence of such an indirect electronic effect is supported by the fact that molecular NO adsorption *is* observed after some NO dissociation has taken place but while there are still open surface sites for further dissociation to occur. Notably, however, molecular NO is only stable with respect to dissociation after the surface has been at least partially oxidized, whether that oxidation takes place via NO dissociation or via deliberate preoxidation of the surface, such as through a reaction with O_2.

Dissociation of NO produces surface atomic oxygen species in both high coordination and terminal (Mo=O) configurations,[22] identified by characteristic Mo—O vibrational modes detected with high resolution electron energy loss spectroscopy (EELS; modes below 1000 cm^{-1} in Figure 2). The presence of N_a produced during NO dissociation seems to promote the formation of doubly bound Mo=O species, so-called "terminal oxygen", even at 100 K. This is particularly remarkable, since terminal oxygen species are only created under higher temperature and flux conditions when O_2 is used as the oxidant. Isotopic labeling studies reveal no vibrational modes which can be readily ascribed to surface atomic nitrogen species because of the limited resolution of EELS. Since nitrogen is clearly present on the surface, nitridation as well as oxidation of the Mo(110) surface no doubt contribute to the stabilization of molecular NO and to its subsequent reactive chemistry.

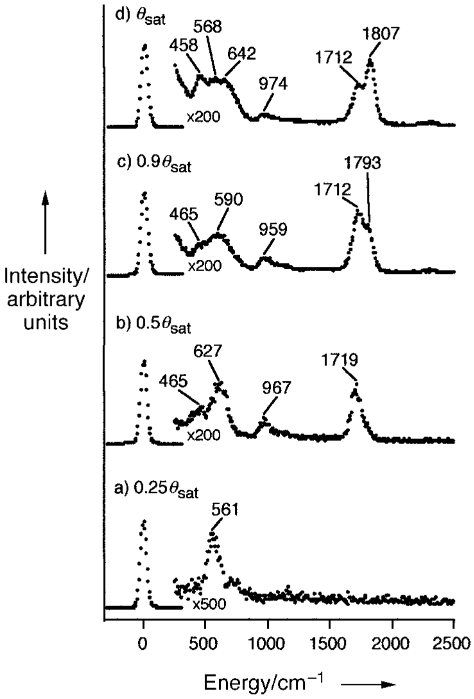

Figure 2. *Electron energy loss spectra acquired after NO adsorption at 100 K on Mo(110), with coverages corresponding to a) 0.2θ_{sat}, b) 0.35θ_{sat}, c) 0.65θ_{sat} and d) θ_{sat}. Reprinted with permission from ref. [22].*

Preoxidation of the Mo(110) surface with O_2 inhibits NO dissociation, as demonstrated by a marked decrease in the amount of recombinant N_2 formation as θ_0 is increased prior to NO exposure (Figure 3). Some evidence for a simple site-blocking mechanism is given by NO reaction on an oxygen overlayer with $\theta_0 = 0.4$ ML (θ_0 = surface coverage, ML = monolayer; Figure 3 a). On this well-defined surface, oxygen atoms

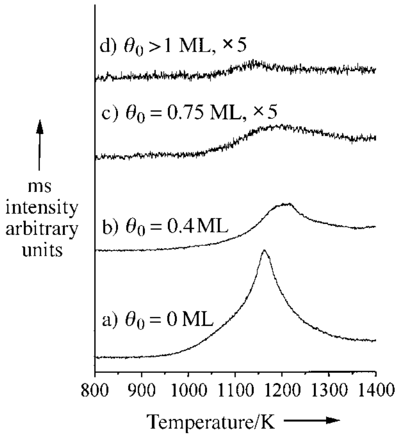

Figure 3. Temperature-programmed reaction of recombinant N_2 formation following reaction of a saturated NO overlayer on a) clean Mo(110), b) an oxygen overlayer with $\theta_0 = 0.4$ ML (see Figure 2a), c) the 0.75-ML oxygen overlayer (Figure 2b), and d) a thin-film oxide with $Mo{=}O$ species (Figure 2c). Mass-spectometric detection at $m/z = 28$. Reprinted with permission from ref. [23].

reside in long-bridge sites; EELS measurements of NO dissociation products on clean Mo(110) shows that these same bridge sites are the first ones populated by oxygen atoms from the NO dissociation.[22] The passivation of these preferred dissociation sites by atomic oxygen is consistent with the approximately 60% decrease in N—O dissociation observed on this surface. However, EELS studies that used isotopically labeled NO[23] also demonstrated that oxygen formed via NO dissociation can displace predeposited atomic oxygen from its initial binding sites, which suggests that electronic modification of the surface by O_a may also play a role in determining NO chemistry on oxygen-modified surfaces.

2.2 Molecular Pathways for NO Reduction

The potentially advantageous characteristics of direct coupling of NO *without* dissociation to nitrogen and oxygen atoms have prompted many researchers to look for evidence of such reaction pathways. There have been several studies that provide evidence of NO dimers, such as those formed in the condensed phase (Figure 1b) on transition metal surfaces above the temperature required for NO condensation. Infrared spectroscopy was used to identify NO dimers on Ag(111) at temperatures as high as 90 K, and N—N bond formation to evolve gaseous N_2O was observed from these dimer precursors.[24, 25] The same type of NO dimers on Cu(111) were subsequently observed using infrared spectroscopy.[26] The fact that the condensed-phase type dimers observed on these surfaces have ν(NO) vibrational frequencies virtually unperturbed from those of true condensed-phase dimers suggests that their interaction with silver and copper is minimal. The metal surface in this case acts more as a physical support to allow the NO molecules to assume a condensed-phase configuration at gas-phase concentrations, than as a chemical participant in the reaction. Such a weak surface/adsorbate interaction is confirmed by the low temperatures at which these species react and/or desorb, which suggests that there would be a low steady-state concentration of such species at the higher temperatures typically used for NO reduction catalysis. Therefore, this type of NO coupling is probably not an efficient route to N—N bond formation.

Dinitrosyl species, such as those identified on MoO_3, should involve stronger binding of NO to the surface, since both NO molecules are bound to a metal atom. This picture is supported by the fact that the intramolecular vibrational features of dinitrosyl species are more strongly perturbed, relative to the condensed phase, than the dimers discussed above. It is important to note, though, that while such intermediates apparently form readily under some catalytic conditions, the sterically crowded nature of dinitrosyl species does not favor their formation under conditions of extremely low pressure. Studying such species under an ultrahigh vacuum is thus intrinsically difficult; however, ultrahigh vacuum (UHV) studies provide a unique opportunity to directly correlate the presence of dinitrosyls with specific NO reaction pathways.

Although NO dissociation accounts for the majority of NO reactions on clean Mo(110) as outlined above, intact NO species are also detected with vibrational spectroscopy (Figure 2b, c). The intramolecular ν(N—O) vibration is extremely sensitive to the degree of metal–NO interaction and ν(N—O) can therefore be used to distinguish between different NO binding sites and/or orientations on the same surface. One of the intact NO species formed on Mo(110) is, indeed, the same dinitrosyl species identified previously on MoO_3 and implicated in the catalytic activity of this material. In fact, dinitrosyl species are formed on *all* Mo(110) surfaces studied, namely over a range of surface oxidation conditions, and provide a low temperature pathway to NO reduction.

While high resolution EELS spectra, such as those shown in Figure 2, allow resolution of distinct NO_a binding environments like those giving rise to $\tilde{\nu}(NO) = 1712$ and $1807\,cm^{-1}$ (Figure 2d), a more exact understanding of the nature of those binding environments can often be derived from surface infrared spectroscopy. In particular, dinitrosyl species (or any other discrete, coupled species) can be definitively identified on the basis of infrared spectra of isotopically mixed overlayers. The infrared spectrum of a saturated overlayer formed from a $\approx 1{:}1$ mixture of ^{15}NO and ^{14}NO is shown in Figure 4a iii, with spectra of both isotopically pure overlayers (Figure 4a i, ii) for comparison. As demonstrated by comparison of the experimental spectrum with a simulated spectrum and the assumption of only isolated nitrosyl species (Figure 4b), the $\tilde{\nu}(^{14}NO)$ peak at $1820\,cm^{-1}$ arises from coupled nitrosyl species; the maximum of this peak in the mixed overlayer, at $1807\,cm^{-1}$, corresponds to a $^{15}NO/^{14}NO$ pair. This general behavior of the isotopically mixed overlayer identifies the $1820\,cm^{-1}$ species as a coupled one; from the nearly exact correspondence of the vibrational peaks in Figure 5a to those in spectra of dinitrosyl species on MoO_3,[13] this peak is assigned specifically to the dinitrosyl species ($(NO)_2Mo$) on Mo(110).

The spectroscopic signature of the dinitrosyl species is identical on all Mo(110)-based oxygen-modified surfaces studied[23] and even on MoO_3. This apparent insensitivity of adsorbate intramolecular bond potentials to oxidation state is

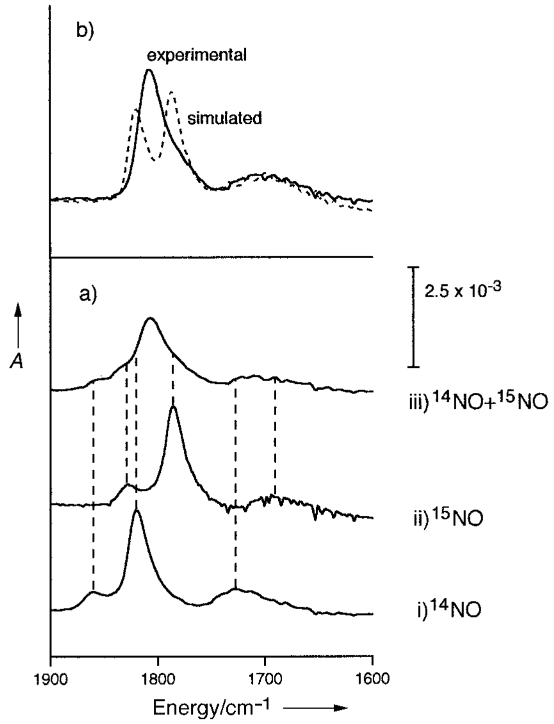

Figure 4. *Identification of surface dinitrosyl species by infrared spectroscopy. Infrared spectra of saturated NO overlayers are shown in a) after adsorption of i) pure ^{14}NO, ii) pure ^{15}NO, and iii) a 1:1 mixture of ^{14}NO + ^{15}NO. Comparison of the experimental spectrum acquired after heating the surface in (iii) to 200 K with a simulated spectrum with assumed uncoupled NO species is presented in (b). Reprinted with permission from ref. [22].*

consistent with results for methoxy (CH_3O) species formed via the reaction of methanol (CH_3OH) on these same oxygen-modified surfaces:[27] namely, that perturbation of these bond potentials is highly sensitive to local electronic structure at the bonding site but not to the overall extent of surface oxidation. What is different in the NO case, as compared to CH_3O, is that the dinitrosyl structure is apparently virtually *identical* on the clean and oxygen-modified Mo(110) surfaces, whereas there is a distinct difference between the bonding of CH_3O on clean Mo(110)[28] and on Mo(110) with even a small amount (0.5 ML) of preadsorbed oxygen. This is almost certainly due to the fact that dinitrosyl species on "clean" Mo(110) form only after approximately 0.5 ML of atomic oxygen is deposited through NO dissociation, so that the "clean" surface is in fact an oxygen-modified one. Methanol on clean Mo(110) also undergoes a significant amount of dissociation[28] but the surface oxygen created either is insufficiently high in concentration or does not populate the correct sites to influence the intramolecular potential of the methoxy adsorbent in the same manner as preadsorbed O atoms from the O_2 reaction. The significance of the apparent insensitivity of dinitrosyl formation to overall surface oxidation is that this effect suggests than even partially oxidized Mo(110) surfaces may approximate the bonding sites available on MoO_3 well enough to describe accurately the NO reduction chemistry that takes place in real catalytic systems.

Identifying dinitrosyl species on Mo(110) is the first step in understanding the role of these species in NO reduction; the well controlled conditions of UHV now allow us to correlate the formation of surface dinitrosyl species with specific reaction pathways. Indeed, dinitrosyl species which are formed on *all* Mo(110) surfaces react via N–N bond formation at relatively low temperatures, as shown by temperature-programmed reaction of isotopically mixed overlayers. For example on clean Mo(110), in addition to the high temperature recombinant N_2 formation discussed above, at high NO coverages both N_2 and N_2O evolve below 400 K along with some NO desorption (Figure 5). By predissociation of a small amount of ^{15}NO on the surface prior to the ^{14}NO reaction, we showed that N_2O production results only from the reaction of two intact NO molecules, since only $^{14}N_2O$ was evolved from the surface. Both infrared and EELS studies show a correlation between the appearance of the vibrational signature of dinitrosyl and N_2O production, which confirms that the dinitrosyl is an intermediate for N–N bond formation on Mo(110).[29] Nitrogen evolution at low temperature is shown to arise partly from reaction of NO_a with N_a but also in part from a dinitrosyl reaction.[22]

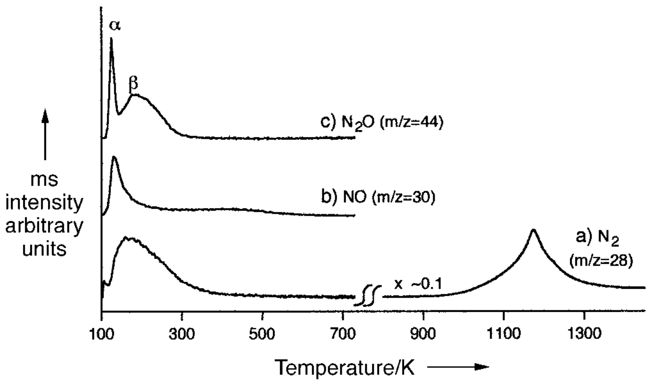

Figure 5. *Temperature-programmed reaction which shows low and high temperature reaction pathways for NO adsorbed on clean Mo(110). Reprinted with permission from ref. [22].*

While predissociation of NO or preoxidation of the surface with O_2 is required for dinitrosyl formation on Mo(110), the presence of atomic oxygen and/or nitrogen species ultimately inhibits the reaction of these NO reduction intermediates. On both the clean and oxygen-modified surfaces, the spectroscopic signature of dinitrosyl species can be detected as high as 500 K, well past the cessation of intermolecular N–N bond formation. This can be understood by recognizing that the formation of NO reduction products via any pathway involves N–O bond scission, which in turn requires empty surface sites for atomic oxygen deposition. The inability of dinitrosyl species to react at high temperatures may again be due to surface-site blocking, electronic effects, or to a combination of the two phenomena. We postulate that the unreacted dinitrosyl species contribute to the long tail of NO desorption observed at temperatures beyond N_2 and N_2O evolution (Figure 5 b).

In fact, although surface oxidation is required for dinitrosyl formation, studies of NO reaction on the various oxygen overlayers reveal that surface oxidation also favors desorption of intact NO rather than NO reduction (Table 1). The increasing

Table 1. *Relative yields of products from NO reaction on clean and oxygen-modified Mo(110) surfaces.*[a, b]

θ_O	N_2O	N_2[c]	NO	N_2[d]	Total reaction[e]
0 ML	0.13	0.11	0.03	0.73	1.00
0.75 ML	0.35	0.28	0.23	0.14	0.23
>1 ML	0.29	0.25	0.46	0.00	0.36

[a] Table adapted with permission from ref. 23. [b] Yields of individual products are expressed as percentages of the total reaction for that surface. [c] At low temperatures. [d] From recombination. [e] The amount of total reaction on each surface is normalized to unity on clean Mo(110).

dominance of NO desorption with increasing θ_0 is largely due to the stabilization of new mononitrosyl species on the oxygen-modified surfaces. The temperature-dependent infrared spectra of saturated NO overlayers on an oxygen overlayer with $\theta_0 =$ 0.75 ML oxygen overlayer and on a thin-film oxide formed by higher-temperature O_2 exposure ($\theta_0 > 1$ ML) are shown in Figure 6; note the appearance of manifold ν(NO) signatures that are not detected after NO adsorption on clean Mo(110) (Figure 4 a i).

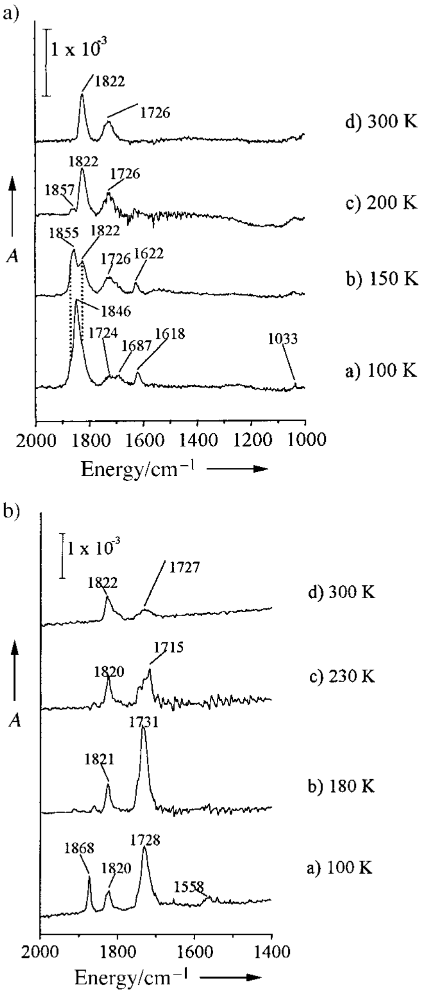

Figure 6. *Infrared spectra of saturated NO overlayers adsorbed on a) a 0.75-ML oxygen overlayer and b) a thin-film oxide with Mo=O species. NO was adsorbed at ~100 K and heated to the temperature shown prior to data acquisition at ~100 K. Reprinted with permission from ref. [23].*

The reactivities of nitrosyl species formed upon NO adsorption on oxygen-modified Mo(110) surfaces are discussed in detail elsewhere[23] but, in general, the strength of the metal–NO interaction, as judged by the resultant perturbation of the intramolecular N–O vibrational frequency, does *not* correlate with the desorption temperature of these species. As outlined in earlier studies of NO on oxygen-modified Ni(111),[30] the simplest interpretation of ν(NO) frequency shifts with surface oxidation is that electronegative surface oxygen species withdraw electron density from the surface and thereby decrease the amount of charge donated to the 2π* antibonding orbital of adsorbed nitrosyl species. Such an effect would tend to increase $\tilde{\nu}$(NO) with increasing oxygen coverage. However, on Mo(110), the presence of surface oxygen stabilizes new nitrosyl binding environments, to lead to both lower *and* higher ν(NO) frequencies relative to the clean surface and therefore such a simplified argument cannot explain the effect of surface oxidation on NO adsorption on these surfaces. Furthermore, since the strength of Mo–NO bonding, as judged by the amount of intramolecular bond perturbation, does *not* scale with NO desorption temperature, it appears that entropic effects are important in determining the stability of surface nitrosyls, whose formation is favored by surface preoxidation. These studies therefore illustrate the complexity of even a model system in describing the effect of surface oxidation state on NO reduction chemistry and highlight the need for companion theoretical studies to link observed behavior (electronic structure as judged by vibrational frequencies, desorption temperature, reaction pathways) with specific catalytic binding sites.

3. The Role of Metal-Mediated Coupling in N–N Bond Formation

Our studies have clearly shown the importance of dinitrosyl species formation in low temperature pathways to NO reduction on molybdenum-based surfaces. In order to understand the general implications of this finding—namely, whether such reaction pathways are a universal template for efficient routes to selective catalytic reduction of NO—we must understand exactly how such intermediates form and what influences their propensity to react in the desired manner. In the following Section, we briefly describe how a combination of experimental and theoretical studies have elucidated these issues.

3.1 Comparison of Dimer versus Dinitrosyl Stability and Reactivity

The relative robustness of dinitrosyl species relative to condensed-phase NO dimers suggests that metal-mediated coupling of two intact NO molecules, where both nitrosyl groups form a metal–NO bond, is the more effective mechanism for N–N bond formation. However, differences in the electronic structures of Mo, which forms dintrosyl species, and metals such as Ag and Cu, which favor dimer formation, introduce other complicating factors into the comparison. Fortuitously, though, both dinitrosyl ($Mo(NO)_2$) *and* dimeric (ON–NO) species can be formed on Mo(110) under certain ultrahigh vacuum conditions.

Specifically, oxidation of Mo(110) at ≈1200 K under about 1×10^{-9} Torr O_2 creates a thin-film oxide that stabilizes both types of coupled nitrosyl species, which allows for a direct comparison of the relative reactivities of these two coupling mechanisms.[31]

Dinitrosyl species on the thin-film oxide are identified by the same infrared experiment described above for the clean surface. The presence of another dimeric species is revealed by the same experiment,[31] as shown in Figure 7. Weak coupling of two nitrosyl groups gives rise to an 8 cm^{-1} splitting of each of the two different, isotopically mixed dimers. The geometry proposed for these species is weak N—N coupling of NO in a second, physisorbed layer to NO directly adsorbed on the surface through interactions similar to those in the condensed phase dimers. Such a picture is supported by an experiment in which the physisorbed species of an isotopically pure NO overlayer were desorbed from the surface and preferentially replaced with isotopically labeled ^{15}NO, to give rise solely to dimers with chemisorbed ^{14}NO and physisorbed ^{15}NO (Figure 7 b).

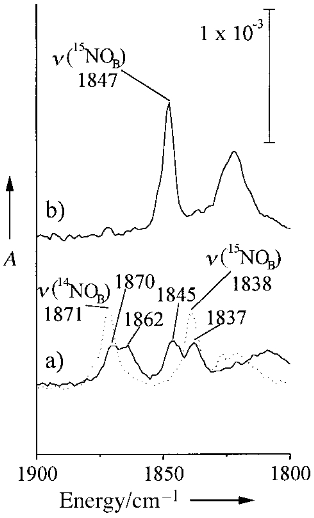

Figure 7. Infrared spectra of ν(NO) of weakly bound NO dimers on oxidized Mo(110). The solid trace in (a) corresponds to the spectrum of a 1/1 mixture of $^{14}NO/^{15}NO$ at 100 K; the dotted line represents the simple addition of the isotopically pure spectra to represent the uncoupled case. The spectrum in (b) was acquired after postadsorption of ^{15}NO at 100 K on a saturated overlayer of ^{14}NO that had been heated to 180 K to desorb the weakly bound species. Reprinted with permission from ref. [31].

In contrast to the chemistry observed for these dimers on Ag(111), where N_2O production is observed at low temperature,[24] the weak N—N bond on oxidized Mo(110) is cleaved to yield NO desorption below 150 K. This difference can be ascribed to the stronger Mo–NO bonding interaction relative to Ag–NO, which anchors one NO of the dimer pair to the metal surface, where it may undergo subsequent reactions. On this same oxidized Mo(110) surface, of course, dinitrosyl species, which are simultaneously present, persist to evolve N_2O and N_2. Therefore, on a metal surface capable of stronger metal–NO interactions, N—N bond formation is favored by metal-mediated bonding in a dinitrosyl over unmediated coupling of intact molecules.

3.2 The Role of Metal Atoms in Dinitrosyl Formation and Reactions

The above experiments demonstrate unequivocally that the specific choice of transition metal has profound implications for the viability of molecular routes to NO reduction. Electronic structure calculations have the unique potential to lend insight into these bonding mechanisms that lead to N—N bond formation and NO reduction. Advances in electronic structure theory and in computational power have now made it possible to study systems of this level of complexity using full, band-structure calculations coupled with a frontier orbital analysis of the bonding.

In our work, we have applied density functional theory to the investigation of monomeric NO and dinitrosyl bound to a $MoO_3(010)$ slab containing a (2×2) array of vacancies at terminal oxygen positions.[32] When dinitrosyl species are adsorbed on the Mo centers, which are in turn exposed by creating the terminal oxygen vacancies, electron density is donated from the Mo d orbitals (primarily the d_{z^2}) to the π^* orbitals of the dinitrosyl moiety. This interaction contributes to the binding to the surface and facilitates the necessary N—O dissociation. In addition, the Mo center mediates a bonding interaction between the N(2p) orbitals of the individual NO molecules in the dinitrosyl; that is, there is N—N coupling in the dinitrosyl group itself.

The density functional calculations also show that the degree of electron donation to the π^* orbitals of NO is higher for a single NO bound to the Mo site at the vacancy, which would indicate that dissociation would be more facile than for the dinitrosyl species. Furthermore, the binding energies of the NO and $(NO)_2$ also indicate that the dinitrosyl will only form by adding gaseous NO to bound NO on the surface. The formation of dinitrosyl from two equilibrated, adsorbed NO molecules is energetically unfavorable by 3.52 eV; the reaction of an adsorbed mononitrosyl with an incoming gas-phase NO molecule is energetically *favorable* by 0.24 eV. This conclusion agrees remarkably well with our experimental results, which show that surface-bound mononitrosyl on a oxygen-modified Mo(110) surface react with incoming NO to convert to dinitrosyl species.[33]

4. Reaction of Methyl Radicals with Adsorbed NO

Methane potentially offers a more effective route for NO reduction. We therefore made use of our detailed understanding of NO chemistry and methyl radical reactions on oxidized Mo(110) to investigate the reduction of adsorbed NO by alkyl species. Since the active species are thought to be gas-phase methyl radicals ($^{\bullet}CH_3$), our studies focus on the elementary step of $^{\bullet}CH_3$ reaction with adsorbed NO on a range of oxidized Mo(110) surfaces.

Our previous studies of $^{\bullet}CH_3$ reaction with oxidized Mo(110) were important in understanding the reactions of methyl radicals with NO. In previous work, we demonstrated that methyl radicals preferentially react with oxygen in high coordination (namely quasi-threefold) sites on Mo(110).[19] These studies were possible because of our ability to selectively populate different types of coordination sites by controlled oxidation of Mo(110), as determined using EELS.[34]

Evidence of methyl addition to oxygen in high coordination sites is obtained from infrared experiments, which consisted of observing the spectrum characteristics of methoxy groups. The same spectrum is obtained following exposure of $^{\bullet}CH_3$ to oxygen in quasi-threefold sites. Importantly, only oxygen in the threefold sites reacted with $^{\bullet}CH_3$. We found no evidence for addition to Mo=O or oxygen in twofold coordination sites, which indicates a kinetic preference for reaction with the oxygen in threefold sites.[19]

In our more recent studies, we found that $^{\bullet}CH_3$ reacts preferentially with *molecular* NO on oxidized Mo(110) at low surface temperatures (100 K).[35] The fact that the methyl radical abstracts oxygen from NO is demonstrated in experiments where gaseous $^{\bullet}CH_3$ is dosed onto a surface containing ^{18}O bound in high coordination sites and $N^{16}O$, present as both mono- and dinitrosyl species. The appearance of a $\tilde{\nu}(^{16}O\text{-}CH_3)$ peak at 1005 cm^{-1} in the infrared spectrum is evidence for reaction with the $N^{16}O$ (Figure 8). There is also a $\tilde{\nu}(^{18}O\text{-}CH_3)$ peak at 935 cm^{-1} due to the reaction of methyl radicals with $^{18}O_a$ surface oxygen, detected after dosing with methyl radicals (Figure 8). Notably, the intensity of the peak derived from the reaction with NO is about three times greater than the peak signifying reaction with surface-bound oxygen. Furthermore, there is a loss of nitrogen-containing species from the surface during methyl radical dosing. Specifically, the amount of NO desorption from the surface measured in temperature-programmed desorption experiments is reduced to 40% of that for a pure NO layer on the same surface by the exposure to methyl radicals. In addition, there is less NO dissociation after radical dosing. These data suggest that there is low temperature coupling, which leads to the evolution of gaseous reduction products (specificially N_2 and/or N_2O). We are in the process of performing isothermal experiments that will enable us to detect gas-phase species produced during dosing.

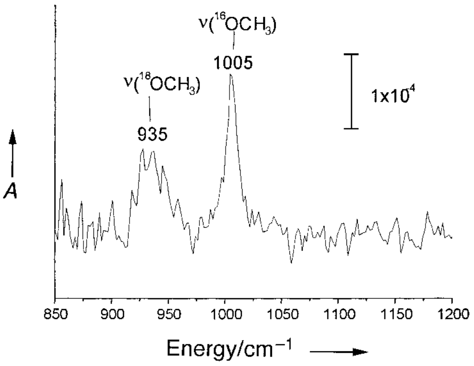

Figure 8. *Infrared spectrum obtained after reaction of methyl radicals with a saturation coverage of $N^{16}O$ on an ^{18}O-labelled surface Mo(110) surface ($^{18}\theta_O = 0.75$ ML) at 100 K. The $\tilde{\nu}(^{16}O\text{-}CH_3)$ peak indicates that there is direct reaction with molecular $N^{16}O$ since there is no dissociation under these conditions.*

The results of our studies of methyl reactions with NO indicate that there is a molecular pathway for this process. Accordingly, we are now investigating the reactions of several possible intermediates in the methyl-plus-NO reaction—CH_3ONO and CH_3NO_2—on oxidized Mo(110). Both of these molecules have been suggested as possible intermediates in this reaction on oxide catalysts.[6, 36, 37] By studying the microscopic pathways by which these molecules react, we will be able to gain insight into whether they are plausible intermediates in the reaction of methyl radicals with NO. Our experimental approach is similar to that taken in our previous work. By combining spectroscopic studies with reactivity measurements, we will develop an understanding of the elementary steps by which these possible intermediates react.

5. Conclusions

Our investigations of NO reduction on oxidized Mo(110) demonstrate that reactions through a dinitrosyl intermediate is a viable pathway. Furthermore, our work provides an example of how detailed mechanistic information is obtained in surface reactions by separating complex problems into elementary reaction steps on well defined materials. This methodology is particularly powerful for the study of fundamental structure–reactivity relationships, which includes issues of site specificity.

In comparing the results of such fundamental studies with the macroscopic trends observed in real catalytic systems, it is important to have experimental checkpoints to evaluate the strength of the correlation between real and model systems. For example, the exact correspondence between the infrared spectra of surface dinitrosyl species on Mo(110) in UHV and the same species on MoO_3 under catalytic conditions demonstrates that the model system, in this case, accurately represents adsorption of NO in the real system. This example also highlights one of the advantages of using infrared spectroscopy in UHV studies, since this technique is also used at higher pressures and therefore allows direct comparison across the pressure gap.

This same example, however, points out the need for using these checkpoints to recognize where the model system diverges from the real one. In the case of NO reduction through dinitrosyl species on Mo(110), the deposition of surface oxygen and nitrogen ultimately limits N–N bond formation on the single crystal surface. This poisoning effect may not be as significant a factor in the real catalyst, where higher operating temperatures and a constant stream of feed gases may remove such poisons from the surface of the catalyst during the course of the reaction. Nevertheless, the self-inhibition of NO dissociation illustrates the importance of oxygen vacancies in the NO reduction process.

Although the model systems employed in these studies are chosen for their simplicity relative to mixed, supported catalysts, it is apparent that even these "simple" systems are often governed by a complex set of interactions. While careful experimental design often allows us to separate the effects of these interactions, it is clear that coupling these experimental studies with state-of-the-art electronic structure calculations vastly improves our understanding of the chemical and physical principles behind the observed chemistry.

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