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Synthesis and Characterization of Ultrathin Metal Oxide Films

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I. INTRODUCTION

Metal oxides, because of their high melting temperature, hardness, chemical resistivity, and low density, have importance in the technological areas of microelectronics and ceramics and are widely used in heterogeneous catalysis. Although the catalytic properties of oxide surfaces have been extensively investigated [1–4], an understanding of the catalytic mechanisms and reaction intermediates is limited because few studies have employed surface science techniques on well-characterized oxide surfaces [5,6]. This is due in part to the fact that most metal oxides used in catalysis are insulators or wide-gap semiconductors. Surface science studies on such systems are hampered by problems associated with sample charging during electron spectroscopic studies and with difficulties related to sample heating and cooling. The use of thin oxide films grown epitaxially on metallic substrates helps to circumvent these problems. These films have been shown to simulate the corresponding bulk oxide very well with respect to their physical and chemical properties, yet have sufficient thermal and electrical
conductivity to preclude temperature inhomogeneities while heating and sample charging when probing with charged particles. The preparation of a well-defined metal oxide layer on top of a supporting metal also offers the opportunity to study the material properties of these ultrathin oxide films as well as the electronic structure of the metal and metal oxide contact barriers.

Epitaxial oxide films can be prepared by controlled oxidation of single-crystal metal surfaces or by evaporating metals onto a dissimilar single-crystal metal substrate in an oxygen atmosphere. Both methods have been used successfully to prepare highly ordered films of NiO, Al₂O₃, SiO, and MgO for surface science studies addressing electronic structure, the adsorption behavior of probe molecules, and supported metal clusters. The latter method, in our view, is preferred in that control of the thickness of the metal oxide layer is possible. In this chapter, we limit the discussion to metal oxides grown on dissimilar metal substrates.

A. Magnesium Oxide

Magnesium oxide (MgO), which exhibits a rock salt structure and an optical bulk bandgap of 7.8 eV, is considered to be a basic catalyst. The MgO surface, for example, catalyzes the isomerization of alkenes and the dehydrogenation of formic acid or methanol. Lithium-promoted MgO, on the other hand, has been found to catalyze the oxidative coupling of methane to ethane.

1. MgO(100)/Mo(100)

Epitaxial MgO(100) with thicknesses ranging from two to 100 mono-layers (ML) can be grown by evaporating Mg onto Mo(100) at 300 K and in 1.0 × 10⁻⁶ torr oxygen. Stoichiometric MgO(100) thin films have been characterized by Goodman and coworkers [7–17] using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HREELS), electron energy loss spectroscopy (EELS), and temperature-programmed desorption (TPD). The films, stable up to 1300 K, were reduced at higher temperatures by the Mo substrate, forming MoO₃ and Mg vapor. XPS, EELS, and HREELS show that both the electron and vibrational structure of the thin MgO
film are very similar to those of the corresponding bulk oxide. EELS has shown the MgO film to be nearly free of point defects, although heating the film higher than 1100 K does produce such defects.

The adsorption of CO on MgO(100)/Mo(100) has been studied by He et al. [8,11], using TPD, XPS, and infrared reflection adsorption spectroscopy (IRAS). On a 7 ML MgO(100) film, the CO vibration shows a blue shift of 35 cm\(^{-1}\) in comparison to gas-phase CO, a shift that has been attributed to electron charge donation from the CO 5\(\sigma\) orbital to the MgO surface. This explanation is supported by XPS measurements that show a 0.4 eV shift in both Mg\(2p\) and O\(1s\) core levels of the MgO thin film to lower binding energy upon CO adsorption. Using an isothermal adsorption method in conjunction with IRAS, the adsorption heat of CO has been determined to be 9.9 kcal/mol, in good agreement with the theoretical result of 9.0 kcal/mol and the desorption activation energy of 10.6 kcal/mol estimated from TPD.

The acid–base properties of MgO(100)/Mo(100) have been characterized by Wu et al. [9,10,12], using HREELS and TPD. Various probe molecules with increasing acid strength from alkanes and alkenes to carboxylic acids were employed in these studies. The use of a high energy electron beam (50 eV) and an off-specular geometry allowed the suppression of the strong surface optical phonons of the substrate. As shown in Fig. 1, multiple phonon losses are attenuated as the electron beam energy is increased. The HREELS results show that acetic acid, formic acid, methanol, and water undergo heterolytic dissociation, with the acidic proton adsorbed on the basic oxygen anion sites and the conjugate base anions adsorbed on the cationic surface sites. Ethylene and ethane, however, were found to adsorb associatively on the MgO(100)/Mo(100) surface. Thermally generated surface defect sites show stronger basicity as indicated by the dissociative adsorption of ethane on these sites. Water and methanol each show similar desorption behavior from this surface. A sharp peak near 150 K is attributed to condensation (of water or of methanol), and a broad peak near 300 K is probably associated with recombinative desorption.

The partial oxidation of methane to ethane on Li-promoted MgO(100)/Mo(100) has been studied by Wu et al. [13–15], using a combination of surface science techniques and kinetics measurements at elevated pressures. The EELS spectra of MgO(100)/Mo(100) and
Li/MgO/Mo(100) after annealing at different temperatures are shown in Fig. 2. The peaks at 1.6, 3.6, and 5.3 eV have been attributed to the [Li\(^+\)O\(^-\)] centers, F aggregates, and F centers, respectively. It has been found that the ethane formation rate correlates well with the F center concentration but not with the concentration of [Li\(^+\)O\(^-\)] centers. The role of Li may be to promote F center formation. These results indicate that [Li\(^+\)O\(^-\)] centers are not likely to be directly involved in the methane activation step. Rather, they promote the production of color centers in the near-surface region that are responsible for this key step in the methane coupling reaction.

2. **MgO(111)/Mo(110)**

The growth of epitaxial and stoichiometric MgO(111) thin films on a Mo(110) surface has been verified using LEED, XPS, AES, and ion scattering spectroscopy (ISS) [18,19]. The MgO(111)/Mo(110) films
are stable up to 1400 K and are reduced by the Mo substrate at higher temperature, forming MoO₃ and Mg vapor. The adsorption of [Re₂(CO)₁₀] and [HRe(CO)₅] onto this thin film has been studied using TPD and IRAS [18,19]. Both molecules decarbonylate on the surface, forming different surface-bound rhenium carbonyls, depending on the surface temperature. The adsorption of formic acid on the MgO(111)/Mo(110) surface has been also studied using TPD [20]. Essentially all of the adsorbed formic acid in the first layer undergoes a dehydration reaction to form H₂O and CO at 610 K.

**B. Nickel Oxide**

Stoichiometric NiO, a typical magnetic insulator that crystallizes in the rock salt structure, shows a bandgap of 4.3 eV. Nonstoichiometric NiO can be either a p- or n-type semiconductor depending on whether it has oxygen or nickel vacancies. Two low Miller index faces have been prepared: NiO(100)/Mo(100) and NiO(111)/Mo(110).

1. **NiO(100)**

Adsorption of formic acid, ammonia, formaldehyde, and alcohols on NiO(100)/Mo(100) has been studied by Goodman and coworkers [21–24] using TPD and HREELS. Formic acid [21] adsorbs associatively at 90 K and undergoes heterolytic dissociation upon heating to > 200 K to form a formate intermediate. The adsorbed formate species is proposed to bond to a Ni cation site via one of the oxygen atoms of the formate in a monodentate configuration. Upon further heating, formic acid desorbs from the surface between 300 and 400 K via recombination of surface formate and surface hydrogen. Methanol and ethanol [24] adsorb associatively at 90 K and desorb reversibly upon heating. Both alcohols are bonded to the Ni cation sites via their oxygen atom with the methyl or ethyl group directed away from the surface. No γ(OH) loss feature has been observed in HREELS, indicating the formation of strong hydrogen bonds between the hydroxyl hydrogen and the lattice oxygen. It has been proposed that the hydroxyl proton of each alcohol fluctuates about the neighboring oxygen anion sites, acting as a mobile proton. Formaldehyde [23] adsorbs molecularly and reversibly desorbs upon heating to 350 K. Extensive polymerization of formaldehyde has been observed. Monomeric formaldehyde is chemisorbed onto Ni
cationic sites in the oxygen end-on $\eta^i$(O) orientation, leading to a shift of the $\gamma$(CO) feature to 1650 cm$^{-1}$. An $\eta^2$(C,O) form of adsorbed formaldehyde is indicated by a $\gamma$(CO) loss feature at 1320 cm$^{-1}$ in the HREELS. Ammonia adsorbs molecularly [22] via the nitrogen lone pair onto the Ni cation site. The HREELS data show that the umbrella mode of ammonia exhibits great charge sensitivity and that the frequency of this mode remains unchanged as a function of NH$_3$ exposure. Accordingly, the frequency of the umbrella mode can be utilized as a fingerprint of the nature of the cations of oxide materials, independent of the ammonia adsorption geometry and coverage.

The interaction of CO with NiO(100)/Mo(100) was also investigated by Vesecky et al. [25], utilizing IRAS. Using isobars constructed from

**Figure 2** EELS spectra of (a) MgO(100)/Mo(100) and (b) Li/MgO/Mo(100), taken after annealing to different temperatures.
measurements in a pressure range of $1 \times 10^{-8}$–1 torr and over a temperature range of 93–280 K, the isosteric heat of CO adsorption was determined to be approximately 10.4 kcal/mol, with the heat of adsorption decreasing slightly with increasing CO coverage.

2. NiO(111)/Mo(110)

The NiO(111)/Mo(110) surface has been studied using LEED, AES, HREELS, and EELS [26]. NiO(111) films of between one and 10 ML are stable only up to 550 K; however, thick NiO(111) films (> 20 ML) are stable up to 900 K, presumably due to kinetic considerations. With heating to higher temperature (> 900 K), the AES signal of the substrate Mo appears, indicating the interdiffusion of the NiO overlayer and the Mo substrate. Epitaxial growth is indicated by a well-formed hexagonal
LEED pattern; annealing to 900 K has virtually no effect on the quality of this LEED pattern. The formation of the (111) surface and its stability are somewhat surprising, as the ideal terminated (111) surface is polar and has a diverging dipole along the surface normal [27,28]. For this dipole to converge, the charge density on the surface must be reduced by 50%. This can be brought about either by reducing the charge on the individual ion or by reconstructing the surface [27–31]. An alternative is to terminate the surface with 50% Ni ions and 50% O ions. The HREELS and EELS spectra show that the NiO(111)/Mo(110) surface has vibrational and electronic structure virtually identical to that of the bulk oxide.

The adsorption of CO, H₂O, CH₃OH, and HCOOH on the 30 ML NiO(111) film grown on the Mo(110) surface has been studied using TPD and HREELS [26,32]. At low coverage limit, CO desorbs at a temperature as high as 215 K. With increasing coverage, the desorption temperature shifts gradually to 175 K, presumably due to dipole–dipole interactions. It is noteworthy that CO desorbs from the NiO(111) surface at a temperature 20 K higher than from the NiO(100) surface [33]. Since the CO–NiO interaction is dominated by electrostatic interactions, the higher binding energy of CO on the NiO(111)/Mo(110) surface is consistent with the polar nature of this surface. Consistent with an increased dipole–dipole interaction, CO adsorbed on the NiO(111)/Mo(110) surface shows a C—O stretching vibration at 2190 cm⁻¹, higher than that for the Ni(100) surface.

On a NiO(111) surface, H₂O and CH₃OH adsorb primarily molecularly. A small fraction of water undergoes decomposition to form hydroxyl groups, as indicated by a sharp peak at 3670 cm⁻¹. Both molecular and dissociatively adsorbed water desorb in a broad feature near 300 K, with the molecular adsorbed water desorbing at the lower temperatures. Molecular methanol, on the other hand, desorbs at 280 K. The HREELS results indicate that methanol is bonded to the surface through the lone pair of electrons on the oxygen with the C—O bond tilted markedly away from the surface normal.

Formic acid (HCOOH) adsorbs dissociatively to NiO(111) even at 100 K, forming a formate species as indicated by HREELS. Upon heating, H₂, CO, CO₂, and H₂O have been shown to be the major desorption products. These results indicate that the dehydrogenation and dehydration reactions are competing processes on this surface.
The interaction of atomic hydrogen with the NiO(111)/Mo(110) surface has been also studied using TPD [32]. Atomic hydrogen was produced by passing H\textsubscript{2} through a tungsten capillary heated to 1900 K. Subsequent TPD shows only H\textsubscript{2}O desorption.

C. Alumina

Aluminum oxide is a widely used support for heterogeneous catalysts. Although aluminum oxide can crystallize in various structures depending on conditions and precursors used to prepare the oxide, \(\alpha\)-alumina is thermodynamically the most stable structure over a wide temperature range.

1. \(\text{Al}_2\text{O}_3(111)/\text{Ta}(110)\)

The heteroepitaxial growth of thin aluminum oxide films on Ta(110) was studied by Chen and Goodman [34] using ISS and LEED, and the initial film growth was found to be largely two-dimensional. The LEED results indicate formation of a long-range ordered epitaxial Al\textsubscript{2}O\textsubscript{3} film with a slightly distorted (\(\beta = 117.9^\circ\)) hexagonal lattice. Detailed structural analysis showed that the observed hexagonal pattern can be interpreted as due to an ordered, close-packed oxygen anion layer associated with either the (0001) face of \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} or the (111) face of \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}. Chemically, the Al\textsubscript{2}O\textsubscript{3}(111)/Ta(110) film is very inert toward a variety of gas molecules, indicating no unsaturated surface bonds.

2. \(\text{Al}_2\text{O}_3(111)/\text{Mo}(110)\) and \(\text{Cu/Al}_2\text{O}_3(111)/\text{Mo}(110)\)

Thin Al\textsubscript{2}O\textsubscript{3} films of various thicknesses were prepared at room temperature on a Mo(110) surface by Wu and Goodman [35]. Film growth, carried out in an oxygen background pressure of \(7 \times 10^{-7}\) torr, was studied by AES, LEED, and HREELS. The AES results show formation of a stoichiometric Al\textsubscript{2}O\textsubscript{3} film without any indication of metallic Al. LEED studies of very thin Al\textsubscript{2}O\textsubscript{3} films (\(d_{\text{Al}2\text{O}3} \leq 8\) Å) showed a hexagonal pattern that was interpreted as described above for Al\textsubscript{2}O\textsubscript{3}/Ta (110).

Wu and Goodman [35] studied the growth of particulate Cu deposits on these Al\textsubscript{2}O\textsubscript{3} films in the 80–800 K substrate temperature range. The films used for supporting the Cu particles were typically 20 Å thick and exhibited excellent thermal stability and chemical inertness toward adsorption. Although particulate metal deposits prepared at relatively
low substrate temperatures exhibit smaller average particle sizes and higher particle densities than those prepared at higher temperatures [36–38], the low temperature preparations are unstable and undergo a major change in morphology and size upon annealing or chemisorption. Wu and Goodman [35] showed that in order to prepare thermally and chemically stable particles of catalytic interest, it is imperative to carry out the metal deposition at elevated substrate temperatures.

Temperature-programmed desorption spectra of Cu deposited onto an Al₂O₃ film at various substrate temperatures, Tₛ, show a shift of the peak maxima to higher temperatures and a narrowing of the TPD peak at Tₛ is increased. It was suggested that the broad TPD peaks observed at low substrate temperatures contain more components and thus reflect a broader size distribution of the Cu particles. Auger measurements showed that Cu particles prepared at Tₛ = 600 K were thermally stable up to an annealing temperature of 850 K, whereas a decrease in Cu Auger intensity was observed upon annealing for those Cu particles prepared at Tₛ = 80 K. A family of TPD spectra of Cu deposited at Tₛ = 600 K is plotted in Fig. 3 as a function of the Cu coverage in equivalent monolayers, θₘ₉. The leading edge of the TPD peak shifts continuously toward higher temperatures as θₘ₉ is increased. At the same time the TPD peak width remains approximately unchanged as θₘ₉ is varied over many Cu multilayers. The inset in Fig. 3 shows that the heat of sublimation of Cu particles decreases rapidly from its bulk value of 80 ± 3 kcal/mol at θₘ₉ ≈ 1.2 to 49 kcal/mol at θₘ₉ ≈ 0.2. This has been attributed to a decrease in the number of neighboring Cu atoms as the Cu particles become smaller. The average size of the Cu particles estimated from the Auger measurements compares favorably with that obtained with direct measurements by TEM.

The reaction of nitric oxide and carbon monoxide with particulate Cu deposits supported on Al₂O₃ films has been studied using TPD and HREELS [35]. The surface was exposed to a ¹⁵NO:CO gas mixture with a ratio of 1:1. At θₘ₉ = 2.7, corresponding to a cluster size of ~ 100 Å, desorption of the parent molecules of ¹⁵NO and CO and the gaseous products ¹⁵N₂ and ¹⁵N₂O, due to ¹⁵NO decomposition, are observed in TPD. A small CO₂ desorption peak is also observed at temperatures between approximately 150 and 250 K, indicating reaction between CO and ¹⁵NO on the supported Cu particles. For small Cu coverages, θₘ₉
Figure 3  A family of TPD spectra of Cu deposited on Al₂O₃ films at $T_s = 600$ K as a function of equivalent monolayers. $\theta_{Cu} = (a) 0.16; (b) 0.33; (c) 0.50; (d) 0.67; (e) 0.98; (f) 1.25; (g) 1.55; (h) 2.09$. The inset shows the heat of sublimation, derived from the leading edge analysis of the spectra, as a function of Cu coverage in equivalent monolayers.

$\leq 0.67$, a CO₂ desorption peak was not observed. However, since the CO₂ yield is very small, the effect of particle size on CO₂ production is unclear. Exposure of the clean surface to the $^{15}$NO/CO gas mixture gives rise to several adsorbate HREELS features in the 1000–2500 cm⁻¹ frequency range. Similar to the case for $^{15}$NO adsorption, the 1255 and 1465 cm⁻¹ losses are attributed to the $\nu(^{15}$NO) mode of adsorbed $^{15}$NO and $^{15}$N₂O, respectively. The loss peak at 2110 cm⁻¹ is due to excitation of the carbon–oxygen stretch, $\nu$(CO), of adsorbed CO.

D. Silica

This SiO₂ films can be synthesized on a Mo(110) substrate by evaporating silicon onto the substrate at room temperature in a $\sim 4 \times 10^{-6}$ torr O₂ background. Such a thin SiO₂ film has been studied by Xu and Goodman [39,40] using AES, EELS, and IRAS. Auger electron spec-
troscopy shows that both silicon and silicon dioxide are formed in the intermediate oxygen pressure range of $1 \times 10^{-6}$ torr. The Auger spectra and the relative intensities of silicon and oxygen do not change for films prepared at oxygen pressure greater than $4 \times 10^{-6}$ torr, consistent with the production of only a silicon dioxide film at the higher oxygen pressure conditions. Furthermore, the line shapes, the peak energies of the Auger electronics, and the electron energy loss spectra are consistent with those of silicon dioxide. The electron energy loss spectrum for the silicon dioxide films after annealing to 900°C displays features identical to those of vitreous silica.

The silicon oxide films prepared at room temperature exhibit additional low energy electron loss features at $\sim 5$ and 7 eV. These features are attributed to a local structure with broken Si—O bonds in tetrahedra of [SiO$_4$] [41]. Defect-free vitreous silica consists of [SiO$_4$] tetrahedra connected by an oxygen bridge to form a long-range 3D network. Thus the $\sim 5$ and 7 eV EELS features indicate some smaller [SiO$_4$] networks.

The intensity of the electron energy loss features at 5 and 7 eV is significantly decreased upon heating and completely disappears after annealing to 900°C. This behavior demonstrates that the silicon dioxide films undergo structural reorganization to form a long-range 3D network of [SiO$_4$].

Infrared reflection adsorption spectroscopy further illustrates the structural changes that occur when the silicon dioxide films are annealed. The asymmetric stretch motion of the Si—O bonds appears as a broad asymmetric peak centered at 1178 cm$^{-1}$ in the IRAS spectrum for the film prepared at a substrate temperature of 50°C. This peak gradually shifts to higher frequency upon heating and reaches a maximum of 1252 cm$^{-1}$ as the silicon dioxide film is annealed to 1100°C.

1. Cu/SiO$_2$/Mo(110)

Model silica-supported copper [42–44] catalysts have been prepared by evaporating copper onto a silica thin film. The preparation conditions control the corresponding metal particle dispersions or average size [43,44]. The structure of the model silica-supported copper catalysts has been investigated with IRAS and scanning tunneling microscopy (STM) [42,43]. The IRAS studies of adsorbed CO indicate that there are several types of copper clusters with surface structures similar to
(111), (110), and other high-index planes of single-crystal copper [42–44]. The STM studies show several types of copper clusters on silica and reveal images of metal clusters on the amorphous support with atomic resolution as shown in Fig. 4 [42].

2. Pd/SiO$_2$/Mo(110)

The adsorption and reaction of CO on silica-supported palladium catalysts over a wide range of temperatures and pressures have demonstrated a continuity between catalysis on Pd single crystals [45,46] and on Pd small particles. The kinetics of CO oxidation at low and high pressures were also shown to be comparable [47,48]. Palladium overlayers of varying thickness on the thin silica films were annealed to 900 K prior to the CO adsorption experiments, producing small metal particles in the range 30–500 Å, with larger particles being formed for the higher Pd coverages.

The IR spectra of adsorbed CO on model silica-supported Pd catalysts are displayed in Fig. 5 for Pd coverages of 1.0, 7.0, and 15 ML.

![Figure 4](image)

**Figure 4** STM images of 1.2 ML copper on silica (100 Å)/Mo(110). A 110 × 110 Å image of a cluster with a Cu–Cu spacing of (4.4 × 2.4) Å. This image was acquired after the sample was exposed to water and dried in air.
Figure 5  A comparison of infrared reflection adsorption spectra of CO on Pd(111), Pd(100), and silica-supported palladium surfaces. The spectra were collected at 100 K with a CO pressure of \(1 \times 10^{-6}\) torr.

The Pd particle size was determined by chemisorption methods [47,48] and verified using scanning probe techniques. For different Pd coverages, three distinct absorption features corresponding to CO adsorbed onto threefold hollow (1880 cm\(^{-1}\)), bridging (1990 cm\(^{-1}\)), and a-top (2110 cm\(^{-1}\)) configurations are observed. At \(\theta_{\text{Pd}} = 1.0\) ML, the dominant absorption feature corresponds to CO adsorbed onto an a-top position, while the peaks originating from threefold hollow and bridging CO are broad, suggesting a nonhomogeneous distribution of these adsorption sites. Increasing the Pd coverage to 7.0 ML and then to 15 ML results in sharpening the absorption features and in the dominance of the peak originating from CO adsorbed in the bridging positions.
These results demonstrate that the larger particles have well-defined crystal orientations whereas the smaller particles have a wide distribution of adsorption sites. A comparison of the IR spectra of equilibrated CO overlayers obtained from the Pd$_{15}$ML/SiO$_2$ sample and from the Pd(100) and Pd(111) single crystals reveals striking similarities. The stretching frequencies of adsorbed CO on the model Pd/SiO$_2$ catalyst (Fig. 5) are identical to the comparable features observed for Pd(100) and Pd(111). The agreement among the IR spectra of the model supported catalysts and the metal single crystals suggests that the metal particles formed on the thin SiO$_2$ film have facets consisting primarily of (100) and (111) orientation. The formation of metal particles with these Miller indices is thermodynamically favored.

The specific activities of the single crystal and the supported catalysts for CO oxidation are essentially identical [47]. The apparent activation energies are similar (∼27 kcal/mol) for the relatively large particles (θ$_{pd}$ > 2 ML) but somewhat lower (∼25 kcal/mol) for the smaller particles (0.6, 0.3 ML). The apparent activation energies for three Pd single crystals with different orientations are similar [45–48] but distinct [29.4 ± 0.3 kcal/mol for Pd(100), 28.1 ± 0.4 kcal/mol for Pd(111), and 30.7 ± 0.5 kcal/mol for Pd(110)].

The effect of particle size on the catalytic properties of palladium was investigated using the decomposition of chemisorbed NO and reactions of NO with CO in flowing conditions. Following a saturation $^{15}$NO exposure on the large particles, $^{15}$NO desorbs in three peaks centered at 315, 515, and 595 K, while $^{15}$N$_2$ is produced in peaks at 545, 595, and 690 K, and $^{15}$N$_2$O is evolved in a peak at 545 K. The 545 K N$_2$ peak is attributed to the fragmentation of N$_2$O. On small palladium particles (∼50 Å), $^{15}$N$_2$O is not produced, $^{15}$NO desorbs in two peaks at 310 and 515 K, and N$_2$ is evolved at 530 and 670 K. The relative yield of N$_2$ with respect to $^{15}$NO desorption (above 400 K) decreases as the particle size grows (from ∼50% for 30 Å to ∼20% for 250 Å particles), suggesting less NO decomposition on the larger particles. In addition, the formation of N$_2$O on the larger particles correlates with the appearance of the NO desorption peak at 595 K. There is no detectable O$_2$ evolution below 1000 K for all sizes of palladium particles. However, O$_2$ desorption is observed in a peak at ∼1250 K,
concurrent with the desorption of palladium. Therefore, the oxygen from nitric oxide decomposition is apparently dissolved into the bulk of the palladium particles.

The reaction of CO with NO under flowing conditions further demonstrates a particle size effect. The relative rate of product evolution was monitored with a quadrupole mass spectrometer during reaction with flowing $^{15}$NO and CO (1:1) at $1 \times 10^{-1}$ torr. The reaction rate increases with increasing catalyst temperature, reaching a maximum at $\sim 580$ K, then declines. On the large palladium particles, the maximum rate of $^{15}$N$_2$O evolution occurs at 570 K, 10 K lower than the maxima for both CO$_2$ and N$_2$ production. On the small particles (<50 Å), $^{15}$N$_2$O is not produced during the steady-state reaction of a 1:1 mixture of $^{15}$NO and CO. N$_2$ is produced by NO dissociation and atomic nitrogen recombination, and CO$_2$ is produced from the oxidation of carbon monoxide. The residence time for CO and NO decreases with temperature whereas the reaction rates increase with temperature, leading to an optimum of about 580 K where product formation rate is maximized.

Both the decomposition of NO and the reaction of NO with CO show that the reaction channel for N$_2$O formation is not available on the small particles (<50 Å). The N$_2$O formation requires the simultaneous presence of adsorbed NO and atomic nitrogen at sufficiently high coverages. The temperature-programmed reaction spectra show that the dissociation of NO occurs along the trailing edge of the main NO desorption peak at 515 K. The formation of N$_2$O correlates with the appearance of the NO desorption peak at 595 K. The formation of N$_2$O correlates with the appearance of the NO desorption peak at 595 K. The higher adsorption energy of the 595 K state increases the NO surface residence time and thus enhances the probability of N$_2$O formation by NO combination with atomic nitrogen. On extended single-crystal surfaces, N$_2$O is also formed during the decomposition of NO [49–51]. However, the decomposition of NO and the formation of N$_2$O correlate with the presence of step/defect (low-coordination) sites on the single-crystal surfaces [49–52]. It is likely that there are surface sites with low coordination and varying reactivities on the large particles and extended surfaces. On the perfect (111) and (100) facets, NO desorbs at < 520 K [51,52], whereas on particles with a variety of low-coordinated sites, NO can decompose to atomic nitrogen and oxygen on some sites or can
be more strongly adsorbed (595 K desorption state) on other sites. The presence of both sites on the large Pd particles, a strong adsorption site for NO and a second site that promotes decomposition, provides a mechanism for the formation of N$_2$O. The absence of the N$_2$O on the small palladium particles can be explained by the lack of the high temperature NO adsorption state (595 K), which is in turn related to the reactivity of the surface sites. The surface of the small particles is more reactive, as indicated by the increased amount of NO dissociation (~50% for 30 Å and ~20% for 250 Å particles), so all NO molecules on the low-coordinated sites are likely decomposed to atomic oxygen and nitrogen at lower temperatures. The presence of atomic oxygen and nitrogen in the near-surface region will likely further decrease the NO adsorption energy.

F. Mixed Oxides

Mixed Al$_2$O$_3$/SiO$_2$ oxide has been studied using TPD, AES, XPS, and ISS [53]. The mixed oxide is prepared by evaporation of metallic Al onto SiO$_2$ supported on the Mo(100) surface and subsequent annealing. Depending on the annealing temperature, the following steps in the Al oxidation have been observed:

\[
\text{SiO}_2/\text{Mo} + \text{Al} \to \text{Al/ SiO}_2/\text{Mo} \quad 100-300 \text{ K}
\]

\[
\text{Al/SiO}_2/\text{Mo} \to \text{Al}_2\text{O}_3/\text{Si/SiO}_2/\text{Mo} \quad 300-800 \text{ K}
\]

\[
\text{Al}_2\text{O}_3/\text{Si/SiO}_2/\text{Mo} \to \text{Al}_x\text{O}_y\text{Si}_z/\text{Mo} + \text{SiO} \quad 800-1200 \text{ K}
\]

Silicon monoxide (SiO) desorbs between 1000 and 1100 K, leaving a homogeneous Al$_2$O$_3$/SiO$_2$ film. The important step for the formation of Si—O—Al bonds is the concerted diffusion of aluminum oxide into the bulk of the SiO$_2$ film with the concomitant desorption of volatile silicon monoxide as a result of the solid-state reaction of Si and SiO$_2$. It was also concluded from the XPS core level shifts that the electronic structure of these films is very similar to that of bulk aluminosilicates.

Epitaxial growth of MgO(100) film on top of NiO(100)/Mo(100) has been studied using LEED, XPS, ISS, and ELS [54]. Owing to the excellent lattice match of MgO (4.211 Å) with NiO (4.168 Å), very good epitaxy was found. MgO grows quite evenly on the NiO(100)
surface. This is demonstrated by the ISS results, which are shown in Fig. 6. As one can see, the NiO surface is almost completely masked for MgO coverages of 2 ML. A 1.0 eV upward shift of Ni (2p$_{3/2}$) XPS binding energy has been observed as the MgO film thickness was increased from 0 to 7.5 ML, which was attributed to the charge transfer from the MgO to NiO.

III. CONCLUSION

Recent studies have shown that model oxide surfaces can be prepared in thin-film form, a preparation strategy that readily enables their exploration with a wide array of charged-particle surface science techniques. Such investigations offer unprecedented opportunities to address the molecular details of the chemistry at oxide surfaces. Furthermore, the addition of metals to the oxides as supports provides a convenient

![MgO/NiO ISS](image)

**Figure 6** Relative integrated intensity of the Ni ISS peak versus MgO overlayer coverage on 10 ML NiO films on Mo(100).
method to model important aspects of supported metal catalysts such as support–particle interactions and quantum size effects of supported metal particles. Using such model catalysts, an array of surface science techniques can be used to study catalysis by metals in systems with well-defined particle sizes and morphology.

In combination with recent technique advances such as in situ IR, this approach to model catalysts allows the so-called pressure and material gaps to be bridged simultaneously. Such investigations offer new opportunities to directly connect studies on single crystals at UHV conditions with analogous investigations of catalytic processes on "real-world" catalysts at elevated pressures.

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