

Interaction of NO with the MgO(100) Surface Studied by Infrared Reflection Absorption Spectroscopy

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Infrared reflection absorption spectroscopy (IRAS) at low temperatures (ca. 40 K) has been used to study the interaction of NO with highly ordered MgO(100) thin films. Dimer formation has been observed in the multilayer regime at (<60 K) and in the monolayer regime at 60–70 K. Using ¹⁵NO, it is shown that dimeric NO, (NO)₂, is the key intermediate in the formation of N₂O above 70 K.

Metal oxides are widely used in catalysis, chemical sensors, corrosion inhibitors, ceramics, and electronic materials.¹ The interaction between crystalline MgO surfaces and simple gas molecules has been studied extensively as a prototype metal oxide system. It has been reported that “low-defect” MgO surfaces are relatively inert and that surface defects play a crucial role in promoting surface reactivity.² Studies using temperature programmed desorption (TPD) have shown that desorption of CO on a low-defect MgO surface is complete below 65 K. On the other hand, for a defective MgO surface, desorption of CO is observed well above 90 K.^{3,4} A previous study has also suggested that NO forms N₂O on a defective MgO surface.^{2,5} Studies using metastable impact electron spectroscopy (MIES) have shown that the extent of N₂O formation on MgO correlates with the defect density.² An investigation with X-ray photoelectron spectroscopy (XPS) concluded that oxygen vacancies on MgO lead to the formation of N₂O from NO adsorbed at 80 K;⁵ however, the NO coverage in these experiments was likely very low since NO is known to desorb well below 80 K on low-defect MgO surfaces.³ To better understand the interaction between NO and MgO surfaces with minimal defects, NO adsorption studies below 80 K are essential.

In the present study the adsorption and reaction of NO on a highly ordered, low-defect MgO(100) surface at 40 K was studied using infrared reflection absorption spectroscopy (IRAS). NO forms a multilayer of NO dimers at 40 K and a chemisorbed layer of NO dimers at 65 K. N₂O is a product of the reaction of NO dimers upon heating the surface to 75 K.

The MgO(100) surface was prepared by depositing Mg onto a Mo(100) surface at 600 K in a background O₂ pressure of 1.3×10^{-6} mbar. The MgO(100) film was then annealed at 1100 K in ultrahigh vacuum (UHV) until a sharp (1 × 1) low-energy electron diffraction (LEED) pattern was evident. This preparation procedure has been

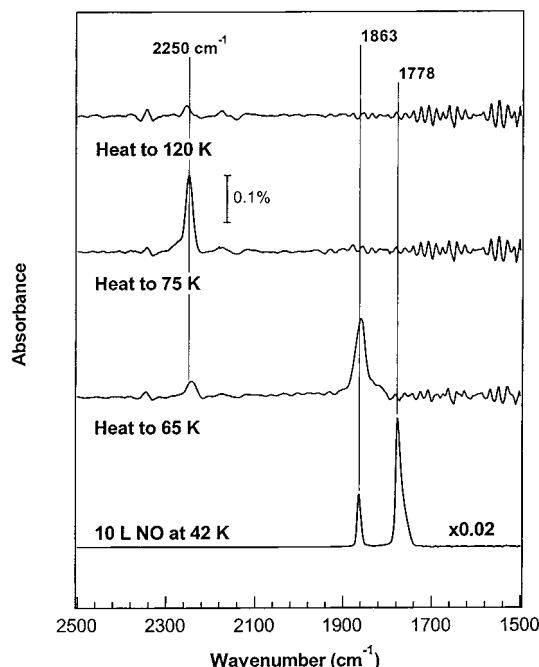


Figure 1. IRAS of NO on MgO as a function of temperature. The spectra were acquired at the temperatures indicated.

shown to be successful in synthesizing highly ordered, low-defective MgO thin films.⁶

The experiments were carried out in an UHV chamber equipped with IRAS, Auger electron spectroscopy (AES), LEED, and a quadrupole mass spectrometer. The instrumentation and data acquisition procedure for IRAS have been described in detailed.⁷ The sample was mounted on a modified heating and cooling sample stage (Vacuum Generators) attached to a continuous flow liquid helium cryostat. The sample could be cooled to 20 K and heated to 1100 K. The temperature was measured using a K-type thermocouple that was calibrated below 80 K using a thermocouple reference junction at liquid nitrogen temperature (77 K). The calibrated temperature was compared to the desorption temperature for multilayer CO (30 K). NO was dosed using a precision leak valve. The NO purity was determined via its gas-phase mass spectrum and the IR spectrum of the condensed gas at 25 K.

Figure 1 shows the IRAS of NO on MgO(100) as a function of the surface temperature. Upon exposure of

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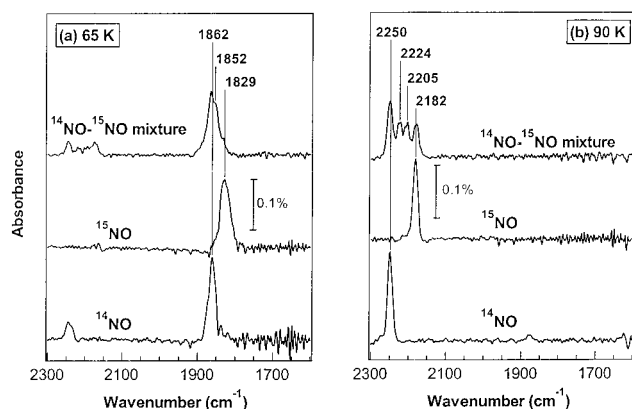


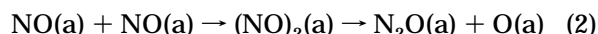
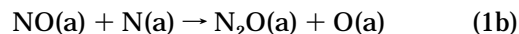
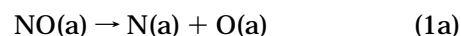
Figure 2. IRAS of ^{14}NO , ^{15}NO , and a mixture of ^{14}NO and ^{15}NO adsorbed on $\text{MgO}(100)$. The surfaces were prepared by exposure of 10 langmuirs of NO at 42 K followed by an anneal to the indicated temperature. In (a) the feature at 1852 cm^{-1} indicates the formation of the $\text{O}^{14}\text{N}-^{15}\text{NO}$ mixed dimer. In (b) the features at 2250, 2224, 2205, and 2182 cm^{-1} indicate the formation of the four possible mixed-isotope N_2O species.

the MgO surface to 10 langmuirs of NO at 40 K, multilayer NO is formed. The two peaks at 1863 and 1778 cm^{-1} can be assigned to the symmetric (ν_1) and asymmetric (ν_3) stretching features of $(\text{NO})_2$. The formation of NO dimers has been observed frequently in the gas⁸ and condensed⁹ phases as well as on metal and metal oxide surfaces.¹⁰ Upon heating to 65 K, multilayer NO desorbs and a chemisorbed $(\text{NO})_2$ layer is formed. Upon further heating to 75 K, the feature at 1863 cm^{-1} completely disappears and a new feature appears at 2250 cm^{-1} . This 2250 cm^{-1} feature, which corresponds to the N–N stretching mode of N_2O , disappears at 120 K. Nitrogen on the surface is not detected by AES after desorption of N_2O at 120 K, which implies intact desorption of N_2O on the $\text{MgO}(100)$ surface.

The formation of NO dimers and N_2O was confirmed using ^{15}N -labeled NO. Figure 2 shows the IRAS of the surface species formed upon dosing ^{14}NO , ^{15}NO , and a mixture of ^{14}NO and ^{15}NO at 40 K followed by an anneal to the indicated temperature. Upon exposure of $\text{MgO}(100)$ to a mixture of ^{14}NO and ^{15}NO , a new feature appears at 1852 cm^{-1} (Figure 2a), characteristic of the mixed dimer, $\text{O}^{14}\text{N}-^{15}\text{NO}$. The orientation of the NO dimer on the surface can be approximated using the IRAS surface selection rule; i.e., only those vibrations with dipole moments perpendicular to the surface are detected. The intensity of the symmetric band is much greater than

that of the asymmetric band, suggesting that $(\text{NO})_2$ is adsorbed in the “U-shaped” geometry with the N–N bond parallel to the surface. At 90 K, four features are resolved in the vibrational frequency region of N_2O following adsorption of a mixture of ^{14}NO and ^{15}NO (Figure 2b). These four features can be assigned to correspond to the N–N stretching frequencies of $^{15}\text{N}-^{15}\text{NO}$ (2182 cm^{-1}), $^{14}\text{N}-^{15}\text{NO}$ (2205 cm^{-1}), $^{15}\text{N}-^{14}\text{NO}$ (2224 cm^{-1}), and $^{14}\text{N}-^{14}\text{NO}$ (2250 cm^{-1}). These values closely match the vibrational frequencies of gaseous N_2O :¹¹ $^{15}\text{N}-^{15}\text{NO}$ (2156.2 cm^{-1}), $^{14}\text{N}-^{15}\text{NO}$ (2177.6 cm^{-1}), $^{15}\text{N}-^{14}\text{NO}$ (2202.5 cm^{-1}), and $^{14}\text{N}-^{14}\text{NO}$ (2223.9 cm^{-1}).

Two possible mechanisms have been proposed for the formation of N_2O from NO on metal surfaces.¹⁰



For MgO , NO is adsorbed primarily as dimers prior to the formation of N_2O , more consistent than with the second mechanism.

The amount of N_2O produced from the NO dimer on $\text{MgO}(100)$ was approximately half of the saturation coverage of N_2O at 100 K. This was estimated by comparing the IRAS intensities. The same NO reaction was investigated using defective MgO surfaces that were produced by extended Ar-ion sputtering. No clear difference was found between “low-defect” and defective MgO surfaces in terms of the amount of N_2O produced. This observation suggests that the reaction of NO adsorbed on MgO below 60 K is different from the reaction of NO adsorbed around 80 K. Below 60 K, the NO dimer is a key intermediate and the role of surface defects may not be crucial for N_2O formation. If NO is adsorbed at a higher temperature than 80 K, on the other hand, formation of NO dimer might be limited because the coverage of NO is low, and different reaction channels might be operative.

In summary, the adsorption and reaction of NO on a low-defect, thin film of $\text{MgO}(100)$ has been studied at 40 K. NO forms a dimer multilayer below 60 K and a dimer monolayer at 60–70 K. N_2O is formed from the NO dimer at temperatures greater than 70 K. These results show that NO reacts on low-defect MgO surfaces to form N_2O via a NO dimer intermediate, which is formed below 70 K.

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