Infrared study of CO on NiO(100)

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The nature of the interaction of CO with NiO(100) thin films (~20–50 Å) grown on a Mo(100) substrate has been investigated with infrared reflection absorption spectroscopy. Isosteric heats of adsorption were measured for CO in a pressure range of 1×10⁻⁸ to 1 Torr and over a temperature range of 93–280 K. The average heat of adsorption was found to be approximately 10.4 kcal/mol, with the heat of adsorption decreasing slightly with increasing CO coverage. This value for the heat of adsorption agrees very well with that measured for CO on MgO(100). The CO stretching frequency was found to decrease with an increase in the CO coverage. At constant coverage, the CO stretching frequency as well as the full width at half-maximum were found to increase with increasing temperature. These results are discussed in the context of current theories of bonding between CO and oxide surfaces.

I. INTRODUCTION

The surface structure and chemisorptive properties of metal oxides are of fundamental interest for a variety of reasons, a particularly significant one being that oxides are widely used as industrial catalysts. Despite this, however, there have been relatively few studies of adsorption on oxide surfaces compared to metal surfaces. While the adsorption energy and IR spectra of CO on MgO(100) have been well characterized, little work has been carried out to address the CO/NiO(100) adsorption system. Recent theoretical investigations suggest that CO interacts with MgO and NiO primarily through an electrostatic bond.

The strength of the bonding interaction between a CO probe molecule and NiO can be readily followed over a wide range of temperatures and pressures using infrared reflection absorption spectroscopy. In this study, the heats of CO adsorption on nickel oxide are addressed over a range of CO coverages. The shifts in CO stretching frequency as a function of temperature and coverage have also been investigated. These results are discussed and compared with respect to the adsorption and bonding of CO to MgO with the goal of generalizing the nature of the bonding between CO and oxide surfaces.

II. EXPERIMENT

These experiments were performed in an ultrahigh vacuum chamber equipped with a Fourier transform infrared spectrometer for reflection absorption studies (IRAS), a mass spectrometer for thermal programmed desorption (TPD), and an Auger electron spectrometer (AES). The pressure in the infrared cell can be varied from 10⁻¹⁰ to 10 Torr. Other electron and ion spectroscopic data were obtained in separate ultrahigh vacuum chambers.

Stoichiometric and epitaxial nickel oxide films were grown on a Mo(100) substrate by evaporating nickel in a ~10⁻¹⁰ Torr background of oxygen. The flux of nickel was monitored with a line of sight mass spectrometer, keeping the evaporation rate constant to within 10%. After annealing to 700 K, low energy electron diffraction (LEED) indicated that the films exhibited a (100) orientation. X-ray photoelectron spectroscopy (XPS) of the Ni(2p) core level showed the films to be characteristic of bulk nickel oxide (Fig. 1). The XPS spectrum of NiO rules out the presence of significant Ni³⁺ and Ni⁰ defects due to the absence of these peaks at +2 and –2 eV, respectively, from the main Ni²⁺ peak at 854.6 eV. The NiO films were stable up to ~900 K, above which NiO was reduced by the molybdenum substrate, forming metallic nickel and molybdenum oxides. Temperature-programmed desorption (TPD) showed that both Ni and MoO₃ desorb at ~1400 K. Ion scattering spectroscopy (ISS) showed that the NiO films completely cover the Mo(100) substrate, and indicates that the surface of the NiO films terminates with an approximately equal number of nickel and oxygen atoms (Fig. 2). Auger electron spectroscopy (AES) also confirmed that the top layer of the NiO film contained no detectable Mo.

III. RESULTS

Figure 3 shows the infrared reflection absorption spectra (IRAS) for CO adsorbed onto a NiO(100) film. At low coverages (10% saturation) at 93 K, the CO exhibits a stretching frequency of 2156 cm⁻¹, which is blue shifted with respect to the gas phase value of 2143 cm⁻¹. As the CO coverage was increased to saturation (50% Ni²⁺ sites occupied), the CO stretching frequency decreased almost linearly with coverage to 2142 cm⁻¹ at θ=1 (Figs. 3 and 4). This is in contrast to CO on MgO(100) where the CO stretching frequency of 2178 cm⁻¹ is essentially independent of coverage.

The IR band at 2142–2156 cm⁻¹ is unambiguously assigned to CO adsorption onto NiO(100). This stretching frequency is in excellent agreement with values reported in the literature. The CO/NiO peak is well separated from the CO/Ni²⁺ peak located at 2094 cm⁻¹. Platero et al. observed shoulders on the main CO/NiO absorption band which were interpreted as being due to NiO(100). Similar shoulders were observed on the NiO thin films; however, annealing to 700 K eliminated these features. Therefore, the shoulders may be due to nonstoichiometric defects, such as Ni⁺ or Ni³⁺ that disappear upon annealing.

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The well defined spectra of Fig. 3 suggest that CO bonding to the NiO substrate is relatively homogeneous. In the zero coverage limit, the singleton CO stretching frequency of 2156 cm\(^{-1}\) agrees well with that predicted for adsorption on a 5-coordinate Ni\(^{2+}\) cation.\(^{12}\) However, the full width at half-maximum (FWHM) for the IR band (10–30 cm\(^{-1}\)) of CO on NiO(100) is much broader than the CO band on signal crystal metal surfaces such as Cu (\(~5\) cm\(^{-1}\))\(^{13}\) or ionic single crystals such as NaCl (\(<4\) cm\(^{-1}\))\(^{14}\) and MgO (4.5 cm\(^{-1}\)).\(^{5}\) This broadening can most likely be attributed to some inhomogeneity of the thin-film NiO(100) surface, which is enhanced when chemical and dynamic interactions among CO molecules become important.

The effect of temperature on the CO stretching frequency and FWHM is shown in Fig. 5. At a constant CO coverage of \(~10\%\) saturation, both the stretching frequency and the FWHM increase with temperature. In order to obtain these spectra at high temperatures, the IR high pressure cell was back filled with up to \(10^{-3}\) Torr of carbon monoxide. The increase in FWHM may reflect the heterogeneity of the surface since less energetically favorable adsorption sites may be populated at higher pressures.

The heats of adsorption for carbon monoxide on NiO(100) thin films (\(~20–50\) Å) were determined using both isothermal and isobaric adsorption conditions. The CO surface coverage was determined from the integrated IR intensity, assuming a linear relationship between CO coverage and IR absorbance. The CO coverage was measured as a function of CO background pressure at a given temperature. The CO surface coverage was measured similarly as a function of temperature at a constant CO pressure (Fig. 6). CO was adsorbed onto NiO(100) at various temperatures and pressures from 93 to 280 K and \(1\times10^{-8}\) to 1 Torr. Data for the CO surface coverage versus pressure/temperature...
were acquired over these ranges of conditions. Isotherms for CO adsorption were then generated by extracting constant coverage data from these isotherms. Isothermic heats of adsorption were determined from the slopes of Clausius–Clapeyron plots.\textsuperscript{15} The assumption that the CO IR intensity is linear with coverage is justified by noting that the isotherms are linear over narrow temperature (pressure) ranges, where the CO frequency is nearly constant, and over broader ranges where the frequency shifts with coverage.

The heat of adsorption for CO on NiO(100) decreases slightly from −12.5 kcal/mol at low coverage (≤0.2 saturation) to −9.2 kcal/mol at higher coverages (0.4–0.6 saturation) (Fig. 7). The average adsorption energy of CO/ NiO(100) is 10.4 kcal/mol, and it is very similar to the heat of adsorption for CO on MgO(100).\textsuperscript{2} A decrease in the heat of CO adsorption with increasing coverage has been observed\textsuperscript{16,17} and attributed to repulsive interactions among the CO molecules at higher coverages. CO heats of adsorption on these films measured by TPD give an average value of 10.5±2 kcal/mol, further supporting the values calculated from the infrared data.

**IV. DISCUSSION**

At low CO coverages (≤10%) at 93 K, the CO stretching frequency on NiO is 2156 cm\(^{-1}\), 13 cm\(^{-1}\) higher than the gas phase value of 2143 cm\(^{-1}\). For CO adsorption on MgO, the corresponding frequency is 2178 cm\(^{-1}\).\textsuperscript{3} This blue shift with respect to the CO gas phase frequency has been observed for singleton CO molecules on several ionic surfaces. This effect is often attributed to the “wall effect”\textsuperscript{18} and/or CO 5σ donation to the substrate.\textsuperscript{19,20} Furthermore, the results of Fig. 4 show there to be a marked red shift of the CO stretching frequency (from 2156 to 2142 cm\(^{-1}\)) with increasing CO coverage. This red shift with respect to the CO coverage has also been observed for other ionic surfaces, i.e., NaCl(100)\textsuperscript{14} and MgO(100).\textsuperscript{2} However, the reported redshifts of 4 cm\(^{-1}\) for CO/NaCl and 8 cm\(^{-1}\) for CO/MgO are significantly smaller than for CO/NiO (14 cm\(^{-1}\)).

The total shift for CO on NaCl consists of a 6 cm\(^{-1}\) shift to higher frequency due to dynamical dipole coupling and a 10 cm\(^{-1}\) shift to lower frequency due to static interactions (dispersion, higher multipole interactions).\textsuperscript{15} For CO on sintered NiO powder, Platero et al. showed that the dynamical shift is 27 cm\(^{-1}\) to higher frequency and the static shift is 43 cm\(^{-1}\) to lower frequency.\textsuperscript{11} Since the total shift for CO on NiO powder is essentially the same as for CO on NiO(100) films, the dynamical and static shifts for CO on NiO films can be reasonably assumed to be the same, 27 and 43 cm\(^{-1}\), respectively.
Both the dynamical and static shifts for CO on NiO are much larger than for CO on MgO and other ionic surfaces, indicating a difference in the nature of CO bonding to NiO compared to MgO. The larger dynamical shift, i.e., the dynamic polarizability, for CO on NiO suggests a more significant covalent interaction between CO and NiO compared with MgO. The frequency shift with CO coverage on NiO is similar to that found on many metals,\textsuperscript{21,22} consistent with the existence of a significant covalent bonding component between CO and NiO.

Pacchioni et al.\textsuperscript{6} conclude from their theoretical study of CO/NiO(100)\textsuperscript{23} that the energetic cost of donating an electron from a Ni\textsuperscript{2+} to a CO 2π\textsuperscript{*} orbital is too high for backbonding to occur (ionization potential = 35.3 eV for Ni\textsuperscript{2+}, 7.6 eV for Ni\textsuperscript{0}).\textsuperscript{23} While it is true that the ionization potential of Ni\textsuperscript{2+} is high, the Ni 3d orbital overlap with the CO 2π\textsuperscript{*} orbital is of proper symmetry and energy to facilitate a measurable change in the dynamic polarizability of CO and thus alter the stretching frequency of the C–O bond.\textsuperscript{24}

Isosteric heats of adsorption also provide a measure of the nature of CO bonding to surfaces. The heat of adsorption of CO on NiO, 10.4 kcal/mol, is very close to the CO heat of adsorption on MgO, 9.9 kcal/mol. In their theoretical study, Pacchioni et al.\textsuperscript{6} conclude that these two heats of adsorption are similar because the primary bonding mechanism between CO/MgO and CO/NiO is the same, namely an electrostatic interaction. The infrared data suggest there to be a more significant covalent contribution in the CO/NiO system compared to CO/MgO. The similar heats of adsorption for CO on MgO and NiO may be fortuitous, i.e., the increase of bonding energy by the covalent interaction is canceled by the decrease of the electrostatic interaction, since NiO is less ionic than MgO.\textsuperscript{25} However, the quantitative contribution of the covalent interaction to the heats of adsorption of CO on NiO remains to be determined.

Both NiO and MgO are predicted to have similar CO singleton frequencies based on the comparable ionic radii and electrostatic bond strengths of Ni\textsuperscript{2+} and Mg\textsuperscript{2+} in their respective 5-coordinate oxides.\textsuperscript{12} Based on the CO singleton frequencies of 2156 cm\textsuperscript{-1} on NiO and 2178 cm\textsuperscript{-1} on MgO, the larger covalent interaction between CO and NiO(100) decreases the CO stretching frequency ~22 cm\textsuperscript{-1} relative to MgO(100). The singleton frequency of CO on MgO(100) may also contain a covalent component due to CO 5σ donation to the oxide substrate,\textsuperscript{19,20} thus the difference in the stretching frequency on NiO compared to MgO is most likely due to Ni\textsuperscript{2+} → CO backbonding. This difference in stretching frequency represents a very small decrease in the C–O bond energy and thus a relatively small backbonding interaction. Therefore, the contribution of a covalent interaction to the heats of adsorption is likely relatively small.

Although several suggestions have been made as to the nature of the CO/NiO(100) interaction, additional studies are required to differentiate the relative importance of chemical and dynamical bonding. It is possible, though not likely, that the observed red shift with respect to coverage is due entirely to a chemical interaction (i.e., reduced CO 5σ donation or increased M→2π* backdonation). Work by Freund et al. has shown that CO may interact more strongly with oxide surfaces than with the corresponding metals by adsorbing in a lying-down configuration.\textsuperscript{26} Since it is not possible to observe parallel oscillators with IRAS, angle resolved photoemission studies may show that the enhanced CO bonding at lower coverages is in fact due to the additional O 4σ bonding of Ni\textsuperscript{2+} → OC.

V. CONCLUSION

In this article, we have shown that the stretching frequency of an isolated singleton CO molecule on NiO(100) supported on Mo(100) is 2156 cm\textsuperscript{-1}. As the CO coverage is increased to saturation, the frequency decreases to 2142 cm\textsuperscript{-1}. This is in contrast to CO on MgO(100) where there is a much smaller coverage dependent frequency shift.\textsuperscript{3} The frequency shift for CO/NiO(100) is rationalized by considering the chemical bonding interaction between CO molecules and Ni\textsuperscript{2+} ions. Chemical bonding is much stronger for ions, such as Ni\textsuperscript{2+}, that contain d electrons which can overlap with CO 2π* antibonding orbitals. The chemical interaction between CO and MgO is expected to be weaker due to the absence of d electrons available for backbonding.

The heat of adsorption of CO on NiO(100) is 10.4 kcal/mol. This compares to the heat of adsorption of CO on MgO(100) of 9.9 kcal/mol.\textsuperscript{3} These similar heats of CO adsorption are attributed to the electrostatic interaction being the major contributor to the heats of adsorption. These results are consistent with there being a significant covalent contribution to the bonding interaction between CO and NiO; however its quantitative contribution to the heats of CO adsorption is at present unknown.

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