Novel properties of ultrathin oxide films: NiO supported on Al_2O_3

C. Xu, Q. Guo and D.W. Goodman

Department of Chemistry, Texas A & M University, College Station, TX 77843-3255, USA

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Ultrathin NiO films have been prepared on an $Al_2O_3(0001)$ surface, supported on a Mo(110) or Re(0001) substrate. The electronic and chemical properties of these NiO films have been studied using electron energy loss spectroscopy (ELS), temperature programmed desorption (TPD), and infrared reflection adsorption spectroscopy (IRAS). TPD and IRAS of adsorbed CO show that the chemical properties of the thin (< 10 monolayers) NiO films are considerably different from those of thick (> 10 monolayers) NiO films. The electronic structure, however, for NiO films with thicknesses between 0.5 and 28 ML are indistinguishable by ELS. Heating monolayer NiO on Al_2O_3 to 800 K in vacuum leads to a substantial reduction of NiO to metallic Ni.

Keywords: carbon monoxide; nickel oxide; alumina; mixed oxide; electron energy loss spectroscopy (ELS); temperature programmed desorption (TPD); infrared reflection adsorption spectroscopy (IRAS)

1. Introduction

Supported transition metal oxides have been shown to exhibit modified catalytic properties compared to their bulk counterparts, and, accordingly, have been used in various technologically important catalytic processes [1–5]. Although the catalytic properties of mixed/supported oxides have been extensively characterized, the origin of their modified chemical and physical properties remains poorly understood. A surface science study of carefully prepared models should add greatly to our understanding of these important but complex systems. Surface science techniques have been applied much less frequently to oxide than metal surfaces because of problems in oxides with poor thermal and electrical conductivity. Recently, thin oxide films, grown epitaxially on refractory metal surfaces, have been successfully used to characterize single component oxide surfaces [6–25]. In this letter we report recent results on the characterization of supported NiO thin films on an $Al_2O_3(0001)$ surface, which, in turn, are supported on a Re(0001) or Mo(110) substrate. NiO supported on Al_2O_3 forms a "spontaneous" monolayer [2], which has been reported to be catalytically active for a number of reactions [2,26]. The understanding of this system is also of interest with respect to Ni/Al_2O_3, a well-known steam reforming catalyst.

2. Experimental

The experiments were carried out in two UHV chambers. One is equipped with capabilities for high resolution electron energy loss spectroscopy (HREELS or ELS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and temperature programmed desorption (TPD). The second system is equipped with a Fourier transform infrared spectrometer for reflection absorption studies (IRAS) and capabilities for TPD, AES and LEED. The base pressure of the two instruments was $\sim 3 \times 10^{-10}$ Torr. TPD experiments were carried out using a line-of-sight, quadrupole mass spectrometer (QMS) and a linear heating rate of 5 K/s. The ELS spectra were taken in the specular direction with an electron beam incident angle of 60° with respect to the surface normal. An electron beam energy of 25 eV was used with a typical resolution of 25 meV. The IRAS spectra were acquired using 4 cm^{-1} resolution and 500 scans (4 min).

Mo(110) and Re(0001) surfaces were used to support the mixed oxide films. Both surfaces were cleaned by annealing in 1×10^{-8} Torr O_2 at 1200 K with a subsequent flash to 2000 K. This procedure was repeated several times until no contamination could be detected with AES.

The Al_2O_3 films were prepared by depositing Al onto the Mo(110) or Re(0001) surface at 900 K in a 1×10^{-6} Torr O_2 atmosphere, followed by an anneal to 1200 K in 1×10^{-6} Torr O_2. The aluminum source was made of a high-purity Al wire inserted into a small cylindrical alumina tube. The cylinder was then tightly fitted into a spiral tungsten filament. After extensive outgassing, the source flux was calibrated using TPD and/or AES of Al deposited on the Mo and Re substrates; the evaporation rate was $\sim$ 1 ML/min. An Al_2O_3 film with a thickness of $\sim$ 30 ML was used for each experiment. These Al_2O_3 films have been characterized previously using LEED, AES, HREELS, ELS and IRAS [27]. A (1×1) hexagonal LEED pattern was observed, indicating epitaxial growth of the Al_2O_3 films with respect to the Mo(110) or Re(0001) substrates. The stoichiometry and purity of the films were verified using AES, while

ELS indicated that their electronic structure were virtually identical to bulk Al_2O_3. AES showed the absence of any metallic Al and IRAS indicated a four-feature spectrum, characteristic of γ-Al_2O_3.

The NiO films were prepared by depositing Ni onto the Al_2O_3 surface at 400 K in an O_2 background pressure of 1×10^{-6} Torr O_2. The Ni source consisted of a 0.25 mm Ni wire (99.997%, Johnson Matthey Chemical limited) wrapped around a tungsten filament. The source was extensively outgassed prior to use and the evaporation rate calibrated using TPD and AES of Ni deposited on the Mo and Re substrates.

3. Results and discussion

3.1. Electronic properties

To probe the electronic structure of the thin NiO films supported on Al_2O_3, electron energy loss spectra were acquired over the 0–10 eV region. Fig. 1 shows a series of ELS spectrum taken at various thicknesses of NiO supported on Al_2O_3. For reference, the ELS spectrum of clean Al_2O_3 is also included in fig. 1 (top curve). Al_2O_3 shows a featureless loss spectrum from 0–7 eV, and thus provides an ideal support for studying the electronic structure of thin overlayer NiO films. The onset of the loss feature for Al_2O_3 at 7 eV is considerably less than the 8.7 eV band gap of Al_2O_3, and can be assigned to the surface-related interband transition associated with surface atoms which have lower coordination than the bulk atoms. Growth of NiO on top of Al_2O_3 introduces various loss features into the ELS spectra; a complete assignment of these features is provided elsewhere [27]. Here we will focus on the differences/similarities between the NiO films with various thicknesses. It is apparent from fig. 1 that the electronic structure of bulk NiO (i.e. 28 ML NiO) has already essentially developed at a NiO film thickness of 1 ML. Furthermore, no significant shifts of the individual features are observed in varying the film thickness from 1.0 to 28 ML. Since the loss peaks below 4 eV correlate with the d–d transitions, the loss energy is primarily a product of the crystal field which, in turn, is defined by the distance between the Ni- and O-ions and their ionicity. These results indicate a very similar electronic structure between the very thin and thick NiO films.

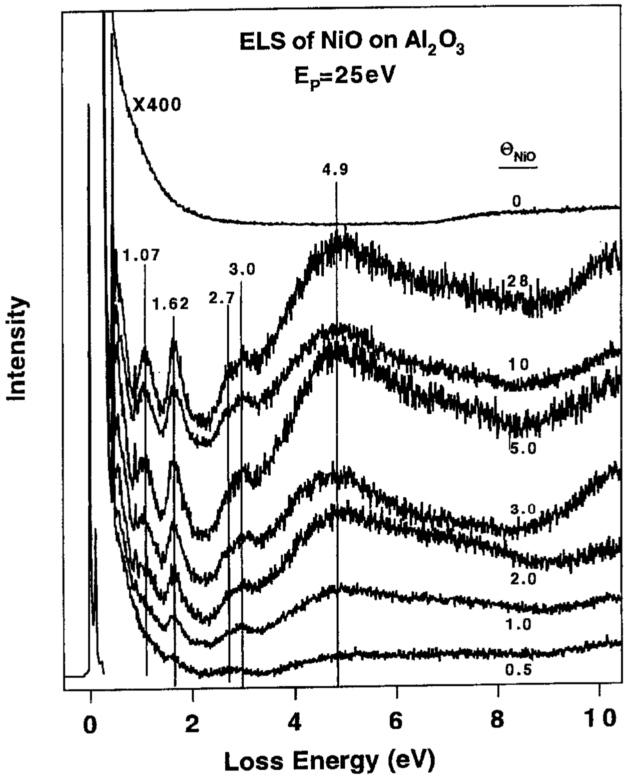

Fig. 1. ELS spectra of NiO with increasing film thickness.

3.2. Chemical properties

Fig. 2 shows two series of CO TPD spectra taken after dosing 0.02 L CO at 90 K onto various NiO/Al_2O_3 surfaces. The NiO/Al_2O_3 surfaces were either freshly oxidized at 400 K and 1×10^{-7} O_2 Torr (left panel) or preannealed at 800 K in vacuum for 5 min (right panel). The exposures were carried out using a directional gas doser and are given without correction for the dose enhancement and ion gauge sensitivity. On the fully oxidized surfaces, only CO desorption below 250 K is observed. With increasing NiO thickness, the CO desorption temperature gradually shifts from 150 K on the NiO_{1ML} surface to 200 K on the NiO_{20ML} surface. The CO desorption temperature on the thin NiO film does not converge to that of the bulk NiO surface until a NiO thickness of $\sim$ 10 ML is reached. Annealing the films to 800 K prior to the CO exposure causes a dramatic change in the TPD spectra. In addition to the desorption feature below 250 K, a desorption peak above 300 K is also observed. On NiO films with thicknesses between 2 and 10 ML, the desorption peak at 420 K, which is very characteristic of metallic Ni, indicates the partial reduction of NiO to metallic Ni due to the vacuum anneal. The extent of reduction correlates well with the film thickness as indicated by both the desorption peak between 100 and 250 K from the oxide phase and the feature at 420 K arising from the metallic phase. For the 1 ML NiO film, the behavior is slightly different. Although the desorption feature at 150 K, which relates to the NiO, is strongly attenuated after annealing to 800 K, a very broad feature extending from 250 K to almost 500 K is observed. Some of the intensity within this feature is likely due to metallic Ni; however, a major part can be attributed to a new Ni species, different from either metallic Ni or NiO. Further evidence for this new Ni phase also is found in the IRAS spectra. Fig. 3 shows a series of IRAS spectra taken at a CO background pres-

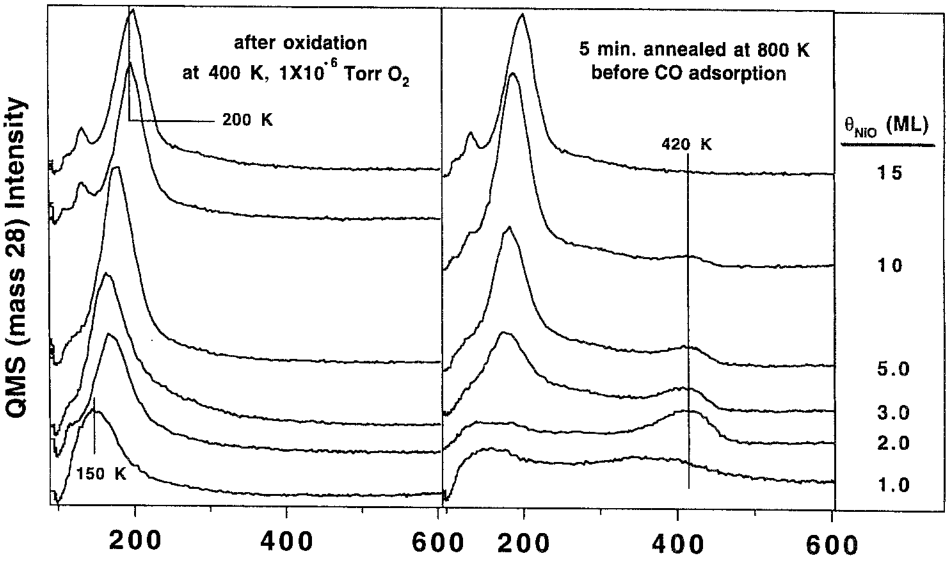

Fig. 2. CO TPD on various NiO films supported on Al_2O_3. The film was as freshly prepared (left) and annealed to 800 K in vacuum for 5 min (right).

sure of 1×10^{-5} Torr and the indicated surface temperature. Curve b was acquired from a 1 ML NiO film freshly prepared and annealed to 800 K in vacuum. The surface was subsequently annealed to 200 K (curve c) and 500 K (curve d) and then cooled to 100 K (curve e). For comparison, the spectra taken from a 30 ML NiO film (curve a) and 1 ML Ni/Al_2O_3 (curve f) are also included. The annealed 1 ML NiO film (curve b) shows two features at 2124 and 2182 cm^{-1}. The feature at 2182 cm^{-1} can be assigned to CO adsorbed on NiO. Heating the surface in 1×10^{-5} Torr CO to 200 K causes desorption of CO adsorbed on NiO and a loss of intensity of the peak at 2124 cm^{-1}. At the expense of the peak at 2124 cm^{-1}, a new peak at 2107 cm^{-1} grows and gradually shifts to a lower wavenumber with increasing temperature, finally reaching 2035 cm^{-1} at 500 K. After cooling the surface to 100 K, the peak shifts to 2097 cm^{-1}; the feature at 2124 cm^{-1}, however, is not repopulated. Based on its peak position and its behavior upon annealing, the feature near 2100 cm^{-1} is assigned to CO adsorbed onto metallic Ni in a atop configuration. The feature at 2124 cm^{-1} has been observed previously by Raschko et al. [28], on NiO supported on powdered Al_2O_3 subsequent to heating in vacuum, and by Peri [29] on Ni supported on powdered Al_2O_3. Both groups have assigned this feature to Ni^{1+} at the interface. Our results support this assignment, since TPD and IRAS of this phase show a desorption temperature and vibration frequency intermediate between metallic Ni and NiO. Furthermore, our results show that heating the surface to 200 K in the presence of CO reduces this phase to metallic Ni. It is also interesting to note that no CO is observed to adsorb on bridging or three-fold hollow sites, implying highly dispersed Ni atoms. This is consistent with the well-known strong interaction of metallic Ni with oxide supports [29–33]. The presence of partial oxidized Ni should serve to further stabilize the Ni particles.

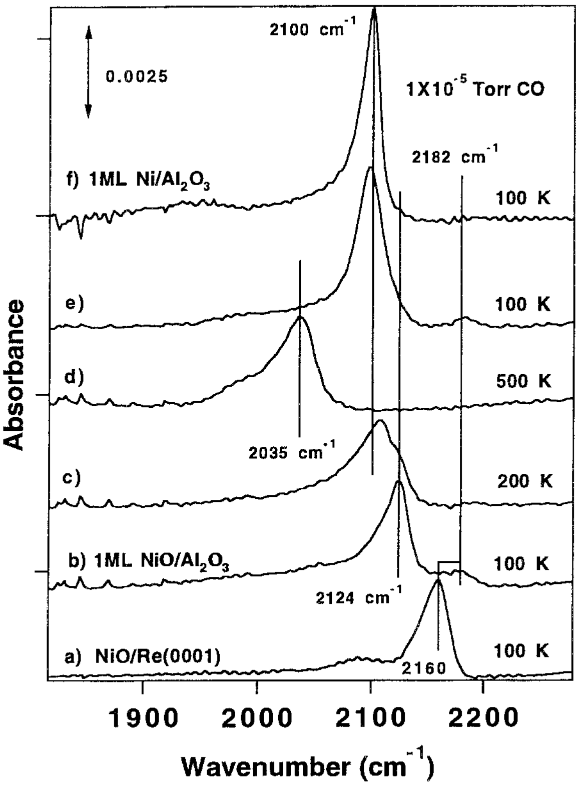

Fig. 3. IRAS spectra acquired in a CO background pressure of 1×10^{-5} Torr and at the indicated temperature.

The high reactivity of thin NiO films is also documented by IRAS using CO as probe. Fig. 4 shows a series of IRAS spectra acquired from various NiO films supported on Al_2O_3 and annealed to 500 K in 1×10^{-5} Torr CO for 5 min. The feature at 2182 cm^{-1} for the NiO_{1ML} and NiO_{2ML} films and the feature at 2160 cm^{-1} for the

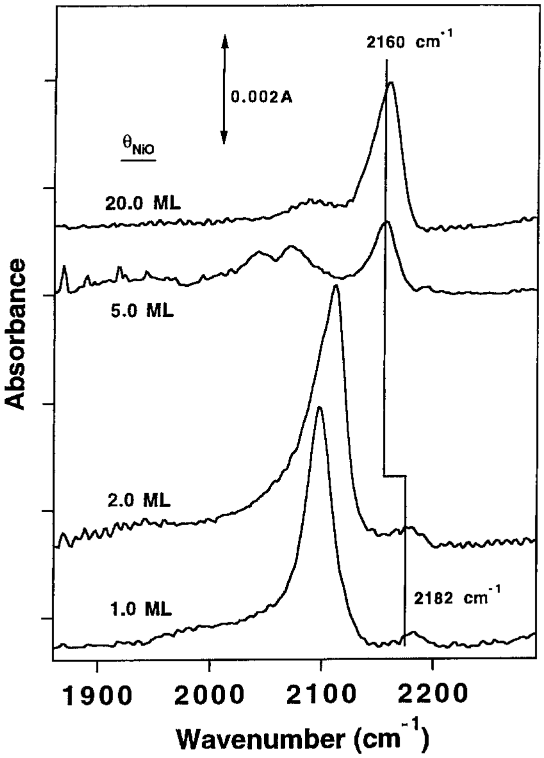

Fig. 4. IRAS spectra of CO adsorbed onto NiO films, pre-annealed at 500 K and in 1×10^{-5} Torr CO for 5 min.

NiO_{5ML} and NiO_{30ML} can be assigned to CO adsorbed on the NiO phase, while the features below 2100 cm^{-1} correspond to CO adsorbed on the metallic Ni phase. It is evident in fig. 4 that heating to 500 K in a CO background substantially reduces NiO films thinner than 5 ML.

To further probe the reactivity of the NiO_{1ML}/Al_2O_3 system, temperature programmed (2 K/s) reaction was carried out at a CO background pressure of 1×10^{-7} Torr. The formation of CO_2 was monitored using a quadrupole mass spectrometer in a line-of-sight configuration (fig. 5). The bottom TPR, acquired for the freshly prepared NiO_{1ML}/Al_2O_3 surface, shows a broad CO_2 feature related to reaction between CO and lattice oxygen. CO_2 formation is apparent even at temperatures as low as 300 K. In a second subsequent TPR, CO_2 formation was substantially attenuated; a third TPR (top curve) shows very little CO_2 evolution. CO/IRAS and CO/TPD following the third TPR indicate the presence of metallic Ni. These results demonstrate the high reactivity of oxygen in the NiO thin film toward CO oxidation. In contrast, the oxygen in Al_2O_3 and in thick NiO films is unreactive toward CO oxidation at surface temperatures as high as 800 K. A quantitative evaluation of the peak areas indicates that ~ 75% of the NiO is reduced in the first run of the TPR experiments.

These results have some interesting implications: First, the weak interaction between the NiO and Al_2O_3 facilitates the reduction of NiO to metallic Ni. On the other hand, the strong interaction between Al_2O_3 and Ni stabilizes the metallic phase and promotes a high dispersion of the Ni. These combined effects make Al_2O_3 an ideal support for metallic Ni. It is interesting to compare the NiO/Al_2O_3 surface chemistry with the surface chemistry of NiO/MgO. Annealing a thin film of NiO supported on MgO(111) to 800 K in vacuum results in interdiffusion of the NiO into the support MgO but no apparent change in the oxidation state of the NiO itself [34].

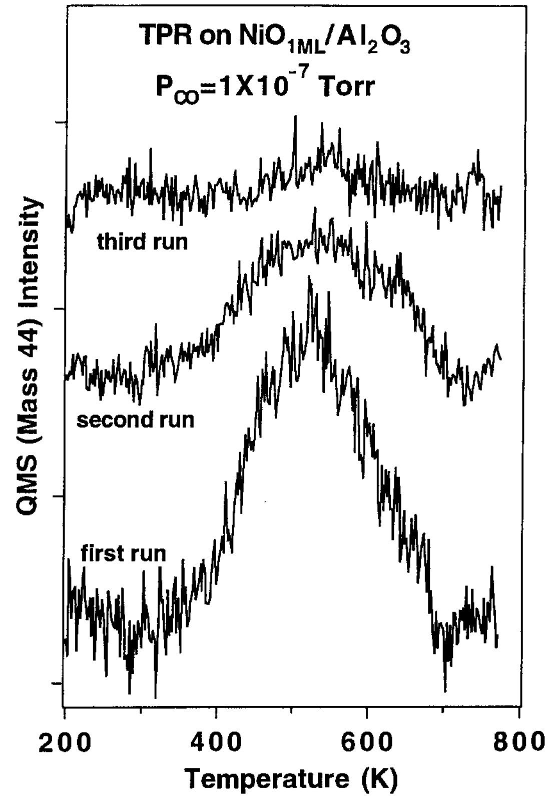

Fig. 5. TPR for a NiO_{1ML}/Al_2O_3 film monitoring CO_2 formation within a CO background pressure of 1×10^{-7} Torr. The heating rate was 2 K/S.

Second, our results provide an alternative explanation for the support-dependent chemistry that is frequently observed for oxide/oxide systems. For NiO on Al_2O_3, our results show the special surface chemistry of the overlayer oxide to be an intrinsic property of low dimensional NiO films. The interaction between NiO 2D (one monolayer) and Al_2O_3 is apparently rather weak and the low dimensional properties of NiO dominate its surface chemistry. On the other hand, a strong interaction between NiO and MgO, comparable to the NiO/NiO interaction, restores the 3D properties of the overlayer NiO. It is also noteworthy that the electronic structure of the NiO overlayer is rather insensitive to the apparent changes in the chemical properties.

Third, the chemical properties of thin NiO films can be significantly different from those found for thick NiO films. If one intends to model the bulk oxide surface with a thin film, a film thickness of ~ 20 ML is essential to avoid misleading results. Similarities based on electronic structure probes is inadequate, that is, documenting similarities with chemical probes is essential to confirm the validity of a thin film oxide model.

In summary, the chemical properties of an ultrathin (< 10 monolayers) NiO films are substantially different from those found for thick (> 10 monolayers) NiO film. The electronic structure of these films is rather insensitive to the changes observed in the chemical properties. The modified chemistry found for the thin NiO films is an intrinsic property related to the low dimensionality of the material.

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