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Acid/base properties of MgO studied by high resolution electron energy loss spectroscopy

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The acid/base properties of model MgO surfaces have been studied using various probe molecules with acid strengths ranging from those of carboxylic acids and alcohols to alkenes and alkanes. High-resolution electron energy-loss spectroscopy (HREELS) data show that carboxylic acids, methanol and water dissociate heterolytically on MgO surfaces. Ethylene and ethane, however, are found to adsorb associatively. Thermally generated surface defect sites exhibit stronger basic character and are capable of dissociating ethane. The present studies demonstrate the capabilities of HREELS for the investigation of the chemical properties of insulating materials.

Keywords: Magnesium oxide; acid/base; high resolution; electron energy loss spectroscopy

1. Introduction

It has long been recognized that acid/base properties of catalysts play an important role in many catalytic reactions, including polymerization, isomerization, cracking, dehydration, alkylation, halogenation and dehalogenation [1,2]. Magnesium oxide is a typical basic oxide whose surface basicity can be altered by adding metal ions [3]. Li-doped MgO catalysts, for example, have been reported to exhibit stronger basicity than pure MgO and are capable of promoting the oxidative coupling of CH_4 to $C_2H_6 + C_2H_4$ through a methyl radical intermediate [4].

It is only recently that surface spectroscopic investigations of the acid/base properties of MgO have been carried out [5–8]. It has been suggested [8] that the dissociation of Brønsted acids on MgO powders can be correlated with their relative acidity in aqueous solution, rather than in the gas phase. Thermal decomposition of alcohols to alkenes and water via surface alkoxides has been found to occur on MgO powders [9]. Dehydration of alcohols, however, did not occur on single-crystal MgO [5], nor was it observed on MgO thin films [7,10].

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These chemical differences between the various forms of MgO relate to the heterogeneous nature of the surface sites of these materials. These sites have been assigned to surface Mg–O pairs with differing coordination numbers. X-ray photoelectron spectroscopy [5], UV-visible and photoluminescence [11,12] studies indicate that the sites of lower coordination exhibit stronger basicity and are capable of reacting with weaker acids.

Recently we have reported a surface study of the growth of ultrathin MgO films on Mo(100) [13]. Our low-energy electron diffraction (LEED) and surface spectroscopic studies have shown that a highly ordered, stoichiometric MgO film can be formed with the (100) face of MgO oriented parallel to Mo(100). In this letter, we present a study of the interactions of Brønsted acids, whose strength ranges from those of carboxylic acids and alcohols to alkenes and alkanes, with these well-characterized MgO films using high-resolution electron energy-loss spectroscopy (HREELS).

Characterization of these Brønsted acids adsorbed on well-defined MgO surfaces has been carried out using primarily spectroscopies which probe electronic structure [5–7]. Surface vibrational spectroscopic studies such as HREELS should provide further information regarding the surface intermediates formed during adsorption and reaction. The formation of surface hydroxyls due to proton abstraction by surface oxygen anions and adsorbed conjugate base anions from Brønsted acids should be particularly amenable to study with HREELS.

In the application of HREELS to adsorbates on ionic substrates, however, a great difficulty encountered is that the accompanying vibrational spectra are dominated by losses due to excitation of surface optical phonons. Since the intense multiple phonon losses generally extend over a wide vibrational frequency range of the HREELS spectra, it is not practical to observe directly adsorbate losses (which are several orders of magnitude smaller in intensity than the phonon losses) in the 0–4000 cm^{-1} spectral range. In recent studies [14], we have developed a new approach to acquiring HREELS data in order to circumvent the difficulties associated with these phonon losses. By utilizing a high-energy incident electron beam in combination with an off-specular scattering geometry, this new approach enables the direct observation of weak loss features due to the excitation of adsorbates without serious interference from intense multiple surface optical phonon losses. HREELS data indicates that carboxylic acids, methanol and water undergo heterolytic dissociation, whereas ethylene and ethane are found to adsorb associatively on MgO. However, an increase in the surface basicity of MgO, achieved by thermal treatment, resulted in the dissociation of ethane.

2. Experimental details

The studies were carried out in an UHV system, described elsewhere [14,15], with capabilities for HREELS, Auger electron spectroscopy (AES), LEED and temperature programmed desorption (TPD), and for sample heating and cooling. The crystal cleaning procedure has also been detailed previously [13].

The HREELS measurements were carried out in the scattering compartment of a two-tiered chamber. The primary energy of the electron beam of the spectrometer (LK-2000, Larry Kesmodel Technologies) can be varied in the 0–250 eV range. The spectral resolution (full-width at half maximum of the elastic peak) of the data presented here was typically 80–120 cm^{-1}.

Spectroscopic grade formic acid (96%), acetic acid (99.9%), methanol (99.99%) and water (99.99%) were used in this study. Further purification was achieved in the manifold via freeze–pump–thaw cycles prior to introduction of these reactants into the vacuum chamber. Ethylene (99.99%) and ethane (99.99%) were used as received.

3. Results and discussion

Ultrathin MgO films were synthesized in a UHV environment by thermally evaporating Mg onto a clean Mo(100) surface in the presence of oxygen. The procedure for the MgO film preparation and the detailed studies regarding characterization of the films have been presented elsewhere [13,15]. Our LEED and surface spectroscopic studies have shown that the MgO films, prepared under optimum oxidation conditions, grow epitaxially in the 200–600 K substrate temperature range and have essentially a one-to-one stoichiometry. The stoichiometric films are nearly free from point-like surface defects, as indicated in our electron energy-loss spectra [15].

3.1. CH_3COOH AND HCOOH

Although much weaker than strong mineral acids, carboxylic acids are considerably more acidic than weakly acidic organic compounds, such as alcohols. It follows then that a carboxylic acid will give up its acid proton more readily on MgO than will a weaker organic acid. Previous X-ray and ultraviolet photoelectron spectroscopic studies [5,7] have shown that carboxylic acids adsorb dissociatively on MgO(100) surfaces and oxidized Mg(0001) surfaces to form stable carboxylate species over the 150–480 K temperature range. Dehydration of the acetate species was reported to occur on MgO powders at higher temperatures, yielding ketene and water [9]. Our HREELS data, however, showed the carboxylate species to be stable on the MgO(100) films up to temperatures > 600 K.

Fig. 1 gives a set of HREELS spectra of acetic acid adsorbed on a ≈ 20 monolayer (ML) MgO film at 90 K as a function of exposure and annealing temperature (T). CH_3COOH exposures were carried out via backfilling the UHV chamber. Exposing the sample to 500 langmuir (L) of CH_3COOH at 90 K gave rise to three distinct peaks in the spectrum (fig. 1a). The losses at 1364,

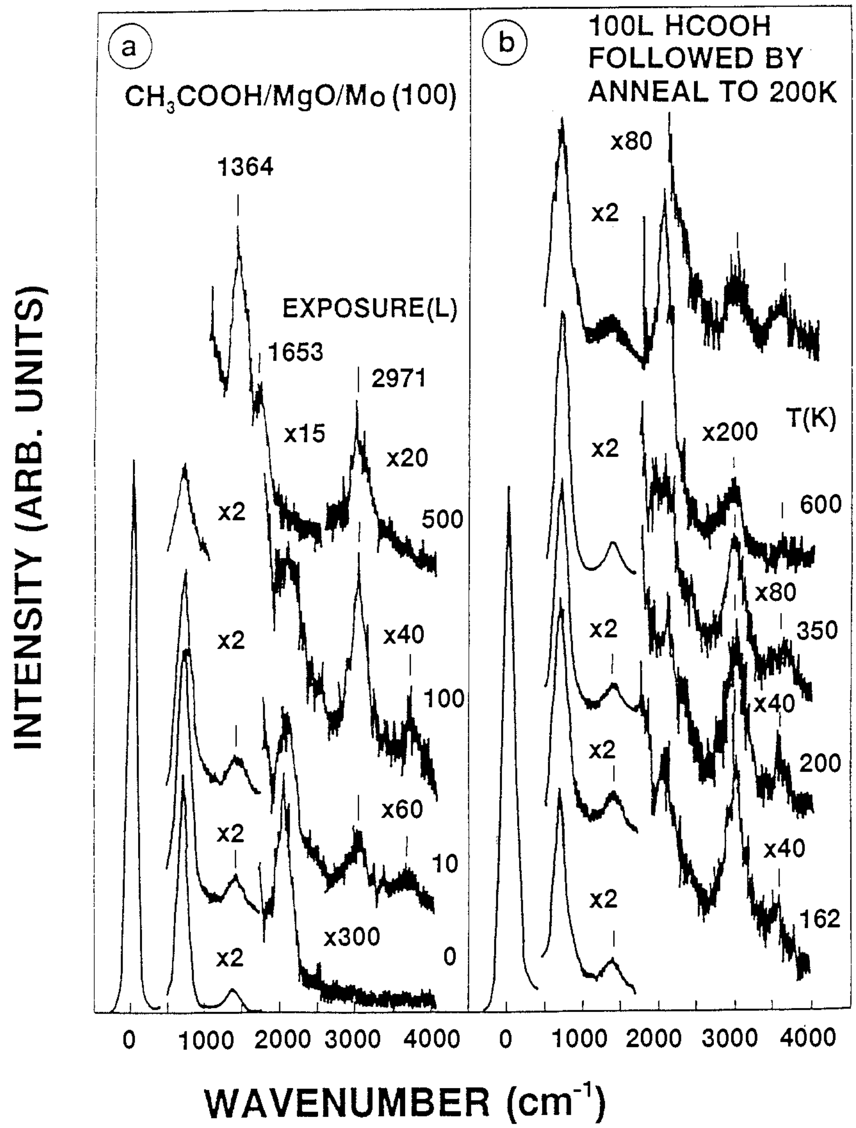

Fig. 1. (a) HREELS spectra of acetic acid adsorbed onto a ≈ 20 ML MgO film at 90 K as a function of the indicated exposure. (b) HREELS spectra of acetic acid adsorbed onto a MgO film at 90 K as a function of the indicated annealing temperature. The surface was previously exposed to 500 langmuir (L) of CH_3COOH. The upper spectrum was acquired after a 100 L exposure of formic acid at 90 K followed by an anneal to 200 K. The spectra were collected at $E_0 \approx 46$ eV and an angle 8.5° off the specularly reflected beam direction.

1653 and 2971 cm^{-1} are due to excitations of the C–H deformation (δ(CH)), the C=O stretching, ν(C=O), and the C–H stretching, ν(CH), modes, respectively [16,17]. The 2971 cm^{-1} loss was broadened at the higher loss energy side due to its superposition with the O–H stretching mode [17]. The lower frequency of the

ν(OH) mode than that observed for gas-phase acetic acid has been attributed to the formation of hydrogen bonding in the solid phase [17]. This feature indicates that multilayers of acidic acid are condensed on the surface at 90 K. At low exposures (fig. 1a), however, a high loss energy peak appeared at 3638 cm^{-1}. The appearance of this loss, which corresponds exactly to the loss feature identified with an OH species (see the next section), indicates the dissociation of acetic acid and the formation of a surface acetate species. The loss features of a surface acetate were not observable in the 500–2200 cm^{-1} spectral region because of interference from losses due to the surface optical phonon and its multiples. However, the increase in intensity of the 1359 cm^{-1} loss relative to that of the fundamental mode at 679 cm^{-1} with increasing exposure can be explained as arising from the symmetric and asymmetric O–C–O stretching modes of the surface acetate in the 1000–1650 cm^{-1} region [16,17].

The evolution of the losses associated with surface acetate as a function of the annealing temperature is shown in fig. 1b. No dramatic changes are observed to take place during the annealing process. The concurrent diminution of the ν(CH) and ν(OH) losses with increasing temperature indicates the gradual desorption of molecular acetic acid formed via recombination of surface acetate and surface hydroxide. There is no evidence for dehydration of surface acetate in our experiments even at high temperatures, nor is there evidence for an irreversible decomposition leading to carburization as reported previously [10]. Auger measurements showed that the surface carbon level was below the detection limit of AES after the surface had been annealed to 800 K. Similar results were found for formic acid adsorption on the MgO films, as shown in fig. 1b (the upper spectrum). Exposing the specimen to 100 L HCOOH, followed by an anneal to 200 K, produced two losses at 2988 and 3556 cm^{-1}, which can be attributed to the C–H stretching mode of surface formate and to the O–H stretching mode of a surface hydroxyl species, respectively.

3.2. H_2O AND CH_3OH

Water and methanol are weaker acids than carboxylic acids; however, dissociation of water and alcohols was found to occur both on well-defined MgO surfaces and on MgO powders [5–7,9].

Adsorption of water and methanol on thin MgO films has been examined using HREELS [14], as shown in fig. 2. Exposing the sample to 100 L of H_2O at 90 K led to the appearance of two distinct peaks in the spectrum (fig. 2a). The losses at 1650 and 3369 cm^{-1} are due to the excitations of the δ(HOH) scissoring and ν(OH) stretching modes, respectively [18]. It is noteworthy that the 3369 cm^{-1} peak was considerably broadened due to hydrogen bonding, indicating that multilayers of water were condensed on the surface. Upon annealing to $T > 160$ K, the ν(OH) feature shifted to higher loss energies (fig.

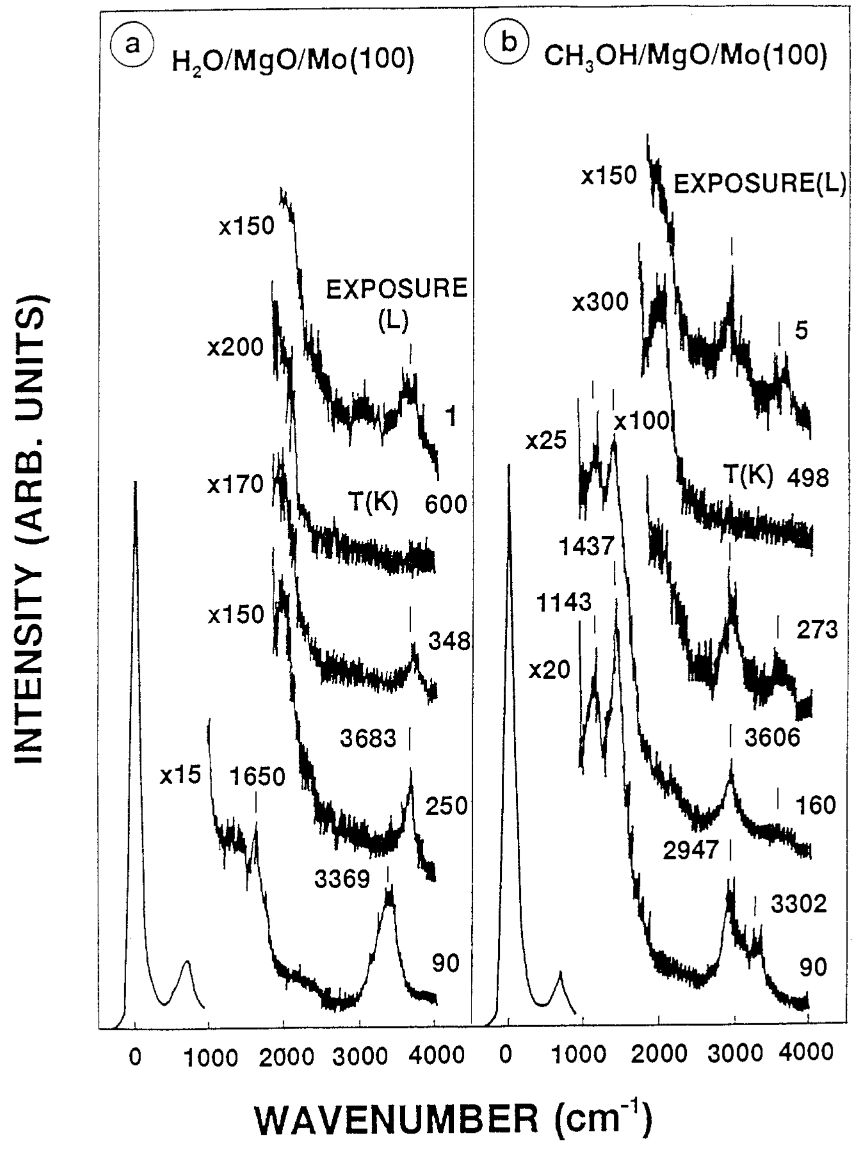

Fig. 2. (a) HREELS spectra of water adsorbed onto a ≈ 30 ML MgO film at 90 K. The surface was exposed to 100 L of water followed by annealing to the temperatures indicated. The upper spectrum was acquired after a 1 L exposure of water at 90 K. (b) HREELS spectra of methanol adsorbed onto a ≈ 30 ML MgO film at 90 K. The surface was exposed to 180 L of methanol followed by annealing to the temperatures indicated. The upper spectrum was acquired subsequent to a 5 L exposure of methanol at 90 K. The spectra were collected at $E_0 \approx 46$ eV and an angle 8.5° off the specularly reflected beam direction.

2a). This shift coincided with the desorption of H_2O multilayers in the TPD spectra. Our TPD experiments [15] have shown that H_2O multilayers desorbed between 131 and 171 K, with a maximum at 154 K. A second desorption peak, which arose from water formed via recombination of surface hydroxyls, appeared in the 171–400 K range.

The shift of the 3369 cm^{-1} peak can be explained as arising from the desorption of the condensed H_2O multilayers, exposing a dissociatively chemisorbed layer of H_2O. Regarding this point, it is noteworthy that the formation of surface hydroxyls on metal [18] and metal oxide surfaces [18–20] usually results in an upward shift in the ν(OH) frequency. Dissociative adsorption of H_2O at low exposures occurred even at 90 K, as shown in the upper spectrum of fig. 2a. The 3586 cm^{-1} peak arising from H abstraction by basic oxygen anions in the upper spectrum is nearly identical to the feature observed in the multilayer annealing experiments.

Fig. 2b shows a set of HREELS spectra of CH_3OH adsorbed onto a $\approx$ 30 ML MgO film at 90 K as a function of annealing temperature. Exposing the surface to 180 L CH_3OH produced four distinct peaks at 1143, 1437, 2947 and 3302 cm^{-1}. These losses can be attributed to C–O stretching (ν(CO)), CH_3 bending ($\delta(CH_3)$), C–H stretching (ν(CH)) and O–H stretching (ν(OH)) modes, respectively [14]. The spectrum acquired following an anneal to 160 K (fig. 2b) exhibits the loss features of the methanol monolayer. This result is consistent with the desorption of methanol multilayers between 140–170 K, as indicated by our TPD measurements [15]. Annealing to $T \geqslant 160$ K resulted in the disappearance of the 3302 cm^{-1} loss, and the appearance of a new peak at 3606 cm^{-1} whereas the 2947 cm^{-1} loss remained essentially unperturbed. The appearance of the new feature at 3606 cm^{-1}, which is identical to the feature assigned above to an OH species, indicates the dissociation of methanol and the formation of a methoxy species upon annealing. Heating to higher temperatures led to a concurrent diminution of the two losses. Features due to the excitation of surface species completely disappeared at 498 K (fig. 2b), consistent with our TPD data. The dissociative adsorption of methanol was also observed at low exposures and at 90 K, as shown in the upper spectrum of fig. 2b.

3.3. C_2H_4 AND C_2H_6

Adsorption of ethylene on thin MgO films has been studied, as shown in fig. 3a. Because of the interference from the phonon losses, the adsorbate losses were not observable in the 0–2000 cm^{-1} spectral range. The 3027 cm^{-1} loss, which was attributed to the ν(CH) stretching mode, remained essentially unchanged with increasing C_2H_4 exposure and annealing temperature, indicating that a saturation coverage has been reached and that the surface species is thermally stable up to 400 K. Further annealing led to the disappearance of the adsorbate losses. No ν(OH) feature was observed in our HREELS measurements, indicating associative adsorption of ethylene on MgO. A similar behavior was observed for ethane adsorbed on the MgO films, as shown in fig. 3b (the lower spectrum).

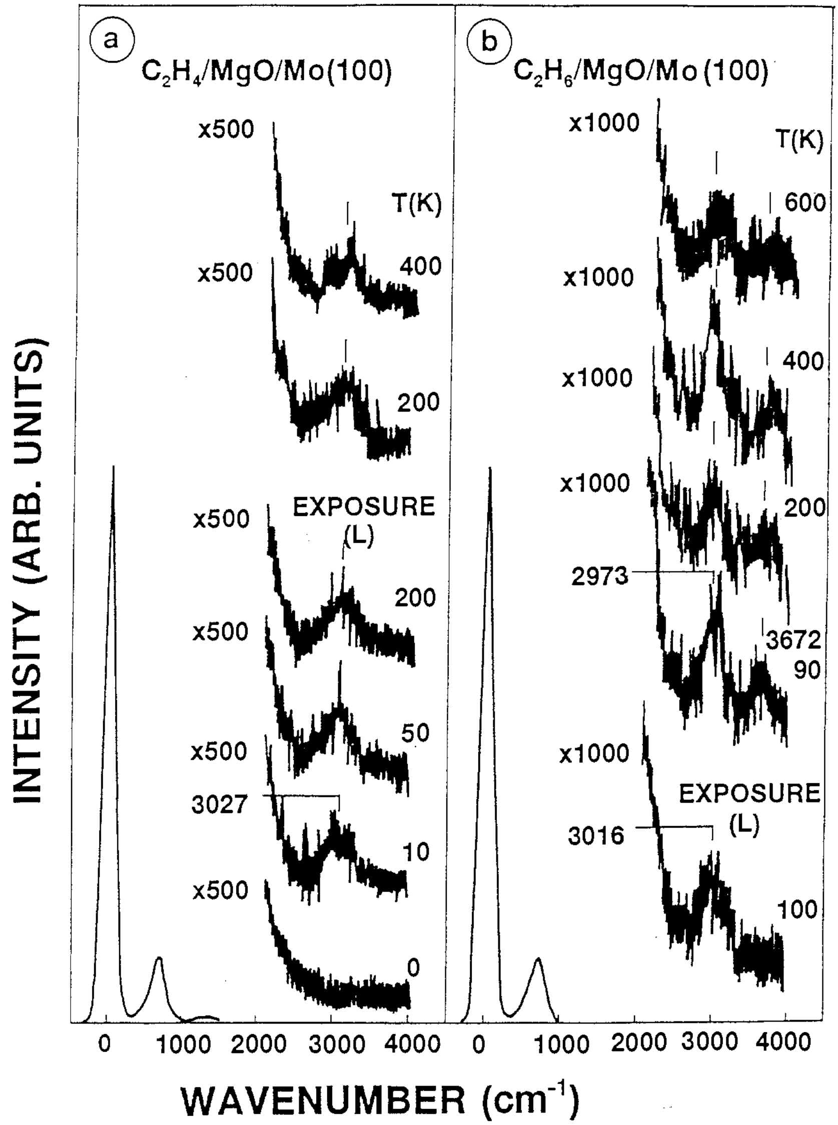

Fig. 3. (a) HREELS spectra of ethylene adsorbed onto a ≈ 20 ML MgO film at 90 K as a function of the indicated exposure. The two upper spectra were acquired after a 100 L exposure of C_2H_4 at 90 K followed by annealing to the temperatures indicated. (b) HREELS spectra of ethane adsorbed onto a MgO film at 90 K. The lower spectrum was acquired from a MgO film nearly free from point-like surface defects and the four upper spectra from the surface that had been annealed to 1300 K. The surface was exposed to 100 L of C_2H_6 followed by annealing to the temperatures indicated. The spectra were collected at $E_0 \approx 46$ eV and an angle 8.5° off the specularly reflected beam direction.

However, a dramatic change occurred upon annealing the substrate to 1300 K. Heating and the subsequent adsorption of 100 L C_2H_6 induced a new feature at 3672 cm^{-1}. The appearance of the new feature, which is identical to

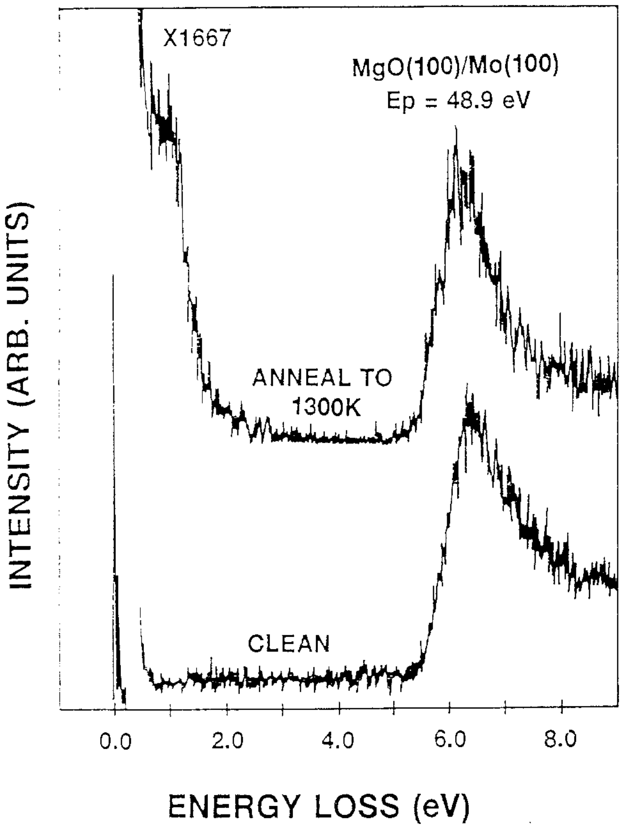

Fig. 4. Electronic interband transitions obtained from a ≈ 20 ML MgO film. The lower spectrum is from an unannealed surface; the upper spectrum was taken following an anneal to 1300 K. The spectra were acquired in the specular direction and at $E_0 \approx 48.9$ eV. The loss assigned to arising from surface defects is centered in the upper spectrum at 0.9 eV.

the feature assigned to an OH species, indicates the formation of a surface hydroxyl species and the dissociation of C_2H_6. This dissociated species was thermally stable up to 600 K (fig. 3b).

The dissociation of C_2H_6 on the annealed surface very likely relates to the presence of surface defects. Fig. 4 shows the electronic interband transitions obtained from a ≈ 20 ML MgO. The electron energy-loss spectra were acquired in the specular direction and at a beam energy of 48.9 eV with an energy resolution of 0.03 eV. The spectrum of the clean surface exhibited a loss feature at 6.3 eV. This feature is believed to be surface related interband transition [21] since its energy is considerably less than the 7.8 eV band gap of MgO [22]. Annealing to 1300 K results in the appearance of a new loss feature in the band gap centered at 0.9 eV *. The nature of this loss has been explored previously

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* The value obtained here should be more accurate than the previously reported loss energy of 2.0 eV, where the spectra were acquired with a much poorer energy resolution of 1 eV.

and attributed to surface defect states [21]. These defect sites have lower coordination numbers, and thus are capable of dissociating ethane.

4. Conclusions

Highly ordered, stoichiometric ultrathin MgO films have been synthesized on Mo(100). Our surface spectroscopic studies have shown that the properties of the MgO films prepared are essentially identical to bulk, single-crystal MgO. The acidic and basic properties of these well-characterized MgO films have been studied using a range of Brønsted acids with strengths ranging from acetic acid and methanol to ethylene and ethane. HREELS data show that acetic and formic acids, 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, are found to adsorb associatively on the MgO surfaces. Thermally generated surface defect sites exhibit stronger basicity, capable of dissociating ethane.

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