Interactions of Alcohols with a NiO(100) Surface Studied by High-Resolution Electron Energy Loss Spectroscopy and Temperature-Programmed Desorption Spectroscopy

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Interactions of alcohols with well-defined NiO(100) films prepared on Mo(100) have been studied using combined high-resolution electron energy loss spectroscopy (HREELS)/temperature-programmed desorption spectroscopy (TPD). The results show that alcohols adsorb associatively on NiO(100) at 90 K and reversibly desorb upon heating under ultrahigh-vacuum conditions. Both methanol and ethanol are bonded to the cation sites of NiO(100) via their oxygen atom with the methyl and ethyl group, respectively, directed away from the surface. At low coverages, there is a repulsive interaction between adsorbed alcohols, resulting in a decrease in the apparent activation energy of desorption. Below monolayer coverages, the change in the relative mode intensities in the HREELS spectra with respect to the methanol coverage correlates excellently with two desorption states evident in the TPD studies, indicating reorientation of a portion of the adsorbed methanol at high coverages. In the case of ethanol adsorbed on NiO(100), however, only a single desorption state above 200 K is observed, consistent with the HREELS data which show that the relative mode intensities remain essentially unchanged within the monolayer coverage range. The absence of the ν(OH) loss feature in the region of OH vibrations below monolayer coverages indicates the formation of strong hydrogen bonds between the hydroxyl hydrogen and the lattice oxygen. This feature, along with consideration of the surface symmetry of NiO(100), leads to the conclusion that the hydroxyl proton of the molecules likely fluctuates about the neighboring anion sites, acting as a mobile proton. This result is important to our understanding of the nature of the precursor to the dissociated state in an acid–base reaction of the following type: 

\[
AH + B \rightleftharpoons A^- + HB^+.
\]

I. Introduction

Interactions of alcohols with well-defined solid surfaces are a subject of both fundamental and practical interest. For example, methanol synthesis from carbon monoxide/carbon dioxide and hydrogen over oxide supported catalysts is a process of major industrial importance. Accordingly, the kinetics and mechanism of this reaction have been studied extensively for the past decade. The key step in methanol synthesis is presumed to involve the formation of adsorbed surface intermediates during the reaction. Thus, in the reverse process, studies of methanol decomposition on well-defined solid surfaces under ultrahigh-vacuum (UHV) conditions should provide useful information regarding adsorbed CH₃O species that may be of importance in this reaction.

Adsorption and decomposition of alcohols on a variety of oxide catalysts have been studied extensively using infrared techniques and other physical chemical methods. A general trend revealed in these studies is that methanol decomposition proceeds via sequentially formed methoxy and formate intermediates. On methanol synthesis catalysts, for example, methanol adsorbs dissociatively to form a methoxy species at relatively low reaction temperatures (400 K) in the presence of gas-phase methanol. The methoxy species decomposes rapidly to form formate and carbonate intermediates upon removal of methanol from the gas phase and upon heating. Heating of magnesium in methanol vapor in the 373–673 K temperature range, however, was reported to give rise exclusively to methoxide, and only in the presence of gas-phase oxygen was a formate species observed. This differs from the early work of Kagel and Greenler in which the production of a formate-like surface compound was found upon heating of magnesium samples at 438 K in pure methanol vapor. The presence of surface carbonates on MgO was reported after heating the sample to 700 K. Desorption products of methanol adsorbed onto powdered oxide catalysts at elevated pressures were found to be primarily H₂, CO, and CO₂. In some cases, the production of methane and water was also reported. Combined infrared/TPD studies of methanol adsorbed on ZnO powdered samples showed that the desorption of H₂ found within the 450–550 K temperature range is due to the decomposition of the methoxy groups as they convert to formate species. Also, concurrent desorption of CO and CO₂ at higher temperatures is a consequence of the decomposition of the formate intermediate. The formation of carbonates on the stoichiometric spinel, ZnCr₂O₄, was also reported and was observed to lead to the desorption of CO₂ at 720 K. In all of the above cases, it has been shown that the participation of substrate oxygen is necessary to form formate and carbonate species on the catalyst surfaces.

Following the above studies, it is clear that although methanol chemistry on oxide materials has been explored extensively, these studies have been carried out primarily on powdered samples. Accordingly, the information obtained necessarily represents an average of the various crystal faces exposed plus a variety of defects present on the polycrystalline powdered samples. In particular, the reaction of methanol over powdered oxide catalysts may well be controlled by various defect sites whose respective contribution to the decomposition mechanism is difficult to identify. The investigation of methanol interaction with a well-defined solid surface is thus of great importance to elucidate the nature of active sites and the microscopies of methanol decomposition. Accordingly, methanol adsorption and decomposition on single-crystal metal surfaces under UHV conditions have been a focus of intensive research for the past decade.

Several studies using ultraviolet photoelectron spectroscopy (UPS) and high-resolution electron energy-loss spectroscopy (HREELS) have shown that methanol is bonded via the hydroxyl oxygen of the molecule with the methyl group directed away from the surface. The decomposition mechanism of methanol on most metal surfaces involves OH bond cleavage to form methoxy, followed by its decomposition to carbon monoxide and additional hydrogen adatoms. No CH₃O or CHO intermediate in the decomposition of methoxy to CO could be...
difficulty associated with losses due to excitation of surface optical
various surface-sensitive techniques such as HREELS, Auger respectively. The CH3 symmetric (v,(CH3)) and asymmetric
of molecular methanol chemisorbed onto several transition-metal
studies of alcohols adsorbed onto metals. The HREELS spectra
different sites.
associations with these hydrogenic features have dipole moment
arise from the CH3 rock (p(CH3)) and deformation (6(CH3)),
coverages of methanol exhibit much more intense n(OH),
features found between 1000 and 1035 cm-1 is due to excitation
electron spectroscopy (AES), and low-energy electron diffraction
environment; and (3) spectroscopic characterization of adsorbates
in the 200-4000-cm-1 spectral region.28-34 A predominant loss
change of the relative mode intensities of molecularly adsorbed
methanol with respect to the methanol coverage.38-90 For example,
OH bending (π(OH)) mode and the oxygen-metal stretching (π(O-M)) mode have been observed in the lower frequency range 235-770 cm-1 in several of these studies.28,30,31

An intriguing feature revealed in these EELS studies is the change of the relative mode intensities of molecularly adsorbed methanol with respect to the methanol coverage.28,39 For example, HREELS spectra of low coverages of adsorbed methanol on Rh(100)30 resemble closely those of methoxy with π(OH) and π-(CO) modes dominating the spectra, while spectra of high coverages of methanol exhibit much more intense π(CH), δ-(CH3), π(CH), and π(OH) modes, similar to the spectra of methanol multilayers. These changes imply that the interaction between the neighboring molecules increases at the higher coverages. Such an increase likely results in reorientation of some of the adsorbed methanol such that the vibrational motions associated with these hydrogenic features have dipole moment components perpendicular to the surface.30

As part of a continuing study of relatively complex organic species chemisorbed on insulating metal oxides, we report here the results of a combined HREELS/temperature-programmed desorption (TPD) investigation of the adsorption of alcohols on NiO(100) films under UHV conditions. These studies focus on the adsorption geometry of alcohols on NiO(100) and on the nature of bonding between alcohols and the oxide surface. The reaction intermediates formed upon adsorption of alcohols on NiO(100) and the desorption products during annealing experiments will be examined.

Our new strategy to study oxides involves the following procedure: (1) preparation of ultrathin metal oxide films on a single-crystal refractory metal surface. Utilization of a refractory metal as a substrate minimizes potential interfacial reactions and interdiffusion at the interface and provides a high melting point conducting substrate; (2) deposition of oxide precursor metals onto the refractory metal surface in a controlled oxygen environment; and (3) spectroscopic characterization of adsorbates chemisorbed on these well-characterized oxide films utilizing combined HREELS/TPD. Such an approach allows us to employ various surface-sensitive techniques such as HREELS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and TPD and for sample heating and cooling. The refractory metal Mo(100) was chosen as a substrate for preparing the thin NiO films. NiO possesses a rock salt lattice, with the anions and cations situated at the corners of two interpenetrating face-centered-cubic sublattices. Since the lattice mismatch between the (100) face of nickel oxide and the Mo(100) structure is only a few percent, NiO films are anticipated to grow epitaxially on the (100) face of Mo.

Thin NiO films were prepared by depositing Ni onto Mo(100) in a controlled oxygen atmosphere, followed by annealing in oxygen ambient. Nickel deposition was performed via thermal evaporation of a high-purity ribbon tightly wrapped around a tungsten filament. The film stoichiometry was adjusted by tuning the flux on the Ni evaporation, which was monitored by a mass spectrometer mounted in line with the metal source, at an oxygen pressure of 7 x 10-7 Torr. The growth of the films was controlled at a rate of approximately one monolayer (ML) per minute, and the films were typically 20 ML thick. Displayed in Figure 1 is the Auger spectrum acquired following the film synthesis which shows features essentially identical to those of single-crystal NiO(100).40 Structural studies using LEED show that the NiO films 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. Recent progress has been made in circumventing the difficulties associated with these phonon losses. For example, deconvolution techniques have been implemented to remove or suppress surface phonon combination peaks from the HREELS spectra.35,36 Clearly, the Fourier deconvolution methods are superior to simply acquiring difference spectra between clean and adsorbate-covered surfaces;35,36 nevertheless, it is still basically an "indirect" technique. Of particular concern are the spurious features that may be introduced in the spectrum by the Fourier deconvolution procedure itself due to difficulties inherent in deconvolution schemes.35,36 In the recent studies,37-39 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, 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 of oxide materials. In the present study, we exploit these recent successes to study the interaction of alcohols with NiO films.

II. Experimental Details

These studies were carried out utilizing an ultrahigh-vacuum (UHV) system containing a two-tiered chamber, described elsewhere,37,38 with capabilities for HREELS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and TPD and for sample heating and cooling. The refractory metal Mo(100) was chosen as a substrate for preparing the thin NiO films. NiO possesses a rock salt lattice, with the anions and cations situated at the corners of two interpenetrating facentered-cubic sublattices. Since the lattice mismatch between the (100) face of nickel oxide and the Mo(100) structure is only a few percent, NiO films are anticipated to grow epitaxially on the (100) face of Mo.
Interactions of Alcohols with a NiO(100) Surface

A. TPD Studies. The adsorption of alcohols on NiO(100) films has been examined using TPD. Thermal desorption products from methanol adsorbed on NiO(100) films at 90 K have been followed by monitoring several masses (m/e = 2, 18, 28, 31, and 32). Displayed in Figure 2 are thermal desorption signals for m/e = 31, the strongest fragment in the cracking pattern of CH$_3$OH. Since during the thermal desorption process the intensity ratio of m/e = 31 to m/e = 32 remained essentially constant, the possibility that the formation of the mass 31 fragment is a consequence of the direct desorption of a CH$_3$0 species can be ruled out. No desorption signal was observed for masses other than the parent peak and its fragments, indicating reversible adsorption of methanol on NiO(100) surfaces under UHV conditions.

This behavior contrasts with that found for methanol chemisorbed on most transition-metal surfaces under UHV conditions where dissociative adsorption leading to further decomposition of methanol to form adsorbed CO and H is generally found. TPD spectra of methanol chemisorbed on Ru(001), Rh(001), and Pt(111), for example, show desorption products of H$_2$ and CO arising from CH$_3$OH decomposition, in the temperature ranges 300–400 and 450–550 K, respectively. Desorption of the parent molecule occurs at a lower temperature range of 150–300 K.

At low exposures (θ < 0.5), TPD spectra (m/e = 31) are characterized by the presence of a single desorption state, designated as a β$_2$ state, shown in Figure 2. Further exposure results in the concurrent appearance of two new states at lower temperatures. The desorption state (β$_1$ state) at 247 K remains unchanged in its peak maximum as the CH$_3$OH exposure is increased, whereas the peak maximum of the β$_2$ state shifts from 298 K at θ = 0.09 to 271 K at θ ≈ 1.00. These β$_1$ and β$_2$ states can be interpreted as arising from the desorption of monolayer methanol. The sharp desorption feature (α state) found at 150 K, whose peak intensity increases continuously with increasing CH$_3$OH exposure, apparently arises from condensed multilayers of methanol. Physically condensed multilayers of methanol on several metal surfaces have been found to desorb at a similar temperature of ~150 K.

It is evident in Figure 2 that population of the multilayers of adsorbed methanol begins prior to completion of the first monolayer. This behavior is likely due to the high sticking probability (by hydrogen bonding) and low mobility of methanol molecules at the low adsorption temperature.

It is particularly noteworthy that the α-state peak in Figure 2 does not exhibit a common "leading edge" on the low-temperature side, behavior frequently observed for many physisorbed systems. It has been argued that the desorption of multilayers of methanol should not be described by zero-order kinetics. Instead, the observed shifts in the leading edge and peak maximum indicate a fractional order rate process, which demonstrates the existence of hydrogen bonding within the condensed methanol phase. The formation of hydrogen bonding in the multilayers of methanol condensed on NiO(100) is confirmed by our HREELS studies which follow.

The evolution of various desorption features as a function of ethanol exposure has also been followed by monitoring several masses (m/e = 2, 18, 28, 31, 45, and 46). Displayed in Figure 3 are thermal desorption spectra of the strongest fragment (m/e = 31) of the parent molecule. There were no detectable desorption signals for masses other than the parent molecule and its fragments, indicating irreversible adsorption of ethanol on NiO(100) under UHV conditions.

In contrast to methanol adsorbed on NiO(100), only a single desorption peak (β state) was found for ethanol above 200 K. Similar to the β$_2$ state of methanol adsorbed on NiO(100), this β state peak maximum shifts from 336 K at θ = 0.05 to 276 K at a coverage approaching saturation of the first layer, as shown in Figure 3. The signal from desorbing ethanol, which levels in the 180–220 K temperature range relative to that of monolayer desorption, was considerably higher in the ethanol TPD spectra compared to the methanol TPD spectra. Likewise, a low-temperature desorption feature at 160 K is assigned to condensed multilayers of ethanol whose peak intensity increases continuously with increasing C$_2$H$_5$OH exposure.

B. HREELS Studies. Adsorption of alcohols on thin NiO(100) films has been further investigated using HREELS.
frequency of this mode shifts slightly downward when adsorbed by 50 cm\(^{-1}\) relative to the gas-phase value of 1033 cm\(^{-1}\). The desorption states designated as \(\alpha\) and \(\beta\) are indicated.

Displayed in Figures 4 and 5 are two sets of HREELS spectra of methanol adsorbed onto a ~20 ML NiO(100) film. Exposure of methanol to \(90\) K gives rise to a number of distinct loss features in the 750–400 cm\(^{-1}\) region. By analogy to the results obtained from infrared\(^{11-24}\) and HREELS\(^{28-34}\) studies of methanol adsorbed onto a variety of surfaces, the assignments of these losses at monolayer coverages are straightforward. The losses observed at \(1080, 1150, 1450,\) and 2920 cm\(^{-1}\) are due to excitations of the CO stretch \(\nu(CO)\), the CH\(_3\) rock \(\rho(CH_3)\), the CH\(_2\) deformation \(\delta(CH_2)\), and the CH\(_3\) stretch \(\nu(CH_3)\), respectively.\(^{28-34}\) Compiled in Table I are HREELS vibrational frequencies and mode assignments for chemisorbed methanol on NiO(100) and on various metal surfaces.\(^{28-34}\)

It is noteworthy that the \(\nu(CO)\) mode is blue-shifted by ~50 cm\(^{-1}\) relative to the gas-phase value of 1033 cm\(^{-1}\). The desorption states designated as \(\alpha\) and \(\beta\) are indicated.

There are differences in the relative mode intensities between the spectra at low coverages and those at high coverages. The spectra at low coverages \((\theta < 0.5)\) resemble closely those at low coverages of methanol on single-crystal metal surfaces,\(^{28-34}\) with a predominant loss peak at 1080 cm\(^{-1}\) and some weaker features found at 1150, 1450, and 2920 cm\(^{-1}\). On the other hand, the spectra at high coverages \((0.5 < \theta < 1.0)\) exhibit much more intense \(\rho(CH_3)\), \(\delta(CH_2)\), and \(\nu(CH_3)\) modes, as shown in Figure 4. The \(\rho(CH_3)\) and \(\delta(CH_2)\) modes, for example, appear as intense as the \(\nu(CO)\) mode as shown in Figure 4b. The origin of these changes in the relative mode intensities will be discussed in the following section. At coverages exceeding one monolayer, the \(\rho(CH_3)\) and \(\nu(CO)\) modes merge into one and become indistinguishable.
The absence of the ν(OH) loss is also clearly evident in the HREELS spectra acquired following the annealing experiments. Heating of a methanol multilayer (θ ≈ 3.33) to 175 K results in the desorption of physically adsorbed multilayers of methanol, the disappearance of the ν(OH) feature, and the appearance of the ν(CO) and ρ(CH₃) loss features, as shown in Figure 5. The reappearance of the ν(CO) and ρ(CH₃) loss features is consistent with the results shown in Figure 4 in which these two losses become indistinguishable as the CH₃OH coverage exceeds one monolayer.

In all of the above HREELS spectra, no loss feature associated with free hydroxyl groups arising from the abstraction of the hydroxyl hydrogen of the molecule could be identified. Such free hydroxyl groups should give rise to a distinct peak at ~3650 cm⁻¹, which is clearly evident in the spectrum of Figure 6c. The insert in Figure 6 shows the intensity ratio of the OH stretch to the CH stretch plotted against methanol coverage. For methanol adsorbed on NiO(100), this intensity ratio increases only at coverages exceeding one monolayer. The above results also eliminate the ambiguity that the ν(OH) frequency might be shifted downward to the region of the OH stretch such that the two spectra overlap.

The absence of the ν(OH) feature of methanol adsorbed on NiO(100) thus contrasts sharply with the results observed for formic acid desorbs on several transition-metal surfaces. These results indicate a distinct ν(OH) feature at ~3300 cm⁻¹, whose intensity is comparable to that of the CH₃ stretch, upon methanol adsorption at θ ≤ 1.0. Figure 6, a and b, shows HREELS spectra of methanol adsorbed on NiO(100) and Mo(100) surfaces, respectively. Exposing Mo(100) surfaces to CH₃OH at monolayer coverages gives rise to a distinct loss feature at 3325 cm⁻¹, which arises from the OH stretch of molecular methanol on Mo(100). The insert in Figure 6 shows the intensity ratio of the OH stretch to the CH stretch plotted against methanol coverage. For methanol adsorbed on NiO(100), this intensity ratio increases only at coverages exceeding one monolayer.

The absence of an OH stretch following methanol adsorption on NiO(100) film at 90 K as a function of CH₃OD coverage (ML): (a) 0.33, (b) 0.67, (c) 1.00, (d) 1.33, (e) 1.67, and (f) 3.33. The spectra were collected at E₀ ≈ 50 eV and at the specularly reflected beam direction.

It is noteworthy that Figure 4 shows no loss feature in the vibrational frequency region of the OH stretch; only at coverages exceeding one monolayer does the ν(OH) loss appear. The frequency of this OH stretching vibration is red-shifted by approximately 430 cm⁻¹ with respect to the methanol gas-phase value of 3681 cm⁻¹ and its bandwidth is considerably broadened. These are clear indications that hydrogen bonding is occurring in the multilayers of methanol adsorbed on NiO(100).

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The absence of an OH stretch following methanol adsorption in the HREELS spectra of methanol-d on NiO(100) film at 90 K as a function of CH₃OD coverage (ML): (a) 0.33, (b) 0.67, (c) 1.00, (d) 1.33, (e) 1.67, and (f) 3.33. The spectra were collected at E₀ ≈ 50 eV and at the specularly reflected beam direction.

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bands are superimposed. The changes of relative mode intensities as a function of methanol exposure and annealing temperature in Figures 7 and 8, respectively, were found to be nearly identical to those found in Figures 4 and 5. Spectrum c of Figure 8, acquired at an angle $\theta$ off the specularly reflected beam direction, clearly shows a decrease of the $\nu$(CO) mode relative to the $\nu$(CH$_3$) mode, indicating the dipole nature of this vibrational mode. Previous HREELS studies have shown that the $\nu$(CO) mode is strongly dipole allowed, whereas hydrogen-associated modes of the molecule are predominantly excited by impact scattering.

Adsorption of ethanol on thin NiO(100) films has also been examined using HREELS. Figures 9 and 10 display HREELS spectra of C$_2$H$_5$OH adsorbed on a ~20 monolayer NiO film at 90 K as a function of exposure and annealing temperature, respectively. Exposing the sample to C$_2$H$_5$OH at 90 K gives rise to several distinct loss features in the 750-4000 cm$^{-1}$ region. The losses observed at 830, 1090, 1415, and 2955 cm$^{-1}$ are due to excitations of the CC stretch ($\nu$(CC)), the CO stretch ($\nu$(CO)), the CH$_{2,3}$ deformation ($\delta$(CH$_{2,3}$)), and the CH$_{2,3}$ stretch ($\nu$(CH$_{2,3}$)), respectively. OH stretching vibrational modes at methanol coverages below one monolayer were also not observed for ethanol adsorbed on NiO(100) (Figures 9 and 10). The $\nu$-(OH) feature appeared only at coverages greater than one monolayer.

IV. Discussion

A. Chemisorbed Alcohol Species and Their Adsorption Geometries on NiO(100). In the preceding section, the conclusion was reached that methanol and ethanol adsorb associatively on NiO(100) at 90 K and undergo reversible desorption upon annealing. The following section will address the adsorption geometry and bonding configuration of these molecules on NiO(100). Since the oxygen lone-pair electrons of the alcohols will likely play a dominant role in adsorption and reaction, the surface chemistry for methanol and ethanol on NiO(100) is expected to be similar. The following discussion will focus primarily on methanol adsorption.

As shown in Figures 4–8, the $\nu$(CH$_3$), $\delta$(CH$_3$), and $\nu$(CH$_3$) loss features at $\theta < 1.0$ exhibit relatively small shifts from their corresponding gas-phase frequencies, indicating a largely un-
perturbed methyl group of methanol following adsorption onto NiO(100). Accordingly, we propose that methanol adsorbs onto the cation sites of NiO(100) via the hydroxyl oxygen with the methyl group directed away from the surface. A bonding configuration of this type is anticipated for the following reason: the lone pairs of electrons on the oxygen atom of methanol constitute a donor ligand, whereas the metal cation is electron deficient, acting as an electron acceptor. In the classic picture of Lewis acid/Lewis base interactions, the adsorption of methanol on nickel oxide can be described by methanol acting as a Lewis base and the nickel cation as a Lewis acid.

The above bonding configuration is also proposed for methanol adsorbed on most metal surfaces. Work function measurements carried out on several metal surfaces have shown a significant decrease of the work function upon methanol adsorption, clearly demonstrating that methanol adsorbs with the oxygen of the molecule pointing toward the surface. This bonding model is also supported by HREELS studies. HREELS spectra of methanol adsorbed on a number of metal surfaces indicate that the ν(OH) and η(OH) vibrational modes shift dramatically from their corresponding gas-phase values, whereas the frequencies of the losses associated with methyl vibrations remain essentially unchanged.

Information relevant to the bonding strength of methanol to NiO(100) can be deduced from the thermal desorption studies. The binding energy of methanol on NiO(100) should correspond approximately to the activation energy of desorption deduced at a coverage approaching zero. Assuming first-order kinetics and a preexponential factor ν = 1 × 10^14 Hz, the activation energy of desorption of the β1 state at θ = 0.09 is deduced to be 19.5 kcal/mol, using Redhead's peak maximum method. This value is significantly higher than the corresponding values (~11 kcal/mol) estimated for methanol desorption from transition metals.

The adsorption of molecular methanol on transition-metal surfaces is, in fact, considered to be chemically weak. Thermal desorption studies performed on several metal surfaces with varying crystallographic structure have shown the binding energies of methanol to be essentially the same. The sign and magnitude of the methanol-induced work function change are also very similar for methanol adsorbed on varying substrates: a decrease in the work function was found in all cases, with an average decrease of approximately 1.5 eV. The decrease in the work function with an increase in CH30H coverage clearly indicates a repulsive interaction between the adsorbates in the β2 state. Given that methanol is a polar molecule with a dipole moment of 1.70 D, lateral repulsion between the neighboring dipoles, which are probably oriented in an ordered fashion at low coverages, is expected. Although the exact orientation of methanol cannot be determined in the present study, the CO axis of the molecule in the β2 state is likely oriented with its dipole component perpendicular to the surface.

Likewise, it is proposed that the dipole axes of the adsorbates in the β1 state are inclined toward the surface with their dipole moments oriented in random directions. This adsorption geometry of the molecules in the β1 state is consistent with the TPD results, which show a constant peak desorption temperature in the CH3OH coverage range. The constant desorption peak temperature likely arises from weaker dipole–dipole interactions (due to randomly oriented dipoles) between CH3OH molecules in the β1 state. Further support for the adsorption geometries of methanol in the β1 and β2 states comes from the HREELS studies which follow.

In Figures 4, 5, 7, and 8, HREELS spectra show the change of relative mode intensities with respect to the methanol coverage. This feature correlates well with that found in the HREELS spectra in which the relative mode intensities remain unchanged as a function of ethanol coverage, as shown in Figures 9 and 10. In view of the complexity of ethanol, the orientation and desorption state of the molecules are not as discrete as those of methanol. This also accounts for the rather broad desorption peak of the ethanol monolayer and the higher desorption signal levels in the 180–220 K temperature range.

B. Delocalization of the Hydroxyl Proton of Alcohols. Adsorption of alcohols on NiO(100) gives rise to a number of distinct loss features which can be unambiguously attributed to the corresponding vibrational modes of alcohols in the gas phase or on the surface. However, in all the cases, no loss peak in the region of ν(OH) (or ν(OD)) vibrations was found at θ ≤ 1.0. The absence of the ν(OH) (or ν(OD)) mode thus contrasts sharply with the results found for methanol adsorbed on several metal surfaces. The origin of this “invisibility” of the ν(OH) (or ν(OD)) mode will be discussed in this section.

In the proceeding section, we have shown that alcohol molecules in the first layer are bonded to the surface cation sites of NiO(100) via the oxygen atom, with the methyl/ethyl group directed away from the surface. Depicted in Figure 11 is a ball model for methanol adsorbed on NiO(100). In this bonding configuration,
the hydroxyl hydrogen of methanol is located at a distance with respect to the surface anion sites such that formation of hydrogen bonds to the surface oxygen anions is expected.

Due largely to the development of modern X-ray crystallographic and infrared/Raman spectroscopic techniques, the nature of hydrogen bonding in solids is now well understood. On the basis of data collected for hundreds of solid compounds, Novak and coworkers found a remarkable correlation between the OH stretching frequency and the oxygen-to-oxygen distance; that is, all data lie on a universal curve. Three distinct regions were revealed based on the slope of this universal curve. Accordingly, the hydrogen bond can be classified into three categories: weak, strong, and intermediate. The hydrogen bond is termed to be strong if the O–O distance exceeds 2.7 Å. Typical examples of this type are solid alcohols where the ν(OH) frequency is higher than 3200 cm⁻¹ with a bandwidth of typically 10 cm⁻¹. The hydrogen bond is termed to be strong if the O–O distance falls between 2.60 and 2.50 Å. Typical examples of this type are acid salts, such as NaH(\(\text{CH}_3\text{COO}\))₂, which exhibit extremely low ν(OH) frequencies, somewhere between 2700 and 700 cm⁻¹, and broad ν(OH) bands which can be as wide as 1000 cm⁻¹. Between the above two extremes, there are some compounds having hydrogen bonds of intermediate strength.

In the present study, assuming that the hydroxyl oxygen of the adsorbate is located at 1.5–1.7 Å above a surface cation site, the distance between the hydroxyl oxygen and the surface lattice oxygen falls into the categories for the strong and intermediate hydrogen bonds. Although we are not aware of any theoretical studies having been undertaken for the adsorption of methanol on NiO(100), calculations using an extended Hückel tight-binding approach showed that the total energy of ammonia adsorbed on NiO(100) reaches a minimum when the nitrogen–nickel distance is around 1.6 Å. The absence of the ν(OH) loss feature in the present study may well be explained by forming a strong hydrogen bond between methanol and NiO(100).

More interestingly, the hydroxyl proton in such an adsorption geometry likely fluctuates or “whizzes” around the four adjacent surface oxygen anions, acting as a mobile proton, as indicated by arrows in Figure 11. This is a consequence of the symmetry of the surface geometry of NiO(100): the four nearest anion neighbors are in equivalent positions and thus have an equal probability to form a hydrogen bond with the hydroxyl proton. From the point of view of the surface potential energy, fluctuation of the proton will occur if the rotational energy barrier along the azimuthal direction is relatively low.

In the preceding section, it has been concluded that the methanol and ethanol adsorb associatively on NiO(100). This contrasts with methanol adsorbed on MgO surfaces where dissociative adsorption leading to a stable methoxy species occurs as low as 90 K. This difference in reactivity between NiO(100) and MgO(100) surfaces can be readily explained in terms of their surface basicity. Magnesium oxide is a typical basic oxide whose surface basicity is significantly stronger than that of nickel oxide. In fact, methanol dissociates on most powdered oxide catalysts under catalytic reaction conditions. The initial step for these reactions all involves OH bond cleavage to form methoxy. It is presumed that there is a short-lived transition state involving a proton transfer subsequent to the formation of a hydrogen bond between the hydroxyl hydrogen and the lattice oxygen. This transition state then leads to the dissociated state, forming a conjugated base anion adsorbed on a cation site and a dissociated hydrogen adsorbed on an adjacent anion site. In the present study, this transition state is uniquely demonstrated due to the relatively weak surface basicity of nickel oxide. This observation significantly enhances our understanding regarding the nature of the precursor to the dissociated state in an acid/base reaction.

V. Conclusions

Interactions of alcohols with well-defined NiO(100) films prepared on Mo(100) under UHV conditions have been studied using combined HREELS/TPD. The results are summarized as follows:

1. Alcohol adsorbs associatively on NiO(100) surfaces and undergo reversible adsorption upon annealing under UHV conditions. Both methanol and ethanol are bonded to the cation sites of NiO(100) via their oxygen atom with the methyl and ethyl group, respectively, directed away from the surface.

2. At low coverages, a repulsive interaction between adsorbed alcohols is observed, which results in a decrease in the apparent activation energy of desorption. Molecularly adsorbed alcohols are found to bond stronger to NiO(100) than to most metal surfaces. The change of relative mode intensities in HREELS spectra with respect to the methanol coverage, below monolayer coverages, correlates excellently with two desorption states revealed in TPD studies, indicating reorientation of some of the adsorbed methanol at high coverages. In the case of ethanol adsorbed on NiO(100), however, only a single desorption state above 200 K is evident, consistent with the HREELS results which show a constant mode intensity pattern with respect to the ethanol coverage.

3. The absence of the ν(OH) loss feature in the region of OH vibrations below monolayer coverages suggests the formation of strong hydrogen bonds between the hydroxyl hydrogen and the lattice oxygen. This feature, together with consideration of the surface symmetry of NiO(100), leads to the conclusion that the hydroxyl proton fluctuates or “whizzes” around the neighboring anion sites, acting as a mobile proton. This observation greatly enhances our understanding of the nature of the precursor to the dissociated state in an acid/base reaction.

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References and Notes

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(44) Desorption of metal multilayers on top of a dissimilar metal, for example, exhibits typically a common "leading edge" on the low-temperature side.