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Adsorption of Formaldehyde on Nickel Oxide Studied by Thermal Programmed Desorption and High-Resolution Electron Energy Loss Spectroscopy

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Abstract: Formaldehyde adsorption on NiO(100) ultrathin films grown on a Mo(100) surface has been studied using combined thermal desorption and high-resolution electron energy loss spectroscopies (HREELS). The results show that formaldehyde adsorbs molecularly on NiO(100) film at 90 K and that concurrent polymerization of formaldehyde occurs extensively in the 90–270 K temperature range. Monomeric formaldehyde is chemisorbed onto Ni cationic sites in the oxygen end-on η^1(O) orientation, leading to a shift of the ν(CO) feature to 1650 cm^{-1}. Between 250 and 300 K, an η^2(C,O) form of adsorbed formaldehyde is indicated by a ν(CO) loss feature at 1320 cm^{-1} in the HREEL spectrum. All formaldehyde species desorbed below 350 K without decomposition.

1. Introduction

The chemical properties of metal oxide catalyst surfaces can be examined via adsorption studies of probe organic molecules.[1] Combined calorimetric and spectroscopic measurements of the interactions between the adsorbed probe molecules and the surfaces can help define the chemical nature of the adsorption sites. Calorimetric measurements of the adsorption of simple probe molecules such as CO, NO, and O_2 are commonly used in this type of study.[2–5] However, for the characterization of more specific types of adsorption sites (such as Brønsted/Lewis acid and base sites), relatively complex organic molecules such as carboxylic acids and pyridine, as well as ammonia, water, and others which possess wide-ranging chemical properties, have been shown to be very useful probes.[3,6–8]

To date, there have been relatively few detailed studies of the adsorption of organic molecules on metal oxide surfaces using surface-sensitive and surface-specific techniques, which can provide information regarding the surface bonding, adsorption configuration, and chemistry of the adsorbed molecule. Moreover, the majority of the adsorption studies on oxide materials are commonly carried out on oxide powders. This is partly due to the experimental difficulties in handling oriented, low-surface-area oxide crystals. The most preferred analytical tool for studying adsorption on oxide powders has been infrared spectroscopy. For high surface-area specimens, IR spectroscopy is an unsurpassed method because of its excellent resolution.[9] However, it lacks the sensitivity needed to investigate complex organic adsorbates at monolayer and submonolayer levels on low-area surfaces, especially when the molecules of interest have relatively weak dipole moments.

We recently demonstrated that combined thermal desorption (TDS) and high-resolution electron energy loss spectroscopy (HREELS) measurements can be used to investigate in detail the adsorption of organic molecules and their interactions with model magnesium oxide surfaces.[10] Furthermore, these adsorption studies were carried out on ordered surfaces of epitaxially grown thin magnesium oxide films. This approach allows the surface chemistry of single crystallographic orientations to be probed, thus avoiding the complexities and ambiguities associated with multifaceted powdered samples. In addition, the use of thin oxide films also permits separate investigations of the contributions of surface defects to the catalytic activities of MgO, since controlled amounts of surface defects can be systematically introduced into the oxide thin films.[11]

Until recently, the use of the HREELS technique in these adsorption studies has been hampered by the interference of strong surface phonon losses which are intrinsic to oxide surfaces. Although several authors have utilized data processing techniques based on Fourier deconvolution algorithms to numerically remove the phonon losses from the loss spectra of adsorbates on oxide single crystals,[12,13] this method is still basically an "indirect" approach. Of particular concern are the spurious features that may be introduced in the spectrum by the Fourier deconvolution procedure itself. We have circumvented the problems of interfering phonon losses in our measurements by employing high incident energy and an off-specular scattering geometry.[14] In our approach, the phonon losses are sufficiently suppressed that the infomation-rich adsorbate modes in the spectral region of 1000–4000 cm^{-1} are easily discernible and undistorted.

In this article, we report the application of this approach to our study of the adsorption of formaldehyde on NiO thin films, epitaxially grown on Mo(100) single crystals, using HREELS and TDS techniques. Formaldehyde is a soft base and can be used to probe the NiO cationic sites. It is well known that the mode of coordination of formaldehyde on the surface is strongly affected by the electronic properties of the adsorption sites. Hence, assessments of chemical reactivities of the Ni cationic sites can be made from spectroscopic measurements of formaldehyde adsorbed on these sites.

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The surface chemistry of formaldehyde on nickel oxide catalyst also has industrial significance. Currently, there is considerable concern regarding a possible increase in formaldehyde emissions as a consequence of the use of alcohol-blended fuels in the United States. It has been reported that energies running on alcohols emit significantly more aldehydes than those running on gasoline.[15] At the present time, catalytic conversion of formaldehyde is proposed as a possible way to make alcohol-based fuels more environmentally acceptable.[16,17] In the overall conversion process, formaldehyde oxidation is considered the most important step. In a detailed atmospheric-pressure kinetic study, Foster and Masel[18] chose nickel oxide because of its good catalytic dehydrogenation properties. In their work, NiO was shown to be a very active oxidation catalyst for formaldehyde conversion; however, no reaction mechanism was offered for the very complicated kinetics that were observed. An understanding of the adsorption and chemistry of formaldehyde on a NiO surface is a prerequisite for detailing the mechanisms of catalyzed oxidation processes. In the present work, we have utilized the high sensitivity of HREELS as well as the novelty of oxide thin-film surfaces to examine the adsorption of formaldehyde on a NiO(100) surface.

2. Experimental Section

The experiments were performed in an ultra-high vacuum (UHV) chamber described previously.[19] This UHV system has capabilities for HREELS, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and thermal desorption spectroscopy. The NiO thin films were prepared by evaporating Ni onto the Mo(100) substrate in an oxygen atmosphere. Details of the film preparation and characterization are described elsewhere.[20] The NiO films prepared using our approach exhibit an excellent (1 × 1) LEED pattern, indicating long range order. These films also yield Auger spectra identical to those of single crystal NiO(100).[21]

All HREELS measurements were carried out with the incident beam at 60° from the surface normal. The HREEL spectrometer utilized is a LK2000 digital spectrometer from LK Technologies. All spectra shown in this work were acquired with a primary beam energy of 50 eV. At this energy, the intensities of the fundamental phonon mode as well as its overtones and multiples are greatly reduced. As a result, adsorbate loss features above 700 cm^{-1} are easily discernible. The resolution of the HREELS spectra was maintained typically at 90–100 cm^{-1} (full width at half maximum of the elastic peak).

Gaseous formaldehyde was produced by thermal depolymerization and sublimation of paraformaldehyde (poly(oxymethylene)glycol from Aldrich Chemical Co.) following repeated heating–evacuation cycles to remove impurities. In the HREELS experiments, the sample surface was exposed to the gaseous formaldehyde by back-filling the chamber through a leak valve. In the case of the TDS studies, the formaldehyde was introduced directly onto the sample surface through a nozzle doser. A linear heating rate of 5 K/s was used in all thermal desorption measurements.

A simple digital filter algorithm was used to remove random noise spikes from the HREEL spectra. Standard linear digital time-domain filter algorithms have been shown to yield excellent results. Unlike common spectral smoothing routines such as Savitzky–Golay or Boxcar Fourier Smoothing, digital filters do not distort that portion of the spectrum containing sharp noise spikes.[22]

3. Results and Discussions

3.1. Thermal Desorption Spectra of Formaldehyde on NiO Films.

The thermal desorption spectra of formaldehyde (m/e = 29) from NiO surface, following different exposures at 90 K, are shown in Figure 1. It has been reported that methane, carbon dioxide, water, and methyl formate[23] are common impurities whenever formaldehyde is generated from paraformaldehyde.[24,25] In the present studies, only a small amount of water desorbed from the NiO surface following formaldehyde adsorption. Water exposure is unavoidable since water is one of the products of the depolymerization of paraformaldehyde. However, the amount of adsorbed water was apparently very small since no loss signal associated with ν(OH) was detected in the HREELS measurements.

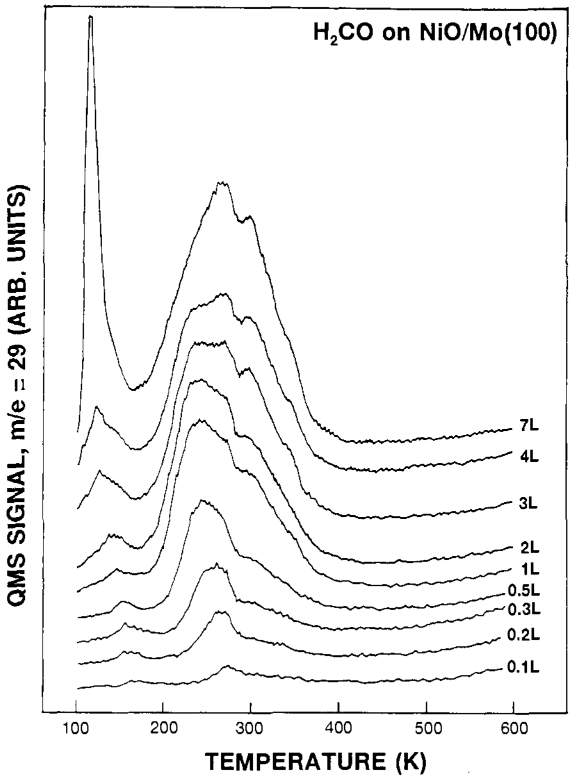

Figure 1. Thermal desorption spectra (m/e = 29) of increasing exposures of formaldehyde at 90 K on a ~20 multilayer NiO film on Mo(100).

The spectra of the parent molecule (m/e = 29) are characterized by a broad feature from 220 to 350 K, peaking at ~270 K, which is attributed to a chemisorbed layer. At higher exposures, a trailing shoulder develops and reaches a maximum a 300 K. The appearance of the multilayer desorption peak at 115–125 K prior to saturation of the chemisorbed peak suggests that formaldehyde grows in 3-D cluster fashion at 90 K rather than layer-by-layer. This tendency toward clustering is likely due to hydrogen bonding in the condensed formaldehyde phase. The width and profile of the chemisorbed feature in the temperature range from 200 to 350 K suggest that it likely corresponds to several chemisorbed formaldehyde species. Detailed discussions of these surface species will be given in section 3.3. In particular, depolymerization of adsorbed paraformaldehyde commonly occurs within this temperature range. In fact, HREEL spectrometric evidence of paraformaldehyde formation on the NiO surface will be presented.

Other masses monitored in the TDS were 2, 18, 28, 30, 44, and 45; however, no species were observed other than the cracking fragments of formaldehyde in the quadrupole mass spectrometer. These results indicate that formaldehyde adsorbs molecularly onto the NiO surface at 90 K and desorbs below 350 K without

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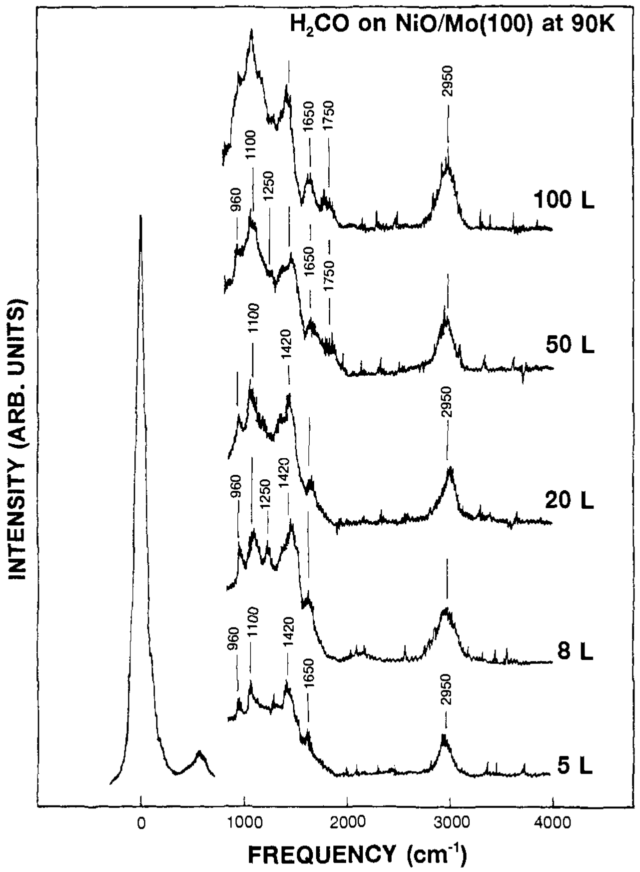

Figure 2. HREEL spectra of increasing exposures of formaldehyde at 90 K on NiO(100) film.

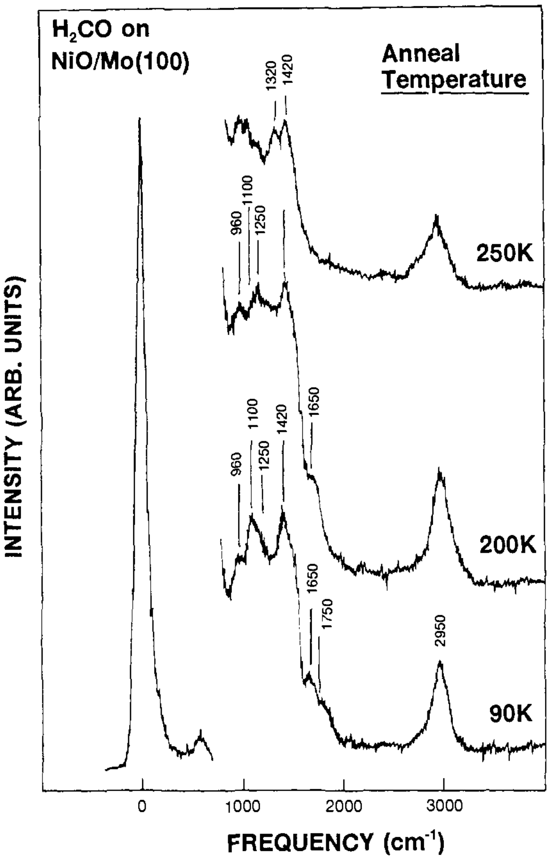

Figure 3. HREEL spectra of formaldehyde adsorbed on a NiO(100) film at different annealing temperatures.

decomposition. Subsequent Auger electron spectroscopic analysis confirmed that the NiO surface was free of carbon residues after the desorption experiments. Our thermal desorption results contrast with published results which report chemical reactions of formaldehyde on metal and metal oxide surfaces. Formaldehyde has been found to decompose readily on polar ZnO[26] and Al_2O_3 and to disproportionate on MgO and ZrO_2 surfaces.[27] Nevertheless, our TDS results are not surprising considering that the NiO surface is relatively unreactive compared to these surfaces. In recent TDS and HREELS studies, NiO(100) was also found to be unreactive with respect to ammonia,[28] methanol, and ethanol.[29] UHV-cleaved NiO(100) has been found to be completely inert to the chemisorption of O_2, H_2O, SO_2, and many organic molecules.[30] There is one report of dissociative adsorption of acetone on NiO powders at high temperatures and pressures;[31] however, this heterolytic dissociation of acetone to surface enolates and hydroxyls is most likely attributable to defect sites on the NiO powders.

3.2. EELS Spectra of Formaldehyde on NiO Films. HREELS spectra of formaldehyde on NiO films at 90 K are shown as a function of exposure in Figure 2. At low exposures (5 Langmuir) the distinct loss features are at 2950, 1650, 1420, 1100, and 960 cm^{-1}. With reference to published results, the feature at 1650 cm^{-1} can be assigned to a C—O stretching mode $\nu(C{=}O)$ of chemisorbed formaldehyde. The frequency of this peak is in good agreement with the reported values for adsorbed formaldehyde on Ru(001)[32] and for acetone on Ru(001) and Pt(111).[33] The magnitude of the shift of the $\nu(C{=}O)$ mode to lower frequency relative to the value of 1740 cm^{-1} [34] reported for solid formaldehyde supports the η^1(O) bonding configuration (hereafter referred to as η^1), in which the adsorbed formaldehyde molecule is bonded to the cationic Ni site through the oxygen end. This adsorption configuration has been proposed for formaldehyde on Ru(001)[32] and for acetone on Pt(111),[33] where a similar red shift of the $\nu(C{=}O)$ frequency was also observed. As shown in Figure 4a, the surface bond (carbonyl O to Ni) is proposed to consist primarily of σ-donation from the $5a_1$ orbital of the formaldehyde molecule to the acceptor level of the Ni cations.[35] The perturbation on the carbonyl group by the Ni cations results in a red shift of the $\nu(C{=}O)$ stretch frequency. Rodriguez and Campbell[36] have performed INDO/S[37] calculations for η^1-formaldehyde on Zn-terminated ZnO(0001) which corroborate the observed frequency shift. The calculations revealed that upon chemisorption of formaldehyde the carbonyl C=O bond order decreases slightly from 2 to 1.8. This bond order reduction is partly due to the depopulation of the $5a_1$ orbital. Nevertheless, this η^1-H_2CO configuration tends to remain stable on the oxide surface due to the lack of any chemisorption-induced increase in the population of the π^*_{CO} orbital $2b_1$.[36] Table I summarizes the assignments of the additional vibrational modes found for formaldehyde on the NiO surface.

With increasing exposures, the features at 960 and 1100 cm^{-1} increase in intensity most rapidly. The frequencies and intensities

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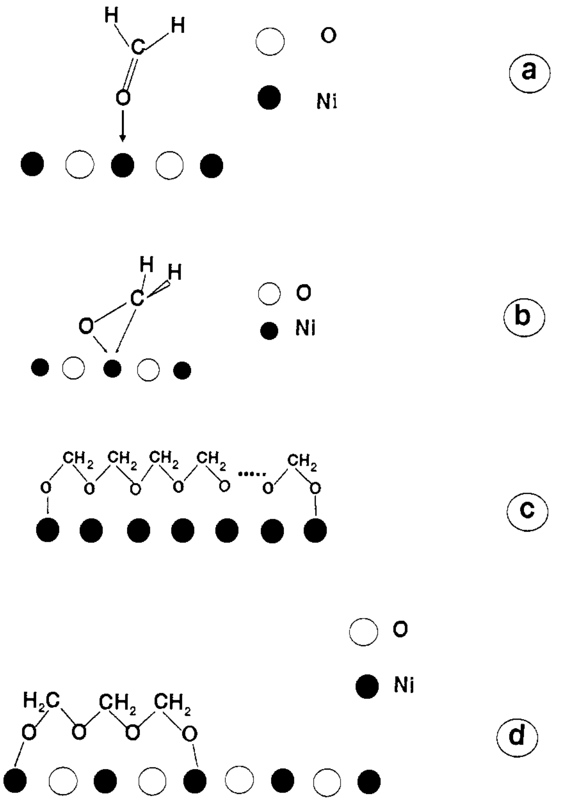

Figure 4. (a) η^1 formaldehyde configuration, (b) η^2 formaldehyde configuration, (c) paraformaldehyde structure on metal surfaces (Ag, Cu), and (d) paraformaldehyde structure on NiO(100) film.

Table I. Assignments of Vibrational Bands (cm^{-1}) for Formaldehyde Adsorbed on NiO Thin Film on Mo(100) at 90 K

modes	H_2CO gas FTIR[57]	η^1-H_2CO HREELS	physisorbed H_2CO
$\nu_a(CH)$, ν_4	2843	unresolved	unresolved
$\nu_s(CH)$, ν_1	2766	~2950	~2950
$\nu(CO)$, ν_2	1746	1650	1750
$\delta(CH_2)$, δ_3	1500	^{a}	^{a}
$\omega(CH_2)$, ν_6	1167	^{a}	^{a}
$\rho(CH_2)$, ν_5	1250	1250	^{a}

modes	$(CH_2O)_n$ paraformaldehyde
$\nu_a(CH)$	unresolved
$\nu_s(CH)$	~2950
$\nu(CO)$	1100
$\nu(COC) + \rho(CH_2)$	960
$\delta(CH_2)$	1420
$\delta(COC) + \rho(CH_2)$	^{a}

^{a} Obscured by broad neighboring modes.

of these two loss features are most consistent with those of the $\rho(CH_2) + \nu(COC)$ (CH_2 rocking/skeletal stretching combination) and ν(C–O) stretching modes[38] of the free formaldehyde polymer (or of polyoxymethylene) and also resemble the symmetric and asymmetric $\nu(CO)$ modes of chemisorbed paraformaldehyde on oxygenated Ag(110), oxygenated Cu(110), and Pt(111).[39–41] HREEL spectra observed for paraformaldehyde adsorbed on oxygen-covered Ag(110) show the 960 and 1100 cm^{-1} modes to be the most prominent loss features.[38] Almost identical features were observed for paraformaldehyde on Cu(110).[40] HREEL spectra of formaldehyde on Ag(110) subsequent to laser-induced polymerization also exhibit these fingerprint features.[42] On these metal surfaces, the paraformaldehyde linear chain is bonded to the surface through the oxygen atom of the oxymethylene linkage (see Figure 4c). The terminal oxygens in the chain are singly bonded to the metal, and the interior oxygen are bonded via weaker electron-donor bonds. However, such a description may not be valid for paraformaldehyde on a NiO surface. The length of the recurrent CH_2O unit in poly(oxymethylene) is 1.92 Å.[43] This allows all of the oxygen atoms in the chain to form weak electron-donor bonds (through the oxygen lone pairs) to the surface sites on Cu(110) and Ag(110) without imposing significant strain on the polymer chain. The Ni–Ni separation in NiO, on the other hand, is on the order of 2.9 Å, much too long for successive CH_2O units to form bonds with the Ni cations (without opening the OCO angle to 180°). Due to this mismatch, it is likely that the paraformaldehyde chain on NiO has fewer oxygen-to-surface linkages where many of the CH_2O units remain detached from the surface or area weakly bonded to the surface via electrostatic interactions. The paraformaldehyde chain on NiO is likely disordered, lacking the structure found on metal surfaces (see Figure 4d). Accordingly, the 960- and 1100-cm^{-1} loss peaks are assigned to the motions of free paraformaldehyde, $\rho(CH_2) + \nu(COC)$ and $\nu(CO)$, rather than to the vibrational modes, $\nu_{asym,CO}$ and $\nu_{sym,CO}$, of the paraformaldehyde structure reported on Ag(110) and Cu(110) surfaces. Other characteristic but less intense paraformaldehyde modes such as the symmetric and asymmetric $\omega(CH_2)$ waggings at 1375–1385 cm^{-1} cannot be clearly resolved and appear as a broad shoulder below the 1420-cm^{-1} mode. The broadness of the feature at 1420 cm^{-1} could also be due to a combination of scissoring modes $\delta(CH_2)$ of paraformaldehyde and chemisorbed and multilayer formaldehydes. On Ag(110) and Cu(110), the $\delta(CH_2)$ mode of paraformaldehyde was reported to occur at 1430 cm^{-1}. For η^1-formaldehyde on Ru(001), a value of 1465 cm^{-1} was reported for the $\delta(CH_2)$ mode.

It is not yet clear how the polymerization process occurs on solid surfaces. Depolymerization and sublimation of paraformaldehyde are known to yield strictly monomeric formaldehyde,[44,45] so it is not likely that the polymers are condensed on the surface from the vapor phase. Anton and Weinberg[32] suggested that adsorbed water catalyzed the polymerization of formaldehyde on solid surfaces. However, the amount of water on the NiO surface in this study is below the detection limit of the HREEL spectrometer. It is possible that only a very small amount of water is needed to react with formaldehyde to trigger the polymerization process. In fact, the water content in paraformaldehyde is only 1–8 mol % of the polymer,[45] consistent with the lack of a $\nu(OH)$ signal in the HREELS experiments. However, in the mechanism of catalyzed polymerization of formaldehyde, the chain initiation is started by either cation or anion attacking groups.[44] For example, on SiO_2 and Al_2O_3 powders, the surface acidic hydroxyl groups are shown to be the catalyst for the polymerization.[27] On the other hand, on the inert NiO(100) and ZnO(0001) surfaces, paraformaldehyde formation was observed, even though H_2O does not dissociate on these surfaces to yield the required initiators.[30] Therefore, adsorbed water molecules or hydroxyl groups are probably not the driving force for formaldehyde polymerization on the NiO surface. Direct formation of formaldehyde with the basic, anionic sites of the oxide surface remains as a possible initiator of polymerization. In fact, this reaction has been proposed for polymerization of formaldehyde on MgO powders.[27] This reaction is analogous to the reaction of formaldehyde with oxygen adatoms on metal surfaces, which can lead to polymerization. On clean Ag(110),

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Table II. Assignments of Vibrational Bands of Paraformaldehyde on Cu(110), Ag(110), Rh(111), and NiO(100) Film

Mode Assignments for Paraformaldehyde Solid[58]

mode	assignment
ν_a(CH)	2978
ν_s(CH)	2920
ω(CH$_2$)	1471
ν(CO)	1120
ρ(CH$_2$) + ν_s(COC)	936 (CH$_2$ rocking + skeletal stretching)
δ(COC) + ρ(CH$_2$)	1235

Mode Assignments for Chemisorbed Paraformaldehyde

Mode	Cu(110)[40]	Ag(110)[39]	Rh(111)[47]	NiO(100) film
ν(CH)	3000, 2920	2960	3000	~2900–3000[a]
δ(CH$_2$)	1420	1430	1500	1420
ν_a(CO)	1090	1100	1150	
ν_s(CO)	960	960	975	
ν(VO)				1100
ν_s(COC) + ρ(CH$_2$)				960

[a] Obscured by broad neighboring modes.

only monomeric formaldehyde was detected; however, with oxygen predosed onto the surface, paraformaldehyde readily formed.[39]

Formaldehyde polymerization has been reported to occur on Zn(0001) and other surfaces.[46] Likewise, formaldehyde polymerization was observed on a clean Cu(110) surface at 90 K; however, an oxygenated Cu surface yielded only formate upon formaldehyde adsorption.[40] On Rh(111), formaldehyde dehydrogenated completely, whereas predosing the Rh(111) surface with oxygen led to the formation of paraformaldehyde and a formate species.[47] Similarly, formaldehyde dissociated on Pt(111) and Pd(111)[41,48] at low exposures, whereas at higher exposures, polymerization was observed, possibly due to initiation by the decomposition products of formaldehyde such as formyl (HC=O) groups. On the other hand, paraformaldehyde was not observed on the Ru(001) surface at any exposure of formaldehyde, whereas the addition of oxygen only served to stabilize the η^1-formaldehyde.[32] For comparison, the vibrational modes of paraformaldehyde on NiO and on oxygenated Ag, Cu, and Rh surfaces and their frequencies are summarized in Table II.

At large exposures (50 Langmuir and above), vibrational modes attributable to monomeric formaldehyde appear. The most notable changes are the appearance of the physisorbed formaldehyde ν(C=O) peak around 1750 cm^{-1} (see spectra, at 5, 8, 20, and 50 Langmuir in Figure 1) and the growth of the very intense peaks at 960 and 1100 cm^{-1} attributed to paraformaldehyde. At formaldehyde exposures of 100 Langmuir or higher, the HREEL spectrum at 90 K shows fingerprints of all possible formaldehyde structures; physisorbed formaldehyde, paraformaldehyde, and η^1-formaldehyde.

3.3. HREELS Annealing Study. HREEL spectra were recorded as a function of annealing temperature and are shown in Figure 3. The spectra were collected after a 30 Langmuir formaldehyde exposure at 90 K. Upon annealing of the sample to 200 K,[49] the multilayer formaldehyde (physisorbed monomer) desorption is apparent in the disappearance of the feature at 1750 cm^{-1}. This change in the HREEL spectrum leads to the assignment of the TDS peak at 115 K as corresponding to physisorbed monomers of formaldehyde. Multilayers or monomeric formaldehyde desorbed at the same temperature on Ag(110)[39] and Cu(110).[40] At 200 K, the remaining species adsorbed on the NiO surface are η^1-formaldehyde, which gives rise to the feature at 1650 cm^{-1}, and paraformaldehyde, which exhibits its characteristic features, at 960 and 1100 cm^{-1}.

Annealing to 250 K leads to several dramatic changes in the HREELS. First, the desorption or transformation of the η^1-formaldehyde is suggested by the disappearance of the 1650-cm^{-1} feature. The formaldehyde species corresponding to this feature can be seen to desorb at ~240 K in the thermal desorption spectra of Figure 1.

In the conventional organometallic picture of formaldehyde or ketone ligands bound to metal centers, the Lewis acidities (or electron deficiencies) of the metal atoms promote the η^1 configuration.[50] On the other hand, metals with weak Lewis base character prefer an η^2(C,O) bonding configuration[51] in which the metal centers are bonded to both the carbon and oxygen atoms of the carbonyl group. In this bonding configuration, the metal–ligand interaction involves simultaneous donation of electrons from the ligand π_{CO} orbital (1b$_1$) and back-donation of d-electron density from the metal to the π^*_{CO} orbital (2b$_1$) of the ligand.[52] In the η^1 orientation, the strength of the metal–ligand bond depends on the ability of the metal center to accommodate the charge donation from the electron pair of the aldehyde or ketone ligand. In the η^2 configuration, this bond is stronger in the systems with metal centers that can best facilitate electron back donation. By applying this relationship between Lewis acidity/basicity of the metal and center and the η^1-/η^2-formaldehyde ligand stability to formaldehyde adsorption on solid surfaces, the acid/base properties of surface sites can be quantitatively assessed.

A Redhead analysis[53] of the TDS data of Figure 1 yields an activation energy for desorption of 14.4 kcal/mol for the η^1-H$_2$CO (T_{des} = 240 K). The substantially lower desorption activation energies of 9 kcal/mol for η^1-H$_2$CO on Ru(001) and 8 kcal/mol for this species on Rh(111)[47] is supportive of the above bonding interpretation. The stronger Lewis acidity of the Ni cationic sites relative to Ru or Rh metal surface sites apparently leads to a stronger η^1-H$_2$CO surface bond. Desorption of an η^1-formaldehyde species within a similar temperature range (~220 K) has been reported on a comparably acidic surface, the polar Zn-terminated ZnO(0001) surface.[26] On Ru(001) and Rh(111) surfaces, formaldehyde adsorption was considerably enhanced following an oxygen predose. For Ru(001), the η^1-formaldehyde

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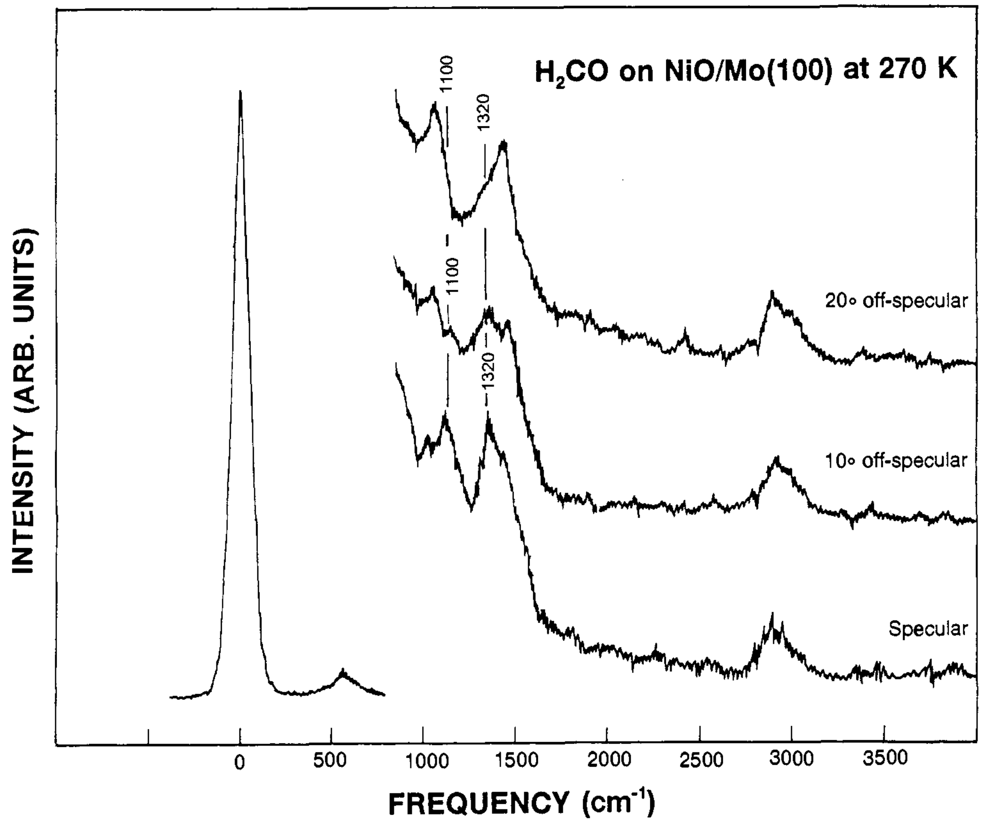

Figure 5. Off-specular HREEL spectra of 30 Langmuirs of formaldehyde, adsorbed at 270 K on NiO(100).

peak desorption temperature shifted from ~120 to 150 K following an oxygen predose. A similar stabilization of the η^1-acetone species was also observed on Pt(111). On Rh(111), the η^1-H_2CO desorption temperature was shifted from 133 to 200 K by coadsorbed oxygen. This stabilization of the η^1-H_2CO is thought to be due to the increased Lewis acidity of the adsorption site, induced by the electron-withdrawing oxygen adatoms.

3.4. Off-Specular HREELS Measurements. As shown in the top spectrum of Figure 3, a new peak appears at ~1320 cm^{-1} upon annealing to 250 K. The surface species giving rise to this loss feature is stabilized on the NiO(100) surface at temperatures between 250 and 300 K. This 1320-cm^{-1} feature was not observed in any measurements below 250 K at any formaldehyde exposure. In an effort to identify the origin of this feature, a series of HREELS measurements were carried out at 270 K, as shown in Figure 5. At this temperature, the η^1-H_2CO species is not present, whereas the paraformaldehyde begins to desorb, as indicated by the overall reduction in the intensities of its HREELS features and by the correspondingly large formaldehyde signal in the TDS spectrum.

All the spectra of Figure 5 were collected at 270 K, following a 50-Langmuir exposure of formaldehyde. The bottom spectrum was recorded with the analyzer set in the specular direction. The most notable features in this spectrum appear at 970, 1100 and 1320, and 2950 cm^{-1}. As the analyzer was moved away from the specular direction, the features around 1100 and 1320 cm^{-1} diminished considerably at 10° off-specular and completely disappeared at 20°. The cross section of the vibrational modes which are of dipole scattering origin sharply peak in the specular direction. With rotation of the energy analyzer away from the specular direction, the vibrational modes due to dipolar scattering (in the case of formaldehyde, those modes which involve C–O vibrations) are attenuated relative to the vibrational modes which show an impact scattering contribution (i.e., C–H vibrations).[54] This effect is clearly illustrated by the spectra of Figure 5. The reduction of the intensity of the peak around 1100 cm^{-1} relative to the 1420-cm^{-1} peaks in the off-specular spectra supports its assignment to a C–O vibration. The observation that the 1100-cm^{-1} peak is attenuated but the 960-cm^{-1} peak is not further supports the assignments of these peaks to adsorbed paraformaldehyde (1100 cm^{-1} to ν(CO) and 970 cm^{-1} to $\rho(CH_2)$ rocking + ν(COC) skeletal stretching).

The feature at 1320 cm^{-1} also attenutes sharply in the off-specular angle measurements; hence, this loss frequency is assigned to a stretching ν(CO) vibrational mode. The frequency of this mode is much higher than the stretch frequency of a single C–O bond in formaldehyde-related molecules, which normally falls within the range of 950–1050 cm^{-1}, and is much lower than the stretch frequency range normally observed for end-on η^1-formaldehyde. The ν(CO) stretching mode, which most resembles this 1320-cm^{-1} feature in our spectrum, was observed for acetone adsorbed on Ru(001) at 275 K. On Ru(001), adsorbed η^2-acetone (i.e., π-bonded, side-on configuration) has a ν(CO) stretch feature at 1300 cm^{-1}.[33] Formaldehyde also chemisorbed in a η^2 configuration (see Figure 4b) on the Ru(001) surface[32] but exhibited a ν(CO) peak at 980 cm^{-1}. This large (320 cm^{-1}) difference between acetone and formaldehyde in the ν(CO) frequency is explained by Anton and Weinberg[32] in terms of the energy level of the π^*_{CO} orbitals of the molecules. On metal surfaces, an η^2 bonding configuration on the surface results from the overlap of the π_{CO} bonding orbital of the formaldehyde (or ketone) with the accepting level of the metal surface atom or cation, along with back-donation from the metal to the π^*_{CO} antibonding orbital of the carbonyl group. The π^*_{CO} orbital in formaldehyde is more stable (approximately 1.3 eV) than the corresponding level of acetone,[55] consistent with more extensive back-donation for formaldehyde, i.e., a smaller energy difference between the π^*_{CO} and the metal highest occupied levels. Back-

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bonding strengthens the π side-one bonding to the surface at the expense of the carbonyl C–O bond, indicated by the red shift of the ν(CO) mode. In fact, η^2-adspecies has been considered to be the precursor to the decomposition of aldehydes and ketones on metal surfaces.

The difference in the observed frequencies also correlates well with the differences in the decomposition temperatures of these molecules on the surface.[31] For example, η^2-formaldehyde decomposition commences at temperatures as low as 90 K on Ru(001). η^2-Acetone, on the other hand, is more stable on Ru(001) and hence decomposes above 250 K.

Significant charge back-donations from the Ni cations of NiO to an adsorbed molecule are unlikely.[56] Therefore, the formation of a surface bond of a η^2-formaldehyde molecule to NiO likely consists primarily of electron donation from the π_{CO} orbital of the formaldehyde molecule to the surface. The higher acidity of the Ni cation relative to Ru metal surface atoms could lead to the side-on formaldehyde-to-Ni bonding configuration being more stable than an end-on η^1 configuration. Furthermore, the C–O bond of an η^2-formaldehyde species on NiO is expected to be stronger than that for η^2-formaldehyde on a metal surface since the bond is weakened only by the depopulation of the π_{CO} orbital upon adsorption. On the basis of this analysis, the species which produces the feature at 1320 cm^{-1} in the spectra of Figure 5 is identified as formaldehyde adsorbed in the η^2 configuration, centered on the Ni cationic site with the C–O axis tilted from the surface normal. A significant attenuation of the electron back-donation in the bonding of η^2-formaldehyde on NiO is consistent with the ν(CO) feature appearing at a frequency of 1320 cm^{-1}.

After correlating the η^2-formaldehyde species with the desorption state at 300 K in the TDS of Figure 1, the desorption activation energy (using the Redhead approximation) can be estimated to be 18 kcal/mol. The stronger binding of the η^2-formaldehyde species compared to the η^1 configuration can be rationalized in terms of the enhanced overlap of the 1b$_1$ orbital of the η^2 species with the surface resulting from the tilt of the molecular axis toward the surface. This is a more optimum bonding configuration compared to the overlap of the 5a$_1$ orbital with the surface in the η^1 orientation.

The thermal desorption data indicate that all of the formaldehyde structures on NiO desorb below 350 K without decomposition. These TDS results contrast the behavior of formaldehyde on metallic surfaces where decomposition is commonly observed, particularly when the η^2 configuration is detected. However, on NiO the dissociation barrier of the C–O bond of η^2-H_2CO is not sufficiently reduced to promote dissociation, as indicated by the much smaller shift to lower frequency. The nature of the bonding of the η^2 species on NiO allows the desorption channel to successfully compete with the decomposition channel.

One notable difference between formaldehyde adsorption on NiO and adsorption on Ru(001) is that on the latter the η^2 structure coexists with the η^1 structure at 90 K. For NiO, in contrast, η^2-formaldehyde is found only within the temperature range of 250–300 K. It is likely that the η^2 configuration on NiO arises from the decomposition of paraformaldehyde beginning at ~250 K.

Conclusions

Formaldehyde adsorbs on NiO film molecularly, and polymerization occurs extensively between 90 and 270 K. Thermal desorption data reveal that the growth of various formaldehyde structures on NiO are nonsequential. Also, chemisorbed monomeric formaldehyde and paraformaldehyde grow simultaneously. Formation of physisorbed formaldehyde initiates before the chemisorbed layer is completely filled. Below 220 K, formaldehyde chemisorbs with the oxygen end toward the surface, i.e., the η^1 structure. Above 250 K, formaldehyde is bonded with the molecular axis tilted from the surface normal, likely via π-bonding.

These results suggest a weak interaction between formaldehyde and the NiO surface. Adsorption of formaldehyde is defined by the acidity of Ni cations; however, the electron donor/acceptor interaction between formaldehyde and NiO does not perturb the molecule sufficiently to lead to decomposition.

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