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Thermal Chemistry of NH₃ on Oxygen-Pretreated Ni(111) Studied by Metastable Induced Electron Spectroscopy and Ultraviolet Photoelectron Spectroscopy

B. Lescop,^{*,†} A. Galtayries,[‡] and G. Fanjoux^{†,§}

Laboratoire des Collisions Electroniques et Atomiques, Université de Bretagne Occidentale, 6 av. Le Gorgeu, CS 93837, 29238 Brest Cedex 3, and Laboratoire de Physico-Chimie des surfaces UMR CNRS 7045, Université Pierre et Marie Curie, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75 005 Paris, France

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Ammonia adsorption on Ni(111) and on oxygen-pretreated Ni(111) has been studied using metastable induced electron spectroscopy and ultraviolet photoelectron spectroscopy at room temperature. Both techniques allowed us to report on the electronic structure of the valence band. The nickel oxidation leads to the existence of an oxygen-adsorbed phase before NiO growth. So we compared the ammonia reaction toward three types of surfaces: Ni(111), NiO/Ni(111), and O–Ni(111). We observed different ammonia reactivities on these three types of surfaces at room temperature: ammonia molecules were molecularly adsorbed on Ni(111), and were decomposed on oxygen-pretreated Ni(111). After surface heating, ammonia products were dissociated, and adsorbed hydroxyl groups were also seen on O–Ni(111). Above 450 K, no ammonia decomposition products were observed on NiO/Ni(111), whereas Ni(111) and the O–Ni(111) were covered by atomic nitrogen. Its coverage is higher on the O–Ni(111) surface than on the clean Ni(111) surface. This observation proves the high ammonia reactivity toward adsorbed oxygen. This study shows that the reactivity of oxygen atoms on Ni(111) toward ammonia depends on their characteristics (adsorbed oxygen or oxygen embedded into NiO).

1. Introduction

The presence of adsorbates on metal surfaces likely alters their structural and electronic properties, and then strongly affects their chemical properties. Understanding the physical origin of any observed change in chemical reactivity and the identification of surface intermediates have potential technical applications, for example, in heterogeneous catalysis or corrosion.

Ammonia interaction with metal surfaces has been extensively investigated^{1–3} since its knowledge is paramount to the fundamental understanding of catalytic processes in industry. However, among these studies, only a few of them have dealt with the adsorption of ammonia on oxygen-pretreated metal surfaces.² Recent investigations carried out with the X-ray photoelectron spectroscopy (XPS) experimental technique have shown that the O-adsorbed phase formed on Ni(111) during the first stages of oxygen exposure at 650 K presents a high reactivity toward NH₃ adsorption at room temperature, contrarily to both clean Ni(111) and NiO thin films.⁴ This result is consistent with scanning tunneling microscopy (STM) data on Ni(110); moreover, it demonstrates that ammonia reactivity depends on the O coverage and is more efficient at low O coverage.⁵ However, open questions remain about adsorption and dissociation mechanisms on oxygen-pretreated Ni surfaces above 300 K. Following previous studies, oxygen pretreatment of Ni surface is assumed to greatly enhance NH₃ decomposition⁶ or to stabilize NH₃ against decomposition to NH or N.⁷

Over a recent study about NH₃ exposure on oxygen-pretreated polycrystalline Ni at high temperature (600 K),⁸ we observed that surface-adsorbed oxygen atoms react with ammonia, and that, finally, water is desorbed while atomic nitrogen partly covers the surface. However, because of the high temperature, neither the intermediate adspecies nor the phases containing oxygen on the surface O-adsorbed and/or NiO islands were identified. At this temperature, both phases may coexist and NiO islands can be transformed into adsorbed oxygen atoms or incorporated into the bulk.^{4,9} Further to extensive studies, the oxidation of the Ni(111) surface, i.e., dissociative chemisorption of O₂, oxide nucleation, and oxide thickening, is now well-known.^{10,11} At the borderline between chemisorption and oxidation, chemisorbed oxygen compounds and oxide-phase NiO coexist on the surface.

Through a fundamental approach along with the use of *in situ* techniques at 300 K, the present study is devoted to investigate the NH₃ exposure on clean and oxygen-pretreated Ni(111) along with the reaction mechanisms on the surface of concern at higher temperatures. Our main focus is to investigate the reactivity of ammonia with surface oxygen in the chemisorbed phase or incorporated in NiO islands. The interaction of O₂ and NH₃ with the Ni(111) surface was thus followed by metastable impact electron spectroscopy (MIES) in combination with ultraviolet photoelectron spectroscopy (UPS). The former technique is nondestructive and based on the interaction of metastable helium atoms (He* 2³S, 19.8 eV) with the surface; in addition, it probes the surface outermost layer *in situ* with a high sensitivity.¹² UPS allows the observation of subsurface spectral contributions that correspond to the integration on the first layers. Then, through the comparison of UPS and MIES spectra, surface and subsurface transformation may be differentiated. Moreover, the used projectiles induce no ammonia

* To whom correspondence should be addressed. E-mail: benoit.lescop@univ-brest.fr.

† Université de Bretagne Occidentale.

‡ Université Pierre et Marie Curie.

§ Present address: Laboratoire d'Optique P.M. Duffieux UMR CNRS 6603, Université de Franche-Comté, route de Gray, 25030 Besançon Cedex, France.

decomposition compared to electron irradiation.¹³ Besides thermal desorption studies, to our knowledge, only a few spectroscopic data are available about the mechanisms of adsorption and reactivity at the highest temperatures on Ni(111).

This paper is divided into two sections. The first one deals with some experimental details about the experimental setup and the reading of MIES and UPS spectra. The second section introduces experimental results about the ammonia exposure on Ni(111), NiO/Ni(111), and the O-adsorbed phase on Ni(111) to observe the evolution of the chemical reaction of the ammonia with a Ni(111) surface covered by different amounts of oxygen from clean Ni(111) to NiO.

2. Experimental Setup

The apparatus is composed of a source for metastable atoms and photons in a UHV chamber where the base pressure is 1.5×10^{-10} Torr. Briefly, a helium cold-cathode gas discharge provides both ultraviolet photons (HeI) and metastable He* atoms ($2^1,3S$) with thermal kinetic energies.¹⁴ The triplet-to-singlet ratio was measured as 7:1 for this type of MIES source.¹⁴ Metastable atoms and photons within the beam are separated by means of a time-of-flight method using a mechanical chopper. The angle of incidence of the probe beam is 45° with respect to the surface normal, and the electrons are collected in the direction perpendicular to the surface. MIES and UPS measurements were performed using a 127° analyzer with a 4 eV fixed energy, leading to a resolution of 250 meV.

The energy scales in the figures were adjusted in such a way that the electrons emitted from the Fermi level (E_F), i.e., electrons with the maximum kinetic energy, were set at the projectile potential energy (19.8 and 21.2 eV for He* and HeI, respectively). It permits the direct measurement of the surface work function from the low-energy cutoff of the spectra. To take into account the analyzer resolution, the work-function value was measured at the central point of the cutoff. Biasing of the sample (6 V negative on the sample) enables one to decrease the secondary-electron peak at low energies without an effect on the spectral features. According to the surface work function, the interaction between a metastable atom, He*, and the surface (MIES technique) is governed by the Auger deexcitation (AD) process or by resonance ionization (RI) followed by the Auger neutralization (AN) mechanism.¹² When the work function is lower than about 4 eV, the electron spectrum is directly proportional to the surface density of states (SDOS) like in the case of the HeI photoelectron spectrum (UPS technique). Therefore, in the description of UPS or MIES (dominated by the AD process) spectra, the energies of the features are given as binding energies (BEs). UPS spectra also give the binding energy scale. For higher work-function values, the RI + AN mechanism dominates. During this process, the 2s electron of He* tunnels into an empty level of the surface; the positive ion thus formed is then neutralized through AN: an electron in the solid transfers to the vacant 1s He* orbital, and another electron in the solid is ejected. The electronic signal created by the AN process, therefore, corresponds to the SDOS self-convolution product.¹⁵ When the RI + AN process dominates the interaction, the Fermi level cannot be located because of the self-convolution process. So the binding energies cannot be reported. However, a vertical line is positioned at the metastable energy (19.8 eV) in our MIES spectra. Note that Pascali et al.¹⁶ have shown that, in a first approximation, the MIES spectrum derivation has to be related to the SDOS and so has to agree with UPS data.

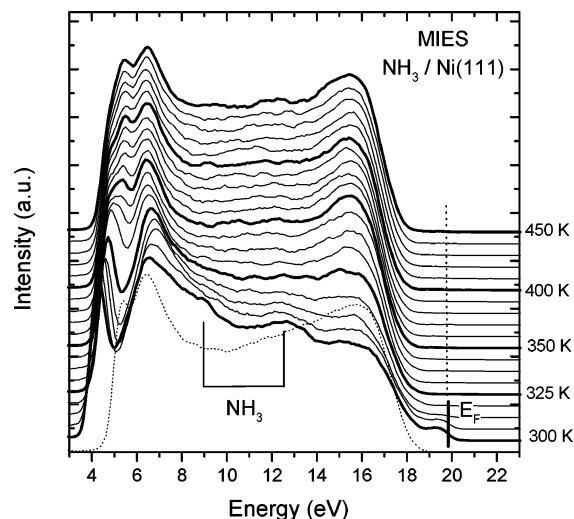


Figure 1. Evolution of the MIES spectra of 3 langmuirs of NH_3 on a clean Ni(111) surface versus temperature. The bottom spectrum (dotted line) corresponds to a clean Ni(111) surface. The next broad spectrum is $\text{NH}_3/\text{Ni(111)}$. The following spectra are functions of the temperature. Electronic structures of $\text{NH}_{3,\text{ads}}$ are positioned.

The Ni(111) sample was, first, mechanically polished before its introduction into the analysis chamber; it was cleaned by repeated cycles of Ar^+ bombardment (2 keV; 7×10^{-7} Torr) and annealing followed with cycles of oxygen and hydrogen atmosphere (10^{-6} Torr). According to Morgner et al.,¹⁷ MIES is sensitive enough to check for surface cleanliness; we thus considered the lack of change in the MIES spectrum, after several cleaning cycles, as a good indicator to end the cleaning process. Exposures to oxygen or ammonia of high purity were performed by admitting the gas through two sapphire leak valves at a constant pressure of 10^{-7} Torr. Oxygen exposures varied between 1 and 100 langmuirs (1 langmuir = 10^{-6} Torr·s). The dose of ammonia was 3 langmuirs obtained at a pressure of 10^{-7} Torr. The gas exposure was always done at room temperature, followed by the sample being heated to 600 K. The rise of the Ni(111) sample temperature was about 5 K/min using a tungsten filament placed behind. One should note that, as the leak valves and ion Ar^+ gun are in the UHV chamber, no sample transfer is needed. Moreover, the MIES and UPS spectrum acquisitions take about 1 min, and therefore, the surface pollution by residual gases is very limited. Between two series of ammonia interactions on the oxygen-pretreated Ni(111) sample, the surface was sputter-cleaned by Ar^+ bombardment and heated in a H_2 atmosphere.

3. Experimental Results and Discussion

3.1. Ammonia Exposure on Ni(111). To study the thermal chemistry of ammonia on Ni(111) pretreated by different amounts of oxygen, NH_3 was first deposited on clean Ni(111). The same experimental protocol was followed to obtain MIES and UPS spectra: NH_3 exposure was made at room temperature, and then the surface was heated to 450 K.

Figure 1 presents the MIES spectrum evolution when the sample temperature is increased; among these spectra, the bottom one corresponds to the clean Ni(111) spectrum (dotted line). The work-function value is extracted from the MIES spectrum; the value we found (5.0 ± 0.2 eV) is in reasonable agreement with previous data.^{18,19} MIES interaction is dominated by the RI + AN process,¹² and then reflects the self-convolution of the SDOS. The structure at about 15.5 eV can be attributed to the self-convoluted Ni 3d band.²⁰

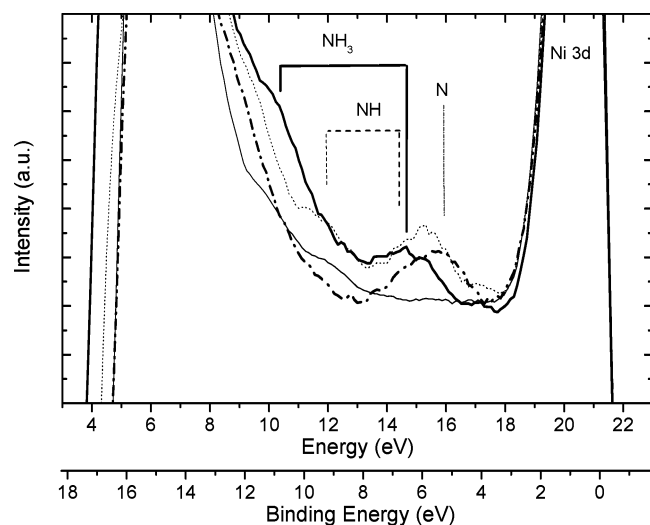


Figure 2. Evolution of part of the UPS spectra of a 3 langmuir NH₃/Ni(111) surface versus temperature: at 300 K (broad line), 310 K (dotted line), and 350 K (broad dashed–dotted line). Note that the clean Ni(111) spectrum is depicted in the solid line. Electronic structures of adsorbed NH₃, NH, and N are positioned. The binding energies are given.

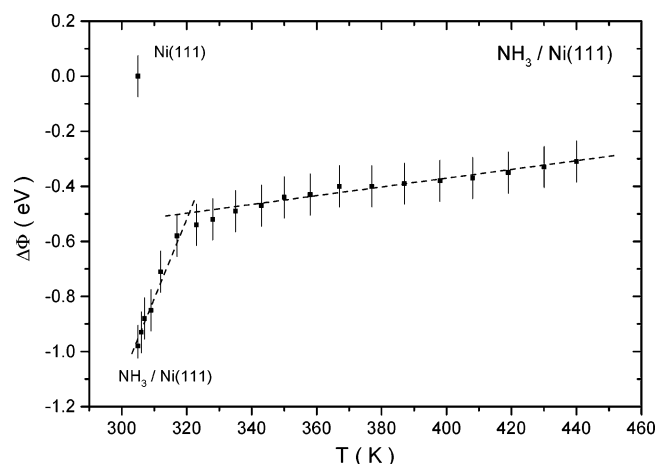


Figure 3. Evolution of the work-function difference $\Delta\Phi$ of NH₃/Ni(111) measured on the MIES and UPS spectra during a temperature increase.

Figure 2 depicts the UPS spectra of Ni(111) at room temperature and of NH₃/Ni(111) at three different temperatures: 300, 310, and 350 K. The features attributed to the adspecies being weak, only a part of the UPS spectra is presented.

Figure 3 shows the evolution of the surface work function of the clean Ni(111) one at 300 K and of the surface after NH₃ exposure and after heating to 450 K.

3.1.1. Ammonia Exposure on Ni(111) at Room Temperature. The 3 langmuir ammonia exposure at 300 K caused several changes in the MIES spectrum (see Figure 1). These modifications can be explained by the switching from the RI + AN to the AD process, whose spectrum is directly related to the SDOS.¹² The process modification must be related to the existence of adspecies on the surface. The adsorption leads to a work-function decrease of about 1.0 eV. Two electronic structures are observable at about 13 and 9 eV, and correspond to BEs equal to 6.8 and 10.8 eV, respectively. The corresponding UPS spectrum (broad line, Figure 2) shows weak electronic structures at energies equal to 10.7 and 6.7 eV BE. These electronic features observed in the MIES and UPS spectra can,

therefore, be unambiguously attributed to the 3a₁ and 1e orbitals of NH_{3,ads} (binding energies 7.0 and 11.5 eV).^{21,22} Consequently, NH₃ is molecularly chemisorbed on the surface at room temperature. It is well-known that ammonia bonds via its lone pair orbital to the ridge atop nickel atoms with its 3-fold axis normal to the surface and three hydrogen atoms pointing outward.²³ After NH₃ exposure, the Ni 3d band structure (15.5 eV) is still clearly visible in the MIES spectrum (see Figure 1). The MIES technique being only sensitive to the external monolayer (ML), our spectrum evidences the existence of bare Ni islands and chemisorbed NH₃.

A signal which results from the AD process obviously appears at the Fermi level in the MIES spectrum. Similar MIES peaks have been reported at the Fermi level for the NH₃/Ni(111),¹⁸ NH₃/Pd(111),²² CO/Ni(111),^{24,25} CO/Ni(100),²⁴ and H₂O/Cu(100)²⁶ systems. Concerning the NH₃/Pd(111) surface, Sesselmann et al.²² have assigned this feature to the metal–adsorbate σ antibonding states. Using molecular orbital calculations on NH₃/Pt(111), Fierro²⁷ has shown that MIES peaks may be due to the partially filled antibonding states formed by the combination of the NH₃ lone pair orbital (3a₁) and the metal d state. Our observations confirm the existence of NH₃-adsorbed-induced states on metals. One should note that these states are not seen by UPS because they are hidden by the metallic d band at the Fermi level.

Since the NH₃ signal in our MIES and UPS spectra is not very intense compared to the Ni signal, the sticking coefficient of ammonia on Ni(111) at room temperature has to be very low. Consequently, traces of ammonia are only present on the surface. Molecular ammonia has to be adsorbed on lowly coordinated Ni atoms. This observation disagrees with recent published XPS data,⁴ which led the authors to consider that ammonia molecules do not adsorb on Ni(111) at room temperature. They supposed that ammonia adsorption needs the presence of O or OH groups.^{4,28} However, given the residual vacuum, the low acquisition time, and the MIES surface sensitivity in our experiment, our data indicate that the surface is not polluted by any oxygen or hydroxyl groups: indeed, no features corresponding to O and OH species are observed.

3.1.2. Thermal Study by Heating the Surface. After NH₃ exposure at 300 K, the surface was heated. The MIES spectra (see Figure 1) evidence the vanishing of the structure up to 20 eV concomitant with the growth of the 15.5 eV one. These changes confirm that the AD mechanism becomes less probable than the RI + AN one. This evolution can be related to adspecies desorption, in agreement with the increase of the work function (see Figure 3). Between 300 and 320 K both processes coexist, which makes difficult MIES spectrum analysis even though the lack of a signal at 19.8 eV above 310 K reveals RI + AN domination. To obtain the SDOS, the derivation of the MIES spectrum can be done.¹⁶ But this procedure leads to an important uncertainty, so we used the UPS spectra depicted in Figure 2 to study the species present on the surface within this temperature range. At 310 K, the UPS spectrum highlights two peaks at 5.9 and 9.3 eV BE. On the other hand, the structures attributed to NH_{3,ads} are no longer visible, which suggests decomposition or removal from the surface of molecular ammonia. The observed peaks must be related to the NH_{x,ads} ($x = 0, 1, 2$) species. Following the data of Grunze et al.²⁹ on Ni(110), the binding energies of the NH_{ads} and N_{ads} orbitals are at 7.0 and 9.3 eV for the former and 5.5 eV for the latter. Consequently, the displayed UPS spectrum indicates the presence of these NH_{ads} and N_{ads} species, the peak at 5.9 eV BE corresponding to the addition of the structures at 5.5 and 7.0 eV. Concerning

NH₂ species, two peaks had to be observed in the spectrum:²¹ the energy separation of these orbitals was found by calculation to be at about 5 eV²¹ on Ni(111) and measured at 5.5 eV on Si(001) by UPS.³⁰ In our spectra, no structure can be attributed to the NH_{2,ads} orbital; its lack exhibits the instability of the NH₂ radical on Ni(111). The above observations suggest that a dissociation mechanism takes place between 300 and 320 K, so within this temperature range, molecular ammonia adsorbed at 300 K should be decomposed into NH_{ads} and N_{ads}. It is likely that NH₃ has been partly removed from the surface. The drastic increase of the work function (Figure 3) between 300 and 320 K confirms the decomposition and desorption of adsorbed ammonia. In a study of temperature-programmed desorption (TPD) of NH₃/Ni(110),²⁸ desorption peaks of NH₃ and H₂ were displayed at about 330 K. Both processes (dissociation/desorption) should occur concomitantly.

Temperatures above 320 K caused a slow increase of the work function (Figure 3) together with poor changes in the spectra, which become closer to the clean Ni(111) spectrum. The final MIES spectrum at 450 K presents not only the structure at 15.5 eV attributed to the Ni 3d band self-convolution, but also a weak feature at 12.0 eV (see Figure 1) not seen in the clean Ni(111) spectrum; this observation reveals the presence of adsorbates on the surface. Other evidence of their presence is provided by the difference in intensity of the 15.5 eV structure at 450 K compared to that in the clean Ni(111) spectrum observed for different measurement series. The MIES spectrum derivation (not shown here) exhibited two peaks, at the Fermi level and 5.5 eV BE, attributed to the Ni 3d band and the atomic nitrogen orbital, respectively. On the spectrum derivation, the Ni 3d band related to the final spectrum is shifted compared to that of the clean Ni(111) one, which proves the charge exchange between the adspecies and Ni atoms. The UPS spectrum at 350 K (Figure 2) displays only one peak that corresponds to the atomic nitrogen orbital; such a feature confirms that the surface is only covered by atomic nitrogen. Moreover, the reduction of this peak in the UPS spectra above 600 K is indicative of nitrogen desorption. Adsorbed nitrogen atoms recombine into N₂ at high temperature:²⁸ a desorption peak of molecular nitrogen was displayed at about 800 K by TPD.²⁸ The weak intensity of this peak in our data proves that desorption of molecular ammonia has to be the major process from 300 to 320 K.

In conclusion, our experimental data prove that, on Ni(111), ammonia adsorbs only molecularly at 300 K, but only traces were seen. Ammonia reactivity on Ni(111) at 300 K is, therefore, very low, in agreement with XPS data.⁴ Adsorbed molecular ammonia is, first, decomposed to NH at 310 K, and finally to N above 320 K. It is obvious that, between 300 and 320 K, the NH_x ($x = 0, 1$) species have to coexist. Our results well agree with previous UPS, XPS, and TPD data on Ni(110).^{3,4,7,13,28,29} The high H₂ and NH₃ peaks displayed at room temperature in the TPD spectra indicate the removal and/or the decomposition of NH₃ adspecies.²⁸ Above 320 K, only N_{ads} species are present on the surface, and the surface heating-induced modifications are caused by nitrogen atom removal from the surface. These conclusions are consistent with previous TPD data^{3,13,28} that showed, at about 800 K, the desorption of N₂ due to N_{ads} recombination.

3.2. Ammonia Adsorption on NiO/Ni(111). **3.2.1. Formation of the NiO/Ni(111) Surface.** To form the NiO surface, 100 langmuirs of oxygen was exposed to Ni(111) at room temperature. Under these conditions, at least 3 MLs of NiO are formed on the Ni(111) surface.^{9,31} The MIES spectrum depicted in Figure 4 is rather similar to the previously published NiO

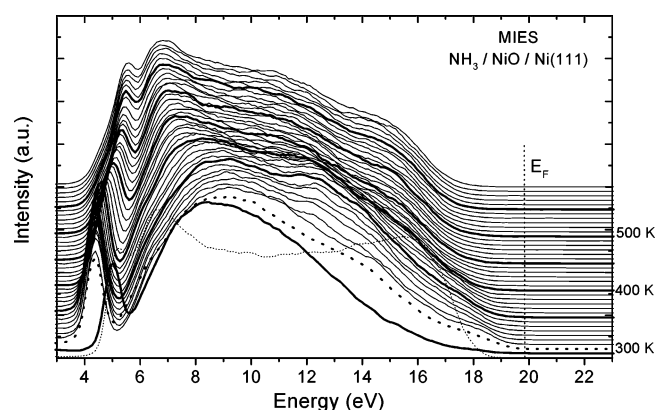


Figure 4. Evolution of the MIES spectra of 3 langmuirs of NH₃ on a NiO surface versus temperature. The bottom spectrum (dotted line) corresponds to a clean Ni(111) surface, the second one (broad line) to NiO/Ni(111), and the third one (dotted broad line) to NH₃/NiO/Ni(111). The following spectra are functions of the temperature.

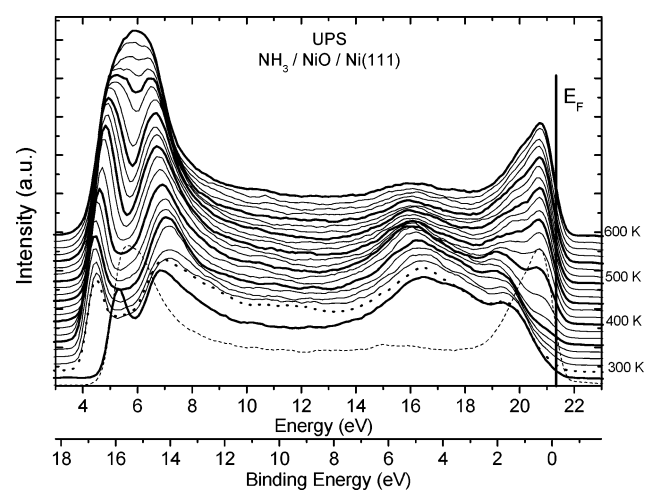


Figure 5. Evolution of the UPS spectra of 3 langmuirs of NH₃ on a NiO surface versus temperature. The bottom spectrum (dotted line) corresponds to a clean Ni(111) surface, the second one (broad line) to NiO/Ni(111), and the third one (dotted broad line) to NH₃/NiO/Ni(111). The following spectra are functions of the temperature.

spectra.^{32,33} Figure 5 reproduces equivalent UPS spectra. The first broad-line UPS spectrum corresponding to the NiO/Ni(111) surface evidences two structures at 20 and 16.5 eV (BE = 1.2 and 4.7 eV), whereas the peak associated with the 3d Ni band is lacking at the Fermi level. Its absence proves the existence of several layers of NiO. The first structure near this level is attributed to the 3d²⁺ Ni band of NiO, and the other one is mainly associated with the O 2p_z orbital.³⁴ As the work-function value is slightly less than the Ni(111) one,³² it evidences the dissolution of adsorbed oxygen atoms into the bulk to further form NiO. This work-function difference and the gap formation both indicate that the AD mechanism is the major one.¹⁷ An intense low-energy peak appears in the MIES spectrum in agreement with the recent results by Aoki et al.³³ The NiO(111) is known to be rapidly hydroxylated.⁹ However, no peaks related to hydroxyl groups are observed in the UPS and MIES spectra. So we suppose that ammonia exposure started before the NiO(111) hydroxylation thanks to our protocol (high vacuum and short time between oxygen exposure and spectrum acquisition).

3.2.2. Ammonia Exposure on NiO/Ni(111) at Room Temperature. Figures 4–6 illustrate the changes induced in the MIES (Figure 4) and UPS (Figure 5) spectra and in the work function

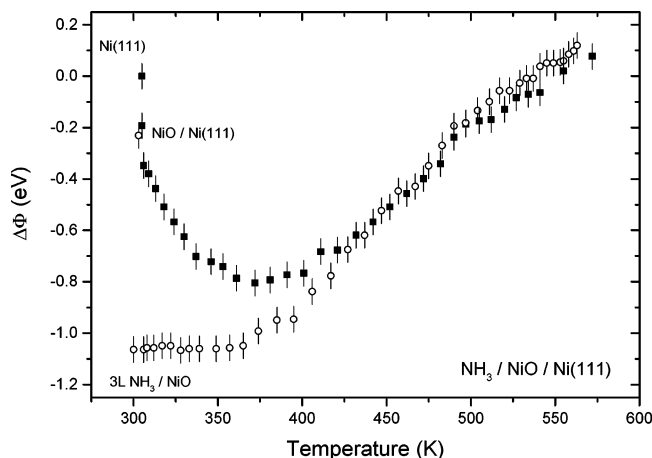


Figure 6. Evolution of the work function of $\text{NH}_3/\text{NiO}/\text{Ni}(111)$ in white circles and $\text{NiO}/\text{Ni}(111)$ in black squares extracted from MIES spectra during a temperature increase.

(Figure 6) by exposure of 3 langmuirs of NH_3 at room temperature. Comparison of NiO with and without NH_3 exposure spectra evidenced superposed structures together with a decrease of the work function by 0.8 eV. One should also note the lack of a band corresponding to $\text{NH}_{3,\text{ads}}$ on the surface; at room temperature, indeed, ammonia molecules are decomposed on NiO . The UPS spectrum shows a plateau from 7 to 13 eV BE. The subtraction of the latter spectrum from the NiO spectrum highlights three weak peaks at 6.8, 9.4, and 12.3 eV BE, respectively. These structures have already been observed at high temperature and attributed to NH_x ($x = 1, 2$) compounds.⁸ Let us note that, at 600 K, the superposition of poorly intense structures leads to a structureless and slight plateau.⁸ The peak at 12.3 eV BE was attributed to NH_2 ,^{29,30} and the other ones were related to NH .²⁹ The lack of structures at about 5 eV BE indicates that no atomic nitrogen is present on the surface; adsorbed ammonia decomposition is thus incomplete. In other respects, the missing hydroxyl-orbital-related structures imply that either the hydroxyl groups have been removed as soon as they were formed by ammonia decomposition as previously reported at high temperature²⁰ or ammonia has been dissociated on NiO without reacting with oxygen.

One should notice the lack of peaks in the MIES spectrum displayed in Figure 4; a broad structure is, however, observed between 11 and 16 eV. The spectrum remains mainly dominated by NiO features: the peaks observed at 18.5 and 14 eV are obtained by the AD process and attributed to the $\text{Ni } 3d^{2+}$ band and $\text{O } 2p_z$ of NiO .³⁴ The RI + AN process seems to be negligible. The ammonia-exposure-induced change in the MIES spectrum also demonstrates the existence of adspecies through the occurrence of a weak superposed structure within 11 and 17 eV. These data can be associated with the NH_x ($x = 1, 2$) formation observed by UPS. The formation of these NH_x adspecies on hydroxyl groups adsorbed on the surface should not be excluded, because of the high reactivity of hydroxyl groups toward ammonia.²⁸

Therefore, at room temperature, ammonia exposure on NiO leads to slight changes in the MIES and UPS spectra, and then confirms the very weak sticking coefficient of ammonia on NiO .⁴ Adsorbed ammonia is totally decomposed to NH_x ($x = 1, 2$); the dissociation seems to be incomplete since no structure attributed to atomic nitrogen on NiO is noticeable in the spectra.

3.2.3. Thermal Study by Heating the Surface. Figures 4–6 present MIES and UPS spectra and work-function evolution for temperatures from 300 to 600 K. Up to 360 K, no major changes

are noticed; the only alterations are a decrease of the features attributed to $\text{NH}_{x,\text{ads}}$, and the temperature-related shifting of the $\text{Ni } 3d^{2+}$ band in the UPS and MIES spectra. The work-function stability is explained by the removal of the NH_x compounds, concomitant with the penetration of NiO -bound oxygen atoms into the bulk; the former increases the work function, whereas the latter decreases it. Figure 6 also presents the work-function evolution of 100 langmuir $\text{O}_2/\text{Ni}(111)$, i.e. $\text{NiO}/\text{Ni}(111)$, without ammonia exposure as a function of temperature. In the same temperature range as above, the work-function decrease proves that oxygen atoms are dissolved into the bulk rather than removed. Further to ammonia exposure, the work-function behavior is almost unchanged and indicates that NH_x desorption counterbalances oxygen penetration. All these data are in favor of $\text{NH}_{x,\text{ads}}$ compound removal between 300 and 360 K.

Above 420 K, Figure 6 shows that the work functions have the same value with or without ammonia pretreatment, so NH_x species are totally removed from the surface, whereas features attributed to $\text{O } 2p$ and $\text{Ni } 3d^{2+}$ are seen in the spectra. This observation confirms the lack of reaction of ammonia molecules with oxygen atoms from NiO , because the oxygen dose on the surface at this temperature is the same with or without ammonia pretreatment after NH_x desorption. Moreover, no hydroxyl groups are observed in our spectra. UPS data evidence a decrease of the $\text{O } 2p$ and $\text{Ni } 3d^{2+}$ contributions together with an increase of the $\text{Ni } 3d$ band with temperature. Above 420 K, the work-function behavior highlights oxygen desorption from the surface and/or a change in the oxygen phase on the surface; indeed, the work function of surface-chemisorbed oxygen is higher than the Ni value.²⁰ At 600 K, the final UPS spectrum exhibits a high peak attributed to the $3d$ Ni band along with a structure at 16 eV corresponding to the $\text{O } 2p_z$ orbital; both indicate that the surface is mainly covered by chemisorbed O , but not by NiO islands. By comparison with previously published MIES data,^{32,33} our MIES spectrum confirms the chemisorption of the whole oxygen atoms on the surface chemisorbed. Consequently, the temperature increase induces the change of NiO into an O -adsorbed phase followed by desorption. These results are in good agreement with published data:^{9,35} at high temperature, oxygen atoms bound into NiO are transformed in adsorbed oxygen before desorption, or diffuse in the bulk. Lorenz and Schulze³⁶ have previously reported the cleaning of the oxygen-pretreated Ni at high temperatures.

To summarize, our experimental data confirm the poorly reactive behavior of a NiO thin film on $\text{Ni}(111)$ observed by XPS at room temperature.⁴ As soon as ammonia enters the chamber, it is decomposed and leads to NH_x formation, and these products are removed below 420 K. Since no hydroxyl groups are observed on the NiO surface, the NH_x radicals may block adsorption sites. From 420 K, ammonia-decomposed elements do not react with the surface. Oxygen of NiO is transformed to an O -adsorbed phase, and then removed; ammonia pretreatment plays no role in this mechanism because dissociation products are desorbed at lower temperatures.

3.3. Ammonia Adsorption on the O-Adsorbed Phase on $\text{Ni}(111)$.

3.3.1. Formation of the O-Adsorbed $\text{Ni}(111)$ Surface. The last part of this paper deals with the thermal chemistry of ammonia on O -adsorbed $\text{Ni}(111)$, because recent works^{4,5,28} have shown that this oxygen pretreatment strongly changes the reactivity of ammonia toward the Ni surface. The O -adsorbed $\text{Ni}(111)$ surface was produced after 1 langmuir O_2 exposure at room temperature. Figure 7 presents MIES spectra of ammonia exposed to 1 langmuir of O_2 on $\text{Ni}(111)$ first at room

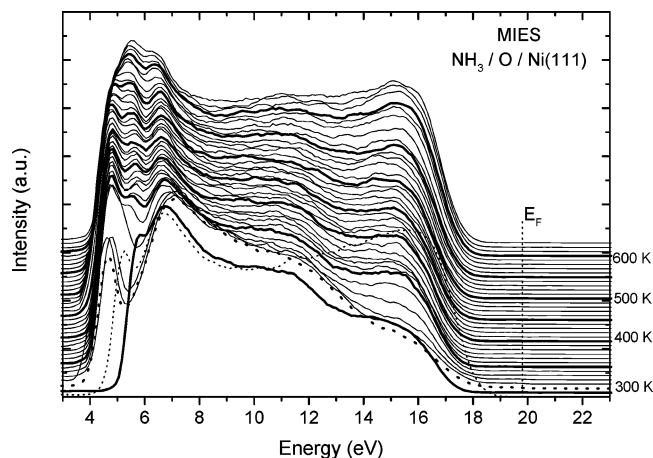


Figure 7. Evolution of the MIES spectra of 3 langmuirs of NH_3 on an O-Ni(111) surface versus the temperature. The bottom spectrum (dotted line) corresponds to a clean Ni(111) surface, the second one (broad line) to O-Ni(111), and the third one (dotted broad line) to NH_3 exposed to O-Ni(111). The following spectra are functions of the temperature.

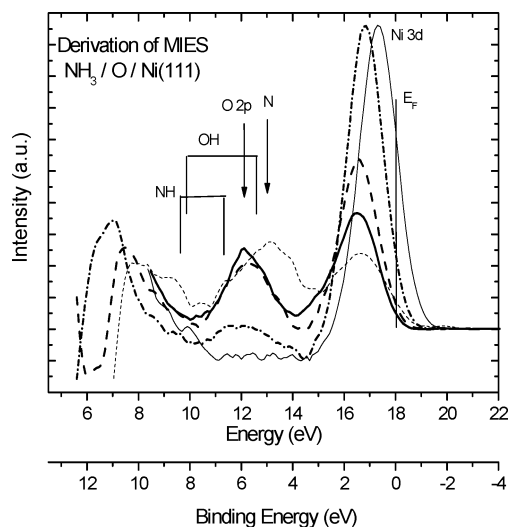


Figure 8. Evolution of the MIES derivation of 3 langmuirs of NH_3 on an O-Ni(111) surface versus the temperature: derivative MIES spectra of Ni(111) at 300 K (straight line) and then O-Ni (broad line), with NH_3 exposure (dashed line), and heated at 350 K (broad dotted line) and 520 K (dashed-dotted line). The binding energies are given.

temperature and then after a progressive heating of the surface up to 600 K. The first MIES spectrum at 300 K (broad line) corresponding to an oxygen-pretreated Ni(111) surface fits well with previously published spectra^{32,33} and evidences the formation of the O-adsorbed phase on Ni(111). As compared to that of Ni(111), the work-function increase (+0.6 eV) agrees with previously published data;³² this increase has been attributed to the permanent dipole of oxygen chemisorbed on the Ni surface. Because of the high work-function value, MIES interaction is dominated by the RI + AN process;¹² the spectrum derivation (see Figure 8) can thus be related to SDOS.¹⁸ The derivation of the 1 langmuir O_2 MIES spectrum (broad line) presents two peaks at 16.5 and 12.0 eV. According to the work-function value, the Fermi level can be positioned at 18.0 eV.¹² We therefore attributed both structures to the Ni 3d band and the O 2p contribution.²⁰ The Ni 3d feature shift in comparison with the clean Ni(111) surface proves the binding between oxygen and Ni atoms, and so proves that no bare Ni is present on the surface, i.e., the surface is totally covered with adsorbed

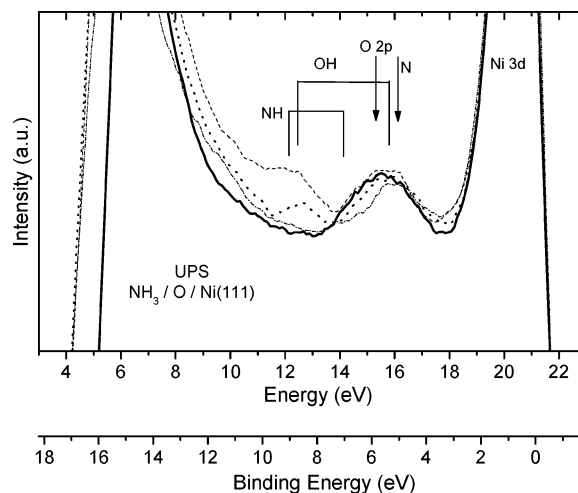


Figure 9. Evolution of the UPS spectra of 3 langmuirs of NH_3 on an O-Ni(111) surface with the temperature: UPS spectra of O-Ni at 300 K (broad line) and then with NH_3 at 300 K (dashed line), 350 K (broad dotted line), and 520 K (dashed-dotted line). The binding energies are given.

oxygen. Moreover, no NiO islands are detected. The same two peaks are clearly displayed in the UPS spectrum (Figure 9).

3.3.2. Ammonia Exposure on O-Ni(111) at Room Temperature. NH_3 exposure was performed at room temperature on the O-adsorbed Ni(111) surface. The MIES spectrum (broad dotted line in Figure 7) indicates that ammonia exposure induced a reduction of the structure at 15.5 eV, and the occurrence of another structure at about 12 eV; moreover, the work function is reduced by 1.2 eV compared to that of the O-adsorbed Ni(111) surface. These observations are in favor of new adspecies. The lack of the signal observed up to 20 eV together with the work-function value indicates the RI + AN process domination with respect to the AD mechanism. MIES spectrum derivation (dashed line in Figure 8) highlights a reduction in intensity of the Ni 3d band and the occurrence of new structures at about 13.2, 11.3, and 9.3 eV (5.8, 6.7, and 8.7 eV BE) instead of the O 2p orbital observed at 6.0 eV BE. One should note that the structures corresponding to energies below 8 eV were not taken into account because of the secondary-electron structure derivation.¹⁷ After NH_3 exposure, the UPS spectrum evidenced a slight decrease of the Ni 3d band intensity (not shown). Figure 9 presents a section of the UPS spectrum and highlights superimposed peaks at the same binding energies as those in the MIES spectrum (5.5 and 8.9 eV BE). They are mainly attributed to orbitals of OH species (1π at 5.7 eV and 3σ at 9.3 eV on Ni(110)³⁷). This observation agrees with TDS data,³⁸ which postulate hydroxyl formation. Figure 8 displays derivation of the MIES spectrum; note the shoulder at 11.5 eV (BE = 6.5 eV) attributed to NH formation. The second NH orbital at 9.0 eV BE is hidden by the peak attributed to the 3σ orbital of OH. However, at room temperature, the existence of N_{ads} species on the surface should be excluded because of the 1π OH peak at 5.5 eV BE. Concerning the $\text{NH}_{2,\text{ads}}$ existence, its orbitals should be seen at about 5 and 10.5 eV BE, and its intensity is negligible compared to those of OH and NH. In conclusion, at 300 K, molecular ammonia molecules are not observed, because they react with chemisorbed oxygen to give NH or N together with OH.^{28,39}

3.3.3. Thermal Study by Heating the Surface. Then the surface is heated from room temperature to 600 K. The MIES spectra displayed in Figure 7 show that the rise in temperature from

300 to 340 K results in the increase of the 3d Ni band (15.5 eV) and the decrease of the 12 eV structure. These observations are in favor of a partial removal of ammonia decomposition products. Up to 350 K, the 15.5 eV signal increase confirms adspecies desorption. On the other hand, the UPS spectrum at 350 K (see Figure 9) highlights the simultaneous decrease of the 12 eV (9.2 eV BE) structure together with the weak variation of the 15.5 eV (5.7 eV BE) peak; it evidences the NH decomposition because of the existence of N_{ads} species on the surface. These data make us suppose also OH desorption: hydroxyls are partly desorbed, forming H₂O by OH disproportionation and/or hydroxyl hydrogenation.^{20,40} These observations confirm the existence of H₂ TDS peaks at this temperature range.²⁸

From 330 to 500 K, only slight changes are noticed in the MIES spectrum (Figure 7). Moreover, the 15.5 eV intensity is rising slowly, though continuously, and a signal is still superimposed at about 12 eV. The OH/NH group removal though continuous seems less efficient. This result confirms recent TDS data,²⁸ where H₂ and NH₃ desorption peaks are observed from 350 to 400 K.

The UPS spectrum at 520 K (Figure 9) evidences a single peak at 5 eV BE in addition to the Ni 3d one; this peak is related to atomic nitrogen. On the MIES spectrum at this temperature, structures are always observed at 15.5 and 12 eV. Derivation of this spectrum (Figure 8) enhanced two peaks that we attributed to the Ni 3d band and atomic nitrogen contribution at 5 eV BE, respectively, in agreement with UPS data. Given the closeness of the O_{ads} and N_{ads} orbital peaks, oxygen existence is also possible. However, following TDS data,²⁸ no oxygen atoms are present on the surface above 420 K. By comparison with the Ni 3d band value in the clean Ni(111) spectrum, it also shows a slight shift of the Ni 3d peak (−0.5 eV) attributed to N_{ads}–Ni bonding. At this temperature, the Ni(111) surface is then partly covered by atomic nitrogen. Moreover, at 600 K, the MIES spectrum shows that the surface is not totally clean. This is in agreement with reported TDS data that evidenced desorption of N₂ around 800 K.²⁸ Guo and Zaera²⁸ have shown that the N₂ desorption peak intensity depends on the oxygen pretreatment. To confirm this observation, we extracted from the MIES derivation (at 450 K) the intensity of the feature corresponding to the nitrogen atom after ammonia exposure with (from Figure 7) and without (from Figure 1) oxygen pretreatment. Oxygen-pretreated Ni(111) increases by a factor of 3 the amount of atomic nitrogen adsorbed. This observation confirms recent TPD data, which evidenced that N₂ was almost only observed after oxygen or hydroxyl pretreatment.²⁸ Thus, we suppose that atomic nitrogen is present on regular sites after oxygen pretreatment, contrarily to clean Ni(111) where ammonia is only dissociated on lowly coordinated Ni atoms. Atomic nitrogen electronic features are confirmed by UPS measurements.

In this part of this paper, we have studied ammonia exposure on the O-adsorbed Ni(111) phase. The studied surface was obtained by 1 langmuir O₂ exposure in agreement with previous results.^{32,33} Ammonia exposure increases the amount of the present adspecies: ammonia reactivity with oxygen leads to the NH₃ dissociation and then to the formation of OH and NH groups. The existence of atomic nitrogen is also supposed. A temperature rise up to 320 K induces the dissociation of the NH species, leading to the increase of the N_{ads} species on the surface in agreement with TPD data.²⁸ The OH groups are removed from 340 to 500 K. Consequently, above 500 K, the surface is only covered by atomic nitrogen. The intensity of

the spectral features of the N is higher than that in the NH₃/Ni(111) case. Consequently, oxygen pretreatment favors the adsorption of NH_x on the Ni(111) surface.

4. Summary and Conclusion

Ammonia exposure to Ni(111) and oxygen-pretreated Ni(111) was investigated by both MIES and UPS techniques at room temperature. On Ni(111), we showed that ammonia is molecularly adsorbed, but surface heating leads to a fragmentation into NH_{ads}, and then N_{ads} below 320 K. Since only traces of N_{ads} were observed above 350 K, the ammonia molecules have been adsorbed on lowly coordinated Ni atoms.

On NiO/Ni(111), ammonia molecules are directly decomposed into NH_{2,ads} and NH_{ads}. No hydroxyl groups were evidenced on the surface, and their lack proves the absence of reactivity of NH₃ toward oxygen of NiO. The surface is not contaminated by the chamber pollution. Above 350 K, the spectra were identical with or without ammonia exposure; as a consequence the NH_{x,ads} (x = 1, 2) species are desorbed from the surface. Above this temperature, the spectrum changes result from only oxygen transformation and desorption: we followed the transformation of NiO into the O-adsorbed phase above 400 K and their desorption from 500 K.

Ammonia exposure on oxygen-adsorbed Ni(111) leads to NH_{ads}, N_{ads}, and OH_{ads} production: ammonia reacts with adsorbed oxygen. When the temperature is increased, OH desorption and NH decomposition are supposed, and the surface is then covered by atomic nitrogen. These results are in perfect agreement with the recent paper by Guo and Zaera.²⁸ The atomic nitrogen coverage is higher on the chemisorbed oxygen surface than on the clean Ni(111) one; this is due to the ammonia reactivity toward adsorbed oxygen and so to the presence of N_{ads} on regular sites. Consequently, the presented results confirm the reactivity difference of oxygen atoms adsorbed on the Ni(111) surface or embedded and bound into NiO toward ammonia. The MIES high sensibility to the outermost layer enables us to report the adspecies behavior.

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