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Ammonia adsorption and decomposition on a Ni(110) surface

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We report UPS/XPS results for ammonia adsorption and decomposition on a Ni(110)-surface. At $T < 130$ K molecular adsorption of NH_3 is observed to proceed with an initial sticking coefficient of $s_0 \sim 0.1$. Increasing the temperature of the nickel surface above 150 K results in partial dissociation of the adsorbed NH_3 molecules. The intermediate species are tentatively identified by their photoelectron spectra as NH-fragments. At temperatures above 350 K only atomic nitrogen is observed to populate the surface after NH_3-exposures. Our data show a similar reactivity of the Ni(110) surface in the NH_3-decomposition reaction as found on iron-single crystal planes. We briefly discuss this result with respect to the negligible activity of nickel as a catalyst for ammonia formation.

I. INTRODUCTION

The mechanism of ammonia formation and decomposition on metal surfaces has attracted considerable scientific interest since the early pioneering studies of Emmett and co-workers.[1]

These reactions have been studied in most detail on iron surfaces because iron has a high catalytic activity and is used as a catalyst in the industrial ammonia synthesis reaction.[2,3] From a more general point of view, however, it is also interesting to understand the physical basis which makes iron a superior catalyst compared to other transition metals. To obtain this understanding it is necessary to make a systematic study for each metal on the structure sensitivity and the microscopic reaction steps of NH_3 formation and decomposition.

From an inspection of the early literature[4] it appears that nickel is a very poor catalyst for NH_3-synthesis but exhibits a reasonable activity towards NH_3-decomposition. Kinetic results on a promoted nickel catalyst obtained under stationary conditions suggest that N_2-chemisorption and desorption are rate determining in the synthesis and decomposition reaction, respectively.[5] The inactivity of nickel in NH_3-synthesis is believed to be caused by its inability to dissociate molecular nitrogen. There are, however, recent reports by Grunze et al.[6] and Wedler and Alshorachi[7] who observed dissociative N_2-absorption on Ni(110) and polycrystalline Ni-films, respectively, with a sticking coefficient comparable to those obtained on iron single crystal planes.[8]

Adsorption of ammonia has been studied by Gundry, Haber and Tompkins on nickel films[9] and by Seabury et al.[10] on a Ni(111)-surface. Gundry et al.[9] concluded from their surface potential measurements that NH_3 decomposes upon adsorption at 195 K into $NH_{2ad} + H_{ad}$. At 293 K and above, evidence for a surface equilibrium between chemisorbed NH_2, NH, and H species was found. The formation of atomic nitrogen through further dissociation of NH, however, was ruled out on the basis of their results. The study of Seabury et al.[10] on

NH_3 adsorption on Ni(111) at 200 K showed no evidence for a thermally activated dissociation of NH_3. Only after electron beam exposure was a stable decomposition fragment observed giving rise to an emission band around 8 eV below E_F in the UPS data. By comparison with the results obtained by Weiss et al. on Fe(110),[11] they tentatively assigned this photoemission feature as originating from NH-species.

Our results presented in the following paragraphs on NH_3-adsorption and decomposition on Ni(110) show a high activity of this crystal plane towards the dissociation reaction. In comparison with the results on Ni(111),[10] they indicate a pronounced structure sensitivity of the ammonia reaction on nickel.

II. EXPERIMENTAL

The experiments were carried out in a commercial (Leybold–Heraeus) photoelectron spectrometer described previously.[12] The angle of incidence of the photons in the UPS and XPS experiments was 60° and the emitted electrons were collected in a plane normal to the surface. The $N(E)$ UPS and XPS spectra were obtained by data collection into a Nicolet Instruments computer. Binding energies refer to the Fermi level of the Ni(110)-substrate. We also present data where the intensity of the N1s core electron emission was measured as a function of exposure or temperature to obtain kinetic data for the decomposition reaction. A description and discussion of this experimental procedure is given elsewhere.[13] The Ni(110) crystal disk used in this study was characterized with respect to its crystallographic orientation in previous experiments.[6] Cleaning of the surface was achieved by flashing the crystal to ~1000 K and Ar⁺-ion bombardment followed by an annealing procedure used in a previous LEED-study to obtain a well-ordered surface.[6]

III. RESULTS

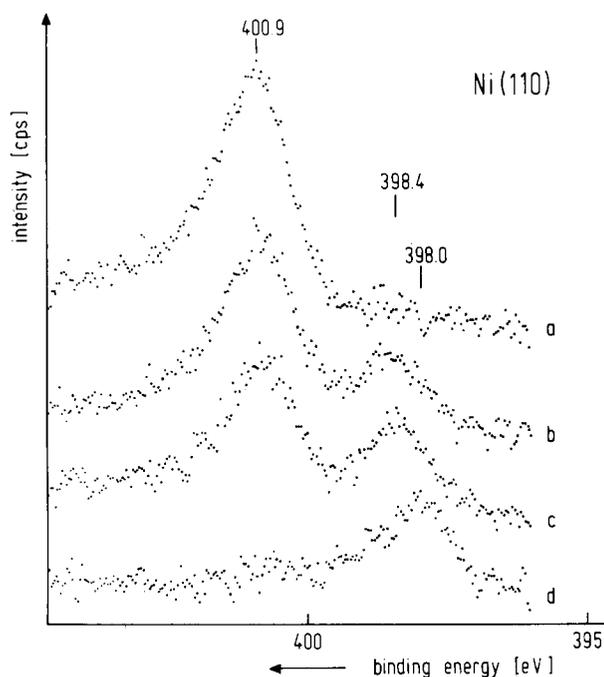Ammonia adsorption at 110 K is nondissociative as evident from the XPS and HeII–UPS data. In Fig. 1a the N1s-spec-

FIG. 1. N1s–XPS data for ammonia adsorption and decomposition on a Ni(110)-surface. (a) adsorption of 0.75 L at 110 K, (b) heated to 191 K, (c) heated to 226 K, and (d) after hydrogen desorption through heating to 426 K.

trum of the Ni(110) surface exposed to ~0.75 L NH_3 is shown. The emission band has a half-width of 1.5 eV and is centered at 400.9 eV below E_F. By comparison with the data obtained on iron surfaces,[12,14] this band is identified as arising from molecularly adsorbed NH_3.

In Fig. 2 the intensity of the N1s-band of molecular NH_3 at 400.9 eV as a function of exposure is shown. The intensity of the peak at a given exposure is proportional to the integrated band envelope and therefore this curve represents directly the relative changes in coverage. Saturation coverage is obtained after an exposure of 4.7 L (Torr $\times$ s $\times$ 10^{-6}). Since the absolute coverage is not known, only a crude estimate of the initial sticking coefficient s_0 can be made by comparison of the NH_3 N1s band intensity to the N1s emission for N_2-saturation coverage on Ni(110).[13] The estimated NH_3-saturation coverage at 120 K on Ni(110) then corresponds to 3.8 $\times$ 10^{14} molecules cm^{-2} or θ ~0.34 ($\pm$30%) with respect to a nickel atom density of 1.1 $\times$ 10^{15} atoms cm^{-2}. With this value an initial sticking coefficient of s_0 ~ 0.1 at 120 K is derived.

Heating the predosed surface above T = 150 K results in the appearance of a new emission band at 398.4 eV (Fig. 1b). This band is indicative of a partial dissociation of ammonia according to

$$NH_{3ad} \rightarrow NH_{xad} + (3 - x)H_{ad},$$

when x = 2,1.

The chemical changes in the adsorbed layer as a function of substrate temperature are plotted in Fig. 3 in terms of relative coverage of NH_3 and NH_x. The full lines were recorded by continuously monitoring the intensity of the 400.9 eV or 398.4 eV emission while heating the surface at a rate of ~7
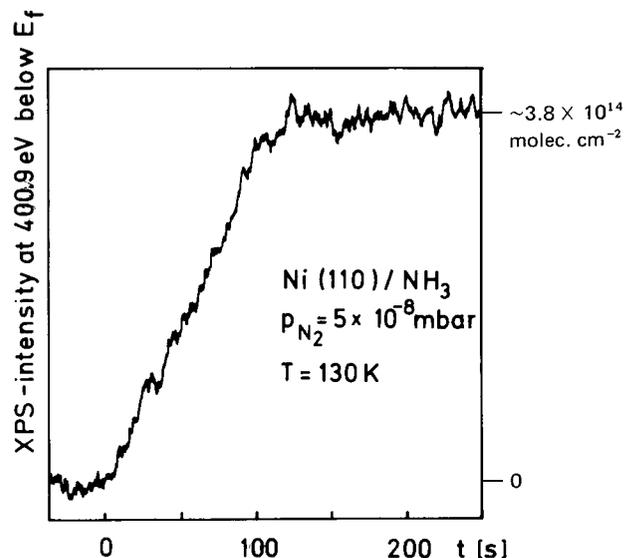
FIG. 2. N1s-intensity at 400.9 eV as a function of exposure: T = 130 K and p = 5 $\times$ 10^{-8}mbar.

K min^{-1}. Data points were obtained by integration of the 400.9, 398.4, and 398.0 eV XPS-bands at the indicated temperatures. As will be described in the following, the 398.0 eV emission is identified as arising from atomically adsorbed nitrogen.

The data points for T > 150 K obtained in a heating experiment are identical within the experimental scatter to those obtained by recording spectra at a constant temperature and therefore represent quasi-stationary coverages in the temperature region where dissociation occurs. The deviation of the data points at T < 150 K from the continuous curve is due to a smaller initial dose of ammonia. That the data points given in Fig. 3 for 150 K < T < 350 K reflect the saturation stationary surface composition at a given temperature (and p < 10^{-9}mbar) was further confirmed by recording adsorption curves at constant temperatures as a function of exposure. At T > 350 K, prolonged exposures to NH_3 of course leads to
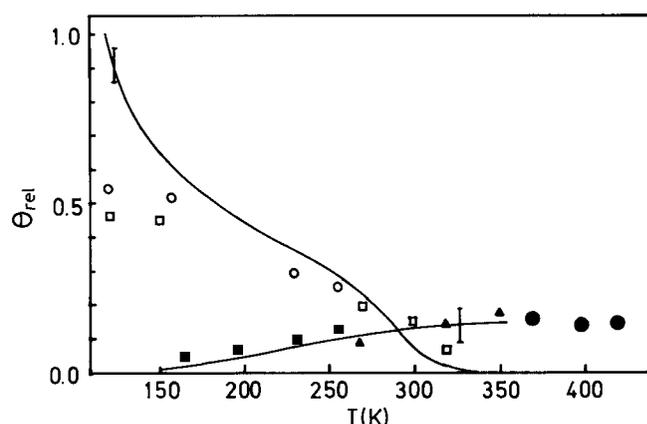

FIG. 3. Relative coverage of NH_3 and NH_x-species as a function of substrate temperature. The full lines represent the experimental traces obtained by continuously monitoring the XPS-intensity at 400.9 and 398.4 eV. The open symbols (O, □) were obtained by integrating the 400.9 eV bands after heating a predosed surface or after saturating the crystal at the indicated temperature with NH_3, the full symbols (——) are the integrated 398.4 eV (■▲) and 398.0 eV (●) bands obtained under corresponding conditions.
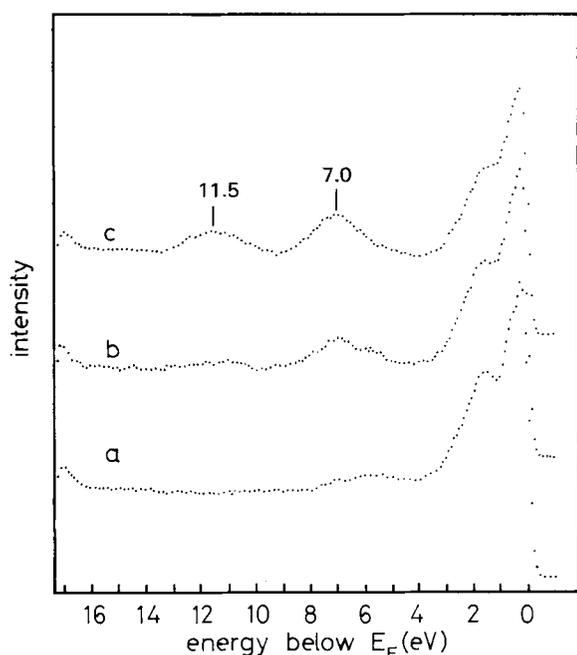
FIG. 4. HeII UPS spectra at 130 K. (a) clean Ni(110)-surface, (b) after 0.4 L NH₃ exposure, and (c) after 1.1 L NH₃ exposure.

the formation of surface nitrides which correspond to a higher nitrogen coverage than obtained in the experiments reproduced in Fig. 3.

The decrease in NH₃ coverage on heating up to 150 K is due to desorption. At $T > 150$ K, desorption proceeds in parallel with partial decomposition of NH₃ as evident from the increase in NH$_x$ coverage. At room temperature about equal concentrations of NH₃ and NH$_x$ populate the surface. An intermediate situation for the surface composition is shown in Fig. 1c. While the NH$_x$ surface concentration remains constant upon heating above 300 K, the residual molecular ammonia molecules continue to desorb from the surface up to ∼340 K. Heating the surface further then leads to a slight shift of the 398.4 eV band to 398.0 eV (Fig. 1d). As evident from hydrogen desorption traces after NH₃ exposure, showing a maximum at 450 K,[15] this shift is due to the dissociation of the NH$_x$-species and the formation of atomic nitrogen on the surface.

Figure 4 shows a sequence of HeII photoemission spectra recorded at $T = 130$ K with increasing exposure. After dosing the clean Ni(110) surface with 0.4 L NH₃ (Fig. 4b) two additional emission bands centered at 7.0 and 11.5 eV below E_F are observed which increase in intensity upon further exposure (Fig. 4c). The spectra reproduced here resemble closely those obtained on iron surfaces and those reported by Seabury *et al.*[10] on Ni(111). Therefore we identify the emission bands as originating from the 1e (11.5 eV) and 3a₁ (7.0 eV) molecular orbitals of ammonia which is chemisorbed through the nitrogen lone pair to the nickel surface. Such a bonding configuration is suggested by a comparison of our photoemission data to those obtained for NH₃-adsorption on iron single crystal planes[11,16,17] and Ni(111)[10] where the results leading to this bonding model were discussed in detail.

In Fig. 5, a sequence of UPS-data (difference spectra with respect to the clean surface) obtained by heating an NH₃-

exposed surface from 130 to 463 K is displayed. Spectrum 5a was obtained after dosing the crystal with 1.1 L NH₃ at 130 K. Subsequent-heating to 184 K causes a decrease in band intensity and a pronounced increase in half-width of the 11.5 eV emission. At 216 K (Fig. 5c) a new feature around 9.2 eV below E_F becomes visible in the spectrum. Further increase in temperature leads to a sharpening of the 9.2 eV band whereas the 7 eV feature remains approximately constant in intensity and binding energy. The HeII-photoemission spectra then remain essentially unchanged until around 374 K [Fig. 5(f)] when the 9.2 eV-band disappears and the 7 eV peak shifts to lower binding energies. After heating to 463 K only one band centered at 5 eV is observed which is attributed to atomically adsorbed nitrogen [Fig. 5(g)]. Besides the described alterations in the valence orbitals of the adsorbate, pronounced changes in the valence band region of the nickel substrate during NH₃-dissociation appear. With progressing dissociation of NH₃ an enhancement in emission appears at 1 eV below E_F which is most pronounced for atomic nitrogen chemisorption. This enhancement in d-band emission can also be seen in the original $N(E)$-data not reproduced here.

IV. DISCUSSION

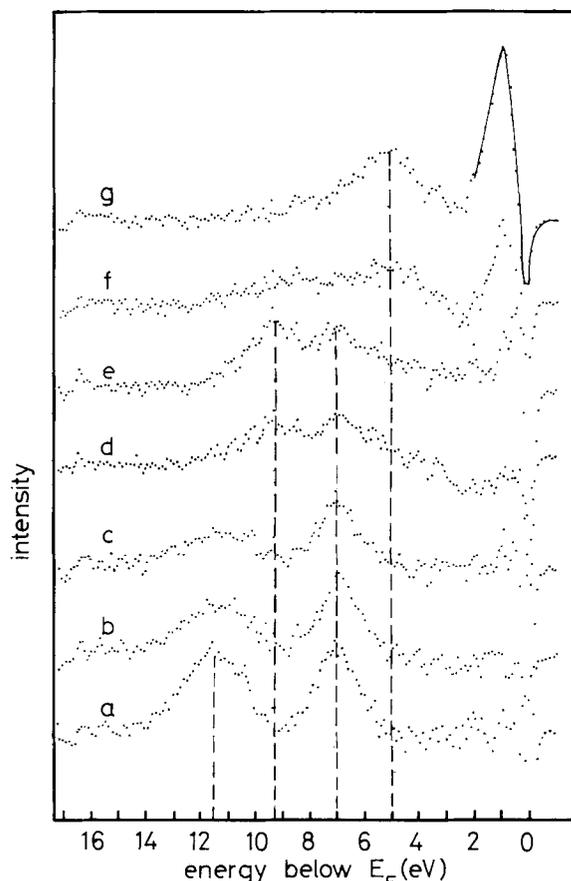The photoemission features observed with UPS and XPS at 110 K clearly indicate undissociated NH₃-adsorption. The

FIG. 5. HeII-UPS difference-spectra with respect to the clean surface spectra obtained after (a) exposing the clean surface to 1.1 L NH₃ at 130 K and heating the predosed surface to (b) 184 K, (c) 216 K, (d) 280 K, (e) 330 K, (f) 374 K, and (g) 463 K.

assignment of the 11.5 eV and 7.0 eV emission to the $1e$ and $3a_1$ orbitals of molecularly adsorbed ammonia has been discussed in detail previously.[17] The N1s-binding energy of 400.9 eV referenced to the Fermi level of the nickel substrate compares well to the value of 400.0 eV for molecular NH_3-adsorption on iron surfaces.[12]

Heating the predosed surface leads to the appearance of new features in the XPS and UPS data which are attributed to partial decomposition of the adsorbed NH_3-molecules. On the basis of the present data an unambiguous assignment of the dissociation intermediate giving rise to an N1s-emission at 398.4 eV and to the bands at 9.2 and 7.0 eV in the UPS data cannot be made. A tentative identification of these species is, however, possible by comparing the present results with those obtained for the NH_3-decomposition reaction on iron surfaces.

It was found that the stability of NH_2 and NH species is different on an Fe(111) and Fe(110)-surface. While on iron-(111) it was found that a mixture of NH_2, NH and atomic nitrogen species populates the surface at 300 K, only NH species were present under comparable conditions on the Fe(110)-surface.[12,17,11,18] A comparison of the XPS-data for NH_3 dissociation on Fe(111) and Fe(110)[12] showed that NH_2-species on Fe(111) are characterized by an electron binding energy of 398.3 eV while NH fragments on Fe(110) give an N1s-emission at a binding energy of 397.3 eV. Atomic nitrogen then leads to an emission band centered at 396.6 eV on Fe(111) and at 397.0 eV on Fe(110). Taking into account that the NH_3–N1s value on Ni(110) come at a 0.9 eV higher binding energy than on iron, the clearly resolved N1s-emission on Ni(110) at 398.4 eV then is identified as arising from NH-fragments. This conclusion is further supported by the observation that the transformation to atomic nitrogen on Ni(110) causes a shift to lower binding energies of only 0.4 eV, while the binding energy difference between NH_2 and N species on Fe(111) is 1.7 eV. An inspection of the XPS-data in Fig. 1 also shows that there is no additional band between the 400.9 and 398.4 eV emission peaks which suggests, according to our interpretation, that NH_2-species are not stable intermediates in the NH_3-decomposition reaction on Ni(110).

The interpretation of the HeII–UPS data in terms of identification of intermediates is less certain. On Fe(111) NH_2-species are characterized by photoemission bands around 9.5 and 6 eV below E_F which are not resolved due to the presence of additional nitrogen species on the surface.[16,17] On Fe(100), however, where an NH-surface-fragment can be isolated, peaks at binding energies of 8.4 and 5.2 eV below E_F were observed.[11] Seabury et al.[10] tentatively assigned a photoemission band at 8 eV below E_F to NH-fragments which were produced by electron beam bombardment of the NH_3-covered Ni(111)-surface. The UPS data reproduced here show two emission bands centered at 9.2 and 7.0 eV below E_F under conditions where predominantly NH_x-fragments populate the surface. In comparison with the cited results they cannot unambiguously be identified as arising from NH_2 or NH species. Their energetic separation of only $\sim$2 eV, however, argues in favor of an assignment as NH-species. This follows from an inspection of the extended Hückel calculation

of Seabury et al.[10] and the INDO-calculations by Grunze[12] for free NH_2 and NH radicals. Those computations gave an energetic separation of $\sim$4 eV[10] (5.5 eV[12]) and 2 eV[10] (2.8 eV[12]) between the low binding energy molecular orbitals of NH_2 and NH, respectively. An unambiguous identification of the UPS-features and the nature of the pronounced resonance in the Ni–d band region observed for atomic nitrogen adsorption will have to await further investigations utilizing angular resolved photoemission allowing an assignment of orbital symmetries.

Finally we want to discuss briefly the adsorption of molecular ammonia and the temperature dependence of the decomposition reaction. The estimated saturation coverage of NH_3 on Ni(110) of 3.8×10^{14} molecules cm^{-2} and the initial sticking coefficient of $s_0 \sim 0.1$ are comparable to the values of 2.9×10^{14} molecules cm^{-2} and $s_0 = 0.16$ on Fe(110).[11] It has to be kept in mind, however,. that the values obtained for Ni(110) are estimates based on relative XPS signal intensities and do not consider possible differences in photo-ionization cross-sections for adsorbed NH_3 and N_2.

Compared to the Fe(110) surface there is, however, a distinct difference in adsorption kinetics: On Fe(110) the coverage dependence of the sticking coefficient is consistent with a first order Langmuir model while on Ni(110) the constant sticking coefficient up to close to saturation coverage indicates adsorption via a precursor state. The data reproduced in Fig. 3 show that the maximum atomic nitrogen concentration remaining on the surface after heating an NH_3-predosed surface corresponds to $\sim$5.7 $\times$ 10^{13} atoms cm^{-2} or to 15% of the saturation ammonia coverage at 120 K. This compares to $\sim$12% and 20% decomposition of the saturation coverage on Fe(110) and Fe(111), respectively.[3] The observation on Ni(110) that the residual adsorbed ammonia on the surface at around 300 K desorbs and does not dissociate indicates that an NH surface coverage of $\sim$5.7 $\times$ 10^{13} molecules cm^{-2} is sufficient to prevent further dissociation of NH_3.

The same atomic nitrogen concentration after heating the predosed Ni(110) surface is obtained with smaller NH_3-starting coverages (Fig. 3). Dissociation of NH_3 is *only* observed at $T \geq 150$ K indicating that decomposition of NH_3 on Ni(110) is a thermally activated process.

In conclusion, the decomposition reaction of NH_3 on Ni(110) resembles the pattern and efficiency found on an iron (110) single crystal plane. It was shown that on clean iron surfaces dissociation of the N_2-molecule is the rate determining step in the synthesis reaction.[2] Because Ni(110) also exhibits a comparable activity in nitrogen dissociation to the low index iron planes, no simple explanation can be given for the catalytic inactivity of nickel in the ammonia synthesis reaction. The comparison of the data presented here with the results by Seabury et al.,[10] however, demonstrate that ammonia decomposition on nickel is extremely structure sensitive (even more pronounced than on iron). Provided ammonia formation also exhibits such a pronounced structure sensitivity, it is possible that the inactivity of certain predominant Ni-crystal orientations causes an overall negligible activity of a nickel catalyst in the NH_3 synthesis reaction. A more detailed discussion of the decomposition reaction on Ni(110) will be given elsewhere.[15]

Note added in proof

Recent results by Netzer and Madey[19] showed some thermal activated dissociation of NH_3 on a Ni(111)-surface. Although no quantitative data on Ni(111) is available, this observation brings into doubt our suggestions on the structure sensitivity of NH_3-dissociation and formation on a nickel-catalyst.

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