The formation of a NO–NH_3 coadsorption complex on a Pt(111) surface: a NEXAFS study

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Received 17 January 1995; accepted 17 January 1996

The adsorption of NO and the coadsorption of NO and NH_3 on Pt(111) has been studied with TDS, work function measurements and near-edge X-ray absorption fine structure spectroscopy (NEXAFS). Pure NO was found to be adsorbed upright at low coverages ($\theta_{NO} < 0.25$) with a bond length of 1.24 ± 0.05 Å which corresponds to an elongation by 0.1 Å as compared to the gas phase. An additional tilted species forms at high coverages. The formation of a coadsorption complex of NH_3 and low coverage NO shows up in an elongation of NO to 1.28 ± 0.05 Å. In the coadsorption complex NO is adsorbed upright. The formation of such a complex which is held together by strong attractive interactions explains the high abundance of the mixed $^{14}N^{15}N$ reaction product in experiments with isotopically labeled educts in the NO + NH_3 reaction.

Keywords: catalytic NO reduction; coadsorption complexes; NEXAFS

1. Introduction

In heterogeneous catalysis the study of coadsorption is an important subject since the energetic interactions between the coadsorbed particles may favor or exclude a certain reaction pathway or even give rise to the formation of a coadsorption complex which plays the role of a reaction intermediate [1]. A well-known example of how a coadsorbed species can influence a catalytic reaction are promoters. Here one typically considers the effect of alkali atoms which modify the bonding of surrounding molecules either via direct or via substrate-mediated interaction [2]. In this letter we present results of a near-edge X-ray adsorption fine structure (NEXAFS) study which show that the NO–NH_3 coadsorption complex which forms on Pt(111) exhibits similar properties as CO coadsorbed with alkali metal. Furthermore, this complex is rather stable and it thus probably represents a relevant intermediate in real catalytic processes involving NO and NH_3 like the SCR (selective catalytic reduction) process [3].

The formation of a NO–NH_3 complex on Pt(111) has first been proposed by Gland and Sexton on the basis of vibrational data and TDS experiments [4]. They observed that the distinct vibrational losses of NO and NH_3 coalesce upon coadsorption into a single broad feature around 1280 cm^{-1}. In TDS they saw that both species, NO and NH_3, desorb simultaneously in a new state at 355 K (heating rate: 10 K/s) which is slightly higher than the highest desorption temperature of each of the constituents. Later on Burgess, Cavanagh and King investigated the rotational accommodation of NO desorbing from this complex [5]. However, no influence of complex formation on the behavior of desorbing NO was detected which apparently means that the dissociation of the complex into its constituents and the desorption occur in two separate steps.

Here NEXAFS was used to study the behavior of the NO–NH_3 complex because of its ability to detect changes in the intramolecular bond length and the orientation of molecules [6,7]. In short, in molecules like NO X-ray absorption causes a transition of 1s core electrons into the antibonding π^* (π^*-resonance) or into the antibonding σ^* molecular orbitals (σ^*-resonance). If the E-vector of the incoming photon beam is perpendicular to the molecular axis then the π^*-resonance intensity is at maximum and the σ^*-resonance is at minimum, while the reverse is true if the E-vector is parallel to the molecular axis. This allows one to measure the orientation of the molecule on the surface with a precision of ±15°. Furthermore, the energy difference between π^*- and σ^*-

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resonance is very sensitive to variations of the intramolecular bond length. Using a simple linear relationship the bond length can be determined from the magnitude of the shift [6]. Since NEXAFS requires no long range order within the adsorbate layer it is the method of choice to investigate NO in a disordered coadsorbate layer.

2. Experimental

The experiments were conducted at the storage ring BESSY at Berlin using synchrotron radiation monochromatized with the high energy plane-grating monochromator HE PGM-2. Preparation of the sample and the NEXAFS measurements were carried out in a standard UHV-chamber equipped with a 4-grid LEED optics, a quadrupole mass spectrometer (QMS) and a partial yield detector (PYD) which was set up in a 45° angle with respect to the incoming photon beam.

The PYD which was used for recording the NEXAFS spectra consisted of 2-grid high pass filter and a channeltron operated as a current amplifying detector. NEXAFS spectra were recorded from the oxygen and the nitrogen K-edge in an energy range from 515 to 615 eV and 385 to 485 eV, respectively, applying retarding voltages of 400 V for oxygen and 300 V for nitrogen. The angle of incidence of the photon beam was varied between 86° (near-normal incidence) and 15° (grazing incidence). All spectra shown here have been background corrected by division with the spectrum of the clean surface. This method eliminates any monochromator structure and transmission characteristics and also the effect of the detector response function. Relative energy shifts between different injection periods were accounted for by using the chromium L-edge absorption dips in the monochromator structure as reference points. The resolution of the spectra was better than 2 eV.

The Pt(111) sample was cleaned by a combination of ion sputtering/oxidation in 5×10^{-7} mbar O_2 at 900 K and annealing to 1050 K. High purity gases were used for the adsorption experiments (NO 99.8%, NH_3 99.7%, ND_3 99.7%). ND_3 has only been used for the TDS experiments in order to get a better background in the mass spectrometer signal. With liquid nitrogen the sample could be cooled down to 100 K, the temperature range in which the adsorption experiments were conducted and in which the NEXAFS spectra were taken. NEXAFS spectra were usually taken from both the oxygen K-edge and the nitrogen K-edge but, due to the smoother background and due to the fact that an additional signal from NH_3 was absent, only the former are used in this paper.

3. Results and discussion

3.1. Pure NO

The adsorption of NO on Pt(111) has been the subject of investigations with thermal desorption spectroscopy (TDS) [8–10], LEED [8–11], X-ray photoelectron spectroscopy (XPS) [10], work function measurements [10] and vibrational spectroscopy both with infrared reflection spectroscopy (IRS) [9] and high-resolution electron energy loss spectroscopy (HREELS) [8]. Due to its low dissociation efficiency (< 2%) a flat Pt(111) surface exhibits only molecular adsorption states of NO, but the interpretation of these molecular states was controversial [8,11,12]. NO adsorption gives rise to a single ordered structure, a p(2 × 2) at $\theta_{NO} = 0.25$. This structure appears already at coverages as low as 5% of the saturation coverage (island growth) and remains visible also at higher coverages, with increasing background intensity [5]. The saturation coverage of NO is $\theta_{NO} = 0.54$ at $T = 120$ K [10]. In the following the term "low coverage" is applied for coverages $\theta_{NO} < 0.25$.

Above $\theta_{NO} \approx 0.2$, an additional molecular state is populated as evidenced by a shift in the XPS O(1s) peak [10], a reversal of the dipole moment of the adsorbate complex [10] and the appearance of an additional NO stretching frequency at 1710 cm^{-1} besides the low coverage stretching frequency at 1490 cm^{-1} [8]. The dynamical LEED analysis of the p(2 × 2) structure ($\theta_{NO} = 0.25$) revealed that NO occupies the threefold-coordinated hollow site (fcc) with only a small, presumably dynamical, tilt of ~ 10° of the molecular axis [11].

NEXAFS spectra of the oxygen K-edge are shown for low (0.5 L) and high NO exposures (5 L) in fig. 1. The spectra have been recorded both close to normal incidence ($\theta = 86°$) and at grazing incidence ($\theta = 15°$). Accordingly, one sees the expected change in the intensities of the π^*- and the σ^*-resonance which is used to determine the orientation angle of the molecule with respect to the surface [7]. Since the σ^*-resonance peak is absent at 0.5 L exposure and near-normal incidence we conclude an upright orientation of the molecule at low coverages. In contrast to this, at high NO exposure, at 5 L, the σ^*-resonance peak does not vanish at $\theta = 86°$ thus indicating the presence of a species which is tilted with respect to the surface normal.

Assuming that a linear relationship between the change of the intramolecular NO bond length ΔR and the shift in the position of the σ-resonance, ΔE, holds as suggested by Stöhr, one can calculate the NO bond length from $\Delta R = m\Delta E$ with $m = 30$ eV/Å [6]. Similar to other authors we use the position of the π^*-resonance as reference point, since the π^*-resonance position is to first-order bond length independent and allows to correct for bonding shifts. The gas-phase spectrum as reference for the bond length is taken from Wight and Brion

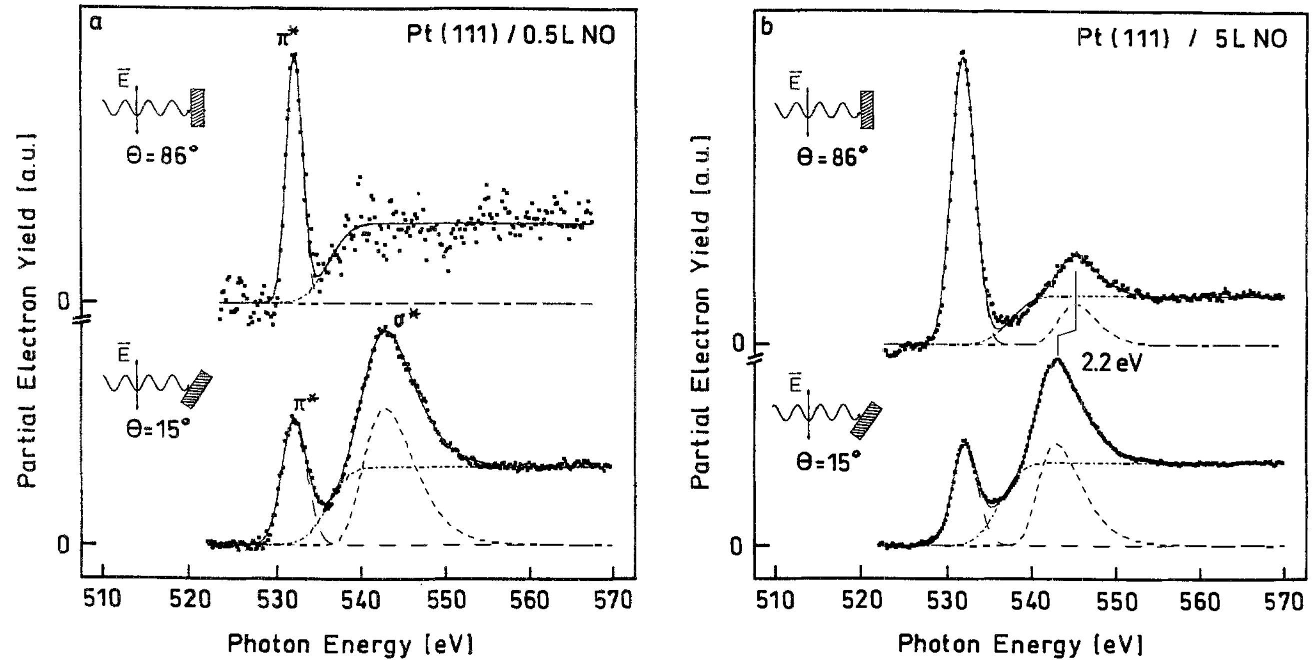

Fig. 1. Oxygen K-edge NEXAFS spectra recorded after exposure of 0.5 L (a) and 5 L NO (b) at $T = 100$ K at 86° normal X-ray incidence and at 15° grazing X-ray incidence. The two peaks in the spectra represent the π^*- and the σ^*-resonance.

[13], who find at the oxygen K-edge an energetic separation between σ^*- and π^*-resonance (σ^*–π^* separation) of 13.6 eV.

Analyzing the low coverage NO adsorption state, we find in the NEXAFS spectrum a σ^*–π^* separation of 10.8 ± 0.5 eV, yielding a bond length of 1.24 ± 0.5 Å (gas phase: 1.15 Å). Upon adsorption on Pt(111), NO is therefore considerably stretched, by about 0.1 Å. The bond length we have determined for low coverage NO is higher than determined by LEED. Materer et al. found in their LEED analysis an intramolecular bond length of 1.18 ± 0.4 Å for NO on Pt(111) in the p(2×2) structure [11].

In the high coverage spectra the σ^*–π^* separation is 13.2 ± 0.5 eV at near-normal incidence, corresponding to a bond length of 1.16 ± 0.05 Å. This σ^*–π^* separation decreases at grazing incidence to 11 ± 0.5 eV, the same separation as for low coverages of NO. The dependence of the σ^*–π^* separation position on the angle of incidence can be explained either by an additional species which is bent with respect to the surface normal, or, as shown by King et al. at No/Pd(110), by an upright standing species but with very soft vibrational modes of the metal–NO bond [14,15]. In the present case the first explanation is more likely because it is not clear why the bond between metal and NO, coordinated in the threefold site, should drastically soften with increasing coverage. That the tilted NO molecule is shorter than the linearly bonded NO can be rationalized with the help of calculations of Sung et al. for NO on Ni(111), who showed that tilting decreases the backdonation at threefold coordinated sites [16].

3.2. Coadsorption of NO and NH_3

The interaction of NH_3 with Pt(111) does not involve substantial dissociation of the molecule at $T < 500$ K [17,18]. At adsorption temperatures $T_{ad} > 160$ K, only the α-state is populated. This state is characterized by a broad desorption maximum in TDS extending from 160 K to almost 500 K and a large apparent dipole moment of 2.0 D which gives rise to a strong work function decrease of nearly -3 eV at the saturation coverage of this state which was estimated to be $\sim 1/4$ of a monolayer [17]. The almost complete absence of the degenerate bending vibration at low coverages in EELS indicates that the NH_3 molecule adsorbs with its threefold axis normal to the surface [19] while no LEED superstructure was detected [5].

In our experiments the coadsorption of NO and NH_3 was studied by TDS, $\Delta\varphi$ and NEXAFS measurements. As shown before, in TDS only a small amount of reaction products (< 10%) like N_2 and H_2O are seen while most of the coadsorbed NO and NH_3 desorb without dissociation [4,5]. As noted before too, the formation of the coadsorption complex depends on the adsorption temperature and on the sequence in which the two components are adsorbed [5]. Fig. 2 displays a comparison of NO-TD spectra produced by adsorption at 120 K of 2 L pure NO (a), adsorbing first 2 L NO and then 2 L ND_3 (b) and first saturating the surface with ND_3 and then saturating the surface with NO (c). The formation of a higher-lying adsorption state at $T = 340$ K (heating rate: 2 K/s) indicates the formation of the complex, but while (b) displays only a partial complexation of NO, the

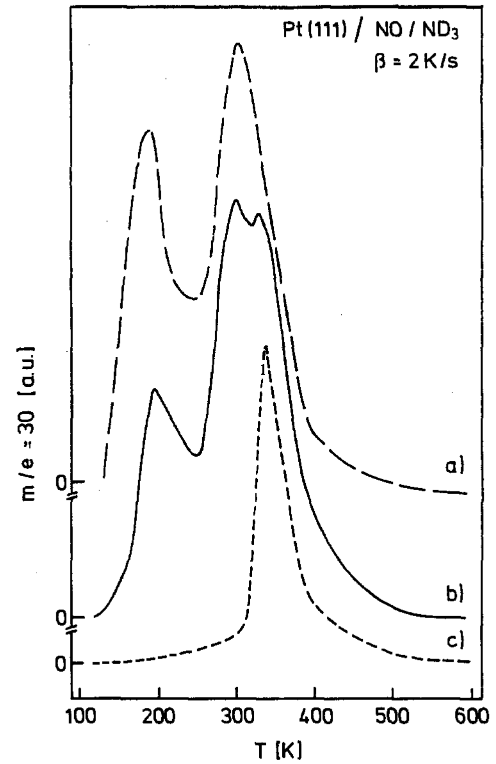

Fig. 2. NO TDS spectra of pure NO (a) and NO coadsorbed with NH_3 (b, c) demonstrating the influence of the preparation conditions on the formation of a NO–NH coadsorption complex on Pt(111). The individual spectra were recorded after adsorption at 120 K of (a) 2 L NO, (b) 2 L NO followed by 2 L ND_3, (c) saturation coverage of 8 L ND_3 followed by 8 L NO. Heating rate: 2 K/s.

preparation in (c) gives exclusively NO in the complexed state.

The difference between (b) and (c) is due to the fact that a NO saturated surface inhibits almost completely the adsorption of NH_3, while NO can still adsorb on a surface saturated with NH_3. As indicated by a strong increase of the work function this happens under displacement of the preadsorbed NH_3. It is therefore plausible that the procedure first NH_3 and then NO leads to an intimate contact of the two admolecules while the reverse sequence of first adsorbing NO and then NH_3 causes complexation at low coverages of NO only.

Fig. 3 shows a comparison of the NEXAFS oxygen K-edge spectra of pure NO and of the NO/NH_3 coadsorption complex recorded both at near-normal incidence ($\theta = 86°$) and at grazing incidence ($\theta = 15°$). The complex was in this case prepared by first adsorbing 3 L NH_3 at 100 K followed by 2 L NO at 100 K and a short annealing to 300 K. The σ^*–π^* separation of 10.8 ± 0.5 eV of pure NO is reduced to a separation of 9.8 ± 0.5 eV in the coadsorption experiment. Using again the linear correlation between ΔE and ΔR, this shift corresponds to an increase of the NO bond length from 1.24 ± 0.05 Å of pure NO on Pt(111) to 1.28 ± 0.05 Å of the NO in the complexed state. In addition one notes that in the coadsorbed state the π^*-resonance peak is shifted by 1.1 eV to lower energies. This shift can be explained as a chemical shift caused by coadsorption of NH_3.

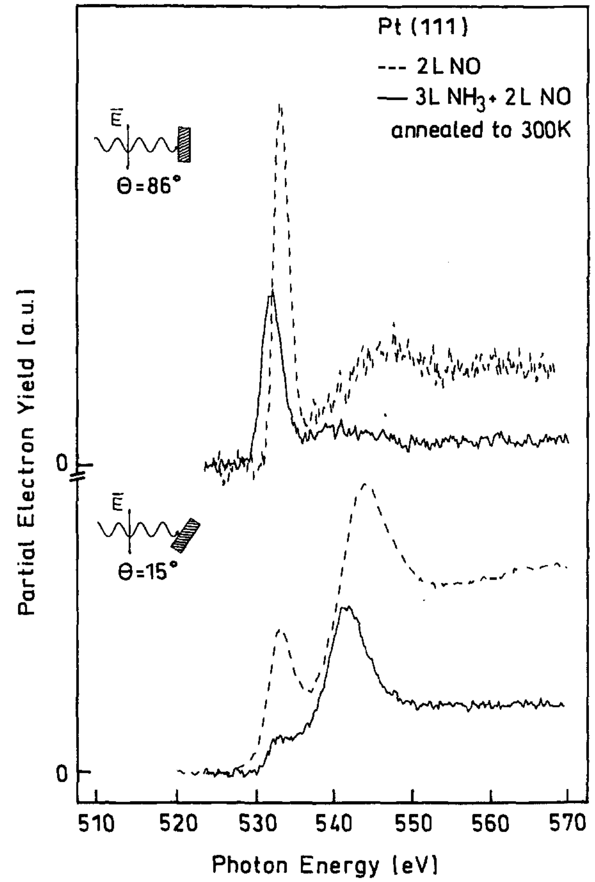

Fig. 3. Oxygen K-edge NEXAFS spectra of pure NO and complexed NO on Pt(111). The dashed lines represent the spectra after adsorption of 2 L NO at 100 K, while the full lines give the spectra after adsorbing at 100 K 2 L NH_3 + 2 L NO followed by annealing to 300 K. The complex formation leads to a shift in the π^*- and the σ^*-resonance position and to a drastic drop in the intensity of the π^*-resonance.

The decrease of the σ^*–π^* separation which correlates with the presence of a higher-lying state in NO TDS is taken as evidence for the formation of a NO–NH_3 coadsorption complex. It is very similar to the results of an earlier NEXAFS study of CO coadsorbed with Na on a Pt(111) surface by Sette et al. [20]. They observed a drastic decrease of the σ^*–π^* separation by 4 eV upon coadsorption, associated with a stronger CO binding state in TDS and a lowering of the CO stretching frequency. Since Na causes, similar to NH_3, a strong lowering of the work function, the explanation in the present system appears to be analogous to CO/Na/Pt(111). The lowering of the work function causes an enhanced backdonation of metal electrons into the antibonding π^*-orbital of NO leading to a weakening of the NO bond. The complex can thus be described as a donor–acceptor complex consisting of the electron donor NH_3 and the acceptor species NO. Since the σ^*-resonance is not discernible in the spectrum recorded at near-normal incidence (fig. 3), NO in the coadsorption complex can be characterized as a molecule which is standing upright on the surface within the experimental uncertainty of ~ ±15°.

$\Delta\varphi$ measurements during thermal desorption showed that the NO–NH_3 complex, if prepared with an approximate 1 : 1 stoichiometry according to Burgess et al. [5], has an apparent dipole moment of 2.3 D similar to pure NH_3 [17]. Experiments, in which the relative amounts of the adsorbates, the sequence of adsorption and the annealing temperature were varied, exhibited a shift of 1 eV or more caused by complexation. The strongest shift of the σ^*–π^* separation, 1.9 ± 0.5 eV, was seen when 1 L NH_3 was adsorbed on a surface precovered with a small coverage of 0.1 L NO. In this case the complex formation could also be seen without annealing.

Complex formation at higher NO coverages is demonstrated in fig. 4. Adsorption of 2 L NH_3 onto 2 L of preadsorbed NO causes only a small shift in the σ^*-resonance position at $T = 100$ K, as demonstrated by figs. 4a and 4b. Annealing up to 300 K is necessary to establish the full shift of 2 eV, as indicated in fig. 4c. This seems to indicate the existence of an activation barrier for complex formation. A careful analysis, however, shows that spectrum (b) in fig. 4 can be decomposed into spectrum (a) and spectrum (c). This means that the increase in the shift is simply due to the fact that the NO which was not in the complexed state desorbed during the annealing procedure. The complex itself, however, was already present at low temperature. As shown by fig. 4c, the intensity of the π^*-resonance decreases drastically in the complexed state, therefore also the normal incidence spectrum is shown (dashed line). The intensity decrease of the π^*-resonance can be explained by an enhanced backdonation into the π^*-orbital of NO and a smaller overlap of the atomic orbitals caused by the increased NO bond length [21].

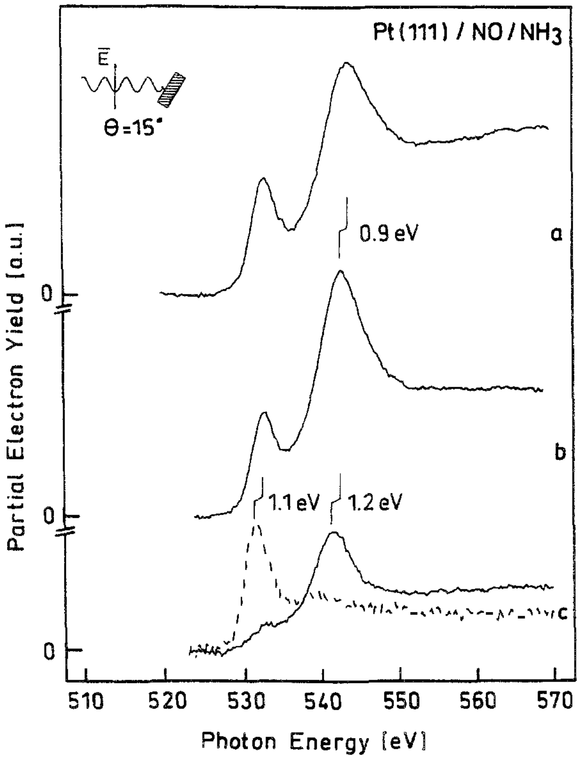

Fig. 4. Oxygen K-edge NEXAFS spectra demonstrating the effect of annealing on the formation of the NO–NH_3 coadsorption complex. The full line spectra are taken at 15° grazing X-ray incidence, the dashed line spectrum in (c) is taken at 86° normal incidence. (a) represents the spectrum after adsorption of 2 L NO at 100 K, (b) the spectrum after an additional exposure of 2 L NH_3 at 100 K and (c) gives the resulting spectrum after a brief annealing to 300 K.

The exact nature of the NO–NH_3 coadsorption complex is still a problem which remains to be solved. HREEL spectra have demonstrated that the vibrational losses of NO at 1490 and 1710 cm^{-1} and of NH_3 at 1090 cm^{-1} all coalescence into a single broad peak around 1280 cm^{-1}, showing that the interaction between NO and NH_3 is quite strong. The drastic changes in the vibrational spectra could indicate the formation of an NOH_x species which then decomposes again into NO upon heating. In an analogous system, where H_2CO was compared to CO, NEXAFS spectra of H_2CO exhibited besides a shift a decrease in the intensity of the π^*-resonance [22]. This lower intensity, however, occurred only at the C K-edge. This intensity decrease for the H_2CO species was attributed to the fact that at the C K-edge the π^*-resonance loses oscillator strength to the resonances associated with the C–H bonds. In the present system, due to the overlap of the signals from NO and NH_3, a quantitative comparison of the π^*-resonances at the N and the O K-edge is difficult to carry out. The higher intensity of the π^*-resonance at the N K-edge seems to suggest the formation of OH bonds in the complex, but in view of the observation that the complex dissociates upon heating into its constituents such a possibility appears to be unlikely.

In any case, the high decomposition temperature of ~ 350 K of the NO–NH_3-complex is indicative for a strong attractive interaction which must be of the order of the desorption energy of NO (20–25 kcal/mol) [5]. This implies that the complex might also be of importance for catalytic reactions proceeding at higher temperature and, since the elongation of the NO bond can be considered as a step towards dissociation, there is a high probability that this complex is a relevant intermediate in the catalytic NO reduction with NH_3. Some evidence for this statement comes from kinetic studies with isotopically labeled educts, i.e. with ^{14}NO and $^{15}NH_3$, on Pt-, Cu- and Ru-surfaces in the millibar range [23]. There the mixed product $^{14}N^{15}N$ appeared in a much higher proportion than expected for perfect isotope mixing and similar observations were made in a study of the interaction of isotopically labeled NO and NH_3 on Pt(100) in the 10^{-6} mbar range [24]. If the reaction proceeds via an NO–NH_3-complex, both results would find a straightforward explanation. The complex formation would explain furthermore that NH_3 is an exceptionally selective reducing agent for NO in flue gases [25].

In the literature, the formation of NH_3 coadsorption complexes has been discussed in connection with O_2 as coadsorbed species [26,27]. For Zn(0001)/$O_2 + NH_3$ a coadsorption complex was suggested as a precursor to O–O bond cleavage [26] and theoretical calculations by van Santen et al. showed that lateral interactions can reduce the activation barrier for N–H bond cleavage [27].

4. Conclusions

The adsorption of NO and the coadsorption of NO with NH_3 have been studied using NEXAFS to detect changes in the orientation and in the intramolecular bond length of NO. NO was found to be adsorbed upright at low coverages and at high coverages a state with a bent geometry was detected. The low coverage NO has a bond length at 1.24 ± 0.5 Å, as determined by the σ^*–π^* separation, and is considerably stretched as compared to the gas phase (gas phase bond length: 1.15 Å). The formation of a coadsorption complex of NO and NH_3 showed up in the NEXAFS spectra by a further increase of the NO bond length to 1.28 ± 0.05 Å. In the NO–NH_3 complex NO is adsorbed in an upright geometry (±15°). The NO–NH_3 complex can be described as a donor–acceptor complex. The weakening of the NO bond can be explained with an enhanced backdonation into the π^*-orbital of NO with NH_3 acting as electron donor. Due to the strong attractive interactions between NO and NH_3 the complex is considered to be a relevant intermediate under real catalysis conditions.

Acknowledgement

The authors would like to thank S. Wasle for the preparation of the drawings, Th. Fink, N. Hartmann and G. Veser for their help with the measurements and the technical staff of BESSY for their assistance. Financial support for some of the authors (SL, SK, AS) by the EU HCM program under BESSY project HCM 31/280194 is gratefully acknowledged.

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