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CO on NiO(100) : orientation and bonding

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Abstract

We use thermal desorption spectroscopy to estimate the adsorption energy of CO on NiO(100) to be 7.0–8.8 kcal mol^{-1}. NEXAFS is employed to determine the orientation of the CO axis. The molecule is oriented perpendicular to the NiO(100) surface. In the present case we have resorted to angle-resolved photoelectron spectroscopy (ARUPS) to find indications that the CO molecule interacts with the surface through its carbon lone pair. The experimental analysis is in agreement with theoretical predictions that CO is held to NiO(100) mainly via electrostatic multipolar forces.

1. Introduction

In recent years the study of adsorption of small molecules on well defined oxide surfaces has gained increasing interest [1,2]. CO and NO adsorption on the non-polar (100) surfaces of simple rock-salt type materials are the prototype systems on which the majority of studies have been performed [3–16]. Notably, the discussion [2] on the electronic and geometric structure of adsorbates on such surfaces has considerably profited from an intense exchange between theoreticians [3–10] and experimentalists [11–16]. From the theoretical studies a clear picture for the bonding of, for example, carbonmonoxide towards NiO(100) or MgO(100) has emerged, even though there still seem to be unresolved problems

with respect to the theoretical reproduction of the experimentally observed enthalpy of adsorption [3–10].

Contrary to metal surfaces, where bonding is strong ($\Delta E_a \approx 1$–2 eV) due to σ/π-charge exchange between the molecule and the surface [17], bonding to a (100) oxide surface of rock-salt type is dominated by multipolar electrostatic forces which leads to rather weak bonding ($\Delta E_a \approx 0.1$–0.5 eV). As a consequence of the rather weak bonding, energy differences between various orientations of molecules, i.e. bonding of CO with it's C-end versus O-end towards the surface or parallel to the surface, are rather small and of the order of 0.05–0.1 eV [4,7,9]. Since these energy values are well within the error range of the theoretical predictions, experimental studies are needed. We report in this paper a full study of the system CO/NiO(100) to complement our previous work on NO/NiO(100) [11]. This will

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allow us to discuss some of the observed differences with respect to the expected different bonding characteristics of both CO and NO molecules on oxide surfaces in relation to the available theoretical calculations [3–10].

2. Experimental

The experiments have been performed in two ultrahigh-vacuum systems. We have used a system equipped with an angle-resolved photoelectron spectroscopy (ARUPS) set-up and thermal desorption spectroscopy (TDS). TDS and ARUPS are located in two separatable chambers which are pumped by a set of turbomolecular and ion pumps as well as a titanium sublimation pump. The sample, a Ni(100) crystal, was attached to tungsten wires, which were spot-welded to two tungsten rods. The rods are mounted onto a saphire block, which is firmly connected to a copper block being part of a liquid nitrogen cooling system. The whole mounting can be moved with a long travel manipulator between the two chambers of the apparatus, including options for translation and rotation. ARUPS was performed by using a resonance lamp.

A second, similar system was used to accumulate the NEXAFS (near edge X-ray absorption fine structure) data. It was located at the Berlin storage ring BESSY-I, where light from the high energy toroidal grating monochromator was used. The procedure used for data accumulation and intensity calibration has been described in detail elsewhere [18].

NiO was prepared as a thin film. This allowed cooling of the sample without charging under photon irradiation. We have reported detailed recepies for preparation of such films and have given a detailed structural characterization. We refer to the literature for any details [11,12]. CO (purity: 99.9999) has been used as received.

3. Results and discussion

Fig. 1 shows the TD spectra of CO/NiO(100) taken as a function of coverage. It is clear from the spectra that the maxima of the desorption features only exhibit a very slight variation with CO cover-
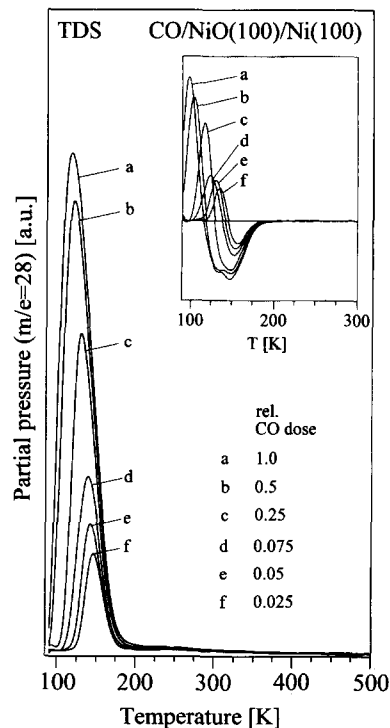

Fig. 1. Thermal desorption spectra of the system CO/NiO(100) as a function of CO coverage. The inset shows the first derivatives of the spectra.

age. The situation becomes more evident by looking at the first derivatives of the TD spectra as shown in the inset of Fig. 1. At low coverage there is a single peak contributing to the spectra while at higher coverage (dose > 0.12) a slightly shifted second peak fills in. We have analyzed the spectra according to a simple Readhead procedure [19] assuming a prefactor of 10^{13}, which is the standard value [20]. Depending on coverage this yields a value of 7.0–8.8 kcal mol^{-1} for the adsorption enthalpy. This may be compared with a value of 9.2–12.5 kcal mol^{-1} recently published by Vesecky et al. [14] on the basis of isosteric measurements using IRAS. The vibrational frequencies determined in the present study on the basis of ELS measurements are not very precise but in line with the values reported by Vesecky et al. [14] for the CO stretching modes.

The adsorption energies of CO/NiO(100) may be compared with those determined for NO/NiO(100) [11]. The latter system is slightly more strongly bound, i.e. by 12.2 kcal mol^{-1} as determined by the

same Readhead procedure [19] and based on TD-spectra. This higher adsorption energy reflects the different bonding characteristics for CO and NO as predicted by theoretical calculations performed in several groups [3–10] but for the CO/NO comparison in detail by Staemmler and his group [3,4]. While CO is held almost exclusively by multipolar electrostatic interactions, NO bonding to NiO(100) does exhibit some covalent chemical bonding characteristics. This is due to the additional unpaired electron on NO as compared to CO as has been discussed in Ref. [11]. This discussion indicated, and was verified experimentally, that the NO/NiO(100) bond leads to a tilted geometry with the ON–Ni bond angle in the neighborhood of 135°. However, for the CO/NiO(100) bond equivalent calculations predict a linear geometry with a Ni–CO angle of 180°.

We have investigated the orientation of CO on NiO(100) via NEXAFS as will be discussed in the following. Fig. 2 shows a set of NEXAFS spectra in the range of the carbon K-edge. The background has been removed from the spectra and the intensities have been normalized to the step edge using well known procedures [21]. The spectra show a pronounced π-resonance but a rather weak σ-resonance, a situation similar to the gas phase [22] but very different from the situation encountered for chemisorbed CO molecules on metal surfaces [23]. To underline this point we show in Fig. 3 a comparison of the C K-edge regions for CO in the gas phase [22] and CO on NiO(100) [23]. In the gas phase as well as on NiO(100) the C K-edge of CO exhibits a rather weak σ-resonance. The series of electron–hole pair excitations in the presence of the core hole, i.e. shake-up excitations, pronounced in the gas phase, are washed out on the oxide surface but a weak feature can still be observed. For strongly interacting systems, such as CO on Ni(100), the intensitiy of this feature is reduced as compared with the widely enhanced σ-resonance [23]. In addition, the position of the σ-resonance in the case of the weakly interacting systems, as well as in the gas phase, is obscured by the so-called two-hole-two-electron excitations which partly exhibit π-symmetry [24] and large half widths. Consequently, the detailed evaluation of the σ-resonance intensity is more difficult in the case of weak interaction as compared with strong interac-
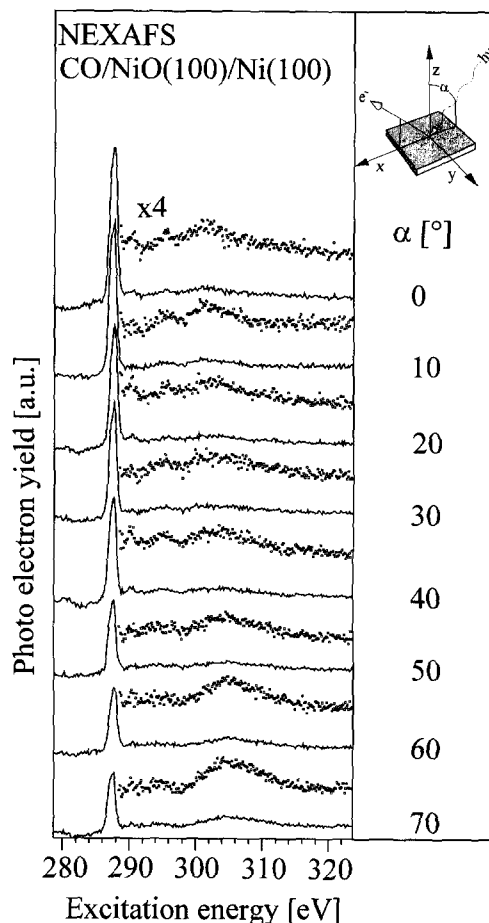

Fig. 2. Carbon K-edge near edge X-ray absorption fine structure of the system CO/NiO(100) as a function of the light incidence angle, as indicated in the inset.

tion. We have therefore restricted ourselves to the analysis of the π-resonance intensity. Fig. 4 shows a plot of the π-resonance intensity as a function of the light polarization varied via changes of the angle of incidence of the synchrotron light. A series of calculated intensity variations according to [11]

$$I_\pi \approx P \sin^2\alpha + 1 + (1 - 3P \sin^2\alpha)\cos^2\delta, \qquad (1)$$

with α being the angle of light incidence, P the degree of linear polarization, and δ the molecular tilt angle, is included in the same figure. Here, the parameter has been the tilt angle δ of the molecular axis with respect to the surface normal. The dashed line is given for the magic angle of 54.7° where we expect no dependence of the intensity on light polar-
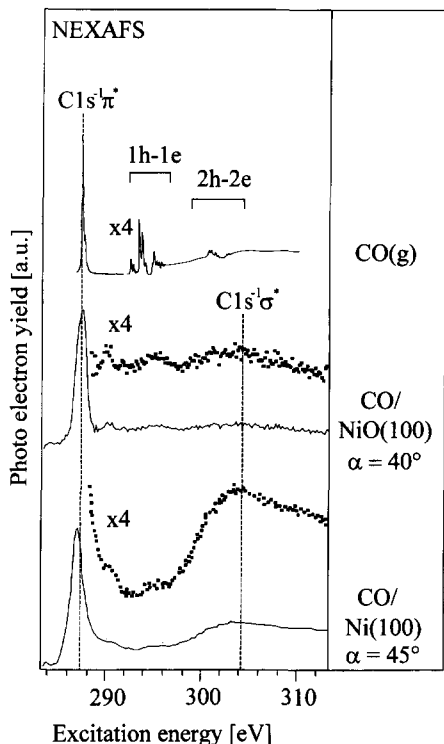
NEXAFS

Fig. 3. Comparison of C K-edge NEXAFS data for gas phase CO, CO chemisorbed on a metal surface, and CO adsorbed on NiO(100).

CO originate from the ionization of the carbon lone pair (5σ), the CO-π-bond (1π) and the oxygen lone pair (4σ). If the carbon atom is involved in the interaction, the 5σ orbital will be shifted relative to the other ionizations. Fig. 5 shows He II (unpolarized) angle-resolved photoelectron (ARUPS) spectra taken at different angles of light incidence and different electron collection angles. These data serve two purposes: they are used to support the orientation determination via NEXAFS as well as to evaluate the bonding mechanism. Fig. 5a shows the raw data with and without CO coverage. Fig. 5b shows the difference spectra within the energy range of the CO-induced features. In order to analyze these data, several points have to be noted. Firstly, at He II photon energies the cross sections of the 4σ-ionization is larger than the one of the 5σ-ionization [25]. Secondly, the σ-intensities peak if the light is polarized along the molecular axis and the electrons are collected near the direction of the oriented axis.
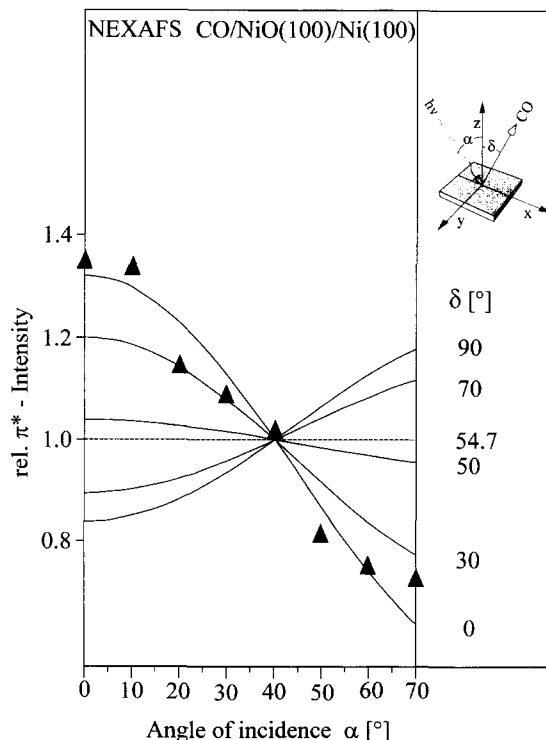
ization direction. Clearly, the data are consistent with an axis of the CO molecule parallel to the surface normal. Of course, there is an uncertainty of $\pm 15°$ but there is no significant inclination angle as indicated by this plot. We therefore conclude that the CO molecule is oriented perpendicular to the NiO(100) surface.

However, with the analysis presented so far it is not possible to decide whether the molecule is oriented with the carbon-end or with the oxygen-end towards the surface. While for typical strong CO–transition-metal bonds there is no question that the molecule binds to the surface via the carbon atom (exceptions are very rare) [17] in the case of oxide surfaces, where bonding is much weaker, the binding energies of the two orientations differ only by less than 0.05–0.1 eV [3–10]. One way to tackle this question is valence photoelectron spectroscopy. The idea is simple and has been applied many times in the past [17]: the three outer valence ionizations of

Fig. 4. Integrated π-resonance intensity as a function of light incidence angle. The full lines represent calculations according to Eq. (1). P equals 0.8.

Therefore, if the CO axis is oriented perpendicular to the surface, the choice of near grazing light incidence and normal detection would lead to maximal σ-intensities [26,27]. Strictly speaking, the analysis is simple only for fully linearly polarized light. In the present case, however, we have to consider unpolarized light [27]. In other words, there is always the possibility to ionize of π-states. We can only hope to vary the relative magnitude of π- and σ-ionizations in the following simplified manner if the axis is oriented normal to the surface: for grazing incidence and near normal emission we expect large σ-intensities. For near normal incidence and grazing excidence we expect dominance of π-ionization. For 45° light incidence and normal emission the σ-ionizations should dominate.

With this in mind we can analyze the spectra in Fig. 5 and find that they are consistent with an orientation of the molecular axis normal to the surface if we place the ionization potentials for the adsorbed molecule as indicated in Fig. 5b. We have collected the values from the present study as measured relative to the Fermi level in Table 1, where we compare them to ionization energies from other CO adsorbate systems. Included are chemisorbates on metal surfaces [28,29], as well as a physisorbed

Table 1
CO binding energies of valence levels (in eV)

	5σ	1π	4σ	Ref.
Ni(100)c(2×2) [a]	8.1	7.5	11.1	[28]
Pd(111)c(4×2) [a]	8.2	7.3	11.0	[29]
Al(111) [a]	8.2	11.1	13.8	[30]
NiO(100)	10.6	11.2	13.9	This work

[a] Value determined at the center of the Surface Brillouin Zone.

system, also on a metal surface [30]. The physisorbed layer behaves similar to a condensed CO layer [31] with relative ionization potentials almost identical to the gas phase [25] and only slightly shifted with respect to the absolute values of gas phase CO if referred to the vacuum level [17]. In the chemisorbed layer, on the other hand, two effects shift the relative and absolute ionization potentials. The strong CO–metal bond via the carbon atom leads to the pronounced shift of the 5σ-ionization to a value below the 1π-ionization energy. In addition, hole-state relaxation in the final ion state due to the screening by the metal electrons shifts the complete spectrum to considerably lower ionization energies giving rise to the strong deviations from the values observed for the physisorbed system [17]. This is
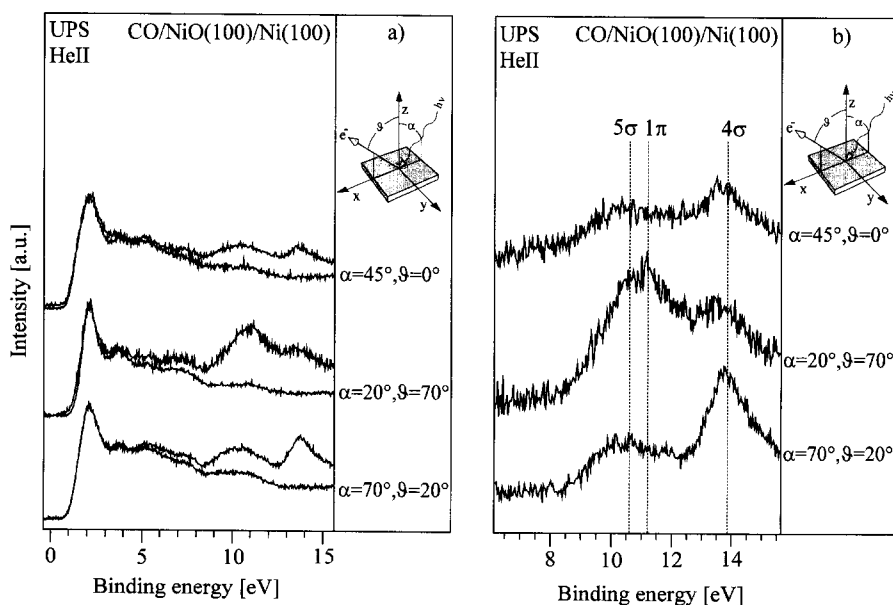

Fig. 5. (a) Angle-resolved photoelectron spectra of CO/NiO(100) in comparison with the clean substrates for different light incidence angles and directions of electron detection. (b) Difference spectra between CO covered and uncovered substrates shown in (a).

well known in the literature [17] and has been repeated briefly here in order to judge the values observed for the oxide surface properly. The analysis is now very easy. 1π- and 4σ-ionizations are slightly shifted with respect to the values of the physisorbed system indicating similar CO–substrate interaction strenghts. However, the carbon lone pair (5σ) is shifted more strongly than the 1π- and 4σ-ionization, indicating a preferential interaction of the molecules through the carbon end. Hole-state screening is of a similar magnitude as in the physisorbate which is reasonable, given that the oxide surface should be less polarizable as compared with a metal.

Therefore, the present analysis of the ARUPS data indicates that the molecule is bound to the surface via the carbon end in an upright position and with relatively low adsorption energy. Thus, the present experimental results are in full agreement with the above-mentioned theoretical predictions [3–9].

4. Summary and conclusions

In agreement with results reported in the literature [14] we find that CO weakly interacts with a NiO(100) surface, leading to an adsorption energy of 7.0–8.8 kcal mol^{-1} depending on CO coverage. The CO axis is oriented perpendicular to the surface as determined via NEXAFS, and the interaction between CO and the substrate is established via the carbon lone pair as revealed through ARUPS measurements. We have not explicitly determined the adsorption site on the NiO(100) surface but we know for NO on NiO(100) and CO on CoO(100) that the molecules reside on the metal ion surface sites. Therefore, we assume the same behavior for CO/NiO(100). This experimental analysis is in full agreement with existing theoretical predictions reported by several groups based on ab-initio and density functional studies [3–10]. The calculations allow us to understand the differences between CO and NO bonding to oxide surfaces: a CO molecule is bonded to a NiO(100) surface mainly via multipolar electrostatic interactions. The more strongly bound NO, on the other hand, is held not only by electrostatic multipolar forces but also chemical, covalent contributions to the bonding play a role. Those in-

duce the tilting of the NO bond with respect to the surface normal and are intimately connected with the partial occupation of the NO-2π orbital interacting with the Ni open shells.

It will be interesting in the future to compare the bonding characteristics of diatomics like CO and NO on the non-polar (100) faces of rock-salt type oxides with the bonding characteristics on the polar (111) faces, which are known to be far more reactive and dynamic once the hydroxyl groups, stabilizing these surfaces, are removed [32–35].

Acknowledgements

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