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Surface Science 325 (1995) 163–168

surface science

NO on CoO(111) /Co(0001) : hydroxyl assisted adsorption

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Received 31 August 1994; accepted for publication 1 November 1994

Abstract

We have investigated the structure of epitaxially grown CoO(111) on Co(0001) and the adsorption of NO on this surface using electron spectroscopic methods. The procedure of oxidation of a cobalt surface to get a single-crystal oxide surface has been chosen for two reasons: first, charging of the sample can be avoided when preparing oxide surfaces of only 20–30 Å thickness. Second, the (111) surface of the ionic rocksalt structure is thermodynamically unstable and thus not otherwise easily accessible for surface studies. We show that the (111) surface is terminated by hydroxyl groups which we think stabilize the surface in the same way as the NiO(111) surface is stabilized [F. Rohr et al., Surf. Sci. 315 (1994) L297; D. Cappus et al., Chem. Phys. 177 (1993) 533], and that the adsorption of NO is affected by the presence of OH.

Keywords: Chemisorption; Cobalt oxides; Electron energy loss spectroscopy; Photoelectron emission; Water

1. Introduction

Transition-metal oxides are often used as the active components in heterogenous catalysis. Therefore, it is interesting to use single-crystal oxides as model systems to understand the mechanisms of the reactions on a microscopic level. Various oxide surfaces have been investigated [1,2]. Especially the (111) surface of the ionic rocksalt structure, which is the structure of some transition-metal oxides, seems to be very reactive towards adsorption of small molecules. This has been established for NiO(111) [3,4].

The (111) rocksalt surface is a polar surface and thus thermodynamically unstable [20,21]. A bulk single crystal for example cannot be cleaved in this crystallographic direction. It is, however, possible to prepare a (111) surface by oxidizing a suitable metal surface such as Ni(111), Co(0001) or Fe(110) [23]. Still, the surface has to be stabilized which can be accomplished either by reconstruction as was demonstrated recently [7] or by reducing the surface charge in some other way [4–7,19]. On Cr_2O_3(111), which is not a rocksalt-type structure but rather a corundum-type structure, the charge of the surface chromium atoms is reduced to 2 + [5,6], whereas on NiO(111), OH is adsorbed in order to reduce the surface charge [7,19]. When the NiO(111) sample is heated, OH desorbs and the surface reconstructs [4,7,22]. In this paper, CoO(111), which is chemically quite similar to NiO(111), is investigated with special attention as to how the surface is stabilized and how this affects the adsorption of NO.

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SSDI 0039-6028(94)00733-0

2. Experimental

The samples have been studied in two different UHV systems by XPS (X-ray photoelectron spectroscopy) and HREELS (high-resolution electron energy loss spectroscopy). The XPS measurements were performed with monochromatized Al Kα radiation which provided a resolution of about 0.5 eV. The HREELS spectra were taken with a double-pass cylindrical electron monochromator and analyzer with a resolution of about 8 meV. Both UHV instruments were equipped with LEED (low-energy electron diffraction) systems, quadrupole mass spectrometers and ion guns for sample preparation.

The Co(0001) crystal was spot-welded to tungsten or tantalum rods which were connected to a liquid-nitrogen reservoir. The sample could be cooled to 100 K. A tungsten filament was mounted behind the sample with which the sample was heated.

Cleaning of the sample was accomplished by repeated cycles of Ne-ion bombardment and annealing. Care was taken not to heat the sample above 650 K to avoid phase transition to fcc cobalt [8].

The oxidation of Co(0001) with O_2 has been described by Ignatiev et al. [9]. In the present study, CoO(111) was grown by oxidation of the Co(0001) sample with 10000 L (1 L = 10^{-6} Torr · s) O_2 at slightly elevated temperatures.

NO of 99.8% purity was used for the adsorption experiments. For the isotope exchange experiments, the sample was briefly heated to 450 K in an atmosphere of 10^{-6} mbar of D_2O (p.a.).

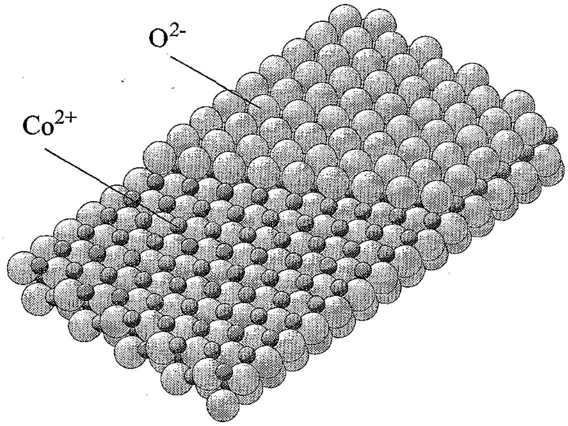

Fig. 1. Schematic representation of the unreconstructed CoO(111) surface.

3. Results and discussion

3.1. Characterization of the oxide layer

Fig. 1 schematically shows a (111) surface of cobalt oxide. The structure consists of alternating layers of Co^{2+} and O^{2-} ions. The surface is idealistically shown, as no reconstruction or surface charge reduction has been taken into account here to stabilize the surface.

The LEED pattern of the oxide in Fig. 2 shows a quite well-ordered (1 × 1)-oxide pattern with some defects as indicated by the broadened spots and the background intensity.

XP spectra of the Co 2p range are shown in Fig. 3. Signals at 780.5 and 796.0 eV binding energy and distinct satellite structures at 787.0 and 804.0 eV binding energy are found, corresponding to the Co $2p_{3/2}$ and Co $2p_{1/2}$ structure of Co^{2+} [10,11]. No indication of the existence of Co^{3+} can be seen [10,11]. A quantitative analysis of the damping of the Co^0 signal in the oxide spectrum gave a thickness of the oxide film of approximately 20–30 Å. The O 1s spectrum of the oxide (see Fig. 4a) not only exhibits the expected oxidic O^{2-} signal at 530.0 eV binding energy [10,11], but also a signal at 531.8 eV binding energy. Upon changing the angle between the surface normal and the electron detection direction from 0° to 80°, thus gaining surface sensitivity, this signal is amplified as compared to the oxidic signal (see Fig. 4b), indicating a surface species. The binding energy of 531.8 eV, also in comparison with NiO(111) [4], suggests this surface species to be OH [12]. Ion scattering spectroscopy results (not shown here) show that the surface contains cobalt as well as oxygen in a ratio of about 6 : 4, and we think that the surface consists of some cobalt- and some oxygen-terminated patches. In order to make certain that a sizeable amount of OH is adsorbed on the surface, probably to stabilize it, HREELS spectra were taken. Fig. 5 shows in the lower trace the spectrum of the clean oxide surface. At 70, 140 and 210 meV, the Fuchs–Kliewer phonon and two overtones can be seen. At 455 meV, there is an intense molecular

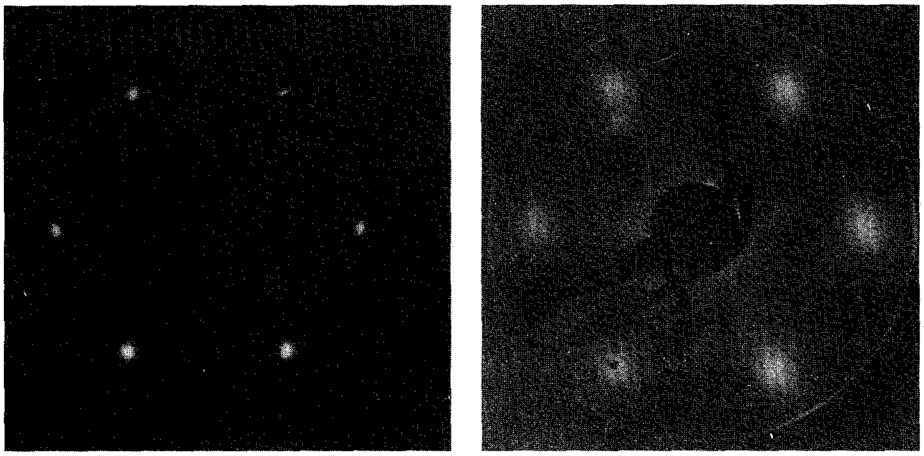

Fig. 2. LEED patterns of Co(0001) and CoO(111)/Co(0001).

vibration. The frequency lies in the same range as the stretching frequencies of surface hydroxyl groups found on other oxides [13]. The feature of lower intensity at higher loss energy is due to an OH–Fuchs–Kliewer-phonon combination mode.

Surface OH has already been found on NiO(111)

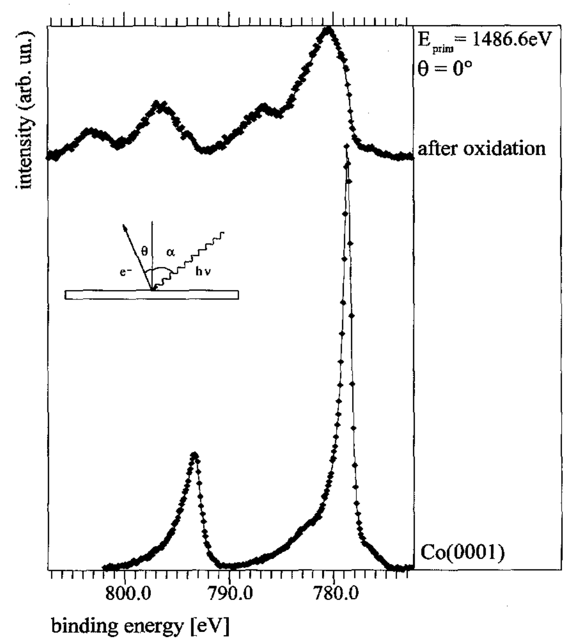

Fig. 3. Co 2p XP spectra of the Co(0001) sample before and after oxidation. The spectra were taken at room temperature.

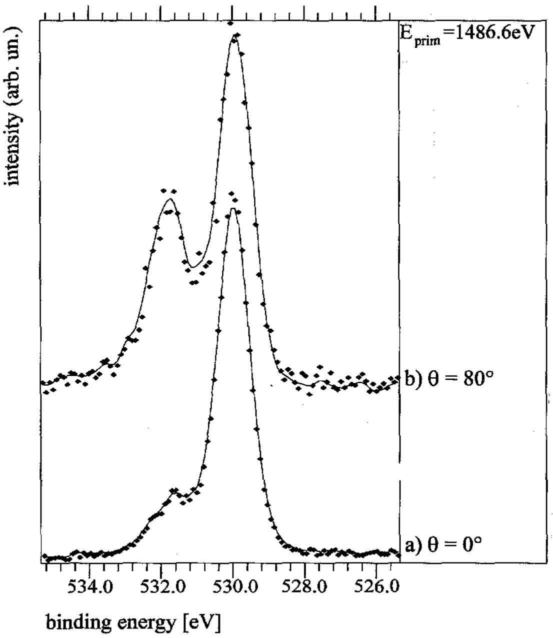

Fig. 4. O 1s spectra of the CoO(111) film at different angles between surface normal and electron detection, θ. The spectra have been taken at room temperature.

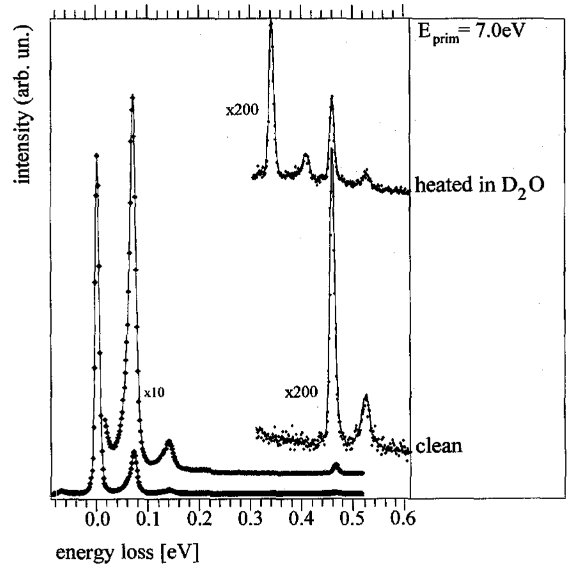

Fig. 5. HREELS spectra of the CoO(111) film (lower trace) and of the D_2O-modified surface (upper trace). All HREELS spectra have been taken in specular geometry and at room temperature, if not denoted otherwise.

as a means of stabilization [4,7]. When the NiO(111) sample is heated above about 600 K, the OH desorbs and the surface undergoes an octopolar reconstruction [22] to regain stability. This process is reversible; after exposing the NiO film to water, the sample showed the same OH presence as before heating [4,7]. Unfortunately the CoO(111) film could not be dehydroxylated by heating to find out if the surface then reconstructs because the oxide film suffered severe damage before the necessary temperature was reached.

3.2. Adsorption of NO

Upon adsorption of NO, a new feature can be seen in the HREELS spectrum. At 205 and 220 meV, N–O stretching vibrations of two different NO species appear (see Fig. 6a). Bending modes cannot be detected because of the intense Fuchs–Kliewer phonons. A temperature series of the adsorbed species (see Fig. 7) shows that the NO species with stretching frequency at 220 meV is the more weakly bonded species with a desorption temperature of about 180 K, while the other species desorbs at 240 K. A stretching frequency of 220 meV is quite common

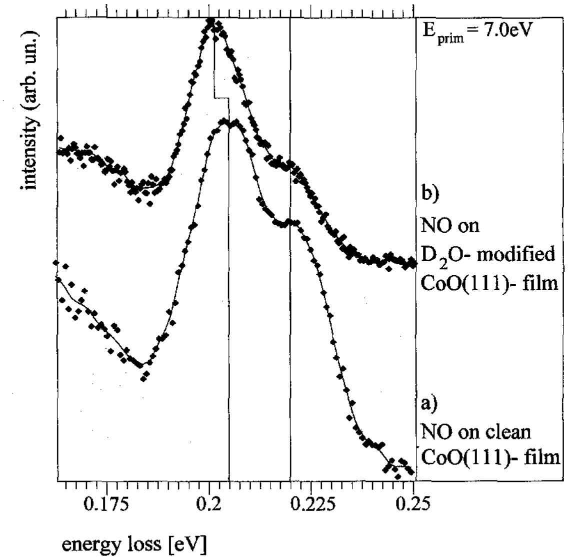

Fig. 6. HREELS spectra of NO (saturation coverage) on (a) the clean and (b) the D_2O-modified CoO(111) film. The spectra have been recorded at 80 K.

for neutrally adsorbed NO on oxides [14–16], whereas a frequency of 205 meV is very low; this frequency is in the range of the N–O stretching

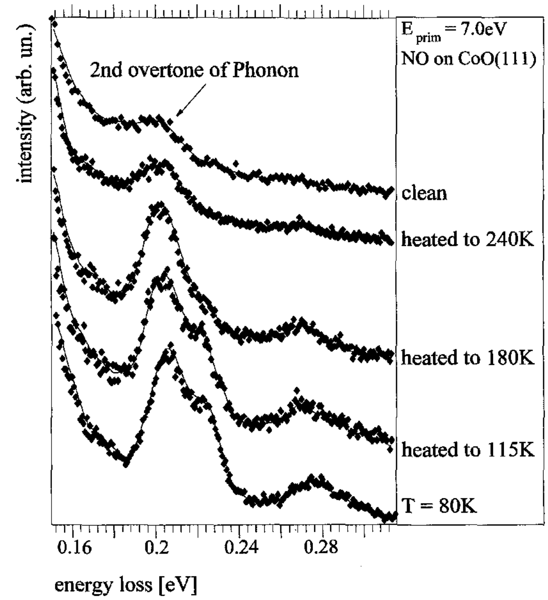

Fig. 7. HREELS spectra of NO (saturation coverage) on the CoO(111) film as a function of surface temperature.

frequency in HNO_2 [17]. Calculations of Pettersson [18] show that "regularly" adsorbed NO, that means NO bonded with N towards the metal ion, should be more weakly adsorbed on CoO than on NiO. This is the case for the NO species with stretching frequency at 220 meV and desorption temperature of 180 K. The desorption temperature, which is a direct measure of the binding energy, of NO on NiO(111) is 220 K [19].

One way to test the assumption that the frequency of the second species is so low because of an interaction between the adsorbed NO with surface OH is to exchange the surface OH against OD. Fig. 5 shows in the upper trace the clean surface after exposing the oxide film to D_2O. There is still some OH left because of the restrictions for heating, but most of the OH has been exchanged against OD. In Fig. 6b, the result of the adsorption of NO on the OD-modified surface is presented. The lower frequency shifts about 4 meV to an even lower frequency, whereas the other N–O loss stays at 220 meV. This shift of 4 meV can be explained by assuming a tendency towards formation of cisoid HNO_2, that means NO bonded with N towards the surface and oriented parallel to the surface OH. Table 1 compares the measured frequencies to infrared data of HNO_2 and DNO_2. Calculations by Pettersson [18] confirm this possibility.

It is also possible that the explanation for this frequency shift has to do with the orientation of the NO molecule towards the surface. Bagus and coworkers [24] have predicted that NO, when binding to the surface through the oxygen atom, experiences a moderate downward shift of the NO stretching frequency. If we assume that somehow the NO surface bond in the latter geometry is stabilized near an OH group, this could also explain the data. However, in which way the OH/OD exchange influences this interaction can only be speculated on at present. Anyway, it will be interesting to see whether theory can help to eventually explain these findings (see i.e. Ref. [25] for calculations of H adsorption on MgO).

The O–H stretching frequency undergoes a slight change upon adsorption of NO as a tailing appears towards smaller frequencies, which would be expected for a species resembling HNO_2. IR measurements are necessary to confirm this as the resolution of the EEL spectra is too poor to give conclusive results.

The conclusion can be drawn that part of the NO adsorbs on sites near the OH that stabilizes the surface. The presence of OH assists the adsorption of NO to form a more stable adsorbed species.

Table 1
N–O stretching frequencies of cis- and trans-HNO_2 and DNO_2 from infrared data and comparison to our measured data

	ν_{N-O} (OH) (cm^{-1})	ν_{N-O} (OD) (cm^{-1})	Ref.
NO/CoO(111)	1653	1621	This work
HNO_2 (cis) O−H | N−O	1640	1625	[17,26]
HNO_2 (trans) O−H | O−N	1699	1692	[26]

4. Conclusions

We have prepared a thin CoO(111) film on Co(0001). The thermodynamically unstable surface is stabilized by adsorption of OH as a means of surface charge reduction. NO adsorbs on this surface on two different sites. One of these sites is situated in the direct vicinity of the surface hydroxyl groups with which the adsorbed NO molecules interact to form a more stable adsorbed species.

Acknowledgements

We have profited from many discussions with Lars Pettersson whom we would like to thank for his input.

Several agencies have supported our work: Deutsche Forschungsgemeinschaft, Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and Fonds der chemischen Industrie. We are grateful for the support.

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