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An in situ XPS study of site competition between CO and NO on Rh(111) in equilibrium with the gas phase

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Abstract

The nature of the adsorption sites of CO and NO as they compete to adsorb on a Rh(111) surface has been determined using by X-ray photoelectron spectroscopy in situ, under gas mixtures of the reactants in the Pascal pressure range. It was found that near room temperature NO readily displaced CO from threefold hollow sites when the NO partial pressure was below 30%. CO is displaced from top sites only at higher NO pressures and after heating. The kinetics of CO:NO exchange at top sites is very slow at room temperature (hours), and requires heating for complete exchange.

Keywords: CO oxidation; NO reduction; In situ photoelectron spectroscopy

1. Introduction

The reaction of CO and NO to form CO_2 and N_2 is one of the most important automobile exhaust control reactions catalyzed by noble metals such as Rh and Pd. For this reason CO and NO adsorption on these metal surfaces has received considerable attention. Understanding the structure and dynamical processes involved in the reaction of these simple gases on surfaces is one of the goals of surface science and catalysis. Electron spectroscopies such as X-ray photoelectron spectroscopy (XPS), Auger spectroscopy (AES), X-ray absorption (XAS), and others, which provide surface-specific electronic structure information, are powerful tools for studying the fundamental aspects of chemisorption and surface reactions. Unfortunately, because of the short mean free path of electrons in gas environments these powerful techniques have been used mostly in high vacuum environments. Under high vacuum and typical reaction temperatures, however, only strongly bound species are detected which are out of equilibrium with the gas phase. This is the origin of the so-called pressure gap that separates surface science from catalysis, where reactions take place at gas pressures in the range of tens or hundreds of Pascals. In automobile exhaust catalysts, for example, the removal of noxious NO_x and CO gases by reactions that form CO_2 and N_2 occurs at partial pressures of tens or hundreds of Pascal and temperatures of a few hundred degrees Celsius. The need to overcome the pressure gap has prompted the development of new techniques. One approach involves pure photon techniques such as infrared (IR), Raman, sum frequency generation (SFG), and X-ray absorption spectroscopies [1,2]. In the case of electron-based techniques, which are intrinsically surface sensitive, differential pumping schemes can be used to extract the electrons from the surface by means of orifices situated within a distance comparable to their mean free path, which for electrons of a few hundred electron volts and gas pressures of hundreds of Pascals is of the order of the millimeter. Such techniques are opening a new era in surface science by allowing molecular-scale studies of surfaces in equilibrium with the gas phase [3,4].

The system of NO and CO on Rh(111) has been studied in the past, both in ultrahigh vacuum (UHV) environments and at high pressures [5]. Low energy electron diffraction (LEED) [6,7], scanning tunneling microscopy (STM) [8] and He diffraction [9] studies have shown that when the surface coverage reaches 0.75 monolayer (ML), both molecules form ordered structures with 2 × 2 periodicity. The

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NO adsorption sites on Rh(111) have also been investigated by photoelectron diffraction [10]. In each case the unit cell contains 3 molecules, one on a top site and the other two in the fcc and hcp 3-fold hollow sites. At coverages lower than 0.75 ML, bridge-site CO species may also exist [11]. When the surface is exposed to mixtures of CO and NO, competition for surface sites takes place and the surface composition depends on partial pressures and temperature. Understanding the structure and site occupation of mixed CO and NO adsorbates is key to understanding the catalytic process. Studies of such mixed system were carried out using thermal-programmed desorption (TPD) by Root et al. [12] and by Witte using He scattering [9]. Using the CO and NO-stretch mode frequencies in the IR spectra as indicators of the adsorption site, Permana et al. [13,14] have shown that under catalytic reaction conditions NO occupies hollow sites while CO occupies top sites. Molecular resolution images have been obtained recently by Rider et al. using STM under catalytic pressure conditions (100s of Pascals) [15]. STM however could resolve only the molecules adsorbed on top sites, which account for 1/3 of the total number. The other 2/3 consists of molecules adsorbed on hollow sites that are invisible in the STM images. The authors proposed a model for the molecular structure based on an analysis of exchange events observed between the top CO and NO molecules in the STM images. In this model as the partial pressure of NO increases in the CO + NO gas mixture, NO displaces CO first in the hollow sites and later on the top sites. To confirm the assignment and the validity of the proposed model other techniques that are sensitive to the molecular adsorption site should be used. XPS is an excellent technique for determining the nature, structure, and chemical state of surface species, as shown by Smedh et al. [11,16]. These authors distinguished the adsorption sites of CO at temperatures up to 410 K and pressures up to 10^{-3} Pa.

2. Experimental

In this paper we present photoelectron spectroscopy results obtained in the important range of 10^{-3} to 650 Pa. Our experiments were performed in situ, i.e., in the presence of the gas phase so that thermodynamic equilibrium can be reached. We used a newly developed high-pressure photoelectron spectrometer (HPPES) capable of operation under several hundreds of Pascals [3]. The instrument is located in the Advanced Light Source of the Lawrence Berkeley National Laboratory. Monochromatized X-ray photons from the synchrotron pass through a thin aluminum window (100 nm thickness) and strike the Rh(111) surface after approximately 1 cm travel in an atmosphere of CO and/or NO gas at an angle of about 20° from the surface plane. Photoelectrons emitted from the sample are transmitted through a 1-mm-diameter aperture located ∼ 1 mm above the Rh(111) surface. The aperture is the entrance to a differentially pumped electrostatic lens system that focuses the electrons into the object plane of a standard electron energy analyzer situated downstream, in the high-vacuum region. The gas-phase composition was checked both by the XPS signal from gas phase molecules in the X-ray beam path, and by quadrupole mass spectrometry in the second stage of the differential pumping system. The overall resolution of the analyzer and beamline monochromator was about 0.4 eV, enough to distinguish the different species present on the surface and to monitor energy shifts down to 0.1 eV.

The sample was precleaned and characterized in a separate UHV chamber by Ar^+ sputtering. Once in the high-pressure chamber is was annealed in oxygen to remove the carbon contamination accumulated during the transfer. The surface oxygen was then reacted away by annealing to 900 K in the presence of CO gas at pressures below 10^3 Pa. The cleanliness of the surface was continuously monitored by XPS, particularly the C peak region near 284 eV, corresponding to graphite and hydrocarbon species. Contamination by nickel carbonyls (from the CO lecture bottle source) was prevented by use of a cold trap.

3. Results and discussion

Fig. 1 shows photoelectron spectra in the binding energy regions of the N 1s and C 1s core levels taken at room temperature (RT). The incident photon energy was set at 450 eV for C 1s and 650 eV for N 1s so that the emitted photoelectrons have comparable kinetic energies close to 150 eV. In this way energy-dependent transmission through the gas phase and the HPPES lens system was normalized. In 18 Pa of pure CO (curve a, Fig. 1), the C 1s spectrum shows two components, which have been assigned to different CO ad-

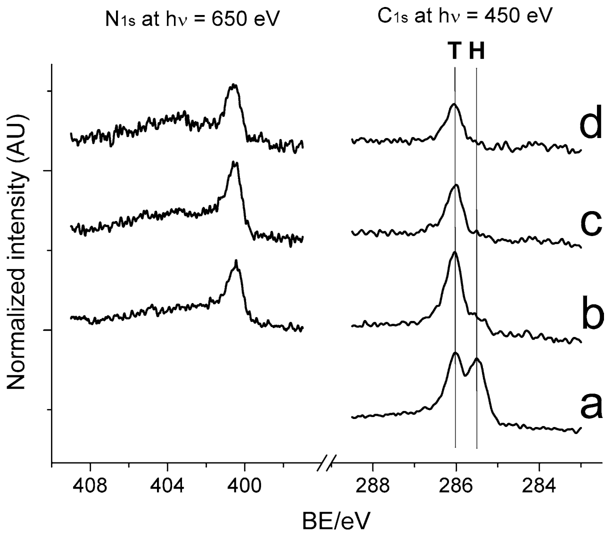

Fig. 1. XPS spectra (without background subtraction or correction due to gas-phase attenuation, but normalized for photon flux) acquired at room temperature in the N 1s binding energy region (left) and C 1s region (right) with the Rh(111) substrate in: (a) 20 Pa CO; (b) 18 Pa CO + 6.6 Pa NO (27%); (c) 18 Pa CO + 13 Pa NO (42%); and (d) 18 Pa CO + 20 Pa NO (53%).

sorption sites [11]. The component at 286.0 eV corresponds to CO on top sites, while the component located at 285.5 eV corresponds to CO on hcp and fcc hollow sites. The structure is known to be 2 × 2 from STM experiments at the same and higher pressures [15] and therefore only hollow and top-site molecules are expected. Since the relative population of top and hollow sites is 1:2, one might expect a similar ratio for the intensities of the two peaks. However, this is not found in general since the ionization cross section is modified by energy-dependent final-state diffraction effects [11].

In the presence of NO the occupation of hollow sites by CO decreases substantially, and after the addition of 6.6 Pa of NO, 27% of the total pressure (curve b, Fig. 1), the CO hollow-site component (labeled H) has practically disappeared. During this time the top-site peak (T) remains largely unchanged. This demonstrates the much higher affinity of NO for hollow sites. At higher NO partial pressures (curves c and d) the peak due to threefold site CO is barely detectable while the top-site population starts to decrease. The much smaller reduction in the top-site CO population is a phenomenon already observed with STM [15], where top-site NO molecules were not visible below a 30% partial pressure of this gas at room temperature. Since the STM results show a well-ordered 2×2 structure under these pressure and temperature conditions, we conclude that near 30% NO partial pressure at room temperature the surface consist of nearly pure NO on hollow sites surrounding CO on top sites. The limited extent of top-site CO displacement by NO is in part a kinetic phenomenon. This is seen by the slow decrease (in the scale of hours, Fig. 3) of the top CO peak intensity in pure NO gas. From the lifetime of CO on top sites we estimate a binding energy of 0.99 eV (95 kJ/mol) (assuming a 10^{13} preexponential factor in the Arrhenius expression). There is also an overall decrease in signal intensity from spectra a to d due to increased electron scattering as the gas pressure increases, which we estimate to account for a 20% loss of signal in the present case. This attenuation depends on pressure and on the position of the sample relative to the collecting orifice.

The N 1s emission at 400.4 eV shown in Fig. 1 is thus attributed to NO molecules that have displaced CO from the hollow sites. Previous low-pressure XPS studies of NO adsorption on Rh(110) (to our knowledge there are no published studies of NO adsorption on Rh(111)) [17] show two components in the 397.2–397.4 and 399.7–400.0 eV ranges, attributed to atomic nitrogen and molecular NO bonded via the N atoms, respectively [18]. The width of N 1s line is broadened by final-state effects (vibrational excitations with an energy quantum of ∼ 0.17 eV, electronic shake-up processes, and lateral interactions between the adsorbed species), as well as multiplet splitting from the unpaired spin density in the adsorbed NO [18,19]. Due to this broadening, it was not possible to resolve the NO top-hollow-site shift.

Fig. 2 shows spectra from an experiment performed at a slightly higher temperature of 320 K in the range of CO:NO pressure ratio where most of the displacement of hollow-site CO by NO takes place. As can be seen, the displacement is already very substantial with only 9% NO in the gas phase and essentially complete at 35%. The reduction in intensity of the CO top-site peak at the higher NO pressure indicates that CO displacement from those sites occurs faster (on the scale of minutes) at this temperature. Differences in gas-phase attenuation in this case are minimized since the total gas pressure does not change appreciably, except for the last spectrum d. It is important also to note that no signal is observed in the binding energy region of graphite and hydrocarbons (near 284 eV), indicating that the Rh surface remains free of hydrocarbon contamination during the experiments.

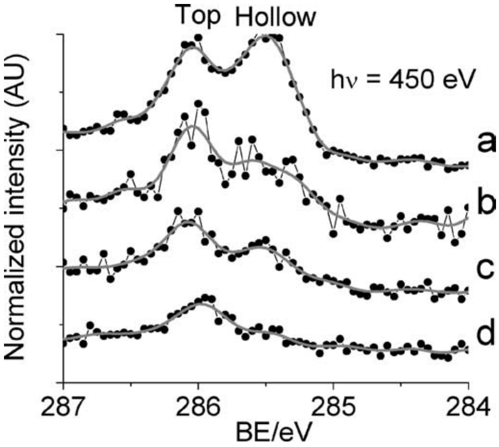

Fig. 2. XPS spectra of C 1s from CO adsorbed on Rh(111) at 320 K. (a) 20 Pa of CO; (b) 17.5 Pa CO + 1.8 Pa NO (9% NO); (c) 14.6 Pa CO + 5.3 Pa NO (27% NO); and (d) 17.3 Pa CO + 9.3 Pa NO (35% NO).

A more detailed analysis of the C 1s peak structure of a pure CO layer is shown in Fig. 3a. The spectrum was acquired at 320 K under 52 Pa of CO at a photon energy of 380 eV to maximize sensitivity to hollow-site CO [20]. The peaks were then decomposed into several contributions that become visible in the Gaussian fits. The on-top and hollow emission peaks were found at 285.9 and 285.35 eV, respectively. These peaks were accompanied by satellites at 250 and 500 meV below the parent peak that are due to excitation of quanta of C–O stretch vibration in the photoemission process [21]. A detailed discussion of vibrational contributions to C 1s photoemission from CO adsorbed on Rh(111) can be found in Ref. [11].

After introduction of 2.6 Pa of NO in the chamber followed by the evacuation of the CO the spectrum of Fig. 3b was obtained after 1 h. As can be seen there is still a small residual top-site CO peak. This residual top-site CO could be completely removed after heating to 623 K (Fig. 3c).

Fig. 4 shows the N 1s region of adsorbed NO in the course of the same experiment. Spectrum a corresponds to the sample under 52 Pa of CO and 2.6 Pa of NO. Spectrum b was obtained in the same run as that in Fig. 3b, under 2.6 Pa of NO and 1 h after evacuation of the CO from the gas phase. The increase in intensity from a to b is largely due to the lower attenuation of the electron signal at the lower

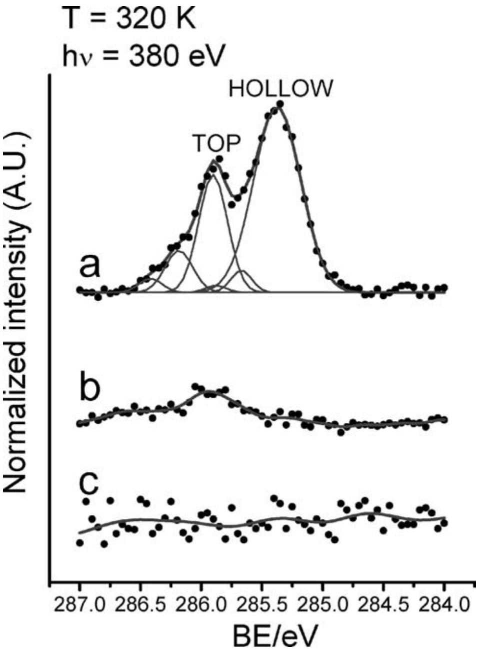

Fig. 3. C 1s XPS spectra of CO adsorbed on Rh(111) acquired at 320 K in various mixtures of CO and NO gas. (a) 52 Pa of CO; (b) 2.6 Pa of NO 1 h after evacuation of the CO; and (c) 2.6 Pa of NO after heating the sample to 623 K. The curves in (a) are Gaussians fits corresponding to the top- and hollow-site peaks plus shake-up satellites corresponding to one and two quanta of 0.25 eV CO-stretch vibrations.

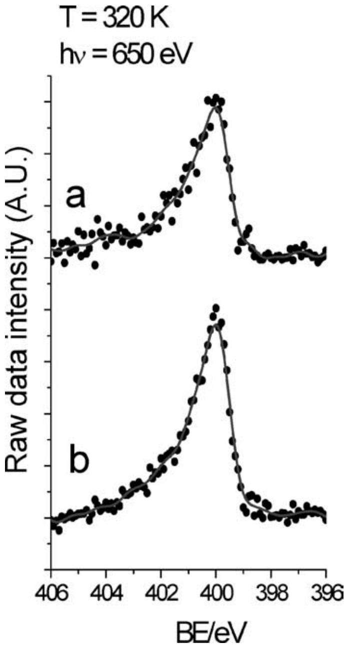

Fig. 4. N 1s XPS spectra of NO adsorbed on Rh(111) acquired at: (a) 52 Pa CO + 2.6 Pa of NO; and (b) 2.6 Pa of NO after 1 h evacuation of the CO gas phase. The increase in intensity for (b) is due to reduced gas-phase signal attenuation.

gas pressure. Although the peak corresponds to a structure containing both top and hollow site NO (in a 1:2 proportion) the peak shape is not resolved into components, indicating that unlike CO, site-dependent binding energy shifts cannot be detected at the resolution limit of our measurements, i.e., 0.1 to 0.2 eV. Similar vibrational losses probably contribute to the NO peak, although they were not resolved due to the smaller energy of the vibration quanta (∼ 0.17 eV) and the NO line broadening.

4. Summary

In conclusion, using a novel photoelectron spectrometer we performed in situ XPS studies of the Rh(111) surface in CO and NO gas mixtures of up to several hundred Pascals. In a mixed atmosphere of NO and CO gases, NO efficiently displaces CO from hollow sites at room temperature. Top-site CO molecules predominantly occupy top sites up to partial pressures containing approximately 30% NO. At this partial pressure CO is almost completely displaced from the hollow sites. Together with information from previous STM results the picture emerges of a surface layer where CO occupies exclusively top sites and is surrounded by NO molecules in the nearby hollow sites. Only at partial pressures of NO above 30% the top-site CO is replaced by NO. We have also shown that the top-site CO remains kinetically trapped for hours at room temperature. The CO displacement rate increases significantly at 320 K and above, and a brief annealing at ∼ 620 K completely displaces top-site CO.

The present results illustrate the potential of in situ photoelectron spectroscopy to determine structure, composition, and reactions under real catalytic conditions. Our current results near room temperature have confirmed models of CO:NO interaction based on STM studies. In situ XPS also has the potential to follow reactions in the CO/NO/Rh system under catalytic conditions, since all of the species believed to be important [5]—atomically adsorbed C, N, and O, molecularly adsorbed CO and NO, and even Rh vacancies (through the Rh surface core-level shift)—can be monitored simultaneously. In combination with in situ crystallographic methods such as STM and X-ray diffraction, these methods advance catalysis research by providing new and fundamental information in the most relevant pressure regime, inaccessible to traditional electron-based surface spectroscopies.

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