Surface Science 602 (2008) 2189–2196

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Density functional theory study of NO on the Rh(100) surface

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ARTICLE INFO

Article history:
Received 21 February 2008
Accepted for publication 24 April 2008
Available online 8 May 2008

Keywords:
Density functional calculations
Surface electronic phenomena
Vibrations of adsorbed molecules
Surface diffusion
Rhodium
Nitrogen monoxide
Single crystal surfaces
Metallic surfaces

ABSTRACT

Density functional theory has been used to perform a systematic study of the adsorption of NO on the Rh(100) surface. A detailed discussion about the structural configurations, work functions, and the frequency modes for all the adsorption sites at several coverages is given. NO has possibly two adsorption sites. NO is found to adsorb in bridge sites at all coverages. A highly inclined NO is present on the surface at low coverages, with a stability close to the NO adsorbed in bridge position. The activation barrier for tilting NO from the inclined to the bridge position is low. A discussion of partial density of states and charge density differences for the stable positions is given. The calculated intensity of the stretching vibration of NO adsorbed in bridge is much higher than the one corresponding to the stretching vibration of NO adsorbed in inclined position. At NO saturation coverage theory predicts various vibrational modes. A discussion about the way in which they might appear is given.

1. Introduction

The adsorption of NO on metal surfaces is of significant interest, both from a scientific and technological point of view. Rhodium is the most efficient metal in the reduction of nitric oxide [1,2]. NO is also an important product in the ammonia oxidation process [3]. The adsorption of NO on transition metal surfaces has been the subject of numerous experimental and theoretical investigations [2–10]. On the Rh(100) surface, NO adsorbs molecularly at low temperatures, and dissociatively above 170 K [6–9].

Several studies conclude that NO adsorbed on Rh(100) surface occupies bridged sites [11–17]. Secondary ion mass spectroscopy (SIMS) studies indicate that NO occupies sites of high coordination, but a definitive site assignment could not be made based on the SIMS results [8,9]. Vibrational studies also could not provide a definitive site assignment [6,18]. Reinterpretation of the EELS results with the frequency ranges proposed by Brown and King [3] indicates that NO is most-likely twofold bridge bonded. Also on other (100) surfaces NO occupies bridged sites, for instance on Pd, Ni, [3] and Cu [19]. Van Tol and Nieuwenhuys found also indications that NO occupies the bridge and highly inclined sites on the Rh(100) at 80 K [7].

In an EELS study, Villarubia et al. observed two vibrational modes at 920 cm^{-1} and around 1580 cm^{-1} for NO on the Rh(100) at 90 K [6,18]. The lower frequency was attributed to a much weakened N–O molecular bond resulting from highly inclined geometry. This loss was only observed at low coverages. The higher frequency is found at higher exposures, and shifts to around 1700 cm^{-1} at saturation. It was assigned to a vertically bound state, although it was not possible to determine this state unequivocally.

Calculations performed by Loffreda et al. [14,15] also indicate that apart from the most stable site for NO being the bridged site, an inclined species is stable. A similar situation was recently reported for the more stable CO molecule on the reactive iron surface [20]. DFT calculations and experimental results by Bondino et al. [16] indicated a bridged adsorption site for NO on the Rh(100) at 140 K. However, the inclined NO at hollow site was found to be only about 0.1 eV less stable, with a calculated stretching frequency of 895 cm^{-1}, which is close to the observed vibrational mode at low NO coverage [6,18]. The results from DFT calculations were supported up by the experimental data of the same group. A further investigation by Bondino et al. [21] showed that only bridged NO is present at saturation coverage. The molecules form a disordered phase which develops in a well ordered $p(4\sqrt{2}\times\sqrt{2})R45^\circ$ structure after heating the adlayer to 353 K. Furthermore, it was concluded that the inclined NO configuration acts as precursor for NO dissociation.

Van Bavel et al. studied the behavior of NO on the Rh(100) using EELS [22]. The measurements of the adsorption of NO on the Rh(100) at low temperatures revealed a strong loss attributed to the bridge bonded NO. After magnifying the spectra, a very weak loss is occasionally and just about discernible around 920 cm^{-1} at

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doi:10.1016/j.susc.2008.04.035

coverages below 0.05 ML. This feature is attributed by several authors to a highly inclined NO [6,15,16,18]. This N–O stretching frequency increases with coverage.

In this paper we present a systematic density functional theory study on the vibrational behavior and stability of NO adsorbed on the Rh(100) surface. We find that NO adsorbs molecularly on the Rh(100) surface occupying bridged sites at all coverages. A discussion about the structural configurations, work functions, partial density of states and charge density differences of NO adsorbed in different sites and surfaces for several coverages is given. In particular, a detailed analysis of the frequency modes for all the structures is presented.

2. Computational details

The electronic structure calculations were carried out using density functional theory (DFT) with the Vienna Ab Initio Simulation Package (VASP), [23,24] with a plane wave basis set and ultrasoft Vanderbilt pseudopotentials, [25] and the generalized gradient approximation (GGA) [26] for the exchange and the correlation energy as proposed by Perdew and Wang [27]. Tests showed that the spin contribution to the total energy of the adsorbated systems is negligible and hence a spin-restricted approach was used except for NO in vacuum [28–30]. Relativistic effects were not included in the calculations. With the pseudopotentials considered, a cutoff energy of 400 eV for the plane wave basis ensures a good accuracy. For the Brillouin zone integration a Monckhorst–Pack $5 \times 5 \times 1$ mesh was used for $p(2 \times 2)$ unit cells and $3 \times 3 \times 1$ for bigger unit cells.

The Rh(100) surface was modeled using the slab supercell approach with periodic two-dimensional slabs. We varied the number of metallic layers from three to six, which were allowed to relax fully, and the same for the equivalent vacuum space in z-direction which separates a slab from its periodic image. Five layers of metal and five or six (the latter in the case of NO in top position) were found to be optimal for the required accuracy of the adsorption energy.

The optimized bulk nearest-neighbor separation of 2.72 Å is in good agreement with the experimental value of 2.69 Å [31]. For NO in vacuum the optimum bond distance was found to be 1.16 Å; the experimental value is 1.151 Å [32].

The molecules were adsorbed on both sides of the metallic slab with an S_2 symmetry center to avoid long-range dipole–dipole interactions between translational equivalent unit cells. Tests performed with different values of cutoff energy and different number of k-points showed that the convergence of the total energy is within $5 \cdot 10^{-2}$ eV. The conjugate-gradient algorithm was used to relax the ions into their equilibrium locations. Equilibrium was assumed to be reached if the Hellmann–Feynman forces on the atoms are less than $0.02\ \text{eV}\ \text{Å}^{-1}$ in each of the Cartesian directions. For the structures on which we have performed vibrational analysis however the forces were smaller than $10^{-3}\ \text{eV}\ \text{Å}^{-1}$ and the energy convergence smaller than 10^{-6} eV.

The adsorption energy for all the adsorption sites of the NO molecules was calculated according to the equation

$$E_{\text{ads}} = [E_{\text{NO/Rh}} - E_{\text{Rh}} - nE_{\text{NO(gas)}}]/n, \tag{1}$$

where $E_{\text{NO/Rh}}$ is the total energy of the Rh slab on which NO is adsorbed, E_{Rh} is the energy of the metallic slab, $E_{\text{NO}}(\text{gas})$ is the energy of an NO molecule in the gas phase, and n is the number of the adsorbed NO molecules on the surface.

The nudged elastic band method (NEB) implemented in the VASP program was used to determine the minimum energy path (MEP) between highly inclined NO and bridge NO [33–35]. All the atomic coordinates were free to change during a NEB calculation. The energy barrier of the change of the adsorption geometry is given by the difference between the energies of the transition state (TS) and of the initial structure. The NEB calculation gives a candidate for the transition state structure. After minimizing the residual forces, a vibrational analysis was used to check if indeed a transition state was found. If a molecule is in a real minimum of the potential energy surface, all frequency values are positive. And a true transition state is a saddle point on the PES and must have one, and only one, imaginary frequency.

The density of states (DOS) or projected DOS were also computed. The work function was computed for various adlayer structures. It equals minus the Fermi energy, when the electrostatic potential is zero at infinite distance from the surface. Because we have a periodic system also in the direction perpendicular to the surface, the work function cannot be directly calculated from the Fermi level. The work function is obtained by shifting the calculated Fermi energy with the constant value of the total electrostatic potential in the middle of the vacuum region.

The frequencies were computed in the harmonic approximation within the VASP program, in which all the atomic coordinates of the Rh and NO were varied, allowing a complete analysis of the possible vibration modes. We applied a finite displacement of 0.02 Å in all directions, for the first layer of the Rh atoms and for the adsorbates. That displacement is a compromise between the accuracy of the force calculations and harmonic approximation. The second derivatives of the potential energy surface were used to calculate the dynamical matrix. By diagonalization of this matrix the frequencies, the surface phonons, and the associated normal modes are obtained.

Tests showed that the phonons of the inner metallic layers hardly couple with the frequencies associated with the adsorbed fragments. This fact makes it possible to freeze the degrees of freedom of the inner metallic atoms in the frequency calculations. The phonon frequencies obtained for the Rh(100)-$p(2 \times 2)$ slab have values between 63 to 245 cm^{-1}. For two NO molecules in the gas phase, while taking into account also the spin contribution to the total energy, there are two possible stretching vibrations, in phase and out of phase (respectively 1892, 1808 cm^{-1}). Other frequencies correspond to translations or rotations. The experimental value of 1873 cm^{-1} [14] is assigned to the N–O stretching vibration. Because of the symmetric approach of the unit cell we have in each case two values for the same frequency, but, as they are coupled, the average value gives the frequency without coupling.

For some structures we also calculated the intensities of the vibrational modes. They are directly related to the dynamical dipole moment, which corresponds to the change of the total dipole moment, μ, of the system as a response to a distortion along a certain normal mode [36]. The intensity, I, of the normal mode q_i [37] in an infrared spectrum is given by

$$I \propto \left| \frac{\partial \mu}{\partial q_i} \right|^2. \tag{2}$$

Therefore the infrared intensities are proportional to the square of the dynamical dipole moment.

3. Results and discussion

The NO adsorption on various Rh surfaces with low Miller indices was studied at 0.25 ML coverage (Table 1). The adsorption energies are −2.72 to −2.57 eV for the most stable sites on the (111), (110), and (100) surfaces. On the (111) surface the most stable adsorption site is the hcp hollow, followed by the fcc hollow. The (110) surface is more open, therefore NO adsorbs on the short bridge. And on the Rh(100) surface NO adsorbs and is stable on the