Coadsorption of CO and NO on the Pd(111) Surface: Combined *Ab Initio* and Monte Carlo Study

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Adsorption and coadsorption of nitric oxide (NO) and carbon monoxide (CO) on the Pd(111) surface are studied by combining first principles (FP) calculations and Monte Carlo (MC) simulations. From FP adsorption energies and molecule-molecule interactions we construct an interaction model, which is used in MC. We do several simulations with different coverages and CO/NO ratios. The simulations provide 0.75 monolayer (ML) for a saturation coverage, which is in excellent agreement with experiments. The results indicate that at 0.75 ML coverage, NO molecules take over the hollow sites and push CO molecules mainly onto bridge sites.

Basic knowledge of carbon monoxide–nitric oxide (CO-NO) coadsorption structures and energetics on the Pd(111) surface is an important initial step towards the understanding of a complex CO-NO oxidation-reduction reaction. According to the traditional interpretation, pure CO adsorbs on the Pd(111) surface just like pure NO: At low coverage the molecules occupy threefold hollow sites, transferring onto bridge sites at intermediate coverages and finally onto atop sites at saturation coverage. Theoretical calculations of Loffreda *et al.* [1] support the model where the molecules occupy hollow sites up to half of monolayer (ML) coverage. According to their first principles calculations at saturation coverage 0.75 ML the top fcc-hcp geometry is more favorable than the top bridge-bridge geometry.

Using infrared (IR) spectroscopy Xu *et al.* [2] compared the CO-NO coadsorption structures on Pd(111) and Pd(100) surfaces and found that the overlayer structure is more complex on Pd(111) than on the open Pd(100) surface. The structure sensitivity studies of the CO-NO mixture on Pd(111) and Pd(100) surfaces reveal that the Pd(100) surface dissociates NO more effectively than Pd(111), which, however, is approximately 5 times more active for NO reduction by CO than the Pd(100) surface. The results of Xu *et al.* [2] show that the reaction between NO and CO is negligible below 500 K and that the molecule coverage ratios and adsorption sites vary as a function of temperature. Between 400–500 K, the dominant adsorbate species is NO. During the cooling process the NO intensity in the IR spectrum decreases while the CO frequency assigned to the bridge position increases. The change in the molecule ratio is interpreted to be a consequence of larger lateral repulsions between NO molecules because the total surface coverage increases with decreasing temperature. Cooling the system down to 200 K strengthens the CO position as a majority adsorbate species and the estimated coverages are 0.5 and 0.25 ML for CO and NO, respectively [2]. The IR spectra show

two peaks: one assigned to atop adsorbed NO and one to a bridge bound CO.

In this Letter we present "first principles" (FP) Monte Carlo (MC) studies for coadsorption of CO and NO on the Pd(111) surface. Stampfl and co-workers applied a similar method combination to study atomic oxygen adsorption on the Ru(0001) surface [3].

We use state-of-the-art first principles density-functional theory (DFT) electronic structure calculations to evaluate self-consistently all the interaction parameters needed in MC simulations. The DFT molecule adsorption energies and two-body molecule-molecule interactions are used to construct total energy in MC, where adsorbates are allowed to change their positions according to a basic Metropolis scheme. This is the very first FP-based MC study to determine molecule coadsorption structures on a metal surface. By combining DFT calculations and MC simulations we can study larger systems and molecule coverages and ratios beyond the limit where all presently available FP schemes become unfeasible. For realistic systems, establishing parameters is a laborious, if not impossible, task. Taking the parameters from the FP calculations is the most reliable way to determine them, when there is not enough experimental data to build up a complete interaction model.

The electronic structure calculations are performed using DFT together with the general gradient approximation by Perdew *et al.* [4] for exchange-correlation interactions. The one-electron equations are solved in a plane-wave basis, and ion cores are treated with pseudopotentials. We use the Troullier-Martins pseudopotential [5] for Pd, while C, N, and O atoms are described with Vanderbilt ultrasoft pseudopotentials [6]. The Pd(111) surface is modeled by a fully relaxed three-layer-thick slab with a 2×2 rectangle or a 3×3 surface cell. The number of k points is fixed to 12 (4), which gives the lattice parameter 3.93 Å. All the calculations are done with the FINGER code [7]. Each *ab initio* calculation takes a few hours with 64 processors using Cray T3E.

Table I shows the adsorption energies of single NO and CO molecules, calculated at four high symmetry sites on both surface cells. The molecules attach first to the surface their carbon or nitrogen head, with the molecular axis parallel to the surface normal. For both molecule species, threefold hollow sites are the most stable adsorption positions. On the rectangular 2×2 surface cell, NO molecules have larger adsorption energies on hollow and bridge sites than CO molecules; the latter are more attracted to top sites than are the former. The adsorption energies calculated at 0.25 ML coverage are in excellent agreement with values published earlier [1].

In addition to these one-body interactions we calculate (in total) 57 CO-CO, NO-NO, and CO-NO interadsorbate interactions according to the following equation on the rectangular 2×2 surface cell:

$$E_{i,j}^{\text{int}} = E_i^{\text{ads}}(X, \text{Pd}) + E_j^{\text{ads}}(Y, \text{Pd}) - E_{i,j}^{\text{ads}}(X, Y, \text{Pd}), \tag{1}$$

where X and Y are CO or NO. Subscripts i and j refer to different adsorption sites. Because of periodic boundary conditions, molecules can form ordered chain structures on the surface. In those cases interaction parameters are divided by two to have a more realistic lateral two-body interaction. We find all the calculated pair interactions to be repulsive. With the same intramolecular distance the repulsion between the adsorbates is larger if the adsorbates share a common Pd atom than in a case where they attach to a different metal atom. The repulsion increases as the intramolecular distance decreases; with distances larger than 3.6 Å the repulsion is very small.

The construction of a perfect interaction model is unfeasible, and we need to make a few approximations. Structures such as top(NO)-bridge(CO) and bridge(NO)-top(CO) have slightly different interaction energies. Instead of using both energies, we take an average of them to describe the bridge-top interaction. Our MC model does not make any difference between the bridge-bridge interactions, where the adsorbates form a straight chain or a "zigzag" chain. In both chain structures the intermolecular distance is the same but the strength of the interaction varies because in the straight chain the molecules share a common Pd atom whereas in the zigzag chain they do not. Again we take an average of different bridge-bridge interactions.

MC simulations clearly show that the results are very sensitive to changes in isolated adsorption energies, bridge-bridge, bridge-hollow, and hollow-hollow interactions. Unfortunately parameters calculated on the rectangular 2×2 cell give physically unrealistic results favoring NO adsorption too much. We recalculate the adsorption energies of individual molecules and the most important CO-NO interactions on the 3×3 surface, and the results are shown in Tables I and II. CO-CO and NO-NO interactions are scaled with factors obtained from CO-NO calculations. Spot checks show that the scaling is a reliable way to correct finite cell effects in the interactions. As one can see from Table I the isolated adsorption energies reduce remarkably from the values calculated on the rectangular 2×2 surface. Note that this is a true finite size effect since our results agree well with the energies of Loffreda *et al.* [1]. The reduction of adsorption energies shows that the molecule-molecule interactions are quite long range and the rectangular 2×2 surface cell is too small to give reasonable isolated adsorption energies for molecules. All results presented in this Letter are calculated with the corrected adsorption energies and interaction parameters shown in Table III. The MC unit cell includes six symmetric adsorption sites (see Fig. 1) and the surface consists of 1600 metal atoms (40×40 surface). We tested various surface sizes but no size effects were found. The total energy of the adsorbate-surface system is expressed as

$$E_{\text{tot}} = \sum_i E_i^{\text{ads}} + \frac{1}{2} \sum E_{i,j}^{\text{int}}, \tag{2}$$

where E_i^{ads} is the adsorption energy of the molecule and $E_{i,j}^{\text{int}}$ is the pair interaction. The range of the interaction is classified by intermolecular distances, and four categories are needed so that there is at most only one interaction per category ($d_1 \leq 0.83$ Å, 0.83 Å $< d_2 \leq 2.22$ Å, 2.22 Å $< d_3 \leq 3.33$ Å, and $d_4 > 3.33$ Å). We emphasize that all the interaction parameters (Table III) used in MC simulations are constructed from first principles calculations and, although tedious, the computation of parameters is straightforward.

The MC simulations are performed as follows. The number of molecules and their types are fixed. All the molecules are put on random positions on the surface at

TABLE I. The molecule adsorption energies on the 3×3 cell ($\theta = 0.11$ ML) and on the rectangular 2×2 cell ($\theta = 0.25$ ML). The energies of Loffreda *et al.* [1] are given in parentheses.

Geometries	E_{ads} (eV) CO	E_{ads} (eV) NO
fcc	$-1.77, -1.99 \, (-2.01)$	$-1.90, -2.26 \, (-2.29)$
hcp	$-1.77, -1.99 \, (-1.98)$	$-1.90, -2.24 \, (-2.26)$
Bridge	$-1.52, -1.83 \, (-1.81)$	$-1.50, -1.93 \, (-1.96)$
Top	$-1.20, -1.44 \, (-1.36)$	$-0.78, -1.10 \, (-1.09)$

TABLE II. CO-NO interaction parameters on rectangular 2×2 (I) and 3×3 (II) cells. "Bri" is a "short-hand" notation for bridge.

Geometry	I (eV)	II (eV)	$d_{\text{NO-CO}}$ (Å)
NO(bri)-CO(fcc)	0.25	0.22	2.89
NO(bri)-CO(bri)	0.29	0.22	2.78
NO(bri)-CO(bri)	0.92	0.74	2.40
NO(hcp)-CO(fcc)	0.15	0.20	3.21
NO(hcp)-CO(hcp)	0.36	0.37	2.78
NO(bri)-CO(top)	0.71	0.58	2.40

TABLE III.   All the interaction parameters used in MC simulations are shown. In each distance category the parameters are in the following order: CO-CO, CO-NO, and NO-NO. Subscripts have values as follows: $n = 1, 2, 3$, $n \neq m = 1, 2, 3$. The value 100 is given to those interactions which have unrealistically high repulsion, or the geometry does not have molecules on that distance category.

Geometry	d_1	d_2	d_3	d_4
top-top	3×100	3×100	0.20, 0.21, 0.22	3×0.0
top-bri$_n$	3×100	6.65, 7.0, 7.35	0.42, 0.46, 0.51	3×0.05
top-fcc	3×100	2.04, 2.3, 2.5	0.05, 0.07, 0.04	3×0.0
top-hcp	3×100	2.04, 2.3, 2.5	0.06, 0.08, 0.05	3×0.0
bri$_n$-bri$_n$	3×100	3×100	0.24, 0.22, 0.27	3×0.0
bri$_n$-bri$_m$	3×100	5.15, 5.72, 6.3	0.73, 0.74, 0.79	0.2, 0.3, 04
bri$_n$-fcc	3×100	1.71, 1.67, 1.48	0.18, 0.22, 0.25	3×0.0
bri$_n$-hcp	3×100	1.73, 1.70, 1.49	0.18, 0.22, 0.25	3×0.0
fcc-fcc	3×100	3×100	0.33, 0.35, 0.37	3×0.0
fcc-hcp	3×100	6.1, 6.4, 6.7	0.18, 0.20, 0.26	3×0.0
hcp-hcp	3×100	3×100	0.35, 0.37, 0.40	3×0.0

very high temperature. The temperature is reduced during the simulation according to a standard annealing procedure so that the final temperature is approximately 150 K. From an adsorption site we allow a molecule to jump to any other site on the surface if that site is empty, exchange the position with a molecule on another site, and desorb from the surface or adsorb back on the surface. The molecules are not allowed to vibrate in the sites. A tentative movement is accepted or rejected according to the standard Metropolis algorithm. After a long enough run time (about 10^8 steps) the system will reach an equilibrium adsorption structure, which is independent of the initial conditions and, as we noticed by warming up the system again, is also independent of the annealing procedure. In saturation coverage studies we expose the surface to a surplus of CO and NO molecules (altogether 4000 molecules). Some of the molecules desorb and stay in gas phase which gives us a ratio of partial pressures although exact total pressure is unknown. These simulations mimic high pressure experiments. The MC results for adsorption of individual CO and NO molecules on Pd(111) are shown in Table IV. Both molecules occupy hollow sites at 0.25 ML coverage. At 0.5 ML, hollow sites are still the most probable adsorption sites but the occupancy of bridge sites is increased with increasing coverage and CO molecules begin to favor bridge sites more than NO molecules. Simulations give saturation coverage of 0.746 and 0.744 ML to CO
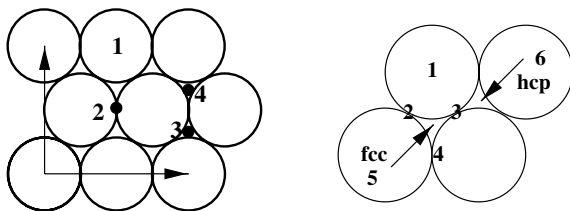
and NO, respectively, and the molecules reside on hollow and bridge sites but none is found from atop sites. This contradicts spectroscopic results, which indicate atop site adsorption [8,9]. However, it is nowadays well established that there are uncertainties in experimental site assignments at high-adsorbate coverage [10]. Theoretical saturation coverages are in excellent agreement with the experimentally determined value 0.75 ML. This indicates that the "volume" of the molecule is correct. NO adsorption is energetically more favorable at low coverage than CO adsorption, but at saturation coverage the difference is only 0.01 eV/mol. The adsorption energies become equal since the repulsive NO-NO interactions are larger than the corresponding CO-CO values.

Table V presents adsorption energies and structures for several CO/NO coverage ratios. The energy per molecule and coverage are independent of the ratio of partial

FIG. 1.   The left side shows the rectangular 2×2 surface cell which has sites top (1), bridge (2), fcc (3), and hcp (4). The MC simulation unit cell is on the right side having six sites: top (1), bridge (2,3,4), fcc (5), and hcp (6).

TABLE IV.   Data about individually adsorbed and coadsorbed CO and NO molecules as a function of coverage. The occupancy of a site is expressed in percentages. The last column shows the energy per molecule.

Molecule	Coverage	Site	%	E_{mol} (eV)
CO	0.25	Hollow	100	-1.77
	0.50	Hollow	77	-1.57
		Bridge	23	
	0.746	Hollow	57	-1.32
		Bridge	43	
NO	0.25	Hollow	100	-1.90
	0.50	Hollow	88	-1.62
		Bridge	12	
	0.744	Hollow	64	-1.33
		Bridge	36	
CO-NO (1/1)	0.25	Hollow	100	-1.84
	0.5	Hollow	76	-1.62
		Bridge	24	
	0.75	Hollow	59	-1.35
		Bridge	41	

TABLE V. Partial pressure ratios, coverage ratios, energy per molecule, and saturation coverage for coadsorption.

p_{CO}/p_{NO}	[CO]/[NO]	E_{tot} (eV)	θ
1/1	1/1	−1.35	0.75
1/2	1/1.72	−1.34	0.75
2/1	1.78/1	−1.34	0.75
1/3	1/2.46	−1.34	0.75
3/1	2.5/1	−1.32	0.75

pressure. The results show that the partial pressure ratio directly determines the surface concentration ratio, i.e., [CO]/[NO] = 1 with an equimolar mixture of gas phases CO and NO. Generally, most of the NO molecules reside on hollow sites regardless of the surface concentration ratio. Whereas CO molecules are more sensitive in the variation of coverage ratio, the occupancy of hollow sites alternates from 3% to 43% and for bridge sites the range is from 57% to 97%, please see Table VI. If the NO concentration on the surface is larger than that of CO, the NO molecules block hollow sites due to their higher adsorption energy and most of the CO molecules end up on bridge sites. When the surface coverage of CO increases and that of NO decreases, the amount of the free hollow sites increases and CO molecules move from bridge to hollow sites.

The coadsorption saturation coverage is always 0.75 ML and no island formation is observed. The CO-NO mixture forms an even overlayer on the Pd(111) surface, as seen in Fig. 2. These results are due to the similarity among NO-NO, CO-CO, and NO-CO interaction parameters.

This work is the first extensive combined DFT and MC study for CO-NO coadsorption and the results are very interesting. Our simulations clearly support the notion that adsorption takes place on hollow and bridge sites up to saturation coverage. This contradicts experimental site assignments which are usually based on the interpretation of IR spectra and indicate atop site adsorption at high coverage. Interpretation of experimental frequencies is done by comparing the molecule frequencies on surfaces to those measured for metal complexes. This is not necessarily a reliable way to determine an adsorption site, and experimental results may need a reexamination. We are currently studying vibrational frequencies and their behavior as a function of coverage using DFT calculations [11], in or-
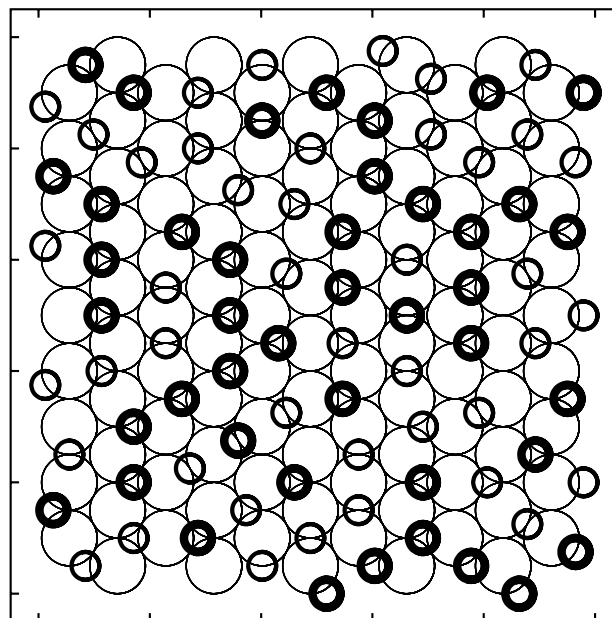

FIG. 2. Simulated coadsorption structure at 0.75 ML coverage with a 1/1 surface coverage ratio of molecule species. NO molecules are marked with thicker circles than CO molecules.

der to make direct comparison to the IR experiments. According to the MC simulations the theoretical saturation coverage is about 0.75 ML for pure CO, pure NO, and coadsorbed CO-NO. The excellent agreement with experimental results indicates that the volume of the molecule is correct.

TABLE VI. The occupation of a site expressed on a percentage with respect to a number of molecules per species and with different partial pressure ratios. The real number of molecules on that site is shown in parentheses.

p_{CO}/p_{NO}	CO: Bridge	CO: Hollow	NO: Bridge	NO: Hollow
1/1	76 (445)	24 (137)	7.8 (48)	92.2 (564)
2/1	61 (466)	39 (295)	4.4 (19)	95.6 (410)
1/2	90 (396)	10 (44)	12 (89)	88 (670)
3/1	57 (489)	43 (369)	5 (16)	95 (329)
1/3	97 (337)	3 (9)	16 (140)	84 (713)

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