Adsorption of carbon monoxide on palladium single crystal (110) *in Silico*

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Abstract
We have performed density functional theory calculations to investigate the adsorption of carbon monoxide, CO on Pd(110) substrate using CASTEP module. One adsorption site and the short bridge site have been focused, as those are known to be energetically preferred at fixed coverage. At 1 ML coverage the CO molecules repel each other preventing them from aligning exactly perpendicular to the surface. The energy contribution of the tilting to the chemisorptions energy by considering a (1×1) and (2×1) surface unit cell has been calculated. The mechanism of interacting the CO molecule with Pd surface has been studied by examining the partial density of states of this system.

Keywords: Chemisorption ; DFT; CASTEP; CO ; Pd (110)

1. Introduction
The design of new catalysts that display higher activity, stability and selectivity is the ultimate goal in the reforming of hydrocarbons since they have enormous potentials as fuel sources and petrochemical feedstock[1].

In the last decades, considerable attention have been focused on an understanding of the interactions between carbon monoxide and single-crystals transition metal surfaces. Not only can the chemisorption of CO on a metal surface be regarded as an exemplary adsorption system, it also has great industrial importance in such areas as the catalysis of CO hydrogenation to produce hydrocarbons and of CO oxidation in controlling automobile exhaust[2, 3]

Bradshaw and Hoffmann[2, 4] combined the infrared (IR) reflection with low-energy electron diffraction (LEED) methods to study the adsorption of CO on Pd (100) surface at room temperature. Their results suggested that there were two stable adsorption sites for CO on Pd (100) surface. At low coverage (Q represents the coverage), CO adsorbed on the bridge site and attained a binding energy of 150 kJ/mol (1.56 eV). The C–O stretch frequency of the bridge site varied from 1895 to 1949 cm^{-1} when the coverage was increased from 0 to 0.5 ML. The second peak at 2096 cm−1 was observed when directly exposing the clean surface to a CO pressure of 10^{-7} Torr with the crystal at 300 K. The authors[4] assigned the second peak to top site adsorption. Behm and coworkers[5] studied the same system by LEED and high-resolution electron energy loss spectroscopy (HREELS), but concluded that the CO molecule only adsorbed perpendicularly on bridge site of the Pd (100) surface. The distance from the carbon atom to the Pd surface was 1.36 ± 0.01 Å, the Pd–C and C–O bond lengths were 1.93 ± 0.07 and 1.15 ± 0.1 Å, respectively. The C–O vibrational frequency was observed within the range 1774–1944 cm^{-1}. Ab initio cluster wave function analysis[6] showed that the C–O stretch frequency decreased from the initially free CO vibration 2270 to 2076 cm^{-1} as the CO approached the surface. But this vibrational frequency has not been assigned.

It is well known that the susceptibility of carbon monoxide molecule to dissociate upon chemisorptions varies systematically depending on the position of the metal in the Periodic Table. Metals on the left side of the Periodic Table (mostly bcc type) dissociatively chemisorb CO,but metals on the right – hand side (mostly fcc type) chemisorb non-dissociatively[7]. The bond strength of the CO chemisorbed on fcc metals, measured as heats of adsorption, tends to decrease as we move rightwards along a row and upwards across a column of the Periodic Table[8].

The geometric and electronic structure of surfaces and adsorbate–substrate systems can routinely be calculated by modern quantum mechanical approaches. Continuous development of theoretical concepts and numerical improvement of existing algorithms allow for reliable simulations which have become an integral tool for the interpretation and microscopic understanding of many surface science experiments[9].

In general, two conceptually different theoretical approaches exist for electronic structure calculations of surfaces and bulk materials. In the first approach, the electronic Schrödinger equation (or Schrödinger-like variational equation for the density) is solved with respect to periodic boundary conditions. However, this super cell ansatz is currently restricted to Hartree–Fock (HF) and density functional theory (DFT). In Hartree–Fock, electron correlation is omitted by definition while in DFT the exact exchange–correlation functional is unknown. Despite recent developments in the construction of new functional [10-12] and promising proposals of theories beyond Hartree–Fock and DFT including periodic boundary conditions [13, 14], no generally accepted theory exists which provides a well-defined treatment of electron correlation with respect to periodic boundary conditions, in particular for systems characterized by a delocalized electronic structure.

In the second approach, a representative section of a surface, a cluster, is treated by either DFT or conventional quantum chemical methods [9, 15]. The latter approach allows for a well-defined treatment of electron correlation, since taking the HF solution of the electronic Schrödinger equation as a starting point, a systematic hierarchy of approximations exists to eventually arrive at the numerically exact solution (complete configuration interaction). Furthermore, the calculation of electronically excited states via configuration interaction (CI) is straightforward [9, 16, 17] in contrast to conventional DFT, although some promising concepts also exist within time-dependent density functional theory and the approximation to the self-energy [9, 18, 19].

The aim of the present work is to examine the Pd surface and its crucial role in a variety of catalytic reactions by understanding the adsorption of CO on Pd(110). The chemisorption of carbon monoxide on transition metals has already been the subject of numerous investigations, mainly because this is the simplest molecule one can use to study with such problems. In this context, DFT simulations can contribute to this understanding by the calculation of adsorption energies of the CO/Pd(110) system.

2. Theory

The CASTEP programme [20] is a first principles quantum mechanical code for performing electronic structure calculations. Within the density functional formalism it can be used to simulate a wide range of materials including crystalline solids, surfaces, molecules, liquids and amorphous materials; the properties of any material that can be thought of as an assembly of nuclei and electrons can be calculated with the only limitation being the finite speed and memory of the computers being used. This approach to simulation is extremely ambitious, given that the aim is to use no experimental (empirical) data, but to rely purely on quantum mechanics [21].

In this study, CASTEP which is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials. CASTEP is a first principles electronic structure code for predicting properties of materials. It employs the density functional theory plane-wave pseudopotential method, which allows to perform first-principles quantum mechanics calculations that explore the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites [22].

Typical applications involve studies of surface chemistry, structural properties, band structure, density of states, and optical properties. CASTEP can also be used to study the spatial distribution of the charge density and wave functions of a system.

CASTEP supports two schemes for geometry optimization: BFGS and damped molecular dynamics. The main advantage of the BFGS minimizer [23] is the ability to perform cell optimization, including optimization at fixed external stress. The BFGS scheme uses a starting Hessian which is recursively updated during optimization. The CASTEP implementation involves a Hessian in the mixed space of internal and cell degrees of freedom, so that both lattice parameters and atomic coordinates can be optimized. When cell optimization is

required, use of a finite basis set correction term is recommended. Calculating the term is not too costly (10-30% of the self-consistent electronic minimization at the first iteration) relative to the advantages that it provides. Cell optimization runs may be problematic if the finite basis set correction is not used or if the energy cutoff is so low that the correction is not accurate. In these circumstances, the optimization run may stop with a message which states that the energy has converged, but that the stress is still non-zero. The minimizer attempts to find the energy minimum rather than the stress zero-point, since the former is more meaningful under the circumstances[22].

Another potential pitfall is the use of the fixed basis size cell optimization setting when the starting geometry is very different from the final one. The finite basis set correction depends on the cell size and shape, although this dependence is disregarded by the minimizer. In addition, the effective cutoff energy changes when the cell geometry is modified with the above setting (it is the number of plane waves that is kept fixed). If this change takes the $dE_{tot}/d(\ln E_{cut})$ function far away from the point that was used to evaluate the finite basis set correction, the results will not be accurate. Therefore, you should compare the starting and final geometries and perform a completely new run starting from the final configuration if the difference between the two structures is large[22].

CASTEP can perform geometry optimization with constraints applied. The simplest type of constraint is to fix the atom positions. In CASTEP, this means fixing the fractional coordinates of the atoms. It is also possible to fix lattice parameters. Once again, it is only necessary to do this for parameters that are not fixed by symmetry. This type of constraint is often useful in phase stability studies when, for example, you want to fix the angles to 90°[24].

It is also possible to impose more general linear constraints on atomic coordinates. These constraints are specified using a matrix that transforms the Cartesian coordinates of all atoms to the subspace of unconstrained coordinates. This facility is intended for fixing, for example, the z-coordinates of atoms in slab calculations of surface processes[22]. Non-linear constraints refer to constraints on interatomic distances (bonds), angles, and torsions. Such constraints can be imposed using the delocalized internals optimizer.

Damped molecular dynamics presents an alternative method for geometry minimization that involves only internal coordinates (the cell parameters have to be fixed). The method uses the critical damping regime as a way of dealing with the ground state. The regime can be implemented either by using one damping coefficient for all degrees of freedom (coupled modes) or by using different coefficients for different degrees of freedom (independent modes). The latter approach allows you to freeze all modes, both fast and slow, simultaneously. Alternatively, you can perform steepest descents damping with a fixed coefficient. However, this is a less efficient approach. Indeed, it is not, strictly speaking, a molecular dynamics technique, since it solves first-order equations of motion and not second-order equations[25].

Both independent modes and coupled modes damped molecular dynamics runs can be performed with a bigger time step than undamped molecular dynamics simulations. When the system gets close to equilibrium, the time step can be increased even further, since the fast modes freeze out before the slow ones. CASTEP can automatically adjust the time step, leading to increased efficiency of the algorithm. It is also recommended recalculation of the damping coefficients periodically during a damped molecular dynamics run. A full description of the method implemented in CASTEP can be found elsewhere[26].

3. Results and discussion

In this study, DFT simulations can contribute to the understanding of the interaction between the carbon monoxide molecule and the palladium surface by addressing the following questions: Where does the molecule want to adsorb? , How many molecules will stick to the surface? , What is the adsorption energy? , What does the structure look like? And What are the mechanisms of adsorption?

We will focus on one adsorption site, the short bridge site, as it is known to be energetically preferred at fixed coverage. At 1 ML coverage the CO molecules repel each other preventing them from aligning exactly perpendicular to the surface. we will calculate the energy contribution of this tilting to the chemisorption energy by considering a (1×1) and (2×1) surface unit cell.

Figure 1 shows the unit cells for Pd bulk, Pd(110) surface , (1×1) CO on Pd(110) and (2×1) CO on Pd(110) constructed by Materials Studio 6.0 software from Accelrys Inc[25].

After construction of these unit cells, optimization of these structures takes place by using CASTEP module in Materials Studio 6.0 software. The quality of optimization is set to fine and the energy task is set to geometry optimization with optimize cell option is chosen. This procedures have been repeated in the optimization of

carbon monoxide molecule, pd(110) surface, (1×1) CO on Pd (110) and (2×1) CO on Pd (110). All these structures are relaxed using CASTEP geometry optimization module.

Figure 2 shows snapshots of the geometry optimization energy calculations for the following systems pd(110) surface, (1×1) CO on Pd (110) and (2×1) CO on Pd (110).

The chemisorptions energy ΔE_{chem} of CO on Palladium can be obtained from the following equation

$$\Delta E_{chem} = 0.5 \times E_{(2\times1)\ CO\ on\ Pd(110)} - E_{Pd(110)} - E_{CO\ molecule}$$

Allowing the CO atoms to tilt against each other, hence reducing the self repulsion of the CO molecules, should result in a gain in energy. The repulsion energy ΔE_{rep} can be calculated from the following equation:

$$\Delta E_{rep} = 0.5 \times E_{(2\times1)\ CO\ on\ Pd(110)} - E_{(1x1)\ CO\ on\ Pd(110)}$$

By using the above equations to calculate ΔE_{chem} and ΔE_{rep}, these have values of -2 and -0.1 , respectively as indicated in Table 1.
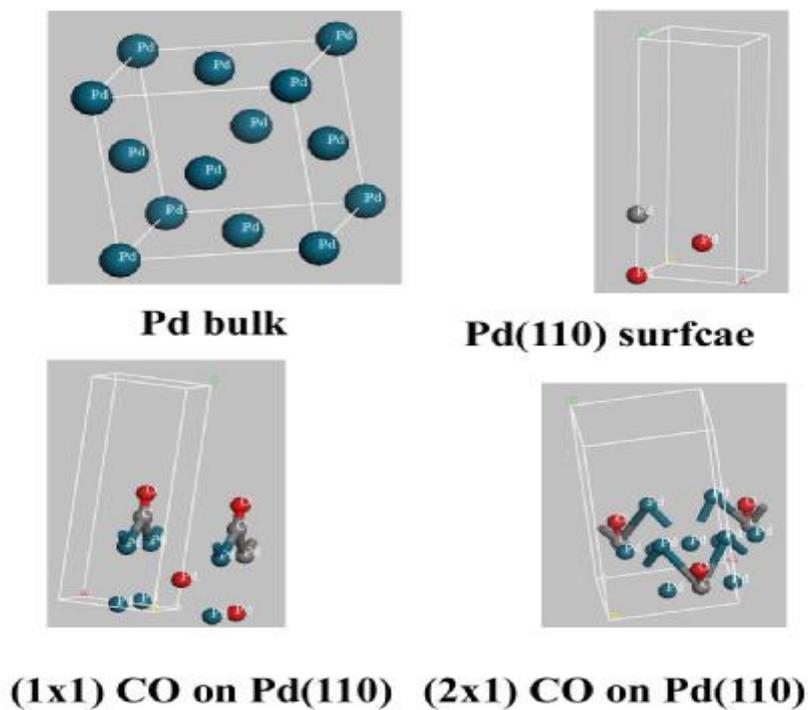
Figure 1 shows the unit cells for Pd bulk, Pd(110) surface , (1x1) CO on Pd(110) and (2x1) CO on Pd(110).

Table 1 shows the energy extracted from the CASTEP geometry optimization calculations.

	Energy in eV
CO molecule	-590.0
Pd(110)	-2393.0
(1×1) CO on Pd(110)	-2980.9
(2×1) CO on Pd(110)	-5962.0

To obtain an insight into the bonding mechanism of CO on Pd (110) we will examine the density of states (DOS).

Figure 3 shows the partial density of states (PDOS) for a single CO molecule and the same molecule adsorbed on the Pd surface. Comparing the graphes in Fig. 3 , it is clear that the electronic states of the isolated CO molecule at approximately -20, -5 and -2.5 eV are considerably lowered in energy as the CO binds to the Pd surface. In case of PDOS for (2×1) CO on Pd(110) it shows the effect of hyperdization with Pd states which manifests itself as broadening of the energy levels and their general shift towards lower energies.
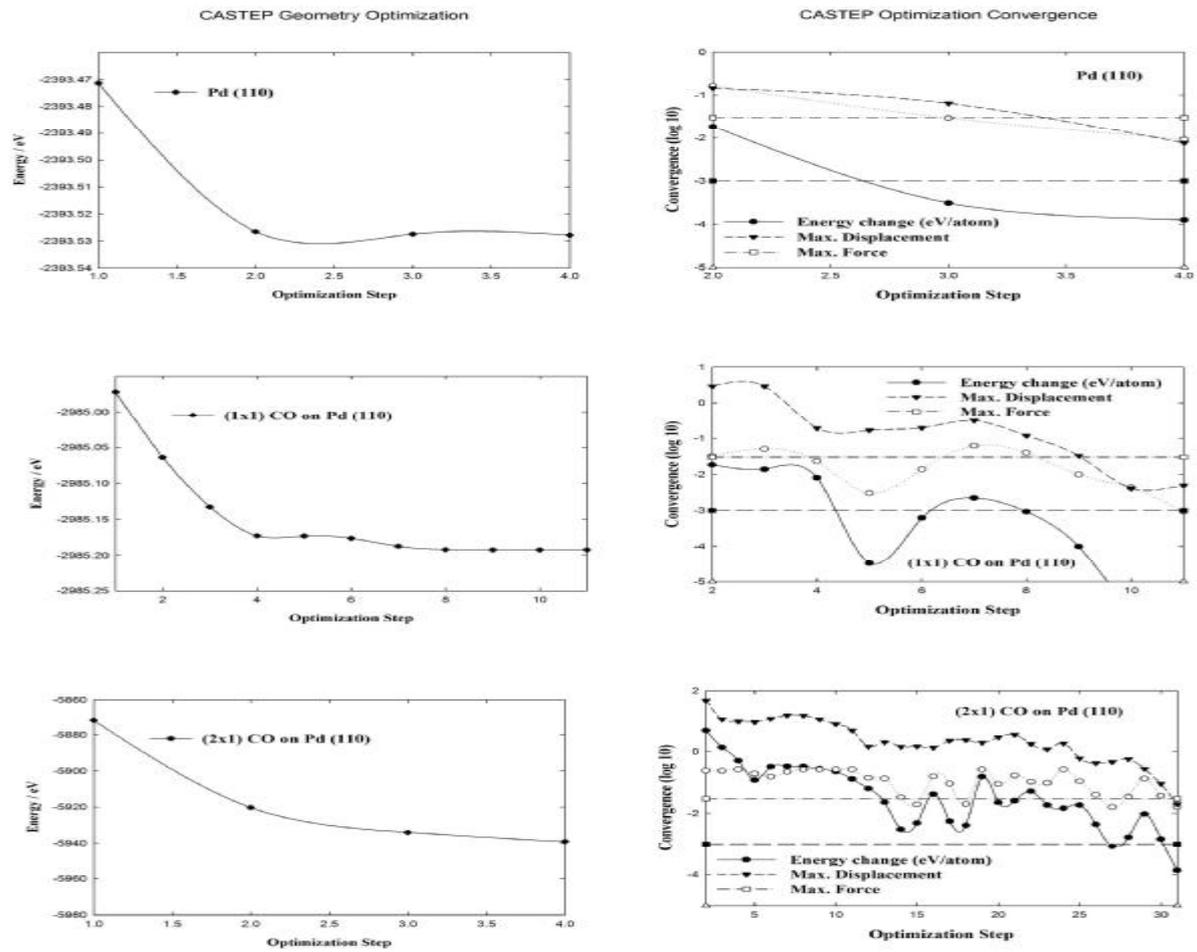
Figure 2 shows snapshots of the geometry optimization energy calculations for the following systems pd(110) surface, (1x1) CO on Pd (110) and (2x1) CO on Pd (110).
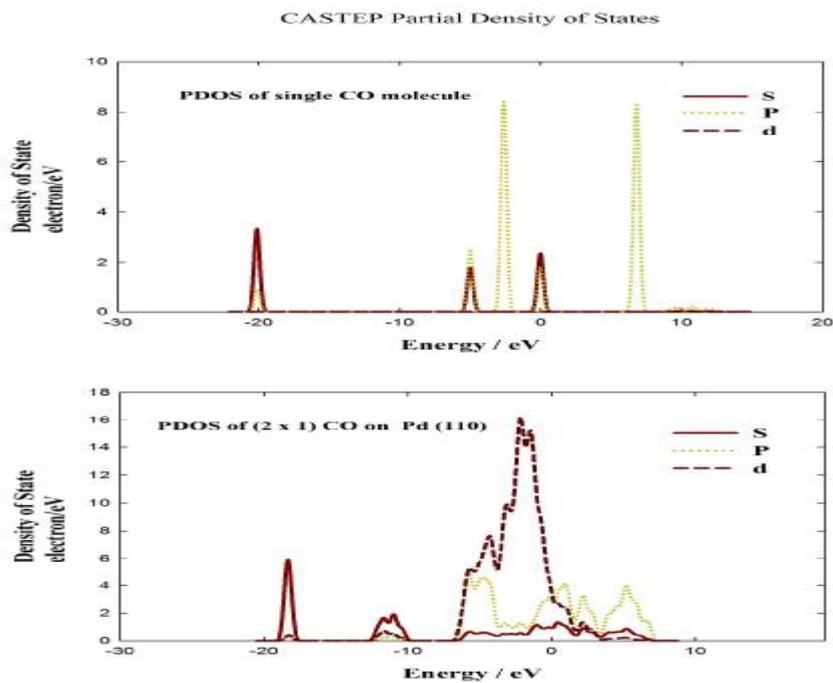
Figure 3 The partial density of states (PDOS) for a single CO molecule and the same molecule adsorbed on the Pd surface.

4. Conclusion

In summary, this study represents one of the first attempts to investigate the use of CASTEP module which is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science to perform first-principles quantum mechanics calculations that explore the properties of crystals and surfaces. The energy contribution of the tilting of CO on Pd(110) to the chemisorptions energy has been calculated by considering a (1×1) and (2×1) surface unit cell. The mechanism of interacting the CO molecule with Pd surface has been studied by examining the partial density of states of this system which manifests itself as broadening of the energy levels and their general shift towards lower energies.

Acknowledgements

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