

First-principles DFT study of ethylene adsorption on Pd(110)

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The structure and energetics of the ethylene-palladium adsorption system were investigated by means of first-principles DFT calculations. The calculations revealed that there exist two minimum energy configurations for the ethylene molecule π -bonded on Pd(110), one with the C = C axis aligned parallelly to the metal surface and the other, at very close energy, with the molecular axis tilted by about 6.5 deg. along the $[1, -1, 0]$ direction. Hence, below 280 K, ethylene is likely to flip between two symmetrical tilted states thereby lowering the local adsorption site symmetry to C_1 , as suggested by experimental observations. The calculated binding energy of the π -bonded ethylene on Pd(110) is about 0.9 eV.

The hydrogenation of ethylene on transition metal surfaces is an important catalytic industrial process. Its chemical mechanism has been investigated by Horiuti and Polanyi almost seventy years ago.¹⁾ Since then, a lot of efforts have been devoted toward its understanding by combining surface science and catalysis.²⁾

By employing surface science techniques, it has been observed that the interaction of ethylene, as well as that of other organic molecules, with various metal surfaces strongly depends on the type of metal and its surface morphology.³⁾ For instance, ethylene interacts weakly with the Ag(110) surface without undergoing decomposition, whereas it strongly binds on Ni and Pt surfaces following decomposition at low coverages.³⁾

Recent STM⁴⁾ and spectroscopic⁵⁾ measurements, carried out at RIKEN by the group of Kawai,^{4,5)} have established that the ethylene molecule is π -bonded on the Pd(110) surface at temperatures below 280 K. In particular, the analysis of the STM images indicated that the C = C axis of ethylene is aligned along the $[1, -1, 0]$ direction. Furthermore, from the assignment of the C-H and C = C stretching frequencies it appeared that the C = C axis is slightly tilted with respect to the metal surface plane. Tilting lowers the local symmetry of π -bonded ethylene from C_2 to C_1 .

To elucidate the nature of the ethylene-palladium adsorption system, we performed first-principles pseudopotential calculations with the CASTEP code.⁶⁾ A serial version of the code is implemented on the Fujitsu VPP-700E supercomputer. This approach, which derives from the Car-Parrinello (CP) method,⁷⁾ combines density functional theory (DFT) and the preconditioned conjugate gradient (CG) method⁶⁾ in order to compute the total force acting on each atom of the system under investigation. The CG method considerably reduces the computational cost of simulation, in comparison to the Verlet algorithm originally adopted by the CP method. The generalized gradient approximation (GGA) was employed in all calculations, along with ultrasoft pseudopotentials for Pd, C and H atoms, respectively.

We firstly investigated the high coverage case by employing a slab model consisting of a $c(2 \times 2)$ surface unit cell and five Pd layers (larger supercells will be considered in future calculations to study the low coverage regimes). The vacuum region in the above supercell corresponds to seven Pd layers. The supercell used here contains two ethylene molecules each one placed on the top of a Pd atom. The resulting structure was optimized by using a plane wave energy cutoff of 340 eV. The atomic positions were fully relaxed except for the unit cell parameters that were kept frozen at the values correspondent to the calculated Pd bulk.

In Fig. 1 it is shown the optimized geometry of ethylene adsorbed on the Pd(110) slab surface model. The C = C axis is oriented parallelly to the metal surface with the middle point of the C = C bond at 2.05 Å from the underlying Pd atom. The C-H bonds of ethylene are slightly bent upward, toward the vacuum, thereby indicating a certain degree of

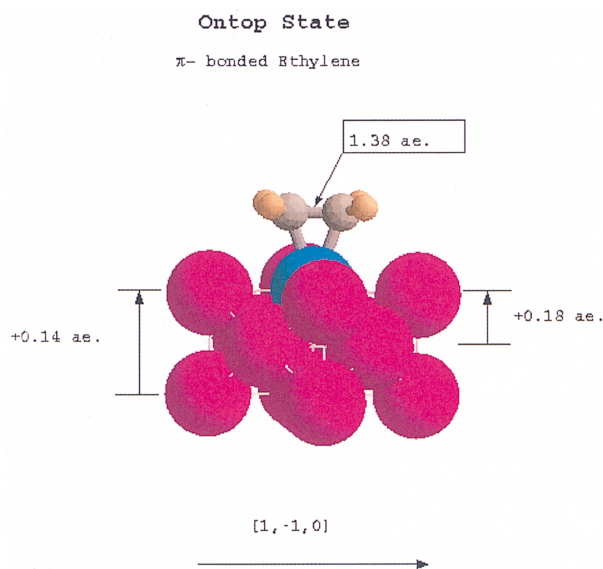


Fig. 1. Optimized slab model of the ethylene-Pd(110) adsorption system.

rehybridization of the carbon atoms upon interaction with the metal surface. The C = C bond length is at 1.384 Å and the C-H bond length at 1.078 Å, whereas in the isolated ethylene molecule these bonds are at 1.317 Å and at 1.079 Å, respectively.

Structural effects do involve the metal surface as well. Menzel⁽⁸⁾ have examined the structural data of over 20 adsorbate systems on the Ru(0001) surface. His analysis indicates that, in comparison to the clean metal surface, electronegative adsorbates expand the distance between the first and the second substrate layer whereas electropositive adsorbates contract it. For the ethylene molecule π -bonded on Pd(110) the present calculations indicate an expansion of the Pd layers. The first Pd layer expands by about +0.18 Å from the second one and by about +0.14 Å from the third one. Furthermore, the Pd atom interacting with ethylene is displaced toward the vacuum by about 0.13 Å with respect to its neighbours lying along the [1, -1, 0] direction.

We calculated the binding energy (ΔE_B) for ethylene adsorption by employing the following equation:

$$\Delta E_B = E_{\text{Pd/et}} - (E_{\text{Pd}} + E_{\text{et}})$$

where $E_{\text{Pd/et}}$, E_{Pd} and E_{et} are the energies of the ethylene-Pd adsorption system, Pd slab and free ethylene molecule, respectively. The ΔE_B calculated for the present model is about 0.9 eV, in satisfactory agreement with that obtained from thermal desorption spectroscopy (TDS) measurements.

An important feature characterizing the adsorption of ethylene on the clean Pd(110) surface at 150 K is the small tilting of the C = C axis along the [1, -1, 0] direction, as revealed by high resolution electron energy loss spectroscopy (HREELS). Interestingly, the tilted state disappears upon co-adsorption of hydrogen on Pd(110).⁽⁵⁾ To investigate the nature of the

tilted state, we performed a series of single point calculations by bending the Pd-ethylene bond axis with respect to the [1, -1, 0] direction. These simulations yielded a potential energy curve with a minimum at a tilt angle Θ of 6 degrees.

Relaxing the above tilted state yields $\Theta = 6.5^\circ$ and a binding energy close to that calculated for the ontop state. Notice that, as a consequence of the local symmetry of the adsorption site, there exists another minimum at $\Theta = -6.5^\circ$ degrees. Hence, at temperature regimes below 280 K, the ethylene molecule is expected to flip back and forth from -6.5 to $+6.5$ degrees, thereby lowering the overall symmetry of the ethylene-Pd(110) adsorption system to C_1 , as revealed by the HREELS measurements.

Further calculations will be performed to investigate the low coverage regimes as well as the co-adsorption of H_2 on the ethylene-Pd system. The final goal of the present study is to shed light on the nature of the chemical species formed upon the chemisorption of ethylene on the Pd(110) surface as well as to provide a theoretical view complementary to the above experimental findings.

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