Theoretical investigation of CO adsorption on Pd(111) and Pd(111) – Zn systems

Imre Bakó¹, Robert Schennach², Gábor Pálinkás¹

¹ Chemical Research Center, Institute of Structural Chemistry, Hungarian Academy of Sciences
² Institute of Solid State Physics, Graz University of Technology, Austria

Corresponding author: baki@chemres.hu

Abstract. The interaction of CO with solid surfaces is a topic of fundamental and applied interest. Nowadays there is an increasing attention on alternative energy carriers, like efficient in situ conversion of methanol to hydrogen. There are several studies in the literature about the catalytic activity of Pd and Rh for dehydrogenation of liquid methanol. It was also shown, that the Cu-ZnO, Pd-ZnO catalysts show a high activity for the dehydrogenation of methanol. At the same time these systems can also be used to catalyze the hydrogenation of CO and CO₂ to form methanol. In this work we performed theoretical calculations of 0.75 ML CO coverages on the Pd(111) and Pd(111)-Zn systems. The adsorption of CO on noble metals was already studied using STM techniques. Using the DFT techniques we can calculate the STM images so, we can delineate the detailed structure of the surface alloy films.

1. Introduction

The Pt-group metals, are among the most widely used catalysts [1]. They are also, however, among the most expensive metals. Thus there is a particular interest in modifying the properties of Pd to achieve higher activity, selectivity and more tolerance against CO poisoning in a catalytic reaction. In addition, a reduction of the amount of expensive Pt group metals needed in the catalyst is an important goal. Catalysts that combine two different metals are frequently used in reaction processes that are the core of the chemical and petrochemical industry. Highly active and selective catalysts for oxidative methanol reforming are based mainly on Cu, Cu-ZnO and Pd-ZnO[2,3]. Recent studies identified that the Pd-Zn alloy is one of the active components of novel efficient Pd-ZnO catalysts. Recent theoretical calculations[4] revealed that, the density of states of the valence band region of Pd-Zn alloys resembles that of metallic Cu. These calculations showed that the most stable overlayer on the Pd(111) surface is a Pd-Zn alloy with a Pd:Zn ratio of 1:1. However, also a Pd:Zn ratio of 3:1 is stable. A subsurface Zn layer is similar in stability to a 3:1 Pd-Zn overlayer.

In this work we calculated the adsorption and vibrational properties of CO molecules on Pd(111) and on Pd₃Zn₂, Pd₃Zn overlayers as well as on a Zn subsurface layer. We performed these calculations using high coverage (2x2-3CO) structures, as these are likely to be present under high pressure catalytic conditions.

Recently STM was used to study the different CO structures on the Pd(111) [5] surface. In this work we also present some calculated STM images of the different investigated surfaces.
2. Methods

All adsorption energies as well as the electronic and vibrational properties were calculated using the Vienna Ab Initio Simulation Package (VASP) [6,7]. Electron exchange and correlation effects were described by the Perdew–Burke–Emzerhof (PBE) [8] GGA type exchange-correlation functional using the spin restricted formalism. We adopted an energy cutoff of 400 eV throughout this work. The total energy of Pd had a minimum at 3.96 Å lattice constant, which is close to the experimental value (3.82). Geometry optimizations were performed on a supercell structure using periodic boundary conditions. The (111) surface is modeled by four layers of metal separated by a vacuum layer of approximately 15 Å. We used a supercell with a (2x2√3) surface unit cell comprising 8 atoms per layer. The three or four uppermost substrate layers and the CO molecules are allowed to relax, while the bottom layer of Pd atoms were held fixed in their bulk position. All atomic coordinates of the adsorbed species and the metal atoms in the relaxed metal layers were optimized to a force of less than 0.025 eV/Å on each atom. Brillouin zone integration was performed using a 7x7x1 Monkhorst–Pack grid and a Methfessel–Paxton smearing of 0.2 eV. In all cases convergence of the total energy with respect to the k-point set and with respect to the number of metal layers included is confirmed. The atomic charges in the molecules and the charge transfers from the metal to the CO molecule were calculated using the Bader decomposition scheme with the help of the Bader program developed by Henkelman et al [9].

Vibrational properties of adsorbed species were calculated by applying the finite–difference method to create the Hessian matrix, which was diagonalized to obtain the characteristic frequencies of the system. We calculated the dipole activity, which is related to the intensity obtained in RAIRS and HREELS spectra. This is proportional to the square of the dipole moment variation with respect to the surface normal for the corresponding mode. The simulated spectra were calculated with a 10 cm⁻¹ Gaussian broadening.

The free CO molecule is characterized by a calculated stretching frequency of 2120 cm⁻¹ at an equilibrated bond length of 1.146 Å. The corresponding experimental values are 2145 cm⁻¹ and 1.128 Å.

3. Results and Discussion

It has already been shown, that in the 2x2-3CO structure the CO molecules occupy the top and the hollow adsorption sites on the Pd(111) surface [5,10]. In our case the investigated structures are shown in Fig. 1. and the calculated geometrical and energetic properties are found in Table 1.

| A: Pd:Zn=2:2, B: Pd:Zn=3:1 | Zn subsurface |
|-----------------------------|----------------|
| -ΔE(eV) 1.52 | 0.70 | 1.141 | 0.85 |
| R_{co}(top, hcp, fcc) 1.158, 1.178, 1.179 | 1.157, 1.172, 1.171 | 1.153, 1.173, 1.175 | 1.149, 1.178, 1.179 |
| R_{pd}(top, hcp, fcc) 1900, 2.127, 2.121 | 1918, 1.958, 2.02 | 1917, 2.051, 2.061 | 1978, 2.147, 2.142 |
| R_{zc}(hcp, fcc) 2.821, 2.494 | 2.661, 2.701 |
| α_{CON}(top, hcp, fcc) 0.0, 0.0, 0.0 | 0.0, 23.0, 18.0 | 0.0, 18.0, 18.0 | 0.0, 0.0, 0.0 |
| ν_{CO}(top) 2081 | 2059 | 2068 | 2078 |
| ν_{CO}(hollow) 1850 | 1879 | 1920 | 1880 |
| Q_{CO}(top) -0.05 | -0.16 | -0.10 | -0.08 |
| Q_{CO}(hollow) -0.28 | -0.18 | -0.25 | -0.27 |
| Q_{ad}(top, hollow) 0.16, 0.23 | 0.00, 0.22 | 0.11, 0.19 | -0.05, 0.06 |

Distances are in Å, charge(Q) in e⁻ unit

The calculated energetic and geometric properties of CO molecules adsorbed on Pd(111) agree well with results from Loffreda et al. [11] The calculated CO distances give different values for different adsorption sites, but for the four investigated systems, the distances do not change significantly.
the Pd(111) and Pd(111)/Zn systems all of the CO molecules are perpendicular to the surface. On the Pd$_2$Zn$_2$ and Pd$_3$Zn the CO molecules adsorbed near the hollow site are tilted from the surface normal at about 18-23° pointing to the Zn atom. On the Pd$_4$Zn$_2$ system all of the hollow positions are closer to the Pd atom than to the Zn atoms (secondary top). The average adsorption energy of CO molecules decreases by about 0.67 eV in the Pd(111)/Zn system compared to the value on pure Pd(111). The adsorption energy also decreases significantly if the Pd:Zn ratio becomes smaller in the overlayer. Very similar results were found on Au, Ru and Ni, Pd and Pt monolayers supported on different transition metals [12-15]. This effect can be explained by the modification of the electronic and surface chemical properties of monolayers due to both strain and ligand effects [12]. The net charge transfer from the metal to the CO molecule was calculated using the Bader program. The charge transfer was different for different adsorption sites. From our calculations it became clear that there is a correlation between the charge on CO and the CO stretching frequencies in the case of top site adsorption. In the hollow sites this relationship is not so well defined. We also found that the positive charge on Pd near the CO molecule became smaller if the adsorption energy decreased. A detailed analysis of this correlation will be described in a following publication.

Figure 1. The investigated adsorption structure of CO on Pd(111) (A) Pd(111)/Zn (B). Pd$_2$Zn (C) and Pd$_2$Zn$_2$ (D)

A.  
B.  
C.  
D.

The STM is a very powerful tool to investigate different structures on metal surfaces. Today several theoretical tools help us to identify the observed structures on STM images. We simulated the STM image of all of the investigated systems using the multiply scattering formalism incorporated in the bSKAM 3.6 code [16] and the results are shown in Fig. 2. We do not show the simulated image for the Pd(111)/Zn system as it is very similar to the calculated image of CO on Pd(111) (A). In these two investigated systems we can observe on the image bright and spherical maxima, which are corresponding to the CO molecules positioned at top sites. These findings agree with earlier results. On the image from 2x2-3CO on the Pd$_2$Zn$_2$ system we can detect bright slightly deformed spherical spots on the same place as in the Pd(111) case. On the image of Pd$_2$Zn$_2$ system we can clearly detect a sombrero shaped [17] bright spot, on the site of the hollow (secondary top) adsorption site.

4. Conclusions
The energy and structures of 0.75ML CO on Pd-Zn surfaces have been calculated using DFT. In the surface alloys the CO molecules are tilted towards the Zn atoms. The calculated STM pictures show that the ordered structures should be observable. STM and IR measurements are currently done.
Figure 2. The simulated STM image for the 2x2-3CO structure on Pd(111) (A), Pd$_3$Zn (B) and Pd$_2$Zn$_2$ (C) surfaces. STM images are calculated with $V=1.0$ bias, constant height mode 6 Å above the surface.

Acknowledgments. This work was supported by the Austrian Science Fund (FWF). I.B. is indebted to the Hungarian Supercomputer center (NIIF) for computer resources and support from the Hungarian Scientific Research Fund OTKA, Project No. K 68140.

References
[1] Satterfield, J.H. Heterogeneous Catalysis in Industrial Practice, 2d, ed. McGraw-Hill: New York 1991.
[2] Trimm, D.L., Onsan, Z.I. 2001, Catal. Rev. 43, 31
[3] Takezawa, N., Iwasawa, 1997, Catal. Today 36 45
[4] Chen, Z.Xh., Neyman, K.M., Röscher, N. 2004, Surface Sci. 548 291
[5] Rose, M.K., Mitsu, T., Dunphy, J., Borg, A. Ogletree D.F., Salmeron, M., Sautet, P. 2002, Surface Sci. 512 48
[6] Kresse, G., Hafner, J. 1993, Phys. Rev. B 47 C558
[7] Kresse, G., Furthmüller, J. 1996 Comput. Mat. Sci. 6 15
[8] Perdew, J.P., Burke, K., Ernzerhof, M. 1996, Phys. Rev. Lett. 77 3865
[9] Henkelman, G., Arnaldsson, Jonsson H. 2006 Comput Mater Sci 36 354
[10] Bradshaw, A.M., Hoffman, F.M. 1978, Surface Sci. 72, 513
[11] Löffler, D., Simon, D., Sautet, P. 1999, Surface Sci. 425, 68
[12] Kitchin, J.R., Norskov, J.K., Barreteau, M.A. Chem, J.G. 2004, Phys. Rev. Lett. 93, 156801
[13] Sakong, S., Mosch, C., Groiß A. 2007, Phys. Chem. Chem. Phys. 9, 2216
[14] Liu, P., Norskov, J.K. 2001, Phys. Chem. Chem. Phys. 3, 3814
[15] Koper, M., Shubina, T. van Santen, R. A. 2002, J. Phys. Chem. B. 106, 686
[16] Palotas K., Hofer W.A. 2005 J. Phys. Cond. Matter 17, 2705
[17] Bocquet, M.L., Sautet, P. 1996, Surface Sci 360 128