



## A bonding study of CO–benzene co-adsorption on Rh(1 1 1)

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### ABSTRACT

The co-adsorption of carbon monoxide and benzene on Rh(1 1 1) has been studied using density functional calculations. We used the ordered  $p(3 \times 3)$  surface unit cell for the study. Besides, a comparison of the co-adsorption with CO and benzene two-dimensional networks is also given. The hydrogen of the benzene ring presents a bonding angle of  $26^\circ$ . The electronic structure reveals that the CO does not interact with benzene. Regarding the bonding, the Rh–Rh overlap population decreases 36.7% after co-adsorption, which is almost, the same decrease after CO adsorption. The CO–benzene interaction is very weak and a small  $H_{\text{benzene}-\text{CO}}$  OP of 0.001 is detected.

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### 1. Introduction

The adsorption of aromatic molecules on metals is of relevance in several fields of chemical sciences and technology [1,2]. The catalytic conversion of aromatic molecules is an important process in the chemical and petrochemical industries, both for environmental and economical reasons [3,4].

The chemisorption of benzene was studied both experimentally and theoretically at low coverage. On close-packed transition metals bonded benzene lies parallel to the surface through the  $\pi$  electron system [5,6]. The co-adsorption with CO presents ordered structures of benzene on transition metals surfaces and has been experimentally studied on Ru(0001) [7,8], Pd(111) [9,10], Pt(111) [11,12], Ni(100) and Ni(111) [13–16] and Rh(111) [11,17–19]. In the case of Rh(111) [11,20], several surface science techniques suggested a 3-fold hollow site for the benzene molecule in presence of CO as an impurity. Theoretical semiempirical methods were used to study the adsorption of benzene on TMS [12,21–23]. On the other hand, ab-initio calculations were performed for benzene on Pt and Ni surfaces [3,24–26].

The co-adsorption of benzene and CO, the subject of this study, provides two additional aspects: mutual structural effects between the different molecules, and contrasting effects on the substrate due to the different adsorbates [27].

Witte et al. studied the low frequency phonon dispersion curves for clear Rh(111) and ordered monolayers of CO and benzene [28]. HREELS determined that the adsorption is in one config-

uration instead of a mixture of bridge and hcp structures [11]. STM studies shown that the mobility of benzene decreases in presence of CO observing two ordered domains [29,30]. Rh pre-covered with CO present a  $3 \times 3$  benzene overlayer with two CO molecules per unit cell [29,30]. LEED experiments examined in detail the co-adsorption either in  $c(2\sqrt{3} \times 3)\text{Rect}$  or  $(3 \times 3)$  structures [18,19,31,32]. Morin et al. calculated that the adsorption of benzene with CO-preadsorbed Rh(111) is more stable on hcp than in bridge location ( $\Delta E = 0.23$  eV). This difference is bigger to that obtained in the case of pure benzene adsorption. This can explain the fact that benzene is experimentally found in hcp sites when CO is preadsorbed [33].

Morin et al. have calculated that the adsorption sites for benzene are bridge positions in Pt(111), while in Pd(111) and Rh(111) bridge and hollow position have similar energies values. For the co-adsorption with CO they found the hcp sites as slightly more stable [33].

In this paper, we present a bonding study of the chemisorption of benzene on Rh(111) based on density functional calculations.

### 2. Theoretical method

All calculations described herein were performed within the framework of density functional theory (DFT) as implemented in the Amsterdam Density Functional 2000 package (ADF2000) [34]. The molecular orbitals were represented as linear combinations of Slater functions. The gradient correction the Becke [35] approximation for the exchange energy functional and the B3LYP [36] approximation for the correlation functional were employed. In order to increase the computational efficiency, the innermost atomic shells of electrons are kept frozen for every atom except

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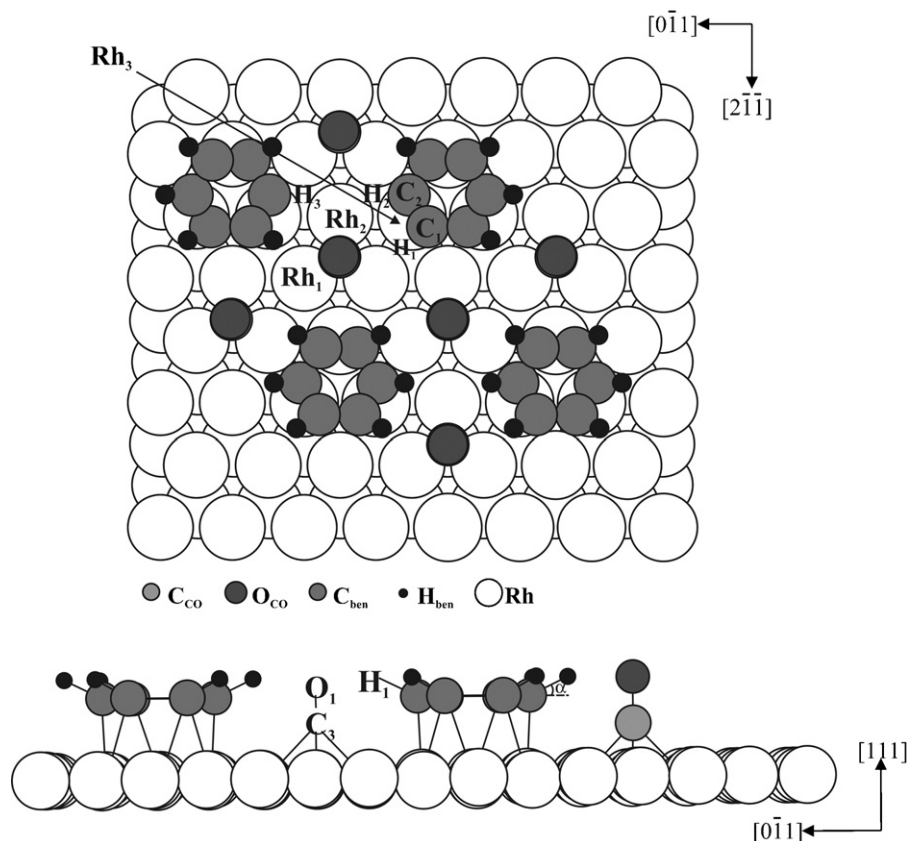


Fig. 1. Schematic top (up) and lateral (down) view of the  $(\text{C}_6\text{H}_6)_4-(\text{CO})_6/\text{Rh}$  system.

hydrogen, since the internal electrons do not contribute significantly to the bonding. We have used a triple-zeta basis set (this means three Slater-type functions for each atomic valence orbital occupied) with polarization functions to express the atomic orbitals of Rh. The basis set of Rh consisted of 4d and 5s orbitals.

Rh is face cubic centered (fcc) metal, and the (111) surface is the close-packed surface. We used the experimental adsorption geometry determined by Barbieri et al. [27]. The carbon monoxide molecules were taken to stand perpendicular to the surface on hcp sites ring and buckling distortions were also considered. Our computed out-of-plane angle was  $26.0^\circ$ . Morin et al. determined the hcp and bridge adsorption sites have almost the same adsorption energy. Minot et al. showed the hcp is the best configuration on an  $\text{Rh}_6$  cluster [23]. Using theoretical calculation Sautet and Joachim proposed the hcp adsorption for benzene [37]. The computed out-of-plane C–H angle was  $15^\circ$  or  $32^\circ$  [33] and  $20^\circ$  [23].

The average perpendicular distance between the aromatic ring and the first Rh layer is  $2.070 \text{ \AA}$ . The shortest Rh–Rh bond distance was  $2.689 \text{ \AA}$ . Carbon–hydrogen bond distances are almost the same to that in the gas phase benzene. The CO distance remains similar (+4.6%) to the vacuum value [38]. The supercell chosen corresponds to a  $p(3 \times 3)$  superstructure of the adsorbed benzene molecule + 2 CO molecule on  $\text{Rh}_{36}$  (see Fig. 1) [27]. A slab consisting of four layers of metal atoms for the surface was used with the two upper most layers allowed to relax. The vacuum space was set to an equivalent of five layers of metal. The molecules were adsorbed on one side of the slab. In fact, the literature reports the accuracy of this methodology [39,40]. The adsorption energies were calculated taking the difference between the total adsorbate/surface system and the individual surface and individual adsorbate. The calculated lattice constant in bulk Rh  $a = 3.845 \text{ \AA}$  compare well with the experimental values ( $3.803 \text{ \AA}$ ).

**Table 1**  
Electron density, overlap population (OP), charge and distances for a Rh, a  $(\text{C}_6\text{H}_6)$  and a  $(\text{CO})$  clusters.

Structure	Electron orbital occupation			Bond type	OP	Distance ( $\text{\AA}$ )
	s	p	d			
Rh						
Rh <sub>1</sub>	0.45	0.29	8.06	Rh <sub>1</sub> –Rh <sub>2</sub>	0.199	2.689
$(\text{C}_6\text{H}_6)_4$ ideal lattice <sup>a</sup>						
H <sub>1</sub>	0.68	0.00	0.00	C <sub>1</sub> –C <sub>2</sub>	0.611	1.367
C <sub>1</sub>	0.94	1.33	0.00	C <sub>1</sub> –H <sub>1</sub>	0.580	1.090
$(\text{CO})_6$ ideal lattice <sup>a</sup>						
C <sub>3</sub>	0.43	0.36	0.00	C <sub>3</sub> –O <sub>1</sub>	0.815	1.180
O <sub>1</sub>	1.63	3.58	0.00			

<sup>a</sup> The ideal lattice is an hypothetical network considered only benzene or CO in the same arrangement as in the adsorbed state without the metal layers.

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