

MODELLING OF THE TRANSITION PHASE AND ENERGY FOR THE ADSORPTION OF CO ON RHODIUM ATOMS INTERFACED WITH NIOBIUM

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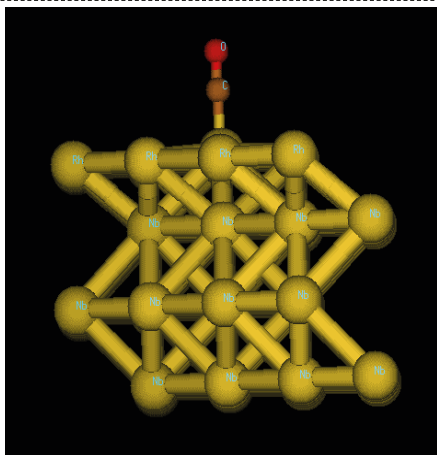
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Side view of optimized adsorption geometry for adsorbed CO on the Rh/Nb interface.

Graphical Abstract (GA)

Abstract: In this study we present a theoretical modeling for the explanation of the transition phase and energy needed for the adsorption of CO on top of the rhodium atoms interfaced with Nb. A periodic method based on the Density Functional Theory (DFT) formalism and PW91 and vdW-DF functional, two different bind sites preferences for CO were investigated. We can demonstrate that the C-O distance indicates a considerable loss of double-bond character upon adsorption. It is observed that the adsorption energy for the adsorption hollow is much more favorable than on top site in both PW91 and vdW-DF functional.

Keywords: CO adsorption; Rh/Nb interface; DFT; vdW-DF; Molecular adsorption.

INTRODUCTION

During the last two decades, CO on catalysts have received much attention due to their catalytic activity in many important processes¹⁻⁶. Many different bimetallic catalysts studies for the carbon monoxide hydrogenation may be considered essential to many industrial catalytic processes because of advantages. In this case we can improved stability and reducibility, slower deactivation,

and noticeable increase in catalytic activity and selectivity in comparison to the monometallic constituents^{7,8}. Friedman et al⁹ were the first who investigated the carbon monoxide hydrogenation activities and product distributions for the bimetallic Co-Rh/Nb₂O₅ catalysts, after low temperature reduction (LTR, 533–573 K) and high temperature reduction (HTR, 773 K) of the catalysts.

We know that kinetics and surface adsorption studies for adsorption on metallic surfaces are very little in the literature, in particular for CO^{1,4,6}. Some authors studied the kinetic parameters for the CO adsorption; however, the reported reaction mechanisms for these reactions cannot be comparing with experiments. Most reactions mechanisms studied for the bimetallic surface reactions were extrapolated for the CO reaction without sufficient evidence on the surface reaction structures under different reaction conditions. Metallic supported catalysts used for the CO reaction deserves specific characterizations. In this case, theoretical modeling for the explanation of the transition phase and energy needed for the adsorption of CO on top of the Rh atoms interfaced with Nb oxide species. Therefore, we believe that the product distribution will depend on the adsorption capacity of the different compounds on surface during the reaction⁹.

The determination of surface structure and reactivity is generally scarce on experimental studies. Nowadays we know that an immense arsenal of available surface techniques that are used as routinely tool in surface science.

The CO adsorption on transition metals and bimetallic surfaces has been studied by many theoreticians and experimenters. There are several technical applications and environmental implications. For this type of system, density functional theory (DFT) has become one of the major tools for theoretical

investigations.

Theoretical studies based on DFT are also of fundamental importance in molecular and materials modeling because can confirm or discard hypothesis about structure and reactivity of the systems. Nowadays with the growing computational facilities make it possible to use total energy methods to compute the structure of reactants and products in a chemical reaction. Modern DFT is less computational demanding than ab-initio wave function-based methods and is also accurate enough to permit the study of rather complicated systems, especially in condensed matter; this is solid and surfaces without or with adsorbents. DFT approach depends on the approximation of the exchange-correlation (XC) functional. Usually go beyond the well-known local density approximation (LDA) and are based either on the generalized gradient approximation (GGA) or on hybrid functionalism¹⁰⁻¹³.

Therefore, became necessary to do studies to understand the interactions between bind molecules to noble metals substrates. In this systems is of crucial importance in molecular scale electronics and self-assembly, where the competition between molecule substrate and intermolecular interactions can lead to template arrangements with specific spectroscopic and transport properties^{14,15}. Is of fundamental importance understand as the forces driving the formation of these molecules-inorganic assemblies often include both local chemical bonding and non-specific long-range interactions, it is essential to have an accurate description of both contributions¹⁶. Knows that density functional theory (DFT) provides a many-particle framework that, in principle, incorporates both local and nonlocal interactions, common semi-local approximations to DFT neglect long-range attractive contributions to van der Waals interactions, so-called "London dispersion

forces". Many different studies show progress has been made towards including London dispersion corrections within standard DFT. Nowadays a fully first-principles van der Waals density functional (vdW-DF)^{17,18} has been developed to accurately include the effects of London dispersion forces. This method has been shown to be relatively accurate and lower computational cost. The term "vdW forces" includes forces due to permanent-dipole dipole interactions, permanent-dipole and induced-dipole interactions, and instantaneous induced-dipole induced-dipole interactions, also called London dispersion forces. The most widely used implementations of DFT do not include the nonlocal London dispersion forces.

In this study the adsorption energies, binding site preferences and geometries of CO on the Rh/Nb interface are determined by means of DFT calculations employing the method PW91 and vdW-DF. Therefore, the purpose is precisely to determine and compare the geometry, binding site preference and adsorption energies of CO on the Rh/Nb interfaces by mean suitable DFT calculation. Consequently, an accurate characterization of the adsorption site, adsorption modes and packing arrangement become to be a necessary step towards understanding the subsequent surface processes, because unfortunately. In literature there is no structural information available for CO on Rh/Nb interface of bimetallic catalysts. We expect that this structural information will help to understand the reactivity of CO on metal surface.

Nowadays we know that there are two major strategies commonly used to model a surface, the cluster approach, and the periodic super cell. The cluster model approach is thought to capture the essential features of the chemisorption bond and to be able to predict local properties such as adsorption geometries and vibrational frequencies in the limit of

extremely low coverage^{19,20}. The alternative much more effective is the super cell approach based on the use of periodic slabs constructed to exploit the translational symmetry of the system.

In literature, the advantage of super cell model is connected to the fact that they are well suited to study the influence of the adsorbate coverage on the surface. Density functional theoretical methods for the prediction of binding and adsorption energies is typically within 5-8 kcal/mol of the reported experimental values²¹⁻²⁴.

In addition, we must highlight that the results reported herein are based only on the electronic energies. A more accurate calculation requires the calculation of zero-point energy corrections as well as changes in the specific heat in going from 0 K to the specified reference temperature.

EXPERIMENTAL

The calculations were carried out using self-consistent density functional theory. The DACAPO package²⁵ and GPAW package²⁶ were employed. For the DACAPO package the ionic cores and their interaction with valence electrons are described by ultra-soft pseudo potentials^{27,28}. We fixed convergence of the plane-wave expansion was obtained with a cut-off energy of 400 eV. For this work tests showed that using this value the converged calculation error was lower than 0.001 eV. Electron exchange and correlation effects were described by the generalized gradient approximation (GGA), using the functional described by Perdew–Wang (PW91)²⁹. In previous works PW91 is known to typically overestimate the adsorption energies. The Kohn Sham equations were solved self-consistently by using an iterative matrix diagonalization scheme. Brillouin zone integrations were performed on a grid of $5 \times 5 \times 1$ Monkhorst–Pack special k-points³⁰⁻³⁵.

In this case a Methfessel–Paxton smearing of width $\sigma = 0.2$ eV was used³⁶.

In this work to describe the adsorption CO on RhNb interface, a molecule interacting with a surface, it is also interesting that the vdW forces has been well described as suggested by³⁷. In previous works were observed that in vdW-DF method the vdW interaction is correctly described as an effect originating in the tails of the electron distribution, and it is well suited to include effects of image planes³⁸.

The GPAW code is an all-electron DFT code based on projector augmented waves³⁹ (PAW) and using finite differences. GGA allows to determine the electron density and part of the total energy followed by non-self-consistent calculations to determine the total energy within vdW-DF. This allowed us to focus on either the GGA need for accuracy in choice of computational⁴⁰⁻⁴² or the vdW-DF need for accuracy in other parameters and methods⁴³⁻⁴⁴. For this work was choosed the real-space grid for representing the wave functions in the PAW procedure to have a distance less than 0.11 Å between nearest-neighbor (nm) grid points. The (valence) electron density is represented on the same grid with additional grid points at half the nm distance, values obtained from interpolation of the electron density grids is important for the quality of the evaluation of the nonlocal correlation contribution⁴³.

Brillouin zone integrations were performed on a grid of $4 \times 4 \times 1$ Monkhorst–Pack special k-points⁴⁵⁻⁵⁰. In this case a Methfessel–Paxton smearing of width $\sigma = 0.2$ eV was used⁵¹. Optimized geometries were found when the forces on atoms were smaller than 0.05 eV/Å².

We using Rh/Nb surface represented with a slab containing four atomic metal layers. A slab with six atomic layers was tested but the results were similar. Therefore, a slab with four layers provides converged results, with accuracy higher than 0.04 eV. Consequently,

a slab with four atomic layers should be appropriate. A three-dimensional periodic cell was constructed including a vacuum gap of 10 Å in the perpendicular direction to the metallic surface. The thickness of this vacuum region was found to be adequate to eliminate any interaction between adjacent metal slabs.

In this present study CO was adsorbed on the Rh/Nb interface. The adsorbate specie was placed in one side of the slab and its geometry could optimize completely together with the two uppermost layers of the surface. Therefore, the remaining atoms of the slab were frozen at the bulk optimized positions. The adsorption energy (E_{ads}) was calculated in both cases as the difference between the energy of the adsorbed molecule ($E_{adsorbate/surface}$) and the sum of the free surface ($E_{surface}$) and the gas-phase molecule ($E_{gas-phase}$) energies, and thus:

$$E_{ads} = E_{adsorbate/surface} - (E_{surface} + E_{gas-phase}).$$

We can see that a negative value indicates an exothermic chemisorption process and releases heat. The calculated energies here refer only to the change of the electronic energy. Our system used a large box of $16 \times 16 \times 16 \text{ \AA}^3$ to obtain the gas-phase molecule energies. The optimized geometries of the CO predict bond distances and bond angles.

Our calculations shown that for the CO molecule in the gas-phase a distance (C1-C2) of 1.12 Å, which agree well with experimental value that is 1.1 Å.

Many different configurations of molecular adsorption on the Rh/Nb interface were examined in order to determine the orientation and site preference of the CO molecule, in accordance with our results. Our calculations yield the attractive adsorbate-substrate interaction only when the molecule is adsorbed on the on top and hollow sites that correspond to stable stationary point with minimum energy.

RESULTS AND DISCUSSION

The two minimum energy structures have quite similar geometries and completely different adsorption energies, indicating that the bonding is dominated by adsorption site. CO adsorbs on Rh/Nb interface with the carbon pointing into the metal surface with a C-O distance of 1.17 and 1.21 Å for the on top and hollow modes in PW91 and 1.16 and 1.23 Å for the on top and hollow modes in vdW-DF, respectively. These distances are a few longer from the calculated value for the gas-phase CO (1.1 Å). The distances from the C to the nearest Rh atoms are 1.85 and 2.05 Å for onto and hollow sites in PW91 and 1.94 and 2.07 Å for onto and hollow sites in vdW-DF. The minima also have quite close geometries. The calculated adsorption energies are -1.6325 eV and -2.5499 eV for the on top and hollow modes in PW91 and -1.8288 eV and -2.2261 eV for onto and hollow sites in vdW-DF, respectively. These results add further support to the conclusion. These data suggest that the two adsorption modes are very different.

The adsorption in hollow site seem to be more favorable. In this presented study we can see that the adsorption energy can be interpreted by decomposing it into two main contributions that are the energy cost to distort CO from its gas-phase structure to that of adsorbed CO and the energy gain to adsorb the distorted molecule. Experimentally we observed that the activity increase in the CO hydrogenation reaction depends on the adsorption of CO molecules caused by mild decoration of Rh metal by support species like NbOx. In this case these species, associated with Rh, enhanced CO dissociation further. Tables 1 and 2 present the binding energies and geometric data for these two stable surface structures.

Surface	Rh/Nb interface	
	ontop	Hollow FCC
E_{ads} (eV)	-1.63	-2.54
E_{ads} (kJ/mol)	-157.51	-246.02
d (C-O)	1.17	1.21
d (C-Rh)	1.85	2.05

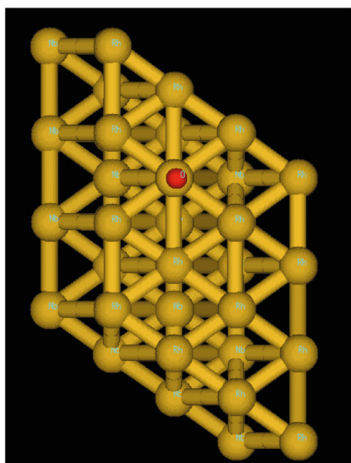
Table 1. Adsorption energies and structural data (distances (d) in Angstroms, h (C-Rh) is the height of the atom C on the surface, taking as zero the most upper metal atom) for CO adsorbed on RhNb bimetallic surface, PW91 results.

Surface	Rh/Nb catalyst	
	ontop	Hollow FCC
E_{ads} (eV)	-1.82	-2.22
E_{ads} (kJ/mol)	-176.45	-214.78
d (C-O)	1.16	1.23
d (C-Rh)	1.94	2.07

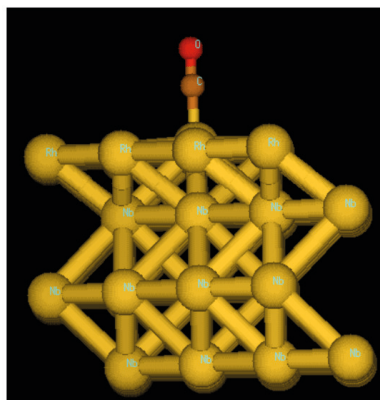
Table 2. In this table we can see the adsorption energies and structural data (distances (d) in Angstroms, h (C-Rh) is the height of the atom C on the surface, taking as zero the most upper metal atom) for CO adsorbed on RhNb bimetallic surface, vdW-DF results.

In Figure 1 the on-top and side view snapshots of optimized structures are shown.

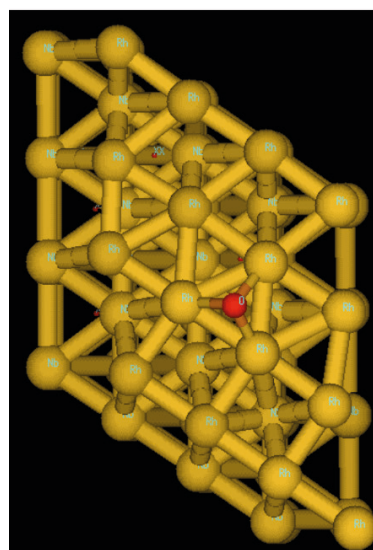
(a)



(b)



(c)



(d)

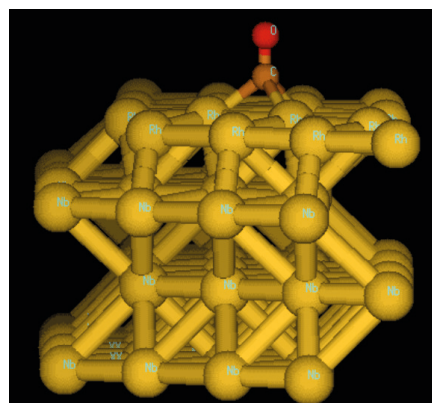


Figure 1: Top and side views of optimized adsorption geometries for adsorbed CO on the Rh/Nb interface. (a-b) on top and (c-d) hollow adsorption modes, respectively.

In previous studies XPS results were reported for the CoNb, RhNb and bimetallic RhCoNb catalysts in the calcined form⁵³ showed that rather thick Co₃O₄ islands exist on 2.7–4.4% of the support surface and that these islands were themselves covered with a Rh oxide layer. In between these islands was a sub-monolayer, fully dispersed Co²⁺ species and Rh₂O₃/Co₃O₄ islands⁵². We can see that this suggests that the calcined Rh+Co islands maintain almost the same surface area after low temperature reduction which are active (and not the dispersed Co species). Therefore, the XPS showed that the topmost atomic layers of these Rh+Co islands are approximately pure Rh, at least in the calcined form. It was shown that the addition of Co inhibited the gain of metal surface area after low temperature reduction of the calcined Rh/Nb catalyst. The high dispersion on the pure Rh/Nb catalyst explains the loss of active metal area upon high reduction temperature, which explains higher susceptible to Rh decoration by support species or to sintering.

The activity increase in the CO hydrogenation reaction was caused by mild decoration of Rh metal by support species, like NbO_x⁵². These species, associated with Rh, enhanced the CO dissociation. Also, can see that when the decoration increased, the Rh sites were completely hindered by those support species, and become inaccessible to chemisorption, and consequently the reaction.

In previous study we observed that higher molecular weight olefins (C₅-12 and C₁₃-18) were detected on the Rh/Nb catalyst only. It is worth emphasizing that the Rh/Nb catalyst, that presented a quite diversified and an uncommon product distribution for a Rh-based catalyst. Among the products, we detected there high-molecular-weight olefins, alcohols from ethanol to butanol, and saturated hydrocarbons from 1 to 27 carbon atoms⁵².

The selectivity to methane and C₂-4 hydrocarbons for the bimetallic did not change markedly with increasing Rh content. In fact, we observed that the activity (TOF) for CO conversion was nearly independent of Rh content in the bimetallic sample. In this work it becomes necessary that this may be due to the topmost atomic layers of the Rh+Co islands, being nearly pure Rh (as shown by XPS in their calcined state).

Our GGA and vdW-DF calculated binding energies are in good agreement with the experimental results. Many different studies shown that the PW91 energy functional is known to give usually somewhat too large chemisorption energies²⁹. We emphasize that GGA is not able to describe the dispersion (i.e. Van der Waals) interactions that are known to be the driving force for physisorption⁵³.

CONCLUSIONS

In summary, the adsorption of CO on the Rh/Nb interface has been investigated by means of DFT calculations using the GGA XC and vdW-DF functional and slab periodic model for the metal surface. The structure of adsorbed CO is a little similar in two on top and hollow sites. In present study we can see that the most stable adsorption mode has been characterized with the C atom bounded to one metal atom. The C-O distances are longer from the calculated value for the gas-phase CO (1.1 Å). It is worth emphasizing that the significant lingering of the C-O distance indicates a considerable loss of double-bond character upon adsorption. In this study our calculations show that the adsorption energy for the adsorption hollow is much more favorable than on top site in both PW91 and vdW-DF functional.

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