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Ab initio cluster model comparative study of atomic oxygen and sulfur chemisorption on Pt(1 1 1) surface: relevance to heterogeneous catalysis

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Abstract

Chemisorption of atomic oxygen and sulfur on Pt(1 1 1) has been studied by means of the ab initio cluster model approach. For both adsorbates, we consider chemisorption on the threefold open site of the Pt(1 1 1) surface which is represented by a Pt_{25} cluster model having 12 atoms in the first layer, six in the second and seven in the third. The ab initio molecular orbital Hartree–Fock method and explicitly correlated wavefunctions are used to obtain a reliable estimate of the interaction energy, vibrational frequency for the normal mode of the adsorbate above the surface, and the equilibrium geometry. The chemisorption bond is analyzed using different theoretical techniques including the constrained space orbital variation, CSOV, method, the analysis of dipole moment curves and the use of projection operators. The influence of electronic correlation effects is analyzed using multireference configuration interaction, MRCI, techniques and also, by using post-Hartree–Fock correlation functionals.

Keywords: Chemisorption; Platinum; Constrained space orbital variation

1. Introduction

Platinum catalysts are commonly employed in many industrial processes. For instance, in petroleum refineries, Pt is widely used in processes involving hydrogenation of unsaturated hydrocarbons and also, in reforming paraffins [1]. Chemisorption of atomic species such as oxygen and sulfur may have dramatic effects on the activity of the Pt surfaces. Hence, oxygen chemisorption seems to have a very important role on the rather recently discovered non-Faradaic electrochemical modification of catalytic activity, NEMCA, effect [2]. The first theoretical study has confirmed a relationship between the change in the work function and the desorption energy of adsorbed oxygen. Furthermore, it has also been shown that the leading mechanism is essentially of electrostatic nature [3]. On the contrary, chemisorption of sulfur on Pt surfaces is known to produce a catalyst deactivation. This poisoning effect is so strong that catalyzed hydrodesulfuration processes on oil crudes are used in the oil refineries to remove sulfur and hence, to prevent catalyst deactivation [1,4].

Because of the important consequences of chemisorption of both O and S on platinum surfaces a considerable experimental effort was devoted to gain information about the nature of the chemisorption

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bond of these two adsorbates [5–8]. The large amount of experimental work contrasts with the lack of reliable, ab initio, theoretical information which, no doubt, has its origin in the difficulties encountered to accurately describe the electronic structure of the Pt atom and of Pt models of surfaces. In fact, even using the well-known pseudopotential approach the computational effort with studying Pt clusters is huge. The remaining difficulty is due to the need to describe at least the 5d electrons of each Pt atom of a given cluster model. To reduce the computational burden we have recently developed a one-electron pseudopotential for Pt [9]. This pseudopotential is meant to be used for environmental cluster atoms whereas the 5d electrons of atoms directly involved with the chemisorption bond should, in principle, be explicitly included. This strategy has been used to study the electronic structure of Pt clusters [10], to describe the electrostatic potential maps of Pt surfaces [11] and some adsorbate–Pt surface interactions such as CO/Pt [12], O/Pt [3,13] and S/Pt [14].

In this work we present a comparative study of chemisorption of O and S on large Pt clusters representing the Pt(1 1 1) surface. One of the major efforts of the present paper is to clarify the chemical nature of the interaction. For instance, work function measurements [15] had been interpreted in terms of a strong covalent bond between sulfur and the metal substrate and a net positive charge had been attributed to chemisorbed sulfur. However, this description is in clear contradiction with the chemical intuition for the interaction of electronegative adatoms with a metal surface. Thus, a realistic estimate of the charge on chemisorbed S is important to understand photoemission experiments and to rationalize its behavior as a catalyst poison.

2. Computational details

The present study is based on the well-known ab initio cluster model approach. Therefore, the Pt(1 1 1) surface is represented by cluster models of different sizes. These are Pt_9(6,3), Pt_{25}(12,6,7) and Pt_{34}(16,9,9) where the numbers in parenthesis give the number of atoms in the first, second and third cluster layers, respectively. To represent the interaction above the threefold open site we use Pt_9 and Pt_{25} clusters whereas Pt_{34} is used to study the migration of S on the surface. Schematic representations of these clusters are given in Fig. 1.

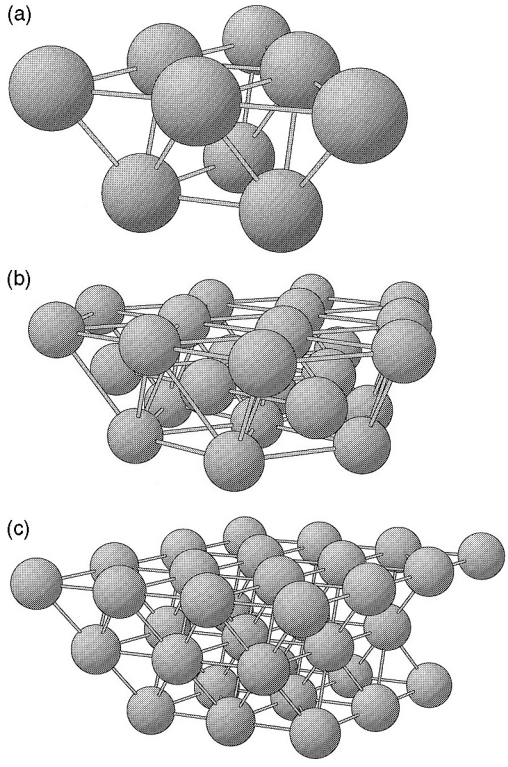

Fig. 1. Schematic representation of the Pt_9(6,3), Pt_{25}(12,6,7) and Pt_{34}(16,9,9) cluster model. Sticks are drawn for clarity purposes.

The interaction of O and S above Pt_{25} is described through ab initio cluster model wavefunctions. In the case of oxygen we have also used a Pt_9(6,3) cluster model in order to study the influence of the cluster size. A Pt–Pt distance of 2.775 Å was taken from bulk Pt. We used either Hartree–Fock or configuration interaction wavefunctions constructed using reasonable large basis sets and appropriate pseudopotentials; the three cluster atoms directly interacting with the adsorbate, which can be considered as a local region, are described using a suitable 10-electron pseudopotential, while the remaining cluster atoms which are the outer region, are described through a recently developed one-electron approach [9] which uses a spherical averaged $5d^9$ core aimed to reproduce average pseudostates. This partition permits to have a better description of the local region while still having

a reasonable description of the neighborhood of the active site, thus enabling us the ab initio treatment of the large cluster model used in this work.

The basis sets and pseudopotentials used in this work are as follows. The three nearest Pt atoms to the adsorbate which belong to the local region are described with a relativistic pseudopotential that leaves explicitly the $5d^{10}$ electrons on the valence shell. For these atoms the GTO basis set is (6s4p6d/3s2p3d). The Pt atoms defining the ''outer'' region are treated with the help of a recently derived one-electron pseudopotential which contains a core with a spherically averaged d^9 shell. Two different GTO sets have been used for these environmental Pt atoms. In the case of sulfur the SCF calculations were done using either a (4s3p/2s1p) basis set (basis 1) or a (4s/2s) set (basis 2) whereas explicitly correlated calculations were carried out using basis 2 only (see [9,12]). In the case of oxygen, only basis 1 has been used. Finally, we include all electrons of the oxygen using a [9s5p/4s3p] basis set [16] and also for the S atom choosing a (13s9p1d/6s4p1d) basis set taken from [17]. Further details and additional information about the Pt pseudopotentials have been reported in [13–15].

For our cluster model representing the Pt(1 1 1) fcc site, electronic correlation effects were introduced through a variety of theoretical techniques. This includes single and multireference second-order perturbation methods, SR-MP2 and MR-MP2, multireference configuration interaction, MRCI and a set of post-Hartree–Fock correlation functionals. For the MP2 level of calculation we have used the barycentric partition as in the CIPSI [18–22] algorithm. The reference space for MR-MP2 was iteratively constructed so as to include in the variational reference space all the determinants contributing to the perturbed first-order wavefunction by 0.1% or 1%. The MRCI calculations start from the MR-MP2 reference space but those determinants with contribution to the first-order wavefunction larger than 0.002 are treated variationally. In the case of oxygen the reference space consists of 13 determinants and the generated space is of about 37 million configurations. In the MRCI procedure about 21 000 of these configurations are treated variationally, while the contribution of the remaining determinants is evaluated perturbatively up to second order. In the case of sulfur the reference space has only five reference determinants and generates about 46 million determinants among which 3×10^4 are included in the variational expansion. With this strategy the second-order contribution to the electronic correlation energy is about 50% of the total value. Further spaces constructed by using smaller thresholds lead to larger second-order expansions without changing the binding energy by more than 0.3 eV.

The influence of electronic correlation on the calculated energies, vibrational frequencies and equilibrium distances has also been investigated by means of correlation functionals applied to the Hartree–Fock density. This approach gave satisfactory results for the interaction of alkali metals on Si(1 1 1) [23] but failed to describe the correlation effects on the O/Pt(1 1 1) system [14]. Here, we will show that correlation functionals represent only a modest improvement in the SCF description and will suggest that the performance of this functionals is related to the contribution of the Hartree–Fock determinant to exact wavefunctions. Of course, the exact solution cannot be obtained and we use the MRCI wavefunction to obtain an estimate of this contribution of the Hartree–Fock determinant.

The introduction of electronic correlation through correlation functionals is based on the so-called post-Hartree–Fock density functional theory (post-HF DFT). The basis of this approach is the solution of the Kohn–Sham equations using an exact expression for the exchange and the resulting method is often referred to as Hartree–Fock–Kohn–Sham [24]. In this approach one finds a set of spinorbitals fulfilling

$$\left[\hat{F} + \frac{\delta E_c}{\delta \rho}\right]|\psi_i\rangle = \epsilon_i|\psi_i\rangle, \tag{1}$$

where F is the Fock operator of the Hartree–Fock approach. In this work the total energy is computed following the approach suggested by Stoll et al. [25] which states that the correlation term from Eq. (1), E_c, is small and has a very small effect on the Fock operator. As a consequence, the Kohn–Sham orbitals and the resulting electron density should be similar to the corresponding Hartree–Fock quantities. This is a very important assumption and it is by no means clear if it is applicable to the case of adsorbates on metal clusters. If ρ_{KS} and ρ_{HF} denote the Kohn–Sham and Hartree–Fock densities, respectively, we are simply

assuming that

$$\rho_{KS}(r) \approx \rho_{HF}(r). \quad (2)$$

It is now possible to prove that the Kohn–Sham functional for the total, $E_{KS}[\rho_{KS}]$, and correlation, $E_c[\rho_{KS}]$, energies can be approximated simply by

$$E_{KS}[\rho_{KS}] \approx E_{KS}[\rho_{HF}] = E_{HF} + E_c[\rho_{HF}], \quad (3)$$

where E_{HF} is the Hartree–Fock self-consistent energy. The above approach and the primary hypothesis have been successfully tested for several atoms and molecules using a variety of expressions of the density functional [26]. The computational simplicity of Eq. (3) permits to test different expressions for the correlation functional by computing exactly the exchange interaction. Here the total energy has been determined according to Eq. (3) and using up to eight different functionals. Within the local spin density approximation [27,28], LSD, we used the expressions suggested by Vosko et al., VWN-LSD [29] and two different approaches aimed to introduce the self-interaction correction, SIC. The first one is that developed by Stoll et al., VWN-SIC [25] and the second due to Perdew and Zunger, PZ-SIC [30]. Gradient corrections to the LSD formalism have been introduced according the methods proposed by either Becke, B-GC [31] or Perdew, P-GC [32]. Methods which are derived from the correlation factor and which do not depend on the first-order density have also been considered. These are the methods proposed by Colle and Salvetti, CS [33], by Moscardó and San-Fabián, MSF [34] and by Lie and Clementi, LC [35,36].

The equilibrium distances, vibrational frequencies and interaction energies are obtained from the potential energy curves at each level of calculation. The potential energy curves have been fitted to a third-order polynomial. The interaction energy is obtained by subtracting the energy of the fragments (SCF, SR-MP2, DFT) from the minimum energy for the super-system or by subtracting the energy of a calculation performed at infinite (i.e. 10^6 a.u.) separation. This latter approach has been used in the MR-MP2 and MRCI calculations as a way to minimize non-size consistent effects derived from the truncated CI inherent to the methods. The SCF interaction energies have been corrected by using the standard Boys–Bernardi counterpoise method. For the MR-MP2 and MR-CI we used a slightly different procedure. Here, the basis superposition to the total energy was estimated by calculating the energy of the Pt cluster with the O or S virtual basis present (but not the nucleus). Since the post-Hartree–Fock methods present a very poor behavior, no BSSE correction is included. Finally, the nature of the interaction will be studied by analyzing the cluster wavefunctions as we will show later.

All the calculations have been carried out using a locally modified version of the HONDO-CIPSI suite of programs [37].

3. Results and discussion

3.1. Structural parameters

We present in Table 1 structural and energetic parameters for both O and S on Pt at different levels of calculation. In order to avoid an exceedingly long

Table 1
Equilibrium distance, vibrational frequency and binding energy for O and S on Pt at different levels of calculation

System	Method	z_e (Å)	ν_e (cm^{-1})	D_e (eV)
Pt_{25}–O	SCF	1.37	456	−1.48
	MSF	1.34	461	0.79
	CS	1.32	466	−0.37
	VWN (SIC)[a]	1.34	460	−0.89
	B(GC)[b]	1.30	467	−0.17
Pt_9–O	SCF	1.42	412	−2.73
	SRMP2	1.42	–	2.55
	MRMP2	1.41	576	1.98
	MRCI	1.36	604	2.46
	MSF	1.37	445	0.06
	CS	1.36	455	−1.21
	VWN (SIC)[a]	1.38	433	−1.69
	B(GC)[b]	1.33	487	−0.78
	Experiment	1.36	480	3.66
Pt_{25}–S	SCF (bs 1)	1.84	311	0.98
	SCF (bs 2)	1.83	318	1.23
	SRMP2	1.88	424	4.98
	MRMP2	1.88	420	4.01
	MRCI	1.80	330	4.09
	MSF	1.79	325	3.57
	CS	1.77	335	1.97
	VWN (SIC)[a]	1.80	321	1.40
	B(GC)[b]	1.74	352	2.67
	Experiment[c]	1.62	375	3.93

[a] VWN(LSD), PZ(LD), LC.
[b] P(GC).
[c] Estimated from thermodynamic data.

list of results we have grouped the DFT results in four main sets according to the proximity between the results arising from each functional.

For both adsorbates, O and S, we obtain structural parameters which are in a rather good agreement with experimental values regardless of whether electronic correlation is included or not. For O on Pt(1 1 1), the perpendicular distance above the surface is about 1.37 Å, and the vibrational frequency, ν_e, for the frustrated translation is 456 cm^{-1}; both these values are in very good agreement with the experimental data (1.36 Å and 480 cm^{-1}, respectively) [38]. On Pt_9 the agreement is not as good, with z(O)=1.42 Å and ν_e=412 cm^{-1}, but still acceptable. For S on Pt(1 1 1) the agreement is not as good as in O but results are rather reasonable; the calculated distance is about 1.80 Å, whereas the suggested experimental value is 1.62 Å [39]. The calculated frequency for S is 318 cm^{-1} whereas the experimental value is 375 cm^{-1} [40,41]. These results are not dependent on the basis set used for the environmental Pt atoms.

As stated earlier, the use of sophisticated correlated methods does not change the distance nor the frequency in a noticeable way. Overall, correlation functionals improve the SCF calculated properties although the final results are very dependent on the form of the functional.

For the interaction energies the situation is more involved. At the SCF level, the energy of $Pt_{25}O$ lies above that of the neutral separated units. However, explicit consideration of electronic correlation effects through MRCI calculations predicts a very stable bond. Interestingly enough, different widely used correlation functionals are not able to predict even an exothermic reaction. This description of the O/Pt(1 1 1) contrast with that of S/Pt(1 1 1) where the SCF interaction energy is already large; ≈1 eV.

In the case of S, the prediction of the bond strength, measured from the computed D_e, is very different for the different correlation functionals. The VWN-LSD, VWN-SIC, PZ and LC behave similarly predicting D_e values of ≈1.5 eV, the gradient corrected functionals, B-GC and P-GC, improve this description considerably with D_e≈2.7 eV. Finally, CS and MSF functionals which usually behave very similarly [23,26] predict quite different values as already found for O on Pt(1 1 1) [14]. The failure of the correlation functionals is related to the poor fulfilment of Eq. (3). This is consistent with the contribution of the Hartree–Fock determinant to the MRCI wavefunction which is ≈0.90 (or 81%) for Pt_{25}–S but only ≈0.83 (or 69%) for Pt_9–O. This seems to explain that correlation functionals were not even able to predict a net bonding for either Pt_9–O or Pt_{25}–O. The failure of the local or semilocal correlation functionals to properly predict dissociation energies has been also discussed by Clementi [42] and Gill et al. [43]. Also, we must point out that correlation functionals are aimed to provide a part of the correlation energy, the one associated to the Coulomb hole whereas standard DFT exchange functional also do contribute to the correlation energy by improving the description of the Fermi hole. Therefore, it is likely that hybrid methods in which the correlation energy is added to the Hartree–Fock energy through a correlation functional will fail when the part of the correlation energy associated to electrons with the same spin will have large differential effects. With respect to the CI calculations, it is worth pointing out that the SR-MP2 value is too large, reflecting the well-know overestimation of the MP2 binding energies. The MR-MP2 and MRCI values are close, suggesting that the more important part of the correlation effects are introduced at the MR-MP2 level through quadruple excitations which introduce high order effects. Finally, it is an interesting fact that correlations functionals lead to binding energies always smaller than the CI ones.

3.2. Nature of the bond

In this section we will comment on the nature of the chemisorption bond for both adsorbates. First of all, we compare the dipole moment curves for both O and S above our Pt cluster model. As shown elsewhere [44], the slope of the dipole moment curve contains important information about the physical nature of a given bond, in particular, the slope is related to the net charge on the adsorbate. We present in Table 2 the values of the absolute dipole moment M_0, the slope, M_1 and the curvature, M_2, for a Taylor series development of the dipole moment curve for the motion of O and S near the equilibrium position.

For O, the dipole curve is rather linear and the slope is −1.31 indicating a large charge transfer to O. On the contrary, for S, the dipole moment curve is much less linear and the slope is small, thus clearly indicating a

Table 2
Analysis of the dipole movement curve for O and S on P(1 1 1) for both uncorrelated and correlated wavefunctions

Model	$Pt_{25}O$	Pt_9O		$Pt_{25}S$		
	SCF	SCF	CI	SCF	SCF	CI
Basis	b1	b1	b1	b1	b2	b2
M_0	−0.84	−1.28	−0.80	−0.96	−0.93	−0.79
M_1	−1.31	−1.28	−0.97	−1.03	−0.74	−0.72
M_2	−0.04	−0.03	−0.54	−0.44	−1.16	−1.00

more covalent bond. Moreover, in the case of O, the introduction of correlation effects, decreases the slope, while for S the change is very small. Results are thus different for O and S, the O/Pt bond being more ionic.

Further information can be obtained from the constrained space orbital variations, CSOV technique [45–47], which permits to decompose the interaction energy in intra-unit (polarization) and inter-unit (charge-transfer) contributions. The first step of the CSOV is the superposition of the electron densities of the fragments. In the case of O the interaction at this step is repulsive by 7.3 eV, while for S is also repulsive, but only by 4.8 eV. This is consistent with the larger equilibrium distance for S. After allowing the adsorbate and substrate to polarize and to donate charge in both directions to form covalent bonds, we have an interaction energy which is still below the full SCF value for both O and S. This is an indication that the final wavefunction contains a strong mixing of the molecular orbitals of the two units. The final SCF wavefunction is very different from the one constructed by superimposing those of the constituent units. In any case, the CSOV analysis confirms a large charge donation towards the adsorbate while a noticeable covalent contribution remains.

A final point of interest is the important contribution of correlation effects to the interaction energy. We could expect such an important contribution in very ionic interactions, but we have seen that the present bonds can be considered as a covalent interaction. A possible explanation can be done by considering that correlation effects try to decrease the initial Pauli repulsion of the interacting fragments. Notice that the difference in Pauli repulsion fully justifies the difference between O and S. The mixing of the ground state configuration with other determinants where electrons are placed on more diffuse virtual orbitals will lead precisely to lower Pauli repulsion.

3.3. Migration of S on the Pt(1 1 1) surface

As a preliminary study of the migration of an adsorbate on a metal surface we have considered a path for migration of S on a large enough cluster model of Pt(1 1 1) as Pt_{34}(16,9,9). In Fig. 2 we present the SCF energy obtained by optimizing the S to surface distance at different positions, starting from the fcc site and going to the hcp site passing across the bridge site. The results were surprising because S on the fcc site of the Pt_{25} cluster model is a true minimum with respect to all S displacements, but this is not the case for the Pt_{34} model, as shown in Fig. 2.

The explanation of this apparent failure is clear when considering that Pt_{34} has a non-negative dipole moment parallel to the surface. As S is largely charged there is a net force on S that disturbs the validity of the model. Thus one must be extremely cautious when

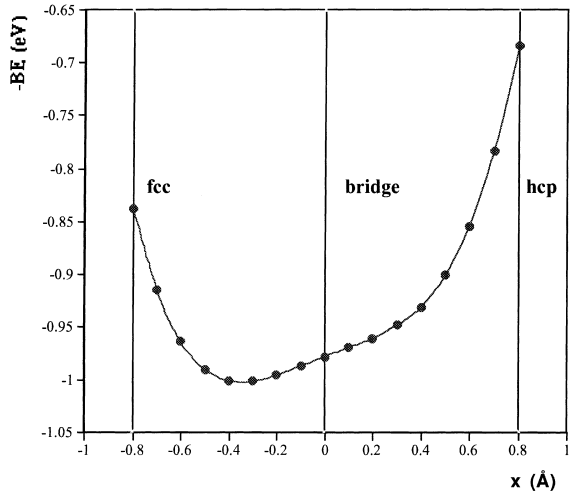

Fig. 2. Binding energy (eV) for S on Pt(1 1 1) along a path from the fcc site to the hcp one.

designing a cluster model to represent a surface because possible cluster artifacts can appear. This problem is likely to appear when periodic boundary conditions are used and one must be very careful in choosing the unit cell.

4. Conclusions

The ab initio cluster model approach has been applied to the study of the chemisorption of O and S on Pt(1 1 1). The calculated structural parameters are in rather good agreement with the experiment, even at the SCF level of calculation while the interaction energy needs an explicit inclusion of electronic correlation effects. Approximate inclusion of these effects through the use of correlation functionals which use the SCF density are found to improve the calculated binding energy in all the cases. However, the resulting values for the interaction energy are still too small independent of the correlation functional employed. Gradient corrected functionals and those based in the correlation factor lead to better values than those derived from the LDA even after corrected for the self-interaction. Moreover, it is seen that different functionals lead to very different numerical values. We have shown that hybrid methods in which the correlation energy is added to the Hartree–Fock energy through a correlation functional will fail when the part of the correlation energy associated to electrons with the same spin will have large differential effects. This is the case when considering chemisorption on cluster models representing metal surfaces. The chemisorption energy is very important and both, Coulomb and Fermi, holes will make similar contributions.

The importance of correlation effects is attributed to the strong initial Pauli repulsion between the adsorbate and surface. The configuration interaction mixing permits to include instantaneous situations in which two or more electrons occupy more diffuse virtual orbitals thus lowering the Pauli repulsion. The bonding mechanism is complex, a large charge transfer occurs, but the bond can be viewed as strongly covalent; this is more clear for S than for O. The analysis of the interaction energies and of the dipole moment curves show that, contrary to what may be expected for isoelectronic elements, the nature of the chemisorption bond is very different. In fact, the interaction of S with the surface is stronger than that of oxygen and involves a strong covalent bond. This difference may serve as a guide to understand the different role played by these two elements when interacting with Pt catalysts.

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