

FIRST PRINCIPLES STUDY OF POISONING BY SULFUR AND DEPOISONING BY CHLORINE OF PALLADIUM BASED HYDROGENATION CATALYSTS: FROM CLUSTERS TO SURFACES

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ABSTRACT

From first-principles calculations we find evidence for a direct effect of co-adsorbed chlorine on the adsorption of dihydrogen and ethylene on sulfur-poisoned palladium. On the model (111) surface, chlorine restores molecular and atomic adsorption energies, and decreases the barrier to H₂ dissociation. By contrast, on Pd₄, one adsorbed sulfur increases, while one co-adsorbed chlorine decreases the adsorption energies compared to the clean cluster. We discuss the implications of such effects in the context of the preparation of noble metals based hydrogenation catalysts of improved thioresistance, needed by the refining industry.

I. INTRODUCTION

As specifications on sulfur and aromatics contents in diesel fuels become ever more severe, the development of more active as well as sulfur tolerant hydrogenation catalysts appears as an increasingly important issue for the refining industry. Halogens incorporated in the solid's formulation, or in the stream of reactants, are known to impart some degree of thioresistance to noble metals (Pt, Pd) based hydrogenation catalysts. Very little is known about the microscopic origin of this effect, although it could provide important guidelines for the preparation of new catalysts. A mechanism involving electrons attraction by halogens bound to the carrier and mediating an electron deficiency of supported metal particles, is usually invoked. However, such a long range effect on electronic structure may appear very unlikely. We have therefore undertaken systematic first-principles simulations aiming at probing the direct effect of adsorbed chlorine on the structural, electronic and adsorptive properties of the Pd (111) surface and Pd₄ clusters, poisoned by sulfur (2), (5), (7).

II. METHODS

The calculations were based on the density functional theory (DFT). For the clusters, we used the Gaussian 94 code (1) under the B3LYP option. Scalar relativistic effects for Pd were incorporated through the use of the LanL2DZ basis set, whereas the standard 6-311(d,p) basis set was chosen for the elements S, Cl, C and H. All geometries were fully relaxed. More details can be found in (2). The calculations on model surfaces were performed using the VASP code (3) using a plane-wave pseudopotential formalism. Exchange and correlation effects were included within the generalized gradient approximation (4) (GGA). We used a supercell geometry consisting of a palladium (or platinum) slab four layers thick with a 3x3 surface cell, and a vacuum gap of thickness equivalent to six layers. Adsorbates and adatoms were introduced on one side of the slab and allowed to fully relax, as well as the first two layers of metal atoms, the remaining two layers being fixed at bulk positions. Full details can be found elsewhere (5).

III. RESULTS AND DISCUSSION

The computed adsorption energies of sulfur and chlorine on palladium substrates are compared in Table 1. The magnitude of these energies correspond to strong chemisorptions. Both on the electron deficient clusters and on the full surfaces, sulfur binds more strongly than chlorine. The nature of these bonds has been demonstrated elsewhere (2), (5) : while the sulfur-palladium bond is essentially covalent, the chlorine-palladium bond has a significant ionic character, both on surfaces and clusters. The adatoms bind more strongly on the surface than on the cluster.

Bulk and surface metal-sulfur bond strengths are compared in Table 2 for Pd and Pt. For the bulk, we use either the cohesive energy per M-S bond as defined in (6), or the standard heat of formation of the isostructural sulfides which also includes the bulk metals cohesive energies. Albeit the surface bonds follow the same tendencies as the bulk bonds, their differences appear much less marked.

The competitive adsorption between sulfur and chlorine is analysed in Table 3: the strong repulsive interaction seen between co-adsorbates sharing two palladium atoms decreases rapidly as the S-Cl distance increases. On Pd₄, S and Cl can even mutually strengthen their adsorption when they share a single Pd atom. On the surface, the destabilization for S and Cl sitting in corner sharing or non adjacent three-fold hollows is quite comparable to that induced by increasing coverage with sulfur alone. Co-adsorption of S and Cl on palladium can therefore be taken as quite likely for systems where externally imposed chemical potentials of chlorine and sulfur are comparable (see (5) for a more detailed discussion).

The molecular chemisorption on ethylene is the first step of its heterogeneous catalytic hydrogenation. The computed adsorption energies of ethylene on our clean model substrates are reported in Table 4. The « top » π configuration is clearly preferred on the Pd₄ cluster, whereas the the di- σ bridging configuration is favoured on both the Pd(111) and Pt(111) surfaces, in accordance with other computational studies and experiment. Platinum binds ethylene a little more weakly than palladium.

As shown in Table 5, sulfur and chlorine co-adsorbed on the palladium surface or the Pd₄ cluster have contrasted effects on ethylene chemisorption. It is slightly enhanced by sulfur, and weakened by chlorine on the cluster. The cooperative effect of S and Cl leads to a significant poisoning of ethylene adsorption, obviously in a non-linear fashion. On the Pd(111) surface, a moderate poisoning is brought about by

0.22 ML sulfur, while chlorine has no effect at the same level of coverage. The mixed ad-layer behaves more like chlorine, which we take as an evidence of effective depoisoning.

We have shown elsewhere (5) the microscopic details of poisoning by sulfur of the dissociative chemisorption of molecular hydrogen on Pd(111), and the depoisoning effect of co-adsorbed chlorine: the latter involves a reduced barrier to dissociation, and restored stability of atomic H bound to the surface with respect to associative desorption. In the mixed ad-layer, the effect of chlorine is again dominant, indicative of another direct depoisoning effect.

IV. CONCLUSIONS

In summary, we have found that although sulfur binds more strongly than chlorine to palladium (or platinum) surface atoms, co-adsorption is likely to occur both on very small clusters and on extended metallic surfaces: in the latter case islands of chlorine may segregate because lateral repulsions between adsorbed sulfur atoms are stronger than between adsorbed chlorine atoms. Co-adsorption of chlorine and sulfur affects the molecular adsorption of ethylene differently on very small palladium clusters and on periodic surfaces, respectively weakening and strengthening the interaction. In both cases the effect is non-linear in the sense it is not the average of the effects of the separate adatoms.

We have demonstrated therefore the likeliness of a direct induction of thioresistance by co-adsorption of an halogen on the palladium surfaces. However, on very small palladium aggregates, chlorine could on the contrary amplify the poisoning by sulfur. For practical purposes, this would imply avoiding too high dispersions of the active metal in the supported catalyst.

Future studies should focus on the diffusion and segregation of adatoms at metal surfaces in presence of activated hydrogen, as well as the determination of energy profiles along reaction paths of hydrogenation reactions, in order to enable evaluations of kinetic data by Monte Carlo simulations (8).

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Table 1. Adsorption energies of sulfur and chlorine on model metallic substrates (kCal.mol⁻¹)

Substrate	Sulfur	Chlorine	Ref.
Pd ₄	-85.3	-56.4	(2)
Pd ₆	-81.4	-65.2	(2)
Pd(111) ($\theta_s=0.33$)	-109.5	-71.1	(5)

Table 2. Comparison of computed bulk and surface metal-sulfur bond strengths (kCal.mol⁻¹)

System	E _{M,S}	ΔH°_f	Ref.
Bulk PdS	45	-16.9	(6)
S @ Pd(111) ($\theta_s=0.33$)	109.5	-	(5)
Bulk PtS	56.3	-19.5	(6)
S @ Pd(111) ($\theta_s=0.33$)	111.1	-	-

Table 3. Changes of the total adsorption energy of S+Cl as a function of S-Cl distance, relative to infinite separation (results from Ref. (5) for Pd(111)).

Substrate	S-Cl distance (nm)	Pd shared	E _{ads} (S+Cl) (kCal.mol ⁻¹)	Change (%)
Pd ₄	(i)	0	-141.7	0
Pd ₄	0.47(ii)	1	-142.9	+5.3
Pd ₄	0.47(iii)	2	-134.3	-5.2
Pd(111)	(iv)	0	-190.7	0
Pd(111)	0.187(v)	2	-16.6	-91.3
Pd(111)	0.323(vi)	1	-174.8	-8.3
Pd(111)	0.485 (vii)	0	-185.6	-2.7

(i): Adsorption of S and Cl on separate clusters, S stabilized in three-fold site (face of the tetrahedron), Cl in bridge site.

(ii): Adsorption of S on a three-fold site and Cl on a bridge site (non adjacent edge) of the same cluster

(iii): Adsorption of S on a three-fold site and Cl on a bridge site (adjacent edge) of the same cluster

(iv): Adsorption of S and Cl in separate cells at the low coverage limit ($\theta_s=0.11$)

(v): Adsorption of S and Cl in two edge-sharing adjacent three-fold hollow sites.

(vi): Adsorption of S and Cl in two corner-sharing opposite three-fold hollow sites.

(vii): Adsorption of S and Cl in two next to next neighbour three-fold hollow sites.

Table 4. Adsorption energies of ethylene on model metallic substrates (kCal.mol⁻¹)

Substrate	E _{ads}	Configuration	Ref.
Pd ₄	-18.5	π	-
Pd ₄	-9.4	di- σ	-
Pd(111)	-14.7	π	-
Pd(111)	-23.5	di- σ	(7)
Pt(111)	-10.6	π	-
Pt(111)	-20.2	di- σ	-

Table 5. Effect of sulfur and chlorine on the adsorption of ethylene on palladium (kCal.mol⁻¹)

Substrate	E _{ads} (C ₂ H ₄)	Configuration	Ref.
Pd ₄	-18.5	π	-
Pd ₄ S	-20.8	π	-
Pd ₄ Cl	-16.1	π	-
Pd ₄ SCl	-7.6	π	-
Pd(111)	-23.5	di- σ	(7)
Pd(111) + 0.22MLS	-19.3	di- σ	(7)
Pd(111) + 0.22MLCl	-23.5	di- σ	(7)
Pd(111) + 0.11MLS	-22.3	di- σ	(7)
+ 0.11 ML Cl			