

## Electric field effects in heterogeneous catalysis

Gianfranco Pacchioni<sup>a,\*</sup>, Julian R. Lomas<sup>a,1</sup>, Francesc Illas<sup>b</sup>

<sup>a</sup> *Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Università di Milano, via Venezian 21, 20133 Milano, Italy*

<sup>b</sup> *Departament de Química Física, Universitat de Barcelona, Martí I Franques 1, 08028 Barcelona, Spain*

Received 6 June 1996; accepted 9 September 1996

### Abstract

Coadsorbed ions on metal surfaces generate electrostatic fields of the order of  $V/\text{Å}$  which induce substantial changes in the rate of catalytic reactions. The mechanism of the interaction of the electric field with adsorbed reactants or products on the catalyst surface is analyzed by means of *ab initio* cluster model wavefunctions. Two examples of catalytic processes modified by coadsorbed ions are considered: (a) The trimerization of acetylene to benzene on the Cu(110) surface and (b) the oxidation of ethylene and other organic molecules on supported Pt catalysts under the effect of an external applied potential. In both cases the trend observed experimentally is reproduced by the calculations and attributed to a field-induced change in the strength of the bond of the reactants or products. The way the field affects the bond, however, is different in the two cases. This can be understood in terms of ionic-covalent character of the adsorbates. For covalent adsorbates, like benzene on Cu(110), the field changes the metal work function and consequently the extent of the adsorbate–surface dative bonding. The effect is entirely chemical. For ionic or partially ionic adsorbates, like the oxygen atoms involved in the oxidation reactions, the effect is largely electrostatic and arises primarily from the interaction of the non-uniform electric field with the polar metal–oxygen bond.

*Keywords:* Electric fields; Heterogeneous catalysis; Electrochemical promotion; Cluster models; *Ab initio* Hartree–Fock

### 1. Introduction

Coadsorbed ions on the surface of metal catalysts often induce changes in the rate of catalytic reactions. The modification of the catalytic rate is connected to the change in the bond strength of the adsorbed species which take part into the reaction. For instance, an

increase in the desorption energy of the final products will result in a considerable reduction of the turnover rate; a decrease in the bond strength of an adsorbed hydrogen or oxygen atom will facilitate the hydrogenation or oxidation of an organic adsorbate, and so on. The effect is well known as ‘promotion’ or ‘inhibition’ in catalysis and several experimental and theoretical studies have been dedicated to this important scientific and technological problem [1]. Various explanations have been proposed to rationalize the promotion effect, starting from the observation that electropositive (electronega-

\* Corresponding author.

<sup>1</sup> Present address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England, UK.

tive) adsorbates on metals form ions at low coverage [2,3]: (a) A direct interaction due to an overlap of the adsorbate and ion wavefunctions; (b) a change in the position of the donor–acceptor energy levels of an adsorbed molecule due to the coadsorbates [4]; (c) short- or long-range electrostatic interactions, etc. [5–8]. A generally accepted model assumes that the coadsorbed ions induce a polarization of the substrate metal with formation of an image charge of opposite sign below the surface [5–8]. The charge pair generates an inhomogeneous electric field at the surface which will affect the properties of the other adsorbates (atoms or molecules). The effect of electric fields on catalytic reactions has been studied experimentally; for instance Block and co-workers [9] have developed a field pulse technique in the field ion microscope that allows the investigation of the field effect on chemical reactions. The way the interaction between the non-uniform field due to the ions and the adsorbates takes place is the subject of this paper.

We will examine two experimental examples of catalytic activity modified by the presence of coadsorbed ions. The first one is the cyclization of acetylene to form benzene on Cu(110) [10,11]; the second one is of more general nature and is connected with the electrochemical promotion in oxidation of organic molecules on supported metal catalysts [12,13]. The two processes have a similar origin, a change of the catalytic activity due to coadsorbed ions, although the way the reaction is modified is completely different. In both cases the ions can be modelled by uniform-electric fields, showing that this is the primary consequence of their presence; the reasons for the different mechanisms in the two examples considered will be rationalized on the basis of the nature of the adsorbate–substrate bonding. We will show in fact that while in the first example the ions induce a change in the chemical bonding of the hydrocarbon molecules, in the second case the inhomogeneous field interacts electrostatically with the adsorbed oxygen atoms on the catalyst surface.

## 2. Computational details

All the calculations presented in this paper have been performed within the cluster model approach [14,15] by determining *ab initio* Hartree–Fock wavefunctions. Relatively large clusters (see below) were used to model the catalyst surface and the interaction with adsorbed atoms or molecules. The coadsorbed ions, on the other hand, have been represented in different ways: (a) By using real ions ( $\text{Li}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ , etc.); (b) by placing point charges (PCs) above and below the cluster surface to represent both the adsorbed ion and the image charge; (c) by applying uniform electric fields,  $F$ , of known magnitude. The applied fields are in the range of 0.005–0.025 a.u.; a field  $F = 0.010$  a.u. corresponds to  $5.7 \times 10^7$  V/cm. For comparison, in semiconductors fields of the order of  $10^6$  V/cm can be maintained, while fields within the double layer at the electrode–electrolyte interface can reach  $10^7$  V/cm. Exposed cations in zeolite cavities create fields of  $10^8$  V/cm ( $1 \text{ V}/\text{\AA}$ ). The upper limit of electric field strength that can be maintained over microscopic distances before field emission or field evaporation takes place is of the order of  $\approx 6 \text{ V}/\text{\AA}$ ; this is also the field experienced by valence electrons in atoms and molecules [4].

The mechanism of the bonding with and without coadsorbed ions has been analyzed to identify the major changes occurring in the interaction. This has been done by decomposing the interaction energy into the sum of intra-unit polarization and inter-unit charge transfer terms according to the constrained space orbital variation technique (CSOV) [16,17]. Details of this method [16,17] and applications to the specific case of field effects can be found elsewhere [7,8]. The dissociation energies,  $D_e$ , have been computed with respect to the cluster with adsorbed ions (or their models) and free benzene or oxygen atom in the respective ground states.

Flexible basis sets of double-zeta plus polarization quality (DZP) were used for the cluster models of the Cu and Pt surfaces; the central

atoms of the cluster were treated with 11-electron (Cu) [18] and 10-electron (Pt) [19–22] Effective Core Potentials (ECP), respectively, while 1-electron ECPs were used for the surrounding Cu [23] or Pt [24] atoms. Cl was described using a 7-electron ECP and DZ basis sets [25]. DZ or DZP all electron basis sets were used for adsorbed benzene [26] and oxygen [27]. For more details about the basis sets see Refs. [11,13]. The calculations have been performed on IBM Risc 6000 workstations with the Hondo 8.5 [28] and Hondo-Cipsi [29]<sup>2</sup> programs.

### 3. Results and discussion

#### 3.1. Coadsorption of Cl and C<sub>6</sub>H<sub>6</sub> on Cu(110)

The presence of coadsorbed Cl atoms during the cyclization of acetylene to form benzene on the Cu(110) surface results in an increase of the benzene desorption temperature from 280 K (no Cl) to 325 K (coadsorbed Cl) [10]. This corresponds to an increase of  $\sim 0.2$  eV in the adsorption energy of benzene. The change has important consequences on the reaction: in fact, while in absence of Cl the cyclization is *surface reaction rate limited*, with Cl becomes *desorption rate limited* [10]. In other words, the change in benzene adsorption energy changes the rate determining step.

To model the interaction of Cl with benzene on Cu(110) we used various models: a Cu<sub>28</sub>/(Cl<sub>2</sub>)<sup>2-</sup>/2PC cluster with two adsorbed Cl<sup>-</sup> ions and two PC = +1 image charges below the cluster; Cu<sub>28</sub>/4PC where the Cl ions in the previous model are represented by PCs of -1; and a Cu<sub>28</sub>/F cluster where the presence of the ions and image charges is simulated by a uniform electric field, *F*, of 0.01 a.u. The simulation of Cl atoms by Cl<sup>-</sup> ions or by -1 PCs is

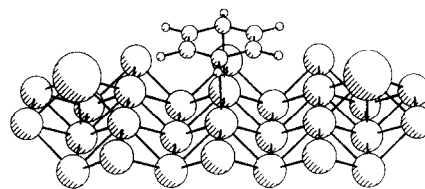


Fig. 1. The Cu<sub>28</sub>/Cl<sub>2</sub>/C<sub>6</sub>H<sub>6</sub> cluster used to model coadsorption of Cl and benzene on Cu(110).

justified by the analysis of the CuCl bond which shows a considerable ionic character [11]. The Cl atoms were fixed at their optimal distance from the cluster first layer, 2.37 bohr. The image charges were placed at -2.37 bohr from the cluster second layer. Hence, we assume that the image plane is half-way between the first and the second layer of the cluster, although in a metal the image plane is slightly above the surface. On all these clusters as well as on a free Cu<sub>28</sub> cluster we have adsorbed a C<sub>6</sub>H<sub>6</sub> molecule placed on a bridge site, Fig. 1.

On Cu<sub>28</sub> benzene is very weakly bound with a *D<sub>e</sub>* of 0.13 eV and an equilibrium distance of 6.45 bohr. If the basis set superposition error (BSSE) [30] is taken into account this weak minimum disappears and the molecule is unbound, a result which is largely due to the use of uncorrelated wavefunctions [11]. When the models of coadsorbed ions are considered, an increase of *D<sub>e</sub>* is observed: The BSSE corrected values are of 0.2–0.3 eV for a surface–benzene distance of 6.1–5.8 bohr. Although weak, this is a real bonding and shows that the calculations correctly describe the increase of bond strength due to the coadsorbed Cl. We also notice that by increasing the bond strength, the surface–benzene distance decreases, as expected in terms of classical theory of chemical bond. The importance of this observation will become clear in the following discussion.

The adsorption strength and the bonding mechanism of benzene on these clusters has been determined with the help of a CSOV analysis [16,17], Table 1. The CSOV analysis, performed for all systems at the same benzene–Cu distance of 5.5 bohr, shows that the two main

<sup>2</sup> Pseudopotential adaptation by J.P. Daudey and M. Pelissier; general ROHF adaptation by R. Caballol and J.P. Daudey; CSOV implementation by J. Rubio and F. Illas.

bonding mechanisms are the donation from benzene to the metal and the back donation from the metal to benzene, Table 1. This result is independent of the surface–adsorbate distance; in fact, the CSOV analysis has been repeated for various Cu–benzene distances and the same trend was found. In terms of energy, these two mechanisms contribute to the stabilization of the  $\text{Cu}_{28}/\text{C}_6\text{H}_6$  complex by 0.17 eV (donation) and 0.14 eV (back donation); the analysis of the dipole moment change associated with each of these mechanisms, a direct measure of the flow of electronic charge in one or the other direction [7,8], shows a more pronounced effect of the  $\text{C}_6\text{H}_6$  donation, Table 1. The charge transfer, however, is small in both directions and *the molecule is covalently bound to the surface*. Although obvious, this conclusion has important consequences for the clarification of the coadsorption effect, as it will be shown below. When the models of benzene coadsorbed with the Cl ions are considered, we found a small increase in the donation, both in terms of energy contribution and dipole moment change, and very little or no change in the back donation, Table 1. Stated differently, benzene is a better donor in the presence of the Cl ions, while the back donation of charge remains stable or decreases slightly. Another bonding mechanism (not reported in Table 1) which changes because of the presence of the coadsorbates is the Pauli repulsion which decreases when the Cl ions are present. The net result is a reinforcement of the bond strength, as experimentally observed [10].

It is worth noting that this effect has been

found for all the models of coadsorbed ions considered, i.e.  $\text{Cl}^-$  ions, PCs or uniform electric fields. Actually, an electric field  $F = +0.01$  a.u. has the largest effect, Table 1. This provides a clear indication that the presence of the Cl ions can be simulated by a uniform field, although inhomogeneities in the field can be very important. *The first conclusion is therefore that the observed effect has an electrostatic origin implying a metal mediated interaction with no direct chemical interaction between the coadsorbates.*

Having established that the presence of the ions creates a field and that the field induces a change in the bond strength, we will examine now the reasons for this change. In particular, we will consider the bond strength of adsorbed benzene in the presence of uniform fields of increasing strength, from  $F = 0$  to  $F = +0.025$  au. At the same time, we have evaluated the metal work function,  $e\Phi$ , derived from Koopmans' theorem [31] as  $-\varepsilon(\text{HOMO})$ , for different field strengths. A positive electric field (i.e. with the same direction of a field induced by negative adsorbed ions) moves the HOMO to lower energies and raises the metal work function,  $e\Phi$ . In the opposite case, the presence of positive ions (e.g. alkali ions) on a metal surface, corresponding to a negative electric field, one would expect shifts of the HOMO to higher energies and a concomitant reduction in  $e\Phi$ .

Therefore, with an applied positive electric field both the benzene  $D_e$  and the metal work function increase. The dependence is almost linear for small fields, and deviates from linear-

Table 1

Donation and back donation contributions to the bonding of benzene on Cu(110) from the CSOV analysis of cluster models of  $\text{Cu}_{28}/\text{C}_6\text{H}_6/\text{Cl}$  (energies in eV, dipole moments in a.u.)<sup>a</sup>

Model	$\text{C}_6\text{H}_6 \rightarrow \text{Cu}$ donation		$\text{Cu} \rightarrow \text{C}_6\text{H}_6$ back donation		$D_e$ (eV)
	$\Delta E$	$\Delta\mu$	$\Delta E$	$\Delta\mu$	
$\text{Cu}_{28}$	0.17	+0.27	0.14	-0.10	0.04
$\text{Cu}_{28}/(\text{Cl})_2^-/2\text{PC}$	0.20	+0.34	0.13	-0.10	0.16
$\text{Cu}_{28}/4\text{PC}$	0.20	+0.37	0.14	-0.08	0.28
$\text{Cu}_{28}/F$	0.25	+0.46	0.12	-0.05	0.27

<sup>a</sup> The analysis is performed for a surface–benzene distance of 5.5 bohr.

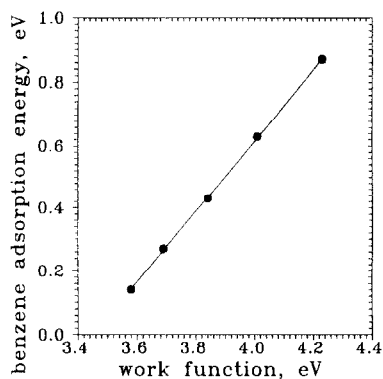


Fig. 2. Relationship between the Cu work function (determined as  $-\epsilon(\text{HOMO})$  at  $\text{Cu}_{28}$ ) and  $D_e$  of benzene ( $D_e$  and the work function have been determined for electric fields of increasing strength, from 0 to  $+0.025$  a.u.).

ity when the field becomes larger. When we plot  $D_e$  versus  $e\Phi$  a linear correlation is found, see Fig. 2. Lowering the Fermi level facilitates charge transfer from benzene to Cu with increase of the bond strength. Of course, this should also result in a reduction of the back donation mechanism but the CSOV analysis has shown that the effect of benzene  $\rightarrow$  Cu donation is more important and dominates. One should mention that the electric field changes also other bonding mechanisms, in particular the Pauli repulsion. The Cu conduction band electrons polarize away from benzene in the presence of a positive field, thus reducing the repulsion with benzene.

These results clearly indicate that *the effect of the coadsorbed Cl is to increase the strength of the benzene–Cu bond by increasing the metal work function hence favoring the benzene  $\rightarrow$  Cu donation (through metal effect)*. In the following section we will present a case where a similar phenomenon has indeed a different origin.

### 3.2. Electrochemical promotion

A few years ago a new example of promotion in catalysis has been discovered and named NEMCA, non-Faradaic electrochemical modification of catalytic activity [12,32,33]. By vary-

ing in a controlled way the catalyst-electrode potential of metal particles supported on solid electrolytes, dramatic changes in the catalytic activity of oxidation reactions have been observed. It has been found that under the effect of an external potential there is a migration of ions through the supporting solid electrolyte to the surface of the metal catalyst. The solid electrolytes used are either anion ( $\text{O}^{2-}$  or  $\text{F}^-$ ) conductors like  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$ , or cation ( $\text{Na}^+$ ) conductors like  $\beta''\text{Al}_2\text{O}_3$ . The effect has been observed for various metals, Pt, Rh, Au, Ni, Ag [32]. Under these conditions the catalytic reaction rate of, for instance, ethylene oxidation on Pt increases by several orders of magnitude. The effect is non-Faradaic since the proportion of oxidized ethylene molecules to deposited  $\text{O}_2$  is of the order of  $3 \times 10^5$ .

It has been observed that the spillover of ions on the catalyst surface is accompanied by a change in the metal work function (in particular an increase of  $e\Phi$  for  $\text{O}^{2-}$  conductors [12]); recently, it has been shown that this increase in work function is linearly correlated with a decrease of the activation barrier for oxygen desorption [33]. Clearly, a less strongly bound oxygen will more easily oxidize another adsorbed molecule (e.g. ethylene) thus increasing the catalytic rate. An opposite effect has been observed for spillover of positive ions ( $\text{Na}^+$ ) on the catalyst surface [34].

The experimentally observed correlation of metal work function and adsorbate bond strength closely resembles the example illustrated in the previous section. It should not be forgotten, however, that the nature of the bond with oxygen is substantially different from that of benzene, in particular in terms of ionic character (see below). In the following we will show that due to the polarity of the metal–oxygen bond other effects have to be considered.

We have used two clusters,  $\text{Cu}_{34}$  and  $\text{Pt}_{25}$ , see Fig. 3, to model oxygen adsorption on the open sites of the Cu(100) and Pt(111) surfaces, respectively. Coadsorbed ions have been modelled, as in the previous case, by placing PCs

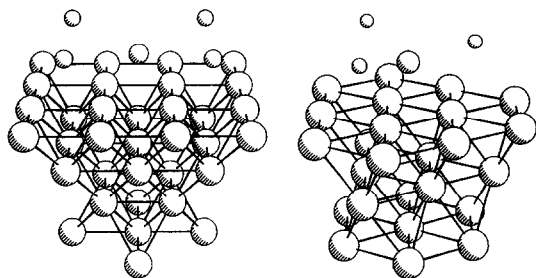


Fig. 3.  $\text{Cu}_{34}$  and  $\text{Pt}_{25}$  clusters used to model the  $\text{Cu}(100)$  and the  $\text{Pt}(111)$  surfaces, respectively. Oxygen has been adsorbed on the central hollow site. The position of the coadsorbed ions (or point charges) is also shown.

above the cluster surface, and by image charges of opposite sign below the cluster first layer. For symmetry reasons, 4 + 4 PCs have been used in the case of Cu and 3 + 3 PCs for Pt. Also in this case we used an uniform electric field normal to the surface to represent the effect of the ions. The PCs and the field models give similar results as clusters with real ions [11]. For a more detailed description of the cluster electronic states, basis sets, etc., see Ref. [11].

The binding energy of adsorbed oxygen has been computed with respect to the ionic dissociation limit,  $\text{M}_n^+$  and  $\text{O}^-$ , where  $\text{M}_n$  is the metal cluster. This choice is justified by the nature of the metal–oxygen bond. It should be mentioned that correlation effects are essential for the correct determination of the metal–O bond strength [35], in particular for Pt [36]. In this work,

however, the focus is not on the absolute values of  $D_e$  but rather on the changes induced by the coadsorbed ions. Before addressing this point it is useful to comment on the nature of the  $\text{Cu}(100)\text{--O}$  and  $\text{Pt}(111)\text{--O}$  bonds. A careful analysis of the bonding nature, based on various theoretical measures, has shown that O on Cu [35] and Pt [36] surfaces has a substantial ionic character. The charge associated to the adsorbed oxygen, not easy to measure in a quantitative way, is not smaller than  $-1$ . This is not surprising giving the high electronegativity of oxygen. The two metals, Cu and Pt, exhibit a slightly different tendency to transfer charge to the adsorbed oxygen; on Cu, in fact, the bonding has a more pronounced ionic character than on Pt where the covalent mixing seems to be more important. This is consistent with the higher experimental work function of  $\text{Pt}(111)$ , 5.7 eV, compared to  $\text{Cu}(100)$ , 4.6 eV. It is also important to stress that the largely ionic nature of the adsorbed oxygen is found with both correlated and uncorrelated wavefunctions [36]. This means that while electron correlation effects are essential for the correct reproduction of  $D_e$ , they do not change significantly the nature of the bonding [36]. Therefore, the conclusions of the present study, based on Hartree–Fock wavefunctions, are valid in general and are not dependant on the level of theoretical treatment used.

We first consider the PCs case. The PCs have been varied from  $q = +0.5$  to  $q = -0.5$ . These

Table 2

Chemisorption properties of an O atom adsorbed on  $\text{Cu}_{34}$  and  $\text{Pt}_{25}$  clusters in the presence of point charges, PCs,  $+q/-q$  (and vice versa) above and below the surface. <sup>a</sup> The  $D_e$  values are computed with respect to the ionic asymptotic limit

PCs	Cu(100)			Pt(111)		
	$e\Phi^b$ (eV)	$z_c$ (bohr)	$D_e$ (eV)	$e\Phi^b$ (eV)	$z_c$ (bohr)	$D_e$ (eV)
+ 0.5 / - 0.5	3.56	1.79	6.60	3.82	2.93	3.45
+ 0.3 / - 0.3	3.89	1.72	6.63	4.13	2.91	3.43
+ 0.1 / - 0.1	4.00	1.64	6.44	4.49	2.90	3.34
No PCs	4.07	1.60	6.29	4.66	2.90	3.26
- 0.1 / + 0.1	4.15	1.55	6.10	4.83	2.91	3.19
- 0.3 / + 0.3	4.22	1.46	5.67	5.16	2.95	2.99
- 0.5 / + 0.5	4.36	1.39	5.34	5.46	3.05	2.77

<sup>a</sup> The PCs are placed at 4.5 bohr above and below the cluster first layer.

<sup>b</sup> The work function  $e\Phi$  is determined as  $-\varepsilon(\text{HOMO})$ .

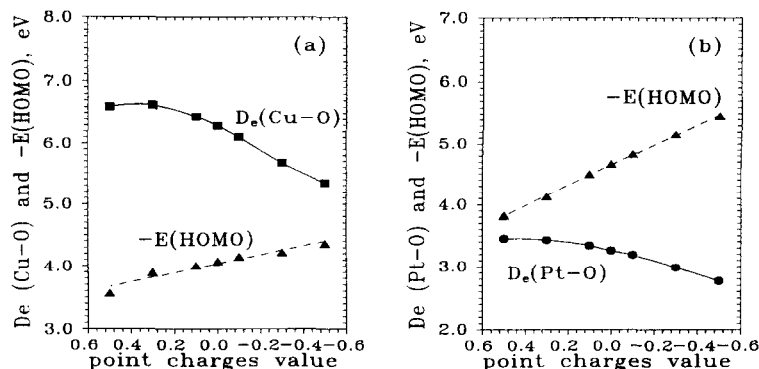


Fig. 4. Dependence of  $-\epsilon(\text{HOMO})$  and oxygen  $D_e$  on the presence of point charges  $\pm q$  above and below the cluster first layer. (a)  $\text{Cu}_{34}$ ; (b)  $\text{Pt}_{25}$ .

are the values of charges at  $+z$  above the surface; opposite charges were added at  $-z$ . The position of the PCs above the surface was estimated from the optimal distances of real  $\text{Li}^+$  and  $\text{F}^-$  ions adsorbed on  $\text{Cu}_{34}$  [11]; the image plane in this case coincides with the cluster first layer. The position of the PCs is such that they are above the O atom in both Cu and Pt, Table 2. On the other hand, the image charges are within the cluster, thus inducing an artificial polarization of the cluster electrons; for this reason it is clear that the PC models should be considered with great care. Nevertheless, they provide a simple representation of the adsorbed ions. The fact that the same qualitative results are obtained with PC models and with uniform electric fields (see below) shows that the main effect of the PCs is to generate a non-uniform field.

The position of adsorbed O has been optimized in the presence of the PCs, Table 2. With  $+q/-q$  PCs (positive adsorbed ions) a considerable increase in the  $D_e$  is found; the opposite is true for  $-q/+q$  PCs, see also Fig. 4. This is the trend experimentally found, a decrease in oxygen  $D_e$  in correspondence with a spillover of negative ions. The change in binding energy is associated to a change in cluster HOMO; in particular, the HOMO is shifted to lower energies by the negative ions (higher  $e\Phi$ ), again consistent with the experimental observations. A simple interpretation is that the

increase of  $e\Phi$  reduces the ability of the metal to transfer charge to oxygen thus decreasing the bond strength. This is the 'chemical' mechanism originally proposed to explain the phenomenon [12]. However, we found that for Cu *the increase of  $D_e$  is associated with an elongation of the metal-O bond length!* This is not what is expected based on classical chemical bonding arguments: A stronger bonding should correspond to a shorter distance. The fact that the distance increases even if the bond becomes stronger suggests that other effects must take place, and in particular that the origin of the change in bond strength can be electrostatic, more than chemical.<sup>3</sup>

To check this hypothesis we have considered the  $\text{Cu}_{34}\text{-O}$  and  $\text{Pt}_{25}\text{-O}$  clusters in the presence of an external uniform electric field,  $F$ . The  $D_e$  of oxygen has then been computed at two levels. According to first order perturbation theory, for small, uniform, electric fields the total energy can be expressed as a function of  $F$  as

$$E_p(r, F) = E_{\text{SCF}}(r, 0) - \mu(r, 0) \cdot F \quad (1)$$

where  $E_{\text{SCF}}(r, 0)$  and  $\mu(r, 0)$  are the energy

<sup>3</sup> The effect is not observed on Pt where the Pt-O bond distance remains almost unchanged, Table 2. This is due to the fact that the  $^1\text{A}_1$  state used for the  $\text{Pt}_{25}\text{-O}$  calculations has a low ionic character compared to the  $^3\text{A}_2$  ground state. For this reason, this state is only moderately affected by an external electric field [36].

Table 3

Chemisorption properties of an O atom adsorbed on a Cu<sub>34</sub> cluster in the presence of a uniform electric field,  $F$ , normal to the surface plane. The  $D_e$  values are computed with respect to the ionic asymptotic limit, Cu<sub>34</sub><sup>+</sup> and O<sup>-</sup>, taking into account the Cu<sub>34</sub> IP and O EA for  $F = 0$

Field (a.u.)	$e\Phi^a$ (eV)	$z_e$ (bohr)		$D_e$ (eV)	
		Stark	Full SCF	Stark	Full SCF
-0.015	2.96	1.73	1.72	6.60	6.40
-0.010	3.29	1.68	1.68	6.49	6.40
-0.005	3.68	1.64	1.64	6.39	6.36
No field	4.07	—	1.60	—	6.29
+0.005	4.48	1.55	1.55	6.19	6.15
+0.010	4.98	1.51	1.51	6.09	5.95
+0.015	5.56	1.46	1.47	6.00	5.65

<sup>a</sup> The work function  $e\Phi$  is determined as  $-\varepsilon(\text{HOMO})$ .

and dipole moments of the system in absence of the field ( $F = 0$ ). This energy represents the first-order Stark effect (simply Stark effect in the following [37,38]). The correction to the  $F = 0$  energy is simply due to the interaction between the dipole of the system (in this case the M<sub>n</sub><sup>+</sup>O<sup>-</sup> polar bond) and the external field (representing the long-range effects of the coadsorbed ions). No change in the electron distribution due to the field is considered at this level. Thus, the Stark interaction energy does include only electrostatic effects with no change in the chemical bonding between the metal and oxygen. These changes are taken into account by relaxing the wavefunction for  $F \neq 0$ . The polarization of cluster and adsorbate electrons and the modifications in chemical bonding mecha-

Table 4

Chemisorption properties of an O atom adsorbed on a Pt<sub>25</sub> cluster in the presence of a uniform electric field,  $F$ , normal to the surface plane. The  $D_e$  values are computed with respect to the ionic asymptotic limit, Pt<sub>25</sub><sup>+</sup> and O<sup>-</sup>, taking into account the Pt<sub>25</sub> IP and O EA for  $F = 0$

Field (a.u.)	$e\Phi^a$ (eV)	$z_e$ (bohr)		$D_e$ (eV)	
		Stark	Full SCF	Stark	Full SCF
-0.015	3.36	2.96	2.96	3.47	3.39
-0.010	3.65	2.94	2.94	3.40	3.41
-0.005	4.13	2.92	2.92	3.33	3.33
No field	4.66	—	2.90	—	3.26
+0.005	5.22	2.88	2.89	3.19	3.18
+0.010	5.81	2.86	2.87	3.12	3.12
+0.015	6.40	2.84	2.86	3.05	3.06

<sup>a</sup> The work function  $e\Phi$  is determined as  $-\varepsilon(\text{HOMO})$ .

nism are thus considered in the Full SCF wavefunction. This separation between Stark (electrostatic) and Full SCF (chemical) terms allows one to identify the importance of the two contributions.

A positive electric field (negative adsorbed ions), results in a decrease of  $D_e$  and a shortening of the surface–O distance, as for the PC models. For small fields, the dependence is linear for both Stark and Full SCF curves; deviations from linearity are observed for larger fields, in particular for Cu, Fig. 5 and Tables 3 and 4. The fact that the change in  $D_e$  found at the first-order perturbation theory level is virtually the same as for a Full SCF wavefunction is a strong indication that the interaction between the adsorbed ions and oxygen is largely electro-

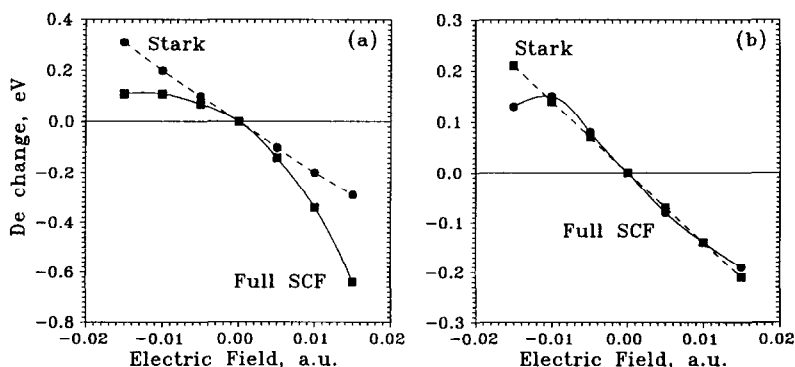


Fig. 5. Stark and Full SCF oxygen  $D_e$  for various field strengths. (a) Cu<sub>34</sub>; (b) Pt<sub>25</sub>.



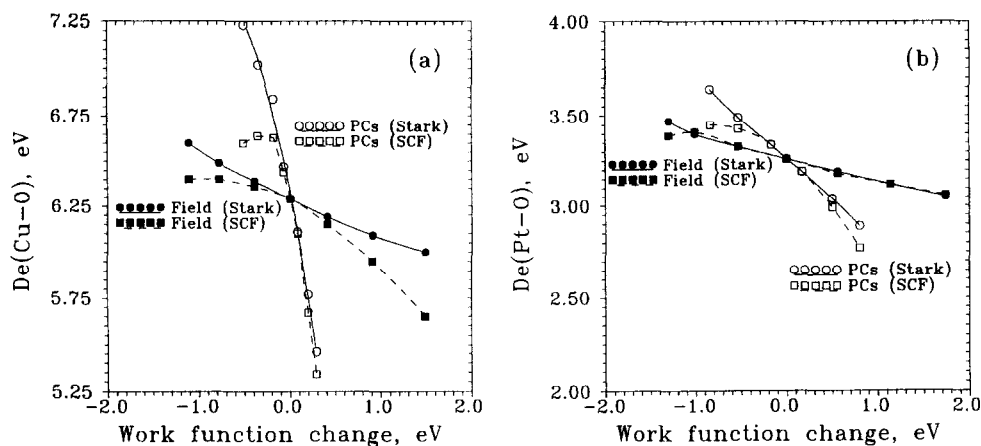


Fig. 6. Work function change,  $-\epsilon(\text{HOMO})$ , versus oxygen adsorption energy,  $D_e$ . The curves refer to the cluster with point charges (PCs),  $\circ$  and  $\square$ , and uniform electric fields,  $\bullet$  and  $\blacksquare$ . Both Stark (solid line) and Full SCF (dotted line) curves are shown. (a)  $\text{Cu}_{34}$ , (b)  $\text{Pt}_{25}$ .

static and does involve only to a minor extent changes in the chemical bonding. The results show a more pronounced dependence of  $D_e$  on the PCs than on uniform fields. This shows the importance of local inhomogeneities in the field.

In both the PC and field models we have determined the position of the metal work function for different values of  $F$ , see Tables 3 and 4.  $e\Phi$  exhibits a similar dependence on uniform fields and PCs, see also Table 2. Since this is not the case for  $D_e$  which changes more rapidly with the PC models, it is interesting to verify whether a direct relationship exists between  $e\Phi$  and the oxygen  $D_e$ . This is done by plotting  $D_e$  computed with the PC and the field models against the corresponding changes in  $e\Phi$ ,  $\Delta(e\Phi)$ , Fig. 6. We see that with the same values of  $\Delta(e\Phi)$  correspond very different oxygen adsorption energies in the two models (PCs and field)! Therefore, the oxygen bond strength is not a direct function of  $e\Phi$ . The first order effect is the electrostatic interaction between the electric field (uniform or non-uniform) and the surface dipole associated to the metal–oxygen bond. The chemical change connected to the shift of the cluster HOMO is a second-order effect. The work function change is an observable consequence of the presence of ions on the surface, but is not directly responsible for the

concomitant change in oxygen desorption barrier and catalytic rate.

#### 4. Conclusions

We have studied two examples of modification of catalytic activity induced by coadsorbed ions. We have analyzed the role of the ions by means of quantum-mechanical ab initio models of their interaction with other adsorbates. The results can be summarized as follows:

- Similar results have been obtained using real ions, point charges, or uniform electric fields. This is a strong indication that there is no direct interaction between the ions and the reactants but rather that the effect is of long-range nature. The ions on the surface create a dipole layer and an associated inhomogeneous electric field. The way this electric field influences the catalytic reaction depends on the nature of the reactants and products.

- A direct, observable, consequence of the formation of the dipole layer is a change in  $e\Phi$ , the metal work function. A positive electric field, induced by adsorbed anions, increases the work function while a negative electric field, induced by adsorbed cations, decreases the metal

work function. Whether the change in  $e\Phi$  has a direct effect on the bonding with other adsorbed molecules (reactants and products) depends on the nature of the surface chemical bond.

- The acetylene trimerization reaction to form benzene on Cu(110) is surface reaction rate limited but becomes desorption rate limited in the presence of coadsorbed Cl. The Cl ions induce an increase in the adsorption energy of benzene which is due to the enhancement of the benzene  $\rightarrow$  Cu donation mechanism. This change in chemical bonding is a direct consequence of the increase of the Cu work function; this favors the charge transfer to the surface. Therefore, the coadsorbed Cl ions induce a through metal change in the benzene bonding mechanism (chemical effect).

- The rate of oxidation reaction of organic adsorbates increases by orders of magnitude by applying a potential on metal catalysts supported on ion conductors (NEMCA). The origin of the phenomenon is the spillover of ions on the catalyst surface. A simultaneous change in metal work function and oxygen desorption barrier has been measured [22,33]. The calculations have shown that the increase in oxygen bond strength is not related to the change in work function but is rather due to the electrostatic interaction between the non-uniform field and the metal–oxygen polar bond. Chemical effects due to the variation in  $e\Phi$  occur only to a second-order. For this process, the effect is primarily through-vacuum (electrostatic).

- Two completely different mechanisms have thus been identified to explain a similar phenomenon, the increase in bond strength of an adsorbate due to the presence of coadsorbed ions. The mechanism, chemical, through-metal, or electrostatic, through-vacuum, is determined in ultimate analysis by the nature of the surface adsorbate bonding. For covalent adsorbates, like benzene on Cu, the chemical effect dominates while for ionic adsorbates, like O on Cu or Pt, the electrostatic interaction is more important.

- The determination of the character of the surface–adsorbate bond, ionic, covalent, or

mixed, is by no means a semantic problem; in fact, this is the property which determines the origin, chemical or electrostatic, of the modification of catalytic activity in the presence of promoters and poisons.

## Acknowledgements

The authors thank Dr. Paul Bagus (Almaden), Professor Costas Vayenas (Patras) and Professor Richard Lambert (Cambridge) for many useful discussions. The work has been supported by the Italian Ministry of University and Research, and the CICYT project PB92-0766-CO2-01 of the Spanish Ministerio de Education y Ciencia. We are grateful to NATO for the Collaborative Research Grant No. 941191. G.P. thanks the Computational Center of Catalunya (CESCA) for support of his visit to the University of Barcelona through the Human Capital and Mobility Program, contract CHGE-CT92-009 “Access to supercomputing facilities for European researchers”.

## References

- [1] I.M. Campbell, *Catalysis at Surfaces*, Chapman and Hall, London, 1988.
- [2] P.S. Bagus, G. Pacchioni and M.R. Philpott, *J. Chem. Phys.* 90 (1989) 4287.
- [3] G. Pacchioni and P.S. Bagus, *Surf. Sci.* 286 (1993) 317.
- [4] H.J. Kreuzer, in: D.J. Dwyer and F.M. Hoffmann (Eds.), *Surface Science and Catalysis. In Situ probes and Reaction Kinetics*, Vol. 482, ACS Symp. Series, Washington, 1992, p. 269.
- [5] J.K. Norskov, *Phys. Rev. B* 26 (1982) 2875.
- [6] S. Holloway, J.K. Norskov and N. Lang, *J. Chem. Soc. Faraday Trans. 1* (1987) 1935.
- [7] G. Pacchioni and P.S. Bagus, *Phys. Rev. B* 40 (1989) 6003.
- [8] G. Pacchioni and P.S. Bagus, *Chem. Phys.* 177 (1993) 373.
- [9] J.H. Bock, H.J. Kreuzer and L.C. Wang, *Surf. Sci.* 246 (1991) 125.
- [10] J. Lomas, C.J. Baddeley, M.S. Tikhov and R.M. Lambert, *Langmuir* 11 (1995) 3048.
- [11] J. Lomas and G. Pacchioni, *Surf. Sci.* 365 (1996) 297.
- [12] C.O. Vayenas, S. Bebelis and S. Ladas, *Nature (London)* 343 (1990) 625.
- [13] G. Pacchioni, F. Illas, C.O. Vayenas and S. Neophitides, *J. Phys. Chem.* 100 (1996) 16653.

- [14] G. Pacchioni, P.S. Bagus and F. Parmigiani (Eds.), *Cluster Models for Surface and Bulk Phenomena*, NATO ASI Series B, Vol. 283, Plenum, New York, 1992.
- [15] G. Pacchioni, *Heterogeneous Chem. Rev.* 2 (1995) 213.
- [16] P.S. Bagus, K. Hermann and C.W. Bauschlicher, *J. Chem. Phys.* 80 (1984) 4378.
- [17] P.S. Bagus and F. Illas, *J. Chem. Phys.* 96 (1992) 8362.
- [18] P.I. Hay and W.R. Wadt, *J. Chem. Phys.* 82 (1985) 270.
- [19] P. Durand and J.C. Barthelat, *Theor. Chim. Acta* 38 (1975) 283.
- [20] M. Pelissier and P. Durand, *Theoret. Chim. Acta* 55 (1980) 43.
- [21] J.C. Barthelat, M. Pelissier and P. Durand, *Phys. Rev. A* 21 (1981) 1773.
- [22] F. Illas, A. Márquez, S. Zurita and J. Rubio, *Phys. Rev. B* 52 (1995) 12372.
- [23] P.S. Bagus, C.W. Bauschlicher, C.J. Nelin, B.C. Laskowski and M. Seel, *J. Chem. Phys.* 81 (1984) 3594.
- [24] I. Rubio, S. Zurita, I.C. Barthelat and F. Illas, *Chem. Phys. Lett.* 217 (1994) 283.
- [25] P.I. Hay and W.R. Wadt, *J. Chem. Phys.* 82 (1985) 284.
- [26] H. Tatewaki and S. Huzinaga, *J. Comput. Chem.* 1 (1980) 205.
- [27] F.B. van Duijneveldt, IBM Res. Rep. N. RJ 945 (1971).
- [28] M. Dupuis, F. Johnston and A. Márquez, HONDO 8.5 for CHEMStation (IBM Co., Kingston, 1994).
- [29] M. Dupuis, J. Rys and H.F. King, HONDO-76, program 338; QCPE (University of Indiana, Bloomington, IN).
- [30] S.F. Boys and F. Bernardi, *Mol. Phys.* 19 (1970) 553.
- [31] T.A. Koopmans, *Physica* 1 (1933) 104.
- [32] C.G. Vayenas, S. Bebelis, I.V. Yentekakis and H.G. Lintz, *Catal. Today* 11 (3) (1992) 303.
- [33] S. Neophytides and C.G. Vayenas, *J. Phys. Chem.* 99 (1995) 17063.
- [34] C.G. Vayenas, S. Bebelis and M. Despotopoulou, *J. Catal.* 128 (1991) 415.
- [35] J.M. Ricart, A. Clotet, F. Illas and J. Rubio, *J. Chem. Phys.* 100 (1994) 1988.
- [36] F. Illas, J. Rubio, J.M. Ricart and G. Pacchioni, *J. Phys. Chem.* 105 (1996) 7192.
- [37] D.K. Lambert, *Phys. Rev. Lett.* 50 (1983) 2106.
- [38] P.S. Bagus, C.J. Nelin, W. Muller, M.R. Philpott and H. Seki, *Phys. Rev. Lett.* 58 (1987) 559.