A study of the interaction of water vapour on clean and oxidized lead surfaces using photoelectron spectroscopy

Mohammed Hashim Matloob

Department of Chemistry, University of Ibb, Ibb 70349, Yemen

The interaction of H_2O vapour with clean and oxidized Pb(100) single crystal surfaces has been studied using photoelectron spectroscopy. The clean Pb(100) surface, does not react with H_2O vapour at 298 K but physisorbs H_2O at a very high sticking probability (~ unity) at 80 K. The adlayer is completely desorbed at 150 K, leaving an atomically clean surface. At 80 K, H_2O is molecularly adsorbed on oxidized lead surface without decomposition, but on warming to 298 K there is a strong evidence for a significant decomposition. Exposure of the Pb(100)–O surface to water vapour at 298 K leads to stoichiometric transfer in intensity from the oxide region to the hydroxyl region indicating the formation of $PbO(OH)_2(s)$. Oxidized Pb(100) single crystal shows no catalytic tendency to decompose ethylene, propylene and acrolein in the temperature range (298-450 K).

The role of oxygen in the activation of O–H, N–H and C–H bonds at Zn, Cu, Mg, Ag, Al, Pt and Ni surfaces has been extensively investigated in order to develop the understanding of chemisorption and the mechanism of surface reactions[1]. In general less attention has been paid to Pb (which is a typical sp metal) even though it has been found to exhibit unique chemistry[2,3]. The object of the present study is to examine the tendency of Pb(100)–O to activate the O–H bond in water vapour and the C–H bond in some hydrocarbons like ethylene, propylene and acrolein and try to fit the data to a plausible model. No such work has been previously reported.

In principle, photoelectron spectroscopy (XPS and UPS) is probably the most informative experimental method, which can be applied to such studies[4,5]. From the energetic position and the intensity of the photoelectron maxima the abundance of specific elements at the surface can be deduced. From the shift with respect to the photoelectron maxima of free elements, information about the binding strengths and positions of the elements at the surface can be obtained. The line shapes in UPS enables to determine the population density of the energy bands, and the angular dependence of the UPS intensities provides information about the electronic band structure[6]. Apart from XPS and UPS low energy electron diffraction (LEED) is widely used as a complementary tool to determine the relative geometry of the surface with respect to the substrate before and after adsorption[7].

Experimental

The spectrometer used for this study is a purpose-built single chamber instrument combining facilities for photoelectron spectroscopy and low energy electron diffraction (VG Scientific, East Grinstead)[8]. The high purity Pb(100) single crystal (from Metals Research, Cambridge) was chemically polished using aqueous acetic acid and hydrogen peroxide, washed and dried before mounting in the apparatus. An atomically clean surface was then generated by several hours' argon ion bombardment (3μA, 900 eV beam energy, 3×10^{-4} mbar) and annealing at 400 K.

Dioxygen (British Oxygen Gasses, 99.99% purity) was admitted to the analyzer chamber from a separately pumped gas handling line via a liquid nitrogen cooled trap. Water vapour (distilled and deionized) was subjected to several freeze-pump-thaw cycles before admission to the chamber of the spectrometer.

Binding energies were referenced to the $Pb(4f_{7/2})$ peak for the clean metal at 136.7 eV. Peak areas were calculated from the smoothed, background-stripped spectra and composite spectra were curve-fitted to Gaussian components using least-squares optimization programme.

Adatom surface concentrations (σ) were estimated[9] using Eq. (1)

$$\sigma = Y_m \mu_s \rho N \lambda \cos\Phi / Y_s \mu_m M \qquad \ldots (1)$$

where Y_m is the integrated photoelectron signal from the adsorbed oxygen species; Y_s is the intensity of the clean $Pb(4f_{7/2})$ peak; μ_m is the ionization cross section of the $O(1s)$ orbital; μ_s is the ionization cross section of the $Pb(4f_{7/2})$; ρ = density of lead; λ is the photoelectron escape depth through the substrate; Φ = angle between collected electrons and normal to the substrate; N = Avogadro's number and M = atomic weight of lead.

Results and discussion

Adsorption of water vapour on clean Pb(100) surfaces

Fig. 1 shows the O(1s) spectral region of the Pb(100) surface after prolonged argon ion bombardment and annealing cycles. The surface was free from contamination and remained unchanged after being left in vacuum for 3 h. The UV spectrum of this surface is shown in Fig. 2a. It indicates the presence of two distinct levels at 0.7 and 2.8 eV below the Fermi level together with broad maxima at 7.0 eV. The "double structure" near the Fermi level arises from predominantly 6p-type states and the broad weaker structure to higher binding energy from 6s-type states[10].

At 298 K, no adsorption was detected even after exposing the clean surface to 60000 L (1L = 10^{-6} Torr s) of water vapour. This obviously reflects the low reactivity of lead (and other sp-metals like Al, Mg and Zn) towards this molecule compared with metals such as Mo, Fe and Co[11], which dissociate H_2O easily at 298 K. The d-band of the transition metals seems to be playing a major role in dissociating the molecule. These results present H_2O as a fruitful molecule to test the activity of different metallic systems. In contrast, no obvious distinction could be made between the relative activities of sp and transition metals using relatively active substrates such as nitric oxide[1] and hydrazine[12].

At 80 K, adsorption of water vapour on lead occurs at a very high sticking probability (~ unity). The O(1s) photoelectron spectrum indicates the presence of only one peak centered at 533.5 eV (Fig. 1). This peak is normally seen after condensing water on a variety of substrates at 80 K and therefore can be attributed to a physically adsorbed H_2O state. As to be expected from the high sticking probability of this molecule at 80 K continued exposure to water results in a rapid enhancement of the 533.5 eV peak; after 20 L multilayer adsorption was observed (Fig. 1).

The corresponding ultra violet changes are illustrated in Fig. 2b. The condensed layer induces essentially three energy levels at about 7.0, 9.0 and 11.0 eV. These peaks match with the strong $1b_1$, $3a_1$ and $1b_2$ emission maxima from H_2O in the gaseous phase[13] (Fig. 1c) after adding 6.5 as a work function correction plus relaxation energy. The ultra violet spectra supports further the XPS data that H_2O is adsorbed in a molecular mode only.

The adsorbed H_2O layer was left in vacuum for 30 min to examine any possibility for dissociation. But
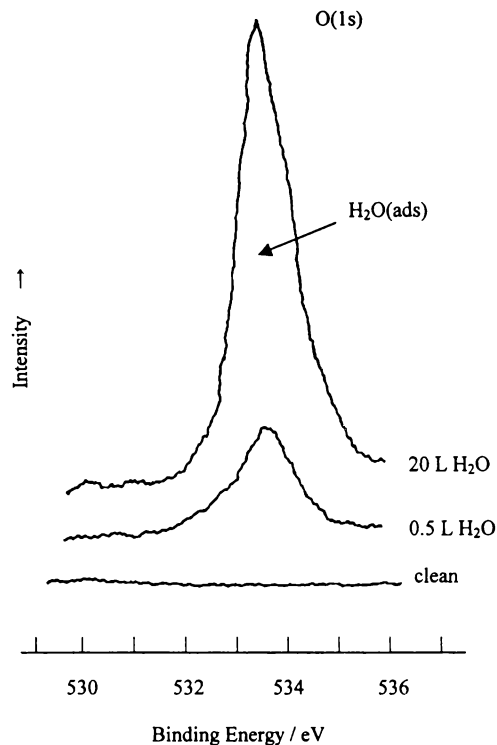
Fig. 1—O(1s) spectra for the adsorption of H_2O vapour on Pb(100) at 80 K. (pass energy = 20 eV)
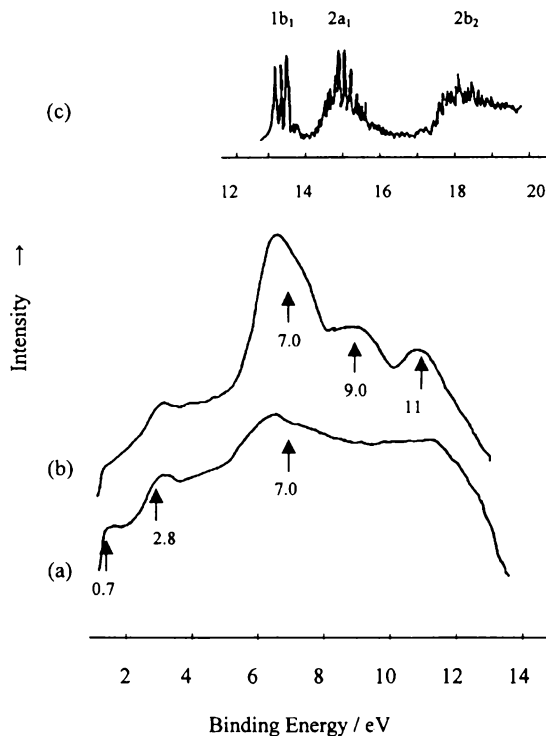
Fig. 2—(a) He(I) spectrum for clean Pb(100). (b) He(I) spectrum of Pb(100) surface after exposure to 20 L of water vapour at 80 K. (c) He(I) spectrum of water vapour. The spectra have been aligned to allow for differences in reference levels.

both XPS and UPS ruled out any of that since no new features emerged. On warming the adlayer to 298 K a rapid diminution of intensity occurs at about 130 K and at 150 K no intensity is present in the 533–534 eV spectral range. The heat of adsorption (ΔH) may be estimated from the observed equilibrium concentration (σ) via the equation[7]

$$\sigma = Z\,\tau \qquad \qquad ...(2)$$

where Z is the molecular impact rate at the surface and τ is the surface lifetime of the adspecies. This in turn is given by the Frenkel equation

$$\tau = \tau_o \exp(\Delta H/R\,T) \qquad ... (3)$$

Taking $\tau_o = 10^{-13}$ s and substituting our experimental values for σ and Z we find $\Delta H = 30$ KJ mol^{-1}.

Interaction of Pb(100) with dioxygen

Due to the difficulty of obtaining oxide single crystals for structural studies, well ordered thin oxide layers generated at the surfaces of metal single crystal have been studied. Exposing the clean Pb(100) surface to 12000 L of dioxygen results in an O(1s) peak at 530.0 eV (Fig. 3) and a skewing of the Pb(4f) peaks to higher binding energy (Fig. 4b). The oxide layer induces a doublet structure near the Fermi level arises from the overlap of the O(2p) and Pb(6p) orbitals (Fig. 5a). These changes were also observed upon the interaction of atomic oxygen with Pb which reflects the adsorption and subsequent dissociation of dioxygen on lead. The dynamic of dioxygen dissociation on metal surfaces is suggested to occur via a sequence of simple steps:

$$O_2(g) \rightarrow O_2(w) \xrightarrow{\ e\ } O_2^-(w) \xrightarrow{\ e\ } 2\,O^-(w)$$
$$\xrightarrow{\ 2e\ } 2\,O^{2-}(ads)$$
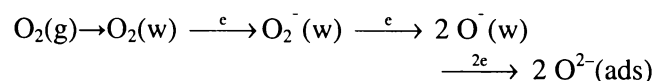
where (ads) refers to a strongly chemisorbed state that can be characterized by electron spectroscopy, while (w) refers to a weakly adsorbed species undergoing rapid surface diffusion[14].

On maintaining oxidized surface in vacuum for 1 h, no change in the O(1s) peak intensity was observed. If this indicates the absence of incorporation at 298 K, an estimate of the oxygen concentration can be established using Eq. (1). After exposure of 12000 L dioxygen the equation gave a σ value of about 6×10^{14} cm^{-2}. Since lead is face-centered cubic with a unit cell of side 495 pm the number of atoms exposed per 1cm^2
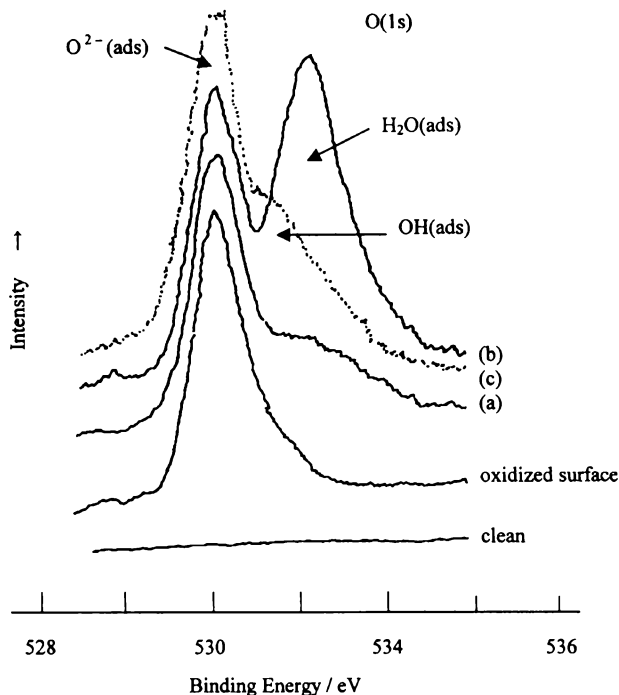

Fig. 3—O(1s) spectral region for (a) oxidized Pb(100) surface, after exposure to 0.5 L of H_2O at 80 K; (b) after exposure to 20 L of H_2O at 80 K; (c) after warming the adlayer to 298 K. (pass energy = 20 eV).
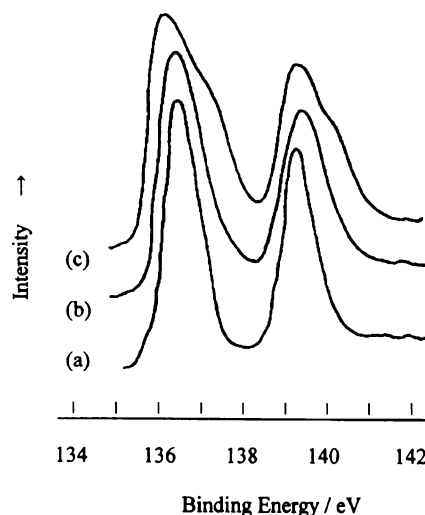

Fig. 4—Pb(4f) spectral region of Pb(100) at 298 K; (a) clean surface; (b) after exposure to 120000 L $O_2(g)$; (c) after exposure to 120000 L water vapor.
(pass energy = 20 eV)

of Pb(100) plane is therefore 8.16×10^{14} and the coverage will be about 75% of a monolayer if it is assumed that every surface lead atom is involved in bonding to oxygen. Increasing the exposure to 120000 L results in slight increase in the O(1s) peak intensity ($\sim 6.5\times10^{14}$ cm^{-2}) which obviously suggests a drastic drop in the rate of the adsorption.
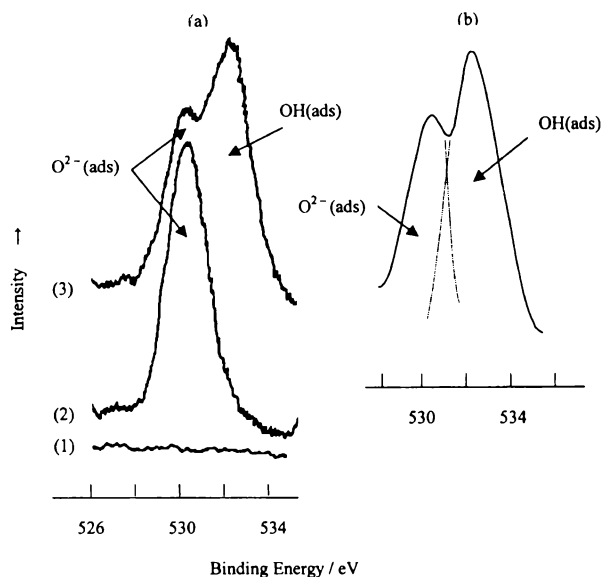
Fig. 5—(a) O(1s) spectra for a clean Pb(100) surface (1), after exposure to 120000 L dioxygen (2) and subsequently to120000 L water vapour at 298 K (3). (b) Corresponding smoothed and curve – fitted spectrum to a (3)
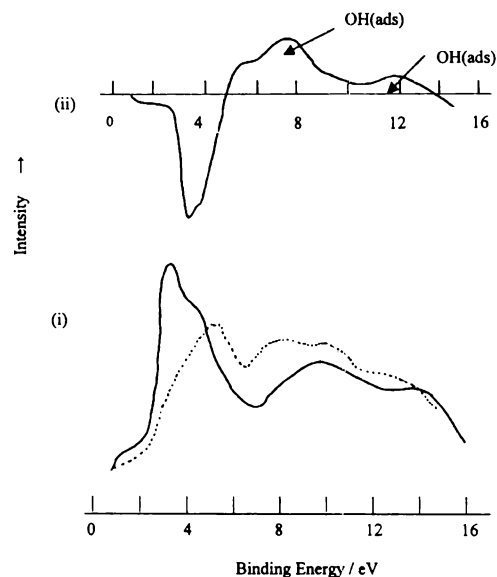
Fig. 6—(i) He(I) spectrum for: (a) oxidized lead surface (b) the surface after exposure to 120000 L H₂O vapor at 298 K. (ii) He(I) difference spectrum b – spectrum a.

Adsorption of water vapour on oxidized lead surfaces at 80 K

The preoxidized crystal was cooled to 80 K and exposed to a very low water vapour pressure. After 0.5 L of water vapour a broad hump appeared on the high binding energy side of the 530.0 eV peak, which developed into a clear peak centered at 533.5 eV after 5 L (Fig. 3b). Both XPS and UPS data indicated that this adlayer is simply physically adsorbed H₂O (due to dispersion forces). On warming the surface to 298 K, disappearance of this peak with some intensity gain in the 532.0 eV region is observed. The O(1s) shoulder at 532.0 eV, is analogous to the O(1s) peak observed on copper and other substrates and the general conclusion suggests the formation of a strongly adsorbed hydroxyl species due to H₂O dissociation on the surface[1].

The question naturally arises as to why H₂O dissociates on an oxidized lead surface and not on a clean one. The answer to this emerges from the role of the highly electronegative oxygen species in creating a significant deficiency in the metal sites. These "positive' lead centers are more susceptible to attack by a nucleophile such as H₂O or OH⁻.

Adsorption of water vapour on oxidized lead surfaces at 298 K

The following remarkable changes were observed upon exposing Pb(100)–O surface at 298 K to10⁻⁴ mbar H₂O vapour for 20 min:

(i)   The O (1s) peak at 530.0 eV partially diminishes whereas an O(1s) peak develops at 532.0 eV (Fig. 5a) These events are shown quantitatively in Table 1.

(ii) The Pb(4f₇/₂) peak at 136.7 eV broadens to a full-width at half-maxima (FWHM) of 2.2 eV compared with 1.4 eV and 1.9 eV for the clean and oxidized surfaces (Fig. 4).

(iii) The doublet structure near the Fermi level was affected as shown in Fig. 6. The figure also indicates the appearance of a complicated structure between 6 and 12 eV.

It is clear that the transfer in intensity from the oxide region to the hydroxyl emission region (Fig. 5) suggests that H₂O vapour dissociates on Pb(100)–O to give chemisorbed hydroxyl species

$$H_2O(g) + O^{2-}(ads) \rightarrow 2OH(ads)$$

This reaction induces a significant shift in the lead core level peaks much larger than that noted during interaction with molecular oxygen. A possible explanation for this interesting shift behaviour seems to be that the adsorbed oxygen species acquire a partial negative charge as the surface reorganizes in the presence of gaseous oxygen, thus enabling the positive charge on Pb to increase as the surface, initially PbOₓ (x<1) in stoichiometry, oxidizes to PbO. The positive charge on the metal increases further on adsorbing hydroxyl species probably to

Table 1—Surface coverage observed during the interaction of water vapour with Pb(100)–O surface at 298 K

	O(ads)	OH(ads)	H$_2$O(ads)	OH(ads) formed /
		/10^{14} cm^{-2}		O(ads) consumed
Oxidized lead	6.5	-----	-----	-----
Oxidized lead + 3.9 H$_2$O vapor	7.7		-----	2.7

achieve a Pb^{+4} valence state through the formation of PbO(OH)$_2$. The corresponding curve fitted data (Fig. 5 and Table 1) indicate that the OH(ads)/O(ads) peak intensity ratio is about 2:1. This interesting result provides unambiguous evidence that the new chemisorbed state consists formally of two hydroxyls and one oxygen species.

The strongly chemisorbed hydroxyl species may be located either within the lattice or on the top of the positively metal atoms. In both cases adsorbed oxygen seems to play a dual role: first the activation of the O–H bond in H$_2$O and secondly conferring stability on the oxyhydroxide formed. The O(1s) spectra observed with nickel at 295 K, which had been first exposed to oxygen and then to water at 80 K , were also interpreted as being due to an overlayer of an oxyhydroxide analogous to βNiO(OH)[1]. Calculations by Anderson[15] have drawn attention to the distinct role that surface and subsurface oxygen can play in chemical reactivity. Unfortunately, the geometrical distribution of the OH(ads) species over the surface is not clear since the adlayer failed to give any LEED features other than a high increase in the background intensity.

Table 1 also indicates that the concentration of OH(ads) formed on the surface is 2.7 times the O^{2-} (ads) consumed . To account for these stoichiometric ratios we propose that at 298 K H$_2$O vapour dissociates on oxidized lead surface to give adsorbed hydroxyl species and hydrogen atoms, which either react with O^{2-}(ads) or recombine and desorbs as H$_2$(g)

$$H_2O(g) \rightarrow OH(ads) + H$$

$$O^{2-}(ads) + H \rightarrow OH(ads)$$

$$H + H \rightarrow H_2(g)$$
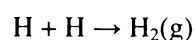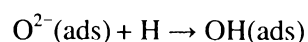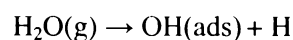
Based on our results the concentration of H$_2$O vapour that dissociates on lead surface may be sufficient to initiate coadsorption-induced chemisorption (with e. g. NO, N$_2$O, NH$_3$, CO$_2$) leading to highly selective reaction pathways.

The valence level spectra (Fig. 6) provides strong additional support for the oxidation-hydroxylation model based on the XPS data. There are three main peaks to the difference spectra: a peak at 3.2 eV due to emission from the attenuated O(ads) (2p) orbital and two peaks at 7.0 and 12 eV we assigned to emission from the surface hydroxyls. The formation of OH(ads) species on lead surfaces was confirmed further by exposing a clean Pb(100) surface to oxygen then to hydrogen atoms. An O(1s) peak developed at 532.0 eV and the He(I) difference spectra indicates an extra intensity at 7.0 and 12 eV.

Most studies to date have focused simply on the decomposition of hydrocarbon fragments[16]. Of more catalytic relevance would be studies of reactions between hydrocarbon fragments as well as reactions of hydrocarbon fragments with coadsorbed species such as H, O, OH, and NH$_2$. Relatively few studies of these processes were investigated using XPS[17].
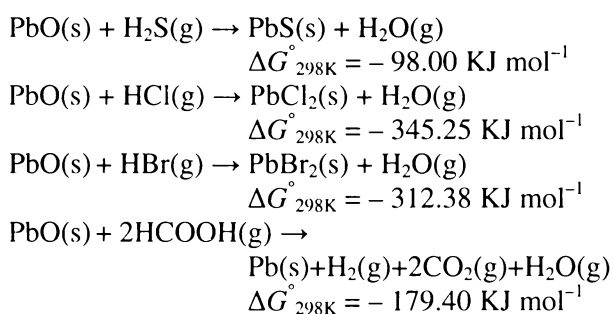
The possibility of Pb(100)-O to activate the C–H bond in some organic molecules such as ethylene, propylene and acrolein were examined in the temperature range 80–450 K through the following experiments: (a) exposing the clean Pb(100) surface to O$_2$(g) and subsequently to each olefine at 80 K; (b) warming the adlayer formed at 80 K to room temperature in 10^{-4} mbar olefine; and (c) exposing the clean surface simultaneously to O$_2$(g) and olefine mixture at 298 K and also at 450 K.

In all these attempts dioxygen was adsorbed to form O^{2-} (ads) and the olefins were only adsorbed in the molecular mode at 80 K. No significant chemisorption was observed throughout the entire temperature range. Roberts observed similar features on clean and preoxidized magnesium surfaces[14] using propylene as a probe molecule. However, very limited chemisorption was detected when Mg(0001) surface was exposed simultaneously to a very low pressure of O$_2$ and olefin mixture at 298 K. This result may reflect the possibility of forming intermediates on Mg(0001) and probably on Pb(100) surfaces. The concentration of these short-lived species on lead surface is too small for spectroscopic detection and study.

In contrast to lead and magnesium oxides, Cu(111)–O activated the carbon-hydrogen bond in ethylene[18] at 298-373 K to form a relatively stable mixed ligand adlayer "OH. C$_2$H$_3$". To understand such observations, information concerning the strength of all chemisorbed species must be established. Within the framework of our XPS and

UPS data such information cannot be extracted. Alternatively, if we follow the traditional assumption that a correlation "apparently" exists between the heats of chemisorptions and the heats of formation of the corresponding bulk compounds.

Then the chemisorbed oxygen-copper interaction will be the weakest (ΔH°_f for Cu_2O, CuO, PbO, PbO_2, Pb_3O_4 and MgO are ∼166.7, –155.2, –217.9, –276.6, – 734.7 and –601.8 KJ mol^{-1} respectively). This would explain the relative ease of hydrogenation of the oxygen – copper bond to form the complex. "OH. C_2H_3" compared with lead and magnesium oxides. At the same time the strong interaction between lead and oxygen would only allow surface reactions that are thermodynamically compensative. In the present work the surface reaction between $Pb(100)$–O and H_2O vapour seems to be driven by the formation of lead oxyhydroxide, while reactions with H_2S, HCl, HBr and formic acid are driven by the formation of water:

$$PbO(s) + H_2S(g) \rightarrow PbS(s) + H_2O(g)$$
$$\Delta G^{\circ}_{298K} = - 98.00 \text{ KJ mol}^{-1}$$
$$PbO(s) + HCl(g) \rightarrow PbCl_2(s) + H_2O(g)$$
$$\Delta G^{\circ}_{298K} = - 345.25 \text{ KJ mol}^{-1}$$
$$PbO(s) + HBr(g) \rightarrow PbBr_2(s) + H_2O(g)$$
$$\Delta G^{\circ}_{298K} = - 312.38 \text{ KJ mol}^{-1}$$
$$PbO(s) + 2HCOOH(g) \rightarrow$$
$$Pb(s)+H_2(g)+2CO_2(g)+H_2O(g)$$
$$\Delta G^{\circ}_{298K} = - 179.40 \text{ KJ mol}^{-1}$$

The interaction of formic acid with oxidized lead and copper surfaces[2] provides further evidence for the stability of these complexes. In both cases "hydroxy formate" (– OH.COOH) species form below 298 K apparently with little thermodynamic gains. The formate at the lead surface is highly unstable and decomposes spontaneously at 298 K on continued exposure to HCOOH(g) leading to regeneration of the clean surface. In contrast, the more stabilized Cu(OH)(HCOO) surface cannot be reduced by formic acid alone at 298 K. To regenerate the copper surface,

the adlayer has to be heated in vacuum to 520 K. In the light of these results, there does, appear to be a correlation between the strength of the metal – oxygen bond and its ease of hydrogenation by coadsorbed molecules.

Acknowledgement

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