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Electronic, chemisorption and catalytic properties of Pd overlayers on Ru(100) probed by CO and O_2 adsorption and reaction

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We have employed UHV surface sensitive techniques together with CO and oxygen adsorption and reaction to link the chemical, electronic and structural properties of ultra-thin Pd films vapour-deposited on Ru(100). At low Pd coverage the properties of the Pd overlayer are considerably modified relative to the bulk-like properties exhibited by thick Pd films. A Pd coverage of 6 ML seems to mark a critical transition to bulk-like Pd behaviour. The strongest modifications in the Pd overlayer occur for coverages up to 2 ML and are exemplified by a reduction in the CO desorption temperature, a low DOS at Fermi level, E_f, and a lower activity toward CO oxidation.

Keywords: oxygen; Ru(100); palladium; CO oxidation

1. Introduction

Bimetallic systems are widely used in catalysis as they may display beneficial properties compared with those of their individual components [1]. An improved understanding of bimetallic systems can be obtained by ultrahigh vacuum (UHV) modelling of these systems carried out by vapour depositing one metal onto a single crystal of a different metal. In this respect Pd overlayers on transition metal surfaces have been extensively studied, not only in terms of overlayer structure, growth mode and electronic properties but also to investigate the chemical/catalytic properties of thin Pd films [2–6]. In particular the adsorption of simple probe molecules such as CO has attracted considerable attention [2,3].

The vapour deposition of Pd overlayers on Ru in particular has attracted several studies concentrating mostly on the basal plane Ru(001) [1,2,5]. The Ru(100) substrate employed here differs in that the surface structure is both more open and anisotropic. We have previously characterised the growth mode and thermal stability of Pd overlayers on Ru(100) using low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) measurements [6]. These results are consistent with a layer-by-layer type growth of Pd at 300 K to coverages of at least 4 ML (1 ML = 8.6×10^{14} atoms cm^{-2}). LEED indicated a pseudomorphic (1×1) pattern for coverages of ~ 2–6 ML, coverages < 2 ML yielding $1 \times n$ $(n = 2, 3)$ patterns. Pd films in excess of 2 ML were unstable towards agglomeration on annealing at temperatures > 650 K. Pd thermal desorption profiles show a single desorption peak (α_1) at ~ 1380 K for coverages up to 2 ML. For > 2 ML Pd a second desorption state (α_2) appears at lower temperature, which is due to multilayer desorption from increasingly large three-dimensional agglomerates.

Here we present photoemission data of the Pd/Ru(100) system to elucidate the electronic properties of Pd overlayers with varying coverage. In addition, chemisorption and catalytic properties were investigated using CO and oxygen chemisorption and CO–O coadsorption/reaction as a function of Pd coverage. Changes in the electronic and structural properties of the overlayer are related to the chemisorption and catalytic properties.

2. Experimental

Experiments were performed in two separate UHV chambers operated at a base pressure of about 1×10^{-10} Torr. The first was equipped with a retarding field analyser, glancing incidence electron gun for Auger measurements, quadrupole mass spectrometer, ion gun and capillary array gas doser. The second was similarly equipped but with additional facilities for photoemission experiments: twin anode X-ray source, He discharge lamp and hemispherical analyser mounted on a turntable for angle-resolved measurements. Pd deposition in both chambers was carried out using a home-built vapour deposition source consisting of a W filament wrapped with Pd wire. In all cases the Pd overlayers were prepared by deposition with the substrate at ~ 300 K and coverages were calibrated using a combination of LEED, TPD and AES as described in ref. [6].

The sample was cleaned using a well established procedure [7] involving cycles of argon bombardment,

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annealing at 1500 K and oxygen adsorption/desorption. X-ray photoelectron spectroscopy (XPS) measurements were carried out using Mg(Kα) radiation (1253.6 eV) with the X-ray source operated at 180–240 W. XPS binding energies were referenced to the Ru($3d_{5/2}$) peak at 279.9 eV. Angle-resolved ultra-violet photoelectron spectroscopy (ARUPS) binding energies were referenced to the Fermi level (E_f) and obtained using HeI radiation (21.2 eV). The analyser acceptance angle was $\sim 2°$. Gas exposures are quoted in langmuirs (L) where $1\,L = 1 \times 10^{-6}$ Torr s.

Adsorption sequences on Ru(100) are represented by abbreviations of the type O_1/Pd_x/Ru(100) which indicates oxygen adsorption on a Pd overlayer where the suffices x and 1 represent the Pd and oxygen coverages in monolayers.

3. Results and discussion

3.1. XPS and ARUPS of Pd/Ru(100) system

Fig. 1 shows Pd(3d) XPS spectra for several Pd coverages on Ru(100). For coverages > 1.5 ML no significant shift was observed in the Pd($3d_{5/2}$) binding energy at 335.2 eV. For the lowest coverage, 1 ML, there was a small shift of 0.3 eV to lower binding energy. This shift could be accounted for by the lower coordination of the Pd atoms in the thin film compared with bulk Pd atoms. This explanation has been used to account for the reported shift in the Pd(3d) peak of 0.4 ± 0.1 eV to lower binding energy for the surface atoms relative to those in the bulk for pure Pd [8]. Using XPS to study the deposition of Pd on Ru(001) Rodriguez et al. [3] found no change in the position of the Pd($3d_{5/2}$) peak with increasing Pd coverage. They interpreted this as indicating a shift of $\sim$ 0.4 eV in the binding energy of the 1 ML Pd film relative to the surface atoms in bulk Pd. This shift, however, was attributed to charge transfer from Pd to Ru.

Fig. 2 shows the HeI ARUPS spectrum with increasing Pd coverage and indicates considerable changes with Pd coverage therefore proving a much more sensitive probe of the electronic properties of the overlayer than XPS. At coverages up to 2 ML the spectrum was dominated by a single feature and there was no substantial increase in the density of states (DOS) at E_f. For coverages > 2 ML there was both a broadening of the valence band and from 5 ML a steady and pronounced increase in the intensity of a second feature at 0.4 eV. At coverages > 12 ML the spectrum had developed a double peak structure broadly resembling that of a bulk Pd(111) sample. The peak at 0.4 eV has been attributed to a surface state and has been reported to form on Pd(111) like films on Nb [9,10] from coverages of 3 ML as well as single crystal Pd(111) [11].

It is of particular interest to note that the Pd spectrum for a 2 ML film has a significantly lower DOS at E_f than the thick film. Previous studies report a relatively low DOS at E_f for monolayer Pd films on Nb [11,12] and Ta [12]. Unfortunately, in the Pd_2/Ru(100) system it is difficult to separate the features of the Ru substrate and the Pd overlayer as they overlap. The effect of the Pd can, however, be seen in the changes in the overall peak shape. The addition of Pd does not initially (< 2 ML) lead to any increase in intensity at E_f which would tend to support a noble metal like low DOS at E_f for the Pd overlayer at coverages up to 2 ML. The low DOS at E_f for low Pd coverages has been variously attributed to charge transfer, orbital rehybridisation or final state

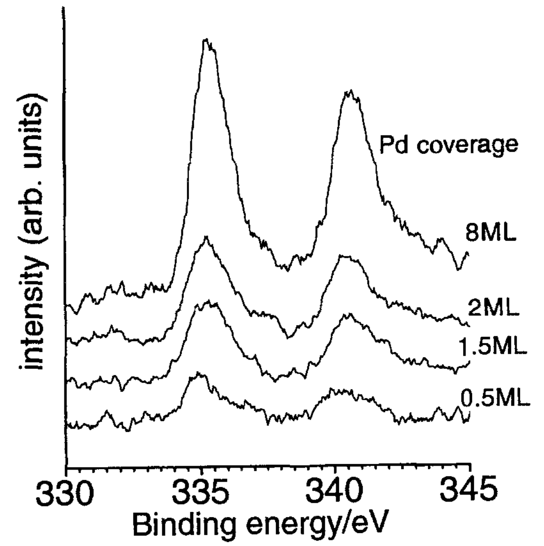

Fig. 1. Pd(3d) XPS spectra with increasing Pd coverage on Ru(100).

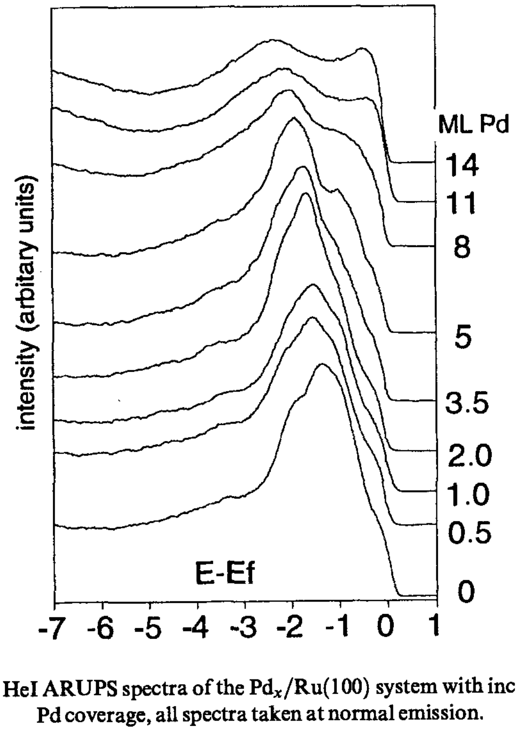

Fig. 2. HeI ARUPS spectra of the Pd_x/Ru(100) system with increasing Pd coverage, all spectra taken at normal emission.

effects and there is considerable debate as to which effect is dominant [13]. One explanation is that at low Pd coverages the photoemission intensity is dominated by Pd atoms of low co-ordination relative to bulk Pd. The metal states are therefore shifted below E_f because the metal d–d overlap is reduced as a consequence of a reduction in the Pd co-ordination. In addition, the hybridisation energy terms that serve to broaden the d band are reduced. An alternative explanation favoured by Goodman [2,3] is that charge transfer from Pd to the substrate dominates. It is, however, difficult to conclusively identify a single factor to account for changes in the ARUPS spectra.

Fig. 3 shows the changes in the HeI ARUPS spectrum for a thick (~ 12 ML) Pd film on annealing. For temperatures up to 650 K the spectra remained as a fairly low intensity feature similar to that on deposition. For temperatures > 700 K a sharp intense feature developed at 1.8 eV. This energy corresponds to the peak maxima of the 2 ML Pd spectrum obtained on deposition. With further annealing to 1000 K the spectrum very closely resembles that of a 2 ML Pd film. Further annealing to 1240 K led to little change in the spectrum. All these changes are consistent with agglomeration of the overlayer beginning at ~ 650 K and leading to development of a 2 ML thick pseudomorphic overlayer surmounted by islands which contribute little to the overall spectrum. This description of the annealing behaviour is supported by LEED and AES results on annealing [6]. The latter is illustrated in fig. 4 which shows the variation in the intensity of the Pd(328 eV) Auger transition as a function of annealing temperature for a range of initial Pd coverages. Thus for Pd coverages below 2 ML, no change in the Pd intensity occurred until the onset of desorption; for thicker films agglomeration of the overlayer began at around 650 K. The agglomeration process resulted in the ratio of the Pd(328 eV)/Ru(274 eV) Auger peak intensities dropping to very similar levels for coverages in the range 2–15 ML; though the final value did increase with the initial Pd loading. This suggests formation of an overlayer with a common thickness which is surmounted by three-dimensional Pd islands, which contribute much less to the overall Pd Auger signal. Consistent with this the LEED pattern developed after annealing Pd films of all coverages to > 650 K is well ordered (1 × 1) indicating a pseudomorphic Pd overlayer with additional diffraction features from the Pd islands for Pd coverages > 6 ML.

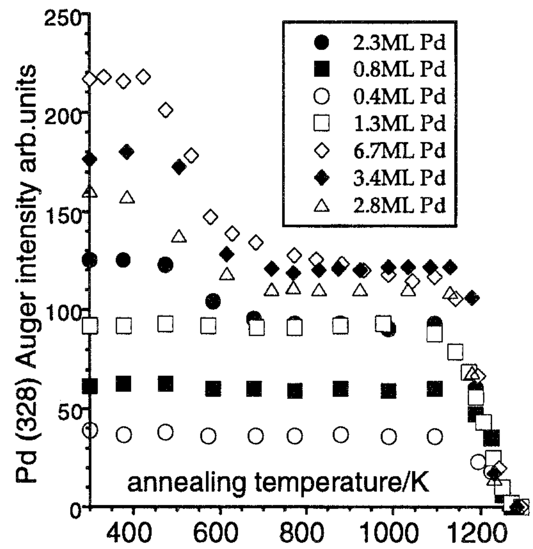

Fig. 4. Variation of Pd(328 eV) Auger intensity as a function of annealing temperature for several Pd loadings on Ru(100). Annealing time of 2 min, sample allowed to cool to < 400 K before Auger spectra were taken.

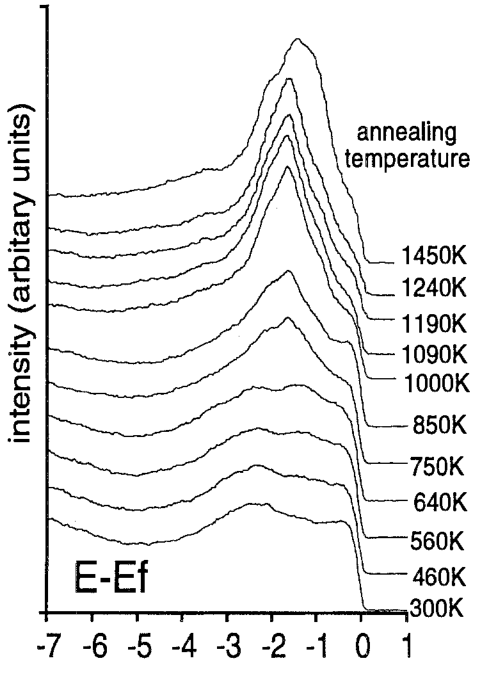

Fig. 3. HeI ARUPS spectra of $Pd_{12}/Ru(100)$ system taken after annealing the sample to the temperature indicated. All spectra at normal emission.

3.2. O_2 adsorption on Pd-precovered Ru

Fig. 5 shows oxygen thermal desorption profiles for a saturation (50 L) oxygen exposure on Pd-precovered surfaces of varying Pd coverage. With increasing coverage up to 2 ML there is gradual development of an O–Pd related desorption state α_1 at ~ 1043 K together with a decrease in the O/Ru(100) related desorption states. By 2 ML Pd, oxygen desorption from the O/Ru(100) states is completely quenched. With increasing coverage there is little further change in the oxygen desorption trace. AES indicates a small attenuation in the Pd(328 eV) and Ru(274 eV) Auger intensities on oxygen adsorption, consistent with oxygen adsorption on the Pd overlayer without a significant change in its morphology.

It is interesting to note that the α_1 oxygen desorption feature differs substantially from O/Pd(110) desorption

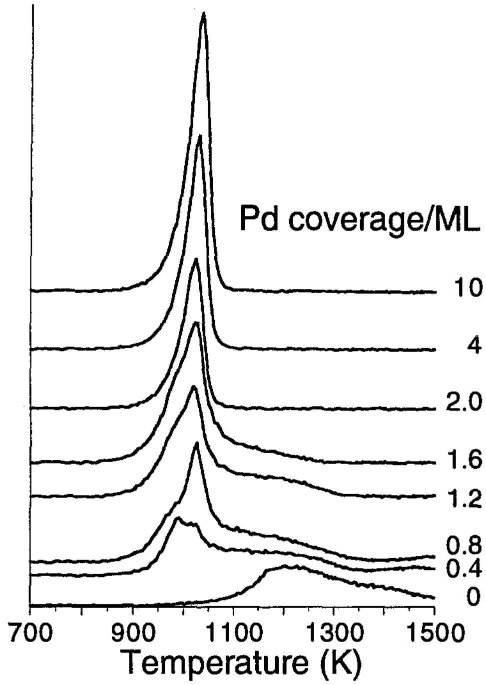

Fig. 5. Oxygen (mass 32) thermal desorption spectra of the $O_{sat}/Pd_x/Ru(100)$ system.

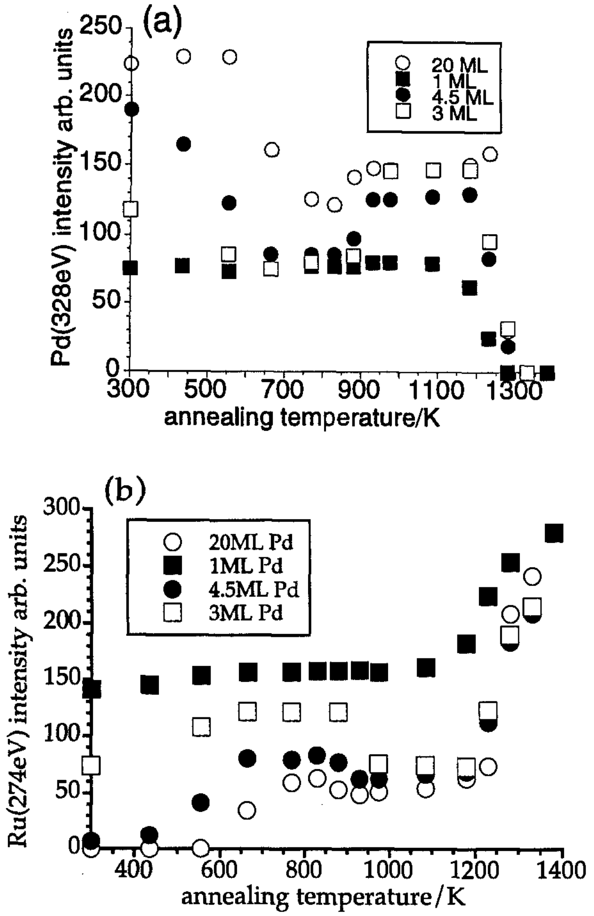

Fig. 6. Annealing behaviour of the $O_{sat}/Pd_x/Ru(100)$ system, showing variation in Auger intensities as a function of annealing temperature; (a) Pd(328 eV), (b) Ru(274 eV).

spectra where the Pd is structurally similar to the pseudomorphic Pd overlayer. For O/Pd(110) the oxygen desorption consists of two peaks at 710 and 790 K [14]. The α_1 peak therefore lies somewhere between this temperature and that for oxygen desorption from Ru(100), indicating a strong modification of the Pd overlayer relative to bulk Pd.

The temperature dependence exhibited by the $O_{sat}/Pd_x/Ru$ system as monitored by AES is illustrated in fig. 6. Comparison with fig. 4 shows that the dependence is similar to that exhibited by the Pd/Ru(100) system though with some additional oxygen-assisted agglomeration. Pd coverages above 2 ML showed a pronounced agglomeration in the Pd overlayer on annealing which was partly reversed on oxygen desorption at ~ 1000 K indicating a rewetting of the Ru. This rewetting process is reflected in both an increase in the Pd(328 eV) and a decrease in the Ru(274 eV) Auger intensities. Confirmation of oxygen-assisted agglomeration in O/Pd overlayers was found for addition of oxygen to preannealed thick films. An 8 ML Pd film was preannealed to 850 K prior to oxygen exposure. This oxygen resulted in a decrease of the Pd(328 eV) and Ru(274 eV) Auger intensities consistent with attenuation from the oxygen overlayer. However, if the system was again annealed to > 600 K further attenuation of the Pd Auger signal occurs indicating a further, oxygen-assisted, agglomeration of the Pd overlayer. The agglomeration of the Pd overlayer prior to oxygen desorption accounts for the lack of change in the oxygen desorption profile with increasing Pd coverage beyond 2 ML. The oxygen is therefore desorbed from a Pd film of similar thickness (probably ~ 2 ML) in all cases, the remaining Pd being contained in three-dimensional islands which have little influence on the oxygen desorption. This conclusion is additionally supported by LEED observations made after annealing of the $O_{sat}/Pd_x/Ru(100)$ overlayers. For all Pd coverages of 2 ML or above the LEED pattern observed after annealing for 2 min at 1000 K, (2 × 1)p2mg, is essentially identical to the pattern observed for 1 ML oxygen on Ru(100) [15] and also 1 ML oxygen on $Pd_2/Ru(100)$. The pattern is sharp with a very low background indicating that the oxygen is adsorbed on a well ordered pseudomorphic Pd overlayer. This data demonstrates that oxygen desorption is a relatively poor probe of the properties of the as deposited, thick Pd films.

3.3. CO adsorption on Pd-precovered Ru

CO thermal desorption spectra for saturation CO coverages on Pd-precovered Ru(100) are shown in fig. 7. These spectra show a decrease in the CO desorption temperature with increasing the Pd coverage to 2 ML after which point the CO desorption temperature increased to around that expected for CO desorption from bulk Pd

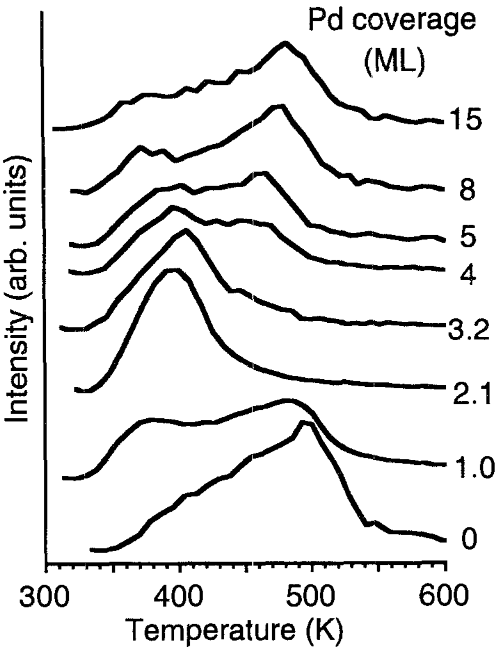

Fig. 7. CO thermal desorption spectra of CO/Pd_x/Ru(100) system following 30 L CO exposure at 300 K for increasing Pd coverages.

(~ 480 K for low index Pd planes [16]). The CO desorption peak maximum of 380 K for the 2 ML Pd overlayer is very close to the value reported for a complete monolayer of Pd on Ru(001) reported by Park [5]. Unlike the O/Pd_x/Ru(100) system the CO desorption spectra continue to change significantly for coverages > 2 ML. This is due to the Pd overlayer being relatively stable up to ~ 500 K. The CO spectra therefore reflect more clearly the Pd layer as deposited and not the system after completion of the agglomeration process as is the case for O/Pd_x/Ru(100). A lowering of the CO desorption temperature from thin Pd films has been interpreted as due to a reduction in the electron density of the thin Pd film relative to a bulk-like Pd overlayer. This reduces the ability of the overlayer to backdonate electron density to the CO and so in the Blyholder model for metal–CO bonding [17] reducing the CO–Pd bond strength. As shown above ARUPS results do in fact support an alteration in the electronic properties of the Pd overlayer with coverage, and most notably a reduced electron density at E_f for low Pd coverages and a recovery to a bulk-like valence band by ~ 12 ML. Changes in the CO desorption can therefore be related to the structural and electronic properties of the overlayer as deposited.

3.4. CO titration of oxygen-precovered Pd overlayers on Ru

Probably the most extensively studied catalytic reaction on Pd studied using surface sensitive techniques is CO_2 formation from CO and O_2 [18]. In contrast to the efficacy of Pd surfaces for this reaction Ru(100) is completely inactive towards CO oxidation in UHV at 300 K [15]. CO titration experiments of oxygen-covered Pd overlayers on Ru(100) were performed to investigate the alteration in the catalytic properties of the Pd overlayer as a function of Pd coverage. Fig. 8 shows the integrated thermal desorption yields of CO, O_2 and CO_2 as a function of Pd coverage following exposure to 20 L O_2 then 50 L of CO at 300 K (higher CO exposures had no effect on the desorption yields). For O_1/Ru(100) CO exposure yields only the saturation oxygen coverage of 1 ML. Deposition of Pd resulted in an immediate and radical alteration in the reactive behaviour of the surface. The most striking feature was total elimination of oxygen desorption after the deposition of ~ 3 ML Pd (at which point the surface is completely covered by Pd). This was accompanied by a corresponding increase in the CO and CO_2 yields. The CO_2 desorption yield exhibits a maximum and is quenched at ~ 6 ML Pd coverage. At this point the only desorption product is CO.

The catalytic behaviour of the system can be explained as follows. In common with other Pt group metals in UHV conditions CO oxidation is likely to occur via a Langmuir–Hinshelwood [19] mechanism between adsorbed CO and oxygen. In this respect it is important to note that even at low temperature (< 600 K) it has been established that CO can adsorb on oxygen-covered Pd surfaces, though a high coverage of CO inhibits O_2 adsorption [20]. Deposition of Pd therefore leads to the adsorption of CO (which is blocked on an oxygen-saturated Ru(100) surface at 300 K) and reaction with adsorbed oxygen at 300 K leading to CO_2 formation and immediate desorption. This process frees adsorption sites for the adsorption of more CO which is desorbed during TPD. For coverages < 3 ML some oxygen is unreactive and so desorbed during TPD. Oxygen desorption traces resembled those of the O/Pd_x/Ru(100) system though with a reduction in the intensity of the state associated with oxygen desorption from the Pd overlayer such that for Pd coverages > 3 ML

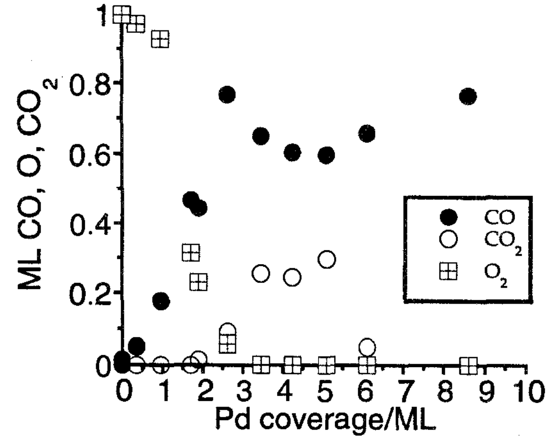

Fig. 8. CO, O_2 and CO_2 thermal desorption yields as a function of Pd coverage for TPD taken after O_{sat}/Pd_x/Ru(100) systems were titrated with a 50 L CO exposure. Desorption yields for oxygen atoms, CO and CO_2 are quoted in monolayers (ML) relative to the Ru(100) substrate.

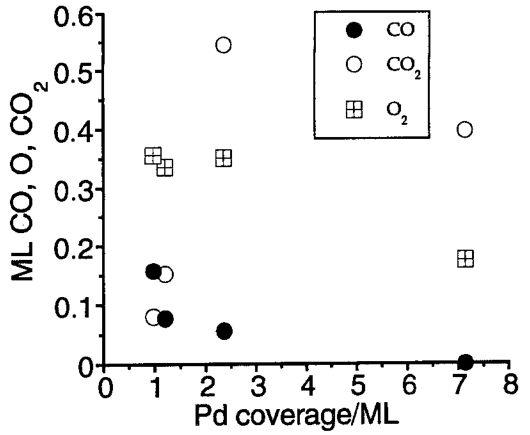

Fig. 9. CO, O_2 and CO_2 thermal desorption yields as a function of Pd coverage for TPD taken after $O_{sat}/Pd_x/Ru(100)$ systems were titrated with a 1 L CO exposure. Desorption yields for oxygen atoms, CO and CO_2 are quoted in monolayers (ML) relative to the Ru(100) substrate.

no oxygen is observed. For Pd coverages between 2 and 6 ML some or all of the remaining oxygen left after CO exposure reacts with adsorbed CO above 300 K and produces CO_2 during TPD, CO_2 desorption occurring between 300 and 500 K. For Pd coverages > 6 ML all the preadsorbed oxygen is reactively removed by CO at 300 K and the surface is repopulated with CO.

Further evidence for this process was provided by lowering the CO exposure to 1 L (fig. 9). This resulted in an increased CO_2 and O_2 desorption yield at the expense of CO as the CO exposure becomes insufficient to completely remove all the reactive oxygen.

The threshold Pd coverage for complete reactive removal of preadsorbed oxygen by CO at 300 K is 6 ML. This coverage corresponds to the transition point for a number of properties in the overlayer: First, it is the coverage at which little further change is observed in the CO desorption profile; second, where the Pd overlayer structure begins to become disordered and the pseudomorphic overlayer structure breaks down; third, it is the point where ARUPS begins to exhibit a bulk-Pd-like surface state at 0.4 eV. All these observations point to bulk-like Pd characteristics being adopted by the overlayer and the influence of the Ru substrate on the properties of the Pd surface being overcome.

4. Conclusions

ARUPS indicates a strong coverage dependence of the valence band electronic structure of Pd overlayers. Low Pd coverages display a lower DOS at E_f compared with the bulk Pd characteristics associated with coverages in excess of 10 ML. This variation is most pronounced for Pd coverages < 2 ML.

The strong variations in the valence band structure are reflected in the chemisorption and catalytic properties of the overlayer. CO desorption from a 2 ML Pd film at 370 K exhibits a peak maximum at ~ 100 K lower temperature than that of a 8 ML Pd film which exhibits a bulk-Pd-like CO desorption profile. Oxygen desorption occurs at 1070 K from Pd films of 2 ML thickness though the desorption temperature does not change with increasing Pd coverage beyond 2 ML due to substantial agglomeration of the Pd at a temperature well below the oxygen desorption threshold.

No CO_2 formation was observed on clean Ru(100) for titration of preadsorbed oxygen with CO, but the addition of even submonolayer amounts of Pd triggers its formation. By a Pd coverage of 6 ML all the preadsorbed oxygen is reactively removed at 300 K by CO exposures of 50 L.

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