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Authors

Tysoe, W.T.
Zaera, F.
Somorjai, B.A.

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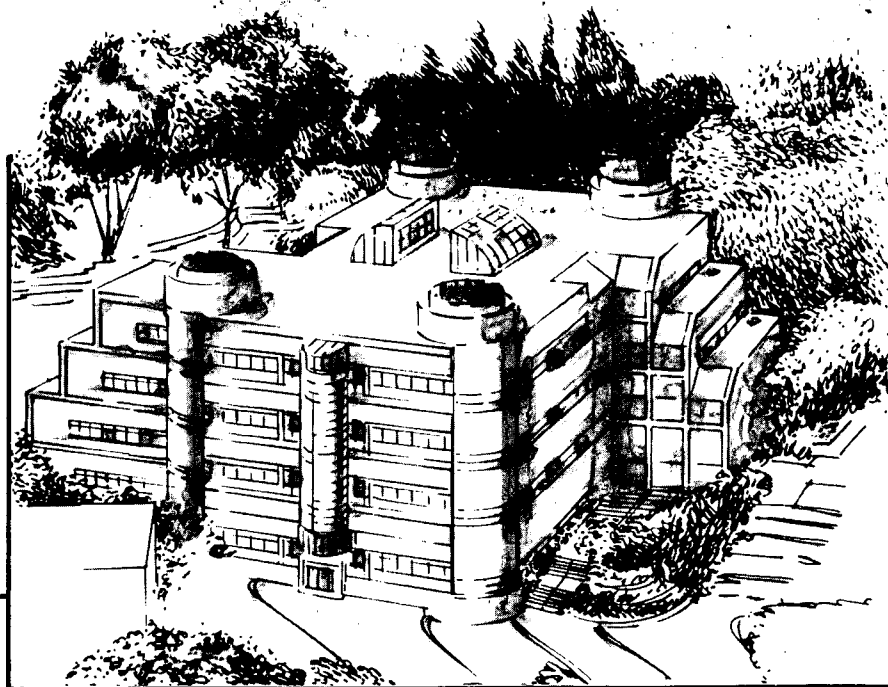
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Lawrence Berkeley Laboratory • University of California
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AN XPS STUDY OF THE OXIDATION AND REDUCTION OF THE
RHENIUM-PLATINUM SYSTEM UNDER ATMOSPHERIC CONDITIONS

by

W.T. Tysoe,^a F. Zaera,^b and G.A. Somorjai

Department of Chemistry, University of California, Berkeley,
and Materials and Chemical Sciences Division,
Lawrence Berkeley Laboratory, 1 Cyclotron Road,
Berkeley, California 94720

ABSTRACT

The oxidation and reduction of the platinum-rhenium system has been studied by using x-ray photoelectron spectroscopy (XPS). Rhenium films about 10 layers thick were formed by evaporation onto a platinum foil under vacuum. These samples were sequentially exposed to 1 atm. of oxygen at different temperatures and then reduced with 1 atm of H₂. XP spectra were taken after each high pressure experiment. A mixture of rhenium oxides were formed after oxidation at above 475K, and depletion of the surface rhenium due to the formation of the volatile Re₂O₇ was observed after treatments above 575K. Subsequent hydrogen treatment did not completely reduce these oxides, and a remaining low oxidation state rhenium, perhaps ReO, could be detected by XPS. The behavior of alloys of platinum-rhenium after similar treatments was also studied. Oxidation for this system was even more facile than for the rhenium overlayers, but almost complete reduction to the metallic state was achieved by hydrogen treatment of the oxides, indicating that platinum may catalyze this rhenium reduction step.

^aPresent address: Dept. of Chemistry, Univ. of Wisconsin,
Milwaukee, WI 53201

^bPresent address: Dept. of Chemistry, Univ. of California,
Riverside, CA 92521

INTRODUCTION

There is significant lack of consensus in the literature concerning the oxidation state of the metals in the platinum/rhenium reforming co-catalyst following preparation, that is, after calcination and reduction of the deposited salts. There is agreement on the fact that the rhenium portion of the catalyst is oxidized to some reasonably high oxidation state (+VI or +VII) after oxygen treatment.¹ Although Re_2O_7 is volatile, it appears that its interaction with the alumina support prevents it from disappearing from the catalyst.^{1,2} The oxidation state following reduction in hydrogen, however, is less clear. Values between Re(IV) ³ and Re(0) ⁴ have been suggested. Re_2O_7 is easy to reduce between 575K and 625K,^{5,6} but lower oxidation states of rhenium are more difficult to reduce to the metallic form, especially when water is present.^{7,8} However, platinum is known to catalyze the reduction of a number of metal oxides (including rhenium) by hydrogen.⁹ In addition, the calcination temperature appears to be crucial in the subsequent response of the rhenium to reduction.¹⁰

Most measurements of oxidation states have relied on indirect methods such as titrations, chemisorption, or reactivity studies. These experiments yield average values, and they have been performed on supported catalysts, where uniformity between samples is difficult to attain.¹¹⁻¹³ More direct techniques such as x-ray absorption^{14,15} and x-ray photoelectron spectroscopy (XPS)^{15,16} have also not given any definite answer to this problem.

We have chosen therefore to study a somewhat simpler, but more reproducible system, that is, rhenium deposited onto or alloyed with a platinum metal film. The oxidation states were measured using XPS;

rhodium being particularly amenable to this method of analysis since chemical shifts of 5 eV are observed between rhodium metal and its highest oxidation state (Re(VII)).¹⁷ In our experimental set-up, the freshly prepared sample was isolated in a high pressure cell and heated while exposing to 1 atmosphere of hydrogen or oxygen. This cell was then evacuated and the sample reintroduced to UHV without any intervening exposure to air.

The degree of mixing between the rhodium and platinum was varied between two extremes, from a rhodium metal layer deposited onto the platinum (in which mixing is minimal) to an extremely intimate mix, in which the alloy is formed. Both these samples got oxidized to Re(VI) and Re(VII) after oxygen pretreatment, although the oxidation process was much faster on the alloy. However, alloying had a marked effect on the oxidation state following reduction, since for the alloy hydrogen treatment results in almost complete reduction of the rhodium to its metallic state. In contrast, the metal overlayer remained in a low oxidation state (perhaps Re(II)) following a similar hydrogen exposure. These results imply that the degree of mixing between the platinum and the rhodium affects the oxidation state of Re following hydrogen reduction, a conclusion that may account for the discrepancy between the data obtained on various catalysts.

EXPERIMENTAL

The experiments were performed in a bakeable diffusion pumped stainless-steel ultra-high vacuum (UHV) chamber operating at a base pressure of $\sim 1 \times 10^{-10}$ torr. The system was equipped with a coaxial isolatable high pressure reactor used for high pressure treatment of the sample, as shown in Fig. 1. The sample is mounted on a rotatable manipulator, which, when the high pressure cell is closed, can be

removed for fast sample transfer without compromising UHV. XPS was done by using a X-ray source equipped with a magnesium anode and a double-pass cylindrical mirror analyzer. The latter was also used for Auger analysis. The sample used in these experiments was a platinum foil which was cleaned using standard techniques. Rhenium was deposited onto this sample from a resistively heated Re wire, as described in detail elsewhere.^{18,21}

The chemical shifts of the various oxides of rhenium were calibrated by pressing a thin film of the respective pure oxides onto a platinum foil under an argon atmosphere in a glove box. The samples were then transferred under argon into the high pressure cell, which was then immediately evacuated and the sample introduced into UHV. In order to ensure that there were no shifts in XPS signal due to charging, spectra were taken at two x-ray source emission currents. Any charging shift would have manifested as a change in peak position as a function of emission current (i.e. x-ray flux). No such shifts were detected. All binding energies were reference to a value of 70.9 eV for the platinum $4f_{7/2}$ peak,¹⁷ that remained constant regardless of treatment. All spectra were analyzed by a routine that subtracts the background contribution due to secondary electrons and deconvolutes the peak shape of the excitation source.

RESULTS

Re 4f photoelectron spectra were taken for a group of rhenium oxide compounds: Re_2O_7 (Re(VII)), ReO_3 (Re(VI)), ReO_2 (Re(IV)) and metallic rhenium Re(0). The resulting spectra, taken at the Re 4f region, are shown in Figure 2. There are clear shifts in photoelectron peak positions as a function of oxidation state. The positions of the $4f_{5/2}$ and $4f_{7/2}$ peaks are presented in Table 1

and shown plotted as a function of oxidation state in Fig. 3. Also plotted for comparison are the data from other studies.^{16,19,20} Our spectra compare well with those obtained by other workers. Oxygen 1s photoelectron spectra were also taken, but since those did not yield significant information on the nature of the rhenium oxides, they are not presented here.²¹

The X-ray photoelectron spectrum of a rhenium layer deposited onto platinum is shown in Fig. 4(a). This spectrum includes 4f peaks from both the platinum substrate (~70 eV binding energy) and the rhenium layer (~40 eV energy). Since the sampling depth in XPS is dominated by the photoelectron escape depth, these data can be used to estimate the thickness of the rhenium layer. Using known values for the electron mean free path and for photoionization cross sections, we calculated the thickness of our rhenium films to be about 10 monolayers,^{17,22} enough so they behave like pure rhenium samples. Additionally, working with such rhenium films increases the surface sensitivity of the technique: 4f Re photoelectrons can penetrate more than 30 layers deep into the sample, so if a monolayer of surface oxide is formed on top of a pure rhenium sample the signal from the oxidized atoms will only contribute to about 10% of the total signal. In our case where we have only 10 layers of rhenium on top of a platinum foil, that same oxide will yield about 20% of all 4f Re photoelectron detected, a factor of two improvement in surface sensitivity with respect to the bulk sample.

Shown also in Fig. 4 are the Pt 4f and Re 4f spectra following various atmospheric pressure treatments. Heating to 475K (spectrum 4(b)) and 525K (spectrum 4(c)) in 700 torr oxygen for 5 minutes does not substantially alter the intensities of the platinum and rhenium

peaks. However, these ratios are considerably changed following treatment after heating to 625K under identical pressures. A more prolonged treatment at 575K shows a further decrease in rhenium signal and a concomitant increase in platinum signal. These data indicate a significant loss of rhenium from the surface due to the formation of the volatile Re_2O_7 . Fig. 4(f) displays the photoelectron spectrum after exposure to 700 torr H_2 at 575K and shows no further loss of rhenium, confirming that oxygen is indeed implicated in the loss of rhenium from the surface.

The Re 4f peaks are shown in more detail and at higher resolution in Fig. 5. Chemisorption of oxygen under UHV does not change the 4f XPS results, indicating that no oxidation takes place under those conditions. This result is in disagreement with that reported by Ducros et al.,²³ since they observed a shift of 1.1 V in the Re 4f peaks following oxygen chemisorption that they attributed to a surface oxide of composition between Re_2O and ReO . However, exposure to 700 torr of oxygen at 475K yields a spectrum with several additional features including peaks at 40.7 and 43.5 eV, and small shoulders at 45.2 and 47.1 eV (Fig. 5(b)), indicating formation of some oxides up to ReO_3 even at these temperatures. The peaks at about 1 eV higher binding energy than those from metallic rhenium correspond to an oxidation state below +4. This new state grows further after treatment at 525K (Fig. 5(c)). Above 600K, a small shoulder extends up to around 49 eV (Fig. 5(d)) indicating the presence of some Re_2O_7 , which is implicated in the loss of rhenium. Reduction in 1 atm. H_2 at 575K (Fig. 5(e)) results in the disappearance of most of the surface oxides. However, the peaks at 40.7 and 43.7 eV persist, indicating that the low oxidation state is stable towards further

reduction.

A similar series of experiments were performed on a platinum/rhenium alloy, which was formed by heating a rhenium covered platinum foil to 900K for a few seconds in vacuo.^{18,21} Fig. 6 shows the platinum and rhenium photoelectron spectra for the alloy before any treatment. The rhenium 4f peaks of the alloy are shown in Fig. 7 following various treatments. Fig. 7 (a) shows a spectrum from the untreated alloy. Fig. 7 (b) shows the spectrum after heating in oxygen at 575K. Clearly, in contrast to the case of rhenium deposited onto platinum, no photoelectron peaks due to metallic rhenium persist. This spectrum corresponds to rhenium in +2 and higher oxidation states. The major difference between the two situations is evident in the spectrum after reduction in hydrogen (Fig. 7(c)). This shows a spectrum essentially identical to the one in Fig. 7(a), indicating virtually complete reduction of rhenium to the metallic state.

DISCUSSION

A common feature of the oxidation of rhenium in 1 atm. of oxygen for both the evaporated metal layer and the alloy is a decrease in the rhenium peak intensity (Fig. 4) after heating above about 600K. This implies loss of rhenium from the surface either by evaporation or by diffusion to the bulk. However, heating the sample to an identical temperature in either vacuo or 1 atmosphere of hydrogen results in no change in relative peak intensities, so that surface to bulk transport is unlikely to be the cause of the rhenium loss. Since it occurs under oxygen environments, this phenomenon can be explained by the formation of a volatile oxide, i.e. Re_2O_7 . This suggests that under these mild conditions, rhenium can undergo facile oxidation to

Re(VII) in both cases, in a metal film or in an alloy, irrespective of the degree of mixing of the two components.

Further evidence of a rapid rhenium oxidation is furnished by the chemically shifted peaks in the more detailed photoelectron spectra of Figs. 5 and 7. The detection of some rhenium in the +7 oxidation state corroborates the observation that rhenium disappears by sublimation of Re_2O_7 . An interesting observation from these spectra is that the rhenium in alloy form shows no remaining Re(0) (within the depth probed by photoelectron spectroscopy) after oxidation, whereas in the case of the metal film, significant amounts of metallic rhenium remain present. Presumably, the diffusion of either oxygen or rhenium (whichever is limiting in the oxide formation mechanism) is facilitated by the formation of an alloy. Unger and Baunack have recently reported data that shows that rhenium segregates to the surface in platinum-rhenium alloys upon oxygen treatment.²⁵ The conclusions, however, remain the same; the final oxidation state of rhenium is high independent of whether the rhenium is present as a thin film or as an alloy, i.e. independent of the degree of mixing.

While the oxidation state of Re depend little on the mixing between rhenium and platinum, the subsequent reduction in 1 atm of hydrogen at 600K is very sensitive to this parameter. Fig. 7(c) shows that the rhenium alloy reverts almost completely to the metallic form following reduction, yielding a Re $4f_{7/2}$ peak at 39.7 eV binding energy. Also, the XPS peaks after reduction are narrower and more asymmetric than those from the original alloy. At present we have no explanation for this change.

The alloy results differ from the case of a metallic layer of rhenium, where reduction in hydrogen at 600K results in the removal of

the features due to high oxidation states (Re(IV) and greater), but where there are peaks remaining in the spectrum of Fig. 4(e) shifted by about 1 eV from the metallic peak. The scatter of data in the calibration of oxidation state versus chemical shift (Fig. 2) precludes a definitive assignment of these peaks, but it is clear that they correspond to an oxidation state less than +4. The best estimate for this oxidation state is that it is Re(II), so that, following reduction of the oxidized rhenium layer, the surface appears to consist predominantly of a mixture of metallic rhenium and Re⁰. It should be noted that the platinum remains in a metallic state during all the above treatments. A possible explanation of the difference in the ease with which the rhenium oxide is reduced is that this reaction may be catalyzed by platinum. It is well known that hydrogen dissociates on metallic platinum, and that, in the case of oxide supported platinum, hydrogen may diffuse to the oxide support; the so called "spillover" effect.^{15,24} A similar mechanism may operate in the case of the reduction of rhenium in platinum/rhenium mixtures depending on the degree of mixing between the platinum and rhenium. In the case of the deposited rhenium layer, the platinum is underneath the rhenium oxide and therefore unable to chemisorb and dissociate H₂ molecules, so reduction reactions are less effective and leave a large portion of the rhenium in a +2 oxidation state. In the case of the rhenium alloy, hydrogen that dissociates on the metallic platinum can easily diffuse to the rhenium oxide, effecting a rapid and almost complete reduction to the metallic state.

Finally, it should be emphasized that the working catalyst consists of many components that are not included in our model system, for instance, oxide supports or discrete particles. Other factors,

such as the presence of halides, which are added to the working reforming catalysts, or sulfides which may be present in the feedstock, may also significantly affect the catalyst properties during oxidation and reduction.

CONCLUSIONS

While the final oxidation state of rhenium after exposure to an oxidizing environment does not depend strongly on the degree of mixing between the rhenium and the platinum (forming up to Re(VII)), the final oxidation state after hydrogen reduction does. Thus, in the case of a platinum/rhenium alloy in which the platinum and rhenium are intimately mixed, the rhenium oxides reduce rapidly to the metallic state. In contrast, when the rhenium and platinum are less intimately mixed as in the case of an evaporated rhenium layer, oxides are not completely reduced to a metallic state but form an oxide in which the metal has an oxidation state less than +4, probably ReO. A possible explanation for this phenomenon is that the rhenium oxides reduction is catalyzed by platinum which remains metallic under all treatment conditions. A mechanism whereby this might operate is that hydrogen, which can dissociate on metallic platinum, then diffuses rapidly into the rhenium oxide when the phases are intimately mixed, thereby facilitating reduction.

ACKNOWLEDGEMENT

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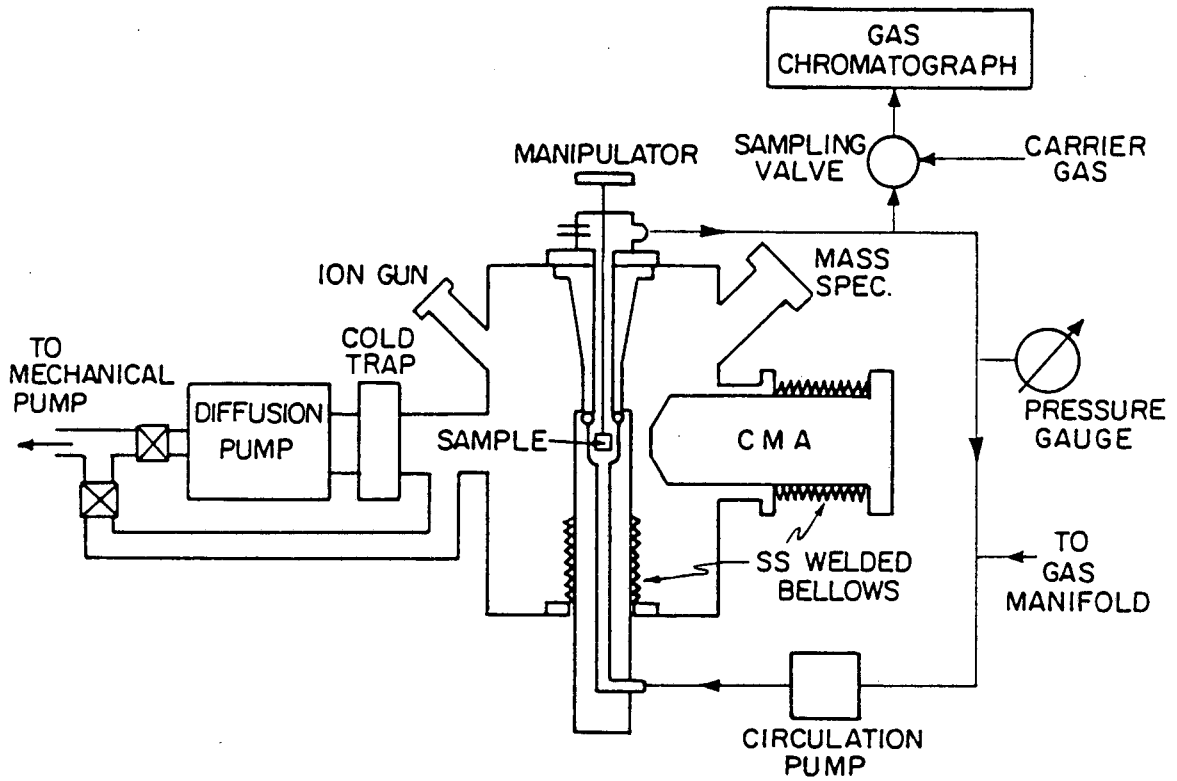
FIGURE CAPTIONS

- Fig. 1 Diagram of the vacuum system showing the isolatable high pressure reactor which also functions as a fast transfer cell. The x-ray source is located behind the sample.
- Fig. 2 XPS of the Re 4f region of various oxides of rhenium.
- Fig. 3 Binding energies of the Re $4f_{7/2}$ photoelectron peak as a function of formal oxidation state. Our data (.) is compared to literature values Ref. 16 (o), 19 (\square), and 20 (Δ).
- Fig. 4 Rhenium and platinum 4f XP spectra for rhenium films deposited onto a platinum foil, (a) clean; and following oxidation and reduction treatments: (b) 475K, 700 torr O_2 , 5 min; (c) 525K, 700 torr O_2 , 5 min; (d) 625K, 700 torr O_2 , 5 min; (e) 575K, 700 torr O_2 , 10 min; (f) 575K, 700 torr H_2 , 5 min.
- Fig. 5 Rhenium 4f photoelectron peaks for deposited rhenium films following oxidation and reduction: (a) clean; (b) 475K, 700 torr O_2 , 5 min; (c) 625K, 700 torr O_2 , 5 min; (d) 575K, 700 torr O_2 , 10 min; (e) 575K 700 torr H_2 , 5 min.
- Fig. 6 Platinum and rhenium 4f XP spectra for the Pt-Re alloy.
- Fig. 7 Rhenium 4f XP spectra of a surface Pt-Re alloy, (a) clean; and after oxidation and reduction treatments: (b) 575K, 1 atm O_2 , 5 min; (c) 575K, 1 atm H_2 , 5 min.

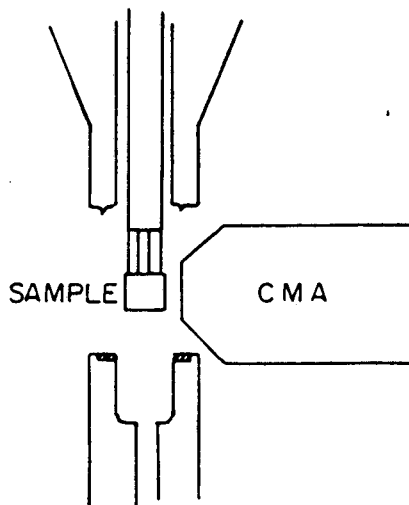
TABLE I

Binding energies, in eV, for Re 4f electrons in several rhenium oxides

Compound	Re 4f _{5/2}	Re 4f _{7/2}
Re (metal)	42.3	39.7
ReO ₂	45.0	42.5
ReO ₃	47.2	44.9
Re ₂ O ₇	49.5	46.7

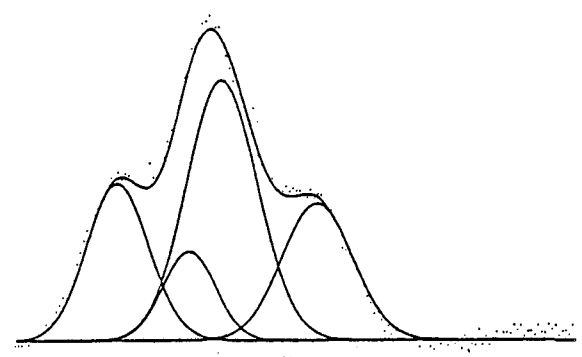


(a)

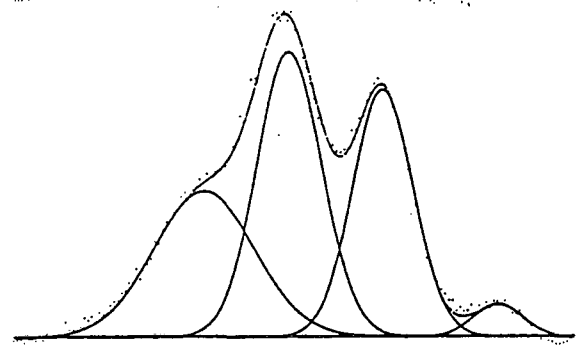


(b)

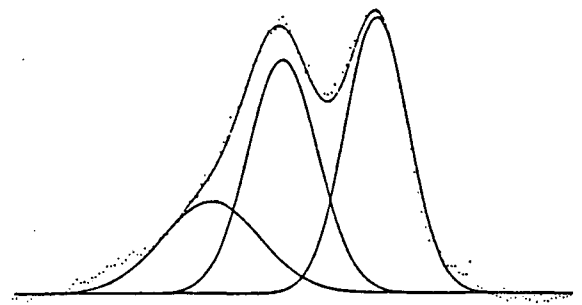
Re oxides 4f XPS



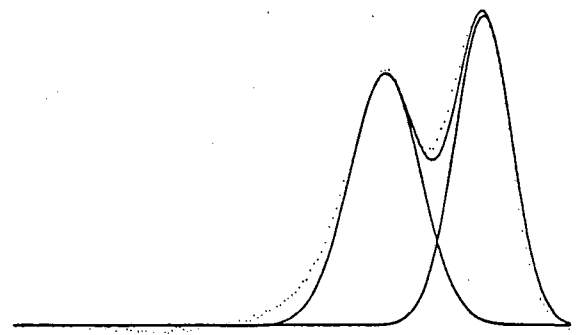
Re₂O₇



ReO₃

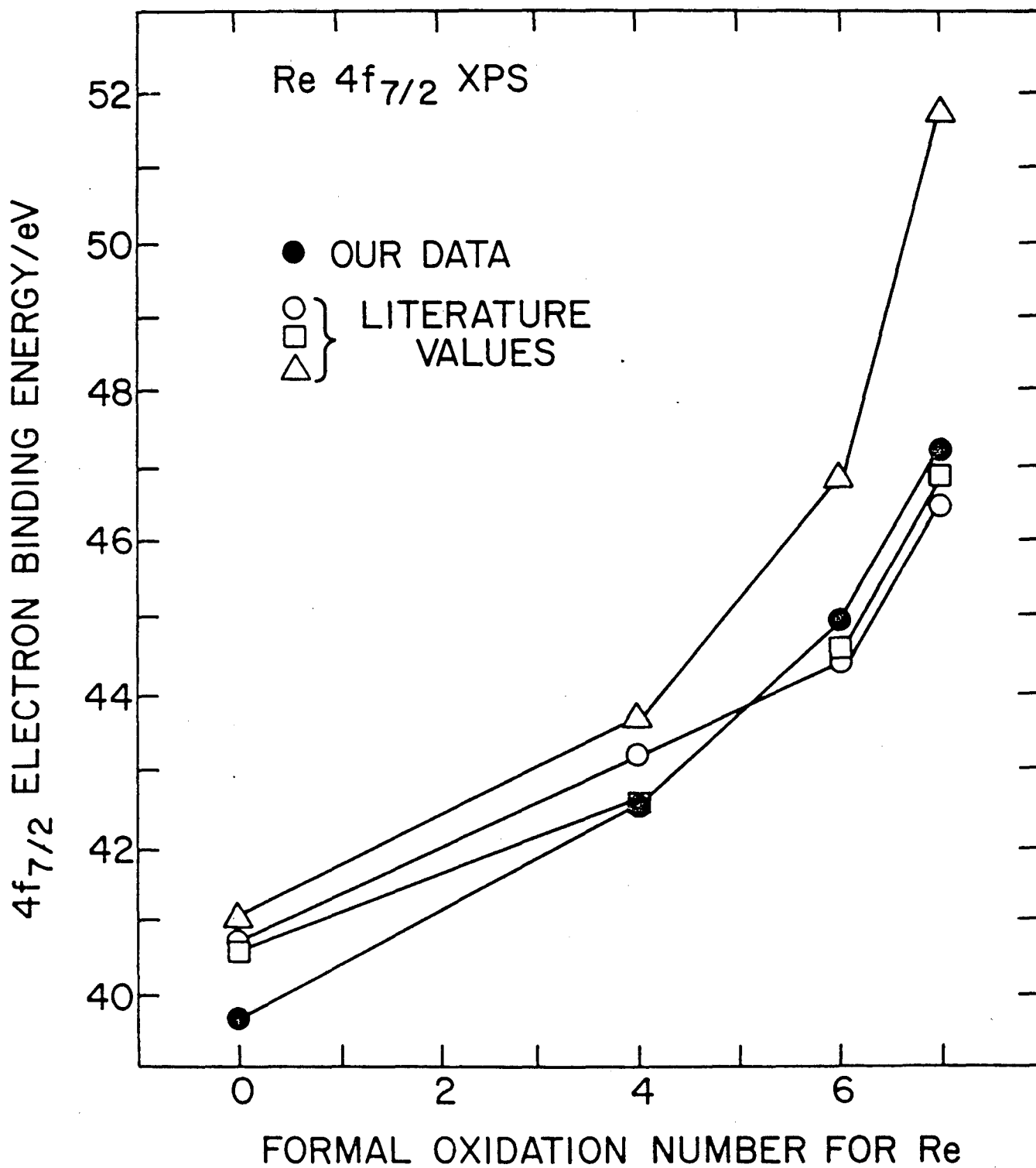


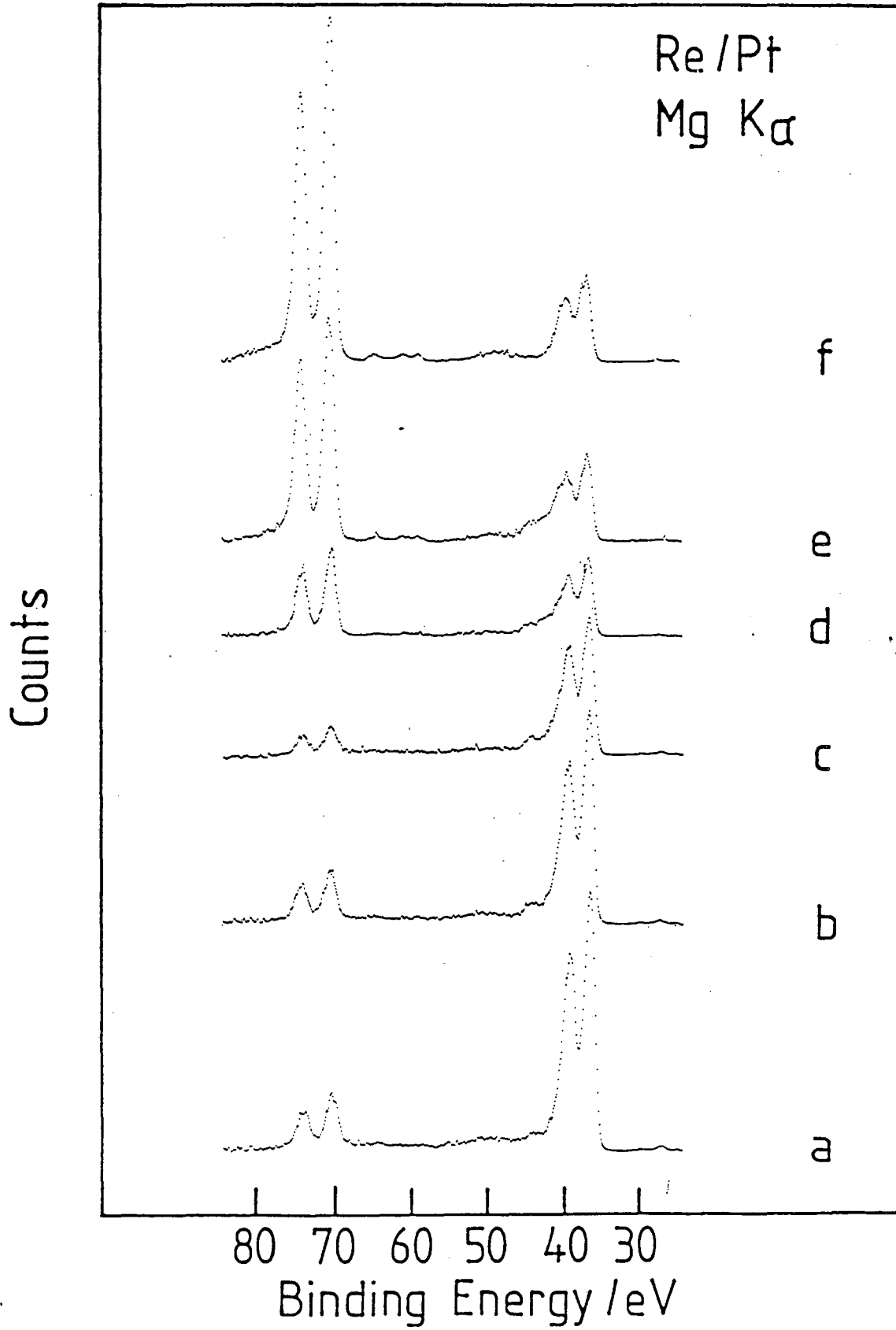
ReO₂

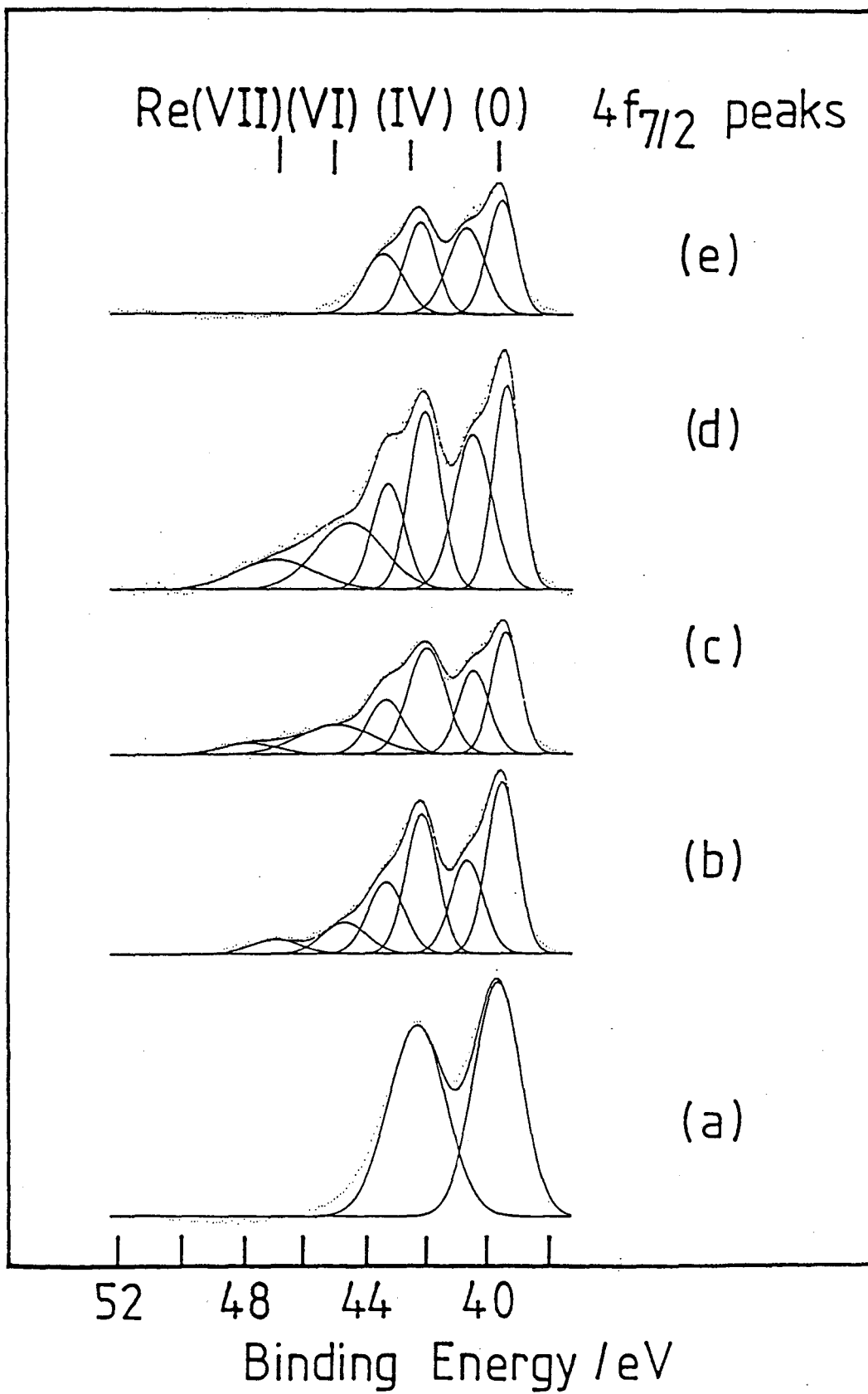


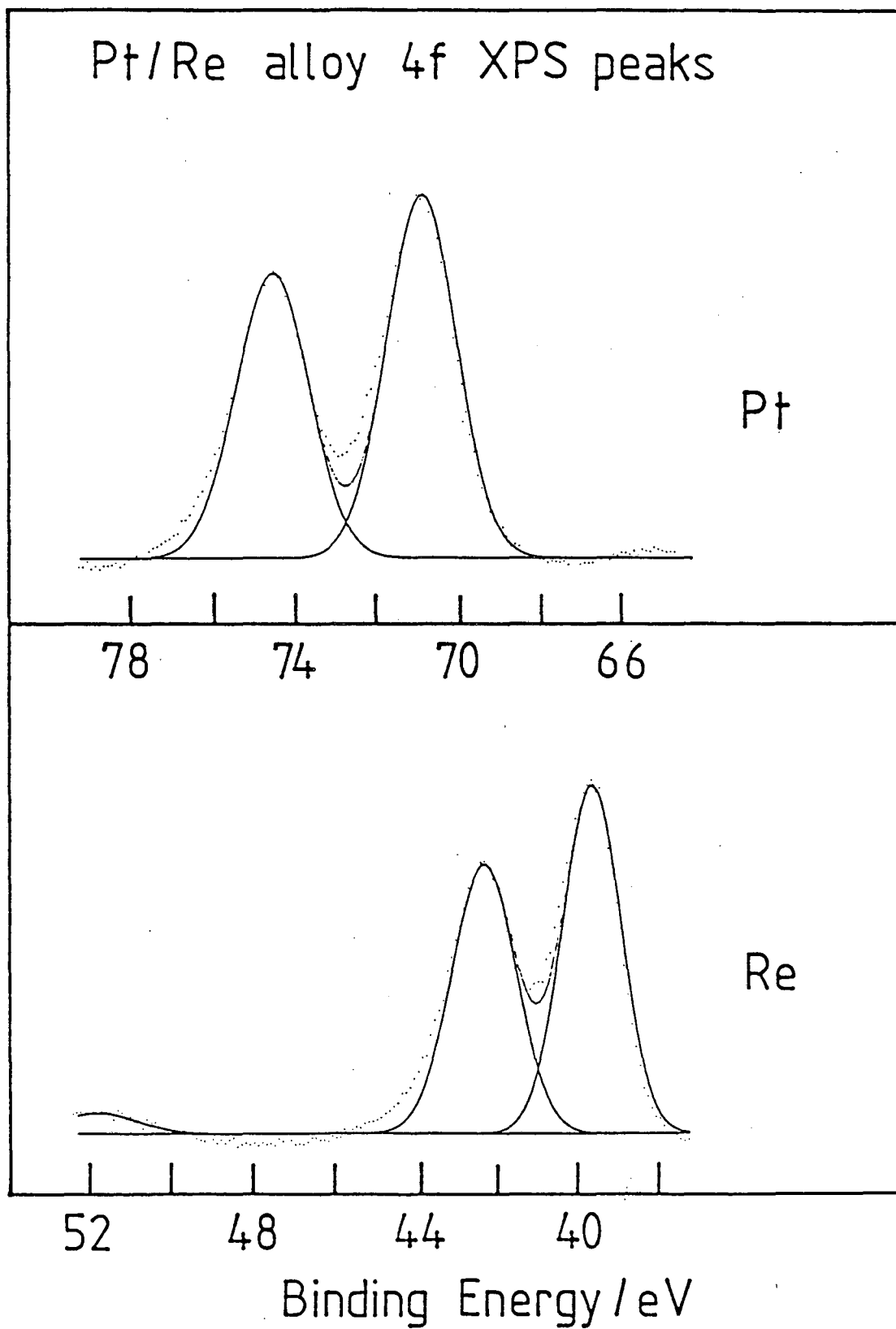
Re metal

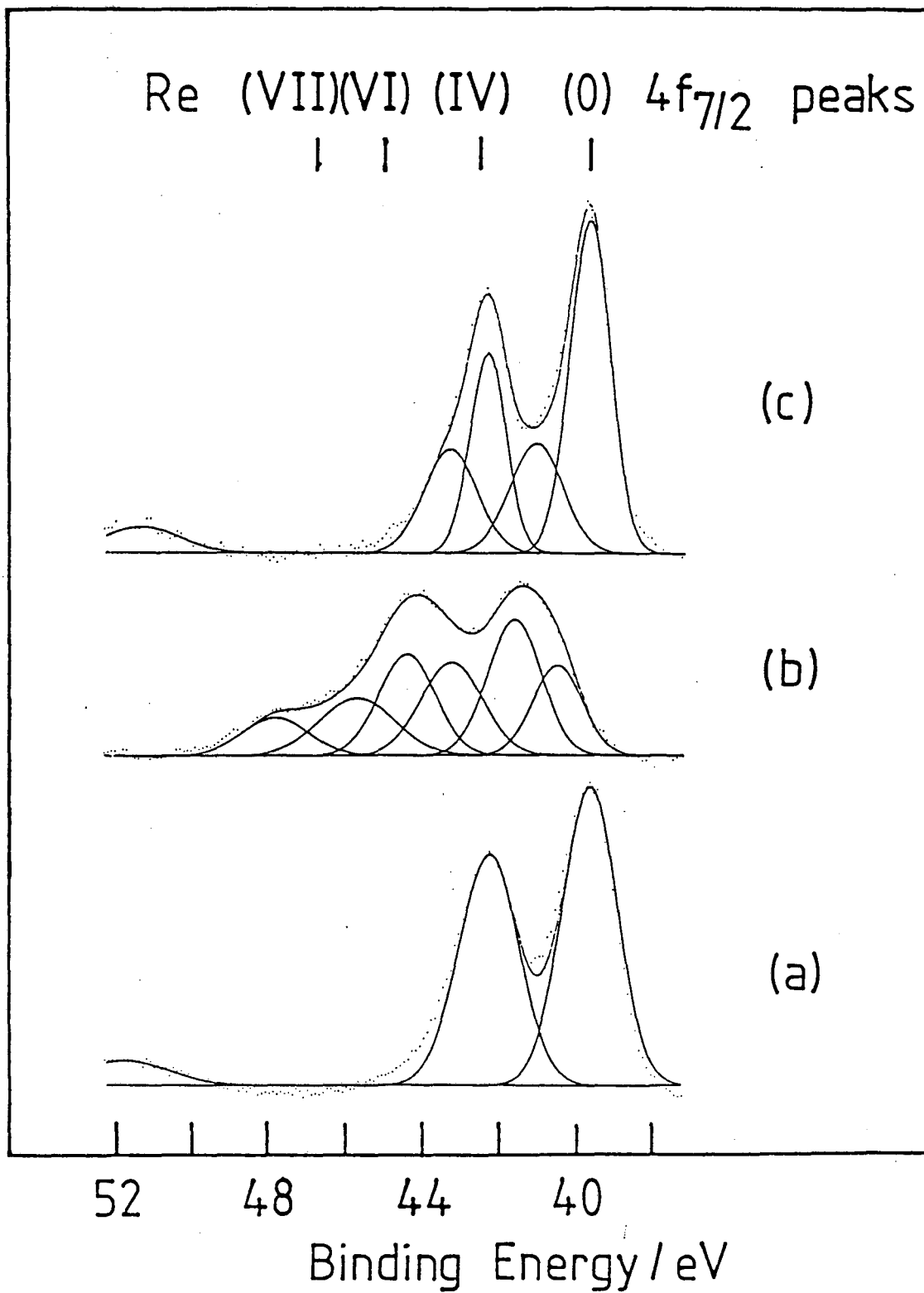
52 48 44 40
Binding Energy / eV











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