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OXIDIZED ZIRCONIUM DEPOSITED ON THE Pt(100) SINGLE CRYSTAL SURFACE

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I. OXIDIZED ZIRCONIUM DEPOSITED ON THE Pt(100) SINGLE CRYSTAL SURFACE

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ABSTRACT

Metallic zirconium was deposited on a single crystal Pt(100) surface by thermal evaporation in UHV conditions. The deposit was oxidized by exposure to oxygen immediately after deposition. Oxidized zirconium was found to grow on the platinum surface by the layer-by-layer mechanism. The adsorption of carbon monoxide on the surface was studied as a function of the zirconium coverage. The results show that oxidized zirconium forms a chemically inert layer which blocks the adsorptive sites of the underlying platinum substrate. The properties of the free Pt surface were unaffected by the presence of the oxidized zirconium layer.

1. INTRODUCTION

The present study is aimed at understanding the properties of bimetallic surfaces where a catalytically active metal (platinum) coexists with an oxidized electropositive metal (zirconium). In a previous study,¹ we reported that zirconium deposited on platinum maintained the high reactivity of the pure metal and that it could be easily oxidized by exposure to oxygen. It was therefore concluded that the stable surface of a Pt-Zr system in an environment other than ultra-high vacuum must be a ternary (Pt/Zr/O) system. In the present paper (part 1 of a two part work) we report the result of a study of such a ternary surface which was prepared by depositing and oxidizing zirconium on a single crystal Pt(100) sample. The results of the complementary procedure (e.g. depositing platinum on pre-oxidized zirconium) are reported in part 2. The structure of these ternary surfaces may be similar to that of SMSI type systems, where oxidized moieties of support metal are believed to be present on the surface of the particles of the catalytically active metal.²⁻⁵

In general, effects on the chemical and adsorptive properties of bimetallic systems depend on surface structure: if the two metals form a single phase, that is if they are dispersed at the atomic scale on the surface, the chemical reactivity may be altered either by electronic effects due to the intermetallic bond (ligand effect) or by the variation of the density of adsorptive sites (ensemble effects). However, under oxidizing conditions, the most reactive metal may segregate as an oxidized phase on the surface, as we reported to occur for the

Pt/Zr¹ and Pt/Ti⁶ systems. If two separate phases are present, ligand or ensemble effects of the type described before are not expected. However, if the oxidized metal forms flat islands on the surface, effects due to the intermetallic bond can still take place at the edges of the islands. Such effects have been reported for the TiO_x/Rh system.⁷

In the present work we used LEED and AES to obtain information on the structural properties of a single crystal Pt(100) surface after zirconium deposition and oxidation. CO was used as the probe molecule to study the reactivity of the surface. The results show that, in general, the properties of the Pt/Zr/O surface can be explained in terms of a two-phase surface (oxide islands and free metal), where the adsorptive properties of the platinum surface are not significantly perturbed by the presence of oxidized zirconium moieties. However, chemical effects at the edges of the oxidized islands cannot be excluded, as the relative concentration of these sites may be too small to produce a detectable effect in our experimental conditions.

2. EXPERIMENTAL

We used a stainless steel UHV chamber equipped with 3-grid LEED optics, single pass CMA for Auger electron spectroscopy with a glancing incidence electron gun, and quadrupole mass spectrometer. AES spectra were recorded in derivative mode with a modulation of 2V_{p-p} and a primary beam energy of 2KeV. The sample was a single crystal

platinum disk about 10 mm diameter and 1 mm thick. The faces were parallel (± 1 deg) oriented along the (100) direction. The sample was held by platinum wires spotwelded to the edge and annealing could be obtained passing current through the wires. Metallic zirconium could be evaporated on the sample surface by means of an electron beam evaporator located in a separately pumped chamber.

Before all the CO thermal desorption tests, both surfaces of the platinum sample were cleaned by the same treatment, consisting of argon ion bombardment and annealing. Subsequently, the same amount of zirconium was deposited on both faces. This procedure insured that the TDS spectra observed were due to surfaces of uniform composition. After exposing to CO, the sample was heated in vacuum at a rate of 84 deg/sec, linear as a function of time up to about 900 K. Temperatures were measured by a chromel-alumel thermocouple spotwelded on the sample edge. TDS peaks were recorded by the mass spectrometer.

3. RESULTS

In Fig. 1 we report the intensity of the Zr and Pt AES signals as a function of the deposition time (AES growth curves). When clean zirconium was deposited on the surface, the linearity of the growth curves shows that the growth mechanism was layer-by-layer type, as we reported in a previous study.¹ If the deposited zirconium was oxidized by exposure to oxygen at room temperature immediately after each deposition, the AES growth curves remained linear, showing that the

growth mechanism did not change. From the AES growth curves, it is possible to obtain a quantitative calibration of the coverage of oxidized zirconium as a function of the relative intensity of the Zr(116 eV) and Pt(237 eV) dN/dE AES signal. The first break in the curves of Fig. 1, corresponds to the completion of the growth of a compact Zr layer ("monolayer"). In the present work, the zirconium coverage on the surface will be always expressed in terms of fractions of monolayer, i.e. as a fraction of the coverage of this compact phase.

Before all CO thermal adsorption experiments, the deposited zirconium was saturated either with CO or with O_2 at room temperature at 1×10^{-7} torr. Exposure to O_2 led to the formation of a surface oxide, whereas for exposure to CO, zirconium oxide and carbide were formed on the surface. However, as reported in Ref. 1, the carbide could be completely eliminated from the surface upon annealing, so that both procedures led eventually to a surface where only oxidized zirconium was present. AES data showed that the O/Zr ratio in the surface could vary, depending on the treatment of the surface, so that in the following we shall refer to the oxidized zirconium layer as " ZrO_x ".

After saturation dosing with CO, the AES spectrum of the clean Pt(100) surface showed the double carbon peak characteristic of molecularly adsorbed CO.¹⁰ The same double peak, although reduced in intensity, could be detected if the Pt surface was partially covered with ZrO_x . No significant CO adsorption could be detected in AES for ZrO_x coverages higher than the monolayer. The results of TDS tests

were consistent with the AES measurements. The CO TDS spectra after saturation dosing are shown in Fig. 2, for different values of the coverage of oxidized zirconium. The curve shown for the clean Pt surface is comparable to the results reported in the literature for Pt(100).^{8,9} The presence of oxidized zirconium on the Pt surface reduced the CO TDS peak intensity, but did not significantly change the peak shape. The peak shape was not affected by the previous thermal treatments of the surface, nor was it affected by the choice of the gas used to saturate the Zr layer (CO or O₂). On the clean Pt(100) surface we observed that the maximum in the CO peak shifted towards higher temperature for lower exposures, in agreement with the results reported by others.^{8,9} Partial coverage of the surface with oxidized zirconium did not affect this behavior. We remark also that traces of CO₂ desorbing from the surface after CO exposure could be detected only in the presence of ZrO_x deposit (a similar result was reported for the TiO_x/Pt system¹⁵). The amount of CO₂ desorbed appeared to depend on the previous thermal and chemical treatment of the surface and it was always more than one order of magnitude smaller than the amount of desorbed CO.

A quantitative measurement of the amount of adsorbed CO on the ZrO_x/Pt surface can be obtained either by integration of the CO TDS peak or by the measurement of the intensity of one of the two carbon AES peaks. However, some graphitic or carbidic carbon contamination was always detectable in AES immediately after Zr deposition, so that a quantitative AES measurement of the adsorbed CO was possible only if

the sample was annealed after Zr deposition and oxidized in such a way as to remove all carbon. In order to measure the amount of adsorbed CO as a function of the ZrO_x coverage, we used two different methods to vary the Zr content of the surface:

- 1) The clean Pt(100) surface was dosed with Zr metal and subsequently saturated with O_2 at room temperature. After determining the coverage from the AES data, the surface was exposed to CO and the TDS peak recorded. The procedure was then repeated for a different amount of deposited Zr.

- 2) Two to three layers of Zr were deposited and subsequently saturated with CO or O_2 at room temperature. As described in Ref. 1 successive annealings over 900 K caused partial diffusion of zirconium into the Pt bulk; in this way a range of coverages from several layers to nearly zero could be obtained. Between successive annealings, the sample was cooled to room temperature and the ZrO_x coverage was measured by AES after exposure to CO, the AES carbon peak intensity or the CO TDS peak were recorded.

In Fig. 3a we have plotted the amount of desorbed CO, as determined by TDS, as a function of the coverage of the oxidized zirconium. For the curve relative to surfaces obtained by the first method, i.e. Zr deposition and oxidation at room temperature (curve 1), the total suppression of CO adsorption, corresponding to the complete coverage of the Pt surface with a monolayer of ZrO_x , occurs for a value of the coverage close to unity, which is the expected result. The experimental points can be fitted with a straight line which indicates the

growth of flat ZrO_x islands on the surface, in agreement with the AES determination of the growth mechanism. However, for surfaces prepared by the second method, i.e. annealing at high temperature (curve 2), the limit of complete blocking of the substrate surface occurs for a Zr coverage smaller (about 0.6) than a compact monolayer phase. The AES measurement of the amount of adsorbed CO (Fig. 3b) was consistent with the TDS measurements for a surface where coverage was varied by bulk diffusion (Fig. 3a, curve 2).

Both TDS and AES data show that the annealed ZrO_x/Pt surface adsorbs a smaller amount of CO than one would expect from the AES determination of the Zr coverage. Since the amount of adsorbed CO (measured by AES) is approximately equal to the amount of desorbed CO (measured by TDS), we can rule out that this effect derives from CO decomposition on the surface or from reaction with the surface oxide to form CO_2 .

4. DISCUSSION

In general, the AES and LEED results relative to the Zr/O/Pt system can be interpreted in terms of a structural model where oxidized zirconium (" ZrO_x ") forms flat, "two-dimensional" islands on the Pt surface.¹ We found in the present study that when the Pt surface was covered in part with oxide islands, the amount of CO adsorbed was reduced, but adsorption was still molecular and the desorption peak shape remained unchanged. The amount of CO desorbing from the surface

was directly correlated to the independently measured uncovered Pt surface area. From these data it appears therefore that the ZrO_x islands were only blocking part of the surface and had a negligible chemical effect on the platinum free surface.

However, on annealed ZrO_x/Pt surfaces we found a significant discrepancy in the extent of free Pt surface and the amount of adsorbed CO. This discrepancy could be caused by two possible effects:

1) Electronic effects: these effects could cause part of the Pt atoms to be deactivated towards CO adsorption/desorption as a result of the Pt-Zr bond.

2) Structural ("matrix") effects. changes in the structure of the overlayer upon annealing could lead to overestimate the fraction of free Pt surface from the AES measurements.

As it will be discussed in the following, structural effects appear a more likely explanation in light of the LEED results reported previously.¹ However, we will examine in detail both possibilities.

Considering first electronic effects, we remark that a study¹⁷ of the electronic properties of the Pt-Ti bond (which is expected to have similar properties as the Pt-Zr bond) has shown that a destabilization of the CO-Pt bond may occur as a consequence of the intermetallic bond. In a surface where an active metal substrate is partly covered with oxide islands, only the substrate atoms which are located around the edge of the islands could be affected in this way. Such an "edge" effect was claimed to be the explanation of results for CO adsorption on TiO_x/Rh surfaces⁷ which were qualitatively similar to

those reported in the present paper. "Edge effects" have been claimed to account for the enhanced methanation activity of some SMSI type catalysts,¹⁴ but no edge effect affecting CO adsorption was found in a recent study of the TiO_x/Pt system,¹⁶ an SMSI type system. Some "edge" effect on the adsorption of CO may occur on the ZrO_x/Pt surface in the conditions of the present study. For instance, the observed CO_2 formation could occur at the ZrO_x island edges by reaction of the oxide with CO adsorbed on platinum. However, it does not appear possible to account for the partial suppression of CO adsorption (Fig. 3) by means of a model based on such effects. First of all, it is difficult to explain in terms of electronic effects why the suppression occurs only after annealing. Since the overlayer appears to form two-dimensional islands independently of the previous thermal treatment, intermetallic bonds (and therefore electronic effects) should exist at the island edges even if the surface is not annealed. This problem, alone, does not necessarily rule out the model, since it is conceivable that the extent of the effect depends on the degree of oxidation of the Zr overlayer (as it was shown to occur for the TiO_x/Rh system⁷) and it was shown previously¹ that strong annealing could cause a reduction in the oxygen content of the overlayer. Rather, the most important argument against the electronic "edge" model is the incompatibility with the number of edge sites indicated by the analysis of the LEED results.

In the "edge" model, the extent of suppression of CO adsorption depends on the extension of the perimeter of the oxide islands. The fraction of affected Pt surface can be calculated by means of the simple geometric model developed by Levin et. al.⁷ If the suppression distance is equal to one Pt interatomic distance, a fair agreement with the experimental results of Fig. 3 can be obtained using the geometric model⁷ with a density of nucleating sites equal to $3 \times 10^{-3} \text{ \AA}^{-2}$. In this model, the radius of the islands of ZrO_x varies with coverage: for a coverage close to unity, the radius is always less than 20 Å, and it is smaller for lower coverages. The LEED results rule out that possibility that the ZrO_x islands can be so small. The sharp overlayer patterns reported¹ for ZrO_x coverages under 0.2–0.3 monolayers indicate that the diffracting domains (that is the islands) must have a radius at least an order of magnitude larger, even for such low coverages. This argument does not rule out "edge" effects entirely, but it seems clear that the number of edge sites is not sufficiently large to account for the results of Fig. 3.

Considering now geometric/structural effects, it should be remarked that in the discussion of electronic "edge" model it was implicitly assumed that the surface density of the islands (i.e. the number of zirconium atoms per unit surface in the island) remains constant over the whole range of coverages from zero to one monolayer. The same assumption is implicit in the model developed by Levin et. al.⁷ for the TiO_x/Rh system. However it is also conceivable that, during

annealing, phase transformations occur, causing the formation of progressively less dense overlayer structures for lower coverages. In such cases, a lower AES overlayer signal does not necessarily correspond to a smaller fraction of area occupied by the islands, but it may correspond to a lower two-dimensional density of the islands.

The hypothesis of a variation in the structure of the overlayer is supported by the LEED results,¹ summarized in Table 1. When the ZrO_x coverage was reduced upon annealing, the surface layer underwent a phase transition from the rhombic "monolayer" phase to either the $\begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix}$ phase or to the $\begin{bmatrix} 7 & 0 \\ 0 & 4/3 \end{bmatrix}$ phase, depending on the initial oxygen content. This transition involves a variation in the surface density in terms of the number of Zr atoms per unit area. In the monolayer rhombic phase, assuming one Zr atom per cell, the surface Zr density is equal to $1.13 \text{ atoms}/\text{\AA}^{-2}$, (a value very close to that relative to the (111) plane of ZrO ($1.11 \text{ atoms}/\text{\AA}^{-2}$).¹²) In the $\begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix}$ phase, the area of the unit cell is sufficient to accommodate two Zr atoms per cell, in the same plane. In this case, the Zr surface density is $8.6 \times 10^{-2} \text{ atoms}/\text{\AA}^{-2}$. In the $\begin{bmatrix} 7 & 0 \\ 0 & 4/3 \end{bmatrix}$ phase, the area of the unit cell is 72.1 \AA^2 and it seems likely that the periodicity observed in LEED is caused either by zirconium vacancies or by oxygen vacancies. However the Zr atomic density in the $\begin{bmatrix} 7 & 0 \\ 0 & 4/3 \end{bmatrix}$ phase must be similar to that of the $\begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix}$ phase, since we observed that the $\begin{bmatrix} 7 & 0 \\ 0 & 4/3 \end{bmatrix}$ can be converted into the $\begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix}$ by exposure to oxygen and annealing without causing a significant variation in the zirconium coverage.¹ Since a discrete number of Zr atoms must exist within the cell, the most

likely conclusion is that the Zr density of the $\begin{bmatrix} 7 & 0 \\ 0 & 4/3 \end{bmatrix}$ phase is 8.3×10^{-2} atoms/Å², assuming 6 Zr atoms per cell.

The foregoing models, derived from LEED observations, show that both the $\begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix}$ phase and the $\begin{bmatrix} 7 & 0 \\ 0 & 4/3 \end{bmatrix}$ phase are less dense than the "monolayer" phase in terms of Zr atom/unit surface, within the island. The consequence is that, when annealing and reducing the Zr coverage by bulk diffusion, the zirconium surface concentration is lowered not by forming islands of constant density with less total area, but by transforming into a less dense, but still flat phase. After this phase transformation is completed, further reduction in Zr concentration causes a decrease in the area occupied by the islands. Consequently, free Pt surface appears and CO adsorption/desorption becomes detectable. The $\begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix}$ and $\begin{bmatrix} 7 & 0 \\ 0 & 4/3 \end{bmatrix}$ phase have a Zr surface density equal, respectively, to 0.78 and 0.75 of the monolayer phase. Therefore, only for values of the coverage smaller than 0.75-0.78, is the onset of CO adsorption expected to occur. This value is to be compared with the experimental results (Fig. 3), from which we obtain a value for the coverage corresponding to onset of CO adsorption of ca. 0.6 monolayer (CO TDS data) or 0.7 monolayers (AES data). A small residual discrepancy (about 0.1 of a monolayer of ZrO_x) remains, which might be attributed to electronic edge effects or to CO₂ formation. However, it appears that the aforementioned structural models of the surface can account almost completely for the experimental results.

4. CONCLUSION

The principal result of the present study is that oxidized zirconium acts as an inert overlayer which sterically blocks the underlying platinum surface. The properties of the exposed platinum surface are not affected by the islands of oxidized zirconium. The apparent discrepancy in the area of exposed platinum surface after annealing, as measured by CO adsorption, can be explained almost completely by taking into account the LEED results which indicate that annealing causes a relaxation of the zirconium overlayer structure. However, the possibility of chemical effects due to an intermetallic bond at the edges of the oxide islands cannot be excluded. The patchwise structure of oxidized zirconium moieties on the platinum surface is similar to the model proposed by some authors²⁻⁵ for SMSI type catalysts where complete oxide decoration of the metal surface can cause the suppression of CO adsorption. The results of the present study show that in the ZrO_x/Pt system, the effect of these oxidized moieties is mainly steric.

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Table 1

ZrO_x phases observed by LEED on the Pt(100) surface

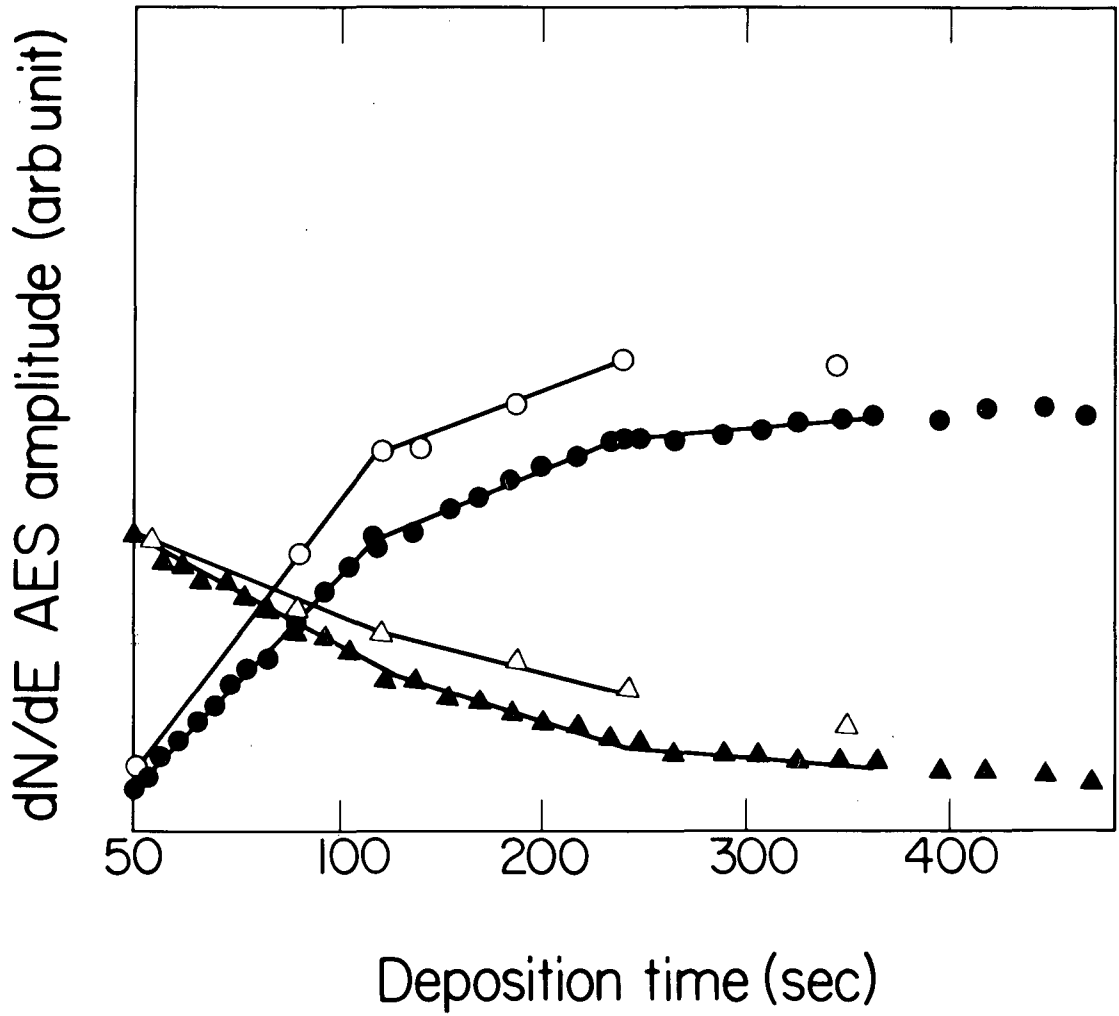
Phase	Cell area(A ²)	Zr atoms/cell	Zr atoms/A ²
Zr(0001) plane	8.87	1	1.1x10 ⁻¹
$\begin{pmatrix} 0.77 & 0.77 \\ -0.57 & 0.92 \end{pmatrix}$ (monolayer)	8.8	1	1.1x10 ⁻¹
$\begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$	23.1	2	8.6x10 ⁻²
$\begin{pmatrix} 7 & 0 \\ 0 & 4/3 \end{pmatrix}$	71.8	6	8.3x10 ⁻²

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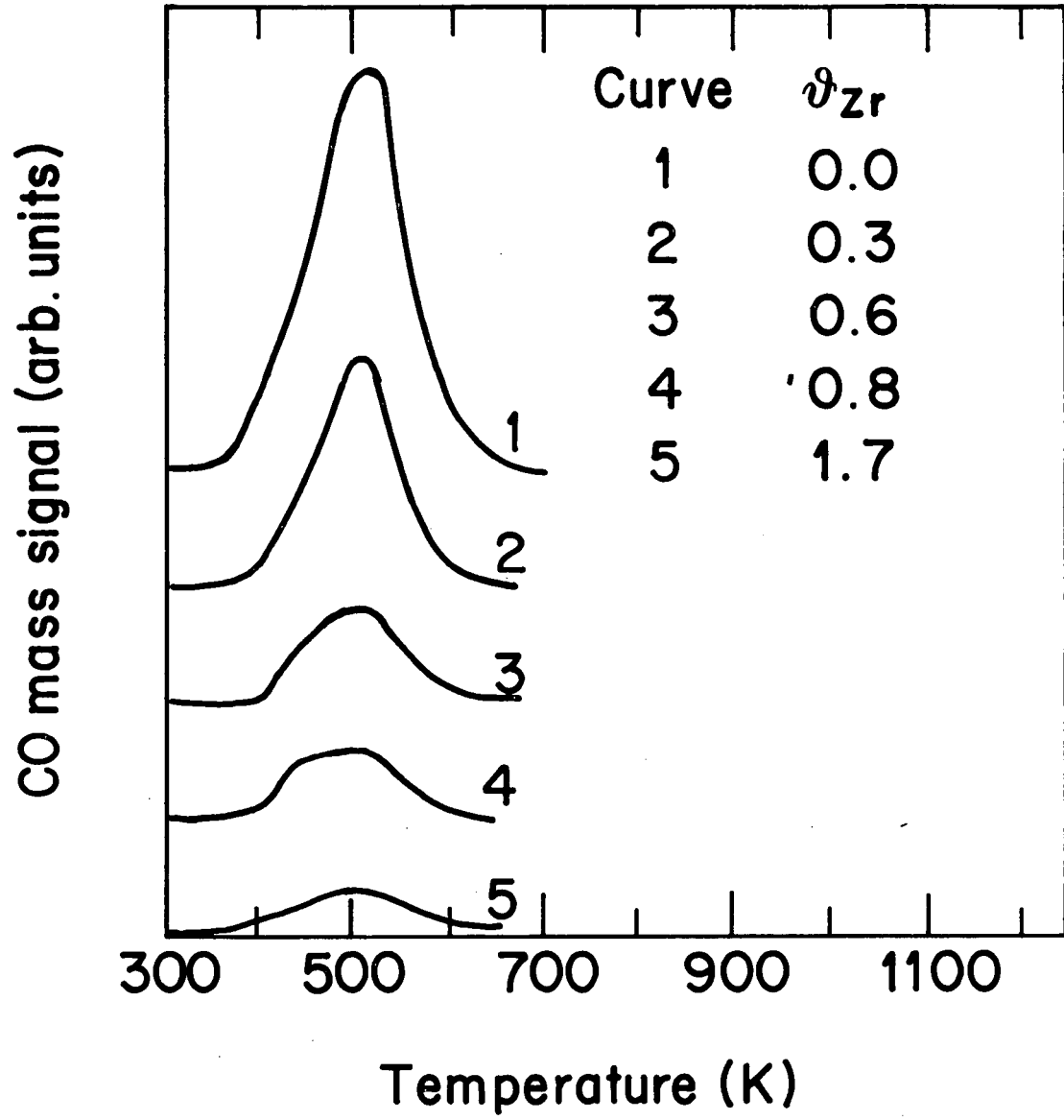
Figure Captions

- Fig. 1. AES growth curves for successive deposition of zirconium by thermal evaporation on the Pt(100) surface. Triangles: Pt(237 eV) signal. Circles: Zr(116 eV) signal. Open symbols: deposition of clean zirconium. Full symbols: deposition of zirconium and oxidation between each successive deposition by exposure to oxygen at $p = 1 \times 10^{-7}$ torr. In both cases the shape of the curves (linear with well defined breaks) indicates a layer-by-layer growth mechanism.
- Fig. 2. CO TDS spectra from the Pt(100) surface for different values of the coverage (θ) of oxidized zirconium measured by AES. CO exposure: 20 L at $p = 2 \times 10^{-7}$ torr at room temperature.
- Fig. 3. A) Results of the titration of the active sites (Pt) of the Pt/Zr/O surface by quantitative measurement of the desorbed CO by TDS. Curve 1: data relative to surfaces which were not annealed before CO adsorption. Curve 2: surfaces annealed over 900 K before CO adsorption. B) Amount of adsorbed CO by AES measurement of the intensity of the 257 eV peak as a function of ZrO_x coverage θ (surfaces annealed over 900 K before CO adsorption).



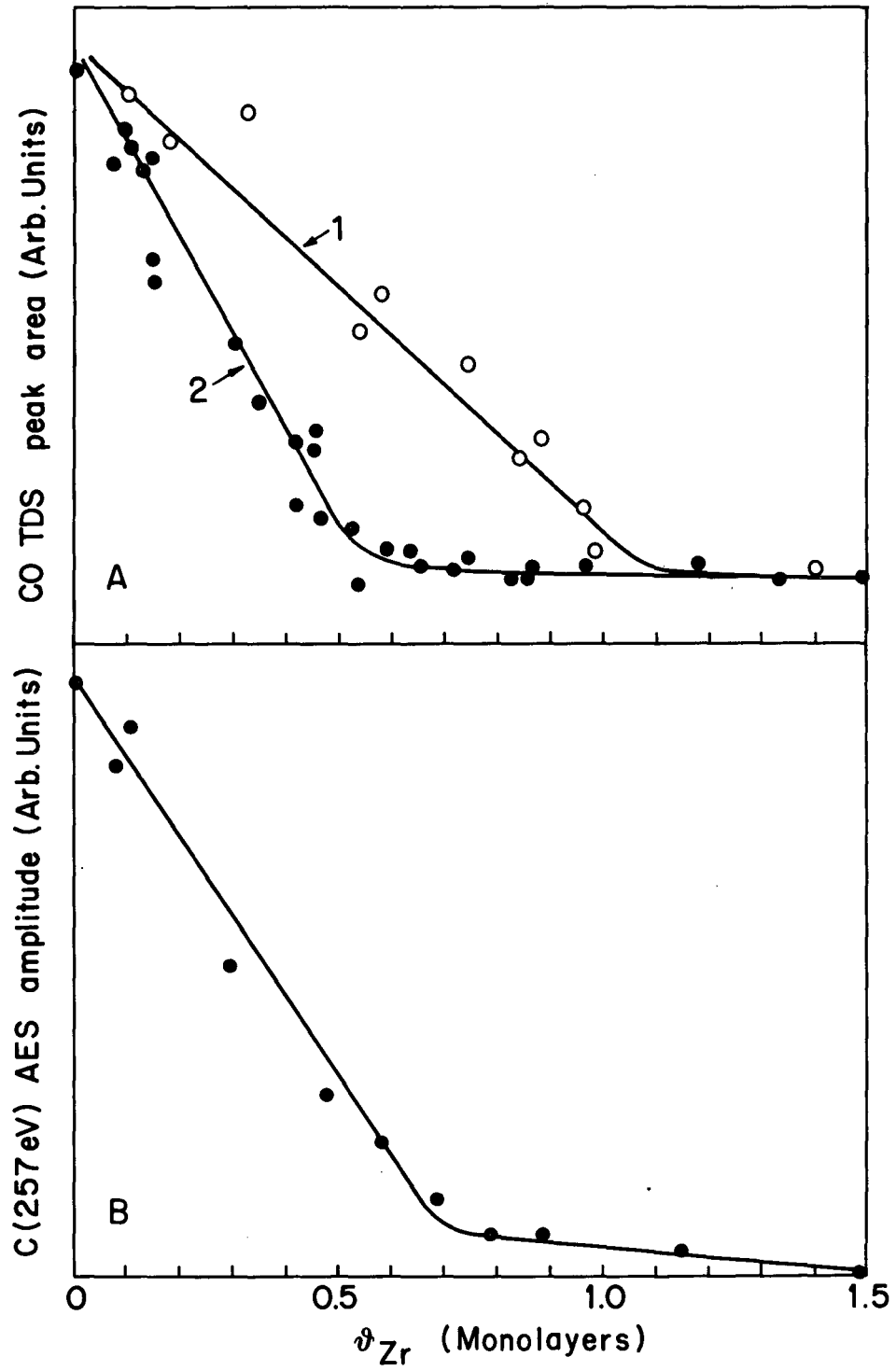
XBL 829-4563 A

Fig. 1



XBL 867-2698

Fig. 2



XBL 867-2704

Fig. 3

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