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EFFECT OF HIGH TEMPERATURE REDUCTION IN HYDROGEN ON Pt DEPOSITED ON THE $TiO_2(100)$ SURFACE: AN ANGLE RESOLVED X-RAY PHOTOEMISSION STUDY

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The effect of high temperature reduction in hydrogen was studied by angle resolved XPS in a system formed of platinum deposited on the (100) surface of a TiO_2 single crystal sample. The analysis of the variation of the Pt/Ti XPS signal ratio as a function of the electron collection angle showed that partially reduced titanium oxide is present on the Pt film after the reduction treatment. The amount of oxide on the Pt surface is of the order of one monolayer equivalent.

1. Introduction

The effect of high temperature reduction in hydrogen on the chemisorption properties of supported metals (Strong Metal to Support Interaction, or SMSI) was observed for the first time in the Pt/TiO_2 system [1]. Various theories have been proposed to account for this effect [2–6]; at present it is generally accepted that SMSI properties are related to the migration of partially reduced support material on the surface of the metal particles [7–12]. This model is commonly referred to as the "encapsulation" or "decoration" model.

Within the framework of this model, several points remain to be clarified. In particular, the reduced chemisorption capability of SMSI systems could be due simply to the blocking of the active sites of the metal by the oxide or, at least in part, to electronic interactions at the edges of the oxide "moieties" [7,11,13,14] on the metal surface, even though these effects appear to be only short ranged [15,16]. It is clear that the role of the "decorating" oxide in SMSI can be understood only starting from the knowledge of its amount and of the fraction of covered metal surface, but there are only few quantitative data available on this point. It is commonly assumed that the decorating oxide is partially reduced

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("suboxide"), but the data obtained by surface sensitive techniques (mainly X-ray photoelectron spectroscopy) on metals dispersed on oxides showed either no suboxides at all [6,17–19] or very small amounts [12–14,20–23]. In general, in these studies no quantification of the results was attempted and only in some cases was it possible to prove that at least part of the suboxide is located on the surface of the supported metal [14,22]. Other studies on "model" systems have shown that the active sites of the surface of a massive metal sample can be completely covered by a single atomic layer of oxide [24,25]. However, the results for such systems may not be directly transferable to supported metals, i.e. to systems where the active metal is in the form of dispersed particles on the surface of an oxide.

In order to obtain quantitative data in this field, the choice of the experimental techniques and of the parameters of the system under study appears critical because of the difficulty of separating the signal of the "decorating" oxide from the much larger signal of the supporting oxide. In the present work we used angle resolved XPS (ARXPS) to study platinum deposited on the flat surface of a massive TiO_2 sample. In this case, the capability of XPS to provide chemical information, coupled with the variable probing depth as a function of the collection angle permits – in principle – to obtain data about the surface distribution of the platinum and of the oxide species. Although a qualitative use of ARXPS in this field has already been reported [22,26], to our knowledge the present work is the first attempt to quantify ARXPS data for a metal/support system where significant diffusion phenomena take place. We will show that the ARXPS data can be analyzed by means of detailed surface structural models. From this analysis it is possible to obtain an estimate of the amount of oxide present on the Pt surface, which was found to be of the order of a single atomic layer.

2. Experimental

Measurements were performed in a vacuum system capable of base pressure in the low 10^{-10} Torr range, equipped with an Al Kα X-ray source and a hemispherical electron analyzer with multichannel detector. The solid angle of electron acceptance was less than 2 degrees. The sample holder permitted both azimuthal and polar rotation of the sample. The results presented in this article are relative to a TiO_2 (rutile) single crystal sample with a surface cut and polished along the (100) plane. Some experiments were also conducted on samples oriented along the (001) and (110) planes, obtaining qualitatively similar results. The sample was annealed in the vacuum chamber by means of a halogen lamp. The lamp could be moved close to the sample surface and it could be operated in the presence of gases at near atmospheric pressure. A sample temperature up to ca. 1000 K could be reached, as measured by a chromel-alumel thermocouple spotwelded near the sample. A clean, stoichiometric $TiO_2(100)$ surface could be obtained after introduction of the sample in the vacuum chamber by ion bombardment and annealing [27,28]. Platinum was deposited by thermal evaporation from a Pt filament.

Before treating in hydrogen, the sample with the deposited Pt film was preannealed in vacuum at $T = 873$ K. The high temperature reduction treatment (from here on, referred to as "HTR") was performed directly in the analyzer chamber, where the sample was kept at 773 K and exposed to pure hydrogen at near atmospheric pressure for 30 minutes.

The XPS peak areas were obtained by an automatic data collection system which integrates the signal intensities in a kinetic energy window comprising all significant peaks. Therefore, in the case of the Ti 2p signal, this measurement sums up the contributions of all titanium oxidation states present. The data separating the contributions of the different Ti oxidation states in the 2p spectrum were obtained by a procedure of curve fitting, as described in detail in [26].

3. Results

X-ray photoelectron diffraction (XPED) data have shown that the thermal treatment in vacuum leads to the formation of ordered, epitaxial Pt crystallites on the $TiO_2(100)$ surface [29,30]. We found that the subsequent treatment in hydrogen at high temperature (HTR) did not cause significant changes in the XPED curves of the Pt 4f or of the Ti 2p signals, even though in the presence of deposited platinum the HTR treatment led to the detection of some XPS signal of titanium in a lower oxidation state [26]. The XPED curves are sensitive to the surface structure, therefore this result indicates the absence of major structural transformations, such as extensive intermixing of the deposit and the substrate. These data do not exclude, however, the migration of small amounts of oxide onto the Pt surface and are also compatible with the transformation from hemispherical to raft shaped particles reported in [31,32], provided that the Pt rafts maintain the same epitaxial relationship with the substrate as the original clusters. A sample which had undergone HTR was also examined by SEM at a nominal resolution of 100 Å after removal from the vacuum chamber. No distinct Pt particles could be detected, indicating that no massive sintering of the Pt film occurred during HTR in our experimental conditions, again in agreement with the TEM results [31,32].

As a consequence of the use of a single crystal substrate and of the growth of the Pt layer as an ordered, epitaxial overlayer, photoelectron diffraction effects caused significant oscillations in the curves of the signal intensity as a function of the angle, as it has been described in detail in [29,30]. The oscillations remained

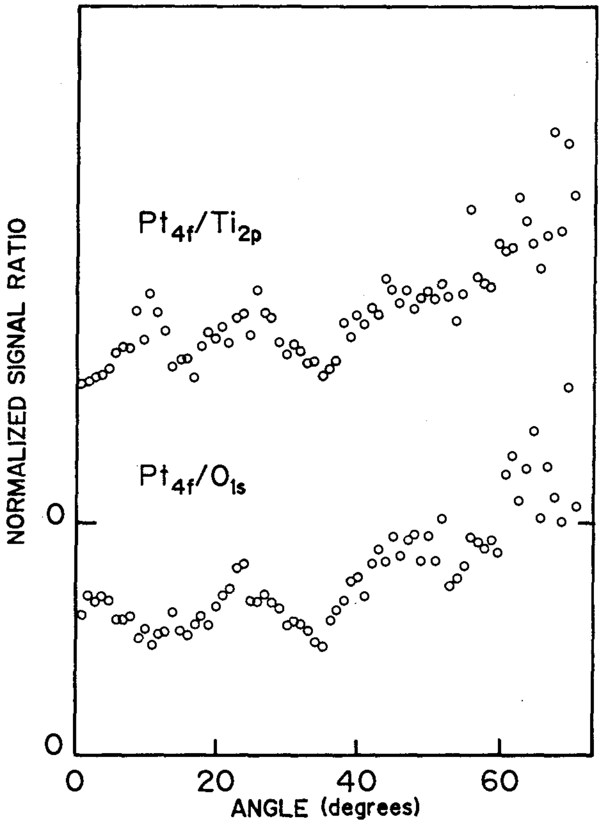

Fig. 1. Experimental signal area ratio versus electron take off angle from the normal to the surface. Both curves are the average of two measurements at non equivalent azimuthal angles.

important also in the Pt/Ti and Pt/O signal ratio curves. In order to remove these XPED effects, we averaged the data over two non equivalent azimuths. Even though this procedure does not completely smooth the curves, it has been shown [33] that the residual oscillations do not prevent the analysis of the averaged data by means of relatively simple physical models. In fig. 1 we show the Pt 4f/Ti 2p and Pt 4f/O 1s averaged signal area ratios after HTR as a function of the electron collection angle. The normalized angle dependence for the Pt 4f/O 1s and Pt 4f/Ti 2p signal area ratios are approximately the same within the experimental error, indicating that the titanium in the surface region remains mostly in the form of an oxide after HTR. These results were reproducible if the sample was exposed to oxygen and subsequently reduced again in hydrogen in the same conditions.

While the data of fig. 1 are relative to the *total* Ti 2p signal intensity, the variation of the intensity ratio of the suboxide and TiO_2 signals was recorded for three different values of the electron collection angle.

4. Discussion

4.1. ANGLE DEPENDENCE OF THE Pt 4f/Ti 2p SIGNAL RATIO

In general, the relative XPS signal intensity is expected to increase for more grazing collection angles for those components which are present in higher amount in the outermost surface region. Since the Pt/Ti and Pt/O signal ratios increase at more grazing angles (fig. 1), a qualitative interpretation of the data indicates that the deposited Pt remains located mainly above the $TiO_2(100)$ surface after HTR. A small amount of "decorating" titanium oxide ("TiO_x") over the Pt surface would scarcely affect the qualitative trend of the signal ratio vs. angle curves, but its presence should be detectable by a quantitative analysis. For this purpose, one needs to take into account all factors which affect the XPS signal ratios. In what follows we will describe a detailed model of the surface which can be used to calculate theoretical ARXPS curves. By means of a comparison with the experimental data it is then possible to estimate the amount of TiO_x present over the Pt surface.

The first parameter to be considered in the model is the shape of the Pt particles. Here, we based the calculation on the TEM results of Baker et al. [31,32], which show that the particles are "raft shaped" after HTR. The "raft" models considered are shown schematically in fig. 2. The simplest conceivable one (model "A") assumes that the Pt rafts have coalesced together to form a uniform layer of constant thickness. A second possible model ("B") considers identical rafts with gaps leaving free a fraction of the substrate surface. A third model ("C") considers rafts of variable thickness. In the last case, to calculate the thickness distribution we used the "Poisson" distribution model which was found in [34] to be a satisfactory model for Pt crystallites on gold surfaces. In this model, the distribution function $P(n)$ = fraction of surface occupied by "n" atomic layers, is described by the expression:

$$P(n) = (\theta^n e^{-\theta})/n!$$

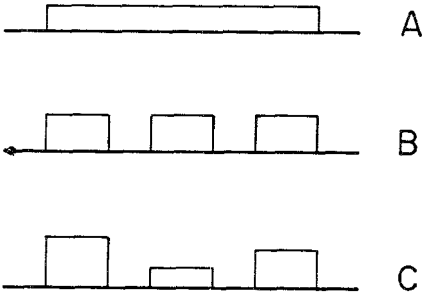

Fig. 2. Schematic representation of the models of the Pt thickness distribution used for the calculation of the Pt 4f/Ti 2p signal area ratios. A: Continuous Pt layer; B: Pt "rafts" of constant thickness; C: Pt "rafts" of variable thickness.

where θ is the coverage in monolayer equivalents. To determine the thickness of a single atomic layer, Pt crystallites were assumed to grow with the (111) plane parallel to the surface of the substrate, as found in [29,30] by XPED.

The decorating titanium oxide was assumed to form a flat layer of constant thickness covering a variable fraction of the Pt surface. All calculations also took into account a variable fraction of Ti present *inside* the Pt film (assumed to be homogeneously distributed), since titanium appears to be able to diffuse as an oxide into the Pt bulk [15]. Moreover, our XPS measurements may not be sufficiently sensitive to detect the presence of a small fraction of Ti as a metal in the Pt bulk to form an alloy [35,36].

In summary, within each assumed Pt thickness distribution, the following parameters were considered: (i) the (average) thickness of the Pt film, (ii) the fraction of Pt surface covered by TiO_x, (iii) the atomic fraction of Ti inside the Pt film and, (iv) the thickness of the decorating TiO_x layer. The "identical rafts" Pt distribution model (model "B") has one further variable parameter: the fraction of "free" substrate surface. The number of parameters can be reduced taking into account that the results reported in [35,37] show that TiO_x on Pt tends to form a single atomic layer with parameters similar to those of low index planes of the bulk TiO oxide. Therefore, in an initial phase of the calculations, the number of variable parameters was reduced to 3 (4 for model "B"), keeping constant the TiO_x thickness as equal to the thickness of one Ti + O layer along the compact (111) plane of the fcc TiO oxide (2.5 Å).

For each set of values of the above parameters, the signal intensities were calculated assuming exponential attenuation as a function of the electron path. The paths were calculated assuming that the "shadowing" effects at the edge of the Pt rafts could be neglected, i.e. that the rafts are large [33]. The mean free paths for the Pt 4f and Ti 2p electrons were calculated according to Penn [38] and to Seah [39]. For propagation in Pt, the two methods gave identical results: λ(Ti 2p) = 13 Å and λ(Pt 4f) = 17 Å. For propagation in TiO_2, the MFPs derived from Seah's method resulted somewhat larger than those calculated according to Penn. Comparative calculations showed however that the use of either set of values had only a marginal effect on the results. For the present work, we used the values derived from Penn, that is λ(Ti 2p) = 17 Å and λ(Pt 4f) = 22 Å. The relative sensitivity for the Pt 4f and Ti 2p transitions was measured experimentally from the Ti signal of a clean TiO_2 surface and from the Pt signal of the same surface covered by a thick Pt layer. The Pt $4f(\infty)/TiO_2\ 2p(\infty)$ ratio was found to be equal to 2.7.

Separate calculations were performed for each Pt distribution model. In each calculation, the adjustable parameters were varied to find the lowest mean square error fit with the experimental Pt/Ti area ratio vs. angle data. The final result of the fitting procedure is shown in fig. 3, where the agreement of theory and experiment appears acceptable in comparison to the results obtained in other works examining the angle dependence of XPS signal ratios [33]. The agreement

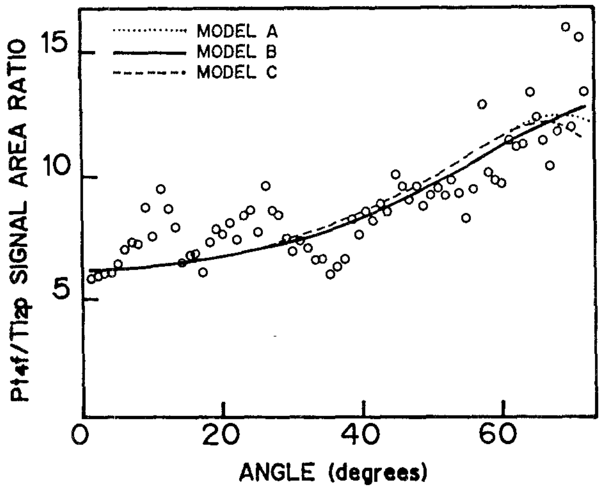

Fig. 3. Circles: experimental Pt 4f/Ti 2p XPS signal area ratio as a function of the electron take off angle from the normal to the surface. Curves: Best fit of the data for the three assumed Pt distribution models, as described in the text. The parameters of the calculation are shown in table 1.

was found to be scarcely dependent on the choice of the Pt distribution parameters and all three models converged to provide a "best fit" for similar values of the thickness of the Pt film. Clearly, our calculation does not permit a choice among the three distribution models, which are to be considered mainly as an approximate description of the morphology of the Pt film. Instead, the fitting was sensitive to the values of the Pt thickness and of the fraction of Pt surface covered by TiO_x. The sensitivity of the calculation for various values of the assumed TiO_x coverage is graphically shown in fig. 4 for the "Poisson" distribution model as an example (a similar sensitivity was obtained with the other two distribution models). It is clear from these results that the presence of some TiO_x on the Pt surface is required for a satisfactory fitting. In fact, if one considers a model where it is assumed that no TiO_x overlayer is present on Pt, no set of the other variable parameters can produce an acceptable fit to the experiment. As shown in table 1, the fitting procedure permitted to determine an optimum value for the TiO_x coverage which, for all three Pt distribution models, was found to be lower than unity. The remaining variable parameter, that is the fraction of Ti inside the Pt layer, was found in general to tend to low values on optimizing the fit. Only for the "uniform layer" Pt distribution model, this fraction was found to be appreciably different from zero.

Calculations were also performed to test the effect of the variation of the assumed thickness of the TiO_x overlayer. Within the assumption that this oxide forms a single atomic Ti + O layer, the effect of a variation of its assumed thickness was found to be marginal, at least in a reasonable range (2.2–2.8 Å). For lower values, the fitting of the experimental data became progressively less satisfactory and no set of the other structural parameters could produce an

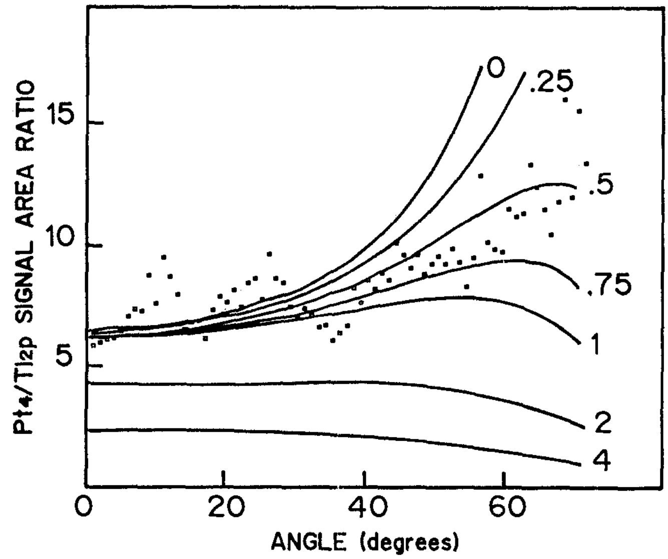

Fig. 4. Sensitivity of the calculation to various thicknesses of the TiO_x overlayer for a constant average thickness of the Pt layers (22 Å) for the "Poisson" distribution of the raft thickness (Model C). The thickness of a single layer of TiO_x is assumed to be 2.5 Å.

acceptable fit for a TiO_x thickness of less than 1.5 Å. Conversely, assuming two layers or more of TiO_x, the experimental data could be fitted for approximately the same thickness of the Pt particles, but for a lower fraction of covered Pt surface. For instance, for the "Poisson" distribution model (model "C"), assuming that the TiO_x islands are two layers thick (5 Å), the fitting indicates a TiO_x coverage equal to 30%, instead of the value of ca. 50% obtained in the assumption of a single layer thickness.

Table 1

Summary of the results of the calculations. The parameters and the three Pt distribution thickness models are discussed in detail in the text. The thickness of the TiO_x layer located on the Pt film is assumed to be 2.5 Å. A: Uniform Pt layer; B: Pt rafts (uniform thickness); C: Pt rafts (variable thickness: "Poisson" distribution)

Model	Best fit parameters				
	Pt average thickness (Å)	Fraction of TiO_2 substrate covered by Pt	Fraction of Pt surface covered by TiO_x	Ti at. fraction *inside* the Pt film	Mean square error
A	20.3	1	0.45	0	0.2
	22.6	1	0.32	0.16	0.16
B	19.9	0.88	0.24	0	0.16
C	22.0	0.99	0.51	0	0.16

Table 2

Experimental and calculated signal ratios for the Pt 4f/Ti 2p and Ti(suboxide)/TiO_2 signal ratios for a Poisson type Pt thickness distribution (model C), as described in the text. C1: The TiO_x overlayer is assumed to be composed of titanium suboxide only. Parameters producing the best fit: Fraction of TiO_x covered Pt surface: 30%, Pt film average thickness = 13 Å. C2: The TiO_x overlayer is assumed to be a variable mixture of suboxide and stoichiometric TiO_2. The calculation takes into account also the presence of suboxide at the Pt/substrate interface and inside the Pt particles. Parameters producing the best fit: Fraction of TiO_x covered Pt surface: 53%, atomic fraction of Ti suboxide in TiO_x moieties = 41%, fraction of Ti suboxide at the Pt/substrate interface: 100%, fraction of Ti suboxide in Pt = 0%, Pt film average thickness = 21 Å.

Angle from normal	Pt 4f/total Ti 2p signal ratio			Ti suboxide/total Ti 2p signal ratio		
	Exp	Best fit, calculated		Exp	Best fit, calculated	
		C1	C2		C1	C2
$\Theta = 0°$	6.5	3.3	6.5	0.22	0.08	0.24
$\Theta = 50°$	10.6	10.5	10.6	0.43	0.18	0.44
$\Theta = 70°$	11.3	11.3	11.3	0.67	0.77	0.67

The result shown in table 1 indicates that the Pt surface is not completely covered by the oxide, a result which appears consistent with those of Takatani and Chung [13] for the Ni/TiO_2 system. It would appear therefore that "decoration" rather than "encapsulation" of the Pt particles takes place in our experimental conditions. However, there are several sources of uncertainty in the calculation, mainly due to the approximations in the models and in the estimation of some parameters. Therefore, although it is possible to exclude Pt encapsulation by several layers of oxide, the accuracy of the procedure appears insufficient to rule out that the TiO_x layer completely covers the Pt surface.

4.2. SUBOXIDE SIGNAL VARIATION VS. ANGLE

The signal intensity ratios separating the contribution of stoichiometric TiO_2 and suboxide at 3 different electron collection angles are listed in table 2. A qualitative interpretation of these results has been reported in [26]. A quantitative analysis can be performed by means of the same type of calculation described in the previous section, with additional assumptions about the distribution of the different oxidation states of titanium in the surface region. It is generally believed that the reduced titanium moieties are located over the Pt particles [11]. Taking also into account that, in the absence of deposited Pt, no suboxide can be detected by XPS after HTR on TiO_2 [26], the simplest conceivable model assumes that the TiO_x overlayer is wholly composed of titanium suboxide, whereas all the substrate titanium is in the formal +4 oxidation state (TiO_2). For each Pt distribution model, therefore, the variable parameters are the (average) thickness of the Pt layer and the fraction of suboxide covered Pt surface.

The calculation was required to fit *both* the angular dependence of the ratios of the Pt/Ti signal and of the Ti(suboxide)/TiO_2 signals. A further constraint was that the parameters producing the best fit should be compatible with those reported in table 1. Given these requirements, we found that the calculations could only reproduce the qualitative trend of the experimental data, but that the calculated Ti(suboxide)/Ti(TiO_2) ratio showed a significantly steeper increase as a function of the angle than experimentally observed.

In order to improve the agreement, we tested the effect of a number of additional structural parameters, namely that (i) the suboxide over the Pt film may contain a variable amount of Ti in the +4 oxidation state (ii) the Pt/substrate interface may be in part composed of a single layer of titanium suboxide and, (iii) some titanium suboxide (homogeneously distributed) may be present inside the Pt layer. We found that the introduction of the first parameter (variable stoichiometry of the TiO_x moieties) did produce a marked improvement in the agreement of theory to experiment. A marginal improvement was produced by the second parameter (suboxide at the Pt/substrate interface), whereas the third parameter (titanium inside the Pt film) only worsened the agreement. As an example, in table 2, we show the best fit obtained for the "Poisson" Pt thickness distribution for two calculations: the simple model which assumes no TiO_2 on the Pt surface (model "C1") and a more complex model where the above described parameters were taken into account (model "C2"). The set of parameters producing the best fit for model C2 involved a fractional TiO_x coverage on the Pt surface ($\approx 50\%$) and a Pt film average thickness (≈ 21 Å), in good agreement with the values reported in table 1.

The calculations based on the other two Pt thickness distribution models produced qualitatively similar results, however the values of the fraction of TiO_2 in the TiO_x overlayer ranged from a minimum of 15% for model "B" (identical rafts) to a maximum of 60% for model "C" (Poisson distribution). Therefore it appears that this analysis can only lead to the generic conclusion that *some* TiO_2 may be present after HTR onto the Pt surface. The presence of the "4+" oxidation state of titanium in the decorating TiO_x layer appears compatible with the results of XPS studies where Ti was deposited and oxidized on Pt [40] or where the Pt_3Ti alloy was oxidized [35,36,41]. In these studies, variable amounts of stoichiometric TiO_2 were found to be associated to the suboxide. The fact that the HTR treatment does not appear to reduce completely the decorating oxide may be tentatively attributed to oxygen migration from the support. In any case it is clear that the decorating oxide layer is composed, at least in part, of titanium suboxide, in agreement with the generally accepted models for SMSI systems [11]. It is also worth noting that the presence of suboxide at the Pt/substrate interface, which was found to optimize the fit in the present work, was assumed to explain the "wetting" transition observed by TEM after HTR for the Pt/TiO_2 system [31,32]).

5. Conclusion

The results of the present work show that ARXPS can be used to obtain quantitative data for a complex system such as the Pt/TiO_2 interface after high temperature reduction in hydrogen. The analysis of the data confirms the generally accepted models for SMSI systems, that is we found that the best fit of theory to experiment requires the presence of partially reduced titanium oxide over the surface of platinum. From this analysis it is also possible to rule out that the reduction in hydrogen causes the formation of significant amounts of Pt-Ti alloy or the migration of titanium oxide inside the Pt layer.

The fraction of Pt surface covered by titanium oxide was found to be lower than unity for all models considered. However, given the uncertainty inherent to the procedure of analysis it is not possible to exclude that the Pt surface is fully covered by a single layer of oxide. It appears therefore that the main conclusion that can be drawn from our results is that the amount of titanium oxide over the Pt surface is of the order of a monolayer.

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