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ON THE COMPOSITION AND STRUCTURE OF THIN LAYERS OF TITANIUM OXIDE ON PLATINUM SURFACES

U. BARDI

Dipartimento di Chimica, Università di Firenze, Via G. Capponi 9, 50121 Firenze, Italy

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This work reviews the available data about the structure and composition of thin layers of titanium oxide on the surface of platinum. These systems can be prepared by vapor deposition and subsequent oxidation of Ti on a massive Pt substrate or by oxidation at low pressure of the Pt_3Ti alloy. For both types of substrate, the XPS data show that two distinct Ti states in the oxide layer can be detected. The structure and the composition of the oxide layer varies depending on the substrate composition and on the conditions of preparation. On pure Pt, the preferential formation of a defective "TiO_{2-x}" oxide was observed. On Pt_3Ti, the oxide film a layer was formed of TiO of thickness of the order of a single atomic layer and of crystallites of nearly stoichiometry TiO_2.

In supported metal catalysts, the migration of a thin layer of oxide onto the surface of the active metal is believed to play an important role in affecting the chemisorptive and catalytic properties of the system. This effect is often referred to as "strong metal to support interaction" (SMSI) [1–3]. In this field, despite the number of studies performed so far, several points remain to be clarified. In particular, it is generally accepted that the oxide which "decorates" or encapsulates the active metal is partially reduced ("suboxide"), i.e. it is in a lower oxidation state than in the support. Photoelectron spectroscopy and other surface sensitive techniques have been used to verify the presence of suboxides in SMSI type supported catalysts, however the detection of the signal from a thin oxide overlayer is difficult because it overlaps in part with the stronger signal of the support. In the studies performed so far the XPS signal of the suboxide was found to be too weak to permit to determine the composition [4–10] and it was not possible to prove that the signal actually derived from a species located over the surface of the active metal. Furthermore, in several studies, the suboxide signal was not detectable at all [11–14].

In order to remove the interference of the signal of the support, a number of studies has been performed on simplified "model" systems, where a massive metal sample is used as substrate and a thin oxide film is formed on the surface.

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Perhaps the most studied among these systems is the Pt/TiO_x one [15–22], owing to the fact that it was the first case reported to show SMSI properties [1]. As substrates, massive Pt or the Pt_3Ti alloy have been used. In these systems, the presence of suboxides in the surface region has been clearly demonstrated, however several points still appear in need of clarification and the available results do not appear to be completely consistent, for instance the suboxide composition was given as "Ti_2O_3" in one case [20], but as "TiO" in others [15,18,19]. The composition and structure of the oxide as a function of different conditions of preparation appear as a fundamental element in order to understand the behavior of these systems. Hence, the main purpose of the present note is to review the available data on this subject in order to verify their consistency and to propose models for the structure of the titanium oxide-platinum interface. Furthermore, the relation of these model systems with actual catalysts will be discussed.

Films of titanium oxide of average thickness of the order of a few atomic layers can be prepared on the surface of a massive Pt sample by vapor deposition of titanium and subsequent low pressure oxidation [15,16]. In the case of Pt_3Ti, titanium oxide segregates on the surface of single crystal or polycrystalline samples by exposing to oxygen at pressures in the range from 10^{-5} to 10^{-18} Torr at temperatures higher than approximately 700 K [17–20]. For both types of substrates, the TiO_x overlayer appears to interact only with platinum atoms of the substrate, since it has been shown that the stable termination of the Pt_3Ti alloy is a layer of pure platinum [17,18].

The published XPS results [15–18,20] for both the Pt and Pt_3Ti substrates are in agreement in showing that only two distinct states of oxidized titanium can be observed in these conditions (see table 1). In fig. 1, the Ti 2p region is shown as observed after oxidation of Pt_3Ti. The higher oxidation state shows a Ti $2p_{3/2}$ binding energy at approximately the same energy as bulk TiO_2 (table 2), so the ion in this phase can be labeled as "Ti^{4+}". Regarding the lower oxidation state, the data of table 2 clearly show that the binding energy is intermediate between

Table 1
Observed values for the Ti $2p_{3/2}$ peak of the low binding energy oxide phase (TiO) in the TiO_x/Pt system

System	B.E. Ti $2p_{3/2}$	Measured oxide composition	Ref.
$TiO_x/Pt_3Ti(111)$	456.9	–	[17]
$TiO_x/Pt_3Ti(510)$	456.3	TiO-$TiO_{0.6}$	[18]
TiO_x/Pt_3Ti(polycryst)	456.8	–	[20]
$TiO_x/Pt_3Ti(111)$–(100)	–	TiO	[19]
TiO_x/Pt(polycryst)	456.2	TiO	[15]
TiO_x/Pt(polycryst)	456.6	–	[16]

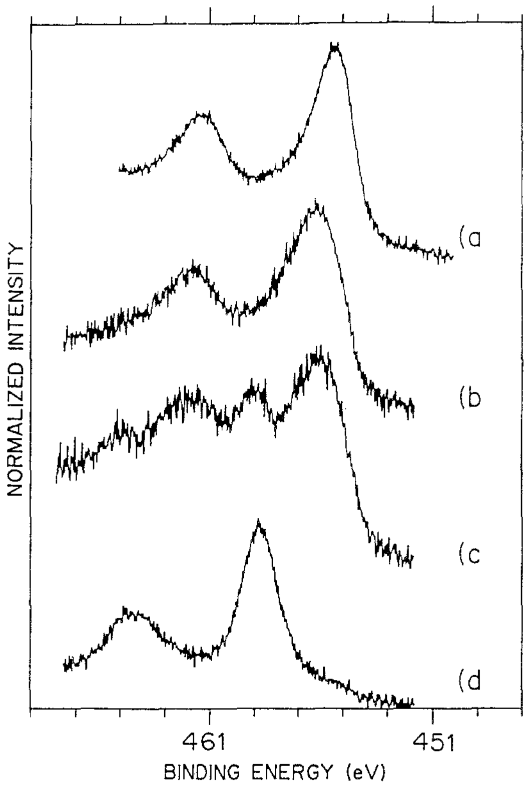

Fig. 1. Evolution of the XPSTi2p peaks for progressively higher exposure to oxygen at high temperature of the $Pt_3Ti(510)$ single crystal surface. A) Clean Pt_3Ti surface, B) nearly pure TiO after exposure to 5×10^{-6} Torr O_2 at 1073 K for 30 sec, C) mixture of TiO and TiO_2 after exposure to 7×10^{-5} Torr O_2 at 973 K, D) Nearly pure TiO_2 after exposure to 1×10^{-4} Torr O_2 at 973 K and cooling in oxygen at the same pressure.

the "2 + " and "3 + " state. In this case, therefore, it is not possible to assign a formal charge to the Ti ions. As a consequence, the composition of the oxide cannot be derived simply from the values of the binding energy of the metal transitions, as commonly done in XPS studies. Rather, only a quantitative measurement based on the relative intensity of the oxygen and titanium peaks can determine the composition of this oxide.

It was found that in most cases oxidation leads to a titanium oxide layer formed of a mixture of the two oxidation states (see for instance fig. 1, curve C). It is obvious that in these conditions one can only measure an average composition, since conventional XPS cannot separate the oxygen signals associated to the two states. However, in certain conditions it has been possible to prepare nearly "pure" layers, where a single state can be detected [15,18]. In this case, the composition of the associated oxide phase can be determined by XPS from the intensity of the O1s and $Ti2p_{3/2}$ peaks, after an appropriate calibration with

Table 2
Binding energy of the Ti $2p_{3/2}$ peak for various species in the TiO_x/Pt system

System	B.E. Ti $2p_{3/2}$	Ref.
Metals		
Ti	454.0	[18]
	453.8	[27]
Pt_3Ti	455.5	[18]
	455.6	[17]
Bulk oxides		
TiO	455.3	[26]
	454.8	[27]
Ti_2O_3	457.5	[26]
TiO_2	459.2	[26]
	459.0	[27]
	459.0	[18]
Thin oxide layers		
TiO/Pt_3Ti	456.3	[17]
	456.9	[18]
	456.8	[20]
TiO/Pt	456.2	[15]
	456.6	[16]
TiO_2/Pt_3Ti	458.8	[18]
	459.4	[17]
TiO_2/Pt	458.9	[15]
	457.9–458.6	[16]

oxide standards. By means of this procedure, it was found for a Pt_3Ti substrate [18] that the O/Ti atomic ratio for the lower binding energy state is equal to one or lower, depending on the conditions of preparation, and that the formation of Ti_2O_3 can be excluded. This result is consistent with those of an earlier LEED/AES study on Pt_3Ti [19]. For the Pt substrate, Greenlief et al. [15], also found an O/Ti ratio equal to one for the low binding energy phase. Regarding the higher binding energy phase ("Ti^{4+}"), quantitative measurements showed that the oxide composition is TiO_2 [18].

Since the data from independent sources are consistent, the "TiO" stoichiometry can be assigned with reasonable certainly to the lower binding energy oxide.However, at this point one is faced with the problem of the shift in binding energy of the Ti 2p peaks of this phase with respect to the data for bulk TiO (table 2). This shift can be explained taking into account the Pt-Ti interaction, which has been shown to affect the binding energy of the titanium peaks. For the clean Pt_3Ti surface a shift towards higher binding energy of the Ti metal peaks was observed [16,18]. Moreover, the calculations performed by Horsley [23] have shown that if an intermetallic Pt-Ti bond is present in a compound where titanium is also bonded to oxygen, a significant electron charge transfer from titanium to platinum should occur. As an initial state effect, this tranfer is expected to cause a shift towards higher binding energy of the titanium core levels. Also final state effects related to the formation of an image charge in the metallic substrate could play a role in altering the binding energy of the Ti levels. Although it is not possible to calculate the exact magnitude of these effects, both imply a direct interaction of most of the Ti atoms in the oxide with the substrate (e.g. an intermetallic Ti-Pt bond), suggesting therefore that the TiO film spreads on the surface forming a uniform layer of near monoatomic thickness. This conclusion is in agreement with the structural models derived in [19] from LEED data. Obviously, one would not expect these effects to modify the Ti binding energy if the oxide forms instead multilayer crystallites on the surface, as it appears to be the case when only TiO_2 is formed [16].

From the knowledge of the stoichiometry associated to each titanium oxide state, one can proceed to examine surface where both states are present. A point to be carefully considered here regards the distribution of the species in the surface region, that is, if the two Ti XPS *states* correspond to two distinct *phases* of well defined stoichiometry, or if both states are dispersed in a single phase of variable stoichiometry. In this respect, an important parameter is the variation of the Ti 2p binding energy for variable fractions of the two states. On the Pt_3Ti substrate, the binding energy of the Ti 2p peaks of both oxides was found to be nearly constant for a variable composition of the layer [17,18,20], (see also fig. 1). In contrast, Dwyer et al. [16], working with a Pt substrate, found a significant variability in the Ti $2p_{3/2}$ peak position as a function of different fractions of suboxide. A similar behavior was observed for the TiO_x/Rh system [24]. Greenlief et al. [15], working on a Pt substrate, do not explicitly report a continuous variability in the Ti binding energies of the oxide, but the examination of the published spectra shows that the transition from a phase composed of nearly pure TiO_2 to one where both oxides are present appears to lead to a shift in the Ti 2p levels of the same order as that reported in [16].

Dwyer et al. [16] attribute the binding energy shift of the Ti 2p peaks to the immission of free electrons in the conduction band from partially reduced centers ("Ti^{3+}"). As a consequence, the rigid shift of the Fermi energy in the "TiO_{2-x}" solid causes a shift in the measured binding energy of all Ti levels. It is obvious that such a model implies that the two states are homogeneously or nearly homogeneously distributed, i.e. that the reduced Ti centers are dispersed *inside* the TiO_2 matrix. So, a continuous variation of the concentration of the Ti^{3+} ions would lead to a continuous shift in the measured binding energies. Conversely, if the two titanium states form two distinct phases of constant stoichiometry, the Fermi levels of each phase are equalized upon contact, independently of the amount of each phase. So, the binding energies cannot change as a function of variable fractions of the two oxides.

It appears therefore that the XPS results reflect a fundamental difference in the structure of the oxide, at least in some conditions of preparation: in one case (Pt

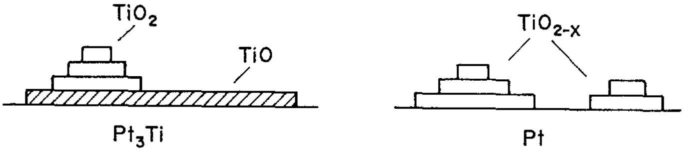

Fig. 2. Schematic model of the oxide overlayer structure. Left: flat "monolayer" of TiO (shaded) plus TiO_2 crystallites. This structure was preferentially formed on the Pt_3Ti substrate. Right: Crystallites of "TiO_{2-x}", which form preferentially on a pure Pt substrate.

substrate) the two oxide states are mixed in a single phase (TiO_{2-x}) of variable composition, in the other (Pt_3Ti substrate) they form two distinct phases (TiO + TiO_2) of constant or nearly constant stoichiometry, with the TiO_2 phase probably forming crystallites over the TiO layer (see fig. 2 for a schematic structural model). This interpretation of the XPS data is confirmed by other techniques: On the Pt_3Ti substrate, the LEED results [19] show that the suboxide tends to form discrete epitaxial phases of thickness of the order of one atomic layer. For the TiO_x/Pt system, even though no LEED study was performed, the LEISS results [16] indicate the preferential direct growth of multilayer crystallites, although the formation of a layer of TiO appears to occur in certain conditions of preparation [15].

If we consider now the thermodynamic parameters of the Pt + Ti + O system, it is evident that, in spite of the negative enthalpy of formation of Pt-Ti alloys [25], the formation of titanium oxide is always favored in the presence of a measurable pressure of oxygen [25]. Furthermore, the formation of TiO_2 should also be favored in the presence of oxygen. In order to explain the preferential formation of TiO on the Pt_3Ti surface, one should consider an important factor favoring reduction, i.e. that the Pt_3ti bulk can be considered a nearly infinite supply of metallic titanium at a sufficiently high temperature to permit rapid migration of Ti to the surface. Hence, the formation of a suboxide on the Pt_3Ti substrate is favored in comparison to a substrate which does not contain metallic Ti. In this system, the formation of TiO as a flat layer of atomic thickness can be explained as due to the stabilizing effect of the formation of the highly stable Ti-Pt bond (as obvious, such bond cannot be formed in the case of TiO_2, since Ti atoms are fully coordinated to oxygen atoms). It should also be remarked that conditions of preparation which maximize the reducing or oxidizing properties of the environment may lead to the same oxide structure on both types of substrates: Nearly pure TiO_2 can be formed on Pt_3Ti by cooling in the presence of oxygen [18], whereas pure TiO may be formed on the Pt substrate at high temperature and very low oxygen pressure [15].

From the above discussion, some general conclusions can be drawn. First of all, it appears important to remark that the simple correlation of binding energy to composition may not hold for a compound in the form of a layer of near monoatomic thickness, in the presence of a strong substrate-overlayer interaction. Therefore, care is to be taken in the interpretation of the XPS data in this type of systems. In the Pt/TiO_x case it is certainly impossible to venture hypothesis on the stoichiometry of the oxide (as done in [20]) on the basis of the supposed identification with the "3 + " formal charge.

Regarding the capability of this type of systems to act as "models" for supported catalysts, it should be noted that the structure of the oxide layer has important consequences on the chemisorptive and catalytic properties of the surface: A flat atomic layer of oxide tends to stop all the capability of the metal surface to chemisorb gases even for a relatively small amount of oxide. It appears interesting to note that the different structure and composition of the oxide layer on reducing (Pt_3Ti) or non reducing (Pt) substrates appears to mirror the transition which occurs in SMSI systems depending on the treatment by reducing (H_2) or oxidizing (O_2) agents [1–3]. It may be speculated that the formation of oxide clusters or monolayer observed on model systems may occur also in supported catalyst, causing the blocking (or the freeing) of a significant fraction of the Pt surface, leading therefore to the reversibility of the SMSI effect.

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