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STRONG METAL-SUPPORT INTERACTION IN THE Pt-$Na_{0.7}WO_3$ SYSTEM: A STUDY BY LOW ENERGY ION SCATTERING SPECTROSCOPY AND OTHER SURFACE SENSITIVE TECHNIQUES

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The system formed of platinum deposited on the (100) surface of a $Na_{0.7}WO_3$ single crystal was studied by low energy He^+ ion scattering and other surface sensitive techniques. After Pt deposition, flashing at or over approximately 500 K leads to the blocking of the Pt adsorptive sites by sodium oxide and to the consequent suppression of the capability to chemisorb CO at room temperature.

The chemical and structural modifications which occur in some oxide supported metal catalysts during high temperature reduction are commonly referred to as "strong metal-support interaction" (SMSI) [1–4]. These phenomena were found to be linked to the partial reduction of the oxide support [1,2]. From this observation, a model was developed which involved electron transfer from the oxide to the metal [4–6], a phenomenon which was correlated to the partially occupied conduction band of the reduced oxide [7]. In later studies, oxide migration phenomena were observed, which led to correlate SMSI properties to the encapsulation or "decoration" of the active metal surface [3,4,8–10]. However, charge transfer phenomena were still claimed to play an important role in affecting the chemical properties of the system [4,7,9].

In the present work we aimed to elucidate the relation between the adsorptive properties of a deposited metal and the presence of "free" electrons in the conduction band of the supporting oxide. For this purpose, we chose an oxide which is stable in a conducting form: Na_xWO_3 ("sodium tungsten bronze"), which is well known for having metal-like conductive properties [11]. Platinum was chosen as the deposited metal in view of the interest of the Pt/Na_xWO_3 system in electrocatalysis [12–16]. Some preliminary results of this study were presented in [17,18]. In the present work, we will show that in this system charge

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transfer phenomena do not appear to play a significant role in the suppression of CO adsorption (a typical SMSI property), which is caused instead only by the blocking of the Pt adsorptive sites by sodium oxide.

The study was performed on the (001) oriented surface of a single crystal sample of composition $Na_{0.7}WO_3$, prepared as described in [19]. The sample was introduced in a vacuum system capable of base pressure in the 10^{-10} Torr range. Heating was performed by means of a halogen lamp mounted inside the system or by resistive heating of the sample holder. XPS and LEISS were performed by means of a hemispherical analyser with multichannel detector. Mg KA radiation was used as excitation source for XPS. For LEISS, a beam of 0.6 keV He^+ ions was used at a sample current of approximately 3×10^{-8} A/ cm^2 ($\sim 2 \times 10^{11}$ ion/sec/cm^2). The ion scattering angle was 135° and the angle of incidence of the beam was near to the normal to the surface. Platinum was deposited by evaporation from a Pt rod heated by electron bombardment. TDS experiments were performed exposing the sample to CO at room temperature and subsequently heating in vacuum at a rate of 8 degs/sec, detecting the CO signal by a quadrupole mass spectrometer.

The $Na_{0.7}WO_3$ surface was cleaned by a treatment consisting of Ar^+ ion bombardment and annealing in the presence of oxygen [17–19]. The XPS, AES and LEED results for the clean surface were found to be in agreement with those reported by other authors [19–23]. The LEISS spectrum of the clean and annealed $Na_{0.7}WO_3$ (001) surface (fig 1, top curve) showed only the peaks of oxygen and sodium, in agreement with the structural models proposed in [19,20]. The weak signal at E/E_0 equal to approximately 0.65 can be attributed to potassium, which was also detected by XPS. The tendency of the Na_xWO_3 surface to accumulate traces of potassium was also observed in [19].

Over several tests of Pt deposition, the Pt LEISS peak was always found to be weak or not detectable at all, even for amounts of deposited Pt of the order of several monolayer equivalents, as estimated from the intensity of the Pt XPS signal. The intensity of the Pt LEISS peak (fig. 1, middle curve) was found to be always at least a factor 5 lower than the peak for a clean and annealed Pt foil in the same apparatus. This result implies the presence of some substance partially covering the surface of the deposited Pt layer. The available data indicate two possible substances responsible for this effect: One is sodium oxide migrating from the substrate and the other adsorbed carbon monoxide, i.e the largest component of the residual atmosphere during deposition. The presence of a fraction of sodium oxide over the Pt surface appears to be indicated by the persistence of the Na LEISS signal even for relatively large amounts of deposited platinum (as determined by XPS). However, the adsorption of carbon monoxide during deposition was also evident. The desorption of carbon monoxide was observed in TDS after Pt deposition and, although carbon is not detectable in LEISS in our experimental conditions, the relative increase of the O LEISS signal (fig. 1, middle curve) may be considered an indication of the presence of

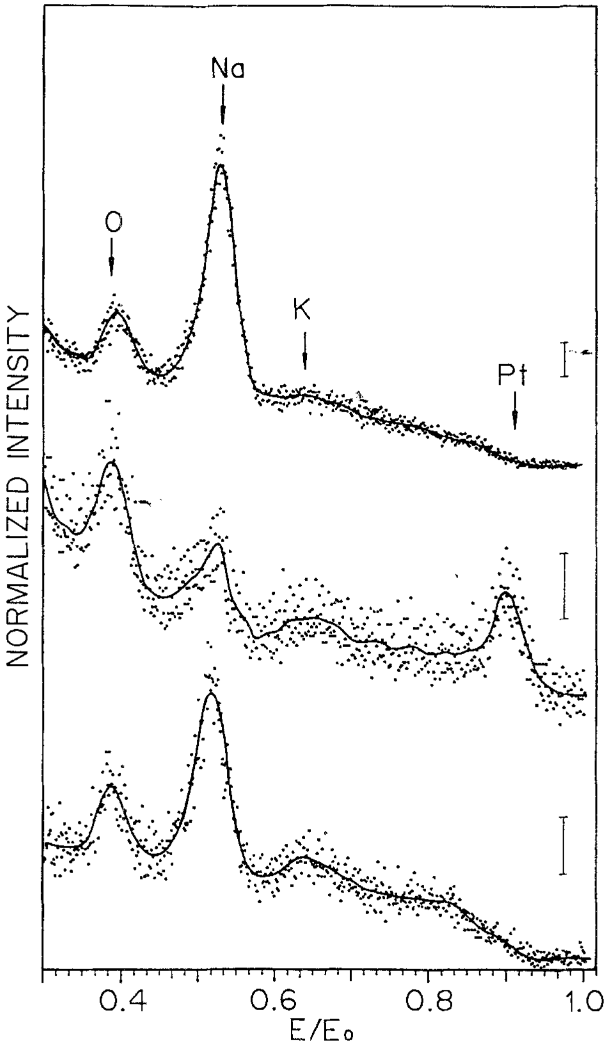

Fig. 1. LEISS results obtained with He^+ ions at an energy of 600 eV. Top curve: Clean $Na_{0.7}WO_3(001)$ surface. Middle: surface after deposition of Pt at room temperature. Bottom: after annealing in vacuum at 600 K.

adsorbed CO. It appears therefore that *both* sodium oxide and CO cover part of the Pt surface after deposition at room temperature. In these conditions, the heat of condensation of Pt during deposition may be considered the driving force for the surface migration of sodium oxide at room temperature.

Flashing in vacuum at or over approximately 500 K after Pt deposition caused the complete disappearance of the Pt signal from the LEISS spectrum (fig. 1, bottom curve). Since the XPS results ruled out a significant carbon surface contamination and since we observed that CO is completely desorbed from the Pt surface at or over ca. 500 K, we can conclude that sodium oxide (plus a minor

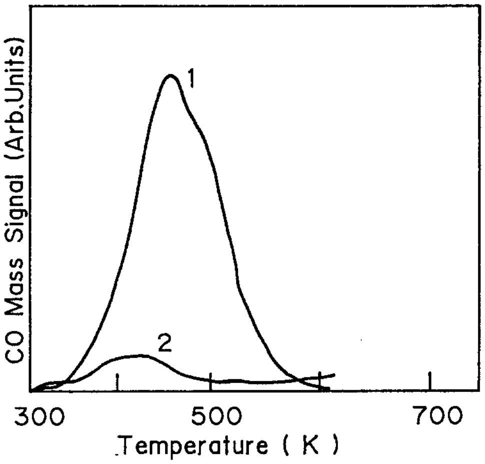

Fig. 2. Carbon monoxide thermal desorption results: Top curve: surface saturated with CO (20 L at 5×10^{-7} Torr) after Pt deposition at room temperature. Bottom: Same CO exposure after annealing at 600 K.

amount of potassium oxide) is the only substance present in the outermost surface layer after annealing. At high temperatures ($T >$ ca 700 K), Pt bulk migration and substrate-deposit interdiffusion were clearly indicated by the strong reduction –and eventually by the near disappearance– of the Pt XPS or AES signal [18]. However, flashing at temperatures not higher than ca 600 K did not cause a substantial reduction of the Pt XPS signal. It appears therefore that the phenomenon that takes place in these conditions may be described as mainly due to the migration of sodium oxide onto the Pt surface. However, partial Pt dissolution into the substrate cannot be excluded.

A further confirmation that a layer of sodium oxide covers the Pt surface after flashing in vacuum was derived from depth profiling of the surface by Ar^+ bombardment at 1 keV. In these conditions it was impossible to remove the sodium oxide overlayer without removing also a large fraction of the Pt deposit, as indicated by the substantial reduction of the Pt XPS signal. However, we observed that ion bombardment could restore a fraction (ca 20%) of the initial Pt LEISS signal.

Typical TDS results for carbon monoxide are shown in fig. 2. Regardless of the amount of deposited Pt, if the sample was not annealed before deposition, a desorption peak could be detected after saturation with CO at room temperature. The position of the peak of the first curve of fig. 2 is compatible with the results for CO thermal desorption from pure Pt surfaces [24]. However, only a minor fraction of the initial CO TDS peak (fig. 2, curve 2) could be observed for a new exposure after the first TDS thermal flash, even though the XPS Pt signal remained well detectable. The CO TDS peak was strongly attenuated also if the "as deposited" surface was preannealed in vacuum at or over 500 K. This behavior was well reproducible over a number of tests for different amounts of platinum deposited on the surface, estimated by XPS to vary from less than a monolayer to several monolayers. Treatment in oxygen at room temperature or up to 900 K at $p = 5 \times 10^{-5}$ Torr did not restore the capability of the surface to adsorb CO. Only a short argon ion bombardment in the same conditions which lead to the partial restoring of the Pt LEISS signal could restore a corresponding fraction of the initial CO TDS peak.

The suppression of CO adsorption is a typical SMSI property [1–4] and our results show that it can be easily induced in the Pt/Na_xWO_3 system simply by moderate annealing. The relation of this system to SMSI ones is also evidenced by the tendency of the Pt deposit to form islands of uniform thickness [17], since the formation of flat islands ("pillboxes") of the active metal was reported [2,4] to be associated to SMSI properties. These properties of the Pt/$Na_{0.7}WO_3$ system might be –in principle– related to the presence of free electrons in the conduction band of the substrate [7], which favor a strong substrate-deposit bond, in analogy with the case of Pt/TiO_2 after high temperature reduction [2,4,6]. However, our results clearly show that the Pt sites which are not blocked by sodium oxide retain the "normal" chemisorptive properties of metallic Pt. Therefore, at least for the Pt-$Na_{0.7}WO_3$ system, the metal-oxide bond does not appear to play a significant role in the blocking of CO adsorption.

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