

An ISS, AES, and ESCA Study of the Oxidative and Reductive Properties of Platinized Titania

INTRODUCTION

The phenomenon of strong-metal-support interaction (SMSI) which was first reported by Tauster *et al.* (1, 2) has been a controversial topic in the field of catalysis for many years. SMSI phenomena are characterized by suppression of the amounts of H₂ and CO which chemisorb on oxide-supported metal crystallites. This occurs after a high-temperature (500°C) reduction in hydrogen, particularly for reducible oxide supports. Annealing in oxygen followed by a low-temperature (200°C) anneal in hydrogen usually restores most of the chemisorption capacity. Numerous explanations of SMSI phenomena have been proposed, including suggestions of an electronic interaction between the supported metal and the oxide, i.e., charge transfer (3-9); changes in metal crystallite morphology (10); encapsulation of the metal crystallites by support species which form during reduction of the support (11-22); encapsulation of the metal crystallites by impurity species; creation of special active sites at the metal-support interface; hydrogen spillover; and others.

From the studies cited above, it appears that encapsulation of the metal crystallites does occur and that the electronic effects can be insignificant (23), small (17), or quite significant (10). However, the techniques used in most studies have not been capable of directly observing encapsulation or of determining the composition of the species which are responsible for the encapsulation. In this study ion scattering spectroscopy (ISS), electron spectroscopy for chemical analysis (ESCA), and Auger

electron spectroscopy (AES) have been used to examine platinum crystallites supported on polycrystalline titania before and after inducing encapsulation. This study is an extension of a previous ISS and static secondary ion mass spectrometry (SSIMS) study (24) of the same system. It also is in qualitative agreement with the ISS results of Dwyer *et al.* (25).

ISS is an excellent technique to use for this type of study due to its extremely high surface sensitivity (essentially outermost layer sensitivity). This high surface sensitivity is due to two factors. The first is that primary ions which penetrate beneath the outermost layer have a very high probability of being neutralized and, thus, do not contribute to the ISS signal. The second is that ions which penetrate beneath the outermost layer of atoms and are not neutralized have a very high probability of scattering inelastically and, therefore, do not contribute to the inelastic peaks in the ISS spectrum but become part of the background. It is also possible to estimate the composition of the outermost layer of atoms using ISS (26). Thus, an effort is made in this study to identify the composition of the encapsulating species after induction of the SMSI state.

EXPERIMENTAL

The platinized titania sample was prepared by first heating a Marz grade polycrystalline titania foil (obtained from Materials Research Corp.) at 500°C for 15 min in air to form an oxide layer. Since the ESCA results show no peak due to metallic Ti, the

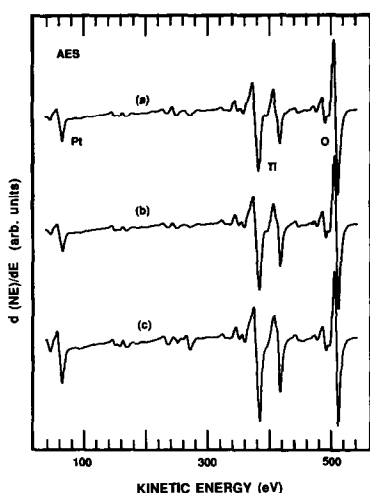


FIG. 1. AES spectra taken from the platinumized titania sample after (a) cleaning and annealing the sample in 10^{-6} Torr O_2 for 4 h at 400°C , (b) annealing the sample in 10^{-5} Torr of H_2 for 1 h at 500°C , and (c) lightly sputtering the sample with 1 keV Ar^+ .

oxide layer was at least 60 \AA thick. Next the surface was platinumized by spraying an aqueous solution of 1.5 M chloroplatinic acid onto the titania surface which was maintained at 500°C .

The sample was mounted in an ultrahigh vacuum system (27) which was used for the characterization studies. The base pressure of this system was less than 2×10^{-10} Torr during these studies. The sample was heated resistively by passing a direct current through the Ti foil, and its temperature was measured using an iron-constantan thermocouple spot welded to the back of the Ti foil. ISS, ESCA, and AES were performed using a double-pass cylindrical mirror analyzer (CMA; Perkin-Elmer PHI Model 15-255GAR) which contained a coaxial electron gun and a movable aperture for angle-resolved studies. ISS was performed using 1 keV $^4\text{He}^+$. A primary beam current of 100 nA defocused over a spot diameter of about 1 cm was used to minimize damage. It required about 20 s to collect an ISS spectrum. The fact that spectra collected repeatedly exhibit no change confirms that beam damage is negligible in this study. ISS

spectra were collected by operating the CMA in the nonretarding mode (28) and using pulse counting detection (29). ESCA spectra were collected using $MgK\alpha$ X-rays and a pass energy of 50 eV. AES spectra were collected using a 3-keV primary electron beam of $10 \mu\text{A}$ with a spot diameter of about 0.1 mm. Very mild sputtering treatments were carried out using a $1\text{-}\mu\text{A}$ primary beam of $^4\text{He}^+$ defocused over an area of 1 cm in diameter for about 40 min.

RESULTS AND DISCUSSION

After insertion into the vacuum system and pumpdown, the sample was cleaned by sputtering, annealing under vacuum at 400°C , and exposure to 10^{-6} Torr of O_2 at 400°C for 4 h. The AES, ESCA, and ISS spectra taken from this surface are shown in Figs. 1, 2, and 3, respectively. The AES spectrum (Fig. 1a) shows features due to Pt, Ti, O, and C. The shape and size of the C feature indicates that a very small amount of graphitic C remains after the sample was cleaned. Based on published cross sections (30), the O-to-Ti peak height ratio of 1.72 indicates that the Ti is present as TiO_2 , and the Pt-to-Ti ratio of 0.38 indicates that a substantial amount of Pt was deposited on this surface. The shapes and

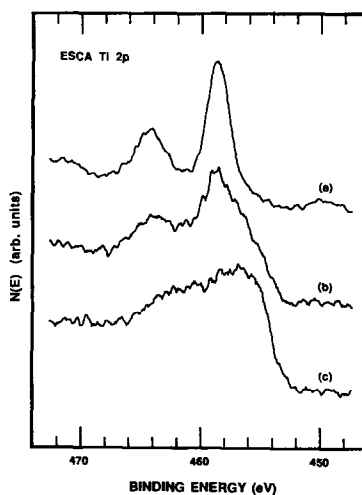


FIG. 2. ESCA spectra showing the Ti 2p peaks. (a), (b), and (c) correspond to those shown in Fig. 1.

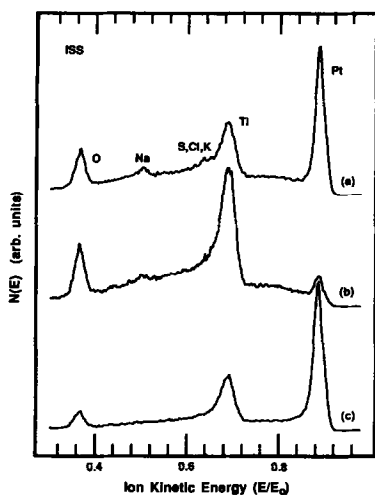


FIG. 3. ISS spectra corresponding to the AES and ESCA spectra shown in Figs. 1 and 2, respectively.

binding energies of the ESCA Ti $2p$ peaks shown in Fig. 2a also indicate that the titania in the surface region is present as TiO_2 (31). The predominant ISS features observed in Fig. 3a are due to O, Ti, and Pt. A very small contaminant feature due to Na is present at an E/E_0 of 0.5, and the small shoulder on the low energy side of the Ti peak is due to the presence of K, Cl, or S. The ISS O-to-Ti peak height ratio also suggests that TiO_2 is the predominant surface Ti species (32, 33). Apparently, the outermost surface layer of atoms contains more than 40 at.% Pt after consideration of the relative cross sections of O, Ti, and Pt (34).

An ESCA spectrum showing the Pt $4f$ peaks after the sample was cleaned is shown in Fig. 4. The binding energy of about 71.0 eV is essentially that of metallic Pt at 70.9 eV (31). In this study it was found that the lineshape of the Pt $4f$ features does not vary with treatment and that the binding energies vary by less than 0.3 eV. One possibility is that these binding energy changes are due to work function changes at the surface caused by changes in the oxidation state of the Ti.

The cleaned and oxygen-annealed sample was then annealed in 10^{-5} Torr of H_2 for

1 h at 500°C . An AES spectrum taken from this surface is shown in Fig. 1b. Comparison with Fig. 1a shows that the O-to-Ti peak height ratio has decreased from 1.72 to 1.65 and that the Pt-to-Ti peak height ratio has decreased from 0.38 to 0.30. Peak height ratios cannot be taken as quantitatively meaningful because peak shape changes are substantial in this system (34), but peak height ratios are qualitatively indicative of surface compositional changes. However, it is apparent from Fig. 1b that the amounts of O and Pt relative to the Ti have decreased during the reductive process. It is important to realize that AES probes at least several atomic layers and is not particularly sensitive to the outermost layer. This makes it difficult to understand what surface processes are responsible for the compositional changes detected by AES.

The ESCA Ti $2p$ spectrum taken from the reduced sample is shown in Fig. 2b. The Ti $2p_{3/2}$ binding energies used by Raupp and Dumesic (35) are consistent with the ESCA data presented in this and a previous study of $\text{TiO}_2(001)$ (34). They are TiO_2 , 458.7 eV; Ti_2O_3 , 456.6 eV; TiO , 454.5 eV; and Ti, 451.9 eV. The presence of a shoulder at 456.6 eV and the reduced valley between the Ti^{4+} $2p$ peaks indicate that a portion of the Ti^{4+} has been reduced to Ti^{3+} during the

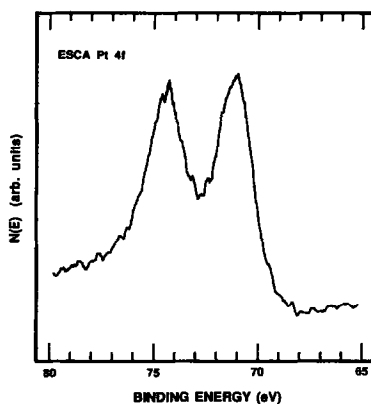


FIG. 4. ESCA spectrum showing the Pt $4f$ peaks taken from the cleaned sample.

reductive treatment. Work function differences between the oxides and varying stoichiometry with depth make quantification quite difficult.

A very dramatic change appears in the ISS spectrum shown in Fig. 3b which was taken from the sample after reduction. The O and Ti peaks are both larger than the Pt peak. This is due to coverage of the Pt by titania species. Only a relatively small amount of Pt remains uncovered after the reductive treatment. This conclusion is also consistent with the previous studies of Hoflund *et al.* (24) and Dwyer *et al.* (25). The O-to-Ti peak height ratio is about one-half that of TiO_2 shown in Fig. 3a and may correspond to a mixture of one or more reduced species. However, the approximate composition of the reduced titania overlayer is estimated to be TiO. Although the ESCA Ti $2p$ spectrum suggests that the reduced titania is Ti_2O_3 , a very thin layer of TiO may be present at the surface and would remain undetected by ESCA since ESCA probes much more deeply beneath the surface than ISS. There are several difficulties which must be considered with regard to assigning a composition to the encapsulating species. Calculated cross sections (33) yield compositions corresponding to TiO_2 for oxidized surfaces and TiO for reduced surfaces, but, nevertheless, they must be applied cautiously since the theoretical derivation of cross sections is extremely difficult. However, experimental support of the calculated cross sections is derived from previous studies of titania supported on polycrystalline Pt (32) and a $\text{TiO}_2(001)$ surface (34). Another potential problem is that the surface may be spatially nonuniform in that ISS is detecting ions scattered off both support regions and encapsulated regions. This would not be a problem if the compositions of the two regions are similar. Finally, the orientation of surface species is important in ISS. If a certain element bonds so that it is at the outermost layer, then ISS detects only that element and not other species which bond to it

but are beneath the outermost layer. It is difficult in this case to determine if orientational effects cause a problem with regard to interpretation of the ISS spectra. With consideration of these possible difficulties, the composition of the encapsulating species is assigned as TiO.

Next the sample was sputtered to determine if the encapsulating titania species could be removed so that Pt would again be the predominant species present in the outermost layer. The AES, ESCA, and ISS spectra are shown in Figs. 1c, 2c, and 3c, respectively. The O-to-Ti AES peak height ratio has decreased further from 1.65 to 1.36. The selective sputtering of O from titania surfaces and inherent reduction of Ti^{+4} has been observed and discussed previously (34). A change in the AES Ti peak shapes is also observed after the sputtering as shown by high-resolution AES spectra presented in the previous study (34). It was found that certain spectral features (or lineshape changes) are due to the presence of oxygen vacancies produced by sputtering. The corresponding ESCA spectrum shown in Fig. 3c indicates that features due to TiO_2 , Ti_2O_3 , and perhaps a small amount of TiO comprise the spectrum. Clearly, sputtering results in a greater extent of reduction than annealing in 10^{-5} Torr of H_2 for 1 h at 500°C .

Sputtering causes an increase in the AES Pt-to-Ti peak height ratio from 0.30 to 0.47 suggesting that more Pt now lies more closely to the surface. This is demonstrated by the ISS spectrum shown in Fig. 3c. Sputtering again restores the predominant Pt peak by removal of the encapsulating titania layer. Sputtering also removes the small amount of contaminating K, Na, Cl, and/or S observed in Figs. 3a and b. The ISS O-to-Ti ratio does not change significantly by sputtering, thereby supporting the assignment of the composition of the peak height encapsulating species as TiO.

Based on the fact that the chemisorption behavior of platinumized titania in the SMSI state can be restored by an oxidative treat-

ment followed by a low-temperature reductive treatment, it has been postulated that oxidation of the reduced titania overlayer causes the encapsulating titania species to move off the Pt and back onto the support. This also has been tested in this study. Figure 5a shows an ISS spectrum taken from a sample which was sputtered and then annealed in 10^{-5} Torr of H_2 for 1 h at $500^\circ C$, and the corresponding ESCA spectrum of the Ti $2p$ peaks is shown in Fig. 6a. Initially, the titania is reduced since the O-to-Ti peak height ratio is 0.4, and much of the Pt is encapsulated since the Ti-to-Pt peak height ratio is 1.47. This surface was then annealed in 10^{-6} Torr of O_2 for 2 h at $400^\circ C$. The resulting ISS spectrum is shown in Fig. 5b. The O-to-Ti peak height has increased to 0.73 which indicates that the reduced surface titania has been oxidized to TiO_2 . The ESCA Ti $2p$ spectrum shown in Fig. 6b also indicates that the reduced titania in the near-surface region has been oxidized to TiO_2 in agreement with the ISS results. After oxidation the ISS Pt peak is increased with respect to the Ti peak. The ISS Ti-to-Pt peak height ratio decreases from 1.47 to 0.92. Therefore, oxidation of the encapsu-

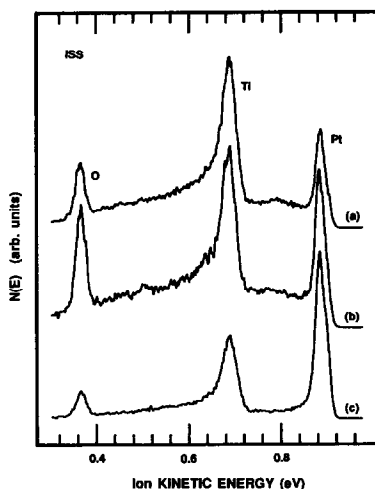


FIG. 5. ISS spectra taken after (a) annealing the surface in 10^{-5} Torr of H_2 for 1 h at $500^\circ C$, (b) annealing the surface in 10^{-6} Torr of O_2 for 2 h at $400^\circ C$, and (c) sputtering lightly with 1 keV He^+ .

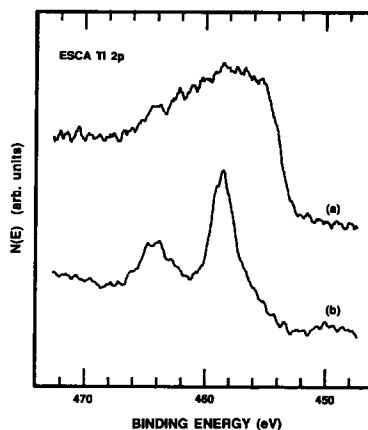


FIG. 6. ESCA Ti $2p$ spectra corresponding to the ISS spectra shown in (a) Fig. 5a and (b) Fig. 5b.

lating, reduced titania features does result in their movement off the Pt thereby exposing more Pt. This is consistent with the results of Dwyer *et al.* (25).

Finally, the surface was sputtered again, and the ISS spectrum shown in Fig. 5c was obtained. Again, the titania is reduced by the sputtering, and the encapsulating titania is removed exposing more Pt. These changes all appear to be completely reversible.

CONCLUSION

In this study a platinumized titania layer has been examined after various treatments including sputtering, annealing in H_2 , and annealing in O_2 using ISS, AES, and ESCA. Annealing in hydrogen causes reduction of the outermost layer of titania from TiO_2 to TiO . These species move over the Pt and cover it. ESCA shows that the titania in the near-surface region of an oxidized sample is reduced from TiO_2 to Ti_2O_3 predominately. Sputtering also reduces TiO_2 to Ti_2O_3 even more effectively than annealing in H_2 . After encapsulation of the Pt has been induced, the encapsulating, reduced titania species can easily be removed by sputtering with inert gas ions. This process restores the high Pt concentration in the outermost atomic layer. Exposure to O_2 then oxidizes the reduced titania back to TiO_2 . The en-

capsulated Pt can also be reverted back to the original state by annealing in O₂. As the encapsulating species are oxidized they migrate off the Pt and back onto the support.

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