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NOTES

XPS Studies of Strong Metal–Support Interactions (SMSI)—Pt/TiO_2

Recently Tauster, Fung (*1–3*), and Garten (*1, 2*) have reported that strong metal–support interactions (SMSI) occur between Group VIII noble metals and transition metal oxide supports when the catalysts are hydrogen-activated at sufficiently high temperatures. The SMSI effect alters the basic properties of these noble metals and renders them inactive for H_2 and CO adsorptions. Transmission electron microscopy studies by Baker *et al.* (*4*) of Pt on titanium oxide clearly showed an unusual structural relationship between the metal and oxide. The Pt particles appear to have a thin pill-box structure and to acquire the same crystal modification as the underlying substrate, since the lattice images of the titanium oxide substrate are not interrupted by the presence of the platinum particles. A strong chemical bonding between the metal and support has been postulated to account for the above phenomena. However, the exact electronic perturbation of the metal particles has not been identified.

The present paper deals with XPS studies of Pt on TiO_2 following reduction at various temperatures. It was anticipated that the chemical nature of this strong metal–support interaction could be elucidated by the observed chemical shifts in the binding energies of the Pt4f electrons. Silica-supported platinum was also investigated for comparison.

The titanium dioxide- and silica-supported Pt samples were prepared first by depositing the respective oxides of about 75 nm onto a 5×10^{-3} cm thick stainless-steel foil. Platinum was evaporated at 10^{-6} Torr (1 Torr = 133.3 N m^{-2}) onto these supports from a spectrographically pure platinum wire mounted on a tungsten filament. This produced a Pt film approximately one atom thick (*4*). Platinum supported on TiO_2 powder at 2 wt% was prepared by impregnating TiO_2 (P-25), obtained from Degussa Co., as previously reported (*2*). The TiO_2 was pretreated 3 hr in H_2 at 600°C before impregnation. This treatment stabilized the BET area of the TiO_2 at 25 m^2/g. The catalyst was reduced with 20% hydrogen/helium at 150°C for 4 hr.

The 2 wt% Pt/TiO_2 sample was examined as a powder pressed onto a 100 × 100 mesh stainless-steel screen. All the samples were cut into a 2-cm strip and mounted onto a sample holder. The latter was contained in a reaction vessel which could be isolated from the spectrometer. Hydrogen treatment of the samples were carried out at 150 to 600°C with 20% hydrogen/helium mixture at 30 liters/hr for 1 hr. After each reduction, the sample was cooled under the gas mixture and evacuated before inserting into the spectrometer. XPS measurements were performed with a Model 200A AEI Scientific Instruments Spectrometer according to (5).

The binding energies were determined with reference to the ClS line at 284.5 eV. Additionally the main oxide line (e.g., Ti^{4+} 2P 3/2 at 458.7 eV) served as an internal reference for the oxide-supported Pt catalysts. This provided an excellent correction for charging. Sample charging is a result of photoemission of electrons from insulators and semiconductors. Maximum charging of about 1.2 eV was observed on the silica-supported sample. The low value was mainly due to the thin film nature of the silica support.

In addition to the XPS measurements, dihydrogen sorption and X-ray diffraction studies were carried out with the 2% Pt/TiO_2 powder sample. Dihydrogen sorption studies were performed with a conventional glass vacuum system as previously reported (*2*). The H/Pt ratios were calculated by assuming that H_2 uptakes at ambient

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temperature and zero pressure of H_2 corresponded to saturation coverage of platinum. A Phillips Electronics X-ray diffractometer (XRG-3000) with nickel-filtered Cu *K* radiation was used for X-ray diffraction studies of the samples.

Figure 1A shows the effect of reduction temperature on the Pt4f binding energies of the Pt/TiO_2 film. The Pt4$f_{7/2}$ binding energy of the sample which had received no hydrogen treatment was 1.6 eV higher than the one which had been hydrogen reduced at 350 and 600°C. The Pt species formed after hydrogen activation of the Pt/TiO_2 film at and above 350°C had a Pt4$f_{7/2}$ binding energy close to that of the bulk metal. The effect of reduction temperature on the Ti2P binding energies is shown in Fig. 2. A lower oxidation state titanium species was observed after the sample was reduced at 600°C. Its intensity was greatly diminished when it was exposed to air, at ambient temperature, whereas little change in its intensity with time was observed when the sample was in the spectrometer. This suggested that the back ground pressure of oxygen in the spectrometer was insufficient to oxidize any reduced species, including Pt, in the time period of obtaining the XPS spectra.

A similar effect was observed for the 2% Pt/TiO_2 powder sample as is illustrated in Fig. 1B. The 150°C reduced sample showed a major fraction of platinum was in the high binding energy state. Reduction of this sample at 200°C decreased the fraction of high binding energy Pt and it disappeared after 550°C reduction.

Hydrogen sorption studies of the 2% Pt/TiO_2 powder sample are summarized in Table 1. After 150°C hydrogen reduction, H_2 uptake on this sample was appreciable and resulted in a H/Pt ratio of 0.63. Increasing the reduction temperature of this sample to 500°C resulted in a marked reduction in the H_2 uptake with H/Pt ratio decreasing to zero. The loss of hydrogen sorption property is not due to encapsulation of the metal particles as has been discussed in an earlier publication (*2*). Furthermore the dihydrogen sorption property of the 500°C reduced sample can be reinstated with a 500°C air calcination followed with a 110°C H_2 reduction. The H/Pt ratio increased from 0 to 0.08 after the above treatment. Increasing the reduction temperature of this sample to 500°C again resulted in zero H/Pt ratio.

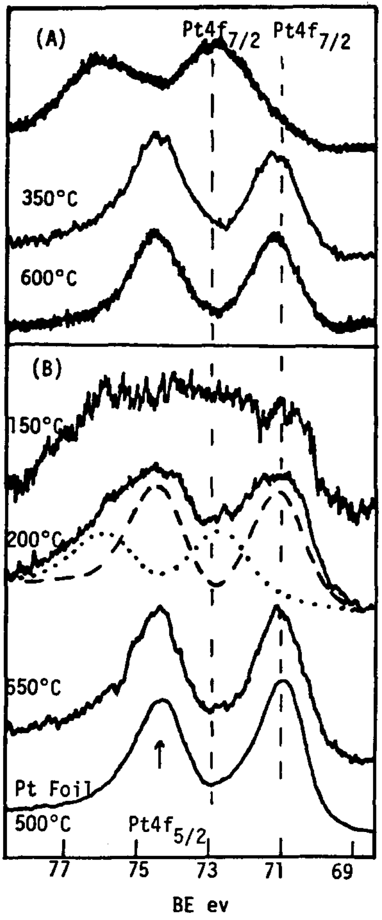

FIG. 1. Effect of H_2 reduction on the binding energies of Pt4f electrons: (A) Pt/TiO_2 film (B) 2% Pt/TiO_2 powder.

The X-ray diffraction patterns of the 2% Pt/TiO_2 powder sample which has undergone the above dihydrogen sorption studies are shown in Fig. 3. The crystallite sizes of platinum calculated from the broadening of the Pt (111) line are summarized in Table 1. The as prepared catalyst after 150°C H_2 reduction showed no Pt line. An increase in the reduction temperature to 500°C pro-

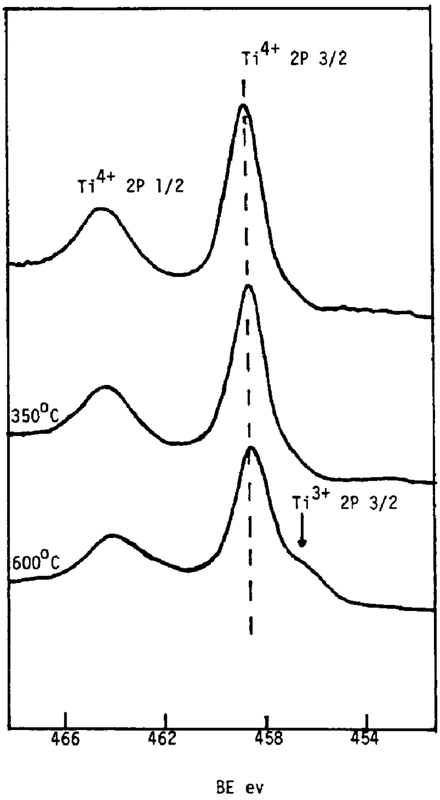

FIG. 2. Effect of H_2 reduction on the binding energies of Ti2P electrons—Pt/TiO_2 film.

duced no significant change in the X-ray diffraction pattern. However, after the 500°C air calcination significant Pt agglomeration was observed. Reduction of the calcined sample at 110 and 500°C produced essen-

TABLE 1

Effect of Treatment Conditions on H_2 Sorption and Pt Crystallite Size of 2% Pt/TiO_2 Powder Sample

Treatment conditions	H/Pt	Crystallite size by X-ray
150°C H_2	0.63	N.D.[a]
250°C H_2	0.17	—
500°C H_2	0.0	N.D.[a]
500°C air	—	100 Å
500°C air, then 110°C H_2	0.08	100 Å
500°C air, then 500° H_2	0.0	100 Å

[a] Pt peaks were not detected.

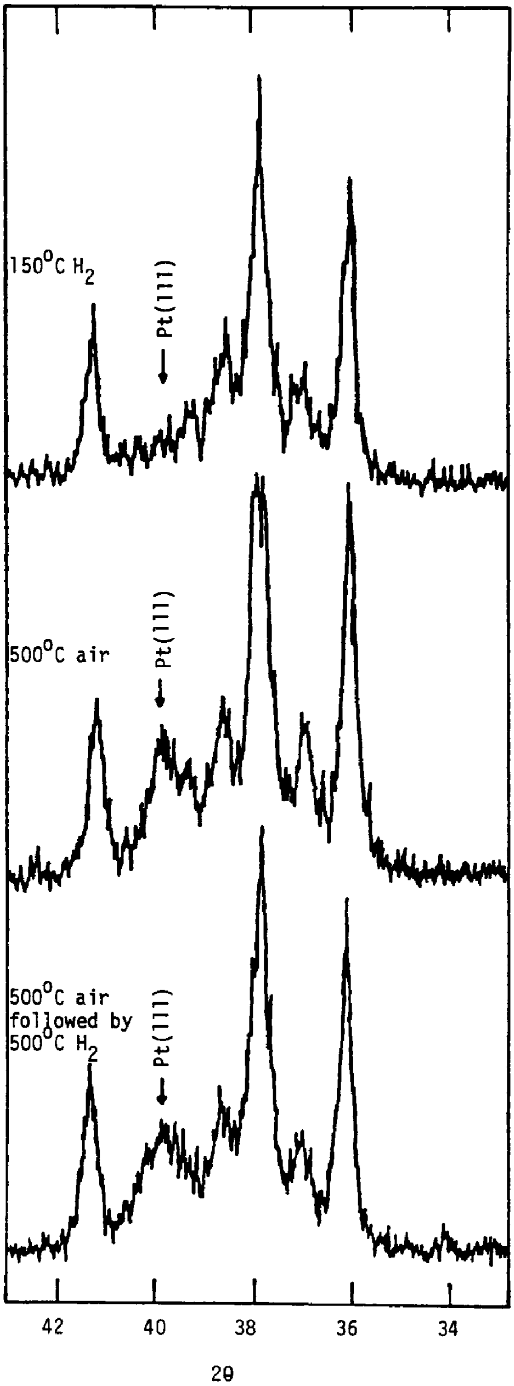

FIG. 3. X-Ray diffraction spectra of the 2% Pt/TiO_2 powder sample at various treatment conditions.

tially no change in the crystallite size of platinum.

XPS studies on the agglomerated Pt catalyst indicated no large effect of reduction temperature on the Pt4f binding energies. The binding energy of Pt4$f_{7/2}$ was 71.3 and 71.2 eV after the agglomerated Pt catalyst was reduced at 110 and 500°C, respectively.

Completely different behavior was observed for the silica-supported sample. No large shift in the Pt4f binding energies was observed between the reduced and nonreduced samples, although the Pt4$f_{7/2}$ binding energy was about 0.6 eV higher than that of the bulk metal. Table 2 lists the Pt4$f_{7/2}$ binding energies of all the samples investigated.

DISCUSSION

It has been generally observed that Group VIII noble metals supported on SiO_2 and Al_2O_3 (*6–8*) exhibit higher binding energies of the core levels than the corresponding bulk metals. These shifts of core levels to higher binding energies are assumed to indicate decreased electron density at an atomic site. However, one must bear in mind that extra-atomic relaxation (or polarization) (*9, 10*) plays an important role in determining the observed binding energies of the core levels of a particular atom. A core hole is created during photoemission of a core electron. Extra-atomic relaxation occurs through a flow of electronic charge from the surrounding atoms toward the host atom during photoemission. It has the effect of lowering the binding energy of the emitted photoelectron. From his own work and that of others, Kowalczyk (*11*) showed that the extra-atomic relaxation associated with photoemission of a core electron in a metal resulted in a lowering of the core level binding energy within a range of 2 to 15 eV as compared to that of the free atom.

TABLE 2

Binding Energies of the Pt4$f_{7/2}$ Electrons

System	Treatment conditions	BE eV[a]
Pt Foil	500°C H_2	71.0
Pt/SiO_2	Vacuum deposit	71.5
	300°C H_2	71.6
Pt/TiO_2	Vacuum deposit	72.7
	350°C H_2	71.1
2% Pt/TiO_2	200°C H_2	72.5
		71.1
	550°C H_2	71.1

[a] Reference to ClS 284.5 eV. Internal standard for charging correction Ti 2P 3/2 at 458.7 eV.

A simple equivalent cores screening model has been developed by Shirley (*12*) to estimate the magnitude of extra-atomic relaxation in small molecules. Kowalczyk (*11*) successfully applied this screening model to metals by utilizing Friedel's (*13*) proposed exciton screening. According to Friedel, the core hole is screened by a newly formed occupied semilocalized state (exciton) via the dropping of a conduction band state below E_F at the hole site. There must also be a newly unoccupied orbital for charge balance. For a bulk metal, the unoccupied orbital is relatively diffused through the lattice and thus interacts with the hole much less strongly than does the occupied semilocalized state. In the case of highly dispersed metal particles, their extremely small crystallite sizes result in a less diffuse unoccupied orbital and its interaction with the core hole is significant. Additionally, the occupied semilocalized state in a small particle is expected to be sufficiently different from the one in the bulk metal. Both effects contribute to decrease the extra-atomic relaxation of a small metal particle and as a result its core level binding energies are higher than the bulk metal. Decreases in the extra-atomic relaxation energy was employed by Takasu *et al.* (*14*) to account for the increases in Pd core level binding energies with decreasing particle size in their UPS and XPS studies of varying Pd coverage on SiO_2 films. Kim and Winogard (*15*) showed that the binding energy shift in small supported metal particles were due to changes in extra-atomic relaxation.

In accordance with the above observation and argument, the observed positive shift in the Pt4f energies of the silica-supported Pt sample may be attributed to a decrease in the extra-atomic relaxation associated with small Pt particles. This is in agreement with the observed chemical properties of the SiO_2-supported Pt particles. There is no significant difference in the adsorption property (e.g., H_2 and CO adsorption) and the catalytic property between bulk Pt and the SiO_2-supported Pt particles. Therefore, the observed 0.6 eV increase in the $Pt4f_{7/2}$ binding energy of the silica-supported Pt particles is not due to charge transfer. A similar argument is applied to the observed increase in the $Pt4f_{7/2}$ binding energy of the titanium oxide-supported Pt particles at low reduction temperature. The origin of the observed difference in the magnitude of the positive shift in the $Pt4f_{7/2}$ level between the SiO_2 and TiO_2-supported samples is not certain. It is possible that the Pt particles supported on TiO_2 are much smaller than those supported on SiO_2. Additionally the polarizability of the support may have a substantial influence on the extra-atomic relaxation of the highly dispersed Pt particles (*15*). Nevertheless, the high binding energy Pt species in TiO_2 is not due to oxide formation since the SiO_2 and TiO_2 film samples were prepared under identical conditions. The reduction of the SiO_2 sample at high temperature essentially has little effect on the $Pt4f_{7/2}$ binding energy. In addition, the 150°C reduced Pt/TiO_2 *powder* sample exhibited hydrogen adsorption, with a H/Pt ratio of 0.63. Therefore, if the reduction of platinum was not complete at this temperature the maximum amount of oxidized Pt would be 37%. However, the high binding energy Pt species was estimated to be 80% from the XPS spectrum of the 150°C reduced sample. Therefore, the assignment of the high binding energy Pt species as the one which adsorbs hydrogen is preferred. Furthermore, higher reduction temperature at 250°C decreased the H/Pt ratio from 0.63 to 0.17. A decrease in the peak area of the high binding energy Pt species was observed in the XPS spectrum of the 200°C reduced sample. This species decreased from 80 to 30%.

The experimental evidence here shows that a 1.6 eV negative shift of the $Pt4f_{7/2}$ level occurs concurrently with the drastic alternation of the hydrogen adsorption property of the TiO_2-supported Pt particles. However, the large negative shift is not solely due to electron transfer to platinum. According to the discussion on extra-atomic relaxation, the growth in the Pt crystallite size between 150 and 600°C may account for part of the negative shift since extra-atomic relaxation increases with increasing particle size. There was indeed a subtle change in the cluster size of Pt particles as was indicated by the decrease in the Pt4f/Ti2P intensity ratio from 0.072 to 0.055 between 150 and 550°C. The intensity ratio Pt4f/Ti2P is calculated from the area of the Pt4f peaks and the area of Ti2P peaks. A detailed discussion in the relationship between the size of supported metal particles and the XPS intensity ratio of the supported metal/support has been reported by Fung (*5*) and others (*16, 17*). Bahl *et al.* (*18*), in their XPS study of Pt/$SrTiO_3$ films, devised a method to separate the relaxation shift from the electron transfer by varying the amount of platinum on the $SrTiO_3$ film. Their results indicated about 0.6 electron per atom transferred to platinum.

In order to obtain a better definition of the contribution of electron transfer to the observed 1.6 eV negative shift, the strong metal–support interaction between Pt and TiO_2 of the powder sample was decoupled by a 500°C air calcination, as has been previously reported for Pd/TiO_2 (*2*). Hydrogen sorption after lower temperature reduction indicated that the supported Pt particles regained their ability to chemisorb hydrogen, but the H/Pt ratio was 0.08. Further investigation of the catalyst by X-ray diffraction revealed that the Pt particles were agglomerated to about 100 Å crystallites. High-temperature reduction again yielded zero H/Pt ratio but with no significant change in the Pt crystallites size as indicated by X-ray diffraction. XPS measurements showed that there was only a 0.1 eV negative shift going from low-temperature to high-temperature reduction. It is not surprising to observe this very small shift since the number of platinum atoms in the 100 Å particles is much larger than the number of titanium sites which make contact with the Pt particle and donate their electrons. However, it is of interest to note that suppression of hydrogen sorption still exists in these large particles and indeed we have observed that the hydrogen absorption property of large Pd particles was suppressed.

Recent theoretical calculations in this laboratory by the multiple scattering x-alpha method on a $(PtTiO_5)^{6-}$ cluster indicate that when Ti^{4+} is replaced by Ti^{3+}, the Ti3d electron is largely transferred to the Pt atom (*19*). The observed initial large negative shift of the $Pt4f_{7/2}$ level, though it may include relaxation shift, is in agreement with the above calculation.

In conclusion, the present study suggests that electrons are transfered from the reduced Ti centers to the Pt particles and probably this results in a strong metal–support interaction (SMSI). Air calcination of the SMSI system can reverse the process but lead to highly agglomerated Pt particles and this results in a decrease in electron transfer per platinum atom as is indicated by the very small negative shift.

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REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., "Strong Metal-Support Interactions." Presentation at ACS National Meet, Chicago, Ill., August 28–September 2, 1977. Excerpt appeared in *C & E News*, Sept. 19, 1977, page 22.
2. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
3. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).
4. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **56,** 390 (1979).
5. Fung, S. C., *J. Catal.* **58,** 454 (1979).
6. Escard, J., Pontvianne, B., and Contour, J. P., *J. Electron Spectrosc. Relat. Phenom.* **6,** 17 (1975).
7. Ross, P. N., Kinoshita, K., and Stonehart, P., *J. Catal.* **32,** 163 (1974).
8. Shipro, E. S., Avaew, V. I., Antoshin, G. V., Ryashentseva, M. A., and Minachev, Kh. M., *J. Catal.* **55,** 402 (1978).
9. Martin, R. L., and Shirley, D. A., "Electron Spectroscopy: Theory, Techniques, and Applications" (A. D. Baker, and C. R. Brundle, Eds.). Academic Press, New York. (1979)
10. Hedin, L., and Johansson, J., *J. Phys. B* **2,** 1336 (1969).
11. Kowalczyk, S. P., "Photoelectron Spectroscopy and Auger Electron Spectroscopy of Solids and Surfaces." Ph.D. Thesis, Univ. of California, Berkeley, 1976.
12. Davis, D. W., and Shirley, D. A., *Chem. Phys. Lett.* **15,** 185 (1972); Shirley, D. A., *Chem. Phys. Lett.* **16,** 220 (1972).
13. Friedel, *J. Adv. Phys.* **3,** 446 (1954).
14. Takasu, Y., Unwin, R., Tesche, B., Bradshaw, A. M., and Grunze, M., *Surface Sci.* **77,** 219 (1978).
15. Kim, K. S., and Winogard, N., *Chem. Phys. Lett.* **30,** 91 (1975).
16. Brinen, J. S., Schmitt, J. L., Doughman, W. R., Achorn, P. J., Siegel, L. A., and Delgass, W. N., *J. Catal.* **40,** 295 (1975).
17. Angevine, J. P., Delgass, W. N., and Vartuli, J. C., *Proc. Sixth Int. Congr. Catal.* **2,** 611 (1976).
18. Bahl, M. K., Tsai, S. C., and Chung, Y. W., *Phys. Rev. B* **21,** 1344 (1980).
19. Horsley, J., *J. Amer. Chem. Soc.* **101,** 2870 (1979).

SHUN C. FUNG

Corporate Pioneering Research
Exxon Research and Engineering Company
P. O. Box 45
Linden, New Jersey 07036

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