

## Dopant-Induced Metal-Support Interactions

### 1. Influence on Chemisorptive Behavior

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Titania supports doped with cations of valence lower than, equal to, and higher than the parent cation were used as carriers for Pt crystallites, and the concept of dopant-induced metal-support interactions (DIMSI) was investigated. Platinized titania doped with cations of lower or equal valence ( $K^+$ ,  $Mg^{2+}$ ,  $Ge^{4+}$ ) exhibited normal  $H_2$  and  $O_2$  chemisorption behavior. Platinized  $TiO_2$  doped with cations of higher valence ( $Ta^{5+}$ ,  $Sb^{5+}$ ,  $W^{6+}$ ) exhibited drastically reduced  $H_2$  and  $O_2$  chemisorption capacity, especially at high Pt dispersions. Transmission electron microscopy analysis showed that these results cannot be attributed to reduced Pt dispersion of the doped catalysts, while electron spectroscopy for chemical analysis showed no surface enrichment of the catalyst supports with the dopant. Results are then interpreted in terms of electronic interactions at the metal-support interface, involving electron transfer from the doped support to the metal particles. Significant changes in the electronic structure of the doped carriers were detected by electrical conductivity measurements. © 1987 Academic Press, Inc.

### INTRODUCTION

Many investigations have been inspired by the possibility that an interaction between metal crystallites and support materials can alter chemisorptive and catalytic properties of the former. Strong evidence for this concept has been provided by Sinfelt and his co-workers (1) and later by other investigators who showed that kinetic parameters of certain catalytic systems were influenced by the particular support employed. Early work by Schwab (2, and references therein) and Solymosi (3, and references therein) attempted to explore and manipulate metal-support interactions, which were induced by doping of supports with altermultivalent cations. It was observed that the activation energy of certain reactions, such as formic acid decomposition, were affected by the doping process. The significance of these early experiments is obscured by the lack of sophisticated catalyst characterization techniques which are now routinely available.

In recent years, the concept of strong

metal-support interactions (SMSI) was introduced by Tauster *et al.* (4) who observed that Group VIII metals supported on titania or other reducible oxides lose their ability to chemisorb  $H_2$  and CO when they are reduced at temperatures higher than 773°K. Significant changes in kinetic parameters in hydrogenation, dehydrogenation, and hydrogenolysis reactions have also been observed over SMSI catalysts (5-7). A number of models have been proposed to explain the origin and mechanism of this phenomenon which include formation of intermetallic bonds with localized charge transfer, electron transfer from the reduced titania support to the metal crystallites, and diffusion of a titanium-oxygen species to the surface of the metal crystallites rendering them partially inaccessible to chemisorption and catalytic action. This last model has recently gained popularity since significant evidence of such species covering the surface of the metal has been obtained from Auger surface analysis and other techniques (8, 9, 23).

The purpose of this study is to investigate

the concept of dopant-induced metal-support interactions (DIMSI) and to determine if there is any connection between the phenomena observed by Schwab (2) and Solymsi (3) and the recent observations of SMSI. For this purpose, titania carriers were doped with cations of valence lower or higher than the parent cations and were subsequently platinized. The effects of dopants on chemisorptive and catalytic properties of platinum are investigated. In the present communication, results of chemisorption studies of hydrogen and oxygen are reported, as well as some results of electrical conductivity measurements, transmission electron microscopy (TEM), and electron spectroscopy for chemical analysis (ESCA) studies. In future papers, the effects of dopants on the catalytic properties of platinum under CO hydrogenation and CO oxidation will be reported along with further characterization procedures.

#### EXPERIMENTAL

The parent titania carrier used in this work was obtained from Degussa Company (P-25) while niobia was obtained from Alfa Products. X-ray diffraction analysis of  $\text{TiO}_2$  showed it to be 20% rutile and 80% anatase. The dopant materials,  $\text{KNO}_3$ ,  $\text{MgO}$ ,  $\text{GeO}_2$ ,  $\text{WO}_3$ ,  $\text{Sb}_2\text{O}_5$ , and  $\text{Ta}_2\text{O}_5$ , all puratronic, were obtained from Alfa Products. To prepare the doped supports, weighted amounts of  $\text{TiO}_2$  and the dopant were slurried with distilled water and thoroughly mixed. The water was evaporated and the residue was dried overnight at  $110^\circ\text{C}$ , then fired in air at  $900^\circ\text{C}$  for 5 hr. The  $\text{TiO}_2$ - $\text{KNO}_3$  residue was first heated at  $400^\circ\text{C}$  for 2 hr to decompose the nitrate and the temperature was subsequently raised to  $900^\circ\text{C}$  and maintained for 5 hr. In all cases the dopant level was 1% by weight.

Catalysts were prepared by incipient wetness impregnation of the support with appropriate amounts of aqueous solutions of chloroplatinic acid. Impregnated supports were dried overnight at  $110^\circ\text{C}$  and reduced in flowing hydrogen, either at  $200^\circ\text{C}$

(LTR) or at  $500^\circ\text{C}$  (HTR) for 2 hr. Platinum content ranged from 0.06 to 5%.

Adsorption isotherms were determined using a constant-volume, high-vacuum apparatus (Micromeritics, Accusorb 2100 E), consisting of cold traps, oil diffusion pump, and forepump. An ultimate dynamic vacuum of  $10^{-6}$  mm Hg is obtained in this apparatus. Pressure detection is by means of a specially designed, autoranging, digital readout capacitance manometer with dual transducers. Total surface area of the catalysts was determined by physical adsorption of argon at liquid nitrogen temperature, employing the BET method. Prior to all adsorption measurements, samples in the adsorption cells were evacuated overnight at  $200^\circ\text{C}$  and cooled to room temperature or liquid  $\text{N}_2$  temperature under vacuum. Adsorption isotherms of  $\text{H}_2$  and  $\text{O}_2$  were determined at room temperature between 10 and 300 mm Hg. Uptakes of  $\text{H}_2$  and  $\text{O}_2$  of the supported Pt crystallites were obtained by extrapolating the adsorption isotherms to zero pressure and subtracting small uptakes by blank supports. The gases used were all of ultrahigh purity and they were further purified by passing them through a DEOXO purifier and a molecular sieve trap.

Metallic dispersions, expressed in terms of H/Pt, or O/Pt ratios, and platinum crystallite sizes were calculated assuming that each surface metal atom chemisorbs one hydrogen or one oxygen atom and that the Pt particles are spherical in shape.

The structure of doped titania supports was characterized by X-ray diffraction. These analyses were performed on a modified General Electric XRD-5 diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation.

To perform transmission electron microscopy analysis, the catalysts were ground to a fine powder and dispersed in methanol using an ultrasonic cleaner. A drop of the suspension was placed onto a carbon-coated electron microscope grid. The samples were examined in a Phillips EM400 analytical TEM/STEM system equipped with energy dispersive analysis of

X-rays (EDAX). The maximum attainable point-to-point resolution was 2.5 Å. Images were recorded using 100 keV accelerating voltage at instrument magnification of 410,000. Pt crystallite sizes were measured from the photographic print in the form of surface mean diameter ( $d$ ) obtained using the following equation in which  $n_i$  is the number of particles having a characteristic diameter  $d_i$ :

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

High-resolution ESCA was performed on a DuPont Model 650-B instrument, at Micron Inc. Measurements were taken with  $MgK\alpha$  radiation. The sample was examined as a powder, dispersed on the surface of a double-sided, stainless-steel sample holder. Binding energies were determined with reference to the carbon 1s line at 285.0 eV. Integrated line intensities were corrected for differences in photoionization cross section to approximate relative atom abundance. They were normalized to the C 1s line at 285.0 eV and the Ti  $2p_{3/2}$  line at 459.0 eV.

Electrical conductivity measurements were performed in a flow cell, using the conventional two-probe direct-current technique. Powdered catalysts were compressed into pellets ( $1.3 \times 0.5$  cm) by applying a pressure of 12,000 psi. Resistances were measured using a EICO Model 950 bridge, with a useful range of 0.1  $\Omega$  to 500 M $\Omega$ , calibrated with precision resistors. Resistance measurements lower than  $10^5 \Omega$  were verified with a Keithley 177 multimeter. Further details of electrical conductivity measurements will be reported in a subsequent communication.

## RESULTS AND DISCUSSION

### (A) Adsorptive Properties of Pt/TiO<sub>2</sub> and Pt/Nb<sub>2</sub>O<sub>5</sub> Exhibiting SMSI

In order to be able to compare the effects of DIMSI with those of SMSI (induced by high-temperature reduction), some preliminary studies were conducted on catalysts

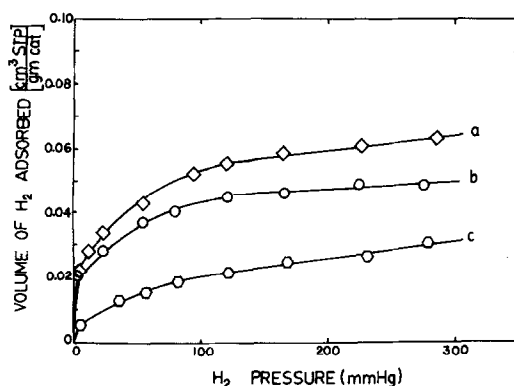


FIG. 1. Hydrogen adsorption isotherms of 0.06% Pt/TiO<sub>2</sub> catalysts. (a) LTR. (b) HTR, exposed to ambient conditions for 5 months. (c) HTR, exposed to ambient conditions for 30 min.

exhibiting SMSI behavior. The effects of metal loading, or crystallite size, on the SMSI character of the catalysts were investigated by preparing a series of platinumized titania with platinum loadings ranging from 0.06 to 5.0% by weight. Niobia was also platinumized and the SMSI character exhibited by this support was compared to that of titania. Typical hydrogen adsorption isotherms of platinumized TiO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub> containing 0.06% Pt are shown in Figs. 1 and 2, respectively. Suppression of hydrogen adsorption is observed when the catalysts are reduced at 500°C. Nevertheless, complete suppression, as reported by Tauster *et al.* (4), is not observed in all cases. Other in-

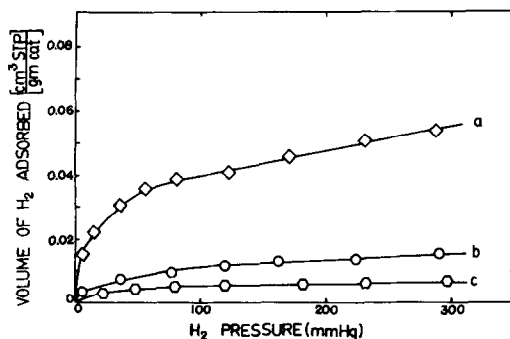


FIG. 2. Hydrogen adsorption isotherms of 0.06% Pt/Nb<sub>2</sub>O<sub>5</sub>. (a-c) Same as Fig. 1.

TABLE 1  
SMSI Character of 0.06% Pt/TiO<sub>2</sub> and 0.06% Pt/Nb<sub>2</sub>O<sub>5</sub> Catalysts

	0.06% Pt/TiO <sub>2</sub>	0.06% Pt/Nb <sub>2</sub> O <sub>5</sub>
Crystallite size, Å	8	12
(H/M) <sub>LTR</sub>	1.45	0.94
(H/M) <sub>HTR</sub> /(H/M) <sub>LTR</sub>	0	0
(H/M) <sub>HTR</sub> /(H/M) <sub>LTR</sub> <sup>a</sup>	0.26	0.06
(H/M) <sub>HTR</sub> /(H/M) <sub>LTR</sub> <sup>b</sup>	0.94	0.27

<sup>a</sup> Exposed to air for 30 min after HTR.

<sup>b</sup> Exposed to air for 5 months after HTR.

investigators (10, 11) have also reported incomplete suppression. This may be due to the fact that the samples were briefly exposed to atmospheric oxygen after HTR which tends to destroy the SMSI character of the catalysts.

It is well established in the literature that exposure of SMSI catalysts to oxygen at elevated temperatures tends to destroy their SMSI character. The isotherms shown on Figs. 1 and 2 (curves b) indicate that similar destruction of SMSI character occurs when the catalysts are exposed to air at room temperature over a long period of time. These isotherms were determined after the catalysts were exposed to ambient conditions for a period of 5 months. Prior to adsorption measurements, catalysts were reduced *in situ*, evacuated overnight at 200°C, and allowed to cool to room temperature under dynamic vacuum for chemisorption measurements. Hence, adsorption of oxygen and/or contaminants such as organics and sulfur-containing compounds can be eliminated as responsible for the observed behavior.

To quantify the SMSI character of the various catalysts exposed to different conditions, a normalized ratio of the amount of hydrogen adsorbed per atom of metal on the catalyst, (H/M), to the amount of hydrogen adsorbed per atom of metal when the catalyst is reduced at low temperature, (H/M)<sub>LTR</sub>, is used. This ratio is a conve-

nient measure of SMSI as it tends toward zero with increasing SMSI character of the catalyst. Table 1 shows such ratios for the 0.06% Pt/TiO<sub>2</sub> and 0.06% Pt/Nb<sub>2</sub>O<sub>5</sub> samples exposed to different conditions. It is obvious that platinumized titania loses its SMSI state much easier than platinumized niobia, although the average crystallite size of Pt on Nb<sub>2</sub>O<sub>5</sub> is somewhat larger than that on TiO<sub>2</sub>. Similar conclusions have been reported by Ko *et al.* (12) for Ni/TiO<sub>2</sub> and Ni/Nb<sub>2</sub>O<sub>5</sub>. Since Nb<sub>2</sub>O<sub>5</sub> is more easily reduced than TiO<sub>2</sub>, these results seem to indicate that the reversibility of the SMSI state is a function of the reducibility of the carrier.

The effects of metal loading or metal crystallite size on the SMSI character of the support were investigated by preparing a series of Pt/TiO<sub>2</sub> catalysts with Pt loadings ranging from 0.06 to 5.0%, reducing these at 200°C (LTR) or 500°C (HTR) and determining room temperature adsorption isotherms of H<sub>2</sub> and O<sub>2</sub>. The results are shown in Table 2 in terms of the H/M and O/M ratios obtained. Pt crystallite sizes were calculated from adsorption data in the standard manner, as stated earlier.

It is generally believed that small metal crystallites may behave differently from bulk metal. Neglecting any possible metal-support interactions, the average coordination number of surface atoms is lower in small metal particles, and in the limit, practically every metal atom is a surface atom. Hence, given the peculiar chemisorption properties of small metal crystallites, it is not surprising to observe H/Pt ratios greater than unity for very small platinum particles as reported in Table 2. Wilson and Hall (14), using the chemistry suggested by Mears and Hansford (15), showed that H/Pt ratios greater than unity can be obtained for Pt crystallites less than 17 Å in diameter. These values of H/Pt or O/Pt greater than 1 correspond to 100% dispersion. Values of H/Pt > 1 have been reported in the literature for Pt/SiO<sub>2</sub> (13) and Pt/Al<sub>2</sub>O<sub>3</sub> (16, 24).

It is interesting to observe that the O/M

TABLE 2  
Chemisorption Behavior of Pt/TiO<sub>2</sub>, under LTR  
and HTR

Metal content (%)	Reducing temperature (°C)	H/M	O/M	Crystallite size, Å	
				H <sub>2</sub>	O <sub>2</sub>
0.06	200	1.45	1.26	8	12
0.06	500	0	1.16	—	10
0.10	200	0.90	0.87	13	14
0.10	500	0	0.85	—	14
0.50	200	0.73	0.70	16	17
0.50	500	0	0.68	—	17
1.0	200	0.30	0.29	39	39
1.0	500	0.03	—	—	—
5.0	200	0.22	0.24	54	49
5.0	500	0.11	—	—	—

ratios, of both LTR and HTR catalysts, are approximately the same as the H/M ratios of the LTR catalysts, consistent with observations in the literature (17). In view of the fact that oxygen adsorption isotherms were obtained immediately following hydrogen chemisorption and evacuation at 200°C, this observation indicates either that the SMSI phenomenon does not affect O<sub>2</sub> adsorption or that the phenomenon is destroyed, almost instantly, after exposure to oxygen at room temperature. Furthermore, this observation suggests dissociative adsorption of both H<sub>2</sub> and O<sub>2</sub> on Pt and that oxygen can be used to determine the degree of dispersion and crystallite size of SMSI catalysts. The effect of metal loading or crystallite size on the SMSI character of the catalysts is shown in Fig. 3, where the ratio  $(H/M)_{HTR}/(H/M)_{LTR}$  is plotted versus metal loading and crystallite size. It is apparent from this plot that the SMSI character of the catalysts decreases with increasing metal loading or Pt crystallite size, which is consistent with observations reported in the literature (18).

### (B) Adsorptive Behavior of Pt Supported on Doped Carriers

The concept of DIMSI arises from the possibility that an electronic interaction between small metal particles and support

materials may alter the chemisorptive and catalytic properties of the former (2, 3). Thus, the hypothesis underlying this study is that metal-support interactions can be induced by electronic interactions between metal crystallites and the support due to different Fermi energy levels at the interface. If this hypothesis is correct, then such interactions can be induced if the Fermi energy level of the support is changed by any means, such as by altermultivalent ion doping or ion implantation. This hypothesis is rationalized by the metal-semiconductor boundary layer theory. To test this hypothesis, the methodology of this investigation involves modification of the electronic state of the support by introduction of foreign ions into its lattice structure. TiO<sub>2</sub> was doped with cations of higher valence (Ta<sup>5+</sup>, Sb<sup>5+</sup>, W<sup>6+</sup>) in order to raise its Fermi energy level, increase its *n*-type semiconductivity, and increase the availability of free electrons, and with cations of lower valence (Mg<sup>2+</sup>, K<sup>+</sup>) in order to lower its Fermi energy level, decrease the *n*-type semiconductivity, and increase the concentration of defect electrons (or positive holes). Finally, TiO<sub>2</sub> was also doped with cation of the same valence (Ge<sup>4+</sup>), which does not alter

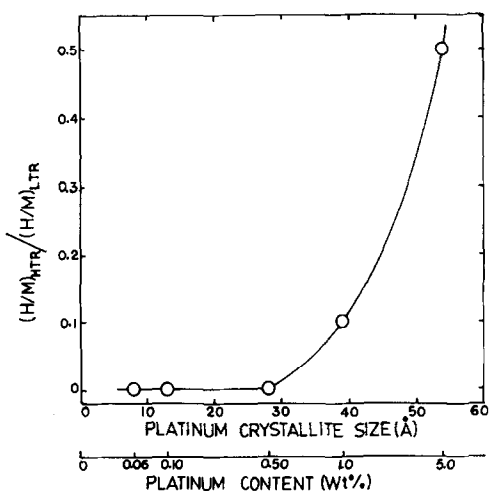


Fig. 3. Effects of metal crystallite size and metal content on SMSI characters of Pt/TiO<sub>2</sub>.

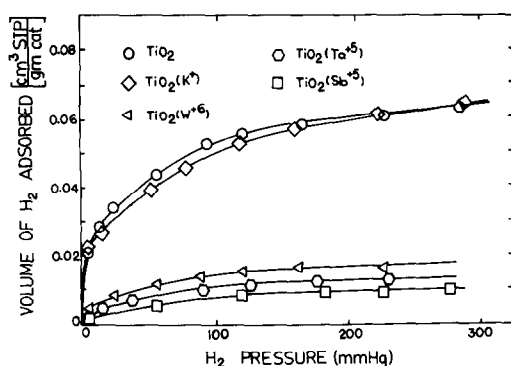


FIG. 4. Hydrogen adsorption isotherms of 0.06% Pt catalysts supported on pure and doped titania.

the Fermi level or the concentration of electrons of the support. These doped supports were employed as carriers for platinum crystallites.

There are some advantages to the doping technique as compared to the conventional HTR associated with SMSI:

(i) With the doped sample, surface reduction of the support is avoided, which serves as a check to localized electron transfer models.

(ii) The Fermi level of the support can be systematically altered by appropriate dopants, allowing the freedom to control the direction of electron flow.

(iii) Any sintering or morphological changes of the metal crystallites that can occur under HTR in hydrogen are avoided since the doped samples are exposed to low temperatures only (<200°C).

(iv) Finally, any diffusion of species from the support to the surface of the metal crystallites would be very slow at such moderate temperatures (<200°C).

All doped supports were prepared following the procedure described earlier. To assure incorporation of the dopants into the matrix of the parent support, all doped supports were sintered at 900°C for 5 hr. As a result of this treatment, the surface area of titania was reduced from approximately 40

to 7 m<sup>2</sup>/g, as determined with argon adsorption at liquid N<sub>2</sub> temperature. Three series of catalysts were prepared on the doped TiO<sub>2</sub> supports with Pt contents of 0.06, 0.5, and 2.0%. All catalysts on doped supports were reduced at 200°C in flowing hydrogen for a period of 2 hr. For ease of reference these catalysts are designated as X% Pt/TiO<sub>2</sub>(D), where X denotes the Pt content and D the dopant.

Typical hydrogen adsorption isotherms, measured at room temperature, on the 0.06% Pt/TiO<sub>2</sub> (D) series of catalysts are shown in Fig. 4. In addition to hydrogen, oxygen adsorption isotherms were also obtained at room temperature and the results are summarized in Table 3. Platinized TiO<sub>2</sub> exhibiting increased *n*-type semiconductivity (Sb<sup>5+</sup>, Ta<sup>5+</sup>, W<sup>6+</sup>-doped) shows suppression of hydrogen chemisorption. On the other hand, platinized TiO<sub>2</sub> exhibiting decreased *n*-type semiconductivity (K<sup>+</sup>, Mg<sup>2+</sup>-doped) exerts almost no effect on the chemisorption behavior of H<sub>2</sub>. The same is true for oxygen chemisorption. Thus, in addition to H<sub>2</sub>, O<sub>2</sub> chemisorption is also suppressed on catalysts exhibiting DIMSI behavior. The normalized ratio, (H/M)<sub>d</sub>/(H/M)<sub>und</sub>, which is defined as the H/M ratio of doped samples to that of the undoped samples, is also reported in Table 3. This ratio, as was suggested earlier, is a

TABLE 3

H<sub>2</sub> and O<sub>2</sub> Adsorption on 0.06% Pt/TiO<sub>2</sub> (D)

Carrier	Reducing temperature (°C)	H/M	O/M	(H/M) <sub>d</sub> /(H/M) <sub>und</sub>
TiO <sub>2</sub> (LTR)	200	1.45	1.26	1.00
TiO <sub>2</sub> (HTR)	500	0	1.16	0
TiO <sub>2</sub> (HTR) <sup>a</sup>	500	0.38	1.16	0.26
TiO <sub>2</sub> (K <sup>+</sup> )	200	1.34	1.22	0.92
TiO <sub>2</sub> (Mg <sup>2+</sup> )	200	1.25	—	0.86
TiO <sub>2</sub> (Sb <sup>5+</sup> )	200	0.23	—	0.16
TiO <sub>2</sub> (Ta <sup>5+</sup> )	200	0.23	0.20	0.16
TiO <sub>2</sub> (W <sup>6+</sup> )	200	0.29	0.32	0.20

<sup>a</sup> Catalyst exposed to air for 30 min after HTR.

good indication of metal–support interaction character as it approaches zero with increasing degree of metal–support interactions, and unity when such interactions are absent. If a similar ratio was computed for O<sub>2</sub> chemisorption, the trend would be similar to that of H<sub>2</sub> adsorption.

Results of similar studies conducted on the 0.5% Pt catalysts are shown in Table 4. The behavior of this 0.5% Pt series of catalysts follows the same trend as that of the 0.06% series reported in Table 3. In the SMSI catalyst, total hydrogen chemisorption suppression is observed while oxygen chemisorption is insensitive to SMSI. On the DIMSI catalysts, H<sub>2</sub> and O<sub>2</sub> chemisorption is normal on samples doped with lower valence ions (Mg<sup>2+</sup>), while suppression of chemisorption capacity is observed on the samples doped with higher valence ions (Sb<sup>5+</sup>, Ta<sup>5+</sup>). In addition, no suppression of chemisorption capacity is observed with the Ge-doped support, in accordance with expectations since Ge is of the same valence as Ti and no changes in the electron structure of TiO<sub>2</sub> are expected by doping with Ge. A sample of platinumized titania doped with a lower valence cation (Mg<sup>2+</sup>) was reduced at 500°C for 5 hr to determine if the doping process can affect the induction of SMSI character. The results shown in Table 4 indicate that the resulting suppression of H<sub>2</sub> chemisorption capacity is less drastic than that of the undoped sample. Although the undoped sample experiences a complete elimination of chemisorption capacity, the doped sample experiences an approximately 40% reduction. This phenomenon might be due to reduced conductivity of the Mg-doped sample (Table 7), since the induction of SMSI has often been correlated with the conductivity of the support. The fact that this support was exposed to high temperatures during its preparation, with a resulting transformation from predominantly anatase to predominantly rutile, is another possible explanation.

It is well known that SMSI catalysts lose

TABLE 4  
H<sub>2</sub> and O<sub>2</sub> Adsorption on 0.5% Pt/TiO<sub>2</sub> (D)

Carrier	Reducing temperature (°C)	H/M	O/M	(H/M) <sub>d</sub> /(H/M) <sub>und</sub>
TiO <sub>2</sub>	200	0.73	0.70	1.00
TiO <sub>2</sub>	500	0	0.68	0.00
TiO <sub>2</sub> (Mg <sup>2+</sup> )	200	0.68	—	0.93
TiO <sub>2</sub> (Mg <sup>2+</sup> )	500	0.40	—	0.54
TiO <sub>2</sub> (Ge <sup>4+</sup> )	200	0.78	—	1.07
TiO <sub>2</sub> (Sb <sup>5+</sup> )	200	0.14	0.14	0.19
TiO <sub>2</sub> (Sb <sup>5+</sup> ) <sup>a</sup>	200	0.12	—	0.17
TiO <sub>2</sub> (Ta <sup>5+</sup> )	200	0.12	0.11	0.17
TiO <sub>2</sub> (Ta <sup>5+</sup> ) <sup>b</sup>	200	0.16	—	0.21

<sup>a</sup> Catalyst exposed to air at 500°C for 90 min.

<sup>b</sup> Catalyst exposed to oxygen at 300°C for 60 min.

their peculiar adsorption characteristics when exposed to oxygen or air at high temperatures (20). This study (Table 3) has also shown that these catalysts partially lose their SMSI character when exposed to atmospheric conditions for a period as short as 30 min. In order to investigate whether DIMSI catalysts follow the same trends, catalysts supported on TiO<sub>2</sub> doped with Sb<sup>5+</sup> were exposed to air at 500°C for 90 min or to oxygen at 300°C for 60 min. Catalysts were then reduced in hydrogen at 200°C and evacuated overnight under dynamic vacuum, and hydrogen adsorption isotherms were determined following the procedures described earlier. Results of H<sub>2</sub> chemisorption capacity, also shown in Table 4, indicate that the DIMSI phenomenon is irreversible and normal H<sub>2</sub> chemisorption capacity (as observed on undoped LTR Pt/TiO<sub>2</sub>) is not regained even under these severe conditions. The fact that the SMSI state is an easily reversible one while the DIMSI state is irreversible constitutes a major difference between the two states.

It is possible, as suggested earlier, that the phenomena observed on small metal crystallites or low metal content catalysts may have a different origin than the phenomena observed on higher metal content

TABLE 5  
H<sub>2</sub> Adsorption on 2.0% Pt/TiO<sub>2</sub> (D)

Carrier	Reducing temperature (°C)	H/M	(H/M) <sub>d</sub> /(H/M) <sub>und</sub>
TiO <sub>2</sub>	200	0.25	1.00
TiO <sub>2</sub> (Mg <sup>2+</sup> )	200	0.18	0.72
TiO <sub>2</sub> (Ta <sup>5+</sup> )	200	0.12	0.48
TiO <sub>2</sub> (Sb <sup>5+</sup> )	200	0.14	0.56

catalysts. Hence, to test this hypothesis, H<sub>2</sub> adsorption was investigated on 2% Pt on doped- TiO<sub>2</sub>. The results are shown in Table 5. The H/M ratio of the 2% Pt/TiO<sub>2</sub> (Mg<sup>2+</sup>) catalyst is approximately 30% lower than that of the 2.0% Pt/TiO<sub>2</sub> catalyst. This reduction in the H/M ratio is attributed to the larger Pt crystallite size of the 2.0% Pt/TiO<sub>2</sub> (Mg<sup>2+</sup>) catalyst, resulting from the reduced surface area of the carrier from 40 to 7 m<sup>2</sup>/g. It is then implied here that the reduction of the specific surface area of the carrier affects the dispersion of the high metal loading (2%) catalysts, while it does not significantly affect the dispersion of the low metal loading (0.06 and 0.5%) catalysts. Evidence of this is presented later in a section on TEM studies. The H/M ratio of the Sb<sup>5+</sup>- and Ta<sup>5+</sup>-doped catalysts is approximately 50% less than that of the undoped sample and only 30% less than that of the Mg<sup>2+</sup>-doped sample. This indicates that the DIMSI phenomenon is a strong function of the size of the metal particles, being inversely affected by it. The effects of metal crystallite size on the strength of the DIMSI phenomenon is shown in Fig. 5. For ease of comparison, the same parameter of the SMSI catalysts is shown in the same figure. It is apparent that both phenomena are sensitive to metal crystallite size. Although the SMSI phenomenon seems to be more sensitive, this may be misleading due to the fact that the (H/M)<sub>d</sub>/(H/M)<sub>und</sub> ratio of the high metal loading catalyst is obscured from changes of the degree of dispersion of the

metal, as was discussed earlier. In both cases, the phenomena become weaker when the average Pt crystallite size exceeds approximately 40 Å.

Before attributing the observed results of reduced H<sub>2</sub> and O<sub>2</sub> chemisorption capacity of small Pt crystallites supported on higher valence-doped titania to some form of metal-support interaction, it must be established that the exposed Pt area has not decreased significantly. Since a significant reduction in the specific surface area of the support is observed as a result of the doping process, it is conceivable that Pt dispersion on these supports is considerably smaller, resulting in reduced exposed metallic area. TEM was used to address this issue and to obtain an independent estimate of the size of the Pt crystallites on all catalysts used in this study. Two representative micrographs from the 0.5% Pt/TiO<sub>2</sub> (Mg<sup>2+</sup>) and 0.5% Pt/TiO<sub>2</sub> (Sb<sup>5+</sup>) samples are shown in Fig. 6. The small, dark spots on the micrographs represent Pt crystallites, as detected by EDAX. The lighter spots did not show any Pt signals; thus they do not represent Pt particles. These micrographs show that the size and the morphology of the Pt crystallites is not altered significantly when the carrier is doped with cations of lower or higher valence.

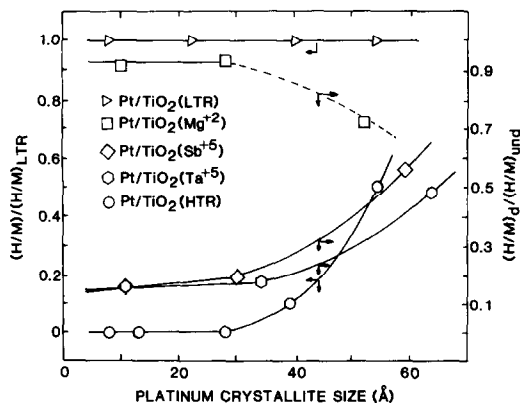


FIG. 5. Sensitivity of DIMSI phenomenon to Pt crystallite size.



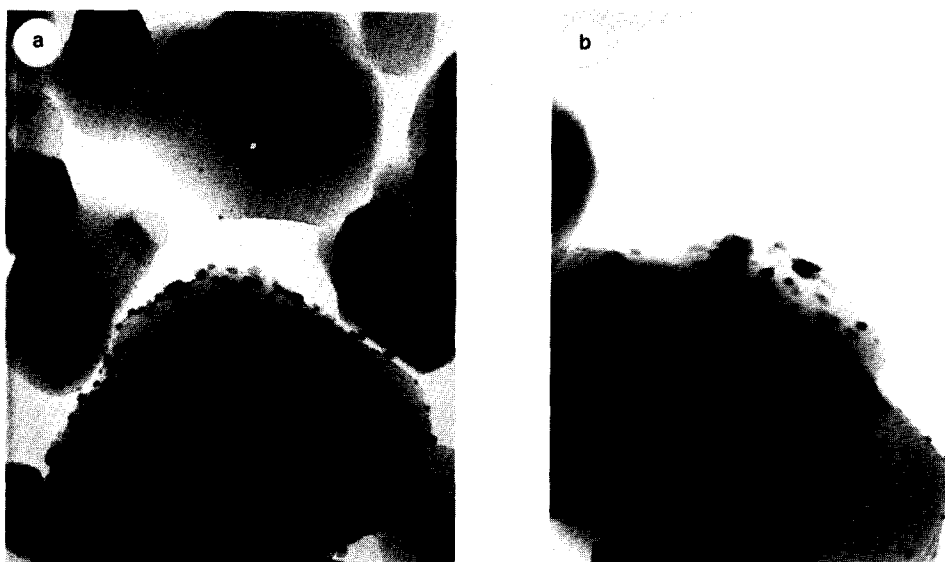


FIG. 6. Transmission electron microscopy micrographs for Pt supported on doped carriers: (a) 0.5% Pt/TiO<sub>2</sub> (Sb<sup>5+</sup>), (b) 0.5% Pt/TiO<sub>2</sub> (Mg<sup>2+</sup>).

Analysis from micrographs of a very large number of Pt crystallites was used to determine the average Pt crystallite size of the various samples. The results are shown in Table 6 along with crystallite sizes estimated from hydrogen adsorption. No significant growth of Pt crystallite sizes is noticed when doped titania is used as the carrier. Crystallite sizes of the higher valence-doped catalysts, estimated from hydrogen adsorption isotherms, shown in Table 6 in parentheses, represent the size that the Pt crystallites would have if no metal-support interactions were present. The large difference between the TEM values and the hydrogen adsorption values clearly indicates the presence of metal-support interactions which suppress hydrogen chemisorption capacity of the Pt crystallites. Therefore, the values in parentheses are erroneous because they do not account for the effects of DIMSI. It is also apparent from Table 6 that the degree of DIMSI is considerably more pronounced in the 0.5% Pt catalysts than in the 2.0% Pt catalysts. The difference between TEM and H<sub>2</sub> adsorption values of crystallite sizes is ap-

proximately 80% in the 0.5% Pt catalysts while only 20% in the 2.0% Pt catalysts.

The suppression of chemisorption capacity of Pt particles supported on higher valence-doped titania could possibly be explained in terms of other factors. Decreased dispersion of Pt on these carriers with loss of exposed metallic area has been ruled out as a possible mechanism by detailed TEM

TABLE 6  
Comparison of Average Pt Crystallite Size as Obtained by TEM and H<sub>2</sub> Adsorption

Catalyst	Average crystallite size, Å	
	TEM	H <sub>2</sub> adsorption
0.5% Pt/TiO <sub>2</sub>	22	16
0.5% Pt/TiO <sub>2</sub> (Mg <sup>2+</sup> )	28	17
0.5% Pt/TiO <sub>2</sub> (Sb <sup>5+</sup> )	30	(154) <sup>a</sup>
0.5% Pt/TiO <sub>2</sub> (Ta <sup>5+</sup> )	34	(169) <sup>a</sup>
2% Pt/TiO <sub>2</sub>	40	47
2% Pt/TiO <sub>2</sub> (Mg <sup>2+</sup> )	52	65
2% Pt/TiO <sub>2</sub> (Sb <sup>5+</sup> )	59	(83) <sup>a</sup>

<sup>a</sup> Erroneous because of suppressed H<sub>2</sub> chemisorption.

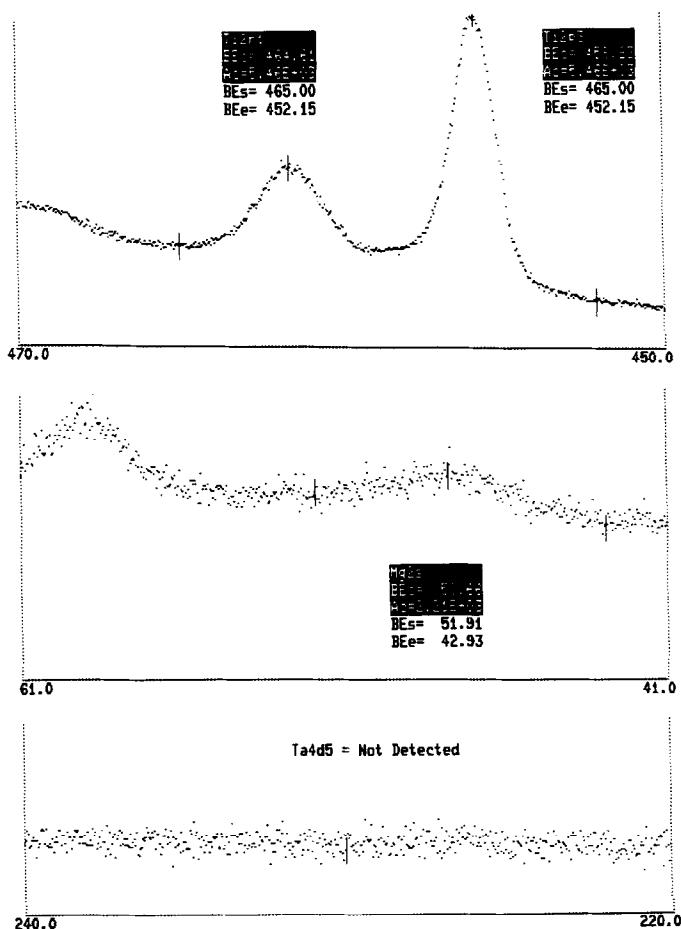


FIG. 7. High-resolution ESCA of MgO- and Ta<sub>2</sub>O<sub>5</sub>-doped catalysts.

analysis of all samples. Diffusion of the dopant to the surface of the metal particles is another potential explanation. To address this possibility, high-resolution ESCA was performed on samples doped with MgO and Ta<sub>2</sub>O<sub>5</sub> to determine if surface segregation of the dopants occur. Various X-ray photoelectron spectra are shown in Fig. 7. The Ti 2*p*<sub>1/2</sub> and 2*p*<sub>3/2</sub> lines appear at binding energies of 464.61 and 458.83 eV, respectively. A very weak Mg 2*s*<sub>1/2</sub> photoelectron line is detected at a binding energy of 50.66 eV, while no Ta is detected on the Ta<sub>2</sub>O<sub>5</sub>-doped sample. The detectability of Ta is approximately 0.005 atoms of Ta per atom of Ti, which corresponds to approximately 1% Ta<sub>2</sub>O<sub>5</sub> in TiO<sub>2</sub>. The fact that Ta is

not detected on the surface of the catalyst implies that no surface segregation of this dopant occurs. On the other hand, some MgO must segregate at the surface of the catalyst, since Mg is detected by ESCA, although the line is very weak. Apparently, the existence of MgO on the surface of titania does not alter the chemisorptive behavior of Pt. Furthermore, the fact that TiO<sub>2</sub> is indeed doped with MgO is obvious from electrical conductivity measurements (Table 7).

A number of arguments can also be made against the mechanism of dopant diffusion to the surface of the metal particles. (i) Diffusion of a cation which is incorporated into the crystal matrix of the solid would be ex-

pected to be an extremely slow process with significant activation energy requirements. It is unlikely that this process could occur at the low temperature (200°C) at which the samples were exposed, for a short period of time (2 hr). (ii) The lower valence cations would be expected to diffuse to the surface of the metal particles with the same ease as the higher valence cations. Nevertheless, no suppression of chemisorption capacity is observed over these samples. Furthermore, it has been demonstrated (21) that K-promoted Pt exhibits significantly reduced ability to chemisorb H<sub>2</sub>, which is contrary to observations in this study since catalysts supported on K-doped carriers exhibit normal H<sub>2</sub> chemisorption capacity (Table 3). Reduced chemisorption capacity would be expected if K was diffusing to the surface, interacting directly with the Pt particles. (iii) Further evidence against this mechanism is provided from kinetic results which will be reported in a future communication. These considerations do not prove that diffusion of the doping cations to the surface of the metal crystallites does not occur, but they provide strong arguments against it.

Indirect evidence of the fact that the work function of the parent support is significantly altered by altermvalent doping is provided by electrical conductivity measurements. A summary of electrical conductivity data of the doped carriers employed in this study is presented in Table 7. A more comprehensive study of electrical conductivity measurements will be reported in a future communication. The data presented in Table 7 show that both in an atmosphere of hydrogen and under vacuum the electrical conductivity of the parent titania is decreased significantly when it is doped with a cation of lower valence (Mg<sup>2+</sup>) while it is not altered when it is doped with a cation of equal valence (Ge<sup>4+</sup>). On the other hand, when titania is doped with cations of higher valence, the electrical conductivity is increased significantly. It is reasonable to expect that the work function of

TABLE 7  
Electrical Conductivity of Pure and Doped TiO<sub>2</sub><sup>a</sup>  
at 450°K

Support	Electrical conductivity (Ω <sup>-1</sup> cm <sup>-1</sup> )	
	in hydrogen (× 10 <sup>5</sup> )	under vacuum (× 10 <sup>8</sup> )
TiO <sub>2</sub> (Mg <sup>2+</sup> )	4	3
TiO <sub>2</sub>	75	20
TiO <sub>2</sub> (Ge <sup>4+</sup> )	70	20
TiO <sub>2</sub> (Ta <sup>5+</sup> )	116	180
TiO <sub>2</sub> (Sb <sup>5+</sup> )	447	224
TiO <sub>2</sub> (W <sup>6+</sup> )	316	180

<sup>a</sup> All samples contain 0.5% Pt.

these samples follows the exact opposite trend. These results correlate very well with the H<sub>2</sub> and O<sub>2</sub> chemisorption results presented earlier.

Electrical conductivities measured in an atmosphere of hydrogen are higher than those of same samples measured under vacuum. This is probably due to the fact that hydrogen reduces TiO<sub>2</sub> (22), generating anionic vacancies, which in turn are ionized further to create electrons. Electrons are also generated as a result of dissociative H<sub>2</sub> adsorption on Pt/TiO<sub>2</sub> and subsequent migration of atomic hydrogen to the support (spillover) where it forms hydroxide ions, thus releasing free electrons to the support. Extra electrons, generated by these processes, contribute to the increased electrical conductivity in the presence of hydrogen. These processes might also be responsible for the fact that conductivity differences between heating in hydrogen and under vacuum are a function of the dopant.

The results presented above clearly demonstrate that doping titania carriers with cations of valence higher than the parent cation results in significantly reduced H<sub>2</sub> and O<sub>2</sub> chemisorption capacity of supported platinum crystallites. On the other hand, doping with cations of lower or equal

TABLE 8  
Comparison of DIMSI and SMSI Phenomena

	SMSI	DIMSI
Suppression of H <sub>2</sub> adsorption	Yes, total	Yes, partial
Suppression of O <sub>2</sub> adsorption	No	Yes
Reversibility	Yes	No
Sensitivity to metal crystallite size	Sensitive	Sensitive

valence does not alter the chemisorption characteristics of the metal. Evidence indicating that this phenomenon is not due to reduced dispersion of Pt particles, or due to diffusion of the dopants to the surface of the metal, was presented.

It is tempting to compare the effects of DIMSI with those of SMSI because a number of similarities are immediately obvious and because it has often been speculated that electronic interactions play at least a partial role in the SMSI phenomenon. The similarities and dissimilarities of the two phenomena are summarized in Table 8. The significant differences shown probably indicate that the two phenomena are of different origins.

The results discussed above are consistent with a mechanism involving electron transfer from the semiconducting support to the metal crystallites, based on the requirement that the Fermi energy level of the two solids in contact must be the same at the interface. Doping titania with cations of higher valence results in increased Fermi energy level or decreased work function, which facilitates this transfer of electrons from the semiconductor to the metal. Thus, the work function of Pt (5.36 eV) decreases because of its alignment with that of the doped carrier and may approach that of gold (4.5 eV) (19). This process would also result in partial filling of the *d*-orbitals of Pt, which would then tend toward the electronic configuration of gold which chemisorbs neither H<sub>2</sub> nor O<sub>2</sub>. The effects of this

process on the chemisorptive properties of the metal would be expected to be a strong function of the size of the metal crystallites. Indeed, an 80–85% reduction of the chemisorptive capacity of Pt is observed when the crystallites are between 10 and 20 Å in diameter, while a 30% reduction is observed when the crystallites are 50–60 Å in diameter.

This mechanism of metal-support interaction was first proposed by Schwab (2) and Solymosi (3), based on observed alterations of kinetic parameters of catalysts supported on doped carriers. The criticism of this theory is well known: Metals have a high concentration of free electrons and, as a result, only minimal perturbations of the electron state of the metal via electron transfer from the support would be expected. In fact, if electrical conductivity is used as a measure of free electron concentration, the discrepancy between Pt metal and the carriers used in this study is on the order of 10<sup>7</sup>.

The fact that in metal-semiconductor contacts the Fermi level of the two solids is at equal heights is well established. Unlike covalent semiconductors in which the Fermi levels is pinned at a specific energy level, in ionic semiconductors (such as TiO<sub>2</sub>) the barrier height is a strong function of the work function of the metal (25). There is no doubt, then, that charge is indeed transferred from the semiconductor to the metal. The real issue is whether the magnitude of charge transferred is sufficient to alter the electron configuration of the metal to an appreciable extent.

To address this issue, in addition to the relative concentration of free electrons in the two solids, the "affected volume" of each must be considered. The electrons which cross the metal-semiconductor interface into the metal form a thin sheet of negative charge contained within a distance of approximately 0.5 Å (25) (Thomas-Fermi screening distance) and also are distributed to the surface metal atoms in conformity with electrostatic principles. On the

other hand, the "depletion region" in the semiconductor, in which a potential gradient exists, is significant. This depletion region can be estimated using classical Schottky barrier equations. We will illustrate this, considering the case of  $\text{TiO}_2$  ( $\text{W}^{6+}$ ).

$\text{TiO}_2$  was doped with 1.0 wt%  $\text{WO}_3$  which is equivalent to 0.112 at.% W in the sample, or a concentration of  $3.578 \times 10^{19}$  atoms W/ $\text{cm}^3$ . Assuming complete ionization, with an excess of two electrons per atom of W, the donor electron concentration,  $N_d$ , is  $7.155 \times 10^{19}$   $e/\text{cm}^3$ . The concentration of free electrons in the sample,  $n$ , is given by (25, 26)

$$n = (N_c N_d)^{1/2} \exp[-E_d/2K_B T], \quad (2)$$

where  $N_c$  is the effective density of states in the conduction band;  $E_d$  is the difference in energy between the conduction band and donor level, which is approximately equal to the activation energy of electron conduction; and  $K_B$  is Boltzmann's constant.  $N_c$  can be estimated from (25, 26)

$$N_c = 2(2\pi m_e^* K_B T/h^2)^{3/2}, \quad (3)$$

where  $m_e^*$  is the effective mass of an electron and  $h$  is Planck's constant.  $m_e^*$  is not easily predictable. As a first approximation it can be taken as  $0.3 m_0$ , where  $m_0$  is the electron rest mass. Then, at 300°K,  $N_c$  assumes a value of  $4.124 \times 10^{18}$   $e/\text{cm}^3$ . Taking  $E_d$  to be equal to the activation energy of electron conduction, a value of 0.20 eV was experimentally determined (27) under vacuum. Thus, at 300°K, the free electron concentration,  $n$ , of  $\text{TiO}_2$  ( $\text{W}^{6+}$ ) is estimated to be  $3.589 \times 10^{17}$   $e/\text{cm}^3$ .

The Fermi energy level for an  $n$ -type semiconductor (for  $n < N_c$ ) is given by (28, 29)

$$E_{F_s} = E_g + K_B T \ln(n/N_c), \quad (4)$$

where  $E_g$  is the energy gap between the conduction band and valence band, 3.0 eV for rutile titania. Thus, at 300°K,  $E_{F_s}$  is 2.937 eV. The semiconductor work function,  $\Phi_s$ , is given by (25)

$$\Phi_s = \chi_s + E_g - E_{F_s}, \quad (5)$$

where  $\chi_s$  is the electron affinity of the semiconductor, which is independent of doping, and is equal to 4.007 eV. Then, a value of 4.07 eV is estimated for the semiconductor work function. The Fermi energy level and work function of undoped  $\text{TiO}_2$  were estimated using the same formulations and found to be 1.513 and 5.50 eV, respectively. As expected, the Fermi energy level of the semiconductor increased as a result of doping with a higher valence cation, while the work function decreased.

The contact, or built-in, potential,  $V_i$ , can be estimated from (25)

$$V_i = (\Phi_m - \Phi_s)/q, \quad (6)$$

where  $\Phi_m = \Phi_{\text{Pt}} = 5.36$  eV and  $\Phi_s = \Phi_{\text{TiO}_2(\text{W}^{6+})} = 4.07$  eV, and  $q$  is the electron charge. Thus, the contact potential is 1.29 V. The depth of the depletion region,  $W_0$ , is given by (25, 28)

$$W_0 = (\epsilon_s |V_i|/2\pi q n)^{1/2}, \quad (7)$$

where  $\epsilon_s$  is the permittivity of the semiconductor. Assuming a value of  $\epsilon_s$  of  $1.146 \times 10^{-11}$  F/cm, which is an average of two values reported in the literature (30), the depth of the depletion region,  $W_0$ , is estimated to be 640 Å.

Thus, the volume of the semiconductor which is partially depleted of electrons is a cylindrical volume of radius equal to the radius of the particle and a length of 640 Å and a hemispherical volume of 640-Å radius. For a 20-Å Pt particle, this volume is approximately  $5 \times 10^8$  Å<sup>3</sup>. On the other hand, the volume of metal which is affected by electron transfer is approximately 150 Å<sup>3</sup>. The discrepancy between the two is on the order of  $10^6$ . This discrepancy in "volume affected" is similar in magnitude to the discrepancy in free electron concentration between Pt metal and the semiconducting carriers.

This analysis indicates that the electron transfer model of metal-support interactions should not be dismissed merely on the basis of free electron concentration differences between metals and semiconducting

supports. Further work must be conducted in order to prove or disprove the model. Modern techniques of surface science can be utilized for this purpose.

#### CONCLUSIONS

The following conclusions can be drawn from the results of this study:

(i) Metal-support interactions affecting chemisorption properties of metal crystallites can be induced by doping titania carriers with cations of higher valence.

(ii) These interactions are very sensitive to the size of metal crystallites, their intensity decreasing with increasing crystallite size.

(iii) The origin of this phenomenon is probably an electronic interaction at the metal-support interface.

(iv) Significant differences between SMSI and DIMSI phenomena indicate that their origins are probably different.

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