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Metal–Support Interaction. Catalytic Properties of TiO_2-Supported Platinum, Iridium, and Rhodium[1]

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The reduction of Pt/TiO_2, Ir/TiO_2, Rh/TiO_2 in the range 473–773 K of temperature induces a strong metal–support interaction as evidenced by the change in catalytic properties of these metals used for ethylene, benzene, and styrene hydrogenations, cyclohexane dehydrogenation, and butane hydrogenolysis. Treatment under O_2 partially restores the usual properties of these metals. The origin of this strong metal–support interaction is discussed.

INTRODUCTION

Recently, Tauster *et al.* (*1*) have reported that TiO_2-supported noble metals, H_2-reduced at low temperature (473 K), showed a significant H_2 and CO chemisorption, while H_2-reduction at high temperature (700–800 K) caused a decrease to a very low level of H_2 and CO uptake. This effect was associated with the so-called "Strong metal–support interaction (SMSI)." Since then the catalytic properties of TiO_2-supported noble metals in CO–H_2 reactions (*2*, *4*), in ethylene hydrogenation (*5*) and in benzene hydrogenation (*6*) have been investigated. In general the results were interpreted in terms of strong metal–support interaction.

The present investigation was undertaken to study further the catalytic behaviour of TiO_2-supported noble metals. Particular emphasis has been placed on determining how the temperature at which the catalysts have been reduced by hydrogen will affect their catalytic properties. Since the temperature of H_2 treatment influences also the semiconductivity of TiO_2, special attention has been paid to this point. In this work we consider the reactions of hydrogenation of benzene, styrene, ethylene, the dehydrogenation of cyclohexane, and the hydrogenolysis of *n*-butane on platinum, iridium, and rhodium supported on TiO_2. The metal dispersion was determined by electron microscopy, and by hydrogen and oxygen chemisorption.

EXPERIMENTAL

Catalysts. TiO_2-supported noble metals were prepared by impregnation of TiO_2 (Degussa P25, anatase structure 50 m^2/g^{-1}) with $RhCl_3 \cdot xH_2O$, $IrCl_3 \cdot xH_2O$, or $H_2PtCl_6 \cdot 6H_2O$. For Ir and Rh, the support material was vigorously stirred in distilled water while the metal salt solution, with the appropriate amount of the metal salt, was added drop by drop; for Pt, the incipient wetness method was used. After completion, the water was evaporated to dryness under reduced pressure at 333 K using a rotary evaporator. The impregnated materials were then dried in air at 373 K. Metal loading in each sample was respectively 4.8% wt (Pt), 2.7% wt (Ir), 3.2% wt (Rh). The reduction of the TiO_2-supported noble metal was carried out in a conventional flow cell, the temperature being raised (4K min^{-1}) from 293 K to the desired reduction temperature while H_2 passed continuously through the cell.

Particle size measurements. Transmission electron microscopy was used to mea-

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sure the metal particle size; the extraction replication procedure similar to that described in Ref. (*7*) was employed. Hydrogen and oxygen adsorption measurements were performed on a conventional volumetric adsorption apparatus equipped with a Texas Instruments precision pressure gauge.

Catalytic reactions. The catalytic activities were measured at atmospheric pressure in a differential flow reactor with a fixed bed catalyst. The effluent gases and vapors were analyzed by means of gas chromatography using an IGC 12 FB Intersmat gas chromatograph. The columns were 1-m stainless-steel tube of 3 mm diameter filled respectively with 5% $\beta\beta'$ oxydipropionitrile on Spherosil XOB 75 for benzene and cyclohexane, with 5% SP 1200, 1.75% Bentone 34 on Chromosorb W 100/120 mesh for styrene, with 20% dimethyl sulfolan on Chromosorb W for *n*-butane and finally with Porapak Q for ethylene.

RESULTS

Chemisorption Measurements and TEM Studies

In Table 1 are reported the metal dispersion, for all samples, calculated respectively from hydrogen chemisorption (HC), oxygen chemisorption (OC), hydrogen titration (HT), and oxygen titration (OT) assuming a stoichiometry of one hydrogen (or oxygen) atom adsorbed per surface metal atom. The particle sizes derived from the adsorption data and those directly measured from the electron micrographs are also summarized in Table 1.

The transmission electron microscopy (TEM) data have indicated that in the case of Ir/TiO_2 and Rh/TiO_2, the metal crystallites were present in the form of individual spherical particles with a particle size distribution in the range 1.5–4.0 nm, the average particle sizes being those given in Table 1. It is interesting to note that heat treatment in H_2 at 793 K produced only a small particle growth. The electron micrographs of Pt/TiO_2 were significantly different from those of Ir/TiO_2 and Rh/TiO_2. No individual platinum particles were observed. Instead Pt appeared like a film (pillbox structure, raft-like structure) covering TiO_2 particles. This pillbox-like structure renders difficult the determination of the size of each individual Pt particle. Table 1 shows that there is a good agreement between the average particle diameters obtained from electron micrographs and those calculated from hydrogen adsorption data at least for the samples reduced at low temperature (~573 K). It is significant to note that, on the contrary, there is a discrepancy between H_2 adsorption and electron microscopy studies for TiO_2-supported noble metals reduced at high temperature (773 K). This seems to indicate that the 773 K heat treatment in hydrogen resulted in a strong decrease of the hydrogen adsorbed by the metal al-

TABLE 1

Data for Metal Dispersion

Sample	Treatment 2 hr under H_2 at	Dispersion as measured by				
		HC H/M = 1 (*d* in nm)	OC O/M = 1	HT H/M = 3	OT O/M = 3/2	TEM (*d* in nm)
4.8% Pt/TiO_2	473 K	25%	26%	25%	26%	
	770 K	6%	25%		25%	
2.7% Ir/TiO_2	473 K	61% (1.7)	68% (1.6)			2.3
	793 K	6% (17.5)	70% (1.5)			2.3
3.2% Rh/TiO_2	473 K	25% (4.4)	47% (2.3)			2.3
	793 K	5% (22.0)	47% (2.3)			2.5

though the particle size remained almost unchanged. These results corroborate the conclusion put forward by Tauster *et al.* (*1*) and Baker *et al.* (*8*) that the high H_2-reduction temperature does not act by a sintering effect but rather by producing a strong metal–support interaction which suppresses hydrogen chemisorption.

The data for oxygen chemisorption and for hydrogen titration as a function of the H_2-reduction temperature, shown in Table 1, clearly indicate that the particle sizes calculated from oxygen chemisorption or from hydrogen titration measurements are in fair agreement with those determined from electron micrographs. This trend was observed not only for the samples reduced at low temperature but also for those heat-treated in H_2 at high temperature. These findings imply the intriguing fact that while high-temperature reduction in H_2 decreases or suppresses the capacity, for TiO_2-supported noble metals, to adsorb H_2, it has no effect on the capacity for oxygen adsorption. Moreover, samples which have been H_2-reduced at 773 K, and subsequently contacted with oxygen at 293 K, recovered their capacity for H_2 adsorption.

Catalytic Measurements

TiO_2-supported platinum, iridium and rhodium, H_2-reduced according to the procedure previously described, were tested for benzene–cyclohexane hydrogenation–dehydrogenation activities, for styrene hydrogenation, and for ethylene hydrogenation. The results are summarized in Table 2. Reaction conditions and the mode of activation of the catalysts are also listed in Table 2. Reaction rates were evaluated as mmole per hour per gramme of metal. Turnover numbers were avoided since the number of metal surface atoms calculated from H_2 adsorbed on samples reduced at 773 K appeared meaningless. The results presented in Table 2 show that TiO_2-supported Pt, Ir and Rh reduced in H_2 at 473–523 K were reasonably active for hydrogenation–dehydrogenation reactions. Furthermore, the rates measured in the present work are comparable to those found for SiO_2- or Al_2O_3-supported Pt, Ir and Rh. The TiO_2-supported metal catalysts reduced in H_2 at 773 K showed very little activity. It is important to note that if before catalytic measurements the high-temperature H_2-reduced samples were contacted with oxygen, their catalytic properties were partially or totally restored. Thus Tables 1 and 2 clearly indicate that the capacity for hydrogen adsorption and the hydrogenating–dehydrogenating properties of TiO_2-supported noble metals follow the same trend upon H_2-reduction at 773 K and O_2-oxidation at 293 K.

TiO_2-supported Pt, Ir, and Rh catalysts were also tested for *n*-butane hydrogenolysis. The reaction involves the central C–C bond rupture to form ethane and the terminal C–C bond rupture to form methane and propane. In Table 3 are reported the rates, expressed in moles per hour per gramme of metal, of methane, ethane, propane, and isobutane formation. Table 3 gives also the reaction conditions and the catalyst activation procedures. The data summarized in Table 3 show again the deactivating effect of H_2-reduction at 773 K. The hydrogenolysis activity was almost suppressed. A progressive reactivation was observed on prolonged exposure to oxygen at 293 K. These results parallel those already reported for the hydrogen adsorption and the hydrogenation reactions.

It is interesting to note that at 623 K Pt/TiO_2 exhibited both isomerization and hydrogenolysis activity, the former reaction being a little more affected by the activation mode of the catalyst. Further study on this particular aspect is in progress and will be reported in a future paper.

ESR Measurements

In order to arrive to a better understanding of the nature of the metal–support interaction we have carried out some preliminary work to determine the nature of the paramagnetic defects which might be

TABLE 2

Rates (mmol h^{-1} g^{-1} metal) for Catalytic Reactions on Pt/TiO_2, Ir/TiO_2, and Rh/TiO_2

Catalyst	Treatment	C_6H_6 hydrogenation at 288 K $P_{C_6H_6}$ = 30 Torr P_{H_2} = 127 Torr P_{N_2} = 603 Torr	C_6H_{12} dehydrogenation at 523 K $P_{C_6H_{12}}$ = 35 Torr P_{H_2} = 127 Torr P_{N_2} = 598 Torr	C_2H_4 hydrogenation at 196 K $P_{C_2H_4}$ = 84 Torr P_{H_2} = 676 Torr	Styrene hydrogenation at 288 K $P_{styrene}$ = 1.5 Torr P_{H_2} = 127 Torr P_{N_2} = 631.5 Torr	
					Ethyl benzene	Ethyl cyclohexane
4.8% Pt/TiO_2	473 K H_2 2 h			317	14	2500
	523 K H_2 12 h	40	1740			
	+O_2 273 K 30 min	56				
	773 K H_2 12 h	3.5	217	39	0	500
	+O_2 273 K 30 min	29	1087	110	9	1260
2.7% Ir/TiO_2	473 K H_2 2 h			281	18	2550
	523 K H_2 12 h	81	1400			
	+O_2 273 K 30 min	159				
	773 K H_2 12 h	0	304	30	0	181
	+O_2 273 K 30 min	18.5		120	9.3	2011
3.2% Rh/TiO_2	473 K H_2 2 h			Too high to be measured in our experimental conditions	31	4220
	523 K H_2 12 h	281	2054			
	+O_2 273 K 30 min	719				
	773 K H_2 12 h	21	1000	300	0	1250
	+O_2 273 K 30 min	381	1395		34	3960

TABLE 3

n butane Hydrogenolysis and Isomerisation $P_{n-C_4H_{10}} = 30$ Torr, $P_{H_2} = 304$ Torr, $P_{N_2} = 426$ Torr

Catalyst	Treatment	Temperature of reaction	Rate in mmol h^{-1} g^{-1} metal			
			C_1	C_2	C_3	iC_4
4.8% Pt/TiO_2	623 K H_2 2 h	623 K	35	46.9	24.9	88
	773 K H_2 2 h		0.65	1.1	0.7	0
	$+O_2$ 298 K 30 min		6.7	7.8	4.4	5
	$+H_2$ 623 K 30 min					
2.7% Ir/TiO_2	503 K H_2 2 h	503 K	3259	9592	930	
	773 K H_2 2 h		0	0	0	
	$+O_2$ 503 K 30 min					
	$+H_2$ 503 K 15 min		537	1178	330	
3.2% Rh/TiO_2	503 K H_2 2 h	503 K	19500	17656	859	
	773 K H_2 2 h		359	656	197	
	$+O_2$ 503 K 30 min					
	$+H_2$ 503 K 30 min		7719	8375	969	

present following the various treatments to which TiO_2-supported noble metals have been subjected. $Pt-TiO_2$, $Ir-TiO_2$, and pure TiO_2 were reduced as previously by H_2 at 473 K and 773 K. All the samples exhibited at 77 K an anisotropic ESR signal with $g_\perp = 1.966$ $g_\parallel = 1.946$. This signal has been previously assigned to Ti^{3+} ions (*9*). The formation of Ti^{3+} ions was due to the removal of lattice oxygen. A double integration of the ESR spectrum allowed us to determine the concentration of Ti^{3+} ions formed on each sample. The number of Ti^{3+} ions formed on samples H_2-reduced at 773 K was found to be approximately the same on both pure TiO_2 and TiO_2-supported metals. However, on Pt/TiO_2 and Ir/TiO_2 reduced at 473 K, the concentration of Ti^{3+} ions was ten times more than on pure TiO_2 reduced at the same temperature. Adsorption of oxygen at 293 K on these samples resulted in the formation of a new 3-g-value ESR signal, $g_1 = 2.030$, $g_2 = 2.008$, and $g = 2.003$, characteristic of the signal observed for O_2^- species (*10*). Simultaneously the signal intensity of Ti^{3+} ions decreased and even disappeared for those samples reduced at 473 K.

DISCUSSION

The overall results presented in this paper fit well with those reported previously by Tauster *et al.* (*1*), Baker *et al.* (*8*) and Ellestad *et al.* (*6*). It follows from these works and our data that the reduction at high temperature of TiO_2-supported noble metals results in a strong metal–support interaction (SMSI) leading to the suppression of the metal capacity for hydrogen chemisorption and also to the suppression of the metal activity for hydrogenation and hydrogenolysis reactions. In addition the SMSI is partially or totally destroyed when the catalysts are reoxidized either at room temperature or at 573–773 K.

There is little doubt that the extent of the SMSI depends on the degree of reduction of the support; the more reduced the support the stronger the SMSI. However, although the origin of the SMSI appears now to be well established the mechanism by which the adsorption capacity for H_2 and the catalytic properties are suppressed is not yet well understood. Nevertheless, it is possible to propose a mechanism which takes into account all the experimental facts and which will describe the observed trends.

To begin with one can imagine that under H_2 atmosphere at high temperature part of the metal becomes inaccessible by either encapsulation or poisoning by impurities which could migrate over the support and deposit on the metal. This mechanism appeared unlikely for Tauster *et al.* (*1*). Indeed it seems reasonable to expect that, once the metal was "poisoned" by impurities or encapsulation, it will not be regenerated by oxygen at room temperature, in contrast with the regeneration effect of O_2 at 293 K observed in this work. Therefore we conclude, following Tauster *et al.* (*1*), that the mechanism of SMSI does not involve encapsulation or deposition of impurities.

Based upon studies of Pt/Al_2O_3, den Otter and Dautzenberg (*11*) showed that the H_2 adsorption capacity decreased when Pt/Al_2O_3 was pretreated in H_2 at high temperature. These authors suggested the formation of Pt_3Al alloys to explain their observations. It is possible that a similar mechanism is operative in the case of TiO_2-supported noble metals as well. In fact the formation of Pt_3Ti, Ir_3Ti intermetallic compounds has been proposed for the SMSI mechanism (*1*). Although it is difficult to exclude totally such a hypothesis, this interpretation does not seem plausible for several reasons:

(i) In general, reduction of TiO_2 to metallic Ti as well the formation of intermetallic compounds such as Pt_3Ti, Ir_3Ti occurs only above 2000 K.

(ii) Intermetallic alloys are rather stable in oxygen and would not be decomposed by oxgen at room temperature. Recently it has been shown (*12*) that the Ni_5Th intermetallic compound decomposes into the ThO_2–NiO system above 573 K.

(iii) Based upon our preliminary XPS analyses, we have not been able to detect the presence of metallic titanium.

(iv) In alloys or bimetallic catalysts the function of the second metal is mainly to isolate the active metal atom rather than to modify the intrinsic activity per atom (*13*). The alloying results in smaller metal ensembles leading to the suppression of reactions requiring more than one metal atom, but has no effect on reactions involving one single surface atom. For example, alloying nickel with copper resulted in a marked decrease of the catalytic activity for ethane hydrogenolysis while for cyclohexane dehydrogenation the catalytic activity remained almost unchanged (*14*). Hence if intermetallic compounds such as Pt_3Ti, Ir_3Ti, and Rh_3Ti have been formed one would expect a decrease of the hydrogenolysis rate of reaction but almost no change in the hydrogenation–dehydrogenation properties of the catalysts, in contrast with our results. Furthermore the SMSI, if due to the formation of intermetallic compounds, will not be destroyed by oxygen at 293 K, since it is most unlikely that oxygen would produce a phase segregation of the alloy at a temperature as low as 293 K. Phase separation of Pt–Pd alloy supported on SiO_2 has been produced by oxidation between 573 and 973 K (*15*).

Another possible mechanism for SMSI has been suggested by Baker *et al.* (*16*). These authors observed by electron diffraction and electron microscopy that under severe conditions of reduction, the surface of TiO_2 was transformed into Ti_4O_7 and the three-dimensional metal crystallites into a flat thin pillbox-like structure. They correlate these structural changes with the SMSI provided by the bond created between Pt atoms and exposed titanium cations. They concluded that the noble metals in the form of the thin pillbox structure will exhibit different catalytic properties compared with systems without SMSI and further that this structure will be responsible for the suppression of H_2 adsorption. One can reasonably consider that the size, the shape of the metal crystallites, and the extent to which they would spread on the support will depend on the degree of metal–support interaction but there is no valid reason to expect that spreading of the crystallites would cause a lowering of the metal capacity for H_2 or CO adsorption. On the contrary, Yates et al. (*17*) showed that raft-like supported rhodium does adsorb H_2 and CO.

The transfer of electronic charge from

Ti^{3+} cations, formed upon H_2-reduction of the support, towards the metal has also been considered as a possible mechanism for the SMSI. Horsley (*18*) has carried out a molecular orbital calculation of the interaction between platinum and a Ti^{3+} cation and concluded that the SMSI resulted from a covalent bonding between platinum and Ti^{3+}, the bond having a partial ionic character due to electron transfer from Ti^{3+} to Pt. Similarly Auger and photoemission studies of platinum sputtered on a clean $SrTiO_3$ surface seemingly indicated transfer of electronic charge from Ti^{3+} to platinum (*19*). However, although the "electron transfer" mechanism between individual Ti^{3+} cations and Pt atoms appears to have a strong basis the following experimental data do not favour this explanation.

(i) TiO_2-supported noble metals reduced at 473 and 773 K both possessed Ti^{3+} cations while only the high-temperature reduced sample exhibited SMSI.

(ii) Ti^{3+}-exchanged Y zeolite with supported rhodium was studied: ESR experiments have shown that Ti^{3+} cations are located in the supercages and transmission electron microscopy has shown that the rhodium particles are also located in the supercages. Thus there is a great probability that Ti^{3+} cations and the metal particles are in contact or at least at very short distance from each other. Preliminary experiments on these samples have shown that the adsorption capacity for H_2 and CO, as well as the hydrogenating properties of supported rhodium, were maintained whatever was the temperature of reduction by H_2. These results would indicate the absence of SMSI when only isolated Ti^{3+} are in the proximity of the metal (*20*).

For these reasons we would favour for the SMSI a mechanism involving the collective property of electrons in reduced TiO_2, that is, the *n*-type semiconductivity property of TiO_2. The Fermi levels of slightly reduced TiO_2, metal (like Pt) and strongly reduced TiO_2 are respectively pictured in Fig. 1a, b, and c: at low H_2 reduction temperature the Fermi level of the support is located near the Fermi level of Pt since the work functions for TiO_2 (*22*) and Pt (*23*) are respectively 5.5 and ~5.6 eV. Reduction at high temperature under H_2 produces a high concentration of surface defects (Ti^{3+} ions and oxygen vacancies (*24*)) and the work function of TiO_2 decreases to 4.6 eV (*22*): the Fermi level of reduced TiO_2 is now higher than the Fermi level of the metal (Fig. 1); hence when the metal particles are in contact with reduced TiO_2 there is an adjustment of the Fermi levels at the interface resulting in a flow of electrons *from the reduced TiO_2 to the metal* and a negative charge appears on the metal particles.

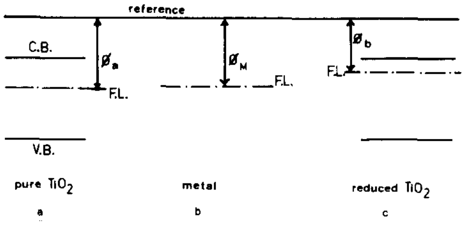

FIG. 1. Schematic energy level diagram for pure TiO_2 (a), metal (b), reduced TiO_2 (c); ϕ_i is the work function of material *i* and *FL* the Fermi level.

According to the rigid band theory, a number of authors have claimed a relationship between catalytic activities and the *d*-band structure of the metal. Accordingly, the proposed mechanism for the SMSI would lead to a completely filled *d*-band and would thus transform the active metal to an almost unreactive system. The Fermi level adjustment theory would explain well the effect of the oxygen adsorption and the reduction temperature on SMSI: it is well known that the adsorption of oxygen at 293 K on reduced TiO_2 decreased considerably its conductivity, thus lowering the Fermi level to near its initial value which removes the SMSI.

The activities of Pt/TiO_2 for dehydrogenation of C_6H_{12} or hydrogenation of C_6H_6 decrease monotonically as the H_2 reduction temperature increases from 473 to 773 K and simultaneously the conductivity of the support increases (*20*); thus the adjustment of the Fermi levels occurs by transfer of an increased number of electrons from reduced TiO_2 to the *d*-band of the metal.

In conclusion, we would stress that the SMSI observed for TiO_2-supported noble metals is probably due to the collective properties of reduced TiO_2; the greater the reduction of the support, the stronger will be the metal–support interaction. In order to confirm this type of mechanism for SMSI some spectroscopic evidence is needed and in this regard XPS experiments now planned will be of great interest.

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