

Electronic Effects in Strong Metal-Support Interactions on Titania Deposited Metal Catalysts

J. M. HERRMANN¹

*Institut de Recherches sur la Catalyse, C.N.R.S., 2 avenue Albert Einstein,
69626 Villeurbanne, Cédex, France*

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The electrical conductivity of Pt, Rh, and Ni catalysts deposited on titania was followed *in situ* during all the pretreatment phases leading either to a "normal" state after reduction in H₂ at low temperature (473 K) or to a strong metal-support interaction (SMSI) state after reduction at 773 K. In both cases, an electron migration from the support to the metal was evidenced under vacuum. This excess of electrons in the metal was highly accentuated by the SMSI conditions. The partial or total inhibition of hydrogen chemisorption on the metals was attributed to an electronic effect, the extra electrons saturating the unfilled *d*-orbitals of the surface metal atoms or inducing long distance electronic interactions which counteract the establishment of M-H bonds. The sensitivity to SMSI for the three samples used was found to vary in the order Ni > Pt > Rh. This was qualitatively explained for rhodium by its greater number of unfilled *d*-orbitals per atom, whereas the case of nickel was found more difficult to interpret because of its low dispersion (or large particle size) and its tendency to be partly irreversibly oxidized. The absence of inhibition by SMSI for reactions involving hydrogen like spillover presently evidenced and explicited by an isotherm law ($\sigma = \sigma_0 + kP_{H_2}^{1/2}$) or CO methanation, is explained by the fact that only a fraction of the hydrogen coverage is needed to let the reaction run.

INTRODUCTION

Group VIII metals deposited mainly on titania but also on other similar semiconductor oxides are known to induce strong metal-support interactions which greatly affect their chemisorptive and catalytic properties in reactions involving H₂ and CO. This SMSI effect, as first stated by Tauster *et al.* (1), commonly occurs after a high temperature reduction of the catalysts in hydrogen and can disappear, at least partially, by introducing either gaseous oxygen or water. Various hypotheses have been proposed and discussed to account for the inhibition of chemisorption and reactivity at the surface of the metals. The agglomeration or encapsulation of the metal particles, the influence of impurities or contamination, the existence of an alloy have been

rejected as possible sources of the SMSI state (see for instance ref. (2)). The same authors propose the occurrence of an electron transfer from the support to the metal, this assumption being based on the necessity for obtaining a SMSI effect, of dealing with reducible transition metal oxide supports (3) as later observed in refs. (4) and (5).

Moreover, it is known that surface migration of TiO_x can occur readily under the conditions of the formation of SMSI characteristics according to the conclusions drawn from the study of various titania supported metals such as Fe (6), Rh (7), or Ni (8).

Any electron transfer from an oxide to a metal can readily occur, when they are put into contact, by the spontaneous alignment of their Fermi levels, provided the work function of the metal (ϕ_n) be greater than that of the oxide (ϕ_{ox}). The latter will depend upon the reduction state of the oxide:

¹ Present address: Laboratoire de Physico-Chimie des Interfaces, U.A. CNRS n°404, Ecole Centrale de Lyon, 69131 Ecully-Cédex, France.

the more reduced the oxide, the smaller ϕ_{ox} and the stronger the electron migration to the metal (5, 9). Several spectroscopic studies (10–14) have evidenced such an electron transfer in agreement with electrical measurements (5, 15) or molecular orbital calculations (16).

In the same line, an "artificial" SMSI effect was even recently induced by replacing the high temperature reduction of Pt/TiO₂ by the introduction of an alkaline additive. This was interpreted by an electron donor effect of potassium to platinum (17). Another artificial way to increase the concentration in free electrons in TiO₂ and consequently to favor the electron transfer to the metal consists in illuminating the solid with suitable wavelengths ($h\nu \geq E_G(\text{TiO}_2) = 3.02 \text{ eV}$). A direct correlation between the amount of deposited platinum (with a constant dispersion) and the photoconductance of the solid has been evidenced and interpreted (18).

A previous electrical conductivity study (15) has shown that platinum in SMSI conditions is strongly enriched in excess electrons coming from the reduced support and is consequently losing its normal adsorptive properties with respect to hydrogen because of an alteration of its normal *d*-electron configuration, which tends to make it progressively resemble its *d*¹⁰ neighbor in the periodic table, namely gold, known as a poor hydrogen sorbent and a poor hydrogenation catalysts (19).

In the present work, the electrical conductivity study was extended to Ni and Rh, thus allowing comparisons between three metals, each one belonging to a different row in group VIII. An attempt was made to explain the differences due to the nature of the metal, as for instance the smaller sensitivity to SMSI of rhodium in comparison with platinum and nickel (20).

EXPERIMENTAL

Catalyst preparation. The various M/TiO₂ catalysts were prepared by the impregnation of non porous Degussa P-25 anatase (50 m² g⁻¹) with the required quantity

of a soluble salt of the metal chosen: chloroplatinic acid, rhodium trichloride, and nickel hexamine nitrate.

The suspension was then dried in a rotating flask by evacuation at 80°C and then in an oven at 110°C for 2 h. The reduction by H₂ at 480°C for 15 h was preceded and followed by a nitrogen flush during the increase and decrease in temperature.

Chemical analysis gave metal loadings close to the nominal weight contents (~5 wt%).

Catalyst characterization. Transmission electron microscopy (TEM) showed that platinum and rhodium were present as well homodispersed particles of 2 and 3.5 nm, respectively, whereas no Ni particles could be detected because of a lack of contrast between metal and oxide particles of similar orders of magnitude. However, magnetic measurements could provide an estimate of the mean diameter (13.5 ± 2.5 nm) of the nickel crystallites. Moreover this mean diameter was very close to that determined by TEM on another 5 wt% Ni/TiO₂ sample, obtained with larger spherical TiO₂ particles (170 nm) previously used in ref. (21), which could allow a neat and unambiguous distinction between Ni and TiO₂ particles.

Dispersion measurement for Pt and Rh by chemisorptions and titrations are presented in Table 1. H₂-O₂ chemisorptions and titrations are in good agreement for the catalysts reduced at low temperature (LTR

TABLE I

Amounts of Gases Which Have Reacted^a during H₂ and O₂ Adsorptions and H₂-O₂ Reciprocal Titrations on Pt and Rh/TiO₂

	5-Pt/TiO ₂		5-Rh/TiO ₂	
	T _R = 473	T _R = 773	T _R = 473	T _R = 773
H ₂ ads	42	6	67	24
O ₂ tit.	65	56	112	100
H ₂ tit.	126	105	224	201
O ₂ ads	45	37	106	88
H ₂ tit.	134	114	298	244
O ₂ tit.	66	53	122	112

^a In micromoles per gram of catalyst.

samples). For what concerns the rhodium-oxygen stoichiometry, the surface species seem to be closer to Rh_2O_3 than to Rh-O .

For nickel, since oxygen chemisorption is partially irreversible and corresponds to an oxidation of the metal, only H_2 chemisorptions were carried out. Moreover, to make sure that all the nickel is 100% reduced as Ni^0 atoms according to magnetic measurement (22), the low reduction temperature was chosen equal to 623 K. The amounts of chemisorbed H_2 were respectively equal to $8 \mu\text{mol H}_2 \text{ g}_{\text{cat}}^{-1}$ for $T_R = 623 \text{ K}$ and $0 \mu\text{mol H}_2 \text{ g}_{\text{cat}}^{-1}$ for $T_R = 773 \text{ K}$.

Electrical conductivity measurements. They were carried out in the same static cell as that previously used for the study of Pt-TiO₂ electronic interactions (15).

The electrical conductivity was measured *in situ* during all the pretreatments and the chemisorption-titration phases corresponding to the first column of Table 1. It has to be recalled that the experimental data obtained do not provide absolute intrinsic electrical conductivity values since the solid is not a single crystal but a powder. However, the relative variations are significant. Moreover, one must underline that the conductivity measured refers exclusively to that of the support since the highly divided state of the metal as well as its moderate weight percentage (5%) cannot allow an electric conduction through the metal crystallites as confirmed by TEM examination.

Procedures. Two reducing treatments were applied to the different catalysts, one at a low temperature (473 K; LTR samples) and the other at a higher temperature (773 K; HTR samples). Of M/TiO₂ 500 mg was inserted between the two electrodes, evacuated at room temperature for 1 h, reduced overnight at 473 K under 250 Torr H₂ (1 Torr = 133.3 Pa), then evacuated (10^{-6} Torr) at 673 K for 2 h to make sure that all hydrogen was evolved according to ref. (23) and finally cooled down to room temperature. Increasing pressures of H₂ in the 10–250 Torr range were introduced in contact

with the solid to follow the influence of P_{H_2} on the electrical behaviour of the Pt-TiO₂ system. After H₂-O₂ titrations, the solid was reduced at 773 K under 250 Torr H₂ for 2 h, then evacuated at the same temperature for 2 h, cooled down to room temperature, and submitted to the same H₂-O₂ sequences as for LTR samples.

RESULTS AND DISCUSSION

Samples Reduced at 473 K (LTR Samples)

The variations of the electrical conductivity σ of the different M/TiO₂ catalysts for the various subsequent phases mentioned above is represented with a logarithmic scale in Fig. 1.

TiO₂ and Pt/TiO₂. The behavior of these two solids has been already described in ref. (15). In the case of TiO₂, the effects of hydrogen at 473 K and of vacuum at 673 K were based on:

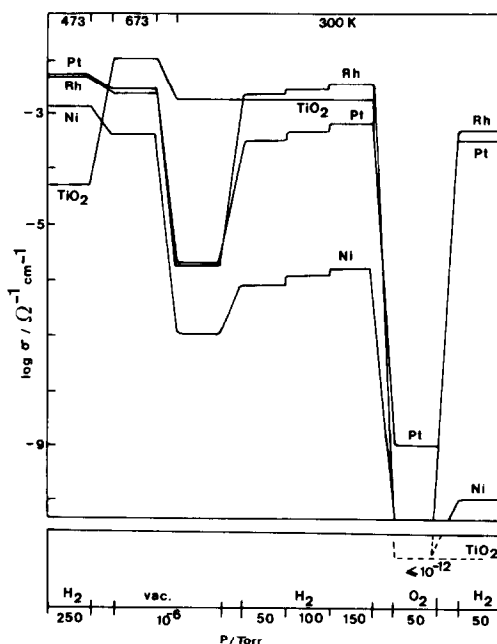


FIG. 1. Variations of the electrical conductivity of the LTR samples as a function of various sequences (lower x axis: atmospheres with pressures in Torr; upper x axis: temperature (K)).

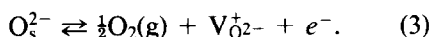
(i) the dehydroxylation of the surface and the subsequent formation of anionic vacancies V_{O2^-}



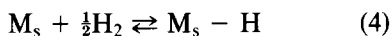
(ii) the ionization of the first electron of these vacancies



(iii) the loss of surface lattice oxygen creating additional singly ionized anionic vacancies



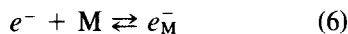
In the case of Pt/TiO₂, the higher conductivity in H₂ at 473 K has been explained by a catalytic effect of the metal which (i) chemisorbs dissociatively molecular hydrogen



where M_s represents a surface metal atom, and (ii) enables the migration of atomic hydrogen onto the support (spillover effect) via the formation of OH_s⁻ groups with surface lattice anions O_s²⁻ with release of one free electron per proton formed



The lower conductivity of Pt/TiO₂ under vacuum at 673 K (Fig. 1) was interpreted in terms of an electron enrichment of the metal due to the alignment of the Fermi levels in agreement with the respective values of the work functions: ϕ (reduced TiO₂) 4.6 eV (24); ϕ_{Pt} = 5.36 eV. This electron transfer can be symbolized by



where e_M^- represents an excess electron in the metal.

Since equilibrium (6) is exothermic because of the electron affinity of the metal, it will be displaced to the right by decreasing the temperature. The partial depletion of TiO₂ in free electrons by the metal enables the samples to conserve a semiconductor behaviour in the whole temperature range investigated (300–673 K) as evidenced by the constant activation energy of conduc-

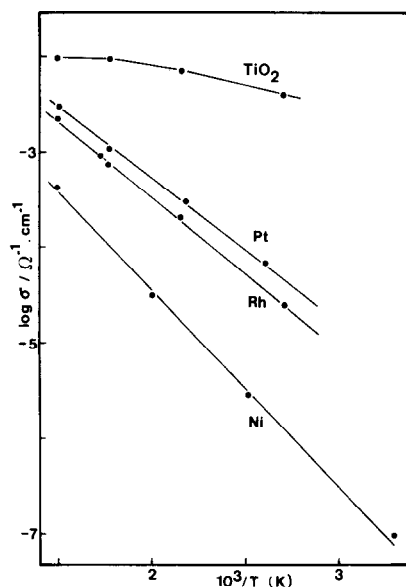


FIG. 2. Arrhenius plot of the electrical conductivity σ under vacuum after reduction in H₂ (250 Torr) at 473 K and evacuation at 673 K.

tion (Fig. 2) in contrast with pure TiO₂ which behaves as a quasi-metallic conductor with a very small and variable apparent activation energy of conduction. The variations of the electrical conductivity σ of Pt/TiO₂ measured at steady state as a function of hydrogen pressure follow an isotherm law in $P_{H_2}^{1/2}$:

$$\sigma = \sigma_0 + kP_{H_2}^{1/2} \quad (7)$$

which can be accounted for by Eqs. (4)–(6) with the condition $d\sigma/dt ad[e]/dt = 0$ as previously discussed in ref. (15).

Finally, the introduction of oxygen produces a strong electron capture by reoxidation of the support [Eq. (–3)], evidenced by a high decrease in electrical conductivity (Fig. 1). The smaller decrease for σ_{Pt/TiO_2} was explained by a higher content in deeper defects which could not be reoxidized at room temperature by oxygen because of its low diffusion coefficient.

Rh and Ni/TiO₂: Rhodium. The results are qualitatively the same as for platinum, thus confirming the model previously proposed. Actually, the respective values of

the work functions of reduced titania (4.6 eV) and of Rh (4.98 eV) (25) as well as the requirement of an alignment of the Fermi levels, are in agreement with an electron migration from the support to the metal as for platinum [Eq. (6)]. The consequent electron deficit of titania allows it to conserve a semiconductive behavior under vacuum between 673 and 300 K, i.e., with a constant activation energy of conduction, despite its high reduction level and in contrast with titania alone (see the Arrhenius plot in Fig. 2).

The same isotherm variations $\sigma = f(P_{H_2})$ [Eq. (7)] are found for hydrogen spillover at room temperature showing that Eqs. (4)–(6) are still observed.

When oxygen is introduced after a brief evacuation, the hydrogen titration occurs on the metal (see Table 1), while the electrical conductivity drops by several orders of magnitude (Fig. 1). This is due essentially to the reoxidation of titania which fills its anionic vacancies [Eq. (–3)], thus scavenging the free electrons of the oxide, including those restituted by the metal to its support.

Finally the last hydrogen introduction shows that, once the oxygen titration is accomplished, the surface metal atoms are covered with dissociatively chemisorbed hydrogen which can then spill over the surface of the support with the same isotherm law [Eq. (7)].

Nickel. According to Fig. 1, the nickel sample behaves qualitatively as Pt and Rh. The nickel work function ($\phi_{Ni} = 5.03$ eV) is also compatible with an electron enrichment of the metal due to the Fermi level alignment. The linear Arrhenius plot of Fig. 2 confirms the semiconductor nature of Ni/TiO₂—in contrast with TiO₂—linked to a partial depletion in free electrons of the support. However, some differences with Pt and Rh can be evidenced: the initial reduction by H₂ (see Fig. 1, phase 1) is less important, the establishment of the electrical conductivity steady state is very slow at room temperature, and the effect upon conductivity of the second exposure to hydro-

gen which corresponds to the titration of oxygen by H₂ is very small in comparison with Pt and Rh.

The two first phenomena can be explained by the lower dispersion of nickel whose crystallites ($d \approx 13.5$ nm) can only affect the support particles which they are in contact with, since there is statistically only 0.15 Ni particle present per particle of TiO₂, instead of ~ 10 for both Pt and Rh samples.

The third phenomenon is directly connected with the partial irreversibility of the chemisorption of oxygen which cannot be stoichiometrically titrated by hydrogen.

Sample Reduced at 773 K (HTR Samples). SMSI State

The same sequences as in Fig. 1 were repeated on the same samples after reduction at 773 K in order to observe the modifications induced by the strong metal-support interactions.

At 773 K under 250 Torr H₂, all three metal catalysts have the same high conductivity level (Fig. 3). Note that σ_{TiO_2} is very close to σ_{M/TiO_2} , which tends to indicate that the thermal reduction of pure titania is very high in these conditions and almost independent of the presence of a supported metal.

The evacuation of hydrogen at 773 K produces only very small variations of σ with the same tendencies as for LTR samples (Fig. 1), i.e. (i) with an increase of σ_{TiO_2} , due to a supplementary creation under vacuum of anionic vacancies [Eq. (3)] and (ii) with a decrease of σ_{M/TiO_2} due to an electron transfer to the metal [Eq. (6)]. When the temperature is lowered, all the solids behave as quasimetallic conductors ($d\sigma/dT \approx 0$) between 773 and 473 K, whereas below 473 K the apparent activation energy of conduction increases (Fig. 4). This partial recovery of a semiconductive behavior at the lower temperatures can be accounted for by a progressive exhaustion of TiO₂ in free electrons because of the simultaneous enrichment of the metal due to the shift to

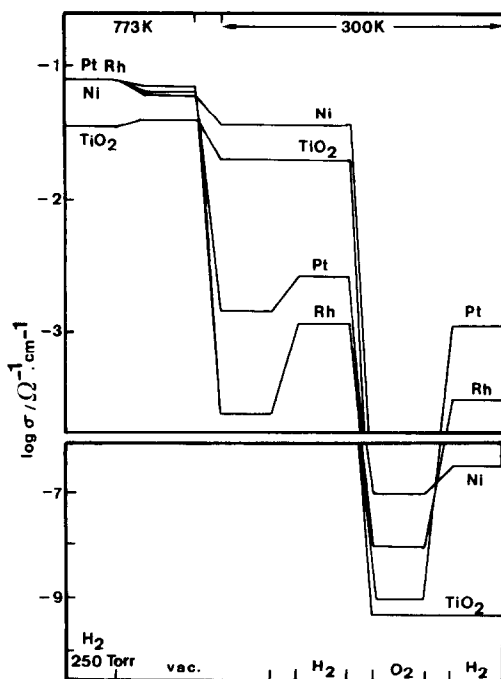


FIG. 3. Variations of the electrical conductivity of HTR samples as a function of various atmospheres (pressures equal to 50 Torr otherwise stated).

the right side of reaction (6) which is exothermic and favored when T is decreased. According to Fig. 3, qualitatively, the *relative* extent of this electron transfer between the support and the metal seems to occur in the sequence $Rh > Pt \gg Ni$.

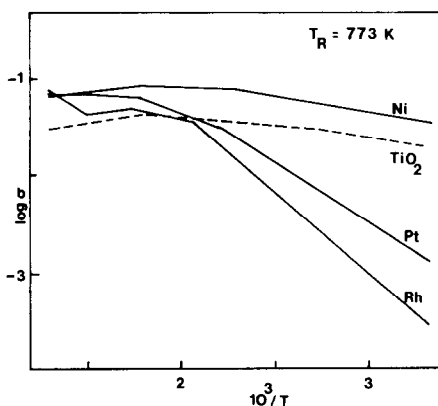


FIG. 4. Arrhenius plot of the electrical conductivity σ under vacuum after reduction in H_2 (250 Torr) and evacuation at 773 K.

The subsequent hydrogen introduction only increases the conductivity of the solids which are able to chemisorb some H_2 in the SMSI state, namely Pt and Rh samples as evidenced by Fig. 1 and Table 1. For these two metals, the same isotherm law [Eq. (7)] is observed. On the contrary, the conductivity of Ni/TiO₂ remains unaffected by hydrogen pressure ($d\sigma/dP_{H_2} = 0$). This means that reactions (4) and (5) do not occur because of a complete inhibition of hydrogen chemisorption on nickel due to an SMSI effect at its maximum level. This behavior is identical to that of a Pt sample with a low loading (0.5%) (15), which tends to show that nickel would be specially sensitive to SMSI. In particular, one can notice that Ni dispersion or percentage exposed deduced from H_2 chemisorption on a LTR sample is substantially lower than that based on magnetic measurements which would mean that, even after a low temperature treatment, a partial SMSI state exists which reaches completion after reduction at 500°C.

The subsequent introduction of oxygen drastically decreases the conductivities of all samples, following the same reoxidation process of TiO₂ described above for LTR samples [Eq. (-3)].

Finally a new introduction of H_2 (Fig. 3) increases again the conductivities of all the metal containing samples, including nickel which exhibits, however, very slow σ variations as for the LTR sample. This confirms that the SMSI state which affects H_2 chemisorption is destroyed, at least partially, by an exposure to oxygen at room temperature.

CONCLUDING REMARKS

By measuring *in situ* the electrical conductivities of titania deposited Pt, Rh, and Ni catalysts and comparing them to that of the bare support, it has been possible to establish the balance in free electrons between the metal and its support in the normal and SMSI states respectively.

The deposited metals favour titania's sur-

face reduction in H_2 by initiating a spillover process of atomic hydrogen which generates OH groups able to desorb as water molecules, thus creating superficial anionic vacancies. Under vacuum, free electrons are able to migrate from the support to the metal through the metal-oxide interface because of the alignment of the Fermi levels which operates in conformity with the respective work function values.

Since titania's work function ϕ_{TiO_2} decreases when the oxide is more reduced, passing from 5.5 eV in the oxidized state to 4.6 eV in the reduced one (24), a higher reduction temperature will render easier the electron migration to the metal which leads to the conclusion that the existence of the SMSI state of M/TiO₂ catalysts corresponds to a strong electron excess within the metal. If the establishment of a metal-hydrogen bond consists in an electron sharing between a H atom and an unfilled *d*-band surface metal atom, a progressive filling of these *d*-orbitals will gradually affect the chemisorptive properties of the metal with respect to H_2 as recently discussed for NO (26). Qualitatively, the electronic configuration of Ni, Rh, and Pt atoms would partially and progressively resemble that of their *d*¹⁰ neighbors of the 1B-group, namely Cu, Ag, and Au, which are known as poor hydrogen adsorbents and poor catalysts for hydrogen involving reactions (19). From electrical conductivity it is not possible to quantitatively estimate the relative electron enrichment *e*/*M* of the metal, but values as high as 0.6 and 0.13 electron/metal atom were given for Pt (10) and Ni (11, 12) respectively from spectroscopic observations. However, we suggest that an important electron transfer, i.e., with a ratio *e*⁻/*M* close to unity, is not necessarily required to induce a SMSI effect if the excess of electrons suffices to partially counteract the electron sharing during H_2 chemisorption.

In Table 2, the SMSI intensity has been tentatively quantified by the ratio *R*, denoted "inhibition factor," of the hydrogen

TABLE 2
Inhibition Factor *R* for Various Catalysts with Different Crystallite Size^a

	Metal content (wt%)	<i>d</i> (nm)	Inhibition factor <i>R</i> $R = n_{H_2(ads)LTR}/n_{H_2(ads)HTR}$
Pt/TiO ₂	5	2	7
Pt/TiO ₂	0.5	2	∞
Ni/TiO ₂	5	13.5	∞
Rh/TiO ₂	5	3.5	2.8

^a *R* is defined as the ratio of the number of H_2 molecules chemisorbed on the LTR sample to the number of H_2 molecules chemisorbed on the HTR sample.

quantities chemisorbed on LTR and HTR samples. For the same given weight percentage (5%), the SMSI effect follows the order Ni > Pt > Rh. According to the metal loading, the total amount of Ni atoms on the support is close to 2 times that of Rh and 3 times that of Pt. For the same amount of electron transferred from TiO₂ to the metal particles, each nickel particle would have much less electrons than Pt and Rh particles. Therefore, one would expect that Ni shows the least SMSI effect. Three reasons can be invoked to account for the opposite result obtained: (i) further Ni agglomeration, (ii) a much lower dispersion of Ni, and (iii) a special aptitude of nickel to SMSI. The first reason, commonly observed in SMSI, cannot apply in the present case since all solids have been previously treated in H_2 at high temperature (480°C) during preparation and before characterization. A further treatment in H_2 at a comparable temperature (500°C) does not modify the mean size of Ni particles as observed by magnetic measurements (see for instance Table 1 in ref. (27)). For the two other reasons, it is difficult to separate their respective effect upon SMSI. One must consider the possibility that the morphology of the metal particles depends on the extent of reduction of the titania surface. According to Fig. 3 (step 1), all three metals give the same σ level, i.e., the same reduction degree for titania. However different morphologies may be favored for different

kinds of metals. This is true for nickel which could be obtained only as large particles with the same reduction procedure as for Pt and Rh. Consequently, because of this textural factor (big particles) and of its tendency to be irreversibly oxidized, nickel should be considered as a special case among the three metals studied.

The inhibition factor of rhodium is the smallest, in conformity with the weaker sensitivity to SMSI generally observed for this metal (20). This can be explained by a greater number of unfilled *d*-orbitals per metal atom, which makes more difficult a progressive electron saturation responsible for the decrease of H₂ chemisorption.

For a given metal (see Pt in Table 2), with constant dispersion and crystallite size (2 nm), a decrease in the metal content by a factor of 10 makes the metal move more easily to a complete SMSI because of an equivalent number of free electron available from the support for a 10 times smaller total number of metal atoms.

The restoration of a normal behavior of the metal after an exposure to oxygen at room temperature is then easily explained with the back-donation of excess electrons by the metal to its support whose reoxidation is highly electrophilic.

The electronic explanation of SMSI does not exclude systematically the occurrence of other simultaneous phenomena which could be also responsible for SMSI such as the possible migration of TiO_x on the metal particles (6–8). However, since the electrical conductivity measured reflects essentially that of the support, as recalled in the experimental part, its variations cannot be physically perturbed—and hence accounted for—by the presence of TiO_x suboxide located on the metal grains, except if an electron exchange is involved via the metal-support interface.

To summarize, when a metal is in SMSI conditions, it is enriched with excess electrons coming from its reduced support. However, other concepts such as the exact influence of the nature of the metal have to

be considered with care since important factors like dispersion, particle size, and morphology can strongly modify the extent of SMSI upon chemisorption and catalysis (see for instance nickel).

Some catalytic reactions involving H₂ are not inhibited by SMSI as for instance CO methanation. This can be easily accounted for, if one considers, as in refs. (28, 29), that only a small fraction of adsorbed hydrogen atoms is reacting. The hydrogen pool adsorbed in the SMSI conditions is then sufficient, if not nil, to supply the reaction with active hydrogen. Moreover one has to take into account the reaction temperature which, if it is high enough, will favor the back-reaction of electron transfer [Eq. (–6)], thus limiting the electronic cause of the SMSI effect.

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REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100**, 170 (1978).
2. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211**, 1121 (1981).
3. Tauster, S. J., and Fung, S. C., *J. Catal.* **56**, 29 (1978).
4. Sexton, B. A., Hughes, A. E., and Foger, K., *J. Catal.* **77**, 85 (1982).
5. Bor-Her Chen, and White, J. M., *J. Phys. Chem.* **86**, 3534 (1982).
6. Santos, J., Phillips, J., and Dumesic, J. A., *J. Catal.* **81**, 147 (1983).
- 7a. Resasco, D. E., and Haller, G. L., *J. Catal.* **82**, 279 (1983).
- 7b. Sadeghi, H. R., and Henrich, V. E., *J. Catal.* **87**, 279 (1984).
8. Chung, Y. W., Xiong, G., and Kao, C. C., *J. Catal.* **85**, 237 (1984).
9. Herrmann, J.-M., and Pichat, P., in "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.*, Eds.), p. 27. Elsevier, Amsterdam, 1982.
10. Bahl, M. K., Tsai, S. C., and Chung, Y. W., *Phys. Rev.* **B21**, 1344 (1980).
11. Kao, C. C., Tsai, S. C., Bahl, M. K., and Chung, Y. W., *Surf. Sci.* **95**, 1 (1980).

12. Kao, C. C., Tsai, S. C., and Chung, Y. W., *J. Catal.* **73**, 136 (1982).
13. Sanchez, J., Koudelka, M., and Augutynski, J., *J. Electroanal. Chem.* **140**, 161 (1982).
14. Fung, S. C., *J. Catal.* **76**, 225 (1982).
15. Herrmann, J.-M., and Pichat, P., *J. Catal.* **78**, 425 (1982).
16. Horsley, J. A., *J. Amer. Chem. Soc.* **101**, 2870 (1979).
17. Bor-Her Chen, and White, J. M., *J. Phys. Chem.* **87**, 1327 (1983).
18. Disdier, J., Herrmann, J.-M., and Pichat, P., *J. Chem. Soc. Faraday Trans. 1* **79**, 651 (1983).
19. Libby, W. F., *Catal. Rev. Sci. Eng.* **23**, 615 (1981).
20. Bond, G. C., in "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.*, Eds.), p. 1. Elsevier, Amsterdam, 1982.
21. Herrmann, J.-M., Vergnon, P., and Teichner, S. J., *J. Catal.* **37**, 57 (1975).
22. Choplin, A., Dalmon, J. A., and Martin, G. A., *C.R. Acad. Sci. Paris* **293**, 137 (1981).
23. Menon, P. G., and Froment, G. F., *Appl. Catal.* **1**, 31 (1981).
24. Chung, Y. W., Lo, W. J., and Somorjai, G. A., *Surf. Sci.* **64**, 588 (1977).
25. Nieuwenhuys, B. E., Bouwman, R., and Sachtler, W. M. H., *Thin Solid Films* **21**, 51 (1974).
26. Fang, S. M., and White, J. M., *J. Catal.* **83**, 1 (1983).
27. Turlier, P., Dalmon, J. A., and Martin, G. A., in "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.*, Eds.), p. 203. Elsevier, Amsterdam, 1982.
28. Vannice, M. A., Twu, C. C., and Moon, S. H., *J. Catal.* **79**, 70 (1983).
29. Vannice, M. A., and Twu, C. C., *J. Catal.* **82**, 213 (1983).