



## **CHAPTER IV**

### **SUPPORTS AND METAL-SUPPORT INTERACTIONS IN CATALYST DESIGN**

#### **4.1 Introduction [43]**

Catalysts involving group VIII metals are usually prepared by dispersing the metal onto a high surface area support, to assure that a high proportion of the metal atoms is available for interaction with gaseous reactants. For most industrial applications, supports are sought which possess high surface area, high thermal and high chemical stability, and high mechanical strength. While it was originally thought that the support was simply an inert carrier of the active component, work conducted in the late 1950s by Schwab and Solymosi revealed that significant changes in the catalytic properties of a metal could be achieved by varying support composition. Extensive evidence supporting this view has appeared over the past 20 years, engendered by an interest in the so-called strong metal-support interaction (SMSI) reported by Tauster and coworkers at Exxon.

#### **4.2 Classification of metal-support interaction**

For a given metal, variations in support composition can influence the size and morphology of the supported metal particles, the surface electronic properties of the particles and the nature of the sites present at the points of contact between the metal and the support. Only the latter two of these three effects should properly be attributed to metal-support interactions, since changes in particle size and morphology can be achieved in other way (e.g., sintering, redispersion). Thus, we might refer to changes in particle size and morphology with support composition as a nonspecific effect and refer to all other changes as specific effects of support composition.

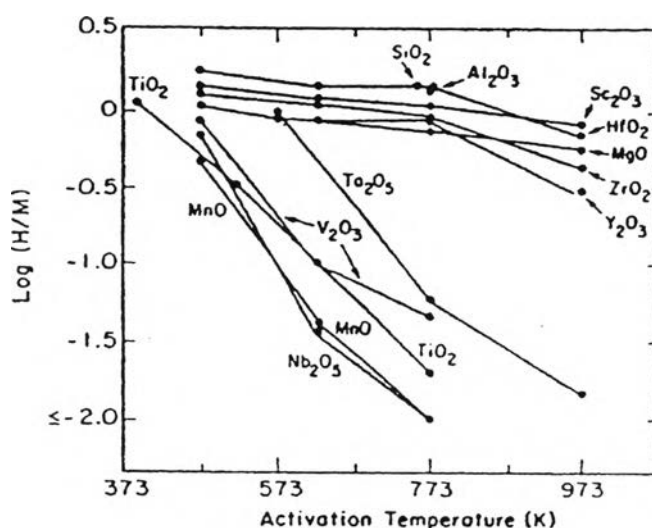
The distinctions between specific and nonspecific effects of support composition are particularly important to recognize for structure-sensitive reactions. For such reaction, the overall changes in the activity and selectivity of a given metal upon changing support may be due only in part to the alteration of support composition, the balance being due to

changes in particle size and/or morphology. To properly assess the influence of metal-support interactions for structure-sensitive reaction, it is therefore, necessary to know a priority the degree to which specific activity and selectivity are influenced by metal dispersion. Unfortunately, though, much of the recent literature on metal-support interactions has failed to distinguish between the effects of particles size and specific supports. This has made it difficult to compare the results of different authors and to properly quantify the magnitude of specific support effect for various metal-support systems.

### **4.3 Influence of metal-support interactions on adsorptive properties**

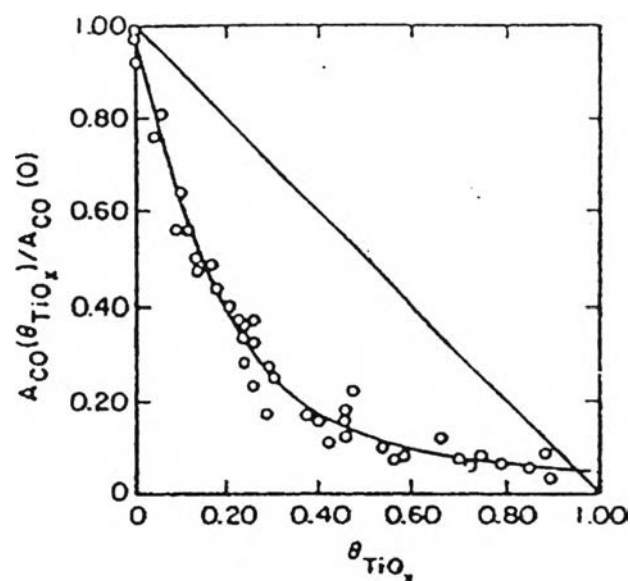
The influence of metal-support interactions on the chemisorption of H<sub>2</sub> and CO has been investigated for virtually all of the group VIII metals. It is generally observed that an increasing degree of metal-support interaction is manifested by a decrease in H<sub>2</sub> and CO chemisorption capacity with increasing temperature of catalyst reduction. An illustration of this effect is shown in Figure 4.1 for H<sub>2</sub> chemisorption on Ir. It is significant to note that the strongest suppressions of H<sub>2</sub> chemisorption is observed for the oxides of Nb, Mn, V, Ta, and Ti, all of which can be reduced more readily than the remaining oxides listed in Figure 4.1. This correlation suggests that the creation of anionic vacancies in an oxide facilitates the migration of oxide moieties onto the surface of the supported metal particles. The validity of this interpretation is supported by the work of Resasco and Haller, which shows that the chemisorption capacity of Rh/TiO<sub>2</sub> decreases proportionally with the surface diffusion of TiO<sub>x</sub> species. Further substantiation of the decoration model of chemisorption suppression comes from the observation that similar effects are observed with small as well as large metal particles. If, for example, the modification in chemisorption behavior were due solely to interactions occurring at the point of metal-support contact, then the influence of such interactions on large particles would be expected to be smaller than that observed for small particles.

The means by which metal oxide moieties present on the surface of metal particles alter the chemisorptive properties of the metal particles is not yet fully understood. It is obvious that the primary effect is simple site blockage, but there is now growing evidence that metal sites adjacent to metal oxide moieties might also be affected. An illustration of this is shown in Figure 4.2 for the case of  $\text{TiO}_x$  deposited on the surface of a Rh foil, with increasing  $\text{TiO}_x$  coverage, the CO chemisorption capacity falls off more rapidly than would be predicted by simple site blockage.



**Figure 4.1** Hydrogen chemisorption on Ir supported on various oxides as a function of activation in hydrogen for 1 hr at various temperature.  $\text{H}/\text{M}$  = atomic ratio of hydrogen adsorbed to Ir in catalyst

Levin and co-worker have demonstrated that the data can be explained by assuming that CO chemisorption is suppressed on those sites that are immediately adjacent to the  $\text{TiO}_x$  islands covering the surface of the Rh foil, in addition to those Rh site covered by the  $\text{TiO}_x$  islands. The authors postulate that the Rh sites along the perimeter of the  $\text{TiO}_x$  islands are affected by a perturbation in the density of states at the Fermi level, along the lines described by Feibelman and Hamann.



**Figure 4.2** Normalized CO adsorption capacity of a Rh foil decorated with  $\text{TiO}_2$ , as a function of  $\text{TiO}_2$  coverage. Adsorption temperature 298 K

In addition to altering the chemisorptive capacity of a metal oxide moieties may also alter the distribution of adsorption states. Two cases are illustrated in Figures 4.3 and 4.4. In both instances the chemisorptive properties of  $\text{Pd}/\text{SiO}_2$  have been altered by the promotion on the catalyst with  $\text{TiO}_x$ . It is evident from both figures that with increasing addition of  $\text{TiO}_x$ , the initial level of CO chemisorption, given by  $\theta_{\text{H}}$  or  $\theta_{\text{CO}}$ , decreases. While  $\text{TiO}_x$  promotion appears to have no effect on the distribution of  $\text{H}_2$  adsorption states, the distribution of CO adsorption states is affected significantly. The most pronounced effect is the preferential suppression of CO chemisorption on Pd (100) surfaces, characterized by the peak at 630 K. A further effect of  $\text{TiO}_x$  promotion is the shift in the onset of  $\text{CO}_2$  formation to lower temperatures. Since  $\text{CO}_2$  is formed via CO dissociation and subsequent reaction of the released oxygen atom, the downscale shift in the  $\text{CO}_2$  peak is evidence of an enhancement in the case of CO dissociation.

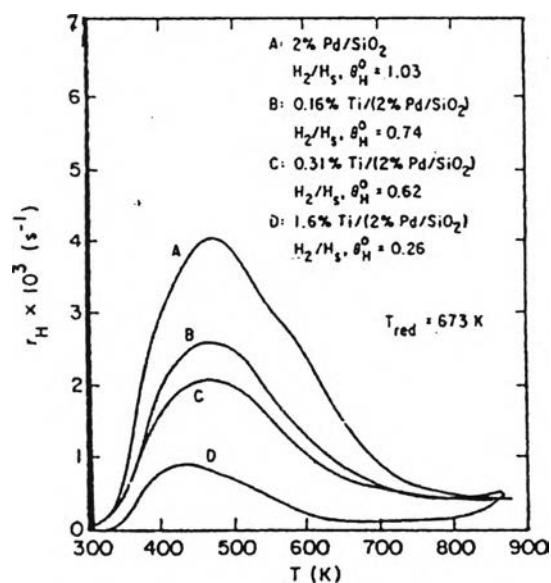


Figure 4.3 Temperature-programmed desorption spectra for H<sub>2</sub> adsorbed on Pd/SiO<sub>2</sub> and TiO<sub>2</sub>-promoted Pd/SiO<sub>2</sub>

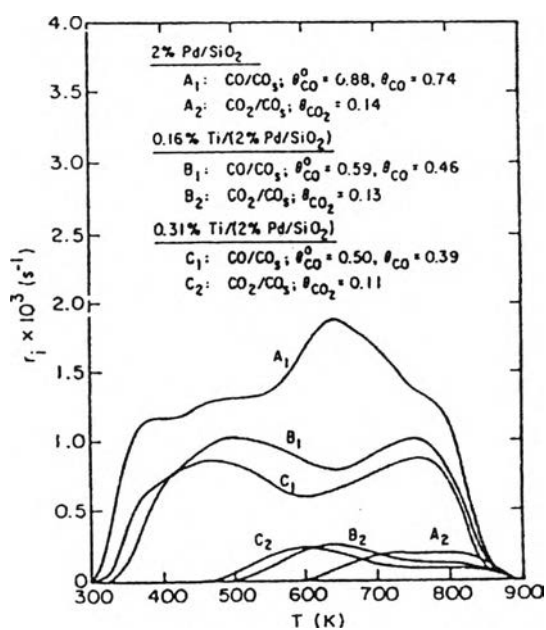
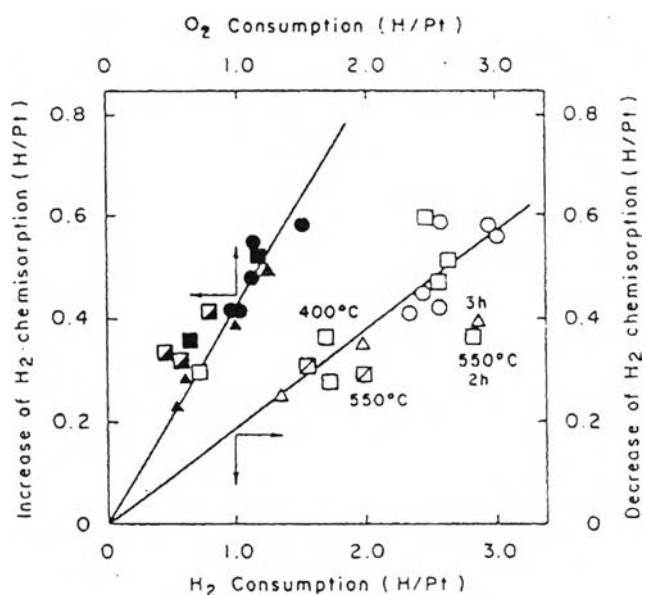


Figure 4.4 Temperature-programmed desorption spectra for CO adsorbed on Pd/SiO<sub>2</sub> and TiO<sub>2</sub>-promoted Pd/SiO<sub>2</sub>

#### 4.4 Strong metal-support interaction [44]

It was observed that the reduced support interacts so strongly with noble metal that it lowers the precious metals  $H_2$  chemi-adsorption capacity at room temperature.

Figure 4.5 shows the result of reduction of oxidation of Pt-supported on  $TiO_2$  at 400-500 °C under hydrogen or oxygen atmosphere. It is evident that as  $TiO_2$  reduces, the  $H_2$  uptake decreases; as reduced  $TiO_2$  is oxidized, the  $H_2$  uptake increases. This is also observed for  $Pt/Al_2O_3$  reduced and oxidized at 400-500 °C in hydrogen or oxygen atmosphere, respectively. When  $Pt/Al_2O_3$  or  $Pt/TiO_2$  are reduced at high temperatures, the hydrogen adsorption capacity for Pt is greatly reduced. This is known as the SMSI phenomenon (strong metal support interaction). There are two explanations for SMSI:



THE DECREASE OF  $H_2$  CHEMISORPTION VS THE AMOUNT OF THE  $H_2$  CONSUMPTION AND THE INCREASE OF  $H_2$  CHEMISORPTION VS THE AMOUNT OF  $O_2$  CONSUMPTION. UNLESS OTHERWISE STATED, EACH TREATMENT (IN  $H_2$  AT 500°C AND IN  $O_2$  AT 400°C) WAS CARRIED OUT AT THE GAS PRESSURE OF 50 TORR FOR 1h (  $\blacksquare$  ; THE GAS PRESSURE WAS ABOUT 5 TORR )

**Figure 4.5** Result of reduction of oxidation of Pt supported  $TiO_2$  at 400°C-500°C under hydrogen or oxygen atmosphere

1. Pt alloys with reduced a aluminum or titanium and losses its hydrogen adsorption capacity

2. The reduced titanium or aluminum oxide becomes an n-type electrical conductor (semiconductor or insulator) and transfers electrons to Pt. This reduces the hydrogen uptake capacity of Pt

The later explanation is preferred

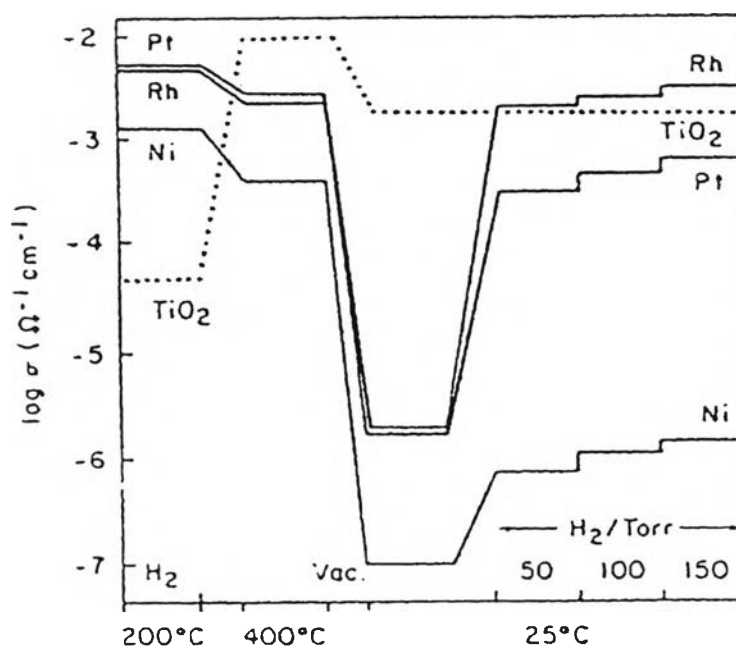
In another study, three samples were prepared by impregnation of TiO<sub>2</sub> with Pt, Rh, and Ni. A fourth sample was prepared without any metal. The electrical conductivity of the four samples was measured under the following conditions: catalyst treatment at 200°C temperature, 250 torr H<sub>2</sub> pressure, then evacuation at 400°C followed by reducing the temperature to 25°C, and finally introducing H<sub>2</sub> at 50, 100, and 150 torr pressure.

The data indicate that TiO<sub>2</sub>, after evacuation, behaved as degenerate semiconductor with low activation energy. However, metal, which is the primary source of hydrogen spillover, partially reduces the TiO<sub>2</sub> under hydrogen atmosphere. The hydrogen donates electrons to TiO<sub>2</sub> and increases conductivity. After evacuation at 400°C, the reverse takes place, and TiO<sub>2</sub> loses electrons, thus reducing conductivity due to reverse spillover. Reducing the temperature from 400°C to 25°C reduces conductivity by an order of magnitude. This is an activating process with activation energy of 8 kcal/mole. The addition of H<sub>2</sub> increases the conductivity at 25°C. Hydrogen behaves as a donor impurity and converts to H<sup>+</sup>, which accounts for the increased conductivity.

In the evacuation step at 400°C, hydrogen is removed by reverse spillover, and TiO<sub>2</sub>



conductivity decreases (see Figure 4.6). The reduced Pt/TiO<sub>2</sub> has high electron density and low hydrogen uptake capability. The reverse is true with an oxidized catalyst. This indicates that SMSI is due to increased electron density of TiO<sub>2</sub> and, possibly, the transfer of electrons to Pt crystallites.



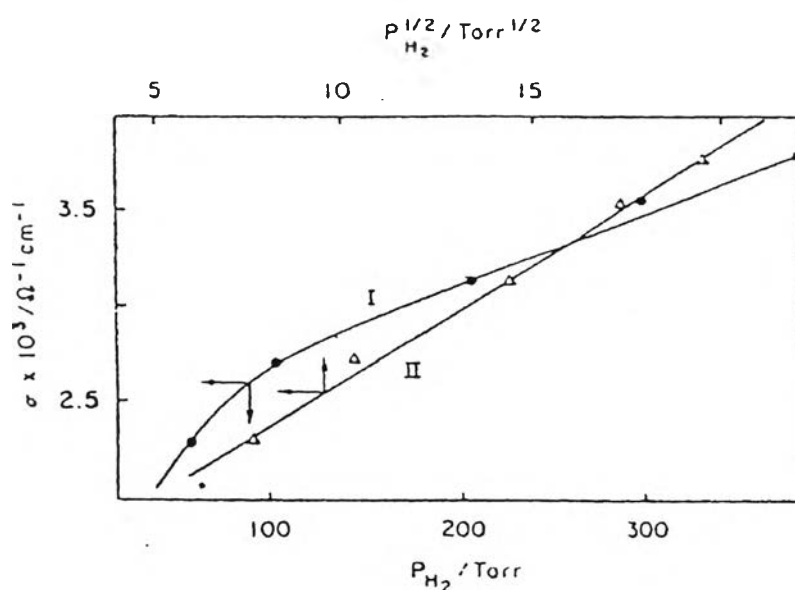
**Figure 4.6** Electrical conductivity of  $\text{TiO}_2$  and of Pt, Rh, and Ni/ $\text{TiO}_2$  under indicated conditions

Figure 4.7 shows Rh/ $\text{TiO}_2$  conductivity versus  $\text{H}_2$  (lower scale) and  $\text{H}_2^{1/2}$  (upper scale) partial pressure. The data confirm the theory that adsorbed H donates electrons to Rh/ $\text{TiO}_2$ . It has been shown that  $\text{TiO}_2$  surface is reduced by a beam of H atoms generated by a microwave discharge or by hydrogen spillover produced by Rh. In both case, the  $\text{TiO}_2$  surface is reduced. Reduced titanium oxide behaves as n-type semiconductor with increased electropotential (Fermi energy). The increase of electropotential and transfer of electrons to noble metal prevents the noble metal from adsorbing H at room temperature. This condition is favorable for the creation of SMSI between metal and  $\text{TiO}_2$ . SMSI has been observed between Pt/ $\text{Al}_2\text{O}_3$ , Pt/ $\text{ZnAl}_2\text{O}_3$  and others.

Strong metal-support interaction was reported in 1978 for Pd/ $\text{TiO}_2$ . The catalyst was reduced at  $500^\circ\text{C}$  in a hydrogen atmosphere. After evacuation, the catalyst was cooled to room temperature. It was found the Pd catalyzed the reduction of  $\text{TiO}_2$  with the result that there was a significant loss of  $\text{H}_2$  or uptake capacity. This property is also known as



SMSI. However, the SMSI does not affect catalytic activity significantly. The SMSI is normally associated with partial reduction of oxides and increase of their electron density of semiconductor or insulator oxides. SMSI occurs with other noble metals and most oxides and zeolites.



**Figure 4.7** Rh/TiO<sub>2</sub> conductivity isotherm as a function of  $P_{H_2}$ (I) and linear transform (II)

In the presence of spillover hydrogen, stoichiometric metal oxides reduce to a nonstoichiometric oxidation state. Some oxides lose all their oxygen and reduce to a metallic state. This depends on the temperature of reduction and the specific oxide. Hydrogen spillover lowers the reduction temperature of oxides significantly. Pt and Pd are most effective in this case. A large number of metal oxides have been reduced by spillover from Pt or Pd, at a much lower temperature than is the case when the reductant is molecular H<sub>2</sub>. The metals are Co<sub>3</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, VO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, Re<sub>2</sub>O<sub>7</sub>, CrO<sub>4</sub>, Ni<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, NiO, CuO, Cu<sub>2</sub>O, ZnO, SnO<sub>2</sub> and Ag<sub>2</sub>O. SMSI takes place between many metals and oxides. They usually do not lose their catalytic activity, but they may lose CO and H<sub>2</sub> uptake capability. It is important to mention that reduced metal oxides have oxygen vacancies, and their SMSI property frequently is reversed with oxidation.

#### 4.5 Influence of reduced oxides on the properties of transition metals [45]

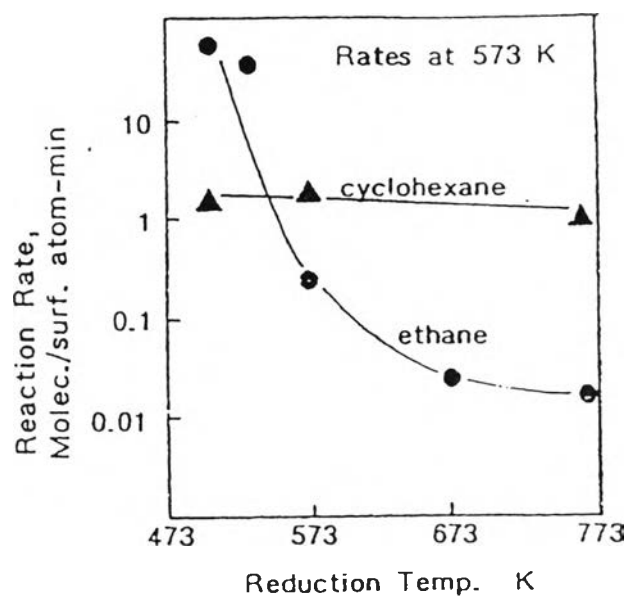
It was first reported about twenty years ago that certain transition metal oxides can have a dramatic effect on the chemisorptive and catalytic properties of metals when they are in close contact with the metal. This effect was originally termed Strong Metal-Support Interaction, but is currently referred to as decoration effect. The first report of this effect was on the suppression of hydrogen and carbon monoxide adsorption capacity of noble metals. It has been found that when a noble metal is supported on  $\text{TiO}_2$ , the material chemisorbs  $\text{H}_2$  or  $\text{CO}$  at a stoichiometry of roughly one H atom or  $\text{CO}$  molecule per surface exposed noble metal atom, if the material is reduced at  $200^\circ\text{C}$ . If the material is reduced at  $500^\circ\text{C}$ , its ability to chemisorb H or  $\text{CO}$  is essentially completely suppressed. This is illustrated with typical data in Table 4.1. It was later found that this effect is not unique to  $\text{TiO}_2$  as the support. Figure 4.8 shows the extent of suppression of the hydrogen chemisorptive capacity as a function of reduction temperature of various oxide supports. In general, oxides that are readily reducible at intermediate temperatures all show this effect. The effect is reversible. That is, reoxidation with oxygen followed by a low temperature reduction at  $200^\circ\text{C}$  restores most of the adsorptive capacity.

The influence of the decoration effect on the catalytic properties of the metal depends on the reaction. It can be seen that the decoration effect suppresses the activity of Pt for benzene hydrogenation and cyclohexane dehydrogenation, but enhances the activity in  $\text{CO}$  hydrogenation. The activity of the Fe catalyst in ammonia synthesis is slightly decreased, but the activation energy is greatly increased. In the case of butane hydrogenolysis, the selectivity and the activity are both altered.

In the past, it was thought that this effect was not due to the formation of alloy (e.g., Pt-Ti alloy). The encapsulation of the metal by the support, sintering of the metal, poisoning of metal by impurities in the support, or simply electron transfer between the bulk of the support and the bulk of the metal crystallite. These conclusions follow from a variety of experimental observations.

**Table 4.1** Suppression of H<sub>2</sub> adsorption capacity due to decoration effect

2% Metal on TiO <sub>2</sub> Supported	H atom adsorbed/Total metal atoms	
	Reduction at 200°C	Reduction at 500°C
Ru	0.23	0.06
Rh	0.71	0.01
Pd	0.93	0.05
Os	0.21	0.11
Ir	1.6	0
Pt	0.88	0

**Figure 4.8** Ethane hydrogenolysis and cyclohexane dehydrogenation on Rh/TiO<sub>2</sub> catalyst as a function of catalyst reduction temperature

For example, transmission electron microscopic studies as well as X-Ray diffraction show no evidence of sintering, and Mössbauer spectroscopy shows that the bulk of the

iron crystallites is the same whether or not the sample is exhibiting the decoration effect, even though the titania support near the metal crystallite is reduced from  $\text{TiO}_2$  to  $\text{Ti}_4\text{O}_7$ .

The current picture is that the origin of the effect is the migration of small particles of reduced titania (or other reduced support) onto the metal crystallites to “decorate” the metal surfaces. These decorating reduced oxide particles may partially block the metal surfaces from gas molecules, affect the electronic structure of the neighboring metal atoms, or provide an oxide-metal interface for interaction with molecules. Depending on the reaction, one or more of these effect may participate to affect the observed characteristics of the reaction.

That decoration is the physical picture was first suggested by Dumesic on the Fe/ $\text{TiO}_2$  system. Using Mössbauer spectroscopy, it has been observed that the bulk properties of Fe crystallites are the same whether they are in the decorated state or not. Thus the effect must be a surface phenomenon. It is then proposed that titania species cover the iron crystallites. Such a decoration model would suggest that the extent of the effect should depend on the time allowed for the reduced oxide particles to migrate onto the metal crystallites and the interface between the metal and the oxide. These have been confirmed. It is observed that using the rate of ethane hydrogenolysis as a measure, the extent of the decoration effect depends linearly on the square root of the reduction time, which is characteristic of diffusion processes. For a given reduction time, the hydrogenolysis activity decreases as the inverse of the particle diameter. Finally, the increasing suppression of the hydrogenolysis activity as the reduction time increases is found to parallel a similar suppression by the addition of copper to a nickel catalyst, which is interpreted by the breaking-up of nickel ensembles on the surface by copper atoms. Thus the data are consistent with the model that the surface metal ensembles are broken up by reduced titania particle decorating the surface.

It fourteen year ago, it has been further proposed that the metal-oxide interaction occurs through the interaction of metal atoms with oxygen ion lattice vacancies in the reduced oxide. At temperatures sufficiently high to induce the decoration effect, the oxide support is reduced so that it has a high concentration of anion vacancies. The high

concentration of anion vacancies enhances the diffusion of metal atoms into the near-surface region of the bulk, and results in the formation of a raft-like metallic cluster covered by a thin (atomic) layer of the support. When the support is reoxidized, the anion vacancies are filled, driving the metal atoms back to the surface.

When titania particles are deposited on model catalysts of a Ni (111) single crystal surface or a Pt foil, a similar suppression of the H<sub>2</sub> or CO chemisorption capacity is observed which is similar to that resulting from high temperature reduction of supported metals. Enhanced catalytic activity in CO hydrogenation has also been observed on these low surface area catalysts. In the case of Pt foil, the activation energy is reduced from 126 to 80 kJ/mole. Furthermore, a small amount of deposited TiO<sub>x</sub> particles is found to enhance the methanation of Ni. At an optimum coverage of 8%, the activity is four times that of a clean Ni surface. On the other hand, complete suppression of the chemisorptive capacity requires complete coverage of the metal surface by the oxide particles.

The extent of electron transfer between the metal and the decorating particles is not established. For example, a study of Pt crystallites supported on a TiO<sub>2</sub> single crystal surface by XPS and AES suggests electron transfer from TiO<sub>2</sub> to Pt, while a XANES study suggests electron transfer from Pt to TiO<sub>2</sub>.

The influence of the decorating effect on the heat of absorption depends on the system. On Pt supported on titania, the effect results in a decrease in the initial heat of absorption of H<sub>2</sub> from 92 to 82 kJ/mole, but no change for CO absorption. The integral heats of absorption of both CO and H<sub>2</sub> are substantially reduced. However, the integral heat of absorption of CO and H<sub>2</sub> on Pd is not affected.