

Strong Interactions in Supported-Metal Catalysts

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Supported-metal catalysts are among the most important materials in heterogeneous catalysis. In such large-volume applications as gasoline octane improvement, manufacture of edible fats and oils, and automotive exhaust purification, the catalyst consists of small particles of metal dispersed on the internal

particles inhibits their agglomeration.

Clearly the primary function of the support is physical in nature, and effective dispersion is not dependent on any degree of metal-support interaction. Nevertheless, the potential for such interaction, in view of the close association of these phases, has long been rec-

Summary. Many commercially important catalysts consist of small metal particles dispersed on inorganic oxide surfaces. Although in most cases there is no significant interaction between the metal and the support, strong bonding can be demonstrated in a recently discovered class of supported-metal catalysts. These cases typically involve group VIII metals dispersed on transition metal oxides whose surfaces can be reduced to form cations with lower valences. Spectroscopic measurements indicate that an electron is transferred from the cation (such as Ti^{3+} or Nb^{4+}) to the metal particle. This, in turn, leads to profound changes in the catalytic and chemisorption properties and the morphology of the metal particles.

surface of a porous inorganic oxide such as alumina. Support oxides typically have surface areas of 200 square meters per gram or more. Thus, if a precursor salt of the metal can be effectively distributed over this area (say, by solution impregnation) and then decomposed, metallic particles as small as 10 angstroms will result. In the case of costly materials, such as noble metals, small particles are economic necessities since they represent a larger surface-to-volume ratio and thus greater catalytic utilization of the metal. Maintenance of this dispersion under severe processing conditions is another function of the support, since the separation of the metal

particles inhibits their agglomeration. Clearly the primary function of the support is physical in nature, and effective dispersion is not dependent on any degree of metal-support interaction. Nevertheless, the potential for such interaction, in view of the close association of these phases, has long been recognized.

Schwab and colleagues (1) in particular demonstrated that in certain cases the catalytic activities and activation energies associated with supported metals could indeed be influenced by the substrate. In this article we discuss a newly discovered class of metal-support interactions. The interactions appear to differ significantly in type and degree from those previously reported. In addition, the sizes and shapes of the metal particles in these systems indicate the existence of strong bonding. These "strong metal-support interaction" (SMSI) catalysts are under investigation for possible use in $CO-H_2$ (Fischer-Tropsch) synthesis (2-4). Their superior activity and selectivity for this reaction appear to be related to their unusual CO and H_2 chemisorption properties.

Derivation from Solid-State Chemistry

Heterogeneous catalysis often draws on ideas and findings that originate in more specialized disciplines, such as solid-state chemistry. Several years ago the late Roland Ward and colleagues (5) at the University of Connecticut found that a number of base metal and noble metal cations can be incorporated into the lattice of $BaTiO_3$ to form strong bonds with the host titanium cations. This finding was unusual because metal-metal bonding (which involves the overlap of the d orbital electrons of adjacent transition metal cations) usually involves like atoms. The finding of heteroatomic metal-metal bonding suggested that titanium cations at surfaces (and perhaps other transition metal cations as well) might be capable of bonding to metal cations or metal atoms in a supported phase.

Our real interest, in fact, concerned supported-metal atoms, because most petroleum-related processes take place in highly reducing environments. Ward had found the oxidation state of the "guest" cation to be flexible, ranging from $2+$ and $4+$, as indicated by magnetic measurements. Of course, an atom with a valence of 0 cannot be incorporated as such into an ionic lattice. At the surface of an oxide, requirements are much more relaxed due to the added spatial degree of freedom. There seemed to be no reason to exclude the possibility of an interaction between the d orbital electrons of the surface cations and those of the supported metal atoms. Beyond this concept we had no idea of the details of such an electron transfer at the interface or of the effect it might have on catalytic behavior. We initiated an empirical investigation in the hope of demonstrating significantly different properties for those systems in which SMSI's might occur.

Chemisorption of Hydrogen

Our first tests, involving $Ru/BaTiO_3$, showed a strong support-induced change in the catalytic properties of the metal. A greater surprise, however, came when we examined the hydrogen chemisorption properties of these catalysts. This

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technique is ubiquitous in catalysis laboratories working with supported metals. It gives a precise measure of the dispersion of the metal since each surface atom chemisorbs (in most cases) a single hydrogen atom. The routine use of hydrogen chemisorption, starting in the early 1960's, represented a major advance since it allows rate constants to be normalized on the basis of surface metal atoms instead of total metal atoms. As a result, differences in dispersion of the supported metal could be factored out, and interlaboratory results were brought into much closer agreement.

It was soon realized, however, that hydrogen chemisorption could not be used to determine metal dispersion in SMSI catalysts because these catalysts did not chemisorb hydrogen. In fact, suppression of hydrogen chemisorption was soon adopted as a simple test for the SMSI state. Data showing this effect for the group VIII noble metals supported on TiO_2 (6) are given in Table 1. Chemisorption was measured at ambient temperature after reduction at 200° and 500°C. This treatment was applied in situ to the metal salt-impregnated TiO_2 and followed by evacuation at the reduction temperature or slightly below to remove any hydrogen that might have been adsorbed on the metal. The values obtained after reduction at 200°C vary widely. This variation is consistent with the tendency of the group VIII noble metals to disperse on any carrier. Even the apparently anomalous uptake by Ir/TiO_2 has been found for iridium on another substrate (7).

In contrast, following reduction at 500°C the titania support induced a drastic alteration of the chemisorption properties of the metals. For three of these, hydrogen adsorption was virtually undetectable. The two highest values are associated with low dispersion of the metals, which mitigates the influence of the substrate. It can be concluded that the metal-support interaction reduces the uptake of hydrogen on the metal essentially to zero when measured by conventional methods.

X-ray diffraction and electron microscopy have demonstrated that metal dispersion in SMSI systems is high (6). The possibility that low chemisorption of hydrogen results from encapsulation of the metal due to structural collapse of the support was ruled out by measurements of total surface area, which showed an absence of such collapse (6). Another explanation for the observed suppression of hydrogen chemisorption was that SMSI strengthens rather than weakens the adsorption of hydrogen on the metal

Table 1. Hydrogen chemisorption on TiO_2 -supported group VIII noble metals.

Metal (2 percent by weight)	Ratio of hydrogen atoms adsorbed to total metal atoms	
	Reduction at 200°C	Reduction at 500°C
Ruthenium	0.23	0.06
Rhodium	0.71	0.01
Palladium	0.93	0.05
Osmium	0.21	0.11
Iridium	1.60	0.00
Platinum	0.88	0.00

surface. Thus, if hydrogen present on the metal surface after reduction of the catalyst were bonded with such tenacity that it could not be removed by evacuation, no further hydrogen adsorption could take place. To probe this possibility, Ir/TiO_2 in the SMSI state was treated in O_2 at 500°C, a procedure that destroys the SMSI state and thus restores normal properties to the metal. Any hydrogen present on the iridium surface should have been converted to water, and, since water adsorption by the support is minimal at 500°C, H_2O should have been detected in the gas phase. None was found, despite the fact that subsequent exposure to hydrogen did lead to measurable H_2O production, since oxygen adsorbed on iridium was titrated by hydrogen.

These experiments lead to the conclusion that the group VIII metals, when supported on titania by conventional procedures and reduced at low temperature, exhibit hydrogen chemisorption properties typical of corresponding well-reduced metals on familiar supports such as alumina or silica. Hydrogen activation at 500°C converts these materials to a strongly altered state in which the metals, although well dispersed, have a greatly weakened interaction with hydrogen.

Chemisorption of Carbon Monoxide

Studies of supported-metal catalysts also commonly include measurements of CO chemisorption. Although these can be used to estimate the dispersion of the supported metal, their chief value comes from the "chemical" information that can be gained from studies of the CO stretching frequency. This can, for example, reveal the presence of alloying in supported bimetallic catalysts (8). Although we had hoped to use CO chemisorption to study metal-support interactions in SMSI systems, this proved impossible because the metals in the SMSI

state did not chemisorb CO (6). As shown in Table 2, low-temperature reduction of TiO_2 -supported metals led to results that are similar to those routinely obtained with conventional supports such as Al_2O_3 and SiO_2 , whereas reduction at 500°C brought about a striking suppression of chemisorption.

SMSI Properties of Other Oxides

These initial chemisorption studies demonstrated that there are strong interactions between the titania surface and the supported metals, provided the systems are activated in hydrogen at sufficiently high temperature. Such treatment reduces the surface of TiO_2 , removing oxygen through H_2O formation and creating Ti^{3+} ions.

Another study (9) further delineated the relation between surface reduction and SMSI behavior. This involved supporting iridium on a number of substrates. The purpose was to determine how widespread SMSI behavior is among the binary oxides, the study being confined to the nonlanthanide and nonactinide groups. Strong metal-support interaction was inferred from the ability of the oxide to suppress the chemisorption of hydrogen onto the metal. Hydrogen activation requirements of the various supports were studied by testing each catalyst several times, each measurement (at 25°C) corresponding to activation at a different (increasing) temperature.

The oxide supports tested were those of magnesium, scandium, yttrium, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, and manganese (sufficient data for $\text{Ir/Al}_2\text{O}_3$ and Ir/SiO_2 were already available). Oxides that are prone to the formation of stable superficial carbonate, such as BaO or La_2O_3 , were rejected, as were oxides considered thermodynamically susceptible to reduction to the metallic state under the planned experimental conditions, such as MoO_3 or Fe_2O_3 . Where necessary, the supports were pre-sintered in hydrogen to avoid any structural changes in the presence of iridium, since this might have caused the latter to agglomerate.

The results, shown in Fig. 1, are informative in several respects. Titania is obviously not unique in possessing SMSI properties, nor is activation at 500°C necessary for this. Oxides of titanium, vanadium, manganese, and niobium are able to suppress the adsorption of hydrogen onto iridium by an order of magnitude when activated in hydrogen for 1

Table 2. Carbon monoxide chemisorption on TiO_2 -supported group VIII noble metals.

Metal (2 percent by weight)	Ratio of carbon monoxide molecules adsorbed to total metal atoms	
	Reduction at 200°C	Reduction at 500°C
Ruthenium	0.64	0.11
Rhodium	1.15	0.02
Palladium	0.53	0.02
Iridium	1.19	0.00
Platinum	0.65	0.03

hour at only 350°C. The adsorption of hydrogen continues to decline steeply when the activation temperature is raised to 500°C, although in the case of vanadia a low surface area (7 m^2/g) apparently results in a small fraction of poorly dispersed iridium; less than 5 percent would account for the observed value. In the case of $\text{Ir}/\text{Ta}_2\text{O}_5$, the response of the system is noticeably more sluggish. The formulas in Fig. 1 do not identify the actual surface valences of these materials. They simply represent the phases revealed by x-ray diffraction analysis at the conclusion of the experiments. (Surface reduction would not be indicated by this.) The x-ray investigations also ruled out the possibility of iridium agglomeration accounting for the profound changes in hydrogen chemisorption, since such agglomeration would lead to distinct iridium peaks, which were not found.

As shown in Fig. 1, no SMSI properties are evident for alumina, silica, magnesia, scandia, hafnia, zirconia, or yttria. Hydrogen chemisorption continues at a high level for activations $\leq 500^\circ\text{C}$, then drops somewhat when the temperature is raised to 700°C. Some agglomeration of iridium is to be expected following such severe treatment, and, in fact, electron microscopy of the Ir/ZrO_2 catalyst revealed an average iridium particle size that agreed well with the observed uptake. In the case of $\text{Ir}/\text{Cr}_2\text{O}_3$, a similar analysis revealed the possibility of weak suppression of hydrogen chemisorption, but by no more than a factor of 2.

Correlation with Reducibility

The investigation of binary oxides thus shows that some transition metal oxides give rise to SMSI behavior and that some do not. How is this difference accounted for?

To pursue this, it is helpful to temporarily confine our attention to the saturated transition metal oxides; that is, those whose cations are in their maxi-

mum oxidation state (d^0 electron configuration) before being activated in hydrogen. These materials are listed in Table 3 in order of increasing reducibility. This is expressed in terms of the thermodynamic equilibrium ($p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ at equilibrium at 1000 K; p denotes partial pressure) between the starting saturated oxide and an oxide with a lower valence or, if none exists, the corresponding metal (10). Thus in the cases of scandia, yttria, hafnia, and zirconia, no oxides with lower valences have been characterized, and in the case of tantalum, TaO_2 has only been reported as a metastable phase. However, NbO_2 is well known and there are many oxides with lower valences in the Ti-O system; Ti_3O_5 has been arbitrarily chosen. Our interest is not in these absolute values but in their relative order, which can also be expected to apply to the surface reducibilities of these oxides.

Table 3 indicates that there is a direct correlation between SMSI behavior and reducibility. Transition metal oxides that are highly refractory to reduction do not exhibit SMSI properties; TiO_2 and Nb_2O_5 , both easily reducible, do. The sluggish behavior of Ta_2O_5 can be correlated with its intermediate reducibility.

Three oxides tested for SMSI properties were nonsaturated: those of vanadium, manganese, and chromium. The need for surface reduction found for the saturated oxides implies that the unsaturated (hence, reduced) supports have SMSI properties. This is true for vanadia and manganous oxide but not chromia. As mentioned above, activation of $\text{Ir}/\text{chromia}$ at 700°C brings about a reduction in hydrogen chemisorption which is at most 50 percent greater than can be attributed to iridium agglomeration.

Table 3. Correlation of SMSI properties with reducibility for saturated transition metal oxides.

Metal oxide	X_{1000}^*	SMSI activity
Sc_2O_3	-18.1 (Sc)	Negative
Y_2O_3	-18.0 (Y)	Negative
HfO_2	-14.0 (Hf)	Negative
ZrO_2	-13.6 (Zr)	Negative
Ta_2O_5	-6.8 (Ta)	Positive (sluggish)
TiO_2	-3.9 (Ti_3O_5)	Positive
Nb_2O_5	-1.1 (NbO_2)	Positive

* $X_{1000} = \log (p_{\text{H}_2\text{O}}/p_{\text{H}_2})$ at equilibrium between oxide in column 1 and phase in column 2 at 1000 K.

Nevertheless, a correlation of the SMSI state with the need for a reducible transition metal oxide succeeds with 12 of the 13 oxides investigated; only chromia is anomalous. Recent work, both theoretical and spectroscopic, has provided insight into this relation.

Electron Microscopy Studies

In view of the changes in the adsorptive properties of metal particles affected by SMSI, we wondered whether direct observation of these particles would reveal changes in their size or shape. This was studied by Baker *et al.* (11), who prepared films of platinum on titania, alumina, silica, and carbon and then annealed the specimens in hydrogen at various temperatures before examining them in an electron microscope. A clear difference was found between $\text{Pt}/\text{titania}$ and the other systems. For the former a much smaller mean particle diameter was found after treatment at high temperature (700° to 800°C). The shape of

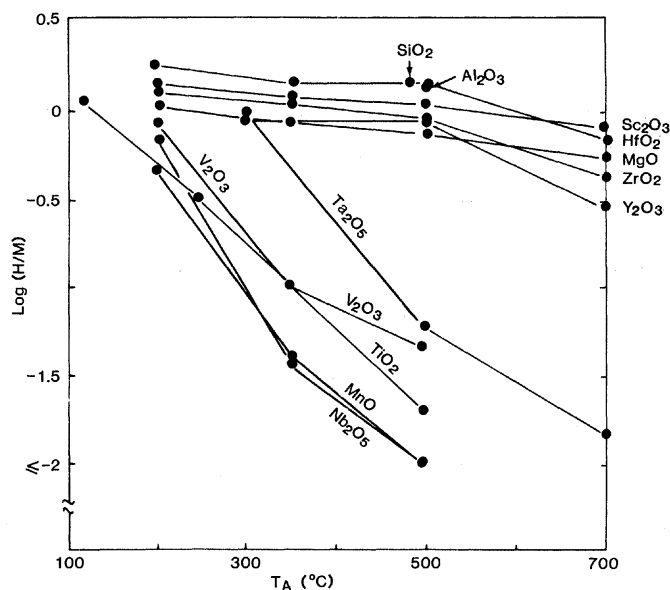


Fig. 1. Hydrogen chemisorption on iridium supported on various oxides as a function of activation in hydrogen for 1 hour at each of various temperatures (T_A , activation temperature; H/M , atomic ratio of hydrogen adsorbed to iridium in catalyst). Iridium is 1 percent (by weight) for SiO_2 , Al_2O_3 , V_2O_3 , and HfO_2 and 2 percent for the other supports.

the platinum particles in this system was particularly revealing. Instead of the usual hemispherical aggregates, they resembled flat pillboxes a few atoms—possibly as little as one atom—thick. Figure 2 shows the morphological difference between platinum particles supported on silica and those supported on titania.

Baker *et al.* (12) also examined the effects of high-temperature (600°C) oxidation on the morphology of platinum particles in the Pt/titania system. This treatment destroys the SMSI state, as evidenced by a return to normal chemisorption properties. The electron microscopy results clearly confirmed this. The pillbox structures were converted to much larger and thicker hemispherical aggregates. However, a return to high-temperature reducing conditions once again brought about the pillbox configu-

ration, with considerable redispersion of the metal particles. This “melting” of the thickened platinum aggregates into pillbox structures provides graphic evidence for the strength of the metal-support interaction in this system, which must outweigh the cohesive forces in the metal aggregates.

Along with these changes in platinum morphology, the support itself was found to transform. Surface reduction to form Ti^{3+} ions was expected, but Baker *et al.* (12), using electron diffraction, found that reduction at 600°C or more led to formation of a stoichiometric lower oxide, Ti_4O_7 . The fact that surface reduction was found to proceed to Ti_4O_7 and no further is consistent with this being the most reduced member of the $\text{Ti}_n\text{O}_{2n-1}$ compositional series. Further reduction

to Ti_3O_5 requires a radical reorganization of structure.

Just as high-temperature oxidation agglomerated the platinum particles, it oxidized the surface Ti_4O_7 phase to TiO_2 (Fig. 3). Correspondingly, rereducing the sample caused the reappearance of Ti_4O_7 and a return to the pillbox structure. This close association of surface reduction of the support and SMSI characteristics is of course consistent with the pattern of results described above for the various transition metal oxides.

Molecular Orbital and Spectroscopic Studies

The changes in chemisorptive, catalytic, and structural properties which characterize the SMSI state strongly suggest an electronic interaction at the metal-oxide interface. Although the early hypothesis envisaged surface cations and supported metal atoms as the bonding centers, the details were obscure.

Some clarification was suggested by the finding that the distribution of SMSI properties among saturated transition metal oxides is correlated with their reducibilities. This focused attention on reduced cations. A possible additional role of surface reduction—that of promoting the exposure of these cations (to the suprajacent metal) by removing oxygen from the surface—was also considered. A localized bonding model was preferred to any involving collective properties of the support, since the substrates included an insulator (MnO) as well as a metallic conductor (V_2O_3).

A theoretical study by Horsley (13), who used the $X\alpha$ molecular orbital method to study the Pt/ TiO_2 system, did much to sharpen our understanding of SMSI behavior. First, the calculations confirmed the need for removal of oxygen anions from the surface in order that the approach of the metal atom and the surface cation be close enough for bonding. Second, the calculations were able to provide an electronic description of the bond; there is a weak covalent contribution from the overlap of metal atom and cation d orbital electrons. The dominant interaction, however, was found to be an ionic attraction as the result of a charge transfer from the reduced cation to the adjacent metal atom. Thus, the need for surface reduction in the SMSI state is twofold. The surface transition metal cations must be reduced, thereby acquiring d orbital electrons, and the concomitant loss of surface anions facilitates approach between metal atom and reduced cation so that the electrons can be

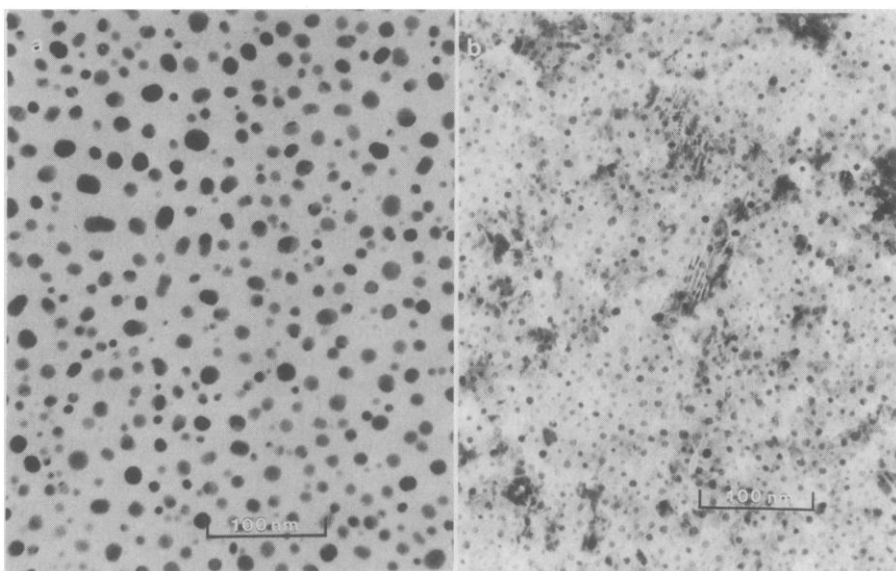


Fig. 2. Electron micrographs of platinum on (a) silica and (b) titania after treatment in hydrogen at 800°C.

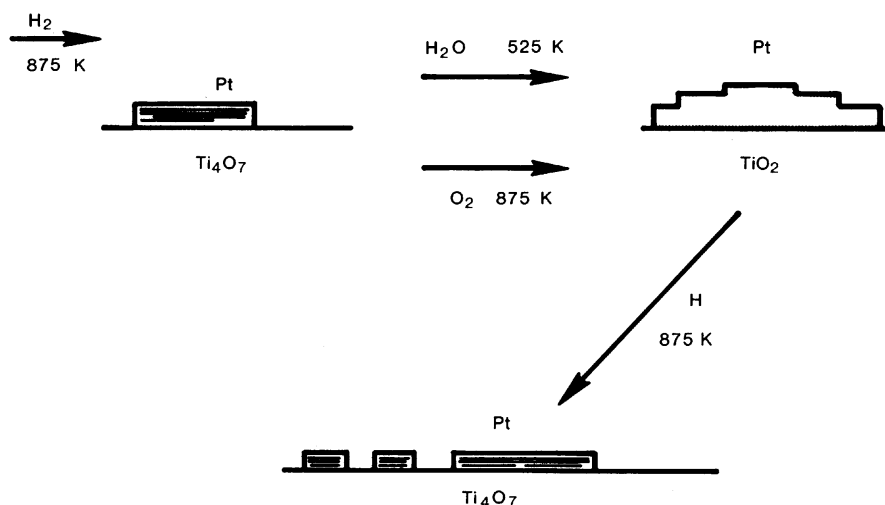


Fig. 3. Behavior of Pt/ TiO_2 under consecutive reduction-oxidation cycles. Both the thickness of the platinum particles and the chemical composition of the substrate surface undergo change.

transferred to the metal. This is our present conception of the nature of SMSI systems.

Evidence for a charge transfer from reduced surface cations to the supported metal has been provided by two spectroscopic studies of the Pt/TiO₂ (14) and Pt/SrTiO₃ (15) systems. In both cases, the chemical shift of the platinum 4f core level indicated that the platinum atoms had acquired a substantial negative charge. Chung and Weissbard (16) used electron energy-loss spectroscopy to monitor the disappearance of the surface Ti³⁺ ions on a reduced SrTiO₃ surface upon deposition of platinum. They simultaneously observed an increase of about 0.8 electron volt in the work function, and on the basis of these two observations concluded that an electron was being transferred from the Ti³⁺ ion to the platinum atom, with the formation of a Schottky barrier at the interface.

This model of SMSI behavior does not readily account for the observed suppressions of H₂ and CO chemisorption. It is possible that the strong interactions increase the distance between neighboring metal atoms and that this leads to a weakened interaction with the gases. An alternative interpretation is that the electrostatic attraction between the subjacent cations and the electrons of the supported metal inhibits the transfer of these electrons to substrate molecules such as H₂ and CO.

The ionic bonding between metals and cations in SMSI systems may be contrasted with another type of metal-support interaction that has recently been described. In the Ru/SiO₂ system, a covalent interaction is indicated between ruthenium atoms and surface anions (17, 18). The manifestations of this type of interaction are quite different from those described for ionic metal-support interactions.

Fischer-Tropsch Reactions

In view of the close relation between chemisorption and heterogeneous catalysis, the strongly altered chemisorption properties of metals in the SMSI state should be reflected in their catalytic properties. This is true in many instances, but the changes are not always in accordance with what one might expect. Thus, in the case of the CO-H₂ synthesis reaction, the chemisorption of both reactants is, as we have seen,

strongly suppressed, and this might be expected to apply to the catalytic activity as well. Instead, studies involving supported nickel catalysts show tenfold greater activity for Ni/TiO₂ than for Ni/Al₂O₃, Ni/SiO₂, or Ni/C (2). These comparisons were made on a per gram basis since chemisorption suppression on Ni/TiO₂ prevented an assessment of the relative nickel surface areas. Further advantages found for Ni/TiO₂ were greater selectivity for the formation of higher molecular weight products and decreased formation of nickel carbonyl.

The chemisorption suppressions cited thus far refer to measurements carried out in the standard manner at ambient temperature. Recent studies have gone further, in confirming that suppression of CO chemisorption is maintained under Fischer-Tropsch reaction conditions as well. This was done with the aid of a specially constructed cell that allowed infrared absorption measurements in situ on catalysts actually carrying out CO-H₂ synthesis. In a study involving supported platinum (3), large quantities of CO were found on the metal under reaction conditions when the carrier was alumina, silica, or silica-alumina, while only a very small amount was detected when the platinum was supported on TiO₂. Yet the latter catalyst was the most active. Similar results were obtained in a corresponding study in which the supported metal was palladium (4).

This relation between chemisorption and catalysis may appear to be paradoxical. However, a very low measured uptake of an adsorbate, implying a short lifetime on the surface, does not necessarily mean that this lifetime is insufficient for the adsorbed species to react. A weakened adsorbate-surface interaction can be beneficial. For example, the CO-H₂ reaction is adversely affected by an excessive heat of adsorption of CO (19). It seems that in many cases the SMSI-induced alterations in the heats of chemisorption of CO and H₂ result in improved catalytic properties for this reaction.

Summary

Strong metal-support interactions have been shown to occur in a number of systems comprising small metal particles dispersed on the surface of an inorganic oxide. The latter must be a transition metal oxide, which, upon activation in

hydrogen, can undergo superficial reduction to form reduced cations that are exposed to the suprajacent metal particles. Manifestations of the ensuing interaction include a profound change in chemisorption properties and an unusual structure of the metal particles as shown by electron microscopy. Catalytic properties are also altered.

Although the original hypothesis was vague about the nature of the interaction between surface cations and the supported metal, molecular orbital (X α) calculations have produced a precise model. This involves the transfer (whole or partial) of an electron from a subjacent cation to a supported metal atom, resulting in a strong ionic bond between a negatively charged "pillbox" of supported metal atoms and the associated surface cations. This model is consistent with recent spectroscopic studies.

Among the many outstanding questions at the present time, it would be important to learn approximately how the cation-to-metal charge transfer varies across the wide range of conceivable systems. The response of catalytic and chemisorption properties to this transfer may be of considerable fundamental interest in the study of heterogeneous catalysis. In addition, studies of this type will hopefully uncover new catalysts with improved properties for CO-H₂ synthesis or other reactions.

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