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Strong Metal–Support Interactions

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Introduction

The term "strong metal–support interaction" was introduced in 1978 to describe the drastic changes in the chemisorption properties of group VIII (8–10)[73] noble metals that were observed when these substances were supported on titanium oxide. For years the adsorption of hydrogen had been used to indicate the particle sizes of catalytic metals such as platinum. At ambient temperature, these metals chemisorb one hydrogen atom per surface metal atom, regardless of whether they are unsupported or dispersed on common carriers such as aluminum oxide. However, the ability to chemisorb H_2 (and CO) either was strongly suppressed or vanished entirely when these metals were supported on titanium oxide and activated in H_2 at ordinary temperatures. Trivial causes such as sintering were easily dismissed, and it was concluded that a strong metal–support interaction had somehow deprived these metals of one of their most characteristic properties.[1]

Much effort has been directed at understanding these phenomena, which are by no means limited to titanium oxide. The key to progress has proved to be the elucidation of the solid-state transformations that occur in these systems. This information has forced us to change our picture of supported metal catalysts, particularly with regard to their morphology. It has become clear that the traditional view of metal particles resting unperturbed on an oxide surface is not always correct. In many systems, the oxide support can invade the metal surface, masking significant portions of it but also creating special contact zones with enhanced catalytic properties for some reactions. In other cases, the metal spreads to increase its coverage of the oxide. These phenomena indicate bonding interactions. The primary focus of this Account will be the direct evidence for this bonding and what has been learned about its fundamental nature. The term "strong metal–support interaction" will refer to the bonding itself rather than to properties (e.g., catalytic) that derive from it.

There are unique features of this bonding that preclude its existence anywhere but at an interface. Understanding these systems thus becomes critically dependent on advanced surface probes, and there is perhaps no subject in contemporary catalysis in which these techniques have had a greater influence.

The Migration of Reduced Titanium Oxide onto Metal Surfaces

The suppression of H_2 and CO chemisorption was initially attributed to an electronic perturbation of the metal atoms, caused by their interaction with titanium cations at the oxide surface. This is quite possible for thin metal crystallites, and evidence for it will be discussed later. However, the surface of a metal particle cannot be significantly affected by titanium ions more than a few atomic units away, owing to screening effects within the metal. Nevertheless, chemisorption suppression had subsequently been found with metal crystallites as large as 50 Å. It was speculated[2–4] that titania was somehow in direct contact with at least a portion of the metal surface.

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Surface science investigations reported in 1984[5-8] confirmed this. Surprisingly, titanium oxide was found to migrate considerable distances in short terms and to appear on initially pristine metal surfaces. This mobility meant that regardless of a metal particle's size, its surface was vulnerable to interaction with titania.

There was an important prerequisite. Titanium oxide had first to be reduced, at its surface, to a lower valency; invariably, the species appearing atop the metal was found to be "TiO_x" with $x < 2$. This critical role of support reduction had in fact been inferred from previous findings concerning chemisorption suppression.[9] It has proved to be a central theme throughout this research.

The distance covered by migrating TiO_x is remarkable. The surface of a TiO_2-supported Ni film 120 Å thick shows signs of TiO_x encroachment after 10-min exposure to H_2 at 425 °C.[8] This includes time necessary to reduce the surface of the substrate to TiO_x. A 30-Å-thick Pt or Rh film on prereduced titania is covered with half a monolayer of TiO_x after 2 min at 400 °C.[10] With temperature ramping, the onset of TiO_x attack is placed at 200 °C.[6]

The mechanism of TiO_x migration to the metal surface is not well-understood and represents a challenging materials science problem. The migration appears to occur via grain boundaries, since it is far too rapid to be accounted for by diffusion of titanium and oxygen through the metal.[11] This migration requires the rupture of the titania lattice. It can only occur if the loss of Madelung energy is outweighed by the strength of the TiO_x–metal surface interaction. Thus, an important aspect of TiO_x overlayer formation is the demonstration of this strength.

None of the phenomena mentioned so far are restricted to titania. This oxide was singled out in early studies because titanium cations had been shown to bond to various other transition-metal cations in a group of oxides known as "hexagonal barium titanates".[12] This suggested the possibility of d-orbital overlap between titanium cations and supported metal atoms, but it was soon obvious that strong metal–support interactions were far broader. Suppressed H_2 chemisorption was demonstrated for iridium supported not only on titania but also on the oxides of niobium, vanadium, and manganese.[9] Of these three transition metal oxides, only the last has been studied for possible overlayer formation. (Two main group oxides, Al_2O_3[13] and SiO_2,[7] have been investigated, with negative results.) Like titania, manganese oxide will invade the surface of a superjacent metal, and this migration, in fact, occurs more rapidly than with TiO_x. A 150-Å-thick Ni film, deposited on MnO, shows substantial amounts of MnO_x on its surface after 100 s of vacuum annealing at 230 °C.[14] Clearly, titania is not unique either in giving rise to strong metal–support interactions or in the time and temperature required to do so.

The Spreading of TiO_x on Metals and of Metals on TiO_x

Closely related to TiO_x overlayer formation is the behavior of increments of titania that are added to a metal surface. Normally, an adlayer will agglomerate to form three-dimensional islands, but if an interaction exists it may spread. The covered metal will be unavailable for chemisorption of H_2 or CO, and the adsorption suppression produced by a given amount of oxide measures its tendency to "wet" the surface.

Ko and Gorte showed in this way that both TiO_x and NbO_x wetted a Pt surface 5 times as efficiently as either Al_2O_3 or SiO_2[15] and that one equivalent monolayer of titania was sufficient for complete coverage of Pt, Pd, or Rh.[16] Studies comparing titania and alumina adlayers on nickel have had analogous results. Their effects were qualitatively similar with regard to the strengths of H_2 and CO adsorption and the catalytic decomposition of formic acid. However, 0.1 equivalent monolayer of titania was equal to 0.7 equivalent monolayer of alumina in bringing about these changes.[17] Direct observations of the titania/Ni system, by means of controlled atmosphere electron microscopy, have shown that large aggregates of TiO_2 spread, upon reduction to TiO_x, to cover the metal surface.[18]

If the above geometry is reversed by depositing a metal onto titania, the interaction is sometimes sufficient to bring about or stabilize a raftlike configuration of the metal. An early electron microscopy study by Baker[19] compared Pt/titania with Pt on the noninteracting support SiO_2. After treatment in H_2 at 800 °C, the Pt particles on SiO_2 (see Figure 1a) were large and globular, while those on titania (Figure 1b) were much smaller and thinner. Electron diffraction showed that TiO_2 had been reduced to Ti_4O_7. At higher magnification (Figure 2) the lattice fringes of the Ti_4O_7 substrate were visible through many of the Pt particles. A later study[20] showed that the morphology of Pt particles on titania could be changed reversibly by alternating oxidation and reduction treatments at high temperature (600 °C). Following treatment in O_2, the particles were large and dense, i.e., similar to Pt on SiO_2, while treatment in H_2 reduced TiO_2 to Ti_4O_7 and caused the metal particles to spread into thin, flat structures. Baker subsequently determined that spreading occurred within 10 s at 565 °C.[21]

Not all metals have been found to exhibit this behavior. Pd[22] and Rh[23] do not, whereas Ag,[24] Ni,[25] and

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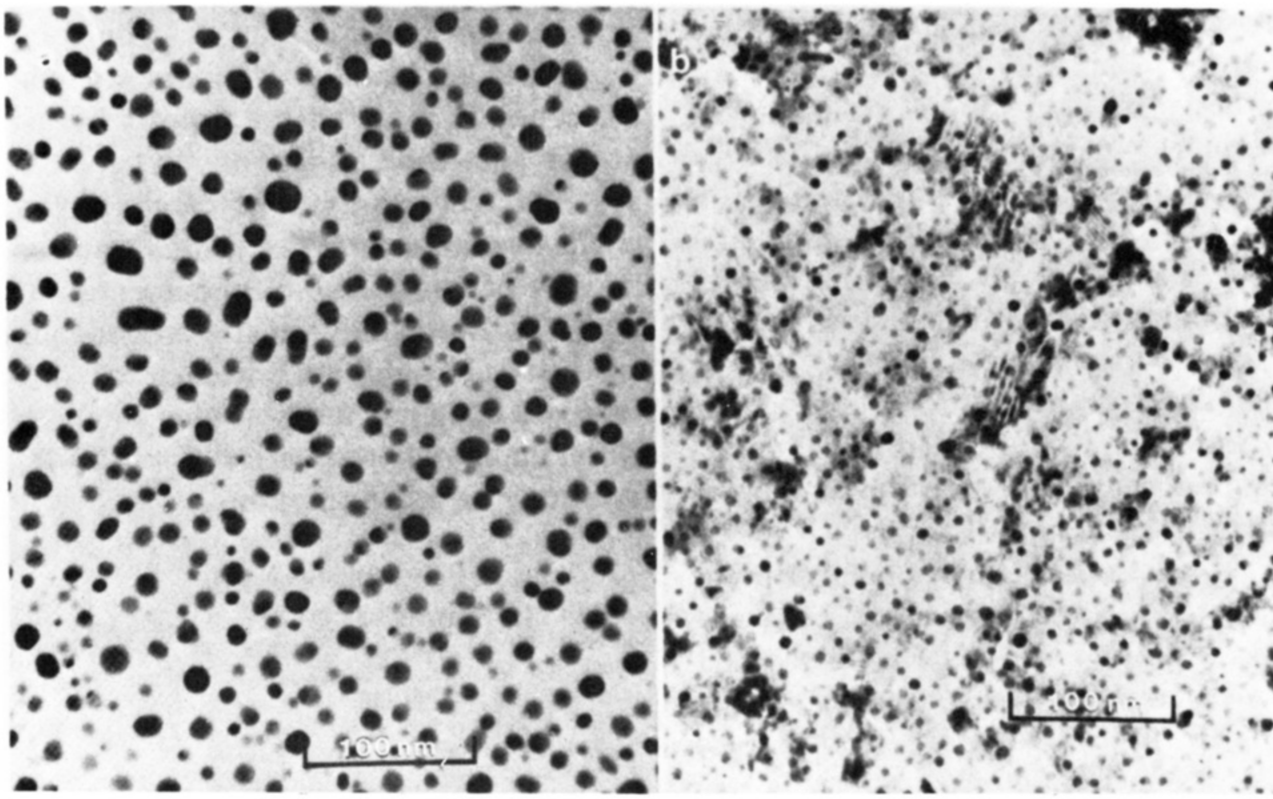

Figure 1. (a, left) Electron micrograph of Pt on SiO_2 after treatment in H_2 at 800 °C for 1 h. The lack of metal–support interaction is indicated by the large, globular shape of the metal particles. A bar representing 100 nm is shown at the bottom of the micrograph. (b, right) Electron micrograph of Pt on titania after treatment in H_2 at 800 °C for 1 h. Before this reduction the support was in its fully oxidized form (TiO_2), but afterward its surface was shown to have been reduced to Ti_4O_7. The small, thin metal particles (contrast with (a)) are indicative of a strong metal–support interaction. A bar representing 100 nm is shown at the bottom of the micrograph.

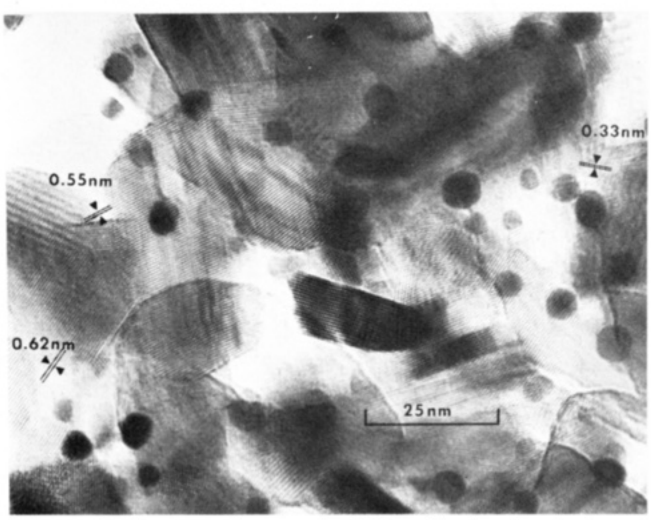

Figure 2. Electron micrograph of Pt on titania after treatment in H_2 at 550 °C. The magnification is about 9 times greater than in Figure 1a,b. The support surface has been reduced to Ti_4O_7, and the thinness of many of the raftlike Pt particles permits the Ti_4O_7 lattice fringes to be seen through them.

Fe[26] do. Spreading, if it occurs, does so only on the reduced titania surface. Thus, the transformation of large, globular Ag particles into small, thin rafts takes place only in the vicinity of Pt particles, which catalyze the reduction of the surface by the hydrogen spillover mechanism.[24] The spreading of Fe on titania, induced by reduction at 500 °C, leads to a doughnut configuration of the metal particles.[26] Apparently, those atoms at the center of the particle are attracted to the periphery, due to the greater concentration of reduced (Ti^{3+}) centers there; the flux of spillover hydrogen is greatest in this zone. This may also explain the breakup of large (>40 Å) Ni particles on titania caused by reduction at 475 °C.[25]

Metal–Ti^{3+} Interactions

The consistent observation that strong metal–titania interactions require reduction to TiO_x suggests that reduced titanium ions (e.g., Ti^{3+}) are central to this chemistry. An important finding is that these cations interact *directly* with group VIII (8–10) metals. If a surface containing Ti^{3+} ions is exposed to a flux of metal atoms, the spectroscopic signature of these ions is either decreased or eliminated. Six studies have shown this, involving Ni,[27–29] Pt,[30] Pd,[31] or Rh[32] as the vapor-deposited metal and TiO_2 or $SrTiO_3$[30] as the substrate. Surface Ti^{3+} was produced by Ar ion sputtering, reduction in H_2, or vacuum annealing. The presence of these ions and their subsequent attenuation were followed with electron energy loss spectroscopy,[30] X-ray photoelectron spectroscopy (XPS),[27–29,31] or, in a recent report, by these two techniques plus ultraviolet photoelectron spectroscopy (UPS).[32]

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The attenuation of Ti^{3+} was not a simple masking of the substrate, since the amounts of deposited metal (usually 0.5–3 monolayers) were far too small. In one study, analysis of the XPS spectrum showed that the metal did not significantly interact with surface oxygen ions, and UPS indicated that Rh was essentially physisorbed on the fully oxidized (TiO_2) surface.[32] Clearly, the reaction of the metal atoms with Ti^{3+} cations is specific.

This bond, of course, can only exist at an interface, since metal atoms and cations are mutually incompatible within a solid lattice. It appears to be partially ionic, with net electron transfer from Ti^{3+} to the metal. It was observed, by means of Auger electron spectroscopy (AES), that the titania surface was more "oxidized" after Rh deposition, and the UPS change was similar to that brought about by the adsorption of O_2.[32] This agrees with an early Xα molecular orbital calculation by Horsley.[33]

There have also been two recent efforts to *structurally* identify a direct Rh–Ti^{n+} bond, using extended X-ray absorption fine structure (EXAFS) analysis. Koningsberger et al.[34] reported a Rh–Ti^{n+} coordination at 3.4 Å, which is obviously too long to represent a strong interaction. Haller and co-workers,[35] however, have reported a coordination at 2.55 Å, which occurred in a Rh/titania catalyst after reduction at 500 °C. This distance is significantly shorter than found in a Rh–Ti alloy (2.68 Å) and suggests the titanium is cationic. Further EXAFS studies of metal/titania and related systems are clearly desirable.

Metal–TiO_x Interaction Effects with and without Overlayers

A small metal particle placed on a TiO_2 surface finds itself in a precarious situation as the system is reduced in H_2. As TiO_x evolves, a strong interaction is unleashed that has the potential of enveloping the metal and obliterating its catalytic properties.

This simple picture, in fact, is in good agreement with several features of metal/TiO_2 catalysts after high-temperature reduction. Their H_2 and CO chemisorption capacities often decrease to near-zero values.[36] Their catalytic activities for hydrogenolysis (i.e., the breaking of carbon–carbon bonds in the presence of H_2) are frequently suppressed by orders of magnitude.[36] Both these observations are most easily accounted for by a simple blanketing of the metal surface by TiO_x.

Attractive as the simple-site-blocking model may be, not all observations are in agreement with it. (We exclude for now CO–H_2 synthesis reactions, which present special features.) Some studies of metal/titania catalysts have found sharp decreases in hydrogenolysis activity with only slight effects on dehydrogenation activity.[37–39] Apparently, an incomplete overlayer can exert different effects on different reactions. Strong metal–support interactions have been reported to increase selectivity for the reduction of trienes to dienes in fats and oils[40] and for the hydrogenation of carbonyl groups.[41] In cases where chemisorption suppression is not total, atypical features are found. H_2 becomes much more competitive with CO for the available surface,[42,43] and a fraction of adsorption sites with unusual lability for both H_2 and CO is observed.[44,45]

There is evidence that chemisorption suppression can be induced by *underlying* TiO_x.[6,25,46,47] Since overlayer formation must be prevented in these investigations, they involve low-temperature deposition of the metal with carefully controlled subsequent heat treatment. Reducing the substrate before metal deposition has a strong effect on the capacity of the metal to chemisorb H_2 or CO, indicating electronic perturbation by TiO_x. Temperature-programmed desorption (TPD) indicates TiO_x-induced adsorption states of lower binding energy. These effects disappear if the metal film is more than a few monolayers thick.[46]

If overlayers are present, the question becomes whether sites other than those directly covered by TiO_x are affected. This has become one of the most debated topics in this field. Some investigators of the TiO_x/Pt system have concluded that the degree of chemisorption suppression agrees with the fractional coverage by the overlayer.[15,16,48–51] TPD used in these studies revealed no changes in adsorption energy on the uncovered surface. Other investigations of TiO_x/Pt have reported TPD evidence for weaker adsorption of H_2 and/or CO.[6,13] TiO_x overlayers on Ni have been found to suppress CO adsorption on uncovered sites[8] (MnO_x did not give this effect)[52] and to weaken the adsorption of CO, viz., that of H_2.[17,53,54] Simple geometric blocking has been claimed for NbO_x on Pt[15] and for TiO_x on Rh and Pd.[16] Other studies of TiO_x on Rh report low-energy CO adsorption states on the metal and suppression of chemisorption within a perimeter region one Rh–Rh bond length around each TiO_x island.[55] It is obviously impossible to arrive at a general conclusion in the light of these conflicting results. The fact that TiO_x *underlayers* can perturb thin metal films suggests that a TiO_x overlayer should have this effect on nearby metal atoms, but not all evidence is in agreement with this.

CO–H_2 Reactions

The catalytic effect of titania on metals is, in general, neutral or deactivating, but an important exception is the reaction of CO with H_2 to form methane or higher hydrocarbons. Introducing TiO_x onto a Pt film in-

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creases the rate of methane formation at low temperature by an order of magnitude or more.[49,56] NbO_x has a similar effect.[57] Ni supported on titania is about an order of magnitude more active than when supported on alumina or silica and shows an increased propensity to form higher hydrocarbons.[58] Similar, although smaller, effects have been seen with some other metals as well.[59]

The reason for this behavior is not entirely clear. One suggestion is that the metal–TiO_x contact perimeter provides active sites for the dissociation of CO;[60] the molecule is thought to straddle the interface, with the O atom coordinated to the titanium (or similar) cation and the C atom to the metal. This implies that TiO_x and the metal are joined to within atomic dimensions. Metal–TiO_x bonding is conducive to such a contact perimeter and may be required for it to occur to a significant extent.

The above explanation may be applicable to Pt or Pd, for which CO dissociation limits the reaction rate. In the case of Ni, enhanced activity and selectivity have been related to changes in the relative adsorption strengths of H_2 and CO, as revealed by TPD. They predict an enhanced ability of hydrogen to compete with CO for the metal surface.[54] Of course, in certain instances the predominant effect of the TiO_x interaction may be simply to inhibit agglomeration of the metal under reaction conditions.

In any case, it is important to establish whether TiO_x is stable in the CO–H_2 reaction environment. The question arises because H_2O, a coproduct, is an oxidant which, by itself, will convert Ti^{3+} to Ti^{4+}. The reactants H_2 and CO are both reductants and have the opposite effect. The result is a dynamic competition. Particularly important is "spillover" hydrogen: H_2 that dissociates on the metal into atoms that spill onto the surrounding support to provide highly active reducing species.

It appears, in fact, that an appreciable concentration of Ti^{3+} exists under reaction conditions. Dwyer et al., using XPS, found that Ti^{3+} was clearly evident in a TiO_x/Pt model catalyst after 16 h of CO–H_2 synthesis.[51] Ion scattering spectroscopy studies of this system showed a marked tendency for TiO_x to spread on the Pt surface, and this coverage (indicative of bonding) was only slightly decreased by the reaction.[61] Gorte et al. reported that the O/Ti atomic ratio (measured with AES) of a TiO_x/Pt catalyst used for CO–H_2 synthesis continued to indicate reduced titania.[49] Indirect evidence supports this, too. Suppressed $Ni(CO)_4$ formation during the CO–H_2 reaction was found for a titania-supported NiFe catalyst.[62] This points to the continued presence of a TiO_x overlayer and corresponds to earlier reports (using in situ IR spectroscopy) of suppressed CO adsorption on Pd/titania and Pt/titania during CO–H_2 synthesis.[42,43] The spreading of Fe on titania (noted earlier) occurred in the presence of 1% H_2O in H_2.[26] Gorte and co-workers, using XPS[63] and AES,[49] have inferred that TiO_x is stabilized against oxidation by its interaction with Pt.

The Extent of Strong Metal-Support Interactions

The question of scope is an important one that bears on the nature of the bonds involved. Until recently, it appeared that these interactions required transition-metal cations with d electrons. This explained the need for reducing TiO_2 to "TiO_x" since this converted Ti^{4+}, with a d^0 electron configuration, to, e.g., Ti^{3+} with a d^1 configuration. The absence of strong metal–support interactions with some transition metal oxides (e.g., ZrO_2) was attributed to the difficulty of reducing their d^0 cations to the d^1 state.

It appears, however, that even difficult to reduce oxides, such as ZrO_2, can sometimes undergo superficial reduction, particularly with a supported metal providing spillover hydrogen.[64,65] Why this is observed in some studies while not in others is not clear. In any case, surface-reduced zirconia ("ZrO_x") inhibits the chemisorption of H_2 onto supported Rh.[64] Even alumina, which in countless investigations has given no evidence for support reduction or chemisorption suppression, has twice (with supported Pt or Pd) been reported to exhibit both.[66,67] In one of these studies, reduction was found to be promoted by sulfur.[66]

Surprising reducibility has also been found for lanthanum oxide, described by Bell and co-workers in reports covering the Pd/lanthana system.[68–71] La_2O_3 is reduced to "LaO_x", and its interaction with the Pd surface weakens the adsorption of CO but not that of H_2, which is able to compete more effectively for the metal surface. These observations are reminiscent of metal/titania systems.[72] There are some differences as well. LaO_x has a smaller effect on H_2 adsorption capacity than TiO_x and interacts with both the Pd (100) and Pd (111) surfaces, whereas TiO_x selectively interacts with the former.[72] Both LaO_x and TiO_x increase the CO dissociation rate of a Pd catalyst.

What is the nature of the reduced centers formed by the reduction of ZrO_2? of La_2O_3? of Al_2O_3? What is the symmetry of the orbitals in which their valence electrons reside, and how do they interact with metals? These questions await future studies.

Summary/Conclusions

It is clear that several metals, including noble metals, form interfacial bonds with the surfaces of reduced transition metal oxides. The most direct evidence for

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(73) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

this is the spontaneous increase in the metal–oxide interfacial area that is observed in many systems, often at the expense of rupturing strong bonds in order to bring these phases together. In the case of titanium oxide, which has received the most attention, direct interactions between metal atoms and reduced titanium ions are seen with a variety of spectroscopic techniques.

This chemistry appears to extend to several other transition metal oxides and even to some that are nontransitional and nominally nonreducible, provided that surface reduction actually occurs. The best documented cases (other than titania) are the oxides of niobium, manganese, and lanthanum.

When metals are dispersed on titania or similar substrates, the onset of the strong metal–support interaction convulses the system. If the particles are large, the oxide moves rapidly to inundate their surface, so that the term "support" is no longer descriptive. With small metal particles, the major morphological change is sometimes a flattening to form thin, raftlike structures. In either event, the metal's ability to chemisorb H_2 and CO, and to crack carbon–carbon bonds, is drastically decreased. A general loss of activity for hydrocarbon conversions is observed. There are cases, however, in which hydrogenation and dehydrogenation activity are only mildly affected, and selectivity for a preferred conversion is sometimes improved. CO–H_2 synthesis is unusual in that activity is substantially improved for some metals; for others, changes in selectivity (toward higher hydrocarbons) are the major consequence.

A precise explanation of these catalytic effects is a difficult undertaking. In the case of CO–H_2 synthesis, the metal–TiO_x contact perimeter may be important in some systems, whereas with other metals altered competition between CO and H_2 may be the significant factor. A combination of kinetic and surface characterization studies will be required to firmly establish these mechanisms.

But it is the materials science aspects of these interactions that pose the most provocative questions. The rapid migrations of TiO_x and MnO_x are mechanistically unexplained. The interactions of metal atoms with reduced cations other than Ti^{3+} have not been studied. There is much chemistry to be learned from these unusual systems, and it is to be hoped that the progress made in the past few years will continue into the future.