Strong Metal-Support Interactions

EDITED BY
R. T. K. Baker,
S. J. Tauster,
and J. A. Dumesic

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R. T. K. Baker, EDITOR
Exxon Research and Engineering Company

S. J. Tauster, EDITOR
Exxon Research and Engineering Company

J. A. Dumesic, EDITOR
Department of Chemical Engineering
University of Wisconsin—Madison

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FOREWORD

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PREFACE

THE DISCOVERY OF STRONG METAL–SUPPORT INTERACTIONS in 1978 led to a renaissance in the study of the effects of supports in supported metal catalysts. The importance of the support has been appreciated for many years. In fact, the concept of electronic interactions between metal particles and semiconducting supports was the basis for intense research on supported metal catalysts in the 1950s. In the late 1960s and early 1970s, research on the effects of metal particle size on refractory supports such as SiO_2, Al_2O_3, and MgO became an active discipline. When it was found in 1978 that the properties of Group VIII metals could be altered dramatically by supporting these metals on reducible supports such as TiO_2, research on metal–support interactions became an active area once again. This book focuses on the advances that have been made recently in this area.

The origin of strong metal–support interactions has been the subject of much research during the past seven years. It has been proposed, for example, that these interactions are due to electronic interactions between the metal and the support, changes in a metal surface structure or particle size induced by the support, or the presence of support species on the metal surface. In general, any of these effects may be dominant for a given catalyst system as documented by the papers in this book. Undoubtedly, the origin of strong metal–support interactions for large metal particles is the presence of support species on the metal surface. This phenomenon is developed at length in this book by a number of papers that address the evidence for the presence of oxide species on metal surfaces and that probe the effects of these species on the catalytic and chemisorptive properties of the metal.

We hope that this collection of papers on metal–support interactions will serve as a "catalytic support" for further research and lead to new applications or to discoveries of new classes of metal–support interactions.

R. T. K. BAKER
Corporate Research Science Laboratories
Exxon Research and Engineering Company
Annandale, NJ 08801
S. J. TAUSTER
Corporate Research Advancement and Transfer
Exxon Research and Engineering Company
Annandale, NJ 08801
J. A. DUMESIC
Department of Chemical Engineering
University of Wisconsin—Madison
Madison, WI 53706

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Strong Metal–Support Interactions

Facts and Uncertainties

S. J. Tauster

Corporate Research Advancement and Transfer, Exxon Research and Engineering Company, Annandale, NJ 08801

Studies of metal-support interactions have yielded significant progress in the past few years. It is appropriate, at the outset of the Metal-Support Interaction symposium, to review our current state of knowledge. We will focus on those facts that seem firmly established as well as on the major items that remain controversial.

A brief synopsis of the older literature will be given first. The finding that the chemisorption properties of Group VIII metals are drastically altered by titania supports following high-temperature-reduction (1), later generalized to include other reducible transition metal oxides (2), was interpreted to mean that a strong interaction occurred between these phases. A theoretical model (3) indicated covalent bonding between a Ti^{3+} cation and a Pt atom and further suggested that cation-to-metal charge transfer would strengthen the interaction. This electronic perturbation of the metal atoms was held responsible for the suppressed chemisorption of H_2 and CO, although the observation that even large metal particles suffered this suppression was difficult to explain on this basis. Evidence for the strength of metal-titania interactions came from electron microscopy which revealed that some metals (Pt (4), Ag (5)) had a tendency to spread on the reduced-titania surface. These interactions drastically suppressed activity for alkane hydrogenolysis (6,7); however, the same systems showed increased activity for CO-H_2 synthesis, often accompanied by improved selectivity to higher hydrocarbons.

TiO_x Overlayer Formation in Metal/Titania Model Systems

More recent research has greatly improved our understanding of these systems and has led to new questions as well. Of major importance is the discovery that reduced-titania (usually referred to as TiO_x) is surprisingly mobile and can migrate onto the surface of metals at temperatures commonly used for catalytic reaction or pretreatment. This remarkable structural dynamism introduces a new dimension to the interpretation of metal/titania systems.

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As an example of this behavior, a 100Å-thick layer of Ni atop a layer of TiO_2 shows, initially, only Ni Auger peaks. Reduction at 723K of TiO_2 to TiO_x leads to the detection of both Ti and O signals. Evidently TiO_x has migrated a distance of 100Å, presumably along grain boundaries or the lateral surface of the Ni layer, appearing on top of the Ni (8). If a layer of SiO_2 is interposed between the Ni and TiO_2, no Auger peaks of Ti or O are seen, indicating the absence of artifacts. Similar results have been obtained with a 30Å-thick Rh layer (Ti and O peaks seen with Auger spectroscopy and SIMS) (9) and in another study involving Ni (120Å thick) on titania (Ti and O peaks seen with Auger spectroscopy) (10). In the latter two cases, Ar ion sputtering led to a decrease in the Ti and O Auger signal intensities, indicating removal of the TiO_x overlayer.

The detailed mechanism of TiO_x-overlayer formation, occurring within minutes at moderate temperatures (9) is still obscure. It must be understood, however, as a chemically-specific effect, driven by the interaction between the TiO_x and metal surfaces. The interaction is strong enough to compensate for the partial loss of Madelung energy caused by the disruption of the titania lattice. TiO_x migration is therefore not to be confused with ordinary sintering which leads to a decrease in the total surface area. Early experiments had in fact shown that high-temperature-reduction of metal/titania systems did not cause such a decrease (1).

The formation of TiO_x overlayers thus serves to demonstrate the existence of a metal-support interaction. The latter should be thought of, primarily, in materials-science terms; that is, a bonding between the phases. The effect of this interaction on catalytic properties is a separate question. Additional evidence for metal-titania interaction comes from three surface science studies in which metals were vapor deposited onto titania or $SrTiO_3$ surfaces pretreated so as to contain Ti^{3+} as shown by XPS or EELS. The important result was that surface Ti^{3+} was eliminated (11,12) or decreased (13) by the metal flux. These experiments, involving Pt, Ni or Pd as the deposited metal, point clearly to a metal-Ti^{3+} interaction. This finding appears to have been obscured by the inconclusive results of experiments aimed at establishing the degree of charge transfer in metal-titania interactions, usually involving XPS. Regardless of how the question of charge transfer is ultimately resolved, the fact of metal-Ti^{3+} interaction seems established by the results just cited.

THE EFFECT OF TiO_x-OVERLAYERS ON ADSORPTION-DESORPTION PROPERTIES

The significance of TiO_x-overlayer formation extends beyond the question of bonding between metals and titania. It suggests that the suppression of H_2 and CO chemisorption in metal/titania systems can be explained as simple site blockage due to the overlayer. Despite the appealing simplicity of this model the question is still open and evidence can be cited that points to a more complicated situation. Experiments have been performed under conditions chosen to minimize the likelihood of overlayer formation. In one case a monolayer of Pt was vapor deposited at 130K on a prereduced titania film. H_2 adsorption at 130K was determined before and after annealing at 370K. The treatment reduced the adsorption capacity by 2/3 although this low temperature would not be expected to lead to an overlayer and, in fact, none was indicated by Auger spectroscopy(14). A similar result was obtained by depositing Pt (0.5 ML) at 298K on a titania film that was either oxidized or, alternatively, prereduced before deposition. Prereduction led to a 2/3 decrease in the amount of H_2 adsorbed at 120K (15).

Another approach to the chemisorption-overlayer question is to determine the degree of coverage with Auger spectroscsopy and compare this with the amount of chemisorption suppression. Two such studies have been reported and have reached opposite conclusions. In one case, varying amounts of Ti were deposited onto Pt and then oxidized to TiO_x. H_2 and CO adsorptions were found to vary linearly with TiO_x coverage and complete coverage was required for complete suppression. Thus no effect other than simple site blockage could be discerned (16). In another study Ni (120Å layer) was deposited onto TiO_2. Reduction at 698K produced a TiO_x overlayer. The coverage of Ni, as well as its effect on CO adsorption, was monitored as a function of time. At low TiO_x coverge between 5 and 9 Ni sites were deactivated for CO adsorption per Ti atom in the overlayer (10,17).

If a TiO_x overlayer is able to do more than block sites, i. e., if neighboring metal atoms are affected, this perturbation should lead to changes in the Temperature Programmed Desorption (TPD) spectra. Some studies have found this. For example, annealing a Pt/TiO_x sample at 370K lowered the H_2 desorption peak temperature 33K viz. annealing at 130K (14). Similarly, depositing Pt (at 298K) on prereduced titania lowered the H_2 peak temperature 75K viz. deposition onto an oxidized (TiO_2) film (15). Changes in the CO TPD spectrum were seen as well. In both these studies TPD changes were accompanied by other evidence of electronic perturbation of the Pt, i. e., suppressed adsorption in the apparent absence of TiO_x- overlayer formation (cited above). Correspondingly, an experiment in which suppressed H_2 and CO adsorptions were attributed to simple site blockage of Pt by TiO_x (cited above) also failed to detect any TPD changes induced by TiO_x (16). Finally, the effect of a TiO_x overlayer on Ni was investigated (18). The activation energy for CO desorption was found to be significantly decreased, whereas in the case of H_2 both stronger and weaker binding states were induced by TiO_x.

PROPERTIES OF HIGH-TEMPERATURE-REDUCED (HTR) METAL/TITANIA CATALYSTS

TiO_x-overlayer formation has been amply demonstrated in model systems amenable to surface science characterization. In the case of well dispersed metal particles on high-surface-area titania, firm evidence for overlayer formation is not available; still, one might reasonably expect it to occur. As pointed out above, one might attribute the near-total suppression of H_2 and CO chemisorption to near-total encapsulation of the metal.

Some recent reports, however, argue against such a drastic interpretation. Although some degree of overlayer formation may well occur following high temperature reduction of a metal/titania catalyst, total coverage of the metal surface is not indicated. One example is the ability of the catalyst to generate spillover hydrogen. Metal/titania catalysts that are reduced and outgassed at 773K and subsequently contacted with H_2 at 298K show rapid formation of hydroxyl groups (19) and Ti^{3+} (20) and an increase in electrical conductivity (21), resulting from the spillover-reduction of titania. In another study, the desorption isotherm of HTR Pt/titania, constructed by stepwise decreases in the equilibrium pressure, extrapolated to H/Pt = 0.27 although the conventional adsorption isotherm indicated H/Pt=0. The former value agreed with the particle size derived from electron microscopy. Apparently, spillover hydrogen led to hydroxyl formation, most of which occurred in the vicinity of the metal particles.

Spillover hydrogen can also be demonstrated through its participation in catalytic processes. A recent report (22) described HTR Pt/titania as more active for acetone hydrogenation than Pt/SiO_2. This reaction is believed to occur via coordination of acetone to the oxide surface followed by attack of spillover hydrogen.

In addition to supplying spillover-hydrogen, HTR metal/titania catalysts have been reported to be active for dehydrogenation. (CO-H_2 synthesis reactions are not considered in this section due to the special problems they present). Despite the drastic loss in ethane hydrogenolysis activity (1000-fold) caused by high temperature reduction of Rh/titania the rate of cyclohexane dehydrogenation decreased only ~ 20% (23) viz. the low temperature reduced catalyst. It has also been reported that HTR Ni/titania is about 0.5% as active for ethane hydrogenolysis as Ni/alumina but ~ 50% as active for cyclohexane dehydrogenation (24). Other studies (25) have yielded contrasting results, i. e., a sharp decrease in dehydrogenation activity following high temperture reduction of metal/titania. One may suspect that the details of catalyst pretreatment are important. It appears, however, that at least in some cases activity can be severely suppressed for one reaction while relatively unaffected for another, which runs counter to the model of gross encapsulation of the metal particles.

For a given degree of TiO_x-overlayer coverge, it is important to know how this phase is distributed on the metal surface. One possibility is "gross coverage", i. e., complete blockage of large areas of the metal with, perhaps, large metal areas remaining unblocked. If the TiO_x does not electronically perturb nearby, unblocked sites, the unblocked portion of the metal would be expected to exhibit normal adsorptive and catalytic properties. Thus a HTR 5% metal/titania catalyst with 80% gross coverage of the metal by TiO_x should behave similarly to a 1% loading of the same metal on, say, SiO_2. The above-cited changes in hydrogenolysis-versus-dehydrogenation selectivity are not accounted for by such a model. Further evidence against this simple picture comes from the observation that Pt/titania and Pd/titania exhibit an unusual relationship between H_2 and CO adsorptions, with the former able to partially displace the latter (26,27). In addition, the technique of "frequency response chemisorption" has been used to demonstrate the existence of labile H_2 chemisorption sites in Ni/titania and Rh/titania that are not found with the silica-supported metals (28).

Although gross coverage cannot account for the selective suppression of hydrogenolysis viz. dehydrogenation activity cited above, the possibility of a finely distributed TiO_x overlayer must be considered. It has been pointed out (29) that this behavior is characteristic of bimetallic systems (e.g., Cu-Ni) for which the selective hydrogenolysis-suppressing effect of Cu is explained on the basis of the large Ni ensembles required for this reaction. Additional support for the metal/titania-bimetallic cluster analogy comes from the faster disappearnce of bridged CO viz. linear CO with increasing reduction of metal/titania (10,29,30). Also, H_2 reaction orders for hydrogenolysis are changed in the same way in both types of systems (31). These observations point out the need for information concerning the distribution, on an atomic scale, of TiO_x moieties on the metal surface.

INFLUENCE OF THE METAL/TiO_x INTERACTION ON CO-H_2 SYNTHESIS PROPERTIES

Studies have shown that metal/titania catalysts often show enhanced activity and/or selectivity for the CO-H_2 synthesis reaction. This literature will not be reviewed here. Instead we will concentrate on the question of how these reaction features relate to the properties of metal/titania catalysts previously discussed in this review. An important problem is that H_2O is a by-product of the CO-H_2 reaction, raising the possibility that reduced titania, "TiO_x", cannot exist in these systems. Since there is much evidence that TiO_x is intrinsically related to the results obtained in H_2O-free systems, the relationship between the effects observed in these different environments is called into question.

It must be remembered that, despite the presence of H_2O, CO-H_2 synthesis reactions occur under net reducing conditions. There will be a dynamic equilibrium between Ti^{3+} and Ti^{4+} governed by the relative activities of all oxidants and reductants: H_2O, CO_2, spillover hydrogen, CO and hydrocarbons. Indeed there is some evidence that the properties associated with anhydrous metal/titania systems can occur under H_2O-containing (but net reducing) conditions as well. Suppressed CO chemisorption has been found with in situ IR during CO-H_2 synthesis at 548K over Pt/titania (26) and Pd/titania (27). Suppressed $Ni(CO)_4$ formation has been found during CO-H_2 synthesis over NiFe/titania (32). The spreading of Fe on titania has been observed with TEM upon reduction at 773K in H_2 containing 1% H_2O (33). In another study of Fe/titania under similar conditions, controlled atmosphere electron microscopy revealed that Fe atoms migrate from the center of the metal particle to reduced titania created at the metal periphery by hydrogen spillover, resulting in a doughnut-shaped configuration (34). As a final note on this topic, a cyclic voltammetry study of Pt/TiO_x/Ti showed suppression of CO chemisorption from a CO-saturated aqueous solution (35).

The CO-H_2 synthesis properties of metal/titania catalysts have been found in several studies to be essentially unaffected by the temperature of reduction, in contrast to the strong effect this factor has on chemisorption properties. This problem has focused attention on the special nature of the metal-titania contact perimeter. Reduction of titania, undoubtedly through hydrogen spillover, begins there. It is important to note that Ti^{3+} cations are produced by reduction temperatures as low as 473K, as shown by O_2 adsorption/H_2O decomposition measurements (36) or by temperature programmed reduction. In the latter study, the amount of Ti^{3+} produced at temperatures below 503K was equivalent to a Ti^{3+}/Pt atom ratio of 0.6 (37).

These reduced cations may be involved in the creation of special CO adlineation sites which have been proposed to exist at the metal/titania contact perimeter (38-40). The concept of CO adlineation, i.e., of a CO molecule simultaneously coordinated to a cation and a metal atom, obviously demands an intimate association between these centers and thus, in fact, presupposes a bonding interaction between the metal and reduced titania. This could conceivably affect CO-H_2 synthesis properties in other ways. One is by simply inhibiting sintering of the metal particles. Another possibility would be the creation of metal sites near the contact perimeter with altered adsorption properties for H_2 viz. CO. Such sites might be capable of supplying an incresed flux of dissociated hydrogen to the metal surface. It should be noted that the H_2-displacing-CO effect, referred to above in connection with Pt/titania and Pd/titania, was also observed following reduction of these catalysts at 473K, although the effect was increased by reduction at 773K.

Thus, it is quite conceivable that the metal-titania interaction influences the CO-H_2 synthesis reaction through effects that are concentrated at the contact perimeter and that, since reduction begins here, high temperature reduction is not required for changes in CO-H_2 synthesis properties to be observed. On the other hand, major suppression of H_2 (or CO) chemisorption, or of hydrogenolysis activity, requires that nearly the whole metal particle be affected. Even if suppression does not require blockage of all sites, i.e., if this can come about by the disruption of ensembles or the electronic perturbation of sites near the contact perimeter, overlayer formation will probably be required except, perhaps, in the case of very thin metal crystallites. It has been reported that the hydrogenolysis activity of a Rh/titania catalyst decreased 25% by reduction at 513K for 2 hours (41). This undoubtedly reflects the deactivation of sites near the contact perimeter. Deactivation increases continuously with temperature/time and becomes nearly total only following high temperature reduction.

To conclude this section, there is a need for a better understanding of the unusual CO-H_2 synthesis properties of metal/titania catalysts and related systems such as metal/niobia. The primary question to be answered in this regard concerns the stability of reduced titania in the CO-H_2 system. The fact that several reducible oxides (titania, niobia, vanadia, MnO, etc .) have been found to impart unusual CO-H_2 synthesis properties to supported metals suggests that support-reducibility is an important factor that is not cancelled by the CO-H_2 reaction environment.

SCOPE OF METAL-SUPPORT INTERACTIONS

Although most of this review has concerned metal/titania, it has been mentioned that other easily reducible oxides have similar support properties. Earlier publications pointed out that they differed as a class from main-group oxides such as alumina, silica and magnesia as well as from refractory (to reduction) transition metal oxides such as zirconia and hafnia (2, 42).

It appears, however, that support surfaces are not always as refractory to reduction as chemical intuition would dictate. An important new finding is that lanthanum oxide undergoes reduction, in the presence of a supported metal, to "LaO_x", and the properties of Pd/lanthana are similar in several respects to those of metal/titania (43,44). Even with alumina supports, surface reduction has been found in some instances (45-47). The reason for this anomalous behavior is not fully understood, although sulfur has been found capable of promoting the reduction (46). A recent report has described suppressed H_2 chemisorption on Rh/zirconia (48) although this was not found in an earlier study of Ir/zirconia (2). One may suspect differences in surface reducibility between the supports used in the two cases.

Although this review has dealt with the interactions of metals with reduced oxide surfaces, metal-support interactions are certainly not limited to these. Evidence for metal-support interaction involving non-reduced surfaces exists even in the metal/titania system. Enhanced hydrogenolysis activities have been found for low-temperature-reduced Rh/titania (7) and Ru/titania (49). These effects presumably involve interaction with Ti^{4+} ions.

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