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LETTERS TO THE EDITORS

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

Much interest is currently expressed in titania as a support, mainly due to the interesting observation that the reduction of TiO_2-supported metals at or above 773 K suppresses H_2 and CO adsorption (*1*). Several hypotheses have been proposed to account for this inhibition of chemisorption [(*1–4*) and references therein]. The recent paper by Herrmann (*4*) represents the view that a transfer of an electron from TiO_2 to the metal is responsible for the observed changes in the chemisorptive properties of the metal. While the aim of the present letter is to comment on the conclusions inferred by Herrmann from electric conductivity measurements, it is also to draw attention to the current attitude toward references to previous work, and to some misleading statements concerning the support effect.

The story of the electronic interaction between metal and titania. It must be pointed out at once that the idea of electronic interaction between metal and TiO_2 is not a new one. It was proposed almost 25 years ago when Szabó and Solymosi (*5*) applied TiO_2 as a metal catalyst support. They examined the effects of the following factors on the catalytic behavior of Ni deposited on TiO_2:

(i) Variation of the electric properties of TiO_2 induced by doping it with altervalent ions, (ii) unreduced NiO still present, and (iii) the temperature of reduction. They came to the conclusion that the electric properties of n-type TiO_2 play a dominant role in its support effect. This was attributed to an electronic interaction between TiO_2 and Ni: electrons flowing from the reduced titania to the Ni. Work was also performed on Ni/Cr_2O_3 (*5*) and Ni/NiO (*6, 7*) (both oxides are p-type semiconductors, and their electric conductivities are markedly altered by doping). These articles provided the first experimental evidence of the importance of the electric properties of the support in the carrier effect. This idea was first proposed by Schwab *et al.* (*8*) in connection with alumina-supported metals, but as we have pointed out on several occasions (*5, 7, 9–11*), their experimental results provided practically no confirmation for this explanation. The electric conduction of the insulator Al_2O_3 depended hardly at all on doping of the Al_2O_3 with altervalent ions (variation within $2.5–7 \times 10^{-6}$ ohm^{-1} cm^{-1}), and the activation energy of dehydrogenation reaction differed by only $\pm 10\%$. An exception was when Al_2O_3 was doped with 5% NiO, but in this case an effective Ni/NiO system could be formed (*6, 7*).

The pioneering papers were followed by a number of publications, and experimental data obtained on other systems also demonstrated the importance of the electric properties of the support, and the role of the electronic interaction in the support effect. The results were surveyed by the present author in the Catalysis Review in 1967; the article covered all views and critical remarks available at that time (*9*).

It is interesting that only few Americans became interested in this phenomenon before 1967. One notable exception was Baddour and Deibert (*12*), who examined the role of the electronic interaction between a Ni catalyst and a Ge support, the type of the conductance and the electric conductivity of the support being varied by doping.

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Their results strongly support the occurrence of the electronic interaction described above and its possible role in the support effect.

Apart from the continuing work of Schwab (*13*), there was very little activity in this field following the publication of the above-mentioned review (*9*). Significant progress in this field stemmed from application of the ESCA technique, pioneered by Escard *et al.* (*14, 15*).

A major breakthrough in the use and extension of this idea (i.e., the role of an electronic interaction between metal and support, and particularly TiO_2) occurred when Tauster *et al.* (*1*) observed that the reduction of metal/TiO_2 at ca. 773 K almost completely suppressed H_2 and CO chemisorption without significantly altering the particle size. The term "strong metal–support interaction" was introduced for the observed effect. In the explanation of this phenomenon, an electron transfer from the TiO_2 to the metal was assumed (*2*), with no mention at all that *the behavior of the Ni/TiO_2 catalysts had been examined previously from the aspect of a possible electronic interaction* (*5*).

This omission may well explain why most subsequent authors using the idea of electronic interaction gave credit to Tauster *et al.* (*1, 2*) and fail to refer to the original papers published in this field. This is the situation in the present paper of Herrmann (*4*), who attempts to demonstrate an enhanced electron transfer between metal and TiO_2 in the SMSI state, i.e., after reduction of metal/TiO_2 at 773 K.

It is a well-known fact that evacuation and reduction at high temperatures of *n*-type semiconducting oxides, such as TiO_2, increases the extent of deviation from the stoichiometric composition on the surface, and in most cases leads to an enhanced conductivity (*16*). It is also well established that transition metals, by activating H_2, increase the rate and extent of reduction of these oxides (*17*). This process is very sensitive to the dispersity, shape, and structure of the metals and to the metal–support contact. Accordingly, it is very doubtful that measurement of the electric conductivity of the TiO_2 support would give a reliable indication of the occurrence of *enhanced electron transfer* in the sample reduced *at 773 K* and provide a solid basis for comparisons of the effects of different metals. To this general remark I may add the following. (i) To detect *enhanced* electronic transfer in the SMSI state, i.e., in samples reduced at 773 K, their electric behaviors should be compared with those determined after reduction *not at 473 K, but at 673 K.* The drastic change in the chemisorptive capacity of TiO_2-supported metal occurs in the temperature range 673–773 K. In other words, it is just possible that the differences registered by Herrmann (*4*) between solids reduced at 473 and 773 K, also exist for samples reduced at 473 and 673 K, where there is no SMSI phenomenon at all! (ii) While investigating the reduction of nickel oxides deposited on TiO_2, we found in 1960 that complete reduction cannot be attained at 473 K (*5*). This feature could influence the properties of the Ni/TiO_2 catalyst, and could cause the basically different behaviors of Ni/TiO_2 experienced after reduction at 473 and 773 K (compare Figs. 2 and 4 in Herrmann's paper). (iii) While the conductivity of M/TiO_2 (reduced at 473 K) was lower than that of TiO_2 at 473 and 673 K after evacuation, which was explained by an electron transfer from the TiO_2 to the metal, just the opposite can be observed after reduction and evacuation at 773 K, which apparently does not prove the occurrence of *enhanced* electron transfer.

As concerns the neglect of the first works on this subject, it is often said that we should not refer to papers and ideas published 20–25 years ago and involving old techniques. Such statements may well be right. But if the application of modern techniques or new approaches only *confirm* (or possibly disprove) ideas proposed long before (obtained by the methods that were available and "modern" at that time), *it is* *absolutely unfair not to refer to the earlier work at all.* (As regards the validity or invalidity of our old assumption concerning the electronic interaction between TiO_2 and a metal (Ni), this is the right place to mention the results of Kao *et al.* (*18, 19*). By using modern spectroscopic methods (the combination of UPS, XPS, and Auger electron spectroscopy) and TiO_2 single crystals, they confirmed not only our view as to the occurrence of the electronic interaction between Ni and TiO_2, but also the direction of the electron flow we had concluded from the effects of doping the TiO_2 support (*5*).)

One might accept the attitude of the users of modern, very powerful techniques (UPS, XPS, EXAFS, SEXAFS, etc.) in neglecting the results and conclusions obtained via old-fashioned methods. But *how can the electric conductivity measurements applied in Herrmann's paper (4) be considered a modern physical surface method* which would give the author the questionable right to neglect the papers in which the idea of electronic interactions in metal/TiO_2 and other systems were first proposed?

The complete neglect of the pioneering work on the TiO_2 support, and of the early assumptions on the possible role of the electronic interaction between metal and support, is so extensive among the new generation in the catalysis world that it is disapproved not only by the authors of the early papers, but by neutral observers too. To illustrate this, we refer to the introductory lecture of Bond (*20*) at the International Symposium on Metal–Support and Metal-Additive Effects in Catalysis in Lyon in 1982. He said:

> The first deliberate attempts to explore metal–support interactions, and to manipulate them, were made by Schwab (*13*) and by Solymosi (*9*) who showed that changing the semiconducting properties of the support by altervalent ion doping affected the activation energies of a number of reactions. It is essential from time to time to inspect the older literature, for otherwise we run the risk of rediscovering the wheel.

I myself consider that the neglect of work from the recent past may well lead to the very early devaluation of our present work, which no one would like.

Use of the term "strong interaction" between the metal and the support. As regards the metal–support interaction, there are many confusing and misleading statements and expressions in the recent literature. I feel that it is time to point out some of these. Before the idea of an electronic interaction was proposed (*5–8*), it had been recognized that the support, by *interacting* with the catalyst, can drastically modify the properties of the latter, including its catalytic effect. We refer here to the work of Adadurov (*21*) (polarizing effect) and Selwood (*22*) (valence inductivity).

It is true that at that time the word "strong" was not used, but this was perhaps not necessary as the term "electronic interaction," and the other terms mentioned above, signified a quite strong interaction. Although the "SMSI" phenomenon is not yet clear and completely understood, one can already wonder whether the term "strong interaction" is not a misleading one to describe this phenomenon. If the formation of a new compound between the metal and the support is responsible for the "SMSI" phenomenon, then this is a result of a reaction and not of an interaction. If only an extended electronic interaction occurs at higher reduction temperature, it would qualitatively not be a *new* type of interaction. If *only* a migration of the support material onto the metal causes this phenomenon (*23*), we can hardly speak about a "strong interaction."

It is depressing, therefore, to view a growing and undesirable tendency in the literature: if a phenomenon, to which the term "SMSI" can be applied, is not observed, the authors seem to think that *there is no interaction at all* between the catalyst and the support in their system.

It is also disturbing that if the experimental results indicate that the support exerts an influence on the catalytic behavior of the metal, in other words when there are indications that the support cannot be considered as a totally inert substance, but interacts with the catalyst, the authors at once talk about an "SMSI," forgetting the origin of this phenomenon and that *an interaction between the metal and the support can be very different from an "SMSI."* To go further, Herrmann (*4*) uses the term "artificial" SMSI effect to describe the situation when potassium (which donates an electron) is added to Pt!

TiO_2 as a effective support. I should emphasize in advance that TiO_2 is *an effective support for many catalytic reactions,* even when the metal/TiO_2 catalyst *has been reduced only at 473–673 K.* This has been particularly well demonstrated in the reactions involving the dissociations of NO or CO. To mention only a few examples: before the "SMSI" phenomenon was observed, we found that the formation of NCO surface species in the NO + CO catalytic reaction occurs much faster on Pt/TiO_2 (*reduced at 673 K*) than on Pt/Al_2O_3, Pt/MgO, or Pt/SiO_2 (*24*). It was shown that TiO_2-supported Pt metals are much more efficient catalysts for the NO + CO reaction than the same metals deposited on other supports (*24–27*). TiO_2 proved to be the most effective support in the methanation of CO_2 (*28*) and CO (*29*), and also in the dissociation of CO (*10*).

As concerns the origin of the high efficiency of the TiO_2 support, the present author suggested that the electronic interaction between metal and TiO_2 could be a dominant factor, particularly when the metal is highly dispersed on the TiO_2 support (*10, 28, 29*). This type of interaction can operate even at lower dispersity, when the boundary lines between the catalyst and the support may be the active sites for the reaction, as proposed earlier (*9*). There is no doubt that there are certainly other factors which could be important, depending on the type of the reaction and the experimental conditions.

In the above works, the reduction of Rh/TiO_2 at or above 773 K did not produce better catalysts. This means that the advantageous performance of the TiO_2-supported metal *is not connected with the high-temperature reduction of the metal/TiO_2 system or with the phenomenon causing the suppression of H_2 and CO adsorption.* This possibility has been almost completely neglected, but it is currently receiving increasing attention (*30*).

The fact is that, partly due to the difficulty of determining the dispersity or surface area of the metal in high-temperature reduced metal/TiO_2 samples, there is hardly any convincing evidence indicating that the high-temperature reduction results in a more effective catalyst. In other words, it is very doubtful whether the phenomenon responsible for the suppression of H_2 and CO chemisorption "SMSI" is involved at all in the favorable effect of the TiO_2 support.

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