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Electronic Effects in Strong Metal–Support Interactions on Titania-Deposited Metal Catalysts: Reply to F. Solymosi's Comments

The comments of F. Solymosi (*1*) on our paper published last year in *Journal of Catalysis* (*2*) can be divided into three parts:

(i) Criticisms concerning the omission of references to pioneer papers on metal–titania interactions, published previously to the basic article of Tauster *et al.* devoted to SMSI (*3*), and some comments on electrical conductivity results.

(ii) A philosophical dissertation about the right of using the term "strong interaction" between the metal and the support.

(iii) Examples of the use of TiO_2 as an effective support for metal—especially Rh—catalysts.

For what concerns point (i) it is true that the paper of Szabó and Solymosi (*4*) as well as the review of Solymosi (*5*) should be considered as precursors for the works on electronic interactions occurring on Ni/TiO_2 and Pt/TiO_2 catalysts. For literature citations on SMSI, most of the authors have referred to papers published after the initial work of Tauster *et al.* (*3*), which clearly defined the conditions of obtaining the SMSI effect. In fact, my article is only one among many others about electronic interactions which did not mention Solymosi's early works (see, for instance, Refs. (*9–11, 13–17*) in Ref. (*2*)).

Consequently, Solymosi's letter could have appeared after any of these papers. Solymosi made an oral rectification during the session devoted to SMSI at the International Congress on Catalysis in Berlin in July 1984. At that moment, my paper was already in press and could not be corrected by including Refs. (*4, 5*).

The indication by electrical conductivity measurements of an enhanced electron transfer in the samples reduced at 773 K is not "doubtful" as discussed hereafter. If the electrical conductivity σ_{TiO_2} of titania increases during evacuation after reduction by hydrogen (Figs. 1 and 3, Ref. (*2*)), this is because of the creation of new singly ionized vacancies by a supplementary oxygen loss due to vacuum (Eq. (3) in Ref. (*2*)). This also occurs for titania supporting metals, but because of the electron transfer to the metal (Eq. 6, Ref. (*2*)), σ_{M/TiO_2} decreases. The fact that σ_{TiO_2} is not higher than σ_{M/TiO_2} in the SMSI state (Fig. 3, Ref. (*2*)) conversely to the normal state (Fig. 1, Ref. (*2*)), does not mean that the electron transfer is not higher than after reduction at 473 K. It is because of the very high conductivity ($\sim 10^{-2}$–10^{-1} ohm^{-1} cm^{-1}) corresponding to a degenerate semiconductor character of titania that σ relative variations in log scale are smaller than those encountered for the normal state, where σ is $\sim 10^{-2}$–10^{-3} ohm^{-1} cm^{-1}, with still a semiconductor character shown by the linear Arrhenius plots of Fig. 2. Moreover, if one compares σ_{M/TiO_2} values in H_2 and after evacuation before cooling for $T_R = 473$ and 773 K (Figs. 1 and 3, Ref. (*2*)) it appears semiquantitatively that the relative decrease in σ_{M/TiO_2} due to electron transfer is 8, 3.4, and 18 times higher for SMSI than for the normal state for Pt, Rh, and Ni catalysts, respectively.

Concerning the choice of 673 K instead of 473 K for the low reduction temperature recommended by Solymosi because of the absence of SMSI for $T \leq 673$ K, I disagree with this suggestion, since SMSI, defined as the phenomenon responsible for the decline of H_2 (or CO) chemisorption after reduction at high temperature, already occurs at 673 K and even at 573 K. This was ob-

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served, for instance, on iridium deposited on various transition metal oxides (*6*). This was also observed on one of our Pt samples, whose H_2 chemisorption capacity was divided by a factor of 1.1, 2.2, and 9 when the reduction temperature was increased from 473 K to 573, 673, and 773 K, respectively. This is also the case for nickel (5 wt%) whose mean particle diameter (~13.5 nm) obtained from magnetic measurements is smaller than that calculated from H_2 chemisorption (8 μmol H_2 $g_{catalyst}^{-1}$), done after reduction at 623 K to make sure that all nickel atoms are really zero valent. This shows that the SMSI effect is already operating at 623 K on Ni/TiO_2 as clearly written on p. 409, 2nd column in Ref. (*2*).

Concerning the uncomplete reduction of nickel oxide by H_2 at 473 K, recalled by Solymosi (*4*), it was taken into account for choosing the reduction temperature before dispersion measurement by hydrogen chemisorption (see p. 406, Ref. (*2*)). This uncomplete reducibility of nickel is clearly evidenced by the second exposure of Ni/TiO_2 to hydrogen following a sequence in O_2 (see Fig. 1 and comment on p. 408, 2nd column in Ref. (*2*)).

Concerning the detection of electronic interactions between the metal and its support on real catalysts—not model ones—electrical conductivity measurements constitute a choice technique to follow *in situ* their behavior from the beginning of their initial pretreatment up to their subsequent exposures to various gases at different temperatures including the transient periods between sequences.

The second part of Solymosi's comments is more general and considers the right of using the term of "strong interaction." I agree with him that concepts should be defined more precisely now, as many results are available. In fact, the term "strong" in the collective acceptance of the SMSI concept, concerns more the effect than the cause. The effect is the sharp decrease in H_2 (or CO) chemisorption, whose extent can vary either with the nature of the metal or with its particle density (Table 2, Ref. (*2*)). The merit of Tauster *et al.* in their initial work (*3*) consists in having clearly established the rules for obtaining the "SMSI" state. Moreover, it is remarkable that this effect was universally observed: as far as I know, nobody, respecting these rules, found a discordant result.

It is correct that "if the formation of a new compound between the metal and the support is responsible for the 'SMSI' phenomenon, then it is a result of a reaction and not of an interaction." It is also correct that "if only a migration of the support material onto the metal causes this phenomenon, we can hardly speak about a 'strong interaction'." However, "if only an extended electronic interaction occurs at higher reduction temperature," it would perhaps "qualitatively not be a new type of interaction" but it would certainly be a *stronger* one and, in this case, the denomination SMSI is correct.

It is also true that the absence of an observed SMSI effect does not mean the absence of interaction. In Ref. (*2*), the electronic interaction between the metal and its support, symbolized by Eq. (6), exists permanently. It only becomes *stronger* when the reduction temperature is increased, corresponding for titania to an elevation of its Fermi level and to the passage from the semiconductor state to the quasimetallic one. Moreover, it is because of the same electronic origin that the term "artificial SMSI" was used in Ref. (*7*), where potassium was introduced as an additive to platinum. The term "artificial" meant: same result (suppression of H_2 chemisorption), acting on the same cause (charge transfer to Pt) but with a different technique (use of an alkaline additive instead of a high-temperature reduction in hydrogen).

Another possible way of modifying the electron density in TiO_2 consists in illuminating it as mentioned in the introduction of Ref. (*2*). The same type of electronic transfer between Pt and TiO_2 occurs under illumination but with photoelectrons, either *in vacuo* or hydrogen (*8*) or under SMSI conditions (*9a*) or even under oxygen (*9b*).

The third part of Solymosi's comments refers to several papers on titania as an effective support, mainly for Rh catalysts, and questions "whether the phenomenon responsible for the suppression of H_2 and CO chemisorption "SMSI" is involved at all in the favorable (catalytic) effect of the TiO_2 support." As mentioned at the end of Ref. (*2*), the absence of inhibition by SMSI for certain reactions like CO methanation implies that H_2 and CO active species are those whose chemisorption is not inhibited by SMSI.

In conclusion, if my article has acted as a catalyst or a promoter for the rejuvenation of the collective memory concerning papers on metal–support interactions—especially electronic ones—which are previous to SMSI (1978, Ref. (*3*)), I would feel satisfied.

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