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Metal–Support Interaction in Pt/Al_2O_3: Reply to Margitfalvi *et al.*

Margitfalvi *et al.* (*1*) have commented on our papers (*2, 3*), in which the experimental results obtained by the high-temperature H_2 or O_2 treatments of Pt/Al_2O_3 catalysts were described and the redox reaction of the alumina support during the pretreatments was proposed as possible mechanism. We found the good correlation between the decrease (or increase) in the amount of hydrogen chemisorption and the amount of H_2 (or O_2) consumptions during the pretreatments (*3*). We also showed clear evidences by XPS and ir for that S and SO_4^{2-} species in the 5% Pt/ALO-2 (No. 4, Ref. (*3*)) did not change during these high-temperature treatments.

Margitfalvi *et al.* (*1*) have claimed that our method of the correlation mentioned above is not sufficiently correct, and additional surface reactions may be also involved in the H_2 consumption during the pretreatments.

First, it is important to note that our discussion in paper (*3*) was mainly concerned with the 5% Pt/ALO-2 (No. 4) with relatively low sulfur content (S/Pt = 0.3). We have never claimed that the same behavior in S and SO_4^{2-} species as in the 5% Pt/ALO-2 should be found generally in all kinds of supported Pt catalysts with different specifications. Formation of S by reduction of SO_4^{2-} could occur by the high-temperature reduction (HTR) in other Pt/Al_2O_3 of higher sulfur content, for which we have some experiences and evidences.

In our preliminary paper (*2*), we did not pay attention to the role of sulfur in Al_2O_3 onto the SMSI behavior of Pt/Al_2O_3. The data in Fig. 3 of Ref. (*2*) are mainly concerned with 0.5% Pt/ALO-2 catalyst with rather high sulfur content, i.e., S/Pt (atomic ratio) of nearly 5. In this catalyst, the higher value of H_2 consumption (about 10 in terms of H/Pt) during HTR probably came not only from the reduction of the Al_2O_3 support, but also from that of SO_4^{2-} contained in Al_2O_3 as an impurity.

Afterwards, we realized that the degree of suppression of H_2 chemisorption after HTR depended strongly on the sort of Al_2O_3 supports, and could be related to sulfur content in Al_2O_3. In paper (*3*), we investigated the relation between the change of H_2 chemisorption and the gas consumption (H_2 and O_2) after and during the high-temperature H_2 and O_2 treatments with special attention paid to the behaviors of sulfur during these treatments. In the case of the 5% Pt/ALO-2, the suppression of hydrogen chemisorption cannot be explained with such a simple mechanism as poisoning by sulfur, as discussed in paper (*3*). The role of sulfur is presumably to promote the partial reduction of alumina. We like to call this phenomenon a sulfur-aided SMSI, where the term SMSI is used in the sense that the partial reduction of support materials is responsible for the phenomenon of the suppression of hydrogen chemisorption. However, the mechanism could be different from the original system (Pt/TiO_2) (*4, 5*).

Recently, we applied a temperature-programmed reduction (TPR) technique to the 5% Pt/ALO-2 to measure quantitatively H_2O formed during HTR. The amount of H_2O coincided well with the result by the H_2 consumption measurements. This result also supports our proposed redox model for the SMSI behavior. The details of this work shall be published in near future.

Second, they have commented that the data in Table 2 of Ref. (*3*) are very scattered. However, we believe that, for in-

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stance, H/Pt = 1.25 in run No. 2 should be regarded as twice that of O/Pt = 0.46 in run No. 4. It is not appropriate to discuss the difference between 1.25 and 0.92 (0.46 × 2), because some experimental errors are unavoidable. In order to measure the gas consumption, we used a closed circulating system with large dead volume (about 120 cm^3) including a circulation pump and a liquid N_2 trap. Correction was done carefully for temperature changes in these parts as well as the sample tube. All the data obtained as above were plotted in Fig. 2 of Ref. (*3*). The figure shows obviously the linear relations, as a whole, between the changes in H_2 chemisorption and the consumption of H_2 (or O_2) during the H_2 (or O_2) treatments. These relations should be accepted as an overall trend, but it is not adequate to discuss some discrepancies from point to point, because of the above reason. The average ratio of slopes of 2 to 1 indicates a reversible redox process occurring during the pretreatments.

We are confident of the above relations in the catalysts examined here, i.e., the 5% Pt/ALO-2 and 2% Pt/ALO-4. However, we have never claimed that there are generalized linear relations which should be applicable to all kinds of supported platinum catalysts with different loading of Pt, different types of Al_2O_3 (especially in terms of sulfur content), quite different dispersion of Pt, and so on. This is an interesting subject for future work. We are not ready to discuss whether residual chlorine has an important role in SMSI or not. This is also an interesting subject for further work.

In conclusion, we cannot accept their criticism which claims the contradictions in our results. We believe that the partial reduction of the alumina support is the most plausible interpretation in the case of the 5% Pt/ALO-2 as discussed in paper (*3*).

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