On the Mechanism of Strong Metal–Support Interaction in Pt/TiO_2: Temperature Programmed Reduction Measurement of H_2O during the High-temperature Treatment

Kimio Kunimori, Ikufumi Maezawa, and Toshio Uchijima*

Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

The number of water molecules formed by H_2 treatment of Pt/TiO_2 at 773 K, which brought about strong metal–support interaction, was of approximately the same magnitude as the number of Pt atoms in the catalyst.

We have shown previously that there is a good correlation between the extent of suppression (or recovery) of hydrogen chemisorption and the amount of H_2 (or O_2) consumption during the high-temperature H_2 (or O_2) treatment of Pt/TiO_2 catalysts, and the strong metal–support interaction (SMSI) model with partially reduced titania has been discussed in terms of the amounts of H_2 and O_2 consumed.[1] The partial reduction of the support has been generally accepted by workers who proposed the model for SMSI (*e.g.*, the formation of the pill-box structure[2] and the migration of reduced titania onto the metal particles[3]). However, alternative models have been proposed to explain the hydrogen uptake during the high-temperature reduction (HTR) of Pt/TiO_2: *i.e.* stronger chemisorption of hydrogen on Pt itself,[4] and spillover and back-spillover of hydrogen.[5,6] On the basis of these models, water would not be desorbed during HTR. In order to discriminate these models of non-reduction of support from the ones with partial reduction of titania, it is important to know whether the hydrogen consumed during HTR is removed from the catalyst as H_2O or not. We now report the result of a quantitative analysis of water during HTR and compare the observed H_2O : Pt ratio in this study with the amount of H_2 (or O_2) consumption (the O : Pt value) from the reported correlation obtained by the volumetric technique.[1]

The analysis of water was performed using a temperature programmed reduction (TPR) apparatus with a quadrupole mass spectrometer as a detector.[7] Special care was taken to detect only water produced by reduction of the support, without any loss of such water by its adsorption on the support, as well as any extra water arising from desorption of that which is preadsorbed. The typical procedures for the pretreatments and the measurements were as follows: (i) O_2 treatment of a Pt/TiO_2 catalyst at 673 K followed by low-temperature reduction at 473 K (the normal treatment), (ii) H_2 temperature programmed desorption (TPD) measurement in flowing He gas (up to 773 K) to check the normal chemisorption behaviour,[7] (iii) He treatment at 773 K to confirm that no extra water is evolved from the system, (iv) analysis of water during TPR (20 K min^{-1}, up to 773 K) and during HTR (at 773 K for 1 h) in flowing 2% H_2–He gas, (v) He treatment at 773 K again to confirm that there is no extra water, and (vi) H_2 TPD measurement in He (up to 773 K) after H_2 adsorption at 473 K to check the decrease in the amount of the hydrogen chemisorption (SMSI behaviour).[7] The portion between the catalyst tube and the detector was heated to 453 K in order to avoid the possible severe effect due to adsorption of water on the inner wall of the stainless steel tube. Samples of Fe_2O_3 (controlled amount to produce water by hydrogen reduction in the same order of magnitude as in the typical TPR study) were used to calibrate the amounts of water produced.

A 1 wt% Pt/TiO_2 (Degussa, P-25) catalyst was prepared by the incipient wetness technique using H_2PtCl_6 (aq.). The catalyst (0.6 g) was treated in O_2 at 723 K then reduced at 473 K before use. The amount of hydrogen chemisorption measured by the volumetric adsorption technique[1] at room temperature gave H : Pt (the ratio of H atoms to the total number of Pt atoms) = 0.41 after the normal treatment, and this decreased to 0.02 after HTR at 773 K for 1 h (SMSI treatment).

In this study, 5 runs were performed. The TPD spectra [steps (ii) and (vi)] were consistent with the previous ones.[7] No water signal was observed in steps (iii) or (v), while a reasonable amount of water was evolved in step (ii). The response of the water signal was as follows during TPR and HTR [step (iv)]. The intensity of the signal increased sharply at around 700 K, decreased gradually after the temperature attained 773 K, and became negligible in *ca.* 1 h after the HTR treatment.

The average amount of water determined from the observed peak area in each run was 1.16† in terms of H_2O : Pt; in other words, the number of oxygen atoms removed (as H_2O) from the oxide support during TPR and HTR was 1.16 in terms of O : Pt. This result is approximately consistent with our previous one from the H_2 and O_2 consumption measurements.[1] The O : Pt value, deduced from the correlation in Figure 1 of ref. 1, is about 1.0, based on the change in the hydrogen chemisorption value (*i.e.*, 0.39 = 0.41 − 0.02). Therefore, it is shown that most of the hydrogen atoms spilled-over (or chemisorbed, if present) were desorbed as water molecules owing to the reduction of titania during HTR. Therefore neither the model invoking the stronger chemisorption of hydrogen on Pt itself,[4] nor the one involving the spillover and back-spillover of hydrogen,[5,6] can be the major mechanism for SMSI. More extensive studies will be needed for the detailed discussion of the SMSI mechanism (*e.g.*, either the pill-box structure model[2] or the migration model[3]).

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† The reproducibility was good, considering the experimental difficulties: 0.96, 1.07, 1.16, 1.47, 1.14 H_2O : Pt (*i.e.* the number of water molecules produced: the total number of Pt atoms in the catalyst).