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NOTES

On the SMSI State in Pt/TiO_2 System: Measurements of Gas Consumption during the High-Temperature Treatments

Recently Tauster *et al.* (*1*) have reported that Pt/TiO_2 exhibited strong metal-support interaction (SMSI) when it was reduced in H_2 at high temperature (773 K). The main characteristic of SMSI is the drastic decrease of hydrogen chemisorption capacity on the supported metal after H_2 treatment at 773 K and its recovery after O_2 treatment at 673 K followed by low-temperature reduction at 473 K. Since then, metals in the SMSI state have been subjected to numerous investigations to elucidate this phenomenon (*2–10*). Morphological study by electron microscope on the model Pt/TiO_2 catalyst (*2*) showed that the three-dimensional Pt crystallites were transformed into flat thin pillbox-like structures on the partially reduced titania, Ti_4O_7. Horsley's (*3, 4*) molecular-orbital calculation suggested the existence of a chemical bond between Pt and Ti^{3+}, and the XPS studies (*5–7*) indicated some electron transfer from Ti^{3+} to Pt. However, the exact nature of SMSI seems to be still controversial (*8–10*). In this note, we report results of our study to measure the gas consumption during the high-temperature treatments of Pt/TiO_2 in H_2 and O_2, respectively, and to correlate the amounts of the consumption with those of the change in hydrogen chemisorption.

The TiO_2 support used in this study was obtained from Degussa Company (P-25, BET surface area 50 m^2/g). Three 1 wt% Pt/TiO_2 catalysts (designated by A, B, and C) were prepared by incipient wetness technique using H_2PtCl_6 aqueous solution. After drying them in air at 383 K overnight, the catalysts were reduced in H_2 for 1 h at 473 K (A, B) or at 773 K (C) with the space velocity of 12,000 h^{-1}.

The adsorption apparatus was a conventional glass vacuum system, base pressure of 10^{-5} to 10^{-6} Torr (1 Torr = 133.3 Nm^{-2}) being attained by an oil diffusion pump with a liquid nitrogen trap. The reduced catalyst samples of 0.5 g were placed in a Pyrex tube. The amounts of hydrogen adsorbed on the catalysts were determined from pressure measurements with an MKS Baratron pressure gauge. Calibrated and dead volumes were determined using helium gas. The procedures used for the chemisorption measurements have been described previously (*11, 12*). The isotherms were not studied in detail, but the H_2 chemisorption measurements were performed at room temperature and the lower equilibrium pressures (2 to 5 Torr) (*11, 12*).

Before the H_2 chemisorption, H_2 and O_2 pretreatments of the catalysts were performed *in situ* using a closed circulating system with a liquid nitrogen trap in the same adsorption apparatus. The two typical procedures were as follows: (a) the H_2 treatment at 773 K and 50 Torr for several hours (up to ca. 5 h), followed by evacuation *in vacuo* at 723 K for 1 h; and (b) the O_2 treatment at 673 K and 50 Torr for 1 h, followed by low-temperature reduction at 473 K and evacuation *in vacuo* at 723 K for 1 h. The consumption of H_2 during the H_2 treatment at 773 K in (a) was measured from the decrease of the H_2 pressure using the closed circulating system. The consumption of O_2 was also measured from the decrease of the O_2 pressure during the O_2

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treatment at 673 K in (b). It should be noted that the high-temperature treatments were performed on the bare (i.e., free from any hydrogen or oxygen adsorbed) Pt surface.[1] Consequently, the amount of H_2 consumed during the H_2 treatment at 773 K did not include that of H_2 for reduction of platinum oxide. In other words, it was not necessary to make a correction for reduction of platinum oxide in the case of the H_2 consumption measurements. On the other hand, the amount of O_2 consumed during the O_2 treatment at 673 K was determined by subtracting the amount of oxygen chemisorbed on platinum at 673 K (blank) from the observed uptake of O_2. The blank value was determined by hydrogen titration (*13*) after the O_2 treatment, and found to be 1.0 in terms of O/Pt (the number of O atoms/the total number of Pt atoms) at this experimental condition. This value is in good agreement with the case of the Pt/Al_2O_3 system (*11*).

The original H_2 chemisorption value after the O_2 treatment (b) of each catalyst was as follows: 0.81 (A), 0.69 (B), and 0.65 (C) in terms of H/Pt (the number of H atoms/the total number of Pt atoms). We regard the difference in the H/Pt ratio between the catalysts A and B as a difference in lot of preparation. For the three catalysts, the drastic decreases (or increases) in the amounts of H_2 chemisorption were observed by the treatments (a) (or (b)). This phenomenon (the SMSI phenomenon) was in good agreement with that reported by Tauster *et al.* (*1*). The original H/Pt values, which correspond to true dispersion of the catalysts, were reproducible if the O_2 treatment (b) was performed. The data for the amounts of H_2 and O_2 consumption and, correspondingly, the changes in H_2 chemisorption values were thus obtained by repeating cycles of the treatments (a) and (b).

Figure 1 shows relations between the changes in the H_2 chemisorption values and the amounts of H_2 and O_2 consumed during the H_2 and O_2 treatments, respectively. Linear correlations were found: the ratio of the slopes in the figure is approximately 2 to 1, which indicates the occurrence of a reversible redox of TiO_2 during the treatments. Spill over of hydrogen from the Pt particles adjacent to the TiO_2 surface may lead to the reduction of the TiO_2 support (with H_2O formation). Small part of the spilled over hydrogen may be also desorbed as H_2 (without reduction of the oxide) during the evacuation *in vacuo* at 723 K, considering that the ratio of the slopes in Fig. 1 appears to be slightly greater than 2.

In most of the published models for SMSI (*1–10*), the reduction of TiO_2 to TiO_{2-x} has been considered in relation to the SMSI phenomenon. This work also supports the idea of redox process. The important aspect of this work is quantitative determination of the amount of oxygen eliminated from the TiO_2 lattice (with H_2O formation), which is responsible for the SMSI state. The complete suppression of hydrogen chemisorption (*1*) was not observed in our system. The maximum change in the H_2 chemisorption value was

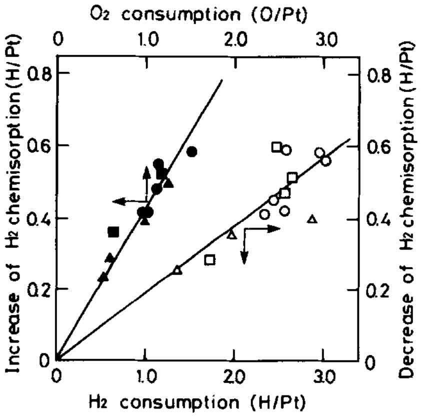

FIG. 1. The decrease of H_2 chemisorption vs the H_2 consumption at 773 K and the increase of H_2 chemisorption vs the O_2 consumption at 673 K. The blank value (1.0) was subtracted from the observed uptake of O_2 (see text). ○,● (A); □,■ (B); △,▲ (C).

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[1] The bare Pt surface was obtained by the treatment of the catalyst in H_2 at 473 K followed by evacuation *in vacuo* at 723 K, or by the evacuation *in vacuo* at 723 K after the hydrogen chemisorption measurement.

ca. 0.6 in terms of the H/Pt ratio as shown in the figure. We note that the incomplete suppression of hydrogen chemisorption was also reported by other authors (*8*). As shown in the Fig. 1 the amount of oxygen consumed (which is responsible for the SMSI state) was almost 2 in terms of the O/Pt ratio, based on extrapolation to the complete suppression. In other words, the consumed value corresponds to the removal of about 8×10^{-3} g-atom O per formula weight of TiO_2, or to the production of nonstoichiometric titania of the composition $TiO_{1.992}$ (i.e., x is ca. 0.008). If we assume the reduction of the support to be limited to the topmost surface layer, the number of the oxygen vacancies was estimated to be about 1×10^{14} atoms/cm^2 (ca. 10% of the surface) based on the BET surface area. It should be noted that, from this work only, it cannot be concluded which model (*1–10*) for SMSI is reasonable. However, the quantitative determination of the amount of the consumed oxygen may be useful for the discussion of the SMSI state. For example, if we adopt the Baker's model (*2*), the surface complex in the SMSI state may be written schematically as $Pt_n(Ti_4O_7)_{2n}$, where n represents the number of Pt atoms of each crystallite in the normal state.

This method may be one of the direct ways to obtain information on the SMSI state. Further experiments for other systems such as Rh/TiO_2 and these metals on the other oxides etc. will be useful to elucidate overall aspects of the SMSI phenomenon.

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