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Combined Temperature-Programmed Reduction (TPR)-Temperature-Programmed Desorption (TPD) Study of Supported Platinum Catalysts

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Successive temperature-programmed desorption (TPD) after temperature-programmed reduction (TPR) (Combined TPR-TPD) was performed in order to characterize supported platinum catalysts (Pt/SiO_2, Pt/Al_2O_3, Pt/ZrO_2 and Pt/TiO_2) as well as to judge the validity of the apparent TPR profiles. In successive H_2-TPD runs obtained after cooling in the absence of hydrogen from 450 °C to room temperature, the hydrogen desorption peak was observed only for the Pt/TiO_2 sample, indicating that the hydrogenic species were kept on Pt/TiO_2 sample, while no hydrogenic species were retained on the other samples after TPR up to 450 °C. For both Pt/Al_2O_3 and Pt/TiO_2 samples, hydrogen spillover seemed to proceed. Hydrogen incorporation during TPR was greater for Pt/TiO_2 than for the others. This hydrogen spillover causes an overestimation of the consumed H_2/Pt value determined by the apparent TPR profile for Pt/TiO_2. For Pt/SiO_2 and Pt/ZrO_2 samples, the apparent TPR profiles were mostly due to a reduction of the supported Pt oxides. For the Pt/TiO_2 sample, the hydrogen incorporation/emission at different temperatures during TPR was investigated. To generate SMSI states, desorption of the spiltover hydrogen is suggested to play a significant role; the role of hydrogen incorporation/emission in the generation of SMSI states is also discussed.

Since Tsuchiya et al. revealed by a temperature-programmed desorption (TPD) method that four types of hydrogen adsorption occurred on platinum surfaces,[1)] TPD has been frequently used to characterize the surface properties of catalysts. Temperature-programmed reduction (TPR) is a method similar to TPD, and has especially been developed to characterize supported metal catalysts.[2—4)] In principle, a hydrogen-containing stream perfuses over a catalyst sample while the temperature is being raised linearly. By measuring the concentration of hydrogen in an effluent stream as a function of the temperature, the TPR profile is obtained. The direct, useful information provided by TPR profiles is the reducibility of the supported metal precursors. The preparative method, pretreatment temperature, modifications with the other metal components, and morphology were reflected in the reducibility of the metal oxides.[2,5—8)]

The "reducibility" of metal oxides has usually been discussed based on the features and areas of the apparent TPR profiles. However, the apparent TPR profiles (hydrogen consumption profiles) are not completely due to a reduction of the metal cations. As suggested by Huang et al.,[9)] a reduced metal is capable of adsorbing hydrogen from the gas phase, and the adsorbed hydrogen on metallic sites can desorb into the carrier gas. Also, the migration of adsorbed hydrogen on metallic sites to the support (hydrogen spillover[10,11)]) and/or its reverse process (back-spillover[12)]) should be taken into consideration regarding an analysis of the apparent TPR profiles. From this point of view, Huang et al. carried out successive TPR experiments while trying to remove any contribution of chemical processes other than reduction to the apparent TPR profiles for monometallic Pt/Al_2O_3, Ir/Al_2O_3, and bimetallic Pt/Ir/Al_2O_3. However, only repetitions of TPR runs cannot be used to distinguish hydrogenic species retained on a surface at the end of the 1st run from those formed by a low-temperature adsorption of hydrogen. We wish to report here on the combined TPR-TPD results concerning supported platinum catalysts (Pt/SiO_2, Pt/ZrO_2, Pt/Al_2O_3 Pt/TiO_2) in order to judge the validity of the apparent TPR profiles of these catalysts. Furthermore, we examined the combined TPR-TPD for Pt/TiO_2 by changing the upper temperature of the TPR measurement in order to elucidate the role of H_2 consumption/emission in the generation of the Strong Metal Support Interaction (SMSI) state, which is well known as the temperature-dependent process.[13,14)]

Experimental

Catalyst Preparation and Apparatus. The supported Pt catalysts were prepared by impregnation with a H_2PtCl_6 aqueous solution. We prepared 2 wt% Pt/SiO_2 and 0.6 wt% Pt/Al_2O_3 catalysts with Fuji Davison-Type ID SiO_2 and JRC-ALO-4 (Reference catalyst of Catalysis Society of Japan), respectively. The 0.5 wt% Pt/ZrO_2 and 0.6 wt% Pt/TiO_2 catalysts were prepared with $Zr(OH)_4$ and $Ti(OH)_4$, respectively. $Zr(OH)_4$ and $Ti(OH)_4$ were obtained by the hydrolysis of $ZrOCl_2 \cdot 8H_2O$ and $TiCl_4$, respectively, with 25% aqueous ammonia followed by filtration. The obtained hydroxide gel was washed with distilled water until no Cl^- ions could be detected. These catalysts were dried at 110 °C and calcined at 400 °C. Prior to TPR experiment, each sample was calcined at 300 °C for 2 h, and then heated in Ar flow in situ at 300 °C for 2 h.

The TPR apparatus used in this study is shown in Fig. 1. A mixture of 3% H_2 in Ar was used as a reductive gas. This mixture was purified over reduced copper in order to remove any trace oxygen, followed by passing it through 13X molecular sieves to remove water. The change in the concentration of H_2 as a function of the temperature was monitored by a thermal conductivity detector (TCD), yielding the TPR pro-

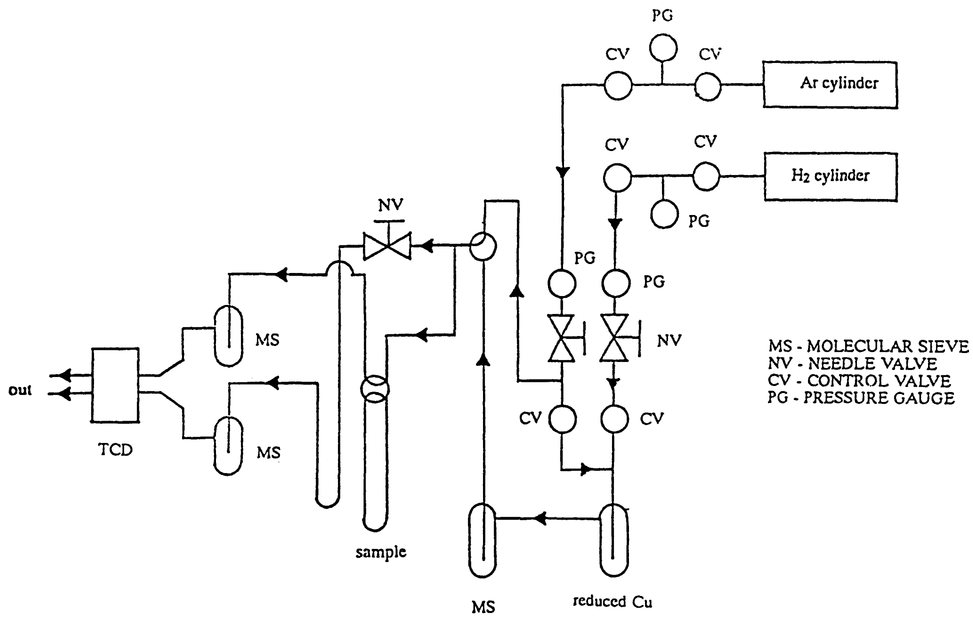

Fig. 1. Schematic diagram of the TPR apparatus.

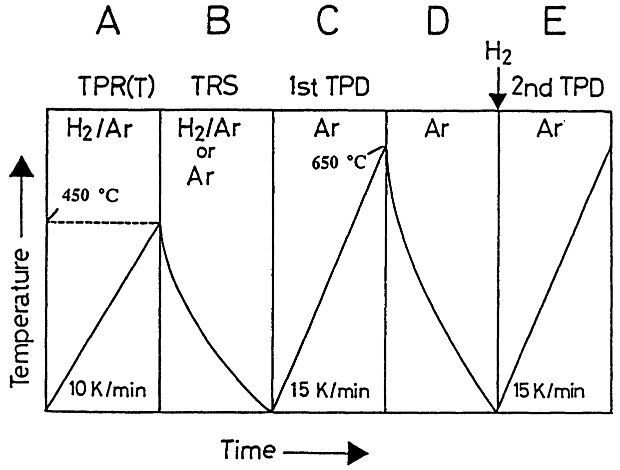

Fig. 2. Sequence of the combined TPR-TPD.
A) TPR, B) TRS (Temperature-Resolved Sorption), C) 1st TPD, D) Cooling, E) 2nd TPD.
The heating rates are indicated.
At the end of D), 23 Torr H_2 was introduced over the sample for 1 min.

file. Since water is formed during the reduction process, gas coming from the reactor was dried over 5A molecular sieves before entering the TCD.

The TPD experiment was carried out succesively after the TPR experiment in the same apparatus. As a carrier gas, pure Ar was used. The Ar gas was purified by the same procedures described in the TPR section. The heating rates for TPR and TPD were 10, and 15 K min^{-1}, respectively. The amounts of consumed hydrogen were calibrated to the amount for reducing of CuO.

Combined TPR-TPD. Although the methodology used in this work was essentially the same as that reported by Huang et al.,[9] we used pure Ar as a carrier gas for the TPD measurement instead of a H_2/Ar mixture in order to avoid any H_2 adsorption during the TPD experiment.

The procedures in this work are illustrated together with a thermoprofile in Fig. 2, and are as follows:

(1) The apparent TPR profile is obtained up to T (T is usually 450 °C).

(2) The sample is cooled to room temperature in a H_2/Ar gas stream.

(3) At room temperature, the H_2/Ar gas mixture switches into pure Ar gas. Then, without H_2 adsorption, the temperature of the sample is raised in an Ar gas stream to 650 °C. The resulting TPD profile is designated the 1st TPD profile.

(4) The sample is cooled to room temperature in an Ar gas stream.

(5) The H_2 gas (3 vol% H_2 in Ar) is then exposed to the sample at ca. 40 °C for 1 min. The temperature of the sample is raised in an Ar gas stream to 650 °C. The resulting TPD profile is designated the 2nd TPD profile.

The difference between the 1st TPD obtained after cooling in the presence of hydrogen and the 2nd TPD reveals the effect of adsorption temperature on the desorption of the hydrogenic species. In some experiments, the sample was cooled to room temperature under a pure Ar stream instead of a H_2/Ar mixed-stream in the procedure (2).

Results and Discussion

Combined TPR-TPD. Figure 3 shows the apparent TPR profiles up to 450 °C of the supported platinum catalysts. Single apparent hydrogen consumption peaks were observed for Pt/ZrO_2, Pt/Al_2O_3, and Pt/TiO_2, appearing at 225, 254, and 145 °C, respectively. These peak temperatures are in good agreement with those reported for Pt/Al_2O_3[5–7] and Pt/TiO_2.[15] On the other hand, two apparent consumption peaks at 130 and 240 °C were observed for the Pt/SiO_2 sample. The appearance of two consumption peaks was reported by Augustine and Sachtler for Pt/Al_2O_3,[16] who suggested that they are due to two-dimensional PtO_2 and three-

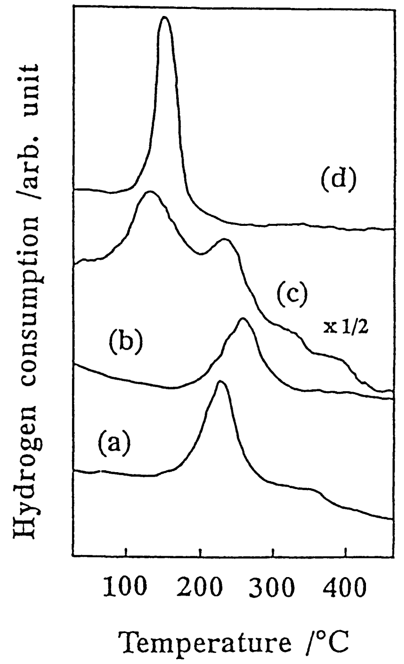

Fig. 3. The apparent TPR profiles of the supported platinum.
(a) Pt/ZrO$_2$, (b) Pt/Al$_2$O$_3$, (c) Pt/SiO$_2$, (d) Pt/TiO$_2$.

dimensional platinum oxide. The apparent consumption peak temperatures are tabulated in Table 1 together with the ratio of the consumed hydrogen during the TPR experiment to the total platinum content in the sample (consumed H$_2$/Pt). It is clearly shown in Table 1 that the consumed H$_2$/Pt value for Pt/TiO$_2$ is larger than those for other samples.

The 1st TPD profiles obtained after cooling in the presence of hydrogen are shown in Fig. 4. These TPD profiles were measured by increasing the sensitivity of the detector. In the 1st TPD, hydrogen desorption was not observable for Pt/ZrO$_2$. For Pt/Al$_2$O$_3$, the desorption peaks were broad and appeared over a wide temperature range (70—600 °C). For Pt/SiO$_2$, the desorption peak was more clear than that for Pt/Al$_2$O$_3$, and appeared at 125 °C. In the case of Pt/TiO$_2$, at least three desorption peaks appeared at 215, 280, 635 °C. The amount of desorbed hydrogen from Pt/TiO$_2$ was larger than that for other samples. This means that a large amount of the hydrogenic species was kept over the Pt/TiO$_2$ sample after cooling down in the presence of hydrogen.

Table 1. Results for the Apparent TPR Profiles of Supported Platinums

Sample	Peak temp/°C	H$_2$/Pt[a)]
Pt/ZrO$_2$	225	1.9
Pt/SiO$_2$	130 340	0.5
Pt/Al$_2$O$_3$	254	1.0
Pt/TiO$_2$	145	3.4

a) The ratio of the consumed hydrogen determined by the apparent TPR profile up to 450 °C to the platinum.

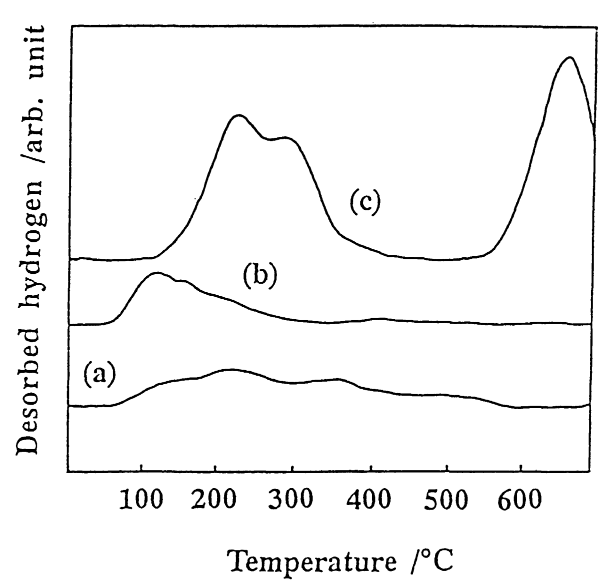

Fig. 4. The 1st TPD profiles of the supported platinum obtained after cooling in the presence of hydrogen.
(a) Pt/Al$_2$O$_3$, (b) Pt/SiO$_2$, (c) Pt/TiO$_2$.

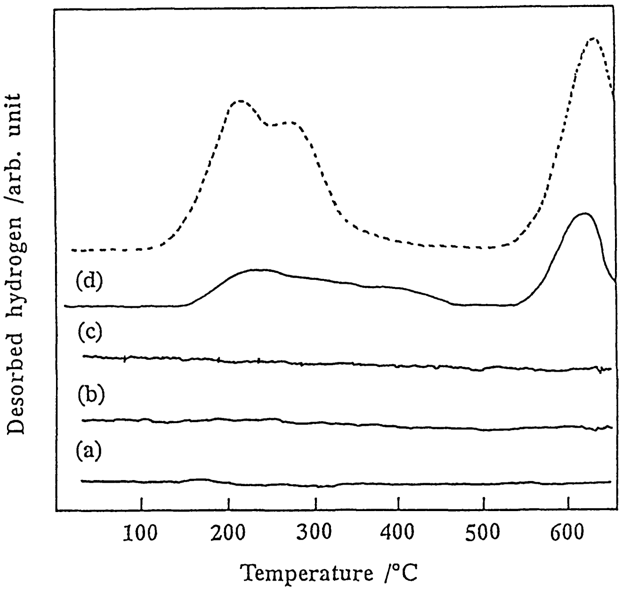

Fig. 5. The 1st TPD profiles of the supported platinum obtained after cooling in the absence of hydrogen.
(a) Pt/ZrO$_2$, (b) Pt/Al$_2$O$_3$, (c) Pt/SiO$_2$, (d) Pt/TiO$_2$. Broken line; Fig. 4-(c).

When a sample was cooled in the absence of hydrogen after the 1st TPD, a hydrogen desorption peak was observed only for the Pt/TiO$_2$ sample. However, the area of the observed TPD profile for Pt/TiO$_2$ was smaller than that obtained after cooling in the presence of hydrogen (Fig. 5). No desorption of hydrogen was found for Pt/Al$_2$O$_3$ or Pt/SiO$_2$, indicating that the origin of the desorbed hydrogen in 1st TPD shown in Fig. 4 occurs during cooling to low temperature in the presence of hydrogen; the surfaces of Pt/Al_2O_3 and Pt/SiO_2 were free from any adsorbed hydrogenic species at the end of the TPR measurement up to 450 °C. On the other hand, for Pt/TiO_2, the existence of desorptions in the 1st TPD obtained after cooling in the absence of hydrogen confirmed that hydrogenic species are formed over Pt/TiO_2 during the TPR measurement; these species remained at the end of TPR measurement up to 450 °C.

Judging from the appearence of a peak in the 1st TPD obtained after cooling in the absence of hydrogen and a consumed H_2/Pt value greater than 1 (Table 1), the apparent TPR profile of Pt/TiO_2 shown in Fig. 3 must be due to both a reduction of the supported platinum oxides and hydrogen incorporation over Pt/TiO_2.

Figure 6 shows the 2nd TPD profiles which were measured after hydrogen adsorption (23 Torr, 1 Torr=133.322 Pa) at ca. 40 °C for 1 min. Single desorption peaks were observed for Pt/ZrO_2, Pt/Al_2O_3, and Pt/SiO_2 at 100, 90, and 140 °C, respectively. These desorption temperatures are close to those for the hydrogen species adsorbed at platinum metallic sites.[17] For the Pt/TiO_2 sample, two desorption peaks were observed at 80 and 290 °C. No desorption peak was observed around 600 °C, which is the most prominent difference. The 2nd TPD profiles of Pt/TiO_2 and Pt/Al_2O_3 are different from the 1st TPD profiles obtained after cooling in the presence of hydrogen (Fig. 4-a,c). It should be noted that these desorption temperatures are lower than those at which hydrogen consumption occurs during the apparent TPR measurements shown in Fig. 3.

The difference between the 1st TPD obtained after cooling in the presence of hydrogen and the 2nd TPD is considered to show the effect of the H_2 adsorption temperature on the binding state of the adsorbed hydrogenic species. In other words, the hydrogenic species formed during cooling in the presence of hydrogen can be detected in the 1st TPD profile. It is well-known that the hydrogen adsorption temperature affects the hydrogen adsorption states;[9,11,18–23] high-temperature hydrogen adsorption causes a hydrogen spillover for both Pt/TiO_2[18–23] and Pt/Al_2O_3.[9,11] It is thus postulated that the difference between the 2nd and 1st TPD obtained after cooling in the presence of hydrogen is due to spiltover hydrogens. The concentration of these species for Pt/TiO_2 (Fig. 4-c) is much greater than that for Pt/Al_2O_3 (Fig. 4-a).

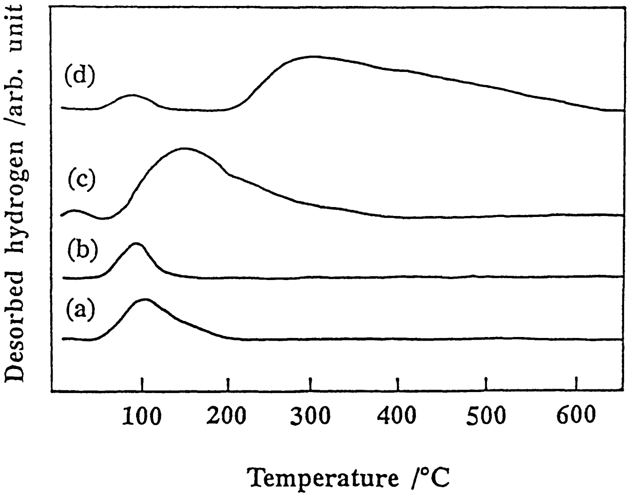

Fig. 6. The 2nd TPD profiles of the supported platinum.
(a) Pt/ZrO_2, (b) Pt/Al_2O_3, (c) Pt/SiO_2, (d) Pt/TiO_2.

The above-mentioned results clearly show that Pt/TiO_2 posesses the hydrogenic species, even at 450 °C, in the TPR measurement and that these hydrogenic species were formed by exposure to hydrogen at high temperatures via a hydrogen spillover process. The formation of these hydrogenic species on Pt/TiO_2 created by exposure to hydrogen at high temperatures causes an overestimation of the consumed H_2/Pt value if determined by the apparent TPR profile. The apparent hydrogen consumption (TPR) profile of Pt/TiO_2 contains the hydrogen adsorption (spillover) process in addition to a reduction of the supported platinum oxides. Chang et al.[24] also reported that the hydrogen consumption peak below 300 °C in the TPR profile for Pd/TiO_2 is due to hydrogen spillover to the TiO_2 support.

For Pt/SiO_2, Pt/ZrO_2, and Pt/Al_2O_3, the apparent TPR profile is mostly due to a reduction of the supported platinum oxides, since the desorption rate is faster (Fig. 6) than the adsorption rate at the temperatures at which hydrogen consumption occurs in TPR measurements (Table 1). The low consumed H_2/Pt value observed for Pt/SiO_2 might indicate the presence of unreduced platinum oxides after a TPR measurement up to 450 °C. An alternative explanation might be that Pt/SiO_2 was not completely oxidized by calcination at 400 °C.

Interaction of Hydrogen with Pt/TiO_2. It is well-known that a high-temperature reduction causes the Strong Metal-Support Interaction (SMSI) state of the supported platinum for Pt/TiO_2.[13,14] The occurrence of SMSI is believed to contain the hydrogen incorporation/emission process, which is temperature dependent.[17–22] We thus examined the effect of the upper temperature of the TPR on the 1st TPD in order to clarify the role of the hydrogen incorporation/emission process in the generation of SMSI states.

The apparent TPR profile of Pt/TiO_2 over a wide range of temperatures is shown in Fig. 7. We chose three temperatures (350, 450, 650 °C) as the upper temperature of the TPR measurement; they are indicated in Fig. 7. The 1st TPD profiles obtained after TPR measurements up to 350, 450, and 650 °C are shown in Fig. 8. These TPD profiles were obtained after cooling in the absence of hydrogen and, thus, reflect only changes in the upper temperatures of the

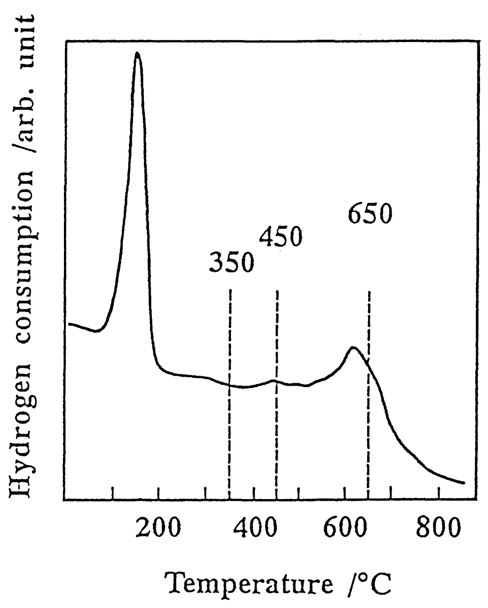

Fig. 7. The apparent TPR profile of Pt/TiO_2 up to 830 °C.

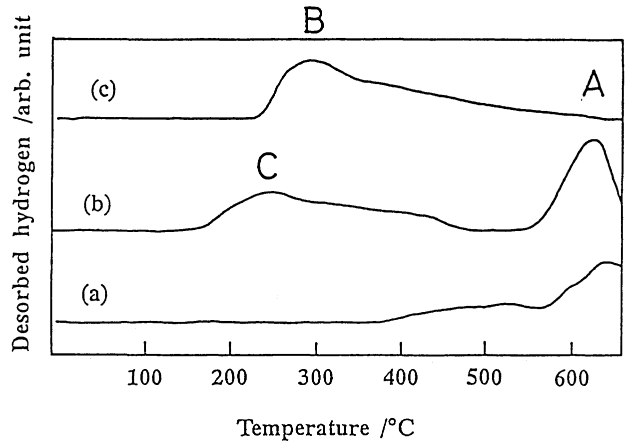

Fig. 8. The 1st TPD profiles of Pt/TiO_2 obtained after the TPR measurement up to (a) 350 °C, (b) 450 °C, (c) 650 °C, and cooling down in the absence of hydrogen.

TPR measurement. In the TPD profile obtained after a TPR measurement up to 350 °C, a single desorption peak above 600 °C was observed. Upon increasing the upper temperature of the TPR measurement to 450 °C, a new desorption peak at around 250 °C appeared in the successive TPD. Following TPR to an upper temperature of 600 °C, the desorption peak became single at 290 °C. At least three hydrogen desorptions were observed. These desorption peaks have been designated as peaks A (above 600 °C), B (around 290 °C), and C (at 250 °C), as indicated in Fig. 8.

The change in the hydrogen exposure temperature changed both the hydrogen adsorption state and the state of Pt/TiO_2. Hongli et al. studied hydrogen TPD from the Pt/TiO_2 related to the SMSI states,[12] and reported that the single desorption peak at 290 °C is a characteristic of the SMSI states. The single desorption peak B at 290 °C, obtained for a sample run up to 650 °C, suggests that a hydrogen treatment up to 650 °C creates SMSI states.

A desorption temparature of 290 °C, obtained for the SMSI state of Pt/TiO_2, is higher than those for the other supported platinum catalysts such as Pt/Al_2O_3 (90 °C), Pt/ZrO_2 (100 °C), and Pt/SiO_2 (140 °C). Raupp and Dumesic studied hydrogen adsorption on titania-deposited Ni polycrystalline, and reported that the adsorption strength of Ni toward hydrogen was enhanced by the presence of titania moieties in the vicinity of Ni metal.[25] The existence of the titania species over metal particles has recently been evidenced by a high-resolution transmittance electron microscopic investigation.[26] It is, therefore, considered that the higher desorption temperature for the SMSI state of Pt/TiO_2 is caused by the presence of titania moieties located in the vicinity of Pt particles.

As seen in Fig. 8, desorption peak A disappeared upon a hydrogen treatment up to 650 °C, indicating that the hydrogenic species producing peak A were desorbed during a TPR measurement between 450 and 650 °C. It is suggested that the desorption of hydrogenic species A plays an important role in the generation of SMSI states.

Hydrogen desorption peak A was observed in the TPD profile after a TPR measurement up to 350 °C. Huizinga and Prins[18] as well as Beck et al.[19] have attributed the hydrogenic species over Pt/TiO_2 formed by hydrogen adsorption below 220—300 °C to represent the spillover state on the TiO_2 support. We therefore consider desorption peak A as being the desorption of spiltover hydrogens on the TiO_2 support. A desorption of these spiltover hydrogens is thought to be necessary to generate SMSI states from this work.

Munuera et al.[22] and Sanz et al.[23] claimed that a further incorporation of hydrogen into the Ti^{3+} cations to form diamagnetic hydride-like species, such as $[Ti–H]^{3+}$, is necessary to generate SMSI states. If their conclusion is correct, hydrogen adsorption would have occurred between 450—650 °C. However, in this work, since hydrogen desorption occurred for the SMSI state, their suggestion is not plausible. A suggestion by Munuera and Sanz[22,23] was made in terms of the ESR result: that the number of Ti^{3+} centers decreases upon reduction at 500 °C, in spite of a continuous incorporation of H_2 into TiO_2 support which occurs under these conditions. The decrease in the Ti^{3+} number during an increase in the reduction temperature seems to be due to both spin pairing and spin–spin relaxation, as interpreted by Bonneviot and Haller.[27]

The role of hydrogen desorption in the generation of the SMSI states has been proposed.[12,18,22] Huizinga and Prins[18] as well as Kunimori et al.[20] have proposed that a dehydration of the support takes place at 500 °C in the neighborhood of the metal particles, thus producing a reduced form of $TiO_2(Ti_4O_7)$[28] in the vicinity of the Pt particles. They proposed that hydrogen is desorbed in the form of water. On the other hand, Hongli et al.[12] as well as Conesa et al.[21] suggested that any back-spillover of the hydrogen species from the support to the metal (metal-catalyzed hydrogen desorption) plays an important role in producing SMSI behavior. In this case, hydrogen is desorbed in the form of hydrogen molecules.

It was also shown in the present work that the role of the hydrogen desorption at around 450—650 °C in the generation of the SMSI states is significant. Since hydrogen was desorbed in the form of molecular hydrogen within the temperature range 450—650 °C, a desorption of spiltover hydrogens seems to be plausible, even though it is not certain whether dehydration also occurs or not. It is proposed that titania migrates with the adsorbed hydrogen onto platinum particles to create the SMSI state. On platinum particles, hydrogen-containing titanium suboxides release hydrogen atoms which recombine to form molecular hydrogen while leaving the surface.

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