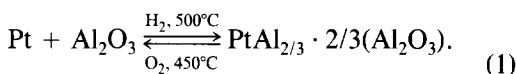


On the Sulfur-Aided Metal-Support Interaction in Alumina-Supported Pt Catalysts

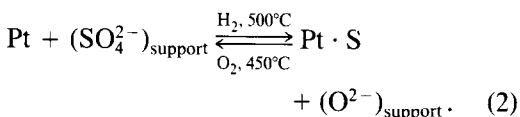
The suppression of hydrogen chemisorption after H₂ pretreatment at high temperature (e.g., 500°C) has been reported in Pt/Al₂O₃ catalysts (1-4). The phenomenon is rather similar to that observed in Pt/TiO₂ by Tauster *et al.* (5). They introduced the acronym SMSI (strong metal-support interaction) which has recently attracted considerable attention in the field of supported metal catalysts (6). The common feature of these phenomena is that a mild oxidation (in O₂ at 400-500°C) followed by low-temperature reduction at 200-300°C almost fully restores the original H₂ chemisorption capacity, although the mechanism could be different between these catalyst systems (6).

In a Pt/Al₂O₃ catalyst system, we have found that the degree of suppression of H₂ chemisorption after the high-temperature reduction (HTR) depends strongly on sulfur content in Al₂O₃ (2). However, the suppression could not be explained with such a simple mechanism as poisoning via a reversible redox reaction of sulfur. On the basis of the observed amount of H₂ (or O₂) consumption during the H₂ (or O₂) pretreatment, and other evidences (2), we have proposed the formation of a superficial alloy between Pt and reduced Al according to the redox reaction



The decrease in the H₂ chemisorption capacity is attributed to the partially reduced state formed in reaction (1). The role of sulfur is presumably to promote the partial reduction of surface alumina. Such a phenomenon may be called a sulfur-aided SMSI (3).

On the other hand, Apestequia *et al.* (4) have recently reported that the SMSI behavior of sulfided (and subsequently sulfated) Pt/Al₂O₃ catalysts was better explained in terms of the following redox reaction of sulfur,



The H₂ chemisorption is suppressed by the sulfur poisoning of the Pt surface, which is common phenomena in the fundamental and industrial studies of metal catalysts. However, our XPS and IR results (2) showed little change in the amount of sulfide and sulfate through the course of the H₂ (or O₂) pretreatments in the case of the Pt/Al₂O₃ (S/Pt = ca. 0.3, where S/Pt means the number of total sulfur atoms/total number of Pt atoms in the catalyst). Therefore, in our case, we discarded the redox reaction (2), and have proposed the sulfur-aided metal-support interaction (i.e., the redox reaction (1)) on the basis of the results of the H₂ and O₂ consumption measurements (2).

In this paper, we present additional data of the Pt/Al₂O₃ catalysts including the characteristic of CO and O₂ chemisorption in order to elucidate more detailed aspects of the sulfur-aided SMSI.

The Al₂O₃ supports (JRC-ALO-2 and 4) used in this work were γ -alumina, which were provided as the Japan Reference Catalysts (JRC) from the Catalysis Society of Japan (7). The JRC-ALO-2 includes originally the sulfur impurity owing to the preparation method (i.e., its precursor was Al₂(SO₄)₃) (2, 7). On the other hand, the

TABLE I
Pt Catalysts Used in This Work

| No. | Pt (wt%) | Al ₂ O ₃ support | Sulfur content (S/Pt) ^a |
|-----|----------|--|------------------------------------|
| 1 | 5.0 | JRC-ALO-4 ^b | <0.004 |
| 2 | 5.0 | JRC-ALO-2 ^c | 0.32 |
| 3 | 0.5 | JRC-ALO-2 ^c | 4.8 |

^a Atomic ratio of sulfur to the total Pt atoms in the catalyst.

^b BET surface area: 177 m²/g.

^c BET surface area: 285 m²/g.

sulfur content of the JRC-ALO-4 was less than 0.01 wt%. As shown in Table I, Pt/Al₂O₃ catalysts (No. 1–No. 3) were prepared by impregnating the Al₂O₃ support with an aqueous H₂PtCl₆ solution, followed by H₂ reduction at 500°C for 1 h. The sulfur content of the Pt catalysts was measured by a chemical method (2).

Detailed procedures for the chemisorption measurements and the H₂ and O₂ pretreatments were described previously (2, 8). Briefly, the volumetric adsorption of H₂, O₂, and CO was studied by 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 amounts of gas adsorbed on the catalysts were determined from pressure measurements with an MKS Baratron pressure gauge. The isotherms were not studied in detail, but the adsorption measurements were performed at room temperature and the lower equilibrium pressures (2 to 5 Torr). The amount of the gas uptake (H/Pt, O/Pt, or CO/Pt in terms of the atomic or molecular ratio of the total Pt atoms) was measured at 1 h after the admission of the gas. Reversible adsorption of H₂ as well as CO was observed, and this quantity (H_{rev}/Pt or CO_{rev}/Pt) was determined from the readsorption after evacuation of the gas at room temperature for 10 min (8). Because the reversibly adsorbed CO (CO_{rev}) molecules are mainly associated

with Al₂O₃ support (8), the CO chemisorption value (CO/Pt) were obtained by subtracting CO_{rev}/Pt from the total adsorption. No reversible O₂ chemisorption was observed in this study.

Before the H₂ chemisorption, H₂ and O₂ pretreatments of the catalysts were performed *in situ* using a closed recirculating system with a liquid nitrogen trap. The two typical procedures were as follows: (i) the H₂ treatment at 500°C and 50 Torr for several hours (0.5 to 24 h), followed by evacuation *in vacuo* at 450°C for 1 h; and (ii) the O₂ treatment at 450°C and 50 Torr for 1 h, followed by low-temperature reduction (LTR) at 300°C and evacuation *in vacuo* at 450°C for 1 h. The O₂ or CO chemisorption was carried out after the H₂ chemisorption followed by evacuation *in vacuo* at 450°C for 1 h.

In a separate experiment, the ethane hydrogenolysis and ethylene hydrogenation reactions over the Pt catalysts were also performed after the H₂ chemisorption measurement in the closed recirculating system ($P(\text{C}_2\text{H}_6)$ or $P(\text{C}_2\text{H}_4) = 10$ Torr, $P(\text{H}_2) = 20$ Torr; total pressure: 500 Torr with He balance). The analysis of CH₄, C₂H₄, and C₂H₆ was carried out by gas chromatograph.

Table 2 shows the changes in the H₂ chemisorption value (H/Pt) after the pretreatments of the catalysts Nos. 1, 2, and 3. It has been well established (2) that the H/Pt values after the O₂ treatment at 450°C followed by H₂ reduction at 300°C (Run No. 1: treatment (ii)) correspond to the percentage (Pt dispersion) of the catalysts exposed, respectively, assuming that the adsorption stoichiometry of hydrogen atom/surface Pt atom (H/Pt_s) is approximately equal to unity (8). The drastic suppression of the H₂ chemisorption ability (H/Pt) by the H₂ treatment at the high temperature (500°C: treatment (i)) was observed in the Pt/JRC-ALO-2 (Nos. 2 and 3). The H₂ pretreatment at 500°C for a longer time (6–24 h) or at higher temperature (550°C) resulted in a more drastic decrease in H₂ chemisorption. It should be noted that the H/Pt values were recovered

TABLE 2

The Changes in the H₂ Chemisorption Values and the Catalytic Activities by the H₂ Treatment of Pt/Al₂O₃ Catalysts

| Cat. No. | Run No. | Pretreatment ^a | H/Pt(H _{rev} /Pt) | Catalytic activity | |
|----------|---------|---------------------------|----------------------------|-----------------------------|----------------------------|
| | | | | Hydrogenolysis ^b | Hydrogenation ^c |
| No. 1 | 1 | H ₂ 300°C 1 h | 0.52(0.18) | 2.0×10^{-2} | 7.3×10^{-3} |
| | 2 | H ₂ 500°C 6 h | 0.40(0.14) | 2.2×10^{-3} | 5.5×10^{-3} |
| No. 2 | 1 | H ₂ 300°C 1 h | 1.02(0.30) | 2.0×10^{-2} | 1.5×10^{-2} |
| | 2 | H ₂ 500°C 3 h | 0.36(0.15) | 1.6×10^{-4} | 1.0×10^{-2} |
| | 3 | H ₂ 500°C 24 h | 0.13(0.07) | — | — |
| No. 3 | 1 | H ₂ 300°C 1 h | 1.28(0.40) | 4.5×10^{-3} | 1.5×10^{-2} |
| | 2 | H ₂ 500°C 1 h | 0.72(0.31) | 1.2×10^{-4} | — |
| | 3 | H ₂ 500°C 6 h | 0.33(0.13) | 1.9×10^{-5} | 1.1×10^{-2} |
| | 4 | H ₂ 550°C 1 h | 0.24(0.11) | 1.6×10^{-7} | 3.8×10^{-4} |

^a The O₂ treatment at 450°C was performed before each H₂ treatment.

^b TOF (s⁻¹) at 300°C.

^c TOF (s⁻¹) at 0°C; the turnover frequency was based on the H/Pt value of Run No. 1.

to the original ones by treatment (ii). The slight suppression was also observed in catalyst No. 1 (S/Pt < 0.004) by the prolonged H₂ treatment at 500°C for 6 h.

As also shown in Table 2, the change in the amount of reversible H₂ chemisorption (H_{rev}/Pt) seems to be in parallel with those in the H/Pt value. The data of the H/Pt and H_{rev}/Pt values for the catalyst No. 2 are collected in Fig. 1. It has been considered that the reversibly adsorbed hydrogen (H_{rev}) is associated with Pt metal (7): H_{rev} may be attributed to terminal Pt-H species. On the other hand, irreversible adsorbed hydrogen (i.e., H_{total} - H_{rev}) may be attributed to a hydrogen in interaction with two or three Pt atoms (multicentered chemisorption), although detailed interpretations of the chemisorbed states are as yet unclear in the present stage (9, 10). As can be seen in Fig. 1, the ratio of H_{rev} to H_{total} was almost constant (ca. 30%) when the H/Pt value was around 1.0. However, it was increased slightly to ca. 50% when the H/Pt values was decreased to ca. 0.2 by the prolonged H₂ treatment at 500°C.

The effects of the pretreatments on the

catalytic activities are also shown in Table 2. For the ethane hydrogenolysis reaction, the activity decreased significantly by the H₂ treatment at 500°C (by one order of magnitude for No. 1 and by two orders of magnitude for Nos. 2 and 3). In contrast, the high-temperature H₂ treatment caused only a slight decrease in the activity of the ethylene hydrogenation. However, the activity of

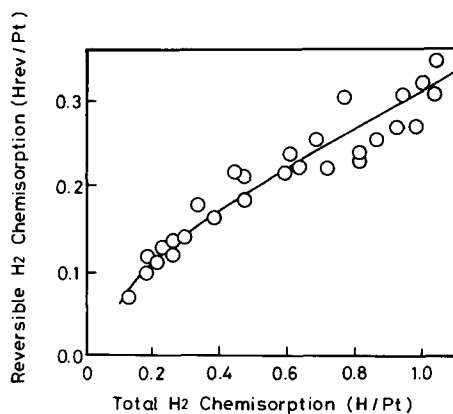


FIG. 1. Correlation between the H_{rev}/Pt and H/Pt values for the Pt/Al₂O₃ catalyst (No. 2).

TABLE 3

H₂, O₂, and CO Chemisorption Values after a Series of the O₂ and H₂ Treatments

| Cat. No. | Pretreatment ^a | H/Pt | O/Pt | CO/Pt |
|----------|---------------------------|------|------|-------|
| No. 2 | H ₂ 300°C 1 h | 0.96 | 0.41 | 0.38 |
| | H ₂ 500°C 12 h | 0.21 | 0.71 | 0.26 |
| No. 3 | H ₂ 300°C 1 h | 1.26 | 0.68 | 0.58 |
| | H ₂ 500°C 12 h | 0.29 | 0.42 | 0.35 |

^a The O₂ treatment at 450°C was performed before each H₂ treatment.

catalyst No. 3 was decreased significantly after the H₂ treatment at the higher temperature (550°C). The ethane hydrogenolysis activity was also decreased drastically after the same H₂ treatment (Run No. 4).

The behaviors of CO and O₂ chemisorption were studied when the H/Pt values were changed by the O₂ and H₂ pretreatments (see Table 3 as an example). The data of O₂ and CO chemisorption (O/Pt, CO/Pt) as a function of the H/Pt value of the catalyst No. 2 are presented in Fig. 2. The O/Pt value (0.4 to 0.5) was almost half of the H/Pt one after the O₂ treatment at 450°C followed by the H₂ reduction at 300°C (treatment (ii); solid circles). The stoichiometry of O₂ chemisorption is in good agreement with that both in our previous work (7) and in the

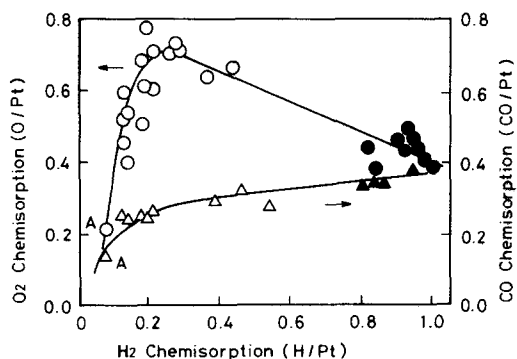


FIG. 2. The changes of the O/Pt and CO/Pt values as a function of the H/Pt value of the catalyst No. 2 (see text).

study of Wilson and Hall (11). As shown in Fig. 2, the O/Pt value was increased as the H/Pt value was decreased by the H₂ treatment at 500°C (treatment (i); open circles), and attained a maximum value (ca. 0.7) when the H/Pt value was ca. 0.3. However, it was decreased significantly when the H/Pt value was below 0.2 after the prolonged H₂ treatment at 500°C, and further decreased to 0.2 by the H₂ treatment at 550°C (as indicated by A in the figure). On the other hand, the CO/Pt value was almost constant (and decreased rather gradually) as the H/Pt value was decreased from ca. 1.0 to ca. 0.1, but finally decreased significantly after the H₂ treatment at 550°C (mark A in Fig. 2).

Figure 3 shows the data of O₂ and CO chemisorption against the H/Pt values in the case of catalyst No. 3. When the H/Pt value was decreased to about 0.3 by the prolonged H₂ treatment at 500°C, the O/Pt value was not increased, but decreased gradually (as indicated by the open circles). The CO/Pt value was also decreased monotonously as the H/Pt value was decreased from 1.2 to 0.2, as shown in Fig. 3. The H₂ treatment at 550°C gave the points indicated by A. When a 0.5 wt% Pt/JRC-ALO-2 catalyst (similar to catalyst No. 3 but different from it in a preparation lot) was first treated in H₂ at 500°C for a long time (24 h), the H/Pt value was diminished to zero as shown by the B in Fig. 3. At the same time, the O/Pt and CO/Pt values were decreased to almost zero.

The H₂ chemisorption behaviors for the Pt/Al₂O₃ catalysts after the H₂ treatment at high temperature are in good agreement with the previous ones (2). In catalyst No. 2 (S/Pt = 0.32), the redox reaction (2) did not occur, judged from the XPS and IR results (2), and we have proposed the redox reaction (1) which was also consistent with the results of H₂ (or O₂) consumption measurements (2). In the catalyst No. 3 (S/Pt = 4.8), however, it is difficult to conclude definitely which mechanism ((1) or (2)) plays an important role in this phenomenon by the XPS and IR techniques because of the

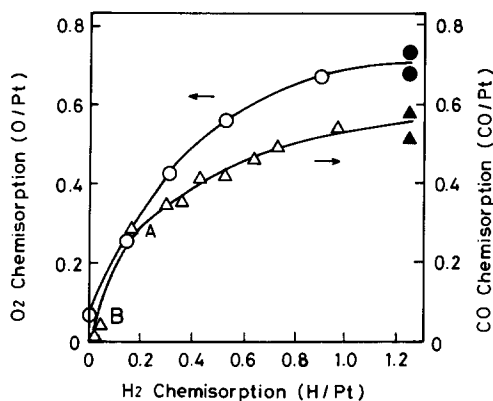


FIG. 3. The changes of the O/Pt and CO/Pt values as a function of the H/Pt value of the catalyst No. 3 (see text).

experimental uncertainty of about 10% (2). The change of less than 0.5 in S/Pt would not be detected by these techniques because of the higher S/Pt value.

The two catalytic reactions studied here may be classified into two categories (12): the ethane hydrogenolysis is the so called "demanding" or structure-sensitive reaction and ethylene hydrogenation is the so called "facile" or structure-insensitive reaction. The catalytic behaviors shown in Table 2 may be consistent with the PtAl_x alloy model (1, 2) because of only a modest change in the activity of the structure-insensitive reaction and a significant decrease in the activity of the structure-sensitive reaction by the high-temperature H₂ treatment. However, these behaviors would not be distinguished from what is known as a selective poisoning phenomenon; i.e., sulfur would be adsorbed predominantly on those sites responsible for hydrogenolysis (13).

The increase in O/Pt value in Fig. 2 may be consistent with the PtAl_x alloy model (1, 2), in which Dautzenberg *et al.* observed the increase in O₂ chemisorption capacity by the alloy formation. On the other hand, Leclercq and Boudart (14) reported that the O₂ chemisorption value was not decreased when the H₂ chemisorption value was decreased by high-temperature H₂ treatments

of sulfur-poisoned Pt/Al₂O₃ catalysts. For their catalysts, however, the H₂ treatment at lower temperature (200°C or 300°C) made the poisoned Pt surface clean (14), while, in our case, there was no recovery in the H/Pt value by the lower-temperature H₂ treatment of the catalyst Nos. 2 and 3 which had been treated in H₂ at 500°C. Few data are available concerning the influence of sulfur on the chemisorption characteristics of H₂, CO, and O₂. Bonzel and Ku (15) studied the effect of sulfur on the chemisorption of CO on Pt(110). They found that the amount of CO chemisorption decreased linearly with the surface sulfur coverage (θ_s) and that the Pt surface with $\theta_s = 0.75$ did not adsorb any CO. Because the CO chemisorption was not suppressed significantly when the H/Pt value was above 0.2 as shown in Fig. 2, the suppression of the H/Pt value (from 1.0 to ca. 0.2) cannot be explained by a simple sulfur poisoning. However, we cannot exclude the possibility that the H₂ chemisorption is hindered by a very small amount of sulfur (2). On the other hand, as already discussed in the previous paper (2), the reduction of surface alumina (the redox reaction (1)) should be considered to explain the quantity of H₂ consumed (ca. 2 in terms of H/Pt) during the H₂ treatment.

The CO and O₂ chemisorption behaviors of catalyst No. 3 are different from those of the catalyst No. 2, as shown in Figs. 2 and 3. As the H/Pt value was decreased to 0.2, the O/Pt value was decreased in the case of No. 3, while it was increased in the case of No. 2. In both catalysts, the CO/Pt and O/Pt values were decreased drastically when the H/Pt value was below 0.2 (Figs. 2 and 3), which may suggest that the Pt surface was poisoned by sulfur. For catalyst No. 3, the sulfur poisoning can also occur, because the O/Pt and CO/Pt values decreased gradually when the H/Pt value was decreased from 1.2 to 0.2. The significant decreases in the catalytic activities (Table 2) after the H₂ treatment at 550°C may also result from the sulfur poisoning.

Even though the two papers (2, 4) came

to different conclusions concerning the role of sulfur for Pt/Al₂O₃, we do not find them incompatible. In one case, the IR result showed a sulfide/sulfate reduction cycle (4), and in the other case, it did not (2). It should be pointed out that the difference in the nature of sulfur (SO₄²⁻) in the Al₂O₃ support results in different mechanisms in these phenomena. The Pt/Al₂O₃ samples of Apestequia *et al.* (4) were sulfided at 500°C in a flow of H₂S/H₂ mixture and subsequently sulfated by air oxidation at 450°C, while the JRC-ALO-2 includes originally the sulfate impurity owing to the preparation method (2, 7). The nature of sulfate (and sulfide) may be different between these Pt/Al₂O₃ catalysts. Yamaguchi *et al.* (16, 17) have found different behaviors in sulfur-promoted iron oxide (SO₃/Fe₂O₃) catalysts by two kinds of preparation methods, namely, "a post sulfation method" and "a simultaneous sulfation method." In practice, when the JRC-ALO-4 was sulfated by impregnating (NH₄)₂SO₄ (2), the H/Pt value of the Pt/Al₂O₃ catalyst decreased drastically even after H₂ reduction at 400°C for 1 h (the sulfur poisoning). The sulfate in a fresh Pt/JRC-ALO-2 catalyst with a higher S/Pt ratio may be reduced partly by the H₂ treatment at 500°C (B in Fig. 3), while there was almost no change in the amount of sulfate in the Pt/JRC-ALO-2 (S/Pt = 0.3) catalyst stabilized by several cycles of the oxidation–reduction treatments (2, 18).

In summary, both redox reactions (1) and (2) can occur simultaneously. Which one dominates depends on the S/Pt ratio, the nature of sulfate in the Al₂O₃ support, and the temperature of H₂ treatment, etc. Further characterization of the catalysts will be needed to obtain direct physical evidence for Pt–Al bonding, etc.

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