JOURNAL OF CATALYSIS 79, 185–195 (1983)

Metal–Support Interaction in Alumina-Supported Pt Catalysts

KIMIO KUNIMORI, YASUO IKEDA, MITSUYUKI SOMA,* AND TOSHIO UCHIJIMA

*Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki 305, Japan, and *National Institute for Environmental Studies, Yatabe-machi, Ibaraki 305, Japan*

Received July 8, 1982; revised September 16, 1982

The suppression of hydrogen chemisorption (a drastic decrease of the H_2 chemisorption capacity by H_2 pretreatment at 500°C and its recovery by O_2 pretreatment at 450°C followed by reduction in H_2 at 300°C) in the case of Pt/Al_2O_3 was studied by volumetric adsorption of H_2, the consumption measurements of H_2 and O_2 during the pretreatments, XPS, and ir. The extent of the suppression was increased remarkably when the sulfur content in the catalysts became high (as high as 0.3 in terms of the atomic ratio S/Pt). However, XPS and ir results showed little change both in the total amount of sulfur and in the relative amount of sulfide and sulfate through the course of the pretreatments. Furthermore, there was the close correlation between the decrease (or increase) in the amount of H_2 chemisorption and the amount of H_2 (or O_2) consumption during the pretreatments. These results indicate that the suppression cannot be explained with such a simple mechanism as poisoning via reversible redox reaction of sulfur. We propose the following reaction as a plausible redox reaction taking place during the pretreatments:

$$\mathrm{Pt} + \mathrm{Al_2O_3} \underset{\frac{1}{2}\mathrm{O_2},\ 450^\circ\mathrm{C}}{\overset{\mathrm{H_2},\ 500^\circ\mathrm{C}}{\rightleftarrows}} \mathrm{Pt} \cdot \mathrm{Al_2O_2}\ [\text{or } \mathrm{PtAl_{2/3}} \cdot \tfrac{2}{3}(\mathrm{Al_2O_3})],$$

where $Pt \cdot Al_2O_2$ represents the composition of surface species consistent with the quantity of H_2 (and O_2) consumed. This mechanism suggests the existence of a metal–support interaction in the Pt/Al_2O_3 system. The role of sulfur is presumably to catalyze (as a promoter) this reaction, although the detailed mechanism will be the subject of further investigation.

INTRODUCTION

Recently Tauster and co-workers found that H_2 and CO chemisorption was severely inhibited when TiO_2-supported Group VIII noble metal catalysts were reduced at 500°C, while oxidation at 400°C recovered the normal chemisorption behavior (*1*). This phenomenon was attributed to a strong metal–support interaction (SMSI); in the SMSI state Pt was ascertained to be in the form of hexagonal thin pillbox structures grown on a partially reduced titania, Ti_4O_7 (*2*). Because such a type of metal–support interaction had not previously been recognized, many works have been induced on related subjects, e.g., the physical characterization of the several TiO_2-supported catalysts (Ni/TiO_2 (*3, 4*), Fe/TiO_2 (*5*)). The catalytic properties such as CO hydrogenation (Ni/TiO_2 (*6, 7*), Pd/TiO_2 (*8*), Ru/TiO_2 (*9*)) have also been studied, and their behaviors have been compared with the catalysts supported on the conventional supports such as SiO_2 and Al_2O_3 which exhibited no SMSI behavior according to Tauster and Fung (*10*).

However, similar phenomena have been observed in the case of both SiO_2 (*11–13*) and Al_2O_3 (*14–16*), although the mechanism of the phenomena could be different among them. Wilson and Hall (*11*) observed the apparent decrease in H_2 chemisorption after treatment of Pt/SiO_2 in H_2 at 770°C in spite of no change of average Pt particle size. Moss *et al.* (*12*) reported for Pd/SiO_2 that the increase of reduction temperature to 600°C caused formation of a new phase with a metal–support interaction as indicated by extra X-ray diffraction lines, although the chemisorption capacity was not affected significantly. Recently, Praliaud and Martin (*13*) also reported evidence of SMSI in the Ni/SiO_2 system. For Pt/Al_2O_3

0021-9517/83/010185-11$03.00/0

catalysts, Gonzalez-Tejuca *et al.* (*14*) reported a decrease in H_2 chemisorption capacity due to decomposition of Pt particles into an atomic form of Pt incorporated into the alumina support. Dautzenberg *et al.* (*15*) observed the apparent decrease in H_2 chemisorption capacity after H_2 treatment of Pt/Al_2O_3 at high temperatures (above 500°C up to 675°C), and suggested the alloy formation between Pt and reduced Al (*17*). We have also reported that the pretreatments of some Pt/Al_2O_3 catalysts in H_2 at 500°C cause a drastic decrease in the amount of H_2 chemisorption, while the metal crystallite sizes remain constant as observed by transmission electron microscopy and X-ray diffraction, and the O_2 treatments at 450°C followed by reduction in H_2 at 300°C restore the ability to chemisorb H_2 (*16*). According to these observations, most of published studies concerning "sintering" and "redispersion" should be reconsidered when only the chemisorption method was used to determine the percentage exposed.

In this work, more detailed aspects of the phenomenon in the case of the Pt/Al_2O_3 catalysts have been studied by the chemisorption behaviors of H_2, the measurements of the consumption of H_2 and O_2, X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (ir) during the pretreatments. In particular, attempts have been made to clarify whether or not the apparent dependency of the extent of the suppression of H_2 chemisorption on the sulfur content of the supports can be related to the poisoning effect of sulfur. It was reported that when Pt supported on an alumina containing sulfur (in the form of sulfate) was reduced at high temperature, the Pt catalyst was poisoned with elemental sulfur which resulted in the change in catalytic selectivity (*18, 19*). Although the study of the sulfurization is important from the viewpoint of industrial use of Pt-reforming catalysts (*20–22*), the fundamental aspect such as the effect of sulfur on H_2 chemisorption is far from clear (*23*). This paper will reveal that the suppression of H_2 chemisorption cannot be explained with such a simple mechanism as poisoning by sulfur, and a possible interpretation, which suggests metal–support interaction promoted by sulfur, will be proposed.

EXPERIMENTAL

The catalyst supports used in this work were γ-alumina, three of which were provided as the Japan Reference Catalysts (JRC) from the Catalysis Society of Japan (*24*). The two other supports, Al_2O_3(A) and Al_2O_3(B), were prepared in our laboratory by a method similar to that of Dautzenberg and Wolters (*15*); a precipitate from aqueous $Al(NO_3)_3$ solution by addition of NH_4OH at final pH of 10.5 (A) or 5.8 (B) was calcined at 650°C. Their main characteristics are given in Table 1. They were all used as powders after grinding and sieving. Pt/Al_2O_3 catalysts (0.5 or 5.0 wt% Pt) were prepared by the impregnation technique using H_2PtCl_6 aqueous solutions, followed by H_2 reduction at 500°C for 1 h with the space velocity of 1200 h^{-1}. The total amount of sulfur in both the supports and the Pt catalysts obtained therefrom was measured by a chemical method (CA) (*25*); the sample was treated at 800°C with flowing hydrogen to remove the sulfur (present mainly in the form of sulfate owing to the preparation methods (*24*)), and then the exit gas was directed, through a Pt plate converter to form H_2S, into an absorber solution, and its

TABLE 1

Al_2O_3 Supports Used in This Work

Support	BET (m^2/g)	Degree of crystallinity	SO_4^{-2} (wt%)[a]
JRC-ALO-1	160	Medium	0.05
JRC-ALO-2	285	Low	2.0
JRC-ALO-4	177	High	Trace
Al_2O_3(A)	99	High	Trace
Al_2O_3(B)	135	Low	Trace

[a] In this column, "trace" means a sulfur content of less than 0.01 wt%.

concentration was determined photometrically.

The volumetric adsorption of H_2 was studied by a conventional glass vacuum system, base pressure of 10^{-5} to 10^{-6} Torr (1 Torr = 133.3 N m^{-2}) being attained by an oil diffusion pump with a liquid nitrogen trap. Reduced catalyst samples of 0.1 to 0.5 g were placed in a Pyrex tube. The amounts of gas 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 isotherms were not studied in detail, but the adsorption measurements were performed at room temperature and the lower equilibrium pressures (2 to 5 Torr) to keep adsorption on the support as well as hydrogen spillover negligible (*26*). The adsorption of H_2 at room temperature was instantaneous. However, it was followed by a slow gas uptake, the rate of which became negligible after 1 h. Therefore, typically, the amount of the uptake was measured at 1 h after the admission of H_2 gas. Blank experiments for the alumina supports revealed that adsorption of H_2 by the supports was negligible at this condition.

Before H_2 chemisorption, H_2 and O_2 pretreatments of the catalysts were performed using the same closed circulating system with a liquid nitrogen trap. The two typical procedures were as follows: (a) the H_2 treatment at 500°C and 50 Torr for several hours (up to ca. 24 h), followed by evacuation *in vacuo* at 450°C for 1 h; and (b) the O_2 treatment at 450°C and 50 Torr for 1 h, followed by H_2 treatment at 300°C for 1 h to reduce Pt oxide and evacuation *in vacuo* at 450°C for 1 h. The consumption of H_2 (or O_2) during the pretreatments ((a) or (b)) was also measured from the decrease of the H_2 (or O_2) pressure with the closed circulating system. It should be noted that the treatments were performed on the bare Pt surface, which was obtained by treating in H_2 at 300°C followed by evacuation *in vacuo* at 450°C. Consequently, the quantity of H_2 consumption thus obtained does not include the amount of H_2 consumed by reduction of Pt oxide. Besides, it was assumed that the Pt surface is bare at 500°C in the H_2 atmosphere (*27*). On the other hand, the amount of oxygen consumed during the O_2 treatment at 450°C was determined by subtracting the amount of oxygen chemisorbed on platinum at 450°C (blank) from the observed uptake of O_2, as will be shown later (Table 2).

TABLE 2

The Changes in H_2 Chemisorption by the Sequence of Pretreatments and the Uptake of H_2 or O_2 during the Pretreatment (5.0% Pt/ALO-2, No. 4 in Table 3)

Run No.[a]	Pretreatment[b]	Observed uptake of H_2 or O_2 during the pretreatment	H_2 chemisorption value[c]
1	O_2 450°C[d]	1.09[e]	0.97
2	H_2 500°C 5 h[f]	1.25[g]	0.31
3	O_2 450°C[d]	1.45[e]	0.95
4	O_2 450°C[d]	0.99[e]	0.95
5	H_2 500°C 15.5 h[f]	1.41[g]	0.22

[a] These runs were conducted in sequence on the same catalyst.

[b] Unless otherwise stated, the time of each treatment step was 1 h.

[c] In terms of H/Pt. After each H_2 chemisorption, the sample was treated *in vacuo* at 450°C to obtain the bare Pt surface.

[d] Followed by H_2 treatment at 300°C and evacuation *in vacuo* at 450°C.

[e] In terms of O/Pt (the number of O atoms/the total number of Pt atoms).

[f] Followed by evacuation *in vacuo* at 450°C.

[g] In terms of H/Pt (the number of H atoms/the total number of Pt atoms).

The XPS spectra were obtained using a VG ESCA LAB-5 spectrometer equipped with both AlK_α and MgK_α X-ray sources, a preparation chamber, and a signal averager. The spectra were taken with a spectrometer resolution of 1 eV. During a series experiment, an aliquot of the sample was transferred from the adsorption apparatus into the quick-entry chamber of the spectrometer, and treated with hydrogen at room temperature to remove oxygen on the Pt surface (H_2 titration (*28*)) followed by evacuation *in vacuo* in the preparation chamber. It should be pointed out that the catalysts after exposure to the atmosphere showed no change in chemisorption behaviors if they were reduced in H_2 at 300°C for 1 h and evacuated *in vacuo* at 450°C for 1 h; that is, the O_2 adsorption at room temperature did not affect the state of the suppressed hydrogen chemisorption unless the catalyst was treated in O_2 at 450°C. The Au $4f_{7/2}$ line (83.7 eV) was used as a primary standard, and the Al 2s line (119.2 eV) of the alumina supports was used as an internal standard. The peak areas of S 2p and Pt $4d_{5/2}$ were normalized by that of the Al 2s for comparison among the samples in a series experiment.

Infrared spectra were obtained using a JASCO infrared spectrometer A202. The sample wafers (20 mmϕ) were prepared by pressing about 100 mg of the catalyst, and placed in an ir cell, with which *in situ* measurements were performed after the H_2 and O_2 treatments.

RESULTS

Changes in H_2 Chemisorption by the Pretreatment Procedures

Some aspects of the phenomenon in the case of 0.5% Pt/Al_2O_3 catalysts were reported previously (*16*). The same phenomenon was also observed in the case of 5.0% Pt/Al_2O_3 catalysts. An example of the changes in H_2 chemisorption by the pretreatments of 5.0% Pt/Al_2O_3 catalyst is shown in Table 2. After the treatment of a sample in O_2 at 450°C (Run No. 1), the amount of H_2 chemisorption (H_2 chemisorption value) was 0.97 in terms of H/Pt, where H/Pt shows the number of chemisorbed H atoms/the total number of Pt atoms in the sample. After evacuation *in vacuo* at 450°C for 1 h to remove hydrogen on the Pt surface, the H_2 treatment at 500°C was performed for 5 h (Run No. 2). As shown in Table 2, the H_2 chemisorption value decreased to 0.31. However, it was recovered to the original value (0.95) after the O_2 treatment at 450°C (Run No. 3). The drastic change in H_2 chemisorption value was quite reversible, as will be shown later (Table 4).

Consumption of H_2 and O_2 during the Pretreatments

The uptake of H_2 (or O_2) during the pretreatments was observed, as shown in Table 2. As defined in the experimental section, the amount of hydrogen consumed during H_2 treatment at 500°C (Run Nos. 2 and 5) was 1.25 and 1.41, respectively, in terms of H/Pt. The uptake of O_2 was 1.45 in terms of O/Pt during the O_2 treatment at 450°C (Run No. 3) which resulted in recovery of H_2 chemisorption capacity. However, the amount of oxygen chemisorbed on the Pt surface at 450°C (blank) should be taken into account. The blank value was measured at the same O_2 pressure and temperature on the recovered catalyst (Run No. 4), and found to be always constant (ca. 1.0 in terms of O/Pt) among the catalysts studied. The "extra-uptake" of O_2 (1.45–0.99; the O_2 consumption) as well as the H_2 consumption can be related to the changes in H_2 chemisorption value. Therefore, the consumption measurements of H_2 and O_2 were performed in detail as shown below.

The time course of the consumption of H_2 during H_2 treatment at 500°C is shown in Fig. 1. The amount of H_2 consumed increased rapidly in the initial stage, reaching a stable level within ca. 15 h of this experiment. The consumption of O_2 during O_2 treatment at 450°C was very rapid. In fact, the O_2 treatment at 450°C for 1 h was enough to restore the H_2 chemisorption value to the original one (*16*). Figure 2 shows relations between the changes in H_2 chemisorption and the consumption of H_2 and O_2 during H_2 and O_2 treatments, respectively. Linear correlations were found: based upon extrapolation, the H_2 chemisorption value fell to zero when the amount of hydrogen consumed was ca. 2 in terms of

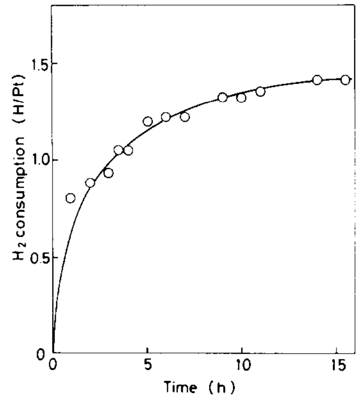

FIG. 1. The amount of H_2 consumed during H_2 treatment at 500°C of the reduced 5.0% Pt/ALO-2 (No. 4 in Table 3).

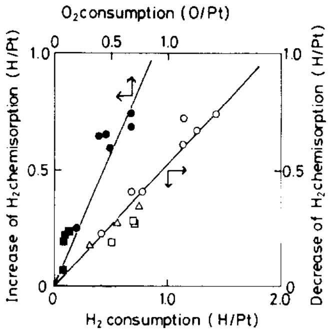

FIG. 2. The decrease of H_2 chemisorption vs the H_2 consumption at 500°C and the increase of H_2 chemisorption vs the O_2 consumption at 450°C. The blank value was subtracted (see text). ○, ●, 5% Pt/ALO-2 (No. 4 in Table 3); △, 5% Pt/ALO-2 (No. 12 in Table 4); □, ■, 2% Pt/ALO-4 (No. 6 in Table 3).

the atomic ratio H/Pt; while it recovered to the original value (100% dispersion) when the amount of oxygen consumed was ca. 1 in terms of the atomic ratio O/Pt. The ratio of 2 to 1 seems to indicate the occurrence of a reversible redox process during the pretreatments.

Relation between the Sulfur Content and the Change in H_2 Chemisorption

The extent of the change in H_2 chemisorption value (H/Pt) according to the pretreatment procedures was studied in connection with the total amount of sulfur in the various Pt catalysts supported on the aluminas in Table 1. The data are listed in Table 3, where S/Pt means the number of total sulfur atoms/total number of Pt atoms. S/Pt is used as a measure of the total sulfur content, in spite of the concept that sulfur is distributed throughout the alumina support. The original values of H/Pt indicated that all the catalysts (except No. 2) were highly dispersed (100% dispersion). It may be worthy to comment here that the H/Pt values are slightly greater than unity. The adsorption stoichiometry (H atoms/surface Pt atoms; H/Pt_s) may be greater than unity when Pt is highly dispersed, probably due to multiple adsorption of hydrogen on certain Pt sites (*29*). The sulfur content of the Pt/ALO-2 (Nos. 3 and 4) was about half of that of ALO-2 itself. It was confirmed by the sulfur analyses (CA) in each preparation step that the partial removal of sulfur did not occur during the impregnation and drying steps, but during the reduction step

TABLE 3

The Sulfur Content (S/Pt) in the Pt Catalysts Determined by CA and the Change in H_2 Chemisorption Value (H/Pt)

Catalyst		Sulfur content by CA		Change of H/Pt	
No.	Metal/Support	SO_4^{-2} (wt%)[a]	S/Pt[b]	Original[c] value	Min[d]
1	0.5% Pt/ALO-1	0.03	0.12	1.25	0.63
2	5.0% Pt/ALO-1	0.03	0.01	0.66	0.46
3	0.5% Pt/ALO-2	1.17	4.75	1.21	0
4	5.0% Pt/ALO-2	0.78	0.32	1.09	0.09
5	0.5% Pt/ALO-4	Trace	<0.04	1.28	1.06
6	2.0% Pt/ALO-4	Trace	<0.01	1.17	0.89
7	0.5% Pt/ALO-4[e]	1.11	4.51	1.04	0
8	0.5% Pt/Al_2O_3(A)	Trace	<0.04	1.34	1.07
9	0.5% Pt/Al_2O_3(B)	Trace	<0.04	1.28	0.90
10	5.0% Pt/ALO-2[f]	0.23	0.09	0.99	0.42
11	0.5% Pt/ALO-2[g]	<0.02	<0.08	1.11	0.84

[a] In this column, "trace" means a sulfur content of less than 0.01 wt%.

[b] S/Pt means the number of the total sulfur atoms/the total number of Pt atoms.

[c] The original value which indicates true dispersion was obtained with the catalyst subjected to the O_2 treatment at 450°C for 1 h followed by H_2 reduction at 300°C (see text) (*16*).

[d] H/Pt value after H_2 treatment at 500°C for 15 to 24 h.

[e] Before impregnation with the Pt solution, $(NH_4)_2SO_4$ was adsorbed on ALO-4, followed by calcination in air at 550°C.

[f] ALO-2 was treated beforehand in H_2 at 550°C.

[g] ALO-2 was treated beforehand in H_2 at 660°C.

with flowing H_2 at 500°C for 1 h. Probably, the sulfate was reduced to elemental sulfur and/or H_2S, and removed from the catalyst at the temperature. Once reduced at 500°C for 1 h, however, minor changes in total amount of sulfur were observed through the course of the pretreatments unless the temperature of the H_2 pretreatment was raised above 500°C, as will be seen in Table 4.

As shown in Table 3, the drastic changes in H/Pt were observed in the catalysts with S/Pt larger than ca. 0.3 (Nos. 3, 4, and 7), and H/Pt decreased to half of the original value even when S/Pt was ca. 0.1 (Nos. 1 and 10). However, the extent of the changes in H/Pt became small when the S/Pt ratios were very low (Nos. 2, 5, 6, 8, 9, and 11). Furthermore, in the preparation of the catalysts Nos. 10 and 11, the ALO-2 was treated beforehand in H_2 at 550 and 660°C, respectively, to control the sulfur content, while the crystallinity was unchanged. Comparing the results among the catalysts supported on the same ALO-2 (Nos. 3, 4, 10, and 11), it is apparent that the extent of the change in H/Pt depends upon the sulfur content in the catalysts. The behavior of catalyst No. 8 was similar

TABLE 4

The Results of XPS, Together with Those of H_2 Chemisorption Value (H/Pt) and the Sulfur Content (S/Pt) Measured by CA, after the Sequence of Pretreatments

Catalyst	Pretreatment[a]	H/Pt	Total amount of sulfur by CA		S/Pt[b] measured by XPS			Pt/Al[d] measured by XPS
			SO_4^{-2} (wt%)	S/Pt	Sulfide[c]	Sulfate	Total	
No. 3	1 O_2 450°C, H_2 300°C	1.21	1.17	4.75	0	8.5	8.5	—
	2 H_2 550°C 5 h	0	—	—	0.6	2.7	3.3	—
	3 O_2 450°C, H_2 300°C, H_2 500°C 15 h; repeated 9 cycles	0.05	0.25	1.01	0.1	2.4	2.5	—
No. 4	A1 O_2 450°C, H_2 300°C	1.09	0.78	0.32	0.13	0.72	0.85	0.94×10^{-2}
	A2 O_2 450°C, H_2 300°C, H_2 500°C 15 h; repeated 5 cycles	0.09	0.66	0.27	0.14	0.45	0.59	0.76×10^{-2}
	B1[e] O_2 450°C, H_2 300°C	1.37	0.71	0.29	0.42	0.49	0.91	0.82×10^{-2}
	B2 H_2 500°C 24 h	0.12	0.80	0.33	0.41	0.29	0.70	0.84×10^{-2}
No. 12[f]	1 O_2 400°C, H_2 300°C	0.75	0.58	0.24	0.09	0.60	0.69	0.73×10^{-2}
	2 H_2 450°C 3 h	0.11	—	—	0.10	0.41	0.51	0.63×10^{-2}
	3 O_2 400°C	—	—	—	0.08	0.50	0.58	0.67×10^{-2}
	4 H_2 300°C	0.69	—	—	0.08	0.50	0.58	0.60×10^{-2}

[a] After the treatment, the evacuation *in vacuo* at 450°C for 1 h was performed in every case. Unless otherwise stated, the time of each treatment step was 1 h.

[b] The atomic ratios S/Pt were derived from the observed S 2p/Al 2s intensity ratios, using the atomic intensity ratio 2.56 determined from the measurement of $Al_2(SO_4)_3$ and the theoretical atomic ratio of Pt/Al, 1.38×10^{-2} and 1.31×10^{-3}, based on the Pt content for 5.0 and 0.5 wt% catalysts, respectively.

[c] Corrected for the $K_{\alpha_{3,4}}$ satellite of the sulfate peak.

[d] The atomic ratios Pt/Al were derived from the observed Pt $4d_{5/2}$/Al 2s intensity ratios, using the cross-section ratio of 13.5 (*32*).

[e] Before this treatment, the H_2 chemisorption value had been 0.17 in H/Pt by the pretreatment at 500°C.

[f] 5.0% Pt/ALO-2; but it was different from No. 4 in lot of preparation. The temperatures of treatments were lowered by 50°C, because this catalyst tended to sinter at the higher temperatures.

to that of No. 9. They are similar in the sulfur content, but quite different in crystallinity. It is shown from these results that the effect caused by the alumina support does not arise from a difference in crystallinity (*16*), but rather from the sulfur content.

Nevertheless, it should be noted that the apparent changes in H/Pt were also observed in catalysts with low S/Pt values (Nos. 2, 5, 6, 8, 9, and 11) and that the extent of the decrease at 500°C was comparable to that reported by Dautzenberg and Wolters (*15, 16*). In particular, it should be pointed out that the quantity of H_2 consumed (Fig. 2) was ca. 0.7 in terms of H/Pt even in the case of catalyst No. 6 in which the sulfur content was very small (less than 0.01 in terms of S/Pt). Summing up, these results show that the extent of the change was remarkable when the sulfur content became high (ca. 0.1 to 0.3 in terms of S/Pt).

XPS Study

An example of S 2p spectra after H_2 and O_2 treatments of 5.0% Pt/ALO-2 (No. 4) is shown in Fig. 3. Although the widths of the observed peaks are rather broad, the XPS technique offers a convenient method of assessing "reduced" and "oxidized" sulfur (*30*); namely, the peaks at ca. 161 and 169 eV are assigned to sulfide and sulfate, respectively (*31*), although it is difficult to determine whether each species is located on the Pt particles or on the Al_2O_3 support. Table 4 shows the XPS results of the several series experiments. The H_2 chemisorption value (H/Pt) and the sulfur content (S/Pt) determined by CA after each treatment are also shown in Table 4. In the case of 0.5% Pt/ALO-2 (No. 3), the drastic change in H/Pt was still observed even after H_2 and O_2 treatments were repeated 9 cycles. Furthermore, the change in H/Pt was also quite reversible even in the case of 5.0% Pt/ALO-2 (S/Pt = ca. 0.3) as shown in the series experiment (No. 4, A).

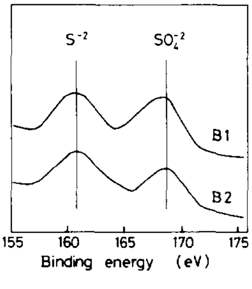

FIG. 3. XPS spectra of sulfur 2p level from the treated catalysts (No. 4), (MgK_α excitation). The label (B1 and B2) should be referred to Table 4.

The XPS study showed that the intensity of the sulfide peak remained almost constant within each series experiment (No. 4, A and B), in spite of the drastic change in H/Pt. Another series experiment (No. 12) also revealed that only a slight change in the relative amount of sulfide and sulfate was observed through the course of the pretreatments and that the H_2 treatment at 300°C for the reduction of Pt oxide did not affect the chemical state of sulfur. The difference in the peak intensity of sulfide among the series experiments might be attributed to a difference in the thermal history of the catalysts. As for the 0.5% Pt/ALO-2 (No. 3), the intensity of the sulfide peak was relatively large when H/Pt was decreased to zero. However, this may be attributed to the higher temperature (550°C) of the H_2 pretreatment. Since the Pt content of this catalyst (0.5 wt%) was too small to discuss a mechanism of the phenomenon quantitatively using the XPS data, we will adopt the results of 5.0 wt% Pt/ALO-2 (Nos. 4 and 12) for further discussion.

No chemical shift of the Pt $4d_{5/2}$ peak (314.3 ± 0.3 eV) was observed among the treated catalysts. Because the Pt 4d lines had a halfwidth of ca. 6 eV, there might be some ambiguity in determining the binding energy. No attempt was made to resolve the overlapping Pt 4f and Al 2p lines.

Infrared Study

Infrared spectra were obtained after a sequence of treatments of 5.0% Pt/ALO-2 (No. 12). A strong band at 1380 cm^{-1} was observed after evacuation *in vacuo* at

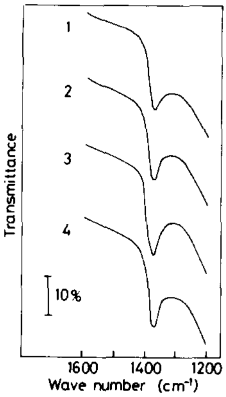

FIG. 4. Infrared spectra taken after the sequence of treatments of 5.0% Pt/ALO-2 (No. 12). Numerals in the figure correspond to those in Table 4: (1) O_2 400°C, H_2 300°C; (2) H_2 450°C 3 h; (3) O_2 400°C; (4) H_2 300°C.

450°C, which was attributed to surface sulfate groups (*33*). Good correlation has been found between the intensity of the band at 1380 cm^{-1} and the sulfur content of the reference aluminas (JRC-ALO-1 to 5) (*34*). In our experiments, the band at 1130 cm^{-1} (*33*) was hardly observed because of large background absorption of Al_2O_3 below 1200 cm^{-1}. As shown in Fig. 4, *in situ* measurements of the band at 1380 cm^{-1} during the treatments corresponding to the series experiment given in Table 4 revealed that the band intensity remained almost constant during the treatments.

DISCUSSION

The possibility that the low chemisorption capacity results from encapsulation of the metal due to structural collapse of the support was ruled out in our system, since the BET surface areas of the catalysts were essentially the same regardless of whether they were in a state of suppressed hydrogen chemisorption or not.

We shall discuss the mechanism of the phenomenon on the basis of three prominent observations: first, the apparent dependency of the extent of the change in the amount of H_2 chemisorption (the extent of the effect) upon the sulfur content of the catalysts; second, the positive correlation between the extent of the effect and the amount of H_2 (or O_2) consumption during the treatments; third, little change both in the total amount of sulfur and in the relative amount of sulfide and sulfate through the course of the treatments which result in the suppression of H_2 chemisorption and recovery of the normal chemisorption behavior.

Behavior of Sulfur

With the first two observations, one is tempted to attribute the loss of the chemisorption ability and its recovery during the treatments to a reversible redox reaction of sulfur expressed schematically as

$$(SO_4^{-2})_{\text{support}} + Pt_s \underset{\frac{3}{2}O_2,\ 450°C}{\overset{3H_2,\ 500°C}{\rightleftarrows}} Pt_s \cdot S + (O^{-2})_{\text{support}}, \quad (1)$$

where $(SO_4^{-2})_{\text{support}}$ represents sulfate on alumina surface, and Pt_s denotes the surface Pt atom. Reduced sulfur bound to Pt_s would inhibit the chemisorption of H_2 (*18, 19*). However, XPS and ir results contradict with this scheme. The XPS study revealed that the peak intensity of sulfide did not vary in spite of the drastic change in H_2 chemisorption (Table 4). The S/Pt values obtained by XPS were at the same order of magnitudes as those by CA. Also, the atomic ratios of Pt/Al calculated from the observed intensity ratios were almost in good accordance with the theoretical one (1.38×10^{-2}) based on the Pt content (5.0 wt%), assuming no surface enrichment. Besides, the S/Pt value from XPS varied reasonably with the change of the sulfur content (No. 3 in Table 4). Therefore, it is reasonable to assume that the behaviors studied by XPS represent almost the total picture of catalysts during the treatments. Although XPS provides information only about the surface region of each catalyst particle, the surface region includes not only the outer surface, but also the subsurface layer (less than ca. 30 Å) (*35*). The ir study also revealed that the band intensity of sulfate remained almost constant during the treatments, while the H_2 chemisorption value was changed drastically (No. 12 in Table 4). If the consumption of H_2 and O_2 during the treatments is due to reaction (1), the results in Fig. 2 mean that almost all sulfur in the 5.0% Pt/ALO-2 (S/Pt = 0.3) must take part in the reaction. However, such drastic interchange from sulfide to sulfate and *vice versa* was not observed, in spite of the drastic change in H_2 chemisorption, as shown from the XPS and ir results. The idea that the reversible reaction (1) was taking place during the treatments, therefore, can be discarded.

Bonzel and Ku (*36*) 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, where θ_s was defined as the atomic ratio S_{ad}/Pt_s. A few data are available concerning the influence of sulfur on the H_2 chemisorption. The initial sticking coefficient of hydrogen on polycrystalline Ni decreased almost linearly to zero at θ_s = ca. 0.5 (*37*). In supported metal catalysts, the fraction of decrease of H_2 adsorption is also generally proportional to the amount of sulfur (*38*). Ng and Martin (*39*) studied the effects of H_2S on Ni/SiO_2, and found that H_2 and CO chemisorptions are specific to the free Ni surface, and have the same characteristics as on pure Ni. As has been seen above, it has been considered that the chemisorption is inhibited with higher sulfur coverage, $0.5 < \theta_s < 1$, although enough data are not available at present. If that is the case in the present system, all the sulfur in the 5% Pt/ALO-2 (S/Pt = 0.3) must act quite reversibly as poison, considering that the catalysts have 100% dispersion ($Pt_s/Pt = 1$). As stated above, this is improbable.

Another possibility which must be taken into consideration is that small Pt crystallites may lose the ability to chemisorb H_2 by a very small amount of sulfur, in contrast with the case of the flat Pt surface. The net change of less than 0.03 in S/Pt could not be detected by XPS and ir because of the experimental error of about 10%. If this hypothesis is correct, the chemisorption should be hindered when one sulfur atom is adsorbed on a Pt crystallite, considering that these catalysts are highly dispersed ($Pt_s/Pt = 1$) and that such a small Pt crystallite consists of less than ca. 30 atoms (*26*). The sulfur might alter the electronic properties of the metal crystallite itself (*20*). In the present stage, there is no direct information for this hypothesis, while structure sensitivity (or selective poison) for catalytic reactions has been reported (*18*). As for the H_2 adsorption on flat Pt surfaces, the difference in the behavior between low and high index planes with atomic steps has been considered to be rather small (*40*), though contradictory results have been also reported (*41, 42*).

There is a good relationship between the H_2 and O_2 consumption and the change in H_2 chemisorption, while reaction (1) does not occur. Therefore, we come to the interpretation that part of the surface alumina in the neighborhood of the Pt crystallites is reduced by H_2 treatment, and reoxidized by O_2 treatment.

Interpretation of the Results in Terms of the Reduction of Surface Alumina

We propose the following reaction as a plausible redox reaction taking place reversibly during the treatments:

$$Pt + Al_2O_3 \underset{\frac{1}{2}O_2,\ 450^\circ C}{\overset{H_2,\ 500^\circ C}{\rightleftarrows}} Pt \cdot Al_2O_2 \quad (2)$$

Note that $Pt \cdot Al_2O_2$ was represented schematically to explain the quantity consumed (2 in H/Pt and 1 in O/Pt, respectively, based on extrapolation).

Weller and Montagna (*43*) studied the reaction of H_2 with pure Al_2O_3, and suggested the partial reduction of the surface Al_2O_3 at 450 to 550°C. They stated that thermodynamic data of bulk crystalline phases are of little use in predicting the possibility of "surface reduction." Furthermore, they observed the surprisingly high value of O_2

uptake (3.7 in O/Pt) on Pt/Al_2O_3 at 525°C which was also attributed to partial reduction of Al_2O_3, catalyzed by the Pt, during the catalyst prereduction with H_2 at 550°C (*44*). Though they did not observe the drastic change in H_2 chemisorption, their results are in accordance with our own consumption measurements. Den Otter and Dautzenberg also assumed alloy type bonding between Pt and Al of the partially reduced Al_2O_3 (*17*), although they did not perform the consumption measurements of H_2 and O_2. Reaction (2) may be rewritten schematically in terms of the alloy model:

$$Pt + Al_2O_3 \underset{\frac{1}{2}O_2,\ 450°C}{\overset{H_2,\ 500°C}{\rightleftarrows}} PtAl_{2/3} \cdot \tfrac{2}{3}(Al_2O_3) \quad (3)$$

The decrease of H_2 chemisorption may be easily rationalized by assuming that H_2 chemisorption, which does not take place on Al, is dissociative and needs two adjacent Pt sites (*17*).

Accepting the above model for H_2 and O_2 consumption, the redox process [(2) or (3)] are related to the change in H_2 chemisorption, and this mechanism suggests the existence of metal–support interaction in the Pt/Al_2O_3 catalysts. The new phase formed upon the treatment by H_2 at 500°C [$Pt \cdot Al_2O_2$ in (2) or $PtAl_{2/3} \cdot \frac{2}{3}(Al_2O_3)$ in (3)] is considered not to chemisorb H_2. In this model, the role of sulfur is presumably to catalyze (as a promoter) reaction (2) or (3). Small amounts of additives might affect the reduction rate of oxides (*45*). Somorjai has studied reconstruction of single crystal surfaces in the presence of impurities (*46*): sulfur causes gross reconstruction of Pt surfaces (*47*), and, further, the (0001) crystal face of α-alumina undergoes a change of surface structure by a change in the chemical composition of the surface, i.e., by the loss of oxygen (*48*). If these effects could be applied to the highly dispersed Pt–Al_2O_3 interface, such drastic structural changes including reaction (2) or (3) would occur with the aid of sulfur by high temperature treatment. There is no evidence that sulfur is required in the case of Pt/TiO_2 (and related systems) to bring about the suppression of hydrogen chemisorption (*1*). In the case of Pt/Al_2O_3, however, sulfur-promoted surface reduction may lead to a new type of metal–support interaction, which also brings about the suppression.

The XPS study was made because the electronic state of Pt could presumably change, but showed no difference in the Pt $4d_{5/2}$ peak position within the experimental uncertainty, while it has been suggested in the Pt/TiO_2 and Pt/$SrTiO_3$ system that the Pt atoms acquire a substantial negative charge (*49*). More extensive work should be done to elucidate the detailed structure and electronic state of the complex of Pt and partially reduced Al_2O_3.

In conclusion, we propose the partially reduced state in reaction (2) or (3) as the model for the state of the suppressed hydrogen chemisorption and the catalytic role of sulfur in the support, because of the close correlation between the extent of the effect and the amount of H_2 (and O_2) consumption and other evidences as shown above.

ACKNOWLEDGMENTS

The authors are grateful to Messrs. M. Nakajima, N. Ii, and N. Nojiri of Mitsubishi Petrochem. Co. for the chemical analyses of sulfur and fruitful discussions.

REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).

2. Baker, R. T. K., Prestidge, E. B., and Garten, R. L., *J. Catal.* **56,** 390 (1979); **59,** 293 (1979).

3. Smith, J. S., Thrower, P. A., and Vannice, M. A., *J. Catal.* **68,** 270 (1981).

4. Mustard, D. G., and Bartholomew, C. H., *J. Catal.* **67,** 186 (1981).

5. Tatarchuk, B. J., and Dumesic, J. A., *J. Catal.* **70,** 308 (1981).

6. Vannice, M. A., and Garten, R. L., *J. Catal.* **66,** 242 (1980).

7. Bartholomew, C. H., Pannell, R. B., and Butler, J. L., *J. Catal.* **65,** 335 (1980).

8. Vannice, M. A., Wang, S-Y., and Moon, S. H., *J. Catal.* **71,** 152 (1981); **71,** 167 (1981).

9. Vannice, M. A., and Garten, R. L., *J. Catal.* **63,** 255 (1980).

10. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).

11. Wilson, G. R., and Hall, W. K., *J. Catal.* **24,** 306 (1972).

12. Moss, R. L., Pope, D., Davis, B. J., and Edwards, D. H., *J. Catal.* **58,** 206 (1979).

13. Praliaud, H., and Martin, G. A., *J. Catal.* **72,** 394 (1981).

14. Gonzalez-Tejuka, L., Aika, K., Namba, S., and Turkevich, J., *J. Phys. Chem.* **81,** 1399 (1977).

15. Dautzenberg, F. M., and Wolters, H. B. M., *J. Catal.* **51,** 26 (1978).

16. Kunimori, K., Okouchi, T., and Uchijima, T., *Chem. Lett.* 1513 (1980).

17. Den Otter, G. J., and Dautzenberg, F. M., *J. Catal.* **53,** 116 (1978).

18. Maurel, R., Leclercq, G., and Barbier, J., *J. Catal.* **37,** 324 (1975).

19. Leclercq, G., and Boudart, M., *J. Catal.* **71,** 127 (1981).

20. Sivasanker, S., and Ramaswamy, A. V., *J. Catal.* **37,** 553 (1975).

21. Apesteguia, C. R., Barbier, J., Plaza de Los Reyes, J. F., Garetto, T. F.; and Parera, J. M., *Appl. Catal.* **1,** 159 (1981).

22. Menon, P. G., and Prasad, J., *Proc. VIth Int. Congr. Catal. London* **2,** 1061 (1976).

23. Oudar, J., *Catal. Rev.* **22,** 171 (1980).

24. Shokubai (Catalyst) **21,** 62 (1979); **22,** 110, 115 (1980).

25. Nakajima, M., Ii, N., and Imaeda, K., *Bunseki Kagaku* **30,** 234 (1981).

26. Anderson, J. R., "Structure of Metallic Catalysts." Academic Press, New York, 1975.

27. Benesi, H. A., Atkins, L. T., and Mosely, R. B., *J. Catal.* **23,** 211 (1971).

28. Benson, J. E., and Boudart, M., *J. Catal.* **4,** 704 (1965).

29. Kunimori, K., Uchijima, T., Yamada, M., Matsumoto, H., Hattori, T., and Murakami, Y., *Appl. Catal.* **4,** 67 (1982).

30. Briggs, D., *in* "Electron Spectroscopy" (C. R. Brundle and A. D. Baker, Eds.), Vol. 3, p. 352. Academic Press, New York, 1979.

31. Matsumoto, Y., Soma, M., Onishi, T., and Tamaru, K., *J. C. S. Faraday I* **76,** 1122 (1980).

32. Scofield, J. H., *J. Electron Spectrosc.* **8,** 129 (1976).

33. Yao, H. C., Stepien, H. K., and Gandhi, H. S., *J. Catal.* **67,** 231 (1981).

34. Take, J., and Yoneda, Y., Schokubai (Catalyst) **22,** 120 (1980) Data-JRC-0006.

35. Delgass, W. N., Haller, G. L., Kellerman, R., and Lunsford, J. H., "Spectroscopy in Heterogeneous Catalysis," p. 289. Academic Press, New York, 1979.

36. Bonzel, H. P., and Ku, R., *J. Chem. Phys.* **58,** 4617 (1973).

37. Rendulic, K. D., and Winkler, A., *Surface Sci.* **74,** 318 (1978).

38. Bartholomew, C. H., and Katzer, J. R., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), p. 375. Elsevier, Amsterdam, 1980.

39. Ng, C. F., and Martin, G. A., *J. Catal.* **54,** 384 (1978).

40. Christmann, K., and Ertl, G., *Surface Sci.* **60,** 365 (1976).

41. Bernasek, S. L., and Somorjai, G. A., *J. Chem. Phys.* **62,** 3149 (1975).

42. Helms, C. R., Bonzel, H. P., and Kelemen, S., *J. Chem. Phys.* **65,** 1773 (1976).

43. Weller, S. W., and Montagna, A. A., *J. Catal.* **21,** 303 (1971).

44. Weller, S. W., and Montagna, A. A., *J. Catal.* **20,** 394 (1971).

45. Il'chenko, N. I., *Russian Chem. Rev.* **41,** 47 (1972).

46. Somorjai, G. A., *Catal. Rev.* **18,** 173 (1978).

47. Somorjai, G. A., *J. Catal.* **27,** 452 (1972).

48. French, T. M., and Somorjai, G. A., *J. Phys. Chem.* **74,** 2489 (1970).

49. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211,** 1121 (1981).