

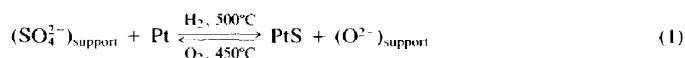
On The Sulfur-Aided Metal–Support Interaction in Pt/Al₂O₃–Cl Catalysts

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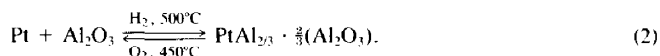
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The SMSI behavior displayed by sulfated Pt/Al₂O₃–Cl catalysts with relatively low sulfur content has been explained by the alternative reactions



or



Redox reaction (2) would be sulfur catalyzed, giving the so-called sulfur-aided SMSI. In this paper the SMSI behavior displayed by sulfided samples with only irreversibly held sulfur (S/Pt = 0.20–0.35) was studied by the changes in H₂ and O₂ chemisorption, infrared spectroscopy, temperature-programmed reduction and H₂S desorption at increasing temperatures. The changes in the 1380-cm⁻¹ band (SO₄²⁻ on the carrier) and in the 2060-cm⁻¹ band (CO adsorption on Pt in linear form) were used to investigate the effects of the high-temperature reduction treatment. The TPR profiles of sulfated aluminas showed only one reduction peak at 650–680°C; the presence of Pt gave rise to a low-temperature peak which appeared at 450–500°C. Such a peak shifted to lower temperatures when the Pt content was increased. The data showed that the SMSI behavior of sulfated Pt/Al₂O₃–Cl samples is better explained in terms of redox reaction (1). During the HTR treatment Pt catalyzes the reduction of sulfate ions. The H₂S formed is adsorbed on the metal so that the H₂ chemisorption is suppressed by the S blockage of the surface. Subsequent oxidation treatment causes oxidized S species in the metal surface to migrate back to the support. The metallic fraction is regenerated and, as a consequence, the H₂ chemisorption capacity is restored. © 1987 Academic Press, Inc.

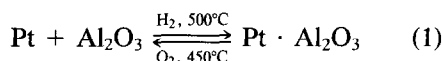
INTRODUCTION

The suppression of hydrogen chemisorption after pretreatment in hydrogen at high temperature had already been noted in Pt/Al₂O₃ catalysts (1–3) prior to the similar phenomenon reported by Tauster *et al.* (4) in Pt/TiO₂. The latter was termed strong metal–support interaction (SMSI). Dautzenberg *et al.* (1, 2) attributed the decrease in the H/Pt ratio after H₂ treatment at temperatures above 500°C to a superficial alloy formed between Pt and reduced Al. González Tejuca *et al.* (3) ascribed the loss in the H₂ chemisorption capacity to a decomposition of Pt particles into an atomic form of Pt

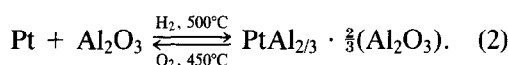
incorporated by the alumina support. On the other hand, Menon and Froment (5, 6) have proposed that after the treatment of Pt/Al₂O₃ catalysts with H₂ at high temperatures, a part of the hydrogen on Pt is “strongly chemisorbed.” This stronger chemisorption of hydrogen would render a fraction of the surface Pt atoms inaccessible to the H₂ chemisorption at room temperature. Thus, the decrease of hydrogen chemisorption will be specific to the platinum metal and not caused by any metal–support interaction. A detailed review has been published concerning the effects of residual hydrogen on physical and chemical properties of the catalyst (7). In all of these

papers, a common feature has been reported: a mild air oxidation at 400–500°C followed by reduction at 250–350°C restores the original capacity of the catalysts to chemisorb hydrogen.

Recently, Kunimori *et al.* (8, 9) have reported that the degree of suppression of H₂ chemisorption after the high-temperature reduction (HTR) depends strongly on the sulfur content in Al₂O₃. On the basis of the correlation found between the decrease (or increase) in the amount of hydrogen chemisorption and the amount of H₂ (or O₂) consumption during the pretreatment, and other evidence, they proposed the formation of a surface compound according to the redox reaction

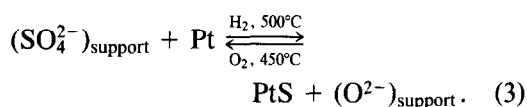


or, alternatively, in terms of the alloy model



Redox reaction (1) or (2) would be sulfur catalyzed. The role of sulfur is presumably to promote the partial reduction of alumina. Such a phenomenon may be called a sulfur-aided SMSI (10).

The effects of the presence of sulfur in Pt/Al₂O₃ catalysts have been extensively studied regarding poisoning and regeneration phenomena. Fundamental (11–13) and industrial (14, 15) studies have explained the sulfurization and regeneration of platinum by the redox reaction



Since the sulfur bound to Pt inhibits the chemisorption of hydrogen (16, 17), redox reaction (3) also explains both the decrease of H₂ chemisorption after the high-temperature reduction and the regeneration of the metal by air oxidation at 400–500°C followed by a low-temperature reduction treatment (LTR). The reduction of sulfates

by H₂ treatment at 500°C is easily verified by analyzing the H₂S removed from the catalyst during the treatment. However, for samples with relatively low sulfur content the consecutive H₂/O₂ treatments do not cause any significant change in the sulfur level (9), thereby indicating that sulfur is not eliminated from the catalysts. Kunimori *et al.* (9, 10) claimed that for low S content (S/Pt ≈ 0.3, where S/Pt means the number of total sulfur atoms/total number of Pt atoms) redox reaction (3) can be discarded so that the decrease of H₂ chemisorption after the HTR treatment has to be attributed to the partially reduced state formed in reaction (1) or (2). The presence of sulfur will be necessary to catalyze (as a promoter) this reaction.

Thus, in order to ascribe the SMSI behavior displayed by a sulfated Pt/Al₂O₃ sample to a sulfur-aided SMSI, it is essential to demonstrate that the sulfur poisoning mechanism of reaction (3) does not take place. In this work we have prepared sulfated Pt/Al₂O₃-Cl catalysts with different sulfur and platinum contents. The changes induced by the consecutive reduction/oxidation treatments were studied by gas chemisorption, infrared spectroscopy, temperature-programmed reduction (TPR), and H₂S desorption at increasing temperatures. The results reveal that the SMSI behavior displayed by the sulfated Pt/Al₂O₃ samples is caused by redox reaction (3) and thus the suppression in the H₂ chemisorption upon applying HTR at 500°C has to be explained by the sulfur poisoning of the metal.

EXPERIMENTAL

The support used in this work was a high-purity commercial Al₂O₃ (Cyanamid Ketjen CK-300) of 180 m² g⁻¹ BET specific area, 0.49 cm³ g⁻¹ pore volume, and a S content of less than 0.004 wt%. The alumina was impregnated with an aqueous solution of chloroplatinic acid and HCl as competitor. After impregnation, the samples were dried 12 h at 120°C and heated in an air stream to 500°C. Then the chlorine content was regu-

lated using a gaseous mixture of HCl, water, and air. Finally, the samples were purged with N₂ and reduced in flowing H₂ for 8 h at 500°C. Five catalysts of 0.18, 0.34, 0.55, 0.93, and 2.72% Pt were prepared. Their main characteristics are given in Table 1.

Accessible metal fractions were determined by H₂ chemisorption (HC) and by titration with O₂ of preadsorbed H₂ (OT). The volumetric adsorption experiments were carried out in a conventional glass vacuum apparatus in which a final dynamic vacuum of at least 10⁻⁵ Torr was attainable. The amount of gas adsorbed on the samples was determined from pressure measurements with an MKS Baratron pressure gauge. In the case of H₂ chemisorption the double isotherm method at room temperature was used (18): the first isotherm gave the total gas uptake and the second, obtained after 2 h of evacuation, the "reversible" or weakly adsorbed gas. By taking the difference between isotherms, the amount of "irreversible" or strongly adsorbed gas was determined. The pressure range of the isotherms was 0–50 Torr and the extrapolation to zero pressure was used as a measure of the gas uptake on the metal. The values of the accessible metal fraction were calculated using stoichiometric ratios (HC)/Pt_s = 1 and (OT)/Pt_s = $\frac{3}{2}$, where Pt_s implies Pt atom on the surface.

The sample wafers for infrared studies were formed by pressing approximately 50 mg of the catalyst powder at a pressure of around 5 ton/cm². The disks were transferred to an all-glass infrared cell where pretreatment of the sample could be performed *in situ* in static or flowing gases at high temperature. The CaF₂ windows were sealed with Viton O rings. In order to avoid contamination of the catalysts, sample holders made of quartz were used. The standard pretreatment involved reduction in flowing H₂ at 500°C for 3 h followed by prolonged degassing at the same temperature. Spectra were always recorded at room temperature.

TABLE 1

Chlorine Concentration and Metal Dispersion of the Catalysts Used in This Work

Catalyst	% Pt	% Cl	D(%)
1	0.18	0.96	72
2	0.34	0.90	76
3	0.55	0.91	67
4	0.93	0.96	62
5	2.72	0.86	56

The TPR experiments were carried out with 5% H₂ in argon. Samples were heated with a linear temperature programmer-controller electric furnace at 6°C min⁻¹ within the temperature range of 20–800°C. The gases were carefully purified to remove water and traces of oxygen. Because of the water formed during reduction of the samples, the gas coming from the reactor was passed through a cold trap before entering the thermal conductivity cell.

The samples were sulfided at 500°C and atmospheric pressure in a flow of H₂S/H₂ mixture with 0.05% H₂S. After sulfidation the catalysts were treated in flowing hydrogen at 500°C for 5 h to remove the weakly held sulfur (reversible sulfur). Under these conditions only the strongly held sulfur (irreversible sulfur) on the metal remains on the catalyst (19). In some cases, in order to have higher sulfur content, the temperature and the length of the hydrogen treatment after sulfidation were diminished. The sulfur level on the catalysts was measured by chemical analysis and X-ray fluorescence.

The reduction of sulfated catalysts was studied by analyzing the H₂S removed from the catalysts at increasing temperatures. The experiments were carried out at atmospheric pressure in a flow system provided with a fixed-bed reactor. Hydrogen was purified by passage through a Deoxo unit and then through a bed of MnO on celite to remove traces of oxygen. The temperature was raised at 6°C min⁻¹ starting from room temperature, and 0.3 g of catalyst was used. The H₂S eliminated was trapped in an alka-

line solution and titrated with mercury acetate, employing dithizone indicator.

RESULTS

I. Gas Adsorption and H_2/O_2 Treatments

The HC and OT values obtained after H_2 and O_2 pretreatments of catalysts 2, 3, 4, and 5 are given in Table 2. The H_2/O_2 pretreatments were first performed on unsulfided samples (runs I to III). Thereafter, the catalysts were sulfided (run IV) and another cycle of H_2/O_2 treatments was carried out (runs V to VII). Prior to the gas uptake measurements, all samples were degassed for 3 h at 500°C. The unsulfided catalysts were treated according to the following procedure: reduction at 270°C for 3 h (run I); reduction at 500°C for 3 h (run II); air oxidation at 450°C for 1 h followed by LTR at 270°C (run III). For each catalyst, the HC values determined after runs I to III were similar, thereby indicating that neither the H_2 reduction at 500°C nor the air oxidation at 450°C modified H_2 chemisorption.

In run IV, the catalysts were sulfided under the conditions described under Experimental. Catalysts 3, 4, and 5 were sulfided at 500°C and then treated at the same temperature in flowing H_2 for 5 h. After this H_2 treatment only the irreversibly held sulfur on the metal remains on the catalysts (19). The S/Pt_s atomic ratios of catalysts 3, 4, and 5 were respectively 0.44, 0.52, and 0.41, which fall within the range (S/Pt_s = 0.4–0.5) determined in previous works for the irreversibly held sulfur on Pt/Al₂O₃ catalysts (19, 20). Thus, taking into account the values of the accessible metal fractions (Table 1), catalysts 3, 4, and 5 had S/Pt atomic ratios of respectively 0.29, 0.33, and 0.23. Catalyst 2 was sulfided and reduced at 300°C. After such a reduction treatment both the sulfur adsorbed on the metal (in the strong and weak forms) and the sulfur adsorbed at the strong Lewis acid sites of the support remain on the catalysts (21). The S/Pt ratio of catalyst 2 was 1.70.

After sulfidation, the metal surface is par-

tially blocked by S so that the gas chemisorption decreases. The H_2 adsorption on sulfided samples occurs only on unpoisoned Pt atoms, whereas O_2 can adsorb to some extent on the atoms of Pt already poisoned by sulfur (13, 16, 17). This explains why the accessible metal fractions determined through OT values were higher than those determined from HC uptakes (run IV, Table 2). The sulfided samples were oxidized with air at 450°C and reduced at 270°C (Table 2, run V). Such a treatment restored the original capacity of the catalyst to chemisorb H_2 and O_2 , thereby indicating that S has been eliminated from the metal. When the reduction temperature was increased up to 500°C, the gas chemisorption decreased and the differences between H_2 and O_2 uptakes were again verified (Table 2, run VI). The sulfur contents of catalysts 3, 4, and 5 were not modified by the treatments of runs V and VI. On the contrary, runs V and VI diminished the S level of catalyst 2 which had a higher S/Pt ratio because both the reversibly and irreversibly held S remained on the catalyst. In this case, the oxidation/reduction treatments of runs V and VI eliminated part of the S adsorbed on the catalyst.

Finally, the air oxidation of run VII did not produce any significant change in the S content of the catalysts and the H_2 chemisorption capacity was restored.

II. Infrared Spectroscopy Results

Catalyst 5 (2.72% Pt) was submitted to the same treatments of runs IV to VI (Table 2) and analyzed by IR spectroscopy. The metallic fraction was characterized by the adsorption of CO. The CO adsorption on Pt gives a band in the region of 2060–2070 cm^{-1} attributed to the linearly adsorbed CO. The presence of SO_4^{2-} on the support was followed by the band at 1370–1390 cm^{-1} . The sulfate ions are well characterized by this band, which has already been employed to measure the sulfate level on alumina samples (22). Results are given in Fig. 1.

TABLE 2
The Changes in H₂ and O₂ Chemisorption by Consecutive Reduction/Oxidation Treatments of Unsulfided and Sulfided Pt/Al₂O₃ Catalysts

Pretreatment	Catalyst 2			Catalyst 3			Catalyst 4			Catalyst 5		
	D(%)	% S	S/Pt	D(%)	% S	S/Pt	D(%)	% S	S/Pt	D(%)	% S	S/Pt
I. Reduced at 270°C 3h	80	76	—	—	—	—	—	—	—	—	—	—
II. I + HTR ^a	75	78	—	—	—	—	65	60	—	56	58	—
III. II + air oxidation at 450°C + LTR ^b	76	78	—	—	—	—	60	62	—	58	56	—
IV. III + sulfidation with H ₂ S/H ₂ + reduction 5 h at 500°C	10	22	0.085 ^c	1.70	18	40	0.026	0.29	22	42	0.050	0.33
V. IV + air oxidation at 450°C + LTR	74	76	0.085	1.52	65	66	0.032	0.35	60	60	0.052	0.34
VI. V + HTR	18	38	0.065	1.16	26	45	0.030	0.33	30	44	0.057	0.36
VII. VI + air oxidation at 450°C + LTR	80	78	0.065	1.16	68	65	0.028	0.31	64	62	0.055	0.35

Note. In all cases, the samples were degassed 3 h at 500°C after reduction and prior to the gas chemisorption.

^a HTR: H₂ reduction at 500°C for 3 h.

^b LTR: H₂ reduction at 270°C for 3 h.

^c Catalyst 2 was sulfided and reduced at 300°C.

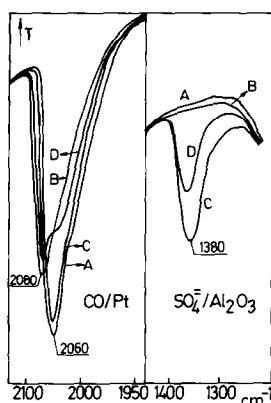


FIG. 1. Infrared spectra of CO and SO_4^{2-} on catalyst 5 (Pt/ Al_2O_3 , 2.72% Pt). CO adsorbed at room temperature; in all cases, $P_{\text{CO}} = 40$ Torr, evacuated 20 min. (A) Unsulfided catalyst; (B) after sulfidation; sulfided catalyst with only irreversibly held sulfur; (C) after (B) and following oxidation with air at 450°C and H_2 reduction at 270°C ; (D) after (C) and following H_2 reduction at 500°C for 3 h.

After the standard pretreatment, 40 Torr of CO was introduced into the IR cell during 20 min at room temperature; then the sample was evacuated for 20 min. The CO adsorbed on the unsulfided sample gave a peak at 2060 cm^{-1} (spectrum A). Thereafter, the catalyst was sulfided as in run IV of Table 2 so only the irreversibly held sulfur on Pt remained on the sample. The CO spectrum was recorded at room temperature (spectrum B). The S adsorbed on Pt diminished the intensity and caused a 20-cm^{-1} shift from 2060 to 2080 cm^{-1} in the band position. Such an increase of the CO band was explained in a previous work by a "short distance" S-Pt interaction considering that the electron-acceptor properties of sulfur decrease the electronic density of the metal (23). But the important fact to be emphasized here is that the upward shift of $\nu(\text{CO})$ indicates the presence of S on the metal.

The sulfided sample was treated with air at 450°C and reduced at 270°C as in run V, Table 2. After degassing at high temperature, 40 Torr of CO was admitted and then the IR cell was evacuated 20 min. As is

shown in spectrum C, the CO band was similar to that obtained for the unsulfided sample (spectrum A) and the band assigned to the sulfate ions on the support appeared at 1380 cm^{-1} . It can be inferred from these spectra that the oxidation treatment caused the elimination of S from the metal and that the oxidized sulfur species were adsorbed on alumina as sulfate ions.

Thereafter, the sulfated sample was reduced at 500°C in the same conditions used in run VI, Table 2. The CO was introduced at room temperature into the IR cell and spectrum D was obtained. The band at 1380 cm^{-1} was diminished upon applying the HTR treatment. The CO adsorption caused the formation of two bands: a band at 2080 cm^{-1} and a superimposed band that appeared as a shoulder at lower frequency.

III. Temperature-Programmed Reduction Results

To obtain more information on the effect of the HTR treatment on sulfated Pt/ Al_2O_3 catalysts, some additional experiments using temperature-programmed reduction were performed. The samples were first sulfided using the $\text{H}_2\text{S}/\text{H}_2$ mixture and then sulfated by air oxidation at 450°C . Prior to the TPR measurements the samples were treated with H_2 at 270°C to reduce the metallic fraction. Catalysts 1, 3, and 5 (Table 1) and samples of alumina and chlorided alumina were used. In the case of catalyst 1, two samples with different S levels were prepared (catalyst 1-A and 1-B). The sulfate levels of the samples are given in Table 3.

TABLE 3

Sulfate Level of the Samples Analyzed by TPR

Sample	% Cl	% Pt	SO_4^{2-} level (% S)	S/Pt	TPR curve (Fig. 2)
Al_2O_3	—	—	0.100	—	a
$\text{Al}_2\text{O}_3\text{-Cl}$	0.90	—	0.080	—	b
Catalyst 1-A	0.96	0.18	0.050	1.69	c
Catalyst 1-B	0.96	0.18	0.085	2.88	d
Catalyst 3	0.91	0.55	0.090	1.00	e
Catalyst 5	0.96	2.72	0.105	0.23	f

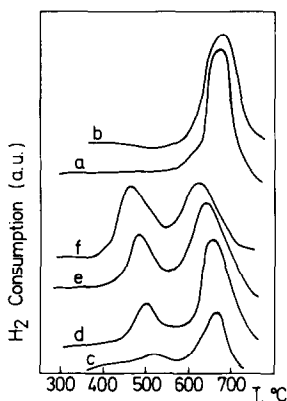


FIG. 2. TPR profiles of sulfated samples. (a) Alumina; (b) chlorided alumina; (c) and (d) catalyst 1; (e) catalyst 3; (f) catalyst 5. The sulfate levels of the samples are given in Table 3.

Except catalyst 1-A (curve c), all the samples had similar sulfate concentrations. The reduction profiles are presented in Fig. 2.

The TPR profiles of Al₂O₃ (curve a) and Al₂O₃-Cl (curve b) showed a single peak at 650–680°C. Hence, if no metal is present, the treatment of sulfated aluminas with H₂ at 500°C will not reduce the sulfate ions, at least for the sulfate levels used in this work. Some TPR experiments performed with Al₂O₃ samples having higher sulfate concentrations showed that the single peak moves to lower temperatures when the S content is increased. Thus, for example, a sulfated alumina sample with 0.35% S gave a reduction peak at 600°C.

Catalyst 1-A with low S content showed a small consumption band at 500–520°C and the second peak at 660°C (curve c). When the sulfate level was increased (catalyst 1-B) the low-temperature peak was clearly defined (curve d). Catalysts 3 and 5 (curves e and f, respectively) had similar S content but higher metal loading than catalyst 1-B (curve d). With increasing Pt content, the following changes in TPR profiles were observed: (i) the low-temperature peak increased and shifted to lower temperatures, (ii) the high-temperature peak decreased and also shifted to lower temperatures.

In summary, the TPR results show that the reduction of sulfate ions in sulfated alumina samples gives a single peak at 650–680°C. The presence of Pt gives rise to a second consumption peak which appears in the region of 450–500°C. The characteristics of the two reduction peaks (relative predominance, temperature at which the reduction takes place) will depend on both the metal amount on the catalyst and the sulfate concentration.

IV. Reduction of Sulfated Samples Studied by H₂S Desorption

The reduction with H₂ of the sulfated samples was also studied by analyzing the H₂S removed from the catalysts when the temperature was raised at 6°C min⁻¹ from room temperature up to 800°C. The details of the experimental system employed are given under Experimental.

The following samples were employed: (i) sulfated Al₂O₃ and Al₂O₃-Cl of Table 3, and (ii) sulfated catalysts 3, 4, and 5 of Table 2, run V. In Fig. 3 the quantity of S eliminated (in reference to the original S concentration of the samples) was plotted as a function of temperature. The curves of H₂S desorption of sulfated alumina and chlorided alumina were similar. Hydrogen sulfide was detected at about 600°C and the temperature of the maximum desorption

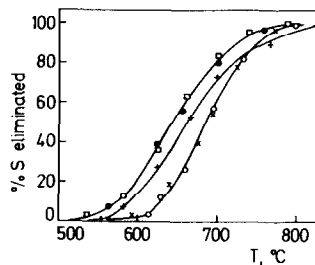


FIG. 3. H₂S removed from the sulfated samples by hydrogen treatment. In the abscissa, the quantity of S eliminated is in reference to the original S level on the samples. ○, Alumina (0.100% S); x, chlorided alumina (0.080% S); ●, catalyst 3; □, catalyst 4; +, catalyst 5. The sulfate level of these catalysts are given in Table 2, run V.

rate was in good agreement with the temperature of the reduction peaks determined by the TPR experiments (Fig. 2, curves a and b). On the contrary, the H₂S desorption curve of sulfated catalyst 5 gave quite different results compared with the TPR profile corresponding to the same catalyst (Fig. 2, curve f). In fact, H₂S was not detected in the region of 440–500°C corresponding to the maxima of the low-temperature peaks in the TPR profiles. H₂S removal from the catalysts was detected at about 560°C, whereas the TPR profiles showed that the low-temperature peaks started from 400°C.

DISCUSSION

The SMSI behavior is characterized by the following changes in H₂ chemisorption: (i) after low-temperature reduction (<300°C) the catalysts exhibit "normal" H₂ chemisorption capacity, i.e., H₂ adsorption stoichiometry corresponds to about one H atom per surface Pt atom; (ii) high-temperature reduction (>450°C) causes a drastic decrease in H₂ uptake (SMSI state); and (iii) a mild oxidation treatment followed by low-temperature reduction eliminates the SMSI state and H₂ chemisorption capacity is restored.

Several authors have reported that unsulfided Pt/Al₂O₃ catalysts display the phenomena described by steps i to iii. Two causes have been advanced to explain this SMSI behavior: (a) after HTR a part of H₂ ("strongly chemisorbed H₂") remains on the catalyst and renders a fraction of the surface Pt atoms inaccessible to subsequent H₂ adsorption (5); and (b) HTR causes the reduction of alumina in the immediate surrounding of the Pt crystals with formation of Pt–Al alloy (2). The H₂ chemisorption is suppressed because reduced Al diminishes the pairs of adjacent Pt atoms which are necessary to adsorb hydrogen dissociatively.

Our results of H₂ and O₂ chemisorption on unsulfided Pt/Al₂O₃ catalysts (Table 2, runs I to III) showed that the SMSI behavior was not verified. In all cases, the HC

and OT values determined after low-temperature reduction at 270°C were not changed by the HTR treatment. Thus, we have to conclude that under the experimental conditions used (HTR at 500°C for 3 h; evacuation at 500°C for 3 h) neither is the Pt–Al alloy formed nor does the strongly chemisorbed H₂ remain on the metal. Although it has been suggested that the reduction of Al₂O₃ carrier with formation of Pt–Al alloy in a "platinum-rich phase" could occur at rather low temperatures (24), our results are consistent with those of Dautzenberg and Wolters (1) who needed "prolonged" pretreatment in H₂ at 500°C or "mild" pretreatment at higher temperatures (>550°C) to have a substantial decrease in H₂ chemisorption. Regarding the presence of strongly chemisorbed H₂ on the metal, our results indicate that either the strongly chemisorbed H₂ is not formed at 500°C or that the high-vacuum degassing at this temperature eliminates the stronger chemisorption of hydrogen. Graham and Wanke (25) have already suggested that evacuation at temperatures lower than 500°C may not be sufficient to remove the strongly chemisorbed hydrogen.

We will now consider the gas chemisorption results on sulfided catalysts (Table 2, runs IV to VII). After sulfidation, air oxidation, and low-temperature reduction (runs IV and V), the catalysts are sulfated. Sulfur has been removed from the metallic fraction so that the samples exhibit the same adsorption properties of the unsulfided catalysts. When HTR at 500°C was performed (run VI) a drastic decrease in H₂ uptake was verified. As mentioned above, this is the SMSI state of step ii. The oxidation treatment followed by LTR restores the normal adsorption behavior (run VII). The SMSI behavior verified through runs VI and VII can be explained indistinctly by redox reaction (2) or (3) given in the Introduction.

Most of the results reported by Kunimori *et al.* (9) were obtained with a Pt/Al₂O₃ catalyst of 5% Pt and S/Pt = 0.32. Catalysts 3,

4, and 5 used in this work had similar S/Pt ratios, ranging between 0.20 and 0.35 (run IV, Table 2). The S level of these catalysts was not changed by the consecutive oxidation/reduction treatments (runs V to VII). This fact can be explained in two ways: (i) either the H₂S produced from the partial reduction of sulfates by the HTR treatment is completely adsorbed by the surface Pt atoms so that no sulfur is eliminated from the catalysts, or (ii) the HTR treatment does not reduce the sulfate ions at low sulfur concentrations. Catalyst 2 was sulfided and reduced at 300°C and had a higher S/Pt ratio (S/Pt = 1.70). In this case the S level was diminished by the consecutive oxidation/reduction treatments of runs V and VI; moreover, the presence of H₂S eliminated from the catalyst was detected during the HTR treatment of run VI. This proves that at least for relatively high S/Pt ratios redox reaction (3) takes place.

It is interesting to note that in the SMSI state (run VI) the accessible metal fractions determined through OT were significantly higher than those determined from HC uptakes. Qualitatively, similar gas chemisorption results were obtained after sulfidation (run IV, S atoms are on the metal) and this fact could be taken as evidence that redox reaction (3) takes place (the quantitative difference between HC values of runs IV and VI would be due to different S coverages). However, if the Pt–Al alloy is formed upon applying HTR treatment, the accessible metal fractions determined by OT uptakes will also be higher than those determined from HC values. As has been pointed out (2), the presence of a Pt–Al alloy suppresses the first H₂ chemisorption more than the subsequent H₂–O₂ titration. In conclusion, the changes in HC and OT uptakes summarized in Table 2 do not allow us to discriminate between redox reactions (2) and (3) as the cause of the SMSI behavior displayed by sulfided Pt/Al₂O₃ samples with S/Pt ratios between 0.20 and 0.35.

To distinguish between these two possibilities catalyst 5 was analyzed by IR spec-

troscopy. The sample was submitted to the same treatments of runs IV to VI and the changes in the bands of SO₄²⁻ on the carrier and CO on platinum were recorded. It is relevant to consider the effect of the HTR in the sulfated sample (Fig. 1, spectra C and D). The SO₄²⁻ band at 1380 cm⁻¹ diminished, which indicates that the H₂ treatment at 500°C reduced to some extent the sulfate ions on the support. The CO adsorption caused the formation of a band at 2080 cm⁻¹ and a superimposed band which appeared at lower frequency. The shift of $\nu(\text{CO})$ from 2060 to 2080 cm⁻¹ indicates that the H₂S produced by reduction of sulfates was adsorbed by the Pt atoms. As stated in Ref. (23), the 2080-cm⁻¹ band should be attributed to the CO molecules adsorbed on the Pt atoms adjacent to the occupied S sites. The low frequency shoulder represents the CO molecules adsorbed on Pt atoms which are not modified by sulfur. The relative predominance and even the possibility to distinguish between the two CO bands depend on the sulfur amount of the metal and on the CO coverage (23). From our IR results we conclude that the HTR treatment reduced to some extent the sulfate species on the support with formation of H₂S which is adsorbed on the metal. The S blockage of the surface Pt atoms will decrease the H₂ chemisorption. In other words, redox reaction (3) takes place even for the low S/Pt ratio of catalyst 5 (S/Pt ratio = 0.23).

The TPR results give additional evidence of the reduction of the sulfate species by HTR at 500°C (Fig. 2). If no metal is present, the reduction peak of sulfates on alumina and chlorided alumina fell between 650 and 680°C. The presence of Pt gave rise to a low-temperature peak at 450–500°C which would indicate that Pt catalyzes the reduction of sulfates. Such an explanation is supported by the fact that the reduction temperature decreased when the metal loading was increased (TPR curves d to f; catalysts with similar S content). Simultaneously, the high-temperature peak corre-

sponding to the reduction of SO_4^{2-} on Al_2O_3 diminished. The catalytic action of Pt represented by the apparition of a low-temperature peak has already been noted in the case of the coke burning in Pt/ Al_2O_3 catalysts (26–28). Such a catalytic action of Pt was explained in terms of the spillover phenomenon (29): oxygen is adsorbed on Pt and, in an activated form, migrates by spillover eliminating the coke at lower temperature than that of the gaseous oxygen. A similar explanation can be proposed to account for the catalytic action of Pt in the sulfate reduction by hydrogen. The migration of activated hydrogen species will reduce the sulfate ions in the immediate surrounding of the Pt particles at a lower temperature than that corresponding to the reduction of SO_4^{2-} on the support by gaseous hydrogen.

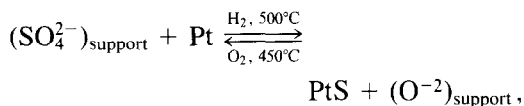
Kunimori *et al.* (9) have related the changes in H_2 chemisorption and the consumption of H_2 (or O_2) during the H_2 (or O_2) treatments (HTR at 500°C ; oxidation with O_2 at 450°C). They found a linear relation with a ratio of slopes of 2 to 1 which would indicate that a reversible redox process according to reaction (2) occurs during the pretreatments. However, Margitfalvi *et al.* (30) observed that during the HTR treatment additional hydrogen-consuming reactions occur which may modify the theoretically expected H/Pt and O/Pt ratios. They reported results concerning the influence of the chlorine content which leads to additional O_2 consumption during the oxidation treatments by the formation of species like PtCl_xO_y . These authors concluded that the linear correlation obtained by Kunimori *et al.* (9) cannot be generalized for Pt/ Al_2O_3 catalysts with different Pt loading. From our TPR results we believe that the influence of the Pt content on the H_2 or O_2 consumptions during the pretreatments is essentially related to the catalytic action of Pt in the reduction of the sulfate ions. For a given sulfate level, the amount of H_2 consumed during the HTR will increase with the surface metal concentration. In the case

of two catalysts with different S and Pt contents but the same S/Pt ratio, the amount of sulfate reduced by the HTR treatment will be greater for the catalyst having the higher Pt surface concentration. On the other hand, it is significant to note that the oxidation treatment does not necessarily transform all the S atoms adsorbed on the metal to SO_4^{2-} species. The formation of oxidized species on alumina follows a rather complex mechanism (31–34) and the amount of sulfate formed depends on the temperature, on the O_2 concentration in the oxidation mixture, on the hydroxyl content, and possibly on the Pt surface concentration. Obviously, the formation of oxidized species other than SO_4^{2-} will occur with different O_2 consumptions. The above reasons explain why a generalized linear correlation between the H_2 (or O_2) consumption during the pretreatments and the decrease (or increase) in H_2 chemisorption should not be applicable to Pt/ Al_2O_3 catalysts with different S and Pt content.

Finally, we will consider our data on reduction of sulfated samples studied by analyzing the H_2S eliminated at increasing temperatures (Fig. 3). The curves of H_2S removal from alumina and chlorided alumina samples were consistent with the H_2 consumption peaks of the TPR profiles. On the contrary, in the case of sulfated Pt/ Al_2O_3 catalysts no H_2S was detected in the range of temperature corresponding to the low-temperature peaks of the TPR profiles (450 – 500°C). This indicates that the H_2S formed at about 400°C is retained by the metal as irreversibly held sulfur. The irreversibly held sulfur is desorbed at temperatures higher than 500°C (19, 35, 36). Thus, for the catalysts with sulfur content of $\text{S/Pt}_s = 0.4$ – 0.5 (which is the irreversible sulfur range) the cycle of mild reduction/oxidation pretreatments as used in this work will not cause any S elimination from the catalysts. This fact is illustrated by the results shown in Table 2, runs IV to VII, with catalysts 3, 4, and 5. The sulfur level of these catalysts, sulfided only with irreversibly

held sulfur, was not changed by the pre-treatments.

In conclusion, our data give strong evidence that the SMSI behavior displayed by the sulfated Pt/Al₂O₃ samples used in the present work was caused by a redox reaction like



even in the case of relatively low S level (S/Pt = 0.2–0.35). Further experimental results are needed to demonstrate that redox reaction (2) can occur simultaneously with reaction (3), especially for “prolonged” HTR at 500°C.

The SMSI behavior produced by sulfur impurities has also been reported in Rh/MgO and Pt/MgO catalysts (37, 38), thereby indicating that poisoning is a cause of the SMSI behavior. In general, redox reaction (3) implies a mechanism which is similar to that proposed by several authors (39–43) as the cause of the SMSI behavior (coverage of the metal by the migration of reduced support species produced by HTR; formation in the metal surface of oxidized species which migrate back to the support during the oxidation treatment). Taking this into account, Wanke *et al.* (38) suggested that the so-called strong metal–support interaction could be renamed to “support induced metal poisoning or promotion” (SIMPP). Nevertheless, from a fundamental point of view the term SMSI represents a specific type of metal–support interaction. If SMSI is not used as a generic term, the results reported in this paper represent a simple case of poisoning, but the support does get into the act by adsorbing the oxidized poison, i.e., makes the process reversible.

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