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The Role of Catalyst Presulfurization in Some Reactions of Catalytic Reforming and Hydrogenolysis

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Three reforming catalysts Pt/Al_2O_3, $Pt–Ir/Al_2O_3$, and $Pt–Re/Al_2O_3$ have been sulfurized by H_2S. By treatment at 500°C in a H_2 atmosphere, only a part of the adsorbed sulfur is easily removed. The remaining sulfur (S_i) is localized on the metal at constant concentration irrespective of the H_2S level in the sulfurizing mixture. The obtained S_i values for each of the catalysts (Pt/Al_2O_3, $Pt–Ir/Al_2O_3$, and $Pt–Re/Al_2O_3$) give an atomic ratio $S_i/Me_{(s)}$ near 0.5. With the same sulfur coverage (S_i) Pt–Re catalysts are more deactivated than Pt and Pt–Ir catalysts. On the other hand, addition of small quantities of Ir to Pt increases sulfur resistance. Finally S_i is a selective poison since the selectivity for hydrogenation–dehydrogenation related to hydrogenolysis is enhanced considerably. Hydrogenolyses of linear hydrocarbons are the most inhibited reactions.

INTRODUCTION

Naphtha reforming catalysts are usually sulfided in order to reduce their initial hyperactivity and to increase their stability. The sulfidation process originally used in Pt/Al_2O_3 monometallic catalysts was later extended to bimetallic and multimetallic catalysts (*1–3*). In spite of the poisoning effect of the sulfur compounds on this kind of catalyst, the addition of small quantities of sulfur improves the behavior of the catalysts and favors their start-up. Different sulfur compounds are used to treat catalysts, but in all cases the catalysts are finally submitted to a treatment with hydrogen at high temperature. Under these conditions part of the deposited sulfur is quickly eliminated as hydrogen sulfide, but some residual sulfur is retained on the catalyst because of its higher resistance to the reducing atmosphere. This strong or "irreversible" sulfur (*4*) will be present in the reforming operation.

We have already shown (*5, 6*) that for Pt/Al_2O_3 catalysts the irreversible sulfur is mainly in interaction with the metal and corresponds approximately to an atomic ratio of 0.5 $S/Pt_{(s)}$. Moreover, the quantity of irreversible sulfur deposited is independent of the hydrogen sulfide concentration in the hydrogen and hydrogen sulfide mixture used to sulfide the catalyst.

Likewise, as has already been pointed out (*7, 8*), sulfur is a selective poison which modifies the intrinsic properties of the metals. Hence it can contribute to a better control of the fresh catalyst activity, reducing coking as well as metal sintering.

The modifications produced by the sulfidation on Pt/Al_2O_3 monometallic catalysts and on $Pt–Re/Al_2O_3$ and $Pt–Ir/Al_2O_3$ bimetallic catalysts are studied in this work.

EXPERIMENTAL

The supported platinum catalyst was made by impregnation of a high-purity γ-Al_2O_3 powder with an aqueous solution of chloroplatinic acid. The γ-Al_2O_3 which had a BET surface area of 200 m^2/g was obtained from the Institut Français du Pétrole. After impregnation the catalyst was dried overnight at 105°C, then calcined in

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an air stream for 5 h at 500°C, and finally reduced in flowing hydrogen for 8 h at 500°C. The Pt and Cl loadings were 0.58 and 1.2%, respectively.

The bimetallic Pt–Ir/Al_2O_3 catalyst was a commercial catalyst of 0.3% Pt and 0.03% Ir supported on the same γ-Al_2O_3 as used to prepare the Pt/Al_2O_3 catalyst. The catalyst was directly reduced for 8 h at 500°C in flowing H_2. The bimetallic Pt–Re/Al_2O_3 catalyst was a commercial catalyst which contained 0.3% Pt, 0.3% Re, and 0.68% Cl. The support was a γ-Al_2O_3 with a BET surface area of 180 m^2/g and 0.5 ml/g of pore volume. The catalyst was reduced in flowing hydrogen as previously described.

The catalysts were sulfided at 500°C for 90 min in a flow of H_2S and H_2 with H_2S/H_2 volume ratios ranging from 1 to 10% and a flow rate of 60 cm^3 min^{-1}g cat^{-1}. After sulfidation the samples were treated in flowing hydrogen for 8 h at 500°C in order to eliminate the reversible sulfur. Table 1 summarizes the different mixtures of H_2–H_2S employed to sulfide the catalysts. The sulfur and chlorine contents were determined by X-ray fluorescence.

The reaction studies were carried out at atmospheric pressure in a flow system provided with a fixed-bed reactor. A measured flow of reactant liquid was delivered to the reactor with a motor-driven syringe. The reactant was vaporized when entering the preheating section of the reactor, and prior to passage down through the catalyst bed, it was brought to reaction temperature in a mixture with hydrogen. The gaseous reaction effluent was analyzed by gas chromatography with a flame ionization detector. Conversion was always less than 20%. The initial activity of the catalysts was determined by extrapolating the deactivation curve to zero.

The activity tests were made under the following conditions: Hydrogenation of benzene: $T = 100°C$; $P_c = 0.05$ atm (2 cm^3/h); $P_{H_2} = 0.95$ atm. Dehydrogenation of cyclohexane: $T = 300°C$; $P_c = 0.023$ atm (3.75 cm^3/h); $P_{H_2} = 0.977$ atm. Hydrogenolysis of cyclopentane: $T = 300°C$; $P_c = 0.1$ atm (2 cm^3/h); $P_{H_2} = 0.9$ atm. Hydrogenolysis of ethane: $T = 420°C$; $P_c = 0.1$ atm; $P_{H_2} = 0.9$ atm; flux = 0.20 mol/h.

Hydrogen was purified by passage through a Deoxo unit and then through molecular sieves at room temperature; the nitrogen was passed over copper filings at 380°C to remove oxygen and then through molecular sieves at room temperature. The ethane N 35 (Air Liquide) was used without further purification. Benzene (Prolabo R.P.) and cyclohexane (Prolabo R.P.) were redistilled and stored over a Pt/Al_2O_3 catalyst containing 1% Pt. Cyclopentane (Fluka) was treated with Zeolite 5 A and activated alumina.

Gravimetric experiments for determination of metallic dispersion were made in a Setaram MTB10-8 electrobalance. 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 obtainable. Gas ad-

TABLE 1

Catalysts and Sulfidation Conditions

Catalyst	Percentage H_2S in mixture H_2–H_2S	Amount of S on catalyst[a] (ppm)	Atom S_i[b] / Atom $Me_{(s)}$
Pt/Al_2O_3	0	40	—
Pt/Al_2O_3-A	12	290	0.42
Pt/Al_2O_3-B	6	300	0.44
Pt/Al_2O_3-C	1	290	0.42
Pt/Al_2O_3-P	4	270	0.39
Pt–Re/Al_2O_3	0	70	—
Pt–Re/Al_2O_3-D	10	320	0.46
Pt–Re/Al_2O_3-E	1	310	0.44
Pt–Re/Al_2O_3-Q	4	310	0.44
Pt–Ir/Al_2O_3	0	45	—
Pt–Ir/Al_2O_3-K	4	290	0.45

[a] Determined after treatment in flowing hydrogen at 500°C for 8 h.

[b] Atom $Me_{(s)}$ was calculated from the metal dispersion of nonsulfided catalysts; see Table 3. Atom S_i was obtained from the third column as the difference in the amounts of S on sulfided and nonsulfided catalysts.

sorption isotherms extrapolated to zero pressure were used as a measure of the metal surface area.

RESULTS

I. MEASUREMENT OF ACCESSIBLE METAL FRACTION OF SULFIDED AND NONSULFIDED CATALYSTS

I.1. Pt/Al_2O_3 Catalysts

The accessible metal fraction of sulfided and nonsulfided Pt/Al_2O_3 catalysts was determined by hydrogen and oxygen chemisorptions and by titration of preadsorbed oxygen (hydrogen) by hydrogen (oxygen), using volumetric and gravimetric methods at room temperature. In the former case, the strongly chemisorbed hydrogen calculated by the double-isotherm method (*9*) was used. Stoichiometric ratios H/Pt = O/Pt = 1 for the hydrogen and oxygen chemisorptions and those proposed by Benson and Boudart (*10*) for titration reactions were employed. Hydrogen chemisorption was also performed at 500°C. In this case, the gas was introduced at room temperature and heated at 500°C for 10 min and then the pressure measurement was performed at room temperature.

As metallic dispersion measurement involves an evacuation treatment at high temperature following hydrogen reduction, some experiments to investigate the influence of the above procedure over the adsorbed sulfur were performed. Thus, successive cycles of titration of preadsorbed hydrogen by oxygen (OT) were measured by gravimetry to evaluate the influence of the time of evacuation. Data are collected in Table 2. It is shown that neither the outgassing treatment nor successive (OT) cycles seem to modify the adsorbed sulfur ((OC) = oxygen chemisorption, (HC) = hydrogen chemisorption, (HT) = titration by hydrogen of preadsorbed oxygen, (OT) = titration by oxygen of preadsorbed hydrogen).

Table 3 presents the results obtained by volumetry. Average values obtained for Pt/Al_2O_3 catalyst give a metallic dispersion of 62%. Two characteristic features concerning the sulfided samples have to be emphasized:

TABLE 2

Accessible Metal Fractions Measurement—Gravimetric Method

Catalyst	Evacuation at 500°C (h)	O_2 uptake (μmol/g cat)			
		$(OT)_1$	$(OT)_2$	$(OT)_3$	$(OT)_4$
Pt/Al_2O_3	8	14.4	15.0	14.4	—
Pt/Al_2O_3-A	1	11.2	11.0	11.6	11.6
Pt/Al_2O_3-A	8	12.2	11.6	11.6	12.2
Pt/Al_2O_3-B	1	11.2	11.9	11.2	—
Pt/Al_2O_3-B	8	11.2	11.0	11.9	11.9
Pt/Al_2O_3-C	8	11.9	10.0	11.6	—
Pt-Ir/Al_2O_3	8	12.2	13.1	13.1	—
Pt-Ir/Al_2O_3K	8	9.7	10.0	9.7	—
Pt-Re/Al_2O_3	8	9.1	8.8	8.8	8.8

(i) A similar accessible metal fraction was obtained from the (OC), (HT), and (OT) values but it sensibly differs from those calculated from the (HC) value. The accessible metal fraction calculated from hydrogen chemisorption (HC) is the one that correlates better with the catalytic activity of the hydrogenation of benzene, a structure-insensitive reaction on platinum (*6*). Furthermore, it may be noted that the Pt/Al_2O_3-A, Pt/Al_2O_3-B, and Pt/Al_2O_3-C catalysts, sulfided with different H_2S concentrations, present similar accessible metal fractions.

(ii) For the sulfided samples, a dramatic change in the hydrogen uptake is produced when the adsorption temperature is varied. This probably indicates that hydrogen may go through the sulfur surface layer and chemisorb on the metal. This assumption is supported by the fact that the accessible metal fraction of sulfided Pt/Al_2O_3 catalyst calculated from the $(HC)_{500}$ value is approximately equal to that of the nonsulfided one ($(HC)_{500}$ = hydrogen chemisorption at 500°C, $(OT)_{500}$ = titration by oxygen at 25°C of preadsorbed hydrogen at 500°C, and $(HT)_{500}$ = titration by hydrogen at 500°C of preadsorbed oxygen at 25°C). In addition, it

TABLE 3

Accessible Metal Fractions Measurement—Volumetric Method

Catalyst	$(HC)_{25}$		$(OC)_{25}$		$(HT)_{25}$		$(OT)_{25}$		$(HC)_{500}$		$(OT)_{500}$		$(HT)_{500}$	
	1[a]	2[b]	1	2	1	2	1	2	1	2	1	2	1	2
Pt/Al_2O_3	10.6	59	11.1	62	34.4	64	16.9	63	11.1	62	—	—	—	—
Pt/Al_2O_3-A	3.8	21	8.9	50	24.7	46	12.9	48	10.7	60	—	—	—	—
Pt/Al_2O_3-B	3.6	20	—	—	25.8	48	12.3	45	10.6	59	—	—	—	—
Pt/Al_2O_3-C	3.1	17	8.6	48	24.7	46	12.3	46	—	—	—	—	—	—
$Pt–Ir/Al_2O_3$	8.7	103	—	—	24.6	97	12.8	101	—	—	—	—	—	—
$Pt–Ir/Al_2O_3$-K	2.7	32	—	—	21.6	85	9.0	71	—	—	—	—	—	—
$Pt–Re/Al_2O_3$	1.42	9	8.3	53	15.6	40	8.6	45	8.8	56	14.2	50	30.7	65
$Pt–Re/Al_2O_3$-E	0.95	6	—	—	7.4	19	4.8	25	8.0	51	8.5	30	25.4	54

[a] 1 = Gas uptake (μmol/g cat).

[b] 2 = Accessible metal fraction (%).

appears that this high-temperature adsorbed H_2 is not removed by evacuation at room temperature since after hydrogen adsorption at room temperature and at 500°C similar amounts of reversible H_2 were found. This agrees with the results reported by Charcosset *et al.* (*11*) using the temperature-programmed desorption (TPD) method to study hydrogen desorption in sulfided Pt/Al_2O_3 catalysts, which showed that H_2 desorption spectra were displaced to higher temperatures when the temperature of previous H_2 adsorption was increased.

1.2. Pt–Ir Catalysts

In order to calculate the accessible metal fraction, hydrogen and oxygen adsorption stoichiometries on Ir were considered to be identical to those used for Pt, as has been proposed by other authors (*12, 13*). The results are shown in Tables 2 and 3. The metallic dispersion of nonsulfided Pt–Ir catalyst is complete as the obtained value is 100%.

When considering sulfided Pt–Ir catalysts it was observed that the successive (OT) cycles do not produce any catalyst regeneration by sulfur desorption. Moreover, it was proved that the value of the accessible metal fraction calculated from (HC) is sensibly different from the values obtained from (OT) and (HT), just as with sulfided Pt/Al_2O_3 catalyst. The results of the catalytic activity in benzene hydrogenation (Table 4) show again a better correlation with the accessible metal fraction calculated from (HC).

1.3. Pt–Re Catalysts

The determination of the accessible metal fraction of Pt–Re catalyst is more difficult than those for the Pt and Pt–Ir cases. Rhenium is a metal easily oxidizable and the Re/Al_2O_3 catalyst can be reoxidized during the outgassing treatment at 500°C. The succession of titration cycles (HT), (OT) and the direct chemisorption (HC) and (OC) will consequently be disturbed by this property. Nevertheless, Pereira (*14*) and Barbier *et al.* (*15*) have indicated that the dispersion of Pt–Re catalyst can be obtained by direct chemisorption of oxygen at room temperature or hydrogen at 500°C, or by titration by O_2 at room temperature of the H_2 adsorbed at 500°C. In order to obtain the metal dispersion of our catalysts, gravimetric and volumetric methods were employed.

1.3.a. Volumetric method. The adsorption reactions used were those described previously (*15*). Considering the number of surface Pt atoms as m and the number of surface Re atoms as n, the surface reactions are:

—Direct adsorption of hydrogen at 25°C—$(HC)_{25}$

$$m\text{Pt} + n\text{Re} + m/2\ \text{H}_2 \rightarrow m\text{PtH} + n\text{Re}. \quad (1)$$

—Titration of the adsorbed H_2 at 25°C by O_2—$(OT)_{25}$

$$m\text{PtH} + n\text{Re} + \left(\frac{3m + 2n}{4}\right) \text{O}_2 \rightarrow m\text{PtO} + n\text{ReO} + m/2\ \text{H}_2\text{O}. \quad (2)$$

—Titration of the adsorbed O_2 at 25°C by H_2—$(HT)_{25}$

$$m\text{PtO} + n\text{ReO} + (3m + 2n)/2\ \text{H}_2 \rightarrow m\text{PtH} + n\text{Re} + (m + n)\text{H}_2\text{O}. \quad (3)$$

—Direct adsorption of O_2—$(OC)_{25}$

$$m\text{Pt} + n\text{Re} + (m + n)/2\ \text{O}_2 \rightarrow m\text{PtO} + n\text{ReO}. \quad (4)$$

—Direct adsorption of H_2 at 500°C—$(HC)_{500}$

$$m\text{Pt} + n\text{Re} + (m + n)/2\ \text{H}_2 \rightarrow m\text{PtH} + n\text{ReH}. \quad (5)$$

—Titration at 25°C of the adsorbed H_2 at 500°C—$(OT)_{500}$

$$m\text{PtH} + n\text{ReH} + \tfrac{3}{4}(m + n)\text{O}_2 \rightarrow m\text{PtO} + n\text{ReO} + (m + n)/2\ \text{H}_2\text{O}. \quad (6)$$

—Titration at 500°C of the adsorbed O_2—$(HT)_{500}$

$$m\text{PtO} + n\text{ReO} + \tfrac{3}{2}(m + n)\text{H}_2 \rightarrow m\text{PtH} + n\text{ReH} + (m + n)\text{H}_2\text{O}. \quad (7)$$

When the gas adsorption stoichiometry on both metals is different (e.g., $(OT)_{25}$, $(HT)_{25}$) the metallic dispersion is derived assuming that the surface and the bulk metal concentrations are similar, as has been stated (*16*). Results are shown in Table 3.

According to Eq. (1) the hydrogen chemisorption at room temperature $(HC)_{25}$ would have to be selective on Pt. Nevertheless, and in coincidence with what was observed by other authors (*5*, *17*), the quantity of H_2 consumed is less than the expected amount considering that the surface and bulk concentrations of the metals are the same. In consequence, the $(OT)_{25}$ and $(HT)_{25}$ values

TABLE 4

Catalytic Activities of Sulfided and Nonsulfided Pt/Al_2O_3, $Pt\text{–}Re/Al_2O_3$, and $Pt\text{–}Ir/Al_2O_3$ Catalysts

Catalyst	Specific activity[a] (mol/h mol metal) × 10^{-2}				Turnover number[a] (h^{-1})			
	a	b	c	d	a	b	c	d
Pt/Al_2O_3	13.7	150	2.54	3.9	2200	25×10^3	400	700
Pt/Al_2O_3-A	4.3	92	0.088	0.014	2150	46×10^3	44	7.1
Pt/Al_2O_3-B	5.1	78	0.105	0.014	2500	39×10^3	53	7.1
Pt/Al_2O_3-C	4.7	100	0.103	0.016	2300	52×10^3	52	8.1
$Pt\text{–}Re/Al_2O_3$	13.3	133	1.52	20.6	2400	25×10^3	280	3,700
$Pt\text{–}Re/Al_2O_3$-D	1.1	65	0.032	0.057	—	—	—	—
$Pt\text{–}Re/Al_2O_3$-E	1.5	53	0.024	0.051	—	—	—	—
$Pt\text{–}Ir/Al_2O_3$	23.0	312	7.6	99.0	2300	32×10^3	760	10,000
$Pt\text{–}Ir/Al_2O_3$	7.8	204	0.6	1.4	2400	63×10^3	190	420

[a] a = Hydrogenation of benzene, $T = 100°C$. b = Dehydrogenation of cyclohexane, $T = 300°C$. c = Hydrogenolysis of cyclopentane, $T = 300°C$. d = Hydrogenolysis of ethane, $T = 420°C$.

will lead to metal dispersion results lower than the real ones.

Moreover, it is confirmed that the metallic dispersion cannot be obtained from $(HT)_{500}$ due to an excess of H_2 consumption registered under these conditions (*14, 15*). It is therefore concluded that the metallic dispersion of our Pt–Re catalyst is 53%, an average of the (OC), $(HC)_{500}$, and $(OT)_{500}$ values.

With regard to sulfided Pt–Re catalysts it is necessary to recall that only the value of $(HC)_{25}$ leads to the truly accessible metallic fraction of the sulfided Pt/Al_2O_3 catalysts. Taking into account that H_2 chemisorption cannot be applied to calculate the metallic dispersion of Pt–Re catalysts, it must be concluded that it is not possible to determine by chemisorption or by titration with H_2 or O_2 the number of accessible metal atoms in a sulfided $Pt–Re/Al_2O_3$ catalyst.

Likewise, the catalytic properties of Pt–Re catalysts are not a linear combination of the properties of each metal. In particular, for the hydrogenation of benzene, there is a synergetic effect that proves that the catalyst activity does not depend only on the metallic area (*18*). In consequence, it is also not possible to use the benzene hydrogenation activity to calculate the nonpoisoned metallic area of sulfided Pt–Re catalysts.

Nevertheless, the results of the different cycles (HC), (HT), (OT), $(HC)_{500}$, and $(HT)_{500}$ obtained for the sulfided Pt–Re catalyst are shown in Table 3.

I.3.b. Gravimetric method. The comparison of successive cycles $(OT)_{25}$ allows us to judge the interaction of both constituents of the Pt–Re catalysts (*16, 19*). When the $(OT)_2$ value is comparable with the $(OT)_1$ value we are facing a characteristic alloy phase, while when the $(OT)_2$ value is lower than the $(OT)_1$ value it shows the presence of isolated Re particles. As may be seen from Table 2, the $(OT)_1$, $(OT)_2$, $(OT)_3$, and $(OT)_4$ values were remarkably similar. We may therefore expect a close interaction between Re and Pt.

Finally, considering the obtained metal dispersion values for the nonsulfided catalysts, the atomic ratio $S_i/Me_{(s)}$ can be calculated. Table 1 shows the values obtained, which are alike and close to 0.5.

II. CATALYTIC ACTIVITY

Catalytic activities of sulfided and nonsulfided Pt/Al_2O_3, $Pt–Re/Al_2O_3$, and $Pt–Ir/Al_2O_3$ catalysts were measured for hydrogenation of benzene, dehydrogenation of cyclohexane, hydrogenolysis of cyclopentane, and hydrogenolysis of ethane. The results are summarized in Table 4. Strongly chemisorbed hydrogen data ($(HC)_{25}$, Table 3) were used to calculate the turnover number of sulfided Pt and Pt–Ir samples. It can be pointed out that:

—Pt/Al_2O_3 (A, B, and C samples) sulfided with different quantities of H_2S present similar catalytic activities.

—On the other hand, sulfidation produced higher deactivation on $Pt–Re/Al_2O_3$ catalysts than on Pt/Al_2O_3 and $Pt–Ir/Al_2O_3$ catalysts. Thus, for a similar sulfur coverage (Table 1) the catalytic activity of benzene hydrogenation for Pt–Re diminishes by a factor of 10 (defined as the ratio: specific rate on nonsulfided catalysts/specific rate on sulfided catalysts), whereas for Pt and Pt–Ir a factor of 3 is found.

—Under the conditions studied, *n*-pentane was the only product obtained when cyclopentane hydrogenolysis was performed on Pt/Al_2O_3 catalysts. However, when performing the reaction on Pt–Re and Pt–Ir bimetallic catalysts, secondary reactions occurred leading to lighter hydrocarbons. Nevertheless, the ratio (% pentane produced)/(% cyclopentane converted) was always greater than 0.90. The catalytic activity data reported in Table 4 were calculated considering the overall rate of cyclopentane conversion. Two features concerning the catalytic activity results have to be emphasized: (i) sulfur toxicity was strongly increased for this reaction, and (ii) Pt–Re catalysts are the most deactivated whereas addition of small quantities of Ir to Pt seems to increase sulfur resistance. Catalytic activity was diminished by factors of 25, 50, and 13 for Pt, Pt–Re, and Pt–Ir samples, respectively.

—Finally, the most inhibited reaction was ethane hydrogenolysis. As previously, it may be noted that Pt–Re catalysts were the most deactivated (diminution factor of 400) and Pt–Ir catalysts have the highest sulfur resistance (diminution factor of 75).

DISCUSSION

In previous work (*5*, *6*) performed on sulfided Pt/Al_2O_3 catalysts, it has been pointed out that by treatment at 500°C in a H_2 atmosphere only a part of the adsorbed sulfur is easily removed. It was found that the remaining sulfur is localized on the metal in constant concentration irrespective of the H_2S level in the sulfurizing mixture. In the same way in Tables 3 and 4 it is shown that the accessible metal fraction and the catalytic activities of the sulfided Pt/Al_2O_3 samples are constant despite the varying H_2S concentration. Pt–Re and Pt–Ir bimetallic catalysts present a similar behavior.

The stability of the irreversibly adsorbed sulfur to H_2 treatment at high temperature suggests a strong S–metal bonding. Surface studies using low-energy electron diffraction (LEED) (*20*) show that the nearest-neighbor metal–sulfur bond distances are less than those for the stable bulk metal sulfides. This indicates that the sulfur adsorbed on the surface is probably bonded more strongly than that in the bulk metal sulfide. Fischer and Kelemen (*21*) have proposed a covalent bonding of sulfur to Pt and in any case, ionically bound sulfur on the surface seems to be improbable. A LEED and Auger electron spectroscopy (AES) study was performed by Heegeman *et al.* (*22*) to investigate surface structures of sulfur on the (100) and (111) faces of Pt. Two distinct adsorption states on each surface were found, referred to as α and β layers. β layers, characterized by a lower degree of order, were rapidly desorbed in the temperature range around 300–400°C. The well-ordered α layers were stable to heat treatment up to a limit temperature of 600°C.

The obtained S_i values for each of the catalysts investigated give an atomic ratio $S_i/Me_{(s)}$ near 0.5. A similar stoichiometry has been reported in a number of studies made on single-crystal planes of various metals (*23–25*). This irreversible sulfur is present in the start-up of reforming industrial processes.

Table 4 shows that with the same coverage the Pt–Re samples are more deactivated than the Pt–Ir and Pt catalysts. On the other hand, addition of small quantities of Ir to Pt increases sulfur resistance, especially in reactions like hydrogenolysis which occur at high temperatures.

The catalytic activity of all the reactions studied was lowered by sulfidation (Table 4). Nevertheless, the selectivity for hydrogenation–dehydrogenation related to hydrogenolysis is enhanced considerably. Ethane hydrogenolysis is the most inhibited reaction. Now, hydrogenolysis of linear hydrocarbons is an undesirable reaction in the catalytic reforming process, since it reduces isomerization and leads to light products with hydrogen consumption. In other words, sulfur is a selective poison that in small concentrations seems to improve the selectivity. This fact probably explains why sulfidation is employed in industrial reforming catalysts.

The selective poisoning has been explained considering the surface heterogeneity (*26*). In this way some reactions are structure insensitive and proceed with the same rate per unit surface area of the metal (e.g., benzene hydrogenation). On the other hand, structure-sensitive reactions are produced only on a fraction of the metallic surface area and this result can be explained by assuming that these reactions are preferably produced on some special sites (e.g., hydrogenolysis of cyclopentane and ethane). In the same way, chemisorption of a poison may be a structure-sensitive or -insensitive reaction. The poisoning produced will be selective if the poison is adsorbed on particular metal surface atoms. For this reason, the catalytic activity of reactions occurring on these sites is strongly diminished. From our results it can be inferred that sulfur is preferentially adsorbed on hydrogenolysis sites producing a selective poisoning of the catalysts.

In the case of Pt/alumina-supported catalysts, the catalytic activity for hydrogenolysis of cyclopentane and ethane increases with the crystallite size (*28, 29*). Irreversible sulfur adsorption occurring on large platinum particles is in good agreement with the greater sulfur resistance observed for the small particles (*30*). Finally, it has been reported (*27*) that the coke formation and hydrogenolysis reactions take place on the same metallic reactive sites. This observation agrees with the greater stability observed in the sulfided reforming catalysts.

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