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Sulfurization of Pt/Al_2O_3–Cl Catalysts

VI. Sulfur–Platinum Interaction Studied by Infrared Spectroscopy

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Sulfur–platinum interaction was studied by ir spectroscopy of the coadsorbed CO, competitive hydrogenation reactions, and chemisorption of O_2, CO, and H_2. Pt/Al_2O_3 catalysts of different metal loadings and mean particle size were used. Infrared spectra for variable coverages of sulfur and CO were obtained. The predeposited S on Pt caused an upward shift of ν(CO) from 2068 to 2083 cm^{-1}; a superimposed band that shifted to the lower frequencies for decreasing CO coverages was detected. The $K_{T/B}$ values ($K_{T/B}$, ratio of the adsorption equilibrium constant) for the competitive hydrogenation of benzene and toluene were determined. It was found that the $K_{T/B}$ ratio increases from 4.2 for unsulfided samples to 6.0 for sulfided samples. On the other hand, the irreversibly held sulfur on the metal increased the ratio of the reversibly adsorbed H_2 to the total adsorbed H_2. These results are discussed considering electronic, geometric, and surface heterogeneity effects. A "localized" modification of the metal by the electron-acceptor properties of sulfur is advanced as a possible explanation.

INTRODUCTION

The sulfidation of naphtha-reforming catalysts is usually performed in order to favor the start-up of the industrial reforming units. The addition of small amounts of sulfur selectively diminishes the initial hydrogenolysis hyperactivity avoiding undesirable exothermic reactions, like demethylation. Although some manufacturers prefer to incorporate sulfur in the preparation of the catalyst, sulfidation is generally achieved during the start-up of the industrial unit. In all cases the hydrogen catalyst treatment at high temperature eliminates part of the deposited sulfur; the residual sulfur is retained on the catalyst because of its higher resistance to the reducing atmosphere. This strong or "irreversible" sulfur will be present in the reforming operation.

As platinum is the basic metal component of this kind of catalysts, we have studied the sulfidation phenomenon on monometallic Pt/Al_2O_3 catalysts (*1–4*). In this paper, the sulfur–platinum interaction is studied by ir spectroscopy. The H_2S adsorption on platinum is difficult to evaluate on Pt/Al_2O_3 catalyst by infrared transmission spectroscopy. In fact, the transparency limit of the alumina wafer is about 1000 cm^{-1} and so, the S–Pt interaction is not directly detected by transmission. Furthermore, the S–H groups produce weak absorption peaks that are not detected for small sulfur concentrations. In order to obtain information on this subject, we investigated the ir spectroscopy of adsorbed CO on sulfided Pt/Al_2O_3 catalysts. As it has been reported (*5*), the frequency shift of the CO vibration can be used to predict the nature of the bond between the adsorbed species and the metal.

The chemisorptions of oxygen, hydrogen, and carbon monoxide, and the competitive hydrogenation of benzene and toluene on unsulfided and sulfided Pt/Al_2O_3 samples were also studied. The competitive hydrogenation of benzene and toluene has been used as a suitable method to study the modifications of the electronic structure of platinum induced by environment effects (*6*).

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EXPERIMENTAL

The catalysts were prepared as previously described (*7*). A high-purity Al_2O_3 powder was impregnated with a solution of chloroplatinic acid and HCl as competitor. The support was a commercial γ-Al_2O_3 (Cyanamid Ketjen CK-300) of 180 $m^2 g^{-1}$ BET specific area and 0.49 $cm^3 g^{-1}$ pore volume. After impregnation, the samples were dried 12 h at 393 K and heated in an air stream to 773 K. Then, the chlorine content was regulated using a gaseous mixture of HCl, water and air. Finally, the samples were purged with N_2 and reduced in flowing hydrogen for 8 h at 773 K.

Two catalysts, A and B, of 2.75 and 0.93% Pt, respectively, were prepared to perform the ir experiments. In order to increase the mean Pt particle size, catalyst A was treated in air at 863 K for 30 min (sample A-I) and at 873 K for 40 min (sample A-II); catalyst B was treated at 873 K for 2 h (sample B-I). The final Cl content of the samples ranged between 0.8 and 0.9% Cl. The catalysts C (0.53% Pt) and D (0.40% Pt) were prepared to perform the activity tests.

The samples were sulfided at 773 K and atmospheric pressure in flow of H_2S/H_2 mixture with 0.1% H_2S. After sulfidation the catalysts were treated in flowing hydrogen at 773 K for 8 h in order to eliminate the reversible sulfur. The irreversible sulfur content was determined by chemical analysis; in all cases atomic ratios of $S_i/Pt_{(s)} = 0.4$–0.5 were obtained, where $Pt_{(s)}$ corresponds to the exposed or surface platinum atoms.

The accessible metal fractions of sulfided and unsulfided Pt/Al_2O_3 catalysts were determined by hydrogen, oxygen, and carbon monoxide chemisorption. In the former case, the strongly chemisorbed hydrogen calculated by the double-isotherm method was used. The volumetric adsorption experiments were carried out in a conventional glass vacuum apparatus in which a final dynamic vacuum of at least 10^{-4} Torr was attainable.

The sample wafers for infrared study were formed by pressing approximately 50 mg of the catalyst powder at a pressure of around 5 ton/cm^2. The disks were transferred to an all-glass infrared cell where pretreatment of the sample was able to be performed *in situ* in static or flowing gases at high temperature. The CaF_2 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 H_2 at 773 K for 3 h followed by prolonged degassing at the same temperature. Spectra were always recorded at room temperature.

The competitive hydrogenation reactions of benzene and toluene were carried out at atmospheric pressure in a flow system provided with a fixed-bed reactor. Rate measurements were carried out at 323 K under constant H_2 pressure (0.95 atm).

RESULTS

1. Gas Adsorption

Table 1 summarizes the results of gas uptake on sulfided and unsulfided catalysts. The accessible metal fractions were calculated through chemisorption of hydrogen (HC), oxygen (OC), and carbon monoxide (CO). Stoichiometric ratios Pt/H = Pt/O = 1 and Pt/CO = 1.15 were employed. The metallic dispersions obtained from chemisorption of different gases were similar for unsulfided samples. In the case of sulfided catalysts the accessible metal fractions calculated from H_2 chemisorption were significantly lower than those obtained from O_2 and CO chemisorption.

The $(HC)_r/(HC)_T$ ratios (reversible chemisorbed H_2/total chemisorbed H_2) were calculated. The reversible chemisorbed H_2 was obtained from the double-isotherm method (*8*); it is the quantity of H_2 eliminated after 2 h of evacuation at room temperature. Table 1 shows that the $(HC)_r/(HC)_T$ ratio was not changed by the loading and the mean particle size of the metal. However, the sulfur deposition on the

TABLE 1

Gas Uptake on Sulfided and Unsulfided Catalysts

Sample	% Pt	(HC)		(OC)		(CO)		$(HC)_r/(HC)_T$
		1[a]	2[b]	1	2	1	2	
A	2.75	47.2	67	44.4	63	73.6	60	0.39
A-I	2.75	24.6	35	24.0	34	40.5	33	0.42
A-II	2.75	21.1	30	20.4	29	36.8	30	0.40
B	0.93	15.5	65	14.7	62	24.0	58	0.38
B-I	0.93	11.4	48	9.8	41	16.6	40	0.45
C	0.53	8.8	65	9.1	67	15.8	67	0.42
D	0.40	7.7	75	7.6	74	12.8	72	0.40
A(S)[c]	2.75	15.5	22	30.3	43	51.5	42	0.62
A-I(S)[c]	2.75	6.3	9	13.4	19	27.0	22	0.67
A-II(S)[c]	2.75	5.6	8	12.0	17	22.1	18	0.62
B(S)[c]	0.93	4.8	20	10.0	42	17.4	42	0.60
C(S)[c]	0.53	3.1	23	6.0	45	10.8	47	0.64
D(S)[c]	0.40	2.6	25	4.8	47	8.9	50	0.64

[a] Gas uptake (μmol/g cat).

[b] Accessible metal fraction (%).

[c] Sulfided catalysts with only irreversibly held sulfur.

metal increased the $(HC)_r/(HC)_T$ ratio from approximately 0.41 to 0.63.

II. Infrared Spectroscopy Results

IIa. CO adsorption, coverage, and Pt particle size. After pretreatment, 30–50 Torr of CO was introduced into the ir cell during 20 min at room temperature; then the samples were evacuated for 20 min. As it has been stated by many authors, the CO adsorption on Pt gives two bands attributed to linear (2060–2075 cm^{-1}) and bridge forms (1840–1870 cm^{-1}). In our experiments the band at 1870 cm^{-1} was very weak after evacuation and in some cases it was not detected.

The shift of the CO band with decreasing coverage was studied on sample A. The amount of CO on the metal was diminished by degassing at increasing temperatures. The elimination of CO shifted the frequency band from 2070 to 2050 cm^{-1} after degassing at 523 K. This downward shift of ν(CO) with decreasing coverage has been explained by the dipole–dipole coupling effect (*9, 10*) and by an electronic effect (*5, 11*).

The effect of the Pt particle size on the position of the CO band was studied by comparing the ir spectra obtained for the samples A (average accessible metal fraction, $D = 63\%$) and A-II ($D = 30\%$), and B ($D = 62\%$) and B-I ($D = 43\%$). A slight increase of the ν(CO) of approximately 5 cm^{-1} was found for particles of a larger size.

IIb. Irreversible sulfur and CO adsorption. Sulfided samples with only irreversible held sulfur were pretreated as mentioned above. The CO spectra obtained for the samples A and A(S) are shown in Fig. 1 (spectra I and II). The effect of preadsorbed sulfur on the ir spectrum of coadsorbed CO was manifested in two ways: (i) decrease in intensity as a consequence of the Pt atoms poisoning, (ii) change of the band position. The addition of sulfur to the Pt/Al$_2$O$_3$ catalyst caused a 15-cm^{-1} shift from 2068 to 2083 cm^{-1}. Similar frequency shifts were obtained for the sulfided samples with larger particle sizes.

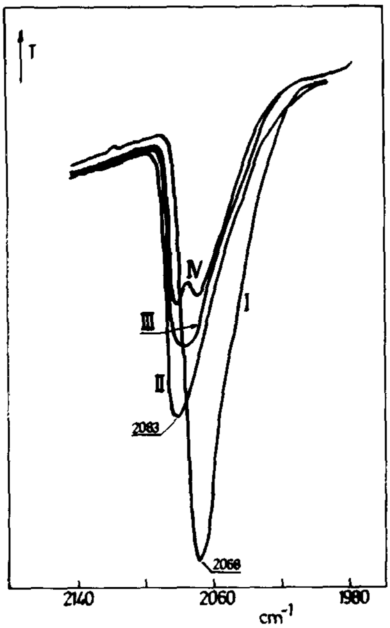

FIG. 1. Infrared spectra of CO adsorbed on catalyst A and A(S). Sulfided catalyst with only irreversible held sulfur. (I) Sample A. P_{CO} = 30 Torr and evacuated 20 min. (II) Sample A(S). P_{CO} = 30 Torr and evacuated 20 min. (III) After (II) and following evacuation for 3 h. (IV) After (III) and following evacuation for 8 h.

IIc. Irreversible sulfur and variable CO coverage. After the adsorption of CO on sample A(S), the CO coverage was diminished by prolonged evacuation at room temperature (Fig. 1, spectra III and IV). The 3-h vacuum treatment diminishes the intensity of the CO peak; the broader shape of this band suggested that it would be a combination of two bands. So, a further degassing for 8 h was performed (spectrum IV). A new peak was detected that shifted to the lower frequencies whereas the position of the original peak at 2083 cm^{-1} was not changed.

IId. Variable coverage of CO and sulfur. To obtain more information on the two peaks detected in the case of fixed sulfur concentration and variable CO coverage, some additional experiments were performed. The sulfur coverage was changed starting from the total poisoning of the metal surface. Sample A was sulfided *in situ* at room temperature. After pretreatment, 30 Torr of H_2S was admitted and then the ir cell was evacuated 20 min. When CO was added to the S-poisoned platinum surface no bands appeared in the region 2200–1800 cm^{-1} indicating a complete blockage of the surface by sulfur (Fig. 2, spectrum I). After partial removal of sulfur by heating in flowing H_2 at 503 K, the addition of CO produced a peak at 2083 cm^{-1} (Fig. 2, spectrum II); subsequent degassing for 3 h diminished the intensity and a shoulder appeared at lower frequencies (Fig. 2, spectrum III). Spectra qualitatively comparable were obtained when the sample was heated at 633 K to eliminate more sulfur on the catalyst (Fig. 2, spectra IV and V).

The spectra presented in Figs. 1 and 2 demonstrate that the CO adsorption on sulfided Pt/Al_2O_3 catalysts causes the formation of two bands: a band at 2083 cm^{-1} and

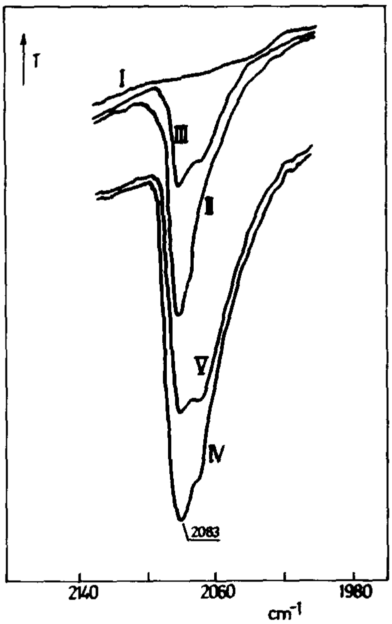

FIG. 2. Infrared spectra of CO adsorbed at room temperature on Pt/Al_2O_3 with variable coverages of sulfur and CO. Sample A. (I) P_{H_2S} = 30 Torr and evacuated 20 min; CO = 30 Torr and evacuated 20 min. (II) After (I) and following reduction in flowing H_2 at 503 K for 15 min. P_{CO} = 30 Torr and evacuated 20 min. (III) After (II) and following evacuation for 3 h. (IV) After (III) and following reduction in flowing H_2 at 633 K for 15 min. P_{CO} = 30 Torr and evacuated 20 min. (V) After (IV) and following evacuation for 3 h.

a superimposed band that shifts toward lower frequencies when CO coverage is diminished. The relative predominance and even the possibility to distinguish between them depends on the sulfur amount on the metal and the CO coverage. It must be taken into account that in our experiments the sulfur concentration corresponds at least to an atomic ratio $S/Pt_{(s)} = 0.4–0.5$, i.e., the amount of irreversible sulfur.

III. Competitive Hydrogenation of Benzene and Toluene

The competitive hydrogenation reactions have been used to study the modifications on the reactivity and selectivity induced by the effect of the additives or the support (*6, 12, 13*). These modifications have been explained by an electronic effect considering a competitive adsorption of the reactants on the same sites of the metal surface.

To obtain more insight into the interaction irreversible sulfur–platinum, we have studied the competitive hydrogenation of benzene and toluene using the samples C, C(S), D, and D(S) (Table 1). From the experimental data the $K_{T/B}$ values can be determined; $K_{T/B}$ is the ratio of the adsorption equilibrium constants of toluene and benzene. Assuming a zero reaction order with respect to the reactants, a simplified method can be applied (*6*). The $K_{T/B}$ values are determined from the slopes of the straight lines obtained when r^0_B/r_B is plot as a function of P_T/P_B; r^0_B and r_B are the rates of benzene hydrogenation without toluene and with toluene, respectively; P_T and P_B are the partial reactants pressures.

The data are represented in Fig. 3. The $K_{T/B}$ value increased from 4.2 for unsulfided catalysts C and D to 6.0 for sulfided catalysts C(S) and D(S).

DISCUSSION

The shift of ν(CO) has been widely employed to study the effect of additive or the support on metal-supported catalysts. The explanation for this shift concerns both electronic and geometric factors and a discussion of their relative importance has already been put forward (*14*).

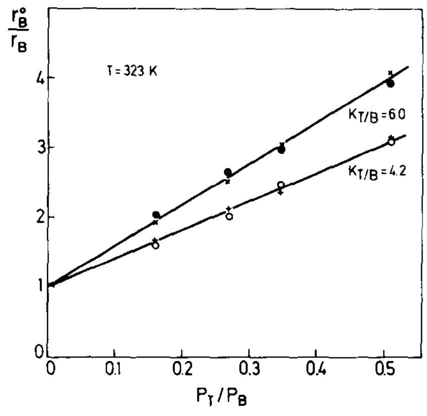

FIG. 3. Simplified method of $K_{T/B}$ determination. Unsulfided catalysts: +, sample C; ○, sample D, sulfided catalysts: ×, sample C(S); ●, sample D(S).

However, and in order to better understand our results, let us consider some general features. We will first consider the case of an electron-donor additive. The electronic effect predicts a decrease of vibration frequency. The CO bond is weakened because the donor increases the back donation of electrons from the metal to the antibonding 2π-orbitals of adsorbed CO increasing the force constant of the metal–carbon bond. The same qualitatively shift is obtained when a dilution or geometric effect is considered. The downward shift is explained considering the dependence of the CO–CO coupling with the mutual distance of the CO molecules adsorbed on the surface. As the additive increases the average mutual distance between CO molecules adsorbed on Pt, the dipole–dipole coupling is reduced and so, the frequency decreases.

A third factor has to be considered when experimental results are analyzed: the frequency shift dependence with the coverage. The CO band shifts toward the lower frequencies when coverage is diminished. A coadsorbed molecule reduces the available surface metal atoms and as a result the CO saturation diminishes. The extent of this effect depends on the amount of the coadsorbed molecule on the metal.

The three above effects could act simultaneously causing the same qualitative downward shift to the ν(CO) when an electron-donor additive is coadsorbed. In order to separate electronic effects from the geometric ones, Ponec *et al.* (*15, 16*) have extensively used the isotopic dilution method in which the dipole–dipole coupling effect is eliminated by diluting ^{12}CO by ^{13}CO.

Our results show that the ν(CO) is *increased* by the predeposited sulfur on the platinum (Fig. 1). This effect is easily explained from an electronic point of view if we consider that sulfur acts as an electron-acceptor molecule, reducing back-donation from the metal. Thus, sulfur weakens the CO–metal bond. This is in good agreement with the results obtained by thermodesorption techniques by Bonzel and Ku (*17*). On the contrary, it is clear that an upward shift cannot be attributed to a simple diluting effect of preadsorbed sulfur in the CO layer as has been analyzed above. Besides, the increase of ν(CO) reported for other coadsorbed electron-acceptor molecules such as oxygen (*5, 18*) and chlorine (*5*) seems to indicate a rather general phenomenon.

In the case of oxygen, an alternative explanation considering a geometric effect has been reported (*15*). Oxygen is known to cause a compression of the CO layer (*19*) which would enhanced the dipole–dipole coupling that increases ν(CO). A detailed study of the coadsorption of CO and oxygen on supported Pt by infrared and pulse microreactor techniques has been recently performed by Sárkány *et al.* (*20*). Their results give strong evidence that the blue shift of CO on oxydized Pt is due to a compression of CO adlayers induced by the preadsorbed oxygen. Such an explanation cannot be excluded from our results as a reason for the blue shift. However, the fact that the CO frequency at 2083 cm^{-1} is not changed by variable coverages of sulfur and CO is hardly explained only by this kind of geometric effect.

On the other hand, it has to be emphasized that the ν(CO) is increased in spite of the reduction of the CO saturation coverage. In fact, as it is shown in Table 1, the CO uptakes are 30% approximately diminished by the irreversible sulfur on platinum.

The superimposed band that shifts to lower frequencies upon partial removal of CO (Figs. 1 and 2) indicates two kind of sites for CO adsorption on sulfided samples. A possible explanation for this observation is that the S–Pt interaction is a "short distance" interaction (*5*). In this case, the ν(CO) is only modified by the sulfur atoms adsorbed on the adjacent or on the same platinum atoms. Further evidence for the formation of species like S–Pt–CO can be extracted from Table 1. The accessible metal fractions of the sulfided samples obtained from oxygen and carbon monoxide adsorptions were similar but higher that those calculated from hydrogen uptake. As it has been already pointed out (*1, 21*), hydrogen adsorbs only on clean Pt atoms suggesting that CO and O_2 can adsorb to some extent on the Pt atoms poisoned by sulfur. Hence, the high frequency band would be attributed to the CO molecules adsorbed on the Pt atoms adjacent to the occupied S sites.

The low frequency shoulder would represent the $\overset{\text{CO}}{\underset{\text{Pt}}{|}}$ species, i.e., the CO molecules adsorbed on Pt atoms which are not modified by sulfur. As for the CO adsorption on unsulfided samples, the ν(CO) will shift to the lower frequencies when coverage is diminished.

The electronic modification of the metal by sulfur is also supported by the results obtained for the competitive hydrogenation of toluene and benzene. The $K_{T/B}$ ratio refers to the adsorption equilibrium C_6H_6(ads) + $C_7H_{8(g)} \rightleftharpoons C_6H_{6(g)}$ + C_7H_8(ads). Toluene is a better electron donor with respect to benzene (*6*) and is therefore expected to form stronger π-bonds with platinum (*22*). If sulfur increases the electrophilic character of platinum, the toluene adsorption will be favored with respect to benzene and as a result the $K_{T/B}$ will increase. This is exactly what we obtain, as $K_{T/B}$ ratio increases from 4.2 for unsulfided samples to 6.0 for sulfided samples (Fig. 3).

Furthermore, the $(HC)_r/(HC)_T$ ratio is enhanced by the irreversible sulfur on Pt (Table 1). This is in good agreement with an electronic modification of the Pt atoms induced by the predeposited sulfur. In a previous paper related with the sulfur effect on the kinetics of cyclopentane hydrogenolysis on Pt/Al_2O_3 catalysts we have already noted that sulfur may modified the chemical bonding of coadsorbates (*23*).

Finally, an alternative explanation based on the surface heterogeneity will be considered. Although our results showed only a slight increase of the $\nu(CO)$ when the metallic dispersion was decreased, the literature reports a significant upward shift when the mean metal particle size is diminished (*24–28*). This effect has been explained considering a stronger adsorption of CO on low coordinate sites (edges, corners) with respect to the high coordinate sites (planes) (*25, 27*). The degree of π bonding CO–Pt is lower when the metal atom has the greatest coordination number (*29*). In this way a blue shift of the $\nu(CO)$ can be expected when the Pt particle size is increased. The same qualitatively effect (a blue shift of $\nu(CO)$) would be produced if sulfur acts as a selective poison (*30*) which preferentially adsorbs on smaller crystallites. However, we have found (*4*) that for the sulfur coverages here studied ($\theta(S/Pt) \geq 0.5$) the atomic ratio $S/Pt_{(s)}$ is not changed when the mean crystallize size is varied from 12 to 41 Å. A structure-sensitive sulfur adsorption at lower coverages cannot be excluded as it has been suggested (*31–33*); still, it is rather the opposite effect that has been noted, being the smaller crystallites the more sulfur-resistant.

CONCLUSION

The results of infrared spectroscopy presented here show that the irreversibly held sulfur on platinum increases the frequency of coadsorbed CO. This shift is better explained by an electronic effect considering that the electron-acceptor properties of sulfur decrease the electronic density of the metal.

The sulfur–platinum interaction would be localized and does not involve the electronic collective properties of the metal. This conclusion is supported by the results of infrared spectroscopy and gas adsorption. In fact: (1) the two bands detected when CO is adsorbed on sulfided catalysts correlate with two CO adsorption sites: CO–Pt–S, that shifts $\nu(CO)$, and CO–Pt that is not influenced by sulfur; (2) gas adsorption results indicate that CO adsorbs to some extent on the Pt atoms poisoned by sulfur.

The results of the hydrogen uptake and of the competitive hydrogenation reactions demonstrate that the strong chemical bond formed with sulfur modifies the chemical bonding of Pt with other coadsorbates.

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