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IRIDIUM SUPPORTED CATALYSTS. VARIATION OF SULFUR COVERAGE WITH THE NATURE OF THE CARRIER

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The study concerns the adsorption of H_2S, at 543 K, on iridium supported catalysts, having a high dispersion of the metallic phase and presenting different resistance to sulfur poisoning. The results show that sulfur coverage of the catalysts decreases when increases the activity of the carrier. This decrease in sulfur adsorption seems another proof that small iridium particles supported on acidic carriers are electron deficient. Finally, it appears that, in a middle temperature range, thiotolerance is linked to sulfur coverage and not to the nature of the sulfur poisoning moities.

1. Introduction

We have recently shown that the thiotolerance of iridium supported catalysts in the dehydrogenation of cyclohexane, contaminated by trace amounts of thiophene, increases when iridium is supported on an acidic support like amorphous SiO_2–Al_2O_3; on the contrary, thiotolerance decreases when iridium is supported on a basic support like MgO [1]. These results were in line with those obtained on Pt supported catalysts [2] and interpreted as being due to a modification of the electronic properties of small metal particles.

On acidic carriers, iridium particles would be electron deficient, leading to the formation of rather loose Ir–S bonds. Consequently, on acidic support, the poisoning by sulfur would be lessened. This electronic model was indirectly confirmed by two sets of experiments:

(i) the use of competitive benzene-toluene hydrogenation, showing clearly a higher toluene reactivity when iridium was deposited on SiO_2–Al_2O_3,

(ii) the use of H_2–O_2 titration, showing that adsorbed oxygen was much more reactive when adsorbed on Ir/SiO_2–Al_2O_3 than when adsorbed on Ir/MgO. In that case, the Ir–O bond, that can be compared, in a first approximation, to the Ir–S bond, was also weaker when Ir was deposited on acidic supports.

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However, we have also shown that the rate of HDS of dibenzothiophene is higher when Ir is supported on MgO than when it is supported on SiO_2–Al_2O_3, in the same temperature range as that used for thiotolerance measurements [3]. Such a different HDS behaviour of iridium catalysts could be responsible for the existence of two kinds (or more) of sulfur poisons, the undecomposed thiophene and H_2S, whose relative concentrations would depend on the type of catalyst. For example, in the case of Ir/MgO, the poisoning would be mainly due to H_2S, whereas for Ir/SiO_2–Al_2O_3, the poisoning would arise from both molecules, thiophene and H_2S, each molecule having different toxicity. Since our model for explaining thiotolerance relies on a single S poisoning species, it is important to see directly whether sulfur coverage, with one single thiocompound, depends or not on catalyst acidity. We therefore dried to measure H_2S adsorption at 543 K, temperature at which thiotolerance has been studied [1], and report here the obtained results.

2. Experimental methods

The catalysts were prepared by impregnation of MgO, Al_2O_3 and SiO_2–Al_2O_3 with an organic solution of $Ir_4(CO)_{12}$. Details on the preparation and the supports are given in [4]. Before H_2S adsorption, the reduced catalysts, previously used for H_2 and O_2 adsorption, were reactivated, *in situ*, at 773 K, under flowing H_2. The heating rate was 8 K/min.

The adsorption of H_2S was done on 0.05 g of the reactivated catalyst, located in a quartz microreactor between two quartz wool plugs. After the reactivation, the catalyst temperature was decreased to 543 K and a gas stream containing 50 ppm H_2S in H_2 was deviated on to the catalyst bed. The H_2S concentration was monitored continuously on a photoionization detector (HNU SYSTEM), equipped with a UV source of 10.2 eV. The 50 ppm H_2S mixture was obtained from a cylinder containing a $H_2 + 1100$ ppm H_2S blend (AIR LIQUIDE). This primary mixture was diluted with pure H_2. The gas flow rates were regulated with electronic mass flowmeters (BROOKS).

Figure 1 gives an example of H_2S adsorption and desorption fronts obtained with Ir/SiO_2–Al_2O_3. This figure defines the parameters designated Atot, Arev1 and Arev2. Each of these parameters includes the contribution of the dead space volume, a constant contribution in all experiments.

After setting the H_2S concentration, the reactor, isolated under pure H_2, is opened to the gas mixture; a rapid adsorption occurs and the detector signal drops to that corresponding to pure H_2. After some minutes, H_2S appears in the exit stream; it reaches its initial concentration after 30 to 50 min. This first adsorption front gives Atot. At that time, the reactor is isolated and pure H_2 is introduced in the tubings. After the detector level stabilization, the reactor is

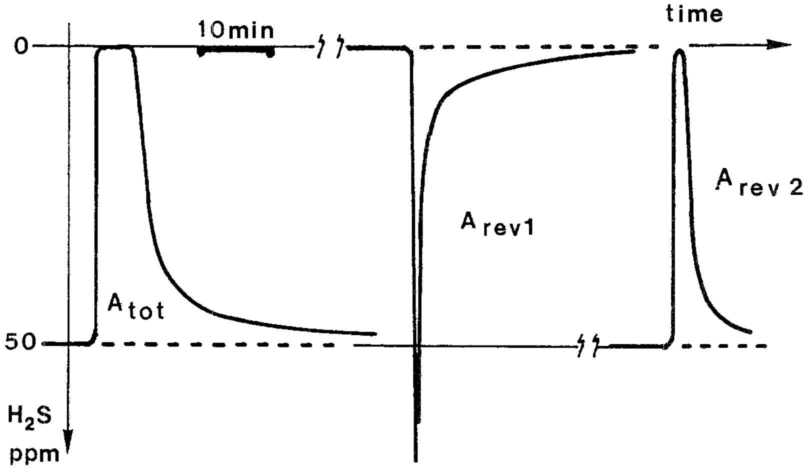

Fig. 1. H_2S adsorption desorption fronts, as followed continuously with a photoionization detector. on $Ir/SiO_2-Al_2O_3$ catalyst, at 543 K.

opened and we observe a desorption peak, the surface of which is designated Arevl. After a period of 40 to 60 min., H_2S desorption becoming negligible, the reactor is again isolated and a stream of the diluted gas mixture is established in the tubings. Finally, on opening the reactor, we observe a new adsorption peak corresponding to Arev2.

In the same equipment, H_2S adsorption at room temperature, followed by TPR up to 773 K is also possible. It is important to point out that all activations, adsorptions and TPR have been performed in situ: some preliminary results obtained by TPR of various catalysts, after H_2S poisoning and air exposure at room temperature, gave quite different data and no clear correlations with other properties.

The number of adsorbed H_2S molecules Stot, Srevl and Srev2 has been calculated after integration of the various adsorption front areas, corrected for the dead space, and compared to the number of surface or total Ir atoms, calculated respectively by irreversible chemisorbed H_2 and chemical analysis.

3. Results

Table 1 gives for the three catalysts, the total number of Ir atoms, the number of Ir* surface atoms, the values of Stot, Srevl and Srev2. It also gives the value Sirr = Stot–Srev2. Two different points are important:

(i) the values of Srevl and Srev2 are in quite fair agreement, showing that we are dealing with a true reversible phenomenon, even at 543 K;

(ii) all the adsorbed quantities decrease when the acidity of the support increases.

Table 1
Adsorbed H_2S amounts for various Ir supported catalysts

Catalyst	Ir content µmole/g cata		Adsorbed H_2S quantity µmole/g cata			
	total Ir	Ir*	Stot	Srevl	Srev2	Sirr
Ir/MgO	35.9	33.2	25.44	8.0	8.3	17.14
Ir/Al_2O_3	24.5	19.6	12.64	4.43	4.45	8.18
$Ir/SiO_2-Al_2O_3$	23.4	23.2	9.51	3.19	3.47	6.04

Figures 2 and 3 show TPR curves respectively for MgO and Ir/MgO and Al_2O_3 and Ir/Al_2O_3 after reactivation of the samples at 773 K under H_2, cooling down to room temperature and H_2S adsorption from the $H_2 + 50$ ppm H_2S mixture. The heating rate, during TPR was 8 K/min.

For MgO, we observe two reduction peaks: the first one of limited intensity, around 400 K and the second, intense, close to 630 K. For Ir/MgO, the low temperature reduction peak is strongly enhanced and the second appears near 470 K, a temperature much lower than observed for pure MgO. With Al_2O_3, three phenomenons are detected during TPR, a very low temperature peak (330 K), a small one at 480 K and a third one, ill defined at 680 K. In the case of Ir/Al_2O_3,

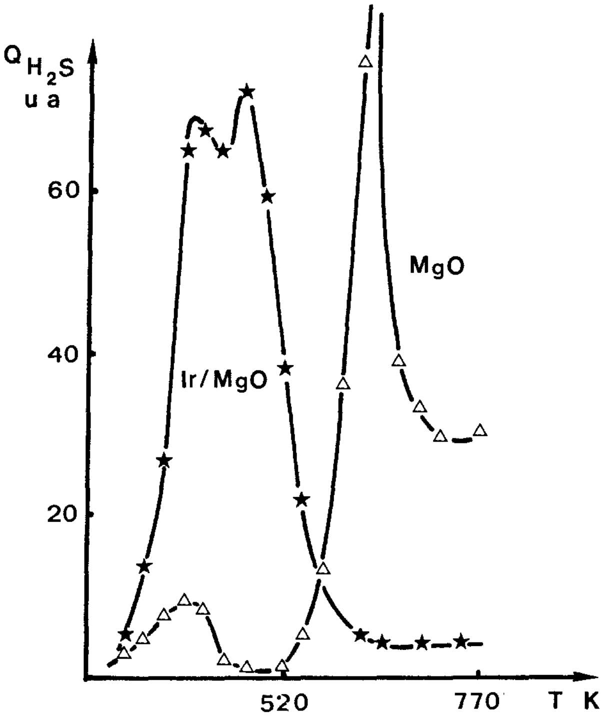

Fig. 2. H_2S release from Ir/MgO and MgO during H_2 reduction, after H_2S adsorption at room temperature from a mixture of $H_2 + 50$ ppm H_2S.

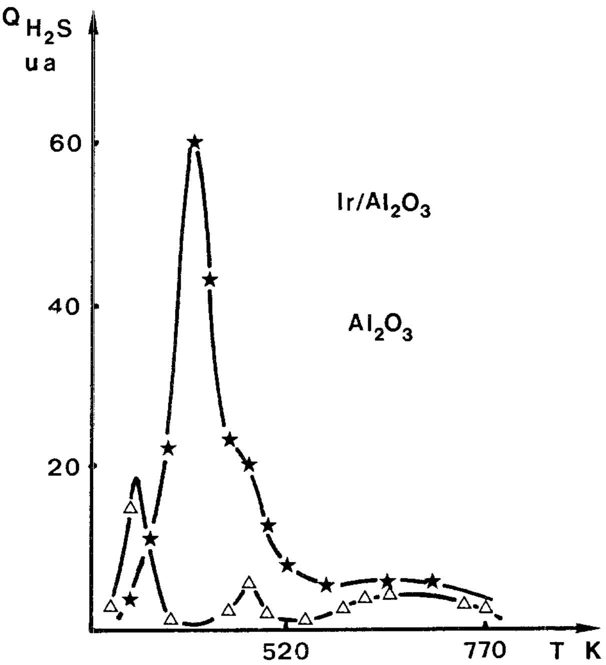

Fig. 3. H_2S release from Ir/Al_2O_3 and Al_2O_3 during H_2 reduction, after H_2S adsorption at room temperature from a mixture of H_2 +50 ppm H_2S.

the second peak appearing as a shoulder and the third one seem to remain unchanged, whereas an intense low temperature peak presents a maximum at 400 K. It is interesting to note that the total amount of H_2S extracted from Ir/MgO is much higher than the amount coming out from Ir/Al_2O_3. From these curves we can say that with Ir supported materials, the majority of H_2S extraction ended at ~ 600 K, in TPR conditions and that the presence of Ir seems to help the H_2S extraction, mainly in the case of MgO supported sample.

4. Discussion

Since H_2S can react with some supports [5–7], it is important to make sure that, when Ir is present, the adsorption of H_2S on the carrier is much lower than on the metallic phase. From TPR carried out after room adsorption, we have shown that, at 600 K, the majority of H_2S has been released; even if this temperature is 60 K higher than the temperature of the isothermal adsorption (543 K), we consider that this difference is unimportant for two reasons:

(i) in a linear temperature program, the temperature corresponding to the maximum of a phenomenon is much higher than the temperature at which the same phenomenon would occur, in an isothermal mode.

Table 2
Adsorbed S per Ir atom

Catalyst	Ir/MgO	Ir/Al_2O_3	Ir/SiO_2–Al_2O_3
Stot/Ir	0.709	0.516	0.406
Stot/Ir*	0.770	0.645	0.406
Srev2/Ir	0.231	0.181	0.148
Srev2/Ir*	0.251	0.227	0.148
Sirr/Ir	0.477	0.334	0.258
Sirr/Ir*	0.519	0.417	0.258
Srev2/Sirr	0.484	0.542	0.574

(ii) at room temperature, the adsorbed quantity is much greater than at 543 K and the desorption of large amounts always retards the maximum of the desorption peak.

For these two reasons, and the fact that the total amount of adsorbed S is in the range of the Ir quantity, we suppose that, in the present conditions, the adsorbed quantities basically refer to Ir. It is also noteworthy that, for low H_2S concentrations, on Pt/Al_2O_3, adsorption on the carrier, even at room temperature, was considered insignificant in comparison to the adsorption on the metallic phase [6]. Therefore, we will, in a first approximation, express our results as ratios of adsorbed sulfur per total and surface Ir.

The results are given in table 2, together with a ratio Srev2/Sirr. This last value gives an idea of the reactivity of adsorbed S with respect to H_2 reduction at 543 K.

From table 2, we can see that, referring either to total or to surface Ir, the total, reversible and irreversible adsorbed S decrease when increasing the acidity of the carrier. In other words, the S coverage of Ir is lower when Ir is supported on an acidic carrier than when it is supported on a basic one. The fact that the ratio Srev2/Sirr increases both when the total amount of S decreases and the acidity of the support increases, indicates also clearly that S linked to Ir/SiO_2–Al_2O_3 desorbs more easily in H_2 flow than S adsorbed on Ir/MgO. These results are in full agreement with the thiotolerance of these catalysts [1]. The origin of thiotolerance seems therefore correlated with S coverage of the metallic particles and not with the nature of the S compound. The S interaction with Ir can be schematized by the equilibrated reaction

$$\mathrm{Ir(0)} + H_2S \rightarrow \mathrm{Ir{-}S} + H_2.$$

This reaction is shifted to the right hand for a poisoned catalyst and to the left hand for a thiotolerant one. A shift to the left side would be favoured, all experimental conditions being constant, by a weaker Ir–S bond. Such a weak bond apparently exists in our Ir/SiO_2–Al_2O_3 catalyst. McCarty and Wise [8] established the isobars of H_2S adsorption on Ir/Al_2O_3 model catalysts, in a rather wide range of experimental conditions. Extrapoling their data to our conditions, we get a value Stot/Ir* = 0.66, to be compared to our experimental value 0.645. The two figures are in excellent agreement eventhough the ways of measuring S coverage and estimating the number of surface Ir* atoms are different. For various Ir/Al_2O_3 catalysts, prepared with hexachloroiridic acid [6], the values Stot/Ir* are in the range 0.86 to 1.22, the highest value being for the smaller Ir particles. The difference with the present data is important but can be, for the major part, explained by slightly different experimental conditions:

(i) the adsorption temperature was 773 K in [7] against 543 K in the present study; higher temperature could lead to more corrosive adsorption;

(ii) the metal area was estimated gravimetrically from hydrogen-oxygen titration that can give, with dispersed catalysts, values 10 to 20% lower than direct H_2 chemisorption [9];

(iii) the dispersion was calculated with the hypothesis of cubic Ir particles, with only 5 faces exposed to adsorption whereas in the present work, the Ir particles are considered fully accessible.

Finally, it is important to compare qualitatively the present adsorption results, not only with thiotolerance but also with the detoxication process obtained when, after reaching the steady state poisoning during the dehydrogenation of cyclohexane containing 3 ppm thiophene, we feed on the catalysts uncontaminated cyclohexane in the presence of H_2. Whereas Ir/MgO recovers only 5% of its original activity, Ir/Al_2O_3 gain is 25% and Ir/SiO_2–Al_2O_3 55% of their respective initial activities with pure cyclohexane. In that case too, the Ir–S bond appears weaker for Ir supported on an acidic carrier.

5. Conclusions

The H_2S adsorption on supported Ir catalysts, at 543 K, is sensitive to the nature of the support. For metallic particles with a dispersion close to 100%, the Ir coverage by S decreases when Ir is supported on amorphous SiO_2–Al_2O_3 and increases when Ir is supported on MgO. The desulfurization by dry H_2 of these Ir particles is also easier when Ir is on the acidic support. The decrease in S coverage, in standard adsorption conditions, is in complete agreement with the thiotolerance and the thiodecontamination of the same catalysts, and with the concept of electronic deficiency of small particles supported on acidic carriers.

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