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NOTES

Determination of the Metallic Surface Area of Ir/γ-Al_2O_3 Catalysts by Selective Chemisorption

The use of iridium as a catalyst has increased quickly since the first studies in the middle of the century (*1*). Iridium was usually included in systematic studies of the catalytic role of its neighbor elements in group VIII (*2*), to later become a common catalyst in different chemical processes: hydrogenation, isomerization, and hydrocarbon synthesis, sometimes alone (*3–5*) and sometimes in bimetallic catalysts (*6, 7*). The evaluation of the metallic surface area was made by chemisorption of hydrogen, but also of oxygen or carbon monoxide. An adsorbate/metal stoichiometry of one was assumed in most works, following the experience with platinum (*2*). However, iridium catalysts of high metallic dispersion were prepared years later, forcing much higher stoichiometries to be postulated (*8, 9*). Nowadays, it is common to admit a H/Ir ratio higher than one or even two (*10–12*), although papers in which a value of one is used still appear (*13, 14*). Due to these uncertainties, a precise, reliable method for the determination of the specific metallic surface area of supported iridium catalysts has not been established yet. This work tries to devise such a method, based on a systematic study of the adsorption of hydrogen and oxygen at different temperatures and pressures and taking account of the adsorption on the support. The influence of iridium particle size on the hydrogen stoichiometry and on the extent of surface oxidation is examined, and the nature of both phenomena is also discussed.

Hydrogen and oxygen (Sociedad Española del Oxígeno, Spain), 99.995% pure, were used as adsorbates. Samples of Ir/γ-Al_2O_3 of various metallic percentages were prepared by the incipient wetness impregnation method with a solution of hexachloroiridic acid (Alfa Products, Germany). γ-Al_2O_3 (Girdler T-126, BET specific surface area 149 $m^2\,g^{-1}$) was used as support, after being heated in air at 973 K for 4 h. The impregnated samples were reduced in hydrogen flow (60 $cm^3\,min^{-1}$) under the following temperature program:

$$T_{\text{room}} \xrightarrow{1\text{ h}} 373\text{ K (1 h)} \xrightarrow{1\text{ h}} 473\text{ K (2 h)} \xrightarrow{2\text{ h}} 723\text{ K (2 h)}.$$

Sintered samples were prepared from the same reduced batch. They were kept in air at room temperature for 10 min (except the 2.5%-2 sample), outgassed at the same temperature, and heated under vacuum for different times and temperatures:

Unsintered
  0.5%
  1%-1
  1%-2
  2.5%-1
Sintered

2.5%-2	790 K	18 h
2.5%-3	783 K	1 h
2.5%-4	823 K	1 h
2.5%-5	829 K	2 h

Samples are identified by the iridium percentage, followed by an order number when necessary.

Amounts adsorbed were measured in a conventional volumetric apparatus whose dead volumes had been calibrated carefully. Pressure was measured with a capacitance

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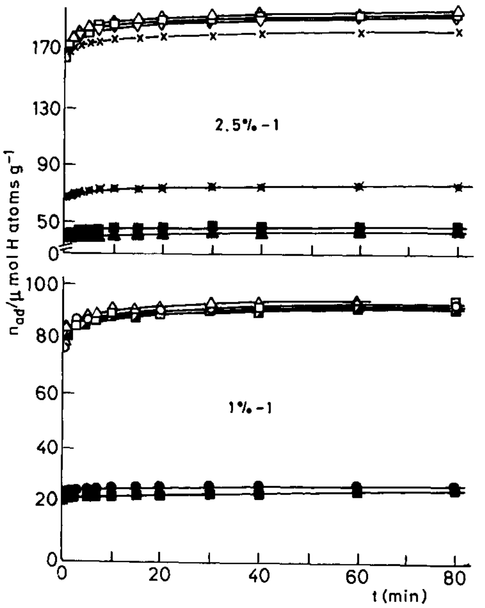

FIG. 1. Hydrogen adsorption kinetic experiments on Ir/γ-Al_2O_3 at different temperatures: (△,▽) 323 K; (□) 343 K; (○) 373 K; (×) 423 K. First (open symbols) and second (solid symbols and ×) experiments.

manometer (Baratron 310, MKS, USA). Reproducibility, measured by cumulative helium expansions, was always better than 0.2 μmol.

Once introduced into the apparatus the sample was reduced in a static hydrogen atmosphere (40 kPa), following the standard temperature program described above, although the final temperature was only 700 K. The treatment was repeated every time the sample had been in contact with oxygen. Before each experiment, the sample was outgassed overnight in a vacuum better than 1 mPa at 673 K. Previous experiments had shown this temperature to be high enough to achieve complete outgassing without producing sintering, in agreement with other authors (*4, 8, 10*).

Kinetic adsorption experiments in which the adsorption of a dose of gas was monitored as a function of time for 80 min were made. Dose sizes were chosen so as to give a final pressure of 20–25 kPa. Adsorption isotherms showed that in this range the uptake is practically independent of pressure. In many occasions, a second kinetic experiment was performed after outgassing for 15 min at the temperature of the experiment, and irreversible adsorption was calculated as the difference between the two runs. Experiments were performed at different temperatures in the range 273–423 K.

The adsorption on the support, although small (2 μmol of H/g, 6 μmol of O/g, at 323 K and 15 kPa), was taken into account. It was obtained by experiments performed on γ-Al_2O_3. Adsorption results are expressed as *net* amounts adsorbed on the metal in micromoles of atoms per gram of catalyst dried under vacuum at 700 K.

Hydrogen *isotherms* are practically independent of temperature and of pressure above 15 kPa. The results of different *kinetic adsorption experiments* are displayed in Fig. 1. Second kinetic experiments, carried out as described above, are also presented in some cases. A well-defined plateau is reached in the first kinetic experiments after about 30 min; this time interval falls to 2–3 min in the second runs, since the intermediate outgassing eliminated the weakly held

TABLE 1

Hydrogen Kinetic Adsorption Experiments on Ir/γ-Al_2O_3[a]

	273 K	298 K	323 K	343 K	373 K	423 K
0.5%[b]	60.4		65.9 66.9		66.3	
1%-1[b]			94.7	93.4 92.1	92.4	
2.5%-1[b]			198.1 194.0	195.4		184.2
2.5%-2			160.2[c]			
2.5%-3	60.3		60.7			
2.5%-4			33.0	33.6	29.2	
2.5%-5	22.0					

[a] Amount of hydrogen in μmol of atoms g-cat^{-1}. Metal content:

0.54%	1.08%	2.64%	of Ir by weight.
28.1	56.2	137.6	μmol Ir atoms g-cat^{-1}.

[b] Reproduced by permission from Ref. (*16*).

[c] From an adsorption isotherm.

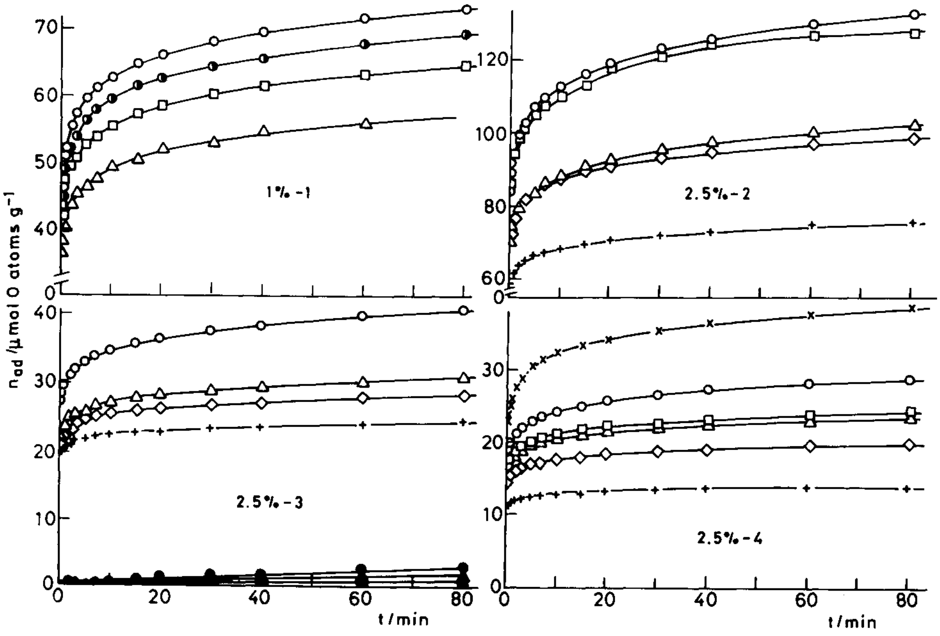

FIG. 2. Oxygen adsorption kinetic experiments on Ir/γ-Al_2O_3 at different temperatures: (+) 273 K; (◇) 298 K; (△) 323 K; (□) 343 K; (○,◑) 373 K; (×) 423 K. First (open symbols) and second (solid symbols) experiments.

species, which readsorbed almost instantaneously. Total amounts of hydrogen adsorbed on iridium after 80 min, H_{Ir}, for all the samples are given in Table 1. They are much higher than the total amount of iridium present, e.g., more than twice in the case of the 0.5% sample. Hydrogen adsorption remains approximately constant up to 343 K. A small decrease is observed at higher temperatures in most cases because of the exothermicity of the adsorption process (Table 1).

These results clearly establish that the hydrogen/iridium stoichiometry, H/Ir_{sf}, is higher than one and unknown, which prevents the calculation of the number of superficial iridium atoms. (The possibility of identifying the hydrogen adsorbed on the metal with a particular species producing a monolayer of stoichiometry $H/Ir = 1$ was tested. In this case the strong bond to the surface would make the irreversibly adsorbed amount to remain constant over a certain temperature range. However, since this amount decreases with increasing temperature this hypothesis had to be rejected.)

Oxygen *isotherms* did not reach a plateau, and the amount of oxygen taken up increases with temperature. Both facts point to the existence of an activated process running parallel to the adsorption. Figure 2 presents oxygen *kinetic adsorption experiments* for some of the samples at various temperatures. A clear increase of both the initial amount adsorbed and the final uptake is observed as the temperature is raised. Table 2 shows values of the amount taken up after 80 min, O_{Ir}, for all the samples. Oxygen consumption at 423 K is about twice as high as at 273 K. The final slopes of the oxygen uptake–time curves follow a similar trend: they are practically horizontal at 273 K and increase with temperature. These results confirm the concurrence of an activated process that runs parallel to the adsorption. It can be considered as a certain kind of superficial oxidation, the nature of which is discussed below.

TABLE 2

Oxygen Kinetic Adsorption Experiments on Ir/γ-Al_2O_3[a]

	273 K	298 K	323 K	343 K	373 K	423 K
0.5%[b] (1.1 nm)[c]	24.3	31.5	36.3	38.2	44.0	50.3
		28.4				
O_0 (Elovich)		23.6	28.5	23.5	26.5	28.2
		23.9				
1%-1 (1.2 nm)[c]			55.7	64.5	72.9	
					69.3	
O_0 (Elovich)			46.0	43.8	53.3	
					47.9	
1%-2[b] (1.4 nm)[c]	38.5	47.9	52.8	57.6	66.4	84.1
O_0 (Elovich)		34.9	37.1	38.8	43.7	50.5
2.5%-1[b] (1.6 nm)[c]			108.2	111.9	131.8	172.2
			106.3			
O_0 (Elovich)			79.2	80.6	87.9	111.2
			75.5			
2.5%-2 (1.7 nm)[c]	75.5	98.3	101.9	127.4	132.9	
O_0 (Elovich)		76.4	76.8	49.2	93.9	
2.5%-3 (5.3 nm)[c]	24.3	28.1	30.3		40.1	
O_0 (Elovich)		23.5	24.9		29.4	
2.5%-4 (8.2 nm)[c]	15.2	19.6	22.7	25.7	32.3	
	15.1	19.6	23.1	24.4	29.5	38.6
O_0 (Elovich)		16.0	16.1	19.0	24.3	
		15.4	18.6	16.3	20.8	18.3
2.5%-5 (11 nm)[c]	10.8	11.3	12.8	14.8		
	8.6					
O_0 (Elovich)			11.2	12.1		

[a] Amount of oxygen in μmol of atoms g-cat^{-1}.

[b] Reproduced by permission from Ref. (*16*).

[c] Particle size as cubes standing on a face: l_c = 0.921/dispersion. (Surface iridium Ir_{sf}, was obtained from O_0 and oxygen adsorption at 273 K.)

Figure 2 also displays results from second kinetic adsorption experiments made on the 2.5%-3 sample. There is no sudden initial uptake; oxygen consumption increased smoothly at a rate that is practically zero at 273 K and increases with increasing temperatures. Therefore, the amount measured in the second kinetic run is not due to oxygen readsorption, but to the persistence of the surface oxidation process.

The existence of surface oxidation prevents us from determining the capacity of the adsorbed oxygen monolayer and therefore from calculating the amount of superficial iridium.

A mathematical treatment was applied to the results of the kinetic oxygen experiments in an attempt to separate the amount adsorbed from the total uptake. The Elovich equation, often useful in similar cases (*15*), was effective when applied in its differential form, following a method developed in our laboratory, which is described in detail elsewhere (*16*). The last row for every sample in Table 2 displays the oxygen monolayer values, O_0, obtained in this way. They have been plotted in Fig. 3 with the maximum oxygen uptake after 80 min. The monolayer capacity thus calculated remains constant with temperature except at the highest ones, 373–423 K, and agrees quite well with the total uptake at 273 K. Only slight or no oxidation seems to take place at this temperature, as we postulated above. The

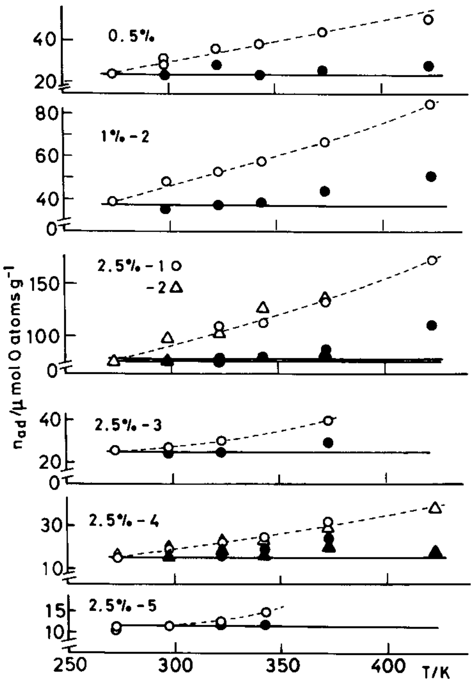

FIG. 3. Oxygen uptake on the Ir after 80 min (open symbols) and value of the oxygen monolayer obtained from the application of the Elovich differential equation (solid symbols) at different temperatures. Results for all the samples of Ir/γ-Al_2O_3.

agreement between the two values lends credence to the calculated value of the oxygen monolayer on the metal and therefore to the amount of superficial iridium.

We can conclude that two kinetic oxygen adsorption experiments at 273 K, on the suport and on the sample, render the net amount of oxygen adsorbed on the metal, and hence the amount of superficial iridium. Moreover, a quick and simple method can be formulated: two consecutive kinetic experiments on the sample at 273 K, with an intermediate outgassing at the same temperature. Since the amount adsorbed is totally irreversible on iridium and reversible on the support, the second experiment measures the adsorption on the latter only. The difference between the amounts adsorbed in the two runs yields the oxygen adsorption on the metal, without the need of a previous run on the support. This procedure can be especially useful in industrial applications.

The existence of hydrogen spillover, a common phenomenon (*17*), does not seem to be the explanation for our high H/Ir_{sf} ratios for two reasons. (i) Of the maximum final adsorption, 90% had taken place in approximately 1 min; i.e., hydrogen would have to spill over the support almost instantaneously, which runs contrary to reported results. (ii) Adsorption rates at the end of the experiments were very low and decreased with increasing temperature.

The existence of unreduced species, Ir(I), has been postulated to explain stoichiometries $H/Ir_{sf} > 1$ (*18*). However, these authors observed a decrease in oxygen adsorption, contrary to our results. On the other hand, it would be necessary to postulate in our case that all the metal was present as Ir(I).

The position of the iridium atom in which hydrogen adsorbs has also been suggested as a possible explanation. Adsorption could take place on the top or bottom rows of Ir atoms with different bond strength in each case (*19*). This proposal is directly related

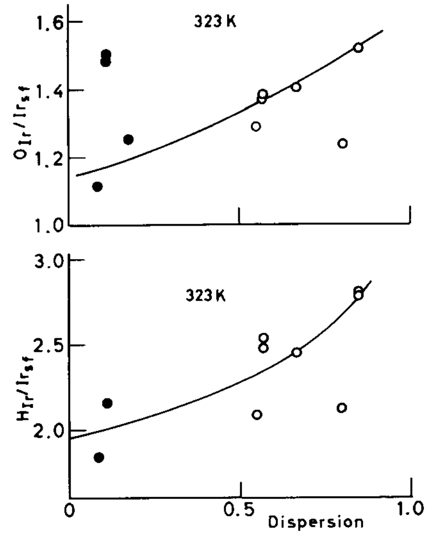

FIG. 4. Ratios of hydrogen (bottom) and oxygen (top) uptakes to superficial iridium vs dispersion degree. Unsintered (open symbols) and sintered (solid symbols) samples of Ir/γ-Al_2O_3.

to the so-called subsurface adsorption postulated some time ago (*12, 20*) and recently revived (*21, 22*), but it cannot explain that H/Ir_{sf} stoichiometries are highest for the most dispersed samples.

It seems more likely that the stoichiometry $H/Ir_{sf} > 1$ is related to crystallite size and shape and metal–support interaction. Figure 4 shows that the H/Ir_{sf} ratio increases with the degree of dispersion. Adsorption on corners and edges has been invoked to explain such a correlation (*23*), since the abundance of these adsorption sites is directly related to the metal dispersion. On the other hand, IR spectroscopy has shown that stoichiometries $CO/Ir \geq 2$ are explained by the presence of plate-like metal particles, with CO adsorbing on the iridium atoms directly bound to the support (*24, 25*). A similar idea had also been postulated for hydrogen adsorption on iridium catalysts (*8*). It is important to point out the decrease of the H/Ir_{sf} ratio produced upon sintering (Fig. 4). A change from plate-like particles existing in the most dispersed samples to cubic particles in the sintered ones can be postulated.

Surface oxidation is proposed in this paper as the process that takes place in parallel to oxygen adsorption. As a matter of fact, oxide formation in bulk iridium starts above 575 K (*26*) and is complete only above 825–900 K (*26, 27*). However, a superficial oxide with an O/Ir stoichiometry of 2 was postulated from gravimetric measurements with iridium powder at 435 K and greater (*27*). This value coincides with that obtained by us at 423 K (Table 2). On the other hand, at higher temperatures two different types of oxides, viz. on the surface or under it, were detected. Above 600 K, a nonstoichiometric oxide embedded near the surface is found by XPS and UPS; whereas at 700–800 K, an oxide bond like that in bulk IrO_2 but with an epitaxial structure was identified (*29, 30*). In our case this superficial oxide is produced in a detectable amount at a lower temperature because of the high degree of dispersion of some of the catalyst samples used. The excess of the O_{Ir}/Ir_{sf} ratio over unity in Fig. 4 shows the correlation that exists for most of the samples between the amount of surface oxide produced and the degree of dispersion.

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