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HYDROGEN–OXYGEN TITRATIONS OVER Pt–Re AND Pt–Ir/Al_2O_3 CATALYSTS IN A VACUUM MICROBALANCE*

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ABSTRACT

Hydrogen–oxygen titrations have been performed at room temperature, over 2% (Pt + Re)/γ Al_2O_3, 0.6 to 0.3% (Pt + Ir)/γ Al_2O_3 and 2% (Pt + Ir)/γ Al_2O_3 catalysts. These experiments allowed us to obtain some information concerning:

(i) the % dispersion of the metal phase (Pt + Re or Ir);

(ii) the interaction between Pt and Re or Ir (taking account of the difference in reducibility of oxygen chemisorbed either on Pt or on Re, Ir, respectively);

(iii) the surface composition of the metal phase (Pt–Re system only, from the selective chemisorption of H_2 on Pt, in appropriate circumstances).

It is concluded that a relatively homogeneous particle composition of the bimetallic phase is obtained more easily in the Pt–Re system than in that of the Pt–Ir.

INTRODUCTION

The catalytic activity of supported monometallic catalysts generally depends on the percent dispersion (%*D*) of the metallic phase. The measurement of %*D* by means of gas chemisorptions (H_2, O_2, CO) or titrations is recognized to have a very reasonable degree of accuracy, at least for Pt[1-3] and Ir[4,5]. Re has been less extensively studied but we have given some evidence that it is possible to measure %*D* (Re) provided the hydrogen titration is carried out above room temperature[3] in agreement with Kubicka's work on unsupported Re powders[6].

More recently, two metals, for example Pt and Re or Ir, have been used to produce bimetallic catalysts in order to improve their performances in reforming

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reactions. Determining the % dispersion, %D (Pt + Re or Ir), keeps the same interest as for the monometallic catalysts. Two further problems are encountered:

(1) Determining if the two metals are combined together (in the form of bimetallic clusters or of alloy particles, the terminology is not established as yet).

(2) Determining the surface composition of the metal phase, that is the % Re_S (or Ir_S)/(Pt_S + Re_S or Ir_S), where the suffix S refers to the exposed metal atoms. In a previous paper[3], we showed that:

(i) The reducibility of oxygen chemisorbed on Re is considerably enhanced, due to the formation of (Pt, Re) bimetallic particles.

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(ii) Hydrogen chemisorption at room temperature is rather specific to Pt_S. These two features allowed us to gain some insight into the interaction between Pt and Re, and into the surface composition of the (Pt + Re) phase.

EXPERIMENTAL

Apparatus

The chemisorption-titration measurements were carried out by means of a Sartorius 4433 microbalance. The vacuum equipment and the anti-contaminant device used in order to decrease the base line drift due to in situ contamination of the sample by residual gases still present in the apparatus were described in ref. 8. The electron microscope was a JEM 100 B, limit of resolution ~3.5 Å. The extraction replication method was applied, using dilute HF aqueous solution to separate the metallic particles from the Al_2O_3 support.

Catalysts

Supports. Two types of Al_2O_3 were used: (a) γ-Al_2O_3 oxide C Degussa, a powder of S ~100 $m^2\ g^{-1}$ (b) γ-Al_2O_3 GBS Rhône Progil in the form of pellets ~3–4 mm length, ϕ ~1.2 mm, S ~200 $m^2\ g^{-1}$.

Impregnation of the active elements. Aqueous solutions of H_2PtCl_6, $HReO_4$ or H_2IrCl_6, or mixed solutions of H_2PtCl_6 with $HReO_4$ or H_2IrCl_6 were used to (co-) impregnate the support. Experimental details are given in ref. 3 for the 2% (Pt + Re)/γ-Al_2O_3 catalysts, and the same procedure was applied to the 2% (Pt + Ir)/γ-Al_2O_3 catalysts. The 0.6 to 0.3% (Pt + Ir) catalysts were prepared according to example 1 in ref. 9.

Activation. (a) 2% (Pt + Re)/γ-Al_2O_3 (0 $\leq$ % Re $\leq$ 100) (% Re indicates the relative % of Re versus (Pt + Re). The standard procedure consisted in reduction under flowing hydrogen during 7 h at 500 °C.

(b) 2% (Pt + Ir)/γAl_2O_3. A first series of catalysts was submitted to the same reduction procedure as for the 2 % (Pt + Re) catalysts. A second series was calcined in air at 500 °C during 15 h, before reduction by hydrogen. These last catalysts are designated as "calcined" to specify the activation procedure.

(c) 0.6 to 0.3 % (Pt + Ir)/γ-Al_2O_3. These catalysts were calcined in air at 520 °C during 4 h only, before hydrogen reduction (16 h at 450 °C).

Procedure followed during the H_2–O_2 titrations

The sample was re-reduced in situ and outgassed at its activation temperature — 450 or 500 °C. Hydrogen was first introduced at room temperature (p ~ 100 Torr; t ~ 15 min). Several O_2–H_2 cycles were performed subsequently, as shown in Fig. 1: gas pressure was ~ 100 Torr, time of gas-solid contact ~ 15 min, evacuation ~ 15 min. HC_{tot} is the increase in weight of the sample during the H_2 chemisorption, HC_{rev} the loss in weight during evacuation and HC_{irr} the net increase in weight of the sample after evacuation.

The first oxygen titration (of irreversibly chemisorbed H) gives rise, similarly, to $OT_{1\ tot}$, $OT_{1\ rev}$, $OT_{1\ irr}$. In the following we do not take account of the reversible oxygen chemisorption which is only very slightly relevant for the present purpose. In

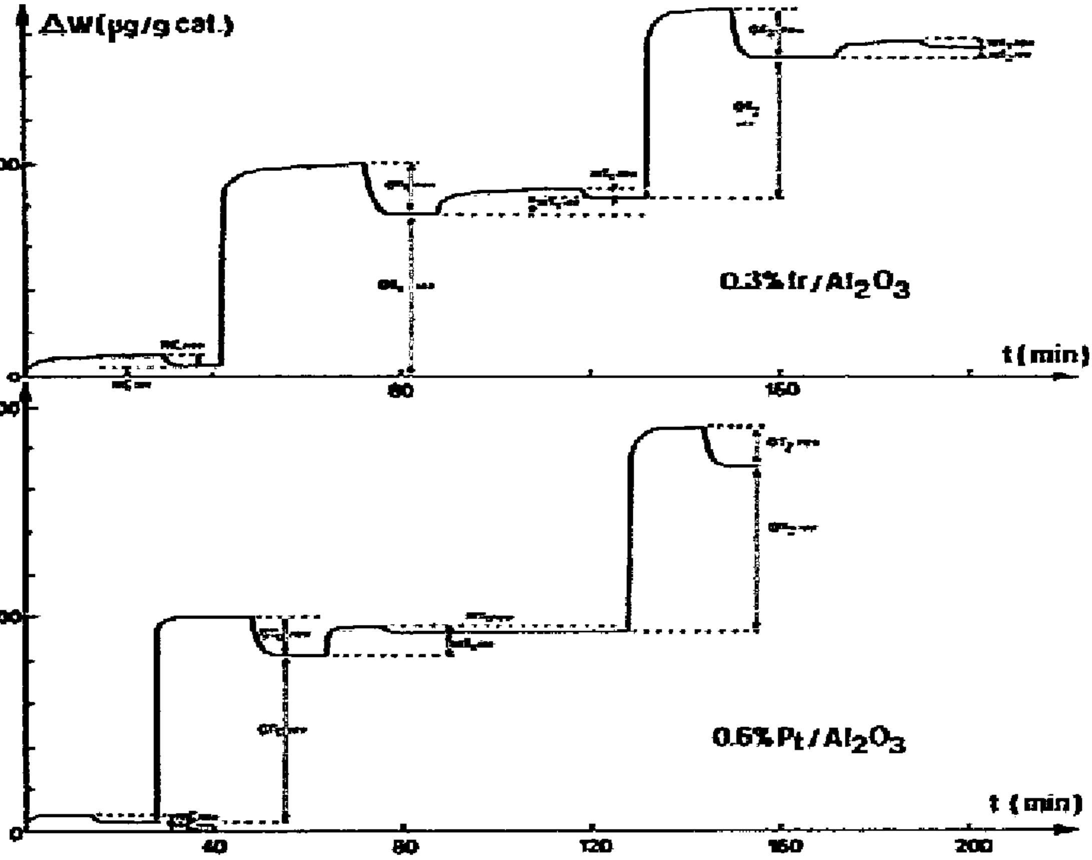

Fig. 1. Weight change of the sample as a function of the time, during H_2 chemisorption and subsequent H_2–O_2 titrations, over: 0.6 % Pt/γ-Al_2O_3 and 0.3 % Ir/γ-Al_2O_3.

TABLE 1

H_2-CHEMISORPTION AND SUBSEQUENT (O_2, H_2) TITRATIONS OVER γ-Al_2O_3 SUPPORTED Pt, Re AND Ir (Values in μg g^{-1} cat.)

Catalyst (% metal)	HC_{irr}	$OT_{1\,irr}$	$HT_{1\,irr}$	$OT_{2\,irr}$	$HT_{2\,irr}$
0.6% Pt (calcined)	20	385	55	350	
2% Pt (non-calcined)	45	1005	140	1110	145
2% Pt (calcined)	80	1570	200	1645	210
2% Re	10	1040	0	90	0
0.3% Ir (calcined)	25	355	40	325	40
2% Ir (non-calcined)	100	1860	205	1715	205
2% Ir (calcined)	25	390	55	300	30

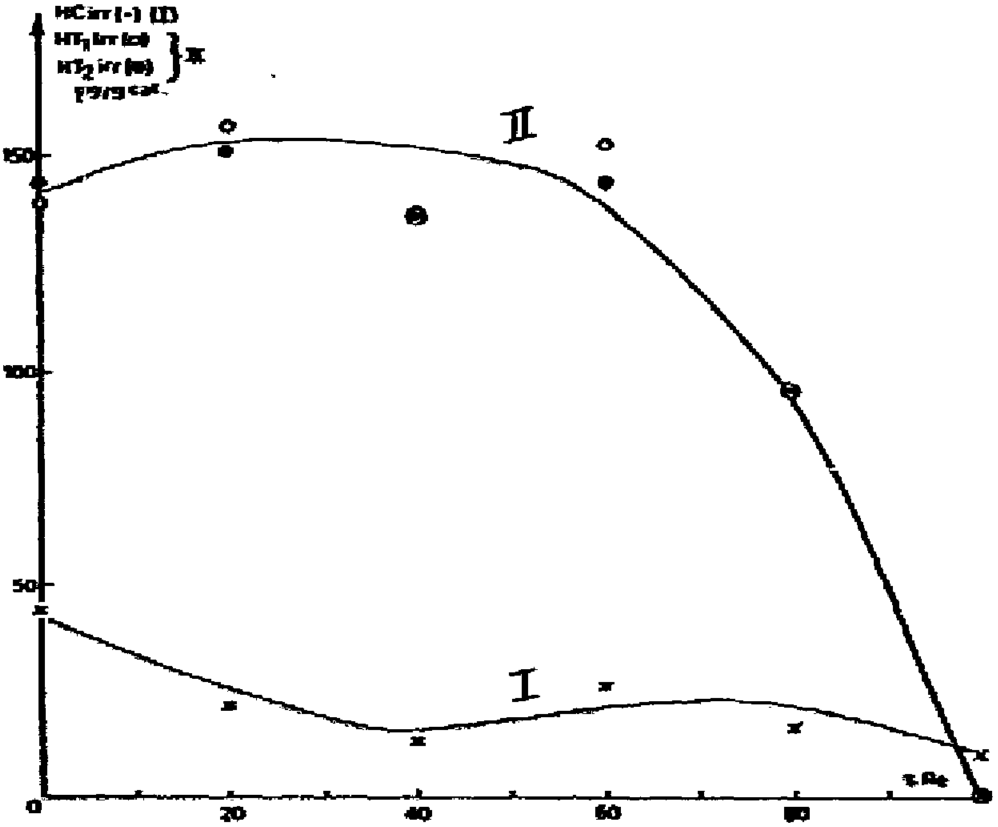

Fig. 2. 2% (Pt + Re)/γ-Al_2O_3 catalysts. Irreversibly chemisorbed H_2 (HC_{irr}, curve I), irreversibly picked up H_2 during the first ($HT_{1\,irr}$) or second ($HT_{2\,irr}$) titration (curve II), as a function of %Re.

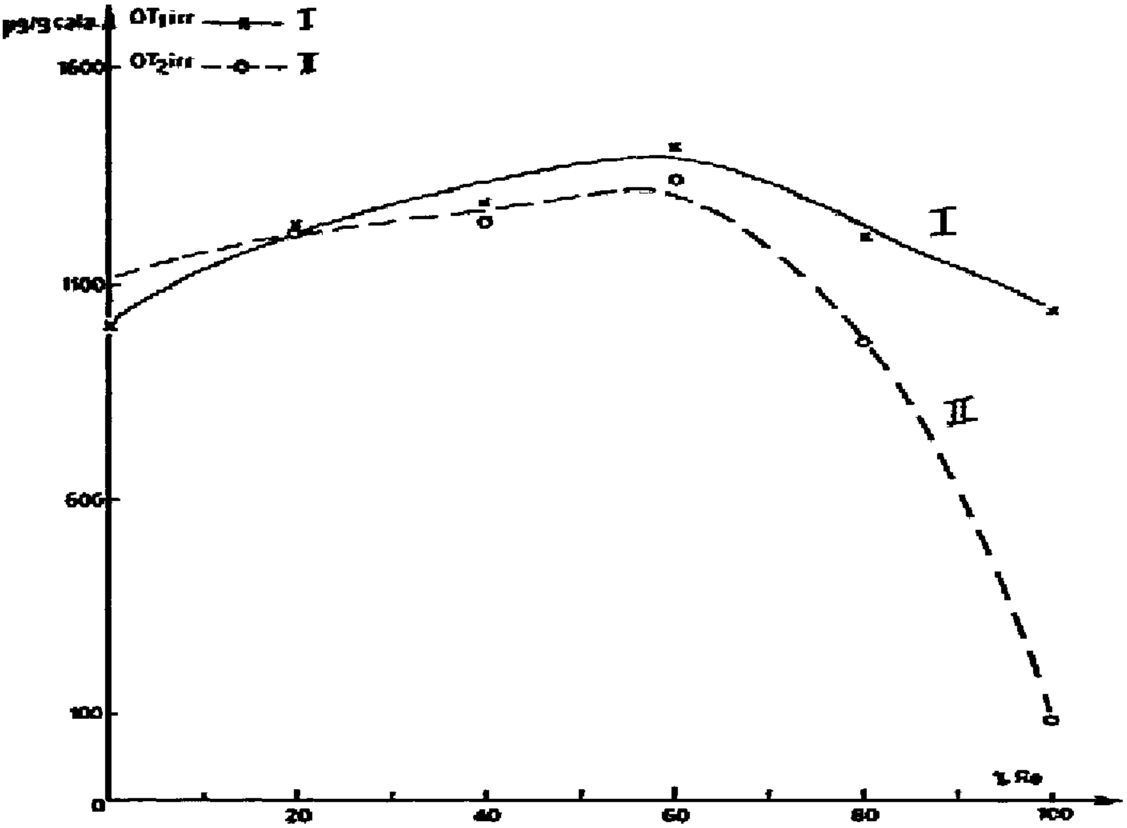

Fig. 3. 2% (Pt + Re) γ-Al_2O_3 catalysts. Irreversibly consumed O_2 during first (curve I) or second (curve II) oxygen titration, versus %Re.

all cases γ-Al_2O_3 chemisorbs H_2O strongly so that the water formed during the O_2, H_2 titrations was trapped by the support of the catalyst.

Results of the (H_2, O_2) chemisorption and titration experiments

Pt, Re, Ir monometallic catalysts. The amounts of irreversibly consumed H_2, O_2, H_2, ··· during the H_2 chemisorption step (HC_{irr}) and the subsequent O_2–H_2 titrations are reported in Table 1. In the case of Re, $HT_{1\ irr}$ appears to be negligibly small and $OT_{2\ irr}$ is less than 10% of $OT_{1\ irr}$: only a small % of oxygen chemisorbed on Re is then titrated by H_2 under the actual conditions, i.e., at room temperature.

2% (Pt + Re)/γ-Al_2O_3. The variation of HC_{irr} (curve I), $HT_{1\ irr}$, $HT_{2\ irr}$ (curve II) versus % Re is reported in Fig. 2. The accuracy of the HC_{irr} values was rather low; $HT_{1\ irr}$, $HT_{2\ irr}$ have similar values and decrease sharply as % Re increases above 60%.

On the other hand, the $OT_{1\ irr}$ values (Fig. 3, curve I) show only a rather small variation versus % Re, while the $OT_{2\ irr}$ values (Fig. 3, curve II) show the same trend as the $HT_{1\ irr}$, $HT_{2\ irr}$ values.

Figure 4 shows the variations in the amount of hydrogen reversibly chemisorbed during the hydrogen chemisorption and the first and second hydrogen titration meas-

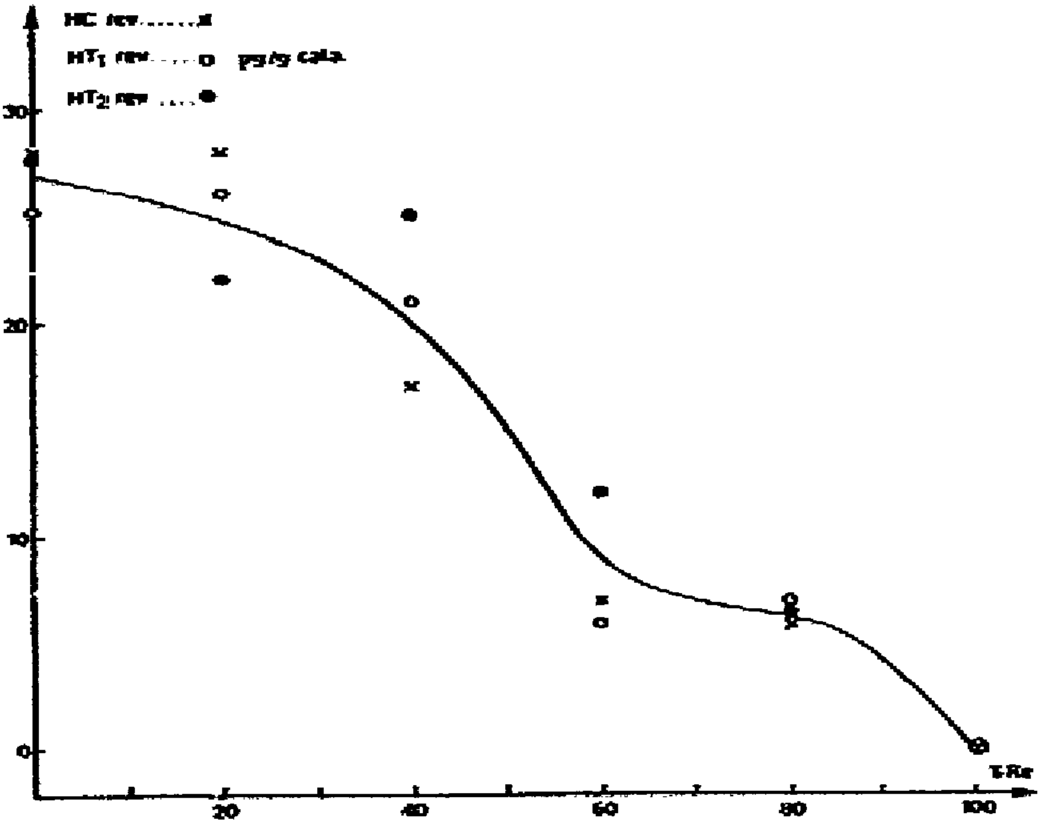

Fig. 4. 2% (Pt + Re)/γ-Al_2O_3 catalysts. Reversibly chemisorbed H_2 during H_2 chemisorption (HC_{rev}), first and second H_2 titrations ($HT_{1\ rev}$, $HT_{2\ rev}$, respectively), versus %Re.

TABLE 2

COMPARISON OF THE NORMAL AND REDISPERSED FORMS OF (Pt + Re)/γ-Al_2O_3 (% Re = 60)
(Values in μg^{-1} g)

Catalyst	HC_{rev}	HC_{irr}	$OT_{1\ irr}$	$HT_{1\ irr}$	$OT_{2\ irr}$	$(OT_{2\ irr}-OT_{1\ irr})$
Normal	25	30	1415	135	1210	205
Redispersed	20	20	1735	95	910	825

urements. There is a progressive decrease of $(HC, HT_1, HT_2)_{rev}$ as % Re increases.

Table 2 gathers the values of HC_{rev}, HC_{irr}, $OT_{1\ irr}$, $HT_{1\ irr}$, $OT_{2\ irr}$ for the routinely activated 60% Re catalyst and for the same catalyst "redispersed" according to a method described by Yao and Shelef[7]. The "redispersion" consists in oxidizing the catalyst with O_2 at 500 °C, subsequently heating in an inert gas stream or in vacuum at 500 °C, before final hydrogen reduction at 500 °C. Our experimental conditions were: O_2 (100 Torr, 4 h) evacuation (15 h), to "redisperse" the rhenium. $OT_{1\ irr}$ appears to be very significantly increased and $OT_{1\ irr}$-$OT_{2\ irr}$ even more so.

(Pt + Ir)/γ-Al_2O_3. Figure 5 reports the variations of $OT_{1\ irr}$ versus % Ir for the three series of catalysts. $OT_{1\ irr}$ does not depend very much on % Ir in the 0.6 to

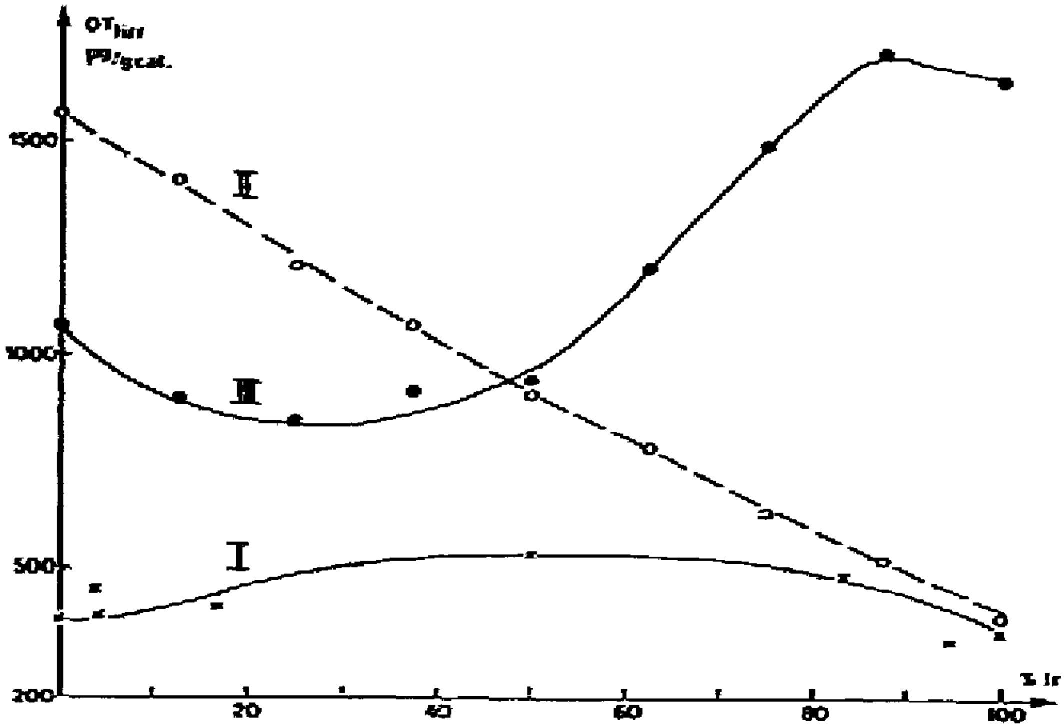

Fig. 5. (Pt + Ir)/γ-Al_2O_3 catalysts. Irreversibly consumed O_2 during the first oxygen titration ($OT_{1\,irr}$), as a function of % Ir: 0.3 to 0.6% (Pt + Ir) calcined catalysts (curve I); 2% (Pt + Ir) calcined catalysts (curve II) 2% (Pt + Ir) non-calcined catalysts (curve III).

0.3% (Pt + Ir) catalysts; it increases significantly at high % Ir, in the non-calcined 2% (Pt + Ir) catalysts; finally $OT_{1\,irr}$ decreases linearly as % Ir increases in the calcined 2% (Pt + Ir) catalysts.

The accuracy in the measurements of $(HC)_{irr}$ was rather low, as for the 2% (Pt + Re) catalysts. $HT_{1\,irr}$ was found to be approximately proportional to $OT_{1\,irr}$, hence it is not necessary to report their values. Concerning the hydrogen titrations, it is of interest to consider the kinetics of the process. It was found in fact that the hydrogen titration is more rapid over Pt/Al_2O_3 than over Ir/Al_2O_3. Therefore, the ratios of $\Delta W_{2\ or\ 4}$ (increase in weight after 2 or 4 min during the first or second hydrogen titration) and ΔW_{15} were evaluated. Figure 6 shows the variations $\Delta W_{2\ or\ 4}/\Delta W_{15}$ versus % Ir for the 0.6 to 0.3% (Pt + Ir) catalysts and Fig. 7 relates to the 2% (Pt + Ir) catalysts: a, calcined; b, non-calcined.

Electron microscopy results

The H_2-O_2 titrations do not give any information about the metallic particle size distribution, electron microscopy being the most useful tool in this respect.

The results obtained over a few typical catalysts are gathered in Table 3. The following remarks may be added:

(1) The difficulty of observation of Re in Re/γ-Al_2O_3 and (Pt + Re)/γ-Al_2O_3 has also been reported by others[10].

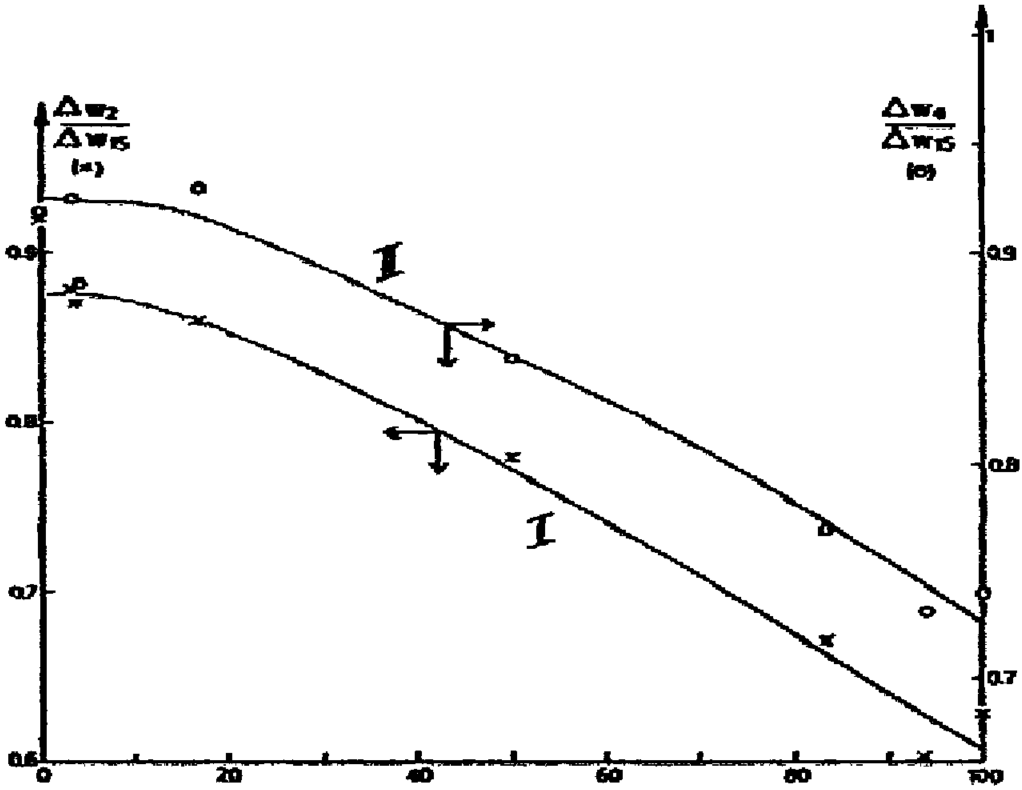

Fig. 6. First or second H_2 titration over the 0.3 to 0.6% (Pt + Ir) calcined catalysts. Increase of weight after 2 min (curve I) or 4 min (curve II) over increase of weight after 15 min, versus %Ir.

(2) A considerable difference was observed between the calcined 2% Ir catalyst and the two other Ir monometallic catalysts. Sintering of Ir as big IrO_2 particles during prolonged heating of Ir/Al_2O_3 in air has already been reported[5,11]. The 15 h calcination in air of our 2% Ir catalyst was clearly not sufficient to permit all of the Ir to be sintered, since small Ir particles were still present besides the ~200 Å large ones.

DISCUSSION

The discussion is successively focused on the % dispersion of the monometallic catalysts, the properties of the metallic phase in the Pt–Re and Pt–Ir bimetallic catalysts [%D (Pt + Re or Ir)], the surface composition and the interactions between Pt and Re or Ir).

The Pt, Re, Ir monometallic catalysts

Method of measurement of %D(Me). The calculation of %D(Pt), %D(Re), %D(Ir) from the H_2–O_2 titrations at room temperature and the comparison with electron microscopy data have been discussed in our previous papers[3-5]. Table 4 reports the stoichiometry of surface reactions which are considered to operate over Pt,

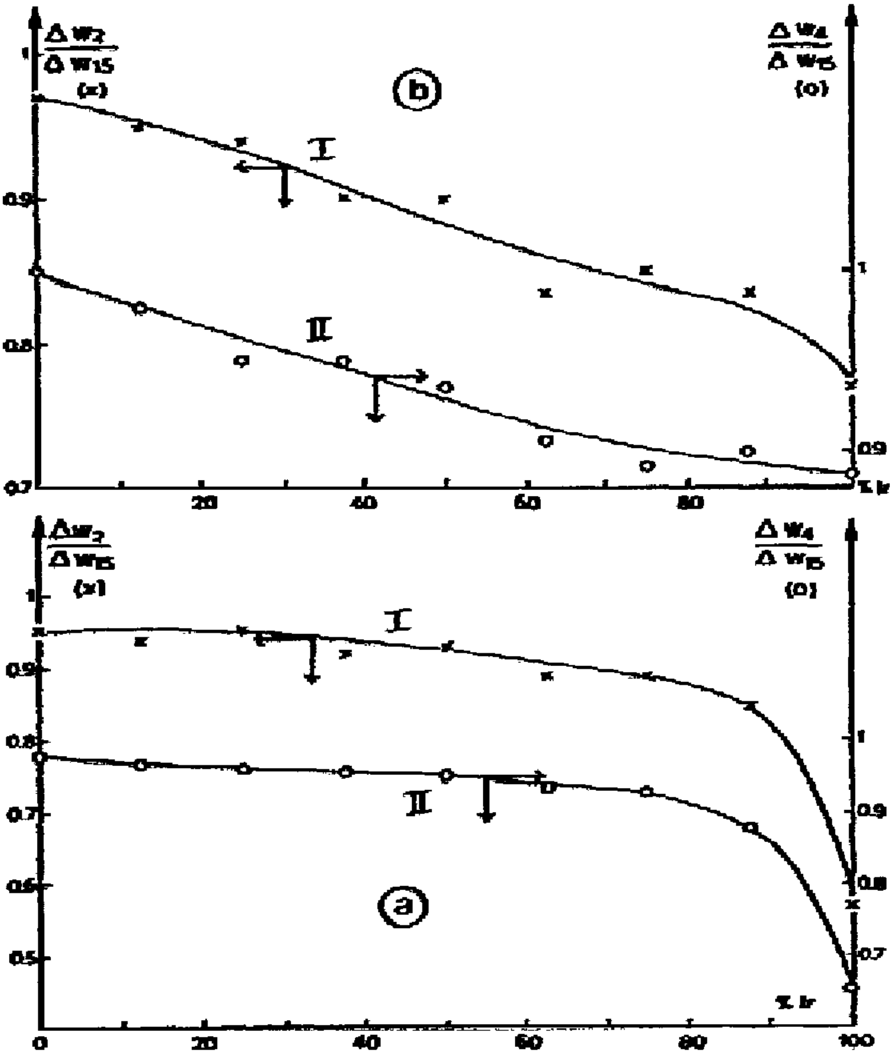

Fig. 7. First or second H_2 titration over the calcined 2% (Pt + Ir) catalysts (a) and over the non-calcined catalysts (b). Increase of weight after 2 min (curve I) or 4 min (curve II) over increase of weight after 15 min, versus % Ir.

in agreement with Barbaux et al.[1], over Ir, in agreement with Brooks[4], and over Re. With regard to Re, we consider the hydrogen coverage to be very low after the hydrogen chemisorption measurement, under our experimental conditions, and the O/Re_x ratio not very different from 1 after the $OT_{I\ irr}$ measurement.

$OT_{I\ irr}$ was then used systematically for the calculation of % *D*(Pt, Ir, Re) (Table 5). When possible, %*D* (Me) was also calculated from the electron microscopy data. The agreement between the oxygen titration and the electron microscopy data may be considered as satisfactory, except for the non-calcined 2% Ir catalyst. The Ir in this catalyst was certainly not completely reduced to Ir^0, since increasing the temperature of reduction from 500 to 700 °C gave rise to a 10% increase in $OT_{I\ irr}$, instead of the decrease that would be expected. It is worth noting the agreement be-

TABLE 3

ELECTRON MICROSCOPY DATA

Catalyst	*Mean particle size (Å)*	*Remarks, in particular as regard to the particle size distribution*
Calcined 0.6% Pt	15–20	
Calcined 2% Pt	15–20	A very small % Pt present as large particles (100–300 Å)
Non-calcined 2% Pt	~ 20	Idem, but large particles are more numerous than in calcined 2% Pt
2% Re	Undetermined	Highly dispersed Re is hardly[3,10] observed by electron microscopy
Calcined 0.3% Ir	~ 10	Smaller undetected particles are probably also present
Calcined 2% Ir	Undetermined	Large particles (~ 200 Å) plus much smaller ones
Non-calcined 2% Ir	~ 10	Narrow particle size distribution
2% (Pt + Re)	Not examined	In similar previously examined catalysts[3,4] ϕ did not vary much from 0 up to ~ 50% Re; at the highest % Re; same remark as for the 2% Re catalyst
Calcined 0.6% (Pt + Ir)		
% Ir = 16.7	10–20	Plus a few larger particles
% Ir = 50	10–15	Relatively narrow particle size distribution
Calcined 2% (Pt + Ir) % Ir = 50	Undetermined	Similar to a 50–50 mixture of the related monometallic catalysts
Non-calcined 2% (Pt + Ir) % Ir = 50	~ 30	Relatively narrow particle size distribution

TABLE 4

THE SURFACE REACTIONS DURING THE H_2 CHEMISORPTION AND SUBSEQUENT O_2–H_2 TITRATIONS OVER Pt, Ir OR Re/γ-Al_2O_3

		Stoichiometric reaction	*Increase of weight of the sample (µg/µatg Me_s)*
Pt : Ir :	: HC_{irr}	$Me_s + H \rightarrow Me_sH$	+ 1
	: $OT_{I\,irr}$	$Me_sH + 1.5\,O \rightarrow Me_sO + 0.5\,H_2O_{supp}$	+ 24[a]
	: $HT_{I\,irr}$	$Me_sO + 3\,H \rightarrow Me_sH + H_2O_{supp}$	+ 3[a]
Re :	: HC_{irr}	θ_H very low	≈ 0
	: $OT_{I\,irr}$	$Me_s + 1\,O \rightarrow Me_sO$	+ 16

[a] The evolved water is assumed to be quantitatively trapped by the catalyst support.

tween the oxygen titration and the electron microscopy data for the 0.3% Ir catalyst which was found to be extremely well dispersed; this suggests that only little deviation if any from the stoichiometry of 1 O per Ir_s takes place as %D (Ir) increases up to very high values. It should be recalled that a change in the stoichiometry from 1 O per Pt_s to 1 O per $2Pt_s$ is currently admitted, as %D (Pt) increases to very high values[12,13].

TABLE 5

% D (Me) IN THE Pt, Ir, RESPECTIVELY/γ-Al_2O_3 MONOMETALLIC CATALYSTS

Catalyst	*%D (Me) from $OT_{1,irr}$*	*%D (Me) from electron microscopy*
Calcined 0.6% Pt	52	~ 60
Calcined 2% Pt	64	~ 60
Non-calcined 2% Pt	43	~ 50
2% Re	60	Undetermined
Calcined 0.3% Ir	95	~ 98
Calcined 2% Ir	15	Undetermined
Non-calcined 2% Ir	66	~ 95

The values of $OT_{1,irr}$, HC_{irr} in Table 1 show $OT_{1,irr}/HC_{irr}$ values significantly lower than the theoretical one[24] relevant to the stoichiometric reactions reported in Table 4. This may be ascribed to some reoxidation of the metal during evacuation in vacuum after in situ re-activation.

The mean value of the reversible hydrogen adsorption on Pt was found to be ~0.75 H per Pt_s and may be regarded as being in reasonable agreement with Barbaux et al.[1] (1 H per 1 Pt_s under p ~200 Torr); the reversible hydrogen adsorption on Pt in fact gives rise to IR bands of increasing intensity with the hydrogen adsorption pressure[15]. The reversible hydrogen adsorption on Ir is probably somewhat less than on Pt (~0.4 per Ir_s).

%D(Pt, Re, Ir) *according to the method of preparation.* The relevant feature about Pt is that %D (Pt) does not depend very much on the support, the wt % Pt, or the method of preparation. Extremely well dispersed pure Pt on γ-Al_2O_3 is certainly not easily obtained and stabilized.

On the other hand, very highly dispersed Ir is easily prepared, in agreement with for instance Boitiaux[16] who prepared 0.35% Ir/γ-Al_2O_3 with %D (Ir) ~ 100 (duration of the calcination step in air, before reduction: 2 h at 530 °C). Sinfelt[11], Rasser[17], some of us also in ref. 5 and in the present work (Tables 3 and 5) have shown that a prolonged calcination (~ 15 h) in air of H_2IrCl_6/Al_2O_3 at 500 °C[5,11] or at a still higher temperature[14] gives rise to a considerable decrease in %D (Ir) in the final catalyst. The variation of %D (Ir) versus the duration of the calcination step before reduction, is most probably the result of two phenomena:

(i) the conversion of only slowly reducible $IrCl_x$ exchanged species into more easily reducible IrO_x aggregates. This phenomenon would result in an increase in the number of Ir_s in the final catalyst. In this regard, recall that Escard et al.[18], Bozon-Verduraz et al.[19] concluded from XPS, UV-visible spectroscopies and selective extraction, that important amounts of Ir (III) may be trapped on the surface of reduced Al_2O_3 supported Ir catalysts.

(ii) The second effect lies in the sintering of the small IrO_2 aggregates into large (200–300 Å) IrO_2 particles, as mentioned above.

TABLE 6

% DISPERSION OF (Pt + Re) IN THE 2% (Pt + Re)/γ-Al_2O_3 CATALYSTS

% Re	0	20	40	60	50	100
%D (Pt + Re)	41	54	60	70	66	60

With regard to Re, we simply note that the % Dispersion is of the same order of magnitude as for Pt.

The 2% (Pt + Re)/γ-Al_2O_3 catalysts

%*D*(Pt + Re). The correct method for evaluating %*D*(Pt + Re) from $OT_{1\ irr}$ was discussed in ref. 3. The variation of %*D*(Pt + Re) versus % Re, (see Table 6) shows a broad maximum at 60–70% Re.

%Re_S/(Pt_S + Re_S) (surface composition). Similar values of the surface and mean compositions of the metal phase were inferred from hydrogen chemisorption volumetric measurements and from CO IR spectroscopy measurements[3]. The present result concerning the reversible hydrogen adsorption (Fig. 4) corroborate this conclusion. It should be noted that if the decrease in $(HC, HT_1, HT_2)_{rev}$ as % Re increases from 0 to 40 is less than 40%, this may be accounted for by the increase in %*D* (Pt + Re).

Interactions between Pt and Re. This question was answered previously by CO IR spectroscopy measurements and by a comparison between $OT_{1\ irr}$ and $OT_{2\ irr}$. In fact the reduction of the oxygen chemisorbed on Pt is very rapid at 25 °C while the reduction of the oxygen chemisorbed on pure Re is extremely slow. A strong increase in the reducibility of Re_SO may be considered as evidence for (Pt, Re) bimetallic particles. This interpretation is strongly corroborated by Mössbauer spectroscopy studies of (Pt, Fe) bimetallic catalysts either supported on carbon[20] or on alumina[21]. Vannice and Garten[21] proved in fact that the oxidation (O_2)–reduction (H_2) of Fe on the surface of (Pt, Fe) alloy particles is reversible at 25 °C, whereas over pure Fe particles it is not.

TABLE 7

SURFACE PROPERTIES OF THE METAL PHASE IN 2% (Pt + Re)/γ-Al_2O_3 (60% Re): COMPARISON OF THE NORMAL AND REDISPERSED STATES

Catalyst (102) *μatg(Pt + Re) g^{-1} cat.*	*(Pt_s)* *μatg g^{-1}*	*(Re_s)* *μatg g^{-1}*	*(Pt_s + Re_s)* *μatg g^{-1}*	*%D (Pt + Re)*	*(Re_s alloy)* *μatg g^{-1}*	*(Re_s unalloy)* *μatg g^{-1}*
Normal	35	36	71	70	~ 36	~ 0
Redispersed	29	65	94	92	12	53

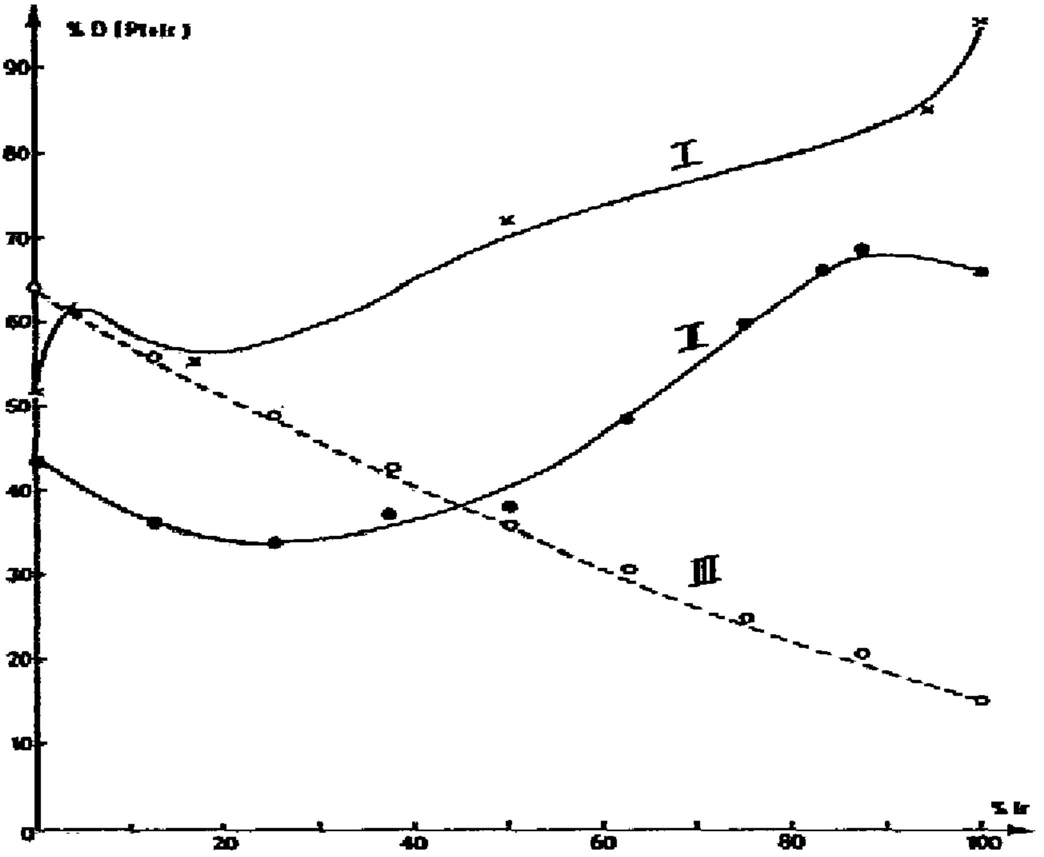

Fig. 8. % Dispersion of (Pt + Ir) as a function of % Ir. Calcined 0.3% to 0.6% (Pt + Ir) catalysts (curve I). Non-calcined and calcined 2% (Pt + Ir) catalysts (curves II and III, respectively).

The very similar values of $OT_{2\,irr}$ and $OT_{1\,irr}$ in the 20, 40 and 60% Re catalysts (see Fig. 3) show that almost all of the oxygen chemisorbed on Re during the first oxygen titration was reduced by H_2 during the first hydrogen titration, although the H_2–catalyst contact time was only ~15 min. Hence Pt and Re may be considered as being mainly alloyed. The more important difference between $OT_{1\,irr}$ and $OT_{2\,irr}$ in the 80% Re catalyst could be accounted for by a kinetic effect rather than by a much more significant amount of unalloyed Re. Increasing the H_2–catalyst contact time up to ~1 h indeed reduced $OT_{1\,irr}$–$OT_{2\,irr}$ down to a negligible value over the 80% Re catalyst, but not at all over the 100% Re catalyst.

The effect of the redispersion treatment. This effect is shown in Table 7, for the 60% Re catalyst, in the standard state and in the redispersed form. (Pt_s) was evaluated from the hydrogen reversible chemisorption, and (Re_s), %*D* (Pt + Re), (Re_s alloyed), (Re_s unalloyed) were subsequently evaluated from $OT_{1\,irr}$, $OT_{2\,irr}$[3].

The redispersion treatment, initially proposed by Yao and Shelef[7] for the Re/Al_2O_3 monometallic catalysts results:

(i) in a significant increase in the %*D* (Pt + Re) (from ~70 up to ~90);

(ii) in a decrease in the interaction between Pt and Re. The metallic phase in the redispersed catalyst is most likely composed of bimetallic (Pt, Re) particles with % Re lower than the nominal composition and of extremely dispersed pure Re particles.

The (Pt + Ir)/Al$_2$O$_3$ catalysts

Overall % dispersion of the (Pt + Ir) phase. The variation of %D (Pt + Ir) calculated from OT$_{1\,\mathrm{ini}}$ versus % Ir is shown in Fig. 8 for the three series of catalysts: 0.6 to 0.3% (Pt + Ir) (curve I), 2% (Pt + Ir) non-calcined (curve II) or calcined (curve III). To a first approximation the variations of %D (Pt + Ir) are progressive, and the deviations from the linearity observed at very small % Ir (curve I) or in the 0–20% Ir concentration range (curve II) do not deserve any specific discussion. Note that curve II does not differ much in its shape from that published by Engels et al.[22] who reduced their 0.6% (Pt + Ir) catalysts without any precalcination in air.

Surface composition of the (Pt + Ir) phase. The surface composition may not be inferred from the O$_2$–H$_2$ titrations since the same stoichiometric equations hold for both Ir and Pt.

Interactions between Pt and Ir. This question is important in that the (Pt + Ir)/Al$_2$O$_3$ catalysts have some practical applications. In fact, the 0.6 to 0.3 % (Pt + Ir) series of the present work has been prepared for an industrial purpose (selective hydrogenolysis of aliphatic hydrocarbons[23]).

Firstly let us consider the main literature data. Sinfelt[11] showed that H$_2$PtCl$_6$ plus H$_2$IrCl$_6$ coimpregnated silica, reduction at 500 °C, contains a (Pt, Ir) alloy phase as detected by X-ray analysis (mean particle size 25 to 50 Å according to the wt % (Pt + Ir) which was between 5 and 20); the % Ir/(Pt + Ir) was ~50. A 50 Pt–50 Ir supported alloy was then obtained even though the solubility of Ir in Pt at ~500 °C is only a very few % and the solubility of Pt in Ir is still smaller[24]. It is not clear as yet if this alloy phase is thermodynamically stable (due to an increase in the mutual solubility as %D (Pt + Ir) increases) or only metastable since the segregation of Pt from Ir when bulk (Pt, Ir) solid solutions are heat treated at ~500 °C should be extremely slow[24]. Sinfelt[11] also showed that a 15 h precalcination in air at 500 °C of (Pt + Ir)/SiO$_2$ or Al$_2$O$_3$ catalysts gave rise, after reduction, to a mixture of large Ir particles and of much smaller Pt particles. Sinfelt[11] tried to characterize 3.5% (Pt + Ir)/Al$_2$O$_3$ catalysts by Mössbauer spectroscopy using a small % Fe as a probe element. The results favoured the hypothesis of a (Pt, Ir) bimetallic phase, provided the calcination in air at 500 °C step was omitted.

The Rasser[17] approach lies in the H$_2$ Thermal Programmed Desorption (TPD) method. The most significant difference between Pt and Ir was found to consist in their respective sensitivity to carbon poisoning, which gives rise to a H$_2$ TPD peak at 224 K and which is much less over Ir than over Pt. Only a small amount of Ir in the surface of Pt was found to be sufficient to remove the carbon deposit from neighbouring Pt sites, in the presence of hydrogen. The Al_2O_3 or SiO_2 supported alloys prepared by Rasser were ~300 Å in metal particle size [% (Pt + Ir) ~6]; calcination in air at 550–600 °C for 15–20 h preceded the reduction.

Let us recall also that a simple mixing of $(NH_4)_2PtCl_6$ and $(NH_4)_2$ $IrCl_6$ powders (50% Pt–50% Ir) followed by calcination for 16 h at 500 °C was sufficient to obtain a heterogeneous alloy phase after reduction[4]. When the same mixture was reduced without any precalcination in air separate particles of Pt and of Ir, identified by X-ray analysis, were obtained. Coming back to the (Pt + Ir)/γ-Al_2O_3 catalysts of the present study:

(1) The electron microscopy data in Table 3 together with the above literature data support the idea that the metallic phase in the 2% (Pt + Ir) calcined catalysts is strongly heterogeneous with regard to its particle composition. On the other hand, Fig. 7(a) shows a Pt like behaviour during the H_2 titrations up to a high % Ir values. The most likely hypothesis to account for all of these data, is that the large metallic particles detected by electron microscopy are iridium particles with a small % of Pt.

(2) The 0.6 to 0.3% (Pt + Ir) catalysts and the 2% (Pt + Ir) non calcined catalysts do not show any evidence (Figs. 6 and 7b) for a synergetic effect between Pt and Ir during the H_2 titrations. Hence we think that the metallic phase in these catalysts contains a high % of the Ir in the form of pure Ir particles, without any interaction with Pt. It should be noticed that this method of appreciation of the Pt–Ir interactions has only little significance in the low Ir concentration range; hence it is very difficult to give valuable conclusions from 0 up to say 20% Ir. It should be pointed out that the synergetic effect between Pt and the second element in (Pt–Me) bimetallic particles, during the O_2–H_2 titrations, is a rather general phenomenon. It has been mentioned above for Me = Fe and Re and was also observed when Me = Ni[25]. The absence of any synergetic effect is strongly indicative, in our opinion, of the presence of at least a part of Me in the form of isolated pure Me particles or of (Me, Pt) particles containing no Pt in their surface.

In conclusion, we have shown that the measurement of overall % dispersion of the metal phase in (Pt + Re or Ir) alumina supported catalysts is possible by means of the H_2–O_2 titrations. Taking account of the kinetics of the hydrogen titration also allowed us to obtain useful information concerning the interactions between the two active elements. The (Pt, Re) alumina supported bimetallic phase appeared to be more easily obtained than the (Pt, Ir) equivalent phase, over a large range of concentrations of Ir or Re.

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