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Hydrogen Titration, Scanning Electron Microscopy, and Associated X-Ray Emission Studies of Pt–Ru/Al_2O_3 Catalysts

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Two series of platinum–ruthenium catalysts deposited on γ-Al_2O_3 pellets and equivalent to 2 wt% Pt in number of (Pt + Ru) atoms were investigated. The first series (I) was prepared by successive impregnation of H_2RuCl_6 and of H_2PtCl_6 in water, and the second (II) by coimpregnation of H_2PtCl_6 and of H_2RuCl_6 in ethanol (75%) plus water. The chemisorption (O_2, H_2) and titration (mainly hydrogen temperature-programmed titration of chemisorbed oxygen) data showed catalysts (I) to be composed of mixtures of Pt and Ru particles, and catalysts (II) to be composed of alloy particles. This conclusion was on the whole corroborated by single particle X-ray emission analysis using X-ray emission in a scanning transmission electron microscope. This last technique further showed that the platinum particles in catalysts (I) contained a small amount of Ru. The reasons for the difference of state of the metallic particles in catalysts (I) and (II) are not totally elucidated but a tentative interpretation is given.

INTRODUCTION

Platinum–ruthenium alumina-supported catalysts have been patented for the reforming of crude oils (*1*). In these catalysts, as well as in many other highly dispersed bimetallics, the main problem is to determine if both elements are alloyed or not.

In previous works (*2, 3*) it was shown that the oxygen chemisorbed on the surface Ru atoms (Ru_s) of (Pt, Ru) alloy particles is much more reducible than the oxygen chemisorbed on pure Ru. A hydrogen temperature-programmed titration (TPT) method was described which showed two hydrogen titration peaks, a low-temperature one related to the Pt_s and to the alloyed Ru_s atoms altogether, and a higher-temperature one corresponding to the unalloyed Ru_s atoms. Previously (*3, 4*) only the qualitative aspect of TPT was presented, but in the present paper the results are tentatively quantified.

Scanning transmission electron microscopes (STEM) are now available allowing determination of local composition down to the nanometer range, either by X-ray emission energy dispersive analysis or by electron energy loss spectroscopy. H_2–TPT and X-ray emission microanalysis available in the STEM were both used in the present study, and showed satisfactory agreement.

EXPERIMENTAL

1. H_2–TPT

After hydrogen reduction at 500°C, the sample was outgassed under helium flow at 500°C. Following cooling down to 20°C, oxygen was chemisorbed from a 1% O_2 in He mixture (frontal katharometer analysis method). The sample was then swept by an argon flow for 20 min. Afterwards the hydrogen titration by a 1% H_2 in argon mixture was carried out first for 20 min at 20°C and subsequently up to 200°C (heating rate: 5°C/min). Finally, the sample was cooled down to 20°C in the 1% H_2/Ar mixture.

The H_2 chemisorption at 20°C followed by O_2 titration at 20°C and by H_2–TPT were similarly measured.

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2. *STEM*

STEM measurements were made with a HB 5 Vacuum Generators instrument using a Kevex X-ray detector (Si/Li crystal 10 mm^2 in area). The point-to-point resolution was 0.45 nm. The minimum analyzable area was about 1 nm^2 (probe diameter ~1 nm). The sensitivity in X-ray emission was about 50–100 Pt atoms.

The studied samples were the extractable replica grids previously used for examination with a JEM 100 CX electron microscope, ~0.3 nm point-to-point resolution (1% HCl + 1% HF in water was used to dissolve the support).

3. *Catalysts*

The support was GFS 400 Rhône Poulenc alumina (pellets ~1.5 mm in diameter, 15 mm in length; $S \sim 200$ m^2/g; $\bar{r}p \sim 7$ nm).

(*a*) *Successive impregnation of* H_2RuCl_6 *and of* H_2PtCl_6 *in aqueous medium.* Aqueous coimpregnation of Al_2O_3 pellets by Ru and Pt salts leads to samples with an inhomogeneous radial distribution of the components. Therefore it was necessary to impregnate the support successively by H_2RuCl_6 in a strongly acidic (HCl) medium and then after water washing, by H_2PtCl_6 without further HCl addition (*2*).

These catalysts were dried in air at 110°C before hydrogen reduction at 500°C.

(*b*) *Coimpregnation of* H_2RuCl_6 *and of* H_2PtCl_6 *in ethanol + water solution.* Reasonably uniform Ru and Pt profiles through the pellets were obtained by coimpregnation of H_2RuCl_6 and H_2PtCl_6 in a 75 vol% ethanol and 25 vol% water solution (*3*, *4*). These catalysts were dried under a dry air flow at 200°C in order to eliminate ethanol completely before hydrogen reduction at 500°C.

All the catalysts contained a constant number of (Pt + Ru) atoms, equivalent to 2 wt% Pt.

Temperature-programmed reduction experiments showed that Pt and Ru were quantitatively reduced to Pt°, Ru° in all of the Pt-containing catalysts while only partial reduction (~55%) of Ru to Ru° took place in the two Ru monometallic catalysts (*2*, *4*).

RESULTS

1. CHEMISORPTIONS AND TITRATIONS

The results obtained over successively impregnated catalysts are reported in Table 1. (OC) is the O_2 chemisorption at 20°C (sequence I), $(HT)_{irr}$ is the overall H_2 consumption due to H_2 titration at 20°C, H_2 titration from 20 up to 200°C, H_2 cooling down to 20°C and final sweeping out of 1% H_2/Ar by Ar for 40 min.

(HC), the irreversible hydrogen chemisorption at 20°C, was measured after reactivation and desorption at 500°C (Sequence II). (OT) is the oxygen titration following $(HC)_{irr}$, and $(HT)_{irr}$ was finally measured and found to be about equal to the value measured after (OC) (Sequence I).

Note that (OC) and $(HC)_{irr}$ increase and

TABLE 1

(Pt + Ru)/Al_2O_3. Successively Impregnated[a]

	Ru/(Ru + Pt) (at.%)	0	43.4	56.7	75.7	100
I	(OC), 20°	0.67	0.784	0.958	0.878	1.15
	$(HT)_{irr}$, 20° ↗ 200° ↘ 20°	2.35	2.00	2.09	2.10	2.42
II	$(HC)_{irr}$, 20°	0.84	0.36	0.22	0.20	0
	(OT), 20°	1.01	1.06	1.02	0.93	1.16
	$(HT)_{irr}$, 20° ↗ 200° ↘ 20°		2.06	2.06	2.09	

[a] Results in at.H or 0 per total at. (Pt + Ru).

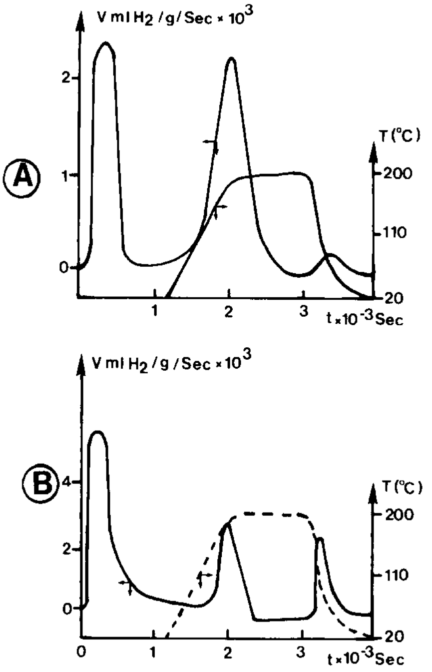

FIG. 1. Hydrogen temperature-programmed titration (TPT) of chemisorbed oxygen. (A) Successively impregnated catalyst (43.4 at.% Ru/(Pt + Ru)). (B) Coimpregnated catalyst (48.2 at.% Ru/(Pt + Ru)).

decrease respectively as the atomic percentage of Ru/(Pt + Ru) increases while the titer values (*HT*), (*OT*) do not vary so much.

The H_2–TPT curve for the 43.4 at.% Ru/(Pt + Ru) catalyst is shown in Fig. 1A. The room temperature peak and the high-temperature peak have a comparable area.

The results obtained with the catalysts prepared by coimpregnation in ethanol + water are reported in Table 2. Significant differences may be observed between (*HT*) following (*OT*) (sequence II) and HT following (*OC*) (sequence I); this is significantly different from what was previously observed (Table 1).

Figure 1B shows the H_2–TPT curve for the 48.2 at.% Ru/(Pt + Ru) catalyst. Note that the ratio of the high-temperature peak area to the room temperature peak area is much smaller than in Fig. 1A.

2. ELECTRON MICROSCOPY (JEM 100 CX) DATA

The results are summarized in Table 3 for some typical catalysts. For both methods of preparation, the mean metal crystallite size decreases as the at.% Ru/(Pt + Ru) increases. While the bimetallics prepared by successive impregnation showed a bidispersion, those prepared by coimpregnation are reasonably well homodispersed.

3. X-RAY EMISSION ANALYSIS DATA OBTAINED WITH THE STEM

(*a*) *Successively Impregnated Catalysts*

The bidispersed 43.4 at.% Ru/(Pt + Ru) was studied. The X-ray emission spectrum of a 2.5-nm-sized particle is shown in Fig. 2. The ratio of the Ru ($L\alpha$; 2.56 KeV) to the Pt ($M\alpha$; 2.05 KeV) intensity is much smaller than 43%. Some Si (1.74 keV) presumably arises from silica impurities in the Al_2O_3 support. The X-ray emission line at 2.31 keV may be ascribed to sulfur contamination. The X-ray emission analysis of a patch of 3 nm^2 with no metal particle larger

TABLE 2

(Pt + Ru)/Al_2O_3, coimpregnated

	Ru/(Ru + Pt) (at.%)	0	13.1	27.3	36.9	48.2	62.4	71.6	85.0	100
I	(*OC*) 20°	0.33	0.479	0.568	0.976	0.977	1.100	1.065	1.307	1.55
	$(HT)_{\mathrm{irr}}$, 20° ↗ 200° ↘ 20°	1.32	1.773	1.948	2.097	2.496	2.722	2.774	2.835	3.15
II	$(HC)_{\mathrm{irr}}$, 20°	0.46	0.543	0.441	0.398	0.336	0.243	0.225	0.134	0
	(*OT*), 20°	0.57	0.757	0.685	0.943	0.984	1.101	1.046	1.179	1.56
	$(HT)_{\mathrm{irr}}$, 20° ↗ 200° ↘ 20°		1.800	1.725	1.710	2.175	2.517	2.591	2.657	

[a] Results in at.H or 0 per total at. (Pt + Ru).

TABLE 3

Electron Microscopy Data

Method of preparation	at.% Ru/(Pt + Ru)	Metal particle size, Ø (nm)
Successive impregnation of Ru and Pt in water	0	1.4–1.5 (+ a few particles ~10 to 20 nm)
	43.4	Bidispersion ~1 ~3
	100	≤1
Coimpregnation of Ru and Pt in ethanol + water	0	2.5
	27.3	2.0
	71.6	1.5
	100	1.0–1.5

than 1 nm in diameter, showed the presence of Ru only (Fig. 3). The very small Pt signal may be ascribed to the contribution of one platinum particle 1 nm distant from the analyzed area.

Clearly this catalyst is essentially composed of a mixture of Pt with about 10 at.% Ru alloyed, and of very small pure Ru particles.

(*b*) *Coimpregnated Catalysts*

Ru/(Ru + Pt) = 48.2 at.%. The X-ray emission analysis of individual metal particles was difficult due to their large density on the grid (only very few particles were separated from a neighbour particle by more than 5 nm). Patches around 140 nm^2 in area, containing 100 metal particles were then analyzed. Figure 4 shows that the Ru/Pt atomic ratio is close to 1 (±20%). In every case Pt ($M\alpha$ = 2.05 keV; $L\alpha$ = 9.44 keV) was found together with Ru ($L\alpha$ = 2.56 keV), and with similar concentrations in Pt and in Ru. The Cu lines in Fig. 4 obviously arise from the copper grid. In Fig. 5, only 10 metal particles were analyzed, with also a Pt/Ru atomic ratio close

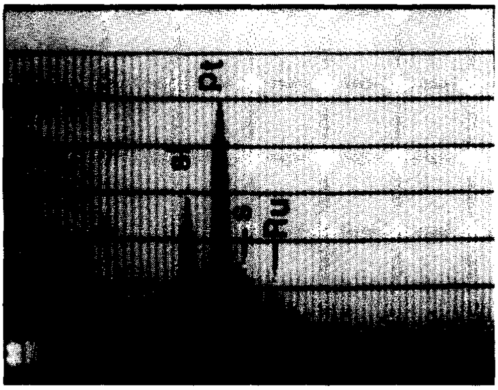

FIG. 2. 43.4 at.% Ru(Pt + Ru) (successive impregnation). Analysis of a single particle, ~2.5 nm in Ø.

FIG. 3. Same catalyst as in Fig. 2. The analyzed patch is 3 nm^2 in area with no metal particle >1 nm, and is 1 nm distant from a 2.5-nm particle identified as Pt.

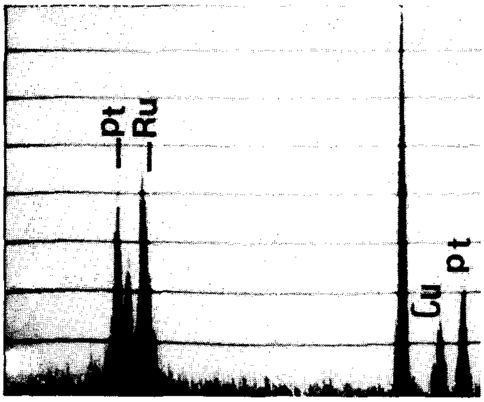

FIG. 4. 48.2 at.% Ru/(Pt + Ru) coimpregnated catalyst. The analyzed patch is about 140 nm² in area, with about 100 metal particles.

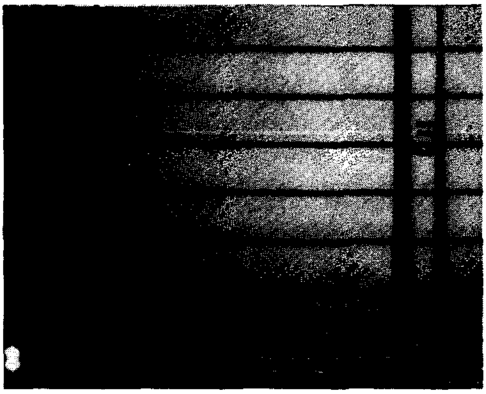

FIG. 6. Same catalyst as in Fig. 4. Tentative analysis of a single metal particle ~1 nm in size.

to 1. In Fig. 6, the analysis of a single 1-nm-diameter metal particle was tentatively made. Even though very low in intensities the *Mα* (Pt) and *Lα* (Ru) lines also showed atomic ratio equal to about 1.

Ru/(Pt + Ru) = 85 at.%. This catalyst was found to be more heterogeneous in metal particle composition than the 48.2 at.% Ru/(Pt + Ru) catalyst. This is shown in Fig. 7 and Fig. 8, where the ratio of Ru to Pt is much smaller in Fig. 8 than in Fig. 7. Since most of the patches analyzed were 0.4 to 0.5 in Ru/Pt, it was concluded that particles presumably composed of pure Ru should be present, to take into account the mean composition of this catalyst. However, experimental difficulty to detect the Ru particles arose from the closeness of the individual metal particles.

DISCUSSION

From the previous (*2*, *3*) simple examination of the H_2–TPT curves completed by transmission electron microscopy examination of the catalysts, it was concluded that:

(i) the successive impregnation of Al_2O_3 by Ru and Pt in an aqueous medium gives rise essentially to a mixture of small Pt and Ru particles. The present X-ray emission analysis data support this hypothesis and further suggest that the Pt particles nevertheless contain a small percentage of alloyed Ru.

(ii) coimpregnation of Al_2O_3 by Ru and

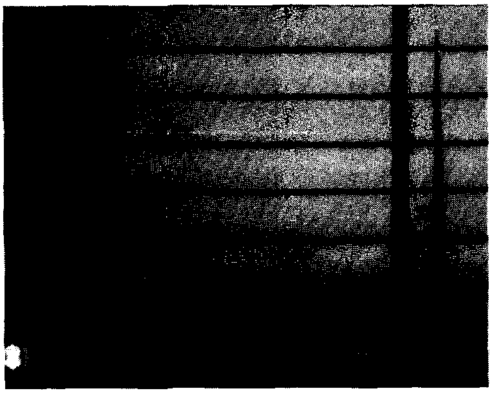

FIG. 5. Same catalyst as in Fig. 4, but the analyzed patch only contains about 10 metal particles.

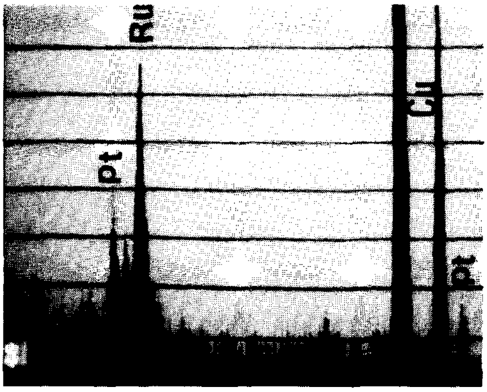

FIG. 7. 85 at.% Ru/(Pt + Ru) coimpregnated catalyst. Each of the two patches analyzed contains ten metal particles. Analysis 1.

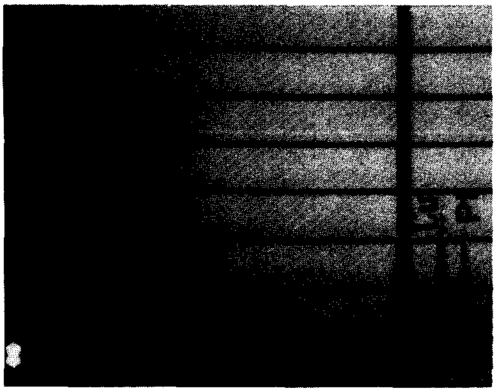

FIG. 8. 85 at.% Ru/(Pt + Ru) coimpregnated catalyst. Each of the two patches analyzed contains 10 metal particles. Analysis 2.

Pt in ethanol plus water gives rise essentially to (Pt,Ru) alloy particles, at least up to 40–50 at.% Ru/(Pt + Ru). The present X-ray emission analysis data also strongly support this conclusion.

It follows that the enhancement in the reducibility of the oxygen chemisorbed on Ru in a bimetallic catalyst does not arise from artefacts such as hydrogen spillover (for review articles on H spillover see, for instance, Refs. (*5*, *6*)) but from a (Pt,Ru) alloy effect. This leads to a semiquantitative interpretation of the chemisorption and titration results. For this purpose the total number of surface Ru atoms, $n(\mathrm{Ru_s})$, may be divided into:

—$\mathrm{Ru_{sp}}$, metallic particles with almost no Pt on their surface. The calculation of the number of $\mathrm{Ru_s}$ atoms, $n(\mathrm{Ru_{sp}})$ is based on the area of the high-temperature peak of the TPT curve and it is known that a few atom percent $\mathrm{Pt_s/(Ru_s + Pt_s)}$ is sufficient to improve the reducibility of $\mathrm{Ru_sO_2}$ to a level nearly equal to $\mathrm{Pt_sO}$ (*2*, *4*).

—$\mathrm{Ru_{sal}}$, metallic particles with at least a few atom percent $\mathrm{Pt_s/(Pt_s + Ru_s)}$ on their surface.

The $\mathrm{Pt_s}$ atoms may be similarly divided into $\mathrm{Pt_{sp}}$ and $\mathrm{Pt_{sal}}$, according to the experimental feature that the hydrogen coverage of well-alloyed (Pt,Ru)/$\mathrm{SiO_2}$ catalysts decreases sharply as the atom percent Ru/(Pt + Ru) increases from 0 to about 20 (*4*, *7*). Hence in the following:

—$\mathrm{Pt_{sp}}$ represents metallic particles poor in Ru, i.e., less than about 10–15 at.% Ru.

—$\mathrm{Pt_{sal}}$ represents the difference between the total number of $\mathrm{Pt_s}$ ($n(\mathrm{Pt_s})$) and ($n(\mathrm{Pt_{sp}})$).

The oxygen chemisorption (*OC*) stoichiometries were discussed elsewhere and found to be close to $\mathrm{Pt_sO}$ and $\mathrm{Ru_sO_2}$, on pure Pt and Ru and on the (Pt,Ru) alloys as well (*9*):

$$(OC) = 1 \times n(\mathrm{Pt_s}) + 2n(\mathrm{Ru_s}). \quad (1)$$

The hydrogen chemisorption (*HC*) may be written:

$$(HC)_{\mathrm{irr}} = a \times n(\mathrm{Pt_{sp}}) + b \times n(\mathrm{Pt_{sal}}). \quad (2)$$

The value of a is close to 1.4 (mean value over Pt/$\mathrm{Al_2O_3}$ catalysts, under the present experimental conditions), and the value of b is close to 1.0 (*7*). Note that Eq. (2) assumes the hydrogen coverage to be close to zero over $\mathrm{Ru_{sp}}$ and $\mathrm{Ru_{sal}}$ as well. This assumption is experimentally proved for $\mathrm{Ru_{sp}}$ as shown in Tables 1 and 2. As far as $\mathrm{Ru_{sal}}$ is concerned, the decrease of $(HC)_{\mathrm{irr}}/(OC)$ as the percentage of Ru/(Pt + Ru) increases (*7*) indicates approximately the same stoichiometry. Concerning the oxygen titration (OT), following (HC), the simple relation:

$$(OT) = 1/2\,(HC)_{\mathrm{irr}} + (OC),$$

was first considered (the oxygen coverages after (*OT*) and after (*OC*) are supposed to be the same). Table 4 shows that hypothesis to be reasonably valid for the successively impregnated catalysts but not for a number of bimetallic catalysts in the coimpregnated catalyst series. It is then suggested that $\mathrm{Pt_{sal}}$ gives rise to $\mathrm{Pt_sOH}$ instead of to $\mathrm{Pt_sO}$ during (OT). The following equation would then apply to (OT) after (HC):

$$(OT) = (1 + a/2) \times n(\mathrm{Pt_{sp}}) + n(\mathrm{Pt_{sal}}) + 2n(\mathrm{Ru_s}). \quad (3)$$

In the case where almost no (Pt,Ru) alloy

TABLE 4

Values of the $\frac{1}{2}(HC)_{irr}$ + (OC) to (OT) Ratio, over (Pt + Ru)/Al_2O_3

Method of preparation	at.% Ru/(Pt + Ru)	($\frac{1}{2}(HC)_{irr}$ + (OC))/(OT)
Successive impregnation	0	1.00
	43.4	0.91
	56.7	1.04
	75.7	0.99
	100	1.0
Coimpregnation	0	1.0
	13.1	0.99
	27.3	1.15
	36.9	1.25
	41.2	1.16
	62.4	1.11
	71.6	1.03
	85	1.17
	100	1.0

particles exist (successive impregnation, Table 1), (HT_{irr} 20 ↗ 200 ↘ 20) is nearly equal following (OT) or (OC). This does not hold any more over the alloyed catalysts (coimpregnated, Table 2), and it is easily shown that the following equations should apply:

$$\begin{aligned}&(HT_{irr}\ 20 \nearrow 200 \searrow 20)\\ &\qquad \text{After (OC)}\\ &- (HT_{irr}\ 20 \nearrow 200 \searrow 20) = n(\mathrm{Pt_{sal}}) \quad (4)\\ &\qquad\qquad \text{After (OT)}\end{aligned}$$

$$(OT) - (OC) = (a/2) \times n(\mathrm{Pt_{sp}}), \quad (5)$$

with $a \sim 1.4$; following the calculation of $n(\mathrm{Pt_{sp}})$ according to (5), $n(\mathrm{Pt_{sal}})$ may be calculated either from (2) or from (4). The values were found to be in reasonably good agreement, especially over the coimpregnated catalysts (at the time of these last measurements the apparatus had been automatized, with consequently a better accuracy in the results).

Since $n(\mathrm{Pt_s}) = n(\mathrm{Pt_{sp}} + \mathrm{Pt_{sal}})$, Eq. (1), (OC) gives rise to $n(\mathrm{Ru_s})$, and then to the overall percentage dispersion of the metallic phase $\%D(\mathrm{Pt + Ru}) = 100\ [n(\mathrm{Pt_s} + \mathrm{Ru_s})/n(\mathrm{Pt + Ru})]$. Table 5 shows the values of $\%D$(Pt + Ru) and the electron microscopy results for the reasonably homodispersed coimpregnated catalysts. Both techniques show that the percentage dispersion increases as at.% Ru/(Pt + Ru) increases.

In order to distinguish between $n(\mathrm{Ru_{sp}})$ and $n(\mathrm{Ru_{sal}})$ it has been considered that the H_2–TPT peak observed during heating added to the H_2 chemisorption peak observed during subsequent cooling corresponds to:

$$\mathrm{Ru_{sp}O_2} + 4\mathrm{H} \rightarrow \mathrm{Ru_{sp}} + 2\mathrm{H_2O}. \quad (5)$$

The H_2 chemisorption peak during cooling is normally ascribed to readsorption of H_2 by the $\mathrm{Pt_s}$ atoms.

From the above equations, the main parameters (see Table 6) are:

—the overall percentage dispersion of the (Pt + Ru) metal phase, $\%D$(Pt + Ru) (column 2),

—the at.% $\mathrm{Ru_{s\,pure}}/(\mathrm{Pt_s} + \mathrm{Ru_s})$ (column 3) which fairly well represents the percentage of the total metal area corresponding to metal particles with practically no Pt on their surface.

—the % $\mathrm{Pt_{s\,pure}}/(\mathrm{Pt_s} + \mathrm{Ru_s})$ (column 4).

Apart from the corroboration of the fact that in the successively impregnated catalysts the metal phase is much more heterogeneous in composition than in the coim-

TABLE 5

(Pt + Ru)/Al_2O_3-Coimpregnated Bimetallic Catalysts: % Dispersion of (Pt + Ru) from the Chemisorption Titration Data, and Mean Metal Particle Size from the Electron Microscopy Results

at.% Ru/(Pt + Ru)	13.1	27.3	36.9	48.2	62.4	71.6	85.00
% D(Pt + Ru)	57	60	93	75	86	91	97
d(nm) microscopy	2.5	2.0				1.5	1.0–1.5

TABLE 6

(Pt + Ru)/Al_2O_3: Characterization from the chemisorption and titration data[a]

CATALYST		% Dispersion (Pt + Ru)	% $Ru_{s\ pure}/(Pt_s + Ru_s)$	% $Pt_{s\ pure}/(Pt_s + Ru_s)$
Medium of impregnation	at.% Ru/(Pt + Ru)			
Water (successive impregnation)	43.4	62	50	50
	56.7	57	73	27
	75.7	58	76	24
Ethanol + water (coimpregnation)	13.1	57	0	90
	27.3	60	6	35
	36.9	93	15	0
	48.2	75	29	0
	62.4	86	48	0
	71.6	91	56	0
	85.0	97	66	0

[a] $Ru_{s\ pure}$: metallic particles with almost no Pt in the surface. $Pt_{s\ pure}$: Pt particles with less than 10–15 at.% Ru in the surface.

pregnated ones, the results in Table 6 further show that even in the coimpregnated catalysts the percentage of the metallic area which corresponds to pure Ru particles is not negligible (30%, at.% Ru/(Pt + Ru) ~ 50). Clearly, the TPT method is very sensitive as regards the determination of the overall metallic area and also of the amount of nearly pure Ru phase.

This semiquantitative aspect of these results is strengthened by the following point dealing with the coimpregnated catalysts. Since the percentage dispersion of the pure Ru phase in these catalysts is roughly 80% (from electron microscopy), the total number of alloyed Ru atoms should be close to $n(Ru_{all}) = n(Ru_{total}) - n(Ru_{s\ pure})/0.8$ and hence a comparison between the surface and the mean compositions of the (Pt,Ru) alloy phase (see Table 7) is possible.

These two compositions are in rather good agreement which means that no significant difference in composition exists between the surface and the bulk of the alloy particles. Ramamoorthy and Gonzales (*10*) arrived at the same conclusion using a different approach (ir spectroscopy of chemisorbed CO and NO on (Pt,Ru) silica-supported alloys (*10*)).

The reasons for the difference in the state of the successively impregnated and coimpregnated catalysts are not completely elucidated. Nevertheless the following remarks may be of interest:

(i) Homogeneous coimpregnation does not necessarily give rise to (Pt,Ru) alloy particles after reduction. In fact, we could deposit Pt and Ru by coimpregnation of the present Al_2O_3 in water, by using H_2PtBr_6

TABLE 7

(Pt + Ru)/Al_2O_3-Coimpregnated Catalysts. Comparison of the Overall Composition of the Metallic Phase, and of the Mean and of the Surface Compositions of the Alloy Phases (Results in at.% Ru/(Pt + Ru)

Overall C	Mean C (alloy)	Surface C (alloy)
13.1	13	
27.3	24	22
36.9	22	32
48.2	27	28
62.4	29	34
71.6	29	25
85.0	26	40

instead of H_2PtCl_6 together with H_2RuCl_6. The final catalysts were found to be altogether poorly dispersed and to be either not alloyed or very little alloyed (*3, 4*).

(ii) The absence of alloy in the present successively impregnated catalysts may not be ascribed to a difference in the temperature of reduction of the Pt and Ru species. In fact, TPR experiments showed that the reduction of Pt and of Ru occured at approximately the same temperature in the two series of catalysts (*2, 4*).

Most probably the distribution of the Pt and of the Ru species is much more statistical in the ethanol + water impregnated catalysts than in the pure water impregnated ones. Adsorption of ethanol by alumina could have an influence but no experiments were performed to check that hypothesis.

CONCLUSIONS

(1) The chemisorption (O_2, H_2) and titration (mainly hydrogen temperature programmed-titration of chemisorbed oxygen) work allows one to determine not only the overall metallic (Pt,Ru) surface area but also the percentage of the metallic area composed of pure Ru.

(2) The results were strongly strengthened by X-ray emission analysis combined with electron microscopy, a technique which, for instance, further allows one to detect a small percentage of Ru in particular particles of Pt as small as about 1.5 nm in size.

(3) The nature of the impregnation medium (ethanol + water in one case, pure water in the other) was found to influence considerably the degree of Pt and Ru alloyed in the final catalysts. Further work is needed to show if that phenomenon is general in nature or if it only holds for the present (Pt,Ru) system.

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