

Platinum-Rhenium-Alumina Catalysts

II. Study of the Metallic Phase after Reduction

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Two percent (Pt + Re)/Al₂O₃ catalysts prepared by co-impregnation of Al₂O₃ with H₂PtCl₆ and Re₂O₇ and generally reduced by hydrogen at 500°C were mainly investigated by thermogravimetry (H₂-O₂ cycles at 25°C), electron microscopy, and infrared spectroscopy (chemisorption of CO at 25°C). The greater reducibility in the presence of Pt of oxygen chemisorbed by Re, and the ν CO frequency shifts of the Pt-CO and Re-CO species against the percentage of Re indicated a strong interaction between both metals. Most probably Pt and Re are alloyed. The H₂-O₂ cycles at 25°C allowed the determination of the overall dispersion of the (Pt + Re) phase while the optical density of the infrared band of CO adsorbed on platinum gave some information about the surface concentration of Pt in the (Pt + Re) phase.

INTRODUCTION

In Part I (1) it has been shown that the reduction of H₂PtCl₆ and Re₂O₇ co-impregnated on Al₂O₃ by hydrogen occurred at a rather low temperature. Pt and Re were both reduced to the metallic state, the reduction of the rhenium compound being strongly catalyzed by Pt. The total reduction of Re₂O₇ in Re₂O₇/Al₂O₃ has been confirmed by Webb (2), while the formation of Al₂O₃ supported ReO₂ postulated by Johnson and LeRoy (3, 4) is probably confined to reduction by hydrogen containing some water vapor. The present paper deals with the characterization of the metallic phase from the points of view of the degree of interaction between Pt and Re metals, and their dispersion was also measured.

EXPERIMENTAL METHODS

1. Techniques

The infrared spectrometer was a Perkin-Elmer 125 instrument with a double monochromator and a slit-width lower than 3 cm⁻¹. The catalyst pellet, pressed at about 2 tons/cm², had a weight of 50-100 mg. After reduction in the infrared cell under various conditions, the samples were evacuated at elevated temperature. After cooling at room temperature, carbon monoxide was adsorbed on the disc under a sufficient pressure (100 Torr) to obtain a complete coverage of the metal surface. The spectra were recorded at 25°C.

The electron microscope was a JEM 100 B model with a resolution of about 3.5 Å.

The sample was examined either as such or by the extractable replica method. In the latter case an aqueous solution of HF (1%) and HCl (1%) was used to remove the Al_2O_3 support.

For the chemisorption and titration measurements we used a Sartorius microbalance with a sensitivity of about $2 \mu\text{g}$ (δ); the weight of the sample was about 300 mg. Pure Re deposited on Al_2O_3 was also studied by means of volumetric measurements in order to ascertain the stoichiometries of the $\text{H}_2\text{-O}_2$ chemisorptions or titrations on Re; a MKS Baratron device was used for the pressure measurements.

Attempts were also made to use X-ray diffraction and electron diffraction to characterize the catalysts but without any significant success.

2. Samples

The supports and catalysts were described previously (1). The supports were Al_2O_3 SCS9 Rhône-Progil (mainly $\alpha\text{-Al}_2\text{O}_3$;

$S = 24 \text{ m}^2/\text{g}$) and Al_2O_3 oxide C Degussa (mainly $\gamma\text{-Al}_2\text{O}_3$; $S = 180 \text{ m}^2/\text{g}$). The catalyst contained 2 wt% (Pt + Re). As previously, we have designated by χ_{Re} the ratio of $100 \times \text{wt}\%$ (Re) over wt% (Pt + Re).

RESULTS

1. Infrared Spectroscopy

a. Preliminary observations. In the absence of metal, no irreversibly chemisorbed CO could be detected on either support, at 25°C . The νCO bands for linear M-CO species were observed near 2075 cm^{-1} (A band) in Pt/ $\gamma\text{-Al}_2\text{O}_3$ and near 2040 cm^{-1} (B band) in Re/ $\gamma\text{-Al}_2\text{O}_3$ (Fig. 1), in agreement with previous work [see for instance Ref. (6)]. The bands attributed to CO adsorbed in the bridged form M_2CO were much weaker and observed near 1860 cm^{-1} in Pt/ $\gamma\text{-Al}_2\text{O}_3$ and 1950 cm^{-1} in Re/ $\gamma\text{-Al}_2\text{O}_3$. In the (Pt + Re)/ Al_2O_3 catalysts only the A band which was much more intense than the B band could be

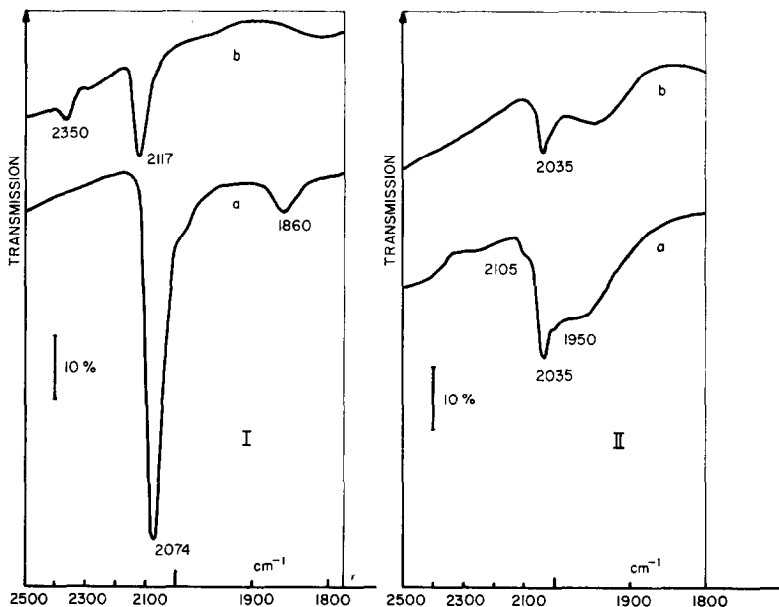


FIG. 1. νCO infrared absorption bands from CO adsorbed on Pt/ $\gamma\text{-Al}_2\text{O}_3$ (I) and Re/ $\gamma\text{-Al}_2\text{O}_3$ (II). (a) CO irreversibly adsorbed at 25°C ; (b) samples (a) heated under oxygen at 100°C for 5 hr.

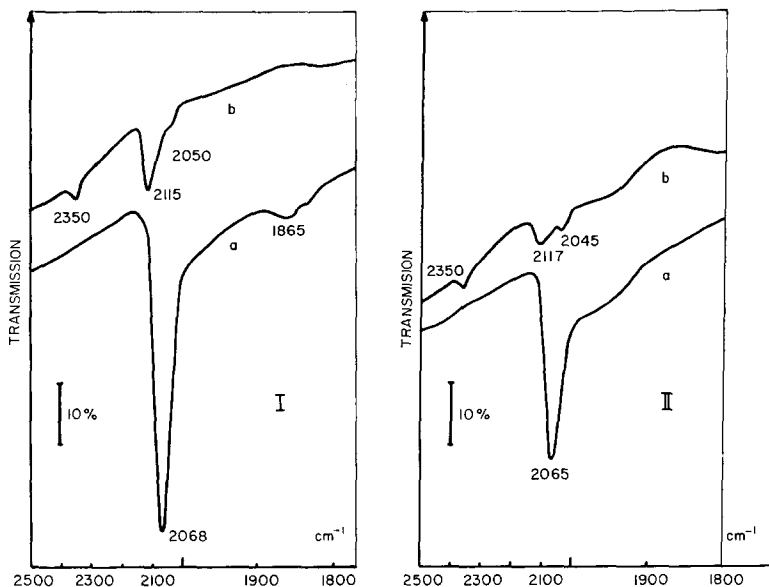
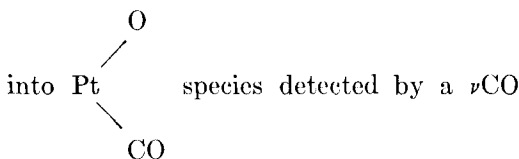


FIG. 2. ν CO infrared absorption bands from CO adsorbed on (Pt + Re)/ γ -Al₂O₃ catalysts. (I) $x_{\text{Re}} = 30$ and (II) $x_{\text{Re}} = 70$; (a) CO irreversibly adsorbed at 25°C; (b) samples (a) heated under O₂ at 100°C for 7 hr.

easily detected in practically the whole range of x_{Re} values because of the proximity of the A and B bands (Fig. 2).

When a CO-covered Pt/Al₂O₃ sample reacted with O₂, a small amount of the Pt-CO groups (~5%) was transformed



band near 2115 cm⁻¹ (γ) (Fig. 1). Practically all the CO chemisorbed on Pt was oxidized to CO₂ partly yielding physically adsorbed CO₂ (band at 7350 cm⁻¹) and partly chemisorbed CO₂ on the support (formation of carbonate species). But the Re-CO species in Re/Al₂O₃ was much less sensitive to the same oxygen treatment; only the intensity of the B band decreased while its frequency remained unchanged (Fig. 1).

During the oxygen treatment of a CO-covered bimetallic catalyst, the Pt-CO species were mainly oxidized while the

Re-CO species were much less disturbed (Fig. 2). Consequently, the oxygen treatment allowed one to distinguish more easily between the A and B bands.

b. (Pt + Re)/ α -Al₂O₃ catalysts. The (H₂PtCl₆ + Re₂O₇)/ α -Al₂O₃ samples were submitted to three hydrogen reducing treatments:

- i. Evacuation under vacuum at 500°C and subsequent reduction at 500°C.
- ii. Evacuation under vacuum at room temperature, and then heating under hydrogen up to 500°C.
- iii. The same as (ii) but the final temperature of heating under hydrogen and vacuum was 700°C.

The optical density and the frequency of the A band were about the same whatever the reducing treatment. Moreover, the band due to the Pt₂CO species was always very weak and the B band could be detected only when x_{Re} was >60.

Figure 3 shows an almost linear decrease of the optical density of the A band, plotted

for a constant weight of sample, when χ_{Re} increased from 0 to 100.

The variation of the frequencies of the A and B bands with χ_{Re} are reported in Fig. 4. The νCO frequency of the (Re-CO) species was evaluated, when possible, after the oxygen treatment of the CO covered sample. A smooth decrease of the νCO frequency of the A band was observed when χ_{Re} increased from 0 to 87.5. The same was apparently true for CO adsorbed on Re for $67.5 \leq \chi_{\text{Re}} \leq 100$ in spite of having only a few experimental points.

c. $(\text{Pt} + \text{Re})/\gamma\text{-Al}_2\text{O}_3$ catalyst. Only the reducing treatment (i) was carried out. A linear decrease of the optical density (OD) of the A band was observed when χ_{Re} increased (Fig. 5). Figure 5 also reports the ratio of the OD of the Pt_2CO band over the OD of the PtCO band as a function of χ_{Re} . The decrease in the intensity of the νCO band as χ_{Re} increases is found to be much more rapid for the bridged species than for the linear species. The variation of the frequencies of the A and B bands are

reported in Fig. 6 as a function of χ_{Re} . As previously, the frequency of the B band is related to samples which were treated under oxygen after the chemisorption of CO. The frequencies of the A and B bands are shifted as for the $\alpha\text{-Al}_2\text{O}_3$ supported catalysts, but the B band could be observed over a larger range of χ_{Re} values.

2. Electron Microscopy

a. $(\text{Pt} + \text{Re})/\alpha\text{-Al}_2\text{O}_3$. The direct observation method was applied. The $\alpha\text{-Al}_2\text{O}_3$ carrier was found to be composed of particles with very different shapes and sizes. The Pt particles in $\text{Pt}/\alpha\text{-Al}_2\text{O}_3$ ($\phi \sim 30$ to 40 \AA) were preferentially deposited on the small Al_2O_3 particles while the big Al_2O_3 particles were less populated. When χ_{Re} increased, the range in the size of the metallic particles increased ($\phi \sim 20$ to 100 \AA). Some metallic Re particles were observed in $\text{Re}/\alpha\text{-Al}_2\text{O}_3$, the mean particle size of which was about 40 \AA .

b. $(\text{Pt} + \text{Re})/\gamma\text{-Al}_2\text{O}_3$. The average size of the metallic particles determined by the

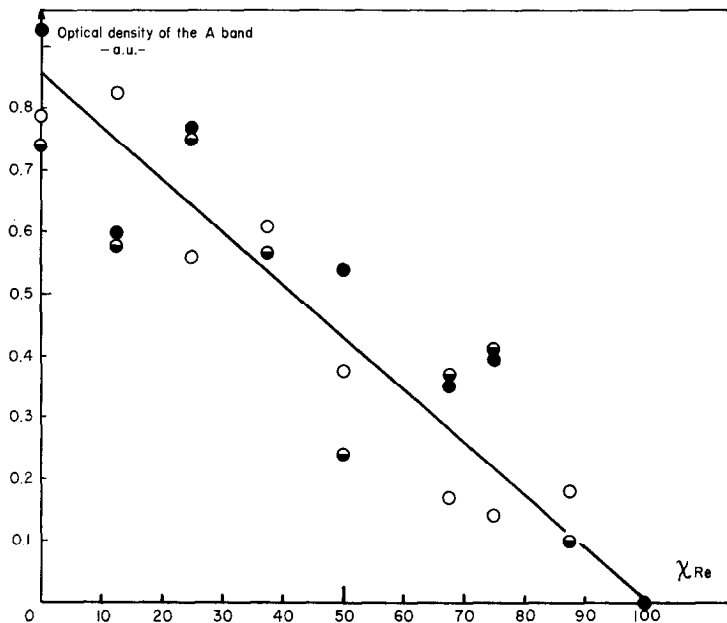


FIG. 3. Optical density of the A band (Pt-CO species) against χ_{Re} in $(\text{Pt} + \text{Re})/\alpha\text{-Al}_2\text{O}_3$. (●) pretreatment (i); (●) pretreatment (ii); (○) pretreatment (iii).

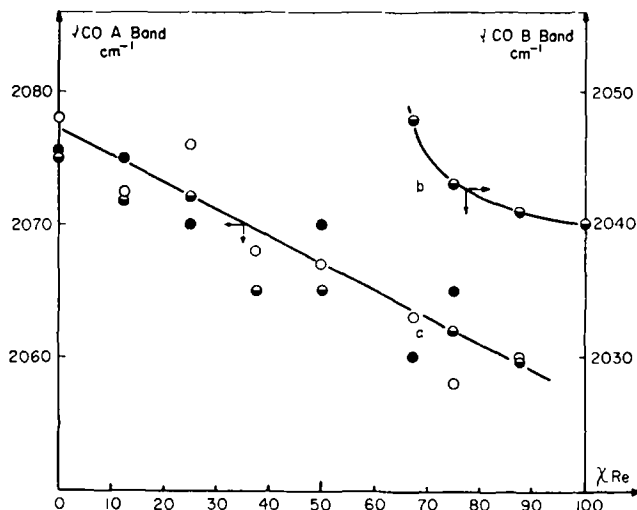


FIG. 4. ν CO frequencies of the A band (Pt-CO species) (a) and B band (Re-CO species) (b) as a function of χ_{Re} in (Pt + Re)/ α -Al₂O₃ catalysts.

extractable replica method was about 25 Å, for $0 \leq \chi_{\text{Re}} < 50$. When χ_{Re} was over 50, the number of metallic particles observed decreased progressively and we have not been able to detect Re particles in Re/ γ -Al₂O₃. It is likely that the metallic phase was partly dissolved during the HCl, HF aqueous solution treatment and the percentage of metal dissolved increased with χ_{Re} .

3. H₂-O₂ Titration Measurements in the Thermobalance

a. Procedure. The hydrogen reduction and desorption pretreatments were performed at 500°C. The adsorption measurements were carried out at room temperature (gas pressure \sim 100 Torr; time of gas-solid contact \sim 20 min; time of gas evacuation \sim 20 min). We only took into account the weight changes observed under vacuum.

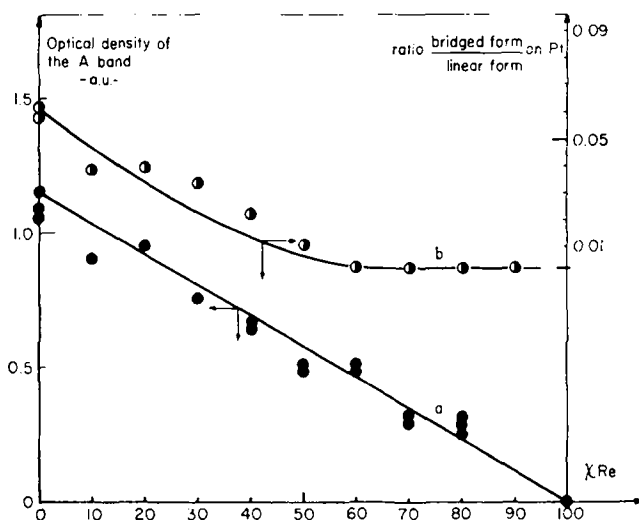


FIG. 5. Adsorption of CO on (Pt + Re)/ γ -Al₂O₃ as a function of χ_{Re} . (a) Optical density of the A band (Pt-CO species); (b) ratio (bridged form)/(linear form) of CO chemisorbed on Pt.

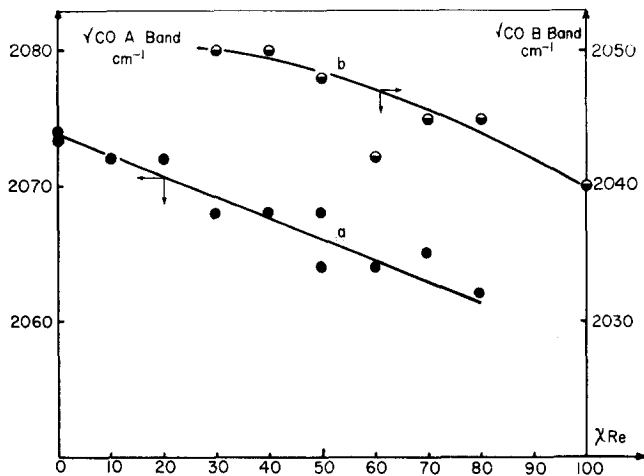


FIG. 6. νCO frequencies of the A band (Pt-CO species) (a) and B band (Re-CO species) (b) as a function of χ_{Re} in (Pt + Re)/ $\gamma\text{-Al}_2\text{O}_3$.

Figure 7 gives the definition of the weight changes observed in each successive step of the $\text{H}_2\text{-O}_2$ cycles. During the initial chemisorption of hydrogen the weight change (HC) was generally too low to be

considered as significant. On the other hand, the following O_2 titration of the irreversibly chemisorbed hydrogen gave a very reproducible increase of weight of the sample $(\text{OT})_1$. The subsequent H_2 titration

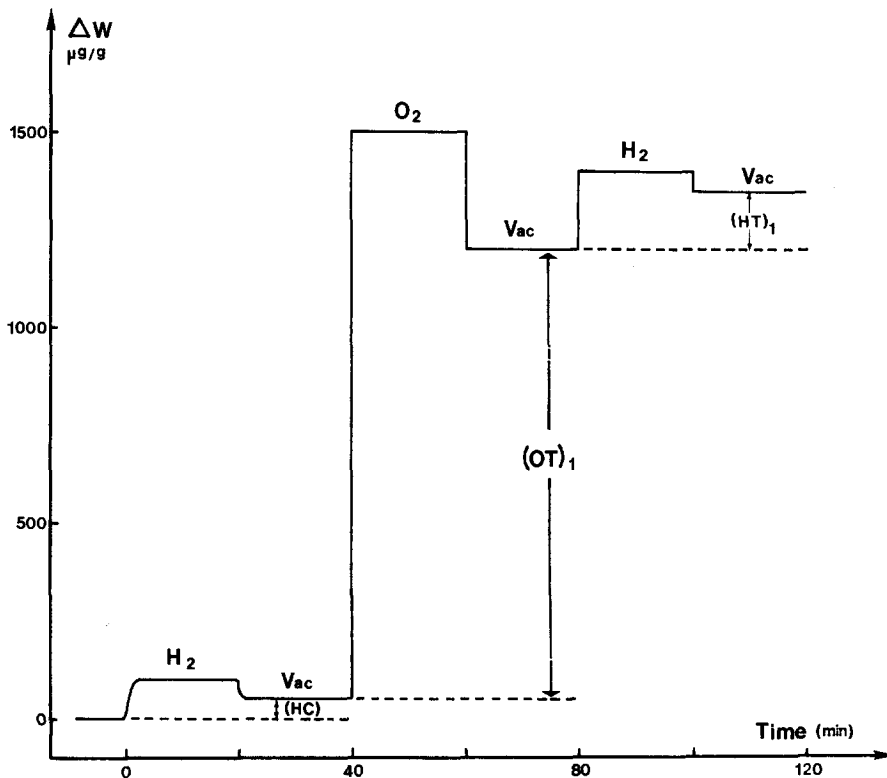


FIG. 7. Schematic representation of the weight change of Pt/ $\gamma\text{-Al}_2\text{O}_3$ in the course of the first $\text{H}_2\text{-O}_2$ cycle performed at 25°C .

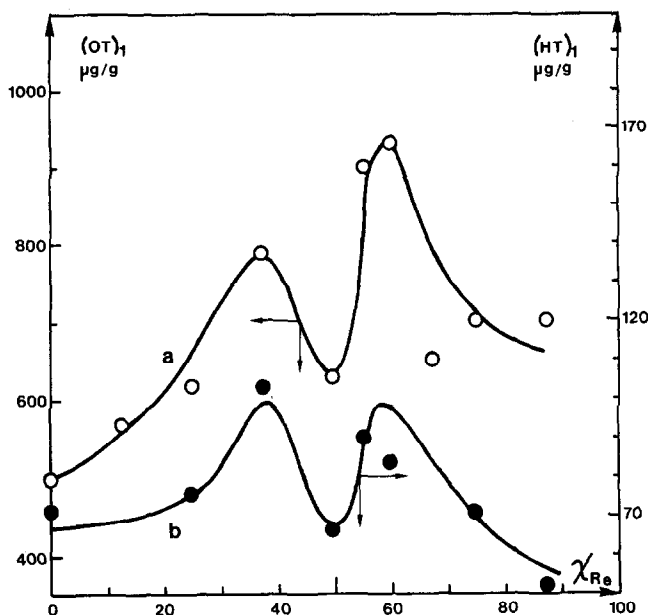


FIG. 8. First oxygen titration $(OT)_1$ (a) and first hydrogen titration $(HT)_1$ (b) as a function of χ_{Re} in $(Pt + Re)/\alpha-Al_2O_3$.

of the chemisorbed oxygen gave a further increase of weight, designated $(HT)_1$. The water formed during the $(OT)_1$ and $(HT)_1$ measurements was quantitatively chemisorbed by either Al_2O_3 support. But only the $\gamma-Al_2O_3$ carrier allowed us to carry out a greater number of successive H_2-O_2 cycles at room temperature, without evidence of water desorption from the support.

b. $(Pt + Re)/\alpha-Al_2O_3$. The variations of $(OT)_1$ and $(HT)_1$ as a function of χ_{Re} are reported in Fig. 8. An increase in the values of both $(OT)_1$ and $(HT)_1$ with χ_{Re} is observed at first, followed by a decrease when χ_{Re} becomes greater than 60. The minima observed when $\chi_{Re} = 50$ may not be considered as definitively established, owing to the insufficient number of experi-

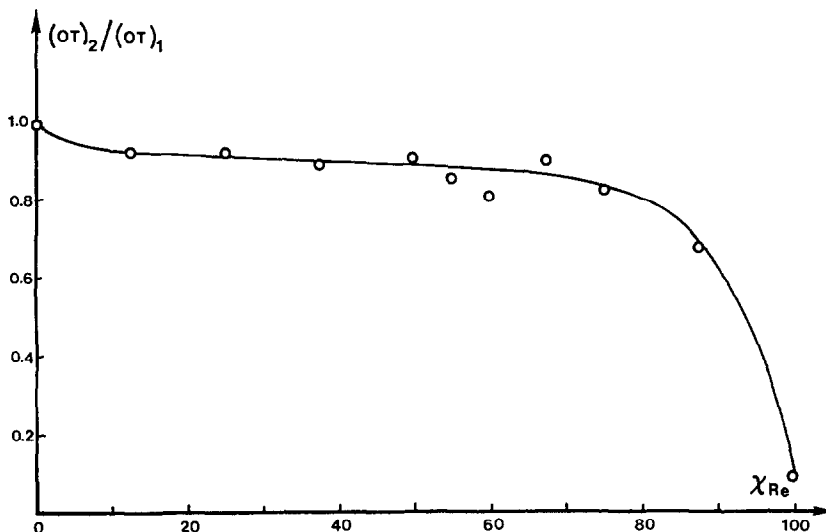


FIG. 9. Ratio of second $(OT)_2$ to first $(OT)_1$ oxygen titration against χ_{Re} in $(Pt + Re)/\alpha-Al_2O_3$.

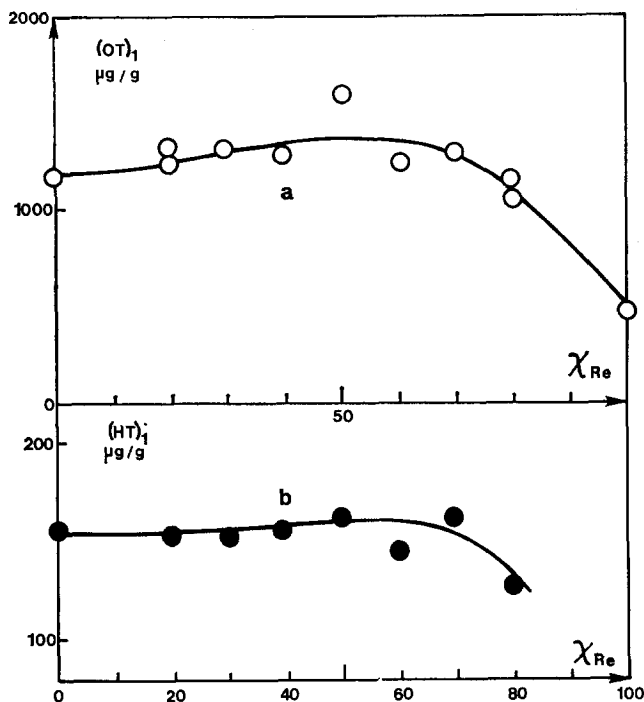


Fig. 10. First oxygen titration $(OT)_1$ (a) and first hydrogen titration $(HT)_1$ (b) against χ_{Re} in $(Pt + Re)/\gamma-Al_2O_3$.

mental points near that particular composition.

The variation of the ratio of $(OT)_2$ (second oxygen titration) to $(OT)_1$ against χ_{Re} is reported in Fig. 9. This ratio is practically 1 on Pt/Al_2O_3 and is slightly lower than 0.1 on Re/Al_2O_3 . It remains practically constant at about 0.9 for a large composition range of the bimetallic catalysts.

c. $(Pt + Re)/\gamma-Al_2O_3$. The variations of $(OT)_1$ and $(HT)_1$ as a function of χ_{Re} are reported in Fig. 10. The values of $(OT)_1$ and $(HT)_1$ do not vary very significantly for a large composition range but decrease somewhat at the highest values of χ_{Re} . The ratio of the second oxygen titration $(OT)_2$ to the first one $(OT)_1$ was only slightly lower than 1 up to $\chi_{Re} = 80-90$ but was only ~ 0.1 in $Re/\gamma-Al_2O_3$. With $\gamma-Al_2O_3$ as carrier, it was possible to measure accurately $(OT)_n$ and $(HT)_n$ during up to about 6(H_2-O_2) cycles

performed successively at room temperature. The variations of $(OT)_n/(OT)_1$ and of $(HT)_n/(HT)_1$ as a function of the number n of the titration experiment are reported in Fig. 11, for $\chi_{Re} = 60$. They show a smooth decrease of (OT) and (HT) when n increases and no evidence for any plateau, up to $n = 6$ at least.

In further experiments over the $\chi_{Re} = 80$, $\gamma-Al_2O_3$ supported catalyst practically the same values of $(OT)_1$ or $(HT)_1$ were found if the O_2 or H_2 titrations were performed at $-78^\circ C$ instead of $+25^\circ C$. The O_2 or H_2 pressure was also found to be of minute importance in the 10 to 100 Torr range. Hence the values of $(OT)_1$ and $(HT)_1$ may be considered as independent of the experimental conditions for a rather large range of temperatures and of gas pressures.

d. *Mechanical mixture of $Pt/\gamma-Al_2O_3$ and $Re/\gamma-Al_2O_3$.* Our purpose was to compare a co-impregnated catalyst ($\chi_{Re} = 80$) with a mechanical mixture of Pt/Al_2O_3 and $Re/$

Al₂O₃ of the same composition. Hydrogen prereduced Pt/γ-Al₂O₃ and Re/γ-Al₂O₃ were hand-mixed in an agate mortar for a few minutes. The value of (OT)₁ found for the mixture (720 μg/g) was not very different from the value calculated from both monometallic catalysts studied separately (600 μg/g). But the ratio (OT)₂/(OT)₁ of the second to the first oxygen titrations performed at 25°C was 0.65 in the mechanical mixture instead of only 0.3 as calculated from the experiments carried out over Pt/γ-Al₂O₃ and Re/γ-Al₂O₃ separately.

4. H₂, O₂ Volumetric Chemisorption and Titration Measurements over Re/α-Al₂O₃

The aim of these experiments was to corroborate the stoichiometries assumed for the surface reactions of H₂ and O₂ with Re, which have been much less investigated in the past than in the case of Pt. Since the gravimetry was rather insensitive in the hydrogen chemisorption measurements, the hydrogen chemisorption and titrations were more especially considered in the volumetric experiments. The H₂ (or O₂) pressure was

TABLE I
H₂, O₂ Chemisorption and Titration over
Re/α-Al₂O₃

No.	Operation	Gas vol (NTP cm ³ /g)	
		H ₂	O ₂
1	Cooling from 500 to 25°C under H ₂	0.28	
2	O ₂ titration of chemisorbed H, at 25°C		0.39
3	H ₂ titration of chemisorbed O: a: at 25°C b: at 500°C, followed by cooling at 25°C	~0	0.87
4	H ₂ chemisorption at 25°C	~0	
5	O ₂ chemisorption at 25°C		0.255

increased by increments of ~10 Torr up to ~50 Torr. The experimental straight lines obtained when reporting the gas volume introduced into the apparatus versus the equilibrium pressure, were extrapolated to zero pressure. The gas volumes determined in this way are reported in Table 1, together with the experimental conditions. The H₂ volume chemisorbed during cooling from 500 to 25°C under hydrogen was first measured (operation No. 1). The sample was then evacuated at 25°C, and the

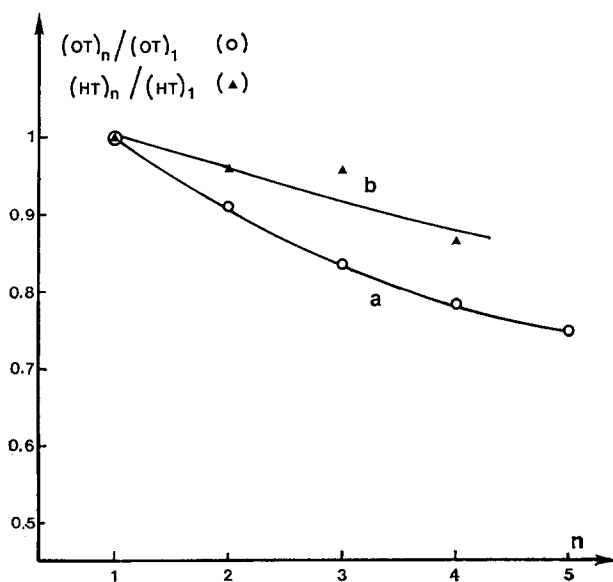


FIG. 11. Variation of (OT)_n/(OT)₁ (a) and of (HT)_n/(HT)₁ (b) with n, the number of the O₂ or H₂ titration experiment ((Pt + Re)/γ-Al₂O₃, χ_{Re} = 60).

chemisorbed hydrogen titrated with O₂ (operation No. 2). The sample was then evacuated again at ambient temperature; only a small fraction of the chemisorbed oxygen was titrated by H₂ at 25°C (operation No. 3a). But heating for a short time (~10 min) in H₂ at 500°C, followed by cooling to 25°C, was sufficient to titrate the remaining oxygen chemisorbed on Re (operation No. 3b). Operation Nos. 4 and 5 refer to H₂ and O₂ chemisorption measurements, carried out after reducing and outgassing the sample at 500°C in each case.

DISCUSSION

Attention will be successively focused on (i) the interactions between both Pt and Re metals (existence of alloy particles or of separated particles of Pt and Re) (ii) the overall dispersion $D(\text{Pt} + \text{Re})$ of the metal phase defined as the relative percentage of (Pt + Re) exposed (iii) the surface composition of the (Pt + Re) metal phase.

1. Interactions between Pt and Re

The X-ray analysis and the electron diffraction experiments did not make it possible to characterize the actual catalysts. Nevertheless, several points may be considered:

a. from the phase diagram of the bulk (Pt + Re) system Pt and Re may dissolve respectively about 40% Re and 40% Pt (8). These limits of solubility are increased in the case of small particles, according to theoretical considerations (9). Therefore Pt and Re, for particle size between 20 and 100 Å, are able to form homogeneous solid solutions in practically the whole range of composition.

b. the reduction by hydrogen of H₂PtCl₆ and Re₂O₇ supported on either α - or γ -Al₂O₃ is largely simultaneous (1), and this coreduction process makes the alloying of Pt and Re easier,

c. in the (H₂-O₂) cycles over Re/Al₂O₃ at 25°C, a large difference between the first (OT)₁, and second (OT)₂, oxygen titrations were observed. The low reducibility of the oxygen chemisorbed on Re by H₂ at 25°C, is in agreement with previous works by Kubicka (10) and Menon *et al.* (11). But in the bimetallic catalysts studied here the oxygen chemisorbed by Re was to a very large extent reducible by hydrogen at room temperature. Hence some interaction between Pt and Re takes place. Nevertheless, the results obtained with the mechanical mixture of Pt/ γ -Al₂O₃ and Re/ γ -Al₂O₃ give evidence that this interaction may be observed to some extent even when Pt and Re are not alloyed. In fact, the migration of active hydrogen H* formed on the surface of Pt on to the Re particles via the support [hydrogen spillover (for review articles, see for instance Ref. (12))] may account for an increase in the reducibility of the oxygen chemisorbed by Re. If some Pt and Re particles were in contact a direct transfer of H* from the Pt to the Re particles could also take place.

The increase in the ratio of (OT)₂ to (OT)₁ at the high values of χ_{Re} in the α -Al₂O₃ supported catalysts (Fig. 9) suggests the presence in those Re-rich catalysts of a small amount of pure Re particles not submitted to the influence of Pt during the H₂-O₂ titration cycles. But the percentage of Re present in that state just after the H₂ reduction and vacuum evacuation at 500°C is difficult to estimate. In fact, the oxygen titrations themselves could cause some segregation of Pt and Re, as suggested by the continual decrease in (OT)_n over (OT)₁ and of (HT)_n over (HT)₁ when n increases (see Fig. 11). It is worthwhile to note that the initial state of the reduced catalysts may be restored by a hydrogen treatment at 500°C, since the values of (OT) and (HT) were then the same as after the first reduction treatment. It follows that the segregation of Pt and

Re due to H₂-O₂ successive titrations has a reversible character.

d. the infrared spectroscopy results showing the changes in frequency for the A (Pt-CO) and B (Re-CO) bands (Figs. 4 and 6) and for the ratio of the optical density of bridged CO on Pt to the optical density of linear CO on Pt (Fig. 5) with χ_{Re} are quite similar to the results obtained using the same technique and the same adsorbate over (Ni + Cu)/SiO₂ catalysts (13). The wt% of (Ni + Cu) was nearly 15, and the alloying between Ni and Cu was proved both by X-ray analysis and by magnetic measurements. An electron transfer from the Cu surface atoms to the neighboring Ni surface atoms was considered to explain the shifts of the νCO bands from CO chemisorbed both on Ni and Cu. The increase in the electron density of Ni increases the electron back donation to the π^* orbitals of CO, and hence decreases the force constant of CO chemisorbed on Ni when the copper content increases. The opposite case applies to the Cu surface atoms, and hence a shift towards higher wavenumbers for the νCO band of CO adsorbed on Cu in the presence of Ni is seen. The more rapid decrease in the amount of the bridged form Ni₂CO compared to that of the linear form NiCO as percentage of Cu increased was ascribed mainly to a geometrical effect, that is to the lowering of the number of Ni-Ni adjacent sites due to the dilution of the surface Ni atoms by Cu atoms (13).

From the analogy mentioned above, Pt and Re are considered to be mainly alloyed. The direction of the electron transfer, from Re to Pt, is not unexpected because of the larger electronegativity of Pt in the Pauling scale (2.23 for Pt instead of 1.92 for Re) and of the lower work function of Re (4.95 eV instead of 5.03 eV for Pt) (14). The alloying of most of the Pt and Re atoms is supported by the identical decrease in the νCO frequency of Pt-CO when χ_{Re} increases in the $\gamma\text{-Al}_2\text{O}_3$ supported catalysts

reduced at 500°C and in the $\alpha\text{-Al}_2\text{O}_3$ supported ones reduced either at 500 or 700°C. Nevertheless the CO infrared experiments are not sufficiently sensitive to differentiate between supported (Pt + Re) alloy particles of constant or of variable composition.

2. Overall Dispersion of the Metal Phase

a. *Pt/Al₂O₃*. The chemisorption and titration reactions generally accepted for Al₂O₃ supported platinum [see for instance Ref. (15)] are reported in Table 2, together with the $D(\text{Pt})$ values found for the two Pt/Al₂O₃ catalysts used in the present study. A satisfactory agreement is observed between the various values of $D(\text{Pt})$ if one takes account of (i) the low precision of the H₂ chemisorption gravimetric measurements (reaction 1) and (ii) the chemisorption of 10–15% CO in the bridged form over Pt/ $\gamma\text{-Al}_2\text{O}_3$, the percentage of the CO bridged form being less in Pt/ $\alpha\text{-Al}_2\text{O}_3$. Accordingly a lower difference was observed between the values of $D(\text{Pt})$ obtained either by H₂-O₂ titration (reactions 2, 3) or by CO chemisorption (reaction 5) over $\alpha\text{-Al}_2\text{O}_3$ than over $\gamma\text{-Al}_2\text{O}_3$. The $D(\text{Pt})$ value obtained by oxygen chemisorption (reaction 4) was somewhat less reproducible than the $D(\text{Pt})$ values determined by H₂ or O₂ titration and is hence considered as slightly less reliable. Finally the mean Pt particle size measured by electron microscopy in Pt/ $\gamma\text{-Al}_2\text{O}_3$ (21 Å) corresponds to a $D(\text{Pt})$ value practically

TABLE 2
Relative Percentage of Pt Exposed in Pt/Al₂O₃

No.	Reaction	$D(\text{Pt})$ (%); in:	
		Pt/ $\alpha\text{-Al}_2\text{O}_3$	Pt/ $\gamma\text{-Al}_2\text{O}_3$
1	$\text{Pt}_s + \frac{1}{2} \text{H}_2 \rightarrow \text{Pt}_s\text{H}$	—	53
2	$\text{Pt}_s\text{H} + \frac{1}{2} \text{O}_2 \rightarrow$ $\text{Pt}_s\text{O} + \frac{1}{2} \text{H}_2\text{O}_{\text{sup}}$	20	48
3	$\text{Pt}_s\text{O} + \frac{1}{2} \text{H}_2 \rightarrow$ $\text{Pt}_s\text{H} + \text{H}_2\text{O}_{\text{sup}}$	21	49
4	$\text{Pt}_s + \frac{1}{2} \text{O}_2 \rightarrow \text{Pt}_s\text{O}$	24	46
5	$\text{Pt}_s + \text{CO} \rightarrow \text{Pt}_s\text{CO}$	19	44

equal to that obtained by hydrogen or oxygen titration, assuming 1.1×10^{19} atoms Pt exposed/m².

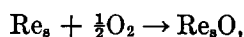
b. Re/Al₂O₃. Only a few papers have been devoted to the measurement of the dispersion of supported Re. Yates and Sinfelt (16) found a very good agreement between the H₂ and CO chemisorption measurements ($p = 100$ Torr; $T = 25^\circ\text{C}$; Re_sH and Re_s-CO supposed surface bonds) and the X-ray line broadening method for a 10% Re/SiO₂ catalyst. Kubicka (17) also obtained a reasonable agreement between H₂ chemisorption measurements and X-ray line broadening for a 1% Re/SiO₂ catalyst; the agreement was less satisfactory when Re was deposited on Al₂O₃.

The situation was not so clear in our case: (i) the X-ray line broadening method was inapplicable, (ii) the extractable replica method which was very suitable for the electron microscope investigations of Pt/Al₂O₃ was more doubtful for Re/Al₂O₃. In fact, the Re particles may be partly reoxidized during their contact with the atmosphere (18) and hence may be partly dissolved in the (HCl + HF) aqueous solution used to remove the Al₂O₃ support. The difficulty of examining Re and (Pt + Re) supported catalysts by electron microscopy has been also mentioned by Freel (19).

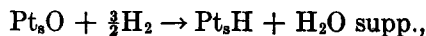
Nevertheless, the values of $D(\text{Re})$ in Re/ α -Al₂O₃ (See Table 3) calculated from the chemisorption titration results reported in Table 1, assuming the same surface reactions as for Pt, are in reasonable agreement. Moreover, the mean Re particle

size measured by electron microscopy (40 Å) corresponds to a $D(\text{Re})$ value $\sim 25\%$ assuming 1.1×10^{19} atoms Re/m² (17) which is in agreement with the chemisorption-titration data. In fact, the main difference between Re and Pt consists in the necessity of a heat treatment under hydrogen in order to obtain (i) complete coverage of Re by H during the H₂ chemisorption measurement and (ii) total reduction of oxygen chemisorbed on Re plus complete coverage of Re by H during the hydrogen titration measurement.

c. (Pt + Re)/Al₂O₃. The first step of the H₂-O₂ titration measurements was the chemisorption of H₂ performed at 25°C. At room temperature, the hydrogen coverage of Re in the bimetallic catalysts is very small as shown by some hydrogen thermal desorption experiments (20). On the other hand the hydrogen coverage of Pt in (Pt + Re)/Al₂O₃ may be supposed to be about the same as in Pt/Al₂O₃, from the same H₂ TPD experiments. Consequently the first oxygen titration (OT)₁ should correspond at least to a first approximation to the following surface reactions



and the first hydrogen titration (HT)₁ to the surface reactions:



It follows that the ratio of (HT)₁ to (OT)₁, both expressed in weight change units, should be theoretically 0.125. Figure 12 shows good agreement between the experiment values of (HT)₁/(OT)₁ and the theoretical one for a large range of composition in both series of catalysts. From the above equations it follows also that knowledge of the surface composition of the metal phase is necessary for an accurate calculation of its overall dispersion $D(\text{Pt} + \text{Re})$ from (OT)₁. In the absence of

TABLE 3

Relative Percentage of Re Exposed in Re/ α -Al₂O₃

Operation described in Table 1 as No.	$D(\text{Re})$ (%)
1 (H ₂ chemisorption)	23
2 (O ₂ titration)	21.5
3b (H ₂ titration)	24
5 (O ₂ chemisorption)	21

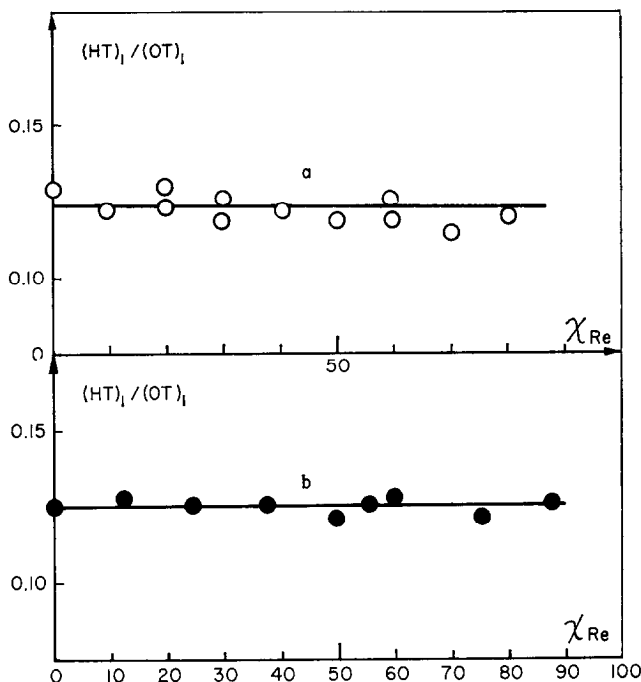


FIG. 12. Ratio of $(HT)_1$ over $(OT)_1$ as a function of χ_{Re} either in $(Pt + Re)/\gamma-Al_2O_3$ (a) or in $(Pt + Re)/\alpha-Al_2O_3$ (b).

quantitative data about the surface composition, we have calculated $D(Pt + Re)$ assuming that the surface composition is equal to the overall composition of the $(Pt + Re)$ phase as given by χ_{Re} . That the surface and overall compositions do not differ very much from each other will be argued below. The mean number of oxygen atoms taken up per exposed metal atom during the first oxygen titration is:

$$1 + 0.5 \times \frac{100 - \chi_{Re}}{100}$$

The values of $D(Pt + Re)$ calculated from $(OT)_1$ (Figs. 8 and 10, curves a) are reported as a function of χ_{Re} in Fig. 13. In the $\gamma-Al_2O_3$ supported catalysts (curve a) the relative percentage of $(Pt + Re)$ exposed is practically constant ($\sim 60\%$) for a very large range of composition of the bimetallic catalysts and slightly greater than in $Pt/\gamma-Al_2O_3$ [$D(Pt) \sim 50\%$]. The variation of $D(Pt + Re)$ over the $\alpha-Al_2O_3$

support is more pronounced, increasing from ~ 20 in $Pt/\alpha-Al_2O_3$ to $\sim 47\%$ when $\chi_{Re} = 60$. But it should be emphasized that $D(Pt + Re)$ over the $\alpha-Al_2O_3$ support depends very significantly on the details in the experimental procedure during the initial hydrogen reduction treatment. In fact, in another set of experiments performed in a different apparatus on the same co-impregnated catalysts the variation of $D(Pt + Re)$ against χ_{Re} over the $\alpha-Al_2O_3$ support was found to be rather small (21). This effect was not observed in the $\gamma-Al_2O_3$ -supported catalysts. This arises from the strong interactions detected between the rhenium oxide and $\gamma-Al_2O_3$. On the other hand the rhenium oxide which is to a large extent simply deposited on $\alpha-Al_2O_3$ is then available for many migration effects during the drying and the initial hydrogen reduction treatments (1, 22).

3. Surface Composition of the Metal Phase

Menon *et al.* (11) report that the first oxygen titration gives the concentration of exposed platinum plus rhenium and that the second one gives the concentration of exposed platinum. It is thus possible to measure the surface composition as well as the overall dispersion of the metal phase. This method necessitates the non-titration of oxygen chemisorbed by Re under hydrogen at 25°C even in the presence of platinum. From the present study this last assumption may only apply to alumina-supported catalysts in which Pt and Re form two separate phases without any interaction. The catalysts studied by us are not relevant to the method proposed by Menon *et al.* (11) since the oxygen chemisorbed by Re was found to be essentially reducible at the room temperature in the presence of Pt. Even after about 5 successive H_2-O_2 cycles no plateau was observed in the value of (OT), (HT), which would

correspond to the separate titration of the exposed platinum.

Another method has been proposed by Savostin *et al.* (23). The catalysts were prepared by successive impregnations of Al_2O_3 by $HReO_4$ and then by H_2PtCl_6 as aqueous solutions, the two impregnations being separated from each other by calcination in air at 500°C. The amounts of metals exposed after hydrogen reduction at 500°C were evaluated by oxygen chemisorption chromatographic measurements. In order to consider more than the overall dispersion of the (Pt + Re) phase, these authors assumed that the concentration of Re exposed in a bimetallic catalyst was the same as in the monometallic Re/Al_2O_3 catalyst with the same content of Re.

Engels *et al.* (24) reported it is possible to show the surface enrichment of the (Pt + Re) phase in one element from CO chemisorption measurements, the CO coverage on Pt being significantly greater than the CO coverage on Re.

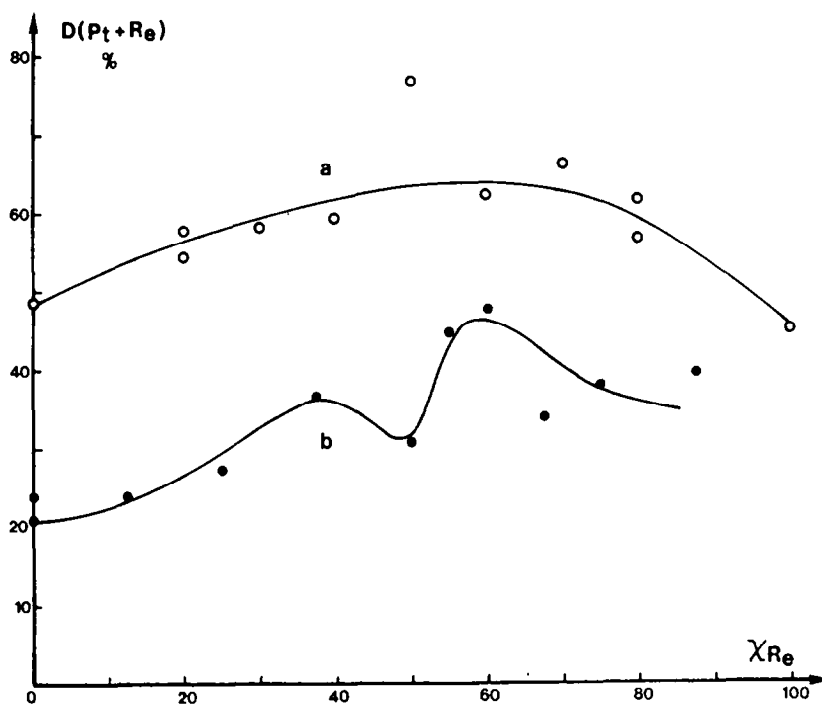


FIG. 13. Overall dispersion (%) of (Pt + Re) in (Pt + Re)/ γ - Al_2O_3 (a) and (Pt + Re)/ α - Al_2O_3 (b).

The experimental results presented above do not give a quantitative method for the separate measurement of the concentration of exposed Pt and Re. Nevertheless, the linear decrease of the optical density of the ν CO band from Pt-CO (Fig. 5, curve a) together with the only small variation of the overall dispersion $D(\text{Pt} + \text{Re})$ of the metal phase (Fig. 13, curve a) when χ_{Re} increases in (Pt + Re)/ γ -Al₂O₃ suggests strongly that in this series of catalysts the surface composition of the metal phase does not differ much from the overall composition as given by χ_{Re} . In the α -Al₂O₃ supported catalysts the optical density of the ν CO band from Pt-CO decreases also linearly when χ_{Re} increases (Fig. 3) while $D(\text{Pt} + \text{Re})$ shows a very significant increase compared to the monometallic platinum catalyst (Fig. 13, curve b). At first sight this would suggest a rhenium enrichment of the surface of the metal phase, compared to the overall composition. But we prefer the alternative explanation based on a smaller variation of the overall dispersion of the (Pt + Re) phase as a function of χ_{Re} for the samples studied in infrared spectroscopy than for those submitted to the H₂-O₂ titration measurements.

In fact, the chemisorption of very little hydrogen on Re either in the mono- or bimetallic form at 25°C, after reduction and evacuation at 500°C, suggested the possibility of titrating the exposed platinum by "selective" hydrogen chemisorption at 25°C. Preliminary experiments have been performed on two α -Al₂O₃-supported catalysts ($\chi_{\text{Re}} = 25$ and 50), the platinum plus rhenium exposed in the same samples being also measured by oxygen titration as discussed above. Identical values have been found for the surface composition and for the overall composition of the metal phase in both catalysts, which may not be fortuitous. However, the chemisorptive properties of Re towards hydrogen necessitate further work since hydrogen chemi-

sorption by alumina or silica supported Re at room temperature has been observed by others (16, 17). Very recently Ducros *et al.* (25) have shown that one oxygen atom chemisorbed on Re prevents the subsequent hydrogen chemisorption of about 6 hydrogen atoms at room temperature. A phenomenon of this kind could account for the behavior of the present catalysts, the rhenium of which appears to chemisorb oxygen normally at room temperature but not hydrogen. We could imagine, for instance, a limited reoxidation of the metal phase during the evacuation at 500°C following the hydrogen reduction treatment, or the presence of small amounts of oxygen dissolved in the metal particles. The presence of platinum does not appear to permit the chemisorption of H₂ on Re at room temperature in the bimetallic catalysts. This is not surprising if one considers that Pt is catalyzing the hydrogen reduction of most but not absolutely all the oxygen chemisorbed on Re, at 25°C; moreover, Pt could not catalyze the reduction of oxygen present in the first sublayers of the metal particles. We consider that the method of titration of the exposed platinum by selective chemisorption of H₂ on Pt at 25°C could well be confined to the actual catalysts reduced and pretreated under our experimental conditions.

In conclusion: (1) platinum and rhenium form alloys in the bimetallic alumina supported catalysts; electron transfer takes place in the direction from Re to Pt atoms; (2) the percentage dispersion of the platinum plus rhenium metal phase is almost independent of the percentage of Pt versus (Pt + Re) for a large range of composition, when the support is γ -Al₂O₃. Larger variations of the percentage dispersion of the (Pt + Re) phase occur over a α -Al₂O₃ carrier; these variations depend on the experimental conditions during the initial reduction by hydrogen; (3) the possibility of variation in the bulk composition of the alumina supported (Pt + Re)

alloy particles cannot be inferred from our experiments; (4) the surface composition of the (Pt + Re) alloy metal phase seems to differ by at most a little from the overall composition.

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