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Platinum–Rhenium/Alumina Catalysts

I. Investigation of Reduction by Hydrogen

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Pure Re_2O_7 when heated in a hydrogen atmosphere, sublimes before reduction. However, when Re_2O_7 is mixed with Pt or Pd or Re powder, instead of volatilization complete reduction to metallic Re occurs below 200°C. A strong activation by Pt of the reduction of Re_2O_7 also takes place on Al_2O_3 samples coimpregnated with H_2PtCl_6 and Re_2O_7. With such catalysts, the reduction of Re_2O_7 to metallic Re under 1 atm pressure of hydrogen seems to be complete at a rather low temperature.

INTRODUCTION

The bimetallic catalysts which contain at least one of the Group VIII elements have been extensively studied, mainly in the powder state. The catalytic activity may change with the composition in several ways, according to the reaction being studied and according to the metal couple (*1*). A regular variation of the activity as well as the presence of one or two maxima in the plot of activity against the percentage composition of one element may be observed.

When both metals are supported on a carrier, several additional effects have to be considered. The accurate characterization of the metallic phase is more difficult, as a consequence of the low metal concentration and of the small particle size. Furthermore, the phase diagrams known for the bulk metals may be significantly modified under these conditions (*2*). A relevant feature of this kind of catalyst is that there is a marked deviation from the additive behavior of the singly supported metals even when no mutual solubility exists in the bulk state (*3*).

The present study deals with Al_2O_3-supported Pt and Re catalysts, which have various practical applications (*4*), and about which very few theoretical investigations have yet been published (*5*).

The activation of the catalysts by hydrogen and especially the catalytic effect of Pt on the reduction of Re_2O_7 are described. To facilitate the interpretation of the results, studies of the reduction of pure Re_2O_7 and of $H_2PtCl_6 + Re_2O_7$ mixtures have also been made.

EXPERIMENTAL METHODS

I. Samples

1. Re_2O_7 and Additives

The following materials were used: Alfa Inorganics Re_2O_7 (99.99%) maintained in a sealed tube under 1 atm of argon; Pt black; Ag prepared by thermal decomposition of Ag_2CO_3 in air at 300°C, and subsequently heated in H_2 at 300°C; Re prepared by thermal decomposition of $ReCl_3$ in nitrogen at 300°C, and subsequently heated in H_2 at 300°C; Pd moss.

2. *Mixtures of H_2PtCl_6 and Re_2O_7*

Aqueous solutions of H_2PtCl_6 and Re_2O_7 were evaporated to dryness by infrared heating below 50°C. Samples prepared by freeze-drying instead of infrared heating gave the same results.

3. *Re_2O_7 and (or) H_2PtCl_6 Supported on an Al_2O_3 Carrier*

a. Supports. (i) α-Al_2O_3 Péchiney SCS9 with a small amount of δ-Al_2O_3 ($S = 24$ m^2/g; granulometry: 0.31 to 0.4 mm, or 0.08 to 0.1 mm). (ii) Poorly crystallized γ-Al_2O_3 Degussa Oxide C with a small amount of δ-Al_2O_3 ($S = 180$ m^2/g).

b. Impregnation. The Al_2O_3 carrier was impregnated with an aqueous solution of $H_2PtCl_6 + Re_2O_7$. The samples were then dried in air at approximately 110°C.

II. Methods

1. *Thermogravimetry*

A vacuum Sartorius microbalance with a sensitivity of $\simeq 5$ μg was employed. For studying the reduction of unsupported Re_2O_7, 10–15 mg of sample was used, the hydrogen pressure was 100 Torr, the heating rate was 2°C/min and water vapor was trapped at 78°K. When SiO_2, Pt, Pd or Re was added to Re_2O_7, the mixture was simply made in the pan of the microbalance.

For studying the reduction of $(H_2PtCl_6 + Re_2O_7)$ supported on Al_2O_3 a sample of 70–80 mg was used. In the case of γ-Al_2O_3-supported compounds, the blank pan was filled with the same amount of γ-Al_2O_3 as contained in the $(H_2PtCl_6 + Re_2O_7)/\gamma$-$Al_2O_3$ sample. The blank γ-alumina and the $(H_2PtCl_6 + Re_2O_7)/\gamma$-$Al_2O_3$ sample were simultaneously submitted to the same thermal treatment (differential thermogravimetry).

Since the weight loss of α-Al_2O_3 was small compared to γ-Al_2O_3, differential experiments were not necessary for studying the reduction of α-Al_2O_3 supported compounds, and the blank pan was in this case filled with quartz.

2. *Differential Thermal Analysis (DTA)*

The cell used was the same as that described by Fouque *et al.* (*6*). The sample weight was $\simeq 200$ mg, the hydrogen flow rate was 3 liter/hr and the heating rate was 10°C/min.

3. *Volumetry*

The consumption of H_2 during the reduction of $(H_2PtCl_6 + Re_2O_7)/Al_2O_3$ was followed using a Pirani gauge. The sample (100 mg) was evacuated at room temperature and then exposed to hydrogen ($p = 0.8$ Torr). During heating (4°C/min), a pressure drop due to the reduction was observed, since H_2O and HCl were trapped at 78°K. The hydrogen pressure was kept at its initial value by introduction of small calibrated volumes of H_2 into the reduction cell. In this way it was possible to obtain the curve of hydrogen consumption as a function of temperature.

4. *Chemical Analysis*

Pt was analyzed colorimetrically (reduction of $PtCl_6^{2-}$ by $SnCl_2$) and Re was analyzed colorimetrically (in presence of α-furildioxime) or by atomic emission spectroscopy.

RESULTS

1. Re_2O_7, Pure or Mixed with Ag, Pt, Pd, Re

Figure 1 shows the weight loss with temperature under H_2 atmosphere for pure Re_2O_7 and mixtures of Re_2O_7 with 20

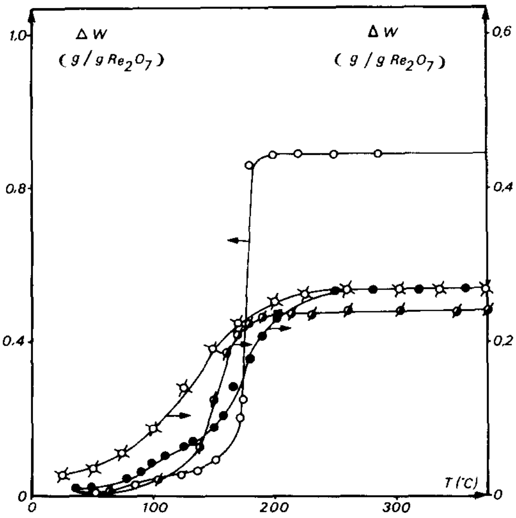

FIG. 1. Weight change of Re_2O_7 at increasing temperature in hydrogen (○) pure Re_2O_7 and Re_2O_7 + SiO_2; (✡) Re_2O_7 + 20% Pt; (∅) Re_2O_7 + 20% Pd; (●) Re_2O_7 + 20% Re.

wt% SiO_2 (quartz), Pt, Pd, or Re. The weight loss of each additive was negligible, compared to the weight loss of Re_2O_7.

The weight loss observed under about 100°C was unreproducible and depended strongly on the time of contact of the sample with the ambient atmosphere. When that time was occasionally very short the weight loss up to about 100°C was negligible compared to the total weight loss of the sample during the thermogravimetry experiment.

Re_2O_7, Pure and Mixed with SiO_2 or Ag

The volatilization of Re_2O_7 gave rise to the marked weight loss observed near 180°C: pure Re_2O_7 deposited on the walls of the reactor tube.

In the presence of Ag, the volatilization of Re_2O_7 was observed at about 200°C, which is a slightly greater temperature than that observed for the $Re_2O_7 + SiO_2$ mixture.

Re_2O_7 + Pt, Pd or Re

No significant volatilization of Re_2O_7 was observed. The weight loss noted above 100°C was due to the reduction of Re_2O_7. The loss of weight between 100 and 400°C was practically equal to the value calculated for the reduction of Re_2O_7 to metallic Re.

When the additive was Pt (10 or 20%) or Pd (20%), the final products at 400°C were mixtures of Re and the additive, as shown by X-ray analysis. In the case of Pd (10%) and Ag (20%) somewhat more complicated diffraction patterns were obtained, which could not be completely identified.

Furthermore, X-ray analysis gave evidence for the presence of metallic Re in a Re_2O_7 + Pt mixture after treatment for a few hours in hydrogen at room temperature.

2. Mixtures of H_2PtCl_6 and Re_2O_7

a. The reduction of H_2PtCl_6 to Pt by H_2 took place slowly at room temperature. It emanated from a few Pt nuclei and was retarded by Re_2O_7. From X-ray analysis, it was concluded that the reduction of Re_2O_7 did not occur under these conditions.

b. During thermal treatment (2°C/min) under hydrogen ($p = 500$ Torr) the mixtures of H_2PtCl_6 and Re_2O_7 were completely reduced to the metallic state at a temperature as low as 200°C, provided that the percentage Pt was greater than 20. X-Ray analysis showed that the final products obtained either at 200 or 500°C were essentially mixtures of Pt and Re.

3. H_2PtCl_6 and (or) Re_2O_7 Deposited on Al_2O_3

Most of the Al_2O_3-supported solids studied had a nearly constant content in (Pt + Re), that is 2 wt%.

In the following we designate 100 × wt% Re/(wt% Pt + wt% Re) by χ_{Re}.

a. Differential Thermal Analysis

($H_2PtCl_6 + Re_2O_7$)/γ-Al_2O_3. Only one exothermic peak due to the reduction was observed. A plot of the temperature of its maximum against χ_{Re} is shown in Fig. 2. The reduction temperature of H_2PtCl_6/γ-

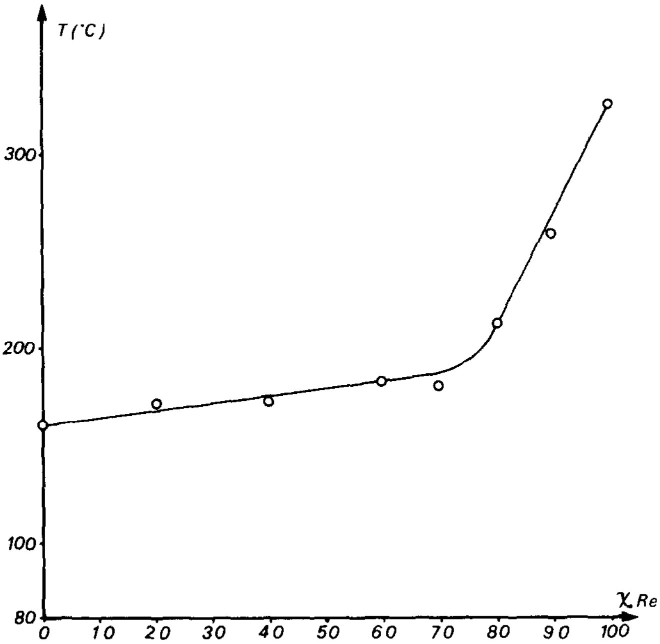

FIG. 2. Temperature of the maximum of the DTA peak in hydrogen, as a function of χ_{Re} in (H_2PtCl_6 + Re_2O_7)/γ-Al_2O_3 coimpregnated catalysts.

Al_2O_3 (near 160°C) is in agreement with the work of Mills *et al.* (7) concerning the reduction of a Pt (0.5%)/Al_2O_3 catalyst. The temperature of reduction (160–180°C) of (H_2PtCl_6 + Re_2O_7)/γ-Al_2O_3 does not change significantly for $0 < \chi_{Re} < 70$. It increases at higher Re content and reaches about 330°C for Re_2O_7/γ-Al_2O_3. For bimetallic catalysts with $\chi_{Re} > 80$ the DTA peak of reduction was broadened because a part of the Re_2O_7 behaved more or less as in Re_2O_7/γ-Al_2O_3.

(H_2PtCl_6 + Re_2O_7)/α-Al_2O_3. A similar variation of the temperature of reduction with the composition was observed. Nevertheless the reduction took place at a lower temperature than with the γ-Al_2O_3 carrier (e.g., peak at 290°C for Re_2O_7/α-Al_2O_3 instead of 330°C for Re_2O_7/γ-Al_2O_3).

b. Thermogravimetry (TG)

Differential thermogravimetry (DTG) of (H_2PtCl_6 + Re_2O_7/γ-Al_2O_3). Heating rate: 4°C/min; $p_{H_2} = 500$ Torr. There was a weight loss of the catalyst when compensated for the carrier alone. The maximum rate of that weight loss occurred at 320, 200 and 180°C for $\chi_{Re} = 100$, 50 and 0, respectively, in agreement with the DTA experiments.

Thermogravimetry of (H_2PtCl_6 + Re_2O_7)/α-Al_2O_3. Heating rate: 8°C/min; $p_{H_2} = 100$ Torr. A few typical curves are shown in Fig. 3. If one considers, for example, the case of $\chi_{Re} = 50$, the weight change below about 220°C is mainly due to the reduction of supported (H_2PtCl_6 + Re_2O_7) while the weight loss above this temperature is mainly due to the support. For $\chi_{Re} = 87.5$, a further change in the slope of the $\Delta W = f(T)$ curve appears near 320°C, that is at the temperature of reduction of α-Al_2O_3-supported Re_2O_7. In the case of $\chi_{Re} = 87.5$ a small part of the Re_2O_7 behaves as in Re_2O_7/α-Al_2O_3.

The TG curves corroborate the DTA experiments, showing that the reduction

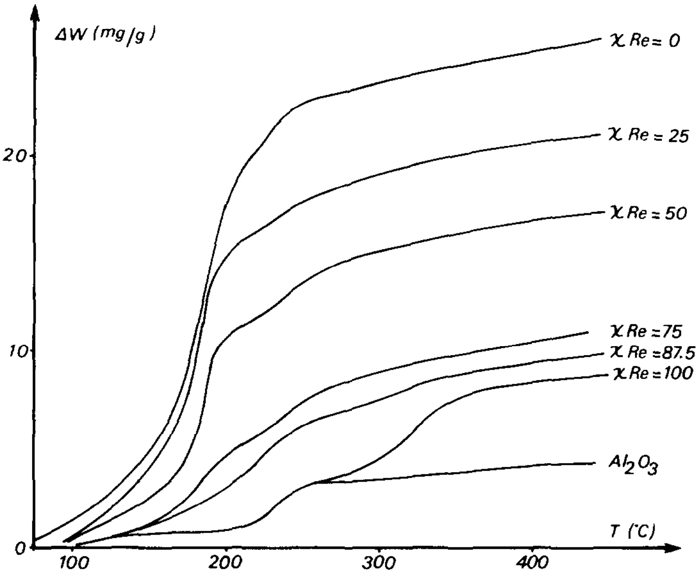

FIG. 3. Weight loss in hydrogen, ΔW, with increasing temperature, of α-Al$_2$O$_3$ and of (H$_2$PtCl$_6$ + Re$_2$O$_7$)/α-Al$_2$O$_3$ coimpregnated catalysts.

occurs in one step at approximately the same temperature in a very large range of the χ_{Re} values.

As far as the difference between the weight losses of (H$_2$PtCl$_6$ + Re$_2$O$_7$)/α-Al$_2$O$_3$ and of α-Al$_2$O$_3$ at 400°C is concerned, its value changes approximately linearly with χ_{Re} over the whole range of composition.

c. *Volumetry*

(H$_2$PtCl$_6$ + Re$_2$O$_7$)/γ-Al$_2$O$_3$. The volume of hydrogen consumed versus the temperature, under a low hydrogen pressure of 0.8 Torr, is shown in Fig. 4 for various values of χ_{Re}. With Re$_2$O$_7$/γ-Al$_2$O$_3$ ($\chi_{Re} = 100$) several hours heating at 600°C were necessary to obtain the equilibrium pressure. Then the reduction was considerably slower than under atmospheric pressure of H$_2$. Figure 4 shows that addition of Pt reduces considerably the temperature of reduction of Re$_2$O$_7$. When $\chi_{Re} < 70$, the temperature of reduction is insensitive to the composition and only slightly dependent on the hydrogen pressure ($T =$ 250–270°C when $p = 0.8$ Torr, $T = 180$°C when $p = 1$ atm from DTA and DTG). Moreover, a release of hydrogen from the catalyst was observed above 350°C when $\chi_{Re} < 50$. This effect is ascribed to the desorption of hydrogen chemisorbed on the metallic phase, in agreement with previous work on the thermal desorption of hydrogen from Pt–Al$_2$O$_3$ catalysts (*8*).

(H$_2$PtCl$_6$ + Re$_2$O$_7$)/α-Al$_2$O$_3$. The shape of the curves $V(\mathrm{H_2}) = f(T)$ was the same as for the γ-Al$_2$O$_3$-supported catalysts. Nevertheless, for a given value of χ_{Re}, the reduction took place at a somewhat lower temperature when the support was α-Al$_2$O$_3$, in agreement with the DTA experiments.

Some values of the volume of hydrogen consumed at the equilibrium H$_2$ pressure of 0.8 Torr at 600°C are reported in Table 1 (second column) both for γ-Al$_2$O$_3$- and for α-Al$_2$O$_3$-supported catalysts.

Since in Al$_2$O$_3$ coimpregnated with H$_2$PtCl$_6$ and Re$_2$O$_7$, these compounds could combine together, it appeared useful to study the reduction of H$_2$PtCl$_6$ (or Re$_2$O$_7$)/Al$_2$O$_3$ samples prereduced before a further impregnation with Re$_2$O$_7$, and

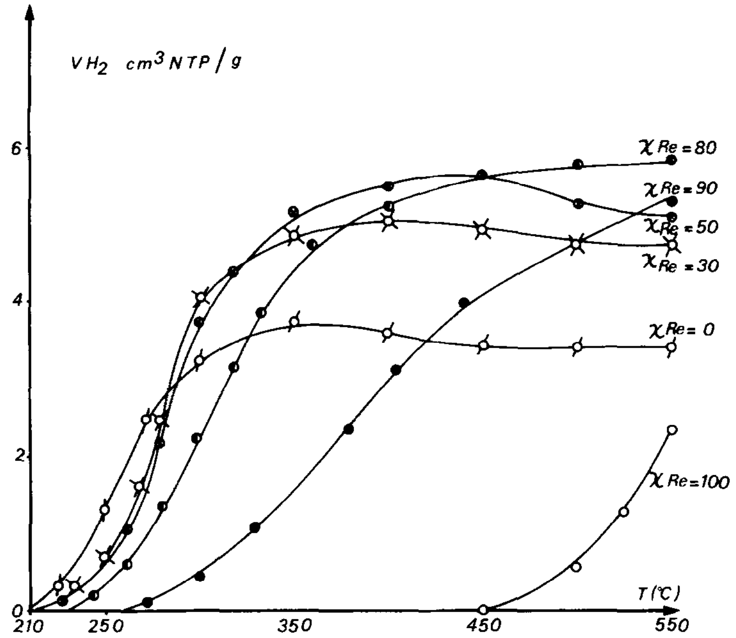

FIG. 4. $V(H_2)$ consumed versus temperature for $(H_2PtCl_6 + Re_2O_7)/\gamma\text{-}Al_2O_3$ coimpregnated catalysts.

the reduction of mechanical mixtures of H_2PtCl_6/Al_2O_3 (or Pt/Al_2O_3) and Re_2O_7/Al_2O_3.

H_2PtCl_6 (or Re_2O_7)/γ-Al_2O_3 prereduced before a further impregnation with Re_2O_7. $H_2PtCl_6/\gamma\text{-}Al_2O_3$ (0.4 wt% Pt) was reduced by H_2 at 500°C and subsequently impregnated with Re_2O_7 in order to produce 2 wt% (Pt + Re) on the support. The reduction curve (Fig. 5, curve I), is similar to that obtained with the coimpregnated solid of the same composition (Fig. 5, curve II) but the prereduction of H_2PtCl_6 to Pt gave rise to a decrease of the initiation reduction temperature of Re_2O_7.

TABLE 1

$V(H_2)$ CONSUMED AT THE EQUILIBRIUM H_2 PRESSURE OF 0.8 TORR AT 600°C

Sample support	χ_{Re}	$V(H_2)$ (cm^3 NTP/g catalyst)	
		Expt	Calc
γ-Al_2O_3	0	3.4	4.5
α-Al_2O_3	0	4.3	4.5
γ-Al_2O_3	100	8.0	7.6
α-Al_2O_3	100	6.4	6.3
α-Al_2O_3	87.5	6.0	6.5[a]
γ-Al_2O_3	80	5.8	6.0[a]
γ-Al_2O_3	50	5.1	5.7[a]
γ-Al_2O_3	30	4.8	4.8[a]

[a] Assuming that the reduction of H_2PtCl_6 requires per gram of Pt the same volume of H_2 as for H_2PtCl_6/Al_2O_3.

A similar experiment was performed with $Re_2O_7/\gamma\text{-}Al_2O_3$ (0.4 wt%Re). Both γ-Al_2O_3-supported Re_2O_7 catalysts (2 wt% Re) prepared in either one or two steps had comparable temperatures of reduction (see Fig. 5, curves III and IV). The total volume of hydrogen consumed at 600°C was about the same, because the prereduced Re was reoxidized to Re_2O_7 in contact with ambient air or (and) with the Re_2O_7 aqueous solution during the second impregnation.

Mixtures of H_2PtCl_6/γ-Al_2O_3 (or Pt/γ-Al_2O_3) and Re_2O_7/γ-Al_2O_3. When a layer ~8 mm thick of $H_2PtCl_6/\gamma\text{-}Al_2O_3$ ($m = 50$ mg) and a layer also ~8 mm thick of $Re_2O_7/\gamma\text{-}Al_2O_3$ ($m = 50$ mg) were superposed in the bottom of the sample pan, the $V(H_2) = f(T)$ curve (Fig. 6, curve I)

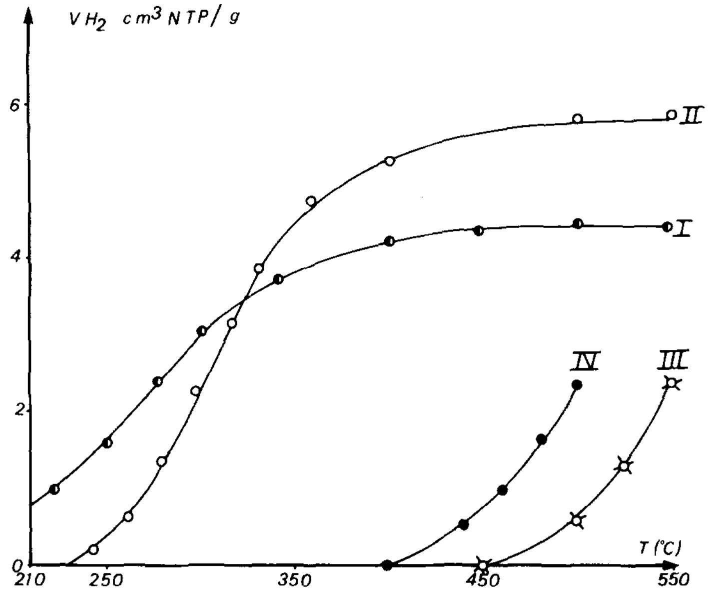

FIG. 5. $V(H_2)$ consumed versus temperature of reduction for: (I) (Pt + Re_2O_7)/γ-Al_2O_3 (χ_{Re} = 80); (II) (H_2PtCl_6 + Re_2O_7)/γ-Al_2O_3 (χ_{Re} = 90); (III) Re_2O_7/γ-Al_2O_3 (one impregnation step); (IV) Re_2O_7/γ-Al_2O_3 (two impregnation steps).

showed clear evidence that the reductions of both catalysts were independent of each other.

On the other hand, when H_2PtCl_6/γ-Al_2O_3 and (Re_2O_7)/γ-Al_2O_3 were mixed (50–50%) in an agate mortar, the $V(H_2) = f(T)$ curve (Fig. 6, curve II) was similar to the curve obtained with the coimpregnated catalyst of the same composition (wt% (Pt + Re) = 2, χ_{Re} = 50).

In a mixture of Re_2O_7/γ-Al_2O_3 with Pt/γ-Al_2O_3, that is with prereduced H_2PtCl_6/γ-Al_2O_3 (Fig. 6, curve III) the consumption of hydrogen began at room

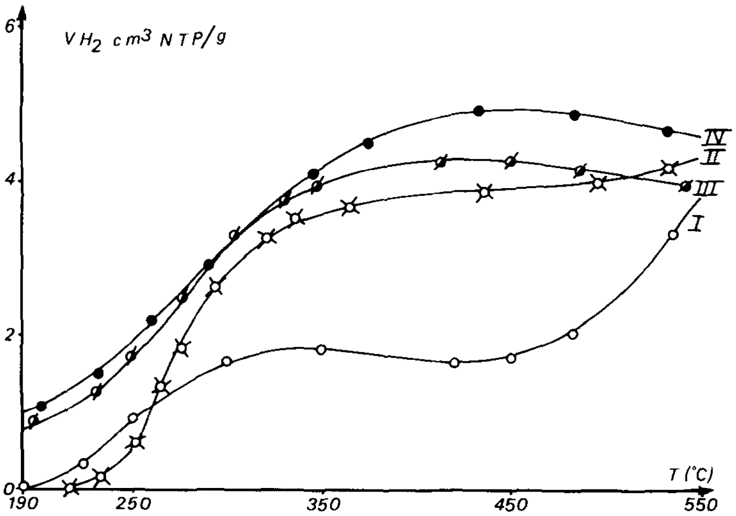

FIG. 6. $V(H_2)$ consumed versus the temperature for: (I) superimposed layers of H_2PtCl_6/γ-Al_2O_3 and Re_2O_7/γ-Al_2O_3; (II) a mixture (50–50%) of H_2PtCl_6/γ-Al_2O_3 and Re_2O_7/γ-Al_2O_3; (III) a mixture (50–50%) of Pt/γ-Al_2O_3 with Re_2O_7/γ-Al_2O_3; (IV) a mixture (50–50%) of (Pt + Re)/γ-Al_2O_3 (χ_{Re} = 30) with Re_2O_7/γ-Al_2O_3.

temperature partly because of the reduction of the oxygen chemisorbed by metallic Pt. Curve IV obtained with a mixture of Re_2O_7/γ-Al_2O_3 with (Pt + Re)/γ-Al_2O_3 ($\chi_{Re} = 30$) is very similar to curve III. Clearly, prereduced H_2PtCl_6/γ-Al_2O_3 and (H_2PtCl_6 + Re_2O_7)/γ-Al_2O_3 ($\chi_{re} = 30$) had approximately the same effect on the reduction of Re_2O_7/γ-Al_2O_3.

d. Chemical Analysis

During the reduction carried out under atmospheric pressure of hydrogen a loss of Re was only observed when the support was α-Al_2O_3 and χ_{Re} was more than about 50 (e.g., Re_2O_7/α-Al_2O_3: % Re after impregnation = 1.9; % Re after reduction = 1.75).

Some experiments were carried out with the purpose of showing a transport of Re oxide inside the catalyst bed during the reduction. Mixtures of 40% H_2PtCl_6/α-Al_2O_3 ($\bar{d}$ = 0.35 mm) and 60% Re_2O_7/α-Al_2O_3 ($\bar{d}$ = 0.1 mm) (mixture I) and of 40% H_2PtCl_6/α-Al_2O_3 ($\bar{d}$ = 0.1 mm) and 60% Re_2O_7/α-Al_2O_3 ($\bar{d}$ = 0.35 mm) (mixture II) were made by shaking together and afterwards were reduced in hydrogen (p = 1 atm) up to 500°C.

The Pt/α-Al_2O_3 and Re/α-Al_2O_3 of mixtures I and II were then separated by screening and submitted for chemical analysis. The results (Table 2) show that the Pt/α-Al_2O_3 catalyst incorporated some Re during the reduction while no transport of Pt to Re/α-Al_2O_3 catalyst occurred at the same time. It is worth while to note that the amount of Re incorporated in Pt/α-Al_2O_3 is larger when the granule size of the Pt-supporting Al_2O_3 is smaller.

TABLE 2

Pt AND Re (wt%) IN H_2PtCl_6/α-Al_2O_3 AND Re_2O_7/α-Al_2O_3[a]

	Support			
Mixture	Composition	Granular size	% Pt	% Re
I	Pt/α-Al_2O_3	0.35 (mm)	1.7	0.2
	Re/α-Al_2O_3	0.1	—[b]	1.69
II	Pt/α-Al_2O_3	0.1	1.8	0.31
	Re/α-Al_2O_3	0.35	—[b]	1.37

[a] Mixed by shaking, then reduced by H_2 at 500°C, and finally separated by screening.

[b] Too low for the analysis to be performed.

DISCUSSION

1. Reduction of Re_2O_7, Pure and Mixed with Ag, Pt, Pd, or Re

The catalytic effect of Pt, Ru or Re on the reduction of Re_2O_7 by hydrogen has already been reported by Smith-Broadbent *et al.* (*9*). Other similar effects are the subject of several recent reviews (*10*). Nevertheless, the magnitude of the effect of Pt on the Re_2O_7 reduction was unexpected, in particular, the formation of metallic Re from Re_2O_7 at 25°C. Pure Re_2O_7 is reduced by H_2 at 300°C to ReO_2 and above 400°C to the metal (*11*), which is a much higher temperature than reported for CuO (nearly 130°C) and NiO (nearly 200°C). CuO, if mixed with Pt, is only slightly reduced by H_2 at room temperature (*12*), and under the same conditions we did not detect any reduction of NiO.

To account for the very pronounced effect of Pt on the reduction of Re_2O_7, it is appropriate to consider the following:

1. Bond *et al.* (*13*) have shown using DTA that the temperature of reduction of oxides by H_2 is decreased by Pd to a greater extent when the cation is initially in a high oxidation state (CrO_3, MoO_3, UO_3, V_2O_5).
2. Re_2O_7, which is strongly deliquescent, is partly transformed into viscous hydrated oxide during contact with air and may thus cover more easily the Pt particles.
3. Because of its low melting point and its high vapor pressure (*11*), Re_2O_7 is able to migrate by surface diffusion and via the gaseous phase to the Pt particles.

4. The activation of hydrogen by Pt is certainly an important step in the process, since Ag does not have the same effect. Re itself can activate hydrogen; the presence of Pt may only be necessary to form the initial Re metallic nuclei. Then, the Re nuclei and Pt can together catalyze the reduction of Re_2O_7. In fact, Smith-Broadbent *et al.* (*9*) have shown that the addition of Re to Re_2O_7 allows the reduction of the oxide to the metal to take place at a lower temperature and under a much lower hydrogen pressure. In the experimental conditions as reported in Fig. 1, Re seems to be effective in reduction of Re_2O_7 at a higher temperature than Pt. This can be related to the slow reduction of oxygen that is chemisorbed on Re (*14*) which is a necessary step before Re can activate H_2.

The ability of the Ag, Re and Pt powders used to activate hydrogen has been tested by the classical WO_3–H_2 reaction, at room temperature. In 5% metal + WO_3 mixtures, the blue color of H_xWO_3 was obtained after 1 hr with Pt and after 15 hr with Re, while no color change was observed for the Ag + WO_3 mixture from the originally yellow sample. Metallic Ni (produced by decomposition of nickel oxalate) was also unable to initiate the color change of WO_3 under the same conditions, in agreement with the work of Ershov *et al.* (*15*). Therefore it is believed that the undetectable reduction of NiO in the presence of Pt at 25°C is partly due to the inability of Ni itself to activate hydrogen in these conditions.

II. Reduction of Re_2O_7 or (and) H_2PtCl_6 Deposited on Al_2O_3

a. Influence of the Hydrogen Pressure on the Temperature of Reduction

The influence of the H_2 pressure is more pronounced in the absence of Pt, as outlined in Table 3. Smith-Broadbent *et al.* (*9*) suggest that the nucleation is the rate determining step in the reduction of Re_2O_7 to metallic Re. Faster nucleation may be obtained using a larger hydrogen pressure or an additive such as Pt (or Re). Hence it is not surprising that the presence of Pt decreases the effect of the hydrogen pressure.

TABLE 3
INFLUENCE OF THE HYDROGEN PRESSURE ON THE TEMPERATURE OF REDUCTION OF (H_2PtCl_6 + Re_2O_7)/γ-Al_2O_3

x_{Re}	p_{H_2} (Torr)	Approx T of reduction (°C)	ΔT (°C)
0	0.8	250	90
	760	160	
50	0.8	270	90
	760	180	
100	0.8	550	220
	760	330	

b. Stoichiometry of the Reduction of H_2PtCl_6 and Re_2O_7

Table 1 (last column) allows us to compare the volumes of H_2 consumed at the equilibrium pressure of 0.8 Torr at 600°C with the values calculated for the reduction of Pt^{4+} to Pt^0 and of Re^{7+} to Re^0 according to the reactions:

$$H_2PtCl_6 + 2\ H_2 \longrightarrow Pt + 6\ HCl, \qquad (1)$$

$$Re_2O_7 + 7\ H_2 \longrightarrow 2\ Re + 7\ H_2O \qquad (2)$$

In these conditions of high temperature and low pressure of H_2, the amount of H_2 chemisorbed by the metal may be neglected (*8*).

H_2PtCl_6/Al_2O_3. The experimental value of $V(H_2)$ is approximately equal to the theoretical value when the support is α-Al_2O_3 and significantly lower when the carrier is γ-Al_2O_3·H_2PtCl_6 is presumably completely reduced to the metal on both supports. H_2PtCl_6 was probably already partly reduced before H_2PtCl_6/γ-Al_2O_3 was exposed to H_2 during the reduction experi-

ment. This may be due to a long storage time of H_2PtCl_6/γ-Al_2O_3 in the ambient atmosphere of the laboratory, where some reducing vapors may occasionally be present. In fact H_2PtCl_6 is very easily reduced to Pt and it has been observed that a mere bubbling of hydrogen in an aqueous solution of H_2PtCl_6 produced metallic Pt particles.

(Re_2O_7/Al_2O_3). The theoretical and experimental values of $V(H_2)$ are similar if we take account of the loss of Re due to the volatilization of rhenium oxide during the reduction (wt% Re after reduction in the volumetric apparatus was 1.8 for Re_2O_7/γ-Al_2O_3 and 1.5 for Re_2O_7/α-Al_2O_3). Hence the reduction of Re_2O_7 to metal is complete at the equilibrium hydrogen pressure of 0.8 Torr at 600°C and this conclusion certainly holds also for a much lower temperature of reduction if the hydrogen pressure is higher, e.g., 1 atm.

($H_2PtCl_6 + Re_2O_7)/Al_2O_3$. The reduction of H_2PtCl_6 and Re_2O_7 to the metals seems also to be complete. To support this view, the theoretical and experimental values of $V(H_2)$ consumed during the reduction are in reasonable agreement (see Table 1), especially when the support was γ-Al_2O_3 which is more efficient than α-Al_2O_3 in avoiding the volatilization of the rhenium oxide.

c. *Remarks About the Mechanism of Reduction*

The temperature of the onset of reduction of Re_2O_7 to metal is determined by the reduction of H_2PtCl_6 itself to the metal which takes place at a temperature nearly independent of the presence of Re_2O_7. Very probably, the reduction of Re_2O_7 to metal starts as soon as some metallic Pt has been formed; hence the reduction of H_2PtCl_6 and Re_2O_7 seems practically simultaneous.

The catalytic effect of supported Pt on the reduction of supported Re_2O_7 may be accounted for by:

The activation of H_2 by Pt and then by Pt and Re;

The migration of Re oxide up to the surface of the metal particles via the gaseous phase or by surface migration on the Al_2O_3 carrier. Whatever the detailed mechanism, the transport of rhenium from particle to particle of Al_2O_3 has been proved by the experiments summarized in Table 2.

An additional effect is the migration of active hydrogen which is formed by contact of molecular H_2 with the metal phase onto the surface of the Al_2O_3 carrier [hydrogen spillover (*10,16*)]. Recently, the existence of this effect has been strongly supported by the experiments of Gardes *et al.* (*17*). These authors have shown that a large amount of active hydrogen may be accumulated on Al_2O_3 if this oxide is heated at about 300°C in the presence of a Ni/Al_2O_3 catalyst in an atmosphere of molecular hydrogen. The active hydrogen accumulated on Al_2O_3 is able to hydrogenate ethylene even at 25°C (*17*). Such a species could certainly promote the nucleation of metallic Re from Re_2O_7 at a lower temperature than molecular hydrogen. Therefore it is likely that hydrogen spillover takes part in the mechanism of the catalysis by Pt of the reduction of Re_2O_7. Nevertheless, this mechanism has not been definitely proved in the present investigation, although we have shown the occurrence of the migration of Re oxide in the catalyst bed.

In conclusion it has been shown that during the activation by hydrogen of $(H_2PtCl_6 + Re_2O_7)/Al_2O_3$ catalysts, H_2PtCl_6 and Re_2O_7 are both reduced to metal, the reduction of Re_2O_7 being strongly catalyzed by metallic Pt.

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