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Effect of Chlorine in the Formation of PtRe Alloys in PtRe/Al_2O_3 Catalysts

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The role of chlorine and the thermal pretreatments of the samples in PtRe alloying during the reduction of Pt/Al_2O_3 and PtRe/Al_2O_3 systems have been examined by using the reaction of *n*-butane hydrogenolysis with the aid of temperature-programmed reduction (TPR) experiments. The presence of chlorine modifies only slightly the TPR profiles, and rhenium reduction is always catalyzed by the presence of platinum. This effect depends strongly on the hydration degree of the support, while it is almost independent of the chlorine content of the sample. However, chlorine greatly decreases the catalytic activity of both Pt and PtRe catalysts in *n*-butane hydrogenolysis. Selectivity to methane (measured as C_3/C_1 ratio) is close to 1 for the platinum samples, while in the PtRe systems it remains close to 0.5 for the chlorine-free catalyst after all the pretreatments, but changes from 0.5 to 1.0 when the chlorinated catalyst is predried at increasing temperatures, indicating differences in the degree of PtRe alloying. Chlorination/dechlorination experiments confirm the role of chlorine on the above results and point to the existence of oxychlorinated Pt and/or Re species that may strongly interact with the progressively dehydrated Al_2O_3 support, leading to higher metallic dispersions and lower PtRe alloying in the chlorinated catalysts after hydrogen reduction. © 1989 Academic Press, Inc.

INTRODUCTION

Several studies using temperature-programmed reduction (TPR) have previously shown (*1–3*) an effect of drying pretreatments on the profile of reduction of PtRe/Al_2O_3 precursors. These studies indicate that the reduction of rhenium in PtRe/Al_2O_3 samples is catalyzed by the platinum and that this effect depends on the degree of hydration of the alumina support, in such a way that both metals are reduced together when the catalyst has been dried at low temperatures (ca. ≤250°C), showing a single low-temperature peak in the TPR profile, while in samples predried at higher temperatures (ca. 500°C) rhenium reduction is retarded and the TPR profile contains at least two peaks. The catalyzed reduction of Re in the samples dried at low temperatures has been explained (*1, 2*) assuming a high mobility of hydrated ReO_x species which can migrate to hydrogen-covered platinum centers, where reduction of rhenium and subsequent alloying with platinum takes place immediately. On the contrary, in samples dried at higher temperatures, the mobility of ReO_x species seems to decrease, so that platinum and rhenium reduce separately and the alloying process is not favored. However, an alternative explanation for the two types of TPR profiles has been given on the basis of spillover of activated hydrogen from the reduced platinum to the rhenium precursor via the alumina support (*3*), assuming that the rate of spillover depends on the degree of hydration of the alumina surface (*4*), so that TPR profiles do not supply direct information on the extent of PtRe alloying.

In fact, rather contradictory results have been reported on the effect of the pretreatments on the state of the metallic phase in PtRe/Al_2O_3 catalysts after hydrogen reduction. So, Wagstaff and Prins (*1*) conclude that, although different TPR profiles are ob-

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TABLE 1

Chemical Analysis and BET Surface Areas of Catalyst Precursors

Sample	%Pt b.w.	%Re b.w.	%Cl b.w.	S_{bet} (m^2/g)
Pt/Al_2O_3-Cl	0.296	—	0.95	183
$PtRe/Al_2O_3$-Cl	0.296	0.311	0.95	187
Pt/Al_2O_3	0.30	—	—	180
Re/Al_2O_3	—	0.29	—	180
$PtRe/Al_2O_3$	0.29	0.29	—	180

tained when the predrying temperature is changed, the same PtRe alloyed phase is always present in the reduced catalyst. On the other hand, from H_2 and O_2 adsorption, Charcosset *et al.* (*5*) find that the amount of unalloyed Re increases and the amount of alloy decreases as the predrying temperature is raised to ca. 500°C, while Isaacs and Petersen (*6*) report that, although the amount of accessible unalloyed rhenium increases as the pretreatment temperature is raised to 300°C, the amount of PtRe alloy is almost independent of the predrying temperature.

In this paper we present a detailed study on the effect of different pretreatments on alloy formation in PtRe catalysts, with and without chlorine. In addition with TPR experiments, catalytic activities and selectivities of the catalysts in hydrocarbon hydrogenolysis have been measured, using this reaction as a test to detect PtRe alloying in the reduced catalysts by measuring their enhanced selectivity to methane, following the method recently proposed by Sachtler *et al.* (*7–9*).

EXPERIMENTAL

Catalysts

The two series of Pt/Al_2O_3 and $PtRe/Al_2O_3$ samples in Table 1 were used. Chlorinated samples, containing a 0.95wt% Cl, were commercial catalysts provided by Akzo Chemie (Ketjen), Amsterdam (Refs. CK303 and CK433). Although details on the preparation of these catalysts were not supplied by the manufacturer, it has been reported (*2*) that commercial precursors are probably calcined at ca. 500°C. Chlorine-free precursors, used as a reference, had been prepared using a Cyanamid PHF γ-Al_2O_3 support, pretreated following the procedure described by Kobayashi *et al.* (*10*), which was impregnated to incipient wetness with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$, NH_4ReO_4, or both. These precursors were dried overnight at 120°C in air, then calcined at 500°C for 3 h, and stored with the commercial samples in a desiccator.

Methods

The same thermal pretreatments were given *in situ* to the samples before all types of experiments (i.e., H_2 adsorption, TPR, and catalytic tests). The temperature was raised at a linear heating rate of 5°C/min under He or synthetic air flows (100 ml/min/g of catalyst), maintaining the selected final temperature for 1 h before the reduction step. Specimens referred to as dechlorinated were prepared from the commercial precursors by flowing wet air (100 ml/min/g) for ca. 100 h at 500°C. When necessary, chlorine-free precursors were chlorinated by injecting pulses of CCl_4 (20 μl) in a He flow (100 ml/min/g) at 200°C before the standard pretreatment. Chlorine contents at the surface of the samples were monitored by XPS with an LHS-10 spectrometer on line with an HP 1000E computer, using the same experimental conditions as those reported elsewhere (*11*).

H/Pt ratios were obtained by extrapolating to zero pressure the linear part of H_2 adsorption isotherms of the samples previously reduced at 390°C under H_2 flow and then outgassed at pressures lower than 10^{-4} Torr for 1 h at the reduction temperature. The isotherms were measured at 25°C with an MKS Baratron (Model 315-BHS-100) capacitance gauge up to an equilibrium pressure of 50 Torr.

TPR experiments were carried out with a conventional TCD system connected to an HP-3054-DL system for data storing and processing. The reactive gas stream (5% H_2

in Ar, 10 ml/min) was passed through 0.5 g of $PtRe/Al_2O_3$ or 1 g of Pt/Al_2O_3 samples, using a constant heating rate of 10°C/min. TC detector response for hydrogen consumption was calibrated using different amounts of CuO (Merck zur analyse, 99% in CuO), being linear in the range 10–200 μmol. Total hydrogen uptakes were obtained by numerical integration of the area under the curve between 200 and 600°C, unless otherwise stated. TPR profiles of the Al_2O_3 supports, after drying under He flow at 25 and 450°C, were recorded without detection of H_2 consumption in the range 25–700°C.

The *n*-butane hydrogenolysis was selected as a "probe" to test the state of the metallic phase obtained after each thermal pretreatment of the precursors since coke deposition, which could change the original state of the metallic phase, does not occur. The reaction tests were performed in a pulse reactor working at atmospheric pressure on 100 mg of catalyst under a hydrogen flow of 25 ml/min, using *n*-butane pulses of 250 μl in the range 300–490°C. Under such experimental conditions reaction rates were dependent only on space velocity (*12*). Products were analyzed by gas chromatography using Porapak Q columns. Activities of samples submitted to different pretreatments were compared taking the total molar conversions at one particular temperature, which was selected in such a way that conversions lower than 75% can be measured for the set of samples. So, due to the high activity of the chlorine-free PtRe catalyst, comparative data including these samples are shown at 340°C, instead of the 390°C used for all other catalysts. Activation energies were calculated from Arrhenius plots for conversions lower than 10%. Up to 490°C the Al_2O_3 supports were totally inactive, and selectivities of the catalysts to isobutane were negligible (<1.5% *M*).

A higher yield to methane in the hydrogenolysis of *n*-butane of $PtRe/Al_2O_3$ catalysts, compared with Pt/Al_2O_3, has been previously reported in the literature (*13*, *14*). The reaction on $PtRe/Al_2O_3$ has been described (*14*) as "multiple hydrogenolysis" (i.e., fission of more than one C–C bond during the reaction of a single hydrocarbon molecule with the surface), contrary to what occurs on Pt/Al_2O_3 catalysts where only "single hydrogenolysis" takes place (i.e., fission of just one C–C bond per molecule). The importance of multiple hydrogenolysis, characteristic of PtRe alloying, was evaluated from the ratio of the molar yields to propane and methane extrapolated to zero conversion, to minimize possible contributions from secondary reactions of the products. This C_3/C_1 ratio takes values ≤ 1 depending on whether single or multiple hydrogenolysis occurs (*14*).

RESULTS

Temperature-Programmed Reduction

(*A*) *Platinum catalysts.* TPR profiles for the Pt/Al_2O_3-Cl precursor, dried under He flow at different temperatures between 25 and 450°C, are shown in Fig. 1A. Hydrogen consumptions included in Table 2 are always slightly lower than the values expected for the reduction process Pt^{4+}/Pt^0 and decrease for increasing drying temperatures. The TPR profiles (Fig. 1A) show two well-resolved reduction steps with maxima at ca. 300 and 430°C for samples submitted

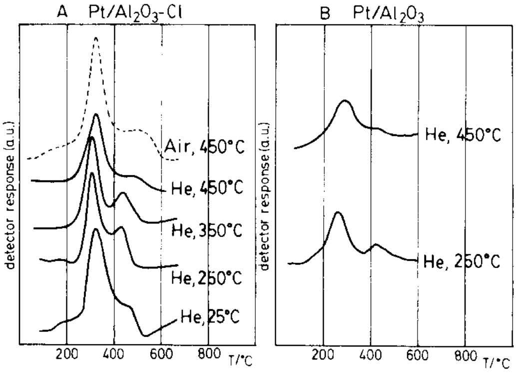

FIG. 1. TPR profiles of Pt catalysts pretreated in flowing He for 1 h at the indicated temperatures: (A) Pt/Al_2O_3-Cl ((---) pretreated in air flow at 450°C, 1 h); (B) Pt/Al_2O_3.

TABLE 2

Temperature-Programmed Reduction: Total Hydrogen Uptakes (μmol/g)

Pretreatment	Pt/Al_2O_3-Cl	Pt/Al_2O_3[a]	$PtRe/Al_2O_3$-Cl	$PtRe/Al_2O_3$[a]
25°C, He, 1 h	28	—	142	—
150°C, He, 1 h	27	—	103	—
250°C, He, 1 h	21	16	111	52
350°C, He, 1 h	22	—	89	—
450°C, He, 1 h	12	13	52	52
450°C, air, 1 h	30	—	56	—
450°C, air, 1 h, H_2O_g, 1 h	29	—	75	—
Reoxidized (350°C) after first TPR run	27	25	54	55

Note. Expected H_2 uptake: $Pt^{4+} \rightarrow Pt^0 = 30$ μmol/g; $Re^{7+} \rightarrow Re^0 = 54$ μmol/g; $Pt^{2+} \rightarrow Pt^0 = 15$ μmol/g; $Re^{4+} \rightarrow Re^0 = 31$ μmol/g; $Re^{7+} \rightarrow Re^{4+} = 23$ μmol/g.

[a] Integrated between 80 and 600°C.

to drying temperatures up to 350°C. However, drying at 450°C produces a net change in the reduction peak at 430°C, which becomes broader and tails toward higher temperatures, while the total hydrogen uptake decreases. These facts suggest that reduction of some platinum has taken place during the preheating at 450°C under inert atmosphere, in good agreement with XANES spectra, that show (*15*) a net reduction of the metallic phase when the sample is outgassed at 450°C.

TPR profiles obtained after preheating the same Pt/Al_2O_3-Cl precursor up to 450°C under air flow have shapes similar to those shown for He in Fig. 1A, although in this case hydrogen uptakes were always closer to the value expected for the Pt^{4+}/Pt^0 reduction (ca. 25–30 μmol/g), indicating that platinum remains fully oxidized when the samples are pretreated under such oxidizing conditions.

On the other hand, as shown in Fig. 1B, TPR profiles for the chlorine-free Pt/Al_2O_3 precursor, dried under a He flow at either 250 or 450°C, are very similar to those obtained for the chlorinated samples, with two slightly broader reduction maxima at ca. 280 and 430°C. However, hydrogen consumptions in this case (Table 2) always correspond to Pt^{2+}/Pt^0 reduction, despite the fact that this precursor had been calcined at 500°C during its preparation. This confirms that reduction takes place during the inert gas heating and occurs in this sample even at 250°C.

(*B*) *Platinum–rhenium catalysts.* TPR profiles of $PtRe/Al_2O_3$-Cl, dried under He flow at different temperatures between 250 and 450°C, are shown in Fig. 2A. Predrying at temperatures up to 250°C gives TPR profiles with a single sharp peak at 320°C indicating that both metals reduce together af-

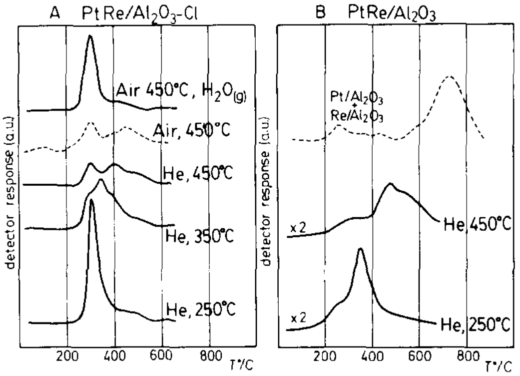

FIG. 2. TPR profiles of PtRe catalysts pretreated in flowing He, 1 h, at the indicated temperatures: (A) $PtRe/Al_2O_3$-Cl ((---) sample pretreated in air flow at 450°C, 1 h; upper trace, pretreated as before and then exposed to water vapor at 25°C); (B) $PtRe/Al_2O_3$ ((---) Pt/Al_2O_3 + Re/Al_2O_3 physical mixture).

ter this low-temperature pretreatment, as previously reported by several authors (*1*–*3*). Total hydrogen consumptions in Table 2 are even higher than those expected for the reduction of Re^{7+}/Re^0 plus Pt^{4+}/Pt^0. Since evolution of CH_4 was detected by mass spectrometry during the TPR, these high values should be ascribed to reduction of carbon-containing impurities adsorbed on the support, pyrolized by rhenium, as previously found by Arnoldy *et al.* (*16*) for Re/Al_2O_3 samples. Unfortunately, this additional hydrogen consumption makes it difficult to establish the actual oxidation state of the metals. TPR profiles of this catalyst predried at increasing temperatures up to 450°C show a progressive decrease in the total hydrogen uptake, which drops to ca. 52 μmol/g at 450°C, while several unresolved peaks (320, 420, 510°C after drying under He at 450°C) are clearly observed. By comparison with the TPR profiles for the Pt/Al_2O_3-Cl catalyst the peak at 320°C can be unambiguously assigned to reduction of platinum, while those at 420 and 510°C correspond to rhenium. A set of experiments using synthetic air instead of He gives similar TPR profiles and hydrogen consumptions although, after the pretreatment at 450°C, minor differences in the relative intensities of the higher reduction peaks (420 and 510°C) occur as shown in Fig. 2A. These results indicate that the presence of a partial pressure of oxygen during the prereduction treatment only slightly modifies the TPR profile of this sample, so that change in the concentration of hydroxyl groups at the surface of the support, prior to the reduction step, can be assumed to be the main origin for the changes observed in the TPR profiles, as previously suggested in (*2*).

In order to assess the effect of surface rehydroxylation in the TPR profile, a PtRe catalyst pretreated at 450°C in air was exposed to a static water vapor atmosphere at 25°C (15 Torr, 1 h) before the TPR run. As shown in Fig. 2A, the TPR profile of this sample is similar to those obtained for the same catalyst pretreated at low temperatures (up to 250°C), showing a single reduction peak, which confirms the role of surface hydroxylation in the reduction process.

The broader TPR profiles for the chlorine-free PtRe/Al_2O_3 precursor in Fig. 2B are also modified by the thermal pretreatments (under He flow at 250 and 450°C) in a manner similar to that for the chlorinated samples. So, the catalyst predried at 250°C gives a TPR profile with a single reduction peak at 300–320°C with a small shoulder at lower temperatures, while the one predried at 450°C shows at least two well-defined reduction steps (320 and 450°C), which should be ascribed to platinum and rhenium reduction, respectively. However, after both pretreatments, total hydrogen consumption in Table 2 is in this sample slightly higher than expected for the reduction of Pt^{2+}/Pt^0 plus Re^{4+}/Re^0 (i.e., 55 vs 46 μmol/g). For comparison, Fig. 2B includes the TPR profile for a physical mixture of the monometallic Pt/Al_2O_3 and Re/Al_2O_3 precursors previously dried under He flow at 250°C. In this case rhenium reduction, associated with the high-temperature reduction peak, was much more difficult than that in the bimetallic catalyst pretreated either at 250 or even at 450°C, so the presence of cosupported platinum clearly promotes rhenium reduction in the bimetallic catalyst even after the pretreatment at 450°C. Small differences in this effect for both samples have been plotted in Figs. 3 and 4 where subtracted TPR profiles of the two sets of Pt and PtRe catalysts, accounting for Re reduction, have been included. These data show that the maximum reduction rate for rhenium was slightly shifted (ca. 30 ± 5°C) to higher temperatures in the chlorine-free sample, whatever the predrying treatment.

(*C*) *TPR of reoxidized samples.* Profiles obtained when a second TPR run is carried out on Pt and PtRe samples reoxidized at 350°C in air flow after a first TPR reduction up to 600°C are shown in Fig. 5. For both Pt

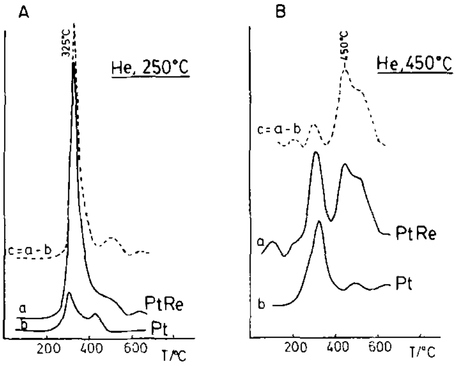

FIG. 3. TPR profiles for PtRe/Al_2O_3-Cl catalysts pretreated in flowing He, 1 h: (A) at 250°C and (B) 450°C ((---) difference spectra for PtRe and Pt samples accounting for rhenium reduction).

catalysts (chlorinated and chlorine free) similar hydrogen uptakes (ca. 25–27 μmol/g, see Table 2) are obtained, corresponding to reduction of a sample with ca. 70–80% of the whole metallic load oxidized up to Pt^{4+}. It is worth noting that while the profile for the reoxidized Pt/Al_2O_3-Cl sample is very similar to those obtained for the precursor (see Fig. 1A), the profile for the reoxidized chlorine-free sample now shows the main reduction peak shifted at ca. 180°C, indicating that reduction of platinum is now easier than that in the original Pt/Al_2O_3 precursor (note the first TPR peak at 280°C in Fig. 1B). Integration of the Re reduction peaks obtained by subtraction in Fig. 5 gives hydrogen uptakes of ca. 29 μmol/g, in good agreement with the value expected for reoxidation of all the rhenium up to Re^{4+}, for both the chlorided and the unchlorided samples. This fact suggests that Re is now probably forming in the two catalysts a bidimensional phase at the surface of the alumina support, as previously reported by Yao and Shelef (*17*) for Re/Al_2O_3 catalysts, which cannot be fully oxidized up to Re^{7+} under such conditions. It is worth noting that, although platinum reduction is now much easier in the Pt and PtRe chlorine-free catalysts, the maximum reduction rate for rhenium appears at ca. 400°C in both PtRe-reoxidized catalysts, indicating again that the presence of chlorine does not affect the reducibility of the rhenium species on the alumina surface, which however is strongly influenced by the presence of water at the surface.

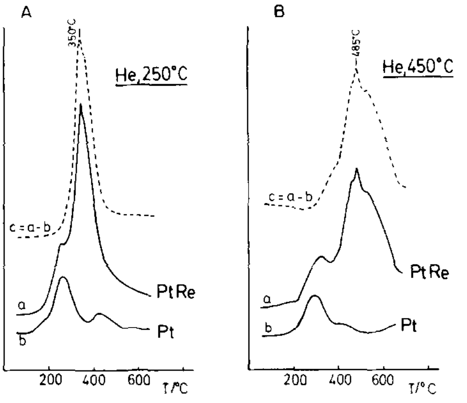

FIG. 4. TPR profiles for PtRe/Al_2O_3 chlorine-free catalysts pretreated in flowing He, 1 h: (A) at 250°C and (B) 450°C ((---) difference spectra for PtRe and Pt samples accounting for rhenium reduction).

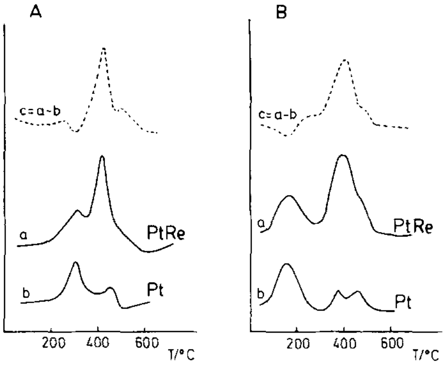

FIG. 5. TPR profiles of samples reduced up to 600°C and then reoxidized at 350°C with air: (A) chlorinated catalysts; (B) chlorine-free catalysts ((---) difference spectra for PtRe and Pt samples accounting for rhenium reduction).

n-Butane Hydrogenolysis

The effect that the prereduction drying treatment has on PtRe alloying in the two sets of catalysts has been examined using *n*-butane hydrogenolysis as a test reaction, according to the method proposed by Sachtler *et al.* (*7–9*), so that the original

TABLE 3

Pt Catalysts: Activities and Selectivities at 390°C for *n*-Butane Hydrogenolysis (Expressed in Molar Units)

Pretreatment	%Conv	$\%C_1$	$\%C_2$	$\%C_3$	C_3/C_1	H/Pt
Pt/Al_2O_3-Cl						
He 250, H_2 390	3.6	31.5	37.7	30.7	0.97	0.44
He 250, H_2 390	6.1	31.7	37.1	31.2	0.98	0.87
He 450, H_2 390	18.7	33.6	34.0	32.4	0.96	0.99
Pt/Al_2O_3						
He 250, H_2 390	39.5	27.2	47.6	25.2	0.93	0.90
He 450, H_2 390	39.7	31.5	39.8	28.7	0.91	0.90
Pt/Al_2O_3-dechlorinated						
He 250, H_2 390	23.8	28.4	45.3	26.3	0.93	0.81
He 450, H_2 390	34.5	30.6	42.1	27.2	0.90	0.83

state of the reduced metallic phase could be monitored in this way.

(*A*) *Platinum catalysts.* Activities and selectivities measured at 390°C of the Pt catalysts reduced in hydrogen at 390°C after different thermal pretreatments under He or synthetic air are summarized in Table 3. From these data we can see that the activity of the chlorided catalyst increases when it is dried at higher temperatures before the reduction step, while its selectivity remains almost independent of the pretreatment, always giving C_3/C_1 ratios close to one (i.e., "single hydrogenolysis"). In principle, the observed increase in activity could be explained on the basis of an increase in the number of sites available for the reaction, as suggested by the H/Pt values included in Table 3. This is confirmed by the constant activation energies, 38 ± 1 kcal/mol for C_1 or C_3, and 46 ± 1 kcal/mol for C_2, in good agreement with the values previously reported in the literature (*18*) for *n*-butane hydrogenolysis on Pt/Al_2O_3.

Data in Table 3 also show that the chlorine-free Pt/Al_2O_3 catalyst is much more active in *n*-butane hydrogenolysis than the chlorided catalyst and that its activity (and selectivity) for this reaction are independent of the pretreatment. This fact suggests that the metallic phase should be in a similar state after both pretreatments in this catalyst. Moreover, since dechlorination of a Pt/Al_2O_3-Cl sample leads to a precursor with activities closer to that measured for the chlorine-free sample, which depend less markedly on the predrying conditions, we must assume that the presence of chlorine in the precursor is actually responsible for the observed changes in activity, although it is worth noting that it does not modify the C_3/C_1 selectivity in these Pt catalysts, where single hydrogenolysis always occurs.

(*B*) *Platinum–rhenium catalysts.* Table 4

TABLE 4

PtRe Catalysts: Activities and Selectivities at 340°C for *n*-Butane Hydrogenolysis (Expressed in Molar Units)

Pretreatment	%Conv	$\%C_1$	$\%C_2$	$\%C_3$	C_3/C_1
Pt/Al_2O_3-Cl					
He 250, H_2 390	2.5	45.7	31.6	22.7	0.49
He 450, H_2 390	0.8	40.7	25.6	33.7	0.83
Air 250, H_2 390	2.8	43.8	31.6	24.6	0.56
Air 450, H_2 390	1.0	41.7	24.8	33.5	0.80
Air 450, $H_2O(g)$, H_2 390	2.4	45.0	28.9	26.1	0.58
He 250, H_2 490	2.2	43.6	32.4	24.0	0.55
He 450, H_2 490	0.6	41.0	25.8	33.2	0.81
$PtRe/Al_2O_3$					
He 250, H_2 390	71.3	59.1	28.1	12.8	0.38
He 450, H_2 390	23.2	44.8	33.7	21.5	0.52
He 250, H_2 490	10.5	47.1	31.7	21.3	0.49
He 450, H_2 490	5.8	41.0	35.5	23.6	0.60

gives a summary of the activities and selectivities of PtRe catalysts, after different pretreatments under He or air flow and final reduction at either 390 or 490°C. Pretreatments up to 250°C (not included in the table) did not affect the activity and selectivity of the chlorinated catalyst. Under such conditions selectivities to methane were always higher than those of the Pt catalysts pretreated at the same temperatures (C_3/C_1 close to 0.5 instead of 1). However, for the sample pretreated at 450°C a lower selectivity to methane (C_3/C_1 of 0.8) is obtained, this change being accompanied by a decrease in activity. Data in Table 4 also show that the use of He or air during the pretreatment did not influence much either the activity/selectivity or the dependence of the reaction rate on the temperature, which always leads to activation energies of 39 ± 1 kcal/mol for C_1 or C_3 and 42 ± 1 kcal/mol for C_2, thus suggesting that the elimination of water before the reduction step can again be responsible for the differences in performance of the catalyst. This assumption was confirmed using a catalyst which had been predried at 450°C and then exposed *in situ* at room temperature to flowing He saturated with water vapor before its standard reduction at 390°C in the pulse reactor. As shown in Table 4 the behavior of this catalyst in the reaction is similar to that of the catalyst which had been predried in air at 250°C, which indicates a recovery of an equivalent surface state during the pretreatment with wet He before the reduction step.

Since the hydroxylation state of the surface affects the reducibility of rhenium (TPR profiles) as well as the activity/selectivity of the reduced catalysts, in principle, both phenomena could be related. TPR profiles in Fig. 2 indicate that rhenium could be only partially reduced in the samples predried at 450°C after reduction at 390°C (although it must be almost fully reduced at this temperature for the catalysts predried to 350°C). So, unreduced rhenium could be responsible for the decreased activity and low selectivity to methane shown in Table 4 for the samples predried at high temperatures. However, as shown in this table, reduction at 490°C does not increase, but slightly decreases, the activity of the samples predried at either 250 or 450°C, while their selectivities still remain very similar to those for the catalysts reduced at 390°C. Therefore, we can discard the incomplete reduction of rhenium as the origin of the changes in performance of the PtRe/Al_2O_3-Cl catalysts predried under different conditions. Therefore, the high selectivity to methane of the catalyst predried at lower temperatures should be ascribed, according to Sachtler *et al.* (*7–9*), to the existence of more PtRe alloy in those samples than in the catalyst predried at 450°C and then reduced at either 390 or 490°C. It is worth noting that the temperature of reduction has only a minor effect in the C_3/C_1 selectivity indicating that the extent of PtRe alloying is mainly determined by the predrying step before reduction.

By comparison with the results above, the data for the chlorine-free PtRe sample in Table 4 show that this catalyst presents a much higher activity for all the pretreatments. Meanwhile, the effect of the predrying temperature in the selectivity of this catalyst (reduced at either 390 or 490°C) was much less marked than that for the chlorinated sample, the C_3/C_1 ratio being always close to 0.5. This fact indicates that in this sample PtRe alloys, highly selective to methane, should always be formed, whatever the predrying conditions, so that the absence of chlorine seems to favor in some way alloy formation, even in the samples predried at 450°C.

To confirm whether the differences between the two samples described above are actually associated to the presence of chlorine, a portion of the Pt-Re/Al_2O_3-Cl precursor was submitted to dechlorination while a chlorine-free precursor was chlorinated *in situ* and their activity in *n*-butane hydrogenolysis measured after predrying and reduction. The results have been in-

TABLE 5

PtRe Catalysts: Surface Contents of Chlorine, Activities and C_3/C_1 Selectivities at 340°C for *n*-Butane Hydrogenolysis

Sample	%Cl[a]	He 250°C		He 450°C	
		%Conv	C_3/C_1	%Conv	C_3/C_1
PtRe/Al_2O_3-Cl					
Original	0.80	2.5	0.49	0.2	0.83
Dechlorinated	0.49	71.3	0.39	45.2	0.53
PtRe/Al_2O_3					
Original	0.00	71.3	0.38	23.2	0.52
Chlorinated	1.34	—	—	4.4	0.97

[a] Atom percentage from XPS analysis.

cluded in Table 5 for two different pretreatments, together with the activities and selectivities of the original catalysts and surface contents of chlorine obtained by XPS. The data clearly confirm that chlorine is responsible for the changes observed in the catalytic behavior of both sets of samples.

DISCUSSION

Platinum Catalysts

TPR profiles obtained for both platinum samples show two maxima, the high-temperature peak probably corresponding, as previously suggested by other authors (*1*, *2*), to platinum more strongly interacting with the support. In spite of these similarities, the influence of the preheating temperature in the TPR profile is somewhat different for Pt/Al_2O_3 and Pt/Al_2O_3-Cl precursors. Thus, for the chlorine-free catalyst the TPR profile after drying in He is almost independent of the predrying temperature of the sample, with a total hydrogen uptake always corresponding to a Pt^{2+} state for all the platinum. In the catalyst precursor containing chlorine the Pt^{4+} state seems somewhat stabilized, as deduced from the higher hydrogen consumption in the TPR of these samples, which is initially close to the expected Pt^{4+}/Pt^0 value, although it progressively decreases for increasing drying temperatures, to finally approach the Pt^{2+}/Pt^0 value at the highest temperature of pretreatment (He, 450°C). In fact, this Pt/Al_2O_3-Cl precursor, when calcined in air, shows a hydrogen consumption always corresponding to Pt^{4+}/Pt^0 reduction, thus suggesting that the platinum could be initially as Pt^{4+} in the supplied precursor, which had probably been precalcined at ca. 500°C, although it progressively decomposes to Pt^{2+} during the heating in He previous to the TPR run. This behavior contrasts with that of the chlorine-free catalyst, where platinum is always as Pt^{2+} even when the precursor has been pretreated in He at 250°C, despite its precalcination at 500°C. This must be because Pt^{4+} either is easier to reduce in this case during the preheating under He or because it was already as Pt^{2+} in the precursor calcined at 500°C during the preparation procedure. Augustine (*19*) has recently reported, for a similar Pt/Al_2O_3 catalyst dried at 500°C in oxygen, a hydrogen consumption in TPR close to the value expected for Pt^{2+}/Pt^0 reduction, so we can assume that platinum is actually as Pt^{2+} in our precursor, and heating under helium at either 250 or 450°C before TPR does not modify much its oxidation state. However, hydrogen consumption for both catalysts reduced to 600°C and then reoxidized in air at 350°C indicates that at least ca. 70% of the platinum becomes reoxidized to Pt^{4+}

under these conditions. All these facts seem to suggest that Pt^{4+} is more unstable in the absence of chlorine, so that it reduces to Pt^{2+} even during the heating under an oxidizing atmosphere (i.e., air or pure oxygen) at 500°C, although it still remains partially oxidized if the same treatment is carried out at lower temperatures. The shift in the most intense TPR maximum (from 280°C for Pt/Al_2O_3 to 300°C for Pt/Al_2O_3-Cl) in Fig. 1 also indicates a slight stabilization by the chlorine of this oxidized platinum, which is again suggested in Fig. 5 by the great shift of this peak to lower temperatures (ca. 180°C) for the reoxidized chlorine-free samples. On the other hand, when the Pt/Al_2O_3-Cl sample is dried at increasing temperatures the smaller TPR peak at 420°C, ascribed to Pt strongly interacting with the support, shifts toward higher temperatures and broadens, suggesting an enhancement of the interaction between this form of platinum and the support when the alumina surface becomes more and more dehydroxylated.

The activity of the Pt/Al_2O_3-Cl catalyst for *n*-butane hydrogenolysis is also strongly dependent on the drying temperature, increasing when the precursor is dried at higher temperatures before its reduction. However, for the chlorine-free sample the activity is always high and almost independent of the pretreatment conditions. This trend follows the H/Pt ratios indicating that in the former catalyst the activity increases with the number of exposed Pt atoms, which remains constant for the latter. However, H/Pt values and activities do not follow a linear relationship, as could be expected from the requirement of "ensembles" of atoms as active sites for hydrogenolysis (*12*).

The results obtained with the dechlorinated sample show that differences in activity should be directly related to the surface content of chlorine. It is worth noting that, although H/Pt ratios are even closer to one in the Pt/Al_2O_3-Cl (pretreated at 450°C) than in the Pt/Al_2O_3 catalyst, this latter shows a higher activity, thus suggesting that active sites for hydrogenolysis could be partially poisoned by chlorine in the former, although they are still accessible to hydrogen adsorption. In fact, dechlorination (see Table 5) produces an enhancement of the activity despite the slightly lower dispersions measured by hydrogen adsorption for this sample. In principle, changes in activity in our Pt samples can be explained by assuming the formation of some kind of oxychlorided platinum species as precursor, which slightly stabilize the higher oxidation state of the platinum against reduction. When water is removed, these platinum species strongly interact with the partially dehydroxylated alumina support (and probably lose part of its chlorine) thus leading, after reduction, to highly dispersed platinum clusters. In the absence of chlorine the stability of the oxidized precursor (now without chlorine) seems to be lower and anchoring to the dehydrated support much less effective, so that reduction occurs at lower temperatures leading to lower dispersions, as shown by the H/Pt values in Table 3.

However, it is worth noting that the C_3/C_1 selectivities of all the samples always remain close to one indicating single hydrogenolysis on the Pt as previously reported in the literature (*18*) with a constant activation energy of ca. 38 ± 1 kcal/mol for C_1 and C_3 (46 ± 1 kcal/mol for C_2), which suggests that the ensembles of atoms acting in the reaction are of the same nature in the two Pt samples, whatever their pretreatment conditions.

Platinum–Rhenium Catalysts

From the TPR data obtained for these two catalysts we may conclude that the predrying treatment at temperatures higher than 250°C progressively modifies the reduction pattern of both samples. These changes are affected neither by the presence of oxygen during the pretreatment nor by the chlorine content of the catalyst, so that they must be related to the elimination of water from the support, as previously suggested by Isaacs and Petersen (*2*) and confirmed by the complete recovery of the single peak TPR profile when samples, which had been predried at high temperatures, are reexposed to water vapor before H_2 reduction (see Fig. 2A).

However, it should be stressed that although the influences of the predrying steps on the TPR profiles of the two samples are very similar (see Fig. 2), their catalytic behaviors, summarized in Table 4, clearly depend on the pretreatment in very different ways. Thus, although the formation of phases with a high selectivity to methane (i.e., $C_3/C_1 < 1$) in the chlorided catalyst is strongly inhibited by high temperatures in the prereduction step, the chlorine-free sample always shows C_3/C_1 ratios close to 0.5. Data for chlorinated/dechlorinated samples in Table 5 indicate that these differences can be unambiguously ascribed to the presence of chlorine in the surface of the precursors. According to recent works by Sachtler *et al.* (*7–9*) an enhancement toward methane selectivity in hydrocarbon hydrogenolysis can be taken as a probe for PtRe alloy formation. Therefore, we can conclude that, while alloying always occurs and is almost independent of the pretreatment in the chlorine-free catalyst, it becomes progressively inhibited in the chlorided precursor when it is predried at increasing temperatures before H_2 reduction. So, the thermal treatment that removes water from the Al_2O_3 support also seems to prevent in this case diffusion of the Re and/or Pt precursors across the Al_2O_3 surface from forming the PtRe alloy. Moreover, catalytic activities of the PtRe catalysts are strongly dependent on the chlorine content of the samples as in the case of the Pt samples, thus suggesting that the resulting active PtRe alloy could be also partially poisoned by chlorine.

In fact, a comparison of the TPR profiles in Fig. 2 indicates that reduction of rhenium is always catalyzed by the presence of cosupported platinum, although this reduction is retarded when the degree of hydroxylation of the Al_2O_3 support decreases during the pretreatment (from ca. 70 to 30% under our conditions (*20*)). As we have previously stated, this fact has been previously ascribed either to differences in the mobility of hydrated Re precursors, strongly dependent on the hydration degree of the sample (*1, 2*), which favors its reduction over hydrogen-covered platinum particles, or to changes in the rate of hydrogen spillover from platinum to them via the alumina support (*3*), a process which also depends on the hydration degree of the support (*4*). Our results clearly suggest that, although differences in the TPR profile for the chlorided samples pretreated in the range 250–450°C lead to changes in the extent of PtRe alloying (measured by selectivities to methane in Tables 4 and 5), for the unchlorided sample similar differences in TPR profiles do not lead to significant changes of alloying, which always seem to occur in this case whatever the predrying conditions. So we must conclude that Re and/or Pt precursors should be highly mobile in the absence of chlorine for any hydration degree of the alumina support, only minor differences in alloying being detected in this case. As a consequence, differences in the rate of the catalytic reduction of rhenium detected in the TPR profiles must be ascribed in this case to differences in the rate of hydrogen spillover from platinum via the partially hydroxylated alumina support, in agreement with previous interpretation by Mieville (*3*). This process seems to be accompanied in this catalyst by diffusion of the chlorine-free Pt and/or Re precursors to form the alloy. In our view, the degree of hydroxylation of the support greatly modifies the rate of hydrogen spillover, while the presence of chlorine only slightly increases the rate of this process, as previously observed by Musso and Parera (*21*). This conclusion seems clearly supported by the TPR profiles for our chlorided and unchlorided samples in Figs. 3 and 4, where only a small shift toward higher temperatures of the maximum reduction rate of rhenium (ca. 30°C) is observed in the chlorine-free catalyst.

Nevertheless, contrary to what is observed for the chlorine-free catalyst, PtRe alloying measured by changes in C_3/C_1 selectivities seems to be strongly affected by the degree of hydroxylation of the support in the commercial PtRe/Al_2O_3-Cl catalyst. Thus, we must conclude that chlorine plays an important role on the surface mobilities of the Re and/or Pt precursors present in this catalyst and therefore on the extent of PtRe alloying so that these species seem to become more tightly anchored to the support when its surface is progressively dehydroxylated, thus preventing PtRe alloying. It is likely that oxychlorided platinum and/or rhenium species could be formed in this case, strongly interacting with the progressively dehydroxylated surface of the support forming Pt–Cl–Al^{3+} (and probably Re–Cl–Al^{3+}) bonds, thus preventing PtRe alloying upon reduction. In this context it is worth noting that a combination of chlorine, air, and water is normally used to redisperse reforming catalysts, where formation of Pt oxychlorided species has been postulated under such conditions (*22, 23*). According to our results, the same type of species would exist at the chlorided precursors, becoming tightly anchored to the Al_2O_3 support during the drying of these catalysts, thus leading, after reduction, to well-dispersed metallic phases, although it might prevent extensive PtRe alloying.

CONCLUSIONS

From the data reported for the two sets of Pt and PtRe chlorinated and chlorine-free catalysts we may conclude that the catalyzed reduction of the Re precursors in the presence of Pt is determined by the rate of hydrogen spillover from reduced Pt to the Re precursors, which greatly depends on the hydroxylation state of the Al_2O_3 support but only slightly on the chlorine content of the catalyst. However, the mobility of such metallic precursors, required to generate PtRe alloys in the PtRe/Al_2O_3 catalyst upon reduction, is strongly dependent not only on the hydroxylation state of the Al_2O_3 support but also on the presence of chlorine. This latter probably forms oxychlorinated compounds of Pt (and/or Re) which become tightly bonded to the Al_2O_3 support when it is progressively dehydroxylated, thus preventing their mobilities and, as a consequence, metallic aggregation and PtRe alloying of the Pt and Re precursors upon reduction.

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REFERENCES

1. Wagstaff, N., and Prins, R., *J. Catal.* **59,** 434 (1979).

2. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **77,** 43 (1982).

3. Mieville, R. L., *J. Catal.* **87,** 437 (1984).

4. Ambs, W. F., and Mitchell, M. M., *J. Catal.* **82,** 226 (1983).

5. Charcosset, H., Frety, R., Leclercq, G., Mendes, E., Primet, M., and Tournayan, L., *J. Catal.* **56,** 468 (1979).

6. Isaacs, B. H., and Petersen, E. E., *J. Catal.* **85,** 8 (1984).

7. Augustine, S. M., and Sachtler, W. M. H., *J. Phys. Chem.* **91,** 5953 (1987).

8. Shum, V. K., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **99,** 126 (1986).

9. Augustine, S. M., and Sachtler, W. M. H., *J. Catal.* **106,** 417 (1987).

10. Kobayashi, M., Inoue, Y., Takahashi, N., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50,** 464 (1980).

11. Espinós, J. P., González-Elipe, A. R., and Odriozola, J. A., *Appl. Surf. Sci.* **29,** 40 (1987).

12. Boudart, M., and Djega-Mariadassou, G., "Kinetic of Heterogeneous Catalytic Reactions." Princeton Univ. Press, Princeton, 1984.

13. Haining, I. H. B., Kemball, C., and Whan, D. A., *J. Chem. Res.* (*M*), 2055 (1977).

14. Leclercq, G., Charcosset, H., Maurel, R., Bertizeau, C., Bolivar, C., Frety, R., Jaunay, D., Mendez, H., and Tournayan, L., *Bull. Soc. Chim. Belg.* **88,** 577 (1979).

15. Caballero, A., Gonzalez-Elipe, A. R., Malet, P., Munuera G., Garcia, J., Conesa, J. C., and Burattini, E., *Physica B.*, in press.

16. Arnoldy, P., Van Oers, E. M., Bruinsma, O. S. L., De Beer, V. H. J., and Moujlin, J. A., *J. Catal.* **93,** 231 (1985).

17. Yao, H. C., and Shelef, M., *J. Catal.* **44,** 392 (1976).

18. Leclercq, G., Leclercq, L., Banleau, L. M., Pretsyk, S., and Maurel, R., *J. Catal.* **88,** 8 (1984).

19. Augustine, S. M., Ph.D. thesis, Northwestern University, 1988.

20. Knözinger, H., and Ratnasamy, P., *Catal. Rev.* **17,** 31 (1978).

21. Musso, J. C., and Parera, J. M., *Appl. Catal.* **30,** 81 (1987).

22. Callender, W. L., and Miller, J. J., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. II, p. 491. Dechema, Frankfurt-am-Main, 1984.

23. Foger, K., and Jaeger, H., *J. Catal.* **92,** 64 (1985).