Redispersion of Platinum on Alumina Support

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The increase in metal dispersion of several Pt/Al$_2$O$_3$ catalysts, following a heat treatment in air or oxygen at 500°C, has been studied as a function of sintering conditions, support pretreatment, and chlorine content. The changes in metal dispersion were followed by hydrogen chemisorption measurements. Heating the catalysts in H$_2$ at 600°C resulted in a slow decrease in metal dispersion and simultaneous loss of chlorine was observed, which depended on the water content of the gas stream. A limiting value of dispersion was obtained after prolonged sintering ($\geq$100 hr) and this behavior is consistent with a crystallite migration mechanism. Hydrogen sintered samples were easily redispersed by air treatment at 500°C, the increase being dependent on the sintering time and the residual level of chlorine. Successive sintering (H$_2$)-redispersion (air) cycles performed on a given sample indicated a slow decrease in the final dispersion, particularly for heavily sintered samples. This trend was reversed by restoring the original level of chlorine. A metal–support interaction involving the platinum atoms and oxidizing sites on the alumina is postulated to explain these results. Heating the catalysts in air at >580°C caused a very rapid decrease in metal dispersion, compared to hydrogen, and the presintered catalysts were redispersed by oxygen treatment at 500°C. In this case the redispersion process was found to depend on time and the final dispersion actually exceeded the original value. These observations suggest that the redispersion of Pt/Al$_2$O$_3$ catalysts occurs by different mechanisms depending on the sintering atmosphere. The origin of the alumina or the support pretreatment did not influence the redispersion process.

INTRODUCTION

The metal surface area of highly dispersed platinum is affected by prolonged exposure at high temperature. Under reducing conditions, such as those prevailing in a reforming reactor the surface area decreases slowly and this is ascribed to particle growth or metal sintering. The process also occurs in an oxygen atmosphere but it has different characteristics. At >580°C the sintering rate is much higher. At lower temperature oxygen actually causes an increase in dispersion. Two models have been proposed to explain the growth of dispersed metal particles on a high area support. One postulates the migration, collision, and coalescence of crystallites and it is known as the crystallite migration model (*1*). Another alternative is the molecular migration model where growth occurs by interparticle transport of metal atoms or molecular species (*2*). Numerous experimental and theoretical studies have been conducted in order to determine the validity of these models. The situation is still open to discussion since the experiments performed so far have failed to provide clear evidence for either mechanism (*3, 4*).

The increase in metal dispersion, or redispersion, is also an important phenomenon because it allows the regeneration of aged catalysts. The process has been known for several years and its industrial applications are covered by several patents (*5, 6*). Johnson and Keith (*7*) followed the changes in surface area of a partially deactivated reforming catalyst upon exposure to air at increasing temperatures. They observed a maximum increase in dispersion at 510°C. Jaworska-Galas and Wrzyszcz (*8*) have also shown that the initial surface area of a used reforming catalyst can be

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restored by oxygen treatment at high temperature. The subject has received considerable attention in the recent literature and the sintering mechanisms mentioned above have been adapted to explain this phenomena. Fiederow and Wanke (9) observed a significant increase in dispersion when a series of fresh Pt/Al$_2$O$_3$ catalysts were treated in oxygen at <580°C. According to the authors the increase is due to migrating platinum oxides that are trapped at high energy sites on the support. Ruckenstein and Malhotra (10) have explained redispersion on the basis of crystallite fracture. They observed the splitting of platinum crystallites in a model catalyst that was exposed to air at 500°C following an air treatment at 600°C. In contrast Dautzenberg and Wolters (11) reported that an air treatment at <580°C cannot restore the original dispersion of heavily sintered samples.

Here again the selection between rival models is not simple and more information will be needed before a definite conclusion can be drawn. Although the effect of gas atmosphere and temperature on the increase in dispersion has been studied in detail (9), other variables are suspected to have an important role. The influence of chlorine, a normal component in reforming catalysts, deserves particular attention. It has been found (12) that in the presence of oxygen, chlorine enhances the formation of an oxidizing form of platinum indicated by the dissolution of the metal at room temperature. This fact may be related to the redispersion process. The increase in dispersion may also depend on the preparation procedure or the support pretreatment. Therefore some important variables may have not been properly identified at the present time and this might explain the divergences in the literature. In this paper we report the effect of different sintering conditions and subsequent air treatment at 500°C, on the dispersion of several platinum on alumina catalysts. We have also focused our attention on the effect of support pretreatment

and chlorine content. It is expected that this study can contribute to a better understanding of the redispersion phenomena.

EXPERIMENTAL

Catalysts

A commercial reforming catalyst (C-1) and several laboratory preparations were used in this work. Table 1 summarizes the catalysts and some of their important characteristics. Catalyst L-1 was supplied by a colleague. It was prepared by wetting the support with an aqueous solution of chloroplatinic and hydrochloric acids. The γ-alumina, Ketjen CK-300, was previously calcined at 650°C for 3 hr. The preparation was dried in air at 120°C for 12 hr and subsequently calcined at 500°C for 2 hr.

The alumina support used for the other preparations was obtained by heating alumina trihydrate at 600°C in different atmospheres as indicated in Table 1. After impregnation with chloroplatinic acid (1.5 ml solution/g support; 24 hr) catalysts L-2 and L-3 were dried in air at 120°C for 12 hr. Catalyst L-4 was prepared by the same procedure but it was maintained under nitrogen during impregnation and drying. Ex-

TABLE 1

Characterization of the Catalyst Samples

Catalyst	BET surface area (m²/g)	Pt content (wt%)	Pt dispersion (%)	Cl content (wt%)
C-1	155	0.375	42[a]	0.85
L-1[c]	165	0.308	90[b]	1.05
L-2[d]	159	0.270	54[b]	0.20
L-3[e]	175	0.260	92[b]	0.28
L-4[f]	—	0.404	45[b]	0.47

[a] Measured by oxygen adsorption–hydrogen titration at room temperature.
[b] Measured by hydrogen adsorption at room temperature.
[c] Alumina calcined at 650°C for 3 hr.
[d] Alumina heated in oxygen at 600°C for 6 hr.
[e] Alumina heated in hydrogen at 600°C for 6 hr.
[f] Alumina heated in nitrogen at 600°C for 3 hr.

cept for a portion of catalyst L-2 all others were reduced, and the initial dispersion measured, before subsequent heat treatments. The platinum and chlorine content were determined by chemical analysis.

Chemisorption Measurements and Sintering Experiments

An amount of 2 to 5 g of catalyst was placed in a Pyrex glass cell and attached to a conventional glass adsorption apparatus for heat treatment or dispersion measurements. Some samples were sintered in hydrogen for prolonged periods of time in a separate experimental set up. Fresh samples were reduced in flowing hydrogen at 500°C for 4 hr, purged with helium for 15 min, and then evacuated for 16 hr at the same temperature. Samples that were exposed to air or oxygen at high temperature were reduced for 8 hr. After degassing they were cooled under vacuum and hydrogen chemisorption measurements carried out at room temperature. The net hydrogen uptake was obtained by extrapolation of the isotherms to zero pressure. In order to calculate the metal dispersion the adsorption stoichiometry was assumed to be one hydrogen atom per metal atom. Values for the fresh samples are listed in Table 1. When the dispersion was estimated to be below 50% and the amount of catalyst employed was less than 2 g the oxygen adsorption–hydrogen titration method was used in order to reduce the experimental errors. The ratio of hydrogen to oxygen uptakes was found to be equal to one in the 10–50% dispersion range.

Hydrogen sintering experiments were carried out at 600°C for varying periods of time. The temperature was then lowered to 500°C and the procedure detailed above was followed to measure the decrease in metal dispersion. The sample was then treated in air at 500°C, usually overnight, to investigate the redispersion phenomena. A small amount of catalyst (0.5 to 0.8 g) was

occasionally removed from the adsorption cell to measure the chlorine content.

The hydrogen used in the chemisorption and sintering experiments was purified by passage over a Cu bed at 300°C followed by a silica gel-molecular sieve drying trap. Oxygen and air from commercial cylinders were only treated for the removal of water. The helium used was Matheson high purity grade.

RESULTS

The main results of this investigation are summarized in Tables 2 to 7. A sample of catalyst C-1 was subjected to successive cycles comprising a prolonged exposure to hydrogen at 600°C followed by air treatment at 500°C for 12 hr (see Table 2). Under reducing conditions a decrease in dispersion and a parallel loss in chlorine was observed. It should be noted that the same final dispersion was obtained in different runs despite the fact that the sintering time was changed. The sample sintered during 88 hr (Run 1) had a dispersion of 23%. Following the treatment in air and subsequent sintering for 154 hr the same value was obtained. When a fresh sample was sintered at 620°C during 54 hr (Run 1') the dispersion decreased again to the same level.

The air treatment at 500°C effected the recovery of the original dispersion although sometimes the final value was lower than the initial one. The ratio between these two numbers was taken as a measure of the redispersion capacity and it provides a convenient parameter to compare the increase in dispersion of different cycles. For the first two cycles the values are 100 and 77%. This decrease was ascribed to the severe loss in chlorine and therefore the catalyst was treated in Run 5 with a stream of air containing 0.85% of HCl and 0.16% of H_2O. In this way we succeeded in increasing the dispersion to nearly 100%. After three additional cycles the redispersion capacity again decreased and the beneficial effect of chlorine to recover the high initial

TABLE 2

Variation of the Metal Dispersion upon Thermal Treatment of Catalyst C-1

Run	Gas atmosphere	Temperature (°C)	Time (hr)	Pt dispersion (%)	Cl content[b] (wt%)
1	H_2	600	88	23[a]	—
2	Air	500	12	43[a]	—
3	H_2	600	154	23[a]	—
4	Air	500	12	33[a]	0.29
5[c]	Air	500	12	93[d]	0.8
6	H_2	600	124	39[a]	—
7	Air	500	12	73[d]	0.39
8	H_2	600	116	32[d]	0.29
9	Air	500	18	69[d]	—
10	H_2	600	168	36[a]	—
11	Air	500	12	46[a]	—
12[e]	Air	500	12	92[d]	0.53
1′	H_2	620	54	24[a]	—
2′	Air	500	10	47[a]	—
3′	Air	600	12	16[a]	0.39
4′	Air	500	12	16[a]	—

[a] Measured by oxygen adsorption–hydrogen titration at room temperature.
[b] Analysis performed after dispersion measurement.
[c] Hydrogen chloride added to the gas atmosphere during oxidation.
[d] Measured by hydrogen adsorption at room temperature.
[e] Catalyst preimpregnated with HCL (aq.) to raise the chlorine level up to 0.6%.

dispersion was confirmed by the results of Run 12.

Analysis performed on the catalyst after these experiments showed that the amount of platinum was not altered. It is also important to mention that the prolonged exposure to hydrogen at 600°C (650 hr) caused only a 10% decrease in the total surface area of catalyst C-1.

Another sample of this catalyst was used to investigate the effect of a higher temperature during the air treatment and the results

TABLE 3

Variation of the Metal Dispersion upon Thermal Treatment of Catalyst C-1

Run	Gas atmosphere	Temperature (°C)	Time (hr)	Pt dispersion (%)[a]	Cl content (wt%)
1[b]	Air	500	2	50	0.66[c]
2	Air	570	6	46	—
3	Air	580	14	27	—
4	Air	500	16	26	0.66[d]
5[e]	Air	500	13	33	—
6	O_2	500	13	37	—
7	O_2	500	12	76	0.84[d]

[a] Measured by hydrogen adsorption at room temperature.
[b] Catalyst used previously in other experiments.
[c] Analysis performed before dispersion measurement.
[d] Analysis performed after dispersion measurement.
[e] Catalyst preimpregnated with HCl (aq.) to raise the chlorine level up to 1.0%.

TABLE 4

Variation of the Metal Dispersion upon Thermal Treatment of Catalyst L-1

Run	Gas atmosphere	Temperature (°C)	Time (hr)	Pt dispersion[a] (%)	Cl content[b] (wt%)
1	H_2	570	99	68	0.62
2	Air	500	12	100	—
3	H_2	590	103	53	—
4	Air	500	12	85	—
5	H_2	570	75	59	—
6	Air	500	12	90	—
7	H_2	590	99	52	—
8	Air	500	17	90	0.27
1'	H_2	600	218	32[c]	—
2'	Air	500	13	41[c]	0.27
1"	H_2	600	320	31[c]	—
2"	Air	500	13	53[c]	0.74

[a] Measured by hydrogen adsorption at room temperature.
[b] Analysis performed after dispersion measurement.
[c] Measured by oxygen adsorption–hydrogen titration at room temperature.

are presented in the lower part of Table 2. At 600°C the dispersion was found to decrease dramatically in only 12 hr, to 16%, and this value was not altered by the standard treatment at 500°C. By lowering the temperature and the length of treatment we were able to sinter the catalyst to the same level achieved in hydrogen (see Table 3). The reason for doing this experiment was to investigate the possibility of redispersion of air-sintered samples. Here again the treatment in air at 500°C was unsuccessful. Successive treatments under the same conditions or the addition of chlorine only

TABLE 5

Variation of the Metal Dispersion upon Thermal Treatment of Catalyst L-2

Run	Gas atmosphere	Temperature (°C)	Time (hr)	Pt dispersion[a] (%)	Cl content (wt%)
1[b]	Air	500	13	77	—
2	H_2	600	96	36	—
3	Air	500	13	64	0.18[c]
1'[d]	Air	500	12	100	—
1"[d,e]	Air	500	13	100	0.83[f]
2"	H_2	600	216	37	0.67
3"	Air	500	12	81	—

[a] Measured by hydrogen adsorption at room temperature.
[b] Catalyst reduced prior to this run (4 hr at 500°C).
[c] Analysis performed after dispersion measurement.
[d] Unreduced catalyst.
[e] Catalyst preimpregnated with HCl (aq.) to raise the chlorine level up to 0.9%.
[f] Analysis performed before oxygen treatment.

TABLE 6

Variation of the Metal Dispersion upon Thermal Treatment of Catalyst L-3

Run	Gas atmosphere	Temperature (°C)	Time (hr)	Pt dispersion[a] (%)	Cl content (wt%)
1[b]	Air	500	13	94	—
2	H_2	600	96	37	—
3	Air	500	13	73	0.15
1'[b]	Air	600	6	69	—
2'	Air	600	13	47	—
3'	O_2	500	8	51	—
4'	O_2	500	22	65	—

[a] Measured by hydrogen adsorption at room temperature.
[b] Catalyst reduced prior to this run.

brought a small increase in dispersion. However, a notable effect was found when pure oxygen was used instead of air (Runs 6–7). The increase actually exceeded the original value. The same behavior was observed when similar experiments were performed on a sample of catalyst L-3 (see Table 6). In accord with these results the redispersion of air-sintered samples seems to be dependent on the oxygen concentration and the length of treatment.

Catalyst L-1 was also subjected to successive sintering–redispersion cycles as seen in Table 4. In contrast to catalyst C-1, the redispersion capacity was near 100% after four cycles, although the chlorine content was considerably reduced. However, it is important to observe that these sintering experiments were carried out under less severe conditions. Consequently, the metal dispersion never decreased below 50%.

When this catalyst was sintered for a long period of time (see Run 1' and 1") the dispersion reached 31–32%. A sample treated in hydrogen for 320 hr showed a redispersion of 58% and a relatively small decrease in chlorine content. The change in dispersion as a function of time for this sample is shown in Fig. 1.

The other laboratory preparations, L-2 to L-4, were treated in air at 500°C after reduction (see Tables 5–7). As a result an improvement in the original dispersion was observed, the exception being catalyst L-3 that has a high initial value. The catalysts were then sintered in hydrogen for 96 hr and the dispersion decreased to 36–37%. After an additional air treatment they showed a redispersion capacity of approximately 80%. Consequently, the differences in support pretreatment or the low initial chlorine content in these samples did not

TABLE 7

Variation of the Metal Dispersion upon Thermal Treatment of Catalyst L-4

Run	Gas atmosphere	Temperature (°C)	Time (hr)	Pt dispersion[a] (%)	Cl content (wt%)
1[b]	Air	500	13	77	—
2	H_2	600	96	37	—
3	Air	500	13	59	0.33

[a] Measured by hydrogen adsorption at room temperature.
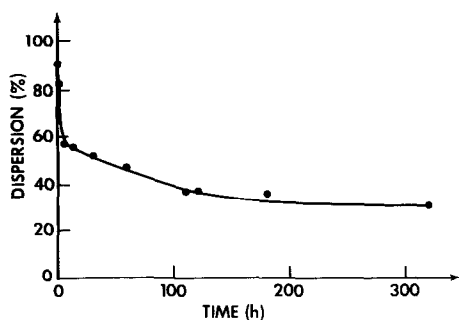[b] Catalyst reduced prior to this run.

FIG. 1. Effect of heat treatment in hydrogen at 600°C on the metal dispersion of catalyst L-1.

cause any appreciable effect in the sintering–redispersion behavior.

An unreduced sample of catalyst L-2 (see Run 1' in Table 5) after being treated in air at 500°C showed a dispersion of 100%. This indicates the beneficial effect of calcination, prior to reduction, in the preparation of highly dispersed platinum catalysts. Finally, catalyst L-2 was sintered in hydrogen for 216 hr and the dispersion was found again to be 37%. This situation is analogous to that found with catalyst C-1 and L-1 where a lower limit of dispersion was also observed despite the differences in sintering time.

DISCUSSION

Identical sintering behavior in H_2 was essentially observed for all samples investigated. At 600°C the loss in metal surface area is a relatively slow process, the rate being strongly dependent on crystallite size, as seen in Fig. 1. Consequently, the kinetics will follow a high order power-law rate equation. Due to the limited number of experiments performed and the error associated with the temperature measurements (± 8°C), we did not attempt to perform a kinetic analysis on our data. It is however interesting to observe that a constant dispersion was obtained after 100 hr of sintering time. As mentioned before similar behavior was observed with catalysts C-1, L-1, and L-2. Although some of these results may be for-

tuitous and without significance, we are inclined to believe that they are related to the sintering mechanism. The limiting growth of the metal particles can be explained on the basis of an increasing resistance to surface diffusion as crystallites become larger. For small particles the metal–support interaction is probably weak, and provided that the temperature is sufficiently high, they can migrate on the support and sinter upon collision. As the particles grow to a certain size they become immobile because of a large number of interaction points with the support, and further growth can occur only through the migration and collision of small particles. If small particles are no longer present on the support, the large crystallites will reach a limiting size. This interpretation supports the crystallite migration model as a mechanism of sintering in a reducing atmosphere.

Published results on sintering in hydrogen at 600°C are scarce but they are in agreement with those given here. Somorjai (13) sintered a high metal content catalyst and followed the growth rate of large particles (>50 Å) by small angle X-ray diffraction. It was seen that the growth process becomes slower as time increases leading eventually to a constant particle size. Dautzenberg and Wolters (11) measured the decrease in dispersion of Pt/Al_2O_3 catalysts that were heated in hydrogen at 600°C. They found that a constant dispersion was reached in less than 100 hr, but a different explanation was given for this result. In their view "platinum loses its ability to chemisorb hydrogen" after treatment in hydrogen at high temperature and consequently the observed decrease in dispersion does not imply crystallite growth. They pointed out that H/Pt ratios as derived from particle size distributions (TEM) were considerably higher than those measured by chemisorption. In addition the amount of Pt detected (by the same technique) was found to be only a fraction of the actual metal content. As the authors pointed out

this quantitative estimation could be subject to errors, in part due to the inherent limitations of the electron microscopy technique. The size distribution of platinum crystallites also becomes questionable when the fraction of particles with sizes below 2.5 nm is important (14). Dautzenberg and Wolters calculated H/Pt ratios of 0.90 and 0.75 based on the average crystallite size, for samples heated in hydrogen at 600 and 675°C, respectively. From the correspondent particle size distributions and using the equations of Van Hardeveld and Hartog (15) for the total number of surface atoms and the total number of atoms, we found the ratios to be 0.78 and 0.56, respectively. It is also important to note that the addition of one particle of large size (5 nm) to the experimental size distributions given in Ref. (11) could further reduce the calculated dispersions. Consequently the electron microscopy experiments do not seem to provide unequivocal evidence of the absence of metal sintering. They do show, however, that the amount of Pt detected increases with the treatment temperature while the particle size distribution becomes broader.

In a subsequent publication (16) the authors further investigated the changes in dispersion of Pt/Al₂O₃ catalysts, treated in hydrogen, by means of hydrogen–oxygen chemisorption and titration. They observed a marked decrease in the hydrogen chemisorption (HC) while subsequent oxygen and hydrogen titration (OT–HT) measurements indicated only a moderate decrease in dispersion. This behavior was ascribed to the formation of a Pt–Al alloy. They also found the HT/OT ratio to be equal to that for the fresh catalyst. Relevant to our interests are the OT values given in Tables 1 and 2 of Ref. (16). They reflect a true decrease in dispersion as a result of the heat treatment in hydrogen. The initial dispersion of 91% went down to 71% after treatment at 550°C and then to 57% after 16 hr at 650°C. The lower HC values of 49 and 24% can be alternatively explained assuming that some

hydrogen was left on the metal surface after the high temperature treatment, due to the relatively mild desorption conditions. In our opinion the removal of surface hydrogen was incomplete after 2 hr evacuation at 400°C. Supporting this view is the fact that the same catalyst (E), when heated in hydrogen under analogous conditions but evacuated at 400°C for 16 hr (see Fig. 3 in Ref. 11), gave a H/Pt ratio of approximately 70%, which is close to the value derived from OT or HT.

Additional evidence for the anomalous HC values is found in Table 3 of Ref. (16) where a sample sintered in air at 600°C or treated in hydrogen at 550°C exhibits the same H/Pt ratio. It has been reported at least on two occasions (3, 17), and confirmed in the present work, that air treatment produces a more rapid decrease in dispersion (as measured by HC) compared to hydrogen. Although we can not rule out completely the possibility of alloy formation and hence a partial reduction in the HC capacity, the experiments discussed above do not provide a definitive answer to this question.

We are also aware of several cases where treatment of Pt/Al₂O₃ catalysts in hydrogen at 500°C caused sintering as detected by CO chemisorption, electron microscopy of X-ray diffraction (18–20). In a recent paper, Yao et al. (21) have shown that treatment at 750°C induces crystallite growth along with a parallel decrease in CO and H₂ chemisorption. Relevant to our work is their finding (by TEM) that redispersion of crystallites in the 1–3 nm range takes place after oxygen treatment at 500°C.

Finally we want to comment on some experiments performed by us on a 4.6% Pt/Al₂O₃ catalyst where CO and H₂ chemisorption was used to monitor the decrease in dispersion. The sample, prepared by the same procedure detailed before for catalyst L-1, had an initial dispersion of 92% and a CO/H ratio of 0.67. Following treatment in hydrogen at 750°C for 48 hr the dispersion decreased to 34% but the CO/H ratio was

not altered. Under the hypothesis of alloy formation we would expect the adsorption of CO to be less affected than hydrogen adsorption since it is not dissociatively adsorbed and is mostly linearly bonded.

The decrease in chlorine content was another important feature of the sintering process. We did not observe a clear correlation between the chlorine content and the sintering time. For example, catalyst L-1 showed a 40% reduction in chlorine after 99 hr at 570°C (see Run 1 in Table 4) and a similar sample treated for 320 hr at 600°C showed only a decrease of 30%. We found this variation to depend mainly on the water content of the hydrogen gas. During the first stages of this work and before systematic control of moisture was established, the long sintering runs were probably conducted under an increasing concentration of water. This was due to the saturation of the molecular sieve traps. An independent study was carried out to establish the dependence of chlorine loss on the water content. It is seen in Fig. 2 that using a water-free gas (<35 ppm) the loss of chlorine is a slow process and this is in accordance with the results shown in Tables 5-7. When the water content increases, the rate of chlorine loss is clearly affected. These qualitative aspects of dechlorination are important because of the fundamental role of chlorine in the redispersion phenomena.

The experiments reported in Table 2 indicate that treatment of Pt/Al_2O_3 catalysts in an oxidizing atmosphere at 500°C, following a prolonged exposure to H_2, leads to a significant recovery of the metal dispersion. We showed that the sintering–redispersion cycles can be repeated several times, although the redispersion capacity does not remain constant. Between Runs 5 and 11, for example, the catalyst had experienced a 50% reduction in metal dispersion while the chlorine content decreased by a factor of three. On the basis of these results we might have expected to find a simple relation between the residual level of chlorine in the catalyst and the redispersion capacity. The results of Runs 4 and 9 indicate that this is not the case. The redispersion was lower in the former run while the chlorine content was the same. When similar experiments were performed on catalyst L-1 (see Table 4) the results were quite different. This catalyst also experienced a marked loss of chlorine but after four cycles it still exhibited a 100% redispersion capacity. Furthermore, catalysts L-2 and L-3 with a very low initial concentration of chlorine showed a redispersion of 83 and 78%, respectively. In order to rationalize all these results we have to take into account another variable, that is, the sintering time. If the redispersion capacity is plotted as a function of sintering time, there is an evident correlation between these variables and the chlorine content. Although the amount of data is certainly insufficient to draw quantitative conclusions, Fig. 3 indicates that there is a tendency to have a lower redispersion capacity as times increase at constant chlorine content. However, for any given time there seems to exist a threshold level of chlorine beyond which a redispersion capacity of 100% is obtained. The higher the chlorine concentration the longer the hydrogen treatment can be carried out without affecting the redispersion capacity. In the case of catalyst L-1, total redispersion was obtained despite the low level of chlorine because the sintering time was relatively short. It is seen in
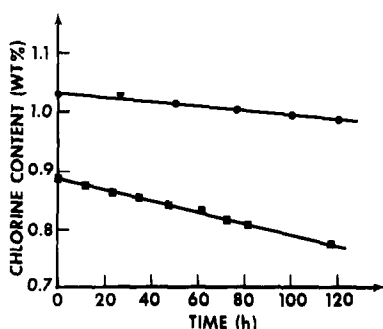

FIG. 2. Decrease in chlorine content of catalyst L-1 during heat treatment in hydrogen at 600°C. Effect of water in the gas phase. ●, 35 ppm; ■, 800 ppm.
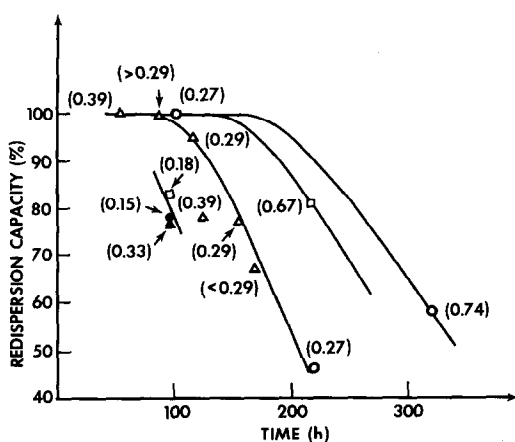
FIG. 3. Effect of chlorine content (wt%) and sintering time in hydrogen on redispersion. Sintering temperature, 600°C. Redispersion conditions, air at 500°C. △, Catalyst C-1; ○, catalyst L-1; □, catalyst L-2; ●, catalyst L-3; ▲, catalyst L-4.

Fig. 3 that a similar sample sintered in dry hydrogen was able to maintain a redispersion of 58% after 320 hr. Our data for the commercial sample seem to fall on a single curve because of the small differences in chlorine concentration. Those catalysts that have a low concentration of chlorine, as L-2 and L-3, show a reduction in redispersion capacity after 100 hr. By increasing both the chlorine content and the sintering time we were able to hold constant the redispersion capacity of catalyst L-2 (see Runs 1″ and 3″ in Table 5).

Another interesting result was the effect of chlorine addition upon samples that have experienced a decrease in redispersion capacity. Regardless of the procedure used for the addition, an increase in chlorine concentration always brought total redispersion. Looking at the results of Table 2 we observe in Run 12 that even a modest addition, below the original level, was sufficient to obtain a very high dispersion. As mentioned before, the increase has been previously associated with the formation of mobile platinum oxides species which migrate from the crystals to the support (9). In order to explain the role of chlorine we need to consider the possibility of interac-

tion between the migrating species and the support. According to our view the support provides the sites where the Pt atoms can be localized, and the concentration of those sites is related to the level of chlorine. When dechlorination occurs, due to the presence of water in the gas atmosphere, the sites are destroyed and consequently the redispersion capacity is affected. Before we attempt to identify the sites we need to explain why redispersion is dependent on sintering time at constant chlorine concentration. During sintering the metal crystallites increase in size and at the same time they decrease in number so we may reach a situation where the concentration of sites in the vicinity of large metal particles becomes insufficient to locate all the Pt atoms on the support. When more chlorine is added to the catalyst, new sites are created and the conditions for total redispersion are reestablished.

Let us now consider the nature of the support sites. It is known that calcination changes the properties of aluminas. Between 300 and 800°C oxidizing sites are formed as a result of condensation of adjacent surface hydroxyl groups (22). It has been suggested that these sites are exposed aluminum atoms with a localized positive charge. Thus, ionic species can be formed through an electron transfer process between adsorbed molecules and the support sites. We postulate the existence of a similar kind of interaction between the metal and the acceptor sites. If platinum atoms or platinum–oxygen species becomes trapped at the sites by this mechanism, the metal will be present in an electron-deficient state. It is well known that a soluble form of platinum in aqueous hydrofluoric acid can be detected in reforming catalysts following an exposure to air at high temperature (23). In accord with this interpretation, the redispersion process can take place in the absence of chlorine because the sites are created during the thermal treatment of the alumina prior to impregnation. In fact, Dautzenberg and Wolters (11) have found

that oxygen treatment of chlorine-free samples leads to an increase in dispersion. Figueras et al. (12, 24) first advanced the idea of an electron-deficient state of platinum due to the presence of oxidizing sites on the alumina. They were able to show that the catalytic activity for cyclohexane dehydrogenation on a series of Pt/SiO₂–Al₂O₃ catalysts of varying alumina content decreased as the concentration of oxidizing sites increased.

The addition of chlorine seems to enhance the oxidizing properties of alumina (25). The electronegative element replaces OH groups and attracts electrons from the Al atom thus reinforcing the strength of the sites. McHenry (23) has found that the amount of soluble platinum increases with increasing chlorine content up to a concentration of 0.6%. We observed that this level was effective to obtain total redispersion in heavily sintered samples. The presence of water during sintering results in the elimination of chlorine and the regeneration of surface OH groups. Consequently, the concentration of sites, and redispersion, are affected.

The interpretation given above agrees with the observation that redispersion is independent on the gas atmosphere used for the support pretreatment. The experiments performed with catalyst L-4 (see Table 7) confirm that the presence of oxygen during the preparation steps is not essential to obtain a catalyst with typical redispersion behavior. Therefore, the role of oxygen at 500°C seems to be restricted to the formation of mobile platinum species.

Another interesting experimental observation was the effect of calcination, prior to reduction, on the metal dispersion. Exposure of freshly prepared catalysts to air at 500°C resulted in a very high dispersion. Catalyst L-1 and a sample of L-2 (see Run 1' in Table 5) are good examples. Uncalcined catalysts, such as L-2 and L-4, with a moderate initial dispersion of 54 and 45%, respectively, increased these values to 77% when heated in air at 500°C. The

variation, although significant, did not reach the value obtained with the precalcined samples. These results are consistent with others in the literature. Fiederow and Wanke (9), working with uncalcined-reduced samples, have found up to a threefold increase in dispersion following an oxygen treatment at 550°C but a value of 100% was not obtained. On the other hand, Dautzenberg and Wolters (11), working with several calcined samples, observed that the H/Pt ratio, following reduction, was always near unity. Jaworska-Galas and Wrzyszcz (8) also found a maximum dispersion in Pt/Al₂O₃ catalysts calcined at 500°C before reduction. The lower initial dispersion in the uncalcined samples (catalyst L-3 seems to be an exception) probably arises from a nonuniform distribution of chloroplatinic acid through the support during impregnation. We cannot explain why the air treatment is not effective to obtain 100% dispersion once the samples have been reduced. We may argue that an unfavorable distribution of Pt and support sites takes place when the acid decomposes in a reducing atmosphere.

The increase in dispersion observed in the uncalcined-prereduced samples indirectly supports our belief that crystallite growth actually occurs during hydrogen treatment at high temperature. Assuming that the hypothesis of Dautzenberg and Wolters (11) is valid it becomes difficult to accept that in the case of catalyst L-4 a mild hydrogen treatment (4 hr at 500°C) has caused a decrease in dispersion from 77 to 45%.

The increase in temperature of the air treatment had a pronounced effect on the metal dispersion. At 600°C the catalyst can be sintered in a short period of time up to a value that was never obtained in hydrogen sintered samples. The transition from redispersion to sintering that occurs at about 580°C is often explained on the basis of PtO₂ decomposition, but it is not clear why the presence of oxygen accelerates the sintering rate. We prefer the hypothesis that

stable platinum oxides are actually formed at this temperature (26) and consequently the metal–support interaction described before ceases to operate. The rapid metal conglomeration observed at 580°C is probably due to surface migration or vapor phase transport of the oxides. The details of these processes cannot be given but the existence of a fundamental change is consistent with the fact that the amount of soluble platinum decreases at temperatures >580–590°C (7).

The redispersion of air-sintered samples is clearly demonstrated in this work according with the results of Tables 3 and 6. There are several distinct features in this process as compared with the redispersion of hydrogen sintered samples. First, the increase in dispersion occurs in the presence of pure oxygen. Second, the redispersion capacity is dependent on the treatment time. In contrast Fiederow and Wanke (9) have found that even an hour treatment in oxygen was sufficient to increase the dispersion of freshly reduced samples. Another observation was the lack of effect of chlorine addition. Finally, it must be pointed out that the ultimate dispersion actually exceeded the initial value. These observations suggest that the catalyst surface is conditioned by the sintering atmosphere. It is unlikely that the support experienced any major transformation during the short treatment at 580°C, and this is consistent with the lack of effect of chlorine addition. If the migration of platinum oxides predominates in the presence of air and the migration of platinum crystallites is the valid mechanism during sintering in hydrogen, some differences may be expected. However, they should be eliminated after the standard reduction procedure at 500°C. It has been reported that platinum forms a stable oxide at high temperature which is difficult to reduce (27). We did not observe any changes in the results when the catalyst was heated in hydrogen at 600°C for 13 hr before the redispersion treatment at 500°C. Undoubtedly, some alterations in the chemical state or the surface morphology of

the platinum crystallites, which are not reversed by hydrogen, take place during heat treatment in air at 580°C. One possibility is the formation of nonreducible oxides in the metal–support interface (28). As a result the mobility of Pt atoms from the crystallites to the support during redispersion may be restricted, and this predicts a time-dependent process.

Although the use of hydrogen chemisorption measurements permits us to follow the change in the number of surface platinum atoms due to sintering, it does not reveal any other structural feature of the metal particles. Thus, catalysts of similar dispersion may exhibit different behavior depending on the pretreatment conditions. For example, it has been found that the specific activity for the hydrogenolysis of ethane on Pt/Al_2O_3 catalyst increases with a decrease in dispersion for air-sintered samples (29), but the opposite behavior was observed when the catalysts were heated in hydrogen at increasing temperatures. Thus, we cannot attempt to establish a mechanism for the redispersion of air-sintered samples on the basis of the experimental evidence obtained in this work. Certainly more information on the surface state of the metal as a function of temperature and gas atmosphere is needed in order to understand the fundamental processes. The present investigation at least has permitted us to demonstrate that there is not a unique mechanism for the redispersion of supported platinum catalysts.

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