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Redispersion of Supported Platinum Catalysts

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The redispersion of platinum on γ-Al_2O_3, SiO_2, and TiO_2 is experimentally studied by means of hydrogen chemisorption, X-ray diffraction, transmission electron microscopy, temperature-programmed reduction, and cyclohexene hydrogenation reaction. The increase in dispersion following treatment in oxygen below 600°C occurs only for Pt/γ-Al_2O_3. For Pt/TiO_2, only the presence of chlorine during oxidation brings about a significant redispersion. For Pt/SiO_2, redispersion does not occur under any condition. Redispersion can occur only in the presence of platinum oxide which could be stabilized by forming a complex with the support. The method for determining whether or not redispersion will occur for any systems and the conditions needed for redispersion are discussed.

INTRODUCTION

Although supported metal catalysts are thermally stable in general, changes in metal surface area still occur with use or treatment for a long period at elevated temperature. The resulting loss of metal surface area generally leads to a decrease in catalytic activity and, very often, to a change in the reaction selectivity (*1*), and it is necessary to restore the original activity of sintered catalysts by a regeneration process, termed redispersion (*2*). The redispersion of crystallites of sintered supported metal catalyst is therefore an important problem. Many investigators (*2–7*) have observed an increase in platinum surface area during thermal treatment of supported platinum catalysts in oxygen-containing atmosphere. Almost all studies of redispersion have been restricted to platinum-alumina system, and carried out with model supported catalyst systems.

Several models have been proposed to explain the redispersion phenomena. The first attributes the redispersion to a physical splitting of the supported particles (*8–11*). A second model assumes the formation of various types of two-dimensional dispersions over the support surface (*2, 5–7, 11–15*). A third model invokes strong metal–support interaction (SMSI) which produces a larger surface area through spreading of particles in hydrogen atmosphere (*16*). A fourth model involves the intraparticle redispersion of alloy catalysts (*17*). However, the conditions and mechanisms for redispersion of metal crystallites are not yet clear.

From the reported results which sometimes contradict each other, many questions arise: Does redispersion depend on treatment time (*2, 10, 18*)? How is the increase in dispersion affected by the initial dispersion (*2*)? Is it possible that dispersion after treatment in oxygen above 600°C is higher than the initial dispersion (*2, 13*)? Is redispersion possible even for catalysts heavily sintered in oxygen (*1, 2, 18*)? Does redispersion take place above the decomposition temperature of the solid platinum oxide (*19, 20*)? How does the addition of chlorine during oxidation affect the redispersion of sintered catalysts (*18, 22*)? Does redispersion occur in hydrogen atmosphere (*16, 22*)?

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The objectives of this study are threefold: first, to obtain some answers to the above questions; second, to select reasonable mechanisms; and third, to search for a simple method for determining whether or not, and under what conditions, the redispersion occurs. To these ends, hydrogen chemisorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature-programmed reduction (TPR), and cyclohexene hydrogenation reaction were carried out on platinum catalysts supported on γ-Al_2O_3, SiO_2, and TiO_2.

EXPERIMENTAL METHODS

Materials. The support materials used in this study were γ-Al_2O_3 (T-374) from United Catalytic Inc., SiO_2 (Grade 57) from Davison Co., and TiO_2 (Cab-O-Ti) from Cabot Corp. The 2 wt% catalysts were prepared by impregnation with chloroplatinic acid. The impregnated catalysts were dried in air for 24 hr at 150°C. All catalysts were reduced for 12 hr in H_2 stream at 400°C unless reduced catalysts were to be examined.

Hydrogen (99.999%) and helium (99.999%) from Matheson Corp. were further purified before use. Oxygen (99.995%, Linde) and nitrogen (99.999%, Matheson) were used without further purification. Cyclohexene (G. R. Grade, Tokyo Chemistry Ind.) was purified by distilling in the presence of sodium metal.

Chemisorption measurements. Adsorption measurements were performed on a conventional BET apparatus equipped with a capacitance manometer (Accusorb 2100E by Micromeritics Instrument Corp.). All samples except Pt/TiO_2 were reduced *in situ* at 400°C in hydrogen atmosphere for 2 hr. The reduced samples were heated to 450°C and then evacuated at the same temperature for 1 hr. The samples were then cooled under dynamic vacuum to room temperature. Pt/TiO_2 sample was reduced at 300°C for 2 hr and then evacuated at the same temperature for 1 hr. Longer period of reduction and evacuation did not affect the subsequent chemisorption results. Uptakes were determined at 25 ± 3°C on the reduced and evacuated samples. Typically 40 min was allowed for each uptake point. At least two successive determinations of hydrogen adsorption uptake were made on each sample.

X-Ray diffraction (XRD). X-Ray diffraction line broadening was measured on a Diano Model 8000 diffractometer using Ni-filtered CuK_α radiation. A slow scan of $0.4°(2\theta)$/min was carried out for 2θ from 35 to 55° and from 75 to 85°. Slow scan provided greater sensitivity for line broadening measurements (*24*).

Transmission electron microscopy (TEM). The electron microscopy was performed using a JEM 100C transmission electron microscope. The samples for TEM were prepared by ultrasonic dispersion after the catalyst powder was ground and passed through a 300 mesh screen.

Sintering treatments. Sintering experiments were done in hydrogen and oxygen streams at temperatures ranging from 300 to 800°C. After sintering at a specified temperature for a fixed time interval, the samples were cooled rapidly to ambient temperature and stored in a stoppered bottle until further use.

Catalytic reaction. The hydrogenation of cyclohexene was carried out in a quartz U-tube microreactor, 8 mm i.d. and 20 cm long. Hydrogen stream at 100 ml/min entered the saturator kept in a constant temperature bath regulated at 35°C to achieve a hydrogen to cyclohexene ratio of 4.52. Nitrogen stream at 100 ml/min, used as a diluent, was mixed with reactants and passed through the reactor heated in a water jacket kept at 60°C. The reaction products were analyzed by a Varian 1420 Gas Chromatograph with a column packed with 20% Carbowax 20M on Chromosorb W.

Temperature-programmed reduction (TPR). TPR was done in a flow system similar to that described by Robertson *et al.* (*24*). The reducing gas was passed through the reference side of the thermal conductivity cell, then through a quartz U-tube reac-

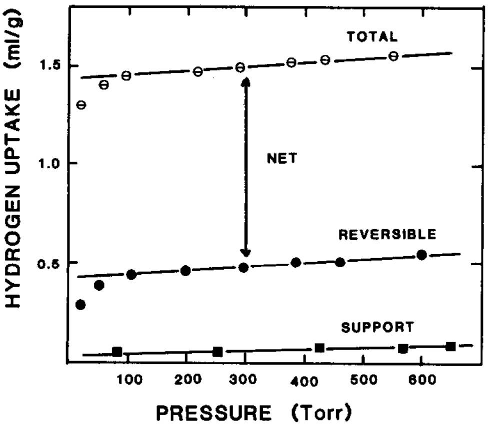

FIG. 1. Typical hydrogen adsorption isotherm at room temperature for 2 wt% Pt/γ-Al_2O_3 (fresh catalysts).

TABLE 1

Dispersion of Catalysts

Catalysts	Treatment	Dispersion
Pt/γ-Al_2O_3	Fresh	0.90
	700°C, 1 hr, H_2	0.44
	700°C, 3 hr, H_2	0.39
	700°C, 5 hr, H_2	0.34
	800°C, 1 hr, H_2	0.31
	800°C, 3 hr, H_2	0.27
	800°C, 5 hr, H_2	0.23
Pt/SiO_2	Fresh	0.21
Pt/TiO_2	Fresh	0.28

tor and a cold trap kept at −78°C back through the sample side of the thermal conductivity cell. A small amount of catalysts was calcined in oxygen at a given temperature and placed in a cold bath at −78°C. The heating rate was 6°C/min and reducing gas composition was H_2/N_2 = 5%/95%. The heating during TPR was regulated around room temperature by a programming controller, but in the range below room temperature, the catalyst was allowed to warm up naturally by simply removing it from the cold bath. The heating in the low temperature region was therefore not necessarily linear.

RESULTS

Chemisorption Measurements

Typical room temperature isotherms of H_2 for 2 wt% Pt/γ-Al_2O_3 catalyst are shown in Fig. 1. The net irreversible uptake was obtained by subtracting the reversible portion from the total uptake. The adsorption of H_2 on supports was found to be totally reversible in preliminary experiments (*26*). Since the amount strongly, i.e., irreversibly, adsorbed is associated with the metal, only the irreversible adsorption is used for comparison of the changes in dispersion.

Table 1 shows the dispersions of freshly prepared catalysts. Since the dispersion of fresh Pt/γ-Al_2O_3 was too great, they were sintered in hydrogen atmosphere to provide various initial dispersions shown in the table before the redispersion study, whereas fresh catalysts were used in the cases of Pt/SiO_2 and Pt/TiO_2. Unless otherwise stated, Pt/γ-Al_2O_3 sintered in hydrogen atmosphere for 3 hr was used.

Figure 2 presents the normalized metal dispersions of three different supported Pt catalysts after treatment in oxygen for 2 hr at various temperatures. For Pt/γ-Al_2O_3 the dispersion after treatment below 600°C was clearly higher than the initial dispersion and

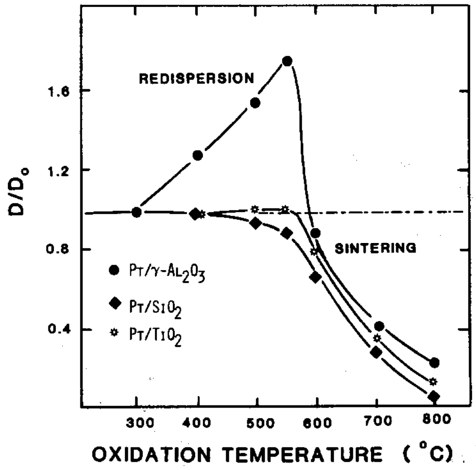

FIG. 2. Effect of oxygen treatment at various temperatures on the normalized metal dispersion. Initial dispersion: Pt/γ-Al_2O_3, 0.38; Pt/SiO_2, 0.21; Pt/TiO_2, 0.28.

TABLE 2

Changes in Dispersion of Pt/γ-Al_2O_3 after Repeated Oxidation–Reduction Cycles[a]

Catalysts[b]	Initial	Number of oxidation–reduction cycles					
		1	2	3	4	5	6
1	0.31	0.65	0.73	0.81	0.83	0.80	0.79
2	0.39	0.79	0.87	0.92	0.93	0.93	0.89
3	0.27	0.53	0.62	0.65	0.68	0.69	0.67

[a] Oxidation at 520°C, reduction at 400°C.

[b] 1, H_2 treatment for 1 hr at 800°C; 2, H_2 treatment for 1 hr at 700°C; 3, H_2 treatment for 3 hr at 800°C.

the maximum dispersion occurred at about 550°C, while for Pt/SiO_2 and Pt/TiO_2 the change in dispersion was small below 600°C. For all catalysts the dispersion decreased severely after treatment above 600°C. The sintering rate was somewhat slower for Pt/γ-Al_2O_3 than for other supported platinum catalysts. The experiments of Fig. 2 were carried out with different samples at various temperatures, but the results had nearly the same trend even when the same experiments had been carried out with a single sample. It is worth noting that dispersion after treatment above 600°C was always smaller than the initial dispersion, which is contrary to the results reported by Fiedorow and Wanke (*2*).

Table 2 summarizes the changes in dispersion of Pt/γ-Al_2O_3 after repeated oxidation–reduction cycles. The catalysts in Tables 1 and 2 are prepared by the same method but subjected to different sintering treatments. The dispersion increased after each oxidation–reduction treatment and reached the saturation value. The higher the initial dispersion, the greater the saturation value was. Since redispersion was found to be insensitive to the treatment time in preliminary experiments, repeated oxidation–reduction cycles might have advantages in regeneration processes.

The effect of dispersion on the redispersion capacity, defined as the ratio of regenerated dispersion after treatment in oxygen at 520°C to sintered dispersion before redispersion treatment, is plotted in Fig. 3. In the case of mildly sintered catalysts the redispersion capacity had maximum with sintered dispersion, while the redispersion capacity decreased monotonically for heavily sintered catalysts. In general, redispersion capacity of mildly sintered catalysts was larger than that of heavily sintered catalysts. On the basis of this result, the hypothesis that redispersion becomes easier as metal particle size increases must be judged incorrect.

Since treatment in oxygen atmosphere for 2 hr at 520°C occurs frequently, we shall refer to this as the *"redispersion condition."* The changes in dispersions of four different Pt/γ-Al_2O_3 samples after various consecutive treatments are shown in Table 3. The increase in dispersion for all catalysts occurred clearly under the redispersion condition. The addition of chlorine during oxidation under the redispersion condition brought about a significant increase in dispersion. The addition of water, however, led to a decrease in dispersion even at redispersion condition. For oxidation at temperature higher than the redispersion condition, dispersion decreased even in the presence of chlorine. On the other hand, the addition of chlorine during reduction showed a significant decrease in dispersion, but it could be increased if the sample was oxidized at a moderate temperature which did not lead to Pt particle size

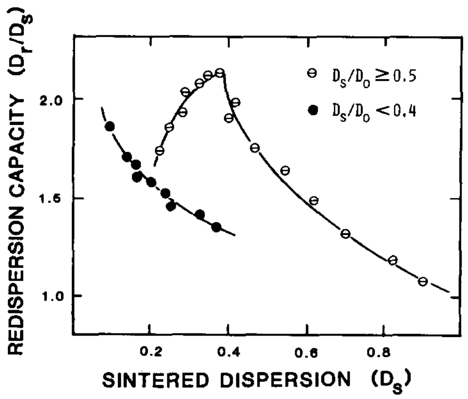

FIG. 3. Effect of dispersion at 520°C in O_2 on the redispersion capacity for Pt/γ-Al_2O_3.

TABLE 3

Dispersion Changes of Pt/γ-Al_2O_3 after Various Treatments

Cat. No.	Initial	Treatments									
		O_2	O_2 + HCl	O_2 + H_2O	O_2 + HCl	O_2 + HCl	H_2 + HCl	O_2	O_2 + HCl	O_2	O_2
1	0.39	0.74 (520)	1.08 (520)	—	0.95 (600)	—	0.29 (600)	0.69 (300)	0.92 (520)	0.07 (800)	0.09 (520)
2	0.30	0.68 (520)	0.96 (520)	0.81 (520)	0.10 (800)	0.49 (520)	0.02 (700)	0.23 (300)	0.69 (520)	0.05 (800)	0.08 (520)
3	0.23	0.47 (520)	0.88 (520)	0.75 (520)	0.35 (700)	0.81 (520)	—	0.79 (300)	—	—	—
4	0.44	—	1.01 (520)	0.38 (700)[a]	0.33 (700)	0.74 (520)	0.03 (800)	0.16 (300)	0.76 (520)	0.05 (800)	0.09 (520)

[a] Hydrogen atmosphere; values in parentheses, treatment temperature.

change. This result implies that the metal–support interaction became stronger in the presence of chlorine (*26*). This strong interaction produced severely suppressed chemisorption capacity, which is in agreement with the hypothesis put forward by Dautzenberg and Wolters (*1*). Furthermore, redispersion occurred even for catalysts heavily sintered in oxygen atmosphere as shown in Table 3.

XRD and TEM Analyses

Since the intensity decreases and the line width increases as the dispersion increases, the changes in dispersion can be measured qualitatively by the change of diffraction peaks. Figure 4 shows the X-ray diffraction patterns of a given sample of Pt/γ-Al_2O_3 treated consecutively at various conditions in the order, a, b, c, d, e, f. The intensity of diffraction peak increased after hydrogen treatment at 800°C, decreased somewhat after treatment at the redispersion condition, but greatly increased again after oxygen treatment at 800°C. This result implies that Pt metal was not changed even in the presence of HCl (*27*). Furthermore, a small decrease in intensity was observed after the redispersion treatment. Changes in X-ray diffraction patterns for Pt/SiO_2 and Pt/TiO_2 were also investigated. For Pt/SiO_2 the intensity did not decrease under any condition. In the case of Pt/TiO_2 the intensity did not decrease during treatment at the redispersion condition alone, but the presence of chlorine during oxidation brought about a significant decrease in intensity.

Figure 5 shows micrographs of Pt/γ-Al_2O_3 catalyst under various conditions. These micrographs reveal clearly the decrease of Pt particle size during oxidation and more significant decrease of Pt particle size in the presence of chlorine. Micrographs of Pt/SiO_2 and Pt/TiO_2 show that Pt particle size did not decrease during oxidation. From these observations we note that the results of chemisorption, XRD and TEM analyses agree well with each other.

Evidence of Metal Oxide–Support Interactions

In general, it is more difficult to reduce the platinum oxide dispersed on large surface area supports than it is to reduce the

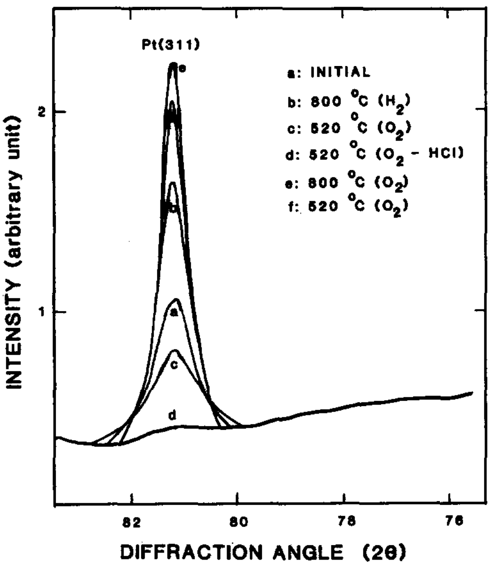

FIG. 4. X-Ray diffraction patterns of Pt/γ-Al_2O_3.

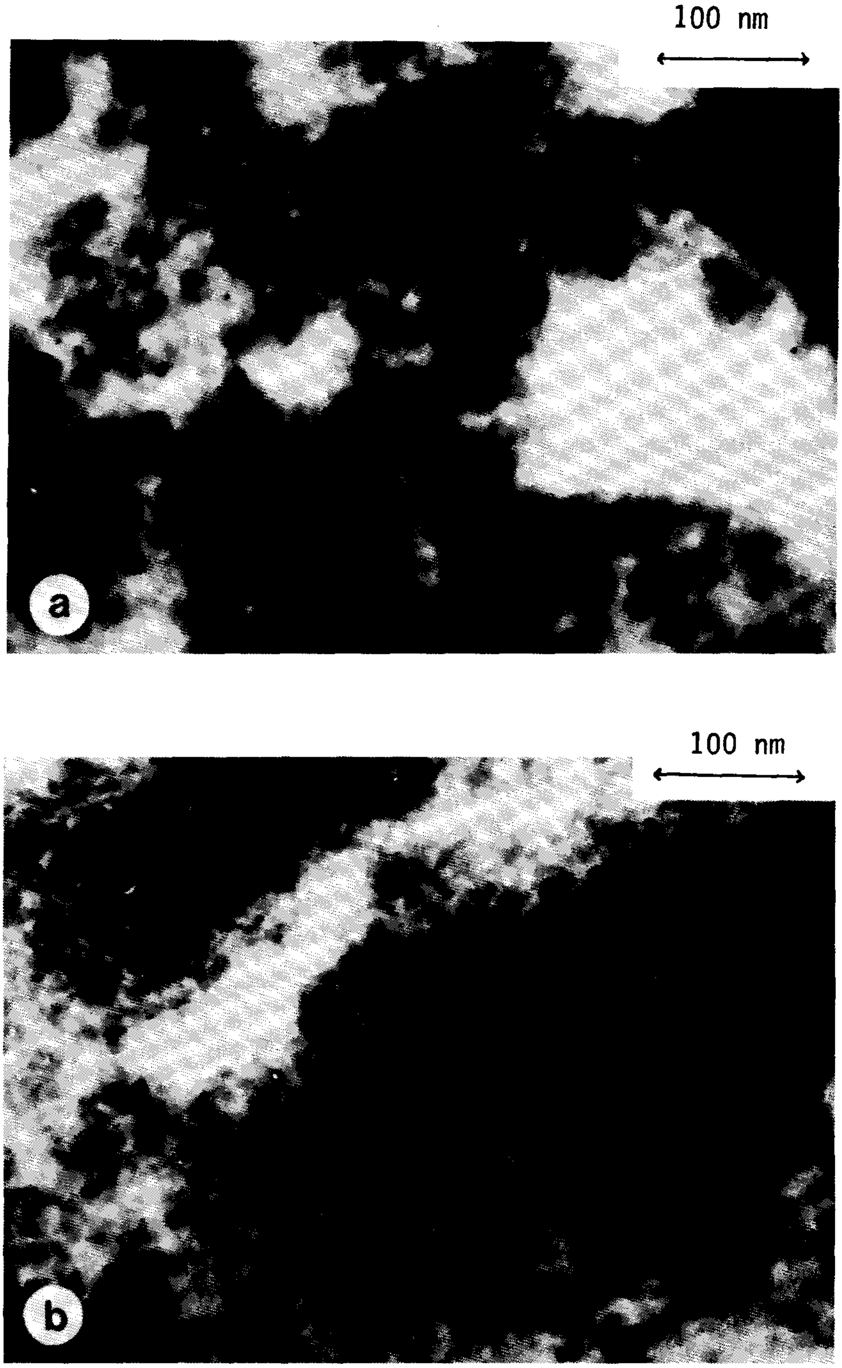

FIG. 5. Electron micrographs of Pt/γ-Al_2O_3. (a) Initial, (b) 800°C (H_2), (c) 520°C (O_2), (d) 520°C (O_2 + HCl).

bulk platinum oxide since the resulting platinum oxide–support interaction impedes the reduction process. Therefore the reducibility of the supported platinum catalysts is an important measure of the strength of metal oxide–support interaction. The TPR

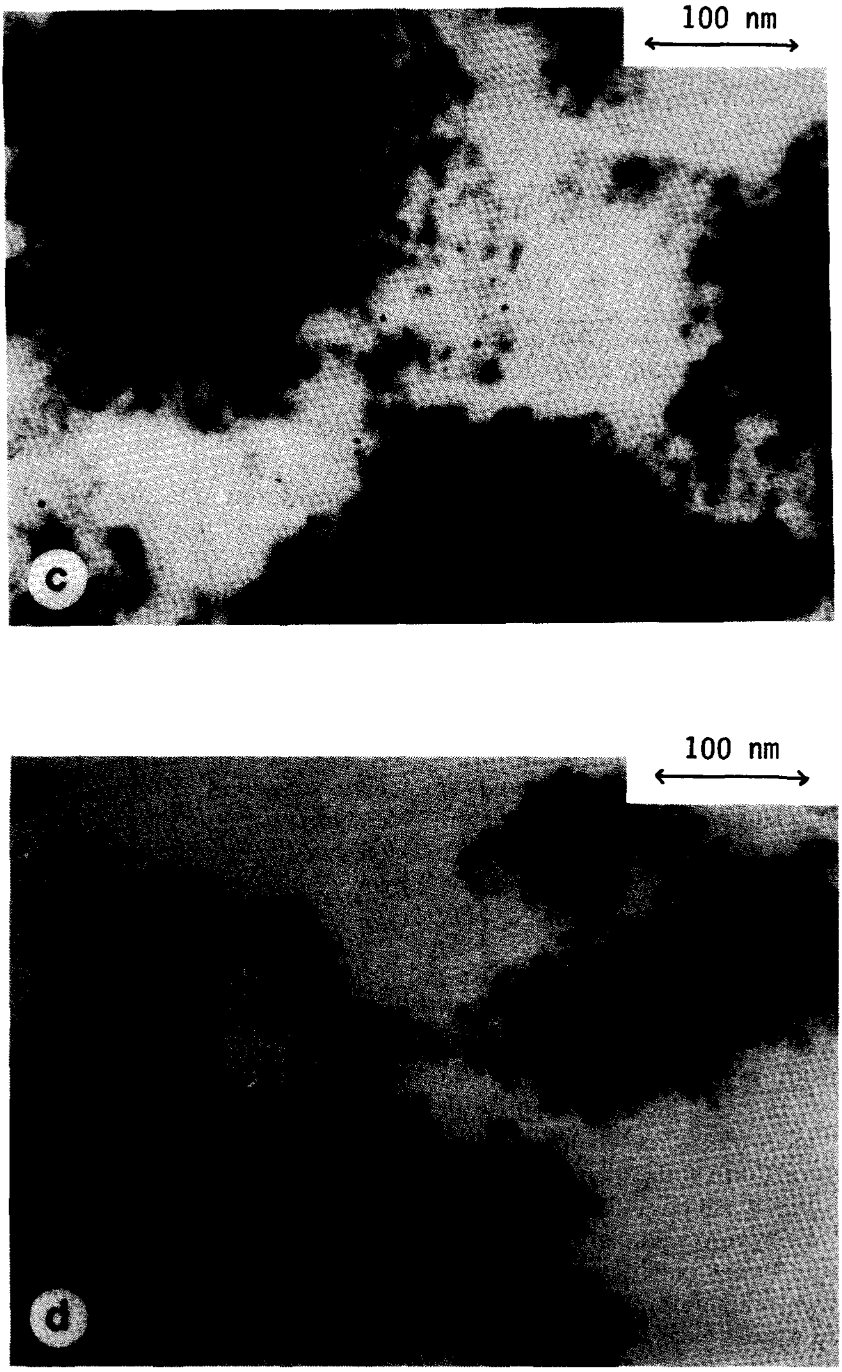

FIG. 5—*Continued.*

profiles of three different supported platinum catalysts after treatment under the redispersion condition are shown in Fig. 6. Like bulk PtO_2 (*15*), Pt/SiO_2 was reduced below room temperature with a maximum rate at 10°C. The TPR profiles of Pt/TiO_2 has two reduction peaks. The low temperature peak might be due to reduction of plati-

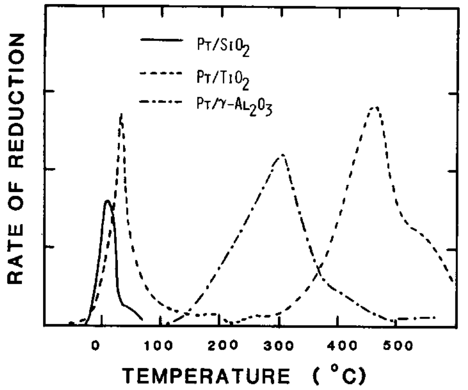

FIG. 6. TPR of catalysts after 520°C oxidation.

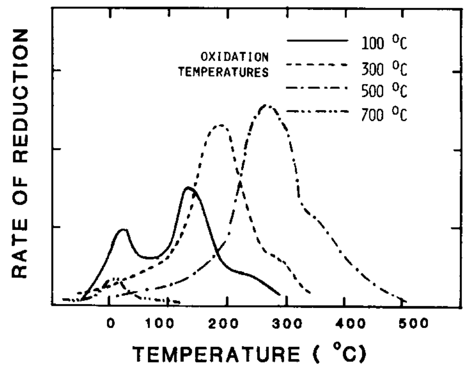

FIG. 7. Effect of oxidation temperature on TPR of Pt/γ-Al_2O_3.

num oxide. The high temperature peak was due to surface reduction of titania to nonstoichiometric oxide (*28*) and did not appear in the other two catalysts. Even though the reduction of pure TiO_2 occurred above 600°C, Pt/TiO_2 could be reduced at lower temperature since the reduction of the support could be catalyzed by Pt (*16*, *26*). In the case of Pt/γ-Al_2O_3, however, a single reduction peak was observed at about 300°C. This result shows that the order of interaction of platinum oxide with supports under the redispersion condition is Pt/γ-Al_2O_3 > Pt/TiO_2 > Pt/SiO_2 ≥ bulk PtO_2.

Figure 7 presents the TPR profiles of Pt/γ-Al_2O_3 at various oxidation temperatures. The reduction of platinum oxide took place at increasingly higher temperature as the oxidation temperature increased. This suggests that higher oxidation temperature enhanced interaction of the platinum oxide with the γ-Al_2O_3 support. The TPR after treatment at oxidation temperature higher than the redispersion condition did not produce the high temperature reduction peak and showed a small peak below room temperature.

The formation and stability of platinum oxide complexed with support have been generally considered crucial to the redispersion process. To investigate this chemisorption experiments were performed in two different ways. The hydrogen uptakes were measured of catalysts oxidized at different temperatures with and without subsequent reduction. The ratios of these uptakes to the initial normal uptakes, measured after reduction at 400°C without oxidation, are given in Figs. 8 and 9. Figure 8 shows that for a single sample of Pt/γ-Al_2O_3 treated consecutively hydrogen uptakes before reduction decreased monotonically regardless of the dispersion (*29*). Very interesting is the result that redispersion can occur only when after reduction hydrogen uptakes are greater than those be-

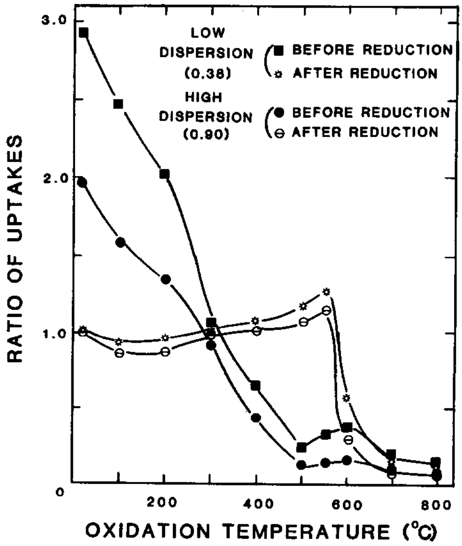

FIG. 8. Hydrogen uptakes before and after reduction of Pt/γ-Al_2O_3.

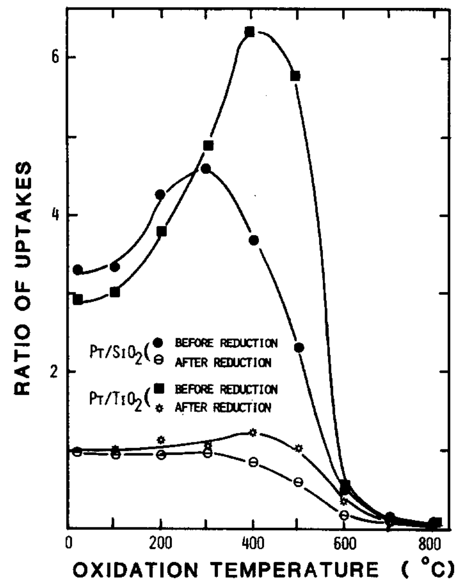

FIG. 9. Hydrogen uptakes before and after reduction of Pt/TiO_2 and Pt/SiO_2.

fore reduction. Figure 9 shows that for Pt/SiO_2 and Pt/TiO_2, on the other hand, hydrogen uptakes after reduction were never greater than those before reduction for any oxidation temperature; that is, redispersion did not take place for these catalysts.

For all three catalysts the hydrogen uptakes measured before and after reduction agreed with each other above the temperature ranges of the decomposition of platinum oxide. From these observations we conclude that redispersion can occur only in the presence of platinum oxide which could be stabilized by forming complexes with γ-Al_2O_3. Dispersion increases with oxidation temperature below the redispersion condition because of the enhancement of the interaction of platinum oxide with γ-Al_2O_3 support. Redispersion cannot occur even in the presence of platinum oxide unless this compound is stabilized by complexing with supports.

Catalytic Activity Measurements

The changes in catalytic activity for Pt/γ-Al_2O_3 after treatment in oxygen and hydrogen atmospheres are shown in Fig. 10. During reduction the activity remained nearly constant up to 500°C, and then decreased, whereas during oxidation the activity increased below the redispersion condition and decreased sharply above it. The activity for the other two catalysts decreased monotonically as the oxidation temperature increased. It was also noted that treating high temperature reduced Pt/TiO_2 samples with oxygen restored their catalytic activity which increased up to 500°C, then dropped sharply. This increase in activity could be attributed not to the redispersion of the metal, but to the destruction of the SMSI since the redispersion phenomenon was not observed in the case of nitrogen- and oxygen-sintered catalysts (*26*).

DISCUSSION

Redispersion of supported Pt catalysts in oxygen atmosphere has been explained by means of one of the two models: one attributes the increase in dispersion to the actual physical splitting of the particles, which is based on crystallite migration model (*30*), while the other invokes the formation and spreading of platinum oxide layers on the support. In general, particle splitting should occur more easily as particle size increased (*9*), but redispersion was observed even in

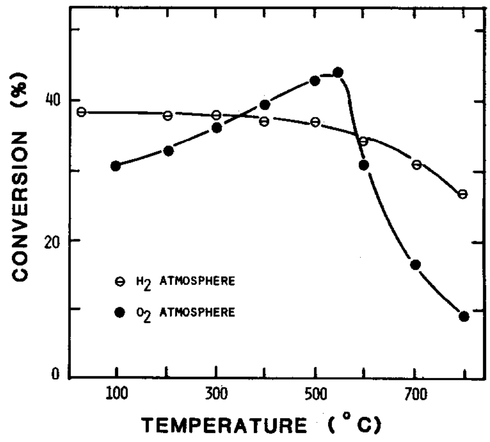

FIG. 10. Conversion of cyclohexene hydrogenation after treatment in H_2 and O_2.

catalysts with very small particle size. According to the splitting model dispersion would increase as treatment time increased (*10*), but the dispersion observed in this work was relatively insensitive to the length of treatment. The resulting dispersion should be independent of initial particle size since splitting occurred continuously until it reached the critical particle size (*10*), but the observed redispersion capacity had a maximum with the variation in initial dispersion. According to the splitting model the increase in dispersion should be independent of the surface area of the support (*2*), but the observed degree of redispersion increased as the available surface area increased. Furthermore, Yao *et al.* (*15*) reported that large particles could continue to be observed after redispersion, and Stulga *et al.* (*31*) proposed that it would be more likely for fracture to take place within the substrate than in the particle. From this we conclude that the splitting model cannot account for redispersion. The formation and spreading of platinum oxide layers on the support appears to be the more reasonable mechanism. This mechanism based on molecular migration (*19*) involves surface migration and vapor phase transport of the migrating species to trap sites on the support that have large interactions and spreading of thin oxidized leading edge of the crystallites.

The results of this study show that treatment below 600°C in oxygen atmosphere leads to increase in dispersion for Pt/γ-Al_2O_3 only. For Pt/SiO_2 redispersion does not occur under any condition, while for Pt/TiO_2 the increase in dispersion was observed only in the presence of chlorine during oxidation. For all catalysts the dispersion decreases drastically after treatment above 600°C. Both continuum concept of surface tension and discrete concept of molecular migration are invoked to explain the results obtained here.

When a metal particle is in thermodynamic equilibrium on a solid support, the three characteristic surface tensions are related through Young's equation

$$\sigma_{gs} - \sigma_{ms} = \sigma_{mg} \cos\theta$$

where σ is the surface tension, θ is the wetting angle, and the subscripts gs, ms, and mg refer to the gas–support, metal–support, and metal–gas interfaces, respectively. If the various metal–gas–support systems are analyzed in terms of this relationship some very interesting predictions emerge. Spreading is due to the changes in surface tension produced by the oxidation of Pt. At 550°C where maximum redispersion reportedly occurs, σ_{gs} for γ-Al_2O_3 is 793 ergs/cm, that for TiO_2 is 582 ergs/cm and that for Pt/SiO_2 is 268 ergs/cm (*32*). Thus σ_{gs} is arranged in the order, γ-Al_2O_3 > TiO_2 > SiO_2. σ_{ms} will be smaller for Pt/γ-Al_2O_3 than for Pt/TiO_2 since metal oxide–support interaction is greater for Pt/γ-Al_2O_3, and SMSI is broken for Pt/TiO_2 during the oxidation treatment (*16, 26*), and the probability of surface Pt-aluminate formation is higher than that of Pt-titanate (*32*). Vannice observed that SiO_2-supported metals could act in the same way as the respective unsupported metals, confirming the lack of strong interactions with the support. Therefore, the order of σ_{ms} is Pt/γ-Al_2O_3 < Pt/TiO_2 < Pt/SiO_2. This is supported by TPR results. As σ_{mg} is the same in these systems, the differences seen for σ_{gs} and σ_{ms} lead to the conclusion that the probability of wetting by a two-dimensional layer of platinum oxide is much higher on alumina than on titania or silica supports. It is therefore not surprising to find that redispersion of sintered metal particles is observed only for Pt/γ-Al_2O_3 system in oxygen atmosphere. When platinum oxide is decomposed at higher temperatures, metal–support interaction is small for Pt/γ-Al_2O_3 since the platinum particles form once again and platinum does not wet alumina (*20*). The platinum atoms are probably very mobile and will be captured by the particles upon collision, thus sintering rate is accelerated regardless of the supports in oxygen atmosphere at high temperature.

On the other hand, the increase in dispersion may be attributed to the formation of mobile species presumably composed of solid and gaseous platinum oxide. A part of the migrating species may be trapped in high energy sites of the support and thus form new particles. This is confirmed by the experimental results that the reversible hydrogen uptakes decreased drastically after redispersion treatment, and that the degree of redispersion increased when reversible hydrogen uptake was large, even in the case of smaller dispersion.

The transport of migrating species from the particle to the support can take two paths: below 600°C the surface diffusion is predominant while at higher temperature the vapor transport dominates because gaseous PtO_2 can exist at high temperature where solid PtO_2 is unstable (*15*). Observed results can be interpreted in terms of the difference between reactivation and thermal deactivation. If reactivation is greater than thermal deactivation, redispersion is obtained. The extent of reactivation can be estimated from the fact that while redispersion clearly occurs in the $Pt/\gamma\text{-}Al_2O_3$ system, it does not in Pt/SiO_2 where only thermal deactivation takes place. This is illustrated in Fig. 2. Below 600°C the formation of mobile species increases with increasing temperature and the energy of adhesion between the oxide formed and the support is very strong, therefore the observed phenomenon is that of redispersion. On the other hand, at higher temperature the observed phenomenon is thought to be that of sintering because the species trapped on the support can move to large particles by overcoming the interaction energy barrier as temperature is raised. If, however, the binding energy between oxide and support remains strong enough even at high temperatures, redispersion may occur. It is possible under this situation that dispersion after treatment in oxygen above 600°C is higher than the initial dispersion. The experimental evidence of redispersion by vapor transport was reported by Baker *et al.* at 800°C (*19*) and Ruckenstein and Chu at 750°C (*20*).

When equilibration between thermal deactivation and reactivation takes place, the observed dispersion is unchanged. This equilibrium depends on experimental conditions, especially chlorine concentration (*22*), oxygen partial pressure (*7*), and the presence of acid sites on the support (*18*). Since interfacial energy and the concentration of mobile phase change with particle size, the particle size is expected to affect the degree of redispersion. The spreading model is probably more valid for relatively large particles, while the trapping model is valid for small particle sizes.

It is apparent that consecutive treatments bring about the increases in dispersion although the rate of dispersion decreases with each cycle. The equilibrium between redispersion and sintering may be obtained during the repeated oxidation–reduction cycles. Equilibrium may be obtained at much lower dispersion as the initial dispersion decreases. Since the observed redispersion is relatively independent of the treatment time and the formation of platinum oxide takes place only a few layers thick (*34*), continued generation of mobile oxides is needed to redisperse the sintered catalyst until dispersion reaches the equilibrium value. Compared with the degree of redispersion of catalysts sintered in oxygen, that of catalysts sintered in hydrogen is larger. Furthermore, for catalysts sintered in oxygen, the dispersion obtained after treatment in hydrogen at high temperature followed by redispersion treatment is much greater than the dispersion obtained after only redispersion treatment.

Another interesting result is the effect of chlorine addition. The addition of chlorine during oxidation brings about a significant increase in the dispersion for the $Pt/\gamma\text{-}Al_2O_3$ system as well as for the Pt/TiO_2 system in which redispersion does not occur during treatment in oxygen alone. It has been found (*18*) that in the presence of oxygen, chlorine enhances the formation of an oxidizing form of platinum as indicated by the dissolution of the metal at room temperature. The evidence of strong interaction between the migrating species and the support in the presence of enough chlorine is found in the formation of oxychloroplatinum complexes which are strongly bonded to the support (*22*) and in the fact that chlorinated compounds create oxidizing sites and destroy reducing centers on the support (*18*). The strong acceptor sites of support were probably enhanced by the addition of chlorine and an electron-deficient state of platinum due to these oxidizing sites was responsible for the significant redispersion observed.

In general, since acidic sites of the supports are oxidizing sites and SiO_2 support has no acidity, redispersion is not expected for Pt/SiO_2 even in the presence of chlorine. Furthermore, unreduced catalyst showed a significant redispersion compared with reduced catalyst since the chlorine remaining after impregnation enhanced the generation of oxidizing sites. This accounts for the beneficial effect of calcination prior to reduction in the preparation of highly dispersed platinum catalysts.

Adsorbed water weakens the metal–support interaction and therefore increases the mobility of platinum particles. While water could oxidize some metals, in general the noble metal such as platinum is difficult to oxidize with water. However, the presence of water during oxidation even under redispersion condition results in the removal of chlorine and regeneration of surface OH groups (*18*); consequently, oxidizing sites are destroyed and sintering rather than redispersion occurs.

A further interesting result is the formation of a complex between the platinum oxide and the support. From the results of TPR it is known that $Pt/\gamma\text{-}Al_2O_3$ exhibits stronger interaction between the metal and the support as compared with Pt/SiO_2 and Pt/TiO_2. This indicates that although platinum oxide can be formed for all catalysts when treated in an oxygen atmosphere below 600°C, only the $Pt/\gamma\text{-}Al_2O_3$ system would be stabilized by forming a complex with alumina. The formation of the complex, which would then be responsible for the high dispersion of platinum, has been observed by many investigators (*5, 7, 8*). Furthermore, Fig. 7 shows that the formation of this complex is enhanced as oxidation temperature increases. As shown in TPR results, it is difficult to reduce this complex. Thus, hydrogen uptake after reduction is larger than that before reduction for $Pt/\gamma\text{-}Al_2O_3$ under conditions where redispersion is possible. For systems other than $Pt/\gamma\text{-}Al_2O_3$, however, hydrogen uptakes after reduction never exceed those before reduction. Therefore, if one were to determine whether redispersion occurs or not for any system, chemisorption measurements with two different methods are needed.

CONCLUSIONS

Dispersion for $Pt/\gamma\text{-}Al_2O_3$ increases after treatment in oxygen below 600°C. For Pt/SiO_2 redispersion does not occur under any condition covered in this study. In the case of Pt/TiO_2, redispersion occurs only in the presence of chlorine during oxidation. The repeated oxidation–reduction cycles play an important role in the regeneration of sintered supported platinum catalysts. Redispersion capacity has a maximum when dispersion is varied, and the rate of redispersion of mildly sintered catalyst is faster than that of heavily sintered catalyst. The addition of chlorine during oxidation enhances redispersion, while the addition of water inhibits redispersion.

Redispersion can occur only under a condition in which interaction is strong enough to produce surface complex between the platinum oxide and the support. The mechanism for redispersion (*2, 14*) based on the molecular migration model which involves spreading of platinum oxide and trapping of migrating species can best account for results obtained in this study.

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