DISPERSION OF SUPPORTED PLATINUM
CATALYSTS IN OXYGEN
I. EXPERIMENTAL EVIDENCES OF REDISPERSION

Tae Jin Lee* and Young Gul Kim

Department of Chemical Engineering

Korea Advanced Institute of Science and Technology

*Department of Chemical Engineering
Yeungnam University, Gyongsan 632, Korea

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Abstract — The redispersion of platinum on γ-Al$_2$O$_3$, SiO$_2$ and TiO$_2$ is experimentally studied by means of hydrogen chemisorption, XRD, TEM, and cyclohexene hydrogenation. The increase in dispersion following treatment in oxygen below 600°C occurs only for Pt/γ-Al$_2$O$_3$. For Pt/TiO$_2$, only the presence of chloride 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 can be stabilized by forming a complex with the support. The methods for determining whether or not redispersion will occur for any system and the conditions needed for redispersion are discussed.

INTRODUCTION

Since almost all supported metal catalysts are expensive to manufacture, methods are needed for the sintered catalyst to recover its original activity. This regeneration process is termed redisperation [1]. The redispersion of crystallites of sintered supported metal catalysts is therefore an important problem. In general, the rate of loss of dispersion increases with increasing temperature [2]. No exception to this rule has been found for non-oxygen containing atmospheres. In oxygen containing atmospheres, on the other hand, many investigators have observed an increase in metal dispersion at certain temperatures [2-8].

Most of studies on redispersion have been restricted to Pt-alumina system, and carried out with model supported catalyst systems. From the reported results which sometimes contradict each other, many questions arise: Does redispersion depend on treatment time [3,9.10]? How is the increase in dispersion affected by initial dispersion [3]? Is it possible that dispersion after treatment in oxygen above 600°C is higher than the initial dispersion [3,11-13]? Is redispersion possible even for catalysts heavily sintered in oxygen [3,10,14]? How does the addition of chlorine during oxidation affect the redispersion of sintered catalysts [10,15]? Does redispersion

occur in hydrogen atmosphere [16,17]?

In the present work, to obtain some answers to the above questions, hydrogen chemisorption, XRD, TEM, and cyclohexene hydrogenation were carried out on platinum catalysts supported on γ-Al$_2$O$_3$, SiO$_2$, and TiO$_2$.

EXPERIMENTAL METHODS

Materials

The support materials used in this study were γ-Al$_2$O$_3$ (T-374) from United Catalytic Inc., SiO$_2$ (Grade 57) from Davision 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 hrs at 150°C. All catalysts were reduced for 12 hrs in H$_2$ stream at 400°C unless unreduced catalysts were to be examined. Table 1 shows the dispersions of freshly prepared catalysts. Since the dispersion of fresh Pt/γ-Al$_2$O$_3$ was too high, they were sintered in hydrogen atmosphere to obtain various initial dispersions show in Table 1 before redispersion study, whereas fresh catalysts were used in the cases of Pt/SiO$_2$ and Pt/TiO$_2$.

Hydrogen (99.999 %) and helium (99.999 %) from Matheson Corp. were further purified by passing them

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* To whom correspondance should be addressed.

Table 1. Dispersion of catalysts.

Catalysts		Treatment	Dispersion
Pt/γ-Al$_2$O$_3$	A $-$ 0	Fresh	0.90
	A $-$ 1	700℃, 1 hr, H$_2$	0.44
	A $-$ 2	700℃, 3 hr, H$_2$	0.38
	A $-$ 3	700℃, 5 hr, H$_2$	0.34
	A $-$ 4	800℃, 1 hr, H$_2$	0.31
	A $-$ 5	800℃, 3 hr, H$_2$	0.27
	A $-$ 6	800℃, 5 hr, H$_2$	0.23
Pt/SiO$_2$	B $-$ 0	Fresh	0.21
Pt/TiO$_2$	C $-$ 0	Fresh	0.28

Fig. 1. Typical hydrogen adsorption isotherm at room temperature for 2wt% Pt/γ-Al$_2$O$_3$ (Fresh).

through a Deoxo purifier (Engelhard Ind.), a molecular sieve trap, and an Oxy-trap (Alltech Asso.) 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 hrs. The reduced sample were heated to 450°C and then evacuted 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 2hrs and then evacuated at the same temperature for 1 hr. Longer periods 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 minutes 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 8,000 doffractometer using Ni-filtered Cu K$_\alpha$ radiation. A slow scan of 0.4° (2θ)/min was carried out for 2θ from 35 to 55° and from 75 to 85°. Slow scan provided greater sensitivity for line broadening measurements [18].

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.

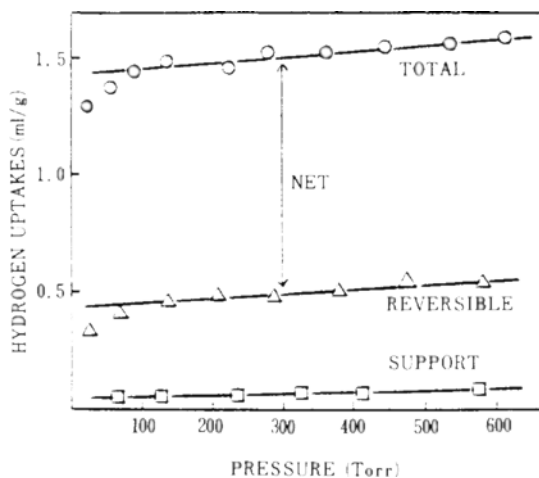**Catalytic Reaction**

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 G.C. with a column packed with 20% Carbowax 20M on Chromosorb W.

RESULTS AND DISCUSSION

Chemisorption Measurements

Typical room temperature isotherms of H$_2$ for 2 wt% Pt/γ-Al$_2$O$_3$ are shown in Fig. 1. The amount of the hydrogen adsorbed per gram of catalyst is expressed in terms of a gas volume corrected to standard condition, i.e., 0°C and 1 atm. In the pressure range studied, adsorption did not reach a saturation value. However, at pressure above 100 Torr the slope of the isotherms was very small and constant. The net irreversible uptake was obtained by subtracting the reversible portion from the total uptake. The reversible adsorption was measured after outgassing the same sample following the total adsorption at the same adsorption temperature for about 30 min [19]. The adsorption of H$_2$ on supports was found to be totally reversible in preliminary experiments [20]. Since the amount strongly (irreversibly) adsorbed is associated with the metal, only the irreversible adsorption is used for comparison of the changes in dispersion. The use of only the irreversible portion had
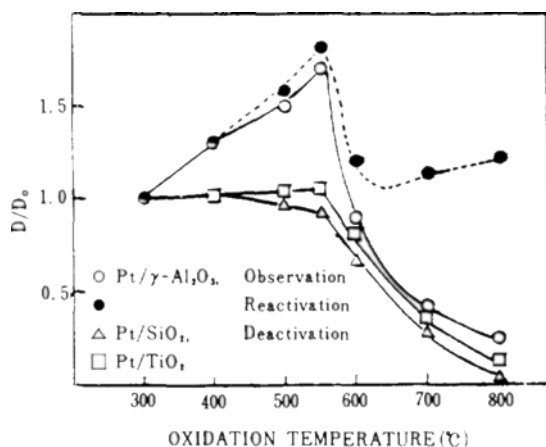
Fig. 2. Effect of oxygen treatment at various temperatures on the normalized metal dispersion. Pt/γ-Al$_2$O$_3$ (A-1).

Table 2. Changes in dispersion of Pt/γ-Al$_2$O$_3$ after repeated oxidation- reduction cycles[a].

Catalysts	Initial	Number of Oxidation-Reduction Cycles					
		1	2	3	4	5	6
A-1	0.44	0.79	0.87	0.92	0.93	0.93	0.89
A-2	0.38	0.71	0.80	0.84	0.85	0.84	0.82
A-4	0.31	0.65	0.73	0.81	0.83	0.80	0.79
A-5	0.27	0.53	0.62	0.65	0.68	0.69	0.67

a Oxidation at 520℃, Reduction at 400℃

two advantages: (1) It was found to be relatively independent of pressure, and (2) it was found to be essentially zero for the supports. Thus the usage of the difference between the total and reversible adsorption isotherms at 300 Torr is arbitrary.

Fig. 2 presents the normalized metal dispersions of three different supported Pt catalysts after treatment in oxygen for 2hr at various temperatures. For Pt/γ-Al$_2$O$_3$ the dispersion after treatment below 600°C were clearly higher than the initial dispersion and 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$_2$O$_3$ 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 (Fig. 6). It is worth noting that dispersion after treatment above 600°C were always smaller than the initial dispersion, which is contrary to the results reported by Fiedorow and Wanke [3].

It is thought that the stability of platinum oxide is closely related to the redispersion phenomenon [10]. Multilayer surface oxidation of poly crystaline Pt wire was studied by Berry [21] at moderate oxygen pressures using a high precision electrical resistance technique. He observed that the electrical resistance increased up to 580°C and then sharply decreased to initial value. He also concluded that the formed oxide was most likely Pto$_2$ and that the maximum growth rate of platinum oxide occurred at the temperature below the dissociation

temperature by aboot 40°C. It is interesting to note that this trend is qualitatively similar to that observed for the dispersion of Pt in Pt/γ-Al$_2$O$_3$ treated in an oxygen atmosphere.

Table 2 summarizes the changes in dispersion of Pt/γ-Al$_2$O$_3$ after repeated oxidation-reduction cycles. The dispersion increased after each oxidation-reduction treatment and reached the saturation value. The higher the initial dispersion was, the greater the saturation value was. It is apparent that consecutive treatments bring about increases in dispersion although the rate of redispersion decreases with each cycle. The equilibrium between redispersion and sintering may be obtained during repeated oxidation-reduction cycles, and this equilibrium may be obtained at much lower dispersion as initial dispersion decreases. 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 of the redispersion capacity, defined as the ratio of regnereated dispersion after treatment in oxygen at 520°C to sintered dispersion before redispersion treatment, is poltted 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. Since interfacial energy and the concentration of mobile phase change with particle size, effect of particle size on the degree of redispersion is expected. According to the Kelvin equation small platinum oxide particles have a higher equilibrium concentration of the mobile species than larger particles [2]. As dispersion increases, redispersion capacity increases and then decreases since dispersion has a limiting value.

Since the treatment in oxygen atmosphere for 2 hrs at 520°C occurs frequently, we shall refer to this as "redispersion condition". The changes in dispersions of four different Pt/γ-Al$_2$O$_3$ samples after various consecutive treatments are shown in Table 3. The increase
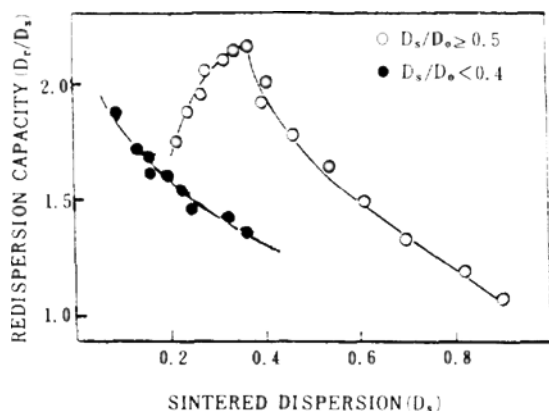
Fig. 3. Effect of dispersion at 520℃ in O_2 the redispersion capacity for Pt/γ-Al_2O_3 catalysts. $D_o =$ Initial dispersion, $D_s =$ Sintered dispersion, $D_r =$ Redispersed dispersion

in dispersion for all catalysts occurred clearly under redispersion condition. The addition of chlorine during oxidation under redispersion condition brought a significant increase in dispersion. The addition of water, however, led to a decrease in dispersion even at redispersion condition. For oxidation at temperatures higher than 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 change. This result implies that the metal-support interaction became stronger in the presence of chlorine [22]. This strong interaction produced severely suppressed chemisorption capacity, which is in agreement with the hypothesis put forward by Dautzenberg and Wolters [14]. Furthermore, redispersion occurred even for catalysts heavily sintered in oxygen atmosphere as shown in Table 3.
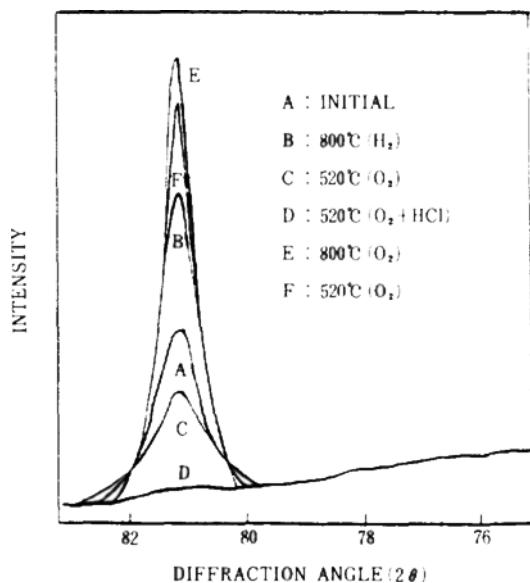

Fig. 4. X-ray diffraction patterns of Pt/γ-Al_2O_3.

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 changes of diffraction peaks. Fig. 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, decreaed somewhat after treatment at redispersion condition. The addition of chlorine led to a significant decrease in intensity, 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 [22].

Furthermore, a small decrease in intensity was observed after 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

Table 3. Dispersion changes of Pt/γ-Al_2O_3 after various treatments.

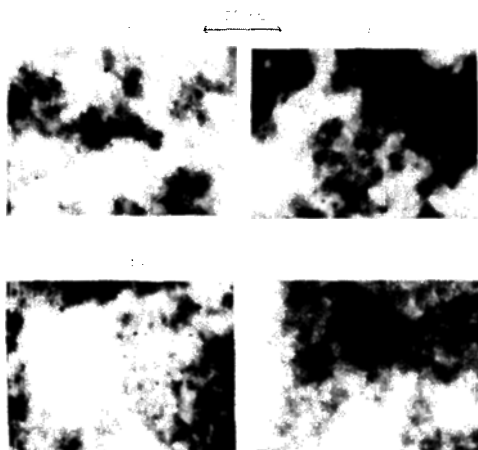| Catalysts	Initial	Treatments									
		O_2	O_2+HCl	O_2+H₂O	O_2+HCl	O_2+HCl	H_2+HCl	O_2	O_2+HCl	O_2	O_2
A-6	0.23	0.47(520)	0.88(520)	0.75(520)	0.35(700)	0.81(520)	–	0.79(300)	–	–	–
A-4	0.31	0.65(520)	0.96(520)	0.8(1520)	0.10(800)	0.49(520)	0.02(700)	0.23(300)	0.69(520)	0.05(800)	0.08(520)
A-3	0.34	0.68(520)	1.02(520)	–	0.95(600)	–	0.29(600)	0.69(300)	0.92(520)	0.07(800)	0.09(520)
A-1	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; ( ) Treatment Temperature in ℃

Fig. 5. Electron micrographs of Pt/γ-Al₂O₃.
a) Initial, b) 800℃ (H₂), c) 520℃ (O₂),
d) 520℃ (O₂+HCl)

OXIDATION TEMPERATURE(℃)

Fig. 6. Hydrogen uptakes before and after reduction of Pt/γ-Al₂O₃.

under any condition. In the case of Pt/TiO₂ the intensity did not decrease during treatment at redispersion condition alone, but the presence of chlorine during oxidation brought about a significant decrease in intensity.

Fig. 5 shows micrographs of Pt/γ-Al₂O₃ 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/SiO₂ and Pt/TiO₂ 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.

Metal Oxide-Support Interactions

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. One was to determine hydrogen uptakes with oxidation state without reduction following treatment at given oxidation temperatures, and the other was to measure hydrogen uptakes after reduction. The ratios of these uptakes to the initial normal uptakes, measured after reduction at 400°C without oxidation, are given in Figs. 6 and 7. Fig. 6 shows that for a single sample of Pt/γ-Al₂O₃ treated consecutively hydrogen uptakes before reduction decreased monotonically regardless of initial dispersion, while hydrogen uptakes after reduction clearly increased below redispersion condition and then dropped sharply. Below 200°C small decrease in dispersion was observed which is consistent
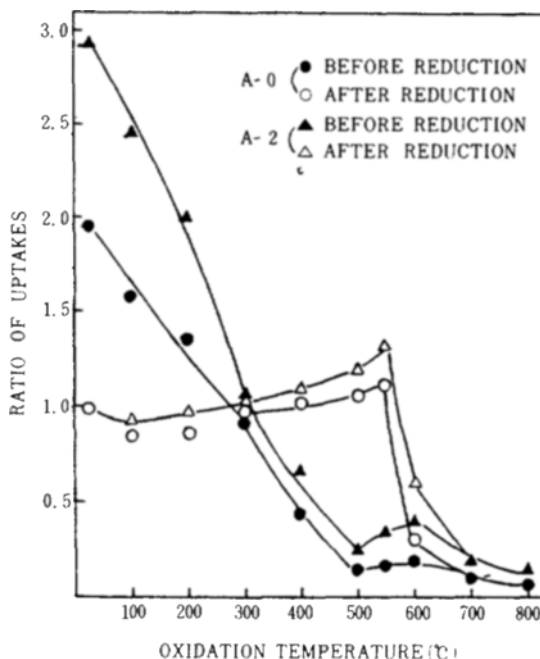
with the result reported by Arai et al [23]. They reported for a Pt/zeolite catalyst that the particle growth proceeded in air at low temperature such as 100°C. For the presintered catalyst (low dispersion) nearly same behavior was observed. In this case the change in dispersion below 300°C was negligible. After treatment above 600°C the values of hydrogen uptakes measured by two ways were nearly the same. This suggests that platinum oxide decomposed completely above 600°C and thus only Pt metal existed [8, 21]. Above 600°C hydrogen uptakes before reduction somewhat increased again although sintering occurred. This is thought to be due to the recovery of chemisorption property by metallic Pt changed from oxide. The observed ratio of uptakes at room temperature agreed with titration stoichiometry which was 2 for highly dispersed cataalyst and 3 for low dispersion [24]. Very interesting is the result that redispersion can occur only when hydrogen uptakes after reduction are greater than those before reduction. Fig. 7 show that for Pt/SiO₂ and Pt/TiO₂, 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 con-
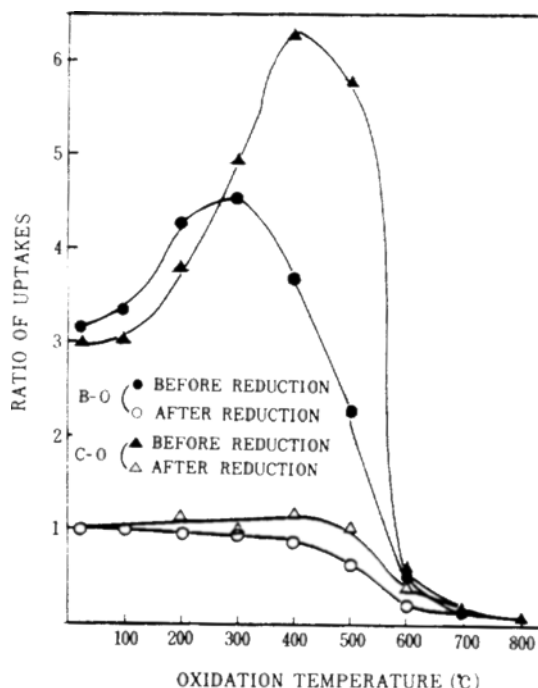
Fig. 7. Hydrogen uptakes before and after reduction
of Pt/TiO₂ and Pt/SiO₂.

clude that redispersion can occur only in the presence of platinum oxide which is stabilized by forming complex with γ-Al$_2$O$_3$ support. Redispersion cannot occur even in the presence of platinum oxide unless this compound is stabilized by complexing with supports.
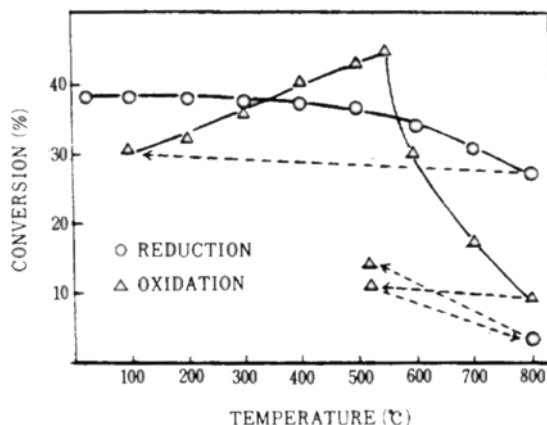

Fig. 8. Conversion of cyclohexene hydrogenation
after treatment in H₂ and O₂ ·····> Rea-
ction sequence.

Catalytic Activity Measurements

The changes in catalytic activity for Pt/γ-Al$_2$O$_3$ after treatment in oxygen and hydrogen atmospheres are shown in Fig. 8. Each oxidation treatments were followed by reduction at 400°C. During reduction the activity remained nearly constant up to 500°C, and then decreased, whereas during oxidation the activity increased below redispersion condition and decreased sharply above it. The rate of sintering in hydrogen was slower than in oxygen above redispersion condition. The increase in activity of sintered catalyst in hydrogen, however, was larger than that of sintered catalyst in oxygen. The activity for the other two catalysts decreased monotonically as the oxidation temperature increased. Consequently, hydrogen adsorption and catalytic activity follow the same trend.

CONCLUSIONS

Dispersion for Pt/γ-Al$_2$O$_3$ 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.

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