DISPERSION OF SUPPORTED PLATINUM CATALYSTS IN OXYGEN

II. Further Studies and Mechanism of Redispersion

Tae Jin Lee* and Young Gul Kim

Department of Chemical Engineering
Korea Advanced Institute of Science and Technology
P.O.Box 131 Chongyang, Seoul, Korea
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Abstract— Further experimental evidences of redispersion on supported platinum catalysts studied by means of TPR, TPD and cyclohexene hydrogenation reaction. $Pt/r-Al_2O_3$ exhibits stronger interaction between the metal oxide and the support as compared with Pt/SiO_2 and Pt/TiO_2. The formation of surface complex is enhanced as oxidation temperature increases. The TPD spectrum of hydrogen on Pt/TiO_2 shifts to higher temperature upon reduction at high temperature and shifts again to its original position upon oxidation. Shift of TPD spectrum does not appear in other catalysts. The suggested mechanism for redispersion is the spreading of platinum oxide and trapping of migrating species.

INTRODUCTION

It is well known that pt/Al_2O_3 is redispersed by oxygen treatment between 400 and 500°C [1-7] whereas at higher temperatures sintering occurs. Although it is generally accepted that during oxygen treatment oxidized platinum is formed, relatively little is known about the nature of the oxidized species. Lieske et al. [8] observed four different oxidized species using TPR: $(\alpha\text{-}PtO_2)_s$ and $(\beta\text{-}PtO_2)_s$ are halogen free, whereas $(Pt^{IV}(OH)_x Cl_y)_s$ and $(Pt^{IV}O_x Cl_y)_s$ include chloride. They also suggested that redispersion of Pt in oxygen is possible only in the presence of chloride and is connected with the formation of $(Pt^{IV}O_xCl_y)_s$.

Several models have been proposed to explain the redispersion phenomena. The first attributes the redispersion to physical splitting of the supported particles [5, 9-11]. A second model assumes the formation of various types of two-dimensional dispersions over the support surface [6, 7, 12-17]. A third model involves strong metal-support interaction (SMSI) which produces a larger surface through spreading of particles in hydrogen atmosphere [18, 19]. A fourth model involves the intraparticle redispersion of alloy catalysts [20]. However, the conditions and mechanisms for redispersion of metal crystallites are not yet clear.

The objectives of this study are twofold: firstly, to in-

vestigate further experimental evidences of redispersion; and secondly to select reasonable mechanisms. To these ends, hydrogen chemisorption, TPR, TPD, and cyclohexene hydrogenation were carried out on platinum catalysts supported on $\gamma\text{-}Al_2O_3$, SiO_2 and TiO_2.

EXPERIMENTAL METHODS

Temperature Programmed Reduction (TPR)

TPR was done in a flow system similar to that described by Menon and Froment [21]. The reducing gas was passed through the reference side of the thermal conductivity cell, thence through a quartz U-tube reactor 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% (mole %). 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 the cold bath. The heating in the low temperature region was therefore not necessarily linear.

Temperature Programmed Desorption (TPD)

The experimental setup for TPD is very similar to that for TPR. The catalyst was loaded onto a quartz U-tube reactor and preheated in a hydrogen stream at a given temperature. The catalyst was then cooled from

Present Address: Department of Chemical Engineering Yeungnam University, Gyongsan 632, Korea
*To whom correspondence should be addressed.

the reduction temperature to the ambient temerature in a hydrogen stream, then in a stream of the nitrogen carrier gas. When the base line of the recorder became steady, the programmed heating was begun and the pattern of evolution of hydrogen from the catalyst as a function of temperature (time) was followed on a dual-channel recorder. The heating rate was 10°C/min, and on reaching 600°C the programmed heating was stopped.

RESULTS

TPR

In general, it is more difficult to reduce the platinum oxide dispersed on supports with large surface area than to reduce to 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 profiles of three different supported platinum catalysts after treatment under the redispersion condition are shown in Fig. 1. Like bulk PtO_2 [16], Pt/SiO_2 was reduced below room temperature with a maximum rate at 10°C. The TPR profiles of Pt/TiO_2 had two reduction peaks. The low temperature peak might be due to reduction of platinum oxide. The high temperature peak was due to surface reduction of titania to non-stoichiometric oxide[22] and did not appear in 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 [18, 23]. In the case of Pt/γ-Al$_2$O$_3$, 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$_2$O$_3$ > Pt / TiO$_2 \geq$ Pt/SiO$_2 \simeq$ bulk PtO$_2$.

Fig. 2 presents the TPR profiles of Pt/γ-Al$_2$O$_3$ at various oxidation temperatures. The reduction of platinum oxide occurred at increasingly higher temperature as the oxidation temperature increased. This suggests that higher oxidation temperatures enhanced interaction of the platinum oxide with the γ-Al$_2$O$_3$ support. The TPR after treatment at oxidation temperatures higher than the redispersion condition did not produce the high temperature reduction peak and showed a small peak below room temperature. As the oxidation temperature increased three important results obtained. First the platinum became more highly oxidized, second this more highly oxidized platinum appeared to react with the γ-Al$_2$O$_3$ support surface forming a more difficult platinum-alumina complex to reduce, and third the dispersion increased as this complex formed. As oxidation temperatures higher than redispersion condition, however, this complex was thermally decomposed, free platinum was evidently formed as large crystallites, and the dispersion was adversely affected. Therefore the formation and stability of platinum oxide complexed with support are generally considered crucial to the redispersion process.

TPD

Typical TPD chromatograms of H$_2$ on Pt/γ-Al$_2$O$_3$, Pt/SiO$_2$, and Pt/TiO$_2$ are shown in Fig. 3. Pt/γ-Al$_2$O$_3$ reduced at 400°C had two or more peaks, and the peak intensity decreased after hydrogen treatment at 700°C. However, the intensity increased again after treatment in oxygen at 500°C. The intensity of Pt/SiO$_2$ which had only one peak decreased by reduction at 700°C, but the intensity did not increase after treatment in oxygen at 500°C and rate decreased somewhat. Pt/TiO$_2$ had also two peaks, with the high temperature peak higher than the low temperature peak. The high temperature peak shifted to higher temperature after reduction at 700°C but the intensity was reduced. The low temperature peak, which did not shift, showed more decrease in intensity than the higher temperature peak. After oxidation at 500°C the low temperature peak increased and
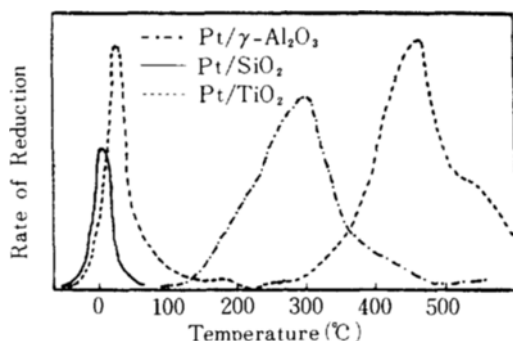

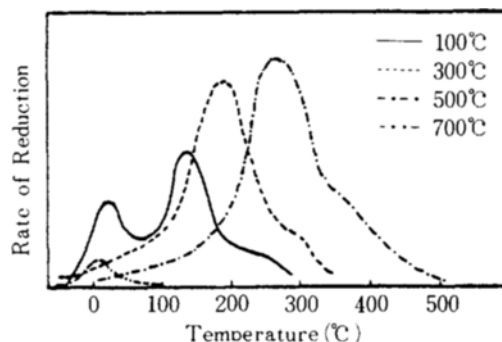Fig. 1. TPR of various catalysts after 520° C oxidation.

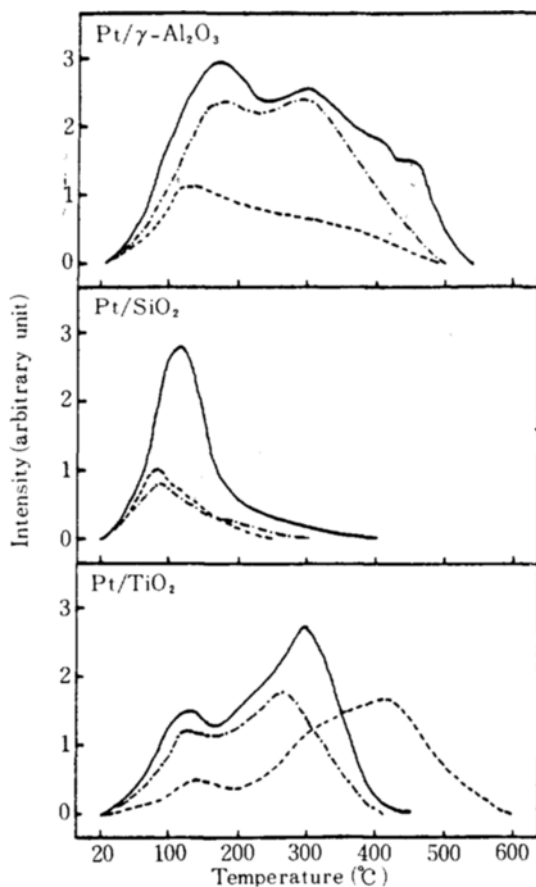Fig. 2. Effect of oxidation temperature on TPR of Pt/γ-Al$_2$O$_3$.

Fig. 3. TPD chromatograms of Pt catalysts at various treatment conditions.

—— 400℃ (H₂), ------ 700℃ (H₂),

—·—· 500℃ (O₂), 400℃ (H₂)

Fig. 4. Changes in catalytic activity of Pt catalysts as a function of pretreatment temperature.

the high temperature peak shifted again to its original position. For the cases of Pt/γ-Al₂O₃ and Pt/SiO₂, however, shift of the peaks was not observed.

Both the TPD chromatogram of Pt/γ-Al₂O₃ and that of Pt/TiO₂ decreased upon reduction at 700°C, and increased upon oxidation at 500°C. However, the peaks of Pt/γ-Al₂O₃ showed a simple decrease or increase, and those of Pt/TiO₂ showed a decrease or increase and a shift. It can be thought that the increase of peak intensity for Pt/γ-Al₂O₃ is due to the redispersion, and that for Pt/TiO₂ is due to SMSI destruction [23]. For the case of Pt/SiO₂ the redispersion or SMSI phenomena do not occur since increase or shift of desorption peak is not observed.

Cyclohexene Hydrogenation Reaction

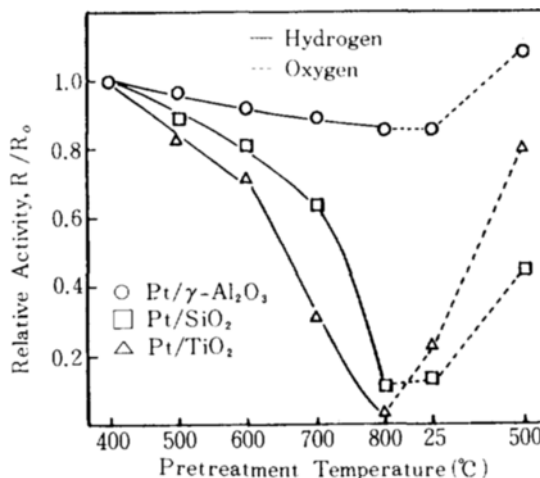The changes in catalytic activity for Pt/γ-Al₂O₃, Pt/Sio₂, and Pt/TiO₂ after treatment in hydrogen and oxygen atmospheres are shown in Fig. 4. The activity is expressed in terms of R/R$_o$ where R is the activity of the catalyst treated at a given temperature and R$_o$ is the activity of the catalyst treated at 400°C. Oxygen and nitrogen treatments were followed by reduction at 400°C. The activity of Pt/γ-Al₂O₃ decreased monotonically up to 800°C. However, it increased to a value greater than the initial value upon oxidation at 500°C. It was also noted that the high-temperature reduced Pt/TiO₂ catalyst restored its catalytic activity after treated with oxygen. 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[23]. Pt/SiO₂ showed an interesting phenomenon: the catalytic activity increased with treating in oxygen for high-temperature reduced sample but the increase in dispersion after oxidation at 500°C did not occur. This disagreement between the catalytic activity and chemisorption property is not well understood at this time. It may be primarily due to the strength of hydrogen-platinum bond and the available surface concentration of hydrogen [24].

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 [25], 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 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 [6], but the observed degree of redispersion increased as the available surface area increased. Furthermore, Yao et al. [17] reported that large particle could continue to be observed after redispersion, and Stulga et al. [26] 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 [26] 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 part I [1] show that treatment below 600°C in oxygen atmosphere leads to increase in dispersion for Pt/γ-Al$_2$O$_3$ 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$_2$O$_3$ is 793 ergs/cm, that for TiO$_2$ is 582 ergs/cm and that for SiO$_2$ is 268 ergs/cm [27]. Thus σ_{gs} is arranged in the order, γ-Al$_2$O$_3$ > TiO$_2$ > SiO$_2$. σ_{ms} will be smaller for Pt/γ-Al$_2$O$_3$ than for Pt/TiO$_2$ since metal oxide-support interaction is greater for Pt/γ-Al$_2$O$_3$ and SMSI is broken for Pt/TiO$_2$ during the oxida-

tion treatment [18, 23], and the probability of surface Pt-aluminate formation is higher than that of surface Pt-titanate [28]. Vannice [29] 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$_2$O$_3$ < 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 suprising to find that redispersion of sintered metal particles is observed only for Pt/γ-Al$_2$O$_3$ system in oxygen atmosphere. When platinum oxide is decomposed at higher temperatures, metal-support interaction is small for Pt/γ-Al$_2$O$_3$ since the platinum particles from once again and platinum does not wet alumina [30]. 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 [17]. 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/γ-Al$_2$O$_3$ system, it does not in Pt/SiO$_2$ where only thermal deactivation takes place. This is illustrated in Fig. 2 of part I[1]. 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 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 [30].

When equilibration between thermal deactivation and reactivation takes place, the observed dispersion is unchanged. This equilibrium depends on experimental conditions, especially chlorine concentration [31], oxygen partial pressure [13], and presence of acid sites on the support [4]. 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 more valid for small particle sizes.

All the expected surface species are summarized in Fig. 5. After oxidation between 200 and 400°C, $(\alpha\text{-PtO}_2)_s$ is formed (R-1) [8]. This oxide is converted at higher temperatures of about 600°C into $(\beta\text{-PtO}_2)_s$ (R-2) [8], or if strong interaction between the platinum oxide and the support is presented, into the surface complex (R-3). In oxygen at temperatures above 600°C ($\beta\text{-PtO}_2)_s$ and the surface complex decompose and crystalline Pt is formed (R-4, R-6). Reaction pathways of R-1→R-3→R-7 and R-5 →R-7 represent redispersion. The reverse pathway (R-6) represents sintering. Although platinum oxide can be formed for all catalysts when treated in an oxygen atmosphere below 600°C, only the formation of a surface complex considers crucial to the redispersion process.

Another interesting result is the effect of chlorine addition. The addition of chlorine during oxidation brings about a significant increase in the dispersion for Pt/γ-Al$_2$O$_3$ system as well as for Pt/TiO$_2$ system in which redispersion does not occur during treatment in oxygen alone [1]. It has been found [4] 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 for-

mation of oxychloroplatinum complexes which are strongly bonded to the support [31] and in the fact that chlorinated compounds create oxidizing sites and destroy reducing centers on the support [4]. 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.

CONCLUSIONS

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 order of interaction of platinum oxide with supports under the redispersion condition is Pt/ γ-Al$_2$O$_3$ >Pt/TiO$_2$ > Pt/SiO$_2$. The mechanism for redispersion based on 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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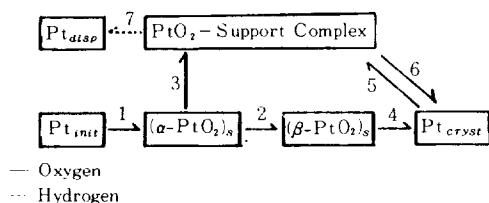12. Adler, S.F. and Keavney, J.J: J. Phys. Chem., 64,

Fig. 5. Proposed reaction pathways of supported Pt species in oxygen and hydrogen.

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