The Sintering of Supported Metal Catalysts

I. Redispersion of Supported Platinum in Oxygen

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The effects of treatment in oxygen at elevated temperatures on the dispersion of five Pt/Al_2O_3 catalysts (0.5 to 4.0 wt% Pt) were determined. Treatment temperatures of 300 to 700°C and treatment periods of 1 to 128 hr were studied. Significant increases in dispersion (at times a two- to threefold increase) were observed at $\leq$600°C. At 500 and 550°C the increases in dispersion were relatively independent of the treatment time. At higher temperatures, rapid, time-dependent decreases in dispersion occurred. The results are in agreement with a molecular migration mechanism.

INTRODUCTION

The high metal surface area per unit mass of metal and the thermal stability of supported metal catalysts are the main reasons for their extensive use. Although the thermal stability of these catalysts is excellent, i.e., relatively small changes in metal surface area occur with extended use at elevated temperatures, changes in metal surface area do occur with use or treatment at high temperatures. The process by which this occurs is termed *sintering*. Several mechanism have been proposed for the sintering process (*1–6*). Attempts have been made to experimentally determine the sintering mechanism (*7, 8*). Unfortunately, discrimination between sintering models on the basis of available experimental data is not possible (*9*).

The present project was undertaken in order to obtain experimental data on the effects of sintering atmosphere, type of metal, and type of support on the rate of sintering. This paper deals with the effect

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of treatment in oxygen on platinum dispersion for alumina supported Pt catalysts. The phenomenon of increasing Pt dispersions for alumina supported platinum catalysts as a result of treatment in oxygen was of special interest. In the following paper (*10*) we will compare the rates of sintering in oxidizing and reducing atmospheres for various Group VIII supported metal catalysts. In subsequent papers we plan to report on the influence of support properties, metal loading and other atmospheres on sintering rates. It is hoped that these experimental data will be useful in elucidating the sintering mechanism(s).

EXPERIMENTAL METHODS

Materials

Five alumina supported platinum catalysts were used in this study; they were: Catalyst 1, 0.5% Pt/Al_2O_3 (Engelhard, Lot 18-381); Catalysts 2, 3, 4, and 5 were 0.53, 1.0, 2.0, and 4.0% Pt supported on Kaiser KA-201 alumina spheres (− 8 + 10 mesh), respectively (all percentages are wt%). The BET surface area of Catalyst 1 was

110 m²/g and the surface area of the Kaiser Al₂O₃ after treatment at 500°C in air for 3 hr was 250 m²/g. Catalysts 2 to 5 were prepared by wetting the support with distilled water (1 cm³ H₂O/g of Al₂O₃), followed by addition of 1 cm³ of H₂PtCl₆ solution/g of Al₂O₃. The mixture was allowed to stand for 24 hr with intermittent stirring before being dried at 110°C for 24 hr. The H₂PtCl₆ solution was prepared by dissolving H₂PtCl₆·6H₂O obtained from Engelhard Industries in distilled H₂O. The amount of Pt in the solution was varied to obtain the various Pt loadings of Catalysts 2 to 5. The BET surface areas of the impregnated catalysts after treatment at 500°C for 3 hr were 230 to 240 m²/g.

All five catalysts were reduced before subsequent sintering experiments. The reduction procedure for Catalyst 1 consisted of treatment at 250°C for 2 hr followed by 16 hr at 500°C in flowing hydrogen. For Catalysts 2 to 5 the procedure was treatment in flowing hydrogen for 16 hr at 150°C, 2 hr at 250°C and 1 hr at 500°C. The reduced catalysts were then split into smaller portions for the sintering experiments and stored in air at room temperature until use.

The majority of the Pt in Catalysts 2 and 3 was concentrated in an outer layer with a thickness of approximately one-third of the pellet radius. For Catalyst 4 the Pt penetration was about $\frac{1}{3}$ to $\frac{1}{2}$ of the radius while for Catalyst 5 the Pt was distributed throughout the pellets. The determinations were made by crushing catalyst pellets and examining the fractured pellets under an optical microscope.

The hydrogen used for reduction and adsorption measurements was produced by a Matheson H₂ generator and was further purified by passing over an Engelhard Deoxo hydrogen purifier. The oxygen, used during sintering, and the nitrogen, used for flushing and as the carrier gas during adsorption, were Linde prepurified grade, 99.995 and 99.997% pure, respectively. The nitrogen was further purified by passing over a Cu/Cu₂O bed at 350°C (*11*), for removal of traces of H₂ and O₂, and a molecular sieve column for H₂O removal.

Sintering and Adsorption Procedures

The catalyst sample to be sintered was placed in a U-shaped Vycor tube and oxygen at 50 cm³ (STP)/min was passed through the U-tube. The size of the catalyst sample used varied with metal loading; 5.0 g were used for Catalysts 1, 2, and 3, 2.5 g for Catalyst 4 and 2.0 g for Catalyst 5. The U-tube was then placed into a modified Thermolyne Model 86 muffle furnace which had been heated to the desired sintering temperature. The temperature of the furnace was controlled by a Thermo Electric 400 temperature controller which resulted in catalyst bed temperatures that were within ±2°C of the set temperature. After the U-tube was inserted 1 to 5 min were required for the temperature to regain the set value. The sintering times were measured from the time that the furnace temperature had attained the desired value after the sample insertion. The oxygen flow was maintained throughout the sintering period. The oxygen pressure was ~93 kPa (~0.92 atm).

After the catalyst had been sintered for the desired period of time the catalyst was pretreated for hydrogen adsorption measurements. For sintering temperatures >500°C the following procedure was employed:

1. The flowing oxygen used during the sintering was replaced by flowing nitrogen (50 cm³ (STP)/min).

2. The U-tube containing the catalyst was immediately removed from the furnace to ambient conditions after the gas change.

3. The furnace was cooled from the sintering temperature to 500°C (20–30 min).

4. The U-tube was again placed into the furnace and kept in flowing nitrogen at 500°C for 1 hr.

5. The nitrogen flow was replaced by hydrogen flow (50 cm³ (STP)/min) and the

catalyst was kept in flowing hydrogen at 500°C for 1 hr (reduction step).

6. The hydrogen flow was replaced by nitrogen and the catalyst was kept at 500°C in flowing nitrogen for 2 hr (degassing step).

7. The U-tube containing the catalyst was removed from the furnace, cooled to room temperature by immersion into a water bath and hydrogen adsorption uptakes were determined by pulse addition of hydrogen to the nitrogen carrier gas (adsorption measurement; procedure described below).

When a sintering temperature of 500°C was used the above procedure with the omission of Steps 2 and 3 was employed. For sintering temperatures below 500°C the above procedure (Steps 2-4) was modified in the following manner: the catalyst sample was left in the furnace; the oxygen was flushed from the system with nitrogen at the sintering temperature (0.5 to 1 hr); the nitrogen flow was maintained while the temperature was raised to 500°C and for 1 hr at 500°C before proceeding with Steps 5 to 7. During this procedure, significant amounts of adsorbed oxygen may be present during the heating stage. To determine whether this influenced the results one experiment was carried out (sintering temperature 300°C) in which, after flushing O_2 from the system, the reduction in flowing hydrogen was carried out at 300°C for 1 hr, heating to 500°C and maintaining at 500°C for 1 hr. This was followed by Steps 6 and 7. This change in procedure did not markedly alter the subsequent adsorption uptake, i.e., results were within the reproducibility experienced with this apparatus (see below).

The hydrogen adsorption measurements were carried out at room temperature after the above pretreatment by addition of hydrogen pulses to nitrogen carrier gas. The nitrogen carrier gas flow rate was 45 cm³ (STP)/min. Experiments to determine whether the carrier gas flow rate influenced

the adsorption uptake showed that at carrier gas flow rates from 25 to 65 cm³ (STP)/min the carrier flow rate did not affect the hydrogen uptake. A two-loop Carle G. C. sample valve was used for the hydrogen pulse injection and a thermal conductivity detector was used to monitor the amount of hydrogen in the nitrogen before and after the catalyst bed. The size of the injected hydrogen pulses was 18.7 μmoles/pulse. Hydrogen pulses were injected at 3 min intervals until no more hydrogen uptake, as indicated by the amount of hydrogen in the exit stream from the catalyst bed, occurred for two or three successive pulses. The standardized time between pulse injection is necessary since some hydrogen is weakly adsorbed and desorption occurs between pulse addition. For a complete description of the equipment and calibration procedures see Ref. (*12*).

At least two successive determinations of hydrogen adsorption uptakes were carried out on each sample. The treatment between adsorption measurements consisted of reduction in flowing hydrogen at 500°C for 1 hr and degassing in flowing nitrogen at 500°C for 2 hr. If the difference in hydrogen uptake between the first two determinations was more than 10% further adsorption measurements were carried out. Deviations of >10% in successive determined uptakes on the same sample occurred only twice in the present work. The average percentage standard deviation (coefficient of variation) (*13*) for repeated determinations was 2.9%. Reproducibility of complete sintering experiments (i.e., starting with fresh catalyst samples) was not as good and variations of up to ±10% were experienced. The average coefficient of variation for repeated runs using fresh catalyst samples was 6.8%. This variation from one catalyst sample to the next from the same batch is largely due to the inhomogeneity that exists between catalysts pellets as indicated by the color variation between pellets. The reported platinum

dispersions, calculated from the hydrogen uptakes, are based on the average value of the measured uptakes; repetitive uptakes on the same sample which deviated by more than 5% from the average were not included.

RESULTS

Various investigators [e.g. (8, 14–17)] have observed increases in Pt dispersion during thermal treatment of supported Pt catalysts in oxygen containing atmospheres. Treatment of deactivated Pt/Al$_2$O$_3$ catalysts in oxygen containing atmospheres is a patented regeneration process (18). The effects of treatment time and temperature in pure oxygen on the Pt dispersion was investigated in the present study. (Dispersion is defined as the ratio of surface metal atoms to total metal atoms.) The Pt dispersions were calculated from the hydrogen adsorption uptakes using the assumption that one hydrogen atom adsorbs per Pt surface atom.

The dispersions of Catalysts 1 to 5 after treatment in oxygen for 1 hr at various temperatures are plotted in Fig. 1. The dispersions of the unsintered catalysts are also shown in Fig. 1. For all catalysts the
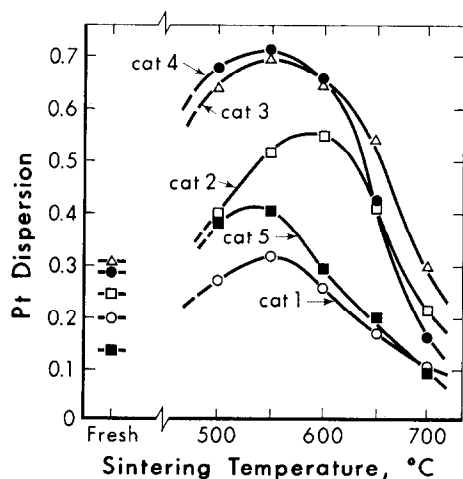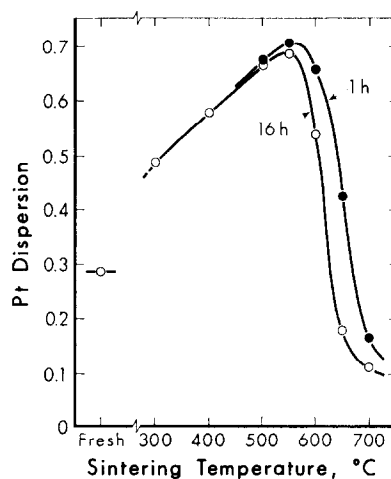

FIG. 2. Effect of treatment time and temperature on dispersion of the 2.0% Pt/Al$_2$O$_3$ catalyst (Catalyst 4).

dispersions after treatment at $\lesssim 600°C$ are higher than the initial dispersions. The maximum dispersion, which generally was two to three times the initial dispersion, occurred after treatment at 550°C (600°C for Catalyst 2).

The effects of length of treatment in oxygen are shown in Figs. 2 and 3. Figure 2 shows a comparison of the dispersion after 1 and 16 hr treatments for Catalyst 4. For temperatures $\lesssim 550°C$ the dispersion is relatively insensitive to the length of treatment, while at higher temperatures

FIG. 1. Effect of treatment in oxygen for 1 hr at various temperatures on dispersion of Pt/Al$_2$O$_3$ catalysts.
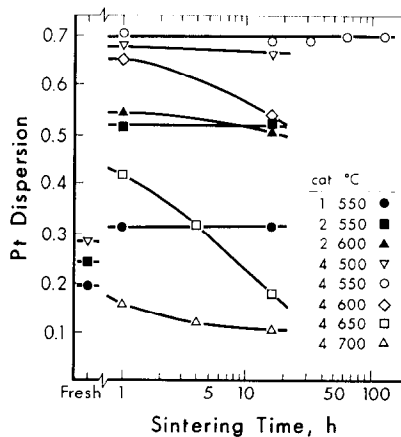

FIG. 3. Effect of treatment time and temperature on dispersion of Pt/Al$_2$O$_3$ catalysts.

the dispersions for the 16 hr treatment are significantly lower than for the 1 hr treatment. The results presented in Fig. 3 show the same behavior. It should be noted that for Catalyst 4 treatment at 550°C and times of 1 to 128 hr resulted in the same dispersion.

A fresh catalyst sample was employed for each of the data points shown in Figs. 1 to 3. In one experiment, the sample obtained after treating Catalyst 4 for 16 hr at 700°C was treated in oxygen for 16 hr at 550°C. The dispersion after sintering at 700°C was 0.11 and after the subsequent 550°C treatment it increased to 0.18. Although this increase in dispersion of 65% is not as large as the increases observed in the treatment of fresh samples, it does show that redispersion occurs even for heavily sintered catalysts. Sintering experiments in hydrogen never resulted in increased dispersion. A comparison of sintering in hydrogen and oxygen of Group VIII metals will be presented in a subsequent paper (10).

Decreases in support surface area during thermal treatment could in part be responsible for the observed losses in Pt dispersion. Total surface areas of Catalyst 4 (2% Pt) after various thermal treatments were determined by the BET method. The unsintered catalyst had an area of 240 m²/g. Treatment for 128 hr at 550°C in oxygen decreased the area to 210 m²/g. The surface areas after treatment in oxygen for 16 hr at 600, 650 and 700°C were 230, 195 and 180 m²/g, respectively. Hence, the most severe treatment conditions (16 hr at 700°C) resulted in a 25% decrease in total surface area while the Pt dispersion decreased by 65%; therefore, the decreases in dispersion were mainly caused by Pt crystallite growth and not by decreases in support areas. (The loss in support area could have been partly responsible for the lower redispersion of Catalyst 4 when treatment at 550°C was carried out subsequent to the 700°C treatment.)

X-Ray diffraction patterns for sintered and unsintered samples of Catalyst 4 showed that no recrystallization of the alumina occurred during the thermal treatments. The diffuse peaks in the diffraction patterns correspond to those of γ-Al_2O_3. Treatment in O_2 for 16 hr at temperatures $\geq 650°C$ resulted in the appearance of Pt lines, but the intensity and position of the alumina lines did not change noticeably.

DISCUSSION

Since the major objective of this work was to obtain information on the sintering mechanism(s), attempts will be made to explain the observations in terms of mechanistic models. A mechanistic model of the sintering process, in order to agree with the above experimental results has to be able to account for the following observations: (1) increases in dispersion at low treatment temperatures ($\lesssim 600°C$); (2) constant increases in dispersions, independent of treatment times, at low temperatures (~ 500–$550°C$); and (3) decreases in dispersion at higher treatment temperatures ($\gtrsim 650°C$).

Two mechanistic models have been proposed for the sintering processes. The first envisages sintering to occur by the migration, collision and coalescences of metal crystallites on the support surface (1, 2). This model will be referred to as the crystallite migration model. The second model envisages the sintering to occur by the dissociation of molecular or atomic species from the metal crystallites followed by migration of these species over the support surface and capture of the migrating species by trapping sites on the support or other metal crystallites (3, 4). This model will be referred to as the molecular migration model. These two models have also been referred to as the Smoluchowski and Ostwald-ripening models (7). Modifications and extensions of these models are required in order to explain the experimental observations in terms of these models.

Crystallite Migration Model

The crystallite migration model always predicts increases in average crystallite

sizes, i.e., decreases in dispersion, as sinter-
ing proceeds. Hence an additional process
has to be included in the model to account
for increases in dispersion during treat-
ment at low temperatures ($\lesssim 600°C$ for
Pt/Al_2O_3). Ruckenstein and Pulvermacher
(2) in their development of the crystallite
migration model attributed the increases
in dispersion to the changes in interfacial
energies (these are a function of the atmo-
sphere to which the catalyst is exposed to
during treatment) which cause a crystallite
to split into smaller crystallites. The break-
up of Pt films into Pt crystallites during
treatment in air at 500 to 1000°C has been
observed (19, 20). The splitting mechanism
can account for increases in dispersion.

This mechanism can also account for the
time independent increases in dispersion if
one assumes that the splitting process is
rapid so that the metal crystallites dis-
sociate to their respective "equilibrium"
sizes (these sizes should be a function of
temperature, atmosphere and metal–sup-
port interactions) in <1 hr. This process
predicts that the increases in dispersion are
only a function of the metal, support, tem-
perature and atmosphere. The increases in
dispersion should be independent of the
surface area of the support, the metal load-
ing, and the initial metal crystallite sizes.

At higher temperatures the migration–
collision–coalescence of crystallites has to
be more rapid than the splitting process in
order to agree with the observed decreases
in dispersion. At the higher temperatures,
the splitting of crystallites may not occur
due to changes in the platinum–oxygen in-
teractions. [The platinum–oxygen system
is not well characterized (21)]. The sta-
bility of platinum oxides is discussed in
more detail below.

Molecular Migration Model

The molecular migration model predicts
decreases as well as increases in dispersion
depending on the treatment conditions
(3, 4). Increases in dispersion result if the
migrating species are trapped at sites on

the support that have large metal–support
interactions or if colliding molecular species
result in the nucleation of new crystallites.

For the platinum–oxygen–support sys-
tem, the transport of Pt as molecular or
atomic species can occur by various routes.
Equation (1) shows the various possible
processes.

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\begin{array}{c}
\text{(see scheme)}
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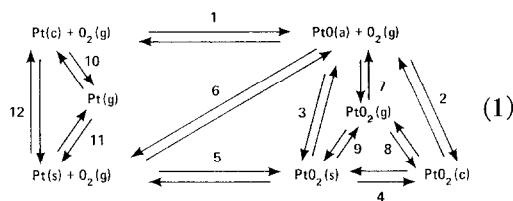
Equation (1) is not intended to be a stoi-
chiometrically balanced equation; it is only
intended to present the various possible
processes. The letters in parentheses indi-
cate the state of the species according to
the following code: (c) = crystalline or
solid phase; (g) = vapor phase; (a) = ad-
sorbed state; and (s) = species on the
support surface as individual atoms or
molecules.

The rates and temperature dependence
of each of the steps in the postulate mecha-
nism are discussed below. This discussion,
due to the lack of knowledge of the $Pt-O_2-$
support system (21), includes a significant
amount of speculation.

Step 1. The adsorption of oxygen on Pt
surfaces is a well-known phenomenon and
occurs at room temperature. Although the
stoichiometry of adsorption may change
with temperature it is certain that even at
elevated temperatures (700°C) some ad-
sorbed oxygen exists. [Note: PtO(a) refers
to Pt crystallites with adsorbed oxygen.]

Step 2. Platinum metal can be converted
to solid platinum oxides of various stoi-
chiometries by exposure to oxygen at 400–
550°C (22). At temperatures above 560°C
solid platinum oxides decompose to plati-
num and oxygen (22, 23).

Steps 3 and 4. The transfer of PtO_2 (or
other platinum oxide) molecules from the
solid to the support surface are the postu-
lated processes which are the basis of the

molecular migration model. It is believed that these steps occur quite rapidly at the temperature used in this study (300–700°C). The concentration of $PtO_2(s)$ in equilibrium with $PtO_2(c)$ or $PtO(a)$ should increase with increasing temperature until $PtO_2(s)$ decomposes.

Step 5. Since $PtO_2(c)$ is unstable at temperatures $\geq 560°C$, it is also likely that $PtO_2(s)$ decomposes at higher temperatures. The temperature of this decomposition is not known and will depend on the interaction of the support with the $PtO_2(s)$. Based on the results of this study it appears that the decomposition occurs at 550–600°C (this is discussed below).

Step 6. The extensive work on nucleation and film growth shows that atoms are mobile on support surfaces, even at low temperatures. At the temperatures ($\geq 550°C$) at which $PtO_2(s)$ decomposes to $Pt(s)$ plus $O_2(g)$, the $Pt(s)$ atoms are probably very mobile and will be captured by $PtO(a)$ particles upon collision.

Steps 7, 8, and 9. $PtO_2(g)$ exists even at high temperatures where $PtO_2(c)$ is unstable. Schäfer and Tebben (*24*) have determined the vapor pressure of PtO_2 over Pt at 1100–1210°C at various partial pressures of O_2. Using the correlation they present for the vapor pressure of PtO_2, the PtO_2 vapor pressure at 500 and 700°C with an oxygen pressure of 93 kPa is $\simeq 9 \times 10^{-10}$ and 2×10^{-7} kPa, respectively. These are very low pressures and hence very little bulk transport of Pt (i.e., loss of Pt to the vapor phase) occurs even if equilibrium vapor pressures of PtO_2 are reached in the oxygen gas stream used during treatment. For example, it would require ~ 55 yr to remove all the Pt from a 5.0 g sample of 0.5% Pt/Al_2O_3 if oxygen at a flow rate of 50 cm^3 (STP)/min and 700°C were saturated with PtO_2 during passage over the sample. Although the rate of Pt loss is small the transfer from $PtO(a)$ and $PtO_2(c)$ to $PtO_2(s)$ by means of $PtO_2(g)$ can be appreciable for small crystallites at temperatures $\geq 600°C$.

Steps 10, 11 and 12. Due to the extremely low vapor pressures of Pt, the contribution of these steps is negligible at the temperatures employed in this study.

The interpretation of the data obtained in this study in terms of the molecular migration model yields the following conclusions. At temperatures $< 600°C$ the Pt transport occurs by Steps 2, 3, and 4. The increases in dispersion are the result of $PtO_2(s)$ formation. Some of the migrating $PtO_2(s)$ may be trapped at high energy sites on the support resulting in the formation of new particles. The decomposition of the $PtO_2(s)$ to $Pt(s)$ and $O_2(g)$ when the oxygen atmosphere is changed to nitrogen (followed by hydrogen) can also result in the nucleation of new Pt crystallites if the $PtO_2(s)$ concentration was sufficiently high. Since the increases in dispersion were found to be independent of treatment time (for ≥ 1 hr) at $\lesssim 550°C$, "local equilibrium" of $PtO_2(s)$ was established rapidly. This "local equilibrium" refers to the $PtO_2(s)$ concentration on individual support grains (out of which catalyst pellets are made) which contain Pt particles. It is believed that migration of $PtO_2(s)$ is restricted to individual support grains and vapor phase transport is required for transfer of Pt from one grain to another. At temperatures $\gtrsim 600°C$ the Pt transport occurs by Steps 3, 5, 6, 7, and 9. This results in decreases in dispersion since the migrating $Pt(s)$ species are captured by Pt or $Pt(a)$ crystallites.

According to the above interpretation, the dispersion after treatment in O_2 and reduction in H_2 depends on the treatment temperature, $PtO_2(s)$–support interaction, support surface area, metal loading and initial Pt crystallite sizes. The major effect of temperature is related to the temperature stability of $PtO_2(s)$ (Step 5). The $PtO_2(s)$–support interaction affects the equilibrium $PtO_2(s)$ concentration; higher interactions result in higher equilibrium concentrations. For large interactions, low metal loadings and/or high accessible support surface areas, it is conceivable that all

the platinum can exist as $PtO_2(s)$. (The accessible support area in the absences of vapor phase transport is comprised of those grains of support which initially contain Pt crystallites, i.e., for surface coated catalyst pellets only that fraction of the support that contains Pt is accessible to the migrating $PtO_2(s)$ species.) The crystallite size affects the $PtO_2(s)$ concentration since small $PtO_2(c)$ or $PtO(a)$ particles, according to the Kelvin equation, have a higher equilibrium $PtO_2(s)$ concentration than larger particles.

Model Discrimination

The crystallite and molecular migration models predict different behavior during redispersion, i.e., for the particle splitting the redispersion should be relatively independent of metal loading and initial metal crystallite size, while the molecular migration model predicts, in general, a dependence on these properties. Catalysts 2 to 5 were prepared to determine the effect of metal loading on redispersion. Unfortunately, the Pt was not uniformly distributed throughout the support pellets (i.e., not all the support surface was accessible) and hence it is not possible to determine the effect of metal loading from the data, but it is possible to determine the effect of average initial crystallite size on the redispersion. The general trend is that the maximum dispersion obtained increases with decreasing initial crystallite size. (The crystallite size is inversely proportional to the dispersion.) This is true for Catalysts 2 to 5 as well as for the redispersion of Catalyst 4 which had been sintered at 700°C for 16 hr. Catalyst 1 does not fit this trend, but this is not surprising since the support for this catalyst was different than that of the other four catalysts.

The dependence of the increases in dispersion on the initial dispersion supports the molecular migration model. The recent results of controlled atmosphere electron microscopy obtained by Baker *et al.* (*25*)

also support the molecular migration model. These investigators observed, from cine films, that detectable Pt particles (>2.5 nm) on Al_2O_3 were immobile. Hence, it is difficult to explain the continued decreases in dispersion at higher temperatures by the crystallite migration model. In our study average crystallite sizes of ∼10 nm were obtained (dispersion ≈0.1) after sintering at 700°C. Experiments to determine the effect of metal loading and support surface area on the degree of redispersion for catalysts with metal evenly distributed over the support surface are planned.

CONCLUSIONS

It has been found that treatment of Pt/Al_2O_3 catalysts in pure oxygen at approximately atmospheric pressure and temperatures ≤600°C results in significant increases in platinum dispersion. The increases in dispersion at ≤550°C were found to be independent of the length of treatment. At treatment temperatures ≥600°C decreases in dispersion occurred. The decreases were a strong function of treatment time and temperature. The molecular migration model is believed to be the mechanism of sintering for supported Pt/Al_2O_3 in oxygen atmospheres.

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