JOURNAL OF CATALYSIS **123**, 486–495 (1990)

Carbon Deposition on Supported Platinum Particles

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Received October 25, 1989; revised January 23, 1990

A combination of electron microscopy and thermogravimetric techniques have been used to investigate the characteristics of coke formation and the associated changes in platinum particle morphology in real and model reforming catalysts. Despite the fact that used commercial catalysts contained large amounts of coke, metal particles were clearly evident and appeared to reach an average size of 1.7 nm, indicative of only a limited degree of sintering during the reforming reaction. Decoking studies showed that the deposit was predominantly isotropic in nature and did not contain any filamentous or graphitic components. *In situ* electron microscopy studies performed on model supported platinum catalyst systems showed that upon reaction in a hydrocarbon environment, the metal particles were capable of hydrogasifying carbon in their immediate vicinity and during this process underwent a wetting and spreading action at the deposit interface which resulted in redispersion of the platinum. This phenomenon was limited to a narrow temperature range between 480 and 600°C, and was believed to be a key factor in the maintenance of the small metal particle size during the reforming reaction. © 1990 Academic Press, Inc.

INTRODUCTION

Carbon deposition on platinum catalysts used for naphtha reforming has become an area of considerable interest (*1–8*). The reaction is carried out over a bifunctional catalyst which consists of a single metal, platinum or various platinum bimetallics, dispersed on an acidic support such as alumina, whose acidity is controlled by the addition of chloride ions (*9, 10*). During the reforming process, which is normally performed at 500°C, carbon is formed from a variety of reactions and appears to have a different deactivating effect on the metal and acidic functions of the catalyst.

Cabral and Oberlin (*5*) used high-resolution transmission electron microscopy to examine spent platinum/alumina catalysts which had been treated under typical industrial reforming conditions. According to these workers the carbonaceous deposits consisted of small stacks of aromatic ring structures less than 1.0 nm in size which formed parallel to the alumina crystal faces and these localized units were believed to form shells which were capable of covering this area of the catalyst. Such units were produced in a random fashion over the entire catalyst, resulting in a deposit with a very porous character, and, since this material had no special relationship with the metallic component, no preferential blocking of the platinum particles was expected.

Gallezot and co-workers (*7*) also studied the location and structure of carbonaceous deposits formed during coking of Pt/Al_2O_3 catalysts in the presence of cyclopentane at 440°C. They used a combination of conventional TEM and electron energy loss spectroscopy (EELS) coupled to high-resolution scanning transmission electron microscopy (HRSTEM). They found that patches of amorphous carbon covered the support surrounding each metal particle and the coke coverage extended as far as 20 nm from a given particle. It was concluded that the local structure of the coke was neither graphitic nor pregraphitic but consisted of a disordered arrangement of polyaromatic molecules. The progression of coke was sometimes limited by the edges of

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0021-9517/90 $3.00

the alumina sheets on which the metal particles were located; however, coke frequently spilled onto neighboring alumina sheets.

Myers and co-workers (*11*) studied the fouling behavior of a number of specific organic compounds on platinum reforming catalysts. They found that small aromatic and cyclohydrocarbons in the presence of hydrogen tended to deactivate catalysts to a small degree, whereas cyclopentane deactivated the catalyst rapidly by producing an intermediate which was not easily formed from *n*-pentane. Large paraffinic molecules also deactivated the catalyst relatively quickly. They suggested the following deactivation mechanism. Initially, unsaturated reaction intermediates are formed mainly at the platinum sites. These precursors are then reversibly adsorbed on the platinum and migrate to acid sites where they are irreversibly adsorbed. These adsorbed precursors can then polymerize to form the cokes having several double bonds per molecule. The polymerization process was viewed as the rate-limiting step, being slower than the platinum-catalyzed reactions and also slower than the process of transferring the precursors to the acid sites.

In the present investigation we have used a variety of techniques including high-resolution and controlled-atmosphere electron microscopy (CAEM) and thermogravimetry to examine the nature of the carbonaceous deposits and the characteristics of the metal particles on real and model catalyst systems.

EXPERIMENTAL

High-resolution transmission electron microscopy examinations of treated catalyst samples were performed in a JEM-200CX electron microscope fitted with a high-resolution pole piece, which provided a 0.24-nm theoretical point resolution. All specimens were examined by bright field techniques. Continuous observations of changes in appearance of specimens undergoing reaction with gas environments at temperatures up to 1000°C were carried out in a JEM-120 microscope equipped with a gas reaction cell. This modification imposed a resolution limit of 2.5 nm. The information generated was monitored by a closed-circuit TV system in conjunction with a video recorder which enabled us to carry out subsequent kinetic analysis of various events.

Specimens for the high-resolution transmission electron microscopy examinations were prepared by grinding deactivated commercial catalyst samples to a fine powder which was then ultrasonically dispersed in butyl alcohol. A drop of this suspension was applied to a holey carbon film mounted on a microscope grid. The catalyst samples contained 0.6 to 1.2 wt% metal on alumina with between 7 and 12 wt% coverage of carbonaceous deposits, which had accumulated during reaction in a naphtha feed for periods of up to 5000 h. When these specimens were examined in the TEM it was possible to find regions of the catalyst which were extremely thin (<25 nm) and which protruded from the carbon substrate. To obtain the representative appearance of a given catalyst sample micrographs were taken of many different regions of the specimen. Metal particle size distributions were obtained from measurements of over 400 particles for each catalyst sample.

Thermogravimetric studies were performed in a Cahn 2000 vacuum microbalance of the gasification rate in a CO_2 environment of the coke formed on a commercial used platinum catalyst. Similar experiments were carried out on high-purity graphite containing the same loading of metal catalyst. From a comparison of the thermograms it was possible to assess the oxidation characteristics of the carbonaceous deposit.

In the model catalyst systems, platinum, approximately one monolayer coverage, was introduced onto transmission specimens of alumina or graphite by evaporation of the metal from a tungsten filament at a residual pressure of 10^{-6} Torr. Graphite specimens were prepared by a standard cleaving procedure (*12*) and γ-alumina substrates were produced according to the method described by Ruckenstein and Chen (*13*). Some of these samples were subsequently treated in the controlled-atmosphere electron microscope in the presence of 2.0 Torr acetylene, and changes in the appearance of the surface were monitored as a function of reaction time and temperature.

Another series of model catalyst specimens were subjected to the following series of treatments in a flow reactor: (a) calcination in air at 500°C for 2 h, (b) reduction in 10% hydrogen/helium at 500°C for 4 h, and (c) reaction in 2% acetylene/helium at 500°C for 0.5 h.

At least two specimens were removed from the reactor after each step for examination by high-resolution TEM and the metal particle size distributions obtained from measurements of over 400 particles in each case. Following reactions b and c, samples were carefully passivated by cooling to room temperature in flowing helium and then treated in a 2% oxygen/helium mixture before exposure to air. Unless this procedure was followed, the specimens underwent an exothermic reaction when taken out of the reactor, which resulted in extensive particle sintering.

RESULTS

Characteristics of a Used Commercial Reforming Catalyst

Transmission electron microscopy examinations. Figure 1 is a high-resolution micrograph showing the typical appearance of the coked catalyst protruding over the edge of the carbon support film, designated as A. This is a specimen derived from a deactivated 0.6 wt% Pt/Al_2O_3 catalyst and some of the metal particles are highlighted by circles. Although it is questionable as to how much of the metal one can actually discern in the micrographs of this type of specimen, it is significant that considerably more particles were evident on a high-metal-loaded catalyst (1.2 wt% metal) than on this sample.

Careful examination of many micrographs showed that there was no evidence for filamentous carbon formation in these systems; moreover, since the metal particles were clearly visible one can conclude that there was not a preferential buildup of carbon at these locations. Indeed it would seem that there was less coke formation in the vicinity of the metal particles than in other regions of the catalyst. Unfortunately the particles are too small to determine any of their morphological characteristics.

Figures 2 and 3 are the respective particle size distributions obtained for the 0.6 wt% Pt and 1.2 wt% coked catalyst samples. In these determinations the lower particle size has been limited to 0.75 nm since it was impossible to make accurate measurements below this size. The distributions are relatively symmetrical in shape and very narrow, indicating that during reaction particle sintering was not a major factor in the deactivation step. The average particle size calculated from these data is 1.7 ± 1 nm, which appears to be independent of both the metal loading and the treatment conditions.

It was evident that during the gasification process some of the platinum particles participated in the reaction. This behavior was seen as the creation of channels through the carbon deposit, and this action resulted in particle mobility and agglomeration.

Microscale oxidation studies. When sections of the coked catalyst dispersed on transmission specimens of graphite were heated in the CAEM facility in the presence of 2 Torr oxygen, the carbonaceous deposit was observed to undergo gasification at 365°C. Continuous observation of the process showed that the deposit gasified very readily and did not contain any filamentous or graphitic components, types of carbon which are usually associated with a metal catalyst (*14*).

Thermogravimetric analysis. The gasification rate in a carbon dioxide environment

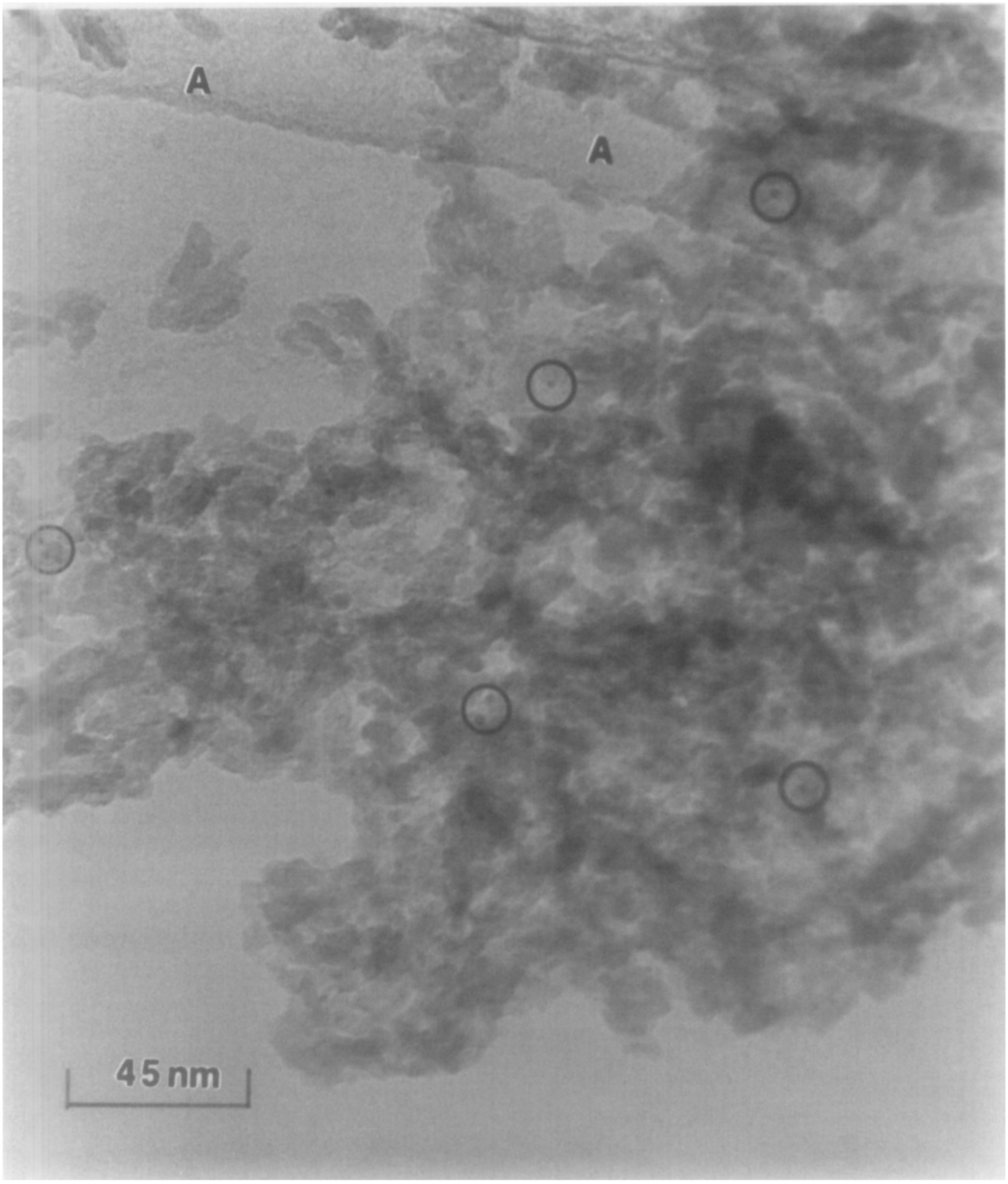

FIG. 1. Transmission electron micrograph of a coked commercial platinum/alumina catalyst mounted on a holey carbon film, designated as A. Some of the metal particles are highlighted by circles.

of the coked 0.6 wt% platinum/alumina catalyst containing 7.9 wt% carbon deposit was compared with that of graphite impregnated with the same weight of metal. From the data presented in Fig. 4 it is apparent that the samples exhibit diverse oxidation behavior, the coked commercial catalysts being significantly more reactive than the platinum/graphite sample. Examination of the thermogram shows that with the coked platinum/alumina catalyst, gasification commenced at about 500°C and was com-

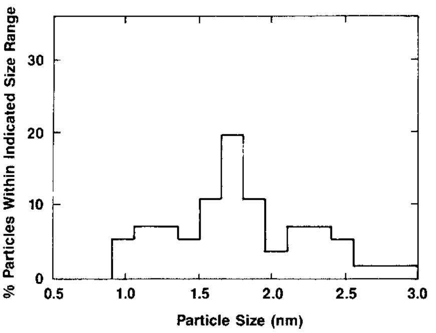

FIG. 2. Particle size distribution of a commercial 0.6 wt% platinum/alumina catalyst which had been on feed for 2500 h.

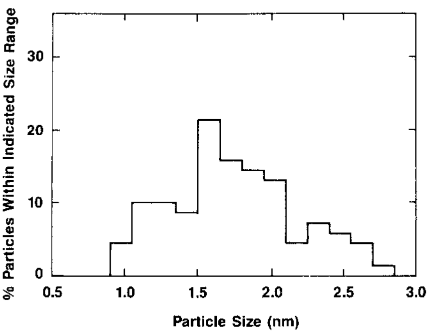

FIG. 3. Particle size distribution of a commercial 1.2 wt% platinum/alumina catalyst which had been on feed for 5000 h.

plete by about 1050°C. However, the onset of gasification of the platinum/graphite system did not occur until about 850°C and about 85% of the carbon still remained after reaction at 1050°C. This result indicates that the coke formed on the commercial catalyst has the characteristics of a material with short-range crystallographic order.

Studies of Model Platinum Catalysts

Controlled atmosphere electron microscopy investigations. Nucleation of small metal particles, 10 to 20 nm in diameter, on platinum/alumina specimens was achieved by sequential treatments in oxygen and hydrogen at 500°C. When these specimens were subsequently heated in the presence of 2 Torr acetylene a uniform coverage of carbon was observed to collect on the surface during prolonged reaction at 425°C. On an increase in the temperature to 480°C, dramatic changes were evident in both the appearance of the carbonaceous deposit and the dimensions of the metal particles. Figure 5 is a schematic representation of the observed sequence of events accompanying the reaction of supported platinum particles in acetylene. At this temperature the metal particles were observed to wet and gradually spread on the support in re-

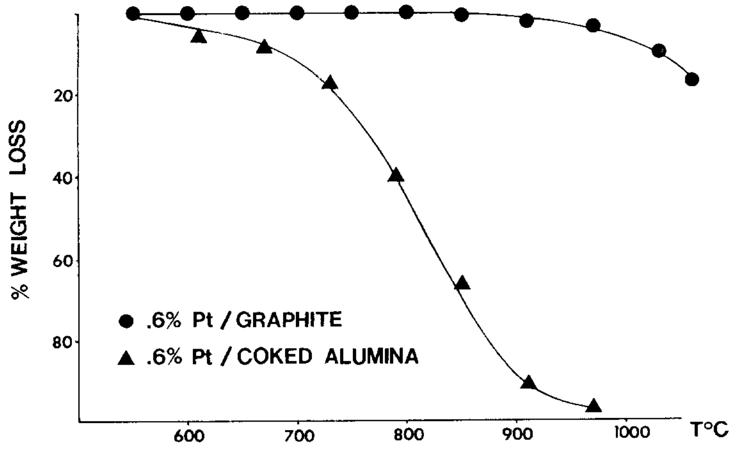

FIG. 4. Comparison of gasification characteristics in carbon dioxide of a commercial coked 0.6 wt% platinum/alumina catalyst and graphite containing the same loading of metal.

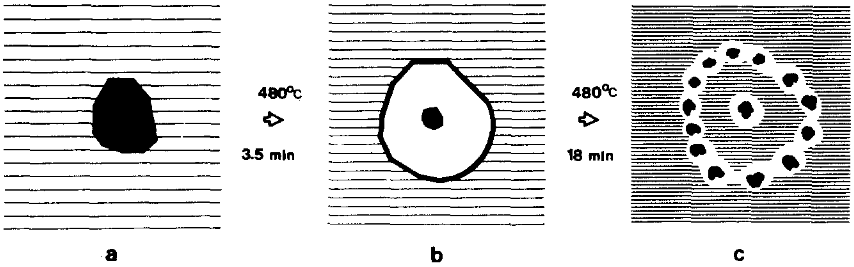

FIG. 5. Schematic representation of the observed changes in appearance of platinum particle supported on alumina when heated in 2 Torr of acetylene at 480°C: (a) platinum particle on γ-alumina, (b) spreading of platinum at the carbon deposit interface, and (c) eventual redispersion and creation of apparently clean islands around each particle.

gions where carbon was deposited. Immediately following this action carbon at the metal interface underwent gasification via the edge recession mode and this resulted in the formation of "clean islands" in the immediate vicinity of the platinum. After a period, the gasification reaction ceased and this coincided with the reappearance of small metal particles, which ranged from 2.5 to 5.0 nm in diameter. Examination of many regions of a specimen showed that this was a general phenomenon; however, there did not appear to be any definite relationship between the size of a given platinum particle and that of the associated "clean island."

As the temperature was raised to 600°C the rate of carbon accumulation on the specimen surface increased significantly and clean regions were no longer maintained around the metal particles. Furthermore, the average platinum particle size increased to 25 nm and in many cases such particles were observed to catalyze the growth of filamentous carbon. During the filament growth process the metal catalyst particle was carried away from the alumina support surface and remained at the tip of the filament. Carbon filament growth continued up to 800°C; however, above this temperature the formation of carbon produced by the direct gas-phase decomposition route became so heavy that it was difficult to discern many of the events occurring on the specimen surface.

In some cases the coked specimens were subsequently reacted in either 1.0 Torr hydrogen or 2.0 Torr oxygen. When the reaction was carried out in a hydrogen environment catalytic gasification of the deposited carbon was observed to commence at about 500°C and took place by the edge recession mode. This process was accompanied by a decrease in the average size of platinum particles which had remained on the support surface during treatment in acetylene. It was necessary to raise the temperature to 800°C to induce catalytic hydrogenation of the filamentous carbon structures.

If the gasification step was conducted in an oxygen environment then at 600°C metal particles located on the support which were not associated with filaments were seen to catalyze the removal of the carbon overlayer. This action took place by the development of channels through the deposit and was responsible for an increased rate of sintering resulting from platinum particle mobility and collisions between particles. At the same time platinum particles located at the tips of filaments were observed to catalyze the oxidation of the filament they had produced during the acetylene cycle and, as a consequence, retraced a pathway back to their original location on the alumina support.

High-resolution transmission electron microscopy experiments. In these investigations two types of specimens were utilized, platinum on graphite and platinum on thin films of γ-alumina. Batches of these samples were treated in a flow reactor tube at 500°C in the following sequence of gaseous reactants: air, hydrogen, and acetylene. At least two specimens of a particular catalyst system were removed from the tube after each reaction step for examination in the electron microscope.

Following the treatment in air it was difficult to discern the presence of platinum particles on either the graphite or the alumina supports. This aspect suggests that most of the metal was dispersed in an atomic state or in the form of monolayer oxide rafts, which were indistinguishable from the texture of the support structure.

Examinations of the data obtained for platinum/graphite specimens (Fig. 6) shows that there is a significant decrease in particle size after the acetylene treatment compared to that after reaction in hydrogen. From the distributions it was found that the average crystallite size decreased from 5.8 to 4.2 nm following reaction in the hydrocarbon. A similar trend was found for the platinum/alumina specimens when they were heated in the same gas environments (Fig. 7). In this case the average platinum particle size decreased from 9.7 to 3.3 nm after the reduced specimen was reacted in acetylene.

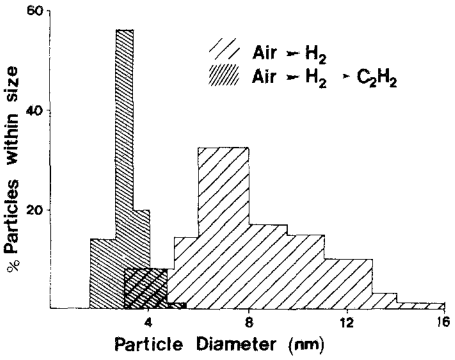

FIG. 6. Particle size distribution of a model platinum/graphite catalyst after heating to 500°C in (a) air for 2.0 h, (b) hydrogen for 4.0 h, and (c) acetylene for 0.5 h.

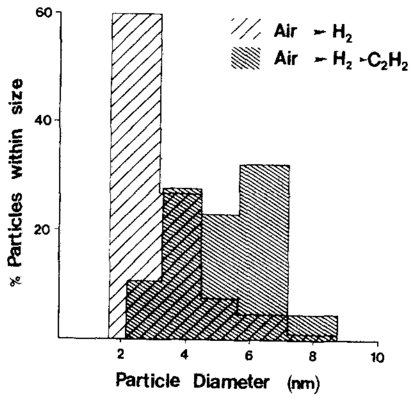

FIG. 7. Particle size distribution of a model platinum/alumina catalyst after heating to 500°C in (a) air for 2.0 h, (b) hydrogen for 4.0 h, and (c) acetylene for 0.5 h.

DISCUSSION

The results of the present investigation provide some basic scientific understanding of the mysteries surrounding the ability of platinum particles to maintain their catalytic activity in systems where carbon deposition is appreciable. Examination of used commercial platinum reforming catalysts shows that the carbonaceous deposit tended to collect at specific sites on the alumina support, leaving the metal particles relatively free of coke. According to decoking studies carried out by thermogravimetry the carbonaceous deposits formed on such catalysts were readily gasified in carbon dioxide at moderate temperatures and no evidence of either filamentous or graphite components was found during controlled oxidation experiments performed in the controlled-atmosphere electron microscope. We therefore conclude that the coke is predominantly isotropic in nature (nongraphitic) which is consistent with the findings of other workers (*5*, *7*). Furthermore since the coke precursors have no special relationship with the metal no preferential blocking of these sites occurs.

A further aspect to emerge from examination of the used commercial catalysts is that sintering of metal particles occurs only to a limited extent during the reforming reaction. The particles reach an average size of about 1.7 nm and this growth process is independent of either the metal loading or the time on feed. In contrast, extensive particle sintering is observed during the decoking step in oxygen and is facilitated by the catalytic gasification reaction which induces mobility of the metal particles.

It is clear from the model catalyst studies that the absence of carbon deposition in the vicinity of platinum particles and the maintenance of a relatively small metal particle size are features which are intimately related to one another. Continuous observations of the interactions of platinum/alumina specimens with acetylene showed that as the reaction proceeded, "clean areas" developed around each metal particle. We believe that this phenomenon is a result of the ability of the platinum particles to hydrogasify coke precursors in their immediate vicinity. The presence of hydrogen during carbon deposition reaction is inescapable since it is a product of dehydrogenation reactions occurring on the metal particle surface. At about 480°C it is probable that decomposition of adsorbed acetylene will occur on the platinum to produce a mixture of carbon species and hydrogen. Under these conditions dissociative adsorption of hydrogen on the metal can lead to methane formation via the hydrogasification of the deposited carbon.

It is well known that noble metals are good catalysts for the hydrogenation of carbonaceous materials (*15*). Tomita and Tamai (*16, 17*) used *in situ* optical microscopy to follow the manner by which several noble metals influenced the graphite–hydrogen reaction. They showed that the metal particles catalyzed gasification of graphite by generating channels across the basal plane surfaces. Recent CAEM studies by Baker and co-workers (*18*) have shown that the onset of catalytic hydrogenation of graphite by platinum-containing particles occurs at 470°C by the edge recession mode. This type of attack results from a strong interaction between the catalytic species and the substrate surface, which causes platinum to undergo a wetting and spreading action along graphite edges. At 645°C, metal particles were observed to reform and the mode of catalytic attack changed from edge recession to channel propagation. This modification in catalytic action indicates that there is a decrease in the interfacial bonding energy between platinum and graphite as the temperature is raised, possibly resulting from the presence of dissolved carbon in the metal.

Rewick and co-workers (*19*) investigated the kinetics of the platinum-catalyzed hydrogenation of a variety of carbon substrates. They interpreted the catalytic effect according to a mechanism involving hydrogen dissociation on the metal surface, followed by surface diffusion across the metal/carbon interface, and finally reaction with carbon to produce methane. An alternative explanation was put forward by Holstein and Boudart (*20*), who claimed that the rate-determining step was the rupture of carbon–carbon bonds with the formation of a carbon–platinum bond. Removal of carbon from the metal via interaction with hydrogen to form methane was the final step in this mechanism.

From the above discussion we may conclude that supported platinum particles are capable of catalyzing the hydrogasification of carbon species as they are formed in the reforming reaction (i.e., they perform a self-cleaning operation), and as a consequence remain essentially free of carbon during this process. In addition, the nature of the interplay between the platinum and the carbonaceous deposit produces a condition where wetting and spreading of the metal interface is facilitated, which helps to maintain particles in a relatively high dispersion when heated in a reducing environment.

A considerable body of information exists on the sintering of alumina-supported noble metal particles; Refs. (*21–28*) are papers from various groups. Although there has been a great deal of argument regarding the mechanism by which supported metal crystallites sinter, it is generally agreed that the nature of the gas environment and the treatment temperature play a crucial role in the process. It has been shown that when platinum/alumina specimens are heated in air or oxygen at 600°C there is a rapid increase in metal crystallite size. However, when these specimens are treated in the same environment at 500°C, there is a decrease in average crystallite size (i.e., redispersion) (*29, 30*). In a subsequent paper, Ruckenstein and Chu (*31*) reported that several cycles of alternating heating of the specimen in oxygen and hydrogen at 750°C and 1 atm pressure were required before platinum crystallites started to redisperse during the oxidation step. These workers introduced the concept of wetting and spreading in catalyst-support systems to account for the observed redispersion of platinum crystallites. They postulated that redispersion occurred in an oxygen environment as a result of spreading of platinum oxide over the surface of the alumina. They further suggested that heating in hydrogen caused sintering as platinum oxide was converted to metal which did not wet the alumina. Other workers (*27*) have also found that alumina-supported noble metal systems undergo redispersion during oxidation–reduction cycling. On the other hand, when alumina-supported metal systems are heated in hydrogen only crystallite growth is observed (*26, 31–33*).

In the present study the behavior of platinum/alumina has been extended to cover the influence of deposited carbon on the sintering characteristics of the metal particles. If the carbon was removed by a subsequent treatment in oxygen then the platinum particles participated in this process and the catalytic channeling action induced motion of the metal particles with a consequent increase in the average particle size. In contrast when the platinum/alumina specimens were maintained in an environment containing a significant amount of hydrogen, then the metal particles exhibited an entirely different pattern of behavior. Both dynamic observations and quantitative determinations of metal particle size are consistent with a concept that a temperature range exists within which the presence of carbon on the catalyst surface can have a direct impact on the redispersion of platinum particles.

Finally, it is interesting to compare the data presented in Figs. 6 and 7. The larger decrease in the average particle size found for platinum on the alumina support compared to that on graphite following reaction in acetylene is a reflection of the stronger interaction exhibited by the metal on graphite than on alumina in a reducing environment at moderate temperatures.

SUMMARY

The following conclusions were reached with regard to carbon deposition on supported platinum particles.

1. In the case of Pt/Al_2O_3 reforming catalysts coke appears to collect at specific sites on the alumina support, leaving the metal particles relatively free of carbonaceous deposit.

2. In this system coke is easily gasified in either O_2 or CO_2 and no evidence of filamentous or graphitic components was found in the carbonaceous deposit produced under typical reforming conditions, i.e., temperatures around 500°C.

3. In a Pt/Al_2O_3 reforming catalyst maintenance of small average metal particle size (1.7 nm) indicates that a limited degree of sintering occurs during the reforming reaction.

4. In such a catalyst, the metal particles remain essentially free of carbon because of their ability to hydrogasify coke precursors as they are formed (i.e., they perform a self-cleaning operation).

5. During the catalytic hydrogasification step the platinum particles undergo a wetting and spreading action with the carbona-

ceous residues on the support and thus maintain a small average particle size.

6. When the model platinum-supported catalysts were reacted in 2 Torr C_2H_2 at low temperatures (about 485°C) the platinum particles were observed to perform a self-cleaning operation, whereas at higher temperatures (590–840°C) they catalyzed the growth of carbon filaments.

ACKNOWLEDGMENTS

The authors thank Dr. G. B. McVicker, Corporate Research Laboratory, Exxon Research and Engineering Company, Clinton, New Jersey, for most valuable discussions and encouragement. The work was carried out under a grant from the Petroleum Research Fund, ACSPRF-19652-AC5.

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