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Electron Microscopy of Supported Metal Particles

I. Behavior of Pt on Titanium Oxide, Aluminum Oxide, Silicon Oxide, and Carbon

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Transmission electron microscopy has been used to investigate the structure and growth characteristics of platinum on thin films of titanium oxide, aluminum oxide, silicon oxide, and carbon. Significant differences in the sintering characteristics of the metal on the various supports was observed after these systems had been treated in hydrogen at temperatures over the range 425 to 1075°K. Sintering occurred on all supports but the metal dispersion was significantly more stable on titanium oxide than the other supports. Examination of platinum on titanium oxide at high resolution showed that the metal particles were predominately hexagonal in outline, of uniform thickness and very thin, indicating a pill-box morphology. Electron diffraction and lattice spacing measurements showed that the titanium oxide support was reduced to Ti_4O_7 in the presence of platinum. In the absence of platinum only the rutile form of TiO_2 was observed. We conclude that platinum catalyzes the reduction of TiO_2 to Ti_4O_7 and deposits as thin pill-box structures on the surface of the Ti_4O_7. The unique structural features of the type observed for platinum on titanium oxide was not observed with the other supports, and is believed to result from a strong metal–support interaction.

INTRODUCTION

It has recently been reported that the ability of the Group VIII metal particles to chemisorb hydrogen and carbon monoxide is related to the nature of the support and the pretreatment of the catalyst (*1*). For well-dispersed and reduced noble metals on silica, alumina, or carbon, the number of surface metal atoms can be counted by selective chemisorption of hydrogen or carbon monoxide providing the stoichiometry of the adsorption is known. The fraction of exposed metal atoms is then calculated from the hydrogen or carbon monoxide uptakes at saturation coverage and the total number of metal atoms for a unit weight of sample. Decreases in the H/M or CO/M ratios for the aforementioned supports is usually associated with growth of the metal particles following thermal treatment. Titania-supported metals show markedly different behavior. Following reduction in hydrogen at 775°K, H/M and CO/M ratios near zero are found. Such ratios are normally indicative of metal particles much greater than 10 nm in size. X-Ray diffraction and electron microscopy examinations of the titania samples, however, showed no large metal particles indicating that the percentage

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metal exposed was much larger than that calculated from chemisorption measurements. The suppression of hydrogen and carbon monoxide chemisorption for titanium oxide-supported metals was attributed to an influence of the support on the chemical and/or structural properties of the metal and has been termed strong metal–support interaction or SMSI (*1*).

In this paper high resolution transmission electron microscopy is used to compare the nature of platinum particles supported on titanium oxide, aluminum oxide, silicon oxide, and carbon films. Films rather than actual catalysts were used to improve the quality and resolution of the micrographs. The objective of these investigations was to determine if there are any identifiable features which would serve to indicate that metal particles on titanium oxide differ from those on common supports such as alumina, silica, and carbon. Both the variation of metal particle morphology and the dependence of particle size distribution on reduction temperature on all the above mentioned supports were examined.

EXPERIMENTAL METHODS

Transmission specimens were prepared according to the following procedure:

Films of titanium oxide, aluminum oxide, and silicon oxide of about 35 nm thickness were produced by sputtering from the respective target materials onto rock salt crystals. The rock salt was subsequently dissolved away in water leaving the oxide films floating on the surface. Sections of the films were washed to remove all traces of salt and then picked up on 200-mesh, stainless-steel, electron microscope grids. Carbon films of similar thickness were prepared by vacuum deposition from a carbon arc onto a Pyrex slide, which had been previously coated with a film of detergent. The resulting carbon film was released from the slide by gradual immersion in water and finally mounted on a microscope grid. Platinum was evaporated at 10^{-6} Torr (1 Torr = 133.3 N m^{-2}) onto these supports from a spectrographically pure platinum wire mounted on a tungsten filament. This procedure produced a platinum film approximately one atom thick.

Specimens were subsequently reduced in a 20% hydrogen/helium mixture under flow conditions for 1 hr at 425, 825, 975, and 1075°K. After cooling, they were examined in a Philips EM 300 transmission electron microscope with a resolution better than 0.25 nm. The microscope and its calibration have been described elsewhere (*2*). Particle size distributions were obtained from measurement of over 600 particles after each treatment.

In some cases a shadowing technique was used to determine the height of metal crystallites on the support. This was accomplished by evaporating uranium atoms onto the specimen at an angle of 14° with respect to the plane of the support film. Areas of the specimen shielded from the impinging beam of atoms by surface relief features are not coated, and, as a consequence, appear as an enlarged shadow when the specimen is examined in the TEM. Under the conditions used, the height to shadow ratio was 1:4, and thus with the available resolution a crystallite thickness in excess of 2 nm could easily be detected.

RESULTS AND DISCUSSION

In this section transmission electron micrographs for titanium oxide reduced in hydrogen at various temperatures are first discussed. This is followed by a discussion of the results pertaining to the nature and behavior of platinum particles on titanium oxide, alumina, silica, and carbon. Finally a comparison of the thermal stabilities of metal dispersions on the various supports is made using particle size distribution data.

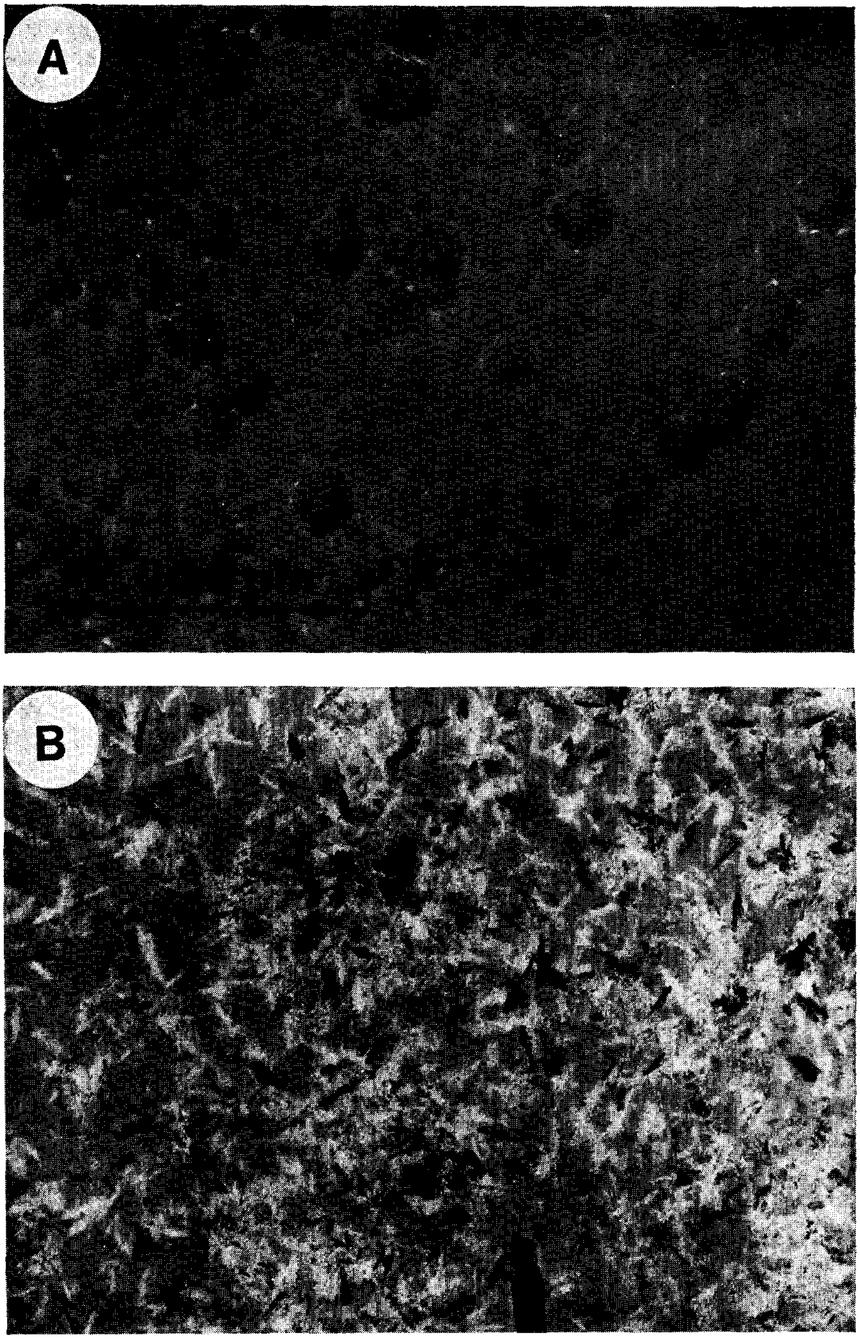

FIG. 1. (A–D) The appearance of TiO_2 after reduction in H_2 at 425, 825, 975, and 1075°K.

Effect of Heating Titanium Dioxide in Hydrogen

The changes which occurred when blank titanium oxide specimens were heated in hydrogen are shown in Fig. 1A to D. The original amorphous structure starts to undergo a change in appearance at some temperature between 425 and 825°K. At

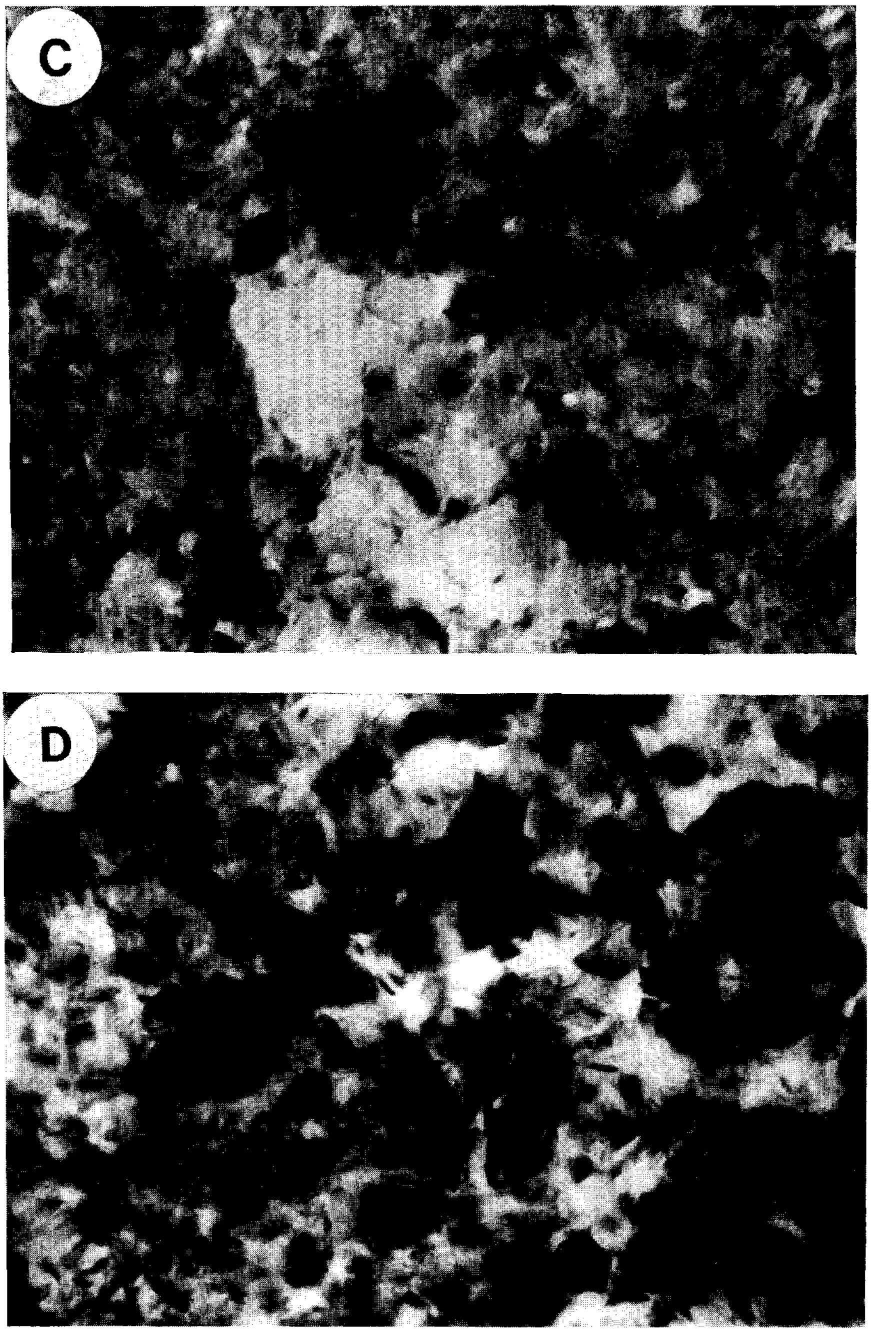

FIG. 1.—*Continued.*

975°K it is apparent that this process is one of crystallization, as evidenced from the appearance of Moiré fringes (*3*) on many areas of the specimen. Moiré fringe patterns can occur where two crystal lattices overlap and are the result of periodic matches and mismatches of the lattice planes of the overlapping crystals. At 1075°K the whole surface has undergone a reorganization. Platelets up to 60 nm in

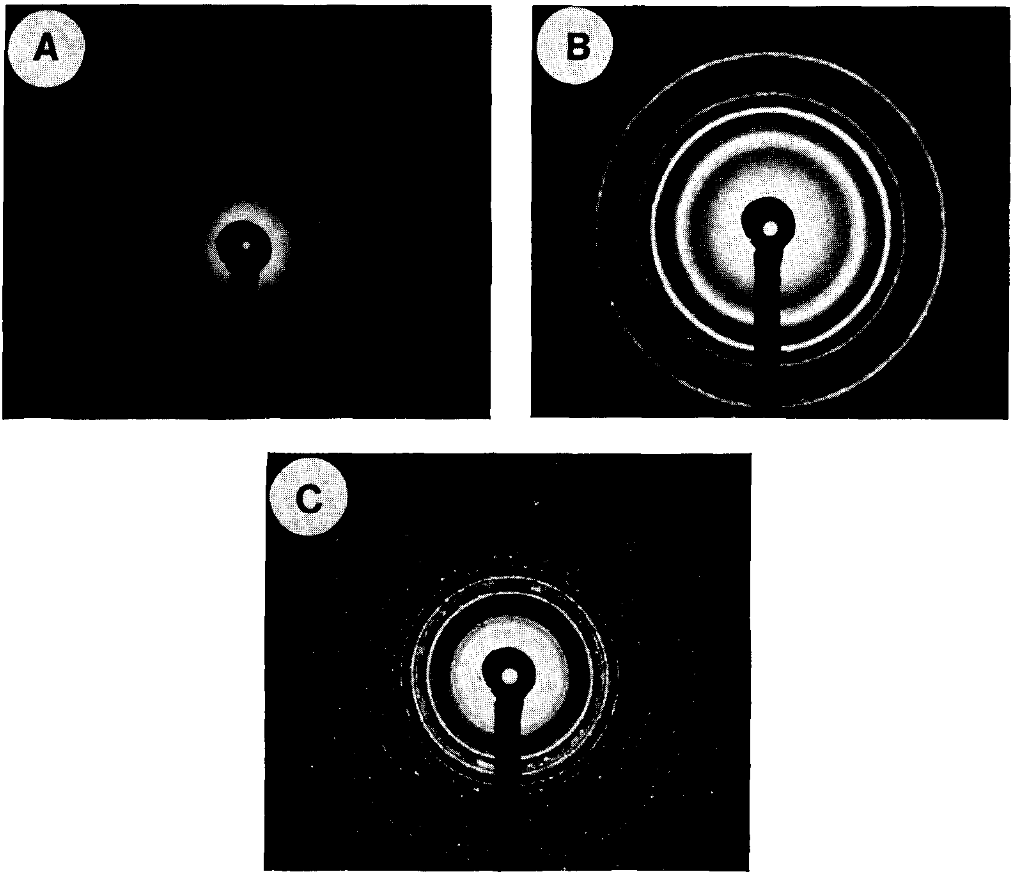

FIG. 2. (A) Selected area diffraction pattern of TiO_2 after reduction in H_2 at 425°K. (B) Selected area diffraction pattern of TiO_2 after reduction in H_2 at 1075°K. (C) Selected area diffraction pattern of Ti_4O_7 after reducing Pt/TiO_2 in H_2 at 1075°K.

width have grown by transport of material from adjacent areas of the surface, the depleted areas showing up as white zones. Selected area electron diffraction examination revealed that as the temperature was increased, the original diffuse ring pattern (Fig. 2A) gradually changed to a well-defined ring pattern, which had many spots superimposed on the rings (Fig. 2B). This latter pattern was identified as that from the rutile form of TiO_2. The mechanism of the observed transformation has been discussed in detail by Shannon (*4*, *5*) and is thought to be due to the creation of oxygen vacancies when the initial anatase form is heated in hydrogen. No evidence for other oxides of titanium in the reduced samples was obtained.

Effect of Heating Supported Platinum Particles in Hydrogen

Examination of the growth characteristics of platinum particles supported on titanium oxide, aluminum oxide, silicon oxide, and carbon showed some profound differences in behavior when these systems were heated in hydrogen. Figures 3 to 6 are transmission electron micrographs taken after heating samples of the four systems to 1075°K in hydrogen for 1 hr. Inspection of these micrographs clearly reveals that there are fundamental differences in behavior of

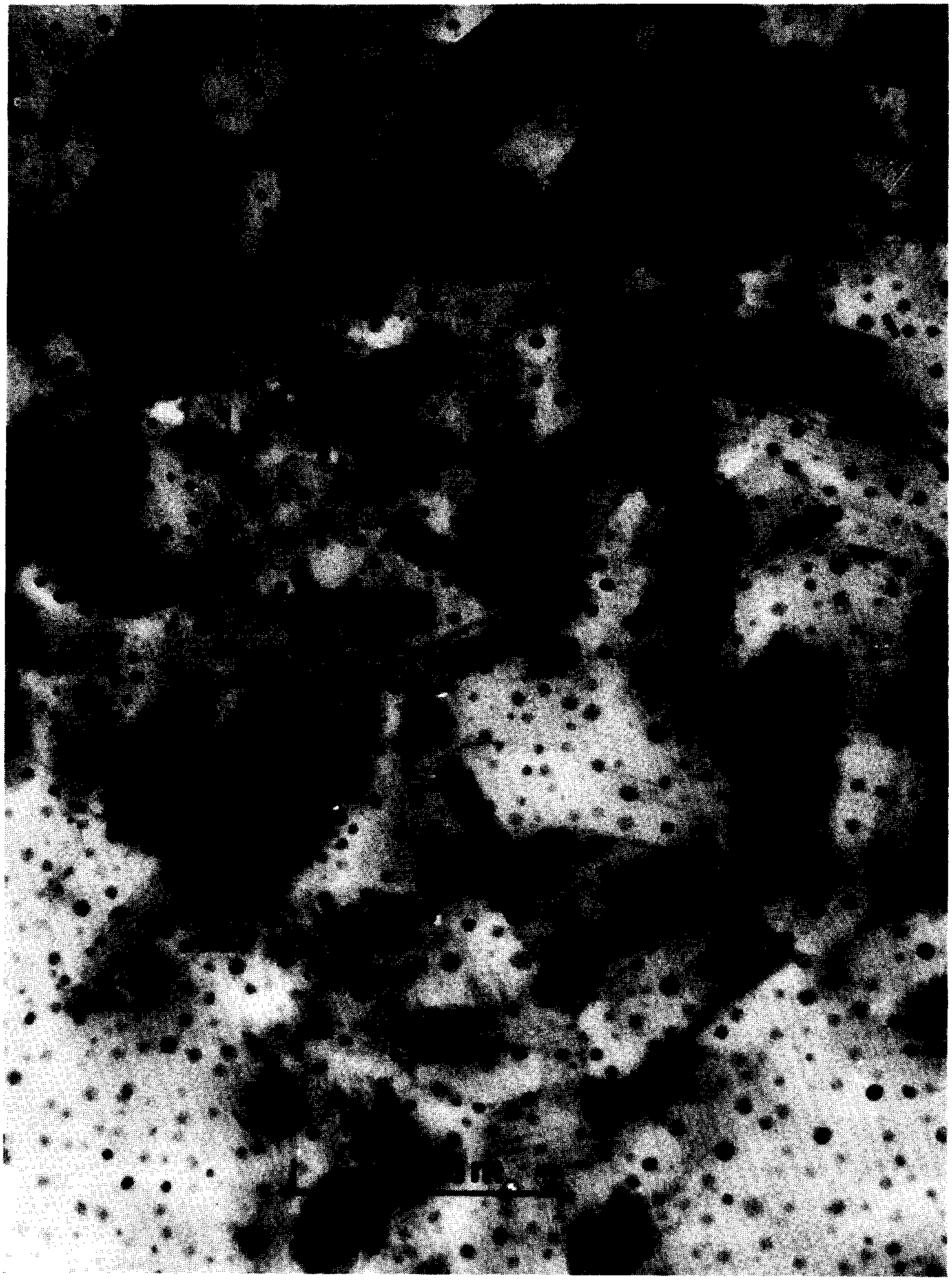

FIG. 3. Micrograph of Pt on titanium oxide after heating in H_2 to 1075°K for 1 hr.

platinum on the four supports following high temperature reduction. Detailed examination of many micrographs showed that after heating to only 425°K, platinum particles were in general of similar size (3 nm) and appearance on all the supports, but, as the reduction temperature was raised, each system behaved differently.

FIG. 4. Micrograph of Pt on aluminum oxide after heating in H_2 to 1075°K for 1 hr.

These differences are discussed in detail in the following sections.

(*i*) *Platinum on titanium oxide: evidence for metal-support interaction.* When compared to the other supports, the platinum–titanium oxide system was unique in many aspects. In the presence of platinum the titanium oxide appeared to undergo the same crystallization process observed for the pure substrate (Fig. 1). However, the

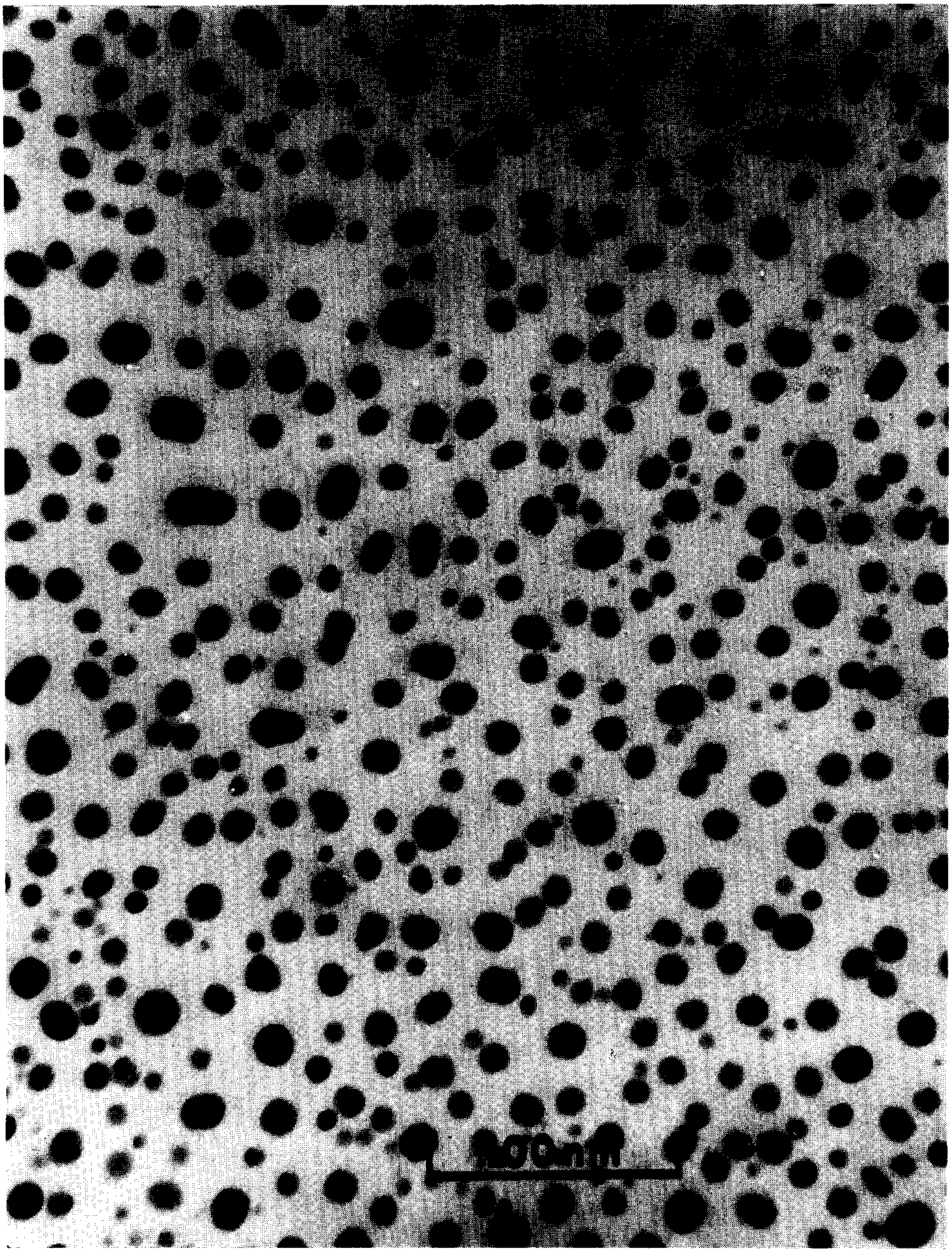

Fig. 5. Micrograph of Pt on silicon oxide after heating in H_2 to 1075°K for 1 hr.

structure of the titanium oxide after reduction at 825°K was markedly different when platinum was present. This feature became more pronounced after reduction of specimens at higher temperatures (Fig. 7). Electron diffraction analysis showed the substrate structure in Fig. 7 to be that of Ti_4O_7 (Fig. 2C) rather than the rutile form of TiO_2 observed in the absence of platinum. The crystal structure of Ti_4O_7 is triclinic

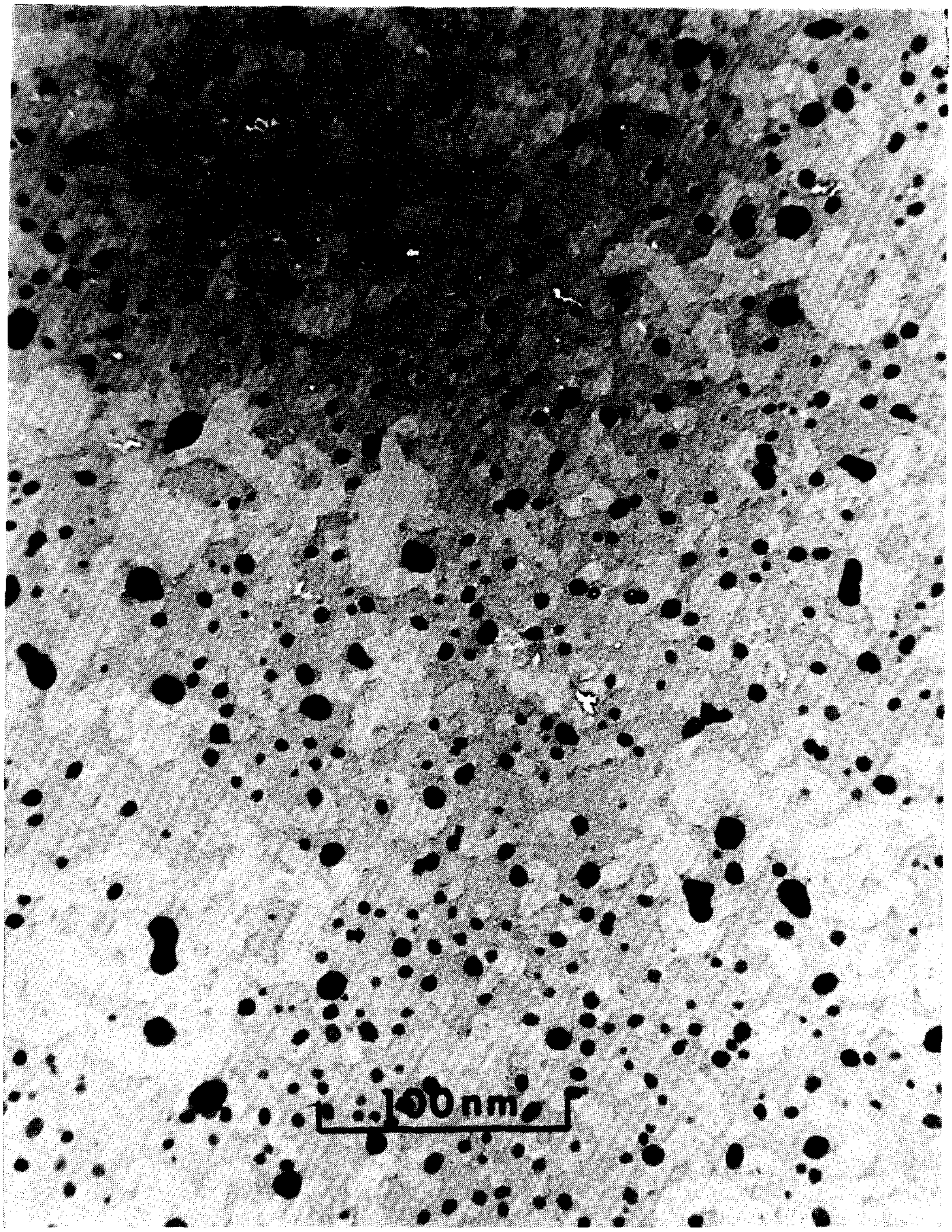

FIG. 6. Micrograph of Pt on carbon after heating in H_2 to 1075°K for 1 hr.

and has been discussed in detail by Marezio and Dernier (*6*). The formation of Ti_4O_7 in the present work was verified by lattice spacing measurements of the lattice images in Fig. 7 and several other micrographs omitted from this paper for the sake of brevity. The measured spacings are presented in Table 1 along with reported values and corresponding crystal planes (*7*). The value of 0.55 nm measured on a number

Fig. 7. High resolution micrograph of Pt on titanium oxide reduced at 825°K showing lattice fringes of Ti_4O_7 and Pt particles on the substrate.

TABLE 1

Lattice Spacing Measurements for Ti_4O_7

Measured d (nm)	Literature d(7) (nm)	[hkl]
0.62	0.617	002
0.43	0.427	$10\bar{2}$
0.33	0.338	$1\bar{2}0$

of micrographs is most certainly the a_0 unit cell dimension (0.56 nm) of Ti_4O_7. The formation of Ti_4O_7 in the presence of platinum demonstrates that platinum catalyzes the reduction of the support.

The nature and growth characteristics of platinum particles on titanium oxide was also unique among the supports investigated. The platinum particles on titanium oxide increased in size over the temperature range 425 to 825°K, but there did not appear to be any further appreciable increase in size as the temperature was raised to 1075°K. On the other supports particle growth continued up to 1075°K. It was also interesting to find that pretreating the titanium oxide in H_2 at 925°K for 1 hr prior to depositing Pt did not produce any significant difference in the subsequent growth characteristics of Pt compared to that on untreated amorphous titanium oxide. The 925°K hydrogen pretreatment caused the titanium oxide substrate to crystallize as was shown in Fig. 1. Since the platinum growth characteristics were the same starting with amorphous or crystalline titanium oxide, the crystallization process has little or no influence on platinum particle growth. In both cases the final structure of the substrate was that of Ti_4O_7.

Another unique aspect of the platinum–titanium oxide system was the observation that the electron scattering density of the platinum particles remained virtually unchanged over the temperature range 825–1075°K indicating that particle growth was not occurring by an increase in particle height. Examination of these specimens at very high magnification ($\sim 2.5 \times 10^6$) revealed several other features of the platinum particles. They were found to be predominately hexagonal in outline and not only were they very thin, but the thickness was uniform across the particle indicating the morphology to be that of a pill-box rather than hemispherical. The failure to find any trace of a shadow after evaporation of uranium places an upper limit on the particle thickness of ~ 2 nm, i.e., a few atomic layers.

Additional evidence for the thin pill-box structure of the platinum particles on titanium oxide was obtained from further inspection of the high magnification micrograph (Fig. 7). It can be seen that lattice images of the Ti_4O_7 substrate are clearly visible through most of the platinum particles. Moreover, the intensity of such fringes appears uniform across the complete width of a given particle confirming the uniform thickness of a particle, i.e., pill-box morphology. Defocusing experiments verified that the platinum particles were on top of the substrate. Similar observations were made by Prestridge *et al.* (*8*) in their studies of metal clusters on silica, which led them to conclude that ruthenium and ruthenium–copper clusters were in the form of rafts, one and two atomic layers thick, respectively. The present results do not allow us to make the same definitive claims, but we do believe that platinum particles are present as extremely thin flat structures.

The observations that the support is reduced to Ti_4O_7 only in the presence of platinum and that platinum is present as thin flat particles, even at 1075°K when the energetically preferred shape would be hemispherical, suggest that a structural relationship may exist between the metal and the support. Two possibilities, epitaxy and pseudomorphism, merit consideration in this regard.

For the case of epitaxy, the metal

particles retain their normal lattice spacing but assume the same orientation as that of the substrate surface (*9*). Crystallites exhibiting epitaxy may be many atomic layers in thickness (*10, 11*). In the case of pseudomorphism, the lattice spacing of the deposit material is identical to that of the substrate (*12*). It appears unlikely that a pseudomorphic deposit would be more than one atomic layer thick if there were an appreciable difference between the normal lattice spacing of the deposit and that of the substrate. In principle, electron diffraction patterns showing the relative orientations of the deposit and substrate can establish if epitaxy exists. The platinum–titanium oxide samples, however, showed no electron diffraction pattern for platinum, so we are in no position to make any strong claims regarding the nature of the interaction in this system. Additional experimental data from techniques such as EXAFS which could provide information on the local environment of platinum or titanium would clearly be valuable in further understanding the Pt–Ti_4O_7 system.

Although the results of this study do not allow us to draw any definite conclusions regarding the precise nature of the interaction between Pt and Ti_4O_7, they nevertheless point to an unusual structural relationship between the metal and oxide. Furthermore, the results are in accord with the chemisorption studies of Tauster *et al.* (*1*) which demonstrated that the suppression of H_2 and CO adsorption on Pt-titanium oxide are indicative of strong chemical perturbations on the platinum due to metal–support interaction. This result provides indirect evidence for a strong chemical bonding between the metal and support that could give rise to pseudomorphism. The fact that the platinum is deposited on a reduced form of titanium oxide, Ti_4O_7, suggests that platinum atoms may form chemical bonds with Ti^{3+} cations. Bonding between platinum cations and Ti^{4+} cations is known to occur in solid-state compounds, namely the hexagonal barium titanates (*13*). For the Pt–titanium oxide system bonding between platinum and titanium would appear to involve a platinum atom

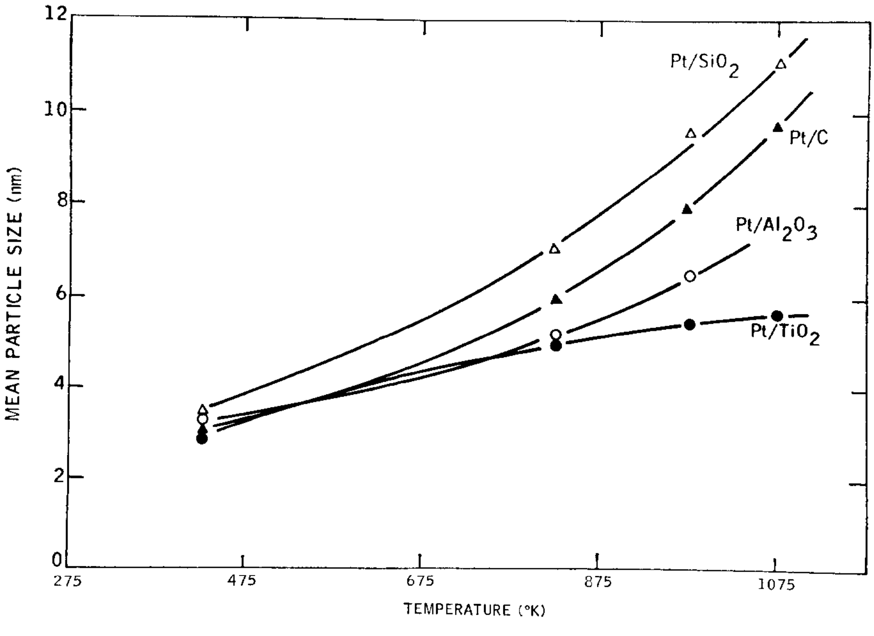

FIG. 8. Variation of mean platinum particle size with reduction temperature on the four substrates.

rather than a cation because Tauster *et al.* (*1*) showed that platinum was reduced to the metal at low temperatures (475°K) and only interacted strongly with the support on further reduction at 775°K. For platinum at the surface of titanium oxide, reduction of the support to a lower oxide may be necessary to provide a sufficient concentration of exposed titanium cations so that bonds to an aggregate of platinum atoms can form. Recent theoretical calculations in this laboratory by the x-alpha scattered wave method indicate that covalent bonding can indeed occur between a platinum atom and titanium cations at the surface of titanium oxide; in addition, an ionic contribution involving Ti^{+3} ions is also under consideration (*14*).

(*ii*) *Platinum on aluminum oxide, silicon oxide, and carbon.* In the platinum on aluminum oxide system expected particle growth is observed as the temperature is increased from 425 to 975°K, but at the upper temperature it is evident that the number of isolated particles present has decreased to a far greater extent than can be accounted for purely on the basis of particle agglomeration. At 1075°K a dramatic change in appearance of the surface is seen; small particles have disappeared and large dense areas have formed. This behavior was observed in dynamic studies of the interaction of Pt/Al_2O_3 with O_2 (*15*). Recently Sprys and Mencik (*16*) found the same effect when Pt/Al_2O_3 specimens were subjected to intense elec-

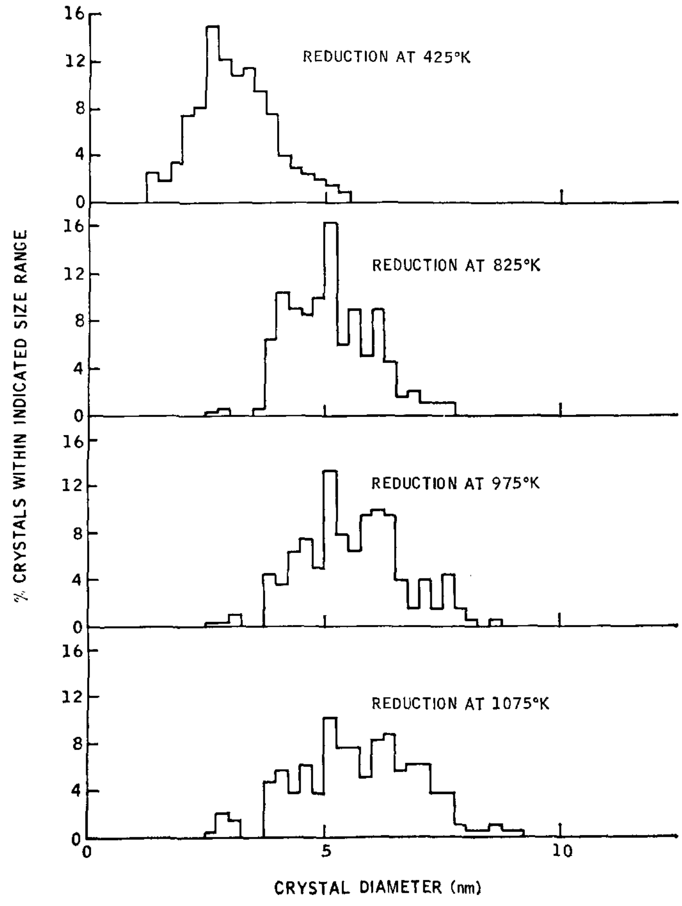

Fig. 9. Variation of PSD with reduction temperature for Pt on titanium oxide.

tron beams within the electron microscope and suggested that it was due to the formation of a Pt–Al alloy. In the present investigation this condition was carefully avoided by the use of low beam intensities and we saw no enhancement of the interaction during the microscopy examination. Clearly the nature of the gas environment does not appear to have any influence over this reaction and raises serious questions as to the formation of a Pt–Al alloy. Although the Pt particles have a faceted outline at 825°K, it is not possible to discern any one particular preferred shape.

A common feature encountered in both the Pt on titanium oxide and Pt on aluminum oxide systems is that all the metal particles remain as discrete entities, there being no tendency for particles to stick together in the form of chains. This observation suggests that once formed, the particles remain static on the support surface and almost certainly grow by migration of atomic species from one crystallite to another.

Examination of the micrographs of the Pt on silicon oxide system indicates that particle growth is quite rapid and that there is extensive agglomeration as the reduction temperature is increased. At the intermediate temperatures, 775 to 975°K, the metal takes the form of elongated "puddles" and there is a great deal of evidence for neck formation between adjacent islands of platinum indicative of liquid-like coalescence.

The behavior of platinum on carbon is similar in some respects to that of the Pt on silicon oxide system in that particles tend to be relatively globular in outline and there is evidence of liquid-like character. The picture is further complicated by the fact that platinum has the ability to catalyze the hydrogenation of the carbon support at temperatures above 775°K (*17*). The results of this action can

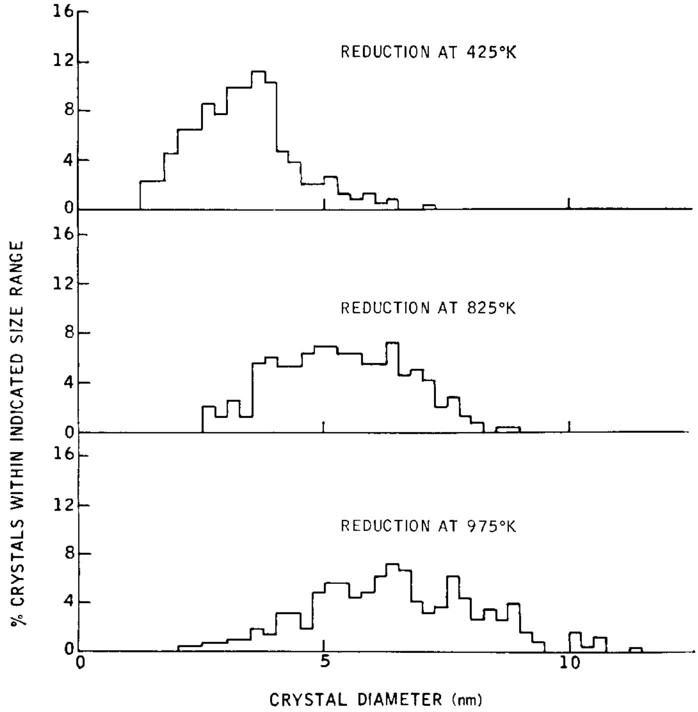

FIG. 10. Variation of PSD with reduction temperature for Pt on aluminum oxide.

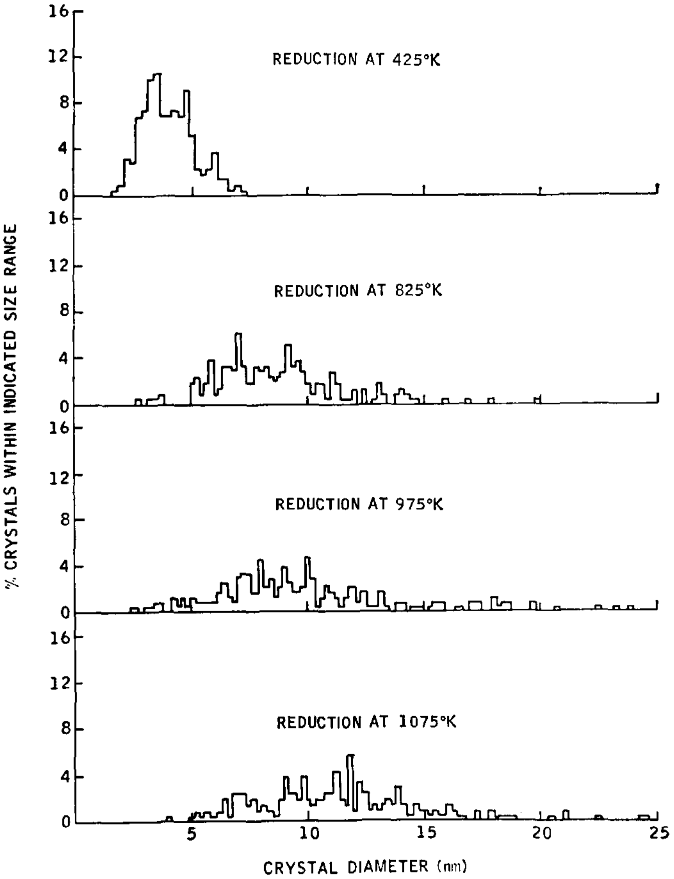

FIG. 11. Variation of PSD with reduction temperature for Pt on silicon oxide.

be seen in Fig. 6, where channels have been created in the wake of almost all the platinum particles. These channels have been caused by the preferential removal of carbon aroms to produce methane at the metal–carbon interface and as a consequence, particles are drawn across the surface removing carbon in their path. This type of behavior would produce the same effects in the carbon as observed during catalytic oxidation of carbon by platinum particles (*18*). Because motion is imparted to the particles by this reaction, there is a high probability of particle collisions leading to coalescence, and a resulting enhancement in the particle growth rate.

(*iii*) *Thermal stability of metal dispersions for the various substrates.* Quantitative determinations of the mean particle size dependence on temperature are presented in Fig. 8, where it can be seen that Pt particles supported on titanium oxide are at least a factor of 2 smaller than on the other supports at the higher temperature range. A detailed analysis of particle size distributions at various temperatures (Figs. 9–12) provides a more enlightening picture of the particle growth characteristics in these systems and reveals significant differences in the behavior of Pt on titanium oxide in comparison to the other supports. It is evident that the distribution from Pt on titanium oxide is narrower than for the other substrates at all temperatures and shows little change in magnitude over

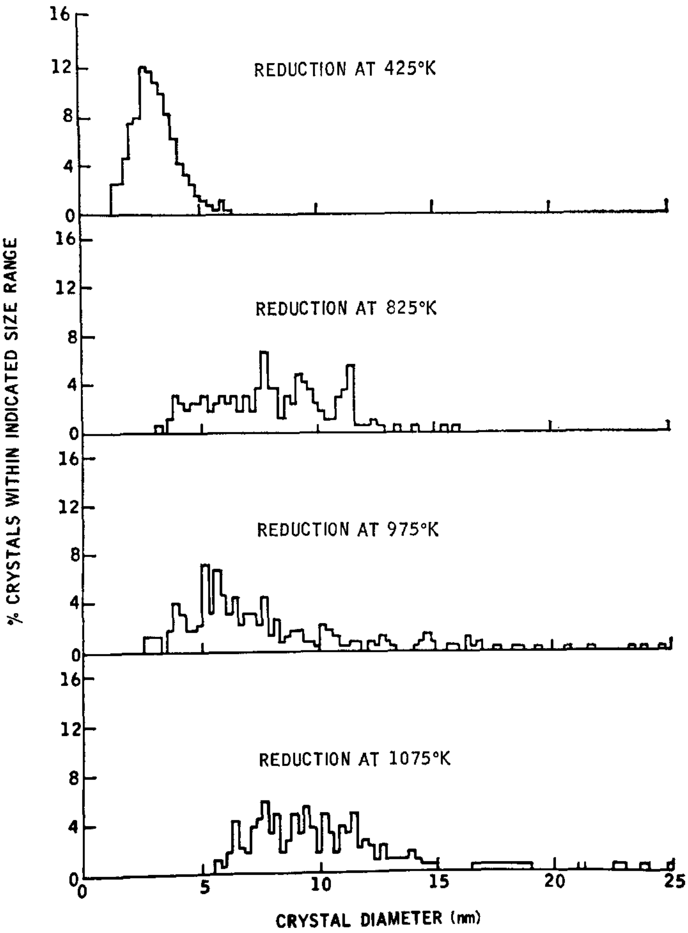

FIG. 12. Variation of PSD with reduction temperature for Pt on carbon.

the range 825 to 1075°K with the exception of the tendency to form a splinter group of small particles. The distribution from Pt on aluminum oxide gets progressively broader with increasing temperature, a trend which is much more pronounced in the Pt on silicon oxide and Pt on carbon systems.

The particle size distributions as a function of reduction temperature give further evidence of strong metal–support interaction for Pt on titanium oxide. Regardless of whether one postulates an atomic migration mechanism or a particle migration mechanism for agglomeration, we expect increased metal–support bonding to inhibit sintering as is observed with Pt on titanium oxide.

SUMMARY

High resolution transmission electron microscopy of Pt on titanium oxide, aluminum oxide, silicon oxide, and carbon shows that following reduction at low temperature (425°K) the platinum particles are similar in size and appearance on all the substrates. Following reduction at 825°K or higher, however, Pt on titanium oxide assumes a pill-box structure of hexagonal shape and the substrate is reduced to Ti_4O_7. In the absence of Pt the titanium oxide is not converted to

Ti_4O_7. Detailed analysis of high resolution micrographs suggest that the Pt forms a structural relationship with the Ti_4O_7. Such a relationship might require the formation of chemical bonds between the metal and the support. The marked alteration of the H_2 and CO chemisorption properties of Pt on titanium oxide reported recently by Tauster *et al.* (*1*) provides evidence that such metal–support bonding exists in this system. No unique structural features were observed with the other supports, aluminum oxide, silicon oxide, and carbon.

Particle size distribution data as a function of thermal treatment in hydrogen demonstrated that the order of stability of the platinum dispersions on the substrates was titanium oxide > aluminum oxide > silicon oxide ≈ carbon. This again is indicative of a metal–support interaction in the Pt–titanium oxide system.

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