Electron Microscopy of Supported Metal Particles
II. Further Studies of Pt/TiO₂

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Hydrogen and carbon monoxide chemisorption on Pt on titanium oxide powders [Pt/TO(P)] and transmission electron microscopy of Pt on titanium oxide films [Pt/TO(F)] have been investigated for a common series of thermal treatments in various gaseous atmospheres. Following reduction at 875 K in H_2, Pt/TO(P) did not adsorb H_2 or CO, and X-ray diffraction examination showed that the Pt had not agglomerated. This behavior is attributed to a strong metal–support interaction (SMSI). The adsorption of H_2 and CO could be partially restored if the sample in the SMSI state were treated with H_2O vapor at 525 K or O_2 at 875 K, the latter treatment being more effective. Transmission electron microscopy studies of Pt/TO(F) treated in the same way as the Pt/TO(P) showed that in the SMSI state the Pt was in the form of hexagonal thin pillbox structures grown on a lower oxide of titania, Ti_4O_7. When Pt in the SMSI state was oxidized, there was an appreciable increase in the growth rate of the Pt particles, comparable to that found on conventional supports. Examination of the individual Pt particles showed that while their shape remained hexagonal, their thickness increased following oxidation so they were no longer present as thin pillbox structures. Electron diffraction analysis demonstrated that the support had also undergone a structural change, Ti_4O_7 reverting to TiO_2. Reduction of the sample to induce the SMSI state showed that although a few large Pt crystallites remained, there was significant redispersion of the metal. Following re-reduction, all particles had again assumed the pillbox structure of the SMSI state and the support had reverted, once again, to Ti_4O_7. A schematic model is presented to illustrate the sequence of events during cycling into and out of the SMSI state.

INTRODUCTION

Although there are several reports in the literature pertaining to the use of titanium oxide as a catalyst (1) there is very little information available on the evaluation of the oxide as a catalyst support. It is probable that in the future

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this will be an area of intense activity because of the discovery by Tauster *et al.* of a series of metal/oxide supports, including titanium oxide, which exhibit unique metal–support interactions (*2, 3*). They found that when the Group VIII noble metals supported on various oxides from Groups IIA–VB were reduced at temperatures in excess of 775 K complete suppression of hydrogen and carbon monoxide chemisorption occurred, a result which was attributed to strong metal–support interaction (SMSI).

In a previous paper we used high resolution transmission electron microscopy to compare the structure and growth characteristics of platinum on a number of supports (4). It was demonstrated that when the noble metal supported on titanium oxide films was heated in a reducing environment, many unique features were observed which were indicative of a strong interaction between the metal and the support. The platinum crystallites took the form of thin hexagonal-shaped flat structures, indicative of a pillbox morphology. Very little change in crystallite dimensions was observed over the range 825 to 1075 K. The behavior of platinum on films of the more conventional supports, aluminum oxide, silicon oxide, and carbon, was in line with previously reported data in the literature, and quite different from that seen on titanium oxide.

In the present investigation we examined the effects of consecutive treatments in various gaseous environments on the structure of platinum on titanium oxide films and on the chemisorption properties of platinum on titanium oxide powders. The objective of this study was to determine whether structural changes observed by transmission electron microscopy studies of films correlated with the chemisorption properties of the real system. If such a correlation were found, it would provide insight as to the structural features of the platinum crystallites when hydrogen or carbon monoxide chemisorption is suppressed (2) and also demonstrate that the information obtained from the model system could be applied to real samples.

EXPERIMENTAL METHODS

The titanium oxide films and the platinum on titanium oxide [Pt/TO(F)] films were prepared as described previously (4). The 2% Pt on titanium oxide powder [Pt/TO(P)] sample for chemisorption studies was prepared by incipient wetness

impregnation of Degussa P-25 TiO_2 with an aqueous solution of H_2PtCl_6. The sample was subsequently dried overnight at 385–395 K and for 4 hr at 535 K, all in air. The surface area of the TiO_2 powder was determined by argon BET surface area measurements to be 51 $m^2 g^{-1}$ assuming a cross-sectional area of 1.46 nm^2 for the argon atom. The composition of the P-25 TiO_2 was ~80% anatase and 20% rutile. The preparation of the powder catalysts and the properties of P-25 TiO_2 are discussed in detail in Ref. (2).

Hydrogen and carbon monoxide chemisorption measurements were performed at room temperature on a conventional glass vacuum apparatus capable of attaining dynamic vacuum of about 10^{-7} Torr. Pressure was measured in the chemisorption studies with a Texas Instruments precision pressure gauge. The procedures for catalyst reductions and chemisorption measurements were the same as those described in Ref. (2). Briefly, the hydrogen uptake at zero pressure of hydrogen was assumed to represent saturation coverage of the metal and was determined by extrapolating the flat linear portion of the hydrogen isotherm.

The CO/Pt ratios were determined by measuring the total CO uptake on the freshly reduced and evacuated sample. This was assumed to represent the sum of CO strongly bonded to the metal and CO weakly bonded to the support. After the initial CO isotherm, the sample was

TABLE 1

Summary of Chemisorption Studies
on 2% Pt/TiO₂ Powders

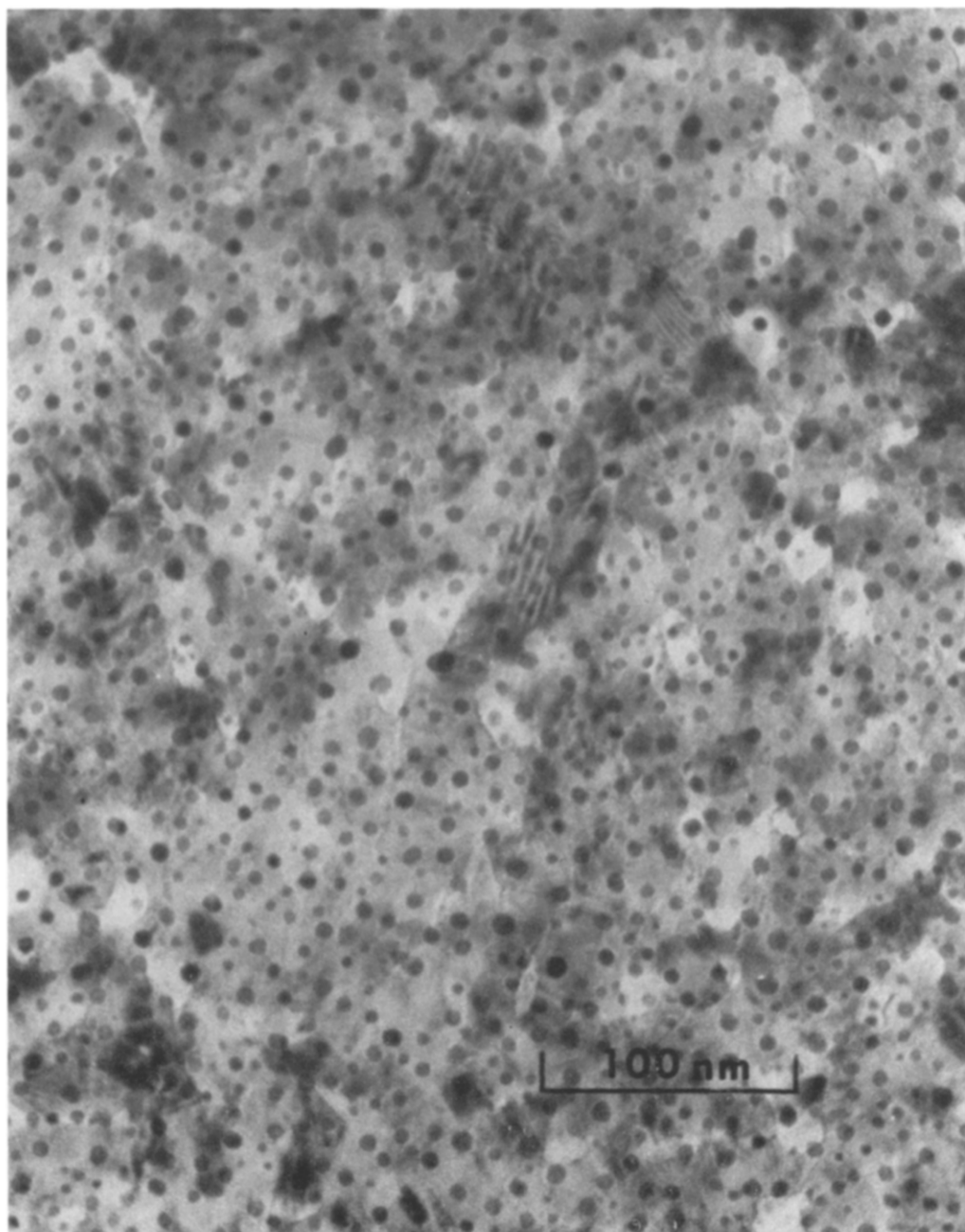| Reduction/oxidation treatment	Evacuation treatment	H/Pt	CO/Pt
(A) H₂, 1 hr, 425 K	2 hr, 425 K	0.61	0.41
(B) H₂, 1 hr, 875 K	0.5 hr, 725 K	0	0
(C) H₂, 1 hr, 875 K			
H₂O (15 Torr), 525 K	2 hr, 425 K	0.13	0.09
H₂, 1 hr, 425 K			
(D) H₂, 1 hr, 875 K			
O₂, 1 hr, 875 K	1 hr, 425 K	0.39	0.26
H₂, 1 hr, 425 K			

FIG. 1. Transmission electron micrograph of a Pt/titania specimen after heating in H_2 at 875 K for 1 hr.

evacuated for 1 min at room temperature to remove the weakly bonded CO. A second isotherm was then determined. Subtraction of the two isotherms then gave the amount of strongly bonded CO from which CO/Pt ratios were calculated.

The hydrogen used in the reductions and chemisorptions was of 99.99% initial purity

and was further purified by flow through a
Deoxo unit and a 5A molecular sieve drying
trap. Carbon monoxide to 99.99% initial
purity was flowed through a dry ice-
isopropanol trap before exposure to the
catalyst. Oxygen of 99.5% purity was
used as received.

RESULTS AND DISCUSSION

Chemisorption Studies

The Pt on titanium oxide powders and
films were subjected to the following series
of treatments:

(a) reduction in H_2 at 875 K for 1 hr;

(b) exposure to H_2O at 525 K for 1 hr;

(c) reduction in H_2 at 875 K for 1 hr
followed by oxidation in O_2 at 875 K for
1 hr;

(d) reduction in H_2 at 875 K for 1 hr.

Table 1 summarizes the results of chem-
isorption studies on the Pt/TO(P) for
the series of treatments along with other
pertinent data. Reduction of the 2%
Pt/TO(P) at 425 K followed by evacuation
at the same temperature (A) gives H/Pt
and CO/Pt ratios indicative of high Pt
dispersion and "normal" adsorption be-
havior. Reduction at 875 K (B), however,
completely suppresses the adsorption of
hydrogen and carbon monoxide. This
suppression is not due to agglomeration
of the Pt since X-ray diffraction examina-
tion of the sample did not show character-
istic Pt peaks or as argued previously (2)
is not likely to result from encapsulation
of Pt by the support. Thus the Pt crystal-
lites in the sample were less then ~5 nm
in size which is the limit of detectability by
X-ray diffraction. This observation we
take as evidence for a metal–support
interaction which suppresses hydrogen and
CO chemisorption.

The Pt/TO(P) was next subjected to a
series of treatments designed to determine
if the metal–support interaction could be
broken. After each treatment of this type,

the sample was reduced and evacuated at
425 K to activate the Pt which would
exhibit "normal" chemisorption behavior.
Table 1 shows that treatment of the 875 K
reduced sample in water vapor at 525 K
(C) restores "normal" adsorption behavior
to a small but significant extent. Oxidation
at 875 K (D), however, is much more
effective in breaking the metal–support
interaction. The fact that the values
following the oxidation at 875 K are below
those obtained in (A) may be due to some
Pt crystallite growth during the oxidation
treatment.

Electron Microscopy Studies

The behavior of the Pt/TO(F) after
consecutive reduction–oxidation cycles is
shown in the series of micrographs in
Figs. 1 to 4. The nature of Pt crystallites
on titanium oxide after reduction at 875 K
(Fig. 1) is identical to that reported
previously (4), the particles being in the
form of thin hexagonal pillbox shapes.
The evidence that the particles are very
thin is provided by the very low contrast
between the majority of the Pt particles
and the underlying support. This aspect
is discussed in detail in Ref. (4). Subsequent
treatment in a water vapor (Fig. 2) or
oxygen (Fig. 3) environment, and in
particular with the latter, produces some
significant changes in the appearance and
structure of the specimens. It is clear that
after oxidation in H_2O or O_2 there has
been an appreciable increase in the average
size of the platinum crystallites. Close
inspection of individual particles shows
that while in many cases they have retained
their hexagonal outline, they are now no
longer flat. After treatment in oxygen,
the majority of particles are quite dense
as indicated by the high contrast between
the metal particles and the support.
Even after milder oxidation in water vapor,
dense nuclei can be discerned in the
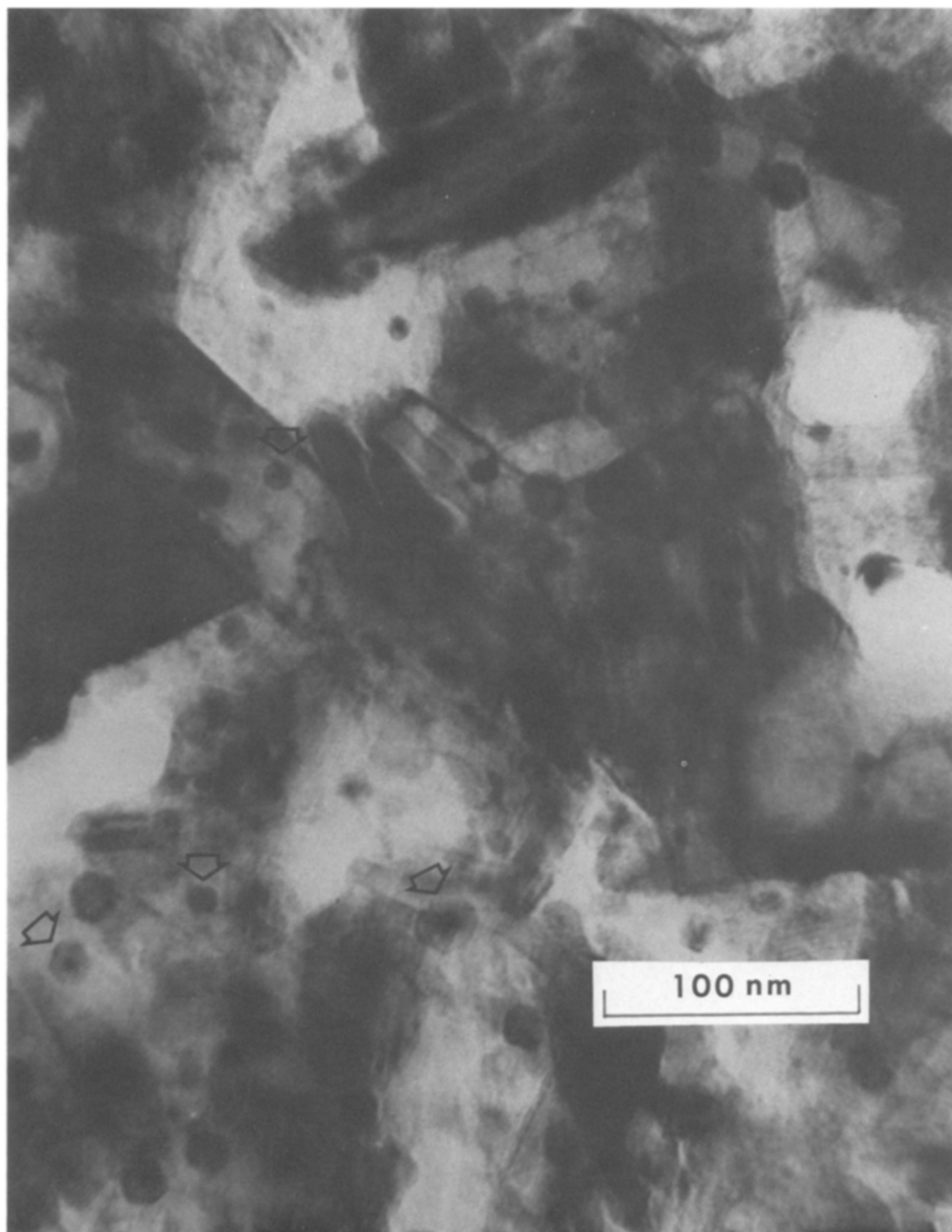center of many of the particles (some are

FIG. 2. Transmission electron micrograph of a reduced Pt/titania specimen, which has subsequently been exposed to H_2O at 525 K for 1 hr.

indicated in Fig. 2), and arrangements of the form depicted in Fig. 5 are frequently encountered, indicating that growth has occurred in three dimensions. Indeed in a separate experiment, where Pt/TO(F) specimens were heated directly in O_2 at 875 K for 1 hr, the metal particles tended to be globular in outline and quite dense,

characteristics of a hemispherical morphology. It is probable, therefore, that in the consecutive experiments longer oxidation periods would have destroyed the faceted outline of the particles.

Electron diffraction examination demonstrated that following the reduction treatments (Figs. 1, 4) the support had a structure corresponding to Ti_4O_7, as reported previously (4), whereas after both
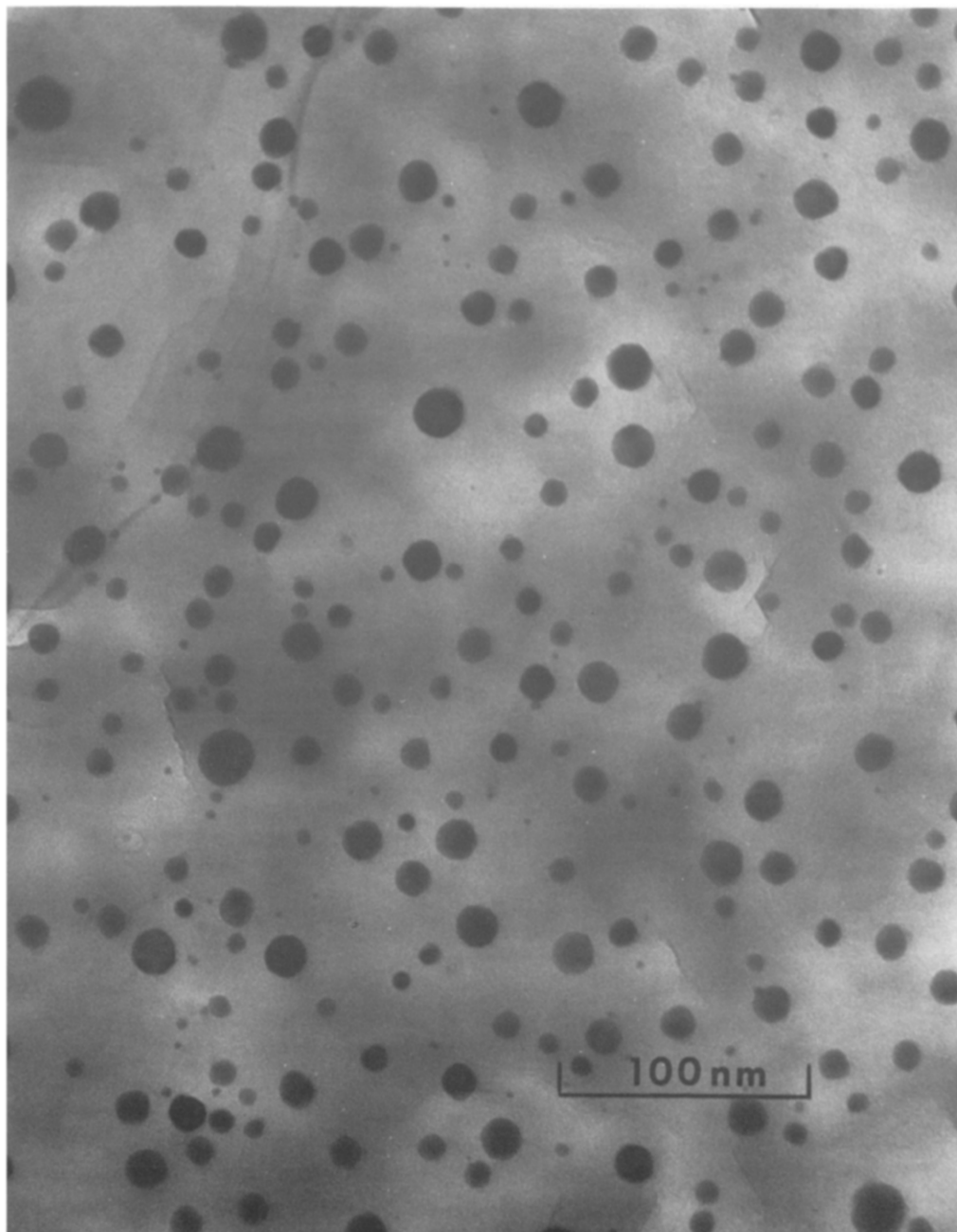

FIG. 3. Transmission electron micrograph of a reduced Pt/titania specimen, which has subsequently been heated in O_2 at 875 K for 1 hr.

FIG. 4. Transmission electron micrograph of a Pt/titania specimen, which has been reduced at 875 K, oxidized in O_2 at 875 C, and reduced at 875 K.

oxidation in water vapor and oxygen (Figs. 2, 4) it was converted back to TiO_2. After the final reduction treatment at 875 K (Fig. 4), it is apparent that although a few particles have increased in size, a few particles have increased in size, there has been a considerable amount of redispersion. In general the particles have maintained the hexagonal shape and have once again assumed a raft-like form. Structural analysis showed that following
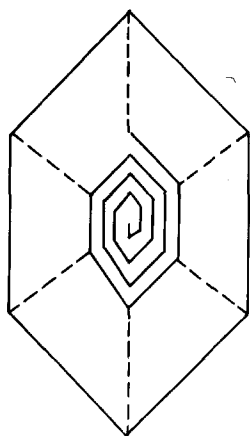
FIG. 5. Crystal growth in three dimensions originating from a screw dislocation.

the re-reduction the support had also reverted to Ti_4O_7.

A more accurate picture of the Pt particle growth characteristics under the various treatments can be seen from the particle size distribution plots (Fig. 6). Oxidation of the reduced catalyst (in the SMSI state) results in a broadening of the distribution, this being most severe·when O_2 is used as the oxidant. This finding is consistent with the chemisorption data, where O_2 at 875 K was found to be more effective for breaking the strong metal–support interaction than was water vapor at 525 K. It is significant that this distribution is similar to that obtained by Flynn and Wanke (5) for the growth of Pt on alumina in O_2, which suggests a comparable metal–support interaction under oxidizing conditions. Redispersion of the Pt particles
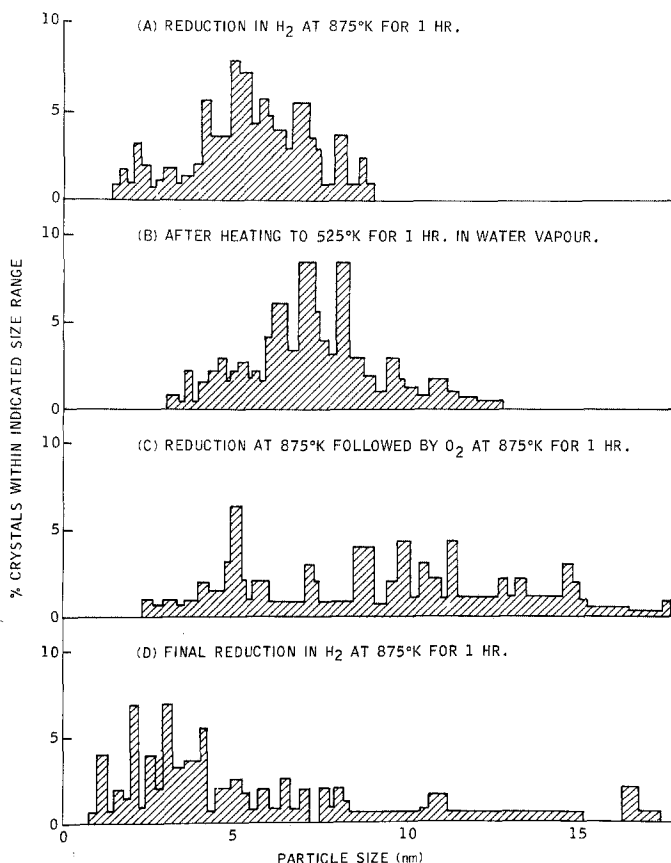
FIG. 6. Particle size distribution of Pt crystallites after consecutive treatments in various environments.

BEHAVIOR OF Pt/TiO₂ UNDER CONSECUTIVE
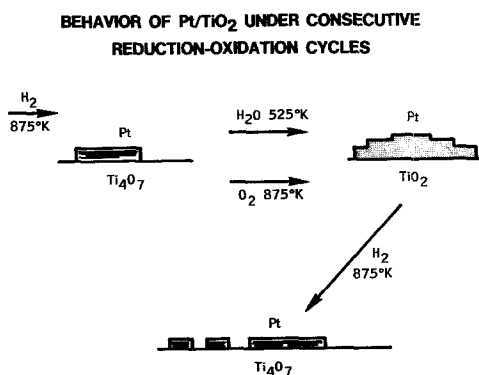REDUCTION-OXIDATION CYCLES

FIG. 7. Schematic representation illustrating the sequence of events during cycling into and out of the SMSI state.

is also quite clear after the final reduction at 875 K. In fact there is an appreciable number of smaller particles present (1 to 2 nm) at this stage than were formed after the initial reduction at 875 K.

A schematic representation of what appears to occur during the sequence of reactions studied is given in Fig. 7. We suggest that during the initial reduction treatment several processes are taking place simultaneously. Molecular hydrogen is dissociated by the Pt and the H atoms produced remove O atoms from the TiO_2 support which is consequently reduced to a lower oxide, Ti_4O_7, with a different lattice spacing. The catalytic role of the Pt in this reaction is demonstrated by the fact that TiO_2 does not undergo the same conversion in the absence of the metal under otherwise identical conditions (4). The vacancies created in the support structure due to the removal of O atoms are satisfied by the formation of bonds between platinum metal and exposed titanium cations, these bonds being stronger than Pt–Pt bonds. As a result the noble metal will be attracted to the vacancies rather than to other Pt atoms, and the growing crystallites will form into thin pillbox structures. In this situation there

is every likelihood that the Pt particles will exhibit different catalytic properties compared to systems where there is little or no interaction between the metal and the support.

When this system is oxidized at moderate temperatures, the Pt–Ti bonds will be ruptured and the lower oxide will revert to TiO_2. There is now no longer a strong metal–support interaction, and the Pt crystallites will tend to restructure forming the more energetically favored configuration of a hemispherical-shaped particle. In this noninteractive state the Pt is free to exhibit normal chemisorption behavior toward H and CO, and the tendency for particles to sinter will be facilitated.

The final reduction treatment would follow the same path as that postulated for the initial treatment, the only difference being that the Pt is now initially present as relatively large particles. If we consider the fate of one of these particles, it is reasonable to assume that Pt atoms at the base of the particle will interact with the reduced oxide support, and those Pt atoms which are remote from this interface will be free to migrate from the parent particle to other exposed titanium cations on the support surface, so that ultimately only the skeleton of the large particle remains surrounded by a sea of much smaller crystallites as is observed.

SUMMARY

The observed hehavior of a model system of Pt on titanium oxide in both reducing and oxidizing environments is compatible with hydrogen chemisorption measurements of the real catalyst system when treated under similar conditions. Reduction of the Pt on titanium oxide at elevated temperature (875 K) suppresses hydrogen and carbon monoxide chemisorp-

tion by the metal and causes the Pt to assume a thin pillbox structure. Treatment of the sample, initially in the SMSI state, with H_2O vapor or O_2 at elevated temperature causes three-dimensional growth of the Pt particles and partially restores the chemisorption capacity of the metal. We have formulated a schematic model to account for our observations.

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