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Electron Microscopy of Supported Metal Particles

III. The Role of the Metal in an SMSI Interaction

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Previous studies with high-resolution electron microscopy have enabled a model to be formulated to account for the strong metal support interaction found in the Pt/titanium oxide system following reduction at 500°C and higher. One of the crucial steps in the model was the postulate that the metal dissociated H_2 to provide a source of H atoms, which then attacked the support reducing it to a lower oxide, $TiO_2 \rightarrow Ti_4O_7$. Subsequently the Pt particles assumed a pillbox structure on the Ti_4O_7, which was believed to be indicative of an SMSI interaction. In an attempt to determine if dissociation of $H_2 \rightarrow 2H$ is a necessary requirement of the metal to form an SMSI interaction, we chose to examine the behavior of Ag on titanium oxide. This system was selected as Ag does not dissociate H_2 and should provide a stringent test of the model. Examination of Ag on titanium oxide at high resolution showed that after treatment in H_2 at 550°C the metal particles were rather large, relatively dense, and globular in outline, indicative of quite normal behavior. Electron diffraction examination revealed that the titanium oxide support was in the rutile form of TiO_2. These observations are consistent with the system being in a normal state. Subsequent introduction of Pt onto these specimens, followed by a further reduction cycle, brought about massive changes in the characteristics of Ag. In this case the crystallites were predominantly thin, pillbox structures and almost indistinguishable from Pt. During this treatment the support underwent conversion from TiO_2 to Ti_4O_7. Similar particle characteristics were also found when Ag was deposited on Pt/Ti_4O_7 and then treated in H_2 at 550°C. It is suggested that in the presence of Pt, Ag exhibits characteristics attributable to SMSI bonding on a reduced titanium oxide (Ti_4O_7) support. Further, it is believed that the function of Pt is to provide a source of H atoms by dissociation of H_2, which are responsible for converting TiO_2 to Ti_4O_7.

INTRODUCTION

High-resolution electron microscopy is an extremely powerful technique for obtaining information on the structural characteristics of supported metal particles. In previous studies we have used TEM to demonstrate that Pt supported on TiO_2 shows many unique features which are not apparent with other more conventional supports, when these systems were treated in H_2 (*1*). Specifically it was found that, following reduction at 550°C, Pt on titanium oxide assumed a pillbox morphology of hexagonal outline and the substrate was reduced to Ti_4O_7. This behavior was thought to be indicative of a strong interaction between the metal and the support, SMSI (*2*).

When specimens in an SMSI state were treated with H_2O vapor or O_2 at elevated temperatures, the Pt particles exhibited normal three-dimensional growth and the support reverted to TiO_2. If specimens were given a final reduction, then the SMSI characteristics of both the metal particles and support were restored. These observations of the behavior of model systems were entirely consistent with hydrogen chemisorption data on real catalysts when treated under similar conditions (*3*).

Based on these observations a model was developed, wherein one of the crucial steps

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was believed to be the ability of the metal to dissociate molecular hydrogen to produce a source of H atoms, which subsequently attacked TiO_2 converting it to a lower oxide. In an attempt to establish that this property is one of the necessary requirements for a system to form an SMSI interaction, we chose to examine the behavior of Ag particles supported on TiO_2. This system was selected because Ag is one of the metals which does not dissociate hydrogen (*4*) and should provide a stringent test of the model.

Experiments were also performed on the mixed metal system, Ag–Pt/TiO_2. Major differences in appearance were found between these specimens and Ag/TiO_2 after both had received identical reduction treatments in H_2. This finding is attributed to the ability of Pt to induce a strong metal–support interaction between Ag and TiO_2, which does not exist in the monometallic system.

EXPERIMENTAL METHODS

Transmission specimens of titanium oxide were prepared according to the procedure described previously (*1*). Spectrographically pure grade silver and platinum were introduced separately onto the oxide support from a tungsten filament at a residual pressure of 10^{-6} Torr. The amounts of each metal were sufficient to produce a monolayer coverage.

In this study three types of experiments were performed:

(a) In the first series Ag alone was deposited onto the oxide surface and then reduced in a 20% hydrogen/helium mixture for 1 hr at 550°C.

(b) Ag was introduced onto the entire surface of Pt/titanium oxide samples, which had previously been reacted in hydrogen at 550°C for 1 hr. These specimens were then subjected to a final 1-hr reduction treatment at the same temperature.

(c) Some of the specimens which had received treatment (a) were coated with a monolayer of Pt in such a manner that only half of the specimen surface was exposed to the Pt flux. These specimens were then reheated in the hydrogen mixture for a further 1-hr period at 550°C.

After cooling, all specimens were examined in the Philips EM300 transmission electron microscope. Particular care was exercised with specimens which had received treatment (c). A number of micrographs were taken in each quadrant of the specimen in order to ensure that representative features were obtained from areas which had both Pt and Ag, or Ag alone.

RESULTS AND DISCUSSION

1. Behavior of Ag on Titanium Oxide

The typical appearance of Ag/titanium oxide specimens after reducing in H_2 at 550°C is shown in the electron micrograph, Fig. 1. It is apparent that the particles tend to be quite globular in outline, and there is an appreciable number of large particles, >15 nm in diameter, which are relatively dense. There are a number of examples of adjacent particles which are in the act of undergoing coalescence, some of which are indicated by arrows. Collectively these features suggest that silver particles are mobile on the support under these conditions. It is interesting to compare these observations with those made from a CAEM investigation of the effect of heating silver particles on graphite in dry H_2 (*5*). Continuous observations of the process showed that particle mobility occurred over the temperature range 320 to 515°C, the onset being at approximately the Tammann temperature for silver, calculated to be 368°C. Virtually all the particle characteristics described above were also seen in the silver/graphite–H_2 reaction. Quantitative analysis shows that the particle size distribution curve (Fig. 2) obtained from Ag/titanium oxide is similar in shape, but significantly narrower in size range, to Ag/graphite. This suggests that although the interaction of Ag with titanium oxide is stronger than with graphite, it is nevertheless relatively weak. One might ar-

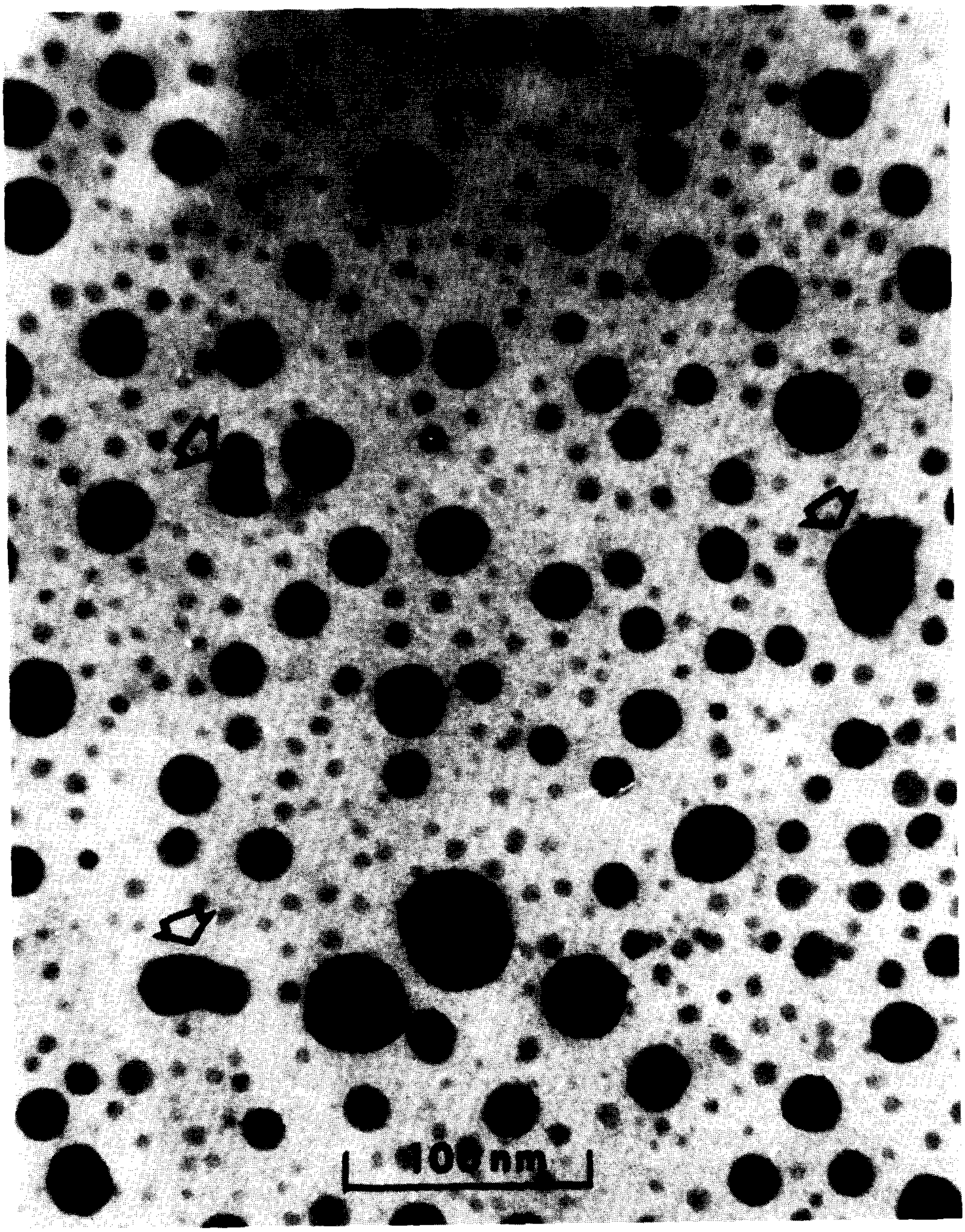

FIG. 1. Micrograph of Ag on titanium oxide after heating in H_2 to 550°C for 1 hr (arrows indicate particles in the act of coalescence).

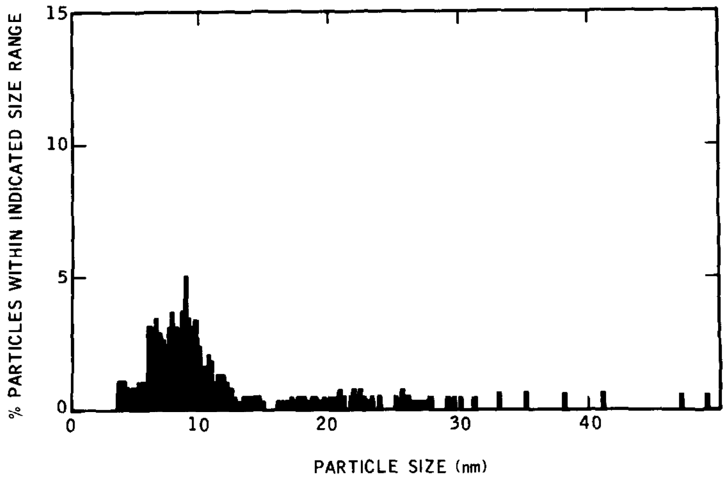

FIG. 2. Particle size distribution of Ag on titanium oxide after heating in H_2 to 550°C for 1 hr.

gue that at a temperature of 550°C silver atoms will evaporate from the corners and edges of crystallites and thus render the particles smooth and globular in outline. Sundquist (6) examined the morphology of silver particles supported on beryllium oxide after treatment in hydrogen at 700°C for 100 hr, and found that although some rounding of corners and edges had occurred, the silver crystallites still exhibited faceted shapes. We, therefore, believe that the globular form of the particles seen in this study is indicative of a relatively weak metal support interaction rather than a result of an evaporation phenomenon.

Another important finding comes from the electron diffraction examination of the sample, which shows that the pattern is that of the rutile form of TiO_2. This behavior is to be compared with that of Pt/titanium oxide, where after reduction under identical conditions the support had a structure corresponding to Ti_4O_7 (1). It was suggested that molecular hydrogen was dissociated by the Pt and that the H atoms produced removed O atoms from the TiO_2 support, which was consequently reduced to a lower oxide with a different lattice spacing (3). Clearly Ag does not fulfill the same mission, probably because of its inability to dissociate molecular hydrogen (4). As a consequence an SMSI interaction does not occur and the metal remains in a normal state, and exhibits behavior characteristic of that condition.

2. *Behavior of Ag on Pt/Titanium Oxide*

Figure 3 is a micrograph showing the effect of introducing Ag onto a prereduced Pt/titanium oxide specimen (sample had been heated in H_2 at 550°C for 1 hr) and then reheated in H_2 for an additional hour at 550°C.

The second heat treatment was necessary to nucleate Ag into discrete particles and the process was conducted in H_2 merely as a precautionary measure to ensure that Ti_4O_7 did not revert back to TiO_2. It is possible that the same result could have been obtained if the heating cycle had been performed in high-purity argon. Comparison of Fig. 3 with Fig. 1 shows some dramatic differences in appearance of the metal crystallites. Indeed, it is impossible from a visual inspection to differentiate between Pt and Ag crystallites. It is apparent that most of the crystallites are small and very thin and only the larger ones are dense. Moreover, all the crystallites tend to be angular in outline. It is evident that there are far fewer large crystallites formed in this system than was found for Ag/titanium

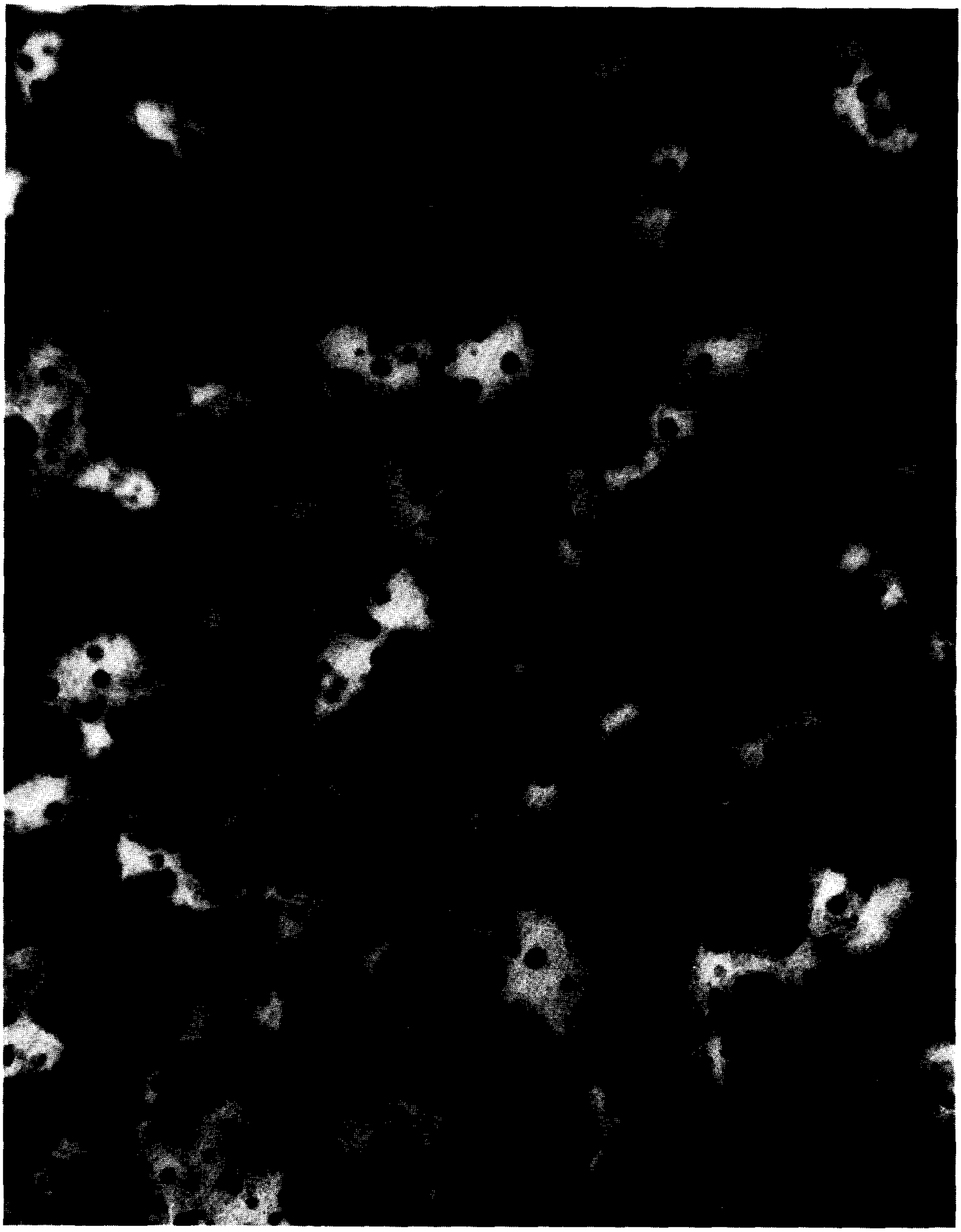

FIG. 3. Micrograph of Ag on Pt/Ti_4O_7 after heating in H_2 to 550°C for 1 hr.

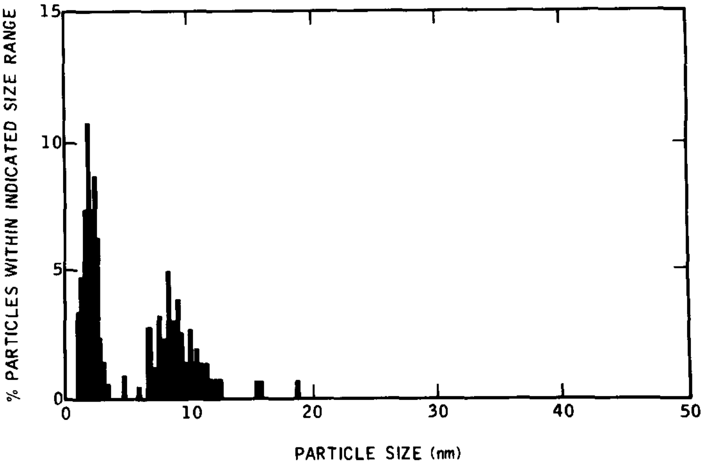

FIG. 4. Particle size distribution of Ag on the specimen shown in Fig. 3.

oxide. This aspect is more obvious when one examines the particle size distribution curve (Fig. 4). This distribution has been obtained by measuring the total distribution of particles (Ag + Pt) and then subtracting that of Pt, obtained from treating Pt/titanium oxide samples under similar conditions. It is implicitly assumed that Pt and Ag remain as discrete entities for this operation and do not form alloy particles, or that Pt forms surface layers on the Ag particles. Electron diffraction examination showed that the nature of the support remained the same after both reduction cycles, the pattern corresponding to that of Ti_4O_7.

A number of facts emerge from this set of experiments. Clearly, Pt is providing the source of H atoms required to reduce the support from TiO_2 to Ti_4O_7. The behavior of Ag is quite different when reduced on Ti_4O_7 than when the reaction is performed on TiO_2. On the reduced support the Ag particles appear to exhibit most of the SMSI morphological characteristics which were found for Pt (*1*).

3. *Behavior of Pt on Ag/Titanium Oxide*

In a final series of experiments Pt was introduced onto some of the reacted samples of Ag/titanium oxide referred to in Section 1. In an effort to discover more about the effect of Pt on the system, it was decided to introduce the noble metal onto only half of the specimen surface. In this way it was possible to see if Pt had a long-range effect on altering the growth characteristics of Ag.

Figures 5 and 7 show, respectively, the appearance of areas in which Pt is intimately dispersed with Ag and in which Pt is at a remote distance from Ag crystallites. Examination of the bimetallic area reveals that there have been some massive changes in the specimen appearance compared to its initial state (Fig. 1). We see that a very large fraction of the particles are <2.5 nm in size and tend to be very thin. The few residual large particles appear to be quite angular in outline and appreciably thinner than in the state prior to reduction with added platinum. The nature of the support has also changed, the rutile TiO_2 being converted to Ti_4O_7, as found from electron diffraction examination.

A clearer picture of the changes in Ag growth characteristics following the addition of Pt can be seen from the particle size distribution curves (Figs. 2 and 6, the latter having been corrected for the contribution from Pt and again assuming no alloy formation). The increase in the number of small Ag particles present (1 to 5 nm) is clear evidence that redispersion is occurring during

FIG. 5. Micrograph showing the effect of adding Pt to a Ag/titanium oxide specimen and heating in H_2 to 550°C for 1 hr.

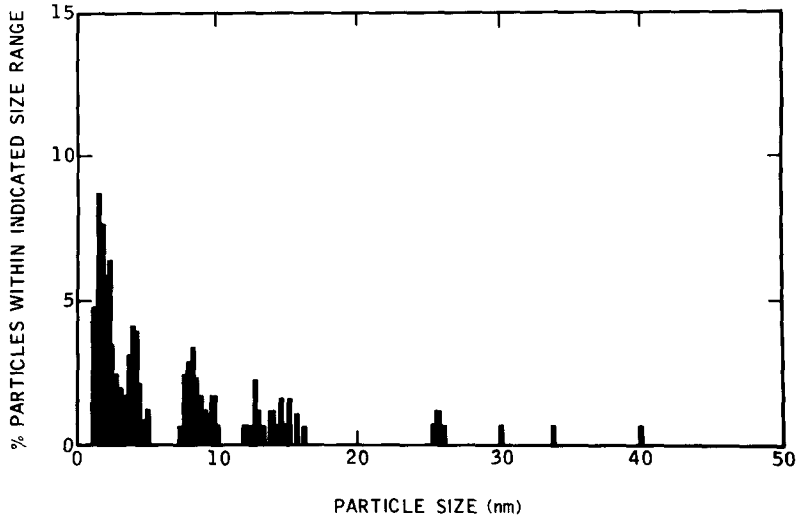

FIG. 6. Particle size distribution of Ag on the specimen shown in Fig. 5.

the second reduction cycle. This change in particle size is about the same as that found for Pt/TiO_2, when this system was cycled from the normal state (after treatment with O_2 at 600°C) to the SMSI state (after a final reduction) (Ref. (*3*), Fig. 6). This observation is entirely consistent with the notion that when Ag is supported on TiO_2, the metal is in the normal state, and when Ag is supported on Ti_4O_7, we have an SMSI interaction.

Examination of areas of these same specimens in which Pt was not present demonstrates that the influence of the noble metal still prevails, albeit on a weaker basis. It is quite apparent from the micrograph (Fig. 7) that the appearance of the support is similar to that where Pt was deposited, and indeed electron diffraction analysis confirms it to be Ti_4O_7. Inspection of the particles shows that Ag has undergone significant structural changes, but many particles are still quite dense and retain their original globular form, these features being particularly noticeable on the larger particles. The particle size distribution curve (Fig. 8) gives a more quantitative summary of the degree to which redispersion and possibly SMSI character has occurred with these particles. It is possible that a longer reduction period might have brought about a more extensive change.

Hydrogen spillover appears to play an interesting role in the extent of reduction of the TiO_2 support in these particular specimens. The spillover of hydrogen has been documented for mixtures of Pt/Al_2O_3 and WO_3 (*7*), and also that water plays an important role in the spillover mechanism (*8*). The effective reduction of an appreciable fraction of the TiO_2 support to Ti_4O_7 when Pt was introduced onto only half of the sample is indicative of the phenomenon of hydrogen spillover. However, the most intriguing result is that the degree of Ag interaction with the Ti_4O_7 surface increases in the vicinity of the Pt boundary. Hydrogen spillover is enhancing reduction of TiO_2 in the vicinity of the Pt boundary and the effect decreases with distance from the boundary. The Ag–support interaction may then be viewed as an indicator of the degree of surface reduction of the TiO_2 support.

Finally, as stated earlier, we assumed that Pt and Ag do not alloy or form bimetallic particles for the purpose of evaluating the Ag particle size distribution in Ag + Pt systems. In reality one probably forms a significant number of particles which contain various amounts of both elements, nev-

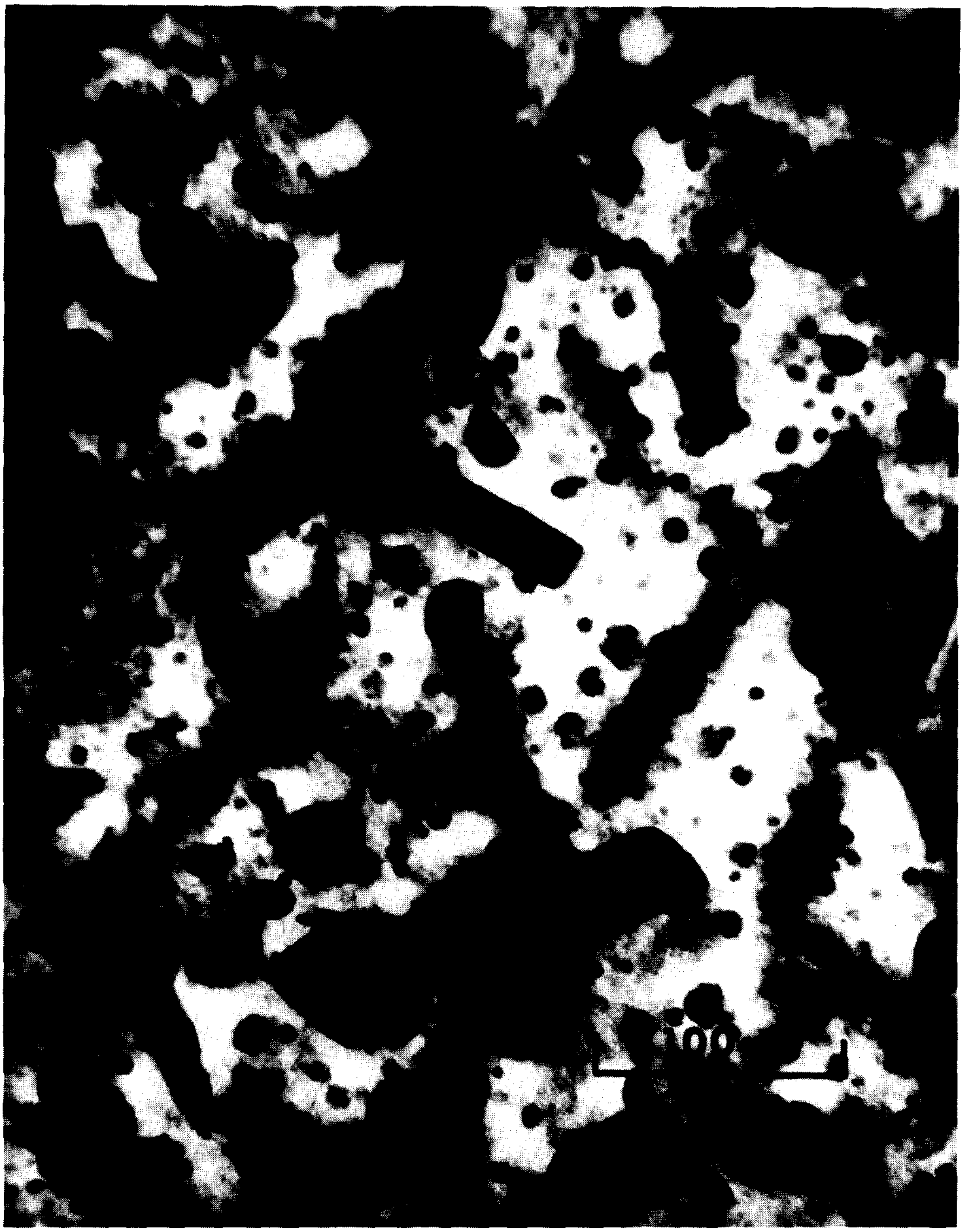

FIG. 7. Micrograph showing the long-range effect of Pt on Ag/titanium oxide specimens which have been heated in H_2 to 550°C for 1 hr. (N.B.: There are no Pt particles present on this area of the specimen.)

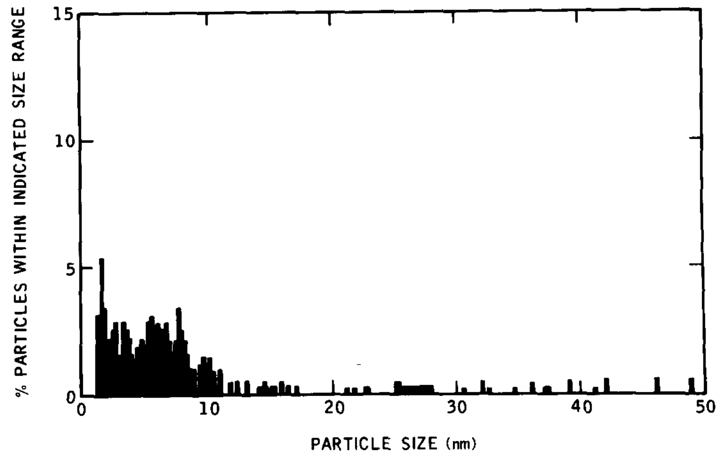

FIG. 8. Particle size distribution of Ag on the specimen shown in Fig. 7.

ertheless, the change in characteristics of Ag particles which were remote from Pt suggests that the noble metal does exert a real effect on the system rather than merely alloying with each Ag particle.

Recent studies by Haller and co-workers (*9*) of Rh–Ag on titanium oxide indicate that the support alters the interaction between Rh and Ag. This indirect effect of the support, which changes the nature of the Rh–Ag interaction, was believed to preferentially influence the smallest particles in the distribution. Our results with Pt–Ag on reduced titanium oxide indicate that the support effect on the nature of the metal–metal interaction extends to relatively large particles.

Finally, an EPR study of Ag on titanium oxide (*10*) suggests that charge transfer may be involved between the oxide and small Ag particles during reduction. Thermal treatment of Ag^+/TiO_2 produced a change of color from white to grayish-blue, with the simultaneous formation of a signal due to Ti^{3+}. The Ti^{3+} signal for Ag on TiO_2 was always much smaller than that observed when TiO_2 alone was treated under similar conditions. The observed color change was attributed to partial reduction of Ag^+ to Ag^0 and formation of small and well-dispersed crystallites all over the reduced TiO_2 surface, with some form of metal–support interaction. Because of the extremely high dispersion for the Ag on TiO_2 samples, comparisons with our studies are difficult.

SUMMARY AND CONCLUSIONS

High-resolution electron microscopy studies of the behavior of model systems of Ag and Ag + Pt on titanium oxide in reducing environments demonstrated several important features of the SMSI interaction. Reduction of Ag/titanium oxide at 550°C results in quite normal behavior of the metal, the crystallites being rather large, relatively dense, and globular in outline. There was very little change in the appearance of the support, analysis showing it to be the rutile form of TiO_2. Introduction of Pt onto these specimens, followed by a further reduction cycle, brought about massive changes in the characteristics of Ag crystallites, which, being predominantly thin, pillbox structures, were almost indistinguishable from those of Pt. During this treatment the support underwent reduction from TiO_2 to Ti_4O_7. This support transformation was also found to occur in areas which were devoid of Pt, although in these regions the changes in Ag crystallites were not so pronounced as those described above. A thin pillbox Ag particle morphology was also obtained if the metal was deposited on a Pt/Ti_4O_7 specimen and then treated in H_2 at 550°C. It is suggested that in the presence of Pt, Ag exhibits characteristics attributable to SMSI bonding on a reduced titanium oxide (Ti_4O_7) support. It is believed that the function of Pt is to provide a source of H atoms by dissociation of H_2, which are responsible for converting TiO_2 to Ti_4O_7.

This work has demonstrated that even though a particular metal does not possess the ability to create H atoms from H_2, it may still be a potential SMSI catalyst through the aid of a second metal capable of performing this role of dissociating H_2.

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