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# Effect of the Strong Metal–Support Interactions on the Behavior of Model Nickel/Titania Catalysts

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The behavior of nickel crystallites supported on titania (rutile) upon heating in $H_2$ and $O_2$ atmospheres has been investigated by using transmission electron microscopy. When $Ni/TiO_2$ specimens were heated in additionally purified ultrahigh-purity hydrogen (APH) at 500 and 700°C, alternate changes in the shapes of the crystallites were observed. This shape alternation is found to be associated with the extension and contraction of the crystallites. During heating of $Ni/TiO_2$ specimens in hydrogen (APH) at 700°C, cavities were formed in the substrate probably because of the migration of $TiO_{2-x}$ away from the substrate underneath and near the particle. The specimens were also heated alternately in oxygen and hydrogen (APH) atmospheres at 700°C. During heating in an oxygen atmosphere, the particles extended considerably over the substrate surface and/or diffused into the substrate. On subsequent heating in a hydrogen atmosphere, large crystallites were formed on the substrate surface. On further heating in hydrogen, the crystallites extended again but to a much smaller extent than in an oxygen atmosphere. These results suggest that in the case of $Ni/TiO_2$ the interactions between the particle and substrate are overall stronger in an $O_2$ atmosphere than in a $H_2$ atmosphere. © 1987 Academic Press, Inc.

## INTRODUCTION

The chemical and physical interactions between the metal particles and the support bring about changes in the morphology of the supported particles and consequently affect the activity and selectivity of the supported metal catalysts. The effect of such interactions on the morphology of the metal particles supported on irreducible oxides such as $Al_2O_3$ and $SiO_2$ has been studied extensively by using transmission electron microscopy (*1–8*). A detailed study in this direction has been carried out recently by Sushumna and Ruckenstein (*9–11*) who investigated the behavior of $Fe/Al_2O_3$ model catalysts in reducing and oxidizing atmospheres. TEM observations of the behavior of metal particles supported on reducible oxides also have been presented (*12–17*). In the case of $Fe/TiO_2$ samples heated in $H_2$, Tatarchuk and Dumesic (*14*) observed thin and flat particles and also an apparent decrease in the observable material on the surface of the substrate. They suggested that the flat morphology was a result of extension and the apparent decrease in observable material was due to a diffuse spreading of iron over the substrate surface and/or into the substrate. They suggested that in an oxygen atmosphere, iron partially diffuses back to the surface and forms large particles which are present as $FeTi_2O_5$ (*15*). Similar behavior was also observed with the $Pt/TiO_2$ system by Baker *et al.* (*12, 13*). Platinum particles had thin morphology upon heating in hydrogen, while they appeared to be thicker upon heating in oxygen. Simoens *et al.* (*16*) reported that the nickel particles were thin and flat at both 150 and 550°C upon heating in hydrogen. The average particle size was, however, somewhat greater at 550°C than at 150°C. On the other hand, heating at 700°C caused severe sintering. In a recent paper (*18*), Raupp and Dumesic reported that nickel particles on titania were relatively resistant to sintering in a reducing atmosphere at temperatures up to 650°C and that the particles had a flat shape, as also confirmed indi-

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rectly by CO temperature-programmed desorption. However, discussions on the role of the metal–support interactions on the morphology of the metal particles supported on reducible oxides have been provided by only a few authors. In addition, it is to be noted that in general the results arrived at in the literature with these systems were based on observations of short-term behavior such as heating for up to only 1 h.

The aim of this paper is to examine in more detail the role of the strong metal–support interactions in affecting the shape of the particles and the behavior, in general, of crystallites supported on titania. For this purpose, Ni/$TiO_2$ model catalysts have been observed over extended periods of heating in reducing and oxidizing atmospheres. The major events observed in this study include an alternate change in the shape of the particles and formation of cavities in the substrate during heating in hydrogen; considerable extension of particles over the substrate and/or diffusion of Ni ions into the substrate during heating in oxygen; and restoration to large nickel particles upon subsequent heating in hydrogen, followed by their extension during additional heating in hydrogen. The latter observations are in contrast to those reported previously by various authors.

## EXPERIMENTAL

*Preparation of sample.* Titania films (rutile form) of approximately 500-Å thickness, used as supports for the model catalysts, were prepared by heating titanium foils (99.98%, 0.025 mm thick, Alfa Products) in oxygen at 300–350°C for 1.5 h and stripping the oxide film off by dissolving the unoxidized titanium. The titania films were then rinsed in distilled water, picked up on gold electron microscope grids, and allowed to dry. Nickel films were deposited onto the titania films by vacuum evaporating nickel wire of 99% purity in an Edwards 306 vacuum evaporator, under a pressure of better than $10^{-6}$ Torr.

*Heat treatment.* The samples were heated inside a quartz tube, placed in a furnace. After the sample was introduced into the tube, the tube was flushed with helium for at least 30 min. The temperature was then raised in a helium atmosphere from room temperature to the predetermined temperature, at which point helium was switched to the desired gas. After it was heated in the desired atmosphere for the predetermined duration of time, the tube was cooled down to room temperature again in a helium atmosphere. The flow rates of the gases during heating were maintained at about 150 $cm^3$/min. The gases used in the experiment were all ultrahigh-purity grade purchased from Linde Division, Union Carbide Corporation. Hydrogen and helium were both 99.999% pure, the former having less than 1 ppm $O_2$ and less than 2 ppm moisture and the latter having less than 3 ppm moisture. Oxygen, 99.99% pure, contained less than 3 ppm moisture. Except for the heat treatments in wet hydrogen, the ultrahigh-purity hydrogen was further purified by successive passage through a Deoxo (Engelhard Industries) unit, a silica gel column, and a bed of 15% MnO on $SiO_2$, and finally a 4A molecular sieve bed immersed in liquid nitrogen. For some experiments in wet hydrogen atmosphere, the as-supplied hydrogen was bubbled through distilled water. Helium was also further purified by passing it through a 4A molecular sieve bed immersed in liquid nitrogen.

*TEM observation.* After each heat treatment, the samples were examined and the same regions of each sample were photographed using a JEOL 100U transmission electron microscope operated at 80 kV.

## RESULTS

Several samples of 10-Å initial metal film thickness have been investigated in hydrogen and oxygen atmospheres at different temperatures. Table 1 summarizes the heat treatments for each sample and the corresponding micrograph numbers.

TABLE 1

Heat Treatments

| Sample | Treatment | Figure |
|---|---|---|
| A | $H_2$ at 700°C for 23 h | 1 |
| | $O_2$ at 700°C for 3 h | 5 |
| | $H_2$ at 700°C for 4 h | 5 |
| B | $H_2$ at 700°C for 16 h | 2 |
| | $H_2$ at 700°C for 115 h | 6 |
| | $O_2$ at 700°C for 6 h | 6 |
| | $H_2$ at 700°C for 4 h | 6 |
| C | $H_2$ at 500°C for 23 h | 3 |
| D | $H_2$ at 250°C for 47 h | 4 |

### *A. Behavior in Additionally Purified Hydrogen at 700°C*

The results on heating a specimen (sample A) at 700°C in additionally purified hydrogen are shown in Fig. 1. The major results observed were (1) alternate changes in the shape of the particles, (2) formation of cavities or channels in the substrate beneath the particles, and (3) severe sintering. These results are described separately.

*Alternate changes in the shape of the particles.* Following the deposition of the Ni film, the sample (sample A) was heated in $H_2$ at 250°C for 2 h to generate very small crystallites. Subsequently, the sample behavior was investigated at 700°C in $H_2$. Figure 1a shows the micrograph following heating at 700°C for 1 h. During the subsequent 4 h of heating, the crystallites agglomerated to form larger particles and maintained a circular shape (Fig. 1b). On heating for an additional 3 h, a change in the shape of the crystallites was observed (Fig. 1c). White (lighter in contrast) annular patches were formed adjacent to the periphery of (but not all around) the particles. The white patch around the particles disappeared after heating for an additional 3 h (Fig. 1d). Two more cycles of such changes were observed on further heating for a total of 23 h (Fig. 1). Another sample (sample B) of the same loading, whose micrographs are not shown, also exhibited similar alternations in the shape of the crystallites. Three cycles of shape alternations were observed over a period of 16 h, and, on further heating for up to 115 h, no further shape alternations were detected with this sample.

The electron diffraction patterns were also obtained after each heat treatment. The *d*-spacing values for sample A are listed in Table 2. They show that titania remained as rutile $TiO_2$ throughout the entire heat treatment. (It is likely that in a hydrogen atmosphere, there is localized reduction of the substrate beneath and in the immediate vicinity of the particles, which is, however, not detected by electron diffraction in our case.) In addition, after heating for 1 h at 700°C, two additional rings appeared in the diffraction pattern. One of them corresponded to Ni, but the other did not correspond to any stoichiometric compound associated with nickel. During the subsequent 2 h of heating, the latter ring disappeared gradually, while another ring corresponding to Ni appeared. This indicates that the unknown compound mentioned above was gradually reduced to Ni and that the particles were finally present as mostly Ni. After a total of 11 h of heating, a new ring whose *d* value was close to the major *d* value of $Ni_3Ti$ appeared. Following a total of 16 h of heating, the intensity of this ring appeared to be much stronger than before, and it increased further on subsequent heating while the intensity of the rings corresponding to Ni decreased gradu-

TABLE 2

Electron Diffraction Analysis for Sample A

| *d*-Spacing from ASTM card (Å) | | | | *d*-Spacing from diffraction pattern (Å) | | | |
|---|---|---|---|---|---|---|---|
| $TiO_2$ | Ni | NiO | $Ni_3Ti$ | 11 h, $H_2$ | 3 h, $O_2$ | 1 h, $H_2$ | 4 h[a], $H_2$ |
| 3.250 | 2.034 | 2.410 | 2.13 | 3.244 | 4.209 | 3.244 | 3.252 |
| 2.487 | 1.762 | 2.088 | 2.07 | 2.485 | 3.676 | 2.488 | 2.482 |
| 2.188 | 1.246 | 1.476 | 1.95 | 2.177 | 3.250 | 2.191 | 2.181 |
| 1.6874 | | | | 2.045 | 2.707 | 2.084 | 2.058 |
| | | | | 1.923 | 2.481 | 1.690 | 1.681 |
| | | | | 1.769 | 2.181 | | |
| | | | | 1.683 | 1.829 | | |
| | | | | | 1.687 | | |

[a] Cumulative heating time in hydrogen.

ally. These results indicate that nickel formed an intermetallic compound with titanium or $TiO_{2-x}$ in hydrogen at 700°C.

The effect of moisture on the behavior of nickel crystallites was investigated by heating a different sample in wet hydrogen at 700°C. The presence of moisture, deliberately introduced in the gas stream by bubbling the hydrogen through distilled water, caused the cessation of the alternate changes in shape described before. In fact, the particles remained circular in shape throughout the entire heat treatment. This is in contrast to the behavior observed with $Fe/Al_2O_3$ (9) where impurities, such as moisture and/or $O_2$, in the as-supplied hydrogen caused changes in shape.

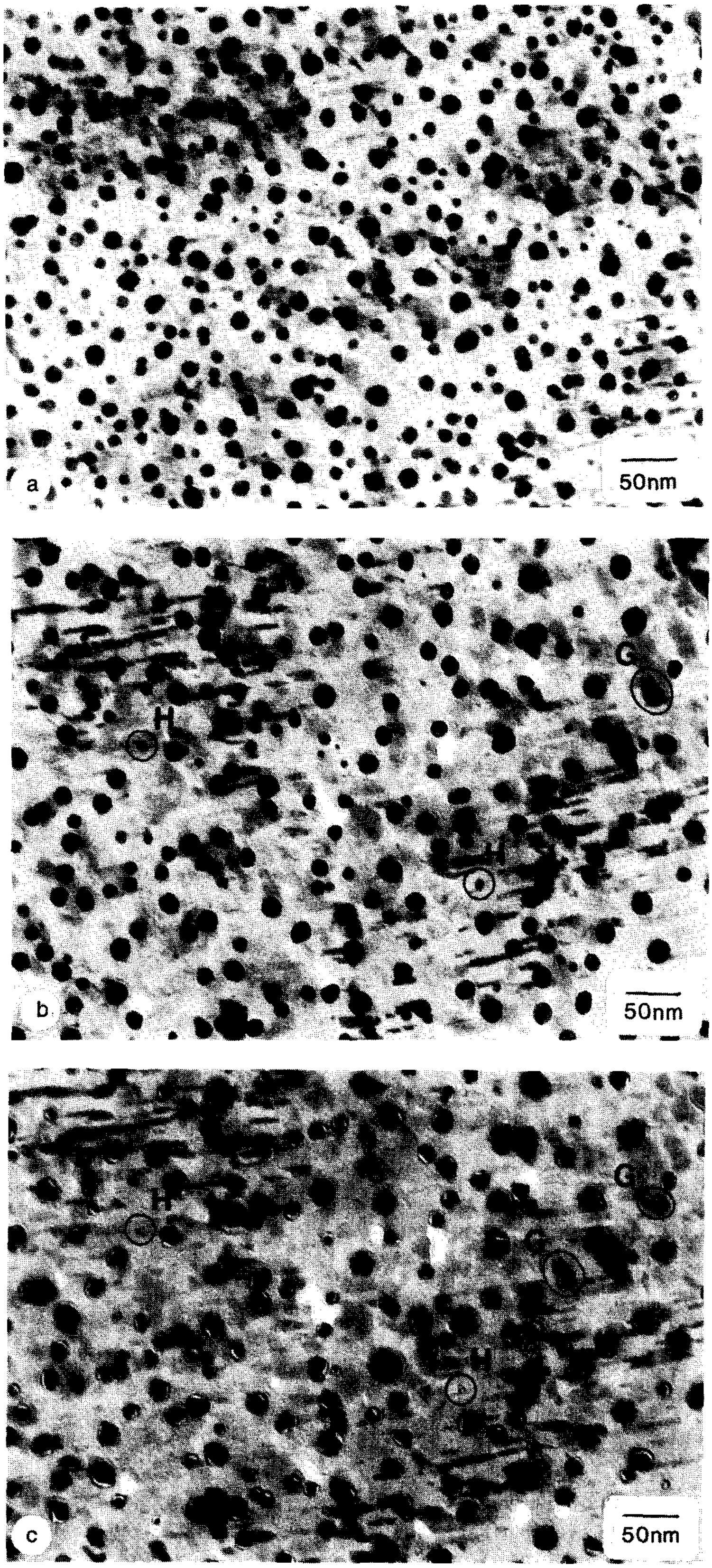
*Formation of cavities or channels in the substrate beneath the particles.* As shown in Fig. 1, the migration of a particle exposes a cavity in the substrate beneath the particle. Some particles generated cavities at their original location only, while others developed channels along their tracks over a fairly long distance. It is likely that there is substrate within the cavities and in the channels which is, however, too thin to be seen in the micrographs. There are particles located in the channels which indicate that there is indeed at least a thin layer of substrate underneath, to support the particles (Fig. 1g, A). Figure 2 shows micrographs of another sample (sample B) which exhibited similar cavity formation. In these micrographs, it is clear that the cavity region is thinner than the other regions of the substrate. Region B in Fig. 2 shows the cavity underneath the particle, exposed as a result of the migration of the particle out of the cavity. A different region, C, shows a particle which migrated completely out of the cavity but did not migrate far away from the cavity. In another region, D, a particle migrated away from the cavity without forming a channel along its track. Region E, on the other hand, shows a particle which formed a channel along its track. It should be noted that the cavity sizes are approximately the same as those of the corresponding particles.

*Sintering.* On heating sample A for 1 h at 700°C in additionally purified hydrogen, large particles were formed (Fig. 1a). The larger of these particles had diameters in the range 150–200 Å, while at 500°C, the larger particles in a different sample of the same loading had diameters of about 50 Å, even after 3 h of heating (Fig. 3). Considerable sintering occurs at 700°C while at temperatures of 500°C or less, relatively little sintering occurs. At 700°C, sintering continued during a total of 23 h of heating and led to the growth of the particles. The larger particles now had diameters between 300 and 400 Å. During heating at 700°C, various events of sintering were observed (Fig. 1): migration and subsequent coalescence with neighboring particles (F), separation of two contacting or overlapping particles (G), disappearance of particles following a gradual decrease in size (H), appearance of new particles (I), and increase in the size of small particles without coalescence (J).

### *B. Behavior in Additionally Purified Hydrogen at 500 and 250°C*

Figure 3 shows selected results for sample C heated at 500°C in additionally purified hydrogen. On heating for 3 h (Fig. 3a), the particles appeared to have a torus shape with a small remnant particle in the cavity. After an additional 8 h of heating, the cavities were filled in (Fig. 3b). A repeated alternation in the shapes of the particles between a torus and a continuous shape was observed on further heating (Figs. 3c–e). The rings in the selected-area electron diffraction patterns were identified to be from the rutile form of $TiO_2$. After a total of 19 h of heating, new rings attributed

FIG. 1. Time sequence of the same region of a specimen (A) heated at 700°C in purified hydrogen. (a) 1 h, (b) 5 h, (c) 8 h, (d) 11 h, (e) 12 h, (f) 13 h, (g) 16 h, (h) 20 h, (i) 23 h.


a
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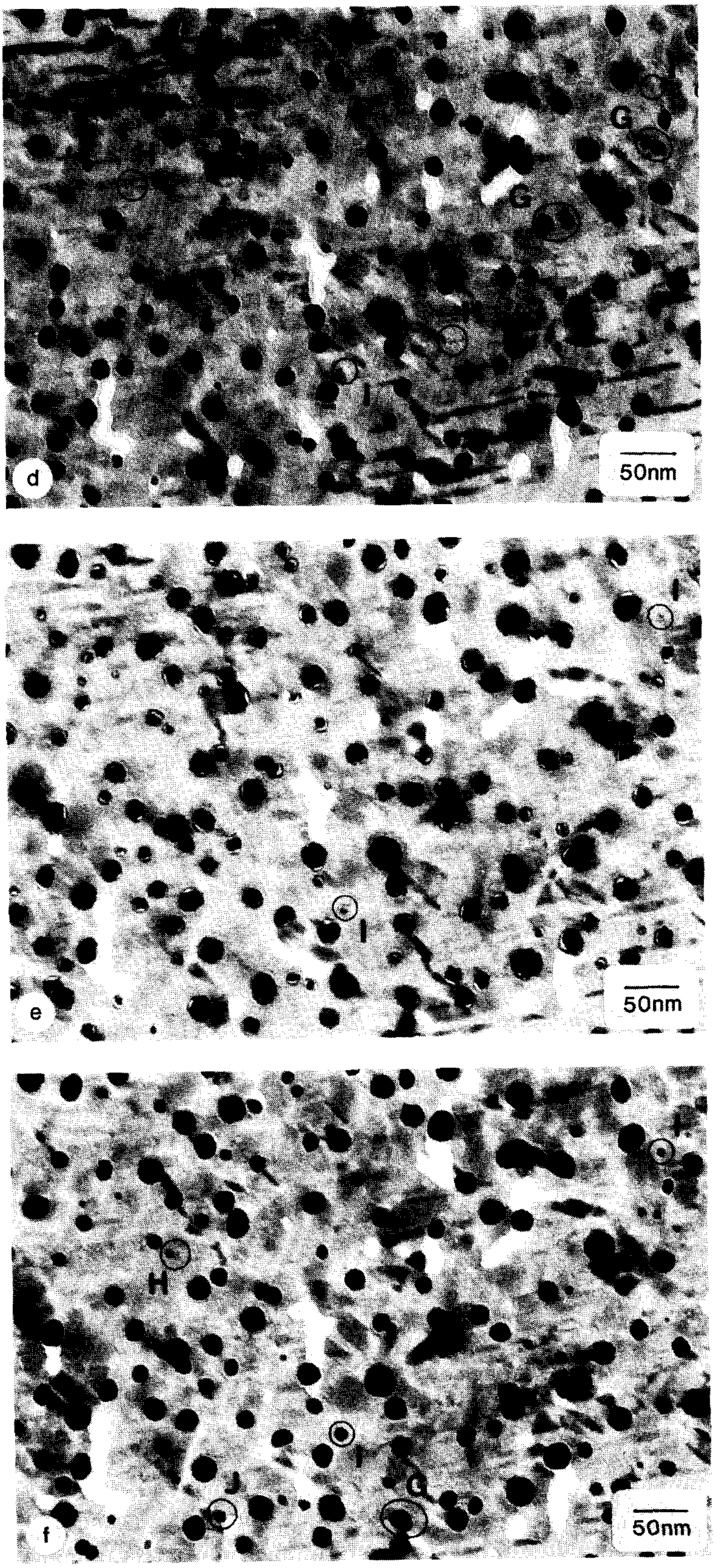


FIG. 1—*Continued.*

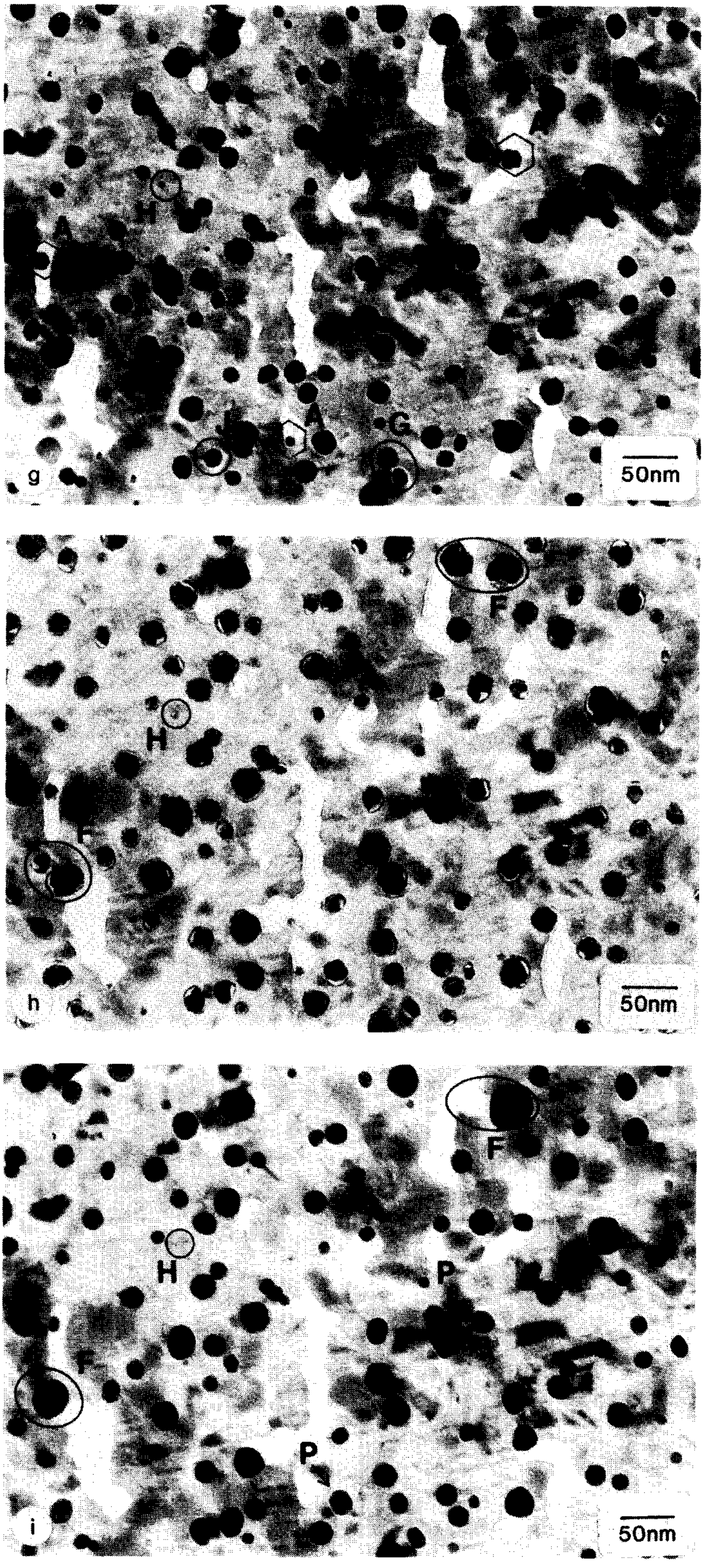


Fig. 1—*Continued.*

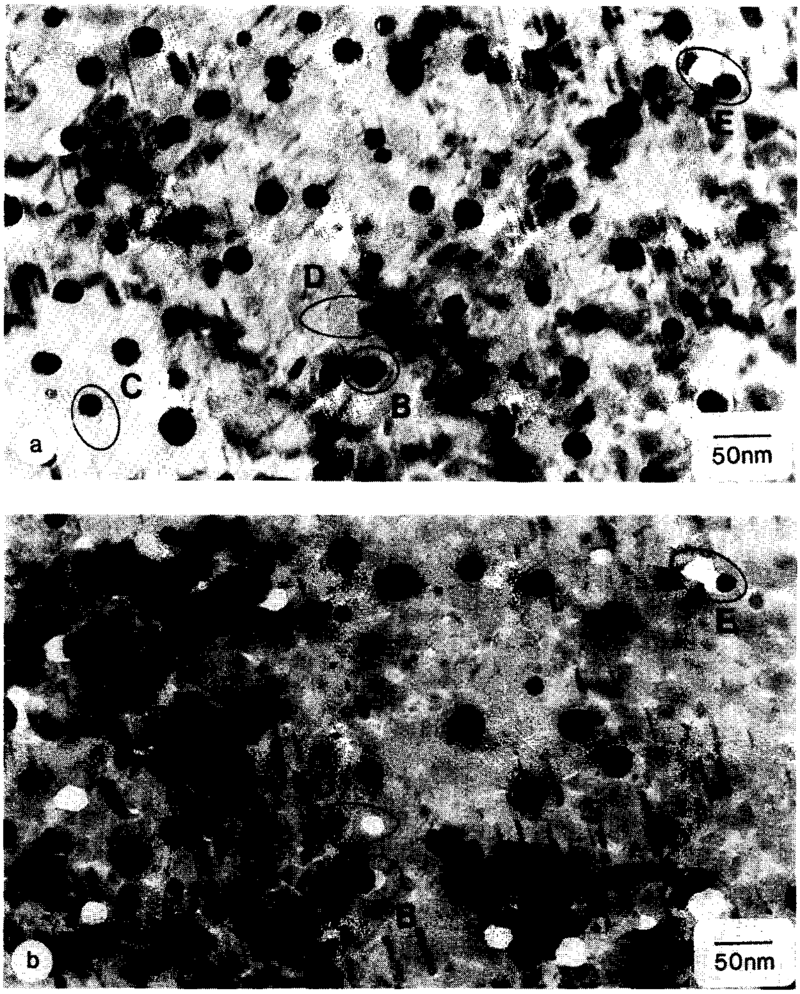


FIG. 2. Sequence of changes in a specimen (B) on heating at 700°C in purified hydrogen. The same region is shown after (a) 10 h and (b) 15 h.

to Ni appeared and the intensity of these rings increased on further heating. One may note that during this period, the growth of the particles and the decrease in the number of particles occurred only to a small extent.

The results on heating at 250°C in additionally purified hydrogen were, however, different and are shown in Fig. 4. Initial particles were formed on heating sample D for 2 h at 250°C (Fig. 4a). On further heating for up to a total of 47 h there was very little change (Figs. 4b and c). However, some particles migrated and coalesced with nearby particles (K). One may also note that some other particles disappeared, probably due either to migration and subsequent coalescence with adjacent particle or to direct ripening (L).

### *C. Behavior on Alternate Heating in Oxygen and Hydrogen*

Sample A, which was heated in hydrogen at 700°C for 23 h before (Fig. 1i), was further heated at 700°C alternately in oxygen and additionally purified hydrogen. The results are shown in Fig. 5. Following 1 h of heating in oxygen (Fig. 5a), most of the particles decreased in size considerably or disappeared. This suggests that the particles probably spread over the substrate as thin films, which could not be seen in the micrographs, and/or diffused into the substrate. In fact, relatively large particles could be observed to have extended over the substrate, as marked in regions P in the Figs. 1i and 5a. In the electron diffraction pattern, several new rings, which had not been detected during prior heating in hydrogen, now appeared. These new rings, whose *d* values did not correspond to any stoichiometric compound, are perhaps from a nonstoichiometric compound of NiO and $TiO_2$. On heating for an additional 2 h in oxygen (Fig. 5b), many small particles further decreased in size (M) or disappeared (N) while the thick films around the large particles further extended over the substrate (P). There was no change in the electron diffraction pattern. The sample was then heated in hydrogen for 1 h at the same temperature (Fig. 5c). A number of large particles with a core-and-ring structure now appeared on the substrate, indicating that during the previous heating in oxygen, the particles had indeed spread out on the substrate or had diffused into it and were not lost. The electron diffraction pattern indicated the presence of NiO. After 3 more hours of heating in hydrogen (Fig. 5d), some particles extended, coalesced, and/or rearranged, while some other particles disappeared completely probably due to extension. The electron diffraction pattern indicates that during the above heating, NiO was gradually reduced to Ni. Sample B, which was previously heated in hydrogen for 115 h at 700°C, was also heated alternately in oxygen and hydrogen at 700°C (Fig. 6). On heating in oxygen for 1 h, the particles extended considerably and formed thick patches with irregular contours (Fig. 6b) and the electron diffraction pattern indicated the presence of NiO. It is worth noting that the extension was perhaps more pronounced with sample A than with sample B, but it had to be inferred from the "loss of material" from the original crystallites as they extended and left behind very small remnant particles following heating in oxygen. On additional heating of sample B in oxygen, most of the particles split to form a few smaller particles (Figs. 6c and d). In the diffraction patterns, NiO rings and rings corresponding to probably some nonstoichiometric compound of NiO and titania (as in the case of sample A) were detected. However, NiO rings were more intense. Subsequent heating in hydrogen for 1 h at the same temperature brought about the contraction of the patches (Fig. 6e). The electron diffraction results indicated the presence of mostly NiO in the sample. On a further 3 h heating in hydrogen, the oxide was reduced to Ni and the particles were observed to have extended again, as a result of the concomitant reduction of titania and its subsequent strong interaction with the particles. Similar results of extension in oxygen, followed by contraction in hydrogen and again extension during additional heating in hydrogen, were observed also with another sample (whose micrographs are, however, not included here) when heated alternately in hydrogen and oxygen successively at 400, 500, 600, and 700°C.

## DISCUSSION

The various phenomena, such as spreading, contraction, shape changes, which were observed during heating of model catalysts of nickel supported on titania in $H_2$ and $O_2$ environments were presented in the previous section. In this section, we employ the concept of wetting to explain the observed results. The wettability of a substrate by a crystallite is determined by the equilibrium of the interfacial free energies as expressed by Young's equation

$$\gamma_{sg} - \gamma_{cs} = \gamma_{cg}\cos\theta, \qquad (1)$$

where $\gamma_{sg}$ and $\gamma_{cg}$ are the surface free energies per unit area of the substrate and crystallite, respectively, $\gamma_{cs}$ is the interfacial free energy per unit area between crystallite and substrate, and $\theta$ is the equilibrium wet-

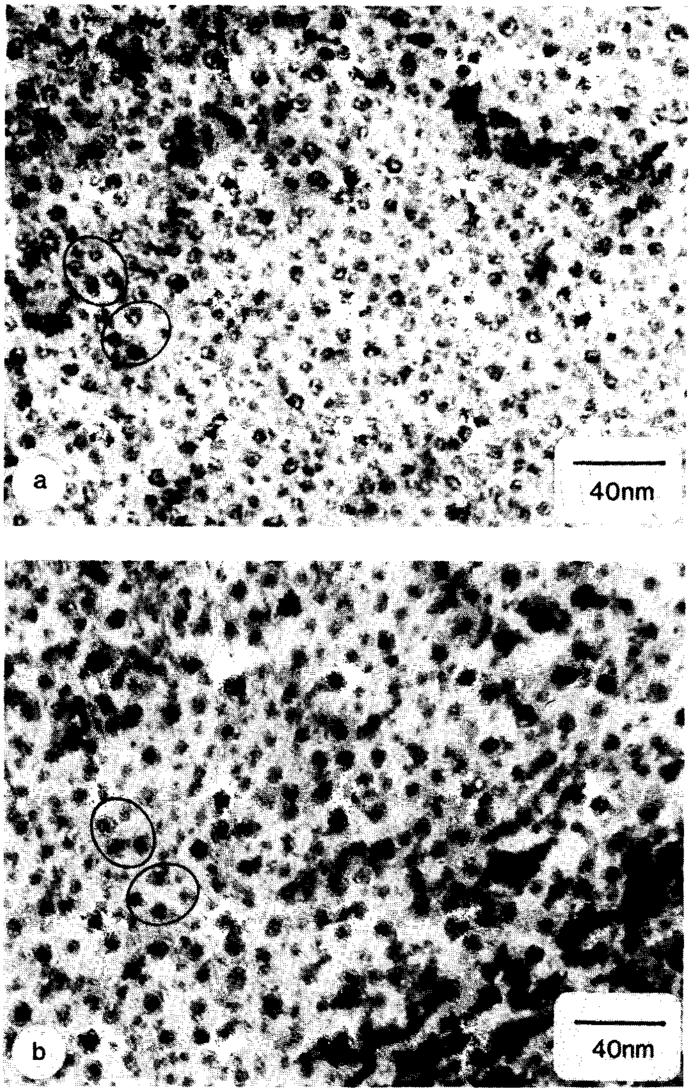


FIG. 3. Sequence of changes in the same region of a specimen (C) heated at 500°C in purified hydrogen. (a) 3 h, (b) 11 h, (c) 15 h, (d) 19 h, (e) 23 h.

ting angle. However, the interfacial free energy between crystallite and substrate is given by

$$\gamma_{cs} = \gamma_{cg} + \gamma_{sg} - (U_{int} - U_{str}) \equiv \gamma_{cg} + \gamma_{sg} - U_{cs}, \qquad (2)$$

where $U_{int}$ is the interaction energy per unit area between crystallite and substrate, and $U_{str}$ is the strain energy per unit area due to the mismatch of the two lattices. When a chemical interaction takes place at the interface between crystallite and substrate, $U_{cs}$ becomes very large and $\gamma_{cs}$ thus decreases. This favors the extension of the crystallite over the substrate. This can happen in a reducing atmosphere, because of the strong interactions between $TiO_{2-x}$ beneath the crystallite and metal, as well as in an oxygen atmosphere, because of the formation of a chemical compound between the oxidized metal and substrate. Increased values of $\gamma_{sg}$ as well as smaller values of $\gamma_{cg}$ also favor the extension of the crystallites.

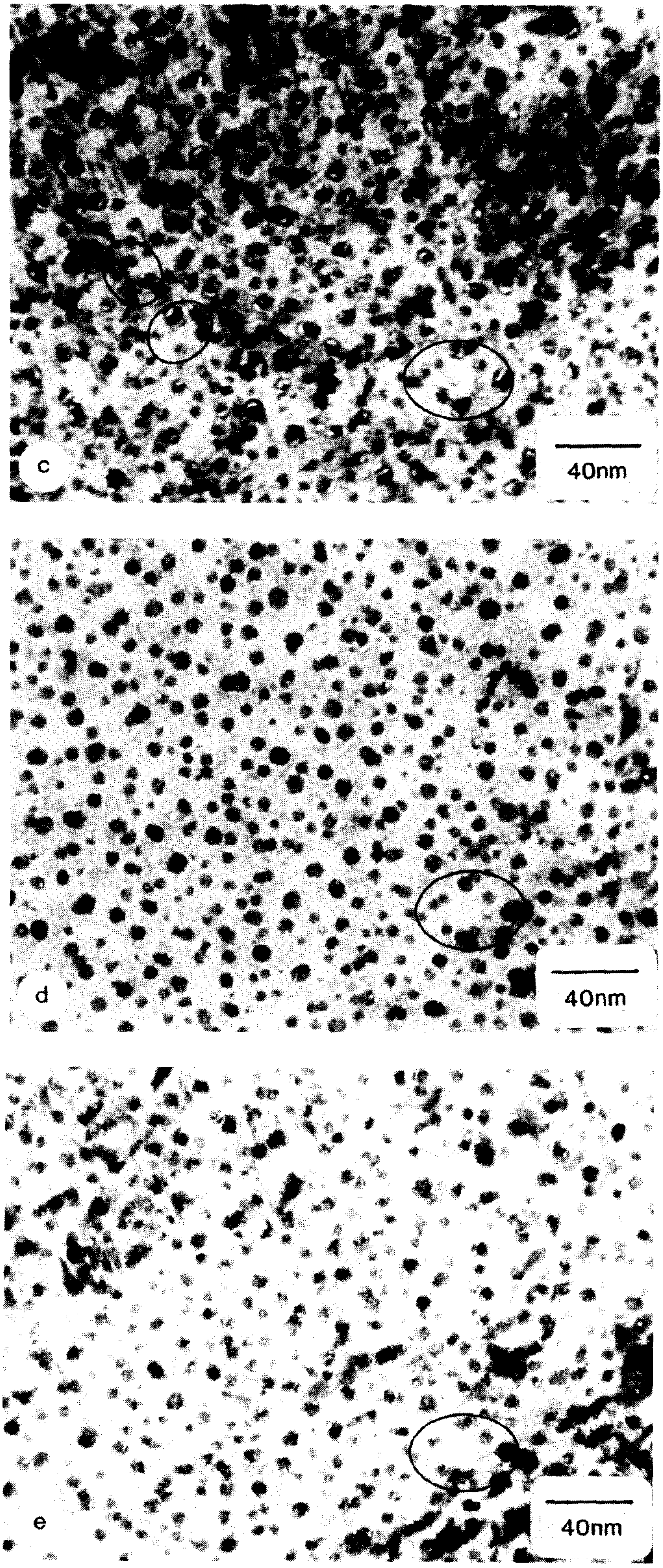


FIG. 3—*Continued.*

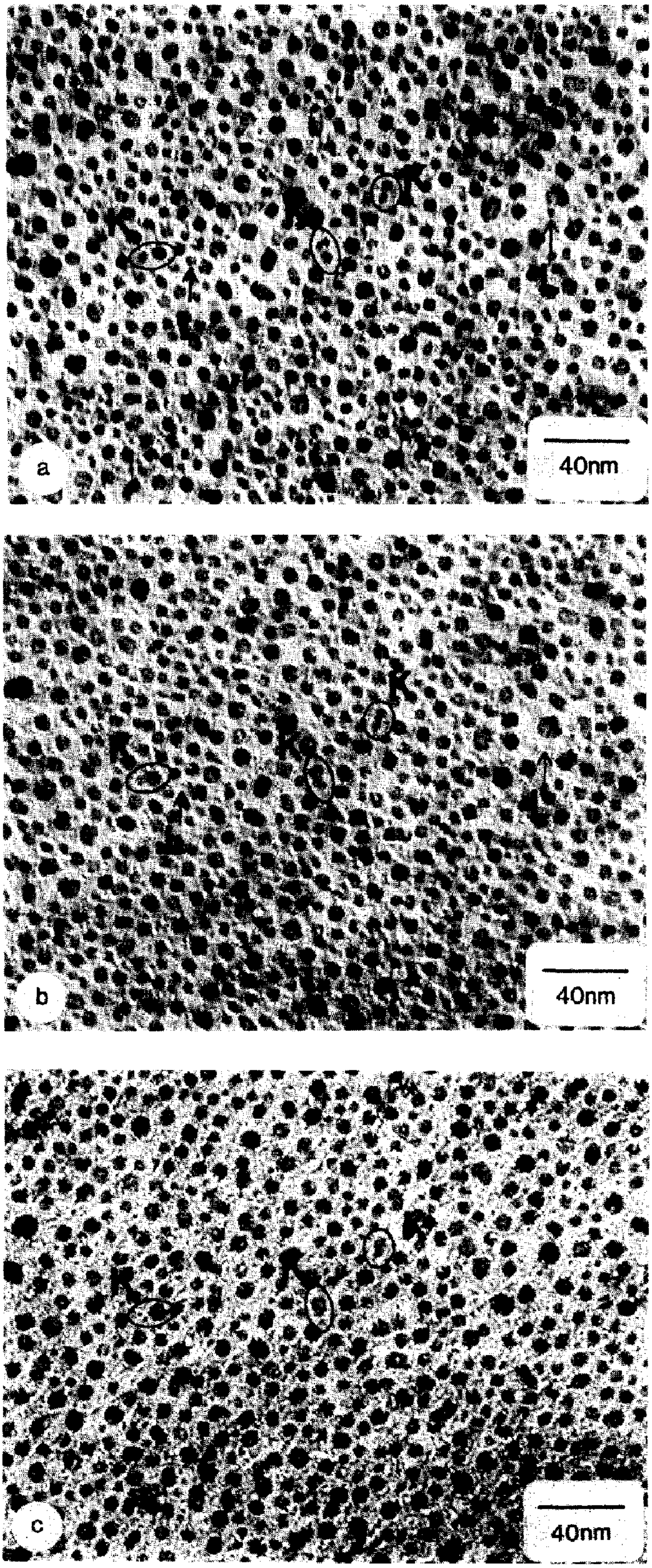
The reduced form, $TiO_{2-x}$, as obtained in a hydrogen atmosphere, being nonstoichiometric, provides a higher value of $\gamma_{sg}$ than the nonreduced form. In addition, the oxidized crystallite has a lower $\gamma_{cg}$ than the metal and, in a reducing atmosphere, the migration of $TiO_{2-x}$ moieties over the surface of the crystallites decreases the value of $\gamma_{cg}$.

### *Shape Changes in Additionally Purified Hydrogen*

It is well known that the Group VIII metals supported on reducible metal oxides such as $TiO_2$, $Nb_2O_5$, $V_2O_3$, and $Ta_2O_5$ exhibit strong metal–support interactions resulting in the low-temperature suppression of hydrogen and carbon monoxide chemisorption after high-temperature reduction (ca. 500°C) (*19–21*). The migration of a monolayer or submonolayer of $TiO_{2-x}$ over the surface of the crystallite because of its "strong interactions" with the metal appears to be responsible for this effect.

Interfacial reactions between nickel and titania have been observed to take place, though at 1500°C (*22*). It is likely that the high dispersion of metal in our system allows the reaction between nickel and titania to occur at much lower temperatures. Indeed, in the electron diffraction patterns a ring whose *d* value was close to the major *d* value of $Ni_3Ti$ was observed on heating Ni/$TiO_2$ specimens in hydrogen at 700°C, suggesting the presence of a compound between Ni and $Ti^{x+}$. The presence of strong interactions at the crystallite–substrate interface decreases $\gamma_{cs}$. The substrate underneath and near the particles is most likely a reduced form of $TiO_2$, even though such a compound was not detected in our electron diffraction patterns. The reduction of $TiO_2$ to such a lower, nonstoichiometric oxide ($TiO_{2-x}$) leads to an increase in $\gamma_{sg}$, since a nonstoichiometric compound has a higher $\gamma_{sg}$ than a stoichiometric compound. In addition, the possible migration of $TiO_{2-x}$ moieties over the surface of the crystallite, as a monolayer or submonolayer, decreases the value of $\gamma_{cg}$, again because of their strong interactions with the metal. Such decreases in $\gamma_{cs}$ and $\gamma_{cg}$ as well as an increase in $\gamma_{sg}$ will lead to an extension of the particles as can be seen from Eq. (1). Furthermore, the gradual increase in the intensity of the ring corresponding to the compound with a *d* value close to that of $Ni_3Ti$ and the gradual decrease in the intensity of the rings corresponding to Ni suggest that there is a material transfer between substrate and particle. The observation of a cavity beneath the particle in the micrographs suggests that the direction of this transfer is most likely from the substrate to the particle. The cavity formation is discussed later in more detail. The migration of the $TiO_{2-x}$ layer away from the surface of the substrate beneath as well as near the particle leads to a contact between the particle and the unreduced $TiO_2$. Consequently, the particle contracts to a higher wetting angle both because $TiO_2$ has a lower surface free energy than a nonstoichiometric oxide ($TiO_{2-x}$) and because the interaction between the particle and the unreduced $TiO_2$ is weaker and hence $\gamma_{cs}$ is larger. When the interactions between the particle and substrate are stronger over a short distance inward from the leading edge, this portion of the particle is strongly held to the substrate. Therefore, when the particle contracts, for reasons explained above, a part of the particle is detached from the main body most probably along the periphery of the cavity, but not all around the particle due to the heterogeneity of the substrate. Thus, a gap is formed between the main body and the detached portion. However, for some particles, the de-

FIG. 4. Sequence of changes in the same region of a specimen (D) on heating at 250°C in purified hydrogen. (a) 2 h, (b) 4 h, (c) 47 h.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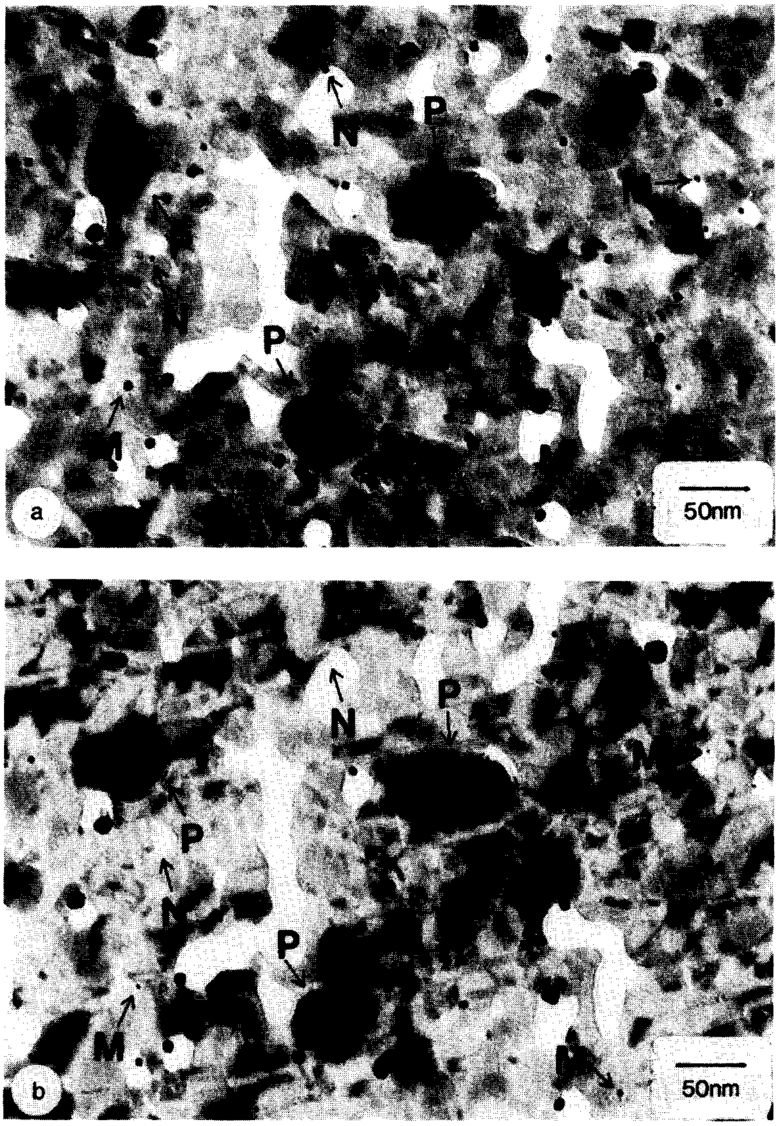


FIG. 5. Sequence of changes in sample A of Fig. 1 on subsequent alternate heating in oxygen and hydrogen at 700°C. The region shown here is the same as that of Fig. 1, after (a) 1 h, $O_2$, (b) 3 h, $O_2$, (c) 1 h, $H_2$, (d) 4 h, $H_2$.

tached portion is not detected because it is too thin to be observed. In the micrographs, the gap appears to be brighter than the other regions of the substrate. This indicates that the substrate in the gap and probably underneath the particle is most likely thinner than in the other regions of the substrate, suggesting that there is a material transfer away from the substrate as already mentioned before.

On subsequent heating in $H_2$, the exposed $TiO_2$ is further reduced to a lower, nonstoichiometric oxide and extension of the particle will follow as a result of the accompanying reaction between the nickel particle and the reduced $TiO_2$. The migration of $TiO_{2-x}$ away from the cavity exposes another layer of the unreduced $TiO_2$ and, as explained above, leads to the contraction of the particle. Such alternate changes in ex-

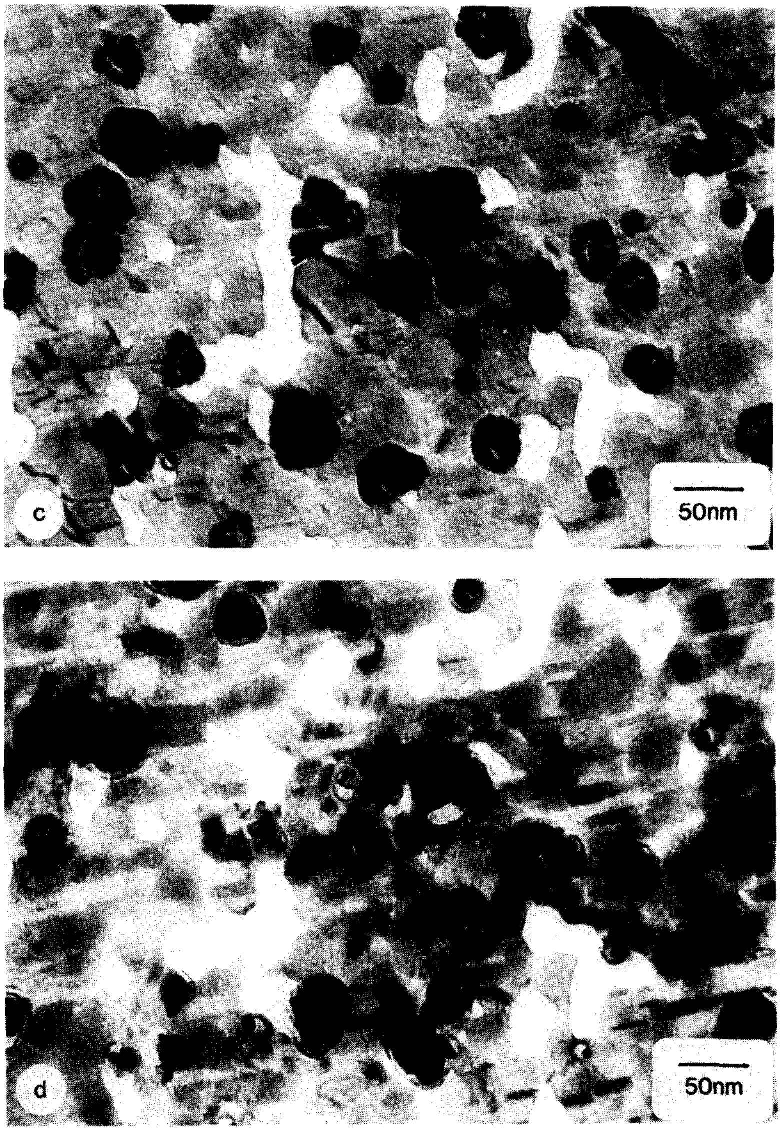


FIG. 5—*Continued.*

tension and contraction will be observed until the rate of reaction between nickel and the reduced substrate and the migration of $TiO_{2-x}$ onto or into the particle are considerably limited kinetically.

The alternate changes of the particles between a circular and a torus shape observed at 500°C in $H_2$ (Fig. 3) are also most likely a result of contractions and extensions. Extension leads to a torus shape, while contraction leads to a circular shape.

### *Behavior of Particles During Alternate Heating in $O_2$ and $H_2$*

As shown in Figs. 5 and 6, alternate heating in $O_2$ and $H_2$ brought about dramatic changes. Baker *et al.* reported that platinum particles supported on titania exhibited an extended, pillbox morphology on heating in hydrogen at 550°C or higher, whereas the particles contracted to a globular morphology on heating in $O_2$ at 600°C

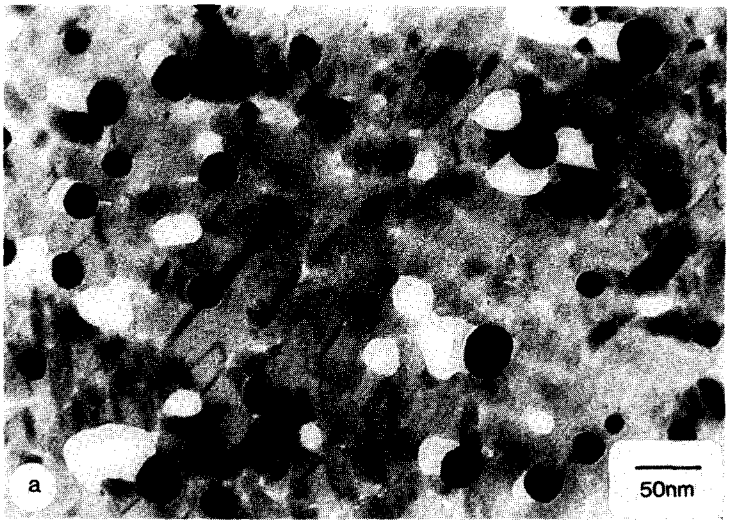
(*13*). Similar results were obtained by Tatarchuk and Dumesic in the case of iron particles supported on titania (*15*). In contrast, in the present experiments at 700°C, Ni particles supported on $TiO_2$ were observed to be in a more contracted morphology in a $H_2$ atmosphere and considerably extended in an $O_2$ atmosphere. Following heating in $O_2$ at 700°C, the drastic decrease in the number of particles and/or in their sizes (sample A, Fig. 5) suggests that either films spread out from around the particles onto the substrate or material diffused into the substrate. Diffraction patterns indicate that the particles were oxidized to NiO and then gradually changed to a nonstoichiometric compound of NiO and $TiO_2$. Such strong interactions between the particles and the support, leading to the formation of a compound, will lead to the diffusion of NiO into the substrate to enable compound formation in the bulk, to further decrease the free energy of the system. It will also decrease the interfacial free energy between the particle and substrate. In addition, $\gamma_{cg}$ for the NiO is lower than that for the metal. The smaller values of $\gamma_{cs}$ and $\gamma_{cg}$ lead to the extension of the particles. When the driving force for spreading is sufficiently large, the particles, especially the small ones (N in Fig. 5), are likely to spread out as a thin film undetectable in the micrographs.

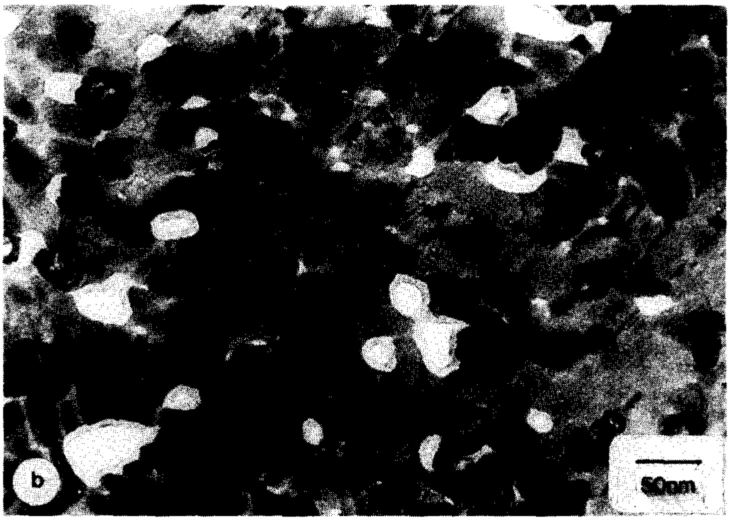
For sample B which was previously heated in $H_2$ for a longer time (115 h), the extension and diffusion of the particles during their heating in $O_2$ occurred to a smaller extent than for sample A, which was prereduced for shorter time. This may be due to the fact that the substrate in the sample prereduced for a long time (sample B) was reduced to a greater extent than the substrate in the sample prereduced for a short time (Sample A). Consequently, sample B is expected to form $TiO_{2-x}$ in greater amounts than sample A. Therefore, on heating in $O_2$ sample B may have residual $TiO_{2-x}$, while sample A may be oxidized to $TiO_2$ completely. The small remnant particles which are shown in Figs. 5b and 6d will have a globular morphology since once the particle has interacted with the substrate and formed a compound at the interface (and most of the particle has extended out as a thin detectable or undetectable film), the remnant particle will be in contact not with $TiO_2$ but with the compound of NiO and $TiO_2$. Since $U_{cs}$ between the particle (NiO) and the latter compound is no longer as large as that between NiO and $TiO_2$, the remnant particle may have a larger wetting angle and may therefore have a globular morphology. In a reducing atmosphere, the interaction compound is probably reduced, and NiO diffuses out to the surface and forms new particles on the substrate surface. After a sufficiently short time of heating in a reducing atmosphere, the latter is present as mostly $TiO_2$. Subsequently the particles are gradually reduced to Ni, and $TiO_2$ is reduced to $TiO_{2-x}$. The interactions between the Ni particles and the reduced $TiO_2$ and the higher $\gamma_{sg}$ of $TiO_{2-x}$ lead to the extension of the particles. However, the extension of the particles in a hydrogen atmosphere occurs to a smaller extent than that in an oxygen atmosphere. This suggests that the interaction between the particle and the substrate is greater in an $O_2$ atmosphere than in a $H_2$ atmosphere. While $\gamma_{sg}$ is larger in the latter case than in the former, $\gamma_{cs}$ is probably much smaller in an oxygen environment than in a reducing one. In addition, $\gamma_{cg}$ could also be smaller in an oxygen atmosphere than in hydrogen. As a result, the extension in the oxygen atmosphere can be greater.

### *Formation of Cavities*

When Ni/$TiO_2$ specimens are heated in

FIG. 6. Sequence of changes in sample B of Fig. 2 on subsequent alternate heating in oxygen and hydrogen at 700°C. The region shown here is the same as that of Fig. 2, after (a) 115 h, $H_2$, (b) 1 h, $O_2$, (c) 3 h, $O_2$, (d) 6 h, $O_2$, (e) 1 h, $H_2$, (f) 4 h, $H_2$.


a
50nm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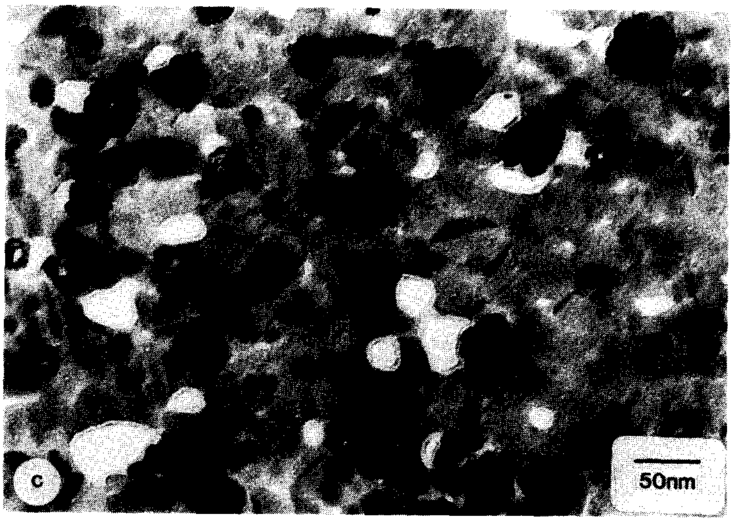
c
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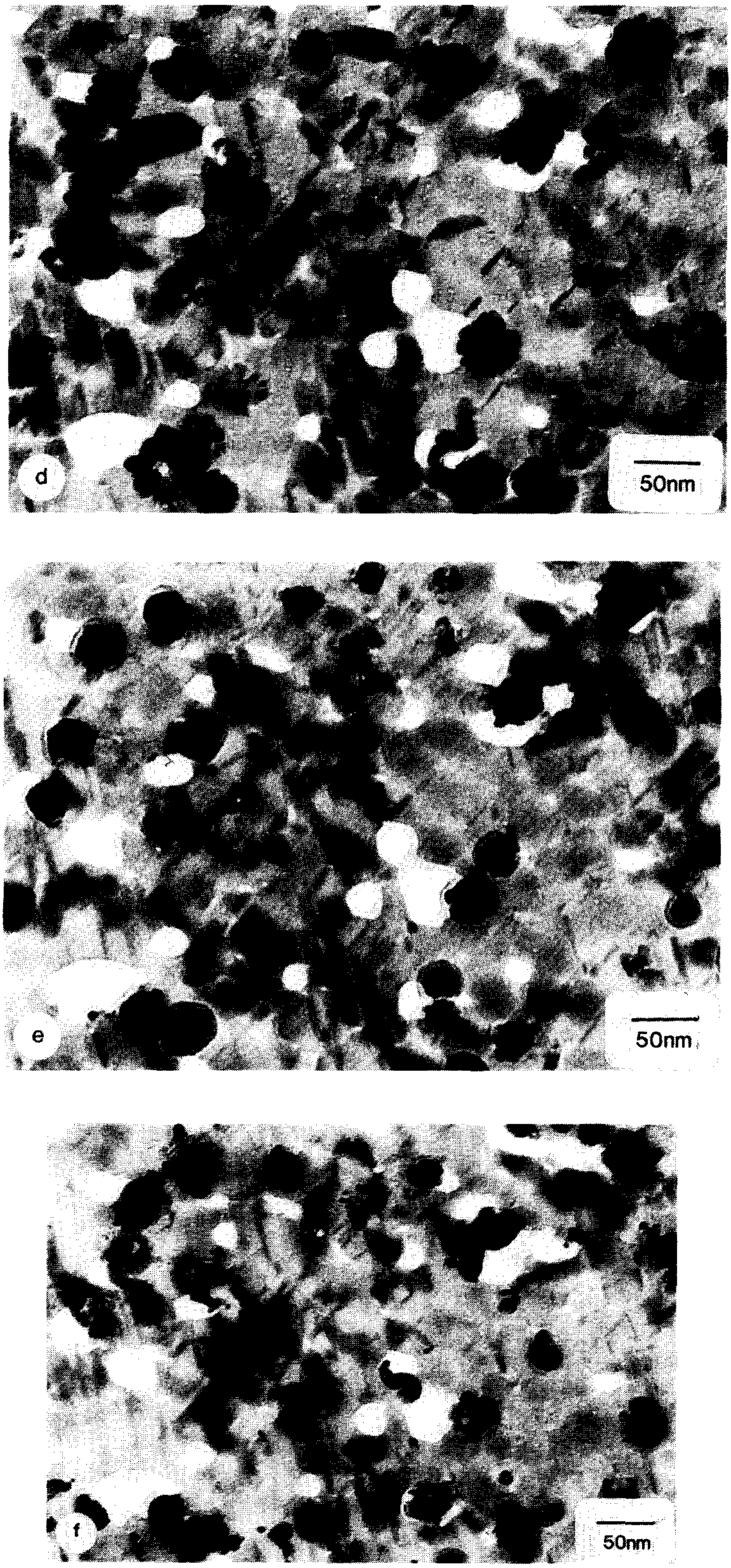

FIG. 6.—*Continued.*

$H_2$ at 700°C, cavities are formed in the substrate via removal of a part of the substrate material as a result of the formation of an intermetallic compound. The material which is removed is transferred most likely onto and/or into the metal particles. It may also migrate onto the substrate surface. Initially the particles were present as Ni. However, on further heating at 700°C in $H_2$, the electron diffraction patterns indicate that a compound whose *d* value is close to that of $Ni_3Ti$ is formed, suggesting formation of a compound between the particles and the reduced Ti species. It was inferred from the electron diffraction patterns that on further heating, the above-mentioned compound increased in amount gradually while Ni decreased. Therefore, it is likely that $TiO_{2-x}$ diffuses into and/or onto the particles, and subsequently an intermetallic compound is formed in the particles. This leads to a thinning of the substrate beneath the particle and to the creation of a cavity. The migration of reduced titania ($TiO_{2-x}$) moieties onto the surface of metal particles supported on $TiO_2$ during reduction in hydrogen has been reported before (*16, 23*). Ko and Gorte (*24*), in addition, reported that the reduced titania probably diffused into the metal particles. The latter is probably true in the present case also as inferred from the compound between Ni and Ti species detected in the electron diffraction patterns. Recently, Dumesic *et al.* also reported the formation of cavities in a Ni/$TiO_2$ system (*25*).

A part of the cavity formed underneath the particle is exposed on one side of the particle in the electron micrographs, as a result of a random displacement of the particle away from the cavity (B in Fig. 2). When the particle actually migrates out of and away from the cavity, the entire cavity can be seen, as marked (C) in Fig. 2.

## CONCLUSION

Various phenomena have been observed to occur during heating of Ni/$TiO_2$ model catalysts both in additionally purified hydrogen and in oxygen atmospheres. Alternate changes in crystallite shape were observed on heating in additionally purified hydrogen at 500 and 700°C. These alternations are suggested to be associated with the extension and contraction of the particles. Extension of the particles is a result of the strong interactions between nickel and reduced $TiO_{2-x}$, which decrease the values of $\gamma_{cs}$ and $\gamma_{cg}$, and of the increased value of $\gamma_{sg}$ for a reduced $TiO_2$ (as compared to a nonreduced one). The above-mentioned reduced species migrates into and/or onto the particles and probably also onto the substrate surface, from the substrate underneath the particles. Such a removal of the reduced $TiO_{2-x}$ layer from underneath the particle exposes the unreduced $TiO_2$ and when the particle comes into contact with this $TiO_2$ layer, it contracts. Electron diffraction patterns indicate that a compound whose *d* value is close to the major *d* value of $Ni_3Ti$ is formed during heating in $H_2$ at 700°C. Migration of the reduced substrate species away from the substrate surface underneath the particles leads to the formation of cavities in the substrate. Some specimens were heated in oxygen and hydrogen atmospheres alternately at 700°C. The results show that the particles considerably extend on, and/or diffuse into, the substrate due to the formation of a compound between NiO and $TiO_2$ in an oxidizing atmosphere. During subsequent heating in $H_2$, the material lost from the particles to the substrate during the previous heating in $O_2$ comes back onto the substrate and forms new particles. These particles are initially composed of NiO and then are reduced to Ni. On further heating in $H_2$, extension of the particles is observed as a result of the interactions between Ni and $TiO_{2-x}$, but the extension in this case occurs to a much smaller extent than in an oxygen atmosphere. These results seem to suggest that overall the interactions between the particle and substrate, in the case of Ni/$TiO_2$, are stronger in an oxygen atmosphere than in a hydrogen atmosphere.

The present results also show that severe sintering occurs at 700°C while sintering at temperatures of 500°C or less occurs to a much smaller extent.

It is emphasized that the extension of the crystallites over rutile in a hydrogen atmosphere is due to (1) the decrease of the interfacial free energy between support and crystallite, $\gamma_{cs}$, caused by the strong interactions between $TiO_{2-x}$ and metal; (2) the decrease of the surface free energy between crystallite and atmosphere, $\gamma_{cg}$, caused by the migration of a monolayer or submonolayer of $TiO_{2-x}$ over the surface of the crystallite because of the strong interactions between the two; and finally (3) the increased surface free energy, $\gamma_{sg}$, of the reduced $TiO_2$ as compared to the nonreduced $TiO_2$. In contrast, the extension of the crystallites over rutile in an oxygen atmosphere is a result of the lower surface free energy of the oxide as compared to that of the metal and of the lower interfacial free energy between crystallite and substrate caused, particularly, by the reaction between the oxidized crystallite and substrate. While the surface free energy, $\gamma_{sg}$, of the present substrate is higher in a reducing atmosphere than in an oxidizing one, $\gamma_{cs}$ is probably much lower in the latter atmosphere, thus ensuring a greater extension during heating in oxygen. In addition, $\gamma_{cg}$ could also be lower in the oxygen atmosphere.

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