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Migration of Nickel and Titanium Oxide Species as Studied by *in Situ* Scanning Transmission Electron Microscopy

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The interactions between nickel and titania were studied by *in situ* scanning transmission electron microscopy during treatments in hydrogen at temperatures near 1000 K. Large nickel particles (e.g., 100 nm) were observed to create pits in the titania films on which they were supported. In addition, the titania films, originally rutile TiO_2, were converted to Ti_4O_7 during treatment in hydrogen at ca. 1000 K. It is suggested that the nickel facilitates reduction of titania in close proximity to the metal particles, thereby leading to the formation of pits in the titania support. The reduced-titania species removed from the support during this process migrate onto and/or into the nickel particles. Evidence is presented that indicates the migration of both nickel and titania may be involved in this process. This mode of migration may be a general phenomenon for metals on reducible supports. The resulting presence of titania species on the metal surface is thought to be responsible for the occurrence of so-called "strong metal–support interactions."

INTRODUCTION

Since the original discovery by Exxon scientists that Group VIII metals supported on reducible oxides (most commonly titania) exhibit unusual chemisorptive (*1, 2*), reactive (*3–6*), and morphological (*7, 8*) properties following reduction at high temperatures, the behavior of such catalysts has been attributed to the presence of "strong metal–support interaction (SMSI)." Several explanations have been proposed to explain the origin of these interactions; however, the majority of the recent results suggest that strong metal–support interactions are due to the presence of oxide species on the surface of the metal particles. Support for this model may be derived from a number of experimental observations. The selectivity of catalysts exhibiting SMSI generally favors facile reactions over demanding ones (e.g., (*9–11*)), suggesting that metal–support interactions affect the surface geometry of the catalyst. Strong metal–support interactions are observed for large (i.e., >5 nm) particles (e.g., (*12–14*)); it is difficult to imagine how interactions between the bulk oxide and the metal particles could affect the metal surface of such samples. Characterization of metal particles exhibiting SMSI using techniques that are sensitive to bulk electronic properties of metals, such as Mössbauer spectroscopy and magnetic susceptibility, show little or no deviation from the properties of the normal metal (e.g., (*12, 15–17*)). This indicates that the metal–support interaction affects only a small fraction of the metal atoms, presumably those at the surface, since catalytic and chemisorptive properties are strongly affected. The promotion of nickel and platinum catalysts with very small amounts of titania has been shown to produce effects similar to strong metal–support interactions (*18, 19*). Metals supported on mixed oxides containing 1–19% titania can also show SMSI (*20, 21*). Furthermore, model systems in which titania is deposited onto the surface of metal foils mimic the chemisorptive properties of high-surface-area materials (*22–24*). In-

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deed, spectroscopic studies performed on model materials indicate that migration of titania species is possible under conditions similar to those required for induction of SMSI (*25–30*).

Nevertheless, a number of questions remain. For example, the mode of transport of oxide species to the particle surface is not well understood. While spectroscopic studies of model materials show that migration of oxide species is possible, it is unclear what role the metal plays in this process. The work presented in this paper is directed toward the mechanism of migration of metal oxide species.

In a previous paper we reported on the effects of depositing powdered titanium oxide on nickel surfaces with respect to catalytic carbon formation from decomposition of hydrocarbons (*31*). It was found that following reduction in hydrogen at 770 K, titanium oxide was an extremely effective inhibitor of carbon deposition from hydrocarbons, whereas following treatment in oxygen, the additive had an almost negligible effect. This inhibition effect was rationalized in terms of the ability of reduced titanium oxide to spread on the surface of a metal, such as nickel, thus preventing the formation of filamentous carbon that would normally be formed when a hot metal surface is exposed to a hydrocarbon environment (*32*). These results provided additional support for the notion that reduced titania species on metal surfaces may be the origin of strong metal–support interactions for titania-supported metal particles.

In the present work we have extended these experiments to study the role of the metal in the nickel/titanium oxide interaction and, in particular, to determine if the metal facilitates migration of reduced titania species onto its surface during reaction in hydrogen. *In situ* scanning transmission electron microscopy has been used to study the behavior of two types of model systems. In the first, titanium oxide crystallites were deposited on a thin nickel film and changes in both the film and oxide particles were monitored as the sample was reduced in hydrogen. In the second, samples consisting of overlapping nickel and titania films were prepared; when heated in hydrogen, large, three-dimensional nickel crystallites formed, and their behavior, as well as their effect on the titania film, could be observed during further heating. Following presentation of the results of these observations, the implications of these experiments for phenomena associated with strong metal–support interactions are discussed.

EXPERIMENTAL

Two types of samples were prepared for these investigations: in the first, the titania was present as particles on nickel film; in the second, nickel and titania thin films were overlapped to produce areas in intimate contact. To prepare the first type of specimen, a film of nickel approximately 30–40 nm thick was evaporated onto a single crystal of sodium chloride. This film was then sprayed with a fine mist of *n*-butanol containing a suspension of TiO_2 (anatase form, Degussa P-25), and was allowed to dry at room temperature. The NaCl substrate was then dissolved in distilled water, and the resulting sample was thoroughly washed and floated onto a 3-mm nickel electron microscope grid.

To prepare the second set of samples, titania films were grown by oxidizing the surface of a titanium metal foil in oxygen at 600 K; the metallic titanium substrate was subsequently removed in an aqueous solution of 10% nitric and 2% hydrofluoric acids (*33*). Previous studies have shown that this form of titania should be rutile (*33*); diffraction studies confirmed that this was indeed the crystal structure obtained. Nickel films were produced by vacuum evaporation onto rock salt, as described above. Nickel grids were then used to pick up two thin films, one of nickel and one of titania, which were overlapped in such a manner that regions of nickel only, titania only, and nickel and titania in direct contact were obtained on the same sample.

All electron microscopy studies were performed in a JEOL 200 CX instrument that could be operated in either transmission or scanning transmission mode. This microscope was fitted with environmental cell and heating stage (*34*), which allowed specimens to be heated in 130 Pa hydrogen up to 1100 K; under these conditions the resolution was better than 1 nm. A further feature of this technique was the ability to perform chemical analysis of the reacting specimen using electron diffraction, energy dispersive X-ray analysis and electron energy loss spectroscopy.

The gas used in this part of the study, hydrogen, was obtained from Scientific Gas Products, Inc. with a stated purity of 99.99% and was used directly.

Postreaction STEM examinations were also performed on a series of nickel–titanium oxide specimens which had been treated in a flow reactor in the presence of 1 atm 10% hydrogen/argon at temperatures between 975 and 1120 K for 1.0 h. Prior to removal from the reaction zone, specimens were passivated according to the following procedure: at completion of the reduction treatment, hydrogen was replaced by an argon flow and the specimens cooled to room temperature and then exposed to a flow of 2% carbon dioxide/argon for 1.0 h before finally transferring in air to the microscope. As will be demonstrated later, careful passivation is a crucial step to ascertain the corresponding chemical state of the specimen from a postreaction examination.

RESULTS

Titania Deposited on Nickel Films

Before studying these model, Ni/TiO_2 systems, the behavior of blank nickel films in ca. 120 Pa hydrogen at temperatures up to 1000 K was studied. It was observed that the nickel foils underwent major restructuring when heated above 800 K, resulting in the formation of large (10–400 nm), three-dimensional crystallites on an extremely thin nickel film.

On the nickel–titania samples prepared by spraying butanol-dispersed titania onto nickel, the titania was present in the form of large (>100 nm), irregularly shaped agglomerates of particles surrounded by large areas of blank nickel. When heated above 800 K in 100 Pa hydrogen, the nickel underwent a restructuring similar to that observed for the blank nickel, resulting in the formation of nickel crystallites supported on a very thin nickel film. At approximately 1060 K, light areas began to appear around the edges of the titania; additionally, the edges of the titania became more rounded and less distinct. Energy-dispersion X-ray analysis of the light areas surrounding the titania indicated that titanium was present in these regions. Electron diffraction analysis of these areas showed the presence of both anatase and nickel. Furthermore, a number of spots were also present at *d*-spacings much higher than can be accounted for by either anatase, rutile, or nickel; these spots may be indicative of some mixed titania–nickel species.

Contacting Nickel and Titania Films

In the studies performed on the samples consisting of overlapping nickel and titania films, the areas containing only nickel underwent a series of changes upon heating similar to those observed for the blank nickel foil described above. In particular, at temperatures above 800 K in ca. 70 Pa of hydrogen, the film restructured into large spherical crystallites supported on an extremely thin nickel film. In contrast, the appearance of those regions of the titania film not in contact with nickel remained visually unchanged at all temperatures investigated (i.e., up to 1200 K). In the areas where the nickel and titania films were in direct contact, nickel particles similar to those present on the blank nickel were observed to form at about 800 K. However, when the sample was heated above 1080 K, these nickel particles began to attack the titania film, leaving behind trails in which no titania appeared to be present. A sequence

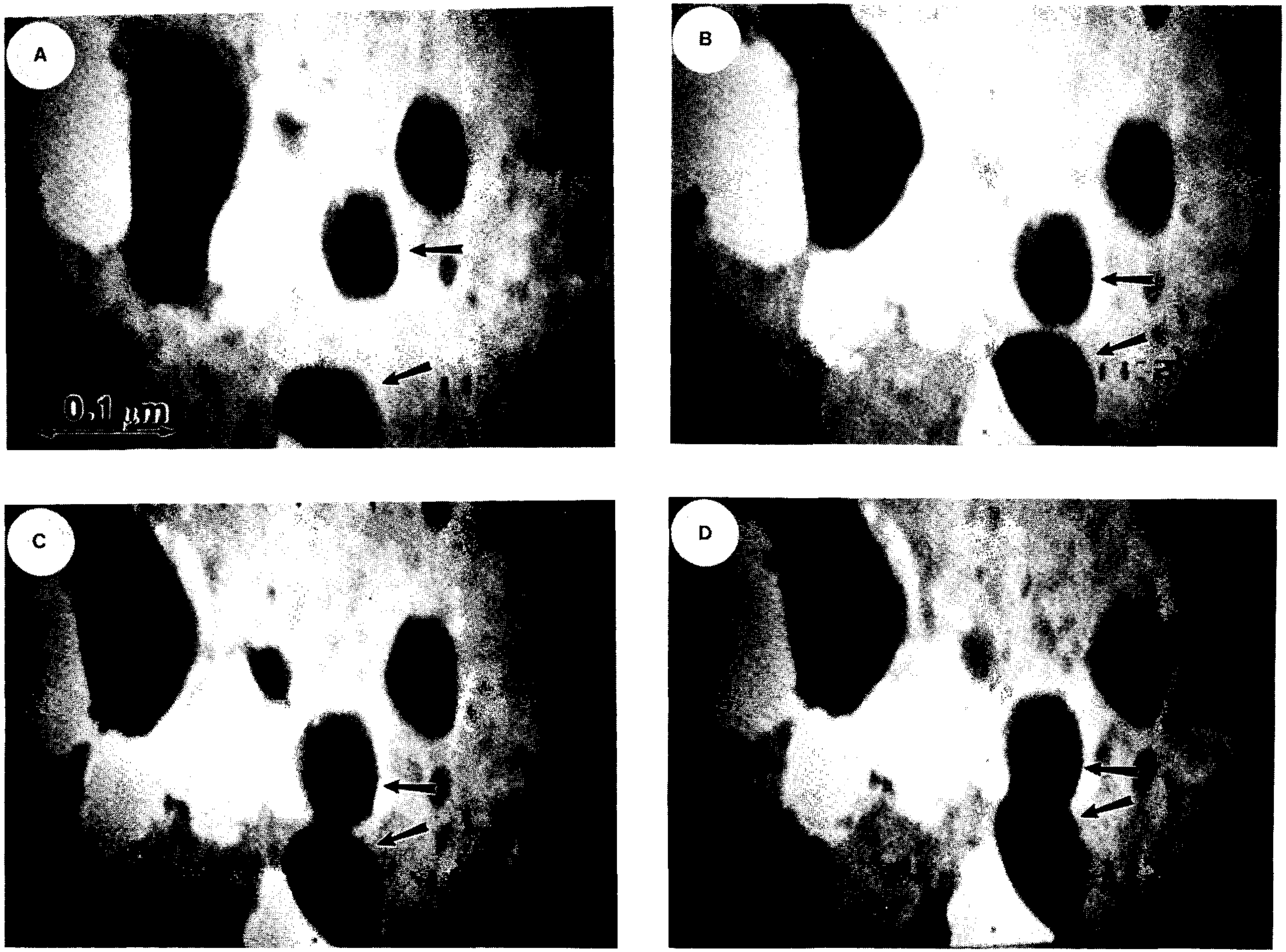

FIG. 1. Sequence showing the interaction of nickel particles with titanium oxide in 70 Pa hydrogen at 1070 K.

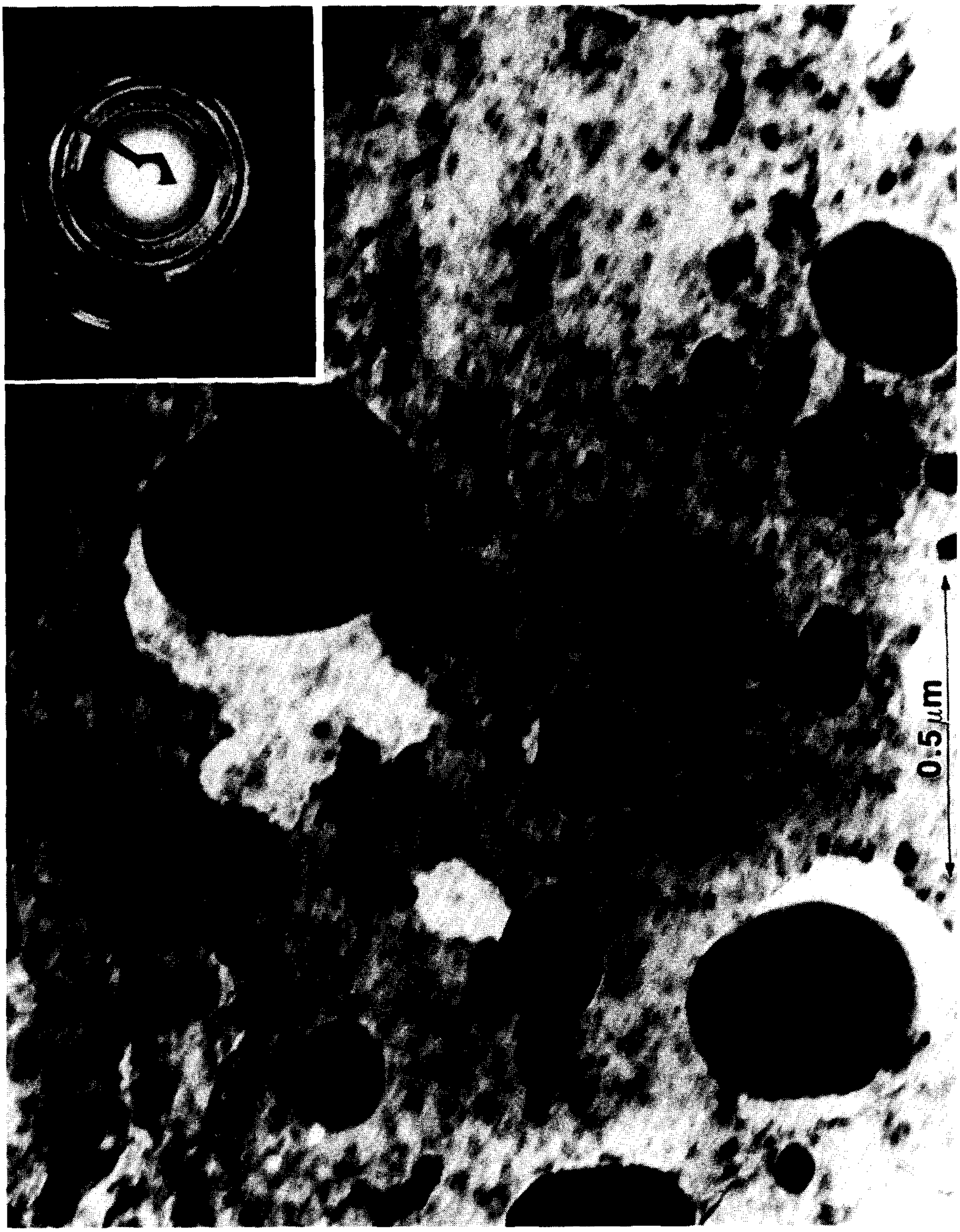

FIG. 2. Electron micrograph showing pits in titanium oxide support produced by nickel particles during reaction in 70 Pa hydrogen at 1070 K. Inset shows the electron diffraction pattern of the sample under these conditions.

showing the movement and coalescence of two nickel particles is shown in Fig. 1; an example of the trails left by this kind of movement is shown in Fig. 2. Electron diffraction analysis under these conditions showed that the titanium was now present in the form of Ti_4O_7 (see inset of Fig. 2 and Table 1). This reduced form of titania was found on all portions of the titania film, even those far removed from the nickel. Since titania cannot dissociate hydrogen, this result seem to indicate that either lattice oxygen or atomic hydrogen has migrated distances of up to several microns across the titania surface at this temperature. Similar behavior has been previously described in the literature (*35*).

It is important to note that the aforementioned attack of titania by nickel in hydrogen observed at temperatures above 1080 K was preceded by a more subtle phenomenon at temperatures near 1000 K. Specifically, light areas (e.g., halos) were observed to form around some nickel particles at these lower temperatures, suggesting that the titania film was becoming thinner in these regions. It is significant that under these conditions electron diffraction analysis failed to show the presence of Ti_4O_7, the observed pattern being that of the rutile form of titania. It is possible that a reduced form of titania was produced at the regions surrounding the nickel but was of such a minor concentration that its pattern was masked by the strong rutile signal.

TABLE 1

Electron Diffraction Analysis of a Titania after Reaction in Hydrogen at 1080 K in the Presence of Nickel

Calculated[a] *d*-spacings (nm)	*d*-spacings of Ti_4O_7 (nm)
0.427	0.427
0.332	0.338
0.308	0.302
0.276	0.282, 0.280
0.258	0.263
0.248	0.252, 0.248
0.241	0.242
0.208–0.222	0.214–0.223

[a] Based on first reflection = Ti_4O_7 $[10\bar{2}]$.

In a related series of experiments, the samples prepared by overlapping the nickel and titania films were treated outside the electron microscope in an atmospheric-pressure reactor and subsequently examined for evidence of attack of the titania by nickel. For example, a sample was treated for 1 h in 10 : 90 H_2 : Ar at 1120 K and a total pressure of 100 kPa. After this treatment, the surface of the sample was observed to have undergone a dramatic change. Many thick regions of titania had developed, and a large number of pits and channels were also present. Although there were many nickel particles, it was difficult to ascertain with any degree of certainty if they were responsible for these pits and channels. However, samples treated in the same apparatus at 970 K were found to have developed channels that were associated with the nickel crystallites; indeed, these samples looked similar to those treated in the electron microscope, although the amount of pitting was not as extensive.

The electron diffraction patterns of these samples paralleled that found for the *in situ* reacted samples, i.e., the samples reduced at 1120 K showed that the titanium oxide had been completely converted to Ti_4O_7, whereas samples treated at 970 K showed only the rutile form of TiO_2, a result reported by Bell and co-workers (*36*). One anomalous finding occurred with a sample that was reacted at 1120 K, and where the passivation procedure was inadvertently omitted; the pattern showed no evidence for Ti_4O_7.

DISCUSSION

As outlined in the Introduction, the presence of titania on the surfaces of metal particles has been proposed by a number of investigators to explain the origin of so-called "strong metal–support interactions" for titania-supported metal catalysts. The mode of transport of titania species onto the surface of the metal particles, however, is not well understood. The results of the present study provide important information about this process.

One limiting case can be imagined in which titania species are mobile on the surface of the support under reducing conditions at temperatures where strong metal–support interactions are induced (i.e., above 800 K). Accordingly, these titania species are then able to diffuse onto the surfaces of metal particles. This hypothesis, however, is not consistent with the results of the present study shown in Figs. 1 and 2. It appears instead that the metal particles attack only those regions of the support in close proximity. Thus, the migration of titania species in hydrogen at elevated temperatures cannot be an intrinsic property of the support itself, but must be related to a reaction that takes place at the interface between the metal particles and the support, where more complete reduction of neighboring titania species and their detachment from the oxide lattice may take place. This is in agreement with the reported observations that metals facilitate the reduction of titania (*35, 37–41*).

The results of experiments where samples of titania powder on nickel films were heated in hydrogen show that an interaction between nickel and titania may also be initiated at 1060 K by the migration of nickel toward titania. In these experiments, the nickel film became thinner in the regions of the sample that were near titania, as evidenced by the increase in electron transmission through these regions. Although energy-dispersive X-ray analysis showed that some titania may be migrating onto the nickel film, the change in contrast indicates that the net mass transfer must be away from the nickel films and toward the titania particles. Indeed, this behavior is consistent with the reported observations that metal particles may spread over titania supports (*7*) or diffuse into titania in hydrogen at high temperatures (*42, 43*). Furthermore, the mobility of nickel at temperatures near 1150 K is demonstrated by the observation of coalescence of nickel particles (see Fig. 1) and restructuring of the nickel film at even lower temperatures.

The conclusion that is suggested by this study is that the migration of *both* titania and metal species may be involved in the initiation of strong metal–support interactions during high temperature treatments in hydrogen. For the case of the large metal particles in contact with the titania films, it appears that the titania is first reduced at the metal–support interface, and it then diffuses into the metal particle and/or onto the metal surface. From the size of the holes created in the titania film from the attack by nickel (see Figs. 1 and 2), it may be suggested that either a fraction of the titania removed from the support must be present inside the metal particles or volatile titania species are being removed from the surface of the nickel particles. While bulk titanium oxides have very low vapor pressures at these temperatures, titania surface species may have different properties once detached from the oxide lattice. A bulk diffusion hypothesis is supported by the observation that upon cooling, needle-like crystals appeared on the surface of several of the nickel particles. This suggestion is also consistent with the results of Ko and Gorte (*44*), which suggest that titania species may, in fact, diffuse into metals. In addition, other investigators have suggested that titania species may diffuse through metal films (*30*). While it is clear from magnetic susceptibility and Mössbauer spectroscopy data that significant quantities of titanium or titanium oxides are not present inside the nickel particles after reduction at 770 K (*15, 17*), the higher temperatures used in this study may favor the dissolution of titania species. For the case of titania particles present on nickel films, however, it appears that nickel diffuses toward titania. The difference between the above two cases seems to be that nickel is the particulate phase in the first case, while titania is the particulate phase in the second case.

The above arguments suggest that the nature of interaction between nickel and titania may depend on the states of dispersion of these two phases. For the set of samples comprised of nickel particles on titania films, the titania appears to diffuse into and/or onto large nickel particles due to the higher stability of these particles compared to a titania film. In contrast, for titania particles on nickel films, the nickel appears to diffuse into and/or onto large particles due to the higher stability of large titania particles compared to a nickel film. This may have implications in determining the morphology of metal particles supported on titania. For example, small metal particles may spread over titania supports, adopting raft-like morphologies, while larger metal particles may not.

It should be noted that the observations of titania and nickel mobility in this study were made at temperatures near 1080 K. In studies of titania-supported metal catalysts, strong metal–support interactions are typically initiated by treatment in hydrogen at temperatures near 800 K. It is important to remember, however, that the measurable attack of titania by nickel particles was also observed in the present study temperatures as low as 1000 K. Indeed, for similar studies of samples composed of platinum thin films in contact with titania thin films, visible manifestations of an attack on the titania were observed at temperatures as low as 910 K. We suggest that this attack on titania by metals may begin at even lower temperatures (e.g., 800 K), but that the extent of reaction may be restricted to the surfaces of the metal particles and is undetectable by electron microscopy.

It should be emphasized that although Ti_4O_7 was the only phase which was detected by electron diffraction after reduction of samples at 1120 K, other Magneli phases (TiO_{2n-1}) (*45*) may be present. Such phases may have been formed in lower concentration or of a less crystalline nature and therefore been difficult to detect under these conditions.

Finally, one may ask why the pitting form of attack of titania by nickel particles was not observed in previous studies where nickel/titanium oxide samples had been treated in hydrogen and were examined by electron microscopy (*30, 46, 47*). In these cases, the nickel particles were considerably smaller (5 to 10 nm) than the ones formed in the present experiments (~100 nm); therefore, the extent of reaction may have been only sufficient to cause removal of a few monolayers of titania, which would have been difficult to detect.

SUMMARY

The results of the present study demonstrate that migration of both titania and metal species may be involved in the initiation of so-called strong metal–support interactions during treatment in hydrogen at temperatures in excess of 775 K.

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