JOURNAL OF CATALYSIS **111**, 440–444 (1988)

Sintering and Pit Formation of Ni Particles Supported on a Thin TiO_2–SiO_2 Film

Several research groups indicated evidence of strong metal–support interactions (SMSI) in Ni/TiO_2 systems from measurements of catalytic and chemisorptive properties (*1–10*). When Ni/TiO_2 samples are reduced in H_2 at temperatures above about 700 K, they markedly lose their adsorptive capacity for H_2 and CO and catalytic activity for certain reactions. In their recent paper, Ko and Wagner noted that when TiO_2 was added to SiO_2, supported Ni showed lower activities in ethane hydrogenolysis and H_2 chemisorption than that with Ni/SiO_2, in particular, after reduction at 773 K (*7*). For Ni/SiO_2 and Ni/Al_2O_3 (*11–13*) as well as for other systems (*14–17*), certain treatments with O_2 and H_2 were recently found to induce some metal–support interactions leading to interesting morphological changes. An O_2 treatment produces pitted and horseshoe-shaped NiO particles and a cyclic O_2–H_2 treatment causes redispersion due to the splitting and/or spreading of Ni particles.

With regard with the above results, we intended to obtain information about Ni–TiO_2 interactions and the influence of TiO_2 additive on Ni/SiO_2 in H_2, in O_2, and under vacuum. For this we prepared a sample of Ni supported on a thin film such that a number of TiO_2 islands were dispersed on SiO_2 and we examined it by transmission electron microscopy (TEM). Our previous TEM studies revealed the effects of metal–support interactions and temperature on the sintering and morphological characteristics of Ni particles for Ni/SiO_2 together with Ni/Al_2O_3 and Ni/C (*11, 18–20*). To clarify the effect of TiO_2, therefore, it seems useful to compare previous results for Ni/SiO_2 with those for Ni on SiO_2 and TiO_2 in the Ni/TiO_2–SiO_2 sample.

An amorphous SiO_2 film was prepared by the procedure used previously (*8*). A Ti film was deposited onto the SiO_2 by vacuum evaporation and treated at 573 K in air for 2 h, under vacuum for 1 h, and in air at 773 K for about 2 h. The treatment at 773 K broke the Ti film into small islands. They became stable in about 2 h and were little changed by further heat treatment at 773 K or above (<950 K). Table 1 gives electron diffraction data and may show the islands to be a polycrystalline, anatase form of TiO_2. Ni was deposited onto this TiO_2–SiO_2 to a thickness of 1–2 nm by vacuum evaporation. Ni was uniformly dispersed over the surface of TiO_2 islands and SiO_2 substrate in the sample as prepared (Fig. 4a). The sample was (i) heat treated under vacuum in a Hitachi H-300 TEM and examined *in situ* or (ii) heat treated with H_2 and O_2 at 8 kPa in an electric furnace and then examined by the TEM at room temperature.

Electron micrographs of Ni/TiO_2–SiO_2 during heating under vacuum at 823 and 883 K are presented in Fig. 1, where the TiO_2 islands are seen to be darker than the SiO_2 substrate. The heat treatment produced larger Ni particles on TiO_2 than on SiO_2. Side view observations showed the Ni particles to be three-dimensional. It is evident from Fig. 1 that particle growth occurred on either TiO_2 or SiO_2 and particle and atomic migrations concurrently contributed to it. In Ni/SiO_2, however, particle migration was predominant at these temperatures as reported previously (*8*). Figure 2 shows changes in the diameter of Ni particles on either TiO_2 islands or SiO_2 substrate. The

0021-9517/88 $3.00

TABLE 1

Lattice Spacings in Nanometers for TiO_2–SiO_2 and Ni/TiO_2–SiO_2 Samples from Electron Diffraction Patterns

TiO_2–SiO_2 oxidized at 500°C for 2 h	Ni/TiO_2–SiO_2 reduced at 600°C for 3.5 h	Ni/TiO_2–SiO_2 oxidized at 600°C for 1 h
0.349[a]	0.358	0.299
0.239[a]	0.329	0.238[c]
0.190[a]	0.217	0.222
0.169[a]	0.203[b]	0.209[c]
0.147[a]	0.187	0.191
0.133[a]	0.174[b]	0.179
0.124[a]	0.164	0.162
	0.130[b]	0.142[c]
		0.123

[a,b,c] Assigned to anatase TiO_2, Ni, and NiO, respectively.

effect of temperature was small for SiO_2 but it was significant for TiO_2, on which Ni particles grew rapidly at 883 K.

Furthermore, we prepared another support in which TiO_2 wholly covered the surface of SiO_2 and we examined the behavior of Ni on this TiO_2 overlayer. The thickness of the TiO_2 layer was roughly estimated to be larger than 10 nm, and its surface properties seemed to be little influenced directly by the presence of the SiO_2 underlayer. The characteristics of particle morphology and growth for the TiO_2 overlayer were found to be the same as observed for the TiO_2 islands in Ni/TiO_2–SiO_2 described above. The change in particle diameter at 873 and 973 K is shown in Fig. 3.

The above results demonstrate the support effect that Ni on TiO_2 is less stable and sinters more rapidly under vacuum than Ni on SiO_2, and this effect becomes more pronounced at higher temperatures. The effect may be due to differences in Ni–support interactions and in surface roughness between TiO_2 islands (uneven) and SiO_2 substrate (flat). In addition, the TiO_2 seemed to modify the SiO_2 substrate, resulting in the sintering mode for Ni on SiO_2 in TiO_2–SiO_2 being different from that on SiO_2 alone (*8*).

Next the influence of H_2 and O_2 was examined. When the Ni/TiO_2 (islands)–SiO_2 was treated with 8 kPa H_2 at 873 K, the TiO_2 was presumed to be reduced from the electron diffraction given in Table 1, although the phases present could not be identified. The H_2 treatment produced larger Ni particles on reduced TiO_2 than on SiO_2 as seen in Fig. 4b. These Ni particles were three-dimensional from side view observations. Previous works reported raftlike, flat particles as well as three-dimensional ones for a few metal–support systems (*3, 4, 21–23*). Mustard and Bartholomew first demonstrated such a particle morphology for Ni on high-surface-area TiO_2 and SiO_2 when reduced at 725 K (*3*). Smith *et al.* also noted raftlike Ni particles on TiO_2 (*4*). These authors believed that the flat particles were indicative of strong Ni–support interactions (*3, 4*).

Figure 3 shows the change of particle diameter for Ni/TiO_2 (overlayer)–SiO_2 in H_2 at 873 K, indicating little influence of H_2 on the rate of particle growth. The Ni particles were seen to grow by particle and atomic migrations. The characteristics of particle morphology and sintering in H_2 were similar to those under vacuum although the H_2 treatment probably reduced the TiO_2 (Table 1). It was previously confirmed that TiO_2 was reduced by H_2 treatment above about 770 K and the significance of reduced species was discussed in terms of SMSI effects for TiO_2-supported metal catalysts (e.g., (*10*)). In the recent CAEM study of Dumesic *et al.*, TiO_2 in a thin Ni/TiO_2 film sample was shown to be reduced to Ti_4O_7 at 1070 K (*9*). Furthermore, they observed the formation of pits in the support around Ni particles and this was ascribed to the attack of the particles onto the support. In our Ni/TiO_2–SiO_2 sample reduced at 873 K, however, such a morphological change was not seen. The results of Ko and Wagner (*7*) cited above might partly be explained by the present result that the degree of dispersion of Ni on TiO_2 is lower than that on SiO_2.

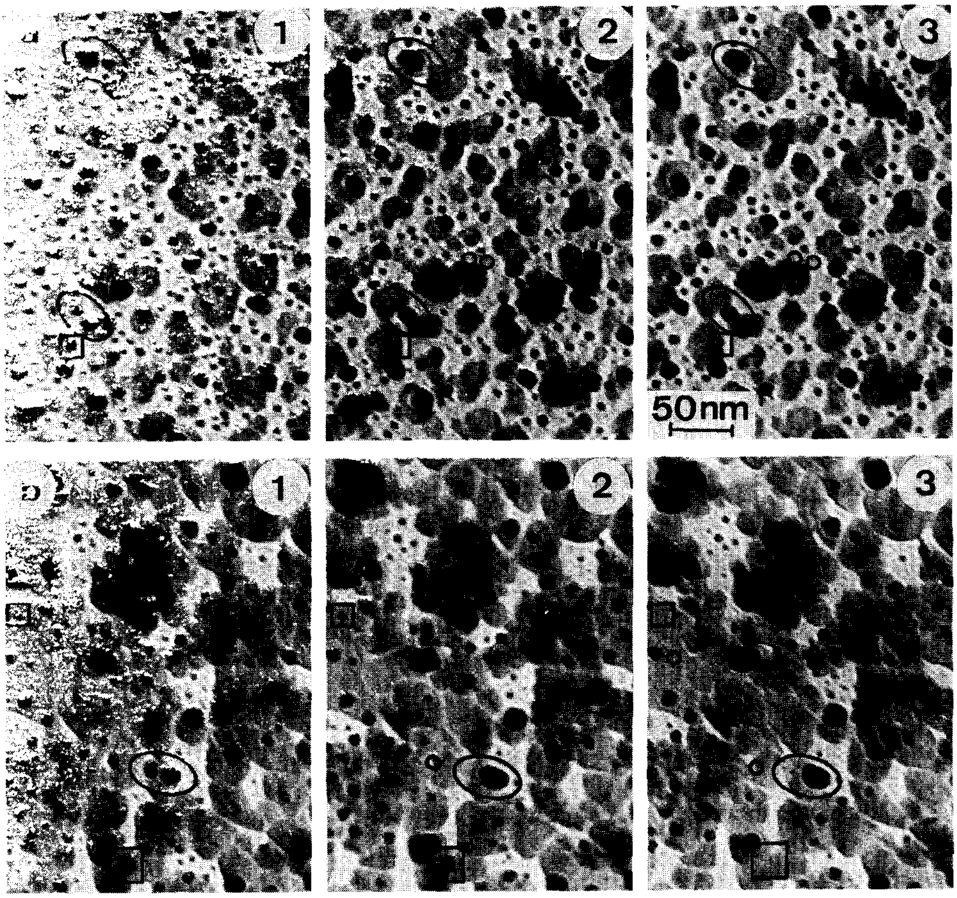

FIG. 1. Electron micrographs of Ni/TiO_2–SiO_2 during heating under vacuum (a) at 823 K for (1) 40, (2) 77, (3) 120 min and (b) at 883 K for (1) 20, (2) 40, (3) 60 min. Typical changes are noted: The particles in ellipses show the growth by particle migration and coalescence. Those in squares contract and disappear at the same positions. Circles indicate the positions on which particles have been present before.

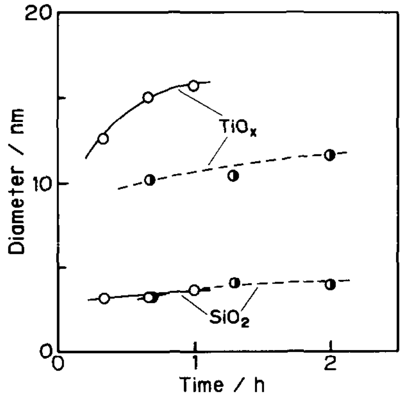

FIG. 2. Sauter-average diameter of Ni particles on TiO_2 islands and SiO_2 substrate in Ni/TiO_2–SiO_2 heated under vacuum at 823 K (◑) and 883 K (○).

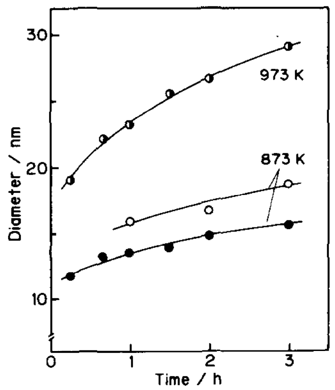

FIG. 3. Sauter-average diameter of Ni particles on TiO_2 overlayer on SiO_2 heated at 873 K (●) and 973 K (◑) under vacuum and at 873 K in hydrogen (○).

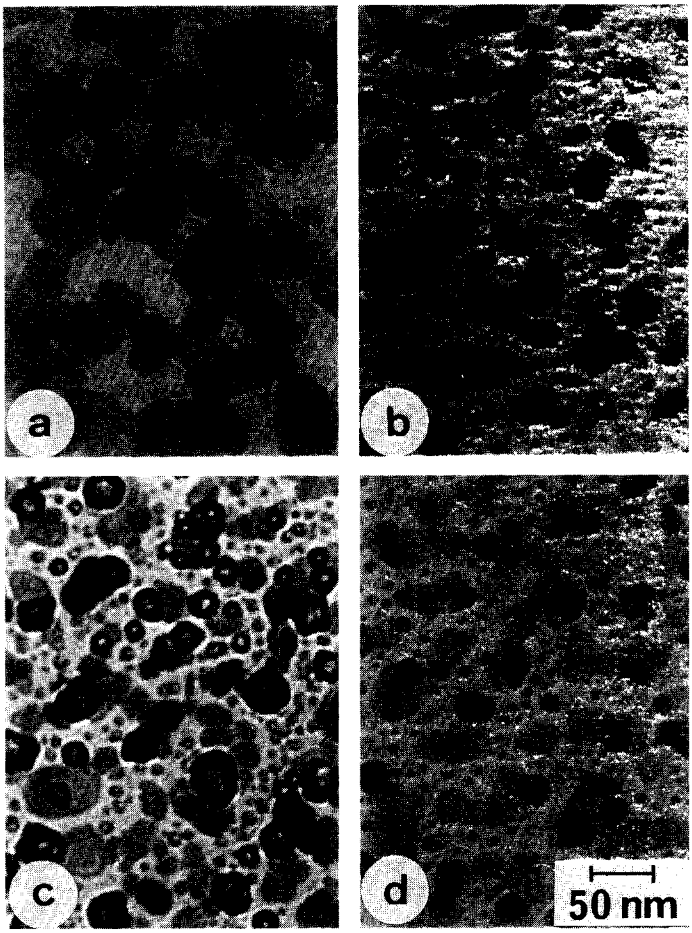

FIG. 4. Electron micrographs of Ni/TiO_2–SiO_2 (a) as prepared and after being heating (b) in H_2 at 873 K for 3 h; (c) then in O_2 at 673 K for 1 h; (d) again in H_2 at 873 K for 1 h.

Following the above H_2 treatment, the Ni/TiO_2 (islands, reduced)–SiO_2 was treated with O_2 at 673 K for 1 h. A micrograph in Fig. 4c clearly indicates that pits were formed in not only small particles on SiO_2 but also larger ones on reduced TiO_2. It is interesting to see that some particles stretch over the uneven surface of a few islands adjacent to one another and a larger pit was formed in a larger particle. Electron diffraction showed these pitted particles to be NiO and further suggested that the reduced TiO_2 was oxidized to some extent but not completely to TiO_2 (Table 1). When this sample was treated again with H_2 at 873 K for 1 h, the pits disappeared and the particles were reduced to Ni and again assumed the morphology that was seen before the oxidation as shown in Fig. 4d. The H_2 treatment seemed to reduce the oxidized TiO_2 but the phases of the resultant TiO_2 were not the same as those observed before the O_2 treatment.

These morphological changes of Ni particles with H_2 and O_2 treatments are quite similar to those for Ni/SiO_2 and Ni/Al_2O_3 observed previously (*11–13*). Therefore, the redispersion would take place by an oxidation–reduction cycling for Ni/TiO_2 as well if proper conditions could be used. A difference between metal–support and metal oxide–support interactions may be responsible for both pit formation and redispersion and it is dependent on the metal–support system considered. Indeed it was found that a higher reduction temperature of cyclic O_2–H_2 treatment was required for Ni/Al_2O_3 to redisperse than that required for Ni/SiO_2 (*11*). Current works in this and other laboratories on pit formation and redispersion in various systems during O_2 and H_2 treatments have produced suggestive information about the mechanism of these phenomena and metal–support interactions (*11–17*).

REFERENCES

1. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1987).
2. Bartholomew, C. H., Pannell, R. B., and Butler, J. L., *J. Catal.* **65,** 335 (1980).
3. Mustard, D. G., and Bartholomew, C. H., *J. Catal.* **67,** 186 (1981).
4. Smith, J. S., Thrower, P. A., and Vannice, M. A., *J. Catal.* **68,** 270 (1981).
5. Burch, R., and Flambard, A. R., *J. Catal.* **78,** 389 (1982).
6. Jiang, X. Z., Hayden, T. F., and Dumesic, J. A., *J. Catal.* **83,** 168 (1983).
7. Ko, E. I., and Wagner, N. J. *J. Chem. Soc. Chem. Commun.*, 1274 (1984).
8. de Bokx, P. K., Bonne, R. L. C., and Geus, J. W., *Appl. Catal.* **30,** 33 (1987).
9. Dumesic, J. A., Stevenson, S. A., Chludzinski, J. J., Sherwood R. D., and Baker, R. T. K., *in* "ACS Symposium Series No. 298" (R. T. K. Baker, S. J. Tauster, and J. A. Dumesic), p. 99. Amer. Chem. Soc., Washington DC, 1985.
10. Stevenson, S. A., Dumesic, J. A., Baker, R. T. K., and Ruckenstein, E. (Eds.), "Metal-Support Interactions in Catalysis, Sintering, and Redispersion." Van Nostrand Reinhold, New York, 1988.
11. Nakayama, T., Arai, M., and Nishiyama, Y., *J. Catal.* **79,** 497 (1983); **87,** 108 (1984).
12. Ruckenstein, E., and Lee, S. H., *J. Catal.* **86,** 457 (1984).
13. Lee, C., Schmidt, L. D., Moulder, J. F., and Rusch, T. W., *J. Catal.* **99,** 472 (1986).
14. Ruckenstein, E., and Chu, Y. F., *J. Catal.* **59,** 109 (1979).
15. Chen, J. J., and Ruckenstein, E., *J. Catal.* **69,** 254 (1981); *J. Phys. Chem.* **85,** 1606 (1981).
16. Ruckenstein, E., and Chen, J. J., *J. Colloid Interface Sci.* **86,** 1 (1982).
17. Wang, T., and Schmidt, L. D., *J. Catal.* **70,** 187 (1981).
18. Arai, M., Ishikawa, T., and Nishiyama, Y., *J. Phys. Chem.* **86,** 577 (1982).
19. Arai, M., Ishikawa, T., Nakayama, T., and Nishiyama, Y., *J. Colloid Interface Sci.* **97,** 254 (1984).
20. Arai, M., and Nishiyama, Y., *J. Colloid Interface Sci.* **104,** 175 (1985).
21. Prestridge, E. B., Via, G. H., and Sinfelt, H. J., *J. Catal.* **50,** 115 (1977).
22. Yates, D. J. C., Murrell, L. L., and Prestridge, E. B., *J. Catal.* **57,** 41 (1979).
23. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **56,** 390 (1979); **59,** 293 (1979).

MASAHIKO ARAI[1]
TETSUNORI NAKAYAMA
YOSHIYUKI NISHIYAMA

Chemical Research Institute of Non-aqueous Solutions
Tohoku University, Katahira 2-1-1, Sendai 980, Japan

Received June 15, 1987; revised January 6, 1988

---

[1] To whom correspondence should be addressed.