JOURNAL OF CATALYSIS **86**, 457–464 (1984)

Redispersion and Migration of Ni Supported on Alumina

INTRODUCTION

The main goal of this note is to provide evidence for the spreading of Ni crystallites on alumina substrates, to a lower equilibrium wetting angle, during heating in O_2 and their contraction, to a larger wetting angle, after their subsequent heating in H_2, as well as on their change in shape, splitting, and sintering. In addition, evidence will be brought concerning rapid migration of Ni crystallites supported on a carbon-contaminated alumina. The method of preparation of thin films of alumina of about 300 Å in thickness which can be used in transmission electron microscopy, as well as the method of deposition of the metal on these films have been already described (*1*, *2*).

Similar phenomena have been already reported from this laboratory. For instance, a few extended Pt crystallites supported on alumina, which formed during heating in wet H_2, fractured into smaller crystallites, after subsequent heating in O_2 (*1*). This happened, however, only after a large number of alternate heatings in O_2 and H_2, during which no changes in the original state of the crystallites occurred. It is interesting to note that some of the crystallites resulted from splitting are located along a torus (see Fig. 3 of Ref. (*1*)). Spreading as well as splitting have been observed for Pd crystallites supported on alumina under less severe conditions than for Pt (*2*). Indeed, during heating in O_2 of Pd crystallites supported on alumina, pits and cavities developed in the crystallites and spreading to a lower wetting angle took place. Spreading was accompanied by tearing and fragmentation (*2*). The few micrographs presented here reveal more clearly that similar phenomena occur for Ni crystallites supported on alumina as well. A thermodynamic explanation for the torus shape which the crystallites of Ni acquire during heating in O_2 is attempted.

WETTING BEHAVIOR OF Ni CRYSTALLITES

Thin films of alumina containing Ni crystallites with sizes in the range of 75 to 450 Å have been heated at 530°C in O_2 and subsequently in H_2, for various periods of time. After each heat treatment, the same areas of the samples were examined by a JEOL 100U transmission electron microscope to follow the changes occurring in individual crystallites. The electron micrographs (Figs. 1a to f) show the time sequence of the same area of a specimen. Figure 1a represents the initial state of Ni crystallites supported on alumina, while Fig. 1b shows the changes which took place during 0.5 h of heating at 530°C in O_2. Crystallites with diameters greater than about 175 Å extended on the substrate and changed their shape from circular to toroidal. However, the torus is divided into a number of interlinked subunits and, in addition, contains small crystallites within the ring. The crystallites with diameters in the range of 50 to 150 Å spread over the surface of the substrate, to a lower equilibrium wetting angle, keeping their original shape. Very small crystallites disappeared. The electron diffraction patterns indicated that most of the Ni crystallites have been oxidized to NiO. Heating in O_2, at the same temperature, for additional 2.5 h did not produce any significant changes (Fig. 1c). A few crystallites spread further on the substrate to a lower equilibrium wetting angle, the width of some of the toroidal crystallites decreased and their edges sharpened. Subsequently, the specimen was heated in H_2 for

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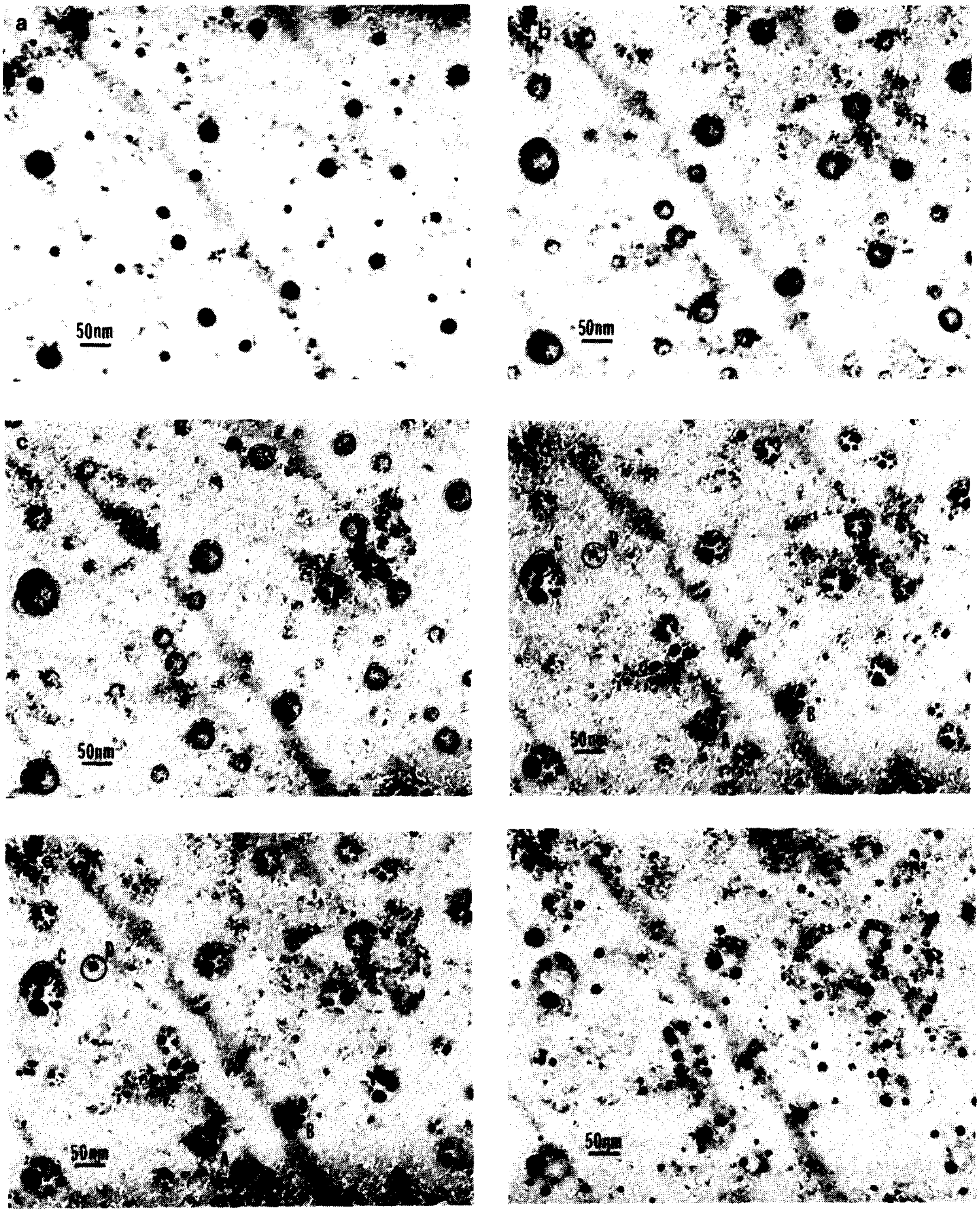


FIG. 1. Time sequence of the same region of a specimen of Ni/Al_2O_3: (a) initial state; heated in 1 atm of O_2 at 530°C for (b) 0.5 h; (c) additional 2.5 h; subsequently heated in 1 atm of H_2 at 530°C for (d) 1 h; (e) additional 1 h; (f) 1 more hour.

1 h at the same temperature (Fig. 1d). A somewhat dramatic change took place during this treatment—the interlinked units of the torus contracted to a greater wetting angle and the splitting of the torus became more obvious. Now, the electron diffraction patterns indicated that NiO was reduced to Ni. Additional heating for 1 h, also in H_2 and at 530°C, produced sintering of crystallites; the resulting crystallites re-

mained however inside the ring of the torus (Fig. 1e). One more hour of heating in H_2 at 530°C produced additional sintering; the sintered crystallites were now located not only inside but also outside the initial ring of the torus. It is clear that some kind of migration of crystallites had taken place.

A few events are marked in Fig. 1. Two neighboring crystallites come in contact (event A in Figs. 1d and e) and coalesce (event B in Figs. 1d and e). A small crystallite disappears, being probably captured by the larger one, either because of migration, or because of direct ripening (events C and D in Figs. 1d and e). We recall that in direct ripening, atoms emitted by a small crystallite move directly to a larger neighboring crystallite. In Ostwald ripening the small crystallites emit atoms to a bulk surface phase of atoms and the large crystallites capture such atoms from this surface phase (*3*).

DISCUSSION

Spreading to a Lower Wetting Angle

The spreading of the crystallites to a lower equilibrium wetting angle during heating in O_2 and their contraction to a larger equilibrium wetting angle during subsequent heating in H_2 is a consequence of the changes in interfacial tensions. Indeed, during heating in O_2, Ni is oxidized to NiO which has a lower surface tension than Ni. In addition, the interfacial tension γ_{sc} between the alumina substrate and crystallites is also decreased (for reasons explained below). The quantity γ_{cs} is related to the surface tensions γ_s of the substrate and γ_c of the crystallites via the expression

$$\gamma_{cs} = \gamma_c + \gamma_s - U_{cs} + U_{str},$$

where U_{cs} is the interaction energy between support and crystallite and U_{str} is the strain plus dislocation energies induced by the disregistry between the lattices of the support and crystallites. The value of γ_{cs} is smaller for NiO on alumina than for Ni on alumina because γ_c and U_{str} are smaller and U_{cs} is likely to be larger for the former. U_{str} is smaller because the disregistry is smaller for NiO/Al_2O_3. Regarding U_{cs}, one may note that the interactions between NiO and Al_2O_3 include not only van der Waals and ionic interactions but also chemical interactions, since, as reported in Ref. (*4*), a chemical compound, namely, an aluminate forms. Even though γ_{cs} can be smaller for NiO than for Ni even without the chemical interactions, the occurrence of the latter greatly decreases the value of γ_{cs}.

The lower values of both γ_{cs} and γ_c for NiO than for Ni lead to a lower equilibrium wetting angle for the former.

CONDITIONS FOR TORUS FORMATION

The torus constitutes the thermodynamically stable shape if the free energy of the system is a minimum for this configuration. It is difficult to perform such a calculation. A comparison between the free energies of droplet and torus like crystallites can, however, suggest a condition in which the torus is preferred thermodynamically to the droplet.

First, let us observe that, in an O_2 atmosphere, the Ni crystallites are oxidized to NiO and the molecules of NiO located at the bottom interact with alumina to form an aluminate. For this reason, it is likely that the part of the substrate, within the central cavity of the torus, in contact with the atmosphere of O_2, is covered with aluminate. Let us assume, for the sake of simplicity, that the surface areas in contact with the substrate and with O_2 are not changed much when the droplet shape is replaced by the torus. This means that when the droplet is replaced by the torus, a part of the substrate, which has the interfacial tension γ_s, is replaced with the central cavity of the torus, where the aluminate covered substrate with an interfacial tension γ_{sa} is in contact with O_2. If $\gamma_{sa} < \gamma_s$, the free energy of the torus configuration is smaller than that of the droplet. Of course, in reality, the surface areas which were assumed to be equal are not really so. A detailed calculation is, however, complicated by the fact

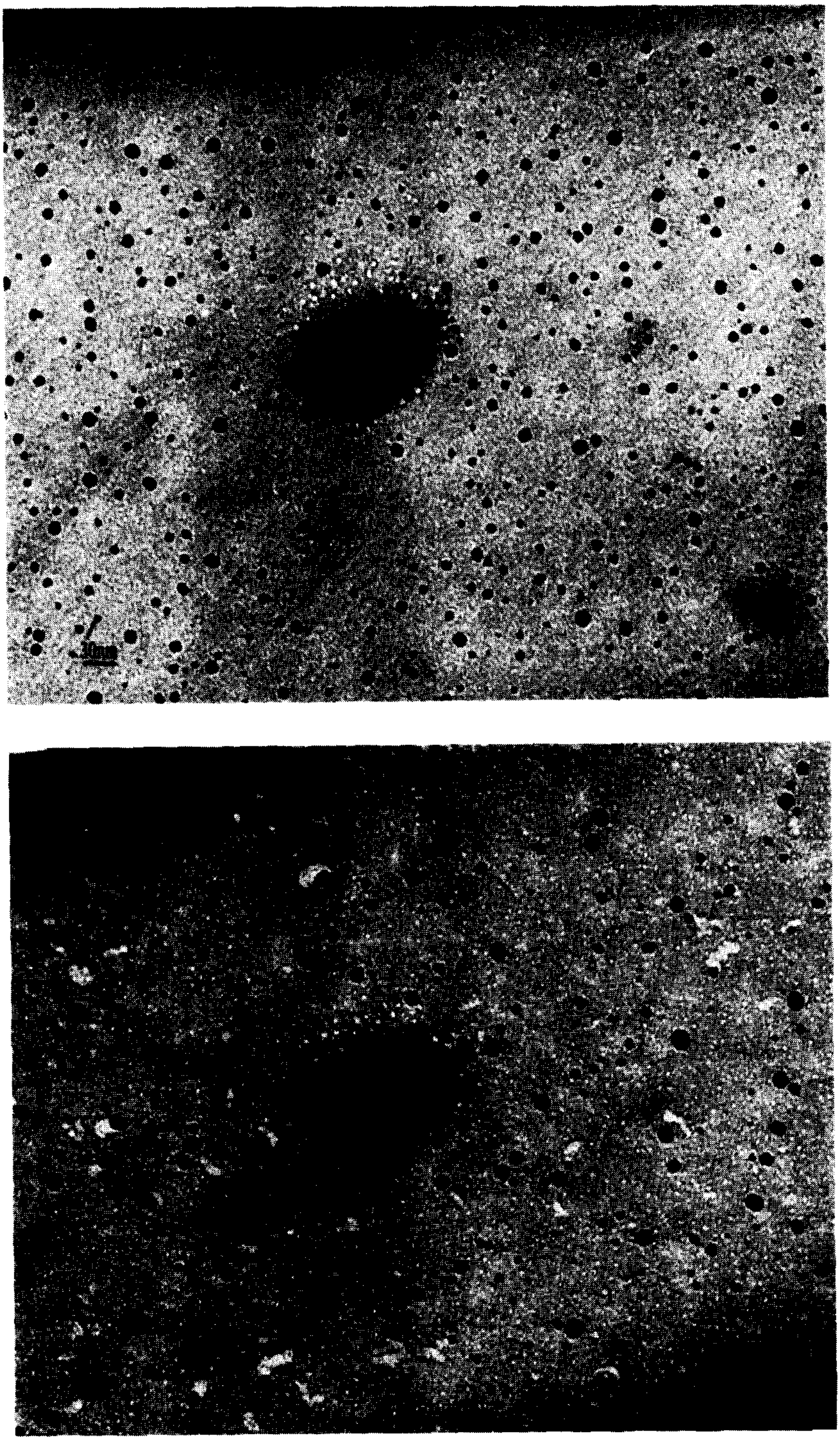
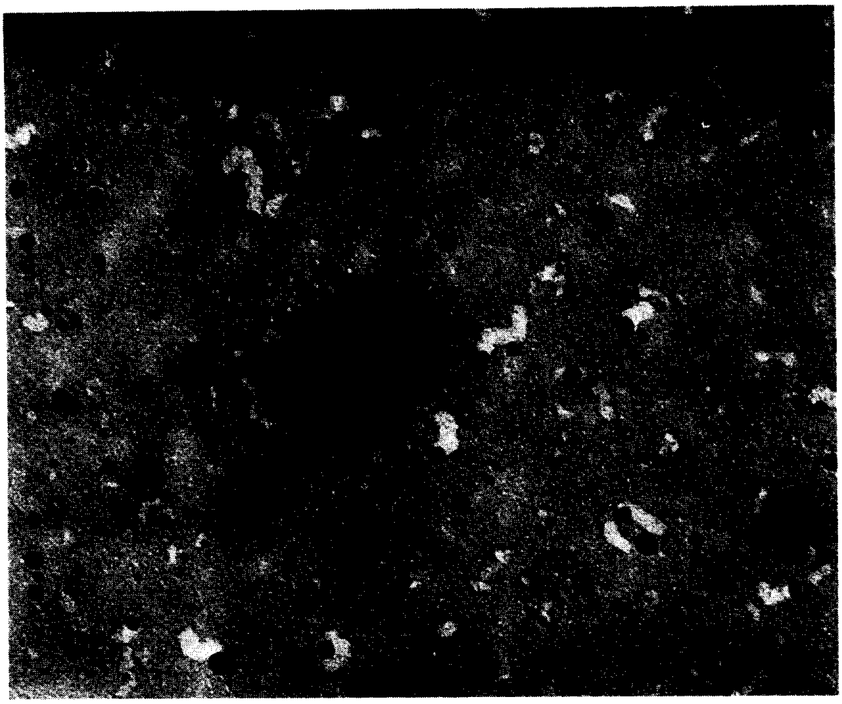


FIG. 2. Time sequence of the same region of Ni/Al_2O_3 specimen: (a) initial state; heated in 1 atm of H_2 at 730°C for (b) 0.33 h; (c) additional 0.5 h; (d) additional 1 h; (e) additional 6 h; (f) 12 more hours.



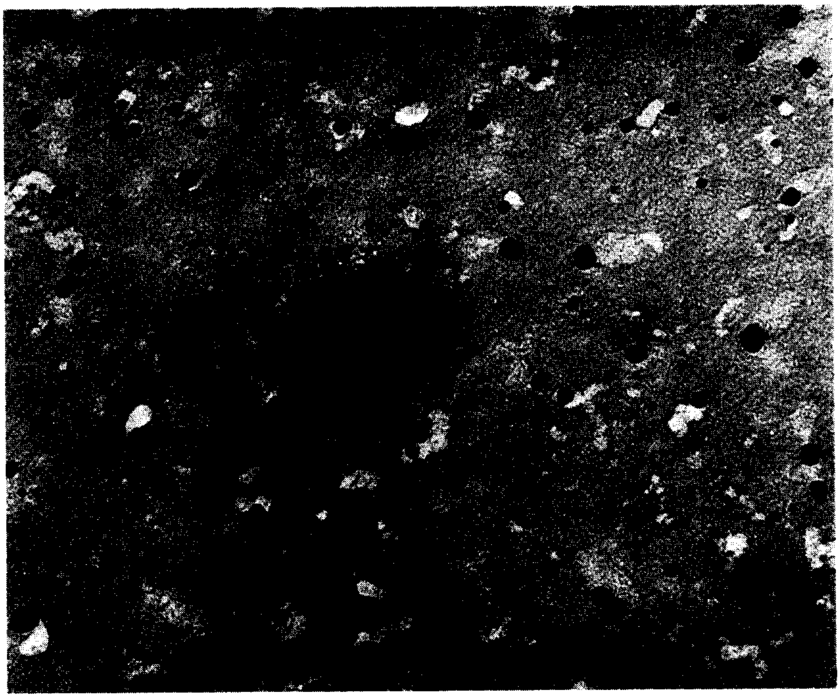


FIG. 2—*Continued.*

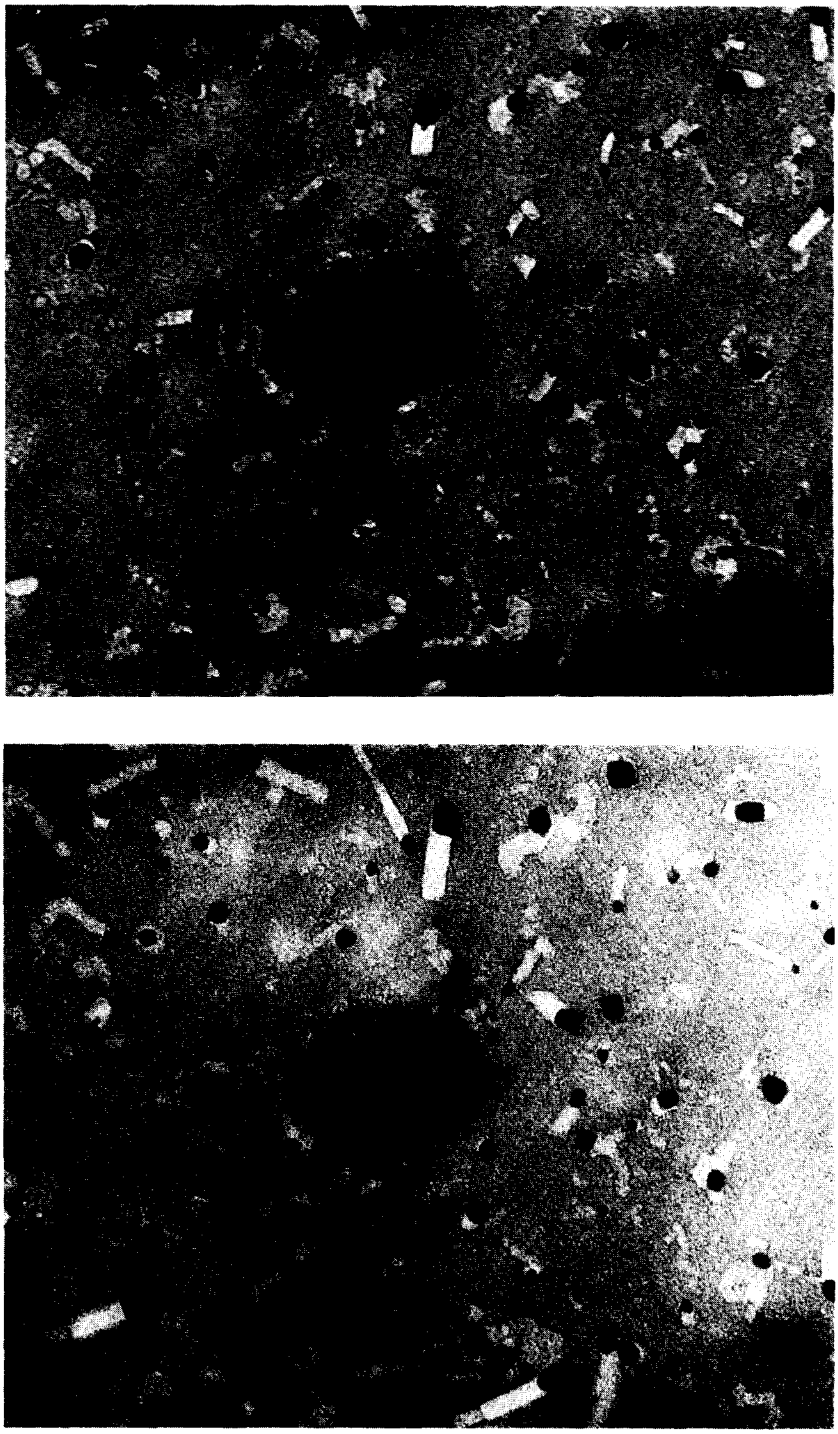


FIG. 2—*Continued.*

that the torus does not have a constant radius of curvature. This happens because the outside equilibrium wetting angle θ differs from the inside equilibrium wetting angle θ', the former being determined by γ_s while the latter is determined by γ_{sa}. It is, however, reasonable to consider that if the above inequality is sufficiently strong, the torus is preferred to the droplet.

Baker *et al.* (*5*) have studied the behavior of platinum particles supported on TiO_2 and observed that during heating in H_2 the platinum crystallites acquired thin hexagonal-shaped flat structures. This happens because, in the presence of Pt, TiO_2 is catalytically reduced by H_2 to Ti_4O_7, and Pt spreads over the substrate as a result of the strong interactions between Pt and Ti_4O_7. (The fact that a "droplet" can have a planar configuration with a very rapid variation of angle near the leading edge had been earlier predicted by Ruckenstein and Lee (*6*) who demonstrated that this occurs when the interactions between the molecules and substrate are moderately strong.) The torus is in this case less stable than the droplet, since the interfacial tension γ_{sa} is likely to be larger than that between Ti_4O_7 and H_2, if a compound is formed between Pt and Ti_4O_7, or equal to the latter, if such a compound does not form.

We cannot yet provide an explanation for the torus observed for Pt on alumina (*1*) (see the Introduction). The large number of alternate heatings have probably introduced in the system impurities, which might be responsible for this behavior.

A possible qualitative kinetic description of the pocess is as follows: Ni is oxidized to NiO and the crystallite spreads over the substrate to a lower wetting angle. The formation of an aluminate at the leading edge of the crystallite accelerates the diffusion of the NiO as well as the rate of oxidation on the surface of the crystallite. The resulting extended configuration is not stable to perturbations. Any thinning of the extended configuration produced by perturbations (such as thermal fluctuations) in some regions will tend to grow, leading finally to the torus which is the more thermodynamically stable configuration.

The more obvious splitting which occurs after subsequent heating in H_2 is due to the contraction of the reduced interlinked subunits of the torus to a greater wetting angle.

The above considerations indicate that the strong interactions between the atoms (molecules) of the crystallite and substrate are responsible for both spreading to a new equilibrium wetting angle as well as the formation of torus. Because the crystallites are relatively thick and the chemical interactions are short range, the support–crystallite interactions can affect directly the catalytic process only at the leading edge of the crystallites and in the enclosed cavity of the torus. However, if aluminate would decrease the surface tension of the torus, it will cover it and this will also affect the catalytic process. Of course, there is also an indirect effect via the shape of crystallites.

MIGRATION OF Ni CRYSTALLITE ON CARBON-CONTAMINATED ALUMINA

In addition to the above observations we like to include here a few electron micrographs (Fig. 2) showing migration of large crystallites on carbon contaminated alumina substrates during the heating of the specimen at 730°C in H_2. Tracks which indicate the rapid movement of the crystallites can be easily identified in the micrographs. Channels have been previously reported for Pt crystallites supported on carbon and heated in O_2 (*7, 8*) and explained as a result of the reaction between O_2 and carbon catalyzed by the metal. A similar explanation is probably valid in the present case also. The reaction between carbon and hydrogen catalyzed by the metal is responsible for the tracks. We note that by heating the above specimen in O_2, the carbon was completely eliminated. The subsequent heating of this specimen alternately in O_2 and H_2 led to phenomena similar to those presented in Fig. 1.

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Received July 1, 1983; revised September 15, 1983