

NOTES

Controlled Atmosphere Electron Microscopy Investigation of Iron Supported on Titania

Previous studies using electron microscopic (1) and spectroscopic techniques (2, 3) have highlighted the complex behavior of iron supported on titania when treated in hydrogen at temperatures above ca. 750 K. In particular, postreduction transmission electron microscopy (TEM) analysis (1) of metallic iron particles formed by H₂/H₂O (100:1) reduction at 700 K revealed two important phenomena upon hydrogen treatment at higher temperatures. First, spreading (or wetting) of iron on the support surface was observed upon treatment at 775 K, as evidenced by the transformation of three-dimensional iron crystallites into particles possessing a "pillbox" or "thin-crystal" morphology. Second, diffuse spreading of iron over the support or diffusion of iron into the support upon treatment was seen at temperatures of 875 K or higher, as evidenced by a decrease in the amount of iron present as distinct crystallites on the titania support. Complementary studies (2, 3) using X-ray photoelectron spectroscopy (XPS) and conversion electron Mössbauer spectroscopy (CEMS) indicated that iron was being removed from the surface and evidenced a change in the chemical state of iron (e.g., γ -Fe; Fe_xTi, 1 $\leq x \leq 2$) upon hydrogen treatment at temperatures of 875 K or higher.

In the present study, controlled atmosphere electron microscopy (CAEM) was used to verify that earlier TEM analyses were indeed representative of the appearance of specimens *during* the various reduction treatments and also to capture transient information that would be lost from a postreaction examination (4). Transmission specimens of titania, 50 to 100 nm thick, were prepared according to the method

described previously (1). Iron was introduced onto the oxide as a thin film approximately 1.5 nm thick, by evaporation of spectrographically pure iron wire at 5×10^{-6} Torr from a tungsten filament. These specimens differed from those utilized in the XPS and CEMS studies, in that TiO₂ films for these latter two spectroscopic techniques were in contact with metallic titanium backings required to support the larger sample areas (ca. 1 cm² for XPS and 25 cm² for CEMS) needed for analysis.

Initial experiments performed with iron-free titania films showed that upon treatment with 2 Torr H₂/H₂O (160:1) at 1200 K, the oxide restructured, with possibly some reduction at the surface. However, this behavior was not uniform across the entire surface, being restricted to those regions of the specimen nearest (ca. $\sim 1 \mu\text{m}$) to the edge of the resistance heater on which the TiO₂ film was suspended. This observation suggests that with nonconducting support media there may well exist an appreciable temperature gradient across the surface. In order to remove the ambiguities created by this edge effect, micrographs were taken only at specimen locations far from the heater edge, where uniform behavior was in all cases observed.

The Fe/TiO₂ specimens were first heated to 670 K in H₂/H₂O (160:1) at 2 Torr. This nucleated the iron overlayer into discrete iron particles which could then be monitored during further hydrogen treatment at progressively higher temperatures. At reduction temperatures of ca. 770 K an unexpected transformation in the particle morphology was observed which is depicted in Figs. 1A and B. These are micrographs taken from the video record of the same





FIG. 1. Fe/TiO₂ during reduction at 770 K. (A) Upon commencement of reduction; (B) same field after 1 h reduction.

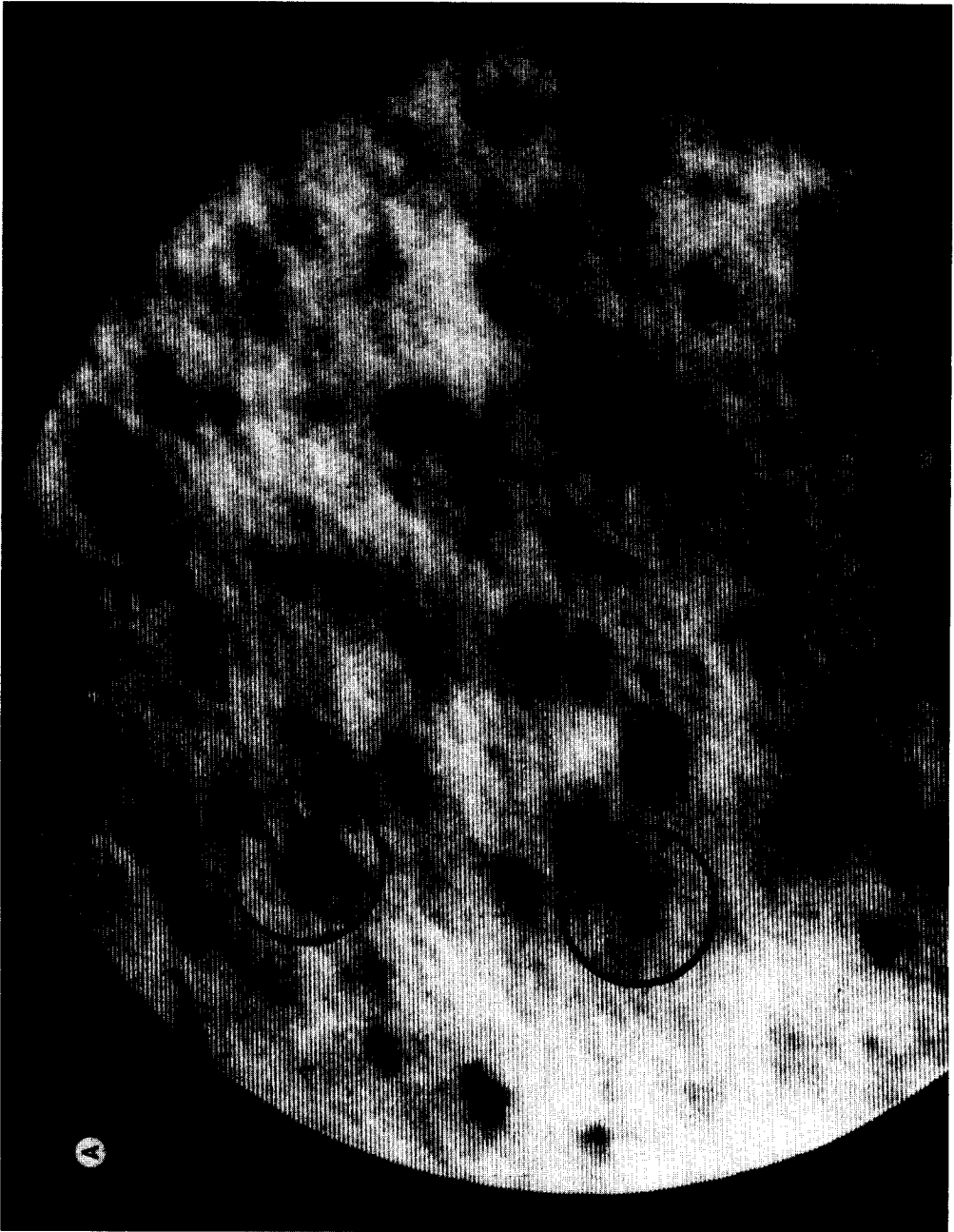




FIG. 2. Fe/TiO₂ during reduction at 1000 K. (A) Upon commencement of reduction; (B) same field after 60 s reduction.

area of the specimen over a time period of about 1 h. It can be seen that the iron particles change from a three-dimensional to an annular morphology. Close inspection of a number of micrographs indicated that on average the particles increased in diameter by about 10% during this restructuring sequence. The observation suggests that spreading of material may be one of the crucial steps involved in the process. Continuous observation of the reaction showed that particles less than 15 nm in size underwent this transformation first, followed by particles in the size range up to 65 nm. Particles greater than 125 nm in size maintained their initial three-dimensional form. That the presence of these annular particles is not the result of experimental artifacts is confirmed by the observation that these annular particles could be formed in the absence of the electron beam, and the continued presence of these particles during (i) defocusing experiments, (ii) cooling of the specimen to room temperature, and (iii) evacuation of the gas atmosphere at this latter temperature. Instead, these annular particles are suggestive of a metal-support interaction. Over a period of several hours at 770 K, the annular particles were observed to divide into a number of smaller crystallites exhibiting low contrast with respect to the support. This behavior conforms with the results of earlier postreduction TEM analyses (1) which noted both the adoption of "thin-crystal" morphologies and a decrease in particle sizes following reduction for similar periods of time at this temperature. It should be noted that annular structures could be observed using such postreduction TEM techniques, provided that appropriate reduction histories (e.g., short reduction times at 770 K) were employed.

These results are consistent with a model in which iron atoms migrate from iron surfaces to freshly reduced regions of the titania support adjacent to the particles. If, in fact, hydrogen is better able to reduce titania adjacent to iron particles compared

to titania beneath iron particles, then a driving force is established for transporting iron. In short, the enhanced metal-support interaction at the more reduced regions of the support drives iron from those regions of the support that are covered by iron to those adjacent regions of the support that are exposed to hydrogen. By analogy with previous studies of the spreading of iridium on graphite in hydrogen (5, 6), it may be suggested that the iron particles do indeed possess sufficient atomic mobility, particularly in the surface layers, to show this transport at 770 K.

When Fe/TiO₂ samples, that had been treated in hydrogen at 670 K, were quickly raised in temperature to 1000 K a different type of metal-support interaction was observed. Figure 2A shows the appearance of the specimen immediately after raising the temperature to 1000 K. Two particles have been selected (circled) to illustrate the change which occurred after remaining at this temperature for approximately 60 s, which is the case shown in Fig. 2B. Comparison of Figs. 2A and B suggests a disappearance of iron particles. Continuous observation of this same field of view also revealed that in some cases crystallites which had apparently disappeared could reappear seconds later, indicating that at least part of this effect might arise from diffraction phenomena (7). However, these diffraction effects are transitory, since prolonged observation of this field of view indicated a net decrease in the number of distinct iron crystallites. This latter result is in accord with the observations from earlier postreduction TEM studies (1). In addition, spectroscopic studies (2, 3) suggest that at least part of this disappearance of iron particles results from the diffusion of iron into the support, accompanied by the formation of dispersed and strongly interacting iron (e.g., γ -Fe, Fe_xTi).

In summary, CAEM investigation of model Fe/TiO₂ systems has enabled direct observation of the morphological changes of Fe particles during reduction. This capa-

bility has been used not only to verify the results of earlier work, but also to uncover a transformation of Fe crystallites (into annular particles) not previously appreciated using postreduction TEM techniques.

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