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# Effect of Wetting on the Morphology of Supported Platinum Crystallites

In a recent paper, Ruckenstein and Chu (*1*) introduced some very interesting concepts to account for the observed redispersion of platinum crystallites supported on alumina in oxygen at 1025°K following several cycles of alternating oxygen and hydrogen treatments at the same temperature. They postulate that redispersion occurs in an oxygen environment as a result of spreading of platinum oxide over the surface of the alumina. Two situations are considered, one in which the crystallites are completely oxidized and as a consequence no wetting angle exists between the crystallites and the support, and the other, where partial oxidation of the crystallites produces a "two-dimensional fluid" layer of oxide which coexists with the metal crystallites. They further suggest that heating in hydrogen causes sintering as platinum oxide is converted to metal which does not wet the alumina.

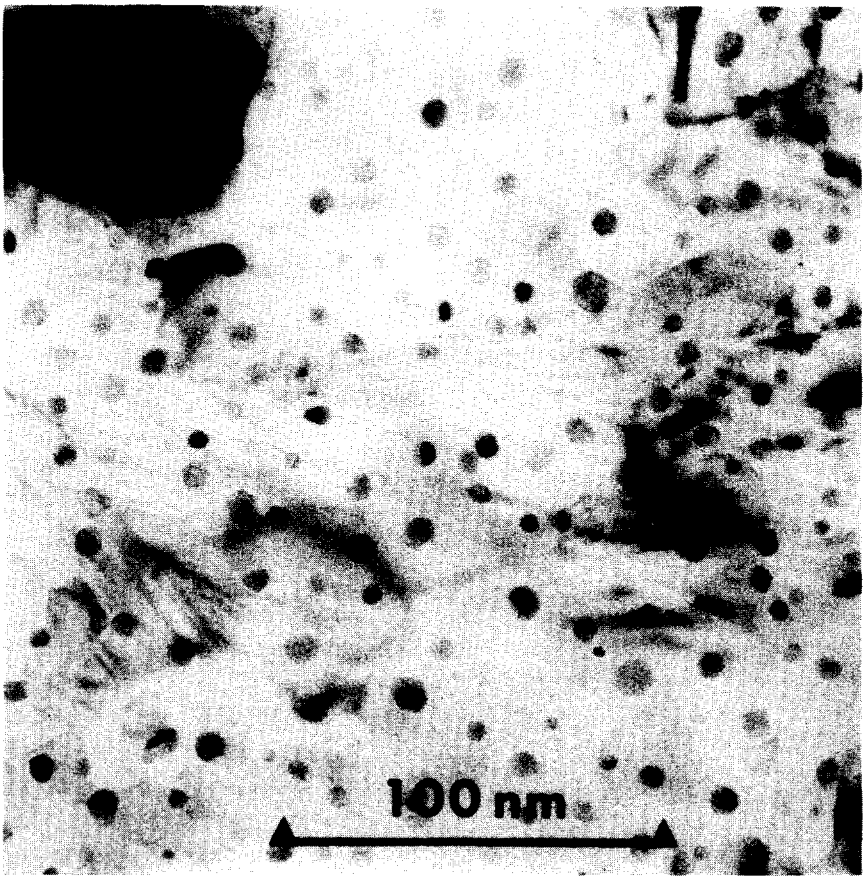

FIG. 1. Transmission electron micrograph of a Pt/titania specimen after heating in $H_2$ at 1025°K for 1 hr.

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The purpose of this paper is to present further support for these concepts and demonstrate how they can be extended to explain the differences in behavior of Pt on titanium oxide when heated in oxygen and hydrogen atmospheres. Earlier studies performed in this laboratory (*2*, *3*) have shown that if the Pt/titanium oxide system is heated in hydrogen at 825°K or higher, then the Pt crystallites were predominantly hexagonal in outline, of uniform thickness and very thin, suggestive of a pillbox morphology, Fig. 1. At the same time the substrate also transformed to a lower oxide, $Ti_4O_7$. Treatment of the sample in this condition with oxygen at 875°K caused the Pt crystallites to not only increase in average size, but also to become quite rounded in outline and dense, characteristics of a globular morphology, Fig. 2. Electron diffraction examination of the support showed that after oxidation it was converted to $TiO_2$.

At first sight it would appear from examination of Fig. 3, a schematic comparison of the observed behavior of the two systems, that the results are in direct conflict. This apparent contradiction is readily resolved when one examines the critical factors controlling the shape of metal crystallites on a support.

Consider the equilibrium situation of a metal particle sitting on a support surface in the presence of a gaseous environment. If the particle is cap shaped, its contact angle $\theta$ in a metal–gas–support system is determined by Young's equation:

$$\sigma_{gs} = \sigma_{ms} + \sigma_{mg} \cos \theta, \qquad (1)$$

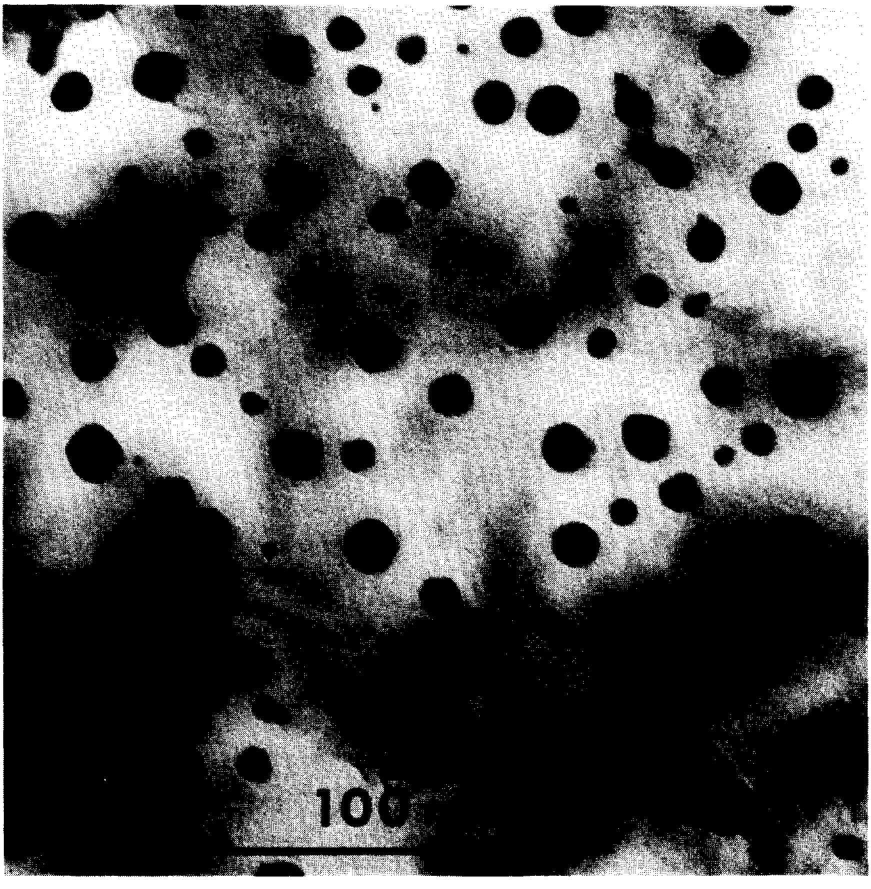

FIG. 2. Transmission electron micrograph of a Pt/titania specimen after heating on $O_2$ at 1025°K for 1 hr.

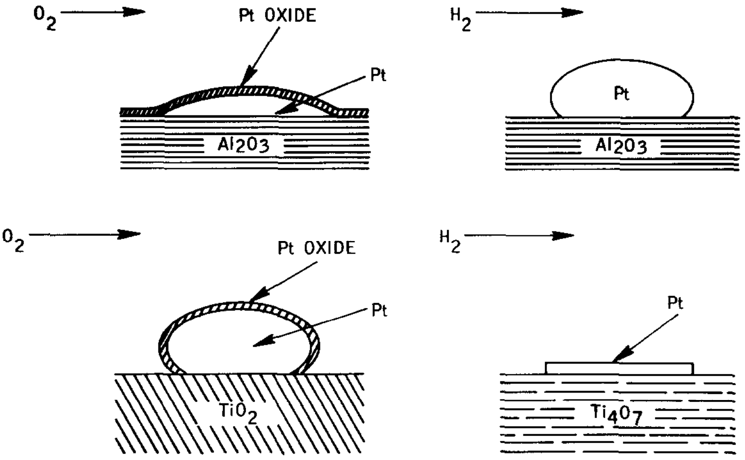

FIG. 3. Schematic representation of the growth characteristics of Pt crystallites on alumina and titania in $O_2$ and $H_2$ environments.

where the notations are the same as those used by Ruckenstein and Chu (1). Transforming Eq. (1),

$$\cos \theta = \frac{\sigma_{gs} - \sigma_{ms}}{\sigma_{mg}}.$$

If the two systems are now analyzed in terms of this relationship some interesting predictions emerge. First, for the case where both are heated in oxygen:

At 1025°K, $\sigma_{gs}$ for alumina is 769 ergs $cm^{-2}$ and that for titania, 546 ergs $cm^{-2}$ (calculated from expressions given in Ref. (4)). Also $\sigma_{ms}$ will be smaller for $Pt/Al_2O_3$ than for $Pt/TiO_2$, since the likelihood of formation of a surface Pt aluminate is higher than a Pt titanate. As $\sigma_{mg}$ is the same for both systems, then the differences seen for $\sigma_{gs}$ and $\sigma_{ms}$ lead to the conclusions that the probability of wetting by a two-dimensional layer of platinum oxide is much higher on an alumina than on a titania support. It is therefore not surprising to find that Pt crystallites on $TiO_2$ tend to assume the energetically preferred shape of a globule.

In contrast, the nonstoichiometric oxide, $Ti_4O_7$, produced by heating the Pt/titanium oxide system in hydrogen at temperatures >825°K, will have an extremely high value for $\sigma_{gs}$. Consequently in this case one would anticipate that wetting and spreading of the metal on the support will be facilitated and as a result the crystallites will grow as very thin flat structures.

It is evident that the behavior of Pt/titanium oxide treated in oxygen and hydrogen is completely compatible with the arguments of Ruckenstein and Chu (1), but it is also apparent from these experiments that the nature of the support can also be a factor in inducing changes in the morphology of a given metal.

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