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Direct Observation of Wetting and Spreading of Copper Particles on Magnesium Oxide

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Supported metal catalysts were exposed to various oxidizing and reducing gas atmospheres during their preparation, operation, and regeneration. Interaction with these gases had profound effects on their morphology. In the present investigation a controlled atmosphere electron microscope was used to follow the changes of the morphology of copper particles supported on magnesium oxide in oxygen and hydrogen environments. When the system is heated in oxygen at 200°C, the metal particles undergo an unusual transformation, discrete solid crystallites changing to toroid shaped oxide structures. Subsequent treatment in hydrogen at 200°C results in a conversion back to the initial metallic form. These results are discussed in terms of a volcano structure, in which particles consist of a molten core surrounded by a porous solid skin.

INTRODUCTION

In a previous paper (*1*) we reported on the wetting and spreading behavior of iridium particles supported on graphite when heated in hydrogen at 965°C. The results were rationalized in terms of a model in which particles had a cherry-like structure, consisting of a "hard-core" surrounded by a "viscous" layer. One of the implicit assumptions made in the development of the model was that no chemical compound was formed between iridium and hydrogen at 965°C.

In the present investigation we have attempted to extend this approach to cover the situation where a chemical compound is formed between the supported particles and the gas to see how this new set of circumstances modifies the previous arguments. The system selected for this purpose was copper supported on magnesium oxide, which was expected to exhibit diverse behavior in oxygen and hydrogen environments.

Previous workers (*2*) have examined copper/magnesium oxide catalysts in the electron microscope but only for the purpose of determining the average particle size of the metal crystallites, and no mention was made of their morphological characteristics. The shapes of copper particles supported on α-alumina have been determined by elegant transmission electron microscopy experiments (*3*) and, from this work, an attempt was made to evaluate the interfacial energy parameters of the system. Unfortunately, these measurements were made after the specimen was cooled to room temperature and removed from the reactive gas environment, and, as a consequence, the conclusions may be subject to considerable error.

The present dynamic approach not only overcomes these drawbacks but enables the kinetic aspects of spreading as a function of time and particle size to be determined. When the copper/magnesium oxide system is heated in oxygen at 200°C, the metal particles undergo an unusual transformation, discrete globular crystallites changing to toroid structures. Subsequent treatment in hydrogen at 200°C results in a conversion back to the initial form or smaller particles.

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These results are discussed in terms of a volcano structure, in which copper particles consist of a molten core surrounded by a porous solid skin when heated in an oxygen environment.

EXPERIMENTAL

The work described here was performed in the controlled atmosphere electron microscope (*4*) using model and conventionally prepared copper–magnesium oxide catalyst systems. Efforts to make self-supporting thin films of magnesium oxide proved to be unsuccessful, and so an alternative approach was adopted. The model catalyst was prepared by placing a single drop of a dispersion of magnesium oxide in butanol onto transmission specimens of single crystal graphite. Magnesium oxide was obtained by heating magnesium hydroxycarbonate in air at 550°C for 2.0 h. Copper was introduced onto these specimens by evaporation of spectrographically pure copper wire from a tungsten filament at a residual pressure of 10^{-6} Torr. The metal was added in an amount sufficient to produce at least a monolayer coverage on the support surface.

Conventional catalysts were made according to the following procedure. Appropriate quantities of $MgCl_2$ and $CuCl_2$ were coprecipitated with K_2CO_3 at 70°C to yield approximately 8% copper on MgO. The catalyst was activated under hydrogen at 520°C for 16 h. Electron microscopy specimens were produced by dispersing the powdered catalyst onto single crystal graphite substrates.

There are a number of advantages in using this type of specimen design. Graphite is an excellent conductor of energy in a radial direction, consequently heat transfer from the platinum heater ribbon is uniform across the specimen, and heating effects from the electron beam are minimized as the energy is dissipated through the support. Occasionally thin sections were found to protrude from the edge of the underlying graphite making these particularly good regions for unambiguous observations of the Cu/MgO interaction. However, since the behavior of copper on graphite in both H_2 and O_2 had been previously established (*5*), it was not a difficult task to isolate the interaction of Cu with MgO superimposed on the graphite. Finally, separate experiments where Cu was omitted from the system showed no evidence of an interaction between MgO and graphite, under the conditions used in this work.

The reactant gases used in this work, helium, oxygen, and hydrogen, had a stated minimum purity of 99.999% (Scientific Gas Products, Inc.) and were used without further purification.

RESULTS

(*a*) *Model Copper/Magnesium Oxide–Graphite System*

Nucleation of the evaporated copper film into discrete particles was achieved by heating specimens in 1 Torr helium to about 175°C. This process was terminated at 415°C, a condition where the particles had grown in size to between 10 to 40 nm.

A dramatic change in particle morphology was observed when these specimens were heated to 200°C in 5 Torr oxygen. Particles changed from a solid to toroid (or donut) geometry over a period of about 1.0 min at this temperature. This transformation is shown in the two photographs, Figs. 1A and B, taken from the TV display, and schematically in Fig. 2, process (A). Defocusing experiments verified that these were real structures and not merely artifacts produced by perturbations in the transmission image. Detailed analysis indicated that this behavior was restricted to particles between 18 ± 4 and 47 ± 7 nm in width, and that the smaller particles within this size range underwent the transformation process first. There was also a change in particles <18 nm diam.; in this case the original dense globular form gave way to a thinner appearance. In contrast, large particles, >47 nm in size, did not appear to exhibit

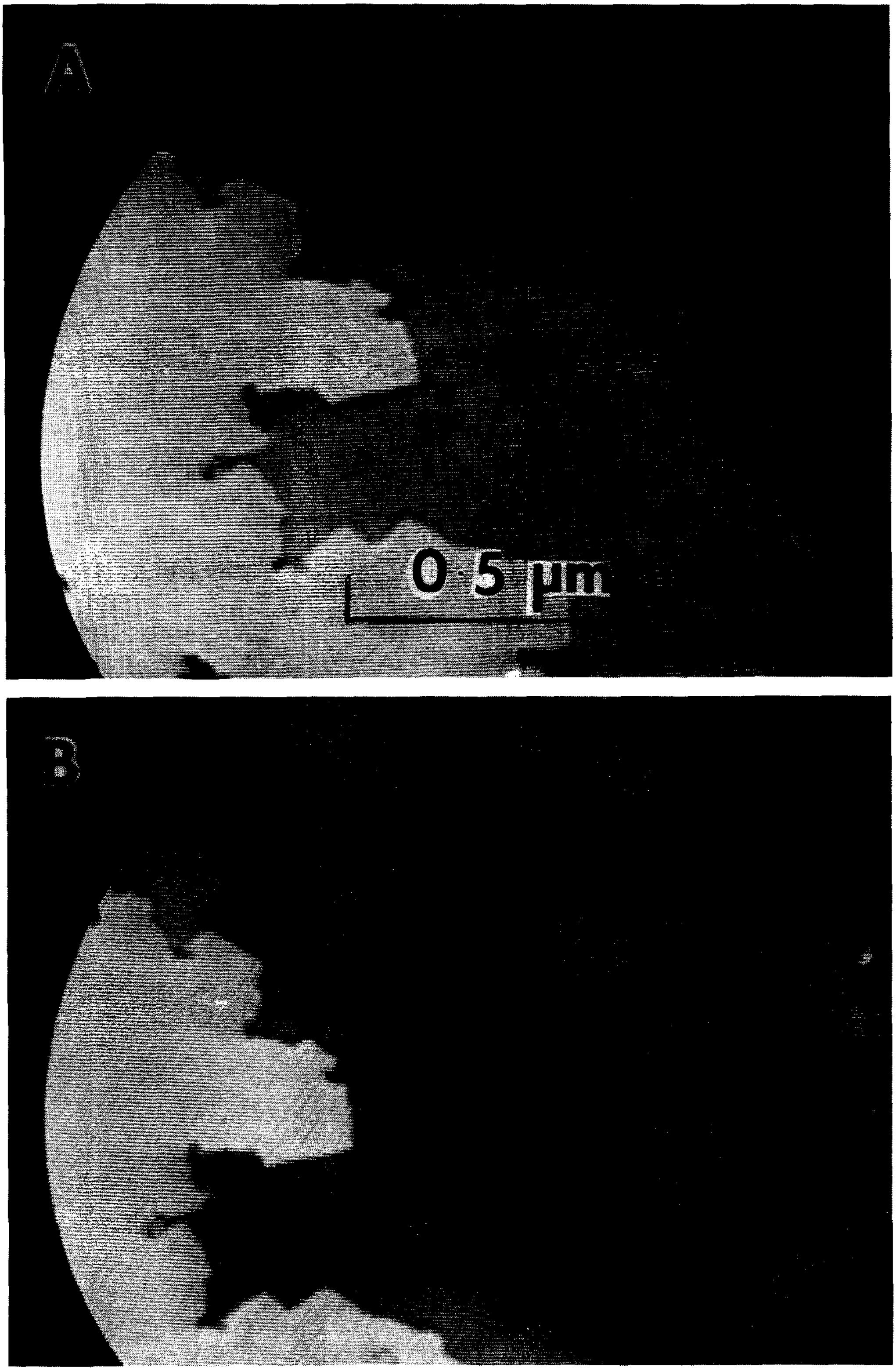

FIG. 1. Sequence (A)–(B) showing the change in the morphology of copper particles supported on magnesium oxide at 200°C in 5 Torr O_2. Time interval between frames is 60 s.

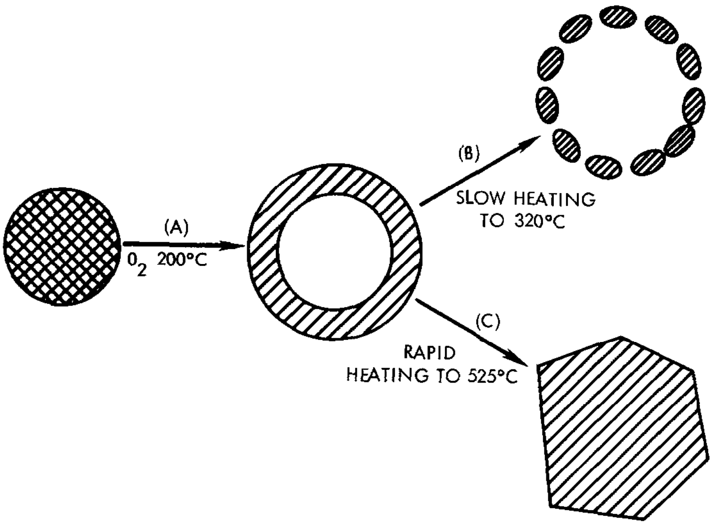

FIG. 2. Schematic representation of the change in particle morphology on heating Cu/MgO in oxygen.

any appreciable change. Quantitative kinetic analysis of the recorded particle spreading sequences also provided valuable information on the criteria surrounding the transformation of particles from a globular to a toroid form. Figure 3 shows spreading data for four typical particles of initial sizes; 24.7 nm (A), 41.1 nm (B), 46.0 nm (C), and 63.8 nm (D) when heated in 5 Torr O_2 at a set temperature of 200°C. On this plot the closed and open symbols relate to the outer and corresponding inner particle

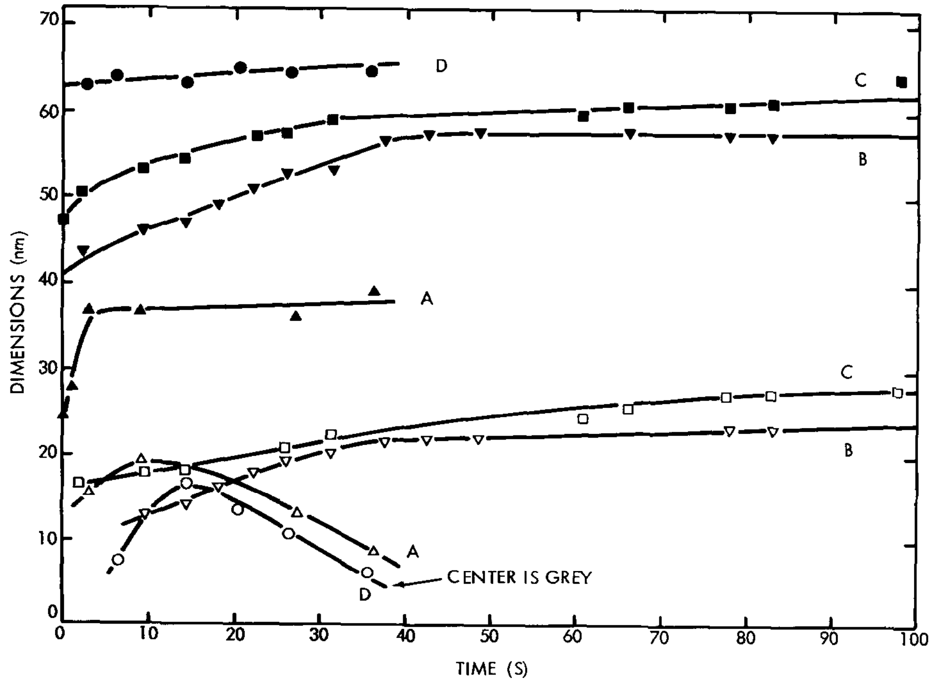

FIG. 3. Spreading data of four particles as a function of time.

diameters, respectively. The particles (B) and (C) are examples of particles which readily transform and maintain the toroid shape. (D) is a relatively large particle containing a small greyish core, which quickly disappears while the outer diameter remains constant; no torus was produced in this case. Finally (A) the smallest particle immediately spreads to a large extent, quickly erasing the existence of the annulus.

The eventual fate of the toroid shaped particles was extremely dependent upon the heating rate and temperature to which specimens were raised. Heating slowly to 320°C and holding at this temperature for about 20 min resulted in rupture of the ring to form numerous small particles, Fig. 2, process (B). The pattern of behavior was quite different if the temperature was rapidly raised and held at 525°C. In this case, in-filling of the torus occurred to produce thin, flat faceted particles (Fig. 2, process (C)).

On continued heating to higher temperatures, all particles exhibited the same characteristics. At 600°C the outline of particles became rather diffuse due to spreading of material across the surface. Even though the reaction temperature was well above the Tammann point for either Cu_2O (481°C) or CuO (526°C), no particle motion was observed suggesting that a significantly strong interaction existed between the copper oxide particles and the magnesium oxide support. Specimens were heated to a maximum temperature of 675°C, at which point there was no detectable evidence for the existence of any of the original particles. Rapid cooling of specimens to room temperature did result in the reformation of some particles, a fraction of which exhibited a toroid geometry.

If the oxygen environment was replaced by 1 Torr hydrogen, then, on subsequent reaction at 200°C, many more particles were observed to reform as very dense globular entities about 5 nm in size. It was also noticeable that any particles, which had remained in the toroid form after the oxygen treatment, also transformed to the more conventional solid configuration. As the temperature was gradually raised to 450°C, the average particle size increased to 50 nm, the particles still maintaining a dense globular morphology. As with the previous system, no particle movement was detected, even though the temperature was above the Tammann point for copper (405°C), indicating that particle growth was probably occurring by an atomic migration mode (*6*). As the temperature was increased, not only did sintering cease, but particles actually decreased in size, and ultimately, at 675°C, they completely disappeared from the surface. If the temperature was reduced at this stage to about 365°C, then renucleation and growth of particles was once again observed. The reversible nature of this process was demonstrated in later experiments where the temperature was continuously cycled between 365 and 676°C. Furthermore, the overall differences in particle characteristics observed between oxygen and hydrogen environments were also shown to be reversible from experiments where specimens were alternatively treated by oxygen and hydrogen.

(*b*) *Conventionally Prepared Copper/Magnesium Oxide Catalyst–Graphite*

When the "real" catalyst (8% Cu/magnesium hydroxycarbonate) was treated in 1.0 Torr hydrogen, particles of 3–4 nm diam. became visible at 200°C. On continued heating up to 450°C, the particles increased in average size to 25 nm, and, as with the model system, no particle motion was observed. When the hydrogen was replaced by 5.0 Torr oxygen, the majority of dense metal particles were observed to change to the torus morphology at 200°C. Although the specimens were heated to higher temperatures, the textural features of the support media obscured many of the detailed aspects seen with the model system. However, on switching back to the hydrogen environment, it was apparent that the torus-shaped particles had all reverted back to their initial globular form at 225°C.

DISCUSSION

The most prominent feature to emerge from this work is the finding of a dramatic change in particle morphology accompanying the reaction of Cu/MgO specimens when heated in oxygen. The similarity in behavior of model and real systems confirms that this is a genuine effect and not just an artifact associated with the model catalyst. Before attempting to present a rational argument to account for this phenomenon, it is worthwhile stressing some of the critical features surrounding the formation of these extraordinary particle shapes.

It was found that the torus-shaped particles revert back to a solid geometry on treatment with H_2 at about 200°C. Also, they can be restored by heating in O_2, demonstrating the reversible nature of the process. This type of morphology appears to be restricted to a narrow particle size range 18 to 47 nm, and, furthermore, particles only maintain this conformation at temperatures below 400°C. Finally, perhaps the poignant aspect is that the onset of the transformation occurs at 200°C, i.e., well below the Tammann temperatures of copper or its oxides.

The notion of a certain degree of atomic motion existing within the catalyst particles during the transformation must play an important role in the development of any proposed model. We suggest that, in the present system, the extra heat required to generate such atomic motion arises from the exothermic interaction of copper with O_2. The support for such a hypothesis is seen from a theoretical examination of the relationship between the size of copper particles and ΔT, the initial calculated temperature change due to oxidation of such particles, assuming that there is ideally no, or at most minimal, heat transfer to the support in the very first reaction stages. Since the thermal conductivities of copper and magnesium oxide are 0.95 and 0.087 cal s^{-1} cm^{-1} $°C^{-1}$, respectively (*7*), it is probable that most of the heat created in the transformation is originally retained by the metal particles.

An estimate of the heat imparted to the particles from the interaction of oxygen to form either Cu_2O or CuO can be obtained from the following calculations, where

ΔT	temperature elevation (°C)
C_{sp}	specific heat of copper (0.092 cal g^{-1} K^{-1})
D	particle diameter (nm)
ρ	specific gravity of copper (8.92)
a	the area per surface copper atom (0.065 nm^2); this value is based on a Cu–Cu distance of 0.255 nm, and 2 Cu atoms/unit cell.
ΔH	enthalpy of reaction (kcal mol^{-1}) (for CuO: −37.7; and for Cu_2O: −40.55)
S	reaction stoichiometry (CuO: 1; and Cu_2O: 2)
N	Avogadro's number (6.02×10^{23} mol^{-1})
n	number of oxide layers initially formed.

ΔT is first expressed in terms of Q (the heat released in converting 1.0 g of Cu into either Cu_2O or CuO), M the weight of copper in a given sized particle, and C_{sp}:

$$\Delta T = \frac{Q}{C_{sp} \times M}. \qquad (1)$$

If we assume that the initial shape of the particles is near spherical, i.e., they are in a nonwetting condition, then the volume V is given by:

$$V = \frac{\pi D^3}{6}$$

Then,

$$M = \frac{\pi D^3}{6} \times \rho \qquad (2)$$

and

$$Q = -\Delta H \times \frac{\pi D^2}{a \times N} \times \frac{n}{S} \text{ kcal mol}^{-1}. \qquad (3)$$

Substituting for Q and M in Eq. (1) we get

$$\Delta T = \frac{-6 \times \Delta H \times n}{C_{sp} \times N \times a \times D \times \rho \times S}. \quad (4)$$

Substituting numerical values into Eq. (4) gives

$$\Delta T = \frac{-186.9 \times \Delta H(\text{kcal mol}^{-1}) \times n}{D(\text{nm}) \times S}.$$

Plots of ΔT as a function of particle diameter D, are presented in Figs. 4 and 5, for the cases of CuO and Cu_2O formation, respectively. It is clear from these dependencies that the temperature of the metal particles, particularly those below 50 nm in size, can be significantly increased due to oxidation of only the outer layer of the copper particles and, as a consequence, reach a temperature above that of the Tammann point of the metal. This data also indicates that if only a monolayer of the particle surface is oxidized then formation of a Cu_2O state is doubtful, since the predicted size range of annular particle is extremely narrow and does not correspond to the experimentally determined sizes. If, however, the calculations are extended to cover the condition where $n = 2$ for the formation of Cu_2O, then the predicted size range where annulus formation occurs would be 26 to 38 nm (Fig. 5) and is in good agreement with experimental observations.

A literature search does not allow us to make any definite conclusions regarding the question as to which oxide of copper would be expected to form at 200°C in the presence of 5.0 Torr oxygen. Rao and co-workers (*8*) used Auger electron spectroscopy to study the surface oxidation of copper and found evidence for the existence of copper in an oxidation state higher than +1 at 225°C, at fairly low oxygen exposures. Garnaud (*9*) followed the oxidation of copper sheets in air by thermogravimetry and established that CuO was formed in the temperature range 400 to 600°C. However, according to Oudar (*10*), at 5 Torr oxygen and 550°C a coherent layer of Cu_2O should be formed instantaneously. In view of this

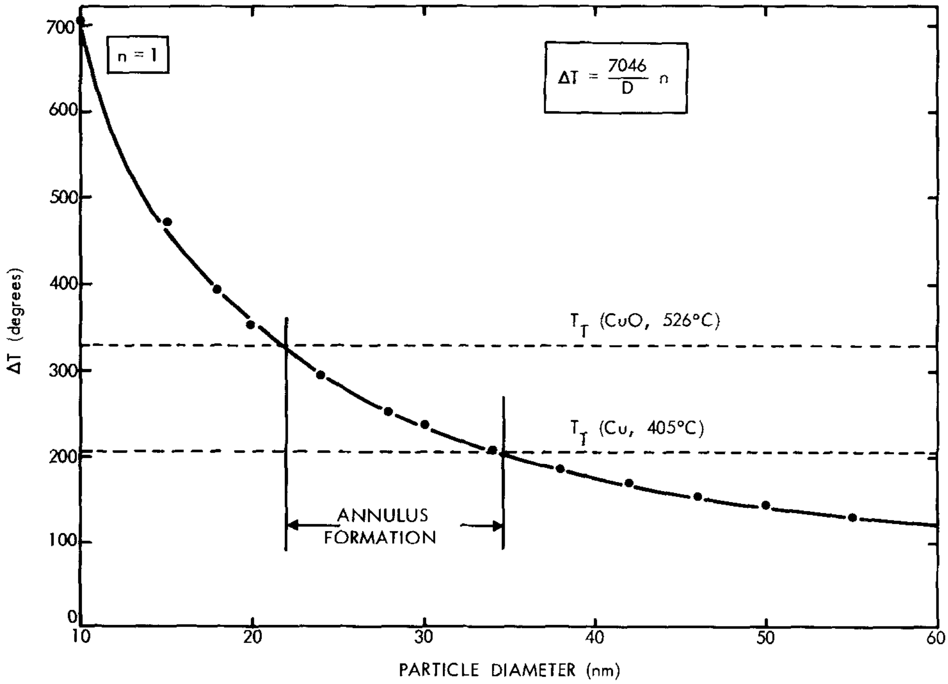

FIG. 4. Calculated temperature elevation as a function of particle size for the reaction Cu + $O_2 \rightarrow$ CuO.

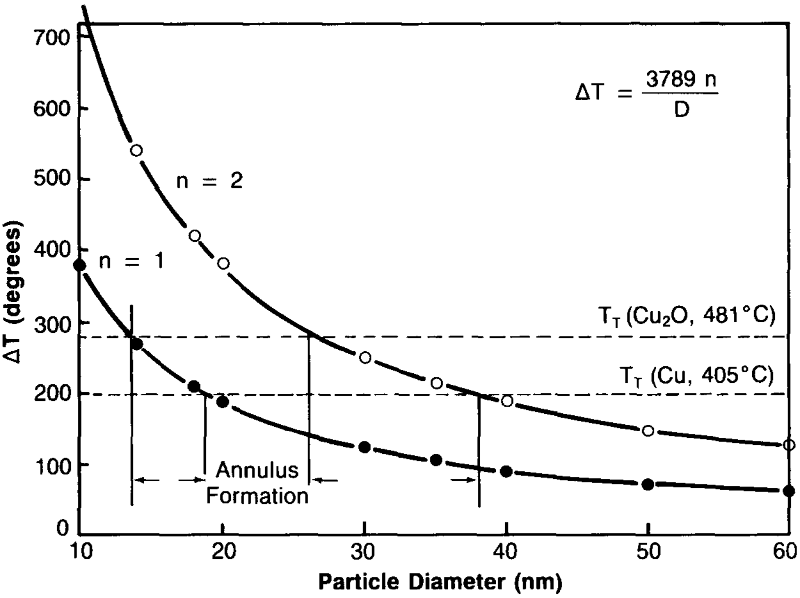

FIG. 5. Calculated temperature elevation as a function of particle size for the reaction Cu + $O_2 \rightarrow Cu_2O$.

controversy, we shall not speculate as to which particular oxide is formed under the current conditions.

THE "SOFT CORE" MODEL

Based on the accumulated experimental information, we have developed the model depicted schematically in Fig. 6 to account for the transformation process of solid to torus-shaped particles. Since it is not known whether copper does or does not wet MgO, we have included two alternative starting situations (A). It should be appreciated that this is not a critical aspect of the mechanism.

It is suggested that, following the initial reaction of copper with O_2 at 200°C, only the outer layers of the particles are converted to oxide. Calculations have demonstrated that this reaction will release sufficient heat to increase the whole particle temperature to 405°C (Tammann temperature of Cu) and provided the temperature does not exceed 526°C (Tammann temperature of CuO), the situation (B) should be attained, where the particles consist of a molten metallic core surrounded by a solid oxide skin. Under these conditions, the core will expand causing the skin to crack or become porous and enable metallic species to diffuse to the surface, resulting in the further build-up of oxide at the particle boundaries (C). Eventually situation (D) will be realized when all the metallic core has disappeared and only a very thin residual oxide layer covers the central regions of the particle, the bulk of the material now residing at the periphery. It follows that this structure, when viewed by electron transmission, would appear as a torus.

From this model, one can explain the behavior of the smaller and larger particles discussed earlier. There should be a minimum and a maximum size for particles which show this effect. This size range will depend on the set temperature. Particles which are too small will immediately tend to spread as both Cu_2O and CuO wet MgO and, the real particle temperature being higher than 526°C, the kinetic limitations will be overcome. By contrast, the reaction heat input for larger particles will be too small to induce Cu atom mobility.

At a set temperature of 200°C, the tem-

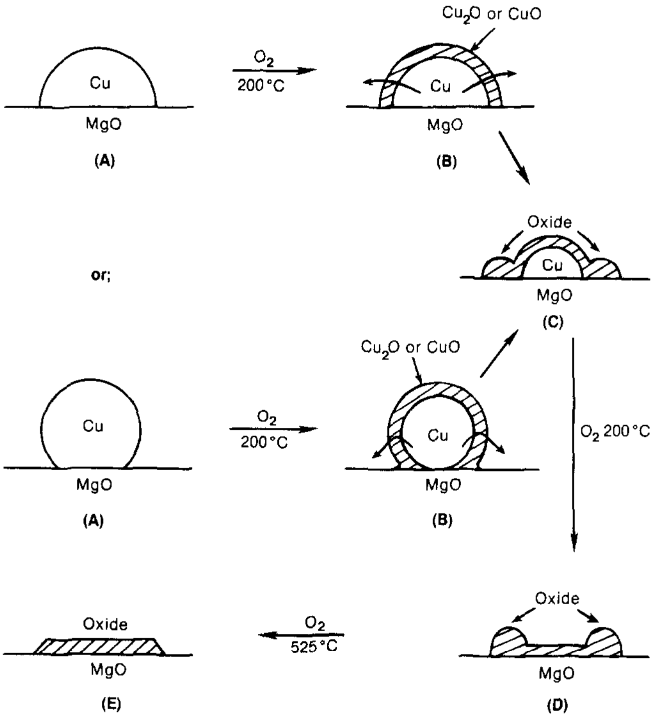

FIG. 6. The "Soft Core" model.

perature elevations required to reach the Tammann temperatures of Cu, Cu_2O, and CuO are 205, 281, and 326°C, respectively. From Fig. 4, it can be seen that the arguments presented above lead to the following limiting particle sizes D_{min} = 22 nm; and D_{max} = 35 nm for the condition where only the outer monolayer of the particles are oxidized and CuO is formed. For the case where the oxidation extends to the two outer layers and Cu_2O is formed then from Fig. 5, the limiting sizes are D_{min} = 26 nm and D_{max} = 38 nm. It also follows that one would expect the smaller particles in these size ranges to undergo the transformation to form toroids first. The agreement between these values and those obtained experimentally, D_{min} = 18 nm and D_{max} = 47 nm, is satisfactory, especially since in the proposed model there is an inherent assumption that all the heat from surface oxidation processes is recovered by the copper core.

As the reaction temperature is progressively raised, a point will be reached where the oxide species become mobile and in-filling of the torus shapes will occur as oxide spreads and wets MgO (E). Reduction of copper oxides by H_2 would be expected to result in the reformation of Cu particles exhibiting the conformation shown in (A), which was observed.

The transformation of particles from a globular to torus form has been reported for other supported metal–gas systems. Tatarchuk *et al.* (*11*) used controlled atmosphere electron microscopy to continuously monitor the appearance of iron particles supported on titanium dioxide when heated in hydrogen. At 500°C, particles up to 65 nm in size exhibited a morphological change from a solid to torus geometry. This observation was rationalized in terms of a strong metal–support interaction which provided the driving force for the migration of iron atoms from iron surfaces to freshly reduced regions of the titanium oxide support adjacent to the particles. Similar morphological changes have been observed when certain supported metal systems were treated in oxygen. Chen and Ruckenstein (*12*) reported that torus-like crystallites were formed on palladium/alumina samples after heating in 1 atm of oxygen at 350°C for 2 h, and other workers have observed similar phenomena for silica- and alumina-supported rhodium and platinum–rhodium (*13*) and nickel on the same oxide supports (*14*). In these cases the explanation has been along the lines discussed in the present work, i.e., oxidation of the metal crystallites results in the formation of mobile metal oxide species which are capable of wetting and spreading on the oxide supports; the driving force for the process being the formation of a strong oxide–oxide interaction.

CONCLUSIONS

Copper particles supported on magnesium oxide have been found to exhibit an extraordinary change in morphological characteristics when heated in O_2 at 200°C. Continuous electron microscopy observation of this process has enabled us to develop a model which accounts for the transformation of a globular to toroid geometry. In the proposed model, one of the necessary requirements is that the surface oxidation processes impart sufficient heat to the copper particle to induce atomic motion in the metallic core, i.e., raise the particle temperature to 405°C or more, but still maintain a solid oxide skin by keeping the surface temperature below 526°C. Under such circumstances, mobile Cu species will diffuse from the inner core through the porous oxide skin to form a progressively thicker oxide region at the periphery of the particle. This process will cease when all the Cu has been drained from the inner region and only a thin residual oxide layer remains, so producing a toroid conformation. We believe that this model, along with the previously described hard core model (*1*) constitute part of a family of such situations, where the characteristics of individual members vary with such aspects as (a) whether reaction at the particle surface is exothermic or endothermic; (b) whether a new chemical compound is formed, and (c) the degree of wetting and spreading of the particle components as a result of their interaction with the support.

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