JOURNAL OF CATALYSIS 29, 253-263 (1973)

Catalysis of Electroless Nickel Deposition by Small Palladium Nuclei

J. F. HAMILTON AND P. C. LOGEL

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received October 2, 1972

Evaporated palladium deposits are used to study catalyst size effects in catalyzed electroless nickel deposition. Comparison is made with results for nucleation of zinc from the vapor by palladium and silver deposits. Conclusions are that single atoms of palladium or silver will nucleate zinc deposition, two-atom palladium nuclei catalyze the decomposition of the reducing agent (dimethylamineborane) and the deposition of boron, but larger palladium particles (4–20 atoms) are required for nickel deposition. Results confirm the direct-impingement mechanism for nucleation and growth of the Pd deposits.

INTRODUCTION

One of the factors that has continued to hold interest in the field of heterogeneous catalysis is the dependence of activity on the particle size of the catalyst (*1–11*). In the range of particle diameters below 100 Å and extending sometimes to as low as 15 Å, there have been conflicting reports as to whether specific activity (i.e., activity per unit surface area) is constant or increases with decreasing particle size. Where a dependence is noted, it is generally associated with the occurrence of particular surface crystallographic configurations. Although the size range below 15 Å is obviously of prime interest, it has not been studied adequately because of the difficulty in preparing and characterizing representative collections of particles in that range of sizes.

One method of producing ultrafine metal particles is by vacuum deposition of very small mounts of metal—in the range of fractions of a monolayer. A number of examples of the use of such deposits have been reported (*9, 11–17*). In no case, however, has it been possible to characterize the deposit well enough to justify sound quantitative conclusions about the size dependence of catalytic activity. The particles of the most interesting sizes are at or below the resolution of the electron microscope, and since they are present in such small concentration, they are very difficult even to detect, not to mention characterize, by available analytical tools. Extrapolation of concentration and size data from heavier coverages requires an understanding of the details of the nucleation and growth processes, and widely differing proposals have been made in this regard.

We have recently reported (*18*) observations on vacuum-deposited films of Ag and Pd on amorphous carbon substrates, together with a model which explains the observations and provides for predictions about the concentrations of all sizes of particles, including those below the limit of direct resolution. We report here the results of experiments dealing with the size dependence of the properties of these particles, particularly their catalytic activity in a reduction–oxidation reaction, namely, the reduction of Ni^{2+} ion from solution, in a process generally known as electroless plating (*19–21*).

As this reaction proceeds, nickel metal is deposited on the catalyst nuclei, and this provides, in principle, a means for enlarging otherwise unresolvable particles to easily recognizable size, provided that such small particles are catalytic. Thus, from these experiments, further data concerning the surface density of particles are produced, in a range of deposit thickness lower than can be studied without the amplification process. In this regard, another useful method for enlarging the nuclei is to deposit a nonselfnucleating metal, such as Zn, over the original particles (*17*, *22*, *23*). The Zn vapor will condense only where a preexisting nucleus of sufficient size is located. The combined results of this type of vapor-phase amplification and the chemical nickel deposition supplement one another and provide a further confirmation of the model for nucleation and growth used to characterize the deposit.

In conjunction with these experiments, a program employing molecular-orbital-type calculations to evaluate the size dependence of the electronic characteristics of small metal nuclei is being conducted within these Laboratories (*23*, *24*). We are able to point out several possible connections between calculated properties and experimental results.

CHARACTERIZATION OF DEPOSITS

Deposits of Pd and Ag on amorphous carbon substrates have been made by the methods already described (*18*). Briefly, the rate of incidence of metal atoms on the substrate is varied and controlled by an oscillating quartz crystal detector. Deposition times are varied by slots in a shutter moving past the substrate plane, over a range from a few milliseconds to a few seconds. Deposit coverages between about 10^{12} and 10^{16} atoms cm^{-2} (about 10^{-3}–10 monolayers) have been studied.

Studies (*18*) of heavier deposits of the two metals by quantitative chemical assay and by electron microscopy have revealed several distinctive features. Although analytically determined sticking coefficients are unity, only a minor fraction of the incident metal is accounted for as visible particles, and the remainder is thought to have diffused into the carbon substrate. Furthermore, although the saturation density of Pd nuclei is several times higher than that of Ag, neither is dependent upon deposit rate, in the way predicted by spontaneous nucleation models. A different model has therefore been proposed (*18*) to account for these observations and the growth kinetics of the particles.

The substrate surface contains at least two distinct types of active sites of unknown nature: one at which either Ag or Pd will nucleate, and another which is inactive for Ag nucleation but active for Pd. An atom incident within the capture area of one of these sites is retained at that site, but failing to strike within that area, it diffuses rapidly into the substrate. Particles grow essentially by direct impingement, and interfacial diffusion appears to be relatively unimportant. Initial capture areas of the active sites have been determined by extrapolation from particle-size measurements (*18*), and although not considered to be highly accurate, they indicate capture dimensions of the order of atomic sizes. The dimensions indicated are slightly larger for Ag than for Pd. With this model, the number per unit area (N_i) of particles containing i or more atoms in a deposit of m incident atoms per unit area is given, for low values of m, by

$$N_i = \frac{\sigma_S\sigma_1\sigma_2 \cdots \sigma_{(i-1)}m^i n_S}{i!}, \qquad (1)$$

where n_S and σ_S are the concentration and capture area of the active sites and σ_i is the capture area of a particle of i atoms. The value of σ_i will generally depend upon i, and for three-dimensional particles of constant shape, $\sigma_i \propto i^{2/3}$, for particle areas larger than σ_S. If log N_i is plotted against log m for various values of i, Eq. 1 gives a family of linear curves with slope i. At higher coverage these curves bend over to saturate at n_S. Their placement along the log m axis is dependent upon the product $\sigma_S\sigma_1\sigma_2 \ldots \sigma_{(i-1)}$.

VAPOR-PHASE AMPLIFICATION

One of the methods used for amplification of the nuclei is to vacuum overcoat the original deposit with a few atomic layers of a nonnucleating metal. Zn, Cd, Mg, and Hg have been reported to be suitable metals which do not self-nucleate at low vapor pressures (*22*). We have found Zn to be most easily controlled and to give the best contrast in electron micrographs. For the higher densities of amplifiable nuclei, Zn particles begin to coalesce before they become large enough for adequate contrast. Pd deposits in this range of nucleus density have been successfully amplified by a silver deposit. In this case the preexisting Pd nuclei cause resolvable silver particles to form in excess of the number which would be present in the absence of Pd. The counts are corrected for the normal silver nucleus density as follows. Let n_A be the density of surface sites active for nucleation by either Ag or Pd. The value of n_A is determined by the saturation density of Ag nuclei as 1.6×10^{12} cm^{-2}. Then let n_P be the density of additional sites active for Pd nucleation only. The total density of active Pd sites is $n_A + n_P$, and is given by the saturation density of Pd nuclei to be 5.4×10^{12} cm^{-2}. After a Pd deposit of m incident atoms per cm^2, a fraction $f(m)$ of these Pd active sites contain Pd nuclei active for further growth by Ag. A subsequent heavy Ag deposit will produce $N_A = n_A + f(m)n_P$ silver particles. Thus, $f(m) = (N_A - n_A)/n_P$. The total density of Pd nuclei is $N_P = f(m)(n_A + n_P)$, so that

$$N_P = [(N_A - n_A)(n_A + n_P)]/n_P. \quad (2)$$

By Eq. 2, the density of Pd nuclei, N_P, may be determined from the counted density of Ag particles, N_A, and the saturation densities of Ag and Pd particles.

ELECTROLESS PLATING

The essential components of an electroless plating bath are a soluble metal ion and a reducing agent, which together are thermodynamically unstable but kinetically stable, at least for workable periods of time. The reaction is strongly promoted by the catalyst. In these experiments we use Ni^{2+} as the ion to be reduced and dimethylamine-borane (DMAB) as the reducing agent. The complete composition of the bath is as follows: 0.1 M $NiCl_2 \cdot 6H_2O$, 0.65 M gluconic acid, NH_4OH to pH9, and DMAB to 1%.

The reaction mechanisms of the catalyzed electroless plating process are not fully understood (*20*). Randin and Hintermann (*25*), for example, list four proposals: (1) the atomic hydrogen mechanism, involving hydrogen as the active intermediate; (2) the hydride transfer mechanism; (3) the electrode mechanism; and (4) a mechanism involving hydrolyzed nickel with hydroxyl ions. At this time, the balance of evidence seems to favor some modified form of hydride transfer process (*26*, *27*). The catalytic evolution of hydrogen and the decomposition of the reducing agent to deposit elemental boron on the catalyst are parallel reactions (*28*), which, in fact, will take place even if the Ni^{2+} is omitted from the solution.

Evaporated Pd deposits with incident coverages of more than 5×10^{14} atoms cm^{-2} effectively catalyze massive nickel deposits in the solution given above. Within a few minutes at room temperature, opaque mirror coatings are formed. For electron microscope study, the deposition must be arrested in the early stages. Optimum treatment times vary with the Pd coverage and for these coverages range between a few seconds and 30 seconds or so. Figure 1 shows how the deposit forms. The upper picture is an electron micrograph of an untreated Pd deposit of 1.08×10^{15} incident atoms cm^{-2}. The lower four micrographs depict different stages of formation of an electroless nickel film on this Pd deposit. Initially, the particles become enlarged rather uniformly, and then, subsequently, a patchy coating forms and becomes progressively more dense. A faint indication of this pattern can be seen even in the first of the plated samples, and there is a suggestion that this coating forms not by a continuous enlargement of the particles, but as a semicontinuous, low-density film superposed on the nuclei. In the last picture of this series there are still discontinuities in the heavy coating, within which enlarged particles can be resolved. Eventually these discontinuities fill in and the film becomes too thick for transmission electron microscopy, but at this stage of deposition these discontinuities are quite reproducible.

Transmission electron diffraction patterns from coatings such as this generally show rings of crystalline nickel, but there is usually a high background of elastically scattered electrons, and part of the nickel may

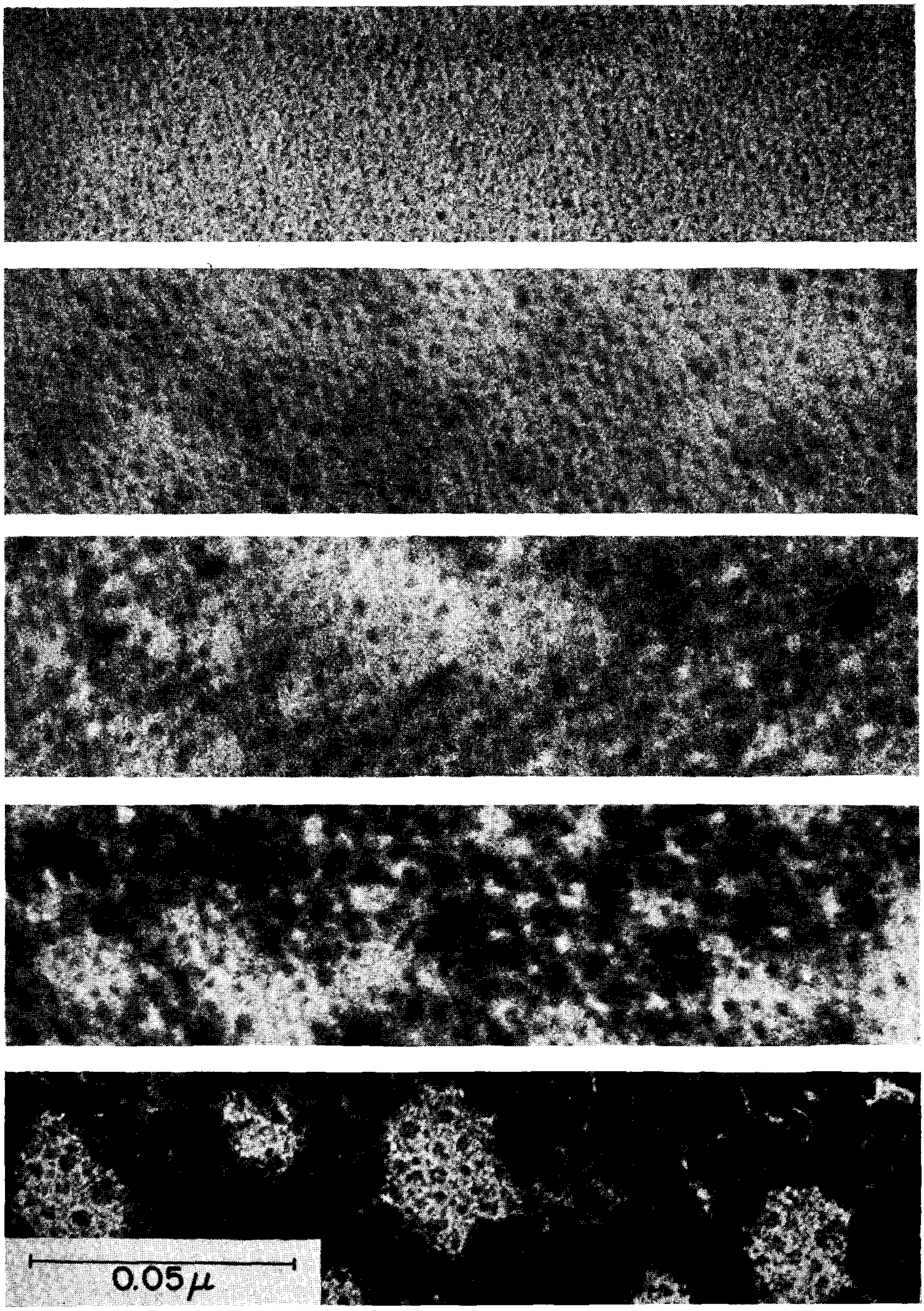

FIG. 1. Evaporated Pd deposit of 1.08×10^{15} incident atoms cm^{-2}, as made (top), and at different stages of electroless nickel plating.

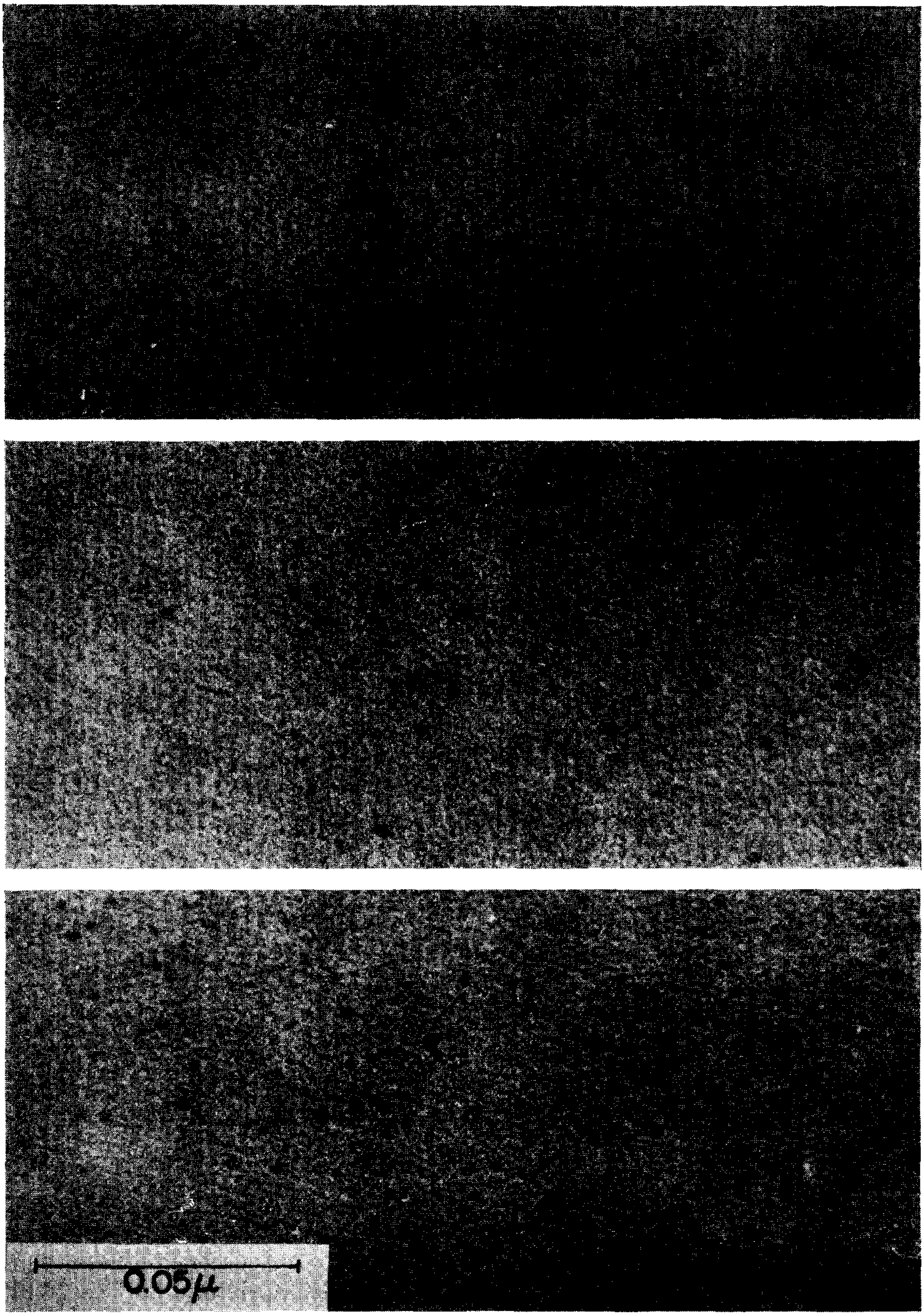

FIG. 2. Particles formed by treatment of evaporated Pd deposits with electroless nickel plating bath. Pd coverages approximately 1×10^{14}, 2×10^{14}, 4×10^{14} incident atoms cm^{-2}.

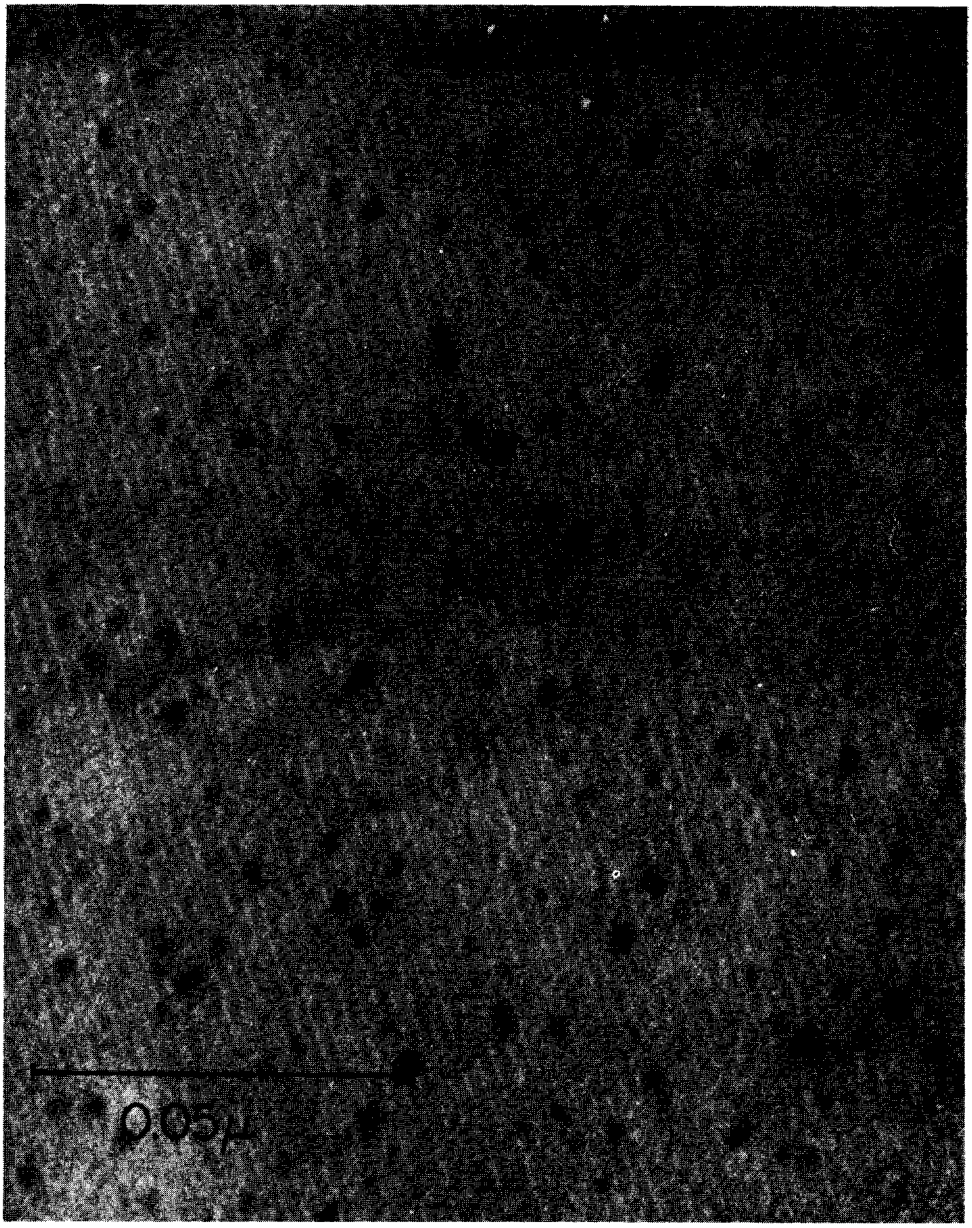

FIG. 3. Particles formed by 30-min treatment of evaporated Pd deposit of 5 × 10^{14} incident atoms cm^{-2} with electroless plating bath with Ni^{2+} ion omitted.

well be in the amorphous state usually found for deposits of this type (*29*).

On Pd deposits with coverage below about 5 × 10^{14} atoms cm^{-2}, the standard Ni^{2+}–DMAB solution produces no visible nickel deposit even for plating times so large that the solution decomposes. However, electron microscope specimens do reveal particles with diameters up to about 50–100 Å in concentrations depending upon the Pd coverage. Examples are seen in Fig. 2. Without the bathing treatment, no Pd particles at all are resolved at these coverages, and the specimens are not distinguishable from carbon control films. Chemical analysis of the films after bathing in the plating solution reveals principally boron, sometimes with smaller concentrations of nickel. Treatment of the samples in a solution similar to the plating bath but from which Ni^{2+} is omitted produces particles with much the same appearance and in the same concentrations (Fig. 3). Thus, although there may be minor amounts of Ni in the particles in question, they are composed principally of boron, formed as the oxidation product of the catalyzed decomposition of DMAB.

PARTICLE COUNTS

Following amplification, specimens for electron microscopy are prepared by stripping the carbon films from the glass support in water and mounting them on support grids. Spot checks have also been made using collodion-carbon support films premounted on support grids prior to the metal deposition. Such specimens can be examined without water contact. Particle density determinations are made by counts of several hundred particles.

Results taken from Pd deposits are shown in Fig. 4, where log particle density (N) is plotted against log incident Pd coverage (m). The open circles are counts of particles left after treatment with the electroless plating solutions. These results include sets of data from Pd deposited at different rates from samples bathed in the solutions for different times, and for solutions with and without Ni^{2+}. These variables make no significant differences in results. The closed circles are data taken from deposits amplified by Zn vapor, such as that shown in Fig. 4. The upper points of this series are in error in the direction of slightly low particle densities as they are beginning to suffer from coalescence effects. The X points are raw data from Ag-amplified Pd deposits, and the squares are these same data corrected for the Ag background by Eq. 2. The triangles are data from unamplified particles, taken from Ref. 18.

The data for vapor amplification of both types fall on a single line with slope 1. They are therefore related to Eq. 1 with $i = 1$. This equation is plotted as the solid line, with σ_S assigned a value of 6.8 $Å^2$ for best fit to the points. The open circles are best fit by a line with slope 2, and the broken line in the figure is a plot of Eq. 1 with $i = 2$, $\sigma_S = 6.8$ $Å^2$, the same value used for the solid line, and $\sigma_1 = 8.7$ $Å^2$ or about $1.3 \times \sigma_S$.

Figure 6 shows a comparison of data from vapor-amplified deposits of Pd and Ag. The broken line is a plot of Eq. 1 with

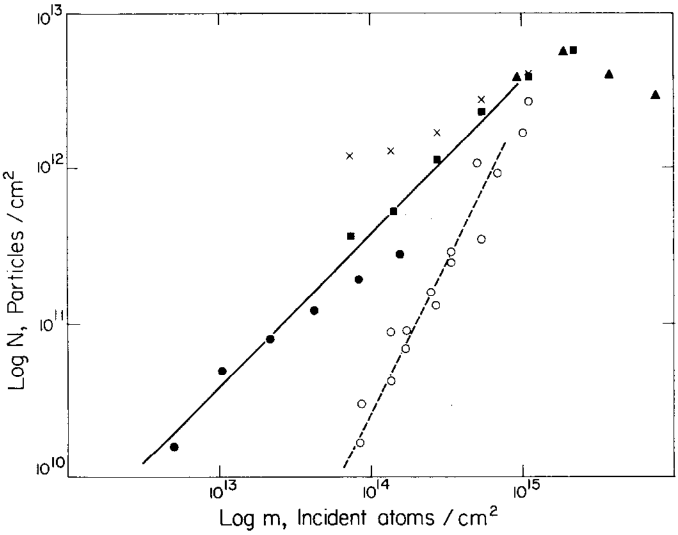

FIG. 4. Plot of log particles cm^{-2} vs log incident Pd coverage for (▲) untreated Pd deposit, and amplification by (×) evaporated silver, uncorrected; (■) evaporated silver, corrected; (●) evaporated Zn; (○) electroless nickel bath. Solid curve, Eq. 1 for $i = 1$; broken curve, Eq. 1 for $i = 2$.

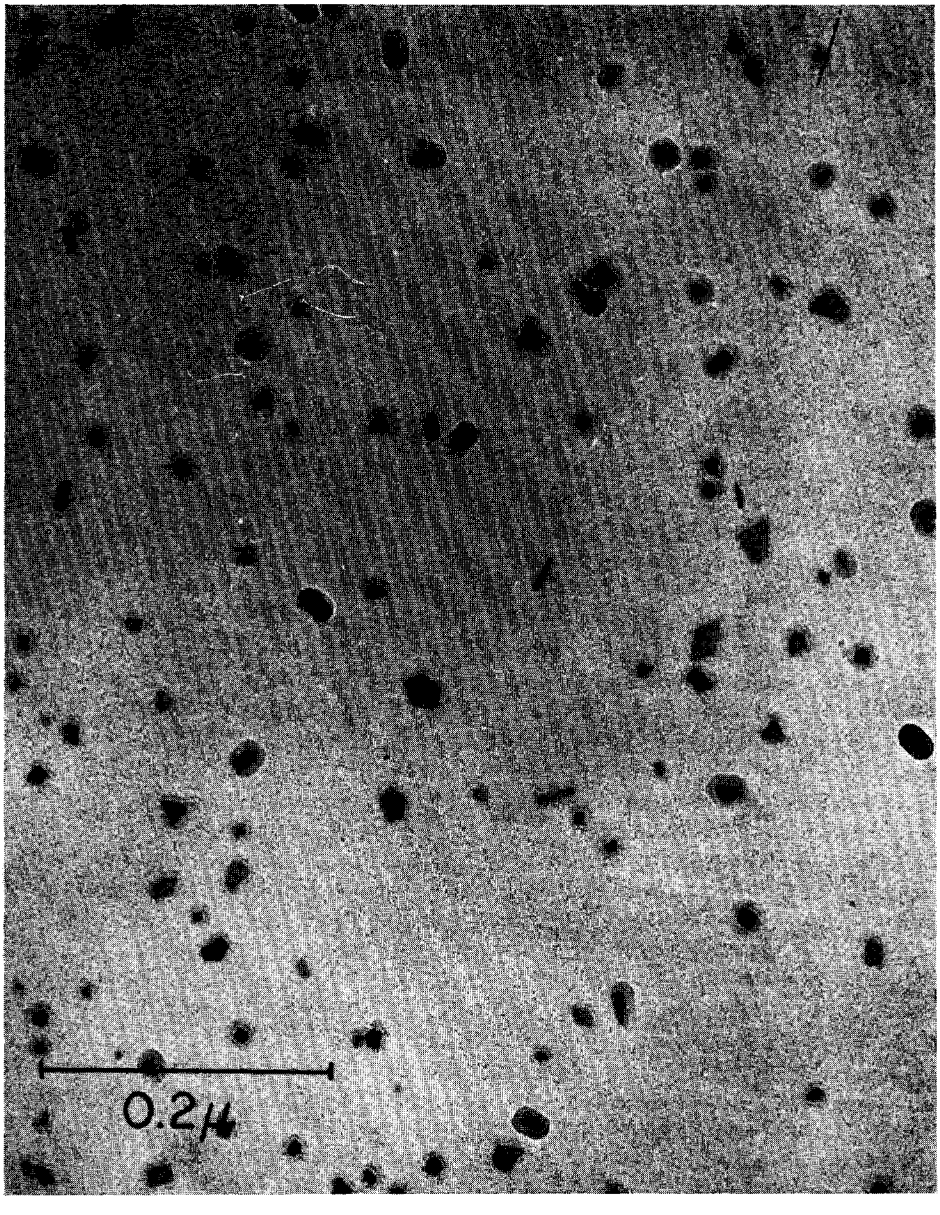

FIG. 5. Particles formed by evaporation of Zn on Pd deposit of 5×10^{12} incident atoms cm^{-2}.

$i = 1$, $n_S = 1.6 \times 10^{12}\ \text{cm}^{-2}$, and $\sigma_S = 63\ \text{Å}^2$. Deposits of Ag do not catalyze the Ni deposition, and we have not found catalyzed reactions which on these substrates do not encounter difficulties from aggregation effects.

DISCUSSION

The fit of the data from vapor-amplified deposits of both Ag and Pd to Eq. 1 with $i = 1$ indicates that single atoms of either of these metals can reside for indefinite periods at the active sites on amorphous carbon substrates, and are capable of nucleating the deposit of Zn vapor. Comparison can be made between these conclusions and those obtained by Baetzold (*23*) from molecular orbital calculations. Baetzold points out that the nonnucleating metals have in common the double occupancy of

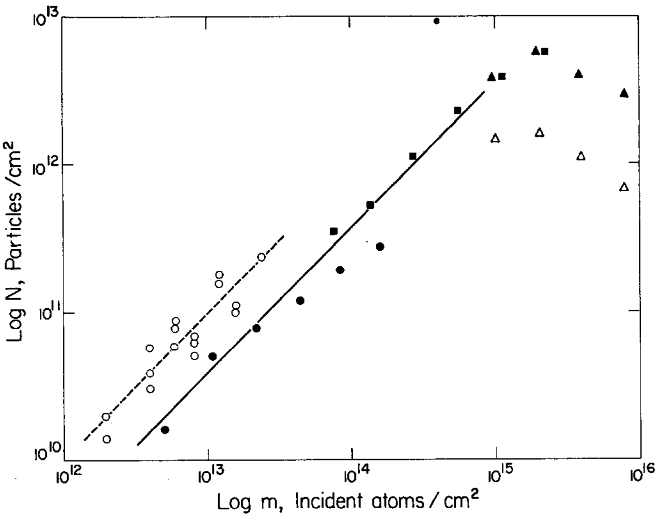

FIG. 6. Log particles cm^{-2} vs log incident atoms cm^{-2} for Ag or Zn evaporation amplification of Pd deposits (■, ●) and for Zn evaporation amplification of Ag deposits (○). Untreated Ag and Pd deposits are represented by △ and ▲.

the highest filled atomic *s*-orbitals. Forming the diatomic aggregate of such metals fills the antibonding molecular orbital and results in very little energetic advantage, if any. In contrast with this behavior, the diatomic species Ag_2 and Pd_2 are strongly bonded.

The presence of a carbon substrate alters this situation (*24*). Bonding is not predicted for any of the 2-atom metal aggregates on a plane carbon surface represented by two graphite rings. This result is in agreement with our proposal of active sites, in that some specific defect in the carbon structure would be necessary to promote growth of an aggregate of Ag or Pd. As an example of a possible defect, an oxygen atom on the graphite surface does provide a site to which the calculations indicate that Pd will bond and continue to grow.

In view of the relatively invariant density of active sites observed experimentally and the fraction of total surface represented by these, adsorbed oxygen seems less likely to be the active site than some sort of physical defect. Limited computer capacity restricts the configurational defect models that may be tried. So far, none has been found that satisfies the experimental observations, though trends toward bonding have been observed.

The calculations indicate that single atoms of silver are not capable of acting as the nucleating sites for Zn, and suggest that a pair of atoms is required. This conclusion, however, must also be qualified by noting that a suitable model for an active substrate site has not yet been included. Again, trends toward stabilization have been observed.

Values for the radii of the capture areas of the active sites, determined from a fit of the vapor-amplified data to Eq. 1, are 4.5 Å for Ag and 1.5 Å for Pd. We consider these values to be more reliable than the corresponding radii of 19 Å and 6 Å, determined by extrapolation of particle size measurements, reported elsewhere (*18*). The general agreement between the two sets of values and the consistent relative sizes for the two metals confirm the concepts of the model used in characterizing the deposits. With capture areas of this size, surface diffusion plays a very minor part in the process. Particles form and grow essentially by direct impingement of vapor atoms.

The data from counts of particles formed in the electroless plating baths indicate that two-atom Pd nuclei will catalyze the DMAB decomposition. Deposition of nickel evidently requires a larger size, which may be evaluated by comparison with Eq. 1,

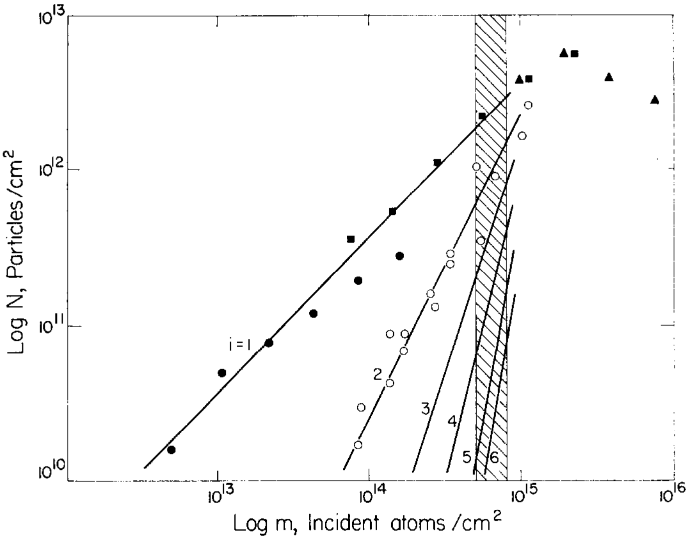

FIG. 7. Curves are Eq. 1 for $i = 1$–6, fit to data for Pd deposits without amplification (▲), and amplified by vacuum evaporation (■, ●) and electroless nickel bath (○). The hatched area represents the threshold coverage for gross nickel deposition.

with the appropriate set of values of σ_i. The value of σ_1, determined by fitting the data to Eq. 1, is 8.7 Å^2. Since $\sigma_1 > \sigma_S$, we may assume that σ_i will in general increase with i, and the 2/3 power dependence characteristic of a three-dimensional particle is a reasonable case to investigate. The family of curves shown in Fig. 7 is the resulting set, for particles sizes $i = 1$–6. The data for vapor-amplified and DMAB-amplified particles are repeated on this graph, and the minimum coverage for gross nickel deposit is indicated by the hatched zone. Nickel deposition starts in the region where the curves are very steep and closely bunched together, and it is not possible to relate this threshold accurately to a specific particle size. We judge, however, that particles of minimum size for nickel deposition in this system must be in the range from four to perhaps ten or twenty atoms.

The specificity of the catalyst size dependence for the two reactions raises intriguing questions concerning the mechanisms involved. A possibility is that the difference is merely configurational. Perhaps catalysis of the reaction producing nickel metal simply involves a larger number of bonds between the catalyst and the active species than does the decomposition of the DMAB. Steric considerations may limit the access of all interacting components simultaneously. On the other hand, the difference may be electronic rather than geometric. Empty *d*-orbitals are generally considered to be important in catalysis, and Baetzold calculates (*24*) that in any planar array of Pd on carbon, where each Pd atom is in contact with the carbon substrate, no vacant *d*-orbitals exist. Only if the aggregate assumes a three-dimensional form, such that one or more Pd atoms contact only other Pd atoms and no carbon atoms, do empty *d*-orbitals appear. The size range of four to ten or twenty atoms may be that over which three-dimensional nuclei begin to form. Perhaps empty *d*-orbitals are necessary for strong interaction with Ni^{2+}, but not for decomposition of the DMAB.

ACKNOWLEDGMENT

Discussions with R. Baetzold and M. Lelental have been very helpful in formulating many of the concepts presented here.

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