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EXPERIMENTAL STUDIES OF CLUSTER PROPERTIES RELATED TO CATALYSIS

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Résumé. — On a utilisé dans des études expérimentales, des agrégats d'atomes métalliques, formés par dépôt de vapeur sur des substrats amorphes. La distribution de la taille des particules peut être calculée en allant des faibles recouvrements, constitués en grande partie d'atomes uniques, jusqu'aux recouvrements plus importants, contenant des cristallites de tailles allant de 10 à 100 Å. Ils sont utilisés pour déterminer la taille minimale nécessaire à l'activité catalytique et pour comparer cette caractéristique à d'autres propriétés mesurables.

Abstract. — Clusters of metal atoms formed by vapor deposition on amorphous substrates are used in experimental studies. The particle-size distribution can be calculated for low coverages, consisting principally of single atoms, through higher coverages containing crystallites 10-100 Å in size. These are used to determine the minimum size for catalytic activity, and to compare this feature with other measurable properties.

1. Introduction. — In conjunction with the theoretical calculations discussed by Dr. Baetzold [1], there is in our laboratory an experimental program dealing with physical and catalytic properties of small metal particles. The samples are either single or multiple layers of clusters deposited on amorphous carbon or silicon dioxide substrates from the vapor phase. These preparations have the advantage that they can be reproducibly prepared and size-characterized over the full range of sizes from single atoms to particles several tens of angströms in diameter. Of particular interest has been the dependence of catalytic activity and chemical reactivity on size, and attempts are being made to correlate the simple chemical data with results of AES and ESCA analysis of surface composition, XPS determination of densities of occupied states, and spectral absorption measurements related to electronic transitions.

The program was initiated as a model study to investigate the development step of the photographic process. This process is a prime example of a catalyzed chemical reaction. The developer contains a reducing agent which, in the presence of a catalyst, reacts with silver ions either in solution or in the solid state to produce metallic silver. The reaction is thermodynamically favored but kinetically retarded, save in the presence of the catalyst. This catalyst is called a latent-image center. It is known to be a cluster of photolytically produced silver atoms, and the photographic evidence convincingly indicates that there is a size limitation on its activity. A critical size larger, but apparently not very much larger, than two atoms must be reached before the nucleus becomes catalytic. The

intriguing question posed by these facts deals with the mechanism of the catalytic activity. One wonders whether the property or properties that change so significantly within this size range as to confer catalytic activity have to do with geometric factors, with thermodynamic stability, with electronic levels, with orbital symmetry, or what.

2. Preparation of nuclei. — The equipment designed to produce the nuclei has been described before [7]. A quartz-crystal detector is used with a feedback circuit to set and maintain a constant flux of metal atoms from a resistively heated boat. A shutter with a series of slots of differing lengths is moved at a constant speed just in front of a sample on which the metal atoms are incident through the slots. The total incident metal flux on any area is, therefore, proportional to the length of the corresponding slot in the shutter. Our usual shutter layout is such that it produces six bands of deposit varying in incident coverage by factors of two. The vacuum system is ion pumped, and pressures are normally in the 10^{-5} Pa range. For convenience, substrates are usually either evaporated carbon or evaporated SiO_2 , but a few experiments have been made on polyester film or on a gelatin coating. In addition to silver, nuclei of gold, copper, platinum and palladium have been prepared and studied.

3. Size characterization. — Although extensive theoretical treatments of the condensation of metal vapors on substrates have been published, they proved not to agree with observations made on these deposits. For example, most treatments predict substantial reevaporation of incident atoms

in the initial stages, resulting in a low measured sticking coefficient. By the time the particles reach resolvable size, this reevaporation is expected to have stopped; integrated sticking coefficients should approach unity, and the particle radius should grow with the one-third power of the incident coverage. Experimentally, apparent sticking coefficients determined from surface concentrations and sizes of particles were in the range 0.01 to 0.1, and the mean particle radius increased linearly with incident coverage. On the other hand, quantitative chemical analysis clearly showed actual sticking coefficients of essentially unity, even down to the very lowest incident coverages. The conclusion was that most of the incident atoms were not being incorporated into the visible nuclei but were, nevertheless, being retained in some way on the substrate. Some novel variations on the depth profiling techniques using AES indicate that these extranuclear atoms diffuse into the substrate and become deactivated for incorporation in the nuclei [3]. The linear growth behaviour further indicates that direct impingement is the dominant growth process. Surface diffusion is of minor importance, and unless an incident atom strikes a nucleus, it suffers an alternative fate, which may be diffusion into the substrate.

Another observation was that over the range tested (10^{14} to 5×10^{15} atoms cm^{-2} s^{-1}) the nucleus density was totally independent of arrival rate. Any homogeneous nucleation process results in a rate dependence of the nucleus density, and the absence of such a dependence is strong evidence for the presence of some particularly active sites on the substrate.

The full model for nucleation of these deposits is simply one of single and then multiple occupancy of the active sites by atoms incident in a random spatial distribution. Size distributions are statistically determined and would be Poisson in form, except for the change in the capture area of a nucleus as it grows. Given this functional relationship, the size distributions can be calculated; they have the general form of the curves shown in figure 1. This set of curves shows how the number of nuclei of i or more atoms increases with the incident coverage, for several low values of i . At low concentrations, each curve approaches a straight line with slope i on this log-log graph. Only the relative horizontal positions of the curves are affected by the changing capture area.

A determination of the initial capture area of an active site can be made by means of an auxiliary evaporation technique [4]. Zinc vapor (and also that of certain other metals, e.g., Cd and Hg) condenses only very poorly on clean substrates [5, 6], owing to the fact that Zn does not self-nucleate. On these substrates, even at the active sites, conditions are easily achieved such that zinc is not deposited.

FIG. 1. — Relative surface nucleus density, size i or larger, as a function of normalized incident atom coverage.

However, a very low coverage of silver, gold, or palladium will provide nucleation centers for the zinc. The amount of zinc deposited can be controlled so that discrete, resolvable zinc particles are produced, each marking a nucleus of the other metal. Data from counts of the surface density of zinc particles, when plotted against the incident coverage of the nucleating metal, give results shown in figure 2. When both axes are logarithmic, the data fit to a line with unit slope, showing that even a single atom at one of the active sites contributes a nucleation center for the zinc vapor.

From curves such as that in figure 2, active-site capture areas are determined. The values found are of the order of atomic dimensions, attesting to the contention that surface diffusion is very limited under these conditions. There are numerical diffe-

FIG. 2. — Counts of surface density of Zn particles as a function of incident gold atom coverage. Open circles are directly visible gold nuclei; filled circles, zinc enlarged.

rences in values among the various metals and substrates ; but each has been characterized individually, and no exceptions to the general scheme have been found.

4. Catalytic properties. — As an example of a catalytic effect, we will examine a reaction which is the solution analog of conventional silver development, in the usual form of which the silver ion is reduced from the solid state. This catalyzed reaction is a simple electrode process : The reducing agent is adsorbed to the catalyst surface, transfers an electron to the catalyst, and eventually is desorbed. The electron is, in turn, transferred to a silver ion in contact, completing the cathodic half of the reaction. Successive silver atoms form on the original catalytic nucleus, and the reaction is, therefore, autocatalytic.

Vacuum-deposited metal nuclei have been used as the catalysts for this reaction, in a solution containing a reducing agent and the silver ions [7, 8]. If the deposit of catalytic nuclei is removed from the solution at an appropriate time, a discrete particle of developed silver, easily resolved in the electron microscope, will have formed at each nucleus large enough to be catalytic (Fig. 3). Counts of the developed silver particles at different coverage of the vacuum deposit then lie along the frequency curve for the minimum developable size. Figure 4 shows such data for nuclei of silver and of gold. The best fits indicate a minimum catalytic size of four atoms for silver and two atoms for gold. The absolute numbers are judged to be accurate to

FIG. 3. — Electron micrographs of developed silver particles for two different values of nucleus density.

FIG. 4. — Particle density counts for silver physical development of silver and gold nuclei and theoretical curves of nucleus density as a function of incident atom coverage.

± 1 atom, but the difference between the two metals is definitely outside experimental error.

5. Observed properties. — X-ray photoelectron spectroscopy studies by Mason have been successful in revealing the density of occupied states in nuclei of this type [9]. Results for silver and gold have been completed, and the agreement with the calculations is encouraging. The threshold of the density of occupied states moves toward the vacuum level and the d-band splits as the size distribution changes from principally single atoms to multiple clusters, with the maximum inflection point where the frequency peak is a few atoms.

Studies are continuing and we are hopeful of being able eventually to establish correlations between catalytic activity and one or another of the basic physical properties of small clusters of metal atoms.

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