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Structure of Aggregated Rhodium Crystallites Prepared from Rh(I) Complexes on Amine-Modified Silica Supports

We have recently reported that one obtains Rh(I)–amine complexes of the form $L_nRh(CO)_2$ (L designates an amine ligand and n is unknown) on attachment from $CHCl_3$ or benzene solution of $Rh_6(CO)_{16}$ onto amine-modified silica supports (*1*). These complexes could be reduced in an H_2 atmosphere of approximately 6×10^4 N/m^2 and temperatures >350 K (*2*). Under these conditions, the Rh atoms aggregated to form small metal crystallites with an average diameter of 2 nm, as shown by ir spectroscopy and electron microscopy (*2*). In this contribution we wish to show that at least the most abundant crystallites develop a well-defined shape. This could be demonstrated by a signal-to-noise enhancement in electron micrographs, utilizing the technique of Filtering Arrays of Images in Reciprocal Space (FAIRS) (*3*). Maximum differential contrast between heavy metal and support had previously been achieved by optimal sizing of the objective aperture (*4–6*).

The sample investigated was identical to the one described in Ref. (*2*). Transmission electron micrographs were obtained with a Siemens EM 102 electron microscope (magnification 314,000×, 100 kV, objective aperture 80 μm, point resolution better than 0.3 nm). Particles of the catalyst material suspended in chloroform were collected on a 2-nm carbon film, which was mounted on a 400-mesh copper grid. As shown in Ref. (*2*), catalysts prepared in this way showed contrast sufficient to allow recognition of the shapes and dimensions of the Rh species.

A typical crystallite size distribution, which is obtained from a total number of 68 individual Rh particles, is shown in Fig. 1. The most abundant particles have diameters of ~2 nm, and 75% of the particles fall in the size range between 1.25 and 2.75 nm.

The determination of crystallite shapes is difficult due to the superposition in the electron micrographs of contrasts originating from the Rh crystallites, the silica support, and the carbon film. Moreover, the shapes of the Rh particles as encountered in the electron micrographs depend on their orientation relative to the support particles and the plane of the carbon film. An unequivocal assignment of contrasts to well-defined particle shapes is thus not possible in all cases. This situation can be improved by a signal-to-noise enhancement by means of the FAIRS technique (*3*), which consists of subsequent light-optical filtering of electron micrographs. For this purpose, a certain number of electron microscopic pictures of individual particles from different electron micrographs are ordered in a two-dimensional array, as shown in Fig. 2a. This pattern then contains regularly repeated object information such as shape and/or overstructures of the variously de-

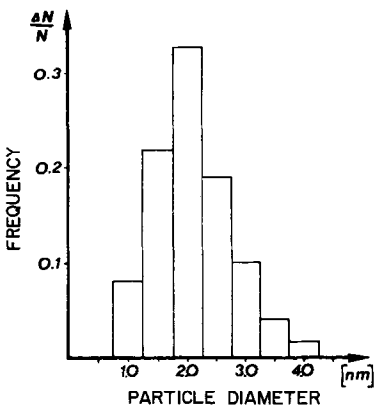

FIG. 1. Rhodium crystallite size distribution.

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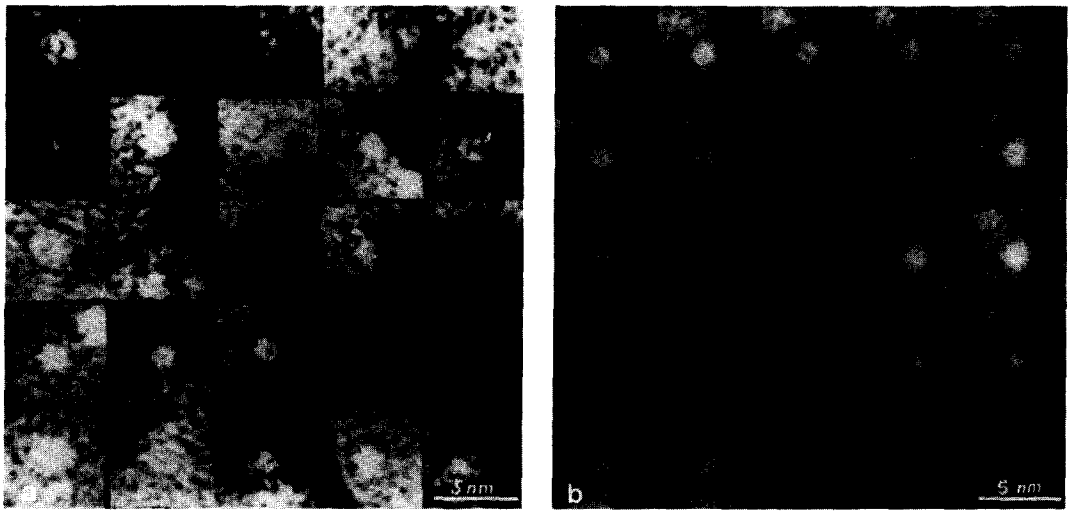

FIG. 2. (a) Two-dimensional array of electron micrographs of individual crystallites. (b) Reconstructed image after light-optical filtering (FAIRS).

lineated individual particles, and in addition irregularly statistically distributed noise which originates from the silica support and carbon film. When a light-optical diffraction is carried out, these components appear separated. By placing a suitable filter into the Fourier plane, the periodic pattern can be selected to reconstruct a picture in which a signal-to-noise enhancement and an averaging over the particle shapes by optical superposition are achieved.

The result of this procedure is shown in Fig. 2b, which now clearly shows shapes of the individual particles. Particles with an average diameter of 2 nm (maximum of the size distribution, Fig. 1) have been selected for this shape determination. The shapes of the particles may be described as cloverleafs, the smallest and largest diameters of which are approximately 1.7 and 2.4 nm, respectively (Fig. 3).

The improvement achieved by this procedure depends strongly on the selection of the individual particle images and their arrangement into the two-dimensional array. These steps, selection and positioning, are the only subjective ones in the interpretation since any misfit would correspond to the introduction of wrong object structures and would contribute to the statistically distributed information which is lost during the filtering procedure. Thus, shapes encountered in the reconstructed image are not necessarily representative for all particles. It can, however, be concluded that a high percentage of the most abundant particles in the 1.75- to 2.25-nm size range should have the observed shape, which is schematically reproduced in Fig. 3. It is not clear yet from this analysis whether the particles have a three-dimensional or only a two-dimensional structure. The position of the Rh atoms in the particles is also still open to question. The model suggested in Fig. 3 is therefore only tentative at present

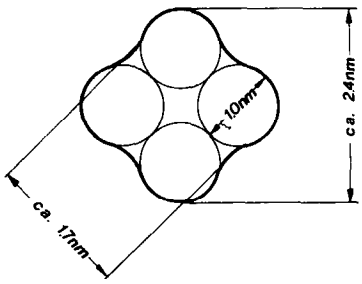

FIG. 3. Schematic drawing of filtered rhodium crystallites.

and a complete structural description—including the possible formation of subaggregates—it not yet possible. Experiments are presently being carried out to elucidate the particle growth mechanism, which should give further insight into the structures of the particles.

CONCLUSIONS

We feel that this relatively simple, rapid, and inexpensive technique, which has been successfully applied for the elucidation of the structure of proteins (*3*), might also be applicable for the structure or shape determination of small supported metal particles, at least in such relatively favorable cases as the present example.

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