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High-resolution transmission electron microscopy of Os-clusters supported on model alumina-films

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Thin planar model alumina films can be successfully used as supports for metal species in the size range $\leqslant 1$ nm, provided the electron optical conditions (defocus setting) are optimized. $Os_3(CO)_{12}$-clusters were anchored on the model support intact and the triatomic clusters (~ 0.6 nm diameter) could be made visible. Metal aggregation in H_2-atmospheres and redispersion in CO and O_2 atmospheres has been studied. It is suggested that CO-induced fragmentation of small osmium particles exposing low-coordinated surface atoms probably leads to mononuclear surface carbonyl complexes.

Keywords: Osmium clusters; model alumina films; particle aggregation; redispersion; transmission electron microscopy

1. Introduction

The determination of dispersion and particle size distributions is of paramount importance for the characterization of supported metal catalysts. Besides chemisorption techniques physical methods such as EXAFS [1–3] and transmission electron microscopy (TEM) [4–7] can be applied. With current conventional transmission electron microscopes (CTEM), it is easy to obtain resolutions of atomic dimensions. Hence, the examination of small metal particles or metal ensembles in the size range $\leqslant 1$ nm in supported catalysts is principally not limited by the instrumental resolution. However, the metal in real catalysts is usually dispersed on high surface area supports (typically 100–200 m^2/g) such as silica or alumina. The characterization by TEM of these materials down to atomic dimensions is not unequivocally possible since the contrast in the micrographs is an unknown superposition of phase and amplitude contrast. This uncertainty may lead to seriously erroneous determinations of particle sizes, shapes and distributions.

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The most direct solution of these problems is, of course, to ascertain that only one contrast mode is operative as for example in high-resolution scanning transmission microscopy (STEM) in the dark field mode [8,9]. Most metal catalysts, however, involve electrically insulating oxide supports which leads to serious charging problems in STEM.

An alternative possibility towards solving the problems involved in contrast interpretation is the use of model systems in which the metal species are deposited on thin *planar* oxide films. As a consequence, the metal clusters or aggregates are distributed in a two-dimensional arrangement. This technique has been sucessfully applied in several studies on metal aggregation and redispersion [10-14]. The distribution and dispersion of MoO_3 and MoS_2 on a model Al_2O_3 support film has also been investigated [15,16].

In the present paper we report on a study of osmium metal species supported on model alumina films which were derived from $Os_3(CO)_{12}$ precursors. Osmium was chosen for two reasons. The first because of its strong scattering power which renders this metal ideal for TEM investigations. Secondly, the surface organometallic chemistry of $Os_3(CO)_{12}$ is well established [17,18], so that the nature of the supported osmium species can be relatively well controlled by the preparation method.

2. Experimental

PREPARATION OF ALUMINA FILMS

The alumina-films were prepared in a bell jar system by reactive evaporation of Al-metal in an O_2-atmosphere at a pressure of 0.01 Pa onto a freshly cleaved NaCl single crystal. Deposition rates and film thicknesses were monitored by a quartz crystal microbalance. The final thickness of the films was limited to 5–7 nm. Electron diffraction indicated that the films have an amorphous structure (see electron diffractogram of the blank Al_2O_3-film inserted in fig. 1).

PREPARATION OF SUPPORTED Os/ALUMINA

The $Os_3(CO)_{12}$ (STREM) cluster precursor was impregnated onto the supports by refluxing an n-octane solution for 3 h under dry N_2, as reported earlier [19]. The n-oxtane solvent was dried over $MgSO_4$ prior to use. The solution was then removed, and the obtained materials were rinsed in dry n-octane to remove excess clusters, which were not chemically anchored to the support surface. The materials were then dried in vacuum at room temperature for 48 h and stored under dry N_2. Since the impregnation in this procedure involved a non-aqueous solvent, namely n-octane, the preparation can equally well be applied with both

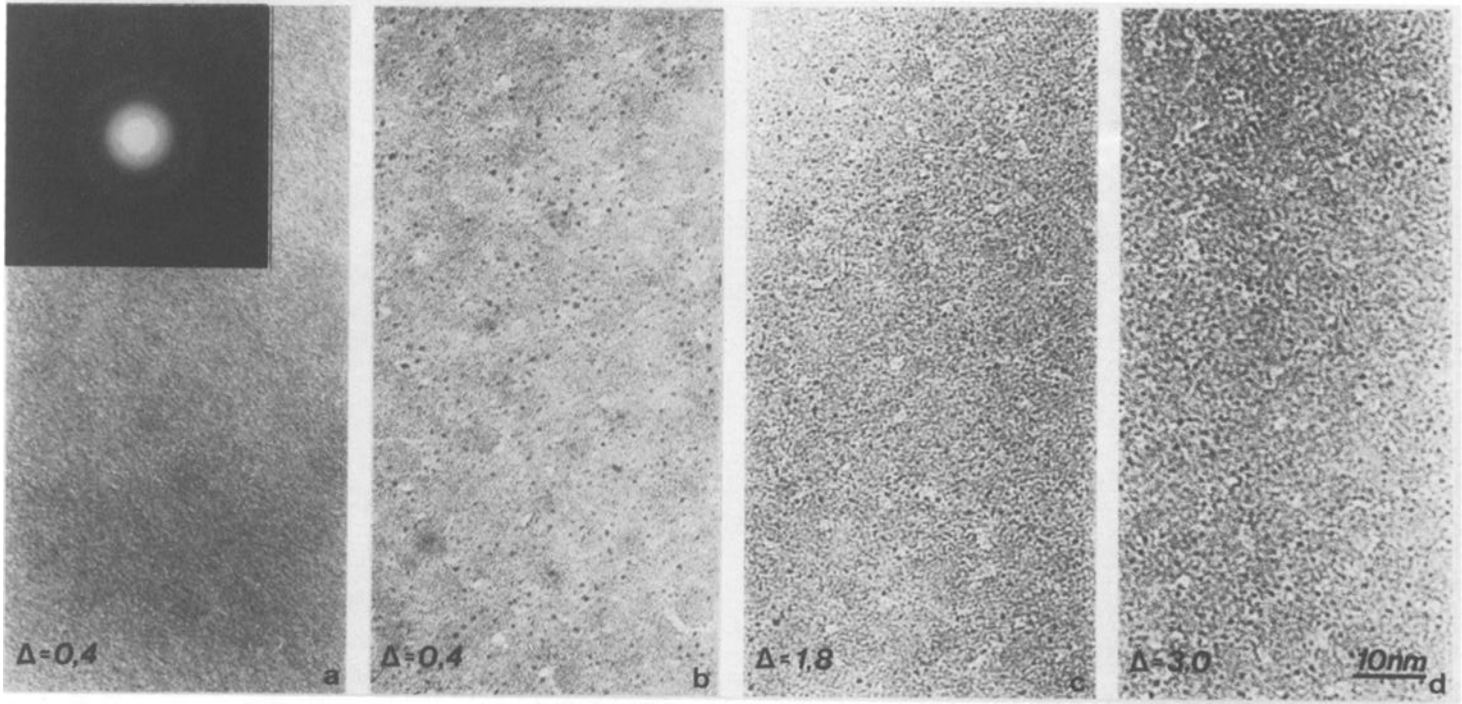

Fig. 1. Electron micrographs of Os clusters on amorphous thin alumina supports at various normalized defocus settings a. The blank Al_2O_3-film with the corresponding diffraction image. b., c., d. The impregnated Al_2O_3-film with $Os_3(CO)_{12}$ clusters which were imaged as fine speckles with nearly homogeneous diameter of 0.5 nm.

types of supports, high-surface area aluminas and the model oxide films supported on the NaCl crystals.

SAMPLE TREATMENTS

The influence of thermal treatments in various gaseous environments on the state of the osmium metal clusters or aggregates was studied using the model catalyst films. For this purpose, a set of several Al_2O_3/NaCl samples was impregnated with $Os_3(CO)_{12}$ simultaneously. These samples were then successively exposed to H_2, O_2 or CO atmospheres (1 bar) at various temperatures and one sample was selected for analysis by TEM after each preparation or treatment step.

PREPARATION OF SAMPLES FOR TEM

In preparation for TEM, the finished self-supporting films containing the osmium species after each respective treatment were floated off in water (net wetting the metal containing side) and mounted on copper grids (400 mesh).

ELECTRON MICROSCOPY

The micrographs were obtained with a Siemens EM 102 microscope with an instrumental magnification of typically 200.000 × and an acceleration voltage of 125 kV. To improve the contrast, the objective aperture was reduced if where necessary to ca. 30 μm, which led to a restriction of the spatial frequency spectrum in the electron microscopic image and a restriction of the phase contrast to $\leqslant 0.3$ nm.

Particle size distributions were obtained by determining the diameters of approximately 200 metal particles or clusters from several micrographs.

3. Results and discussion

Bright field micrographs of the thin amorphous alumina support with (fig. 1b) and without (fig. 1a) osmium clusters in the same defocus setting (normalised defocus $\leqslant 0.4$) are compared in fig. 1. The electron optical diffractogram inserted in fig. 1a demonstrates the structureless character of the support film. Under these electron optical conditions, the phase contrast is minimal in contrast to figs. 1c and 1d where the variation of the film granularity depends on the defocus setting. This through focus series of the osmium cluster containing films exhibits that the defocus of $\Delta = 0.4$ is an optimum for the imaging of such small osmium clusters which are fixed on thin structureless alumina films. By virtue of the almost structureless support film and by exploitation of the optimal defocus setting, one can perform size measurements on the clusters down to dimensions of 0.5 nm.

Fig. 1b shows very uniform cluster sizes of 0.5–0.6 nm; the size distribution for this material (freshly prepared prior to any thermal treatment) is demonstrated in fig. 2 (first column). Clearly about 90% of the detected clusters fall in the size range below 0.75 nm. Based on the preparation method it is to be expected, that the alumina-film contains structurally intact Os_3-clusters anchored to the surface. Infrared spectroscopy [18,19] and EXAFS [20] proved the formation of molecular clusters under the synthetic conditions applied here, which are bonded to the surface via bridging surface oxygen atoms (Os_{surf}):

$$[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_{surf})].$$

The Os–Os distance in the precursor cluster $Os_3(CO)_{12}$ is 0.287 nm. Hence, the dimension of the triatomic cluster core is estimated to be near 0.6 nm, which compares very nicely with the observed cluster size distribution. It is therefore inferred that the clusters seen in fig. 1b and fig. 2 (first column) in fact represent the Os_3 clusters.

When these anchored molecular clusters are thermally treated in a H_2 atmosphere at 580 K, they tend to aggregate and form larger OS° metal particles (fig. 2). A similar effect had been observed earlier, when high surface area alumina supported triosmium clusters were used as catalysts for CO hydrogenation at 10 bars and 520–600 K. Particles in the size range of 1–2 nm were seen by TEM in this case [21]. The formation of metal particles with increasing exposure time in H_2 at 580 K is shown in fig. 2. Clearly the average particle diameter increases with exposure time from 0.85 nm after 1 hr to 1.34 nm after 48 hrs. Similar sintering studies using model supports have been reported earlier by Ruckenstein [22], the materials investigated, however did not include osmium derived from molecular cluster precursors. The present study does not permit any conclusions to be drawn on the particle growth mechanism.

Fig. 3 summarizes a few experiments related to redispersion phenomena of Os° metal particles, when samples were exposed in CO and O_2 atmospheres. For direct comparison, fig. 3 again shows the micrograph and cluster size distribution of the initial surface triosmium clusters in the first column. In the second column, the particle formation in H_2 at 570 K after 2 hrs exposure is evident, the average particle size being 1.22 nm. Treatment for 2 hrs in a CO atmosphere at 470 K leads to a shift of the particle size distribution toward smaller particles (see third column in fig. 3). The average particle diameter is calculated to be 0.92 nm in this case. This observation suggests a redispersion of Os° metal particles in an atmosphere of CO. CO-induced particle fragmentation has been reported and studied in depth for SiO_2- and Al_2O_3-supported Rh° catalysts (see e.g. [18] and references therein). Metal-CO bond energies in noble metal carbonyl cluster compounds are typically greater than the corresponding metal-metal bond energies [23]. This is also true for osmium carbonyls

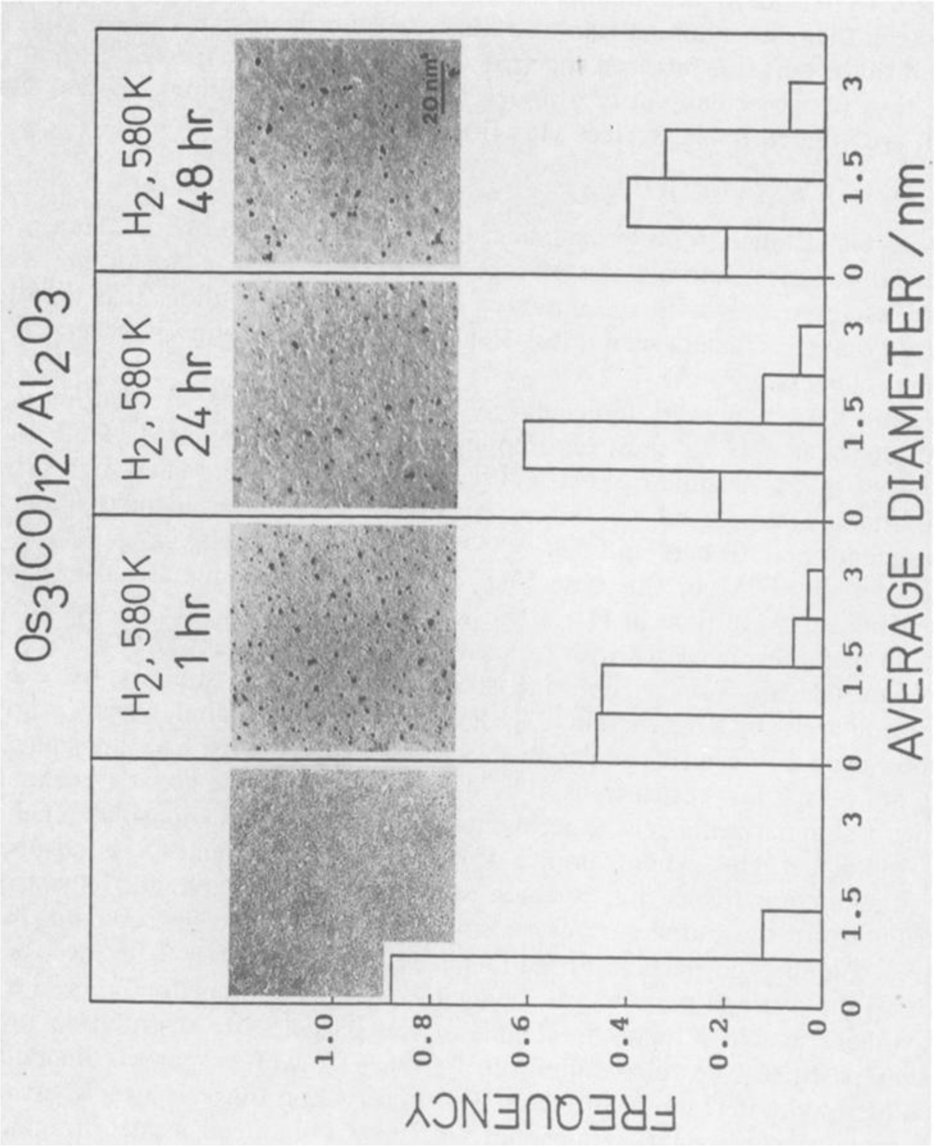

Fig. 2. Electron micrographs of an impregnated Al_2O_3-film with $Os_3(CO)_{12}$ clusters after H_2-reduction at 580 **K** for different time periods with the corresponding cluster size distributions.

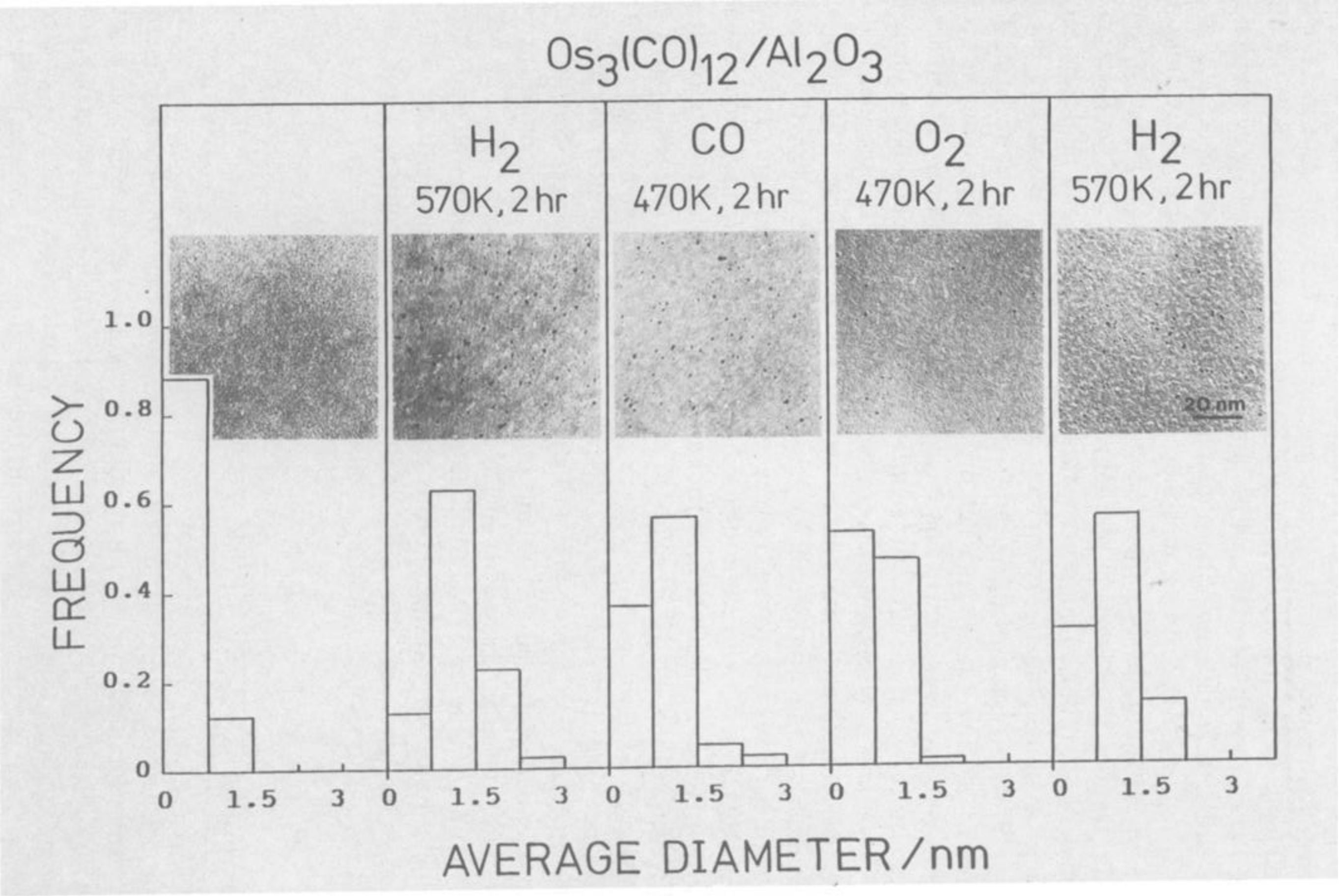

Fig. 3. Electron micrographs of an impregnated Al_2O_3-film with $Os_3(CO)_{12}$ clusters after different treatments with the corresponding cluster size distributions.

despite the relatively strong Os–Os bond. It is to be expected that the heats of chemisorption of CO on highly coordinatively unsaturated surface atoms on the surface of small metal particles is also greater than the respective metal-metal-bond energy [24]. Therefore, metal-metal bond rupture should be possible under the action of CO with formation of mononuclear subcarbonyl species which may possess sufficiently high mobility to enable redispersion to occur [25,26].

Redispersion in oxidizing atmospheres is a technologically very important process in regeneration of supported metal catalysts, such as e.g. reforming catalysts. Details of redisperion mechanisms have been studied by Ruckenstein [27] using model thin film supports with several transition and noble metals not including osmium. Similar experiments were reported by Wang and Schmidt [28]. The fourth column of fig. 3 shows the result of an O_2 treatment at 470 K for 2 hrs of the Os° metal particles produced during H_2 treatment as seen in column two of the same figure. The micrograph shows a few metal particles, the average size of which is shifted to significantly smaller dimensions, namely 0.71 nm. This value is only slightly greater than the diameter of the original triatomic cluster, indicating that the redispersion was in fact very efficient. In addition to the decrease of the average diameters of the visible particles, the very low number of particles seen after O_2 treatment suggests that some of the osmium escapes detection. The possible formation of volatile OsO_4 may indeed lead to metal loss. However, a subsequent reductive treatment in an H_2 atmosphere at 570 K (fifth column in fig. 3) leads to the reappearance of metal particles at higher density with an average diameter of 0.98 nm, although some metal loss can not be fully excluded. Hence, the osmium invisible after O_2 treatment should be present on the surface in extremely high dispersion. Sushumna and Ruckenstein [13] inferred that in the Pt/Al_2O_3 system a thin film of probably PtO extends out around particles after oxidative redispersion. This film was too thin to be detectable by TEM. An analogous explanation may well apply for the osmium-alumina system. Since even triatomic clusters could be made visible, an alternative interpretation may infer the formation of mononuclear OsO_x surface complexes which should definitely escape detection.

4. Conclusions

Thin self-supporting, structureless alumina films have proved very useful for application as model supports for metal clusters (Os_3) and particles in combination with high-resolution electron microscopy. By optimizing the imaging conditions with regard to the phase contrast transfer function of the electron microscope, cluster and particle sizes in the size range $\leqslant 1$ nm can be measured with these specimens. Aggregation and redispersion of osmium particles derived from molecular triosmium surface clusters could thus be studied. It is perhaps interesting to note that conventionally prepared (impregnation of H_2OsCl_6 from aqueous solution followed by H_2-reduction) high surface area catalysts [26] and $Os_3(CO)_{12}$-cluster derived catalysts on high surface area alumina [29] gave very similar particle size distributions, which were in both cases very close to those observed in the present study using model alumina-films after comparable H_2-treatment conditions. This observation may suggest that results of studies with the model support films are at least qualitatively relevant for real high surface area materials.

Acknowledgements

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