Structural analysis of $Au/Mg(OH)_2$ during deactivation by Debye function analysis

W. Vogel

Fritz Haber Institut der Max-Plank-Gesellschaft, Faradayweg 4-6, D14195 Berlin (Dahlem), Germany

D.A.H. Cunningham, K. Tanaka and M. Haruta [1]

Osaka National Research Institute, Midorigaoka 1, Ikeda City, Osaka 563, Japan

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Using a Debye function analysis, the presence of icosahedral and face centered cuboctahedral gold in a 1 : 1 ratio has been found in freshly prepared $Au/Mg(OH)_2$ catalyst. The results support earlier studies which suggest the icosahedral form to be more stable at small nanometer sizes. Interactions between the gold and the $Mg(OH)_2$ support appear to be weak, with the gold rapidly coagulating over a period of three months. Re-analysis of the aged sample shows the gold to be mainly in the form of truncated decahedra.

Keywords: gold catalysis; nano-size; Debye function analysis; TEM

1. Introduction

Over the last decade the high catalytic activity of nano-size gold has become gradually more important [1]. The reason for the interest in gold is that, perhaps unique amongst all the coinage metals, gold is able to oxidize CO to CO_2 at temperatures as low as −76°C. High catalytic activity is usually obtained when the gold is dispersed as ultrafine particles on alkaline earth or transition metal oxide supports, with the most active supports being $Mg(OH)_2$ and $Be(OH)_2$ [2], or semiconductors such as Co_3O_4 and Fe_2O_3 [3]. During detailed studies it has become apparent that major differences occur between the two classes of support, which are mainly related to the size of the gold particle. The critical size at which the behaviour of gold changes is approximately 2 nm. For hydroxides of alkaline earths, high catalytic activity is normally observed when the Au particle is less than 2 nm in size [2]. Transition metal oxides, however, remain active up to 10 nm.

As TEM is limited in its ability to study the structure of 1 nm size particles or amorphous support materials, it is difficult to obtain sufficient information to allow detailed studies to determine the reason for the differences in behaviour. In previous studies on nano-meter size gold, it has been predicted that the gold should undergo a structural change to the icosahedral form to minimize its energy [4]. To try to establish if differences in structure occur in the supported gold catalyst, we carried out a Debye function analysis (DFA) [5] on $Au/Mg(OH)_2$. The Debye function technique is based on modeling the intensity difference between the supported catalysts and catalyst support to obtain the diffraction pattern of the pure Au metal. As our first study, $Au/Mg(OH)_2$ was chosen because of the regular dispersion of the gold and the ability to control the size to less than 2 nm. The catalyst is also known to have one of the highest activities for CO oxidation, but deactivates rapidly on aging, giving us the possibility of studying active and inactive catalyst under similar conditions.

2. Debye function analysis

Previous theoretical studies on the stability of fcc metal clusters predict that the structure of gold should undergo a change from the fcc symmetry to the more thermodynamically stable icosahedral form at 1–2 nm in size [4]. Though the structure of the gold at the nanometer size is important, the study of such materials is difficult because of difficulties in growing materials with well defined size distributions. Because of this, confusion still persists in the literature concerning the structure of highly dispersed gold. In experimental studies by Marcus et al. [6] and Balerna et al. [7] the fcc structure has previously been determined to exist for gold particles as small as 55 atoms in size. However, these studies are limited by the fact that EXAFS is sensitive mainly to changes in bond distances, making a structural analysis based only on the use of EXAFS highly susceptible to error [8].

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[1] To whom correspondence should be addressed.

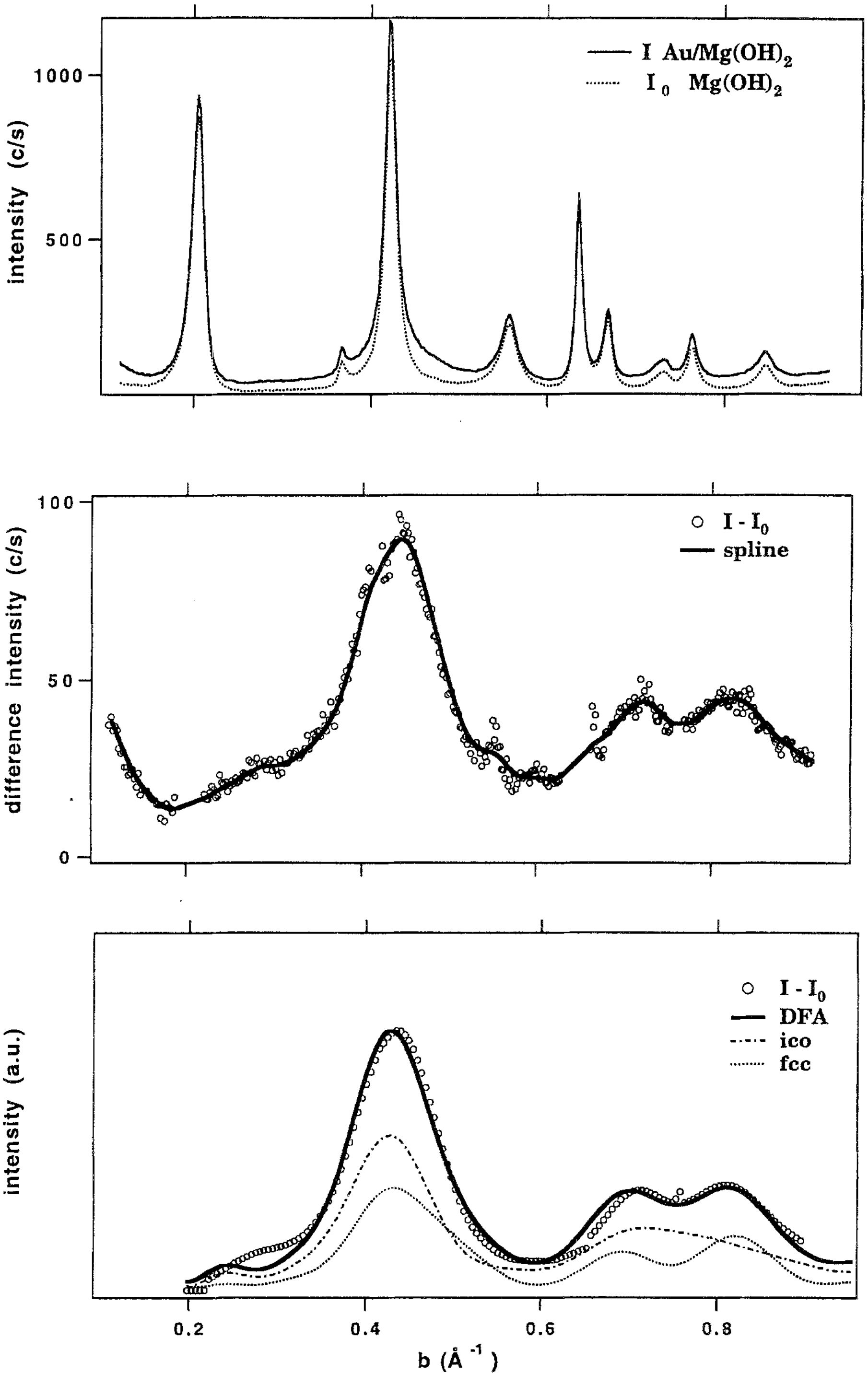

Fig. 1. From top to bottom: (i) original pattern of fresh catalyst and (calibrated) pure support intensity, (ii) difference intensity and spline fit, (iii) icosahedral Au_{13} + Au_{55} (dashed–dotted) and cuboctahedral Au_{55} clusters (dotted).

Using the Debye function (DFA) technique, which is much more sensitive to the symmetry of the particle, Vogel [9,10] has determined that the icosahedral form exists in Au_{55} dispersions. Debye function analysis [5] was first used in 1989 by Hall et al. [11] in the structural analysis of small ultra-fine particles using standard electron diffraction. This was later modified to X-ray diffraction studies by Gnutzmann and Vogel in 1990 [12]. Use of the DFA technique allows analysis of both the size distribution and symmetry of the particle and involves measuring the intensity difference between the catalyst of interest and the support [9–16]. Analysis of the difference spectra is then made with the assumption that strain is absent in small sub-nanometer metal crystals. This is justified because, though multiple twinning defects frequently occur, crystallographic defects such as grain boundaries in nanometer size particles are essentially meaningless and can be ignored. The intensity difference is then directly related to the metal phase and can be simulated by the addition of spherical averaged scattering functions of model clusters with incremental increasing size.

3. Experimental

Ultrafine gold particles supported on $Mg(OH)_2$ were prepared by first dispersing ultra pure magnesia (Ube industries Ltd.) in an aqueous solution of $HAuCl_4$. To the aqueous dispersion, magnesium citrate was added and the mixture stirred for a period of 2 h. During treatment the MgO undergoes a transformation to $Mg(OH)_2$. The precipitate was then washed thoroughly with distilled water to remove chlorine ions. After the precursor was dried under vacuum the sample was calcined at 280°C to produce metallic gold with dispersions approaching 1 nm in size at the surface [17].

All X-ray diffraction patterns were measured in a specially designed in situ cell [14] and mounted on a commercial Guinier diffractometer (HUBER). Samples were aligned 45° to the transmission geometry. X-rays of Cu $K_{\alpha 1}$ wavelength were generated by a conventional X-ray source, with the energy defined using a Johansson-type Ge monochromator. Sample catalysts were pressed under a pressure of approximately 4 tons/cm^2 to produce translucent pellets $8 \times 15 \times 0.2$ mm^3 in volume. For tablets this size, μd was calculated at approximately 1.0, where μ is the linear absorption coefficient of the catalyst under study. High resolution TEM photographs were recorded using a Hitachi H-9000 transmission electron microscope.

4. Results

Fig. 1 shows from top to bottom (a) the original intensity of the Au/$Mg(OH)_2$ catalyst taken one week after preparation compared with the calibrated $Mg(OH)_2$ intensity, (b) the difference signal, and (c) the simulation of the smoothed difference spectra by Debye functions of a mixture of fcc cuboctahedra and icosahedra, respectively. Neither face centered cubic cuboctahedral (fcc) nor icosahedra clusters in isolation reproduce the experimentally obtained diffraction profile (fig. 2).

The size distribution of gold particles supported on $Mg(OH)_2$ taken within 1 week of preparation is well defined and centered at approximately 1 nm (fig. 3). As the particle size of metals approaches atomic dimensions, theoretical calculations predict that, for fcc type metals, the crystal should undergo a structural change

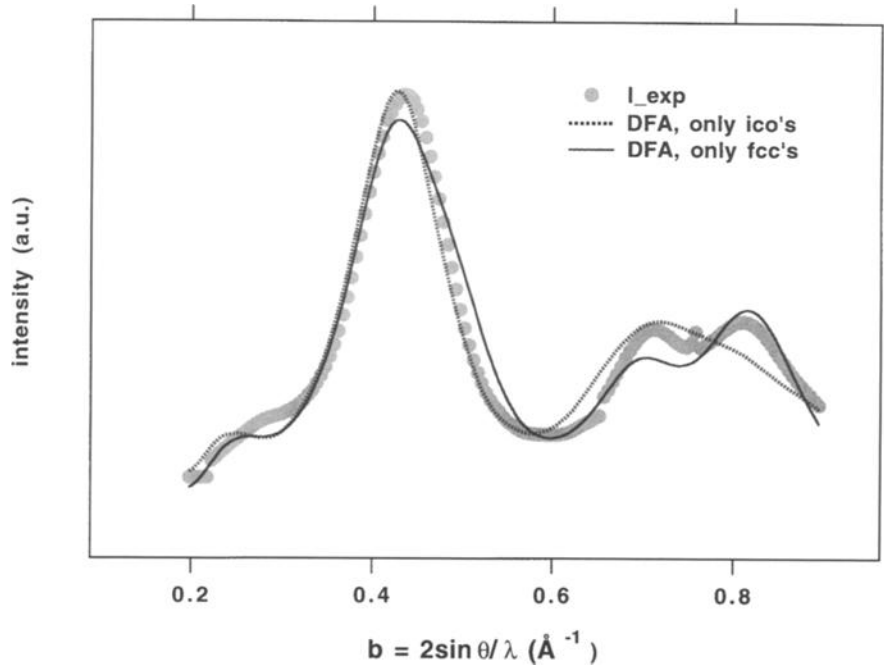

Fig. 2. DFA of fresh Au/$Mg(OH)_2$ using only fcc- cuboctahedra (solid line) and only icosahedral (dotted line). This figure indicates that individual fits using only one cluster type in isolation do not lead to a reasonable result.

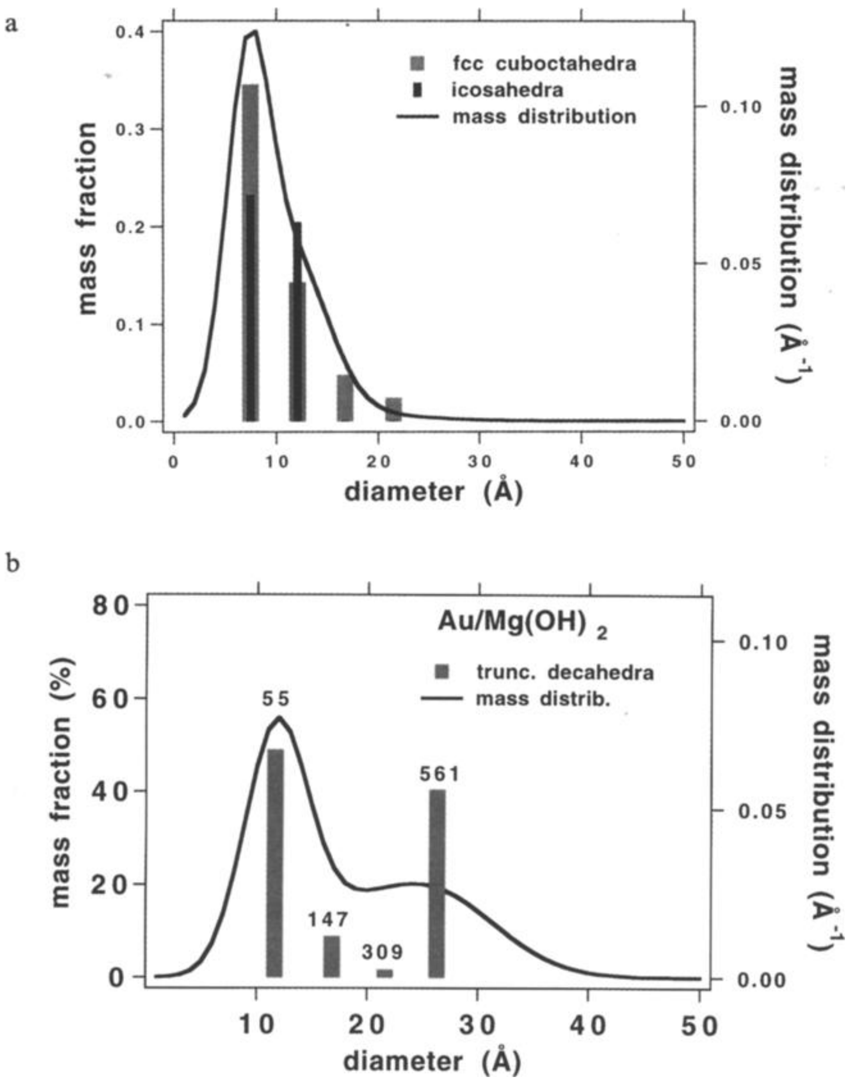

Fig. 3. Mass fractions of clusters corresponding to (a) the DFA of freshly prepared (1 week old) Au/$Mg(OH)_2$ and (b) aged Au/$Mg(OH)_2$ (3 months). The solid line gives the corresponding non-discrete distribution of mass.

from fcc to a Mackay icosahedron [18]. Because of the problem of coagulation, which normally prevents us from obtaining a clear identification of the structure of the gold present, many authors have taken to studying organo-stabilized Au_{55} clusters prepared chemically [19]. Though the study of systems with well defined size distributions aids analysis, care is required in transferring results based on model compounds to the Au particles found in catalysts.

In theoretical work by D'Agostino et al. three possible structures for the Au_{55} cluster prepared by the Schmid method were given [8]: (i) all clusters are icosahedral, (ii) all clusters are cuboctahedra with high static disorder due to the presence of ligands, (iii) the sample is a mixture of icosahedral and cuboctahedral clusters.

As stated previously, analysis of the DFA spectra allows us to determine both the size and the symmetry of the nano-crystalline particles. Looking first at the symmetry of the gold particle, in freshly prepared Au/$Mg(OH)_2$, gold can be divided into two main components. In the greatest concentration is fcc cuboctahedral gold, which ranges from approximately 2.1 nm to 0.8 nm in size. Also present is icosahedral gold, which originates between 13 and 55 atoms in size. By weight, the percentage of gold in the face centered cubic symmetry is approximately 58%. It should be noted that a near equal quality DFA simulation was also possible if the Au_{13} was assumed to exist entirely in the icosahedral form Au_{13} (36%) and the Au_{55} to be a mixture of icosahedral and face centered cubic; icosahedral-Au_{55} (23%) and fcc-Au_{55} (40%), respectively. However, the continuous mass distribution, plotted as a solid line in fig. 3 showed no major change upon this modification and the near 1 : 1 ratio of cubic and icosahedral particles remained unaffected.

Because it is known that Au/$Mg(OH)_2$ deactivates rapidly over a period of three to four months (the TOF per gold atom decreasing from a value greater than

Table 1
Comparison of turnover frequency between freshly prepared and aged 3 months Au/Mg(OH)$_2$. Mass of sample used was 0.15 g in a continuous flow reactor, SV 20 000 ml h^{-1}/g-cat

Au/Mg(OH)$_2$	Conversion (%)			TOF at −70°C
	−70°C	25°C	300°C	
fresh	100	100	100	> 0.1
aged	0	1	3	zero

0.1 s^{-1}, measure at −70°C, to less than 0.007 s^{-1}, measured at 300°C (see table 1)) and because we know that the particle size increases, it was of interest to determine how the gold changes from the active to less active state as a function of time. If the data is analyzed carefully, this provides us not only with information concerning the aging process, but also with information relating to the species responsible for catalysis.

Repeating the DFA analysis for Au/Mg(OH)$_2$ after a period of three months revealed a number of changes in the structure of the catalyst. From the DFA, a marked sharpening of the diffraction peak occurs, which is to be expected upon the particles increasing in size. In Au/Mg(OH)$_2$, growth of gold particles appears to be bimodal and not by atomic migration of unobserved atomicly dispersed gold, with the most notable change in the DFA profile occurring at approximately 2.8 nm in size. This is supported by TEM analysis (fig. 4) which differs from the DFA analysis by separating joined bi-particles back into discrete separate particles (fig. 5). For this reason the TEM analysis shows most particles to have a diameter of 1.0 nm size with no second peak at 2.8 nm. To make the DFA and TEM size distributions comparable, the DFA mass fractions of fig. 3b must be divided by the number of cluster atoms and re-normalized, leading to a number fraction of only 7% in the 2.8 nm range.

The most striking result that we obtain, however, is that after a period of three months both the icosahedra and fcc cuboctahedra apparently disappear, being replaced by the truncated decahedra form. Previously, in earlier studies on gold catalysts we have worked on the principle that the deactivation of Au/Mg(OH)$_2$ is associated with either changes in the electronic properties of the gold, or with changes in the structure of the support; in the Au/Mg(OH)$_2$ system magnesium is able to react with CO to form the carbonate. Because of this, it is difficult at this point to directly relate the changes in symmetry of the gold particle to catalytic activity.

5. Conclusions

From a Debye function analysis of the gold particles supported on Mg(OH)$_2$ a bimodal growth of the gold occurs upon aging. Freshly prepared the gold is present in two different states, with the smaller particles apparently taking the theoretically predicted icosahedral form. Over Mg(OH)$_2$ the icosahedral symmetry is apparently unstable, as is surprisingly the fcc cuboctahedron, with both undergoing change to truncated decahedra at room temperature. Growth over a period of three months is bimodal, indicating the coalescence of neighbouring particles and that the interaction between the gold and Mg(OH)$_2$ support is weak.

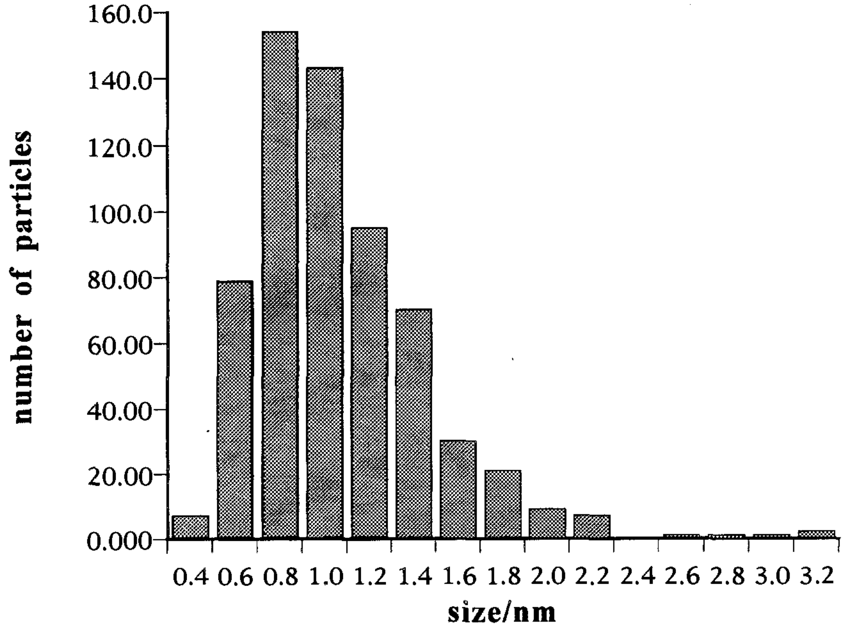

Fig. 4. TEM calculated size distribution of aged Au/Mg(OH)$_2$. In this analysis, bi-particles were frequently observed but for the calculation of size distribution such particles are considered to be two discrete particles.

Fig. 5. TEM photograph of aged Au/Mg(OH)$_2$. Thin needles of catalyst observed in this photograph are of Mg(OH)$_2$ crystals viewed from the side. Representative bi-particles are shown circled.

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