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High resolution Auger electron imaging of supported metal particles

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High spatial resolution Auger electron spectra and images of supported metal particles have been obtained in a UHV scanning transmission electron microscope. An edge resolution < 3 nm has been achieved. The number of atoms in a small particle can be estimated from the integrated intensity of the Auger electrons. This method is very useful for detecting and measuring particles with sizes smaller than the incident probe size. Ag clusters containing less than 20 atoms have been detected when supported on a thin carbon film.

Keywords: Auger electron imaging; Auger electron spectroscopy; small particles; supported catalysts

1. Introduction

A detailed understanding of catalytic processes requires knowledge of both bulk and surface properties of the catalyst system. The surface properties of small metal particles which are highly dispersed on supporting materials play a dominant role in determining this system's catalytic behavior. Therefore, the characterization of surface topography and chemical composition of supported metal particles is of primary interest. Surface morphology of supported catalysts can be examined by secondary electron imaging with subnanometer resolution [1]. The relative positions of the small metal particles on and within the support structure may have significant consequences for catalytic activity. Small metal particles dispersed on model and commercial catalyst supports have also been observed using our secondary electron imaging techniques [2].

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Although surface topography of supported catalysts can be studied with secondary electron signals, a spectroscopic signal such as Auger electrons must be used to extract chemical information of the surface species. In order to observe the active phases (small metal particles) which are highly dispersed on the carrier materials, it is necessary to have nanometer scale resolution in Auger electron images. In this paper we demonstrate the application of high resolution Auger electron imaging and spectroscopy to the study of supported metal catalysts. In addition, we show that with computer assistance, digitized Auger electron images can be used to estimate the total number of atoms contained in a particle with a size smaller than that of the incident probe.

2. Experimental

The carrier materials used were commercially available polycrystalline γ-alumina. Supports were prepared ex situ by dry grinding alumina pellets and dipping a holey-carbon coated molybdenum grid into the powder. The sample was heated to approximately 500°C for 4 h in the microscope UHV preparation chamber before metal deposition.

Silver was used because of its high Auger sensitivity. A deposit of 8×10^{14} atoms/cm^2 (or 0.6 monolayer (ML) mean thickness, referred to the atomic density of Ag (111)) was evaporated in situ onto the sample, at room temperature, from a water cooled Knudsen cell. The deposition was performed at a rate of 0.03 ML/minute. Silver particles with sizes < 5 nm in diameter were formed on the holey-carbon film support and the γ-alumina carriers. These small metal particles were easily observed in high resolution secondary electron and high-angle annular dark-field images.

After being examined in the microscope the same sample was extracted into the specimen preparation chamber and was annealed at 500°C for about 2 h. The number density and the particle size distribution changed due to the annealing. Larger particles with an average size about 10 nm in diameter were formed on the carbon film. Then another 0.6 ML Ag was deposited onto the sample again at room temperature. Therefore, large ($\approx$ 10 nm in diameter) as well as small Ag particles ($\approx$ 1–5 nm in diameter) can be examined at the same time.

The Vacuum Generators HB-501S, codenamed MIDAS (a microscope for imaging, diffraction and analysis of surfaces), was used for these studies. Detailed descriptions of the MIDAS system have been published elsewhere [3–5]. Briefly, this instrument is fully bakeable and has a base pressure $\approx 10^{-10}$ mbar throughout. One unique feature is the collection of secondary and Auger electrons through magnetic "parallelizers" situated inside the objective pole pieces. With this configuration high collection efficiency of the emitted electrons has been realized. The efficiency of electron collection is further enhanced by

biasing the sample negatively. For Auger electron analysis the collection efficiency can be optimized by changing the bias voltage, which in these experiments was -500 V.

For high resolution Auger electron spectroscopy (AES) and Auger electron imaging experiments an electron beam current of $\leqslant 0.2$ nA, within a probe < 2 nm FWHM, was used. A concentric hemispherical analyzer (CHA) was employed as the final detector for AES. All images and spectra were acquired digitally. The energy scales of the acquired Auger electron spectra were shifted to compensate for sample bias. All Auger electron images were acquired with an image resolution of 128 pixels $\times$ 128 lines with a large dynamic range.

3. Results and discussion

3.1. Ag SUPPORTED ON CARBON FILM

Fig. 1a shows an Auger electron spectrum obtained from an area containing deposited Ag particles and the holey-carbon film support. The 512 point spectrum was averaged 8 times with a dwell time per point of 0.1 s. The total acquisition time was about 7 min. The carbon KLL and the Ag MNN Auger peaks are shown clearly. There is no observable contamination on the sample surface as checked by examining the contrast changes in the secondary electron images. Fig. 1b shows a high energy resolution Ag MNN Auger spectrum. The total acquisition time for this spectrum was about 24 min. Because of the high probe energy and very thin specimen used the peak to background ratio in the spectrum is extremely good ($P/B \approx 2$). The Ag MNN doublet is clearly resolved.

Spectroscopic images can be obtained by collecting energy-selected signals. Fig. 2a shows an Ag MNN Auger peak (nominally 350 eV) image of Ag particles supported on a thin carbon film. The Ag particles have an average size about 10 nm in diameter. Fig. 2b shows another image of the same area but formed with the carbon KLL Auger peak (nominally 263 eV) signal. These images were acquired at a dwell time of 6 ms per pixel, resulting in a total acquisition time about 2 min for each 128 pixel $\times$ 128 line image. The Ag particles are shown with very high bright contrast in the Ag MNN Auger peak image as expected. However, the larger Ag particles are also revealed with bright contrast in the carbon KLL Auger peak image although the relative image contrast is much lower than that shown in fig. 2a.

The bright contrast of the Ag particles in the C peak image could occur for either chemical and/or electron scattering reasons, e.g. (1) carbon contamination on the Ag particles, (2) contributions from backscattered electrons and (3) high secondary electron background from the Ag particles. The first factor can

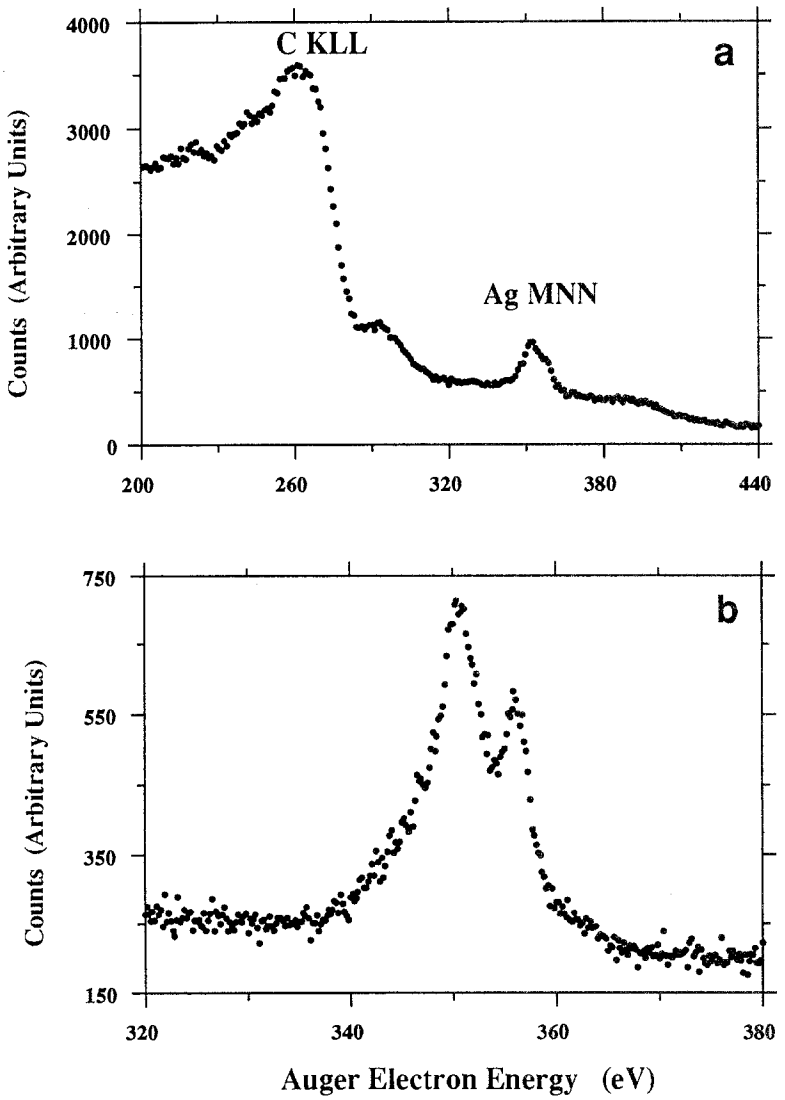

Fig. 1. (a) Survey Auger electron spectrum obtained from an area containing Ag particles on a thin carbon film; (b) high energy resolution Ag MNN Auger electron spectrum.

be ruled out based on our specimen preparation method; we also note that the peak to background ratio in the Ag MNN spectrum shown in fig. 1b is at least as high as that from pure, clean Ag. The second factor, the contribution from backscattered electrons, is not significant for small Ag particles supported on thin carbon films. We have shown that the third factor plays a dominant role in the image of Ag particles taken at (all) energies in the vicinity of the C peak. In fig. 2c, which shows a secondary electron image of the same area, the Ag particles have much higher secondary electron yield than that of the carbon film,

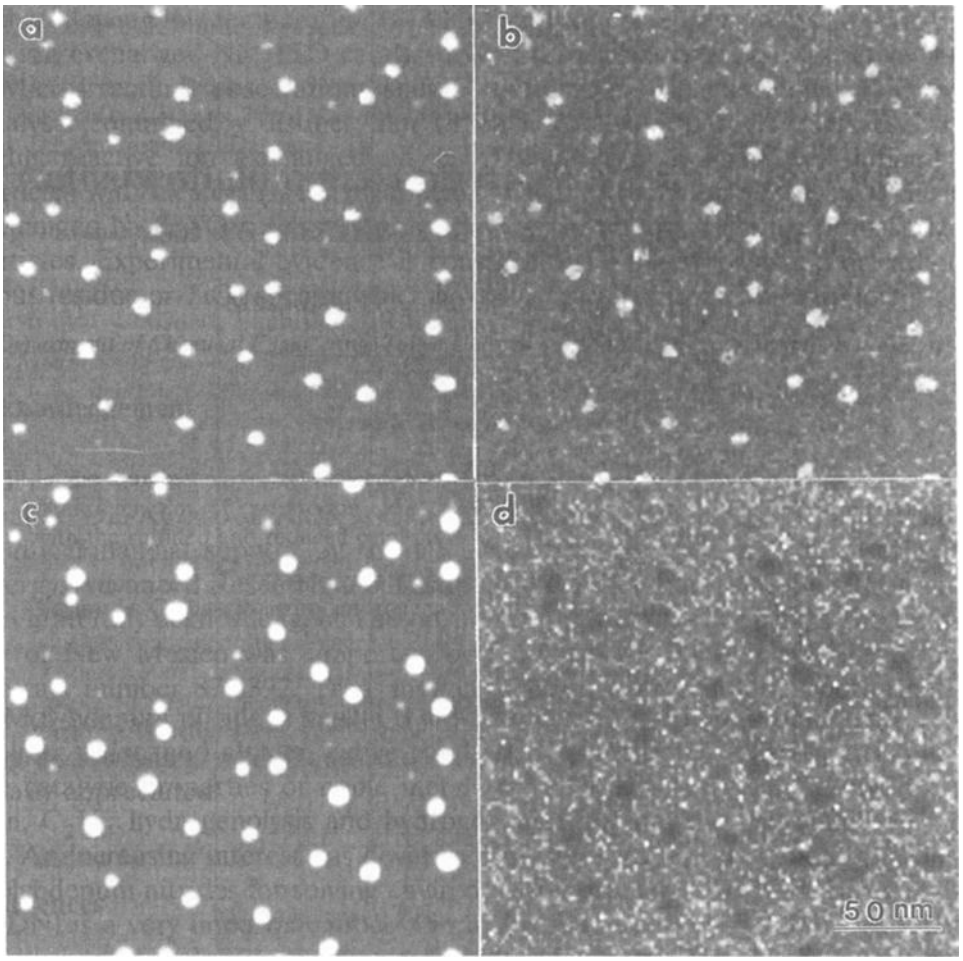

Fig. 2. Ag MNN (a) and carbon KLL (b) Auger peak images of the same area; (c) is the corresponding secondary electron image; (d) is the ratio I_C / I_{Ag} of pictures (a) and (b).

and spectra show that this larger background extends up to the C peak energy and beyond.

Full Auger information for such a sample can be obtained by taking four images, at and above the C and Ag peak energies, and can be displayed in various ratio forms. With two images, only the ratio of peak intensities I_C/I_{Ag} can be obtained, and this is not an element-specific map. Nevertheless this ratio, shown in fig. 2d, indicates the qualitative distribution of carbon as seen by the probing beam. At the high beam energies employed, the Ag background image has very low contrast, so that the element specific (peak − background) image is not much different from the Auger peak image alone [5]. Of course, if we were trying to detect a minor component on the surface of such a particle, such background subtracted images would be essential.

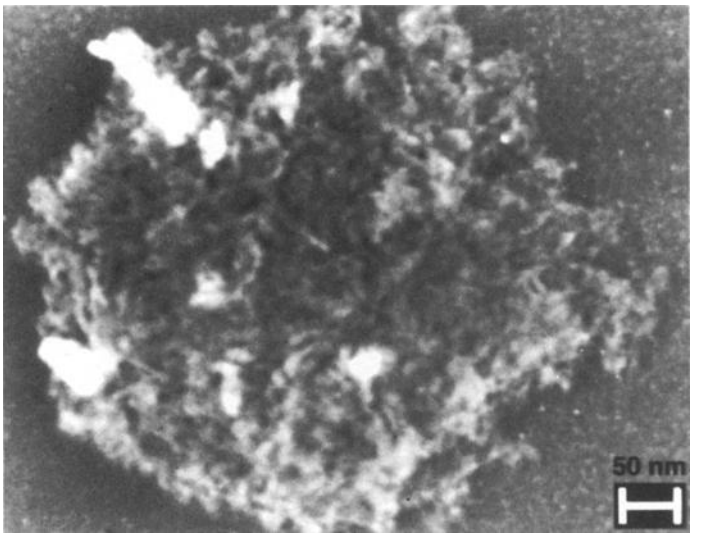

Fig. 3. Secondary electron image of a large agglomerate of uncoated γ-Al_2O_3 carrier, revealing fine surface topography.

3.2. Ag SUPPORTED ON γ-ALUMINA

At the electron beam energies typically used in STEM instruments the surface of electron beam transparent insulators should, in principle, acquire a positive potential which will suppress the emission of secondary electrons. However, our results with 100 keV incident electrons have shown that small crystals of insulators (e.g., α-alumina carriers, MgO smokes, etc.), dispersed on conducting supports, do not charge up substantially. For commercially available high surface area γ-alumina carriers unstable charging of the specimen can occur during electron microscopy observations. But, it is still possible to examine surface topography of the γ-alumina supports, without coating, using secondary electrons. Fig. 3 shows a typical entrance surface secondary electron image of a large agglomerate of high surface area γ-Al_2O_3 carriers. The surface morphology is revealed clearly with high resolution.

Auger electron spectra can be obtained from these γ-Al_2O_3 clusters to yield surface chemical information. Ag MNN and O KLL Auger spectra obtained from a γ-Al_2O_3 cluster, deposited with 0.6 ML Ag, are shown in figs. 4a and 4b, respectively. The acquisition time for fig. 4a was about 10 min. The oxygen KLL spectrum was obtained with higher energy resolution, and was acquired in about 20 min. The Auger peak image of the Ag particles is shown in fig. 5a. The particles are revealed with bright contrast on a relatively uniform background of the γ-Al_2O_3 carrier. Silver particles as small as 2 nm in diameter are clearly revealed. Fig. 5b shows the corresponding secondary electron image obtained simultaneously with fig. 5a. It is interesting to compare these two images. The

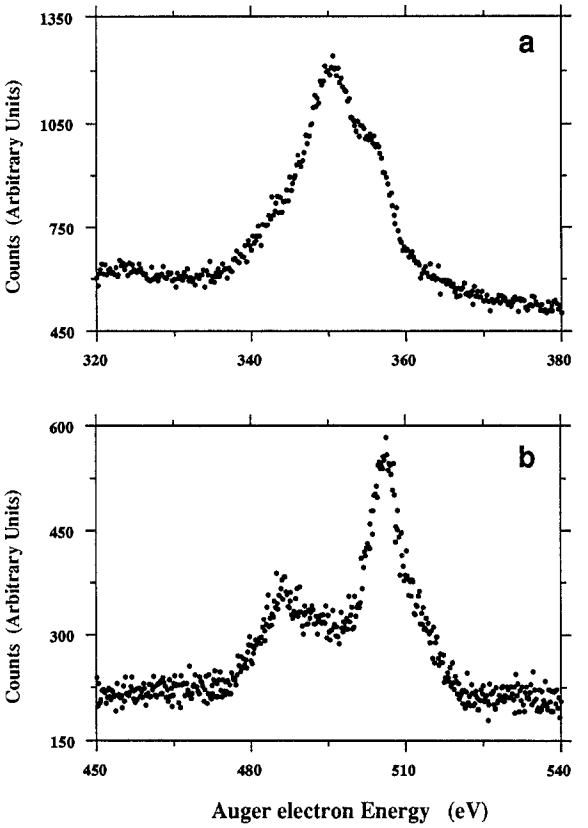

Fig. 4. Ag MNN (a) and oxygen KLL (b) Auger electron spectra obtained from γ-Al_2O_3 carrier deposited with 0.6 ML Ag.

contrast in the Ag peak image comes mainly from the Ag particles. In the secondary electron image small particle contrast can be obscured by support topography or by other effects. For example, the small Ag particles indicated by A and B are clearly revealed in the Ag MNN Auger peak image but are not shown unambiguously in the secondary electron image. On the other hand, fig. 5b shows the support morphology clearly.

3.3. RESOLUTION LIMIT AND DETECTION SENSITIVITY

Fig. 6 shows a Ag MNN Auger peak image of small Ag particles deposited on a thin carbon film. The coverage of the Ag is about 0.6 ML. The image was acquired into 128 pixel $\times$ 128 lines with a pixel size about 0.19 nm. Small Ag particles with sizes < 2 nm in diameter are clearly resolved. Intensity line scans across a big and a small Ag particle are shown in figs. 7a and 7b, respectively. On large islands, an edge resolution < 3 nm has been achieved. An edge

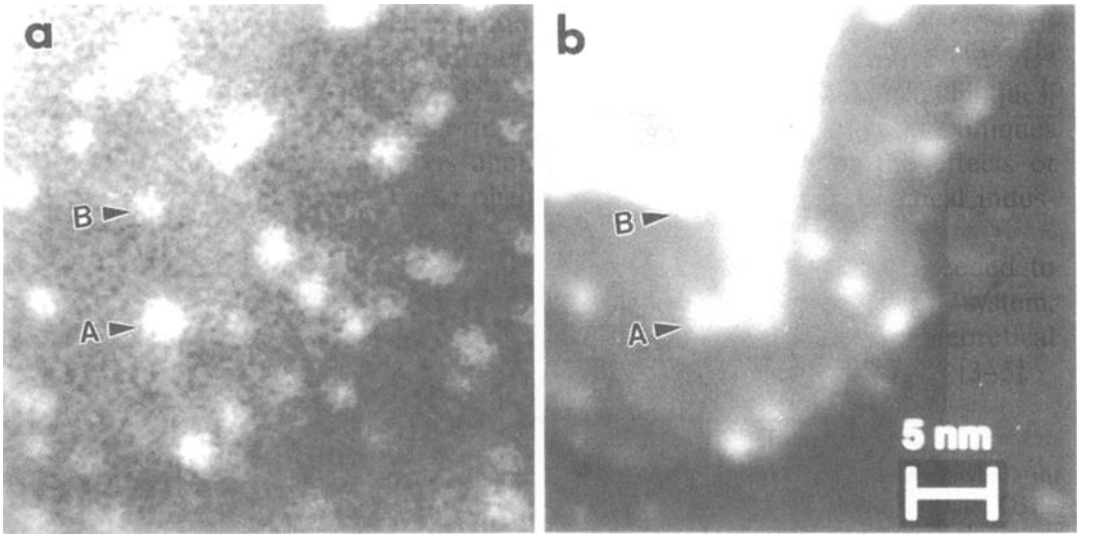

Fig. 5. Ag MNN Auger peak (a) and secondary electron (b) images of $Ag/\gamma\text{-}Al_2O_3$ sample. Ag particles as small as 2 nm in diameter are revealed clearly with high contrast in (a).

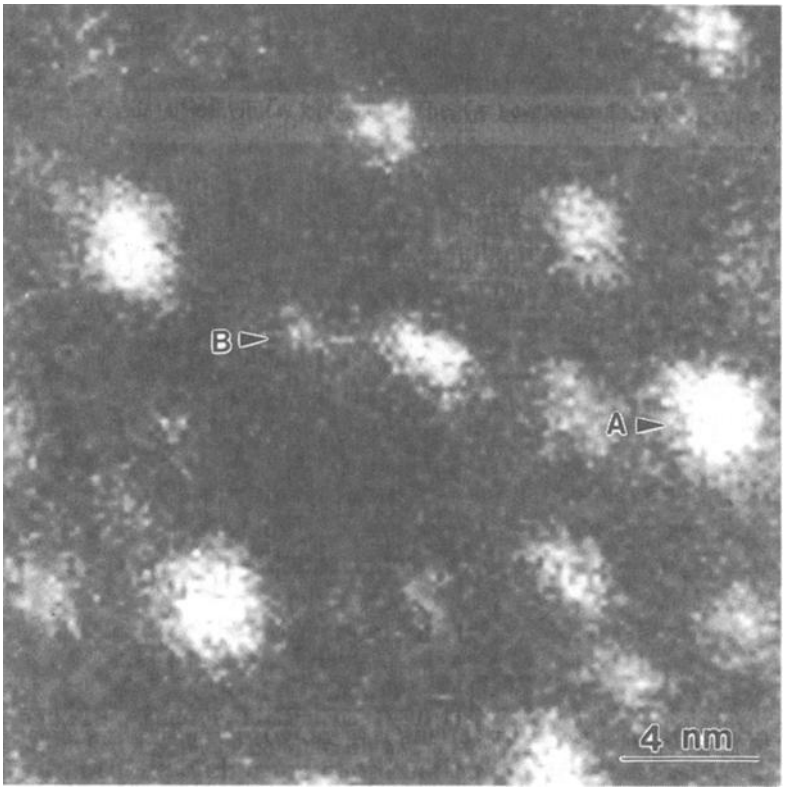

Fig. 6. Ag MNN Auger peak image of small Ag particles supported on a thin carbon film.

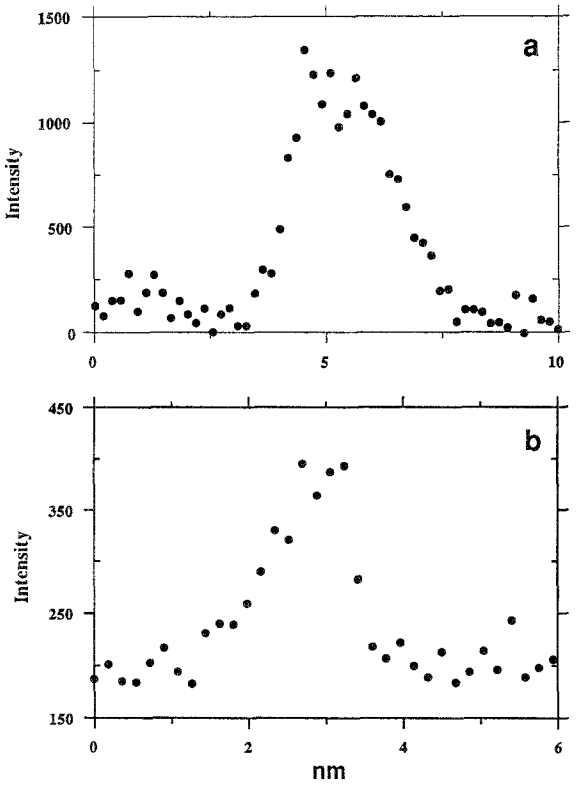

Fig. 7. (a) and (b) show intensity line scans, revealing the intensity profile of a large and a small Ag particle, respectively.

resolution < 3 nm has also been achieved in oxygen KLL Auger peak images of small MgO smoke crystals.

The resolution in Auger electron images is affected by several sample- and instrument-related effects. The sample-related effects include (1) surface topography, (2) Auger electron escape depth, (3) backscattered electrons, and (4) localization of the Auger generation process. Although the last factor would be the ultimate resolution limit, our results indicate that this is not the limiting factor with the present instrumentation. With very thin specimens and high energy incident electrons, the contribution from backscattered electrons should be negligible. For imaging very small particles the first two factors are not relevant for the following reasons. The emission of secondary and Auger electrons from small particles is quite different to that from flat surfaces of bulk material. Electrons generated inside small particles will have a high escape probability, provided that the particle radius is smaller than the inelastic mean free path, λ, of the secondary and Auger electrons. In the small particle limit, the collected Auger or secondary electron current is proportional to the volume of the particle, and the distinction between "bulk" and "surface" signals is no

longer valid. The instrument-related effects include (1) incident probe size, (2) collection efficiency and (3) instability of the microscope. At present, these factors set the limits of the obtainable resolution to < 3 nm in Auger peak images of supported metal particles.

The diameters of particles comparable to, or smaller than, the probe size cannot be measured reliably from electron micrographs because the intensity profile of the particle is a complicated convolution of the probe, topography and escape depth with the real dimension of the particle. However, the integrated Auger signal from a small particle, in the absence of image noise, should be independent of the probe size. As discussed above the integrated intensity (I) of a particle is proportional to the total number of atoms (N) which contribute to the collected Auger signal in that particle: $I = \alpha N$, where α is a parameter determined by the Auger cross-section, collection efficiency, incident beam current and other instrumental parameters. However, α can reasonably be assumed constant in the same micrograph. Thus the number of atoms contained in a small particle, N_1, with an integrated intensity I_1 can be estimated from a large particle (subscript 2) as $N_1 = N_2(I_1/I_2)$, i.e. a larger particle can be used as an internal calibration.

If we apply this ratio method to the particles A and B indicated in fig. 6 we obtain $N_A/N_B = 50$. The diameter of particle A is less than 4 nm. The inelastic mean free path (λ) of the Ag MNN Auger electrons is about 0.82 mm [6]. If we assume that particle A has a hemispherical shape, then $N_B < 20$ regardless of the shape of this particle.

In principle the integrated intensity is independent of the probe size. However, in practice the cluster visibility in the Auger peak image will change with size of the incident probe. With a larger probe the particle edge detection will be susceptible to any noise within the image which introduces errors in the intensity measurement. The minimum detectable dimension is different from the resolution of Auger peak images [7]. While the latter is limited by the incident probe size, the former is related to, but not limited by, the dimension of the probe. It is directly related to the signal-to-noise and signal-to-background ratios. The minimum detectable dimension may eventually be reduced to a single atom provided that the microscope is stable enough, delivers a sufficient dose of electrons, and that the atom in question does not move during observation.

4. Conclusions

Spatial resolution of less than 3 nm has been achieved in Auger peak images of supported metal particles. Silver clusters containing less than 20 atoms have been detected with Auger electron signals. This pushes the minimum detectable mass to less than 3×10^{-21} g for Auger electron spectroscopy. The simultaneous

detection of Auger electron and secondary electron signals yielded topographical as well as chemical information of supported catalysts.

Acknowledgement

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