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S. J. Pennycook and D. E. Jesson
Solid State Division, Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, Tennessee 37831-6030

D. R. Liu
Ford Motor Company, Research Laboratory
20000 Rotunda Drive, Dearborn, Missouri 48121

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S. J. Pennycook, D. E. Jesson and D. R. Liu*

Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6030;
*Ford Motor Company, Research Laboratory, 20000 Rotunda Drive, Dearborn, MI 48121.

Z-contrast imaging in the scanning transmission electron microscope has become the accepted technique for imaging sub-nanometer catalyst clusters, utilizing the high angle annular detector introduced by Howie[1]. The lack of coherent phase contrast effects greatly assists the identification of small clusters, especially near the resolution limit of the microscope[2]. The choice of inner detector angle depends on the system being studied. The highest signal to noise ratio is obtained with the smallest inner detector angle, but increasing this angle significantly reduces the contribution of coherently scattered electrons, which is advantageous for crystalline support materials. In this case, small metal clusters may be unambiguosly distinguished from diffracting regions of the support, and their size distributions determined. Fig 1 compares two preparations of 1 wt% Pd on γ-Al_2O_3, prepared from palladium nitrate solution[3], and aged at 600°C for (a) 6 hours, and (b) 24 hours. Images were taken with a VG Microscopes HB501UX 100 kV STEM, using a probe size of ~3Å. The narrower size distribution resulting from the longer aging time is clearly observed.

Now that cluster sizes are approaching the resolution limit of 100 kV instruments, we might anticipate significant advantages in utilizing the smaller probes available with a 300 kV STEM. Although for size distibution determination we may not require the 1.3Å probe available with this instrument, two potential advantages are immediately apparent. Since the clusters are supported on high surface area support materials, which are naturally three dimensional in form, the microscope depth of focus and the degree of beam broadening in the support are critical considerations. Probe profiles as a function of defocus are shown in Fig. 2. At 300 kV, although the optimum probe profile is much sharper than at 100 kV, the loss of intensity at low defocus values, and the extended tails at high defocus values mean that for a probe size of ~2.5Å the depth of focus is limited to ~800Å in both cases. However, the 300 kV STEM does offer a substantial reduction in beam broadening. Particles on the exit surface of the support will be imaged with a probe that has undergone beam broadening (assuming that no strong channelling condition exists in the support). The thickness dependence of the spatial resolution calculated by the simple formula of Goldstein et. al.[4] is plotted in Fig. 3. Since beam broadening is inversely proportional to accelerating voltage, for a 300 kV probe, 3Å resolution can be expected after passing through 200Å of support, but this reduces to less than 100Å for a 100 kV probe. Evidence of this increased penetration power is seen in the image of Fig. 4a., taken with the VG Microscopes HB603. For comparison, Fig. 4b. shows a bright field phase contrast image, recorded simultaneously, in which no catalyst clusters can be discerned.

In the future it may prove possible to resolve the atomic structure of real catalyst clusters by utilizing the small probe capability of the 300 kV STEM. For sufficient signal to noise ratio it would be necessary to reduce the detection angle to the minimum necessary for incoherent imaging[5], $\theta_i = 1.22\ \lambda/\Delta R$, or ~12 mrad for a 2Å column spacing. Transverse incoherent imaging would then allow column positions to be determined directly from the image. However, since the image would be formed from coherently scattered electrons, the intensity of each column would be proportional to the square of the number of atoms in the column, up to a thickness of $2\lambda/\theta_i^2$ after which scattering from the top and bottom of the crystal destructively interfere. For a 12 mrad inner detector angle this thickness is 267Å, well above the thickness range of interest. Therefore it should be possible to use maximum entropy image analysis to quantify positional and intensity information, and extract the likely three-dimensional form of the cluster[6].

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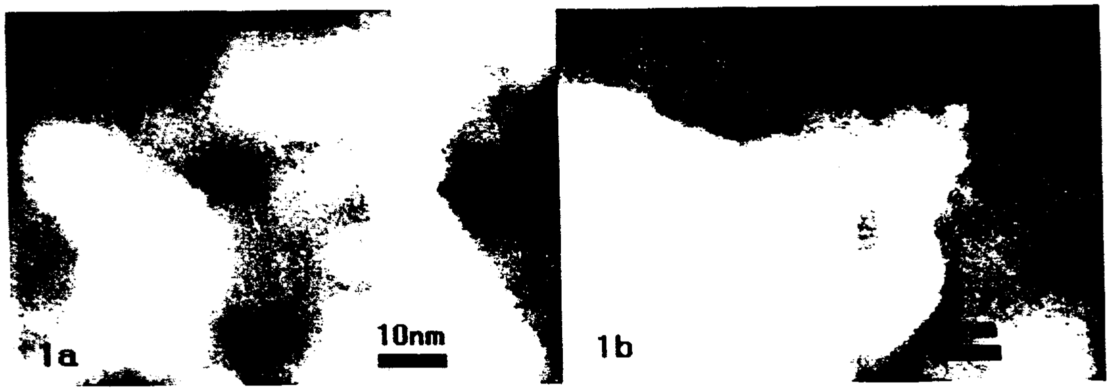

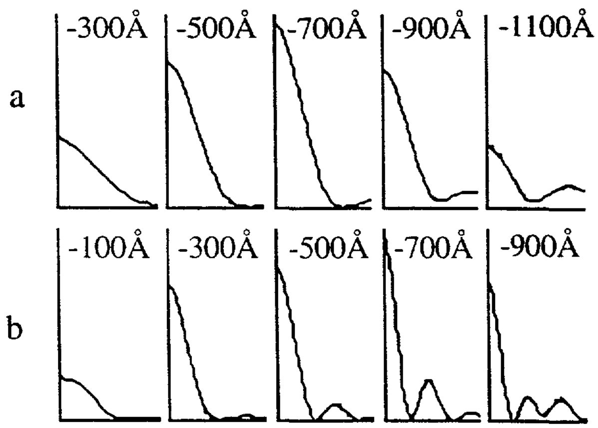

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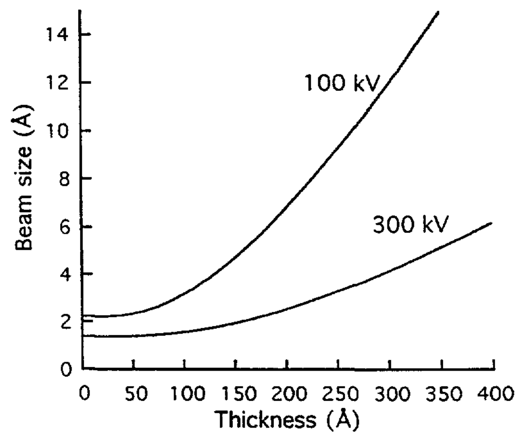

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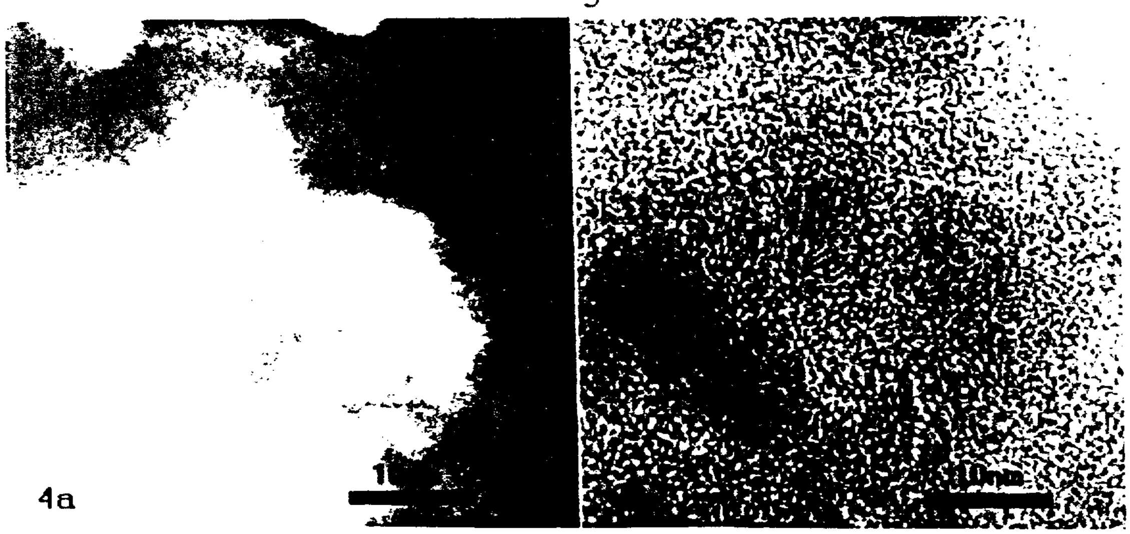

FIG. 1.--100 kV Z-contrast images of Pd clusters on γ-Al_2O_3, aged at 600°C for (a) 6 hours, and (b) 24 hours. FIG. 2.--Probe profiles as a function of defocus at (a) 100 kV, C_s = 1.3 mm, 10.3 mrad aperture, and (b) 300 kV, C_s = 1 mm, 11.3 mrad aperture. Fig. 3.--Beam broadening in γ-Al_2O_3. Fig. 4.--(a) 300 kV Z-contrast image of Pd clusters on γ-Al_2O_3, aged 600°C for 24 hours, (b) Simultaneous bright field image.