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COMPUTER SIMULATED IMAGES OF PLATINUM CLUSTERS IN Y ZEOLITE

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High resolution electron microscopy is a valuable technique for studying catalytic metals and their zeolite supports because it allows direct visualization of their microstructure. The question is: what is the smallest metal particle that can be detected by electron microscopy in such a system? Our goal is to determine the conditions under which a small (13 atoms) platinum cluster inside a Y zeolite channel can be detected by HREM. We chose the Pt/Y system because modified Y zeolites are widely used in commercial catalyst systems and Pt is a common and important catalytic metal.

The image simulations were carried out using the 81D version of the SHRLI programs.[1] The dynamical electron scattering calculation used the multislice method with a slice thickness of 0.4988nm.[2] In order to carry 3017 diffracted beams through the crystal, interactions were considered with 12097 phase-grating coefficients out to $42.2 nm^{-1}$ in the [110] zone (out to h,k=±104). The 0.4988nm slice containing the Pt cluster was incorporated as two "sub-slices" of 0.2494nm thickness. The sum of diffracted beam intensities at 70nm thickness was better than 0.999 for all models. Atom coordinates for the Y zeolite were taken from the work by Baur.[3] Images were computed for JEOL 200CX parameters; viz. C_s of 1.2mm, beam convergence semi-angle of 1.0mrad, spread-of-focus halfwidth of 10nm, objective aperture of $5nm^{-1}$. The zeolite was oriented with the electron beam parallel to the <110> Y zeolite channels. The Pt cluster consisted of one atom surrounded by six atoms in a plane with three atoms above and three atoms below, ie., it retained the three-fold symmetry of the Pt (111) planes.

Figure 1 shows the projected potential map of the Y zeolite unit cell in the [110] projection and how the 13-atom Pt cluster was assumed to fit in the channel. In the 3.5nm thick specimen (fig. 2a), the presence of the Pt cluster is detected in every focus setting, but only by comparing the images. At 7.0nm thick, the images are the same both with and without Pt for -30nm and -120nm defocus (fig. 2b). The presence of Pt creates darker contrast inside the channel when Δf= -60nm and -90nm. The same is true for the 10.5nm and 14.0nm thick specimens except that the contrast of the Pt images inside the channels decreases with increasing thickness.

In all the images calculated near optimum defocus[4](-60nm for the JEOL 200CX), dark patches appear at the tunnel positions even when no Pt is present; this effect occurs even for thin crystals (fig. 2a). The explanation for the "anomalous" dark contrast is provided by the contrast-transfer-function (CTF) for the 200CX microscope. Figure 3 shows how the lowest-frequency reflection from Y zeolite ({111} in the <110> orientation) is largely blocked by phase shifts in the objective lens of the 200CX at -60nm defocus; only approximately 21% of its amplitude is passed to contribute to the image, and it is this missing {111} frequency that produces the dark patch.

The calculations show that unambiguous images of the 13-atom Pt cluster residing in the channel of Y zeolite can be obtained only under very specific conditions. Part of the reason that the 13-atom cluster is difficult to detect in the calculated images is that the contribution of the periodicity of the matrix to the image is very strong. This "overwhelms" the contrast of the Pt cluster. When the zeolite is not oriented exactly along a major zone axis, the matrix contribution to the contrast would be substantially smaller, rendering the Pt cluster more visible. During the observation, the zeolite often loses its crystallinity with time. This should also increase the visibility of small metal particles. Work is underway on image simulation studies of Y zeolite under these imaging conditions.

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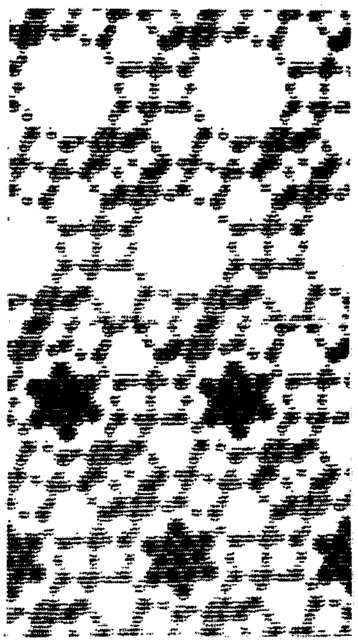

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FIG. 1.--Projected potential map of [110] Y zeolite unit cell, with and without Pt cluster in channel.

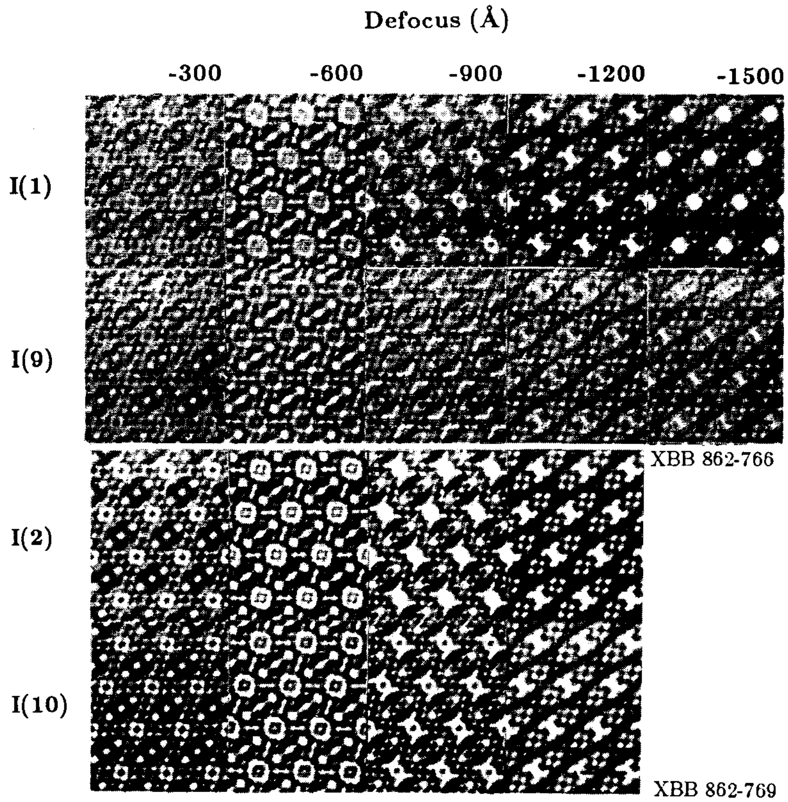

FIG. 2.--Computed Y zeolite images. I(1),I(2) w/o Pt; I(9),I(10) with Pt; Bar=1.43nm. a) 3.5nm thick, b) 7.0nm thick.

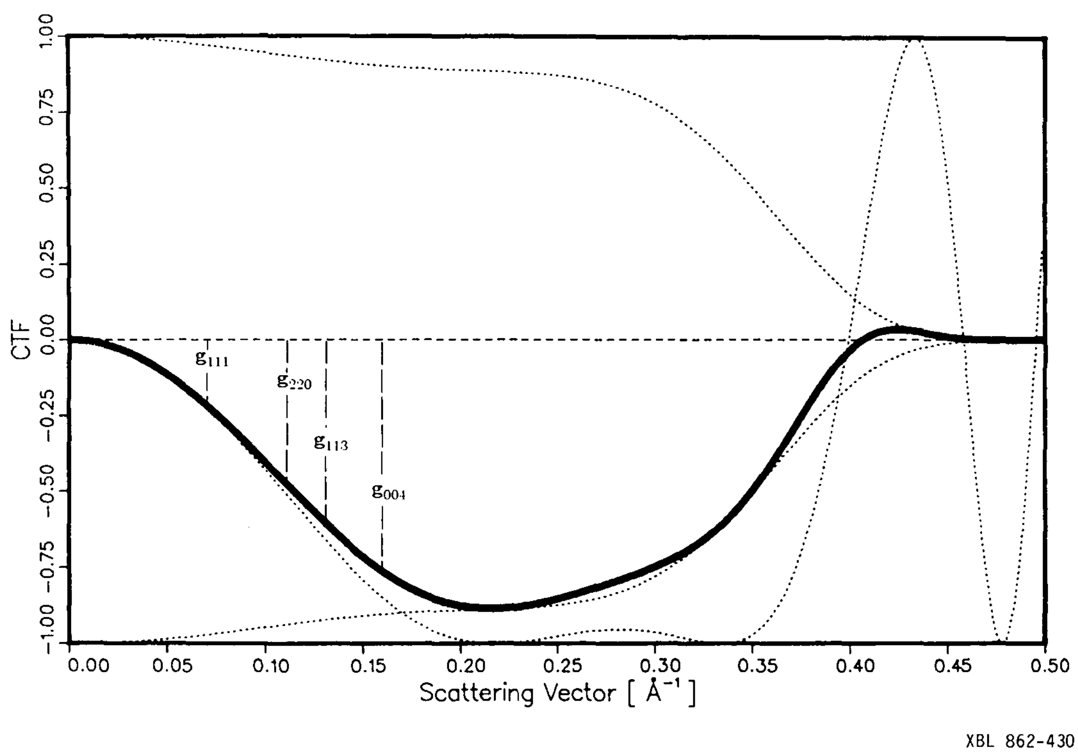

FIG. 3.--Operating CTF for 200CX, Scherzer defocus (-60nm), four lowest frequencies of Y zeolite marked.

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