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Electron Microtomography: A New Method for Studying the Spatial Structure of Catalysts

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Abstract—The spatial arrangement of active component (Pt) particles on the surface of a support (Sibunit globule) has been studied by bright-field electron tomography. A tomographic attachment for a standard specimen holder and tomographic grids have been designed. The tomographic procedure has been refined, and adequate tilt series alignment and tomographic reconstruction algorithms have been chosen. The 3D distribution of the active component in the catalyst grain has been studied: particles hidden in micropores have been directly observed, and the size of the pores connecting internal cavities with the exterior has been estimated.

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INTRODUCTION

Electron tomography (ET) has been used by biologists in the reconstruction of the spatial structure of macromolecules and cell organellas since 1968 [1]. However, the first materials science application of ET was reported only in 2000 [2]. This long ignorance stemmed from the very essence of ET. For a reconstruction algorithm to work correctly, the electron micrographs must satisfy the so-called projection condition: the image intensity at each point must be a monotonic function of two quantities, namely, the specimen thickness and the density of the substance along the imaging beam. This condition is readily met by weakly scattering and amorphous specimens as in biological applications. However, the great majority of the objects of materials science give rise to so-called diffraction contrast due to their crystalline nature (Fig. 1). The projection condition is not satisfied in this case.

In order to solve this problem, it was suggested to make ET reconstruction in the high angle annular dark field STEM (HAADF STEM) or energy filtered TEM (EFTEM) mode [3]. Due to the specific features of contrast formation in these modes, the resulting images satisfy the projection condition and are characterized by a spatial resolution of a few nanometers. Furthermore, both imaging modes are element- or atomic-number-sensitive, providing additional, very valuable information. For example, in the HAADF STEM mode, the image intensity at any point is proportional to the squared atomic number. The diffraction contrast can be avoided by using the annular dark field TEM (ADF TEM) imaging mode [4]. The backbone of this method is the special shape of the diaphragm: the central beam is shuttered with an opaque disc and the image is formed by electrons scattered at an angle of 20 to 40 mrad that have passed through the annular slit of the diaphragm. A drawback of the ADF TEM technique is the strong image delocalization due to the spherical aberration of the objective lens. For a higher resolution, it was suggested to use a spherical aberration (Cs) corrector. However, the introduction of a Cs corrector makes ADF TEM a very expensive technique like HAADF STEM and EFTEM, because an emission field cathode (FEC) should be used along with the Cs corrector.

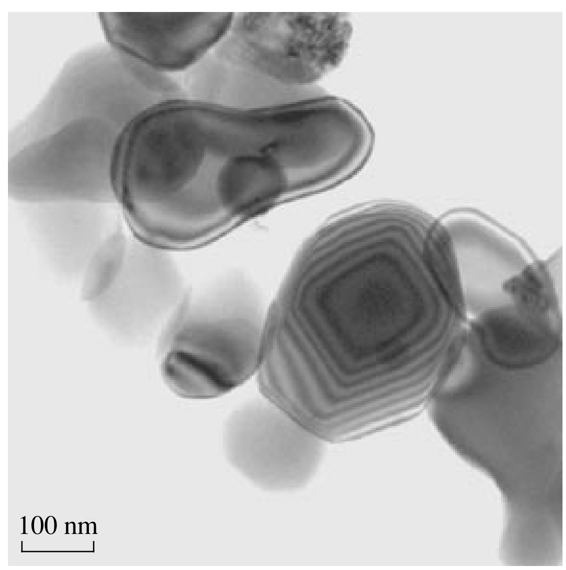

Fig. 1. Diffraction contrast in the image of a crystalline particle: the image intensity varies in a wavelike manner, while the particle thickness decreases monotonically from the center to the periphery.

Some objects of materials science and, in particular, heterogeneous catalysis do not require the above techniques. The purpose of our work was to modify the available equipment so as to realize bright-field ET and to use this method in the reconstruction of a Sibunit-supported Pt catalyst. Because Sibunit globules are poorly crystallized, they do not give rise to strong diffraction artifacts. Catalyst particles of size 2–3 nm are point objects irrespective of the specimen orientation; that is, the projection condition necessary for the correct work of tomographic reconstruction algorithms is fulfilled.

RESOLVING POWER OF ET

Resolution in ET is anisotropic. The z-axis resolution d_z (Fig. 2) is equal to the resolution in the original electron micrographs. The highest theoretical x-axis resolution [3] is

$$d_x = \frac{2\pi D}{N}, \quad (1)$$

where D is the size of the region examined and N is the number of images in the tilt series.

This formula is valid for a full angular range (±90°) uniformly covered with data. However, the imaging range is usually ±60° to ±80° and the actual resolution is, therefore, lower. In our study, D was approximately 50 nm and images were obtained in 1° steps in the angular range ±72°. Therefore, as can be estimated from Eq. (1), the highest x-axis resolution was ~2 nm. Many researchers (see, e.g., [3]) note that Eq. (1) gives an underestimated resolution and that the actual resolution is much higher. Our study is in agreement with this opinion: the x-axis resolution d_x in our tomograms is ~1 nm.

The theoretical y-axis resolution is given by the formula

$$d_y = d_x e_{xy}, \quad (2)$$

where $e_{xy} = \sqrt{\frac{\alpha + \sin\alpha\cos\alpha}{\alpha - \sin\alpha\cos\alpha}}$ is the extension factor and α is the largest specimen tilt angle.

At $\alpha = 40°$ and 72°, $e_{xy} \approx 2.1$ and 1.13, respectively. In other words, in the former case, the y-axis resolution is twice lower than the x-axis resolution, while in the latter case, the loss in resolution is only 13%.

This study was carried out using a JEOL JEM-2010 microscope with a high-resolution pole tip (pole gap ~5 mm). The holder of this instrument allows a tilt of ±40°, which is insufficient for tomography. In order to extend the tilt angle range to an acceptable value of 60°–70°, we designed a tomographic attachment for the holder. This attachment is sufficiently small so as not to graze against the pole tip upon rotation. It does not interfere with the rotation of the holder, so it makes it theoretically possible to obtain images over an angular range of ±90°. However, the design of the specimen grid imposes dome limits on the range of imaging angles. The tangent of the maximum allowable tilt, which is the angle at which the grid is about to screen the specimen, is directly proportional to the diameter of the grid hole (W) and is inversely proportional to the grid thickness (h):

$$\tan\alpha_{max} = W/2h. \quad (3)$$

Furthermore, the grid must be sufficiently narrow to be rotatable without hindrance in the narrow space between the tips of the magnetic lenses. The tomographic grids that we designed allow the angular range to be widened to ±72°, which is quite sufficient for tomographic reconstruction.

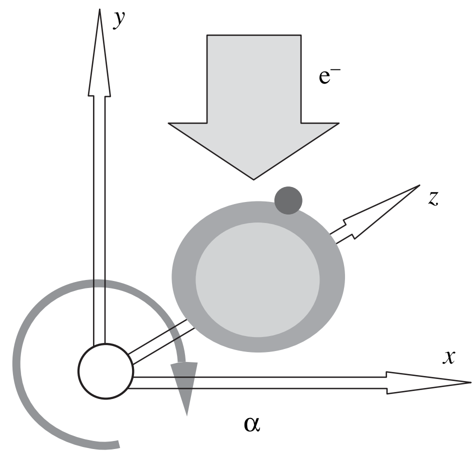

Fig. 2. Schematic of the ET experiment. A globule with a catalyst particle on its outer surface (at the center) is exposed to an electron beam coming from above (in the direction opposite to the y axis). The specimen holder is rotated along the z axis. α is the maximum tilt of the specimen.

EXPERIMENTAL

Tilt series were obtained on a standard JEM-2010 transmission electron microscope operating at an accelerating voltage of 200 kV. The specimen was Sibunit globules containing supported platinum. The platinum loading was 9%, and the platinum particle size was 2–4 nm.

A tilt series was obtained in an angular range of ±72° in 1° steps for agglomerated Sibunit globules supporting metal particles. A total of 145 images were obtained. The magnification was 40000×. The images were recorded on a CCD camera with a 1376 × 1032 pixel matrix.

Microscopic data were processed using the electron tomography program package IMOD and homemade algorithms and programs. Tilt series were aligned using correlation methods and the marker method [5]. Tomographic reconstruction was carried

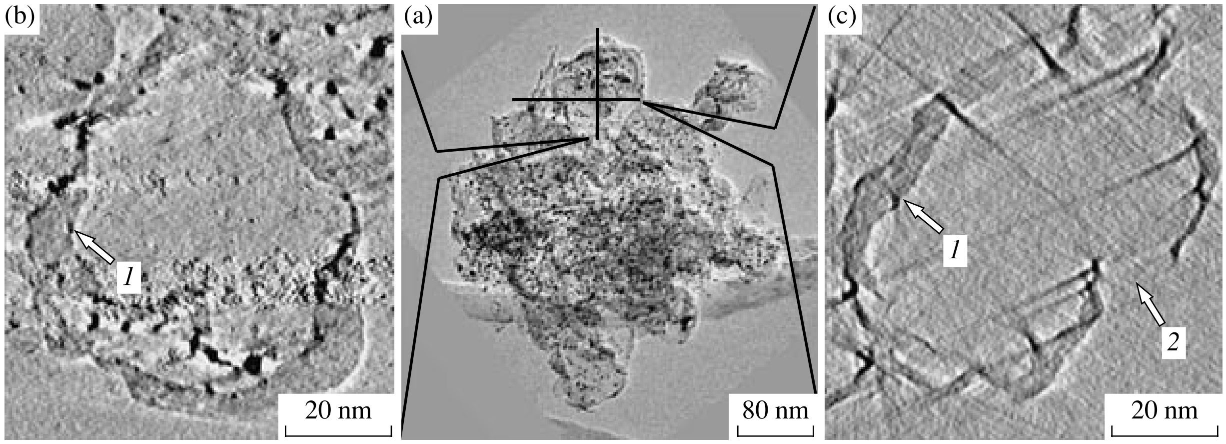

Fig. 3. (a) Original image of a Sibunit particle (not tilted). (b) Vertical and (c) horizontal tomographic cuts of the particle: (*1*) platinum particle of size 2 nm on the inner surface of the globule and (*2*) gap in the wall of the globule.

out using the iterative filtered backprojection algorithm (IWBPJ method) [6].

RESULTS

Figure 3a shows a micrograph of the specimen examined. Figures 3b and 3c show, respectively, a vertical and a horizontal 0.6-nm-thick cut of a tomographically reconstructed globule. The cuts pass through the same Pt particle of size ~2 nm (*1*) on the inner surface of the globule. Providing information of this kind is peculiar to ET. No such information can be obtained by TEM. Furthermore, it can be seen in Fig. 3c that the wall of the globule has a gap of size 15 nm (*2*). This gap can let metal particles into the globule.

CONCLUSIONS

Thus, we have adapted bright-field ET to the study of the spatial structure of heterogeneous catalysts and have tested this method by examining a Pt/Sibunit catalyst with a mean Pt particle size of 2 nm. In spite of the problems associated with diffraction contrast, objects of this type (nanosized particles on a low-crystallinity or amorphous support) allow stable equation and reconstruction algorithms to be developed for bright-field images. The techniques reported here can be applied to a wide variety of weakly scattering objects, either amorphous (e.g., soot) or having a large lattice constant (e.g., zeolites), as well as to composites and composite-supported catalysts. The examination of the Pt/Sibunit catalyst has demonstrated that ET can provide unique spatial structure data that cannot be obtained by using conventional electron microscopy, including the 3D shape of support globules, pore connectivity, the location of particles on the outer and inner surfaces of the globules, and the true distance between Pt particles.

The adaptation of ET to a wider variety of objects, including well-crystallized ones, will require the use of dark-field Z-contrast techniques and is now the subject of our further investigation.

The tomographic grid holder that we designed is easy to make and can be used in a standard transmission electron microscope. This makes ET easily realizable, inexpensive, and widely available.

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