Analysis of Particle Size Distribution of Supported Catalyst by HAADF-STEM

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INTRODUCTION
It has been well recognized that the performance (reactivity and selectivity) of a catalyst depends greatly on its dimensions or size [1,2]. In many cases, tiny clusters and even single atoms on a support have been identified as the main active sites for catalysis [3]. Therefore, an accurate knowledge of the particle size distribution (PSD) of the catalysts is very critical for understanding the involved catalysis mechanism [1,2] which guarantees their effective application in the chemical industry [4]. Consequently, the measurement of particle size occurs ubiquitously in the catalysis community, as well as in other materials research fields.

There are several routine scientific methods to calculate the PSD, such as X-ray diffraction (XRD) [5], transmission electron microscopy (TEM) [6-9] and scanning transmission electron microscopy (STEM) [3,4,10-12]. The intensity of the peaks for metal particles measured by using XRD is very weak if the proportion of supported metal particles versus the support is low in the samples. Therefore, it is inaccurate or not possible to calculate the mean value of particle size of trace amounts of metal. Moreover, the smaller particles can result in a strong peak broadening, also unfavourable for the measurement.

Among these available techniques, high-resolution TEM (HRTEM) may be the most popular for measuring small particle sizes, owing to its direct visibility, accessibility, and its ease of use. Usually, 200–300 particles are counted for PSD analysis [5,8,11]. It is clear that the prerequisite for a meaningful PSD is that all particles from small (<2 nm) to large (>20 nm) can be imaged and counted, and that the size (diameter) of the particles should be measured precisely on the digital images. The calculation of the PSD, however, may be inaccurate by using HRTEM method alone, which will be discussed below. Alternatively, STEM can be a better candidate in some cases [13].

In order to address this issue, here we have compared the PSD of metal particles from the same regions supported on different materials by using both HRTEM and high angle annular dark field (HAADF) STEM. Since few reports do exist and can play a key role in the catalysis.

Figures between HRTEM and HAADF-STEM MODES
Theoretically speaking, in terms of phase-contrast or HRTEM, a large objective aperture or the removal of the objective aperture is required so that both the direct beam and Bragg-diffracted beams are applied to generate an image [7,14]. Because multiple beams are used in these images, variations in the contrast are observed when these beams interact with each other. Increasing the size of the aperture allows more Bragg-diffracted beams to be included in the image; the sharpness improves, but the overall contrast decreases. Sometimes it is almost impossible to identify particles as small as 2 nm and below even by advanced sub-A microscopy [9], although they do exist and can play a key role in the catalysis.

Figure 1: A typical pair of (a) high-resolution transmission electron microscopy (HRTEM) and (b) scanning transmission electron microscopy (STEM) images of the same area of ruthenium nanoparticles supported on carbon nanotubes. The smaller particles, circled in (b), are not visible in the HRTEM image.
The underlying phase contrast can be largely reduced, be much weaker or completely disappear in the HRTEM analysis of these materials [6]. However, HAADF imaging features atomic-number sensitivity (approaching \(Z^2\)), less dependence on the beam defocus and sample thickness, absence of proximity effects at interfaces or surfaces, and higher spatial resolution [10]. Equipped with a HAADF detector, Z-contrast imaging is powerful enough to identify tiny clusters or particles as small as 2 nm and even single atoms in STEM mode [3, 13].

**MATERIALS AND METHODS**

**Preparation of Nanoparticles**

The ruthenium nanoparticles supported on carbon nanotubes (Ru/CNT) were synthesized by using a microwave thermolytic method. Ru\(_3\)(CO)\(_{12}\) was mixed together with CNTs and ground for 20 min. The sample was exposed to an argon flow for 2 h at a flow rate of 100 mL min\(^{-1}\), followed by microwave treatment in a quartz-tube reactor with a frequency of 2.45 GHz as the radiation source for 5 min. The sample was then taken out after cooling to room temperature.

Palladium nanoparticles supported on iron oxide catalysts were prepared by a co-precipitation method. Fe(NO\(_3\))\(_3\)·9H\(_2\)O and Pd(NO\(_3\))\(_2\) were precipitated with the aid of NaOH at pH 9. The precipitated mixture was then dried at room temperature under air, followed by calcination in air and reduction in a temperature programmed reduction (TPR) machine.

The Ru/CNTs sample was ultrasonically dispersed in ethanol, and then a drop of the solution was deposited on a holey C/Cu TEM grid to be used for HRTEM and HAADF-STEM characterization. The TEM specimen of Pd/FeO\(_x\) was prepared by a dry method in the glove box to prevent oxidation.

**High Resolution Transmission Electron Microscopy**

The supported metal catalysts were examined using an FEI Titan 80-300 electron microscope equipped with a CEOS image spherical aberration corrector and a Fischione model 3000 HAADF-STEM detector. The microscope was operated at an accelerating voltage of 300 kV in TEM mode for HRTEM and in STEM mode for STEM imaging. The probe size was about 1 nm as a good compromise of spatial resolution and beam current. The specified probe current for a 1 nm probe is \(\geq 0.6\) nA. Since the probe size in our experiment was about 1 nm, the current should be similar to the specified value.

**RESULTS**

Figure 1 is a typical pair of HRTEM and STEM images of Ru particles supported on a carbon nanotube (CNT) taken from the same area. Many smaller particles, most of which are spherical or quasi-spherical, as indicated by the white circles in Figure 1b, are only visible in the STEM image, but not by HRTEM. Moreover, the adjacent and overlapped particles can be distinguished by STEM, as shown in Figure 2.

Since the HRTEM images were taken by using Cs-corrected conditions with a point-to-point resolution of 1 nm, the STEM images are not directly comparable to the HRTEM images. However, the STEM images provide additional information about the particle shape and size distribution not available in the HRTEM images. The STEM images also show the presence of clusters of particles, which are not visible in the HRTEM images. The presence of these clusters suggests that the particles are not well-dispersed in the sample.

**Figure 2:** A typical pair of (a) HRTEM and (b) STEM images of adjacent and overlapped Ru nanoparticles supported on CNT. The images were taken from the same area.
point resolution of 1Å, and the HAADF-STEM images were taken using a fine probe with a resolution of also around 1Å, clearly it is not the resolution that is critical for an accurate measurement of the PSD in this case.

A focus-series of HRTEM images may visualize nanoparticles, as shown in Figure 3. The small particles (circled in Figure 3d), however, are still invisible in the defocused HRTEM images, which indicates that the focus-series method is not optimum for the measurement of the PSD.

The histograms of the PSD of Ru supported on CNTs shown in Figure 4a, b were obtained from the same region in both HRTEM and STEM modes. The PSD based on HRTEM images can be fitted approximately by two Gaussian functions centered at 2.8 and 4.6 nm (see Figure 4a), which displays a seemingly bimodal PSD [15,16]. The PSD from STEM, however, can be fitted only by one Gaussian function centered at 2.0 nm, as indicated in Figure 4b. The corresponding statistical data for the PSD are given in Table 1.

The numbers of counted particles were 192 and 675 from the measurement based in the same region of Ru/CNTs sample on HRTEM and STEM, respectively. Ru nanoparticles as small as 0.5 nm can be identified in STEM mode, whereas the minimum is 1.6 nm in HRTEM. The mean value shifts to the smaller one from HRTEM to STEM, although the largest particle size and the standard deviation are almost the same with either mode. Since the details of the shape and structure of the nanoparticles are often overshadowed by the dominant phase contrast of the support, some small particles can become invisible in the HRTEM mode.

The dominant fringe contrast from a crystalline support can overshadow or severely interfere with the particle contrast [6]. The optimum-focus (extended Scherzer focus) condition commonly used in HRTEM imaging may,

![Figure 4](https://example.com/figure4.png)

**Figure 4:** Histograms of PSD from (a) HRTEM and (b) STEM images in the same region of Ru nanoparticles supported on CNTs.

![Table 1](https://example.com/table1.png)

**Table 1:** Measurement of central tendency (particle number, mean, min, max, median, and standard deviation) for Ru nanoparticles supported on CNTs and Pd nanoparticles supported on iron oxide by using HRTEM and STEM modes.

![Figure 5](https://example.com/figure5.png)

**Figure 5:** Typical pairs of HRTEM (a,c) and STEM (b,d) images of Pd nanoparticles supported on FeOx. Most of the Pd particles are invisible or blurred, except for the circled particle in (a), whereas it is distinctly revealed in (b).
therefore, not be the most favourable imaging condition for detecting small metal nanoparticles supported on crystalline materials. The visibility of very small particles or clusters generally increases through changing defocus values [6]. However, owing to the roughness of the support, the particles may locate at different heights in the direction of the electron beam. Since a complex change of phase contrast will occur in HRTEM mode, owing to the variation of the contrast transfer functions by changing the focus [17, 18] the application of a focus-series HRTEM images is required [19] which would undoubtedly increase the complexity of the PSD measurement. Thus the change of imaging mode of the microscope may be useful for an accurate PSD in such a context.

A pair of representative HRTEM and STEM images were also acquired from the same region of iron oxide-supported palladium nanoparticles (see Figure 5). The dominant lattice fringes of the iron oxide support do not give any obvious indication of the presence of Pd nanoparticles except for one particle indicated by the white circles in Figure 5a. The Pd nanoparticles become distinctly visible in the same specimen area when the operation mode of the microscope was changed to HAADF-STEM, as shown in Figure 5b. When the sample thickness was very thin, the supported Pd particles could not be unambiguously identified in the HRTEM mode (see Figure 5c). Therefore, it was impossible to conduct an effective measurement of the particle size by using an HRTEM image. Whereas, the particles were highly visible in the STEM image (see Figure 5d).

The histograms of the PSD shown in Figure 6a, b are based on the statistics of HRTEM and STEM images from the same region of Pd nanoparticles supported on iron oxide. In this case, the distributed particle number was only 62 and the average particle size was larger than 1.4 nm, based on HRTEM images from the randomly sampled 20 regions. However, in STEM mode the determined particle number was 321 for the aforementioned identical regions; that is, five times more than the number from HRTEM, and the Pd nanoparticle size determined by STEM is as low as 0.2 nm, as illustrated by the corresponding statistical data for PSD in Table 1. The mean value is clearly smaller in the STEM image than in the HRTEM image, which is similar to the aforementioned Ru/CNT’s case. The PSD based on HRTEM images was fitted approximately by three Gaussian functions centered at 1.5, 2.0, and 2.4 nm (see Figure 6a), which displays an apparently trimodal PSD on these present sampled regions. The PSD from STEM, however, can be fitted only by one Gaussian function centered at 1.5 nm, as indicated in Figure 6b.

Considering that some overlapped or some small particles cannot be identified in the HRTEM images, the partial absence of uncounted particles could result in a seemingly multimodal (bimodal or trimodal) PSD. Therefore, such a limited counting of particles in HRTEM images, compared with that in STEM mode, could lead to the statistical errors. In order to solve the aforementioned intrinsic problem of the imaging techniques, a trade-off must be made: more areas should be sampled in HRTEM mode and then enough particle numbers must be accounted towards an accurate PSD.

**CONCLUSIONS**

In summary, a comparison of methods for determining the PSD of metal nanoparticles supported on CNTs and iron oxide catalysts has been conducted through applying both HRTEM and HAADF-STEM modes.

1. From the exactly same regions, the obtained particle number is much larger in HAADF-STEM mode, whereas the lower number obtained by the HRTEM counterpart can lead to an inaccurate PSD of catalyst, such as the so-called multimodal distribution in this work.

2. Many smaller particles can be identified using the HAADF-STEM mode, while they are invisible in HRTEM mode.

3. Based on (1) and (2), the derived measurement of mean and minimum particle size, as well as the produced PSD, can be largely different in these two modes. Thus the PSD information achieved by using STEM can be more accurate, which is crucial towards a full understanding of the catalytic performance of supported metal catalysts. The determination of mean particle size should be complementarily performed with XRD and gas chemisorption experiments [20].

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**REFERENCES**