

Accurate Determination of the Size Distribution of Nanoparticles in Supported Metal Catalysts: Challenges and Opportunities

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Introduction

Supported-metal catalysts are important for a variety of chemical reactions and alternative energy resources. For example, carbon-supported Pt or Pt alloy catalysts are used in the hydrogen fuel cell. Supported-metal catalysts usually consist of active metal or alloy nanoparticles dispersed onto high-surface-area carriers. The activity, selectivity and stability of a supported-metal catalyst depend not only on the chemical state of the metal but also on its particle size distribution (PSD). The PSD in a supported-metal catalyst is determined by the synthesis conditions and the evolution of these nanoparticles during the catalytic reactions. Accurate determination of the particle sizes and size distributions is critical to understanding the synthesis-structure-performance relationships of supported-metal catalysts.

Challenges

Three methods are usually used to determine PSDs: 1) electron microscopy, 2) wide-angle X-ray scattering (WAXS) and 3) small-angle X-ray scattering (SAXS). Electron microscopy (EM) techniques can provide direct visualization of the nanoparticles. There is, however, a concern about the statistical validity of the data unless a very large number of nanoparticles are analyzed. This problem becomes more critical during the optimization stage of a promising commercial catalyst: one needs to distinguish the structural differences among very similar catalysts. The WAXS technique with various data analysis algorithms (the Sherrer method, the Williamson-Hall method, the Warren-Averbach method and the full profile analysis method) can provide statistically meaningful size distributions of crystalline domains. Complications of strain field, defects, surface-induced disordering and size-induced peak broadening make the WAXS technique less reliable for determining the size distributions of very small particles. For larger particles or complex particles, the domain size may not represent the true particle size. The SAXS technique can be used to determine the size distributions of small particles or pores. For industrial catalysts, the complications of carrier morphology and the complicated data analysis processes prevented the wide applications of the SAXS technique to determining PSDs in supported-metal catalysts.

Results and Discussion

Figure 1 shows an example of the challenges in precisely determining the PSDs. Three methods were independently employed to determine the size distribution of a carbon-supported Pt fuel cell catalyst. As shown in figure 1, the PSDs of the Pt nanoparticles are very different even though the same batch of catalyst was used. High-angle annular dark-field (HAADF) technique (image resolution < 0.2 nm) revealed more Pt particles with sizes < 2 nm in diameter. The conventional TEM technique (images resolution of ~ 0.4 nm) failed to reveal the very small Pt nanoparticles. The SAXS technique provided a size distribution different

from that of the HAADF and the TEM. The challenge is which size distribution represents the true PSD of the carbon-supported Pt fuel cell catalyst. Figure 2 shows the PSDs obtained by the SAXS technique, revealing the effect of sintering gas on the size distribution of Pt nanoparticles in a Pt/C fuel cell catalyst. The HAADF and conventional TEM data, however, provided a very different picture. In this presentation, we will discuss the advantages and disadvantages of the various techniques for accurately determining the size distributions of supported-metal catalysts.

Relevance: The development of methods that can accurately determine the size distributions of nanoparticles is critical to the fundamental understanding of catalysis and catalyst synthesis processes. This study is especially valuable for developing commercial catalysts.

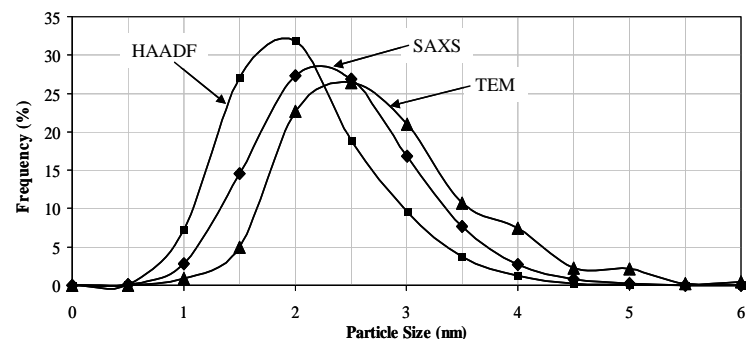


Figure 1. Plots of size distributions of Pt nanoparticles in a Pt/C fuel cell catalyst demonstrate the variations in size distributions of the same catalyst; different techniques provided different size distributions of the Pt nanoparticles.

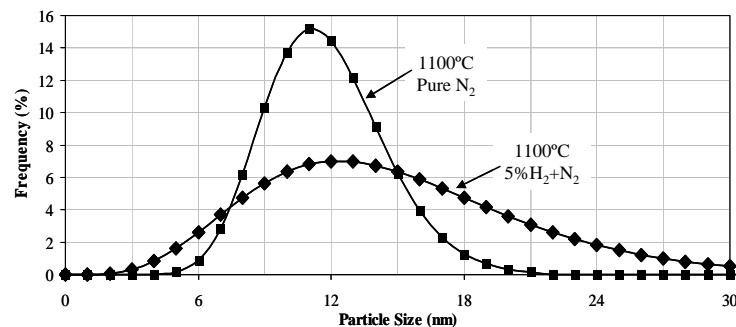


Figure 2. Plots of the size distributions of Pt nanoparticles in a Pt/C fuel cell catalyst sintered at 1100°C for 4 hours in ultra-pure N₂ and 5% H₂ + N₂ gases, respectively.