Catalyst Characterization: TEM vs. STEM

Visualizing Pt Nanoparticles Supported on Cerium Oxide

In (HR)TEM images of catalysts, it is often difficult to recognize metal nanoparticles with a diameter around 1 nm or below on strongly scattering crystalline oxides. For such systems, the combination of information obtained with an aberration-corrected STEM microscope equipped with BF, DF and secondary electron detectors provides a superior means to detect the nanoparticles, as demonstrated here for Pt particles on cerium oxide.

Introduction

Typically, a heterogeneous catalyst comprises small metal particles that are dispersed on a supporting material (mostly a chemically inert oxide). As the activity, selectivity and stability of such a catalyst often strongly depend on the size of the metal particles and the size distribution, the accurate determination of these parameters is crucial in catalysis research. Transmission electron microscopy represents the classical and well-established approach for the characterization of such heterogeneous catalysts. In fact, particles of heavy metals supported on an oxide material can easily be visualized by HRTEM in many systems. Moreover, information about the particle's structure and shape can be gained. However, if the supporting oxide is crystalline and the diameter of the metal particles in the range of only a few nm, then they might hardly be visible in TEM images due to the superposition of mass-thickness and diffraction contrast [1, 2]. In these cases, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) is suitable to image sub-nm sized particles - and even single atoms in favorable cases - with high contrast by forming the image with electrons that are scattered incoherently into high angles. Under these conditions, diffraction and phase contrast are suppressed, and the intensity then mainly depends on the atomic number Z (Z-contrast imaging [3]). If the support itself consists of a heavy scattering material like ceria, then the detection of small metal particles is further impeded.

Cerium-oxide Supported Catalysts
Recently, the use of ceria (CeO$_2$) as support for metal nanoparticles was shown to be advantageous for the heterogeneous catalysis of various reactions [4].

For example, gold particles on ceria represent an effective catalyst for oxidizing dibenzylamine selectively to dibenzylimine by O$_2$ [5]. The comprehensive characterization of such catalysts represents a challenge for the electron microscopist because of the rather small difference in the scattering potentials of the metal and the support, resulting in a relatively poor contrast [6]. Here, we demonstrate this by showing and comparing the results of different electron microscopy methods applied for the detection of the metal nanoparticles in a model catalyst Pt/CeO$_2$.

**Characterization by Conventional TEM and STEM**

The test sample comprises 5 weight% Pt on a ceria support. The difference in the scattering potential of the Pt metal and the support (atomic numbers: Pt = 78 vs. Ce = 58) is rather small but sufficient to reveal metal particles with a diameter of 5 nm or more by HRTEM [7]. If the particles are around 1 nm, however, it becomes difficult to achieve a clear, unambiguous contrast. The particle detection by HRTEM imaging is further hindered by strong diffraction and phase contrast of the crystalline ceria. However, if the supporting ceria crystals themselves are quite small and homogeneously thin, then the additional scattering contribution of Pt nanoparticles with a size of about 1-2 nm is sufficient to give a reasonable contrast (fig. 1a). Note that it is difficult to recognize particles in regions where several CeO$_2$ crystals are stacked upon each other. In comparison to this TEM image, a much clearer contrast is obtained if mainly incoherently scattered electrons are used to build up the image (fig. 1b). Many Pt nanoparticles with a diameter of about 1 nm can be recognized clearly in the HAADF-STEM image as bright patches. Unfortunately, a less clear contrast appears if the particles have a broad size
distribution and if the support has an irregular structure with varying thicknesses. Then, it is difficult to distinguish whether a brighter patch results from a thicker support area, the superposition of two support crystals, or indeed from a looked-for metal particle. Analyses of such spots by EDX or EEL spectroscopy further help to clarify this as recently demonstrated for an Au/CeO$_2$ catalyst [5, 6].

**Aberration-corrected STEM**

Aberration-corrected scanning transmission electron microscopes provide the option to record BF as well as HAADF images simultaneously with a resolution below 1 Å [8]. The Pt particles in the model catalyst are clearly recognizable as bright patches in the HAADF-STEM and as dark ones in the BF-STEM images (figs. 2 and 3 a, b). This already unambiguous interpretation of the image contrast can easily be further confirmed by EDXS spot analysis. As in TEM (fig. 1a), the interpretation of the observed contrast becomes more difficult in thick areas (circles in fig. 2). The high resolution achieved by the microscope used here provides not only valuable information about the size and shape of the Pt particles and ceria crystals but additionally about their structure as well. The highly resolved structure of two ceria crystals is eye-catching; they are oriented along [110] of the cubic fluorite-type structure (fig. 2). Depending on the selected imaging conditions, a certain amount of diffracted electrons can contribute to the formation of the BF-STEM image so that this has similarities with a conventional phase contrast (HRTEM) image [8].

A further detector was used for the comprehensive characterization of this sample, namely a secondary electron (SE) detector installed inside the column of the dedicated STEM microscope, a Hitachi HD-2700CS. Recently, it was shown that SEM images with atomic resolution can be recorded by this quasi in-lens SE detector [9]. Here the SE images demonstrate the morphology of the catalyst (fig. 3c). As the work function for electrons in the conduction band of metals is in general considerably lower than that for oxides, a brighter contrast can be expected for the Pt particles if the low energy secondary electrons can be detected. Although some Pt particles appear indeed as bright dots (fig. 3c), most of them, which can be recognized in the HAADF-STEM image (fig. 3b), are not visible. This is caused by the fact that only a few of the Pt particles are located on the catalyst's top surface where the secondary electrons can escape into the vacuum towards the detector. Secondary electrons generated inside the specimen are absorbed and therefore cannot be detected. Furthermore, even a thin contamination layer blurs the contrast in SE imaging since it hinders a certain portion of the low energy secondary electrons to escape from the surface area.
Conclusions

The possibility to record BF- and HAADF-STEM simultaneously with ultimate high resolution offers unprecedented perspectives for tackling otherwise unsolvable structural problems. The thereby obtained information about the elemental distribution (Z contrast) and the structure (BF imaging) is supplemented by the additional option to study the topology and morphology by SEM imaging which gives rise to a complete characterization of the sample. The results presented here on the investigation of nm-sized Pt particles on cerium oxide exemplify the potential of the new generation of aberration-corrected STEM microscopes for materials and catalyst research.

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