Characterization of catalytically active Au and Pt particles supported on cerium oxide

F. Krumeich[1], L. Aschwanden[2], F. Hoxha[2], B. Schimmöller[3], A. Baiker[2], and S.E. Pratsinis[3]

1. Laboratory of Inorganic Chemistry, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
2. Laboratory of Chemistry and Applied Biosciences, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland
3. Particle Technology Laboratory, ETH Zurich, Sonnegg-Str. 10, CH-8092 Zurich, Switzerland

krumeich@inorg.chem.ethz.ch
Keywords: Z-contrast, catalysis, ceria, size distribution

Transmission electron microscopy represents the classical and well-established method for the characterization of heterogeneous catalysts consisting of small metal particles dispersed on a support material. Since the activity, selectivity and stability of the catalyst often strongly depends on particle size and size distribution, the determination of these properties is crucial in catalysis research. In fact, heavy metals supported on a light oxide material can easily be visualized by HRTEM in many systems. Moreover, their structure and shape can be determined. However, if the support 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]. In such cases, HAADF-STEM is suitable to image sub-nm sized particles - and even single atoms in favorable cases - with high contrast because diffraction and phase contrast are suppressed and the intensity depends only on the atomic number (Z-contrast imaging [2]).

Recently, the use of ceria (CeO_2) as support for metal nanoparticles was shown to be advantageous for the heterogeneous catalysis of various reactions [3]. The characterization of such systems represents a challenge for the electron microscopist because of the rather small difference in the scattering potential of the metal and the support, resulting in a poor contrast [1]. This is shown by the HAADF-STEM image of gold particles on ceria (Fig. 1), an effective catalyst for the selective oxidation of dibenzylamine to dibenzylimine by O_2 [4]. The particles have a diameter in the range of 5-10 nm and appear with approximately the same brightness as the supporting ceria [5]. Nonetheless, they are frequently recognizable as patches. The correctness of this assumption was proven by EDXS spot analyses (Figure 1).

Ceria-supported particles that are 1 nm or less in size are quite difficult to recognize in HRTEM images. This is demonstrated in Figure 2a where Pt particles being 1-2 nm large are hardly visible. However, if the supporting cerium oxide crystals are thin and of homogeneous thickness, many about 1 nm large Pt particles can clearly be recognized in HAADF-STEM images (Figure 2b). Confirmation of the reasonable assumption that these bright patches are indeed Pt particles by analytical means was not possible in this case with our equipment [6].

1. J. Liu, Microsc. Microanal. **10** (2004) p55.
2. P.D. Nellist and S.J. Pennycook, Science **274** (1996) p413.
3. A.S.K. Hashmi, G.J. Hutchings, Ang. Chem. Int. Ed. **45** (2006) p7896.
4. L. Aschwanden et al., J. Mol. Catal. A **300** (2009) p111.

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-429 , © Verlag der TU Graz 2009

5. Experimental: The catalyst powders were dispersed in ethanol and some droplets deposited on a carbon foil (Cu grid). Microscope: FEI Tecnai F30 (V_{acc}= 300kV, Supertwin lens) with EDXS system (EDAX).
6. We thank EMEZ (electron microscopy ETH Zurich) for measuring time.

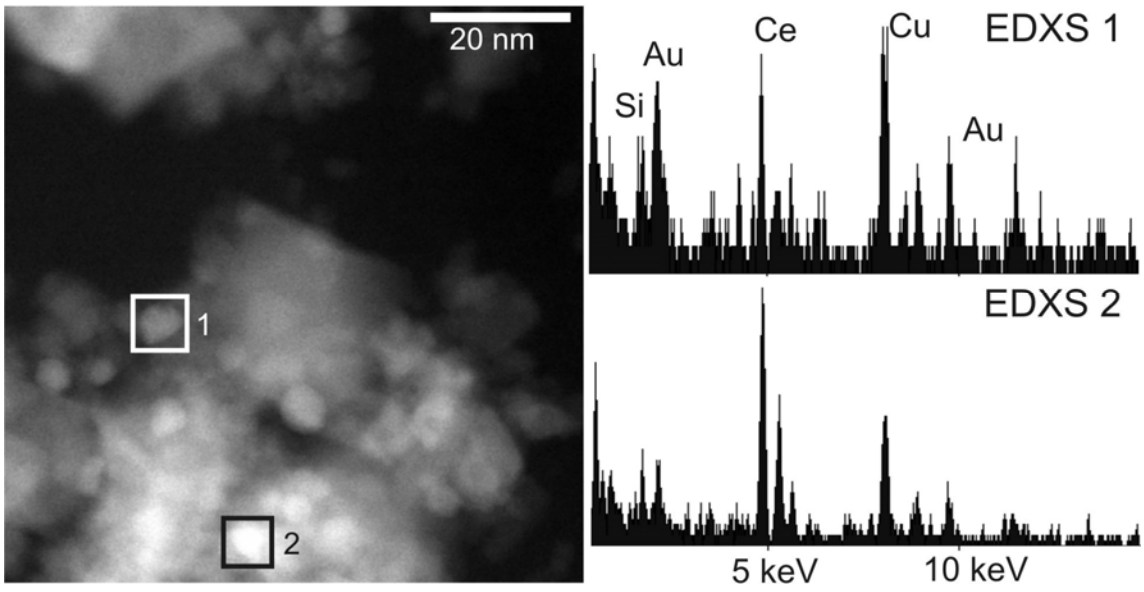

Figure 1. HAADF-STEM image of Au particles on ceria. EDXS analyses of the marked areas prove the presence of Au in the bright patches.

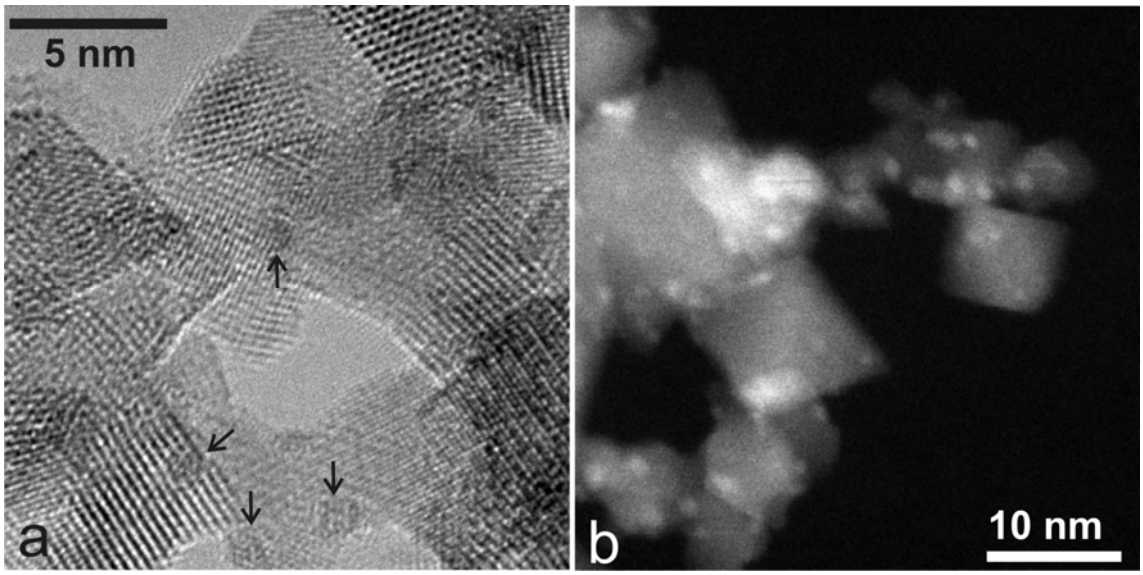

Figure 2. (a) HRTEM and (b) HAADF-STEM images of Pt nanoparticles (5 weight%, diameter 1-2 nm) on ceria. In (a), arrows point to Pt particles.

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-429 , © Verlag der TU Graz 2009