Aerobic catalytic oxidation has been appreciated in view of its application in green chemistry in contrast to non-catalytic methods. By controlling the synthesis methodology, the structures of nanocatalysts can be designed towards specific activity and selectivity for the reaction of interest. Recent developments in analytic electron microscopy techniques have enabled the structure and chemistry of individual catalyst particles to be resolved at sub-nanometer resolution. In this presentation, we will focus on two activated carbon (AC) supported Ru-Au bimetallic catalysts synthesized by sequential deposition following a two-step procedure [1] to correlate the elemental distributions and surface decoration with the activity and selectivity of the catalysts.

For Ru@(Au/AC), Ru(III) was reduced with H₂ at 80 °C in the presence of preformed Au/AC. Au@(Ru/AC) was prepared by depositing PVA stabilized Au nanoparticles onto a commercial Ru/AC. The catalysts were examined in an image aberration corrected FEI Titan 80-300 electron microscope with conventional EDX detector as well as in a probe aberration corrected Titan 80-200 with in column Super-X EDX detector.

Spectrum imaging with probe corrected STEM and Super-X EDX detector offers high spatial resolution and the opportunity to resolve the components by multivariate analysis before changing the structure during electron beam irradiation. In Fig. 1a, components containing Au and Ru are displayed, forming an Au core-Ru shell structure in the case of Ru@Au(AC). The high resolution HAADF STEM image in Fig. 1b shows two Au particles with Ru clusters (lower intensity) situated on their surface. In the case of Au@Ru(AC), we obtained a more inhomogeneous distribution, with the presence of small Ru particles and larger bimetallic particles, as seen in Fig. 2b. Interestingly, the bimetallic particles, as shown e.g. in Fig. 2a, is also composed of an Au core and Ru shell. Both catalysts were tested in oxidation of n-octanol in toluene and oxidation of glycerol in water, respectively. Ru@Au(AC) shows almost no activity in the former case but is highly active for the latter; while Au@Ru(AC) behaves in the contrary, being very active for oxidation of n-octanol but shows only limited activity in glycerol oxidation. The TEM results and catalytic tests therefore suggests that Ru is the main active phase in oxidation of aliphatic alcohols and the addition of Au has a detrimental effect on the Ru particles on it. But this Au core-Ru shell structure leads to distinctly enhanced activity in oxidation of water soluble and highly hydrophilic polyols [2].

Reference
Fig. 1: a) Component maps by multivariate analysis, with red for Au and green for Ru, and b) HAADF STEM image of bimetallic particles showing Ru situated on Au core for the Ru@(Au/AC) catalyst.

Fig. 2: a) Components maps by multivariate analysis, with red for Au and green for Ru, and b) HAADF STEM image of segregated small Ru particles together with big bimetallic particles for the Au@(Ru/AC) catalyst.