Different types of graphitic carbon formed by electron irradiation of carbon-covered Pt-black catalysts studied by HRTEM and EELS.

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A Pt-black catalyst was prepared by reduction of H_2PtCl_6 in aqueous solution by formaldehyde (HCHO) and presintered at 473 K in hydrogen. It was treated with mixtures of n-hexane and H_2, partly followed by exposures to O_2 and, separately, to H_2, at 603 K. For HRTEM and EELS investigations the samples were mounted on holey carbon films. They consist of agglomerates of sintered Pt crystals (sinter-particle size: 10-60 nm) covered with different amounts of carbonaceous deposits. All samples contain agglomerates which show extreme differences in electron irradiation sensitivity. Three types of agglomerates were identified:

Type 1 is stable in the electron beam for several tens of minutes even at electron current densities of 25 A/cm^2. HRTEM images show normal Pt lattice fringes, partly with some distortions. Additionally, there is a large number of cavitated Pt crystals.

Type 2 is sintering at current densities of 1 –10 A/cm^2 within a few minutes leaving behind nanoporous carbon with curved graphitic layers and isolated single loops among thin graphite ribbons. Further irradiation leads to the formation of graphitic layers on the surface of the Pt particles.

Type 3 is fusing into spherical Pt particles (diameters up to some μm) within a few seconds at current densities as low as 0.05 – 0.20 A/cm^2 with segregation of large, highly graphitic particles. The graphitic order is demonstrated by HRTEM imaging and verified by EELS measurements in the low-loss region and at the C K-edge. At local current densities of some 10 A/cm^2 the Pt spheres start moving around and carry away the amorphous carbon film which is converted into graphitic layers surrounding the Pt spheres.