Supplementary material
Materials and methods

The SXRD experiments were performed at the ID03 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) (1), using an incident radiation of 18 keV corresponding to a wavelength of 0.688 Å. An in-situ flow reactor (2) was mounted on a Huber 6-circles, vertical axis diffractometer, equipped with a 2-Dimensional (2D) pixel detector (3) mounted on the diffractometer arm, see Fig. S1. The detector was placed at 560 mm from the sample position and has a pixel size of 55 μm and the dimension of the 2D detector (256x250 pixels) lateral result in a theoretical angular resolution of about 0.005° and to a total angular view of about 1.35°. The gases (Air Liquide, purity N55(O2) and N47(CO)) were fed into the reactor via a remote controlled gas system consisting of four mass-flow controllers (Bronkhorst). A remotely controlled fully closing valve, downstream of each controller allows for a perfect closing of that particular gas supply. The pressure in the reactor was controlled by means of a pressure controller at the gas exit, regulating the leak from the reactor to the exhaust pump, in the range 120-1200 mbar. The gas composition was monitored at all times by a residual gas analyzer (RGA), which is fed by an adjustable leak from the reactor. The experimental time resolution on the gas composition is about 15 sec. The sample temperature controlled through a resistive heater (Pyrolytic Boron Nitride heater by Advanced Ceramics) and was monitored with a thermocouple type E, which was calibrated by a type K thermocouple before each experiment.
Figure S1: Schematics of the detector geometry illustrating the 2D detection of the Ewald sphere as indicated by the pink rectangle.

HPXPS experiments (4,5) were conducted at the 9.3.2.1 (4) and the 11.0.2 (5) beamlines at the Advanced Light Source (ALS, Berkeley, CA, USA), where pressures up to 10 mbar can be reached through an adjustable leak valve.

The Pd particles were produced by aerosol deposition, following a procedure described elsewhere (6,7). Pd particles, with nominal sizes of 35 nm ± 3 nm, and 15 nm ± 1 nm, were deposited on SiO$_x$ and Al$_2$O$_3$ (0001) substrates. The size and distribution of the deposited particles were determined using Scanning Electron Microscopy (SEM, FEI- Nova Nanolab 600) before and after the experiments. To avoid carbon contamination the samples were heated in the measuring environment before the experiments at 572 K in 1 mbar of O$_2$ atmosphere. By HPXPS, we observed the absence of C-1s peak and that the Pd particles were fully oxidized. The Pd oxide could then be removed by reduction in 0.1 mbar of CO at 400 K.

The expansion of the Pd lattice in the particles due to the carbon incorporation can be calculated using Braggs law. This is shown in Fig. S2 (a). From our measurements we find a maximum lattice expansion of almost 4%. The expansion of the lattice from our measurements can be translated into a carbon concentration in the Pd particles by using data from the literature (8), see Fig. 2S(b). The maximum carbon concentration in the particles is found to be almost 16% under our most extreme conditions.
Figure S2: The Pd calculated lattice expansion using Braggs law and the Pd\textsubscript{(111)} reflection. (b) The carbon concentration as a function of the lattice expansion using ref. (8).


