Supporting information for: Effect of the TiO₂ reduction state on the catalytic CO oxidation on deposited size-selected Pt clusters

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Details of the catalysis measurements

Figure S1 shows the data measured on the Pt/LR-TiO₂ sample from which the CO₂ production curves presented in Figure 2c of the manuscript have been derived. The CO₂ signal exhibits peaks synchronized with the injections of the reactants (CO and O₂). The inset shows one sequence of reactant and product pressure peaks. The CO₂ peaks synchronized with the O₂ pulses (blue) are labeled CO₂(O₂) and shown in orange and those synchronized with the CO pulses (green) are labeled CO₂(CO) and shown in red. The maxima of the respective peaks are connected with full lines and displayed in Figure 2c. In Figure 6 of the manuscript we performed the reaction with a constant O₂ pressure and CO pulses. In that case there is only one CO₂ curve (red) which is obtained by connecting the CO₂ peaks synchronized with the CO pulses. For further information, the reader can refer to S. Bonanni, et al., Eur. Phys. J. D 63, 241 (2011).

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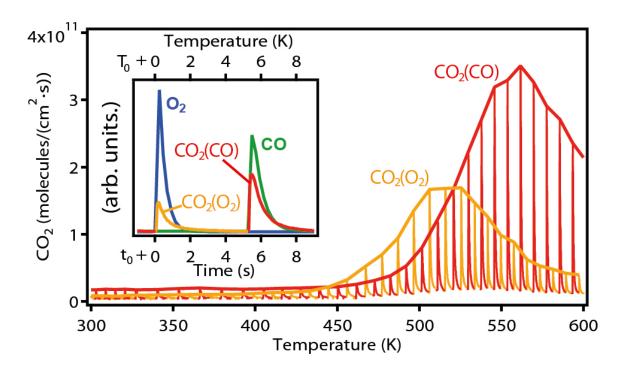


Figure S1: Inset: Single reactant pulse sequence, O_2 blue and CO green, and resulting CO_2 peaks, orange when correlated with O_2 pulse and red when synchronized with CO pulse. Main figure shows individual CO_2 pulses as function of temperature and time (ramp 1 K/s) and their respective peaks connected by curves, such as shown in Figure 2c of the main paper.

Supplementary STM measurements

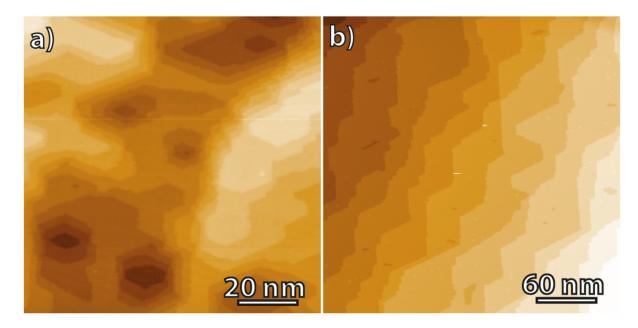


Figure S2: Large scale STM images of the clean (a) LR- and (b) HR-TiO₂(110)-(1×1) surfaces showing terraces with an average width of 5 and 30 nm, respectively (+1.5V, 0.1 nA, 80 K).

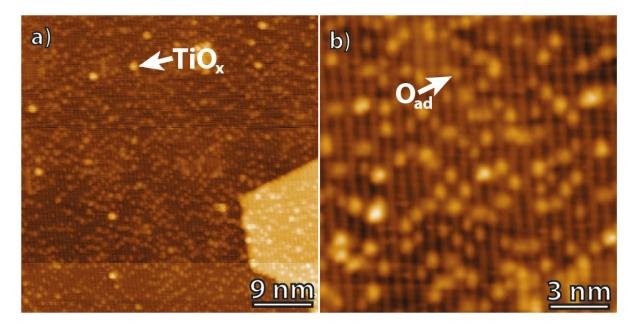


Figure S3: (a,b) Atomic resolution STM images of HR-TiO₂(110)-(1×1) after oxygen exposure of 50 L at 100 K and annealing to 300 K (+1.5V, 0.1 nA, 80 K). The surface exhibits a coverage of 0.10 ML of oxygen adatoms (O_{ad}) all of them adsorbed on the Ti rows. The features with the larger apparent height are attributed to TiO_x nuclei.

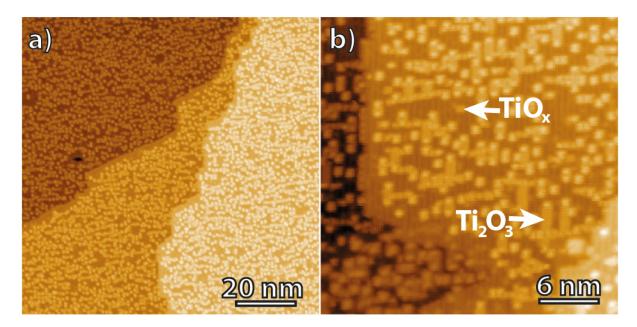


Figure S4: (a,b) STM images of HR-TiO₂(110)-(1×1) after exposure to alternating CO and O₂ pulses while ramping the temperature from 300 K to 600 K identical to the CO oxidation experiments, however, without Pt clusters on the surface (+1.5V, 0.1 nA, 80 K). TiO_x (including Ti₂O₃) structures analogue to those observed in the presence of Pt clusters (see Figure 3b of the main paper) are formed on the surface due to the reaction of Ti³⁺ interstitials with the supplied oxygen.

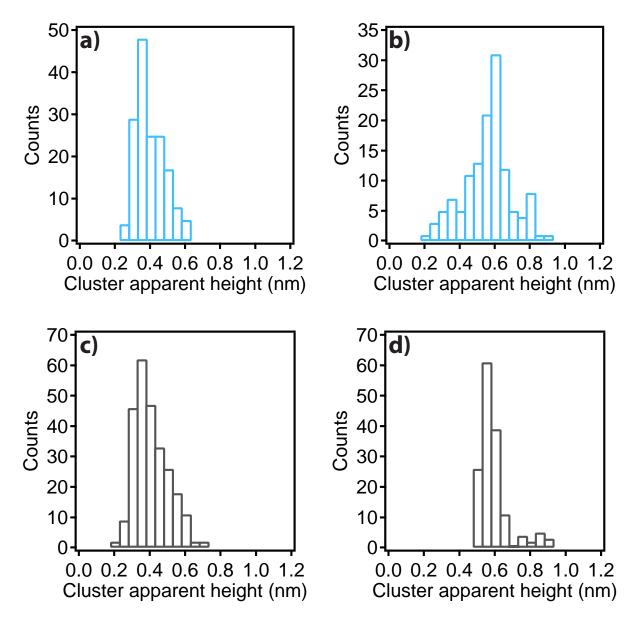


Figure S5: Cluster apparent height histograms before (a) and after (b) the catalytic activity measurement for the Pt/LR-TiO₂ sample and the corresponding histograms for the Pt/HR-TiO₂ sample (c,d). In (d) the clusters having an apparent height below 0.45 nm are not represented because they are hidden by TiO_x .