Self-sustained carbon monoxide oxidation oscillations on size-selected platinum nanoparticles at atmospheric pressure
- Supplemental Material

1 The μ-reactor platform

The experiments were performed in Si-based 20x16 mm μ-reactors[1]. The reactor consists of two inlets, a mixing zone allowing for diffusional mixing of reactants, an outlet, a reactor volume of 240 nL and a 5.4 μm wide, 3 μm high and 1500 μm long capillary used for sniffing gases from the reactor volume. The reactor is sealed by anodic bonding of a pyrex lid to the Si reactor and is able to operate in a pressure range of 0–2.5 bar. The reaction gases are supplied to the two inlets by flow controllers capable of controlling the gas flow from 0–10 mL/min. The capillary flow is fed into a quadropole mass-spectrometer (QMS) for analysis while any surplus of gas from the inlets is passed directly through to the outlet via a pressure controller allowing control of reactor pressure. The design makes sure that all gases exposed to the catalyst under investigation are measured by the QMS ensuring an extremely high sensitivity of the system.

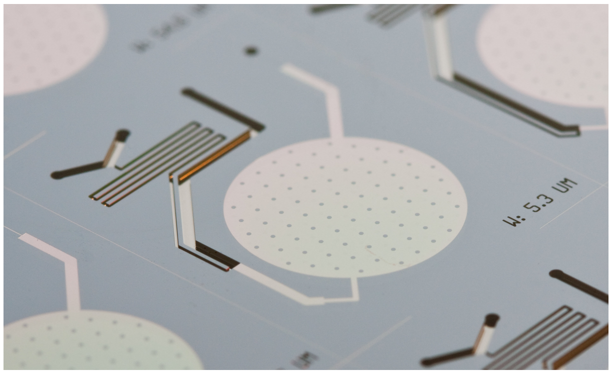

Fig. S1 Image of the 20x16 mm microreactor showing the circular reactor area and gas channel system

Before any measurements are performed the reactor is pumped by a turbopump to minimize contaminants in the system. When an evacuated reactor is mounted the base pressure of the mass spectrometer chamber is $\sim 5 \times 10^{-9}$ mbar and in operation at 1 bar in the reactor volume the pressure is $\sim 5 \times 10^{-7}$ mbar in the QMS chamber.

The reactor is heated by joule heating of a Pt strip evaporated on the backside of the reactor chip. The introduction of two additional contacts on the backside of the reactor allows for 4 wire measurements of the resistance of the Pt strip using it as a RTD for temperature measurement of the reactor. An external thermocouple acts as room-temperature calibration of the RTD as well as sanity check of the RTD measurement during operation. The measured RTD temperature is always compared to the thermocouple at room temperature both before and after an experiment to be sure the RTD did not change resistance due to annealing during the experiment.

The gas handling including flow and pressure controllers and the mass spectrometer is fully automated allowing for measurements during several days without human intervention allowing for self-consistent measurements of many samples.

2 Pt nanoparticle deposition

Pt nanoparticles were deposited in the reactor using a gas-aggregation source (Mantis Deposition Ltd., Nanogen 50). Pt clusters were formed by gas-phase condensation of Pt atoms produced by impinging argon ions on a 99.99% Pt target in a magnetron sputter source. After condensation the ionised fraction (60-80%) of the clusters were size-selected by a quadropole mass selection filter according to their mass-to-charge ratio. Using this setup Pt nanoparticles with diameters in the range of 2–16 nm can be produced[2,3]. The size-selected nanoparticles were after size-selection soft-landed in the reactor volume of the microreactor. The coverage was kept at approximately 0.1% geometric coverage determined by measuring the current on the reactor during deposition. After deposition the reactors were anodicly cold-bonded[4] to a pyrex lid to avoid sintering of the nanoparticles while bonding.

3 TEM Imaging

It is quite obvious that it would be very interesting to aquire good TEM images of the nanoparticles before and after a long oscillation measurement. However, due to the design of the μ-reactor platform it is extremely difficult to get TEM images after reaction. This is partly due to the very thick substrate of seveal hundred μm, as well as the anodic bonding, which cannot be reversed and thus the lid can only be removed by mechanically breaking the device. Images of the as-deposited particles are on the other hand quite easy to acquire by depositing on a substrate more suitable for TEM under conditions identical to those of the deposition into the μ-reactor. Such an image is shown in Figure S4. Images of this kind confirms that our particles actually look like we expect them to do, but does not bring any insight into the oscillation mechanism or an explanation of the decrease in oscillation period as time progresses.

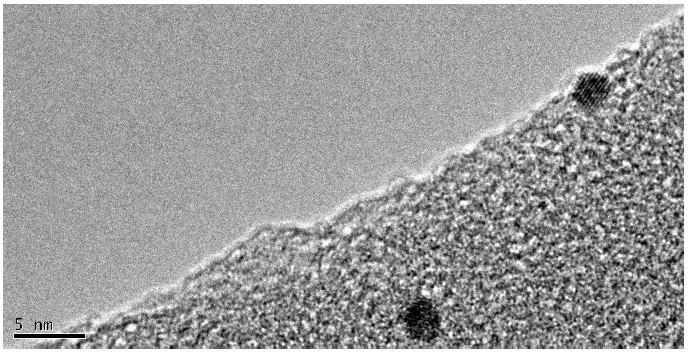

Fig. S2 Image of as-deposited nanoparticles deposited on a thin substrate of SiO_2.

4 CO concentration dependence

The dependence of the CO concentration on the period of the oscillations was investigated. The result shows that the period increases slightly with increasing CO-concentration. However, the effect is small compared to the general trend of slower oscillations as the experiment progresses. In Figure S3 the oscillation periods are summarized and the actual masspectrometry data of the entire experiment is shown in Figure S4.

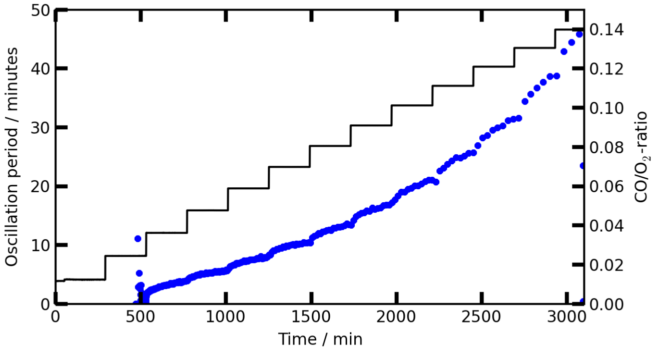

Fig. S3 Oscillation period (blue) as a function of time and CO concentration (black). The overall trend of increasing oscillation period with time is superimposed with small discontinuous steps when the CO concentration is increased.

5 Temperature dependence

As mentioned in the main paper, the oscillations shows a very strong temperature dependence. In Figure S5 we show an example where the oscillations are turned on and off by changing the temperature 20°C.

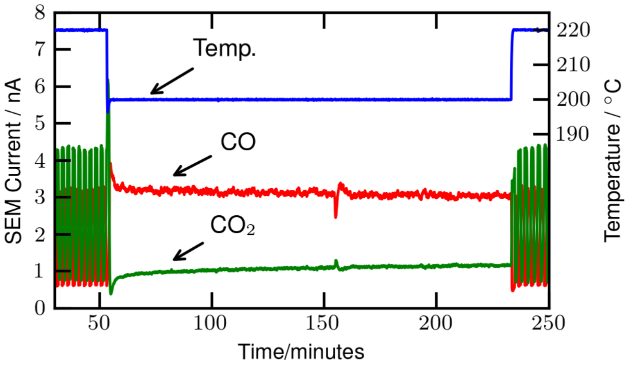

Fig. S5 Another example of the very pronounced temperature dependence.

6 Duty cycle

Even though the period of the oscillations increases with time, the total integrated conversion rate during a complete cycle is almost constant. In Figure S6, the value of the mean value of CO and CO_2 is plotted for every oscillation in the four-day long experiment. It is evident that the ratio between CO and CO_2 is almost constant and thus the average activity of the sample is almost unchanged despite the development in the oscillation frequency.

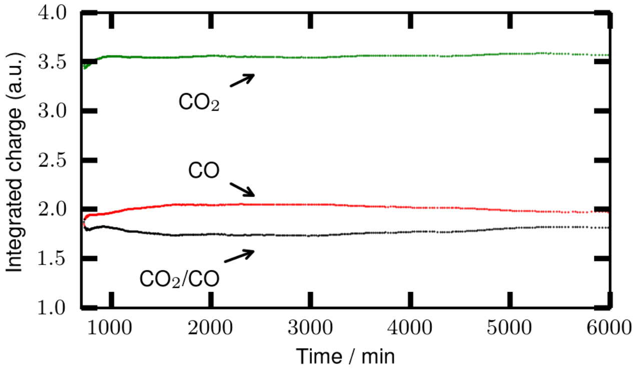

Fig. S6 Running average of the CO and CO_2 concentrations and their ratio during a 4-day long experiment. The individual data-points is calculated as the integral of CO (red) or CO_2 (green) during the individual oscillation periods. The ratio between CO and CO_2 is drawn in black.

References

1 T. R. Henriksen, J. L. Olsen, P. Vesborg, I. Chorkendorff and O. Hansen, *Review of Scientific Instruments*, 2009, **80**, 124101.

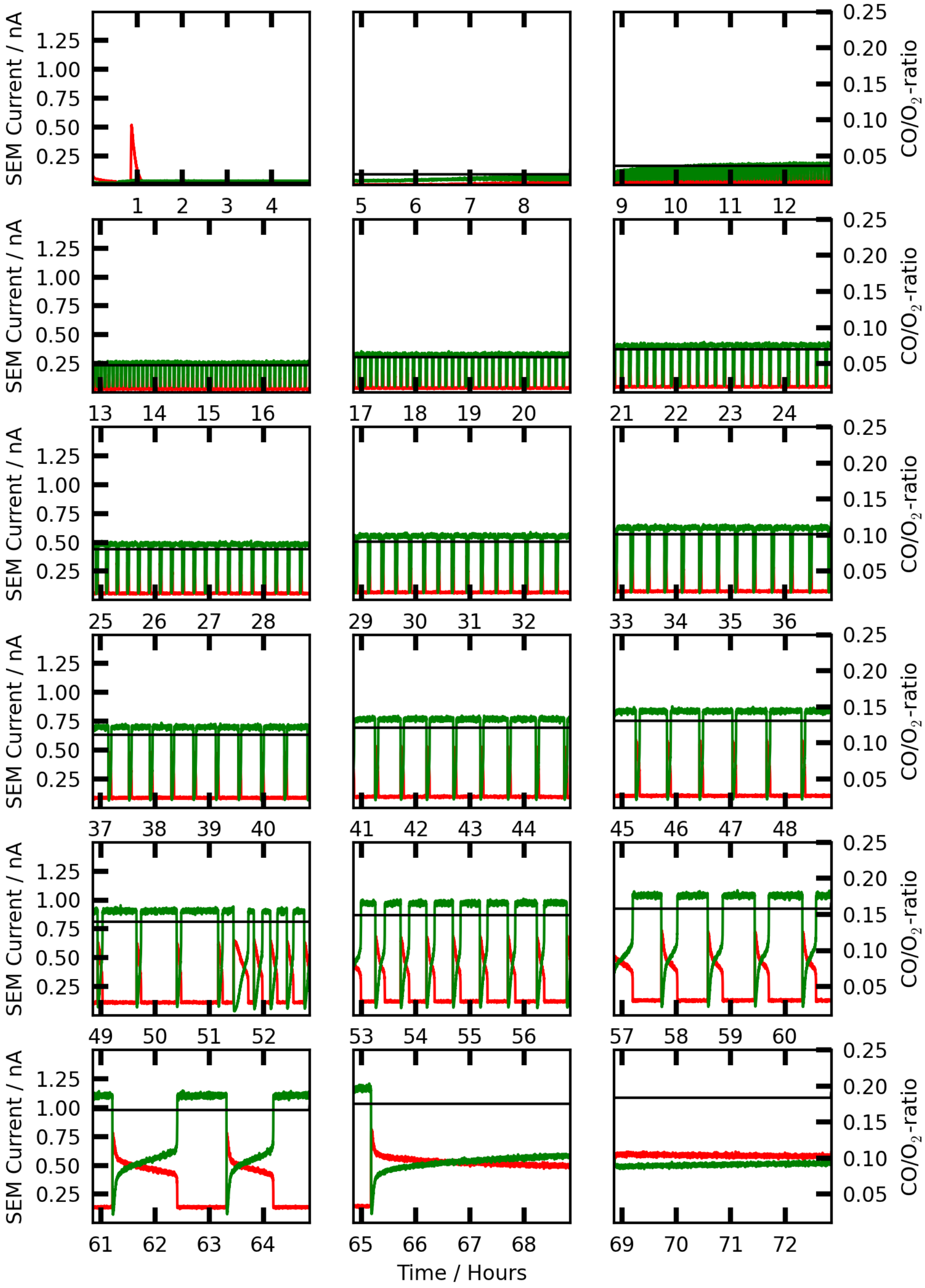

Fig. S4 Complete series of data from an oscillating sample, showing CO (red) and CO_2 (blue). The temperature is constant at 210°C during the entire measurement. For every frame the CO-concentration is increased.

2 R. M. Nielsen, S. Murphy, C. Strebel, M. Johansson, I. Chorkendorff and J. H. Nielsen, *Journal of Nanoparticle Research*, 2010, **12**, 1249–1262.

3 R. M. Nielsen, S. Murphy, C. Strebel, M. Johansson, J. H. Nielsen and I. Chorkendorff, *Surface Science*, 2009, **603**, 3420–3430.

4 P. C. K. Vesborg, J. L. Olsen, T. R. Henriksen, I. Chorkendorff and O. Hansen, *Review of Scientific Instruments*, 2010, **81**, 016111.