

## Atomic-Scale Imaging of Pt and Pd Nanoparticle Catalysts During CO Oxidation at 1 Bar Reaction Conditions.

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Until recently, catalysts have mainly been characterised using traditional high-vacuum transmission electron microscopy (TEM). This means they can only be studied before and after the catalytic reaction, in a sort of frozen state. However, it has been realised that these frozen states probably differ significantly from the active state during the catalytic reaction. The development of differentially pumped ETEM was a significant step in the direction of real in situ TEM, allowing gas pressures of up to 50 mbar and heating up to about 1000 °C [1].

We have developed a micro-electro-mechanical system (MEMS) nanoreactor system to bridge the pressure gap [2; Figure 1]. It confines a thin layer of gas (several microns) in a windowed cell, thus retaining atomic resolution at pressures exceeding 1 bar by limiting the path length of gas the electron have to traverse. The catalyst under study (or its precursor) can be loaded into the nanoreactor prior to the experiments. Small electron transparent windows provide both good transmission of the electron beam and stability against the pressure difference. Heating is possible up to about 600 °C.

This nanoreactor system has now been expanded by adding the possibility of studying gas compositions using mass spectrometry. This means the gas composition can be monitored while simultaneously imaging dynamic changes in eg catalyst metal nanoparticles.

We have used this system to study the Kirkendall effect during oxidation of copper nanoparticles. The Kirkendall effect is used in catalyst regeneration procedures. We can now follow the process using live imaging.

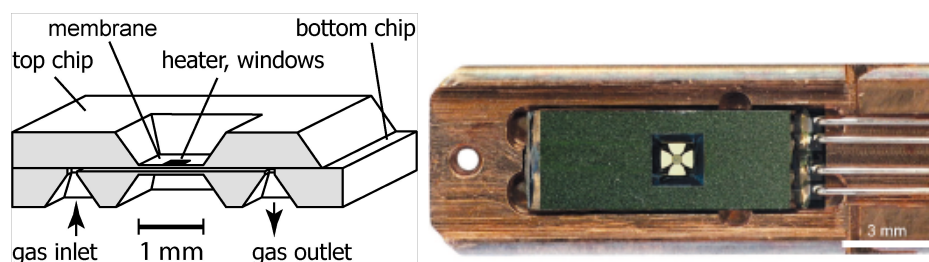
We have studied the oxidation of CO with O<sub>2</sub> on both Pt and Pd nanoparticles. Several process parameters have been varied, such as temperature and CO/O<sub>2</sub> ratio. Figure 2 shows the increase in conversion while increasing the temperature for CO oxidation on Pt. Figure 3 shows atomic resolution images of a Pt and a Pd nanoparticle recorded in situ during the catalytic process.

### References:

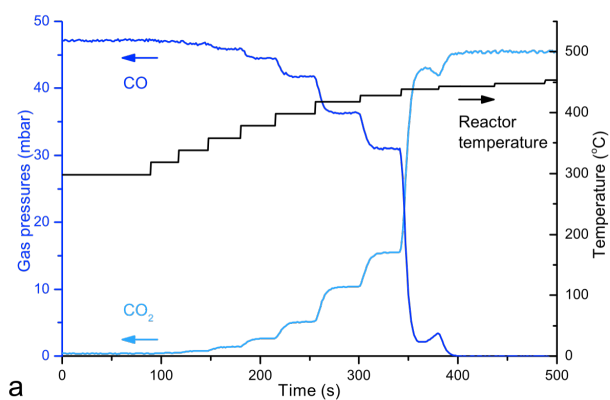
[1] ED Boyes and PL Gai, *Ultramicroscopy* **67** (1997) p. 219

[2] JF Creemer, *et al*, *Ultramicroscopy* **108** (2008) p. 993.

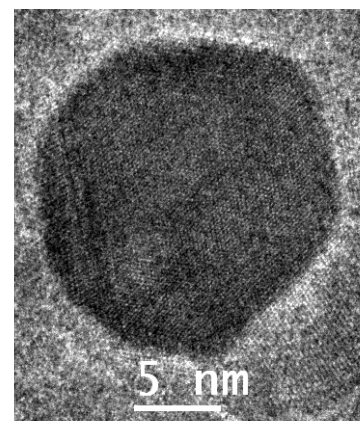
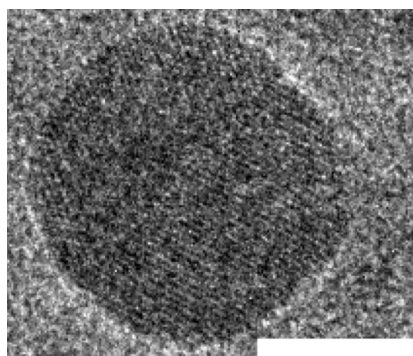
[3] The authors acknowledge funding from the NIMIC SMARTMIX consortium.



**Figure 1.** Left, schematic of the nanoreactor. Right, photo of a nanoreactor in the special TEM holder.



**Figure 2.** Mass spectrometry data (left axis) and nanoreactor temperature (right axis) showing increased CO conversion with increasing temperature. Catalyst used here was Pt.



**Figure 3.** Left, Pt nanoparticle imaged at 400 °C in a mixture of CO, O<sub>2</sub> and He at a total pressure of 1 bar (scale bar = 5 nm). Right, Pd nanoparticle imaged at 400 °C in a mixture of CO and O<sub>2</sub> at a total pressure of 250 mbar.