**Oral presentation**

# CO-induced dynamic behaviour of $Al_2O_3$-supported Pd nanoparticles at room temperature

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It is known that metal nanoparticles (NPs) can undergo surface and/or structural rearrangements in the presence of adsorbates, and this has relevance both in catalysis and in the field of NPs characterization. A typical example is the structural rearrangement of Pd NPs in the presence of CO, which has been reported to occur mostly at elevated temperature (e.g. during CO oxidation reaction) [1]. However, catalysts with small NPs (~2 nm) tend to exhibit high activity under milder reaction conditions. Moreover, CO is commonly used as probe molecule for the characterization of metal NPs close to room temperature (e.g. through pulsed CO chemisorption). Recently, we demonstrated - by coupling gas volumetry, adsorption microcalorimetry and IR spectroscopy - that CO adsorption at room temperature on $Al_2O_3$-supported Pd NPs (size ~ 2.2 nm) causes the corrugation of the (100) facet, entailing the creation of new defective sites [2]. Herein, we delve deeper into the structural evolution of these supported Pd NPs upon CO adsorption by using *operando* Pair Distribution Function (PDF) analysis coupled with mass spectrometry (performed at beamline ID15A at ESRF), allied with complementary *in situ* IR spectroscopy. The catalyst was initially reduced in $H_2$ at 393 K, and flushed in Ar at the same temperature, to expose metallic Pd. Then, it was exposed to CO at 298 K and time-resolved (1s) XRD patterns were collected with a Modulated Excitation (ME) approach [3]. During a longer, preliminary isothermal CO adsorption, the Pd-Pd contributions (triangles in Fig. 1a) grow in intensity, sharpen, and shift to longer distances. Cycle-averaged ME-PDF fit results (Fig. 1b) in CO atmosphere reveal two regimes i) a fast, step-like change in atomic displacement parameter (ADP) and Pd-Pd expansion ($\Delta R/R$) following the ordering of the NPs in the first few seconds; ii) a slower evolution of the same parameters due to the progressive expansion of the NPs (breathing). When the atmosphere is switched to Ar, both phenomena are fully reversed following a similar two-step evolution.

While the breathing and the reordering captured by differential PDF inevitably average over bulk and surface, *in situ* IR spectroscopy of CO adsorbed on the same Pd NPs is only sensitive to surface effects. Fig. 1C shows the IR spectrum of CO adsorbed at 100 K and its evolution upon warming to room temperature (from yellow to blue). The general peak sharpening suggests that CO triggers a surface restructuring of Pd NPs above a threshold temperature, transitioning from an amorphous to a more ordered morphology. This observation corroborates the restructuring pointed out through the ME PDF analysis and validates the potential of this technique to detect adsorbate-induced structural changes in supported metal NPs.

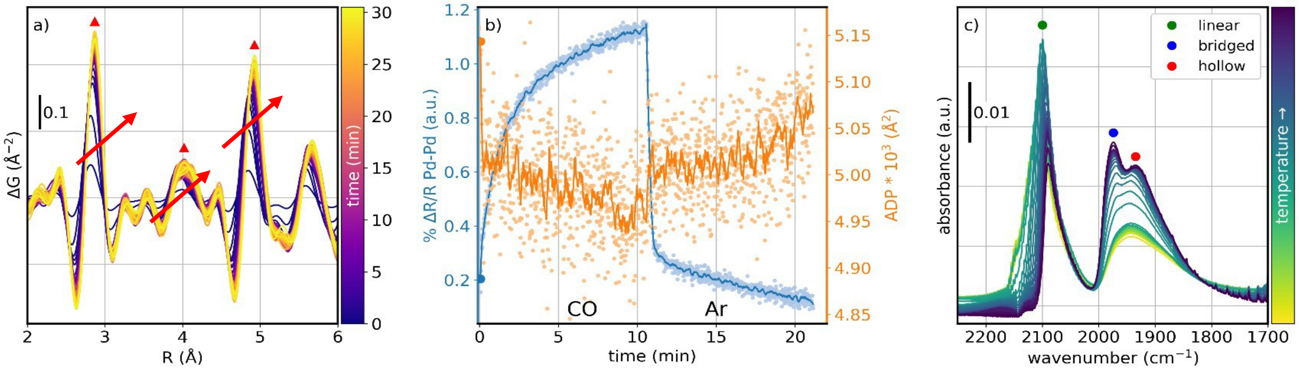

**Figure 1**. a) Differential PDF collected during the isothermal adsorption of CO on Pd NPs at 293 K (Pd-Pd contributions: red triangles); b) cycle-averaged ME data showing time evolution of the structural expansion of Pd (blue) and ADP (orange), c) *In situ* IR spectra of adsorbed CO collected under static CO pressure from 100 K to room temperature.

1] I. Jbir, J. Couble, S. Khaddar-Zine, Z. Ksibi, F. Meunier, D. Bianchi (2016) *ACS Catalysis,* **6,** 4, 2545-2558.

[2] A. Ricchebuono, E. Vottero, D. Bonavia, P. Lazzarini, R. Pellegrini, V. Crocella`, N. Porcaro, S. Checchia, D. Ferri, A. Piovano, E. Groppo (2024) *ACS Catalysis* [submitted].

[3] D. Ferri, M. Newton, M. Di Michiel, G.L. Chiarello, S. Yoon, J. Andrieux (2014) *Angew. Chemie,* **126,** 34, 9036-9040.