

# Role of noble metal-support interaction and *in situ/operando* spectroscopy in the rational design of active and stable catalysts

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Supported noble metal nanoparticles are essential catalytic materials in several application areas such as production of fine chemicals, energy conversion processes and environmental catalysis. Due to the limited availability and high costs of noble metals, maximizing catalyst efficiency is highly anticipated. However, improving the activity and stability of noble metal-based catalysts is only possible with an in-depth understanding of the reaction-induced structural dynamics and identification of the active site motif. [1] In our work, systematic *operando* X-ray absorption spectroscopy (XAS) and IR spectroscopy investigations in combination with DFT calculations were conducted to track the structure of the active sites in the Pd-based catalysts under transient CO oxidation conditions. For this purpose, a universal concept for the preparation of catalytic materials with a modified, local surface noble metal concentration [2] was developed in a first stage. The threshold of the *in situ* Pd cluster formation could be increased at a rather low noble metal loading of 0.5 wt.% by using CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support. This is achieved by exploiting the differences in the noble metal-support interaction that appear for CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> materials in comparison to pure CeO<sub>2</sub> support. To control the localization of Pd on the CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> carrier and ensure the close noble metal-ceria contact, we used flame spray pyrolysis (FSP) in a double nozzle configuration for the catalyst preparation. Based on the findings of our *in situ/operando* investigations, we were able to determine the crucial role of small PdO<sub>x</sub> clusters in combination with the Pd-CeO<sub>2</sub>-interface for a high CO oxidation activity at low temperatures and propose a strategy for the rational catalyst design.[3]

[1] F. Maurer, J. Jelic, J. Wang, A. Gänzler, P. Dolcet, C. Wöll, Y. Wang, F. Studt, M. Casapu, J.-D. Grunwaldt, *Nat. Catal.* 2020, **3**, 824.

[2] F. Maurer, A. Beck, J. Jelic, W. Wang, S. Mangold, M. Stehle, D. Wang, P. Dolcet, A. M. Gänzler, C. Kübel, F. Studt, M. Casapu, J.-D. Grunwaldt, *ACS Catal.* 2022, **12**, 2473.

[3] D. Gashnikova, F. Maurer, E. Sauter, S. Bernart, J. Jelic, P. Dolcet, C. B. Maliakkal, Y. Wang, C. Wöll, F. Studt, C. Kübel, M. Casapu, J.-D. Grunwaldt, *Angew. Chem. Int. Ed.* 2024, e202408511.