Confining Pd on CeO_2 nano-islands for more efficient oxidation catalysts

Daria GASHNIKOVA[1], Florian MAURER[1], Maria CASAPU[1], Jan-Dierk GRUNWALDT[1,2*]
[1] Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe, Germany.
[2] Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Karlsruhe, Germany..
** e-mail corresponding: grunwaldt@kit.edu*

Significance and Relevance

Despite a strong interaction with the support prevents the noble metal (NM) sintering at high temperatures, this can also lead to deactivation due to the formation of highly dispersed and thus inactive species under oxidizing conditions. This study reports a novel concept for stabilizing NM clusters on ceria in low-loaded catalysts during lean operation. Complementary *in situ/operando* characterization revealed that the *in situ* formation of Pd clusters is favored by confining Pd on CeO_2 nano-islands. The proposed strategy leads to highly active and stable CO oxidation catalysts with more efficient NM usage and is attractive for further NM-catalyzed reactions.

Preferred and 2nd choice for the topic: "Automotive and stationary emission control" or "Air cleaning and combustion".
Preferred presentation: Oral preferred

Introduction and Motivations

Noble metal-based systems are crucial materials for numerous catalytic reactions including hydrogen production, synthesis of fine chemicals and emission control. Due to their unique chemical properties, the exhibited activity and stability are hardly replaceable by non-noble metal based catalysts. Considering their limited availability and high costs, a more efficient use of noble metals is desired without negative impact on the catalytic activity. In this regard, the rational design of more efficient noble metals catalysts requires a profound understanding of structure-activity correlations. Due to high structural dynamics of noble metal-based catalysts under reaction conditions, the relationship between the catalyst structure and performance can be derived only by applying complementary *in situ/operando* characterization methods.[1-5]

Besides the impact of the reaction conditions, the noble metal structure is further influenced by the interaction with the used support material. In particular, CeO_2 as a strongly interacting carrier is known to provide alternative reaction pathways due to the perimeter sites at the interface with noble metal particles [2,3] However, in oxidizing atmosphere at high temperatures this interplay also leads to the formation of isolated noble metal species, i.e. single atoms, which for Pt/CeO_2 were found to be only poorly active for CO oxidation.[2]

To overcome this effect, the surface noble metal concentration (SNMC) can be adjusted to promote the cluster formation tendency and therefore of the catalytic performance of noble metal/ceria-based materials[3]. The SNMC can be increased by applying high noble metal loadings, which is, however, not ideal. Therefore, another approach was selected in this study for regulating the noble metal state on CeO_2. By using a combination of differently interacting supports, e.g. CeO_2-nano-islands on Al_2O_3, the SNMC can be increased at a rather low noble metal loadings, as verified in our work for Pd-containing catalysts[4-5].

Materials and Methods

Pd-based catalysts (noble metal loading of 0.5 wt.%) supported on CeO_2, Al_2O_3 and 5% CeO_2-Al_2O_3 were synthesized by flame spray pyrolysis using a double nozzle configuration and palladium and aluminium acetylacetonate, and ceria ethylhexanoate as educts. For Pd/CeO_2-Al_2O_3, the Pd and CeO_2 the precursors were sprayed in one flame, separately from the Al_2O_3 precursor solution. In such a way, the preferential location on Pd on CeO_2 nano-islands could be ensured already during the catalyst preparation.

The catalytic activity of the as-prepared samples was evaluated during CO oxidation in a high excess of oxygen (1000 ppm CO/8 % O_2/N_2) in a tubular quartz reactor with an inner diameter of 8 mm. The gas composition was monitored at the reactor outlet with a Fourier transform infrared spectrometer (Multigas FTIR Spectroscopy, MKS).

To reveal differences in the evolution of Pd species during reaction and verify our approach, we performed systematic *operando* X-ray absorption spectroscopy (XAS) investigations (conducted at Pd K edge at SAMBA beamline of synchrotron radiation facility SOLEIL) and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies.

Results and Discussion

The *ex situ* characterization results indicate the presence of highly dispersed species in Pd/CeO_2 and Pd/CeO_2-Al_2O_3, while small Pd nanoparticles were obtained on the weakly interacting Al_2O_3 despite the identical Pd loading of 0.5 wt.%. The synthesized catalysts showed a significantly different catalytic activity, with Pd/CeO_2-Al_2O_3 reaching the highest CO oxidation performance (temperature of 90 % conversion T_{90} = 90°C). On the contrary, Pd/CeO_2 converted only ~80 % of CO at 300 °C (Figure 1a). The complementary *in situ/operando* DRIFTS/XAS investigations revealed that the noble metal in Pd/CeO_2 remained in an almost fully oxidized state over the entire reaction range, while a slight Pd reduction was detected for Pd/CeO_2-Al_2O_3 (Figure 1b). Supported by electron microscopy data, this structural peculiarities and the high low temperature activity could be correlated with the *in situ* formation of small Pd clusters in Pd/CeO_2-Al_2O_3, confirming the proposed strategy for promoting the noble metal cluster formation and stabilization.

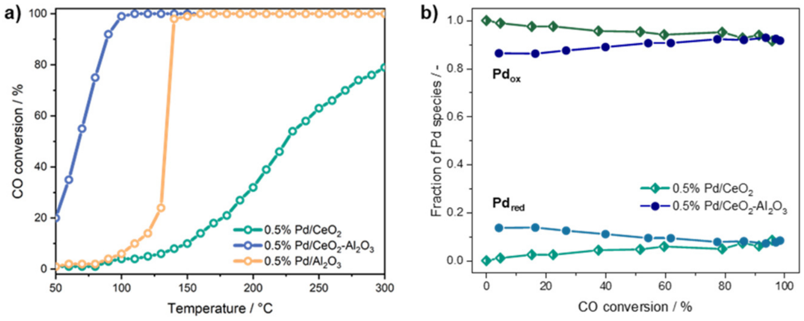

Figure 1 a) Catalytic activity of Pd-based catalysts during lean CO oxidation; b) LCA results of operando XAS spectra recorded during the CO oxidation reaction for Pd/CeO_2 and Pd/CeO_2-Al_2O_3.[4]

References

1. B. B. Sarma, J.-D. Grunwaldt, *Chimia*, **2024**, *78*, 288.
2. 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.
3. 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.
4. 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.
5. D. Gashnikova, F. Maurer, M. R. Bauer, S. Bernart, F. Studt, C. Kübel, C. D. Damsgaard, M. Casapu, J.-D. Grunwaldt *et al.*, *ACS Catal.* **2024**, *14*, 14871.

Acknowledgements

Daria Gashnikova acknowledges the “Fonds der Chemischen Industrie” (FCI) of the Verband der Chemischen Industrie e.V. (VCI) for financial support during her Ph.D. studies. This study was further funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) − SFB 1441 − Project-ID 426888090. The authors thank the synchrotron radiation facility SOLEIL for beamtime at the ROCK and SAMBA beamlines and the KIT light source for beamtime at the CAT-ACT beamline.