

# Structural parameters for high activity and stability of Pd/CeO<sub>2</sub> CH<sub>4</sub> oxidation catalysts

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#### Significance and Relevance

Due their high costs, increasing the efficiency of the noble metal based catalysts is highly important for numerous applications including emission control. A systematic study on the influence of noble metal loading relative to the specific surface area of ceria supports on the activity and stability of Pd-based methane oxidation catalysts is reported. The results show a clear correlation between the noble metal coverage as single site layer and the evolution of the catalyst under reaction conditions. The highest noble metal efficiency and catalyst stability was identified for loadings close to the monolayer coverage <sup>1</sup>.

Preferred and 2<sup>nd</sup> choice for the topic: Automotive and stationary emission control; Air cleaning and combustion

Preferred presentation: Oral preferred or Short Oral

### **Introduction and Motivations**

In combination with noble metal (NM) as active species, ceria is one of the most applied supports in heterogeneous catalysis. As strongly interacting and functional materials, CeO<sub>2</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub> are mostly used to prevent the noble metal sintering and buffer the oxygen concentration in emission control. Additionally, the perimeter sites at the interface with the noble metal particles were found to directly contribute to oxidation reactions<sup>2</sup>. However, the strong NM-CeO<sub>2</sub> interaction leads also to the formation of single sites or highly dispersed NM species, which have been shown to be less active<sup>3-4</sup>. Particularly for reactions involving the exposure to high temperatures such a deactivation mechanism needs to be considered. Although the re-formation of noble metal particles can be induced by reductive treatments, this approach is not favoured during real applications. With our study we propose an alternative path for controlling the formation of Pd particles in CeO<sub>2</sub>-based methane oxidation catalysts by adjusting the noble metal loading and the support specific surface area to slightly exceed the single site monolayer coverage concentration.



**Figure 1.** CH<sub>4</sub> oxidation activity of Pd/CeO<sub>2</sub> catalysts with 20% (a) and 120% (b) noble metal coverage pre-treated at 800°C in oxidizing conditions (black line) and H<sub>2</sub> pre-reduced at 500°C (red line). Gas mixture: 3200 ppm CH<sub>4</sub>, 0-5%H<sub>2</sub>O, 10% O<sub>2</sub> in N<sub>2</sub>; WHSV 20000 L/g<sub>NM</sub><sup>-1</sup>h<sup>-1</sup> (high WHSV). [1]



#### **Materials and Methods**

A series of Pd catalysts with noble metal loadings of 1-3 wt.% were supported on CeO<sub>2</sub>-based materials with different specific surface areas (30-120 m<sup>2</sup>/g) by incipient wetness impregnation. To disperse Pd homogenously over the CeO<sub>2</sub> surface, the obtained samples were calcined for 10 h at 800 °C in static air. The resulting catalysts were characterized by complementary *ex situ* and *in situ/operando* characterization methods including XRD, ETEM/EDXS, DRIFTS, XAS and XPS. The variations in the sample characteristics depending on the catalyst pre-treatment are supported by DFT calculations. Catalytic tests were conducted for the granulated samples (125 – 250  $\mu$ m) in a plug-flow reactor while measuring the reaction products with an FTIR Gas Analyzer (MKS).

#### **Results and Discussion**

The results obtained indicate a pronounced increase in the CH<sub>4</sub> oxidation activity by applying a reductive treatment to Pd/CeO<sub>2</sub> samples containing single noble metal sites and small clusters. Larger particles and a higher catalyst stability were obtained by using CO for the reductive treatment instead of H<sub>2</sub>. Moreover, by adjusting the noble metal loading per surface area unit of CeO<sub>2</sub>-based supports, the spreading of the entire noble metal amount as inactive single sites was prevented. For Pd concentrations slightly exceeding the theoretical single site monolayer coverage an improved activity was measured already in the as prepared catalyst state (Fig. 1b, after oxidation at 800°C for 10h), which was combined with a higher stability during the following activity cycles. In contrast, for lower noble metal loadings, the activity gained after the pre-reduction treatment shows a rapid decay due to the noble metal redispersion. The formation or redispersion of Pd nanoparticles depending on the gas atmosphere and temperature was monitored during ETEM measurements. Further differences in the noble metal structure leading to a higher or lower catalyst activity and durability were uncovered by in situ DRIFTS and operando XAS characterization, and were additionally supported by DFT calculations<sup>5</sup>. Summarizing, a threshold for Pd concentration on CeO<sub>2</sub>-based supports was identified around the monolayer coverage, which ensures an optimal usage of the noble metal and a high stability of the catalyst by preventing excessive sintering or redispersion.

## References

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