

# Pr-doped Pd/CeO<sub>2</sub> catalysts with enhanced CH<sub>4</sub> oxidation activity: unveiling the promoting role of Pr through advanced spectroscopy

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## Highlights

- A mild Pr-doping enhances Pd/CeO<sub>2</sub> activity for both dry and wet CH<sub>4</sub> oxidation
- Pr loading in ceria is correlated with methane adsorption capacity
- More stable carbonates form at the surface of Pr-rich catalysts during CH<sub>4</sub> oxidation
- Most active samples exhibit a mix of reduced and oxidized Pd species during reaction

## 1. Introduction

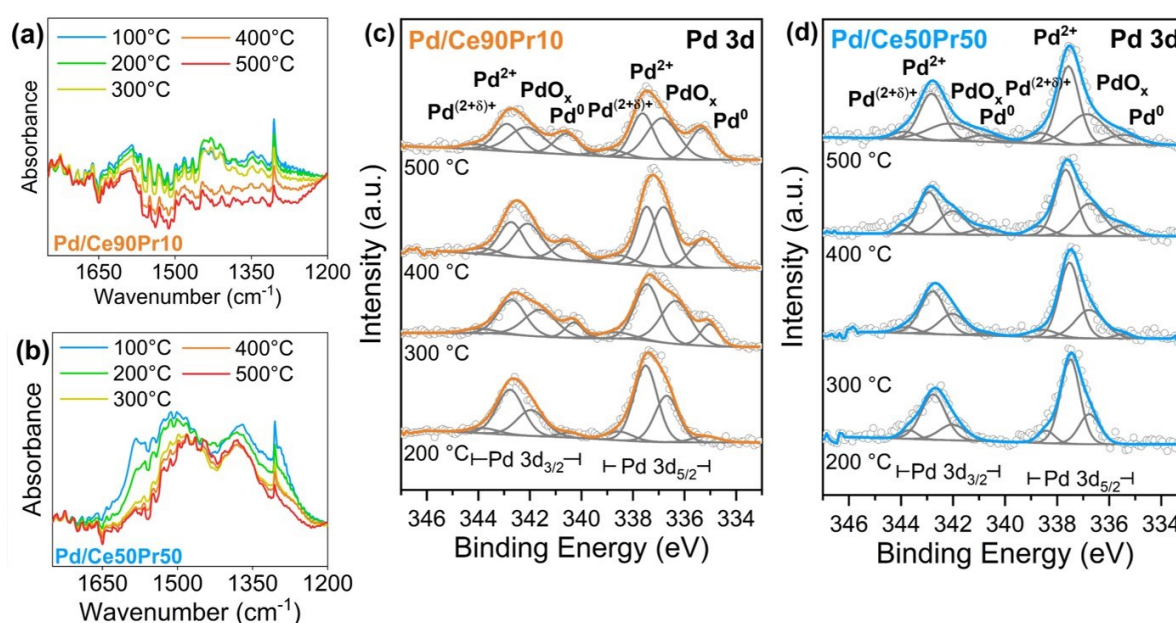
The atmospheric CH<sub>4</sub> concentration has significantly increased in the last decades, mainly due to anthropogenic emissions, and it is likely going to exceed a value of 2000 ppb in the next years [1]. Since methane is considered the second most impacting human-related greenhouse gas, having a high global warming potential, several efforts have been made to reduce its emissions. In this regard, increasingly efficient catalytic systems have been developed to promote CH<sub>4</sub> oxidation to CO<sub>2</sub>. Pd-supported catalysts have been recognized as the most promising materials, while ceria exhibited excellent properties as Pd support [2]. More recently, Pr-doping of the ceria support was proved to enhance metal-support interaction, promoting the presence of active Pd species and counteracting water-induced deactivation phenomena [3 - 5]. In the present study, Pd-Ce-Pr systems with different compositions were tested and deeply investigated with some advanced techniques, such as Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) and in-situ/operando FTIR spectroscopy, gaining new insights into the promoting role played by Pr during methane oxidation.

## 2. Methods

Nanostructured Ce-Pr supports were prepared through hydrothermal synthesis and impregnated with 2 wt.% of Pd [4]. The samples were named Pd/Ce(100-X)Pr(X), where X indicates the atomic percentage of Pr in the support (0, 10, 25, 50%). Catalytic activity tests (0.3% CH<sub>4</sub> + 1.2% O<sub>2</sub> in N<sub>2</sub>, GHSV = 60,000-80,000 h<sup>-1</sup>) were carried out in a fixed bed reactor in both dry and wet conditions (5 vol% of H<sub>2</sub>O added to the inlet flow). The materials were comprehensively characterized through different techniques (XRD, N<sub>2</sub> physisorption, FESEM, TEM, etc.), including some advanced spectroscopic analyses. In-situ transmission FTIR analyses were conducted to study the interaction between the catalysts and H<sub>2</sub>O or CH<sub>4</sub>, using a Bruker Invenio S FTIR spectrometer: the sample was pressed in a tablet, placed in a handmade IR cell connected to a high-vacuum line, pretreated under-vacuum at 500 °C, and then exposed to increasing doses of H<sub>2</sub>O or CH<sub>4</sub>. Operando FTIR analyses were carried out using a Specac HT/HP cell, collecting spectra at different temperatures while flowing a reacting mixture (0.9% CH<sub>4</sub> + 3.6% O<sub>2</sub> in N<sub>2</sub>). Similarly, NAP-XPS measurements were performed at Charles University (Prague, CZ) using a SPECS EnviroESCA system equipped with a monochromated Al K $\alpha$  X-ray source (1486.71 eV): the sample powder was pressed against Ti mesh, and core-level spectra of Pd 3d, Ce 3d, Pr 3d, C 1s and O 1s were recorded while heating the sample under a reacting flow (0.3% CH<sub>4</sub> + 1.2% O<sub>2</sub> in N<sub>2</sub>, pressure of 2.5 mbar).

### 3. Results and discussion

A mild Pr-doping was associated with an enhancement of Pd/ceria catalytic activity towards methane oxidation: indeed, Pd/Ce90Pr10 resulted to be the most performing sample, both in dry and wet conditions. Further Pr addition was instead linked to lower activity. According to in situ FTIR, increasing the Pr percentage in ceria favors CH<sub>4</sub> adsorption, despite also promoting hydrophilicity. Moreover, a higher Pr content was related to a strong affinity with carbonate species: indeed, Pr-rich materials were covered by stable bi- and poly-dentate carbonates, showing a limited CO<sub>2</sub> desorption tendency (Fig. 1a,b). NAP-XPS showed that the catalysts containing a low Pr percentage exhibited a variegated mix of reduced and oxidized Pd species throughout the course of the reaction up to 500 °C (Fig. 1c); a higher Pr loading was instead associated with the presence of too stable oxidized palladium forms (Fig. 1d), with detrimental effects on catalytic activity. An intermediate Pr doping represents therefore the best compromise in terms of stability of both Pd active species and reaction intermediates.



**Figure 1.** FTIR (a,b) and NAP-XPS (c,d) spectra collected at different temperatures over Pd/Ce90Pr10 (a,c) and Pd/Ce50Pr50 (b,d) samples during methane oxidation.

### 4. Conclusions

Doping Pd/CeO<sub>2</sub> systems with a moderate Pr quantity (10%) results in an optimized metal-support interaction, favoring the formation of a mixture of highly active Pd species, promoting CH<sub>4</sub> adsorption and allowing the formation of medium-strength carbonates as intermediates.

### References

- [1] R. B. Skeie, Ø. Hodnebrog, G. Myhre, *Commun. Earth Environ.* 4 (2023) 317
- [2] M. Danielis, L. E. Betancourt, I. Orozco, N. J. Divins, J. Llorca, J. A. Rodríguez, S. D. Senanayake, S. Colussi, A. Trovarelli, *Appl. Catal. B: Environ.* 282 (2021) 119567
- [3] S. Ballauri, E. Sartoretto, C. Novara, F. Giorgis, M. Piumetti, D. Fino, N. Russo, S. Bensaid, *Catal. Today*, 390–391 (2022) 185
- [4] S. Ballauri, E. Sartoretto, M. Hu, C. D’Agostino, Z. Ge, L. Wu, C. Novara, F. Giorgis, M. Piumetti, D. Fino, N. Russo, S. Bensaid, *Appl. Catal. B Environ.* 320 (2023) 121898
- [5] S. Ballauri, E. Sartoretto, M. Castellino, M. Armandi, M. Piumetti, D. Fino, N. Russo, S. Bensaid, *ChemCatChem.* (2024) e202301359

### Keywords

“methane oxidation”, “ceria-based catalysts”, “operando spectroscopy”, “palladium”