Pd-ceria catalysts for complete CH_4 oxidation: influence of Pr-doping on sulfur resistance

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Significance and Relevance

Nanostructured Pr-doped Pd-ceria catalysts for complete CH_4 oxidation were studied in the presence of SO_2, in order to investigate how Pr loading affects the behavior of Pd species and influences their regeneration after sulfation. Sulfur can penetrate the bulk of Pr-rich supports, causing structural distortion and defect formation, but the palladium activity is preserved. Sulfation also results in a global reduction of the material and a weakened metal-support interaction. This reduces the beneficial effect of Pr on PdO stabilization at high temperature, but at the same time promotes activity at low temperature, optimizing the PdO/Pd^0 ratio.

Preferred topic: Automotive and stationary emission control
2nd *choice topic: Air cleaning and combustion*
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Natural gas is regarded as an important energy vector for the energy transition towards a more sustainable society. However, CH_4 emissions must be reduced as much as possible due to its high global warming potential. Catalytic total oxidation is a state-of-the-art method to abate the methane traces in exhaust gases, and Pd-based catalysts are usually employed for activating the CH_4 dissociation.

Since recent research suggested the presence of oxidized Pd^{2+} species to be crucial for catalyzing methane oxidation at high temperature[1], in the last years we synthesized redox Pd supports consisting of pure and Pr-doped ceria[2-4]. We proved that Pr doping enables the conservation of palladium in more oxidized species, thereby reducing the typical loss of activity due to PdO decomposition to Pd, usually observed at 650 – 700 °C during methane oxidation tests[3]. However, the best catalytic activity was achieved with mild Pr-doping (10 at%), since too strong Pd-support interactions is detrimental[2]. An intermediate Pr content also resulted in high activity and stability in the presence of water, thanks to the higher affinity with methane of Pr-doped ceria (observed through in situ FTIR and NMR)[3].

Besides water, sulfur, present in traces in natural gas, is also a known deactivating agent for Pd-based catalysts[5]. Hence, in this work we thoroughly investigated the resistance of Pd/Ce-Pr materials to sulfur poisoning and the role of Pr-doping in this phenomenon.

Materials and Methods

Well-defined nanostructures with different cerium and praseodymium contents were prepared through a hydrothermal synthesis procedure[3] (Ce100 = 100 at% Ce; Ce90Pr10 = 90 at% Ce + 10 at% Pr; Ce50Pr50 = 50 at% Ce + 50 at% Pr; Pr100 = 100 at% Pr). Pd was deposited via incipient wetness impregnation (2 wt%) using a palladium nitrate solution. Catalytic tests of methane oxidation (0.3% CH_4 + 1.2% O_2 in N_2, GHSV = 50 000 h^{-1}), consisting of repeated heating and cooling cycles up to 900 °C (see Figure 1A), were carried out before and after exposure to SO_2 during isothermal reaction (20 ppm, 500 °C, 6 h). The fresh and spent catalysts were comprehensively studied with several techniques, including XRD, N_2 physisorption, Raman spectroscopy, FESEM, TEM, EDX, XPS.

Results and Discussion

Upon exposure to SO_2 during methane oxidation, different behaviors were observed depending on the Pr loading, which seems to influence both the stability and the possibility of the catalyst to be regenerated at high temperature. In particular, Pd/Ce100 exhibited a very rapid drop in activity as soon as SO_2 was sent to the reactor (Figure 1B), whilst Pr doping increased the resistance of the catalyst (only a slight decrease in activity was observed for Ce50Pr50 over 6 h). However, after having exposed the catalyst to higher temperature (900 °C) during a methane oxidation cycle, Pd/Ce100 almost completely recovered its initial activity (Figure 1C). Instead, the Pr-doped samples exhibited increased activity in the second reaction cycle after sulfation (Figure 1D and 1E), but Pd/Ce50Pr50 dramatically lost the ability to avoid PdO decomposition at high temperature. To understand these phenomena, two spent samples for each catalyst were recovered, one at the end of the fourth reaction cycle (Figure 1A) and the other just after the time-on-stream exposure to SO_2 (TOS).

EDX and XPS analyses of these spent samples revealed the presence of sulfates after TOS, whose content increases with the Pr loading. Moreover, sulfates almost completely disappeared after two reaction cycles in Pd/Ce100, while they were only partially eliminated in the case of Pr-doped catalysts. XRD and Raman measurements indicated a good structural stability for Pd/Ce100 and Pd/Ce90Pr10; conversely, the Pd/Ce50Pr50 catalyst exhibited non-reversible XRD peak splitting and a remarkable increase of the defect-related Raman band after exposure to SO_2. Coupled with TEM-EDX investigations, this information suggests that sulfur can penetrate the bulk of Pr-rich supports, causing structural distortion and defect formation, but without damaging the palladium activity. This also results in a global reduction of the material and a weakened metal-support interaction, as revealed by XPS. The latter effect positively influences activity at low temperature, optimizing the PdO/Pd^0 ratio in Pd/Ce90Pr10, but reduces the beneficial effect of Pr on PdO stabilization at high temperature.

This study explores the behavior of Pr-doped Pd-ceria materials for CH_4 oxidation in the presence of SO_2, providing useful insights for the use of Pr as dopant in real applications.

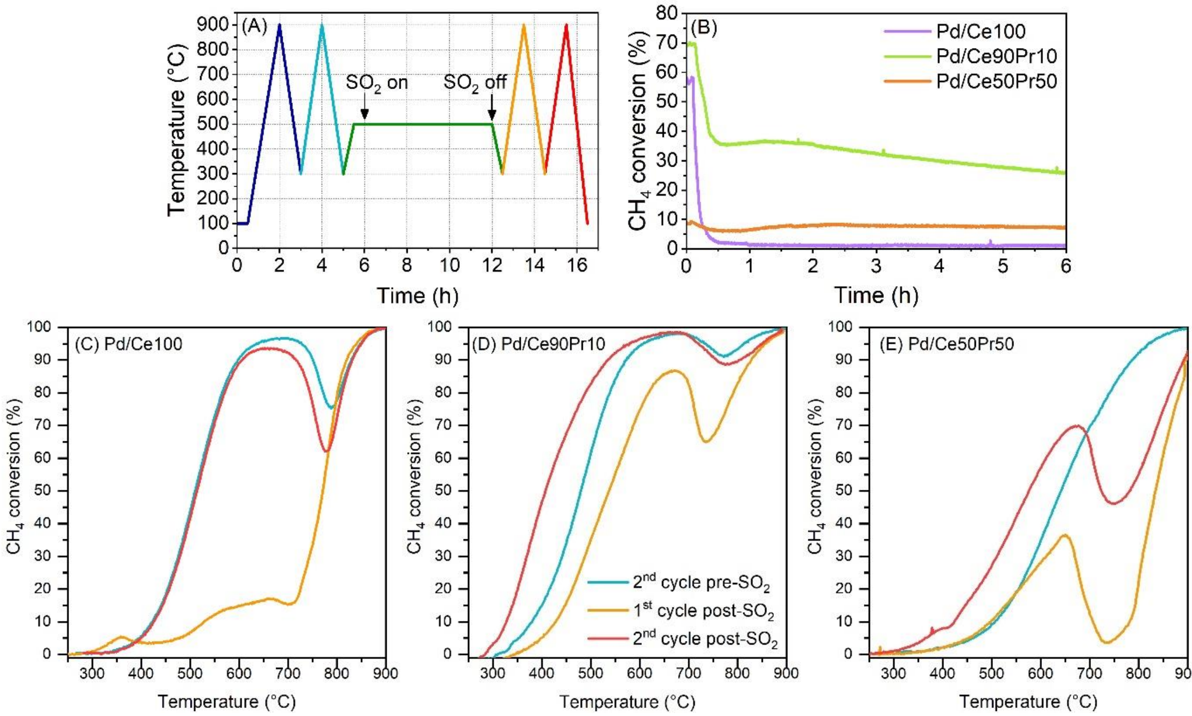

Figure 1 Scheme of the catalytic tests (A). Evolution of CH_4 conversion over time-on-stream (TOS) in the presence of SO_2 (B). Methane oxidation tests (heating runs) performed on the Pd/Ce100 (C), Pd/Ce90Pr10 (C) and Pd/Ce50Pr50 (E) catalysts before and after exposure to SO_2.

References

1. S. Colussi et al., *Chin. J. Catal*. **2020**, *41*, 938–950.
2. S. Ballauri, E. Sartoretti et al., *Catal. Today*. **2022**, *390–391*, 185-197.
3. S. Ballauri, E. Sartoretti et al., *Appl. Catal. B Environ*. **2023**, *320*, 121898.
4. S. Ballauri, E. Sartoretti et al., *ChemCatChem*. **2024**, *16*, e202301359.
5. J. Lin et al., *Appl. Catal. B Environ.* **2024**, *340*, 123283.

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