Optimizing Performance of Ce/Zr/Pr-based Gasoline Soot Oxidation Catalysts by Mechanochemical Synthesis

Rizwan Asghar[1], Carla de Leitenburg[1], Rudy Calligaro[1], Alessandro Trovarelli[1]
[1]*University of Udine, DPIA, Udine, Italy*
asghar.rizwan@spes.uniud.it

Significance and Relevance

Mechanochemical synthesis is an environmentally friendly synthetic approach[1] that is solvent-free and is streamlined compared to other preparation methods. It is also capturing interest for the preparation of efficient heterogeneous catalysts[2]. In this work, mechanochemical synthesis was found to be promising for the synthesis of mixed rare-earth oxide formulations based on Cerium (Ce), Zirconium (Zr) and Praseodymium (Pr) with lower Pr amount respect to what previously reported in literature[3]. This was proven to be associated to the preparation methodology and to the presence of small amount of Zr into CePr which enhanced Oxygen ion mobility and led to improved catalytic activity.

Preferred topic: Automotive and stationary emission control
2nd choice: Air cleaning and combustion

Preferred presentation: *Poster*

Introduction and Motivations

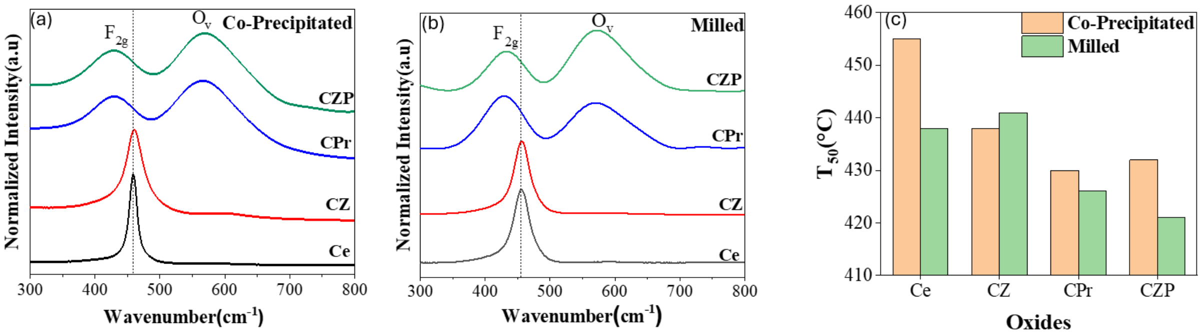
Plug-in Hybrid Electric Vehicles (PHEV) equipped with Gasoline Direct Injection (GDI) engines are of great interest nowadays owing to their fuel efficiency and reduced CO_2 emissions. However, high PM emissions during cold start pose major confront for environmental implication. The combination of gasoline particulate filter with a catalyst is an effective approach for reducing the temperature of soot oxidation. Ceria-based catalyst, with their high OSC and redox cycle are the most studied and promising materials in the field of soot oxidation. Because of its poor thermal stability, ceria suffers from sintering and consequent loss of activity at elevated temperatures. For this reason, CeZr formulations can be used, since better thermal stability can be obtained[4]. The low oxygen content in the gasoline engine exhaust contributes to the difficulty of low temperature soot combustion. Therefore, the use of the highly reducible Pr can significantly improve catalytic performance by boosting the OSC for oxygen deficient environment. The aim of this work is to prepare some CeZrPr formulations to investigate the effect of Zr introduction into the CePr lattice and to explore the feasibility of a more sustainable synthetic approach, namely ball milling, which has the advantages of being solvent-less, faster and easy to scale up.

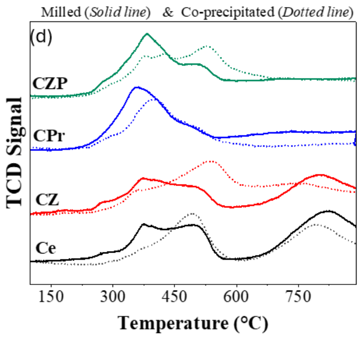
Materials and Methods

CeO_2, $Ce_{0.9}Zr_{0.1}O_2$, $Ce_{0.7}Pr_{0.3}O_2$, $Ce_{0.63}Zr_{0.07}Pr_{0.3}O_2$ were synthesized with mechanochemical synthesis starting from nitrate hydrate salts. The ratio of Ce/Zr was 9/1 for both CeZr and CeZrPr. The prepared samples were characterized using XRD, Raman spectroscopy, BET along with porosimetry measurements, and TPR for the evaluation of structural and catalytic properties. The prepared supports were mixed with commercial soot in a 4.7 wt.% loading and evaluated for soot oxidation activity by means of TGA under different environments (N_2, $1\%O_2/N_2$ and $20\%O_2/N_2$). The materials were compared with some analogues prepared via wet chemistry co-precipitation technique.

Results and Discussion

Both XRD and Raman analysis results support the solid solution formation for doped samples irrespective of the synthesis method. Raman analysis showed a shift and a widening of the F_{2g} peak at around 460cm^{-1} in the doped samples with respect to pure ceria (see Figure 1(a, b)) with a magnitude that depends on dopant cation. The appearance of band around 600 cm^{-1} (A_{ov}) is related to defects or oxygen vacancies present in the material. The intensity and width of the defect band increase moving from Ce to CeZrPr and it was intense for Pr containing samples due to the easy reducibility of Pr. The ratio of the A_{ov}/A_{F2g} reported in Table 1 represents the ease of oxygen ion mobility[5]. This ratio was highest for milled CZP, which were expected to have excellent oxidation and reduction performance. This indication was in accordance with results of H_2 TPR (Figure 1(d)) and soot oxidation in 1% O_2(Figure 1(c)). Interestingly, the performance of milled samples was better than that of the co-precipitated counterparts for low temperature shift of either soot oxidation or H_2 reduction temperature. The better performance of milled CePr and CeZrPr, despite having lower surface area (Table 1), can be attributed to the higher concentration of reduced Pr. Overall, the optimized composition prepared by a mechanochemical approach coalesced in a single formulation the benefits of high OSC of Ceria, thermal stability of Zr and high catalytic activity of Pr in an oxygen deficient environment providing an effective catalysts for gasoline soot oxidation technology.





(e)

Table 1. Morphological characteristics of the prepared catalysts

Symbol	Oxides	Surface Area (m²/g)	Particle size (nm)	Pore size (Å)	Pore Volume (cm³/g)	A_{ov}/A_{F2g}
Ce	CP-CeO_2	59	11.4	191	0.33	0.02
	M20-CeO_2	101	8.0	101	0.31	0.02
CPr	CP-$Ce_{0.7}Pr_{0.3}O_2$	61	6.9	142	0.25	0.08
	M20-$Ce_{0.7}Pr_{0.3}O_2$	56	11.3	177	0.30	0.05
CZ	CP-$Ce_{0.9}Zr_{0.1}O_2$	60	6.4	158	0.27	1.21
	M20-$Ce_{0.9}Zr_{0.1}O_2$	76	8.5	179	0.38	1.24
CZP	CP-$Ce_{0.63}Zr_{0.07}Pr_{0.3}O_2$	63	4.8	189	0.35	1.52
	M20-$Ce_{0.63}Zr_{0.07}Pr_{0.3}O_2$	39	9.8	285	0.31	2.03

Figure 1: (a,b) Raman spectrum of milled (M20) and co-precipitated (CP) samples, (c) Temperature of 50% soot oxidation in 1%O_2 (d) Hydrogen temperature programmed reduction(H_2-TPR) profiles (e) **Table 1**: structural and textural properties of mixed oxides.

References

1 M. Danielis, S. Colussi, N. J. Divins, L. Soler, A. Trovarelli and J. Llorca, *Johnson Matthey Technology Review*, **2024**, *68*, (2), 217–231.

2 M. Danielis, A. Felli, M. Zampol, N. Fonda, P. Brüner, T. Grehl, E. Furlani, S. Maschio, S. Colussi and A. Trovarelli, *ACS Omega*, **2024**, *9*, 12046–12059..

3 S. Fahed, R. Pointecouteau, M. Aouine, A. Boréave, S. Gil, V. Meille, P. Bazin, O. Toulemonde, A. Demourgues, M. Daturi and P. Vernoux, *Applied Catalysis A General*, **2022**, *644*, 118800.

4 W. Chen, L. Fan, X. Jiang, J. Guo, H. Liu and M. Tian, *ACS Omega*, **2022**, *7*, 16352–16360.

5 J. C. Martínez-Munuera, M. Zoccoli, J. Giménez-Mañogil and A. García-García, *Applied Catalysis B*, **2019**, *245*, 706–720.

Acknowledgements

Finanziato dall'Unione Europea – NextGenerationEU - PNRR M4.C2.1.1 - PRIN 2022 – Codice 2022JRT7WZ – CUP G53D23001210006