Doped Ceria Catalysts for NOx Storage and Reduction

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Keywords: Doped Ceria, NOx Reduction, Emission Control

Introduction:

The new Euro 7 protocol, proposed by the Commission on 26th October 2022, concerning emissions of lean-burn engines, presents a need for further optimisation of existing after-treatment technologies. It reveals a 35% reduction to the NOx emission limit for cars and vans, compared to Euro 6 [1]. A well-known technology employed to reduce NOx to clean emissions in light-duty vehicles is the Lean NOx Trap (LNT). LNTs employ catalysts consisting of PGMs supported on ceria (CeO_2) or other mixed oxides. Ceria's redox property makes it an attractive selection, as well as its ability to store NO_x at low temp (<300 ˚C), especially when Pt is present. Storage properties of ceria can be further enhanced by doping. Dopants reportedly allow ceria to function better at low temperature (<300 ˚C), and to reduce the PGM loading required to achieve the same conversion efficiencies. [2] The RE metals Sm, Pr and Nd have been employed as dopants on CeO_2 for LNT applications to increase surface oxygen content, oxygen vacancies, defect densities, and cause changes to the Pt-ceria interaction. These structural changes can allow for higher NSC during lean operation and enhanced activation during rich purge. [3] Sm, Pr and Nd doped catalysts (10 wt.%) were synthesised on a range of ceria based catalysts with different Pt loadings (0-1 wt.%). Morphological changes observed through dopant addition has been investigated and related to catalytic performance increases.

Experimental/methodology:

NOx Storage Capacity experiments were carried out in a fixed bed reactor (tot. flow 200 Ncc/min, 40mg cat). Initial activation and cleaning ran from RT to 450˚C flowing 0.4% H_2 in Ar. Storage conditions consisted of 5% O_2, 400ppm NO, balanced with Ar. For H_2-TPR experiments; catalysts were pretreated to 500°C for 1hr in 10% O_2/He (35ml/min). H_2 consumption was measured from 0-1000°C in 5%H_2/Ar (35ml/min) at 10˚C/min.

Results and discussion:

NSC experiments were performed to assess the differences in NO_x storage capabilities at low temperatures (150-300˚C), on a range of doped ceria and Pt-ceria samples (Figure 1). It is observed that, at 150˚C, the NSC increases by 15% and 40% compared to that of the bare support, upon doping with Sm and Pr, respectively. To understand the dopant effect on NOx storage and oxidation capability, H_2-TPR experiments were also performed. Figure 2 shows reduction profiles of the four supports. Ceria shows the expected H_2 consumption peaks: from ~200-600 ⁰C and >700 ⁰C related to surface and bulk reductions of CeO_2, respectively. Upon 10wt.% addition of Sm, Pr and Nd, more intense peaks of reduction are observed between 250-450˚C along with a continuous H_2 consumption section between 600-700˚C possibly indicating a mixed phase reduction.

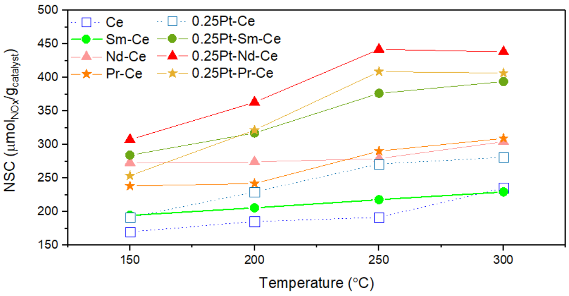

Figure 1. NSC experiments *(Ce = Ceria)

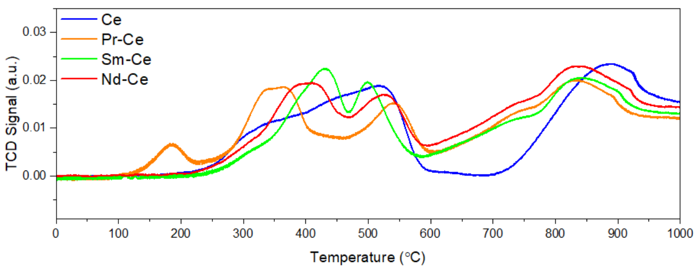

Figure 2. H_2-TPR experiments *(Ce = Ceria)

Many other characterisation techniques have also been used to study catalyst modification with doping. XPS highlighted an increase in surface O content present on the doped samples. Raman spectroscopy investigations showed higher defect densities on doped surface. EELS imaging illustrated partial separation of Pt at the CeO_2 surface caused by Sm doping which affects the Pt-Ce bonding. These studied effects may help explain the greater catalytic performances of the doped catalysts to remove NOx at low temperatures.

References [1] Euro 7 factsheet, doi:10.2873/99010. [2] Chansai, S.; Burch, R.; Hardacre, C.; Breen, J.; Meunier, F. *J. Catal.* **2011**, 281, 98. [3] Filtschew, A.; Hess, C. *Appl. Catal. B Environ.*, **2018**, 237, 2, 1066–1081.

CERIA CATALYSTS FOR NO_X STORAGE AND REDUCTION

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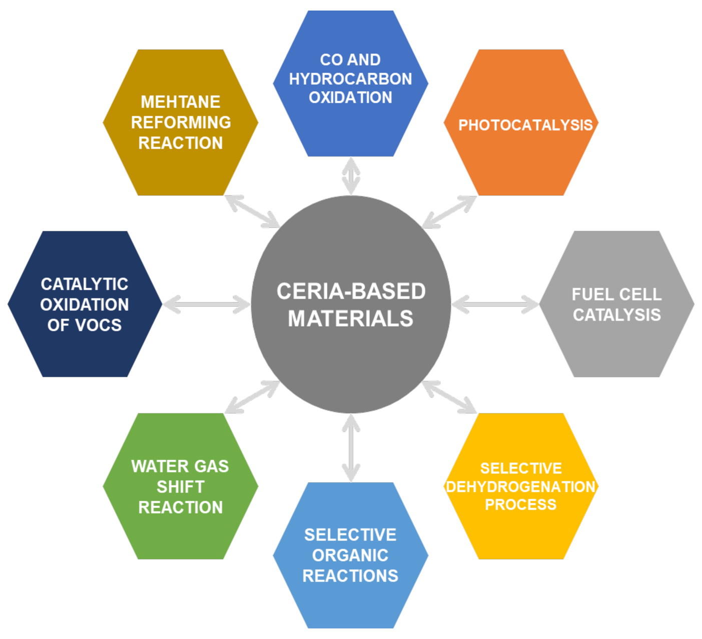
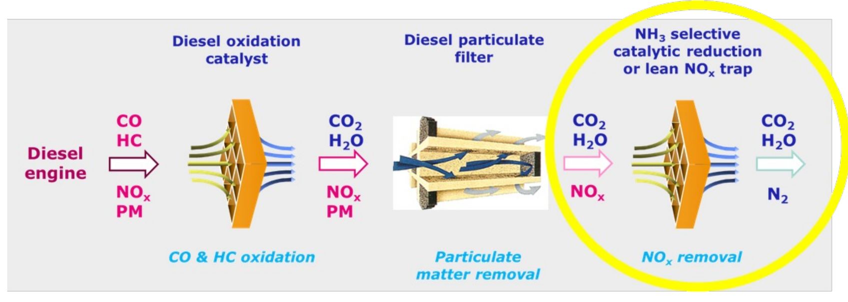
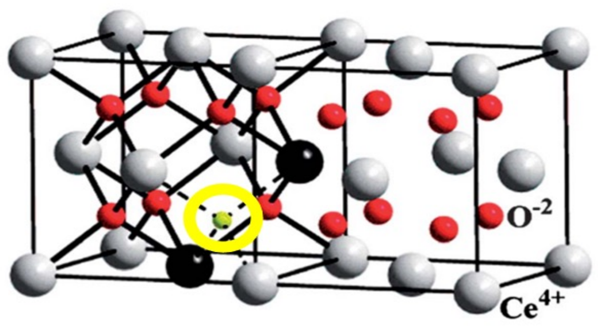
BACKGROUND

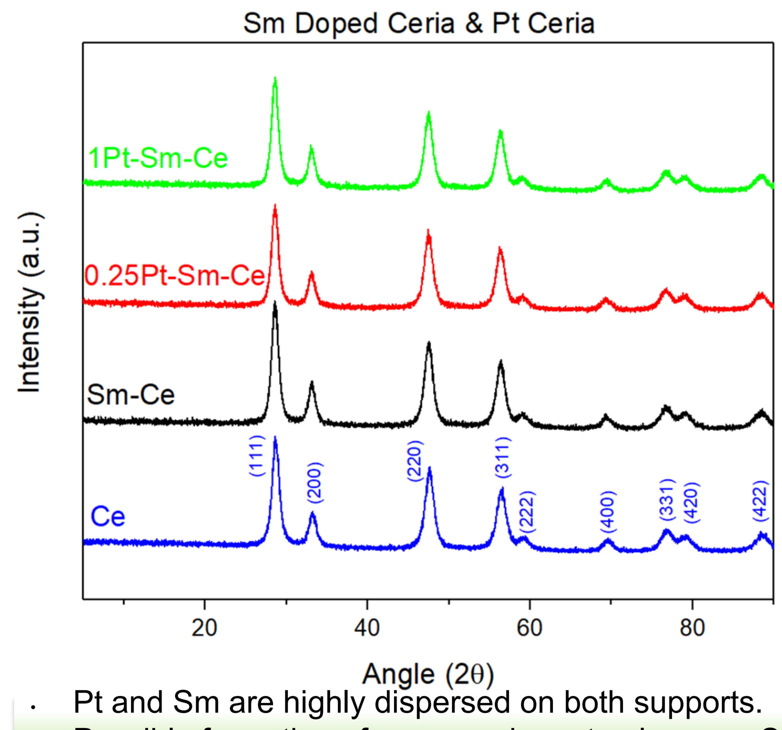
- Ceria (cerium oxide) promotes storage and release independent of reaction conditions. The Ce3+/4+ fluctuation creates oxygen vacancies and defects to influence storage and release mechanisms.
- Ceria is well established as a lean NOx trap (LNT) catalyst.
- The critical redox property can be affected by doping to modify the interaction cerium has with oxygen within the structure of the catalyst.
- Rare-Earth doping can induce structural defects to alter the catalytic performance of the catalyst.
- The main objective of this project is the investigation of this **"structure-performance"** relationship of ceria and how this changes upon dopants and PGM addition.

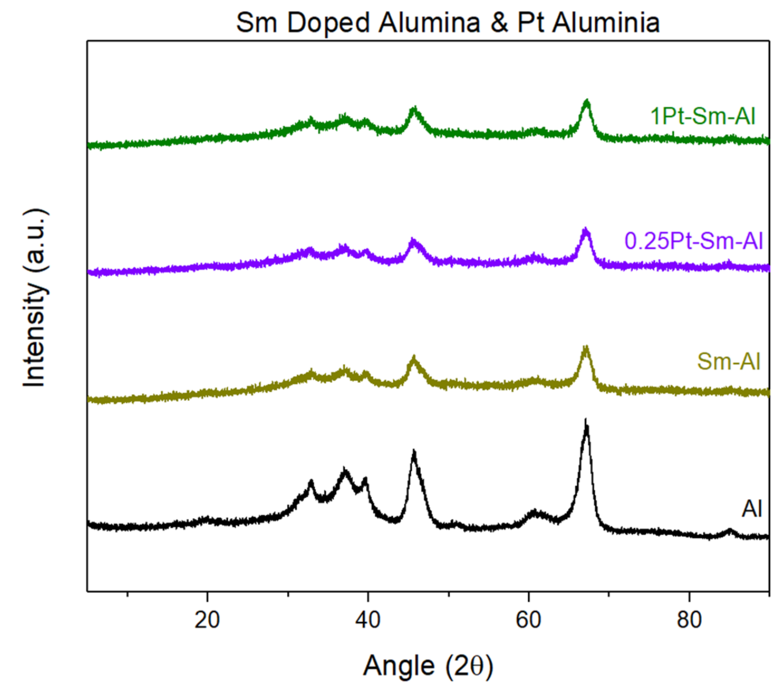




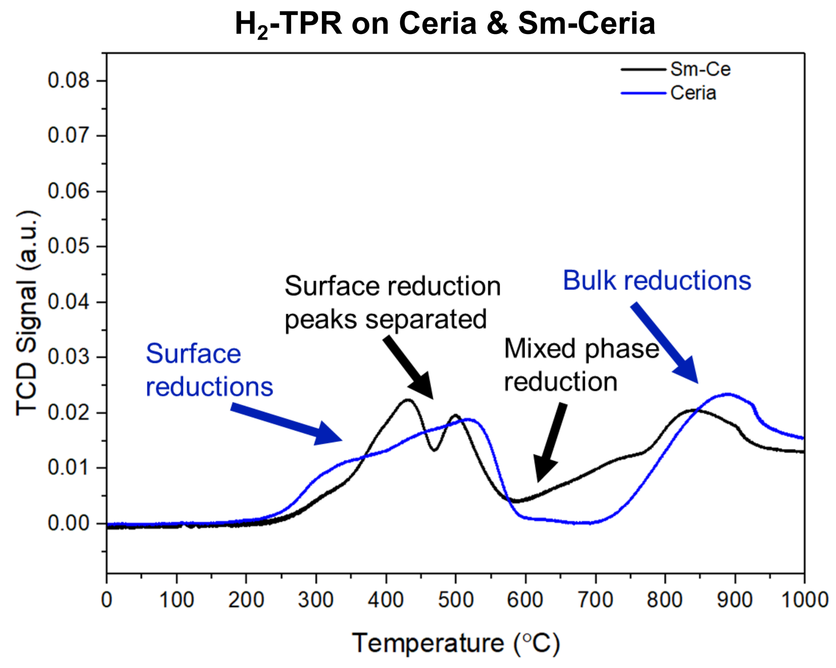


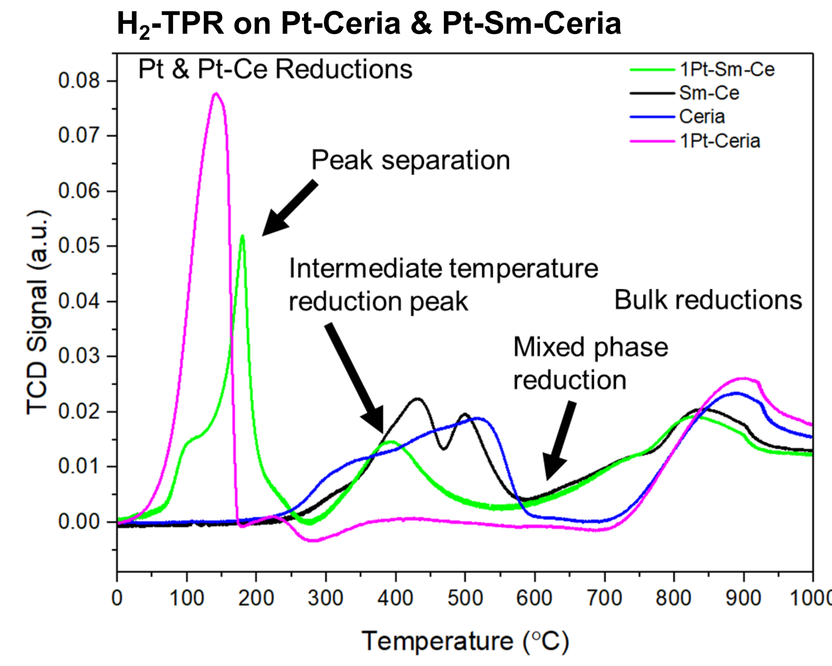
CATALYST CHARACTERISATION: XRD AND TPR





- Pt and Sm are highly dispersed on both supports.
- Possible formation of an amorphous top layer on Sm-alumina as peaks appear reduced in size.





- Modification of surface Ceria reduction (peak separation).
- Change in bulk ceria reduction profile to include mixed phase reduction.

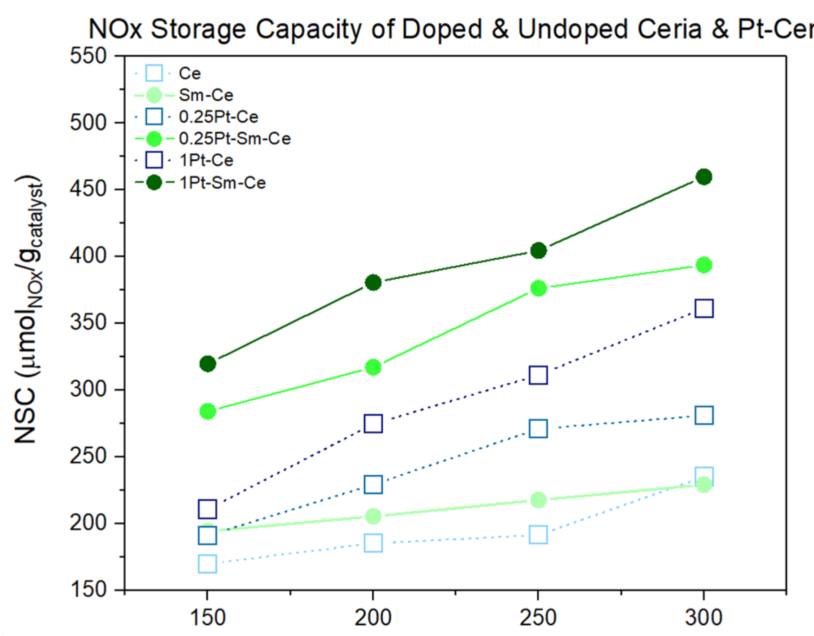
- Low temperature Pt peaks are no longer overlapped.
- Peak shift to higher temperature.
- Additional peak at intermediate temperature ~400ºC.

CATALYST PREPARATION & SYNTHESIS

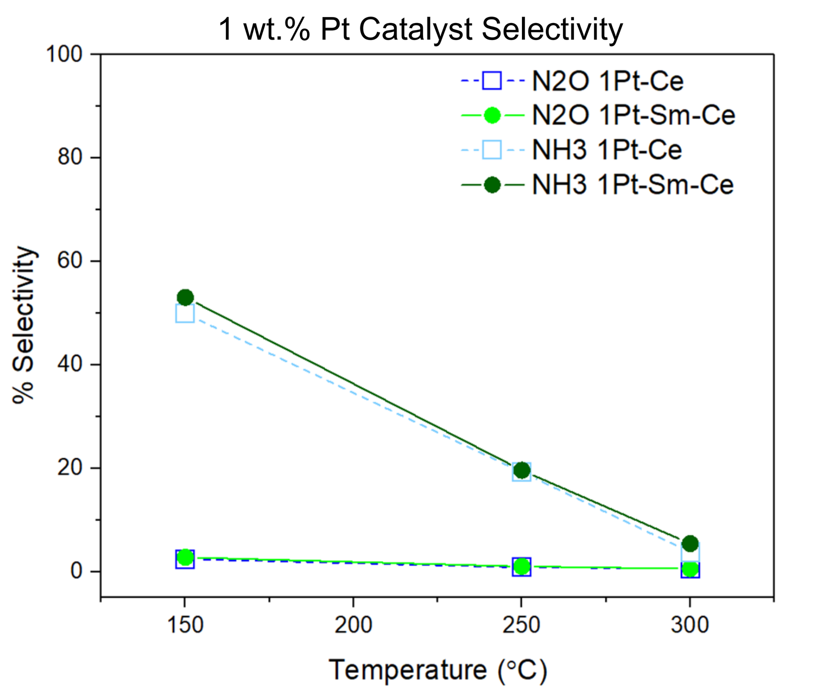
Catalyst Name	Wt.% Sm	Wt.% Pt	BET (m^2/g)
Ce	--	--	130.4
0.25Pt-Ce	--	0.25	131.7
1Pt-Ce	--	1	131.0
Sm-Ce	10	--	106.9
0.25Pt-Sm-Ce	10	0.25	108.9
1Pt-Sm-Ce	10	1	108.1
Sm-Al	10	--	122.6
0.25Pt-Sm-Al	10	0.25	118.5
1Pt-Sm-Al	10	1	118.5

Synthesis Method:
- Incipient wetness impregnation using dopant nitrates.
- Incipient wetness impregnation using platinum salt on ceria and doped ceria supports.
- All dried @ 110 °C for 8hrs and calcined @ 500 °C for 2 hrs.

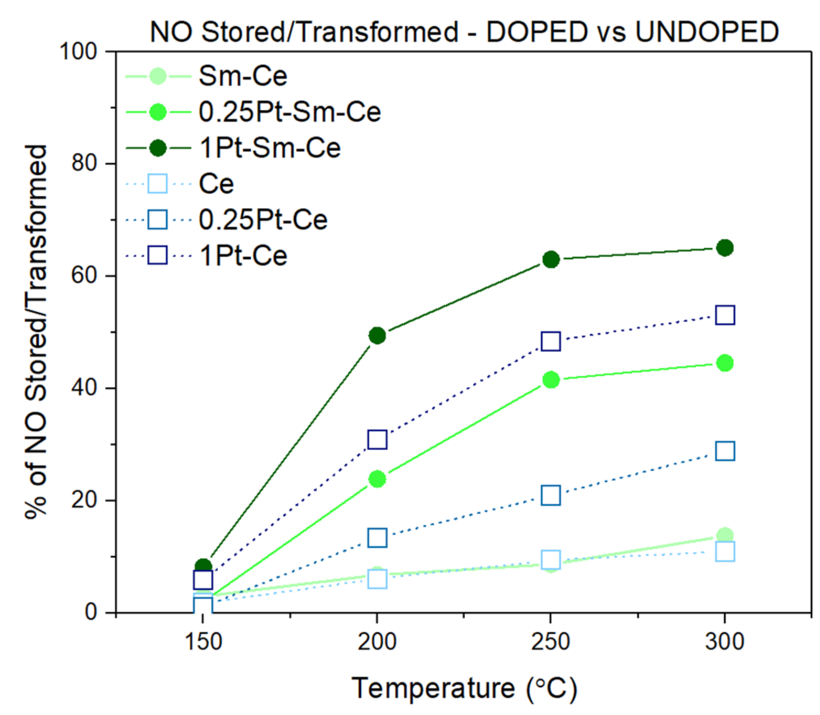
CATALYTIC PERFORMANCE TESTING

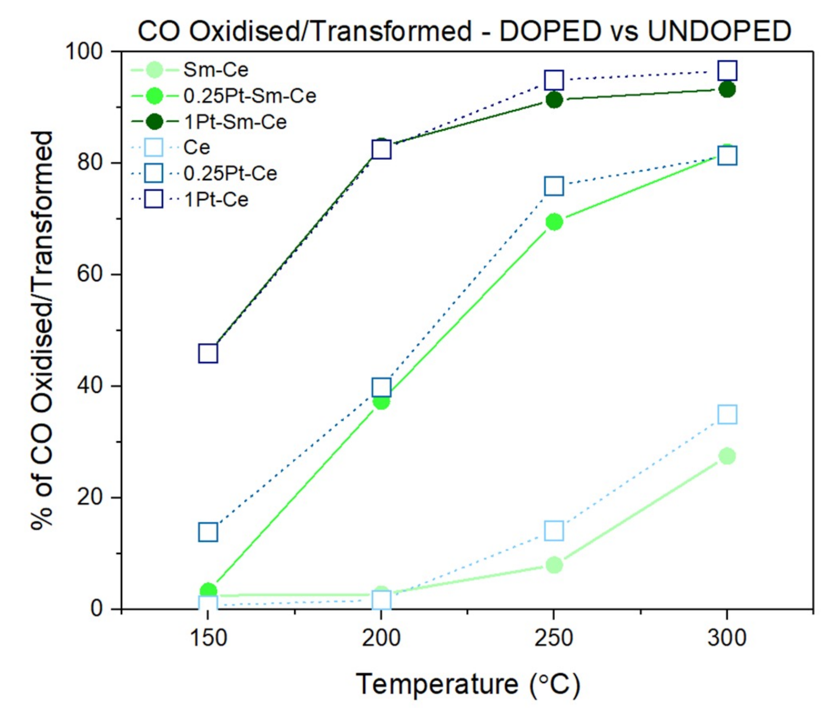


- NSC increased with Pt loading.
- NSC increased with Sm addition.
- Synergistic effect of dopant and Pt: highest NSC on 1.0Pt-Sm-Ce.

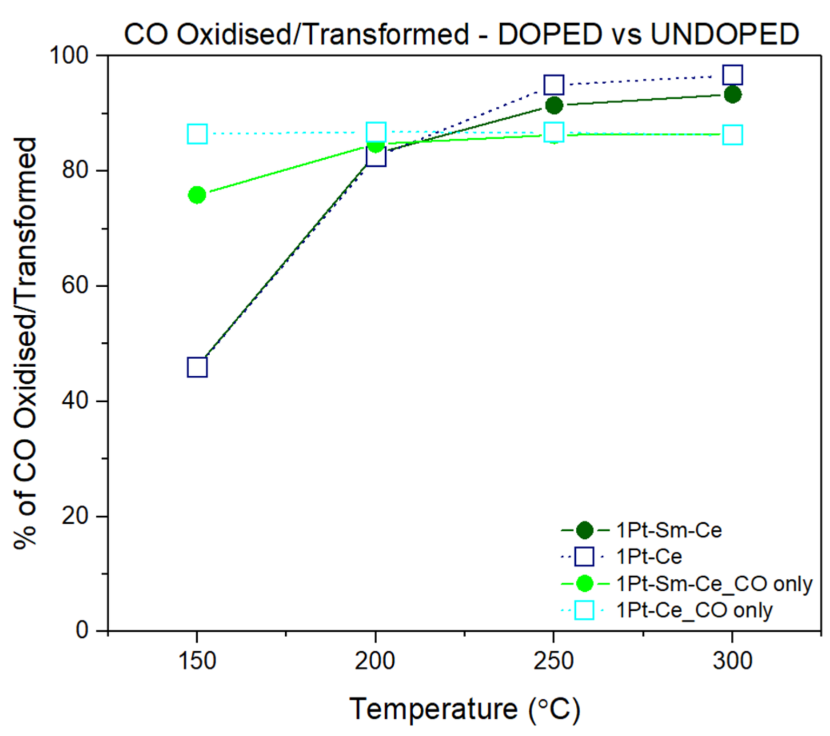


- Presence of Sm does not affect the selectivity to products of the 1wt.% Pt-Ceria catalyst.



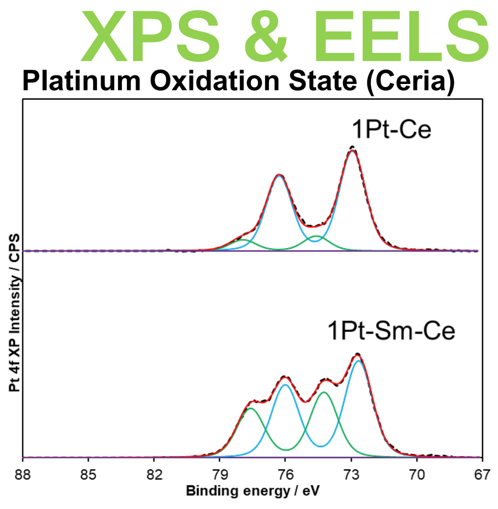


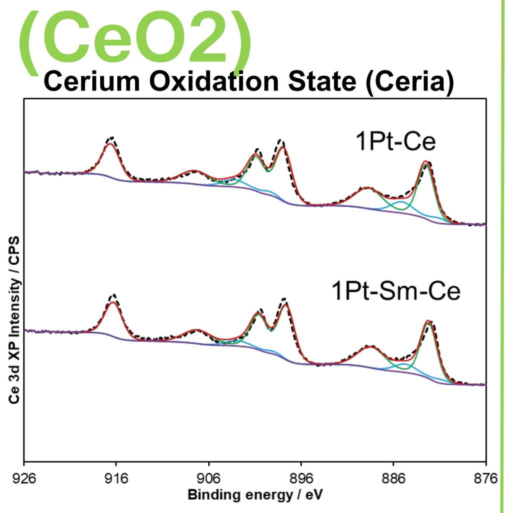
- NSC increases with Pt loading.
- Effect of dopant on Pt-Ceria catalyst enhances the NSC at all temperatures.
- Presence of Sm on Pt-Ceria does not have a significant effect on CO oxidation.



- Presence of C_3H_6 in exhaust mixture reduces CO oxidation potential at low temperatures.
- Presence of Sm slightly reduces amount of CO stored on the catalyst at low temperature.

XPS & EELS (CeO2)



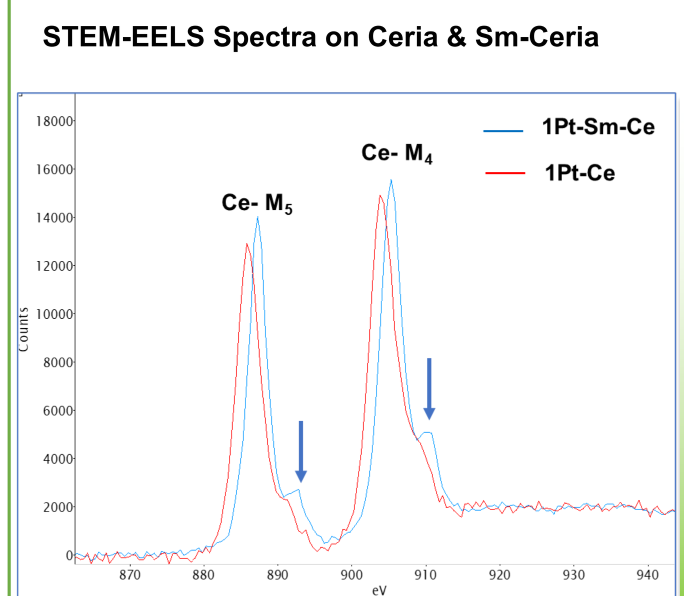


Catalyst	Pt^{2+}	Pt^{4+}
Ce	--	--
Sm-Ce	--	--
0.25Pt-Ce	88.1	11.9
0.25Pt-Sm-Ce	63.6	36.4
1Pt-Ce	87.0	13.0
1Pt-Sm-Ce	59.7	40.3

Catalyst	Ce^{3+}	Ce^{4+}
Ce	19.6	80.4
Sm-Ce	13.9	86.1
0.25Pt-Ce	14.5	85.5
0.25Pt-Sm-Ce	10.6	89.4
1Pt-Ce	12.5	87.5
1Pt-Sm-Ce	9.5	90.5

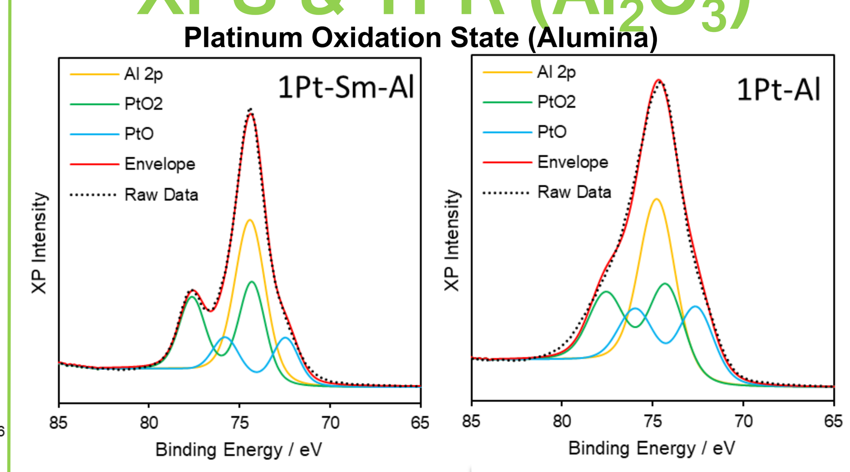
- Ce and Pt oxide are at higher oxidation states when Sm is present.

STEM-EELS Spectra on Ceria & Sm-Ceria



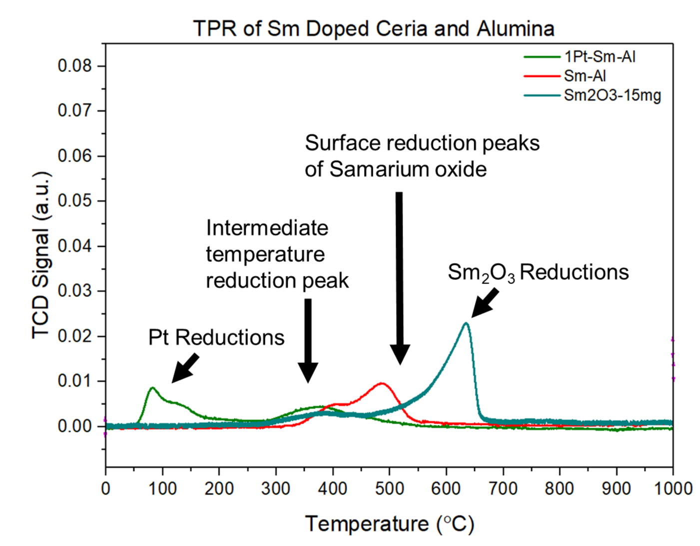
EELS:
- Ce-M_5 and Ce-M_4 peaks shift toward higher energy.
- The shoulders (blue arrows), are an indication of the change in oxidation state.

XPS & TPR (Al_2O_3)



Catalyst	Pt^{2+}	Pt^{4+}
0.25Pt-Al	56.3	43.7
0.25Pt-Sm-Al	31.6	68.3
1Pt-Al	47.8	52.3
1Pt-Sm-Al	32.5	67.5

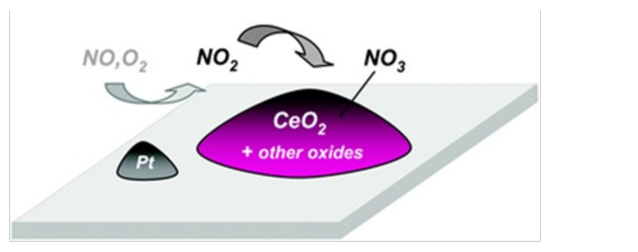
- Pt oxide is at higher oxidation states when Sm is present.



- Similar surface reduction profile for ceria and alumina due to Sm addition.
- Less intense Pt reduction peak for alumina catalyst compared to ceria.
- Similar intermediate temperature peak ~ 400˚C with Pt addition to doped support.

CONCLUSIONS

Effect of Sm Dopant on Ceria:
- Pt and Sm dopant were well dispersed **(XRD)**.
- Higher total H_2 consumption and change in reduction profile. **(TPR)**.
- Altered reducibility due to the combination of reducible ceria and samarium oxide.
- Higher oxidation states of Ce and Pt **(XPS)**.
- Oxygen donation happens more readily = higher NOx storage capacity.
- Increases NSC, as a result of higher oxidising ability.
- Increased availability for sites to store NOx species without significant changes in product selectivity.
- Synergistic effects observed between Pt and dopant from NSC and activity studies.
- Lowers the CO oxidation at low temperature when propylene is not present.
- More effective low temperature Lean NOx Trap catalyst.



Nitrite Formation: $Ce^{4+} - O^{2-} + NO \rightarrow Ce^{3+} - NO_2^-$

Nitrate Formation: $Ce^{4+} - NO_2^- + Ce^{4+} - O^{\bullet} \rightarrow Ce^{4+} - NO_3^- + Ce^{3+} - \square$

Activated surface oxygen = $O^{\bullet}$

Surface oxygen vacancy = $\square$

Effect of Sm Dopant on Alumina:
- Pt and Sm highly dispersed **(XRD)**.
- Amorphous layer formation on support **(XRD)**.
- Bare support becomes reducible = Higher total H_2 consumption **(TPR)**.
- Pt oxidation state changes to become more oxidised **(XPS)**.

REFERENCES & ACKNOWLEDGEMENTS

SuperSTEM Daresbury: Demie Kepaptsoglou, Quentin M. Ramasse, Miryam Arredondo-Arechavala, Praveen Kumar

diamond: Mark Isaacs

]AV: Presentation "Real Driving Emissions—New Requirement and solutions for LD and HD vehicles", Goteborg, Nov 2016
]https://en.wikipedia.org/wiki/European_emission_standards#cite_note-:1-27
]https://www.greencarcongress.com/2013/03/xom-20130309.html
]R. Kopelent et al. Catalytically Active and Spectator Ce 3+ in ceria-Supported Metal Catalysts
[5] M. Stoian et al. Catalysts2021,11, 427
[6] S.A. Kondrat et al. Topics in Catalysis (2019) 62:1218-1227
[7] Catalysis Today 127 (2007) 230-237
[8] ACS Catal 2018, 8, 4354-4363
[9] Primo et al. Journal of American Chemical Society. 2011; 133: 6930-6933.
[10] A.I.Y. Tok et al. Materials Science and Engineering A 466 (2007) 233-299
[11] M Crocker et al. Emiss. Control Sci. Technol. (2017) 3:59-72
[12] Worawat Wattanathana et al. Ceramics International 43 (2017) 9823-9830
[13] Appl. Catal. B Environ., vol. 237, no. 2, pp. 1066-1081, 2018