Nano Innovation 2024 Conference & Exhibition — Rome, 9-13 September

Dry Reforming of Methane on Pt/CeO_2 catalyst starting from a recycled solution containing precious metals

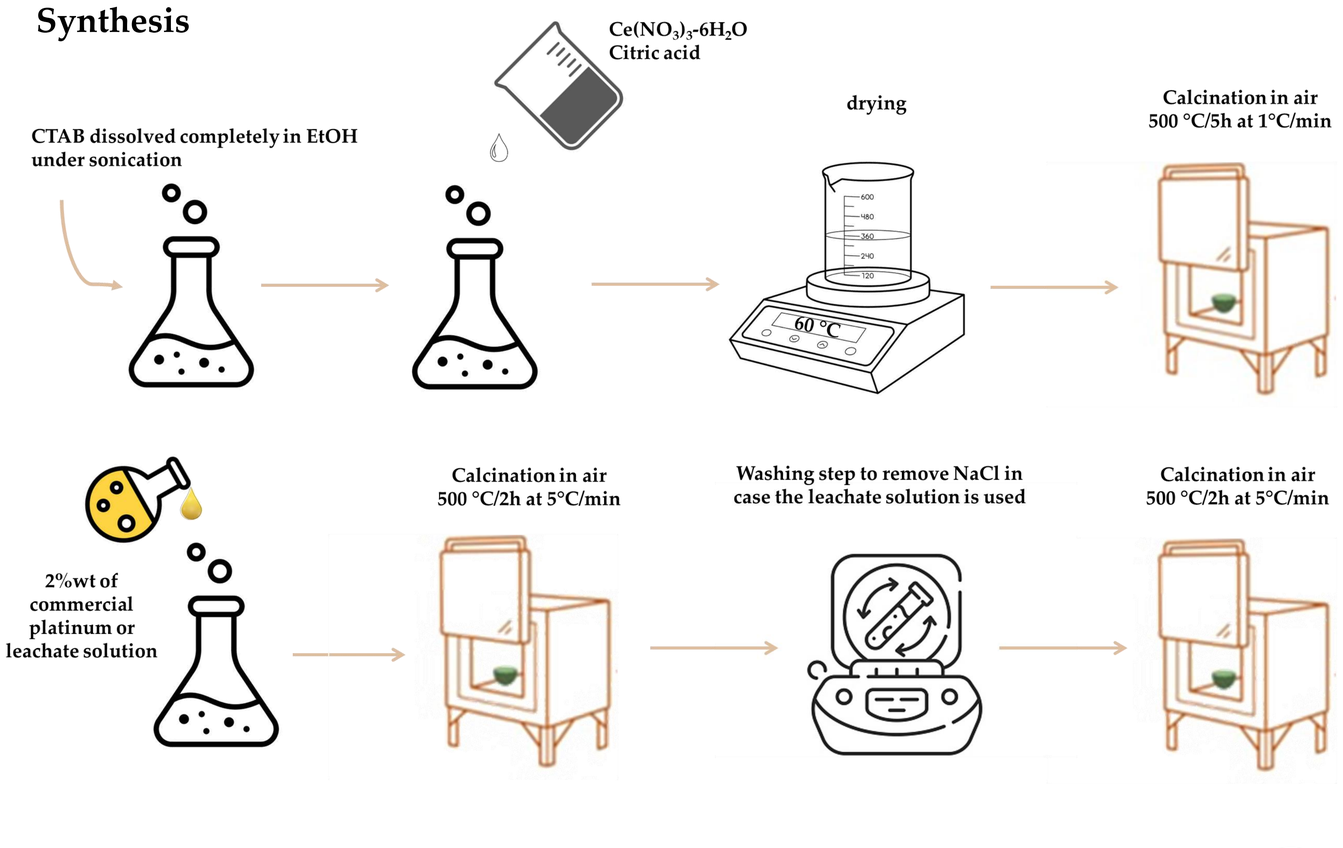
A. Varotto[1,2,*], U. P. Laverdura[1], F. Bozza[1] , A. Moschovi[3] , I. Yakoumis[3] , M. Feroci[2] and M. L. Grilli[1,*]

[1] Italian National Agency for New Technologies, Energy and Sustainable Economic Development-ENEA, Energy Technologies and Renewable Sources Department, Via Anguillarese 301, 00123 Rome, Italy; [2] Dept. Fundamental and Applied Sciences for Engineering (SBAI), Sapienza University of Rome, via Castro Laurenziano, 7, 00161 Rome, Italy ; [3] Monolithos Catalysts & Recycling Ltd., 83 Vrilissou, 11476 Athens, Greece

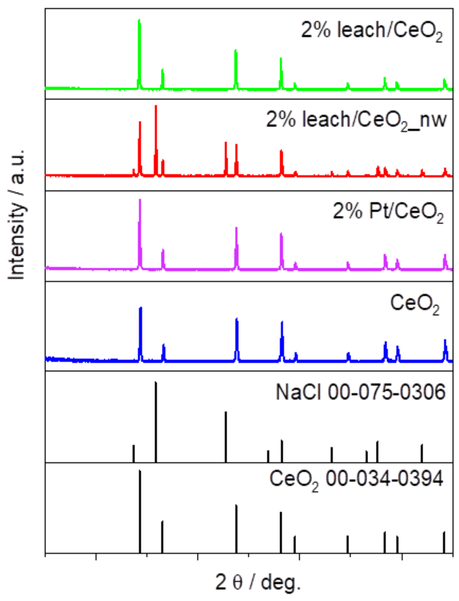
[*] alessio.varotto@uniroma1.it,marialuisa.grilli@enea.it

Due to the continuous emissions of greenhouse gases (GHG) in the atmosphere because of anthropogenic activities, it is very important to reduce their concentration using several approaches. One of the best ways is to use the dry reforming of methane (DRM) reaction that consumes GHG to obtain syngas, a mixture of H_2 and CO. DRM is promoted using catalysts, often based on Pt or other critical raw materials (CRMs) for EU [1] . To face the CRM issue, we fabricated Pt/CeO_2 catalysts, with 2%wt of Pt by direct impregnation of the CeO_2 support with the leachate solution of Spent Automotive Diesel Oxidation Catalysts submitted to a mild hydrometallurgical recycling process [2] , which contains H_2PtCl_6 as Pt precursors. A synthetic leachate solution was also prepared for comparison. CeO_2 has been chosen because of its widely accepted positive influence on the conversion of the products [3] . The results obtained from the catalytic tests were encouraging, as shown in a figure below, where the conversions of CO_2 and CH_4 are reported for the Pt/CeO_2 catalysts obtained from commercial Pt precursors. The ratio of H_2/CO was 0,9 at T=850 °C. Lower conversion efficiency was found in the case of the real leachate solution; 0,5 when the powder is not washed (2%leach/CeO_2_nw) and 0,7 when the powder is washed (2%leach/CeO_2_w). Catalysts were characterized by several techniques.

Synthesis

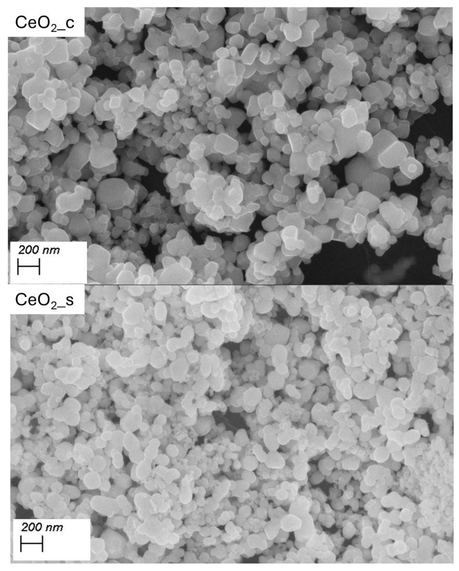


XRD patterns



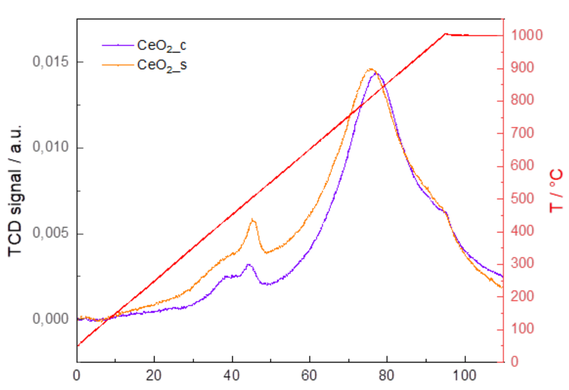
There are only the XRD patterns related to the commercial CeO_2, but there is not a difference in XRD patterns if the commercial or the synthesized CeO_2 is used

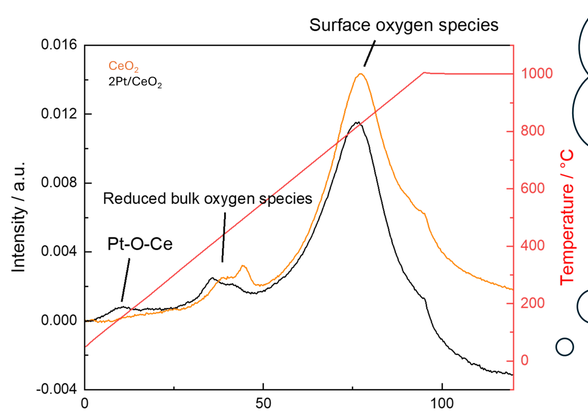
SEM



The commercial CeO_2 powder is formed by round shape particles of uniform dimension of less than 200 nm, while the syntesised one is characterized by less uniform sized particles some round and other rectangular shaped.

Temperature Programmed Reduction (TPR)





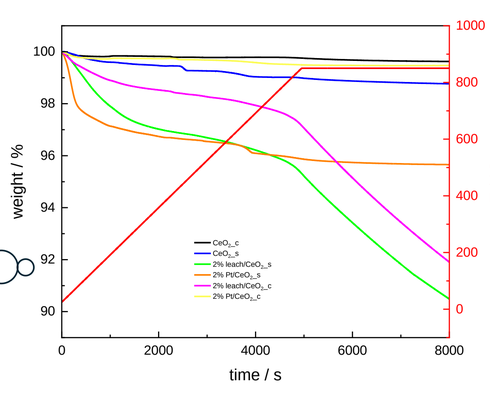
Once platinum is deposited on ceria, peaks are shifted to lower temperatures, due to the weakening of the bond of Ce with oxygen

XRF and ICP analysis have been conducted at Monolithos, in Greece.

Negligible loss at around 100°C due to the evaporation of water. If the leachate solution is used there is a weight loss at around 850°C probably due to the impurities.

Sample name	BET surface area m^2*g^{-1}	Pore volume cm^3*g^{-1}	Average pore diameter nm
2%Pt/CeO_2	6,95	0,028	16,3
2%leach/CeO_2_nw	15,97	0,051	12,7
2%leach/CeO_2	6,89	0,035	20,3
CeO_2	3,37	0,016	19,5

ThermoGravimetric Analysis (TGA)



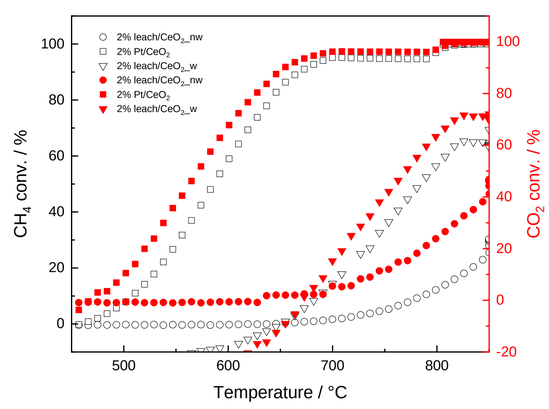
$$2Ce^{4+} + H_2 \rightarrow 2Ce^{3+} \qquad Pt^{4+} + 2H_2 \rightarrow Pt$$

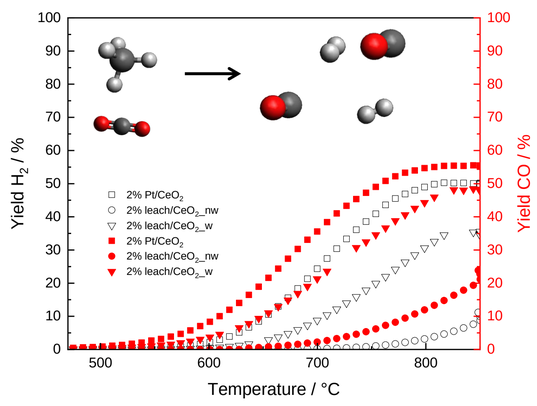
XRF analysis

ICP-OES

Sample	Pt		Ce		Pt		Ce	
	mg/kg_{cat}	%	mg/kg_{cat}	%	mg/kg_{cat}	%	mg/kg_{cat}	%
2%leach/CeO_2_c	6986	0.70	193800	19.38	3301	0.33	13880	1.39
2%leach/CeO_2_s	14176	1.42	341100	34.11	9123	0.91	372330	37.23

Catalytic tests





Conclusions

In this study it has been reported a successful attempt of using the leachate solution of spent diesel oxidation autocatalysts containing Pt precursors for fabricating Pt/CeO_2 catalysts for the dry reforming of methane reaction. Crystallographic peaks of the synthesized CeO_2 and of the 2%Pt/CeO_2 catalyst are associated to the cubic face-centered phase structure of CeO_2 fluorite. For catalysts obtained from the leachate solution, additional peaks are present in the XRD diffractograms due to impurities, including NaCl. The DRM test shows a H_2/CO of 0,9 at 850 °C for 2%Pt/CeO_2 catalyst and almost 0,5 in case of the 2%Pt leach/CeO_2_nw and 0,7 in case of the 2%leach/CeO_2_w Difference in catalytic activity can be attributed both to a different dispersion of the metal on the surface of the CeO_2 support and to the impurities present in the starting leachate solution. Future studies will be devoted to the increase of the surface area of the support to improve active metals' dispersion. The leachate solution of spent gasoline autocatalysts containing besides Pt, also Pd and Rh, will be also investigated to infer the contribution of the other precious metals to the catalytic performances.

SCAN ME

Acknowledgments: This research is partially funded by the European Union's Horizon 2020 research and innovation programme under the Marie- Skłodowska-Curie Grant Agreement No. 101007669, Chemistry of Platinum Group Metals-CHemPGM. Authors acknowledge also the support from Regione Lazio for the fellowship n° 22066DP000000028 and from MASE for project PNRR, «Investimento 3.5 Ricerca e Sviluppo sull'Idrogeno» and Electric System Research Programme, Project 1.6, «Energy Efficiency of Industrial Products and Processes», Work Package 4, «Production of green H_2 from biomass gasification using efficient CO_2 capture, storage and reuse process», financed by the Italian Ministry for the Environment and Energy Security.