Ion beam surface engineering for highly active nanocatalysts

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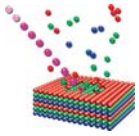
Ion Beam Bombardment

application to Diesel Oxidation catalysts (DOC)



- fragment and disperse the metal in the form of nanoparticles with well-defined characteristics
- enhance the stability and the resistance to aging
- significant reduction of the operating temperature

Ion beam implantor

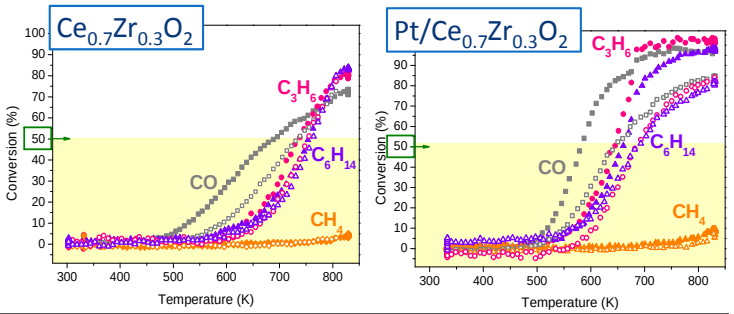
N^+ ion beam at 52.5 keV current density of 3.75 μA/cm²

Materials

- $Ce_{0.7}Zr_{0.3}O_2$
- 1%Pt -Pd/$Ce_{0.7}Zr_{0.3}O_2$

TPO Temperature Programmed Oxidation

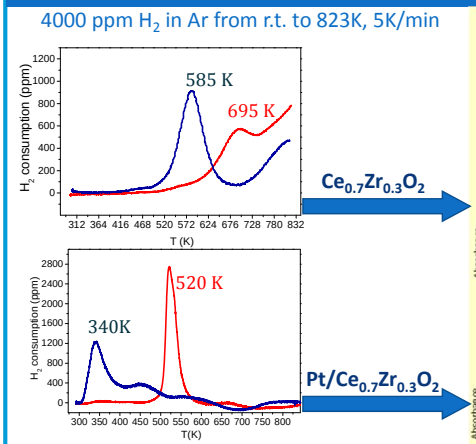
10 % O_2, 2000 ppm CO, CH_4, C_3H_6, C_6H_{14} in Ar from r.t. to 823K, 2K/min

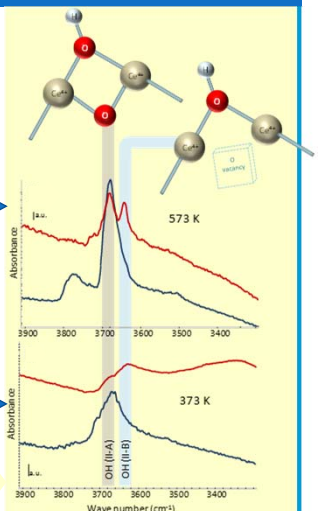


	$Ce_{0.7}Zr_{0.3}O_2$		$Pt/Ce_{0.7}Zr_{0.3}$	
	non treated	bombarded	non treated	bombarded
T_{50} CO (K)	739	696	640	579
T_{50} C_3H_6 (K)	756	738	682	645
T_{50} C_6H_{14} (K)	764	754	693	660
Conversion % CH_4 @550°C	4.2	4.9	8.4	9.4

TPR Temperature Programmed Reduction

4000 ppm H_2 in Ar from r.t. to 823K, 5K/min



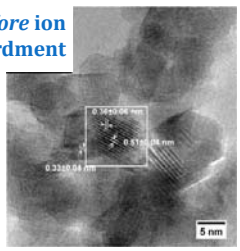


spectra taken after H_2 reduction (before evacuation)

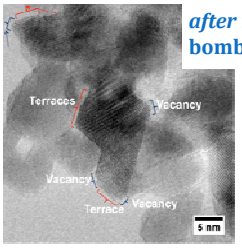
IN SITU FT-IR experiments
hydroxyl species vibrational modes ν(OH) used as probe of the surface oxidation state

HRTEM $Pt/Ce_{0.7}Zr_{0.3}O_2$

***before* ion bombardment**



***after* ion bombardment**

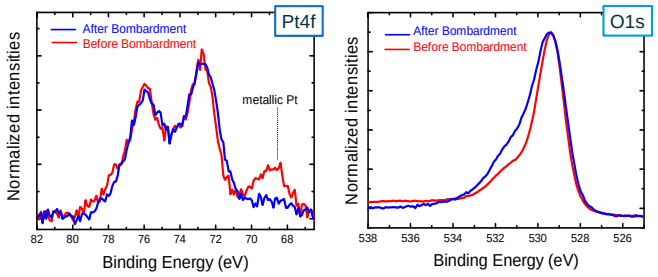


- highly faceted **nanoparticles** before and after the ion treatment
- upon ion bombardment: increment on the surface of defective units. Atomic **vacancies** are visible at the corner of the nanoparticles and extended **terraces**

the presence of **vacancies** and **terraces** is one of the driving causes for the enhanced catalytic activity of nanoscale systems

XPS $Pt/Ce_{0.7}Zr_{0.3}O_2$

EFFECT ON THE ELECTRONIC PROPERTIES



- heterogeneous **charge effect** on catalyst powder after bombardment under the X-Ray excitation
- the global composition of the catalyst is maintained and **novel structure** changes of the active sites.
- the oxygen peak is modified in its high binding energy part

oxygen chemical environment is modified by the bombardment

Conclusions: Effects of Ion Bombardment

MICROSCOPIC

- Formation of **morphologic and structural defects on the surface** upon bombardment (vacancies & terraces)
- Creation of preferential absorption sites and routes for oxygen (increasing the **oxygen activation and mobility**)
- Modification of the local **electronic structure of the sites** (localised charges), affecting both metal and support

- **Enhanced reducibility** of both CZ and Pt/CZ bombarded materials
- **Enhanced catalytic activity** of nanoscale systems
- Better grafting of metal particles, i.e. better **resistance to ageing**

MACROSCOPIC

Jain I.P., Agarwal G., *Surf. Sci. Rep.*66, 77 (2011).
Busardo D., Guernalec F., Method for the ion beam treatment of a metal layer deposited on a substrate WO 2010092297 A1(2010)
Daturi M, Finocchio E., Binet C., Lavallay J.C., Fally F. and Perrichon V., *J. Phys. Chem. B* 103(23), 4884 (1999)