DESIGN OF ACTIVE AND STABLE Au CATALYSTS FOR H_2 PURIFICATION

GOLD2009

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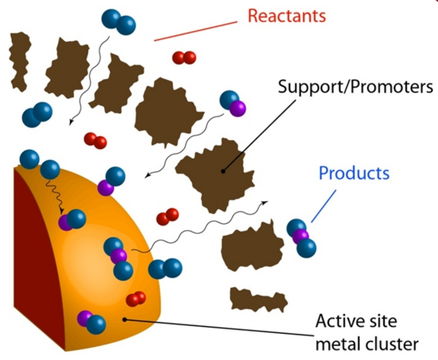
INTRODUCTION

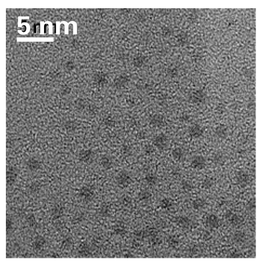
- H_2, in combination with efficient Fuel Cells (FCs), is an attractive energy vector for the future
- most of the H_2-based Fuel Cells, such as Proton-Exchange Membrane (PEM) FCs, still contains catalysts which are sensitive to CO poisoning
- PReferential OXidation (PROX) of CO in the presence of H_2 is an advantageous purification process: $CO + 1/2O_2$ (in H_2) = CO_2
- Au/CeO_2 systems are excellent candidates, joining Au selectivity and CeO_2 oxidation capability
- improvement in activity, selectivity and thermal stability are objects of today's research

AIM OF THE WORK

Design, preparation and characterization of highly active and thermally stable Au catalysts for PROX through **the embedding approach** [1,2]



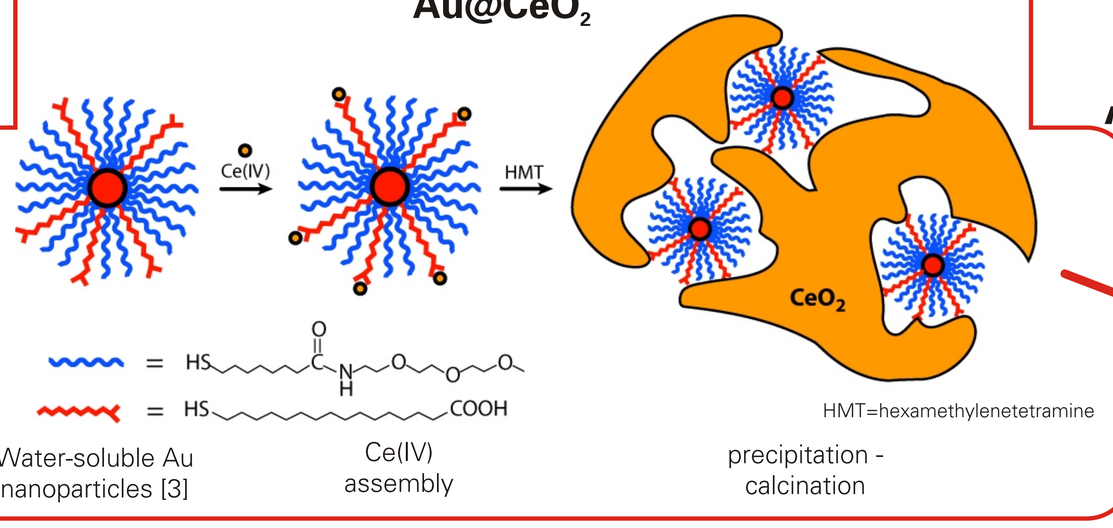
" stabilization against sintering by embedding the active phase inside the support "



HRTEM image of Au nanoparticles

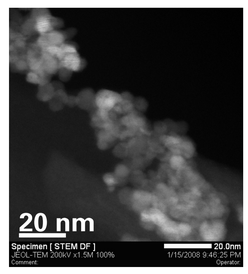
Design

$Au@CeO_2$



Water-soluble Au nanoparticles [3] → Ce(IV) assembly → precipitation - calcination

HMT=hexamethylenetetramine



HAADF-STEM image of calcined $Au@CeO_2$

Au loading: 1 or 3 wt. %

Reference samples: Au/CeO_2 DPU

by Deposition-Precipitation with Urea [4]

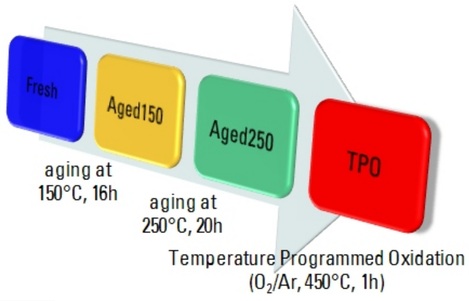
@: embedded catalysts

DPU: Deposition-Precipitation Urea catalysts

CATALYTIC ACTIVITY

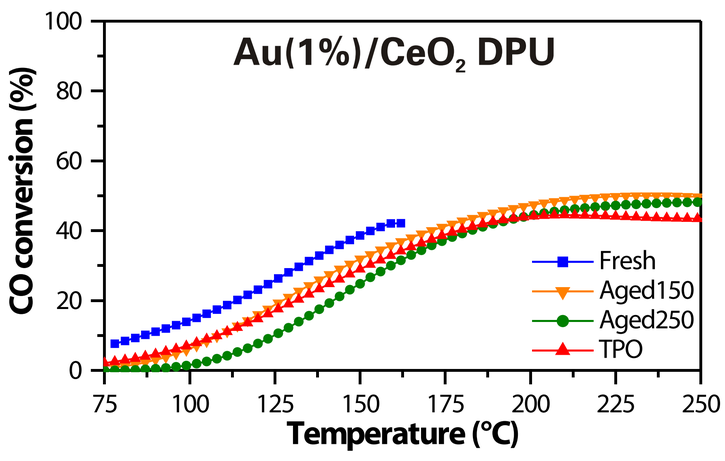
Full PROX mixture: CO (1%) + O_2 (1%) + H_2 (47.5%) + CO_2 (17.5%) + H_2O (5%) in Ar

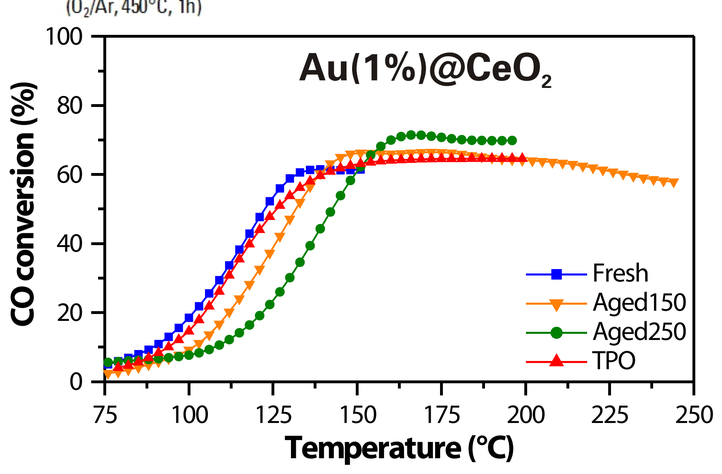
GHSV ~ 75000 mL g^{-1} h^{-1}

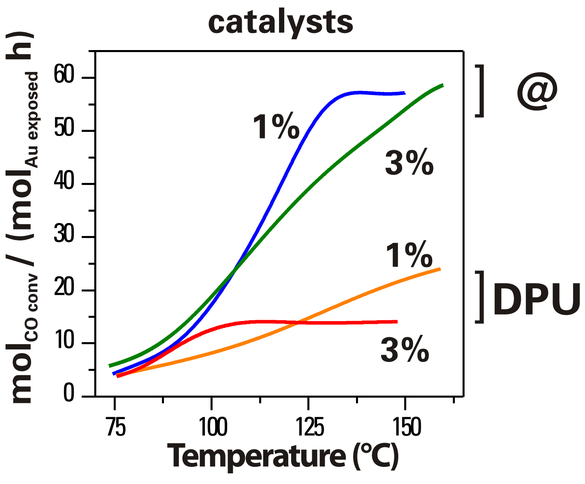


$$CO + 1/2O_2 \xrightarrow{H_2} CO_2$$

aging protocol + mild oxidative regeneration







- @ samples at least **4 times more active** than traditional DPU catalysts
- activity **completely restored** (blue and red curves) after aging/regeneration for 1 % @ sample

CHARACTERIZATION

CO Chemisorption

Sample	Accessible Au*		
	Fresh Catalysts	Aged Catalysts	After TPO Catalysts
$Au(1\%)@CeO_2$	31%	-	-
$Au(1\%)/CeO_2$-DPU	51%	-	-
$Au(3\%)@CeO_2$	11%	7%	11%
$Au(3\%)/CeO_2$-DPU	41%	11%	34%

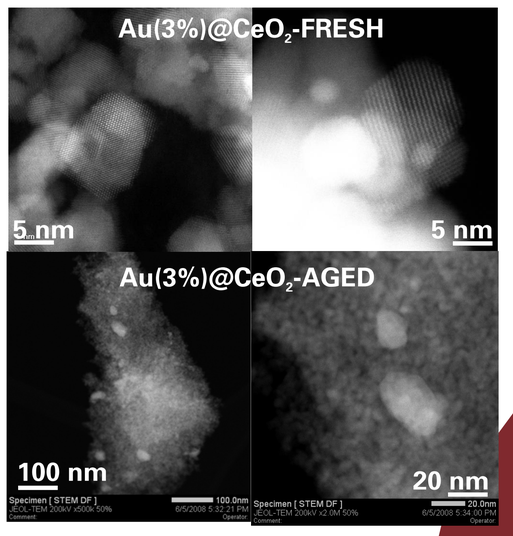
* Determined according to the protocol described in [5].

EXAFS results

Sample	Au particle diameter (nm)*	
	Fresh Catalysts	Aged Catalysts
$Au(1\%)@CeO_2$	0.9	1.0
$Au(1\%)/CeO_2$-DPU	2.0	2.3
$Au(3\%)@CeO_2$	1.3	1.6
$Au(3\%)/CeO_2$-DPU	2.4	3.0

* Determined from the fitting of the first Au-Au contribution.

Advanced Electron Microscopy (HAADF-STEM)



- CO chemisorption and EXAFS confirm the occurrence of sintering in DPU samples
- EXAFS demonstrates that calcination does not increase the dimension of Au particles in @ samples
- Advanced TEM shows some big particles also in the 3 wt. % @ sample

CONCLUSIONS

- **highly active** and **thermally stable** Au catalysts with low Au loading (1 wt. %) have been prepared;
- the embedding approach is **promising** with room for **improvements**

REFERENCES

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