PROJECT 20: SUPPORTED METALS NANOPARTICLES AS CATALYST FOR THE PROX REACTION

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for Gas Innovation
cleaner energy for a sustainable future

V Workshop Interno RCGI
University of São Paulo, Brazil
21 – 22 AUG 2018

Why to study hydrogen purification?

Some hydrogen applications: ammonia synthesis and electric energy generation through polymer electrolyte membrane fuel cells (PEMFC)

Hydrogen production

methane steam reforming

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$$

→

water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Typical composition of the **effluent gas from the water gas shift reactor:**

about **1% or 10.000 ppm of CO in a large excess of H_2**

CO is a poison for the ammonia synthesis catalyst and PEMFC anode catalyst!

What is CO-PROX reaction?

The preferential oxidation of carbon monoxide (CO) with oxygen in hydrogen-rich mixtures

CO-PROX reaction: $CO + \frac{1}{2} O_2 + H_2 \leftrightarrow CO_2 + H_2$ (1)

CO Oxidation: $CO + \frac{1}{2} O_2 \leftrightarrow CO_2 + H_2$ (2)

H_2 Oxidation: $H_2 + \frac{1}{2} O_2 \leftrightarrow \xcancel{H_2O}$ (3)

PROX reaction is interesting for H_2 stream purification

Objectives

To perform **basic studies and technology** on nanostructured catalysts for PROX reaction

To obtain **catalysts more active and selectivity in the range 25 – 200 °C** and to understand the reaction mechanisms involved in this process

In our studies, **two parallel pathways will be followed**:

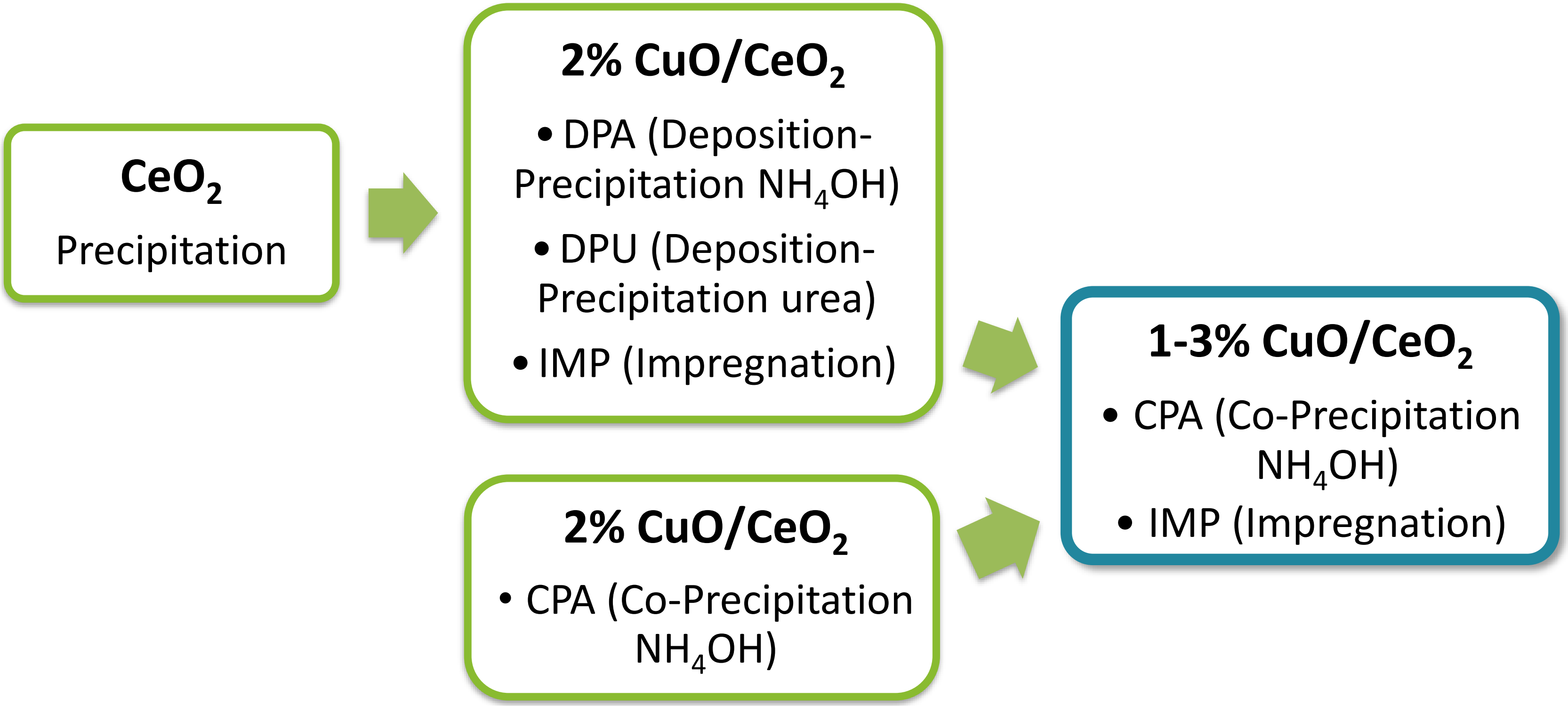
i - Bulk and supported **CuO/ceria compounds** will be prepared. **Pt and Au** will be incorporated as a promoter and the catalysts will be tested in the PROX reaction (**UFSCar and USP-Scarlos**)

ii – **Au and Pt nanoparticles supported on reducible metal oxides** will be prepared and tested in the PROX reaction (**IPEN-CNEN/SP**)

CuO/CeO_2 NANOPARTICLES

UFSCar-USP/SÃO CARLOS

Strategy – UFSCar-USP (São Carlos)



CeO_2

Precipitation

2% CuO/CeO_2

- DPA (Deposition-Precipitation NH_4OH)
- DPU (Deposition-Precipitation urea)
- IMP (Impregnation)

2% CuO/CeO_2

- CPA (Co-Precipitation NH_4OH)

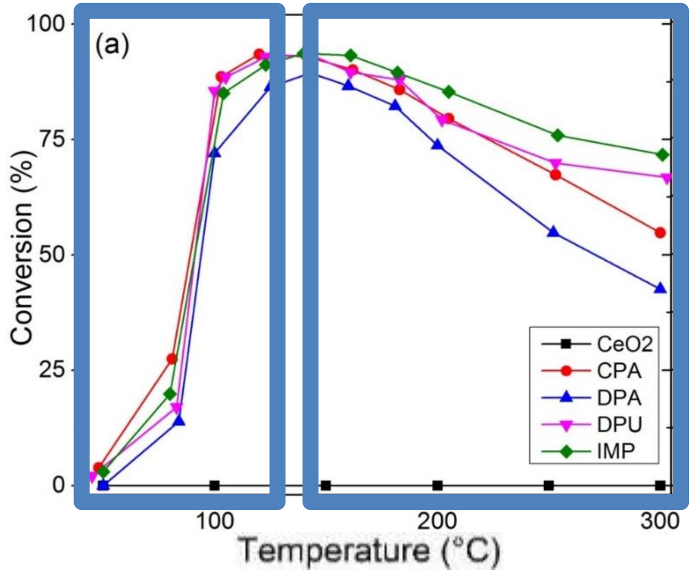
1-3% CuO/CeO_2

- CPA (Co-Precipitation NH_4OH)
- IMP (Impregnation)

Results - UFSCar-USP (São Carlos)

2% CuO/CeO_2: Preparation Method

- ✓ The preparation method influences directly:
  - $Cu\text{-}CeO_2$ interactions;
  - Catalytic performance.
- ✓ Best catalytic performance:



2CuCe-CPA:

- Highest H_2 consumption;
- Highest copper area;
- Smallest particle size;
- Best redox capacity.

2CuCe-IMP:

- Lowest H_2 consumption;
- Lowest copper area;
- Largest particle size.

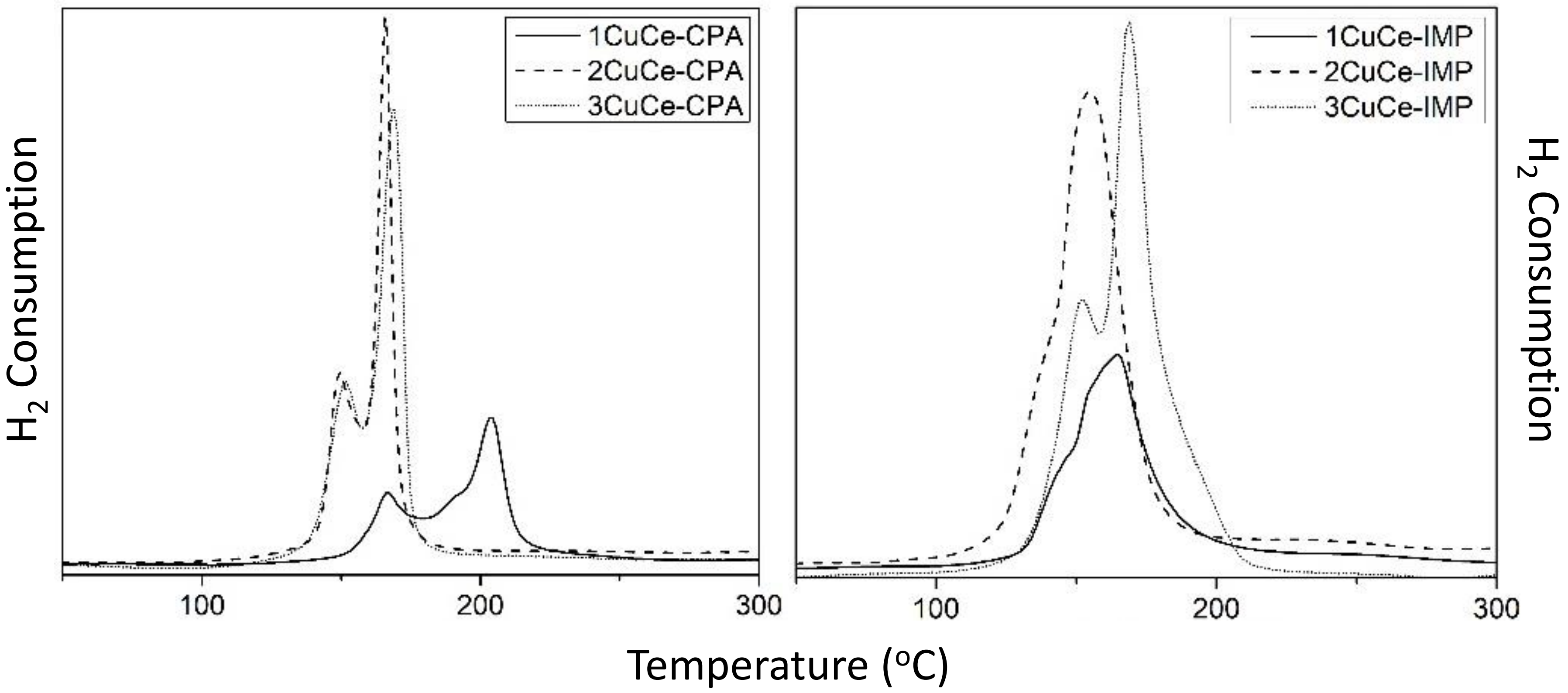
Results – UFSCar-USP (São Carlos)

1-3% CuO/CeO_2: Physicochemical Properties

	SEM-EDS	BET	TPR
	Cu loading (wt.%)	SA (m^2/g_{cat})	H_2 (µmol/g_{cat})
1CuCe-CPA	1.1	44	373
2CuCe-CPA	2.0	56	572
3CuCe-CPA	2.5	72	614
1CuCe-IMP	0.9	35	269
2CuCe-IMP	2.5	37	454
3CuCe-IMP	3.7	31	631

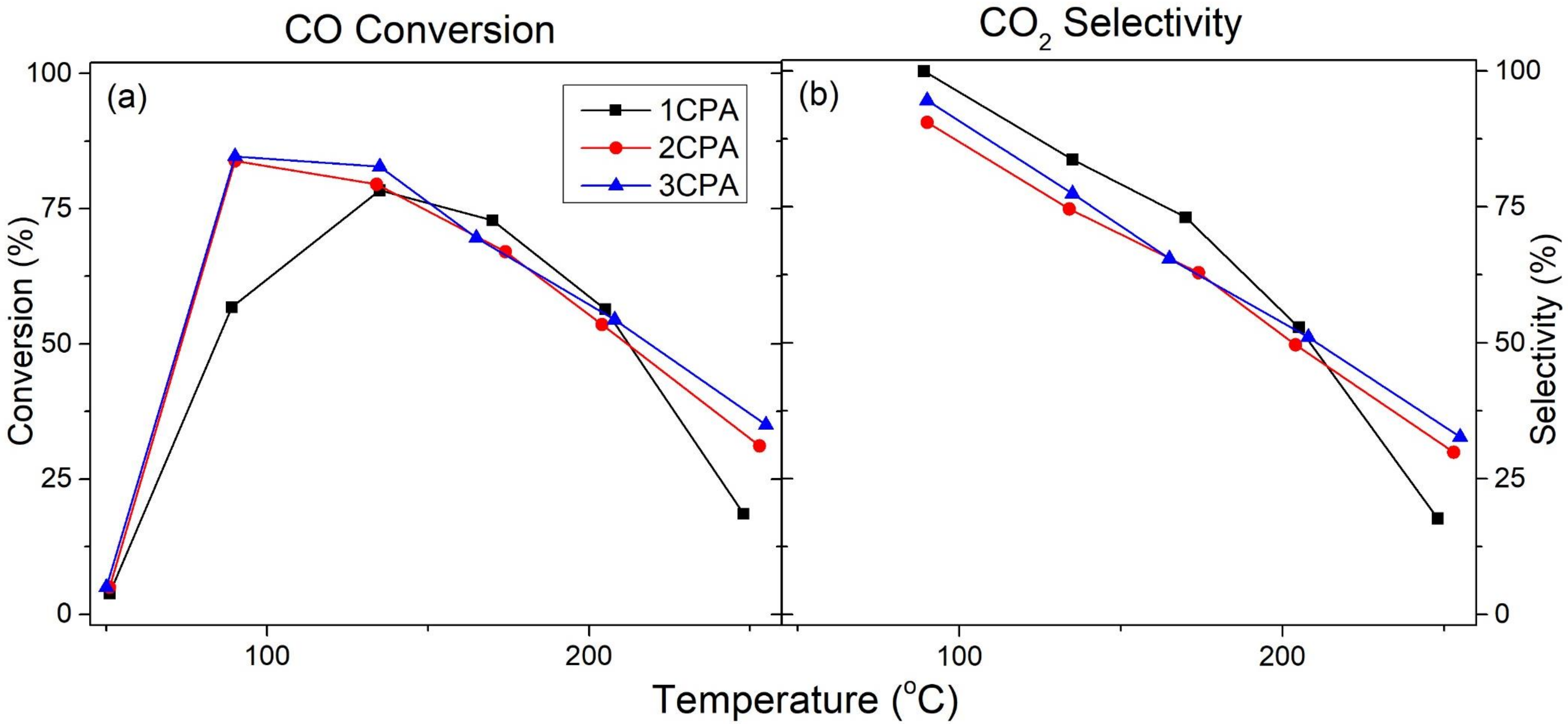
Results – UFSCar-USP (São Carlos)

1-3% CuO/CeO_2: TPR-H_2



Results – UFSCar-USP (São Carlos)

1-3% CuO/CeO$_2$: PROX reaction



Planned Activities - UFSCar-USP (São Carlos)

1-3% CuO/CeO_2:

Characterization the catalysts;

Reaction using IMP catalysts.

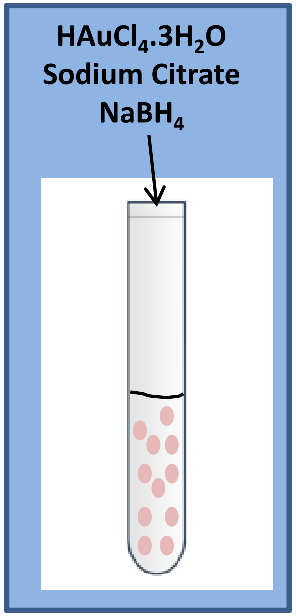
Addition of noble metals:

Analyze the impact of the noble metal addition on the performance of the best catalysts.

NOBLE METALS NANOPARTICLES

IPEN-CNEN/SP

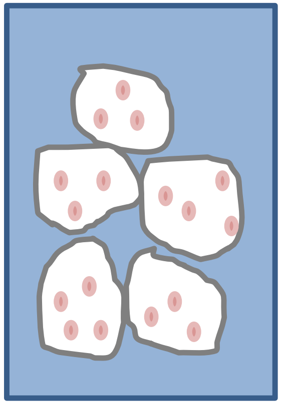
DEVELOPMENT OF A NEW METHOD OF SYNTHESIS TO PREPARE Au/TiO_2 CATALYST



$HAuCl_4.3H_2O$
Sodium Citrate
$NaBH_4$

Preformed Au Nanoparticles

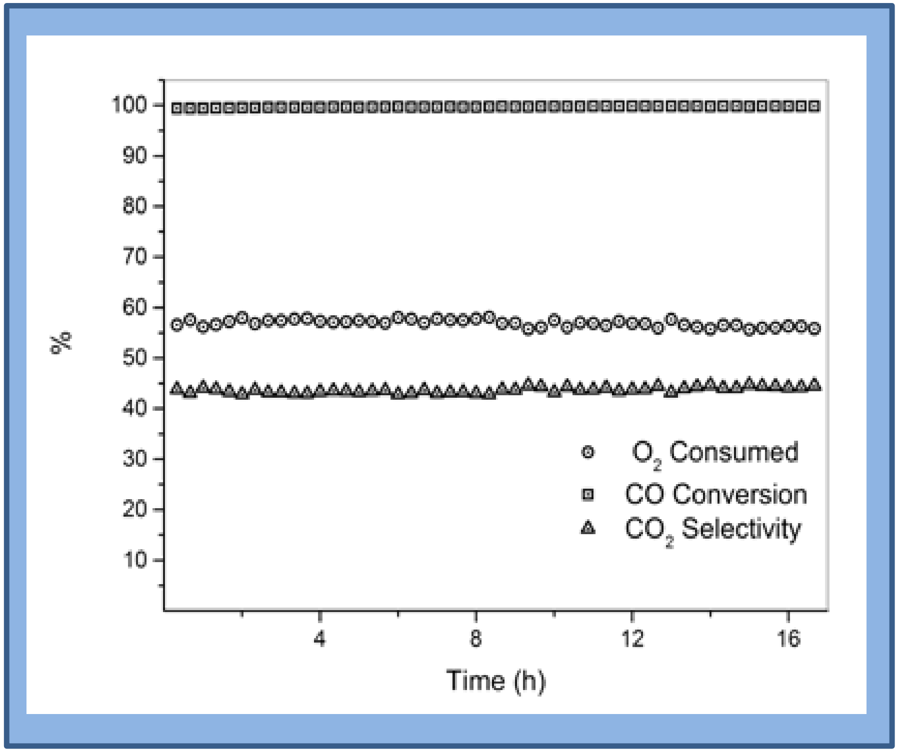
TiO_2 support



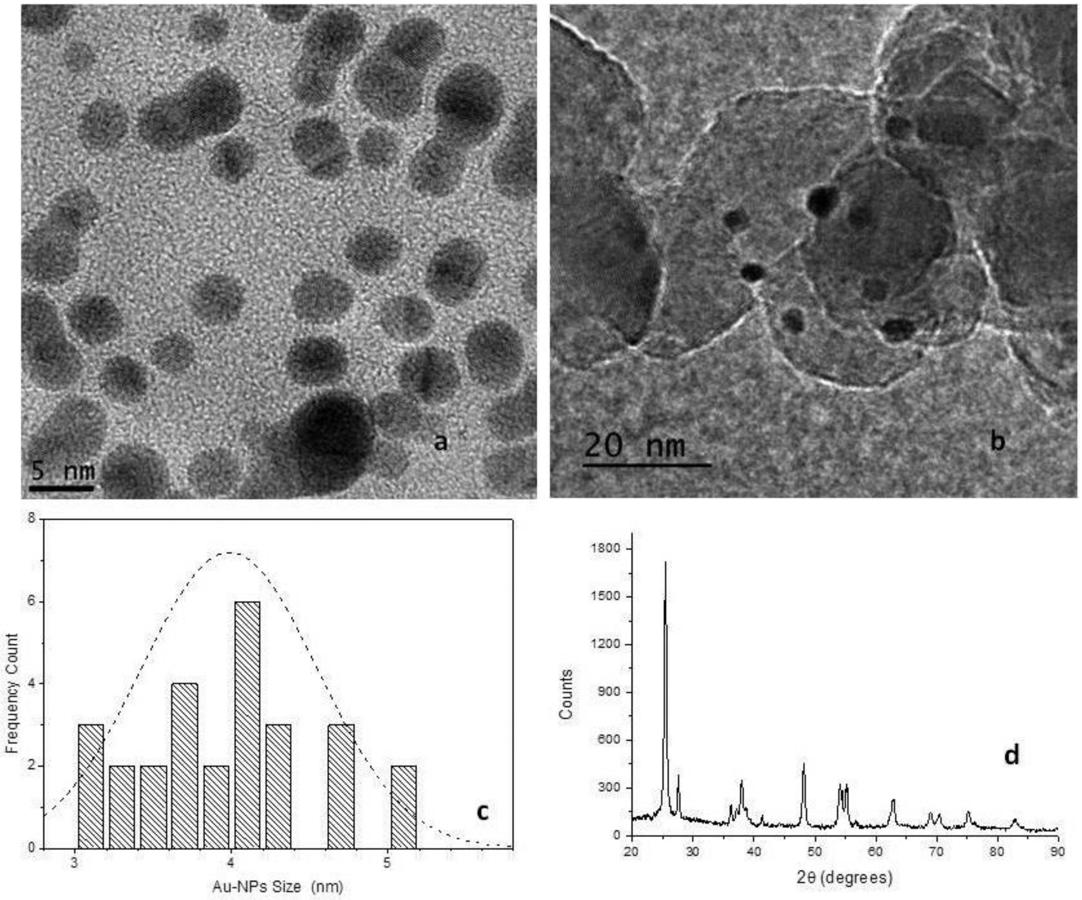
Au/TiO_2

CO-PROX

45ºC

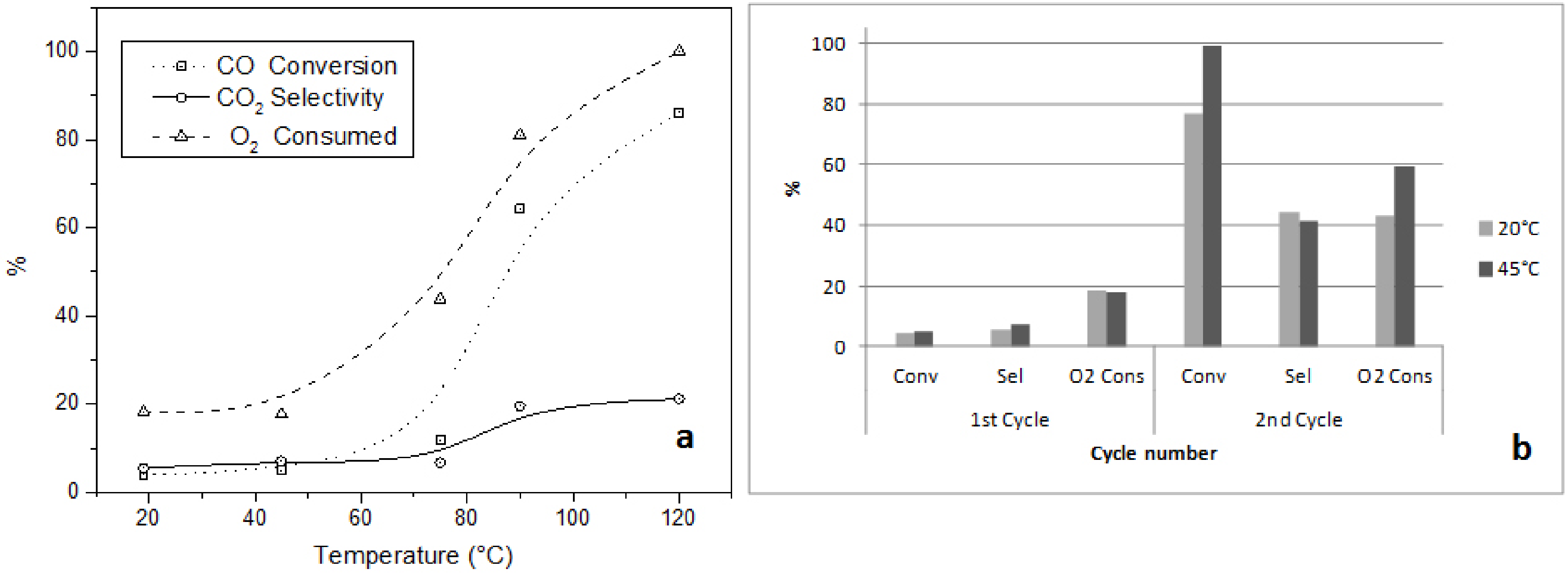


Au/TiO_2 – Catalyst Characterization



TEM micrographs of the pre-formed Au nanoparticles (a) and further supported on TiO_2 (b), particle sizes distribution (c) and X-ray diffractogram of 1 wt% Au/TiO_2 catalyst (d)

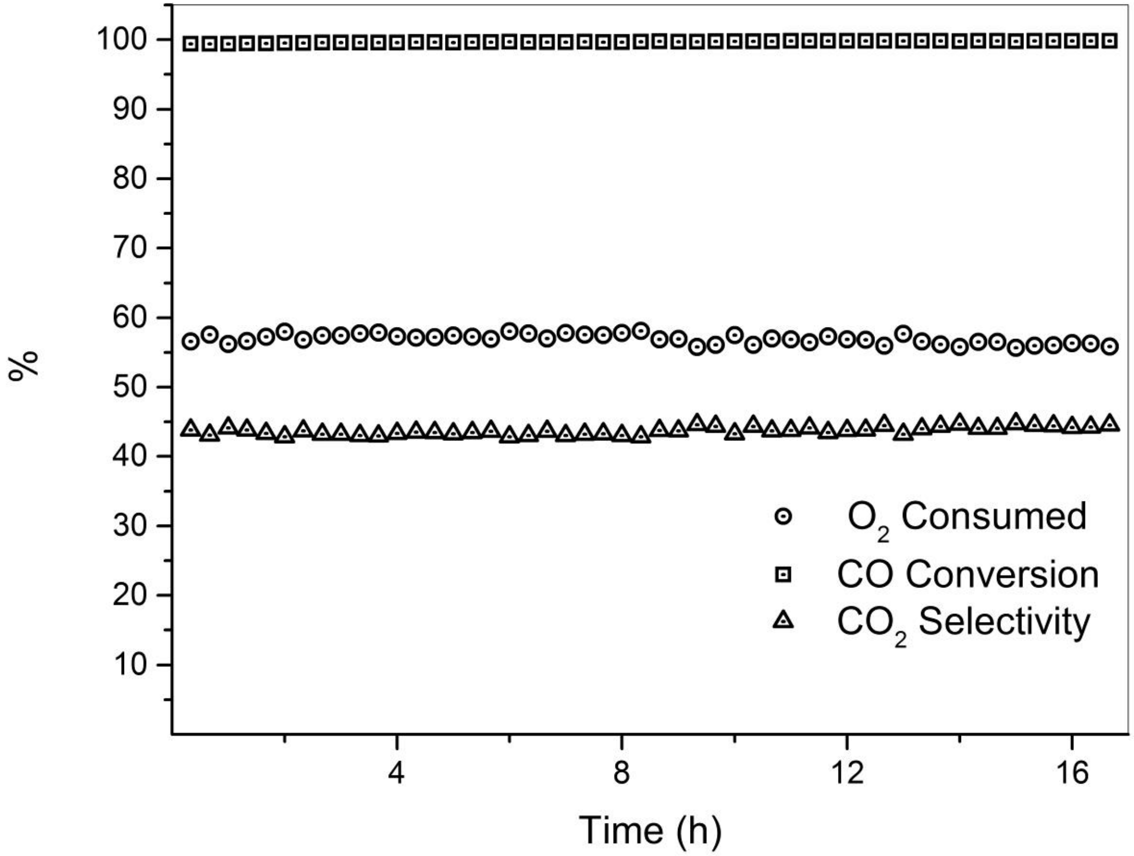
Au/TiO$_2$ - Catalytic Activity



CO conversion (%) and CO$_2$ selectivity (%) as a function of reaction temperature - first cycle (a), and comparison of the catalytic performance results of the first and second cycles (b).

(Feed composition CO:O2:H2 = 1:2:97 (vol%), space velocity 15.000 mL g^{-1} h^{-1})

Au/TiO_2 - Catalytic Activity



CO conversion (%) and CO_2 selectivity (%) at 45°C *vs*. time on stream – stability test

(Feed composition CO:O2:H2 = 1:2:97 (vol%), space velocity 15.000 mL g^{-1} h^{-1})

Au/TiO$_2$ - Catalytic Activity

Table 1. Comparison of the catalytic performance over Au/TiO$_2$ catalysts for CO-PROX reaction reported in the literature

Method	**Catalyst treatment process before reaction**	**Au metal loading (wt%)**	**Au particle size(nm)**	**Feed composition (vol%)**	**0$_2$/CO feed ratio**	**Space velocity**	**T (^{o}C)$^{\#}$**	**CO conversion (%)**	**CO$_2$ selectivity (%)**	**Reference**
Deposition Precipitation	Calcined at 300^{o}C	2	--	CO/O$_2$/H$_2$/CO$_2$/H$_2$O/He 1/2/37/18/5/37	2	40.000 mL g^{-1} h^{-1}	60-80	99.99	20	[5]
Direct anionic exchange (DAE)	Ammonia treatment	1.5	3	CO/O$_2$/H$_2$/He 2/2/48/48	1	3.000 h^{-1}	100	88	45	[6]
Impregnation Au complex	Heating H$_2$ at 500^{o}C and calcined at 400^{o}C	1	4.7	CO/O$_2$/H$_2$/He 1/2/50/25	2	90.000 mL g^{-1} h^{-1}	100	55	30	[7]
laser vaporization of a metallic gold	No treatment	0.023	2.9	CO/O$_2$/H$_2$/He 2/2/48/48	1	4.000 mL g^{-1} h^{-1}	200	60	40	[10]
Deposition Precipitation	**Calcined at 250^{o}C**	**1.3**	**5.7**	**CO/O$_2$/H$_2$ 1/0.5/98.5**	**1**	**20.000 mL g^{-1} h^{-1}**	**22**	**85**	**90**	**[11]**
Photo-deposition	No treatment	1	~1.5	CO/O$_2$/H$_2$/He 1.33/1.33/65.33/32.01	1	30.000 mL g^{-1} h^{-1}	80	95	47	[12]
Deposition Precipitation	**No treatment**	**3**	**≥ 5 nm**	**CO/O2/H$_2$/N$_2$ 1/1/50/48**	**1**	**165.000 mL g^{-1} h^{-1}**	**25-50**	**99**	**50**	**[13]**
Deposition Precipitation	Calcined at < 200^{o}C	0.5	2.5	CO/O$_2$/H$_2$/He 1.33/1.33/65.33/32.01	1	30.000 mL g^{-1} h^{-1}	80	70	35	[14]
Deposition Precipitation	Thermal and Plasma Treatment	1.0	2.8	CO/O$_2$/H$_2$/N$_2$ 1/1/50/48	2	120.000 h^{-1}	100	75	30	[15]
Supported pre-formed Au nanoparticles	**No treatment**	**1.0**	**4**	**CO/O$_2$/H$_2$ 1/2/97**	**2**	**15.000 mL g^{-1} h^{-1}**	**45**	**99**	**45**	**This work**

$^{\#}$ *Temperature of maximum CO conversion*

Conclusions

-Au/TiO_2 catalyst with Au metal average nanoparticles size of ~ 4 nm could be prepared by a facile method at room temperature.

-The catalyst showed to be very active, selective and stable (18 h on reaction stream) for the CO-PROX reaction at low temperatures (20-50°C), even at a high volumetric O_2/CO ratio ratio of 2 ($\lambda = 4$) and high hydrogen concentration (97 vol%) in the inlet feed gas stream.

-Next Steps

-The influence of synthesis parameters, like citrate:Au and BH_4^-:Au molar ratios on Au nanoparticles size and

- The influence of reaction parameters on the CO conversion and CO_2 selectivity, like a volumetric O_2/CO ratio, space velocity, hydrogen concentration and the presence of H_2O and/or CO_2 in the inlet feed gas stream are under investigation.

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