Institut Charles Gerhardt
ICG Montpellier

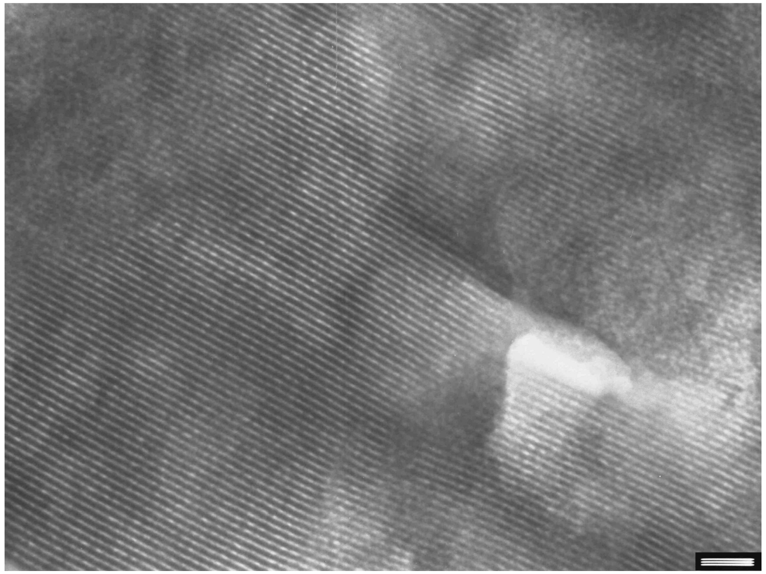
UMR 5253 - Institut de Chimie Moléculaire et des Matériaux de Montpellier

RuO_2@SiO_2 as catalytic filters for gas sensors

Dr. Y. Guari

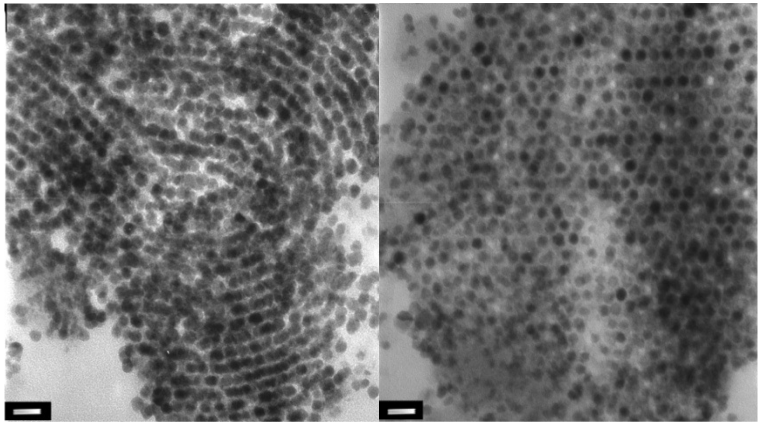
UMR 5253 - CNRS, UM2, ENSCM, UM1

Nanomaterials exhibiting optic and magnetic properties.



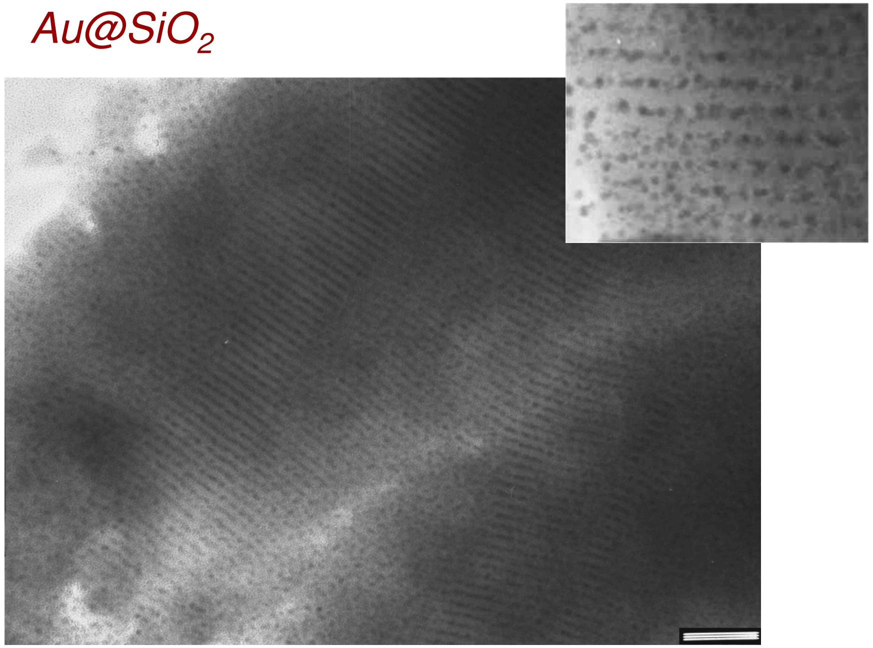
Corriu, R. J. P. . et al. *Chem. Commun.* **2001**, 763,
Corriu, R. J. P. et al. *Chem. Commun.* **2001**, 1116,
Porcherie, O. et al. *New J. Chem.* **2005**, *29*, 538.

In_2O_3@SiO_2



Guari, Y. et al. *New J. Chem.* **2003**, *27*, 1374

Au@SiO_2



Guari, Y. et al. *Chem. Commun.* **2001**, 1374,
Guari, Y. et al. *Chem. Mater.* **2003**, *15*, 2017,
Besson, E. et al. *Chem. Commun.* **2005**, 1775.

Fe_3O_4@SiO_2

Matsura, V. et al. *J. Mater. Chem.* **2004**, *14*, 3026.

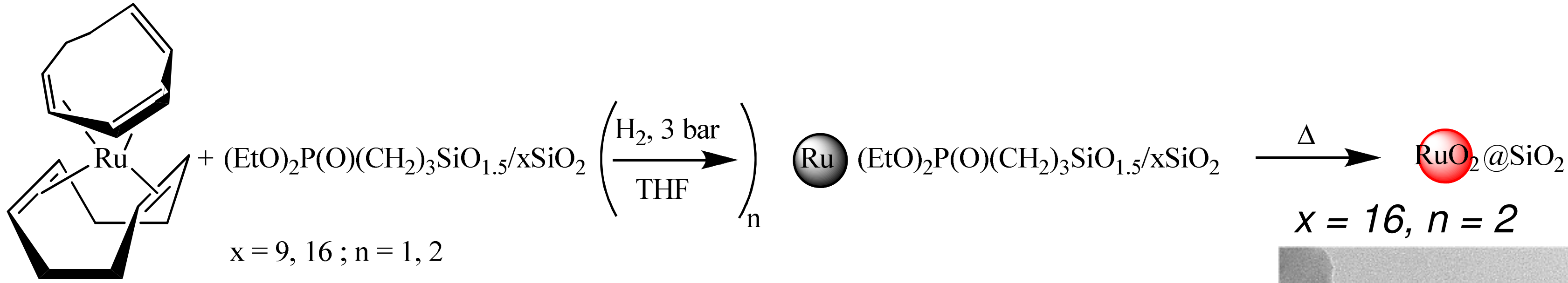
Mn_3O_4@SiO_2

Matsura, V. et al. *J. Mater. Chem.* **2004**, *14*, 2703.

NiFe@SiO_2

Folch, B. et al. *J. Mater. Chem.* **2006**, *16*, 4435.

First route towards RuO_2@SiO_2 nanomaterials



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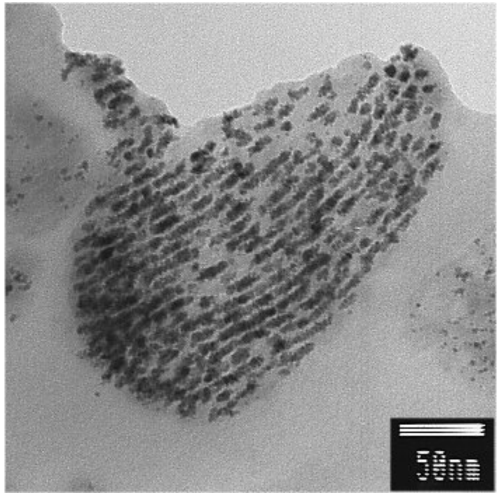

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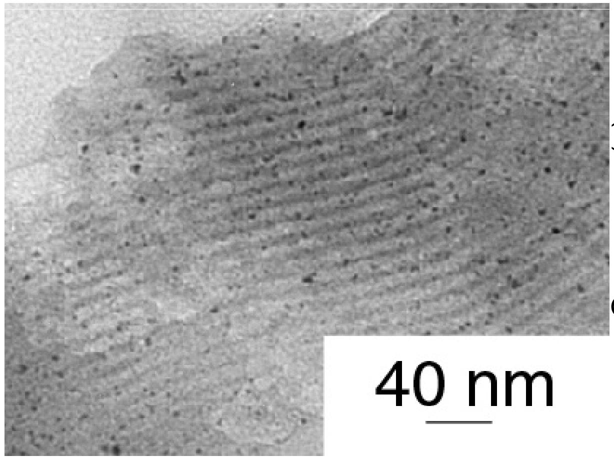

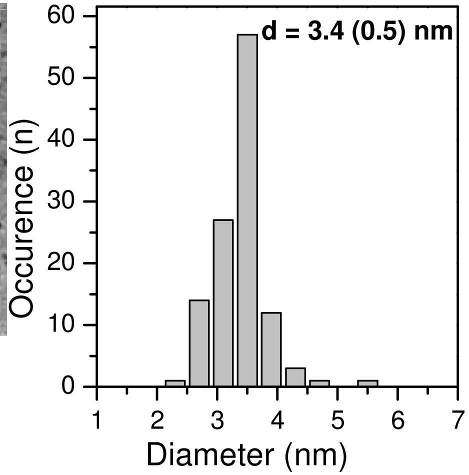

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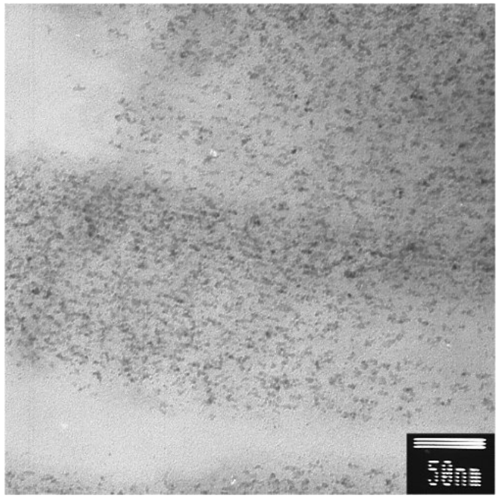
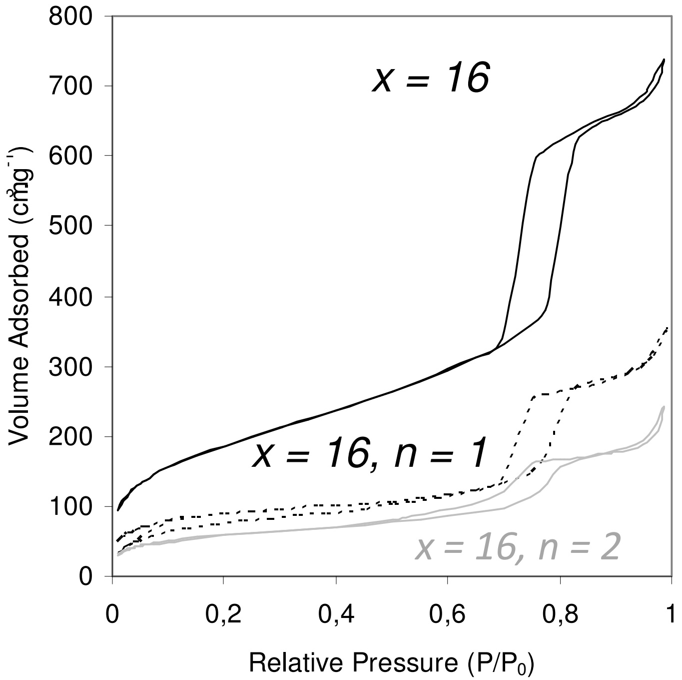
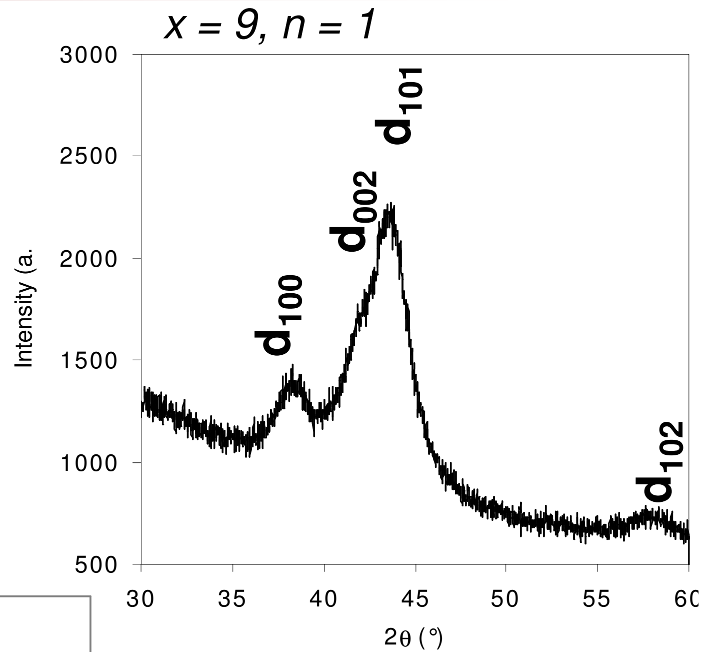
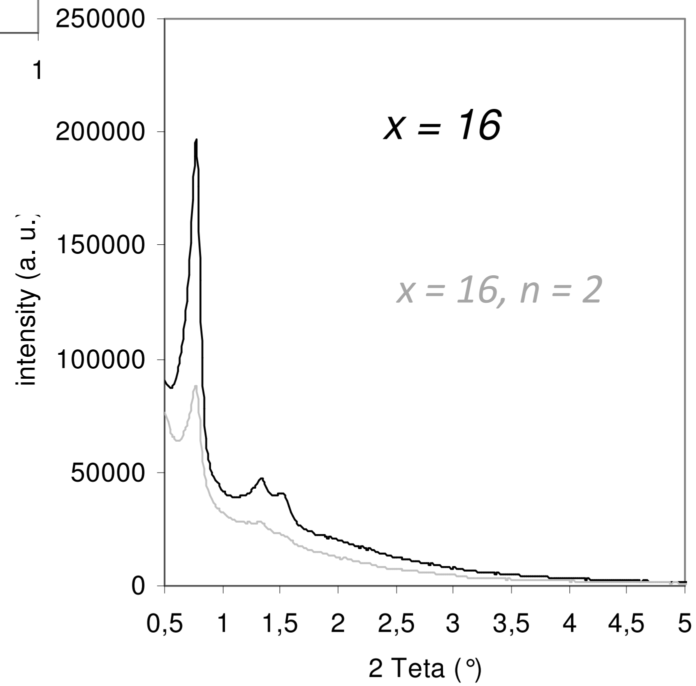


Jansat, S et al. *Adv. Funct. Mater.*, **2007**, *17*, 3339

First route towards $RuO_2@SiO_2$ nanomaterials

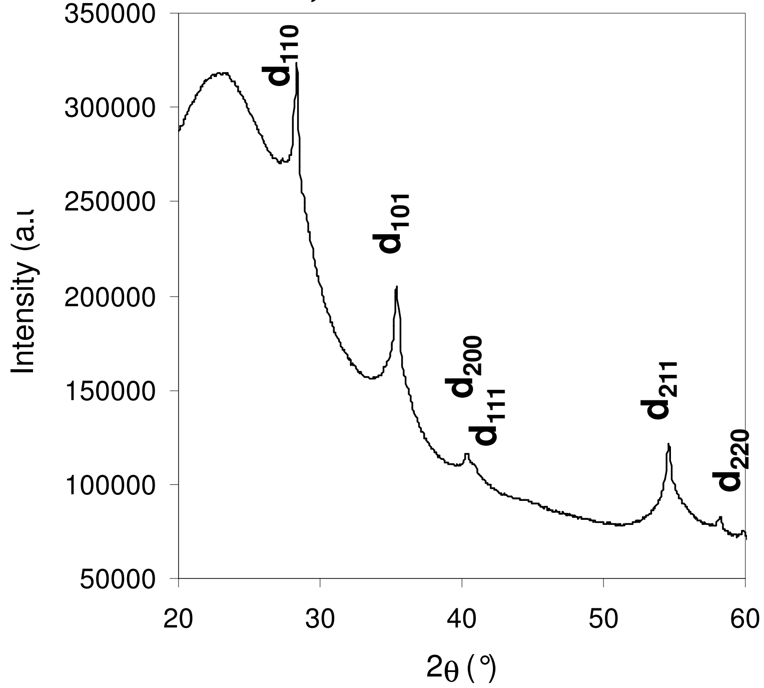




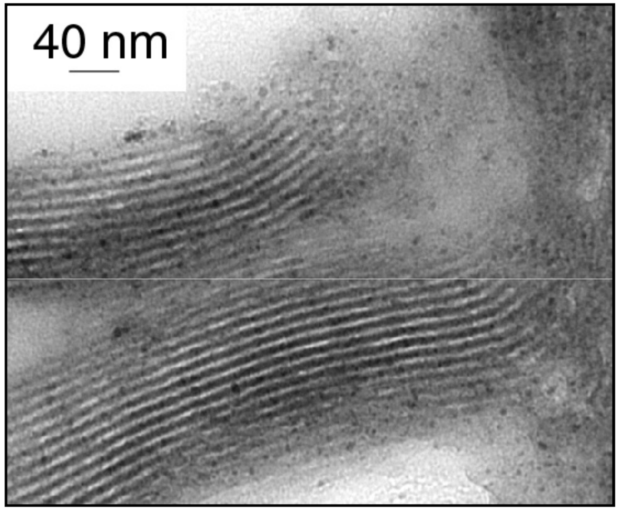


First route towards $RuO_2@SiO_2$ nanomaterials

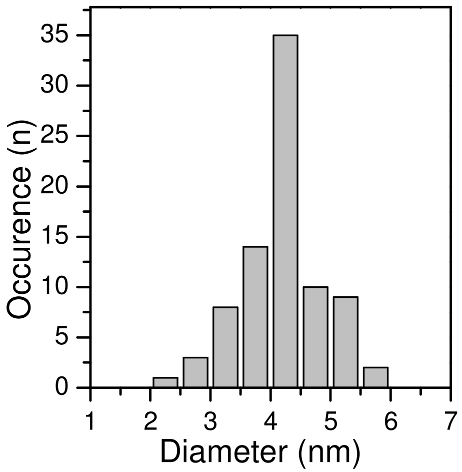
x = 9, n = 2



x = 16, n = 1



d = 4.2 (0.6) nm



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First route towards RuO_2@SiO_2 nanomaterials

X = 9, n = 2

S_{BET} = 253 $m^2.g^{-1}$
D_p = 6.2 nm

$D_{nanop.}$ = 4.2 (0.6) nm

RuO_2 wt % content = 11.0

RuO_2 content

Material	Number of I/H cycle	Ru (RuO_2) [%]
SiO_2 (x=9)	0	0
Ru@SiO_2 (x=9)	1	3.94
	2	7.91
RuO_2@SiO_2 (x=9)	2	8.37 (11.0)
SiO_2 (x=16)	0	0
Ru@SiO_2 (x=16)	1	4.90
	2	10.09
RuO_2@SiO_2 (x=16)	1	5.64 (7.42)

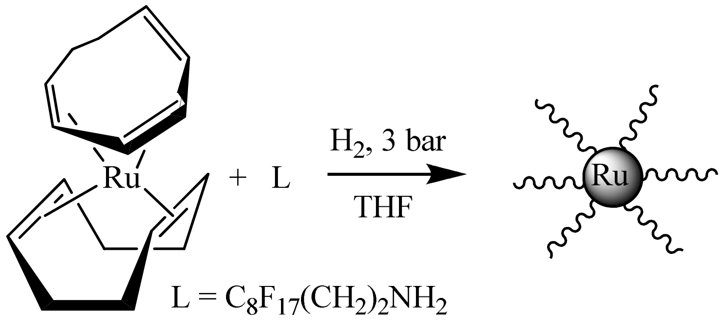
Specific surface and porosity

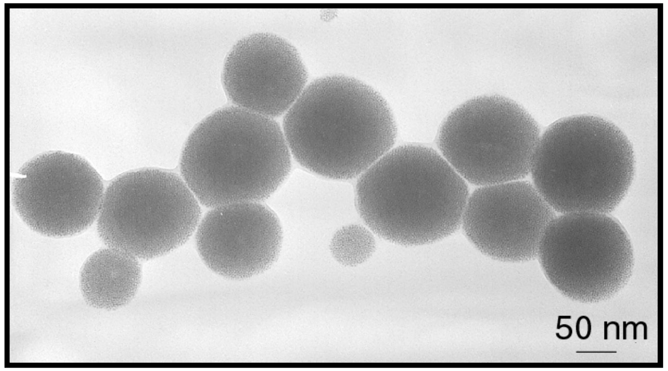
Material	I/H	$S_{Spec.}$ [$m^2.g^{-1}$]	V_p [$cm^3.g^{-1}$]	D_p [nm]
SiO_2 (x=9)	0	722	1.21	6.0
Ru@SiO_2 (x=9)	1	465	0.46	6.0
	2	253	0.40	6.2
RuO_2@SiO_2 (x=9)	2	259	0.35	4.5
SiO_2 (x=16)	0	646	1.14	7.5
Ru@SiO_2 (x=16)	1	289	0.55	7.3
	2	198	0.37	7.3
RuO_2@SiO_2 (x=16)	1	205	0.39	6.0

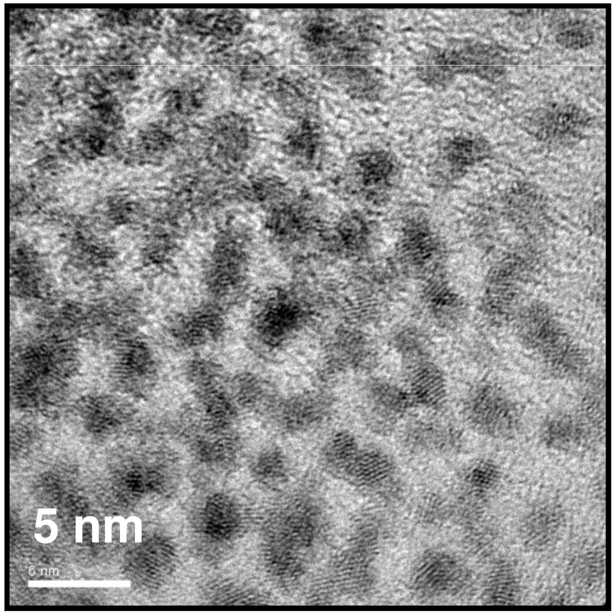
RuO_2 nanoparticles size

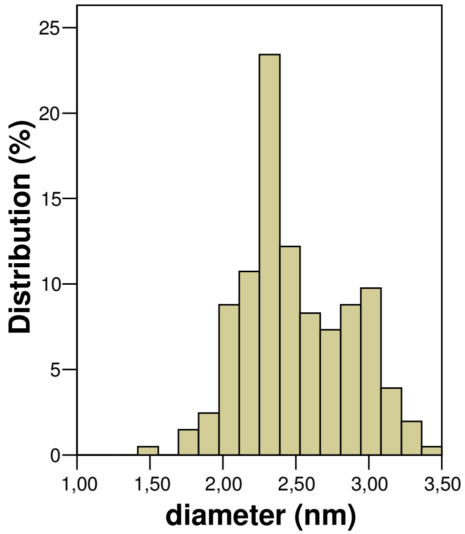
d = 4.2 (0.6) nm

Second route towards $RuO_2@SiO_2$ nanomaterials



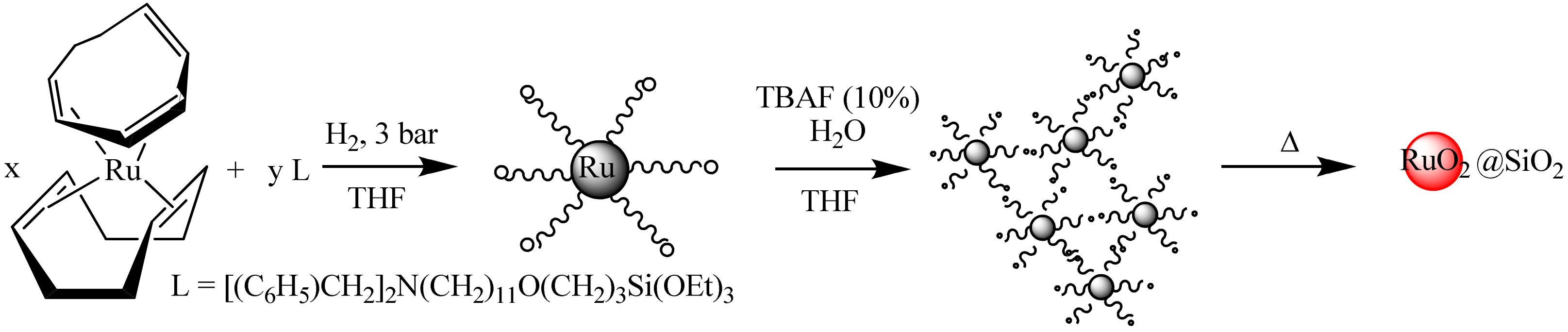


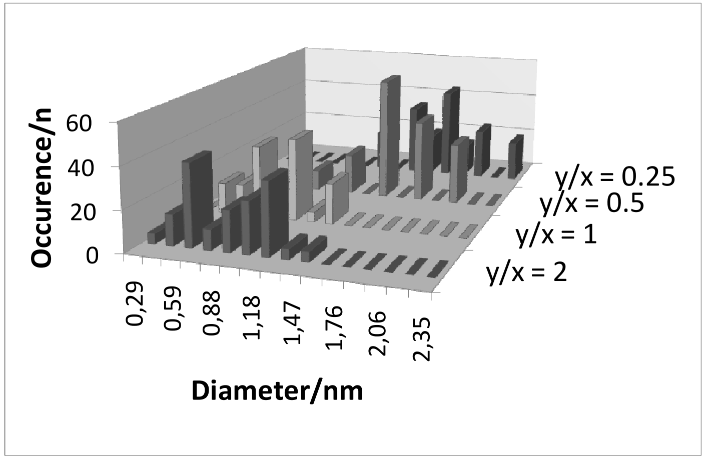


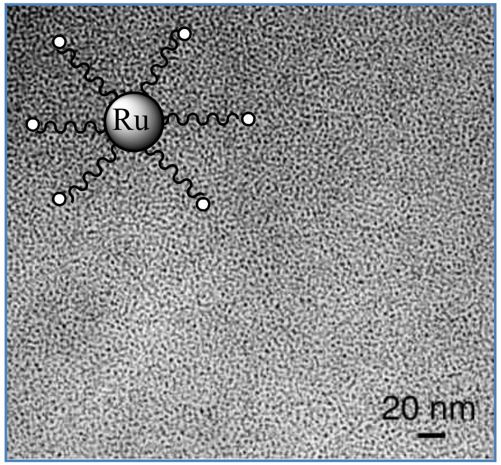


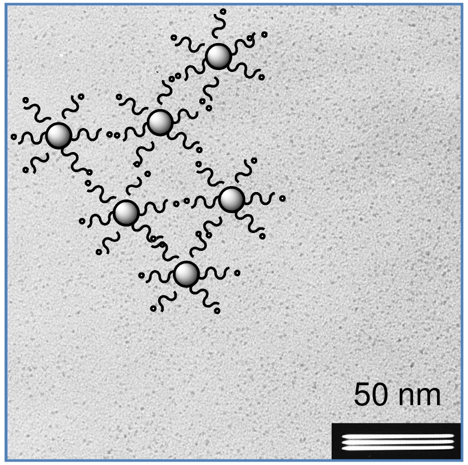
Tristany, M. et al., *Adv. Funct. Mater.*, **2006**, *16*, 2008.

Second route towards $RuO_2@SiO_2$ nanomaterials

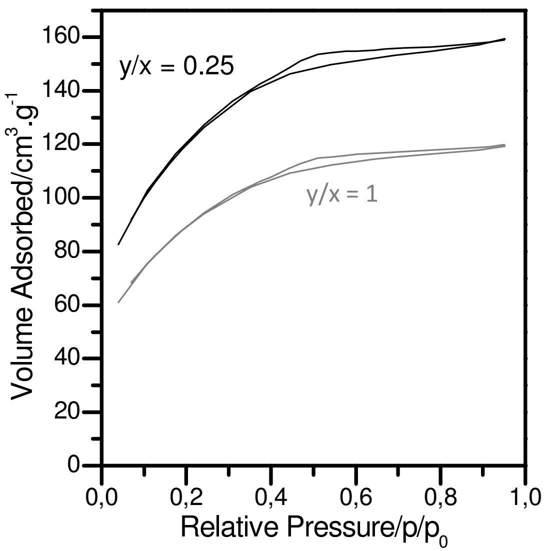


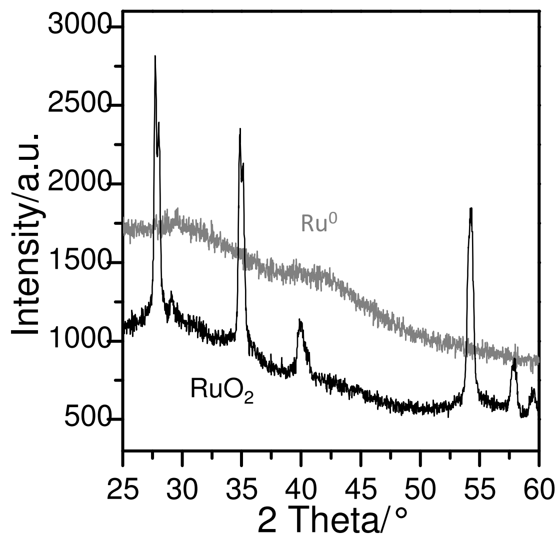


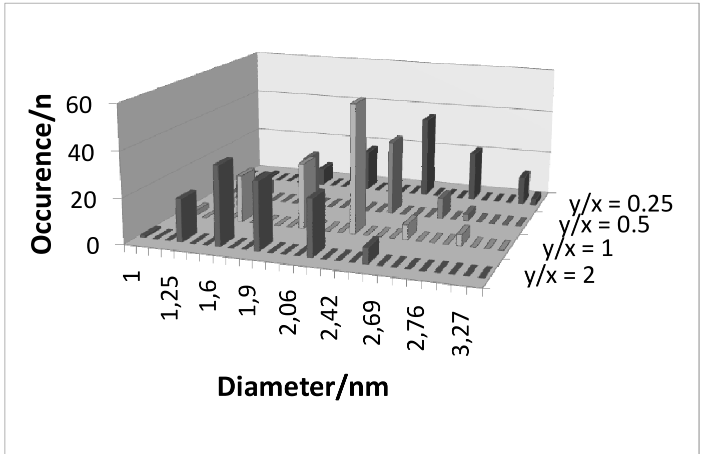


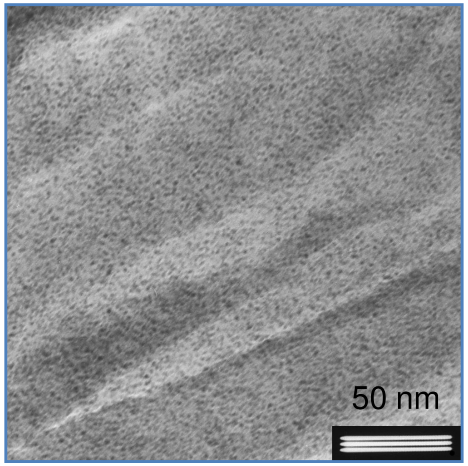


Second route towards RuO_2@SiO_2 nanomaterials









Second route towards $RuO_2@SiO_2$ nanomaterials

RuO_2 nanoparticles size

y/x	$[Ru^0]L'$/nm	$[RuO_2/SiO_2]$/nm
0.25	2.0 (0.4)	2.5 (0.5)
0.5	1.6 (0.3)	2.2 (0.4)
1	0.9 (0.3)	2.1 (0.4)
2	1.0 (0.3)	1.8 (0.4)

y/x = 0.25
S_{BET} = 328 $m^2.g^{-1}$
D_p = 2.6 nm

$D_{nanop.}$ = 2.5 (0.5) nm

RuO_2 wt % content = 57.4

RuO_2 content

y/x	$[Ru^0]L'$/%	$[RuO_2/SiO_2]$/%
0.25	19.6	57.4
0.5	14.1	48.3
1	12.1	43.1
2	8.07	29.1

Specific surface and porosity

$[RuO_2]/SiO_2$	$S_{BET}/m^2.g^{-1}$	D_p/nm
y/x = 0.25	328	2.6
y/x = 0.5	400	2.6
y/x = 1	442	2.6
y/x = 2	476	2.6

Nice materials for catalysis !

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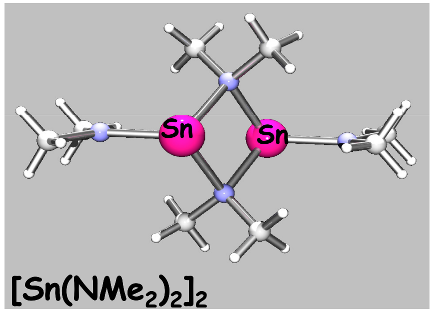
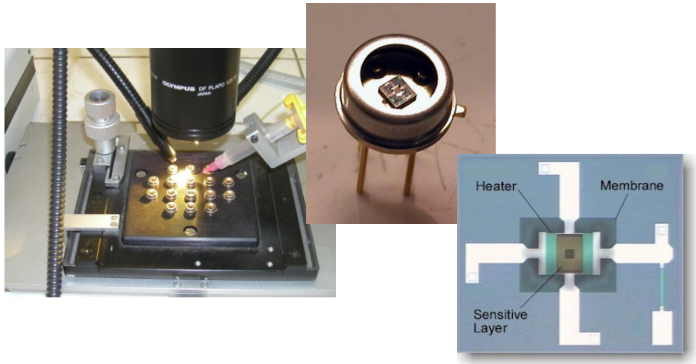
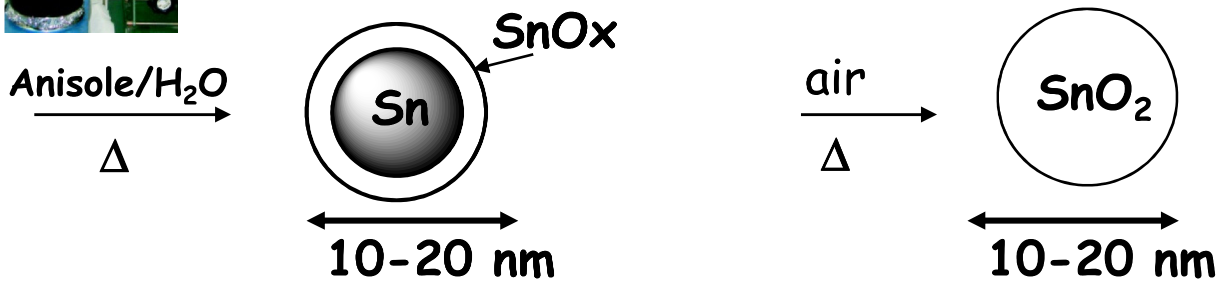
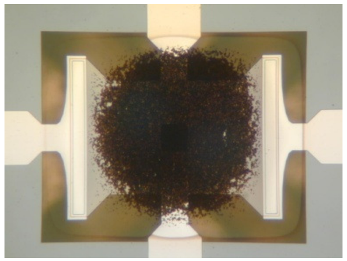
Nanoparticles based sensors

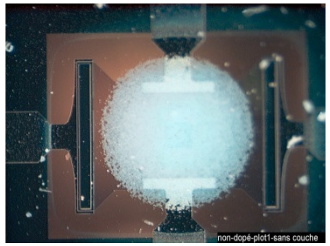






Solution colloïdale

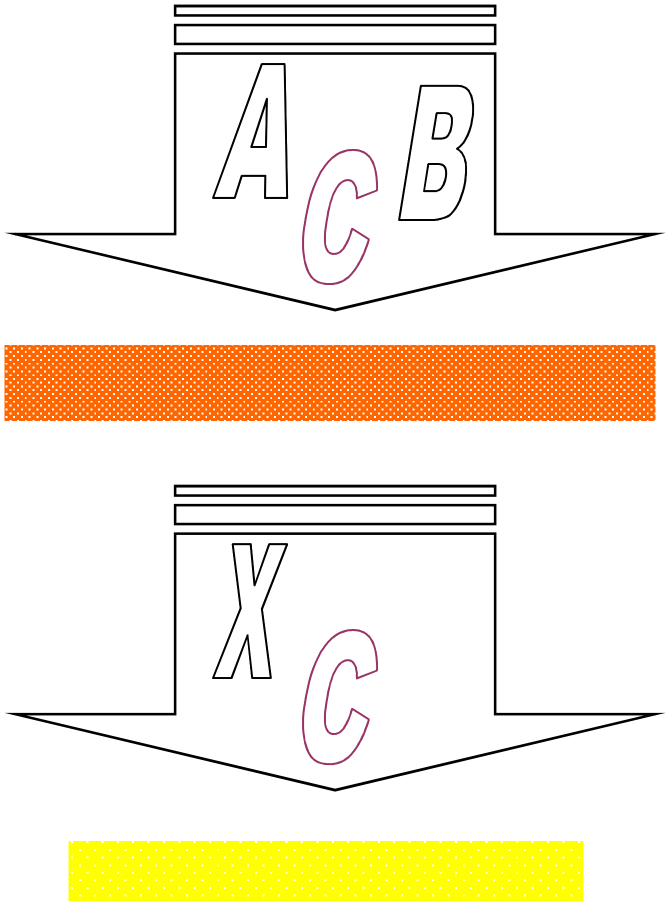




Collaboration : B. Chaudret, K. Philippot.

Chaudret, B. et al, *PCT Int. Appl.*, WO 2001002844, **2001.**

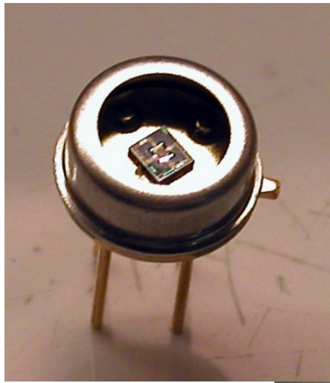
Catalytic filter principle

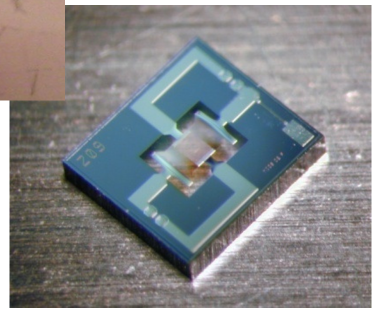


Catalytic filter — RuO_2 nanoparticles within SiO_2

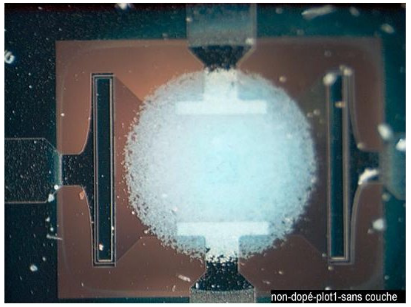
Sensitive layer — SnO_2 nanoparticles

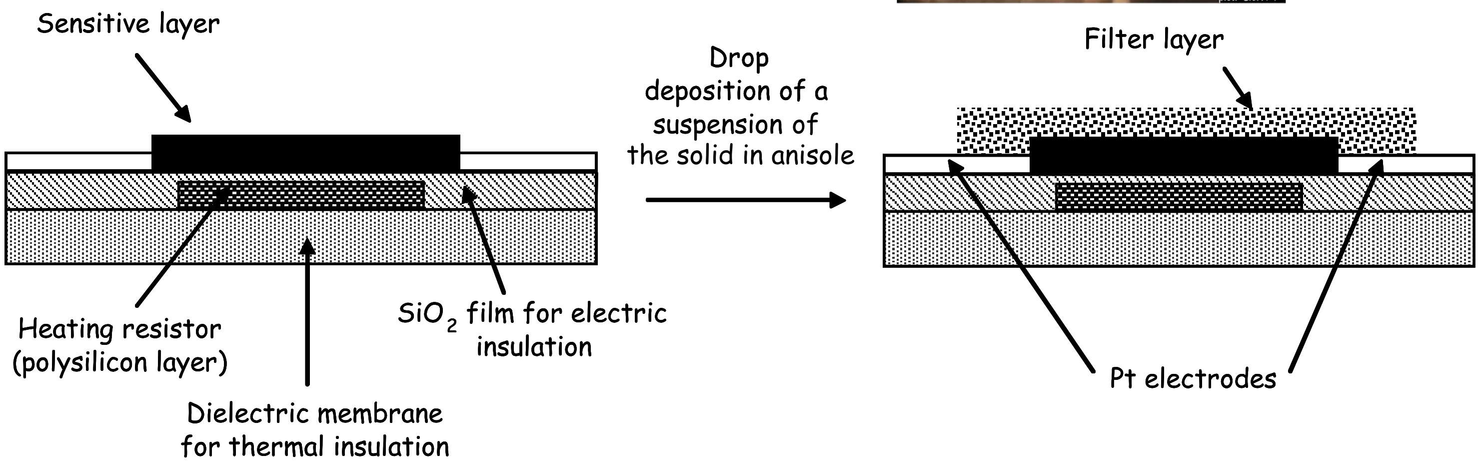
Catalytic filter for selective alkane detection





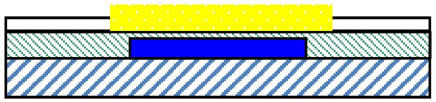
"On chip" catalytic filtering

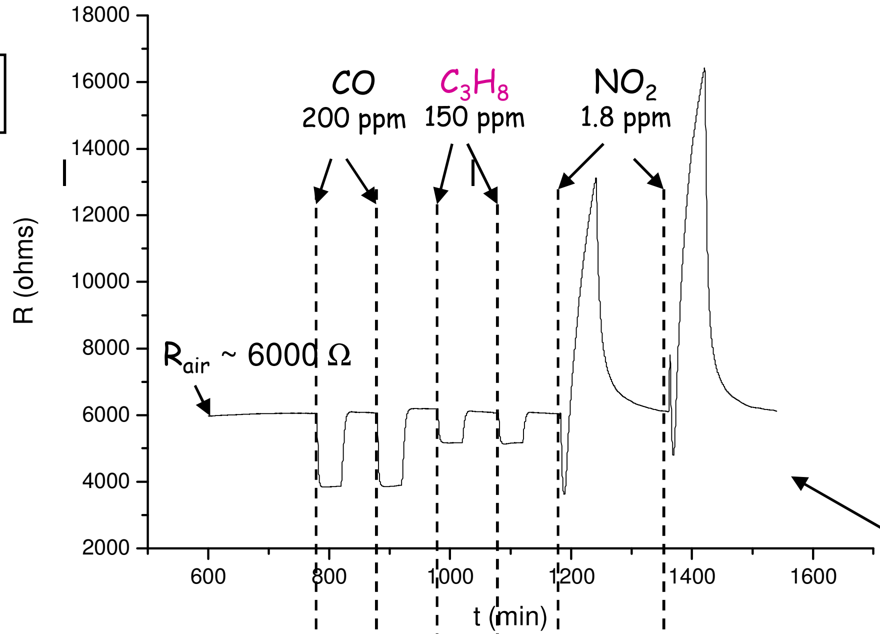




Catalytic filter obtained from the first route

No catalytic filter





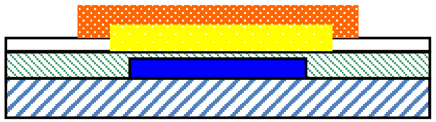
S_{C3H8}/S_{CO} = 0.4

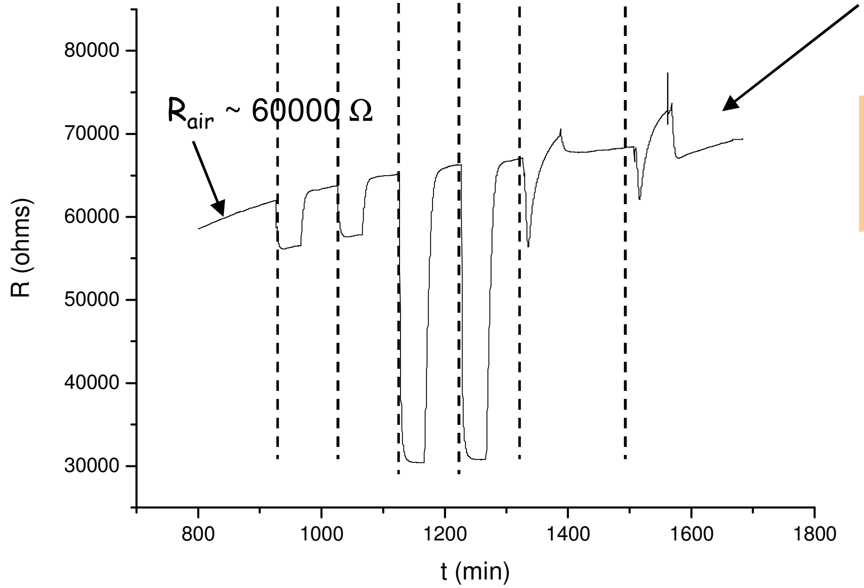
$S_{gaz} = (R_{gaz} - R_{air})/R_{air}$

$S_{CO\ 200}$	$S_{C3H8\ 150}$	$S_{NO2\ 1.8}$
-0.37	-0.16	+ 1.5
-0.09	-0.53	+0.04

<u>Experimental conditions</u>
V_h = 3.2 V
R_h = 50%
Gaz flow = 1000 mL/min

Catalytic filter



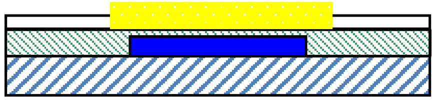


- Sensitivity CO ↘ 4
- Sensitivity NO_2 ↘ 37
- Sensitivity propane ↗ 3.5

S_{C3H8}/S_{CO} = 5.8

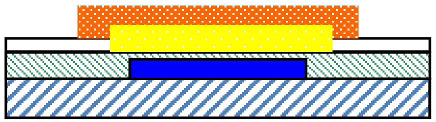
Catalytic filter obtained from the second route

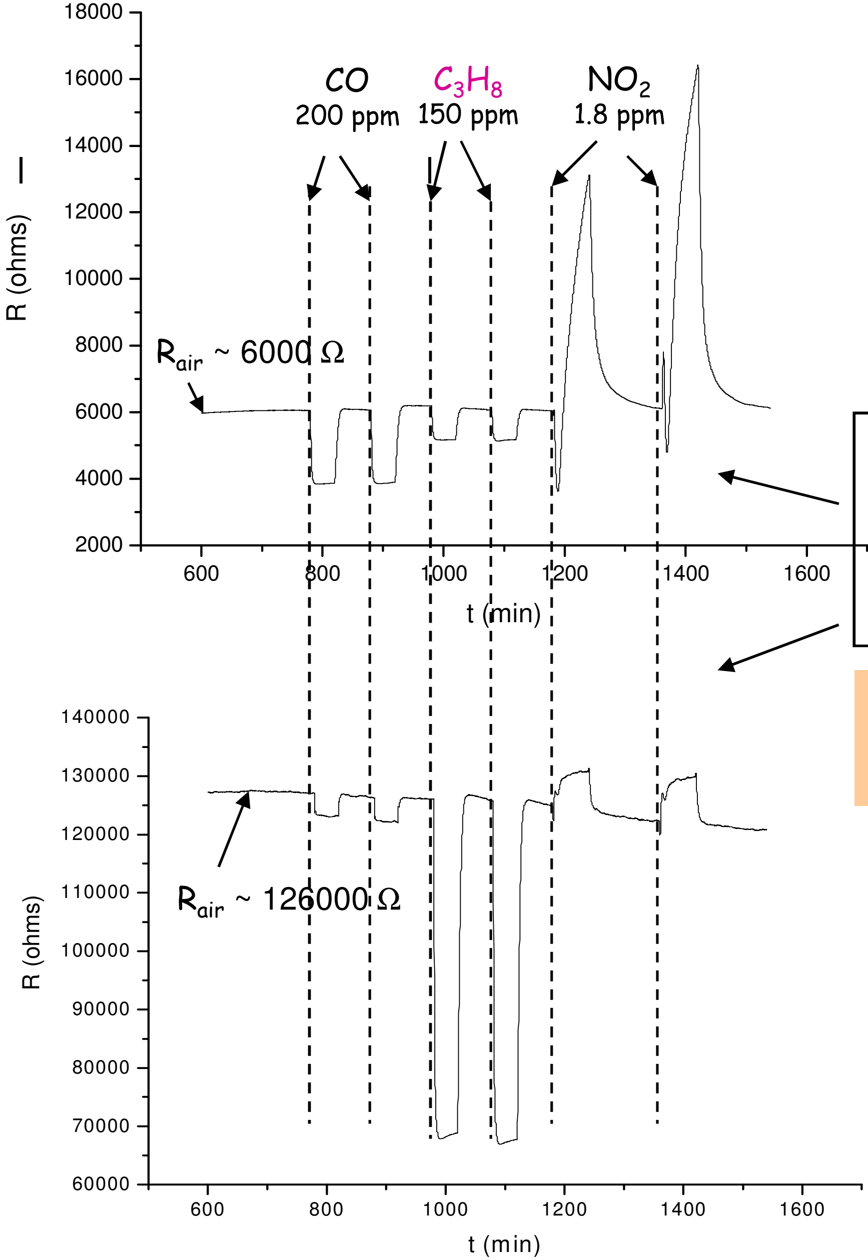
No catalytic filter



Experimental conditions
V_h = 3.2 V
R_h = 50%
Gaz flow = 1000 mL/min

Catalytic filter





S_{C3H8}/S_{CO} = 0.4

$S_{gaz} = (R_{gaz} - R_{air})/R_{air}$

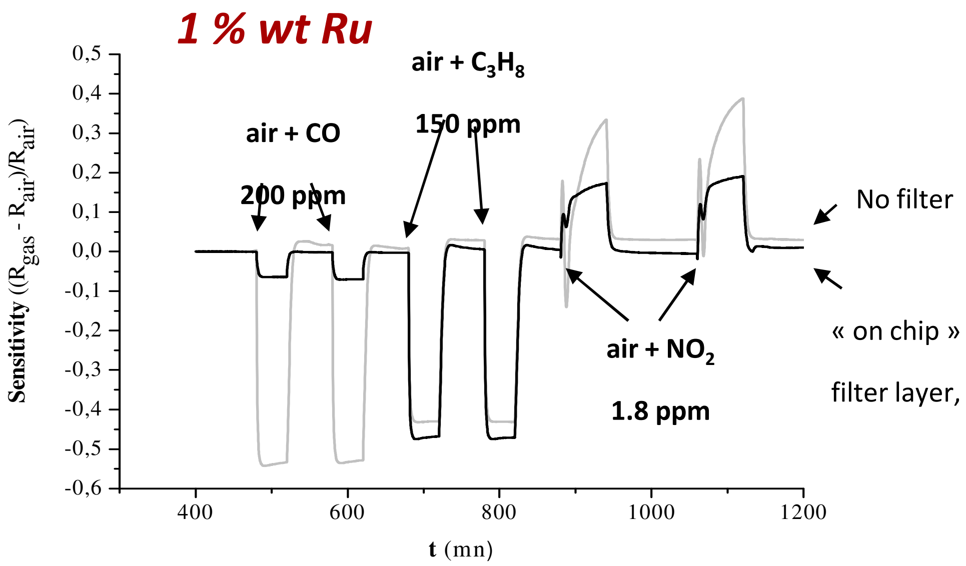
$S_{CO\ 200}$	$S_{C3H8\ 150}$	$S_{NO2\ 1.8}$
-0.37	-0.16	+ 1.5
-0.03	-0.47	+0.05

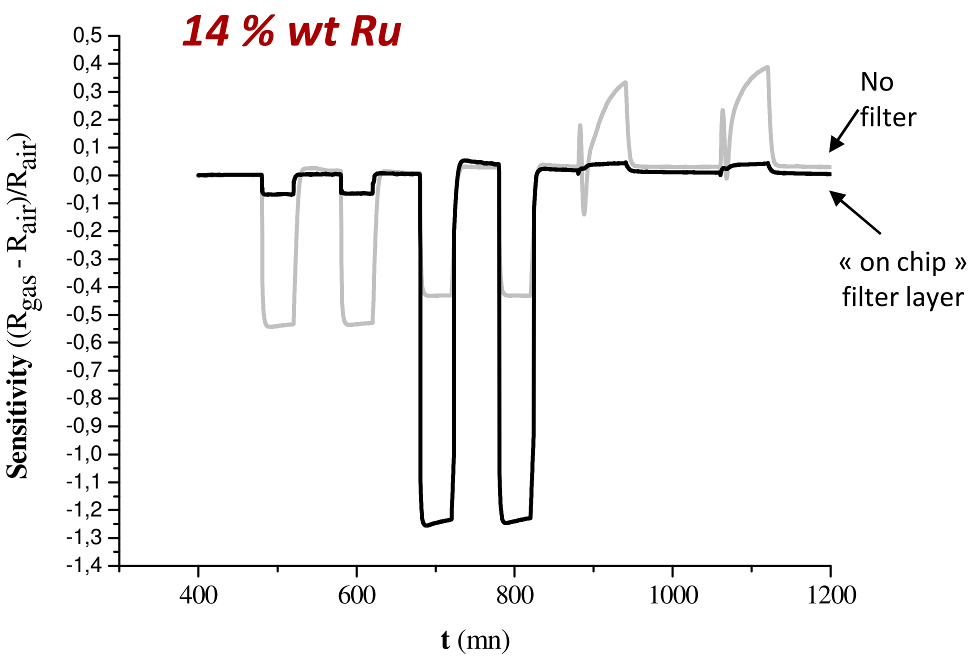
- Sensitivity CO ↘ 12
- Sensitivity NO_2 ↘ 30
- Sensitivity propane ↗ 3

S_{C3H8}/S_{CO} = 15.7

Ru content effect on sensitivity ?

-Sensitivity to CO : 90 % decrease
-Sensitivity to propane : 4-6 % increase





-Sensitivity to CO : 87 % decrease
-Sensitivity to propane : 150 % increase

Catalytic filter effects

- Sensitivity towards CO_2 decreases:

  Catalytic oxydation of **CO towards CO_2 by RuO_2**

- Sensitivity towards NO_2 decreases:

  A partial reversible chemisorption resulting from the interactions between nitrogen and the OH groups at the silica surface. Leads to stable **chemisorbed complexes**.

- Sensitivity towards propane increases :

  Considering the sensitive layer working conditions (T(filter) < T (sensitive layer)), no catalytic oxydation by RuO_2 can be considered. Nevertheless, at the sensitive layer neighbouring (higher temperature) **ruthenium can have a doping effect**.

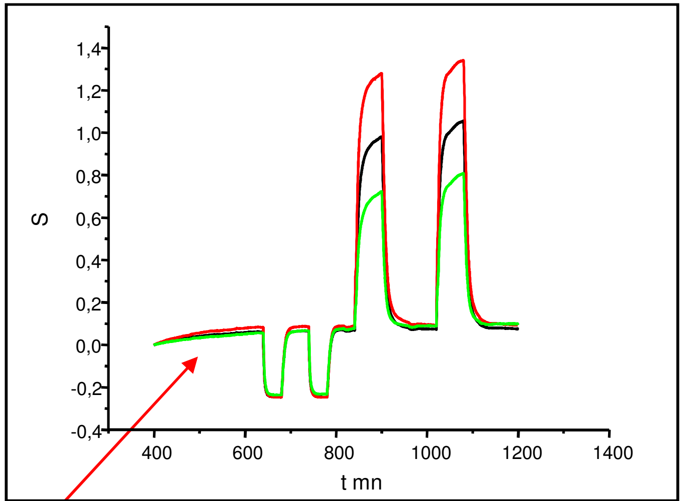
- The filter layer prepared following the second route contains a higher amount of RuO_2 catalyst leading to a better activity for the catalytic CO oxydation.

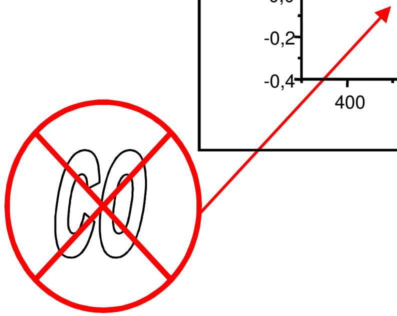
Why residual detection of CO ?

- Partial conversion of CO due to a low catalytic activity.

- Cracks and defaults in the catalytic filter layer.

RuO_2/SiO_2 as an external catalytic filter





Preferential detection of propane in presence of CO.

K. Philippot et al, FR2901715, **2006.**
K. Philippot et al. PCT/. WO2007138197, **2007.**
Matsura V. et al. *Adv. Funct. Mater.*, **2009**, *submitted*

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Many thanks to :

ICG-CMOS, Montpellier

and Dr. B. Folch.

MAGMANet NETWORK OF EXCELLENCE

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