

# Synthèses innovantes de catalyseurs : enjeux et solutions

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*Synthèses innovantes  
de matériaux  
(pour la catalyse)?*

*Synthèses de catalyseurs  
innovants?*

**Synthèses innovantes de catalyseurs?**

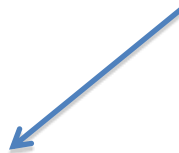
*Synthèses de catalyseurs pour  
des procédés innovants?*

# Synthèses innovantes de catalyseurs

*Quelles nouvelles idées, pour des problèmes anciens ou nouveaux?*

*Quelles nouvelles contraintes?*

**Métaux**  
**Oxydes**  
**Nitrures**  
**Sulfures**



*Systèmes micro/mésoporeux*  
*MOFs*  
*Catalyse organométallique supportée*  
*Catalyse hétérogène énantiosélective*  
*Catalyse enzymatique supportée*

1. Milieux de  
synthèse

2. Milieux de  
réaction

3. Organisation

4. Nouvelles  
phases

## Nouveaux milieux de synthèse

*Dispersion*

*Taille*

*Précurseurs  
commerciaux*

*Supports non poreux*

*Morphologie/texture*

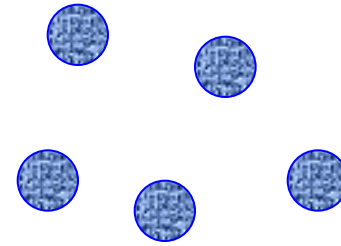
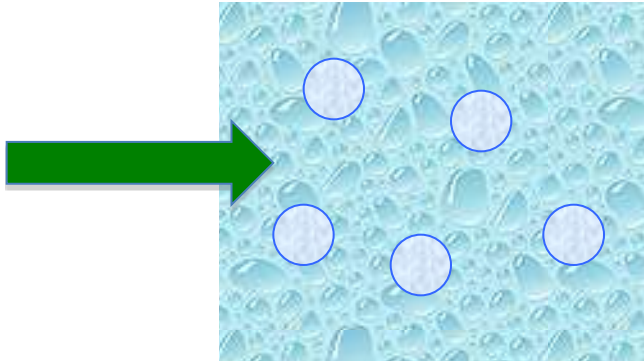
*Réactifs/procédés "verts"*

1. Milieux de  
synthèse

2. Milieux de  
réaction

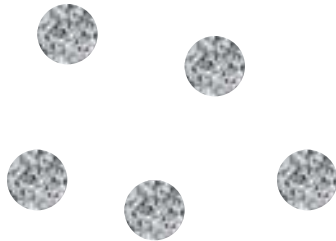
3. Organisation

4. Nouvelles  
phases

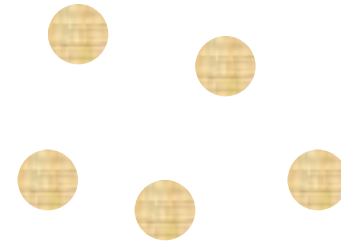


imprégnation  
(déposition-)précipitation

séchage



réduction



calcination



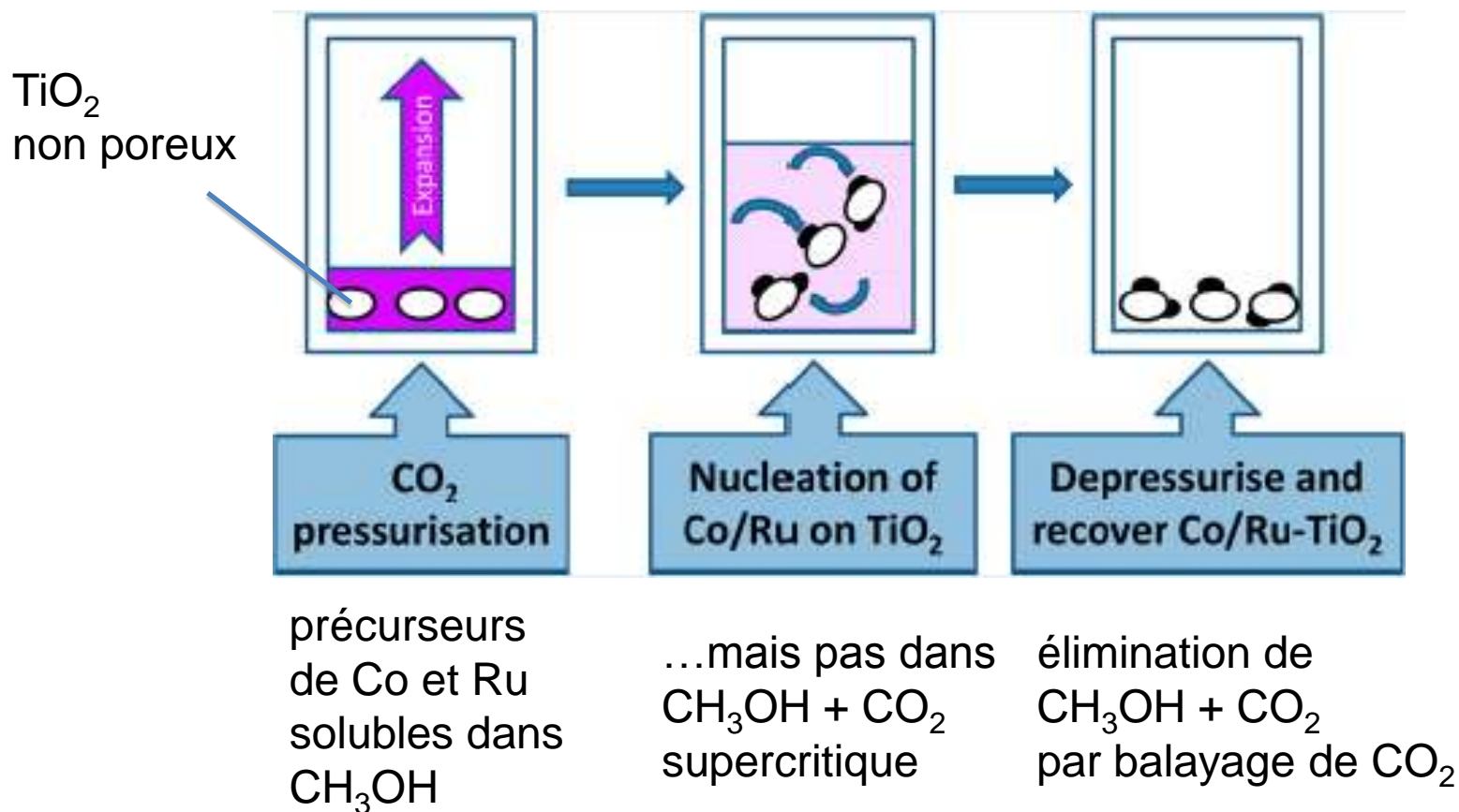
1. Milieux de synthèse

2. Milieux de réaction

3. Organisation

4. Nouvelles phases

## a- Dépôt en milieu "antisolvant" supercritique



1. Milieux de synthèse

2. Milieux de réaction

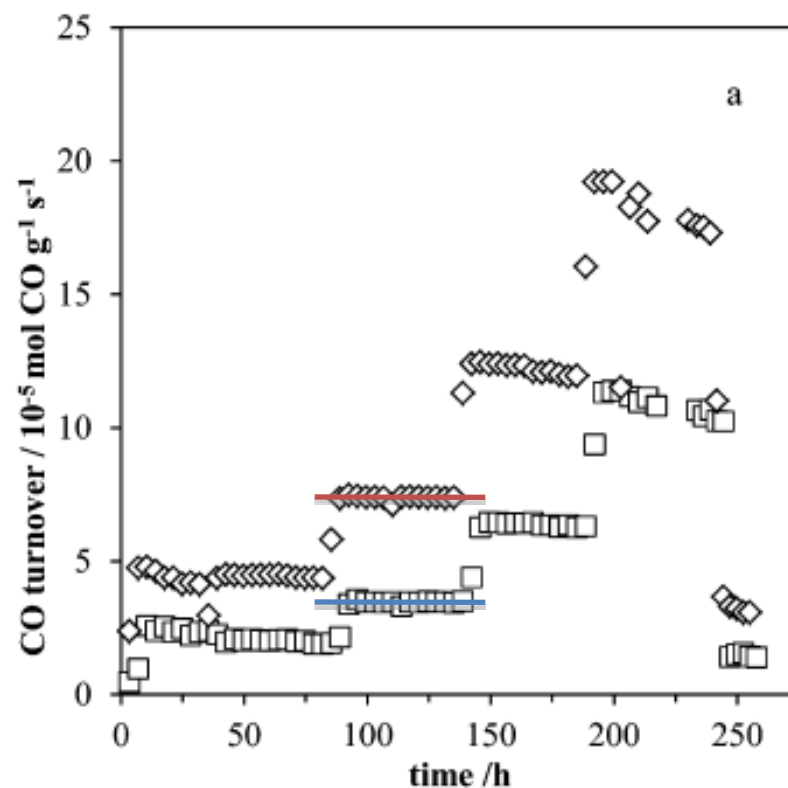
3. Organisation

4. Nouvelles phases

## a- Dépôt en milieu "antisolvant" supercritique

sample	Co <sub>3</sub> O <sub>4</sub> crystallite size (nm)
IMP Co-Ru/TiO <sub>2</sub>	36.0 ± 0.2
GAS Co/TiO <sub>2</sub>	17.0 ± 0.2
GAS Co/TiO <sub>2</sub> Ru IMP	17.1 ± 0.1
GAS Co-Ru/TiO <sub>2</sub>	20.2 ± 0.2

Activité en synthèse Fischer-Tropsch



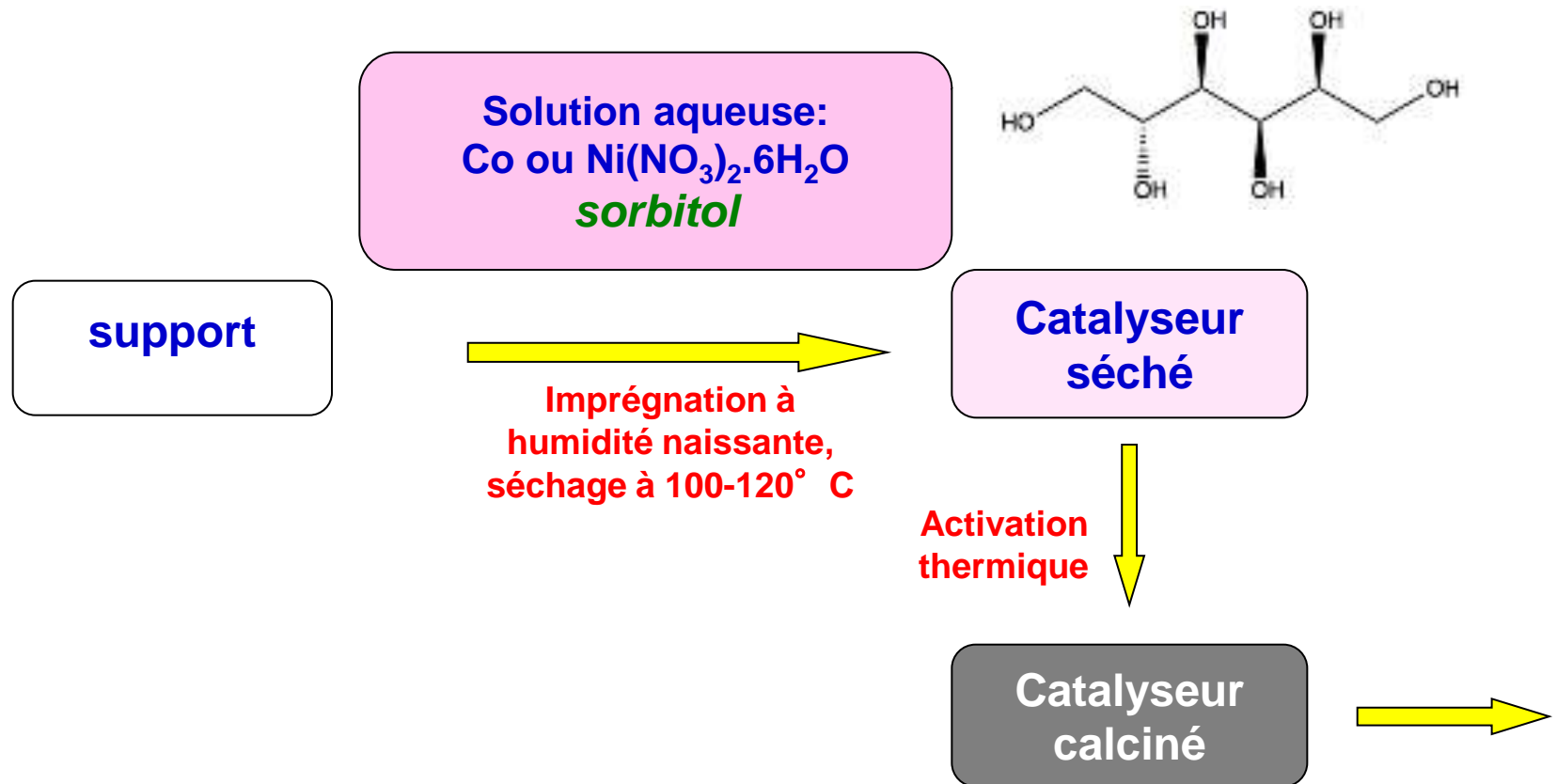
1. Milieux de  
synthèse

2. Milieux de  
réaction

3. Organisation

4. Nouvelles  
phases

## b- Additifs organiques dans la solution d'imprégnation





1. Milieux de  
synthèse

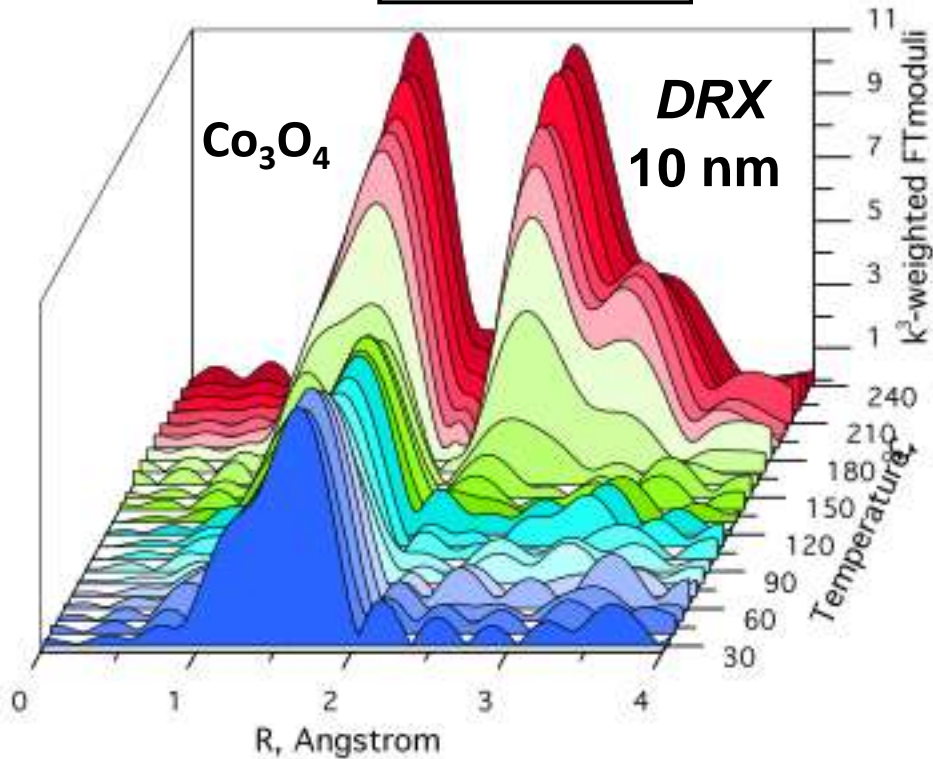
2. Milieux de  
réaction

3. Organisation

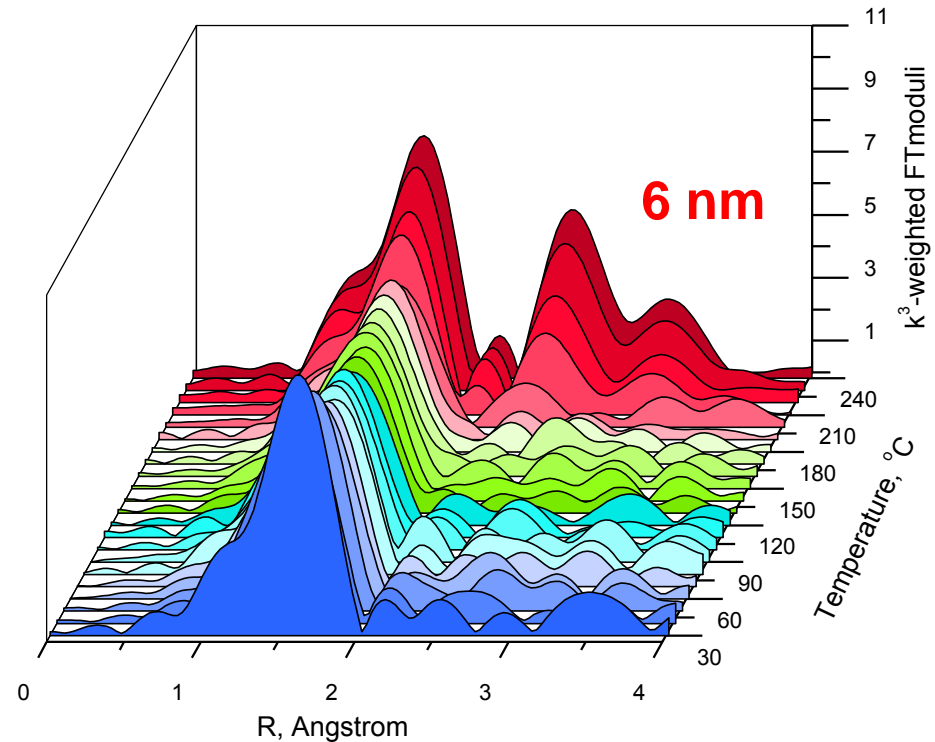
4. Nouvelles  
phases

## EXAFS seuil K de Co

Sans sorbitol



Avec sorbitol



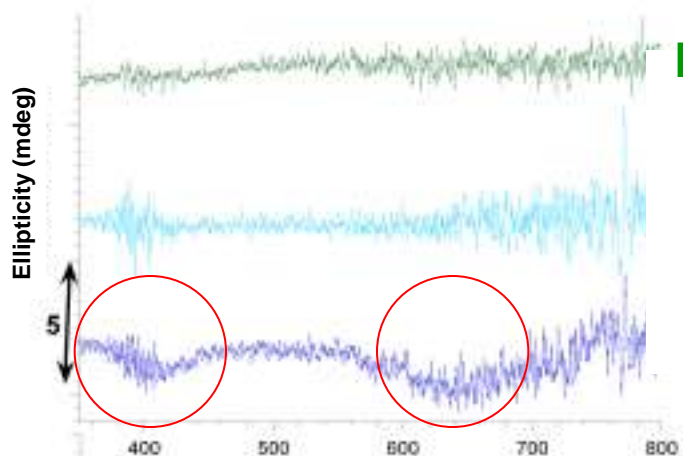
1. Milieux de synthèse

2. Milieux de réaction

3. Organisation

4. Nouvelles phases

## Modes d'action du sorbitol



$\text{Ni}(\text{NO}_3)_2$ , 2.5 M

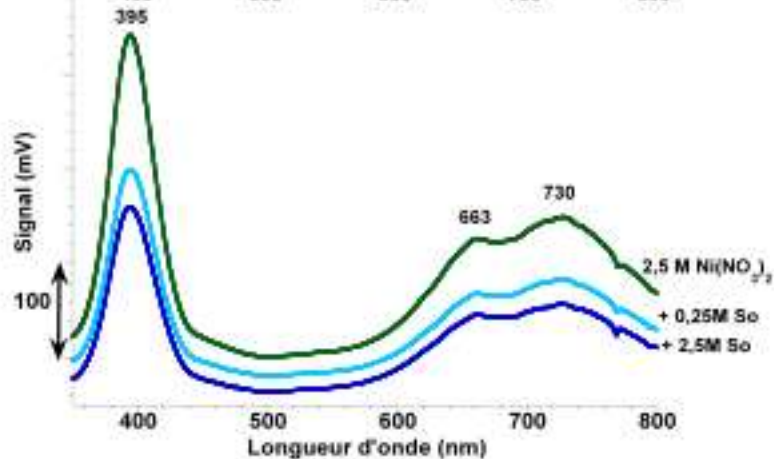
*Dichroïsme circulaire*

$\text{Ni}(\text{NO}_3)_2$ , 2.5 M  
+ sorbitol, 0.25 M

$\text{Ni}(\text{NO}_3)_2$ , 2.5 M  
+ sorbitol, 2.5 M

$$\Delta\epsilon = 2 \cdot 10^{-5} \text{ L} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$$

$$[\text{Ni}(\text{serinato})_2(\text{H}_2\text{O})_2]:$$
$$\Delta\epsilon = 10^{-3} \text{ L} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$$



**Interactions  
de seconde sphère  
entre polyol,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  et  $\text{H}_2\text{O}$   
(liaisons H)**

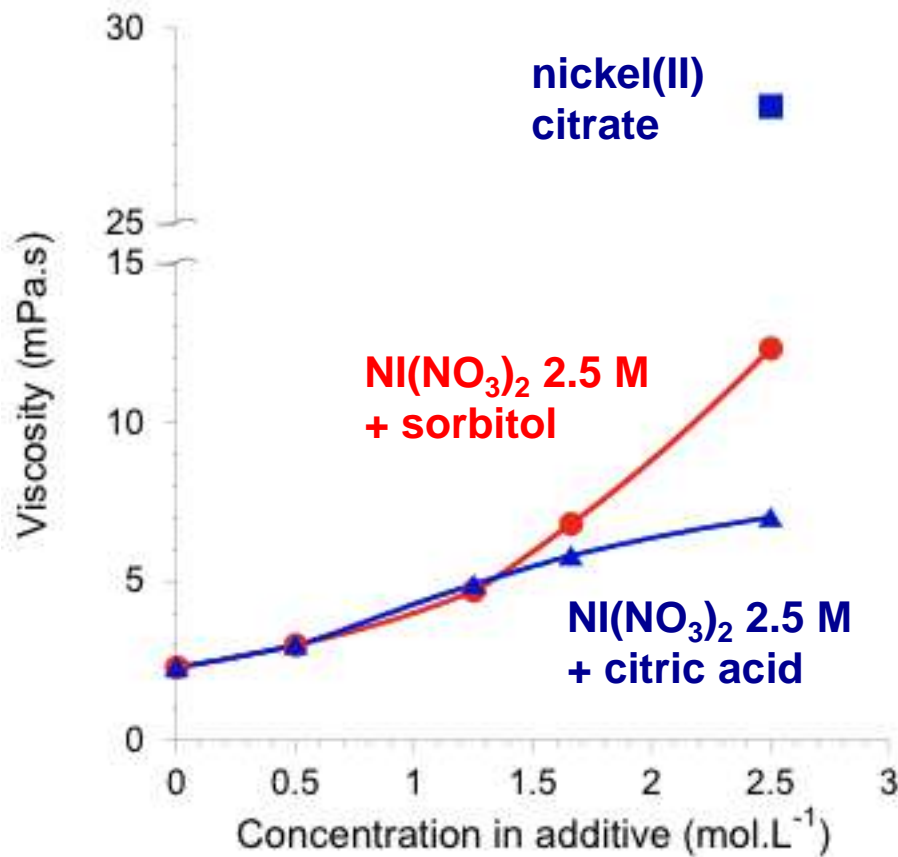
1. Milieux de synthèse

2. Milieux de réaction

3. Organisation

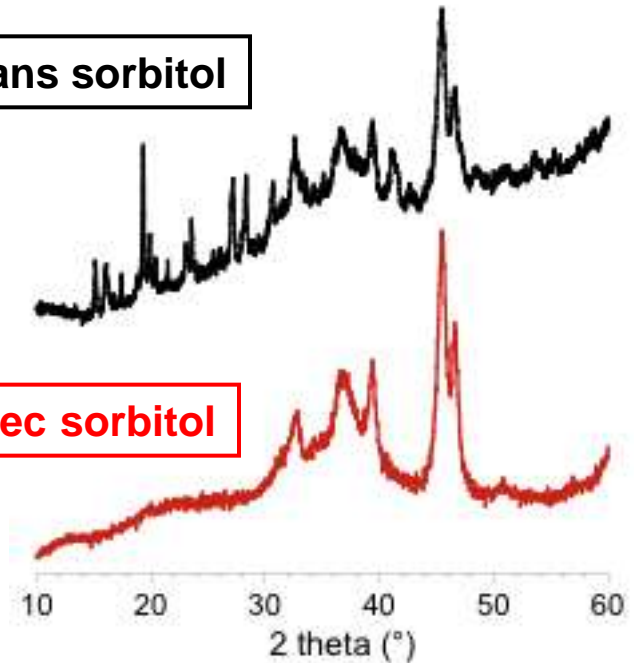
4. Nouvelles phases

## Modes d'action du sorbitol



Sans sorbitol

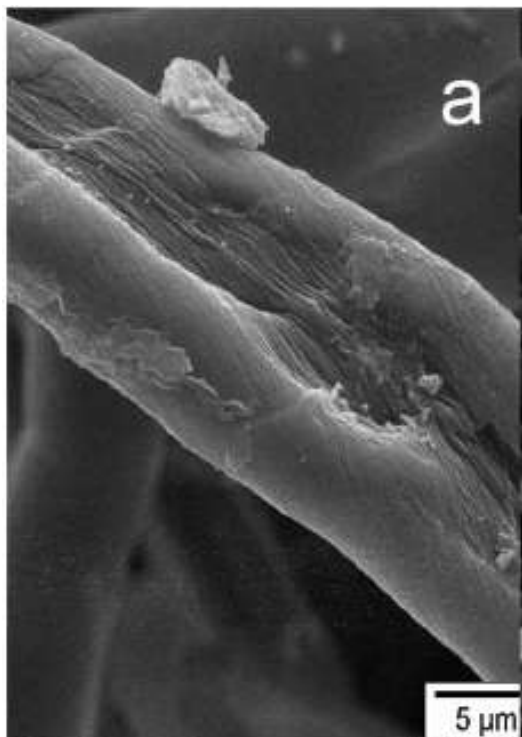
Avec sorbitol



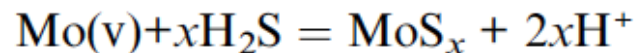
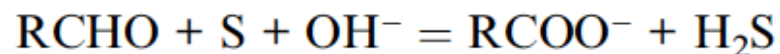
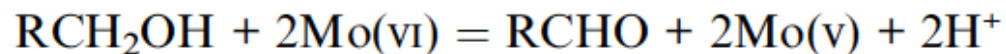
**Augmente la viscosité de la solution**

**Après séchage: rôle dispersant**

## c- Additifs organiques comme réactifs



**cellulose** + éthylène glycol + soufre  
+ heptamolybdate (196° C)



1. Milieux de  
synthèse

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phases

## c- Additifs organiques comme réactifs

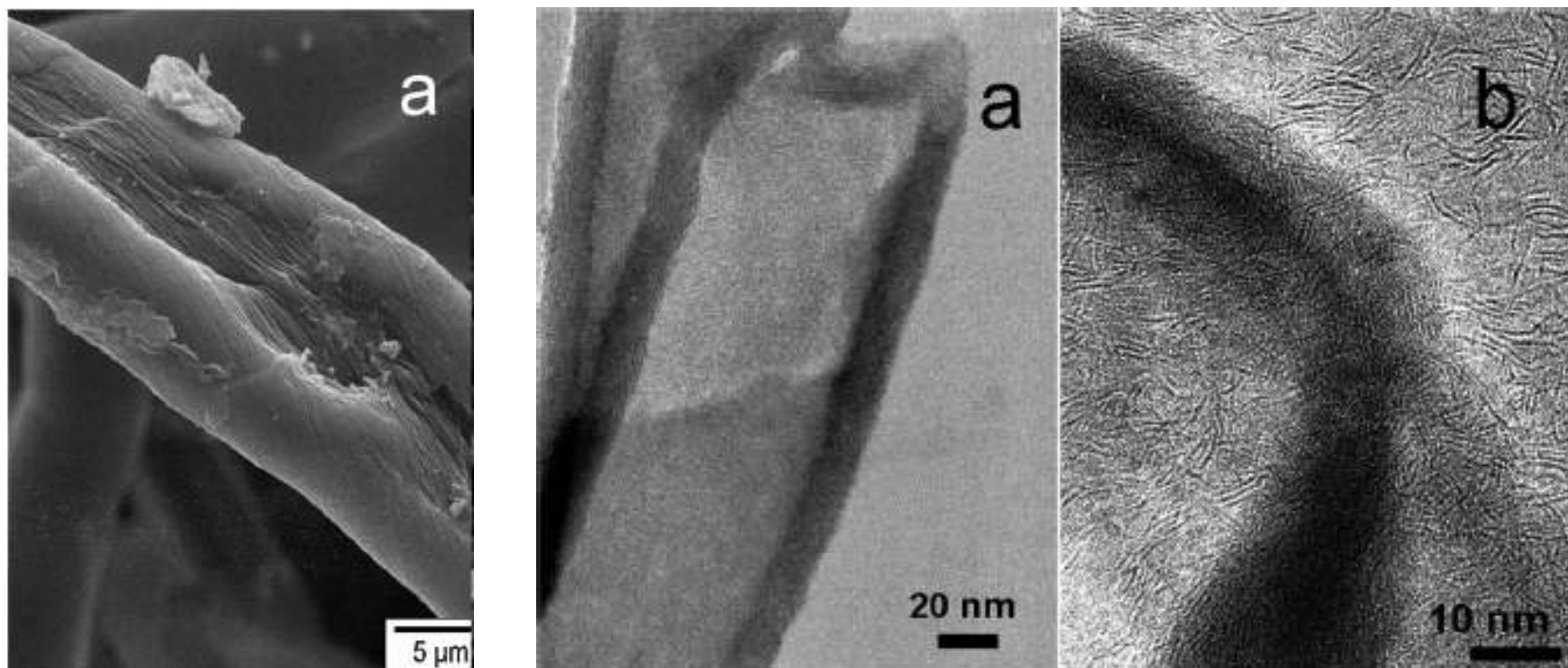


Fig. 2 TEM images of the (cellulose-derived and H<sub>2</sub> treated) solid B at magnifications: 150 000 (a) and 400 000 (b).

1. Milieux de  
synthèse

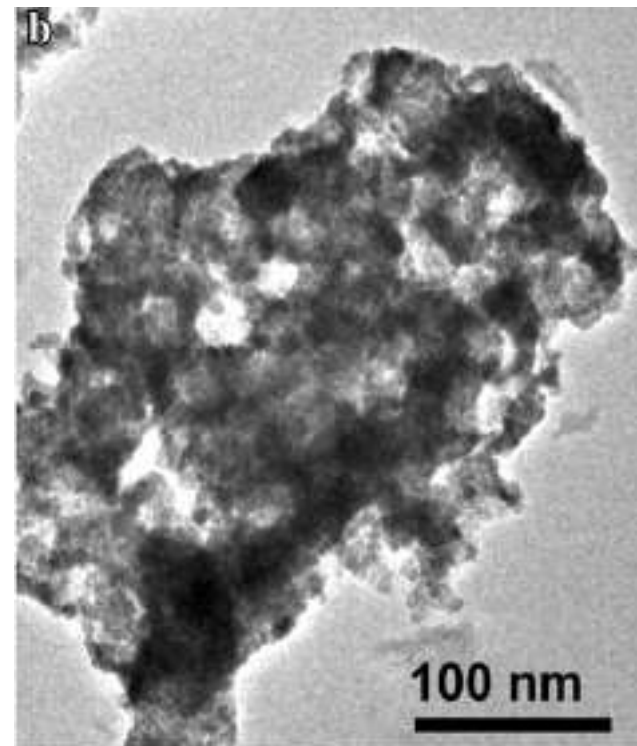
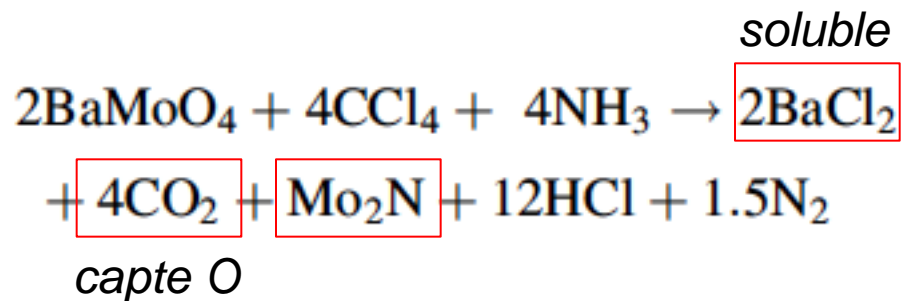
2. Milieux de  
réaction

3. Organisation

4. Nouvelles  
phases

## d- Activation thermique: $\text{NH}_3/\text{CCl}_4$

scheelite  $\rightarrow$  nitrure de Mo poreux



100-140  $\text{m}^2\cdot\text{g}^{-1}$

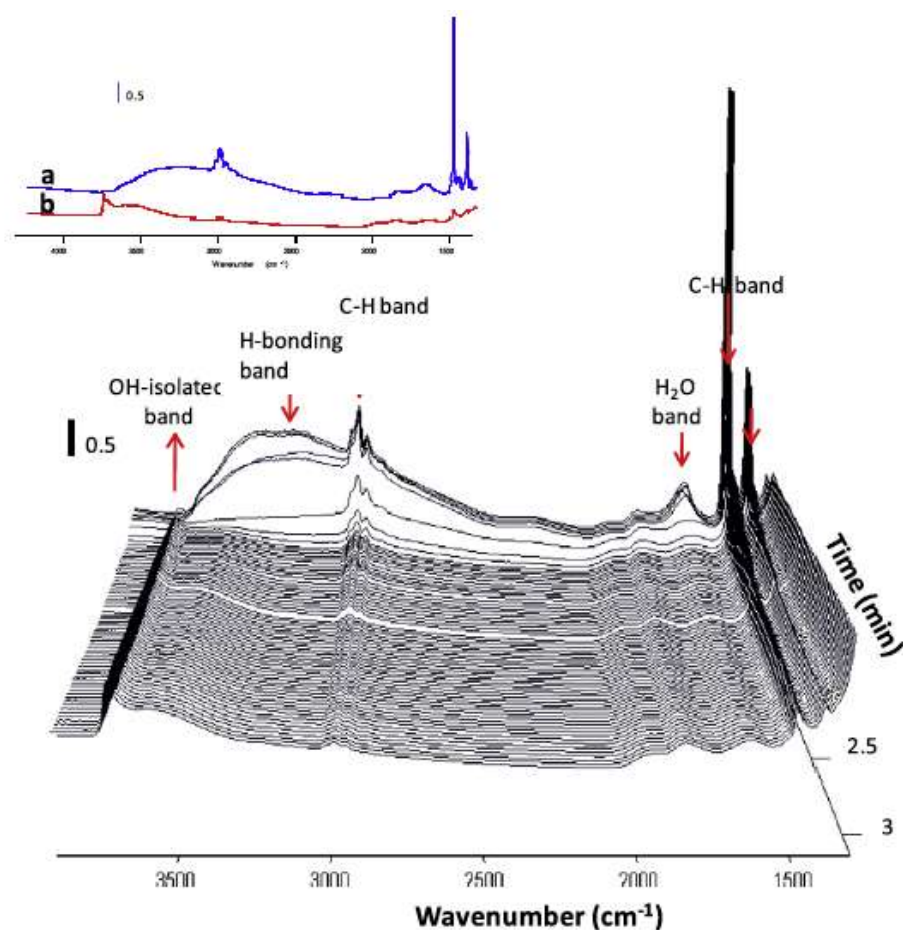
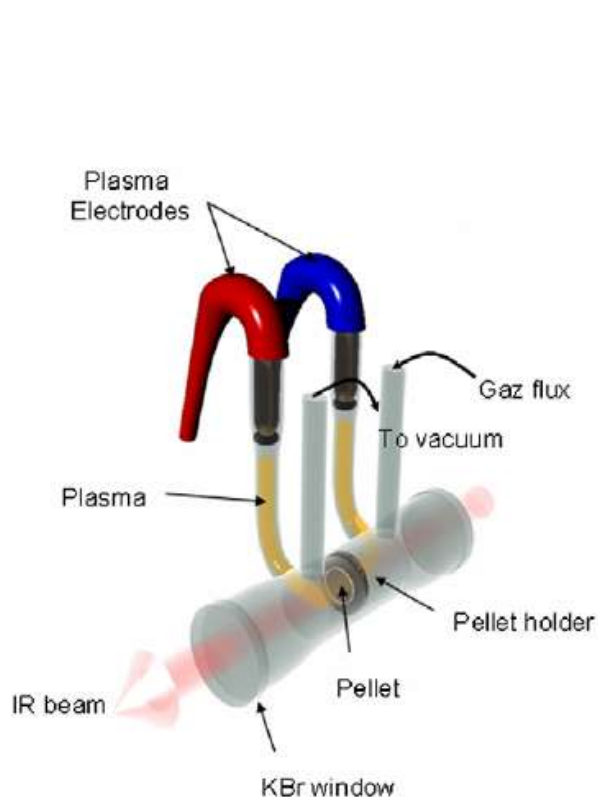
1. Milieux de  
synthèse

2. Milieux de  
réaction

3. Organisation

4. Nouvelles  
phases

## e- Activation par plasma: décomposition d'un template



1. Milieux de  
synthèse

2. Milieux de  
réaction

3. Organisation

4. Nouvelles  
phases

## Nouveaux milieux de réaction

*Transfert de masse*

*Phase gaz/aqueuse*

*Taille des réactifs*

*Phase liquide  
non aqueuse*

*(Biomasse)*



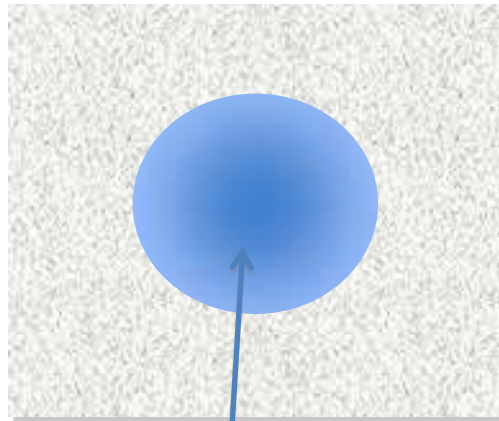
1. Milieux de  
synthèse

2. Milieux de  
réaction

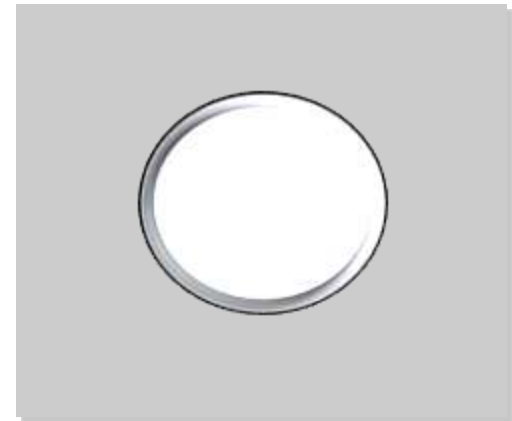
3. Organisation

4. Nouvelles  
phases

## a- Systèmes macroporeux



calcination



template = billes de polymère  
émulsion

1. Milieux de  
synthèse

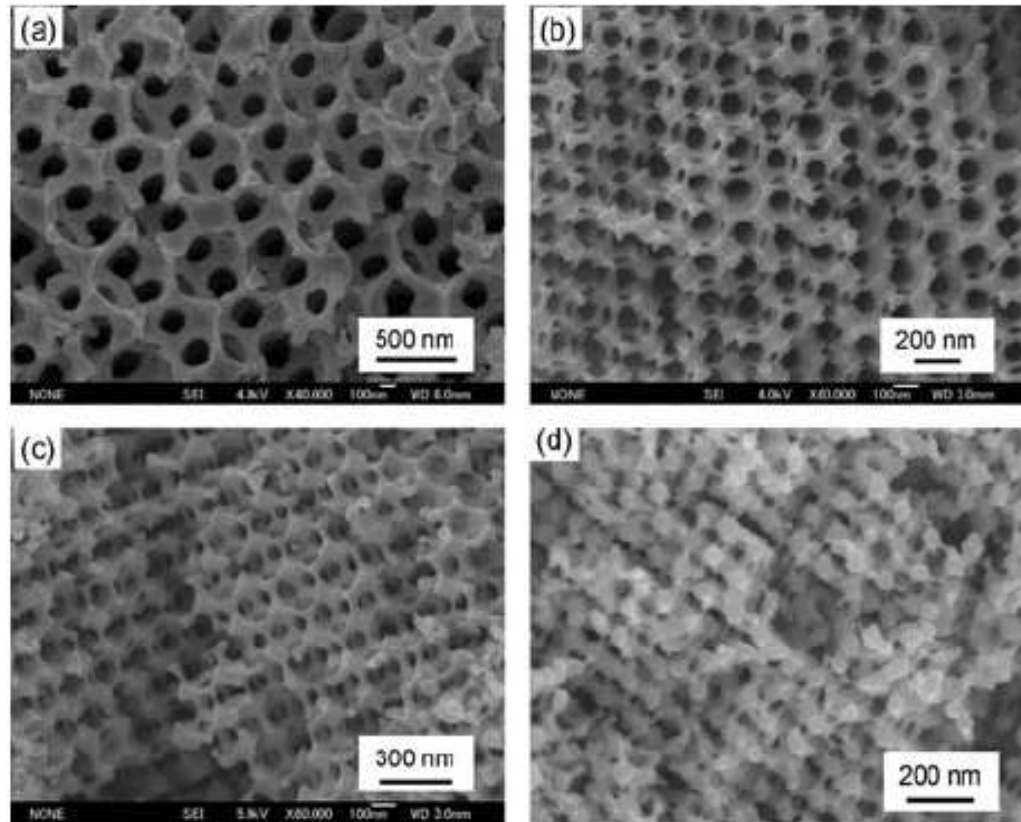
2. Milieux de  
réaction

3. Organisation

4. Nouvelles  
phases

## Systemes macroporeux: oxydes

$\text{WO}_3$  synthétisé  
par imprégnation  
de métatungstate  
d'ammonium autour  
de billes de PMMA  
de taille différente  
(492-86 nm)  
et calcination à  $500^\circ \text{C}$



1. Milieux de  
synthèse

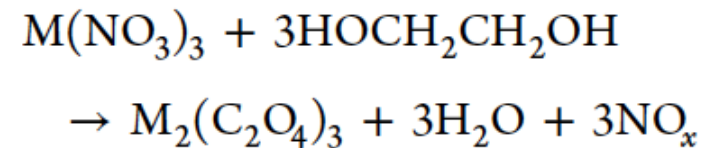
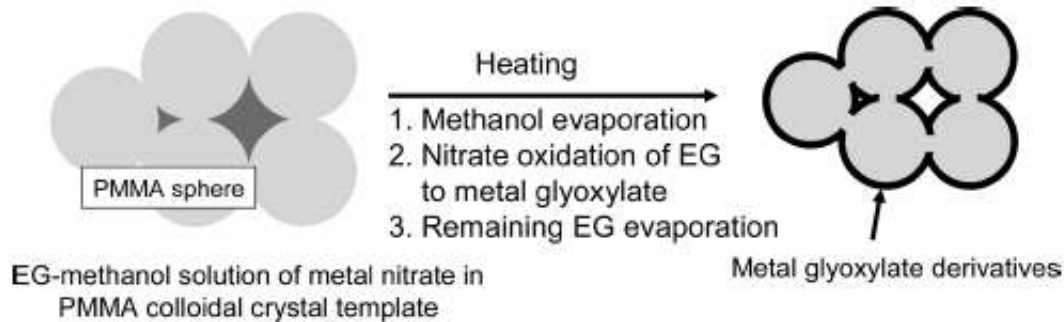
2. Milieux de  
réaction

3. Organisation

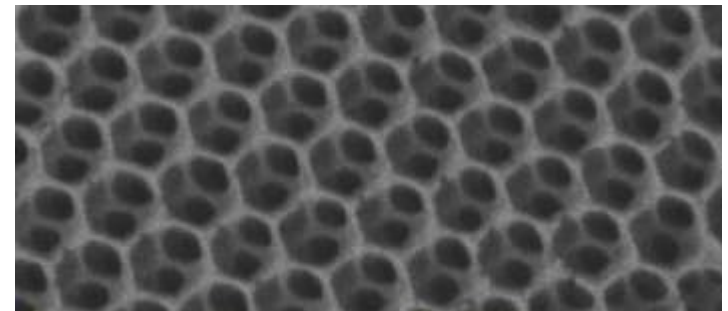
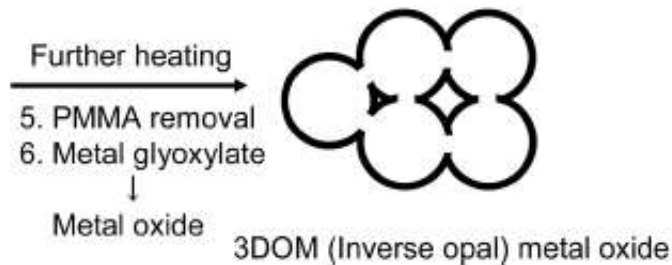
4. Nouvelles  
phases

## Systemes macroporeux: oxydes

oxydes mixtes: spinelles, perovskites, cérines-zircones



$T < T_g$  du PMMA



1. Milieux de synthèse

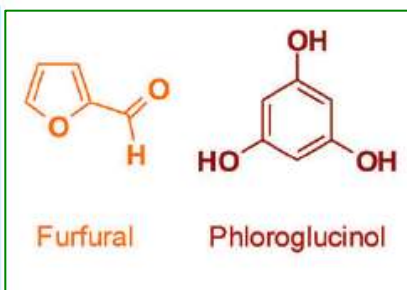
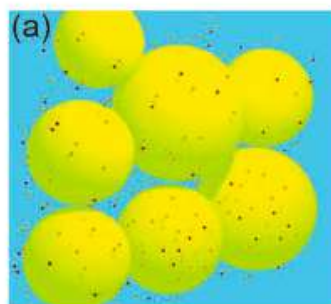
2. Milieux de réaction

3. Organisation

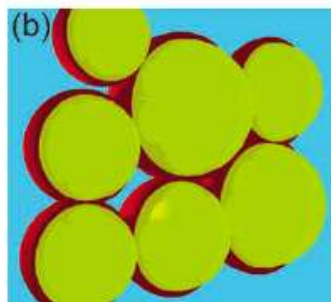
4. Nouvelles phases

# Systemes macroporeux: carbones

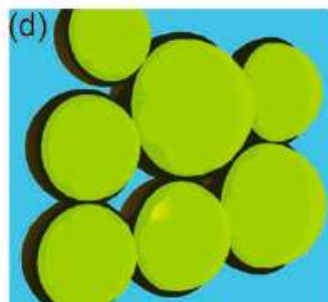
Soft-template: oil-in-water emulsion



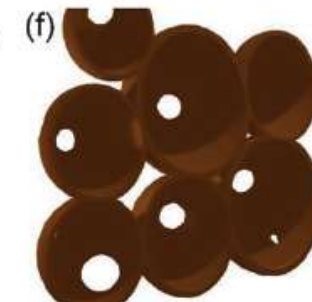
Prepolymerization



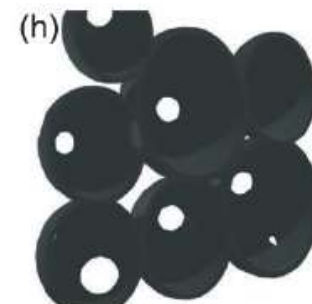
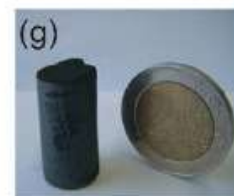
Hydrothermal carbonization



1. Soxhlet extraction  
2. Drying



High Internal Phase Emulsion  
Carbo-HIPE



Pyrolysis

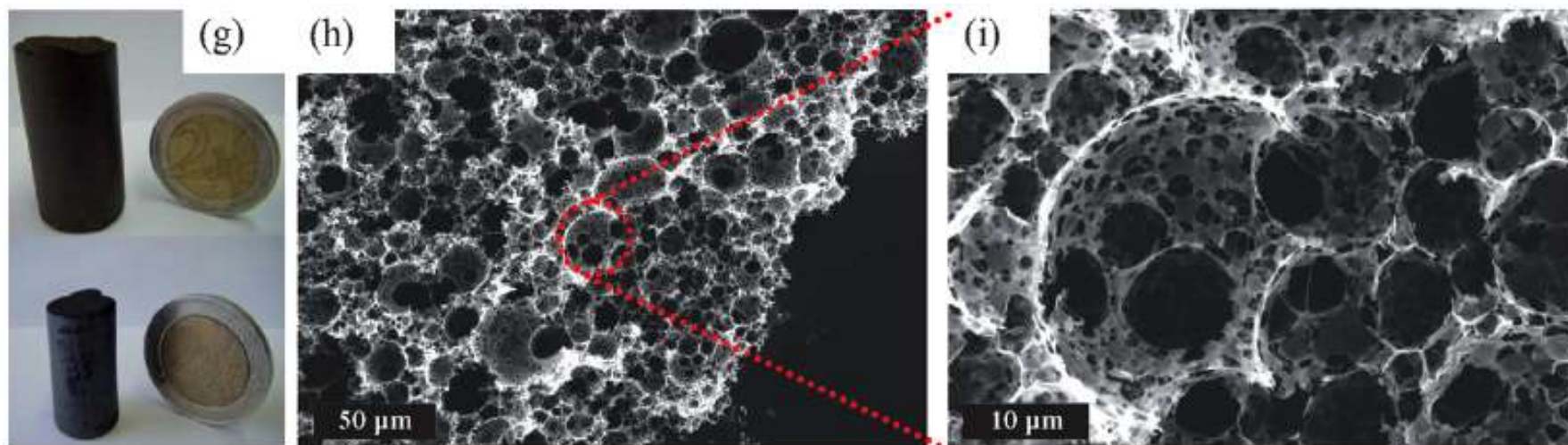
1. Milieux de  
synthèse

2. Milieux de  
réaction

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phases

## Systemes macroporeux: carbones



pyrolyse : 950° C – 535 m<sup>2</sup>.g<sup>-1</sup> – macropores de 4000 nm

1. Milieux de  
synthèse

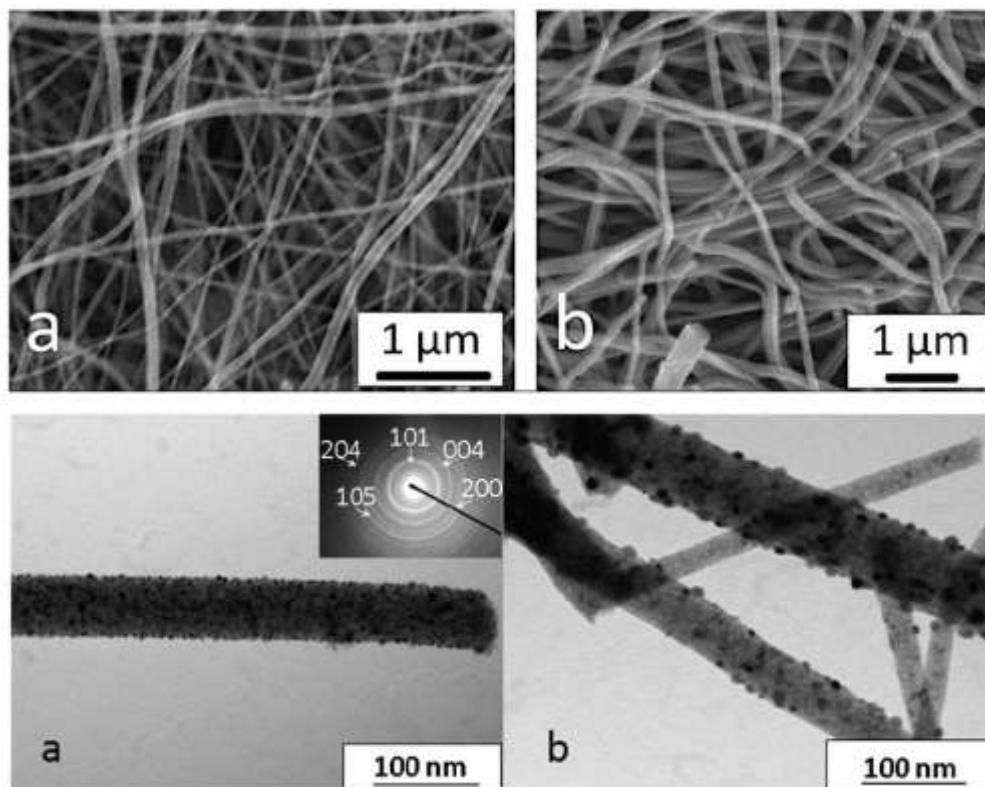
2. Milieux de  
réaction

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## Nanofibres d'oxyde (électrospinning)

fibres de Pt/Ti(Nb)O<sub>2</sub>



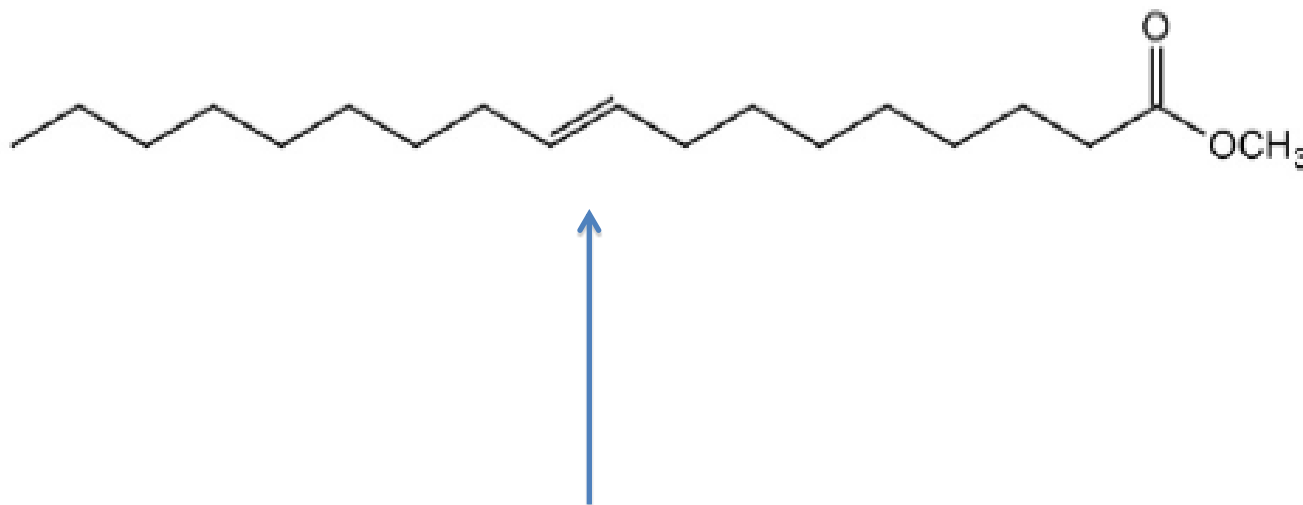
1. Milieux de  
synthèse

2. Milieux de  
réaction

3. Organisation

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phases

## b- Systèmes hydrophobes



époxydation par  $\text{H}_2\text{O}_2$  hydrosoluble /  $[\text{PO}_4[\text{WO}(\text{O}_2)_2]_4]^{3-}$

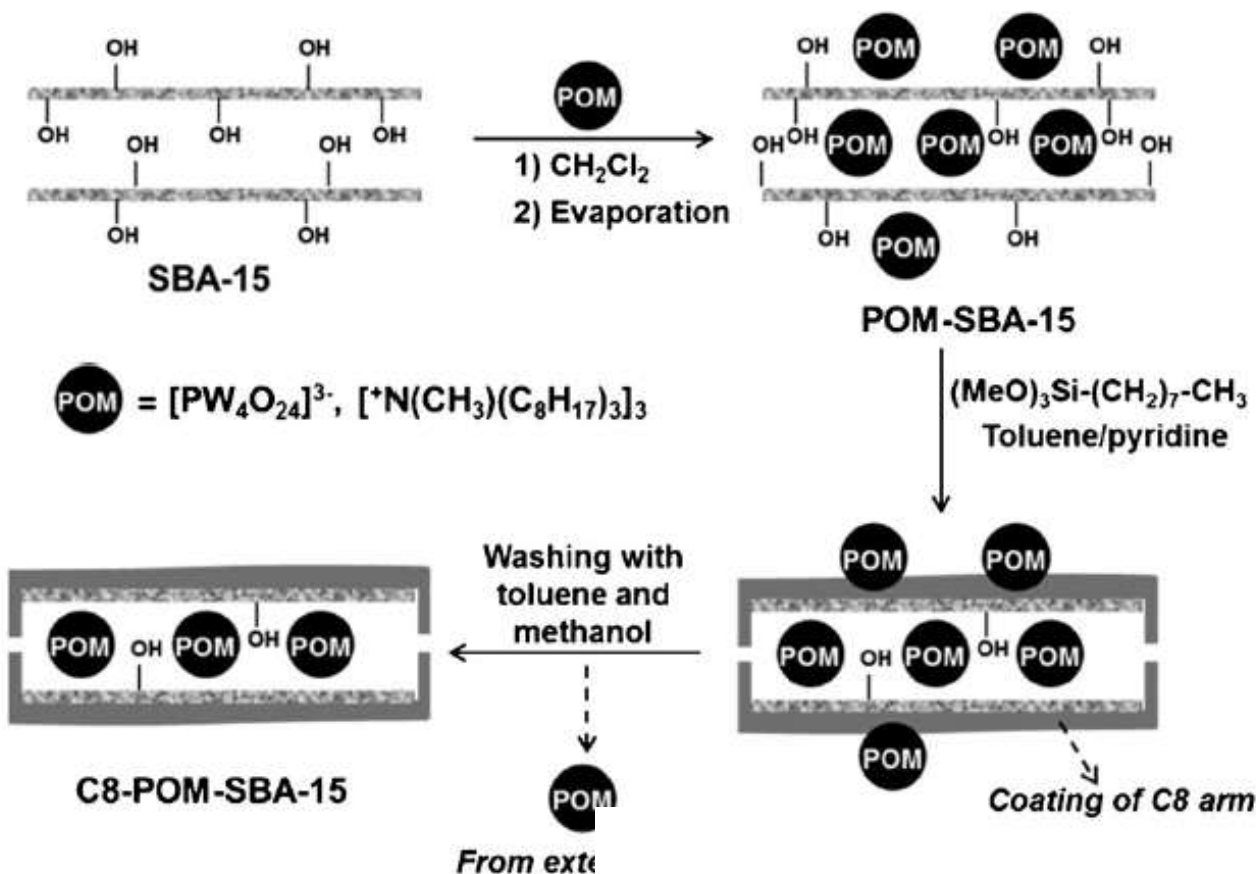
1. Milieux de  
synthèse

2. Milieux de  
réaction

3. Organisation

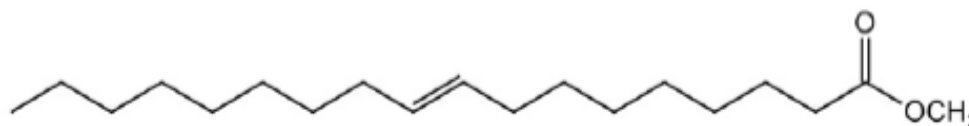
4. Nouvelles  
phases

## Systemes hydrophobes





## Systemes hydrophobes



**Table 3** Epoxidation of methyl oleate with the C8-POM-SBA-15 catalyst<sup>a</sup>

Entry	Catalytic run	Conv. <sup>b</sup> (%)	Epoxide selectivity <sup>b</sup> (%)	W leaching <sup>c</sup> /ppm
1	1	85	5	<0.1
2	2	87	51	0.2
3	3	86	47	0.3
4	4	86	50	0.2

<sup>a</sup> 338 K, 15 h, H<sub>2</sub>O<sub>2</sub>/MO (3/1), O<sub>2</sub> 10 mL min<sup>-1</sup>. <sup>b</sup> Determined by gas chromatography. <sup>c</sup> Determined by ICP.

1. Milieux de  
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Organisation

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phases

## Organisation du site catalytique

***Promoteurs***

***Frittage***

***Hétérogénéité***

***Localisation***

***Distance***

***Nanostructuration***

1. Milieux de  
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phases

## a- Localisation de promoteurs

( $\text{Mn}^{x+}$  sur  $\text{Co}_3\text{O}_4$ )/ $\text{TiO}_2$

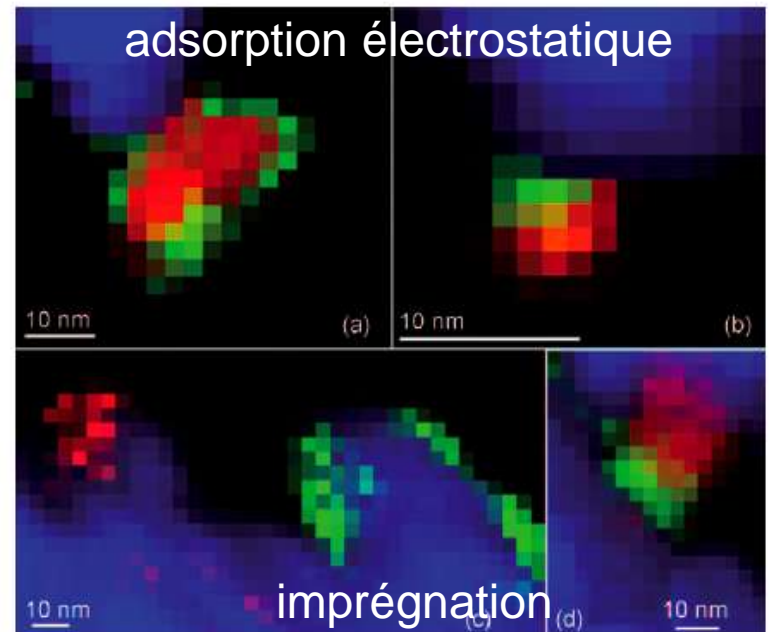
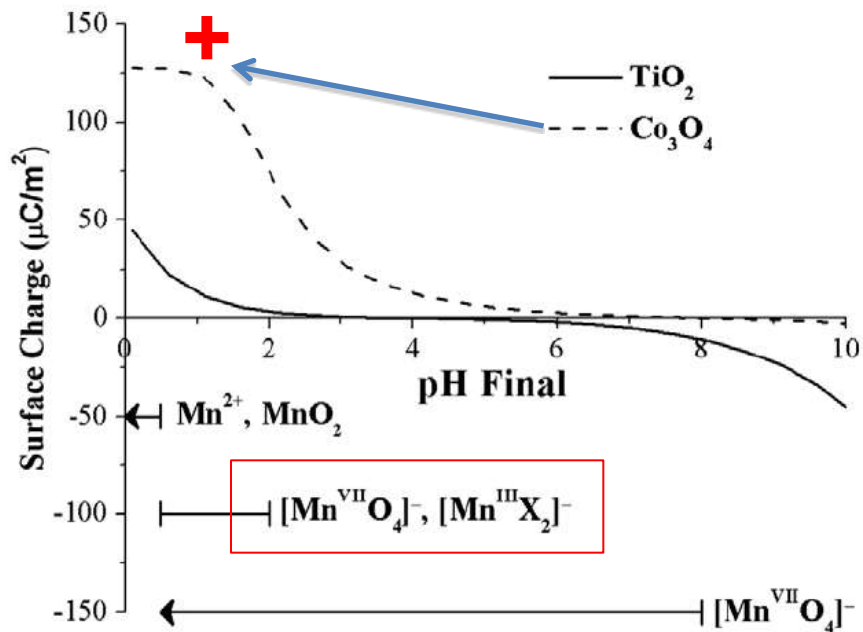


Figure 2. EELS chemical maps (blue:Ti, red:Co, green:Mn) for the a) calcined and b) reduced  $\text{Mn}^{\text{SEA}}/\text{Co}/\text{TiO}_2$  catalyst and the c) calcined and d) reduced  $\text{Mn}^{\text{DI}}/\text{Co}/\text{TiO}_2$  catalyst.

T.E. Feltes, L. Espinosa-Alonso, E. de Smitet al., J. Catal. **270**, 95, 2010

T.E. Feltes, Y. Zhao, R.F. Klie, R.J. Meyer, J.R. Regalbuto, ChemCatChem **2**, 1065, 2010

1. Milieux de  
synthèse

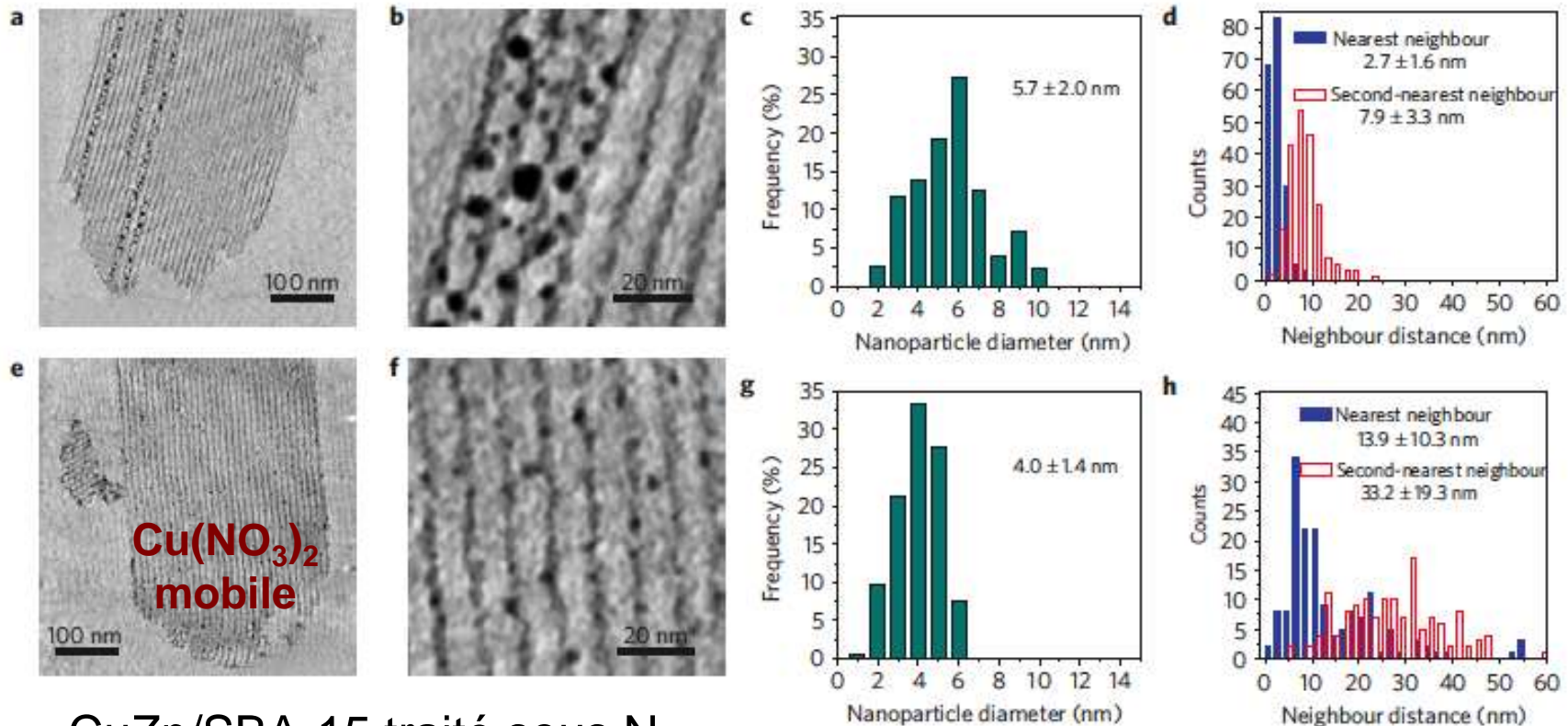
2. Milieux de  
réaction

3.  
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phases

## b- Répartition spatiale de nanoparticules

CuZn/SBA-15 traité sous NO



CuZn/SBA-15 traité sous N<sub>2</sub>

1. Milieux de  
synthèse

2. Milieux de  
réaction

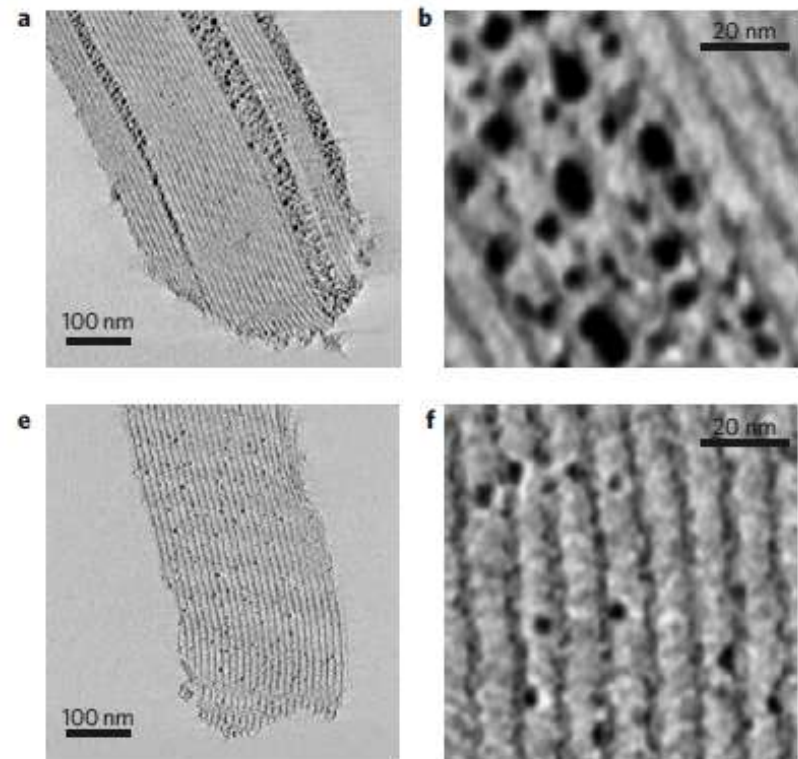
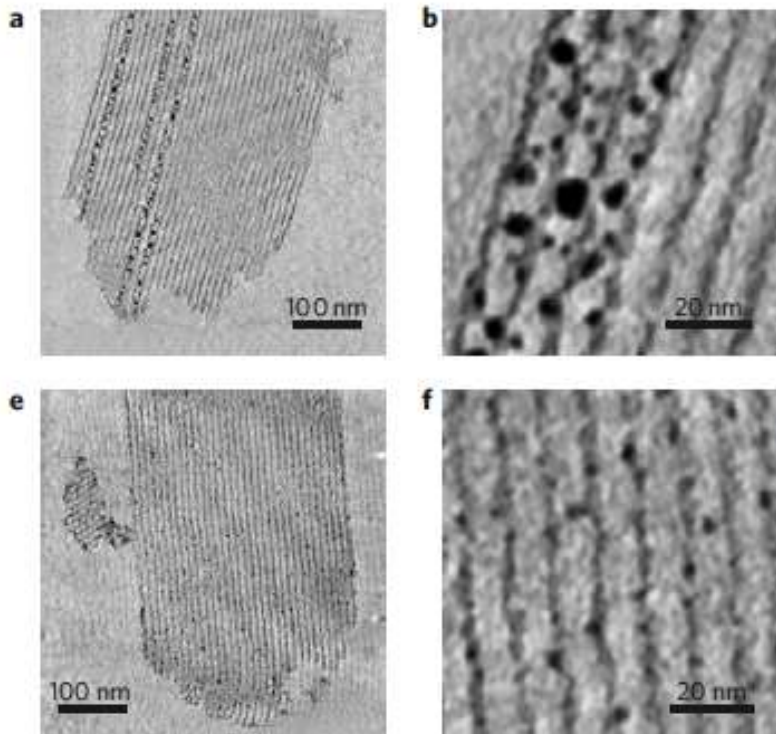
3.  
Organisation

4. Nouvelles  
phases

## b- Répartition spatiale de nanoparticules

CuZn/SBA-15 traité sous NO

après synthèse de CH<sub>3</sub>OH



CuZn/SBA-15 traité sous N<sub>2</sub>

1. Milieux de  
synthèse

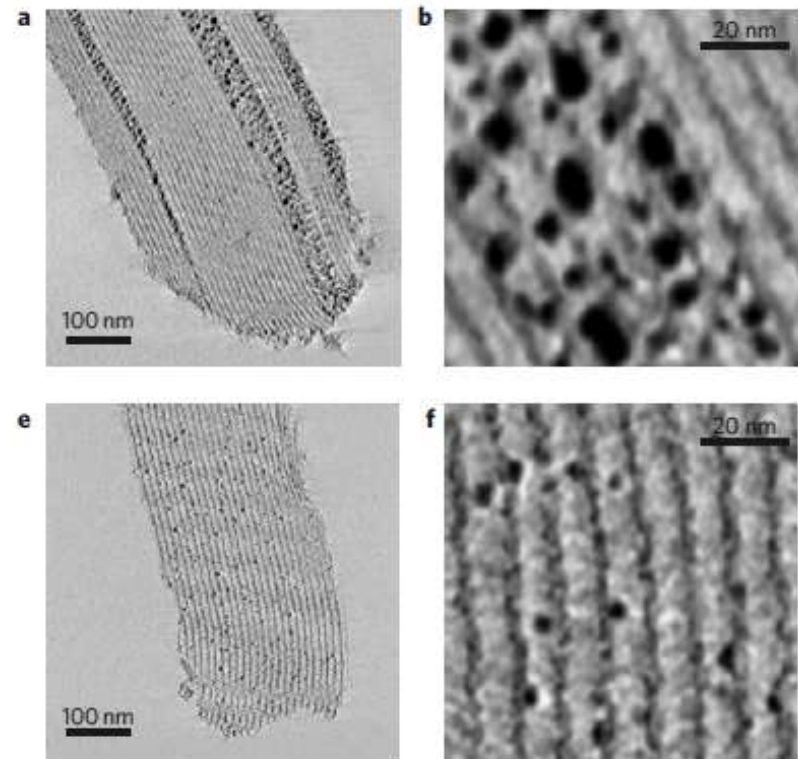
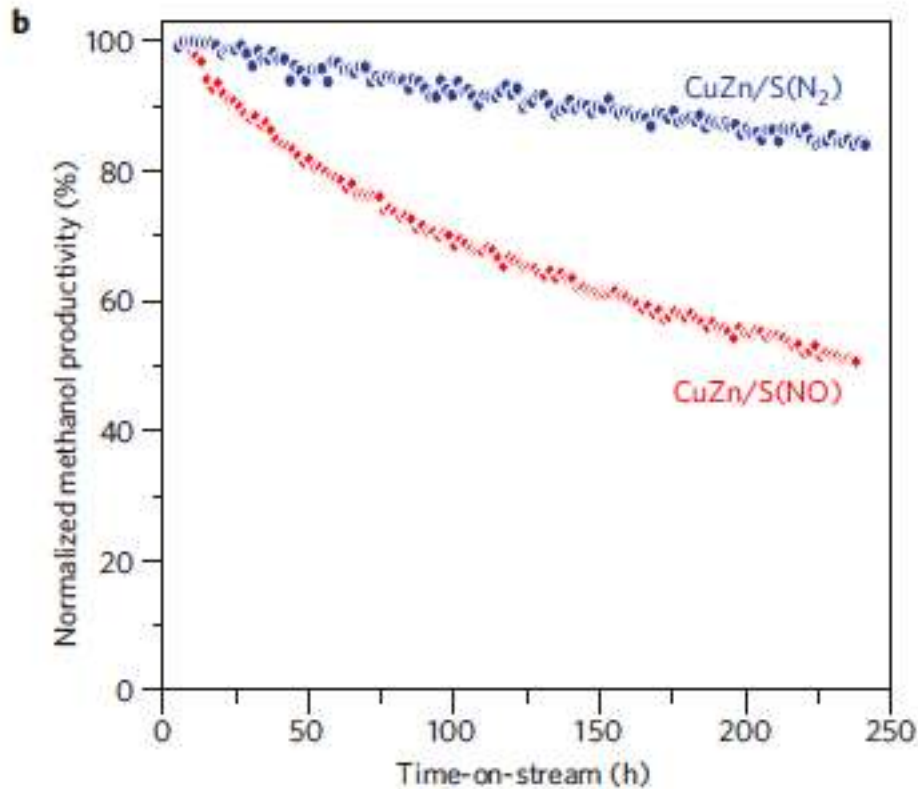
2. Milieux de  
réaction

3.  
Organisation

4. Nouvelles  
phases

## b- Répartition spatiale de nanoparticules

après synthèse de  $\text{CH}_3\text{OH}$



1. Milieux de  
synthèse

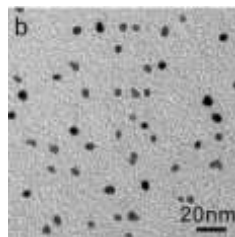
2. Milieux de  
réaction

3.  
Organisation

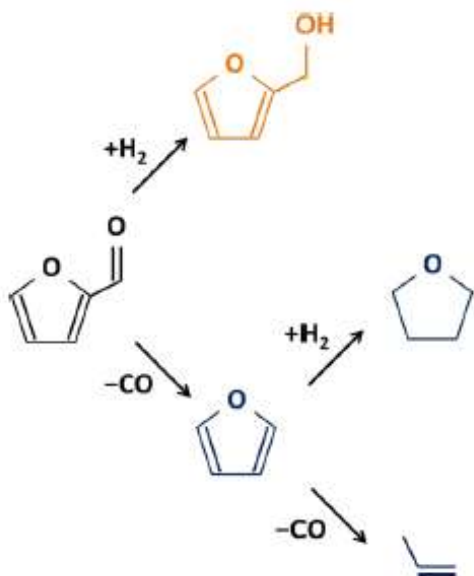
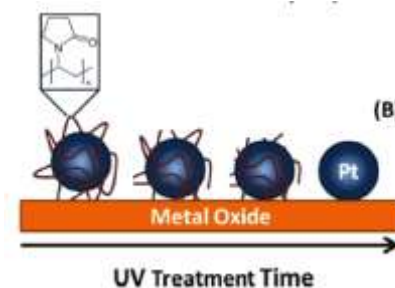
4. Nouvelles  
phases

## c- Réactions aux interfaces

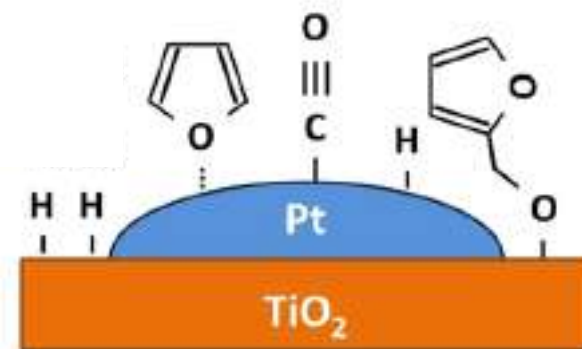
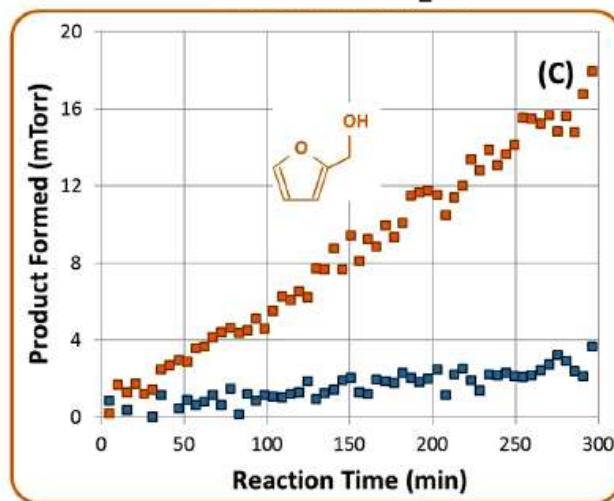
Pt (5 nm)  
+ PVP



LBlodgett  
 $h\nu$  (UV)



UV Cleaned Pt



1. Milieux de  
synthèse

2. Milieux de  
réaction

3.  
Organisation

4. Nouvelles  
phases

## d- Nanostructuration

croissance de nanotubes  $\text{Ti}(\text{Nb})\text{O}_2(\text{N})$  par anodisation de Ti en présence de  $\text{F}^-$

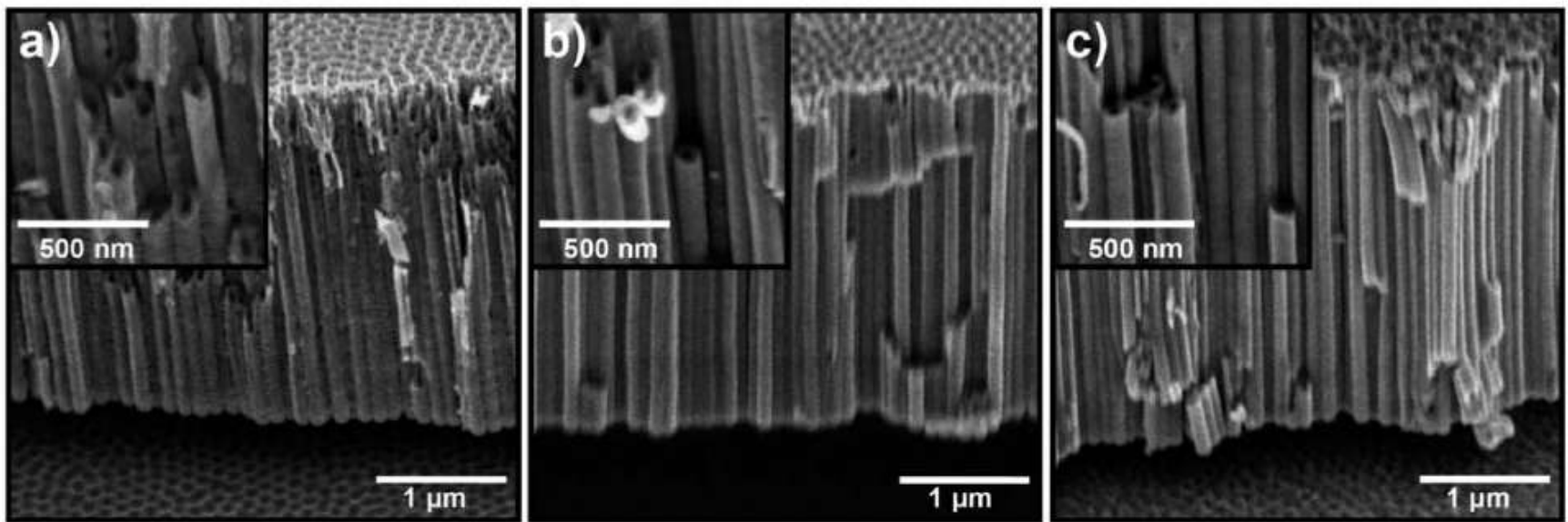


Fig. 2 SEM images at 45° inclined view of: (a)  $\text{TiO}_2$ -NTs; (b) 0.5 Nb/ $\text{TiO}_2$ -NTs and (c) 1.0 Nb/ $\text{TiO}_2$ -NTs. The insets show magnifications of the nanotubular structure.



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**Table 2** Calculated yields for the different samples in the UV, visible and whole spectral domain (AM1.5) for undoped and Nb-doped TiO<sub>2</sub>-NTs samples annealed in air or diluted NH<sub>3</sub>

Sample	Annealing gas	Yield <sup>a</sup>	UV yield <sup>b</sup>	Vis yield <sup>c</sup>
TiO <sub>2</sub> -NTs	Air	0.115(5)	2.439(8)	0.004(5)
TiO <sub>2</sub> -NTs	d.NH <sub>3</sub>	0.032(5)	0.261(8)	0.038(5)
0.50 Nb/TiO <sub>2</sub> -NTs	d.NH <sub>3</sub>	0.117(5)	1.488(8)	0.090(5)

<sup>a</sup> %/whole solar spectrum (280 >  $\lambda$  > 4000 nm). <sup>b</sup> %/ $\lambda$  < 400 nm. <sup>c</sup> %/800 >  $\lambda$  > 400 nm.

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## Nouvelles phases catalytiques

***Activité***

***Stabilité***

***Sélectivité***

***Innocuité***

***Coût***

***Disponibilité***

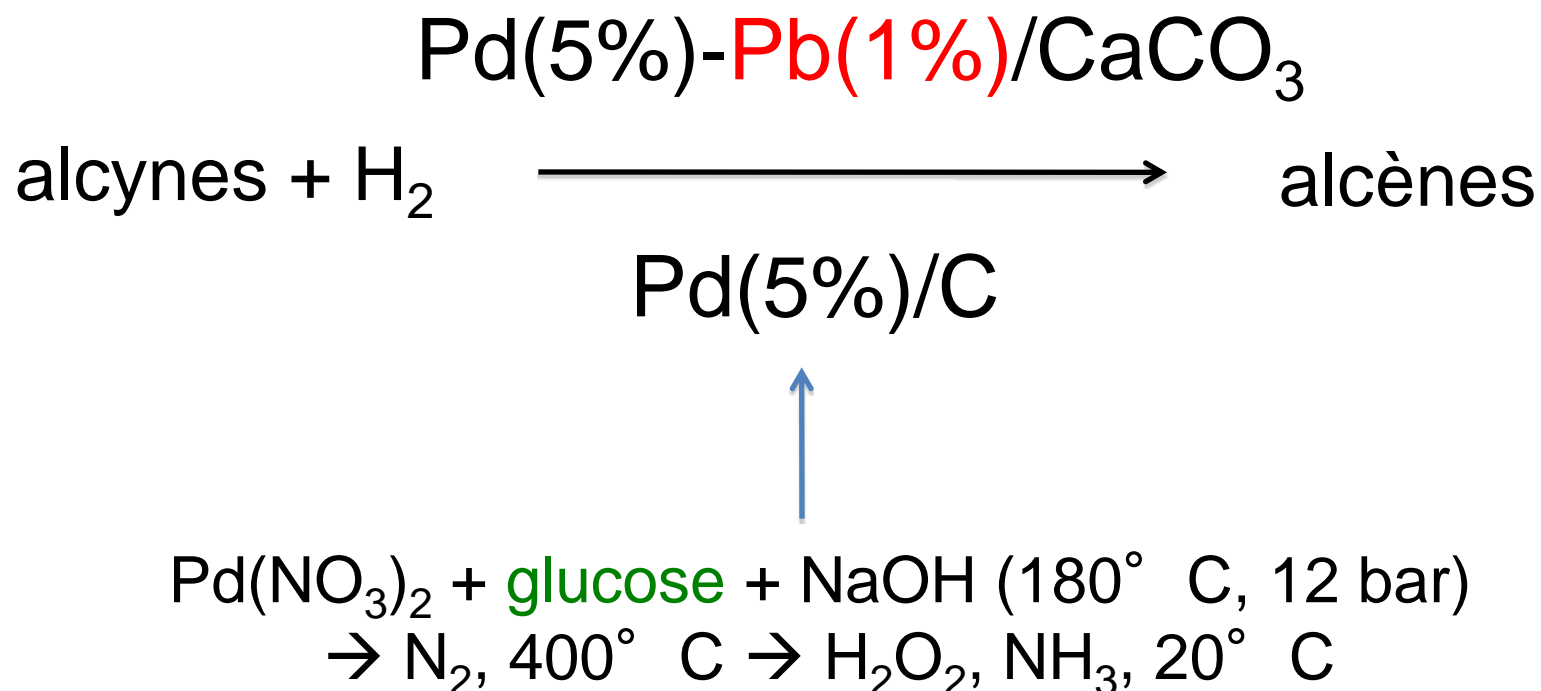
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## a- Catalyseurs monométalliques sélectifs

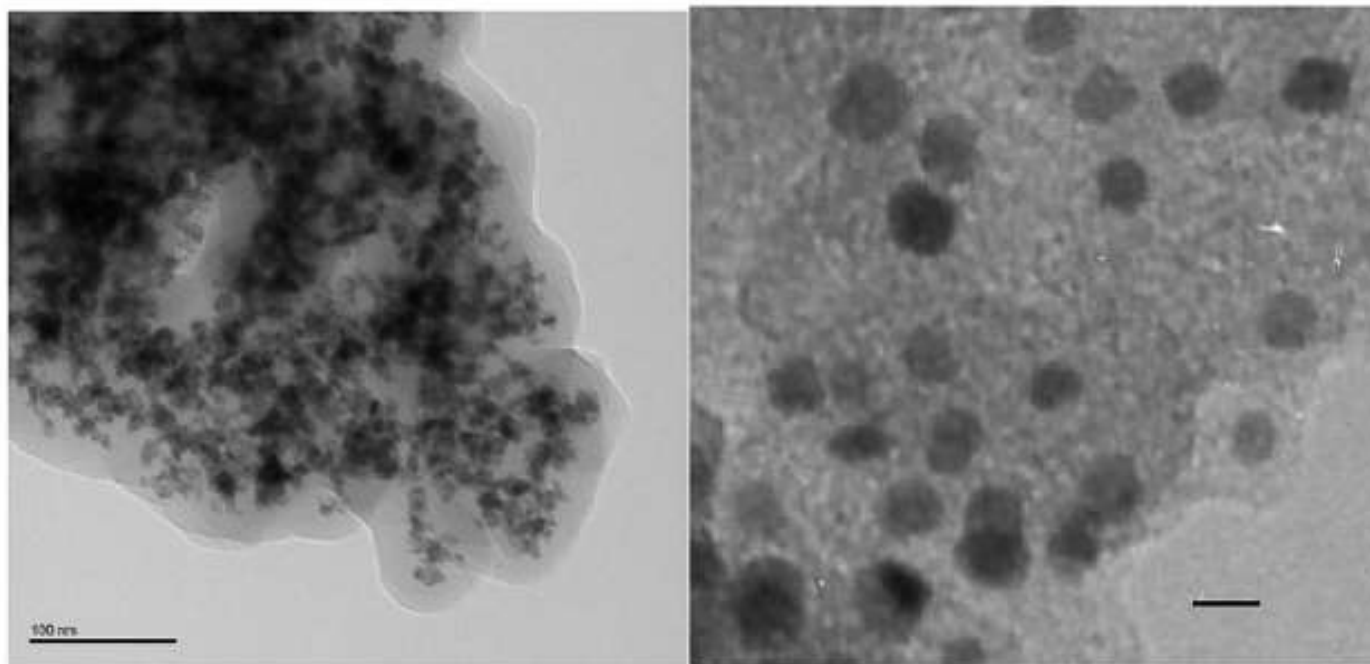


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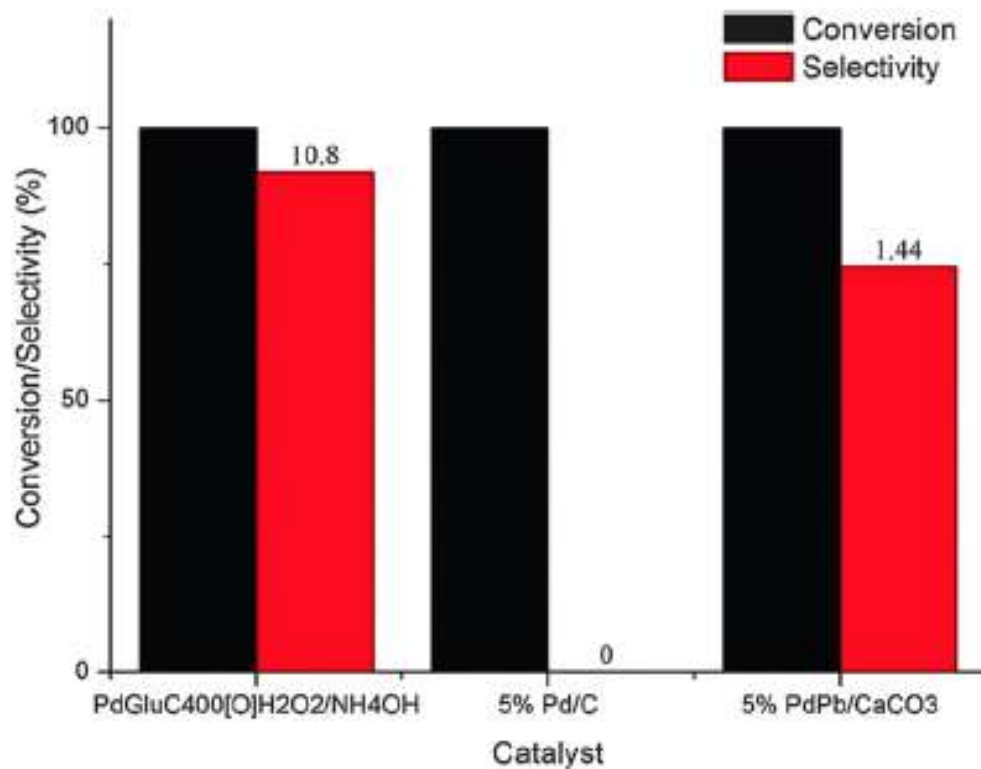
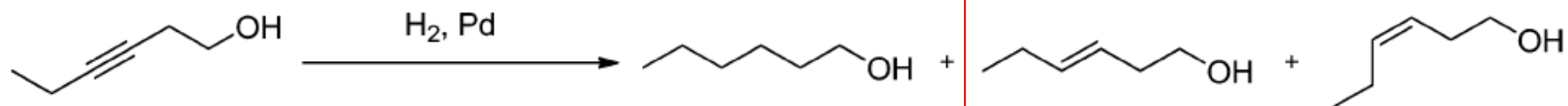
**Fig. 1** TEM of (a) glucose derived carbon embedding 5–6 nm Pd nanoparticles after treatment at 400 °C, scale bar 100 nm (left), (b) HRTEM of the same sample (right), scale bar 5 nm.

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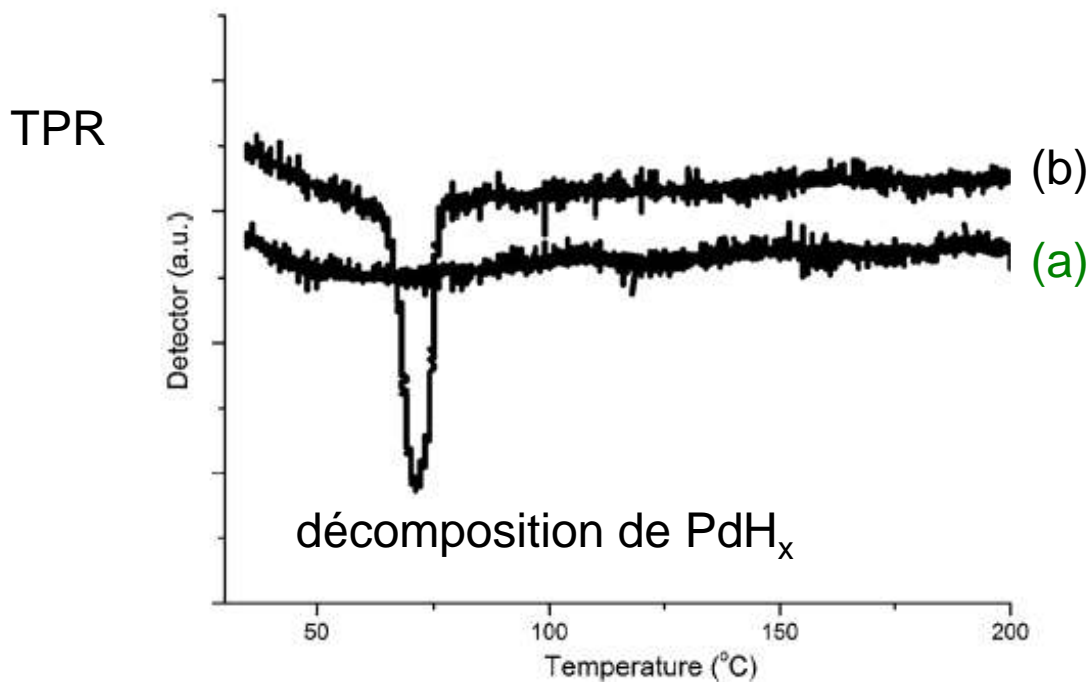
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	Calcination of Pd glucose catalyst/°C	Lattice parameter $a_0^a$	Approx. C at%
(a)	As-synthesised	0.3923(4)	4.7
	400	0.3994(3)	15.1
(b)	400 in H <sub>2</sub>	0.3892(3)	0.3



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## b- Combinaisons bimétalliques

									13	14	15	16	17	18
									5	6	7	8	9	10
									<b>B</b>	<b>C</b>	<b>N</b>	<b>O</b>	<b>F</b>	<b>Ne</b>
									10.81	12.011	14.007	15.999	18.998	20.180
									13	14	15	16	17	18
									<b>Al</b>	<b>Si</b>	<b>P</b>	<b>S</b>	<b>Cl</b>	<b>Ar</b>
									26.982	28.085	30.974	32.06	35.45	39.948
4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Ga</b>	<b>Ge</b>	<b>As</b>	<b>Se</b>	<b>Br</b>	<b>Kr</b>
47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.38	69.723	72.63	74.922	78.96	79.904	83.798
40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
<b>Zr</b>	<b>Nb</b>	<b>Mo</b>	<b>Tc</b>	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>	<b>Ag</b>	<b>Cd</b>	<b>In</b>	<b>Sn</b>	<b>Sb</b>	<b>Te</b>	<b>I</b>	<b>Xe</b>
91.224	92.906	95.96	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
<b>Hf</b>	<b>Ta</b>	<b>W</b>	<b>Re</b>	<b>Os</b>	<b>Ir</b>	<b>Pt</b>	<b>Au</b>	<b>Hg</b>	<b>Tl</b>	<b>Pb</b>	<b>Bi</b>	<b>Po</b>	<b>At</b>	<b>Rn</b>
178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)

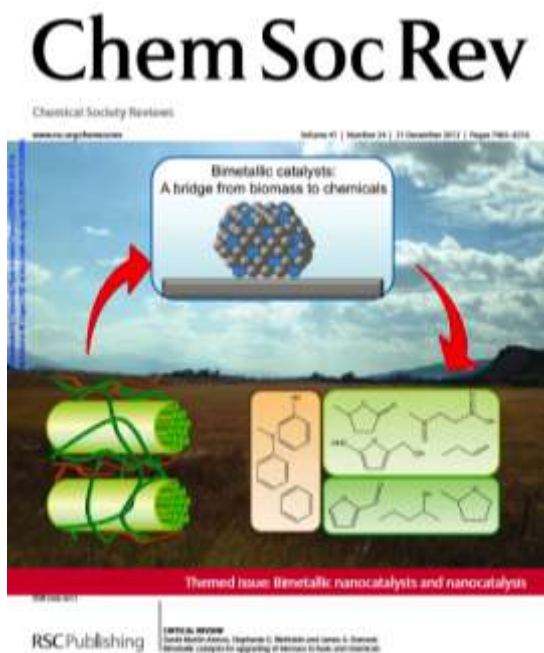
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## Reformage en phase aqueuse



Catalyst	Feedstock	Conversion (%)	H <sub>2</sub> selectivity (%)
RANEY <sup>®</sup> Ni <sub>14</sub> Sn	Sorbitol	> 90%	46
Pt/Al <sub>2</sub> O <sub>3</sub>	Sorbitol	> 90%	46
RANEY <sup>®</sup> Ni <sub>14</sub> Sn	Glycerol	> 90%	76
Pt/Al <sub>2</sub> O <sub>3</sub>	Glycerol	> 90%	51
RANEY <sup>®</sup> Ni <sub>14</sub> Sn	Ethylene glycol	> 90%	95
Pt/Al <sub>2</sub> O <sub>3</sub>	Ethylene glycol	> 90%	88
RANEY <sup>®</sup> Ni	Ethylene glycol	> 90%	28

RuSn: hydrogénations sélectives

PtBi: oxydation sélective du glucose et du furfural



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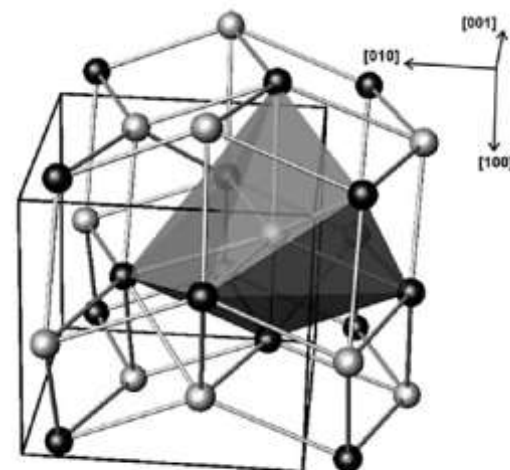
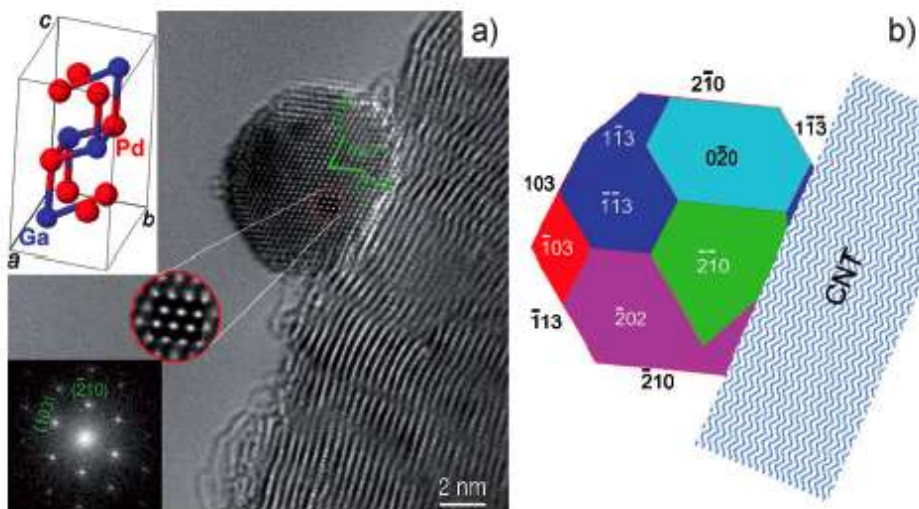


Fig. 1. In the crystal structure of PdGa each Pd atom (white spheres) is surrounded by seven Ga atoms (black spheres). The environment of one palladium atom is shown as polyhedron.

## Pd<sub>2</sub>Ga/CNT

$\text{Pd}(\text{NO}_3)_2 + \text{Ga}(\text{NO}_3)_3$ , calc 250° C, réd 550° C

J. Osswald, R. Giedigkeit, R.E. Jentoft, M. Armbrüster et al., J. Catal. **258**, 210, 2008

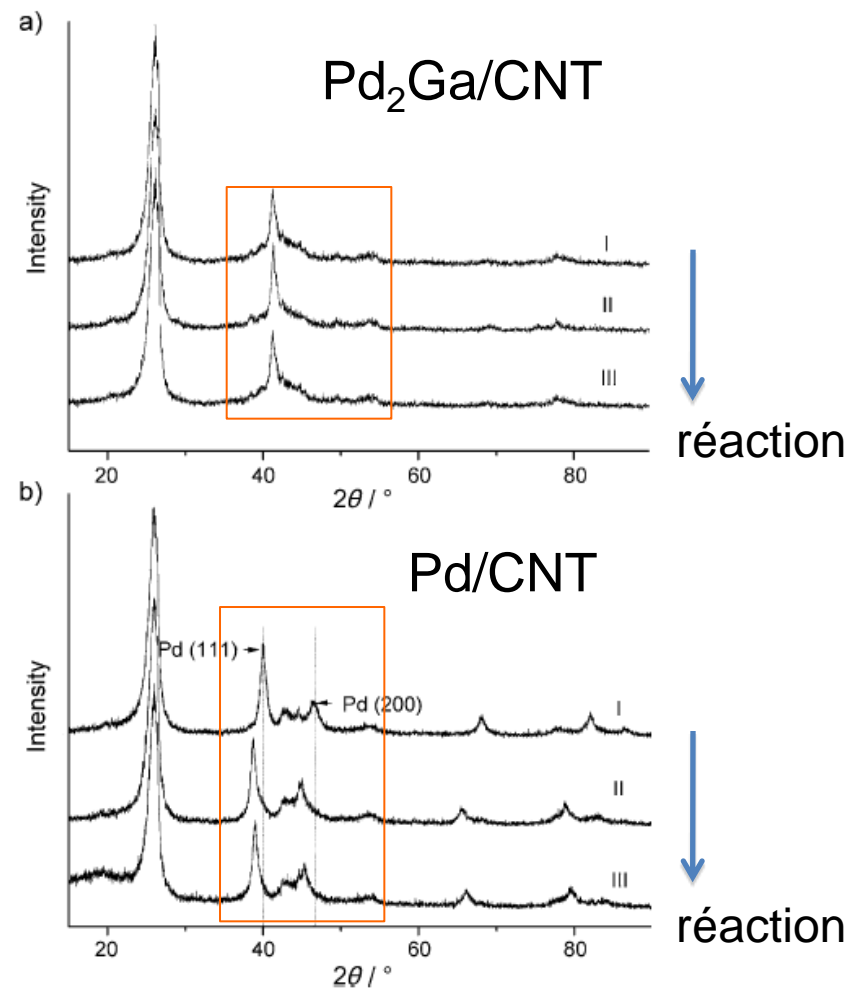
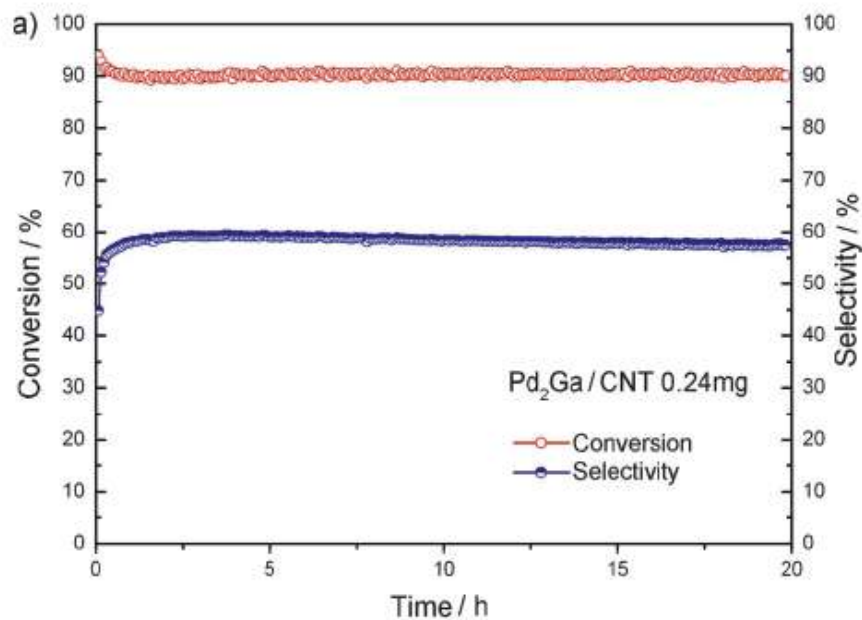
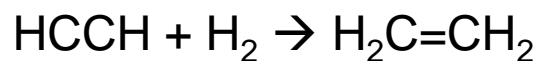
L. Shao, W. Zhang, M. Armbrüster, D. Teschner et al., Angew. Chem. Int. Ed. **50**, 10231, 2011

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LETTERS

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nature  
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# $\text{Al}_{13}\text{Fe}_4$ as a low-cost alternative for palladium in heterogeneous hydrogenation

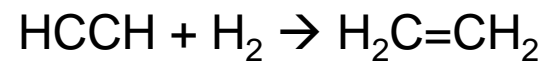
M. Armbrüster<sup>1\*</sup>, K. Kovnir<sup>1†</sup>, M. Friedrich<sup>1</sup>, D. Teschner<sup>2</sup>, G. Wowsnick<sup>1</sup>, M. Hahne<sup>3</sup>, P. Gille<sup>3</sup>, L. Szentmiklósi<sup>4</sup>, M. Feuerbacher<sup>5</sup>, M. Heggen<sup>5</sup>, F. Girgsdies<sup>2</sup>, D. Rosenthal<sup>2</sup>, R. Schlögl<sup>2</sup> and Yu. Grin<sup>1</sup>

1. Milieux de  
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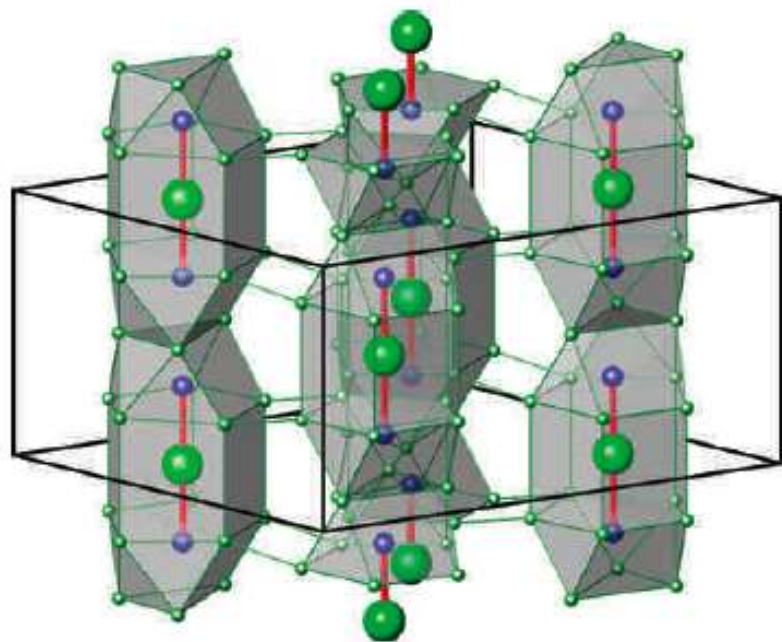
2. Milieux de  
réaction

3. Organisation

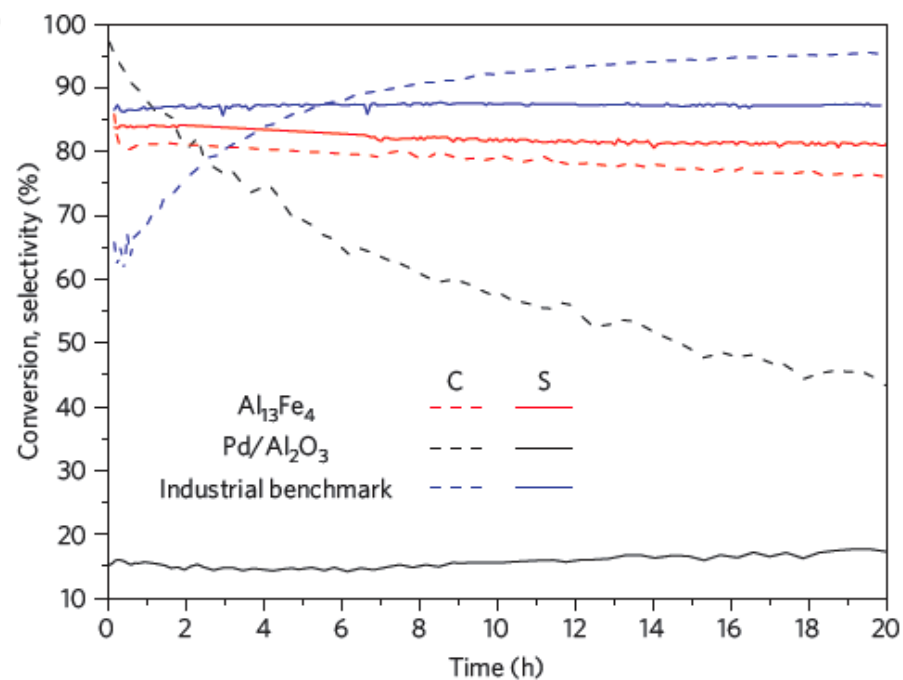
4. Nouvelles  
phases



a



b



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### *Synthesis and Crystal Growth*

Pieces of Al (99.99%) and Fe (99.9%, both CrysTec Berlin, Germany) were etched to remove surface contamination and precisely adjust the desired Al-rich off-stoichiometric composition according to the phase diagram<sup>1</sup>. Al was treated with hot hydrochloric acid followed by aqua regia; Fe was first etched by diluted nitric acid and polished in diluted hydrochloric acid. Between successive steps, the metal pieces were washed with distilled water and, at the end, in acetone (p.a.). Even short-time storage was done under vacuum. Charges of composition  $\text{Al}_{88.5}\text{Fe}_{11.5}$  and approximate totals up to 27 g were melted under Ar 99.999% by high frequency heating in alumina crucibles placed in a graphite susceptor in a fully metal-sealed reactor. Homogenisation times of a few minutes at a maximum temperature of 1300 °C were found to be sufficient to dissolve the Fe pieces in the Al-rich solution. After free cooling to room temperature, the solidified charges could easily be removed from the crucible.

- Nouveaux procédés = nouvelles opportunités
- Nouveaux supports = nouveaux problèmes
- Actualité de la “chimie minérale”
- Richesse de la chimie des **additifs ou templates organiques**
- Catalyse: cinétique + génie chimique