



Speciation of palladium in nuclear fuel reprocessing operation

B. Simon, C. Bouyer, S. de Sio, A. Chagnes, L. Berthon

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FROM RESEARCH TO INDUSTRY



Speciation of palladium in nuclear fuel reprocessing operation

Kudowa Zdrój, August 26-30, 2018

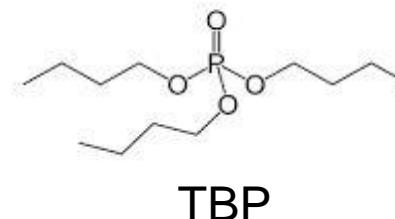
**Bénédicte SIMON, Christine BOUYER, Stéphanie DE SIO,
Alexandre CHAGNES, Laurence BERTHON**

*CEA Marcoule / Nuclear Energy Division,
Research Department on Mining and Fuel Recycling Processes
Unit of dissolution and separation processes*

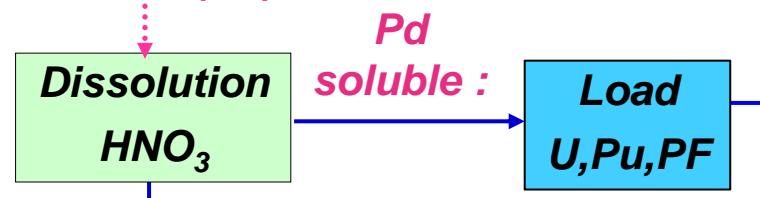


Context: PUREX process

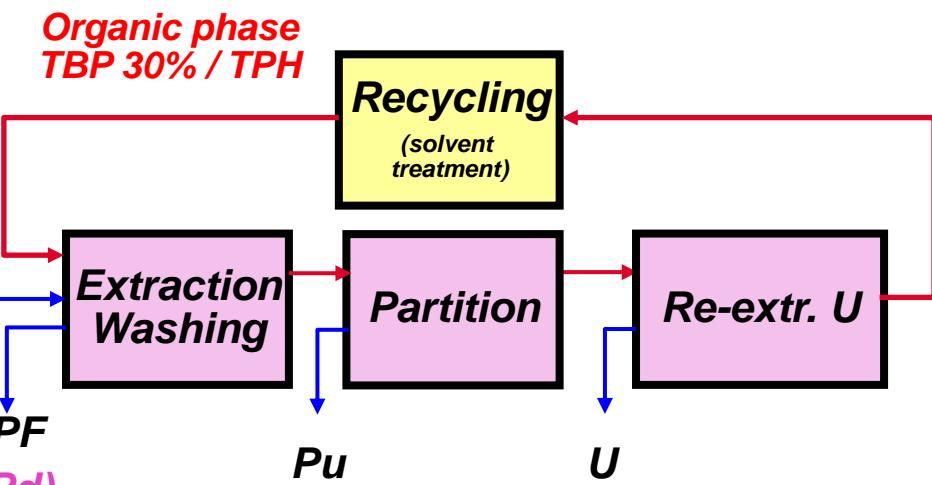
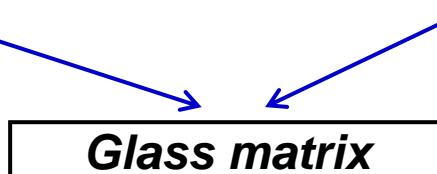
- PUREX process = hydrometallurgical process
- Selective extraction of U and Pu present in the spent nuclear fuel by an organic phase TBP-TPH
- Palladium = fission product
- How to cope with aging equipment:
→ Presence of precipitate with palladium



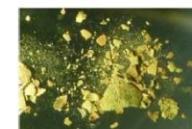
Spent fuel:
U, Pu, FP
(Pd)



FP insolubles
Pd insoluble



De SIO et al., Procedia Chemistry, 21, 2016, 17-23



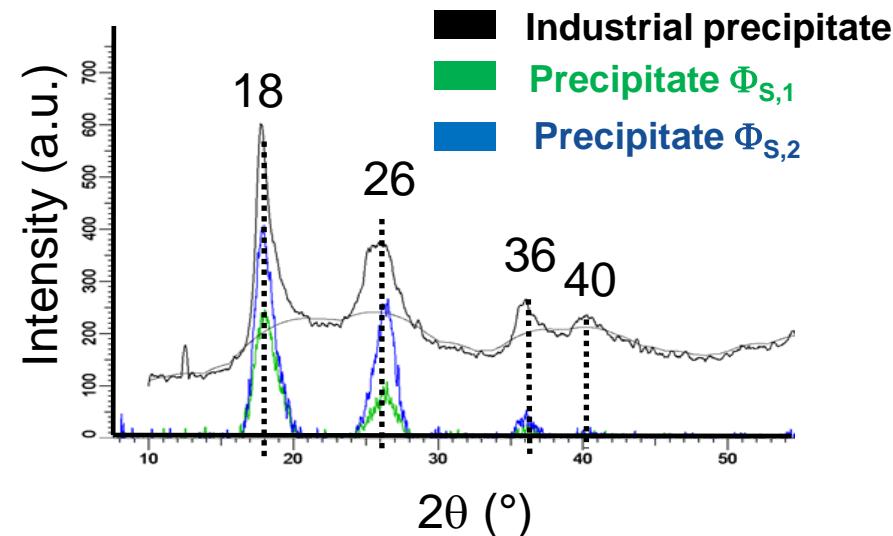
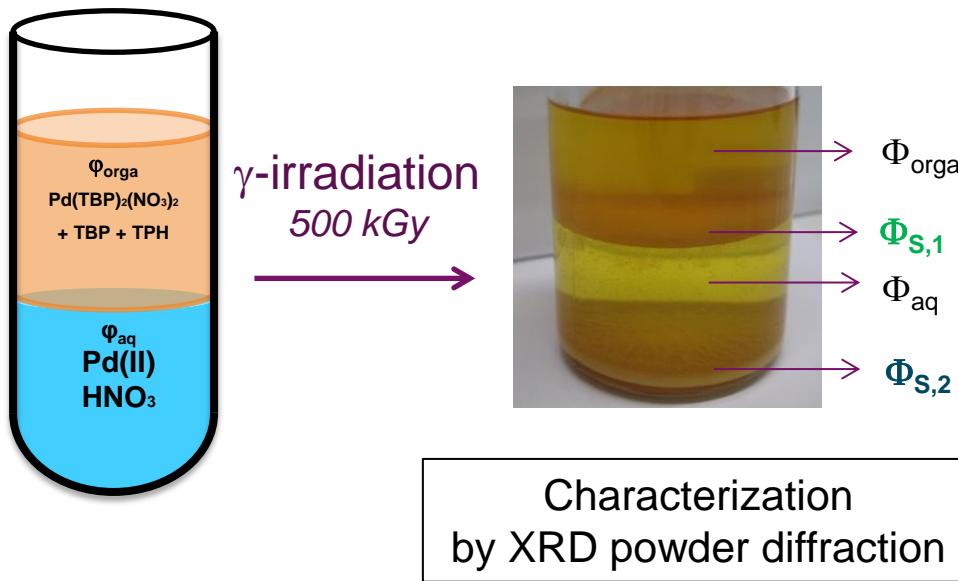
Industrial solid

Objective of the study

Understanding the formation of Pd precipitates in liquid-liquid extraction cycles

→ Identification of the compounds responsible for the precipitation of Pd

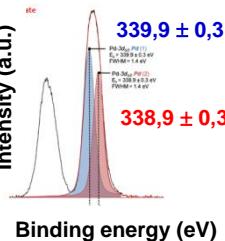
Role of the radiolysis



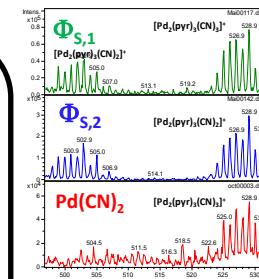
How to explain the presence of precipitate in liquide-liquid extraction cycles ?

- Speciation of precipitates formed by γ -irradiation

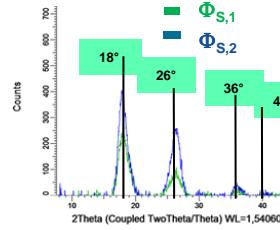
XPS



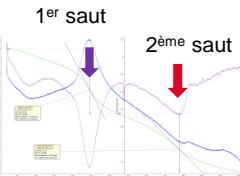
ESI-MS



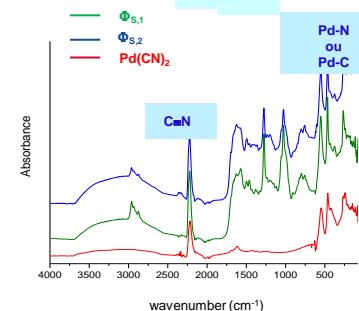
XRD

Precipitate $\Phi_{S,1}$ 

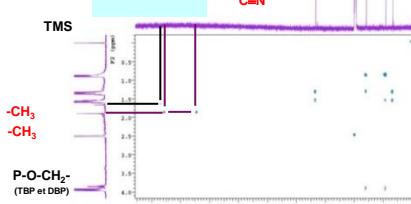
ATG

Precipitate $\Phi_{S,2}$ 

IRFT

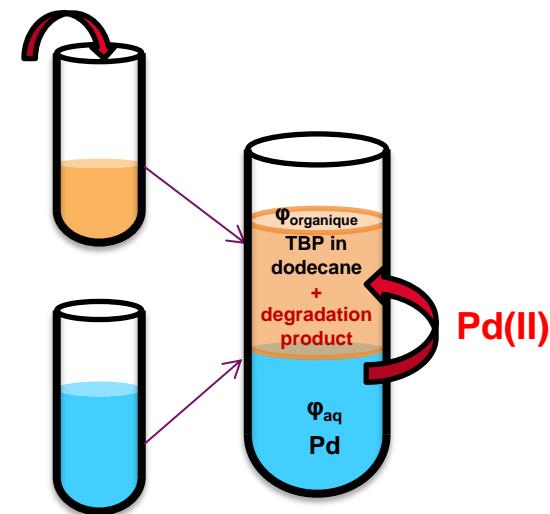


RMN



- Extraction of Pd(II) in presence of degradation product (DP) of the solvent

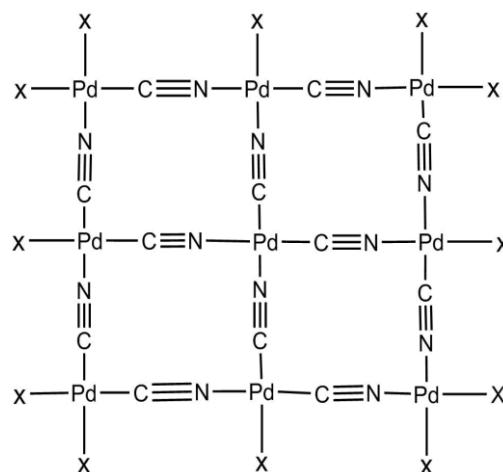
degradation
product



Identification of palladium species formed with degradation products (solid/complexe)



Precipitate

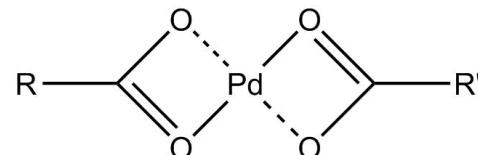
 $\Phi_{S,1}$ 

Functions present in the precipitates $\Phi_{S,1}$ et $\Phi_{S,2}$

XRD, XPS, ATG,
ESI-MSXPS, FTIR,
NMR

NMR, XPS, FTIR, ESI-MS

Pd-carboxylate



Organic compounds

 $R''-NH_2$

and
Phosphorous
compounds
(TBP / HDBP)

with $X = H_2O, CN$, others functions

Presence at least of 2 different compounds

S. J. Hibble, A. M. Chippindale, E. J. Bilb  ,
E. Marelli, P. J. F. Harris and A. C. Hannon,
Inorg. Chem., 2011, **50**, 104–113.

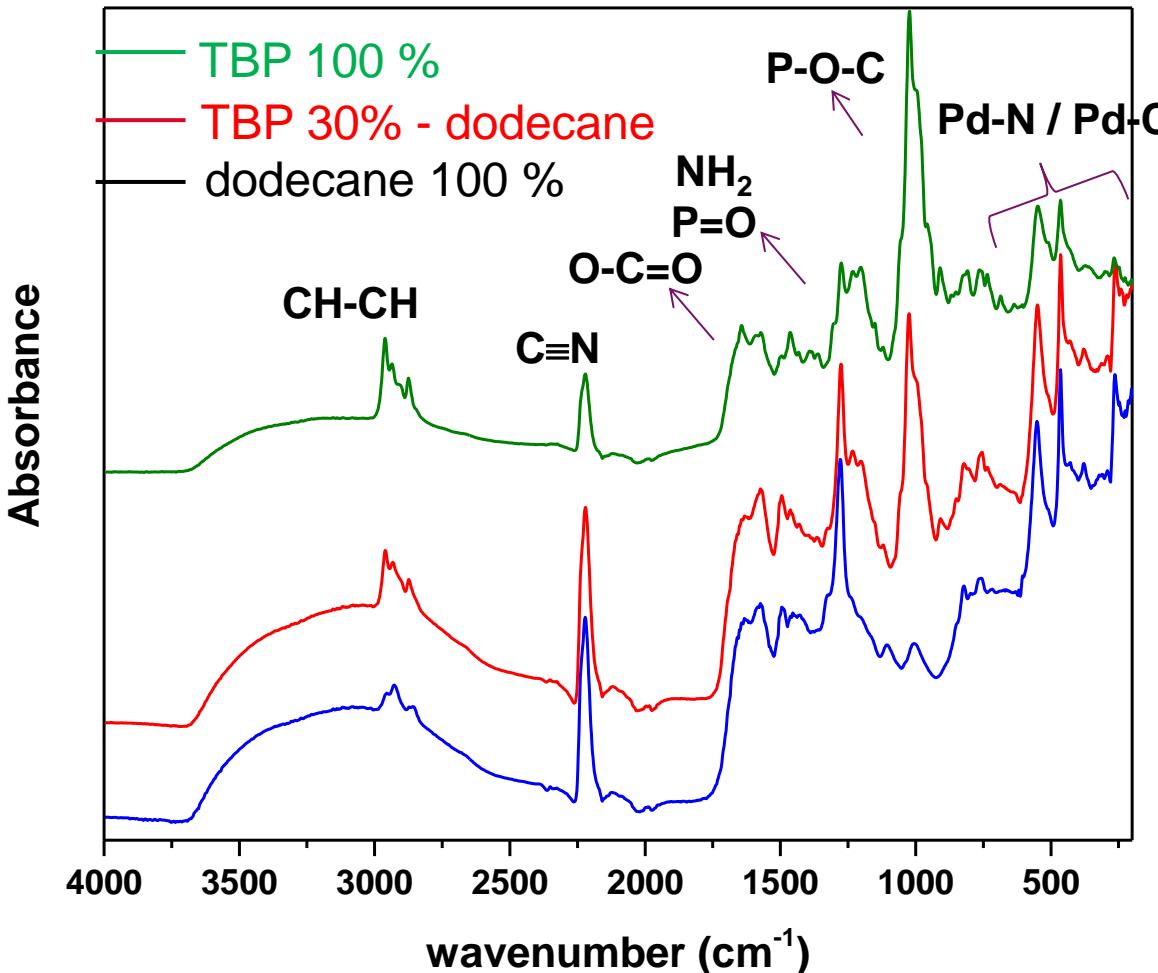
Published manuscript : "Characterization of palladium species after γ -irradiation of a TBP-alkane-
 $Pd(NO_3)_2$ system "
RSC Adv., 2018, 8, 21513-21527



Precipitate

 $\Phi_{S,2}$

Origin of degradation products leading to the formation of precipitates



Initial conditions:

Φ_{aq} : $\text{Pd}(\text{NO}_3)_2$, HNO_3 3 mol.L⁻¹

Φ_{orga} : variable composition



$\Phi_{\text{S},2,\text{TBP}}$



$\Phi_{\text{S},2,\text{TBP-dodecane}}$

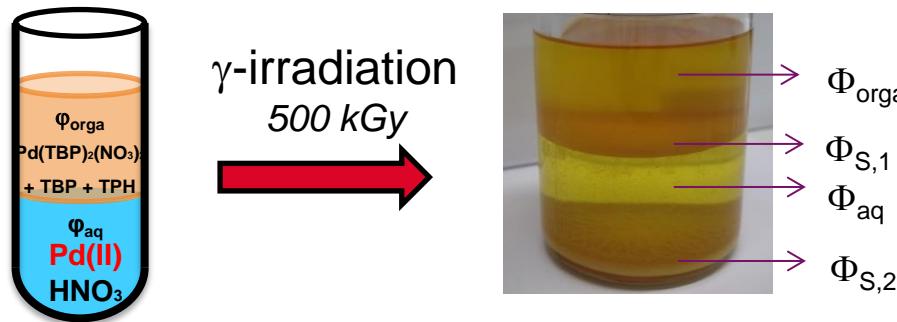


$\Phi_{\text{S},2,\text{dodecane}}$

→ Degradation products from TBP or dodecane allowing the formation of precipitates

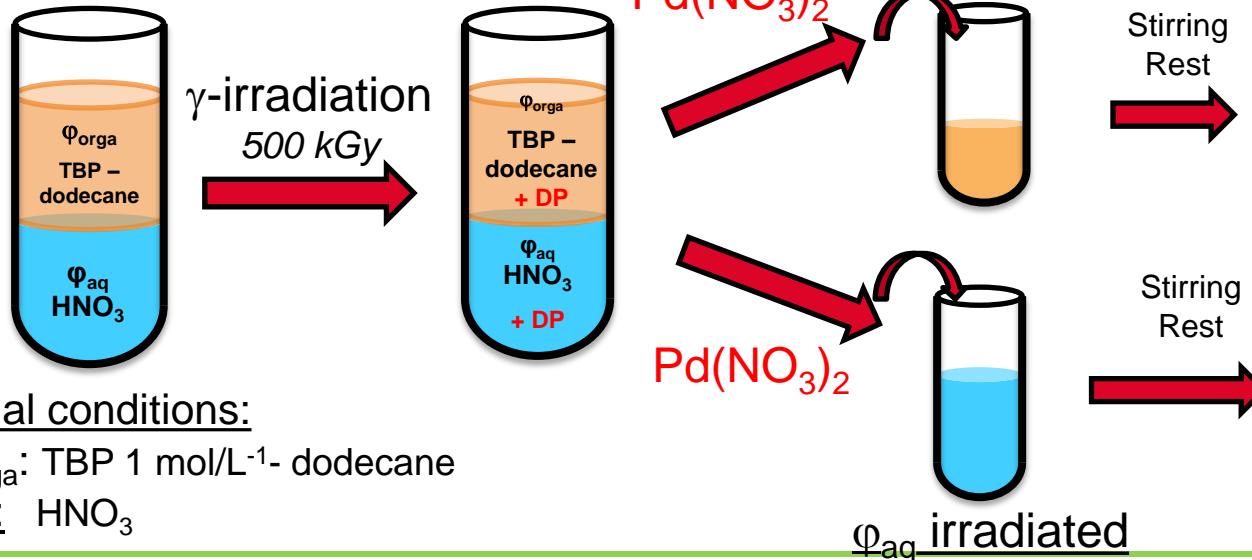
Distribution of degradation products leading to precipitation of palladium

Irradiation with Pd :



$\Phi_{\text{S},2}$

Irradiation without Pd :



$\Phi_{\text{pp},\Phi_{\text{orga}}}$



$\Phi_{\text{pp},\Phi_{\text{aq}}}$

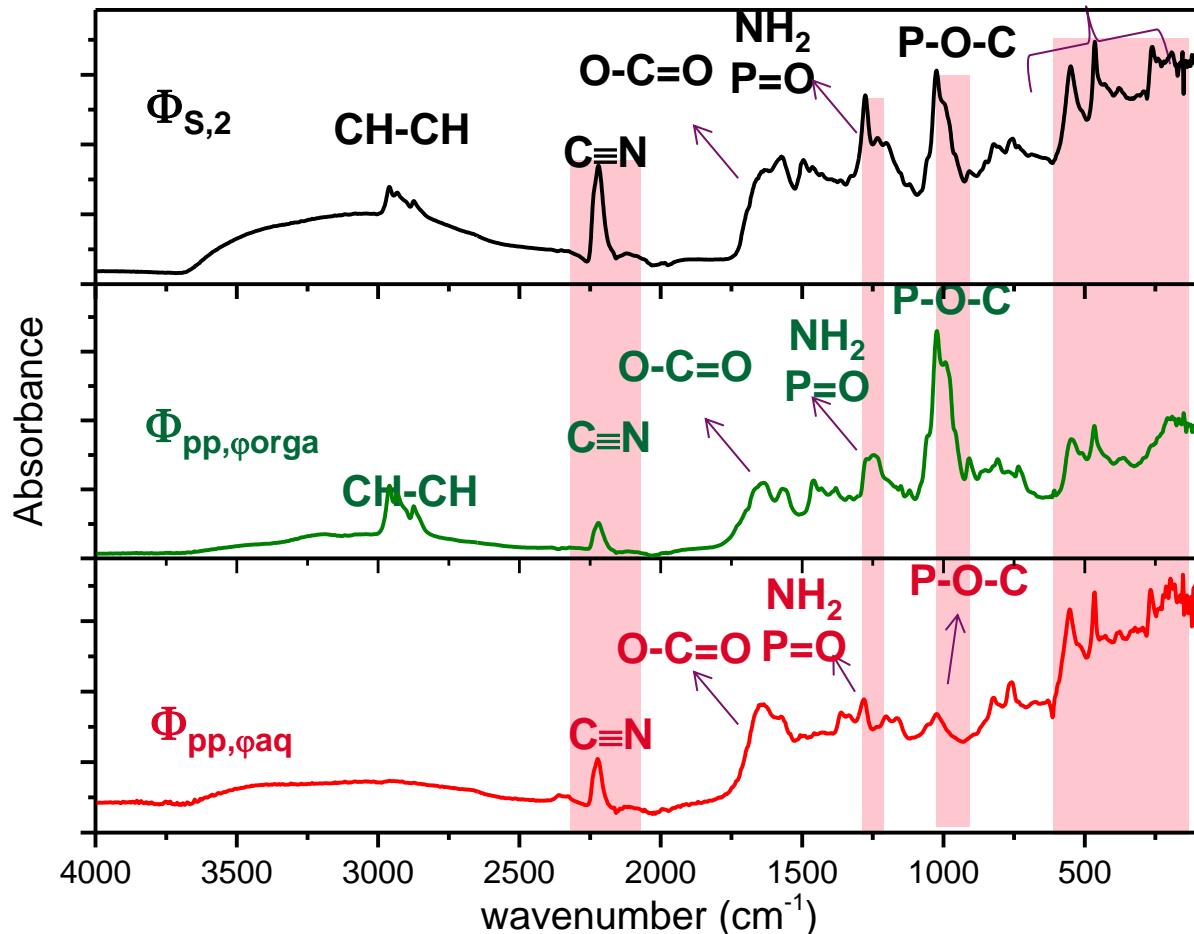
Initial conditions:

Φ_{orga} : TBP 1 mol/L⁻¹- dodecane

Φ_{aq} : HNO_3

Infra-red of $\Phi_{pp,\phi_{orga}}$ et $\Phi_{pp,\phi_{aq}}$ after the addition of $Pd(NO_3)_2$

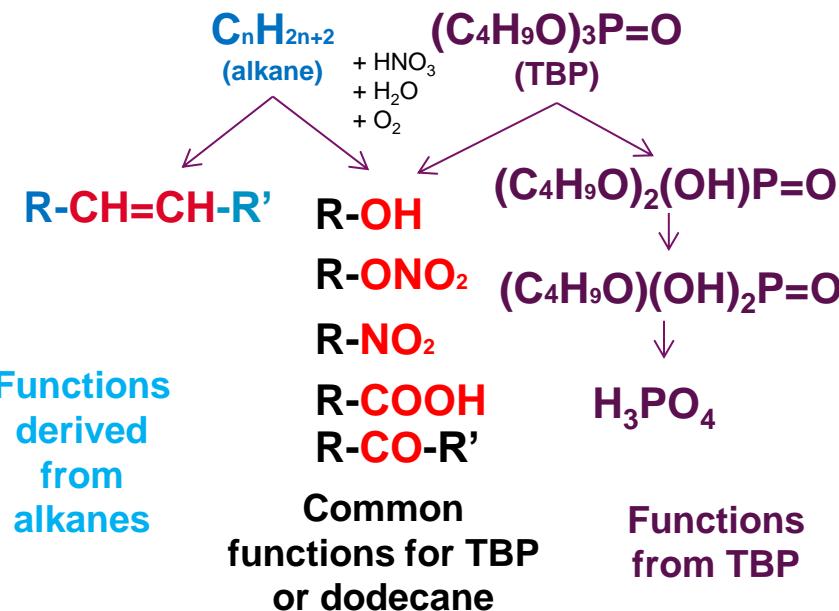
Pd-N / Pd-C

 $\Phi_{pp,\phi_{aq}}$ $\Phi_{pp,\phi_{orga}}$

→ Degradation products responsible for the precipitation of Pd present in ϕ_{aq} et ϕ_{orga}

Extraction of Pd(II) in the presence of degradation products (DP)

Bibliographic review on the degradation of TBP -TPH



Functions
derived
from
alkanes

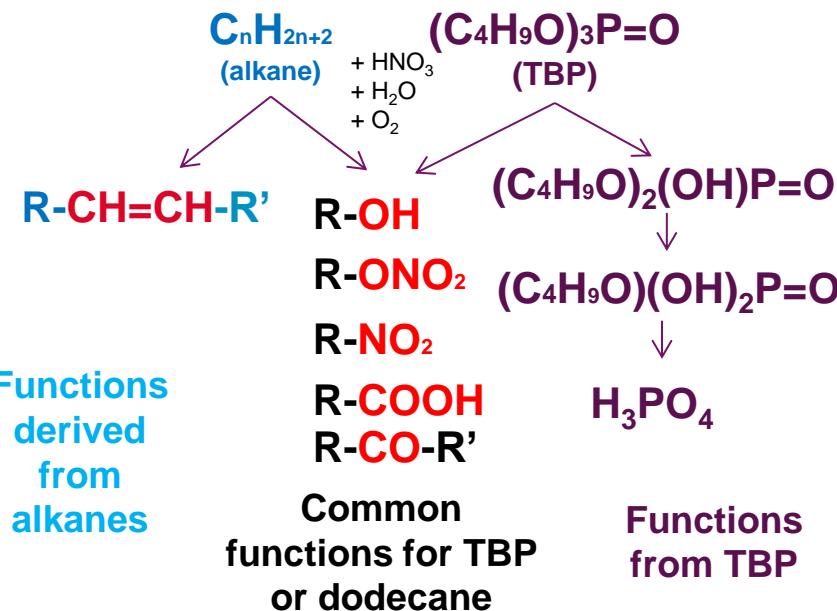
Common
functions for TBP
or dodecane

Functions
from TBP

D. Lesage, 1995
L. Berthon et M. C. Charbonnel, 2009
Tripathi et Sumathi, 1999

Extraction of Pd(II) in the presence of degradation products (DP)

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Functions
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Common
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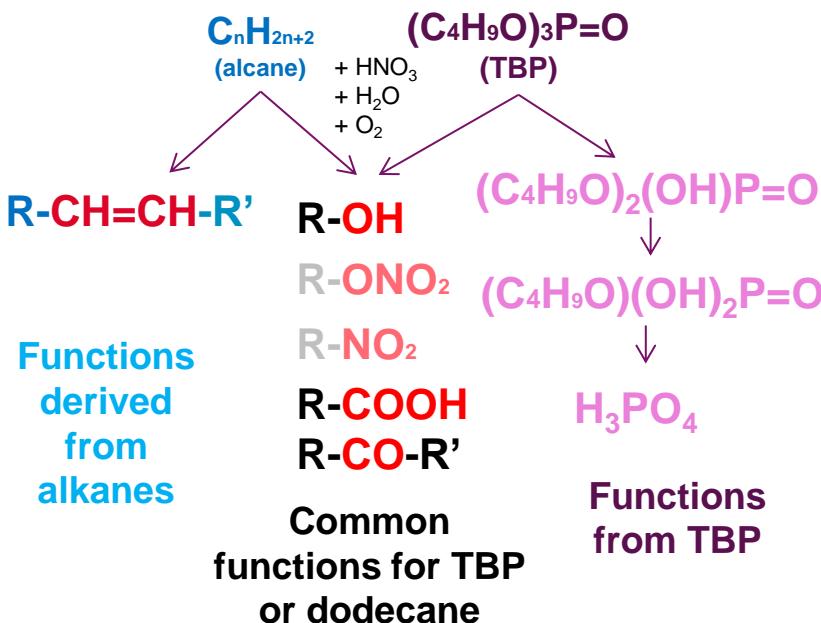
■ DP tested:

- 5-dodecene
- dodecanoic acid
- 1-dodecanol
- 5-dodecanone

D. Lesage, 1995
L. Berthon et M. C. Charbonnel, 2009
Tripathi et Sumathi, 1999

Extraction of Pd(II) in the presence of degradation products (DP)

Bibliographic review on the degradation of TBP -TPH



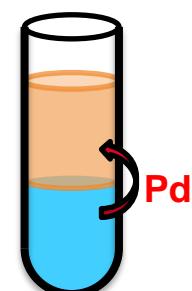
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D. Lesage, 1995
 L. Berthon et M. C.
 Charbonnel, 2009
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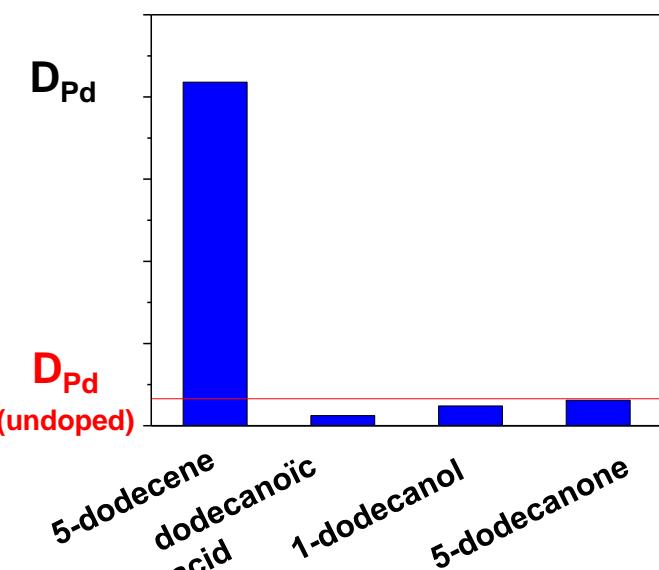
Identification of palladium species formed with these DPs (solids / complexes)

Organic phase:
 TBP 1 mol.L⁻¹ in dodecane
 + addition of DP



Aqueous phase:
 $HNO_3 + Pd(II)$

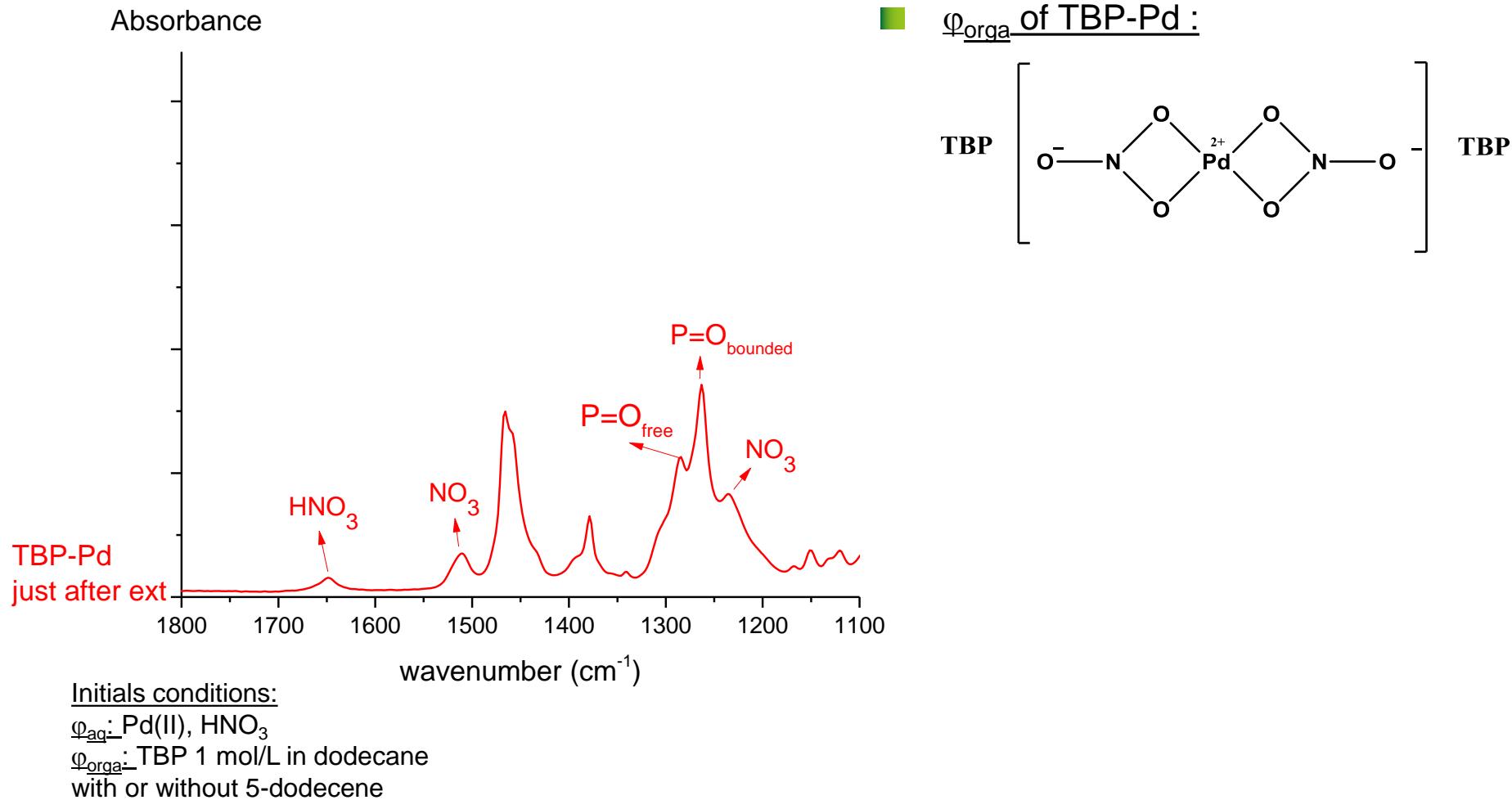
$$D_{Pd} = \frac{[Pd]_{orga}}{[Pd]_{aq}}$$



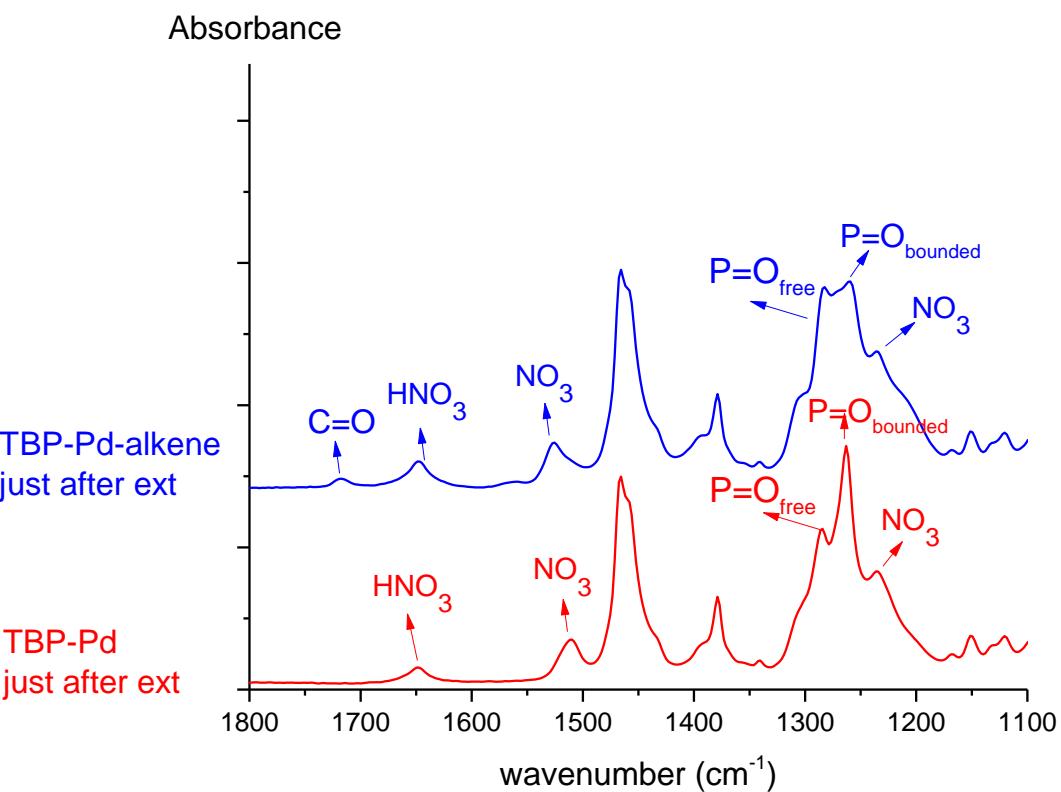
Only 5-dodecene:

1. $D_{Pd}(TBP+alkene) >> D_{Pd}(\text{undoped})$
2. Presence black powder at the interphase Pd et PdO (XRD powder and XPS)

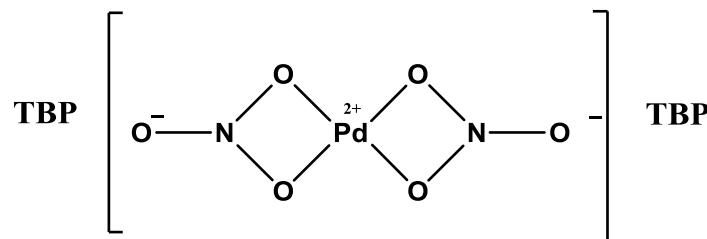
Infra-red of φ_{orga} after Pd(II) extraction in presence of absence of 5-dodecane



Infra-red of φ_{orga} after Pd(II) extraction in presence of absence of 5-dodecane



■ φ_{orga} of TBP-Pd :



■ φ_{orga} of TBP-Pd-5-dodecene :

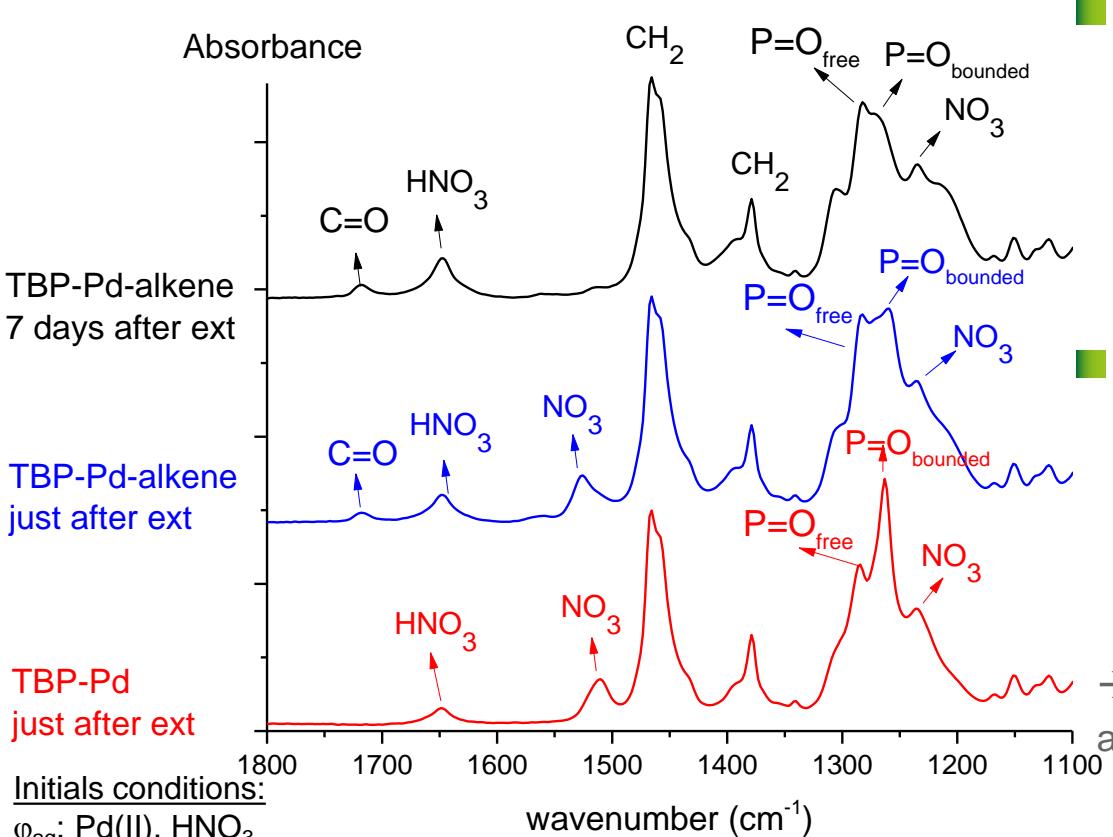
- Presence of C=O at 1718 cm^{-1}
→ function RCOH, R-CO-R' or R-COOH
- NMN : presence of ketone
- ESI-MS : complexes different from $\text{Pd}(\text{TBP})_2(\text{NO}_3)_2$
→ Palladium complexes different with or without alkene

Initials conditions:

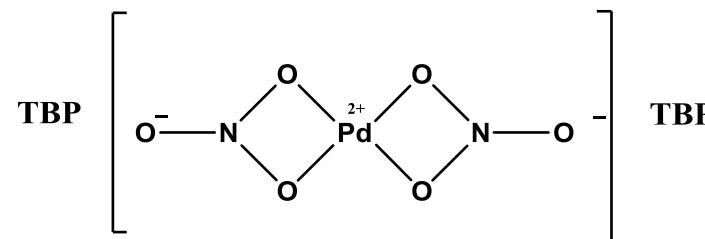
φ_{aq} : Pd(II), HNO_3

φ_{orga} : TBP 1 mol/L in dodecane
with or without 5-dodecene

Infra-red of φ_{orga} after Pd(II) extraction in presence of absence of 5-dodecane



φ_{orga} of TBP-Pd :



φ_{orga} of TBP-Pd-5-dodecene :

- Presence of C=O at 1718 cm⁻¹
→ function RCOH, R-CO-R' or R-COOH
- NMN : presence of ketone
- ESI-MS : complexes different from Pd(TBP)₂(NO₃)₂

→ Palladium complexes different with or without alkene

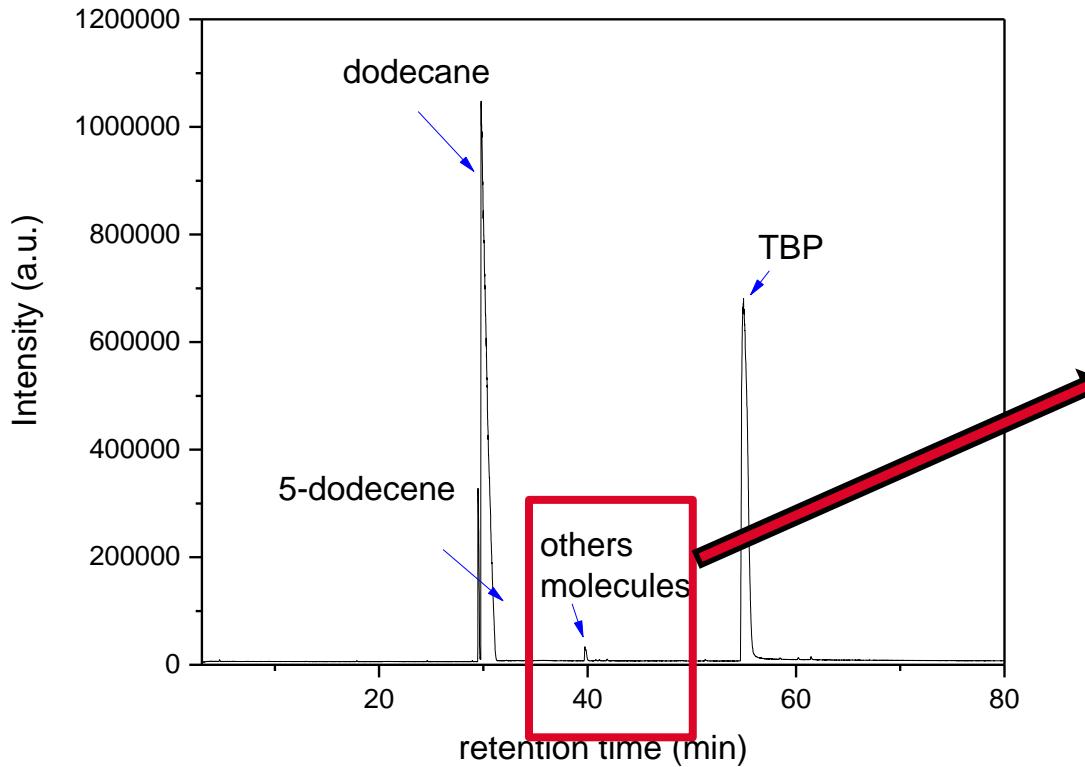
Evolution φ_{orga} of TBP-Pd-alkene :

Functions C=O: C^{te} between t₀ et 7 days
Disapparence of nitrate vibration bands (1527 cm⁻¹)

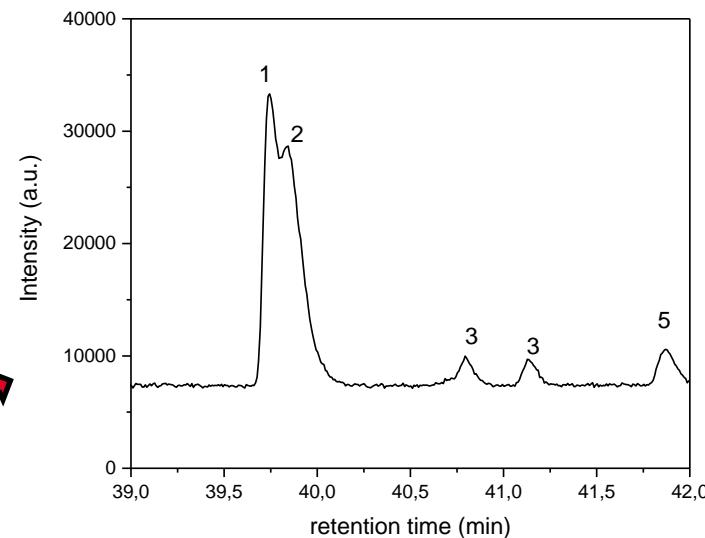
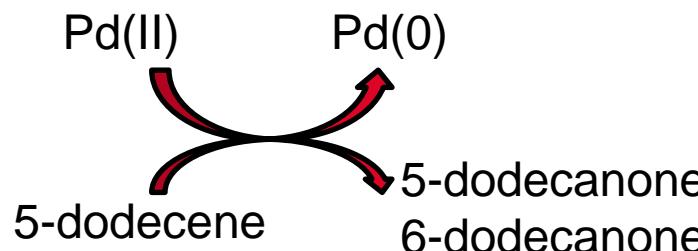
- ESI-MS : Presence of a mixed complexe of Pd-TBP-5-dodecene

**Hyp : mixed complexes Pd-TBP-C₁₂H₂₄
Formation of C=O in presence of alkene**

Characterization by GC-MS of an organic phase of TBP-dodecane-Pd-5-dodecene



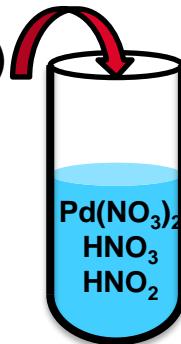
Oxydo-reduction reaction:



| N° | Attribution |
|----|--------------|
| 1 | 6-dodecanone |
| 2 | 5-dodecanone |
| 3 | 3-dodecanone |
| 4 | 2-dodecanone |
| 5 | ? |

Behavior of ketone in presence of palladium

2-butanone
(DP from TBP)



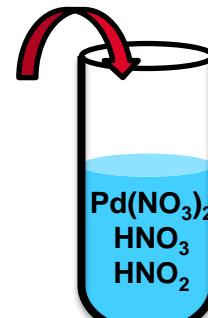
Mixture without stirring



Initials conditions:
HNO₃, Pd(II), HNO₂,
Ketone

M. Nonomura,
Toxicol. Environ. Chem., 1987, 17,
47–57

2-dodecanone
or
5-dodecanone
(DP from dodecane)



Mixture stirred

T_{amb}

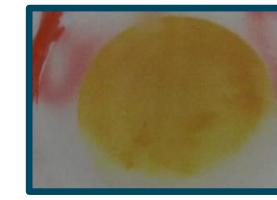
No precipitate

Stirred mixture
100°C

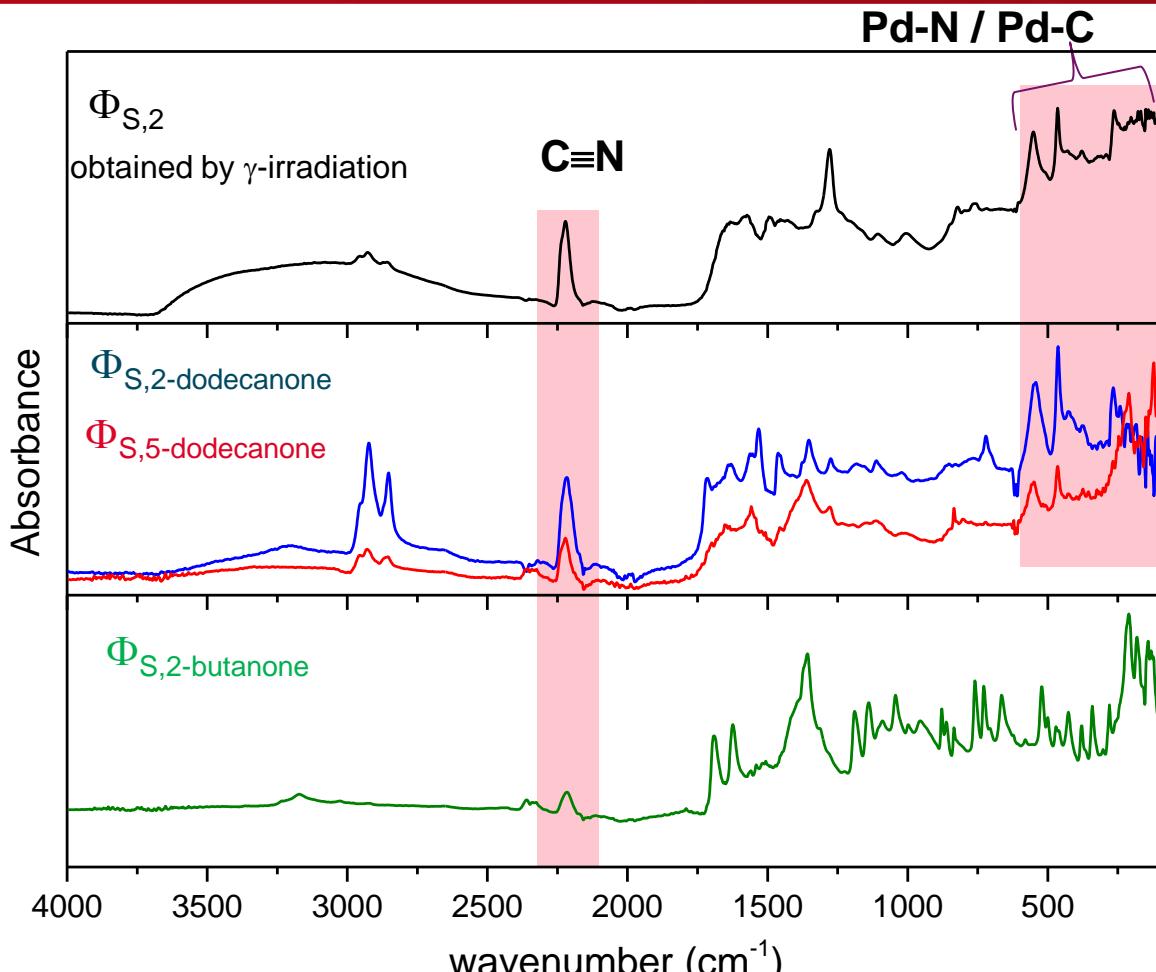
Φ_{S,5-dodecanone}



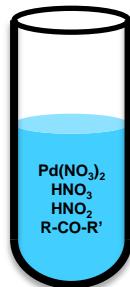
Φ_{S,2-dodecanone}



- without ketone: no solid formation
- without HNO₂: no solid formation



Initials conditions:
 HNO_3 , Pd(II), HNO_2 ,
Ketone



- Presence of $\text{C}\equiv\text{N}$ in the 3 solids
 - whatever the length of the chain and the position of $\text{C}=\text{O}$, formation of $\text{Pd}(\text{CN})_2$



Ketone and HNO_2 : precursors in the $\text{Pd}(\text{CN})_2$ formation

Conclusions and Prospects

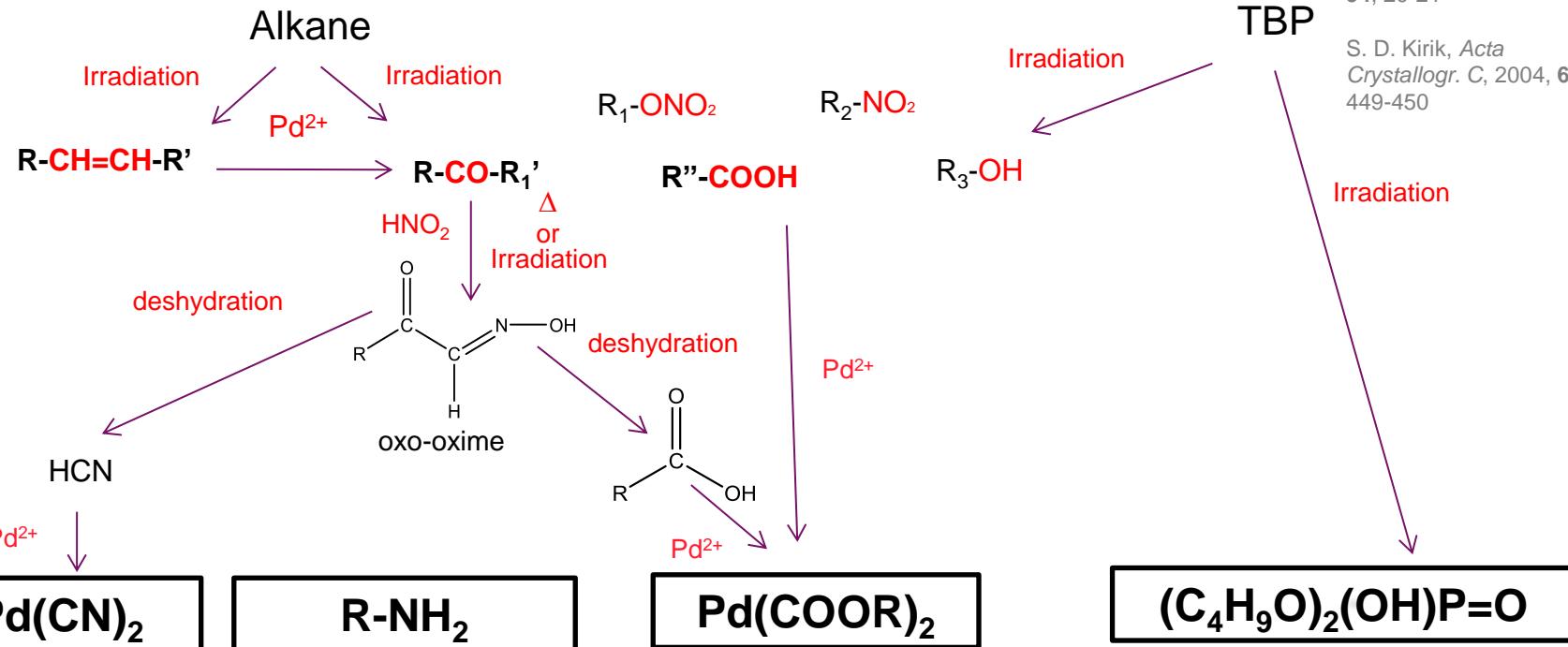
➤ Characterization of precipitates of palladium in {TBP-TPH-HNO₃} irradiated

Several compounds : Pd(CN)₂, Pd(COOR)₂, TBP, HDBP, Amine

DP come from TBP or dodecane

DP leading to the precipitation of Pd present in ϕ_{aq} and ϕ_{orga}

➤ Suggestion of mechanisms formation of precipitates



➤ Prospects: suggestion of NH₂ mechanism formation

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CEA/DEN/MAR/DMRC/SPDS/LILA

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- Georges SAINT-LOUIS
- Nathalie BOUBALS
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Université de Lorraine

- Alexandre CHAGNES

ORANO Cycle

- Stéphanie DE SIO

CEA/DEN/MAR/DE2D/SEVT/LDMC

- Nicolas MASSONI

Thank you for your attention