GDR Groupement de recherche
Prométhée Procédés hydrométallurgiques pour la gestion intégrée des ressources primaires et secondaires

Direct preparation of palladium catalysts by selective extraction of the E-waste leachates

Dmytro Nikolaievskyi

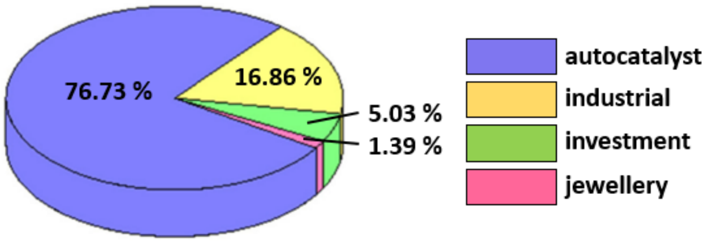
23/05/2024

Journées du GDR Prométhée

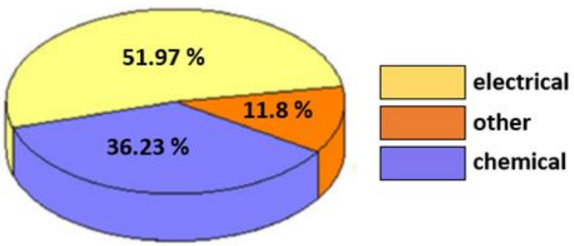
IFPEN, Rueil-Malmaison

Context

Demand by market sectors



Demand by industrial sectors



Global net demand ≈ 193,8 tonnes in 2023

Pd is widely used in catalytic processes

- H_2O_2 production
- Drug synthesis (pharma)
- Polymer production
- Air purification
- …

Pd – critical metal

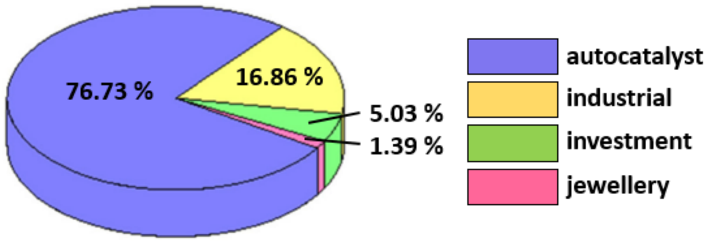
⇓

Secondary sources should be considered

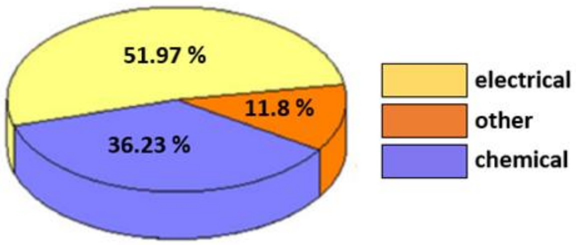
Hughes, A. et al., *Resources,* **2021**, *10*(9), 93.
SFA (Oxford)

Context

Demand by market sectors



Demand by industrial sectors



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Pd – critical metal

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Secondary sources should be considered

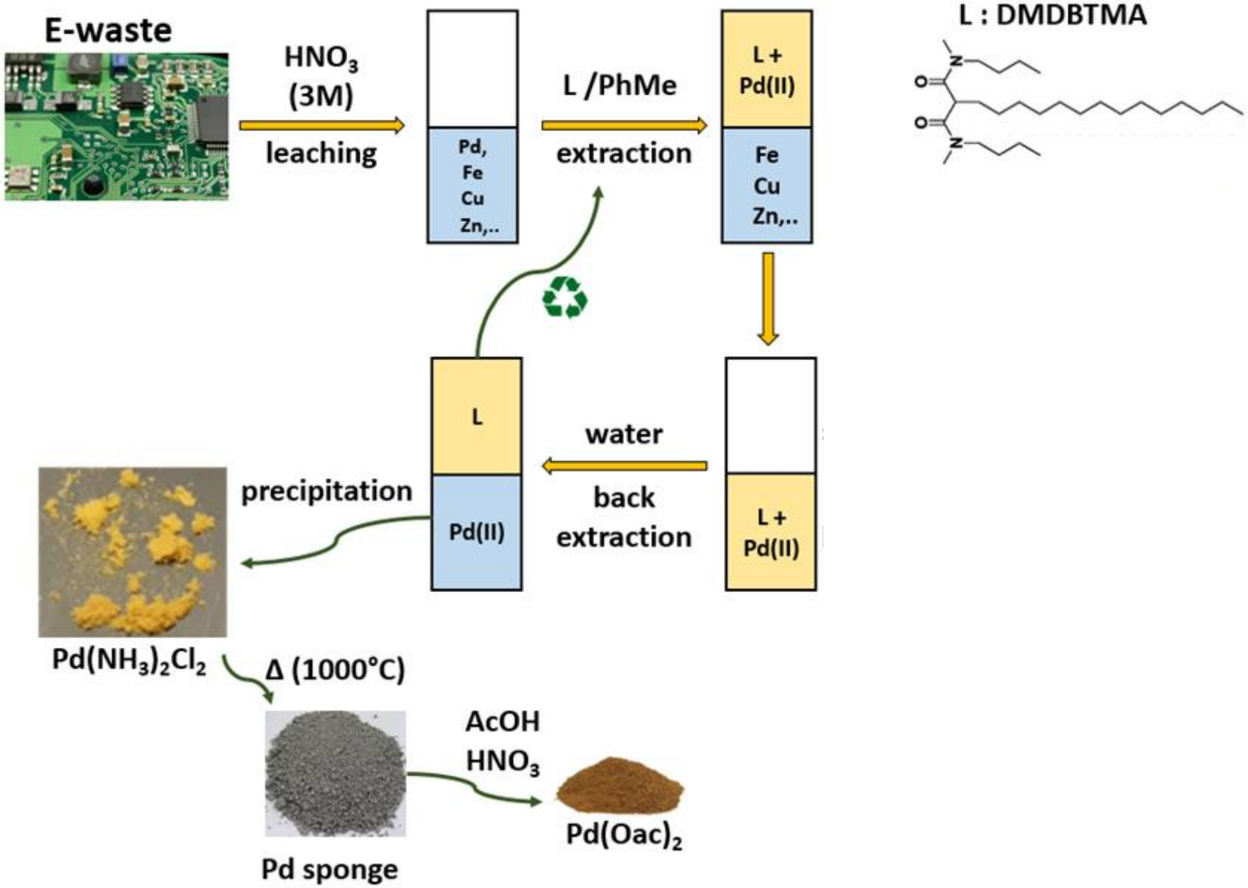
Electronic waste - a promising source for Pd

- High Pd content compared to natural ores

Hughes, A. et al., *Resources*, **2021**, *10*(9), 93.
SFA (Oxford)

Hydrometallurgy for Pd recovery

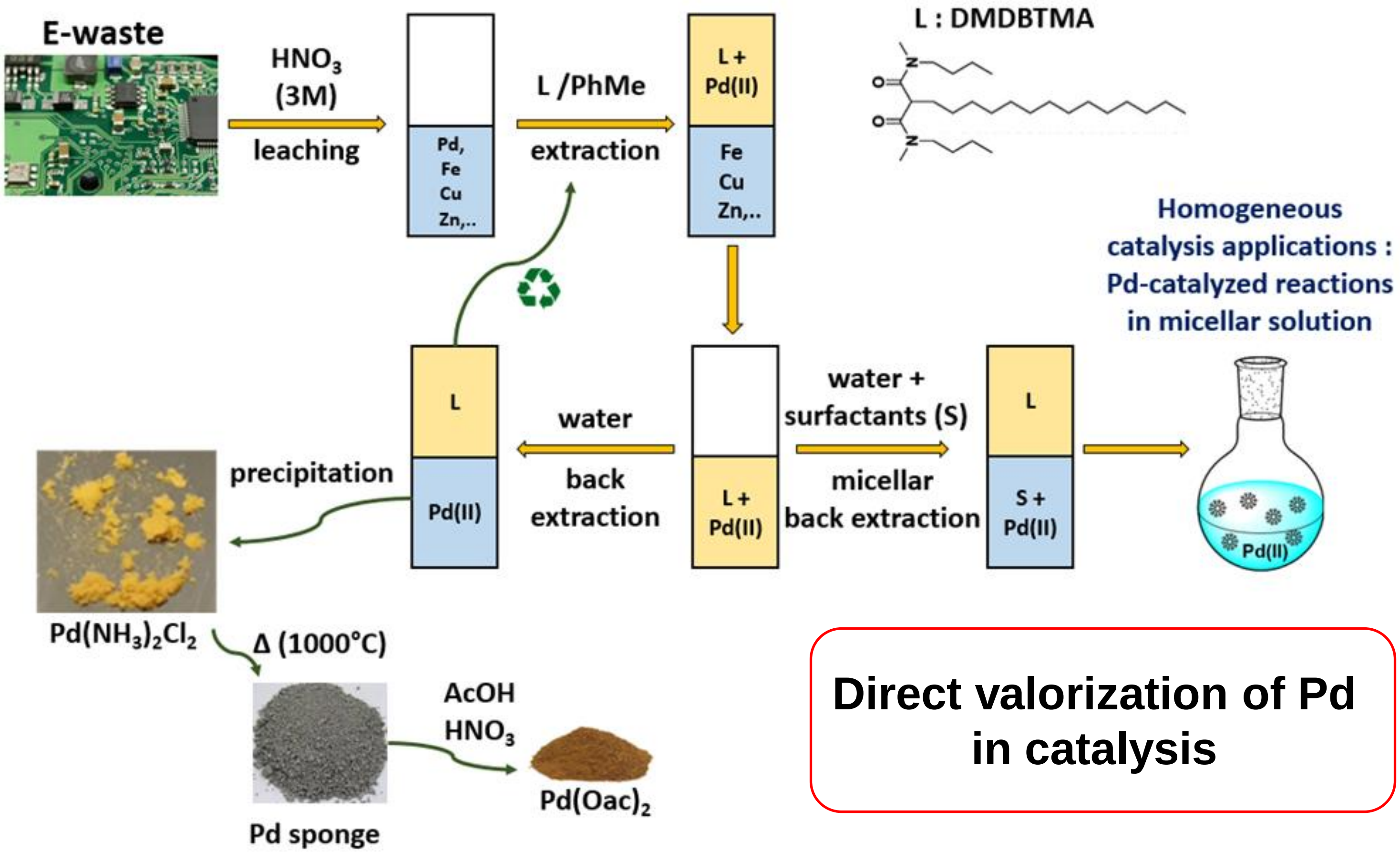
Which processes are used to recover Pd?



Bourgeois, D. et al., *Hydrometallurgy* 191, **2020**: 105241.

Hydrometallurgy for Pd recovery

Is it possible to by-pass the isolation of pure Pd salt?



Direct valorization of Pd in catalysis

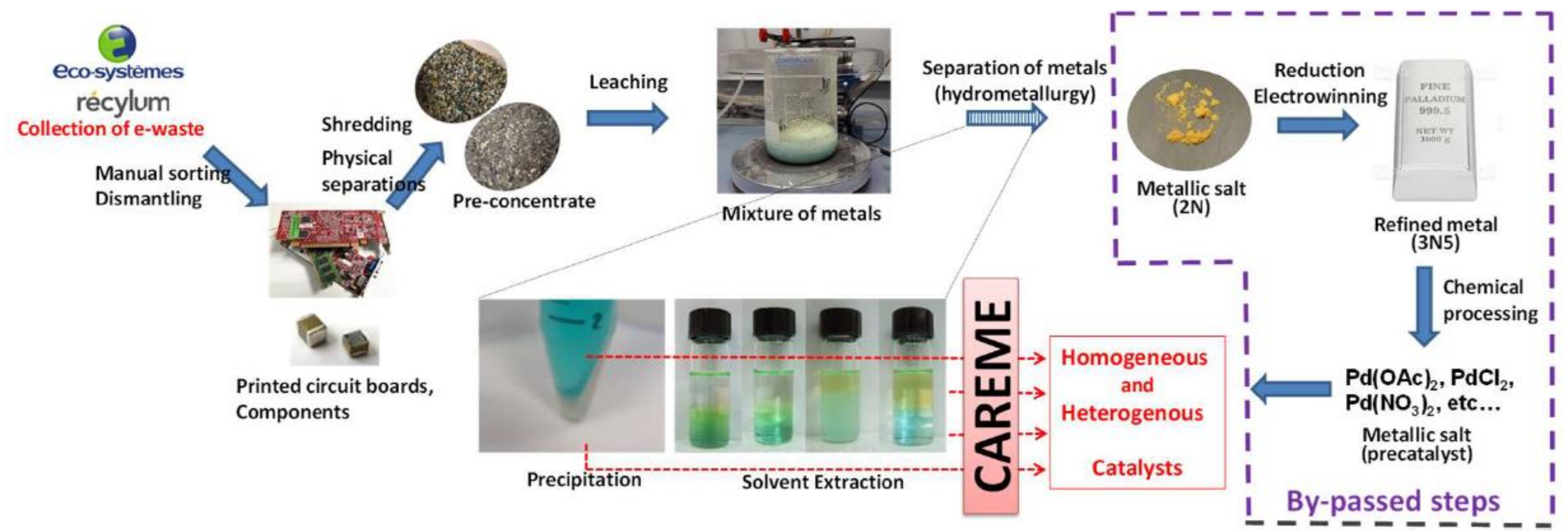
Bourgeois, D. et al., *Hydrometallurgy* 191, **2020**: 105241.

Lacanau, V. et al., *ChemSusChem*, **2020**, *13*, 5224-5230

Project concept

CAREME - CAtalysis with REcycled Metals

- Valorize noble metals (mainly Pd, Au) from electronic waste by direct preparation of hetero- and homogeneous catalysts.



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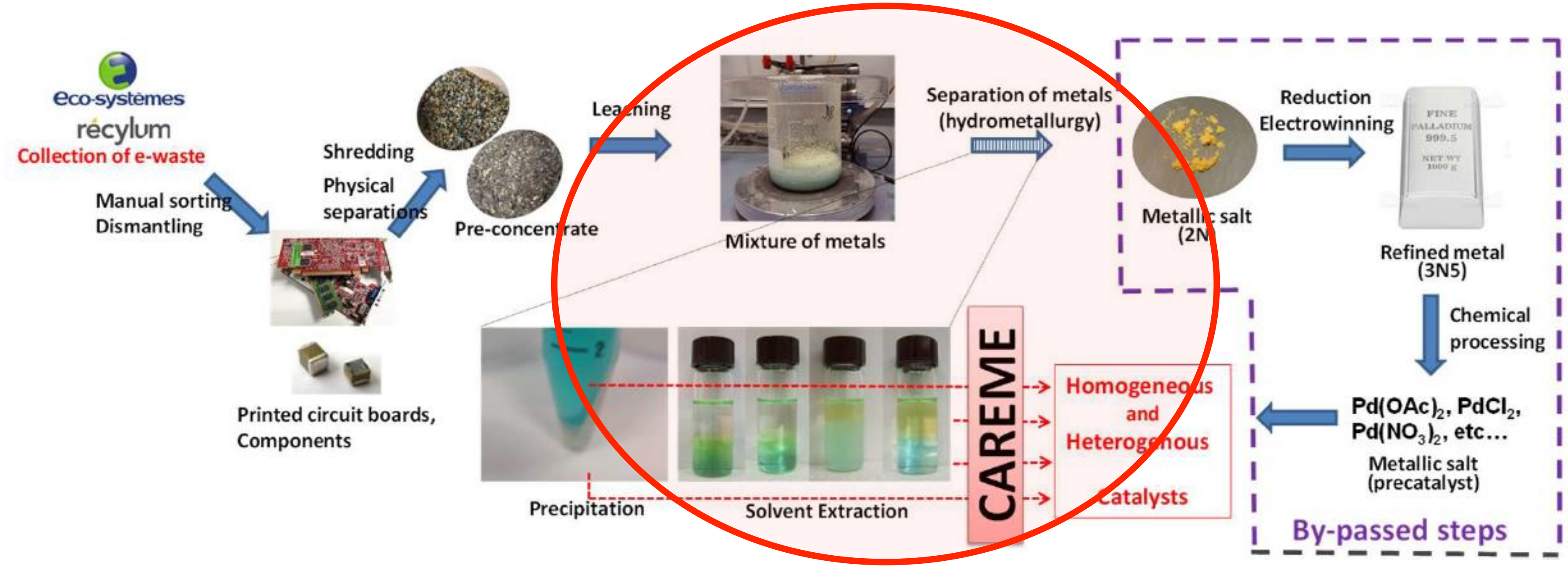
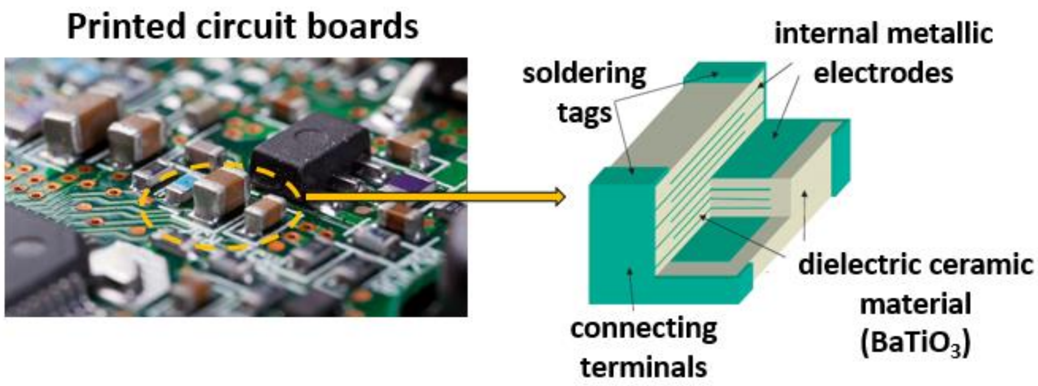
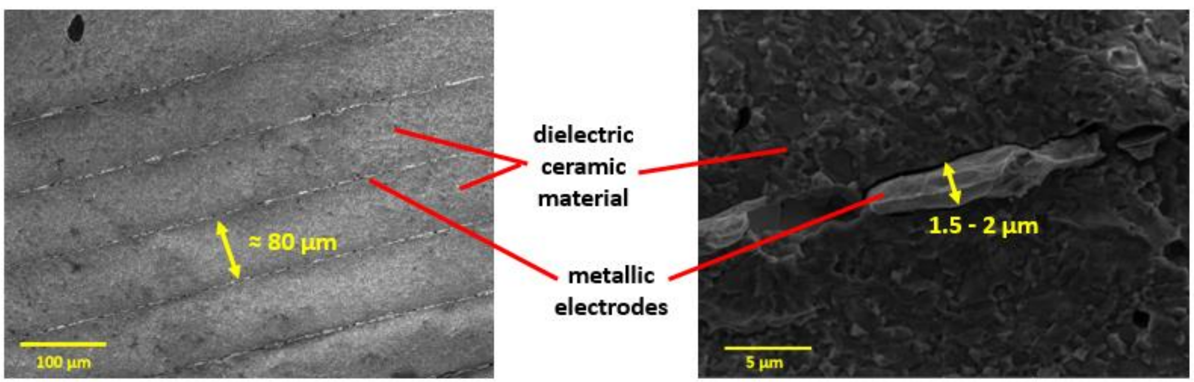


MLCC – Pd source

Multilayer ceramic capacitors

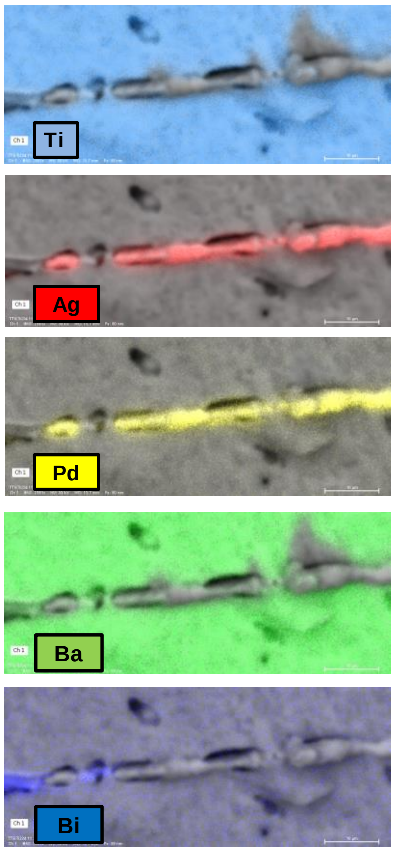




SEM images of MLCC cross-section

Thesis M. M. Romo y Morales

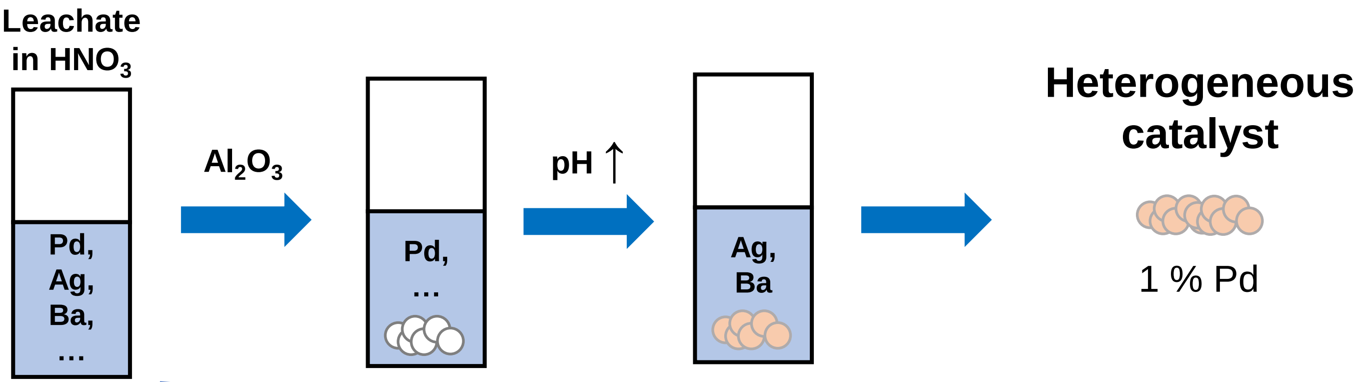
SOVAMEP



Direct valorization of leachates

γ-Al_2O_3 supported catalysts prepared by deposition-precipitation method

Thesis M. M. Romo y Morales

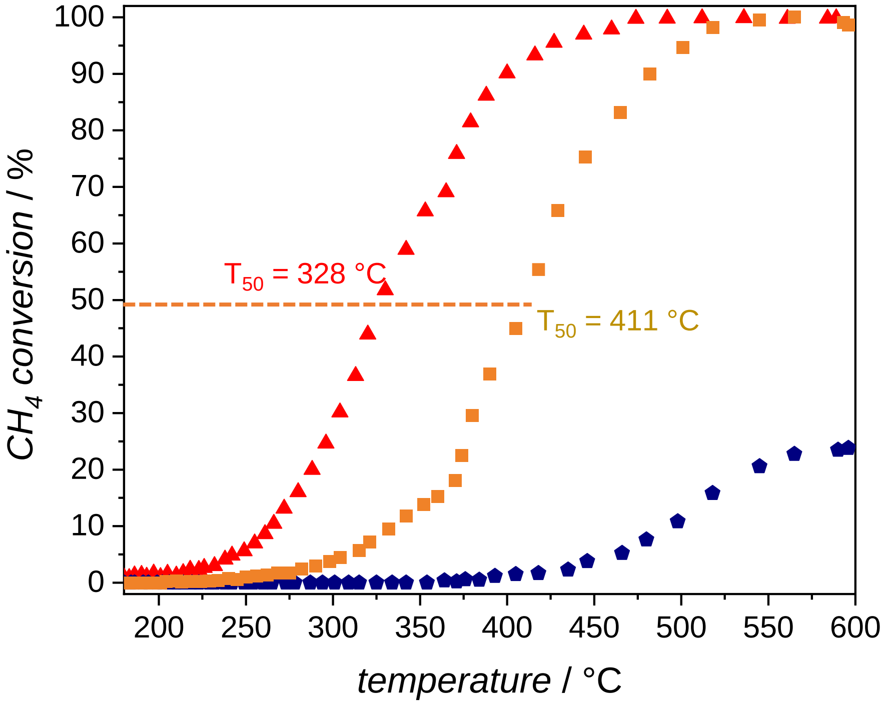


Metal	Pd	Ag	Ba	Bi	Ti	Pb	Cu	Ni	Sn
C, mg / L	1710	4580	2232	2220	4580	373	360	116	71

Direct valorization of leachates

Catalytic test : **Total oxidation of methane**

Thesis M. M. Romo y Morales



pH impact on the catalytic performance

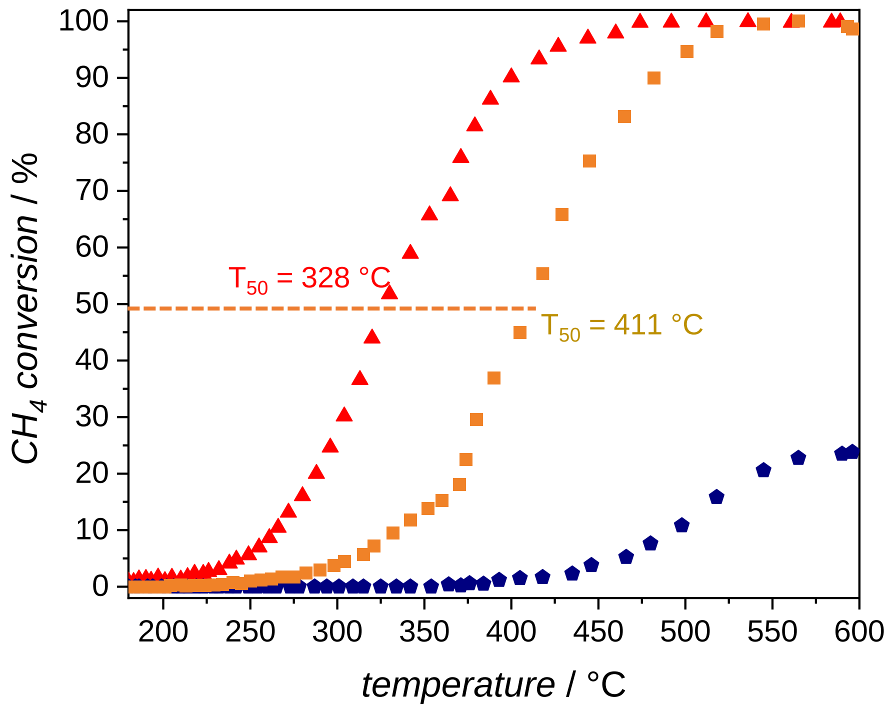
▲ **1.0%Pd/Al_2O_3**

⬟ **DP10.5/Al_2O_3 : 1.0%Pd-2.8%Ag-2.2%Ba-1.4%Bi-3.0%Ti-0.2%Pb/Al_2O_3**

■ **DP4/Al_2O_3: 1.0%Pd-1.0%Ag-0.4%Ba-2.2%Bi-1.9%Ti-0.3%Pb/Al_2O_3**

Direct valorization of leachates

Catalytic test : **Total oxidation of methane**



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Thesis M. M. Romo y Morales

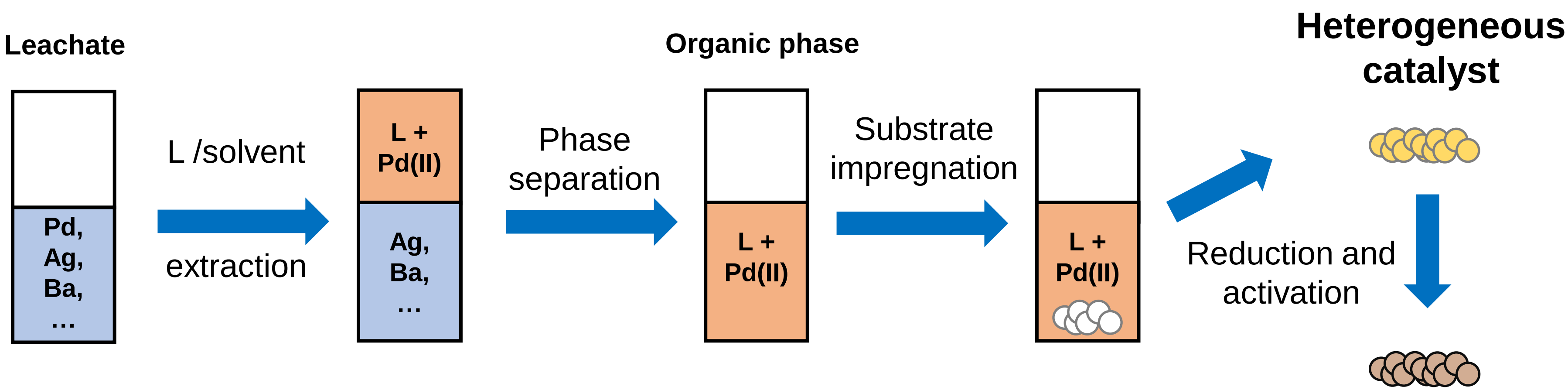
pH impact on the catalytic performance

Good activity compared to the model catalyst

…but works poorly in butadiene hydrogenation

Liquid-liquid extraction

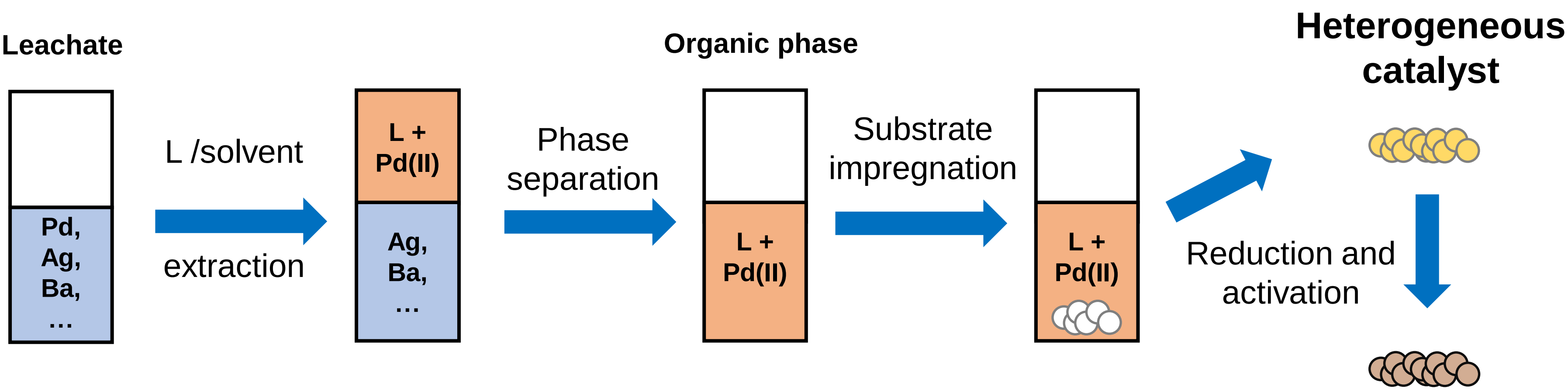
How to improve the performance?



Solvent = dodecane

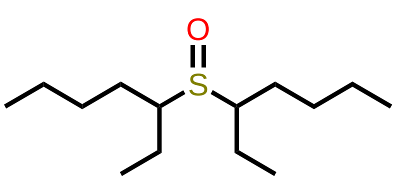
Liquid-liquid extraction

How to improve the performance?

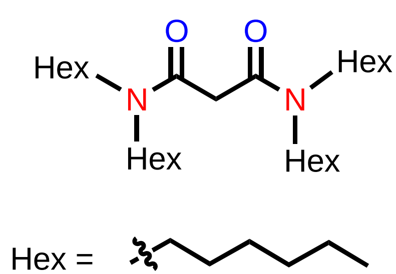


Solvent = dodecane

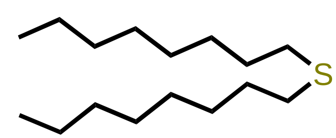
Which ligands to use ?



BESO

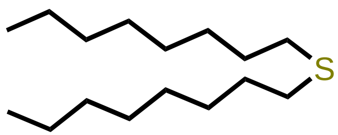


THEMA



DOS

Liquid-liquid extraction



DOS

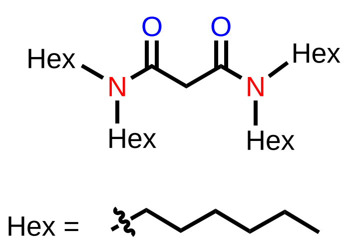
1000 €/kg

Commercial product

0,1 M/ dodecane, A/O = 1, 3h, 23 ˚C, 1000 rpm

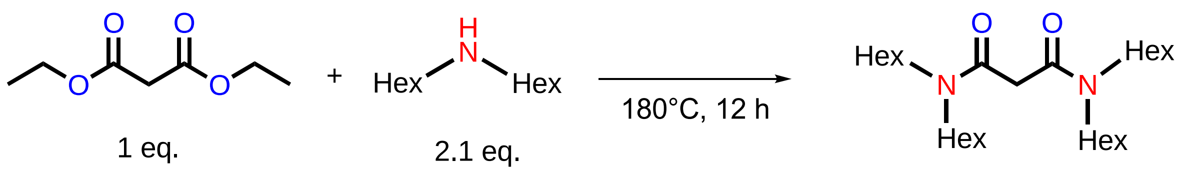
✓ Total Pd extraction
✓ Total precipitation of Pd on Al_2O_3
✗ Contains S – catalytic poison
✗ Inefficient organic phase recycling

Synthesized easily at the laboratory



THEMA

164 €/kg



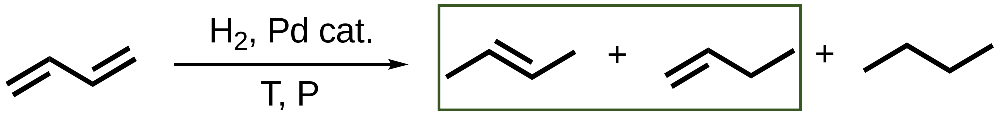
0,2 M/ dodecane, A/O = 1, 3h, 23 ˚C, 1000 rpm

✓ High distribution coeff. (D = 32)
✓ Sulphur free
✓ Efficient recycling
✗ Lower efficiency of precipitation of Pd on Al_2O_3

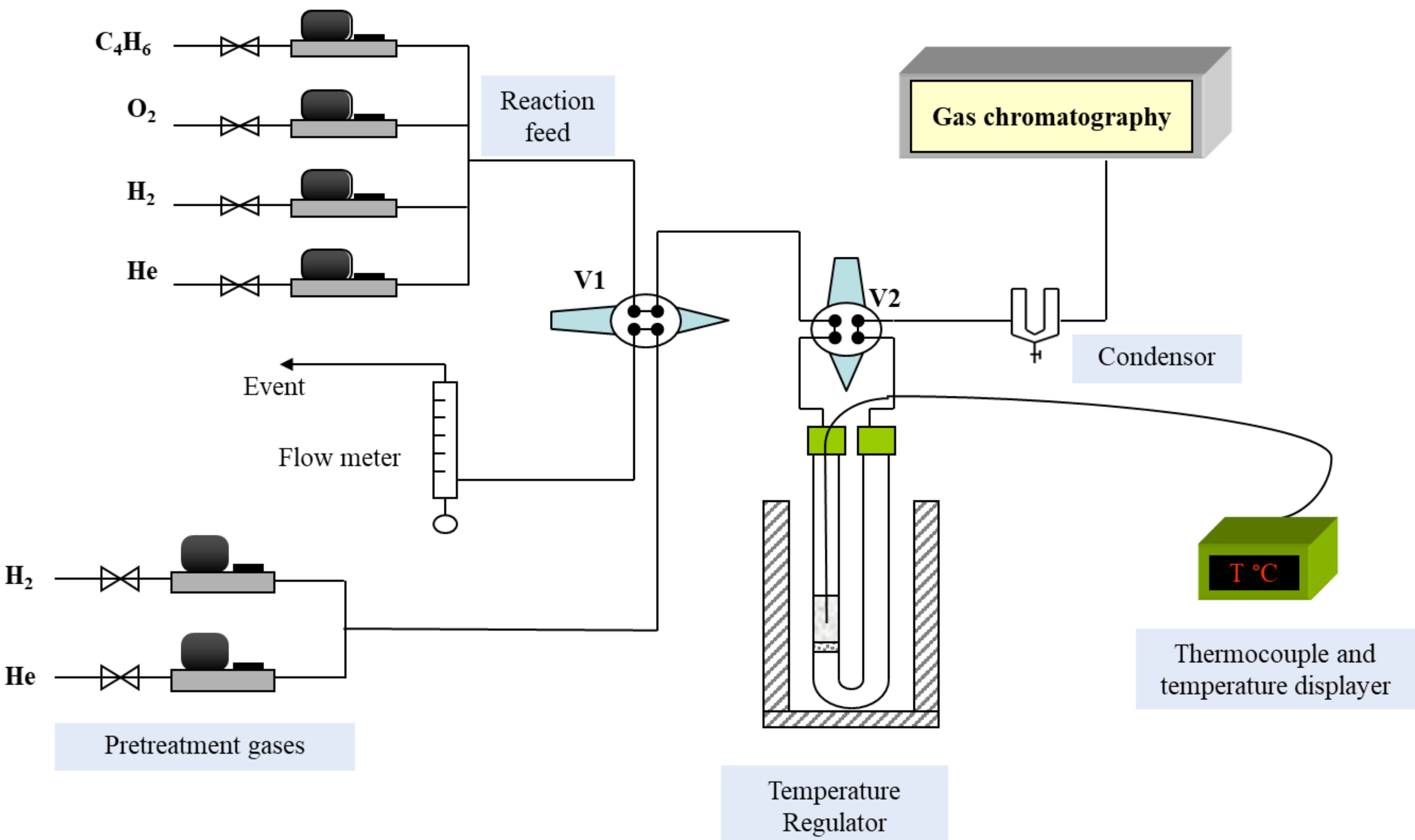
Pd source solution: Leachate (E-waste) or Model solution (Pd 1,7 g/L)

Catalytic tests

Hydrogenation of butadiene

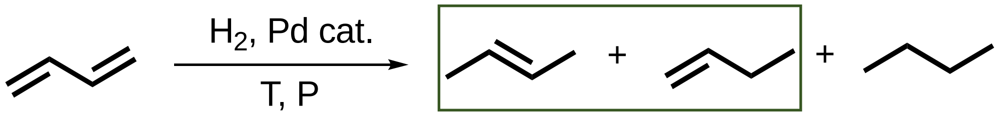


Experimental set-up



Catalytic tests

Hydrogenation of butadiene



Butadiene maximal conversion, %

	Pd source	
Extracting agent	Pd model	E-waste
DOS	66,0	14,0
THEMA	29,2	<1

Selectivity in butenes, %

	Pd source	
Extracting agent	Pd model	E-waste
DOS	59,0	100,0
THEMA	99,5	100,0

Conclusions and Perspectives

Sum up :

- Catalyst directly prepared from leachate by DP demonstrated encouraging results in total oxidation of methane but very poor activity in hydrogenation of butadiene.
- Liquid-liquid extraction was chosen to selectively isolate Pd from leachate.
- DOS and THEMA were used as extracting agents.
- Performance of the catalysts prepared from model solution is higher than the one prepared from leachate.

Perspectives

- Scrubbing of the organic phase with H_2O
- Back-extraction of organic phase to eliminate the impurities
- Preparation of Pd nanoparticles directly in the organic phase

Evaluate the rentability of each step basing on the cost, recyclability and extraction efficiency of the products used

Acknowledgments

LHyS (Systèmes HYbrides pour la Séparation)

Jean-Luc Rousset
Franck Morfin
Noura Haydar

Thank you for attention

Thank you for attention

Heterogeneous catalysts

First experiments

DOS extraction conditions:

- Leachate : MLCC, Pd 1710 ppm (ref. H678)
- DOS (0,1 M) solution in dodecane
- O/A = 1
- 3 h at 1000 rpm, 23°C

WI → No Pd in the org. phase after impregnation → Total deposition

DNc-00X-DOS-WI-MLCC (IRCE) DNc-00X-DOS-WI-MLCC(ACTIV)

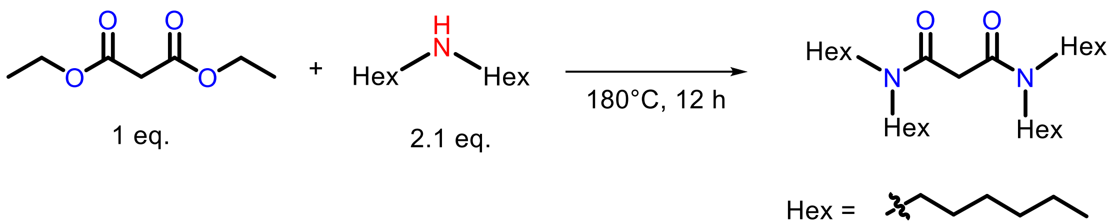
Washing with H_2O:

- O/A = 5
- 0,5 h at 1000 rpm, 23°C
- 2 times

pH of aqueous phase after 2nd washing around 3-4

Heterogeneous catalysts

Synthesis of THEMA



THEMA (neat) pour IRCE

THEMA extraction conditions:

- Leachate : MLCC, Pd 1710 ppm (ref. H678)
- THEMA (0,2 M) solution in dodecane (addition of 10% mol of DHA)
- O/A = 1
- 3 h at 1000 rpm, 23°C

WI

DNc-00X-THEMA-WI-MLCC (IRCE)

DNc-00X-THEMA-WI-MLCC (ACTIV)

S.-A. Moussaoui *et al.*, *Molecules*. **2021**, *276*, 119293.

Conclusions and Perspectives

Sum up :

- Catalyst directly prepared from leachate by DP demonstrated encouraging results in total oxidation of methane but very poor activity in hydrogenation of butadiene.
- Liquid-liquid extraction was chosen to selectively isolate Pd from leachate.
- Catalysts prepared using DOS showed better performance.
- Performance of the catalysts prepared from model solution is higher than the one prepared from leachate.

Perspectives :

- Back-extraction from organic phase to avoid the impurities.
- Preparation of Pd nanoparticles directly in organic phase.
- Evaluate the rentability of the use of DOS and THEMA as extracting agents based on cost, recyclability and extraction efficiency.