Innovative catalytic pathways for the reduction of carbon-oxygen bonds for the oxygenated plastics reductive depolymerization

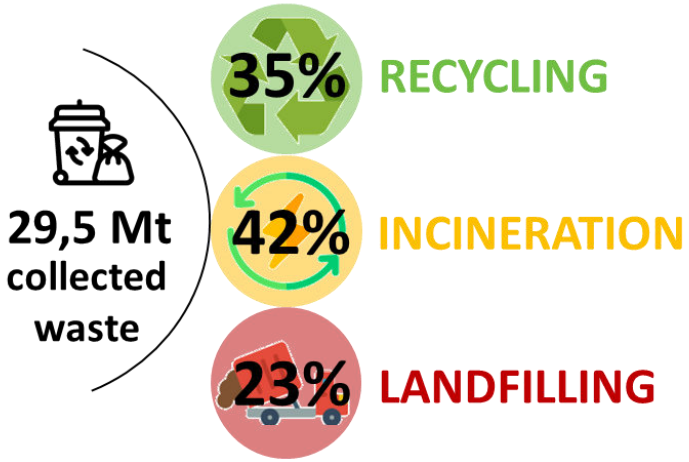
Marie KOBYLARSKI

Thibault CANTAT / Jean-Claude BERTHET

DRF/IRAMIS/NIMBE/LCMCE

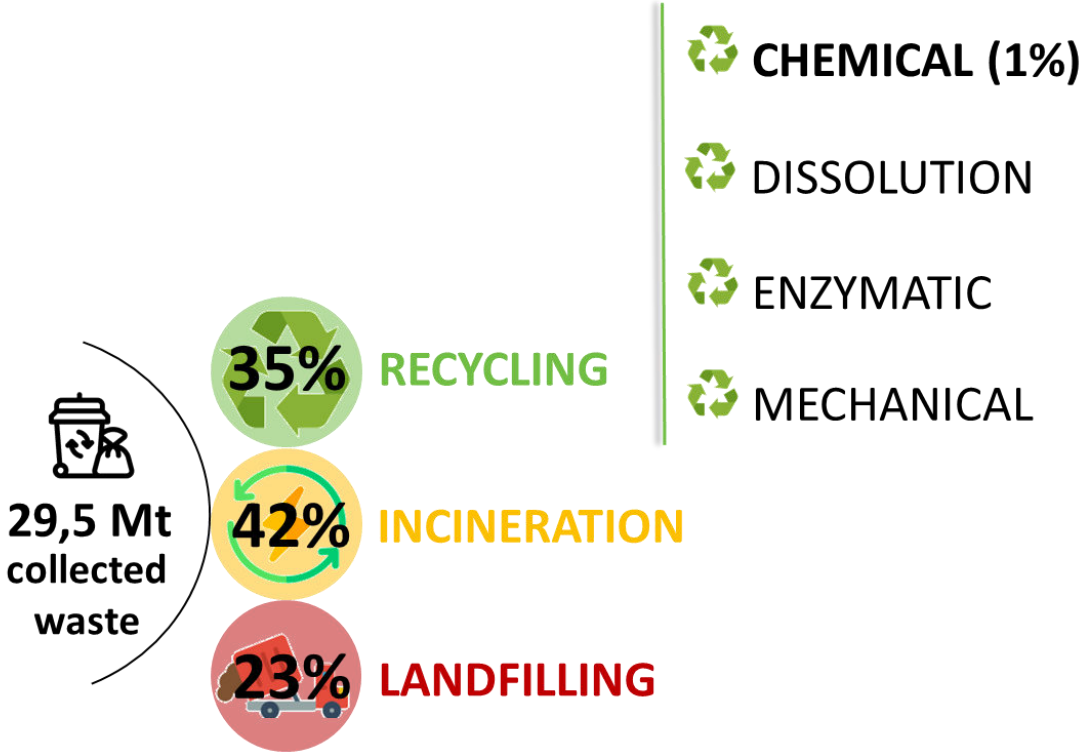
Journée de la Chimie Durable – September 29th, 2023

Plastic waste processing



Figures for Europe - Plastics The Facts, **2022**

Plastic waste processing



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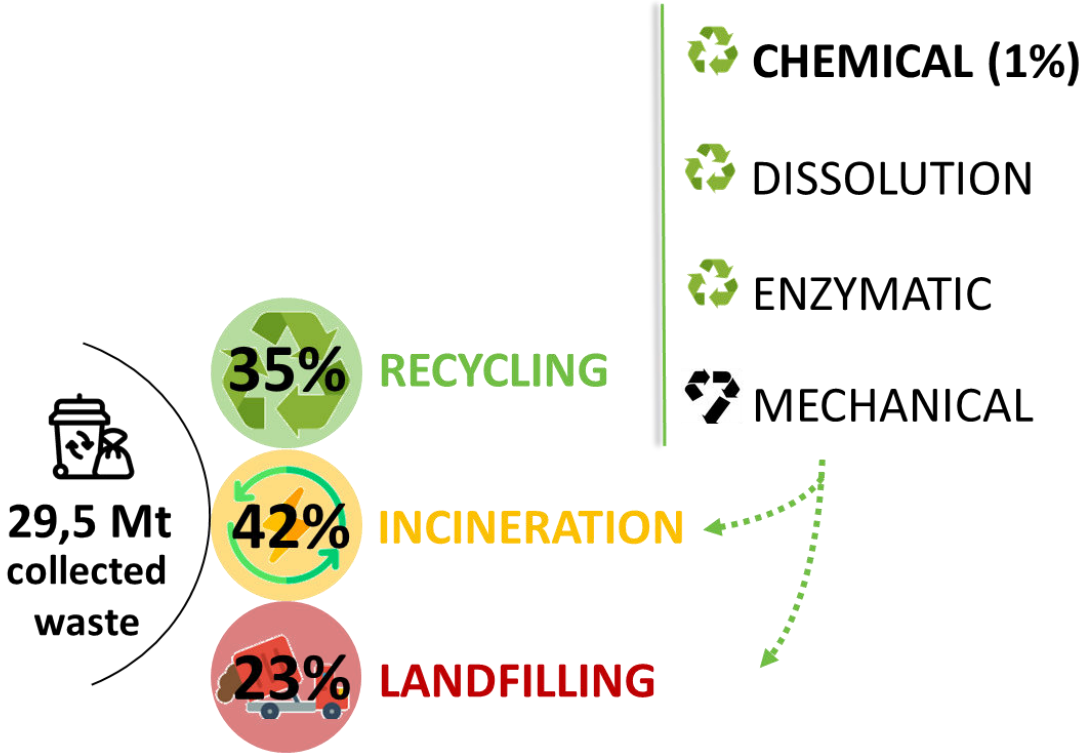

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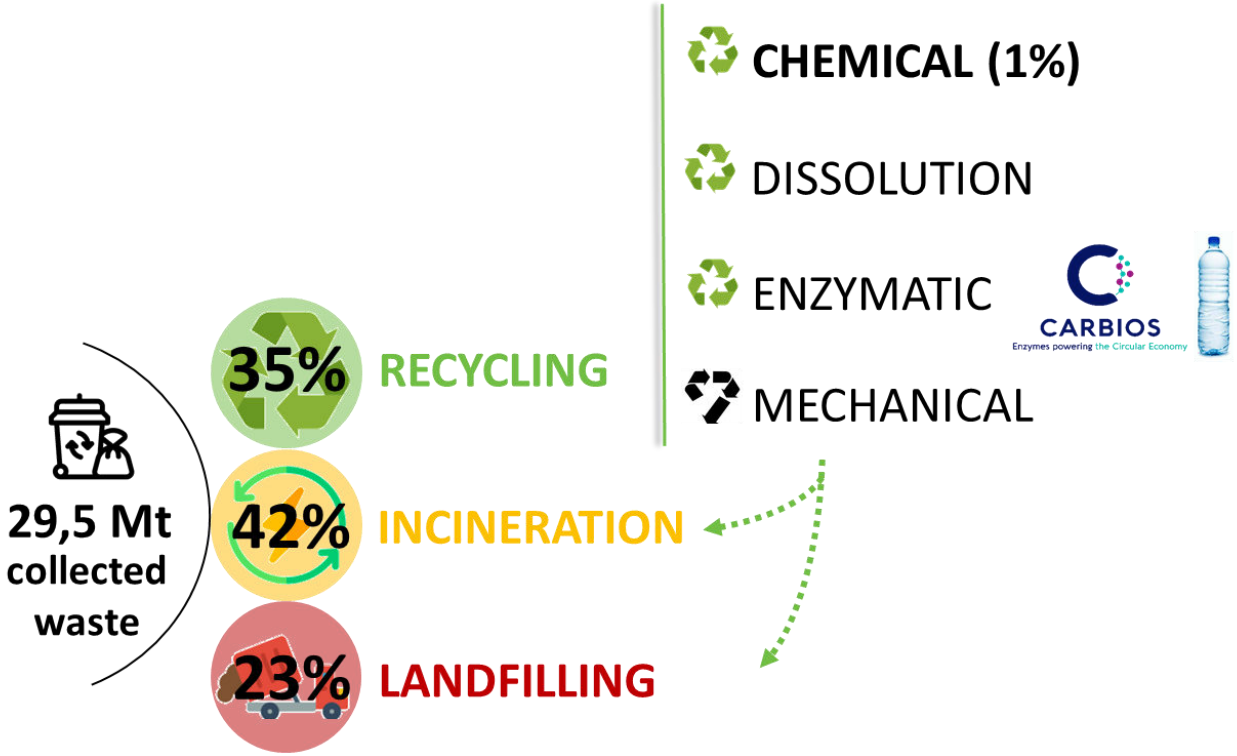

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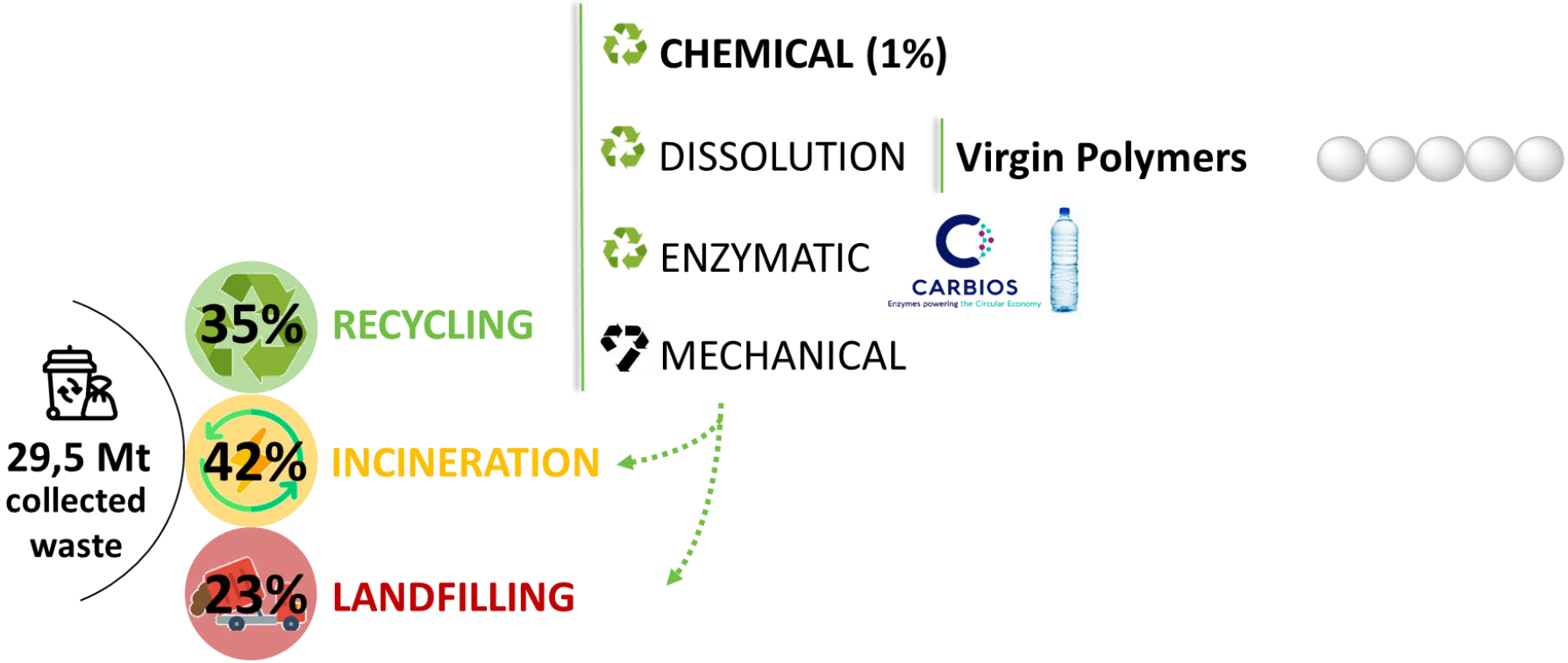


Figures for Europe - Plastics The Facts, **2022**

Plastic waste processing

THERMAL

Gaz
Oils

CHEMICAL (1%)

29,5 Mt collected waste

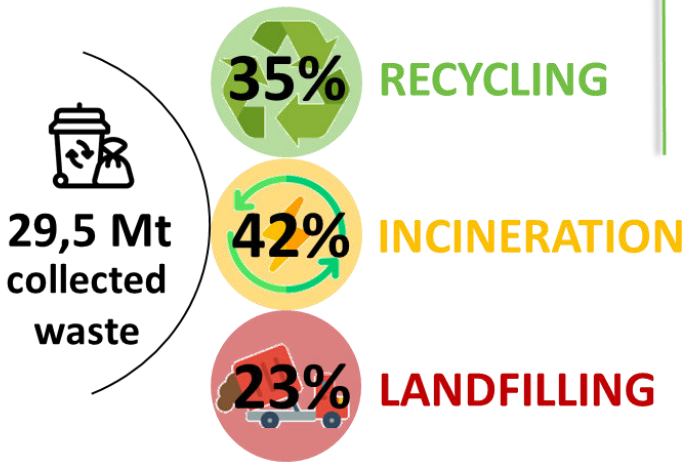
35% RECYCLING

42% INCINERATION

23% LANDFILLING

Figures for Europe - Plastics The Facts, **2022**

Plastic waste processing



CHEMICAL (1%)

THERMAL

Gaz
Oils

DEPOLYMERIZATION

Monomers

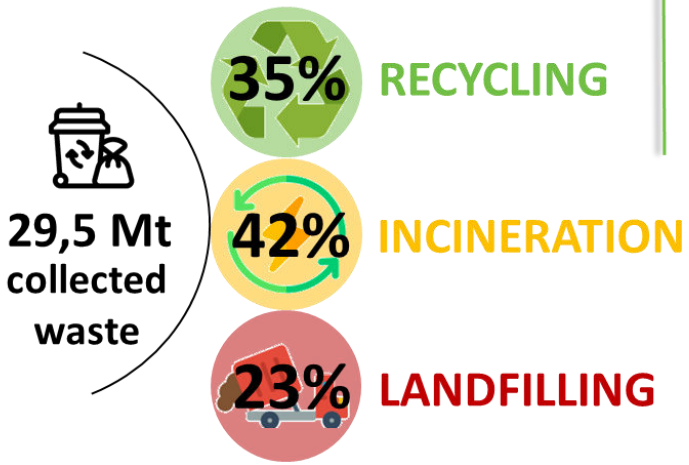
Hydrolysis, Alcoolysis, Aminolysis

Derivatives

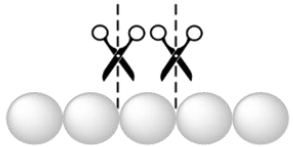
Reduction

Figures for Europe - Plastics The Facts, **2022**

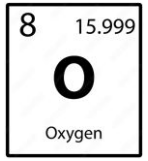
Plastic waste processing



CHEMICAL (1%)



DEPOLYMERIZATION

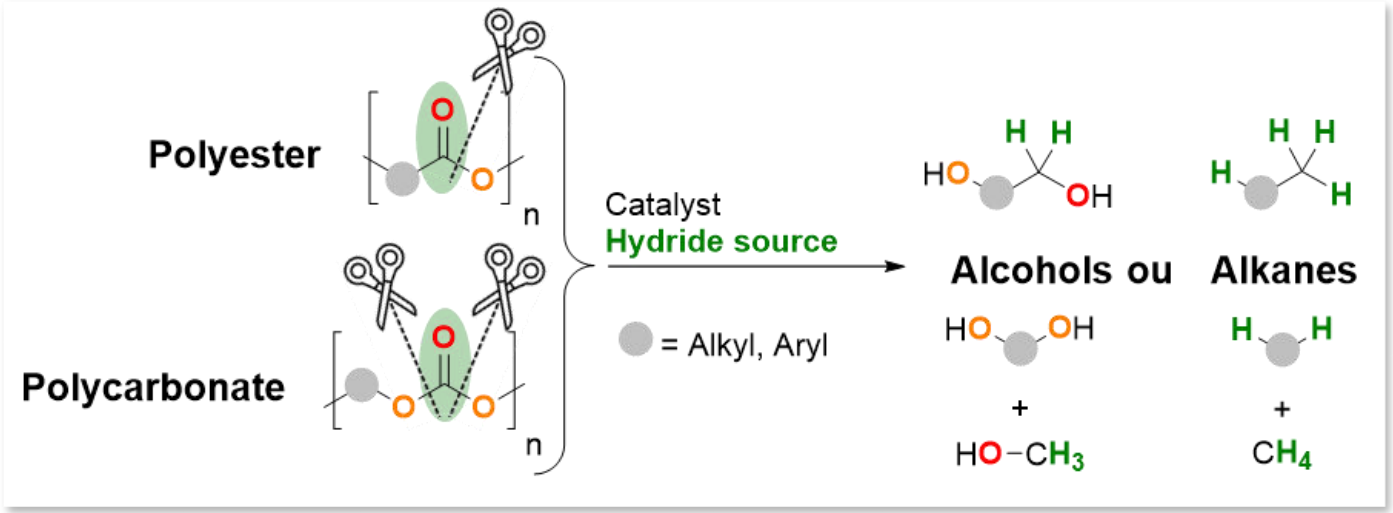


Derivatives

Reduction

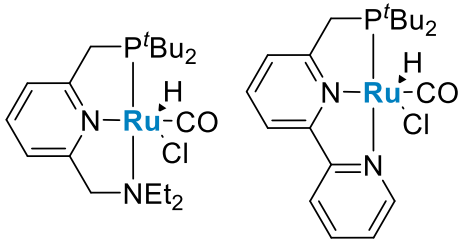
Figures for Europe - Plastics The Facts, **2022**

Reductive depolymerization of oxygenated plastics – State of the art



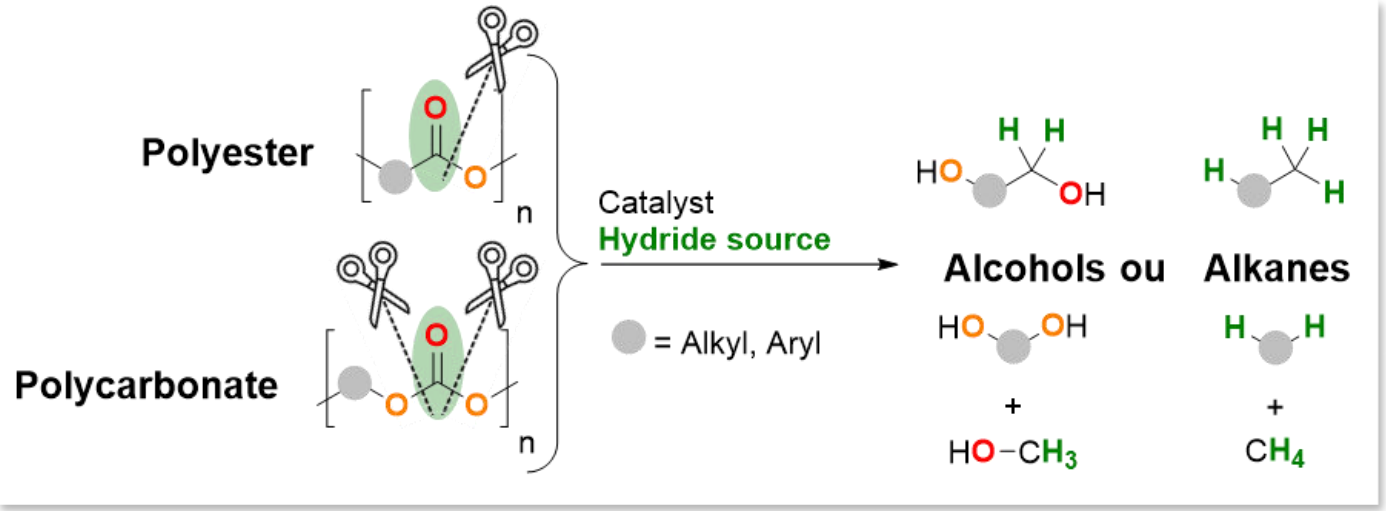
Reductive depolymerization of oxygenated plastics – State of the art

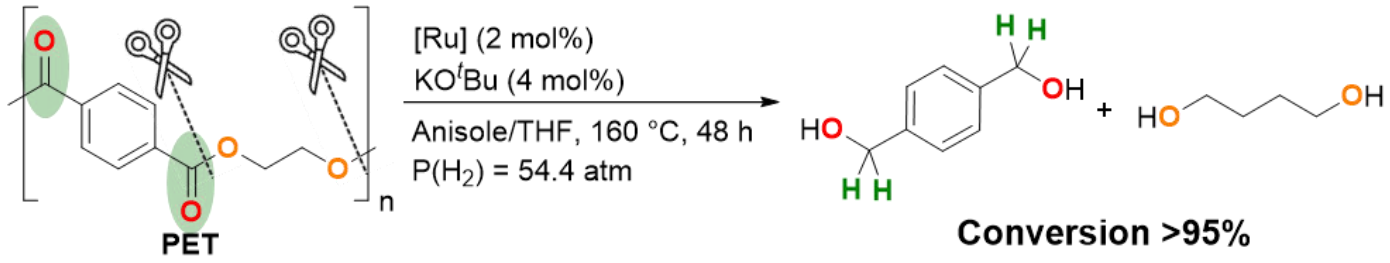
HYDROGENATION



120 €/mmol*

Robertson *et al.*
1-2 mol%
H_2
P(H_2) = 54.4 atm

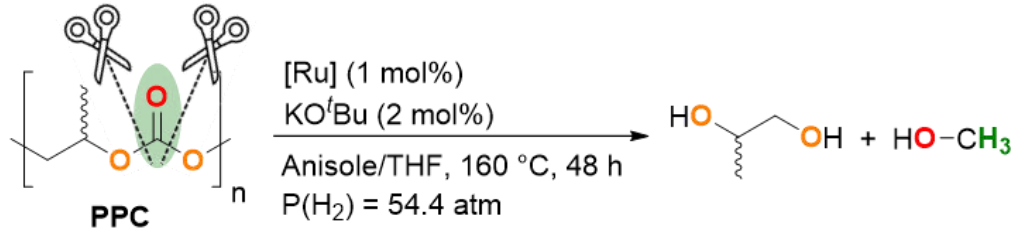




PET

Polyethylene terephtalate

Conversion >95%



PPC

Polypropylene carbonate

Conversion >95%

* Alfa Aesar (26/11/2022) VS $Zn(OAc)_2$: 35 €/mmol)

N.J.Robertson, *Chem. Commun.*, **2014.**

Reductive depolymerization of oxygenated plastics – State of the art

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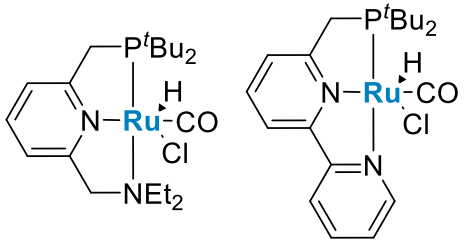

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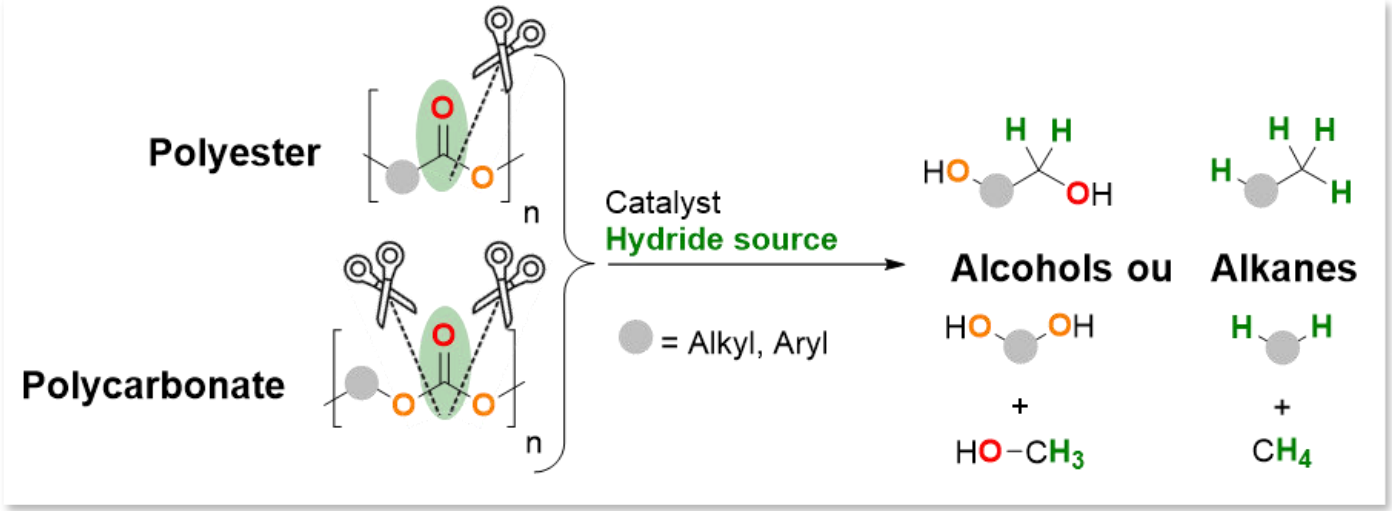
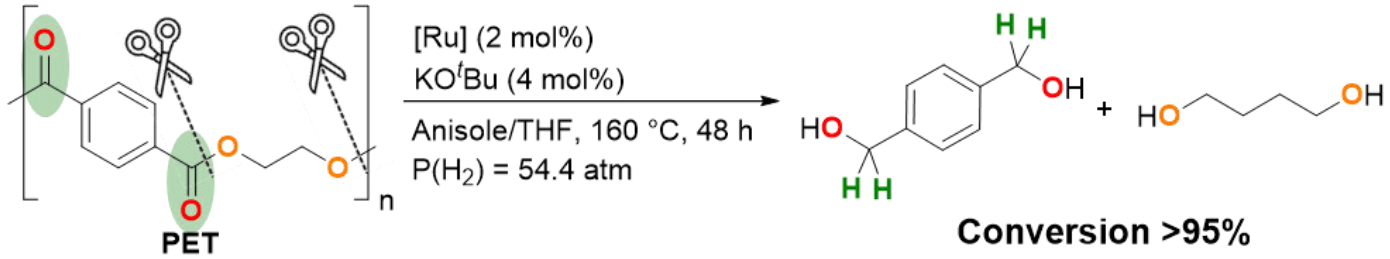


- ✖ ***Expensive catalysts***
- ✖ ***High pressure***
- ✓ ***Abundant reductant***
- ✓ ***No side-products***



Polyethylene terephtalate

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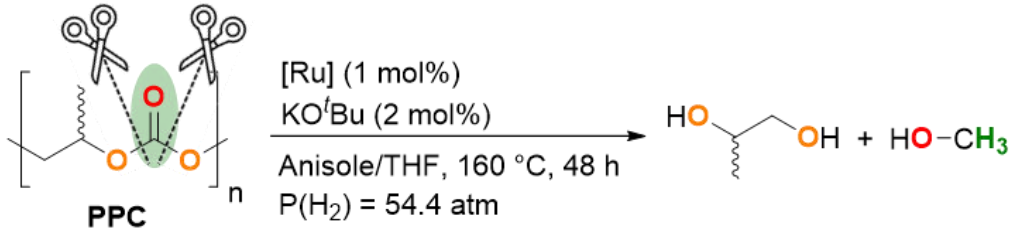

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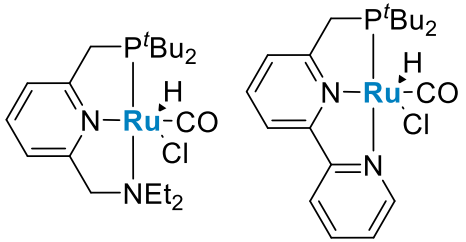

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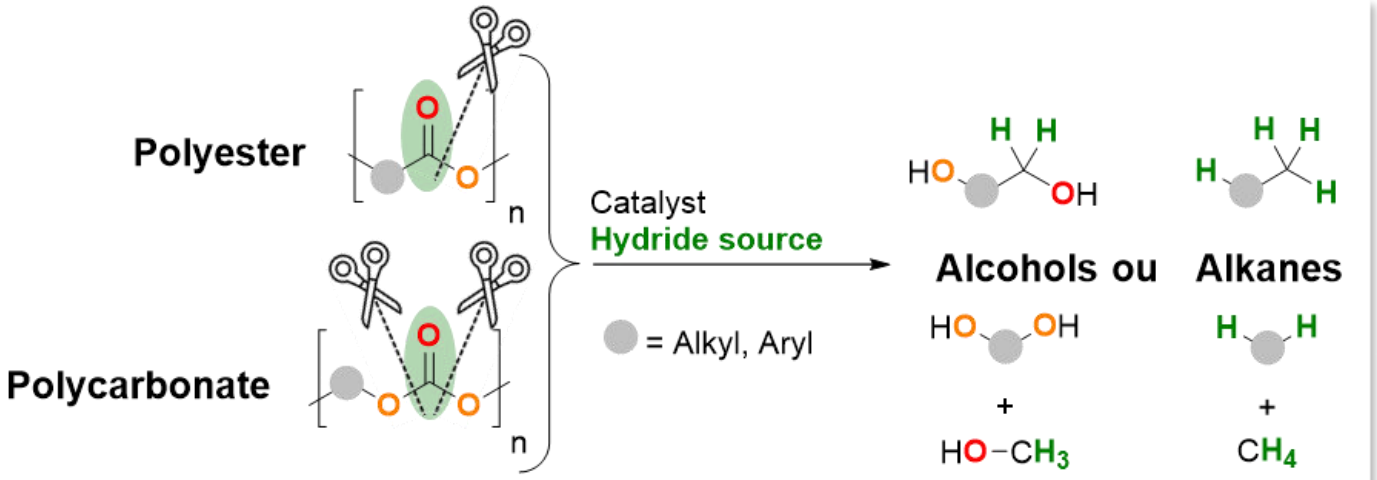
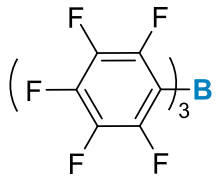
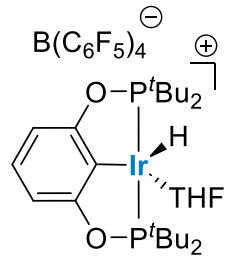


HYDROSILYLATION



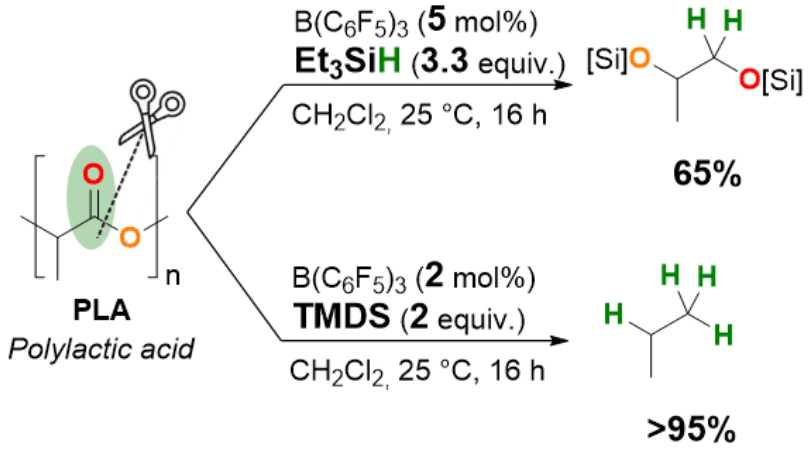
180 €/mmol*

Cantat *et al.*
2-10 mol%
R_3Si-H



410 €/mmol*

Cantat *et al.*
0.3-1 mol%
R_3Si-H



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N.J.Robertson, *Chem. Commun.*, **2014** ; E.Feghali, *ChemSusChem*. **2015** ; L.Monsigny, *ACS Sustainable Chem. Eng.*, **2018.**

Reductive depolymerization of oxygenated plastics – State of the art

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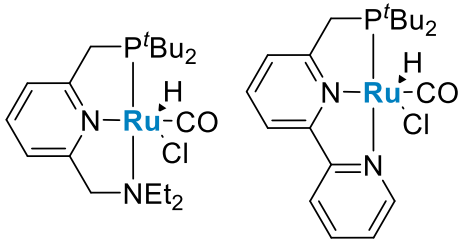

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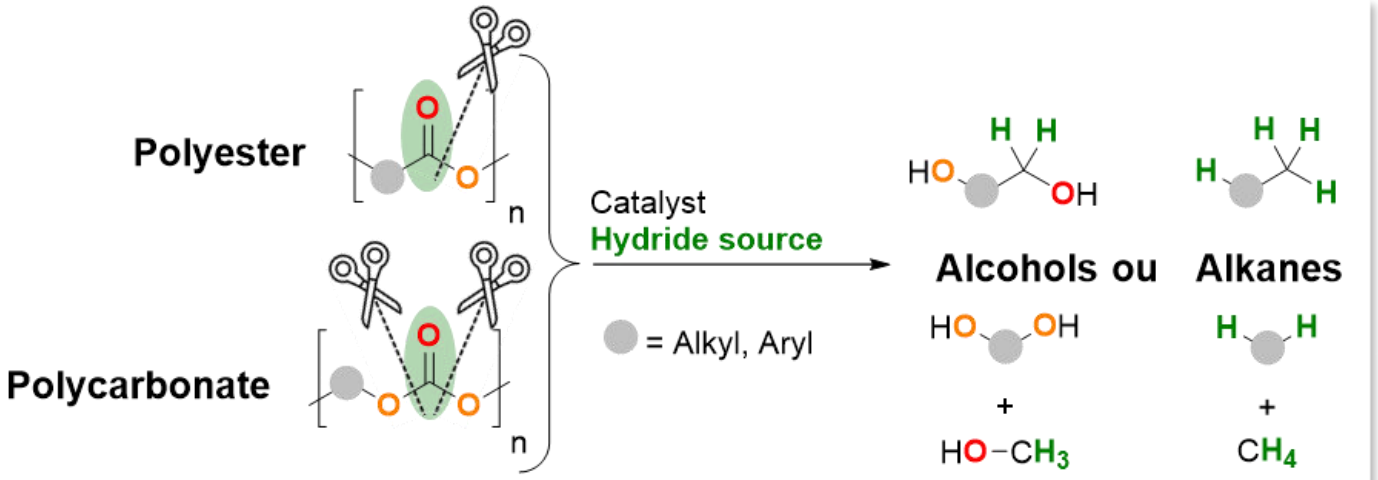

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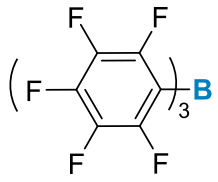

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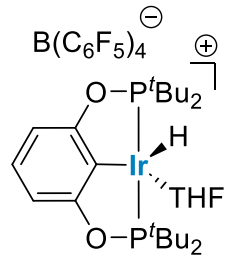

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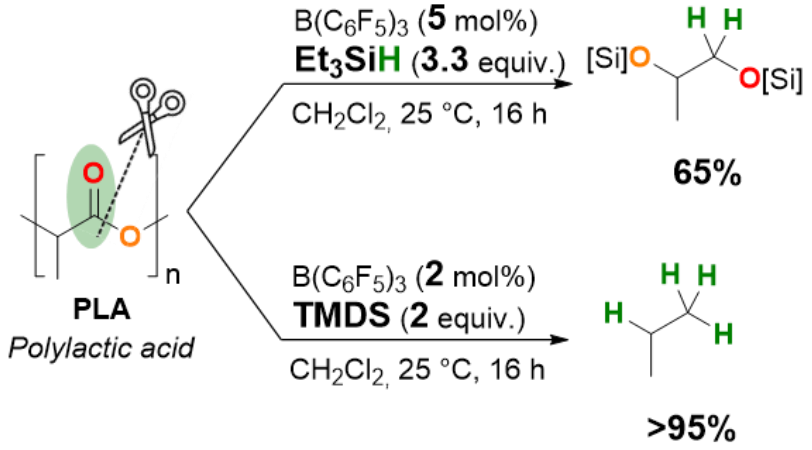
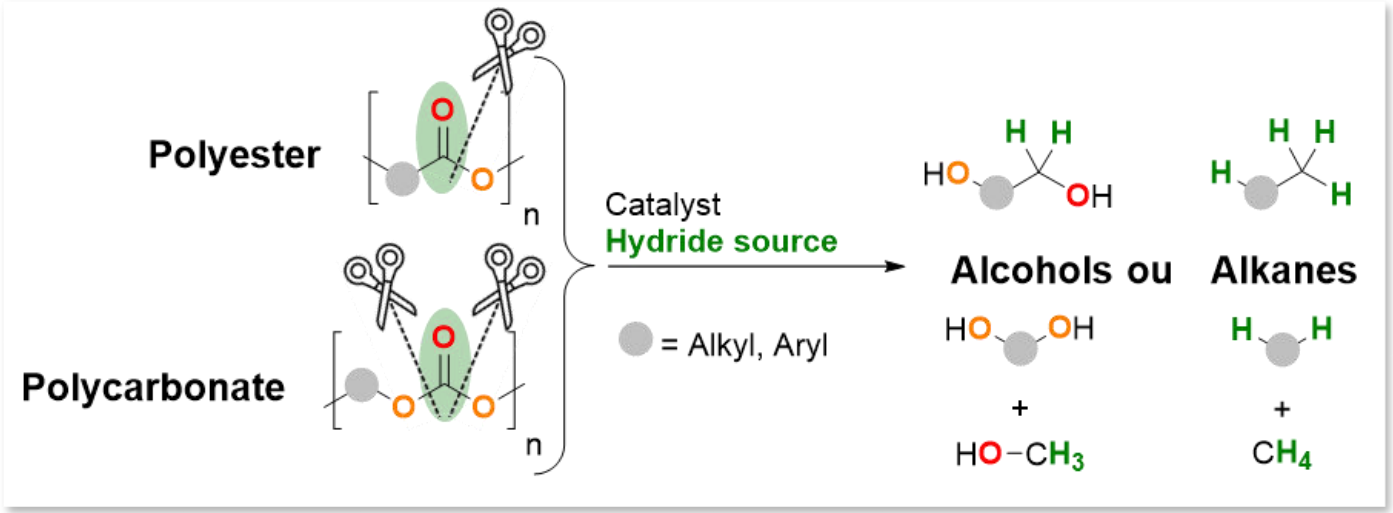


- ✓ *Soft conditions*
- ✓ *≠ reactivities VS conditions*
- ✗ *Expensive catalysts*
- ✗ *Siloxane waste*

* Alfa Aesar (26/11/2022) VS $Zn(OAc)_2$: 35 €/mmol)

N.J.Robertson, *Chem. Commun.*, **2014** ; E.Feghali, *ChemSusChem*. **2015** ; L.Monsigny, *ACS Sustainable Chem. Eng.*, **2018.**

Reductive depolymerization of oxygenated plastics – PhD Goals



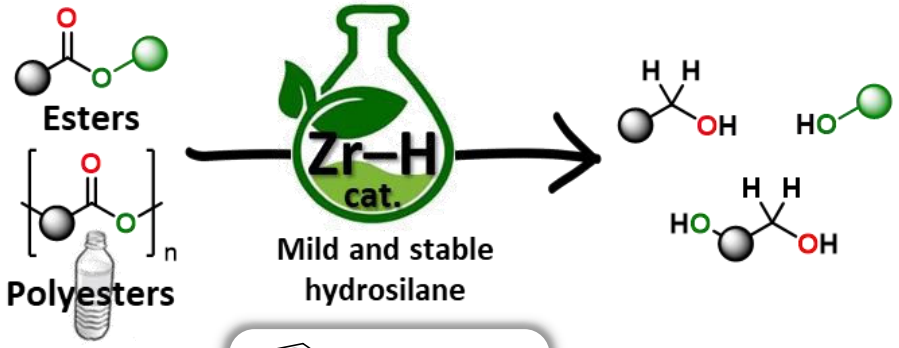
Metal

Hydride source

Mechanism

Oxygenated polymers

1. Reductive depolymerization with R_3Si-H



Green Chem., **2022.**

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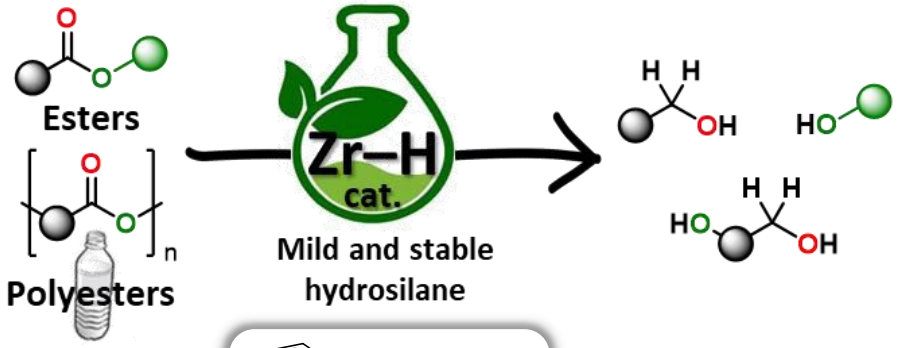
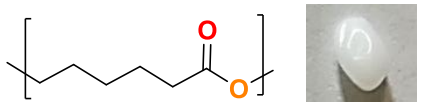


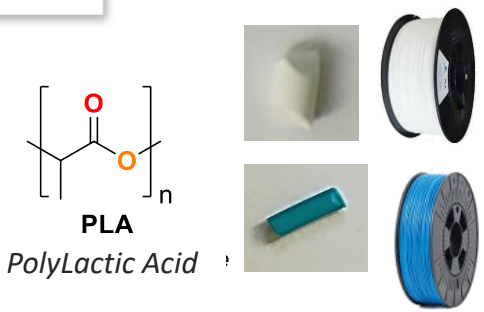
1st use of Zirconium catalyst for :

- ☑ **Reduction of esters**
- ☑ **Reduction depolymerization of polyesters**



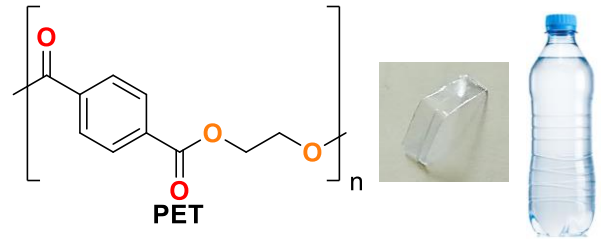
PCL

PolyCaproLactone



PLA

PolyLactic Acid



PET

PolyEthylene Terephtalate

Green Chem., **2022.**

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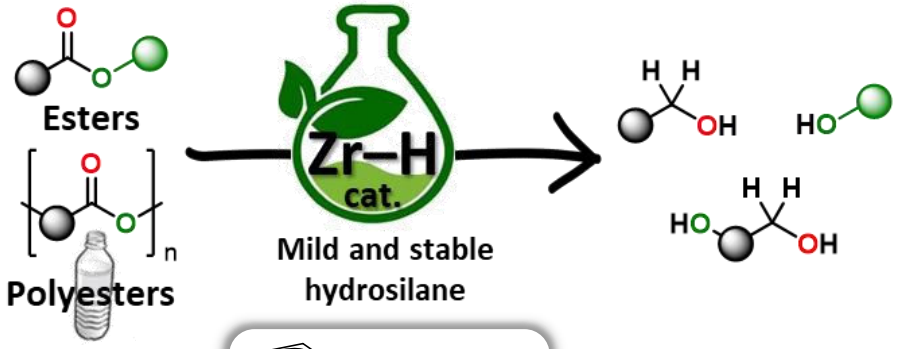

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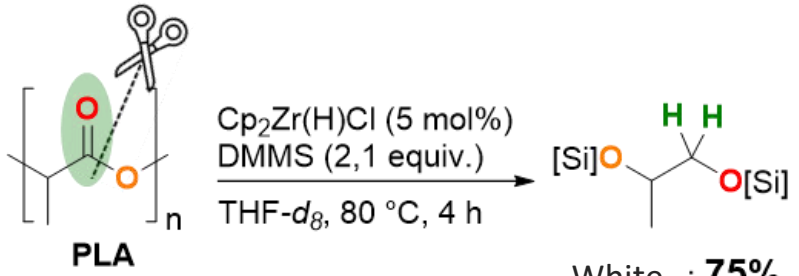
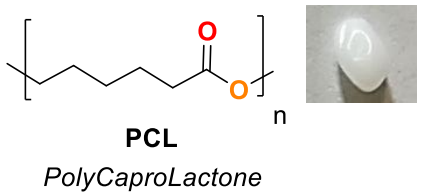


PLA
PolyLactic Acid

White : **75%**
Blue : **>95%**



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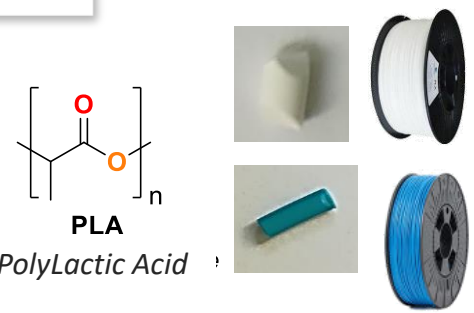

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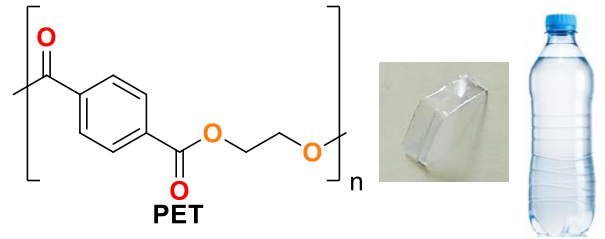

PET
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* Alfa Aesar price (26/11/2022)

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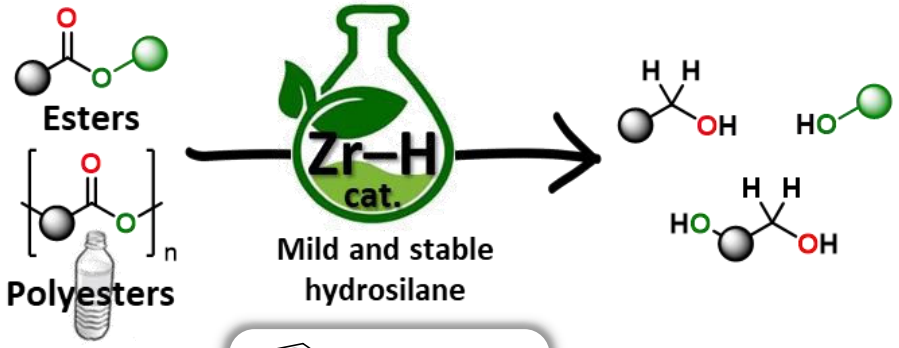

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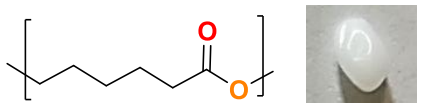
- ☑ **Reduction of esters**
- ☑ **Reduction depolymerization of polyesters**
- ⇨ **High selectivity (no over-reduced products)**
- ⇨ **Quite cheap catalyst (80 €/mmol)***



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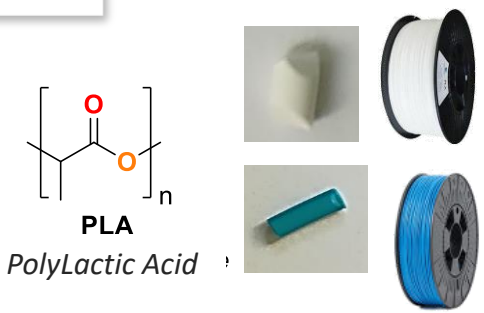

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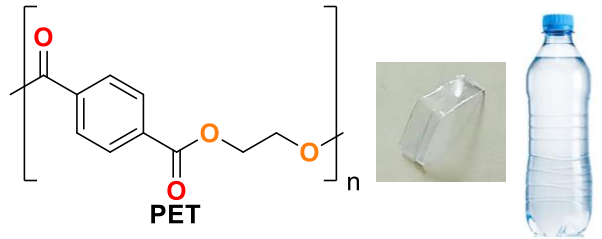

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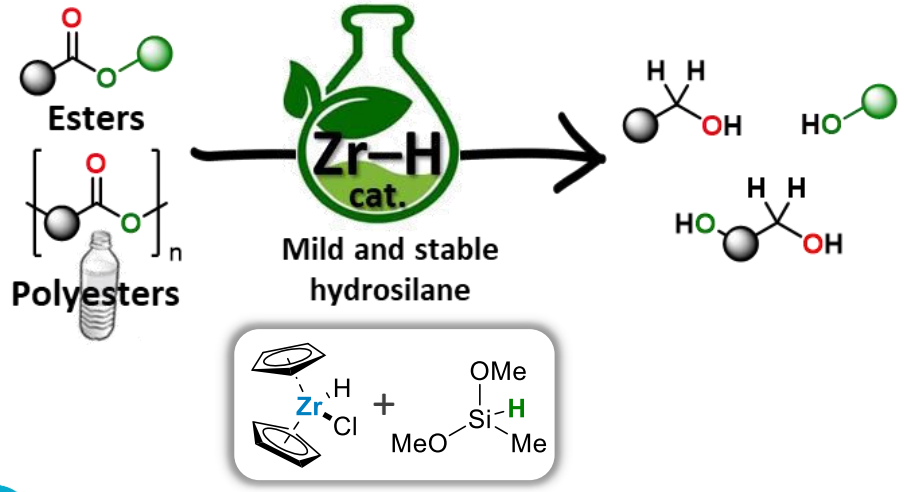

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- ☑ **Reduction of esters**
- ☑ **Reduction depolymerization of polyesters**
- ⇨ **High selectivity (no over-reduced products)**
- ⇨ **Quite cheap catalyst (80 €/mmol)***

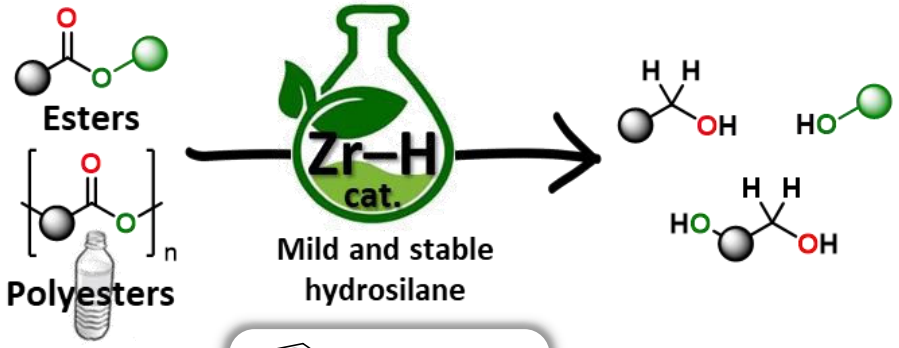
Perspectives :

- ☐ **Extend to other polymers**
- ☐ **Optimize hydrolysis**
- ☐ **Further explore the mechanism**

* Alfa Aesar price (26/11/2022)

Green Chem., **2022.**

2. Reductive depolymerization with R_2B-H



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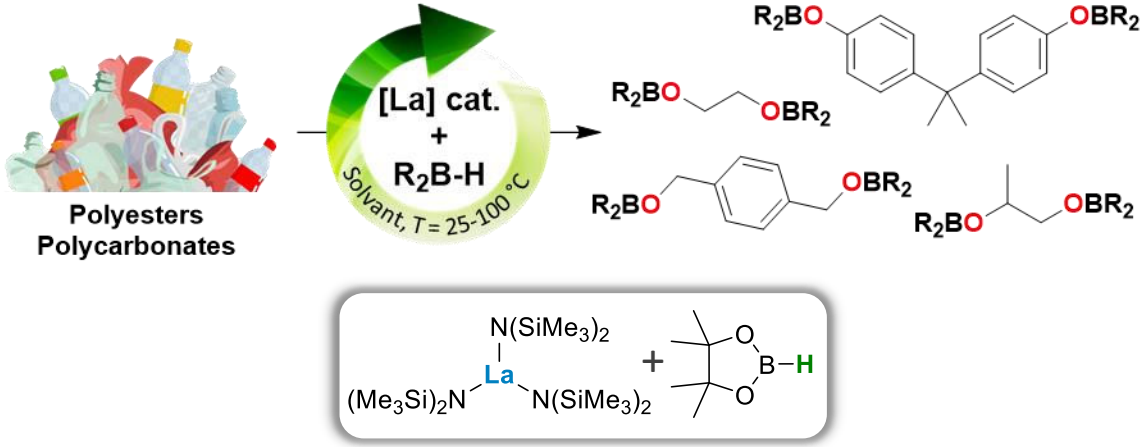

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Green Chem., **2022** ; *Chem. Comm.* **2022.**

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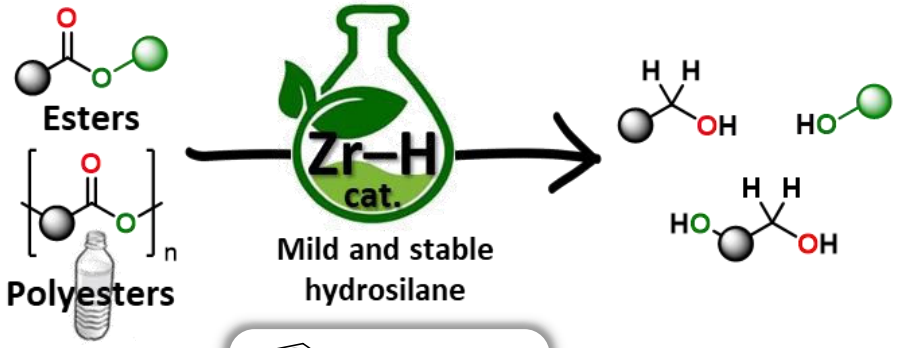

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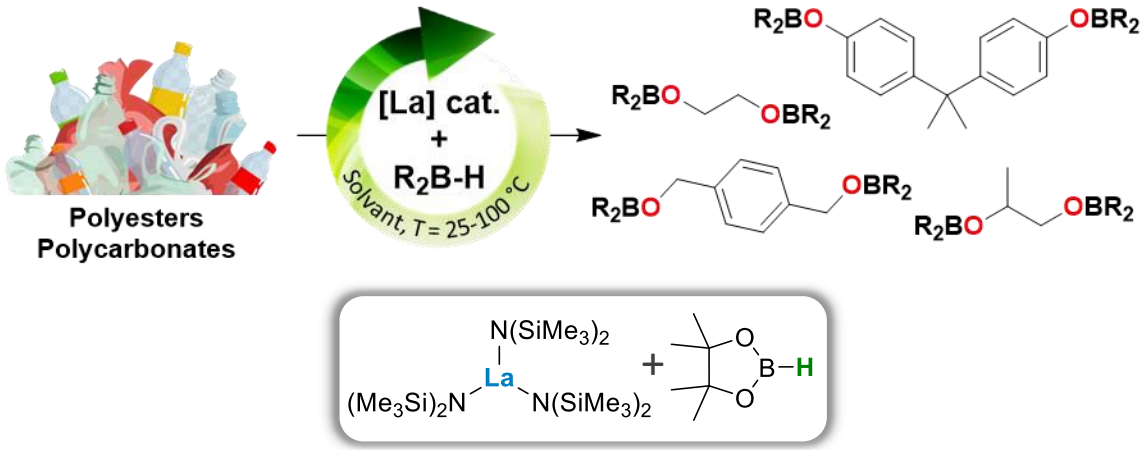


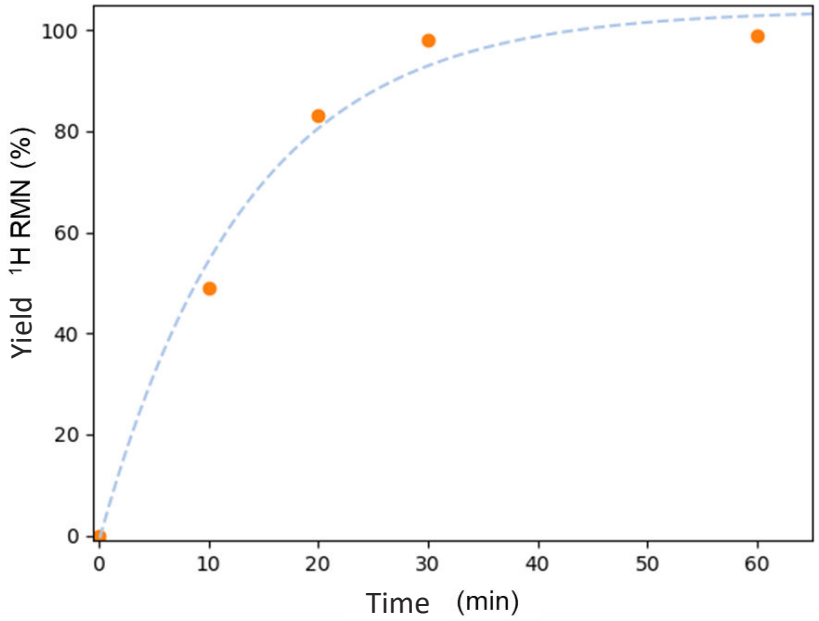
1st reductive depolymerization with :

- ☑ **Metal f catalyst**
- ☑ **Hydroboranes**

* Alfa Aesar price (26/11/2022)

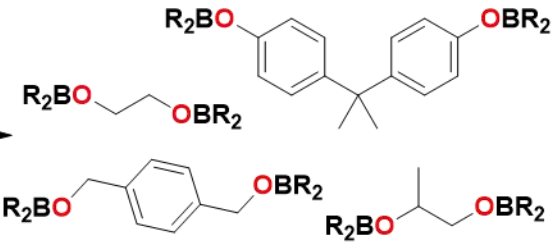
Green Chem., **2022** ; *Chem. Comm.* **2022.**

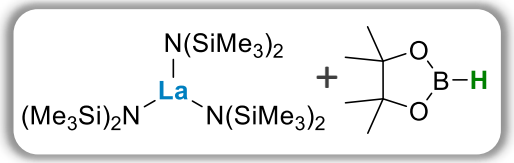
2. Reductive depolymerization with R_2B-H



Polyesters
Polycarbonates

[La] cat.
+
R_2B-H
Solvant, T = 25-100 °C





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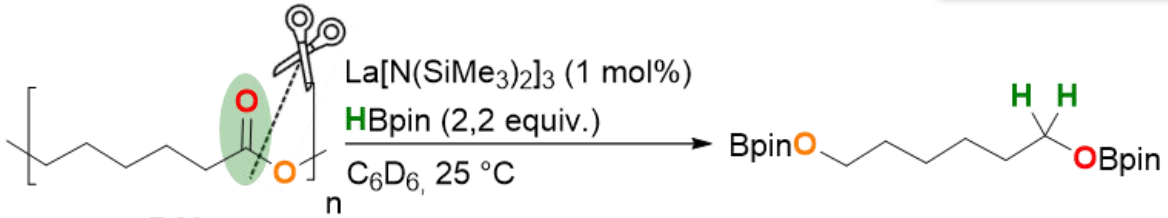


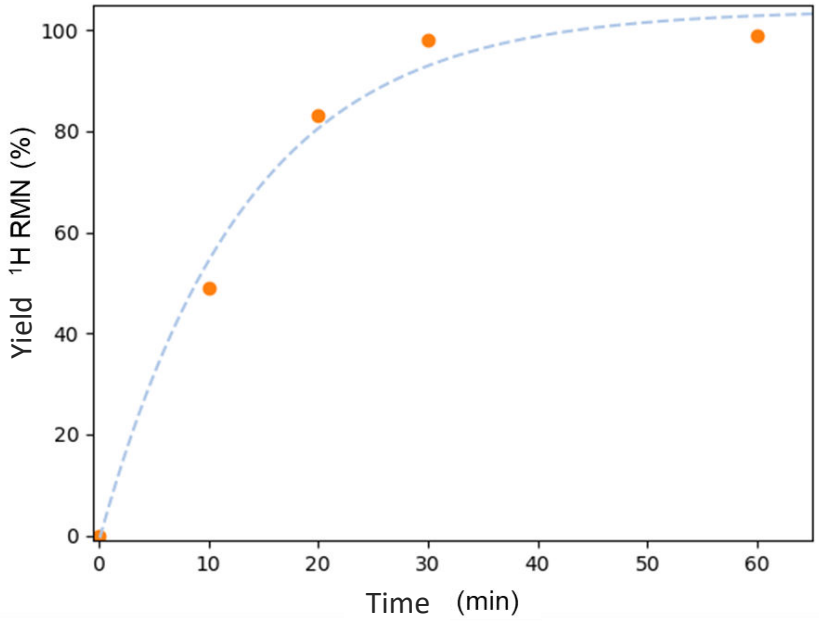
PCL

PolyCaproLactone

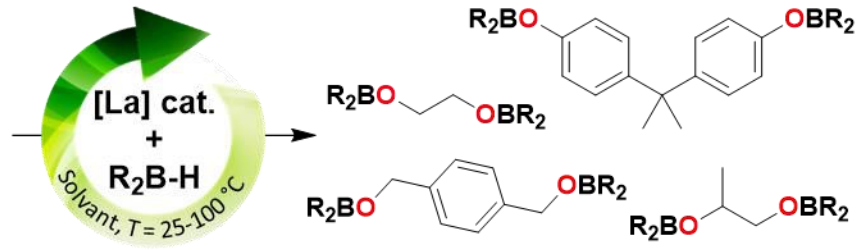
>95%

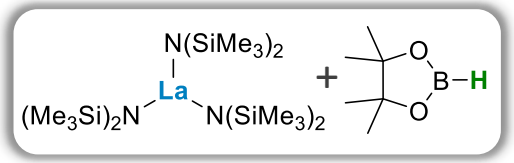
Green Chem., **2022** ; *Chem. Comm.* **2022.**

2. Reductive depolymerization with R_2B-H



Polyesters
Polycarbonates





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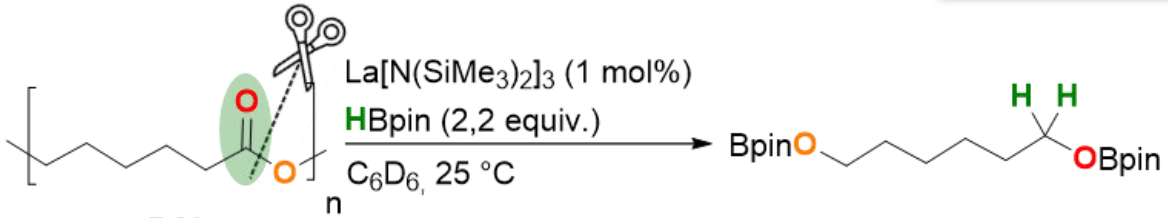


PCL

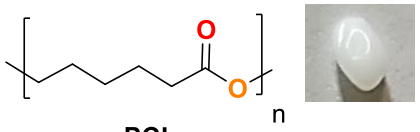
PolyCaproLactone

>95%

87%

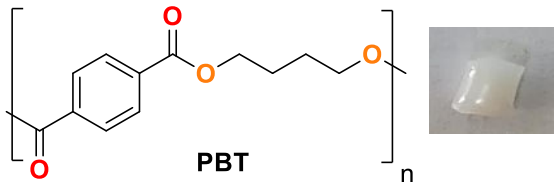
Green Chem., **2022** ; *Chem. Comm.* **2022.**

2. Reductive depolymerization with R_2B-H



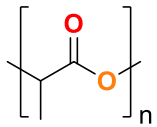
PCL

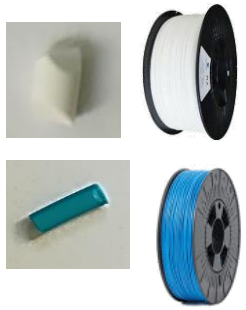
PolyCaproLactone



PBT

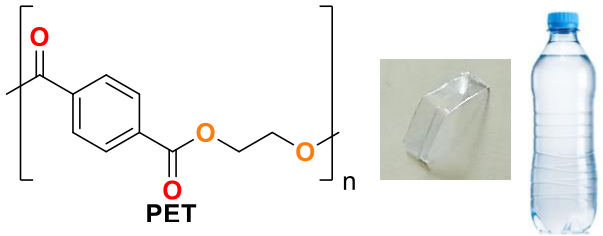
PolyButylene Terephtalate





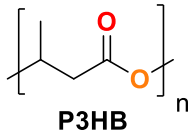
PLA

PolyLactic Acid



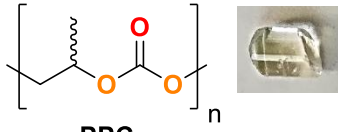
PET

PolyEthylene Terephtalate



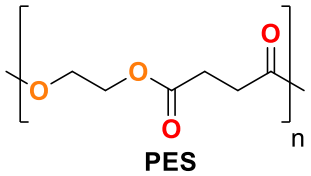
P3HB

Poly-ß-hydroxybutyrate



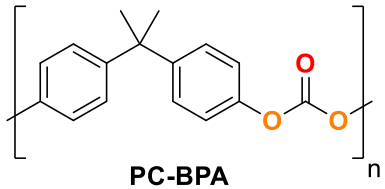
PPC

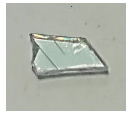
PolyPropylene Carbonate



PES

PolyEthylene Succinate

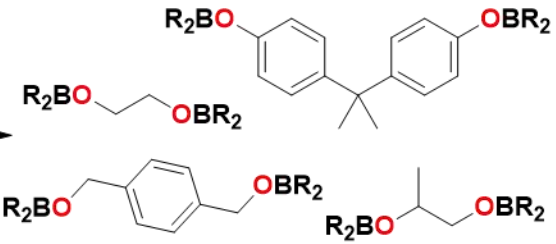


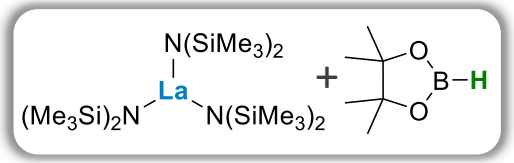


PC-BPA

PolyCarbonate Bisphenol A

Polyesters
Polycarbonates



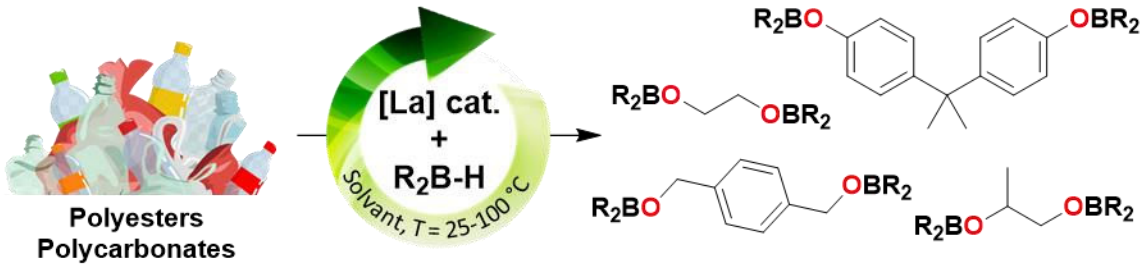


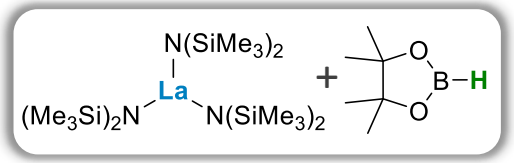
1st reductive depolymerization with :

- ☑ **Metal f catalyst**
- ☑ **Hydroboranes**
- ⇨ **High selectivity (no over-reduced products)**
- ⇨ **Catalyst ~ 170 €/mmol***

Green Chem., **2022** ; *Chem. Comm.* **2022.**

2. Reductive depolymerization with R_2B-H





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Perspectives :

- ☐ **Try on a mixture of plastics**
- ☐ **Reuse of the catalyst**
- ☐ **Study the mechanism**
- ☐ **Extend to others polymers**

* Alfa Aesar price (26/11/2022)

Green Chem., **2022** ; *Chem. Comm.* **2022.**

Thank you

CEA SACLAY

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France

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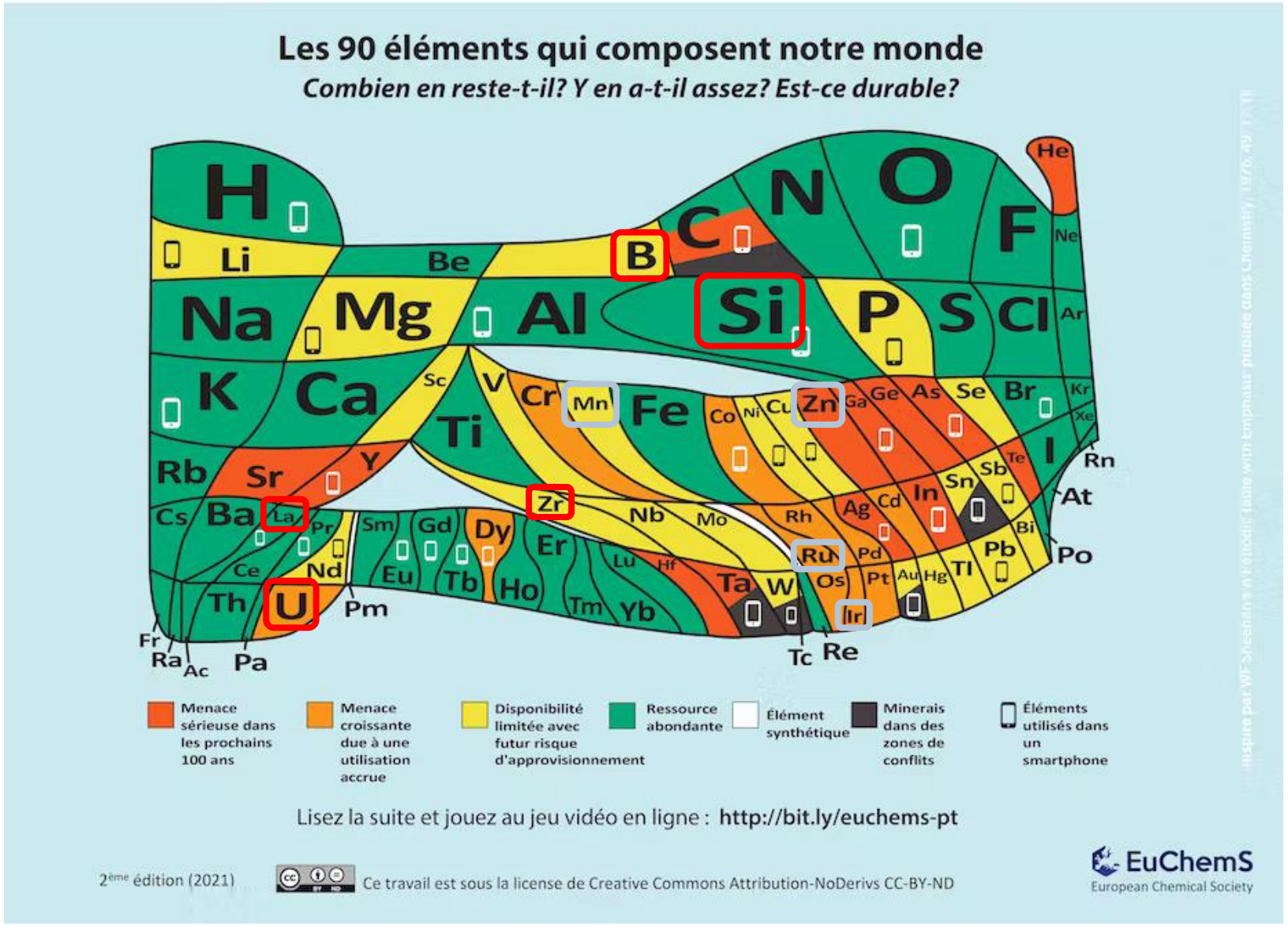

Elément	Prix (€/kg)
Iridium	29 000
Ruthénium	3 000
Bore	2 200
Uranium	53,10
Zirconium	21
Molybdène	15
Lanthane	6
Zinc	3
Silicium	2
Manganèse	2
Fer	<1