A sustainability-driven approach for the comparison of heterogenous and homogenous Cu-based catalysts in the DMTM reaction

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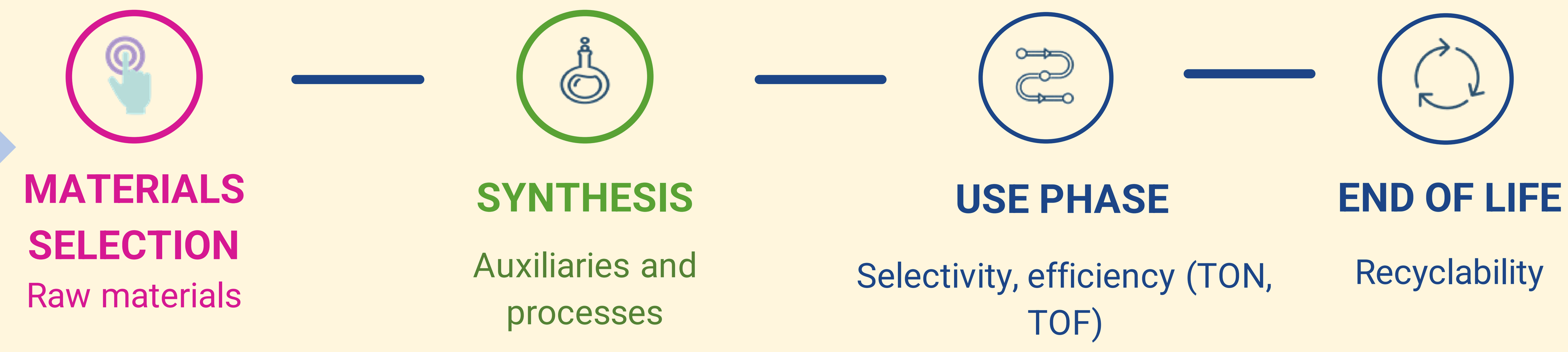
Catalysis and sustainability:

Beside the classical parameters employed to determine the efficiency of a catalytic process (i.e. turnover number (**TON**), turnover frequency (**TOF**)…), other aspects should be introduced. In particular (i) the **environmental** and **economic sustainability** and (ii) the **recyclability** of the catalysts. Process sustainability Is crucial, both in laboratory and in industrial scale. To assess the sustainability of a process, it is necessary to consider all the **life-cycle phases**: firstly, the **row material selection**, then, the **sustainability** of the **synthetic process**, and finally the **recyclability of the obtained catalyst**.[1,2]



Desirable catalysts

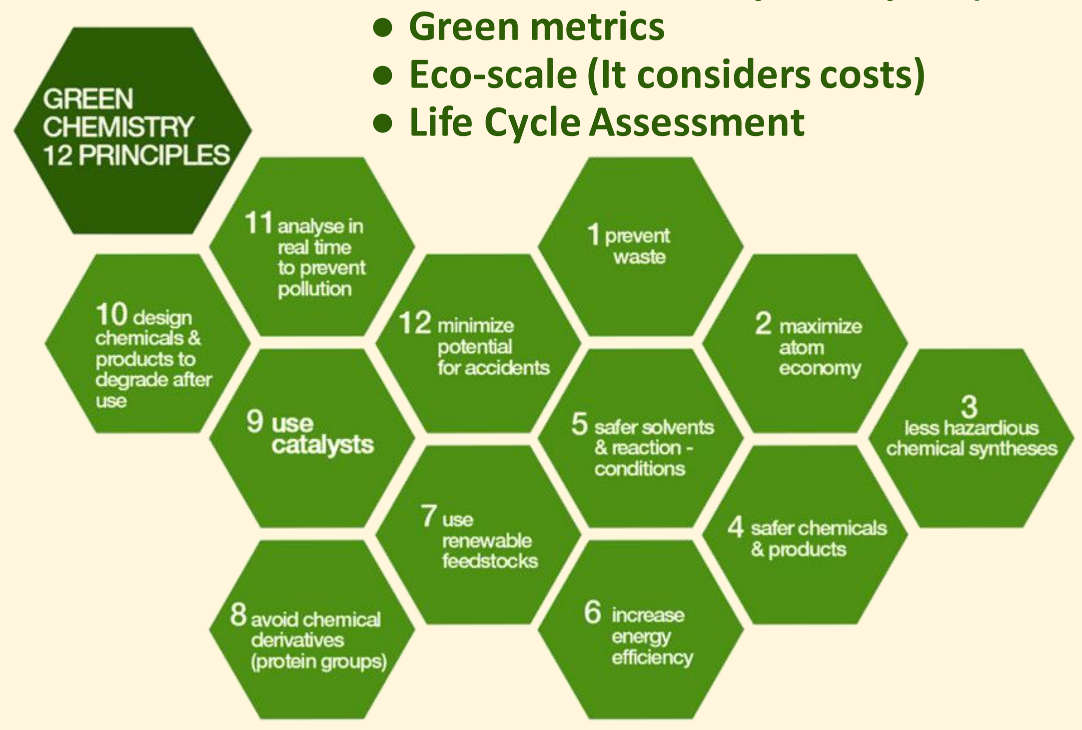
- Sustainable and cheap synthesis
- Excellent activity and selectivity
- Recyclability

What is usually considered?

- **Element availability**
- **Source (Fossil vs. Bio-based)**
- **Toxicity**
- **Cost**

What is usually considered?

- **12 Green Chemistry Principles (Guideline)**
- **Green metrics**
- **Eco-scale (It considers costs)**
- **Life Cycle Assessment**



Case study: preliminary sustainability assessment of two potential catalysts for DMTM

How to assess sustainability?

LAB-SCALE

Copper-based catalyst		SUSTAINABLE MATERIAL		
		RELIABLE AND SECURE (Society)	CLEAN (Environment)	AFFORDABLE (Economic)
LIFE-CYCLE PHASES	RAW MATERIALS	(+) Low Supply risk (-)Low substitutability (https://www.rsc.org/periodic-table/element/29/copper)	(+) Low CED (53.7 MJ-eq/Kg)	(+) $9.78/kg (https://mineralprices.com/base-metals/)
	MATERIALS PRODUCTION	Solvents and materials involved in the final material production should be safe and non toxic	Green metrics Synthesis LCA GHG emissions*	Materials costs, energy costs, production scale**
	USE	Leakages, durability	LCA/ Environment	LCA/Efficiency
	END OF LIFE	Toxicity	Recovery, recycling	Waste management costs

"It is important to include sustainability aspects in decision making at the product development stage, especially **early** in the development process"[3]

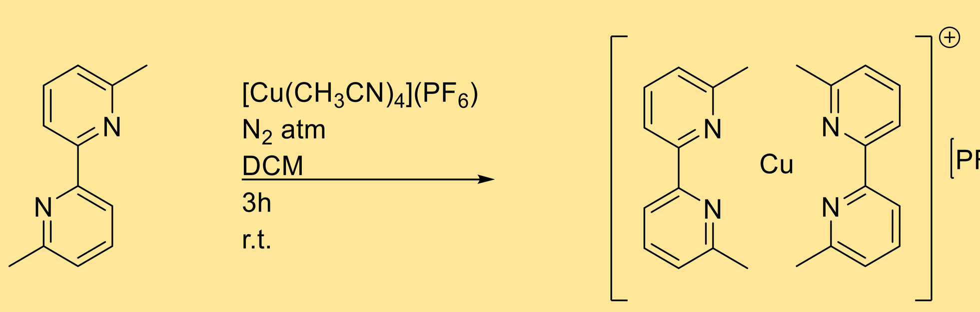
Nowadays, it is a **go/no-go** aspect

*https://www.eea.europa.eu/ **https://it.vwr.com/store/

Direct Methane To Methanol challenge[4]: road toward the perfect catalyst

Aiming at a preliminary comparison we select a copper complex as homogenous catalyst, (left side) whose ligands are suitable for the construction of a MOF as heterogeneous catalyst, (right side) to obtain two chemically comparable catalysts as potential candidates for DMTM. This sustainability-driven comparison has been conducted following two different approaches: (i) the cost per gram of catalyst and (ii) the cost per active site. The second evaluation is necessary since the proposed MOF contains only 10% of the complex's linkers, and consequently a limited quantity of copper centers.

Homogeneous catalyst[5]



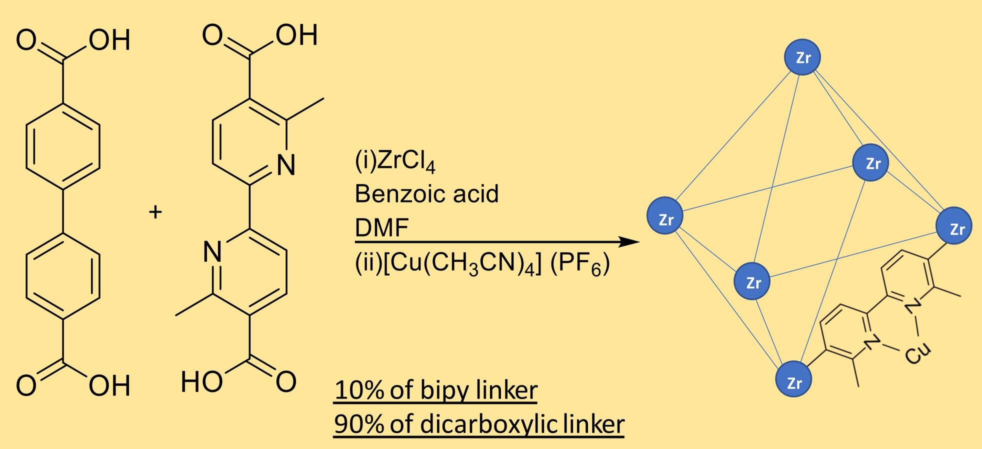
Material	Quantity	Cost	Cost/€	CO_2eq/g
6,6′-Dimethyl-2,2′-dipyridyl	0,67 g	47 €/g	31,49	
$[Cu(CH_3CN)_4]$ (PF_6)	0,64 g	16,2 €/g	10,37	
Solvent	10 mL	0,005 €/mL	0,05	
3h, r.t.	0,01 Kwh	0,082 €/kWh	<0,01	3,524
N_2 atm	2 mol	2,75E-05 €/mol	<0,01	

Cost per gram **41,9 €/g**

Active copper sites per gram[6] **1,73 mmol**

Cost for the same amount of copper sites **41,9 €**

Heterogeneous catalyst[6]



Material	Quantity	Cost	Cost/€	CO_2eq/g
$ZrCl_4$	0,73 g	0,48 €/g	0,35	
H_2BPDC	0,68 g	7,68 €/g	5,22	
$H_2BPyDC66'dme$	0,08 g	360 €/g	36,05	
Benzoic Acid	1,15 g	0,16 €/g	0,18	
DMF	42,63 mL	0,06 €/mL	2,45	
Acetone–work up	25,87 mL	0,009 €/mL	0,22	
$[Cu(CH_3CN)_4]$ (PF_6)	0,105 g	16,20 €/g	1,70	
130° C, 24 h	60,9 kWh	0,08 €/kWh	5,00	14049,63

Cost per gram **49,48 €/g**

Active copper sites per gram[6] **0,28 mmol**

Cost for the same amount of copper sites **305,71 €**

The *homogeneous* catalyst is about 7 times cheaper!

Take-home message:

The proposed analysis could represent the starting point of a go/no-go criteria.

- **Similar cost in terms of euro/g**
- **Significant dilution of the copper in MOF implies a factor of 7 when the cost is normalizes to the amount of copper**
- **Urgent need to evaluate activity and recyclability of the catalysts.**
- **A reduction up to 70%[8] of the environmental impacts are foreseen identifying the sustainability hotspots of both the synthetic procedures.**

The heterogenous catalysts (i.e. the MOF) would be preferred if it would be proved to be at least 7 times more active than the homogenous catalyst (copper complex).

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