# MOF@IL COMPOSITE MATERIALS AS Pd(II) SUPPORTS FOR HETEROGENEOUS ORGANOCATALYTIC REACTIONS

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BASQUE CENTER FOR MATERIALS, APPLICATIONS & NANOSTRUCTURES

ehugroup

- Introduction
- Material preparation and characterization
- Catalytic activity tests

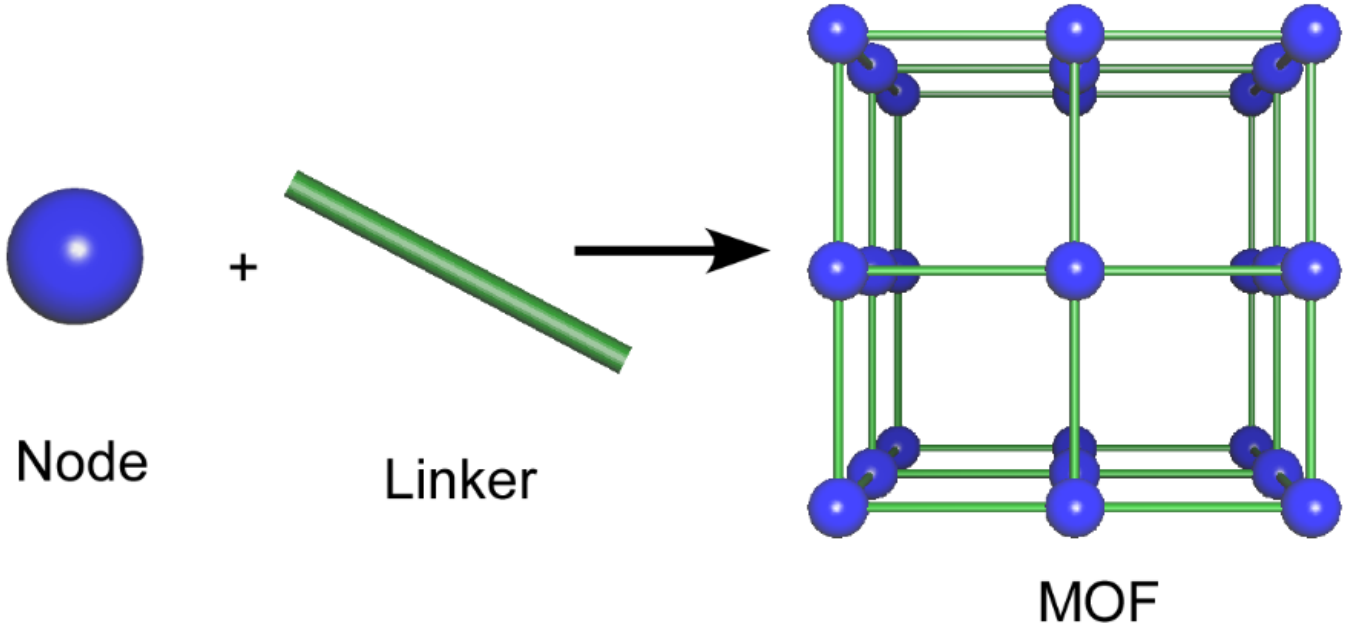
# Aim of the work

To obtain a novel Pd/Cu catalyst.

Stategy: Introduce an ionic liquid able to immobilize Pd into a Cu MOF

# Metal-Organic Frameworks (MOF)

- Compounds consisting of metal ions or clusters (nodes) coordinated to organic molecules (linkers) to form one-, two-, or three-dimensional porous structures.



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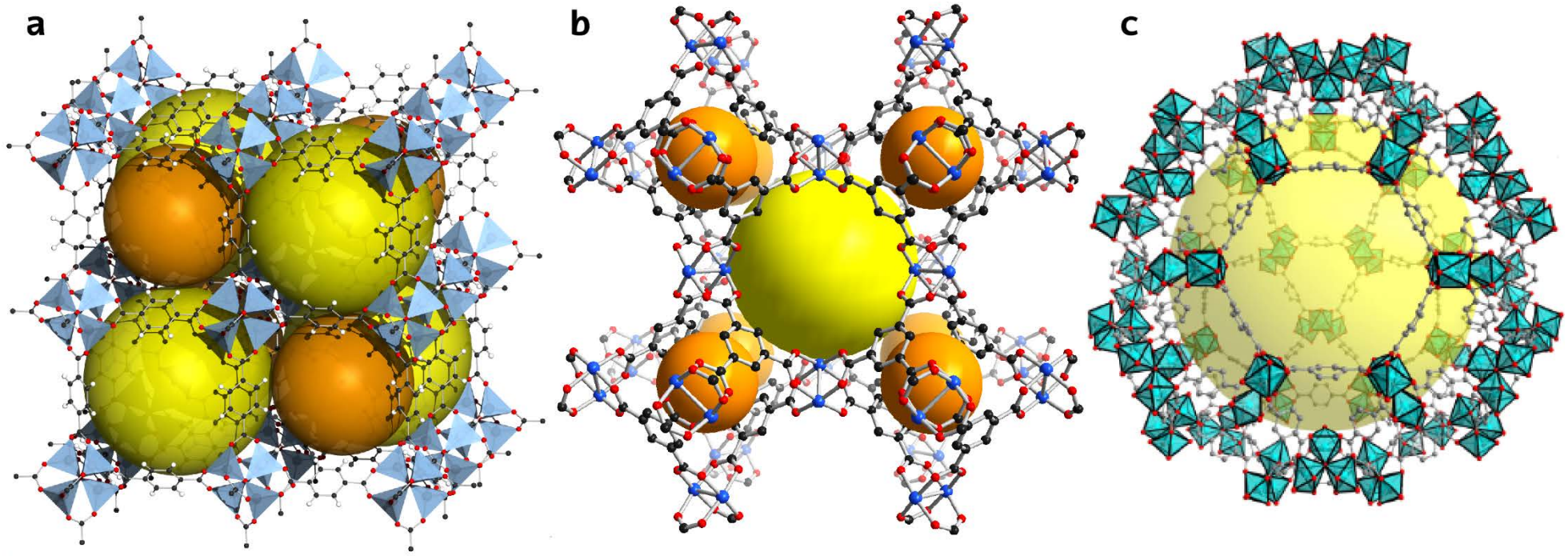
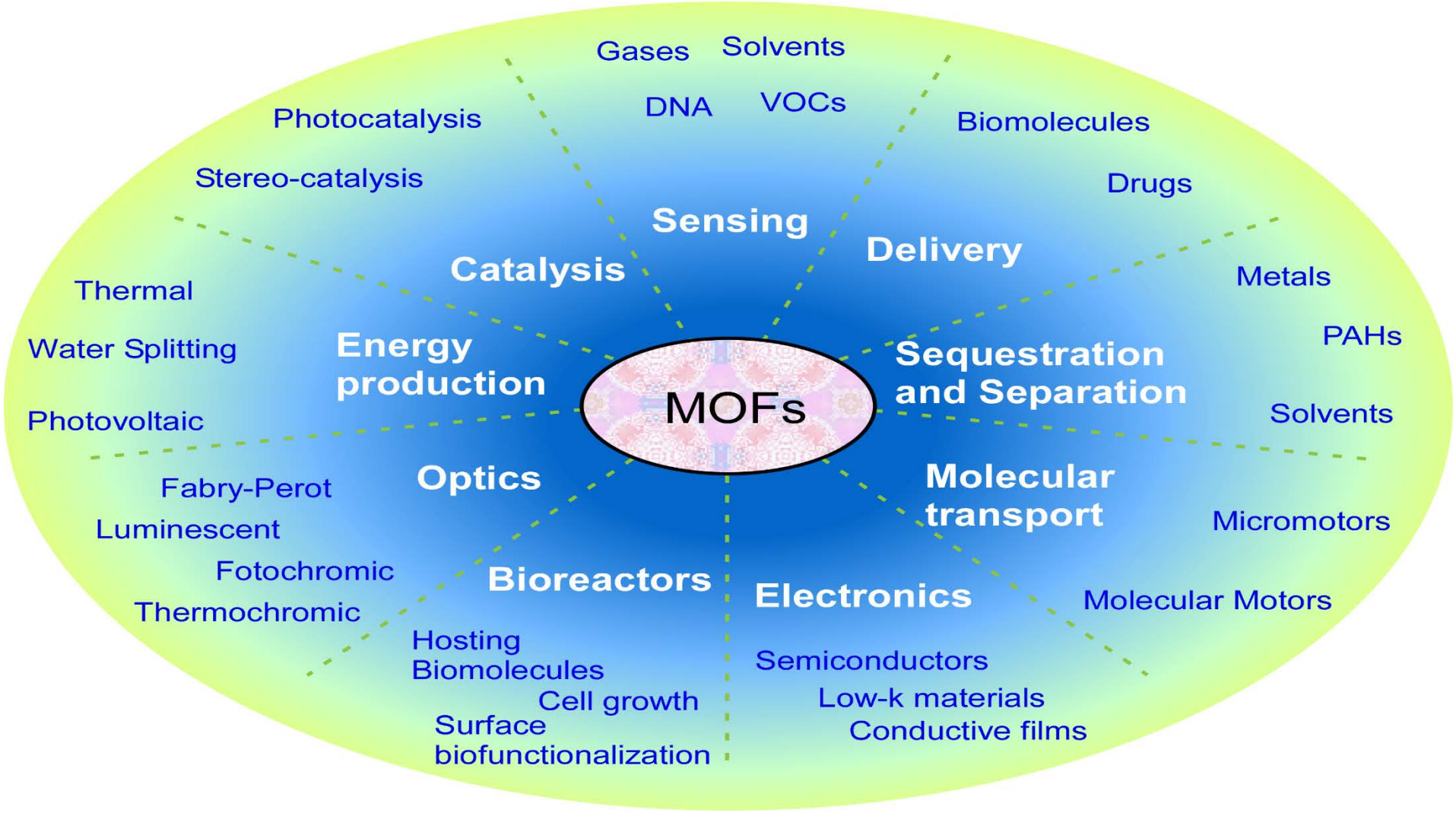



- Porous crystal structures
- Wide variety
- Tunable pores

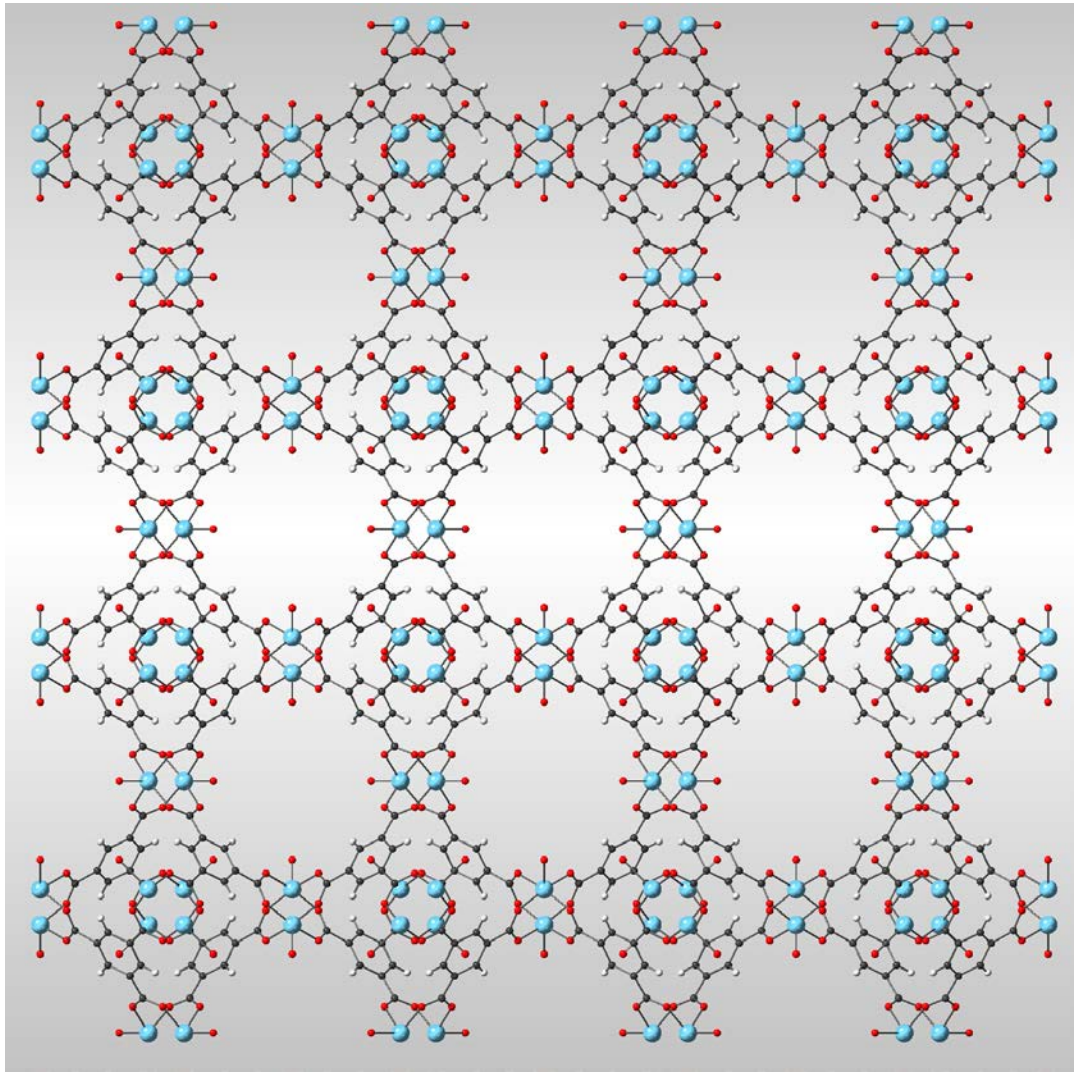
# Metal-Organic Frameworks (MOF)



# Metal-Organic Frameworks (MOF)

- HKUST-1 or CuBTC

| **Chemical Formula:** | **$Cu_3(BTC)_2(H_2O)_3$** |
|---|---|
| Space group: | F m-3m |
| Crystal System: | Cubic |
| a: | 26.3430 Å |
| Cell Volume: | 18280.821 Å³ |
| Density: | 1.0884 g/cm³ |
| BET surf. area: | 1500-2100 $m^2/g$ |



# Ionic Liquids (IL)

Ionic compounds with a melting point below 100ºC

## Properties

- Low vapor pressure
- Wide liquidous range
- High thermal and chemical stability
- Wide electrochemical window
- Nonflammability
- High ionic conductivity
- Good solvents
- Wide variety of cations and anions

## Applications

- Green alternative to organic solvents for synthesis, catalysis, separation, extraction
- Versatile electrolytes for electrochemistry and photovoltaics
- Novel functional materials for lubrication, microfluidics, propellants and sensors

## Drawbacks

- Tedious handling procedures

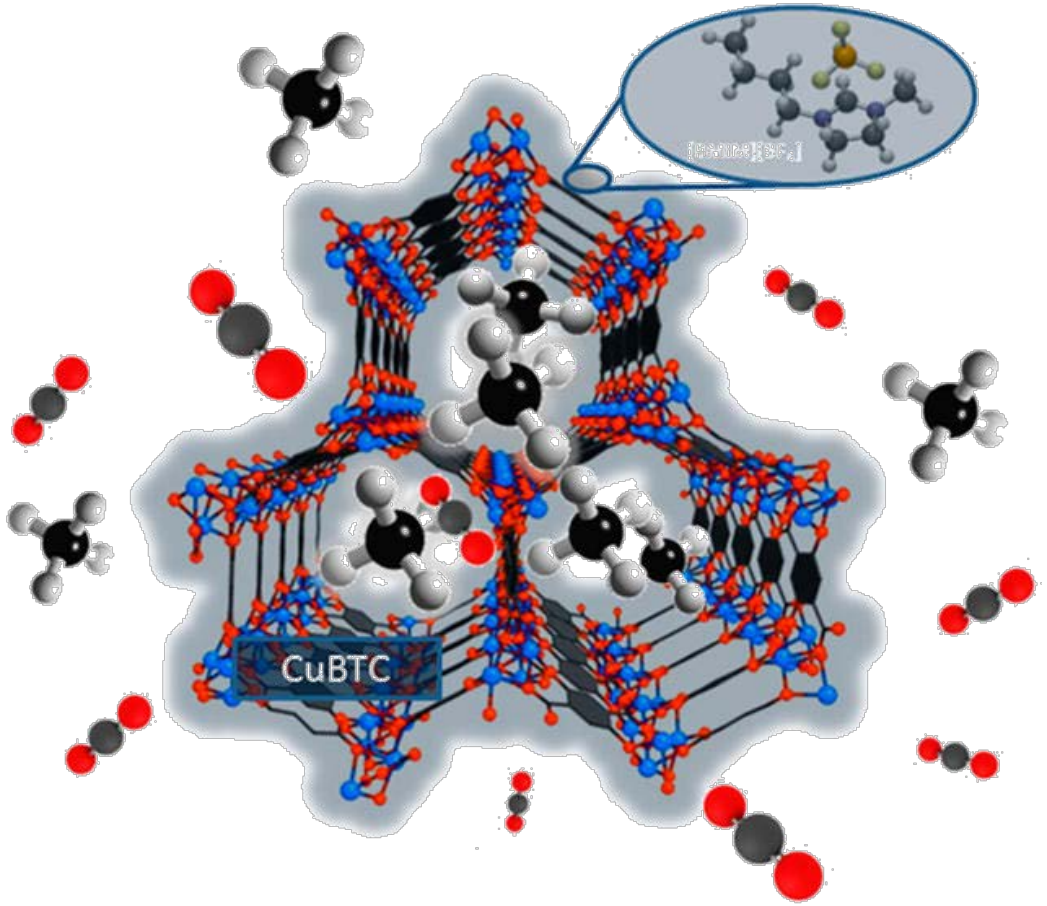
**Confined ILs**

# MOF@IL composite materials

MOFs can act as solid supports for ILs due to their great porosity

**Potential applications**

- Catalysis
- Adsorption
- $CO_2$ capture



# MOF@IL-Pd for catalytic applications

- ILs for immobilization of transition metal sites over solid materials

IL confined into a MOF crystal structure for the immobilization of Pd → Cu/Pd porous material

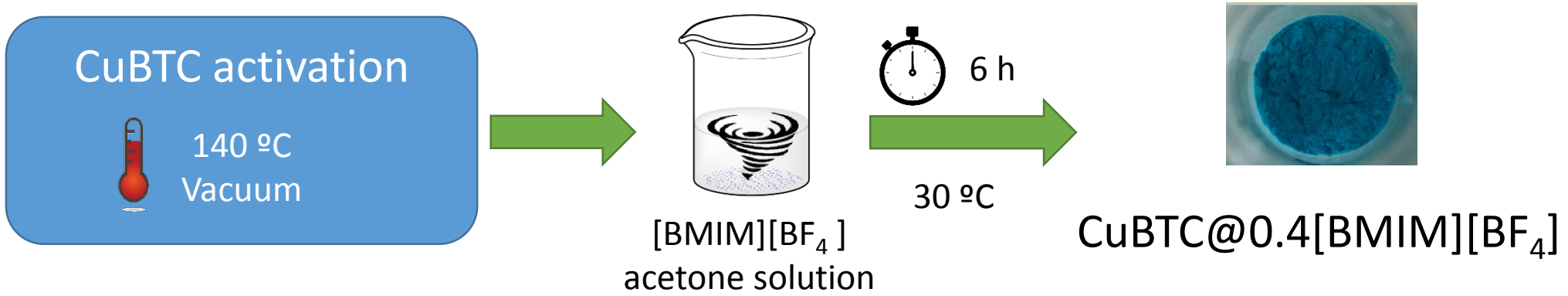
Introduction

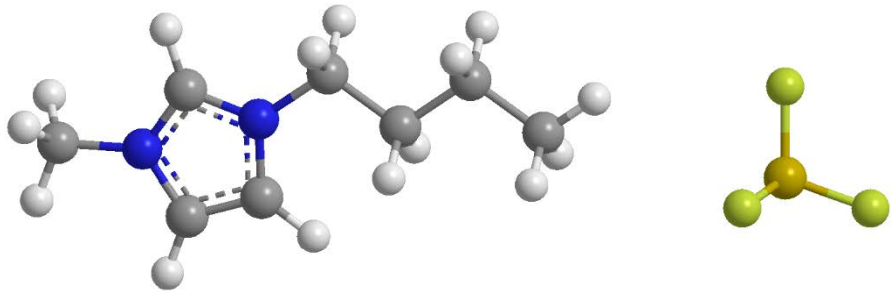
Material preparation and characterization

Catalytic activity tests

# CuBTC@IL-Pd preparation

- 1st step: MOF@IL composite formation – impregnation method



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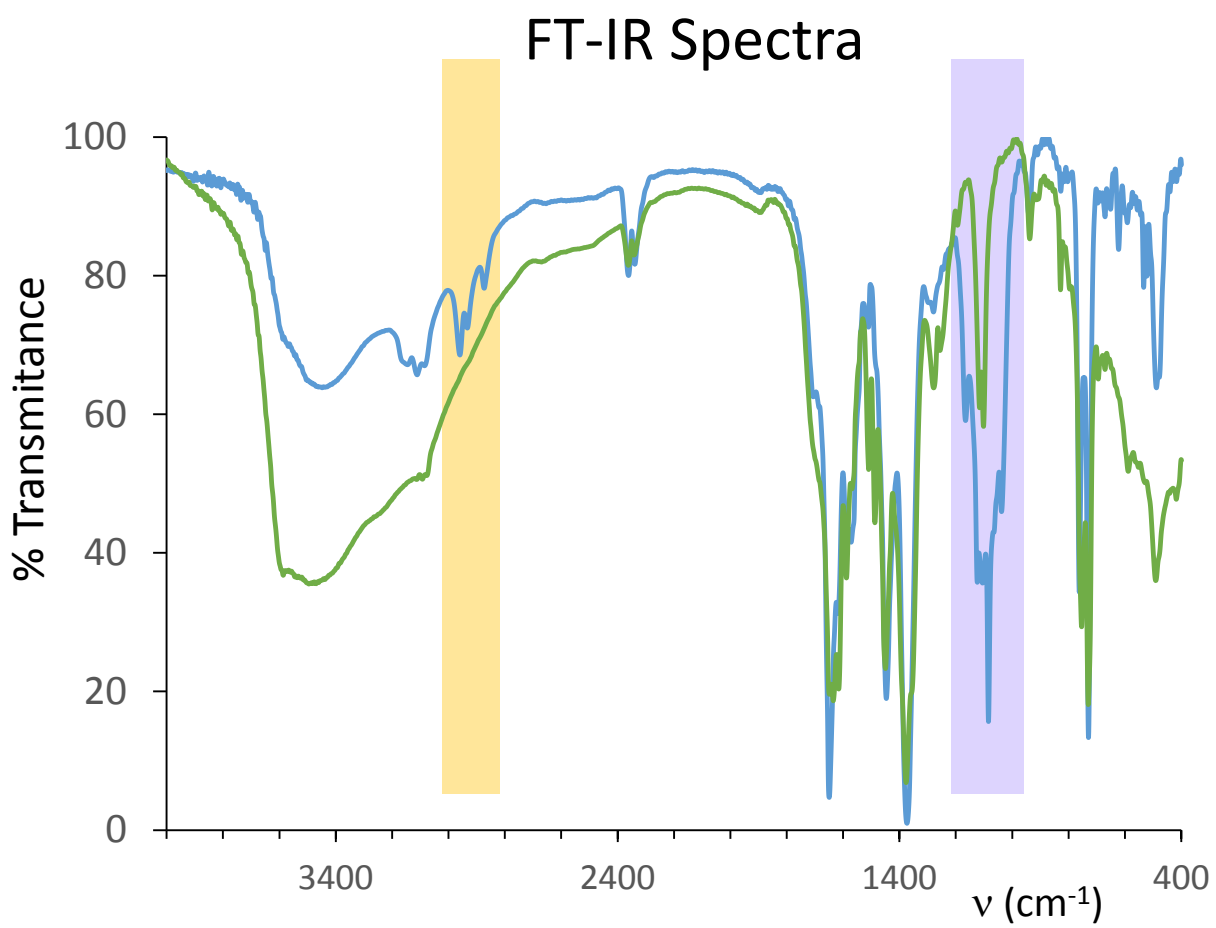


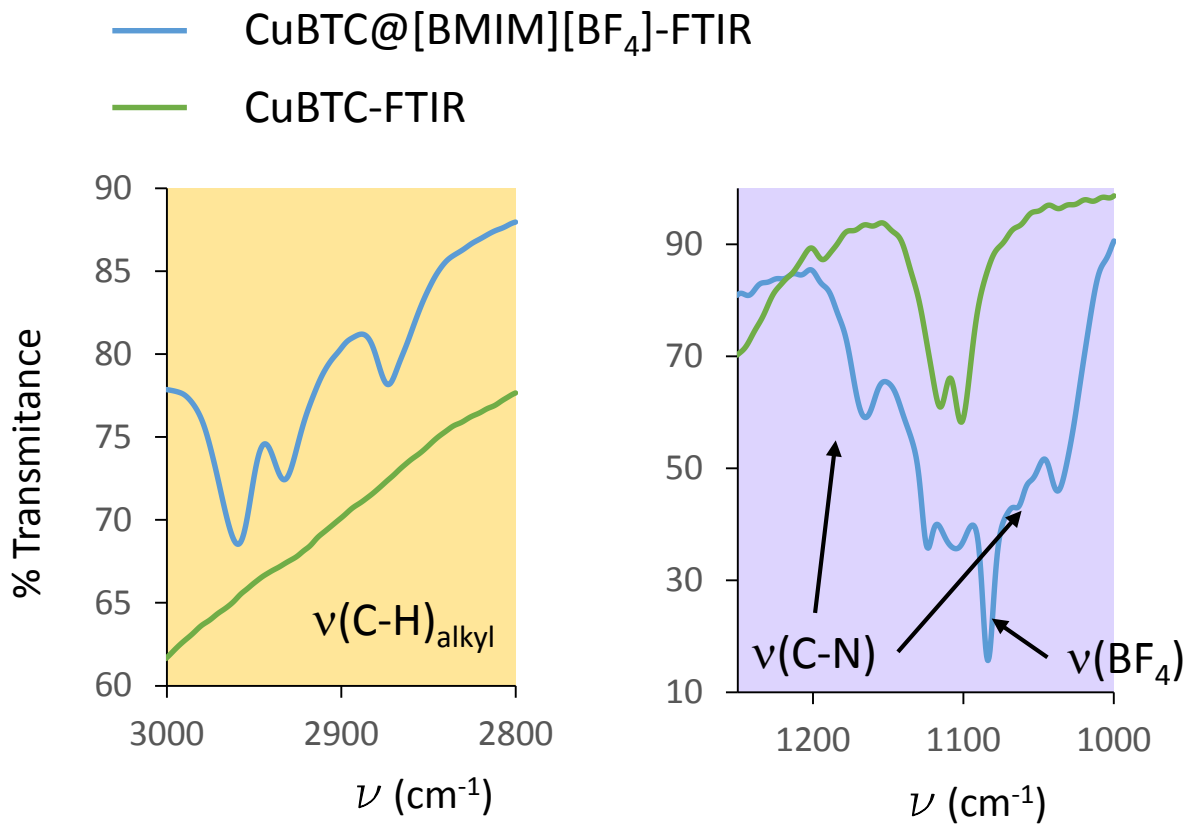

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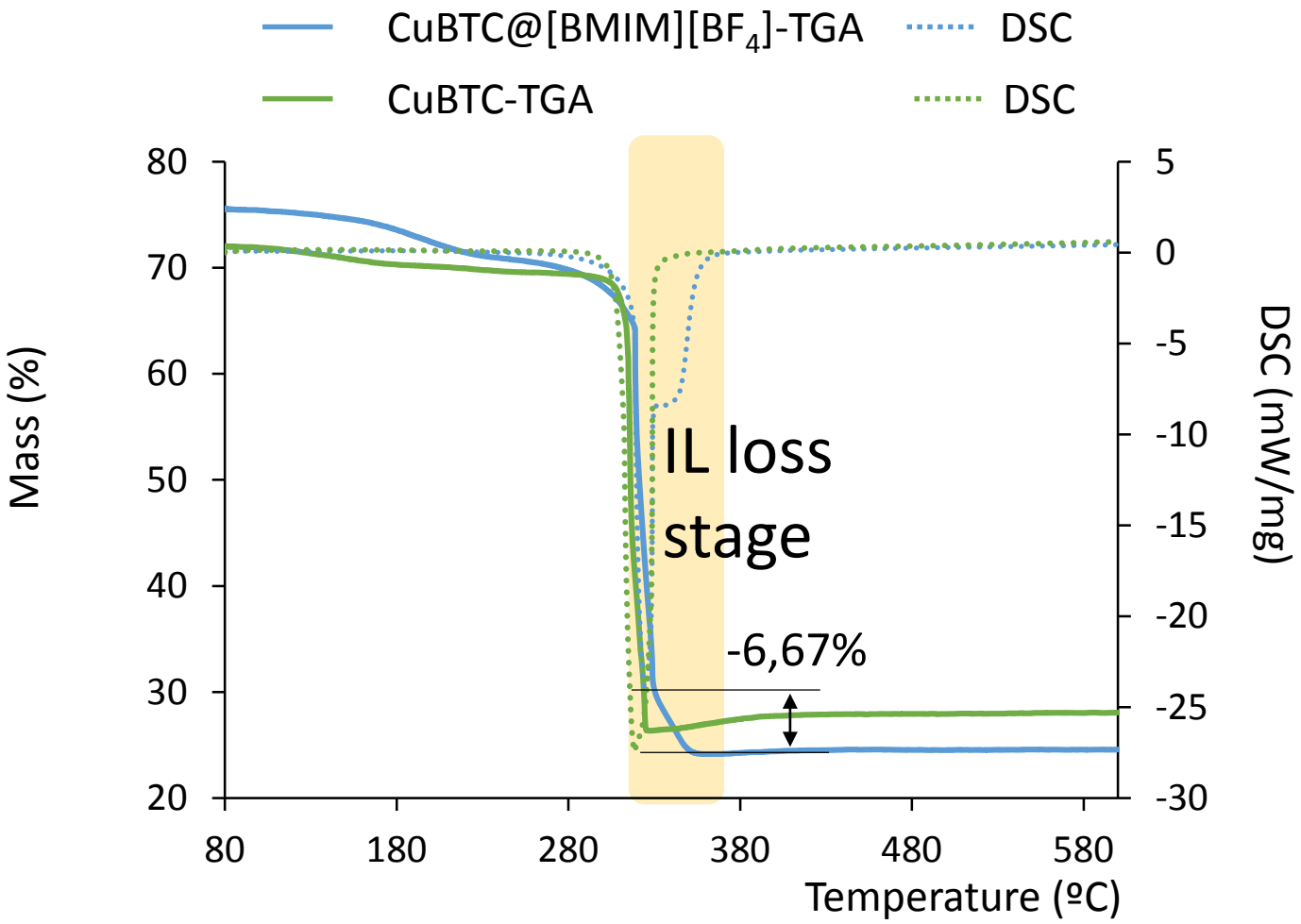
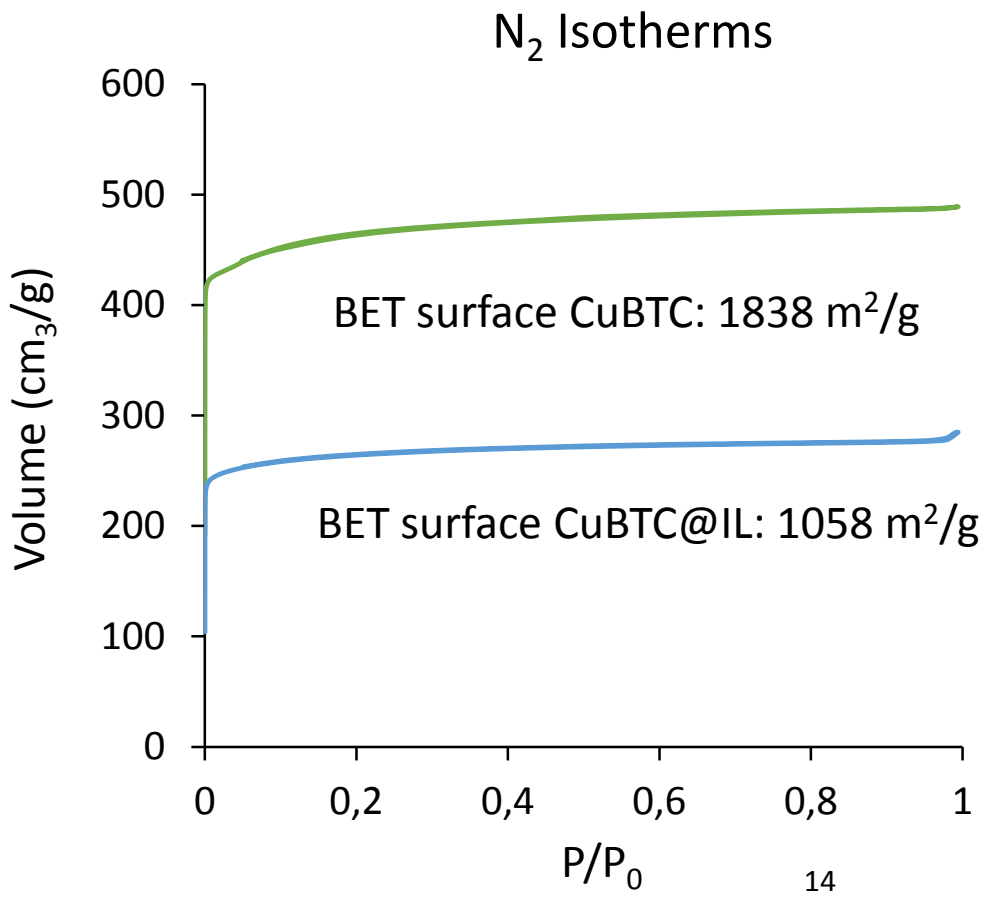


# CuBTC@IL-Pd preparation

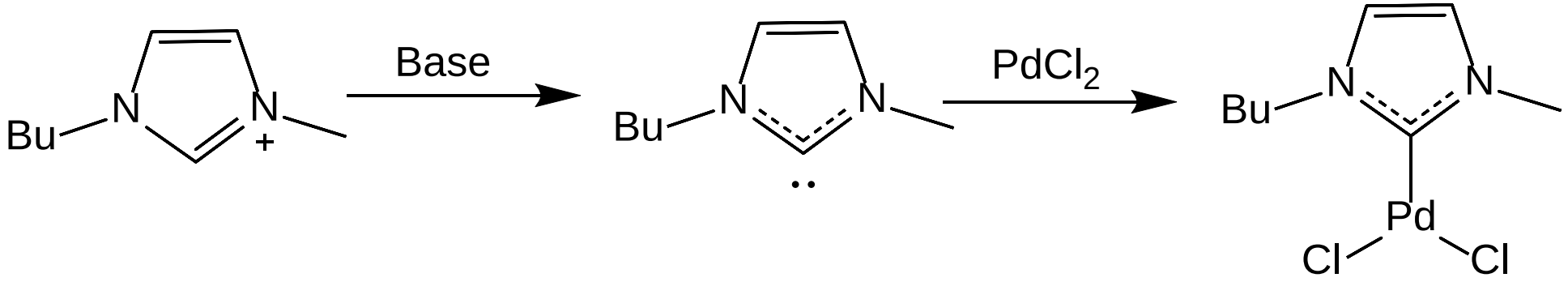
- 2nd step: MOF@IL composite functionalization with Pd

CuBTC@[BMIM][$BF_4$] activation

140 ºC
Vacuum

1. $LiN(Si(CH_3)_3)_2$, Toluene
   30 min, r.t.
2. $PdCl_2$, Acetonitrile
   6 h, 85.5 ºC

CuBTC@0.4[BMIM][$BF_4$]·0.1$PdCl_2$



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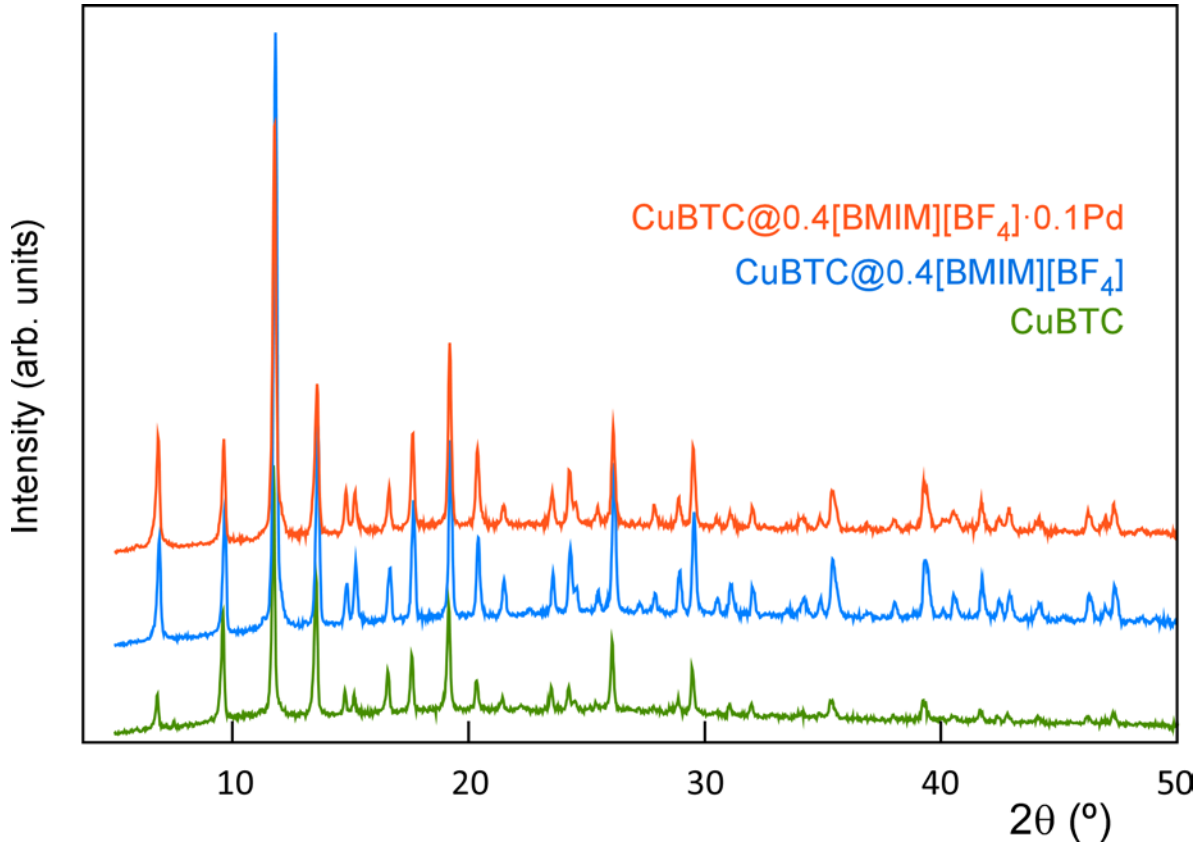
- 2nd step: MOF@IL composite functionalization with Pd

X-ray Powder Diffraction



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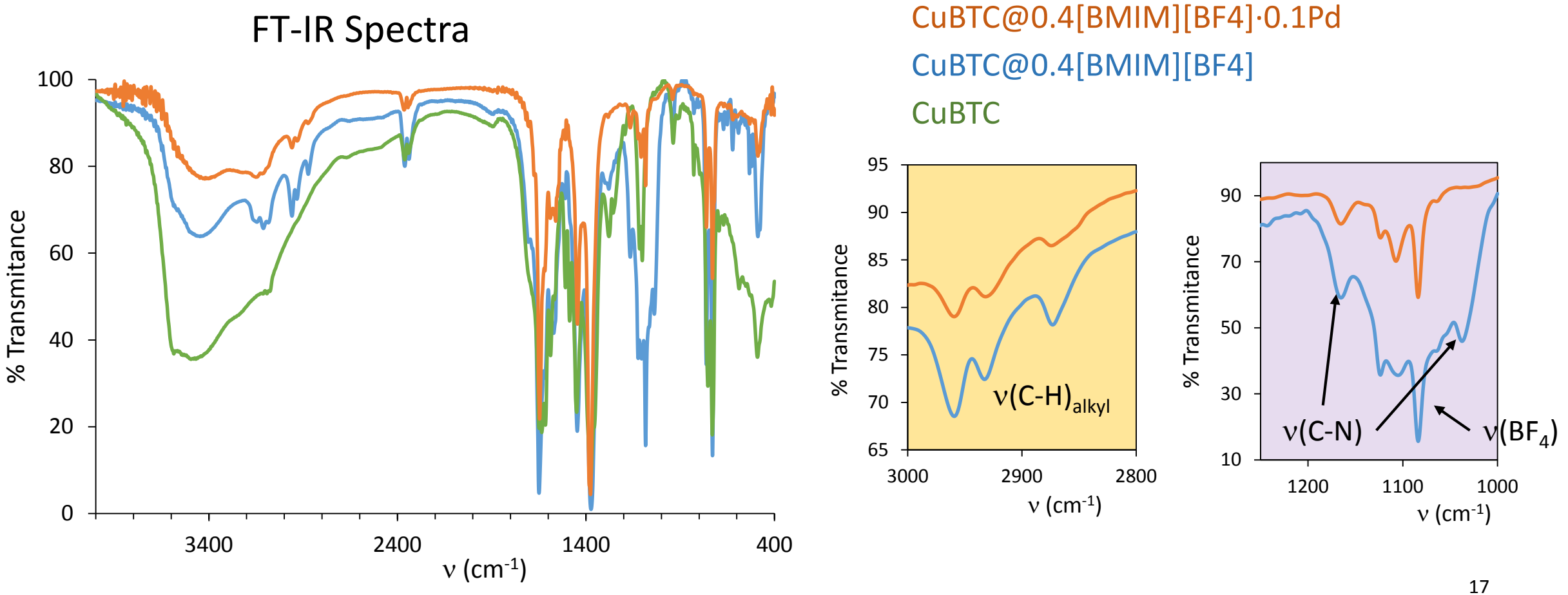

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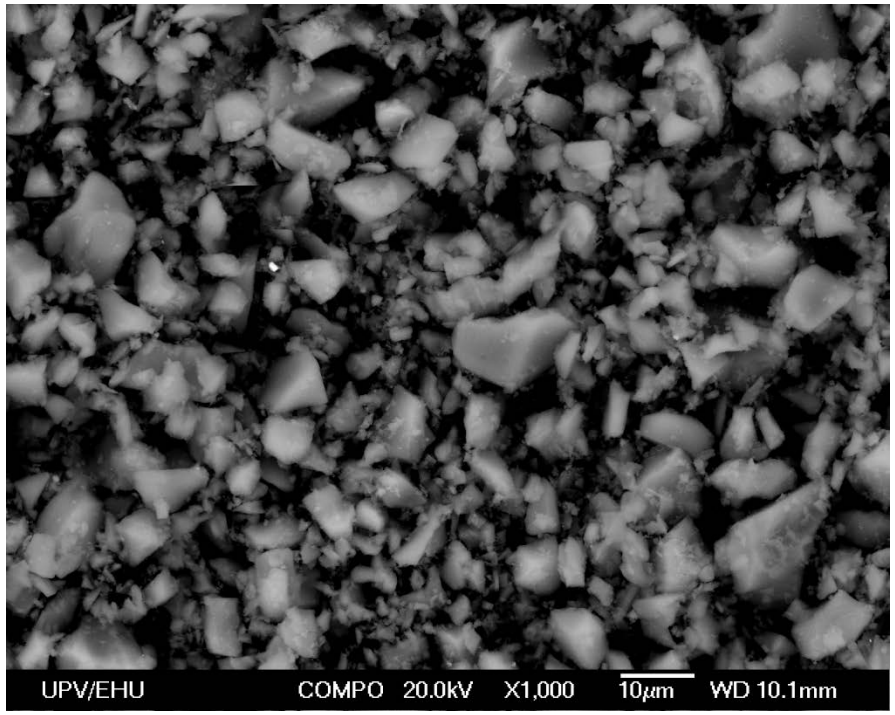
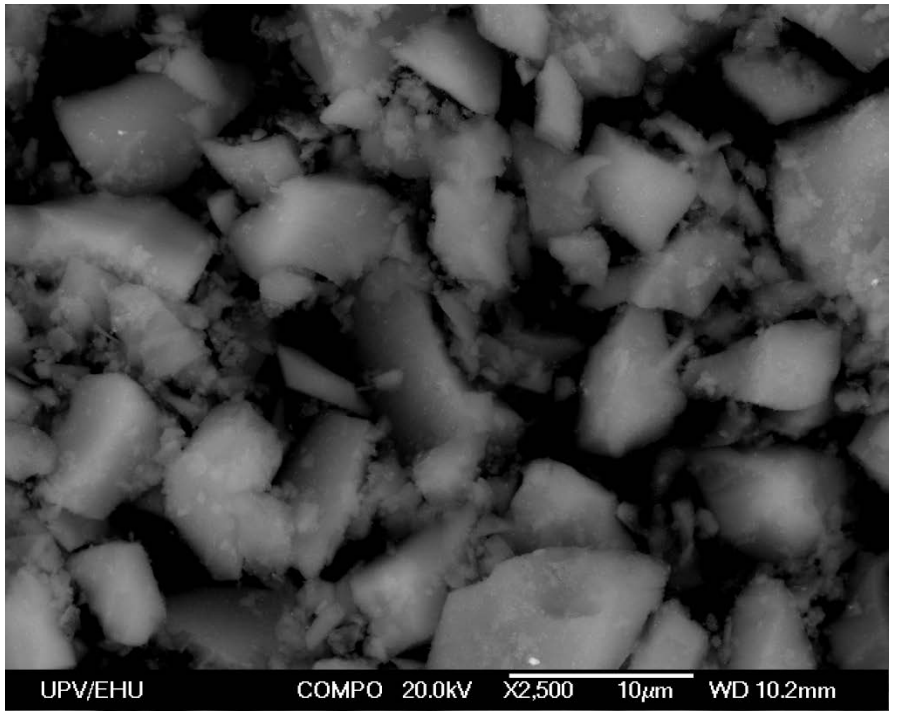


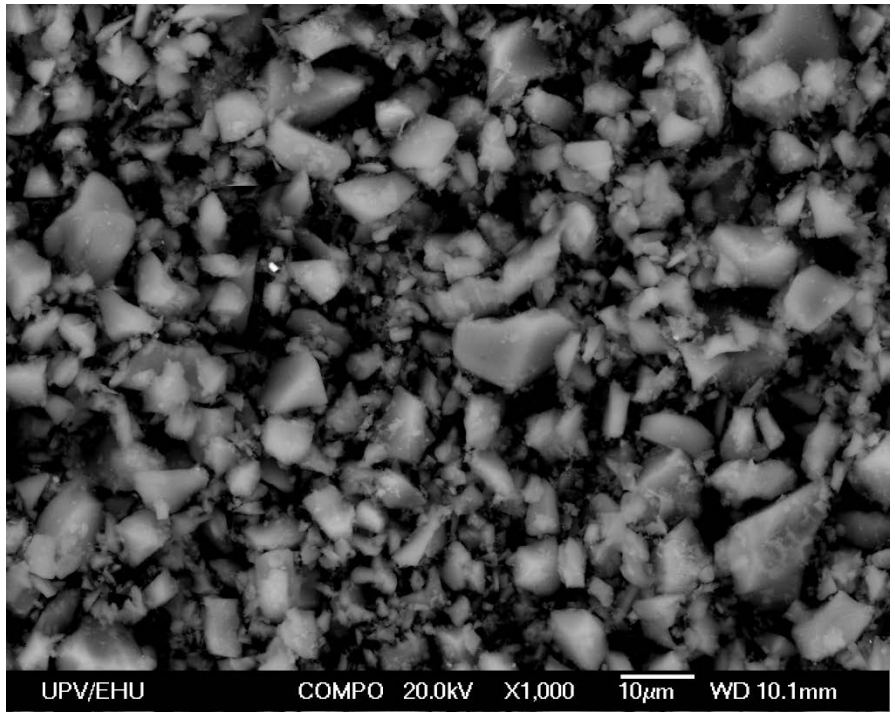

10 μm

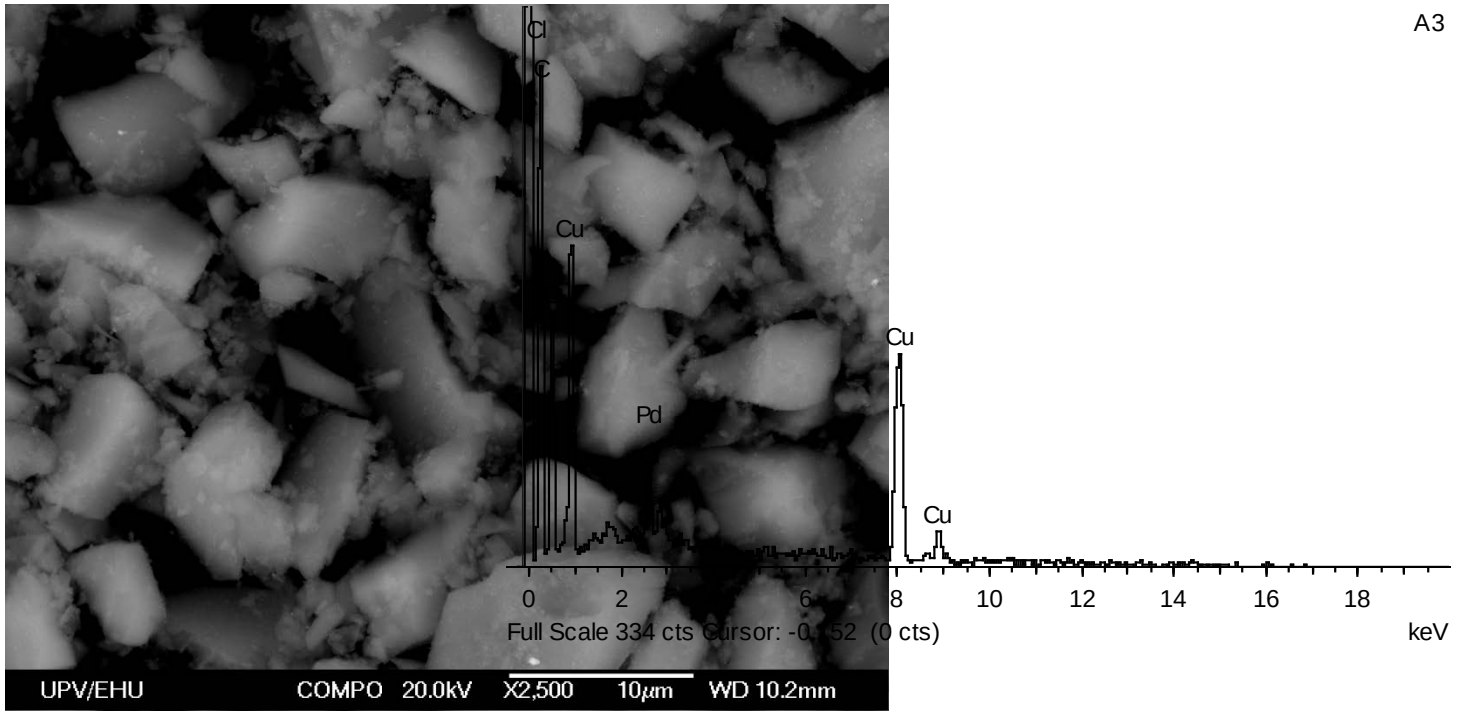



10 μm

# CuBTC@IL-Pd preparation

- 2nd step: MOF@IL composite functionalization with Pd



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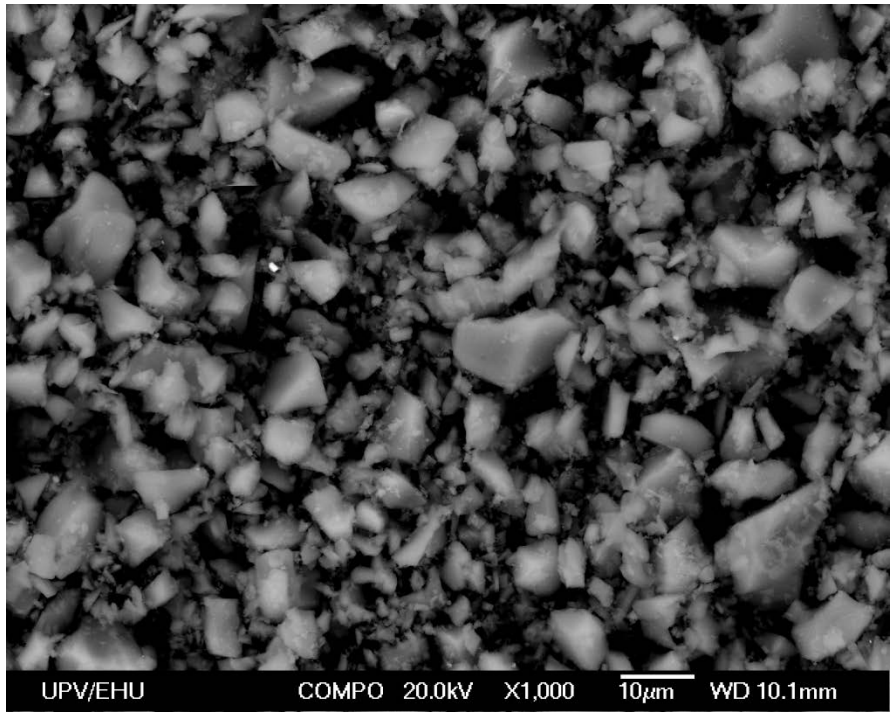
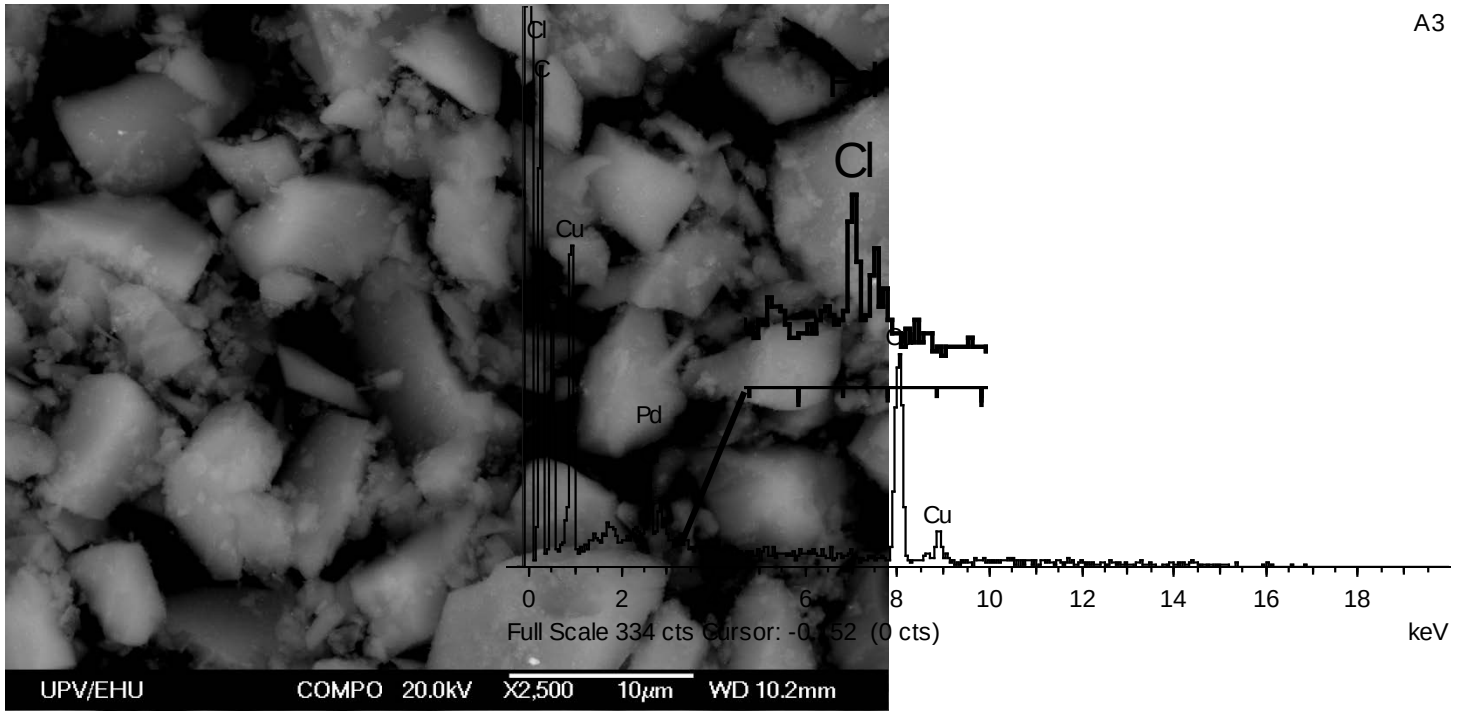


# CuBTC@IL-Pd preparation

- 2nd step: MOF@IL composite functionalization with Pd

ICP-AES → 1 % of Pd → $Cu_3BTC_2$@0.4[BMIM][$BF_4$]·0.1$PdCl_2$

BET analyses

| CuBTC | CuBTC@IL | CuBTC@IL·Pd |
|---|---|---|
| 1838 $m^2/g$ | 1058 $m^2/g$ | 957 $m^2/g$ |

# CuBTC@IL-Pd preparation

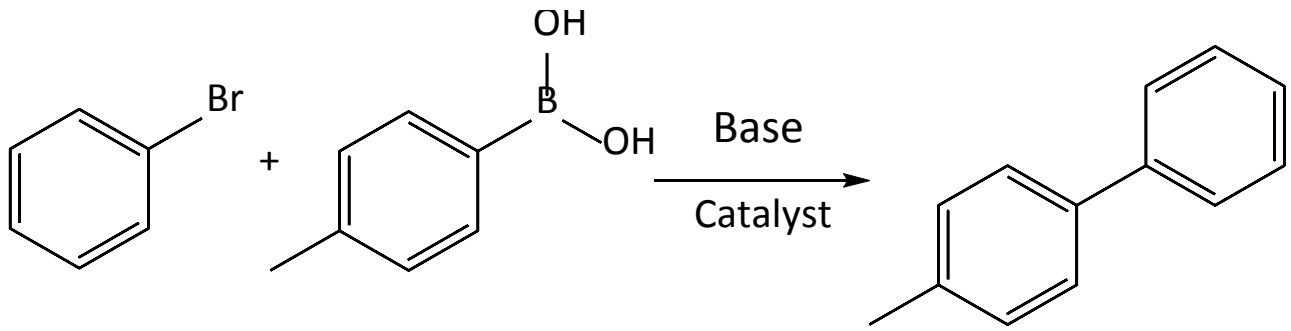
- Porous material
  957 $m^2/g$
- 1 % of Pd
- 20 % of Cu

Introduction

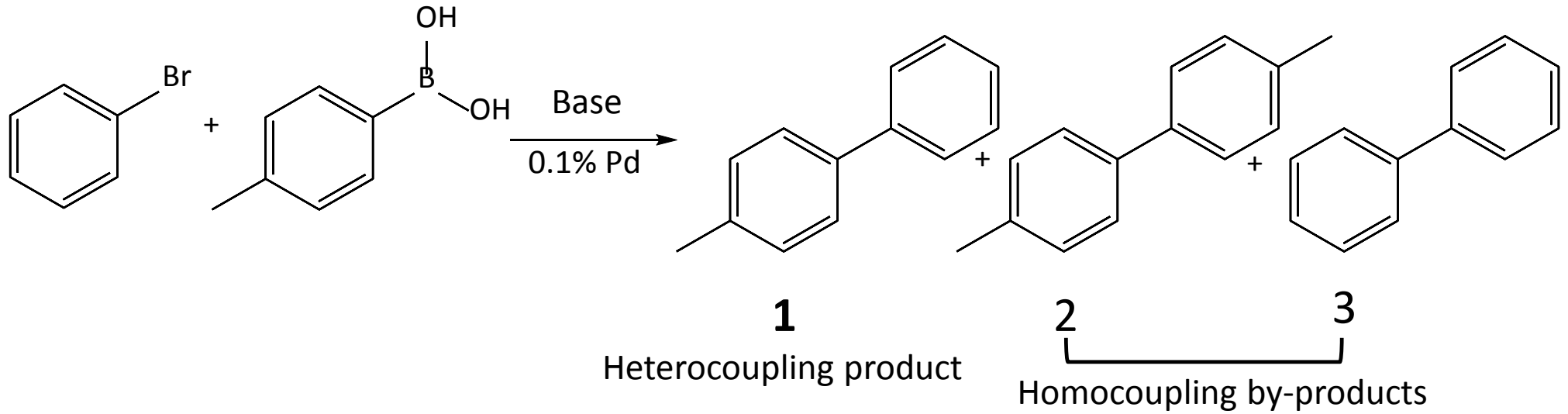
Material preparation and characterization

Catalytic activity tests

# 1. Suzuki-Miyaura

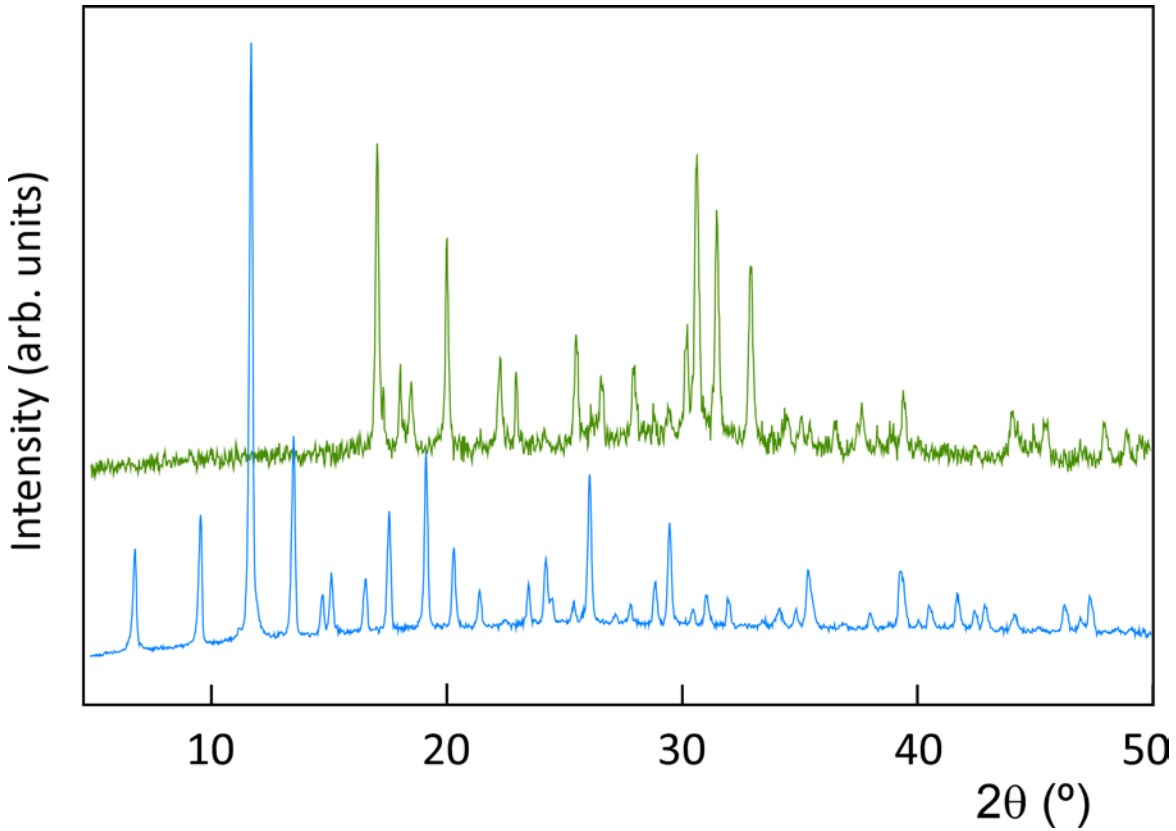


# 1. Suzuki-Miyaura




| Base | Solvent | T (ºC) | Time | $C_T$ (%) | $C_1$ (%) | $C_2$ (%) | $C_3$ (%) | $S_1$ (%) |
|---|---|---|---|---|---|---|---|---|
| $K_2CO_3$ | MeOH | 70 | 1.5 h | **91** | **61** | 21 | 9 | **67** |
| $K_2CO_3$ | MeOH | 100, MW | 15 min | **56** | **52** | 4 | 0 | **93** |
| $Et_3N$ | Toluene | 100 | 24 h | **0** | | | | |
| $^{i}(Pr)_2NH$ | Toluene | 100 | 22h | **12** | **3** | 9 | 0 | **25** |

# 1. Suzuki-Miyaura

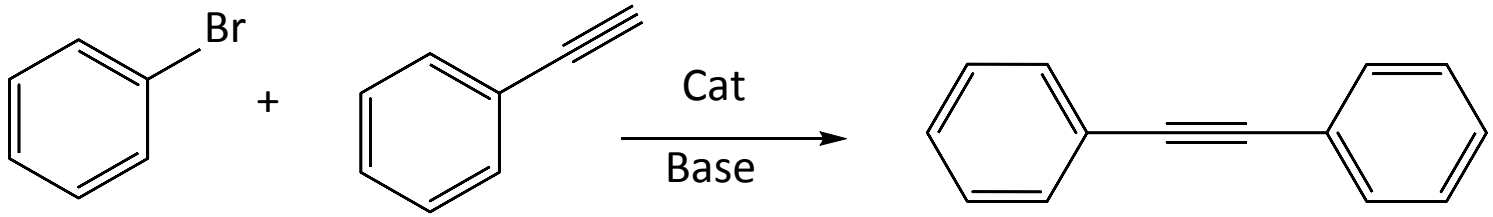



The catalysts suffered a structural tranformation, so the active species im-Pd may not be into it.

After reaction in MeOH, 70 ºC

Fresh catalyst

# 2. Sonogashira



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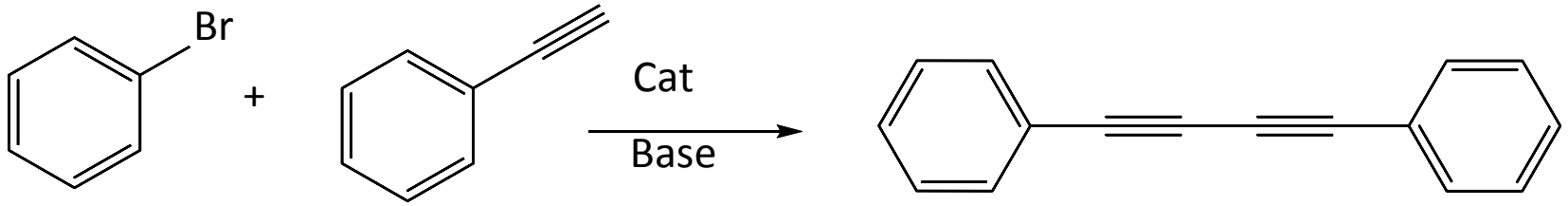
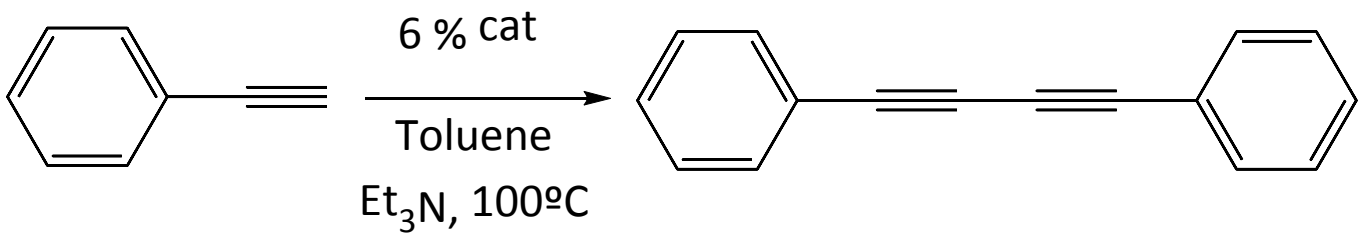
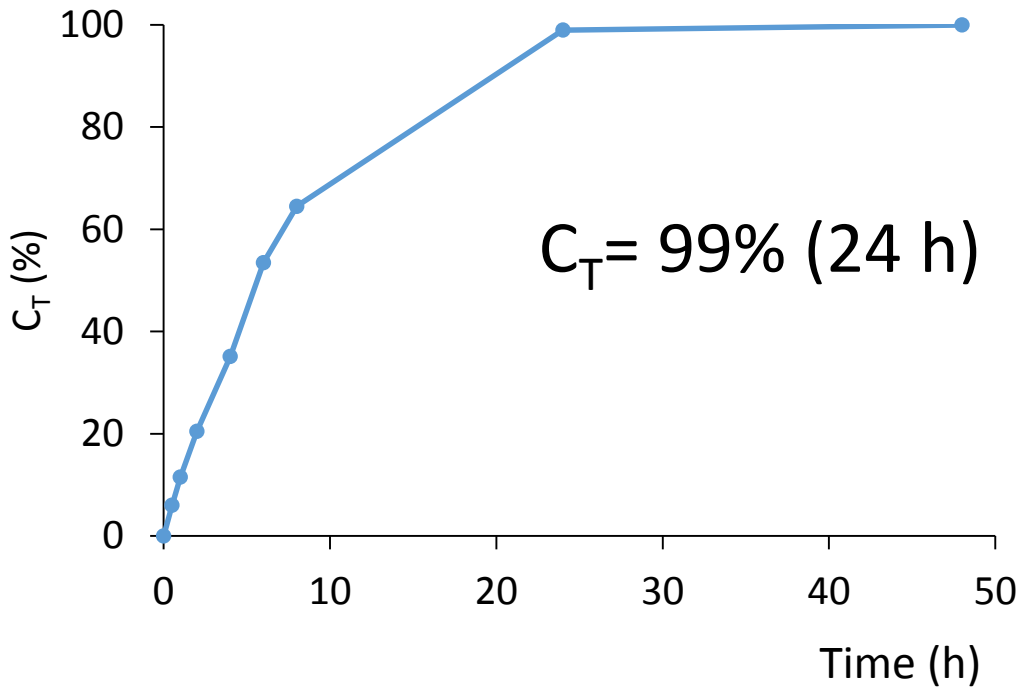



Phenylacetylene homocoupling product

# 3. Alkyne homocoupling

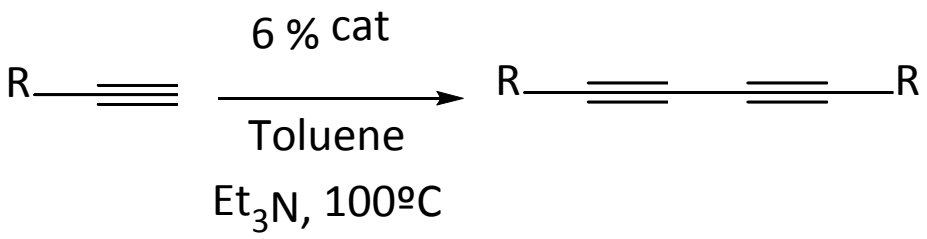


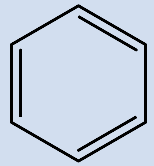
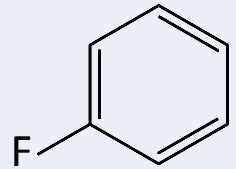
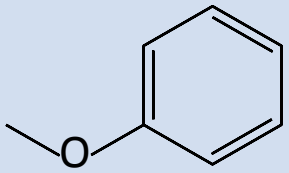



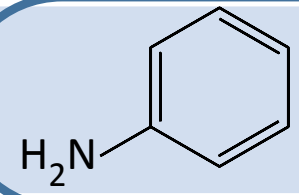
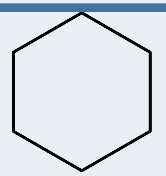
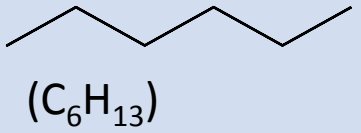

The same reaction with CuBTC@[BMIM][$BF_4$] does not take place

Pd is the catalytic species

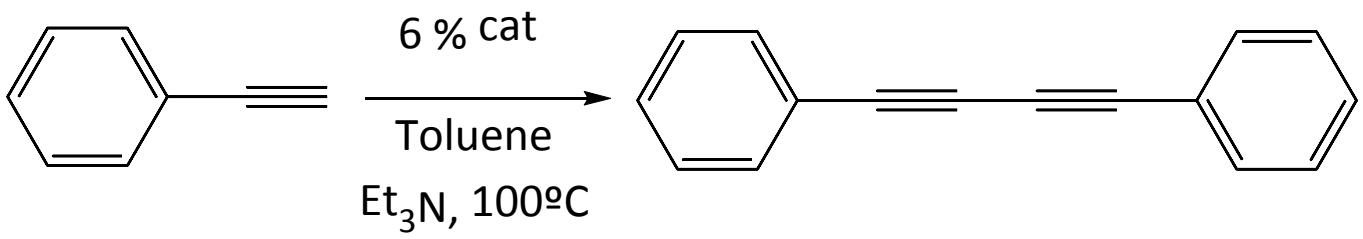
# 3. Alkyne homocoupling

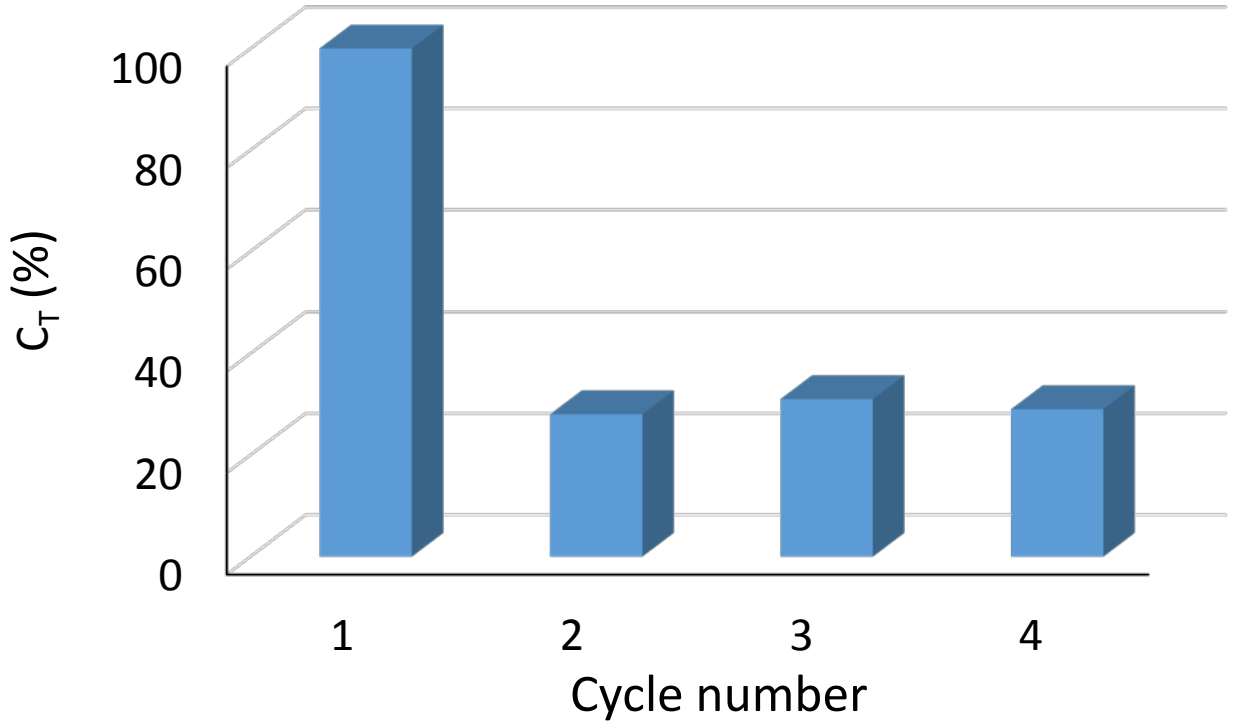



| R | $C_T$ (t) |
|---|---|
|  | 99% (24 h) |
|  | 100% (24h) |
|  | 61% (24 h) |

| R | $C_T$ (t) |
|---|---|
|  | 0% (24h) |
|  | 99% (24 h) |
|  | 100 %(24h) |

# 3. Alkyne homocoupling

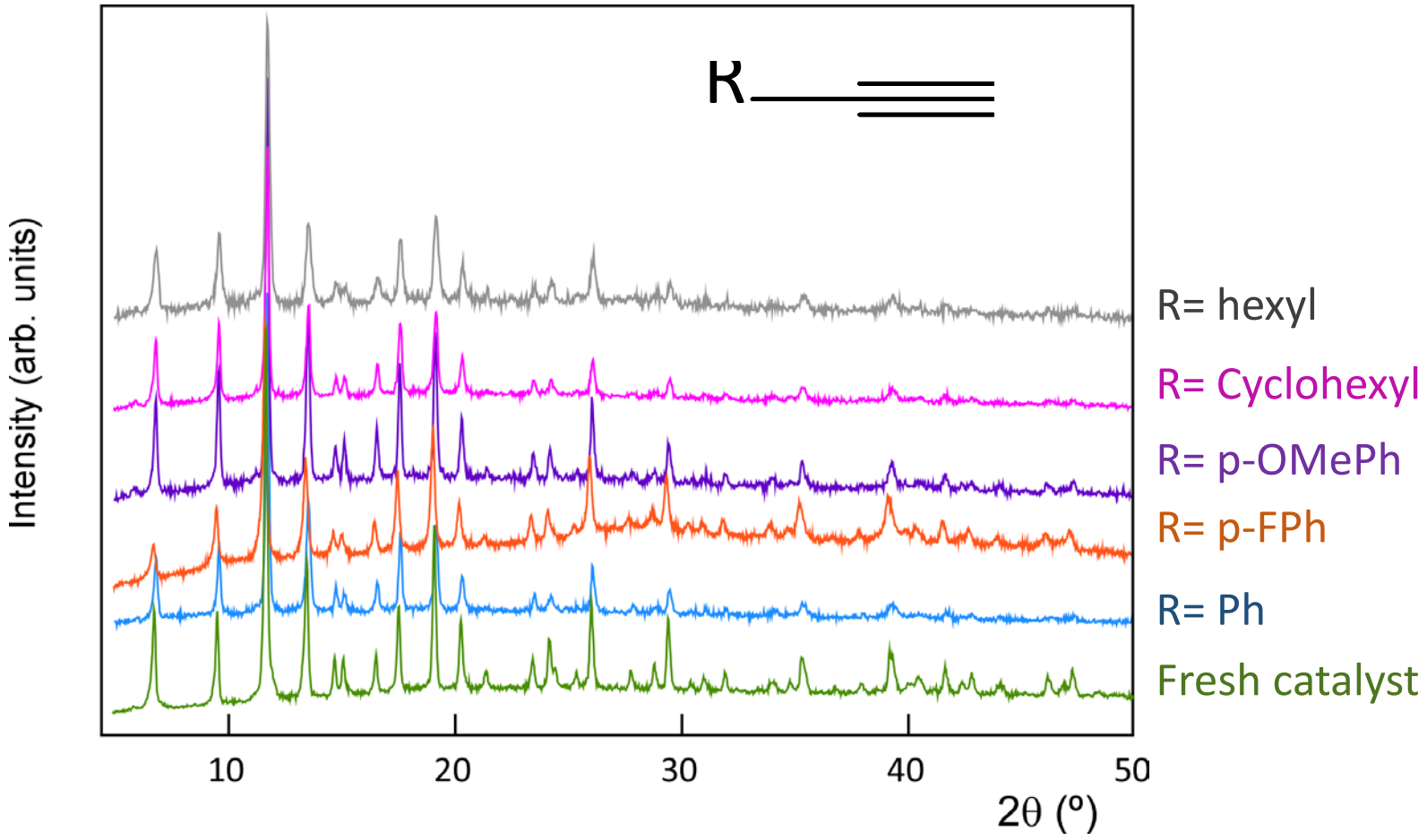



- From the first to the second cycle the conversion rate decreases drastically.
- In the following cycles the conversion is around 30%

# 3. Alkyne homocoupling

X-ray Powder Diffraction

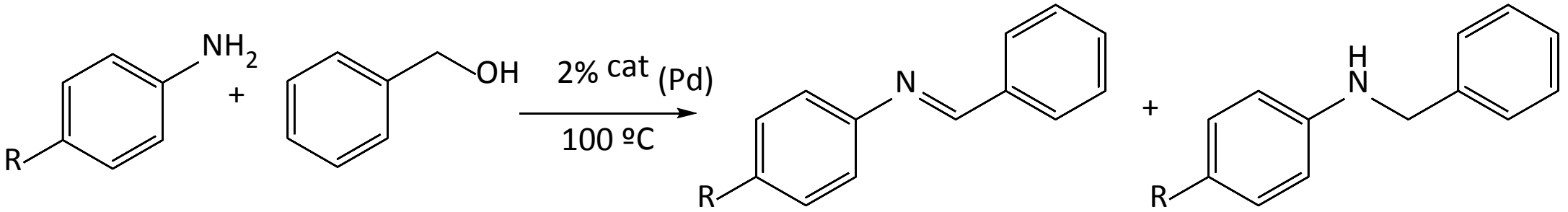



ICP-AES, Pd

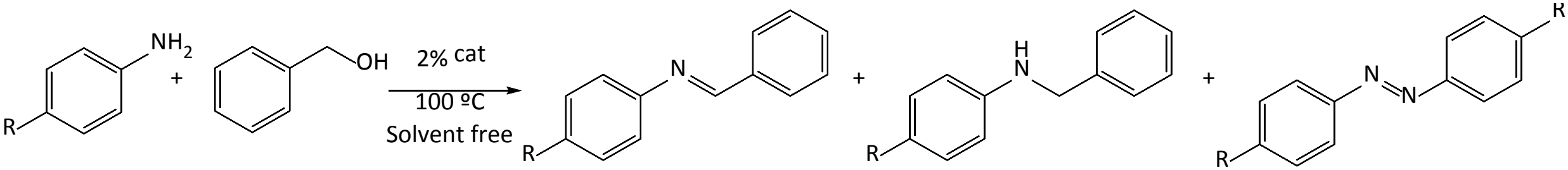
Recovered catalysts= Fresh catalyst

Decrease of activity due to pore occlusion

# 4. Amine alkylation



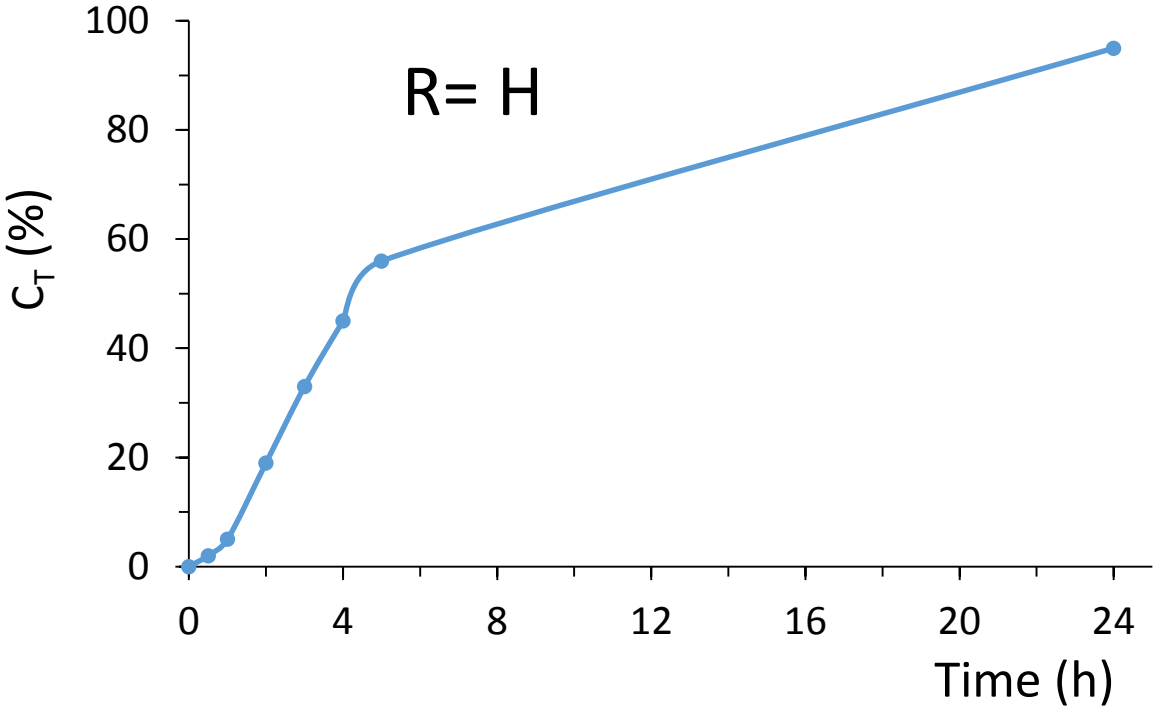
# 4. Amine alkylation




1
Heterocoupling product

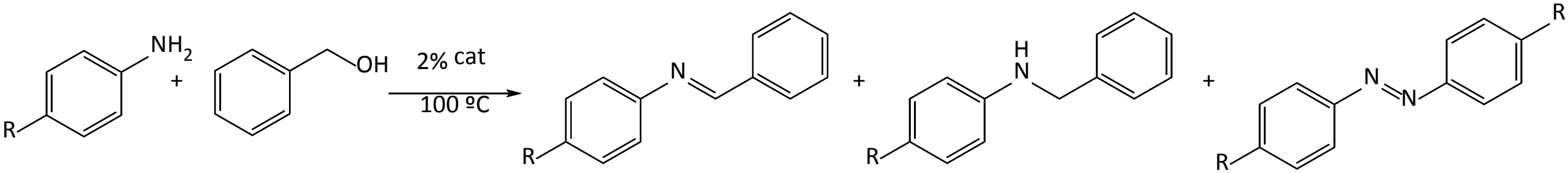
2
Dehydrogenated product

3
Homocoupling product




| $C_T$ (24 h) | 95% |
|---|---|
| $C_1$ | 77% |
| $C_2$ | 9% |
| $C_3$ | 9% |

# 4. Amine alkylation



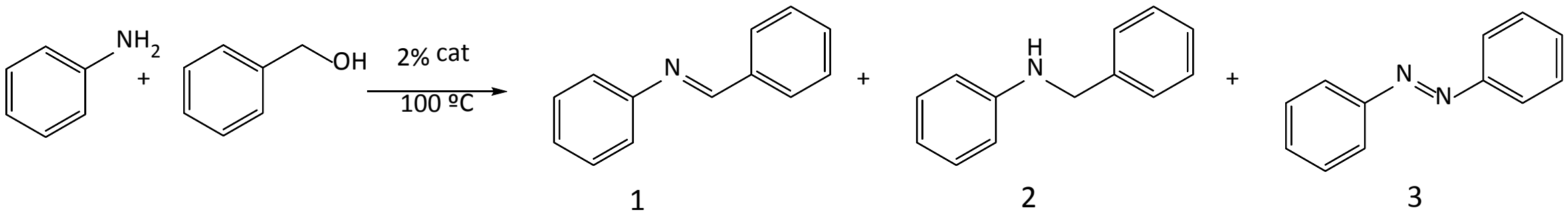

1
Heterocoupling product

2
Dehydrogenated product

3
Homocoupling product

| -R | $C_T$ (24 h) | $C_1$ | $C_2$ | $C_3$ | $S_1$ |
|---|---|---|---|---|---|
| -H | 95% | 77% | 9% | 9% | 81% |
| -Me | 20% | 20% | 0 | 0 | 100% |
| -OMe | 88% | 71% | 0 | 17% | 81% |
| -Cl | 36% | 30% | 0 | 6% | 83% |

# 4. Amine alkylation

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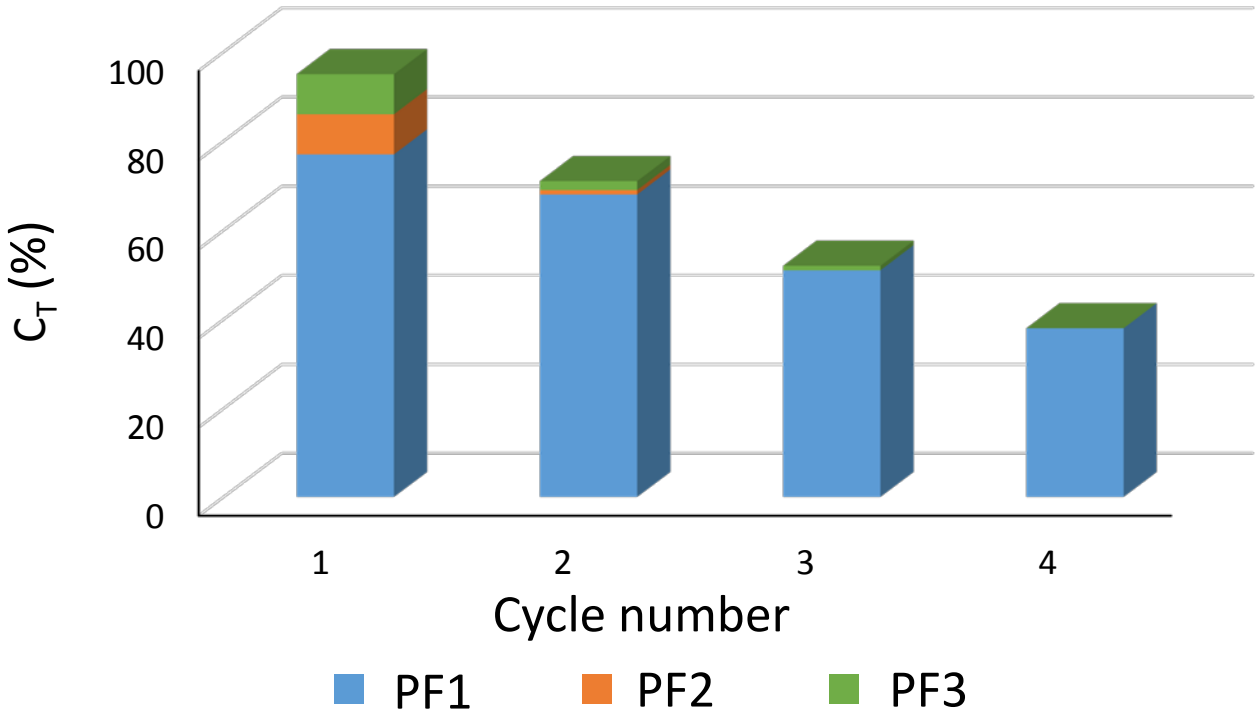
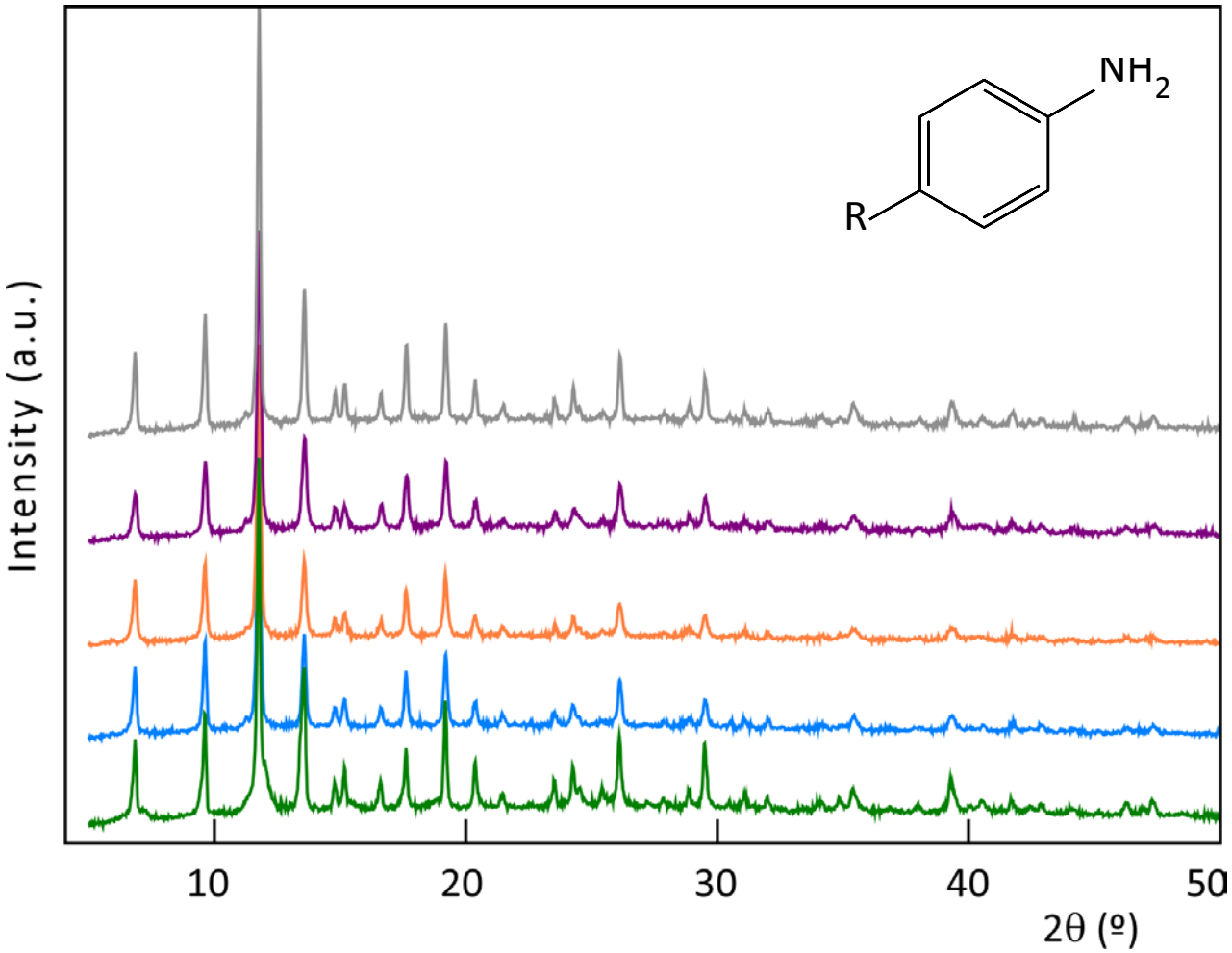



- The conversion rate decreases gradually from one cycle to another.
- The catalyst loses its activity when recycling it

# 4. Amine alkylation

## X-ray Powder Diffraction




R= Cl

R= OMe

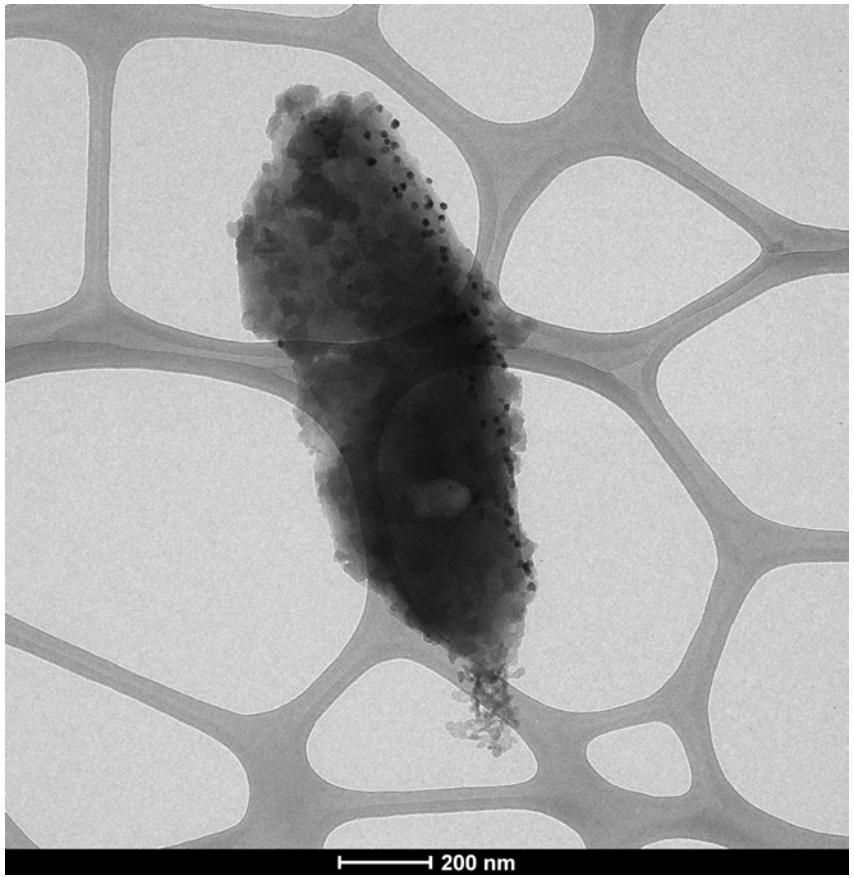
R= Me

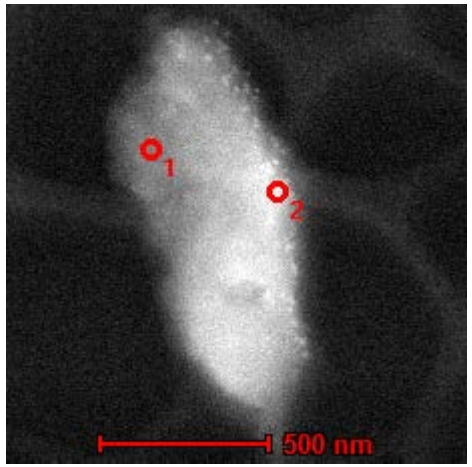
R= H

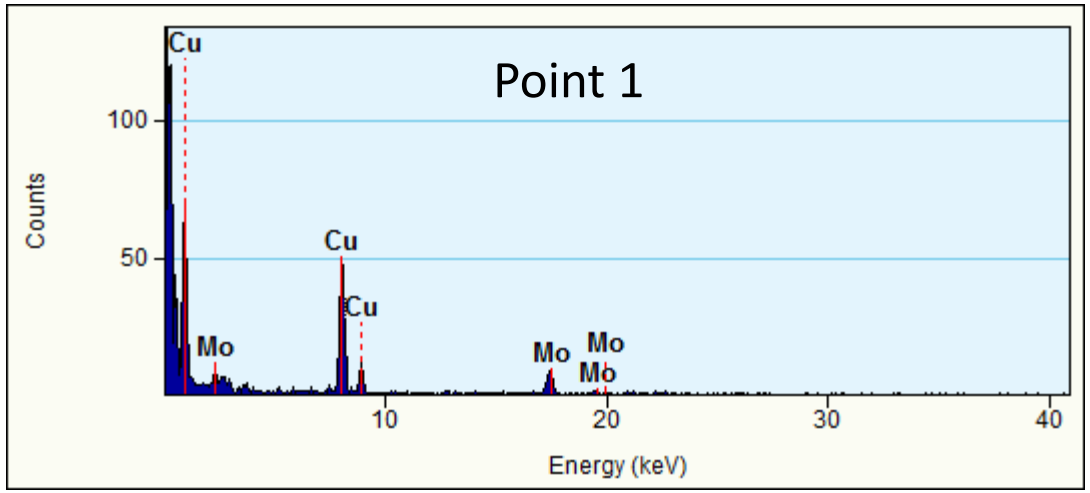
Fresh catalyst

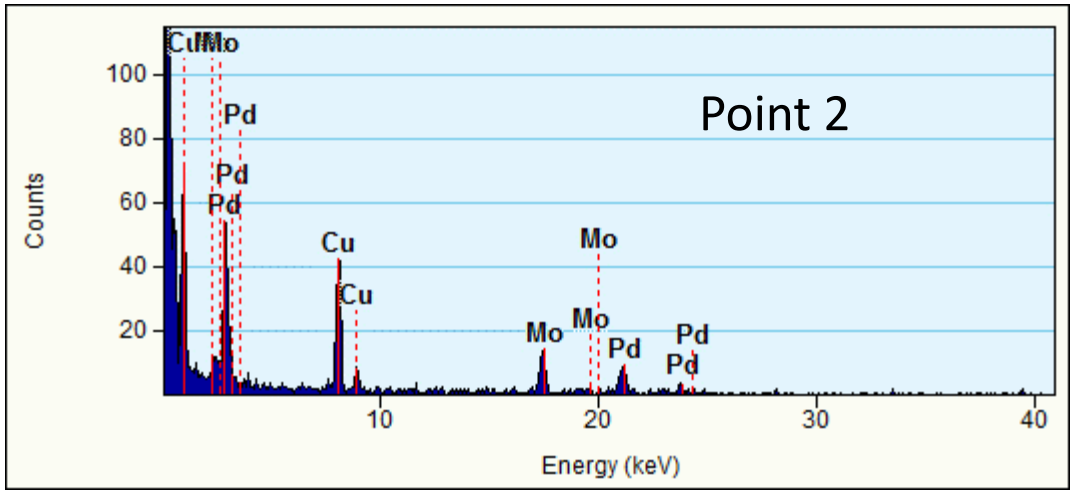
ICP-AES, Pd
Recovered catalysts= Fresh catalyst

# 4. Amine alkylation



# Summary

- We have prepared a new bimetallic material with potential application as catalyst
- We have tested it for the typical Pd-catalyzed reactions with diverse results
- The alkyne homocoupling reaction is catalyzed by the palladium present in the material
- For the alkylation of amines a deactivation process of the catalyst was observed during the successive cycles due to the formation of $Pd^0$ nanoparticles

# Aknowledgements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  Technicians:
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  - Drs. Luis Bartolomé and Juan Carlos Raposo



Thank you for your attention

ご清聴ありがとうございました

Muchas gracias por su atención