UiO : Department of Chemistry
University of Oslo

inGAP
Innovative Natural Gas Processes and Products

" Ethylene oxychlorination catalysis: role of metal promoters on activity and selectivity of the process"

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Trondheim, 3rd Nov '11

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Centre of Excellence
Università di Torino
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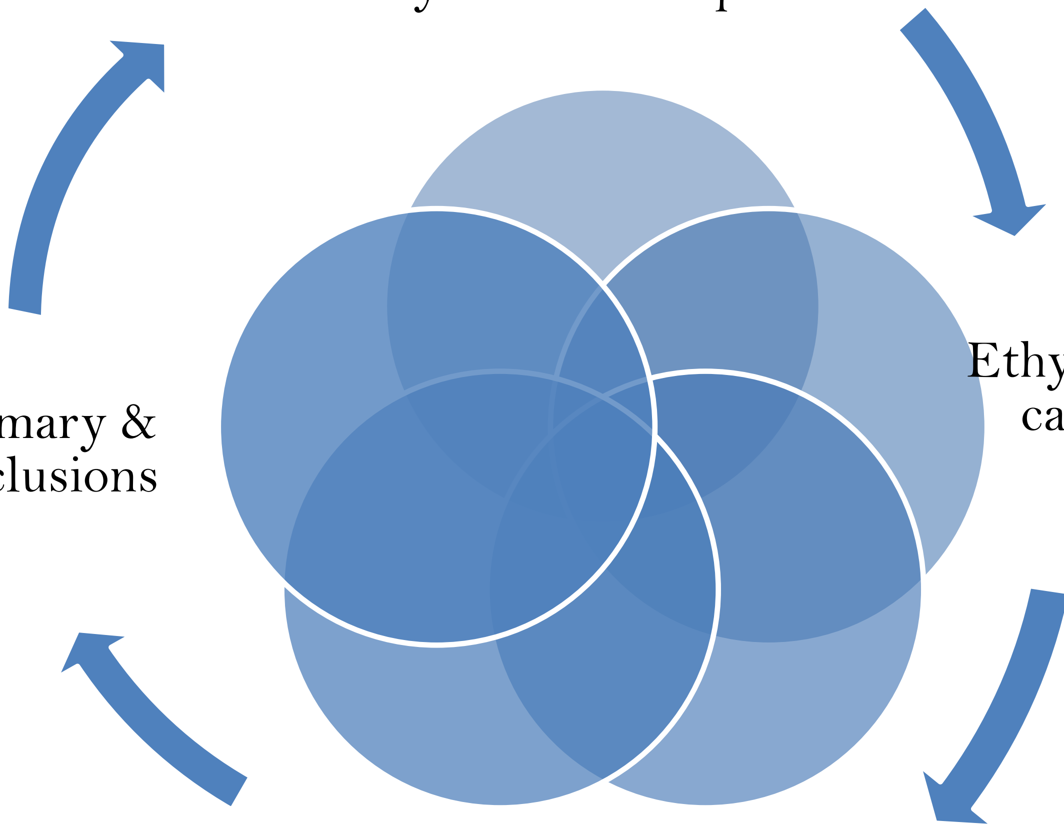
Outlook

The chemistry of PVC and origin of Oxychlorination process



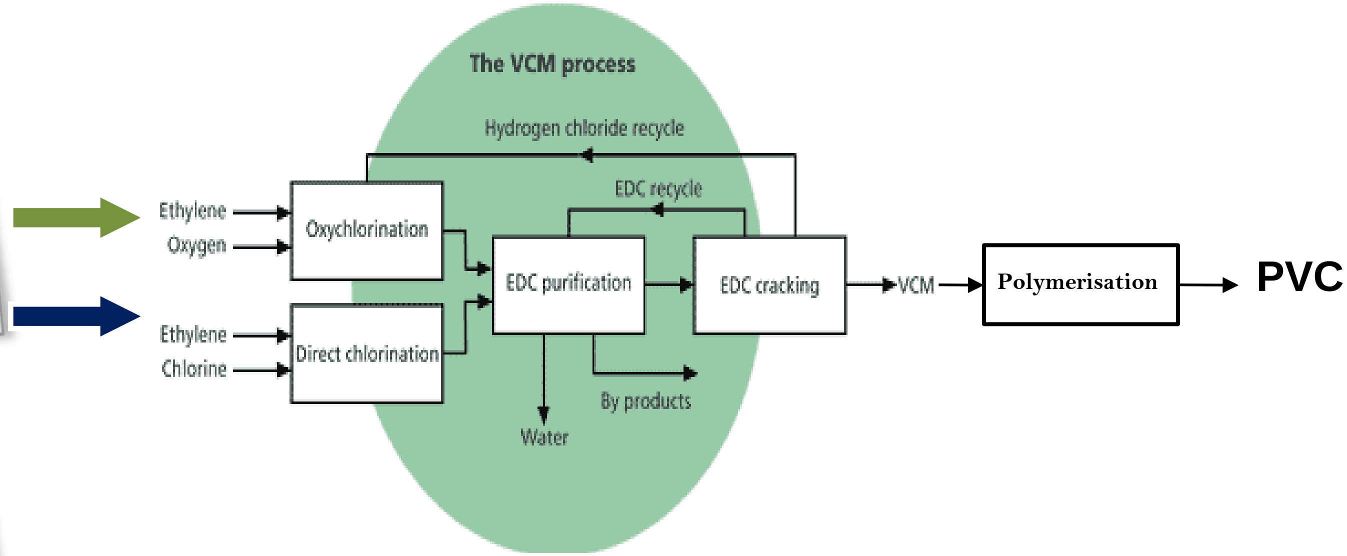
Ethylene Oxychlorination catalyst - state of art

Influence of additives on base catalyst: multi technique approach

Summary & Conclusions

Poly Vinyl-Chloride (PVC)

PVC industry is growing market with recycling efforts



Oxychlorination reaction ($CuCl_2$) @ 230°C

$$C_2H_4 + 2HCl + ½\ O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

Direct chlorination ($FeCl_3$)

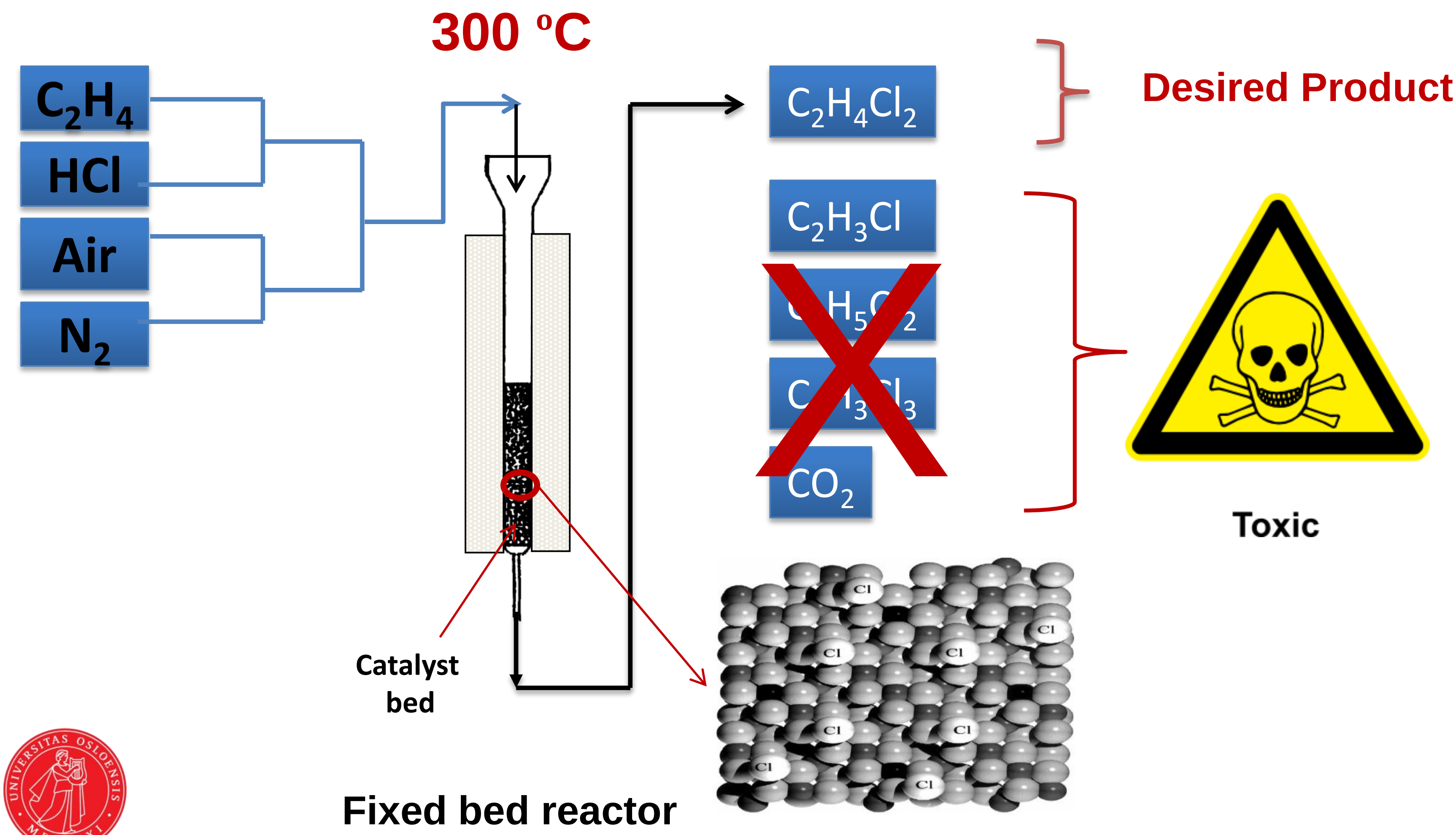
$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Cracking of 1,2-dichloroethane (EDC)

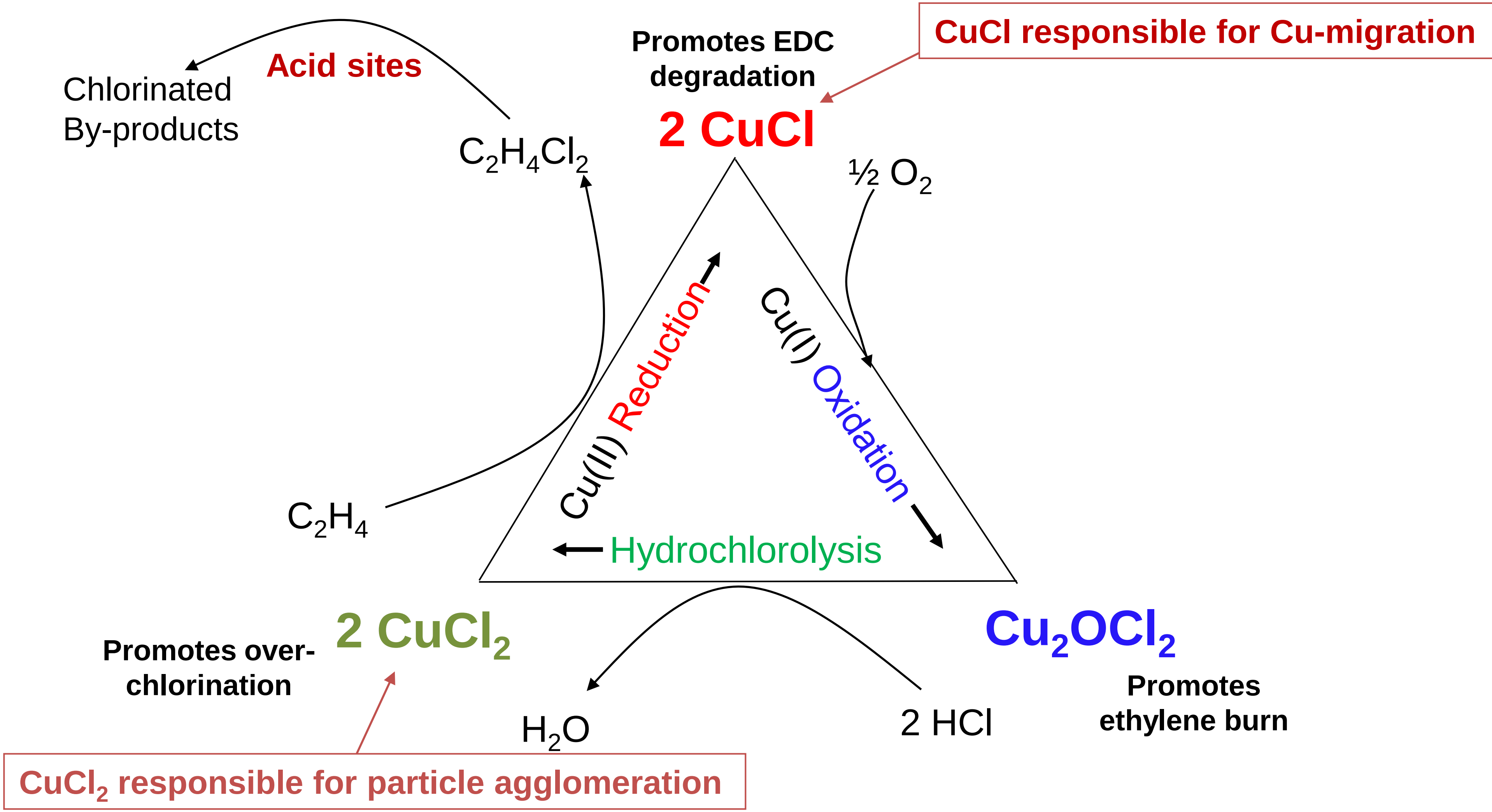
$$C_2H_4Cl_2 \rightarrow CH_2{=}CHCl + HCl$$

Oxychlorination Catalyst – State of Art

The basic commercial catalyst is **$CuCl_2$/ γ-Al_2O_3**



Reaction mechanism



Motivation & Challenges

- **Economic prospect:** Drive to decrease operation costs
- **Chemical & Environmental prospect:** selectivity could still be improved
- $CuCl_x$ is volatile and may be lost during reaction
  Hot spots, thermo–chemical side reactions
- Catalyst becomes sticky under certain reaction conditions (Fluid bed operation)

Adding dopants may solve the above problems

Objective

Our aim is very ambitious and can be summarized in the following four main points:

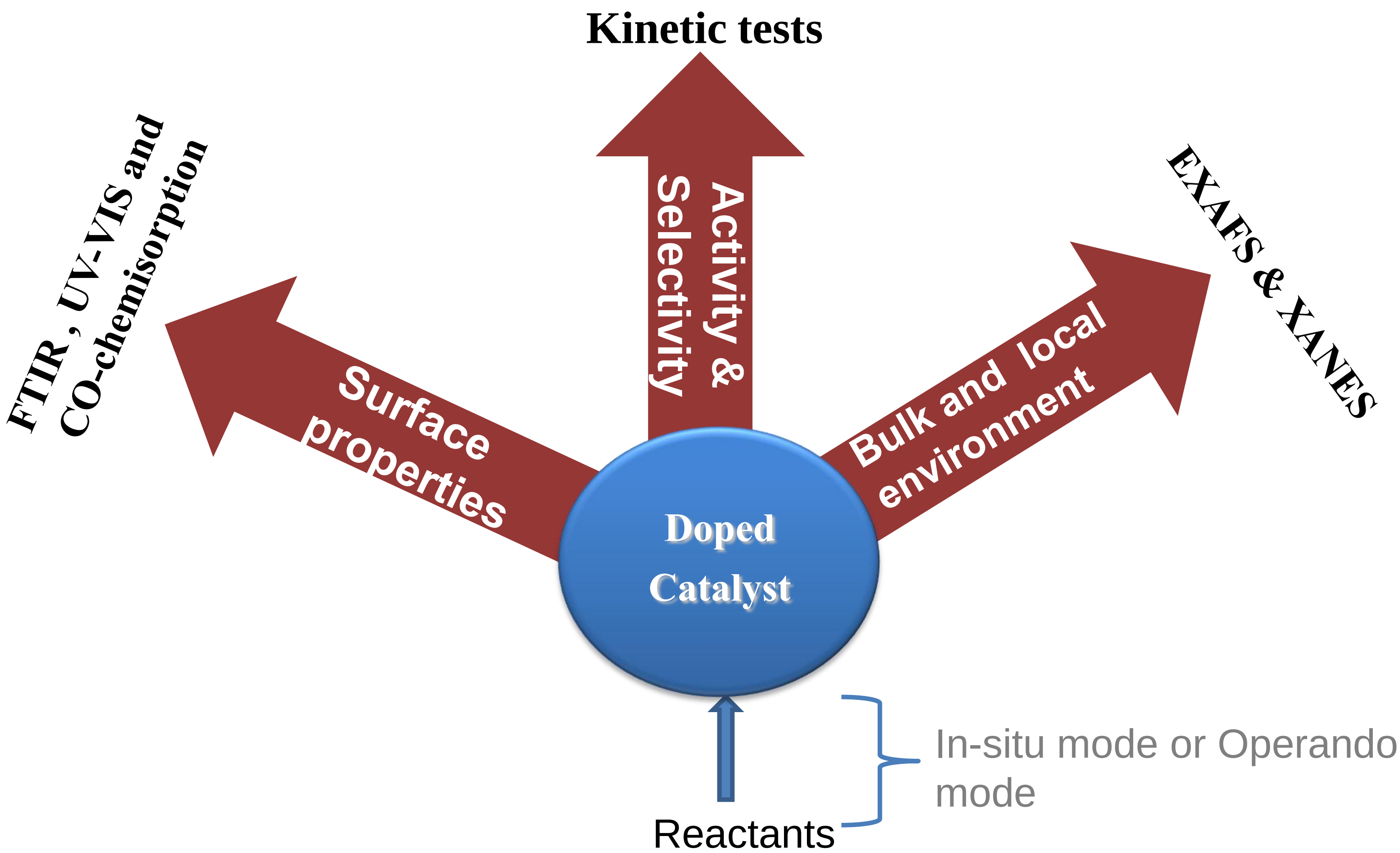
Doped catalyst

Reactants

1) Influence on Surface and its properties
   Dispersion, active phase modifictaion, acidity of the surface….
2) Influence on reaction mechanism and kinetics
3) Influence on thermal & mechanical stability of the catalyst during reaction
4) Influence on Selectivity

Influence of Additivies

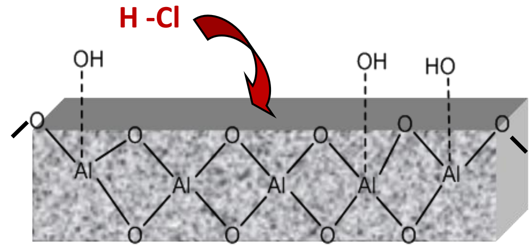
Characterisation using combined spectroscopy

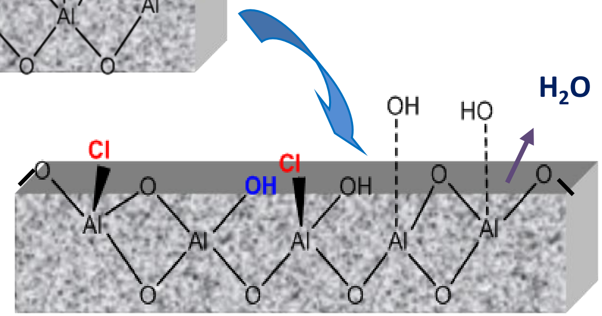


Influence of Additives: On the Support

Modification on Surface acidity upon addition of dopant & chlorine

1)



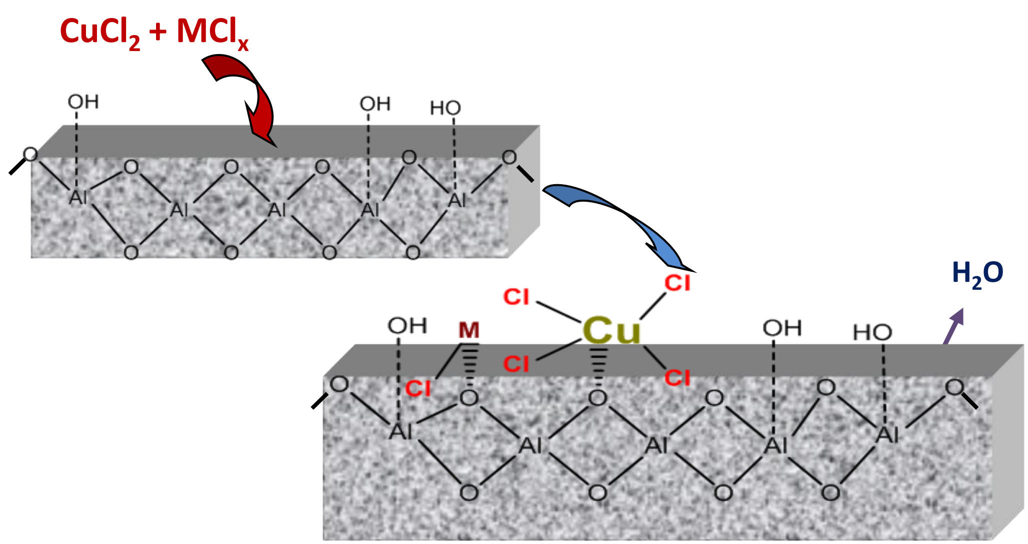


>Al-O-Al< +HCl $\rightarrow$ >Al-OH + Cl-Al<

>Al-OH + HCl $\rightarrow$ >Al-Cl + H_2O

Unwanted species

2)

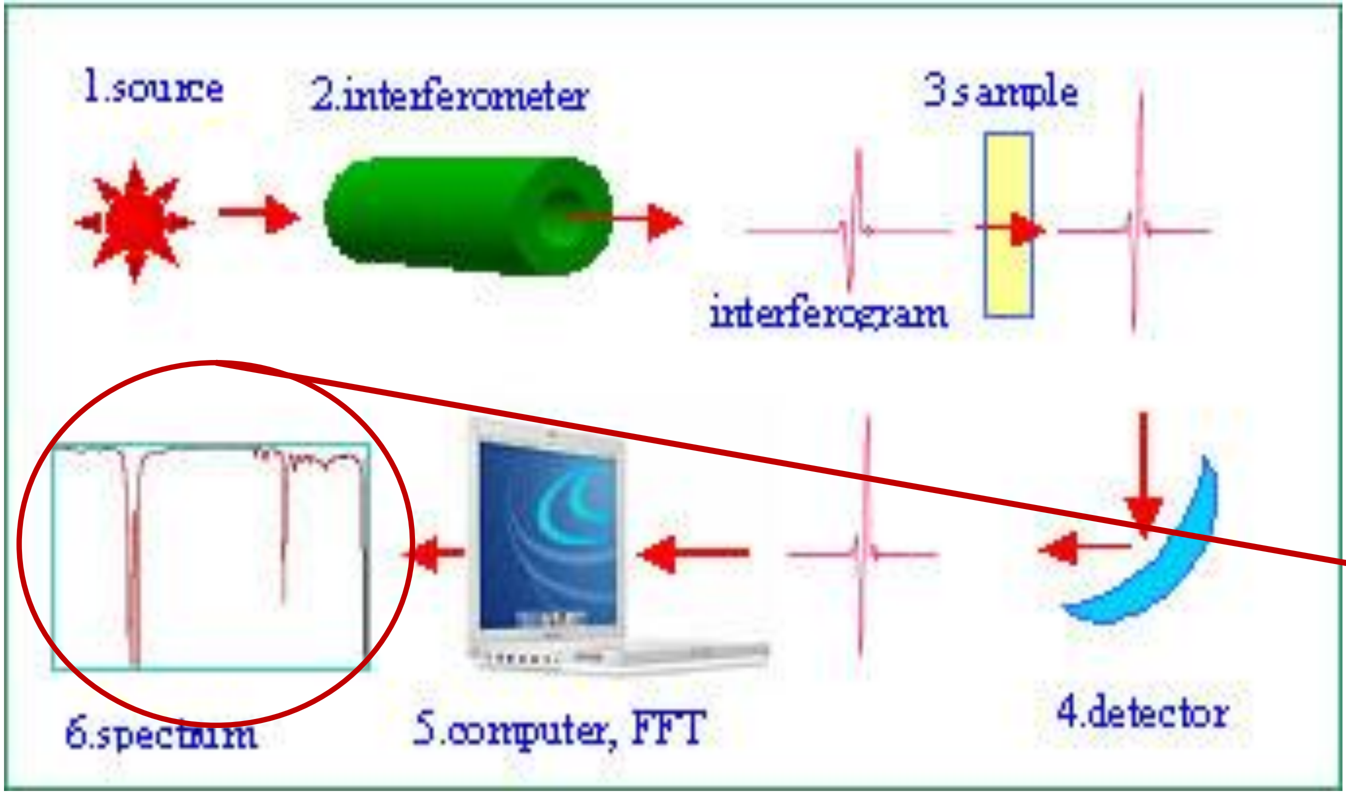


N. B. Muddada *et al*., J.Catal (2011) accepted

Fourier Transform Infrared Spectroscopy

FTIR: a surface technique, basically give information about surface species

$$I/I_0 = \%T$$



Peak position, intensity and width
=>
Nature of species

Influence of Additives: The Surface

CO adsorbed FTIR

FTIR

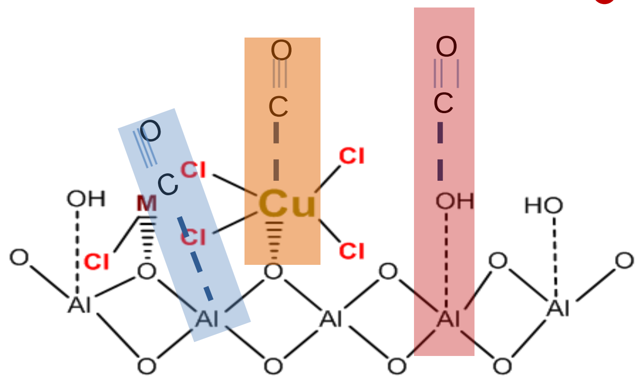
Evolution of the CO adsorbed FTIR spectra on the fresh catalyst activated @230°C under vaccum.

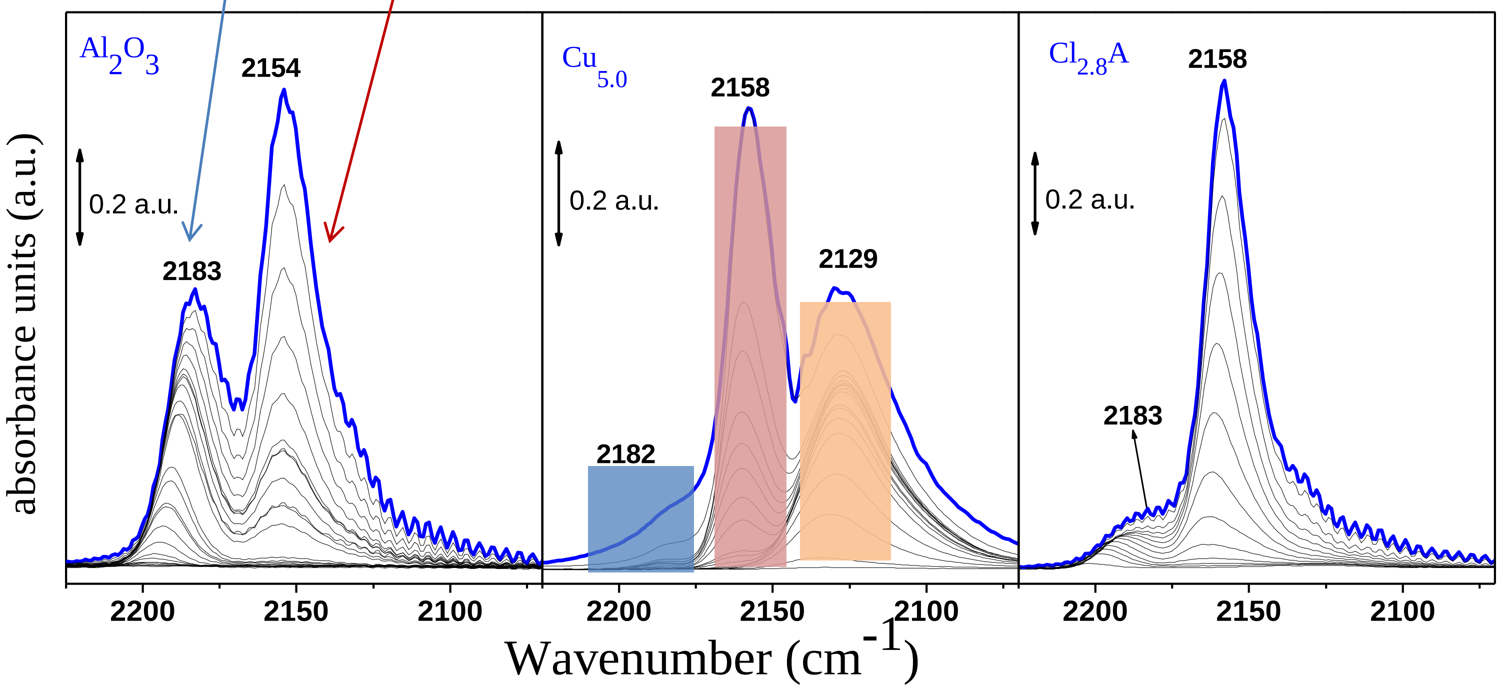
Lewis acid sites:

[= Al^{3+}] ···· CO

Brønsted acid sites

[= Al-OH] ···· CO



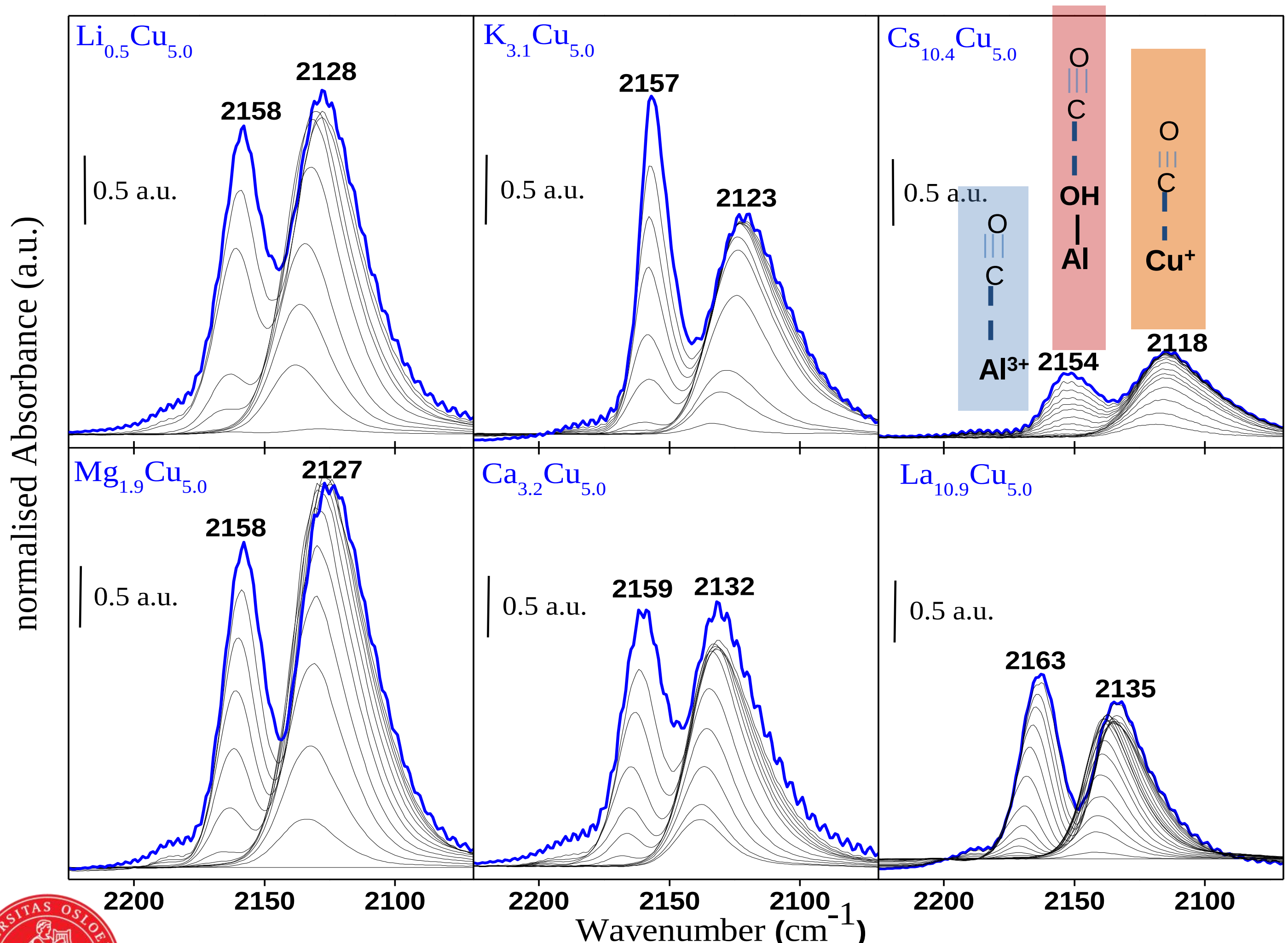


N. B. Muddada *et al*., J.Catal (2011), in press.

Influence of Additives: On the Surface

CO adsorbed FTIR

Catalyst: doped $CuCl_2/\gamma$-Al_2O_3

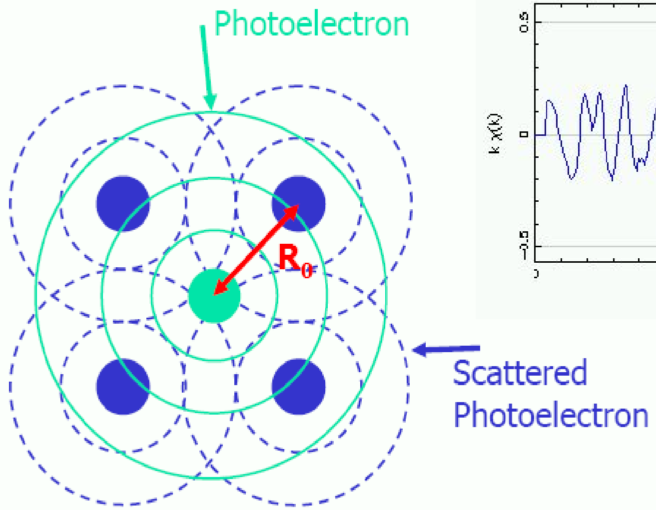


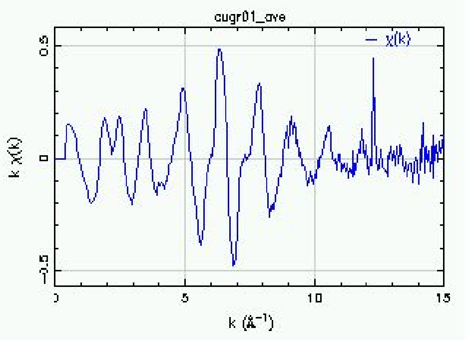
- ❑ Most of Lewis sites are compressed
- ❑ Strength of Brønsted sites follows the order:

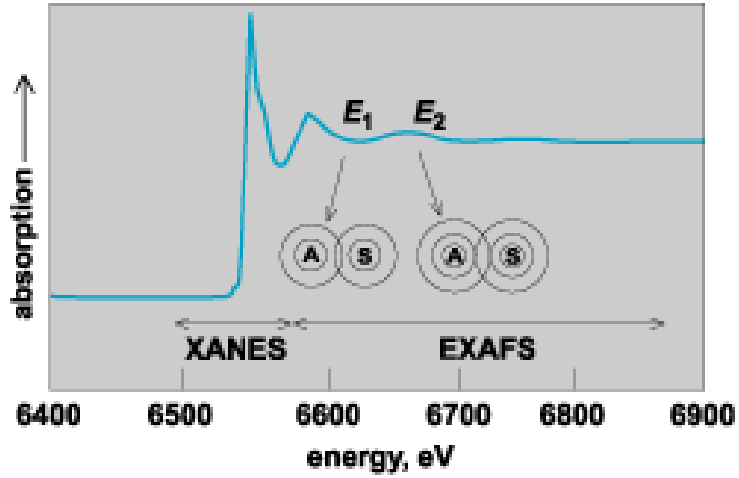
La > Ca > Mg > Li > Cu > K > Cs

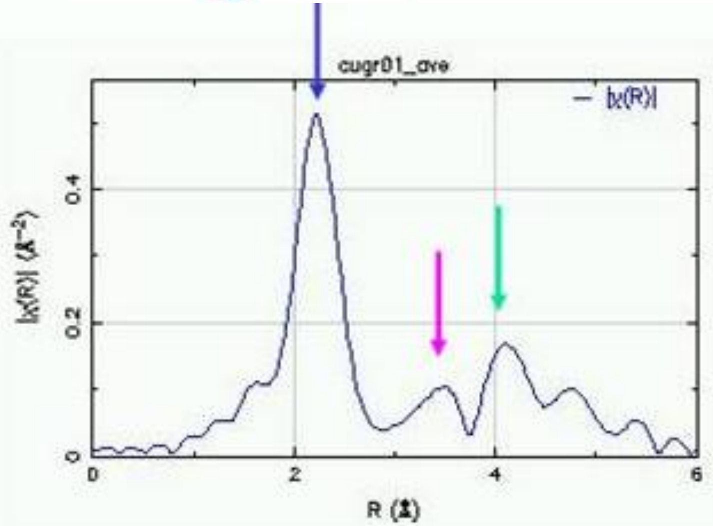
N. B. Muddada *et al*., J.Catal (2011), in press

X-ray-Absorption Fine Structure









$$\chi(k) = S_0^2 \sum_s \frac{N_s A_s(2k)}{R_s^2} e^{-\frac{2R_s}{\lambda}} e^{-2k^2\sigma_s^2} sen(2kR_s + \phi_s(k))$$

Influence of Additives: On the Cu phase

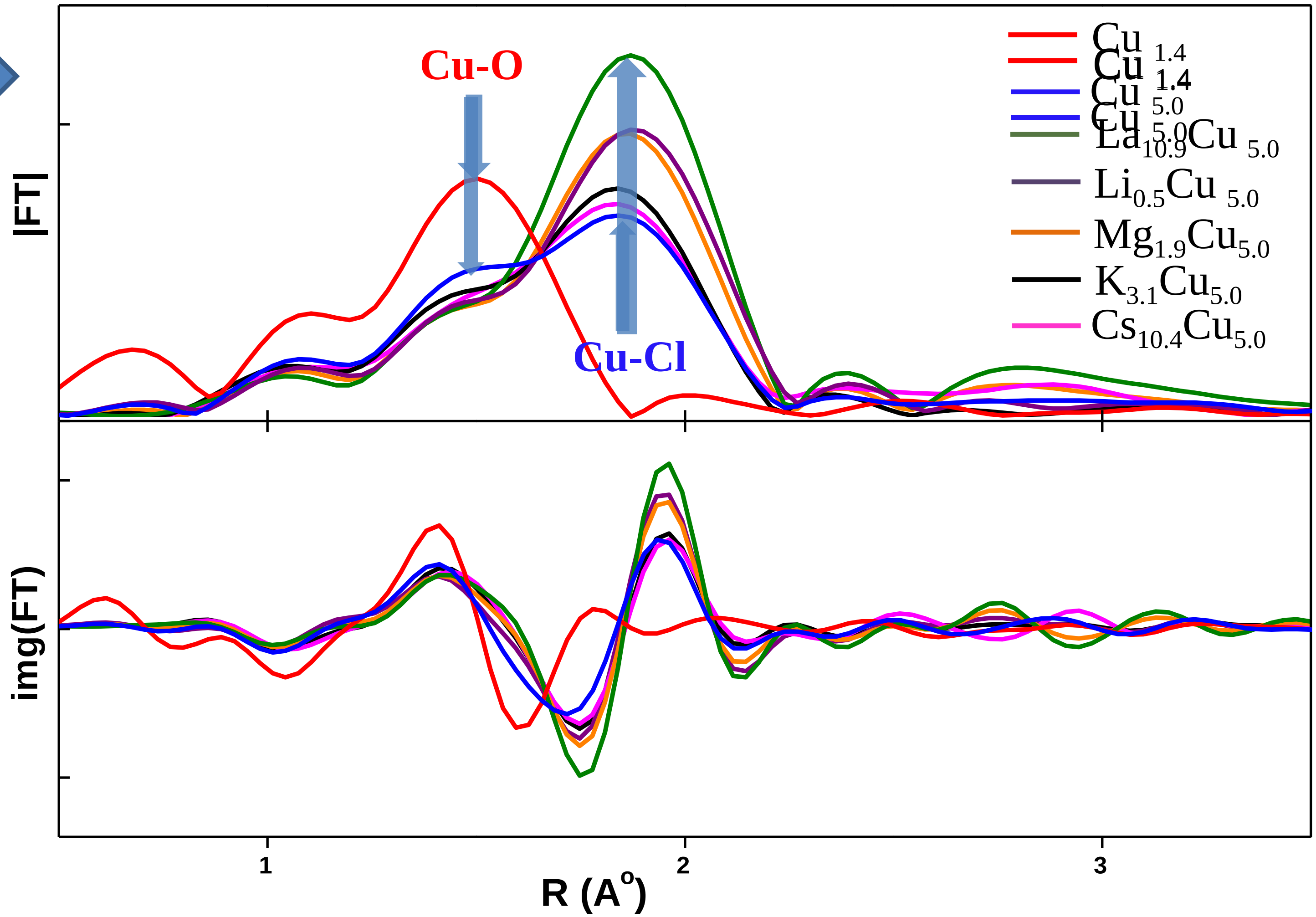
Extended X-Ray Absorption Fine Spectroscopy

All dopants are competing with Cu to occupy alumina octahedral vacancy sites

La>Li>Mg>K>Cs>Cu

EXAFS

Evolution of the EXAFS spectra of the fresh catalyst activated @ 230°C



N. B. Muddada *et al*., Dalton Tran, 39 (2010) 8437.

Collected at EAXFS 13, LURE, France

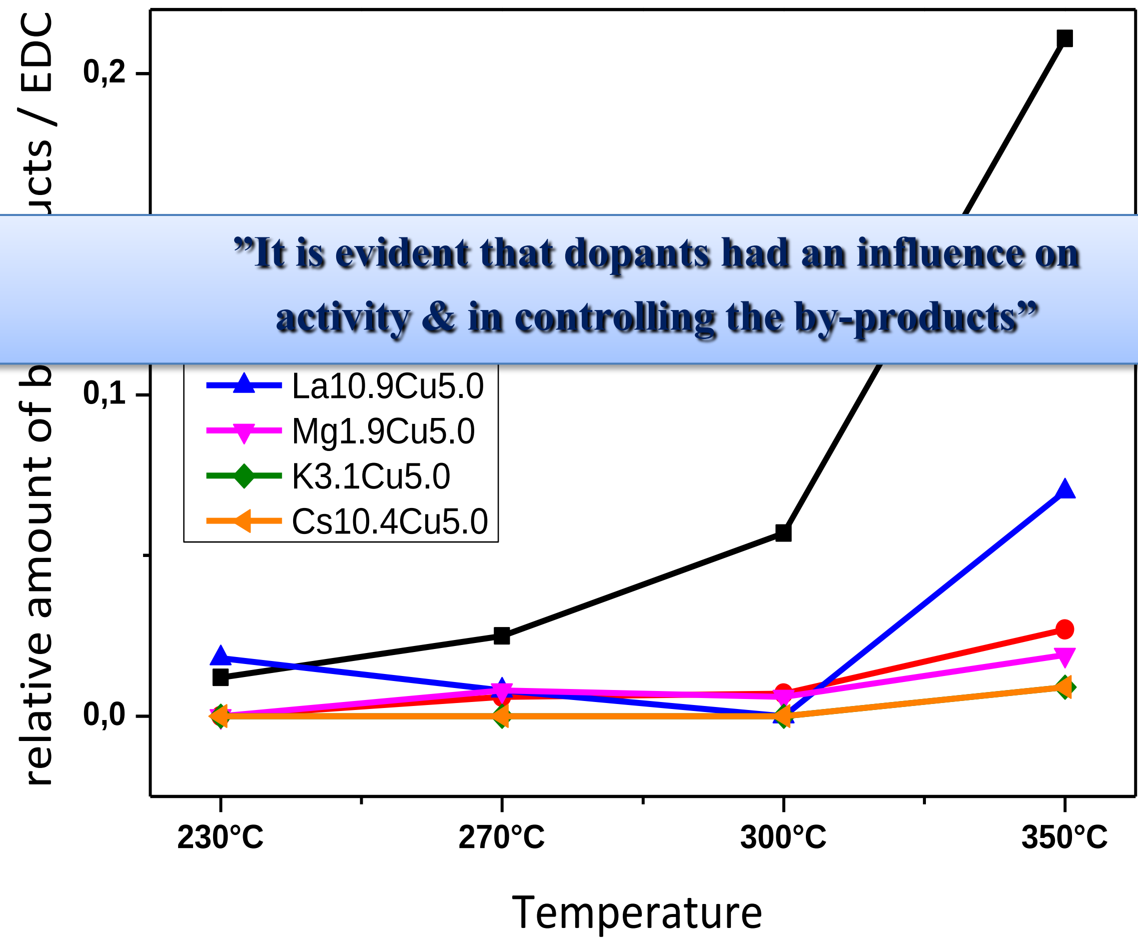
Influence of Additives: Kinetics

Byproduct formation follows the order

$\mathbf{Cu_{5.0} > La_{10.9}Cu_{5.0} > Li_{0.5}Cu_{5.0} > Mg_{1.9}Cu5.0 > K_{3.1}Cu_{5.0} \approx Cs_{10.4}Cu_{5.0}}$

Kinetic tests

Evolution of the products (by GC-MS) of the sieved catalyst interacted with reaction mixture @ 230°C - 350°C under steady state

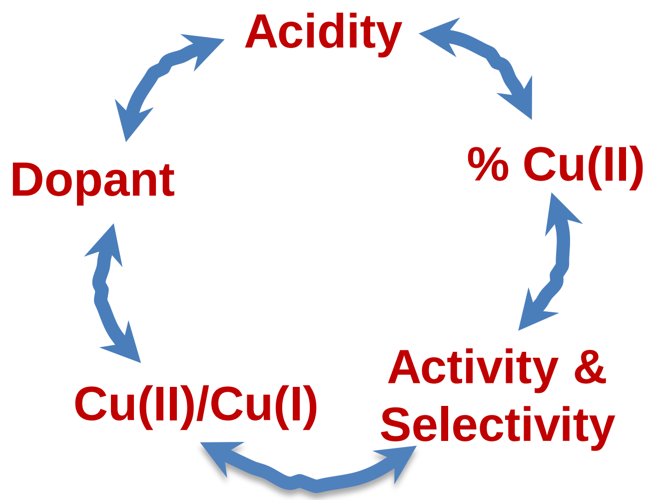


”It is evident that dopants had an influence on activity & in controlling the by-products”

N. B. Muddada *et al.*, J.Catal (2011) accepted

Summary & Conclusions

- **Chlorine has significant influence on acidity of alumina surface.**
- **Dopant metals also influence the acidity of alumina especially in case of Lewis sites.**
- **Dopants increase the fraction of copper specieis on the surface.**
- **Dopants had a significant influence on activity and also in controlling the by- product formation compared to base catalyst $CuCl_2/\gamma\text{-}Al_2O_3$.**



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Thanks for your Attention……☺

Different Supports

Possible Supports:

- Zr-MOF (UIO-66) - An ultra stable Metal Organic Framework (MOF)
- Alumina modified with CeO_2 .
- Mixed metal oxides: $CeZrO_x$, Mg_{10} Al_7O_x.
- Perovskite materials, Zeolites type materials.

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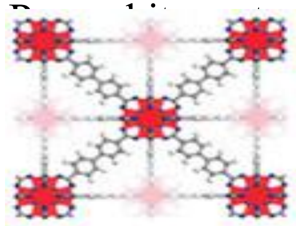
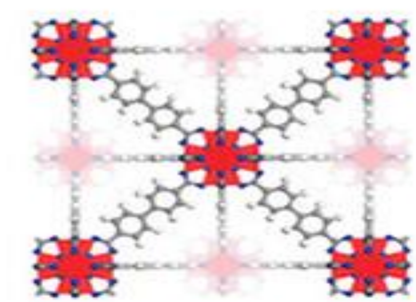
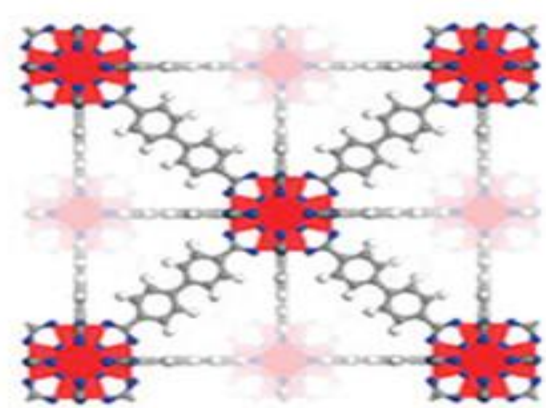




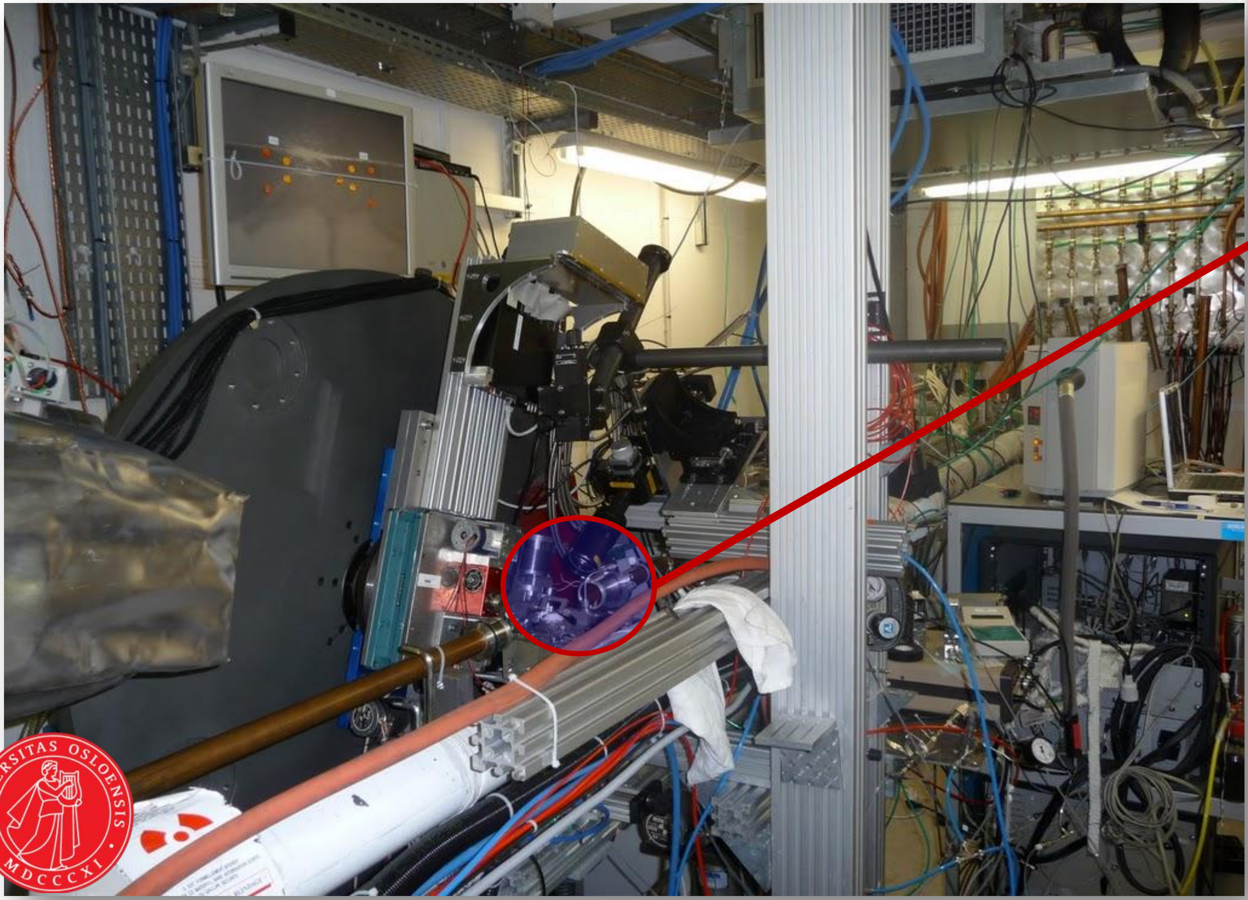


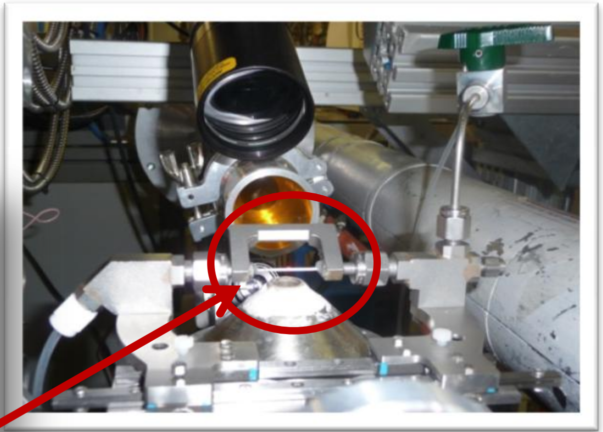
UIO-66: Commerically available Zr- MOF

SNBL - ESRF

- ❑ $CuCl_2$ was loaded during synthesis of Zr-MOF (uio-66)

In-situ EXAFS+MS set-up

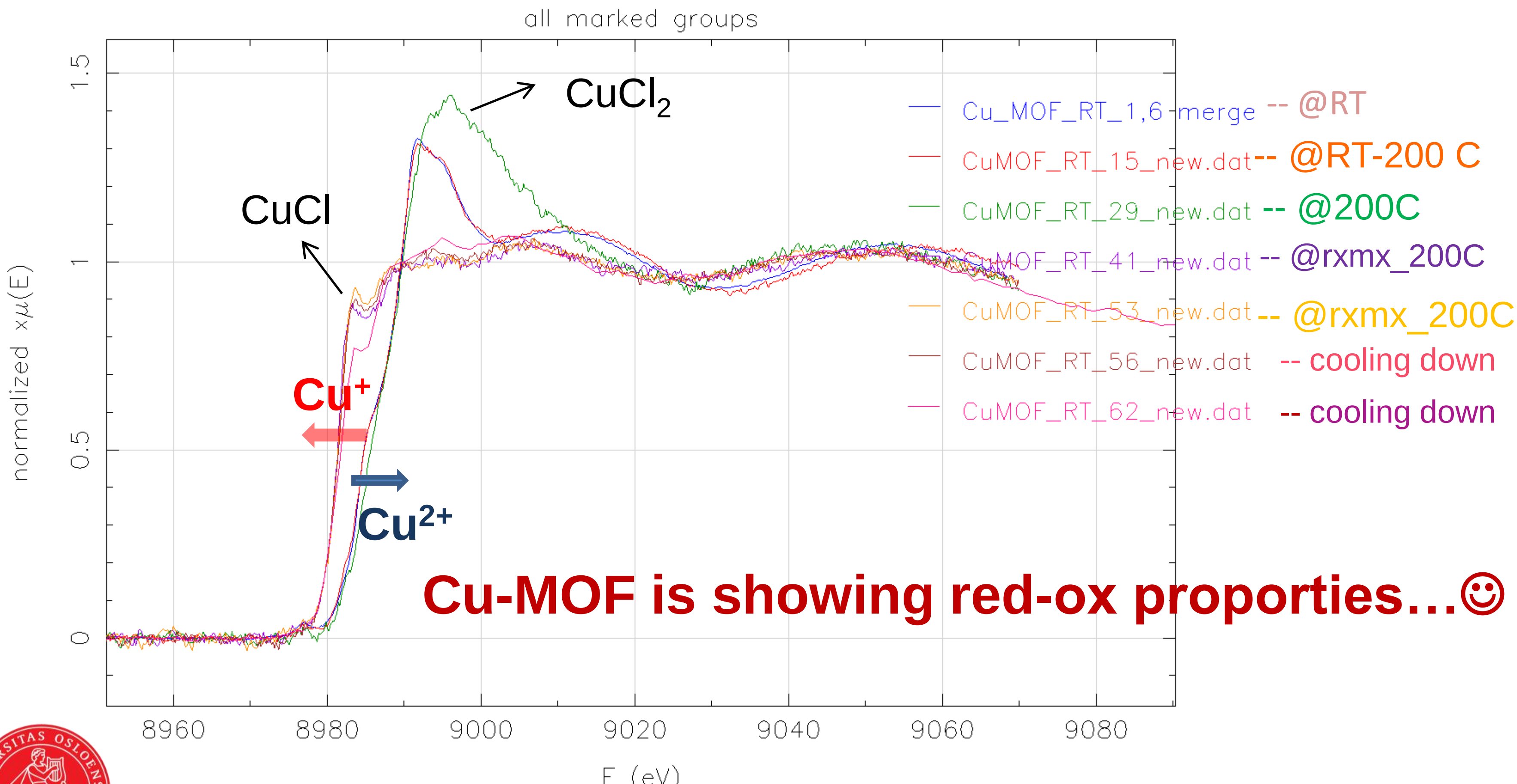




$CuCl_2$-Zr-MOF as redox catalyst - XANES

Ethylene+HCl+Air →  → Mass Spec

Cu wt% ≈ 1,2 %
Conversion is
very very low!!!

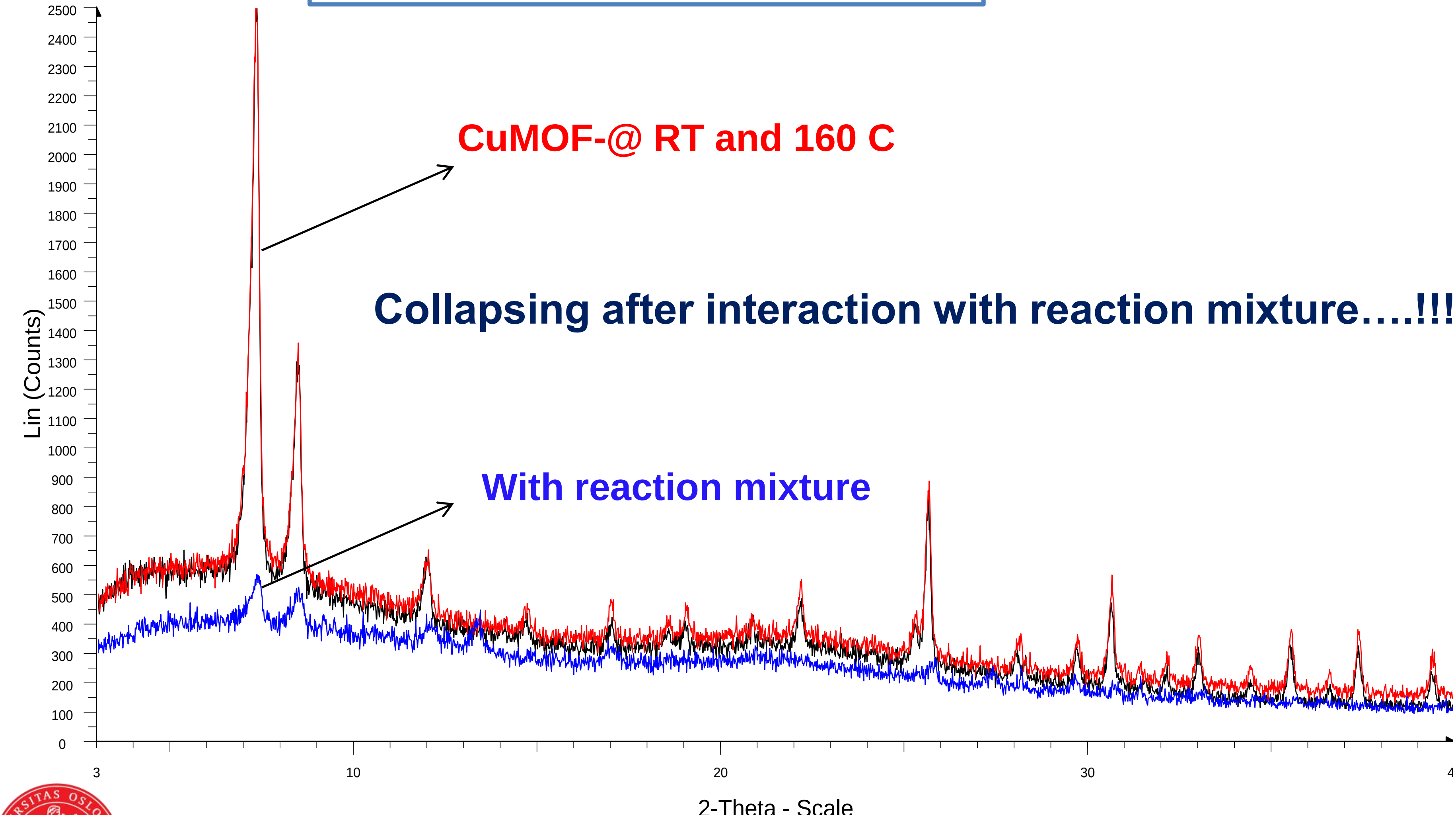


Cu-MOF is showing red-ox proporties…☺

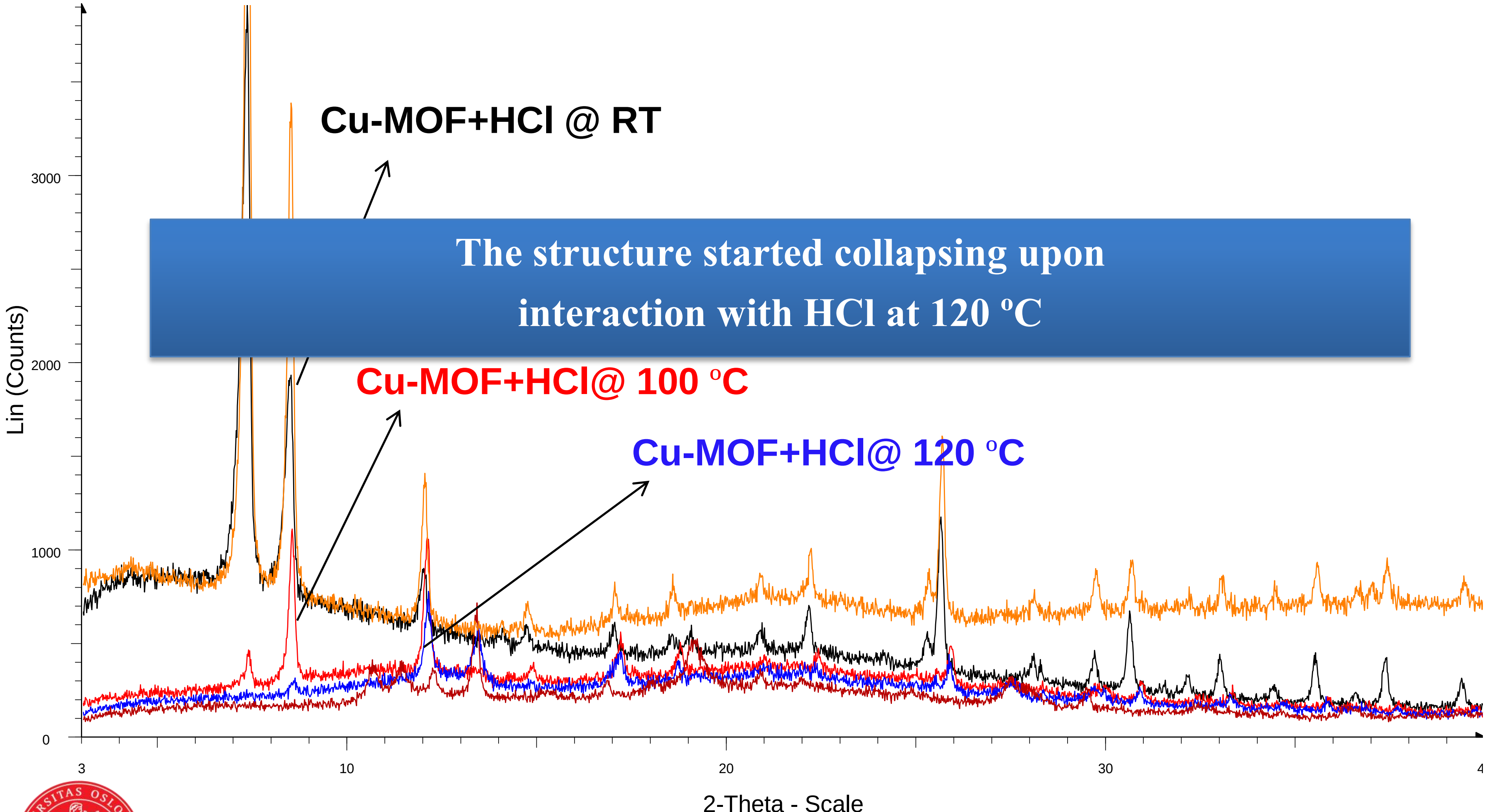
CuMOF : $CuCl_2$ loaded onto Zr-MOF

$CuCl_2$-Zr-MOF as redox catalyst - XRD

CuMOF : $CuCl_2$ loaded onto Zr-MOF



$CuCl_2$-Zr-MOF + gas. HCl - XRD



The structure started collapsing upon interaction with HCl at 120 ºC