→Expertise of the Unité de catalyse et chimie des matériaux divisés (CATA)

Eurokin

February 12th 2009, LLN

E.M. Gaigneaux

Unité de catalyse et chimie des matériaux divisés

Université catholique de Louvain - Belgium

→Expertise of the

Unité de catalyse et chimie des matériaux divisés (CATA)

→ A case study :

catalytic abatement of air chlorinated pollutants

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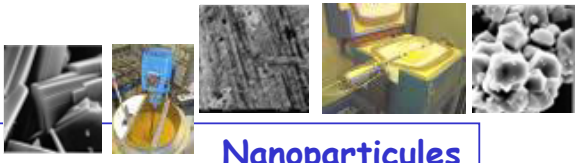
Université catholique de Louvain - Belgium

Université catholique de Louvain **UCL**

Unité de catalyse et chimie des matériaux divisés

Expertise in heterogeneous catalysis

Cata



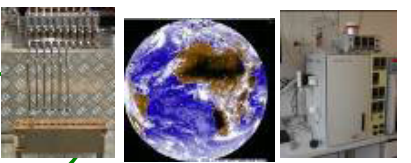
Nanoparticules
Mixed oxides & **Noble metals**
Structuration : monoliths
Scaling-up & Shaping

Preparation of divided inorganic solids

Surface
XPS
Bulk
DRX
IR, Raman
XRF, ICP
Textural
Porosimetry
Chemical
Chemisorption

Physicochemical characterization

Heterogeneous catalytic reactivity



Fine Chemicals
Petrochemistry
Production biofuels & H_2
Air depollution
Activation of CO_2

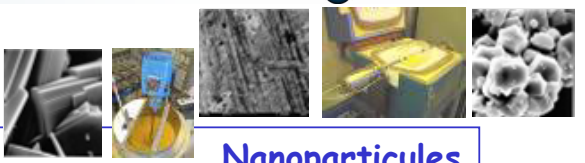
Pointing the parameters & understanding the mechanisms dictating the performances → Specific actions to improve the systems

Synthesis of heterogeneous catalysts

Cata

- Bio-onions route
- (Co-)precipitation
- Complexation (citrate)
- Sol-gel
- Micro-emulsion
- Impregnation
- Grafting
- Deposition-precipitation
- Ion exchange
- Precursors mth
- Spin-coating

Preparation of divided inorganic solids



Nanoparticules
Mixed oxides & **Noble metals**
Structuration : monoliths
Scaling-up & Shaping

Single and mixed bulk oxides

- Doped oxides
- Spinels
- Perovskites
- Hexaaluminates
- Oxynitrides
- Phosphates

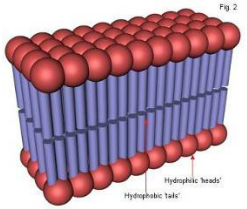
Heteropolycompounds

Other materials: nitrides, carbides, sulfides, etc.

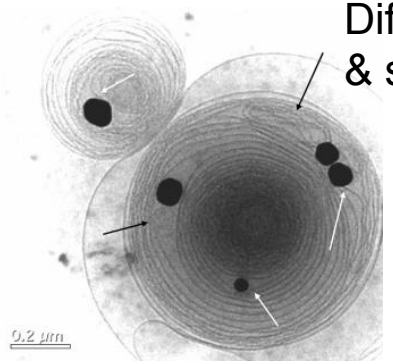
Supported or encapsulated metals in oxide or carboneous matrixes

Synthesis of heterogeneous catalysts

Bio-onions route



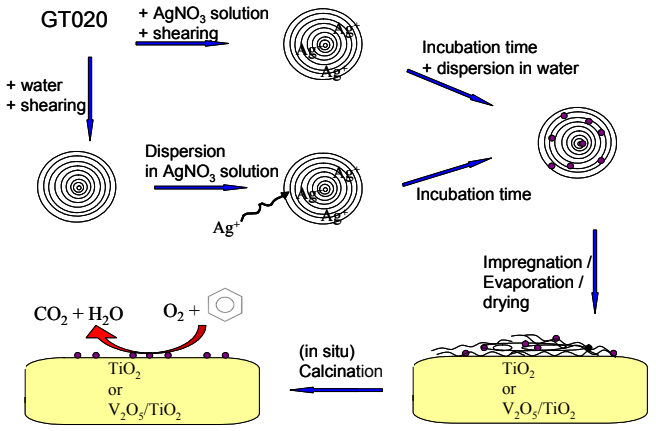
Surfactant

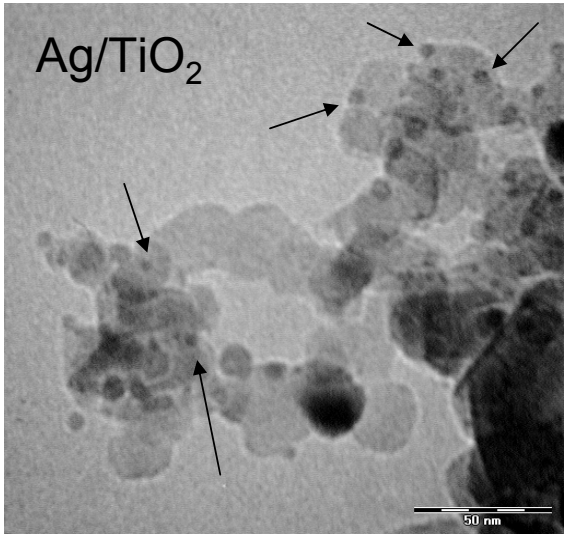


Diffusion of metal salt inside multilayer vesicles
& simultaneous in situ reduction
→ no thermal treatment !!!

Supported metal particles of 5 nm resistant to sintering
Debecker et al, Small 4 (2008) 1806.

Transfer on a support

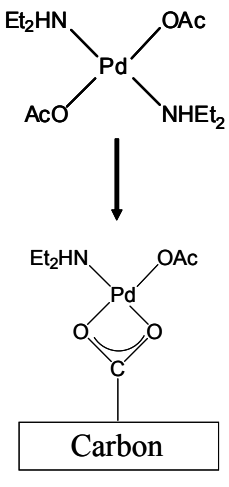


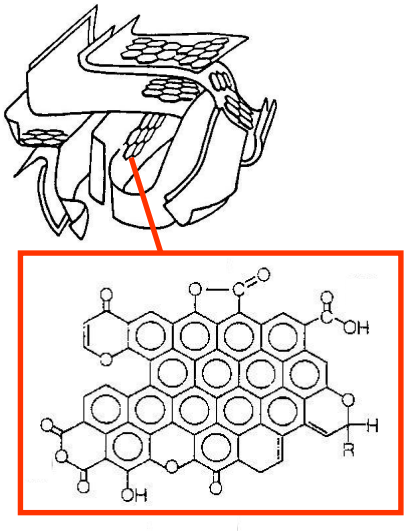


Synthesis of heterogeneous catalysts

Cata

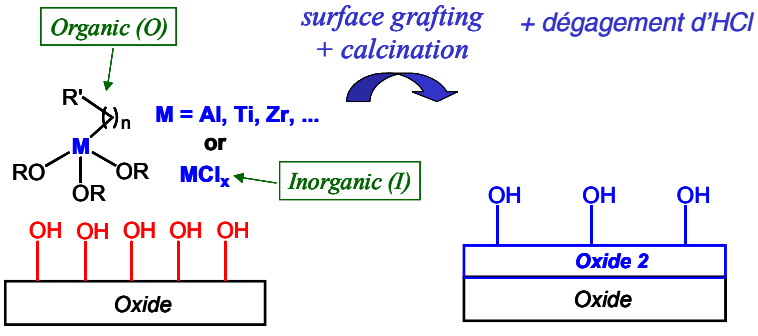
Grafting





On active carbon

On oxide



Sample	Dispersion (%)
Rh/Ti-SiO$_2$/I	17
Rh/Ti-SiO$_2$/O	7

brings chemical properties favorable for the Rh dispersion

brings textural properties

Synthesis of heterogeneous catalysts

Cata

Shaping
Scaling-up

Pellets & Extrudates
from A to Z :
batches up to 1 kg

Characterizing heterogeneous catalysts

Surface
- XPS

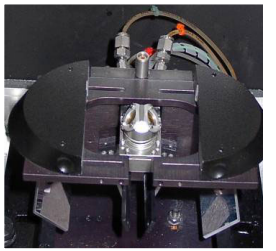
Bulk
- DRX
- IR, Raman
- XRF, ICP

Textural
- Porosimetry

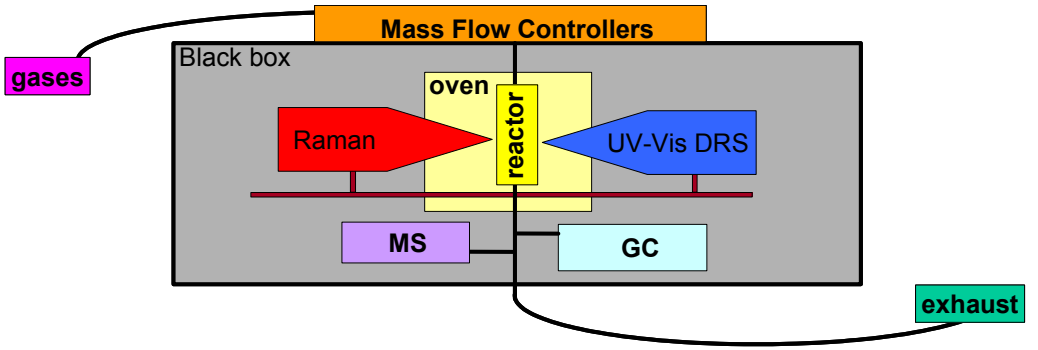
Chemical
- Chemisorption

Physicochemical characterization

Texture : physisorption
Composition : XRF
Surface : XPS including pseudo in situ
Structure : XRD IR Raman
all including in situ at high T
Chimisorption : acidobasicity (CO_2 or NH_3)
dispersion (CO)

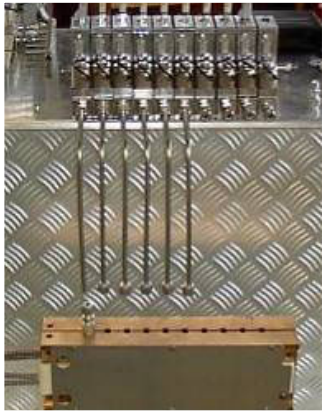


+ operando



Catalyst performances

- **Environmental catalysis**
  - Air: catalytic removal of S, N, Cl-VOCs, O_3, CH_4, NO_x
  - Water: denitrification and elimination of organics
  - Activation of CO_2 at low temperature → P. RUIZ

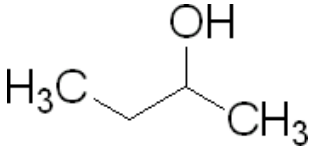


- **Petrochemistry** & **refining**
  - Partial oxidation & epoxidation (propylene)
  - Oxidative dehydrogenation
  - Ammoxidation (propane → acrylonitrile)
  - Isomerization, and metathesis
  - Production of synthetic gas
- **Fine chemistry**
  - Acid-base reactions
  - (De) hydrogenation
  - C sp2 coupling

- **Catalytic combustion and energy production**
  - Hydrogen production
  - Catalytic burner
  - Esterification to biodiesels

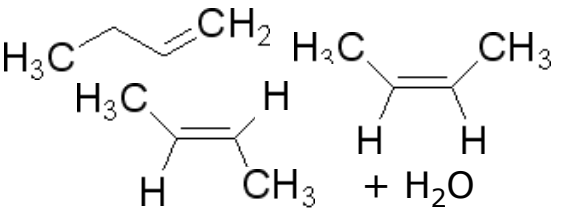
Microreactors + multireactor

Oxidative dehydrogenation of 2-butanol on heteropolycompound (HPAs)



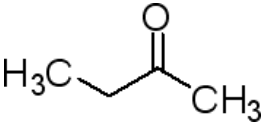
in the presence of O_2

Dehydration ☺



Butenes (But)

Oxidative dehydrogenation ☺



+ H_2O

Methyl-ethyl-ketone (MEK)

Total Oxidation ☹

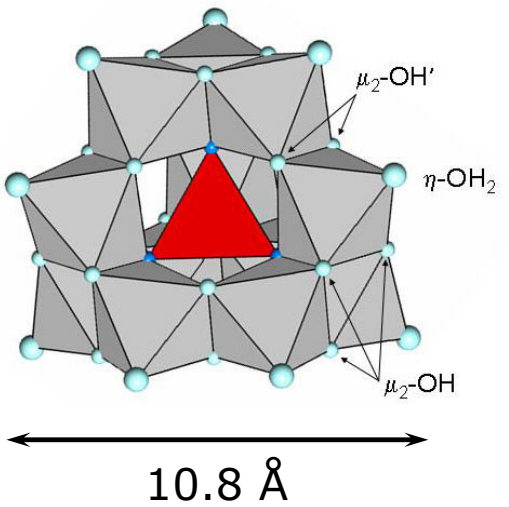
4 CO_2/CO + 5 H_2O

Combustion products

Oxidative dehydrogenation of 2-butanol on heteropolycompound (HPAs)

HPAs = polyoxometalates incorporating anions and a counter ion

➡ i.e. : Keggin-type complex $XM_{12}O_{40}^{n-}$



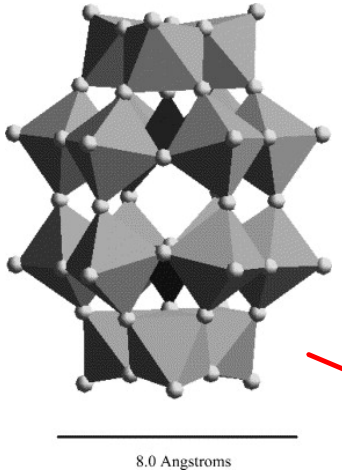
X = heteroatom –tetrahedral
P^{V}, Si^{IV}, (Ge, As, Co, B)

M = atom addenda -octahedral
Mo^{VI}, W^{VI}

+ counter-ion
H^+, NH_4^+, K^+, Ni^{2+} etc

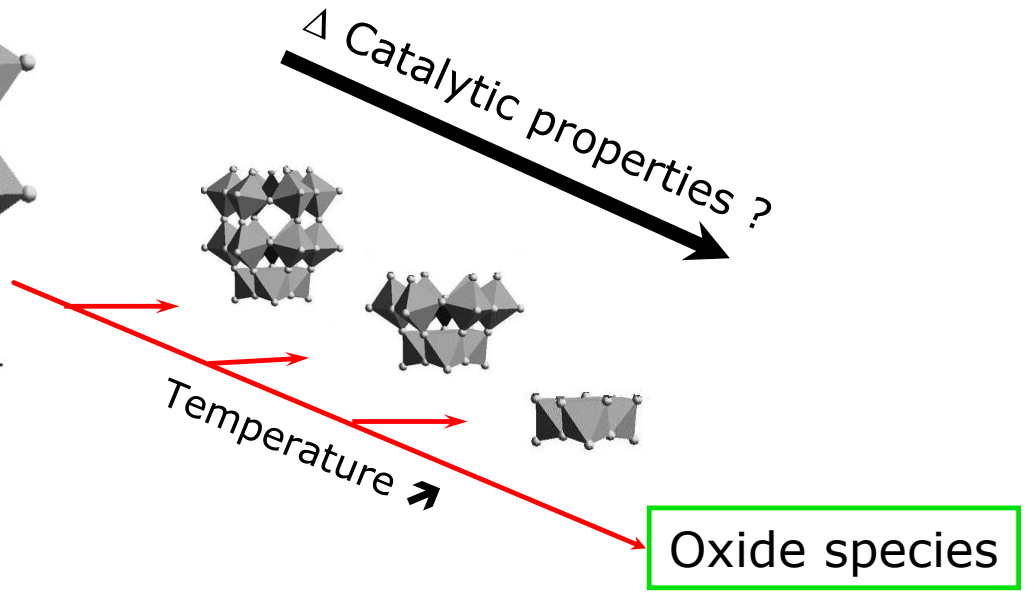
$(H^+)_3\,(PMo_{12}O_{40})^{3-}$
$(Ni^{2+})_2\,(SiW_{12}O_{40})^{4-}$

Oxidative dehydrogenation of 2-butanol on heteropolycompound (HPAs)



Wells-Dawson

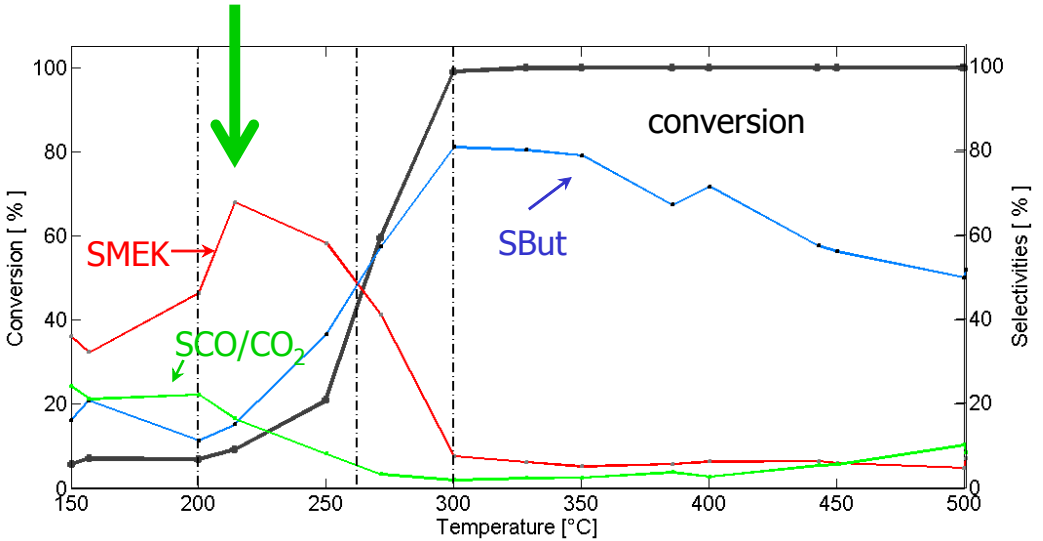
$(NH_4)_6\ P_2Mo_{18}O_{62}\ .12\ H_2O$



Can we tune a
« Wells-Dawson » HPA,
so that it preferentially performs the
oxidative dehydrogenation of 2-butanol ???

Oxidative dehydrogenation of 2-butanol on heteropolycompound (HPAs)

Enhanced selectivity to MEK



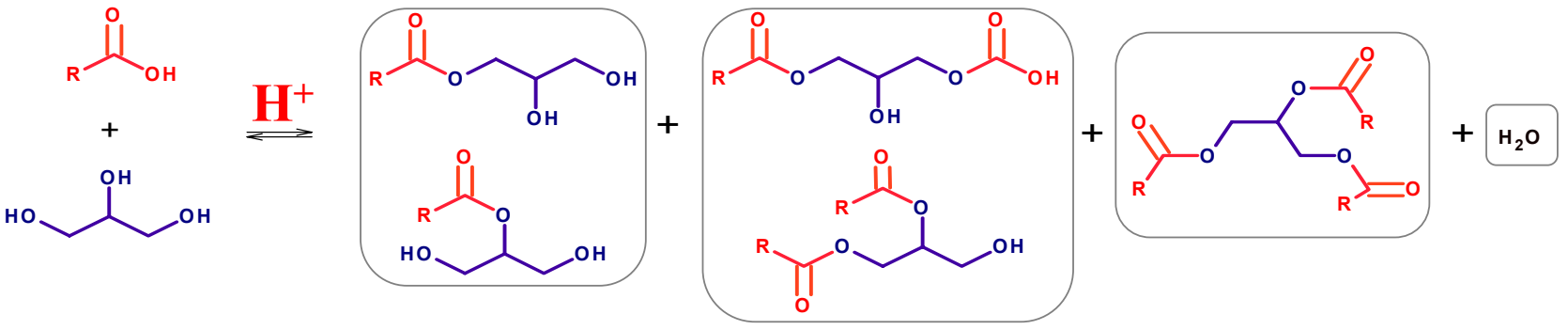
Can we tune a
« Wells-Dawson » HPA,
so that it preferentially performs the oxidative dehydrogenation of 2-butanol ???

→ YES !!!

Production of biodiesels by acid solids

→ Esterification of short-chain acids

with glycerol (by-product from current transesterification of triglyceride)



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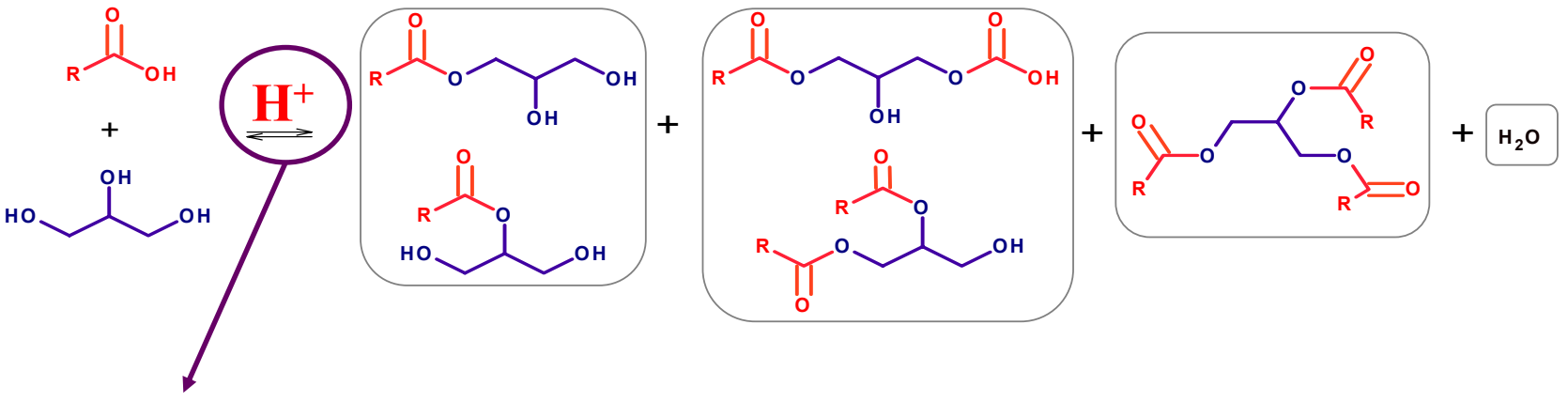
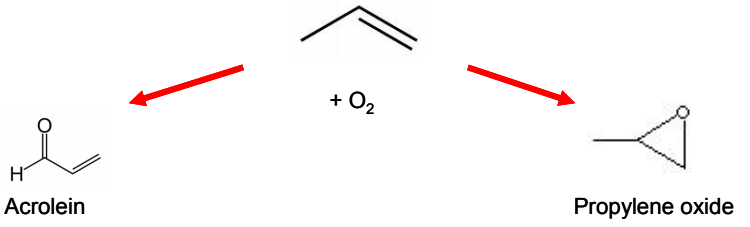


→ Solid acids : modified zirconia, etc → resistance to leaching + selectivity !

Partial oxidation (epoxidation) of C_3=

Working with MoO_3/silica-alumina :

which are the parameters
allowing to direct the tendency of
the catalyst to favor one of the two routes ?



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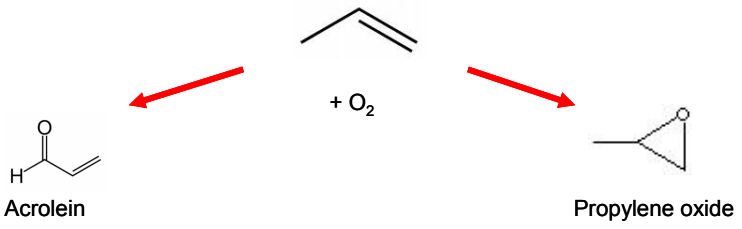

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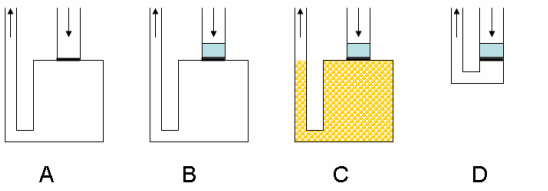

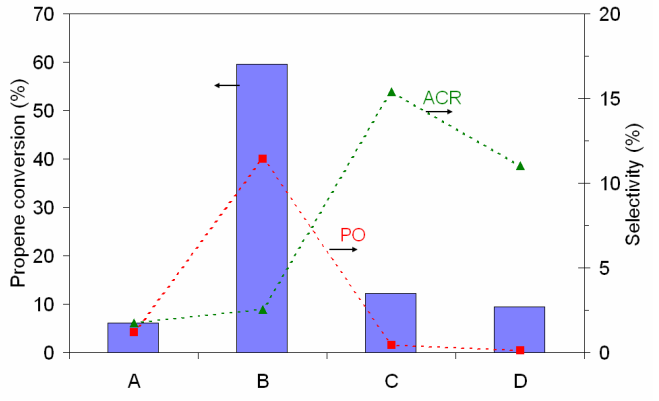

The type of reactor and its filling
is one … which are the others :
Mo precursor, source of oxygen, temperature, dopants ?

Expertise of the
Unité de catalyse et chimie des matériaux divisés (CATA)
in the field of
Catalytic abatement of air pollutants

Eurokin

February 12th 2009, LLN

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Unité de catalyse et chimie des matériaux divisés

Université catholique de Louvain - Belgium

Period 1993 → 2004

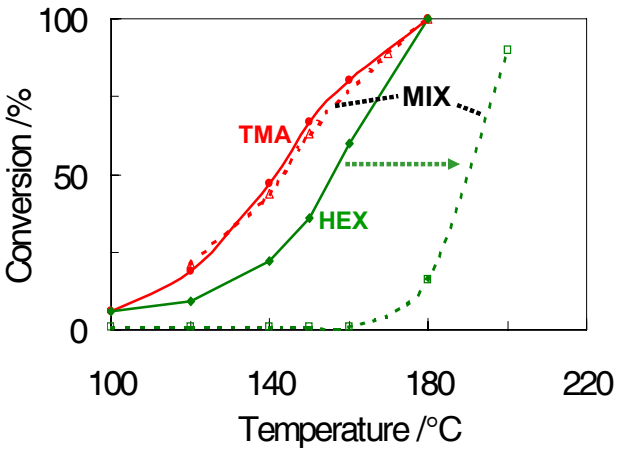
All kinds of air pollutants were considered :

methane

NO_x and SO_x

amines (trimethylamine)
thiols (methylthiol)
linear alcanes (n-hexane)
aromatics (benzene)
esters
O_3

Abatement of a mix of
TMA – 250 ppm
HEX – 125 ppm on MnO_2



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methane

NO_x and SO_x

amines (trimethylamine)
thiols (methylthiol)
linear alcanes (n-hexane)
aromatics (benzene)
esters
O_3

→ Excellent solutions were always found :

→ Perovskites
→ Pd/Al_2O_3
→ (Cu, Sm) doped zeolites
→ V_2O_5/TiO_2 + zeolites

→ Bulk MnO_2

Period 1993 → 2004

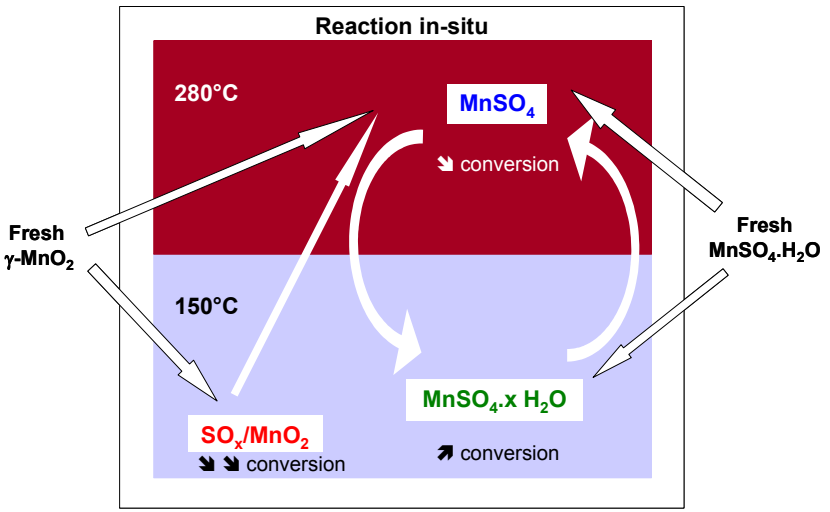
Projects starting from fundamental questions :

e.g. identifying the active Mn species in methylthiol abatement

→ how to activate MnO_2 properly for this reaction

& Projects with
a very applied objective
e.g. development of a
mobile prototype
machine for abatement
of VOCs in confined air

(→ Spinoff project)



Cellier C. et al, J. Phys. Chem. B, 108 (2004) 9989.

Period 2002 → now

Period 1993-2004

= all kinds of « difficult pollutants » but one kind …

→ chlorinated ones

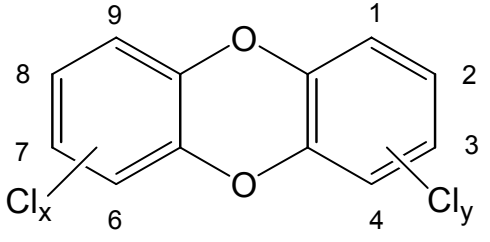
while Cl is a known poison in catalysis !!!

Period 2002 → now

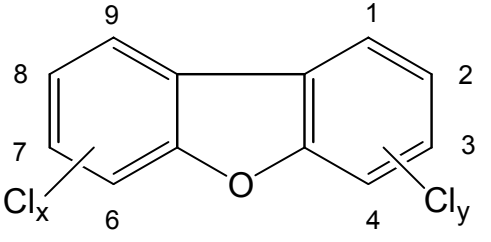
Period 1993-2004
= all kinds of « difficult pollutants » but one kind …
→ chlorinated ones
while Cl is a known poison in catalysis !!!

→ Period 2002 → now
= Cl-containing air pollutants : final target = "dioxin"

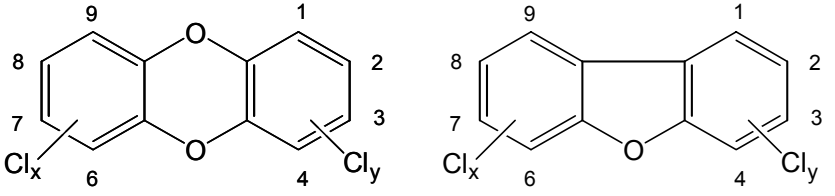
PCDD
(polychlorodibenzodioxins)

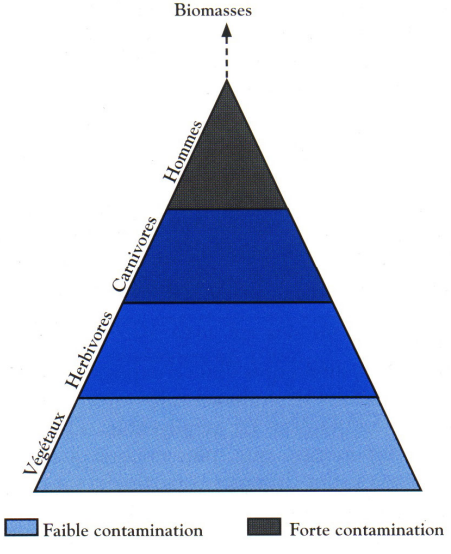


PCDF
(polychlorodibenzofurans)



Period 2002 → now : dioxins



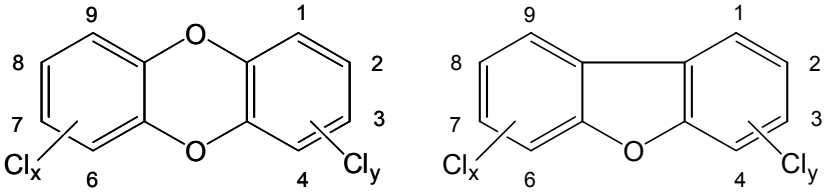


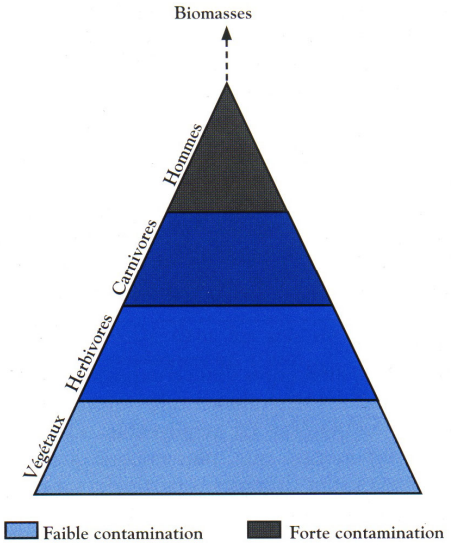
→ Dioxins are persistant pollutants
that accumulate in the fats of
superior organisms

→ are often formed
during incineration of biomass

→ Currently, trapped on active carbon
then stored ? → risk of leaching !?

Period 2002 → now : dioxins





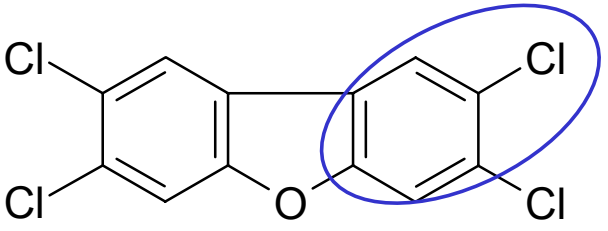
→ Dioxins are persistant pollutants
that accumulate in the fats of
superior organisms

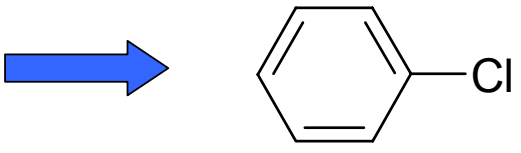
→ are often formed
during incineration of biomass

→ Currently, trapped on active carbon
then stored ? → risk of leaching !?

→ Catalytic abatement of dioxins
via total oxidation

Model molecules for dioxins



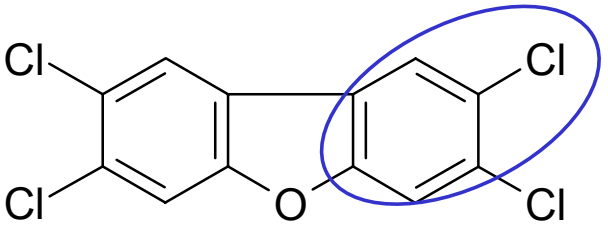


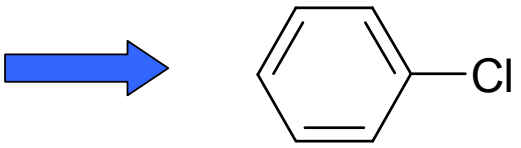
Cl-VOC model = Cl-benzene

→ MnO_2 indeed deactivates quickly
→ Noble metal catalysts produce more toxic polychlorobenzene

→ V_2O_5/TiO_2 catalysts were efficient

Model molecules for dioxins





Cl-VOC model = Cl-benzene

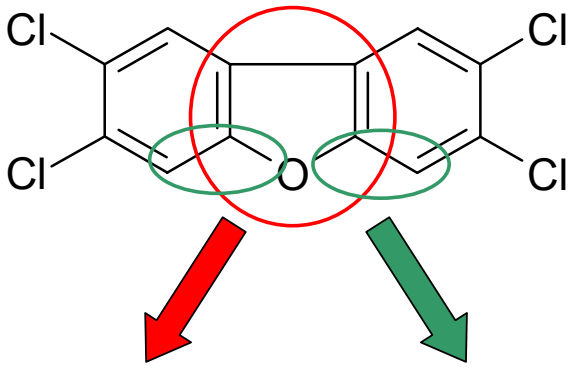
→ MnO_2 indeed deactivates quickly
→ Noble metal catalysts produce more toxic polychlorobenzene

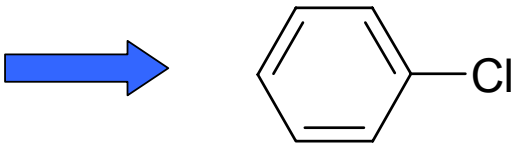
→ V_2O_5/TiO_2 catalysts were efficient but we improved them + sulfation
+ MoO_3 or WO_3
+ work with NO_2
+ Ag or Au

100 ppm of Cl-benzene
in 20% of oxygen
37.000 h^{-1}

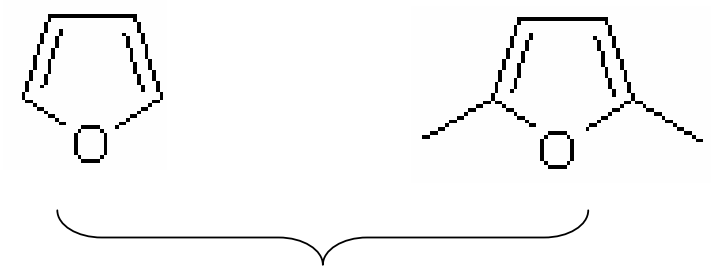
completely
eliminated at 200°C

New model molecules for dioxins





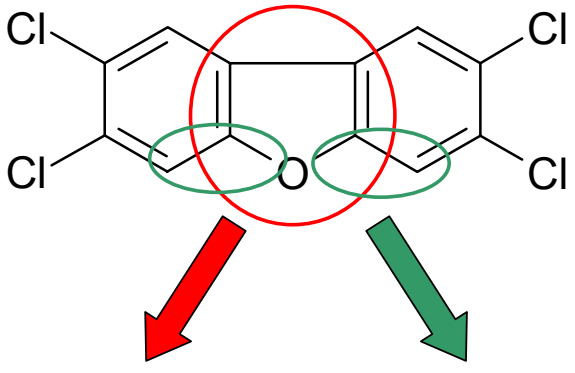
Cl-VOC model = Cl-benzene

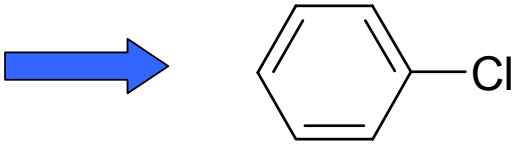


What about the impact of the central oxygenated rings on the catalysis ?
→ adsorption ? coking ? else ?

→ Necessity to study ALSO O-VOC models
→ furane & di-Me-furane

New model molecules for dioxins





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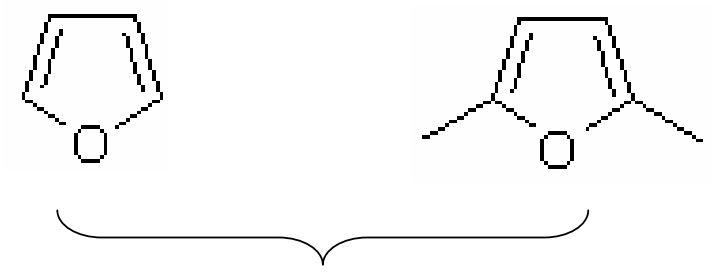

Never really done before !!!

What about the impact of the central oxygenated rings on the catalysis ?
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→ furane & di-Me-furane

Université catholique de Louvain UCL
Unité de catalyse et chimie des matériaux divisés

Relevance of oxygen-containing VOC as model molecule for the study of dioxin total oxidation on VO_x/TiO_2 catalysts

5th International Congress on Environmental Catalysis

Sept 3rd 2008, Belfast

R. Delaigle, D.P. Debecker and E.M. Gaigneaux

Unité de catalyse et chimie des matériaux divisés

Université catholique de Louvain - Belgium

Strategy

Question 1 : Are V_2O_5/TiO_2 catalysts **efficient** in the abatement of O-VOC?

➔ Test on classical V_2O_5/TiO_2 catalysts with the O-VOC models

Question 2 : Are the **"improved"** catalysts also better in the oxidation of O-VOC?

➔ Test on Mo and W-doped formulations
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Question 3 : Which function (Cl or O) wins the intermolecular **competition**?

➔ Competition tests between O-VOC model and Cl-VOC model

Experimental conditions

- Catalysts synthesis

  ➔ Wet impregnation : 0.75 theoretical monolayer of VO_x
  (eventually + 0.75 TML of MoO_x or WO_x)

- Catalytic tests

  ➔ 200 mg of catalyst (200µm< Ø <315µm)

  ➔ 200 ml/min of gas (VVH = 37000 h^{-1}):

  - 100 ppm (vol) of chlorobenzene or 2,5-diMe-furan or 150 ppm (vol) of furan
  - 20% of O_2
  - He as diluting gas

  } VOC conditions

  ➔ Catalyst tested from 100 to 400°C in step mode

  ➔ Catalyst stabilized during 150min at each T°

  } Light-off approach

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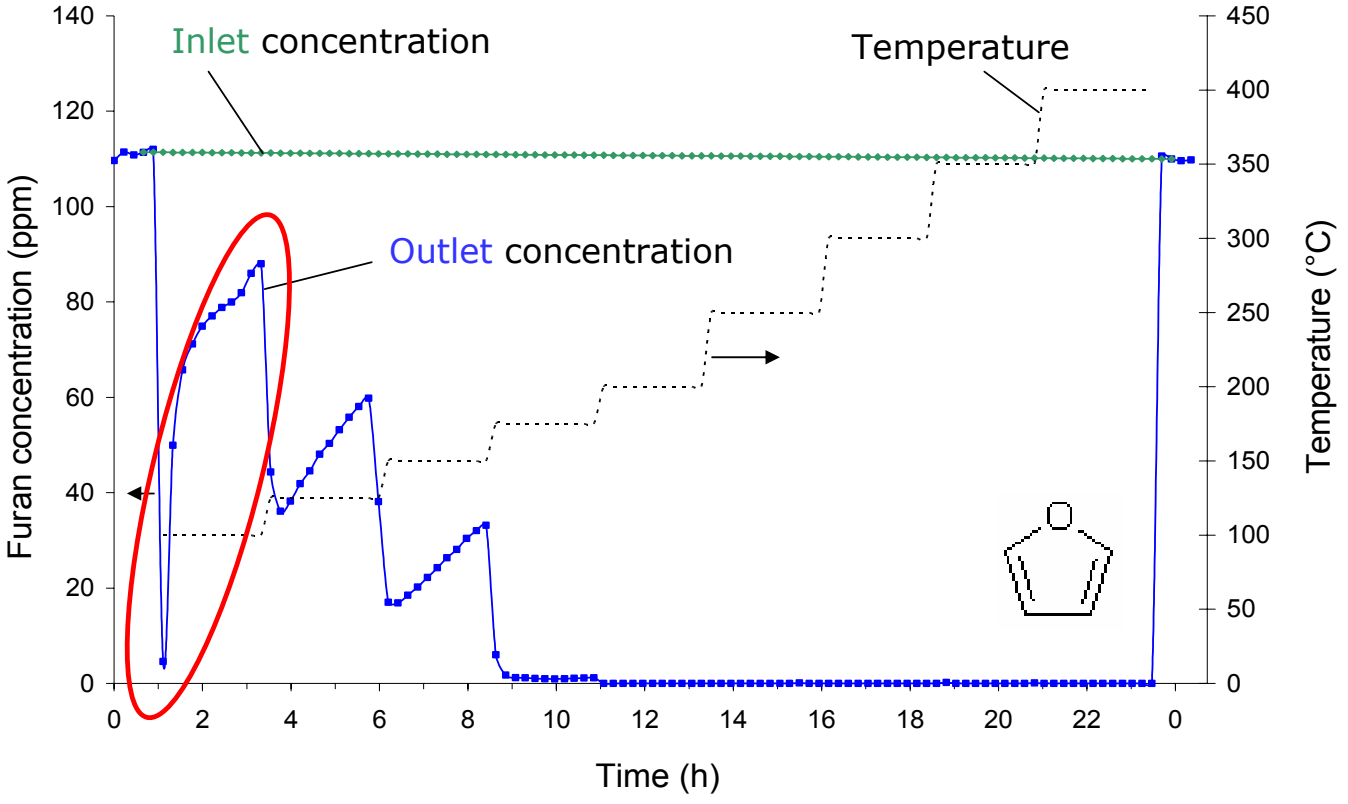

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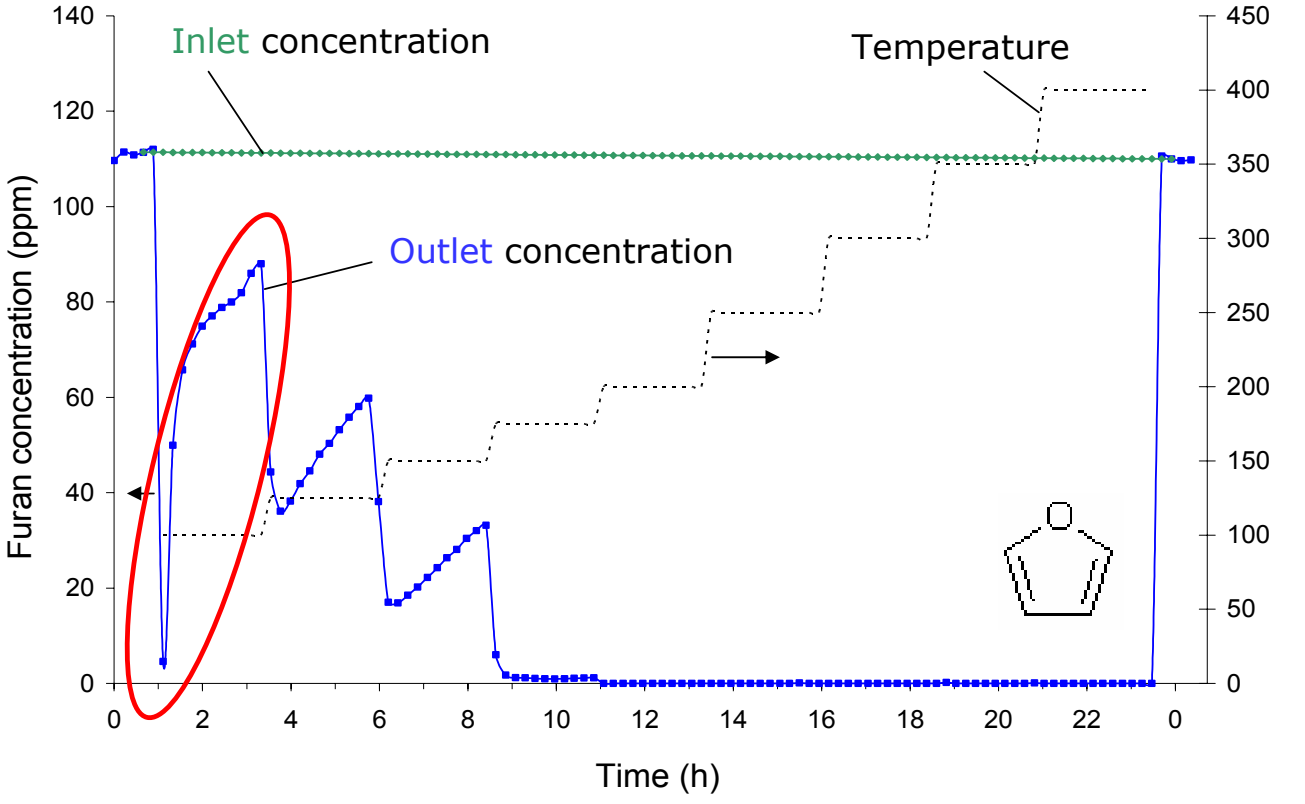


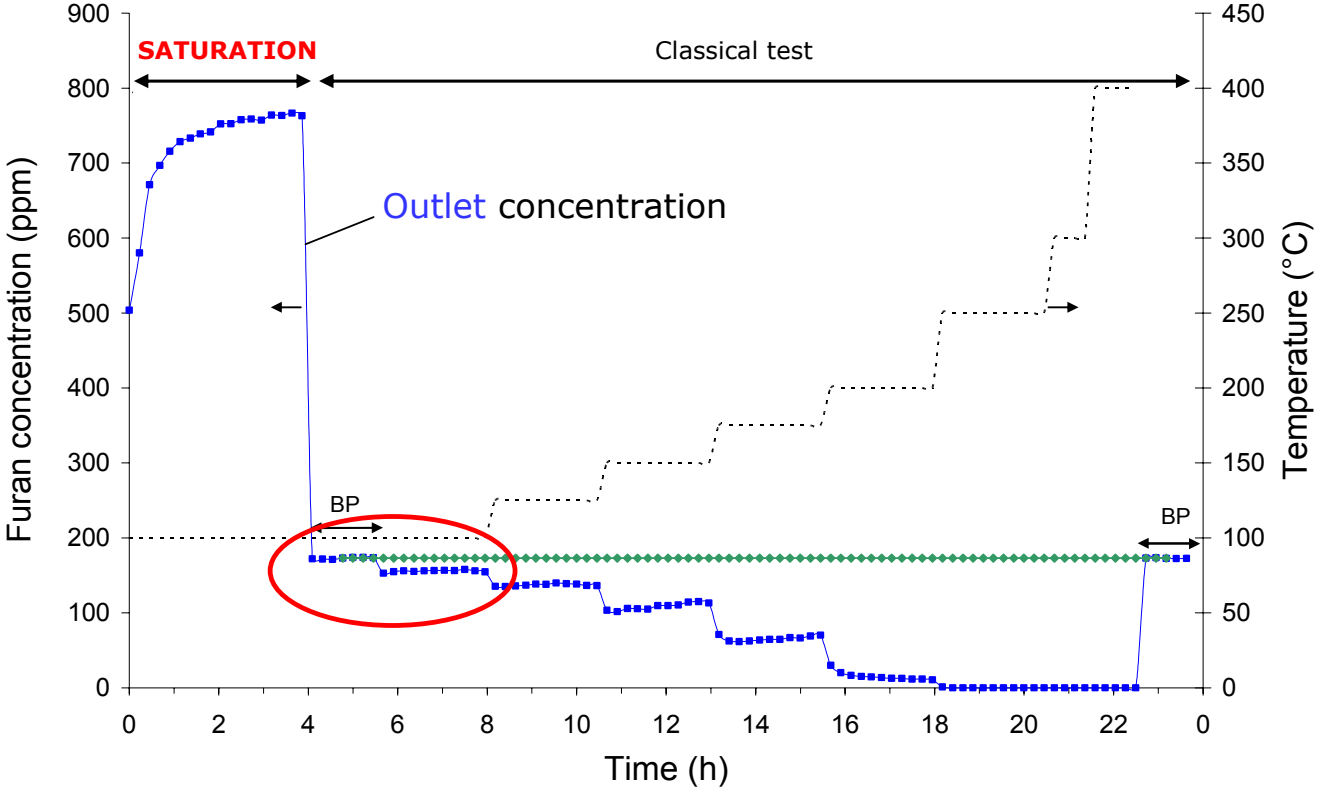
Instability

⬇

Not exploitable

➔ Strong adsorption ?

Are V_2O_5/TiO_2 catalysts **efficient** in the abatement of O-VOC?



Good
- Stability
- Repeatability

Reliable tests & light-off

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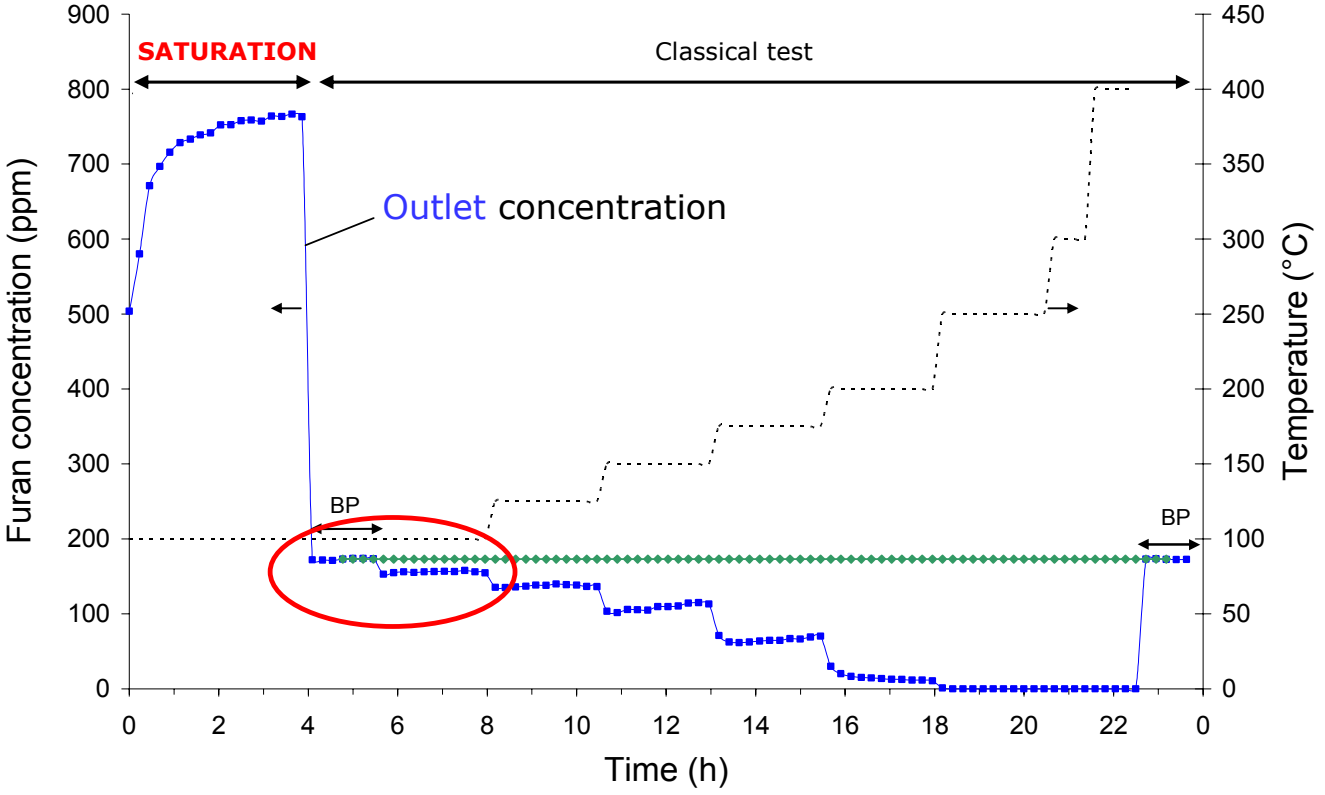


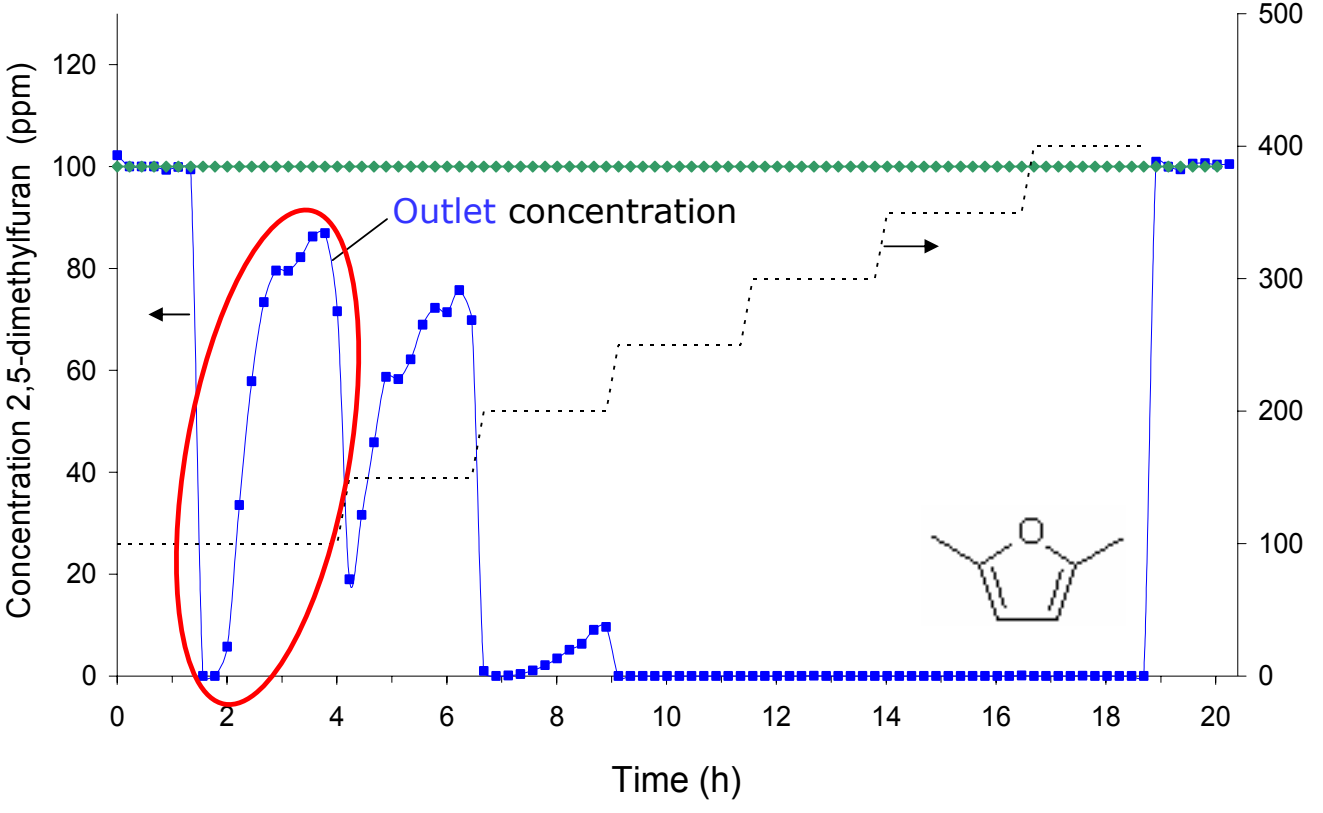
Good
- Stability
- Repeatability

⇓

Reliable tests & light-off

➔ Behaviour due to a strong adsorption of furan on the catalyst

Are V_2O_5/TiO_2 catalysts **efficient** in the abatement of O-VOC?



Instability

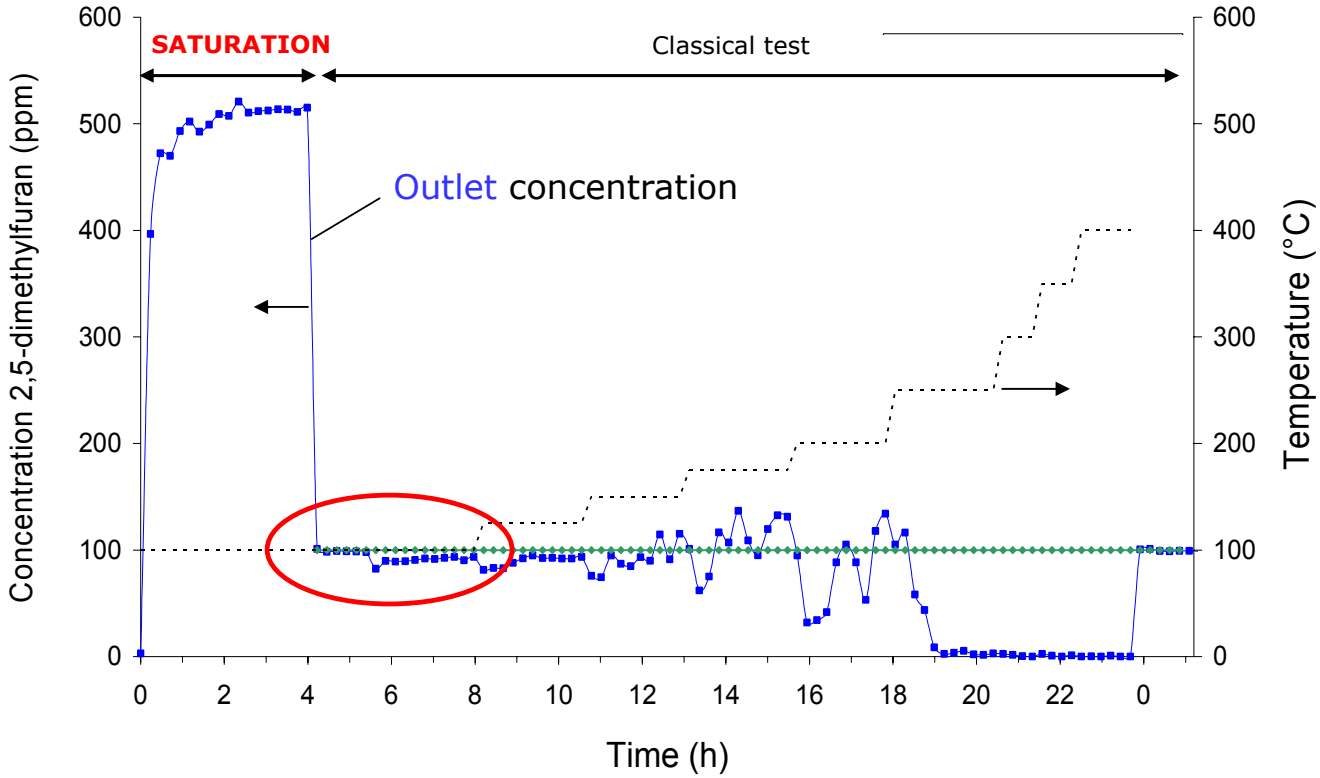
↓

Not exploitable

↓

Same behaviour as furan

Are V_2O_5/TiO_2 catalysts **efficient** in the abatement of O-VOC?



Saturation

↓

Stability

➔ Still strong adsorption although steric hindrance

Are V_2O_5/TiO_2 catalysts **efficient** in the abatement of O-VOC?

Chlorobenzene

↓

Adsorption

is a limiting step

O-VOC

↓

Adsorption

is

strong and easy

↓

Completely opposite behaviour

Are V_2O_5/TiO_2 catalysts **efficient** in the abatement of O-VOC?

Chlorobenzene

- Total oxidation
- No selective oxidation

O-VOC

- Total oxidation
- Some selective oxidation → production of maleic anhydride

V_2O_5/TiO_2 catalysts are also efficient in the abatement of O-VOC

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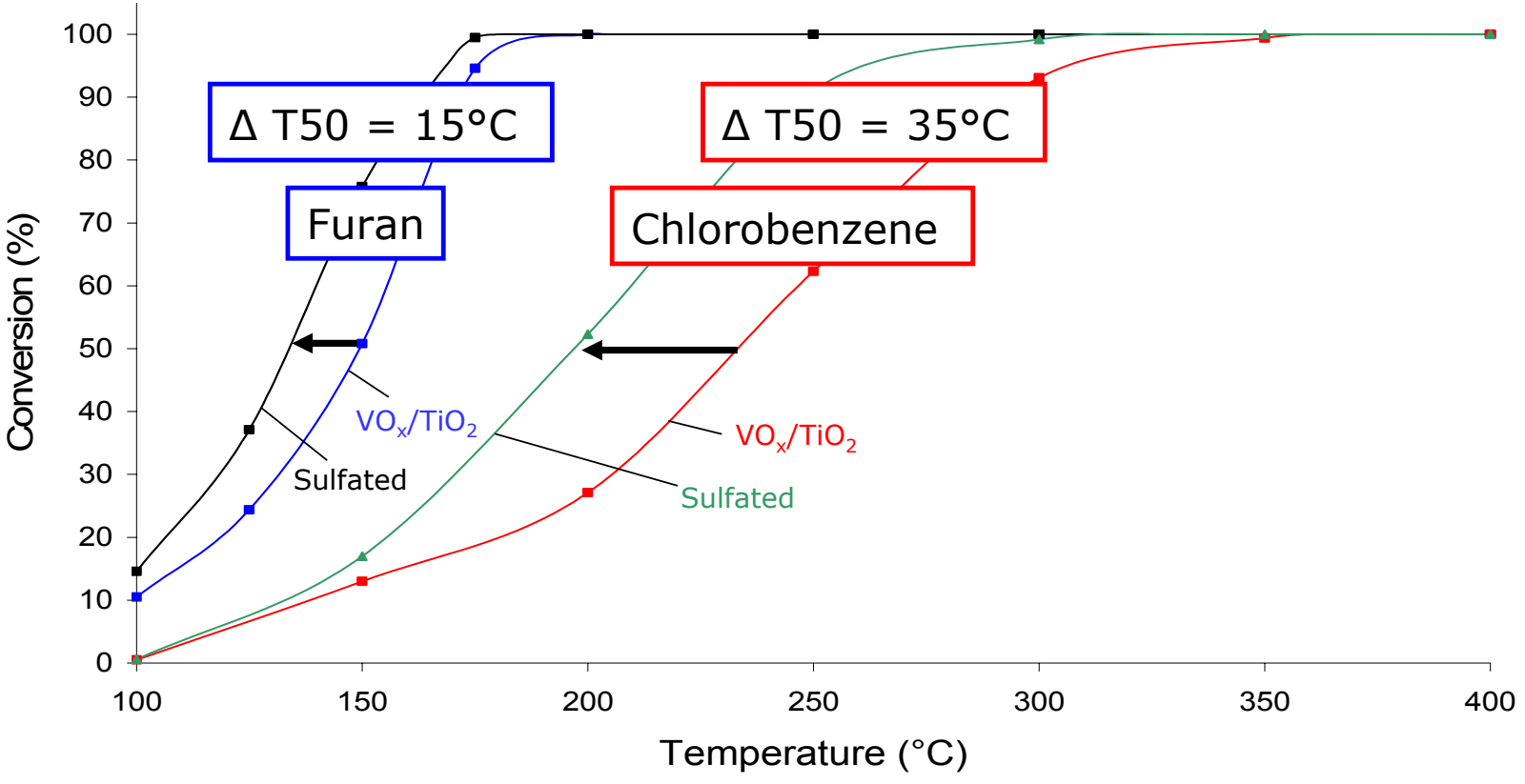
Are the "**improved**" catalysts also better in the oxidation of O-VOC? → sulfation of the support



Are the "**improved**" catalysts also better in the oxidation of O-VOC? → sulfation of the support

Higher activity for catalysts supported on sulfated support

➔ Sulfated TiO_2 promotes the spreading of the impregnated phases
➔ Well spread oxides show more acidic sites

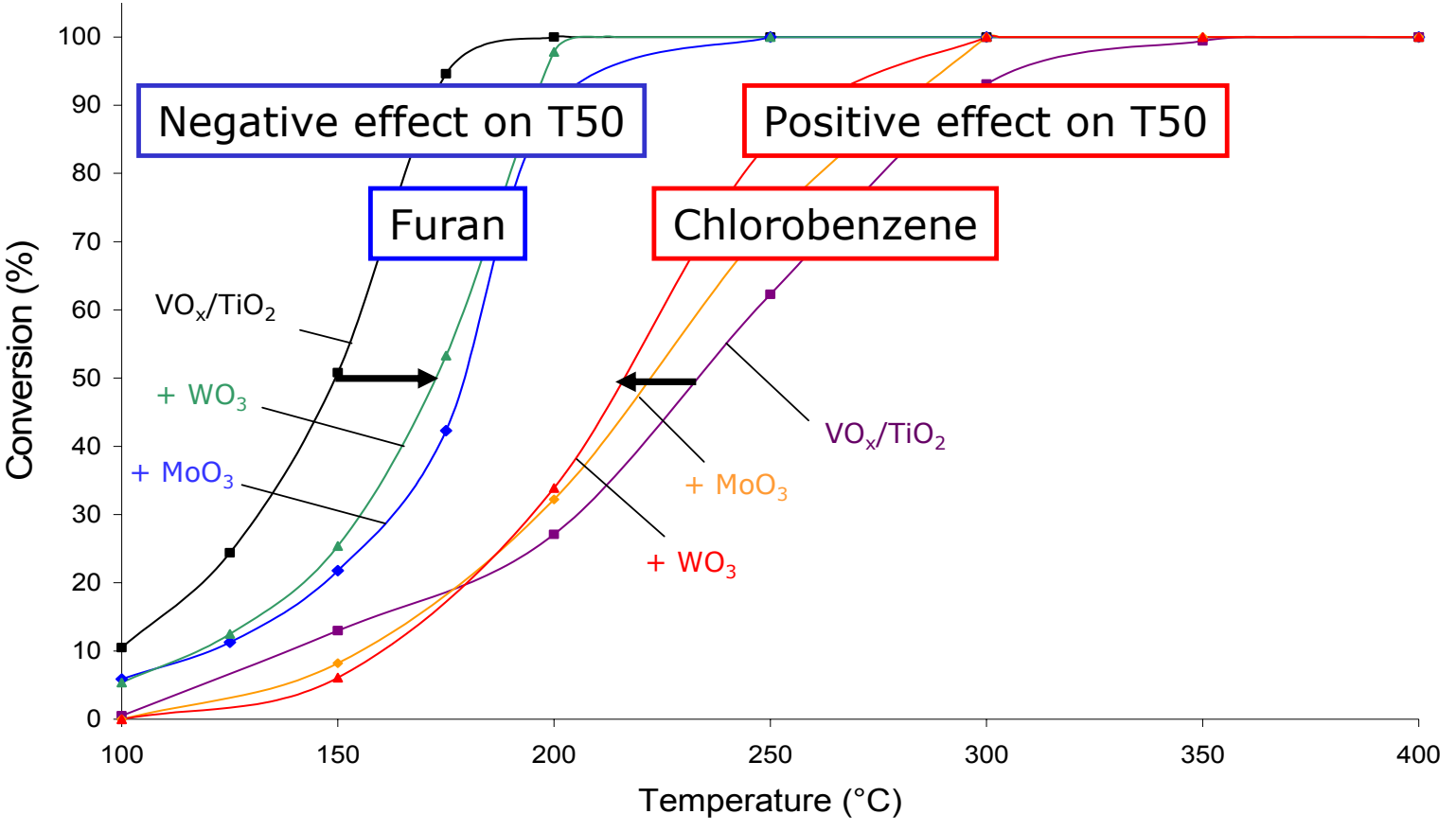
Chlorobenzene :
More acidic sites ➔ easier adsorption

Effect of the sulfated support
=
Facilitation of the adsorption step

O-VOC :
Adsorption is easy whatever the number of acidic sites

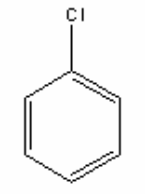
No effect of the support sulfation

Are the "**improved**" catalysts also better in the oxidation of O-VOC? → Mo or W doping

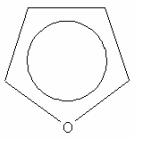


Are the "**improved**" catalysts also better in the oxidation of O-VOC? → Mo or W doping

Lower activity for catalysts with a secondary phase



MoO_3 and WO_3



\- Are NOT good catalysts for VOC total oxidation -

\- Prevent complete spreading of the vanadium phase -

\+ + + Bring Brönsted acidic sites (facilitating adsorption) 0

Doping effect of secondary phase

No doping effect
Negative effect !

Are the "**improved**" catalysts also better in the oxidation of O-VOC?

Chlorobenzene

- Positive effect of the sulphated support
- Positive effect of the secondary phase

O-VOC

- No effect of the sulfated support
- Negative effect related to the secondary phase

Improvements of the catalysts proposed from Cl-benzene are not efficient in the oxidation of O-VOC

↓

Embarrassing !?

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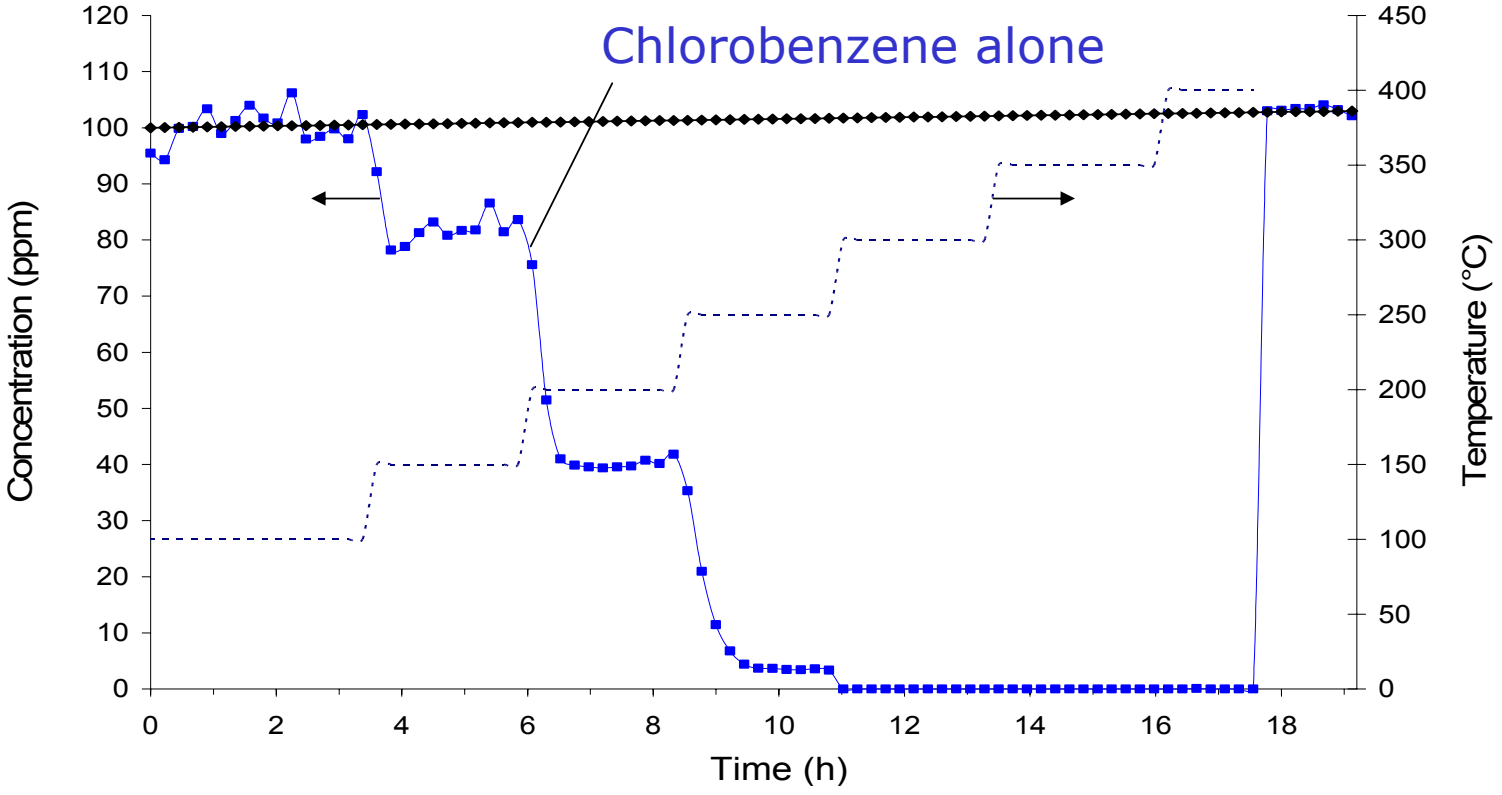
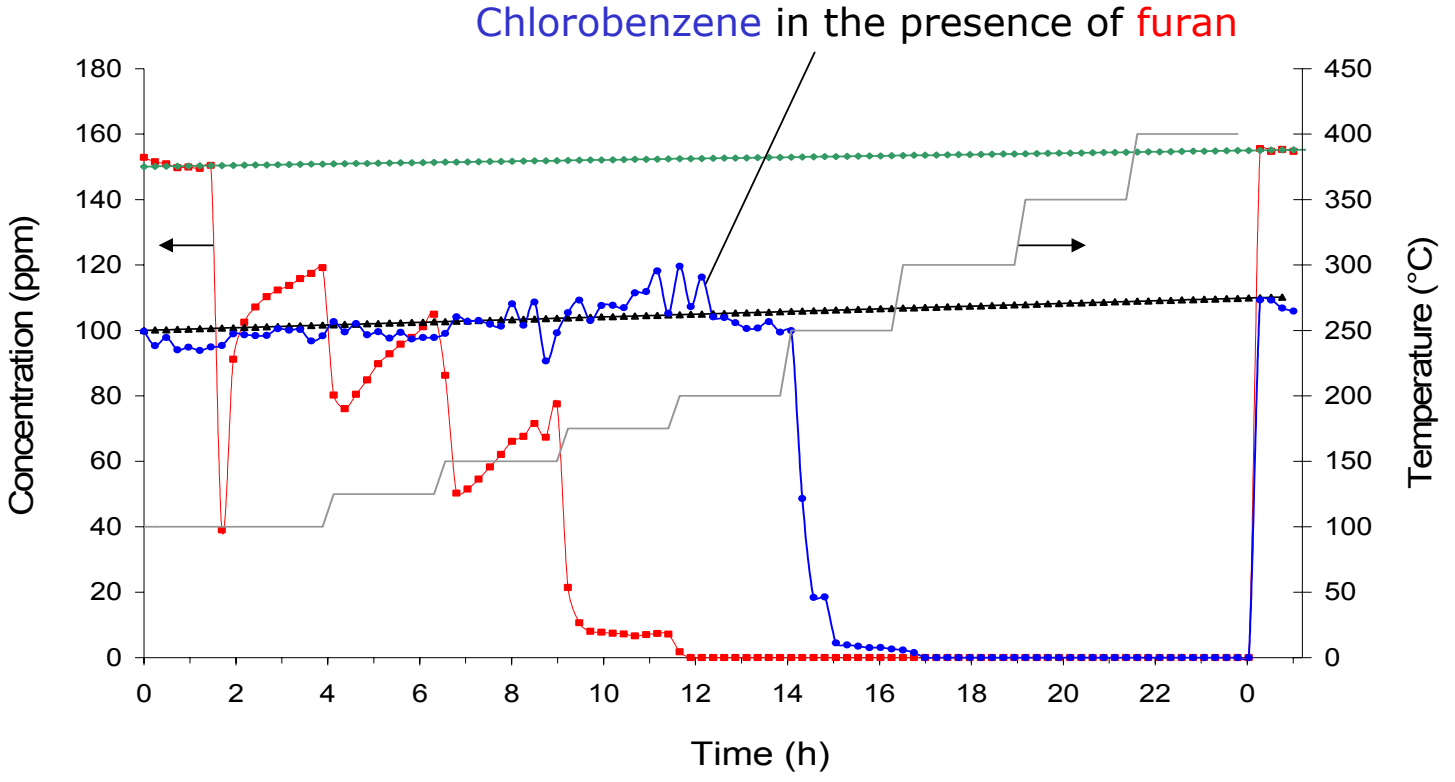


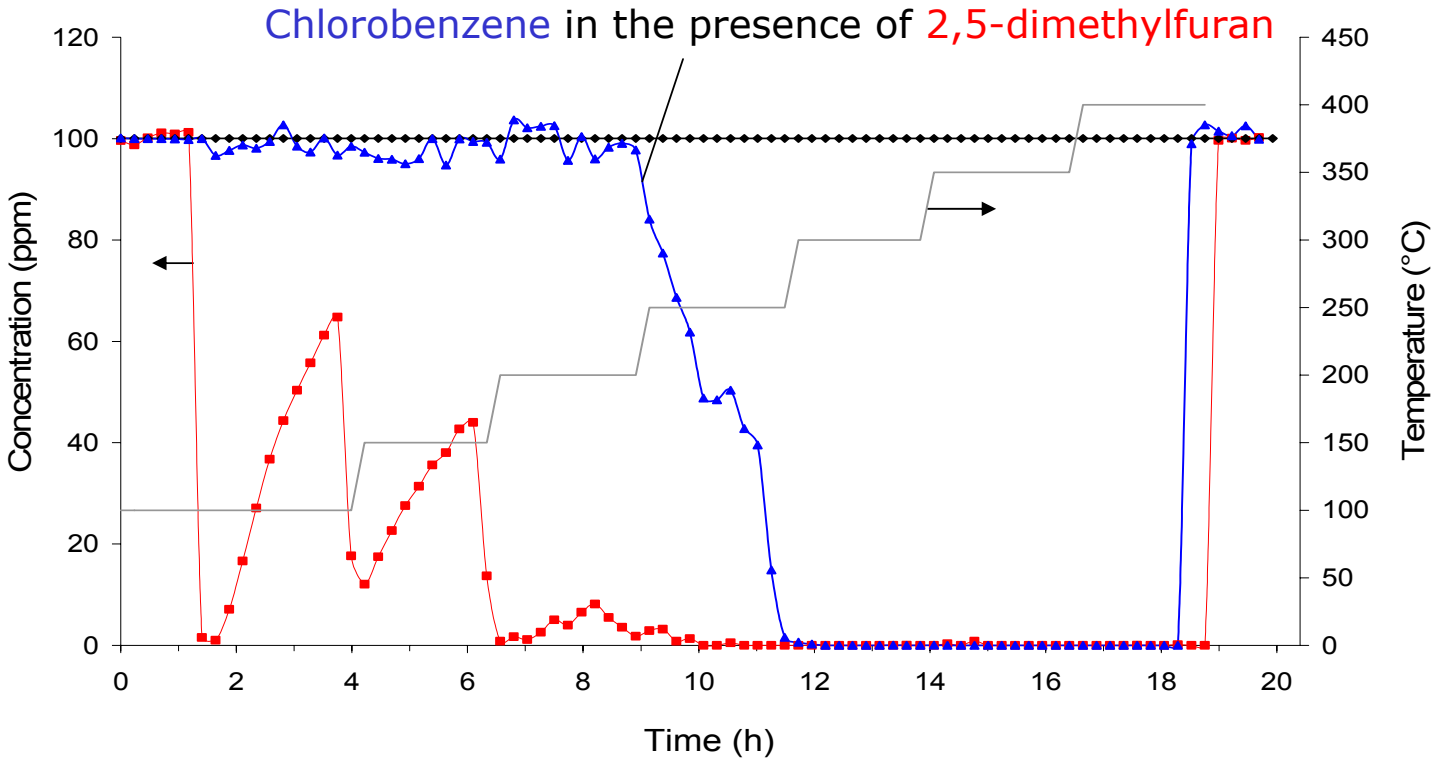
Conversion starts between 100 and 150°C

Which function (Cl or O) wins the intermolecular **competition** ?



Chlorobenzene conversion only starts
after furan conversion has reached 100% (→ 250°C)

Which function (Cl or O) wins the intermolecular **competition** ?



Chlorobenzene conversion only starts
after 2,5-dimethylfuran conversion has reached 100% (→ 250°C)

Which function (Cl or O) wins the intermolecular **competition** ?

The conversion of chlorobenzene is dramatically impeded in the presence of O-VOC

➔ O-VOC adsorption occurs on the same sites as chlorobenzene oxidation

➔ The surface of a saturated catalyst must be cleaned before we observe the "usual" level of conversion for chlorobenzene

➔ The oxygenated function wins the intermolecular competition against the chlorinated function (due to an easier adsorption)

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The conversion of chlorobenzene is dramatically impeded in the presence of O-VOC

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- ➔ The surface of a saturated catalyst must be cleaned before we observe the "usual" level of conversion for chlorobenzene
- ➔ The oxygenated function wins the intermolecular competition against the chlorinated function (due to an easier adsorption)

The oxygenated function will also win the intramolecular competition and thus will induce an easy beneficial adsorption of the full dioxin molecule

Conclusion

- The O-moiety dictates decisively the nature of the pollutant-to-catalyst interaction

- The use of Cl-VOC models is not fully relevant

  guidelines to improve formulations for Cl-benzene may be not beneficial (or even detrimental) for O-VOCs abatement (thus for full dioxin)

- Importance of this information for further studies

Acknowledgments :

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FAME noe

Belgian Science Policy

INANOMAT

RÉGION WALLONNE