Equipe Chimie et Ingénierie des Procédés

Industrial and indoor air treatment by catalytic oxidation over an innovative support coming from recycled glass wastes

Audrey Cabrol[a] - Antoine Lejeune[a] – Pierre-François Biard[b] – Annabelle Couvert[b] – Audrey Denicourt[b] – Alain Roucoux[b] – Ronan Lebullenger[c]

[a] SATT Ouest Valorisation – 35708 Rennes Cedex, France
[b] Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France
[c] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France

OUEST VALORISATION

audrey.cabrol@ouest-valorisation.fr
antoine.lejeune@ouest-valorisation.fr

20/06/2018 – Atmos'fair – Paris

UNIVERSITE BRETAGNE LOIRE — UNIVERSITÉ DE RENNES 1 — cnrs — Ecole Nationale Supérieure de Chimie de Rennes — INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES RENNES

Context of the study

- Air pollution is a major health concern

- Main focus on VOCs (Volatile Organic Compounds) removal
  - → toxic for human health
  - → disturb the chemical balance in the atmosphere

- More and more stringent laws about the decrease in VOCs' emissions
  - → - 43% emissions for 2020
  - → - 52% emissions for 2030

- 2 targeted fields
  - → industrial air treatment
  - → indoor air treatment

OUEST VALORISATION

Context of the study

- Various processes are used to eliminate VOCs

  → recovery processes (adsorption, condensation, physical scrubbing, etc.)

  → destroying processes (biodegradation, chemical scrubbing, **catalytic oxidation**, etc.)

- Among these processes, **catalytic oxidation** has good performances for the treatment of complex mixtures and/or low concentrated pollutants

- Catalytic oxidation needs a catalyst for kinetic improvement

  → increase in production and decrease in reactor volume

  → lower Temperature and Pressure

    → decrease in energy consumption and environmental impact

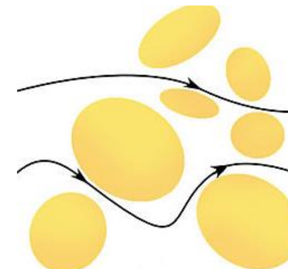
- Use of **heterogeneous catalysts** (easier to recover)

OUEST VALORISATION

Context of the study

❖ Various types of catalysts
- acids
- metal oxides
- **metals : Fe, Co, Ni, Pd, Ru, Rh, Pt…**

❖ Sorption of metals on a porous support → **open cell foams**
→ increase in convection and radial stirring



❖ Different types of foams :
- metal foam (very expensive, need of a Al_2O_3 washcoat layer)

- ceramic foam (multi-step synthesis, energy consuming)

- **glass foam → recycling of glass wastes**

→ Goal : development of an original support (glass foam) for air treatment by catalytic oxidation using O_3 and O_2 as oxidants

Outline

1) Glass foam synthesis

2) Impregnation of metals on the glass foams

3) Use of impregnated glass foams in catalytic oxidation for VOCs removal

Glass foam synthesis

- Use of crushed glass coming from **recycling (circular economy)**
  - glass bottles
  - screens
  - industrial glass wastes…

- Addition of foaming agents (AlN, MnO_2) and doping agents (TiO_2, Fe_2O_3)

- Heating at T around 900°C during 30 min – 4 h

$$3\,TiO_2 + 4\,AlN \xrightarrow{T\approx 900°C} 2\,Al_2O_3 + 3\,TiN + \boxed{0.5\,N_2 \nearrow}$$

Creation of gas bubbles which trigger the porous structure of the glass foam

Properties of the glass foams

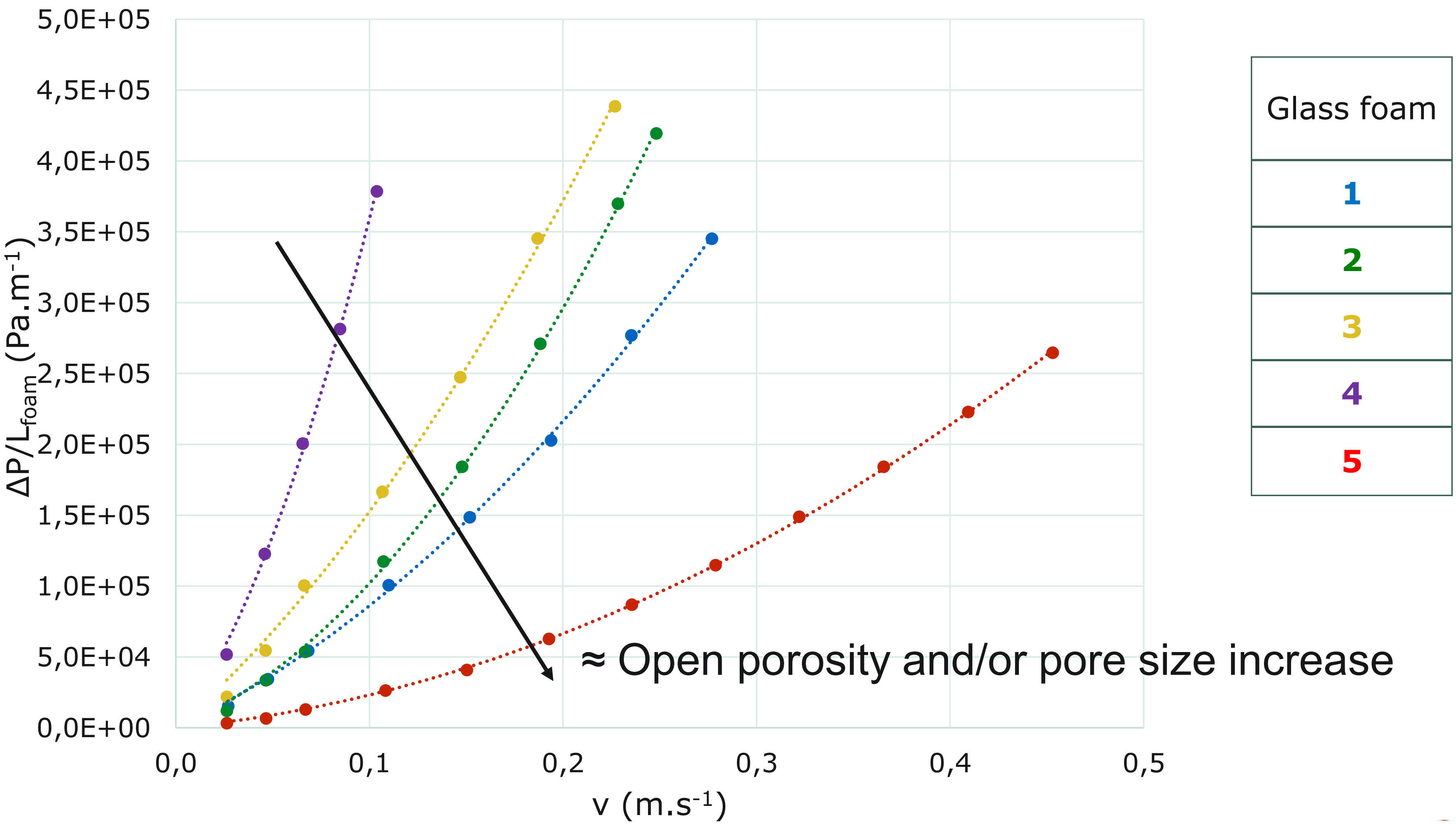
- Different properties depending on the quantity and type of foaming/doping agents

Glass foam	Look of the glass foam	$d_{p\ average}$ (mm)	Open porosity (%)	Contact angle (°)
1		0.199	90	76
2		0.331	90	74
3		0.186	73	-
4		0.109	77	47
5		0.427	92	76

OUEST VALORISATION

Properties of the glass foams

❖ Linear pressure drop in function of the speed of air circulation



Properties of the glass foams

❖ Influence of operating conditions during the synthesis

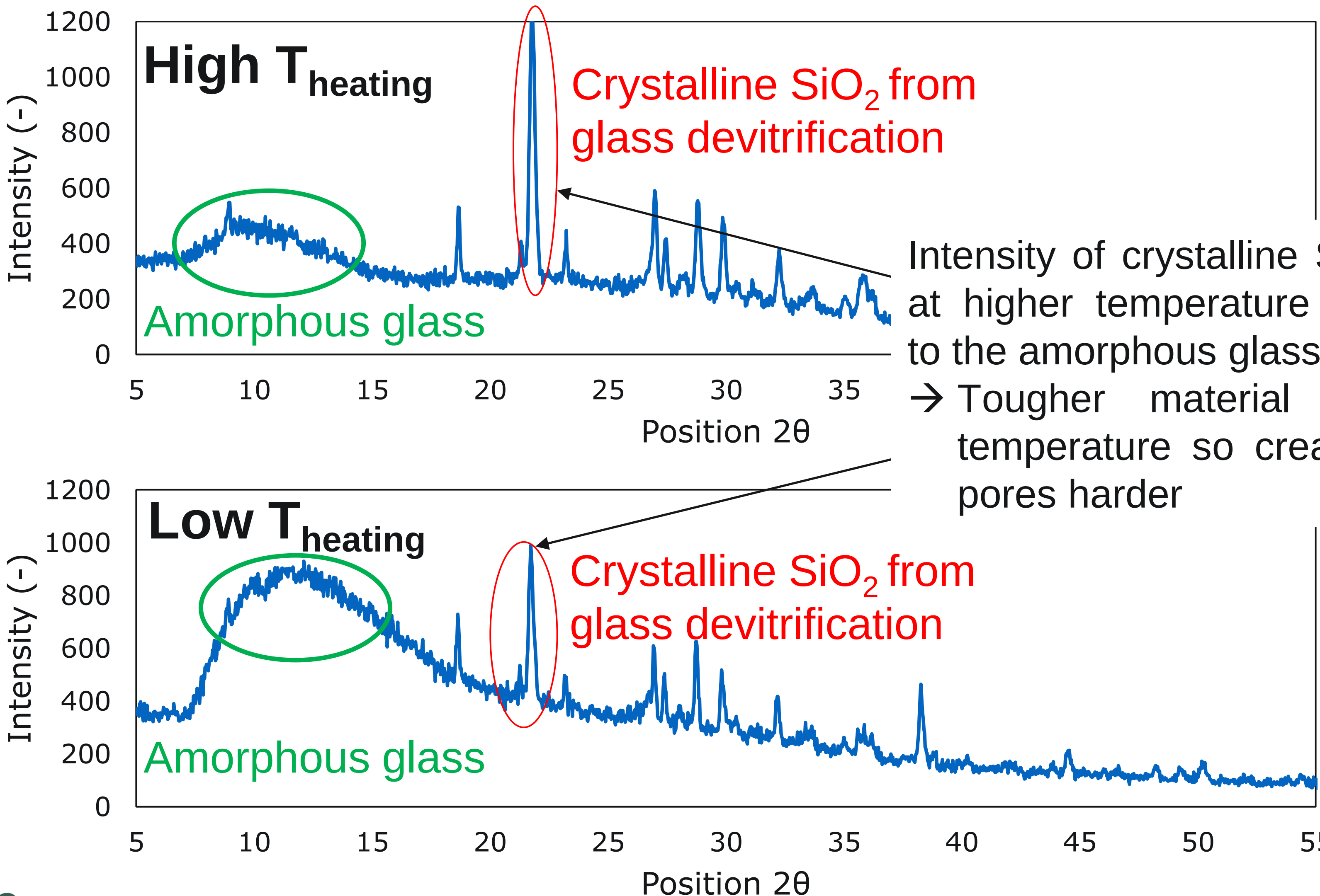
Base case :

- Granulometry of the glass : <100µm
- $T_{heating}$ around 900°C
- $t_{heating}$ between 30min - 4h

	Average pore diameter dp	**Open porosity**	**Linear pressure drop**
$T_{heating}$ decreases	↗	=	↘

Properties of the glass foams

❖ X-Ray diffraction analysis of glass foam #4



Intensity of crystalline SiO_2 higher at higher temperature (compared to the amorphous glass)

→ Tougher material at higher temperature so creation of big pores harder

Properties of the glass foams

❖ Influence of operating conditions during the synthesis

Base case :

- Granulometry of the glass : <100µm
- $T_{heating}$ around 900°C
- $t_{heating}$ between 30min - 4h

	Average pore diameter dp	Open porosity	Linear pressure drop
$T_{heating}$ decreases	↗	=	↘
$t_{heating}$ increases	↗	=	↘
Granulometry increases	↘	↘	↗

→ Modular properties of the glass foams depending on the composition and operating conditions during the synthesis

Comparison with other foams

Type of foam	Synthesis	$d_{p\ average}$ (mm)	Open porosity (%)	Linear pressure drop at 0.1 $m.s^{-1}$
Glass foam	**Eco-friendly** (recycling of glass) and **cheap** (few steps and energy)	0.1 – 1.0	73 - 93	< 250-1500 $Pa.m^{-1}$ for the « best foams »
Al_2O_3 ceramic foam from Vesuvius Inc.	**Multi-step synthesis** (complex) and **energy consuming** (1,500°C)	1.529*	75**	204*
		1.582*	85**	440*
Metal foam (stainless steel) from Glatt GmbH	**Expensive material**, need a **washcoat layer** (Al_2O_3)	0.802*	95**	231*

* Mass transfer and pressure drop in ceramic foams: A description for different pore sizes and porosities, Incera Garrido et al., 2008, Chemical Engineering Science
** Manufacturer data

→ glass foams as support of metals are competitive with ceramic and metal foams

OUEST VALORISATION

Outline

1) Glass foam synthesis

2) Impregnation of metals on the glass foams

3) Use of impregnated glass foams in catalytic oxidation for VOCs removal

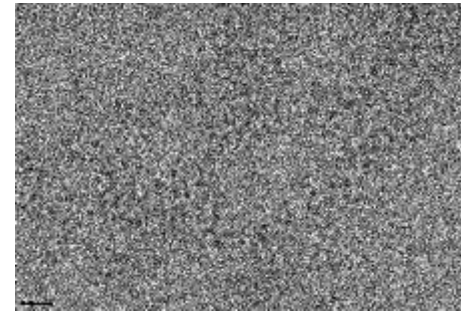
Impregnation of metal catalysts on the glass foam

❖ Synthesis of metal Nanoparticles (NPs)

→ use of various metals (Rh, Ru, Pt, Au…)

→ NPs of 2-5 nm

→ high specific area and lot of active sites



Reduction of the metal salt

Metal salt in **water**

Ex: $RuCl_3$

Room temperature
Atmospheric pressure

→

Surfactant
+ $NaBH_4$

NPs

Impregnation of NPs on the glass foam by immersion*

→ easy and reproducible impregnation method with a low amount of metal (≈0.1 %)

* METAL NANOPARTICLES SUPPORTED ON A GLASS-FOAM SUBSTRATE AND USES FOR THE CATALYSIS OF CHEMICAL REACTIONS, WIPO Patent Application WO/2017/064418

Impregnation of metal catalysts on the glass foam

- Successfull deposits of Rh, Ru, Au, Pd
  - drying in an oven
  - without washcoat

Before impregnation

After impregnation with Ru NPs

Outline

1) Glass foam synthesis

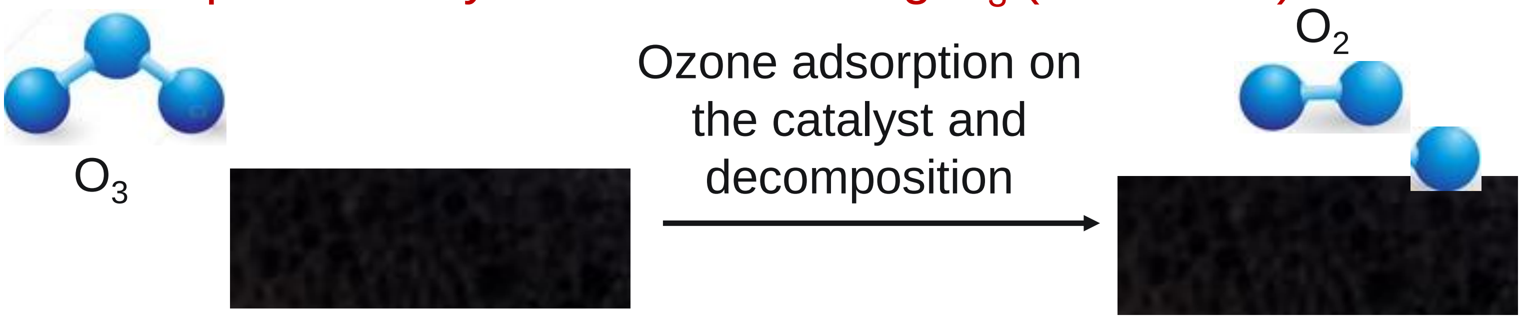
2) Impregnation of metals on the glass foams

3) Use of impregnated glass foams in catalytic oxidation for VOCs removal

OUEST VALORISATION

Performances of the impregnated glass foams in catalytic ozonation

❖ Principle of catalytic ozonation using O_3 (ambient T)



Impregnated glass foam

Active site
→Where the VOCs decomposition will take place

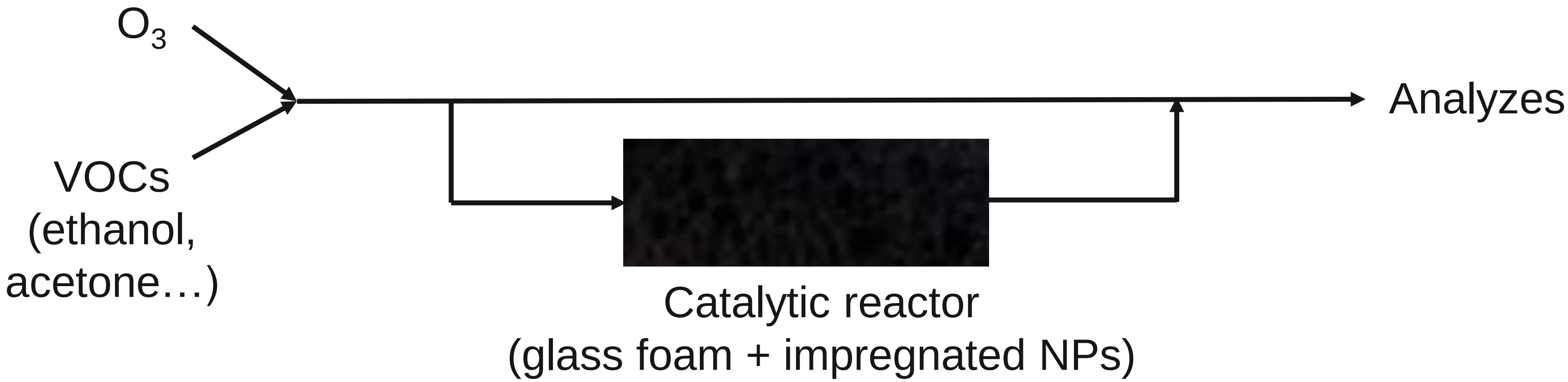
❖ Tests of ozone decomposition at room temperature

- first-order kinetic : $\frac{d[O_3]}{dt} = -k_1 * [O_3]$

Glass foam composition	Metal	k_1 (s^{-1})
No glass foam	**No metal**	**$0.064*10^{-3}$**
$AlN + TiO_2$	**Au**	**$6.7*10^{-3}$**
$AlN + TiO_2$	**Rh**	**$2.3*10^{-3}$**
$AlN + TiO_2$	**Pd**	**$1.2*10^{-3}$**
$AlN + TiO_2$	**Ru**	**$7.0*10^{-3}$**
$AlN + TiO_2 + MnO_2$	**Ru**	**$42.0*10^{-3}$**

Performances of the impregnated glass foams in catalytic ozonation

❖ Tests of VOCs removal at room temperature with a continuous reactor



Glass foam composition	Metal	Acetone removal	Ethanol removal
$AlN + TiO_2$	**Ru**	**30 %**	**75%**

Operating conditions :

- **Low gas superficial velocity → need to improve the mass transfer**
- 13.5 $g.Nm^{-3}$ of ozone at the input of the reactor
- Residence time : 30 secondes

Conclusion and prospect

- ❖ Development of the synthesis of an innovative catalytic material from recycled glass wastes

  → glass foams with modular properties (porosity, pore size, hydrophilicity…) synthesised from recycling glass wastes

  → easy to do NPs solution, various metals can be used, low amount of metal (≈0.1%)

- ❖ Impregnated glass foams are active in catalytic ozonation to remove a lot of VOCs (acetone, ethanol…) for industrial air treatment

- ❖ Other tries in catalytic ozonation are in progress in order to optimize material properties

- ❖ Tests with O_2 as oxidant (250°C ≤ T ≤ 350°C) are in progress for indoor air treatment

OUEST VALORISATION

Equipe Chimie et Ingénierie des Procédés

Industrial and indoor air treatment by catalytic oxidation over an innovative support coming from recycled glass wastes

Audrey Cabrol[a] - Antoine Lejeune[a] – Pierre-François Biard[b] – Annabelle Couvert[b] – Audrey Denicourt[b] – Alain Roucoux[b] – Ronan Lebullenger[c]

[a] SATT Ouest Valorisation – 35708 Rennes Cedex, France
[b] Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France
[c] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France

OUEST VALORISATION

audrey.cabrol@ouest-valorisation.fr
antoine.lejeune@ouest-valorisation.fr

20/06/2018 – Atmos'fair – Paris

UNIVERSITE BRETAGNE LOIRE — UNIVERSITÉ DE RENNES 1 — CNRS — Ecole Nationale Supérieure de Chimie de Rennes — INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES RENNES