Incorporation of Catalytic Compounds in the Porosity of SiC Wall Flow Filters – 4 Way Catalyst and DeNOx Application examples

DEER MEETING
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Jean-Pierre JOULIN  CTI
Bruno CARTOIXA  CTI
Didier TOURNIGANT  CTI
Arnold LAMBERT  IFP
Jean-Christophe RUIZ  CEA
Anne JULBE  IEM

CERAMIQUES TECHNIQUES ET INDUSTRIELLES S.A.
La Resclause - Route de Saint Privat F 30340 SALINDRES - FRANCE
E-mail: ctisa@ctisa.fr Site internet: www.ctisa.fr
Phone: +33 466 858 870 Fax: +33 466 857 009
• Short CTI presentation

• Introduction
  – Why to concentrate in one or two components all the exhaust gas containing HC, CO, NOx and PM

• Exploration of 3 different methods of catalyst impregnation inside the pore of a SiC DPF
  – Supercritical CO₂ method
  – Sol Gel impregnation
  – Incorporation of catalyst with the slurry forcing method

• Zeolith impregnation of SiC DPF for DeNOx function using SCR method

• Conclusions
CTI is specialized in perfecting the design of a wide range of technical ceramics often porous, whose applications are mainly in environment, filtration, catalysis fields and SOFC.

These include:

- **Liquids filtration**: membranes supports in ultra and micro filtration.
- **Gas and particles filtration**: tubular, flat, honeycomb, foam filtration carriers, **diesel particulate filter**.
- **Catalysts supports**: pellets with high specific area, honeycombs, smooth and grooved porous rings.
- **Liquid metals filtration**: honeycombs and foams refractories.
- **Special refractories**: withstanding temperatures higher than 1600°C.
- **Special ceramic washcoast for COx, DeNOx, VOC treatment and SOFC applications**.
Factory area: 6 000 m²
Laboratory and pilot area: 1 000 m²

Scientific manager: JP. JOULIN
Adm. & Financial Manager: N. DELBIANCO
Dr in Catalysis & membranes: E. LOURADOUR D. TOURNIGANT
4 Ceramic engineers: L. ESPIN B. CARTOIXA F. PEY G. GAUDRY
Quality insurance: S. ENJOLRAS
10 Technicians & laboratory people

Created: 8th of march 1990
Independent SME, French Institute Of Petrol as Share holder
Capital: 220 000 €
Numbers of employees: 75

Industrial and laboratory equipment:
mixers (1 to 1200Kg), extrusion press (1 to 400L), high frequency and microwave dryers, gas and electric kilns (0.4 to 10m³ until 1700°C), laboratory equipment, ...
Membrane materials and design for High temperature applications (> 500°C)

Inert porous supports (mainly for filtration):
\[ \text{Al}_2\text{O}_3, \text{SiO}_2, \text{TiO}_2, \text{SiC}, \text{ZrO}_2, \text{Y}_2\text{O}_3\ldots \]

Geometry design
Honeycomb, flat, tubular, granules, foams, tablets, washcoat, membrane

Active materials (for catalysis)
\[ \text{CeO}_2/\text{ZrO}_2 \]
\[ \text{CeO}_2/\text{Al}_2\text{O}_3/\text{Pt}, \text{CeO}_2/\text{Gd zeolites}, \text{ZnO}, \text{V}_2\text{O}_5 \]
Perovskites (LSM), ….
INTRODUCTION

HC, CO, NOx, PM
Vehicle's environmental progress

Diesel emissions reduction legislation trends in Europe

Fiat courtesy

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CURRENTLY DPF SYSTEM + DeNOx TRAP

Exhaust-gas treatment of the Vision GL320 BlueTec

- Oxidizing catalytic converter
- Particulate filter
- AdBlue metering valve
- BlueTec
- SCR catalytic converter

Exhaust-gas treatment of the E320 BlueTec

- Oxidizing catalytic converter
- Advanced DeNOx catalytic converter
- Particulate filter
- SCR catalytic converter
- BlueTec
<table>
<thead>
<tr>
<th>SYSTEMS</th>
<th>PROCESS</th>
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<tbody>
<tr>
<td>Catalysed DPF</td>
<td>- Soot Oxidations with NO₂ with or without catalysis</td>
</tr>
<tr>
<td></td>
<td>[Diagram: Catalyzed DPF system]</td>
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<tr>
<td>SCRT System (JM)</td>
<td>- Soot Oxidations with NO₂ + PM → CO₂ + N₂</td>
</tr>
<tr>
<td></td>
<td>- Catalytic reduction of NOₓ</td>
</tr>
<tr>
<td></td>
<td>[Diagram: SCRT System (JM)]</td>
</tr>
<tr>
<td>DPNR System (Toyota)</td>
<td>4 WAY CATALYSIS</td>
</tr>
<tr>
<td></td>
<td>[Diagram: DPNR System (Toyota)]</td>
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</tbody>
</table>
4-WAY CATALYSIS: eliminate HC, CO, NOx and PM with a single treatment device

Catalytic phase impregnation + NOx deep trapping within the pores of the filtering support

- Favor the NOx trapping and the oxidative catalysis in terms of volume (high $S_{BET}$) together with the important function of absolute particles filtering (no thick covering of the surface that would desactivate the catalyst and blocks the NOx trapping).

- Favor the synergy effect between NOx trapping and particles oxidation

Interest of nanophased materials:

- Homogeneous materials, finely divided with high $S_{BET}$

- Specific properties (surface activity highly increased)
CTI has developed a new composite SiC DPF able to be easily catalysed. The catalyst is impregnated inside the porosity of wall flow:

- Porosity of the CTI SiC DPF is around 46% and pore size around 17/19 µ.

- The great advantage of CTI’SiC composite product is to be already treated against all the oxidation attacks and so to preserve the catalyst performance during ageing.
Since 2003 CTI has explored 3 different ways of catalysis impregnation:

- $\text{CO}_2$ supercritical impregnation with CEA (Pierrelatte, Atomic Energy Center)
- Sol gel impregnation with IEM Montpellier (European Institute of membrane)
- Forced slurry method with IFP (French Petroleum Institute) (patented)
SEM PHOTO OF A CTI’S DIESEL PARTICULATE FILTER (DPF)

Soot Deposit configuration before regeneration
SUPERCRITICAL CO$_2$ METHOD

with collaboration of CEA Pierrelatte - 2004
Phase diagram of supercritical CO₂

Pressure

Solid

7,4 MPa

Liquid

Critical point

Supercritical CO₂

Gaz

Triple point

304,1 K

Temperature
Particularity: The synthesis and macroporous support impregnation was carried out in a single step, in a 1 litre high-pressure vessel. After introducing a specific amount of selected catalyst formulation in the autoclave containing the monolith, the liquid CO$_2$ was pumped into the vessel up to the operating pressure of 30 MPa. The reaction temperature was regulated at 573 K using an external electric heater. The contact time of the reactants in SC CO$_2$ was 1 hour.
RESULTS - SEM - SiC and Cordierite analysis

**thickness of the active layer after 2 impregnations**

Sol composition: Alumina - Zirconia - Ceria - Baryum oxyde
SOL GEL IMPREGNATION

with collaboration of IEM Montpellier
CERAMICS GRIT IMPREGNATED WITH NANOPHASE CATALYST (350 nm layer) ON HONEYCOMB FILTER 1/2

Sol gel composition Alumina, Ceria, Zirconia, Baryum oxide

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CERAMICS GRIT IMPREGNATED WITH NANOPHASE
CATALYST (350 nm layer) ON HONEYCOMB FILTER 2/2

Number of coatings vs. Weight increase (%)

- SiC3092
- SiC1891
MULTI IMPREGNATION RESULTS

* Layer thickness is around 2µ after deposition
* Cracks can appear up to 4 layers
INCORPORATION OF CATALYST WITH THE SLURRY FORCING METHOD

with collaboration of IFP (French Petroleum Institute)
Incorporation of a NOx-trap type catalytic formulation inside the porosity of a SiC wall flow filter (WFF) has been performed, forcing a slurry of the catalyst through the substrate.
SLURRY PREPARATION

NOx trap formulation:
Precious metal Pt, Pd, Rh
Catalyst oxide: BaO - CeO\textsubscript{2} - ZrO\textsubscript{2} - Al\textsubscript{2}O\textsubscript{3}

Adjust the viscosity and particle size distribution
• fluid enough
• $D_{v90}/D_{pores} < 0.25$

$D_{v90}$: measured by laser diffraction
$D_{pores}$: mean pore size of the WFF, measured by Hg porosimetry
SiC cores characteristics:
1" diameter, 3" length, 180 cpsi,
20 µm mean pore diameter,
55% porosity
SEM pictures of a core loaded with 159 g/l catalyst

- Washcoat inside the porosity
- Whole SiC surface coated
  - Thickness 1 to 8 µm
**SCALE UP**

- 5"66 diameter, 6" length, 180cpsi, 19 µm mean pore diameter, 50% porosity

- Washcoat loading: 190 g/l
- Washcoat-induced pressure drop: 15 mbar (50000 h⁻¹)

Scale up succeeded:
- High loading
- Low pressure drop
Pressure drop as a function of washcoat loading

Synthetic gas bench testing of deNOx activity

• Low pressure drop at high loading
• DeNOx activity comparable to that of flow through monoliths
CONCLUSIONS OF IFP/CTI METHOD

• Versatile method to deposit any type of catalytic formulation inside the porosity of wall flow filters
• Method has been scaled up to real size filter
• Key point resides in adapting the slurry's particle size distribution to the mean pore size of the substrate.
FIRST QUALITATIVE CATALYSIS RESULT FOR NOx CONVERSION COMPARISON OF THE DIFFERENT METHODS

Temperature (°C)

Conversion NOx (%)

- 180 g/L
- sol gel route 60g/L
- Supercritical CO$_2$ route 48 g/L

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Zeolith impregnation of CTI SiC DPF for DeNOx function using SCR method.
### Impregnation

<table>
<thead>
<tr>
<th>N° Filter CTI</th>
<th>CTI 039/06</th>
<th>CTI 031/06</th>
<th>CTI 033/06</th>
</tr>
</thead>
<tbody>
<tr>
<td>N° Filter IFP</td>
<td>EC89</td>
<td>EC90</td>
<td></td>
</tr>
<tr>
<td>Mass before impregnation (g)</td>
<td>1817</td>
<td>1877</td>
<td>1811</td>
</tr>
<tr>
<td>Mass after impregnation + Calcination IFP (g)</td>
<td>2156.4</td>
<td>2059.5</td>
<td>Non calcined</td>
</tr>
<tr>
<td>Mass after impregnation + Calcination CTI 500°C/2h00 (g)</td>
<td></td>
<td>2048.2</td>
<td>Impregnated</td>
</tr>
<tr>
<td>Masse addes cata in g</td>
<td>339.4</td>
<td>171.2</td>
<td></td>
</tr>
<tr>
<td>Volume of the filter in liter</td>
<td>2.47</td>
<td>2.50</td>
<td>2.47</td>
</tr>
<tr>
<td>Content cata in g/liter</td>
<td>137.41</td>
<td>68.48</td>
<td>0</td>
</tr>
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</table>

ΔP - mb

<table>
<thead>
<tr>
<th>Stream of air co-current to the direction of impregnation</th>
<th>Flow 100 m³/h</th>
<th>Flow 200 m³/h</th>
<th>Flow 300 m³/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow 100 m³/h</td>
<td>7</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Flow 200 m³/h</td>
<td>16</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>Flow 300 m³/h</td>
<td>27</td>
<td>21</td>
<td>16</td>
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<th>Stream of air against the current of the direction of impregnation</th>
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<tr>
<td>Flow 100 m³/h</td>
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<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Flow 200 m³/h</td>
<td>15</td>
<td>13</td>
<td>9</td>
</tr>
<tr>
<td>Flow 300 m³/h</td>
<td>26</td>
<td>22</td>
<td>16</td>
</tr>
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</table>
PHOTO OF THE CTI’S DPF AFTER IMPREGNATION
Total zeolith deposition is inside the pore. There is no layer at the surface. Porous cavity of the support are sometimes plugged by the zeolith depending on the concentration.
Excellent catalyst penetration with partial plugging of some pores, depending of the slurry concentration.

20/12/2006
B. Cartoixa
$\Delta P = f(\text{wt}\% \text{ cata avec flux d'air à contre-courant de l'imprégnation})$
$\Delta P = f$ (débit d'air à contre-courant de l'imprégnation)
MOTOR BENCH TEST FOR ZEOLITH DeNOx DPF Content 137 g/l
NOx EMISSION BEFORE AND AFTER DPF

- sans injection
- injection d'air
- injection air + injection d'Urée
- injection d'air
- sans injection d'air

- émissions amont FAP
- dilution
- émissions aval FAP
- rétention + dilution

NOx (ppm)

Time (s)
REAL AND RELATIVE EFFICIENCY

DPF NOx efficiency \(((\text{NOx amont} - \text{NOx aval})/\text{NOx amont})\)
DELTA P EVOLUTION OF THE DPF

Graph showing the evolution of Delta P (mbar) over time (s) for two different cases labeled VVH 30000 and VVH 66000.
PM EFFICIENCY OF THE PARTICULATE FILTER
(test made by IFP)

The CTI product when it is virgin (worst condition) is 3 to 4 time below the upper limit requested for Euro V in 2009 (SMPS test done by IFP).

**PM / MVEG Cycle**

**EURO 5**

- **CTI 20µg/Km**
- **CTI 15µg/Km**
- **CTI asymmetric shape**

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CONCLUSIONS

• The 3 different impregnation methods show a real industrial potential for 4 way catalysis technology or separatively CatOx + DPF DeNOx function.

• Today the most easy and cheapest method seems to be the slurry forcing technology (Patent IFP – CTI)

• CTI’s composite SiC product could be easily impregnated with catalyst with very low increase of back pressure.
This work has been done with the financial support of the:

French Research Ministry Predit VP008 convention 04K133 From june 2004 until june 2007 (Cti - Peugeot -Irma –Faurecia- Le moteur moderne Eft )

FSH (Fonds de soutien hydrocarbure) from 2001 until 2004 (A50004/01 – A59009/01) (IFP –CTI)
CERAMIQUES TECHNIQUES ET INDUSTRIELLES S.A.

THANK YOU FOR YOUR ATTENTION

CERAMICS MANUFACTURER AS ENVIRONMENTALLY FRIENDLY MATERIALS

C.T.I. S.A. La Resclause - Route de Saint Privat F 30340 SALINDRES - FRANCE
E-mail: ctisa@ctisa.fr Site internet: www.ctisa.fr
☎: +33 (0) 4 66 85 88 70 Fax: +33 (0) 4 66 85 70 09

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