Emission catalysts

Dr Teuvo Maunula, Dinex Finland Oy
4.2.2019
Introduction of emission catalysts in automotive (mobile) and industrial (stationary) applications
- Emission sources, pollutants and limits
- Variation of solutions by applications
- Automotive catalyst converter structures
- Catalysts and reactions in gasoline and diesel applications
- Complete catalytic Aftertreatment Systems (ATS)
- Challenges in use conditions
- Durability and deactivation
- Research methods in emission catalyst development
- Recent and future trends
Introduction of speaker

Teuvo Maunula:
- M.Sc. and Dr in Technology at Aalto University
- Doctor thesis about NO$_x$ reduction catalyst, reaction mechanism and kinetics
- Development of Industrial emission catalysts since 1985 in Ahlström Oy (2 years) and Dinex Finland (1987-), R&D Fellow
- Docent in Environmental catalysis and reaction engineering at Aalto University (2016)
Emission catalyst development and manufacture in Finland

- Emission catalyst development started in year 1983 from the first ideas in Kemira – since 1985 laboratory and pilot facilities and a development group
- The bases for commercial emission catalyst concepts and systems were created in Catalyst development group, which operated 1985-2016 (31 years) in Oulu (max. number of persons ~30) – Commercial production since 1988
- Dinex Finland (since 7/2018), former Dinex Ecocat, Ecocat and Kemira Metalkat has been a part of Danish-based Dinex Group since 2013
- Dinex Global Catalyst Competence Centre (GCCC) and product management groups were created in 2016 to concentrate the catalyst, pilot and engine laboratories and application engineering in a Dinex Ecocat plant in Vihtavuori (20 km to Jyväskylä)
- In addition R&D groups in Bindlach Germany and Middelfart Denmark
- Development and manufacture of commercial, full-scale emission catalyst systems is a challenge requiring the knowledge and methods in different fields
Dinex Group

Employees: 1300
Companies: 20
Turnover: 150 M€

Family owned Danish company
CEO Torben Dinesen
Dinex Finland: about 100 employees, 50 M€ turnover
Pollution and pollutants

- Pollution is caused by harmful, man-made materials (pollutant) remaining from the industrial processes, transportation and generation of energy. The pollutant can have also a natural source (Volcanic, animals, soil dust, vegetation).
- **Air pollution** is the contamination of the Earth atmosphere by noxious gases, liquids and particles in harmful concentrations.
- Most relevant primary pollutants into the air are nitrous oxides ($\text{NO}_x$), sulfur oxides ($\text{SO}_x$), carbon monoxide (CO), particulates (PM), methane, volatile organic compounds (VOC/hydrocarbons), toxic metals, chlorofluorocarbons (CFC), ammonia, radioactive compounds.
- Secondary pollutants formed by the reactions of primary pollutants: photochemical smog, ozone/peroxyacetylinitrate (PAN) ($\text{VOC}+\text{NO}_x$)
- Persistent organic pollutants (POPs) are resistant to degradation.
- **Water pollution**: the contamination of oceans, lakes, river and ground water.
- Noise control is also a part of environmental protection.
- **Focus on air pollutants and their removal in this lecture**
Greenhouse gases

• A wide concern about Green House Gases (GHG), which absorb and emit radiation within infrared range and cause global warming
• The main GHGs: Water (~50% + clouds 25%), CO₂, methane, N₂O, O₃ and CFCs (toxicity of GHGs varying) → non-condensing as the main environmental concern
• Man-made GHGs: CO₂ is the main but the Global Warming Potential (GWP) of CH₄ (25, after 100 years) and N₂O (298) is much higher (GWP of CO₂ =1)
• CO₂ is a part of carbon cycle → global carbon balance for a product/process (carbon footprint) → alternative energy sources for fossil ones
• Target to minimize the fuel consumption/energy (= CO₂ as g/kWh, g/km, g/product), to cut down CO₂ itself and save raw material consumption
• CO₂ consumption regulated (limits, fuel price, taxes) and a clear decrease per a vehicle during the last 30 years but the total number of vehicles has compensated that saving
→ Emission limits and aftertreatment systems (ATS) for the main air pollutant since 1970s, first in Japan and USA (California).
→ Industry: Integrated pollution prevention/control for air, water, land, waste, energy, noise, accidents
→ Best Available Technics (BAT) /EU
Pollution prevention

Preferably the formation of pollutant emission is prevented

- Primary methods:
  - Process/combustion modification, substitution of hazardous agents

- Secondary methods:
  - Engineering methods, aftertreatment, waste separation/treatment/ storage
Pollution prevention

Preferably the formation of pollutant emission is prevented but methods and effects are opposite to \( \text{NO}_x \) and PM (\( \text{CO}_2 \)) in combustion

**Primary methods:**

- Low \( \text{NO}_x \): Lower temperature and oxygen concentration
- Low PM: Higher temperature and oxygen concentration

→ Optimization

**Question:** Which is causing more emissions, diesel or gasoline car?
EU Emission limits for passenger cars

Emission limits for passenger cars

<table>
<thead>
<tr>
<th>Stage</th>
<th>Date</th>
<th>CO</th>
<th>HC</th>
<th>HC+NOx</th>
<th>NOx</th>
<th>PM</th>
<th>PN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Ignition (Gasoline)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1†</td>
<td>1992.07</td>
<td>2.72</td>
<td>(3.16)</td>
<td>-</td>
<td>0.97</td>
<td>(1.13)</td>
<td>-</td>
</tr>
<tr>
<td>Euro 2</td>
<td>1996.01</td>
<td>2.2</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>2.30</td>
<td>0.20</td>
<td>-</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>1.0</td>
<td>0.10</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Euro 5</td>
<td>2009.09b</td>
<td>1.0</td>
<td>0.10i</td>
<td>-</td>
<td>0.06</td>
<td>0.005i</td>
<td>6.0×10¹¹i</td>
</tr>
<tr>
<td>Euro 6</td>
<td>2014.09</td>
<td>1.0</td>
<td>0.10i</td>
<td>-</td>
<td>0.06</td>
<td>0.005i</td>
<td>6.0×10¹¹i</td>
</tr>
<tr>
<td>Compression Ignition (Diesel)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euro 1†</td>
<td>1992.07</td>
<td>2.72</td>
<td>(3.16)</td>
<td>-</td>
<td>0.97</td>
<td>(1.13)</td>
<td>-</td>
</tr>
<tr>
<td>Euro 2, IDI</td>
<td>1996.01</td>
<td>1.0</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>Euro 2, DI</td>
<td>1996.01a</td>
<td>1.0</td>
<td>-</td>
<td>0.9</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>Euro 3</td>
<td>2000.01</td>
<td>0.64</td>
<td>-</td>
<td>0.56</td>
<td>0.50</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>Euro 4</td>
<td>2005.01</td>
<td>0.50</td>
<td>-</td>
<td>0.30</td>
<td>0.25</td>
<td>0.025</td>
<td>-</td>
</tr>
<tr>
<td>Euro 5a</td>
<td>2009.09b</td>
<td>0.50</td>
<td>-</td>
<td>0.23</td>
<td>0.18</td>
<td>0.005</td>
<td>-</td>
</tr>
<tr>
<td>Euro 5b</td>
<td>2011.09c</td>
<td>0.50</td>
<td>-</td>
<td>0.23</td>
<td>0.18</td>
<td>0.005</td>
<td>6.0×10¹¹</td>
</tr>
<tr>
<td>Euro 6</td>
<td>2014.09</td>
<td>0.50</td>
<td>-</td>
<td>0.17</td>
<td>0.08</td>
<td>0.005</td>
<td>6.0×10¹¹</td>
</tr>
</tbody>
</table>

Almost same limits for gasoline and diesel cars after 2014 but CO₂ emissions are 10-20% lower with diesel cars (weight dependent)8

More information: www.dieselnet.com/standards/eu/ld.php
EU Emission limits for vehicles

- Emission regulation for **gasoline passenger cars** (Euro 4 → Euro 5 → Euro 6, years 2005 → 2014)
  - CO: 1.0 → 1.0 → 1.0 g/km
  - NO\textsubscript{X}: 0.08 → 0.06 → 0.06 g/km
  - Particulate Matter (PM): 5 mg/km/Euro 6; Particle Number (PN): 6x10\textsuperscript{11} #/km /Euro 6
  - **New test cycles (after 2017-2019):** WLTC (World harmonized Test Cycle), RDE (Real-Driving Emissions) with PEMS (Portable Emission Measurement System) to estimate better the real driving conditions – applied also to hybrid and electric vehicles

- Emission regulation for **diesel passenger cars** (Euro 4 → Euro 6)
  - CO: 0.5 → 0.5 → 0.5 g/km
  - NO\textsubscript{X}: 0.25 → 0.18 → 0.08 g/km
  - PM: 25 → 5 → 5 mg/km; PN: 6x10\textsuperscript{11} #/km /Euro 6

- The emission regulation for **mobile Heavy-duty On-road vehicles** will require the use of aftertreatment systems for NO\textsubscript{X} and/or PM (CO/HC easier to remove with oxidation catalysts)
  - NO\textsubscript{X}: 3.5 → 2.0 → 0.4 g/kWh (Euro 4 → Euro 6)
  - PM: 30 → 30 → 10 mg/kWh (Euro 4 → Euro 6, Particle Number (PN) limits)

- Evaluation of emissions by **driving cycles** as new and after long-term use: Passenger cars focused on city and trucks on high-way driving
- Other countries are following US-EPA/EU regulations with a delay
- **OBD (On-Board Diagnostics)** since Euro 3 → Alarm about malfunction of ATS
- Similar limits for mobile off-road applications applied also with a delay

CO₂ emission legislation as a driving force

Fuel economy around the world as normalized CO₂ emissions on European driving cycle (EDC) for passenger cars

- Similar regulations for heavy-duty trucks
- CO₂ emissions are increased by treatments to cut down PM and NOₓ

Ref: SAE Paper 2012-01-0368
Commercial automotive honeycomb catalyst is a good example about intensification and down-sizing of a catalyst reactor.

Ref: SAE Paper 2010-01-0894
Substrate types - Metallic

Open Foil Coating: Simultaneously high cell density (500-1000 cpsi) and high washcoat thickness by spray coating; oxidation resistant AlCr alloy foils in all metallic substrates: Original, innovative Kemira catalyst concept 1985-

[Images of Open Foil Coating with cell density labels: 400 cpsi, 600 cpsi, 1200 cpsi]
Substrate types - Metallic

Ecocat®: self-supporting structure having improved mass and heat transfer
- Can be also brazed with higher cell densities (500 cpsi)
Substrate types- Metallic mixer structures

**EcoXcell®**: welded catalyst structure with good 3D mixing
(if 2 units combined by 90° angel)
- Urea hydrolysis
Ceramic honeycombs are the most common structure in automotive catalysts

Usually cordierite material $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, insulator material

A lot of development during the last 20 years:
- Thinner walls down to 3-4 mils (75-100 µm)
- Higher cell density
- Improved mechanical durability
- Alternative aluminium titanate
- Low price by mass production
## Advantages and Disadvantages by substrate types

<table>
<thead>
<tr>
<th>Property</th>
<th>Ceramic</th>
<th>Metallic</th>
<th>Extruded</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>→ pressure drop</td>
</tr>
<tr>
<td>High cell density</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>Small channel diameter</td>
</tr>
<tr>
<td>Low cell density</td>
<td>+/-</td>
<td>-</td>
<td>++</td>
<td>Large channel diameter</td>
</tr>
<tr>
<td>Catalyst amount</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>Kinetically limited reactions at low T</td>
</tr>
<tr>
<td>Fast mass transfer</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>Thin coating and small channel size</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>--</td>
<td>+++</td>
<td>--</td>
<td>Metal vs insulators</td>
</tr>
<tr>
<td>Mechanical durability</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>Important in mobile applications</td>
</tr>
<tr>
<td>Thermal durability</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>Stoichiometric application</td>
</tr>
<tr>
<td>Flexible shapes</td>
<td>+/-</td>
<td>++</td>
<td>-</td>
<td>Annular, banana, oval, filters</td>
</tr>
<tr>
<td>Price</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>Final price as a complete reactor</td>
</tr>
</tbody>
</table>

**Honeycomb extruded from catalyst material**
Exhaust gas conditions by engine and fuel type

- $\lambda$ (Lambda)=$\left(\frac{m_{\text{air}}}{m_{\text{fuel}}}\right)/\left(\frac{m_{\text{air}}}{m_{\text{fuel}}}\right)_{\text{stoichiometric}}$ /variable describing exhaust conditions where $\left(\frac{m_{\text{air}}}{m_{\text{fuel}}}\right)_{\text{stoichiometric}}$ depends on fuel: 14.6-14.7 (gasoline, diesel), 17 (methane)

- $\lambda \sim 1$ stoichiometric ($\rightarrow$ conventional gasoline, spark-ignited engine)

Rich, $\lambda < 1$  Lean, $\lambda > 1$

$\rightarrow$ Three-Way Catalyst (TWC) invented for stoichiometric combustions, does not work in lean/rich
Types of emission catalysts

- Three-way catalysts (TWC: CO+HC+NO\textsubscript{x}) for stoichiometric gasoline/NG engines: Noble metal \textit{Pt, Pd and Rh} as active metals
- Diesel Oxidation Catalysts (DOC) to oxidize CO, HC and NO on Pt/Pd
- Urea-SCR (Selective Catalytic reduction) with Ammonia slip Catalyst (ASC) for NO\textsubscript{x}: Vanadium, copper and iron on titania or zeolites
- Lean NO\textsubscript{x} trap (LNT) for NO\textsubscript{x}: Pt+Rh with NO\textsubscript{x} trapping agents
- Catalyzed Diesel Particulate Filter (DPF, CPF) for particulate removal
- The latest emission limits require the use of combined ATS to cut CO/HC/PM/NO\textsubscript{x} in mobile diesel applications: Volume of units \textasciitilde 5-6x engine displacement \rightarrow wide optimization potential
Emission purifications of passenger cars

- Emissions evaluated by European driving cycle (EDC, figure) with gasoline and diesel cars
- Main emissions during first 100 s with gasoline cars + TWC
- CO and HC emissions in city driving up to 800 s in EDC with diesel cars + DOC
- Different challenges for catalyst converters with gasoline and diesel cars

Ref: Maunula, Novel reactors -Intensification in Reaction Engineering, June 2015

Aalto University
School of Chemical Engineering

Ref: Maunula, Novel reactors -Intensification in Reaction Engineering, June 2015

4.2.2019
Three-Way Catalysts (TWC) for gasoline cars

- Improved sensor and control technology enable an enhanced TWC light-off
- Improvements in TWCs - thermal durability, new oxygen storage compounds (OSC)
  → Lower noble metal (Pt, Pd, Rh) loadings and costs
  → Today less noble metals in TWC even if more demanding test cycles than in 1990s.

Ref: SAE Paper 1999-01-3625
Reactions on TWCs

**CO, H₂ & HC oxidation**

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 \\
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} \\
\text{C}_n\text{H}_m + (n + \frac{m}{4})\text{O}_2 & \rightarrow n\text{CO}_2 + \frac{m}{2}\text{H}_2\text{O}
\end{align*}
\]

**Oxygen storage → buffer**

\[
\begin{align*}
\text{Ce}_2\text{O}_3 + \frac{1}{2} \text{O}_2 & \rightarrow 2\text{CeO}_2 \\
\text{CO} + 2\text{CeO}_2 & \rightarrow \text{CO}_2 + \text{Ce}_2\text{O}_3
\end{align*}
\]

**NO reduction (stoichiometric)**

\[
\begin{align*}
\text{NO} + \text{CO} & \rightarrow \frac{1}{2}\text{N}_2 + \text{CO}_2 \\
\text{NO} + \text{H}_2 & \rightarrow \frac{1}{2}\text{N}_2 + \text{H}_2\text{O}
\end{align*}
\]

**Water gas shift & steam reforming → promotion**

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{CO}_2 \\
\text{C}_3\text{H}_6 + 3\text{H}_2\text{O} & \rightarrow 3\text{CO} + 6\text{H}_2 \\
\text{C}_3\text{H}_8 + 3\text{H}_2\text{O} & \rightarrow 3\text{CO} + 7\text{H}_2
\end{align*}
\]

Pt, Pd, Rh as active sites

CeOₓ

Alumina
Three-Way Catalysts (TWC) for gasoline cars

Oxygen Storage Capacity compounds are crucial for TWC performance and OBD. Ceria oxidation state oscillates between $\text{Ce}^{4+}$ and $\text{Ce}^{3+}$, promoting TWC and buffering fast $\lambda$ variations:

**Oxygen storage (Lean):**

\[
2 \text{Ce}_2\text{O}_3 + \text{O}_2 \rightarrow 4 \text{CeO}_2
\]

\[
2 \text{Ce}_2\text{O}_3 + \text{NO} \rightarrow 4 \text{CeO}_2 + \text{N}_2
\]

**Oxygen release (Rich):**

\[
2 \text{CeO}_2 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2
\]

\[
2 \text{CeO}_2 + \text{H}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{H}_2\text{O}
\]

\[
4 \text{CeO}_2 \rightarrow 2 \text{Ce}_2\text{O}_3 + \text{O}_2
\]

Ref: SAE Paper 1999-01-3625
Three-Way Catalysts (TWC) for gasoline cars
On-Board Diagnostics (OBD)

Factors related to emission control systems must be monitored by OBD requirements:
1. Methods based on $\lambda$ sensors: amplitude methods, jump (step) methods
2. Methods based on temperature sensors: detection of reaction heat, joint to $\lambda$ responses

Combines catalyst chemistry to control engineering

Amplitude method - $\lambda$ responses / real data:

Before TWC

After TWC

Good TWC

Deactivated TWC (at 1200° C)

Ref: SAE Paper 1999-01-3625
Diesel Aftertreatment systems

NO$_x$ and PM are the main pollutants which are controlled by engine (combustion) modifications (primary method) and aftertreatment methods (secondary). An example for mobile off-road emission control:

Decrease of NO$_x$:
- Exhaust gas recirculation (EGR)/lower temperature
- Selective Catalytic Reduction (SCR)
- Lean NO$_x$ Trap (LNT)

Decreasing particulate matter (PM):
- Efficient combustion (→SCR engine, high temperature
- Catalyzed Particulate filter (CPF, DPF)
- Partial filter

Ref: Maunula 2011
Diesel Aftertreatment systems

- New diesel passenger cars have lower fuel consumption (CO\textsubscript{2}) and exhaust gas temperatures than gasoline cars
- The share of diesel fueled vehicles are increased continuously in 2000’s in Europe (over 40% in many countries) → decrease in near future due to complicity of ATS?
- Euro 4-6 emission regulations required new types of catalytic aftertreatment systems
- Catalyst sizes and thermal stress vary by the functions and locations
- PM oxidation and DPF regeneration the main heat source

<table>
<thead>
<tr>
<th>Temperature Range</th>
<th>Time (hours)</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAX. 900°C</td>
<td>150,000 – 1,000,000 h\textsuperscript{-1}</td>
<td>Engine DOC, MAX. 900°C</td>
</tr>
<tr>
<td>MAX. 700°C</td>
<td>40,000 – 150,000 h\textsuperscript{-1}</td>
<td>DOC</td>
</tr>
<tr>
<td>MAX. 800-900°C</td>
<td>15,000 – 90,000 h\textsuperscript{-1}</td>
<td>DPF/CPF/FSCR</td>
</tr>
<tr>
<td>MAX. 700-800°C</td>
<td>10,000 – 60,000 h\textsuperscript{-1}</td>
<td>SCR/LNT</td>
</tr>
</tbody>
</table>

Preturbo DOC
**NO\textsubscript{x} removal methods**

The main NO\textsubscript{x} removal method is urea-SCR, where urea is a source for ammonia, which selectively reacts with NO in oxygen excess. The main and side reactions:

\[
\begin{align*}
2 \text{ NO} + \text{O}_2 &\rightleftharpoons 2 \text{ NO}_2 & (1) \text{ NO}_2 \text{ formation (on DOC)} \\
4 \text{ NO} + 4 \text{ NH}_3 + \text{O}_2 &\rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O} & (2) \text{ Standard SCR (SCR, ASC)} \\
\text{NO} + 2 \text{ NH}_3 + \text{NO}_2 &\rightarrow 4 \text{ N}_2 + 3 \text{ H}_2\text{O} & (3) \text{ Fast SCR (SCR)} \\
4 \text{ NH}_3 + 3 \text{ NO}_2 &\rightarrow 3.5 \text{ N}_2 + 6 \text{ H}_2\text{O} & (4) \text{ NO}_2\text{-SCR (SCR) - slow} \\
4 \text{ NH}_3 + 3 \text{ O}_2 &\rightarrow 2 \text{ N}_2 + 6 \text{ H}_2\text{O} & (5) \text{ NH}_3 \text{ decomposition (ASC)} \\
4 \text{ NH}_3 + 5 \text{ O}_2 &\rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O} & (6) \text{ NH}_3 \text{ oxidation to NO (ASC, SCR)} \\
2 \text{ NH}_3 + 2 \text{ O}_2 &\rightarrow \text{N}_2\text{O} + 3 \text{ H}_2\text{O} & (7) \text{ N}_2\text{O formation (ASC, SCR)} \\
2 \text{ CO} + \text{O}_2 &\rightarrow 2 \text{ CO}_2 & (8) \text{ CO (from urea) oxidation (ASC)}
\end{align*}
\]

Lean NO\textsubscript{x} traps (LNT) were examined intensively during the last 20 years

- No additional reductant needed
- Require short rich peaks in every few minutes and longer enrichments for desulfation about in every 500-1000 hours

Urea-SCR and LNT in commercial use, many other methods introduced but they are not competitive in commercial use
**NO\textsubscript{x} removal methods- SCR**

**SCR catalysts**

- **Vanadia-SCR**
  - Wide commercial use for Euro 4 – 6 heavy-duty trucks (Europe, Asia, Russia)
  - V-SCR is chemically very durable but the maximum temperature limited to 600-650 °C - Vanadium on TiO\textsubscript{2}-WO\textsubscript{3}-(SiO\textsubscript{2}) support
  - The use of vanadium limited in USA and Japan (toxicity, evaporation)

- **Cu-SCR and Fe-SCR**
  - Based on hydrothermally stable zeolites (Beta, chabazite) developed during the last 15 years
  - Cu-SCR good at low and Fe-SCR good at high temperatures
  - Fe-SCR has a higher dependence on NO\textsubscript{2} (DOC) than Cu-SCR catalysts
Effect of hydrothermal (HT) ageing and NO$_2$ on the V-, Cu- and Fe-SCR catalyst performance (NO only = standard SCR, NO$_2$ present = Fast SCR):
Detailed surface reaction mechanism is complicated and both Langmuir-Hinshelwood and Eley-Ridel (ER) mechanism have been proposed. Mobile oxygen in VO\textsubscript{x} has a role in ER reaction paths:

Ref: Maunula 2007 by Inomata 1980
NO$_x$ removal methods- SCR

LH reaction mechanism on active metal sites (*) is a common reaction path explaining the reaction initiation by ammonia activation:

\[ \text{NO} + * \rightarrow \text{NO}^* \]
\[ \text{NH}_3^* + * \rightarrow \text{NH}_2^* + \text{H}^* \]
\[ \text{NH}_2^* + \text{NO}^* \rightarrow \text{N}_2 + \text{H}_2\text{O} + 2 * \quad \text{NO reduction} \]
\[ 2 \text{H}^* + \text{O}^\# \rightarrow \text{H}_2\text{O} + \# \]
\[ \text{O}_2 + 2 \# \rightarrow 2 \text{O}^\# \]

In addition, more complex mechanisms like NH$_4$NO$_3$ intermediate as a key compound have been proposed particularly for zeolite based catalysts, which have a high ammonia adsorption capacity and coverage during SCR.

Ref: Maunula 2007 by Otto and Shelef 1972
Optimal for DPF regeneration and SCR located on “clean side” but thermally demanding for SCR → Main ATS solution for mobile diesel applications

Ref: Maunula 2013
Low thermal stress and an improved low temperature activity of SCR but DPF regeneration more demanding and SCR on “dirty side” of DPF
NO\textsubscript{x} removal methods - LNT

NO\textsubscript{x} reduced on LNT (Ba, K, La etc. as NO\textsubscript{x} adsorbents) in the exhaust gas which is lean on average

→ Small cars to cut g/km emissions (fuel economy = CO\textsubscript{2})

→ Fuel penalty is an obstacle for the use in heavy-duty applications

Ref: SAE Paper 2001-01-3665
NO$_x$ removal methods - LNT

Mean NO$_x$ conversions with single LNT catalysts with 130 g/cft Pt as hydrothermally aged (700°C/20h) in simulated lean-rich feed mixture (30.000 h$^{-1}$)

→ Developed LNT by Dinex clearly more active than Pt/Alumina+Ba or TWC: Al+Ba+La+OSC+preparation.

Ref: SAE Paper 2001-01-3665
Diesel particulate formation and reactions

- Primary particles accumulating
- HC, SOₓ and water volatile
- VOF oxidized
- SO₂ → SO₃
- C + O₂/NO₂ →
- PM measured by standards contains solid carbon (soot, C) and condensed compounds
- SO₃ → SO₄ (absorbs water)

Ref: Maunula 2010
Particulate aftertreatment method

Variable
PM removal, %
Pressure drop
Regeneration need
Service need
Cost

<table>
<thead>
<tr>
<th></th>
<th>DOC</th>
<th>POC</th>
<th>DPF-skin</th>
<th>DPF-deep</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM removal, %</td>
<td>10-40</td>
<td>30-70</td>
<td>&gt;&gt;90</td>
<td>50-90</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>very low</td>
<td>low</td>
<td>very high</td>
<td>high</td>
</tr>
<tr>
<td>Regeneration need</td>
<td>no</td>
<td>Pass/Act</td>
<td>Act</td>
<td>Pass/Act</td>
</tr>
<tr>
<td>Service need</td>
<td>no</td>
<td>medium</td>
<td>needed</td>
<td>needed?</td>
</tr>
<tr>
<td>Cost</td>
<td>low</td>
<td></td>
<td>very high</td>
<td>high</td>
</tr>
</tbody>
</table>

DPF: Diesel Particulate Filter
DPF-skin: Wall-flow type filters (cordierite, silicon carbide), forced flow through walls, usually catalyzed
DPF-deep: Deep filtration type filters (fibres, foams, wire mesh)
POC (Particle Oxidation Catalyst/partial filter/Open filter): metallic, tortuous flow channels
DOC (Diesel Oxidation Catalyst): conventional oxidation catalysts, oxidize HCs
Pass = Passive
Act = Active

DPF-skin (full-filters) necessary to reach the current PM /PN targets

Ref: SAE Paper 2007-01-0093
Catalyst coated wall-flow particulate filter

Porous walls with ceramic cordierite or SiC:
- Forced flow through walls → Skin PM filtration with efficiency of >95-99% (weight)
- Mean pore size 10-30 μm
- Surface and pore volume reserve for catalyst
  - Oxidation catalyst
  - SCR catalyst
  - LNT
- Accumulated soot requires periodical regeneration

SEM image of SiC wall (Porosity as uncoated 65% and as catalyst coated 50%)

Source: Dieselnet
Carbon oxidation reactions on DPF

\[ C + O_2 \rightarrow CO_2 \] (1) thermal (>550° C) or catalytic /active DPF regeneration

\[ C + 2 NO_2 \rightarrow CO_2 + 2 NO \] (2) thermal (>250° C) or catalytic /passive DPF regeneration

\[ C + 2 NO \rightarrow CO_2 + N_2 \] (3) Catalytic, a minor path, poor selectivity when excess O\(_2\)
Combined C and NO\(_x\) removal

Catalytic oxidations utilize reaction cycles /Catalytic PM/soot oxidation:

\[ C + MO_x \rightarrow CO_2 + MO_{x-2} \] (4) Metal oxides able to oxidize C

\[ MO_{x-2} + O_2 \rightarrow MO_x \] (5) Re-oxidation

\[ MO_{x-2} + NO_2 \rightarrow MO_x + NO \] (6) Re-oxidation

\[ 2 NO + O_2 \leftrightarrow NO_2 \] (7) NO\(_2\) formation, Catalytic, thermodynamical limits

Ref: Maunula 2010
Integration of ATSs for diesel applications

The intensification of DPF+SCR systems for diesel applications: A lot of potential for optimization by engine calibration, thermal management and costs

Main solution

Ideal, compact but too many limitations

Secondary solution
Intensification of diesel ATSSs

Integration of ATS, SCR control, DPF control and OBD in mobile diesel applications
Design and downsizing ATSs for diesel applications

An example about muffler design for ATS (emissions and noise)

All catalytic components in a single muffler/silencer

Complicated urea dosing and DPF regeneration systems
Natural gas

• Methane is very energy rich fuel and produces less CO$_2$ emissions per energy equivalent compared to other HC’s

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad 809 \text{ kJ} \]

• On the other hand it is the hardest HC to oxidize and needs high loadings in the catalyst

• Pd-rich Pt-Pd (MOC) and Pd-Rh (TWC) coating technologies have been used in the methane oxidation catalyst with high loading (100-250 g/cft = 3.5 – 8.8 g/dm$^3$)

• Lean conditions
  • Produces less NO$_x$ emissions
  • Better fuel to energy –efficiency compared to stoichiometric combustion
  • Oxidized poison compounds (like sulfates) can gather on the catalyst surface
ATS for natural gas and dual-fuel applications
Lean and stoichiometric

- NG is an alternative fuel with very low PM emissions
- Composition mostly methane, limited local distribution
- Methane is a much worse greenhouse gas than CO$_2$ and the most difficult HC to be oxidized
- Diesel fuel in low speed region (Lean dual-fuel engines)
- Bi-fuel gasoline-NG for passenger cars
Oxidation catalyst for lean natural gas application

Pd-rich Methane Oxidation Catalysts (MOC) are sensitive for sulfur poisoning in lean. Sulfur deactivation rate and desulfation strategy are key points in catalyst development. MOC recovery requires stoichiometric or lean conditions above 500° C with elevated methane concentration.

Ref: Maunula 2016
Methods and steps for emission catalyst development

- Targets
  - Performance
  - Durability
  - Design

- Catalyst Development
  - Composition
  - Substrate

- Catalyst Preparation
  - Small-scale

- Pilot scale Preparation
  - Full-scale

- Catalyst Testing
  - Ageing
  - Characterization

- Engine testing

- Product design

- Post mortem analysis

- Client

- Products
  - Grams / dl / 1-2x
  - Kgs / L / 1-2x
  - Tons / >100L / 100-10000

- Commercial manufacture

- Production process design

- Catalyst Concept
Characterization methods in catalyst development

- Particle size analysis
- Metal Content (XRF, AAS)
- Composition (XRF)
- Total surface area by BET and Dubin methods (SORPTOMATIC 1990) → effect of thermal deactivation
- Precious metal dispersion (SORPTOMATIC 1990) → effect of thermal or chemical deactivation
- Temperature Programmed Desorption/Reduction/Oxidation TPD/TPR/TPO (Mass spectrometer)
- OSC Measurements (Reactor with mass spectrometer)

TEM, SEM, XPS, AFM, XRD, Drifts-FTIR ETC. IN COLLABORATIONS WITH PARTNERS (Universities, Institutes)
Characterization methods in catalyst development

Chemisorption analysis to evaluate active metal surface:
- CO (or H₂) as reactive gas at room temperature
- Adsorption isotherm from vacuum up to 0.1 bar - low pressure to limit physical adsorption
- Metal – CO stoichiometry assumed by the analysis method: e.g. 1.15 Pt-CO, 1.5 Pd-CO
- Metal dispersion = (Adsorbing metal atoms) / (All metal atoms)
- Methods to eliminate physical adsorption (increase by pressure) 1) Double isotherm, 2) Back Zero extrapolation

Reduction and evacuation → isotherm 1 → vacuuming to remove physisorbed CO → isotherm 2
Characterization methods in catalyst development

Dispersion degree with CO on PtRh-TWC by ageing temperature
- Deactivation mainly thermal on TWCs → stability studies by chemisorption
- Significant drop of catalytic activity when dispersion below 10%
- Particle size increasing correspondingly from 1 nm to tens of nanometers
- Particle size by CO chemisorption is an indirect method, direct methods like TEM to detect noble metal particles

![Graph showing dispersion degree with CO on PtRh-TWC by ageing temperature](image)
Case study: DOC

- Low light-off temperature ($T_{50}$) for CO/HC/NO oxidation required
- Utilization of low heat of exhaust gas in catalytic reactions
- Low sulfate formation, enhanced carbon oxidation, HC trapping
- Pt(Pd) on alumina based support with set of metal oxides (promotors) and zeolites (HC trapping) - noble metals most durable in real exhaust
- Slight 5-10 % deNO$_x$ by HC-SCR
- TEM images of aged Pt- and PtPd-DOC (Pd stabilizes):

Ref: Honkanen et al. 2015
Case study: DOC

Light-off experiments to detect reactant conversions by temperatures (aged DOC)- variable effect study

Aged 30.000 h⁻¹

Light-off experiment
–fixed feed gas in heating ramp:
80 ppm propene
15 ppm toluene
15 ppm decane,
200 ppm NO
1500 ppm CO
14% oxygen
6% water, 6% CO₂
balance nitrogen
30.000 h⁻¹
Case study: DOC

Experimental simulation of the conditions in a diesel car exhaust in European Driving Cycle (EDC) with a laboratory reactor:

Ref: SAE Paper 2004-01-3021
Case study: DOC

Numerical simulation of DOC performance by the conditions of a diesel car exhaust in EDC- Model validation for HC oxidation and adsorption:

Ref: Koci et al. 2005
Numerical simulation of DOC performance by the conditions with two diesel cars and a truck - Conversions in EDC (g/km) and ETC (g/kWh):

CO conversion in EDC with a cold (135°C in UDC) and warm (180°C in UDC) diesel cars with aged DOCs

Utilization of DOC simulator:
→ Estimate for pollutant emissions (g/km) in EDC and required DOC specification by the vehicle raw data or different calibrations
→ Ageing effects included in kinetic parameters
→ Due to very different test cycles for heavy-duty trucks, much smaller DOC volumes and PtPd loadings than with passenger cars

Ref: Maunula YSF, Jyväskylä, 2016
Summary

- Pollutant emission regulated for stationary and mobile processes by international legislations
- Emission control for cars and trucks resulting in very complicated and expensive ATSs requiring wide optimization and R&D
  - Combined development in engine, control and catalyst technologies together with fuel quality and economy
  - New types of TWCs, DOCs, SCR catalysts, LNTs and catalyzed filters developed as ATS solutions

Questions?

Good general information in the field: www.dieselnet.com
Contact for additional information: Teuvo Maunula, tma@dinex.fi
References


Maunula, T., Novel reactors -Intensification in Reaction Engineering, Key note, Saariselkä, June 2015.


Maunula YSF, Key note presentation, Jyväskylä, March 2016.


Books about emission catalysts:

Ronald M. Heck, Robert J. Farrauto, Suresh T. Gulati
Catalytic Air Pollution Control: Commercial Technology, 3rd Edition
ISBN: 978-0-470-27503-0
Mar 2016, 544 pages
Publisher: Wiley
Abbreviations

ASC: Ammonia Slip Catalyst (to remove ammonia after SCR unit)
ATS: After Treatment Systems
BAT: Best Available Technics
CPF: Catalyzed Particle Filter; generally, DOC, LNT or SCR coating
cpsi: cells per square inch (cell/channel density for honeycomb catalysts), use in car industry
DOC: Diesel Oxidation Catalyst
DPF: Diesel Particle Filter
EDC: European Driving Cycle, agreed driving cycle, where emissions are regulated
EGR: Exhaust Gas Recirculation
EMS: Engine Management System
EU: European Union (emission limits)
FSCR: DPF with SCR coating
GHG: Green House Gases
GWP: Global Warming Potential
HC: Hydrocarbons, THC: Total Hydrocarbons
HT: Hydrothermal (ageing)- rapid ageing to evaluate catalyts durability
Lambda (λ): Air/Fuel ratio divide by stoichiometric Air/Fuel ratio, <1 rich (lack of oxygen), >1, excess of oxygen
MOC: Methane Oxidation Catalyst (in lean conditions)
NG: Natural Gas
NOx: Nitrogen Oxides like NO, NO2
OBD: On-Board Diagnostics
PAN: peroxycetylNitrates
PM: Particulate Matter, particles in exhaust gas
PN: Particle Number (regulations), number per km
POC: Particle Oxidation Catalyst, Partial Filter
POP: Persistent organic pollutants, resistant to degradation
SCR: Selective Catalytic Reduction (by ammonia, urea or hydrocarbons)
SOx: Sulfur oxides like SO2 and SO3
VOC: Volatile Organic Compounds, hydrocarbons
TWC: Three-Way Catalyst to remove CO, HC and NOx in stoichiometric conditions