Durability Task Force

Gasoline Engine Catalyst

Deactivation/Ageing
Introduction

- Gasoline engine aftertreatment devices
  - ✔ TWC → standard aftertreatment
  - ✔ GPF → used in GDI engines (either catalyzed or non-catalyzed)
  - ✔ LNT/SCR/TWNSe → used in GDI lean-burn engines

- Literature focuses mainly on **thermal ageing**

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Type</th>
<th>Definition/Brief Description</th>
<th>Relevant device</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poisoning</td>
<td>Chemical</td>
<td>Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction</td>
<td>TWC, catalytic GPF, LNT (NSC), SCR, TWNSC</td>
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<tr>
<td>Fouling</td>
<td>Mechanical</td>
<td>Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores</td>
<td>As above</td>
</tr>
<tr>
<td>Sintering</td>
<td>Thermal / Chemical</td>
<td>Thermally induced loss of catalytic surface area, support are and active phase-support reactions / chemical transformations of catalytic phases to non-catalytic phases</td>
<td>As above</td>
</tr>
<tr>
<td>Degradation</td>
<td>Mechanical</td>
<td>Mechanical malfunction, improper operation of key components or physical damage being inflicted upon the TWConverter Meltdown</td>
<td>GPF (and TWC, loss of catalyst material due to fractures in the monolith)</td>
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Thermal Deactivation

- Thermally induced deactivation of catalysts results from:
  1. loss of catalytic surface area due to crystallite growth of the catalytic phase
  2. loss of support area due to support collapse and of catalytic surface area due to pore collapse on crystallites of the active phase, and/or
  3. chemical transformations of catalytic phases to non-catalytic phases

Processes 1 and 2 are typically referred to as **sintering**

Decay by **sintering**: agglomeration of deposited metal sites
Mechanisms of sintering

Principal mechanisms

1. **(Ostwald) ripening** - particles grow in size due to differences in surface energy. Larger particles grow at the expense of smaller ones.

2. **particle migration and coalescence** – dependent on the mobility of nanoparticles, vapor transport (at very high temperatures)
The prevailing view of catalyst sintering

- The early stages of sintering are dominated by the particle migration and coalescence.
- Ostwald ripening continues as the dominant mechanism of sintering as particles grow larger.
Sintering - What is the contribution from each of these processes?

Each of the 2 sintering principal mechanisms is a simplification which ignores the possibility that all mechanisms may occur simultaneously and may be coupled with each other through complex physicochemical processes:

1. dissociation and emission of metal atoms or metal-containing molecules from metal crystallites
2. adsorption and trapping of metal atoms or metal-containing molecules on the support surface
3. diffusion of metal atoms, metal-containing molecules and/or metal crystallites across support surfaces
4. metal or metal oxide particle spreading
5. support surface wetting by metal or metal oxide particles
6. metal particle nucleation
7. coalescence of, or bridging between, two metal particles
8. capture of atoms or molecules by metal particles
9. liquid formation
10. metal volatilization through volatile compound formation
11. splitting of crystallites in O2 atmosphere due to formation of oxides of a different specific volume, and
12. metal atom vaporization
### Sintering - Factors affecting metal particle growth

<table>
<thead>
<tr>
<th><strong>Variable</strong></th>
<th><strong>Effect</strong></th>
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<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td>Sintering rates are exponentially dependent on $T$; Activation Energy decreases with increasing metal loading; it increases in the following order with atmosphere: NO, O$_2$, H$_2$, N$_2$</td>
</tr>
<tr>
<td><strong>Atmosphere</strong></td>
<td>Sintering rates are much higher for noble metals in O$_2$ than in H$_2$ and higher for noble and base metals in H$_2$ relative to N$_2$; sintering rate decreases for supported Pt in atmospheres in the following order: NO, O$_2$, H$_2$, N$_2$</td>
</tr>
<tr>
<td><strong>Metal</strong></td>
<td>Observed order of decreasing thermal stability in H$_2$ is Ru $&gt;$ Ir $\sim$Rh $&gt;$ Pt; thermal stability in O$_2$ is a function of (1) volatility of metal oxide and (2) strength of metal oxide–support interaction</td>
</tr>
<tr>
<td><strong>Support</strong></td>
<td>Metal–support interactions are weak; with a few exceptions, thermal stability for a given metal decreases with support in the following order: Al$_2$O$_3$ $&gt;$ SiO$_2$ $&gt;$ carbon</td>
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<tr>
<td><strong>Promoters</strong></td>
<td>Some additives decrease atom mobility, e.g. C, O, CaO, BaO, CeO$_2$, GeO$_2$; others increase atom mobility, e.g. Pb, Bi, Cl, F, or S; oxides of Ba, Ca, or Sr are “trapping agents” that decrease sintering rate</td>
</tr>
<tr>
<td><strong>Pore size</strong></td>
<td>Sintering rates are lower for porous vs. non-porous supports; they decrease as crystallite diameters approach those of the pores</td>
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</table>

**In general, sintering processes are kinetically slow (at moderate reaction temperatures) and irreversible or difficult to reverse. Thus, sintering is more easily prevented than cured.**

*Source: Bartholomew, 2001*
Sintering in automotive catalysts

- Thermally deactivation caused by high temperatures (>500°C)
  - affected also by catalytic species (Rh is the most resistant in sintering)
  - affected also by washcoat material (Al₂O₃ is the most common material, most stable chemically and thermally, other common is Zeolite)
  - affected by oxygen concentration (higher O₂ concentration accelerates ageing)
  - affected (usually accelerated) by the presence of water vapor

- Thermal deactivation mechanisms
  1. Catalyst (precious metals, i.e. active material) sintering
  2. Washcoat sintering
  3. Chemical interactions among active sites and between active site and washcoat

- Thermal shock, due to continuous lean/rich operation
  - O₂ storage in Ce during lean operation
  - CO/HC oxidation during rich operation → sharp increase in temperature
Atomic and crystallite migration of active precious metals reduce catalysts activity to the point of total deactivation.

Crystal growth → decrease in catalytic surface area → fewer catalytic sites available to the reactants.

Active sites may also be buried within the crystal.

The experimental observations show that temperature is a dominant factor for sintering of active precious metals.
Washcoat sintering is defined as a loss of the internal pore structure leading to a decrease in the physical surface area of the carrier. In extreme cases, encapsulation of catalyst particles occurs at very high temperatures. Al$_2$O$_3$ and CeO$_2$-based materials are subjected to significant sintering.
Washcoat Sintering - Al₂O₃

- Al₂O₃ sintering is accompanied by thermally induced phase transformation – from γ-Al₂O₃ (100–200 m²/g surface area) to non-porous α-Al₂O₃ (5 m²/g) and to elimination of pore structures.

- Compared to other washcoat materials for TWC, Al₂O₃ has a higher specific surface area and better thermal and chemical stability that is particularly significant for metal dispersion.

- Improving skeleton stability and suppressing phase transformation of Al₂O₃ are necessary.

- These can be achieved through skeletal doping with specific dopants (i.e. La₂O₃, ZrO₂ and Y₂O₃).

- Atomic scale insertion is still a technical challenge and remains an interesting research field.
Washcoat Sintering - CeO$_2$

- CeO$_2$ readily crystallises and sinters with growth of particles and loss of surface area, leading to rapid reduction of the oxygen storage and release properties.

- Improvement with the introduction of Zr$^{4+}$ ions into the CeO$_2$ skeleton to achieve CeO$_2$-ZrO$_2$ solid solution – stabilization and enhancement of catalytic activity.

- Further improvement with the use of Al$_2$O$_3$ particles as diffusion barriers.
Thermal Deactivation: Chemical interactions (solid–solid reactions)

Solid-state reactions that chemically transforms active phase to non-catalytic phase

Examples:
✓ Decomposition of active PdO species to inactive Pd at temperature higher than 800°C
✓ Formation of Pt Pd alloy and Pt Ni alloy
Chemical Deactivation (Poisoning)

✓ Poisoning is the strong chemisorption of reactants, products or impurities on sites otherwise available for catalysis. Thus, poisoning has operational meaning: whether a species acts as a poison depends upon its adsorption strength relative to the other species competing for catalytic sites.

✓ In addition to physically blocking of adsorption sites, adsorbed poisons may induce changes in the electronic or geometric structure of the surface.

1. A strongly adsorbed atom of S physically blocks at least one 3- or 4-fold adsorption/reaction site and 3 or 4 topside sites on the metal surface.

2. By virtue of its strong chemical bond, it electronically modifies its nearest neighbor metal atoms and possibly its next nearest neighbor atoms, thereby modifying their abilities to adsorb and/or dissociate reactant molecules although these effects do not extend beyond about 5 a.u.

3. Restructuring of the surface by the strongly adsorbed poison, possibly causing dramatic changes in catalytic properties, especially for reactions sensitive to surface structure.

Conceptual two-dimensional model of S poisoning of C\textsubscript{2}H\textsubscript{4} hydrogenation on a metal surface
Three kinds of poisoning behavior

Poisoning may be selective, non-selective or anti-selective, depending on whether the poisoning is universal or takes place only at certain sites or crystal faces or affects only certain adsorbed species.

- **Selective** poisoning involves preferential adsorption of the poison on the most active sites at low concentrations.
- **Non-selective** poisoning occurs when the activity loss is proportional to the concentration of adsorbed poison.
- **Anti-selective** poisoning occurs when sites of lesser activity are blocked initially.
Poisoning of automotive catalysts (1)

Poisoning of an exhaust gas catalyst caused by accumulation of impurities on the active sites is typically a slow and irreversible phenomenon. It is possible even with a low level of impurities.

Fuel-bound poisons: S (~5ppm), Mg, Pb (practically eliminated from modern gasoline).

Oil-bound poisons: Zn and P as lubricity enhancers, Ca, S.

LNT sensitive to S (BaO poisoning), but catalyst conditions is reversible following a desulfation process (applying rich operation at high temperature, ~700°C).
Poisoning of automotive catalysts (2)

➢ Chemical deactivation mechanisms

1. Selective poisoning
   - a poison reacts directly with an active site, decreasing its activity for a given reaction
   - if the poison reacts chemically with the catalyst component, the poisoning is permanent
   - if poisoning result from adsorption, then it can be (partially) reversible

2. Nonselective poisoning (fouling or masking)
   - masking of active sites and pores occurs due to a deposition of fouling agents on the washcoat
   - decreasing the available catalytic surface area and blocking access to the pores
All the previous ageing mechanisms apply for catalytic (coated) DPF.

In addition, another important degradation mechanism for GPF is:

- Ash derives from additives in the lubricant
  - **Layer ash**: improves (interception and impaction) filtration
  - **Plug ash**: (diffusion) filtration is reduced

- It affects pressure drop ($\Delta p$) across the filter

- **First effect**: decrease in effective soot storage volume

- **Second effect**: ash reduces the active volume of the filter $\rightarrow$ gas velocity (space velocity) increases $\rightarrow$ exhaust gas residence time decreases $\rightarrow$ catalytic activity deteriorates (for catalytic GPF)

- **Major challenge for GPF**: high exhaust mass flow with high PM concentration $\rightarrow$ fast PM loading $\rightarrow$ if there is enough heat in high temperature fuel-cut conditions then GPF can be damaged due to thermal shock
Discussion

• OSC is reduced by **max. 12%** (with normal quantity of oil additive, 60h ageing), **due to chemical ageing**

• With 10 times higher concentration of oil additive, max. reduction of OSC is 50%

• **Thermal ageing** reduced OSC by **70-90%**, after 60h

• Poisoning can be limited with:
  • high quality fuels
  • reduction in oil consumption in modern engines

• Therefore, chemical poisoning is no longer the major cause for catalyst deactivation or malfunction.

• The industry standard theory assumes that all of the ageing is thermal and that loss of catalytic activity depends on temperature and time

• It seems that, **thermal ageing** affects the gasoline engine catalysts substantially stronger than chemical ageing
Accelerated Thermal Ageing Techniques

➢ **Engine ageing**
  • Catalyst brick placed at the exhaust of an engine, apply specific drive cycle
  • Realistic gas composition and temperature
  • Limited control of gas composition and temperature, variability from engine to engine, cost

➢ **Static ageing**
  • Catalyst brick or sample aged in an oven
  • Known temperature and known gas environment
  • Low operating cost and control
  • Not representative of real world conditions

➢ **Ageing on SGB**
  • Full control of gas composition and temperature
  • Reproduction of transient profiles
  • Usually, ageing of catalyst samples and not the whole brick – ageing effects are not the same for the whole catalyst volume (it follows a radial and axial distribution, major deactivation at the center and in the front of the cylindrical brick, decreasing outwards towards the edges)
Typical aging cycles consist of the following elements simulating these situations:

- Stoichiometric operation with lambda oscillation at the temperature limit, before component protection is switched on in the engine control.
- Rich operation at borderline temperatures, which are used for component protection.
- AFR change from rich to slightly lean, which occurs when excess oxygen reaches the catalyst as can be the case when the lambda control to stoichiometric is switched on, or by uneven cylinder distribution or close catalyst position to the cylinder and exhaust gas post reactions.
- AFR change from stoichiometric or rich mixture to pure air flow representing the fuel shut off operation used in engine control for fuel consumption reduction.
A good correlation between engine test bench aging results and the vehicle fleet testing programs is claimed, when both aging programs provide the same accumulated thermal load to the catalyst.

This is of course only true within certain boundaries of temperature and lambda, which are used for the tests.

The simulation of the vehicle standard road cycle by a simplified standard bench cycle is adopted by EPA and European legislation. This is based on the comparison of the thermal loads and follows to a theoretical Arrhenius approach for catalyst deactivation energy, the bench aging time (BAT) formula:

\[
BAT = A \cdot \sum_{\min}^{\max} \Delta t \left( e^{\frac{R}{Tr} \frac{R}{Tv}} \right)
\]

- **A** = chemical deactivation correction
- **Σ** = sum over all temperature bins
- **Δt** = time at temperature bin in the vehicle
- **R** = reactivity constant = 17500 for LEVII aftertreatment and 18500 for all other vehicles
- **Tr** = effective reference temperature bench
- **Tv** = midpoint temperature vehicle

Source: Ignatov et al, 2010
Engine Ageing (3) - Disadvantages

1. The inability to vary key components of the aging cycle
2. The variability experienced between tests due to the use of different engines or due to engine deterioration added to the inconsistency of test results due to operator approach, often requires a sacrificial catalyst to be used as a comparator to previous tests
3. **The cost of testing** a catalyst assembly on a dyno is substantial.
   - Although economies of scale are applied with multiple test pieces running simultaneously, the cost still remains high
   - The potential drawback of multiple catalysts per test may result in uneven distribution of the flow to each catalyst resulting in aging inconsistencies between bricks

Other approaches include the use of a gas burner in which a lower cost fuel such as natural gas is used. The benefit is the absence of soot Similar to the engine limitations
Static ageing

- Catalyst brick or sample aged in an oven
- Known temperature and known gas environment
- Low operating cost and control
- Not representative of real world conditions

Further work must be conducted in order to see if any correlation exists between static aging and dynamic aging under laboratory conditions.
SGBs have been generally used for steady state tests on cored samples.

Recent work conducted (Adam et al., 2015) has shown successfully that SGB reactors are capable of testing transient engine conditions with comparable results to an engine bench.

The assumption that lambda, temperature and flow rate are the key factors when aging a catalyst are driven by the limitations in the evaluation tools available.

If there were a SGB reactor capable of providing the high flow, high temperature and precision control, combining the capability of transient dynamic engine aging with the precision of an SGB would represent a unique development tool offering capabilities (Catagen Limited).
Some results for gasolines - ZDAKW cycle

ZDAKW cycle on hot gas test bench

FTP emission result comparison with different aging methods for ZDAKW catalysts

FTP emission comparison with different aging methods

ZDAKW cycle repeats a comparable situation for a time originally defined to be 96 hours for the EURO III 80000 km equivalent

Source: Ignatov et al, 2010
Some results for gasolines (2)

The OSC at different temperatures of the 3 differently aged gasoline catalysts and reference, when changing conditions from lean to rich.