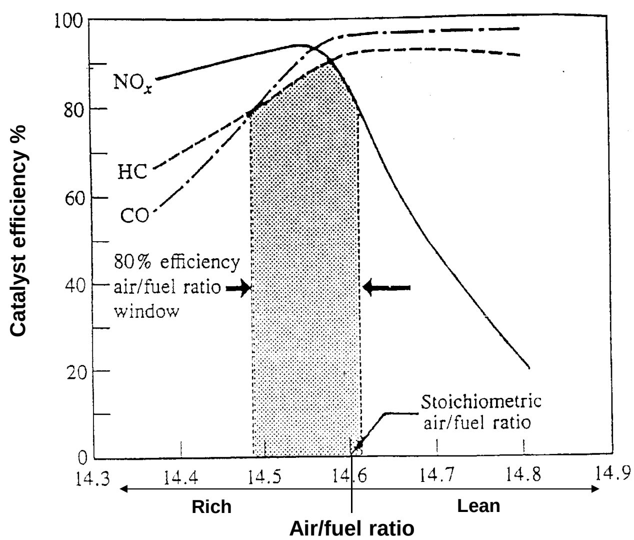
SI Engine Catalyst

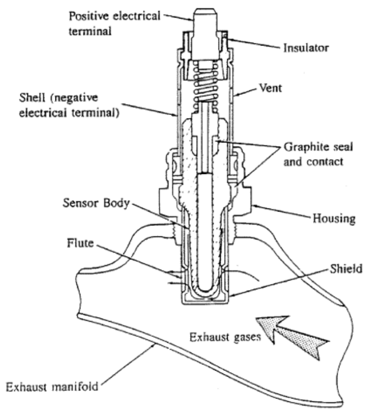
Requirement for the 3-way catalyst

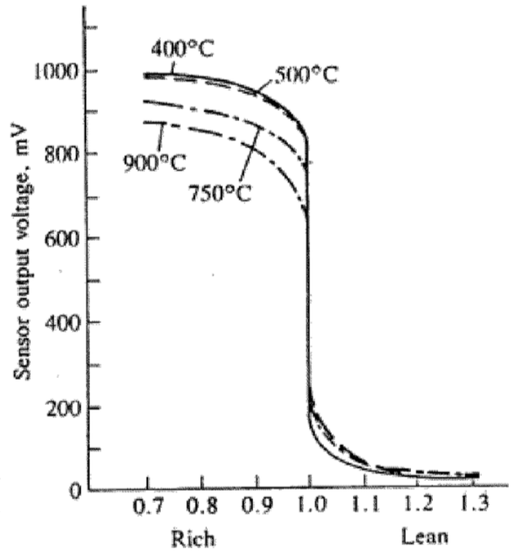


Modern catalyst peak efficiency is better than 97%

Fig 11-57

EGO (exhaust gas oxygen) sensor

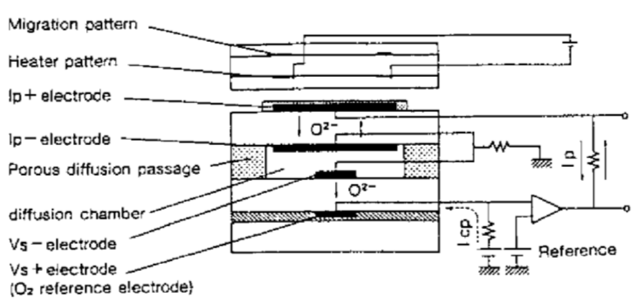


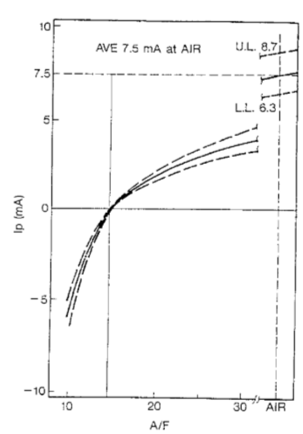


Exhaust	Metal	Ceramic	Metal	Air
p'_{O_2}	M_e	ZrO_2, Y_2O_3	M_e	p''_{O_2}

Nerst Eq.: V_o=(RT/4F)ℓn(P"$_{O2}$/P'$_{O2}$)

UEGO sensor





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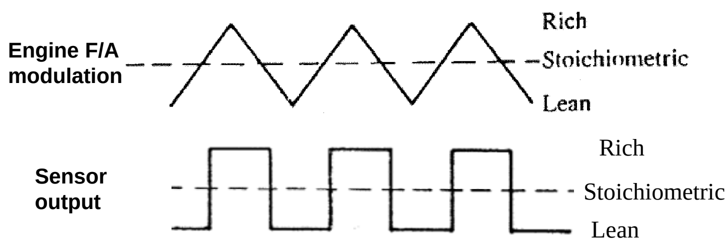
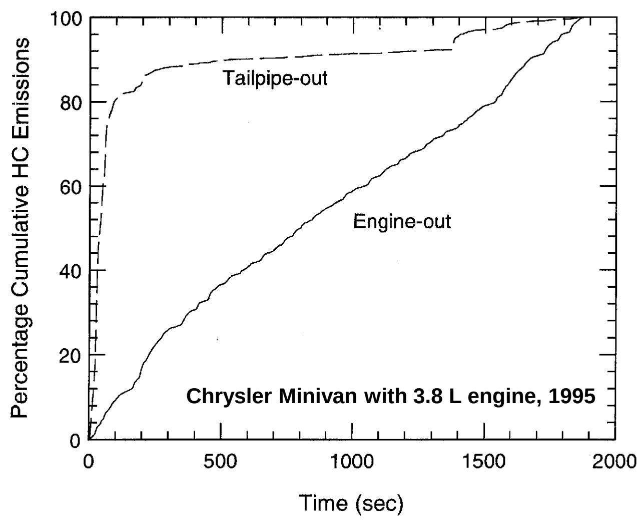
λ control strategy

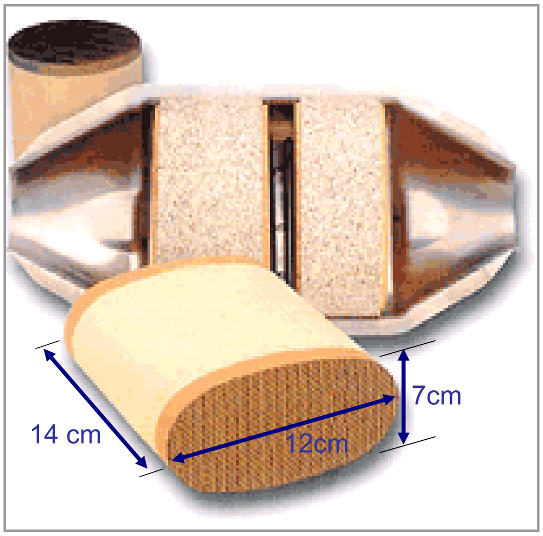
- Modulate A/F ratio around stoichiometric (typically by +/- 2% at around 1 Hz)
  - Enable EGO sensor to read average λ value
  - Make use of O2 storage capability of catalyst so that only average λ = 1 is needed



Engine out and Tailpipe out Cumulative HC emissions in FTP cycle

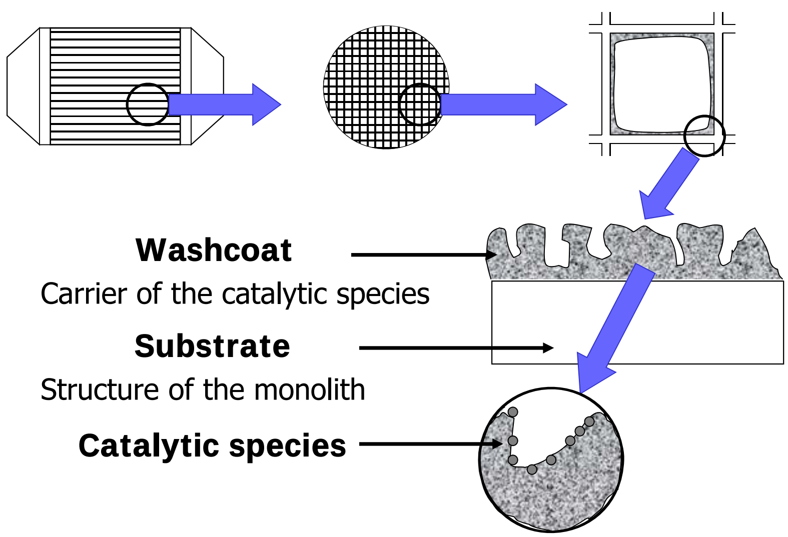


Monolithic reactors



(Typical dimensions for a 2.4 L engine)

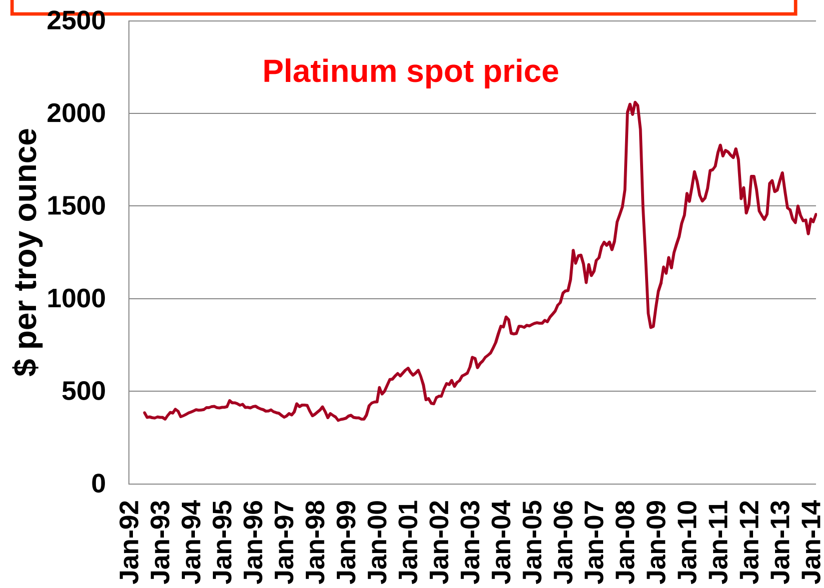
Monolithic catalysts' elements



Materials

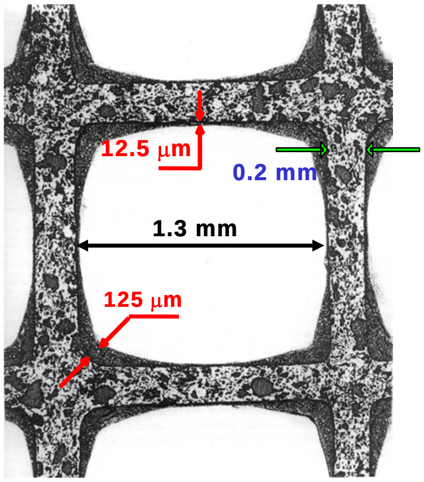
- Substrate
  - Synthetic cordierite ($2MgO \bullet 2Al_2O_3 \bullet 5SiO_2$)
- Washcoat
  - γ-alumina (γ- Al_2O_3)
- Active materials
  - Platinum (~ 1-2 g/L)
  - Palladium (~0.5-1 g/L; usually in front brick)
  - Rhodium (~0.2 g/L; for NOx and HC reduction)
  - Ceria (for oxygen storage)
    - $Ce_2O_3 + 1/2\ O_2 \leftrightarrow 2CeO_2$

Cost of catalyst active material



1 troy ounce = 31.1 g

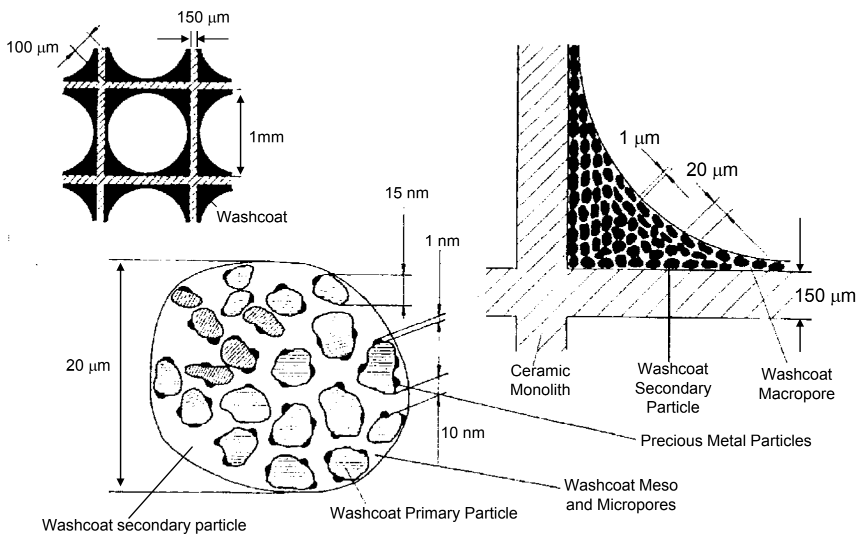
The washcoat



- Provides a high-surface area support to carry the catalytic species: 20 to 100 m^2/g
- Increases the resistance of the catalyst against deactivation processes
- Supports the catalytic function of the catalytic species

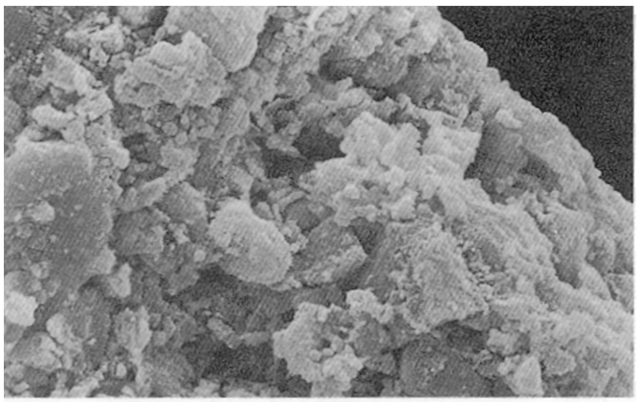
(Heck and Farrauto, *Catalytic Air Pollution Control, Commercial Technology*, Van Nostrand Reinhold, 1999)

The catalyst structure



(Lox and Engler, in *Environmental Catalysis*, Ed. by Ertl, Knozinger and Weitkamp, Wiley-VCH 1999)

The washcoat secondary particles



- **Secondary particle size** ~ 2 to 30 μm
- **Macro-pore dimensions** ~ microns

Scanning electron microscope view of washcoat
(Lox and Engler, in *Environmental Catalysis*, Ed. by Ertl, Knozinger and Weitkamp, Wiley-VCH 1999

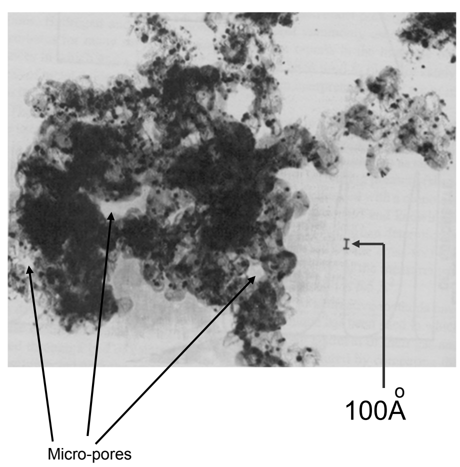
The catalytic species on the washcoat primary particles

- **Primary washcoat particle size** ~ 10-20 nm
- **Typical size of active material (e.g. Pt) on fresh catalysts**

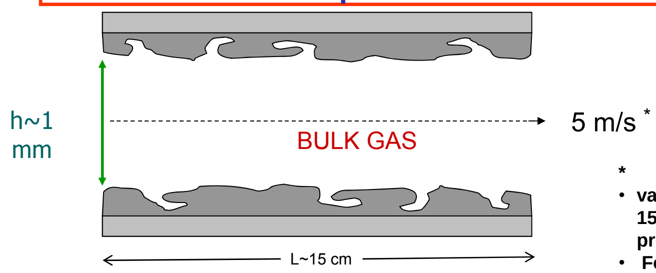
  less than 50 angstroms,

  (30 angstroms on the figure)
- **Atomic spacing of Pt atom** 2.8 angstroms
- **Average distance between two particles**

  65 angstroms
- **Micro-pore dimensions** ~ 10 to 100 nm



Transport time scale



*
- value for 2.0 L Engine at 1500 rpm, 0.4 bar intake pressure.
- For V_{cat} = 1L space velocity is 1×10^5/hr

T=900°K, p=1bar
Mass diffusivity = 4×10^{-5} m^2/s; mean free path = 200 nm;
molecular speed c = 450 m/s

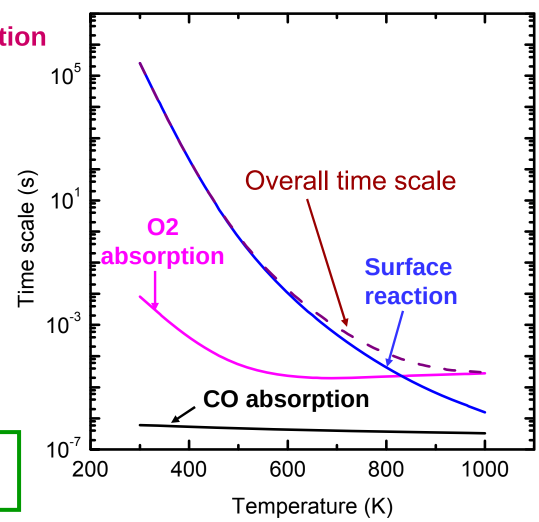
External diffusion time $\tau_{ext} = (h/2)^2/D$ = 6 ms
Internal diffusion time:
Macro-pore (size ℓ = 10 μm; continuum limit)
$\tau_{int,\ macro} = \ell^2/D$ = 2.5 μs
Micro-pore (size ℓ' = 100 nm; Knudson limit)
$\tau_{int,\ micro} = \ell'/c$ = 0.2 ns
Residence time L/U = 30 ms

Transport time dominated by external transport

Chemical time

Example: Catalytic CO oxidation

- O_2 absorption
  - $O_2 + 2\ S \leftrightarrow 2\ O^*$
- CO absorption
  - $CO + S \leftrightarrow CO^*$
- Surface oxidation and CO_2 release
  - $CO^* + O^* \leftrightarrow CO_2$

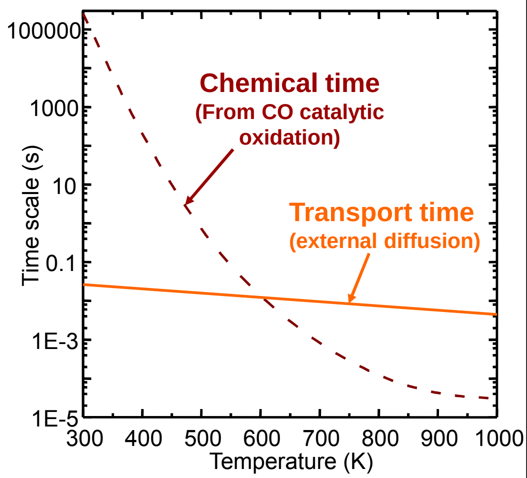


Overall time scale dominated by surface reaction

Limiting time scale

Conclusions:

- For fully warm-up catalyst, overall reaction is rate limited by external diffusion
- At low temperatures, surface chemistry is rate limiting



Catalyst deterioration

- Poisoning
  - Lead
  - Phosphorus (from oil additives)
  - Sulfur (fuel S from 300 to 30 ppm)
    - ➢effect reversible to a large extend
- Thermal degradation
  - Sintering (T>1000ºK)
    - ➢Active ingredients: loss of reactive surface
    - ➢γ-alumina: occluding the active ingredients
    - ➢Oxidation of Rh
- Glazing — lubrication oil covering catalyst
- Erosion