Outline

- ✓ *Emission characteristics and impact*
- ✓ *Three-Way Catalysts principles and targets*
  - *Oxygen Storage*
  - *Thermal stability*
  - *Noble metal loading*
- ✓ *Gasoline vs. Diesel engine*
- ✓ *Lean NOx catalysts*
- ✓ *Particulate*
- ✓ *Conclusions*

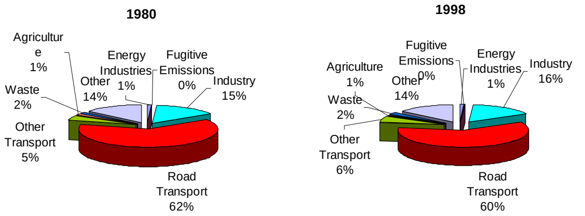
Outline

Nature and origin of atmospheric pollutants

- **STATIC SOURCES: POWER PLANTS**
- **MOBILE SOURCES: AUTOMOBILES**
- **AUTOMOTIVE EXHAUST:**
  - **UNBURNT/PARTIALLY BURNT HYDROCARBONS (HC) to be oxidized to CO_2**
  - **CARBON MONOXIDE (CO) to be oxidized to CO_2**
  - **NITROGEN OXIDES (NOx) to be reduced to N_2**
  - **OTHERS: PARTICULATE, LEAD AND SULFUR COMPOUNDS**

Exhaust

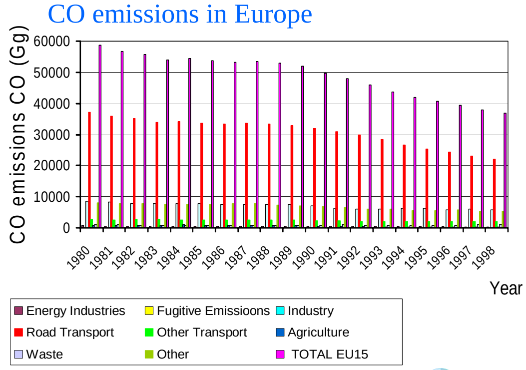
CO emissions in Europe



- 1980: 350.000.000.000 km-passenger
- 1998: 540.000.000.000 km-passenger (+55%)

Exhaust

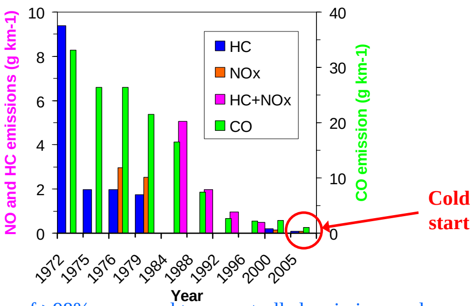
CO emissions in Europe



CO from transport decreased by 40%.

Exhaust

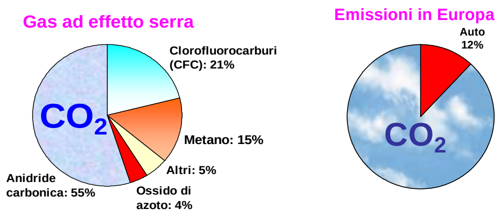
Legislation limits in Europe



Reduction of >98% compared to uncontrolled emissions and durability of 180.000 km^{-1} is required by 2004 in US (TIER2 phase)

Exhaust

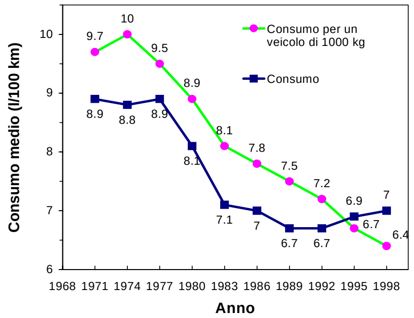
Greenhouse effect gases



- Automotive emissions significantly contribute to greenhouse effect
- Vehicle consumption must decrease

Exhaust

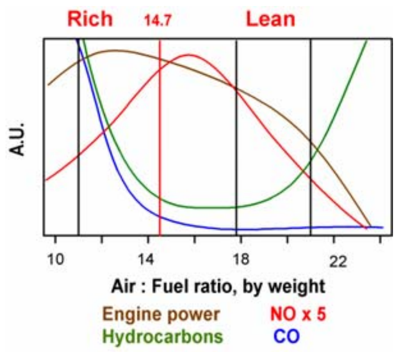
Average passenger car consumption (EU)



High efficiency engines are needed : diesel and lean-engine (up to 35% fuel economy)

Exhaust

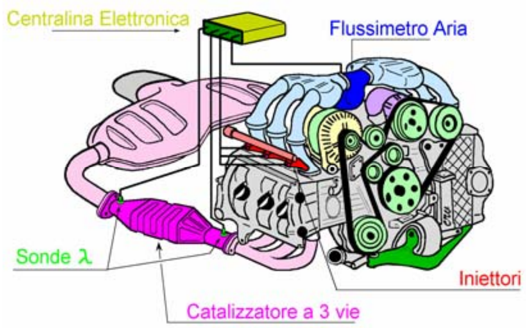
Emissions depend on air-to-fuel ratio (A/F)



A/F = 14.7 stoichiometric ratio (oxidants = reductants)

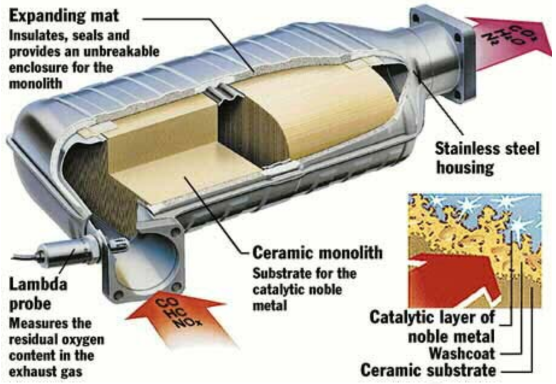
TWC

Engine emission control

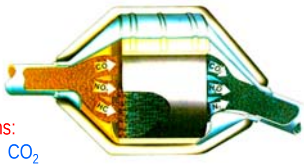


TWC

TWC: Scheme of a Catalytic converter



TWC: How the exhaust is converted?



Oxidation Reactions:

$CO + ½ O_2$ ➔ CO_2

"HC" + O_2 ➔ CO_2 + H_2O

Reduction Reactions:

$NO + ½ CO$ ➔ $½ N_2 + CO_2$

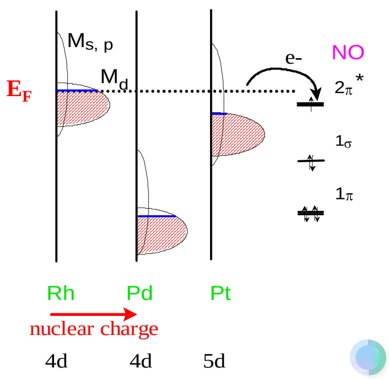
"HC" + 2 NO ➔ $CO_2 + N_2 + H_2O$

Catalyst:

Pt (Pd) / Rh / Al_2O_3 / CeO_2 Pt/Rh = 5/1

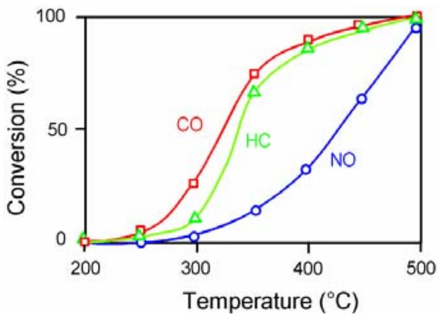
TWC

Why Rhodium in the TWCs?



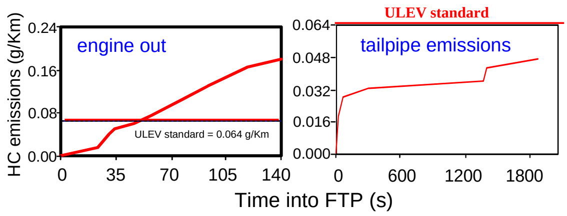
TWC

Drawbacks: Typical light-off curve for a TWC



TWC

Vehicle cumulative exhaust emissions: close coupled catalyst



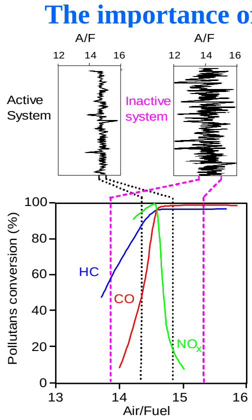
About 70% of HC is emitted during the cold start: need of minimizing heating time

Properties of a suitable catalyst (year 2005)

- Highly active
  - Space velocity (GHSV)= 50.000-150.000 h^{-1}
    20-50 liters of exhaust to be converted (>98%) in 1 sec per liter of catalyst
- Highly selective
  - Only H_2O, CO_2 and N_2 as products
- Thermally stable
  - Working temperatures 300-1100°C
- Long life
  - 180.000 km / On-board diagnostics (OBD)

TWC

The importance of the A/F ratio:

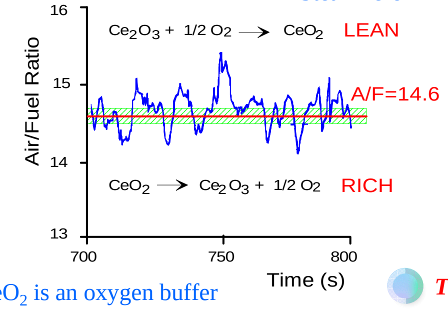


- A/F varies in the engine, which affects the conversions.
- Better A/F control = high pollutant conversion.
- CeO_2 act as an oxygen buffer through its Ce^{4+}/Ce^{3+} redox couple (OSC)

TWC- OSC

TWC: Role of CeO_2

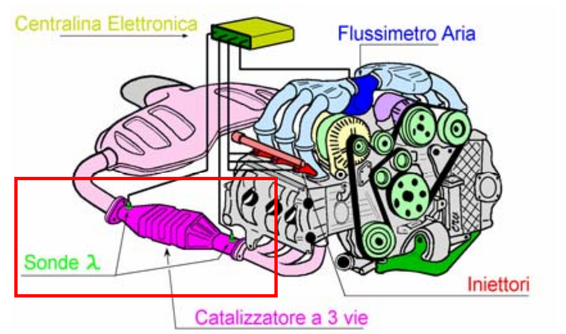
- Oxygen storage
- Water gas shift
- Stabilisation of metal particles
- Steam reforming



CeO_2 is an oxygen buffer

TWC- OSC

Engine emission control: On board diagnostics



TWC

High efficiency gasoline and diesel engines (Lean NO_x)

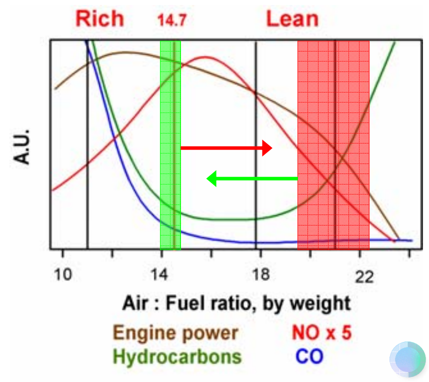
- **Lean technology (Excess of air: A/F > 14.6)**

  $HC + NO_x + O_2 \Rightarrow N_2 + H_2O\ CO_2$

  - **fuel economy (15-35%)**
  - **combustion efficiency**
  - **power output**
  - **and it decreases CO_2 emissions**
  - **BUT : 1000 ppm NO, 1000 ppm HC and 5-12% O_2 : extreme selectivity is needed**

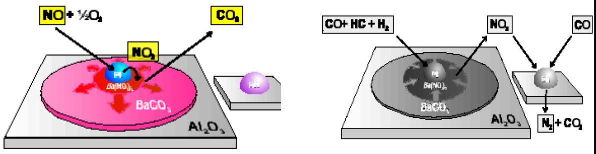
Lean NO_x

NO_x storage(60 sec) – reduction (1sec) concept



Lean NO_x

NO_x-Storage - Reduction Catalysts



- NO_x are fixed on BaO as $Ba(NO_3)_2$ under oxidizing conditions (A/C> 14.6)
- NO_x are reduced on TWCs under reducing conditions (A/C<14.6)

Lean NO_x

Drawbacks of Lean technology

- **Lean Burn Catalysts:**
  - **Cu/Co-zeolite catalyst:** **hydrothermal stability**
  - **Pt/Al_2O_3:**
    - narrow operating regime
    - low N_2 selectivity - high N_2O formation
- **NO_x/Storage/Reduction**
  - **NO_x storage on support (BaO): lean**
  - **NO_x reduction on TWCs: rich**
  - – **sulfur tolerance of the trap**
  - – **BaO dissolution during the preparation**

Extensive research is needed

Lean NO_x

Particulate matter

Mixture of:

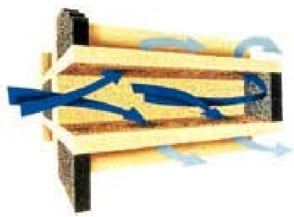
✓Solid (soot, metals, ash, minerals)

✓Liquid (hydrocarbons, sulphuric acid,water)

- Variable composition
- Poorly reactive

Diesel

Particulate honeycomb filter

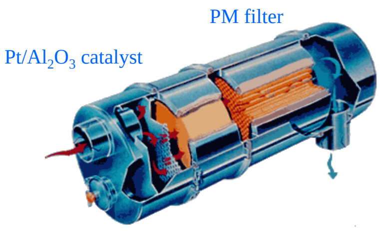


Filter regeneration is exothermic =

thermal sintering/plugging of the filter

Diesel

Continuously regenerating trap



- (1) $NO + ½ O_2 = NO_2$
- (2) $NO_2 + PM = CO_2 + H_2O + N_2$

Sulphur tolerance is an issue

Diesel

AND THE FUTURE ?

Are the Three Way Catalysts the Solution?

- Improvements in durability and low NM loading are needed: Best solution available
- Substantial improvement of lean-NO_x technology is needed, NO_x-storage/reduction catalysts being the most reliable technology
- Continuously regenerating trap appears very promising for PM removal

Conclusion

Auto “pulita” può essere costruita trasformando il carburante in idrogeno per alimentare una cella a combustibile che genera la corrente per il motore elettrico.