Ecole Polytechnique Fédérale de Lausanne

EPFL

Paul Scherrer Institut

PSI

Catalysis for Emission Control and Energy Processes - ChE-410

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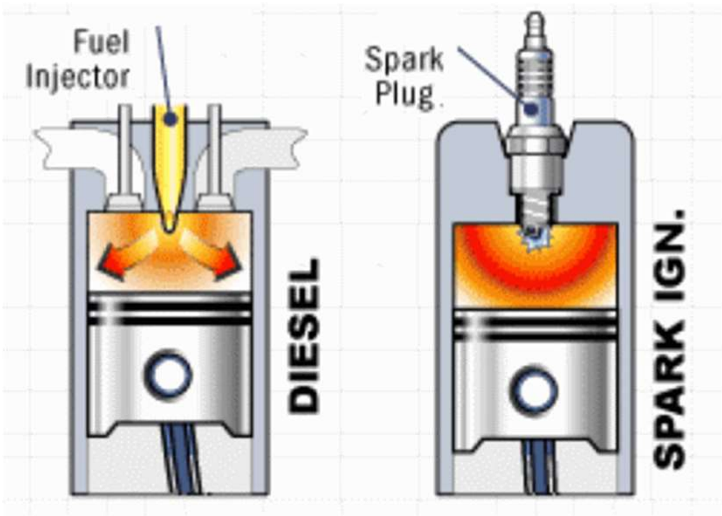
Different fuel and engine – different aftertreatment

diesel gasoline



- Diesel is atomized
- High air/fuel ratio
- compression is sufficient to ignite
- WARM exhaust, 200-500°C

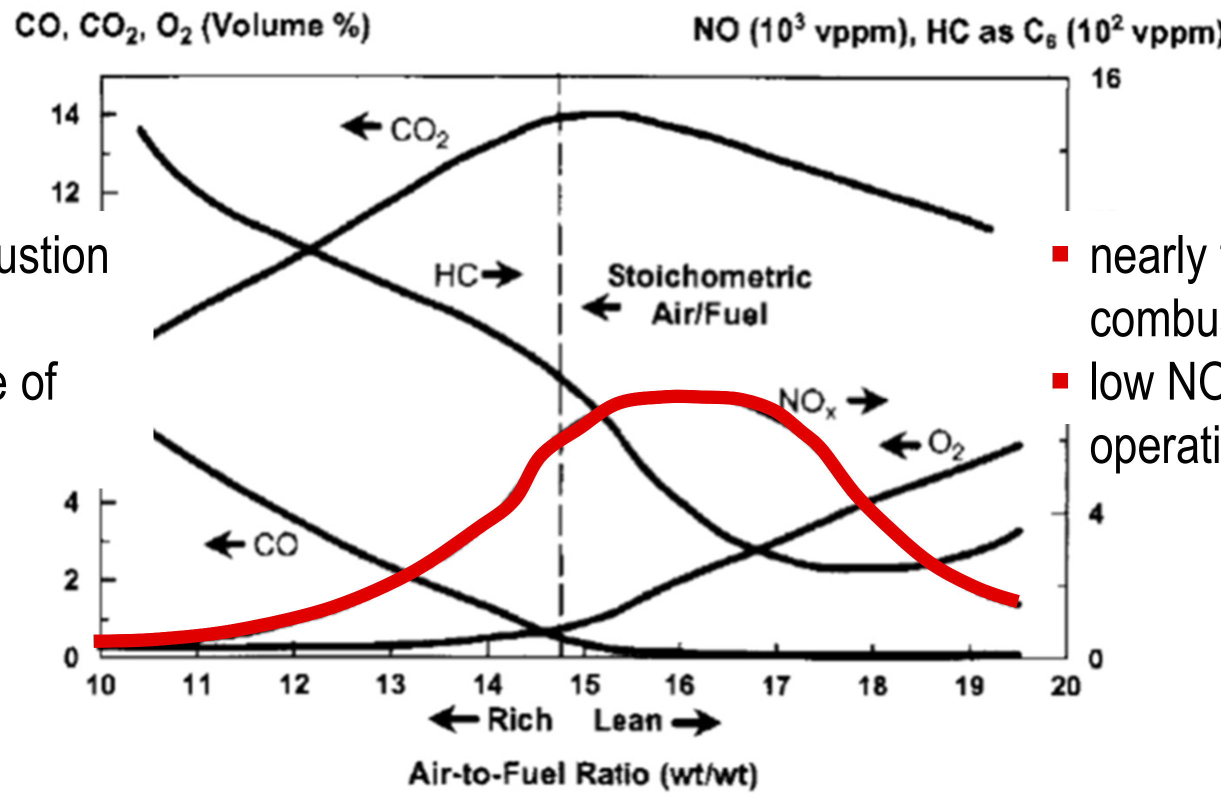
- Gasoline is more volatile
- Low air/fuel ratio
- ignition is induced (spark)
- HOT exhaust, 500-800°C

source: ccrc.kaust.edu.sa

Gasoline exhaust gas

$$CH_x + (1 + x/4)O_2 \rightarrow CO_2 + x/2H_2O + \text{heat}$$

- partial fuel combustion (O_2 deficiency)
- low NO_x because of lowe flame T



- nearly full fuel combustion
- low NO_x because of low operation T

- Exhaust contains variable amounts of CO (1-2 vol%), unburnt HC (500-1000 ppm) and H_2 (0.3 mol/mol_{CO})
- High T combustion produces NO_x (NO, NO_2, N_2O; 100-3000 ppm) from N_2 in the air

Air pollution

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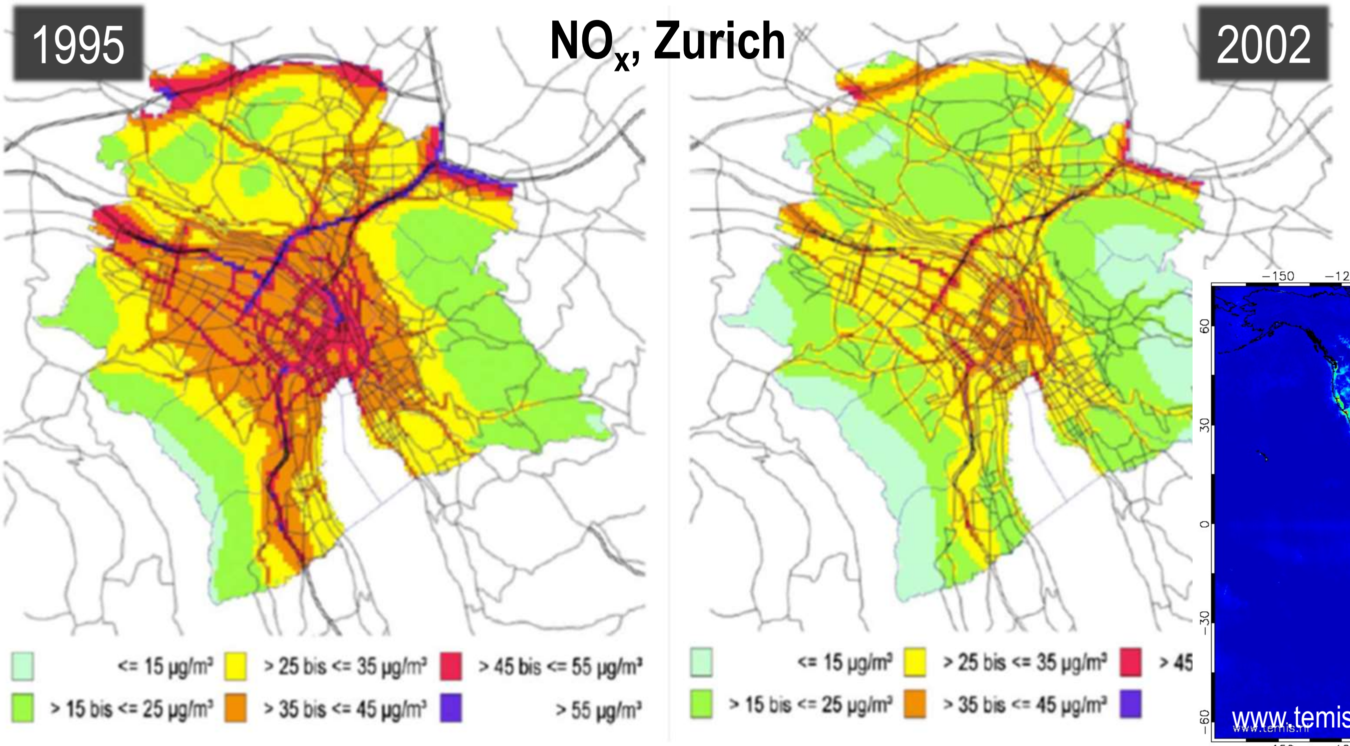
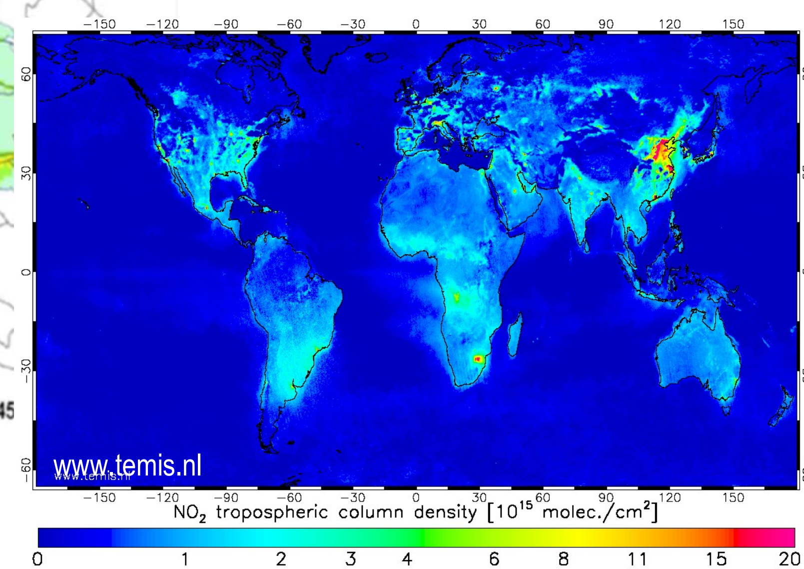
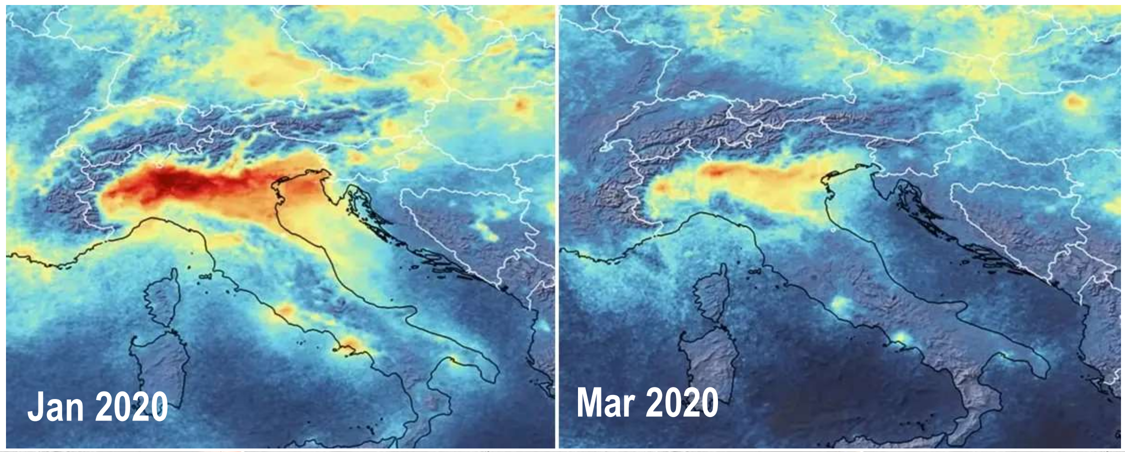
- 1970 – Clean Air Act, USA
- 1976 – CO and HC conversions larger than 90% required, 50’000 miles – high NO_x standards
- late1980’s – catalytic converters in Europe
- 1993 – introduction of European legislation (EuroI)
- 1996 – emissions for 100’000 miles (USA)
- 2014 - EuroVI

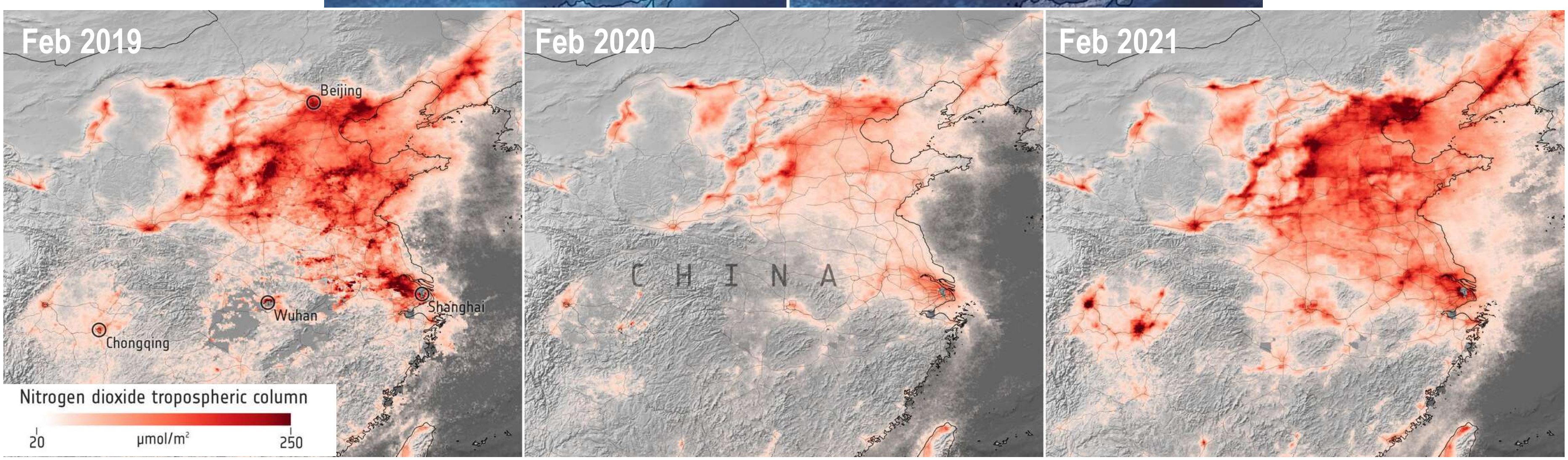




Guzzella, Ann. Rev. Control 33 (2009) 1; source: Dept. of Health and Environment ZH

NO_x emissions





Source: the European Space Agency

The basic reactions

- Oxidation of CO and unburnt hydrocarbons

$$\mathbf{C_yH_n} + (1+n/4)O_2 \longrightarrow yCO_2 + n/2H_2O$$

$$\mathbf{CO} + 0.5O_2 \longrightarrow CO_2$$

$$CO + H_2O \longrightarrow H_2 + CO_2$$ water gas shift reaction (WGS)

- Reduction of NO_x (NO/NO_2)

$$\mathbf{NO} + CO \longrightarrow 0.5N_2 + CO_2$$

$$NO + H_2 \longrightarrow 0.5N_2 + H_2O$$

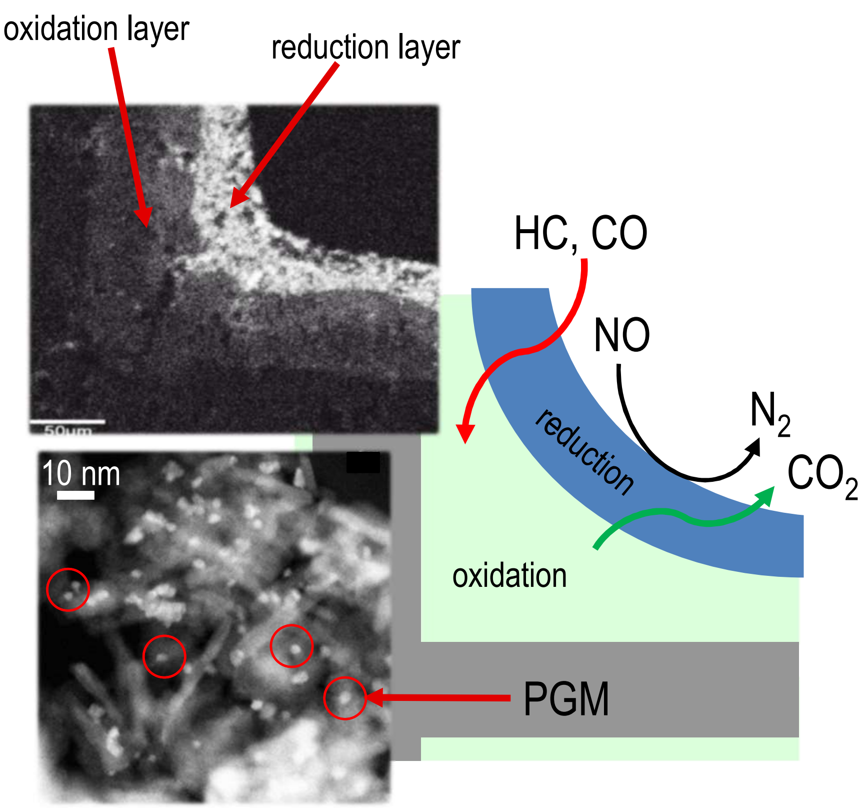
$$(2 + n/2)\mathbf{NO} + C_yH_n \longrightarrow (1+ n/4)N_2 + yCO_2 + n/2H_2O$$

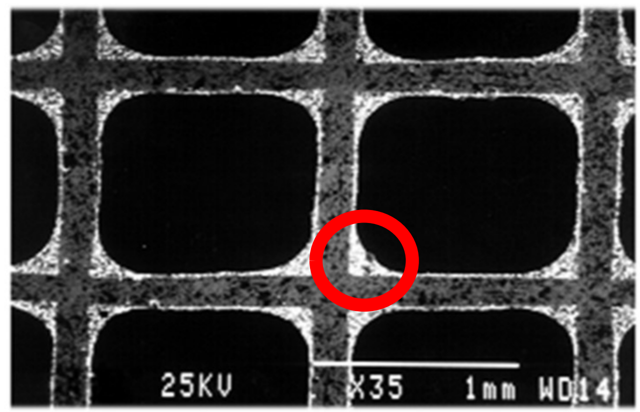
- Ancillary reactions

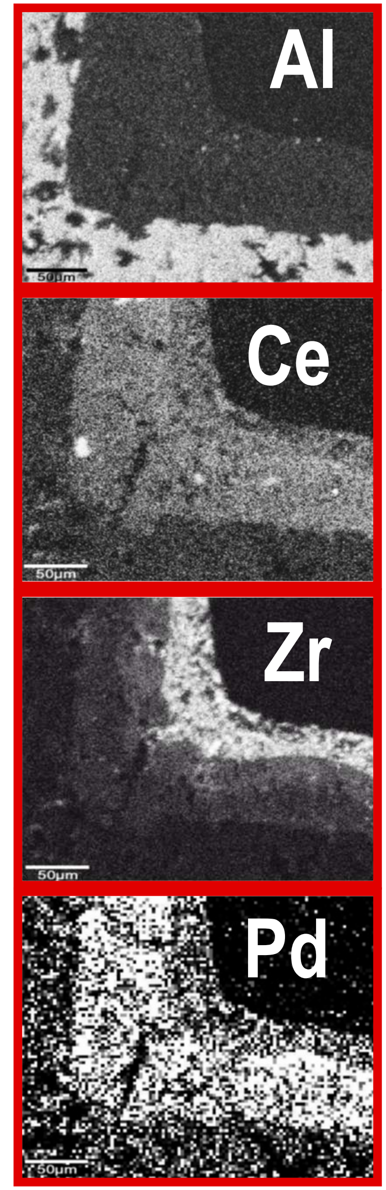
$$C_yH_n + yH_2O \longrightarrow (y + n/2)\, H_2 + yCO$$ steam reforming (SR)

Composition of a TWC

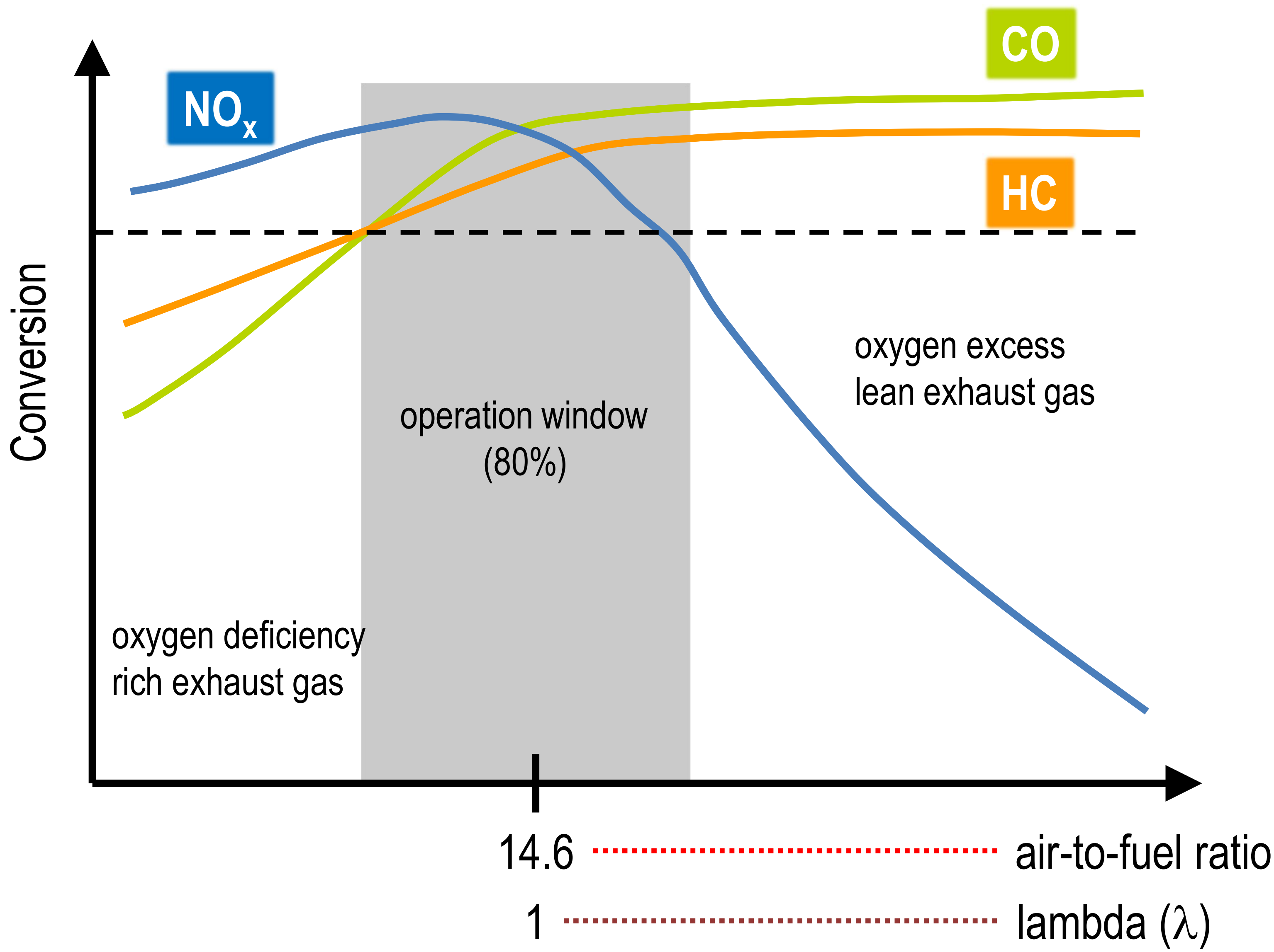
- Platinum group metals (PGM): Pt, Pd, Rh (0-1 wt.%)
- Metal oxide support: Al_2O_3
- Oxygen storage component: CeO_2, ZrO_2, $Ce_xZr_{1-x}O_2$
- Honeycomb material: cordierite ($Mg_2Al_4Si_5O_{18}$), Al_2O_3
- Promoters, stabilizers (La, Ba, Ni, rare earth oxides (REO))







Three pollutants in one shot



Terms and definitions

- Stoichiometric combustion in gasoline engines: 14.6 kg air for 1 kg gasoline (CH_x with x= 1.85), thus the stoichiometric air-to-fuel (A/F) ratio is:

A/F = 14.6

- A/F ratio is also termed λ (lambda):

λ = dosed air mass / required air mass

λ = 1, dosed air mass equals the required air mass, stoichiometric point (A/F = 14.6)
λ < 1, too less air/oxygen → **rich** combustion (A/F < 14.6)
λ > 1, too much air/oxygen → **lean** combustion (A/F > 14.6)
λ ~ 1.4, ignition limit
λ = 1.15-1.25, low fuel consumption
λ = 0.9-0.95, maximum engine power

Terms and definitions

- Definition of lambda (engine)

$$CH_x + aO_2 + bN_2 \longrightarrow bCO_2 + dH_2O + eH_2 + fCO + gC_3H_6 + hC_3H_8 + mNO$$

$$\lambda = \frac{(4\chi + x(2 - 2[H_2] - 2[CO] - 8[C_3H_6] + 2[O_2] + [NO])[O_2]}{(4 + x)([H_2] + [CO] + 9[C_3H_6] + 10[C_3H_8] - 2[O_2] - [NO] + \chi[O_2])}$$

with $\chi = 2 - [H_2] - [CO] + [C_3H_6] + 2[C_3H_8]$

- More practical parameter (e.g. laboratory)

$$\text{red/ox} = \frac{[CO] + [H_2] + (2+0.5n/y)[C_yH_n]}{[NO] + 2[O_2]}$$

the redox ratio, or stoichiometry number (R or also S)

source: Brinkmeier, PhD Thesis, Stuttgart

Evolution

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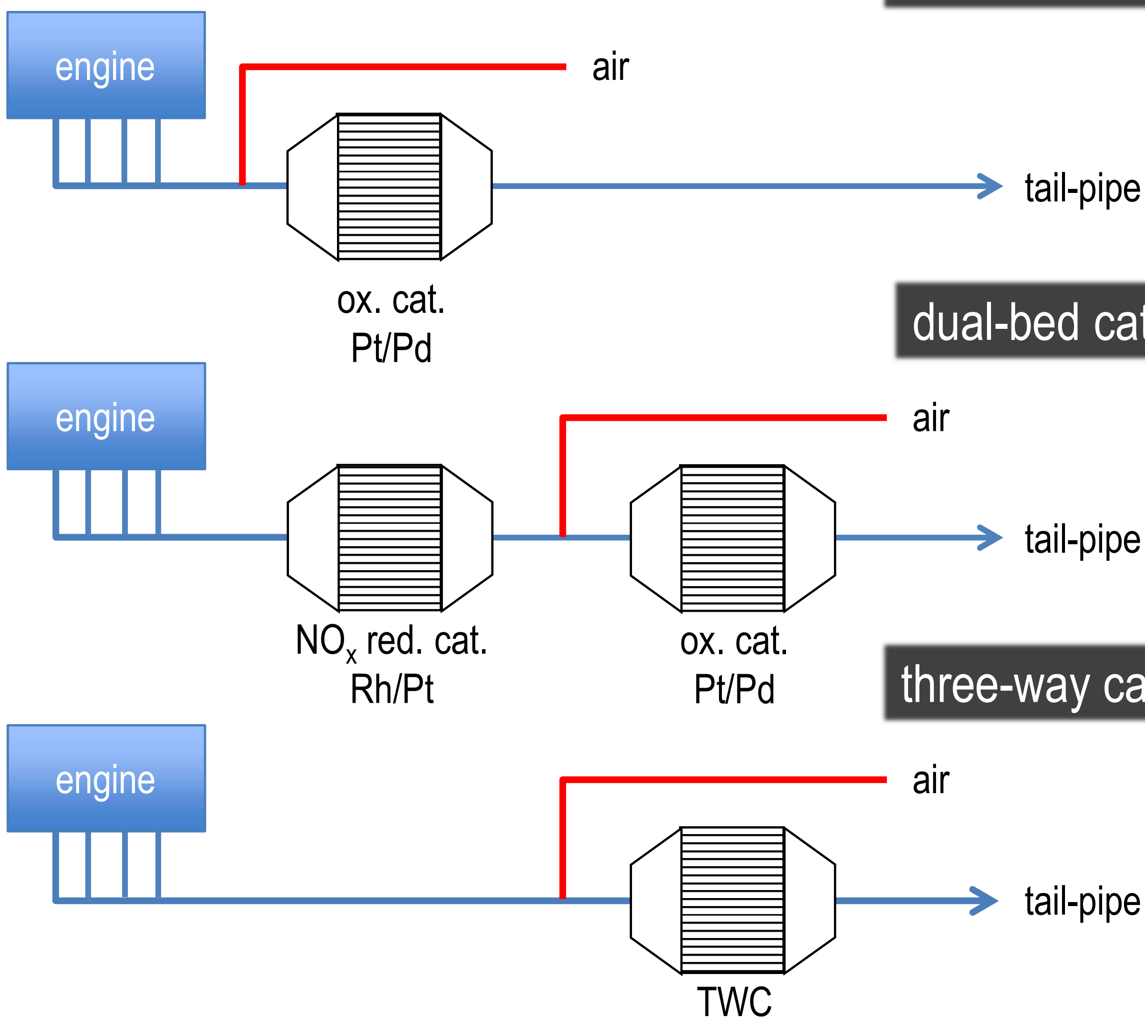
oxidation catalyst

dual-bed catalyst

three-way catalyst |TWC



Main reasons
- increasingly stringent regulations
- precious metal price
- quality of fuel (S)
- air/fuel control

H.S. Gandhi (1941-2010)

precise feedback controlled air+fuel metering system needed
- electronic fuel injection
- oxygen sensor
- microprocessor to control the loop

Evolution

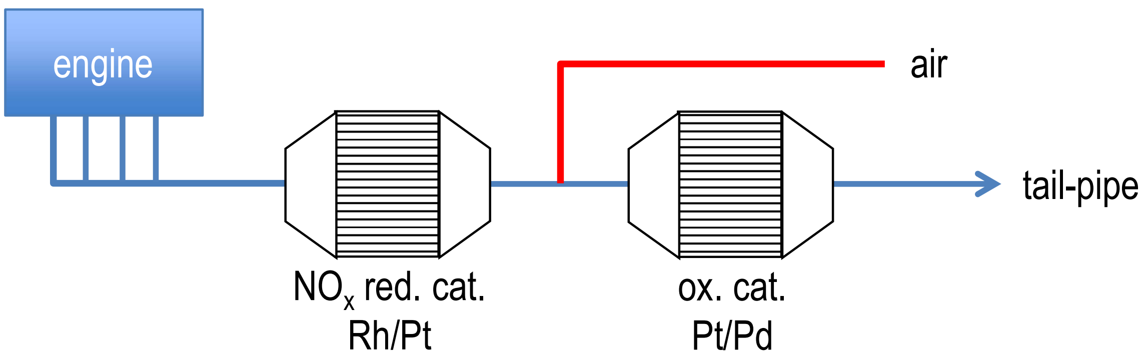
EPFL

First generation (1976-1979)

- Oxidation catalyst only
  - Noble metals (Pt, Pd,) excellent oxidation catalysts, but costly
  - Transition metals (Cu, Cr, Ni, Mn…) also good oxidation catalysts, but
    - much less active than noble metals (larger volume required)
    - more susceptible to poisoning (high [S])
- First generation **oxidation catalyst**: Pt (and/or Pd) on stabilized γ-Al_2O_3 (La or Ba)

Evolution

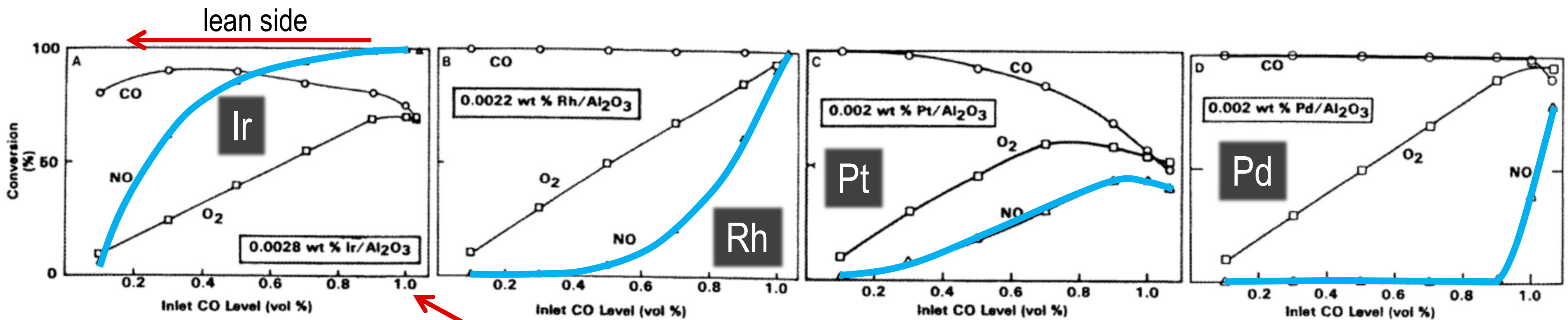
Dual bed automotive catalyst



- Introduced with introduction of NO limits
- Engine runs slightly rich

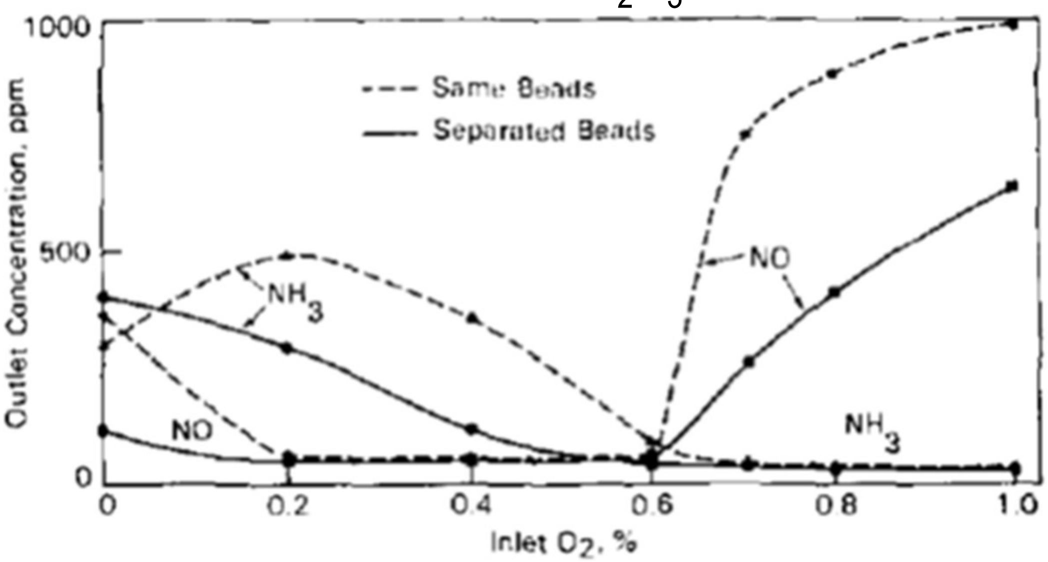
- Ru as possible reduction metal, but
  - forms RuO_2 > 700°C which is volatile
  - stabilization attempts with perovskite-type oxides ($MRuO_3$, M= Ba, Sr, La)
    - NO_x reduction mainly to NH_3
    - lower NO_x reduction activity
  - never commercialized
- Pt and Pd reduce NO_x preferentially to NH_3

NO reduction by Rh



Taylor et al., J. Catal. 63 (1980) 53

Rh-Pd/Al_2O_3



conversions @ 400°C

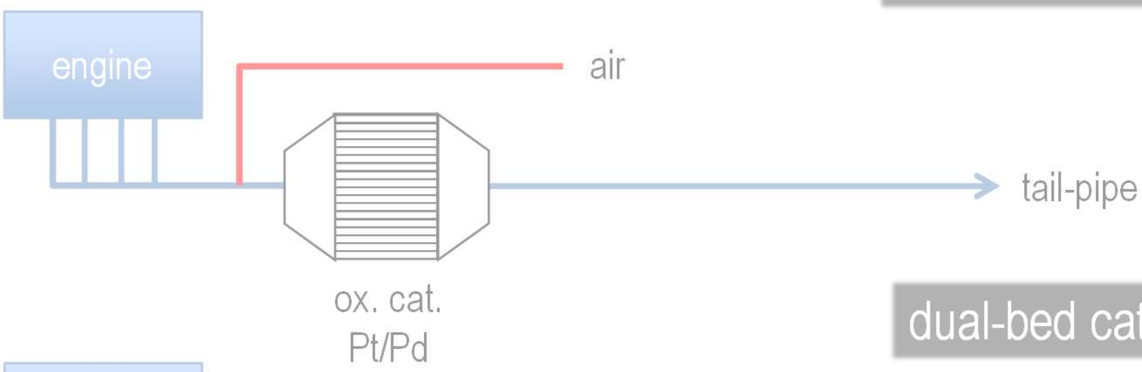
	HC	CO
Rh	41	86
Rh+Pt	83	95
Rh+Pd	93	98

- separation of Rh and Pd/Pt is required → precursor of modern double layer washcoat

Schlatter et al., J. Catal. 49 (1975) 42

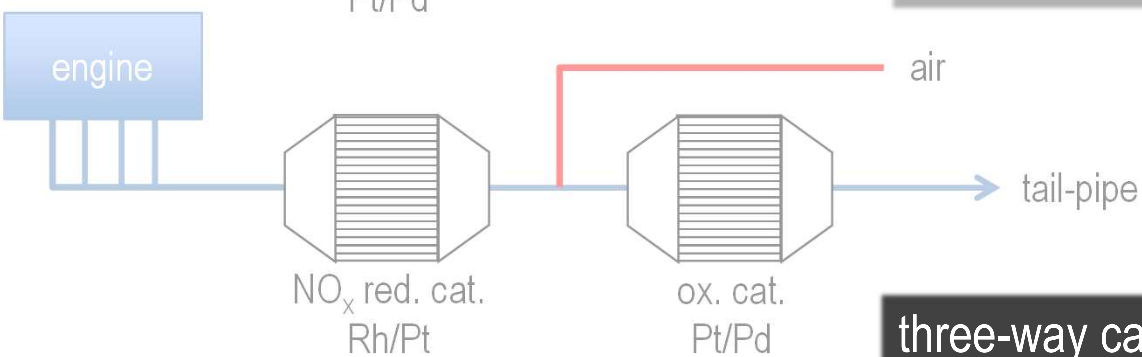
Evolution

oxidation catalyst

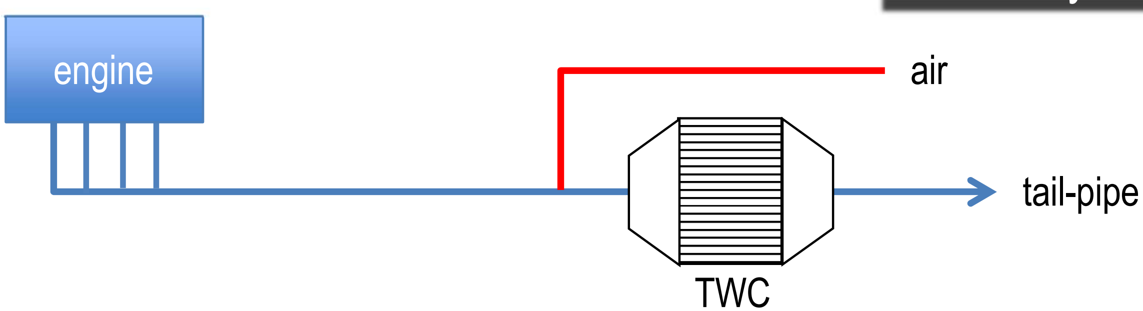


Main reasons
- increasingly stringent regulations
- precious metal price
- quality of fuel (S)
- air/fuel control

dual-bed catalyst

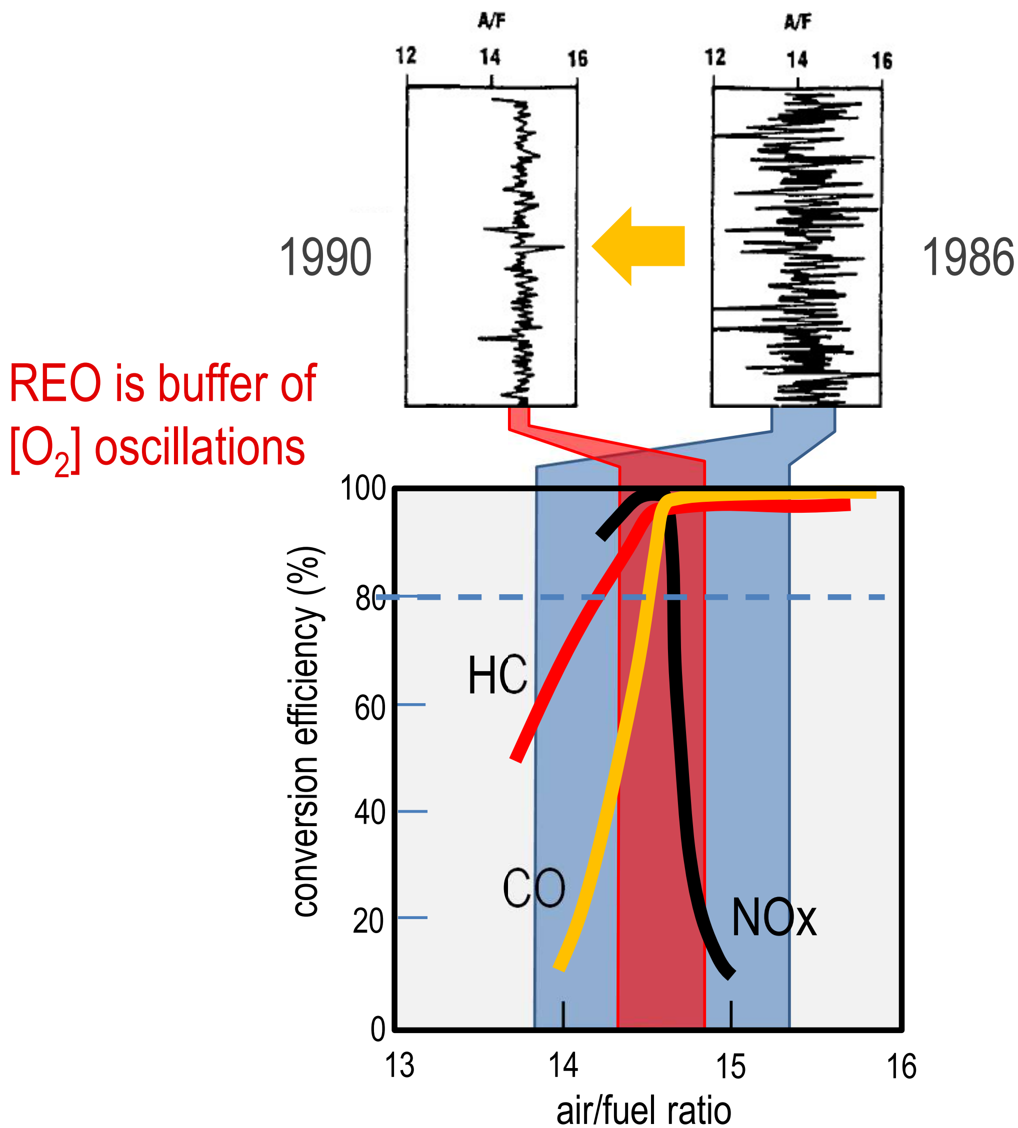


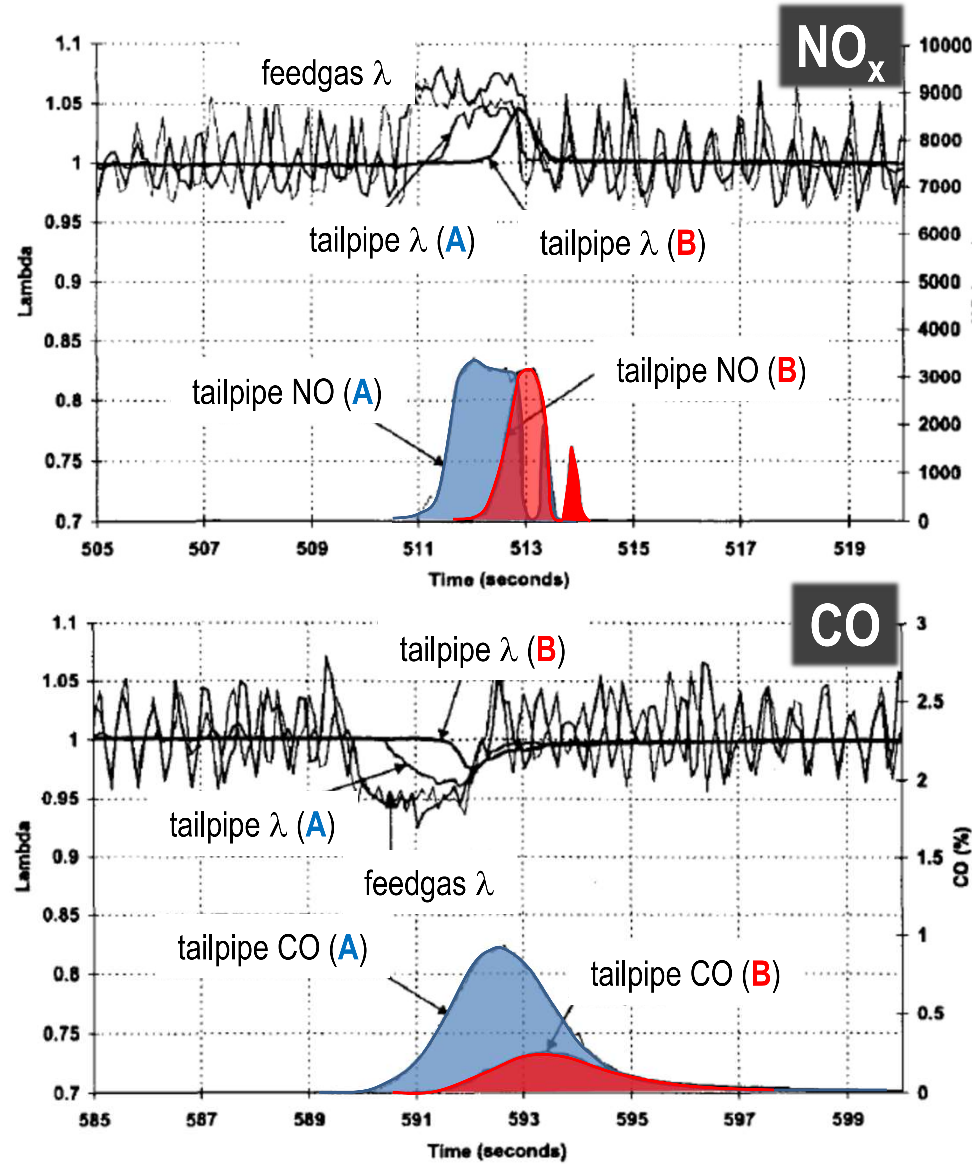
three-way catalyst |TWC



precise feedback controlled air+fuel metering system needed
- electronic fuel injection
- oxygen sensor
- microprocessor to control the loop

Closed-loop control





- improvements due to addition of oxygen storage compounds (rare-earth oxides, REO) and improved control

Why precious metals?

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- Pt, Pd and Rh are noble enough to stay metallic under most TWC reaction conditions
- resistance to poisoning (e.g. less stable sulfates)
- thermal stability
- non-volatile oxides
- lower interaction with support

…compared to transition oxides

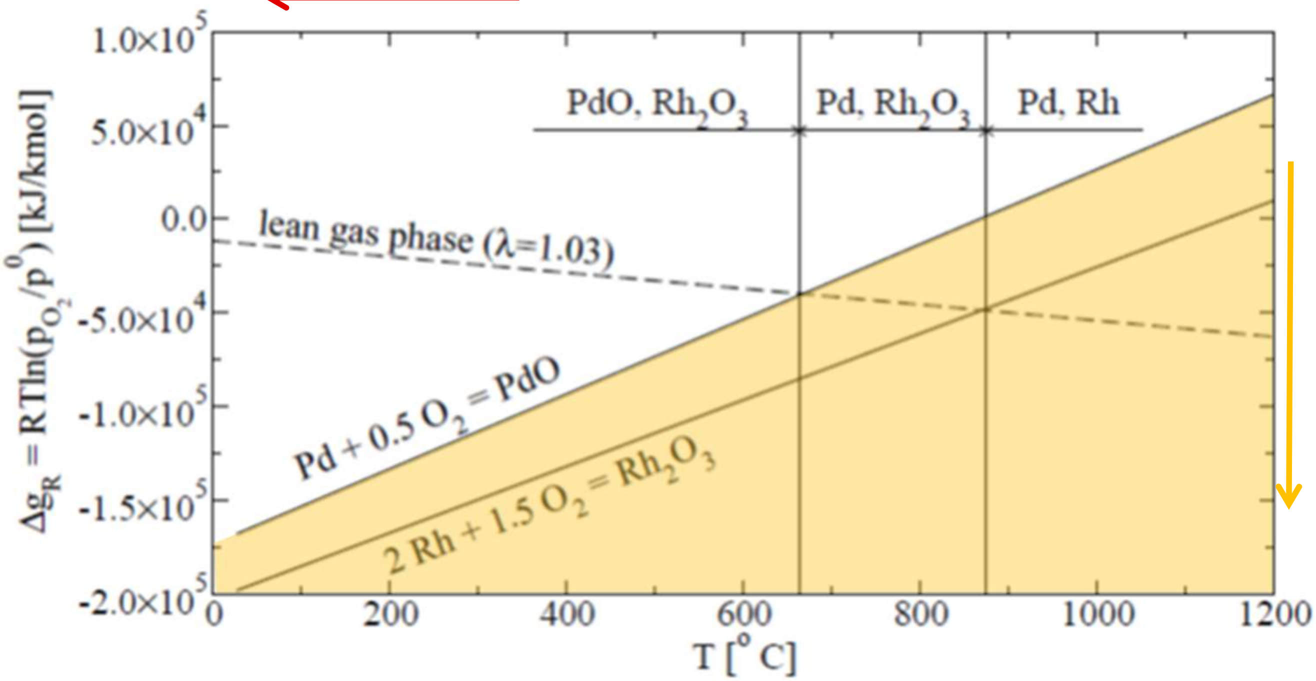
	MP (°C)	Red. potential $Me^{n+} \rightarrow M^0$ (n)	Oxide stability	
Pt	1772	1.19 (2)	Unstable	
Ir	2410	1.16 (3)	moderately stable	Sintering and loss of Ir
Pd	1552	0.92 (2)	Stable	
Rh	1966	0.76 (3)	Stable	
Os	3054	- (2)	Very volatile	Loss of Os
Ru	2310	0.45 (2)	Very volatile	Loss of Ru
Cu	1084	0.34 (2)	Stable	Sensitive to Pb, S, halide
Co	1495	-0.28 (2)	Stable	
Ni	1453	-0.30 (2)	Stable	Sensitive to Pb, S, halide
Fe	1535	-0.44 (2)	Stable	

Twigg, Catal. Today 117 (2006) 407

Precious metals: metal or metal oxide?

- Thermodynamics of: $nMe + mO_2 \rightarrow Me_nO_{2m}$

low T → ΔG<0, oxidation possible



metal is favored

at sufficiently high T ΔG>0 → MeO spontaneously reduces

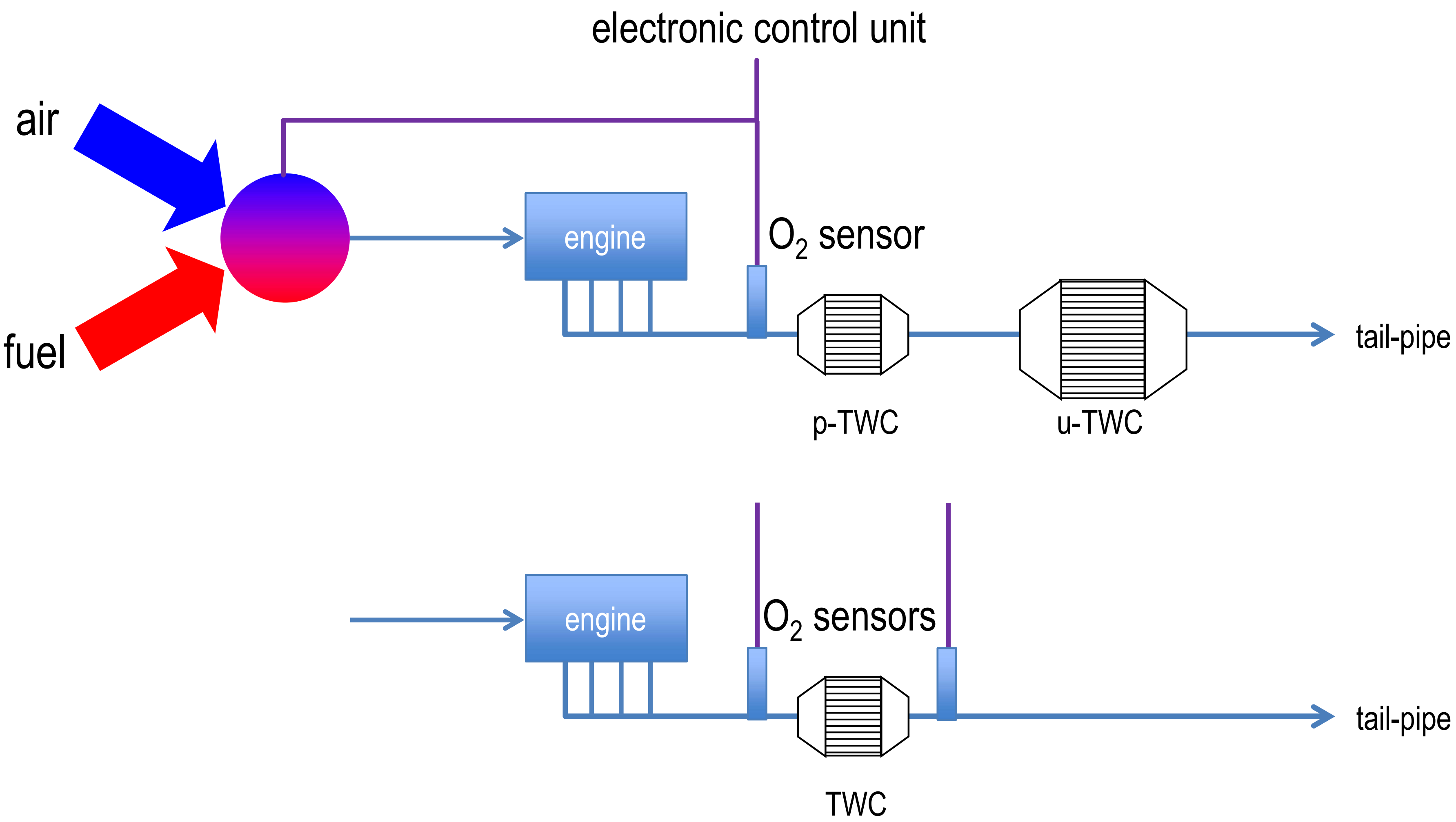
- under the redox lambda oscillations, Pd and Rh will repeatedly (partially) oxidize/reduce

source: Brinkmeier, PhD Thesis, Stuttgart

Evolution

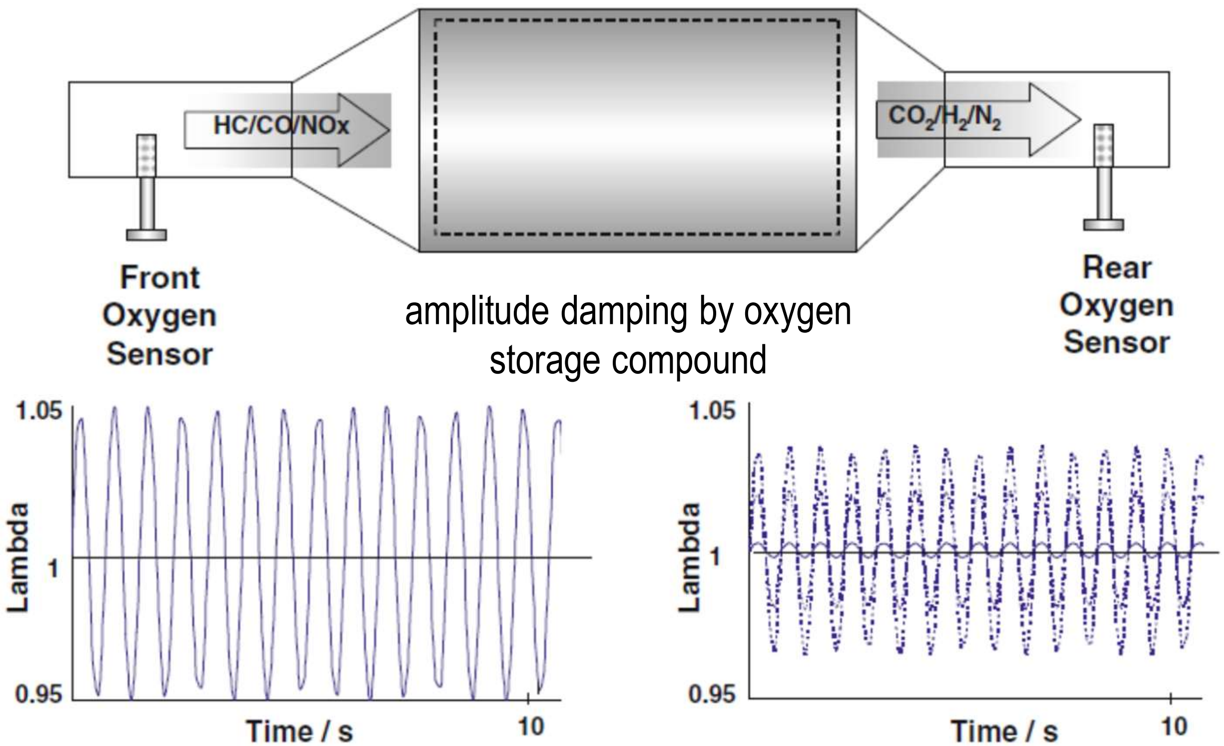
EPFL

- Today



On Board Diagnostics - OBD

1- short lean period: OSC component is fully oxidized
2- short rich phase
3- the time taken for the gas to become rich after the catalyst is the measure of OSC



active catalyst – large difference front-rear EGO
spent catalyst – small difference front-rear EGO

Characterization of a catalyst

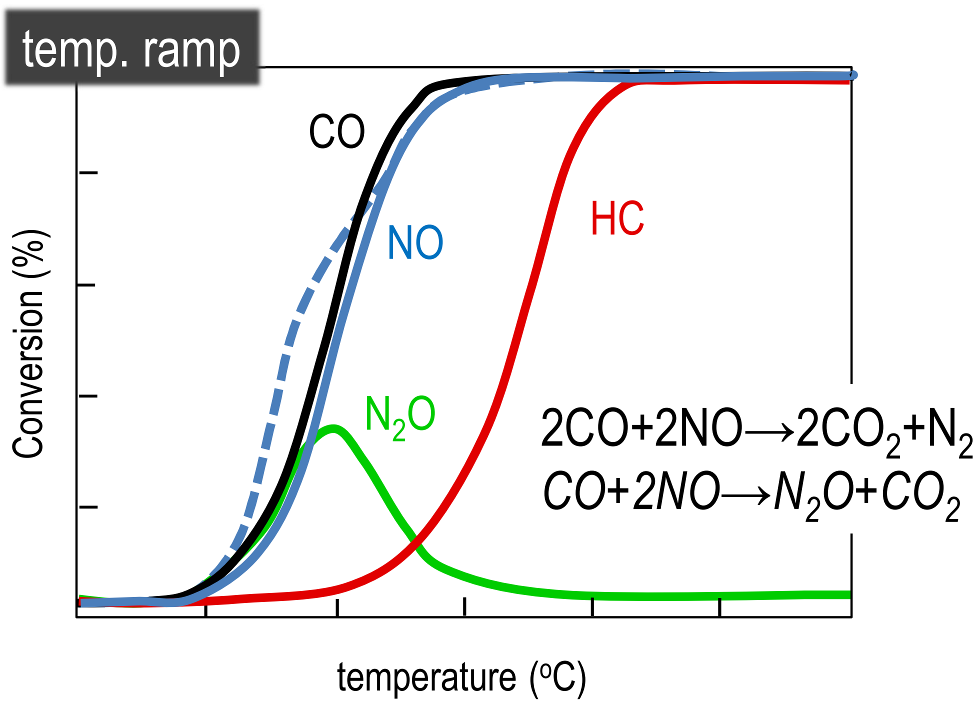
The following properties can be derived at laboratory scale:

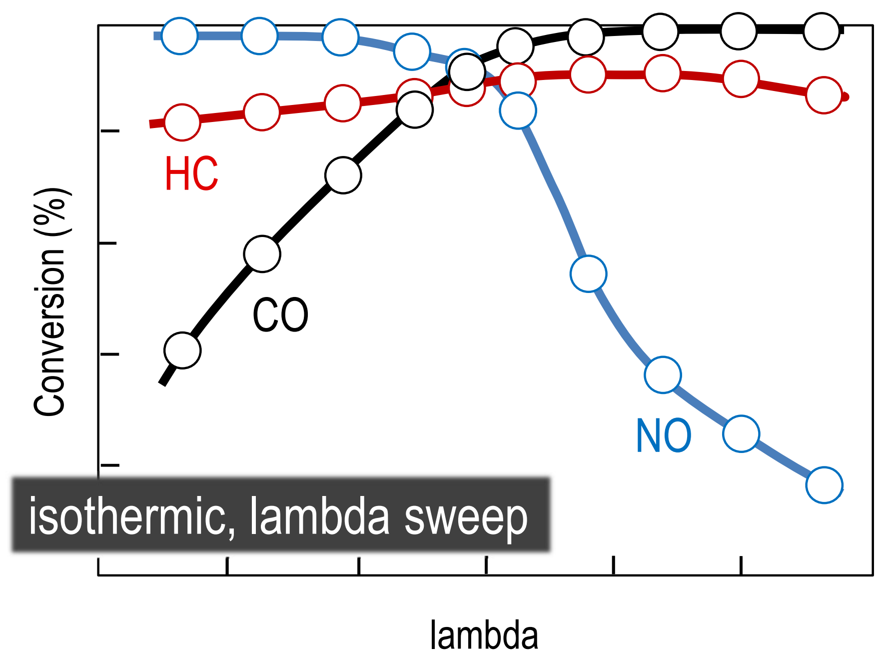
- **Activity**
  - CO, NO and HC conversion
  - temperature ramp
  - lambda sweep
- **Stability**
  - thermal/hydrothermal ageing (high temperature)
  - poisoning
- **Selectivity**
  - product selectivity: N_2, N_2O and NH_3
- **Oxygen Storage Capacity (OSC)**

Temp.: 200 - 1000^{o}C, typically 200-600^{o}C
GHSV: typically 50000-200000 h^{-1} (for monoliths)
Feed composition: variable CO, NO, HC (various), H_2 and O_2, 5-10 vol% H_2O, 5-10 vol% CO_2 and N_2

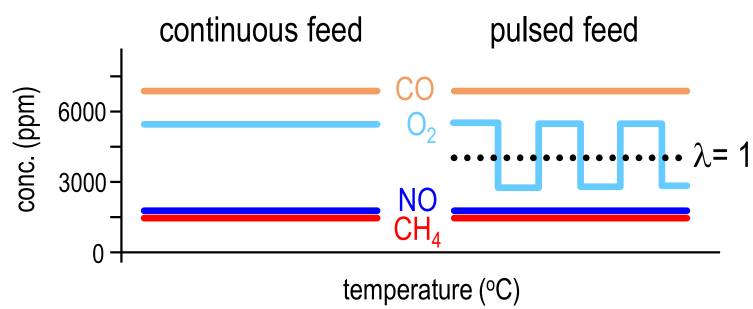
How to measure performance

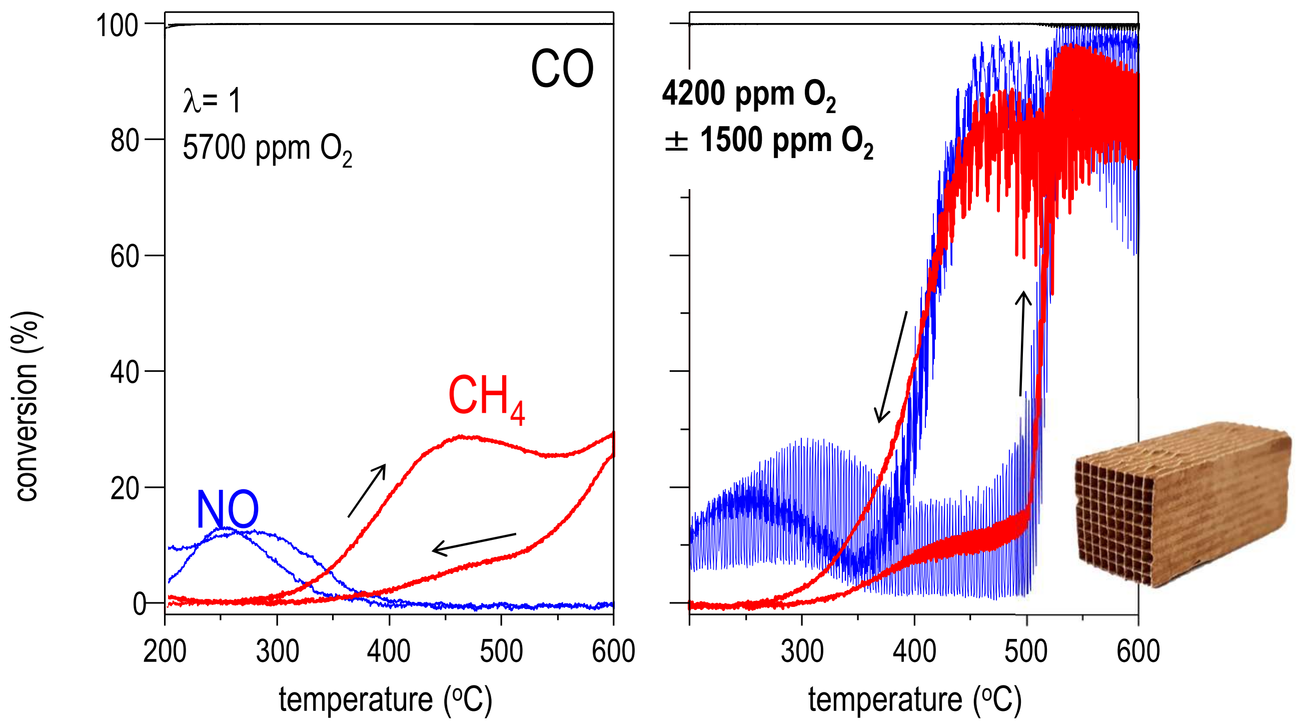
- Conventional microreactor
  - powder samples
  - monolith samples
  - various lambda values
  - various gas feed compositions
- Gas analytics
  - mass spectrometry (fast! but complex)
  - infrared spectroscopy (fast, but no H_2, O_2, N_2)
  - chemoluminescence (NO_x)
  - eletrochemical cell (O_2)
  - thermal conductivity (H_2)

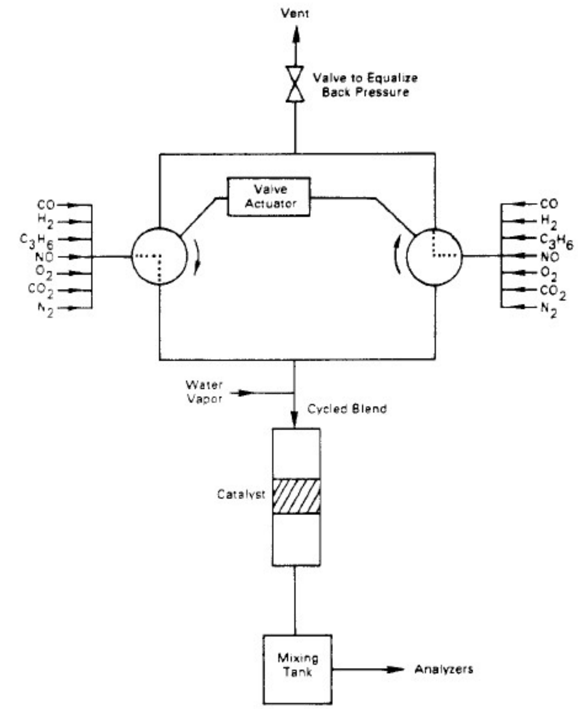




How to measure performance







Pd-only TWC; 56.6 g/ft^2; 600 cpsi

7000 ppm CO/1500 ppm CH_4/1600 ppm NO/5 vol% H_2O

Ferri et al., *Appl. Catal. B* **220** (2018) 67

Schlatter et al., Ind. Eng. Chem. Prod. Res. Dev. 22 (1983) 51

Oxygen Storage Capacity

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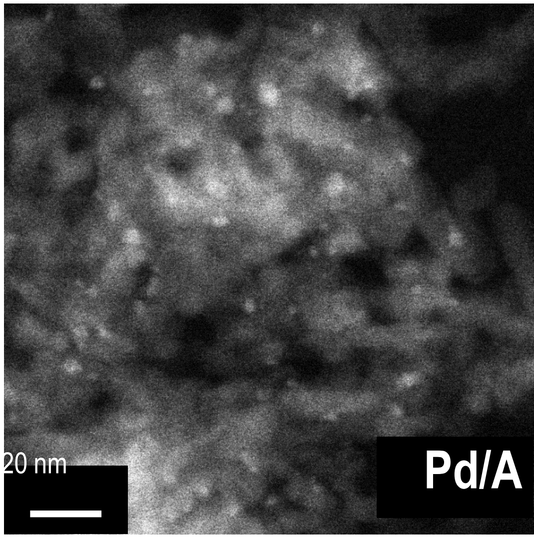
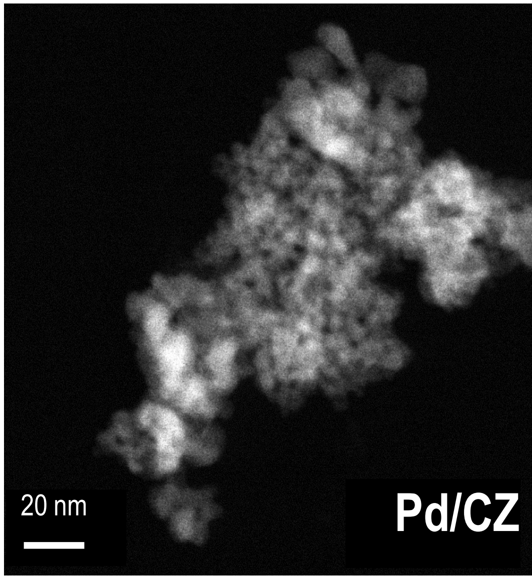
- The attitude to undergo a rapid change of oxidation state upon a change of redox potential
- The change of oxidation state is associated with the reversible removal and addition of oxygen
- Typical OSC compound: **CeO_2**

rich exhaust: $2Ce^{IV}O_2 + CO \rightarrow Ce_2^{III}O_3 + CO_2$

lean exhaust: $Ce_2^{III}O_3 + 0.5O_2 \rightarrow 2Ce^{IV}O_2$





- CeO_2: cubic structure preserved, small volume change
- Additional properties of CeO_2 interesting to TWC (but not only!!!):
  - it prevents SSA loss of TWC upon thermal treatment
  - it stabilizes PM in finely dispersed state
  - it enhances WGS reation to remove CO under rich conditions

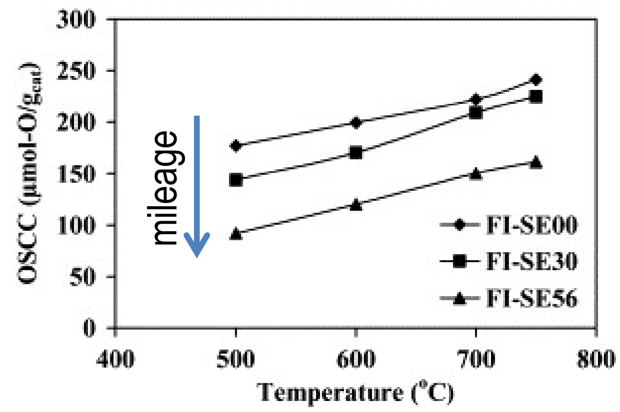
Yao et al., J. Catal. 86 (1984) 254

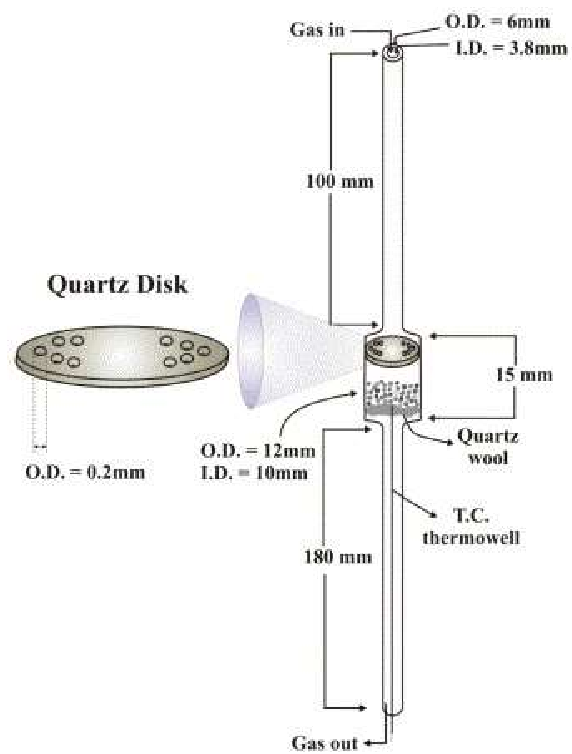
Oxygen Storage Capacity

- Oxygen storage capacity complete (OSCC) - total amount of O_2 consumed in re-oxidation
  - Pulse injection technique (@ given T_{OSC}):
    - 20 vol% O_2/He (1 h) → He (5') → consecutive H_2/CO (50 μmol) pulses → consecutive O_2 (10 μmol) pulses until saturation

- Oxygen Storage Capacity (OSC) - amount of most reactive O_2
  - Pulse injection technique (@ given T_{OSC}):
    - 20 vol% O_2/He (1 h) → He (5') → one H_2/CO (50 μmol) pulse → consecutive O_2 (10 μmol) pulses until saturation

- Dynamic Oxygen Storage Capactiy (DOSC)
  - Step gas concentration switch technique (@ given T_{OSC}):
    - 1.5 vol% O_2/He (30") → He (30") → 3 vol% CO/3 vol% Ar/He (30") → He (30") → repeat

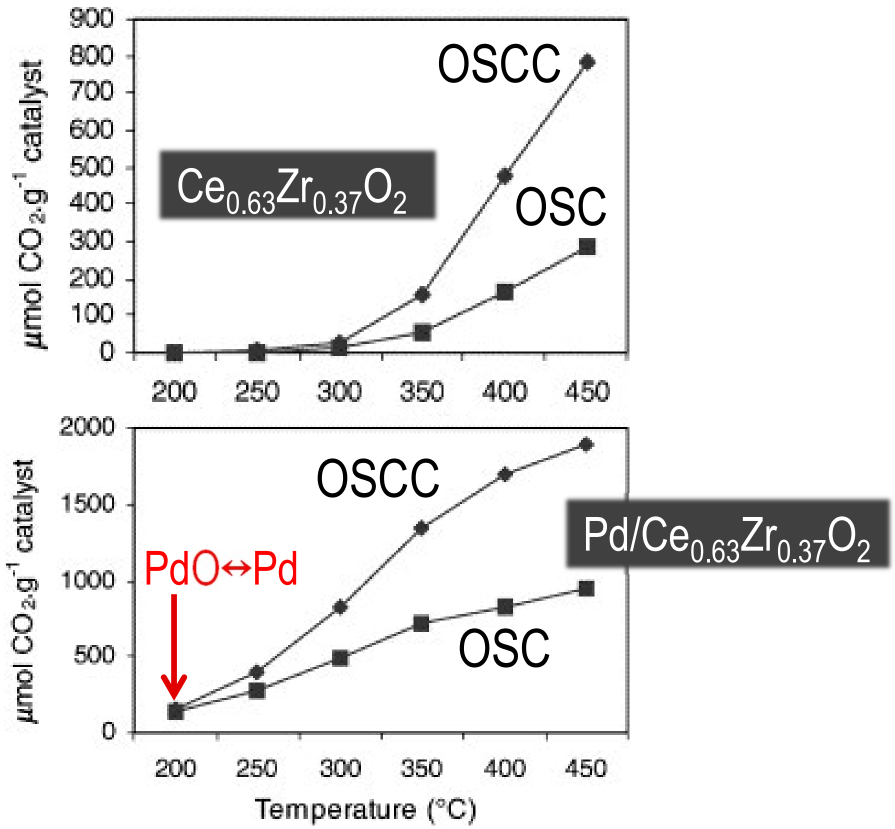




Costa et al., J. Catal. 219 (2003) 259

Oxygen Storage Capacity

- OSCC is not OSC: total available oxygen vs reactive oxygen

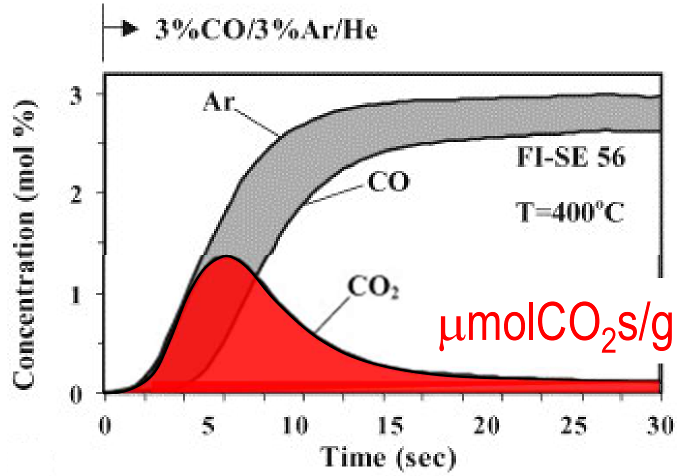


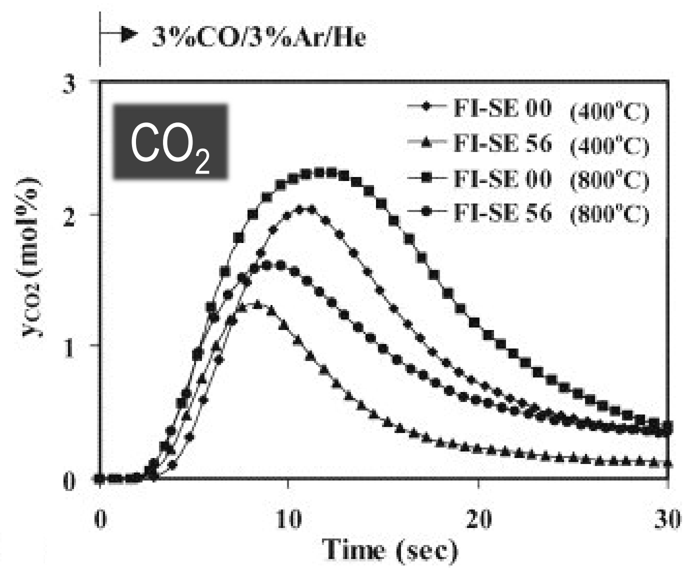
Bedrane et al., Catal. Today 73 (2002) 233

Oxygen Storage Capacity

- Alternated step concentration switches

1.5 vol% O_2/He
↓
He
↓
3 vol% CO/3 vol% Ar/He
↓
He
↓
repeat

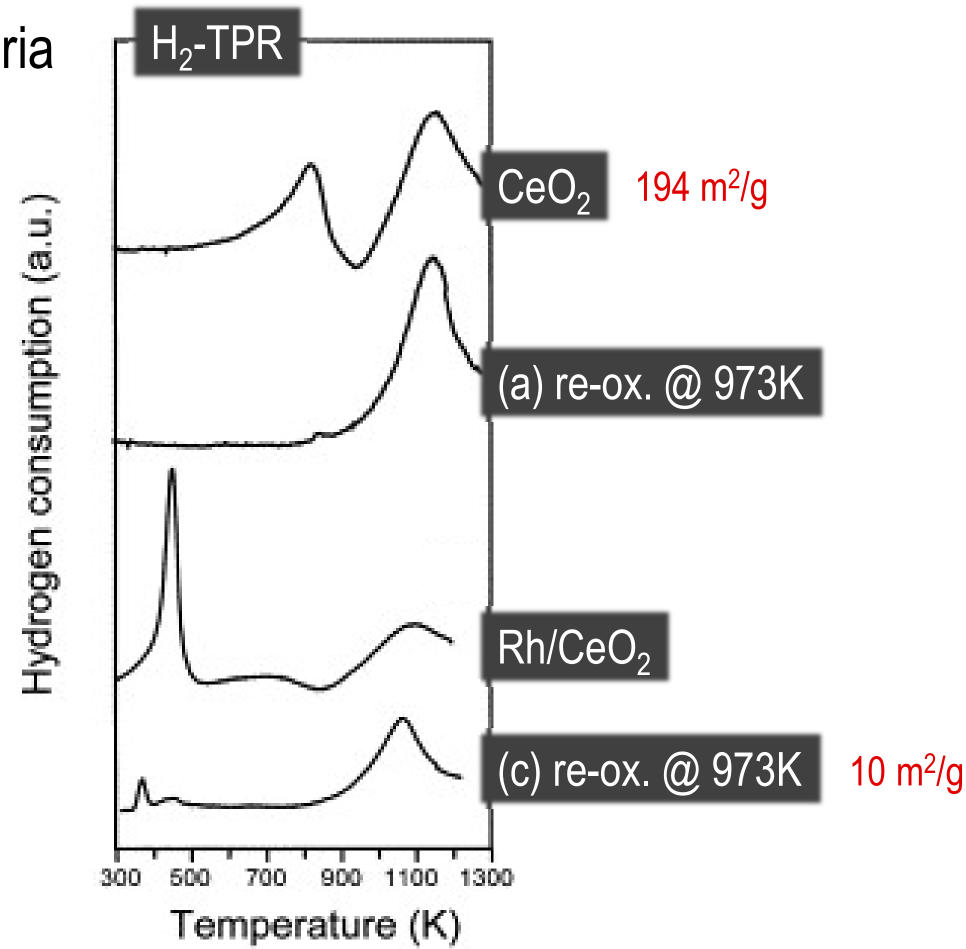




Lambrou et al., Appl. Catal. B: Environmental 86 (1984) 254

Oxygen Storage Capacity

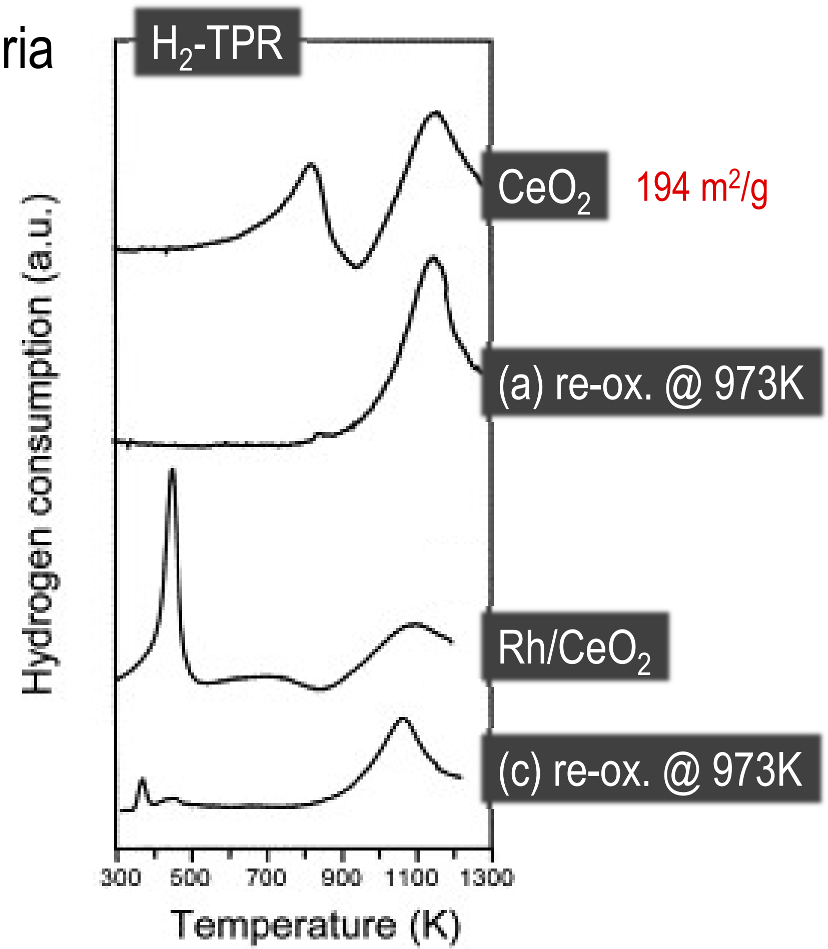
- Ceria

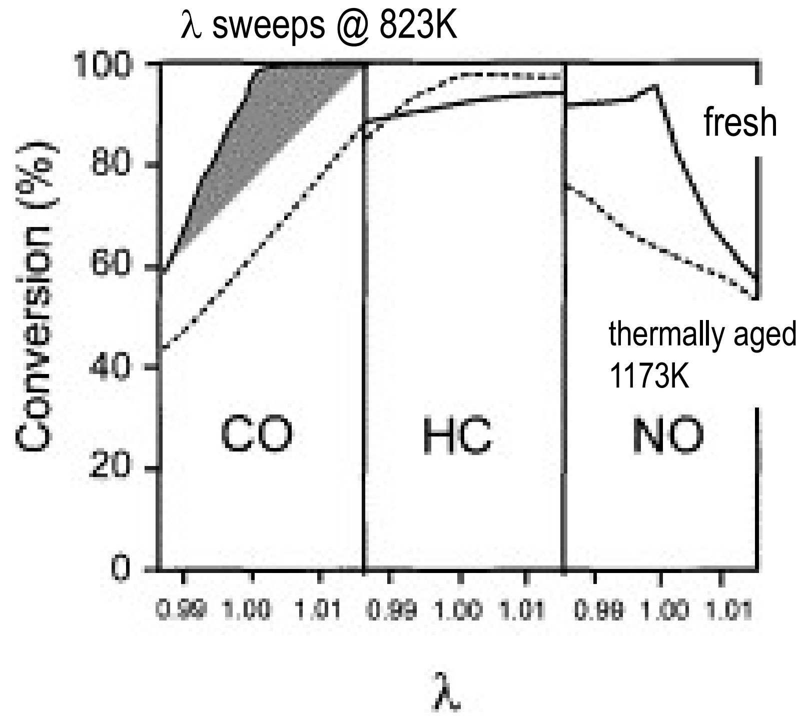


Kaspar et al., Catal. Today 50 (1999) 285

Oxygen Storage Capacity

- Ceria





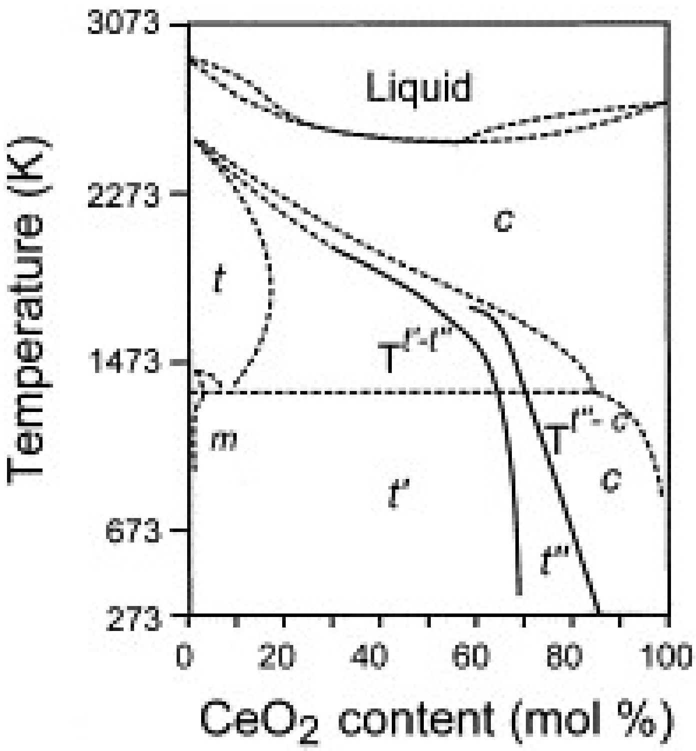
- CeO_2 is not thermally stable → loss of surface area and metal dispersion
- Possible formation of $CeAlO_3$ in CeO_2-Al_2O_3 catalysts
- Loss of TWC activity upon ageing

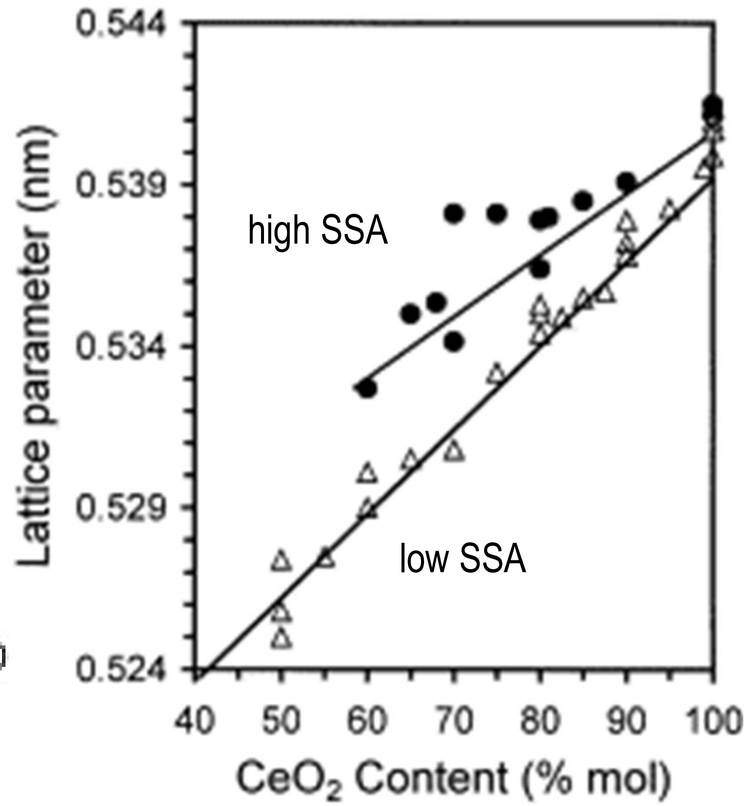
Kaspar et al., Catal. Today 50 (1999) 285

Oxygen Storage Capacity

- Ceria-zirconia

ionic radius: Ce^{4+} (0.97 nm) - Zr^{4+} (0.84 nm)





- Metastable phases
- Synthesis method is crucial (material science)
- Necessity to disperse homogeneously Zr in CeO_2
- Zr decreases overall lattice parameter
- Zr progressively increases structural defects

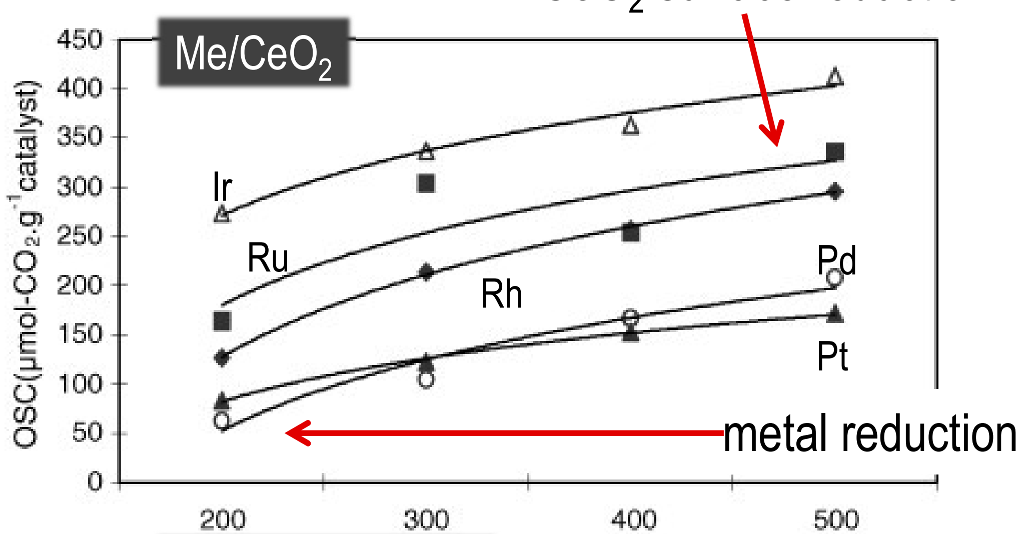
Classification of the phases in the CeO_2–ZrO_2 binary system[a]

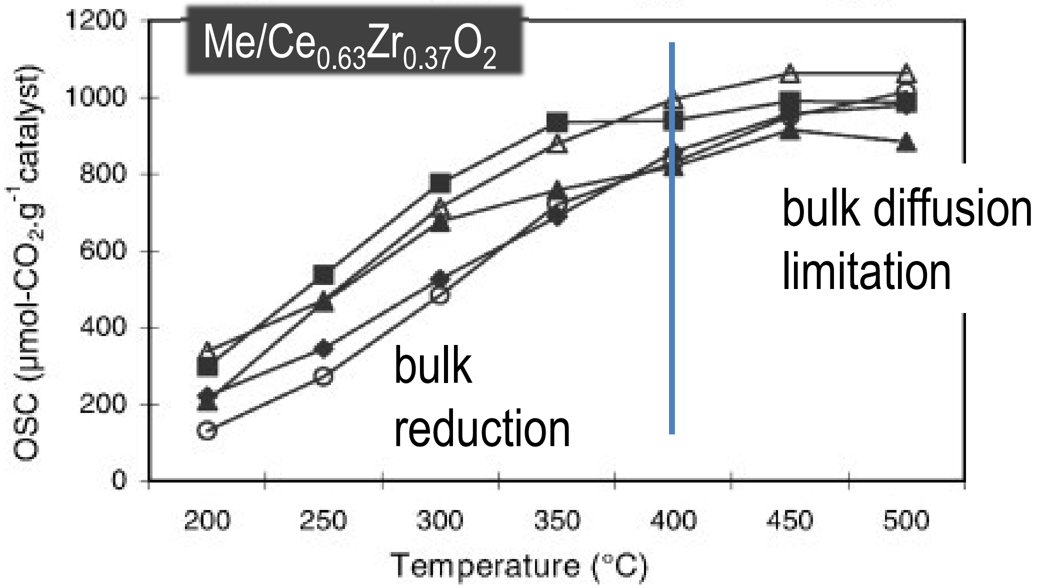
Phase	Composition range (mol% Ce)	Tetragonality[b]	Space group
Monoclinic (*m*)	0–10	–	$P2_1/c$
Tetragonal (*t*)	10–30	>1	$P4_2/nmc$
Tetragonal (*t'*)	30–65	>1	$P4_2/nmc$
Tetragonal (*t''*)[c]	65–80	1	$P4_2/nmc$
cubic (*c*)	80–100	1	Fm3m

Oxygen Storage Capacity

500°C

Catalyst	OSC$_{exp}$ [a]	OSC$_{metal}$ [b]	NL [d]
Rh/Ce	296	115	1.3
Pt/Ce	172	84	0.6
Pd/Ce	208	91	0.9
Ru/Ce	336	196	1.0
Ir/Ce	413	266	1.1
Rh/CeZr	980	128	5.6
Pt/CeZr	883	95	5.2
Pd/CeZr	1015	109	6.0
Ru/CeZr	985	210	5.1
Ir/CeZr	1062	308	5.0
	μmolCO$_2$/g	μmolO/g	involved layers

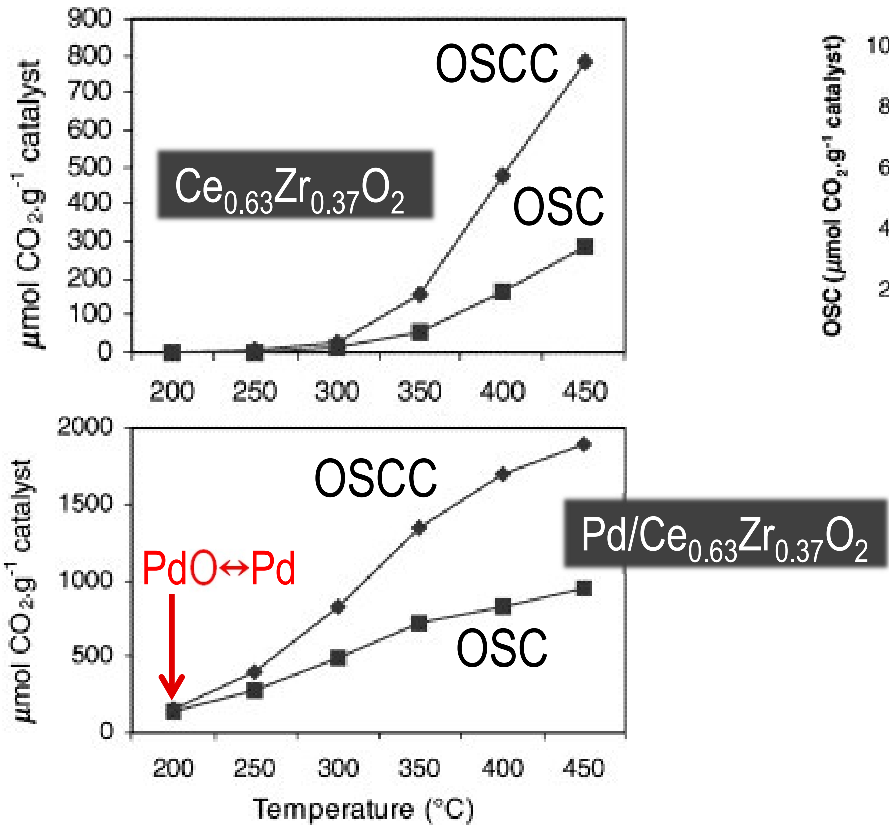




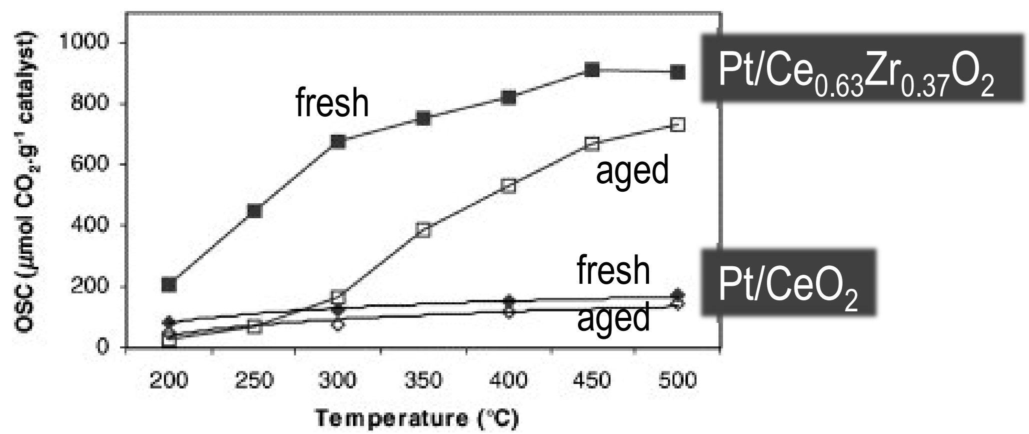
Bedrane et al., Catal. Today 75 (2002) 401

Oxygen Storage Capacity

- Ceria vs. ceria-zirconia



Thermal ageing



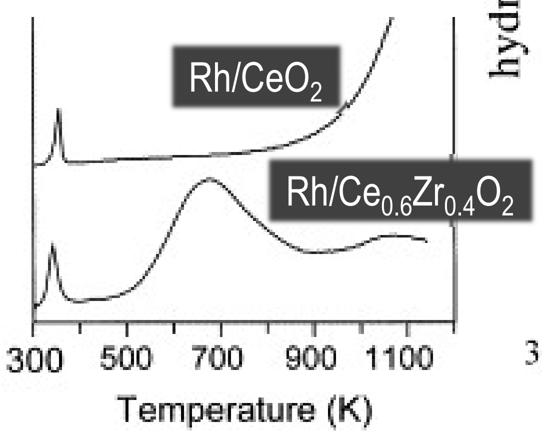
- OSC originates from the bulk
- Zr stabilizes ceria against ageing

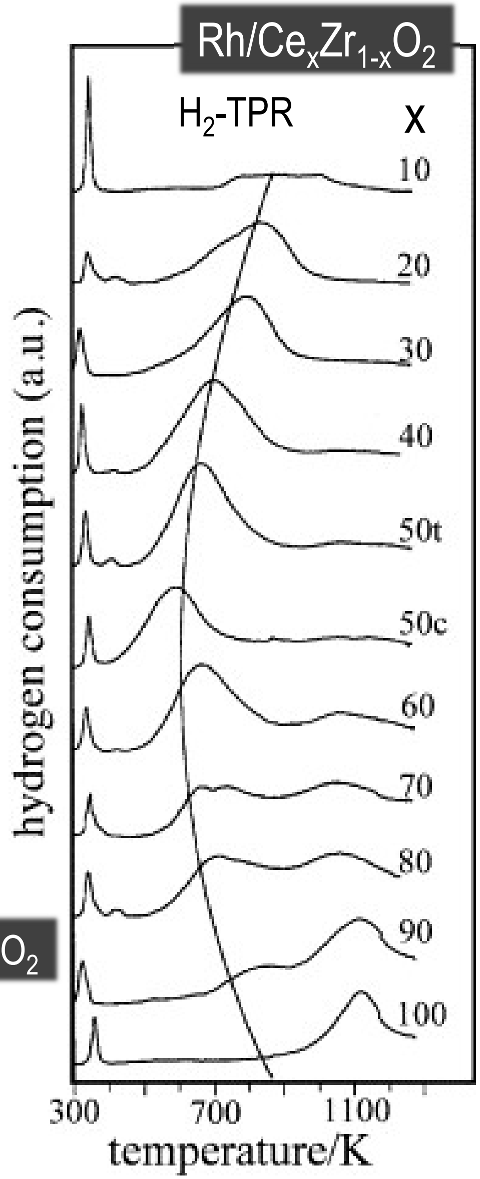
Bedrane et al., Catal. Today 73 (2002) 233

Oxygen Storage Capacity

- Ceria-zirconia

- ZrO_2 promotes bulk reduction
- PM enhances this effect





Boaro et al., Catal. Today 77 (2003) 407; Sugiura, Catal. Surveys Asia 7 (2003) 77

Oxygen Storage Capacity

- Ceria-zirconia

- ZrO_2 promotes bulk reduction
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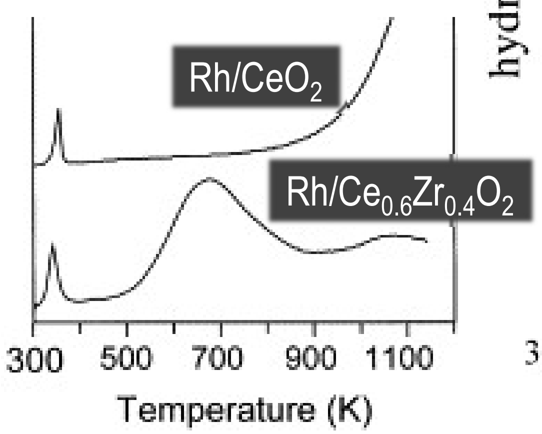
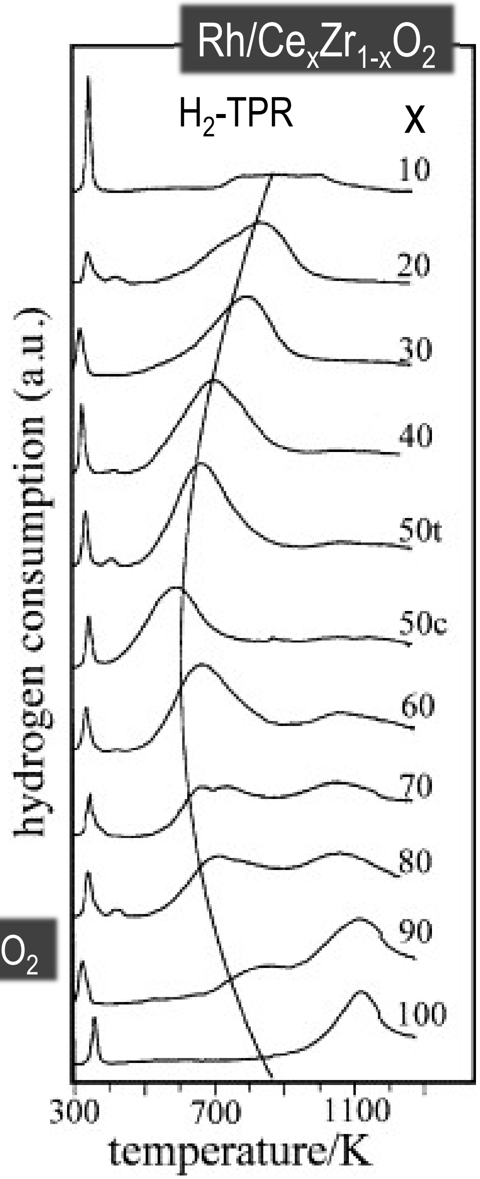
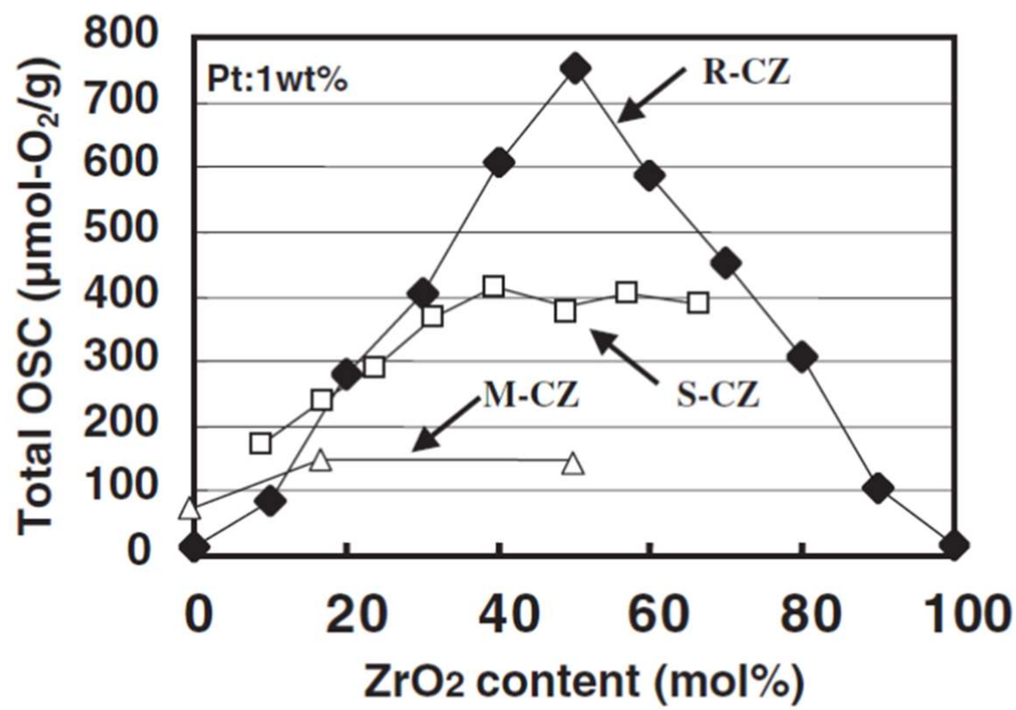




Boaro et al., Catal. Today 77 (2003) 407; Sugiura, Catal. Surveys Asia 7 (2003) 77



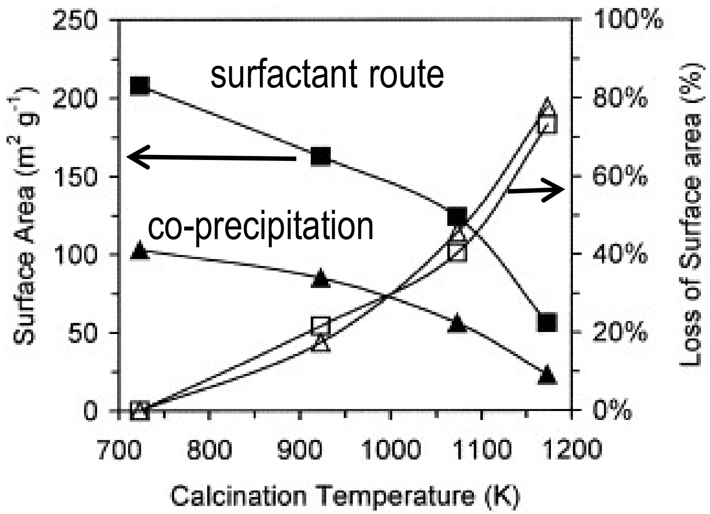
M-CZ: precipitation
S-CZ: milling
R-CZ: precipitation+reduction at 1473K+oxidation at 773K

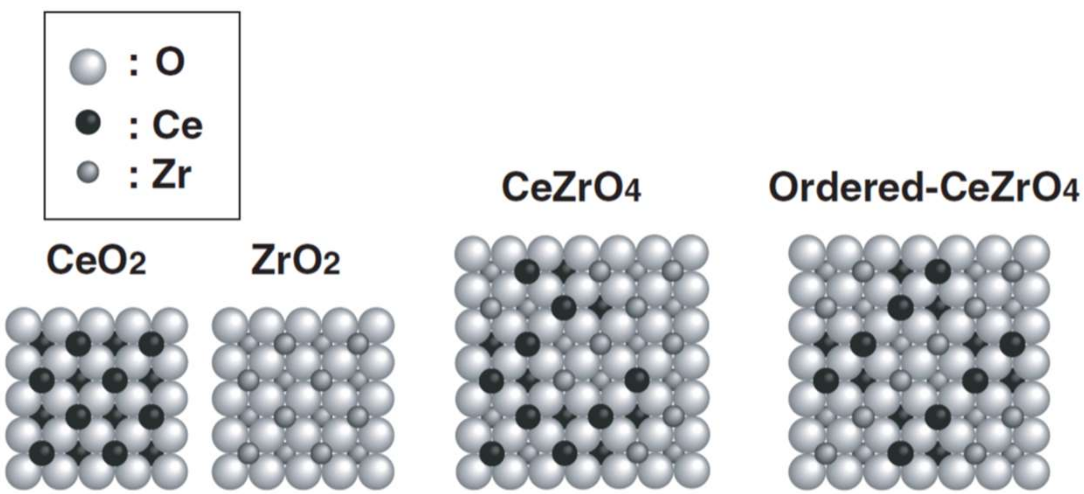
Reducibility and OSC depend on:

- crystal structure
- particle size - surface area
- synthesis method - pretreatment history
- PM dispersion

Oxygen Storage Capacity

- Improved thermal resistance



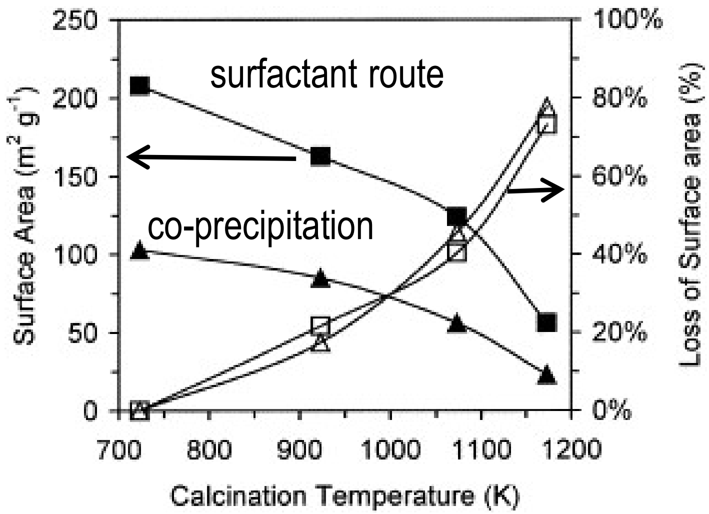


solid solution

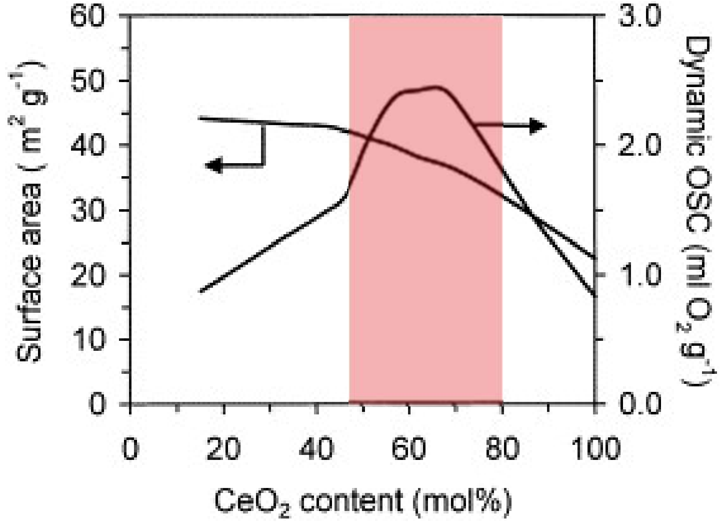
κ-$CeZrO_4$ phase

Oxygen Storage Capacity

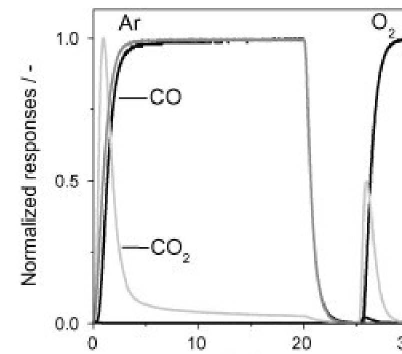
- Improved thermal resistance



ageing @ 1173K, 6h, air

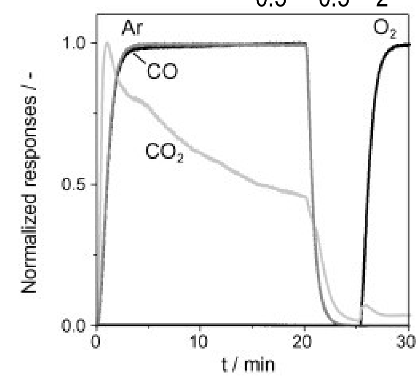


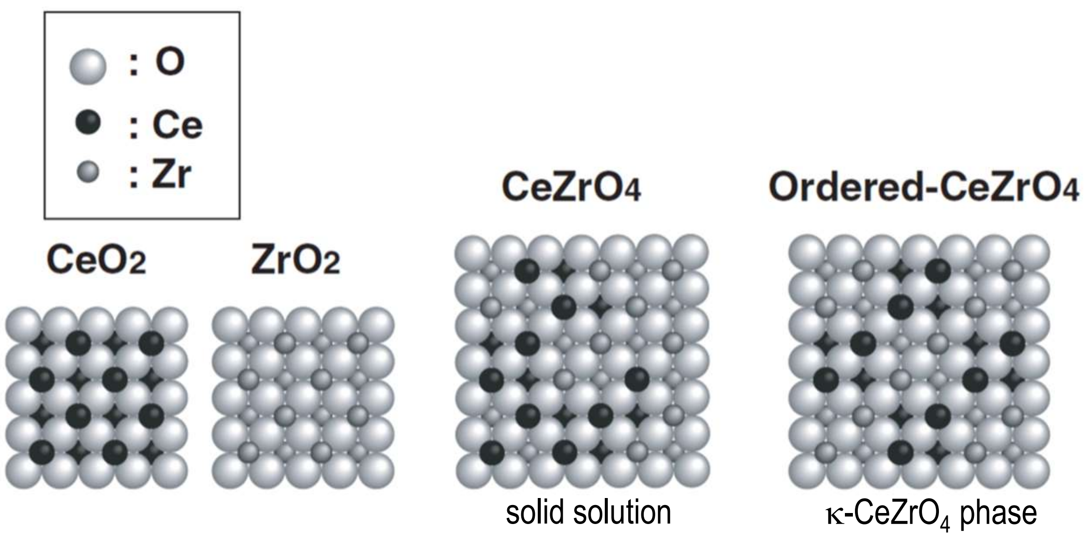
Pt/c-$Ce_{0.5}Zr_{0.5}O_2$



523K

Pt/κ-$Ce_{0.5}Zr_{0.5}O_2$

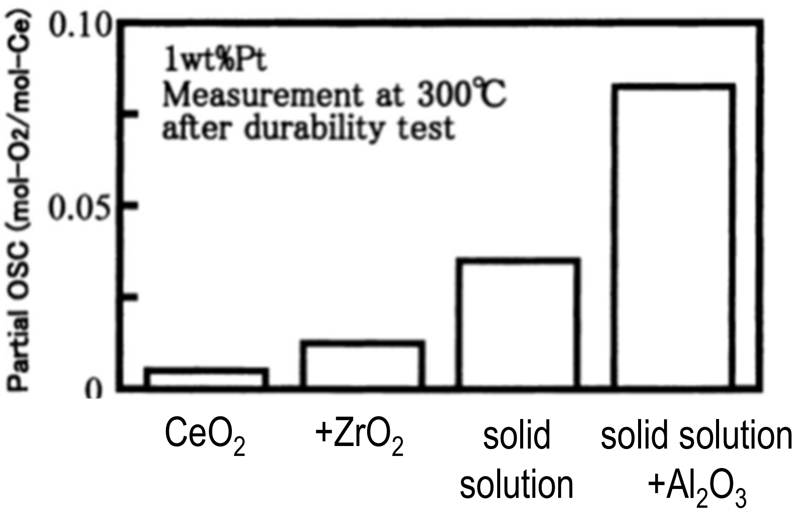


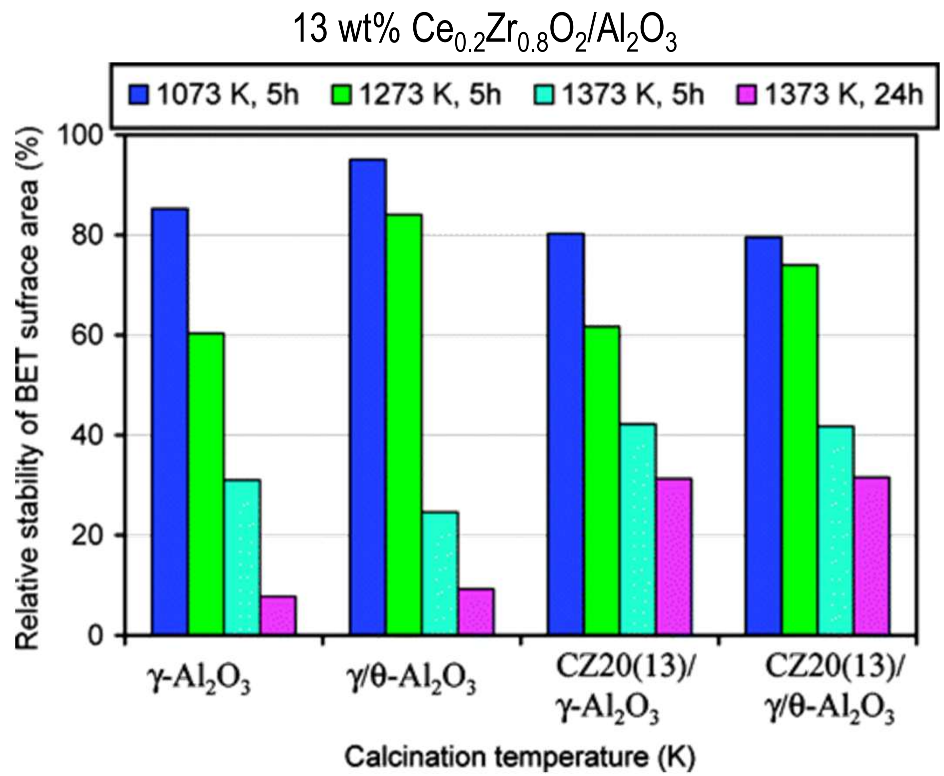


- SSA increases up to 60 mol% ZrO_2
- optimal OSC @ 20-50 mol% ZrO_2
- formation of ordered κ-$CeZrO_4$ is of advantage

Oxygen Storage Capacity

- Al_2O_3-ceria-zirconia

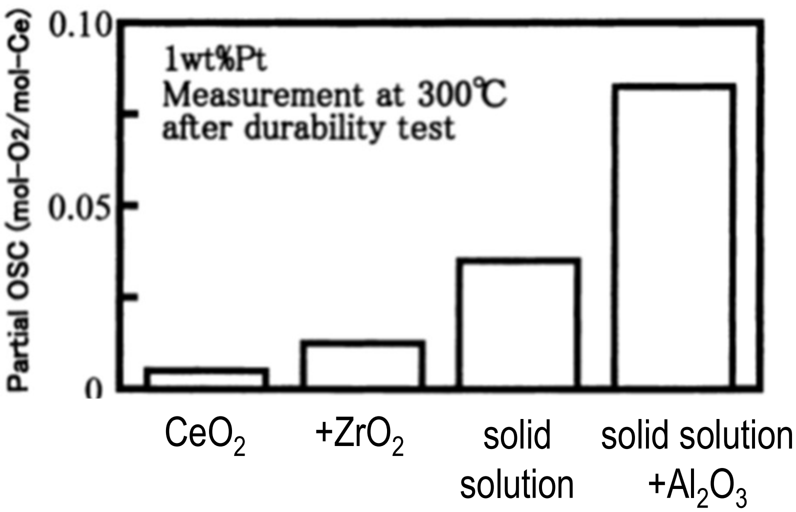


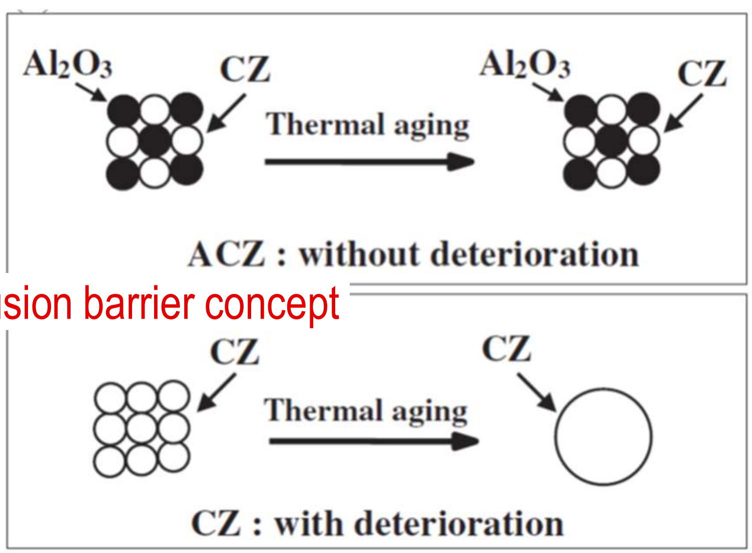


Oxygen Storage Capacity

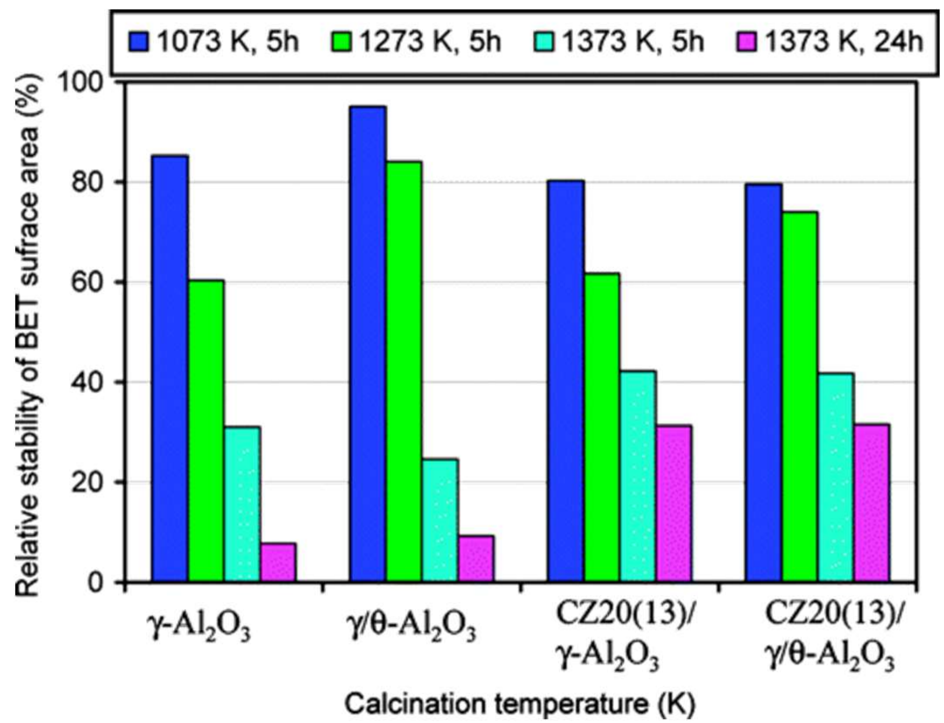
EPFL

- Al_2O_3-ceria-zirconia





diffusion barrier concept



- High Zr stabilizes γ-Al_2O_3
- High Ce stabilizes θ- and δ-Al_2O_3
- Both Zr and Ce stabilize the Al_2O_3-Ce-Zr composite
- Material Science required to design optimized composites

Catalyst deactivation - Ageing

thermal

- washcoat sintering
- alloy formation
- support alterations
- PGM-metal interaction
- metal-MO_X-support interaction
- metal volatilization
- …

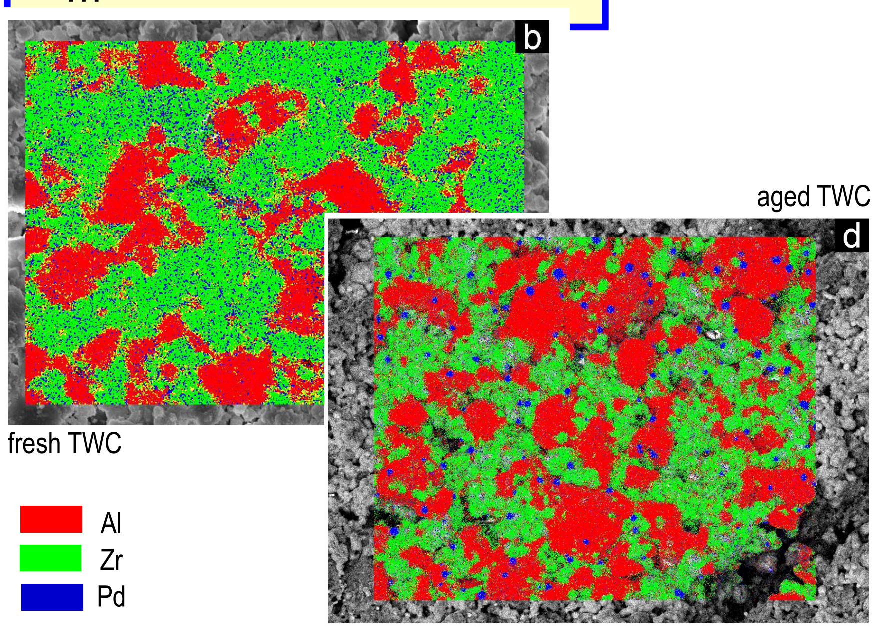
chemical

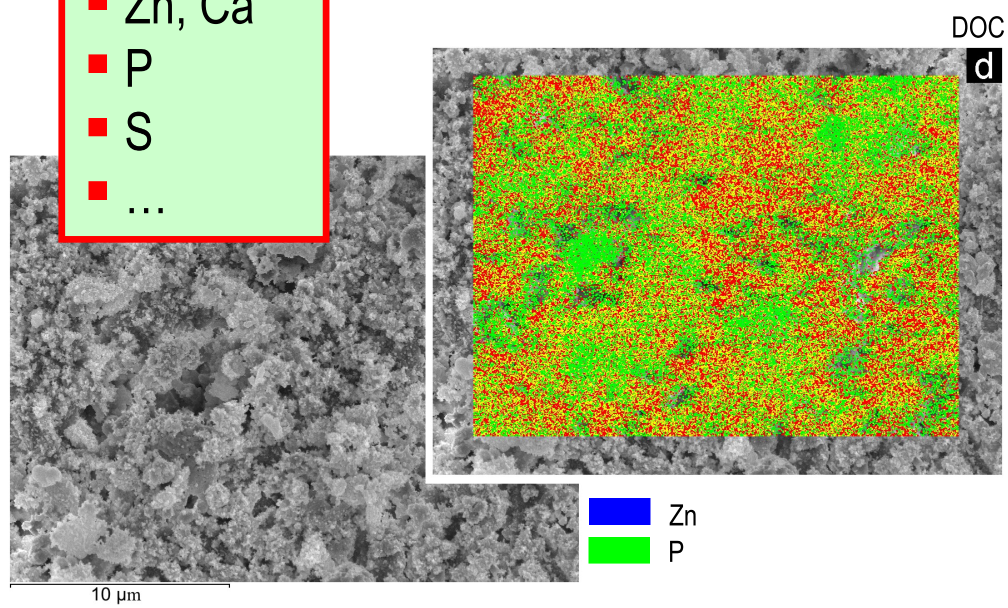
- site poisoning
- competitive adsorption
- pore chemical blocking
- pore physical blocking
- …

- products
- Zn, Ca
- P
- S
- …

mechanical

- thermal shock
- impact
- attrition
- …





images source: Winkler et al. *Catal. Today* 155 (2010) 140

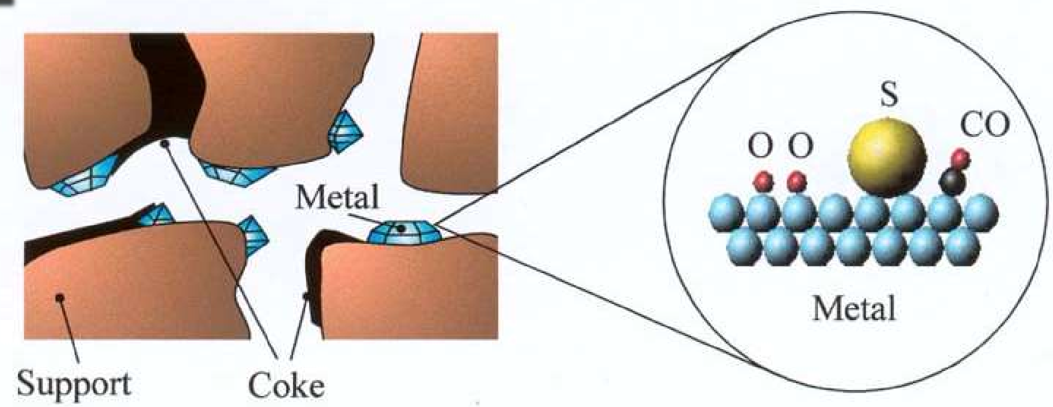
Catalyst deactivation - Ageing

- Ageing is an unavoidable but slow process
- The ageing entails the variation of the catalyst structure on operation
    - loss of PM dispersion - loss of active centres on catalyst surface
    - decrease of catalytic activity
  - Chemical (fuel and oil additives and impurities: S, Zn, P, Ca, Mg)
    - poisoning: irreversible adsorption on or reaction with the catalyst surface
    - inhibition: competitive reversible adsorption of different species
  - Thermal (high temp. exposure, surges/operation)
    - sintering of waschcoat particles
    - alloying of metal particles
    - metal-washcoat interaction
    - thermal oxidation
    - evaporation
    - restructuring of the precious metal surfaces
  - Mechanical (vibrations, exhaust)
    - fracture
    - attrition
  - Fouling
    - coking

Catalyst deactivation - Ageing

chemical ageing

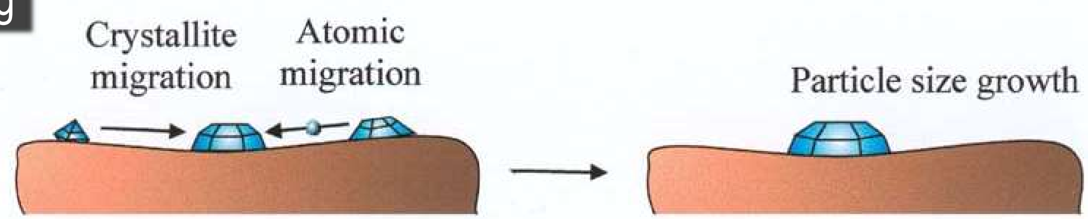
- poisoning (P, S)
- inhibition
- coking
- phase transformation



thermal ageing

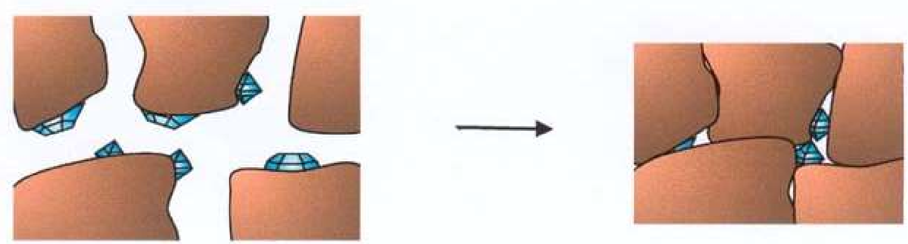
- loss of catalytic surface by crystal growth (sintering)
- start of sintering (empirical):

$$T_{Tammann} = 0.5\ T_{melting}$$



sintering

- loss of washcoat surface by collapse of pore structure (sintering and encapsulation)



Lassi, PhD thesis, 2003, University of Oulu

Catalyst deactivation - Ageing

- Countermeasures
  - Chemical ageing
    - Reduction of impurities and additives
      - fuel (S): sulphur content in gasoline < 10 ppm (Europe)
      - oil quality (S, P, Zn, Ca, Mg)
      - clean catalyst with weak organic acids
  - Thermal ageing
    - Stabilisation of metal oxides by rare earth metal oxides (REO)
      - addition of ZrO_2 to CeO_2
      - Al_2O_3-CeO_2-ZrO_2 composite
      - addition of La to Al_2O_3
      - improved PM-support interaction

Chemical ageing

- Sulfur
  - Chemical reactions
    - SO_2 production:

      $$S + O_2 \longrightarrow SO_2$$
    - under lean conditions (Pt, Pd):

      $$2SO_2 + O_2 \longrightarrow 2SO_3$$
    - SO_3 reacts with water to form sulfuric acid:

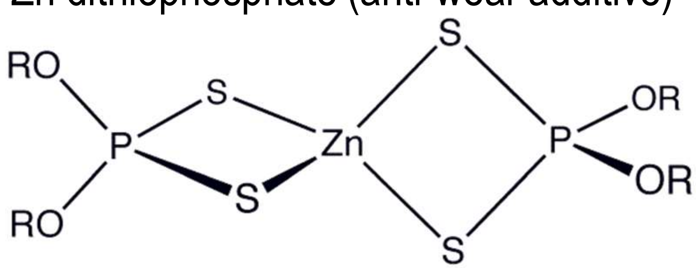
      $$SO_3 + H_2O \longrightarrow H_2SO_4$$
    - SO_3 and H_2SO_4 react with basic oxides to yield sulfates, e.g. $Al_2(SO_4)_3$, $Ce(SO_4)_2$:

      $$CeO_2 + 2SO_3 \longrightarrow Ce(SO_4)_2$$
    - under rich conditions, SO_2 is reduced to hydrogen sulfide (H_2S)

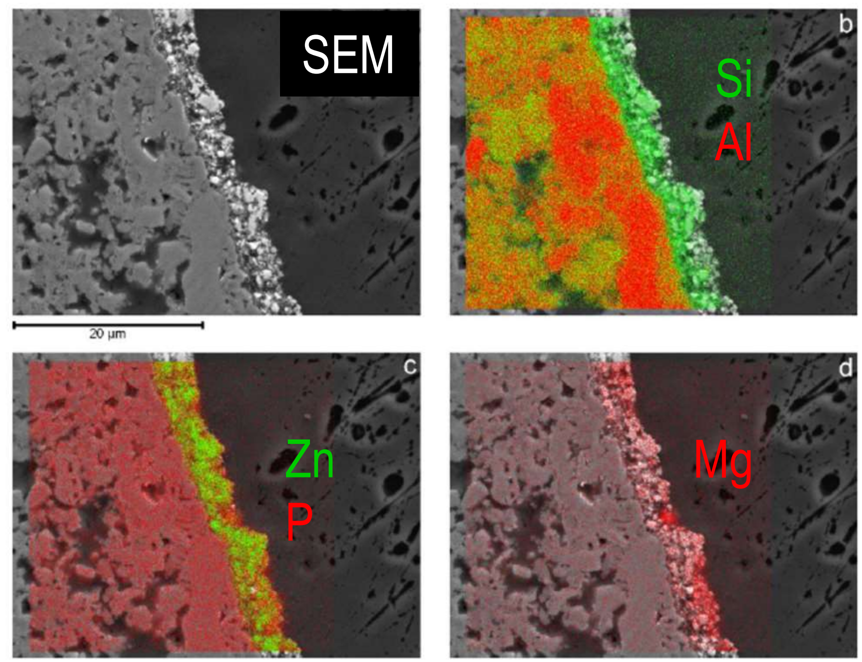
Chemical ageing

- Effect of metals and inorganic elements
  - Lead (Pb), Phosphorous (P), Zinc (Zn), Calcium (Ca) and/or Magnesium (Mg) from engine oil deposit on the catalyst on mileage
    - Effects of compounds of diff. exhaust components can be more severe than the single components. For example, Zn pyrophosphate ($Zn_2P_2O_7$) more than P or Zn.
    - Formation of metal phosphates in various phases (pore blockage)
    - Phosphates form a thin layer covering the PM particles (blockage of active centres)
  - Especially P reacts with washcoat influencing catalytic performance and OSC

Zn dithiophosphate (anti-wear additive)



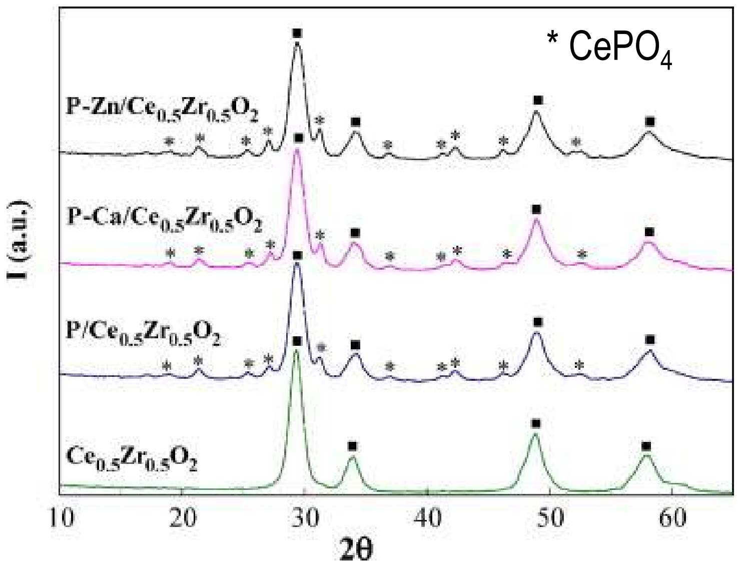
(R = alkyl)

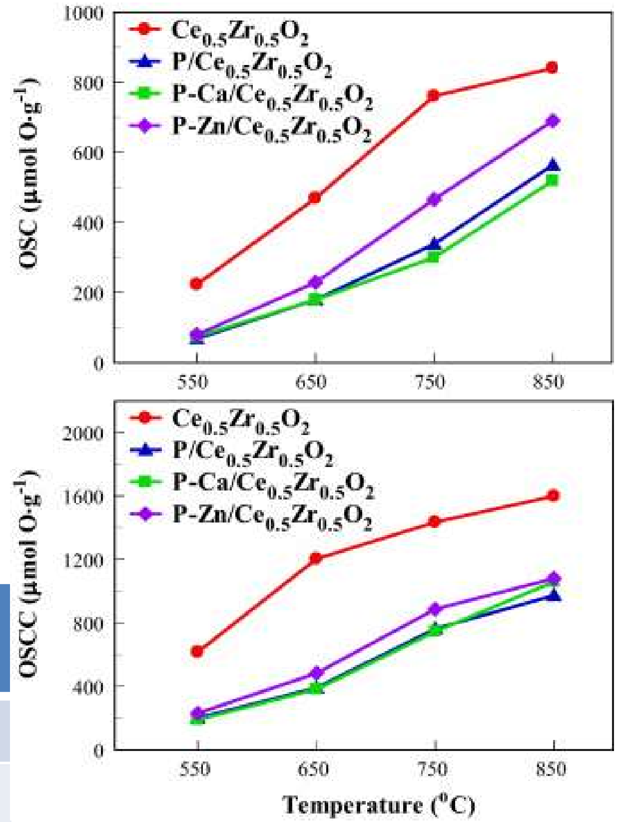


  - Bio-fuels

Chemical ageing

- $P-CeO_2/Ce_xZr_{1-x}O_2$ interaction





	SSA (m^2/g)	pore volume (cm^3/g)	surface Ce^{4+} (%)
$Ce_{0.5}Zr_{0.5}O_2$	52	0.235	82
$P-Ce_{0.5}Zr_{0.5}O_2$	26	0.167	46
$P-Ca-Ce_{0.5}Zr_{0.5}O_2$	27	0.137	43
$P-Zn-Ce_{0.5}Zr_{0.5}O_2$	18	0.136	37

Phosphorous

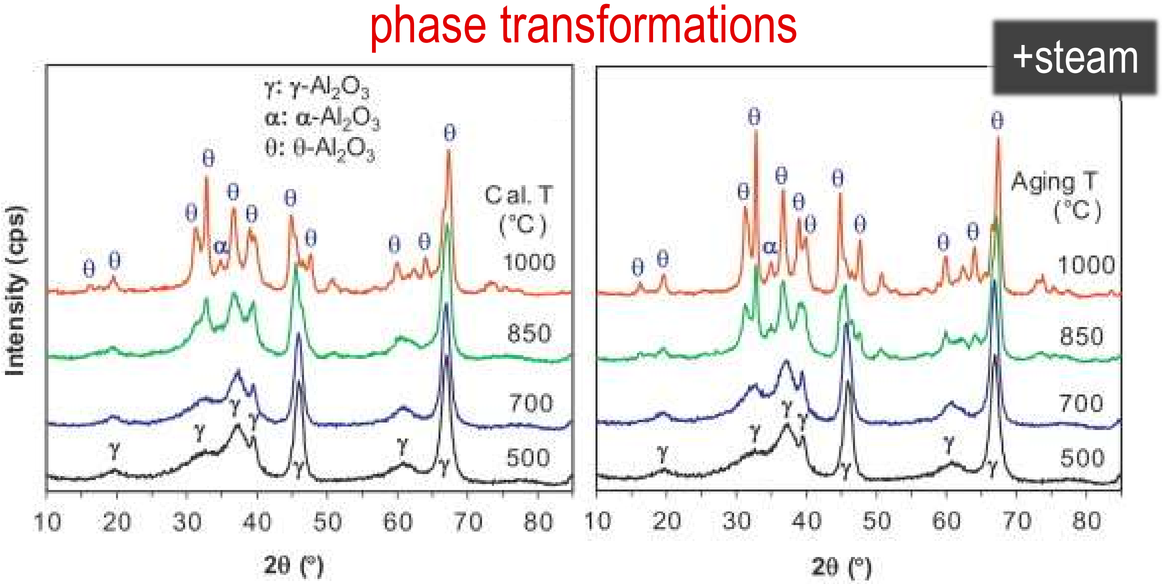
- reacts with Ce
- reduces SSA and blocks pores
- severely reduces OSC/OSCC

Christou et al., Appl. Cata. B: Environmental 106 (2011) 103

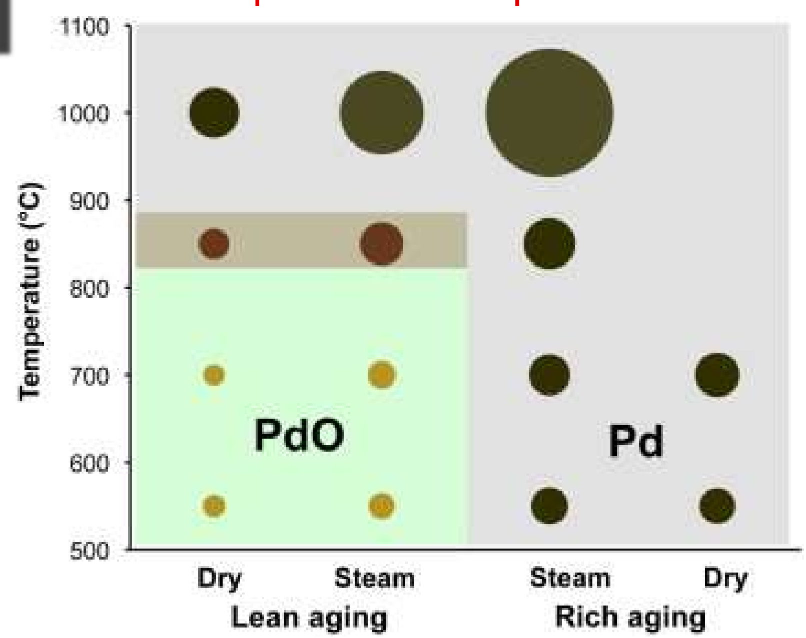
Thermal ageing

- (Hydro-)Thermal ageing manifests as
  - loss of metal dispersion by exposure to high temperature (Pt, Pd)
  - loss of metal by incorporation into washcoat (Rh)
  - loss of metal oxide (washcoat) surface area and phase transformations (e.g. Al_2O_3, CeO_2, $Ce_xZr_{1-x}O_2$)
- Referred to any structural change induced by temperature, in some cases 'positive', e.g. re-dispersion of precious metal

phase transformations



particle re-dispersion



Chen et al., Appl. Catal. B Environmental 163 (2015) 499

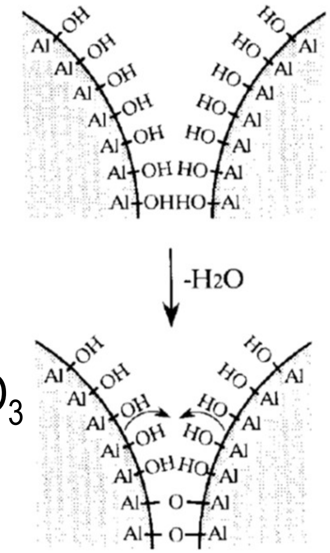
Thermal ageing

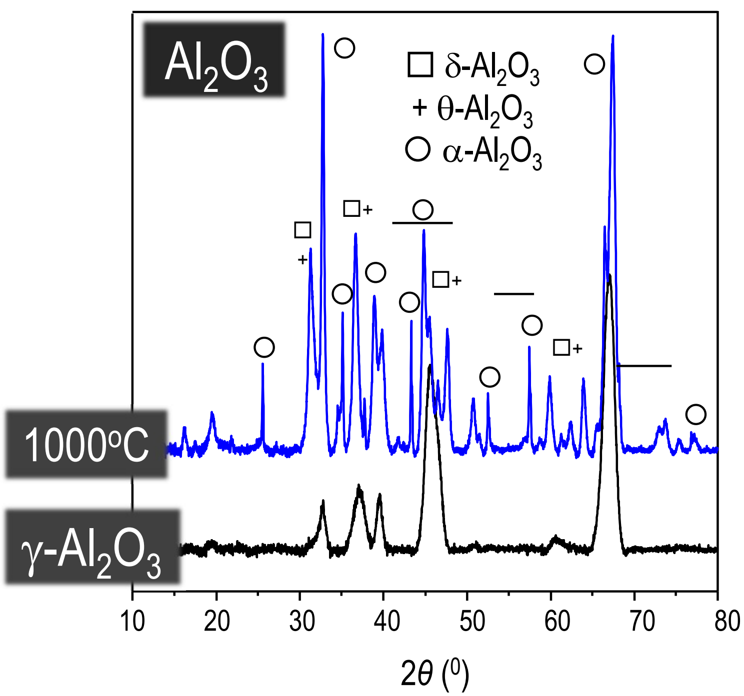
EPFL

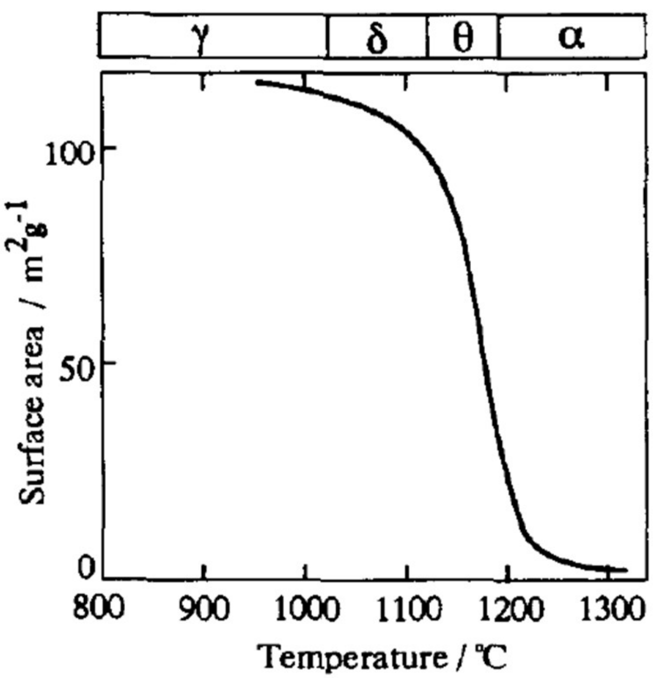
- Ageing of Al_2O_3 – phase transitions

bayerite $\xrightarrow{230^oC}$ η-Al_2O_3 $\xrightarrow{850^oC}$ θ-Al_2O_3 $\xrightarrow{1200^oC}$ α-Al_2O_3

boehmite $\xrightarrow{450^oC}$ γ-Al_2O_3 $\xrightarrow{750^oC}$ δ-Al_2O_3 $\xrightarrow{1000^oC}$ θ+α-Al_2O_3 $\xrightarrow{1200^oC}$ α-Al_2O_3







Phase transformation of Al_2O_3 means:

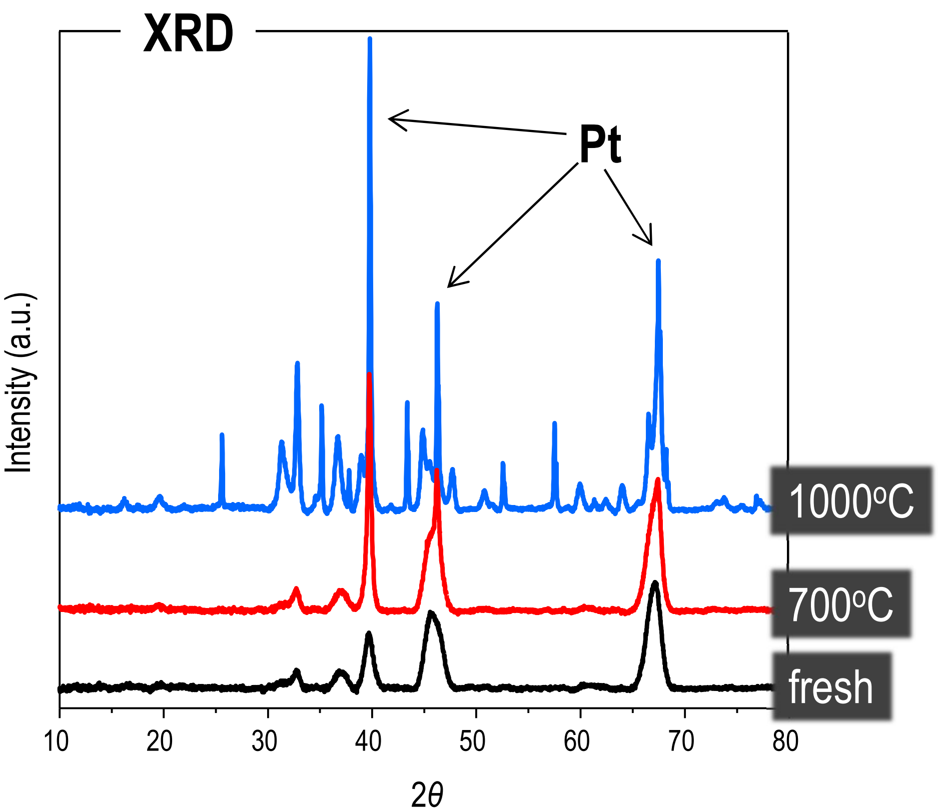
- loss of surface area
- loss of PM dispersion
- less active sites

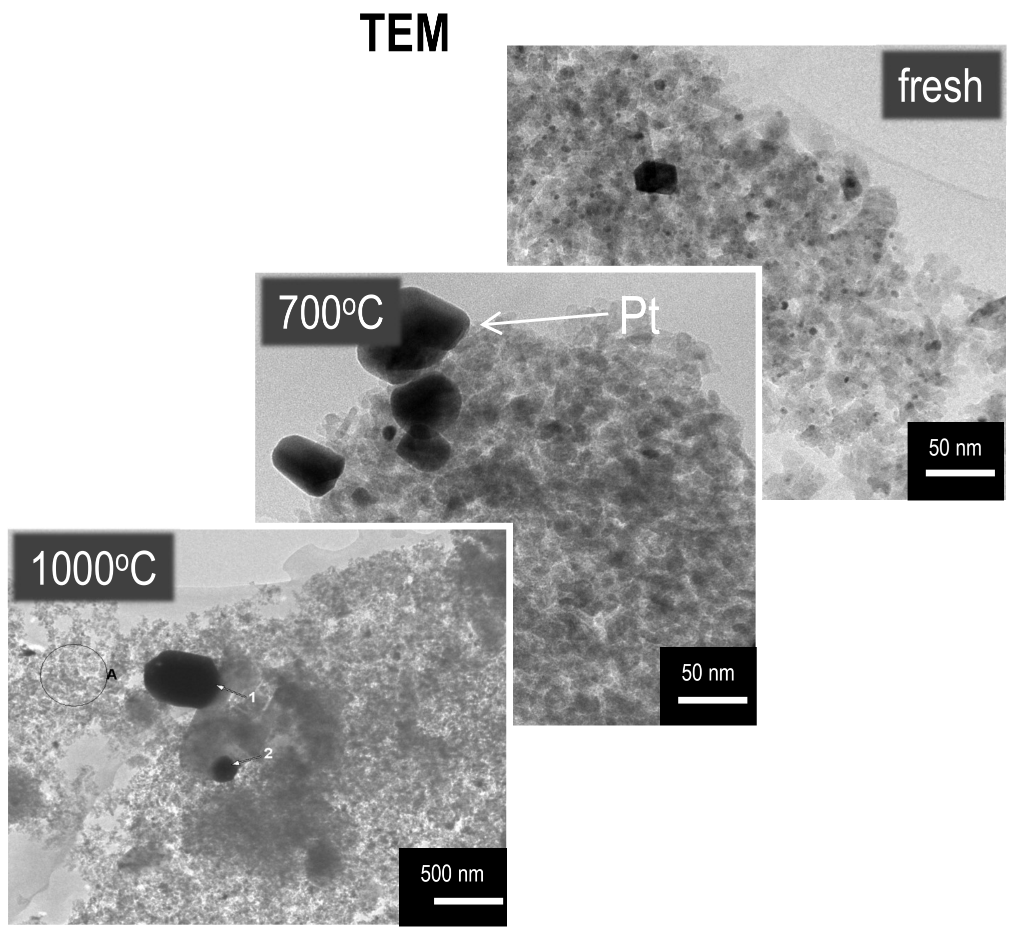
especially when α-Al_2O_3 is formed

- Water facilitates phase transformation

Thermal ageing

- Hydrothermal ageing - Pt/Al_2O_3

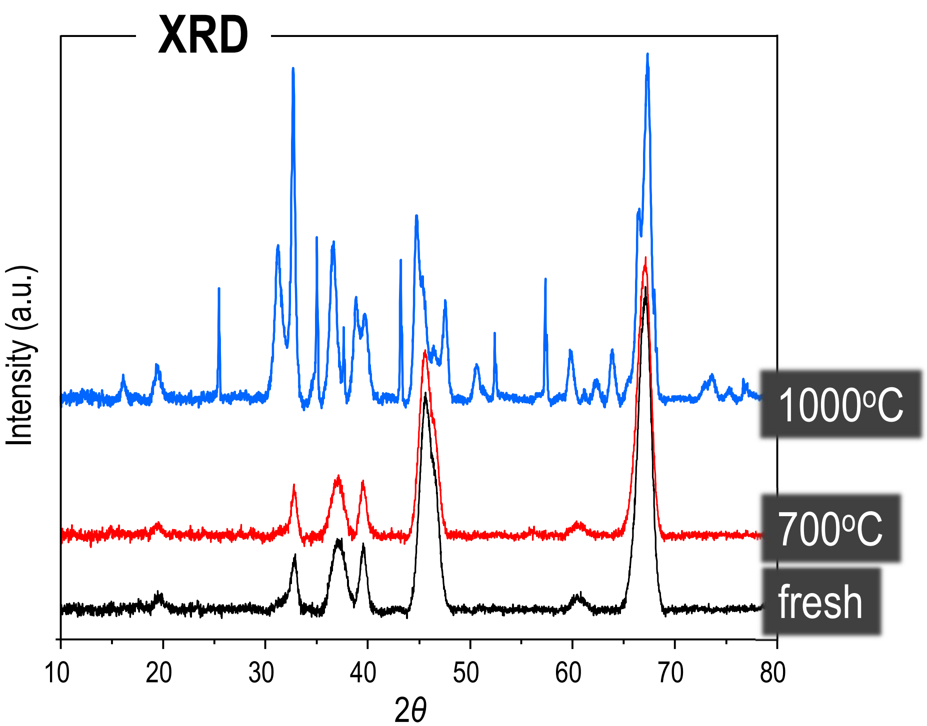




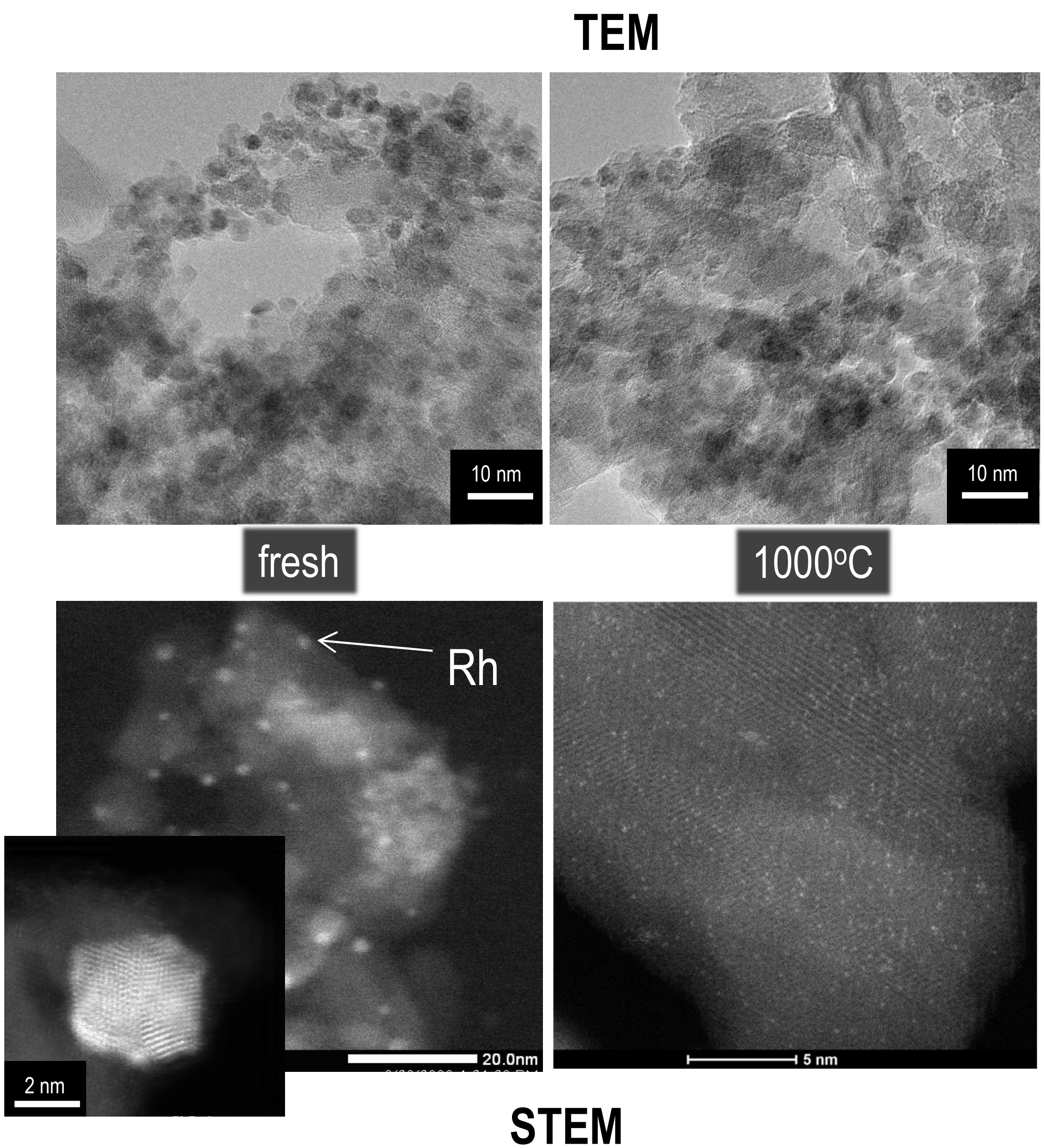
- Ageing drastically changes Pt particle size and morphology as well as dispersion
- XRD and TEM already informative

Thermal ageing

- Hydrothermal ageing - Rh/Al_2O_3



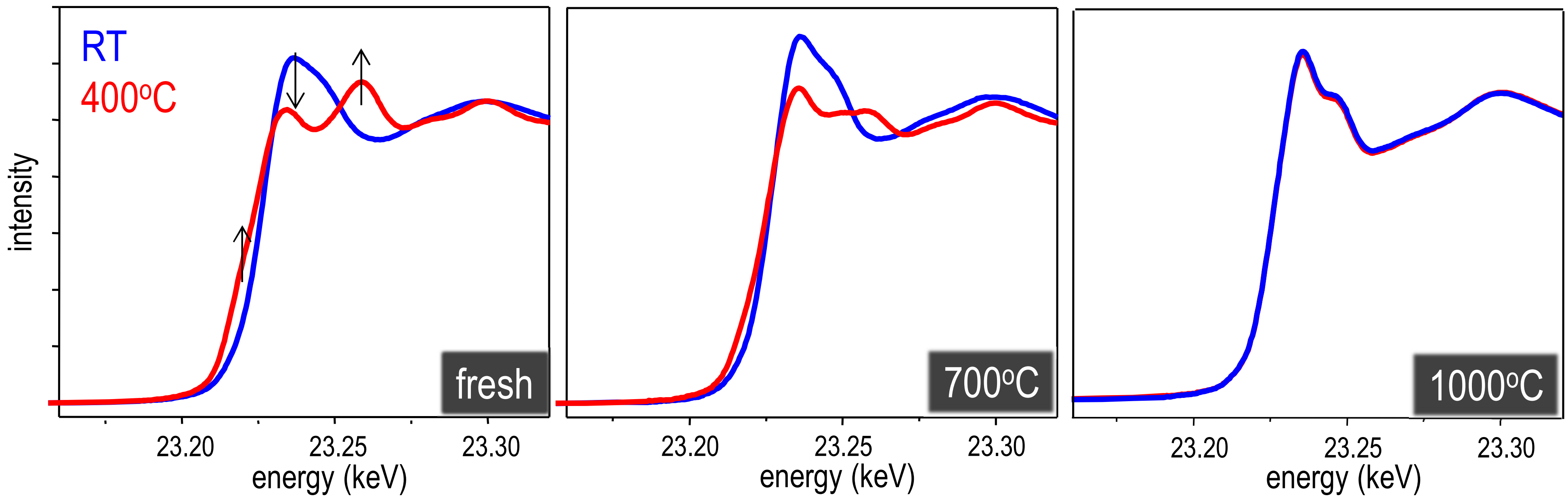
- Rh crystallites are too small to be detected by XRD
- XRD and TEM do not reveal any relevant difference between the samples



Thermal ageing

EPFL

- Hydrothermal ageing - Rh/Al_2O_3



H_2-TPR: 5 vol.% H_2/He at 30ºC and prior to heating;
heating to 400ºC (10ºC/min) in H_2/He

- Rh reducibility - availability for reaction - decreases with increasing aging temperature

$$2Rh + 3/2O_2 \rightarrow Rh_2O_3$$
$$Rh_2O_3 + Al_2O_3 \rightarrow Rh_2O_3{\cdot}Al_2O_3$$
$$Rh_2O_3{\cdot}Al_2O_3 + 3H_2 \rightarrow 2Rh + Al_2O_3 + 3H_2O$$