Université catholique de Louvain UCL

Part II

A case study: catalytic car converter.

→ A pretext to speak about environmental catalysis (mobile sources)

IMCN
Institut de la matière condensée et des nanosciences

Societal needs

Our nowadays mankind needs advanced technology
BUT with less impact as possible on the environment :
less spoiling, less wastes, heat less, etc.

↓

BUT
emissions/formations of harmful byproducts/wastes
cannot always be avoided
→ « Catalytic clean-up technologies »
allow struggling against pollutions

Challenges for the catalysis

Heterogeneous catalysis is a must
to convert air pollutants in molecules not/less toxic
for the environment

$CO \rightarrow CO_2$

$NO_x \rightarrow N_2$

$SO_x \rightarrow H_2S \rightarrow S°$

$O_3 \rightarrow O_2$

Hydrocarbons → $CO_2 + H_2O$

Volatile Organic Compounds (VOC) → $CO_2 + H_2O$

without producing NO_x (→ N_2) / SO_x (→ H_2S) / Cl_2 (→ HCl)
for COV containing heteroatom (N, S, Cl)

Challenges for the catalysis

and water ???

↓

→ Organic molecules :
hydrocarbons + fatty esters (oils : industrial + eatable)
+ dyes + solvents
= same approach as VOC and hydrocarbons in the air :
total oxidation

→ Nitrates :
= denitrification on (membrane) catalysts

Catalysis vs Trapping/Scrubbing

Trapping / Scrubbing =
Washing (for ex : on CaO milk) or
Adsorption on active carbon or other porous solids (for ex : zeolites)

↓

Not everything is trappable : (CO, O_3 = No) vs (NO_x, SO_x = Yes)

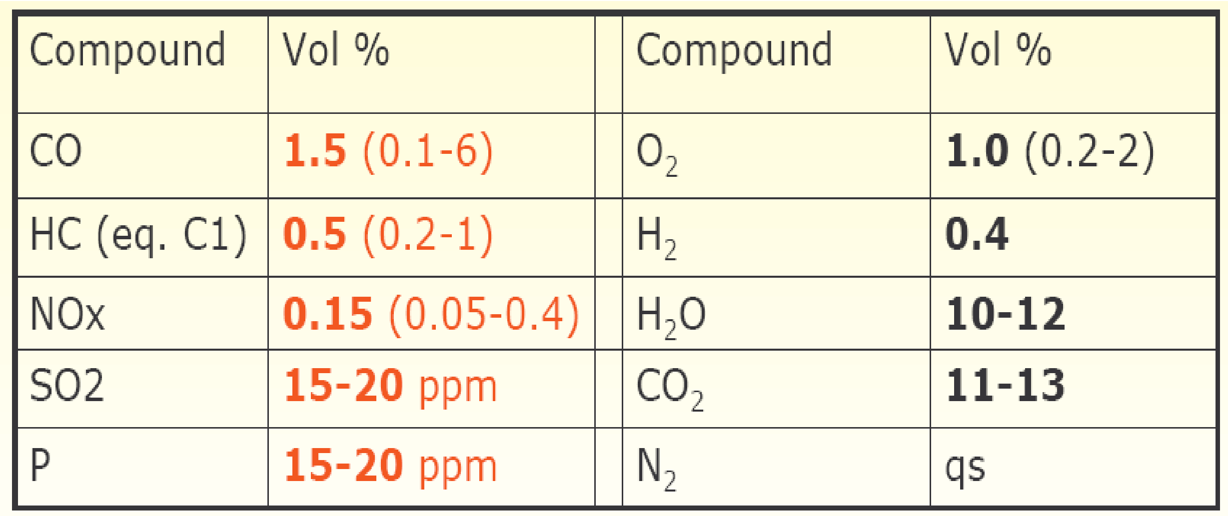
$A^d/_b$sorbing is not eliminating but only shifting a pollution !!!
→ What to do when the adsorbant is saturated ???
(industrial dumping + risk of leaching /combustion + air pollution)

vs destruction of pollutants by catalysis (for ex : dioxins)

Replacement cost of adsorbants vs Starting investment for catalysis

Automotive catalysis

Composition of exhaust gases
gasoline engine

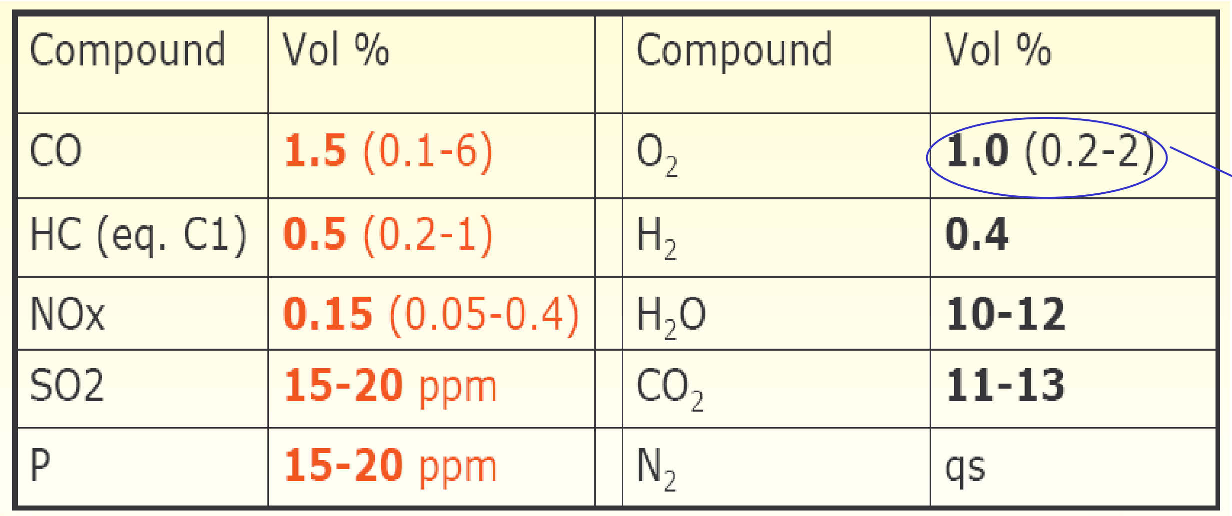


Compound	Vol %		Compound	Vol %
CO	**1.5** (0.1-6)		O_2	**1.0** (0.2-2)
HC (eq. C1)	**0.5** (0.2-1)		H_2	**0.4**
NOx	**0.15** (0.05-0.4)		H_2O	**10-12**
SO2	**15-20** ppm		CO_2	**11-13**
P	**15-20** ppm		N_2	qs

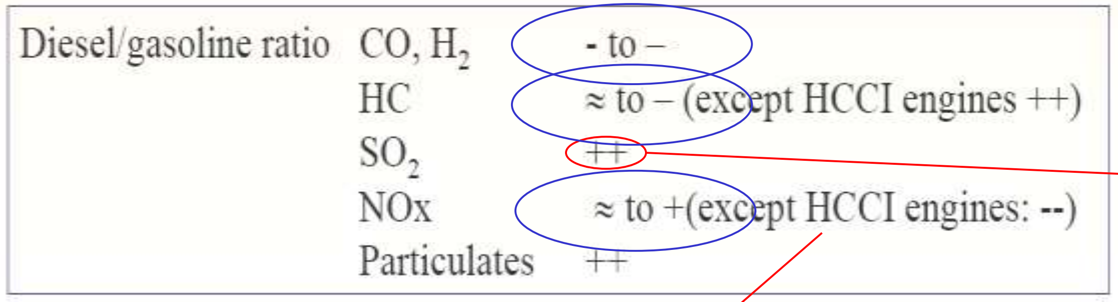
→ 10 times more CO than NOx

!!!
Variations with
tuning of the engine
age of the vehicle
and
type of driving
// age of driver
!!!

Composition of exhaust gases
gasoline engine vs diesel



Compound	Vol %	Compound	Vol %
CO	**1.5** (0.1-6)	O_2	**1.0** (0.2-2)
HC (eq. C1)	**0.5** (0.2-1)	H_2	**0.4**
NOx	**0.15** (0.05-0.4)	H_2O	**10-12**
SO2	**15-20** ppm	CO_2	**11-13**
P	**15-20** ppm	N_2	qs



Diesel/gasoline ratio	CO, H_2	- to –
	HC	≈ to – (except HCCI engines ++)
	SO_2	++
	NOx	≈ to +(except HCCI engines: --)
	Particulates	++

Diesel =
Much more O_2 :
6-10%

Before HDS of diesels
→ Today =

Homogeneous combustion engines (T° <<)
→ less NOx but more unburnt HC
(under development)

Reactions to achieve !!! → 3-ways

Way 1 Way 2

- Oxidation reactions : CO and hydrocarbons

$CO + \frac{1}{2} O_2 \longrightarrow CO_2$ **Pt** or Pd

$HC + O_2 \longrightarrow CO_2 + H_2O$

ex: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ **Pt** or Pd

Way 3

- Reduction reactions : NOx

$NO \longrightarrow \frac{1}{2}N_2$ **Rh** or Pd

but Rh more selective to N_2

Reactions to achieve !!! → 3-ways

Way 1 Way 2

- Oxidation reactions : CO and hydrocarbons

$CO + \frac{1}{2} O_2 \longrightarrow CO_2$ **Pt** or Pd

$HC + O_2 \longrightarrow CO_2 + H_2O$

ex: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ **Pt** or Pd

Way 3 // Way 1

- Reduction reactions : NOx

$NO + CO \longrightarrow \frac{1}{2}N_2 + CO_2$ **Rh** or Pd but Rh more selective to N_2

$NO + H_2 \longrightarrow \frac{1}{2}N_2 + H_2O$

Reactions to achieve !!! → 3-ways

- **Oxidation reactions : CO and hydrocarbons**

$CO + \frac{1}{2} O_2 \longrightarrow CO_2$ **Pt**

$HC + O_2 \longrightarrow CO_2 + H_2O$

ex: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ **Pt**

- **Reduction reactions : NOx**

$NO + CO \longrightarrow \frac{1}{2}N_2 + CO_2$ **Rh**

$NO + H_2 \longrightarrow \frac{1}{2}N_2 + H_2O$

Too much O_2

→ A lot of NO

→ Complete oxidation of CO

(not enough CO to reduce NO)

Not enough O_2

→ complete reduction of NO

→ a lot of CO and

unburnt HC

Heterogeneous Catalysis, E. Gaigneaux, UCL, Belgium

Reactions to achieve !!! → 3-ways

- Oxidation reactions : CO and hydrocarbons

$CO + \frac{1}{2} O_2 \longrightarrow CO_2$ **Pt**

$HC + O_2 \longrightarrow CO_2 + H_2O$

ex: $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$ **Pt**

- Reduction reactions : NOx

$NO + CO \longrightarrow \frac{1}{2}N_2 + CO_2$ **Rh**

$NO + H_2 \longrightarrow \frac{1}{2}N_2 + H_2O$

→ Way 1 // Way 3

Key of 3-ways = tuning the ratio residual O / reductants in the effluent

tuning the ratio air/fuel at the engine admission

Too much O_2

→ A lot of NO

→ Complete oxidation of CO

(not enough CO to reduce NO)

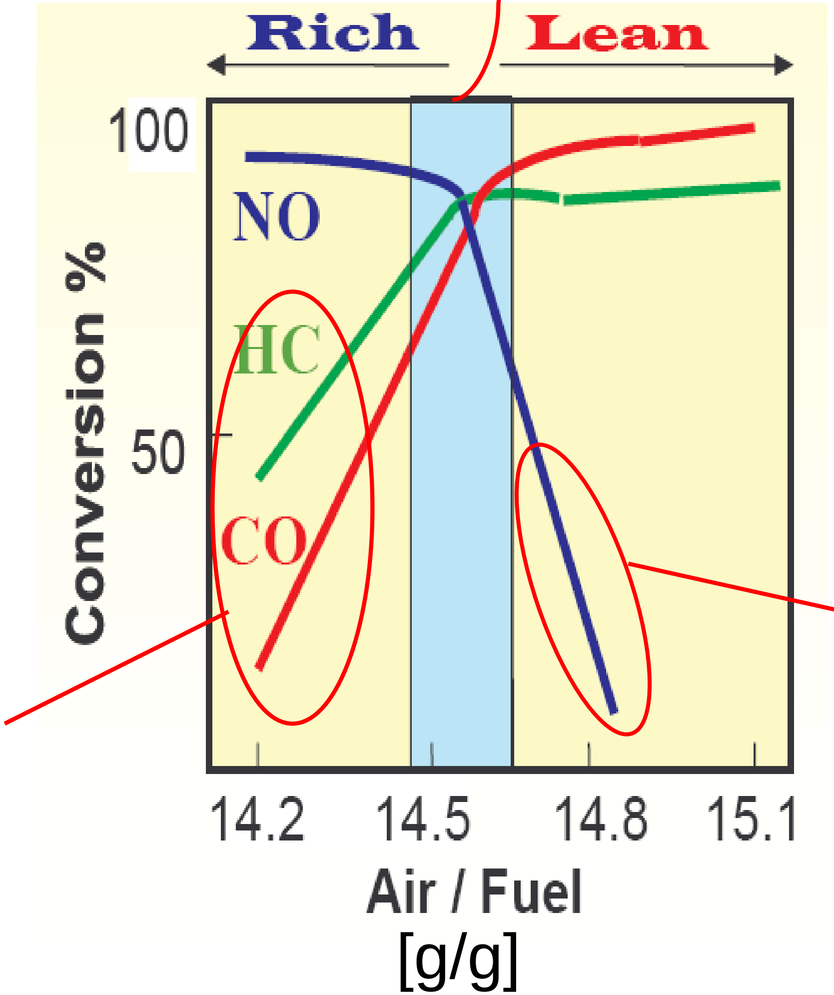
Not enough O_2

→ complete reduction of NO

→ a lot of CO and

unburnt HC

Effect of air/fuel on TWC performances



the window
where to work !!!
= mix
stoechiometry
of
air/fuel = 14.5-14.7

too reducing mix
too « rich »
to oxidize CO
and HC

too oxidant mix
too « lean »
to reduce NO

Lamba / Richness / Schlater

$$\lambda = \frac{{}^{A}\!/_{F}}{14.6}$$

Richness = 1/λ

the motorist vision

Schlater

$$S = \frac{OX}{RED} = \frac{2O_2 + NO}{CO + H_2 + 3nC_nH_{2n} + (3n+1)C_nH_{2n+1}}$$

the chemist vision

ponderating by the number of O atoms effectively available (OX) and by the number of O atoms effectively needed (RED)

Effect of λ on TWC performances

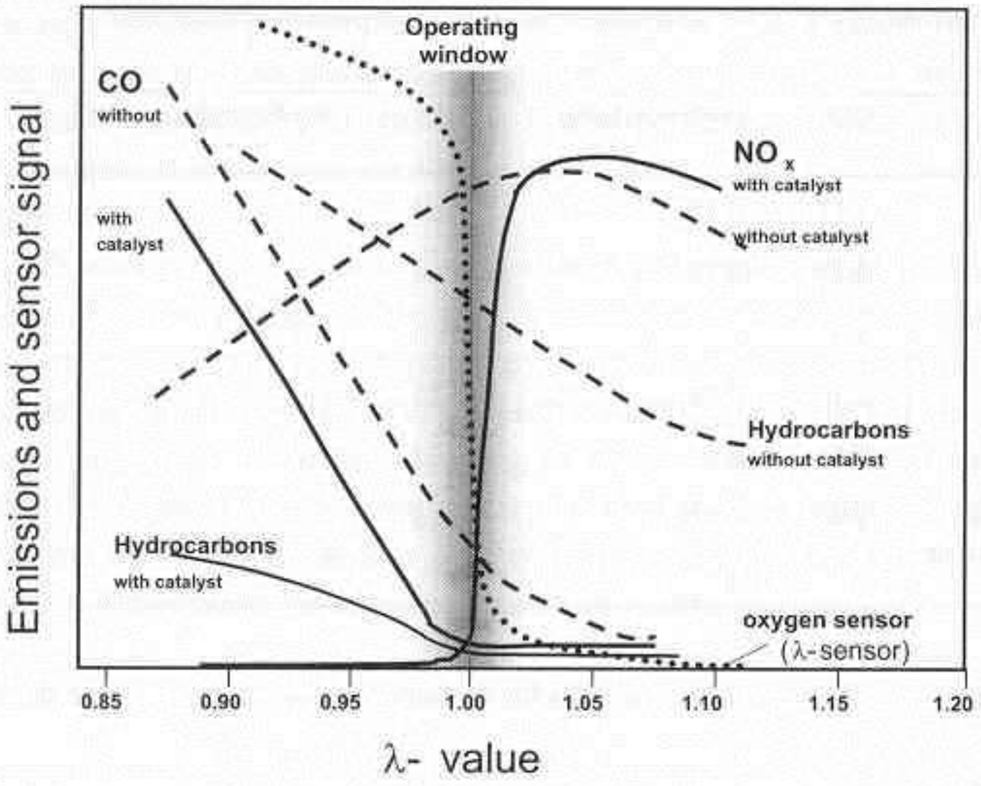


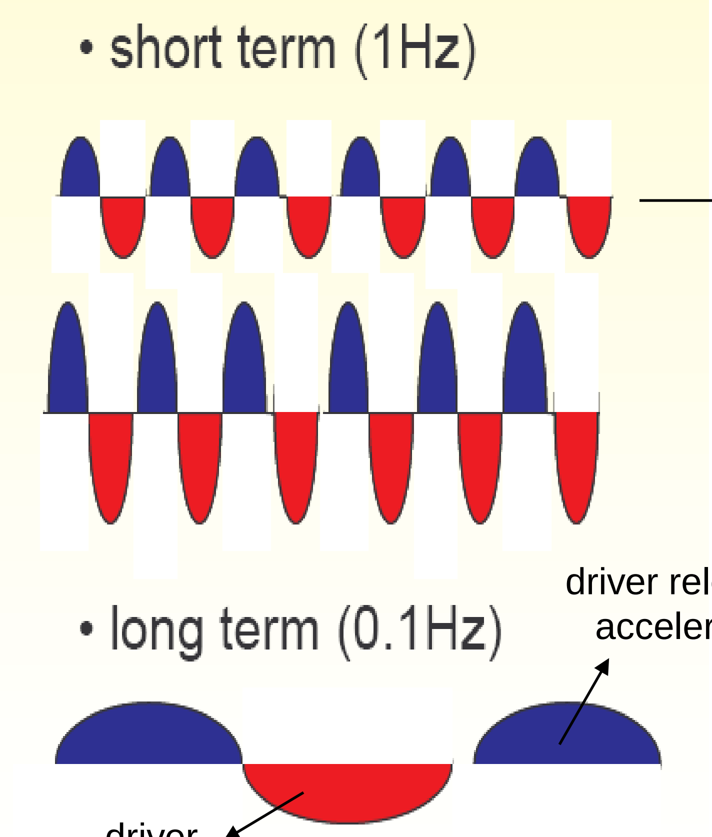
Figure 10.1. Emissions of CO, NO_x and hydrocarbons along with the signal from the oxygen sensor as a function of the air/fuel composition; $\lambda = 1$ corresponds to the air-to-fuel ratio of 14.7. Note that the three pollutants can only be converted simultaneously in a very narrow operating window of air-to-fuel ratios.

Same representation
but expressed in emissions
→ reverse curves !

The effect of the catalyst
is clearly visible :
1° less emissions globally
2° transition around λ = 1
is more marked

How to stay in the right lambda slot ?

Variation of richness
during driving
= f(type of driving)



→ λ=1

fearful/stressed driver (grand mother ?)

young nervous ?

driver releases accelerator

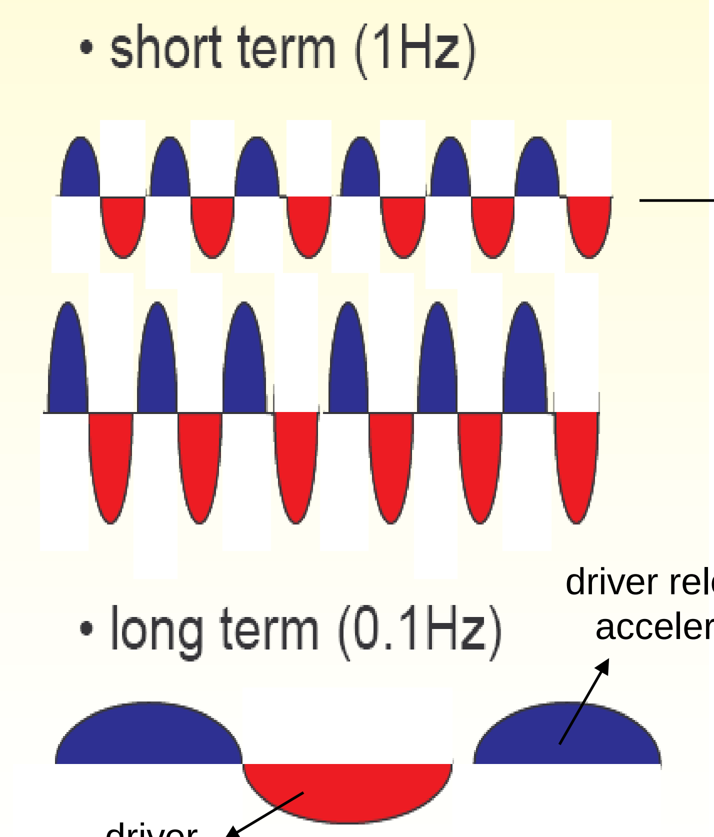
driver speeds up

normal behavior ?
(grand father ?)

→ 1 push on accelerator every 10s

How to stay in the right lambda slot ?

Variation of richness
during driving
= f(type of driving)



→ λ=1

fearful/stressed driver (grand mother ?)

young nervous ?

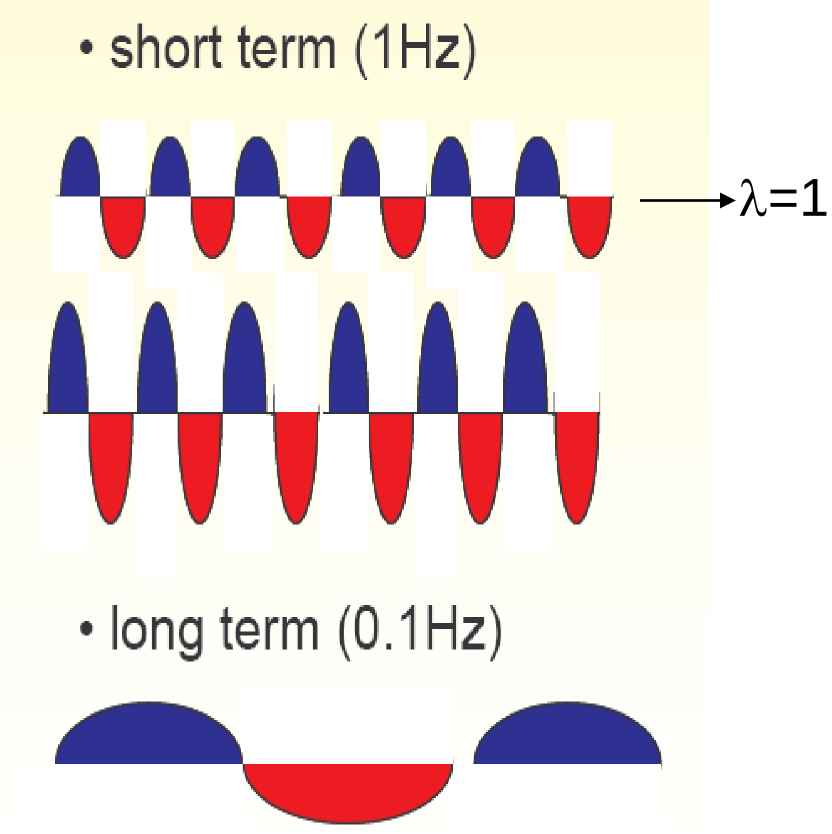
driver releases
accelerator → Problem of NOx

normal behavior ?
(grand father ?) → 1 push on accelerator
every 10s

driver
speeds up → Problem of CO

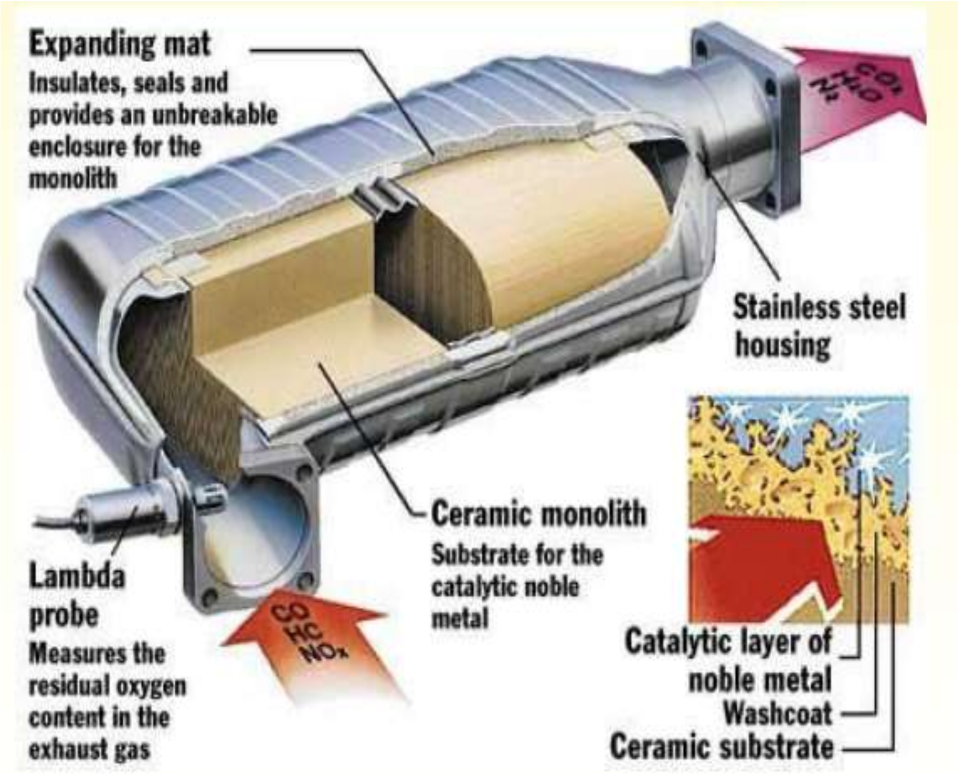
How to stay in the right lambda slot ?

Variation of richness
during driving
= f(type of driving)

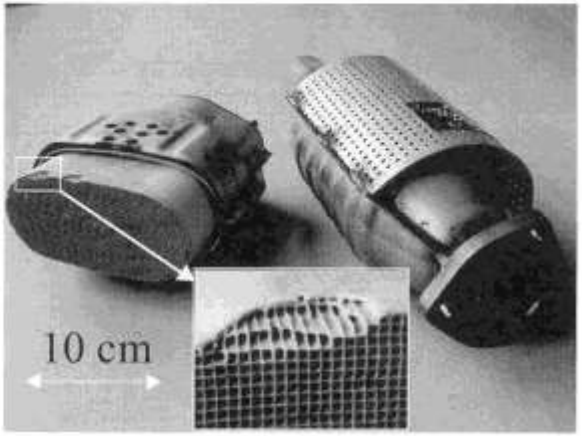


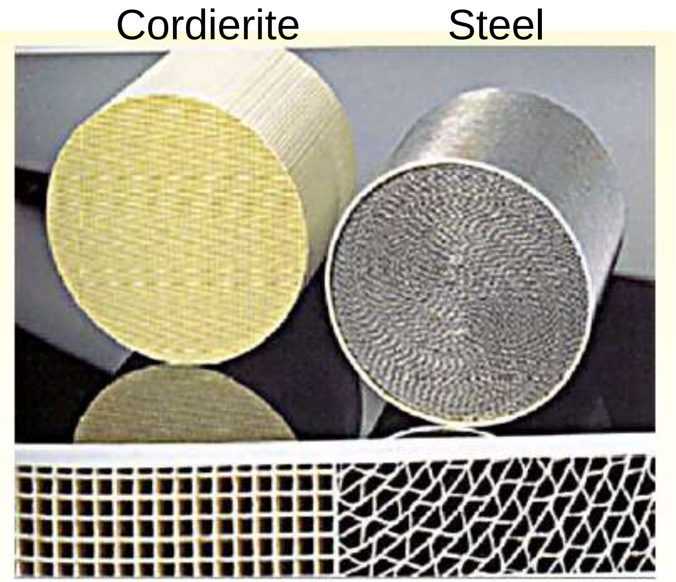
→ LAMBDA PROBE

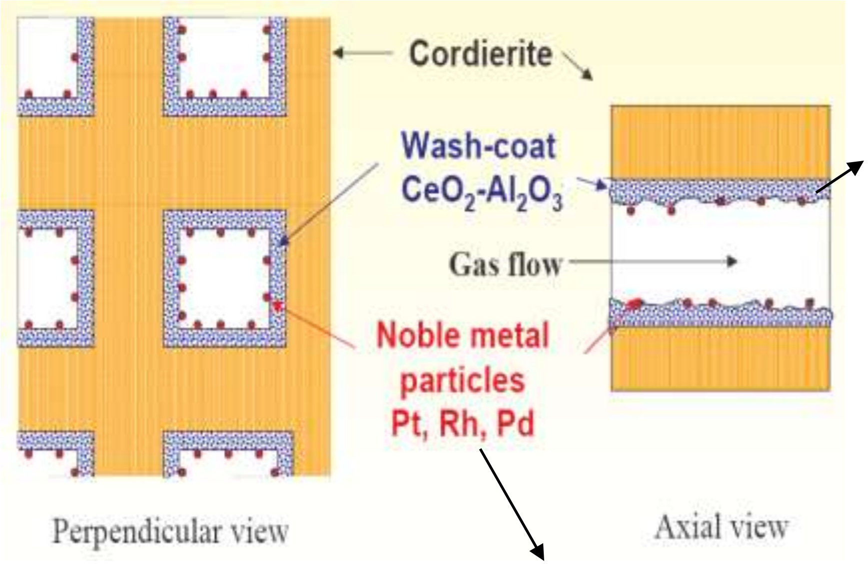
→ CATALYST



The catalyst







30-50 µm

as most dispersed (nano) as possible !!!

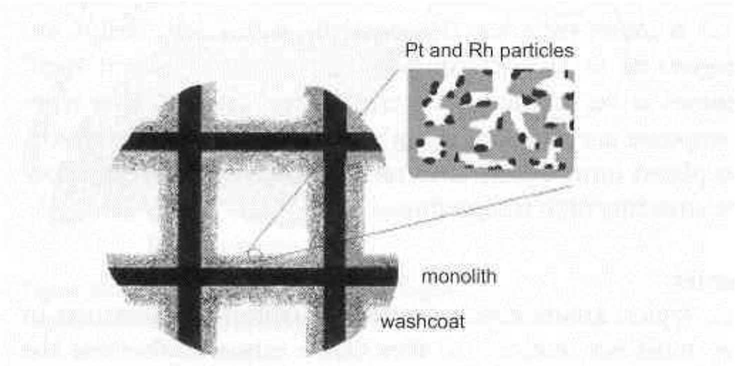
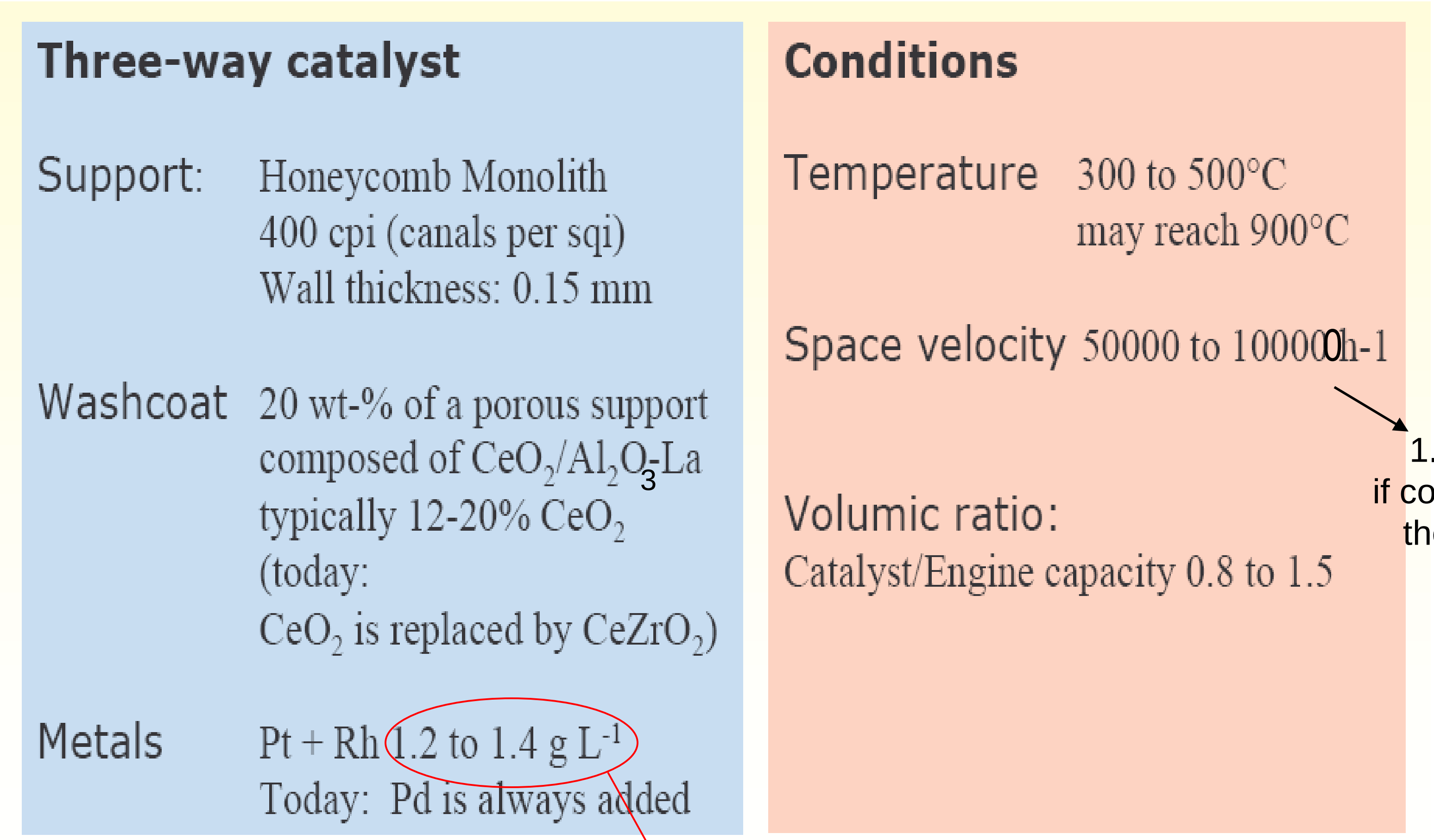


Figure 10.5. Monolith, washcoat and noble metal particles in an automotive exhaust catalyst.

A typical catalyst



Three-way catalyst

Support: Honeycomb Monolith
400 cpi (canals per sqi)
Wall thickness: 0.15 mm

Washcoat 20 wt-% of a porous support composed of CeO_2/Al_2O_3-La
typically 12-20% CeO_2
(today:
CeO_2 is replaced by $CeZrO_2$)

Metals Pt + Rh 1.2 to 1.4 g L^{-1}
Today: Pd is always added

Conditions

Temperature 300 to 500°C
may reach 900°C

Space velocity 50000 to 100000h-1

Volumic ratio:
Catalyst/Engine capacity 0.8 to 1.5

1.000.000 h^{-1}
if considering only
the wash-coat

1-2% wt
of the wash-coat

TWC→ Oxidation of CO

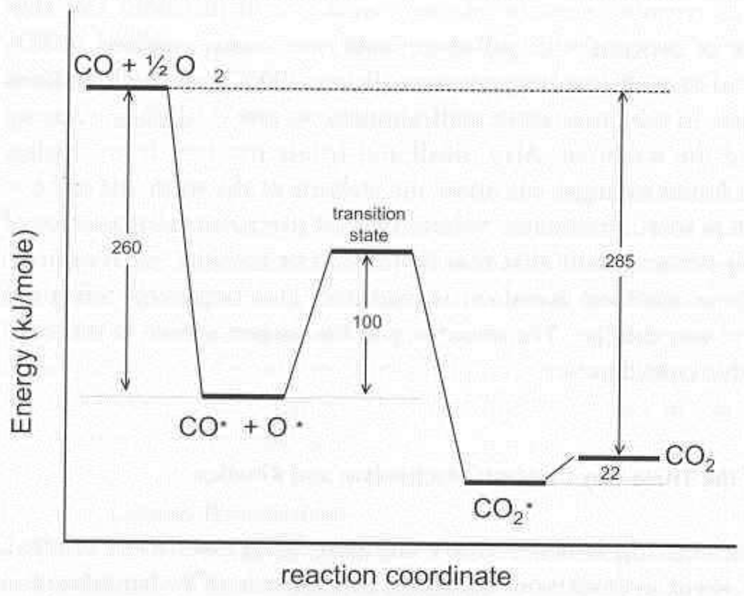


Figure 10.6. Approximate energy diagram of CO oxidation on palladium. Note the largest energy barrier is the CO + O recombination. [Adapted from T. Engel and G. Ertl, *J. Chem. Phys.* **69** (1978) 1267.]

→ $CO + \frac{1}{2} O_2 \rightarrow CO_2$

Highly exothermic reaction (285 kJ/mole)

→ On Pd :

Activation energy = 100 kJ/mole

for the r° CO*+O* (rate limiting step)

vs

Homogeneous phase :

Activation energy = 500 kJ/mole

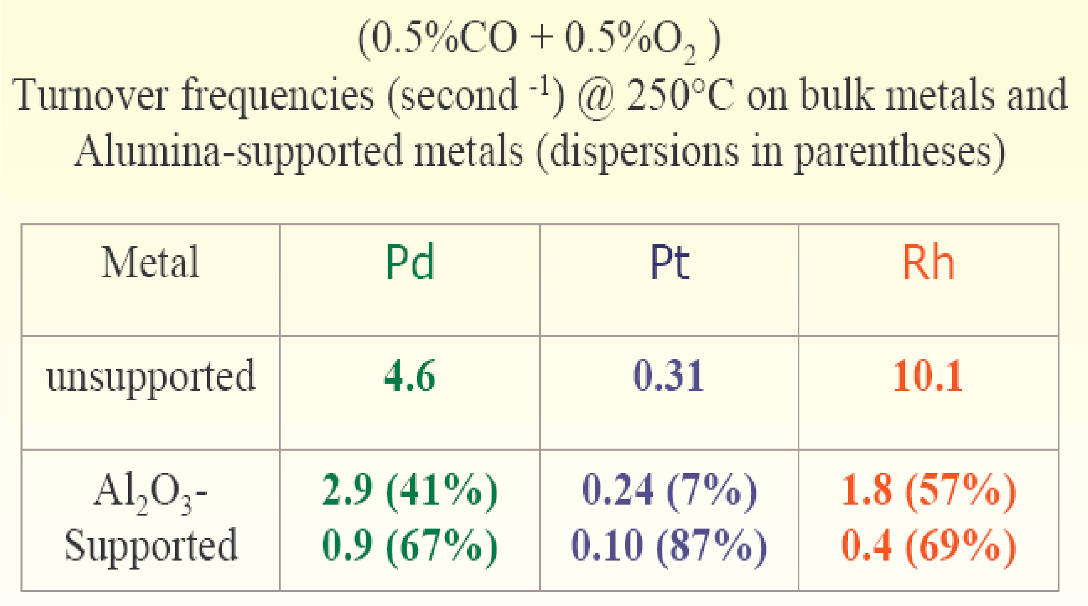
for the dissociation $\frac{1}{2} O_2 \rightarrow O$

(rate limiting step)

→→ The catalyst has modified

the rate limiting step !

TWC→ Oxidation of CO



($0.5\%CO + 0.5\%O_2$)
Turnover frequencies (second $^{-1}$) @ 250°C on bulk metals and Alumina-supported metals (dispersions in parentheses)

Metal	Pd	Pt	Rh
unsupported	**4.6**	**0.31**	**10.1**
Al_2O_3-Supported	**2.9 (41%)** **0.9 (67%)**	**0.24 (7%)** **0.10 (87%)**	**1.8 (57%)** **0.4 (69%)**

→ R° faster on big particles than on small ones :
dispersion ↗ → TOF ↘ (mainly on Rh)

→ Rh and Pd loose activity in presence of NO (not shown)

→→ Best catalyst = Pt

NO = poison !!!

TWC→ Oxidation of CO

NO = poison !!! → CO also (much more) !!! !!! !!!

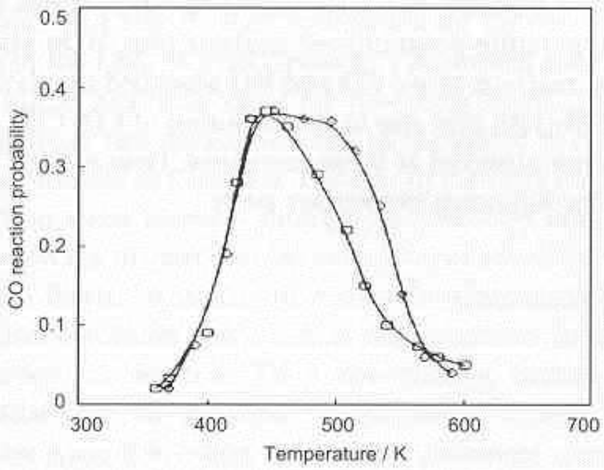


Figure 10.7. CO_2 formation rate from CO and O_2 over Rh(111) and Rh(110) surfaces [Adapted from M. Bowker, Q. Guo, and R.W. Joyner, *Catal. Lett.* **18** (1993) 119]. Note the similarity to the simple model used to describe the rate in Fig. 2.12.

According Arrhenius :
We should have Temp ↗ → Speed ↗
Not the case:
→ There is a speed maximum !!!

TWC→ Oxidation of CO

NO = poison !!! → CO also (much more) !!! !!! !!!

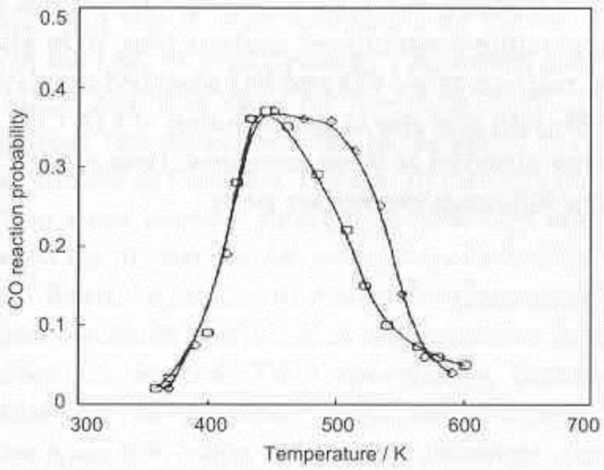


Figure 10.7. CO_2 formation rate from CO and O_2 over Rh(111) and Rh(110) surfaces [Adapted from M. Bowker, Q. Guo, and R.W. Joyner, *Catal. Lett.* **18** (1993) 119]. Note the similarity to the simple model used to describe the rate in Fig. 2.12.

According Arrhenius :
We should have Temp ↗ → Speed ↗
Not the case:
→ There is a speed maximum !!!

Low Temp :
surface mostly covered by CO
→ no place for O*
→→ no r° CO* + O*

High Temp (> desorption temp of CO):
surface covered by O*
→ not enough CO* at the surface
→→ no r° CO* + O*

TWC→ Oxidation of CO

NO = poison !!! → CO also (much more) !!! !!! !!!

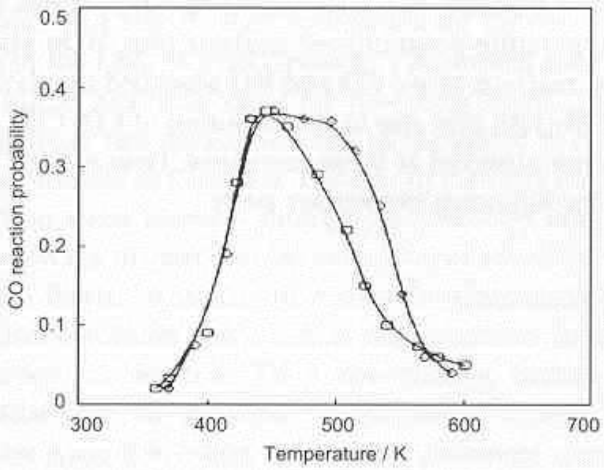


Figure 10.7. CO_2 formation rate from CO and O_2 over Rh(111) and Rh(110) surfaces [Adapted from M. Bowker, Q. Guo, and R.W. Joyner, *Catal. Lett.* **18** (1993) 119]. Note the similarity to the simple model used to describe the rate in Fig. 2.12.

According Arrhénius :
We should have Temp ↗ → Speed ↗
Not the case:
→ There is a speed maximum !!!

Necessity to work at
intermediate temperature
at which
coverage of the surface
by CO and by O are comparable !!!

→ Mechanism of
Langmuir-Hinshelwood
(cf Part Ib – Section 6)

TWC→ Oxidation of CO

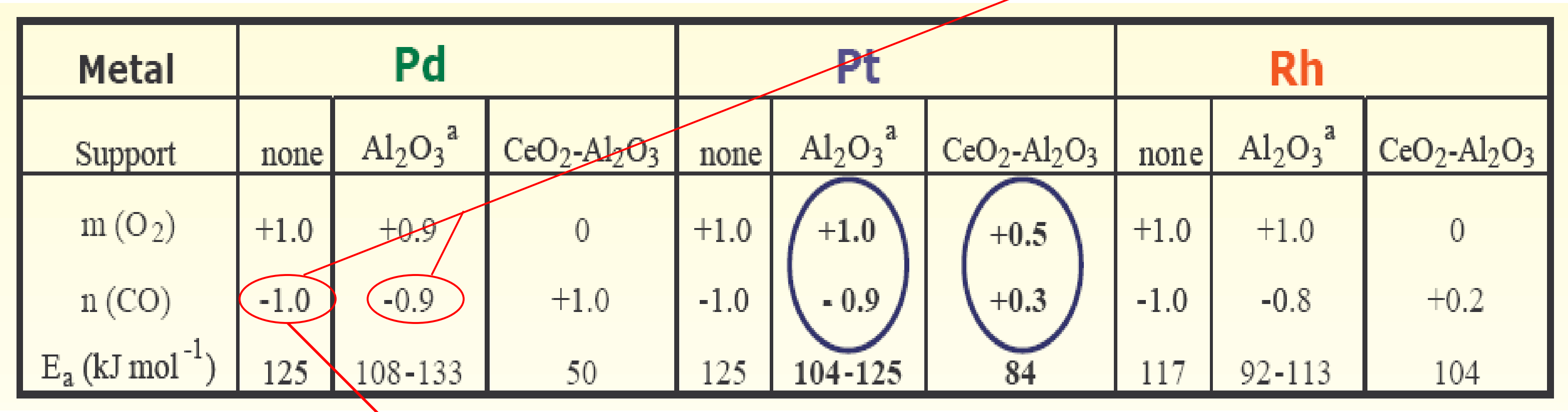
because O_2 → 2O

$$r_{CO} = k\frac{K_{CO}P_{CO}K_OP_O^{1/2}}{(1+K_{CO}P_{CO}+K_OP_O^{1/2})^2}$$

Adsorption CO>>>Adsorption O_2

If $K_{CO}P_{CO} >> 1+K_OP_O^{1/2}$ →

$$r_{CO} = k\frac{K_OP_O^{1/2}}{K_{CO}P_{CO}}$$



Metal	Pd			Pt			Rh		
Support	none	Al_2O_3 ^a	CeO_2-Al_2O_3	none	Al_2O_3 ^a	CeO_2-Al_2O_3	none	Al_2O_3 ^a	CeO_2-Al_2O_3
m (O_2)	+1.0	+0.9	0	+1.0	**+1.0**	**+0.5**	+1.0	+1.0	0
n (CO)	-1.0	-0.9	+1.0	-1.0	**- 0.9**	**+0.3**	-1.0	-0.8	+0.2
E_a (kJ mol^{-1})	125	108-133	50	125	**104-125**	**84**	117	92-113	104

Metal or Metal/alumine
order –1 for the CO → CO = inhibitor
= CO adsorbs stronger on the metal
and does not allow oxygen to adsorb

TWC→ Oxidation of CO

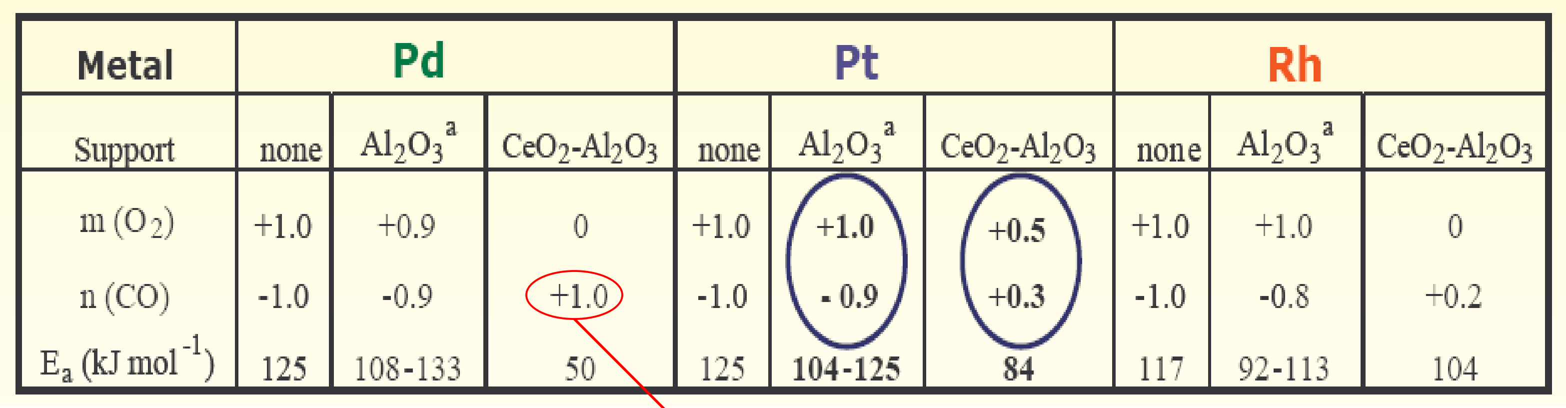
because O_2 → 2O

Adsorption CO>>>Adsorption O_2

$$r_{CO} = k \frac{K_{CO}P_{CO}K_O P_O^{1/2}}{(1 + K_{CO}P_{CO} + K_O P_O^{1/2})^2}$$

$$\text{If } K_{CO}P_{CO} >> 1 + K_O P_O^{1/2}$$

$$r_{CO} = k \frac{K_O P_O^{1/2}}{K_{CO}P_{CO}}$$

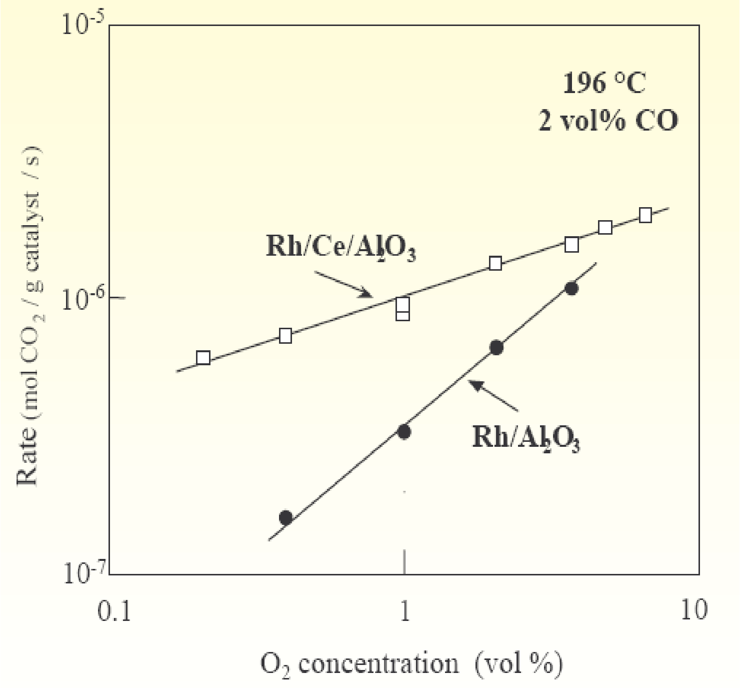


Metal	Pd			Pt			Rh		
Support	none	$Al_2O_3{}^a$	CeO_2-Al_2O_3	none	$Al_2O_3{}^a$	CeO_2-Al_2O_3	none	$Al_2O_3{}^a$	CeO_2-Al_2O_3
m (O_2)	+1.0	+0.9	0	+1.0	**+1.0**	**+0.5**	+1.0	+1.0	0
n (CO)	-1.0	-0.9	+1.0	-1.0	**- 0.9**	**+0.3**	-1.0	-0.8	+0.2
E_a (kJ mol^{-1})	125	108-133	50	125	**104-125**	**84**	117	92-113	104

Metal/ceria+alumina
order +1 for the CO → CO ≠ inhibitor
→ ceria brings new sites
for the adsorption of oxygen !!!

TWC→ Oxidation of CO

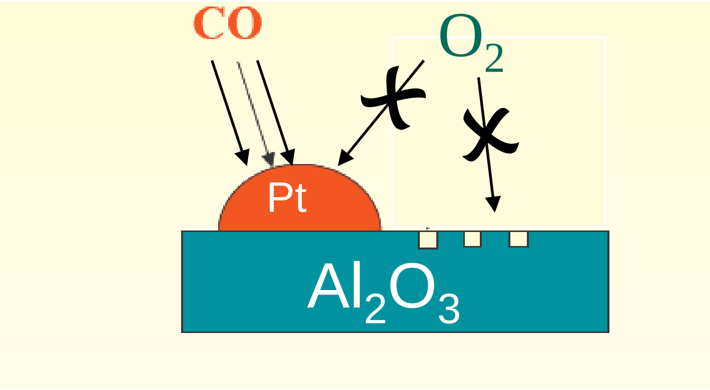
Effect of the addition of ceria

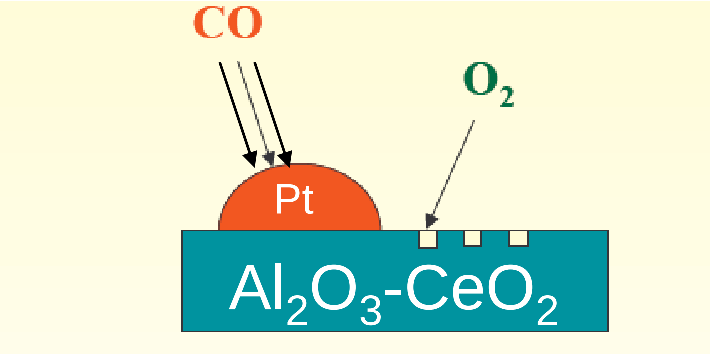


A mixture « rich » in CO inhibits less Rh/Ce-Alumina than Rh/Alumina

TWC→ Oxidation of CO

Effect of the addition of ceria





- CO adsorption on metal (site #)
- O_2 adsortion on O vacancies of ceria (site *)
- CO reaction with O species at the metal/support interface

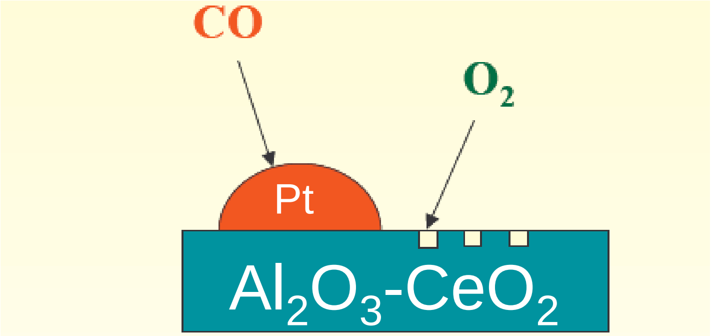
→ The adsorptions of CO and O_2 are no more competitive because there are 2 distinct sites of adsorption for them

TWC→ Oxidation of CO

Effect of the addition of ceria

→ The oxidation of CO happens thanks to O atoms from ceria (and not from the gas phase)

→→ Does it work without O_2 in the reaction gas ?



- CO adsorption on metal (site #)
- O_2 adsortion on O vacancies of ceria (site *)
- CO reaction with O species at the metal/support interface

TWC→ Oxidation of CO

because O_2 → 2O

$$r_{CO} = k \frac{K_{CO}P_{CO}K_O P_O^{1/2}}{(1+K_{CO}P_{CO}+K_O P_O^{1/2})^2}$$

Adsorption CO>>>Adsorption O_2

$$\text{If } K_{CO}P_{CO} >> 1+K_O P_O^{1/2}$$

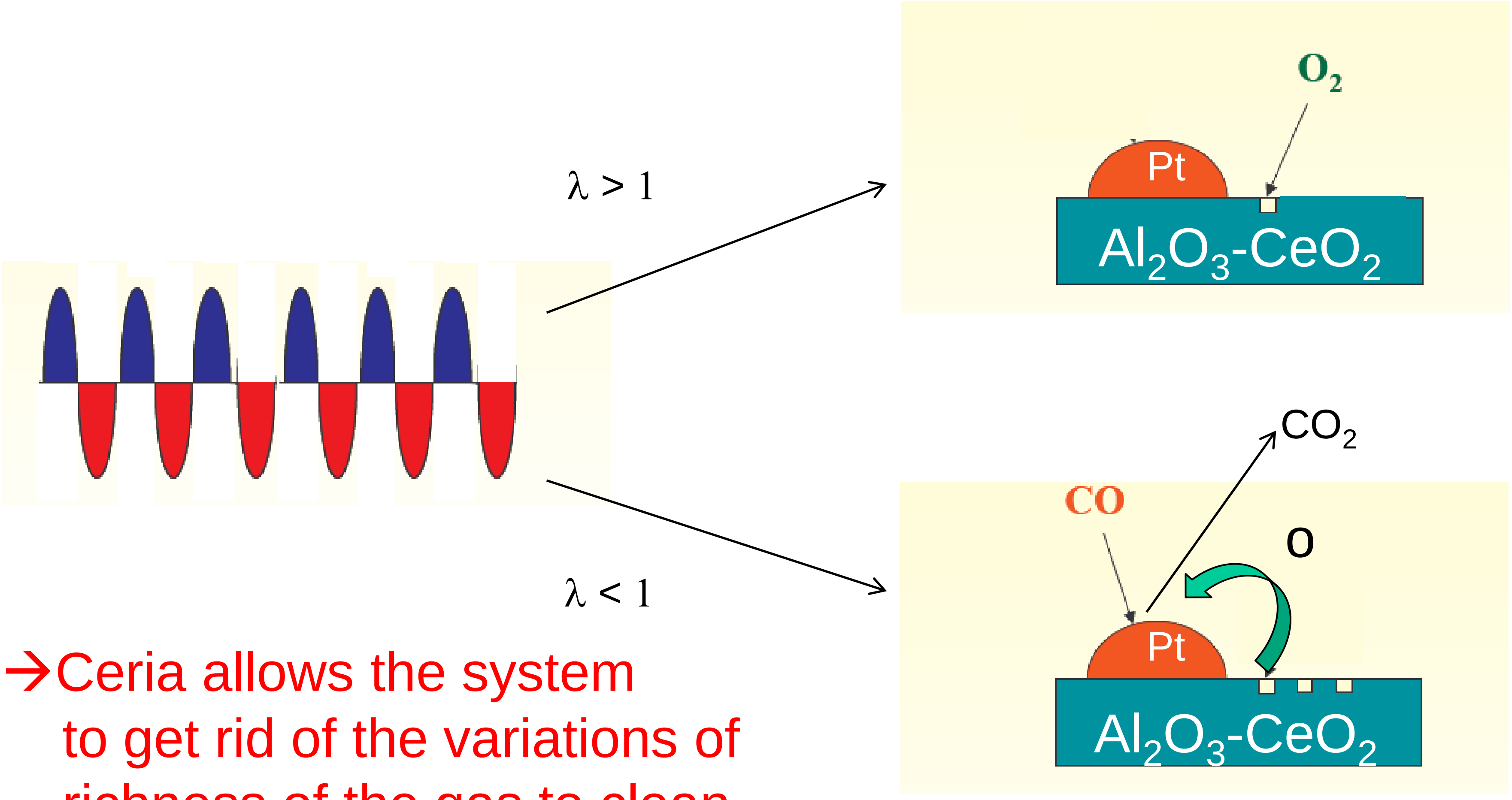
$$r_{CO} = k \frac{K_O P_O^{1/2}}{K_{CO}P_{CO}}$$

Metal	**Pd**			**Pt**			**Rh**		
Support	none	Al_2O_3[a]	CeO_2-Al_2O_3	none	Al_2O_3[a]	CeO_2-Al_2O_3	none	Al_2O_3[a]	CeO_2-Al_2O_3
m (O_2)	+1.0	+0.9	0	+1.0	**+1.0**	**+0.5**	+1.0	+1.0	0
n (CO)	-1.0	-0.9	+1.0	-1.0	**- 0.9**	**+0.3**	-1.0	-0.8	+0.2
E_a (kJ mol^{-1})	125	108-133	50	125	**104-125**	**84**	117	92-113	104

With ceria, order 0 for O_2 !!!
= it works even without O_2 in the gas !!!
→ With ceria : it works more as MVK !!!

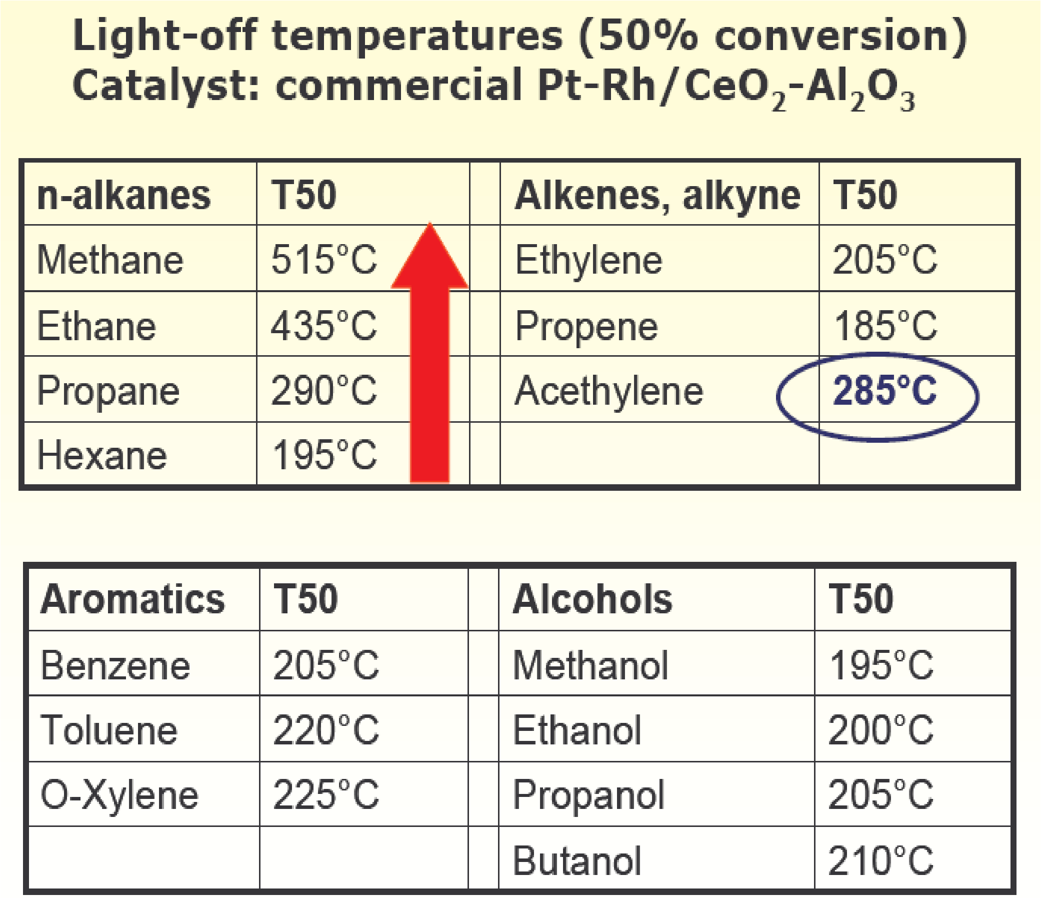
TWC→ Oxidation of CO

Effect of the addition of ceria



→Ceria allows the system to get rid of the variations of richness of the gas to clean.

TWC
→ Oxidation of HC and alcools



Light-off temperatures (50% conversion)
Catalyst: commercial Pt-Rh/CeO_2-Al_2O_3

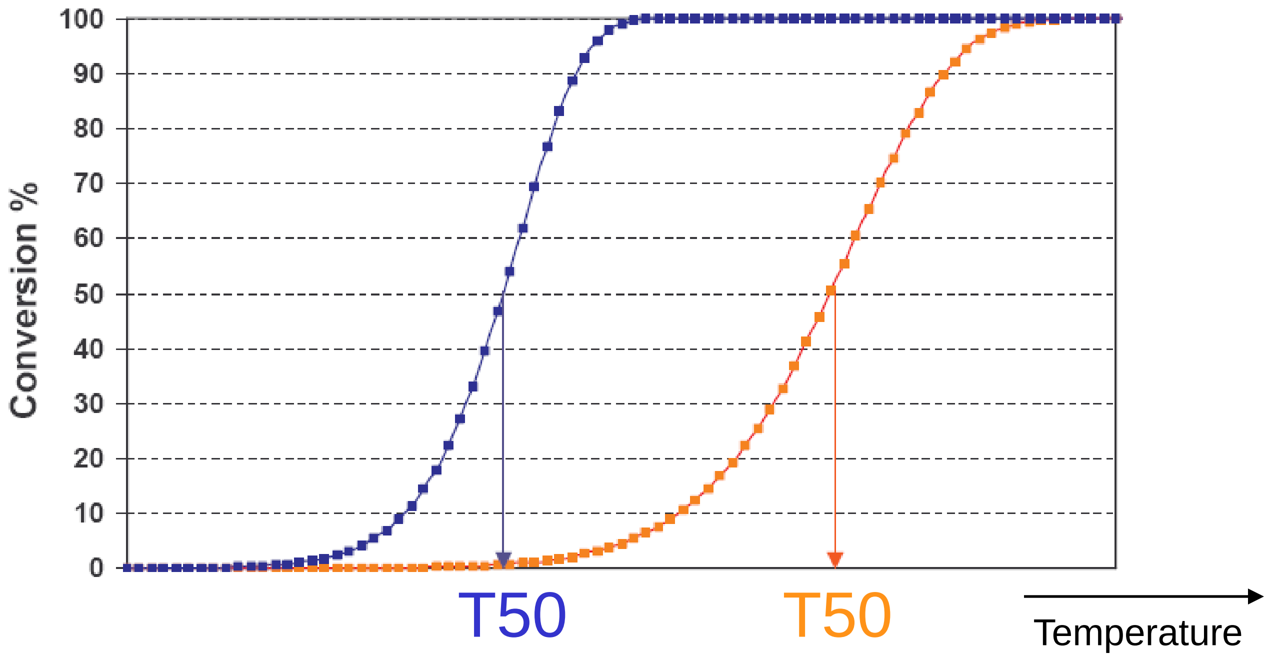
n-alkanes	T50		Alkenes, alkyne	T50
Methane	515°C		Ethylene	205°C
Ethane	435°C		Propene	185°C
Propane	290°C		Acethylene	**285°C**
Hexane	195°C			

Aromatics	T50		Alcohols	T50
Benzene	205°C		Methanol	195°C
Toluene	220°C		Ethanol	200°C
O-Xylene	225°C		Propanol	205°C
			Butanol	210°C

→ Light-off and T50

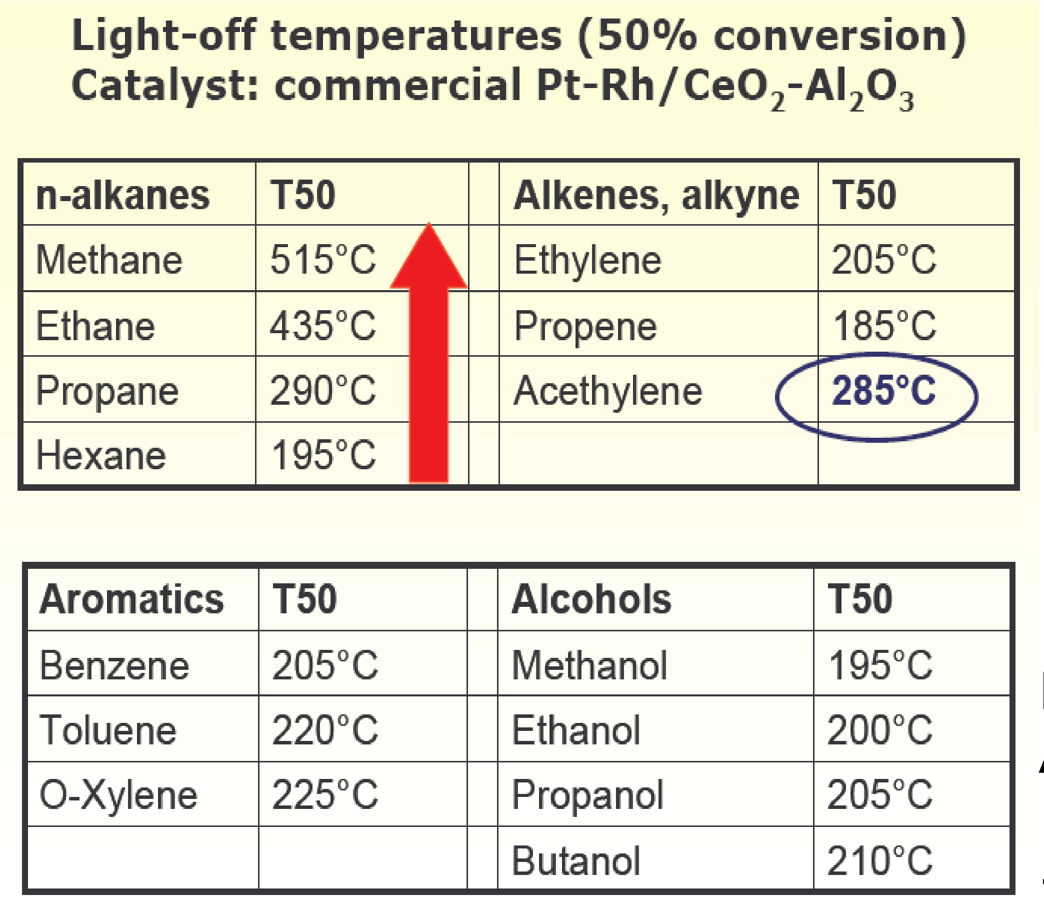
TWC
→ Oxidation of HC and alcools

→ Light-off and T50



T50 : temperature at which catalyst has 50% of conversion
T10, T90, etc …

TWC
→ Oxidation of HC and alcools



Light-off temperatures (50% conversion)
Catalyst: commercial Pt-Rh/CeO_2-Al_2O_3

n-alkanes	T50		Alkenes, alkyne	T50
Methane	515°C		Ethylene	205°C
Ethane	435°C		Propene	185°C
Propane	290°C		Acethylene	**285°C**
Hexane	195°C			

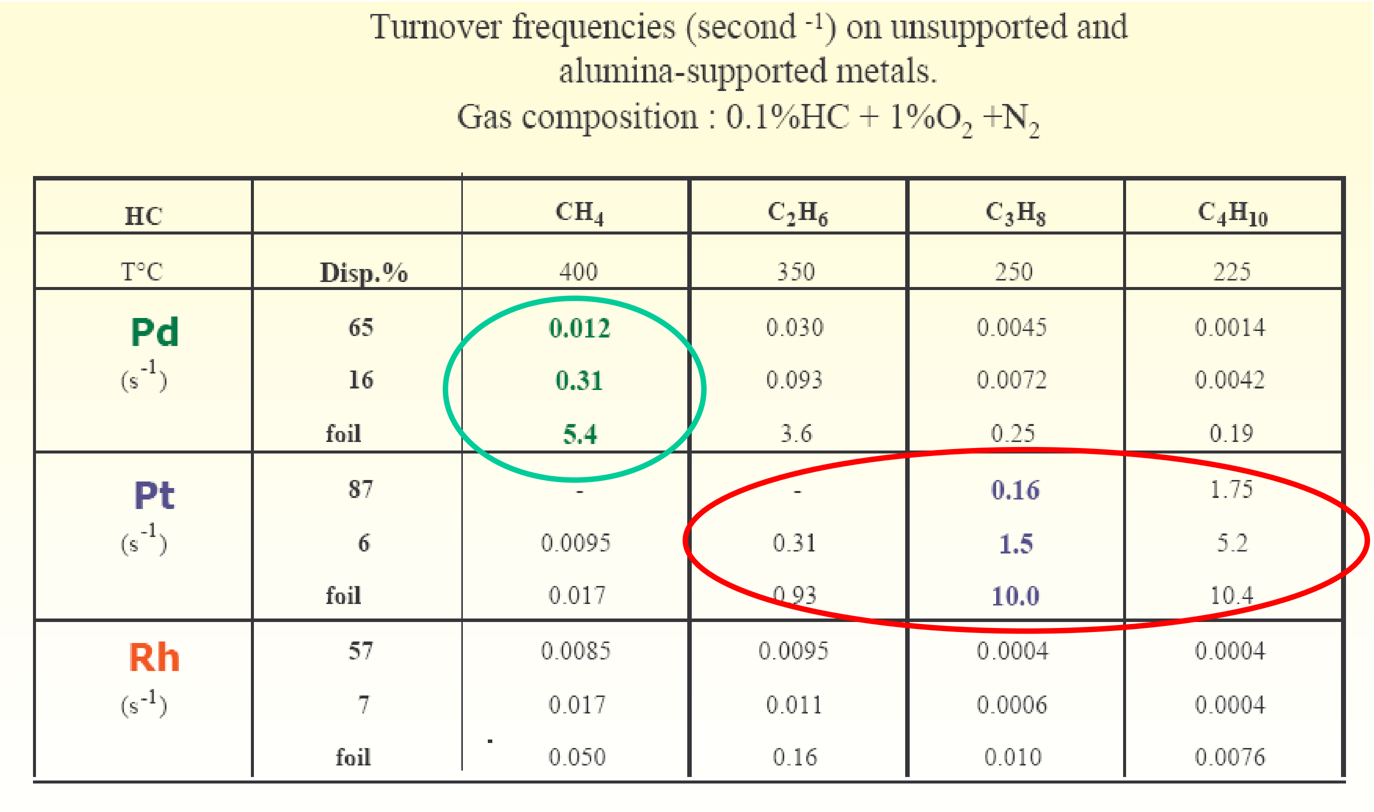
Aromatics	T50		Alcohols	T50
Benzene	205°C		Methanol	195°C
Toluene	220°C		Ethanol	200°C
O-Xylene	225°C		Propanol	205°C
			Butanol	210°C

In general :
Alcohols easier to oxidize than alkanes

→ alkanes more difficult than olefins

→ Lighter alkanes → more difficult
(not true for alcohols)

TWC
→ Oxidation of HC and alcools



Turnover frequencies (second $^{-1}$) on unsupported and alumina-supported metals.
Gas composition : 0.1%HC + 1%O_2 +N_2

HC		CH_4	C_2H_6	C_3H_8	C_4H_{10}
T°C	**Disp.%**	400	350	250	225
Pd (s^{-1})	**65**	**0.012**	0.030	0.0045	0.0014
	16	**0.31**	0.093	0.0072	0.0042
	foil	**5.4**	3.6	0.25	0.19
Pt (s^{-1})	**87**	-	-	**0.16**	1.75
	6	0.0095	0.31	**1.5**	5.2
	foil	0.017	0.93	**10.0**	10.4
Rh (s^{-1})	**57**	0.0085	0.0095	0.0004	0.0004
	7	0.017	0.011	0.0006	0.0004
	foil	0.050	0.16	0.010	0.0076

→ Pt : best metal for C2-C4

→ but Pd : best for CH_4

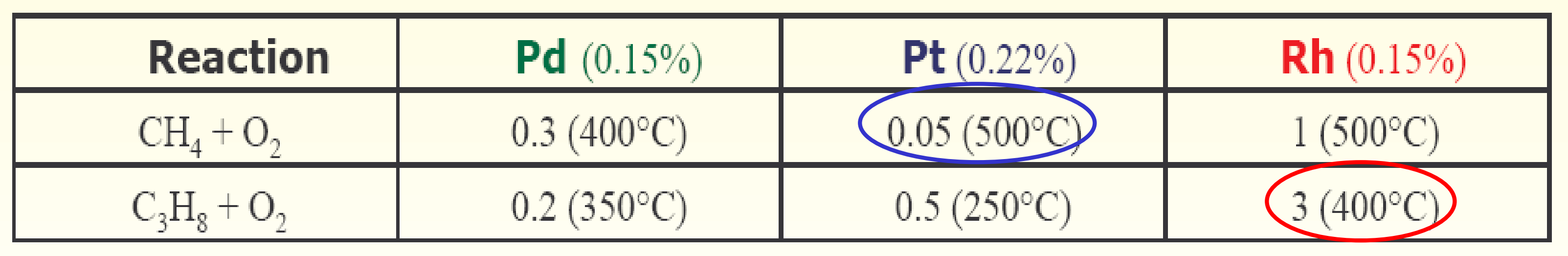
→ Rh always bad !

→ Dispersion ↗ → Activity ↘ (big particles more active)

TWC
→ Oxidation of HC and alcools

Effect of addition of ceria

« Activity ratio » = activity of metal on CeO_2- Al_2O_3 / activity of metal on Al_2O_3



Reaction	**Pd** (0.15%)	**Pt** (0.22%)	**Rh** (0.15%)
$CH_4 + O_2$	0.3 (400°C)	0.05 (500°C)	1 (500°C)
$C_3H_8 + O_2$	0.2 (350°C)	0.5 (250°C)	3 (400°C)

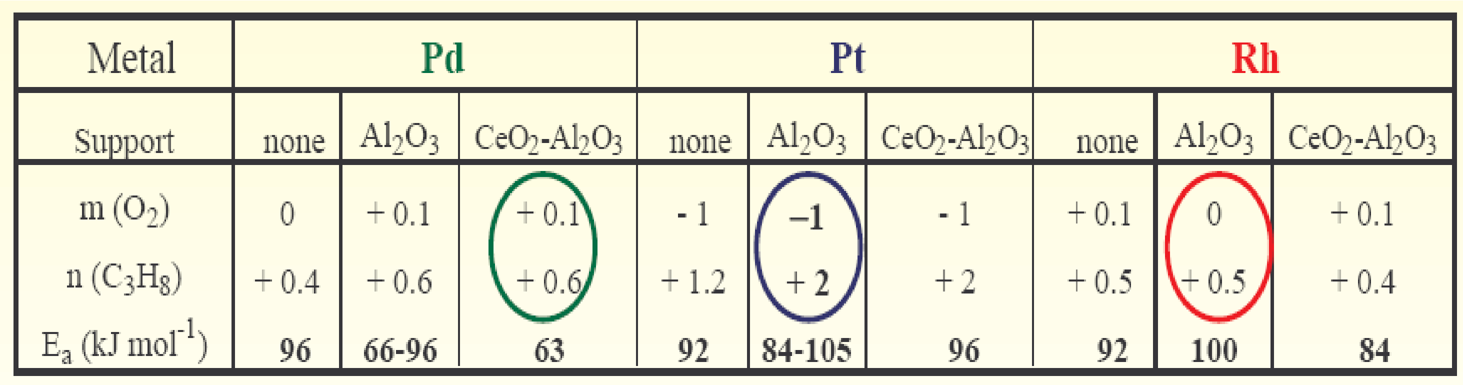
→ Negative effect for Pd and Pt (ratio < 1)

→→ mainly true for Pt

→ « Positive effect » for Rh (ratio > 1)

TWC
→ Oxidation of HC and alcools

Effect of addition of ceria



Metal	**Pd**			**Pt**			**Rh**		
Support	none	Al_2O_3	CeO_2-Al_2O_3	none	Al_2O_3	CeO_2-Al_2O_3	none	Al_2O_3	CeO_2-Al_2O_3
m (O_2)	0	+ 0.1	+ 0.1	- 1	**–1**	- 1	+ 0.1	0	+ 0.1
n (C_3H_8)	+ 0.4	+ 0.6	+ 0.6	+ 1.2	**+ 2**	+ 2	+ 0.5	+ 0.5	+ 0.4
E_a (kJ mol^{-1})	**96**	**66-96**	**63**	**92**	**84-105**	**96**	**92**	**100**	**84**

→ Pt : order for O_2 = -1 vs order for C_3H_8 = +2

→ adsorption O_2 >>> adsorption C_3H_8

→→ opposite situation as for CO

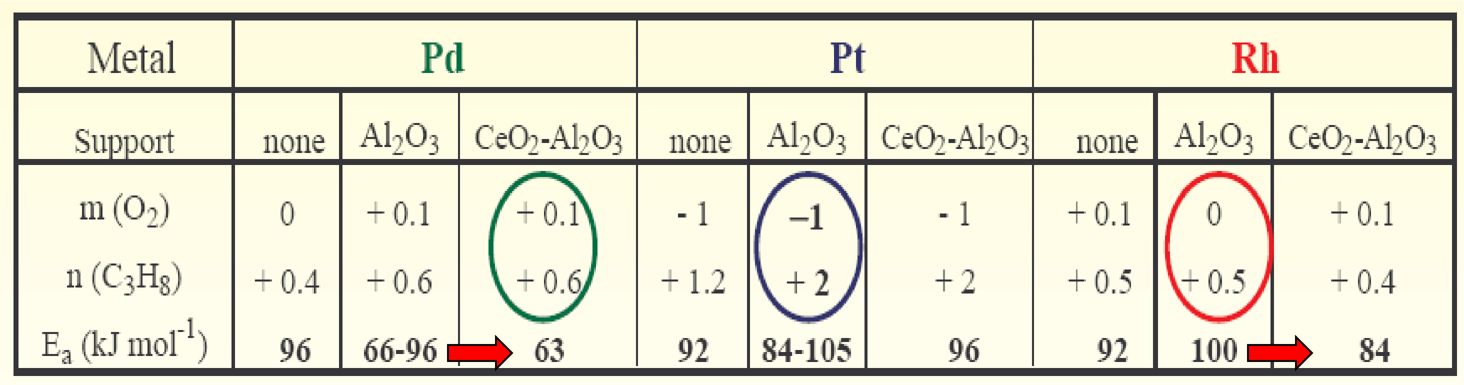
The surface is spontaneously more covered by O_2

→ adding oxygen (via CeO_2) diminishes further the place for C_3H_8

Consequence : activity of Pt ↘ ↘ in presence of ceria.

TWC
→ Oxidation of HC and alcools

Effect of addition of ceria



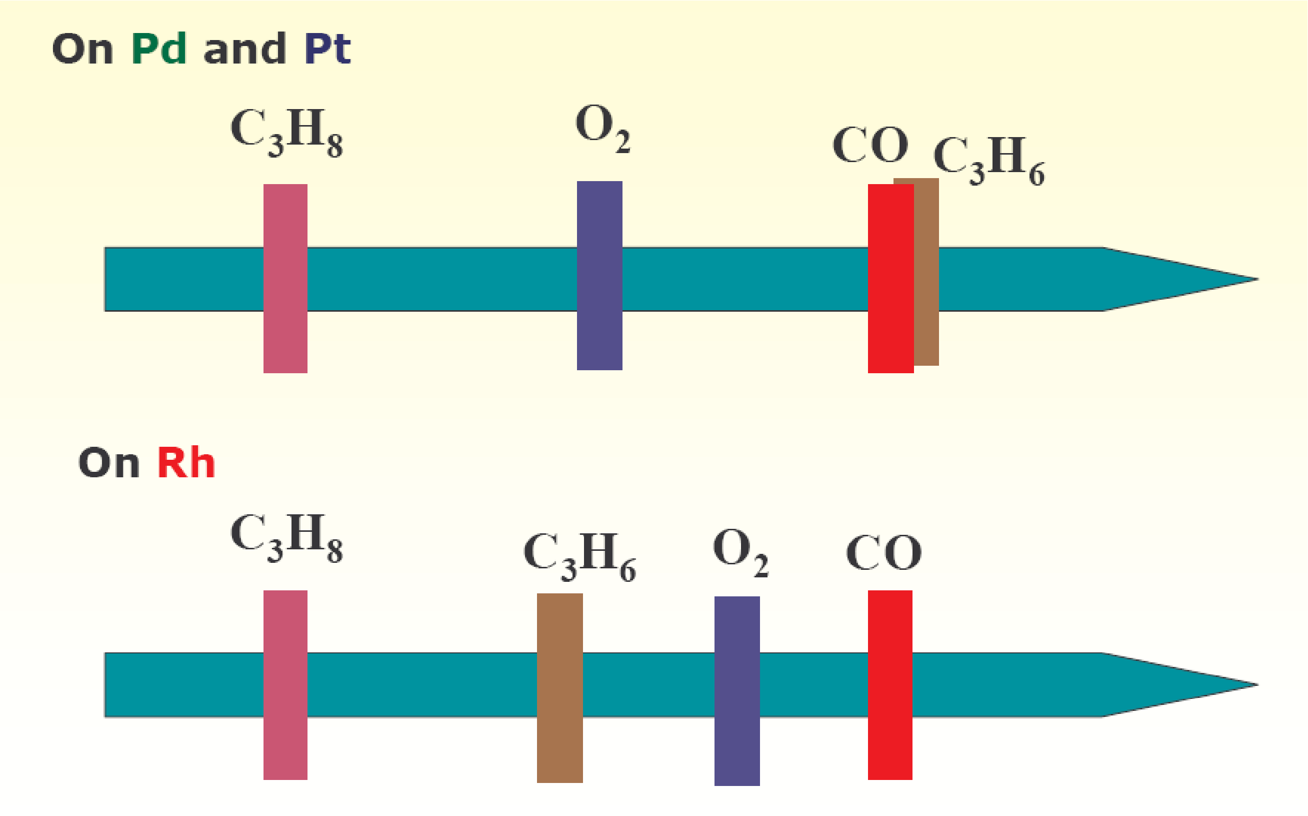
Metal	Pd			Pt			Rh		
Support	none	Al_2O_3	CeO_2-Al_2O_3	none	Al_2O_3	CeO_2-Al_2O_3	none	Al_2O_3	CeO_2-Al_2O_3
m (O_2)	0	+ 0.1	+ 0.1	- 1	–1	- 1	+ 0.1	0	+ 0.1
n (C_3H_8)	+ 0.4	+ 0.6	+ 0.6	+ 1.2	+ 2	+ 2	+ 0.5	+ 0.5	+ 0.4
E_a (kJ mol^{-1})	96	66-96	63	92	84-105	96	92	100	84

→ Pt : adsorption O_2 >>> adsorption C_3H_8

→ Pd and Rh : smaller difference between orders for O_2 and C_3H_8
→→ effect of CeO_2 less negative (or positive) via adsorption but additional activating effect via E_{act} ↘

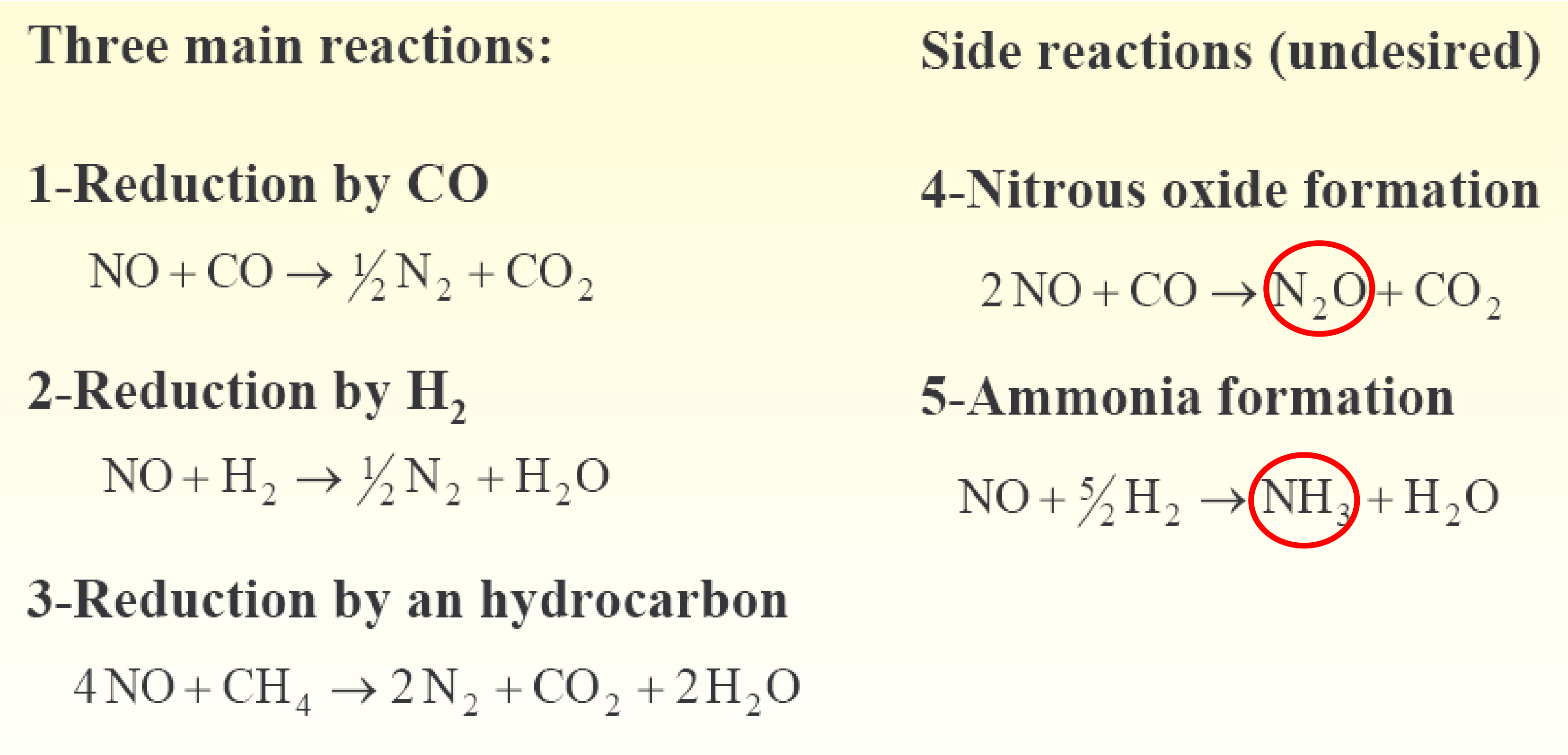
TWC
→ Oxidation of HC and alcools

Constants of relative adsorption



→ Useful to predict the effect of ceria !!!

TWC→ Reduction of NO_x



Three main reactions:

1-Reduction by CO

$$NO + CO \rightarrow \tfrac{1}{2} N_2 + CO_2$$

2-Reduction by H_2

$$NO + H_2 \rightarrow \tfrac{1}{2} N_2 + H_2O$$

3-Reduction by an hydrocarbon

$$4\,NO + CH_4 \rightarrow 2\,N_2 + CO_2 + 2\,H_2O$$

Side reactions (undesired)

4-Nitrous oxide formation

$$2\,NO + CO \rightarrow \boxed{N_2O} + CO_2$$

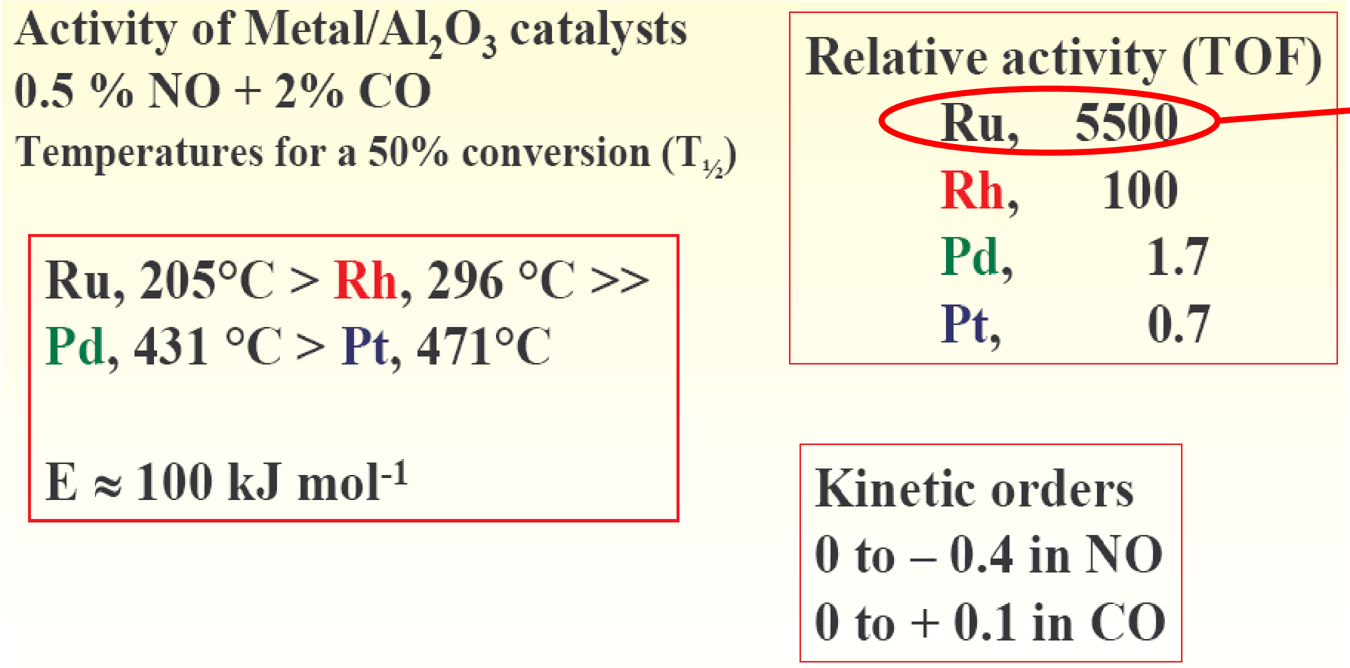
5-Ammonia formation

$$NO + \tfrac{5}{2} H_2 \rightarrow \boxed{NH_3} + H_2O$$

Heterogeneous Catalysis, E. Gaigneaux, UCL, Belgium

TWC→ Reduction of NO_x

Reaction CO + NO



Activity of Metal/Al_2O_3 catalysts

0.5 % NO + 2% CO

Temperatures for a 50% conversion ($T_{½}$)

Ru, 205°C > Rh, 296 °C >> Pd, 431 °C > Pt, 471°C

E ≈ 100 kJ mol^{-1}

Relative activity (TOF)

Ru,	5500
Rh,	100
Pd,	1.7
Pt,	0.7

Kinetic orders

0 to – 0.4 in NO

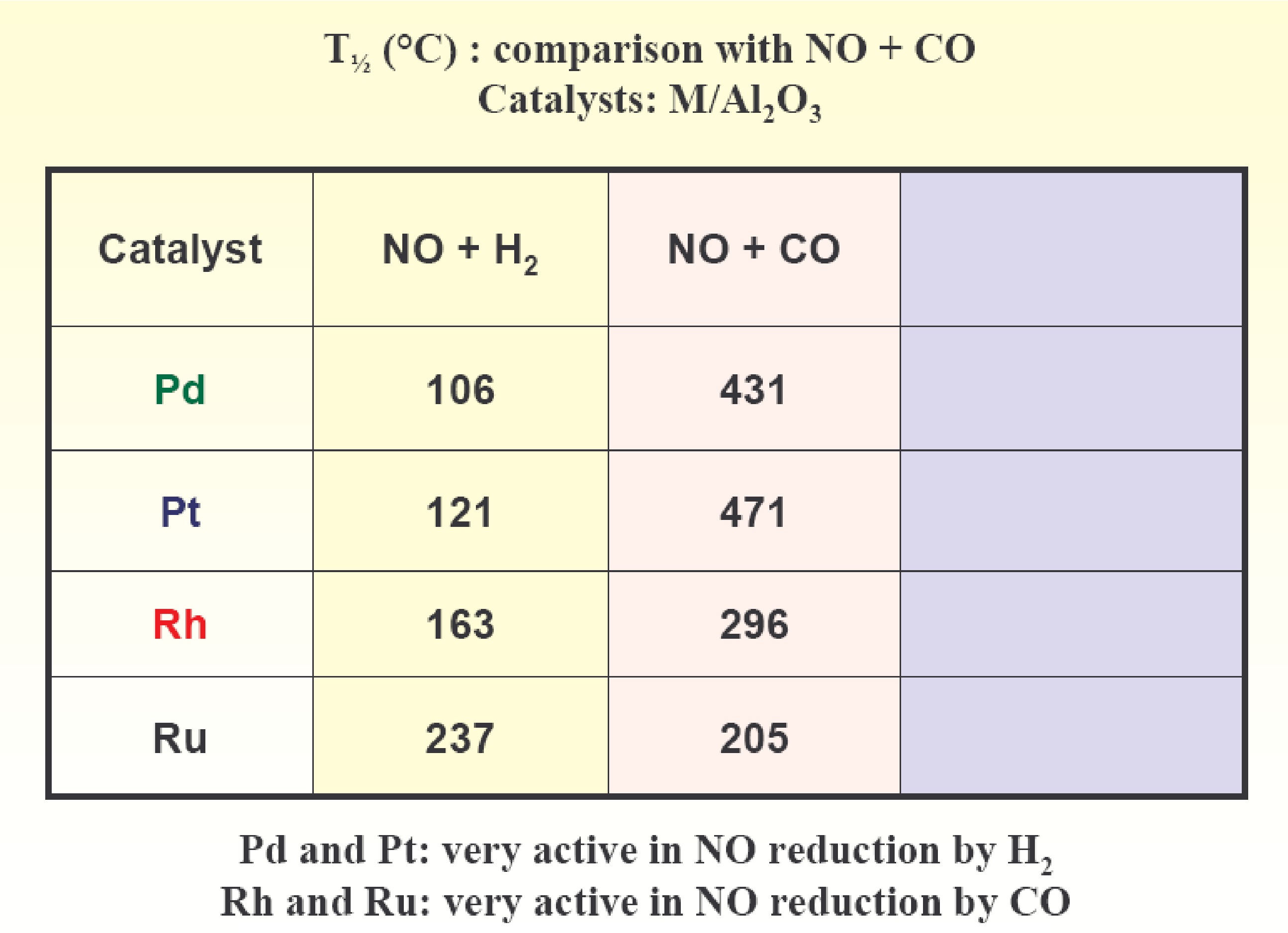
0 to + 0.1 in CO

Ru by far the best !
but !!! in presence of O_2
→ formation of RuO_4
VOLATILE !!!

One puts Rh in converter for its ability to activate CO+NO (Reminder: Rh is not efficient in oxidizing CO in the presence of NO)

TWC→ Reduction of NO_x

Reaction NO + H_2



$T_{½}$ (°C) : comparison with NO + CO
Catalysts: M/Al_2O_3

Catalyst	NO + H_2	NO + CO	
Pd	106	431	
Pt	121	471	
Rh	163	296	
Ru	237	205	

Pd and Pt: very active in NO reduction by H_2
Rh and Ru: very active in NO reduction by CO

Reduction of NO easier with H_2 !

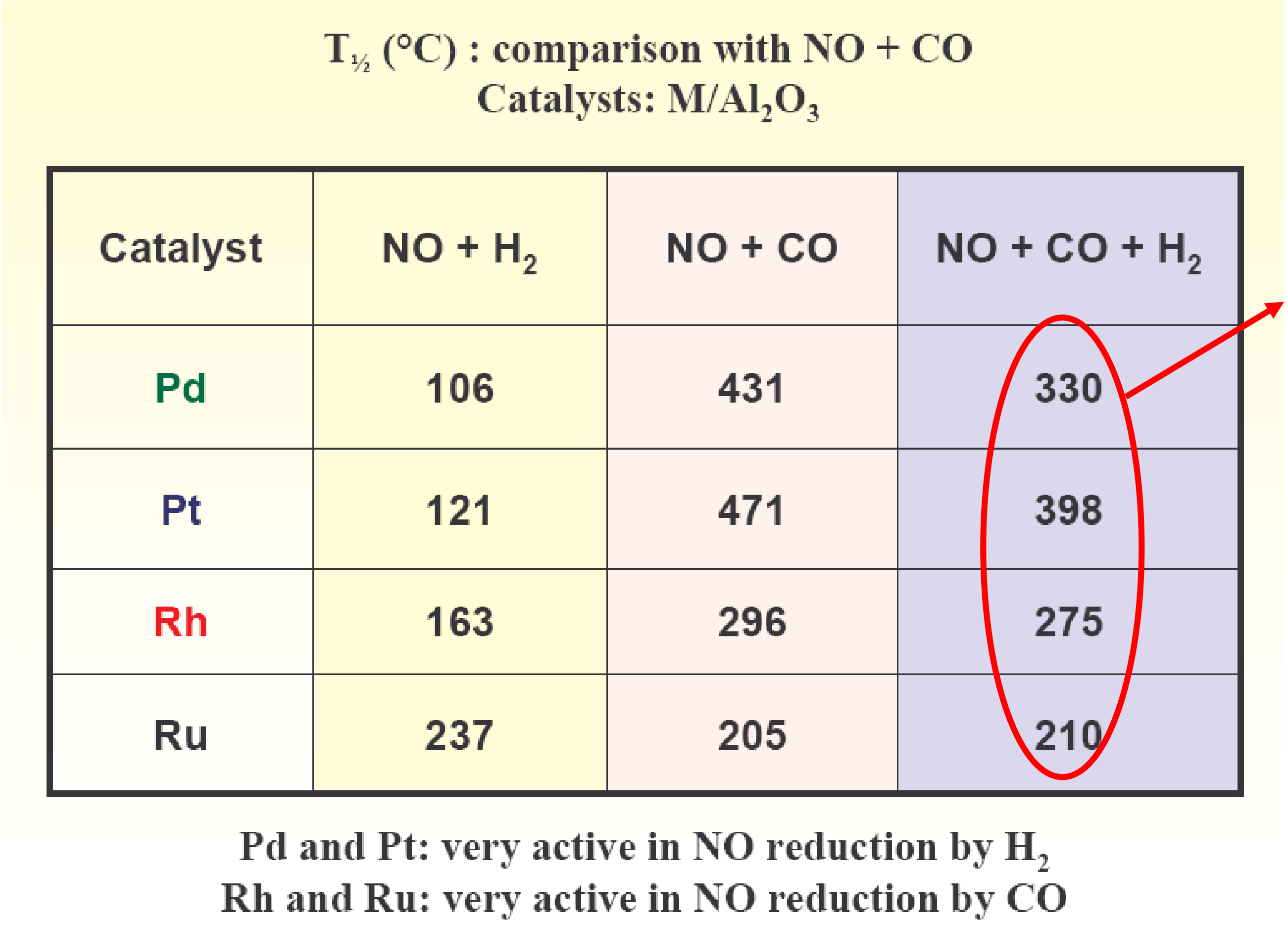
→ Normal !?
H_2 more reducing

Mainly on Pt and Pd
→ Normal !?
Pt and Pd activate easily H_2

→ reverse order of reactivity BUT … (in the real system) ?

TWC→ Reduction of NO_x

Reaction NO + H_2



$T_{½}$ (°C) : comparison with NO + CO
Catalysts: M/Al_2O_3

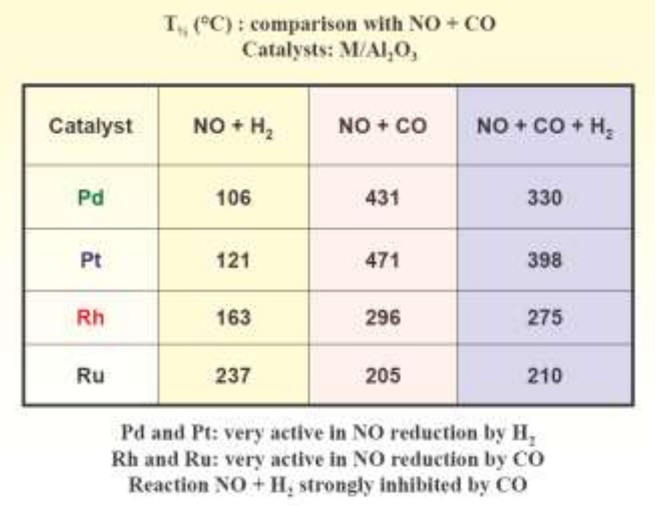
Catalyst	NO + H_2	NO + CO	NO + CO + H_2
Pd	106	431	330
Pt	121	471	398
Rh	163	296	275
Ru	237	205	210

Pd and Pt: very active in NO reduction by H_2
Rh and Ru: very active in NO reduction by CO

temperature
and
order of
reactivity
close
to those
of NO+CO

→ reverse order of reactivity BUT 1° inhibition NO+H_2 by CO

TWC→ Reduction of NO_x



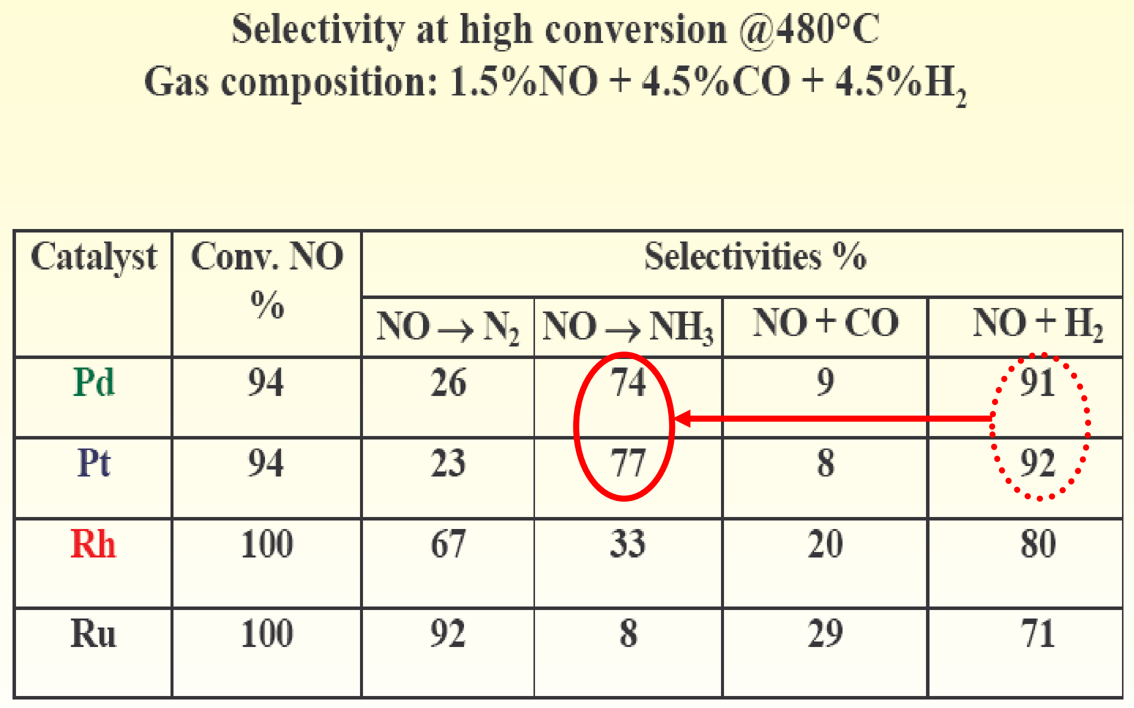
$T_{1/2}$ (°C) : comparison with NO + CO
Catalysts: M/Al_2O_3

Catalyst	$NO + H_2$	NO + CO	$NO + CO + H_2$
Pd	106	431	330
Pt	121	471	398
Rh	163	296	275
Ru	237	205	210

Pd and Pt: very active in NO reduction by H_2
Rh and Ru: very active in NO reduction by CO
Reaction $NO + H_2$ strongly inhibited by CO

Reaction $NO + H_2$

→ BUT 2° reduction of NO not to N_2
in presence of H_2 = $NO+H_2 \rightarrow NH_3$
(mainly on Pt and Pd)



Selectivity at high conversion @480°C
Gas composition: $1.5\%NO + 4.5\%CO + 4.5\%H_2$

Catalyst	Conv. NO %	Selectivities %			
		$NO \rightarrow N_2$	$NO \rightarrow NH_3$	NO + CO	$NO + H_2$
Pd	94	26	74	9	91
Pt	94	23	77	8	92
Rh	100	67	33	20	80
Ru	100	92	8	29	71

Rh remains the best
most active
most selective to N_2
most stable

TWC→ Further challenges !

1° Improvement of engines conditions

→ In order to diminish HC and CO_2 emissions ,
one must better burn the fuel (→ less unburnt)
=
one must work at A/F = 20
= with too much oxygen !!!

→ at LAMBDA (20/14.7) = 1.36
the reduction of NO does not proceed on the TWC !

→→ a lot of NO in the exhaust gas

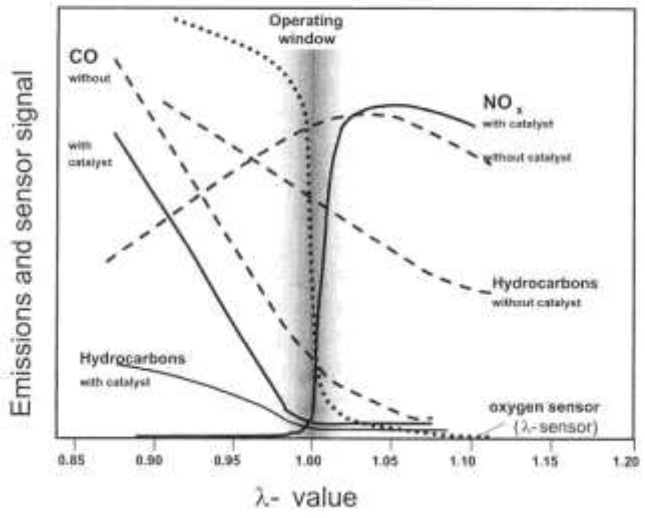


Figure 10.1. Emissions of CO, NO_x and hydrocarbons along with the signal from the oxygen sensor as a function of the air/fuel composition; $\lambda = 1$ corresponds to the air-to-fuel ratio of 14.7. Note that the three pollutants can only be converted simultaneously in a very narrow operating window of air-to-fuel ratios.

TWC→ Further challenges !

1° Improvement of engines conditions
= one must work at A/F = 20
= with too much oxygen !!!
→ a lot of NO in the exhaust gas

2° Diesel cars

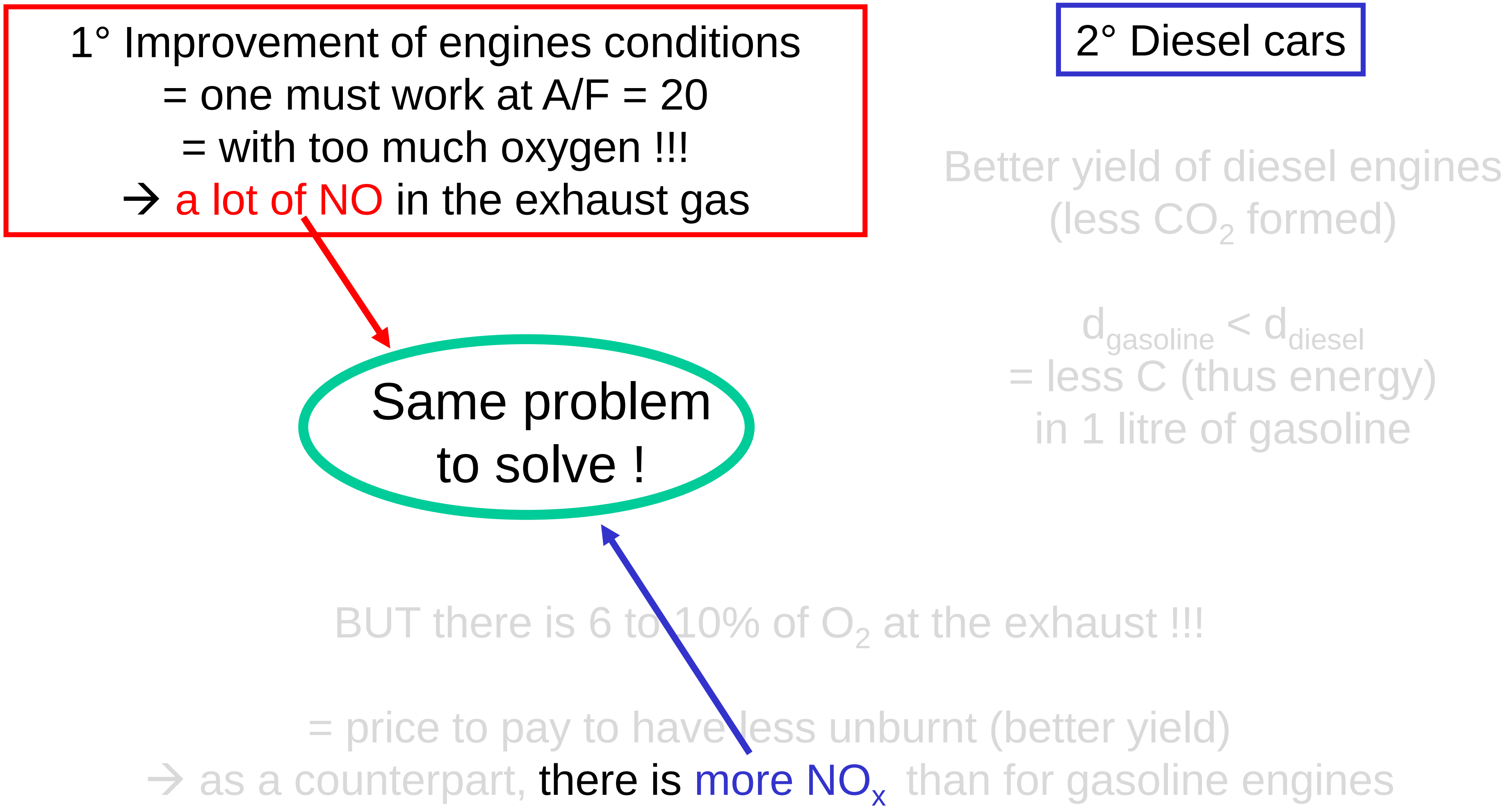
Better yield of diesel engines
(less CO_2 formed)

$d_{gasoline} < d_{diesel}$
= less C (thus less energy)
in 1 litre of gasoline

BUT there is 6 to 10% of O_2 at the exhaust !!!

= price to pay to have less unburnt (better yield)
→ as a counterpart, there is more NO_x than for gasoline engines

TWC→ Further challenges !



1° Improvement of engines conditions
= one must work at A/F = 20
= with too much oxygen !!!
→ a lot of NO in the exhaust gas

2° Diesel cars

Better yield of diesel engines
(less CO_2 formed)

$d_{gasoline} < d_{diesel}$
= less C (thus energy)
in 1 litre of gasoline

Same problem
to solve !

BUT there is 6 to 10% of O_2 at the exhaust !!!

= price to pay to have less unburnt (better yield)
→ as a counterpart, there is more NO_x than for gasoline engines

Towards « NOx-trap »

Concept

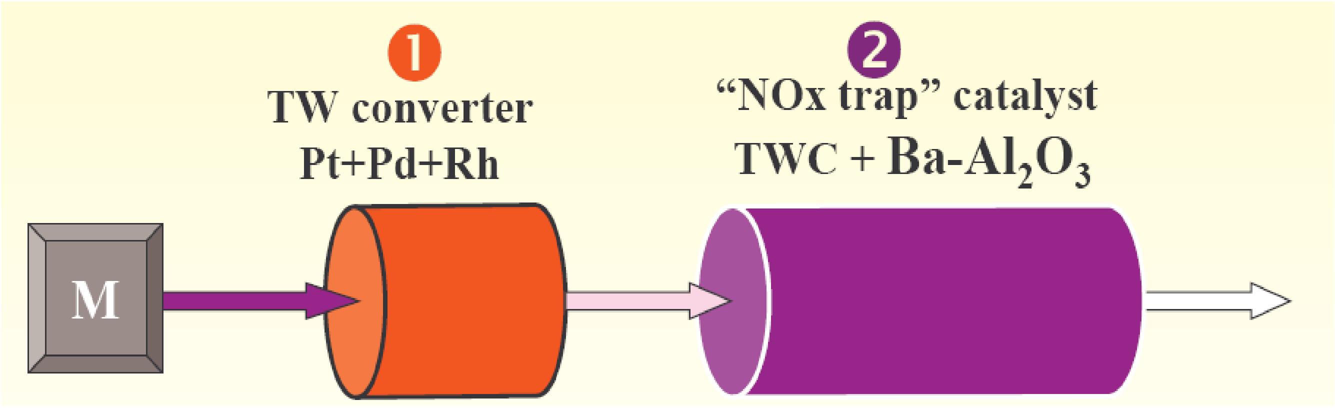
(developed by Toyota → « Toyota Process »)

process in 2 steps
during which the engine shifts successively
from periods at lean regime (A/F ~ 20, 1 minute)
to
periods at rich regime (A/F ~ 10, 2 s).

Towards « NOx-trap »

Concept

(developed by Toyota → « Toyota Process »)



"Lean" phase : Converter ❶ $HC, CO \rightarrow CO_2 + H_2O$

$NO \rightarrow NO_2$

Converter ❷ $BaCO_3 \rightarrow$ Ba-nitrates

"Rich" phase : Converter ❶ $HC, CO \rightarrow$ not totally **converted** and CO_2

converted

$NO \rightarrow N_2$

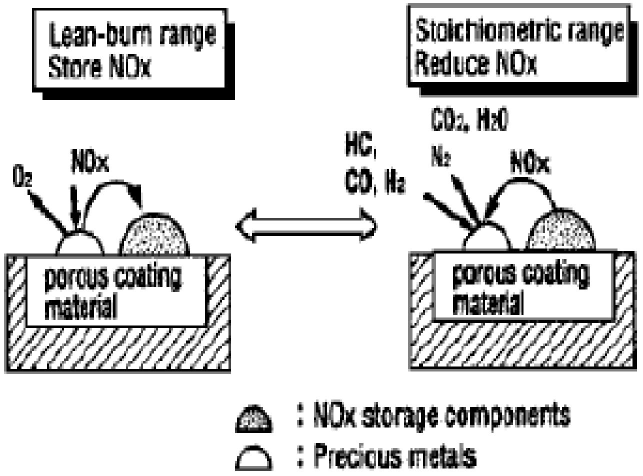
Converter ❷ Ba-nitrates → Ba-carbonates+ NO_x

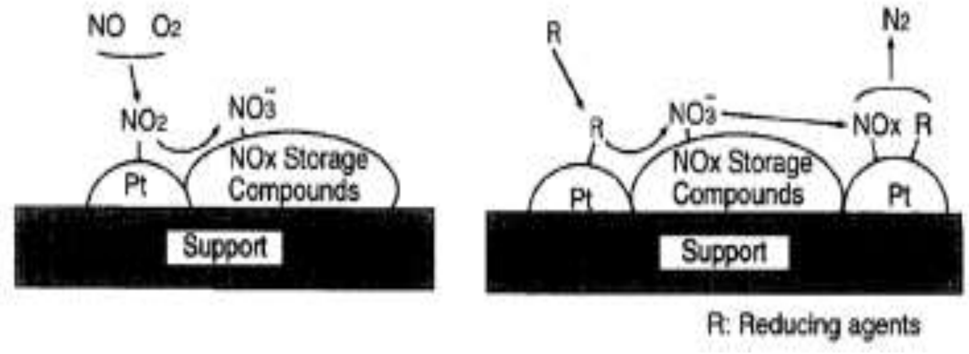
$CO, HC + NO_x \rightarrow CO_2 + H_2O + N_2$

Towards « NOx-trap »

Concept

(developed by Toyota → « Toyota Process »)





Towards « NOx-trap »

Concept

(developed by Toyota → « Toyota Process »)

Why is working in cycles needed ?

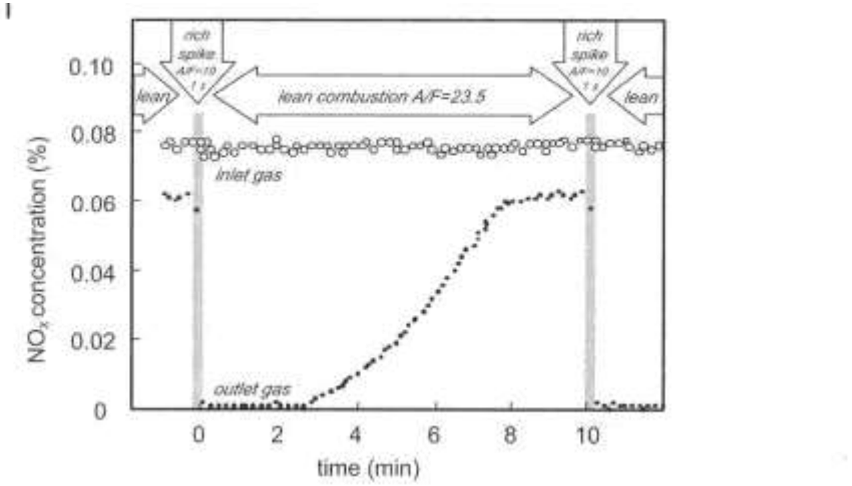
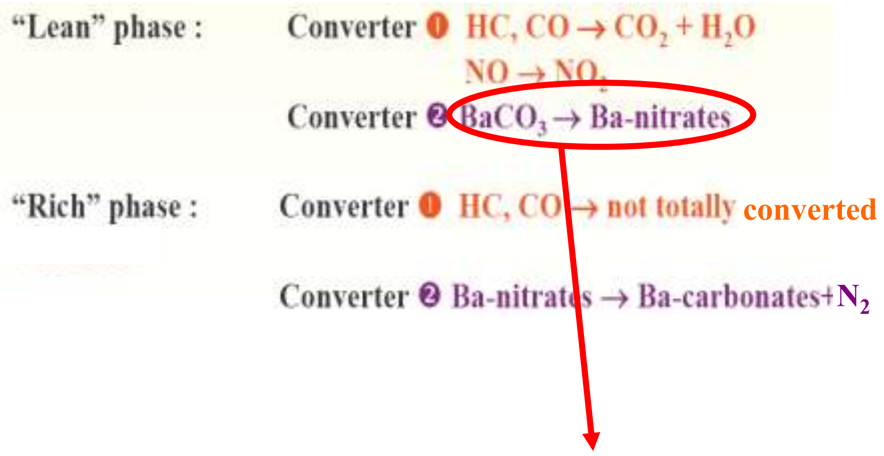


Figure 10.10. Principle of operation of NOx storage catalyst. During lean combustion, NO is oxidized to NO_2 and stored by BaO as barium nitrates. Once the getter is saturated, a short rich excursion of the air–fuel mixture reduces the nitrates and the cycle starts anew. (Adapted from S. Matsumoto, *Cattech* **4** (2000) 2). Note that in an operating system the cycle time from lean to rich conditions will be much shorter than indicated in this figure.



"Lean" phase : Converter ❶ HC, CO → $CO_2 + H_2O$

NO → NO_2

Converter ❷ $BaCO_3$ → Ba-nitrates

"Rich" phase : Converter ❶ HC, CO → not totally converted

Converter ❷ Ba-nitrates → Ba-carbonates+N_2

≠ catalysis

= stoichiometric reaction

What else???

Automotive catalysis is also :

- things about poisoning of catalysts :
S, P, Si, Pb, etc
(solution = heterogeneous catalytic HDS)

- things about soots
in diesel engines
(solution = heterogeneous catalysis)

- things about secondary catalytic reactions
Between co-reactants present in exhaust gas

= many other things to address !!!