Autocatalysis and HC Traps

(mainly for Gasoline Vehicles)

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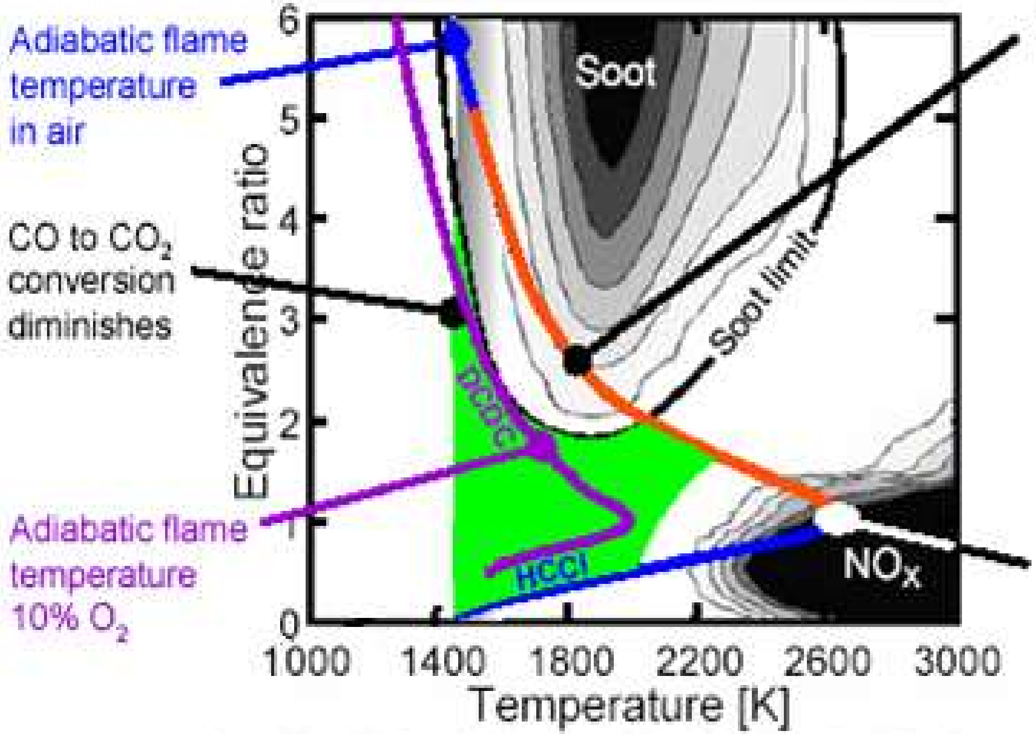
HCs Emissions and Control

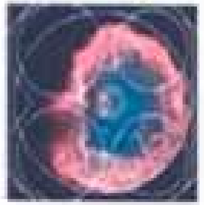
- Future HCs emissions regulations
- Strategies of HCs emissions control
  - Advanced TWCs
  - HC traps
- HC traps

Graphical summary of SI, CI and HCCI engines



Diesel (CI) combustion
- controlled heat release (mixing)
- controlled combustion timing
- wide load range
- high efficiency (relative to SI)
- **NO_x and PM emissions**

Spark ignition (SI) combustion
- controlled heat release (flame propagation)
- controlled combustion timing
- wide load range
- three-way catalyst
- **low efficiency** (relative to diesel)



- offers diesel-like efficiency (high CR & no throttling)
- low NO_x and particulate emissions
- **load range?**
- **combustion timing?**
- **heat release rate?**
- **transient control?**
- **fuel?**

Source: K. Akiyama et al., SAE 2001-01-0655.

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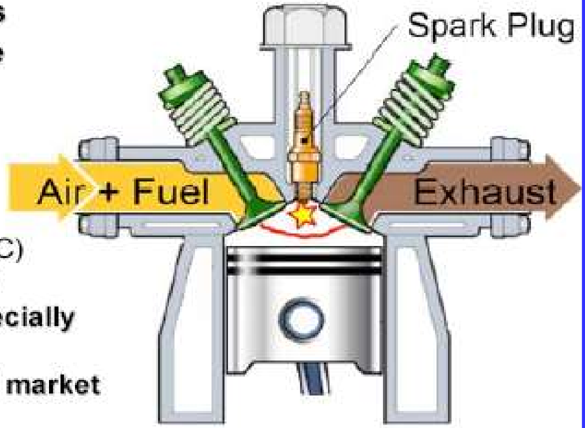
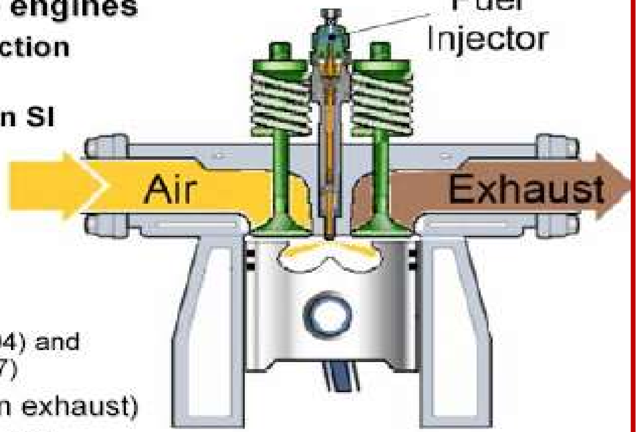
Combustion modes of SI and CI engines

- Spark-ignition (SI) engines
  - Port fuel injected gasoline
  - Non-optimal efficiency
    - Low compression ratio
    - Pumping losses
  - Very low emissions
    - Three-way catalyst (TWC) removes NO_x, UHC, CO
  - Good power density, especially at high speed
  - Dominates light-duty (LD) market in US
    - Low emissions
    - Lower peak cylinder pressure → cheap to manufacture



→ Gasoline vehicles

- Compression-ignition (CI) engines
  - Turbocharged, direct injection of diesel fuel
  - 30-40% more efficient than SI
    - Higher compr. ratio
    - Load controlled by amount of fuel injected
  - Emissions
    - High NO_x and soot
      - LD fails CA LEV II (2004) and Fed. Tier II, Bin 5 (2007)
    - TWC doesn't work (O_2 in exhaust)
  - Better low-end torque than SI
  - Dominates heavy-duty market
    - Highly efficient and reliable



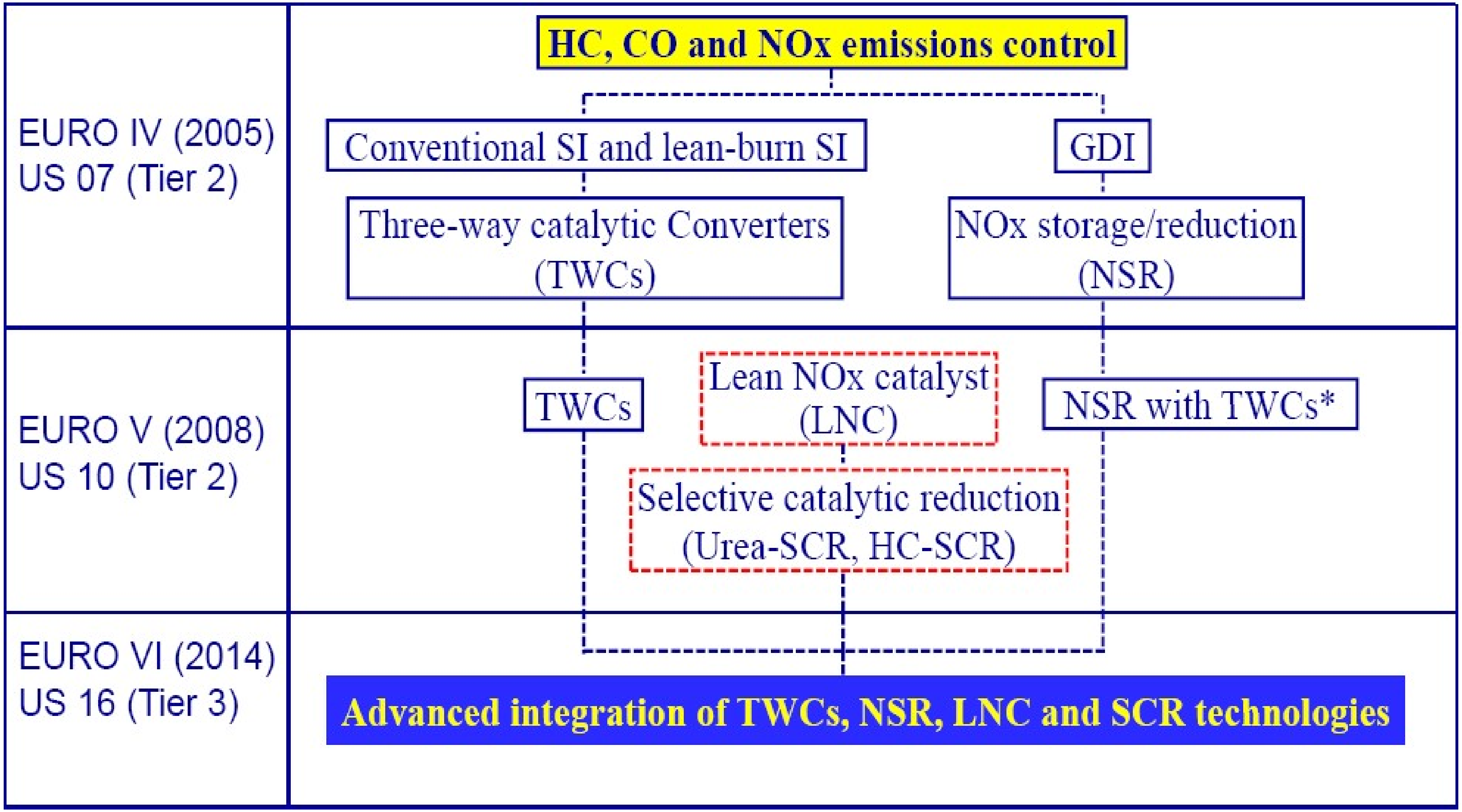
Diesel vehicles ←

Engine-out emissions from PC and LDVs

Engine-out emissions	Conventional gasoline engine	LB gasoline engine	GDI engine	Diesel engine
NO_x (ppm)	100 ~ 4,000	≈1,200	-	350 ~ 1,000
HC (ppm C)	500 ~ 5,000	≈1,300	-	50 ~ 330
CO (ppm)	0.1 ~ 6[a]	≈1,300	-	300 ~ 1,200
O_2 (%)	0.2 ~ 2	4 ~ 12	-	10 ~ 15
H_2O (%)	10 ~ 12	12	-	1.4 ~ 7
CO_2 (%)	10 ~ 13.5	11	-	7
SO_x (ppm)	15 ~ 60	20	-	10 ~ 100
PM (mg/m^3)	-	-	≈65	65
T (°C)	R.T. ~ 1,100	R.T. ~ 850	R.T. ~ 650	R.T. ~ 650
GHSV (h^{-1})	30,000 ~ 100,000	30,000 ~ 100,000	30,000 ~ 100,000	30,000 ~ 100,000
AFR	14.7	17	13 ~ 24 / 30 ~ 40	30 ~ 50

[a] In %.

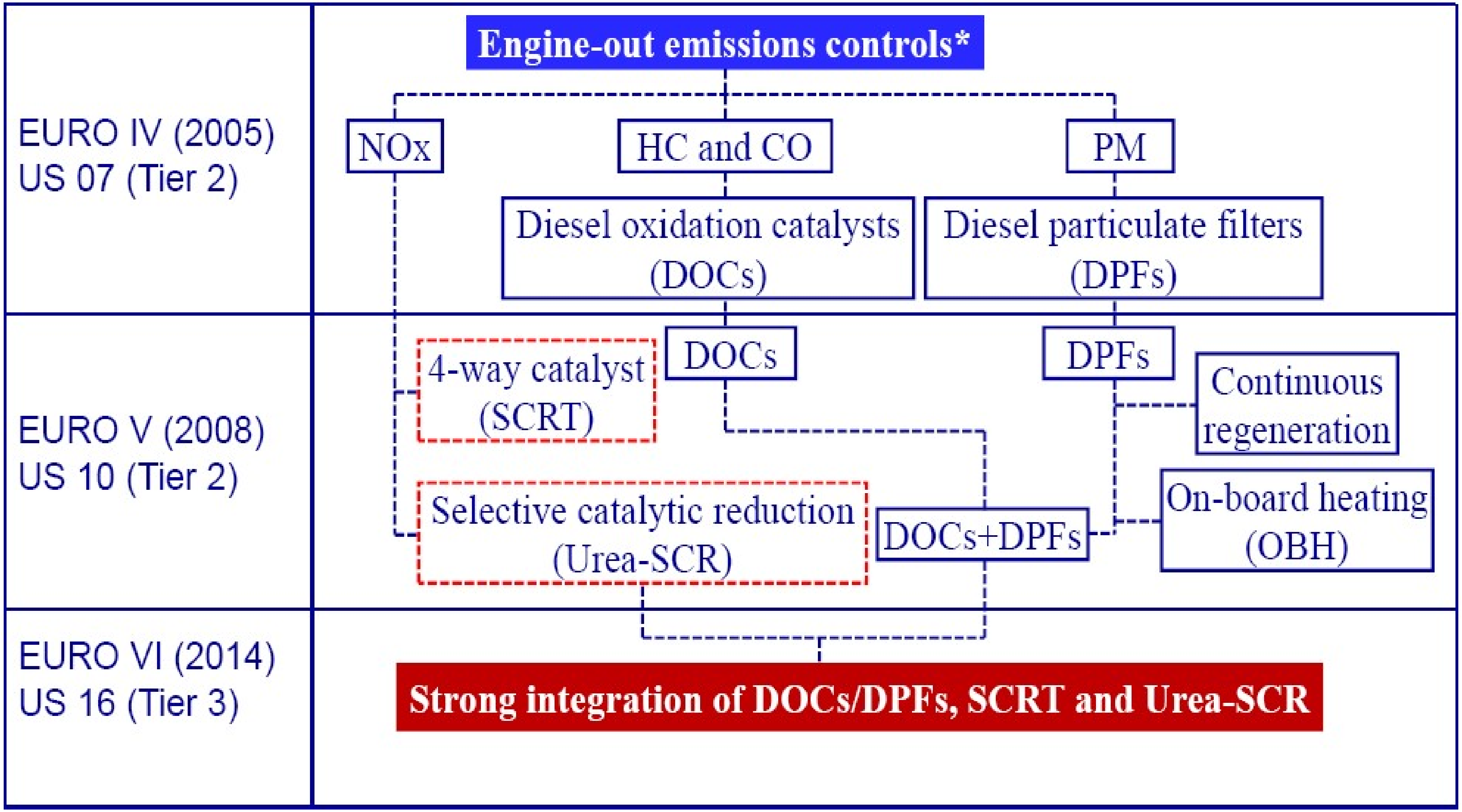
Gasoline automotives emissions controls



: Not yet commercialized.

* Different from the conventional TWCs.

Diesel automotives emissions controls



* Dependent strongly on engine duties.

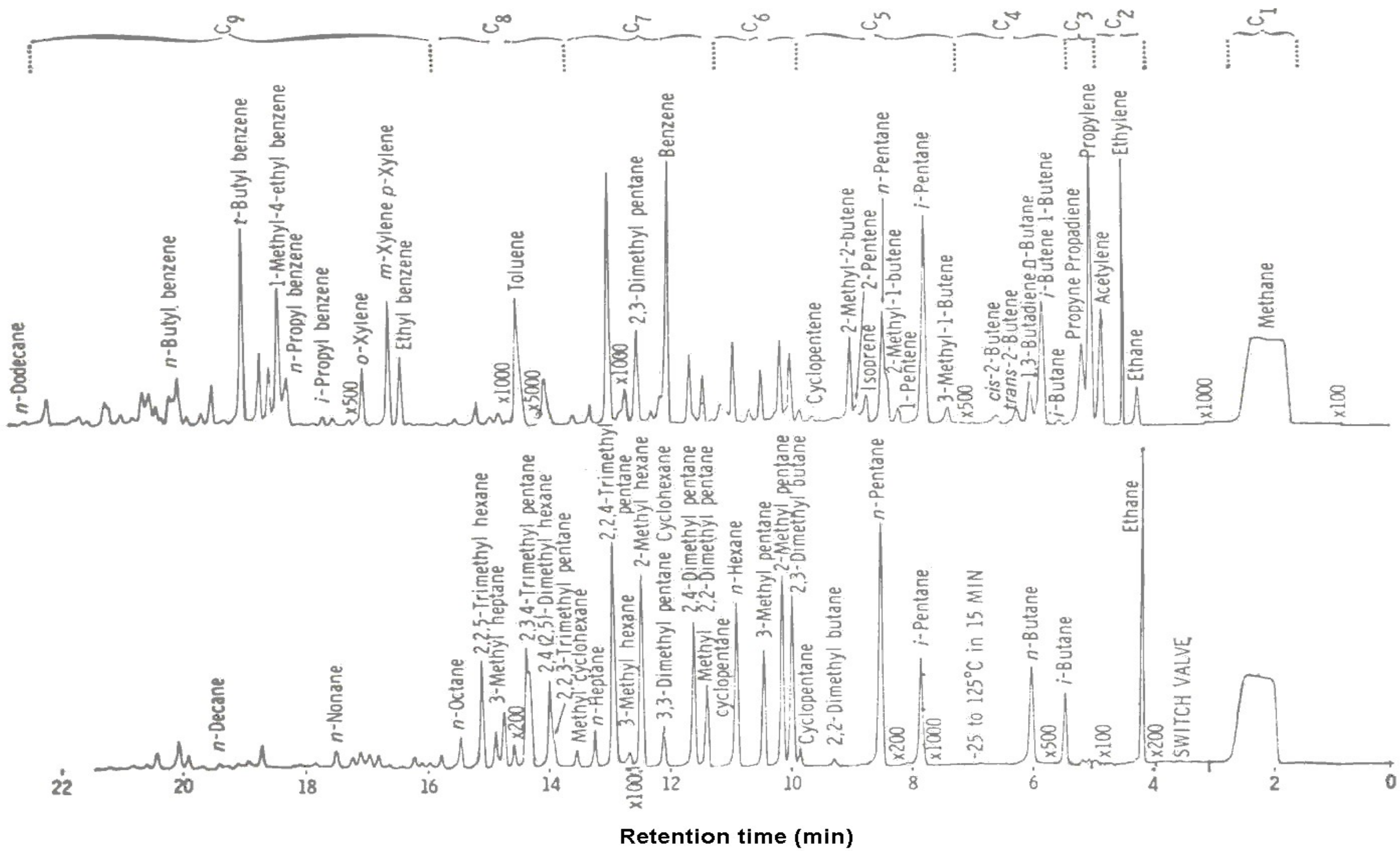
: for HDVs at present time.

Progression of exhaust emission standards for LD vehicles in USA

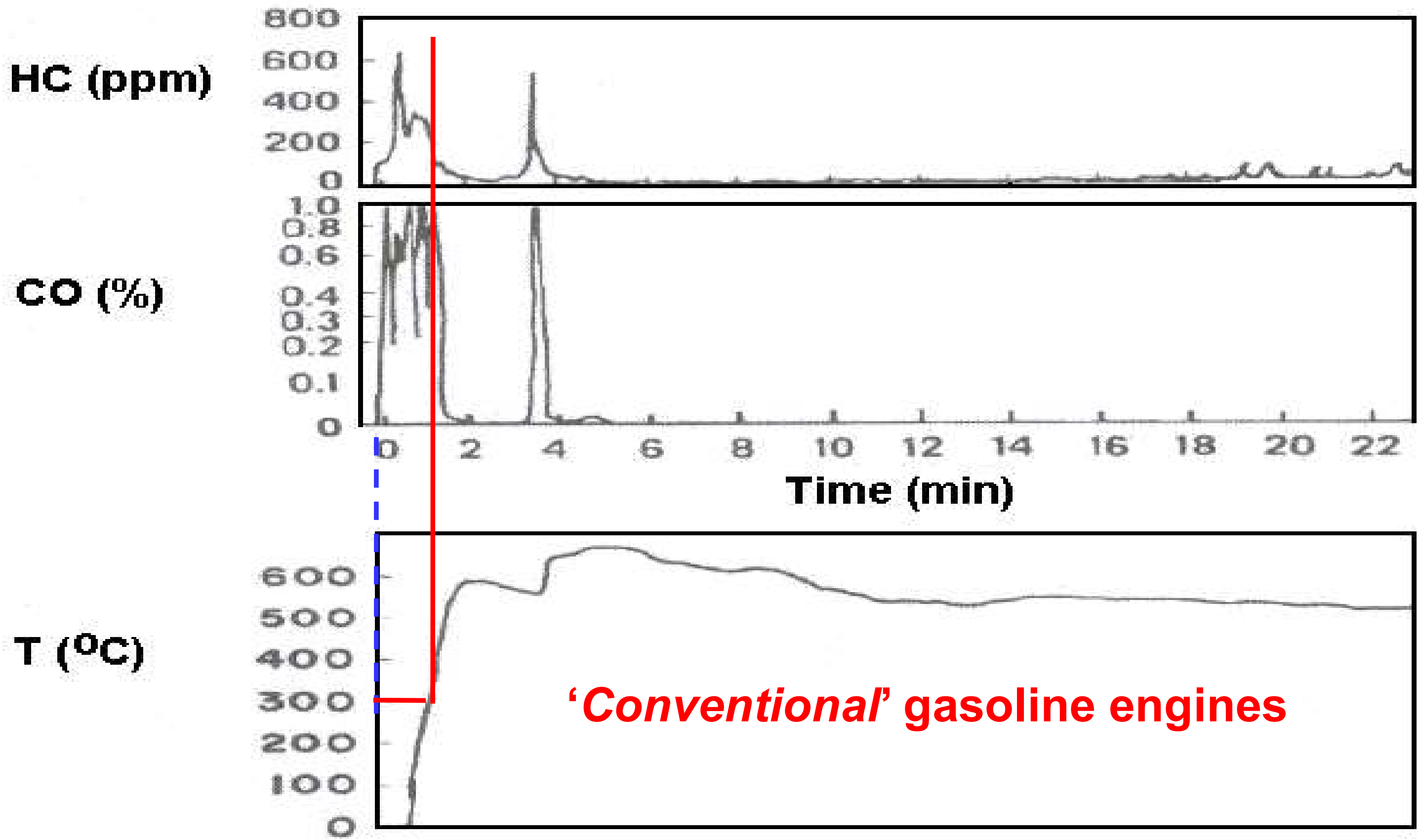
Model year	Emission standards (g/mil)[a]			Comments
	NO_x	CO	HC	
Pre-1968	6.2	90.0	15.0	Uncontrolled
1970	-	34.0	4.1	
1972	-	28.0	3.0	
1973-74	3.1	28.0	3.0	
1975-76	3.1	15.0	1.5	
1977	2.0	15.0	1.5	
1980	2.0	7.0	0.41	
1981	1.0	3.4	0.41	
1991	1.0	3.4	0.41	Tier 0
1994-96	0.4	3.4	0.25[b]	Tier 1
2001	0.2	3.4	0.075[c]	NLEV
2004-09	0.07	3.4	0.075[c]	Tier 2 (all phase-in), NO_x fleet average
2010-2015	0.07	3.4	0.30[c,d]	Tier 2 (phase-in for NMOG), NO_x and NMOG fleet average
2016[e]	? (↓)	? (=)	? (↓)	Tier 3

[a] Applicable over the "useful life" defined as 50,000 miles or 5 years for automobiles.
[b] Non-methane HCs (NMHC).
[c] Non-methane organic gases (NMOG).
[d] Sampling must be on the FTP cycle at -7°C and applicable at 120,000 miles.
[e] The President Obama announces "National Fuel Efficiency Policy", Press Release, The White House, May 19, 2009.

Speciation of HCs in exhausts from SI engines



HC emissions trace over the FTP 75 cycle



The HCs are emitted within 2 min during the test cycle, and this amount is about 70~80% of the total HC emissions.

Sources of cold-start engine-out HC emissions

1. Misfiring
2. Incomplete flame propagation
3. Wall wetting
4. Rich fuel–air charge

Major contributions to the emissions

5. Crevice storage of the fuel–air charge and its release
6. Oil dilution with liquid and fuel vapor
7. Wall quenching
8. Poor post-flame oxidation
9. Exhaust valve leakage
10. Inlet valve leakage
11. Lubricating oil

Small contributions to the emissions, depending on engine-to-engine

Source: N.A. Henein and M.K. Tagomori, Progr. Energy Comb. Sci., 25 (1999) 563.

Historical strategies of HC emissions control

1. TWC-based approaches

■ Usage of advanced TWCs (a-TWC):

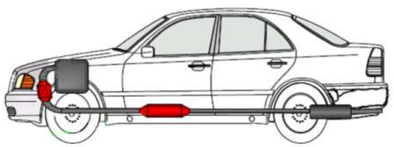
Addition of Pd into conventional TWC (c-TWC) with Rh and Pt

■ Modification in system configuration of a-TWCs:

UBC -> CCC

■ Dual TWC system configuration:

UBC (c-TWC) + CCC (a-TWC)



■ Increase in volumes and PGM loadings of a-TWCs

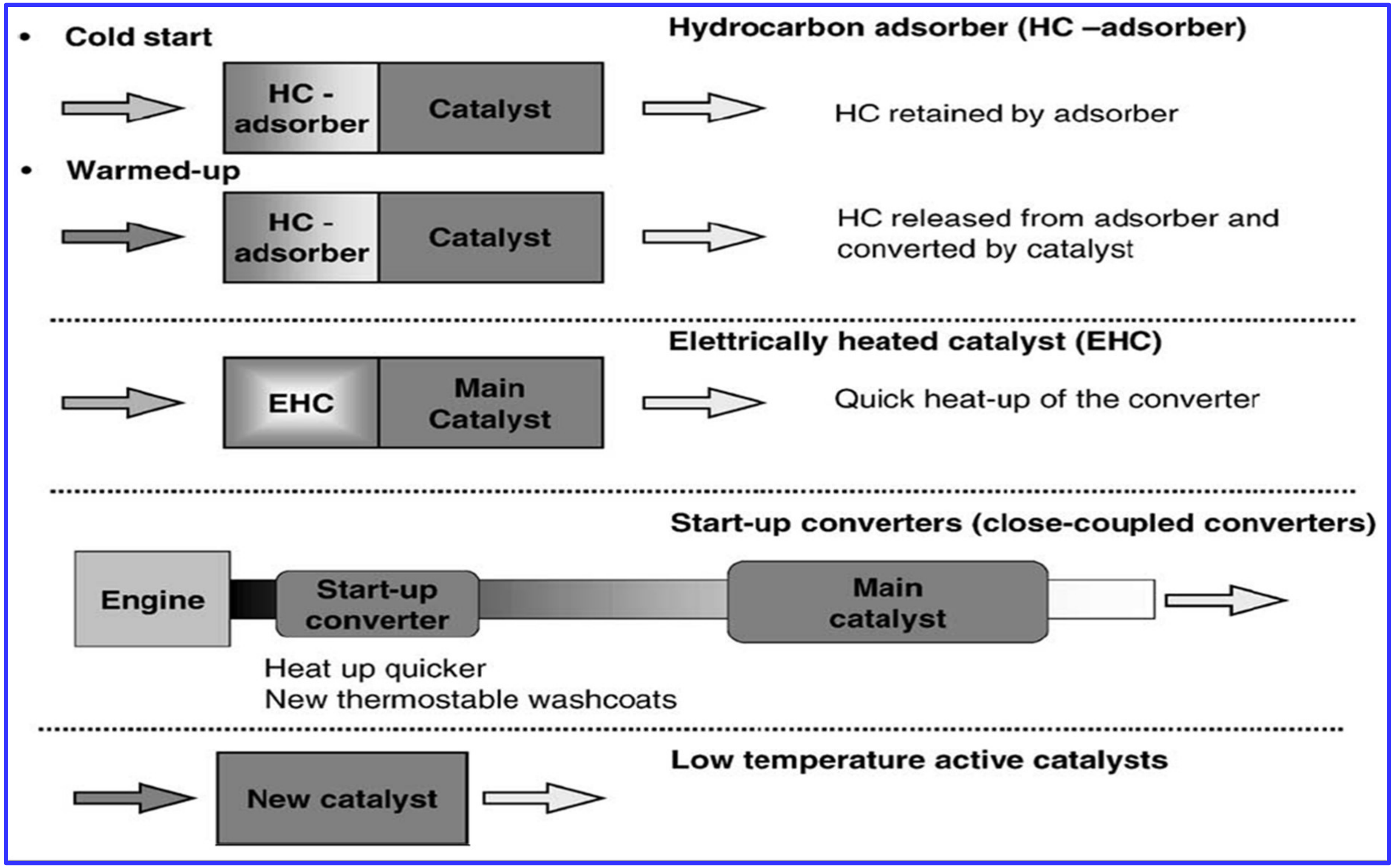
2. Mechanical heat-up of exhaust streams

■ Electric heater

3. Trapping of HCs upon cold-start phase

■ HC traps (adsorbers)

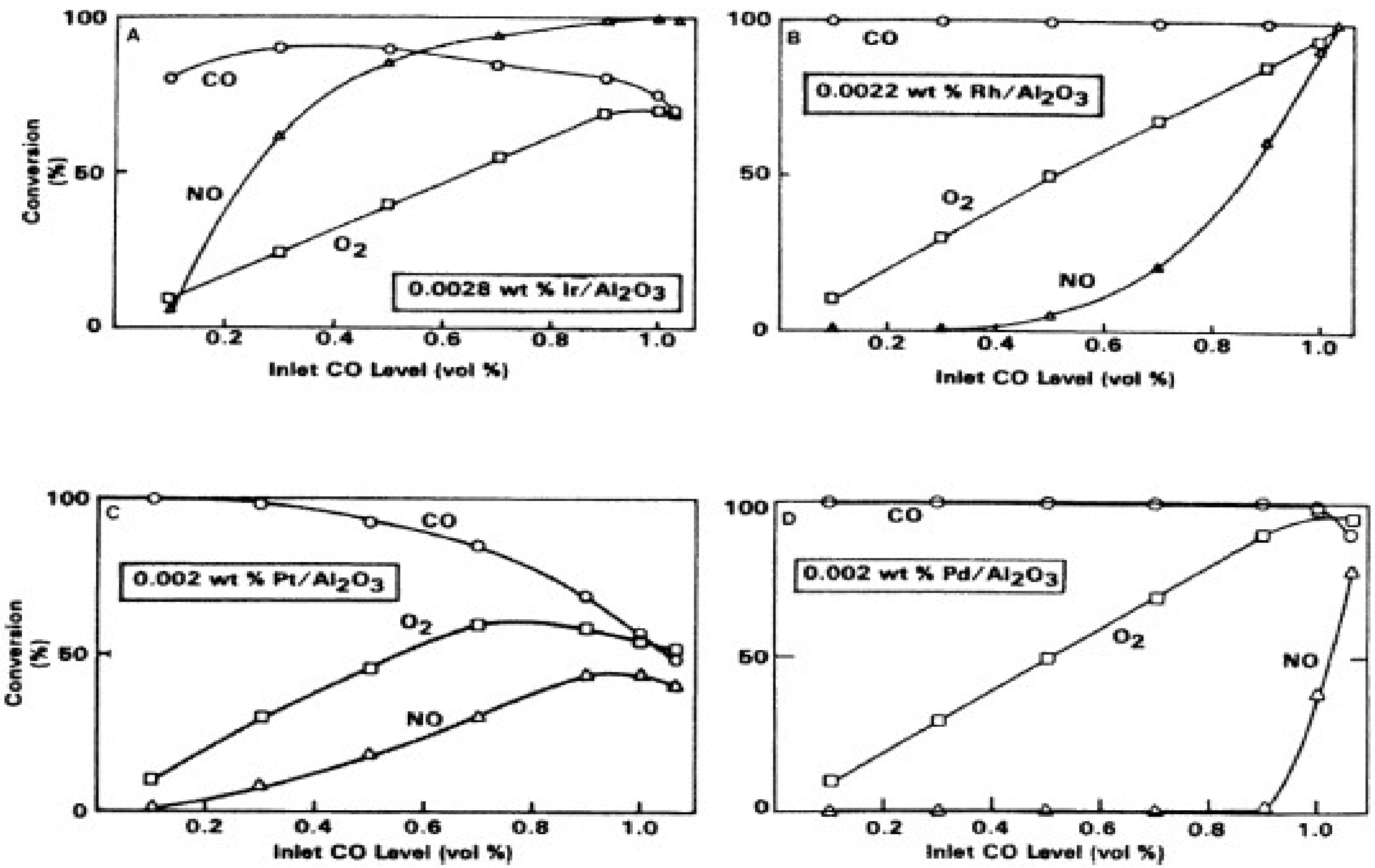
Proposals for HCs emissions control



Source: J. Kaspar et al., Catal. Today, 77 (2003) 419.

The first phase of catalytic emissions control

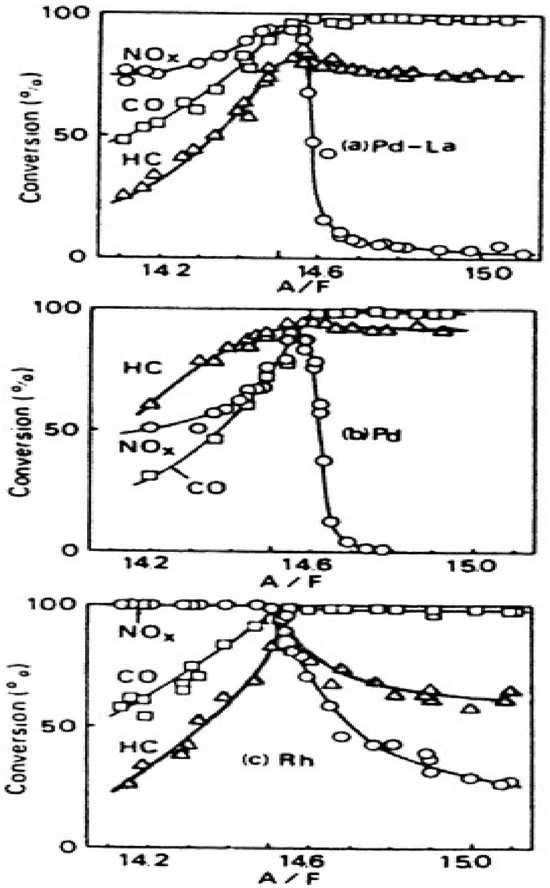
Ir: formation of volatile oxides
Rh: good NO_x control, but lower activity for olefin HCs conversion under oxidizing conditions



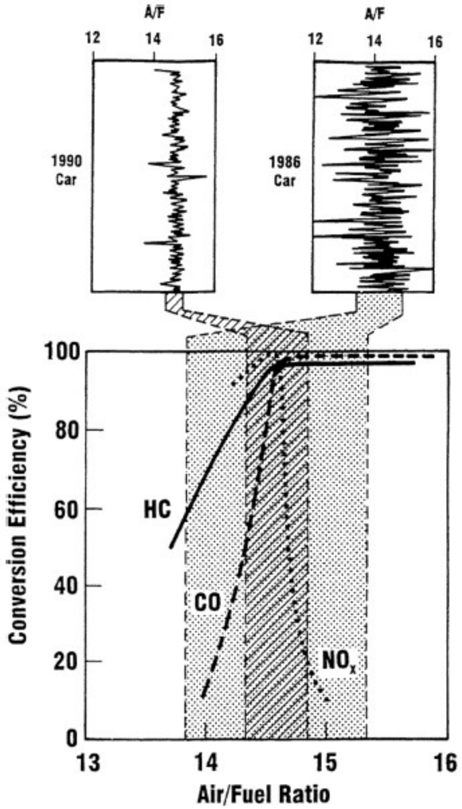
Source: K.C. Taylor and J.C. Schlatter, J. Catal., 63 (1980) 53.

Advanced TWCs components and formulations

Pd: high HCs conversion
Rh: low HCs conversion

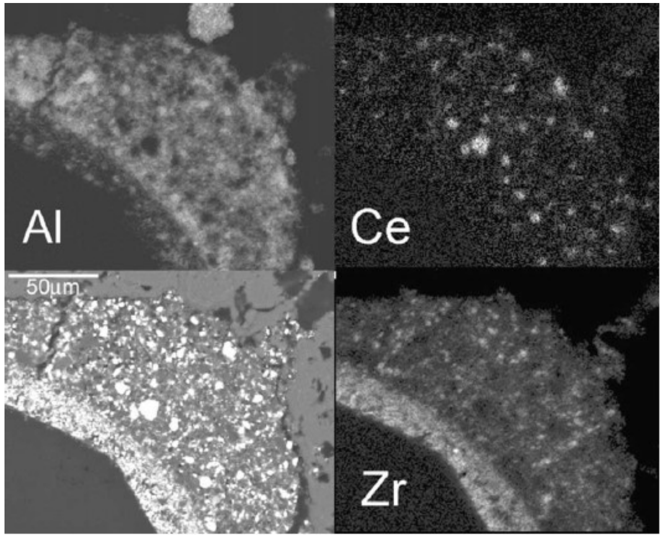


Source: H. Muraki et al., Appl. Catal., 22 (1986) 325.



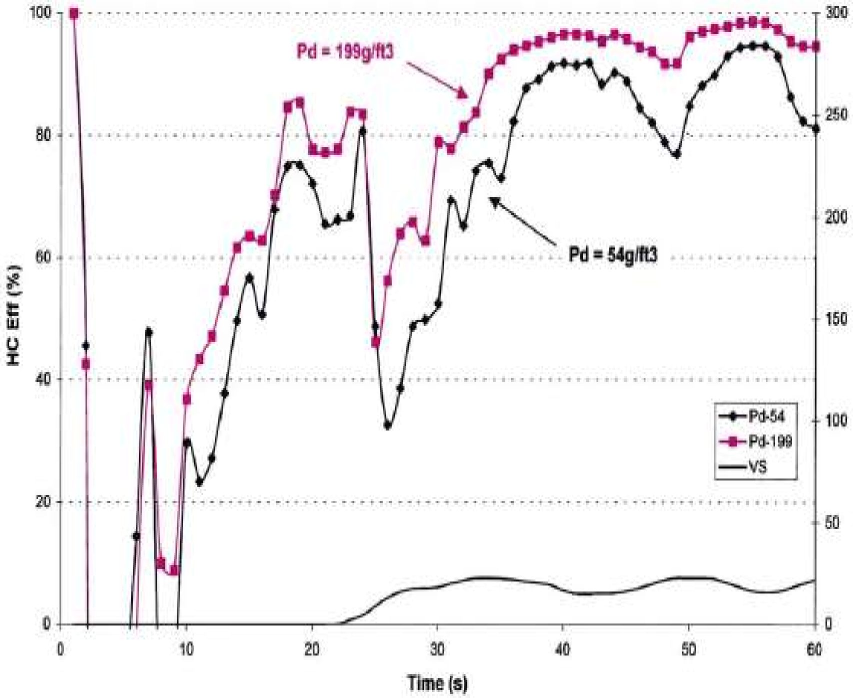
Source: M. Shelef and R.W. McCabe, Catal. Today, 62 (2000) 35.

- Stabilized alumina with La or Ba
- Oxygen storage components (OSCs): High SA ceria
- Layered washcoating



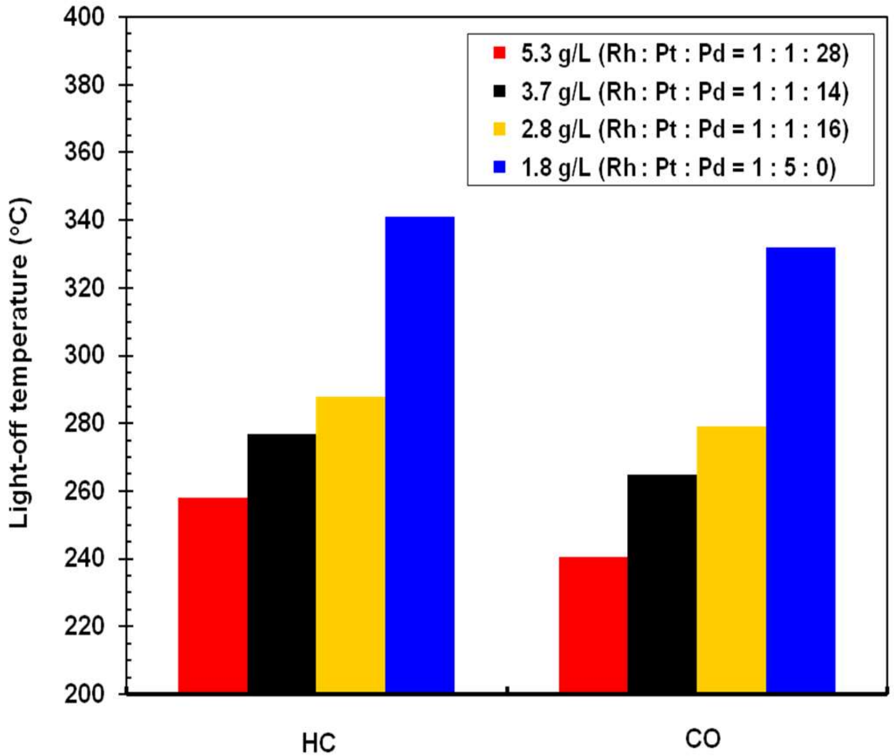
PGM loadings vs. HC & CO light-off performances

High Pd loadings: excellent HC conversion within very short time (50 s)



Source: H.S. Gandhi et al., J. Catal., 216 (2003) 433.

Advanced TWC system configuration: CCC



Source: J. Kaspar et al., Catal. Today, 77 (2003) 419.

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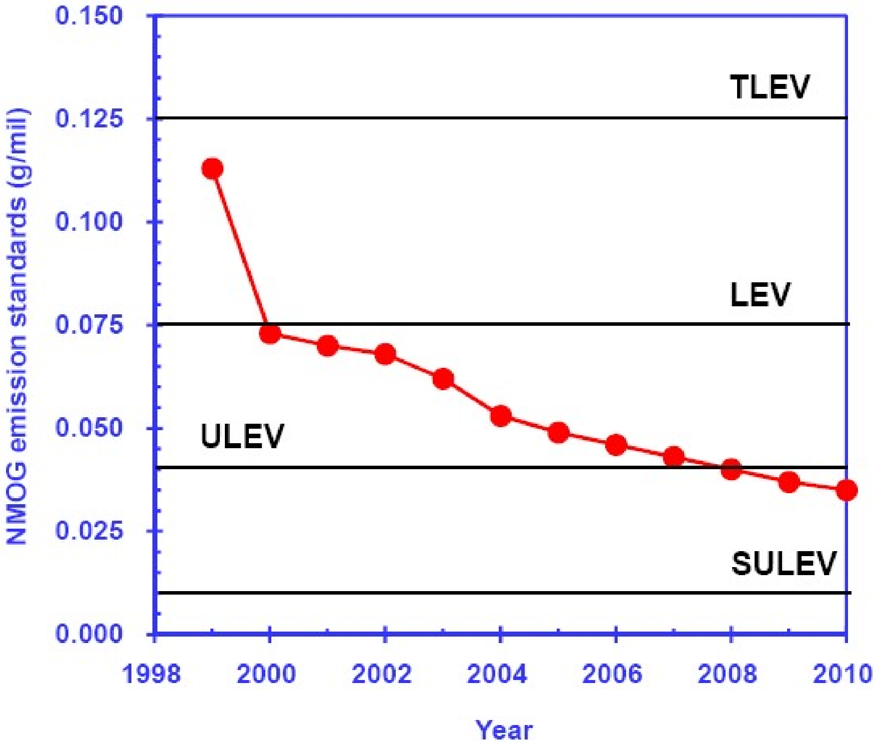
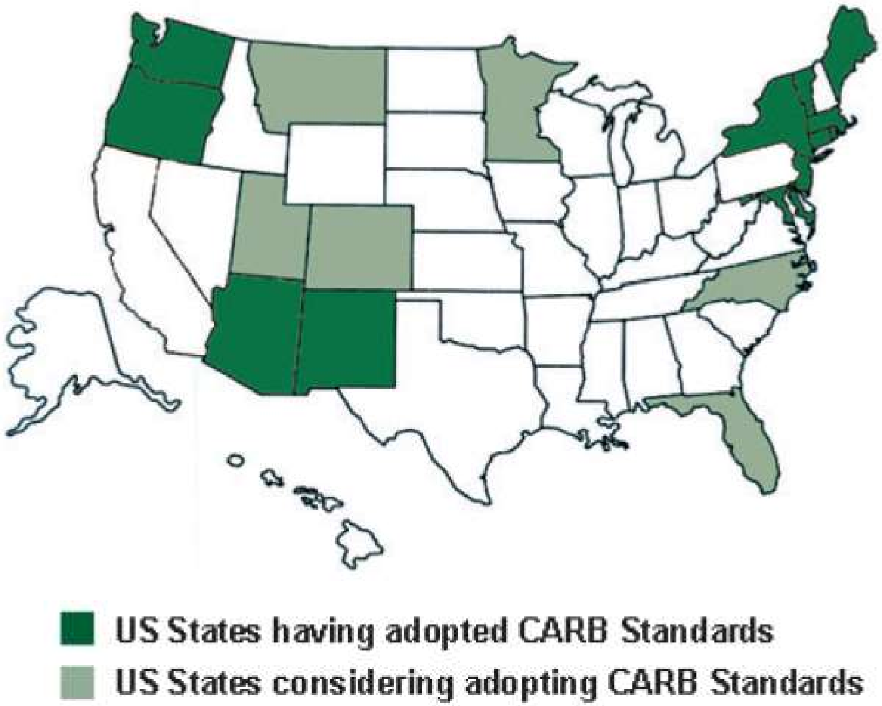
California NMOG emission standards for LDVs

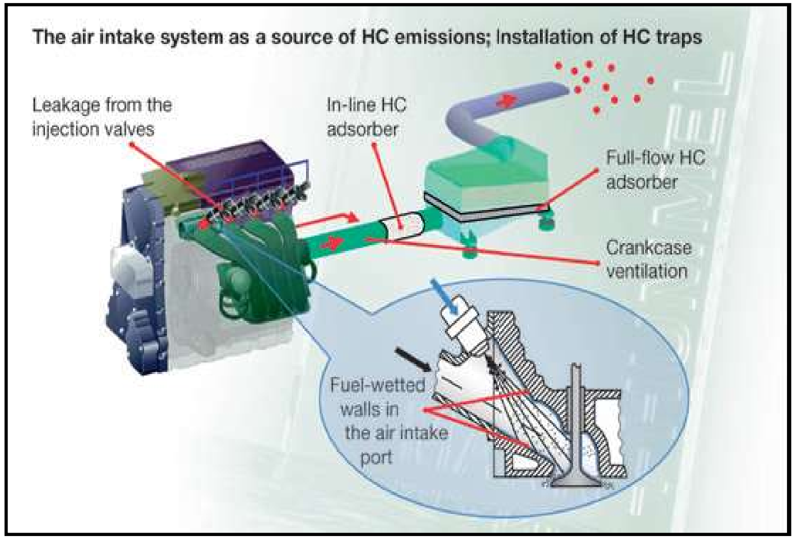




Source: Worldwide Emissions Standards 2010/2011: Passenger Cars & Light-Duty Vehicles, Dephi, MI, USA, 2010.

HC traps in auto industries

There are two kinds of the HC traps (adsorbers) for auto industry applications.



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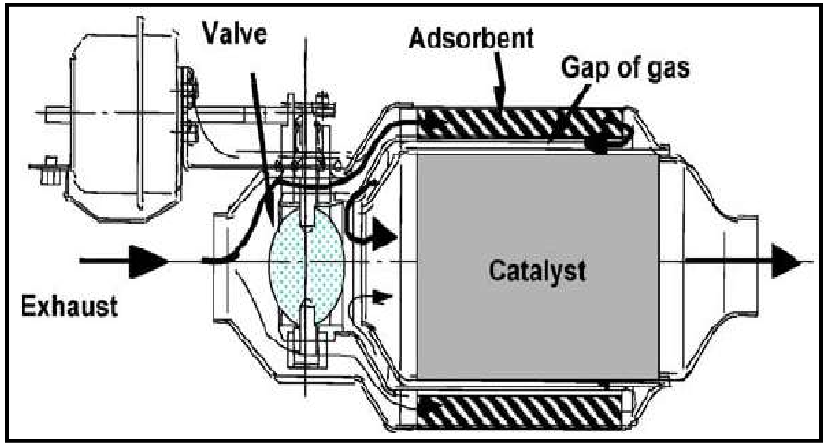
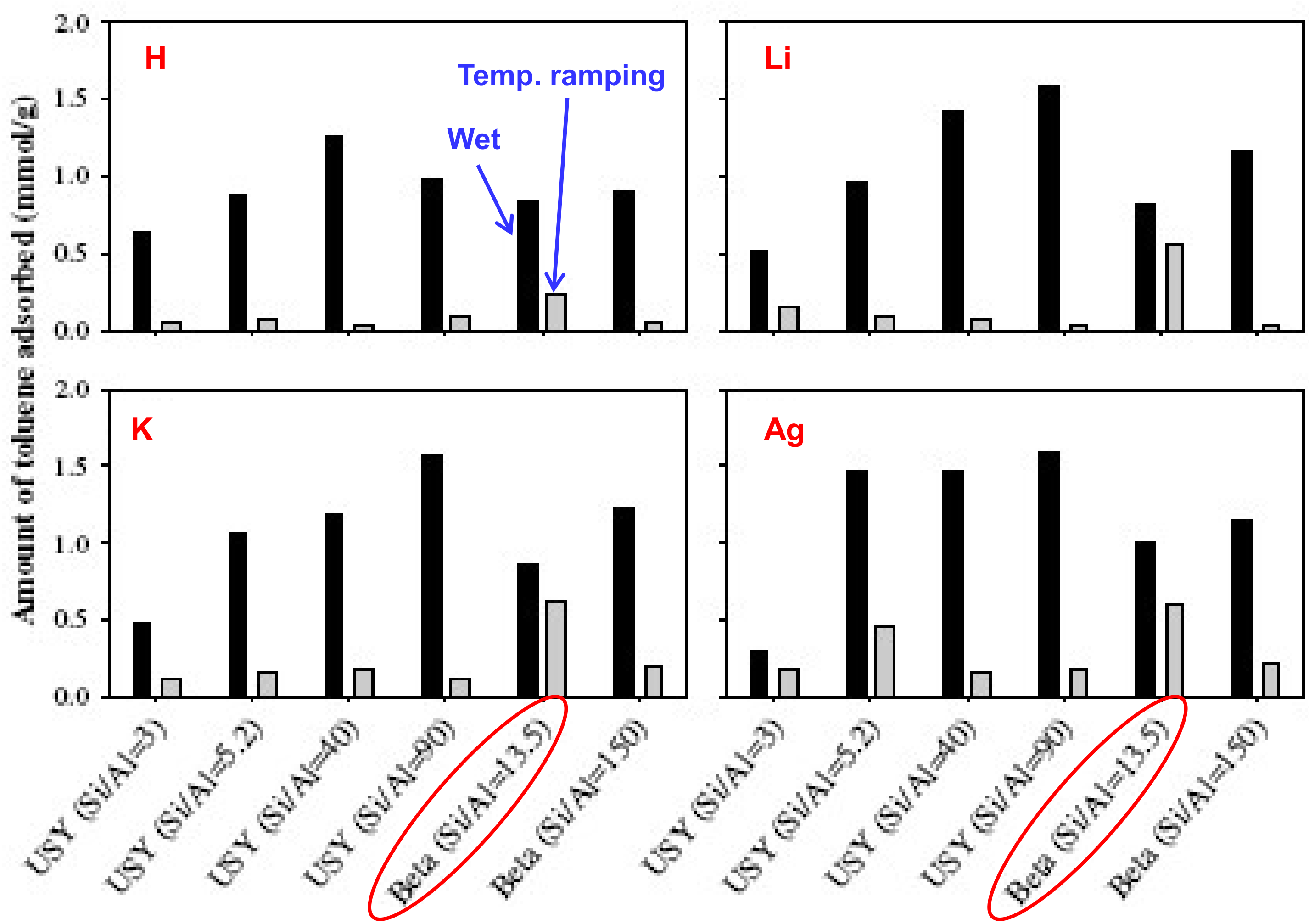


- A system to adsorb the hydrocarbons diffusing from the air intake on layers of activated carbon
- Usually installed directly over the air filter element.
- Being in force from 2007 in the States: NY, MA, VT, ME and CA.

This HC traps are of our particular interest.

Adsorption of toluene on USY and β zeolites



Source: J.H. Park et al., Micropor. Mesopor. Mat., 117 (2009) 178.

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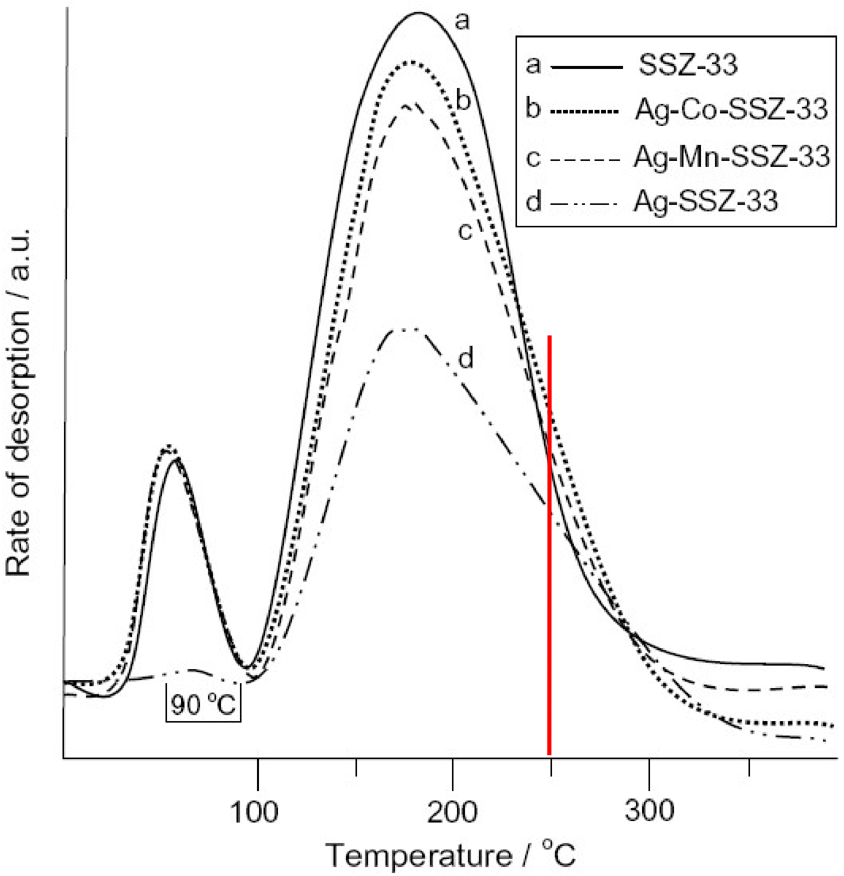
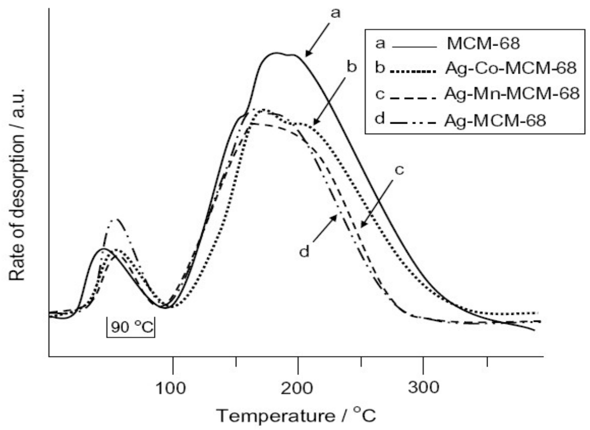
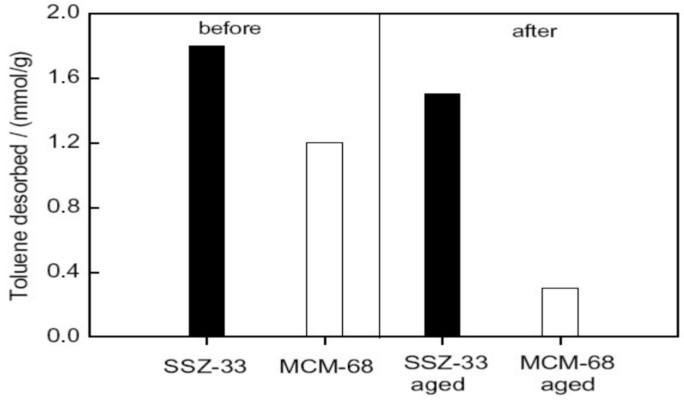
Adsorption of toluene on SSZ-33 and MCM-68

- The desorption temperatures are too low.
- Metal ions exchanged in the zeolites have not a preferred role in moving desorption temperatures up.





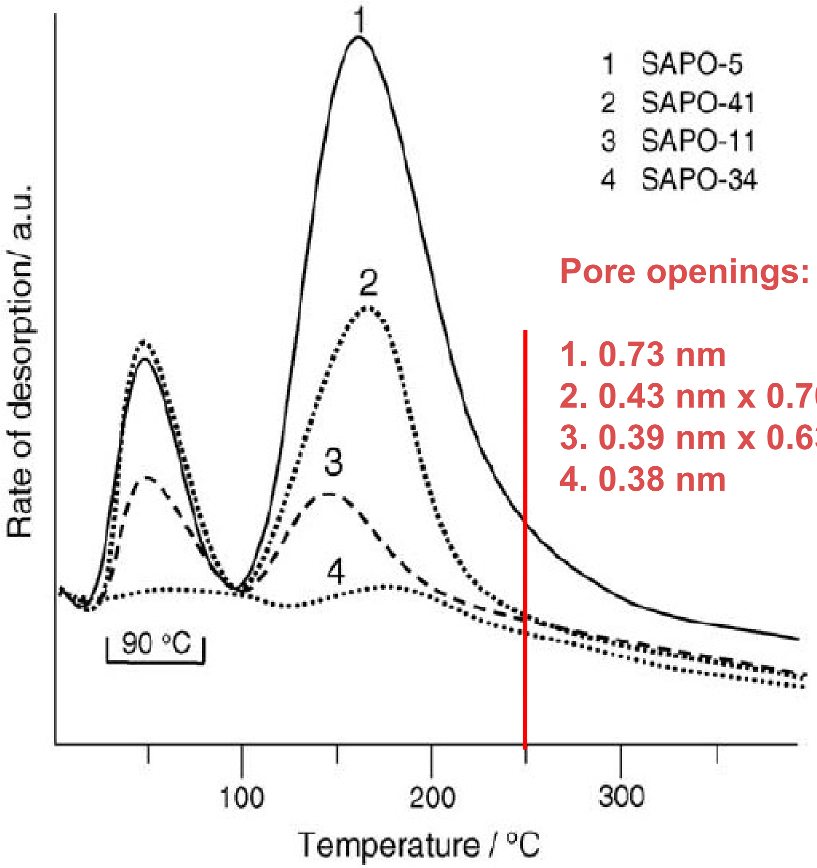
- Hydrothermal aging at 800°C for 5 h with 10% H_2O in an inert gas
- A peak desoprtion temperature = 150°C



Source: S.P. Elangovan et al., Micropor. Mesopor. Mat., 96 (2006) 210.

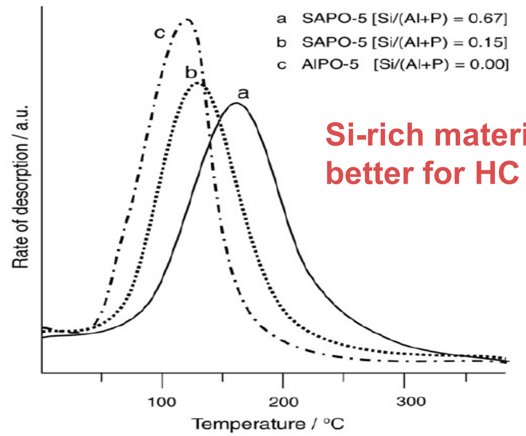
Adsorption of toluene on silicoaluminophosphates

- The desorption temperatures are too low.
- The extent of toluen adsorption is strongly assocated with the pore openings of SAPOs.

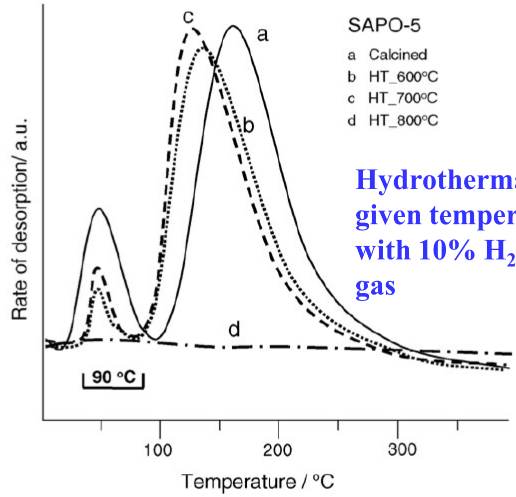


Pore openings:

1. 0.73 nm
2. 0.43 nm x 0.70 nm)
3. 0.39 nm x 0.63 nm)
4. 0.38 nm



Si-rich materials are better for HC traps.

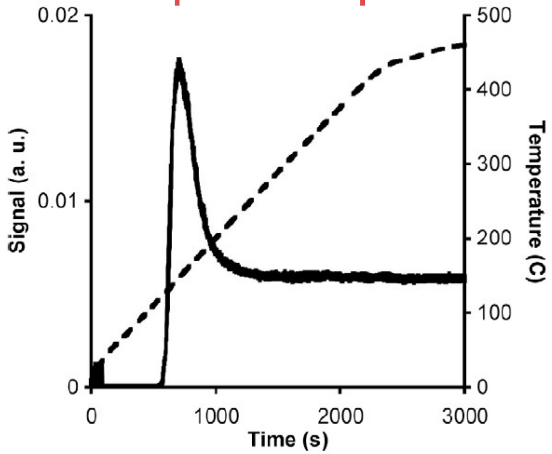


Hydrothermal aging at given tempertures for 5 h with 10% H_2O in an inert gas

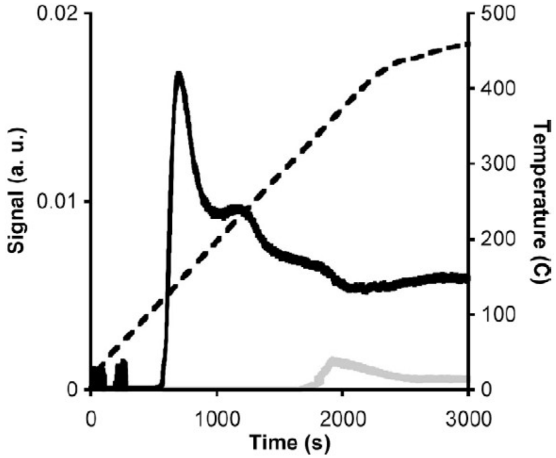
Source: S.P. Elangovan et al., Appl. Catal. B, 57 (2005) 31.

Adsorption of propane/toluene on Cs-MOR

Propane desorption



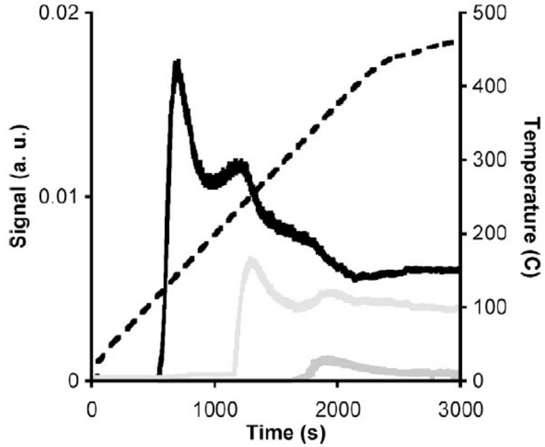
Propane/toluene desorption



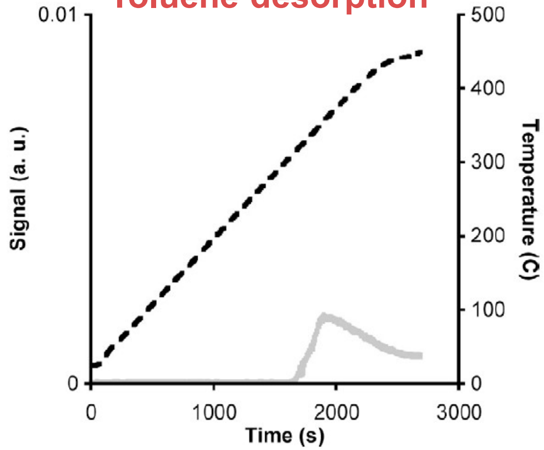
Hydrothermal treatment with a simulated exhaust at 450°C for 40 h

↓

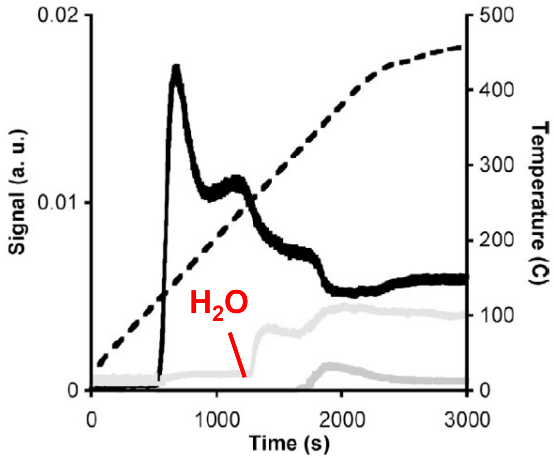
Propane/toluene/water desorption



Toluene desorption



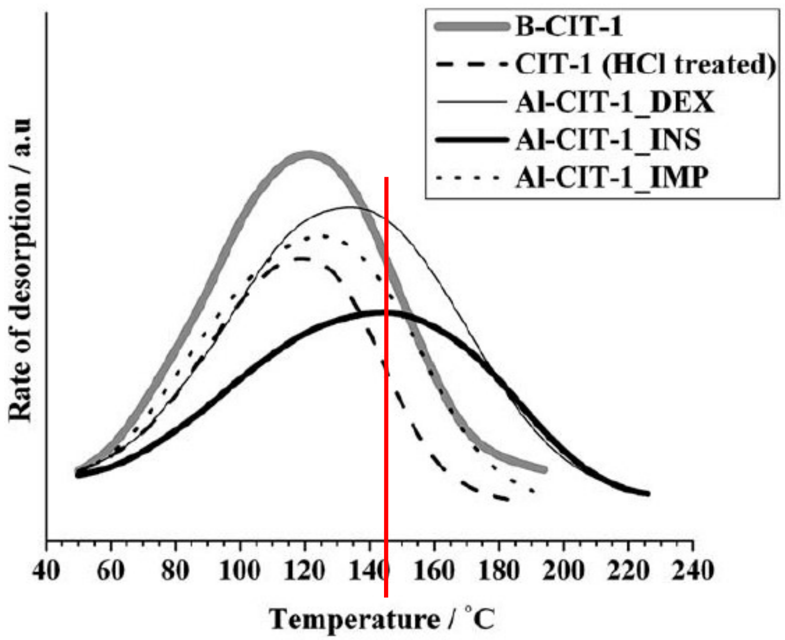
Propane/toluene/water desorption



Source: P.J. Wesson and R.Q. Snurr, Micropor. Mesopor. Mat., 125 (2009) 35.

Adsorption of toluene on CIT-1

- The desorption temperatures are too low.
- An acidity regarding framework Al sites has an influence on the adsorption strength of toluene.



Sample	Chemical analysis (ICP-AES)		N_2 adsorption data		Amount of acid sites[a] (μmol/g)
	Si/B	Si/Al	BET surface area (m^2/g)	Micropore volume (cm^3/g)	
B-CIT-1	26.6	–	627	0.18	30
Al-CIT-1_DEX	∞	55	640	0.18	90
Al-CIT-1_INS	∞	37	648	0.17	40
Al-CIT-1_IMP	∞	173	634	0.15	20

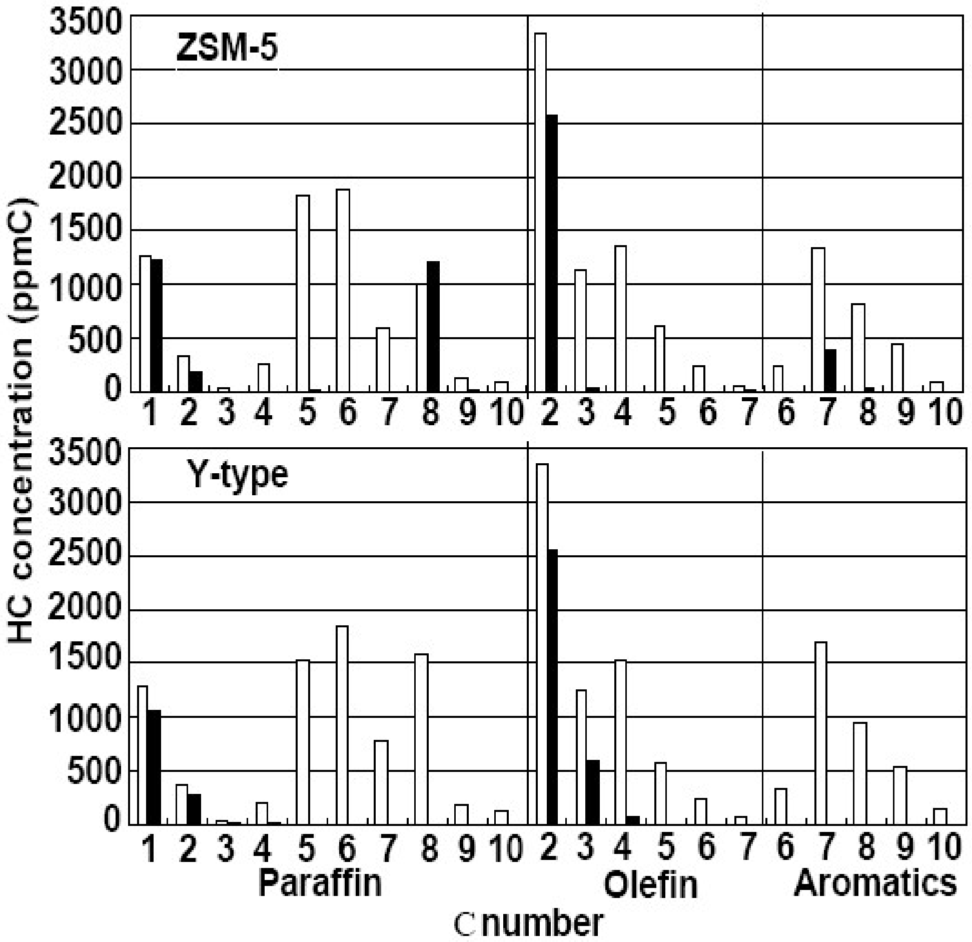
[a] Obtained from NH_3-TPD by considering the high temperature peak alone.

Sample	Amount of toluene adsorbed (mmol/g)	Amount of 2,2,4-TMP adsorbed (mmol/g)	Toluene desorption characteristics[a]	
			Peak maximum (°C)	Desorption end temperature (°C)
Al-CIT-1_DEX	0.60	0.37	134 (126)	223 (188)
Al-CIT-1_INS	0.47	0.06	145 (136)	226 (215)
Al-CIT-1_IMP	0.58	0.17	125 (125)	195 (195)

[a] The data for the corresponding hydrothermally treated sample is given in the parentheses.

Source: T. Mathew et al., Micropor. Mesopor. Mat., 129 (2010) 126.

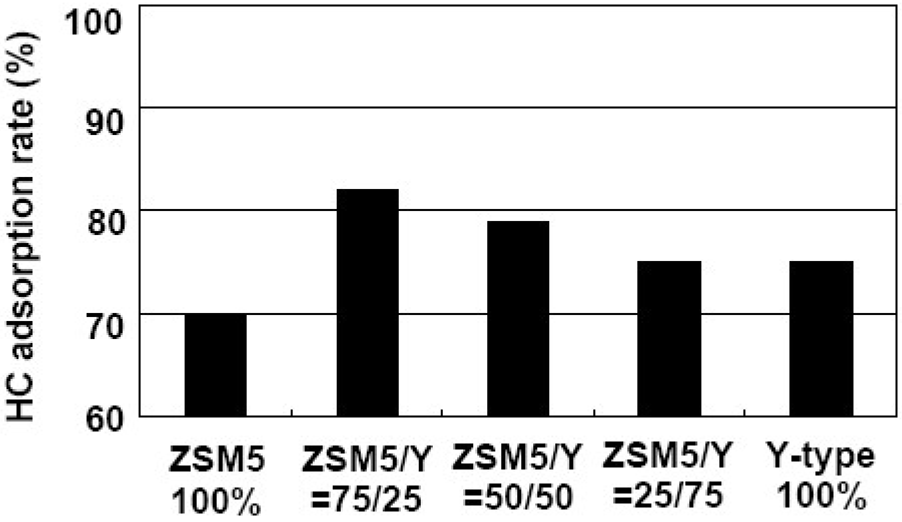
Adsorption of HCs on MFI and FAU

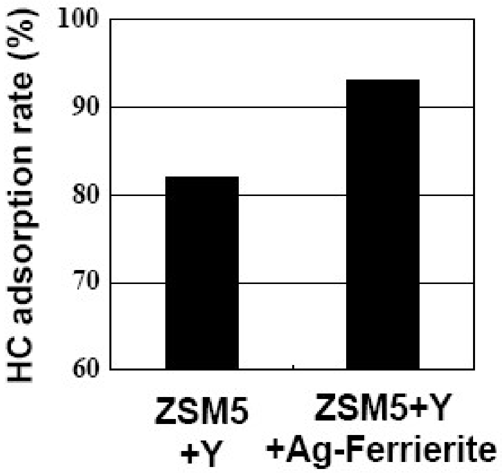


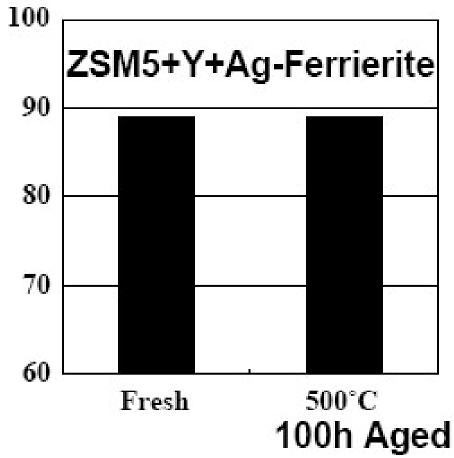
- C_1 is passed through all the zeolites.
- All the zeolites are not good for C_2 paraffins and olefins, particularly C_2 olefins.
- The Y zeolite adsorbs preferably C_8 paraffins and C_7 aromatics.
- The ZSM-5 is good for C_3-C_4 olefins.
- C_4-C_7 paraffins are well trapped on all the zeolites.

Source: T. Kanazawa, Catal. Today, 96 (2004) 171.

Adsorption of HCs on a mixture of zeolites







- The mixture is a good HC trap, and this formulation was applied to the Toyota Prius to meet the SULEV standards in May 2000.
- The Ag-FER can adsorb selectively C_2 olefins.
- The three mixture system has a good hydrothermal stability; however, the aged temperature is somewhat low.

Source: T. Kanazawa, Catal. Today, 96 (2004) 171.

Conclusions: Materials for HC traps

- Fast rate of HCs adsorption
- High adsorption capacity
- Good robustness to HCs (paraffins, olefins and aromatics)

  Exhausts contain C_1~C_{11} HCs, but C_2~C_9 HCs are targeted.

- Strong adsorption strength so as to be:

  (i) desorbed at temperatures > 175°C (Modern TWCs require 175°C or slightly above for an initiation)
  (ii) retained up to temperatures = 250~300°C

- Completely reversible in HCs adsorption and desorption
- Incombustible even in the presence of O_2 (0.2~2%)
- Strong tolerance to H_2O vapor (10~12%)
- Good or excellent hydrothermal stability

  Perhaps, this may be solved through aftertreatment system designs.

- Good resistance to thermal shocks (hot spots)
- Easy to fabricate it to low pressure drop monoliths
- Minimal adsorption of CO