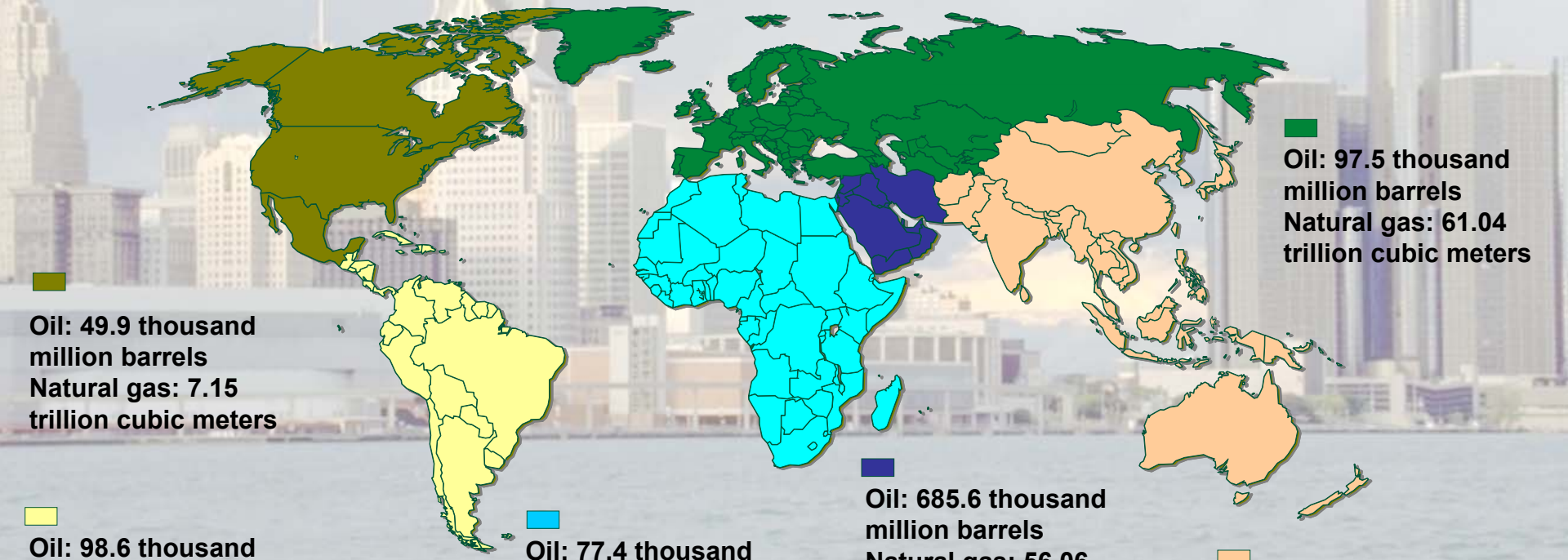
Cleers Workshop 2005

Recent Results for HC-SCR Using Ag-Alumina and Cu-Zeolites

Edward Jobson

Volvo Technology Corporation

Proven resources of crude oil and natural gas



Oil: 49.9 thousand million barrels
Natural gas: 7.15 trillion cubic meters

Oil: 98.6 thousand million barrels
Natural gas: 7.08 trillion cubic meters

Oil: 77.4 thousand million barrels
Natural gas: 11.84 trillion cubic meters

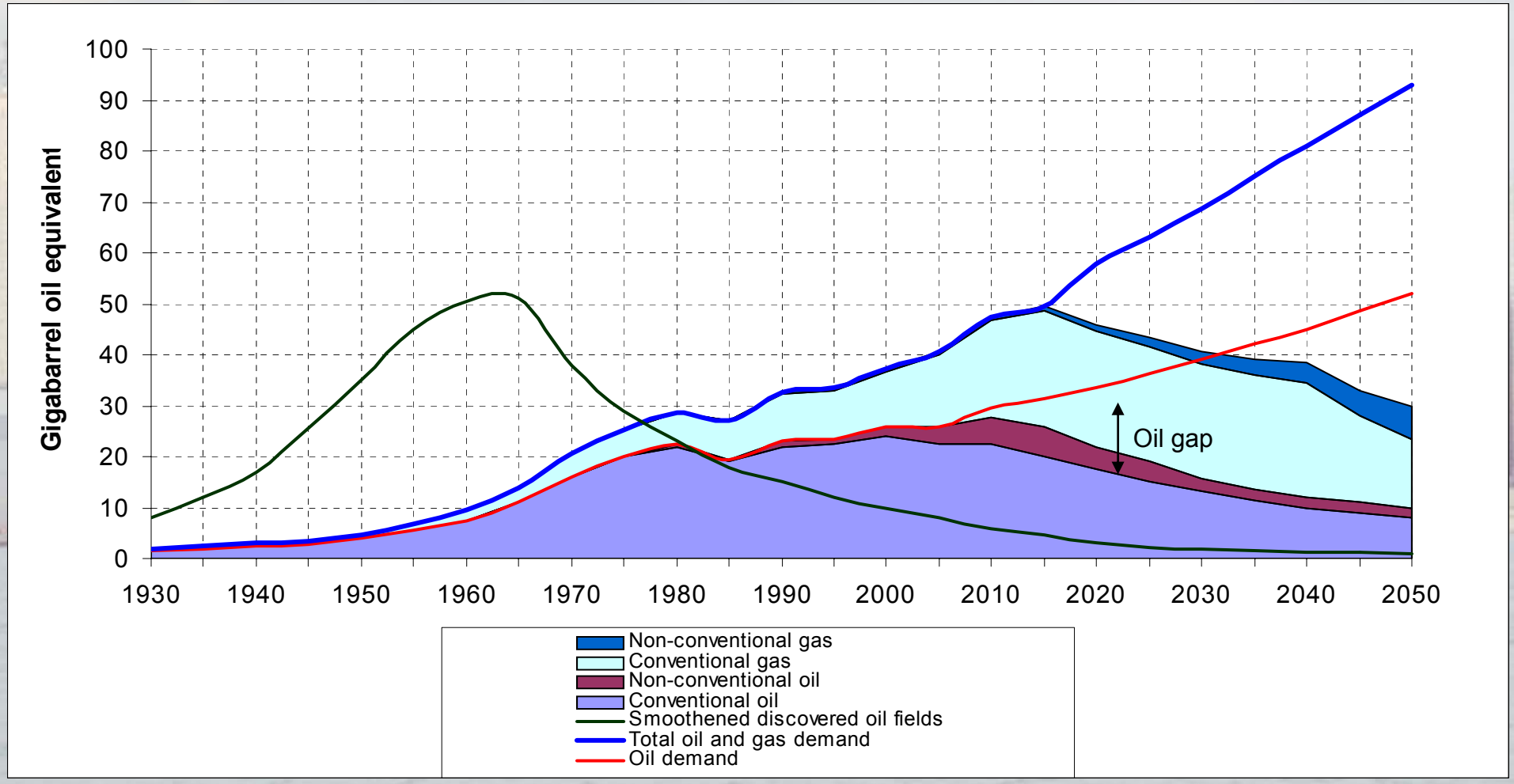
Oil: 685.6 thousand million barrels
Natural gas: 56.06 trillion cubic meters

Oil: 97.5 thousand million barrels
Natural gas: 61.04 trillion cubic meters

Oil: 38.7 thousand million barrels
Natural gas: 12.61 trillion cubic meters

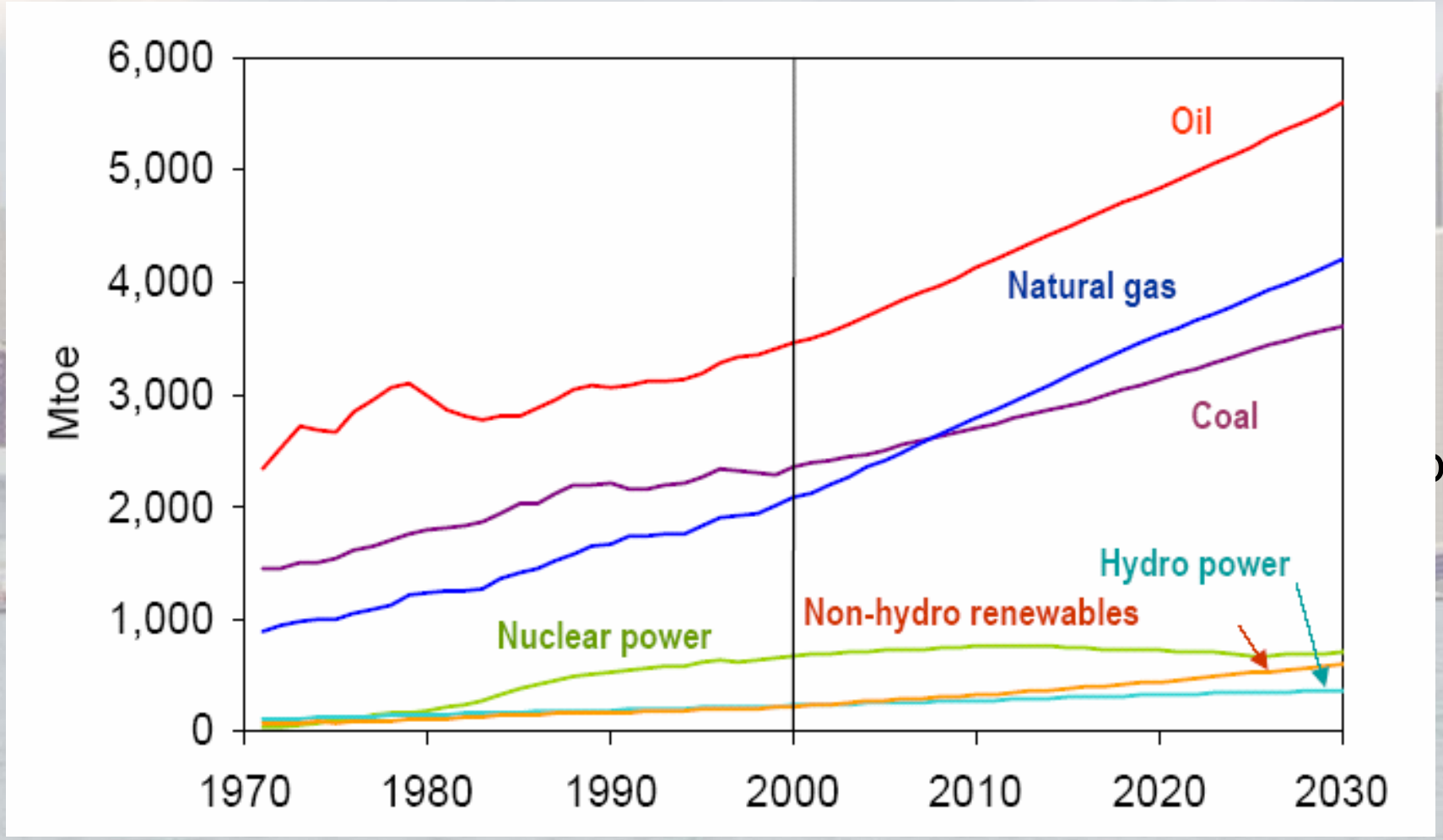
Source: BP Statistical Review of World Energy 2003

Oil production peak



Sources: www.peakoil.net, C.J.Campbell, demand from IEA

Increasing energy demand



Energy demand projections IEA

Greenhouse gases

What is needed to be done?

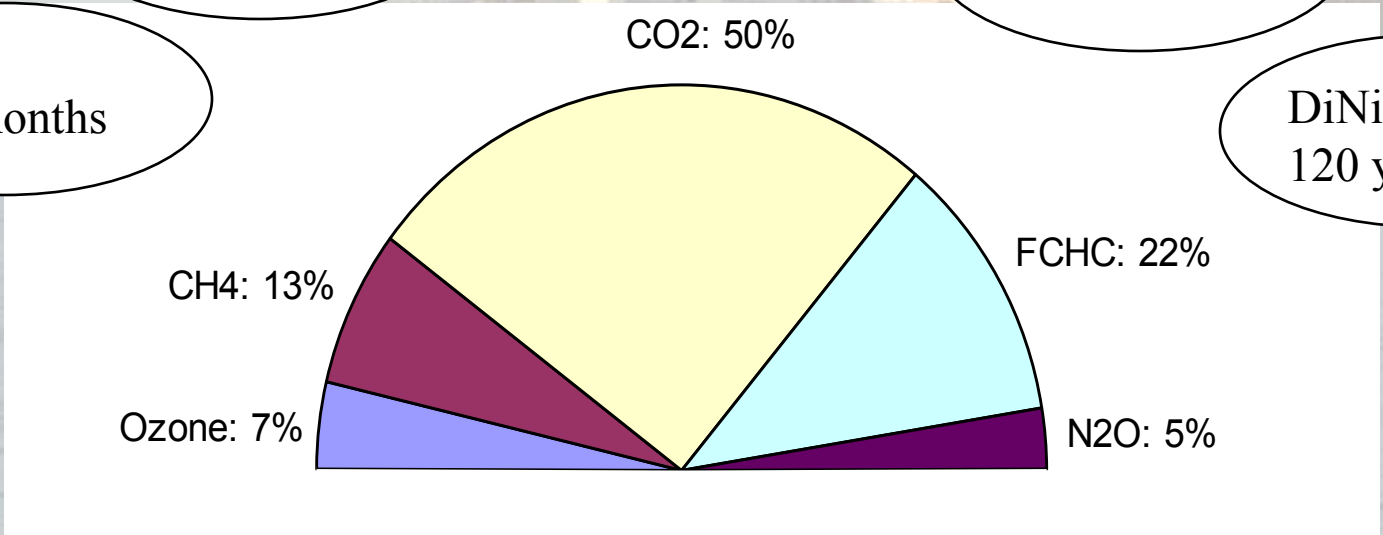
Carbondioxide
50-200 years

Methane
12-17 years

FCHC
45-100 years

Ozone
ca. 4 months

DiNitrogenoxide
120 years



Who needs to act?

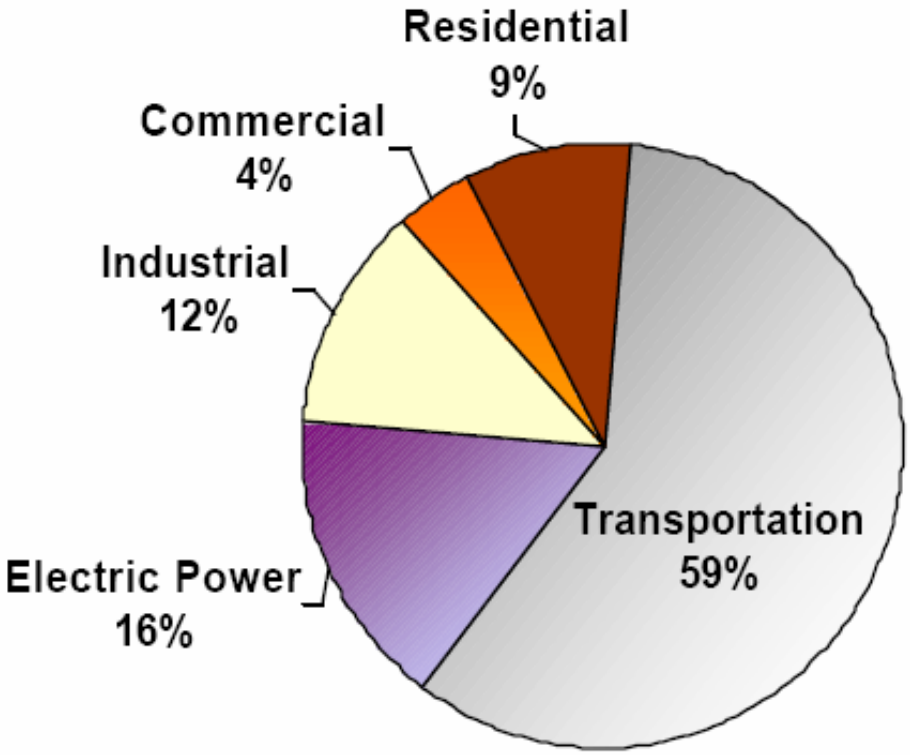


Figure 2-5. CO2 Emissions from the Combustion of Fossil Fuels by Sector for 1999 (adapted from CEC, 2002).

Climate change

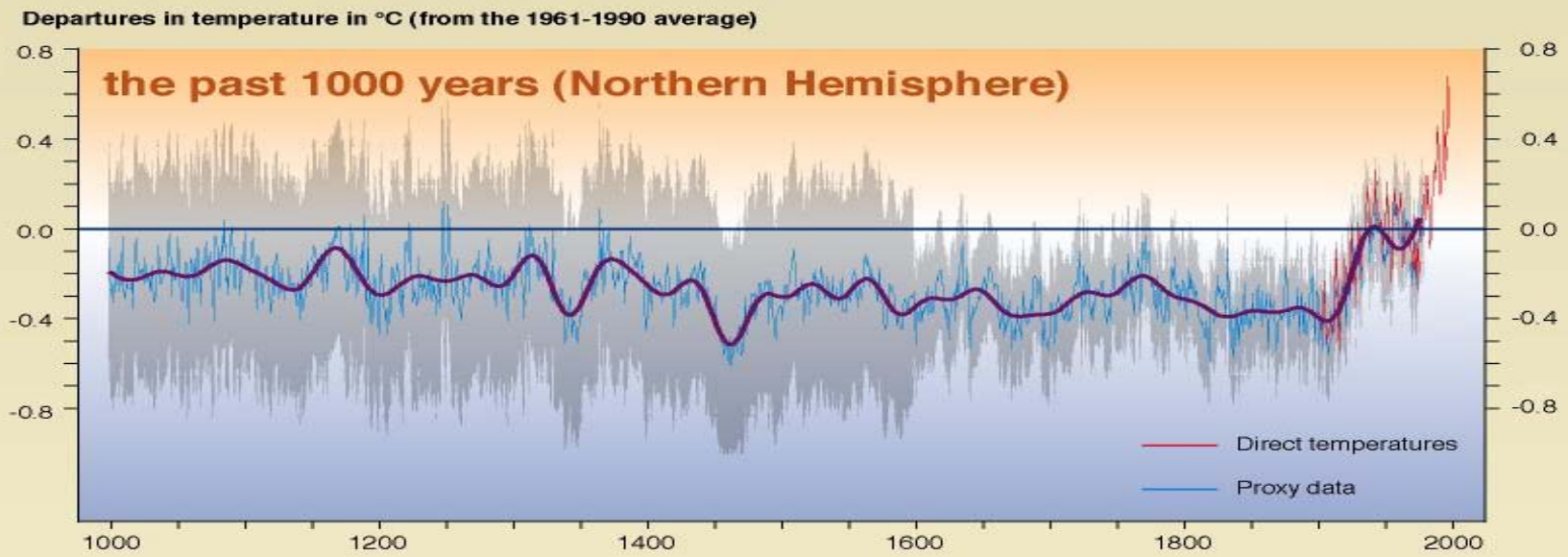
"Climate issues will present the automotive industry with its greatest challenge in the future"

Leif Johansson, CEO and President of Volvo.

Reduction of fossil greenhouse gas emissions is addressed in national and international strategies and programmes.

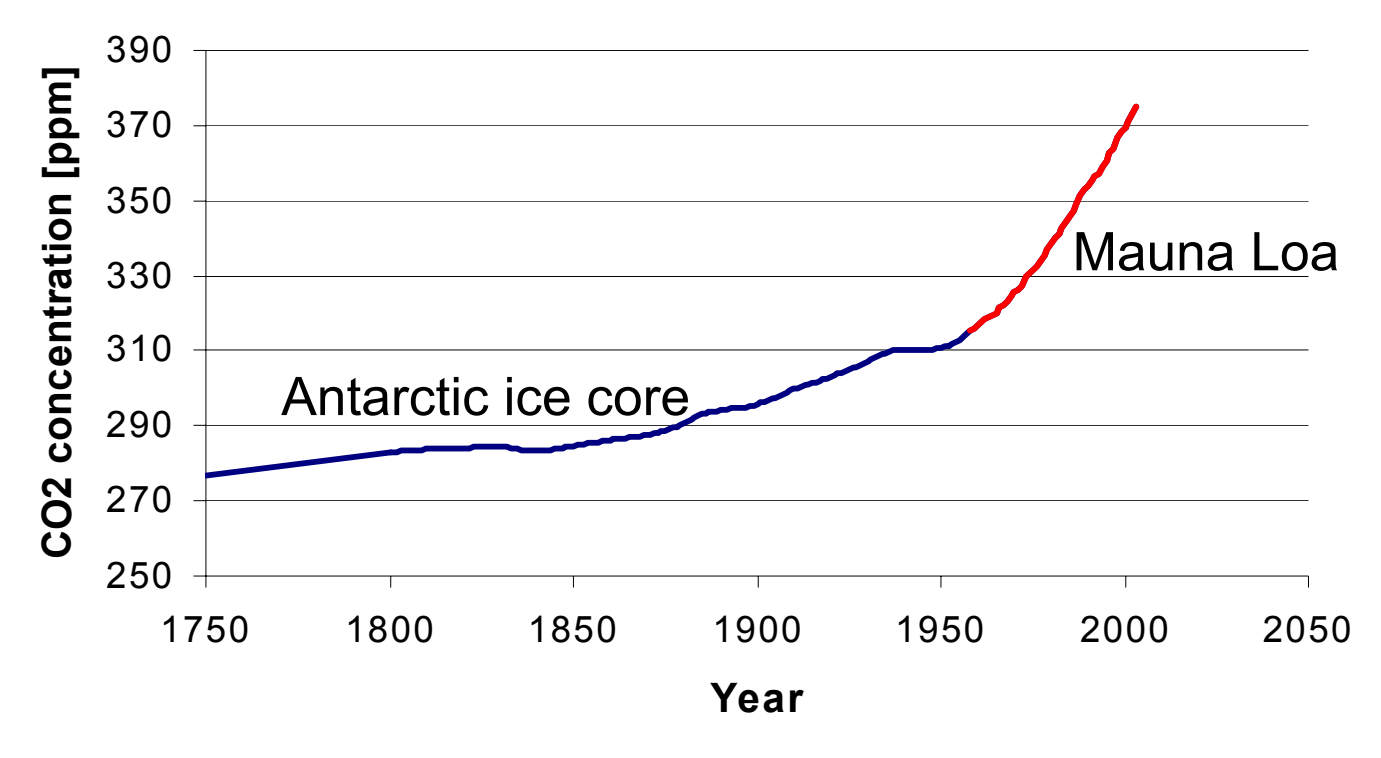
The transport sector is a focused area.

The needed reduction of fossil greenhouse gas emissions will be a very strong driver for low or neutral CO_2 fuels and vehicles.

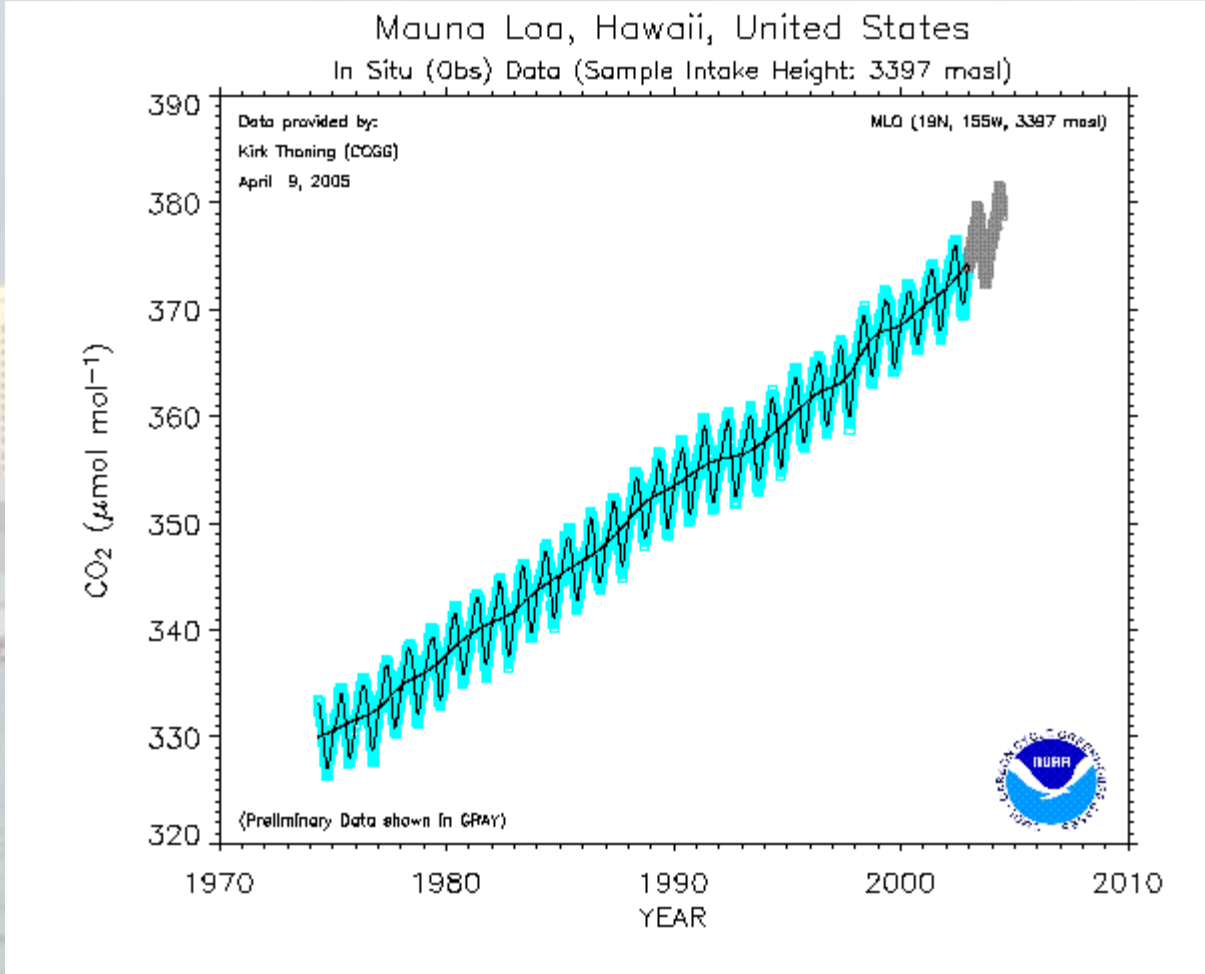


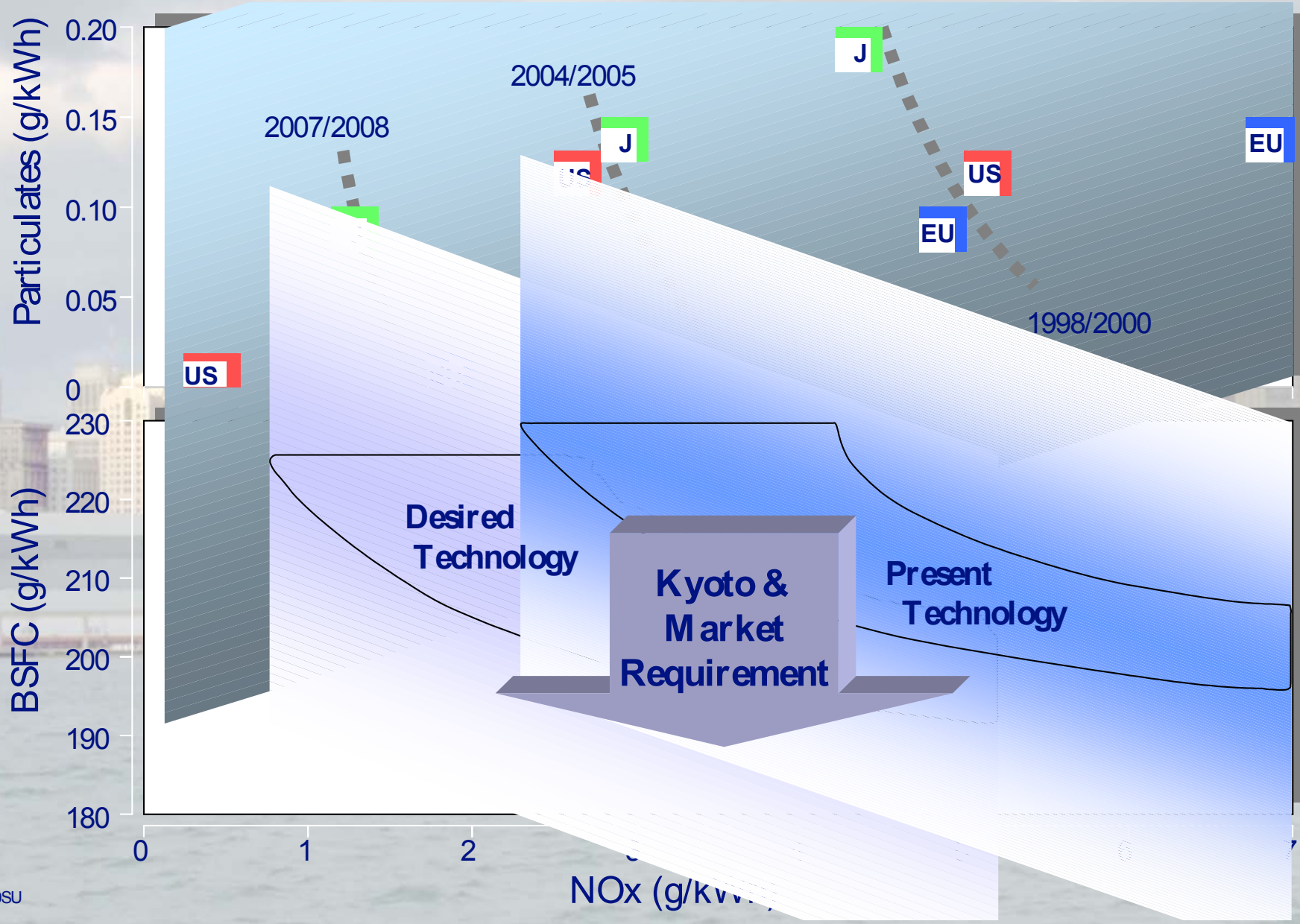
Source: IPCC

Atmospheric CO_2 concentration



Atmospheric CO_2 concentration




Particulates (g/kWh)
0.20
0.15
0.10
0.05
0
2007/2008
2004/2005
1998/2000
J
US
EU
BSFC (g/kWh)
230
220
210
200
190
180
Desired Technology
Kyoto & Market Requirement
Present Technology
0
1
2
NOx (g/kW

24440SU

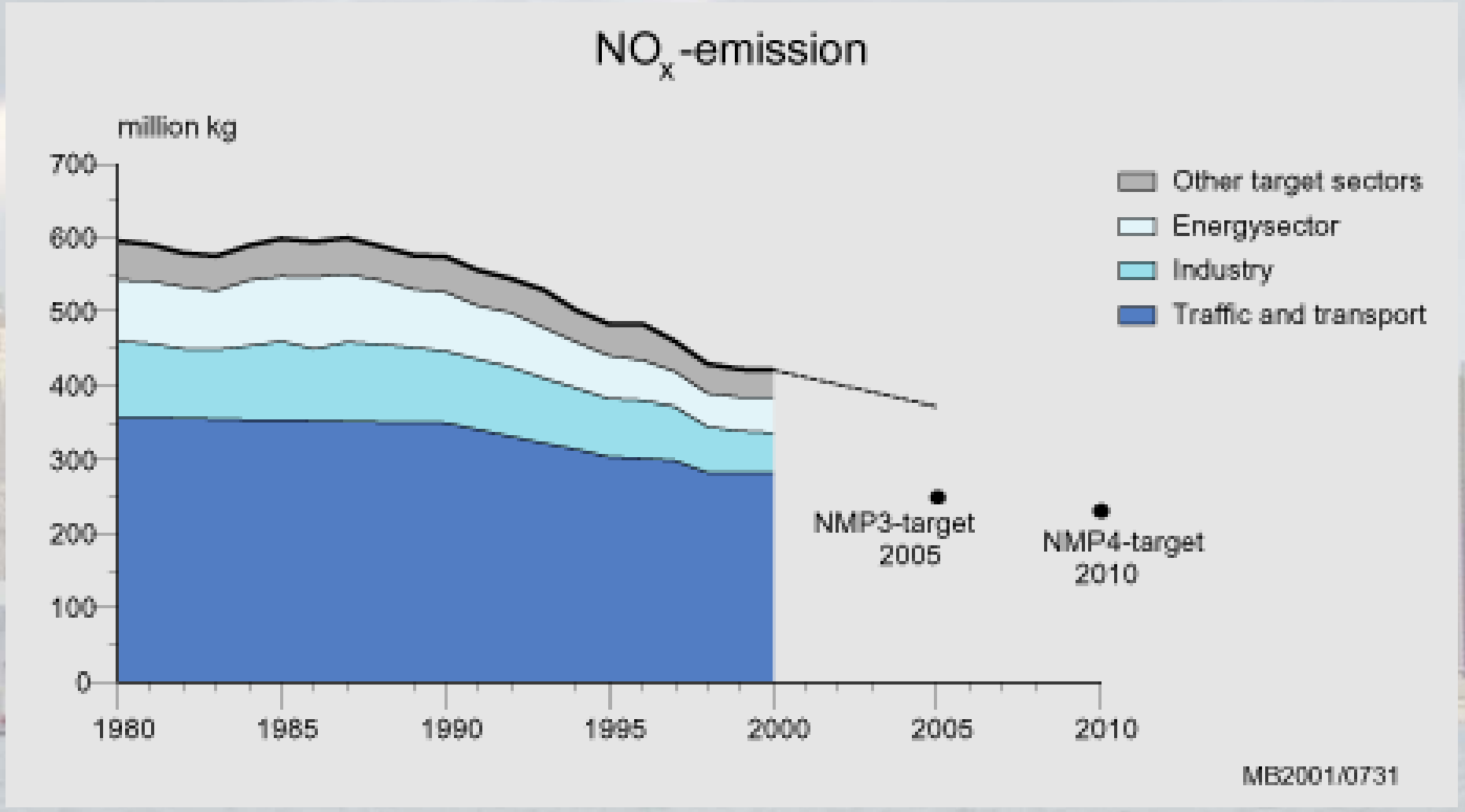


Figure 2.2.4 Emission of NO_X in the Netherlands, 1980-2000

http://www.epa.gov/air/airtrends/pdfs/2003ozonereport.pdf

The present trend is good…

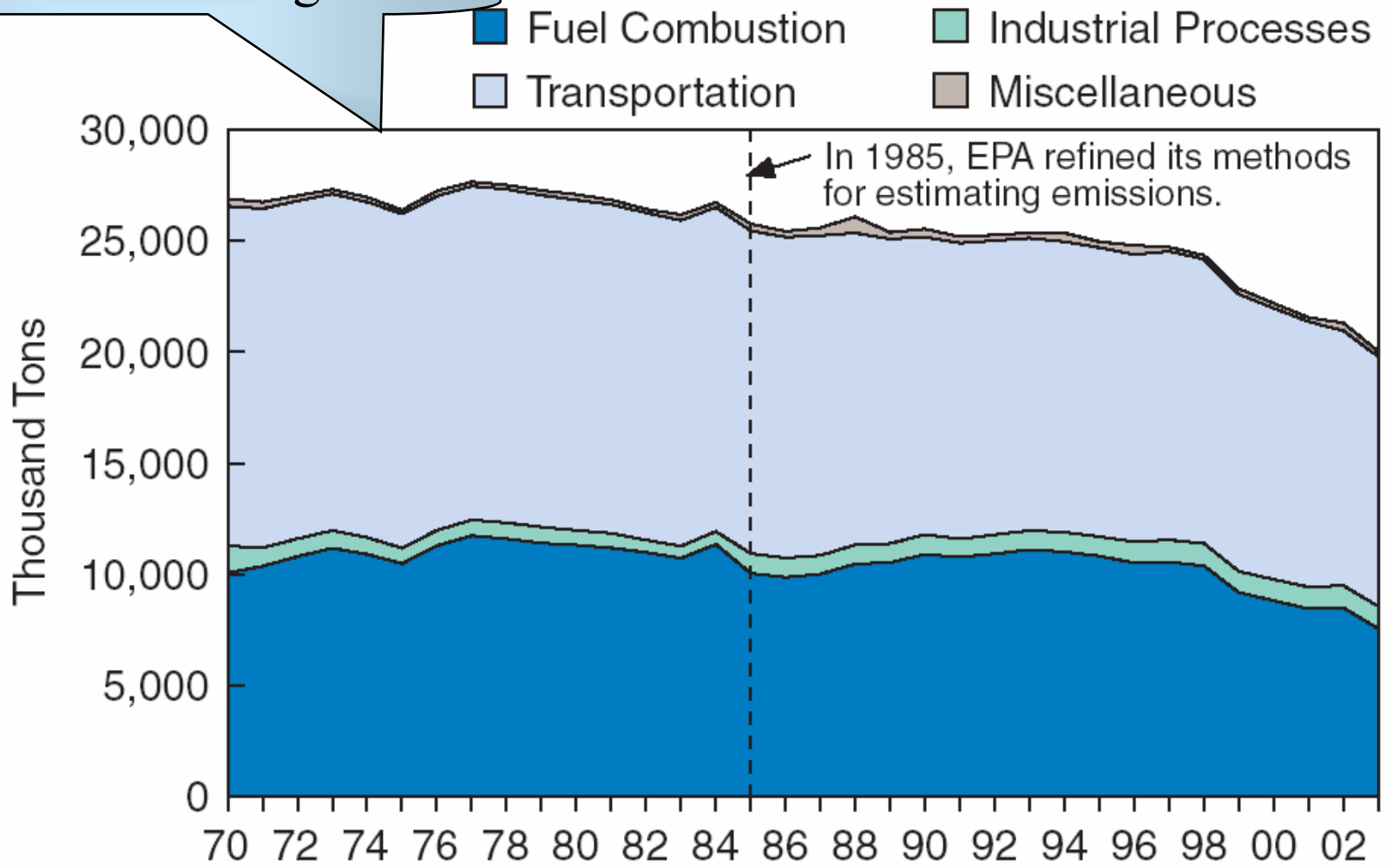
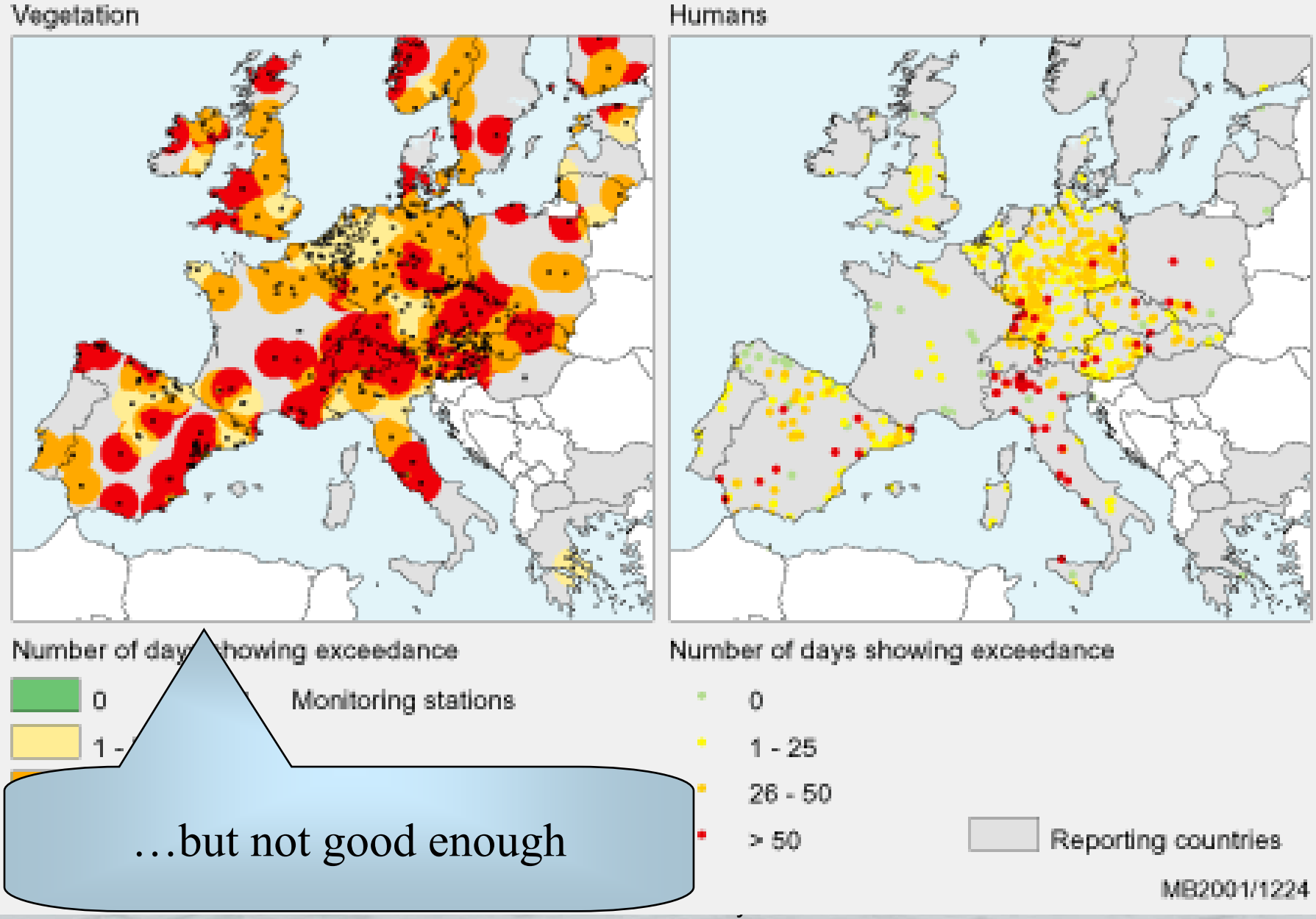


Figure 12. National Trends in NO_x Emissions, 1970–2003.

Exceedance of ozone standards in 1999



…but not good enough

Technical solutions for improved fuel consumption.

Large Car

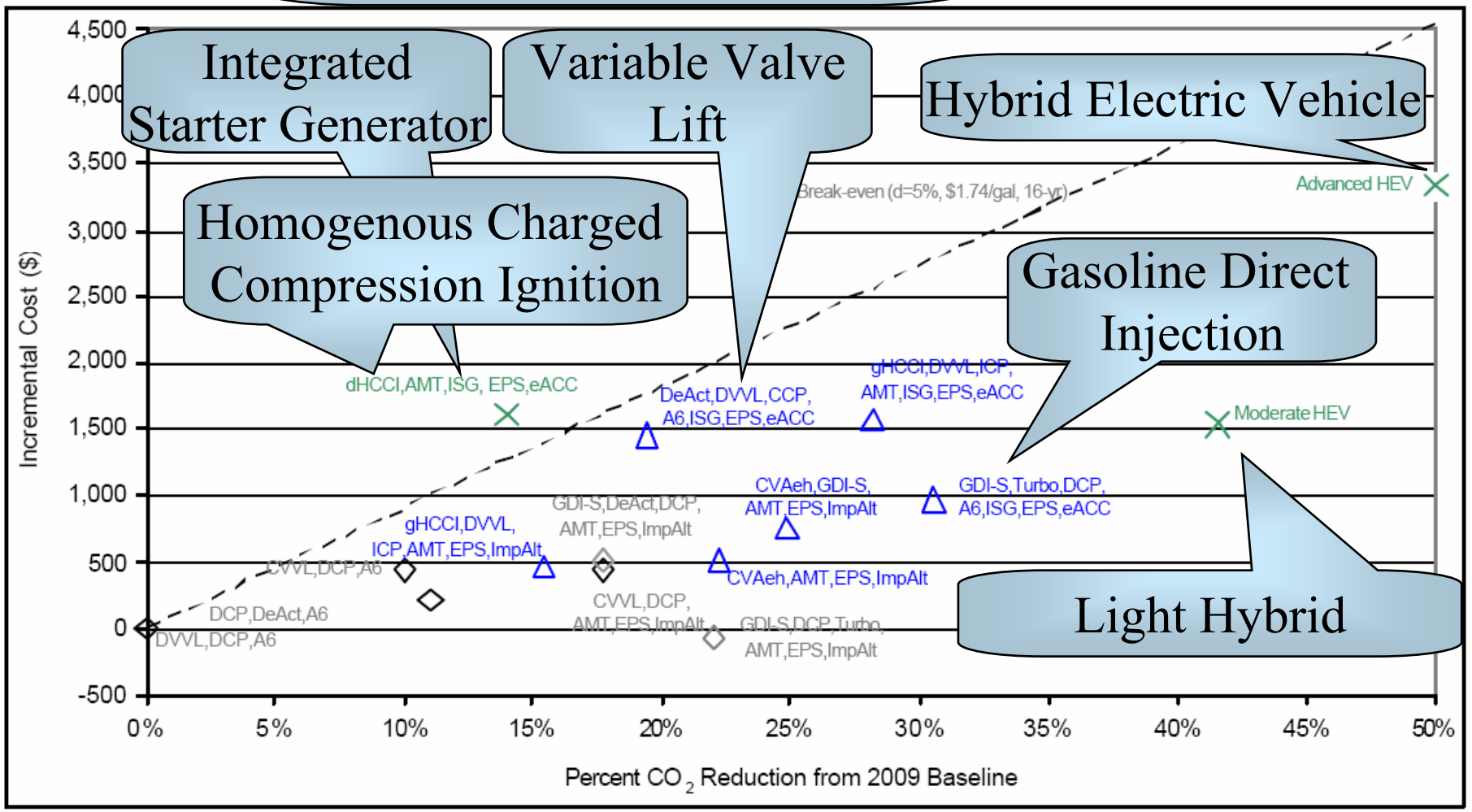


Figure 5-8. Incremental Costs for Technology Packages on 2009 Baseline Large Cars

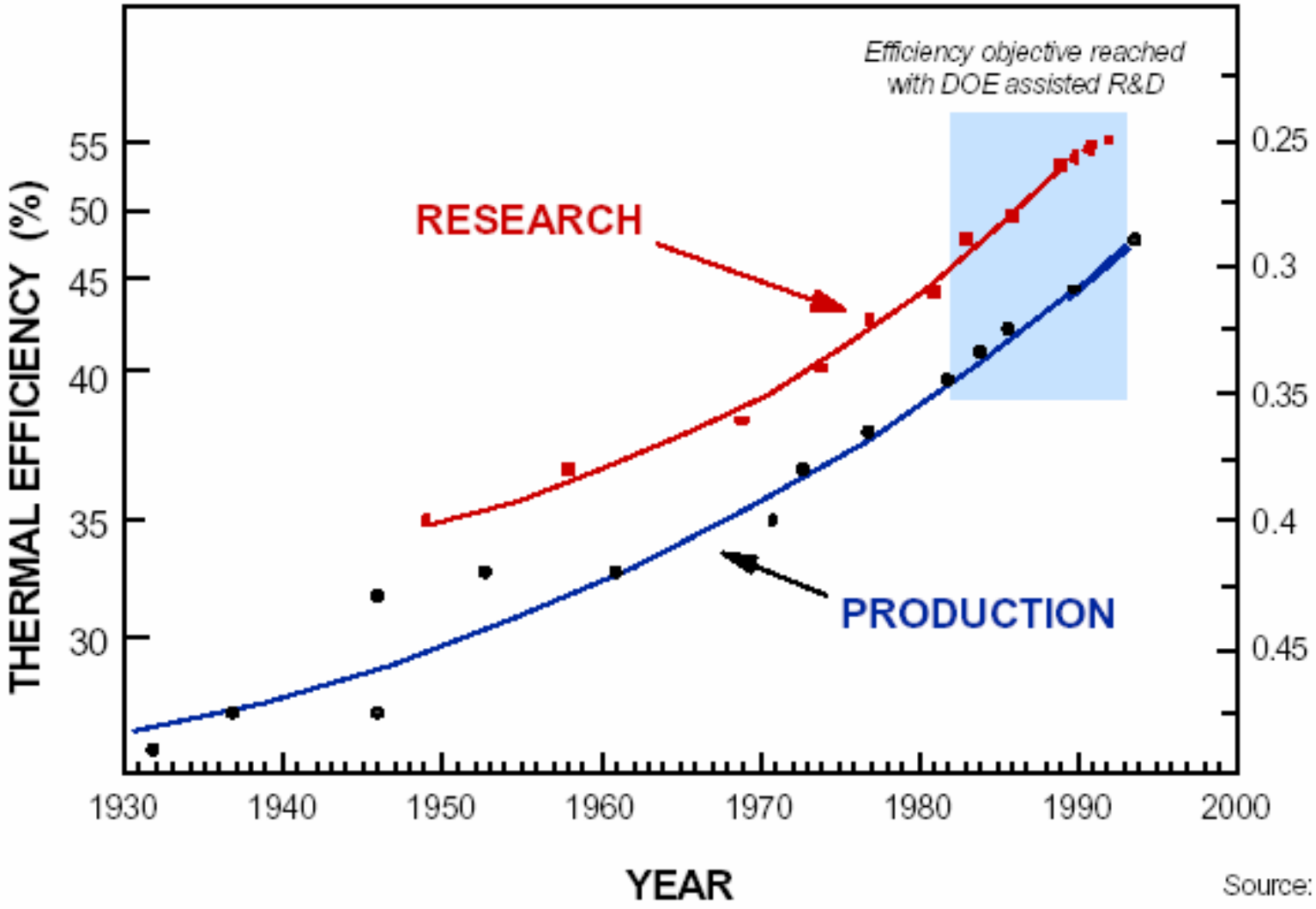


Figure 1. Increasing Diesel Efficiency

Global considerations

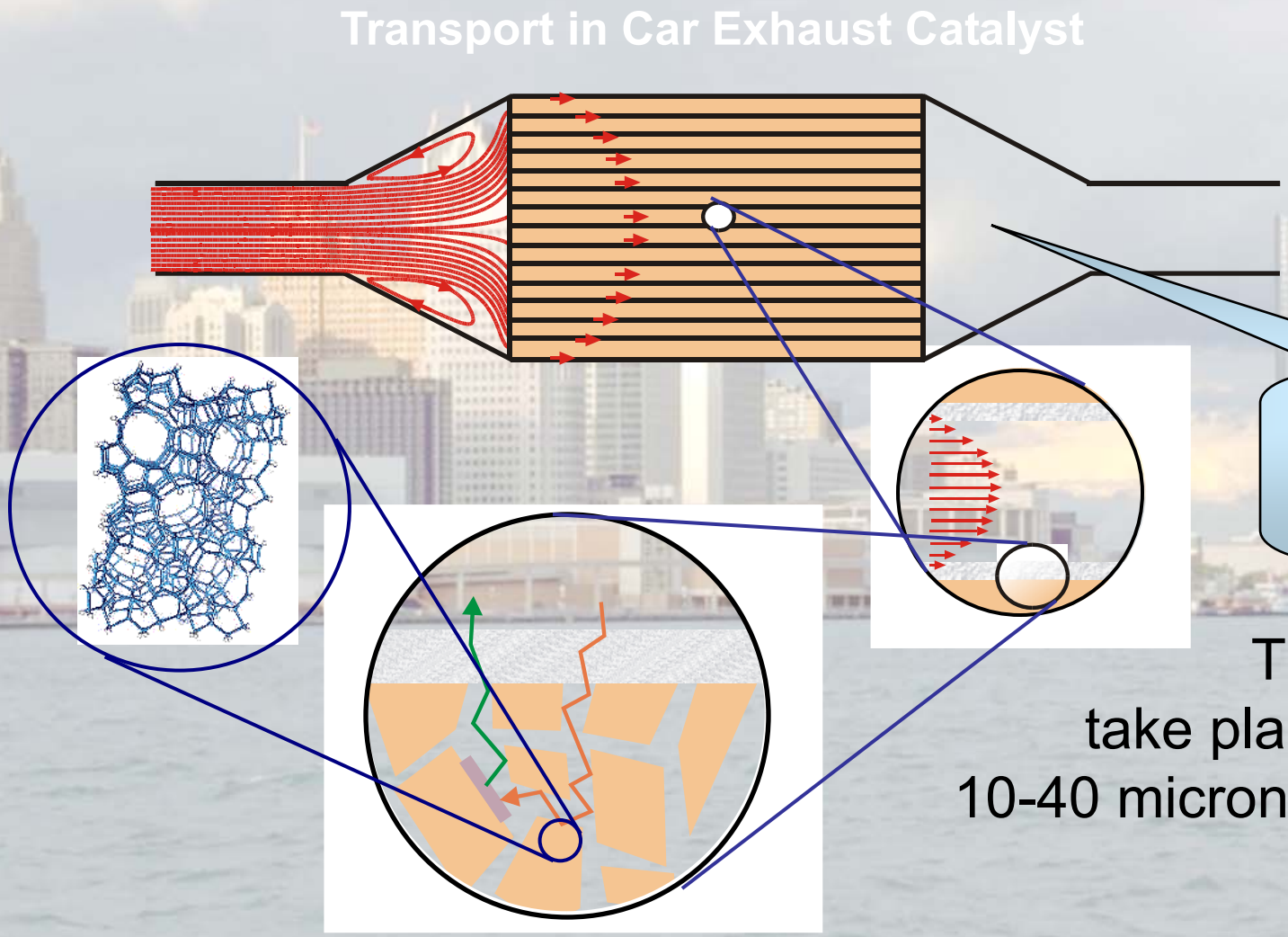
- Transition to sustainable energy production
- Global transport solutions not local, needed to solve global emissions
- Global harmonisation
  - Fuels
  - Test cycles → real world emissions
  - Diagnostics & in use compliance

Risks and opportunities

- Risks
  - Fuel price weak driver
  - Coal for >600 years
  - International destructive competition
  - Responsibility on short term mandate
    - Politicians, Presidents, CEOs, media, (religion)
- Opportunities
  - Technology solutions
  - Sustainable energy
  - International cooperation
    - Development countries
    - Global social development
    - Constructive competition

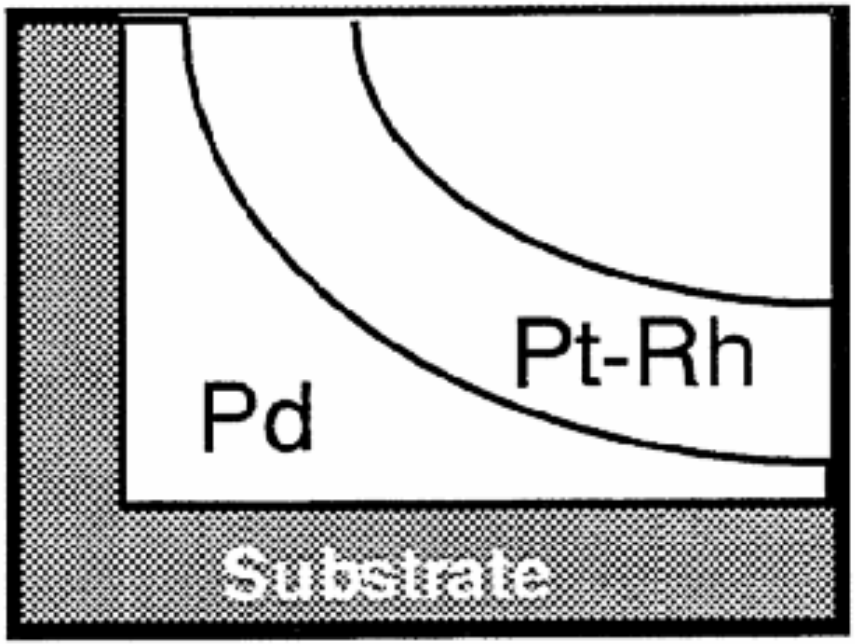
Educated public a condition for GHG abatement
Researchers and scientists are <u>responsible</u>

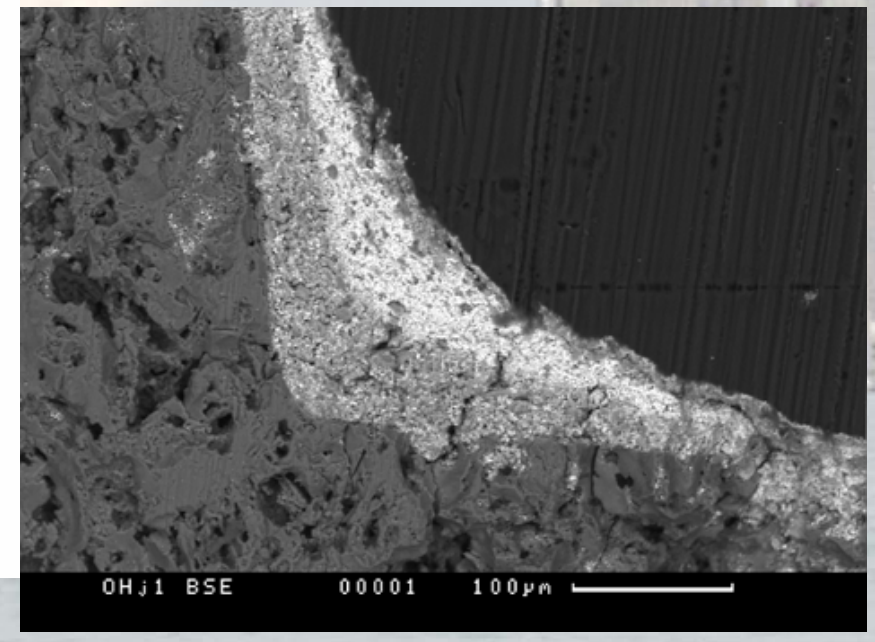
Design of a catalytic converter



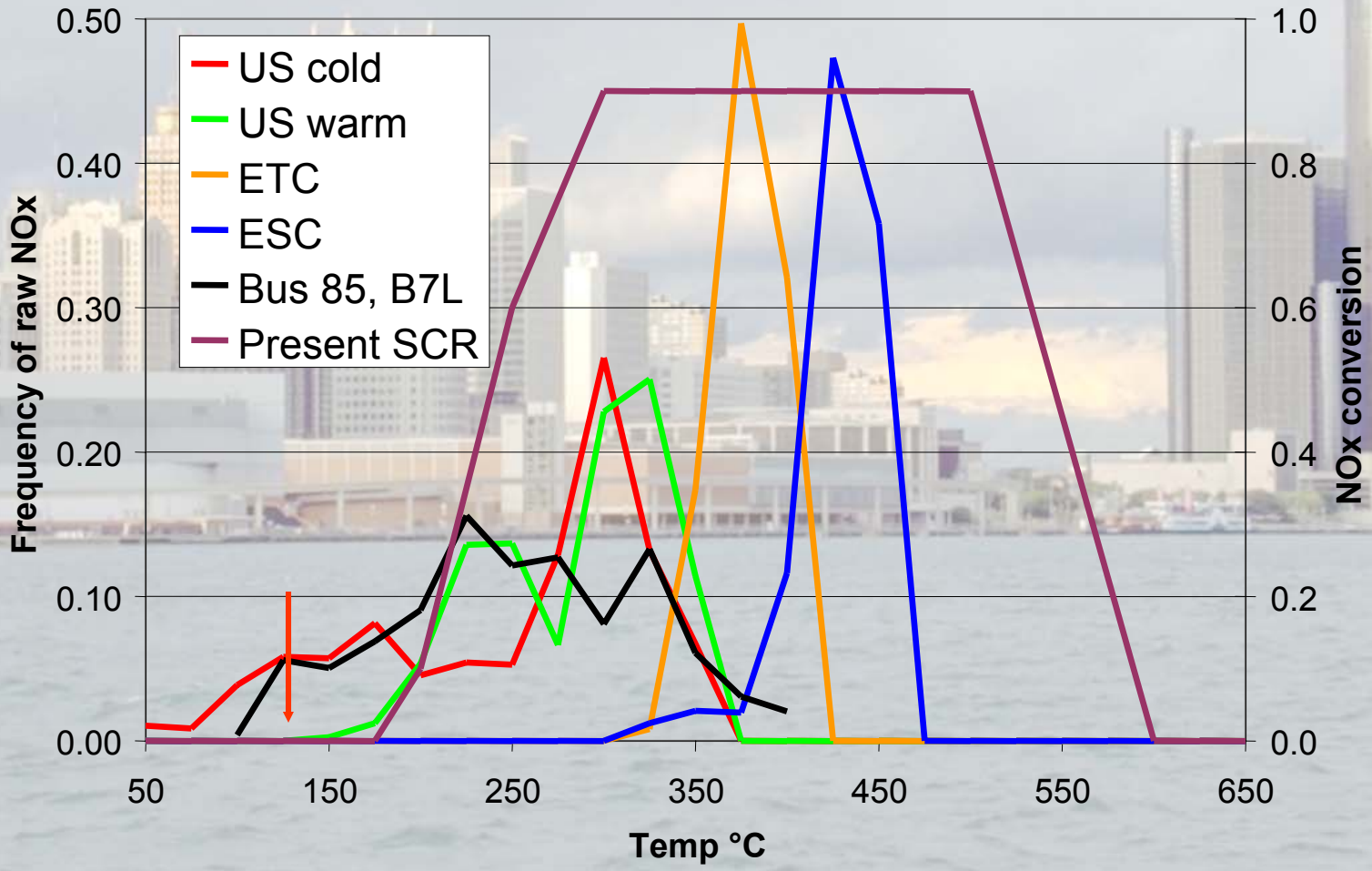
The reactions take place in the top 10-40 micron of the wash coat.

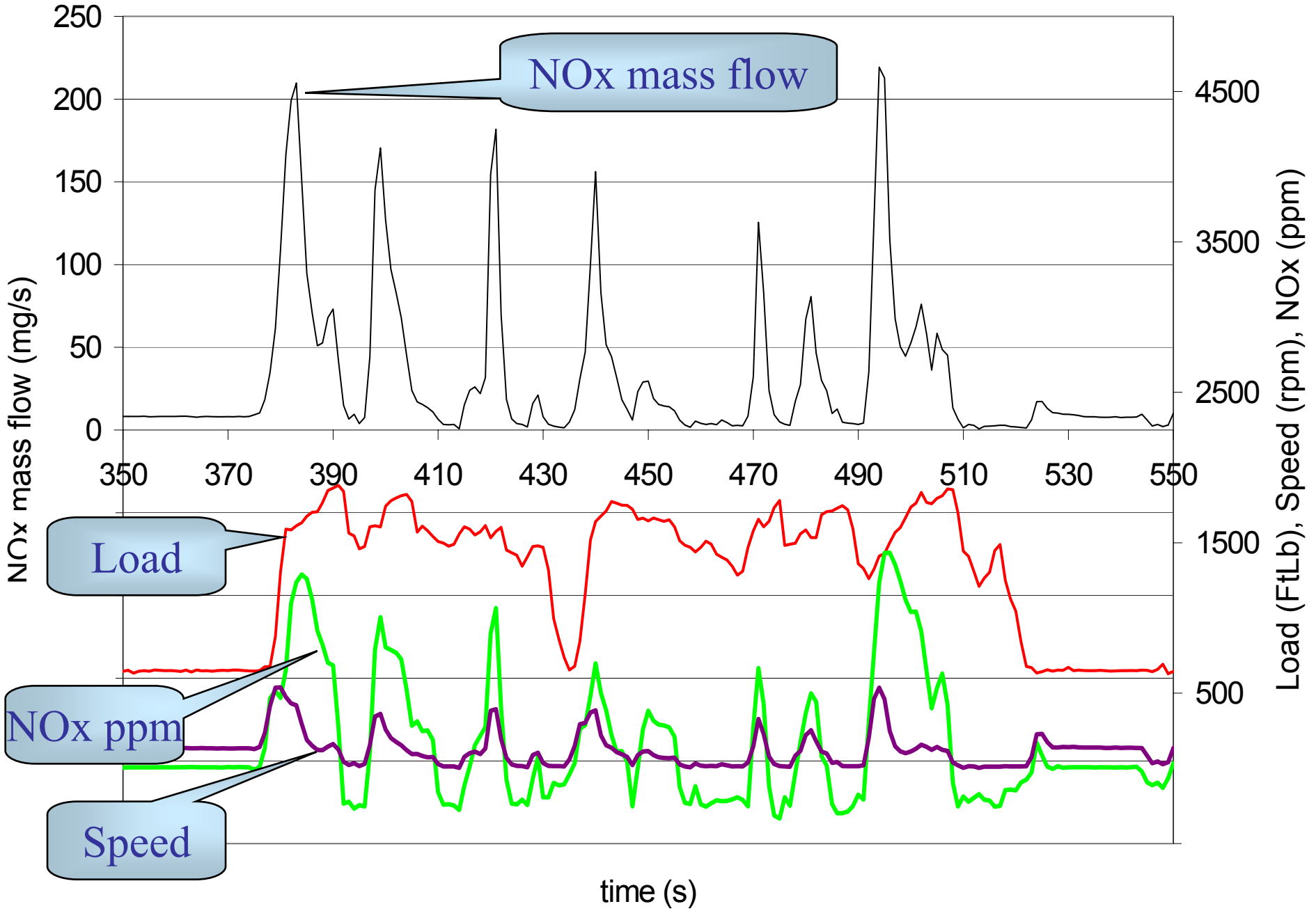
The monolith channels





Active temperature range for SCR




NOx mass flow
Load
NOx ppm
Speed
NOx mass flow (mg/s)
Load (FtLb), Speed (rpm), NOx (ppm)
time (s)
250
200
150
100
50
0
4500
3500
2500
1500
500
350
370
390
410
430
450
470
490
510
530
550

NOx reduction by HC-SCR Challenges by example

- Cold start
- Low temperature activity
- Transient NOx conversion
  - Reducing agent ”matching”
  - Temperature swing
- Soot clogging
- Fuel quality variation (**sulphur** and aromatics)
- Lubrication oil (solid state reactions, ash and masking)
- Water soak and shower

Brief History

- Cu-ZSM5 → transition metal ion exchanged zeolite
- Pt catalysts → Au cluster catalysts
- Sn catalysts
- Ir, Rh, In
- Ag/Alumina

Held, König, Richter, Puppe
SAE 900496
1990

Iwamoto
Proc, Catal. Tech. for Removal of NOx
1990

Lean Green fun to drive machine VW 1996

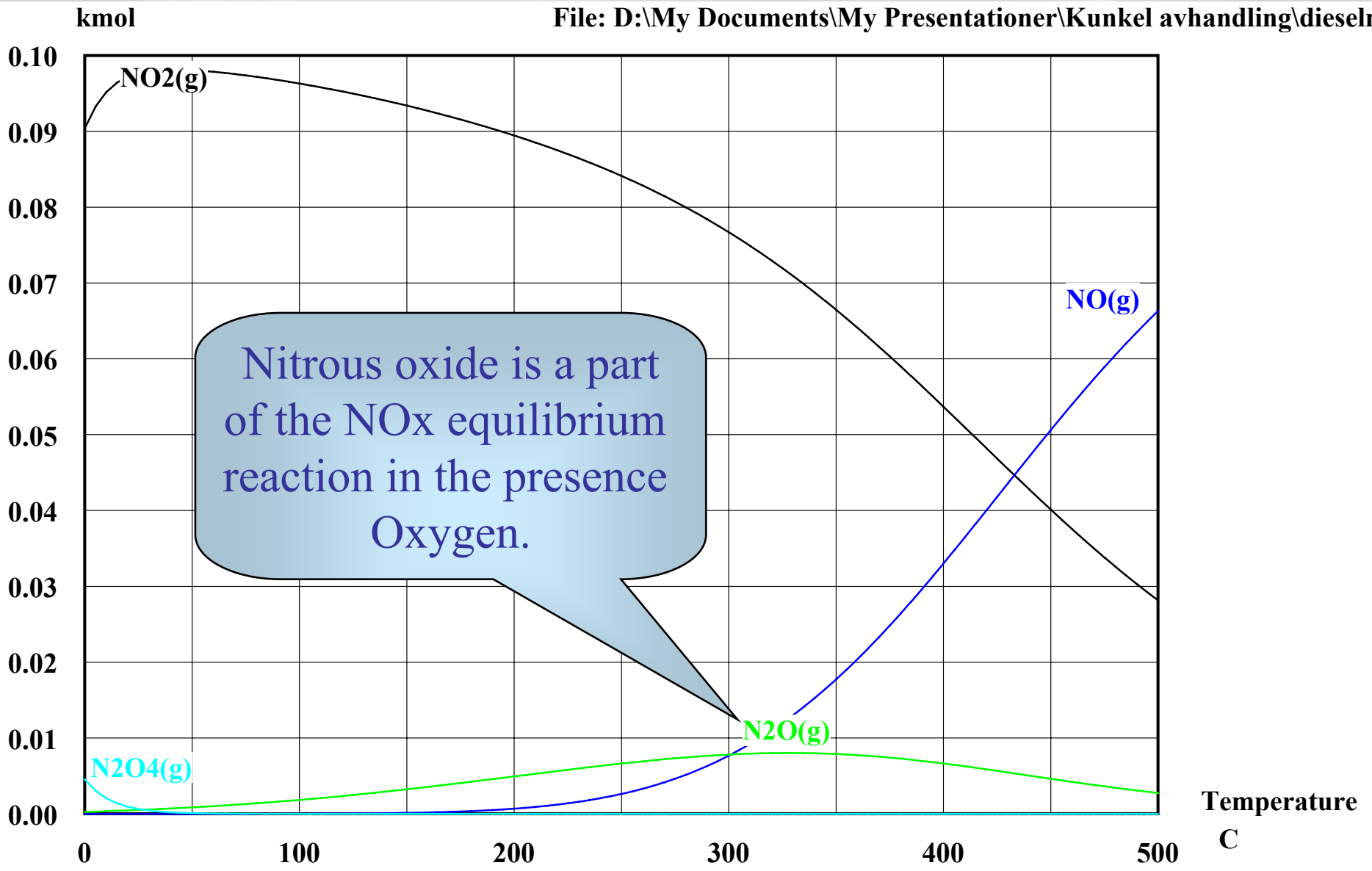
Mitsubishi Iridium Catalyst 1997

Cleaire Retrofit catalyst 2003

Three paths for HC-SCR

- Cu-Zeolite
- Ag-Alumina
- Pt-Alumina

NOx equilibrium in dieselexhaust 1000 ppm



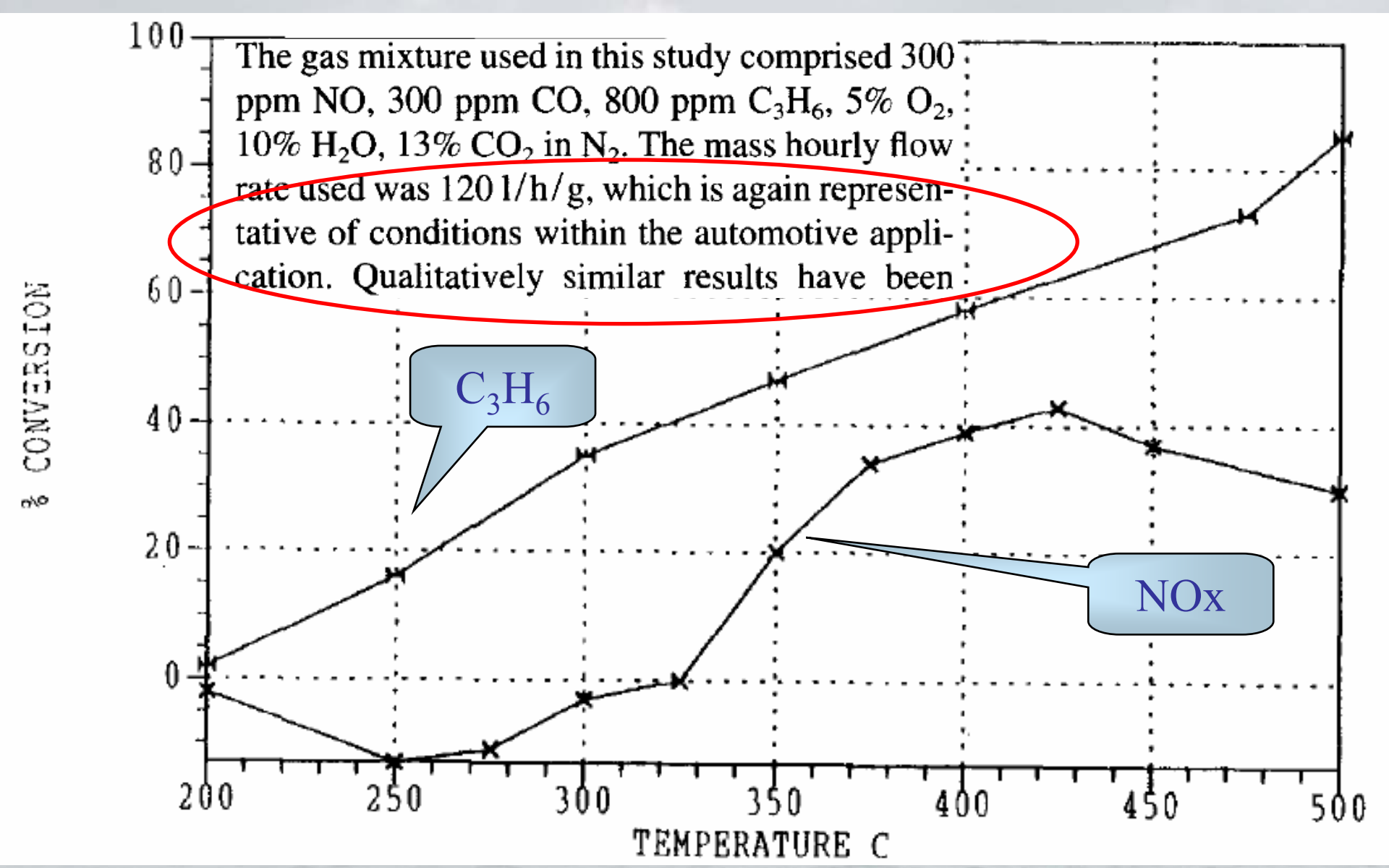


Fig. 1. The NO (X) and C_3H_6 (H) conversion profiles obtained over Cu/ZSM-5 during temperature programmed reaction under a realistic full gas mix. (For details of the conditions, see text). Taken from Ref. [5].

Cu-ZSM5 Observations

- NOx is reduced by HC
- Not by H_2 or CO
- CO is formed (also in HC+O_2)
- Oxygen concentration dependence
- Water concentration dependence
- Temperature dependence

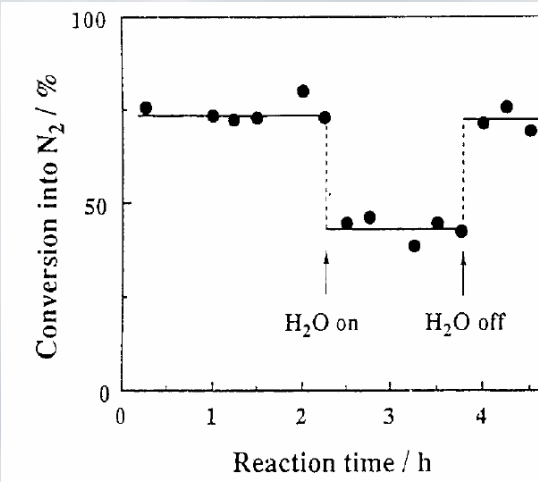


Fig. 3. Effect of the introduction of water vapour on the con of NO into N_2 over Cu/ZSM-5. ($W/F = 0.1$ g s cm^{-3}, te ture = 773 K, $P_{NO} = 600$ ppm, $P_{C_3H_6} = 940$ ppm, P_{O2} = $P_{SO_2} = 250$ ppm, $P_{H_2O} = 3.9\%$). Taken from Ref. [36].

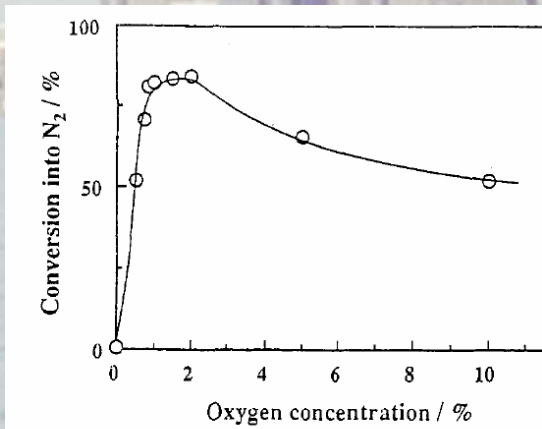


Fig. 2. The effect of oxygen concentration on the conversion o into N_2 over Cu/ZSM-5. ($W/F = 0.3$ g s cm^{-3}, temperature = K, $P_{NO} = 1000$ ppm, $P_{C_3H_6} = 1000$ ppm). Taken from Ref. [36

Mechanistic review Walker 1995

1. Redox: $NO \xrightarrow{\text{decomp. on Cu(I)}} N_2 + Cu(II)$
   $HC + Cu(II) \rightarrow Cu(I)$
2. Partial Ox:
   $HC+O \xrightarrow{Cu} HCO \ldots +NO \rightarrow CO_2 + N_2$
3. Organonitrogen species:
   $HC+NO \xrightarrow{Cu} HC\text{-}NOy \xrightarrow{decomp} N_2$
4. Bi-functional: $NO+O_2 \xrightarrow{Cu} NO_2$
   $NO_2+HC \xrightarrow{ZSM5} HCO$

Redox

- NO + Cu(I) → Cu-NO
- Cu-NO + NO → $Cu(NO)_2$
- $Cu(NO)_2$ → Cu(II) O + N_2O
- Cu(I) + N_2O → Cu(II) + N_2
- CuO + HC → Cu(I) + CO_2 + H_2O
- But why does H_2 and CO not produce N_2?
- Role of O_2 is to oxidise Cu(0) to Cu(I)

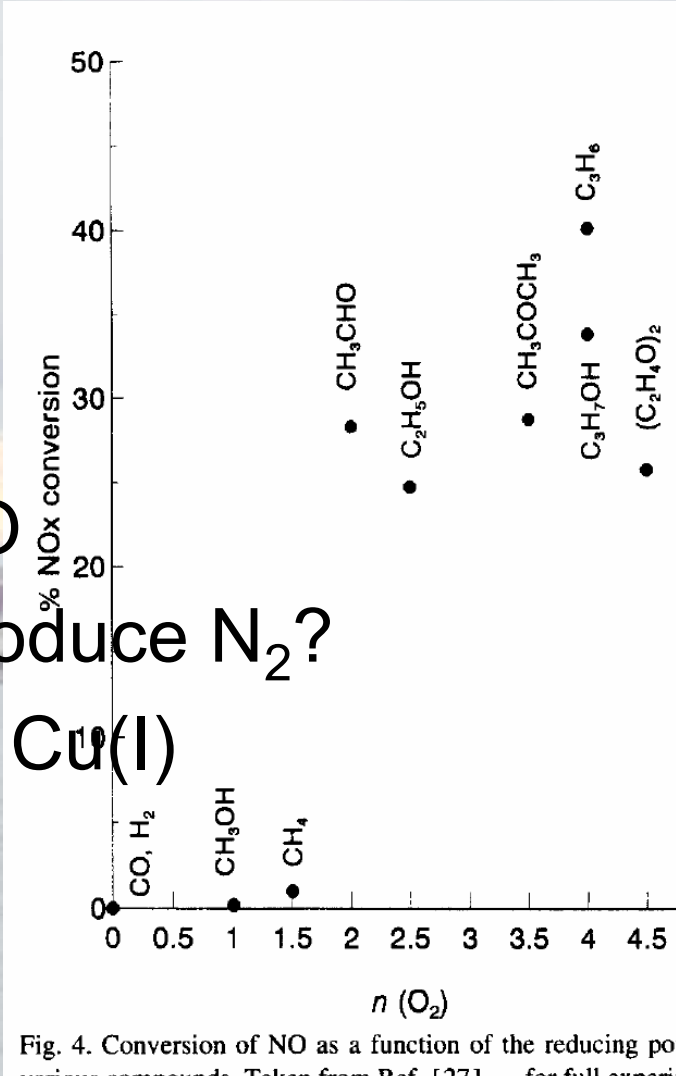


Fig. 4. Conversion of NO as a function of the reducing po
various compounds. Taken from Ref. [27] — for full experi
details see Ref. [6].

Partial oxidation

- Alcohols and aldehydes more active than corresponding alkanes
- Alkenes more active than alkanes
- Role of oxygen logical
- Partially oxidised HCs observed experimentally
- Not clear how N-N bond is formed

Organonitrogen species

- Isocyanate (NCO) species observed by IR
- Subsequent reaction with NO may generate N_2 + CO
- Alternatively a route to C_xH_y-NH_2 and + NOx → N_2 in conventional SCR

Bi-functional

- $NO + ½ O_2 + CuO \rightarrow NO_2 + Cu$
- $NO_2 + HC \rightarrow H_xC_yO_z$
- …?
- The overall activity for NO oxidation also picture overall N_2 formation
- Effect of water is also in line with NO oxidation
- Higher activity for NO_2 observed

Deactivation

- Grinsted et al. Zeolites 13(1993)602
  - Deactivation observed at 410C in the presence of water vapour
  - MASNMR concluded dealumination of tetrahedral sites
  - XRD showed no change in crystallinity
- Kharas et al. Appl. Catal. B. Environ. 2(1993)225
  - CuO formation and pore blocking

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Fuel Vol. 76, No. 6, pp. 507–515, 1997

Printed in Great Britain
0016-2361/97/$17.00 + 0.00

A review of NO_x reduction on zeolitic catalysts under diesel exhaust conditions

Patrick Gilot, Marc Guyon and Brian R. Stanmore*

Laboratoire Gestion des Risques et Environnement, Ecole Nationale Supérieure de Chimie de Mulhouse CNRS EP082, 25 rue de Chemnitz, 68200 Mulhouse, France

** Department of Chemical Engineering, University of Queensland, Q 4072, Australia*

(Received November 1995; revised 15 August 1996)

omponent

Table 1 Maximum reduction of NO by Cu-ZSM-5 catalysts

Reductant	Reductant concn. (ppmv)	NO (ppmv)	O_2 (vol.%)	Space velocity (h^{-1})	Temp. of maximum (°C)	Maximum conv. to N_2 (%)
Propene	500	1000	2	10 000	300	57
Diesel exh.	250	1000	10	20 000	400	28
Propene	700	250	5	20 000	400	30
Propene	2500	250	5	20 000	400	50
Ethylene	250	1000	2	15 000	250	40
Propene	1900	670	4	30 000	430	58

[a] Catalyst in powder form
[b] Catalyst wash-coated

LeaNOx reduction occur for all sorts of hydrocarbons but activation energy seems differs a lot!

Topics in Catalysis Vol. 28, Nos. 1–4, April 2004 (© 2004)

Reaction mechanisms of lean-burn hydrocarbon SCR over zeolite catalysts

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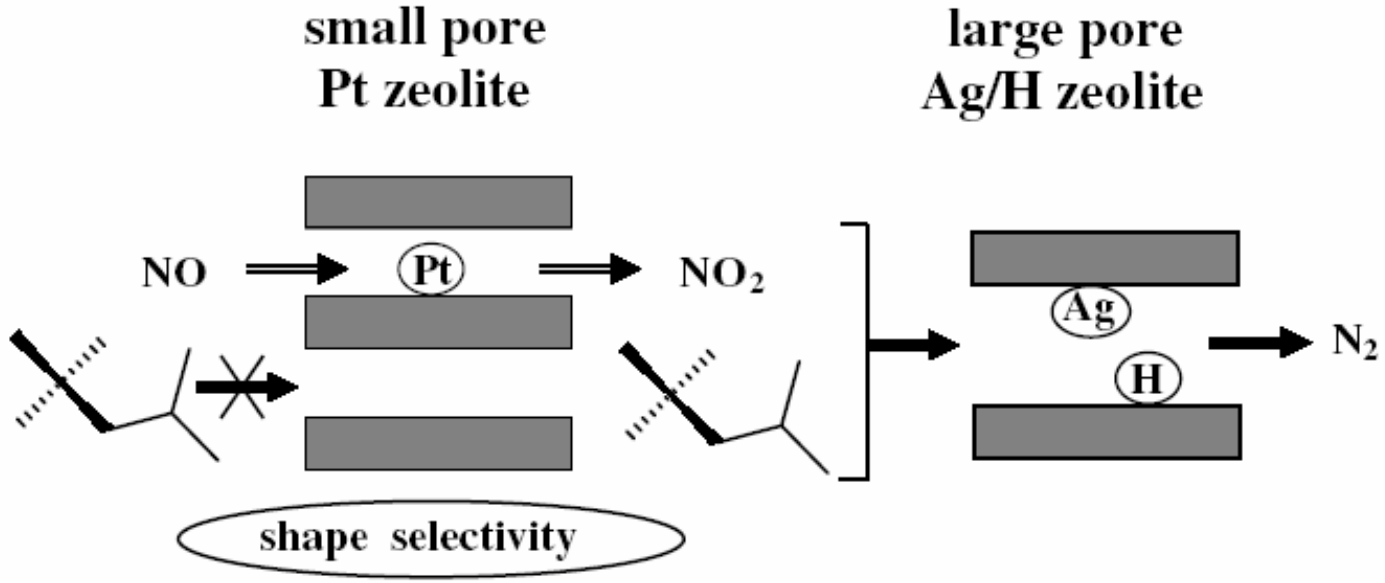

Figure 10. Dual pore concept for hydrocarbon SCR involving oxidation in small pores and reduction in large pores.

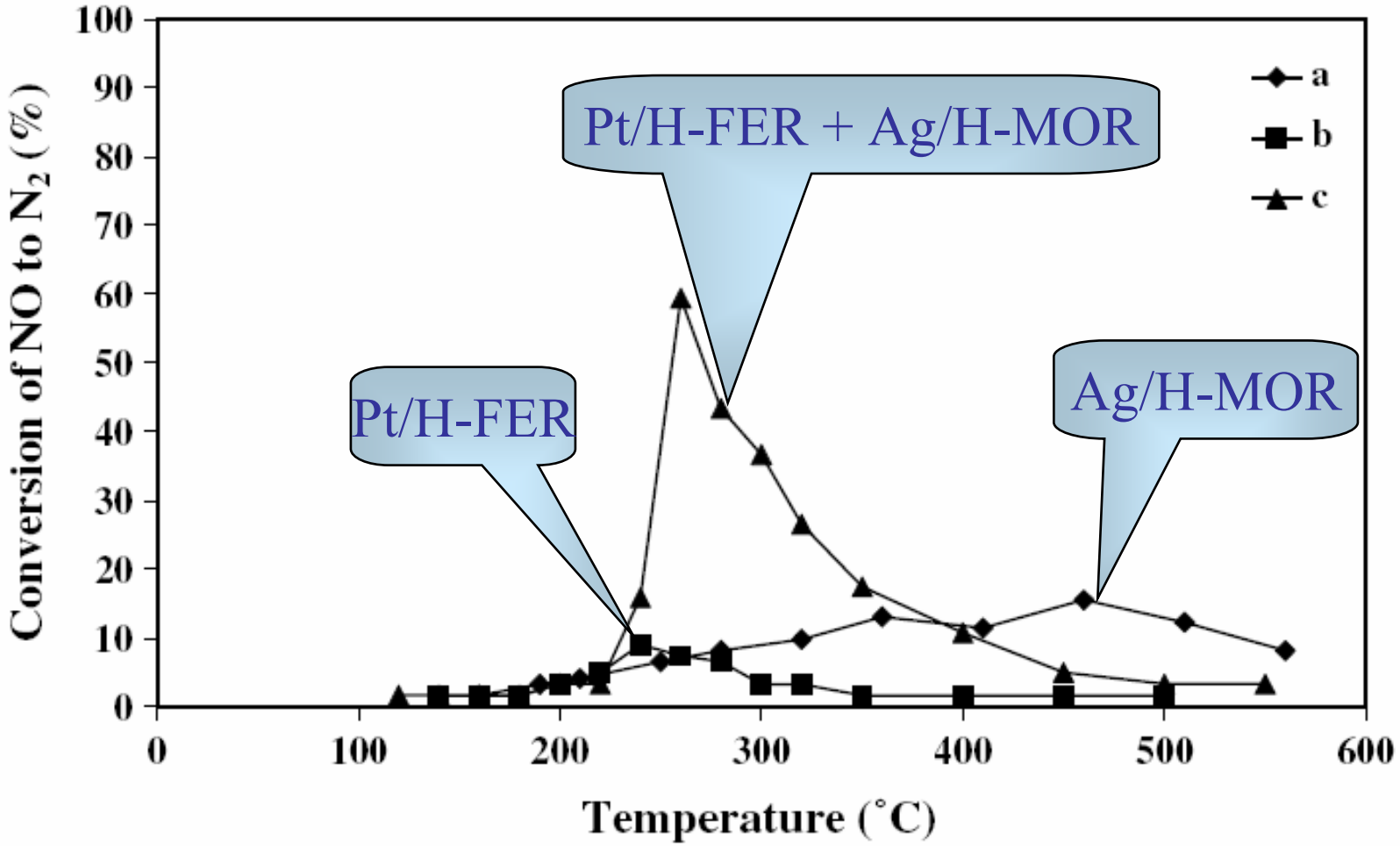

Figure 11. Nitrogen formation in *iso*-octane-SCR experiments over Ag/H-MOR (a), Pt/H-FER (b) and mechanically mixed Pt/H-FER and Ag/H-MOR (c) catalysts. Gas composition: 500 ppm NO_2, 350 ppm *iso*-octane, 6% O_2, 12% H_2O, 10% CO_2, 350 ppm CO in He at GHSV: 60,000 h^{-1}.

Support for ”Bi-functional” theory

- $NO + O_{2\ TM} \rightarrow NO_2$
- $CxHyNO_2$ or HCN or CNO → $CxHyNH_2$
- $CxHyNH_2$ + HNO2 → $CxHyNN^+$

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Study on metal-MFI/cordierite as promising catalysts for selective catalytic reduction of nitric oxide by propane in excess oxygen

Landong Li [a], Jixin Chen [a], Shujuan Zhang [a], Naijia Guan [a,*], Manfred Richter [b], Reinhard Eckelt [b], Rolf Fricke [b]

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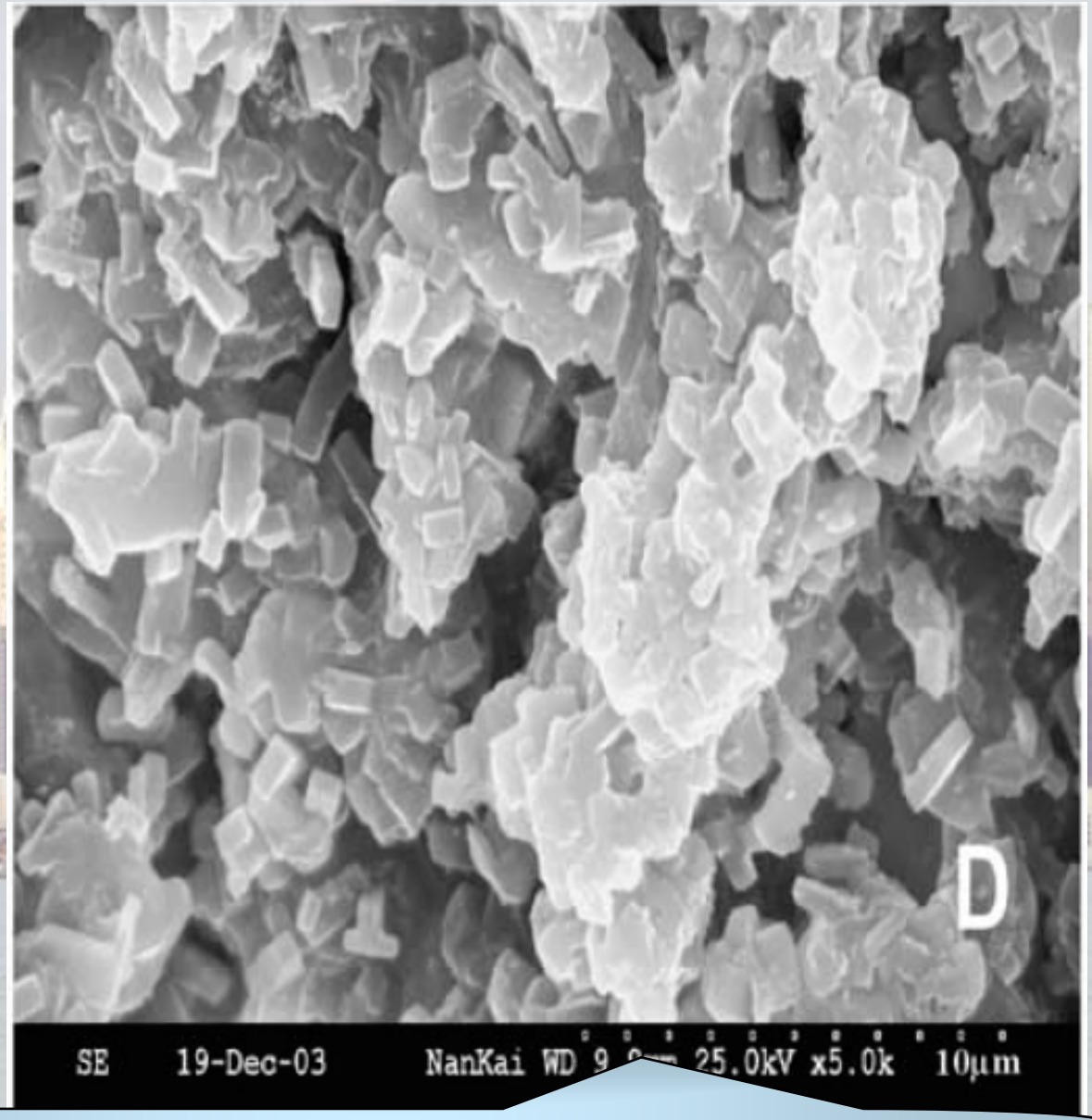
[b] *Institute for Applied Chemistry, Berlin-Adlershof, D-12489 Berlin, Germany*

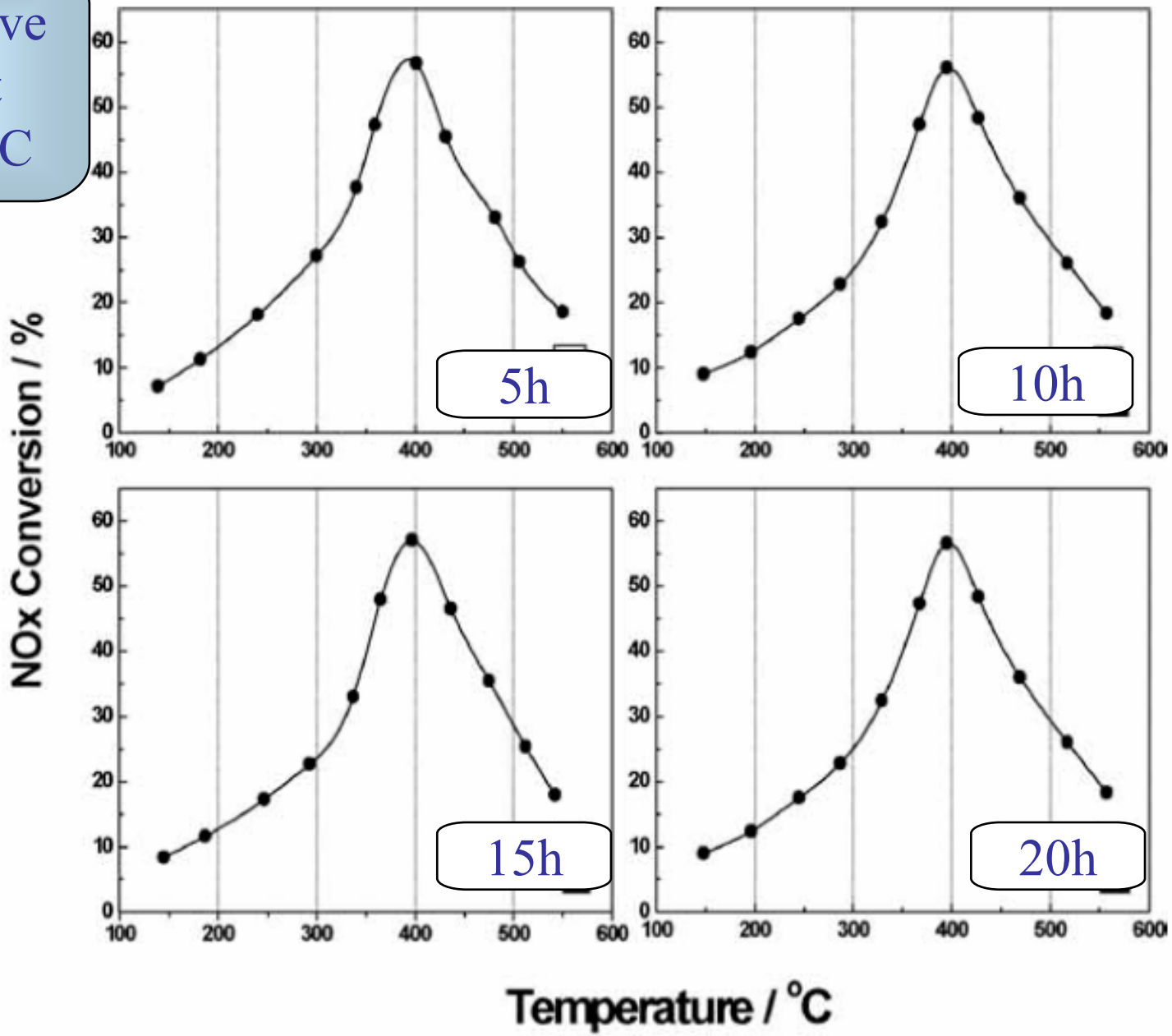
Received 19 May 2004; revised 2 August 2004; accepted 12 August 2004

Available online 22 September 2004



Cu-ZSM5 grown on Corderite monolith

Automotive exhaust 250-550C



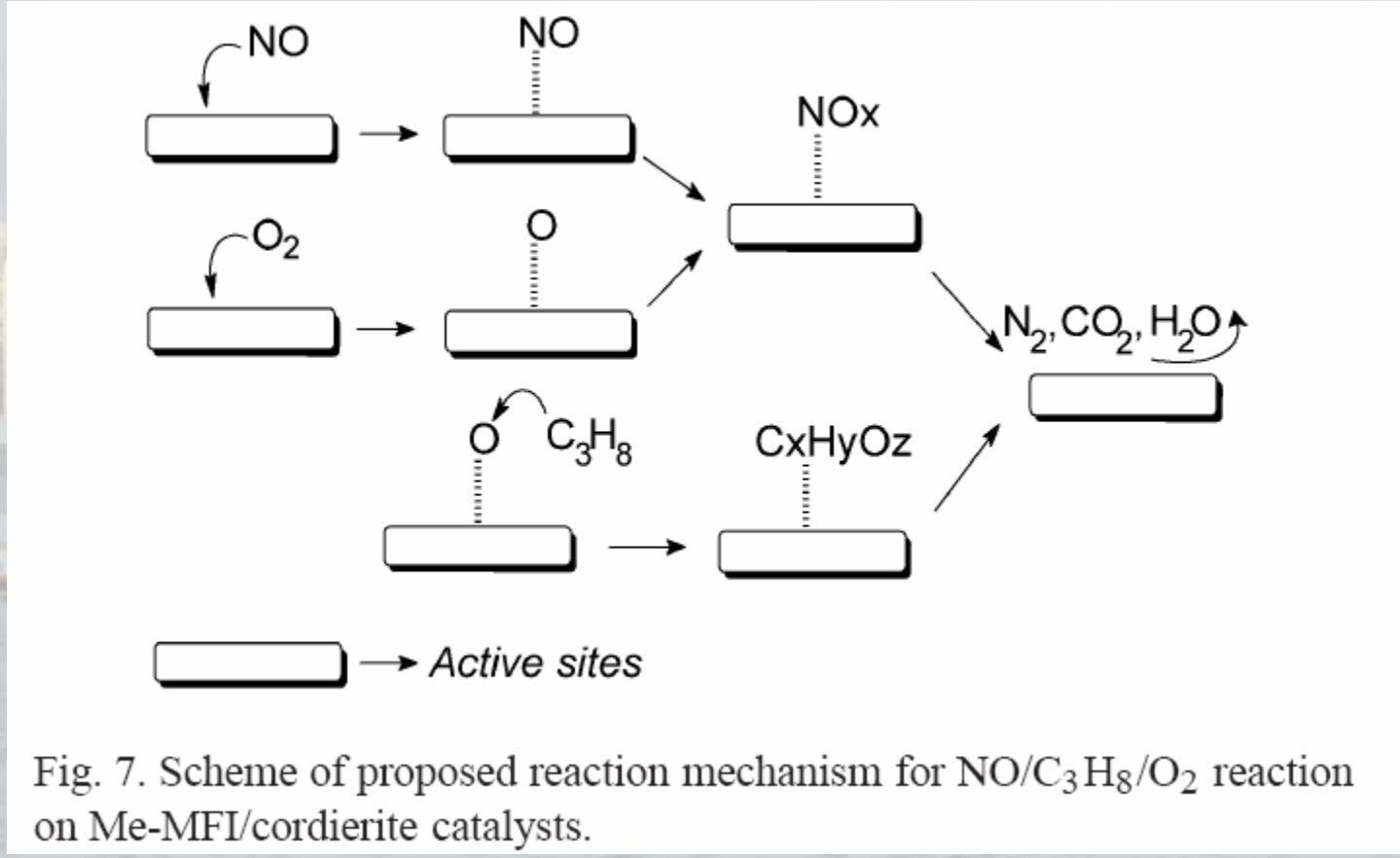


Fig. 7. Scheme of proposed reaction mechanism for $NO/C_3H_8/O_2$ reaction on Me-MFI/cordierite catalysts.

Factors that influence the activity

1. Adsorption ability of the active metal component toward gaseous reactants.
2. Oxidative activity of the active metal components.
3. Brønsted acidities of the supports.
4. Oxidative activities of the supports.

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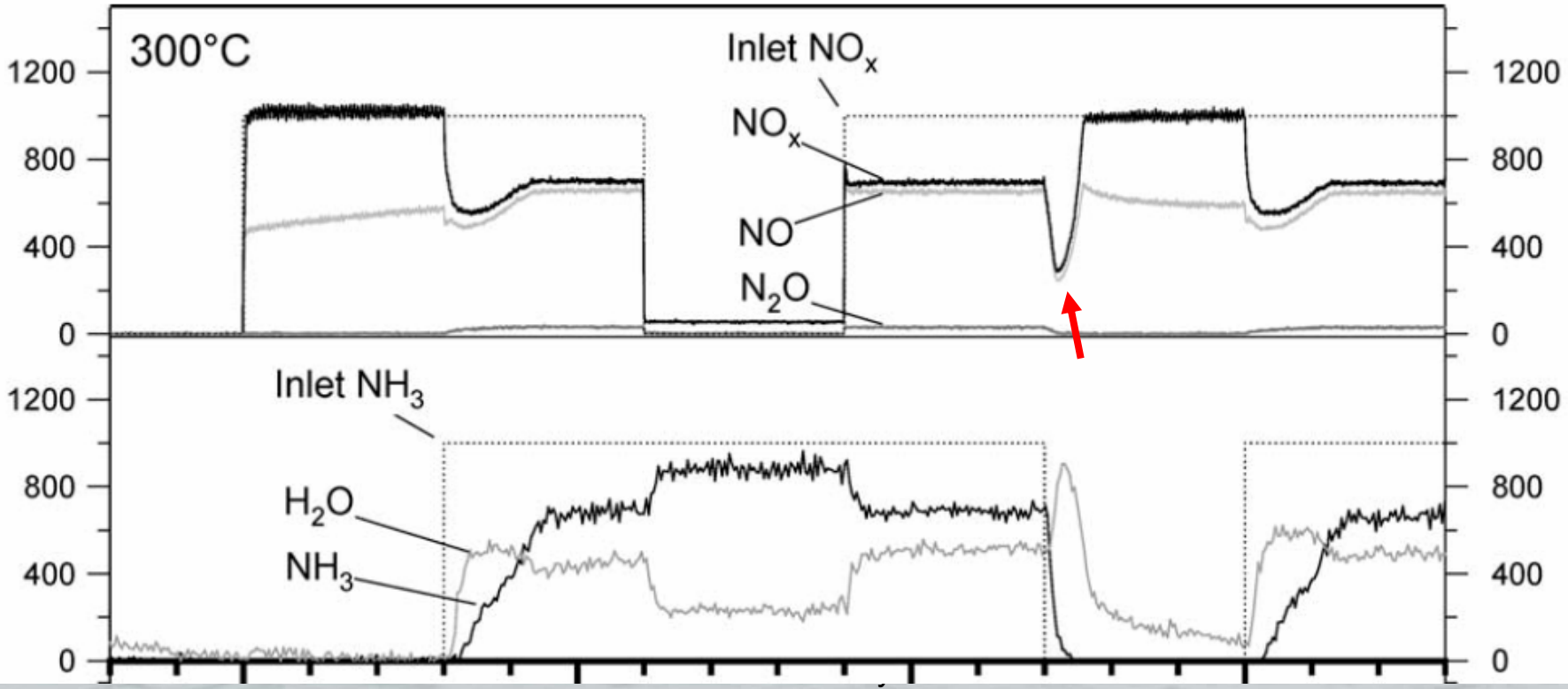
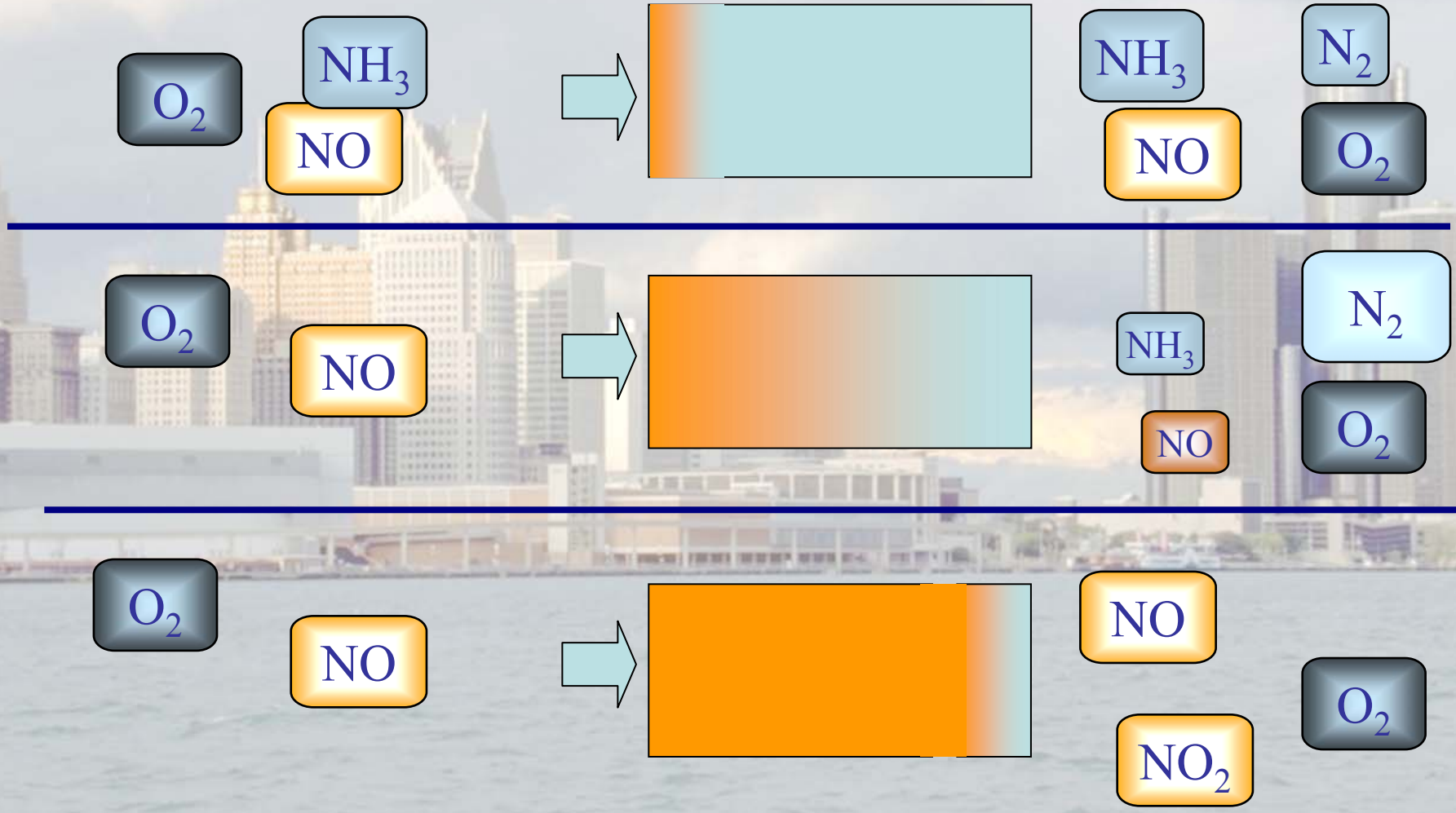
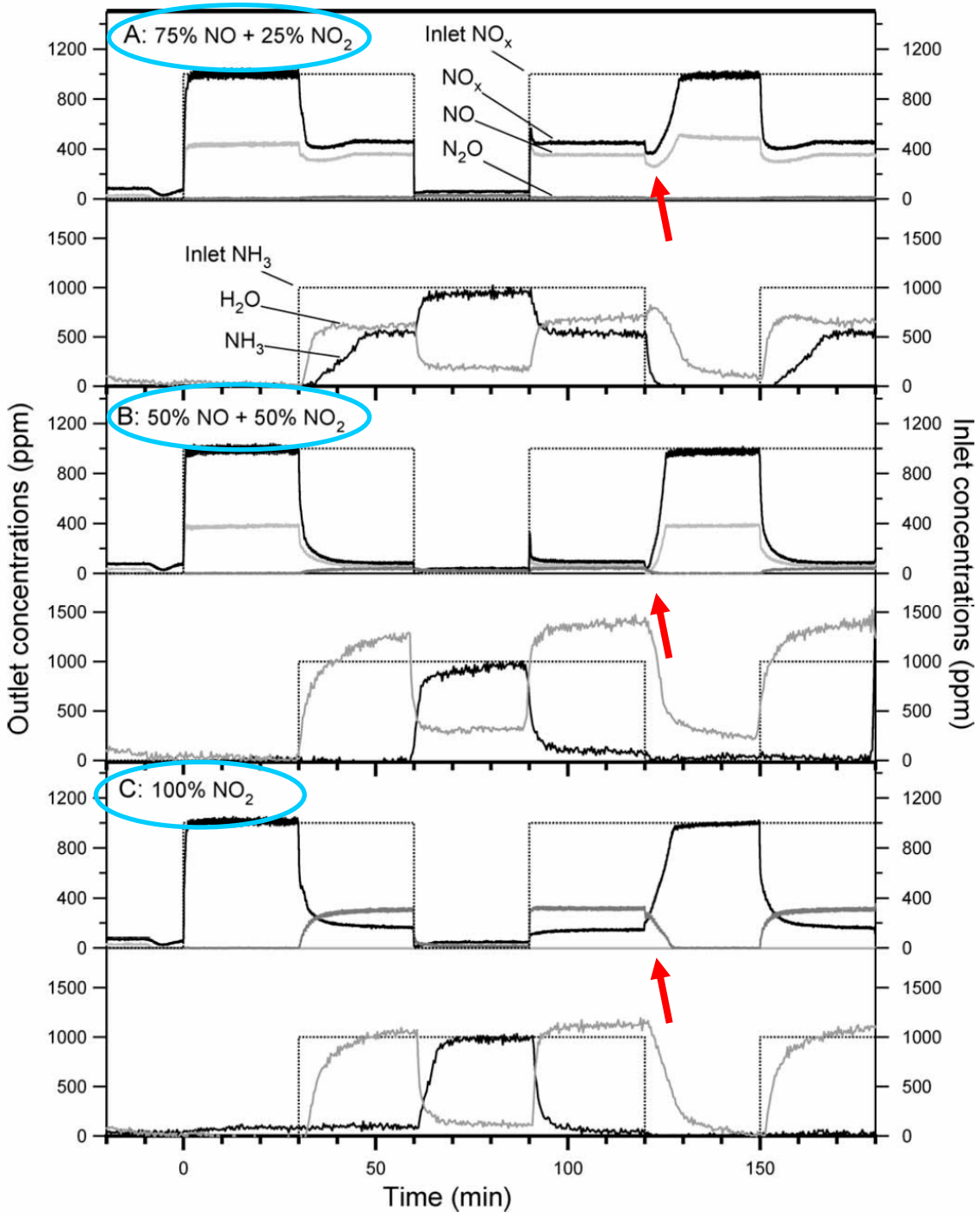
Selective catalytic reduction of NO_x with NH_3 over zeolite H–ZSM-5: influence of transient ammonia supply

Mikaela Wallin,[a,b,*] Carl-Johan Karlsson,[a,b,1] Magnus Skoglundh,[a,b] and Anders Palmqvist [a,b,c]




O_2
NH_3
NO
NH_3
N_2
NO
O_2
O_2
NO
NH_3
N_2
NO
O_2
O_2
NO
NO
O_2
NO_2



Volvo Technol

Cu-ZSM-5 zeolite highly active in reduction of NO with decane. Effect of zeolite structural parameters on the catalyst performance

L. Čapek[a], J. Dědeček[a], B. Wichterlová[a*], L. Cider[b], E. Jobson[b] and V. Tokarová[c]

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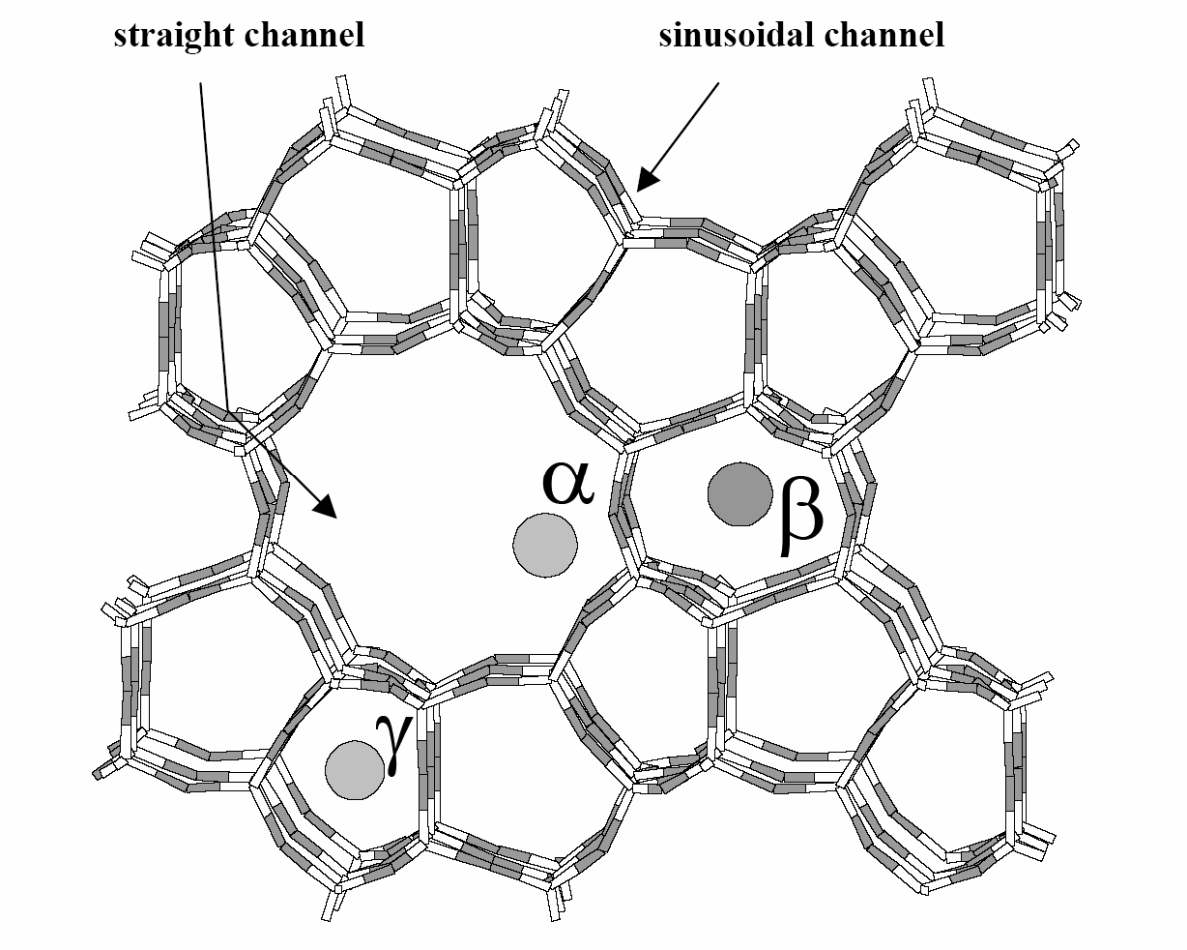
[c]*Research Institute of Inorganic Chemistry, Unipetrol, CZ-400 01 Ústí nad Labem*

Expected to be published in Applied Catalysis B Environmental


straight channel
sinusoidal channel
α
β
γ

- It has been shown that Cu-ZSM-5 zeolites with optimum Cu/Al around 0.5-0.6 and Cu ions located preferably at cationic sites exhibit high and stable in time activity in $C_{10}H_{22}$-SCR-NOx under high concentration of water vapor (12 %) corresponding to its content in real exhaust gases of diesel engines.
- Cu ions located in vicinity of two Al atoms ("Al pairs") localized in the framework rings and forming cationic sites for divalent cations are suggested to be the active sites in $C_{10}H_{22}$-SCRNOx under water vapor presence.
- **Thus, the Cu-ZSM-5 activity is actually controlled by the concentration of "Al pairs" in the framework governed by the content and distribution of aluminium in the framework.**
- **Most of the Cu ions are located in the β-type site at the intersection of the main and sinusoidal channel of ZSM-5 structure.**
- It is to be pointed out that such high and stable activity can be reached by using only hydrocarbon reductant with olefinic character or long-chain paraffin, which in the first step cracks to a spectrum of olefins and paraffins (see Ref. [9]).

NOx reduction by Cu-MFI
Where we stand today…

- Several routs to N_2 production confirmed
- ”bi-functional” rout to N_2 formation is relatively fast
  - NO oxidation to NO_2
    - Possibly both for the nitrogen pairing and →
  - Partial oxidation of HC → R-CNO
- Ion exchanged Cu at Al pairs are among the most active sites
- Acid sites are essential for the nitrogen pairing
- Zeolite – HC combination important

Some recent results

- Progress in low temperature activity
- Progress in hydrothermal stability

Future challenges

1. Lean NOx reduction
   -Scientific & Industrial importance
2. Resistance for sulphur for extended time
3. Hydrothermal stability
4. Catalyst activity for real fuel hydrocarbons
5. Activity in a broad temperature window
6. Low sensitivity to poisoning by lubrication oil additives

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