FHI, Berlin, January 27th, 2017

Lecture Series
Heterogeneous Catalysis

In-Situ Differential Scanning Calorimetry in the Studies of Oxide Catalysts and Mechanisms in Oxidative Heterogeneous Catalysis

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Outline

1. Introduction:
    - energy factor in chemical processes
    - Chemical Thermodynamics vs. Thermochemistry
    - particularity of ‘reaction independence’ principle in heterogeneous catalysis
2. Calorimetric measurements: methods and instruments
3. Signal treatment
4. Case studies
5. Summary & Concluding Remark

Introduction: Energy in Chemistry

Energy Factor:

- intrinsic reactivity
- interaction with environment

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Reactivity:

- thermodynamic aspect (Free Energy – 'driving force', feasibility)
- kinetic aspect (Activation Energy – 'barrier on reaction coordinate')

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Interaction with environment:

- external parameters ('conditions')
- subject to change

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- external parameters (‘conditions’)
- subject to change

⇒ feedback

Introduction: Chemical Thermodynamics *vs.* Thermochemistry

Chemical Thermodynamics –

the study (branch of Physical Chemistry) of interrelations between heat and work in relation to chemical systems, i.e. to substances and their chemical transformations and changes of physical state (e.g., phase transitions)

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Key parameters: enthalpy of formation/transformation (reaction, phase transition), heat capacity

Introduction: Chemical Thermodynamics and Catalysis

Friedrich Wilhelm Ostwald
(1853-1932)

Catalyst does not affect the chemical equilibrium, but only changes (e.g. accelerates) the rate(s) of thermodynamically feasible reaction(s)

Introduction: ‘reaction independence’ and heterogeneous catalysis

Friedrich Wilhelm Ostwald
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Independence of Reactions Principle –

the applicability of the main postulate of chemical kinetics (Mass Action Law) to a particular reaction does not depend on the occurrence of other reactions in the system

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Homogeneous reactions in gas – YES!

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Heterogeneous catalysis – NO:

- non-uniformity (irregularity) of surfaces and ad-layers
- non-stoichiometry of solids and their dynamic character

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In heterogeneous catalysis we cannot rely on ‘tabular’ values of thermodynamic characteristics

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⇓

CALORIMETRY

Calorimetric measurements: methods and instruments

Calorimetry –

experimental methods for measuring thermal effects (heat evolution and consumption) accompanying the processes of various types (chemical, physical, biological) and based on different physical principles

Calorimetric measurements: methods and instruments

Adiabatic Calorimetry

Calorimetric measurements: methods and instruments

Adiabatic Calorimetry –

in a system that is thermally isolated from the environment (no external heat exchange) called *adiabatic*

$$\Delta T = Q/C,$$

where ΔT – temperature change;
Q – heat evolved (consumed);
C – heat capacity

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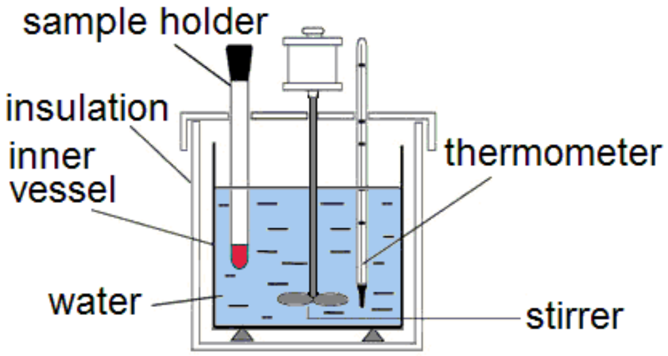

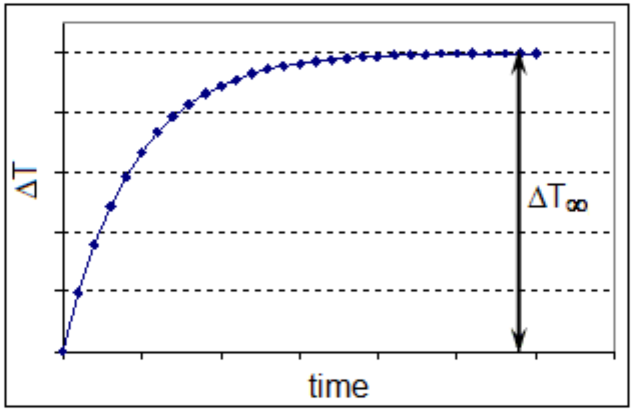

$$Q = C\,\Delta T_\infty$$

Calorimetric measurements: methods and instruments

Adiabatic Calorimetry –

- high precision (ΔH_f, C_P, etc.);
- limited T range;
- long-lasting measurements / low productivity;
- low temporal resolution

Calorimetric measurements: methods and instruments

Differential Scanning Calorimetry (DSC)

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experimental methods for measuring thermal effects (heat evolution and consumption)

- in extended range of temperatures;
- with improved productivity;
- with higher temporal resolution

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Differential Scanning Calorimetry (DSC) –

scheme of measurements
(permanently compared to reference)

Calorimetric measurements: methods and instruments

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experimental methods for measuring thermal effects (heat evolution and consumption)

- in extended range of temperatures;
- with improved productivity;
- with higher temporal resolution

Differential Scanning Calorimetry (DSC) –

measurements at varied (programmed) temperature (permanently and/or stepwise)

Calorimetric measurements: methods and instruments

Differential Scanning Calorimetry (DSC) –

experimental methods for measuring thermal effects (heat evolution and consumption)

- in extended range of temperatures;
- with improved productivity;
- with higher temporal resolution

Differential Scanning Calorimetry (DSC) –

‘near-calorimetric’ (although reduced) precision (typically, 1-2% of measured thermal value) – as a rule, satisfactory for a wide range of applications

Calorimetric measurements: methods and instruments

Differential Scanning Calorimetry (DSC) –

experimental methods for measuring thermal effects (heat evolution and consumption)

- in extended range of temperatures;
- with improved productivity;
- with higher temporal resolution

based on different technical principles and schemes

but fundamentally – on the same physical background:
heat transfer and balance

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heat transfer and balance

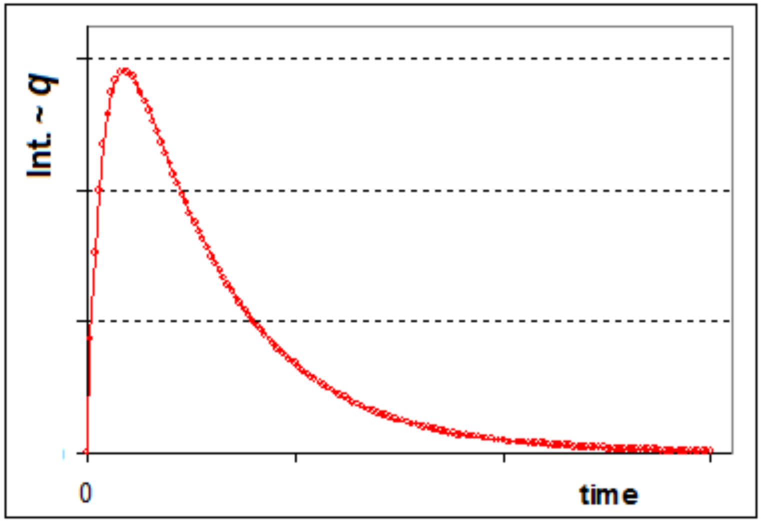
$q = k\Delta T + C(dT/dt)$ – *Tian equation*
(heat removal & storage)

Calorimetric measurements: methods and instruments

Differential Scanning Calorimetry (DSC) –

experimental methods for measuring thermal effects (heat evolution and consumption), based on different technical principles and schemes, but on the same physical principles of heat transfer and balance

$q = k\Delta T + C(dT/dt)$ – *heat removal and stortage*



$$Q = \int_0^\infty q\,dt$$

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

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DSC: different technical principles and schemes

1. ‘Quantitative TA’

TA – *thermal analysis, i.e. measurement of*
ΔT between the sample and the reference
(usually, in a T-programmed regime)

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

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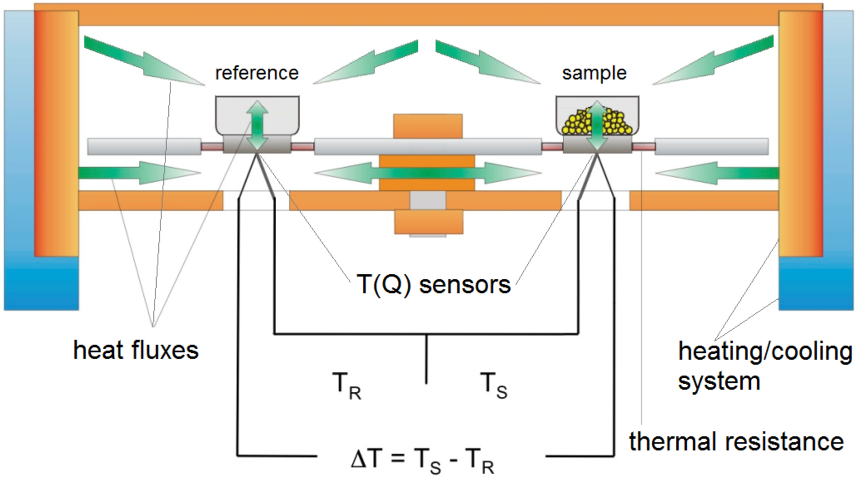

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DSC: different technical principles and schemes

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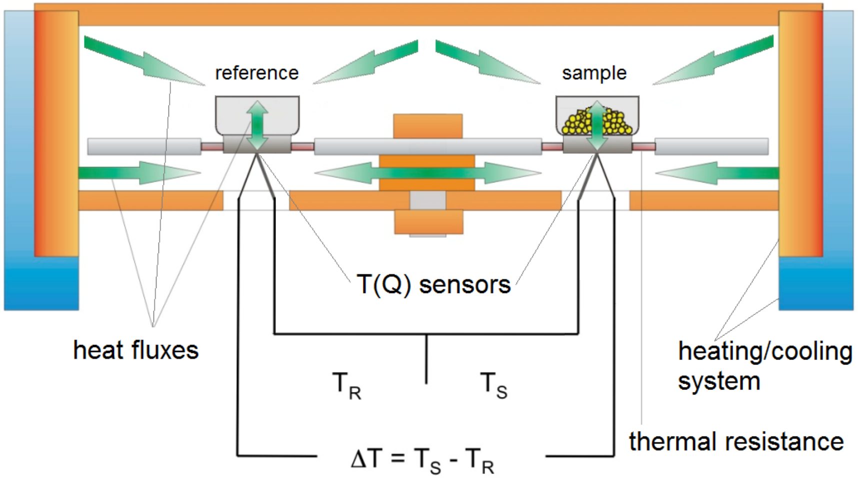


Calorimetric measurements: methods and instruments

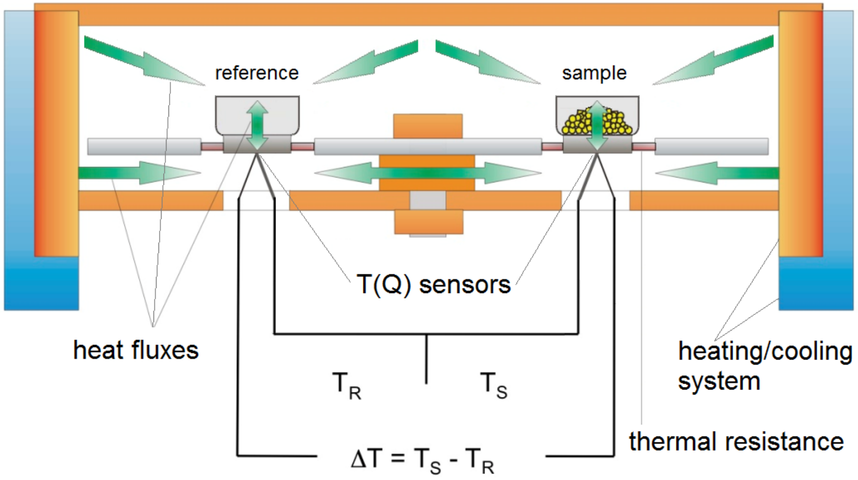
DSC: different technical principles and schemes

1. ‘Quantitative TA’

    – multiple sensors

    – tight contact between sensors and holders

    – rapid heat removal from the sample



Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

1. ‘Quantitative TA’

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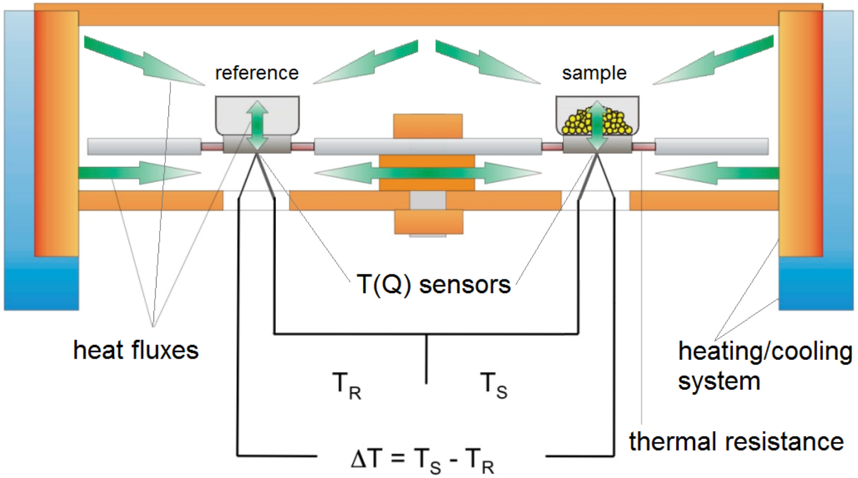
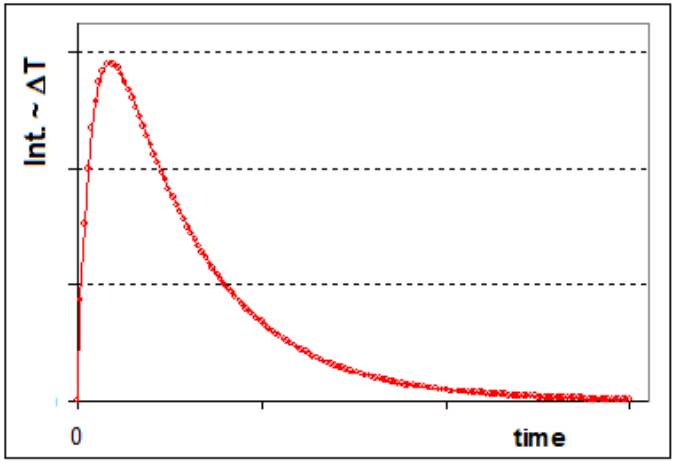
$C(dT/dt) \approx 0$ *and*

$q \approx k\Delta T$





$$Q \approx \int_0^{\infty} \Delta T dt$$

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

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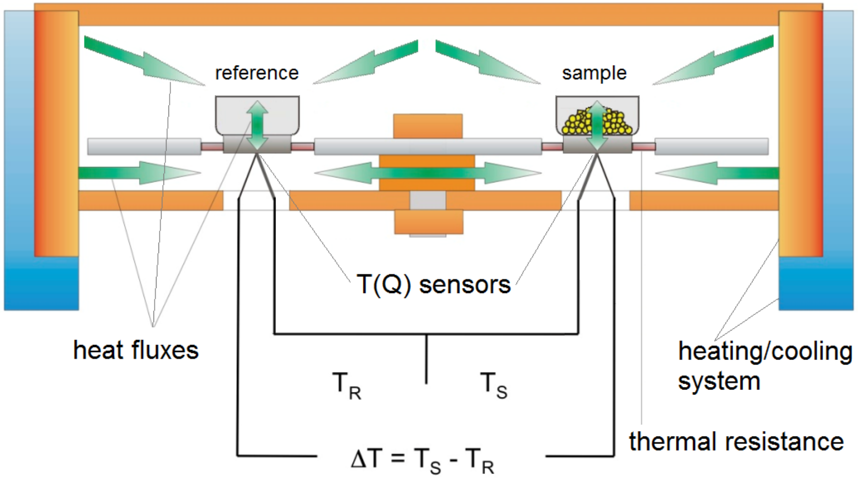


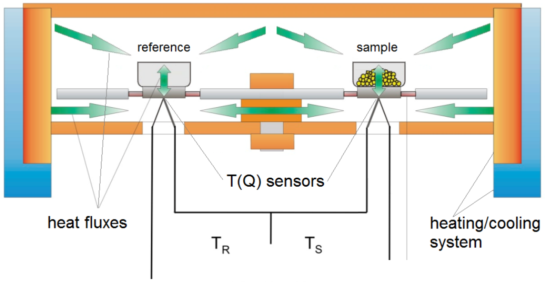
- relatively simple design;
- wide range of T’s;
- compatible with other methods (e.g. TG)

- calibration is critical and can vary from sample to sample;
- gas-solid diffusion

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

1. ‘Quantitative TA’



Calorimetric measurements: methods and instruments

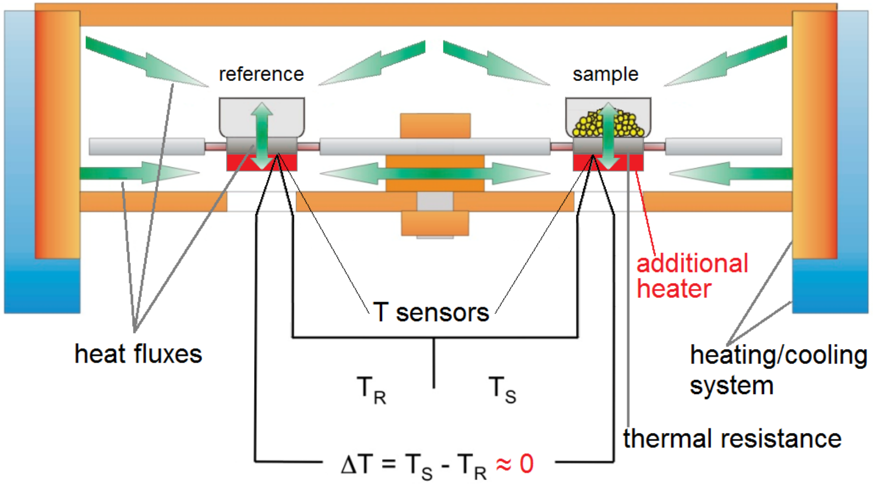
DSC: different technical principles and schemes

2. ‘Zero ΔT’ or ‘heat-compensation’ DSC

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

2. ‘Zero ΔT’ or ‘heat-compensation’ DSC
   - – precise T-sensor + fast feed-back control + thermal compensation (Joule or combined Joule-Peltier elements, i.e. thermoelectric heaters or heater/cooler)
   - – measured parameter – electric power required to compensate thermal effects in the sample



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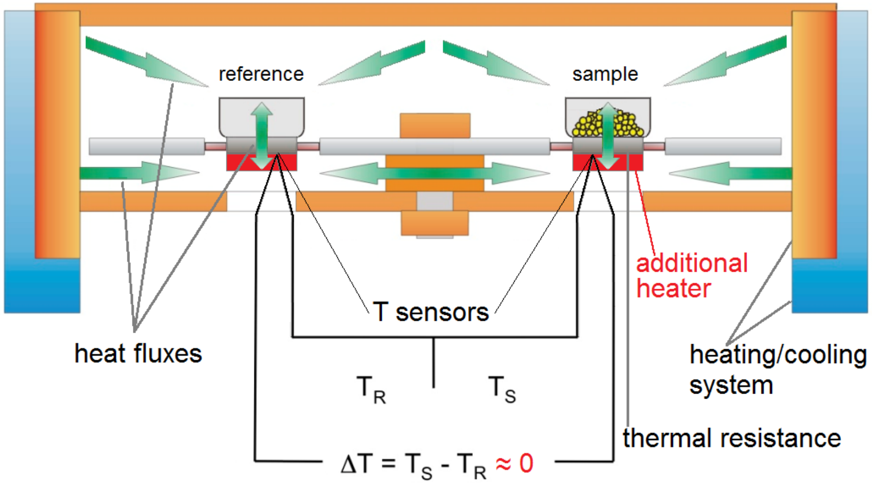

- direct measurement of power;
- precise measurements of T

- calibration is critical and can vary from sample to sample (2D T sensing);
- gas-solid diffusion

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

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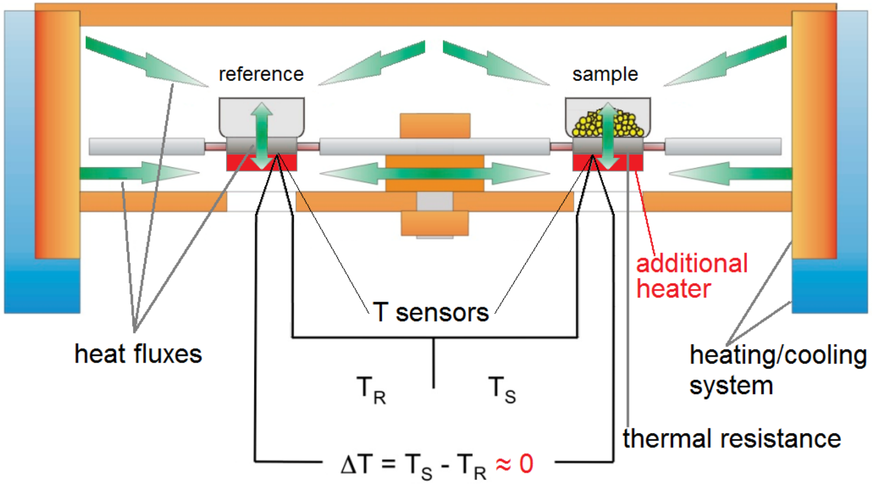

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

3. ‘Heat-flux’, or ‘heat-conductive’, or Calvet-type DSC
   - heat flux is measured outside of the sample assuming that it is proportional to the ΔT on different distances from it

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DSC: different technical principles and schemes

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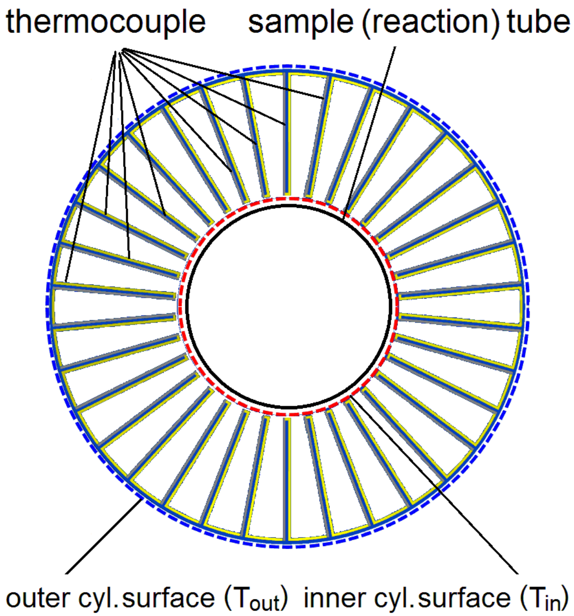
Calvet sensor (top view)



$q \sim (T_{in} - T_{out})$

Calvet calorimetry (incl. DSC):

- none of the TC’s measures the temperature of the sample (!!!);
- the DSC signal is formed as ΔT between two cylindrical surfaces (inner and outer) on different distances from the sample

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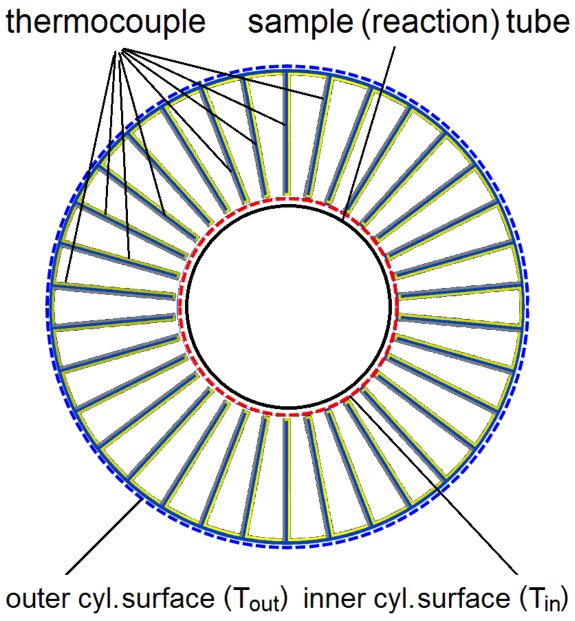
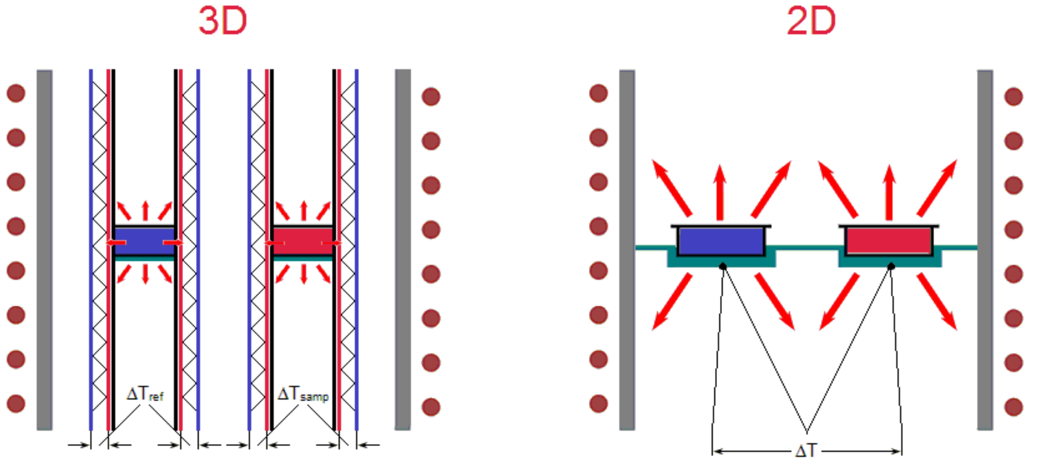


$q \sim (T_{in} - T_{out})$

Side view: Calvet (3D) vs. TA (2D) sensing



$q^{3D}_{diff} \sim (\Delta T_{samp} - \Delta T_{ref})$

$q^{2D}_{diff} \sim \Delta T$

3D vs. 2D sensing: more efficient (complete) capturing of heat fluxes from/to the sample – lower sensitivity to the sample properties !!!

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

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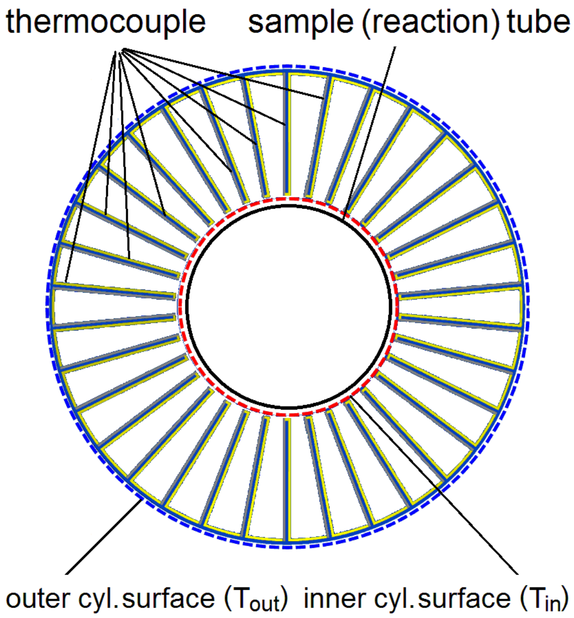

$q \sim (T_{in} - T_{out})$

– fool realization of the potential of *Newton-Richmann law* and *Tian equation*;

– the sample does not play the role of ‘thermal resistance’;

– no tight contact between sample (and reference) holder(s) and the sensor is required;

– 3D heat sensing;

– good gas-solid mass-transfer conditions;

– high compatibility (e.g. with TGA)

– relatively low temporal resolution

Calorimetric measurements: methods and instruments

DSC: different technical principles and schemes

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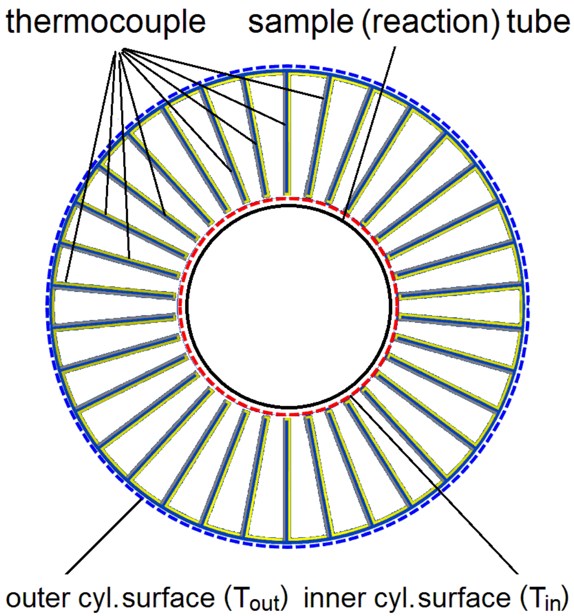

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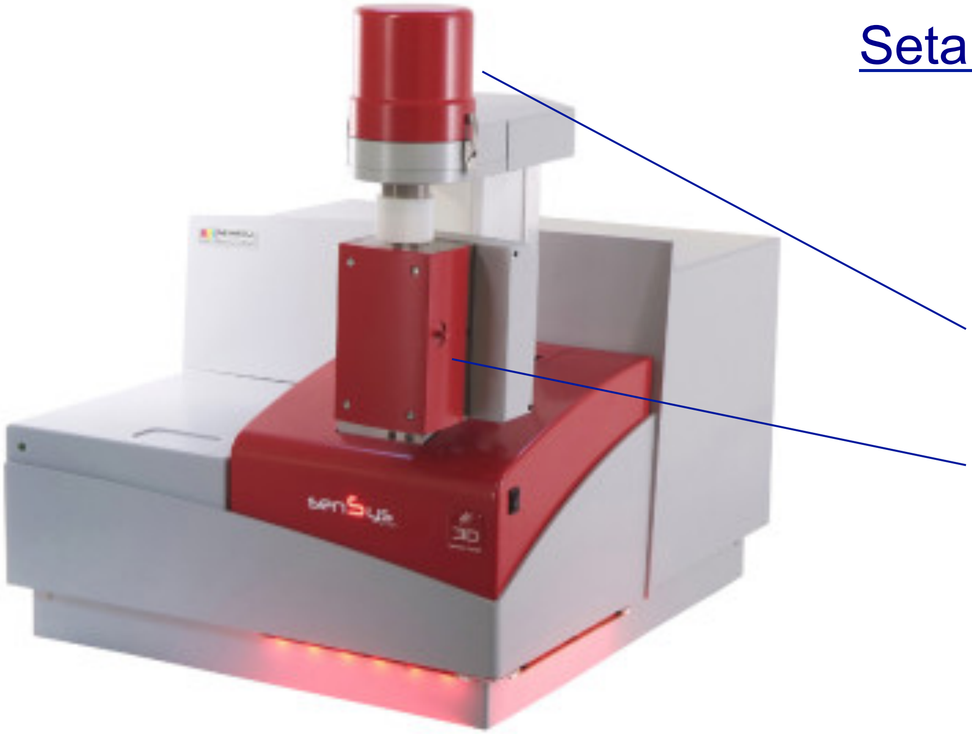

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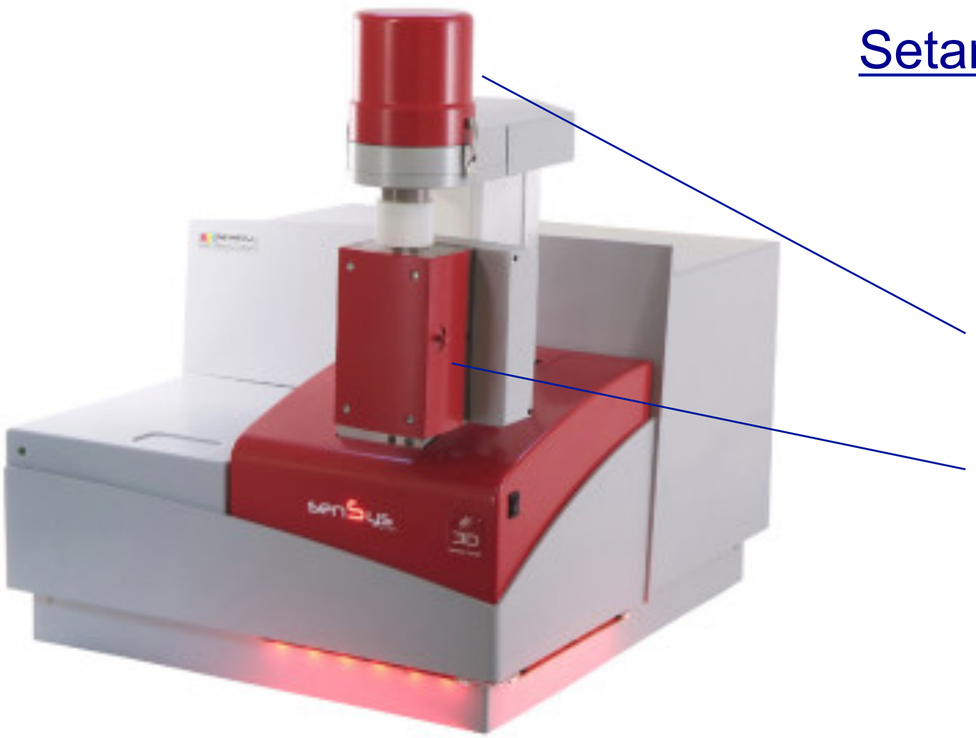


Setaram SENSYS evo TG-DSC

balance (TGA-unit)

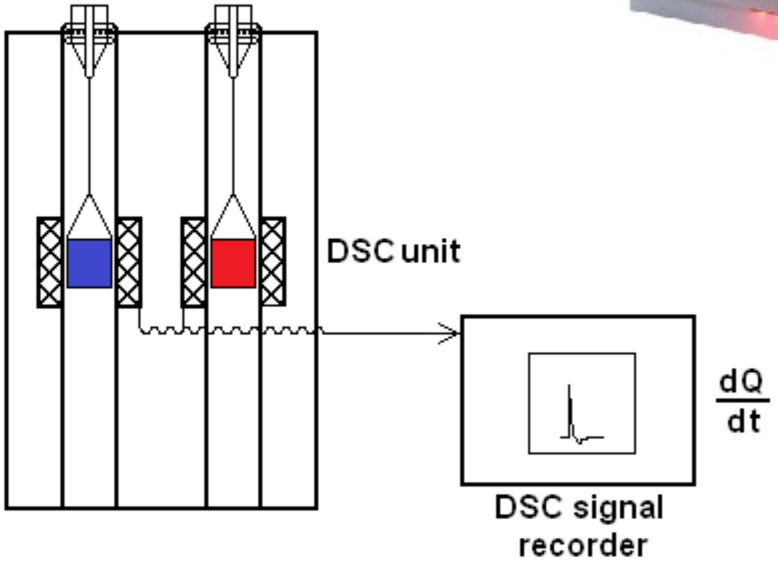
DSC unit (DSC-111)

Calorimetric measurements: methods and instruments

Setaram SENSYS evo (DSC-111)

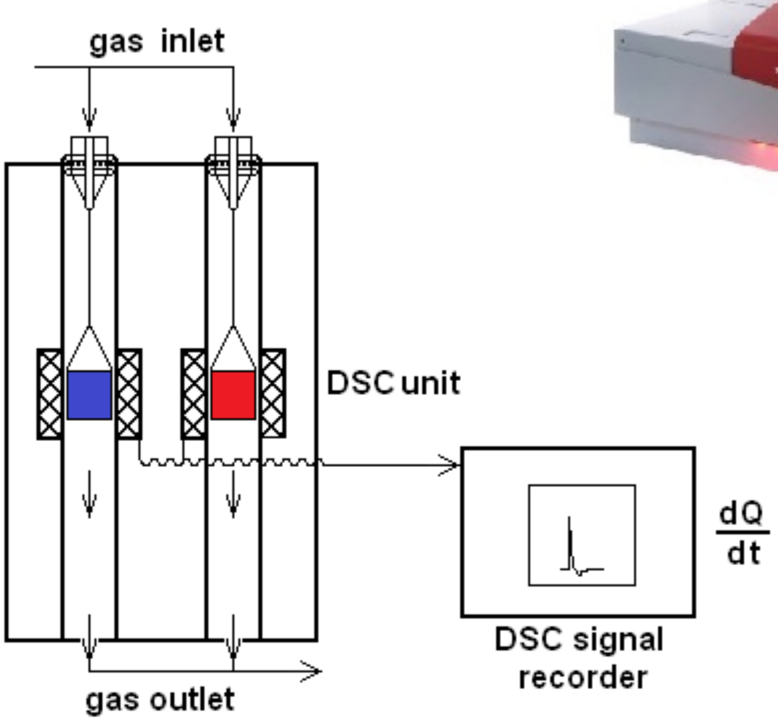
Calorimetric measurements: methods and instruments

Setaram DSC-111



Calorimetric measurements: methods and instruments

Setaram DSC-111



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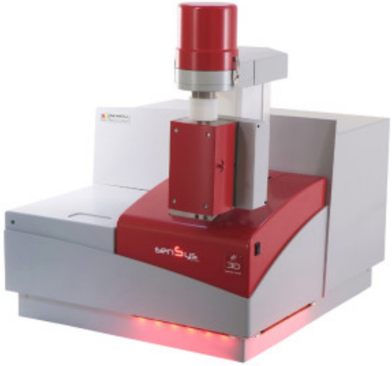
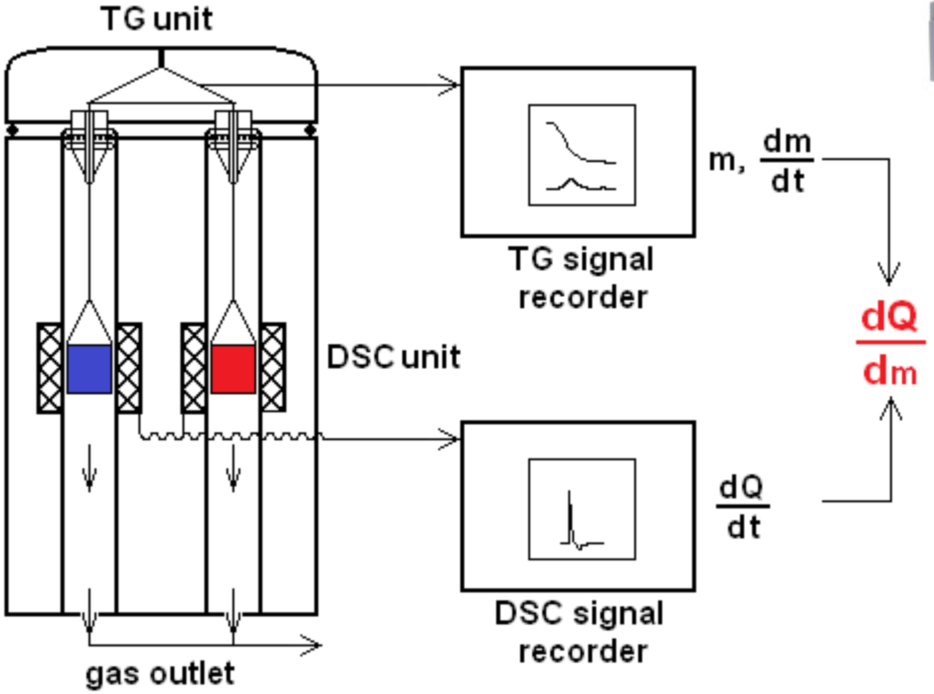


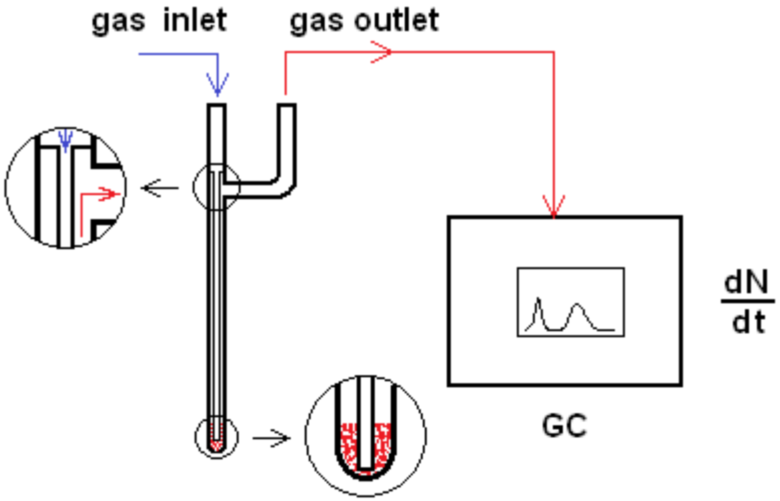


Calorimetric measurements: methods and instruments

Setaram DSC-111 for heterogeneous catalysis

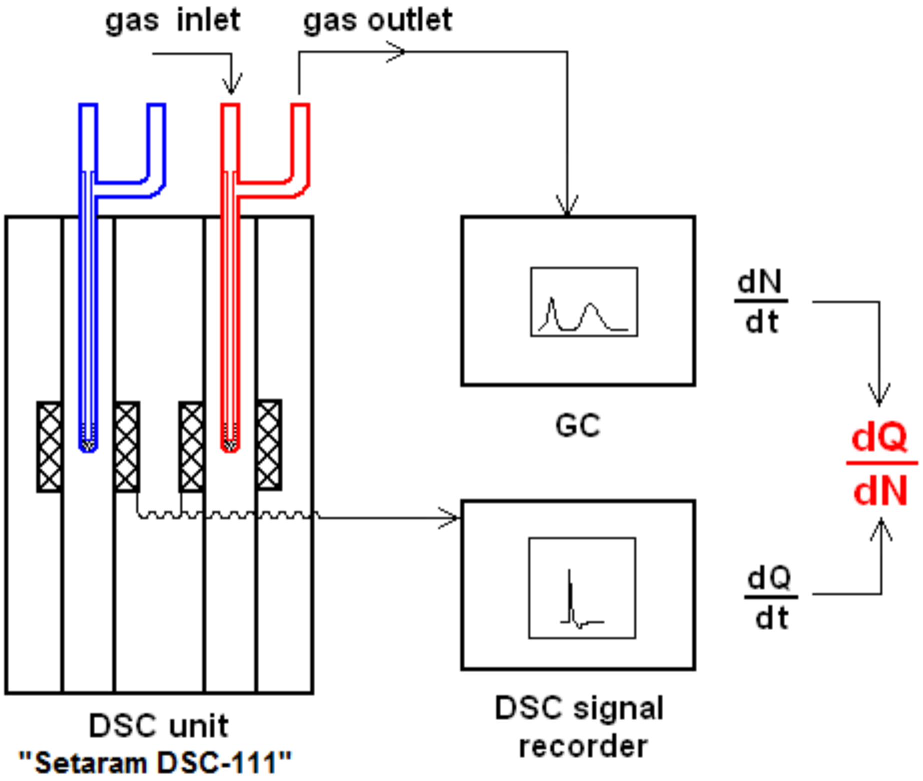
Calorimetric measurements: methods and instruments

Setaram DSC-111 for heterogeneous catalysis – *in situ* cell



Calorimetric measurements: methods and instruments

Setaram DSC-111 for heterogeneous catalysis – *in situ* DSC



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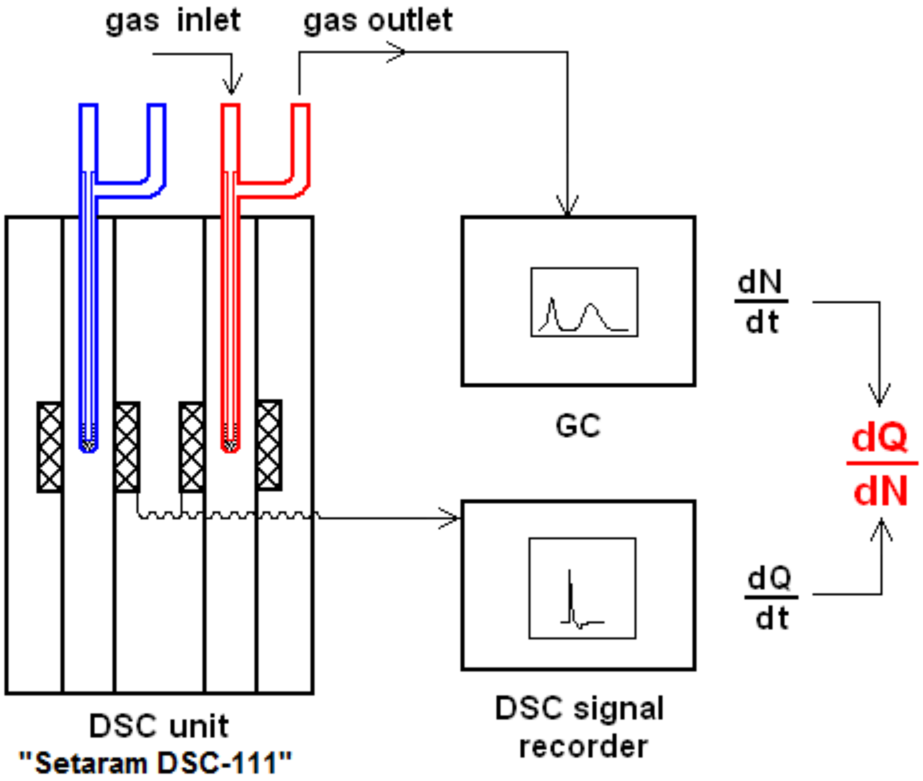
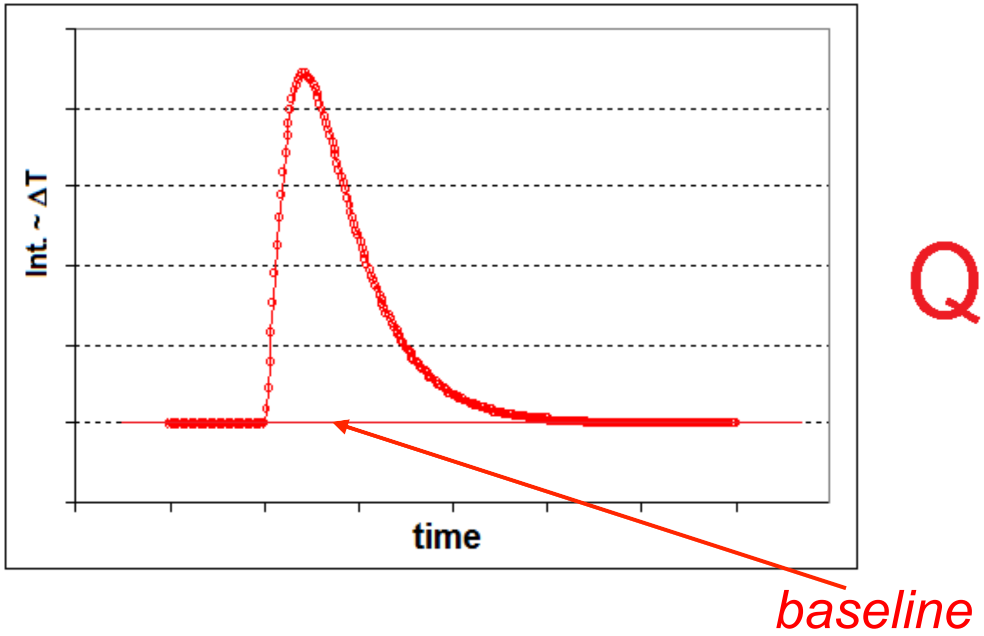


Temperature range: R.T - 1100 K; heating rates: 0-20 K/min.;
‘chemical resolution’ - 10^{15}-10^{16} at. (~0.01 ML @ ~1 m^2/g & m = 25 mg)

Treatment of DSC signal (*q*-curve)



$$Q = \int_0^\infty q\,dt \simeq a\int_0^\infty \Delta T\,dt$$

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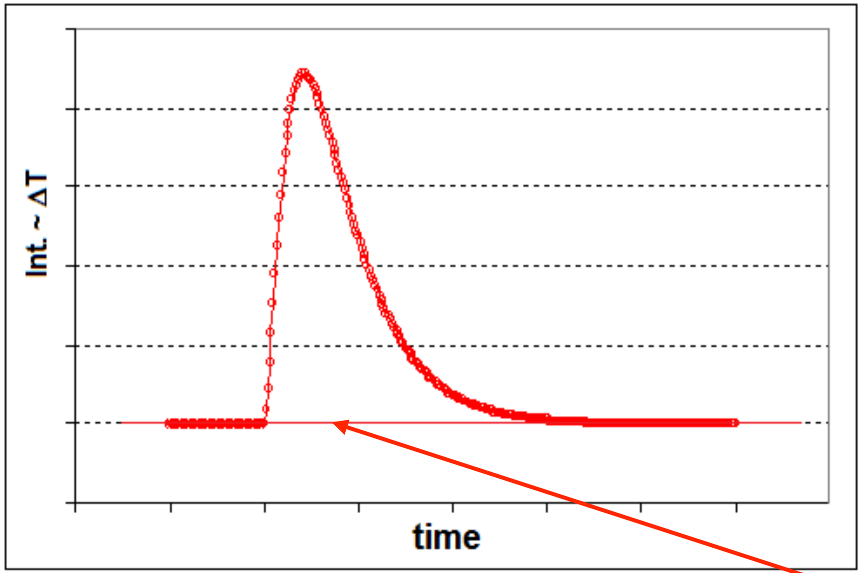
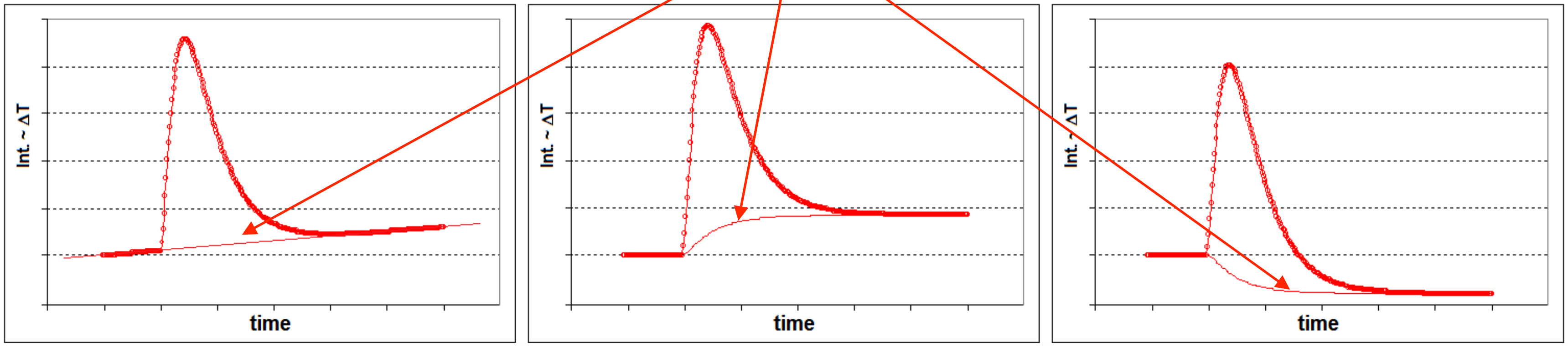
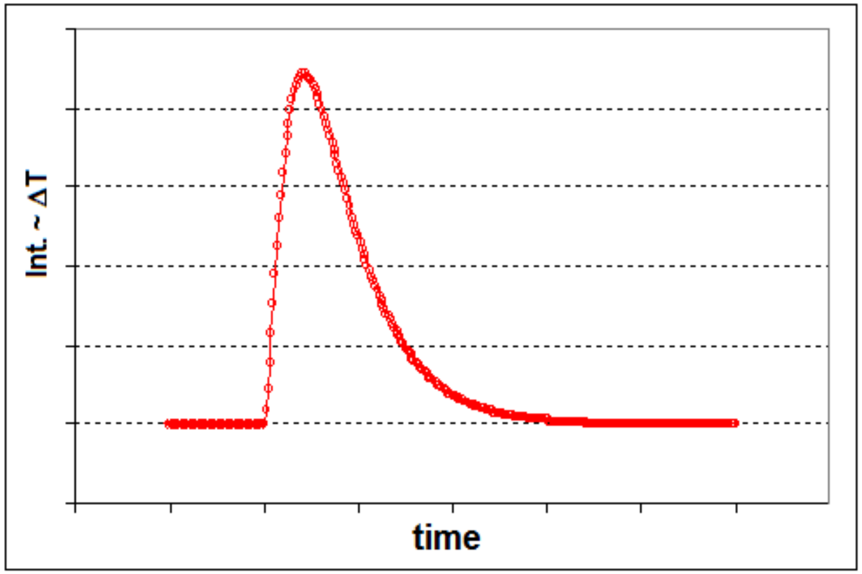


$$Q = \int_0^\infty q\,dt \simeq a\int_0^\infty \Delta T\,dt$$

baseline



Treatment of DSC signal (q-curve)

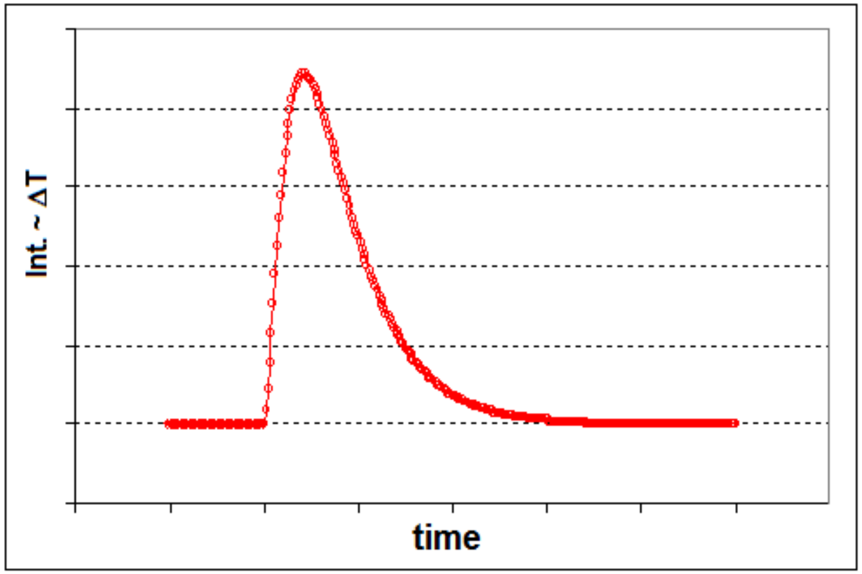


$$Q = \int_0^\infty q\,dt \simeq a\int_0^\infty \Delta T\,dt$$

Treatment of DSC signal:

- baseline

Treatment of DSC signal (q-curve)

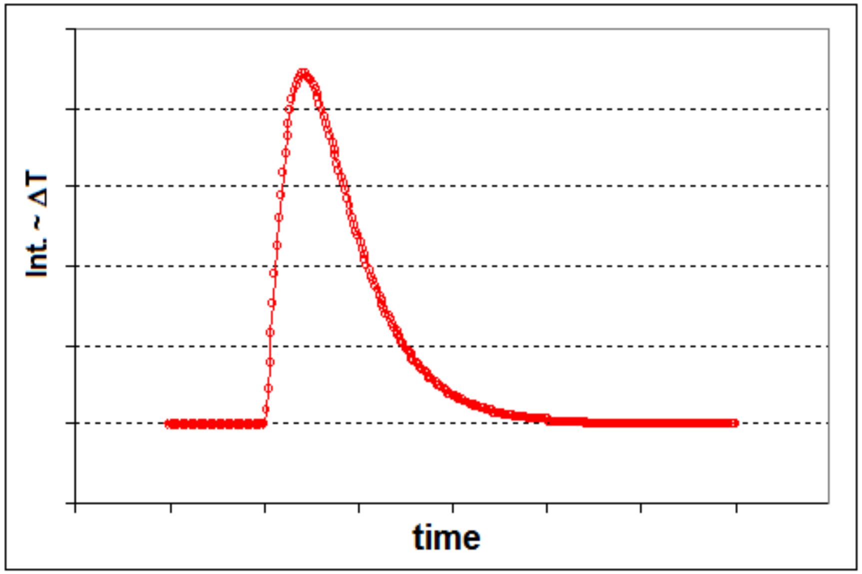


$$Q = \int_0^\infty q\,dt \simeq a\int_0^\infty \Delta T\,dt$$

Treatment of DSC signal:

- *baseline*
- *signal as such*
- *…*

Treatment of DSC signal (*q*-curve)



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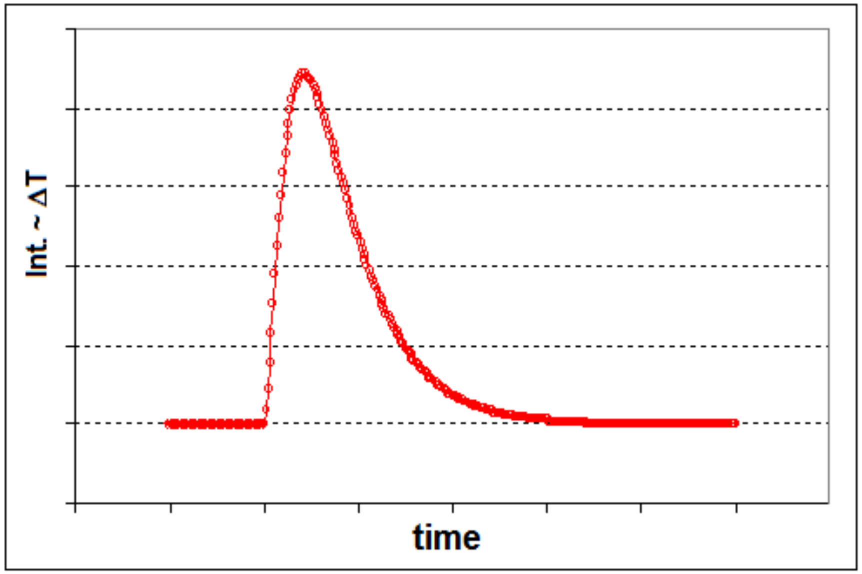

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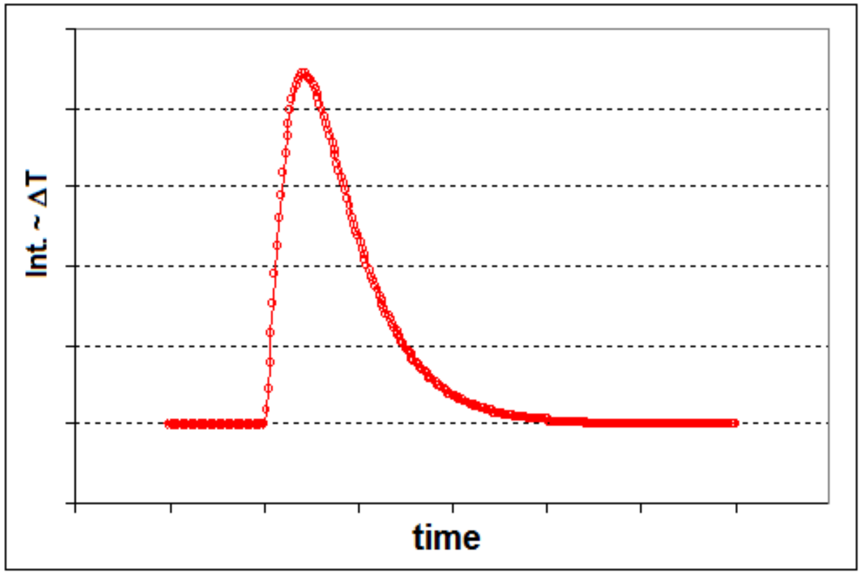
$q = k\Delta T + C(dT/dt)$ – *Tian equation*

Treatment of DSC signal (q-curve)



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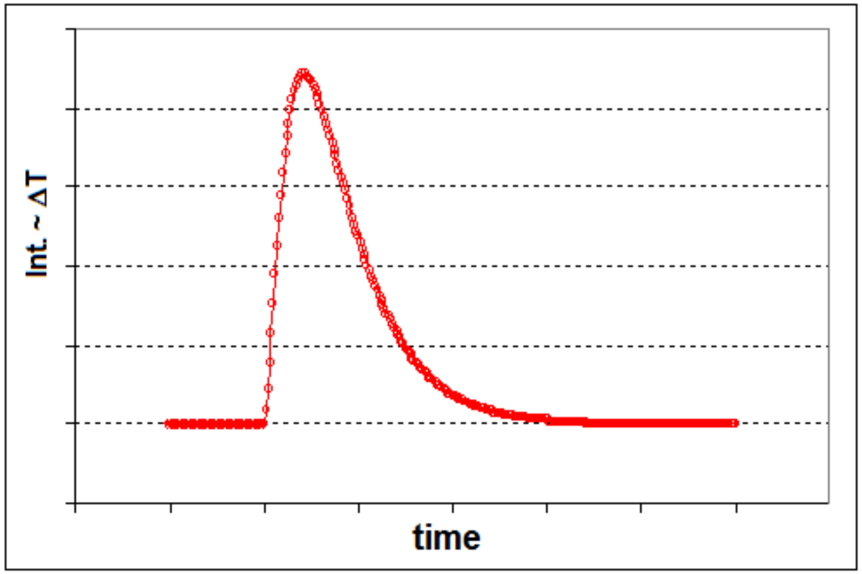

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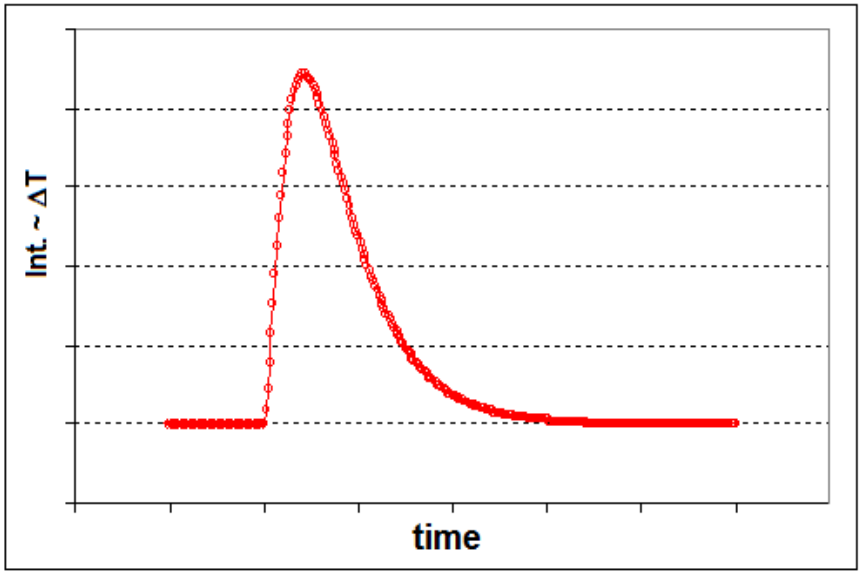
$$\frac{\int_0^\infty q\,dt}{\int_0^\infty \Delta T\,dt} \simeq a, \text{ however } \quad \frac{q}{\Delta T} \neq \text{const.}$$

Treatment of DSC signal (*q*-curve)



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τ^* = C/k – time constant of fluxmeter

for DSC-111 $\tau^* \approx 25$ s

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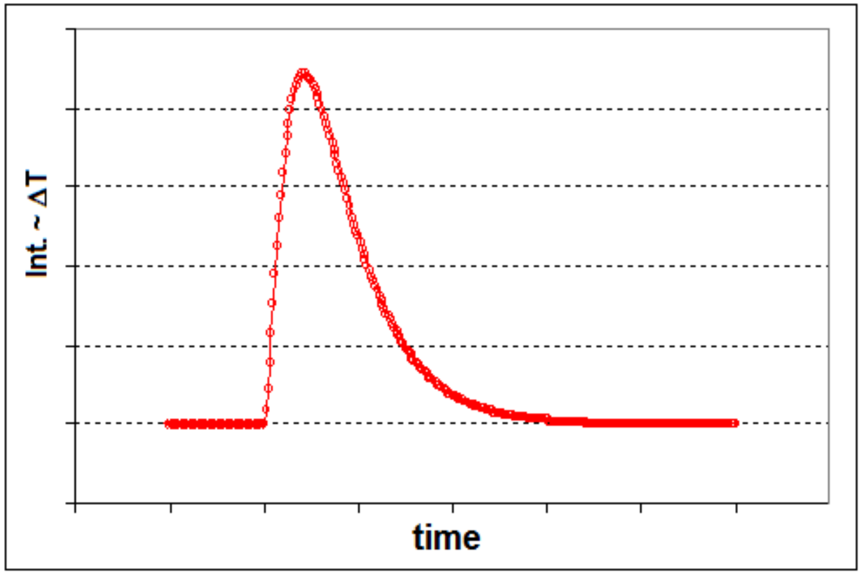

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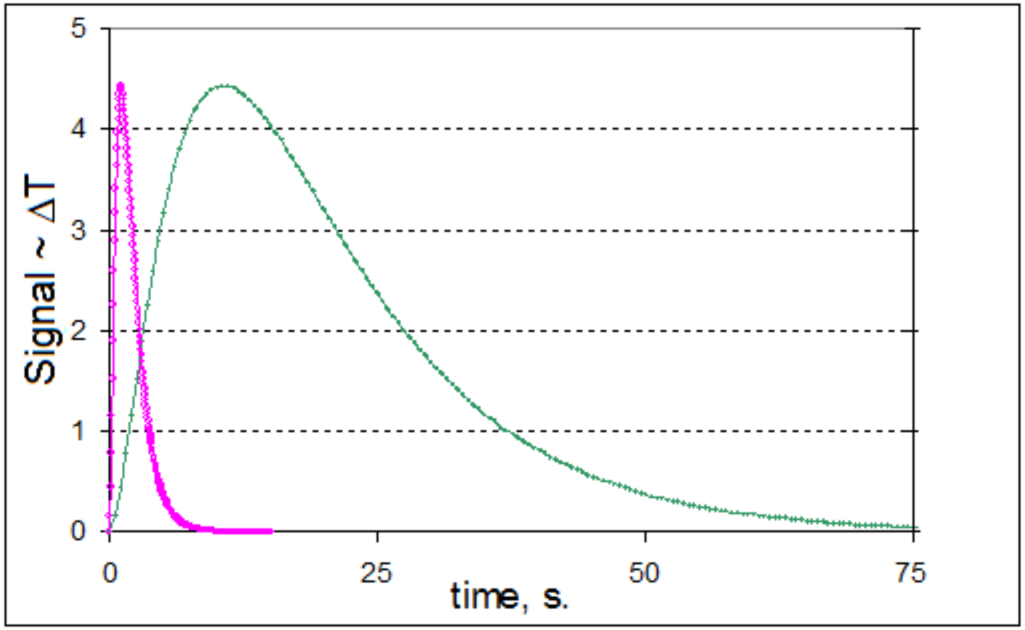
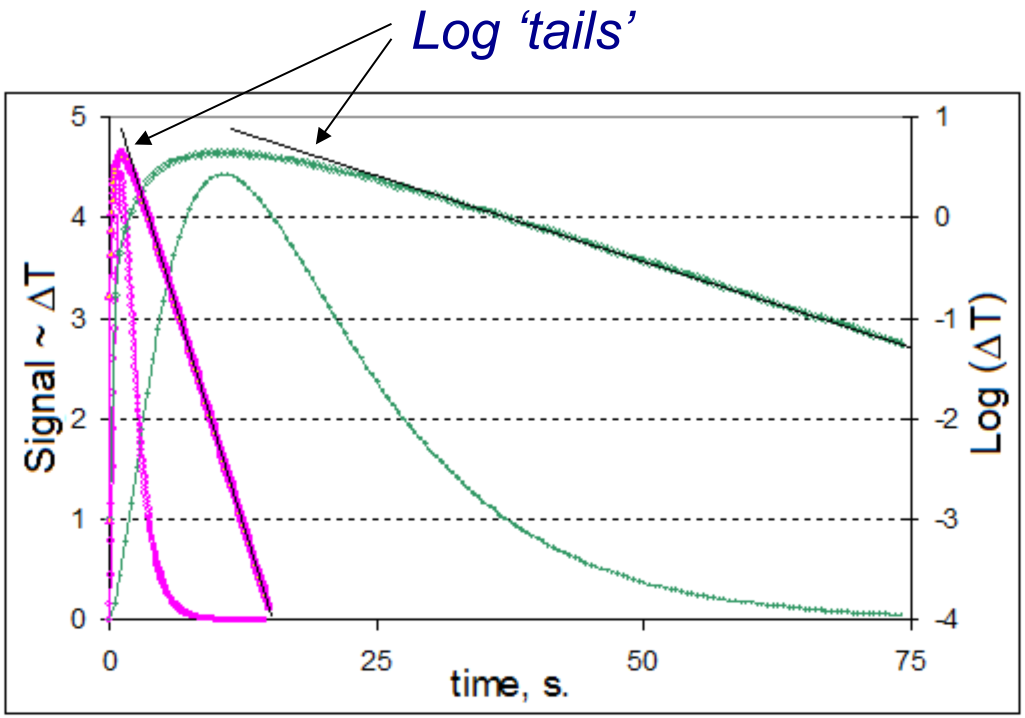


ΔT-curve 'tail': $q = k[\Delta T + \tau^*(d\Delta T/dt)] \approx 0 \Rightarrow$

$\Delta T \sim 1 - \exp(-t/\tau^*)$ and $\tau^* = - d(\mathrm{Log}\Delta T)/dt$

Treatment of DSC signal (q-curve)



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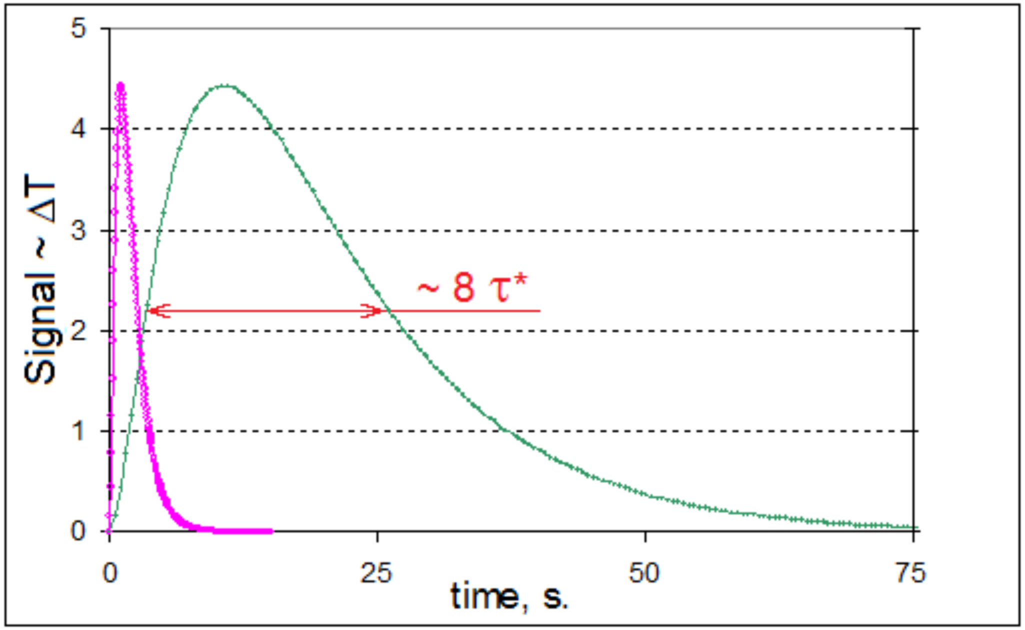

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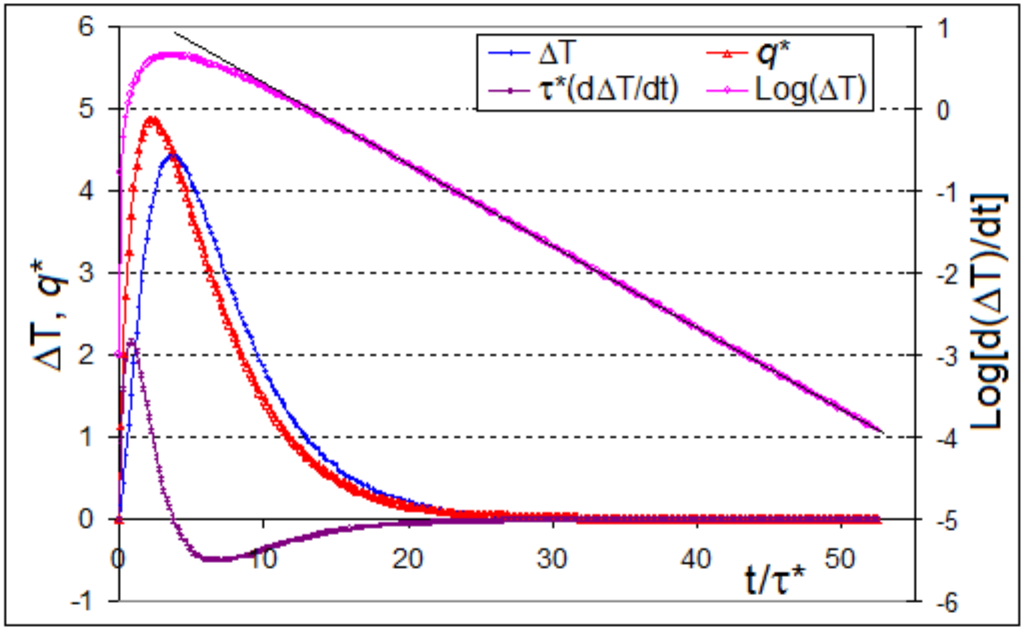

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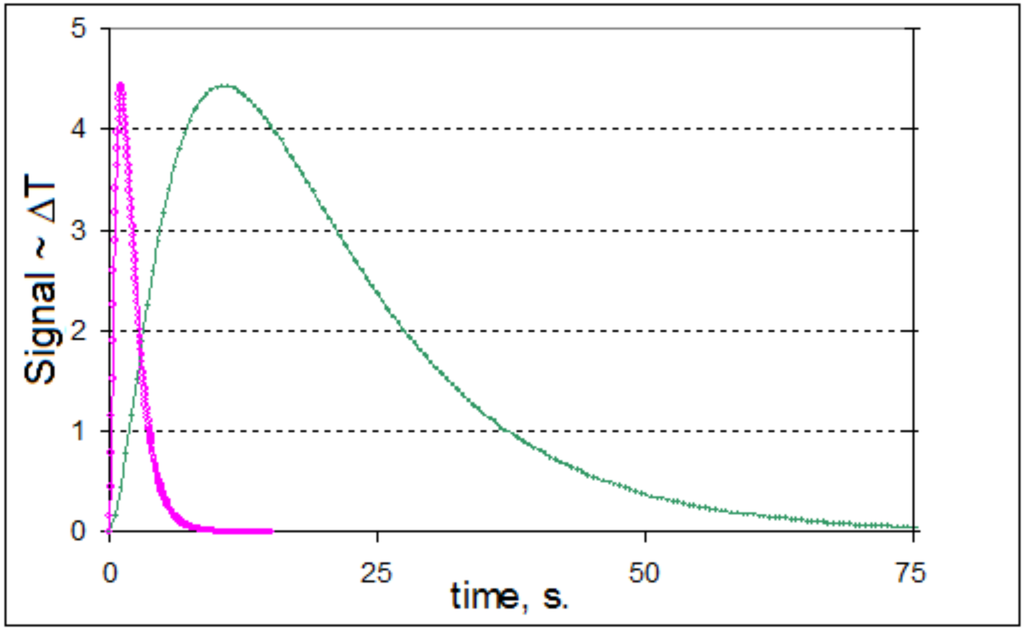

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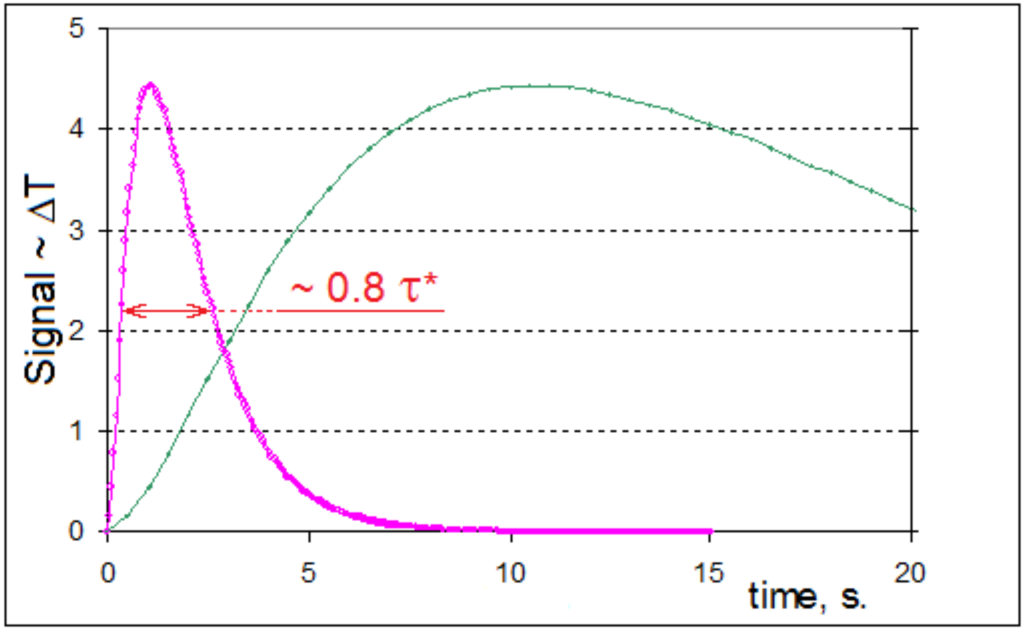

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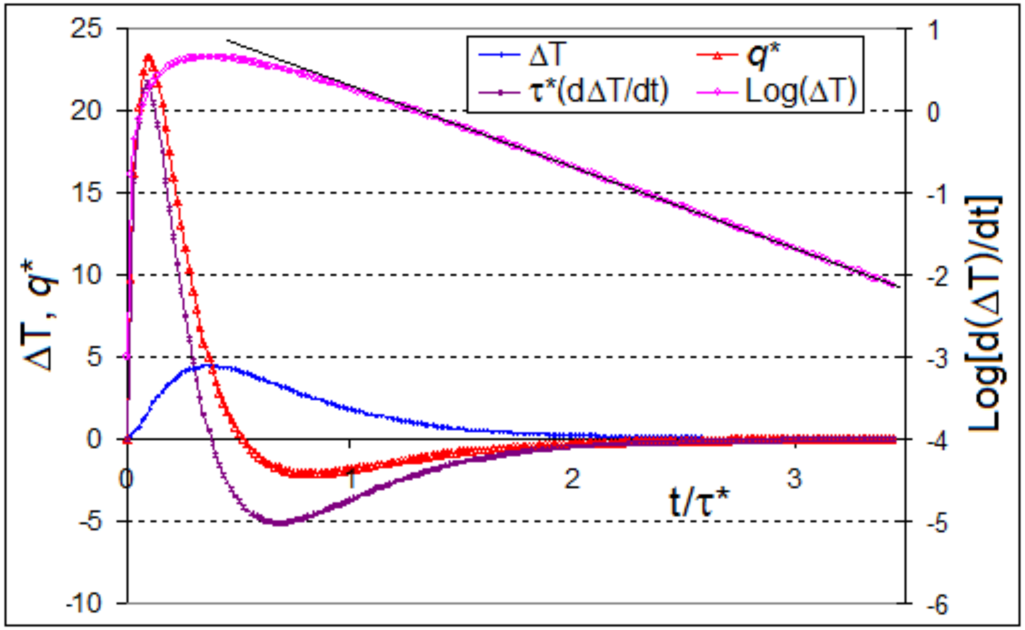

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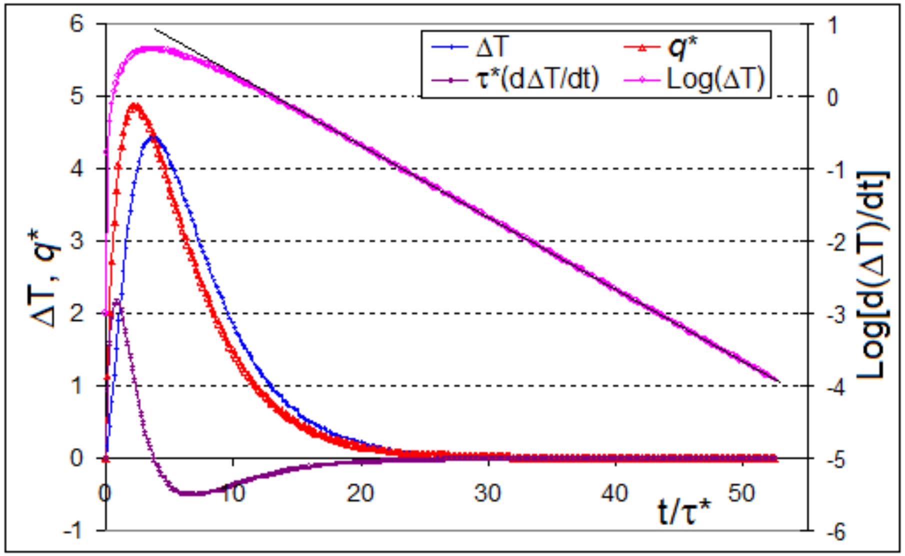
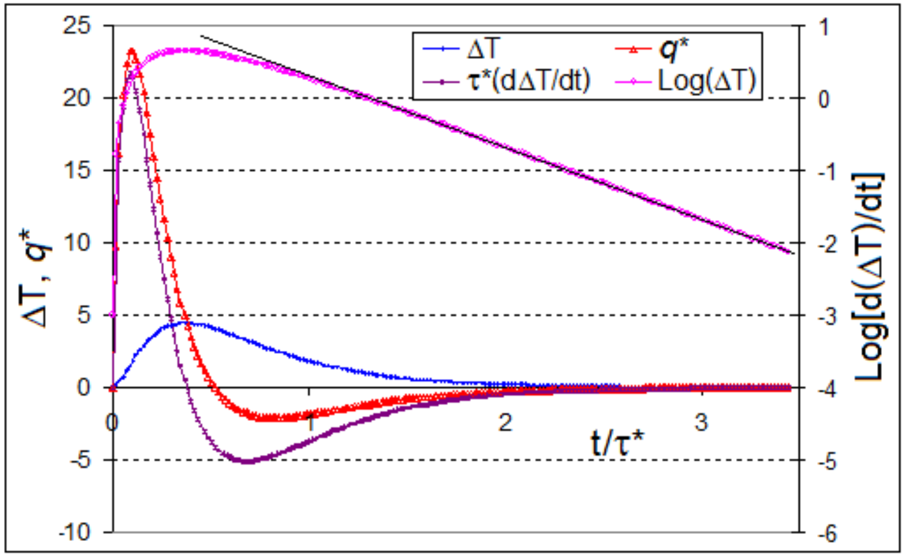
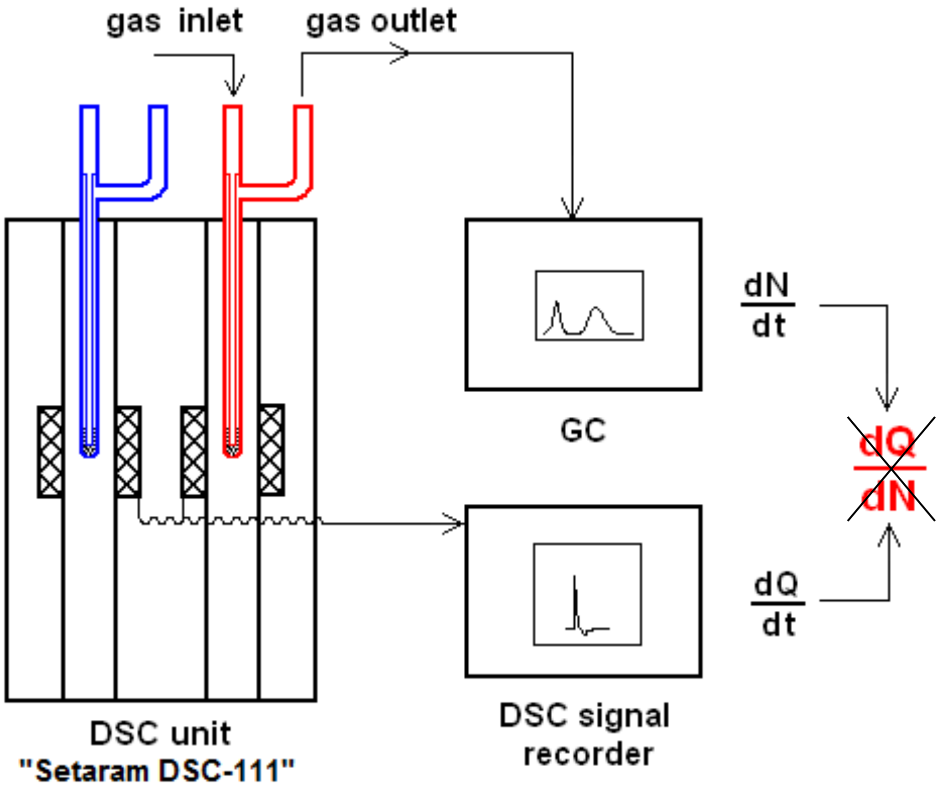
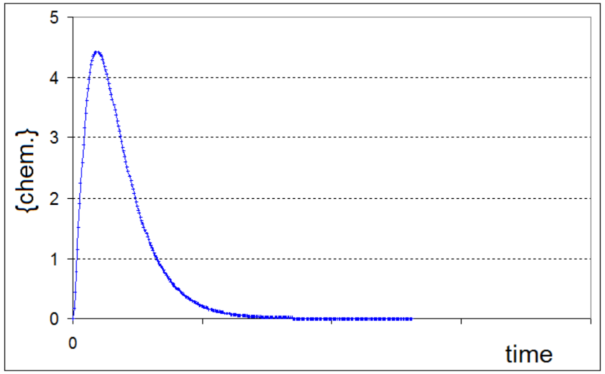


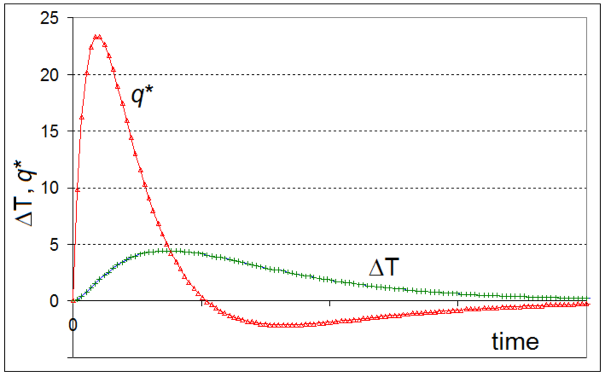


Treatment of DSC signal (*q*-curve)

in situ DSC







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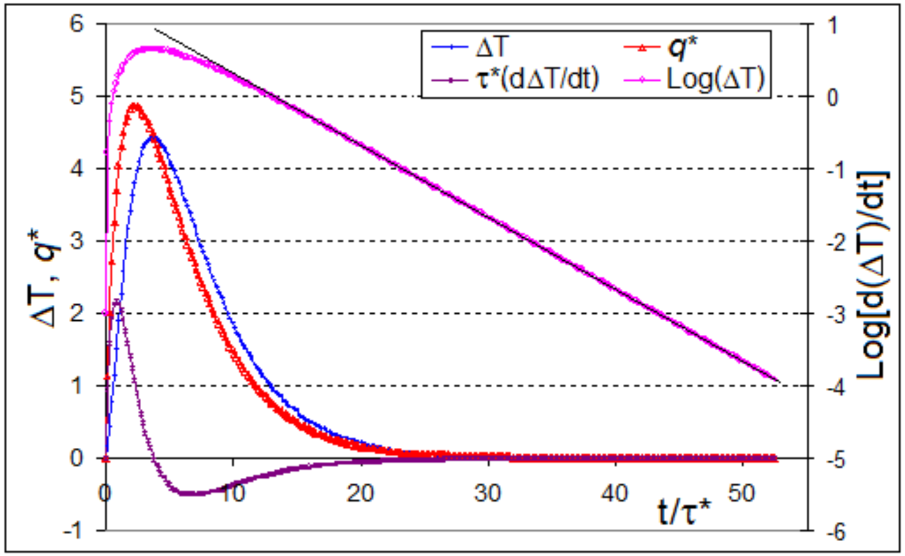

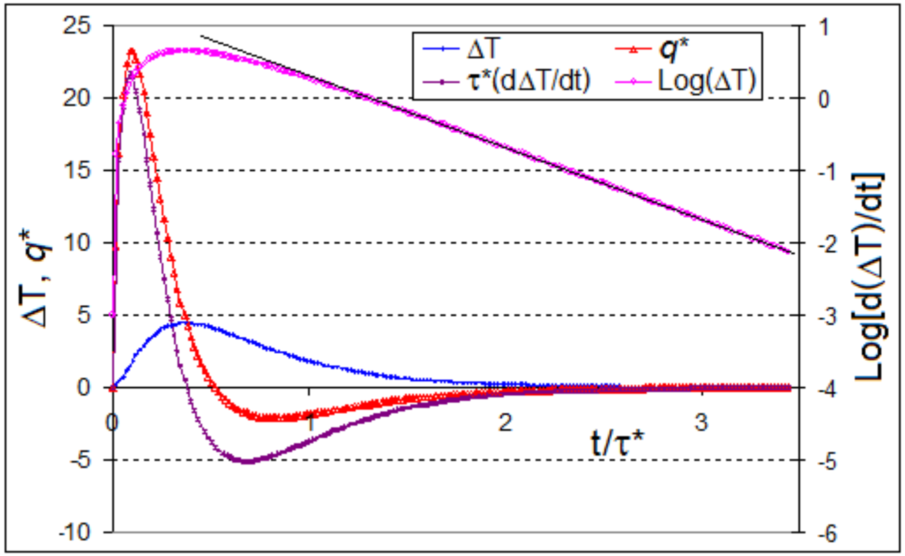

- If $\tau_{chem} \leq \tau^*$, dynamic (e.g., T-prog.) measurements may lead to substantial errors (both kinetic and calorimetric)

Treatment of DSC signal (q-curve)

In Calvet-type DSC

$$q = k\Delta T + C(dT/dt) \approx k\Delta T + C(d\Delta T/dt)$$
$$= k[\Delta T + \tau^*(d\Delta T/dt)]$$

$k\uparrow \Rightarrow \tau^* (\approx C/k)\downarrow$, but $\langle q\rangle \sim \Delta T\downarrow$ $\Rightarrow$

$\langle q\rangle \downarrow$ @ $\tau^*\downarrow$ $(\langle q\rangle\times\tau^* \approx \text{const.})$

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MS80

vs.

SETSYS evo
(DSC-111)

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Measurements: calorimetric dynamic

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MS80

vs.

SETSYS evo
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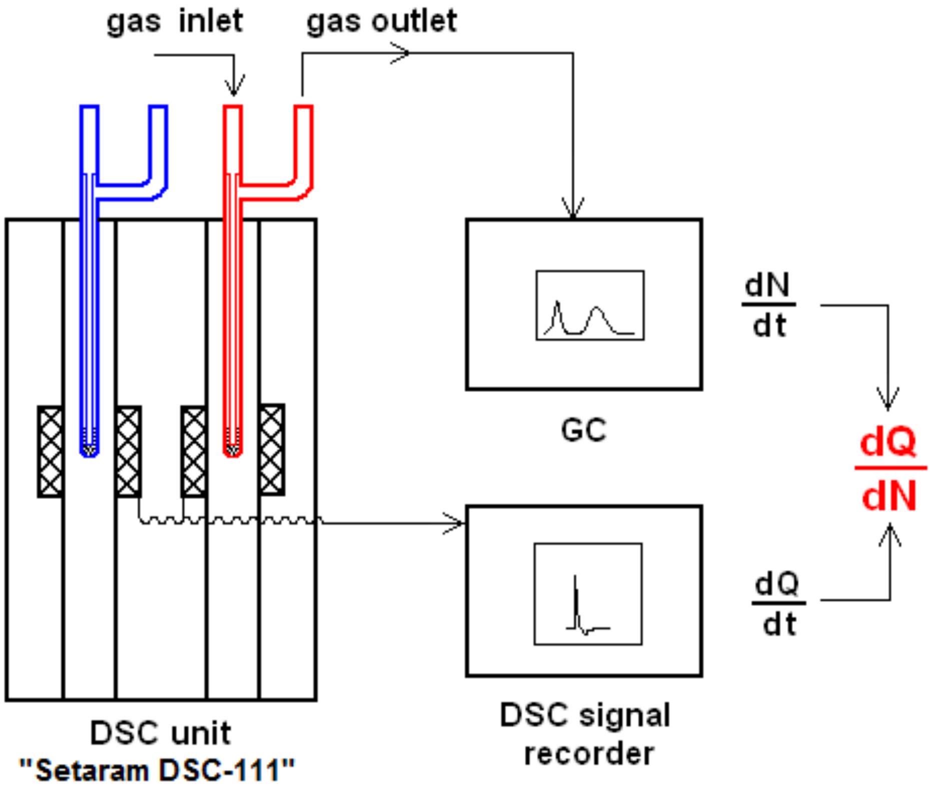
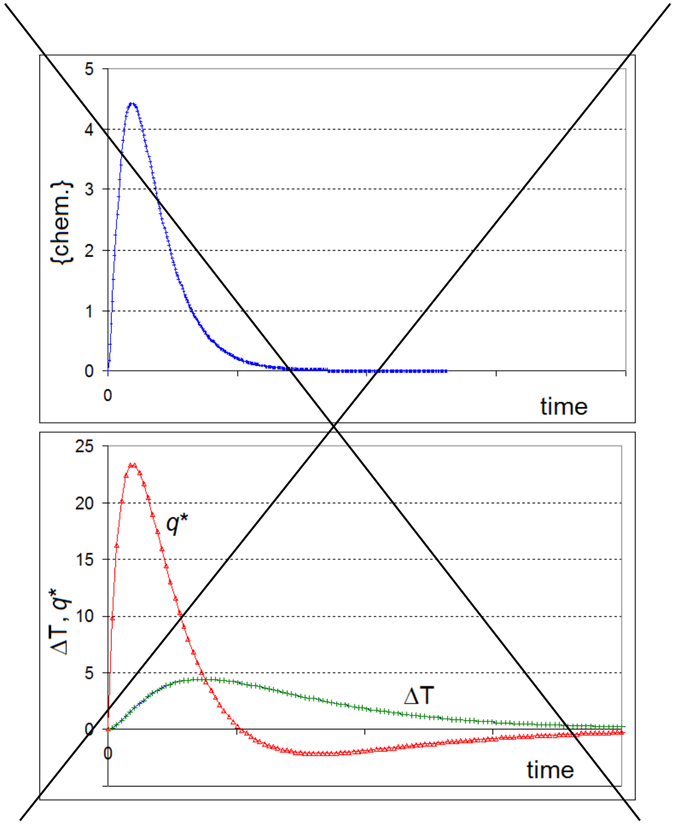
Measurements:	calorimetric	dynamic
$\tau^* \approx$	5-10 min.	~ 25 sec.

Treatment of DSC signal (*q*-curve)

in situ DSC





Pulse suply if active reactants ⇒

‘differential’ heats in each pulse
correct dQ/dN values

DSC – methods & instrumentation: summary

- wide variety of instruments

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- careful selection according to specific needs & requirements

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- wide variety of instruments
- careful selection according to specific needs & requirements
- rough experimental data must be "handled with care"

FHI, Berlin, January 27th, 2017

Lecture Series
Heterogeneous Catalysis

In-Situ Differential Scanning Calorimetry in the Studies of Oxide Catalysts and Mechanisms in Oxidative Heterogeneous Catalysis

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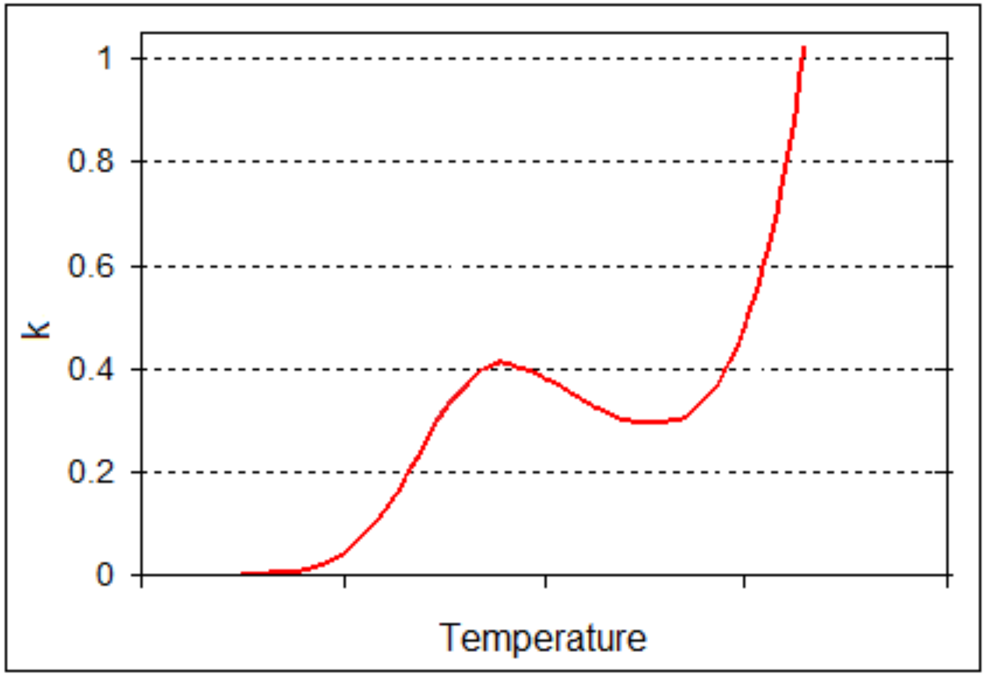
‘Classical’ kinetics of catalytic oxidation

$$A + \frac{1}{2} O_2 \rightarrow AO$$



k – apparent rate constant

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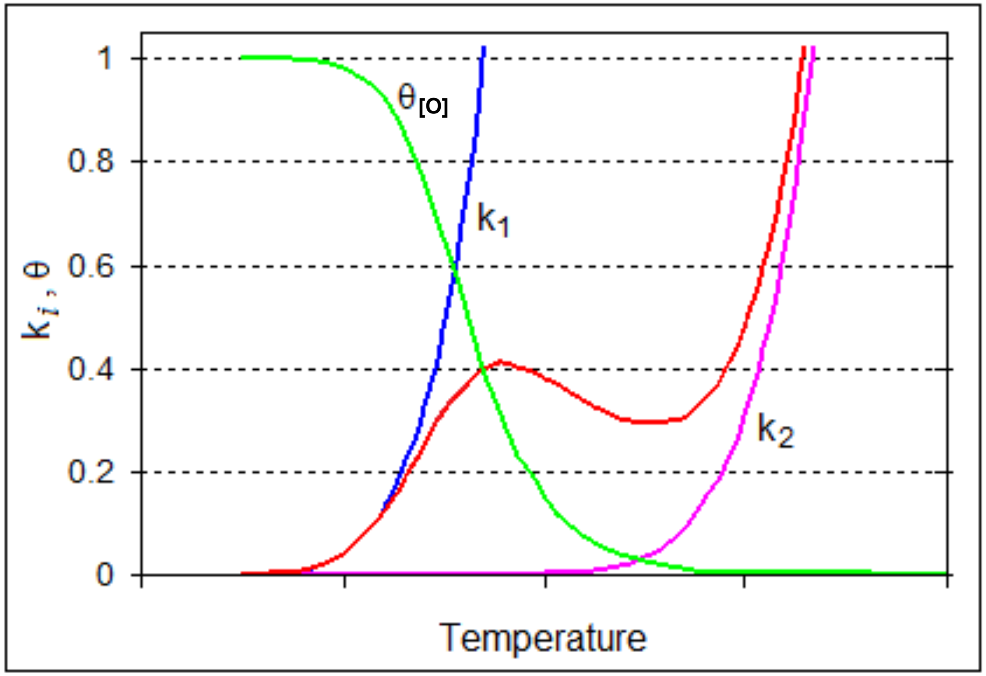

k – apparent rate constant

$$k = k_1{}^* + k_2 =$$

$$= k_1\theta_{[O]} + k_2$$

‘Classical’ kinetics of catalytic oxidation

$[O]_S + A \rightarrow [\ ]_S + AO$

$[\ ]_S + O_2 \Leftrightarrow [O_2]_S \rightarrow \ldots \rightarrow [O]_S$

“Classical” oxygen adsorption-desorption (OAD) mechanism

$$W^*_{AO} = \frac{k^*_{red} P_A \, k_{ox} P_{O_2}}{1 + K_{ox} P_{O_2}}$$

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- None of the two says anything about the ‘nature’ of active O-species (lattice, adsorbed, …)
- In both cases the properties of active O-species and the ‘substrate’ interaction with them are crucial for activity/selectivity

‘Classical’ kinetics of catalytic oxidation

‘Key’ properties of active O-species:

- lifetime (⇒ type of kinetics);
- reactivity – qualitative (types of interactions with other species) and

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‘Substrate’ interactions with active O-species:

- qualitative (types of interactions & products formed);
- quantitative (rates / kinetic parameters)

Energy in Chemistry

Energy Factor:

- intrinsic reactivity
- interaction with environment

Reactivity:

- thermodynamic aspect (Free Energy – ‘driving force’, feasibility)
- kinetic aspect (Activation Energy – ‘barrier on reaction coordinate’)

Interaction with environment:

- external parameters (‘conditions’)
- subject to change

⇒ feedback

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Energy in oxidative catalysis over solid oxides

Energy Factor:

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Oxide catalysts and reactive oxygen:

- O-binding energy (⇒ O-lifetime, defects, etc.);
- reactions with ‘substrates’ (activity, selectivity);
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in situ DSC!!!

DSC *in situ* in oxidative catalysis over solid oxides

‘Non-calorimetric’ techniques:

- oxygen TPD;
- TPR (e.g., H_2, CO);
- TPO (O_2, N_2O, H_2O, CO_2, etc.)

DSC *in situ* in oxidative catalysis over solid oxides

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\+ calorimetry:

- thermodynamics *vs.* kinetics;
- oxygen non-uniformity;
- mechanistic information (e.g., ‘E_a *vs.* ΔH’ and ‘S *vs.* $E_{[O]}$’ correlations)

Case study 1: alkane ODH over VSb/Al_2O_3

$C_nH_{2n+2} + ½\ O_2 \rightarrow C_nH_{2n} + H_2O$

$C_nH_{2n+2} + zO_2 \rightarrow nCO_X + (n+1)\ H_2O$

Catalysts – V-containing bulk and supported oxides

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Catalysts – V-containing bulk and supported oxides

’Classical’ Red-Ox Kinetics over V-containing catalysts –
Mars-van-Krevelen* or oxygen rebound-replenish (ORR) mechanism

$$[O]_S + A \rightarrow [\ ]_S + AO$$

$$[\ ]_S + O_2 \rightarrow \ldots \rightarrow [O]_S$$

* toluene oxidation over V-alumina catalyst

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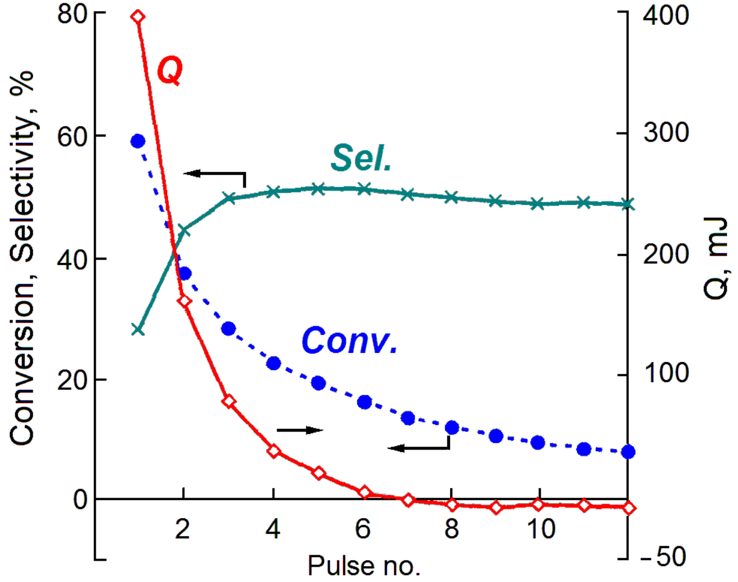
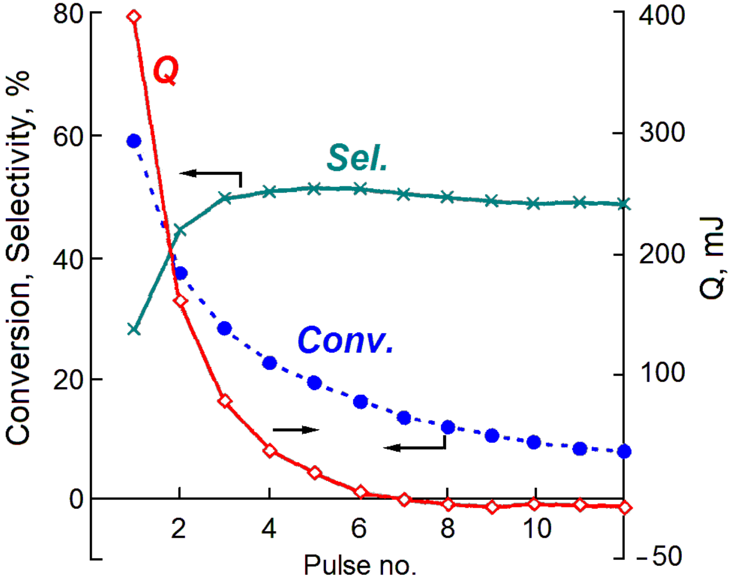
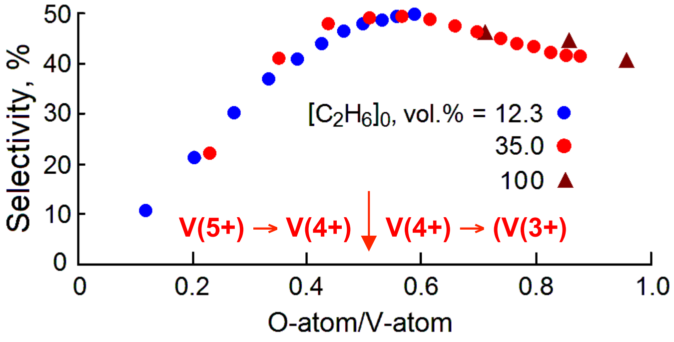
550°C, ethane pulses onto pre-oxidized VSb/Al_2O_3



Case study 1: alkane ODH over VSb/Al_2O_3

550°C, ethane pulses onto pre-oxidized VSb/Al_2O_3





V(4+) state is optimal for high selectivity to ethylene

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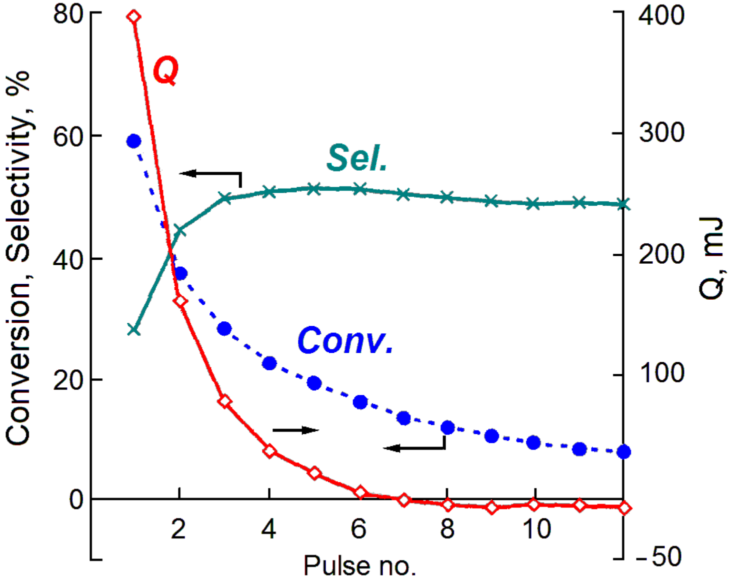

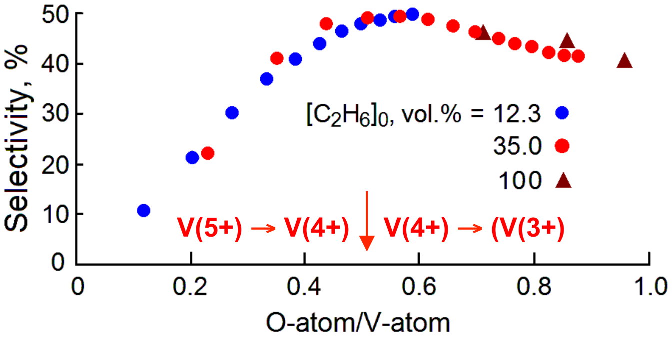

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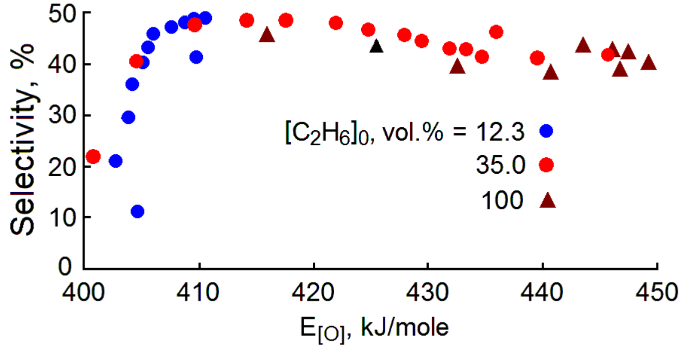

V(5) → V(4+) – jump of S @ small variations of $E_{[O]}$;

V(4+) → (V3+) – slow decrease of S in a wide range of $E_{[O]}$ variation

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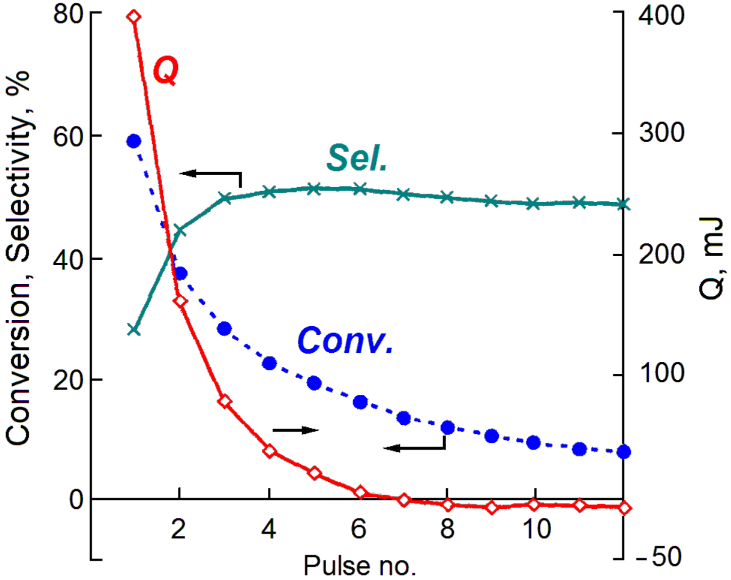
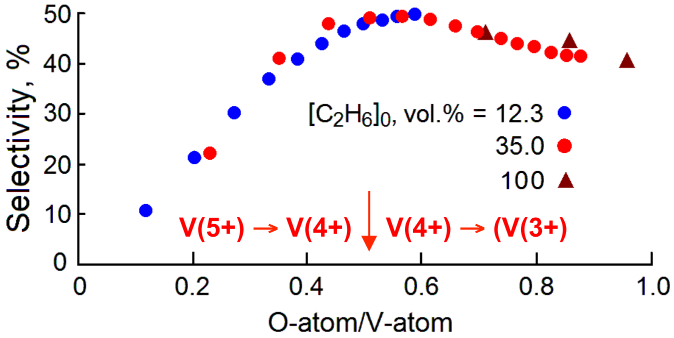
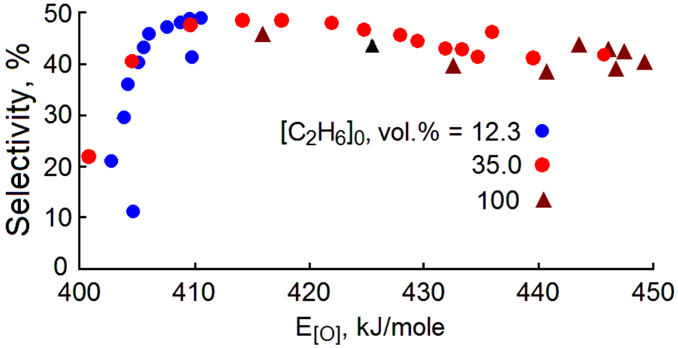
550°C, ethane pulses onto pre-oxidized VSb/Al_2O_3





V(4+) state is optimal for high selectivity to ethylene



V(5) → V(4+) – jump of S @ small variations of $E_{[O]}$;

V(4+) → (V3+) – slow decrease of S in a wide range of $E_{[O]}$ variation

‘Chemical’ factor (i.e. state of surface sites and their interaction with HC’s) is more important than ‘energy’ one

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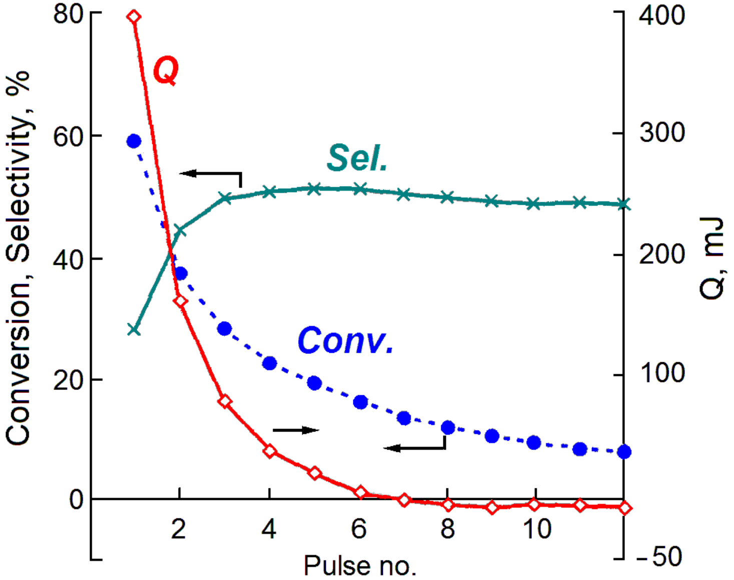

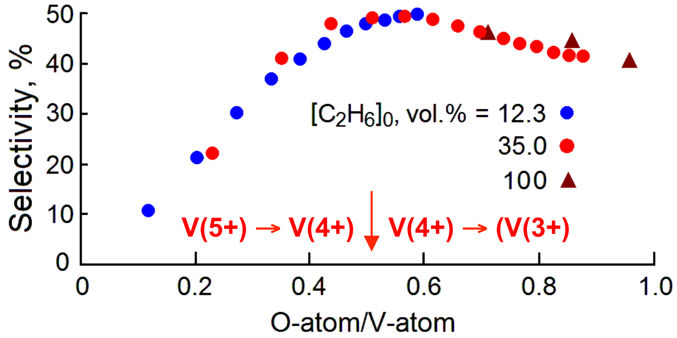

V(4+) state is optimal for
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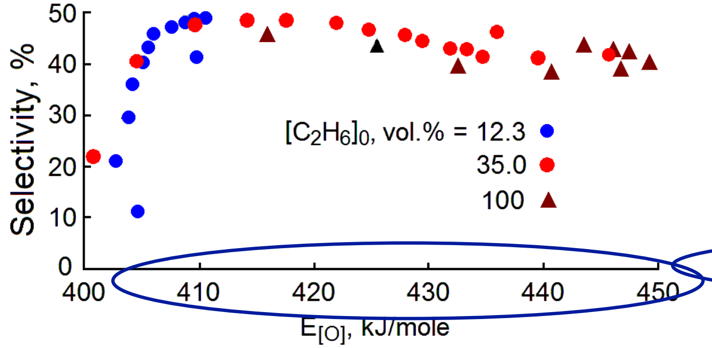
$(\Delta H_f)_{M2OX-1} - (\Delta H_f)_{M2OX} \approx E_{[O]}$



$Sb_2O_5 \rightarrow Sb_2O_4 + ½ O_2$	-171 kJ/mole O_2
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Is $E_{[O]} \approx (\Delta H_f)_{M2OX-1} - (\Delta H_f)_{M2OX}$???

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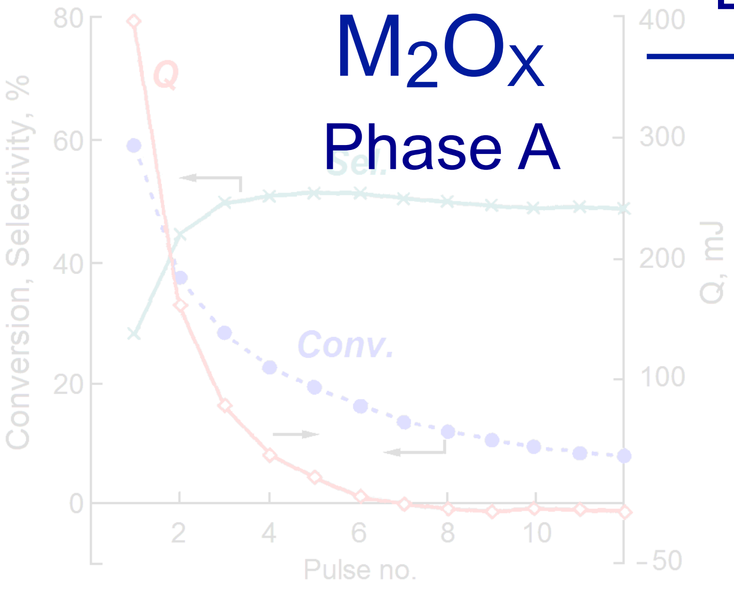
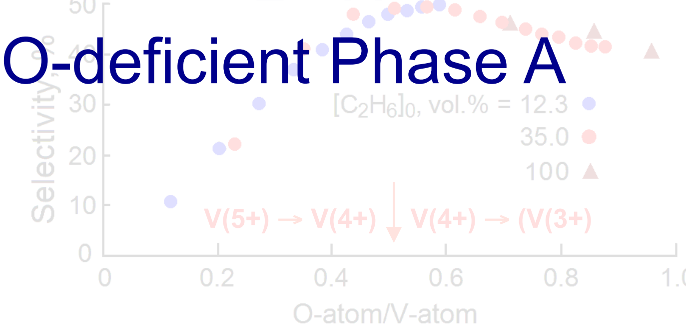
550°C, ethane pulses onto pre-oxidized VSb/Al_2O_3

$$M_2O_X \xrightarrow{-D_{[O]}\ \text{(endo)}} M_2O_{X-1}$$

Phase A → O-deficient Phase A





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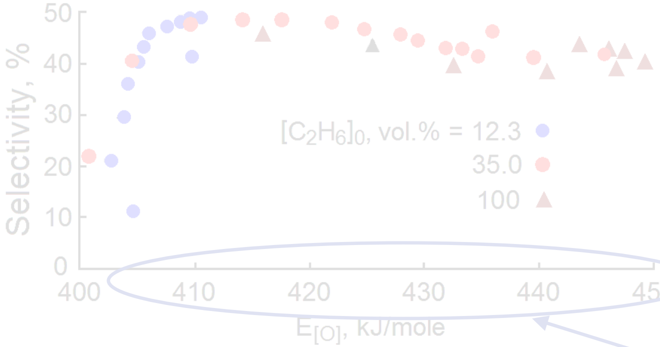

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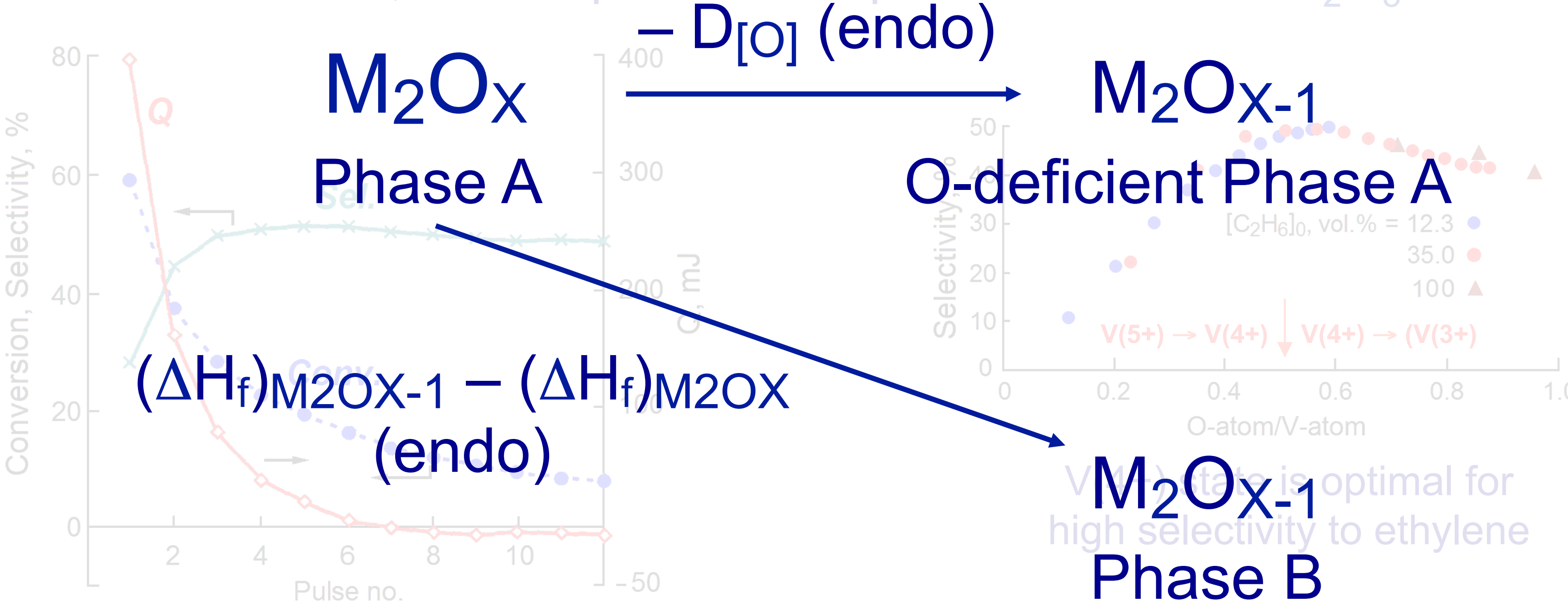


M_2O_X

Phase A

$\xrightarrow{-\ D_{[O]}\ \text{(endo)}}$

M_2O_{X-1}

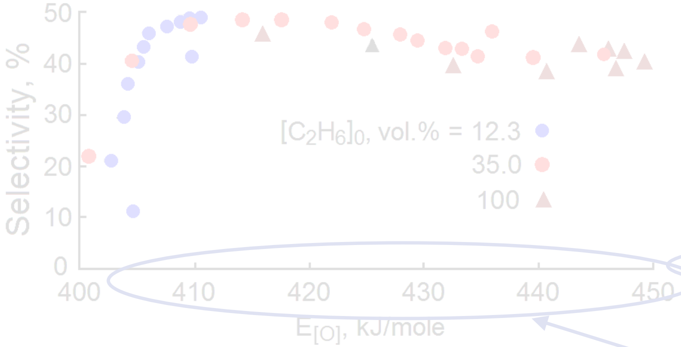
O-deficient Phase A

$(\Delta H_f)_{M2OX-1} - (\Delta H_f)_{M2OX}$ (endo)

M_2O_{X-1}

Phase B

V(4+) state is optimal for high selectivity to ethylene



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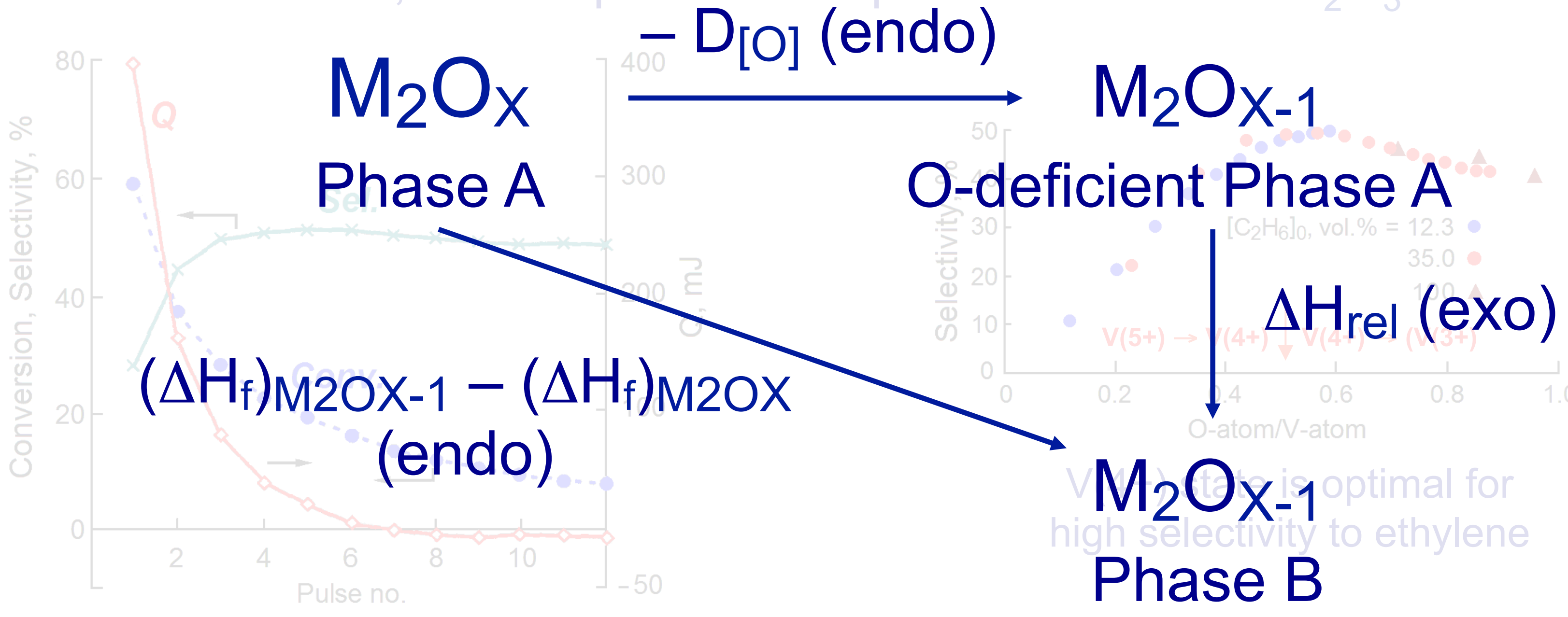


M_2O_X

Phase A

$– D_{[O]}$ (endo)

M_2O_{X-1}

O-deficient Phase A

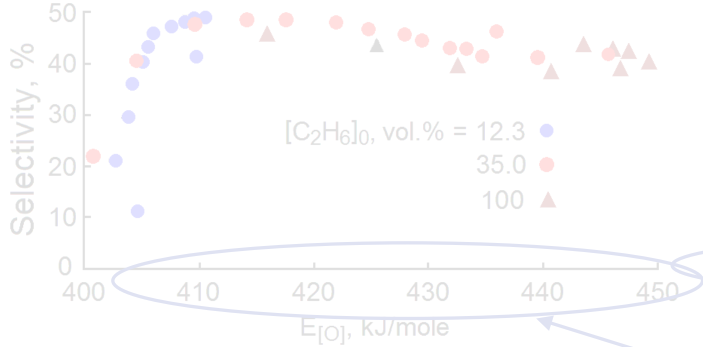
ΔH_{rel} (exo)

$(\Delta H_f)_{M2OX-1} – (\Delta H_f)_{M2OX}$
(endo)

M_2O_{X-1}

Phase B

V(4+) state is optimal for high selectivity to ethylene



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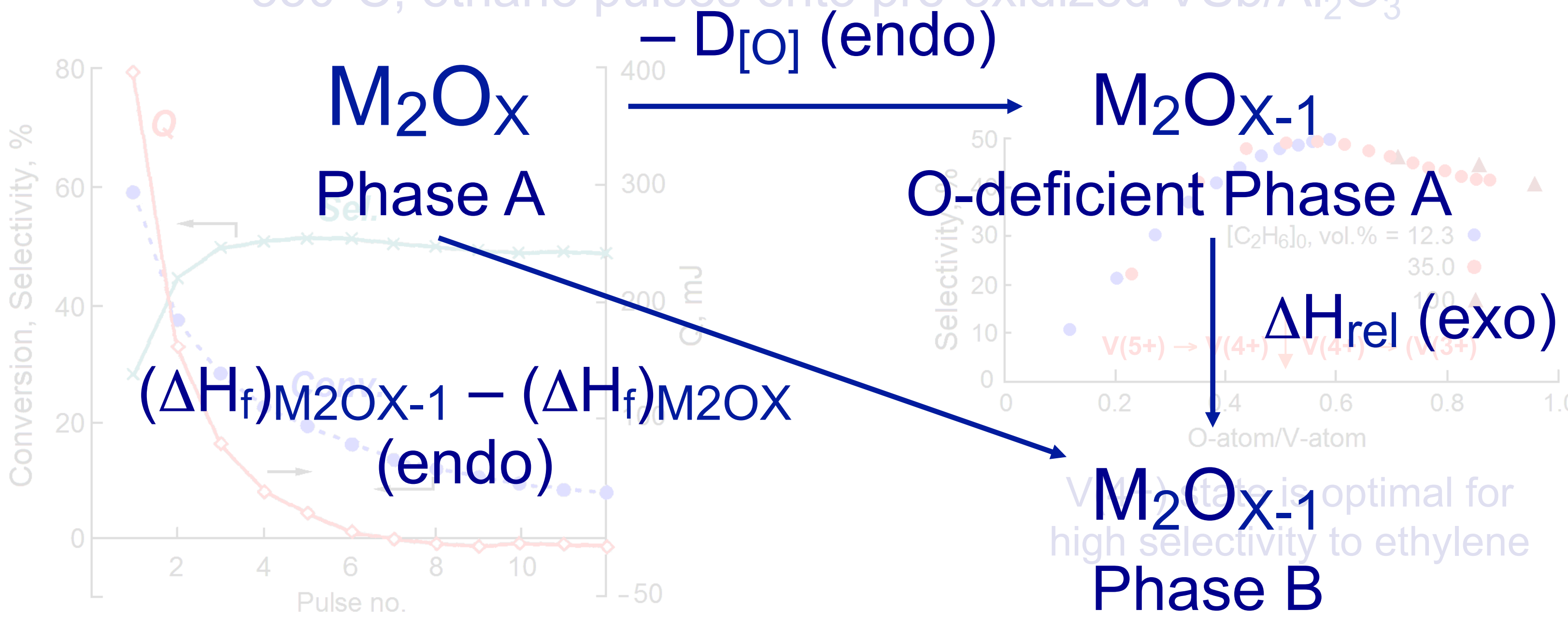

M_2O_X

Phase A

$- D_{[O]}$ (endo)

M_2O_{X-1}

O-deficient Phase A

ΔH_{rel} (exo)

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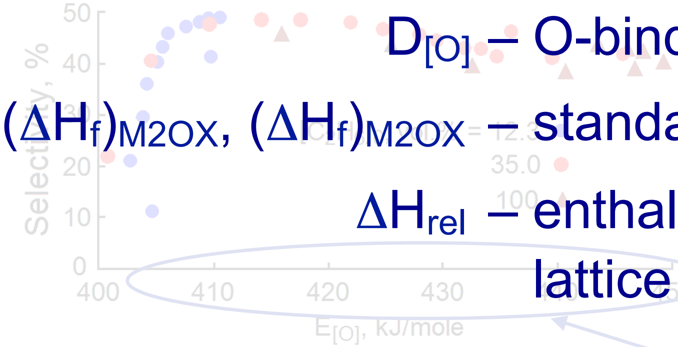

$D_{[O]}$ – O-binding energy (in ‘phase homogeneity’ range);

$(\Delta H_f)_{M2OX}$, $(\Delta H_f)_{M2OX}$ – standard (tabulated) values;

ΔH_{rel} – enthalpy of relaxation (elimination of vacancies, lattice re-organization, etc.)

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$$|D_{[O]}| = |(\Delta H_f)_{M2OX-1} - (\Delta H_f)_{M2OX}| + |\Delta H_{rel}|$$

???

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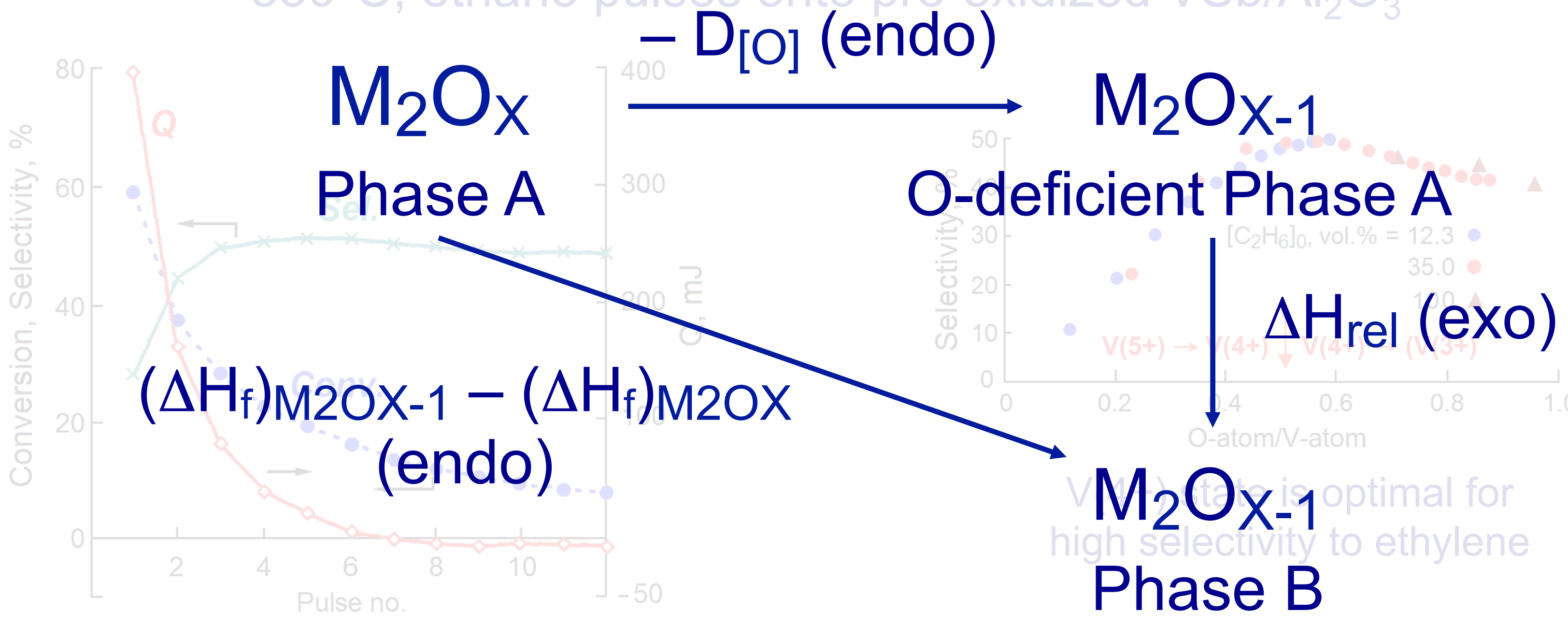

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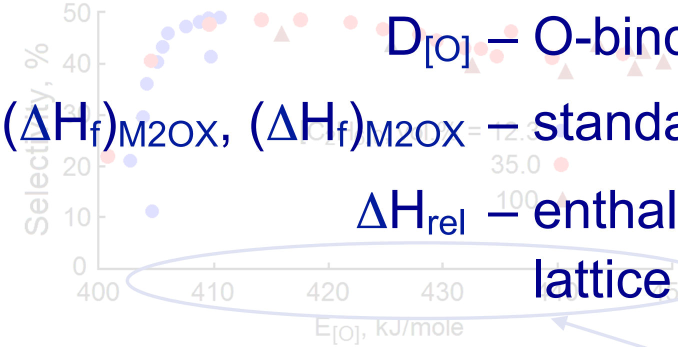

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🗝 $|(\Delta H_f)_{M2OX-1} - (\Delta H_f)_{M2OX}| < |E_{[O]}| < |D_{[O]}|$

Case study 2: oxidative coupling of methane (1)

Oxidative Coupling of Methane (OCM)

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$$\begin{tikzcd} CH_4 + [O]_S \arrow[r] & CH_3^{\bullet} + [OH]_S \arrow[d] \\ & C_2H_6 \end{tikzcd}$$

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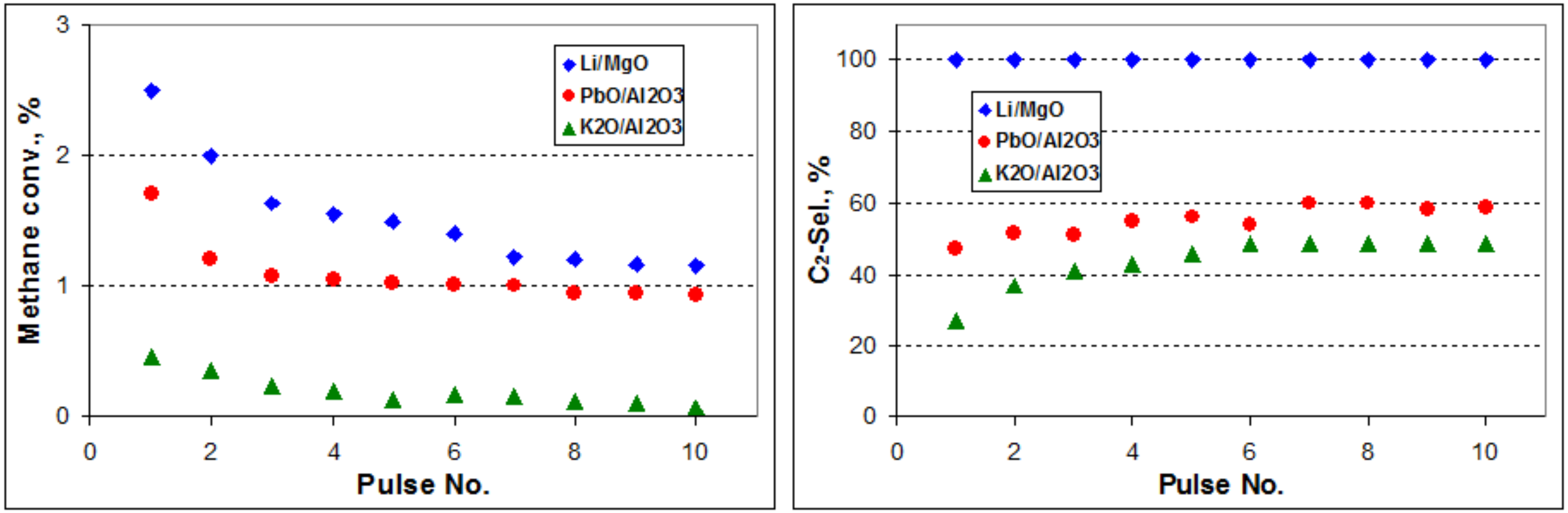
700^{o}C, methane pulses onto pre-oxidized oxide catalysts



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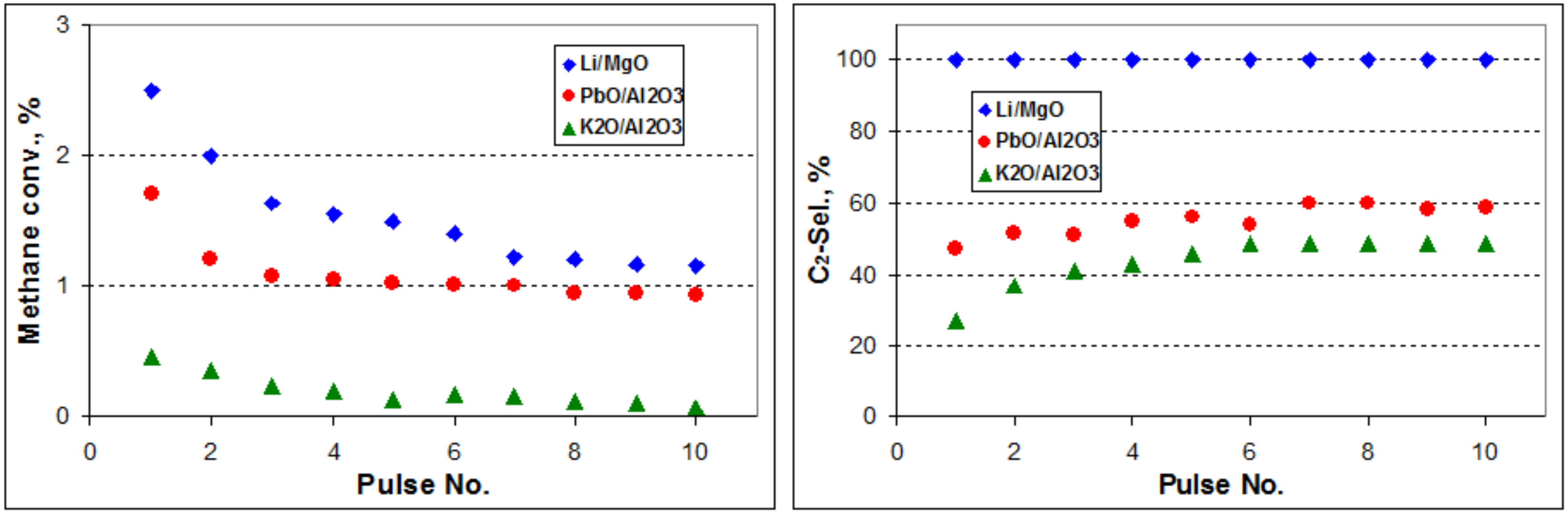
700°C, methane pulses onto pre-oxidized oxide catalysts



Li/MgO – no water evolved into the gas phase during reduction (CH_4, H_2) - !?

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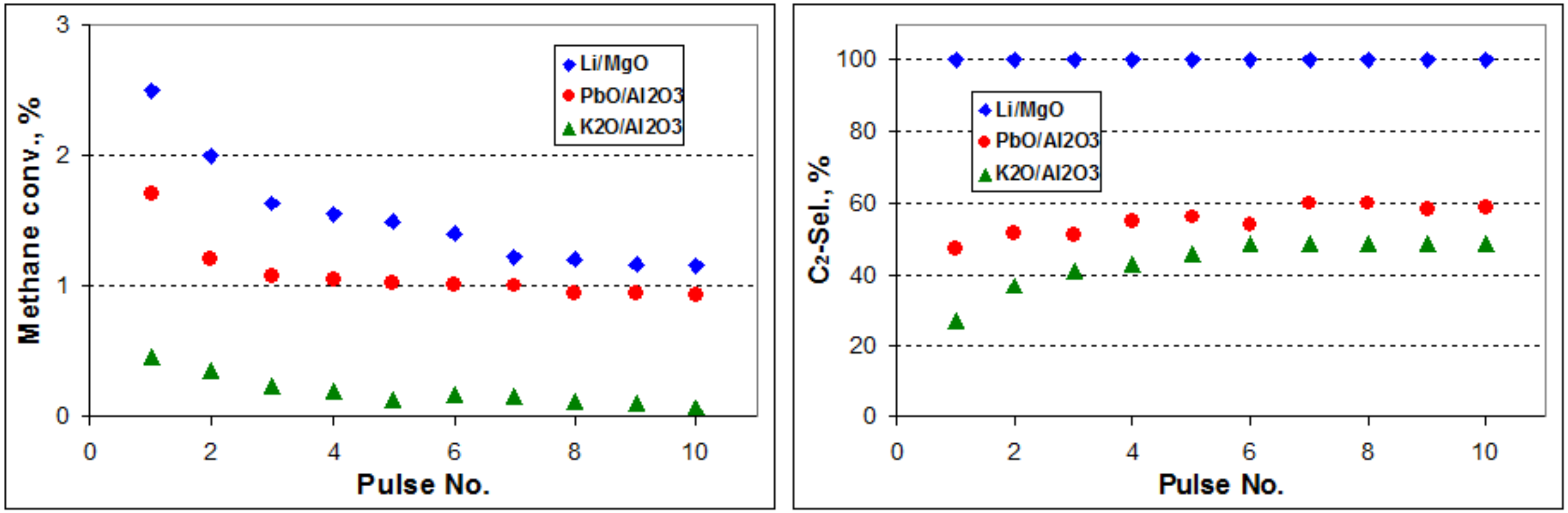

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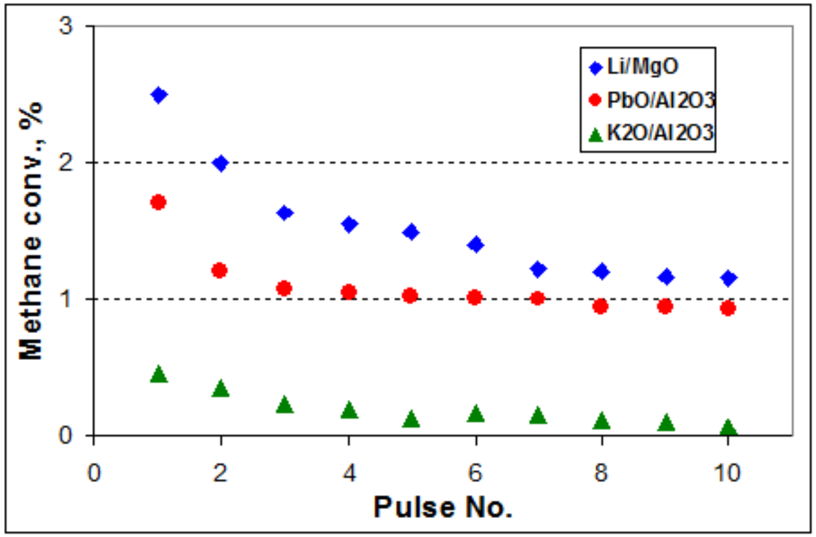

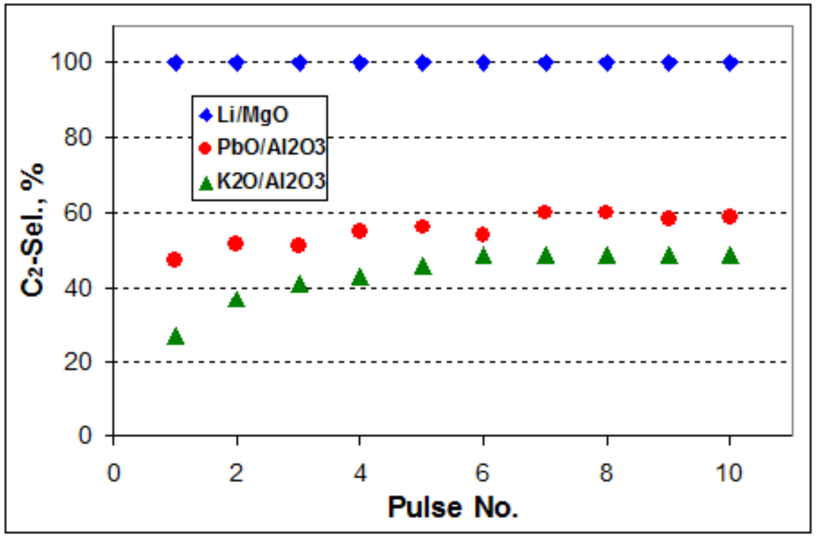

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Reduction: $[O] + CH_4 \rightarrow [OH] + CH_3^{\bullet}$ $\Rightarrow D_{[O\text{-}H]}$

Re-oxidation – ???

Case study 2: oxidative coupling of methane (1)

Alternative mechanisms of re-oxidation

$2\ [OH]_S \rightleftharpoons [O]_S + [\ \ ]_S + H_2O$ (A)

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$H_2O_2 \rightarrow 2\ OH$ (B3)

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$D_{[O\text{-}H]}$, kJ/mole	320	250	270
$E_{[O]}$, kJ/mole	535	407	450

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🗝 relative contribution of routes A and B is determined by thermochemistry

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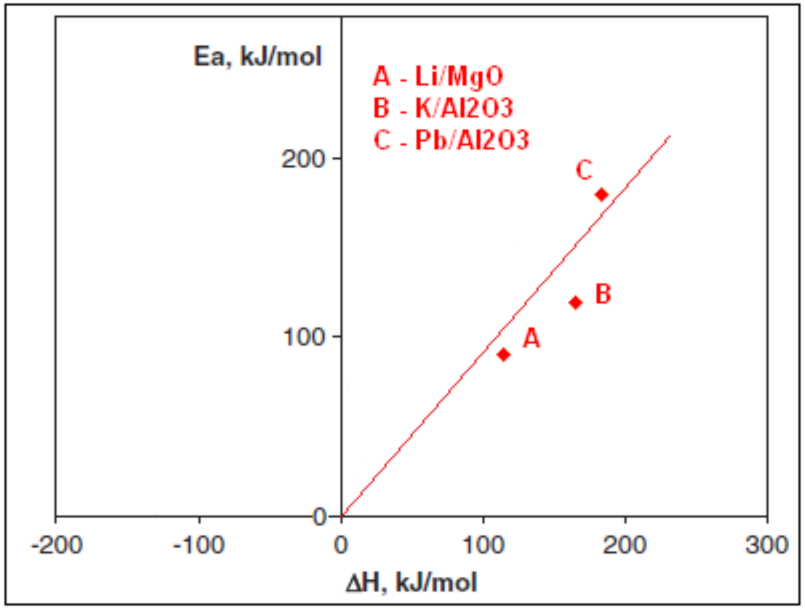
Case study 2: oxidative coupling of methane (2)

E_a - ΔH Correlation

$[O] + CH_4 \rightarrow [OH] + CH_3^{\bullet}$ $\Delta H = D_{[O-H]} - D_{H-CH_3}$



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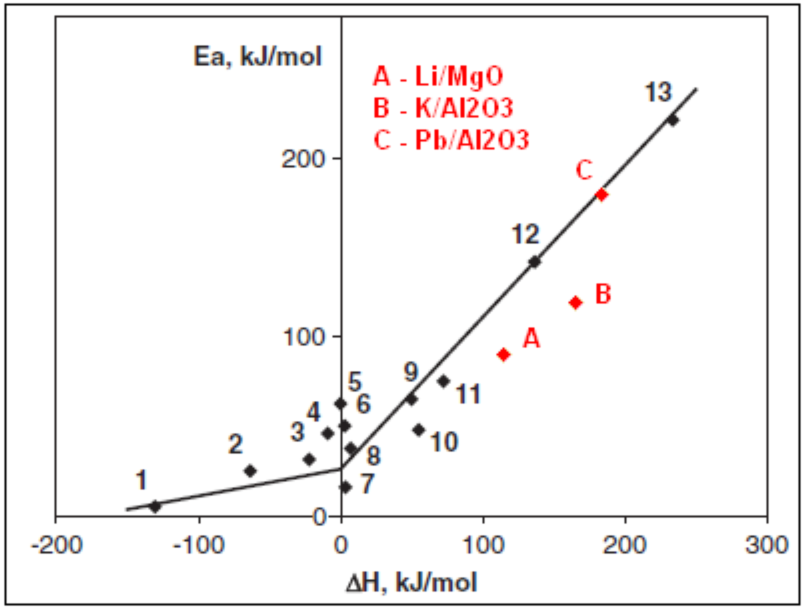

$CH_4 + X \rightarrow CH_3 + XH$ $\quad \Delta H = D_{H\text{-}X} - D_{H\text{-}CH_3}$

X = F (1); OH (2); C_6H_5 (3); CF_3 (4); CH_3 (5); H (6); Cl (7); O (8); SH (9); CH_3O (10); Br (11); I (12); O_2 (13)

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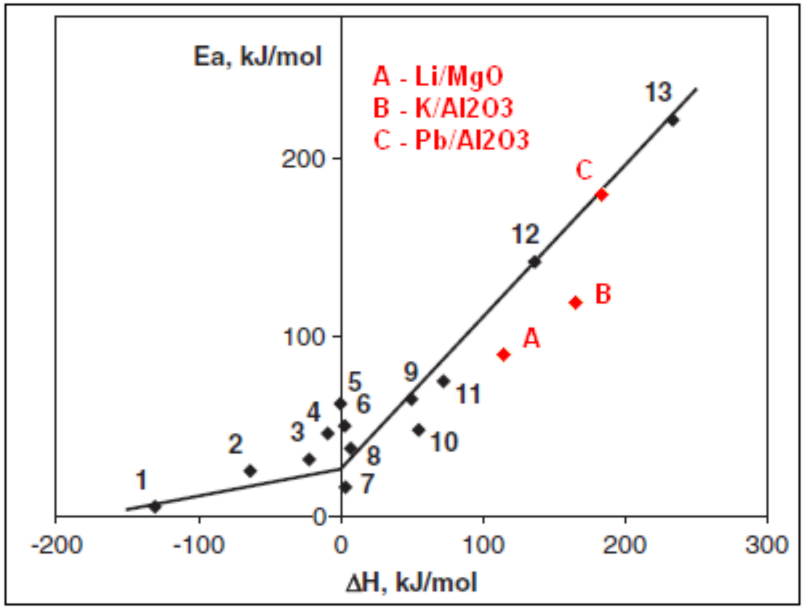

🗝 Analogy between heterogeneous and homogeneous reactions, i.e. $[O] + CH_4 \rightarrow [OH] + CH_3^{\bullet}$ is a collision-type elementary process

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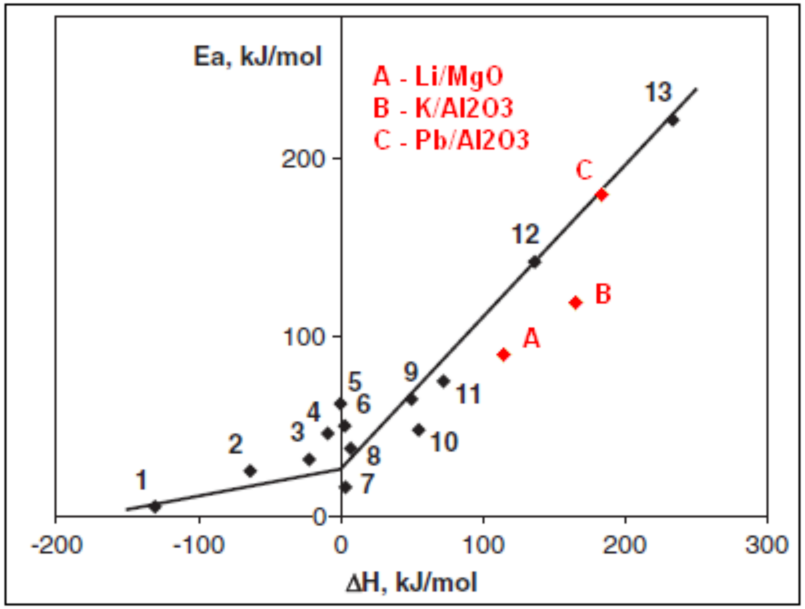

- Analogy between heterogeneous (‘gas – s.s.’) and homogeneous Interactions of the same type (e.g., H-transfer, O-transfer)

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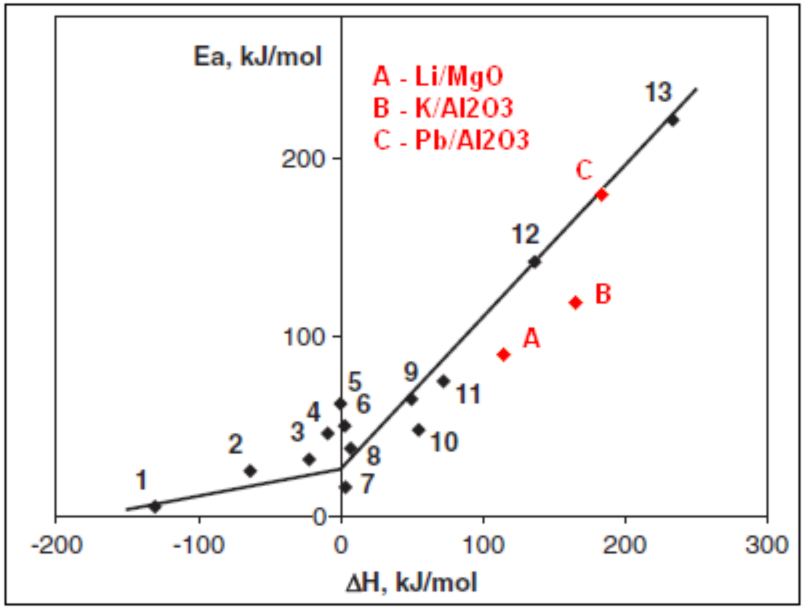

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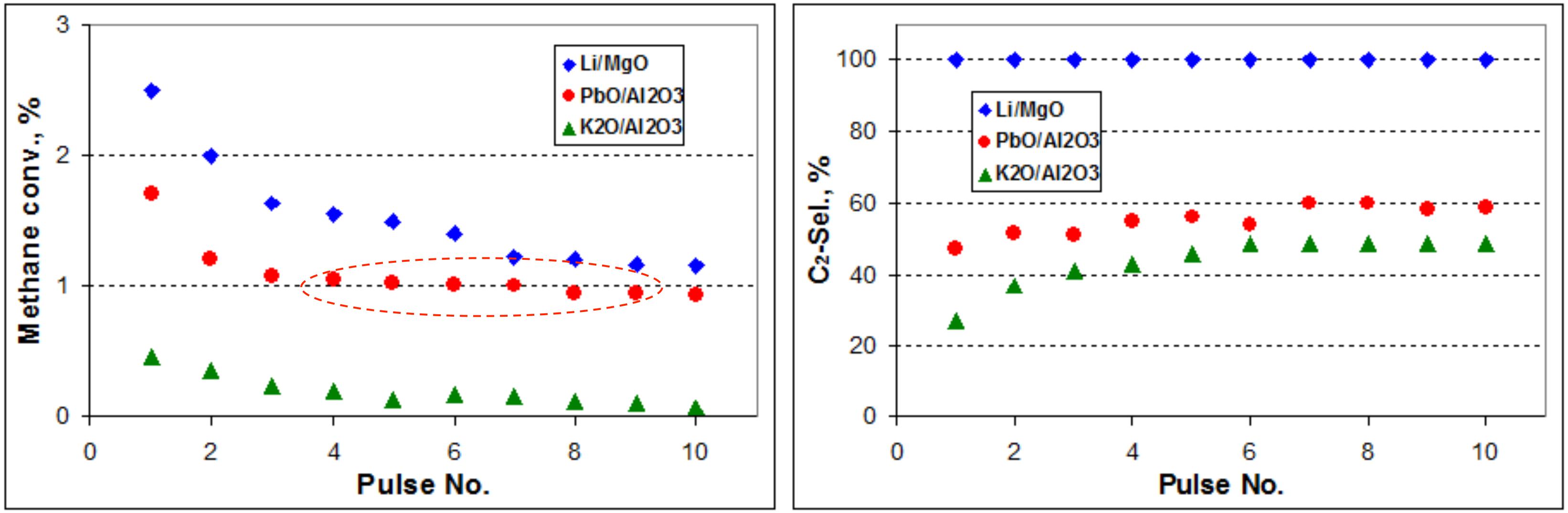
  microkinetic (multi-step) model of OCM and related processes

Case study 2: oxidative coupling of methane (3)

700°C, methane pulses onto pre-oxidized oxide catalysts



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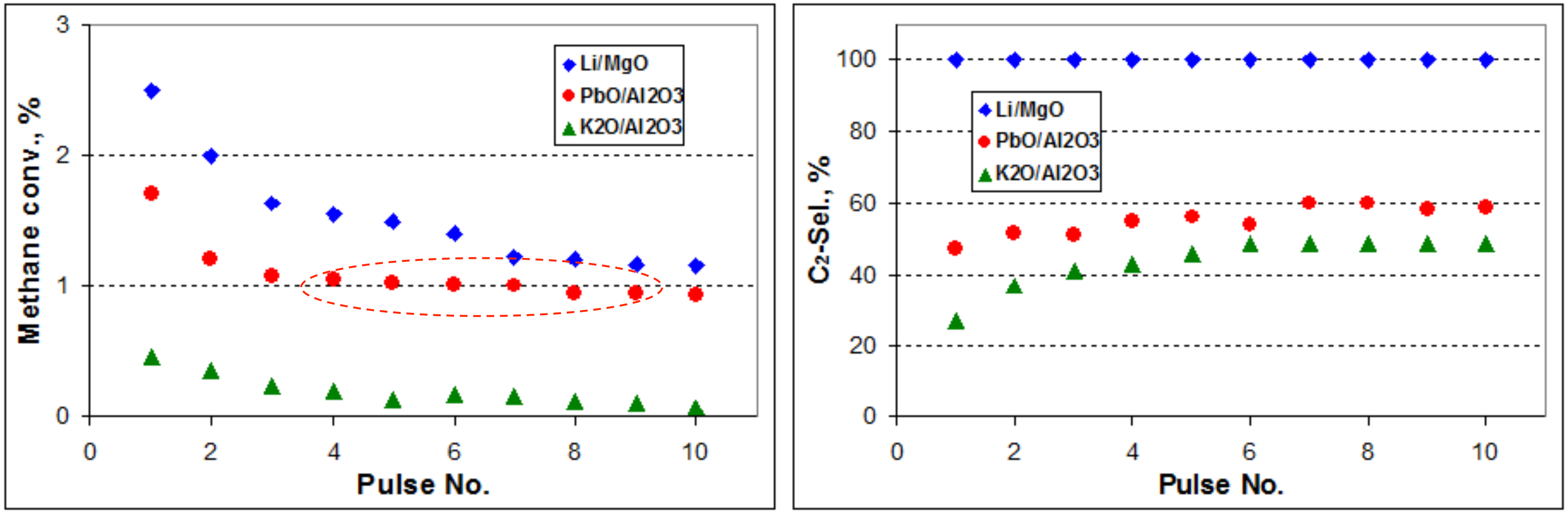

PbO/Al_2O_3 – near-steady-state - !?

Case study 2: oxidative coupling of methane (3)

Re-oxidation of PbO/Al_2O_3 at 700°C after reduction with methane pulse
(varied Δt between reduction and re-oxidation)

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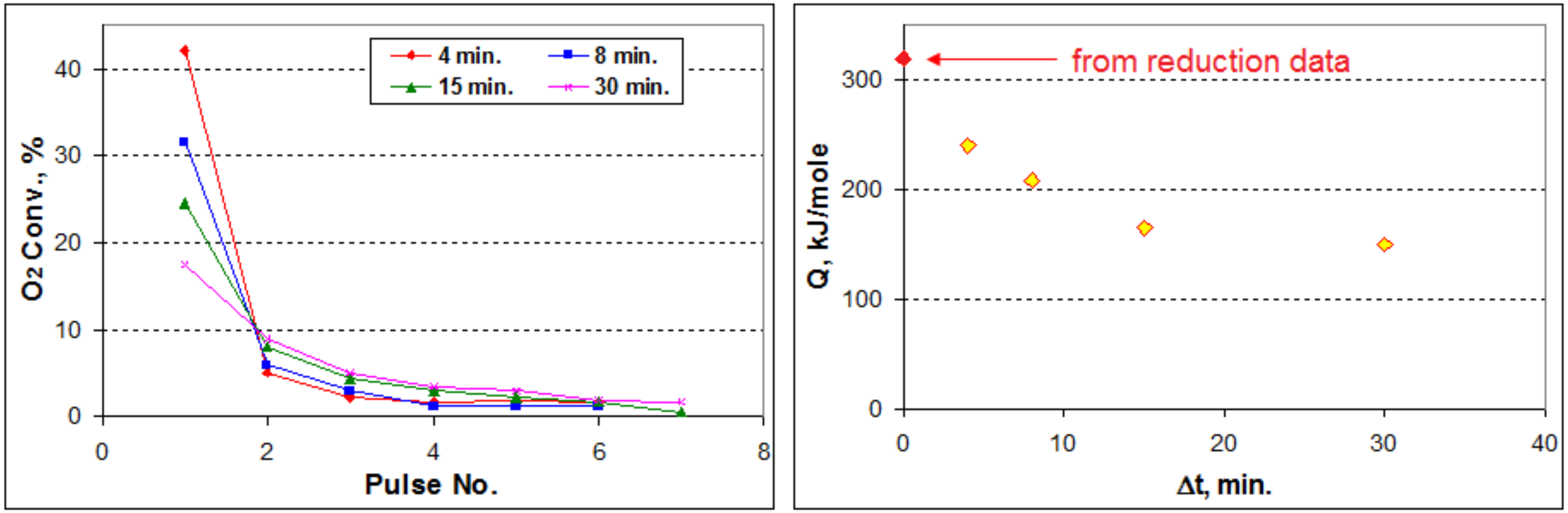

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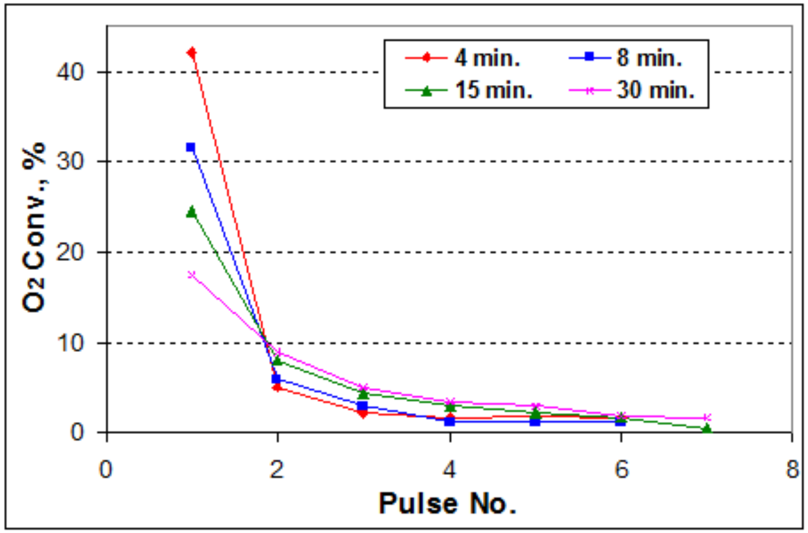

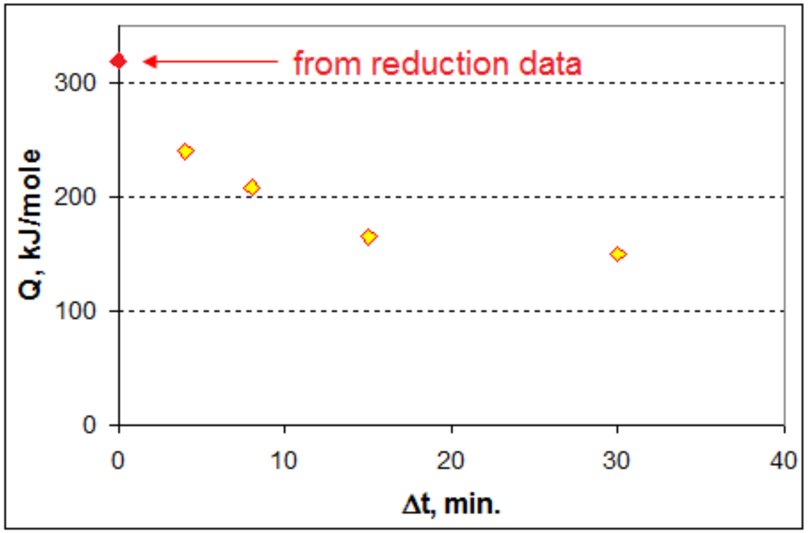

- spatial re-distribution of oxygen / energetic relaxation of reduced lattice

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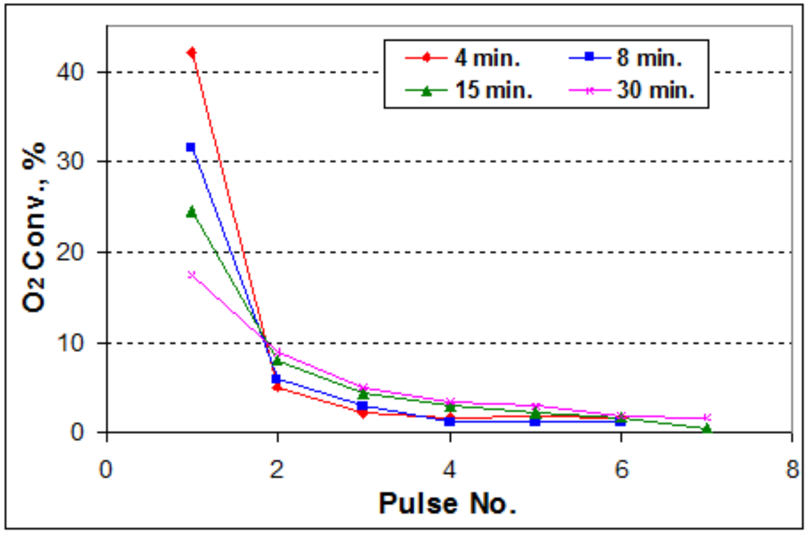

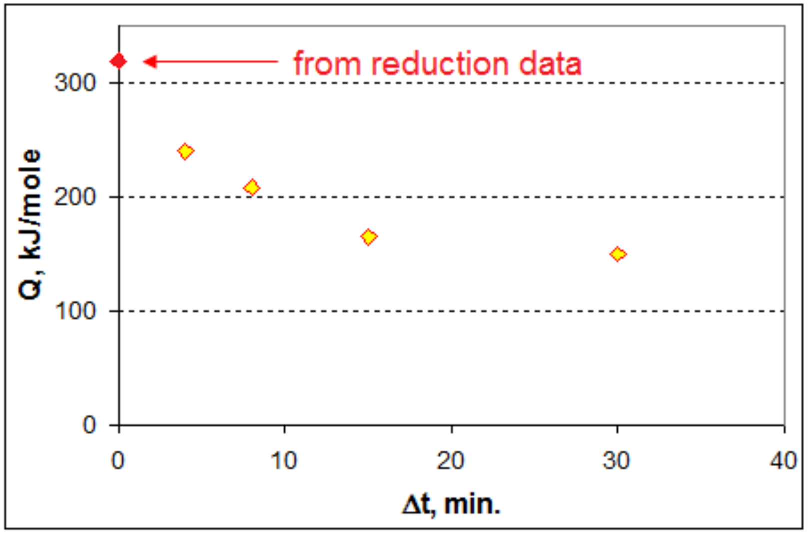

- spatial re-distribution of oxygen / energetic relaxation of reduced lattice
- 'standard' tabulated data do not reflect actual relations taking place under reaction conditions

Case study 3: oxygen storage materials (oxides)

Oxygen-storage materials –

oxides capable of reversible oxygen uptake/release

Areas of application :

- oxygen capture (deep purification of gases);
- gas sensors;
- catalysis (automobile TWC washcoat component);
- …

Key characteristics:

- oxygen storage capacity (bulk storage, i.e. lattice oxygen);
- oxygen uptake/release conditions (O-binding energy)

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| ⇒

ideal objects to study using *in situ* DSC

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Typical oxygen-storage materials –

oxides with cubic or slightly distorted cubic structure,

e.g. spinels, perovskites, fluorites, pirochlores, etc.

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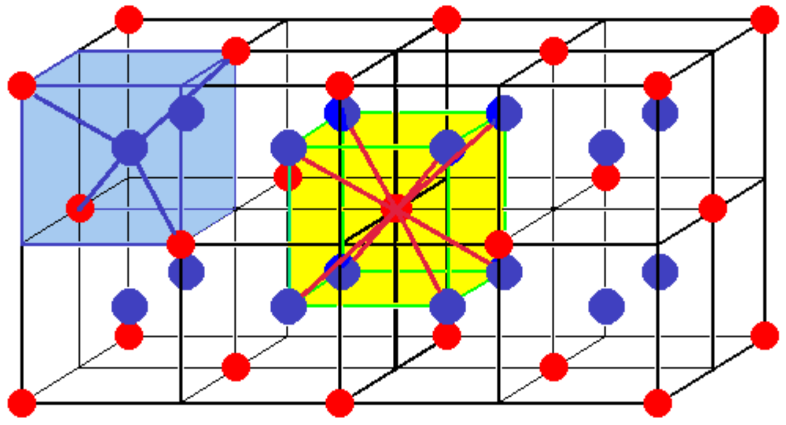

MX_2: ● M^{2n+} ● X^{n-} (n = 1, 2)

Cubic fluorites (e.g., Y/ZrO_2):

- tend to form oxygen vacancies with no restructuring;
- very fast O-transport

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$Ce_{0.55}Pr_{0.45}O_2$ – CeO_2-based cubic fluorite

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$Ce_{0.55}Pr_{0.45}O_2$ – CeO_2-based cubic fluorite

Vacuum / inert gas atmosphere, > 350°C:

$Ce(IV)_{0.55}Pr(IV)_{0.45}O_2 \Rightarrow Ce(IV)_{0.55}Pr(III/IV)_{0.45}O_{2-X} + O_2 \quad (X \leq 0.225)$

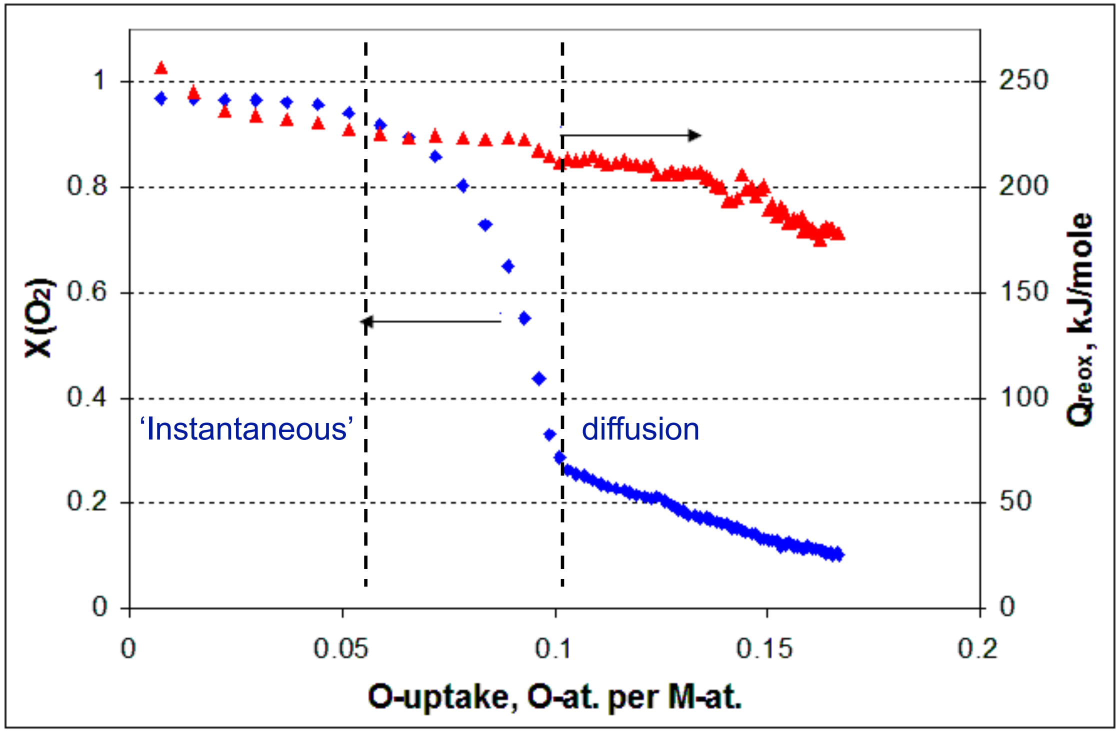
O_2-containing atmosphere, < 250°C:

$Ce(IV)_{0.5}Pr(III/IV)_{0.5}O_{2-X} + O_2 \Rightarrow Ce(IV)_{0.5}Pr(IV)_{0.5}O_{2-X}$ –

nearly instantaneously

Case study 3: oxygen storage materials (oxides)

Pulse re-oxidation of $Ce_{0.55}Pr_{0.45}O_2$
after O-removal in He at 500°C



🗝 different character of O-uptake kinetics on different stages

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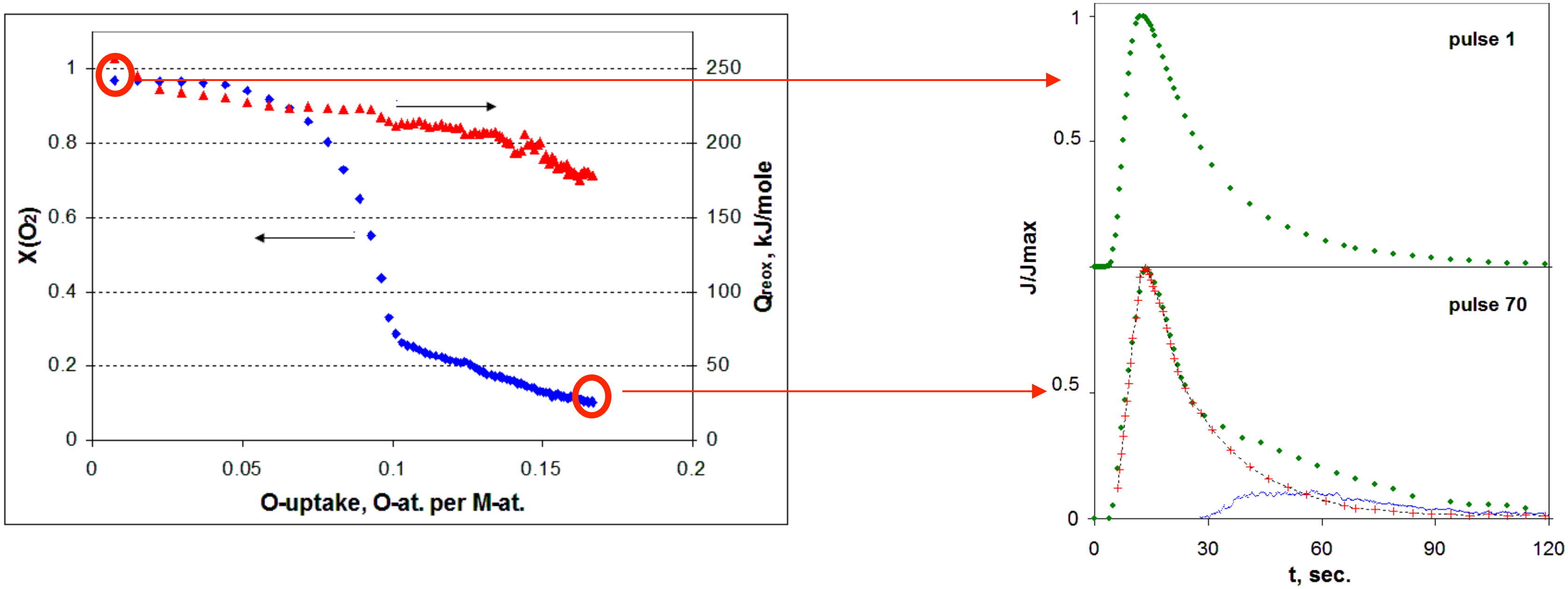

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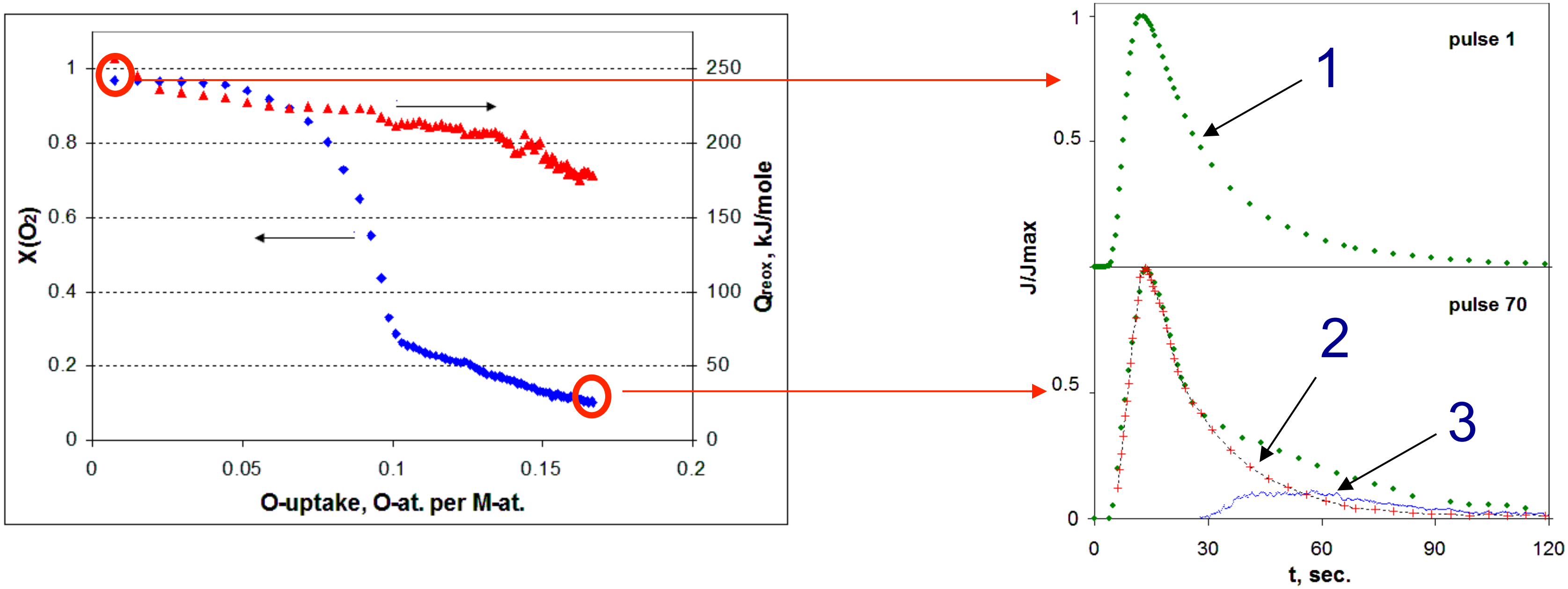

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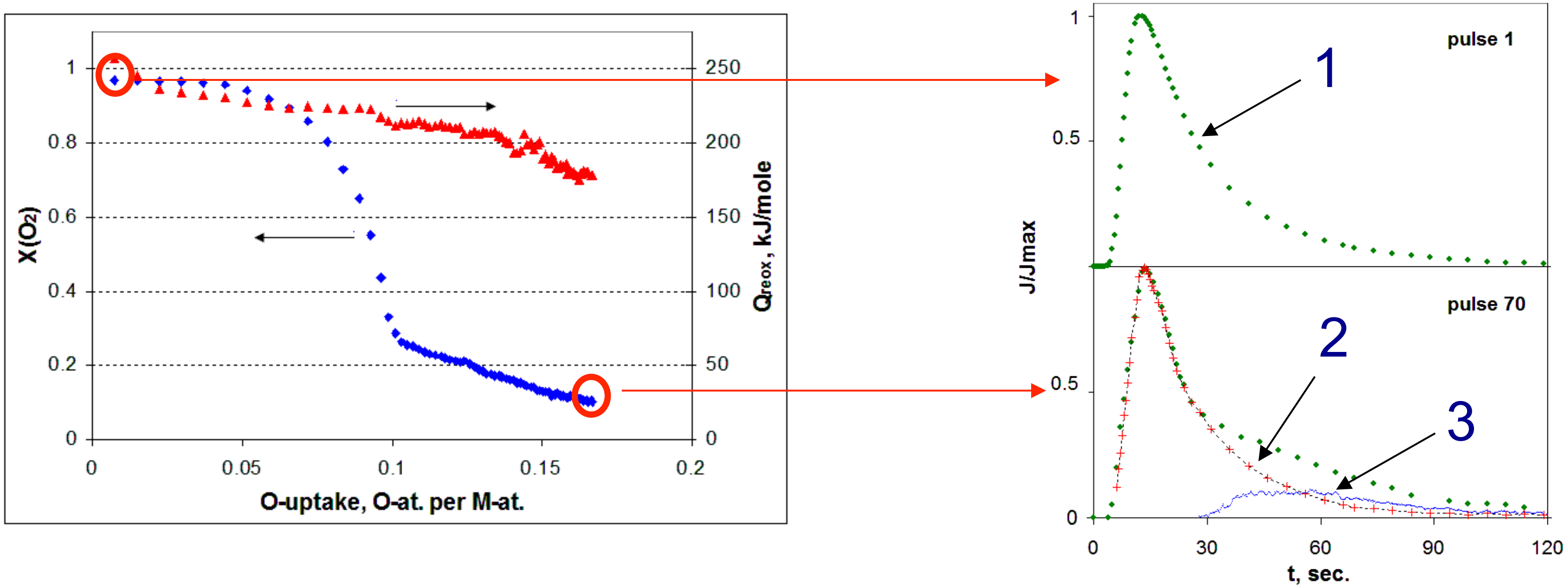

1 – rapid uptake on ‘strong’ surface sites
2 – rapid uptake on ‘weak’ surface sites
3 – slow re-distribution from ‘weak’ surface to ‘strong’ bulk sites

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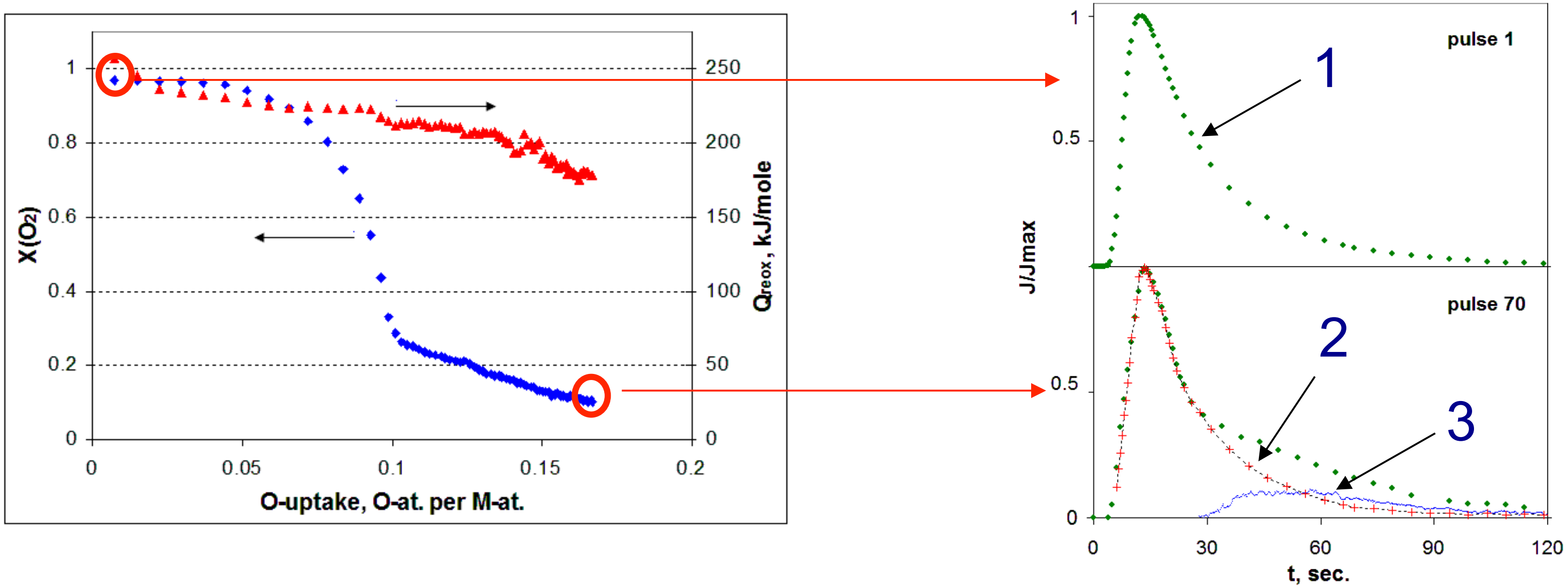

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2 – rapid uptake on ‘weak’ surface sites
3 – slow re-distribution from ‘weak’ surface to ‘strong’ bulk sites

DSC provides with ‘visualization’ of O-redistribution (surface to bulk)

Summary & Concluding remark

1. Direct measurements of thermal effects accompanying interactions of reactants with solid catalysts is a valuable tool that allows one to reveal the role of energy factor(s) in catalytic reactions

2. Like any other method, *in situ* DSC has specific applications, as well as its own advantages and limitations; in some cases it provides with a unique information about dynamic behaviour of oxide systems and valuable complementary information about reaction mechanism(s)

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Combining of calorimetric measurements with other (structure-sensitive) techniques is highly desirable

Acknowledgement

Prof. Oleg V. KRYLOV✝

Dr. Viktor Yu. BYCHKOV

Lecture Series

Heterogeneous Catalysis

Thank You for Your Attention!