Part A: Operando FT-IR Studies of heterogeneous catalytic reactions: pitfalls and benefits.

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cnrs dépasser les frontières

***Operando* FT-IR Studies of heterogeneous catalytic reactions:**

1. **Pitfalls**
2. **Benefits.**

Pitfalls:

- **Temperature control**
- **flow control**

in IR reaction cells

Catalytic reactor and spectroscopic IR cells

U-shaped quartz reactor
in a tubular furnace

Transmission IR cell
(ca. 20 mg wafer)

Heat loss through IR windows

Diffuse reflectance IR cells

Harrick
(powder, up to 80 mg)

Modified Spectra-Tech
(powder, up to 60 mg)

Measure-thermocouple positioning

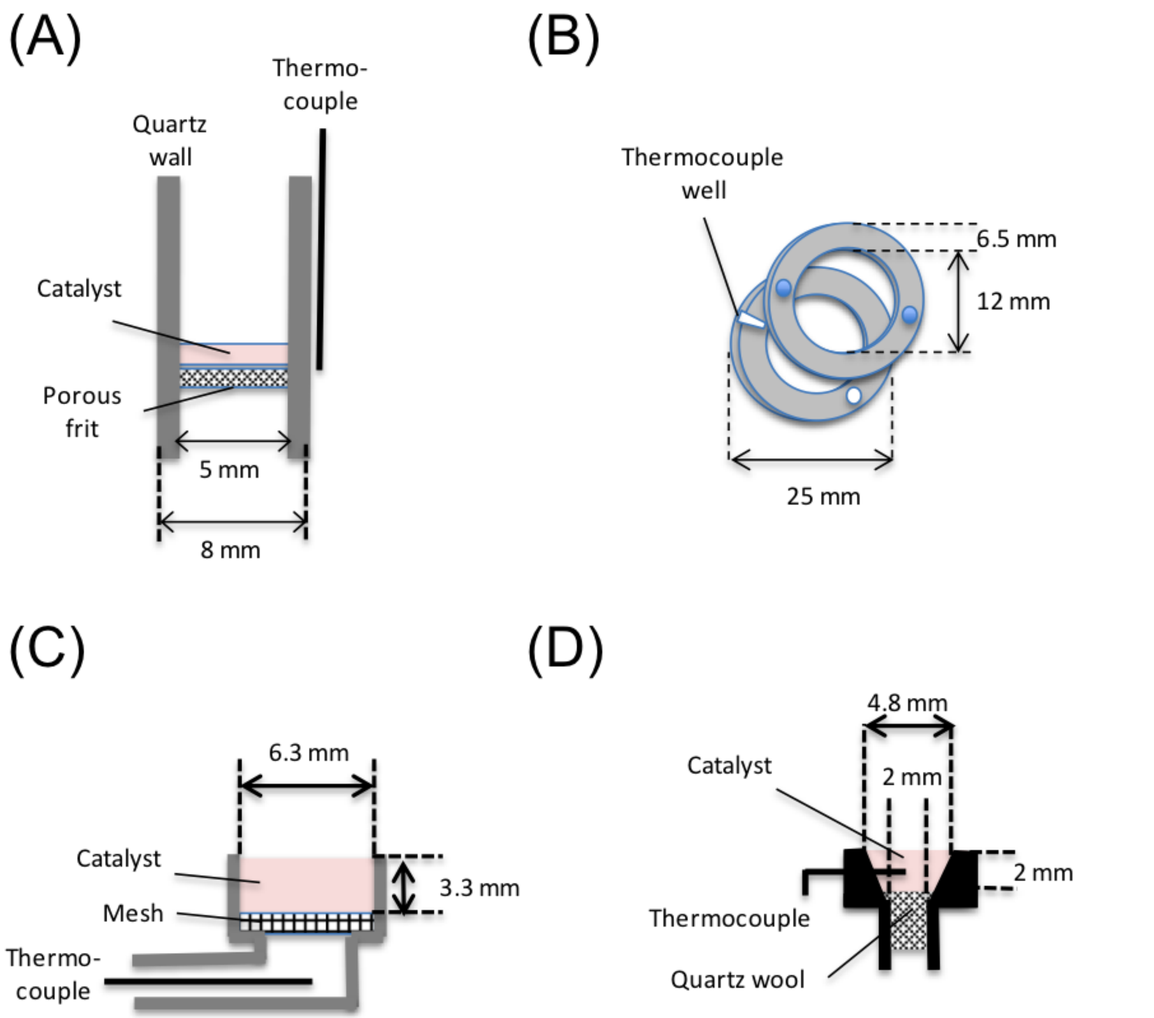
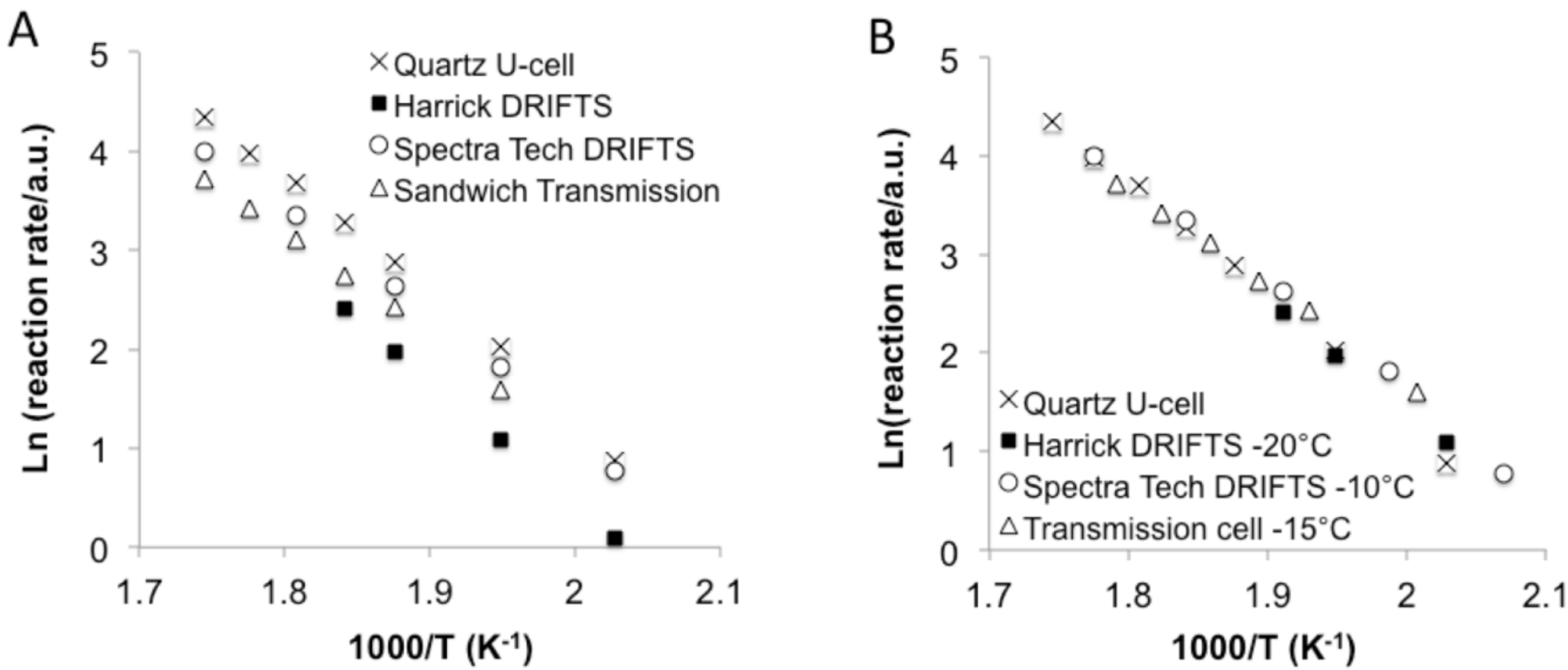


Figure 1. Schematic representation of the various sample beds used in this study: (A) in the U-shaped quartz reactor, (B) in the "Sandwich" transmission cell, (C) in the Harrick DRIFTS cell and (D) in the Spectra-Tech DRIFTS cell

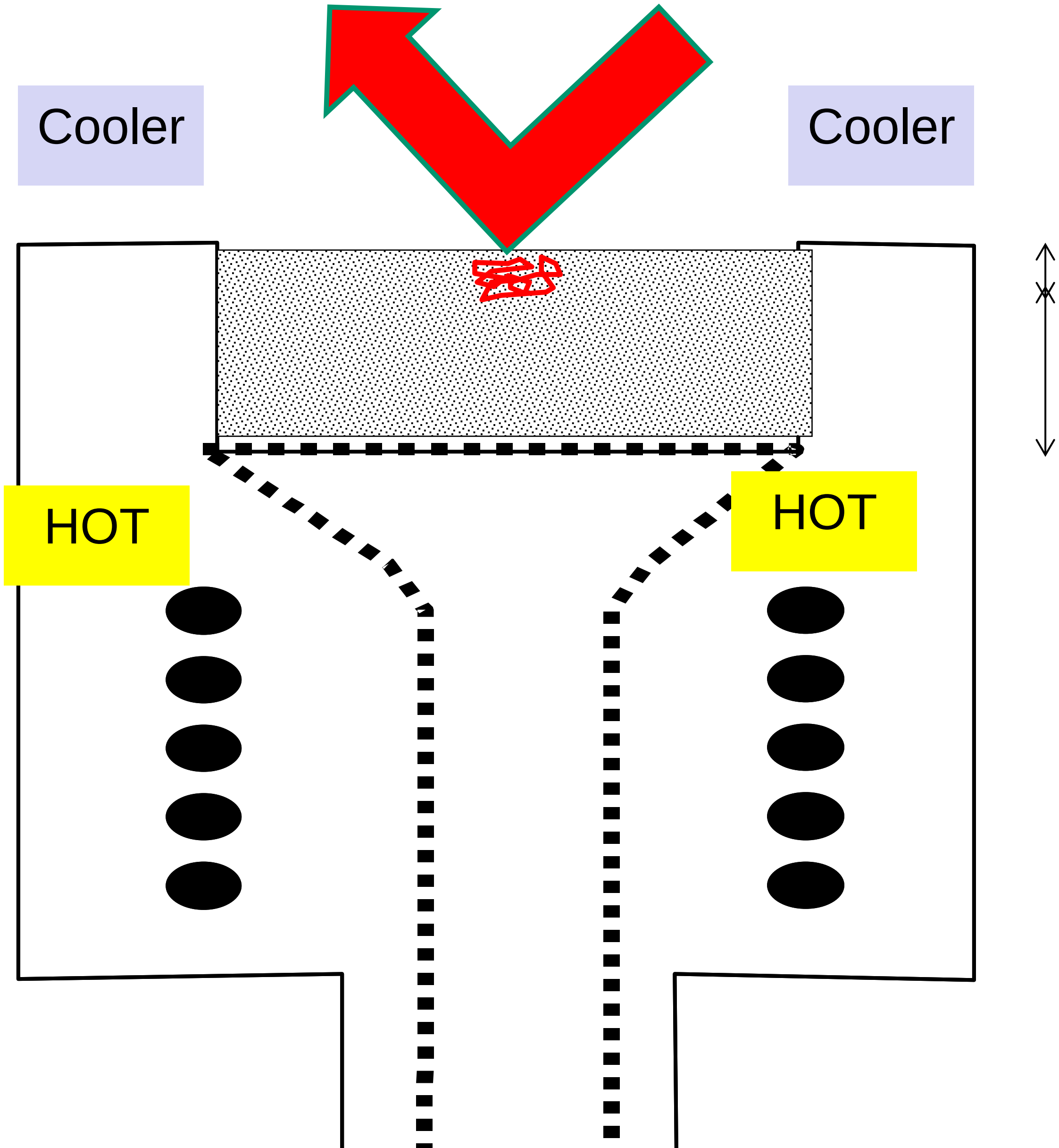
CO methanation as a “bulk temperature probe”



IR cells bed “cooler” than expected

Figure 3. (A) Arrhenius-type plots relating the natural logarithm of the reaction rate of CO methanation to the reciprocal temperature. (B) Same plots as (A), except that the reaction temperature of the IR cells was corrected by the value given in the legend. Feed 10% CO + 35% H_2 in Ar.

DRIFTS: bed surface (top) temperature



Typical analysis depth:
< few 100 μm

Bed depth: 2-5 mm

Surface temperature by optical pyrometry

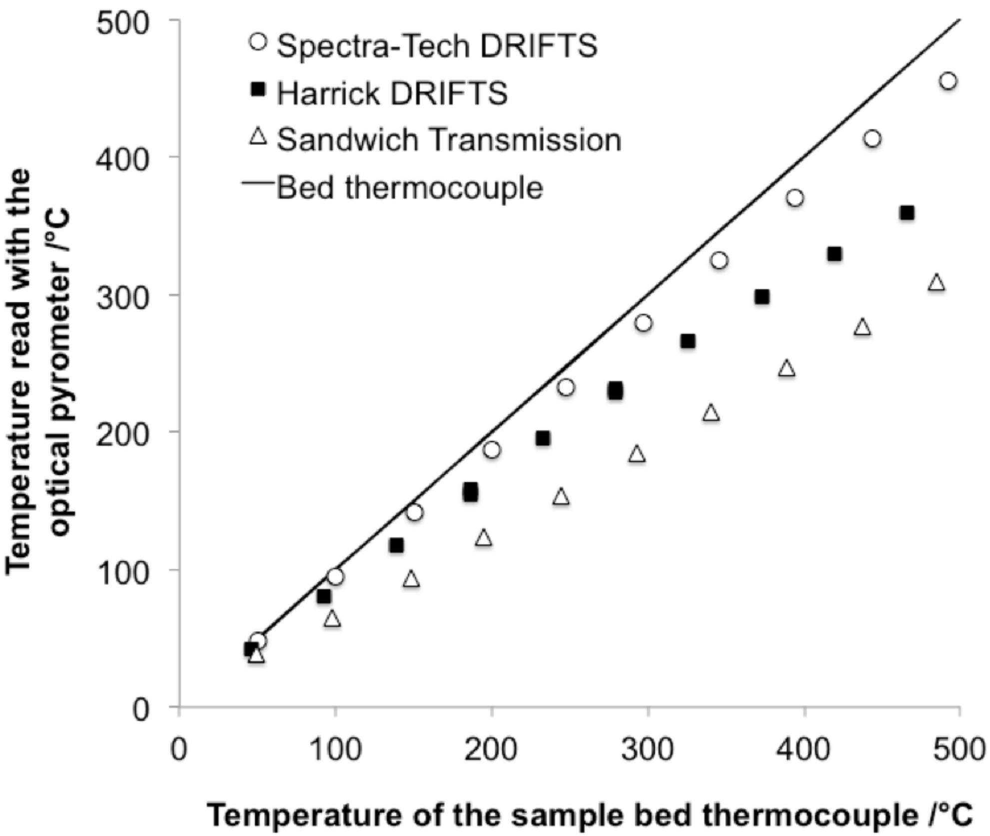
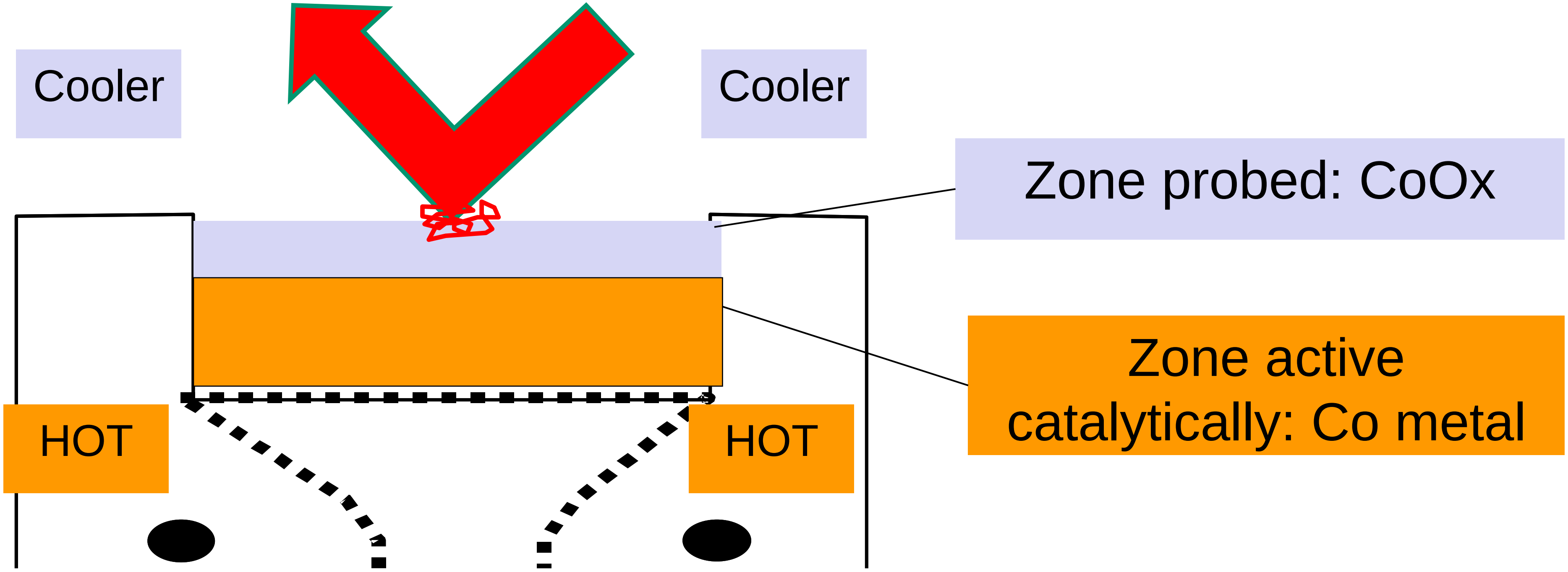


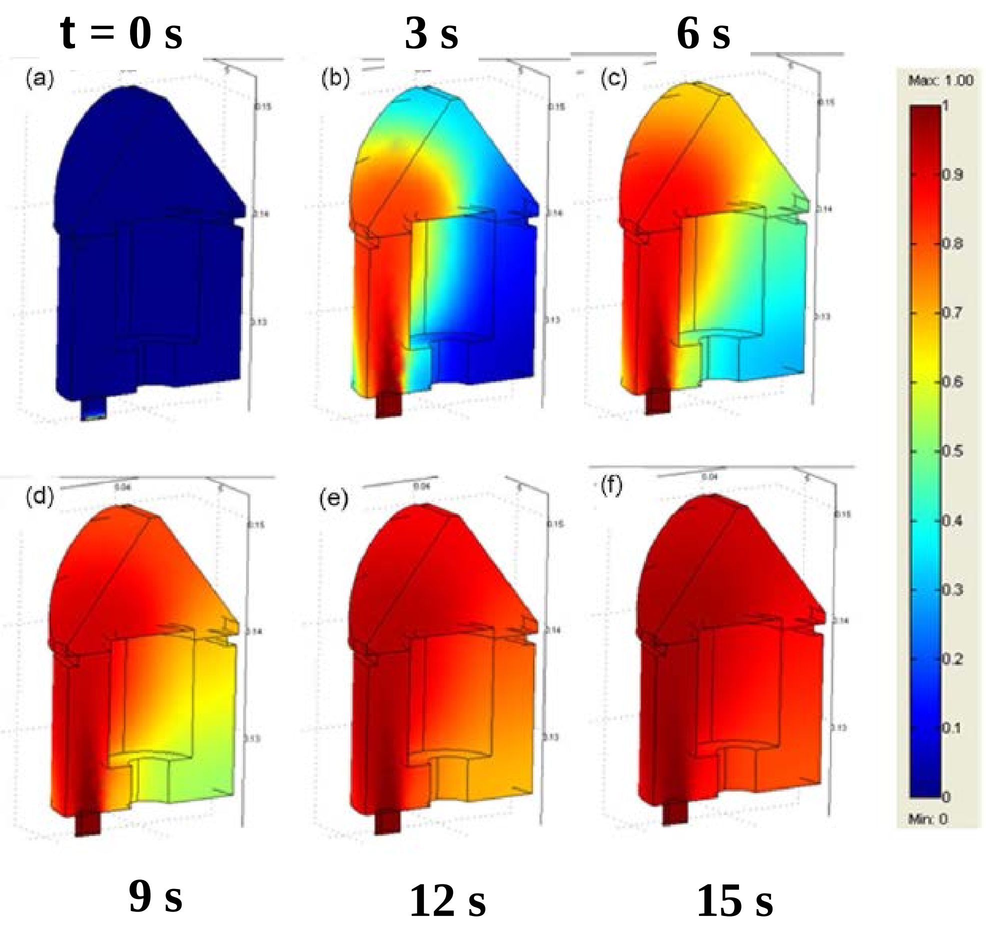
Figure 6. Comparison of the temperature read using the optical pyrometer on the various IR cells and the corresponding sample bed temperature. The sample bed temperature was measured with a thermocouple located in the cell as described in Table 1 and Fig. 1. The optical pyrometer was held at about 20 cm from the sample bed filled with the powdered form (for the Spectra-Tech and Harrick DRIFTS cells) and a self-supported wafer (in the case of the Sandwich transmission cell) of the Ni/alumina

DRIFTS cells
bed surface
"much cooler" than expected at High T

Supported CoOx for CO hydrogenation in custom-made DRIFTS cell: reduction at 450°C?



Spectra-tech DRIFTS cell hydrodynamics: "ill-defined" reactor



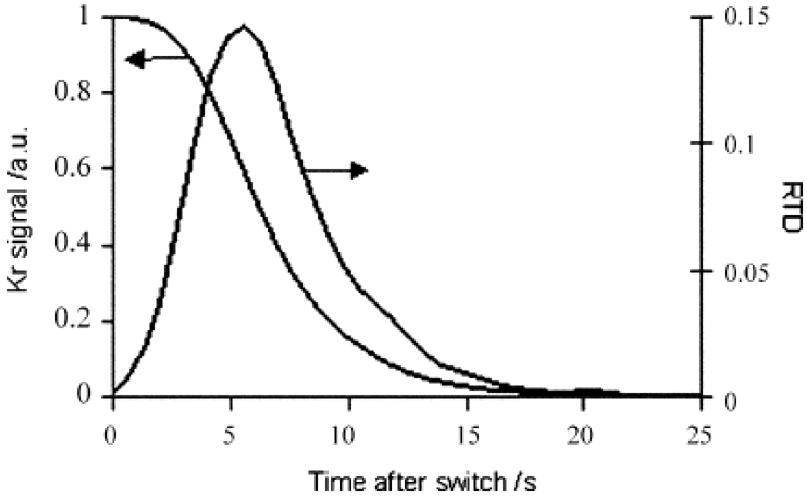
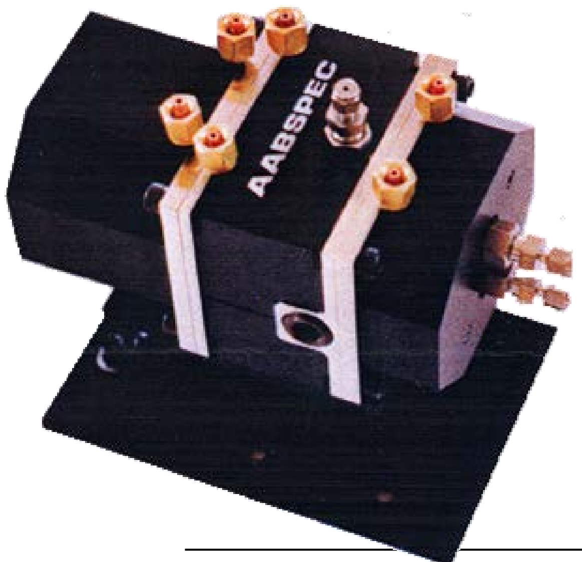


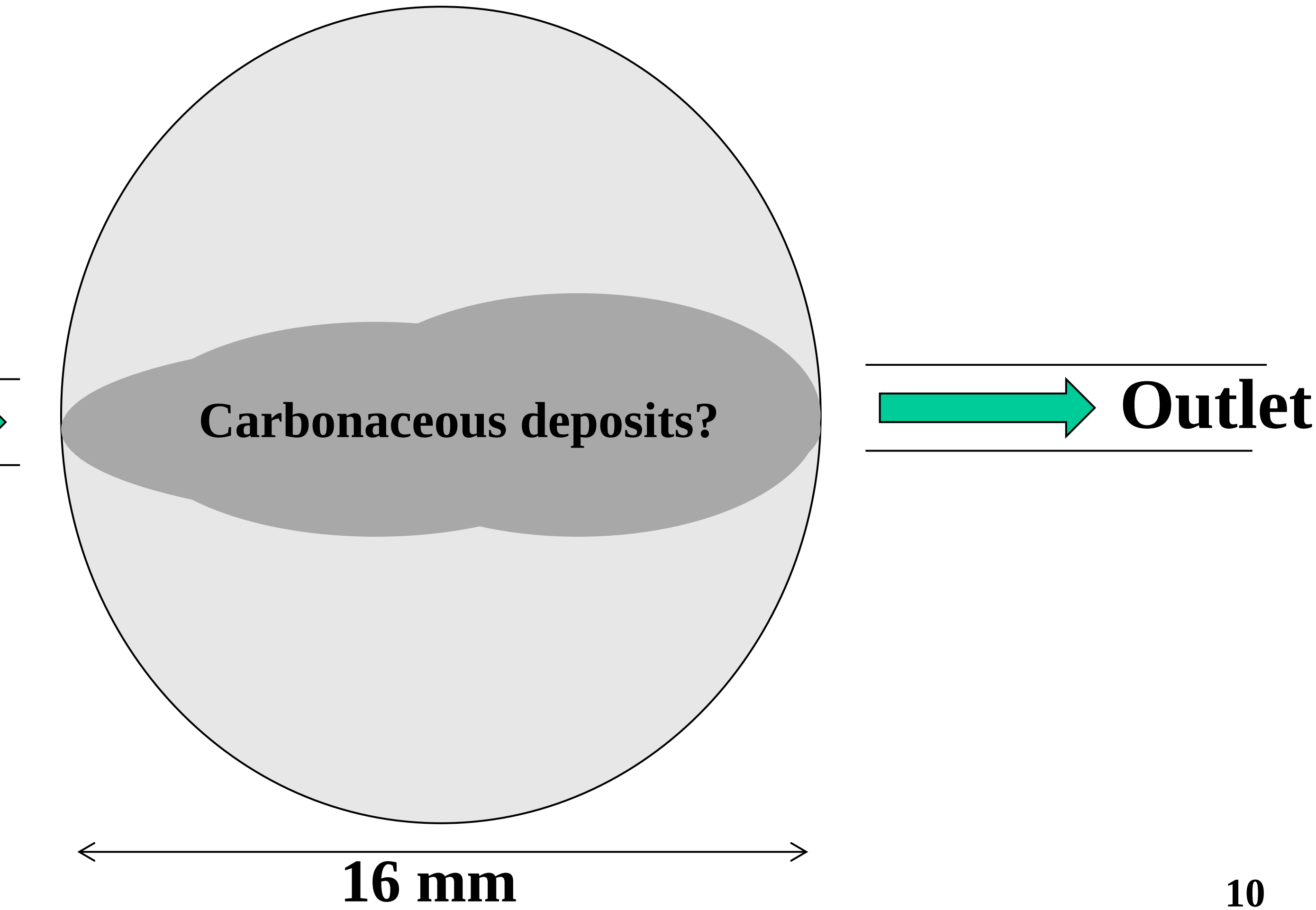
Fig. 4. Kr mass spectrometer signal during a switch from 2% Kr/Ar to pure Ar and the corresponding normalized residence time distribution (RTD). The total flowrate was always 100 ml min^{-1}.

Meunier et al., Appl. Catal. A 340 (2008) 196

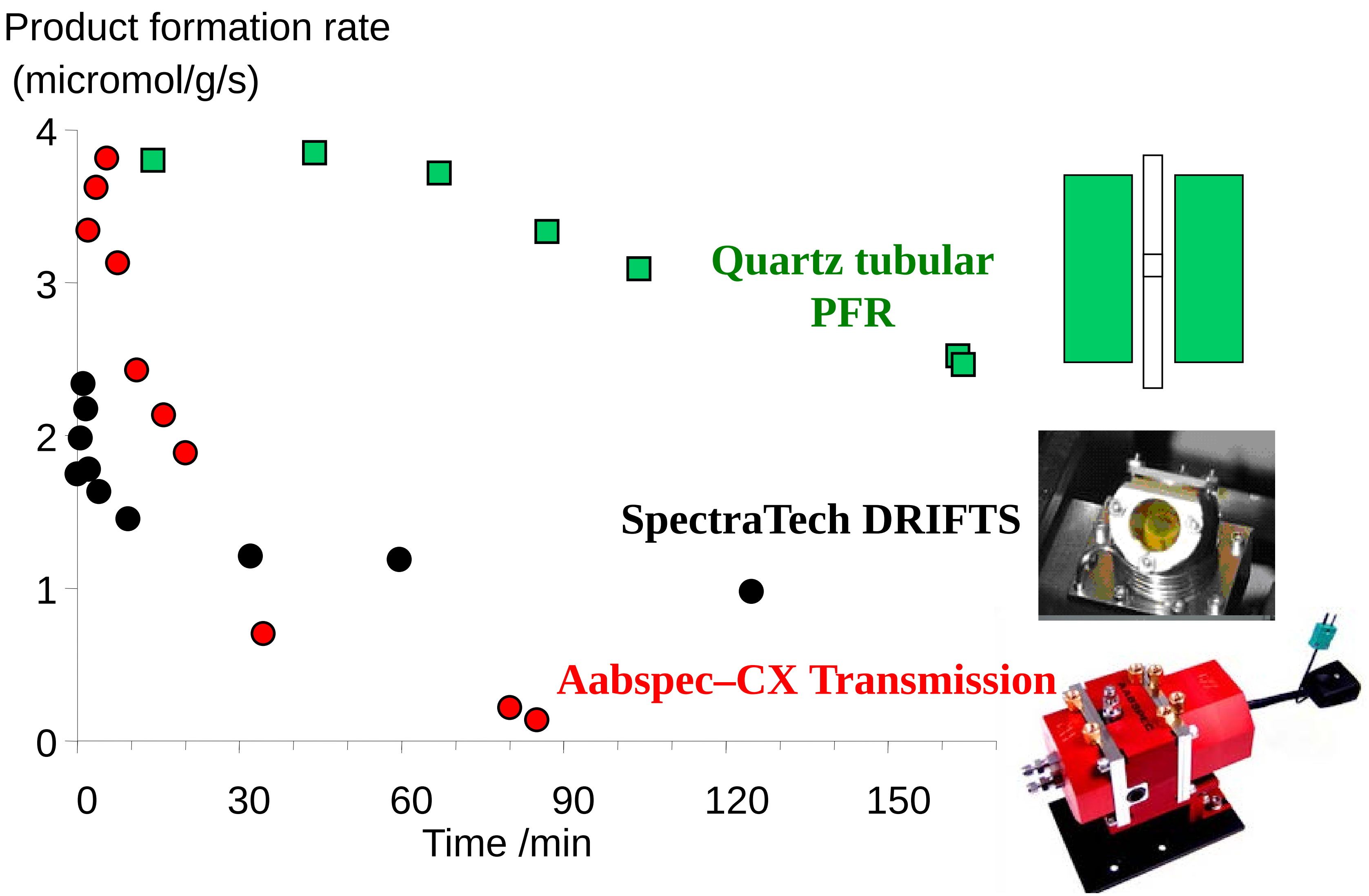
Artistic impression of a post-experiment wafer (NOx storage-Reduction)

Aabspec



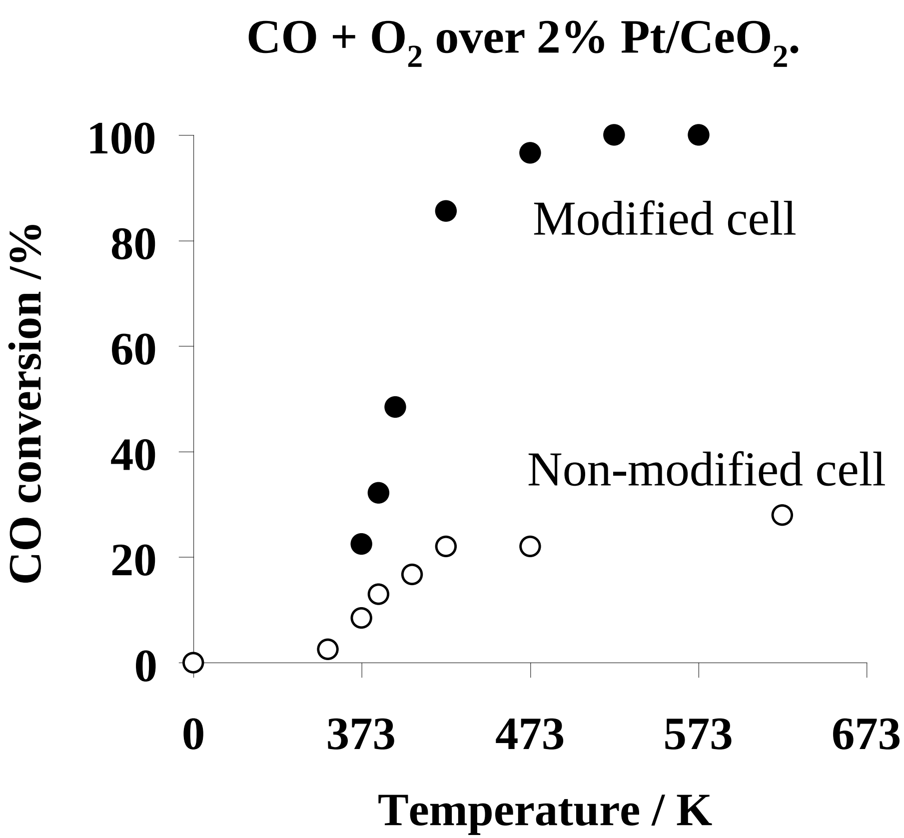


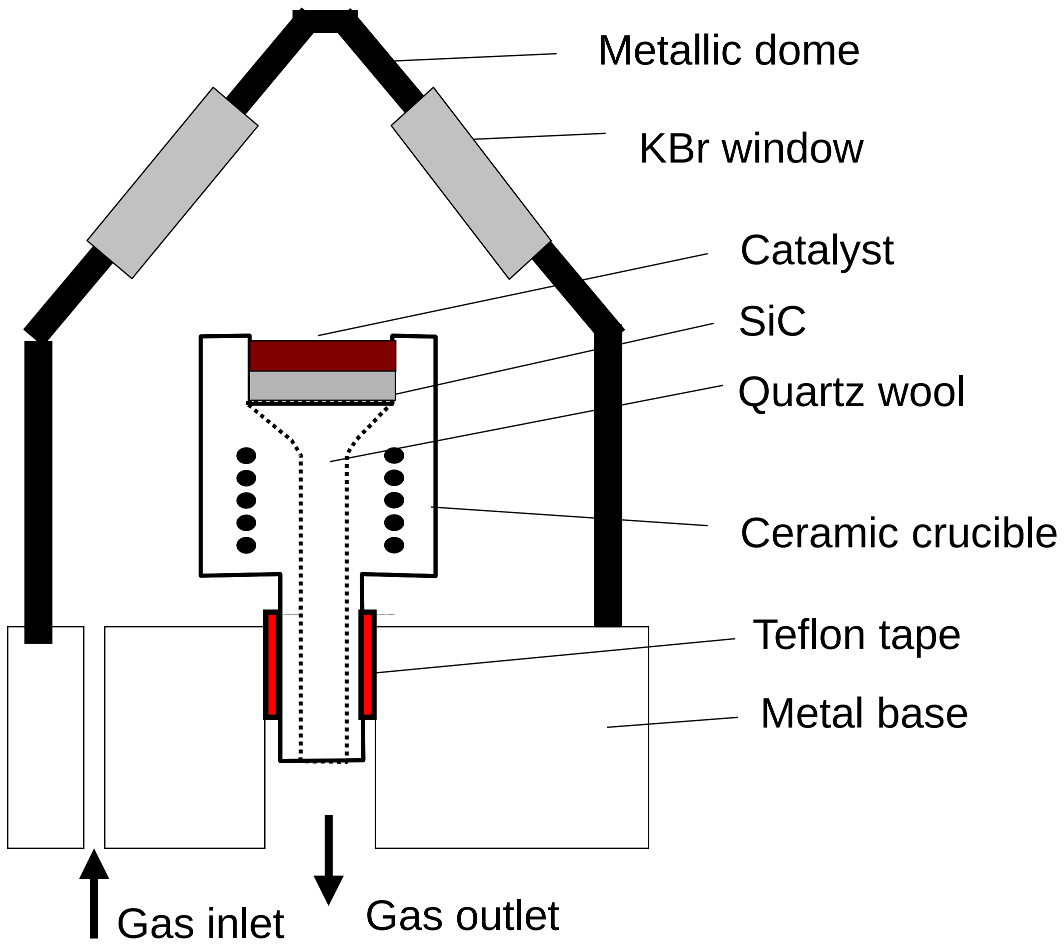
Alcohol condensation at 300 °C using the same catalyst



Temperature (mis)control and bad hydrodynamics?

Modified DRIFTS cell from Spectra-Tech.





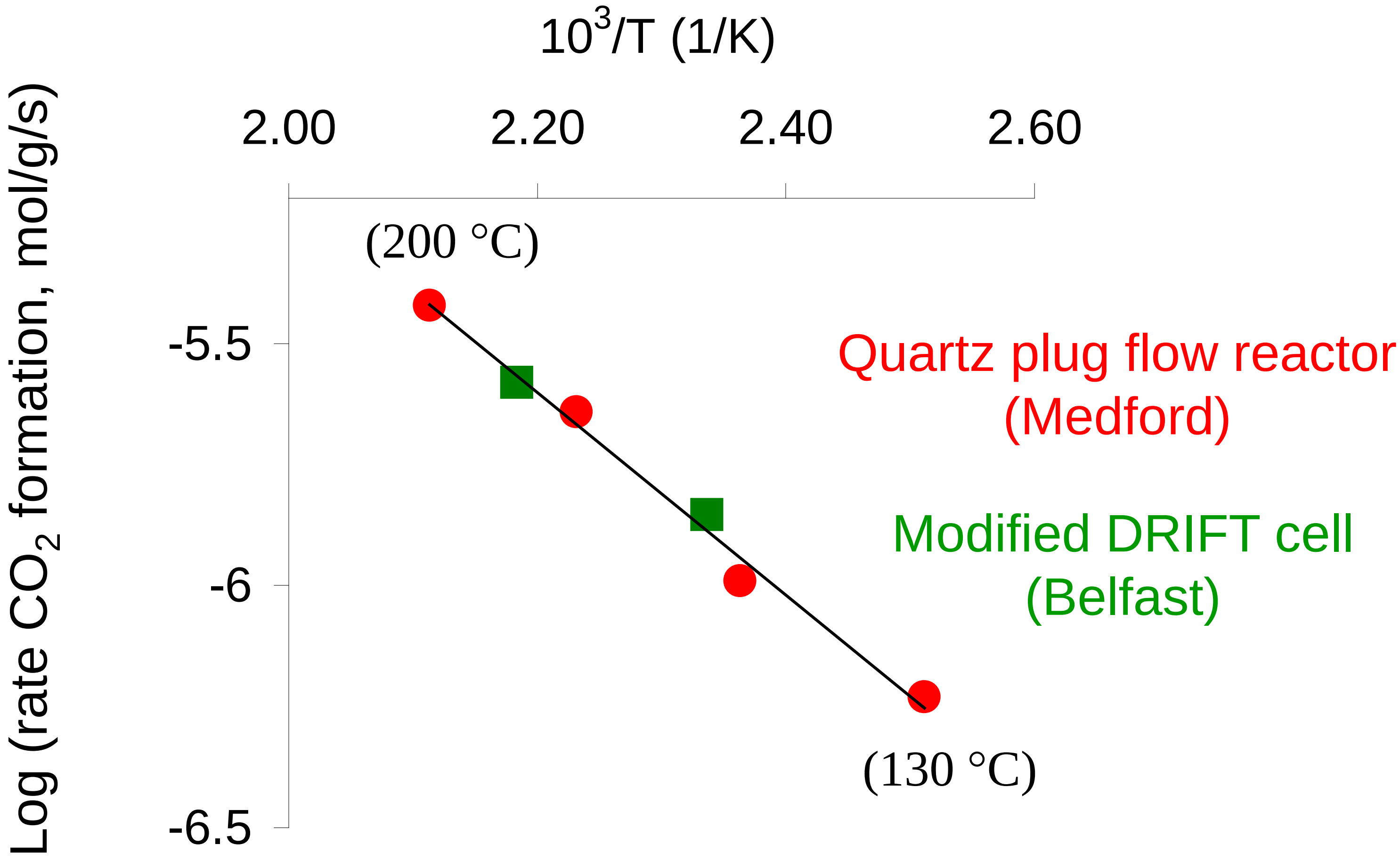
Meunier et al., Appl. Catal. A 340 (2008) 196

Validation of modified DRIFTS cell

Meunier et al., Appl. Catal. A 340 (2008) 196

J. Catal. 247 (2007) 277

Au-Ce-La-O catalyst
Water-gas shift: 2 % CO + 7 % H_2O



Ensure kinetic relevance of the IR cell-based data

Validation of modified DRIFTS cell

CO hydrogenation (30% CO + 60 % H_2 at 1 bar) on 14 wt.% Co (8 nm) /Al_2O_3 : TOF = 14 x 10^{-3} s^{-1}

DeJong et al.., J. AM. CHEM. SOC. 2006, 128, 3956

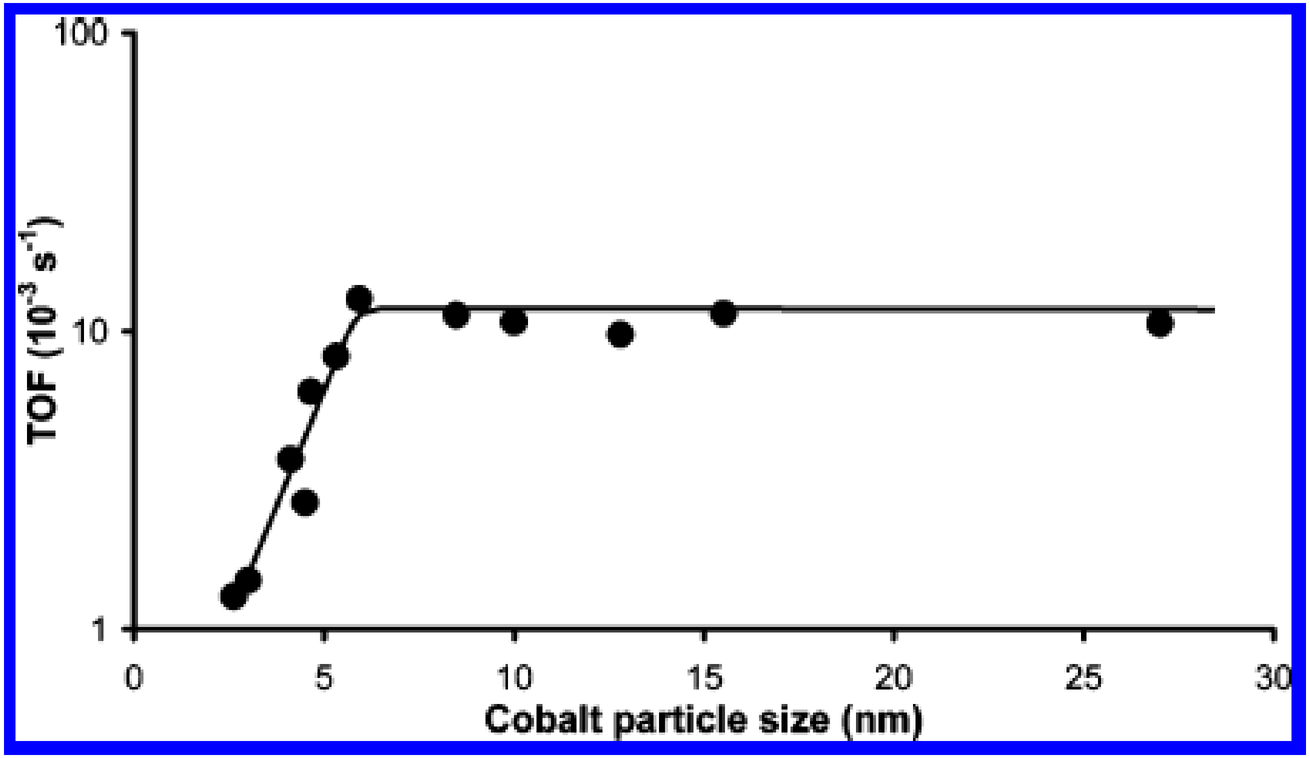


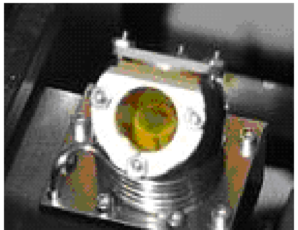
Figure 8. The influence of cobalt particle size on the TOF (220 °C, H_2/CO = 2, 1 bar).

Operando FT-IR Studies of heterogeneous catalytic reactions: pitfalls and benefits.

Benefits:

- transport in zeolites
- CO heat of adsorption
- catalyst surface poisoning
- adsorbate reactivity

Isooctane transport in large and small H-ZSM-5

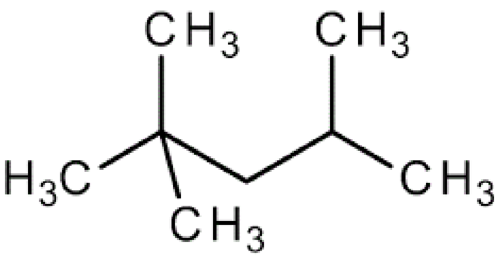


1 mg powder is enough!

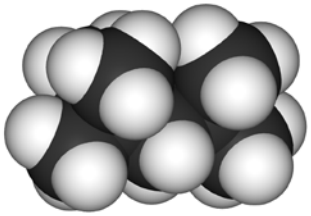
17 µm

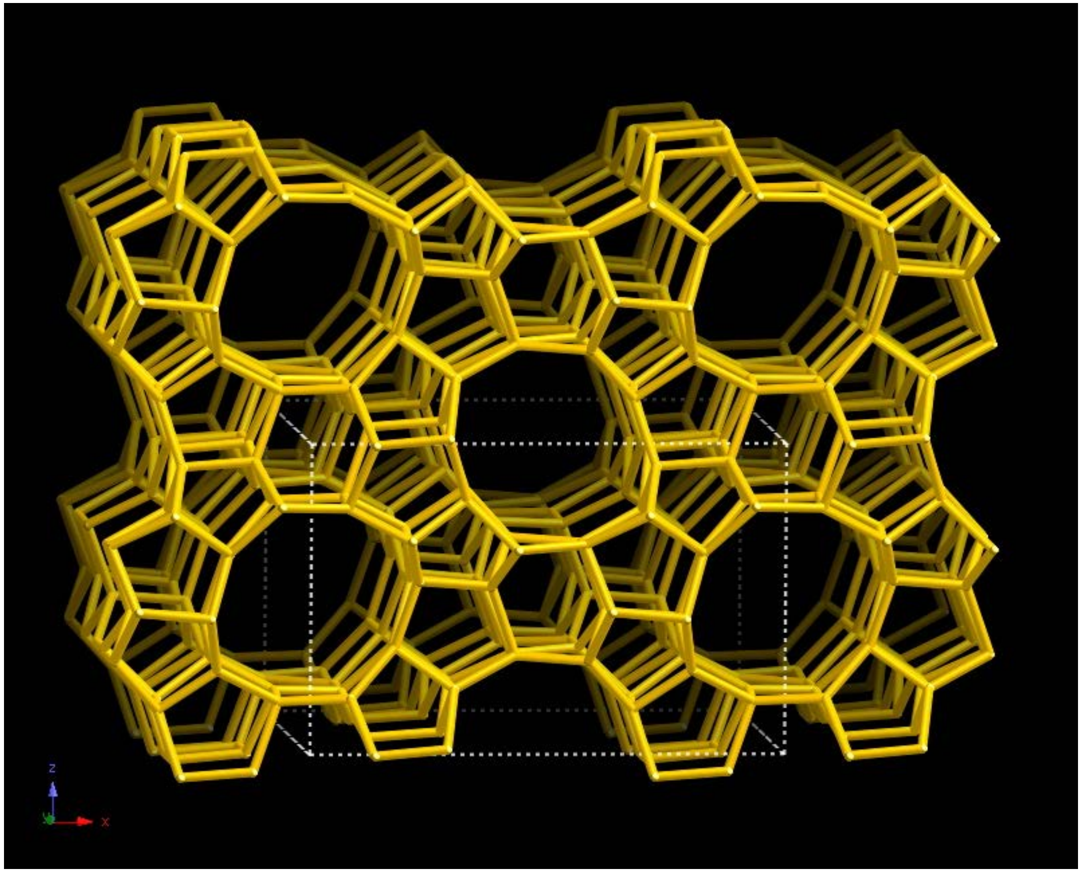
0.25 µm

H-ZSM-5: pore diameter ca. 0.55 nm

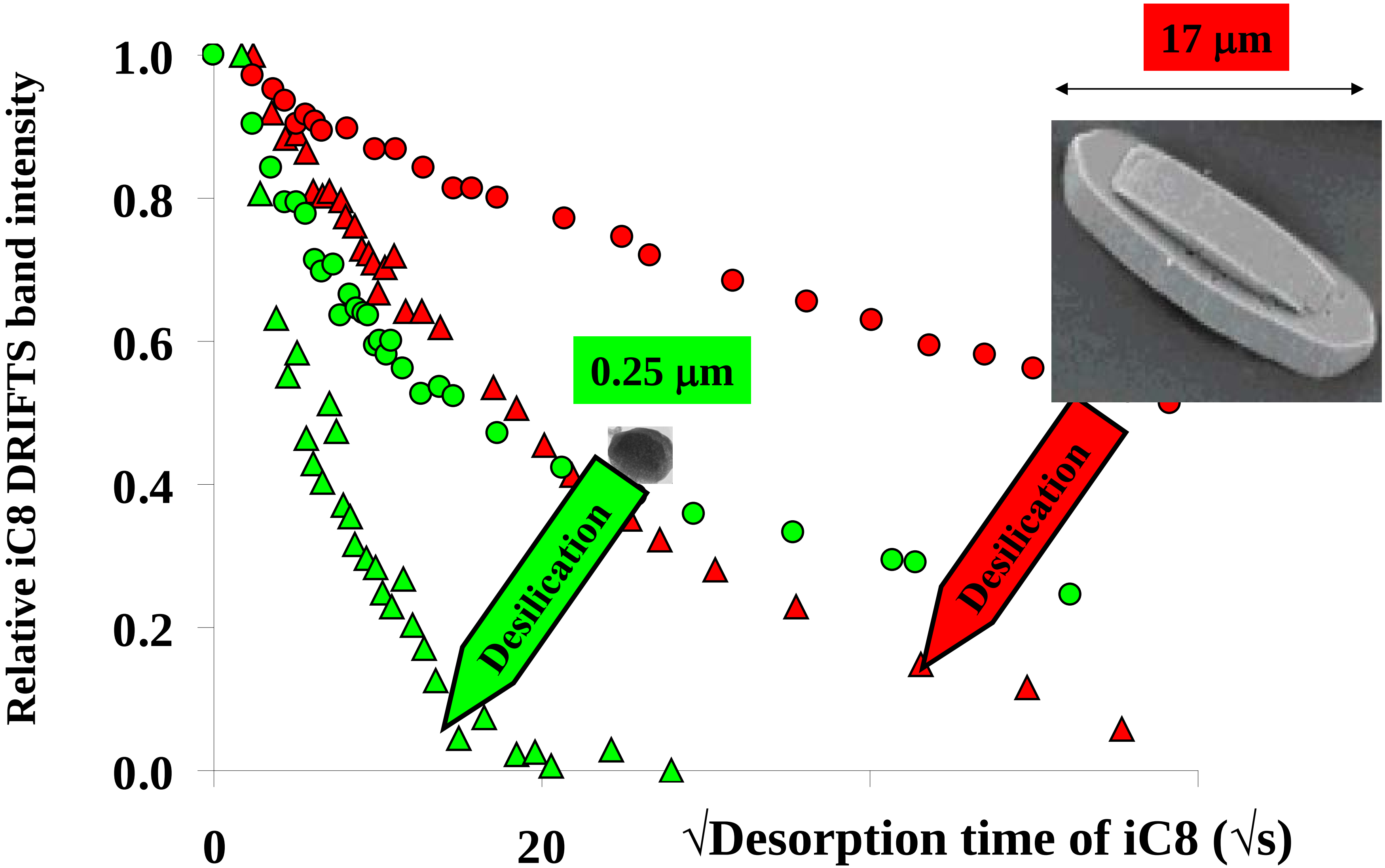


kinetic diameter
= 0.62 nm





Isooctane in H-ZSM-5: effect of mesoporosity

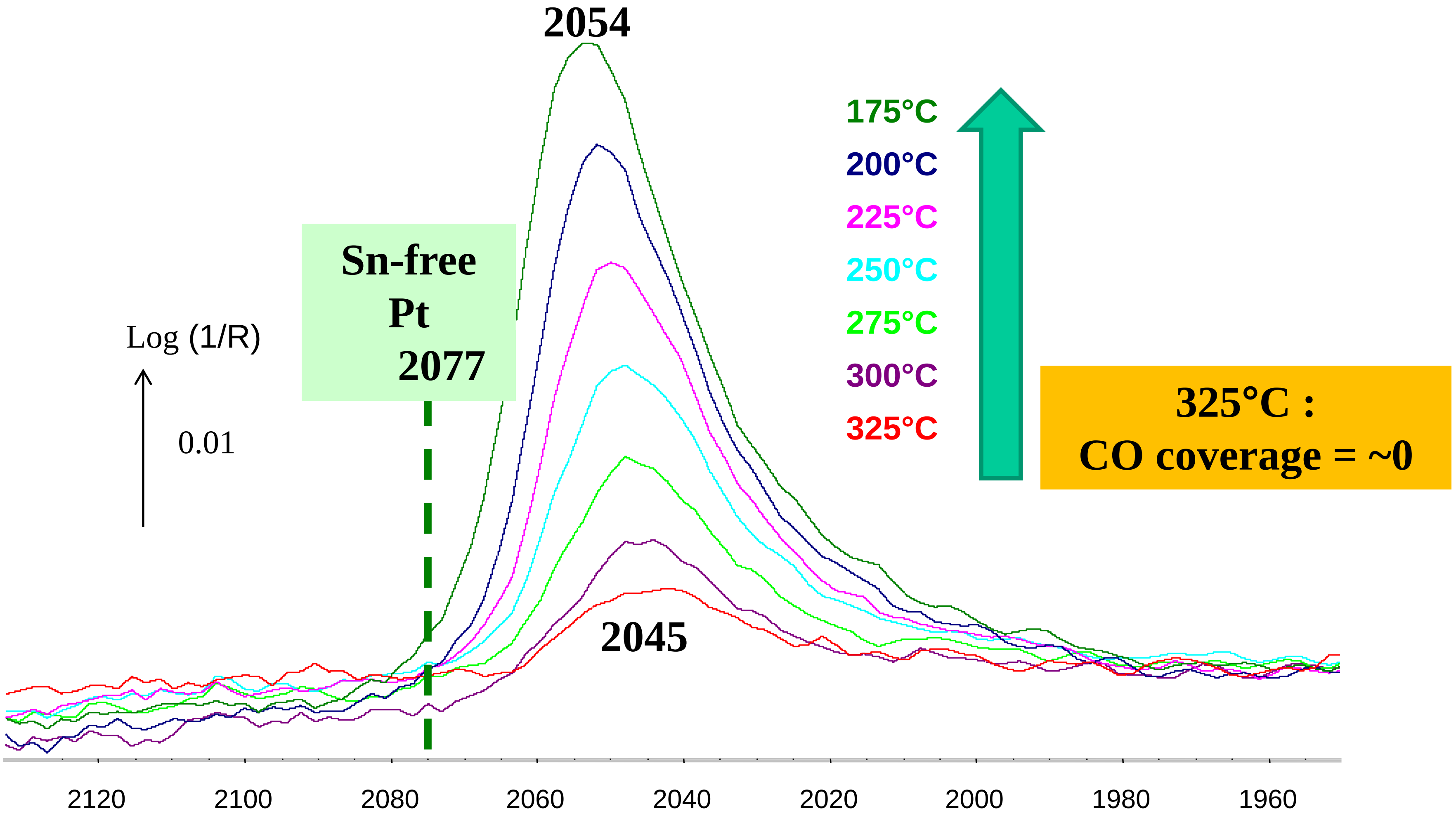


***ca.* 4-fold reduction in the characteristic diffusion path length**

Meunier et al., Micropor. Mesopor. Mater. 148 (2012) 115

CO adsorption on Pt-Sn/Al_2O_3 pre-reduced at 400°C

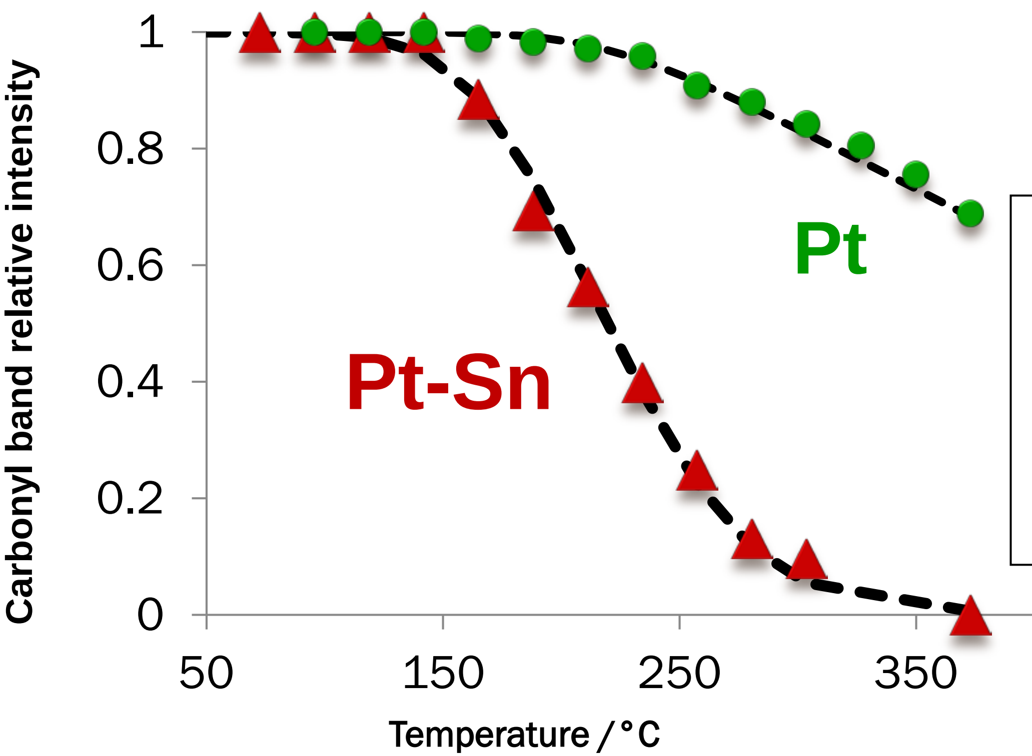
- Feed: 2%CO/H_2
- T decreased from 325-50°C



IR determines the nature and coverage of sites

CO heat of adsorption on Pt/Al_2O_3 and $Pt\text{-}Sn/Al_2O_3$

Moscu et al, *Chem. Commun*., 2014, 50, 8590-8592.



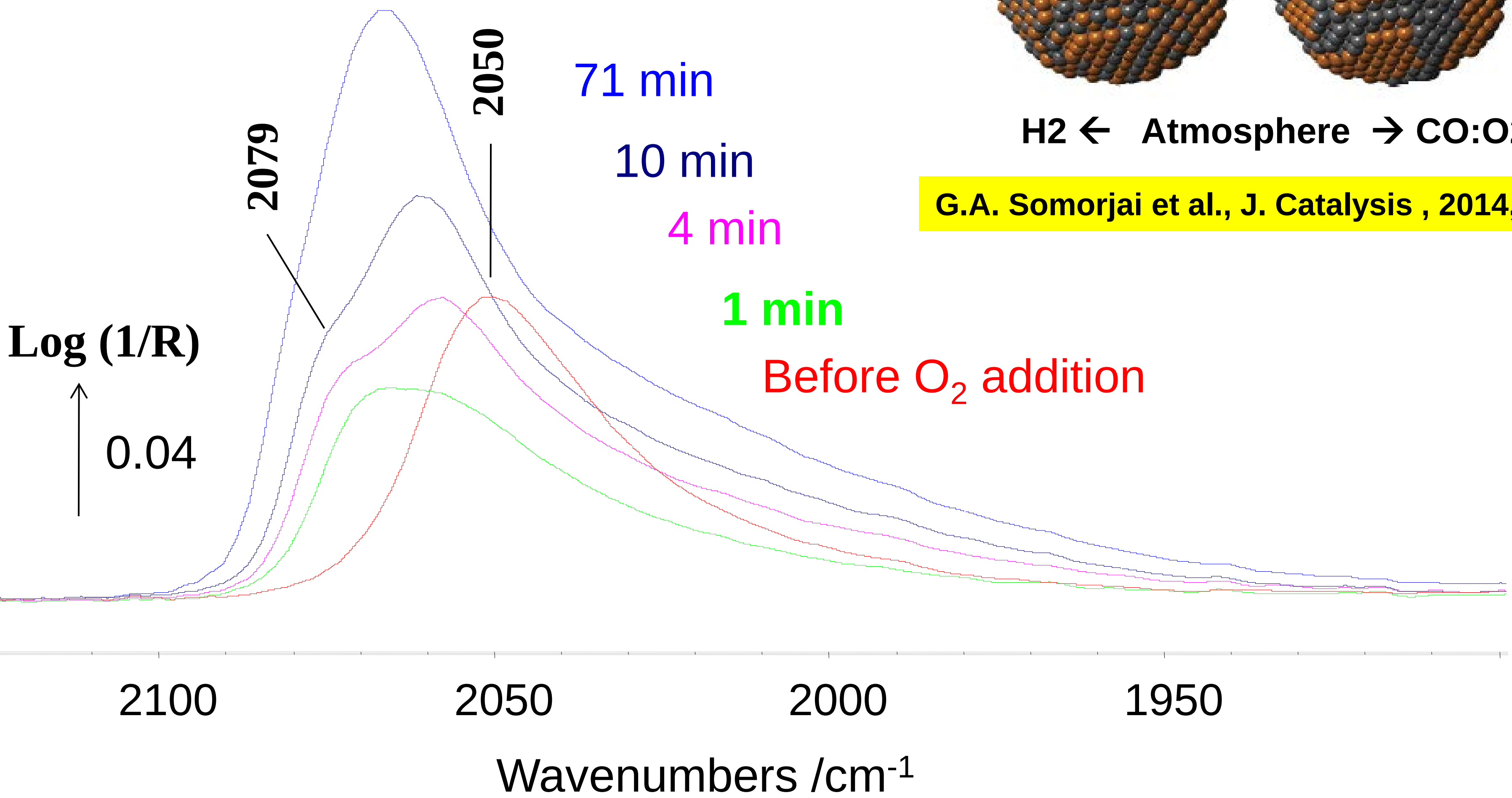
Catalyst	$-\Delta_{ads}H$ (kJ/mol)	
Pt/Al_2O_3	E0 =180	E1 =85
$Pt\text{-}Sn/Al_2O_3$	E0 = 95	E1 =75

1. CO bonding much weaker on Pt-Sn / Pt

2. Effect of surface coverage on ΔH not significant for Pt-Sn

Introduction of O2 at 225°C (Red spectrum is under CO/H2/Ar only)

Moscu et al, *Catal Today*, 2015, in press.



G.A. Somorjai et al., J. Catalysis , 2014, 312, 17-25

J. Phys. Chem. C 2009, 113, 1037–1045

Impact of the Reconstruction of Gold Particles on the Heats of Adsorption of Linear CO Species Adsorbed on the Au Sites of a 1% Au/Al_2O_3 Catalyst

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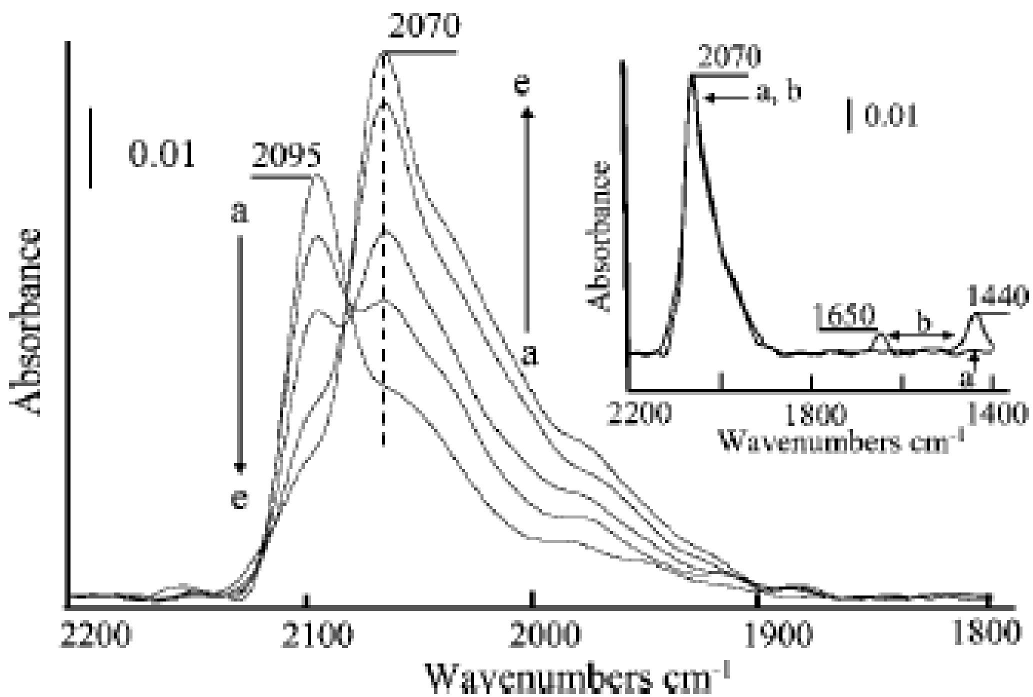


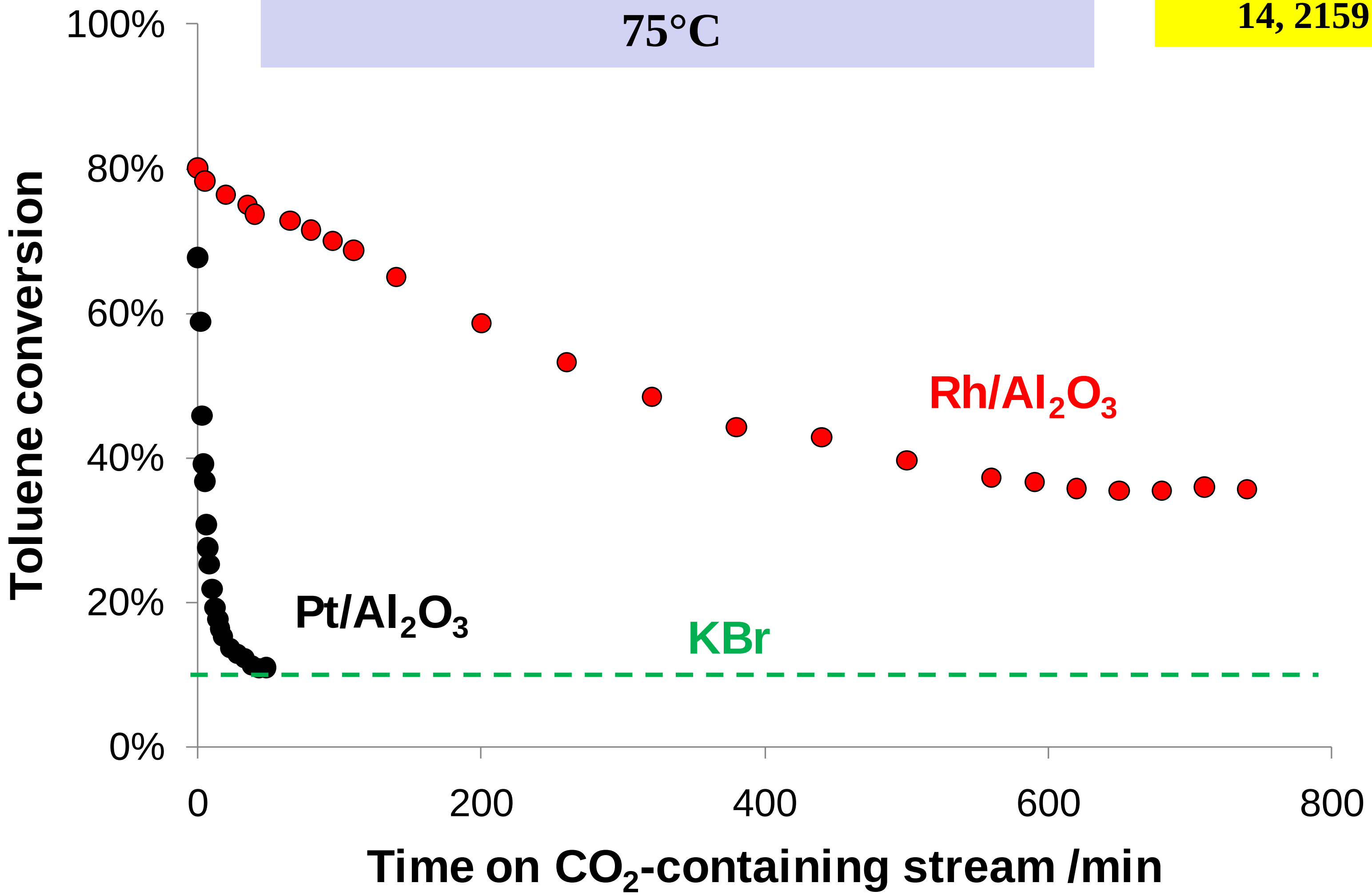
IR is site and coordination-specific!

Toluene hydrogenation: Effect of CO_2

0.17 % toluene + 17 % H_2 + 1.7 % CO_2

75°C

Scalbert et al. *PCCP*, 14, 2159 (2012).

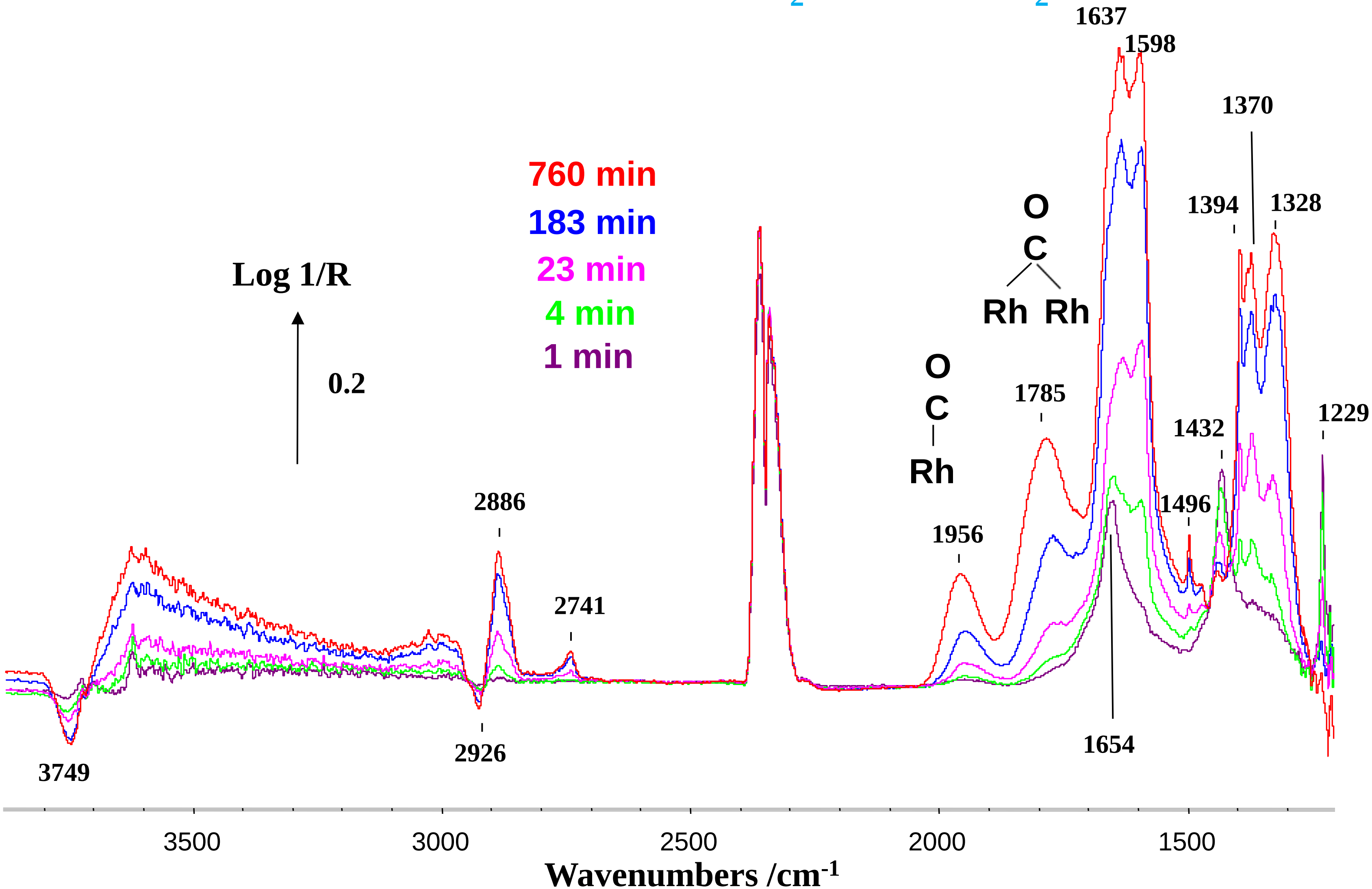


In presence of CO_2: **Pt: fast and total deactivation**

Rh: slow and limited deactivation: why?

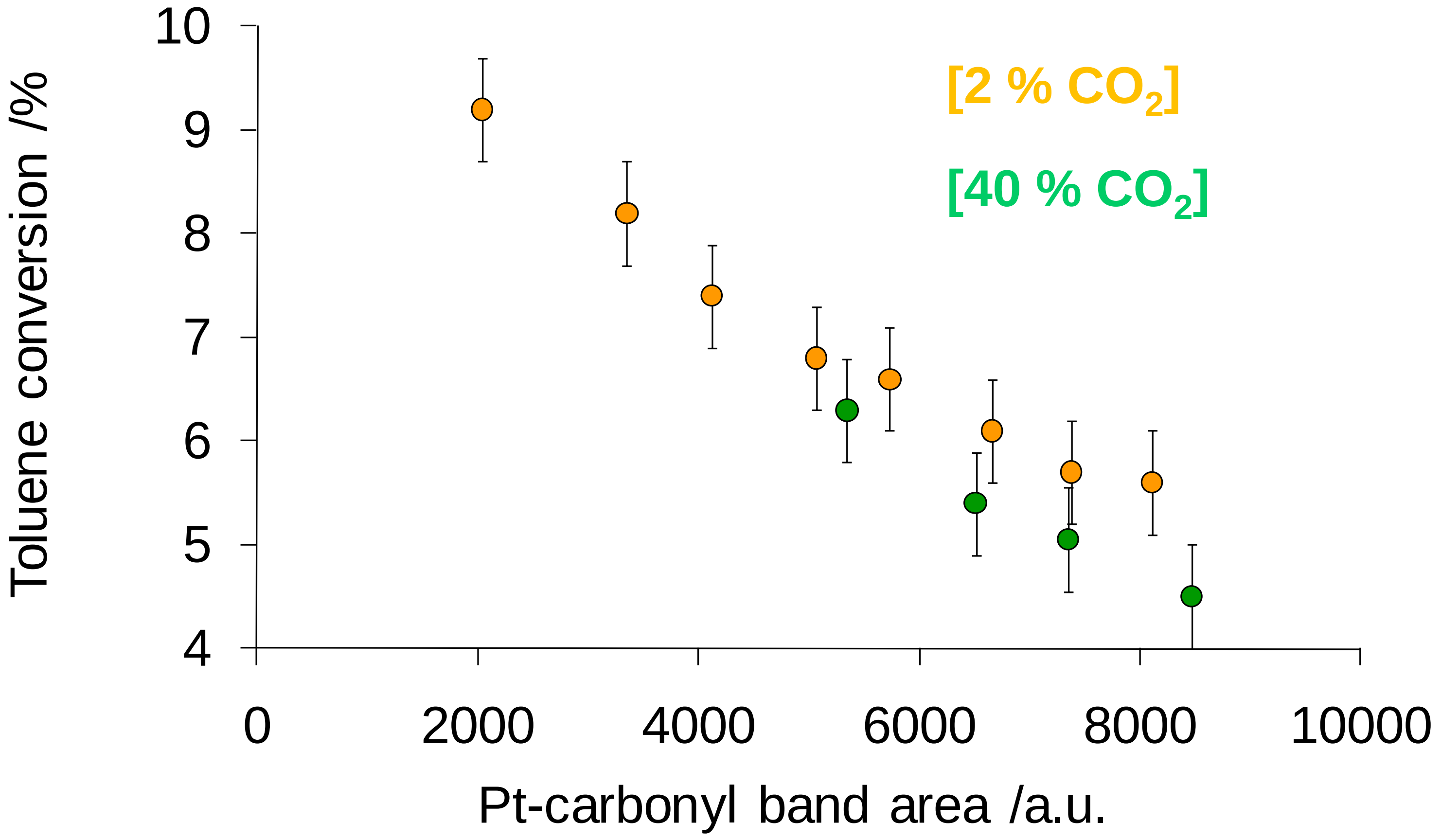
Rh/Al$_2$O$_3$: difference DRIFTS spectra following CO$_2$ introduction

0.17 % toluene + 17 % H_2 + 1.7 % CO_2



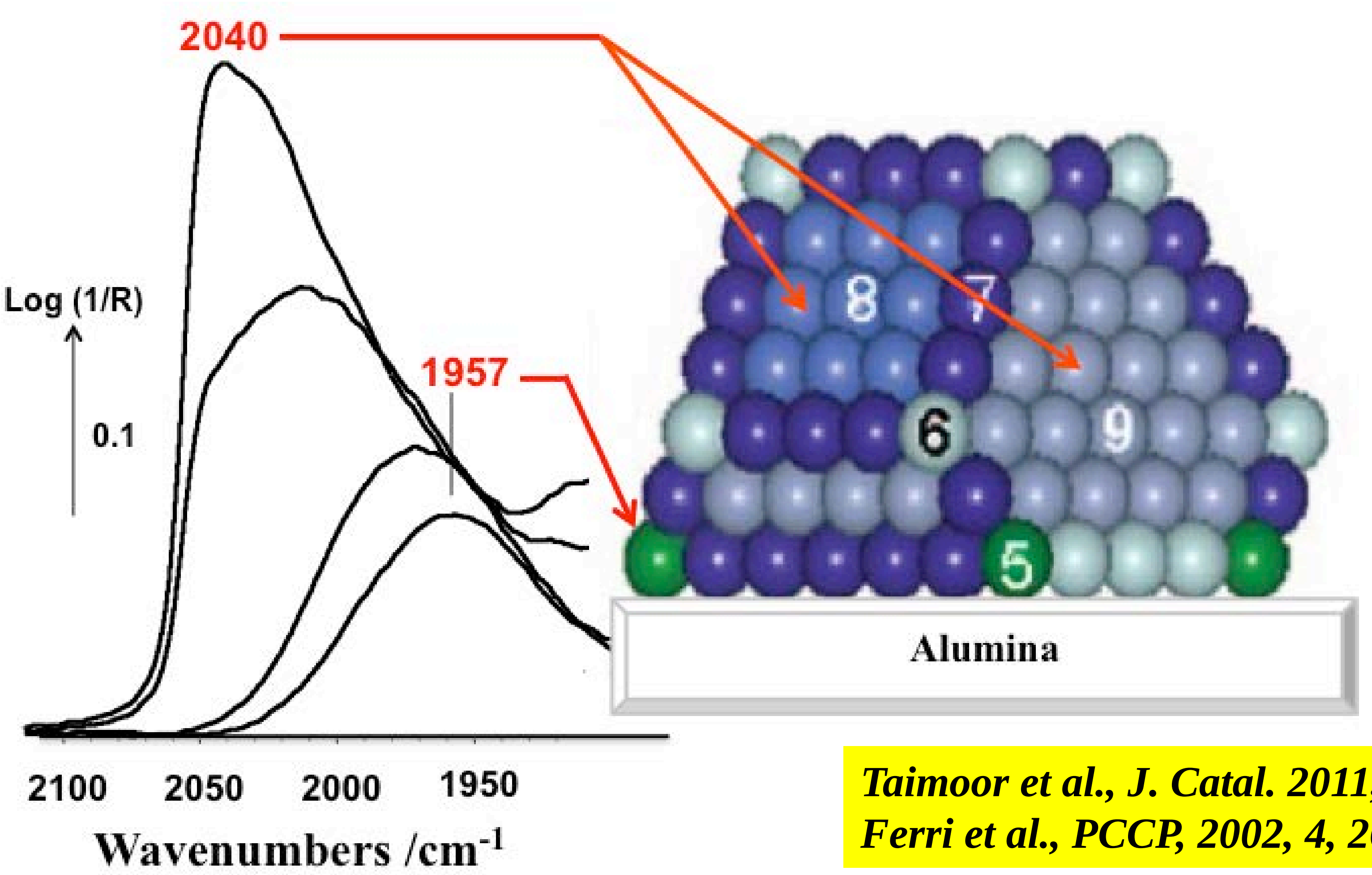
Various Rh-CO are formed, but no CO(g)

Correlation between toluene conversion and Pt-CO



Conversion correlates Pt-CO signal whatever [CO_2]

Rh/Al$_2$O$_3$ (D= 55%): linear carbonyls assignment



Taimoor et al., J. Catal. 2011, 278, 153.
Ferri et al., PCCP, 2002, 4, 2667.

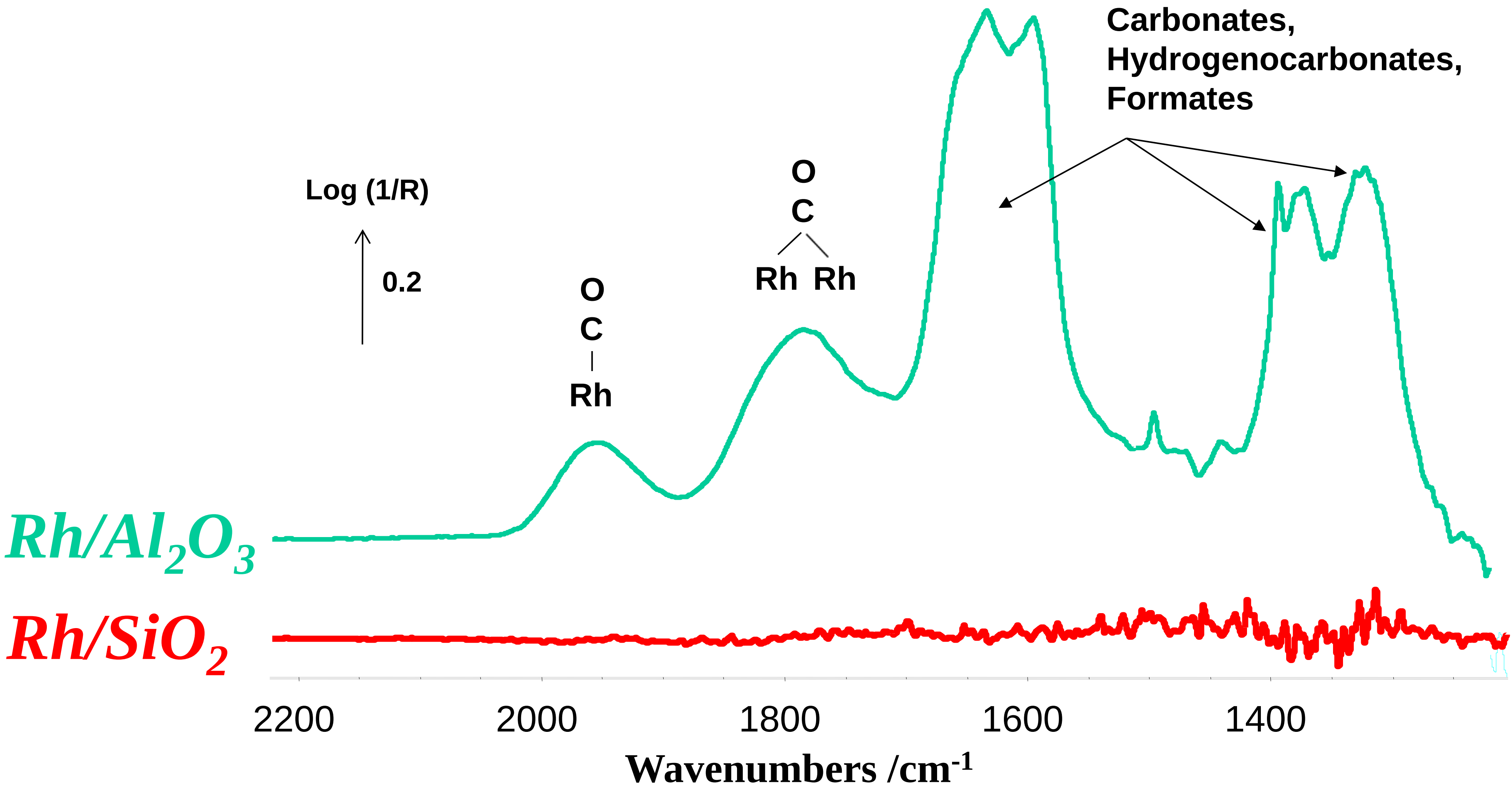
High-wavenumber carbonyls, on dense plans, displaced by toluene.

Low-wavenumber carbonyls, on low coordination sites, more stable.

→ Low dispersion samples should be more resistant to deactivation.

Rh/Al$_2$O$_3$ (D=55 %) vs Rh/SiO$_2$ (D=19 %)

Feed: 0.8 % toluene + 57 % H_2



No carbonyl nor carbonate formation on Rh/SiO$_2$ when CO_2 is added.

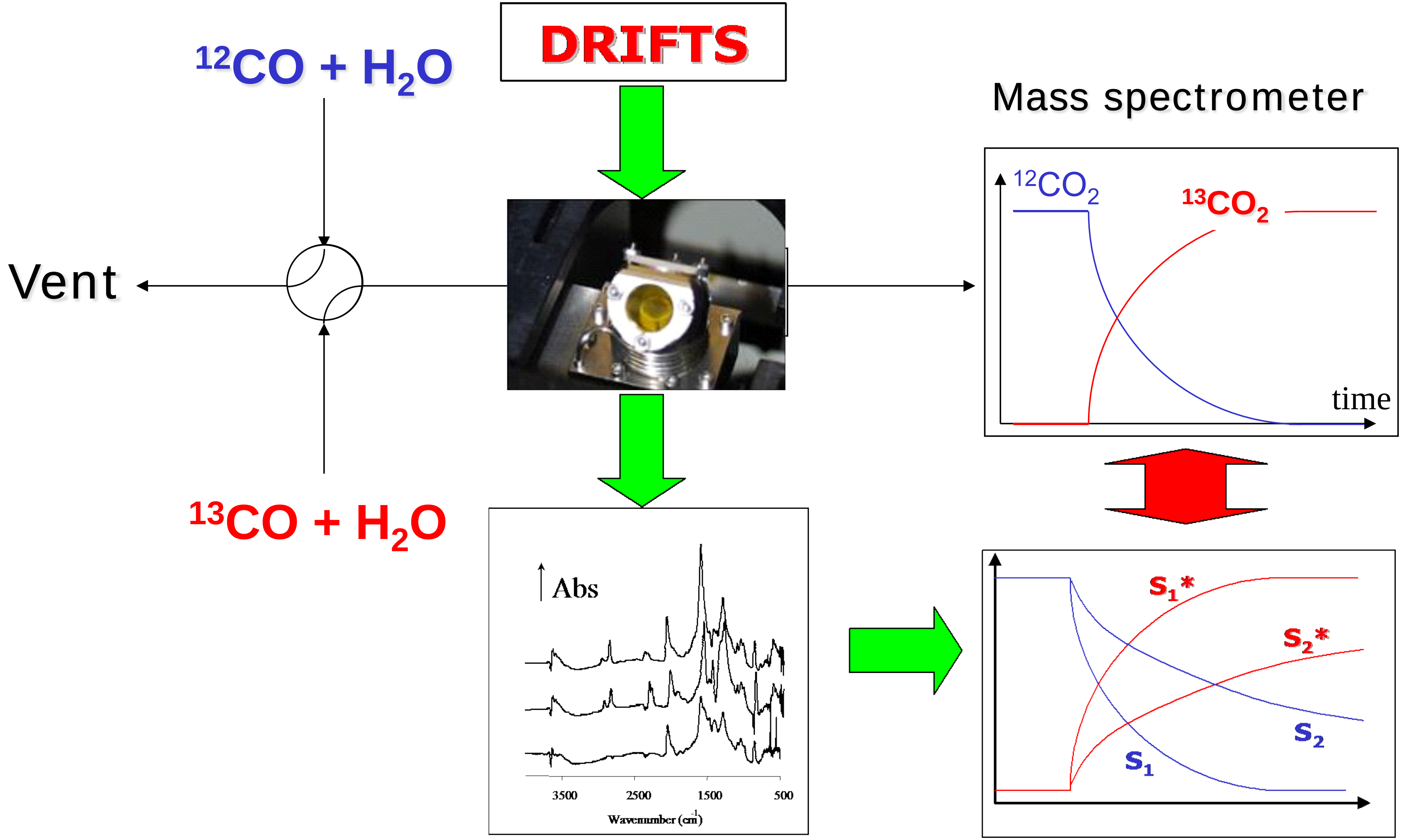
Scalbert et al., J. Catal 318 (2014) 61

DRIFTS + MS + SSITKA

(SSITKA: Steady-State Isotopic Transient Kinetic Analysis)

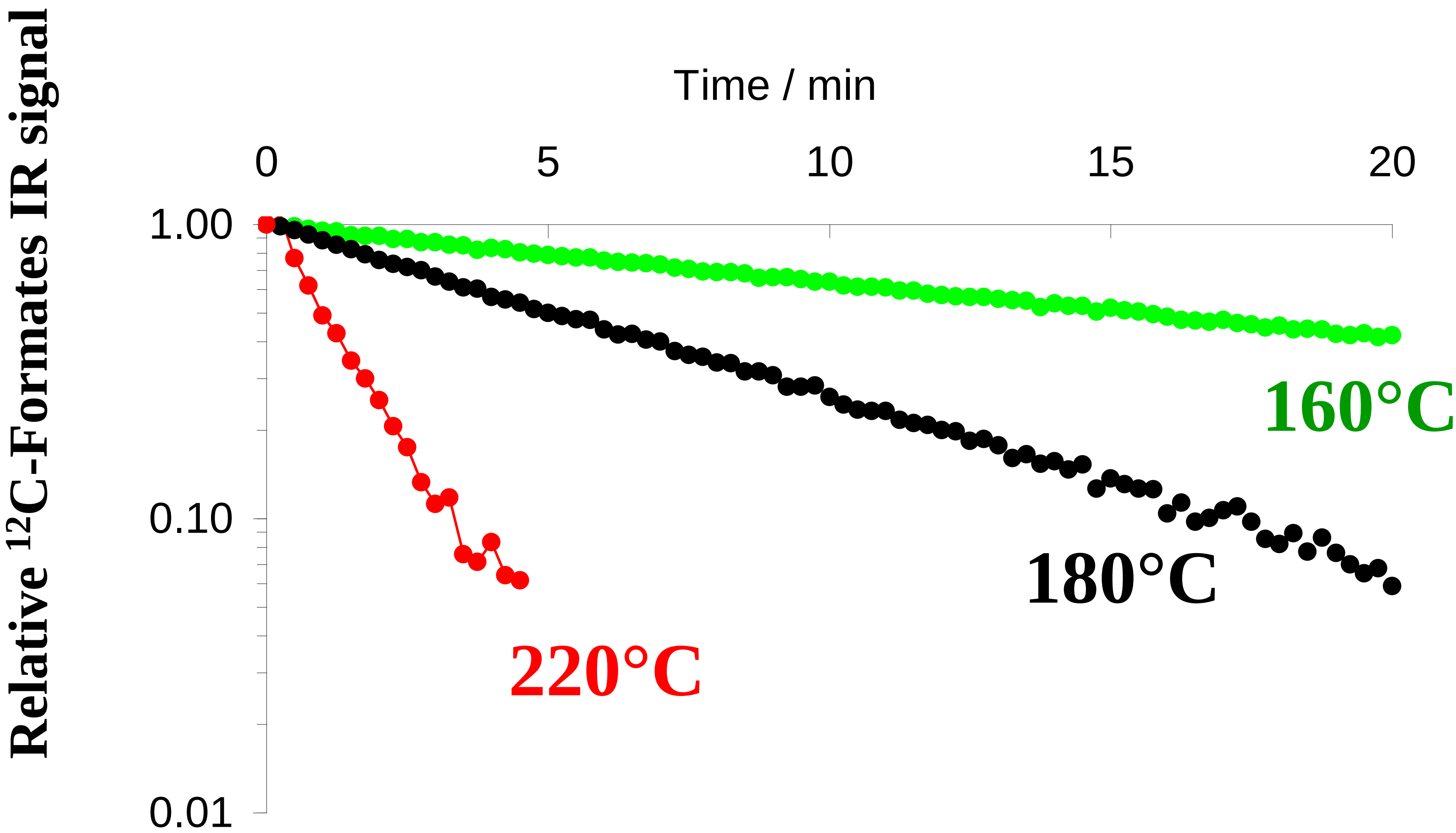
Shannon and Goodwin, Chem. Rev., 90 (1995) 667.

Goguet et al., J Phys. Chem. B 108 (2004) 20240



DRIFTS: Formate exchange over ***Pt-CeO$_2$***

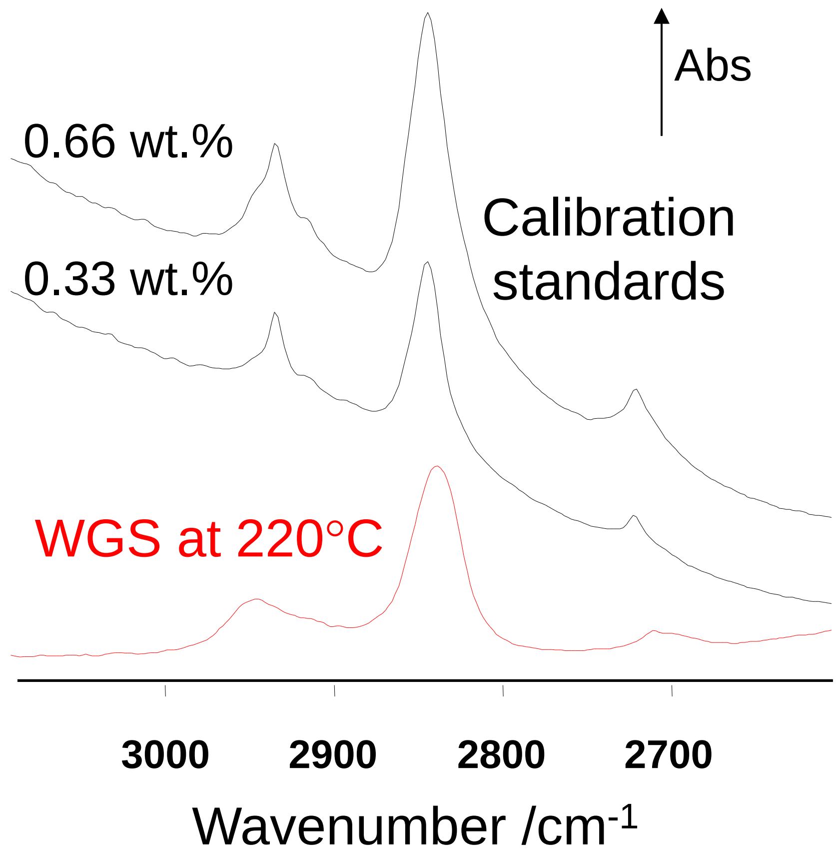
2% ^{12}CO + 7% H_2O $\rightarrow$ 2% ^{13}CO + 7% H_2O

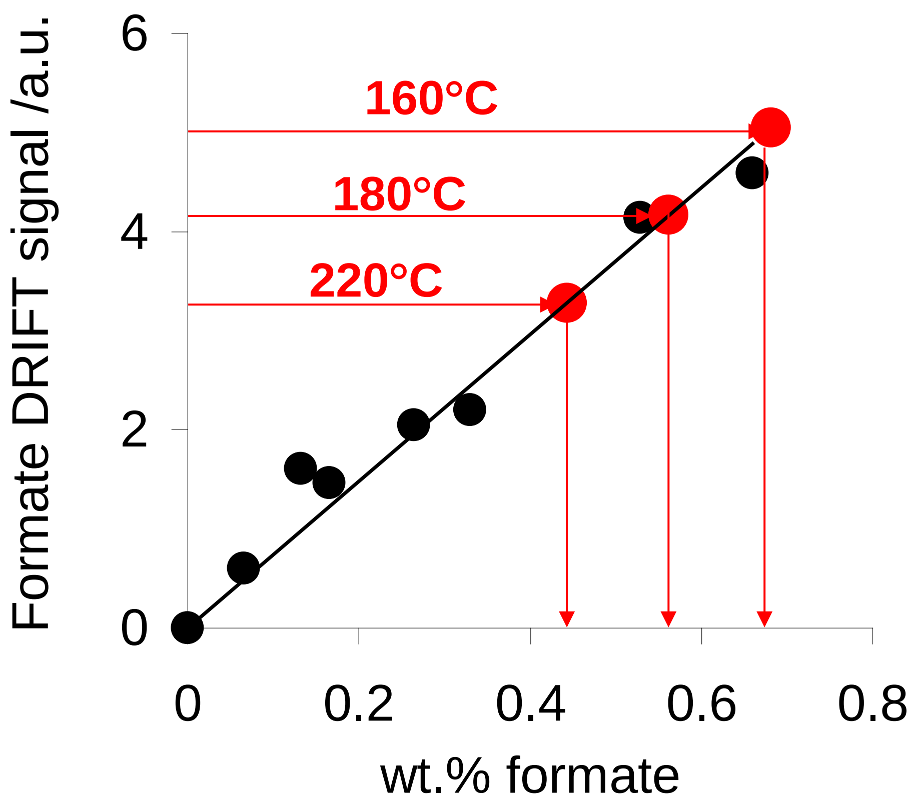


Slope = k

Formate DRIFT signal calibration

Na-formate deposition (by IWI) over the CeO_2 support
Spectra recorded at 100°C under Ar

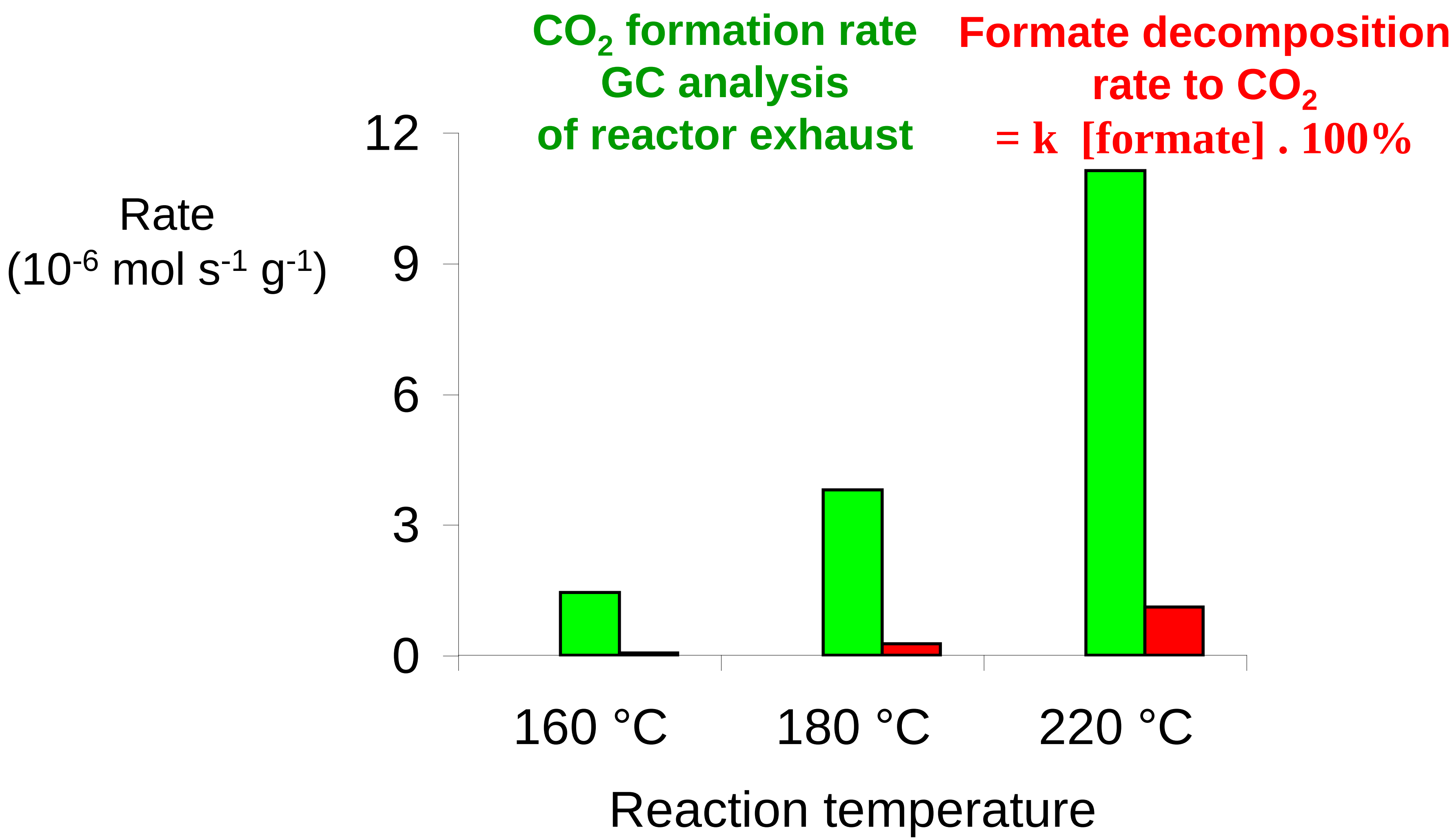




[formates] can be determined accurately

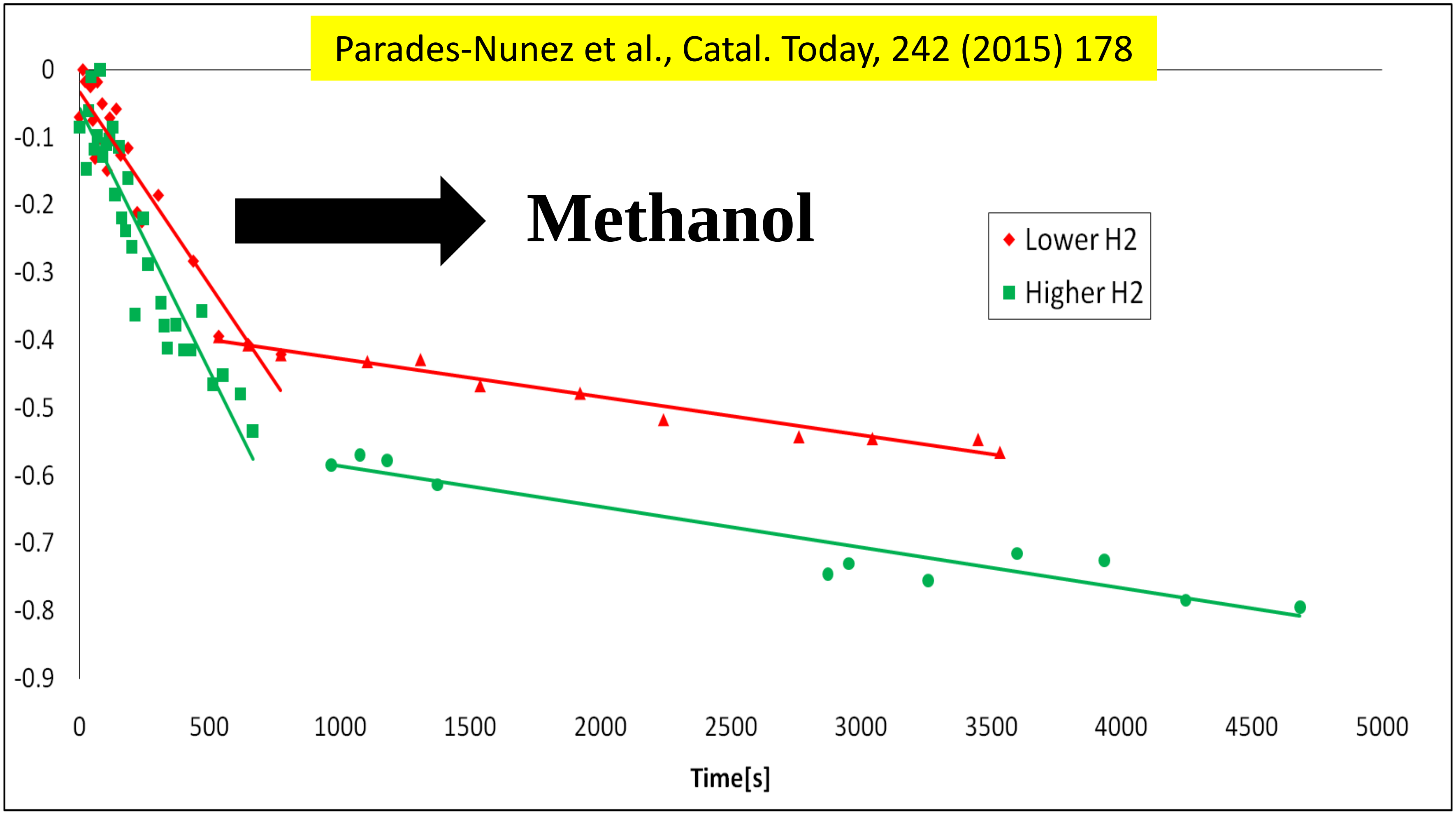
Pt/CeO$_2$: rate of CO$_2$ formation vs. rate of formate decomposition

Meunier et al. J. Catal. 252 (2007) 18



Formate decomposition during CO hydrogenation on 14% Co/Al_2O_3

30% CO + 60 % H_2 at 1 bar, 220°C



Two-type of formates: fast and slow

Conclusions

Operando FT-IR Studies of heterogeneous catalytic reactions: pitfalls and benefits.

- **Necessity to compare activity in IR cell and standard reactor**
- **Understand the origin of the differences, if any.**
  (impurities, bed by-pass, temperature gradients)
- **Improve cell design.**

- **Many relevant information for kinetic modelling can be obtained (using differential conditions): transport, nature(s) and coverage of sites, heat and mode of adsorption, poisoning, adsorbate reactivity….**

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