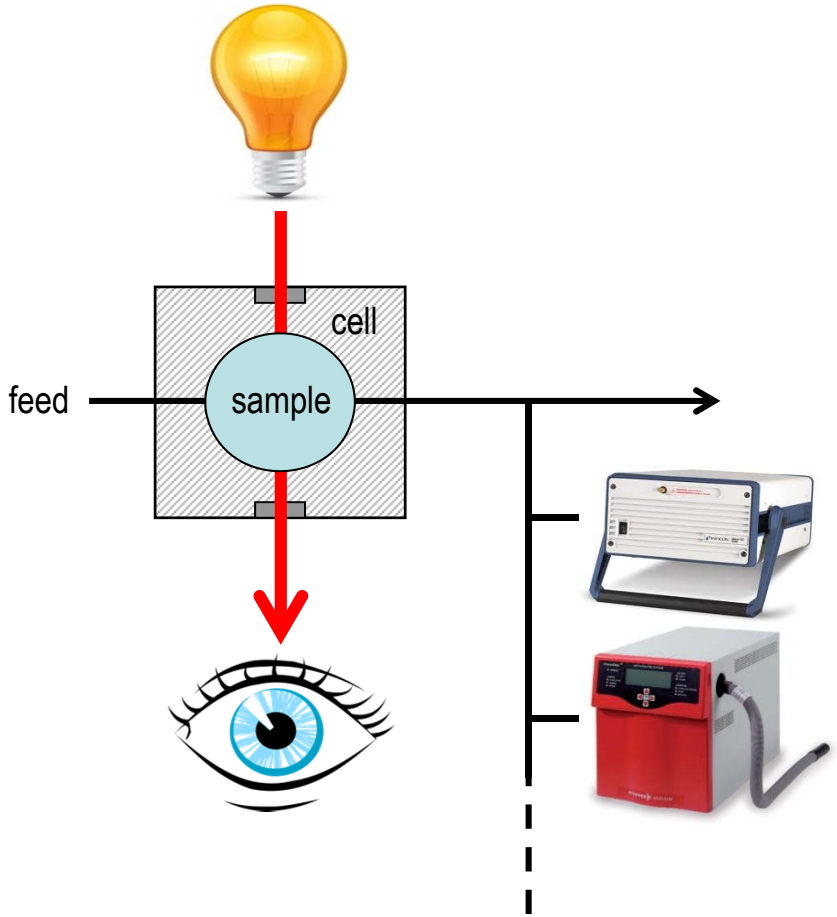
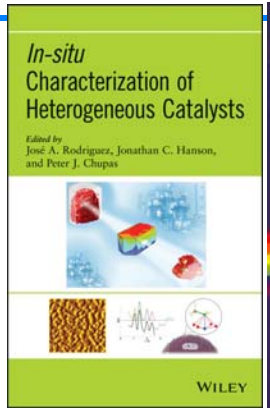
Definitions

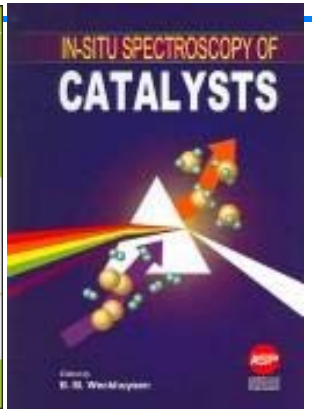
- *Ex situ* spectroscopy
  - *pre-natal/post-mortem* structure of material as is
  - away from sorption/reaction conditions
  - typically, room temperature/pressure
- *In situ* spectroscopy
  - defined sample environment
  - sorption/reaction in presence of reactants
  - relevant reaction conditions (T/P)
  - time-resolved
- *Operando* spectroscopy
  - synchronous measurement of activity/selectivity
  - structure-activity relationship
  - time-resolved
  - strict definition: cell design comparable to real reactor



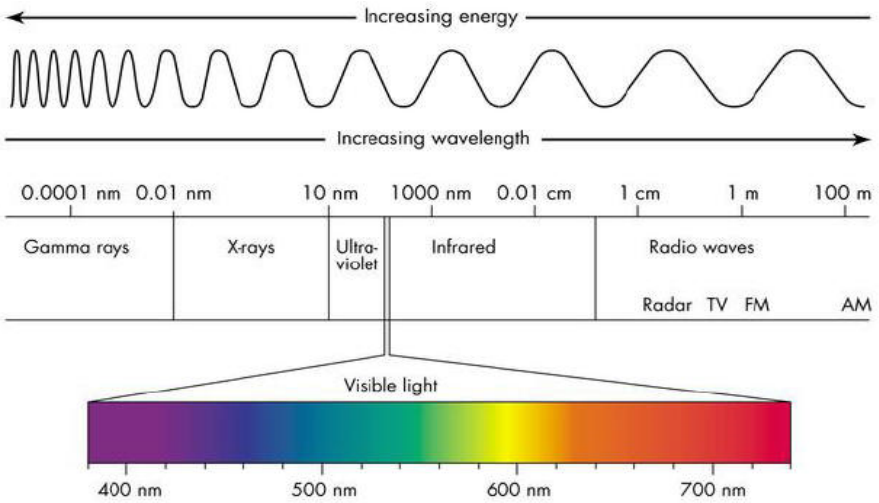
Weckhuysen, *Chem. Commun.* (2002) 97; Banares, *Catal. Today* 100 (2005) 71; Banares et al., *Catal. Today* 113 (2006) 48
In situ spectroscopy of catalysts, Weckhuysen (Ed).; Am. Scientific Publishers, Stevenson Ranch, 2004

Most used characterization methods

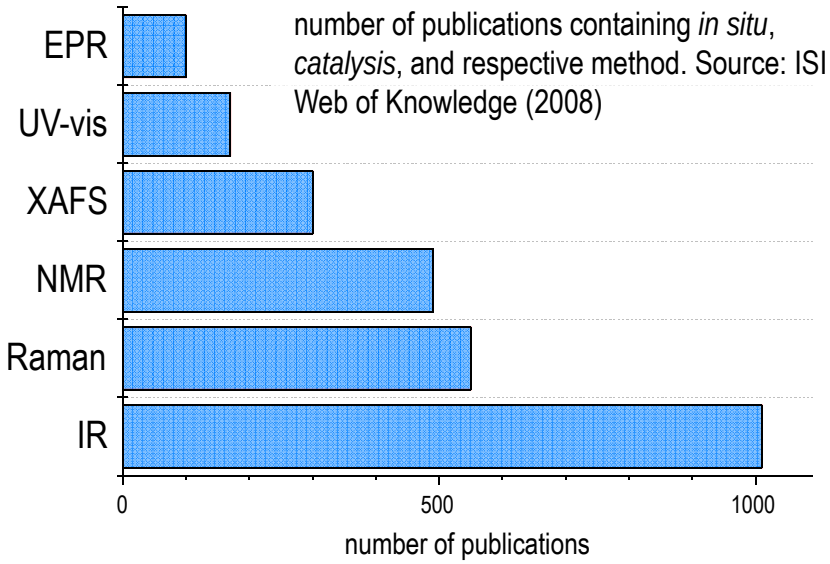




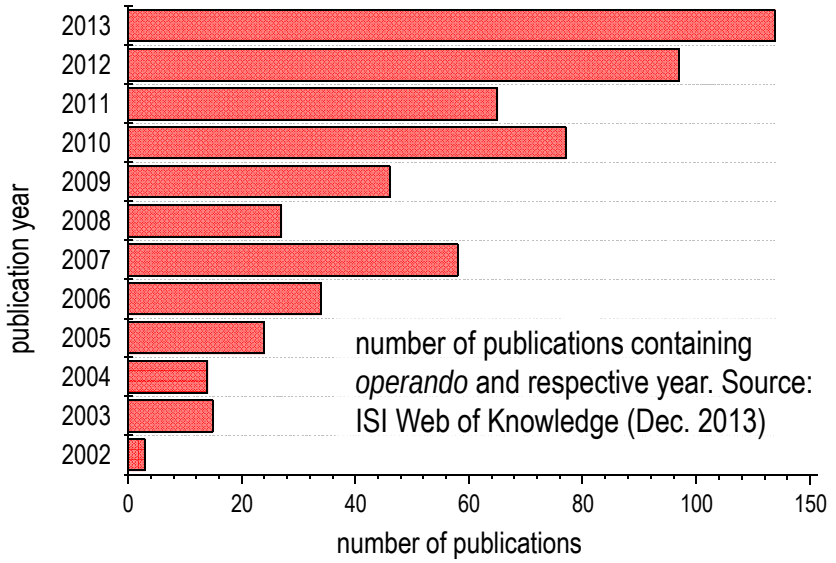
Infrared | IR
Raman
UV-vis
X-ray diffraction | XRD
Extended X-ray absorption fine structure | EXAFS
X-ray photoelectron spectroscopy | XPS
Nuclear magnetic resonance | NMR
Electron paramagnetic resonance | EPR
…



lumenistics.com



number of publications containing *in situ*, *catalysis*, and respective method. Source: ISI Web of Knowledge (2008)



number of publications containing *operando* and respective year. Source: ISI Web of Knowledge (Dec. 2013)

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Most used characterization methods

method	time resolution (s)	information	disadvantages
XRD	0.1-30	long-range structural order phase composition crystallite size	- no information on crystallite size smaller than 2-3 nm - no information on amorphous phases
XAFS	0.003-30	short-range structural order coordination environment and oxidation state of metal and metal ions	- average information - complicated analysis
EPR	60-300	paramagnetic transitions of metal ions	only for paramagnetic nuclei
UV-vis	0.01-1	electronic d-d tansitions and charge transfer transition metal ions/metal oxides	- complicated spectrum - only low metal oxide loadings possible
Raman	0.05-1	vibrational spectra of metal oxides and organic deposits	- Raman effect is weak - low metal oxide loadings difficult
FTIR	0.01-1	vibrational spectra of adsorbed species and reaction mixtures	difficult analysis of supported metal oxides
NMR	7200	geometry of adsorption sites identification of organic molecules	not applicable to many nuclei

- methods can be combined in a single experiment or in independent experiments
- combination of methods is practical to obtain information on different length scales

Weckhuysen, *Chem. Commun.* (2002) 97; Tinnemans et al., *Catal. Today* 113 (2006) 3; Deka et al., *ACS Catal.* 3 (2013) 413

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Most used characterization methods

Table 7.1 Characterization techniques used in heterogeneous catalysis and their potential for the identification of active sites

Technique	Potential	Limitations	In situ/ operando?
XRD	Determination of long-range order, of particle sizes	Averaging technique, on traditional level no potential for disordered structures	yes
Electron microscopy	Visualization of structures down to atomic details, usually in UHV, but environmental versions available	Site concentrations difficult to establish, analysis refers to small assay of material under study (support by averaging technique desirable)	in situ (limited)
XAFS (EXAFS/XANES)	Short-range order, also for disordered or highly disperse phases, electronic structure	On traditional level averaging technique, difficult for situations with many species of an element coexisting	yes
XPS	Atomic concentrations, oxidation states in near-surface layer, sometimes structural information, UHV technique, environmental versions available	Averaging over sampling region (depth differentiation requires synchrotron source[a]), assignment of signals may be complicated, structural information limited	in situ (limited)
LEIS (ISS)	Identification of atoms in topmost layer, concentration gradients via sputter series, vacuum technique	No information on oxidation states, averaging technique, concentration analysis possible, but with risks	no
Raman	Structural information for highly disperse phases, characterization of adsorbates	Qualitative, signal superposition for complex materials, problems with sample fluorescence	(yes)
IR	Characterization of sites (acid–base, redox) by probe molecules, of adsorbates, structural information	Concentration analysis difficult (only in transmission geometry, extinction coefficients required), structural information often limited by signal saturation	yes
UV–Vis	Analysis of oxidation states, of aggregation degree of TMI sites	Semiquantitative, broad signals may create problems with assignment, poor resolution of clustering degrees	yes
EPR	Analysis of paramagnetic sites and their environment, extremely sensitive, gives information also on clustered phases	Not all oxidation states accessible, accuracy of concentration analysis limited	yes
NMR	Concentration, coordination, oxidation states of elements, sometimes information on distances between sites	Only nuclei with nonzero spin, sometimes problems with sensitivity, interference by nearby paramagnetic sites complicates application in redox catalysis	yes
Moessbauer	Oxidation states, coordination to neighbors, clustering degrees of sites	Only a few elements with suitable nuclear levels, in particular Fe, full diagnostic potential only at very low measurement temperatures	no[b]
Chemisorption	Particle sizes (metals), adsorption sites (ionic surfaces)	Particle size determination averaging; adsorption stoichiometry not always clear	no
Adsorption calorimetry	Enthalpy and entropy of adsorption (titration method) for probe molecules and reactants	Limited to simple systems (well-defined surface, one adsorptive)	no
Temperature-programmed desorption	Differentiation of adsorption sites on a surface, depending on test molecule for acid/basic or redox sites, determination of energetics of desorption	Desorption signals remain to be assigned to sites	no
Temperature-programmed reduction/ oxidation	Reduction/reoxidation properties of redox phases in samples; strong in detecting interactions between phases, in simple cases determination of energetics of reduction	Nature of detected interactions remains to be elucidated	no

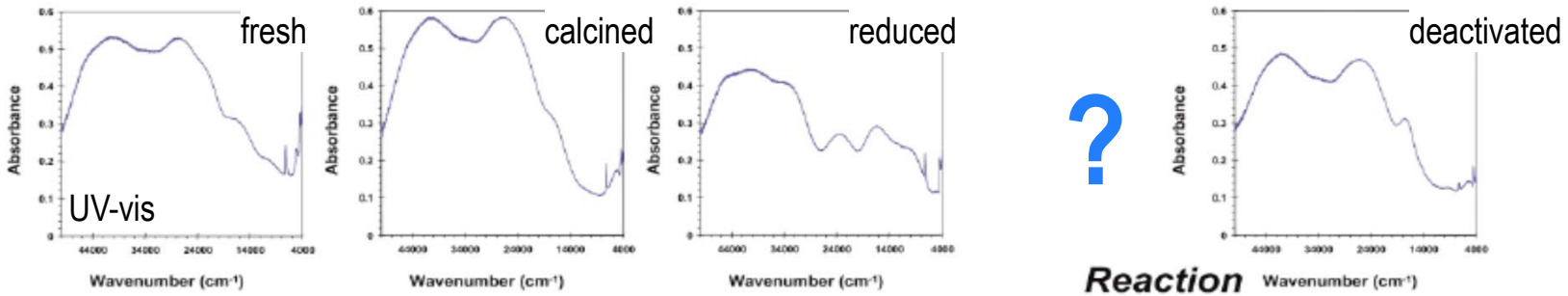
[a] Angle-resolved XPS, which can be performed with lab sources, is a safe tool only for flat sample surfaces

[b] In principle possible, but no examples known; loss of diagnostic potential at elevated temperatures seems to discourage attempts

Grünert, in Urea SCR technology for deNOx after treatment of diesel exhausts, Springer, (2014) p. 181

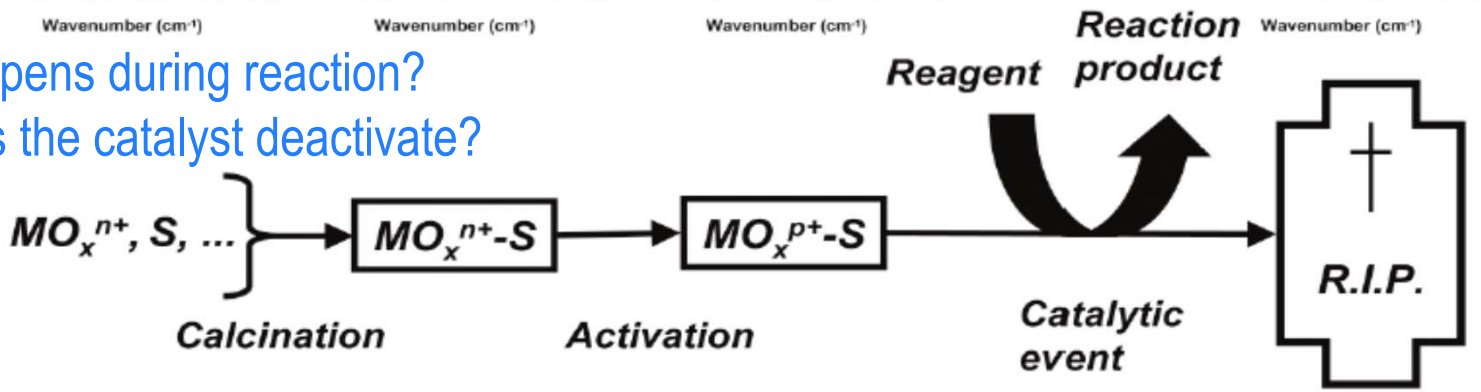
Do we need in situ/operando?

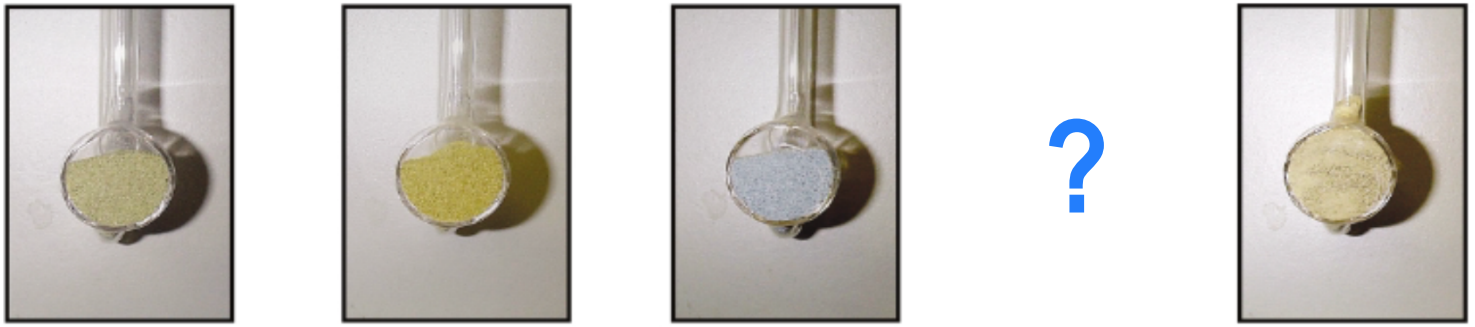
The life time of a catalyst | 8 wt% CrO_3/Al_2O_3



what happens during reaction?

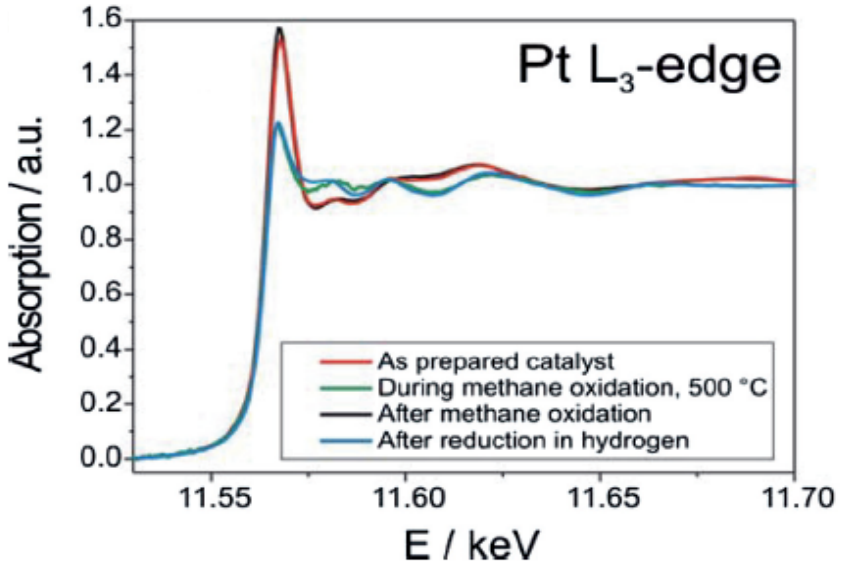
why does the catalyst deactivate?

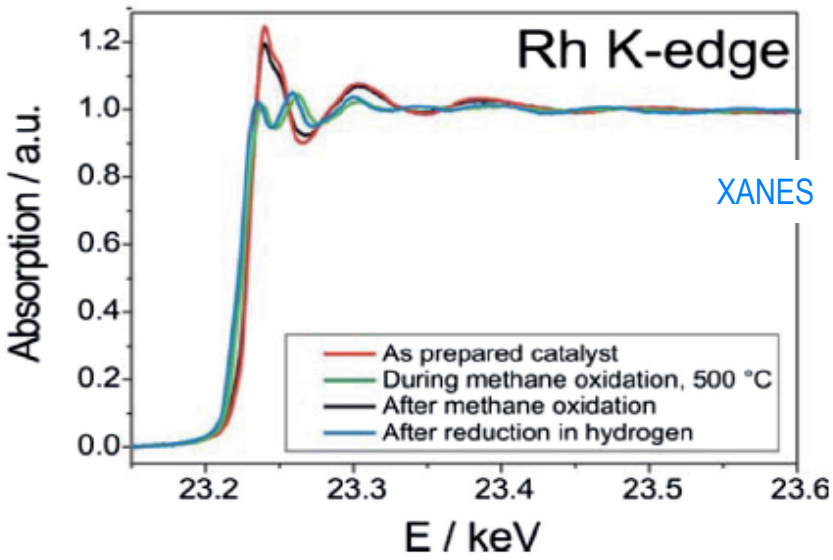




Weckhuysen, *Chem. Commun.* (2002) 97

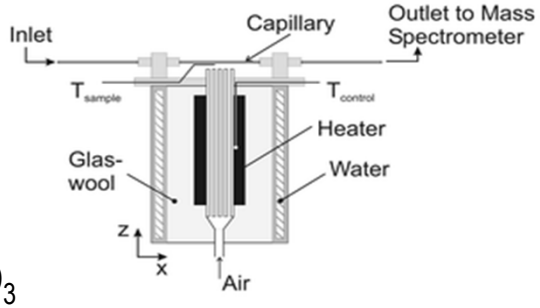
Do we need in situ/operando? YES

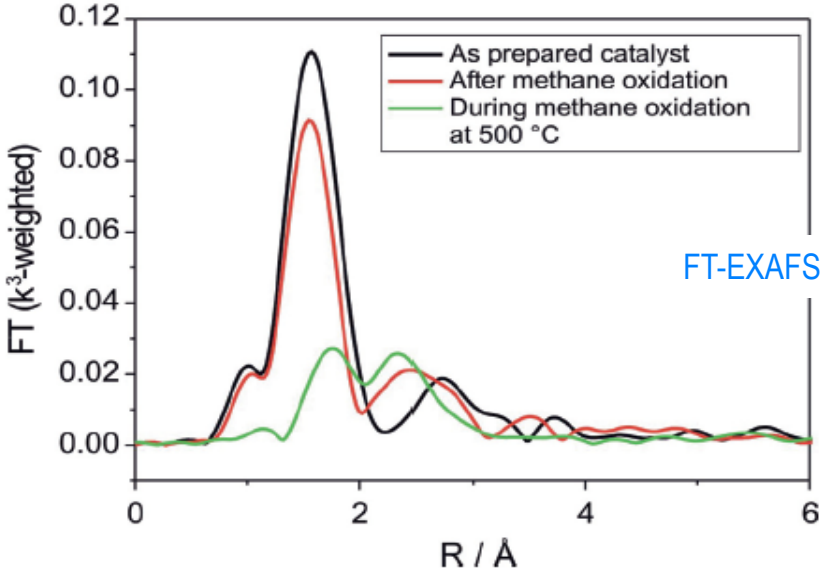




XANES

- Pt and Rh oxidized before and after reaction
- BUT in reduced state during partial CH_4 oxidation



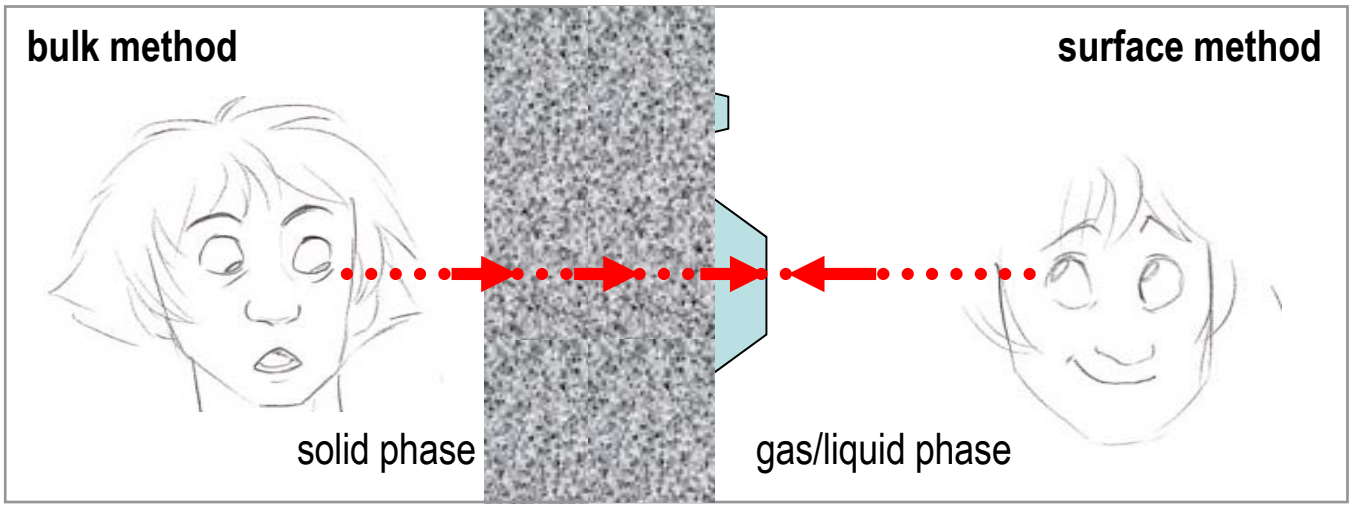


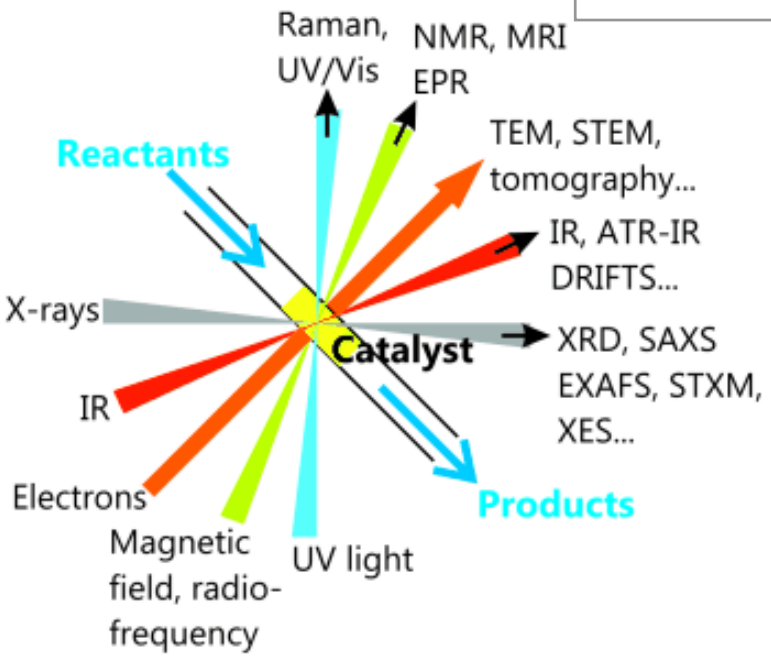
FT-EXAFS

6 vol% CH_4-3 vol% O_2/He
2.5 wt% Pt-2.5 wt% Rh/Al_2O_3

Grunwaldt et al., *Catal. Lett.* 99 (2005) 5

Bulk vs surface information

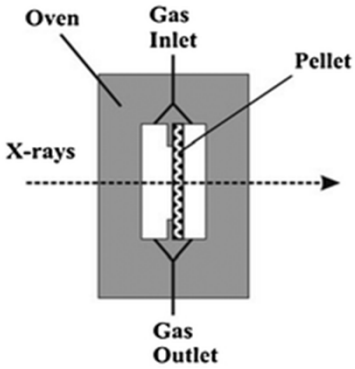




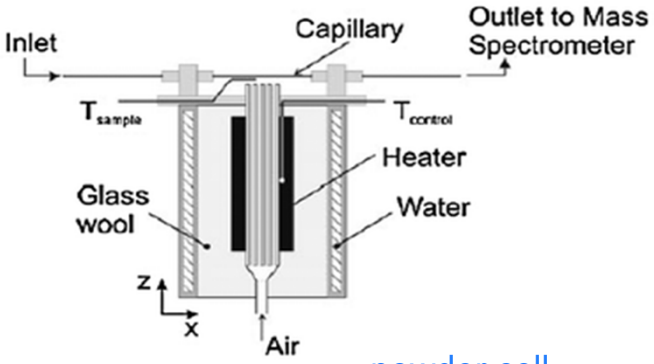
Grunwaldt et al., *ChemCatChem* 5 (2013) 62

The sample form and the cell

- Many methods (IR, EXAFS, XPS) use wafers…

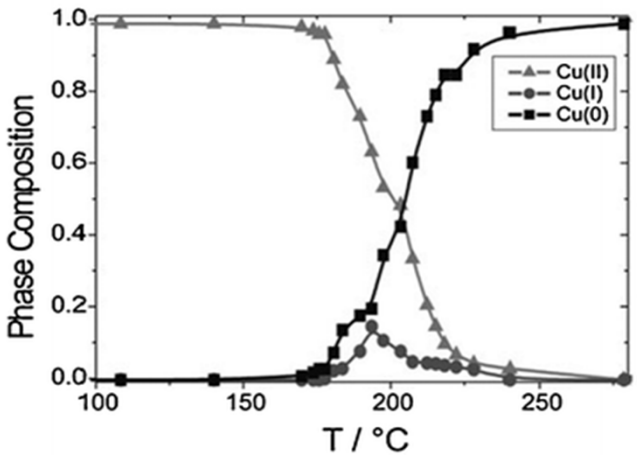


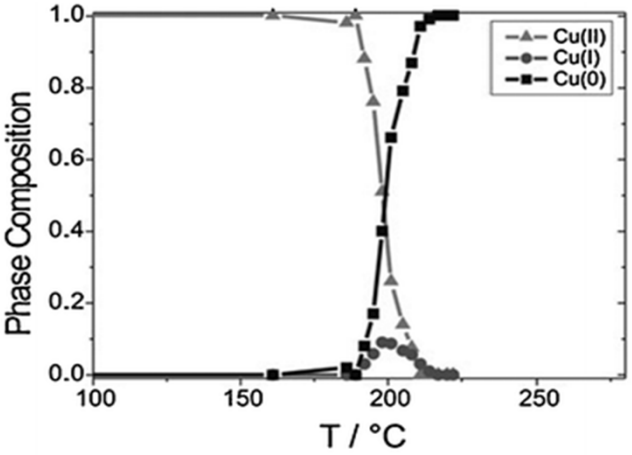
pellet cell
mass transfer coefficient,
1.03x10^{-2} m/s
13 mm x 1 mm



powder cell
mass transfer coefficient, **0.61 m/s**
80-120 μm

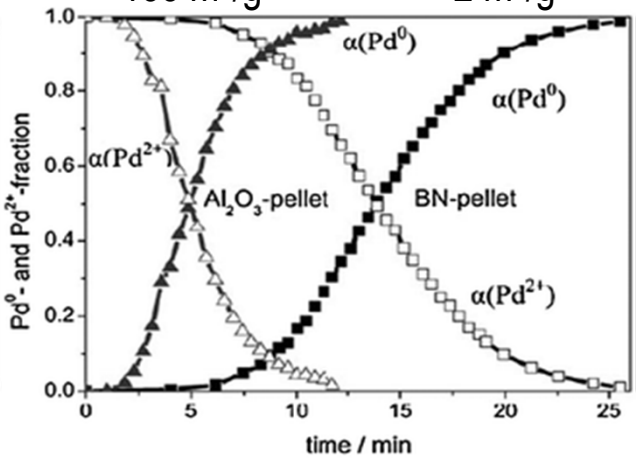
30% CuO/ZnO, 5% H_2/He; 1° C/min

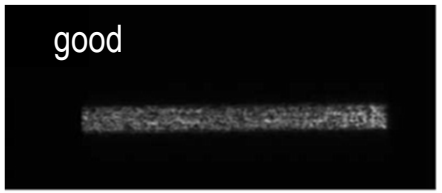


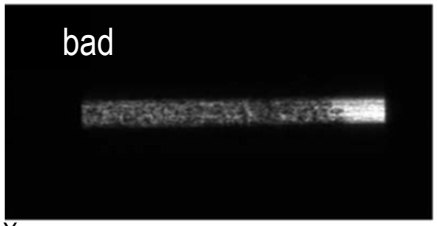


…and diluent

133 m^2/g 2 m^2/g







X-ray eye

Grunwaldt et al., *PCCP* 6 (2004) 3037

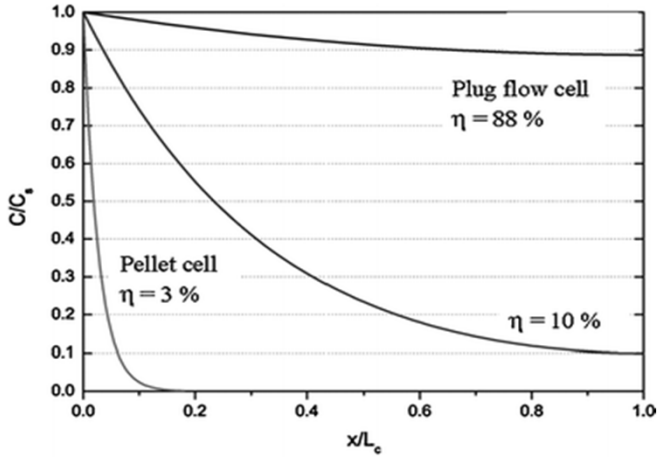
The sample form and the cell

- Catalyst effiency during *operando* XANES experiment
  - methane combustion, $Pd(O)/ZrO_2$, Pd K-edge (24.35 keV)

method	sample form	cell	rate [10^{-4} mol/gs] (conversion)
Pd/ZrO_2	powder	capillary	1 (100%)
Pd/ZrO_2	wafer	pellet cell	0.03 (80%)
PdO/ZrO_2	powder	capillary	0.53 (80%)
PdO/ZrO_2	wafer	pellet cell	0.02 (65%)

1% CH_4/4% O_2/He
wafer: 13 mm x 1mm
powder: 80-120 μm

effectiveness factor - η

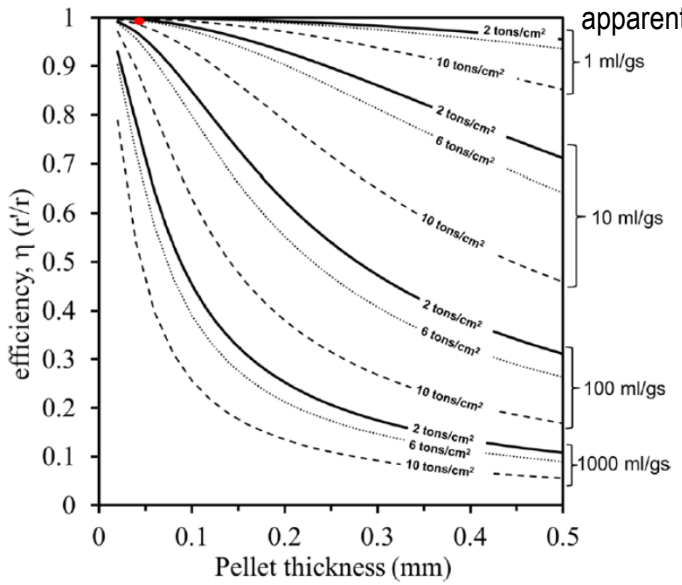


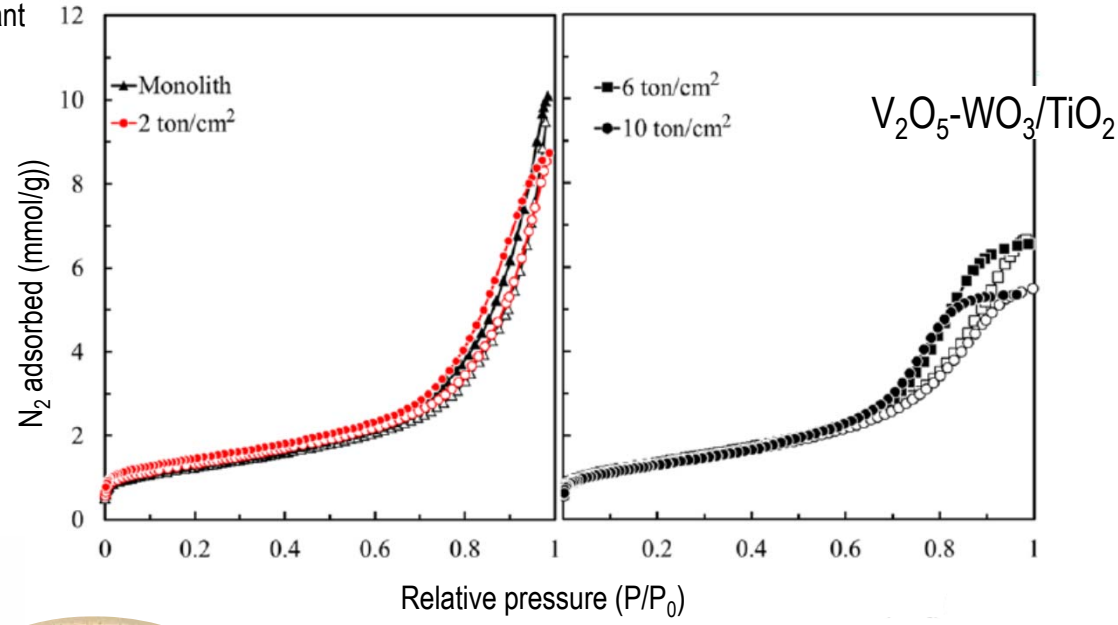
$$\eta = \frac{\tanh \psi}{\psi} \qquad \psi = L_c \sqrt{\frac{k_r}{D_e}}$$

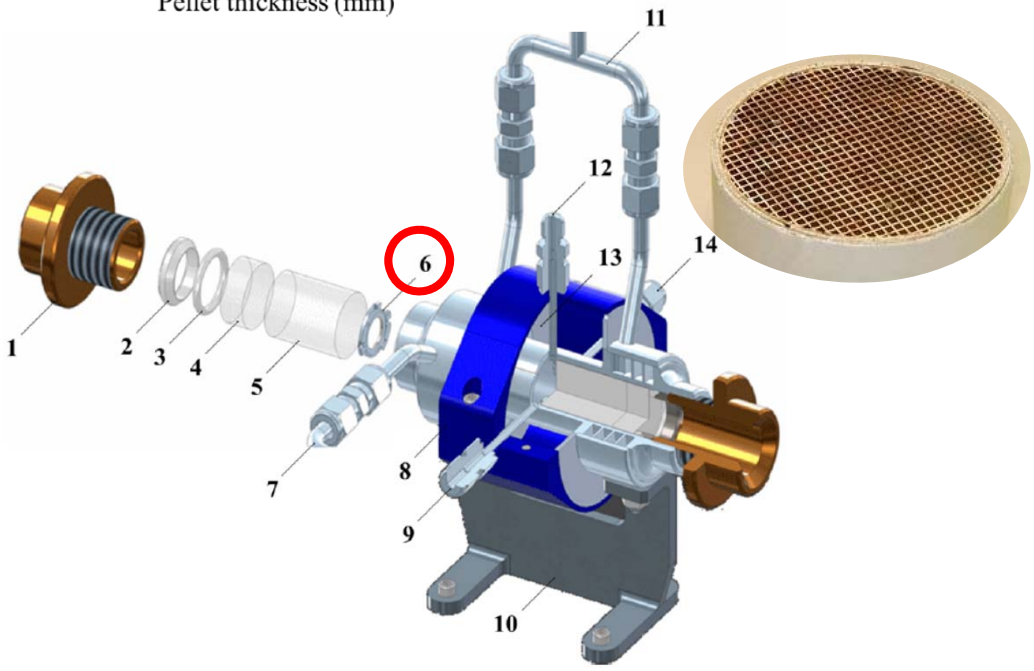
$$L_c = \frac{d}{2}$$

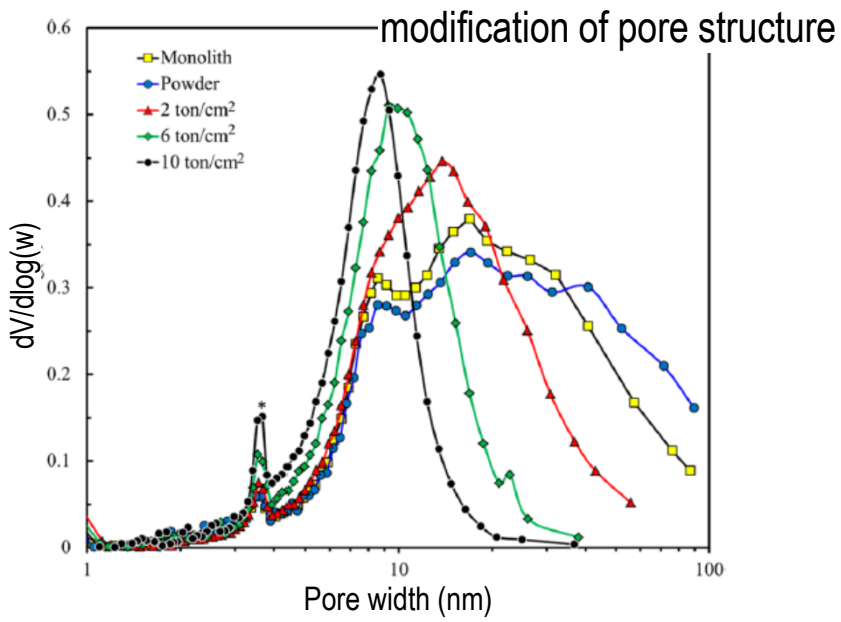
Grunwaldt et al., *PCCP* 6 (2004) 3037

The sample form and the cell





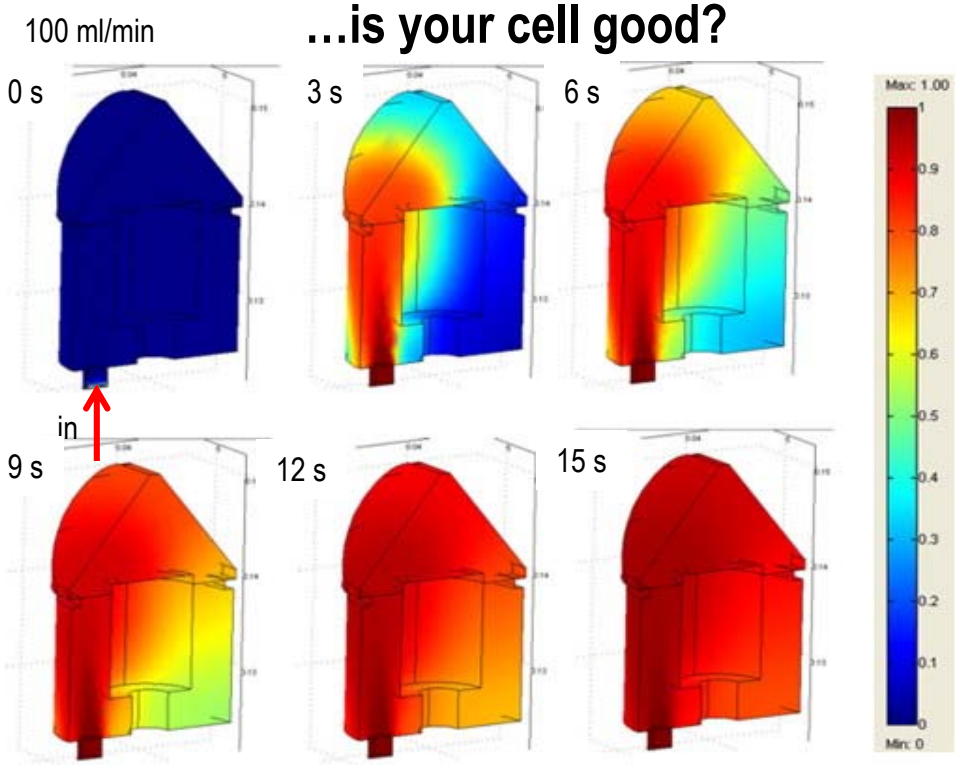


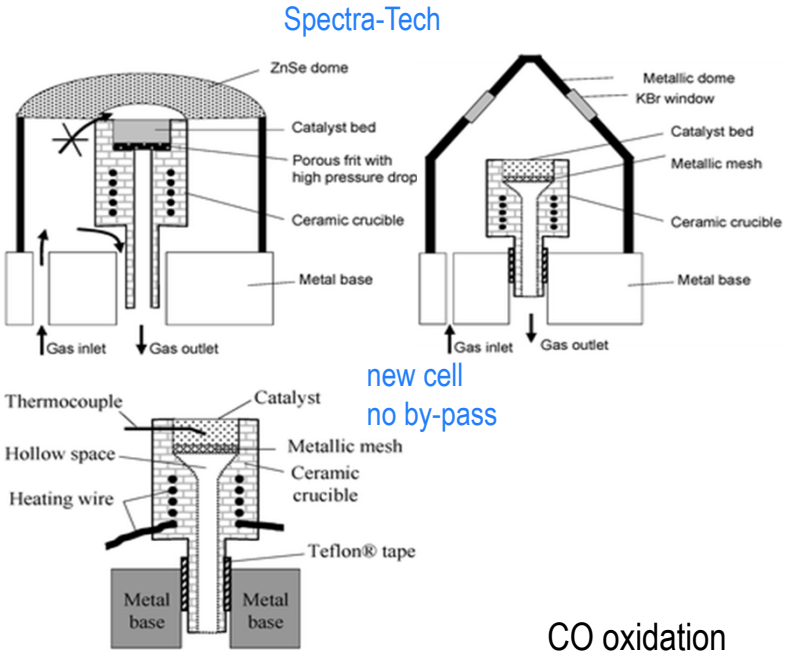


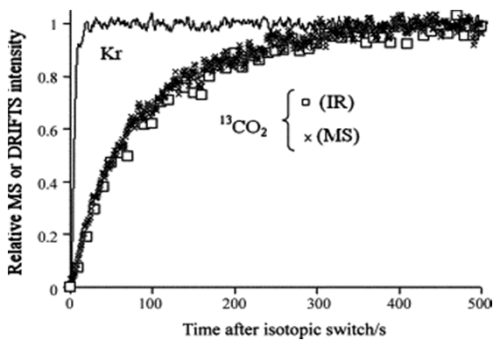
Rasmussen et al., *ACS Catal.* 3 (2013) 86

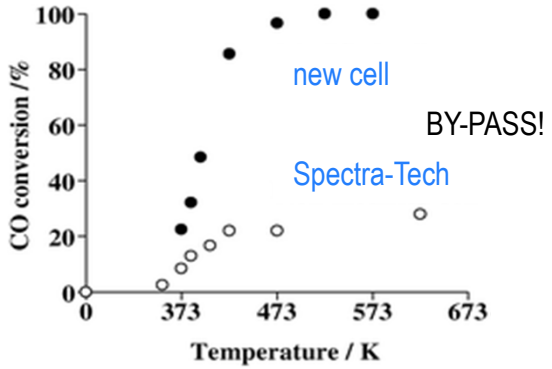
The sample form and the cell

…is your cell good?



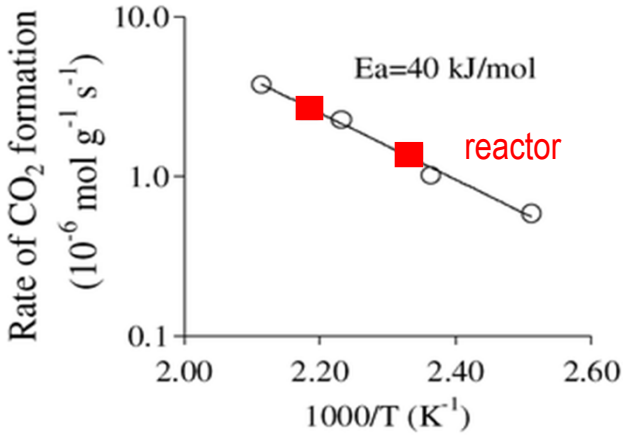






Meunier et al., *Appl. Catal. A* 340 (2008) 196

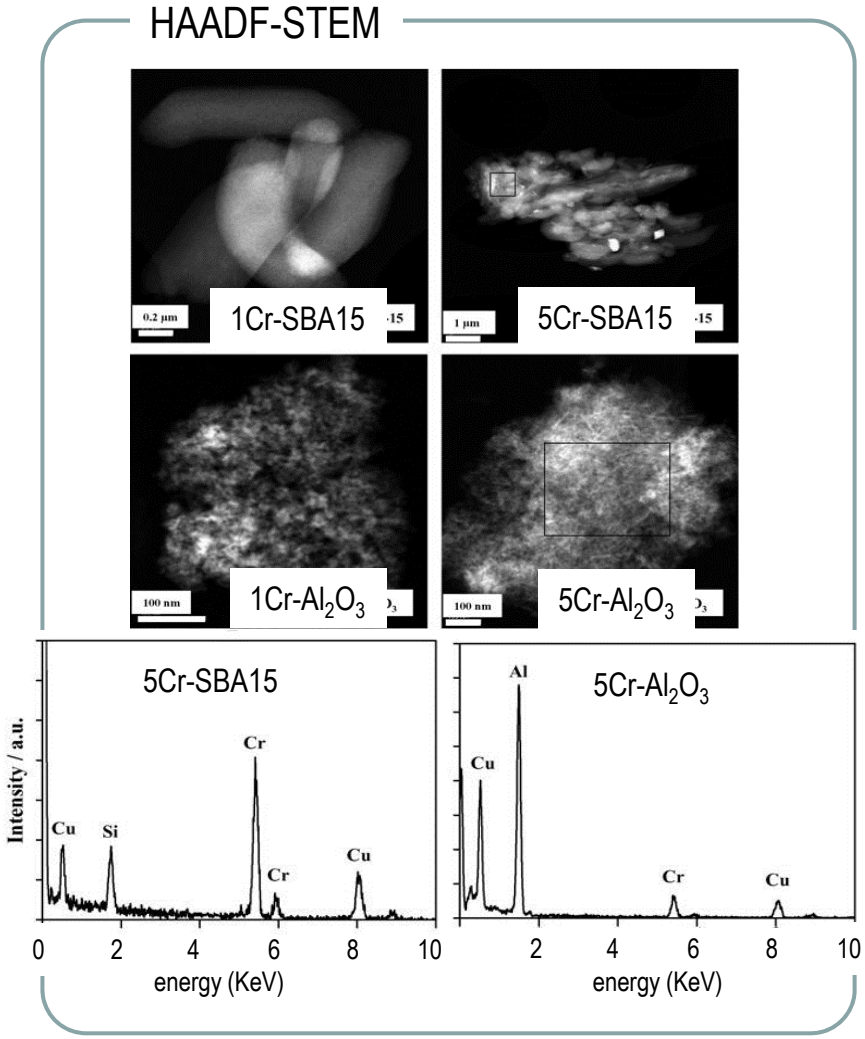
CO oxidation
DRIFT cell vs. microreactor

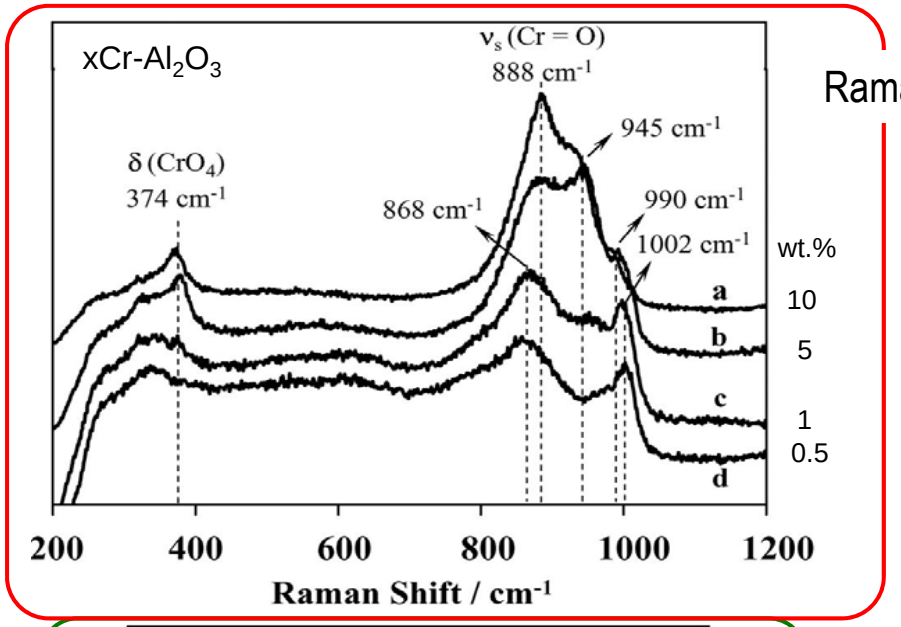


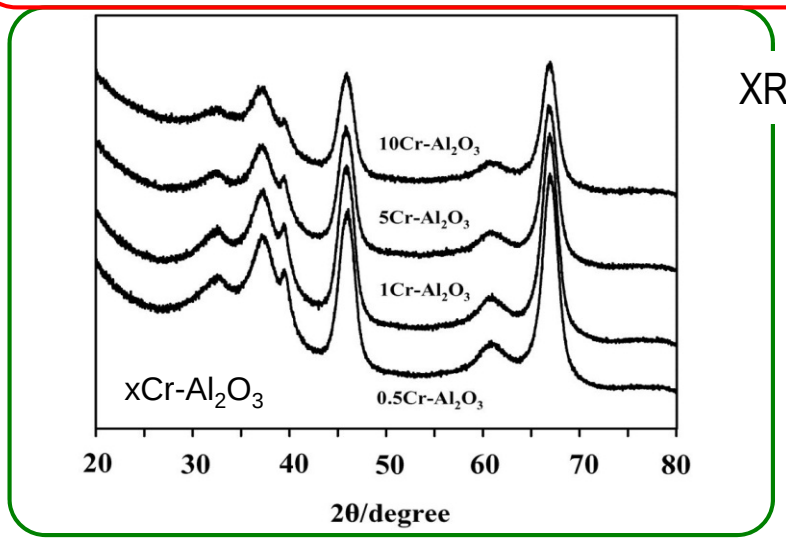
Meunier et al., *J. Catal.* 247 (2007) 277

Meunier, *Chem. Soc. Rev.* 39 (2010) 4602

- **Comparison of techniques: x wt% Cr^{n+}/support**

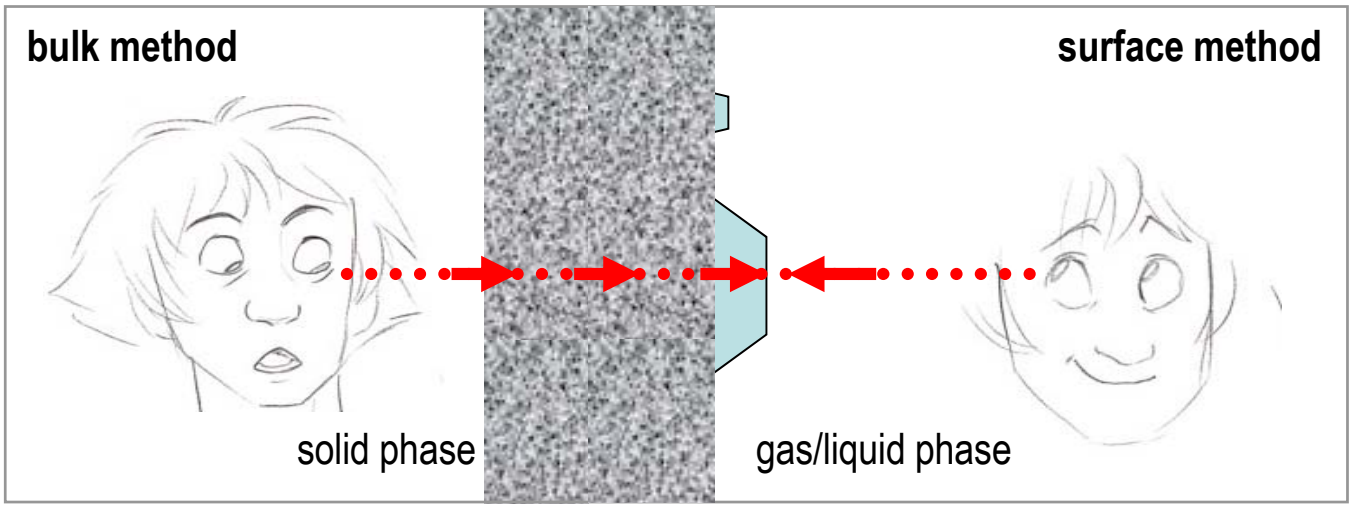


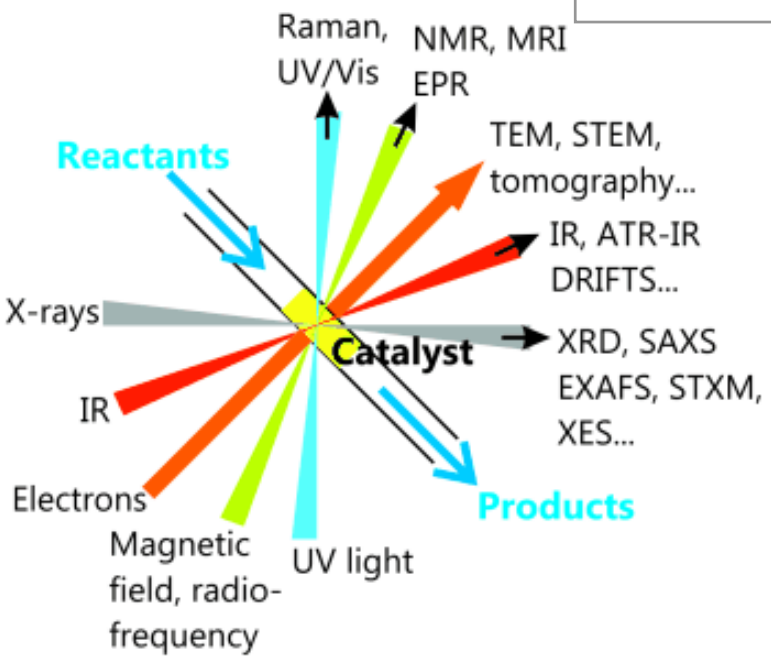




Matam et al., *J. Catal.* **261** (2009) 116

Multitechnique approach



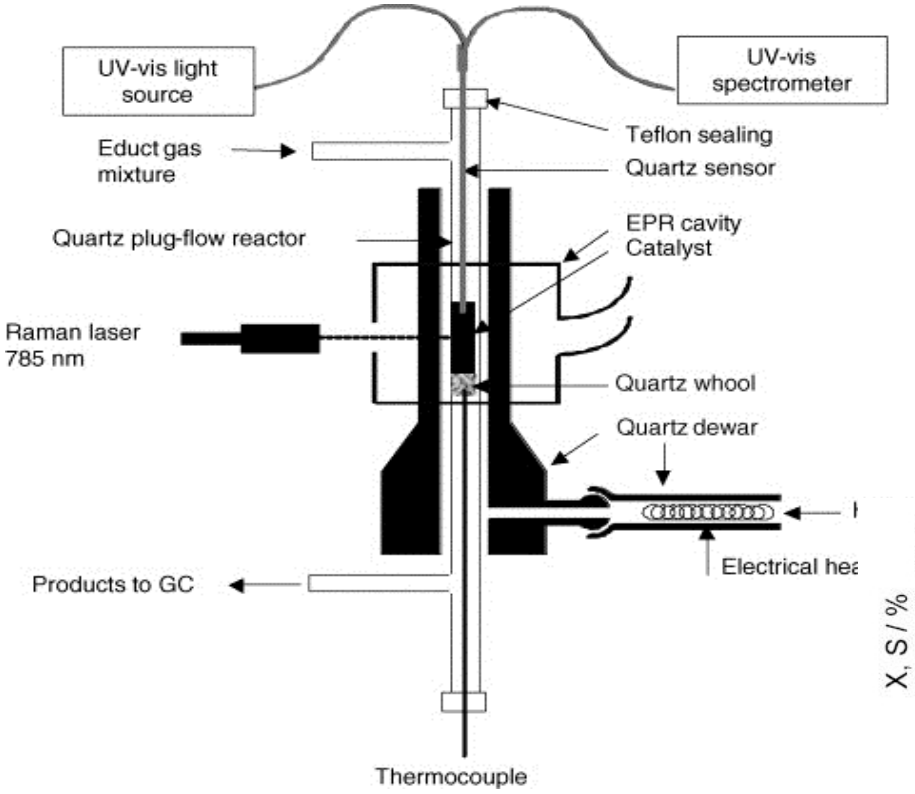


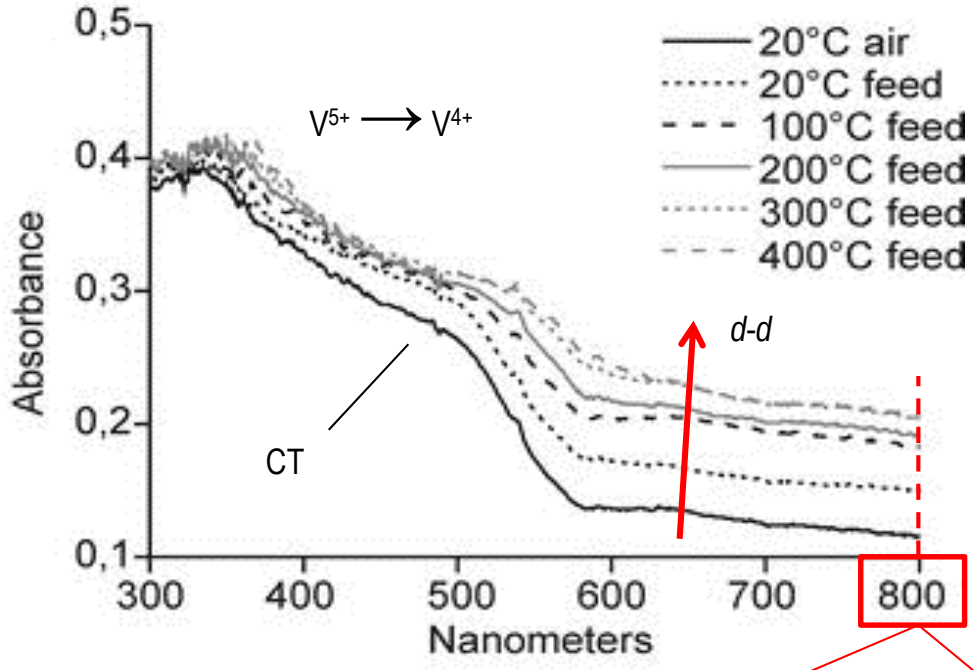
Grunwaldt et al., *ChemCatChem* 5 (2013) 62

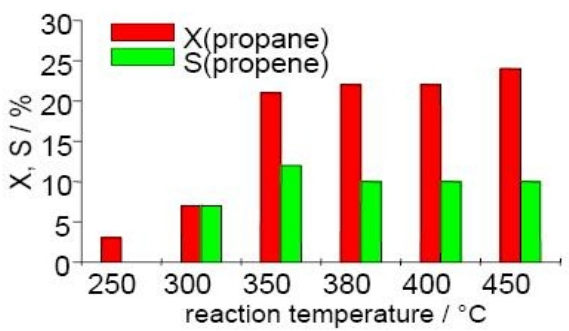
Combination of methods

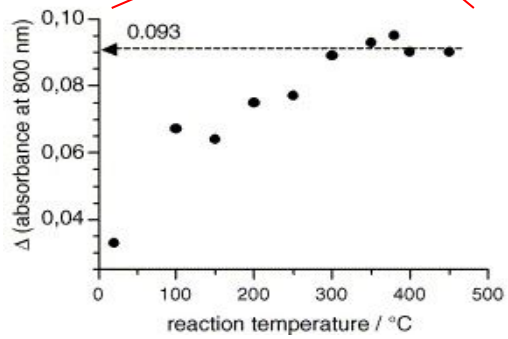
- Reactivity of V/TiO_2 after oxidative treatment

UV-vis: V^{5+} CT (UV)
V^{4+} d-d transitions (vis)





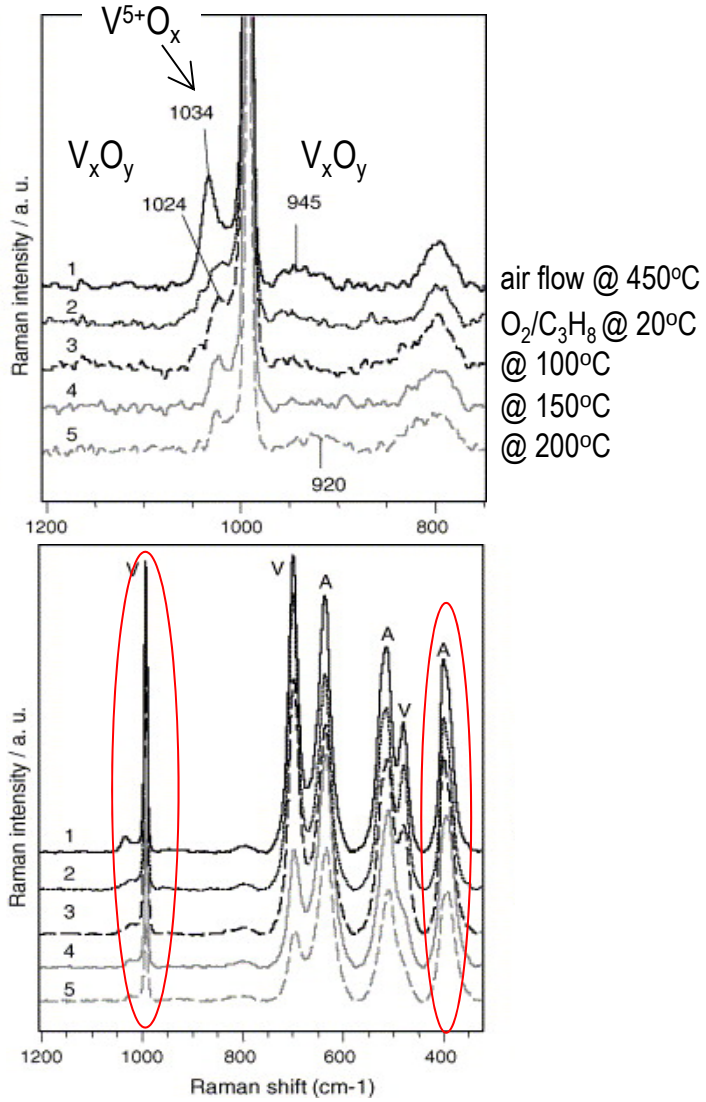


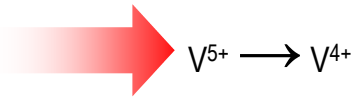


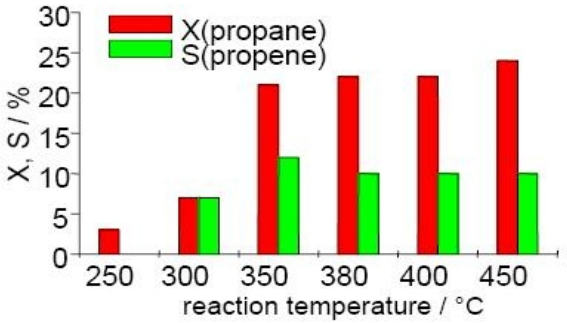
Brückner et al., *Catal. Today* **113** (2006) 16

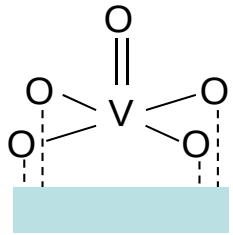
Combination of methods

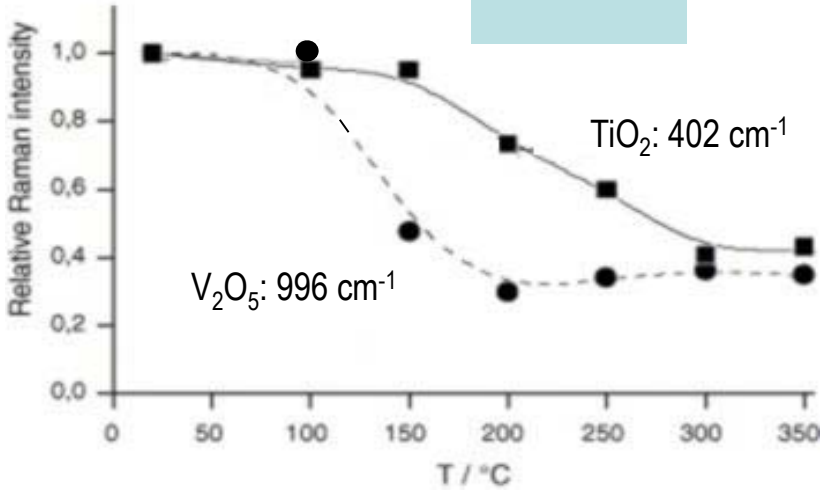
- Reactivity of V/TiO_2 after oxidative treatment





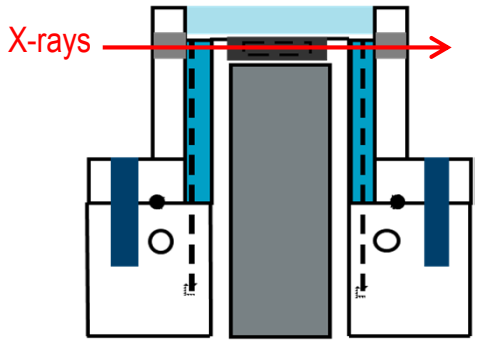




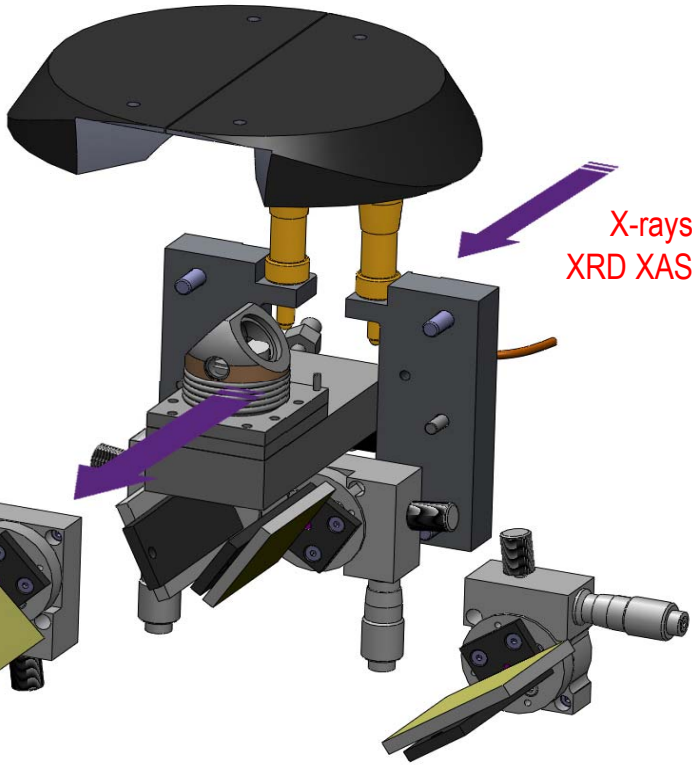


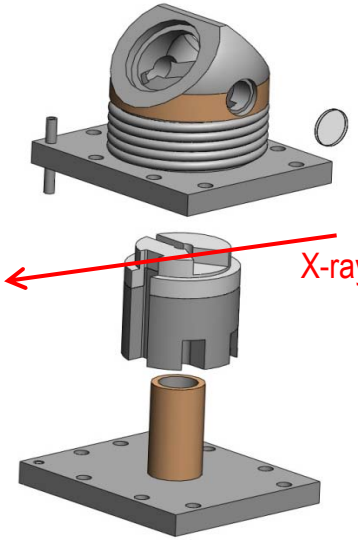
Brückner et al., *Catal. Today* **113** (2006) 16

Combined techniques: XAS/XRD/DRIFTS/MS

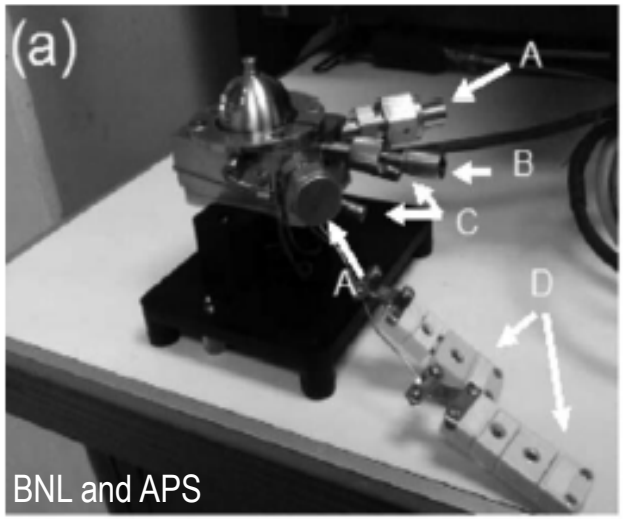


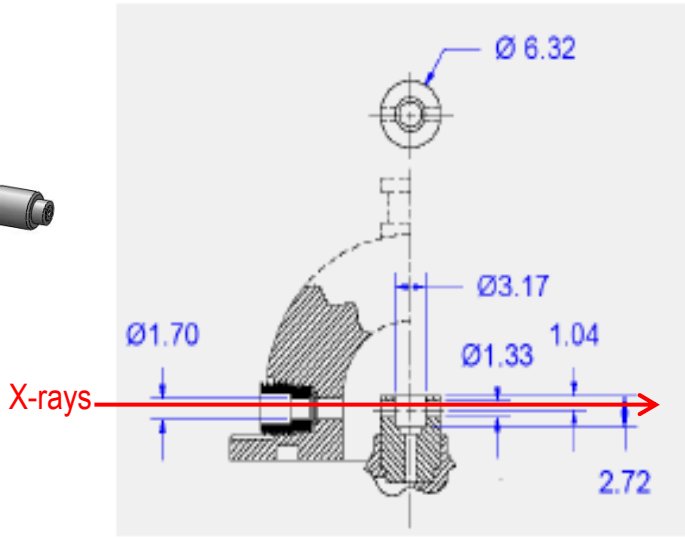
Newton et al, *Chem. Comm*. (2004) 2382





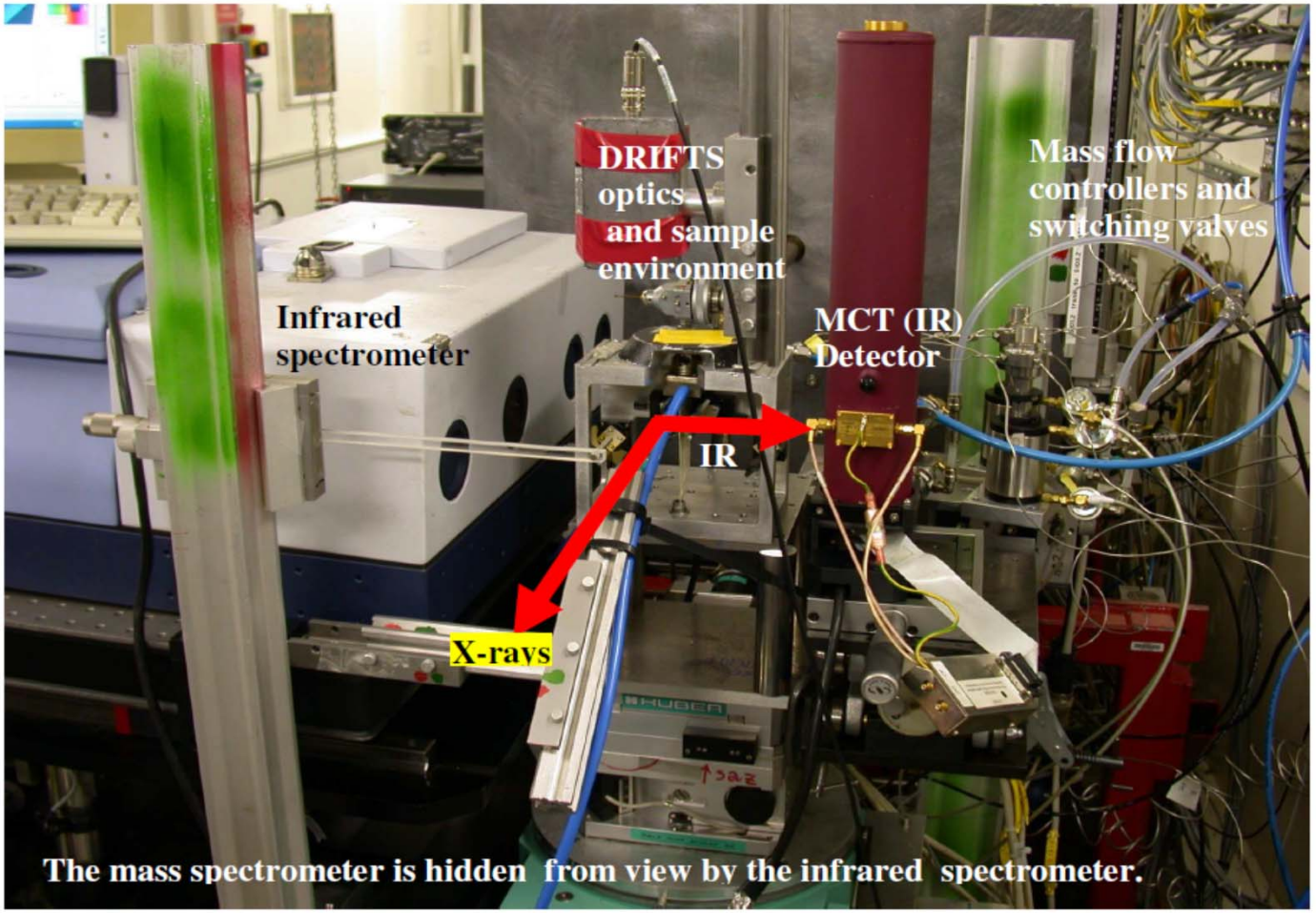
Newton , *Top. Catal*. 52 (2009) 1410





Marinkovic et al, *JSR* 18 (2011) 447

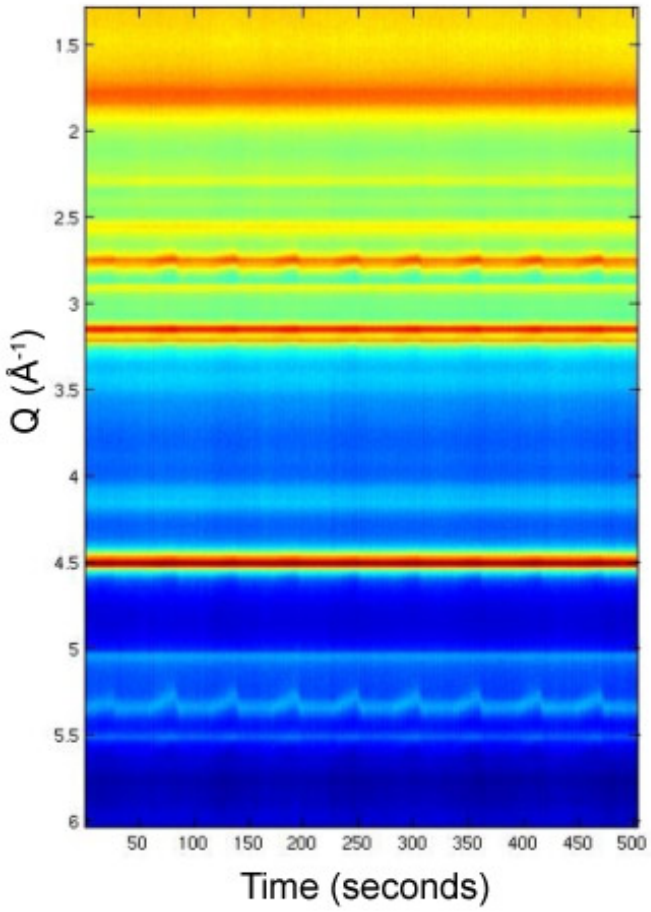
Time-resolved X-ray diffraction

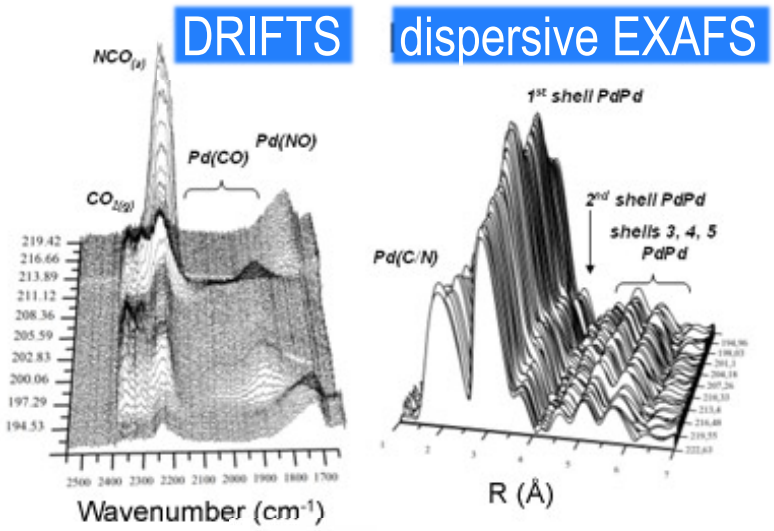


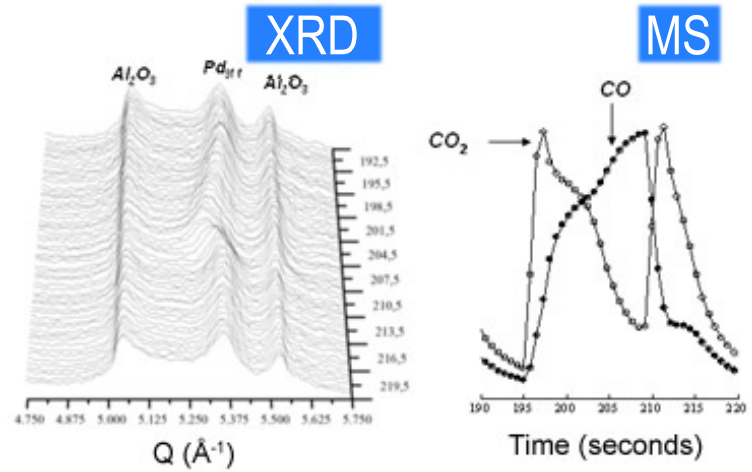
Newton et al, *J. Am. Chem. Soc*. 132 (2010) 4540

Pd/Al_2O_3 – Combined methods

- One experiment – many methods





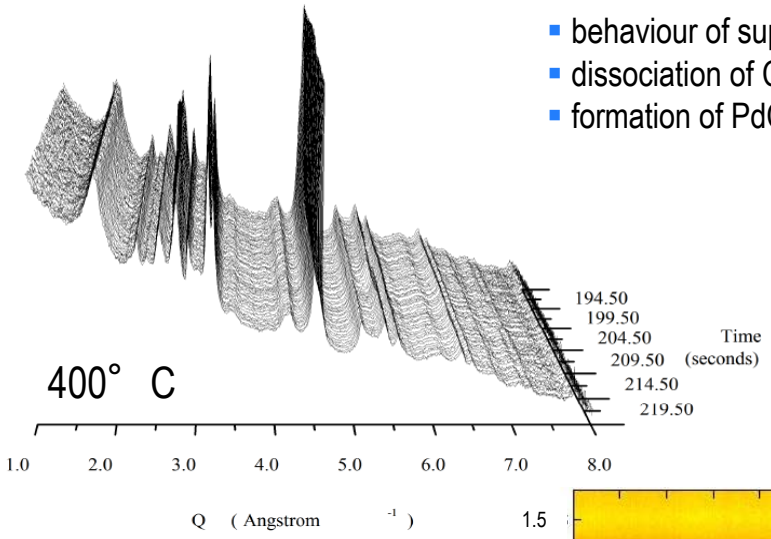


Q= 4πsin(θ)/λ

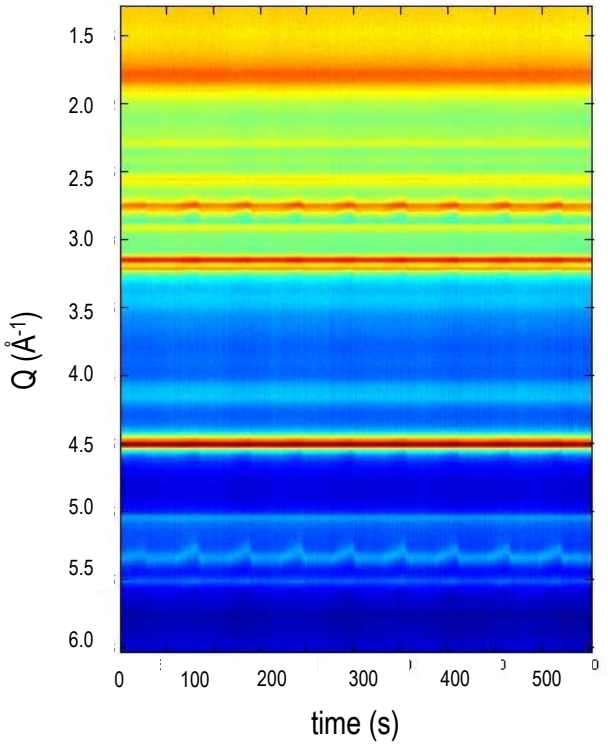
Newton et al., *J. Amer. Chem. Soc.* **12** (2010) 5634

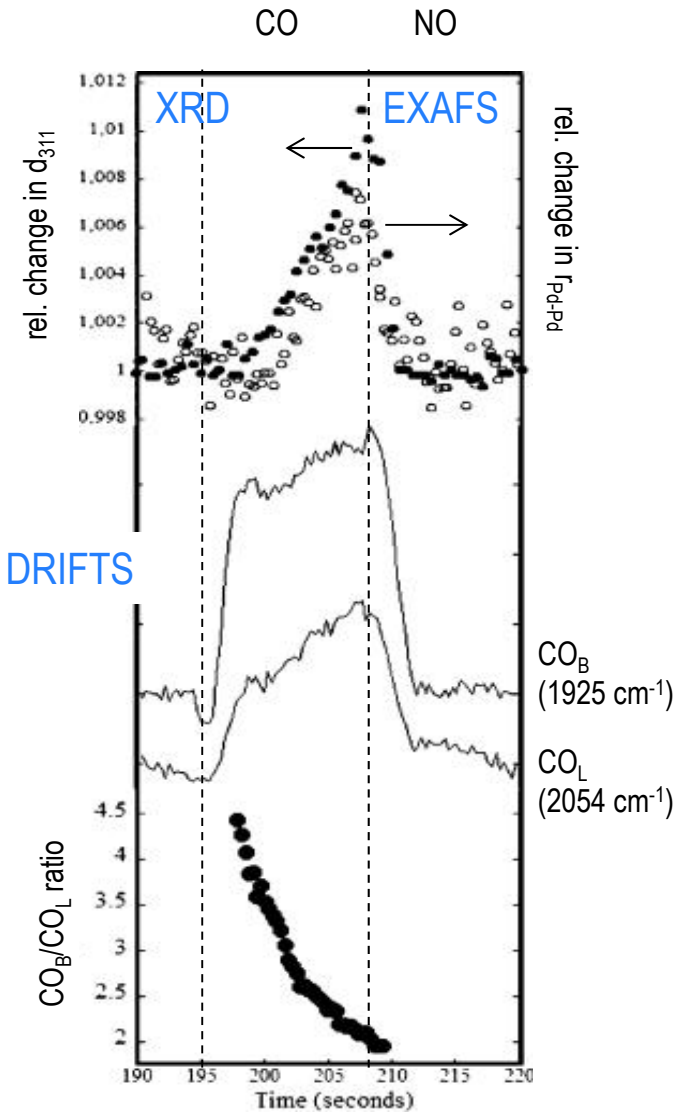
Time-resolved X-ray diffraction

- behaviour of supported Pd nano-particles
- dissociation of CO on Pd
- formation of PdC_x adlayer



$Q = 4\pi\sin(\theta/2)/\lambda$





l=0.143Å
86.8 keV
XRD: 2 Hz, 100 ms/pattern
2% Pd/Al_2O_3 catalyst
(TEM: ca. 3 nm)

Newton et al, *J. Am. Chem. Soc*. 132 (2010) 4540; Newton et al, *Angew. Chemie Int. Ed*. 51 (2012) 2363

Diffraction – Spectroscopy – Microscopy

XRD

- analysis of long range order
- averaging over the whole sample
- limited to large crystallites (> 3 nm)
- amorphous material invisible
- 3D distribution of d-spacings (but collapsed into 1D)
- usually no beam damage
- not element specific
- distinguishes different crystallographic sites
- averages over different elements on the same crystallographic site
- distinguishes different (crystalline) phases

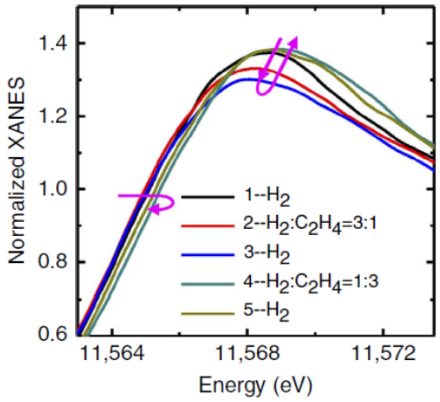
TEM

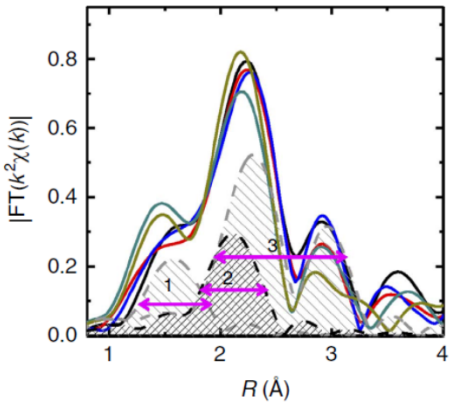
- local
- limited to smaller crystallites (beam transparency required)
- amorphous material visible
- 2D projection of d-spacing
- beam damage quite possible

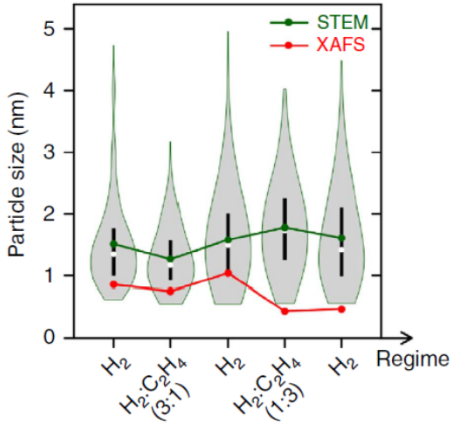
EXAFS

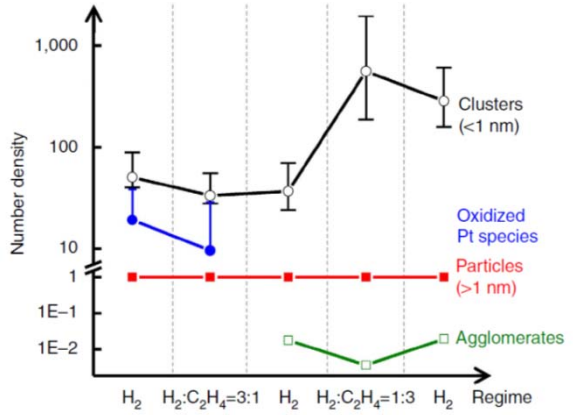
- analysis of short range order
- covers both crystalline and amorphous material
- element specific
- averages over different sites (for the same element)
- distinguishes different elements on the same crystallograpohic site
- averages over different phases (containing the same element)

Combination of spectroscopy and microscopy

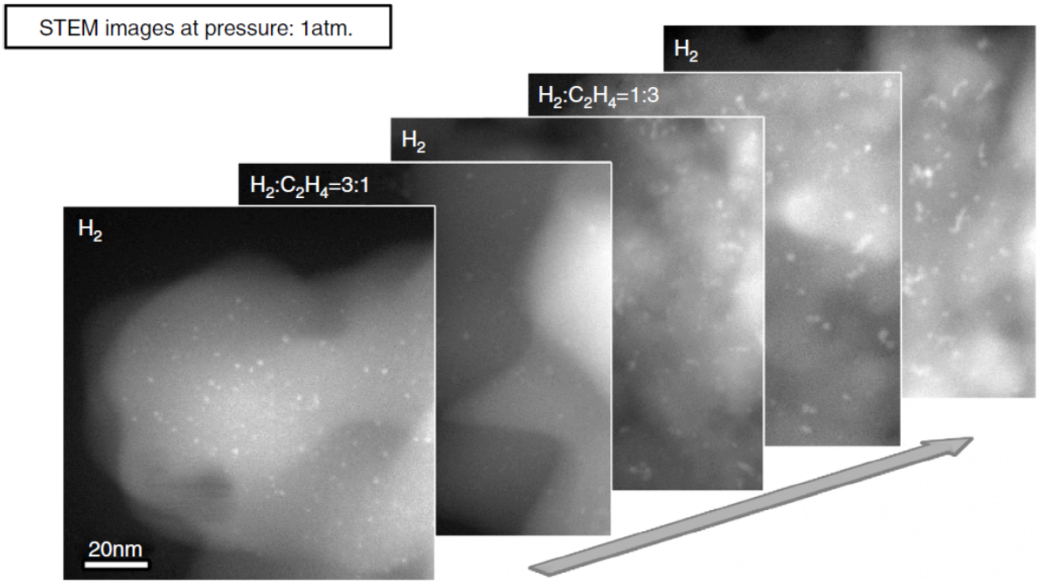


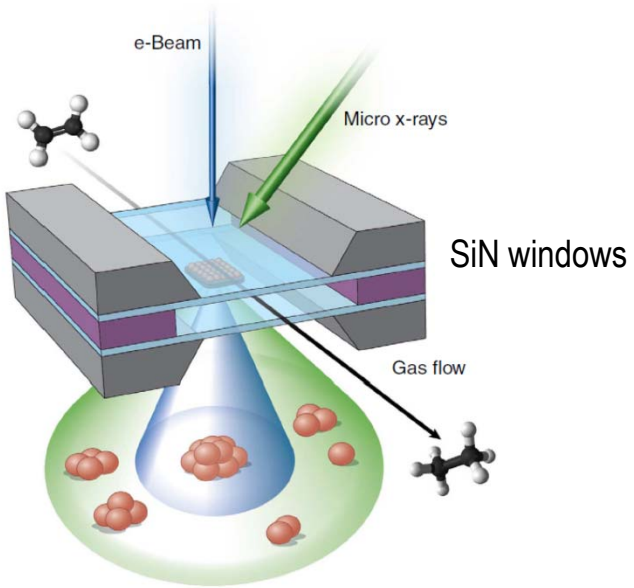






Pt redispersion under reaction conditions



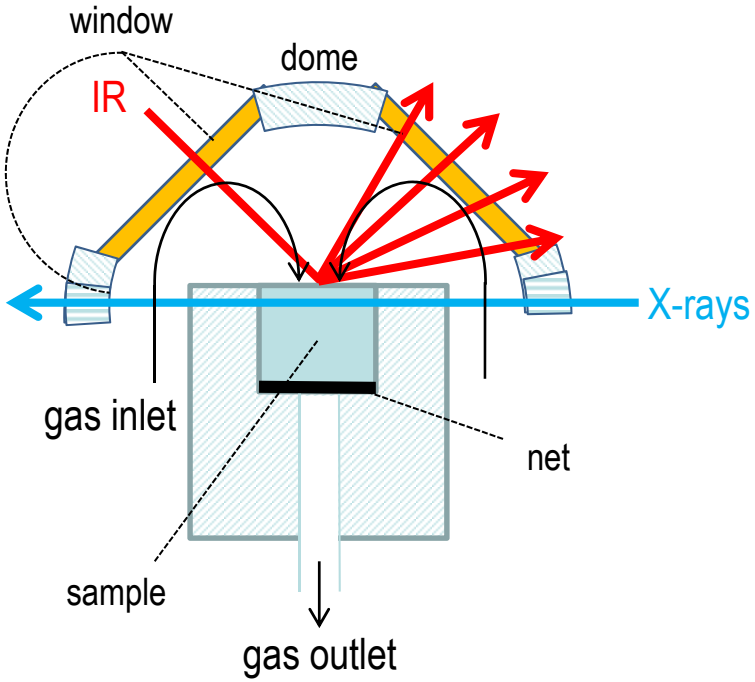


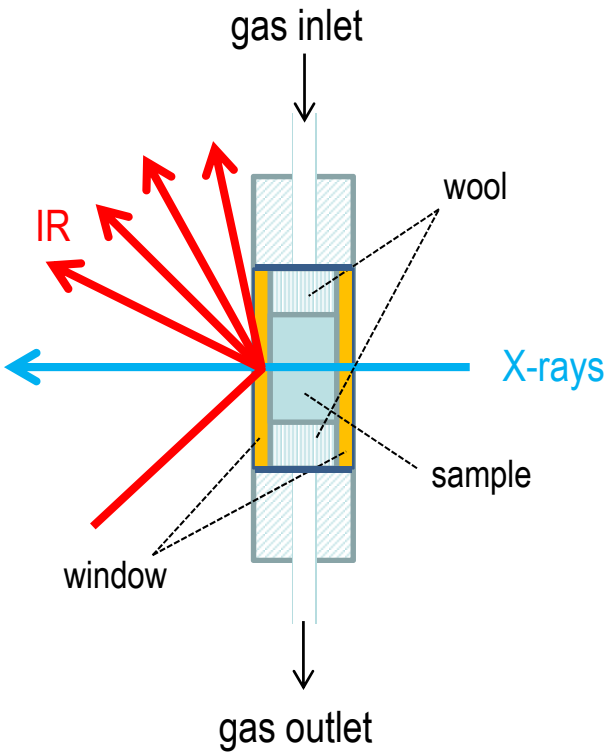
SiN windows

BROOKHAVEN NATIONAL LABORATORY

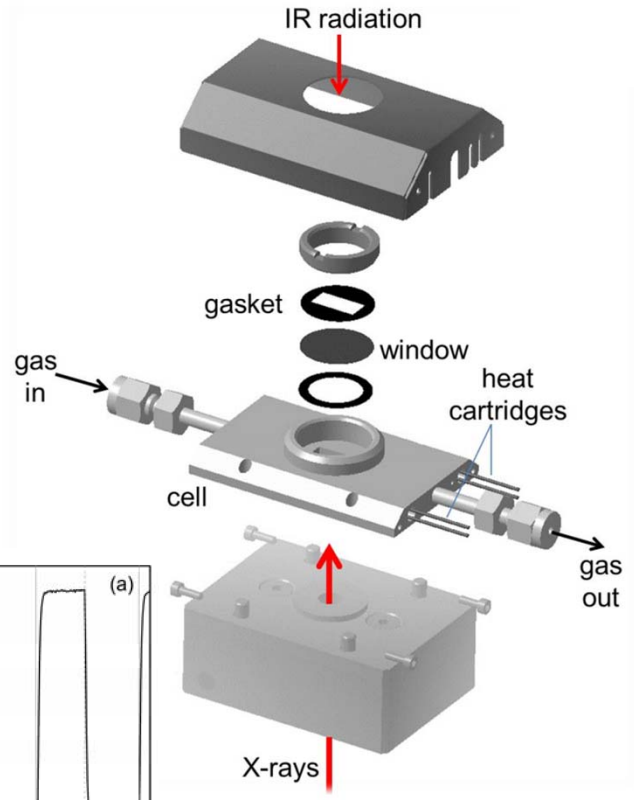
Li et al., *Nature Commun.* **6** (2015) 7583

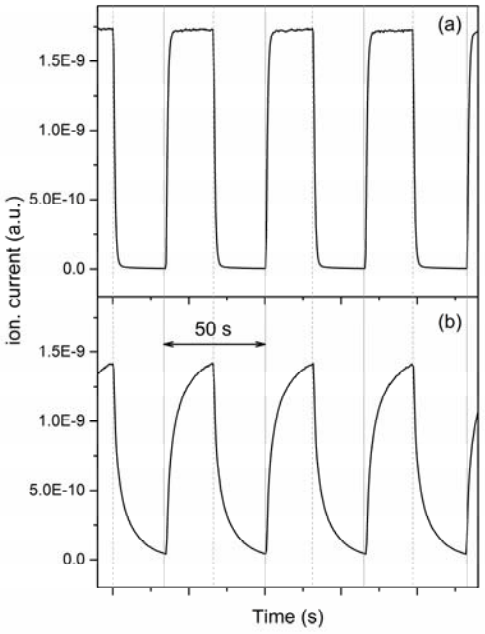
A different approach…



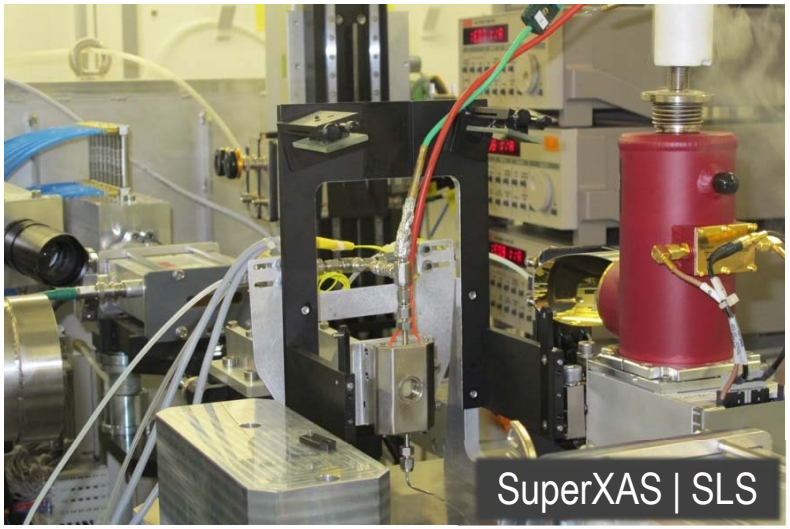


A different approach…



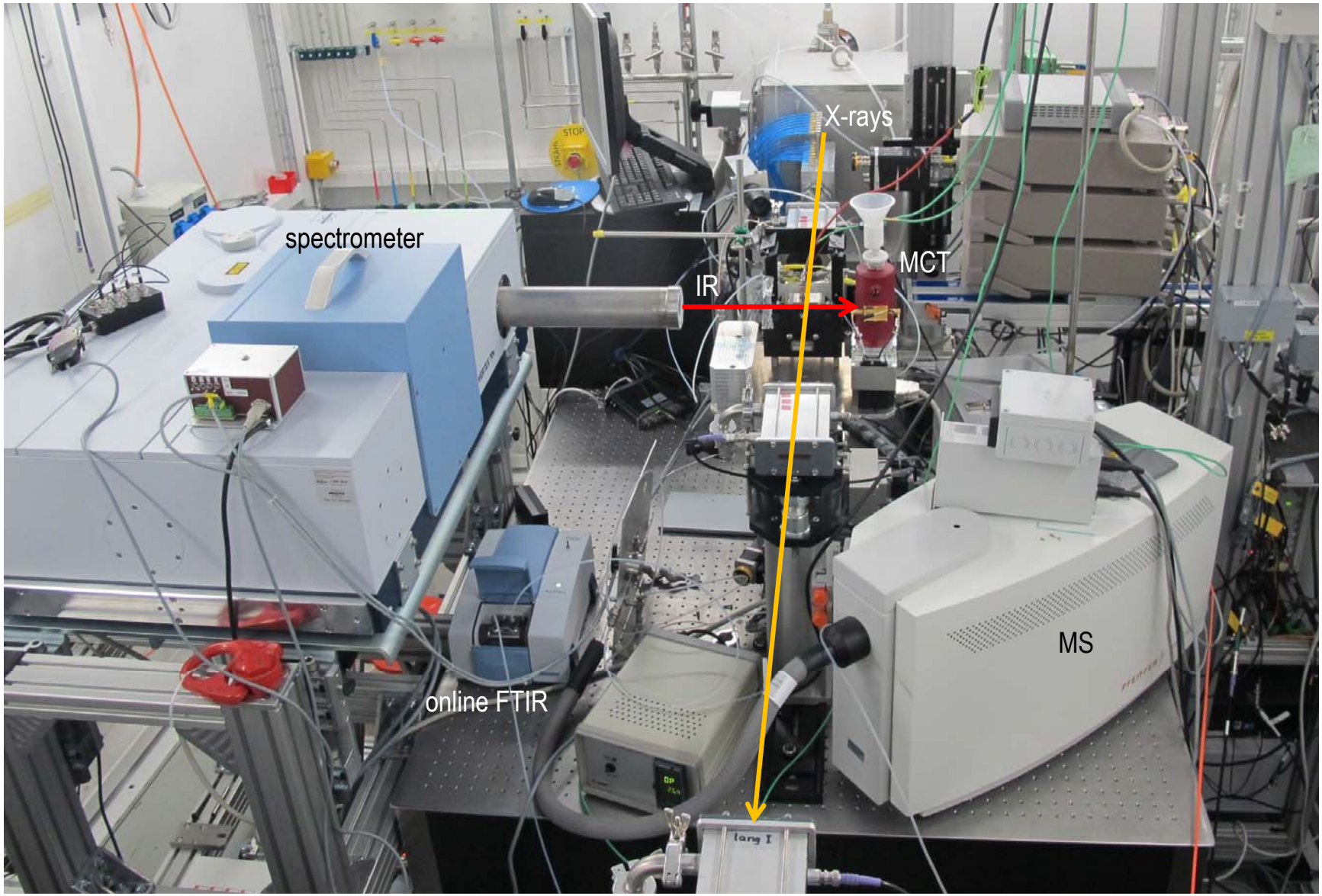


- Versatile cell: interchangeable windows
- Tested for DRIFTS, (quick-, ED-)EXAFS, HE-XRD, XES, PDF
- Simultaneous DRIFTS/quick-EXAFS (SLS)
- Amenable to Raman, UV/vis
- One setup



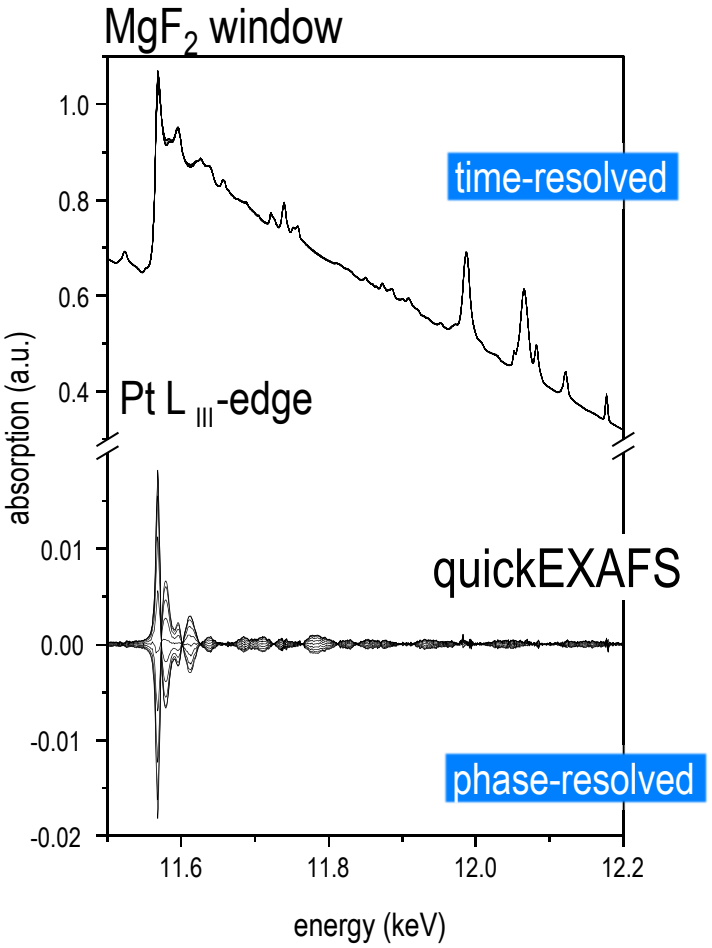
Chiarello et al., *Rev. Sci. Instr.* **85** (2014) 074102

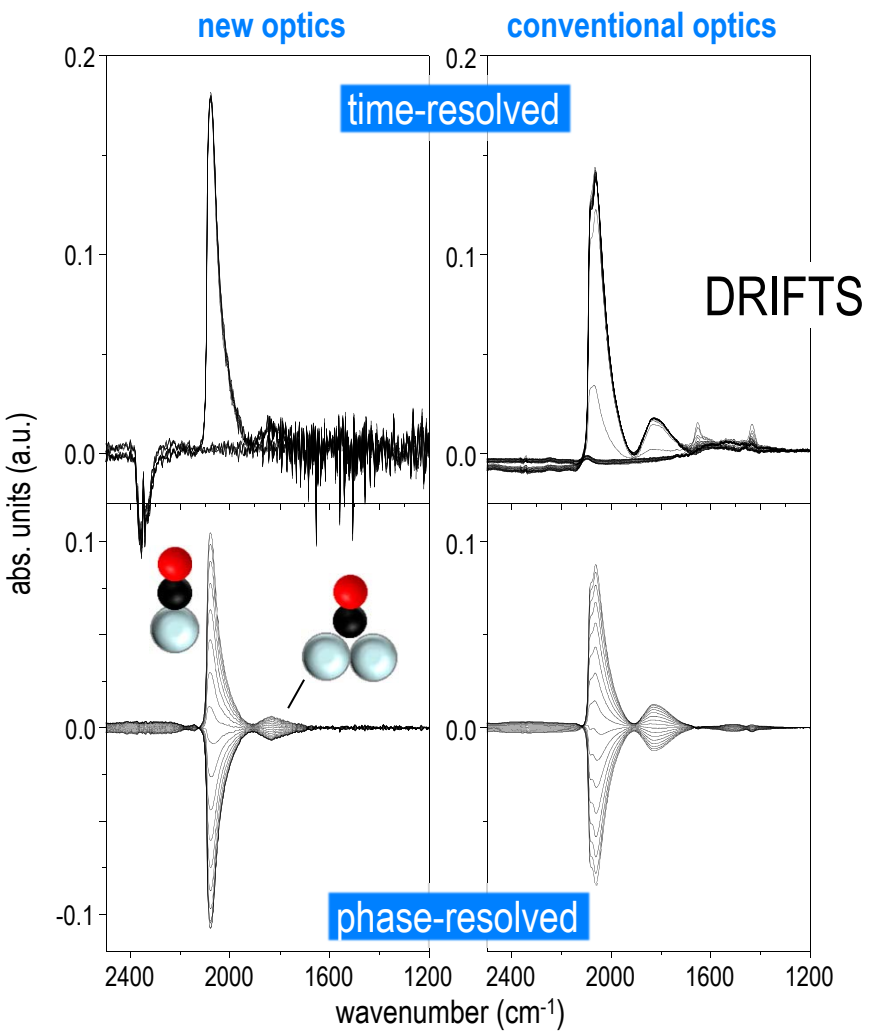
Combined synchronous XAS-IR-MES at SuperXAS

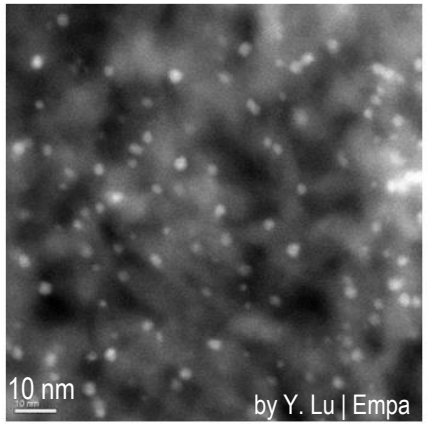


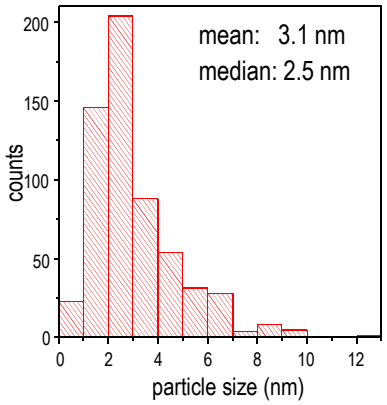
Combined synchronous XAS-IR-MES at SuperXAS

2 wt% Pt/Al_2O_3, CO vs. O_2, 150°C





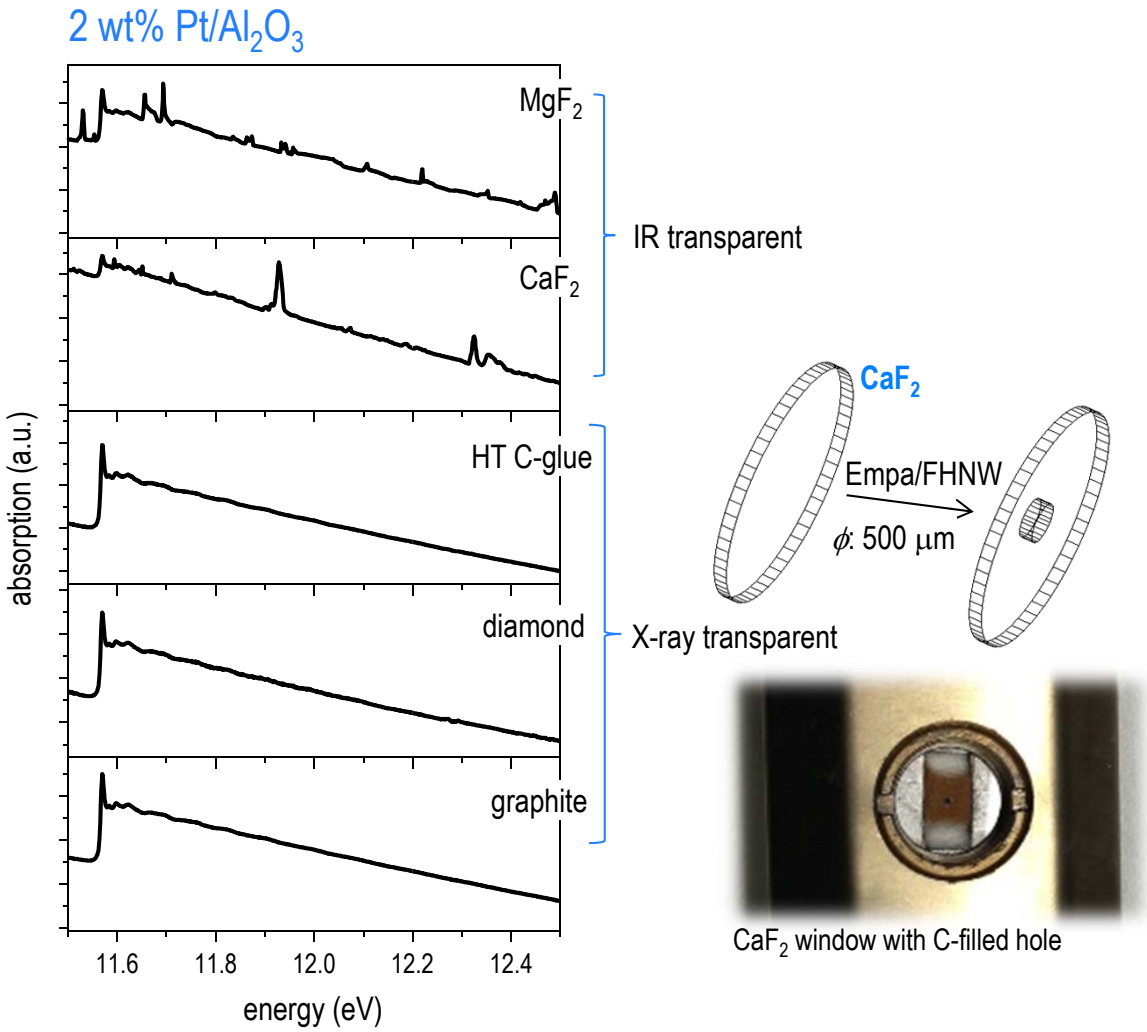




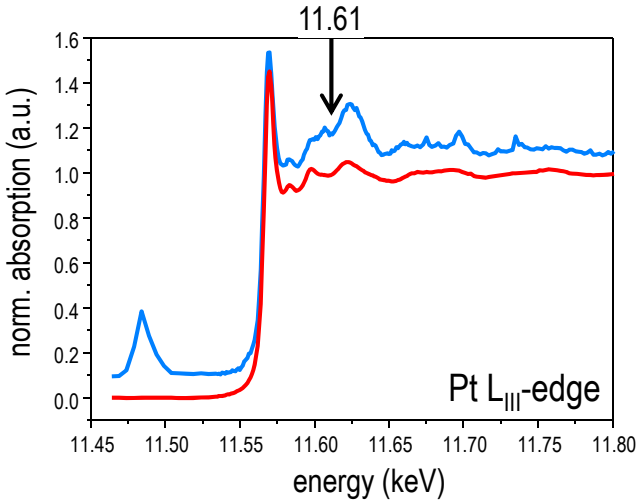
- diffraction peaks removed by PSD
- synchronous adsorption of CO followed by DRIFTS

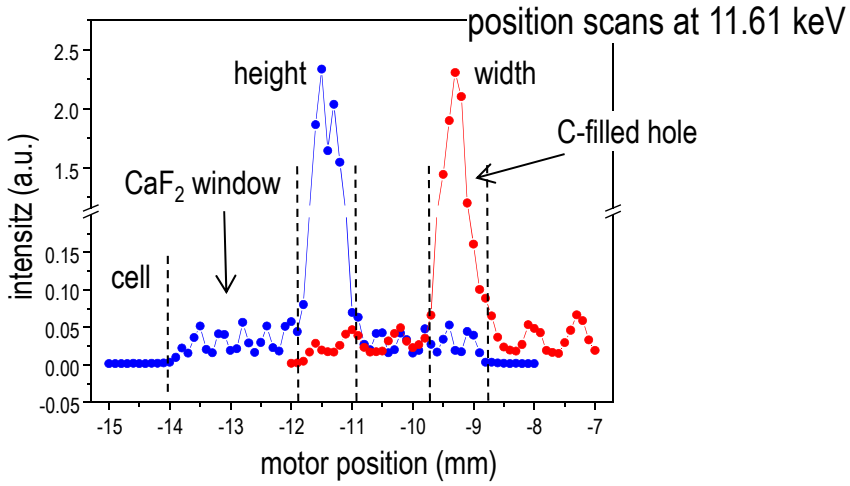
Chiarello et al., *Rev. Sci. Instr.* **85** (2014) 074102

Which window for XAS-IR combination?



CaF_2 window with C-filled hole



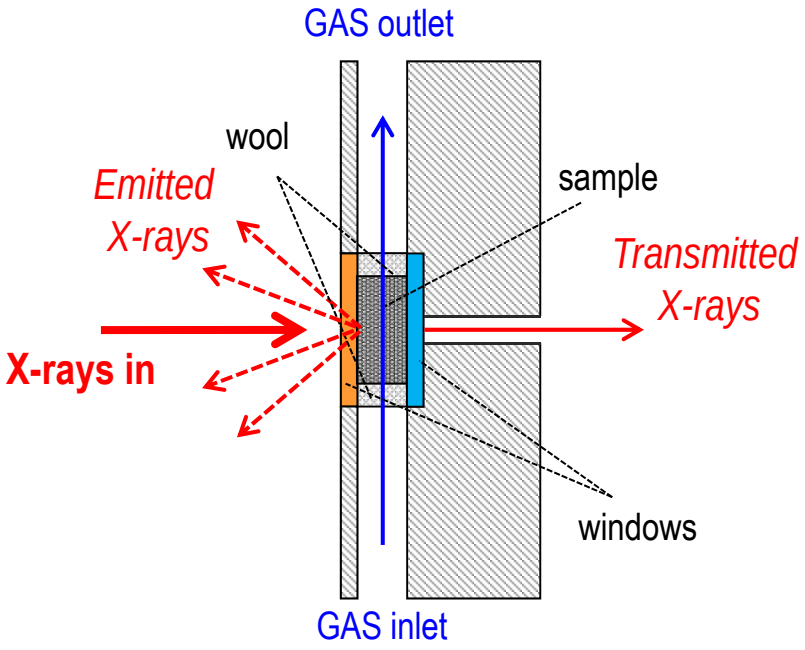


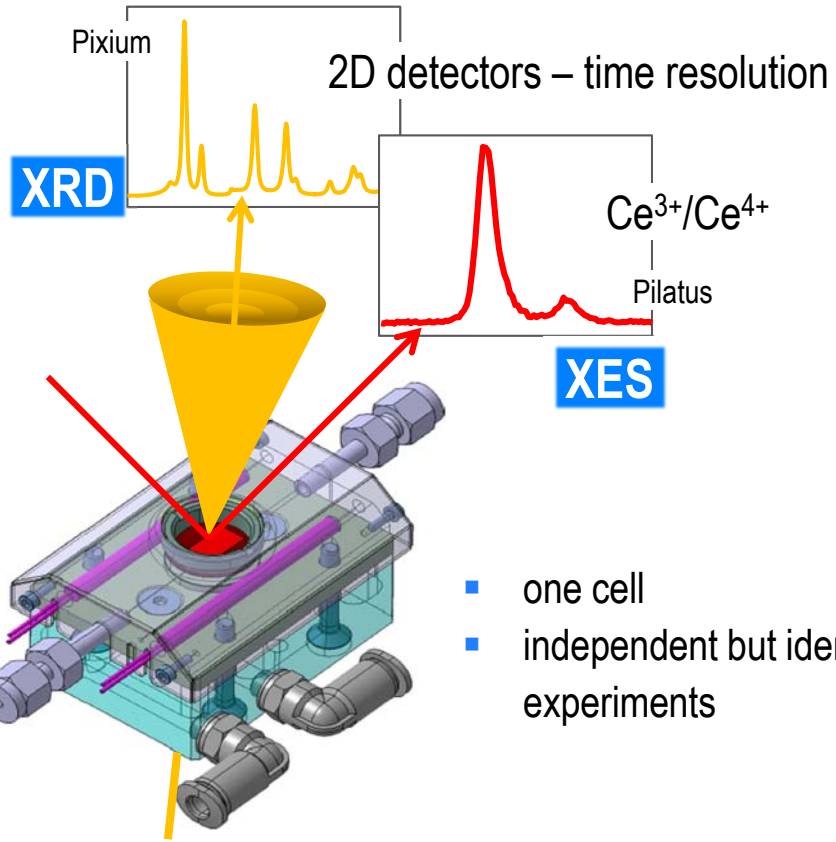
Chiarello et al., *Rev. Sci. Instr.* **85** (2014) 074102

A different approach…

Advantages **new design**:

- Combine different spectroscopic and diffraction methods:
  DRIFTS, Q-EXAFS, ED-XAFS, XES (HEROS and R-XES), XRD
- Reduced dead volume → close to lab scale PFR





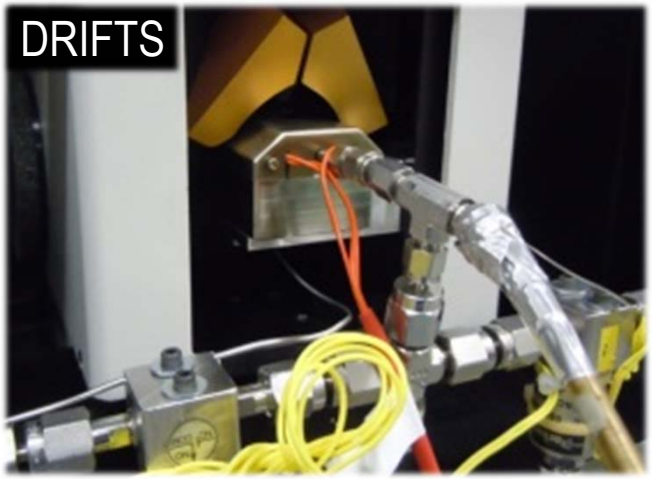
- one cell
- independent but identical experiments

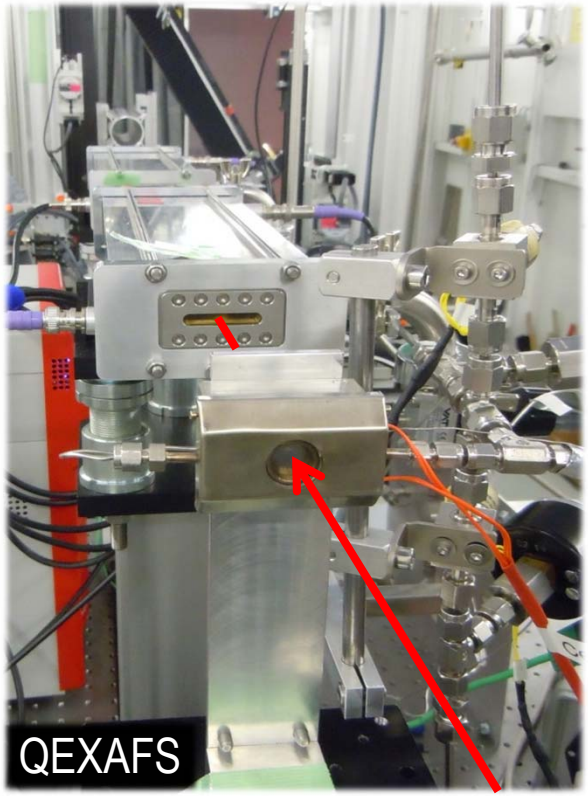
- Two **heat cartridges** and a **thermocouple** inserted along the stainless steel block on the sides of the sample position → guarantee **homogeneous temperature distribution**
- A **thermocouple** inserted at the beginning of the catalyst bed → monitor the **sample temperature**
- Cell tested **up to 450ºC**

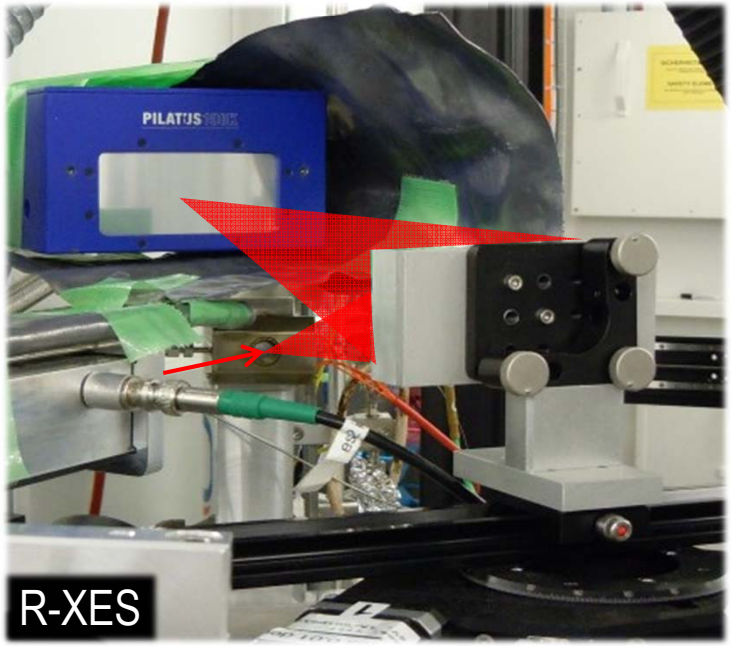
Chiarello et al., *Rev. Sci. Instr.* **85** (2014) 074102

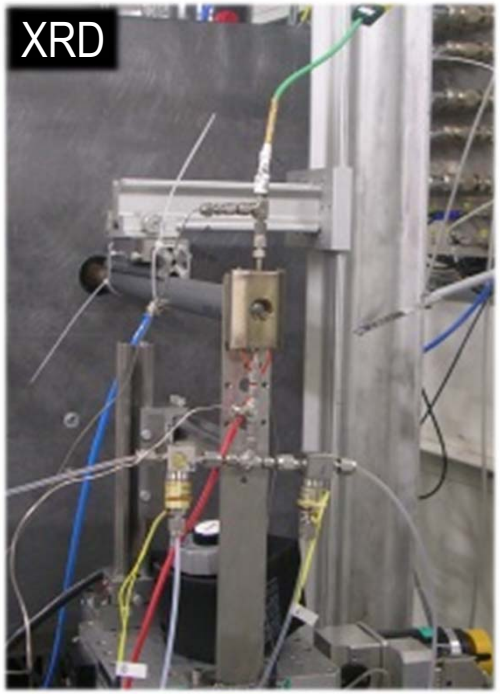
A different approach…

Amenable to Raman and UV-vis-NIR

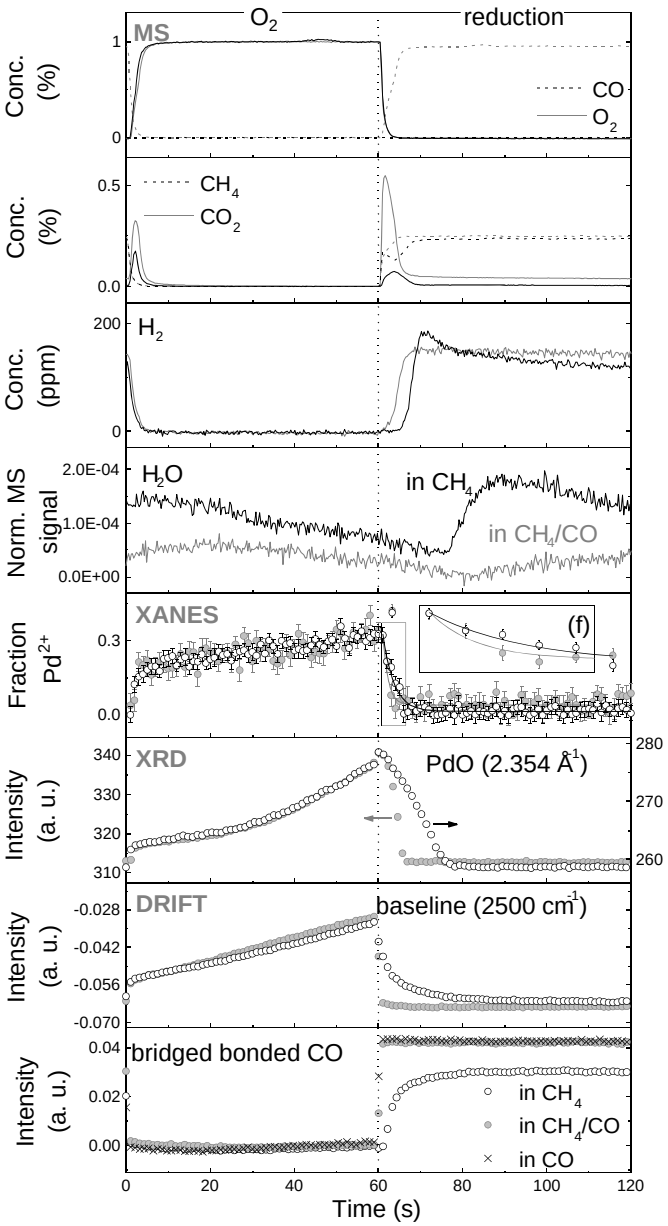


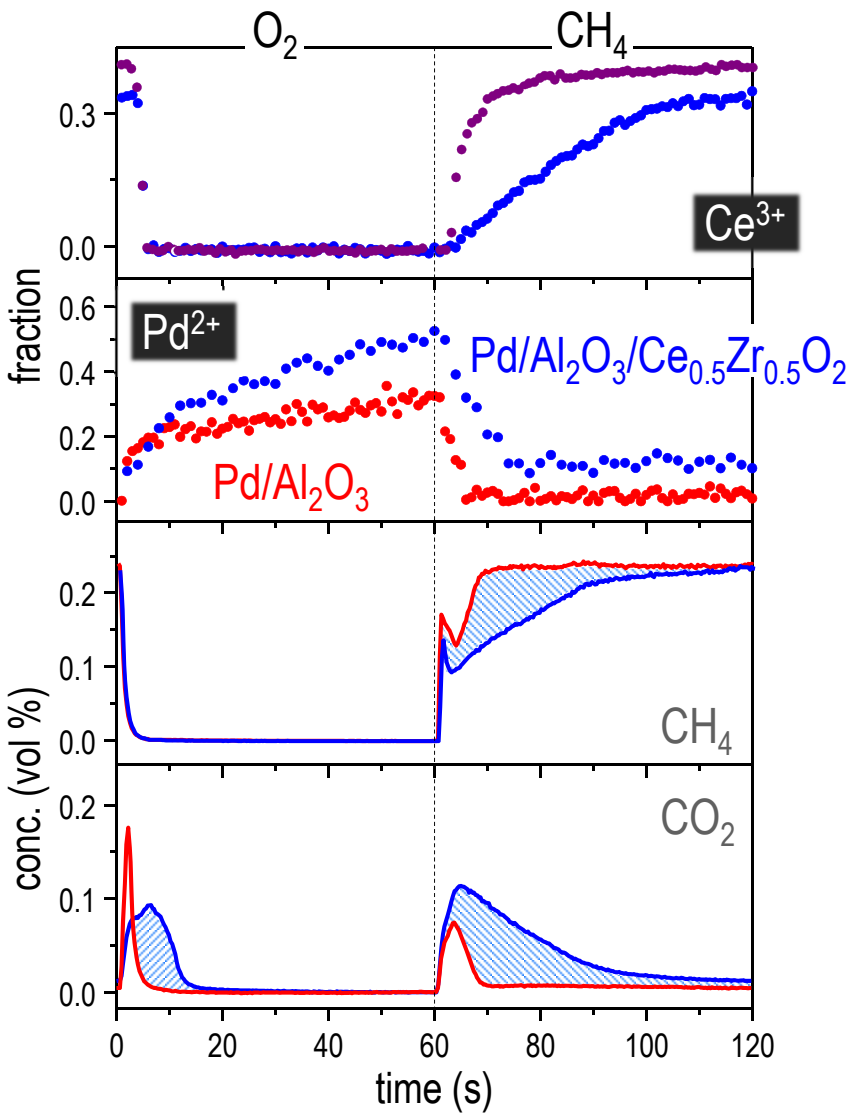






Example

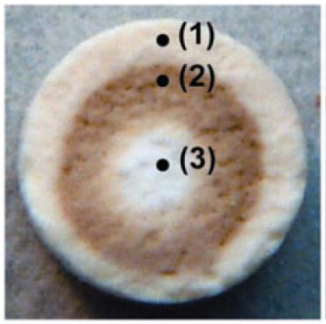

O2
reduction
MS
Conc. (%)
CO
O2
CH4
CO2
H2
Conc. (ppm)
Norm. MS signal
H2O
in CH4
in CH4/CO
XANES
Fraction Pd2+
(f)
XRD
PdO (2.354 Å-1)
Intensity (a. u.)
DRIFT
baseline (2500 cm-1)
bridged bonded CO
in CH4
in CH4/CO
in CO
Time (s)

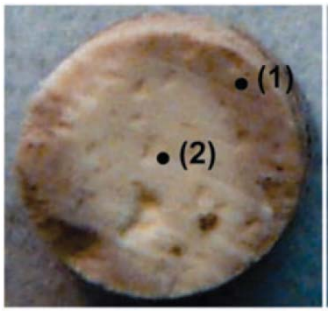

O2
CH4
fraction
Ce3+
Pd2+
Pd/Al2O3/Ce0.5Zr0.5O2
Pd/Al2O3
conc. (vol %)
CH4
CO2
time (s)

PAUL SCHERRER INSTITUT

Supported Palladium catalysts

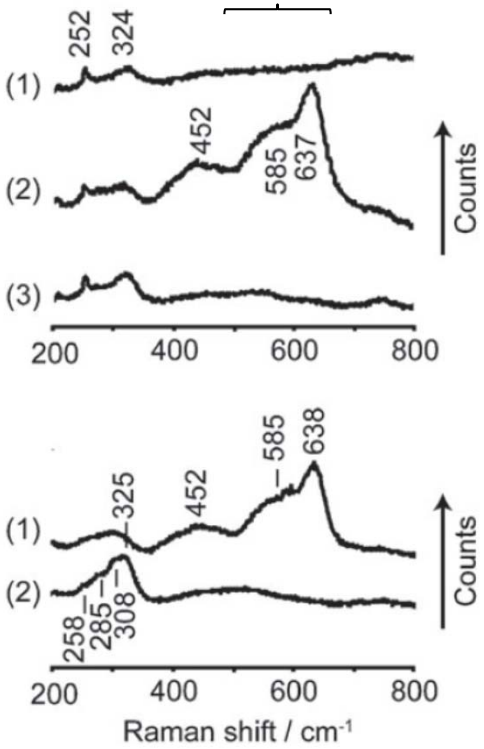
Pd/Al_2O_3 – how good is preparation?





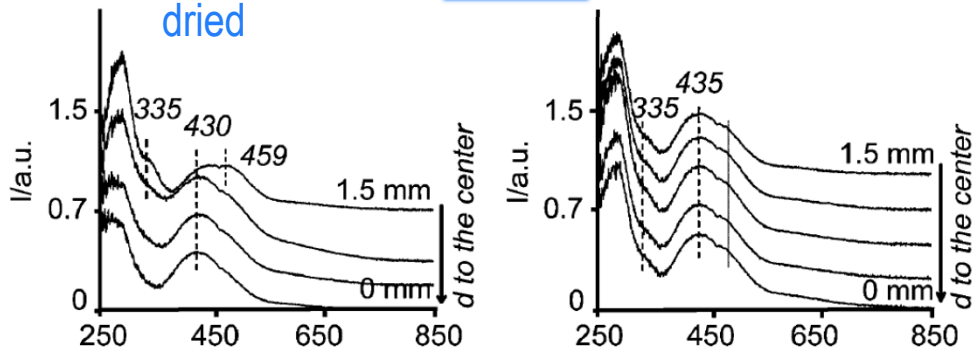
Raman

calcined



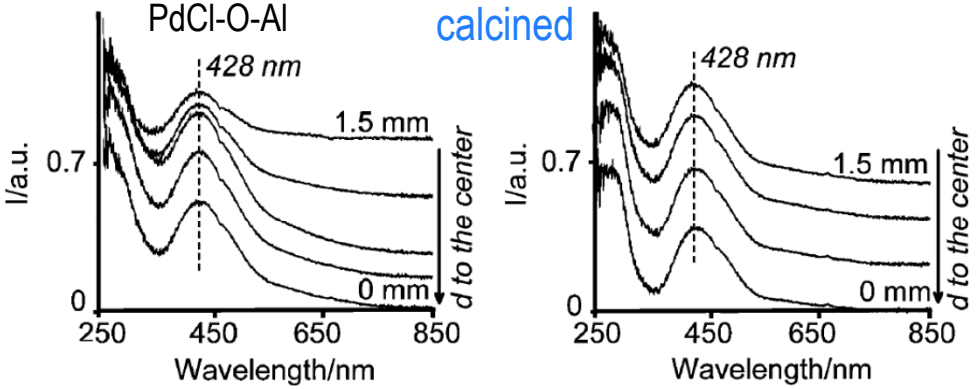
UV-vis

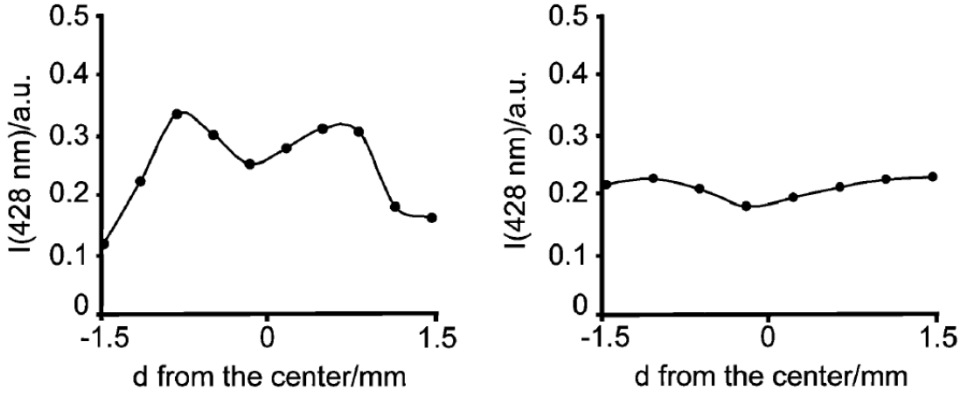
dried



PdCl-O-Al

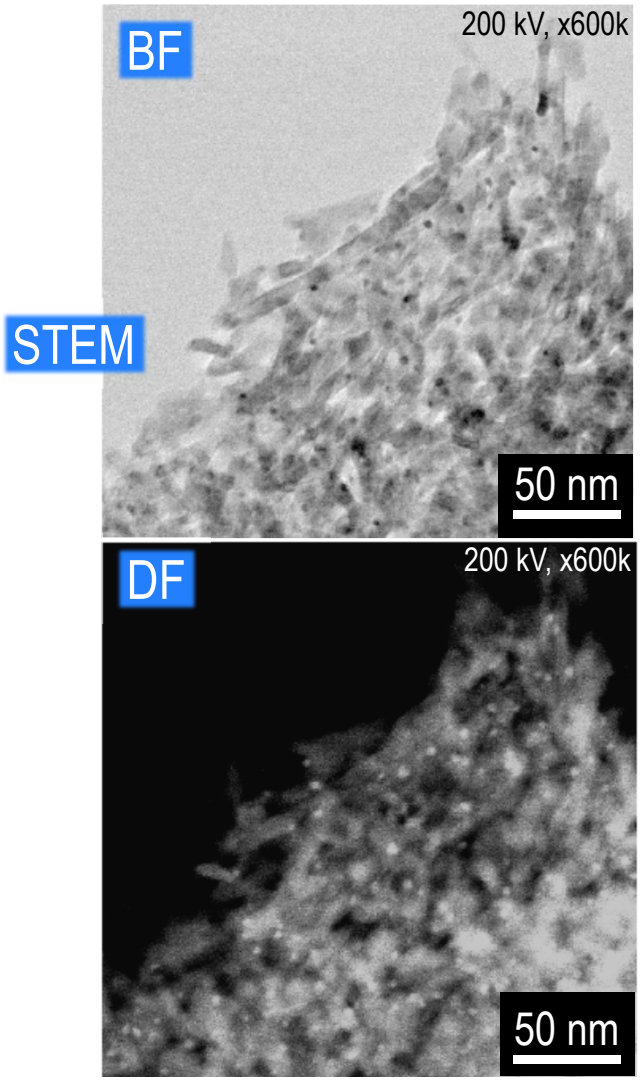
calcined

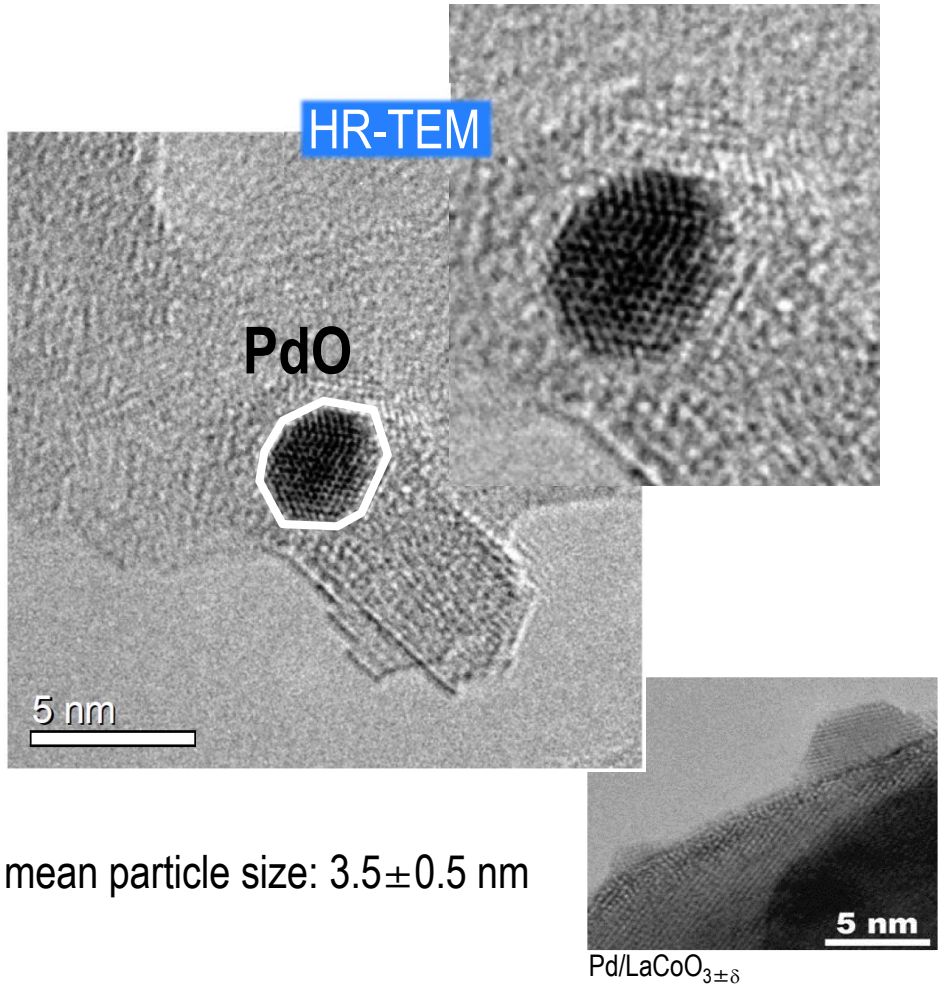




Espinosa-Alonso et al., *PCCP* **12** (2010) 97

Pd/Al_2O_3 – textural properties

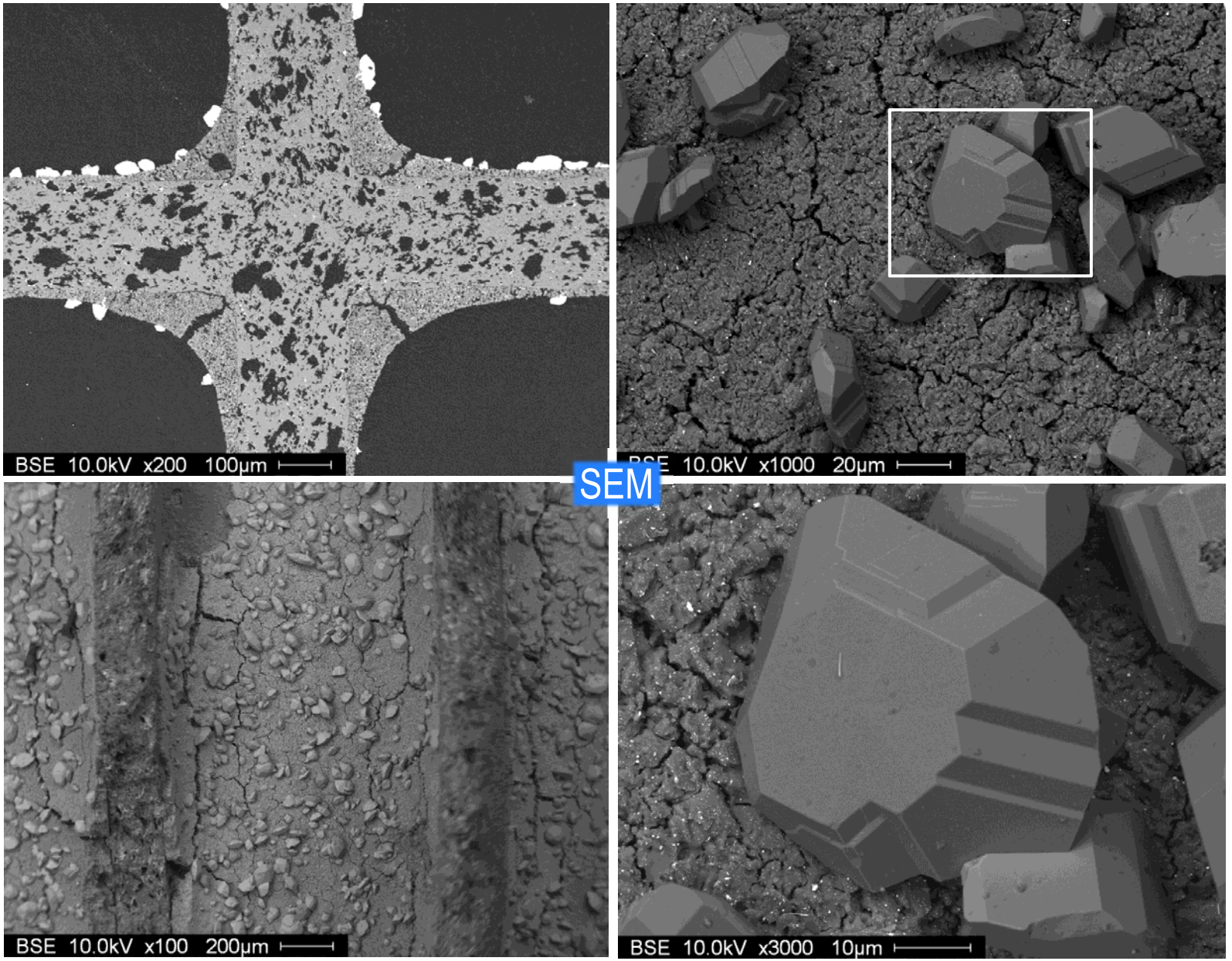




mean particle size: 3.5±0.5 nm

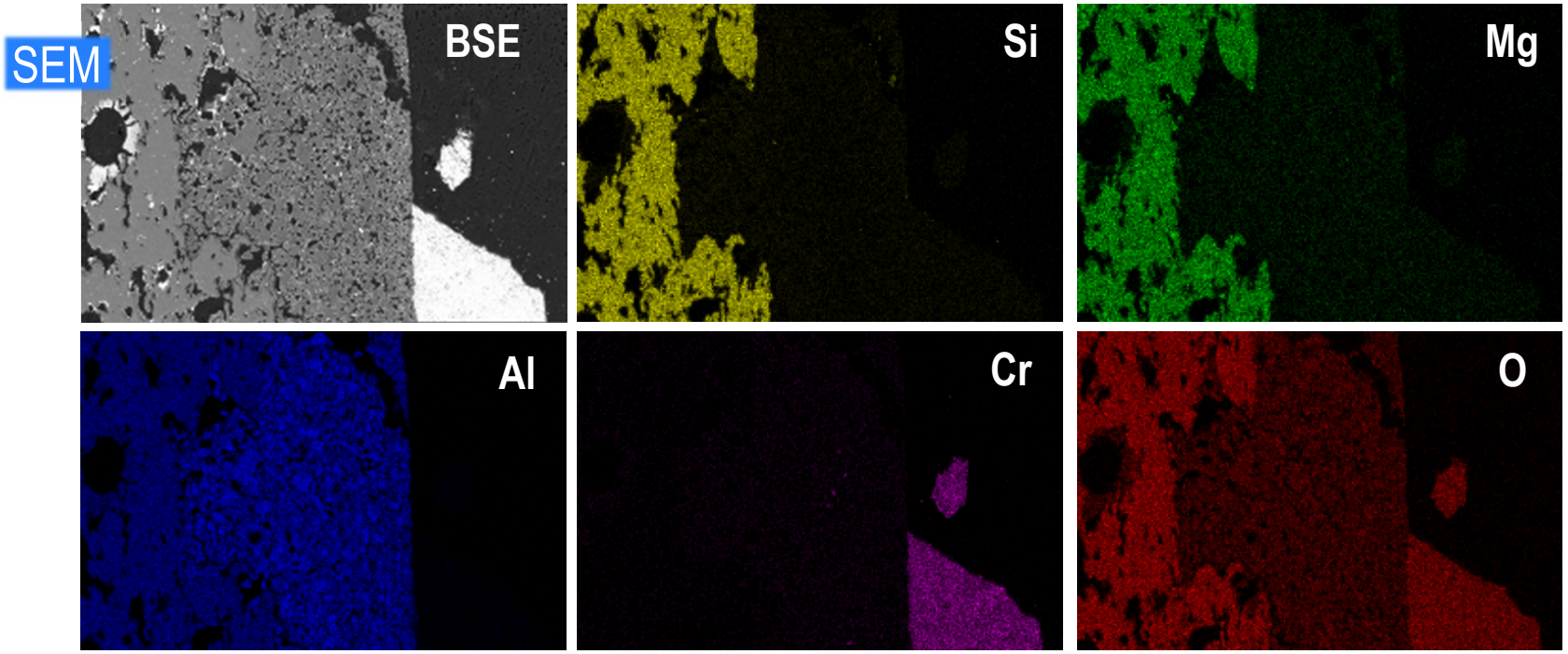
$Pd/LaCoO_{3\pm\delta}$

Pt/Al_2O_3 – Morphology

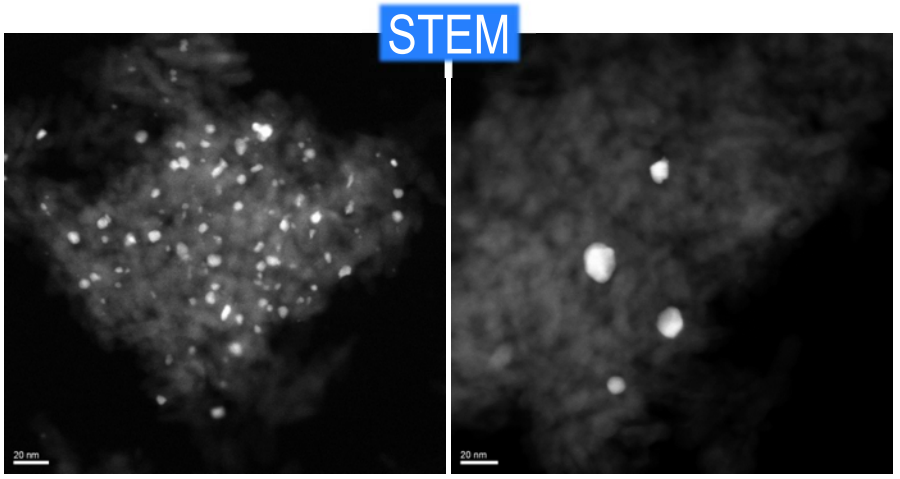


Keav et al., *Appl. Catal. A* **469** (2014) 259

Pt/Al_2O_3 – Morphology

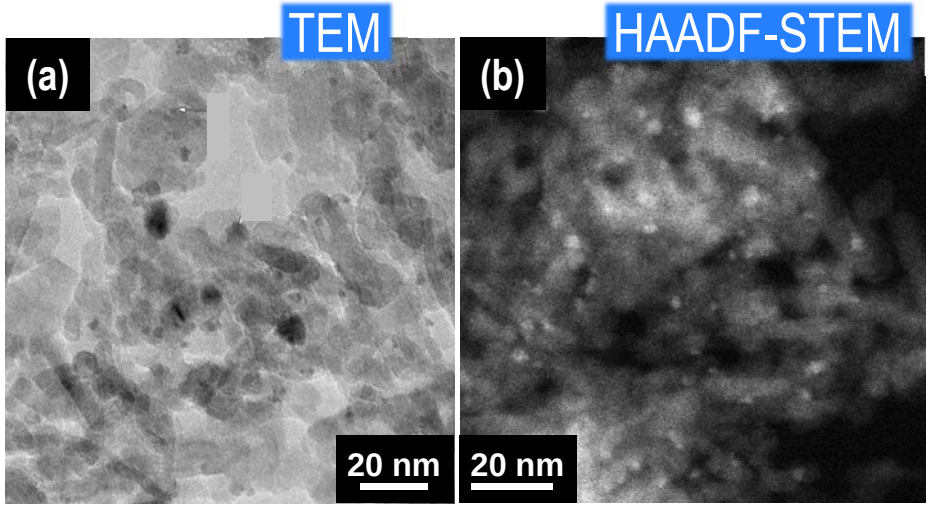


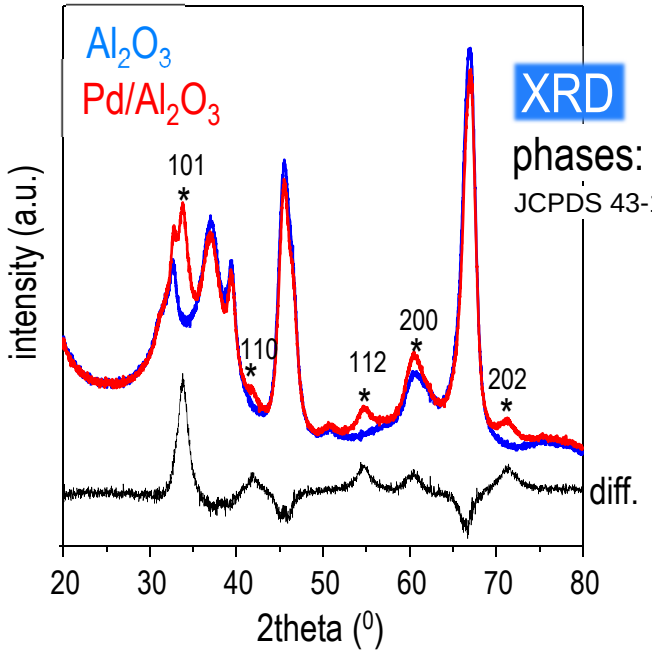
- Cr particles only at the surface of the washcoat
- Pt particles growth



Keav et al., *Appl. Catal. A* **469** (2014) 259

Pd/Al_2O_3 – textural properties

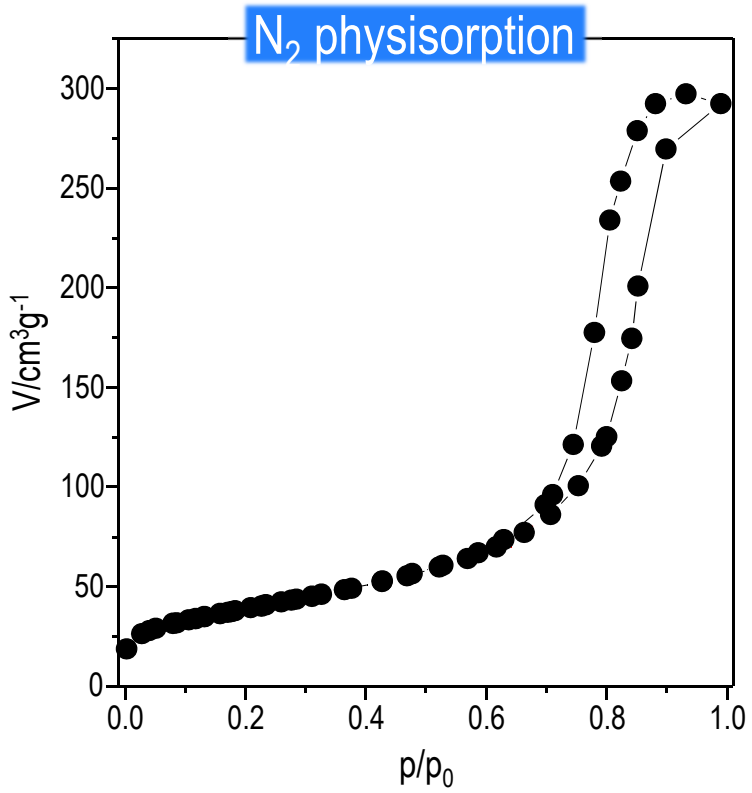




XRD

phases: γ-Al_2O_3, PdO_t

JCPDS 43-1024

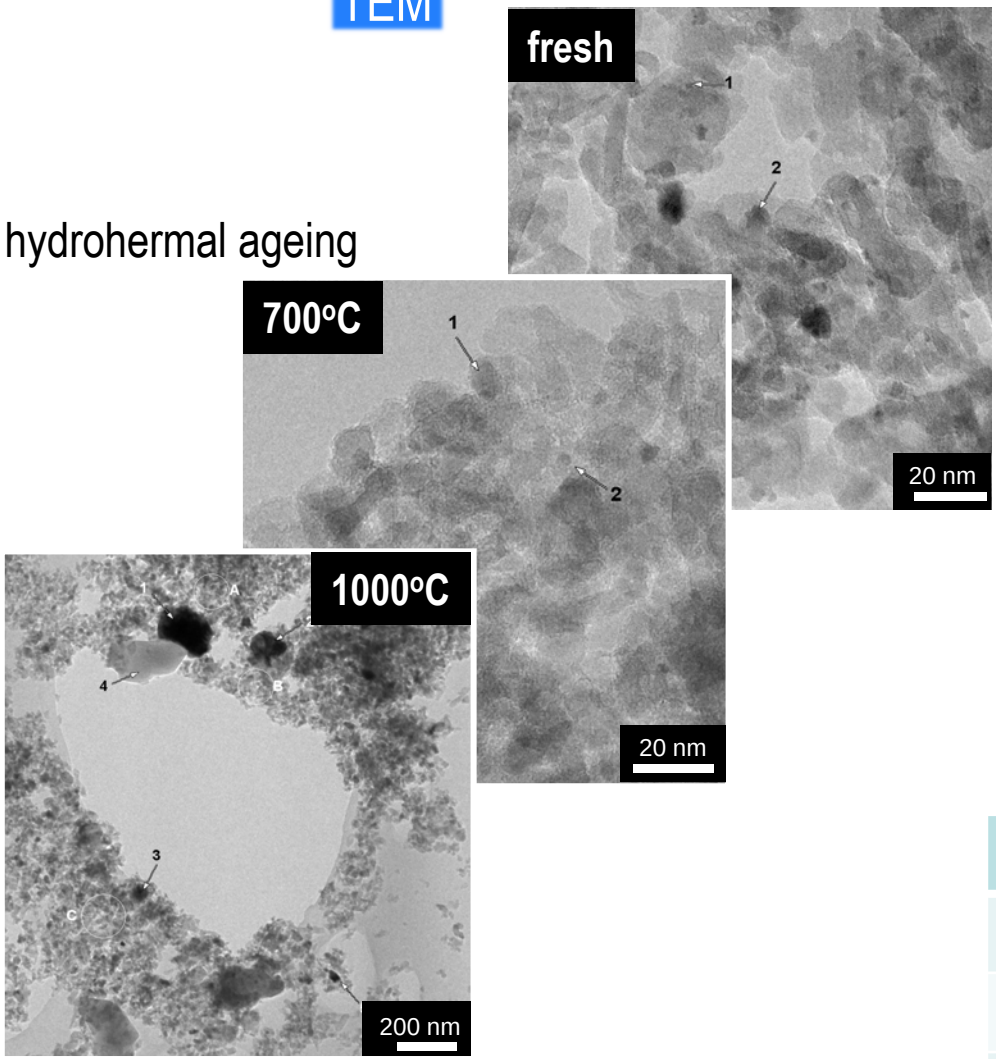


	SSA | m^2/g	V | cm^3/g	D | %	SSA | m^2/g
fresh	135.2	31.0	20	130.3

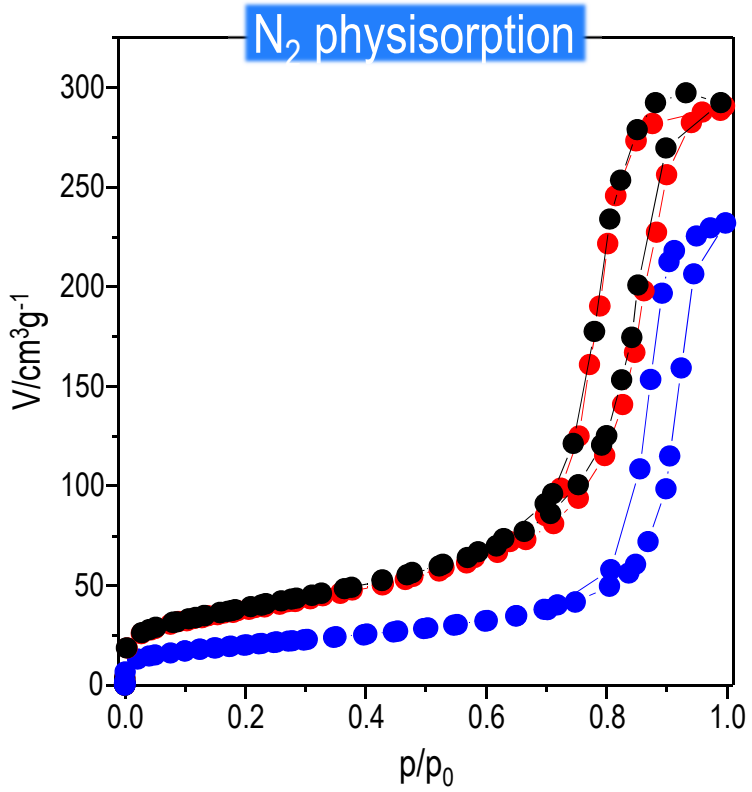
Pd/Al_2O_3 – textural properties

TEM

hydrohermal ageing

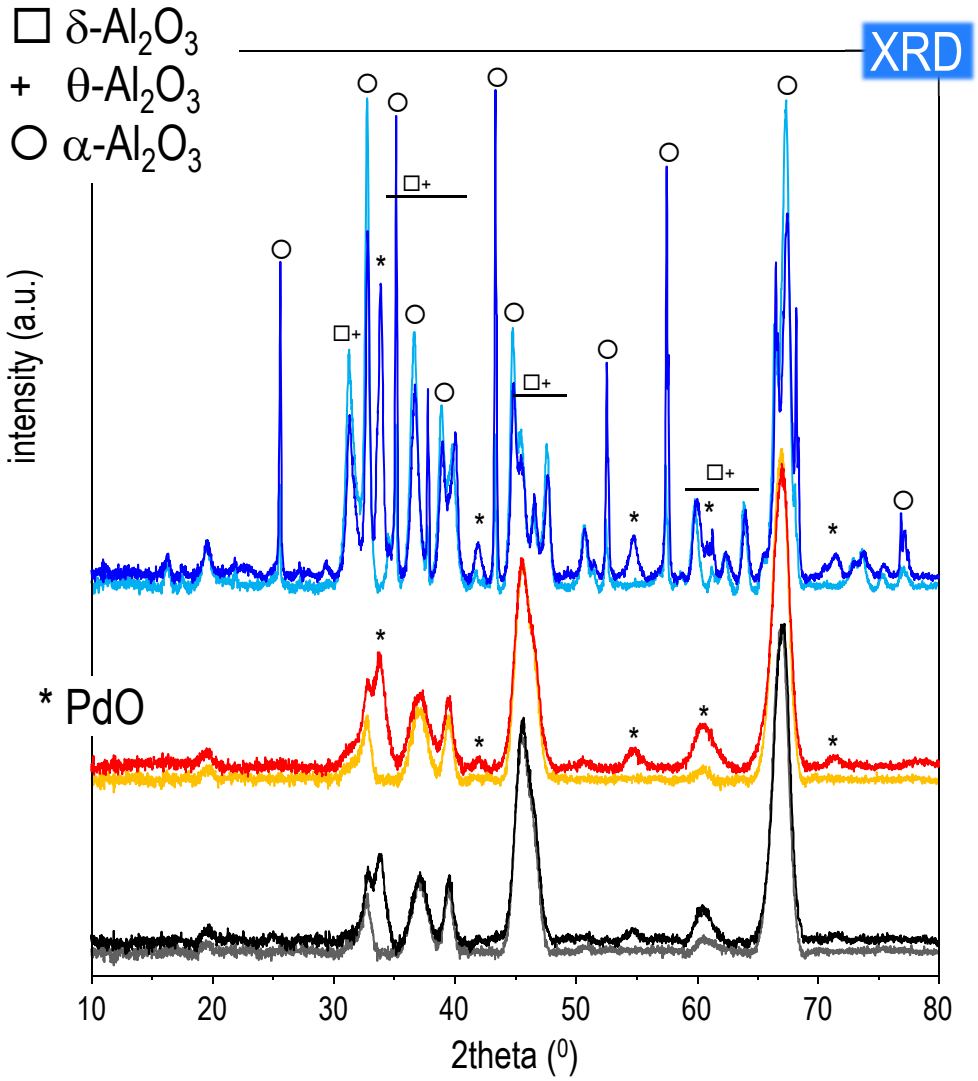


N_2 physisorption



	SSA | m^2/g	V | cm^3/g	D | %	SSA | m^2/g
fresh	135.2	31.0	20	130.3
700°C	123.9	28.5	20	124.6
1000°C	56.7	13.0	1.3	65.9

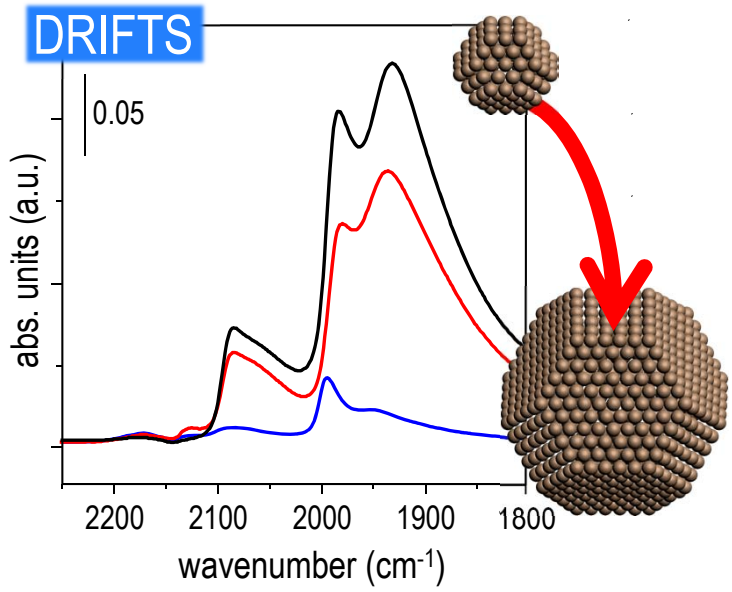
Pd/Al_2O_3 – textural properties



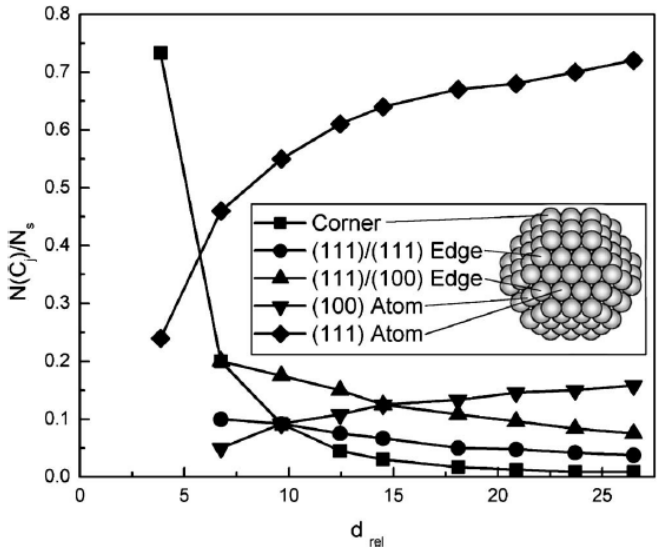
phase transitions

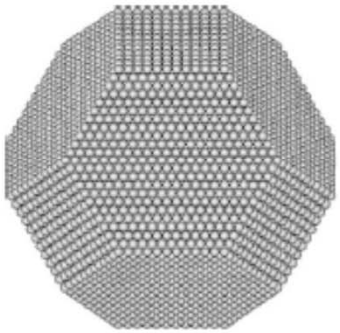
	230°C	850°C	1200°C				
Bayerite	→	η	→	θ	→	α-Al_2O_3	
	450°C	750°C	1000°C		1200°C		
Boehmite	→	γ	→	δ	→	θ+α	→ α –

Al_2O_3



Pd/Al_2O_3 – Pd particle size





azide

(5%) NO_3^{2-}

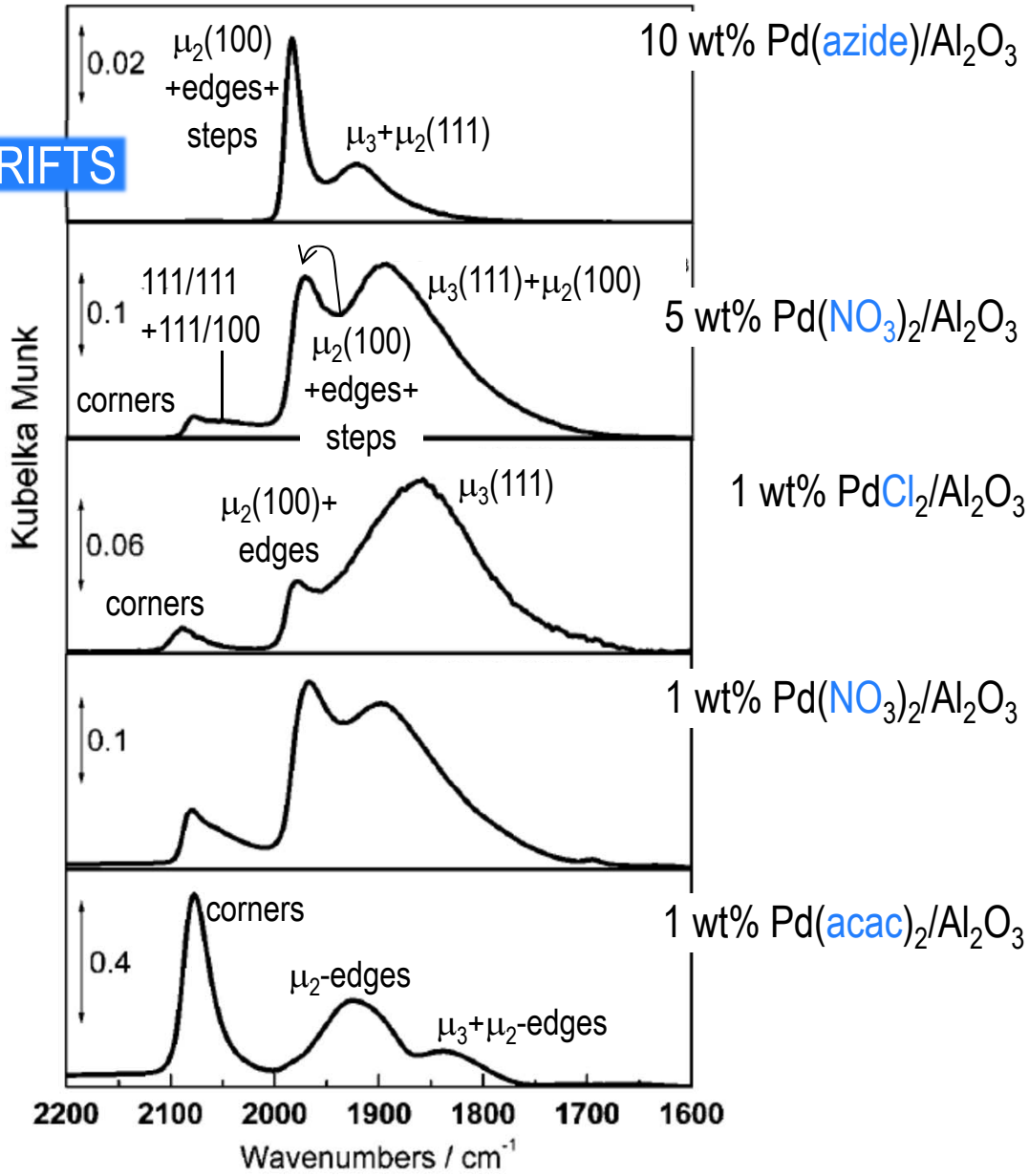
Cl^-

(1%) NO_3^{2-}

acac

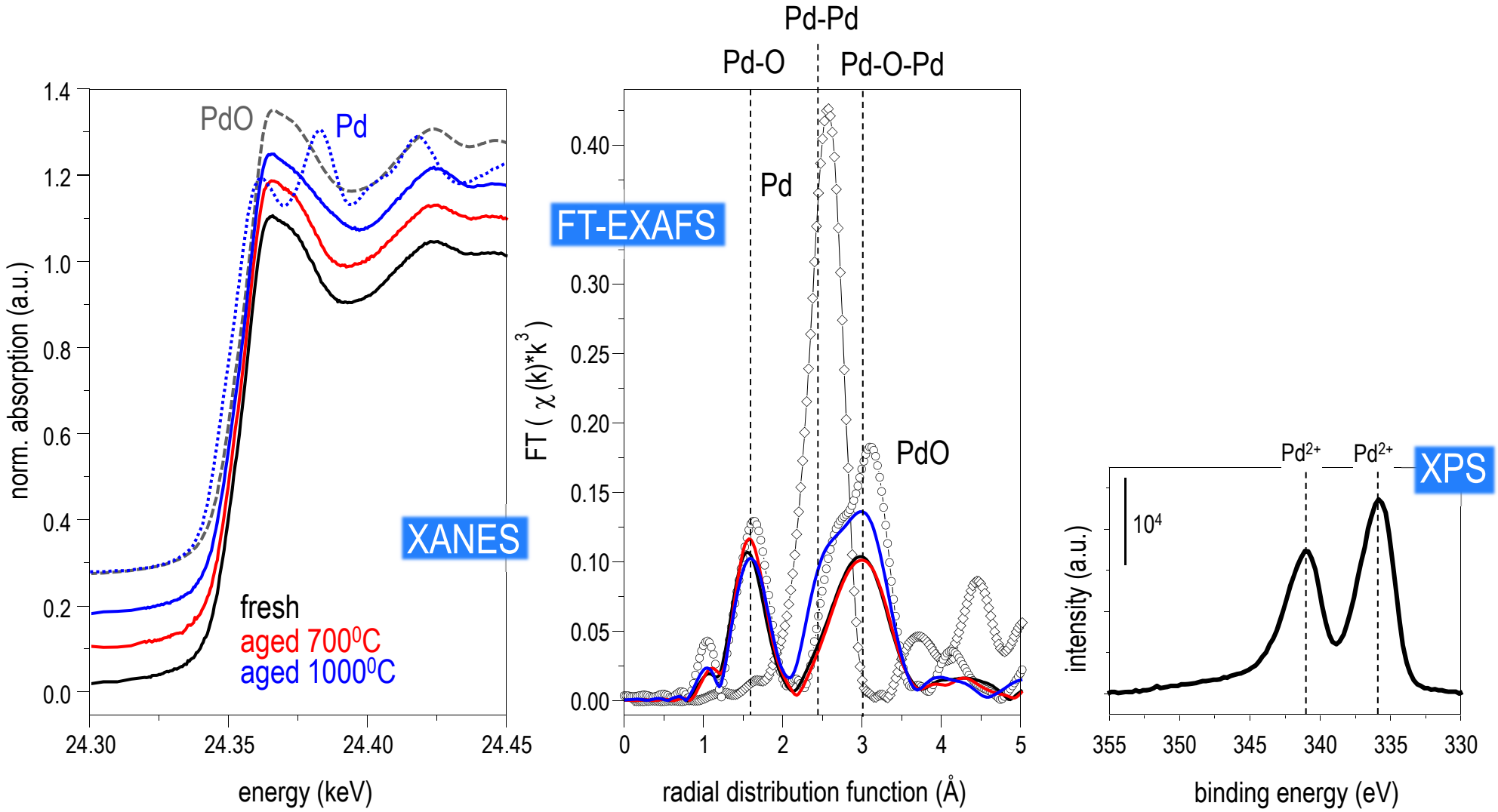
2 nm

DRIFTS



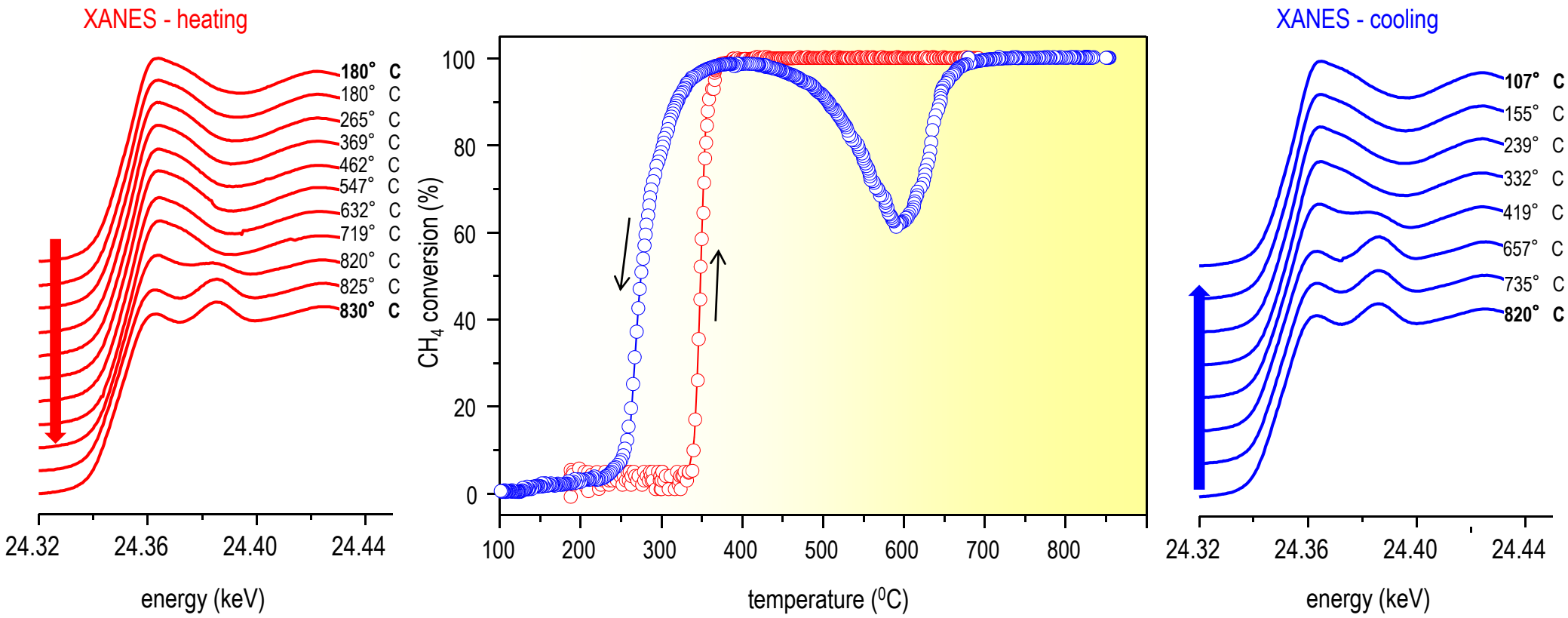
Lear et al., *J. Chem. Phys.* **123** (2005) 174706

Pd/Al_2O_3 – oxidation and coordination states



Pd/Al_2O_3 – CH_4 oxidation

- Operando XANES



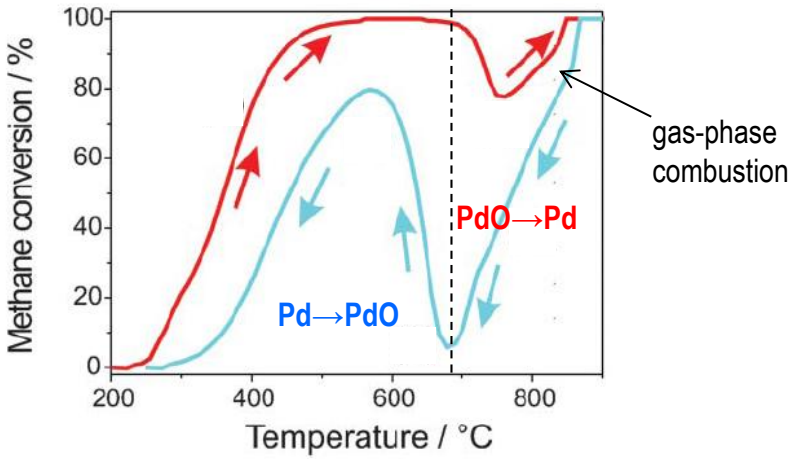
- activity influenced by PdO↔Pd equilibrium
- obvious structural changes during reaction

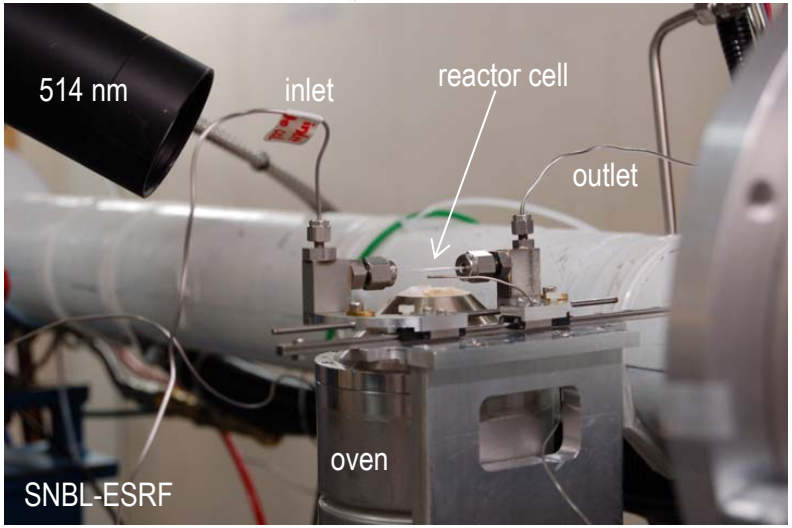
800 ml/min; 0.8 g 2 wt.% Pd/Al_2O_3; 1 vol.% CH_4/4 vol.% O_2; 10^0C/min; Pd K-edge

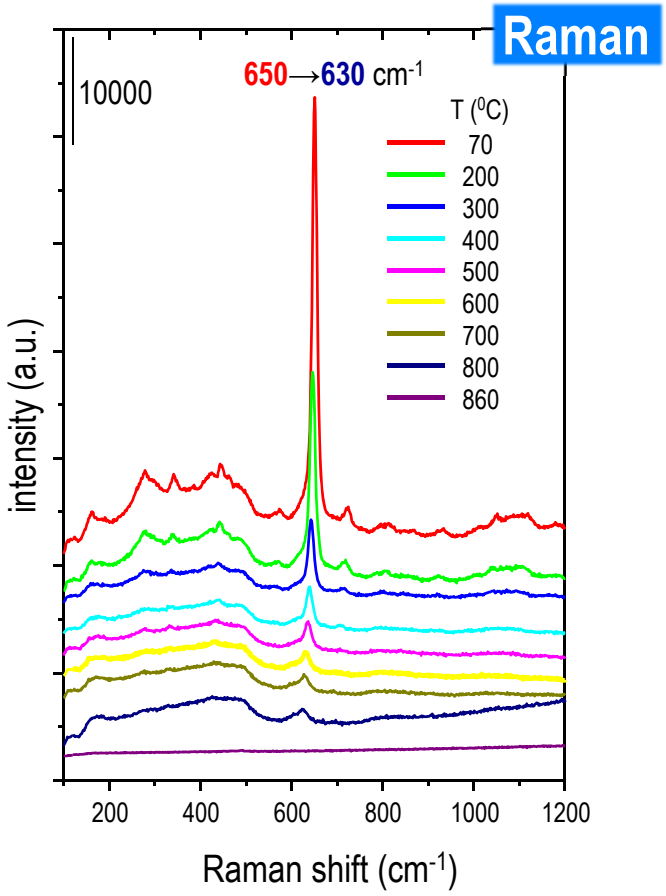
Matam et al., *J. Phys. Chem. C* **114** (2010) 9439

Pd/ZrO_2 – CH_4 oxidation

- Resonance Raman spectroscopy





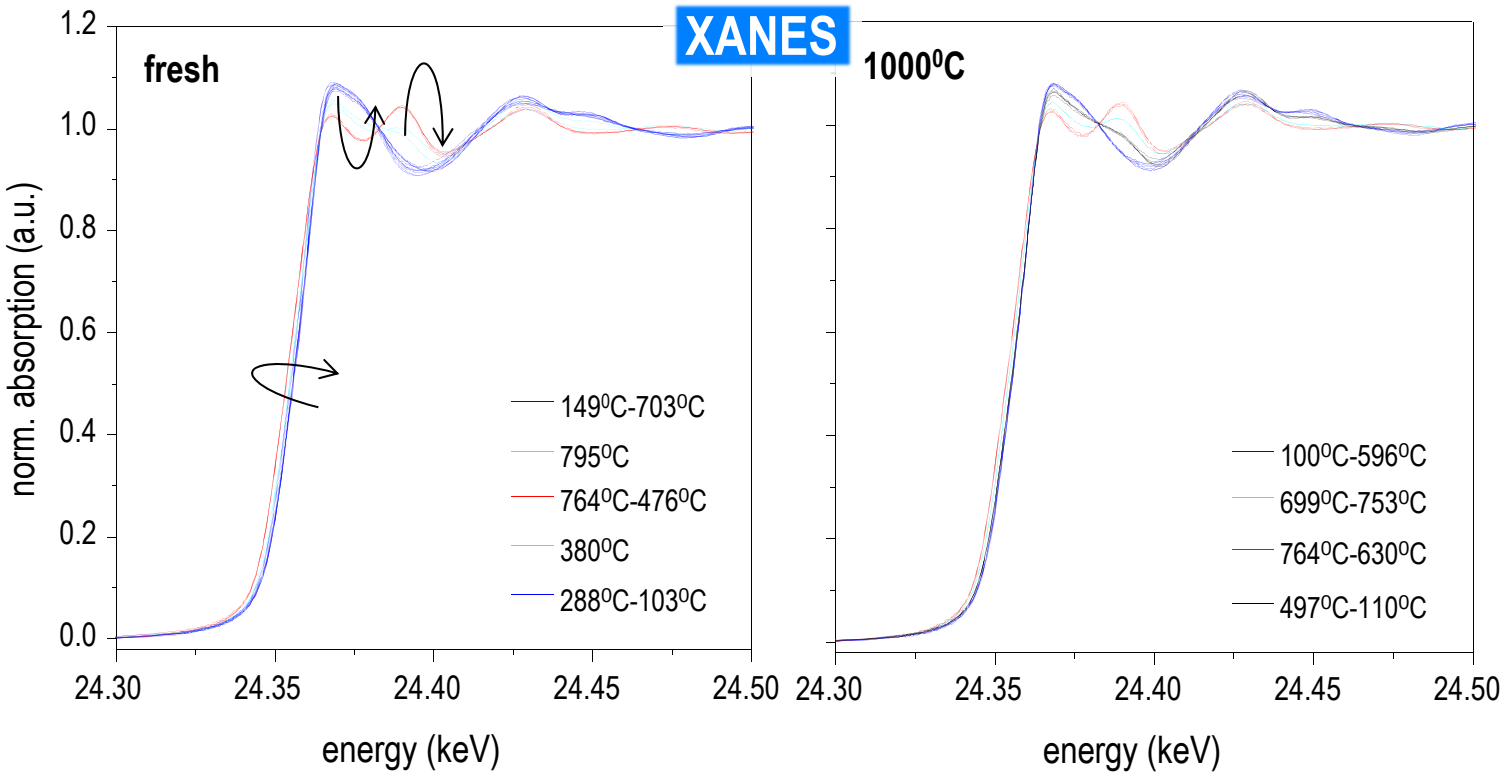


1 vol% CH_4/4 vol.% O_2/He; 10 wt.% Pd/ZrO_2

Grunwaldt et al., *Chem. Comm.* (2007) 4635

Pd/Al_2O_3 – CH_4 oxidation

- Influence of ageing on oxidation state during reaction

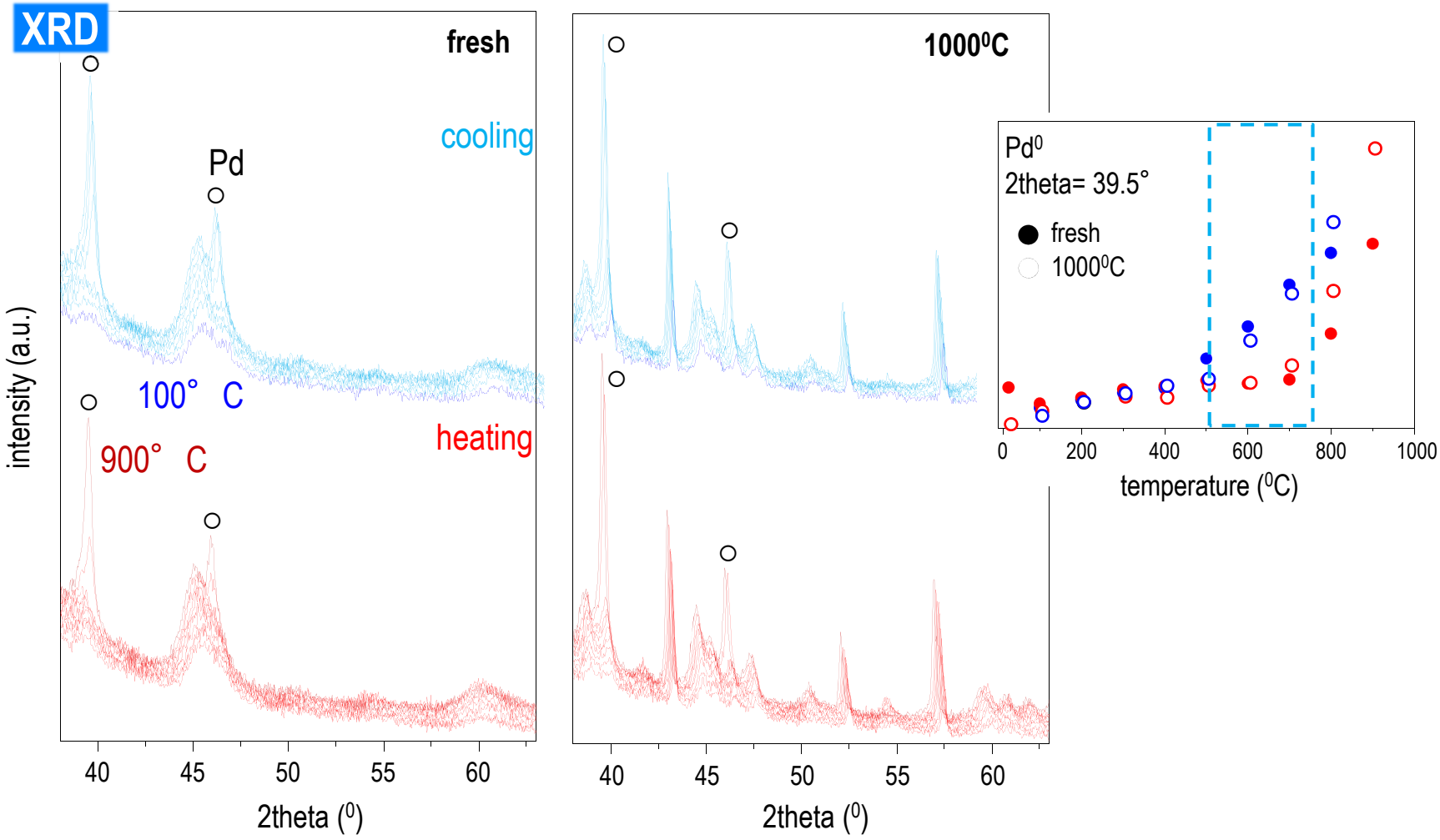


- activity influenced by PdO↔Pd equilibrium
- obvious structural changes during reaction
- Pd always in mixed oxidation state

800 ml/min; 0.8 g 2 wt.% Pd/Al_2O_3; 1 vol.% CH_4/4 vol.% O_2; 10^0C/min; Pd K-edge

Pd/Al_2O_3 – CH_4 oxidation

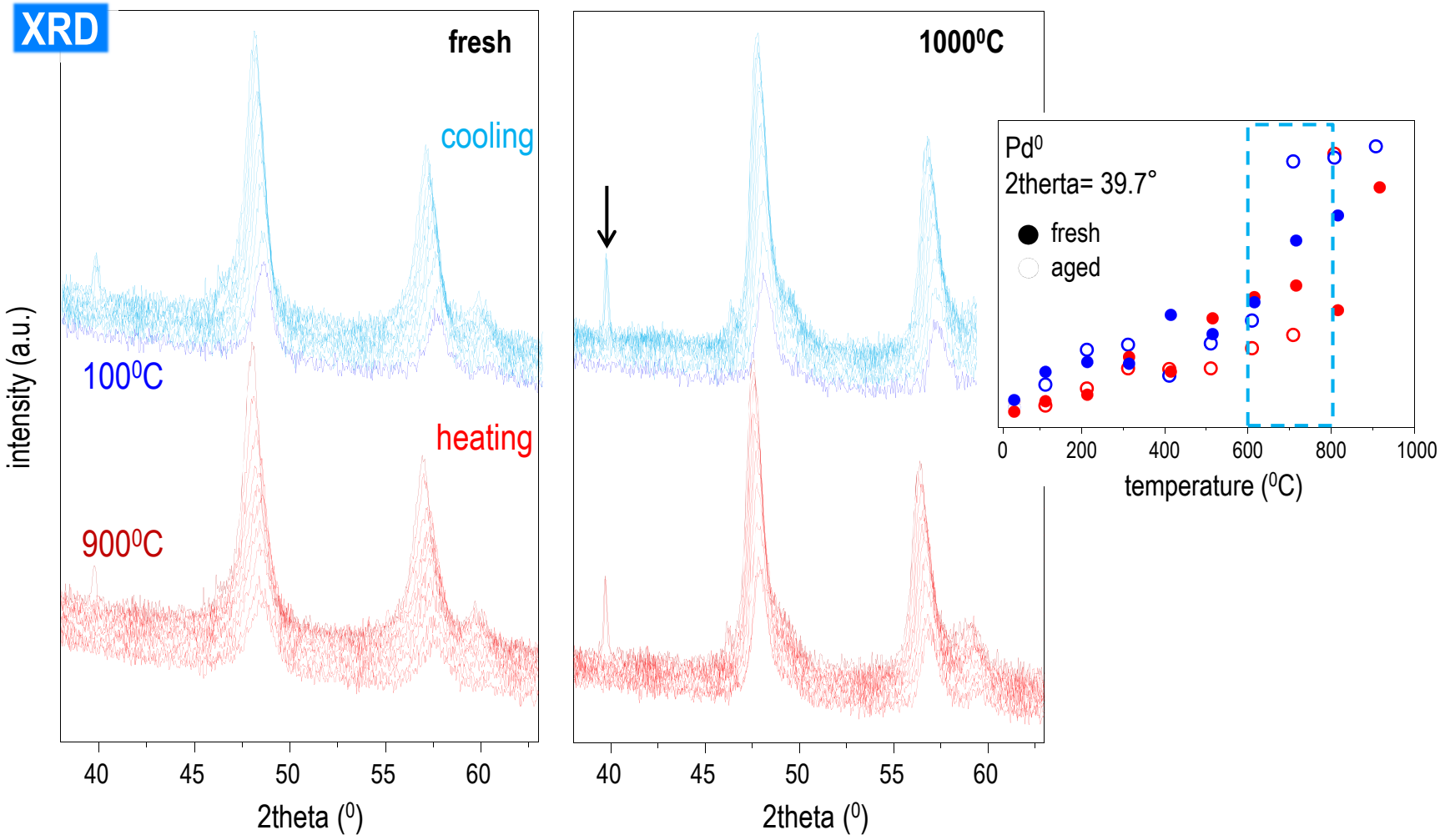
- Influence of ageing on oxidation state during reaction



100 ml/min; 0.2 g 2 wt.% Pd/Al_2O_3; 1 vol.% CH_4/4 vol.% O_2; 10^0C/min

$Pd/CeZrO_2$ – CH_4 oxidation

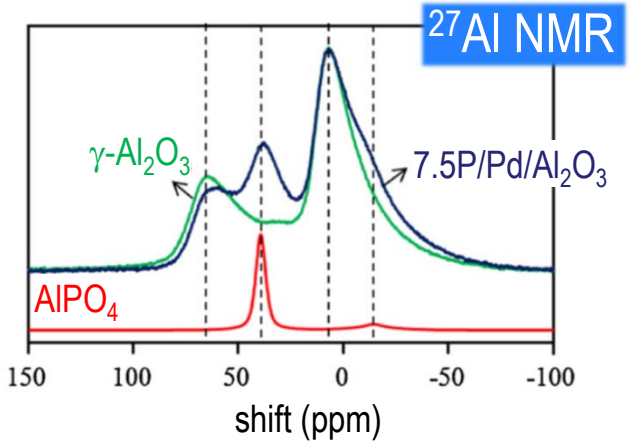
- Influence of ageing on oxidation state during reaction

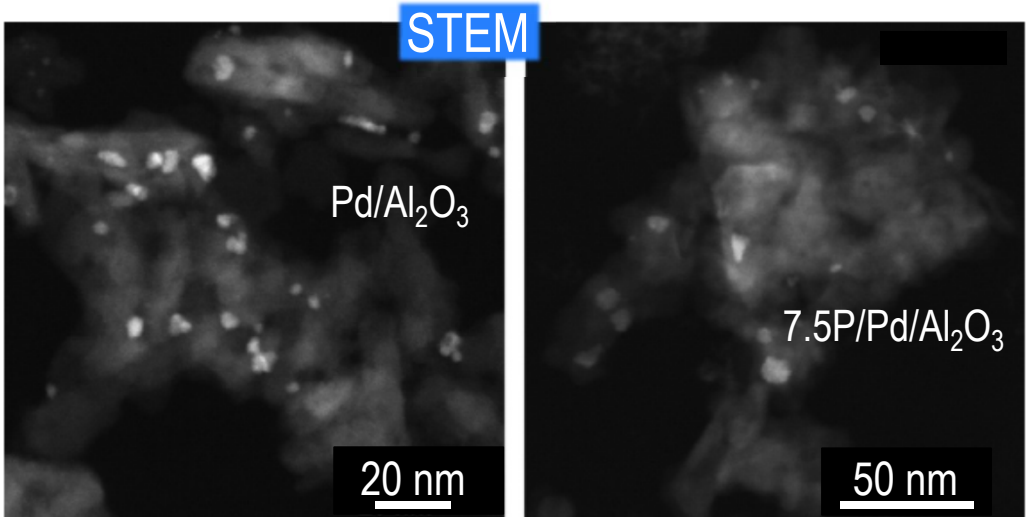


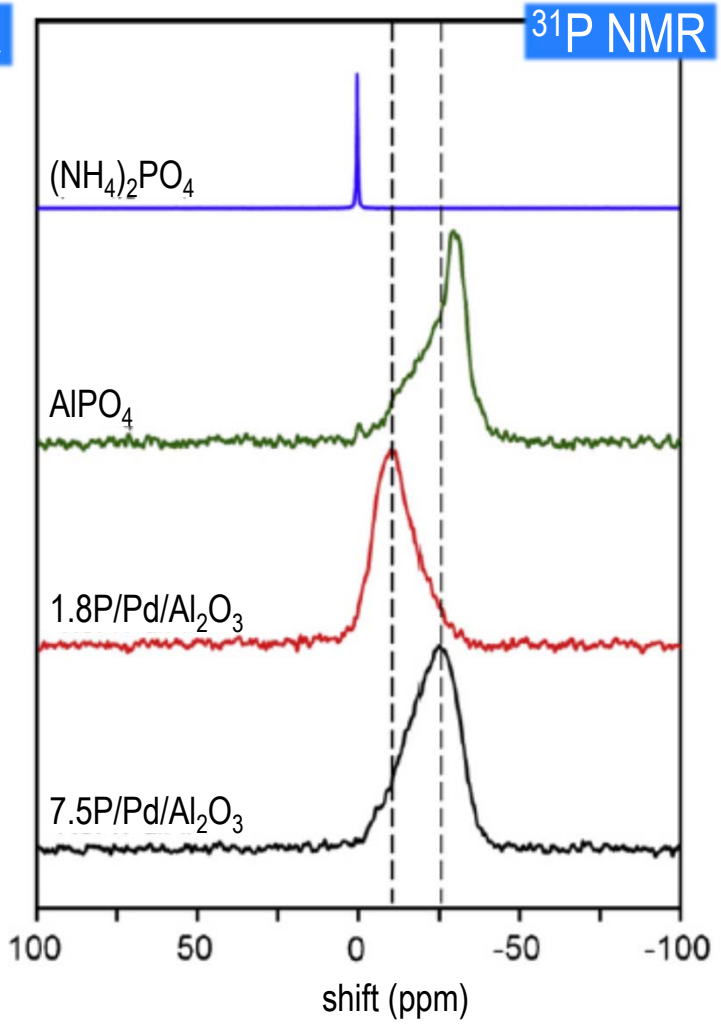
100 ml/min; 0.2 g 2 wt.% Pd/Al_2O_3; 1 vol.% CH_4/4 vol.% O_2; 10⁰C/min

Pd/Al_2O_3 – Chemical ageing

- low amount of P
- not detectable by XRD
- decreased dispersion
- $AlPO_4$ visible by NMR
- dependence on P loading

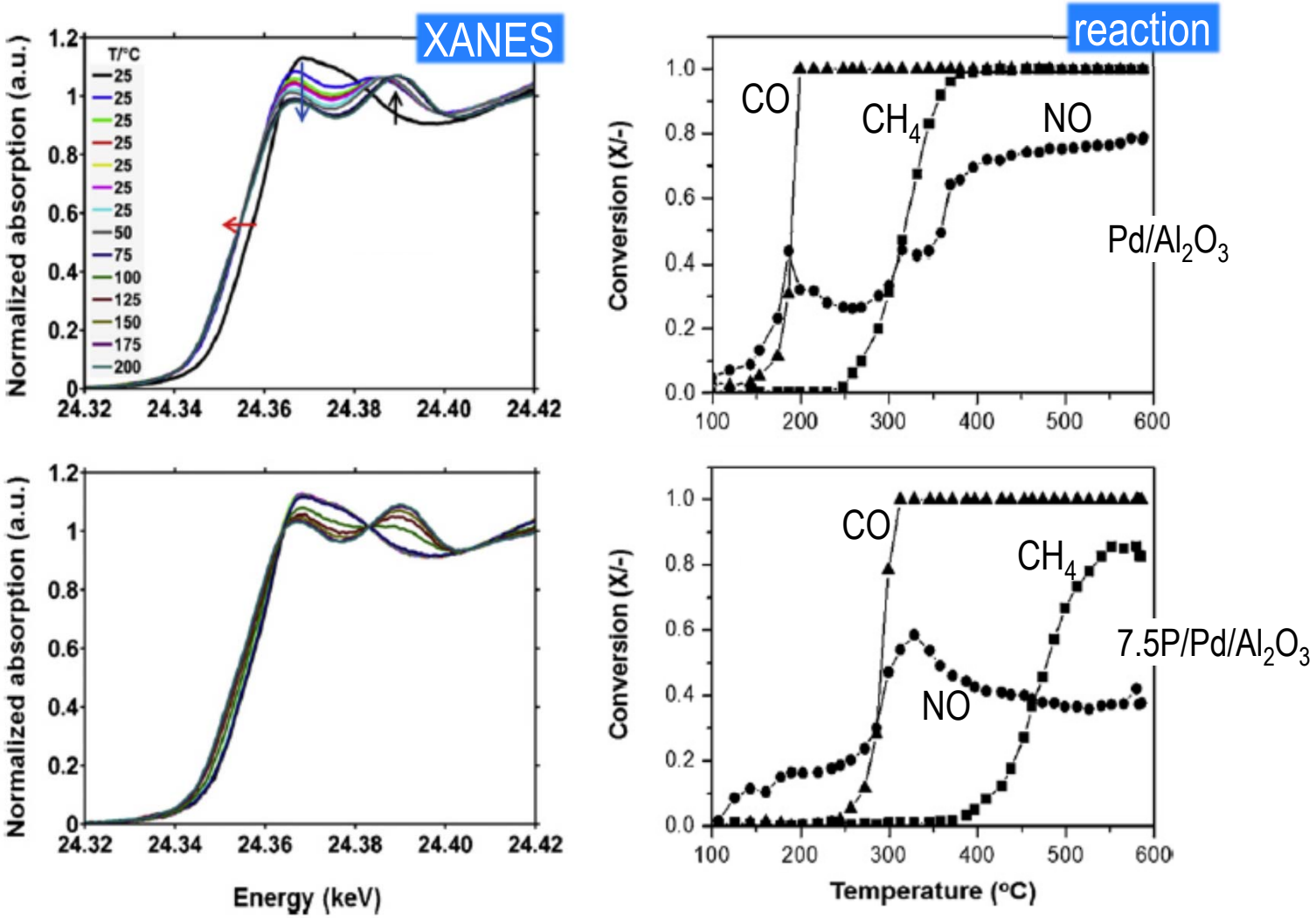






Matam et al., *Catal. Today* **184** (2012) 237; Matam et al., *Catal. Today* **205** (2013) 3

Pd/Al_2O_3 – Chemical ageing



- P shifts the PdO-Pd equilibrium to higher T
- P changes the catalytic properties of Pd

7000 ppm CO, 1300 ppm CH_4, 1600 ppm NO, 5300 ppm O_2; λ= 1

Matam et al., *Catal. Today* **184** (2012) 237