TPX

Temperature Programmed Techniques

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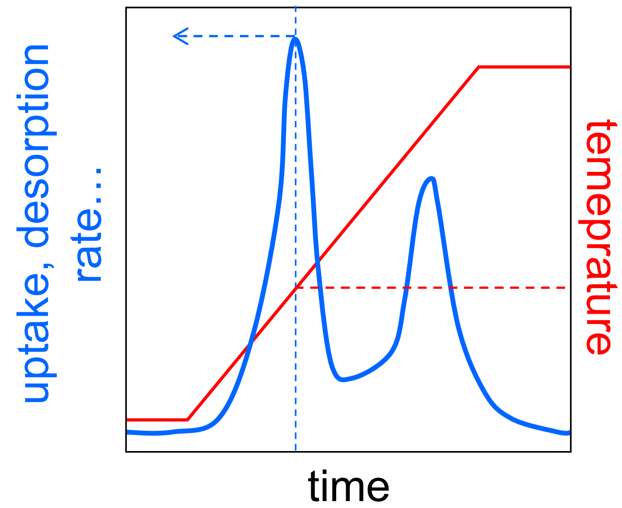
Definitions

- Temperature programmed desorption (TPD) or thermal desorption spectroscopy (TDS)
- Temperature programmed reduction (TPR)
- Temperature programmed reaction (TPR)
- Temperature programmed oxidation (TPO)
- Temperature programmed reaction spectroscopy (TPRS)



Definitions

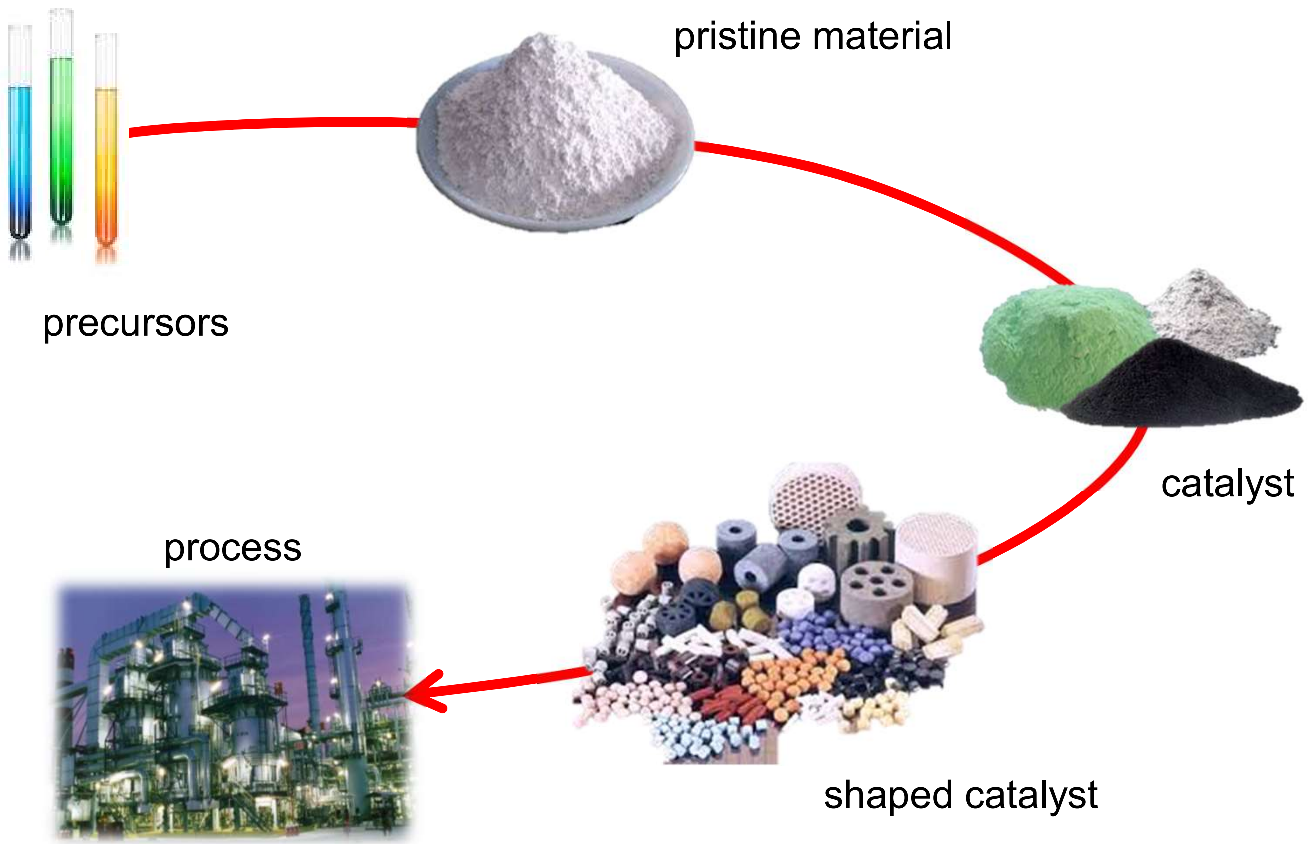
- **TPD**

A solid is first exposed to an adsorbate gas under well-defined conditions (temperature and pressure) and then heated under inert conditions with a temperature program

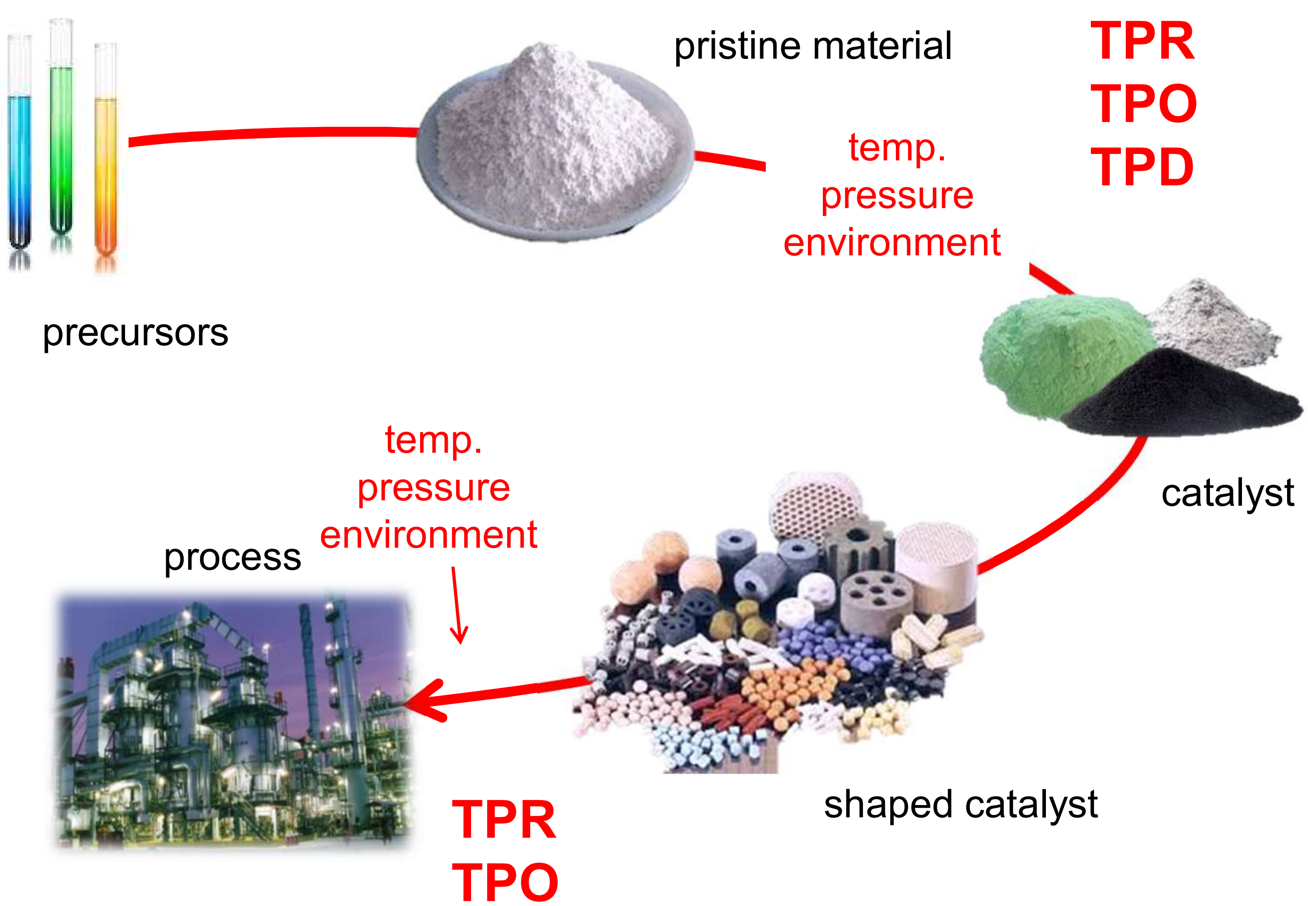
- **TPX** except TPD

Solid and reactants in contact during temperature programmed experiment

Catalyst manufacture

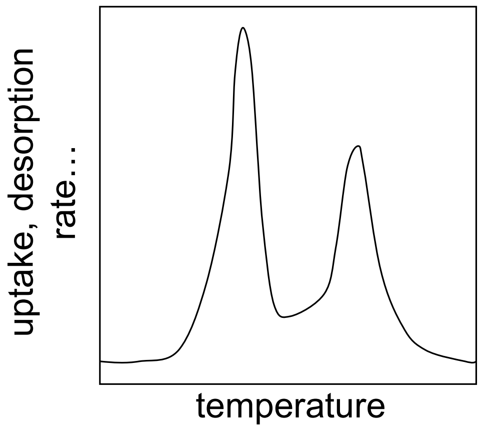


Catalyst manufacture



Information

- T_{red}, T_{des}, T_{ox}, T_{react}
- Adsorption site strength, quality and quantity
- Bond strength, solid-adsorbate
- Surface coverage
- Quantification of desorption
- Adsorption enthalpy + pre-exponential factor for desorption



- **Advantages**
  - Experimentally simple
  - Inexpensive
  - Access to powders and single crystals

- **Disadvantages**
  - Complex determination of activation energies and pre-exponential factors

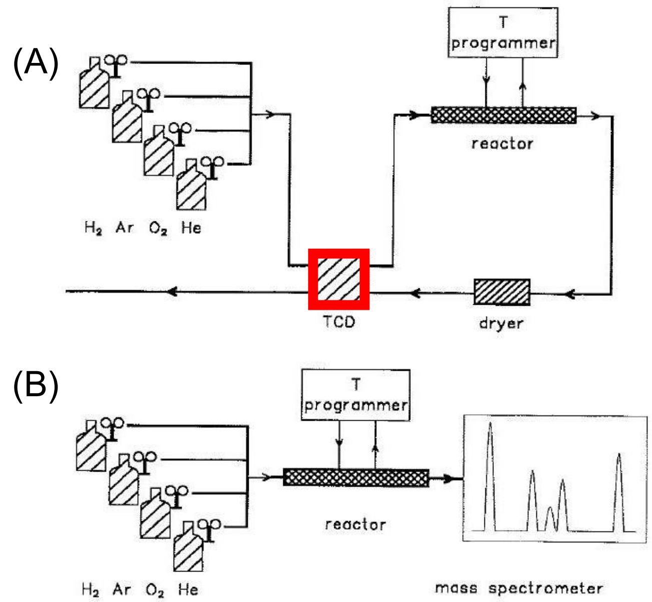
Temperature programmed techniques

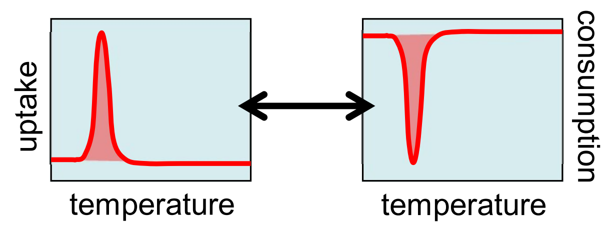
- **Equipment**

Thermal conductivity

gas	$\lambda \times 10^{-3}$ [W/(cmK)]
air	0.277
NH_3	0.270
Ar	0.190
CO_2	0.183
CO	0.267
He	1.574
H_2	1.972
CH_4	0.374
N_2	0.275
O_2	0.285
H_2O	0.195

Reactant and carrier gases
TPR: 5 vol.% H_2/Ar (or He)
TPO: 5 vol.% O_2/He





J.W. Niemantsverdriet, Spectroscopy in catalysis, VCH, Weinheim, 2007

Temperature programmed reduction

- **Reduction of a bulk metal oxide**

$$MO_n + nH_2 \rightarrow M + nH_2O$$

From thermodynamics:

$$\Delta G = \Delta G^0 + nRT\ \ln(p_{H2O}/p_{H2}) < 0$$

If H_2 is the reducing agent,

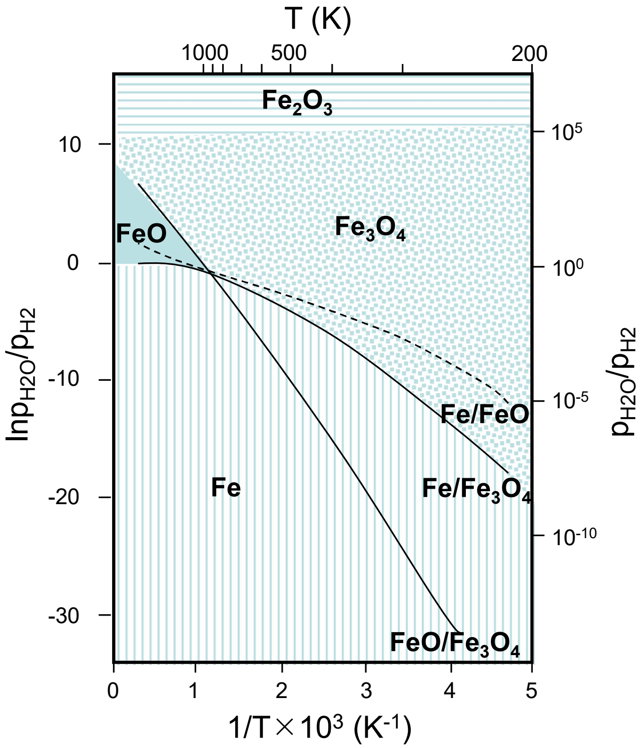
$$\Delta G = nRT\ \ln[(p_{H2O}/p_{H2})/(p_{H2O}/p_{H2})_{eq}]$$

then $\Delta G < 0$, if

$$p_{H2O}/p_{H2} < (p_{H2O}/p_{H2})_{eq}$$

Temperature programmed reduction

- **Reduction of a bulk metal oxide**



thermodynamic data for reduction (400°C)

metal	oxide	$(p_{H2O}/p_{H2})_{eq}$
Ti	TiO_2	4×10^{-16}
	TiO	2×10^{-9}
V	V_2O_5	6×10^{-4}
	VO	2×10^{-11}
Cr	Cr_2O_3	3×10^{-9}
Mn	MnO_2	10
	MnO	2×10^{-10}
Fe	Fe_2O_3	0.7
	FeO	0.1
Co	CoO	50
Ni	NiO	500
Cu	CuO	2×10^{8}
	Cu_2O	2×10^{6}
Mo	MoO_3	40
	MoO_2	0.02
Ru	RuO_2	10^{12}
Rh	RhO	10^{13}
Pd	PdO	10^{14}
Ag	Ag_2O	3×10^{17}
Ir	IrO_2	10^{13}

BUT!

reduction of a supported MO_x can produce completely different TPR patterns

Temperature programmed reduction

- **Reduction mechanisms**

Rate of reduction of $MO_n + nH_2 \rightarrow M + nH_2O$

$$- d[MO_n]/dt = k_{red}[H_2]^p f([MO_n])$$

k_{red}, rate constant of reduction reaction
p, reaction order in H_2
t, time

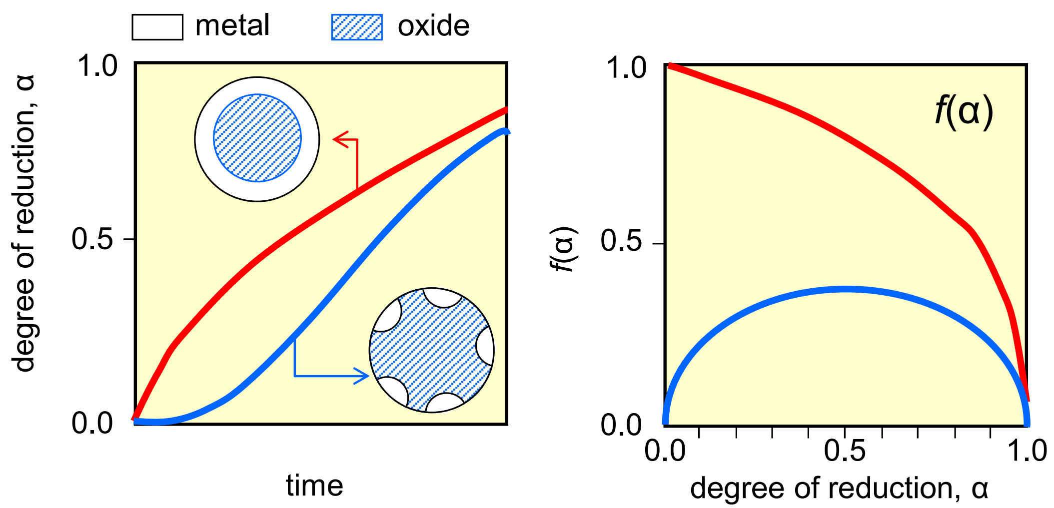
If **α** is the degree of reduction, if p=0 (excess H_2), if linear T-ramp ($dT = \beta\, dt$) and using Arrhenius equation

$$d\alpha/dT = v/\beta\, e^{-Ered/RT} f(1-\alpha)$$

v, pre-exponential factor
β, heating rate
E_{red}, activation energy of reduction reaction

Temperature programmed reduction

- **Reduction mechanisms**



shrinking core $f(\alpha) = 3\,(1-\alpha)^{1/3}$

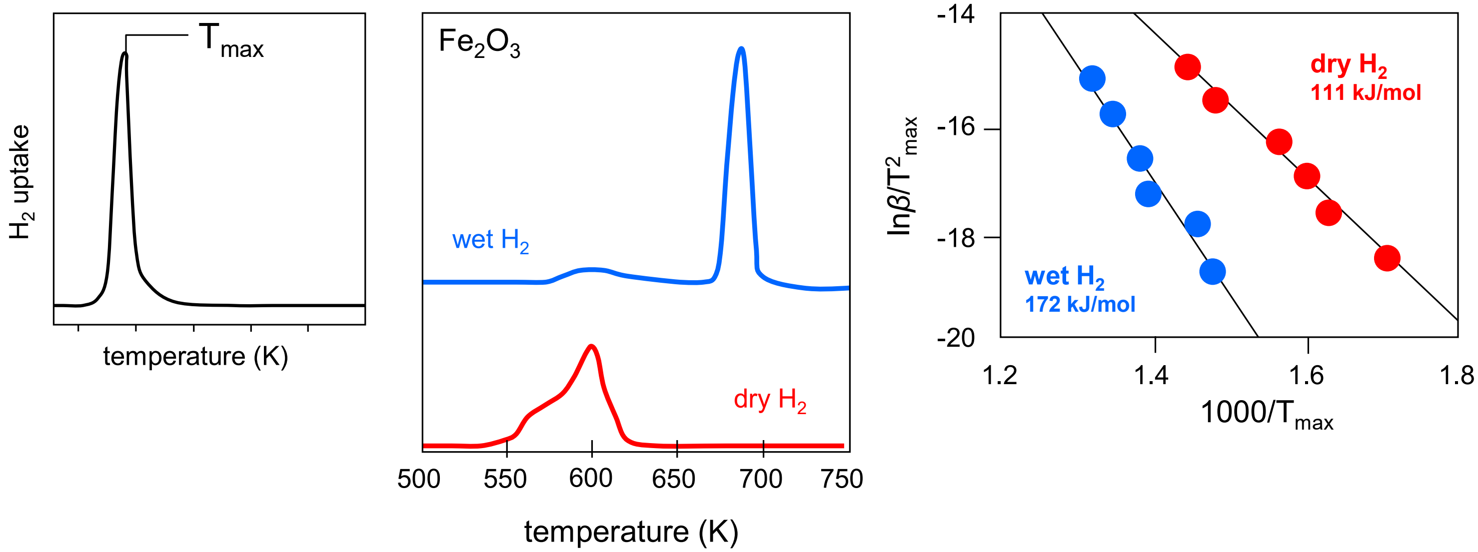
nucleation and growth $f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{2/3}$

Temperature programmed reduction

- **Activation energy of reduction**

$$\ln(\beta/T^2_{max}) = -E_{red}/RT_{max} + \ln(vR/E_{red}) + K$$

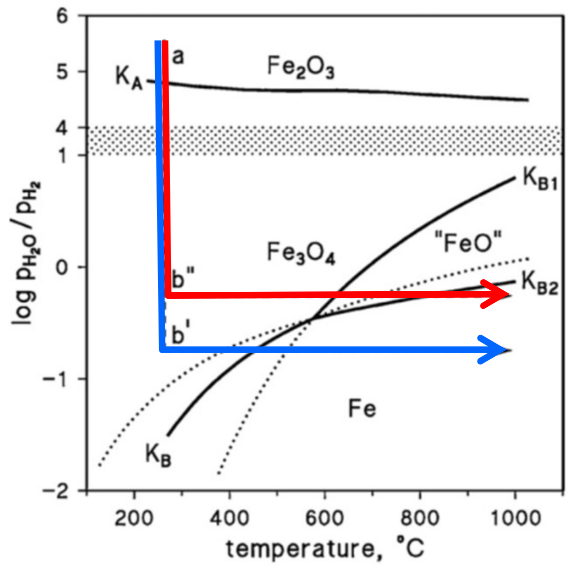
if $f(1\text{-}\alpha)$ and $\alpha(T_{max})$ independent of β.



Temperature programmed reduction

- **Reduction of a bulk metal oxide**

…a somewhat different phase diagram



three-steps mechanism

two-steps mechanism

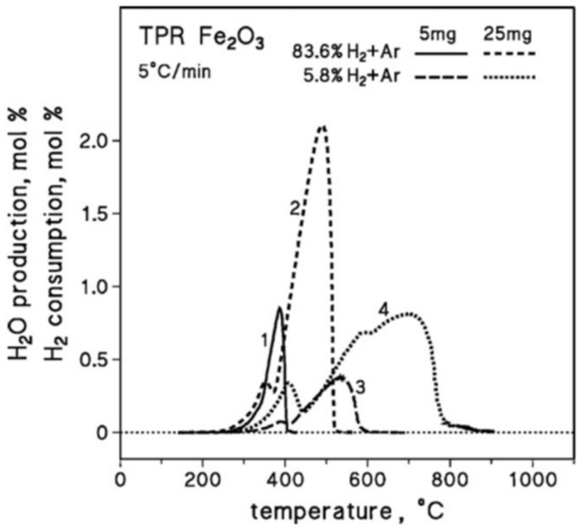
one-step mechanism?

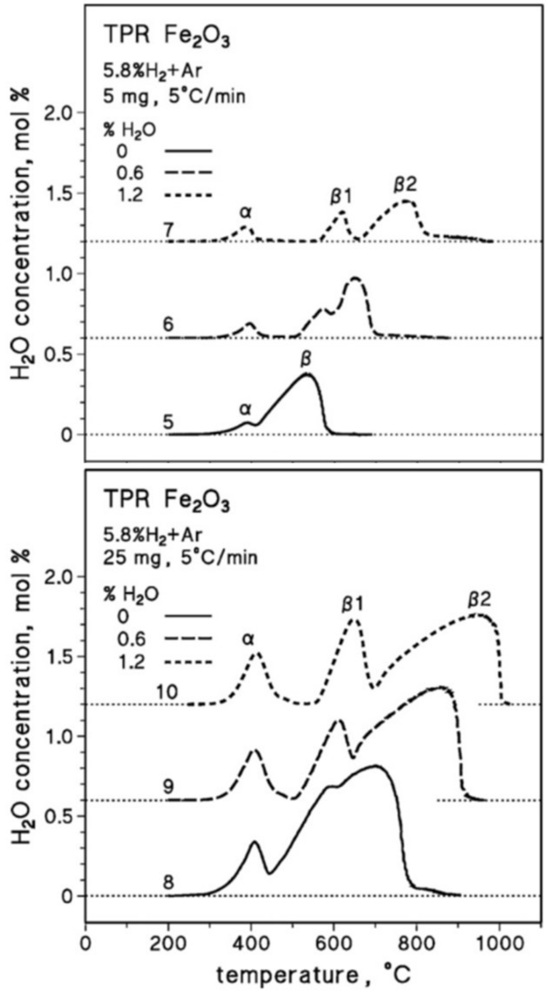
$Fe_2O_3 \rightarrow Fe$

J. Zielinski et al., Appl. Catal. A: General 381 (2010) 191

Temperature programmed reduction

- **Effect of experimental conditions**



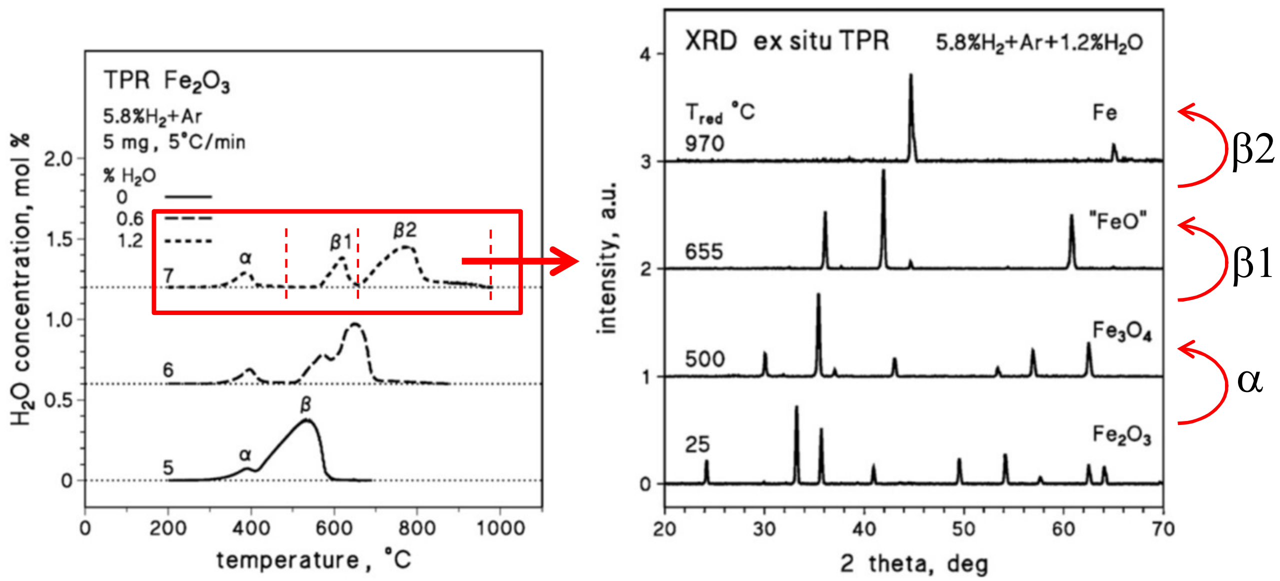


- TPR profile depends on exp. conditions
  - sample amount, H_2 conc., H_2O, T ramp…
- Effect of water conc. on p_{H2O}/p_{H2}?

J. Zielinski et al., Appl. Catal. A: General 381 (2010) 191

Temperature programmed reduction

- **Evidence of mechanism from XRD**

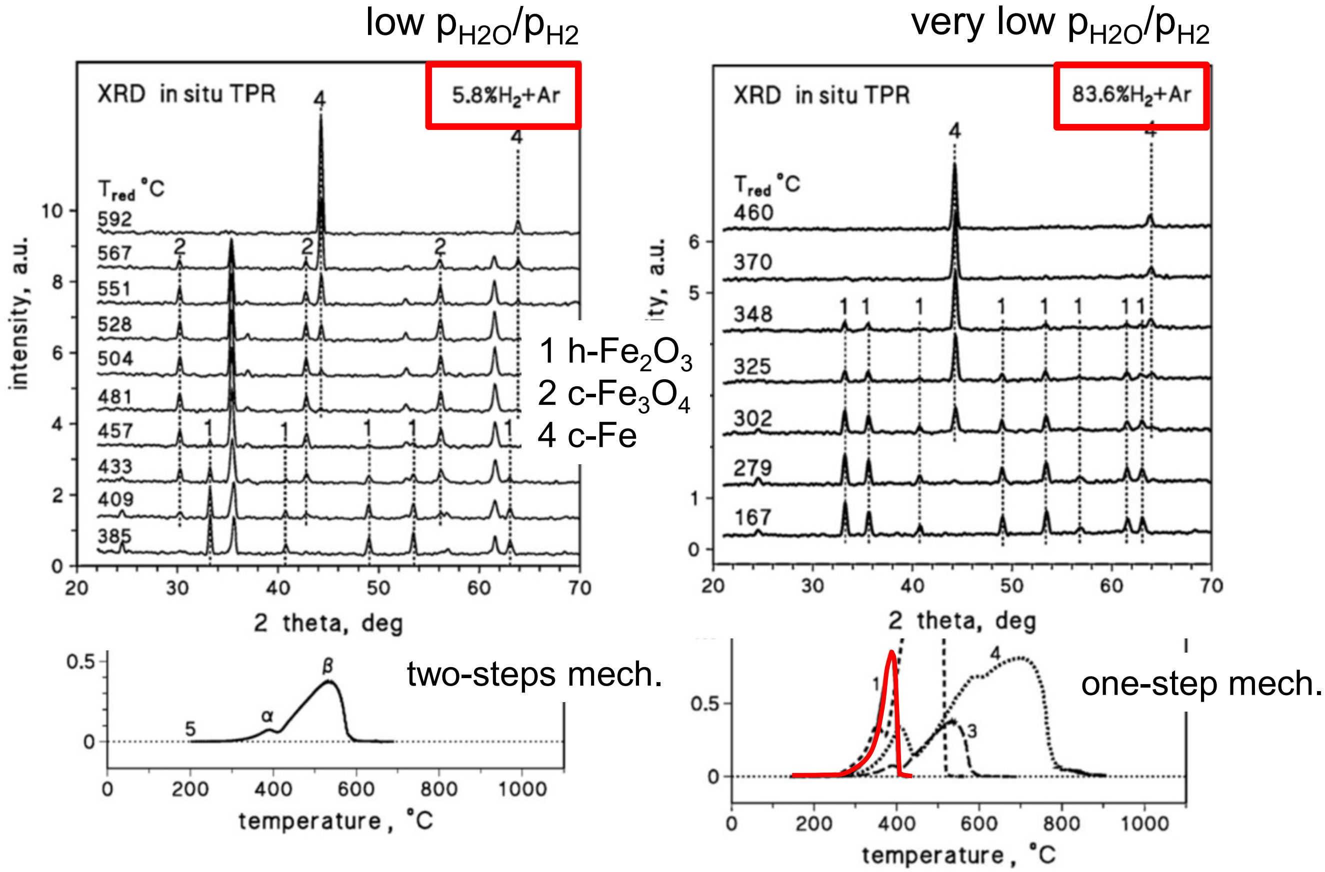


- Effect of fed water on p_{H2O}/p_{H2}
  - High ratio, three step mechanism
  - Low ratio, two step mechanism

J. Zielinski et al., Appl. Catal. A: General 381 (2010) 191

Temperature programmed reduction

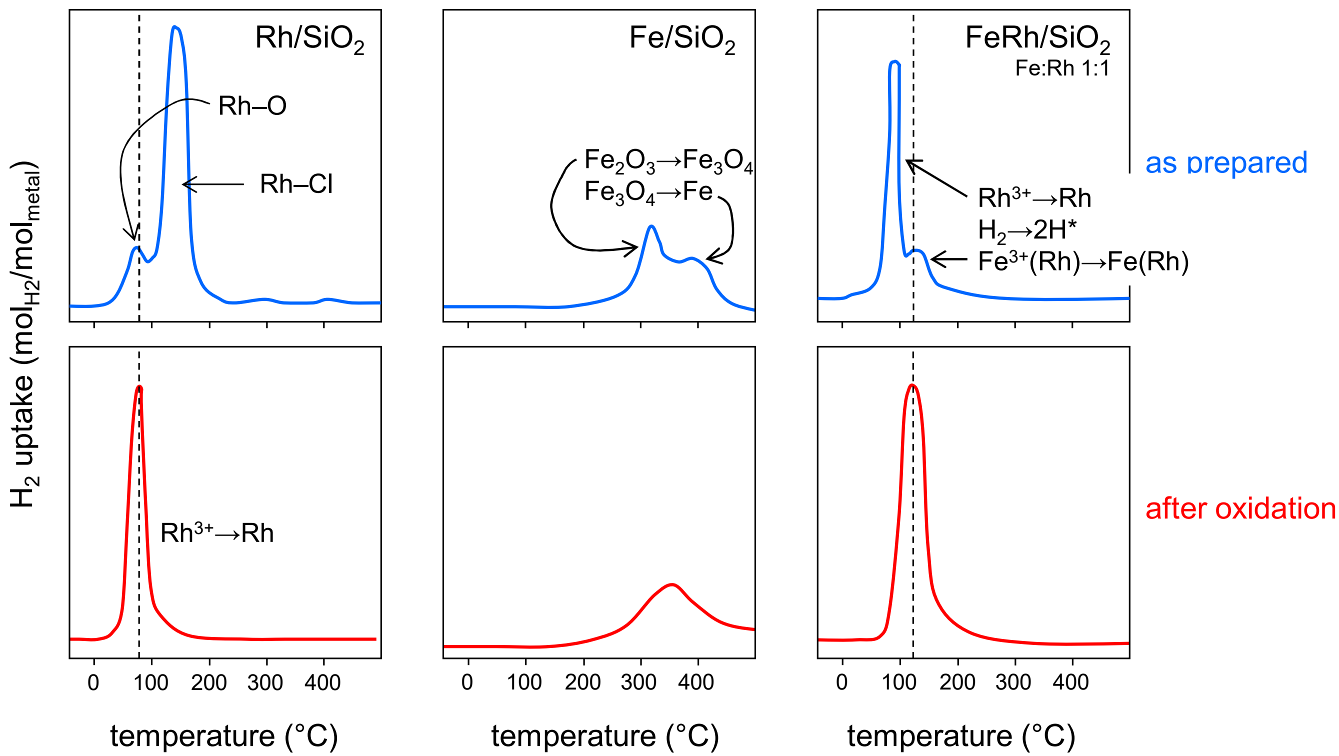
- **Evidence of mechanism from XRD**



J. Zielinski et al., Appl. Catal. A: General 381 (2010) 191

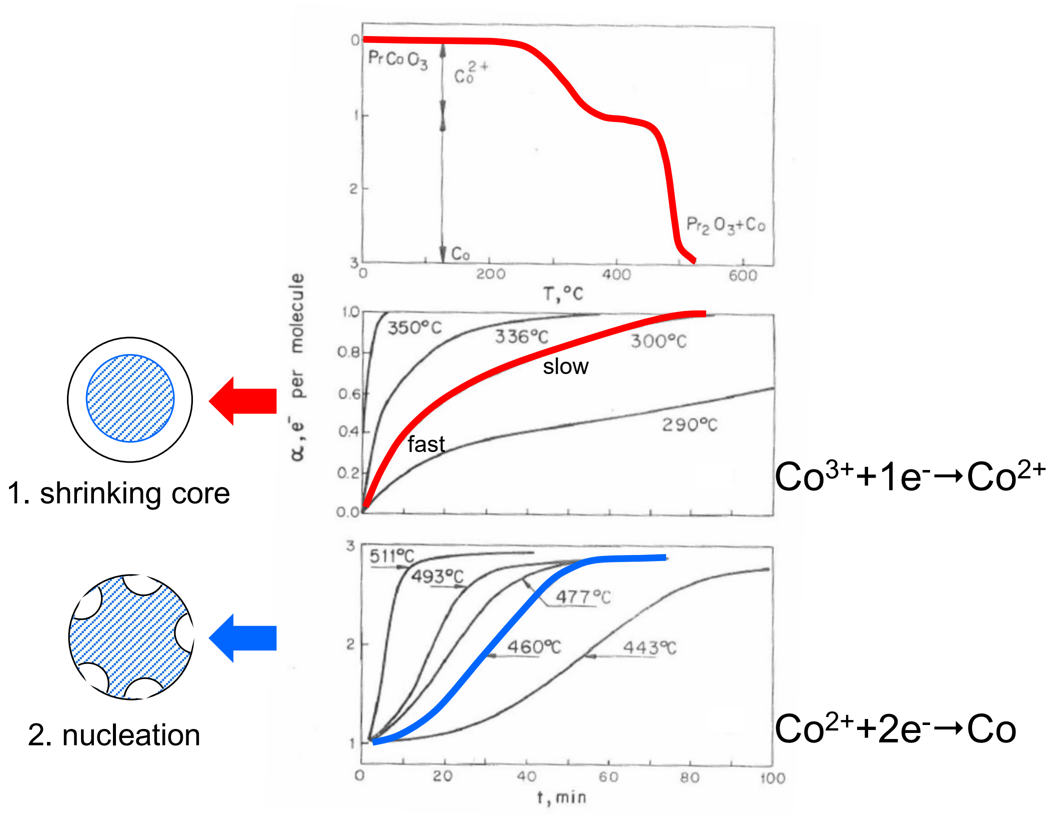
Temperature programmed reduction

- **Supported oxides and bimetallic catalysts**



Temperature programmed reduction

- **Reduction mechanisms, $PrCoO_3$**
  - $Co^{3+} + 1e^- \rightarrow Co^{2+}$
  - $Co^{2+} + 2e^- \rightarrow Co$

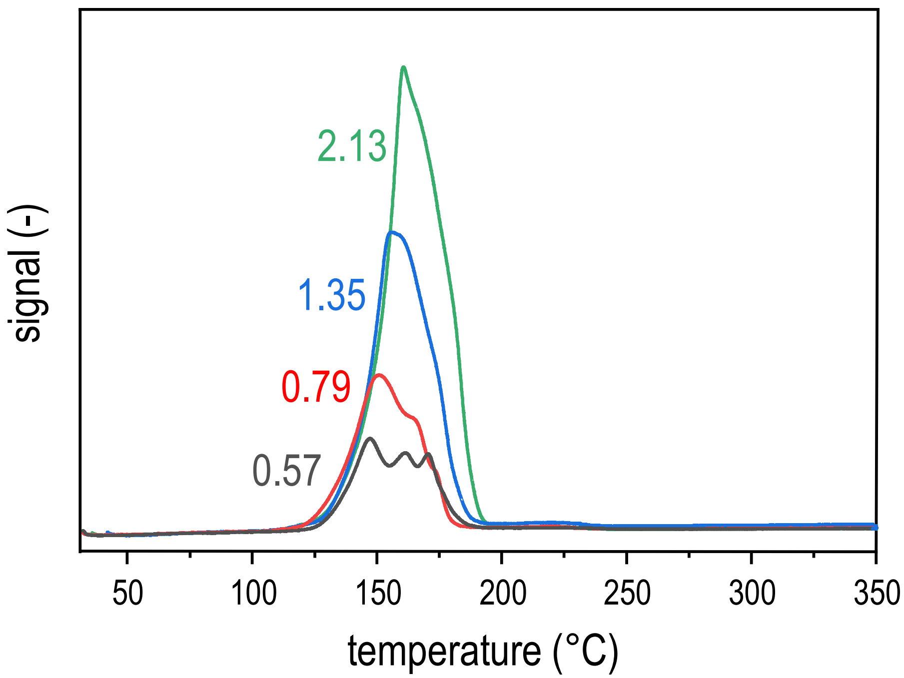


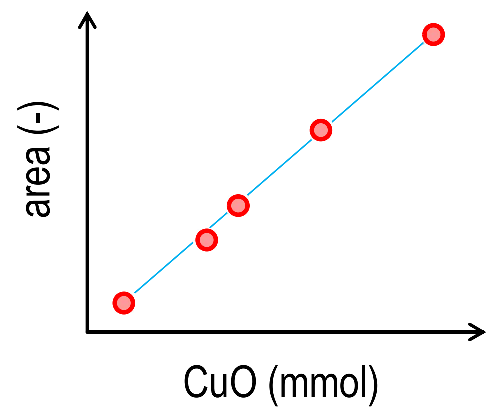
Fierro et al., J. Mater. Sci. 23 (1988) 1018

Temperature programmed reduction

- **Calibration**

$$CuO + H_2 \rightarrow Cu + H_2O$$

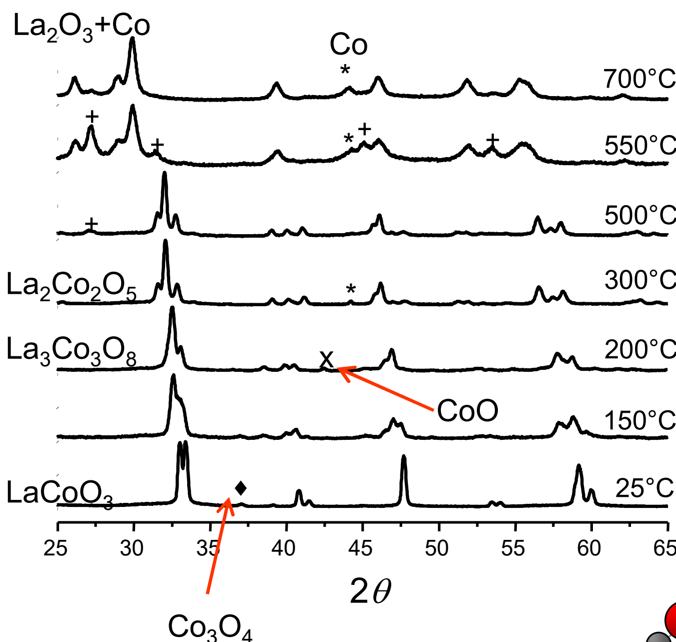


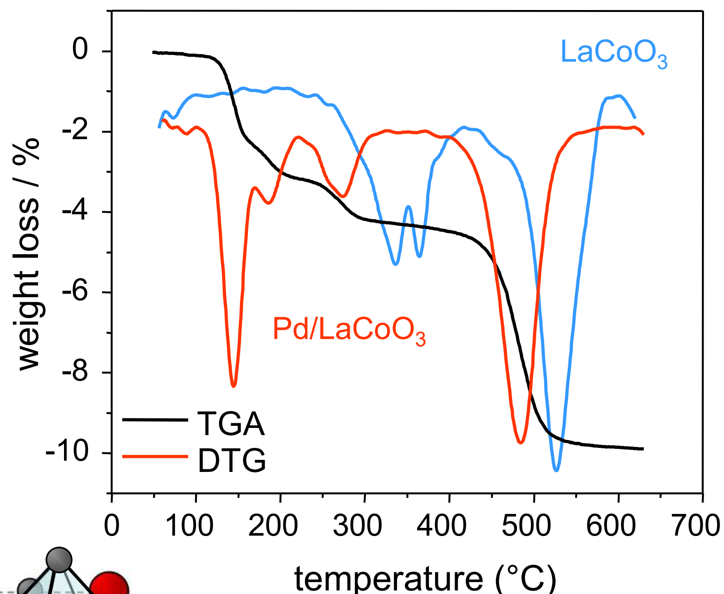


$$CuO:H_2 = 1$$

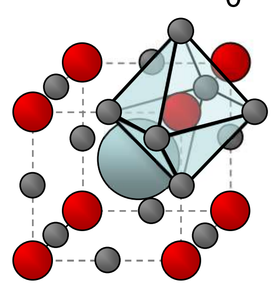
Temperature programmed reduction

- **Reduction of 0.5 wt.% Pd/$LaCoO_3$: H_2-TPR XRD**





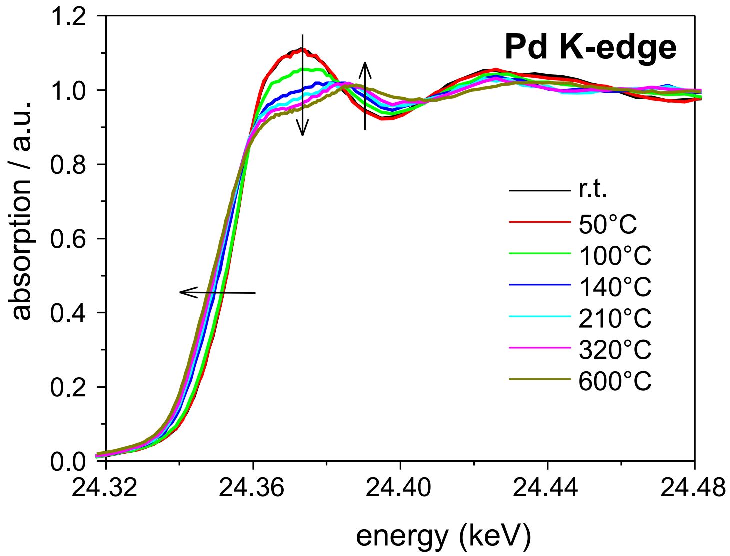
No information on Pd

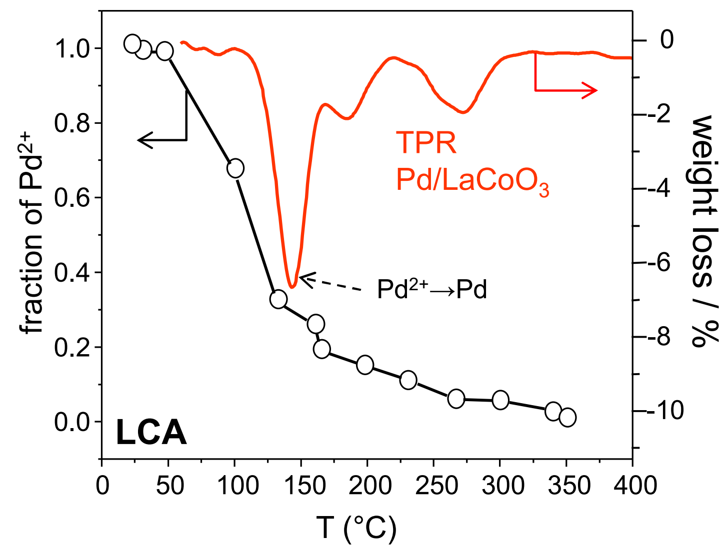


Chiarello et al., J. Catal. 252 (2007) 127 + 252 (2007) 137

Temperature programmed reduction

- **Reduction of 0.5 wt.% Pd/$LaCoO_3$: H_2-TPR XANES**



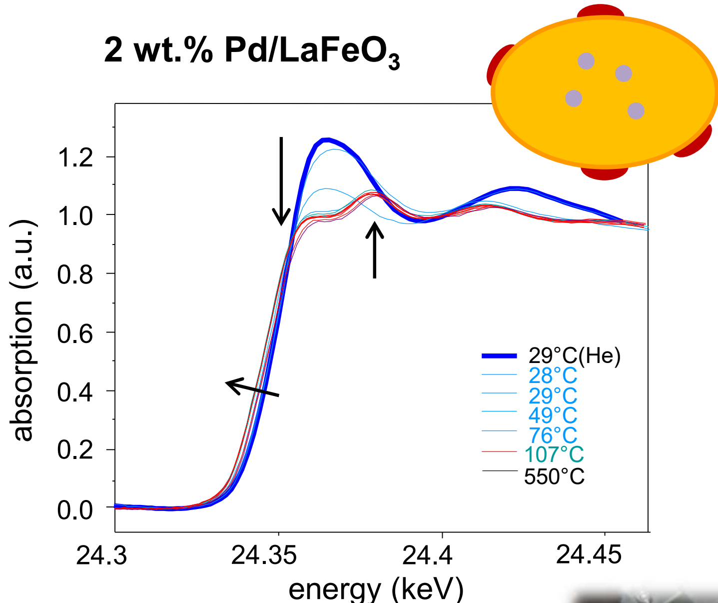


Chiarello et al., J. Catal. 252 (2007) 127 | Chiarello et al., J. Catal. 252 (2007) 137

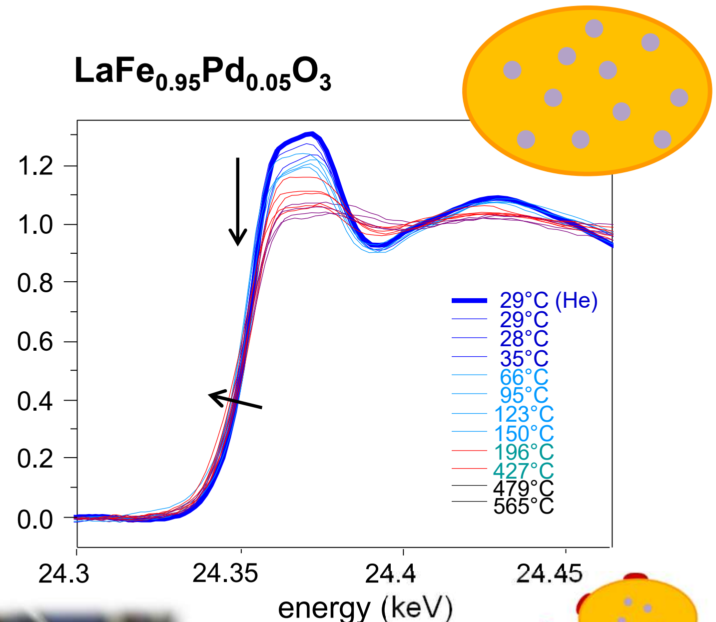
Temperature programmed reduction

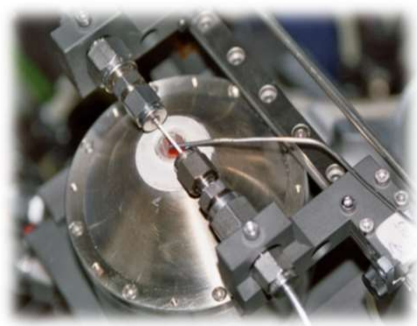
- **Reduction of Pd-containing perovskites**

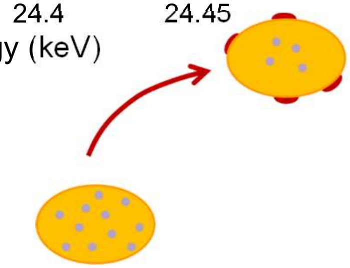
2 wt.% Pd/$LaFeO_3$



$LaFe_{0.95}Pd_{0.05}O_3$







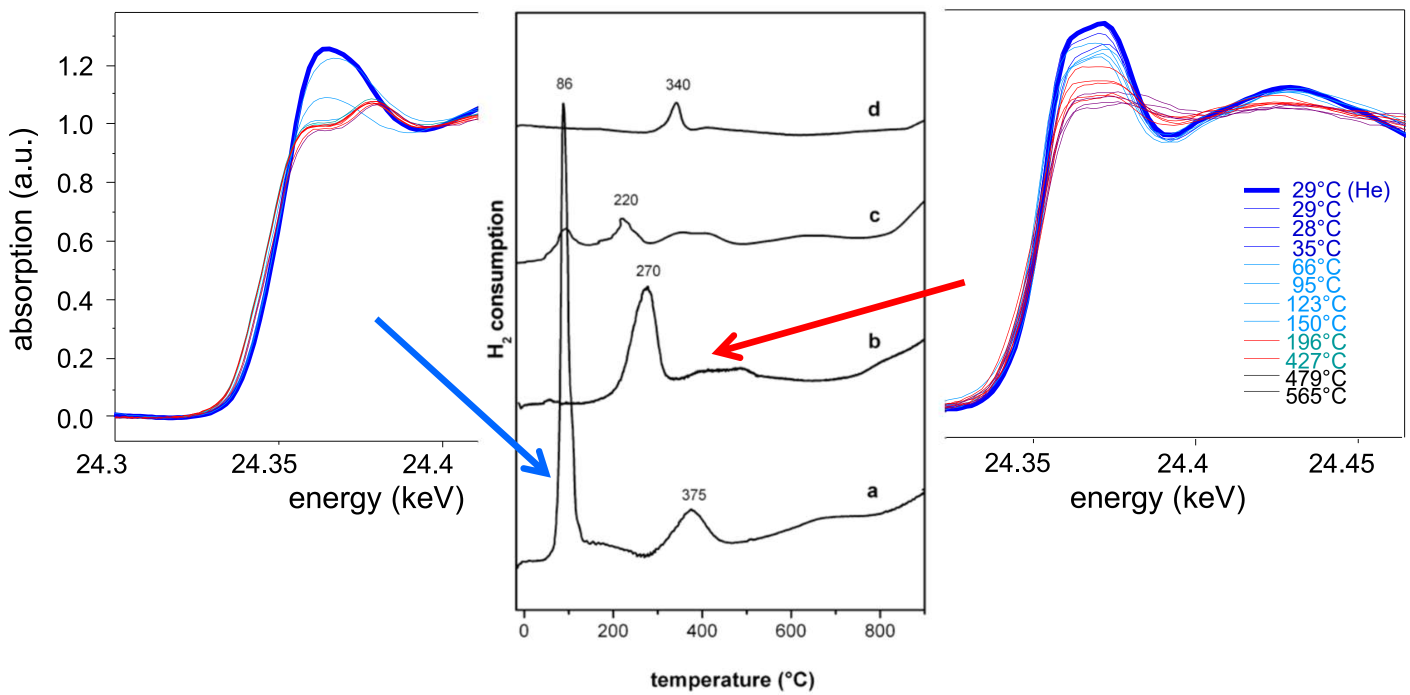
10 vol.% H_2/He, 10°C/min, 50 ml/min

Eyssler et al., J. Phys. Chem. C 114 (2010) 4584

Temperature programmed reduction

- **Reduction of Pd-containing perovskites**

2 wt.% Pd/$LaFeO_3$ | **$LaFe_{0.95}Pd_{0.05}O_3$**



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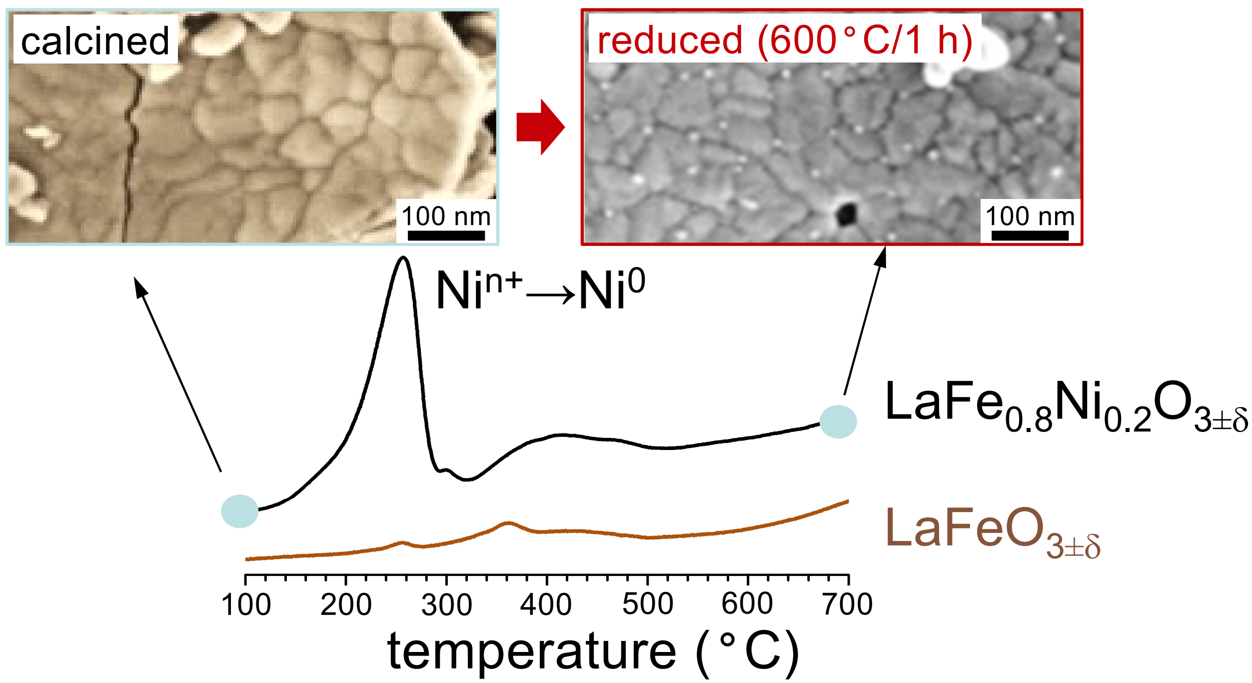
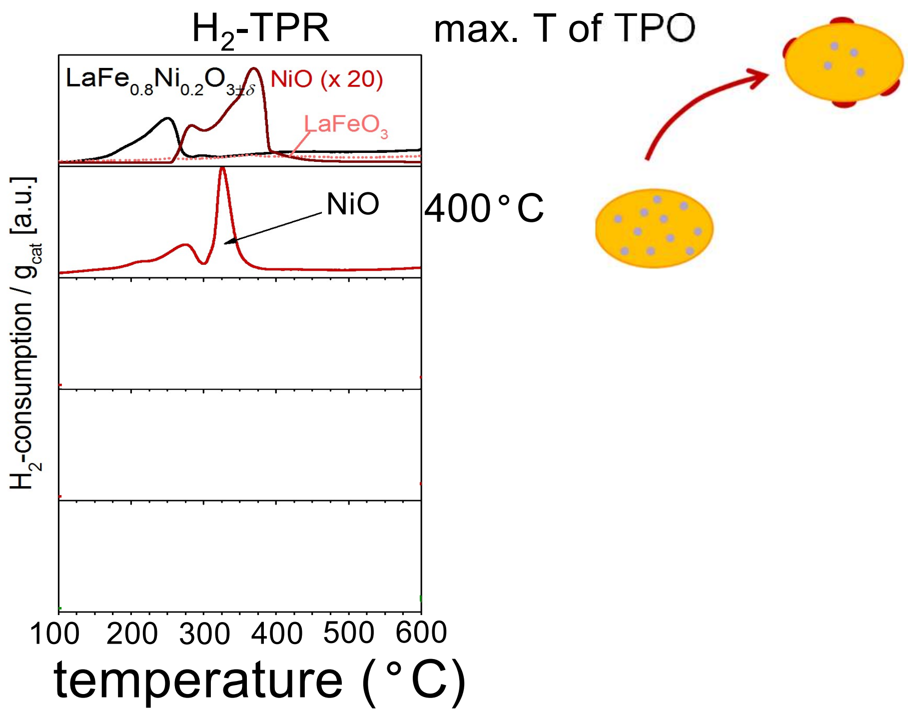
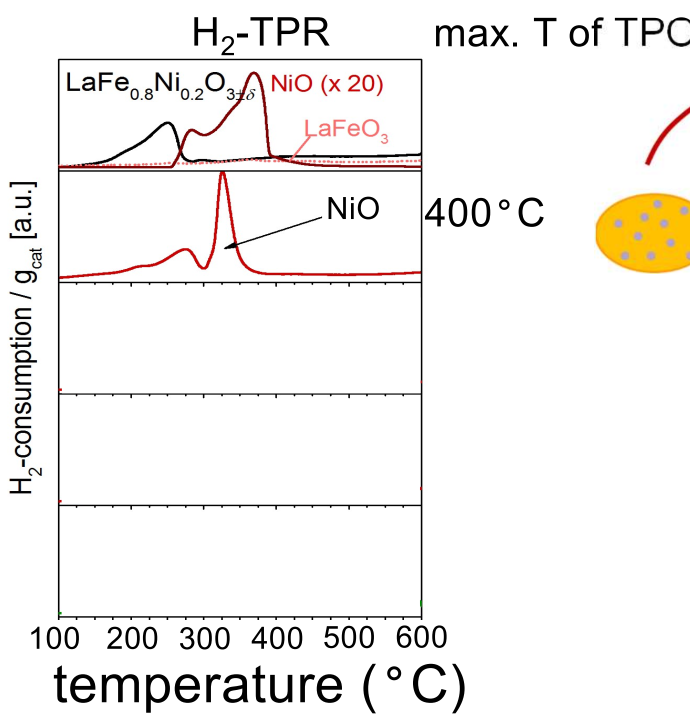
Temperature programmed reduction

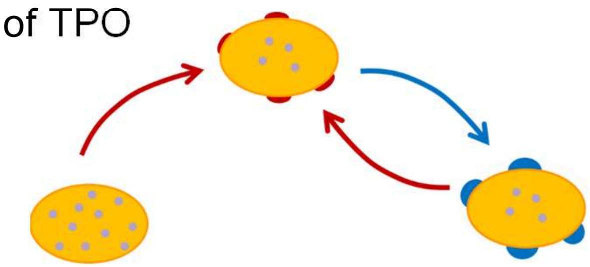


TPR+TPO+TPR

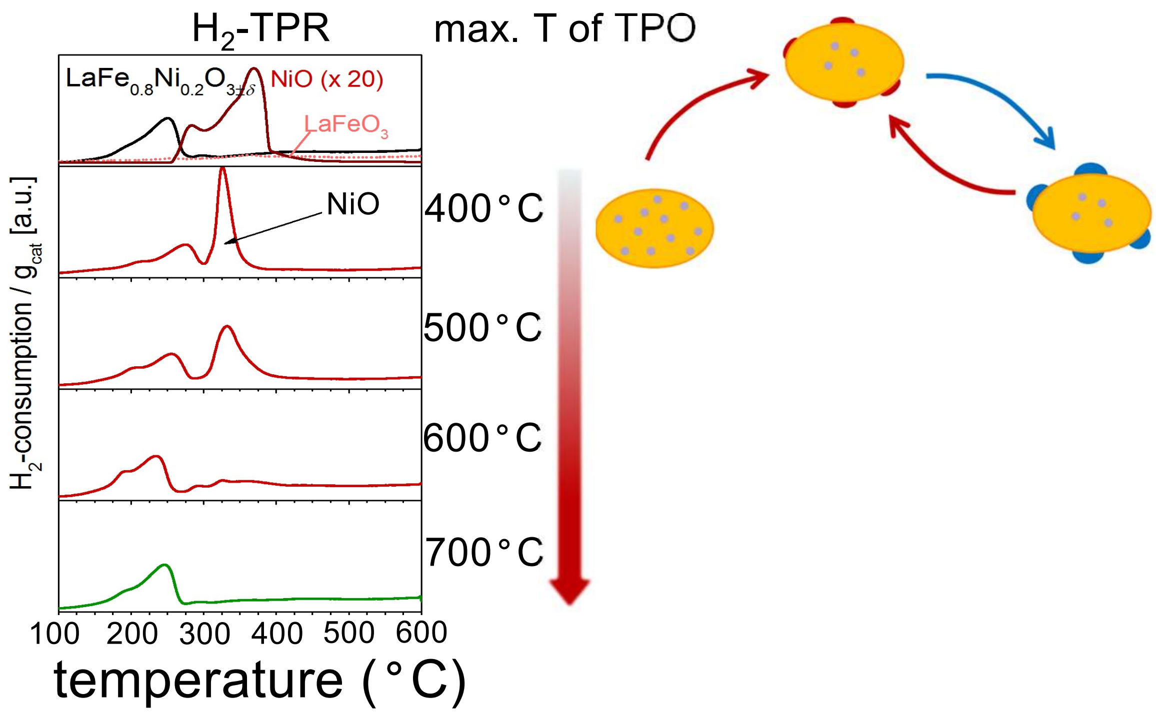

H2-TPR
max. T of TPO
LaFe0.8Ni0.2O3±δ
NiO (x 20)
LaFeO3
NiO
400 °C
H2-consumption / gcat [a.u.]
100 200 300 400 500 600
temperature (°C)

TPR+TPO+TPR


H$_2$-TPR
max. T of TPO
LaFe$_{0.8}$Ni$_{0.2}$O$_{3\pm\delta}$
NiO (x 20)
LaFeO$_3$
NiO
400 °C
H$_2$-consumption / g$_{cat}$ [a.u.]
100 200 300 400 500 600
temperature (°C)

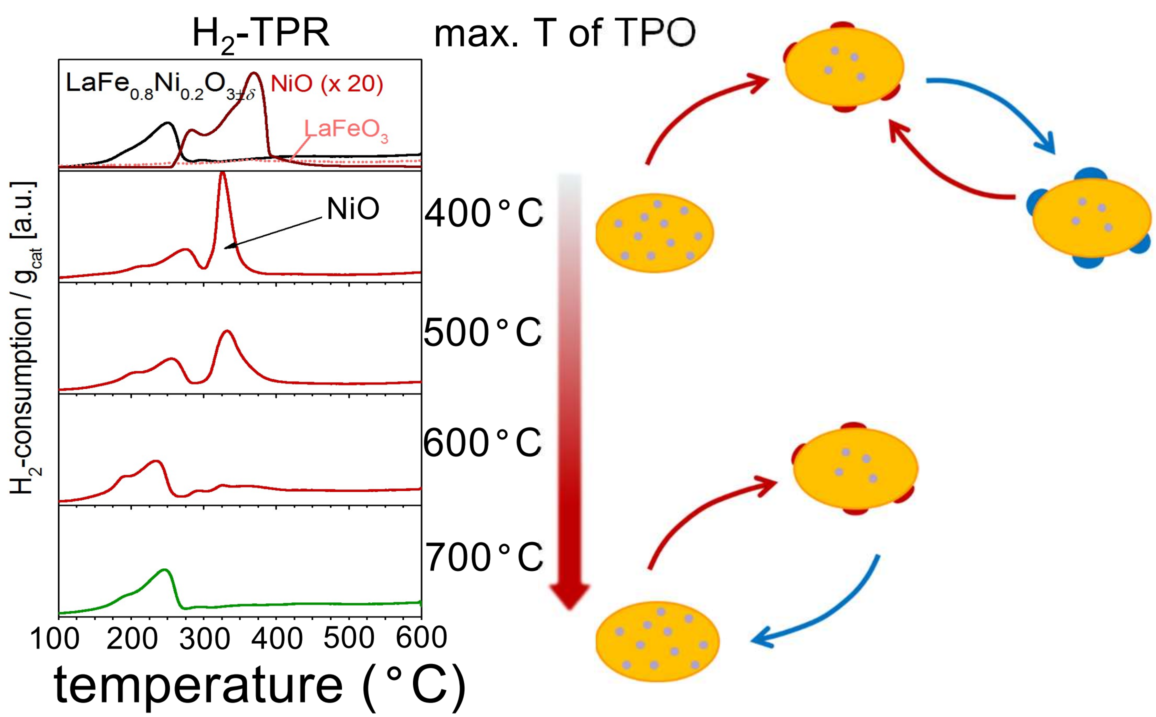


TPR+TPO+TPR



H$_2$-TPR
max. T of TPO
LaFe$_{0.8}$Ni$_{0.2}$O$_{3\pm\delta}$
NiO (x 20)
LaFeO$_3$
NiO
400 °C
500 °C
600 °C
700 °C
H$_2$-consumption / g$_{cat}$ [a.u.]
100 200 300 400 500 600
temperature (°C)

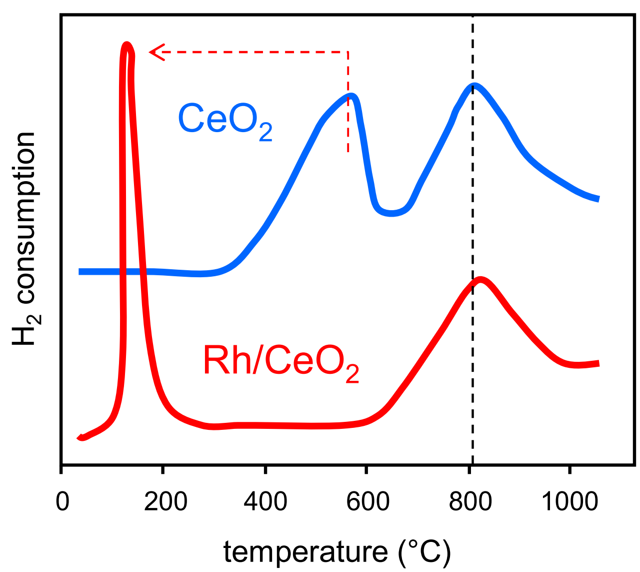
TPR+TPO+TPR

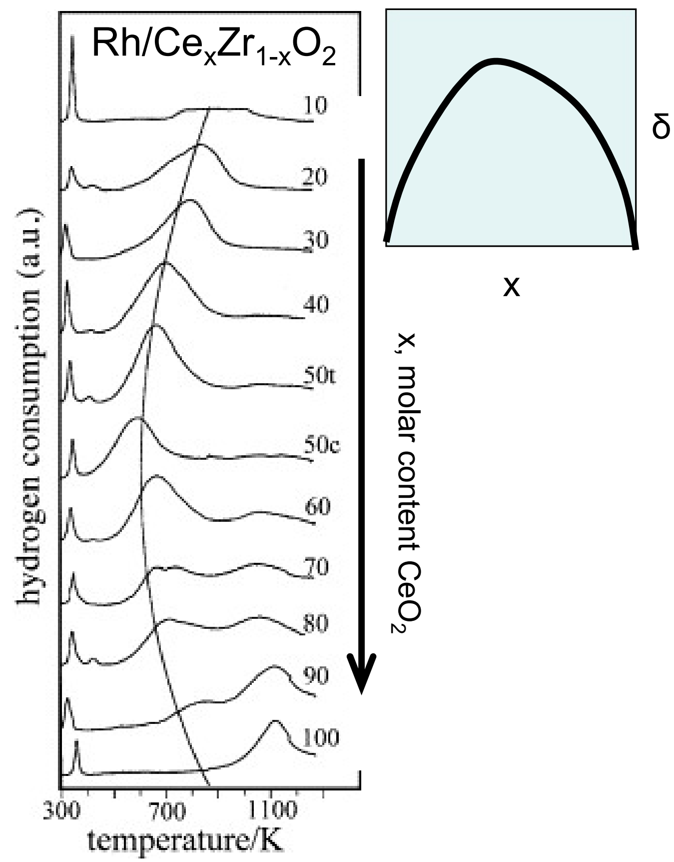


Steiger et al., ChemCatChem 10 (2018) 4456

Temperature programmed reduction

- **Reduction of CeO_2-based catalysts**





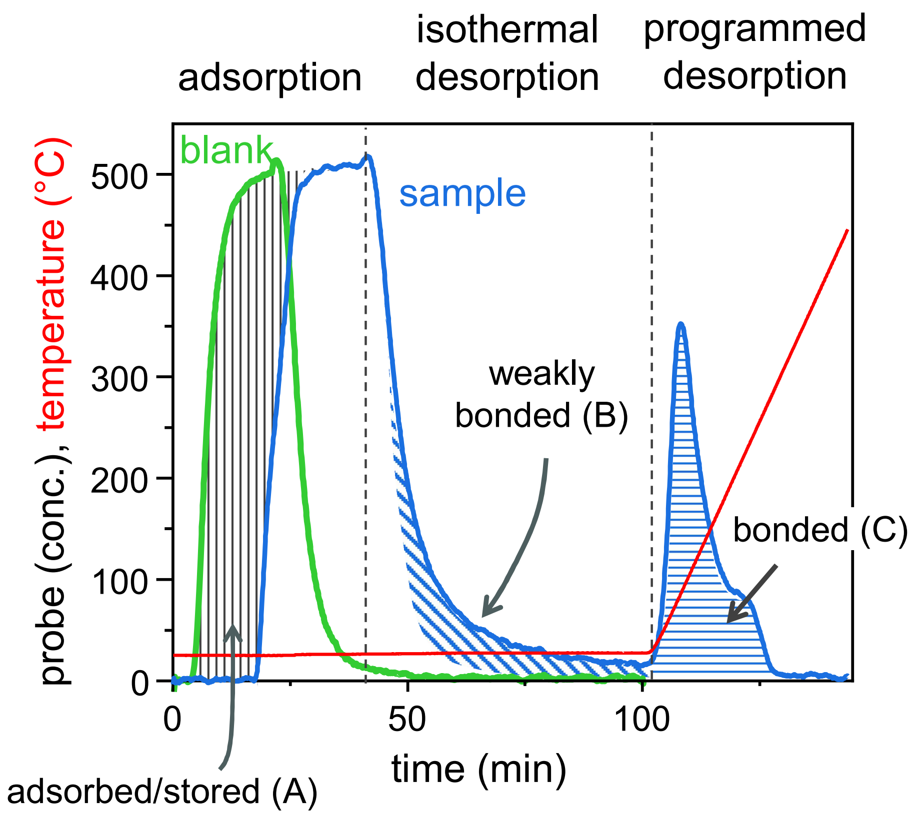
Red. conditions: $CeO_2 \rightarrow Ce_2O_3$
Ox. conditions: $Ce_2O_3 \rightarrow CeO_2$

$Ce_xZr_{1-x}O_2 + \delta H_2 \rightarrow Ce_xZr_{1-x}O_{2-\delta} + \delta H_2O + V_0$

Boaro et al., Catal. Today 77 (2003) 407

Temperature programmed desorption

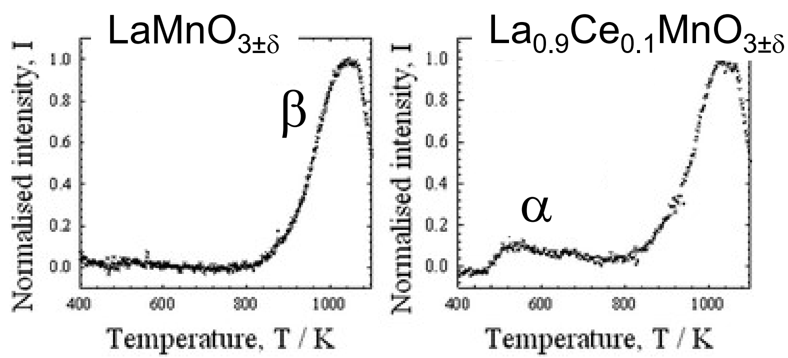
- **Methodology**

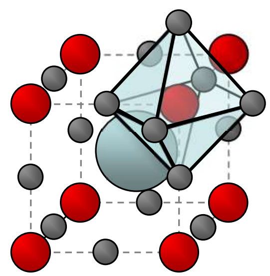


A = B + C

Temperature programmed desorption

- **O_2-TPD - Oxygen mobility in (mixed) oxides**
  - surface oxygen (a): suprafacial catalysis
  - lattice oxygen (β): intrafacial catalysis

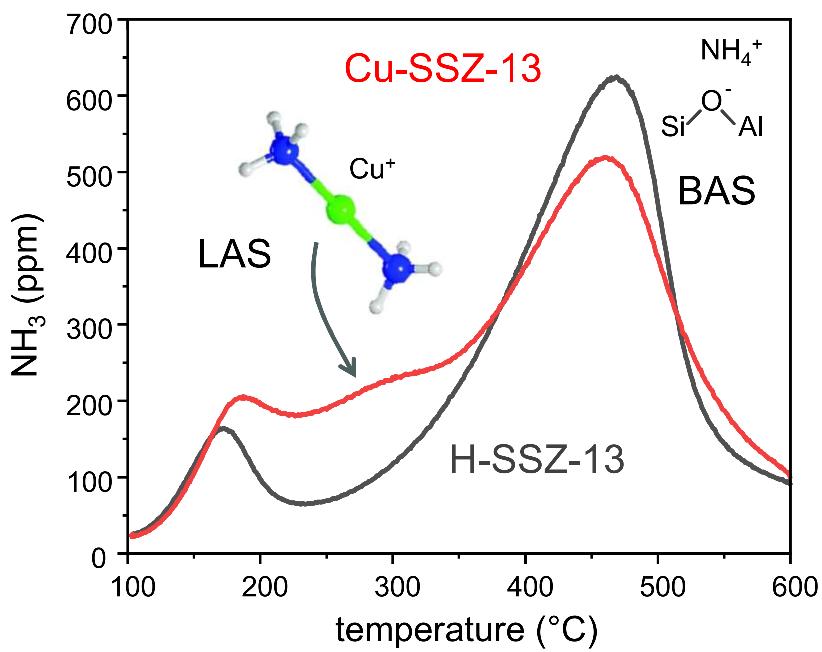


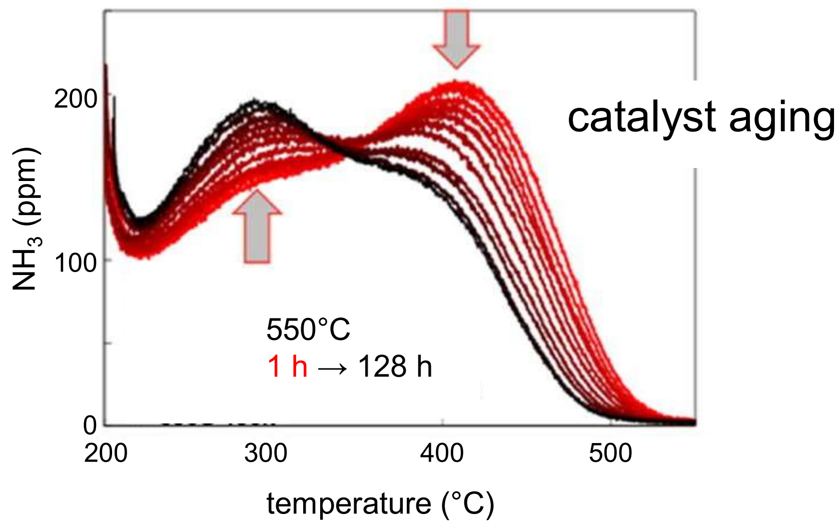


$$t = \frac{r_A + r_O}{\sqrt{2}\left(r_B + r_O\right)}$$

Temperature programmed desorption

- **NH_3-TPD - Acidity**





Marberger et al., Nat. Catal. 1 (2018) 221 | Luo et al., Chem. Eng. Sci. 190 (2018) 60