



Temperature-programmed reduction and oxidation.

Principles and application

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Lecture on TPR/O
13.12.2013



- Reduction of a metal oxide is a frequent process to generate metal catalysts
- Oxidation occurs as deactivation process and is undesired
- In catalytic reactions catalyst undergoes redox dynamics

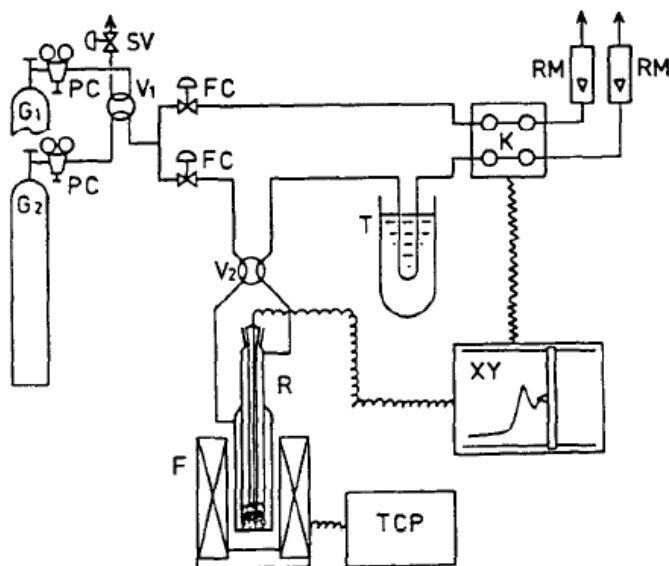
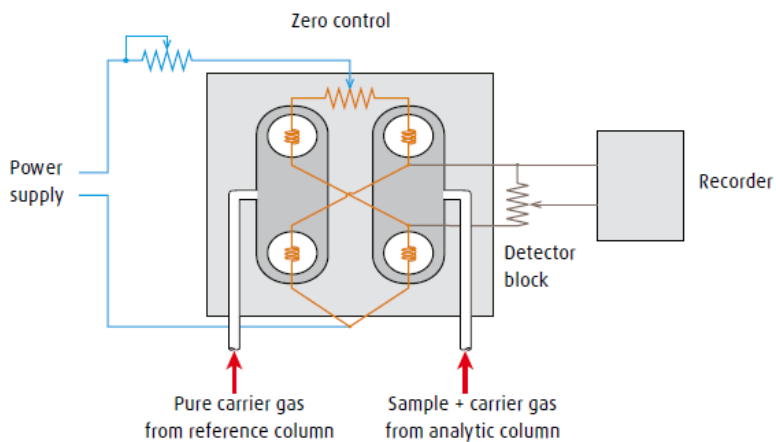
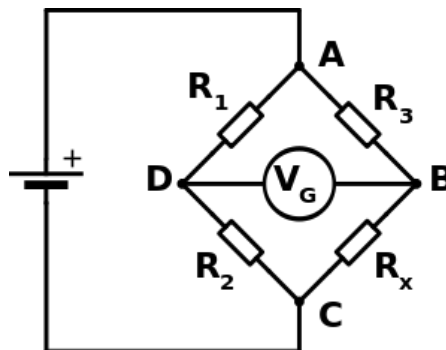


Figure 2. Schematic of the Rogers-Amenomiya-Robertson arrangement for TPD and TPR studies. G_1 and G_2 , gas cylinders (1, pure gas; 2, reducing gas mixture); SV, shutoff valve; V_1 , four way valve for gas selection; FC, Flow controls; V_2 , four way valve for shunting the reactor; R, quartz reactor with quartz thermowell; F, Furnace; TCP, temperature controller-programmer; T, cold trap; K, thermal conductivity detector; XY, recorder; RM, rotameters (From Ref. 5).



Wheatstone bridge



$$R_x = \frac{R_3 \cdot R_2}{R_1}$$

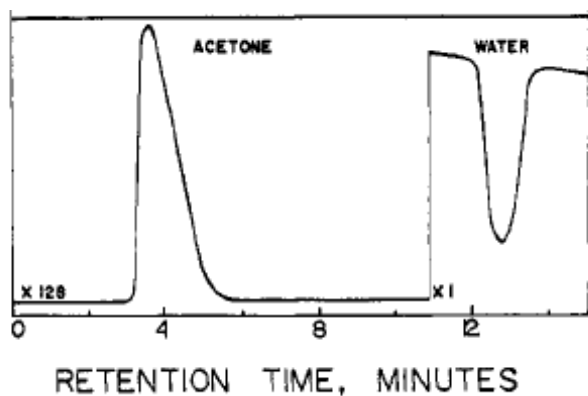
Gas	Thermal Conductivity at 300K (W/m ² *K)
Air	0.026
Ar	0.018
CO	0.025
CO ₂	0.017
H ₂	0.182
He	0.151
N ₂	0.026
O ₂	0.027
CH ₄	0.034
H ₂ O	0.62

Filaments: W-Re, Pt

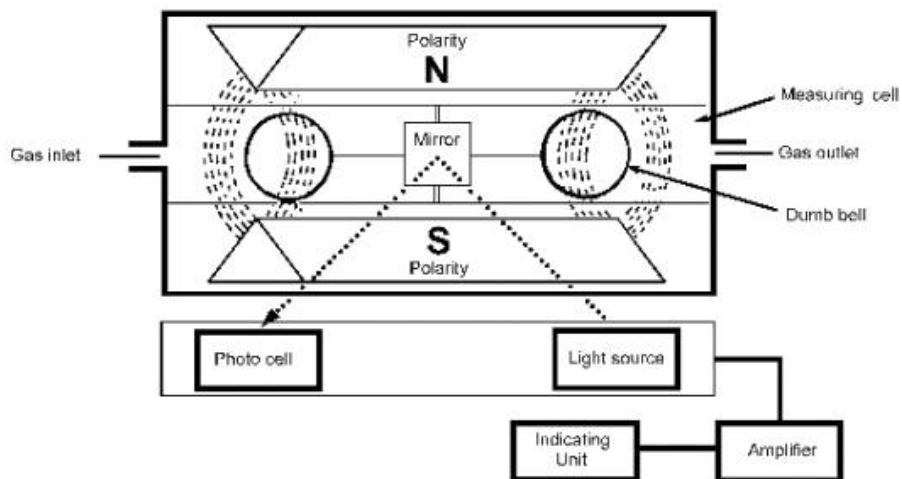
Gasmixtures: H₂/Ar, O₂/He, CH₄/He

Avoid: HCl, HNO₃, Cl₂, F₂, Br₂

CxHy: carbide formation



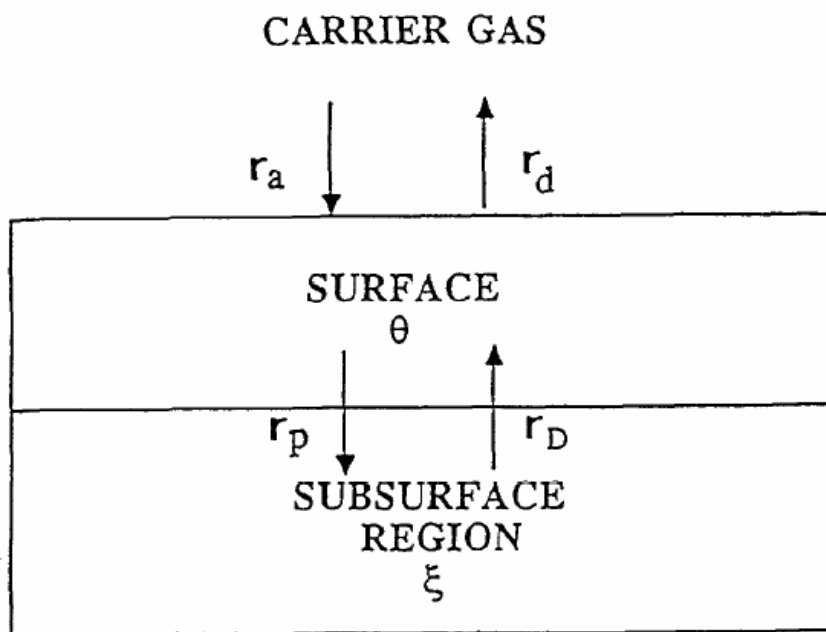
higher thermal conductivity than the carrier gas will produce the negative peak



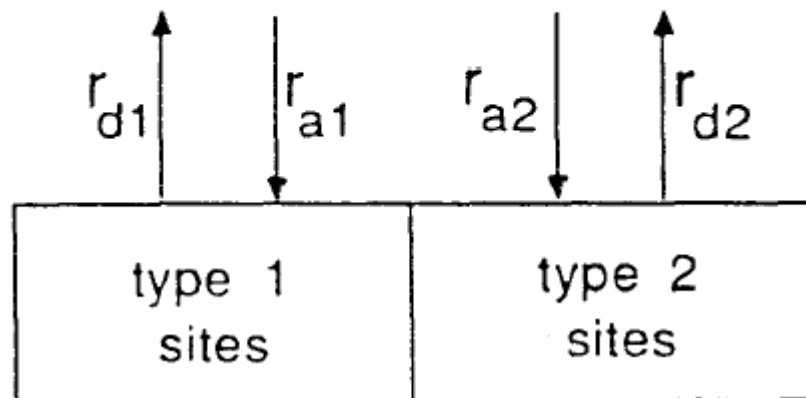
Interfering effect of Paramagnetic sensor

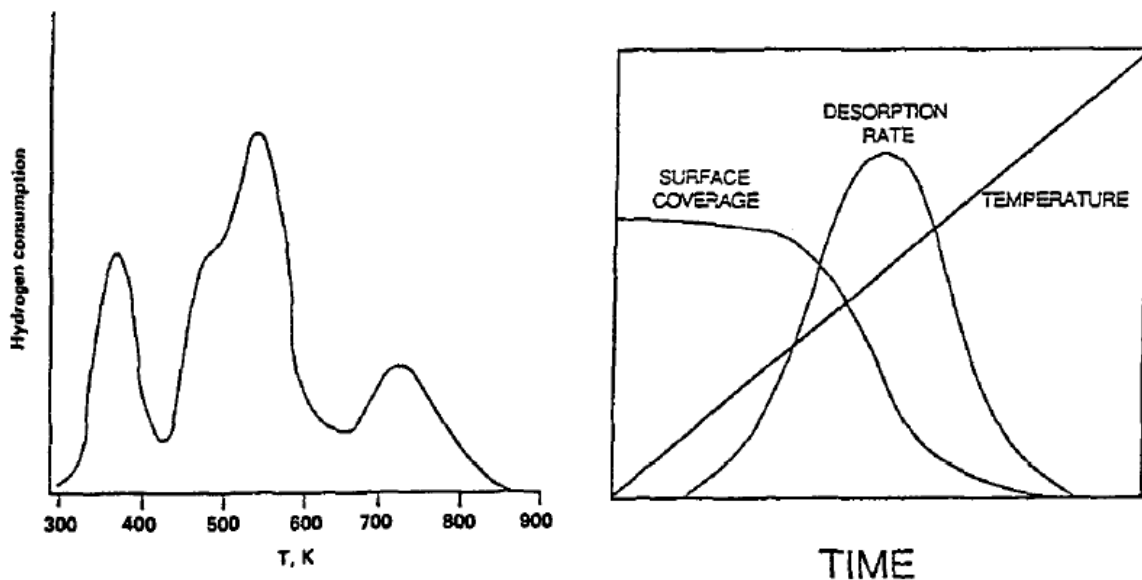
Interfering Gas	Interference Effect
(100% Interferent)	(% O ₂)
N ₂ O	-0.20
CO ₂	-0.26
H ₂ O	-0.03
Halothane	-1.93
Isoflurane	-1.97
Enflurane	-1.97
Desflurane	-2.10
Sevoflurane	-2.90
Chloroform	-1.37
Helium	0.29
NO	42.56
NO ₂	5.00

Process occurring during TPR when both readsorption and subsurface diffusion are important



Catalyst containing two distinct adsorption sites of differing binding energies





Temperature-programmed reduction (TPR) response diagrams

- Number of peaks (shoulders)
- Position, T_{\max} , T_{onset}
- Peak profile

Kinetics Basics

degree of reaction

Activation energy

Arrhenius equation:

$$\frac{-d(\alpha)}{d(t)} = A \cdot f(\alpha) \cdot \exp\left(-\frac{E_A}{RT}\right)$$

isothermal

Pre-exponential factor
(in gas describes the number of particle collisions)

$$\beta = \frac{dT}{dt}$$

$f(\alpha)$ – Reaction type
(e.g. for the second-order reaction $f(\alpha)=\alpha^2$)

$$\frac{-d(\alpha)}{d(T)} = \frac{A}{\beta} \cdot f(\alpha) \cdot \exp\left(-\frac{E_A}{RT}\right)$$

Non-isothermal

$$\alpha, T, t \longrightarrow A, f(\alpha), E_A$$

Measured parameters

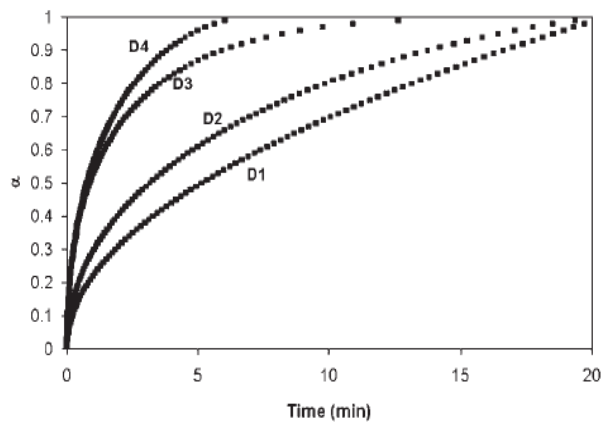
Kinetic triplet

Table 1. Solid-State Rate Expressions for Different Reaction Models, Shapes of These Models Is Given in Figure 3

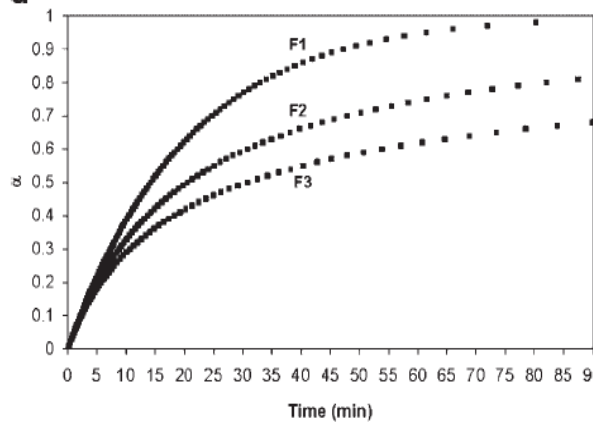
Model	Differential Form ^a $f(\alpha) = \frac{1}{k} \frac{d\alpha}{dt}$	Integral Form ^a $g(\alpha) = kt$
Nucleation models		
Power law (P2)	$2 \alpha^{(1/2)}$	$\alpha^{(1/2)}$
Power law (P3)	$3 \alpha^{(2/3)}$	$\alpha^{(1/3)}$
Power law (P4)	$4 \alpha^{(3/4)}$	$\alpha^{(1/4)}$
Avrami-Erofe'ev (A2)	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
Avrami-Erofe'ev (A3)	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
Avrami-Erofe'ev (A4)	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
Prout-Tompkins (B1)	$\alpha (1 - \alpha)$	$\ln[\alpha/(1 - \alpha)]$
Geometrical Contraction models		
Contracting area (R2)	$2(1 - \alpha)^{1/2}$	$[1 - (1 - \alpha)^{1/2}]$
Contracting volume (R3)	$3(1 - \alpha)^{2/3}$	$[1 - (1 - \alpha)^{1/3}]$
Diffusion models		
1-D diffusion (D1)	$1/2\alpha$	α^2
2-D diffusion (D2)	$[- \ln(1 - \alpha)]^{-1}$	$[(1 - \alpha)\ln(1 - \alpha)] + \alpha$
3-D diffusion-Jander eqn.(D3)	$3(1 - \alpha)^{2/3}/2(1 - (1 - \alpha)^{1/3})$	$[1 - (1 - \alpha)^{1/3}]^2$
Ginstling-Brounshtein (D4)	$(3/2)((1 - \alpha)^{-1/3} - 1)$	$1 - (2\alpha/3) - (1 - \alpha)^{2/3}$
Reaction-order models		
Zero-order (F0/R1)	1	α
First-order (F1)	$(1 - \alpha)$	$- \ln(1 - \alpha)$
Second-order (F2)	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
Third-order (F3)	$(1 - \alpha)^3$	$0.5 ((1 - \alpha)^{-2} - 1)$

^aIn some references $f(\alpha)$ and $g(\alpha)$ have opposite designations.

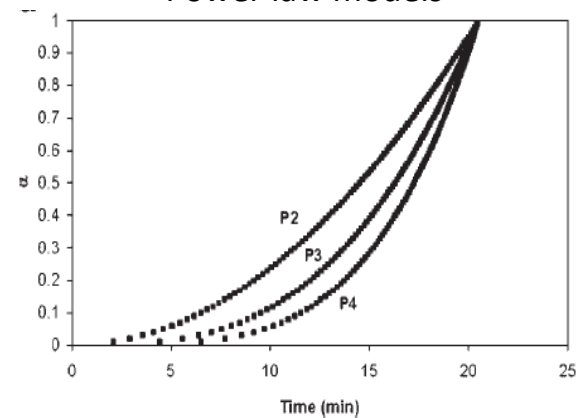
Diffusion models



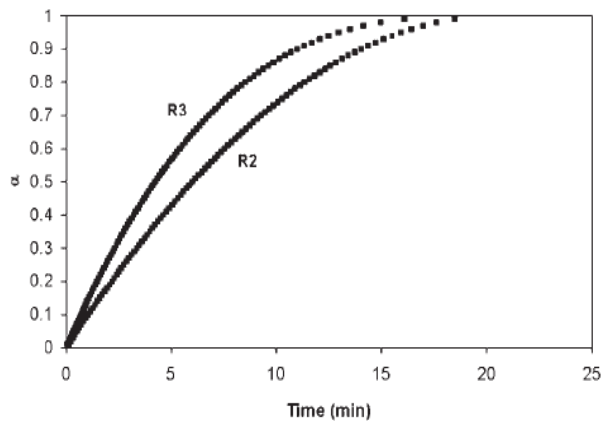
Reaction order models



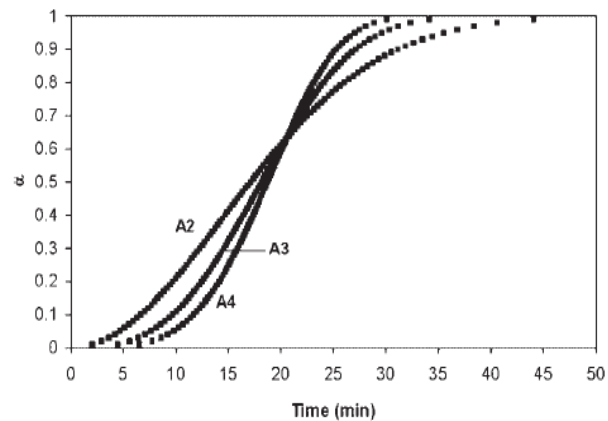
Power law models



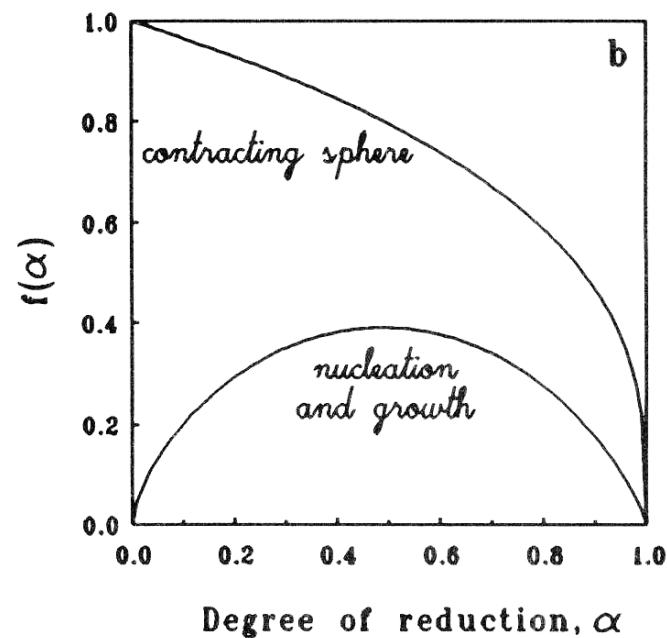
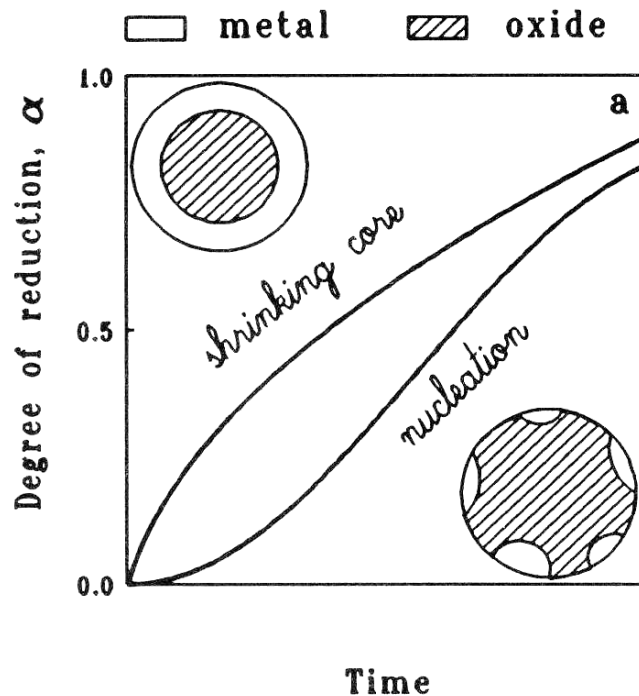
Geometrical contraction models



Avraami Erofeev



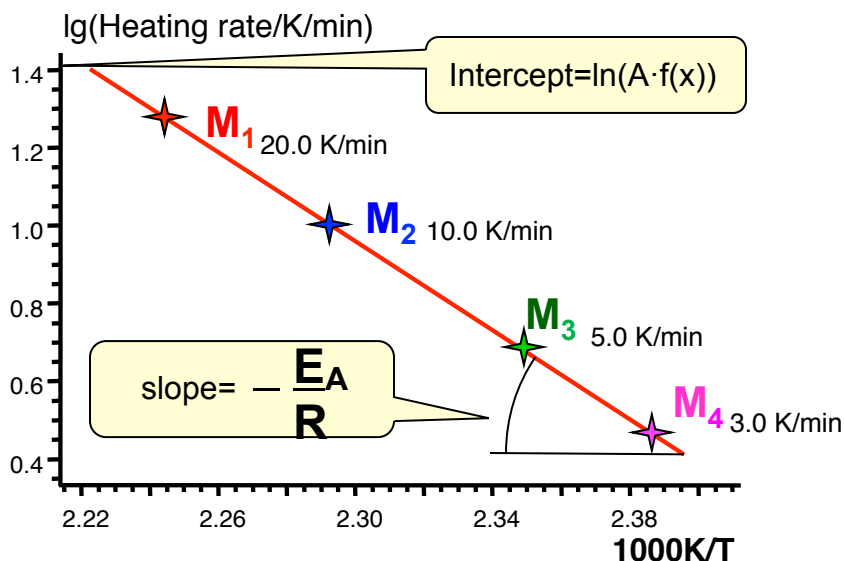
TPR Simple model functions



Model free kinetics

$$\ln(\beta) \sim -\frac{E}{R} \cdot \frac{1}{T}$$

name	Equation
(Ozawa-Flynn-Wall)	$\ln \beta = \ln \left[\frac{AE_a}{RG(\alpha)} \right] - 5.33 - 1.05 \cdot \frac{E_a}{RT}$
(Friedman)	$\ln \left[\left(\frac{d\alpha}{dt} \right) \cdot \beta \right] = \ln A + n \ln(1 - \alpha) - (E / RT)$
(Kissinger)	$\ln(\beta / T_m^2) = (E / R)(1 / T_m)$



Formal kinetics

Aim: finding of mathematical model

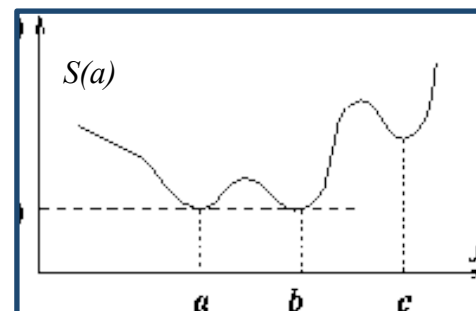
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(1-order)	$f(\alpha) = -\ln(1 - \alpha)$
(Avrami – Erofeev)	$f(\alpha) = [-\ln(1 - \alpha)]^{1/2}$
(Prout-Tompkins)	$f(\alpha) = \ln[\alpha / (1 - \alpha)]$

Way: non linear regression (NLR) to minimise least squares between numerical values of the experiment and calculation

$$S(a) = \sum_{i=1}^N w_i^2 (y_i - f_i)^2 g_i^2$$

y - measured
 f - fitted

$S(a)$ -Objective function



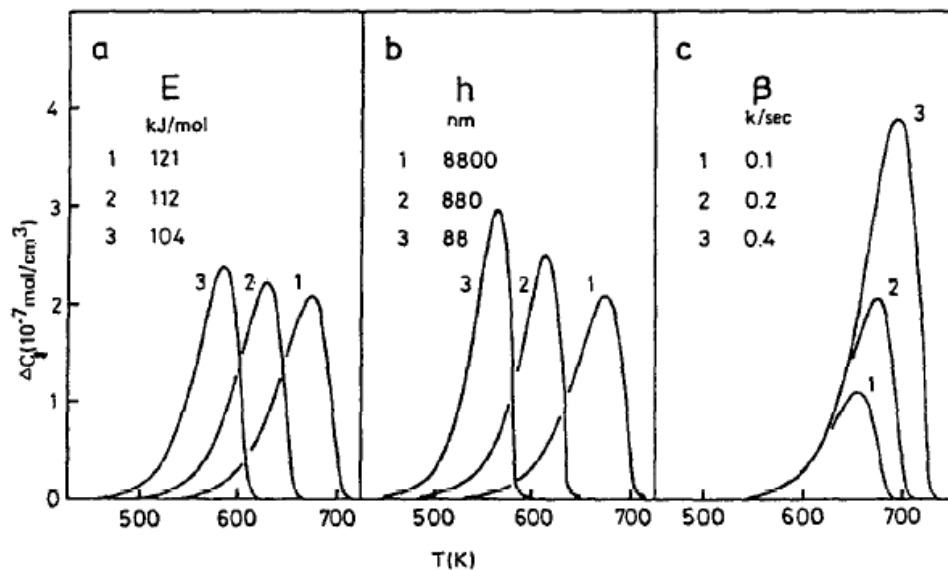
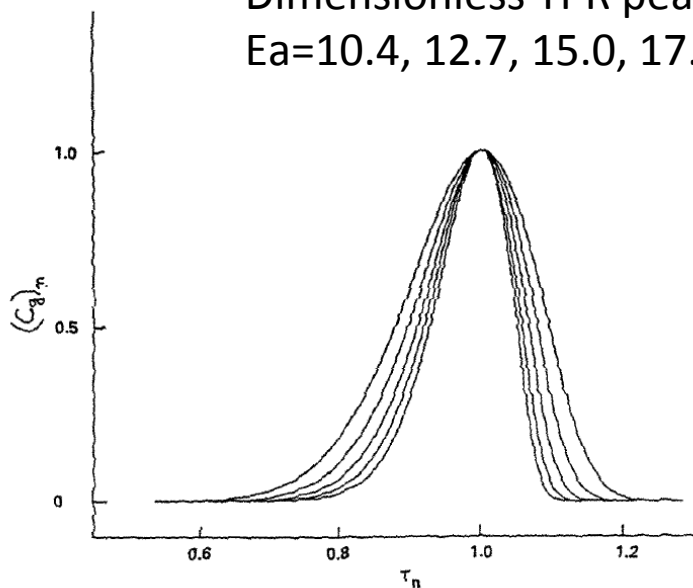
Verified kinetic triplet \rightarrow

The important parameters that have to be optimized in temperature programmed analysis are:

- Flow rate of carrier gas
- Reactant gas/inert gas ratio
- Catalyst sample volume/mass
- Catalyst sample particle size
- Geometry of the reaction vessel (catalyst sample reactor)
- Heating rate
- Signal intensity
- System pressure

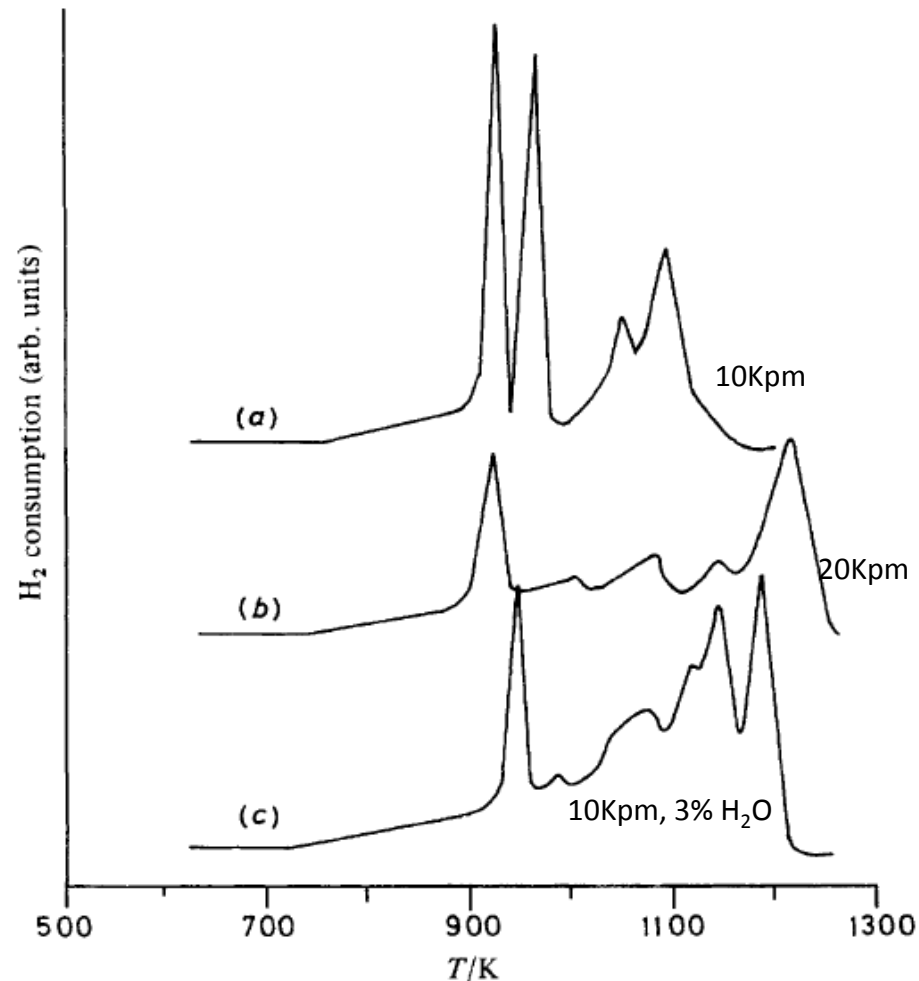
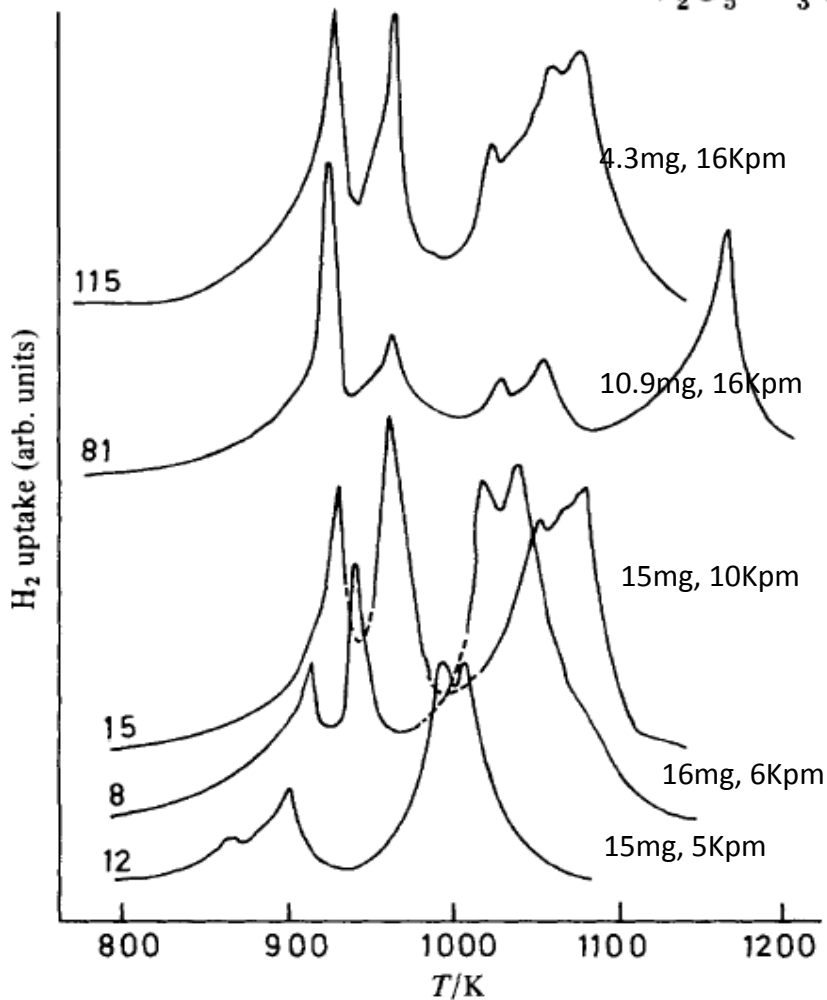
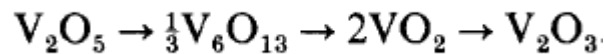
Information obtained depends on the procedure
Not a fundamental property

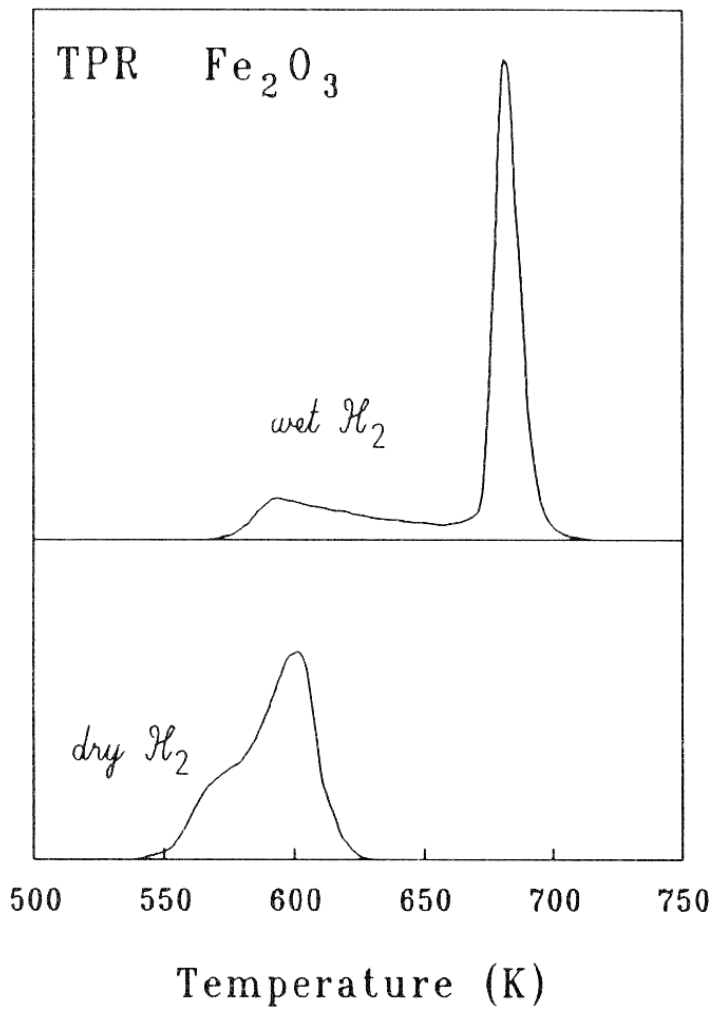
Dimensionless TPR peak shape analysis for different values of E_a , $E_a=10.4, 12.7, 15.0, 17.3, 19.7$. The peaks become sharper with increasing E_a .



Theoretical TPR patterns of of a nucleation controlled reaction

TPR profiles of V_2O_5 – influence of heating rate, sample mass and water vapor.





Reduction of iron oxide particles

Decent TPR profile

$$K = \frac{S_i^0}{C_g \cdot F_o} \frac{[\mu mol]}{\left[\frac{\mu mol}{cm^3} \right] \cdot \left[\frac{cm^3}{s} \right]} = [s]$$

$\beta=5-20Kpm$

S – current amount of reducible species, μmol

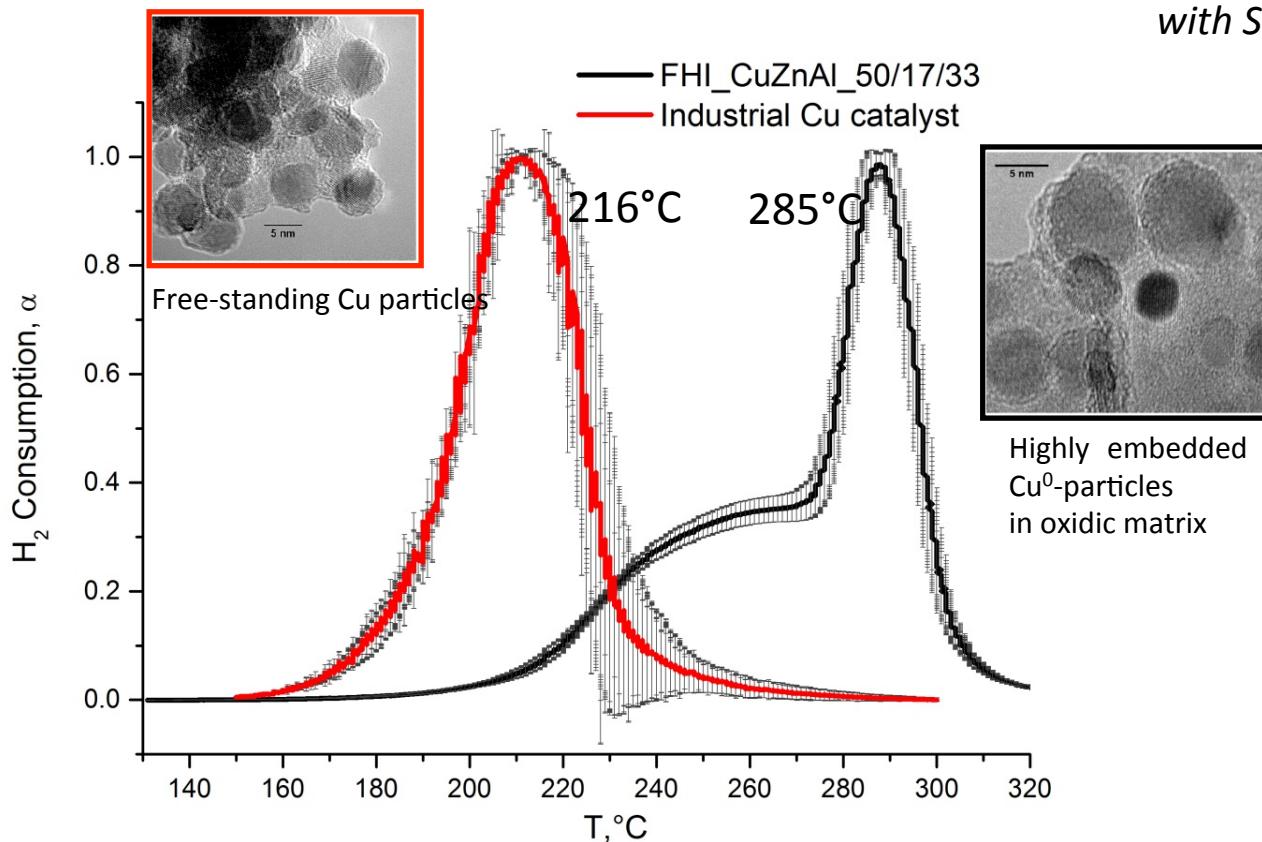
C – current concentration of hydrogen, $\mu mol/cm^3$

V*-total flow rate of the reducing gas, $cm^3(NTP)/s$

$55 < K < 140$

- The amount of hydrogen consumed at the peak maximum should not exceed 2/3 of the hydrogen feed to the reactor $C_m \geq 0.33C_0$
- The minimum conversion at the peak maximum should be 10% $[C_m \leq 0.9C_0]$

with Stefanie Kühl

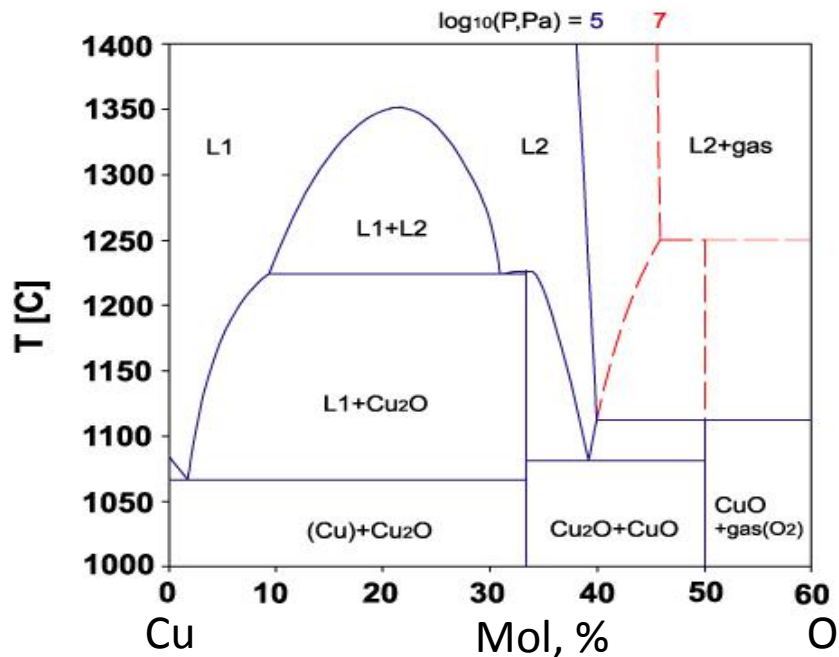


- FHI sample possesses a better homogeneity due to smaller variance

Origin of the shoulder on the TPR profile of FHI sample

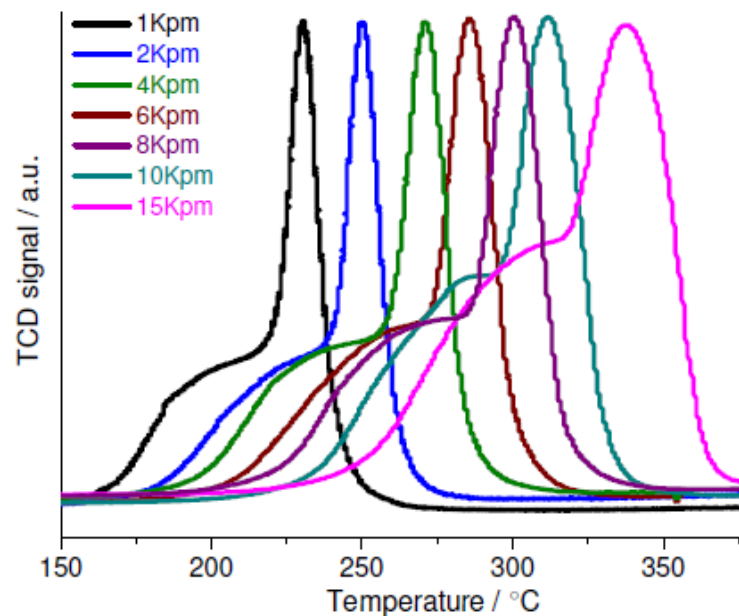
- reduction of finely dispersed CuO?
- 1st step of reduction to kinetically stabilized Cu(I)oxide species?
- the reduction of hydroxy carbonate species?

Phase diagram Cu – O system



Thermodynamically Cu₂O must be present

Heating rate depended TPR profiles



Kinetic mechanism doesn't change with varying heating rate.

Kinetics Basics

degree of reaction

Activation energy

Arrhenius equation:

$$\frac{-d(\alpha)}{d(t)} = A \cdot f(\alpha) \cdot \exp\left(-\frac{E_A}{RT}\right)$$

isothermal

Pre-exponential factor
(in gas describes the number of particle collisions)

$$\beta = \frac{dT}{dt}$$

$f(\alpha)$ – Reaction type
(e.g. for the second-order reaction $f(\alpha)=\alpha^2$)

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Non-isothermal

$$\alpha, T, t \longrightarrow A, f(\alpha), E_A$$

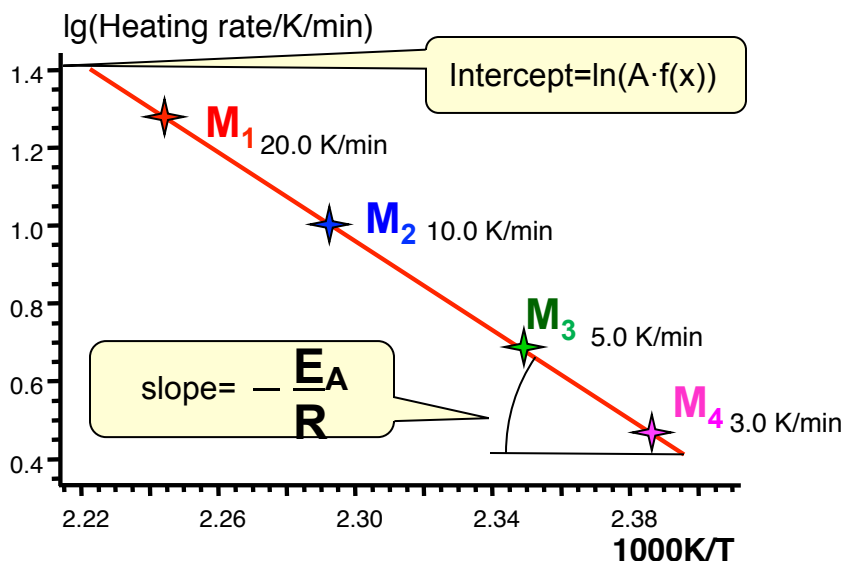
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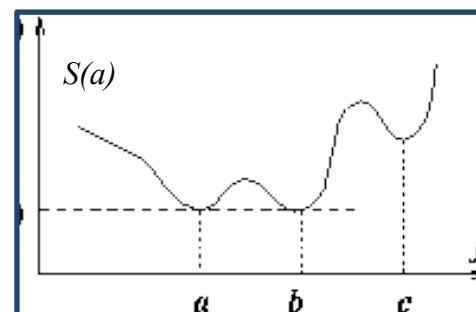
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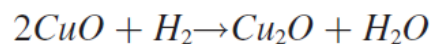
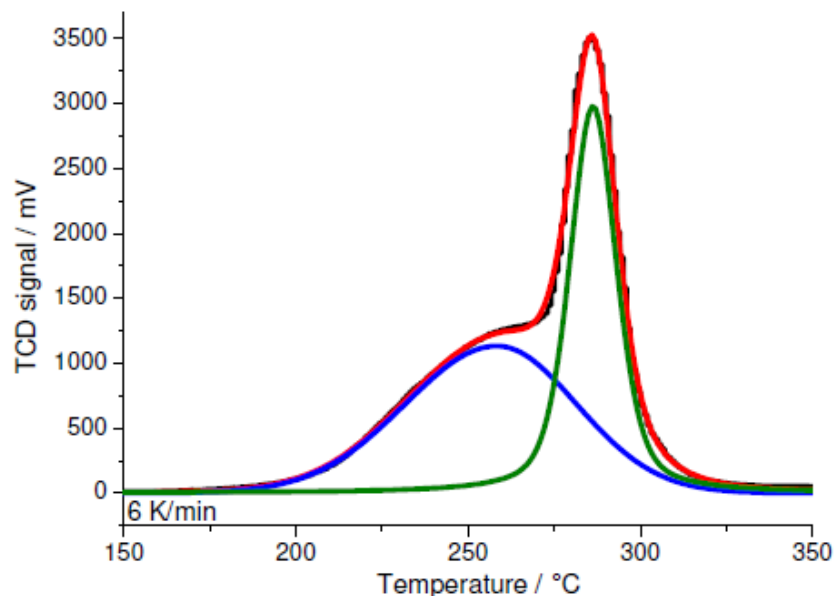
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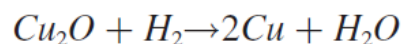
Verified kinetic triplet \rightarrow

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Qualitative deconvolution of TPR profile



$$\Delta_r H_{298}^0 = -100.41 \text{ kJ/mol}$$



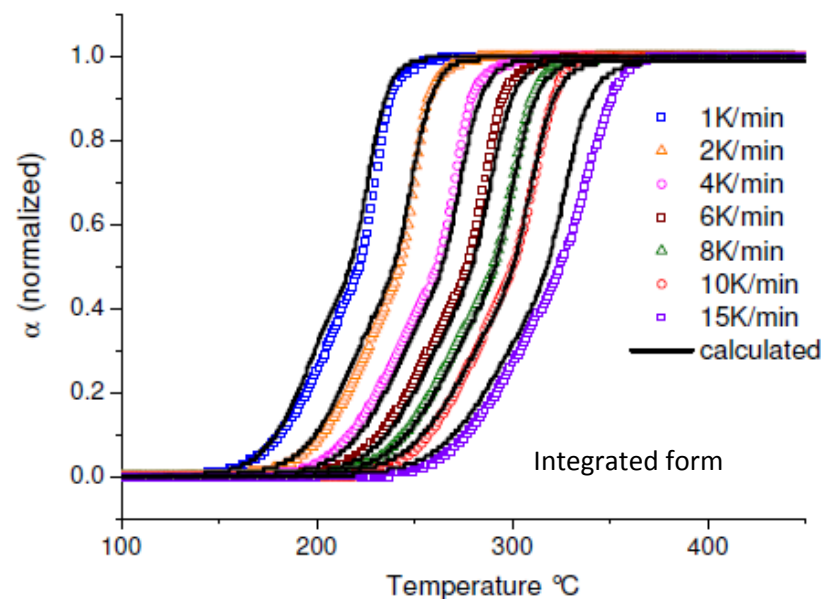
$$\Delta_r H_{298}^0 = -71.12 \text{ kJ/mol}$$

$$\frac{d\alpha}{dT} = \frac{k_0}{\beta} \cdot e^{-E_a/RT} \cdot f(\alpha)$$

$$f(\alpha) = (1 - \alpha)^n \cdot \alpha^a$$

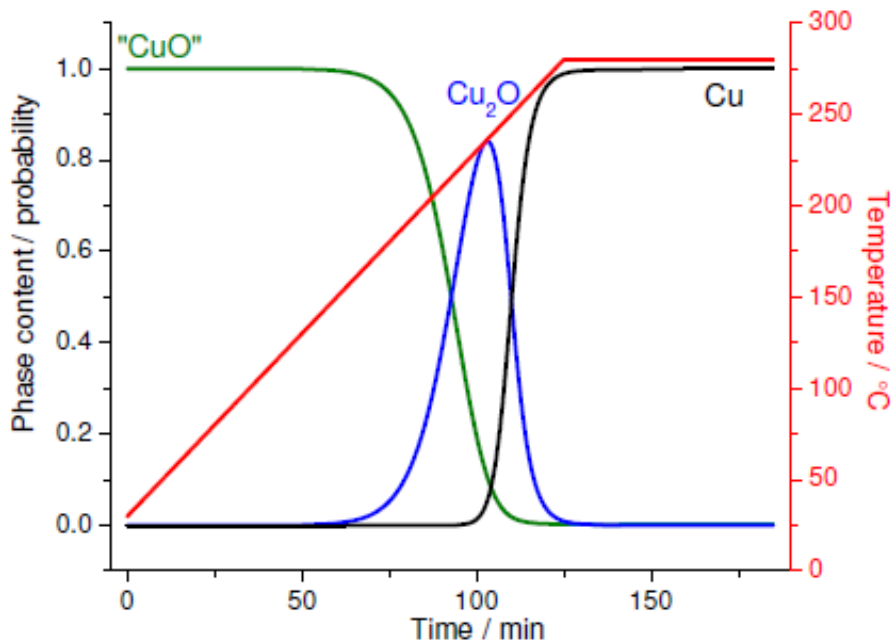
Stage No., i	E_A / kJmol^{-1}	Pre-exponential factor, $\lg(A) / \text{s}^{-1}$	n	a
1	52.9 ± 2.0	3.0 ± 0.2	0.9 ± 0.2	0.6 ± 0.0
2	63.2 ± 3.8	4.1 ± 0.6	1.2 ± 0.4	1.2 ± 0.4

Fitting and refinement of TPR profiles



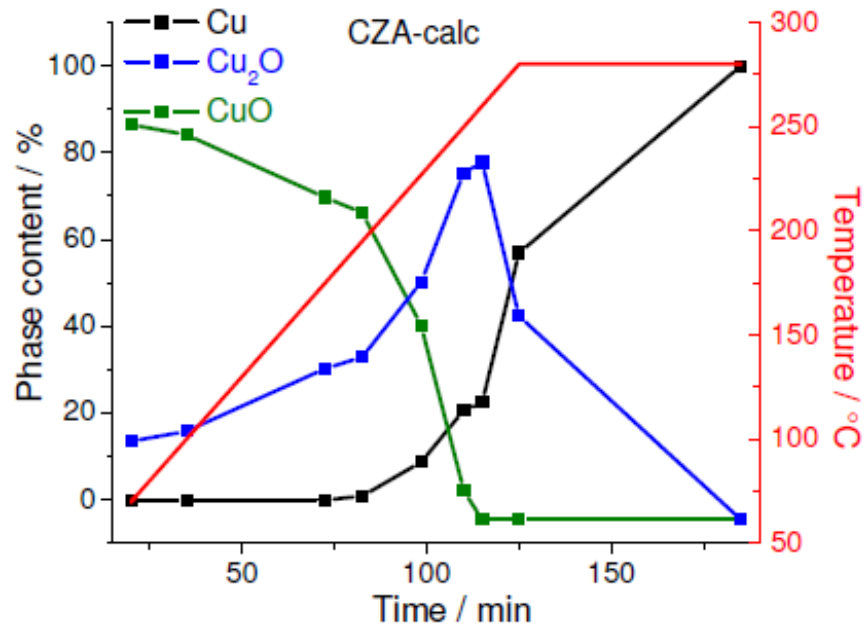
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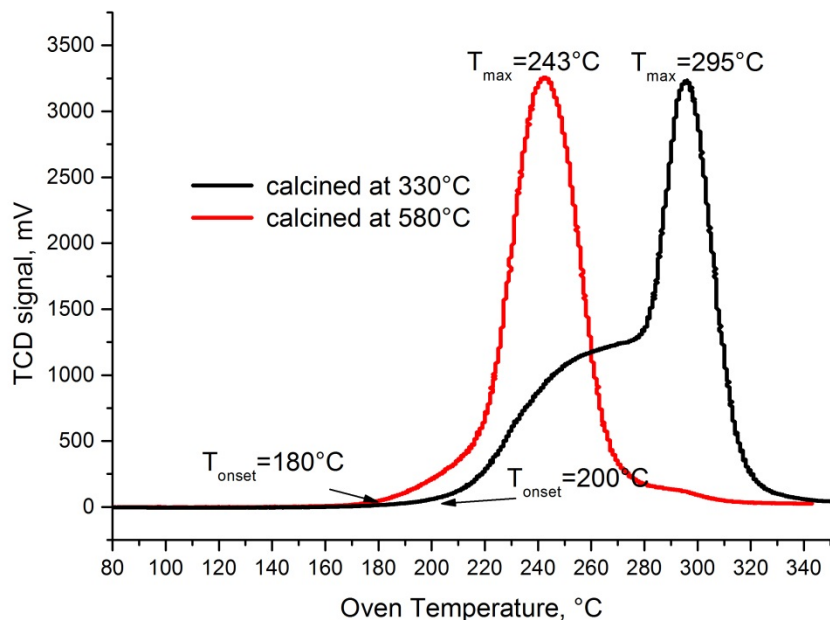
Prediction of phase evolution from TPR data



Two-step consecutive mechanism through formation of kinetically stabilized Cu (I)

Results of quantification of NEXAFS data





Reduction kinetic parameters

T calc, °C	Ea, CuO – Cu ₂ O kJ/mol	Ea, Cu ₂ O-CuO, kJ/mol
330	110	77
580	72	40

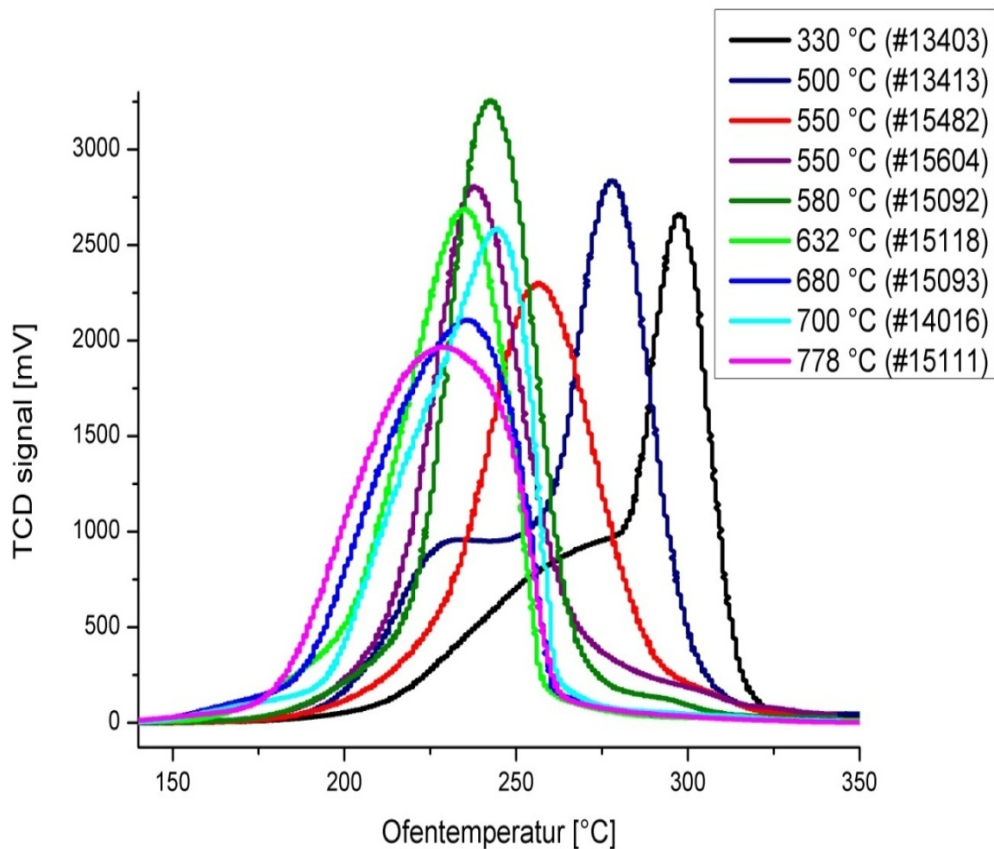
Kinetic results from TG data.

Higher calcination temperature favors faster reaction and promotes higher activity towards MeOH

Tcalc, °C	Cu-SA, m ² / g(cat)	MeOH Activity after 4hrs, μmol/min/ g(cat)
330	5	90
580	19	240

Testing conditions: p = 30.5 bar, T = 230 °C,
gas (CO / CO₂ / H₂ / He): 6 / 8 / 59 / 27 ml/min

Effect of calcination temperature



T°C	Domain size CuO	Cu-SA, m ² /g	μmol/g(cat)/min (after 4hrs)
330		5	90
400		5	
500		8	160
550	2.0	11	165
580	3,0	19	240
600	5,1	19	200
632	5,8	19	
680	20,6	10	130
700	23,4	7	94
778	37,2		

Target Reaction Dry reforming (DRM): $\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2 \text{CO} + 2 \text{H}_2$ $\Delta H^0 = 247 \text{ kJ/mol}$

Side reactions (\Rightarrow catalyst deactivation because of **coking**):

- Boudouard reaction: $2 \text{CO} \rightleftharpoons \text{C} + \text{CO}_2$ $\Delta H^0 = -171 \text{ kJ/mol}$
- Methane pyrolysis: $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$ $\Delta H^0 = 75 \text{ kJ/mol}$

Suppression of side reactions:

- high reaction temperature (900 °C)

\Rightarrow high temperature stable, long term active, non coking materials required

$\Rightarrow \Rightarrow$ Ni/MgAl₂O₄ catalyst

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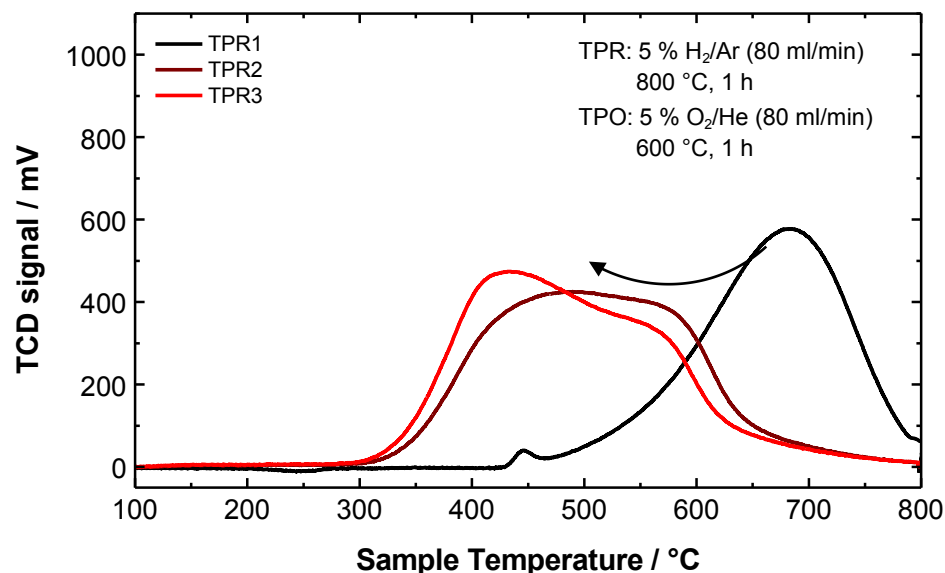
MOTIVATION

- find the carbon source for coking ($\text{CH}_4?$, $\text{CO}_2?$)
- find non coking conditions

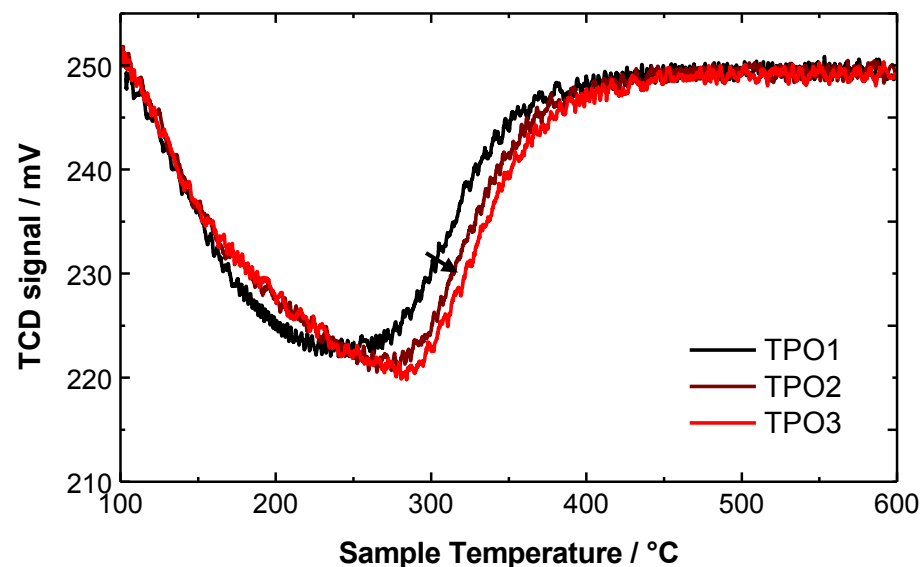
APPROACH

- DRM investigations under various conditions (temperature, feed composition, pressure) with TG-MS using ex-LDH Ni-catalyst
- preparation of a redox stable sample by TP-R-O cycling to overcome sample dynamics

Reduction



Oxidation

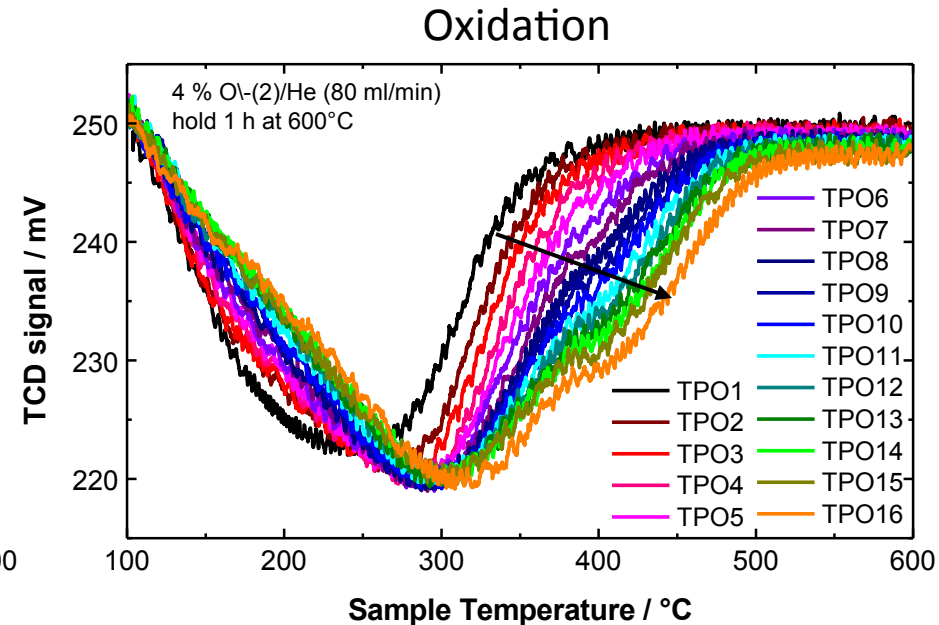
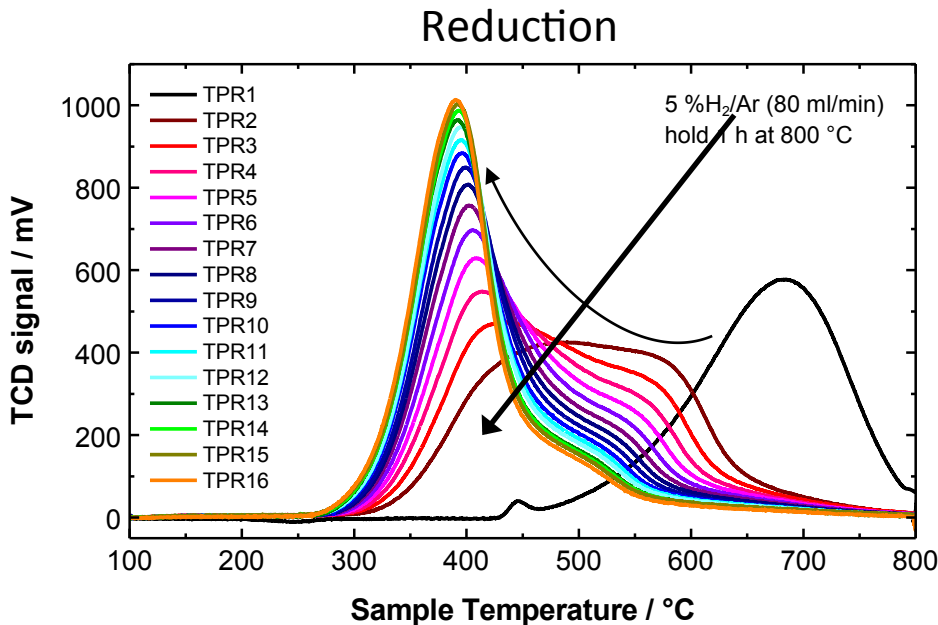


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→ sample is not redox stable after 16 cycles

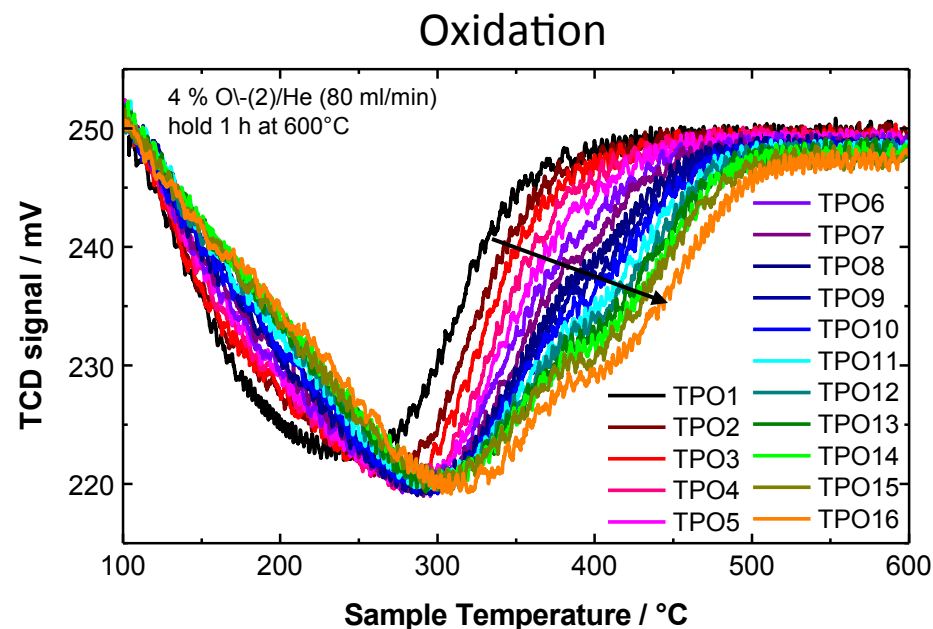
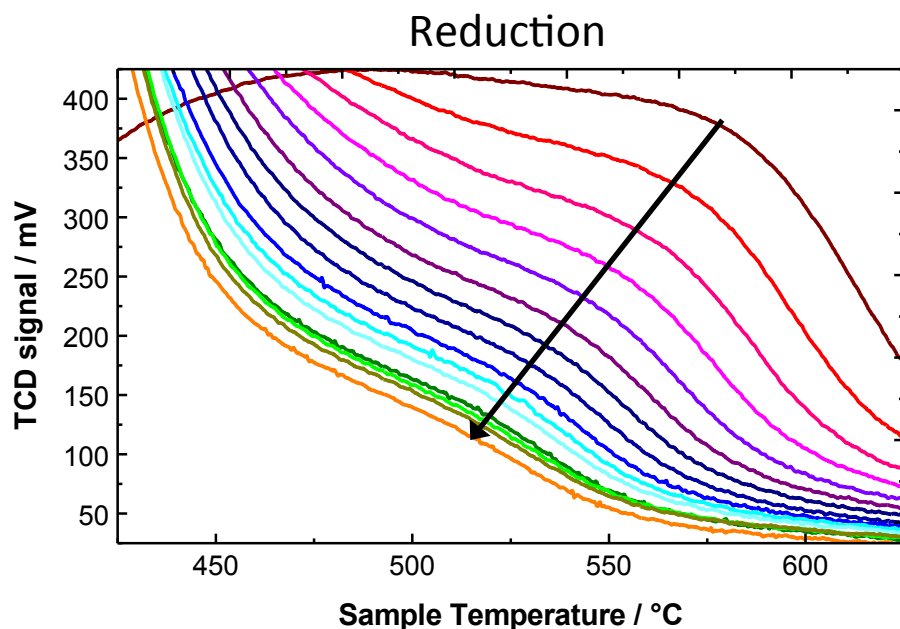
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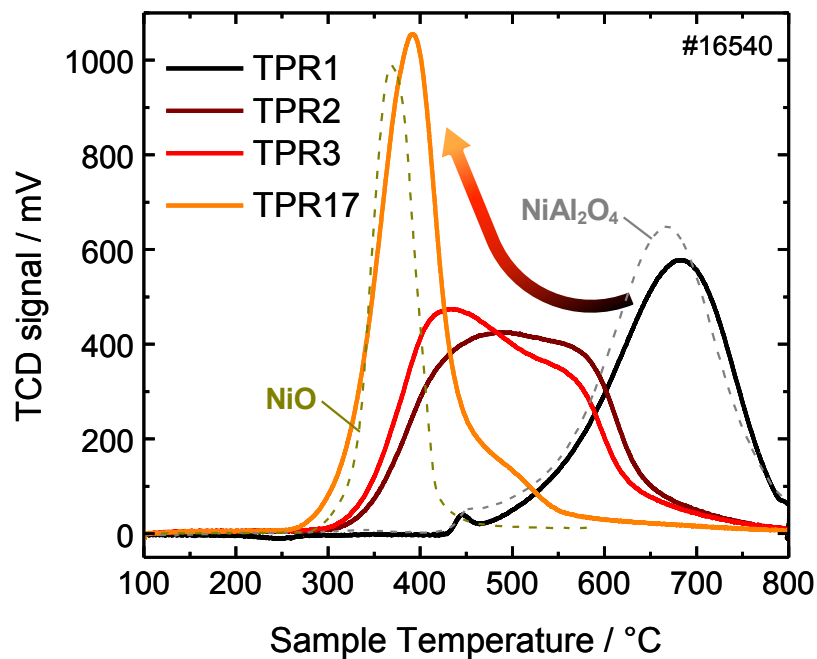
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with Katharina Mette and Stefanie Kühl



Ni surface area

#	cycle	NiSA m ² /g _{cat}	NiSA m ² /g _{Ni}
16715	1	25.0	51.9
16715	2	20.5	42.6
16715	3	14.3	29.6
16737	18	7.0	14.6

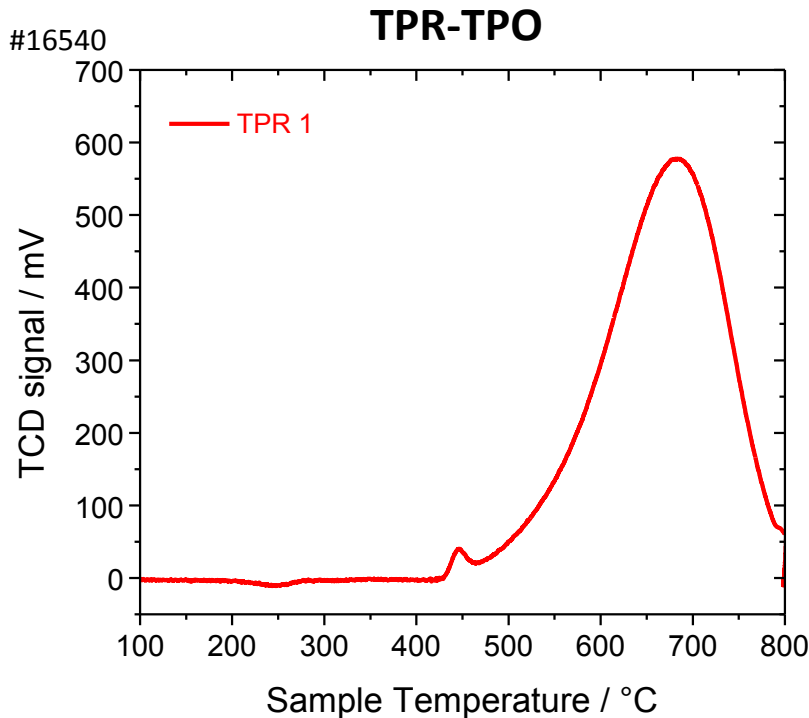
- redox dynamics is influencing Ni dispersion
- Ni surface area is decreasing (cycle 1-18: -72%)
- NiAl₂O₄ → NiO

TPR-DRM-TPO cycles

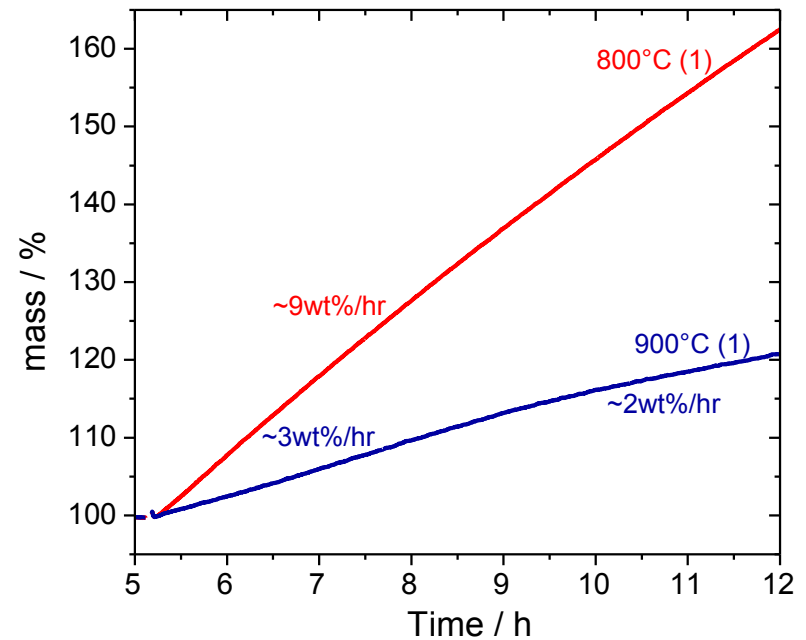
with Katharina Mette and Stefanie Kühl

5.06 %H₂/Ar (80 ml/min), hold 1 h at 800 °C
oxidation at 600°C in 4.99 % O₂/He (80 ml/min), 1h

NiMgAl 50:17:33, Tred=800°C, CO₂/
CH₄=1.25, 120ml/min, 120mg (cat)



TPR-DRM-TPO in Thermobalance



- continuous coke formation at 800 and 900°C in 1st cycle
- redox dynamics is influencing amount of coke deposits
- no coking after 4 cycles at 900°C

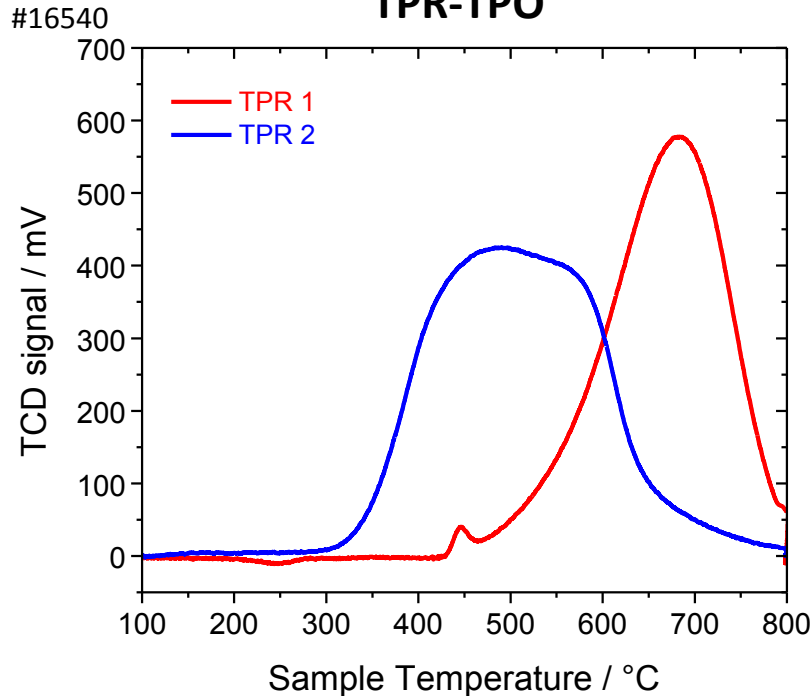
TPR-DRM-TPO cycles

with Katharina Mette and Stefanie Kühl

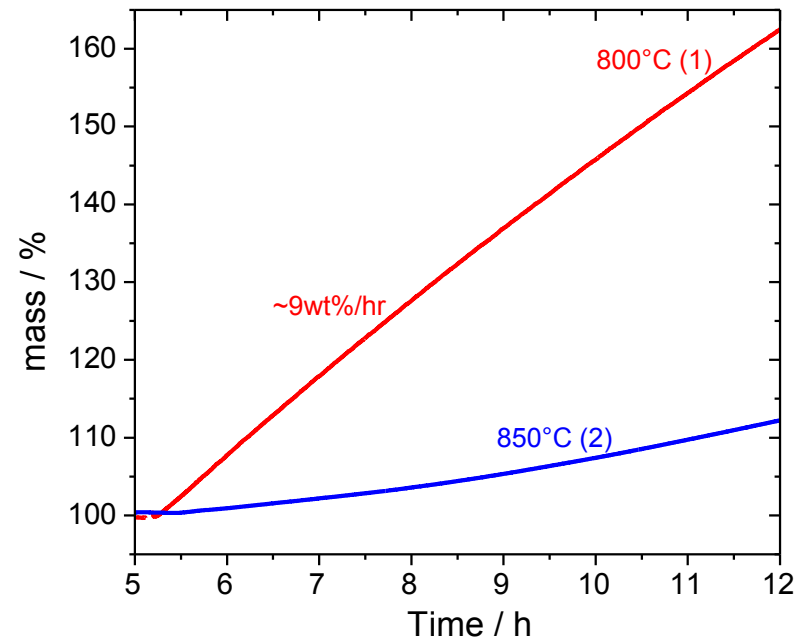
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TPR-TPO



TPR-DRM-TPO in Thermobalance



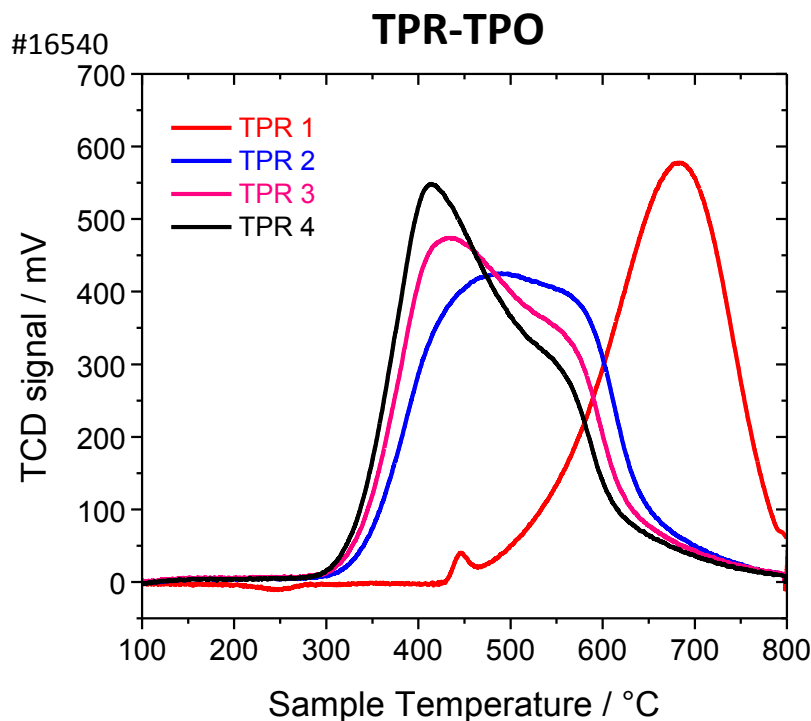
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TPR-DRM-TPO cycles

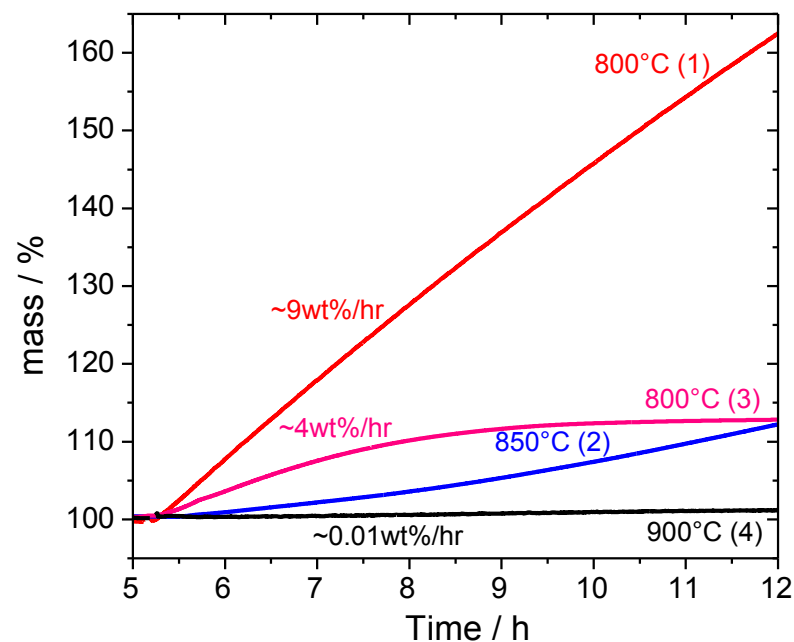
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TPR-DRM-TPO in Thermobalance



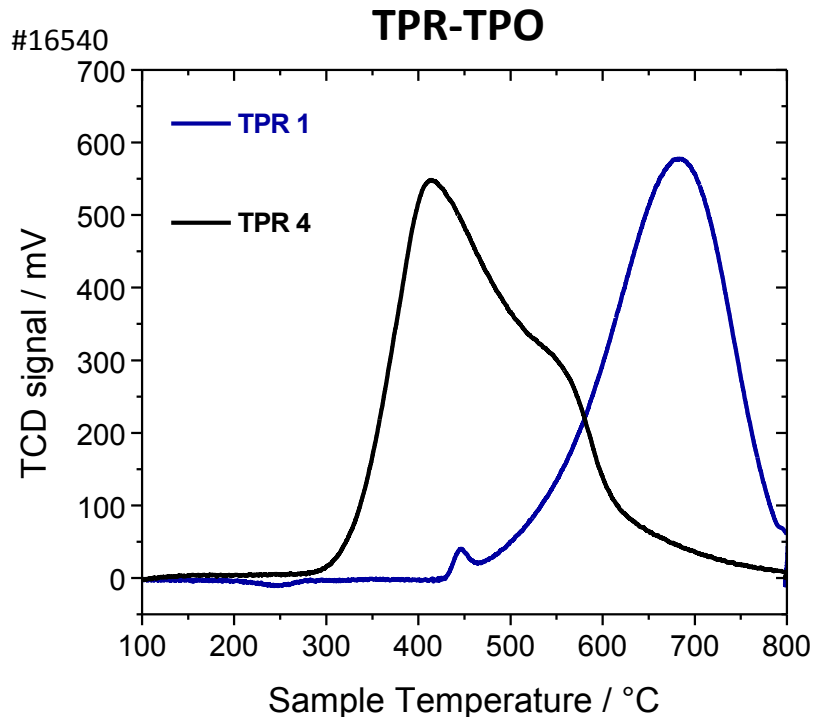
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TPR-DRM-TPO cycles

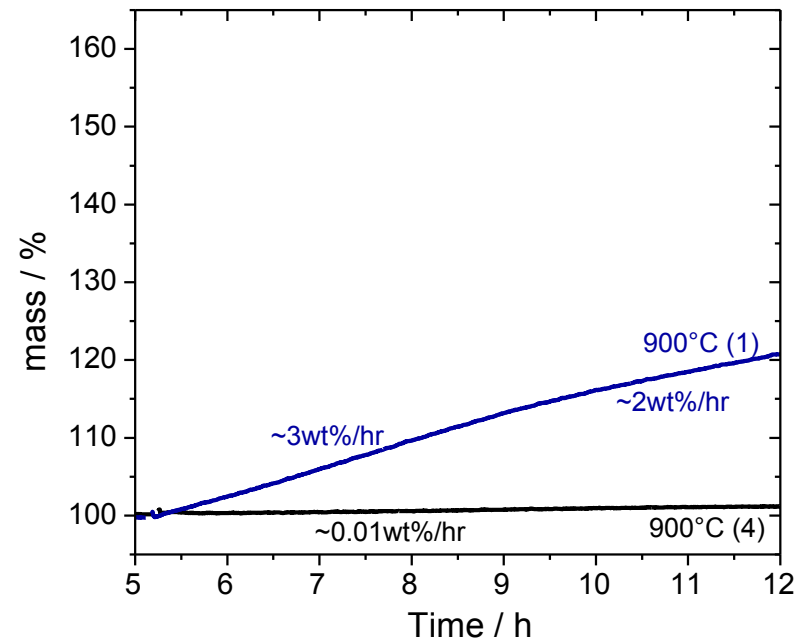
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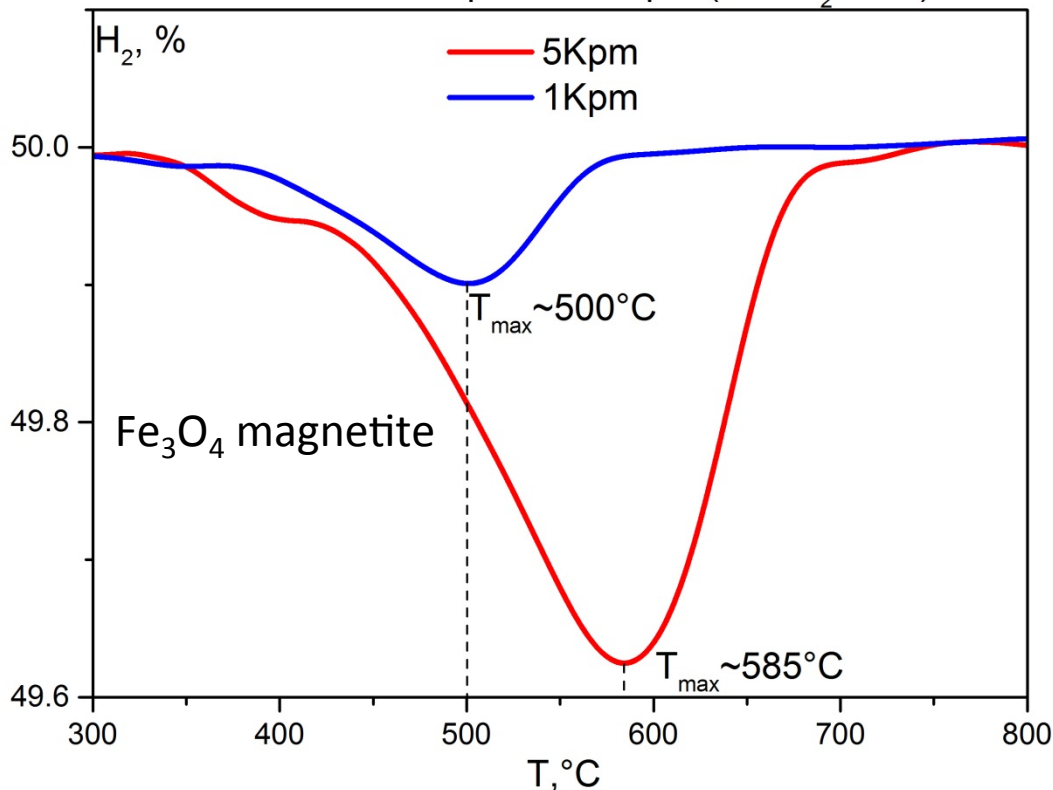
TPR-DRM-TPO in Thermobalance



- continuous coke formation at 800 and 900°C in 1st cycle
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Industrial catalyst for Ammonia synthesis.

TPR Profiles at 5Kpm and 1Kpm (50%H₂ in Ar)

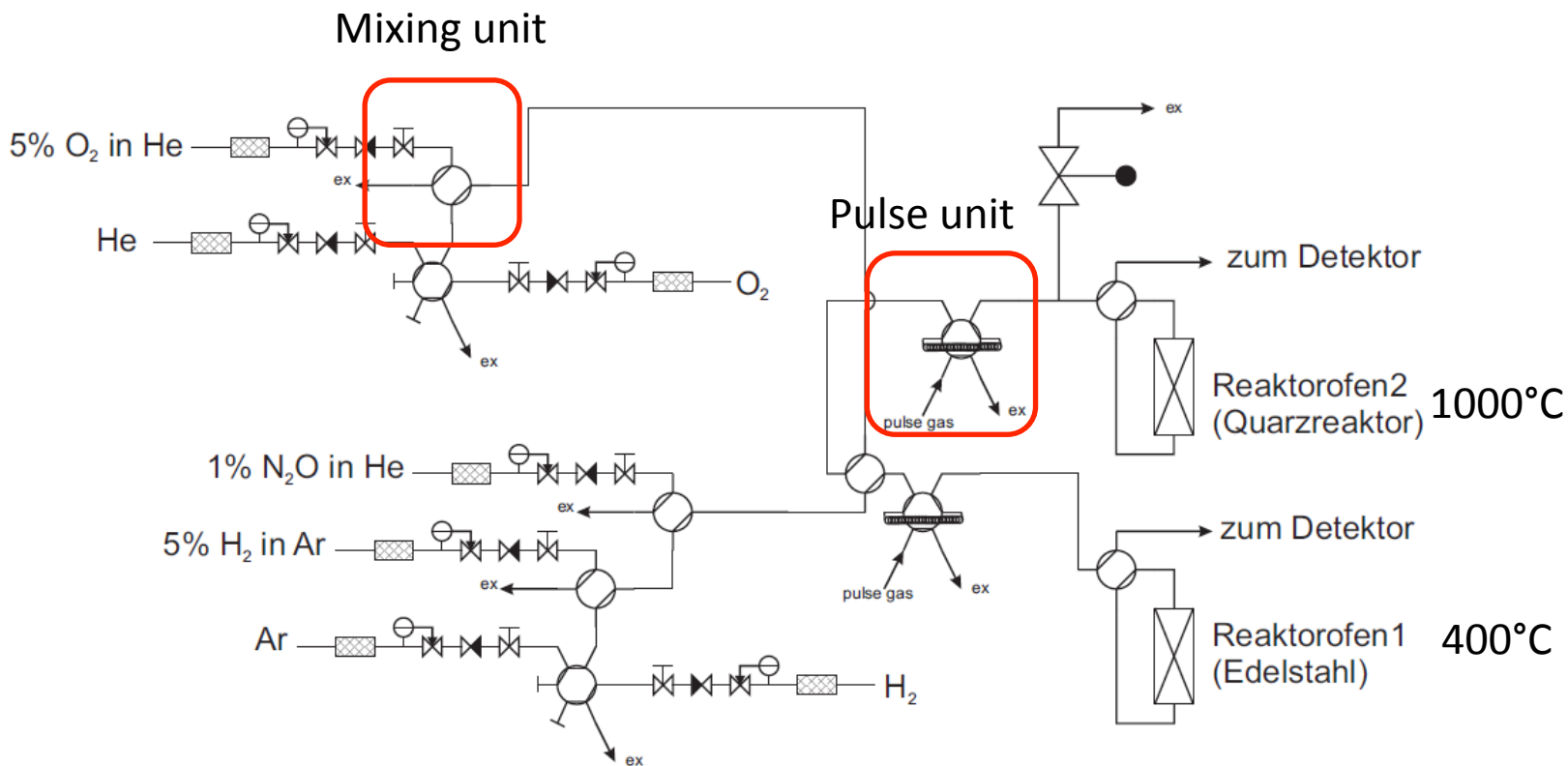


Industrial activation protocol
H₂/N₂=3:1, 20bar
0.2-1 Kpm, 380°C, 24hrs, hold.

Under 1 bar at 380°C we needed
1 week for the complete
reduction of Fe₃O₄ to Fe.

- The amount of the consumed hydrogen doesn't correspond to the complete reduction of Fe₃O₄ to Fe.
- Reduction is hindered due to reduced layer
- High reduction temperatures cause sintering

Monti setup

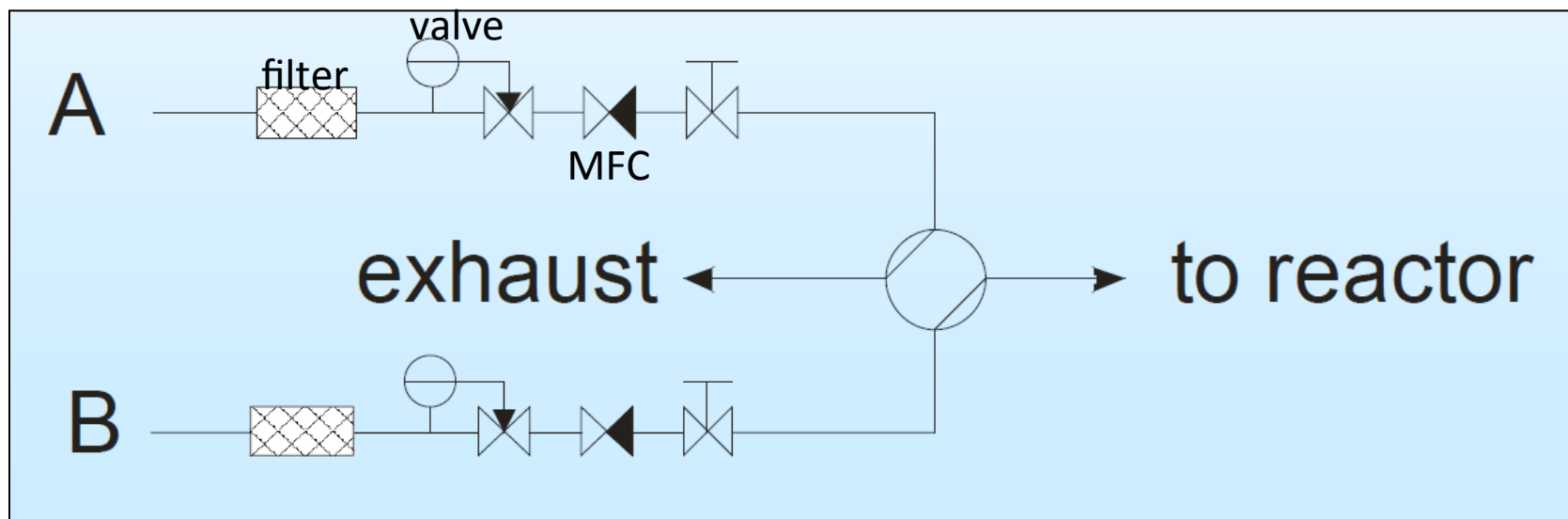


Mixing unit:

- 4 port valve for fast switching
- Purging before switching

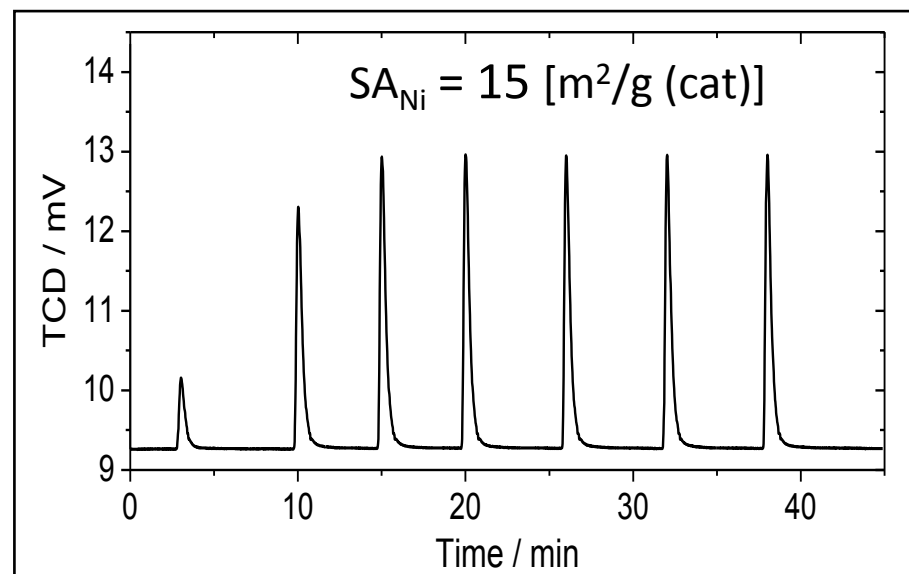
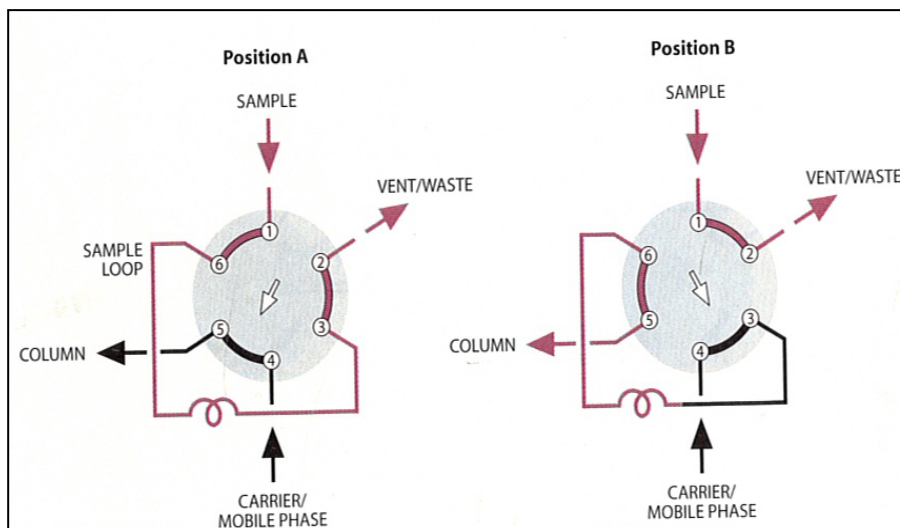


Backpressure



Pulse unit:

- 6 port valve for fast switching
- Fast switching
- Purging before switching

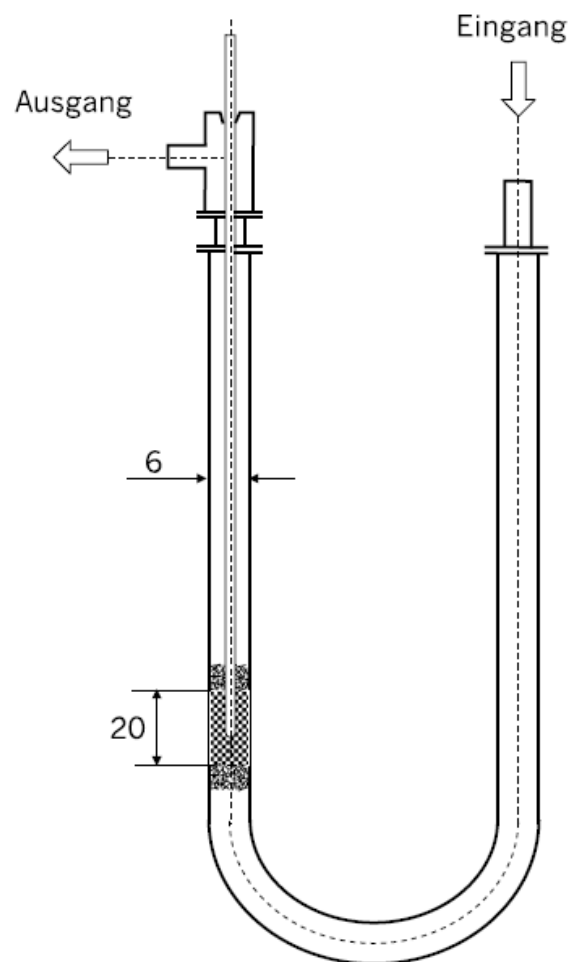


Ni metal surface area (Ni SA) measured by H_2 pulse chemisorption on Monti NiMgAl = 50:17:33

Reactor: geometry

U-tube

- Preheating of feed
- compact



U – tube reactor

Thermocouples

Type	Composition	Temperature range, K		Output voltage (0°C), mV
		T _{min}	T _{max}	
T	Cu /constantan	3	670	20
J	Fe/constantan	70	870	34
E	chromel /constantan	-	970	45
K	chromel /alumel	220	1270	41
S	Pt/PtRh (10)	270	1570	13
R	Pt/PtRh (13)	220	1570	12
C	W/WRe(26)	-	2670	39
N	Nicrosil/Nisil	-	1200	39

Constantan - 58% Cu, 42% Ni

Chromel – 89% Ni, 10% Cr, 1%Fe

Alumel – 94% Ni, 2% Al, 1,5% Si, 2,5 % Mn

Nicrosil/Nisil – Ni, Cr, Silicon/Ni, Silicon



Monti setup



Analytics

Sensor types

TCD – H₂

IR - N₂O, CO₂, CO

Paramagnetic – O₂

QMS - m/z 100



Questions



MAX-PLANCK-GESellschaft



 **APPLAUSE**

