Conductivity of supported VO_x catalysts:

Impedance spectroscopy, oxygen vacancy formation enthalpy and correlation to catalytic properties

B7 M. Harth
B6 C. Carrero (Catalytic Testing)
C11 R. Mitdank (Oxidation State of V_xO_y)

SFB 4th period:

Poly B,

Redox state
XRD, SEM, TEM (B2),
RBS (C11)
ASAXS (HZB)

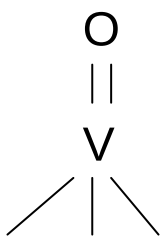
Volume Properties
thermal (XRD)
mechanical
electrical (impedance, DC,
RBS, UV-Vis, XRD, microscopy)

C11
Winter
Mitdank

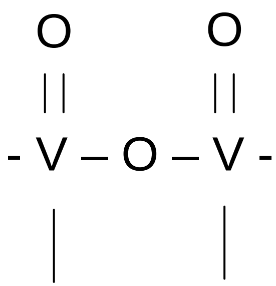
1. **Introduction**
2. **Impedance spectroscopy**
3. **Results**
   1. Determination of ΔH_f
   2. Oxygen vacancies and catalytic properties
4. **Conclusion and Outlook**

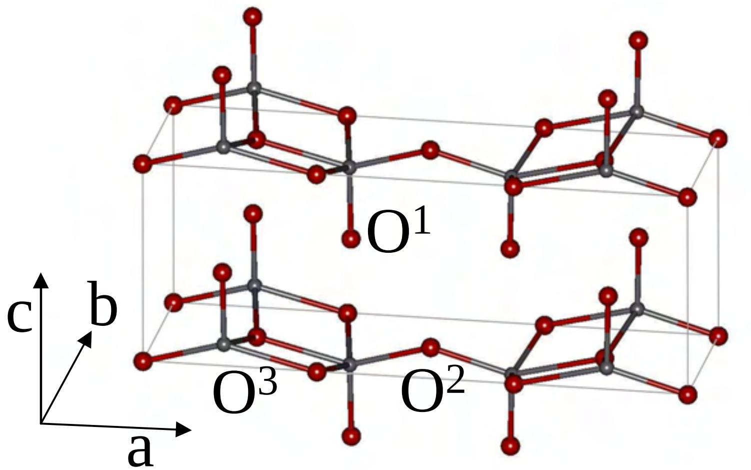
Crystals

Single Sites



Polymers





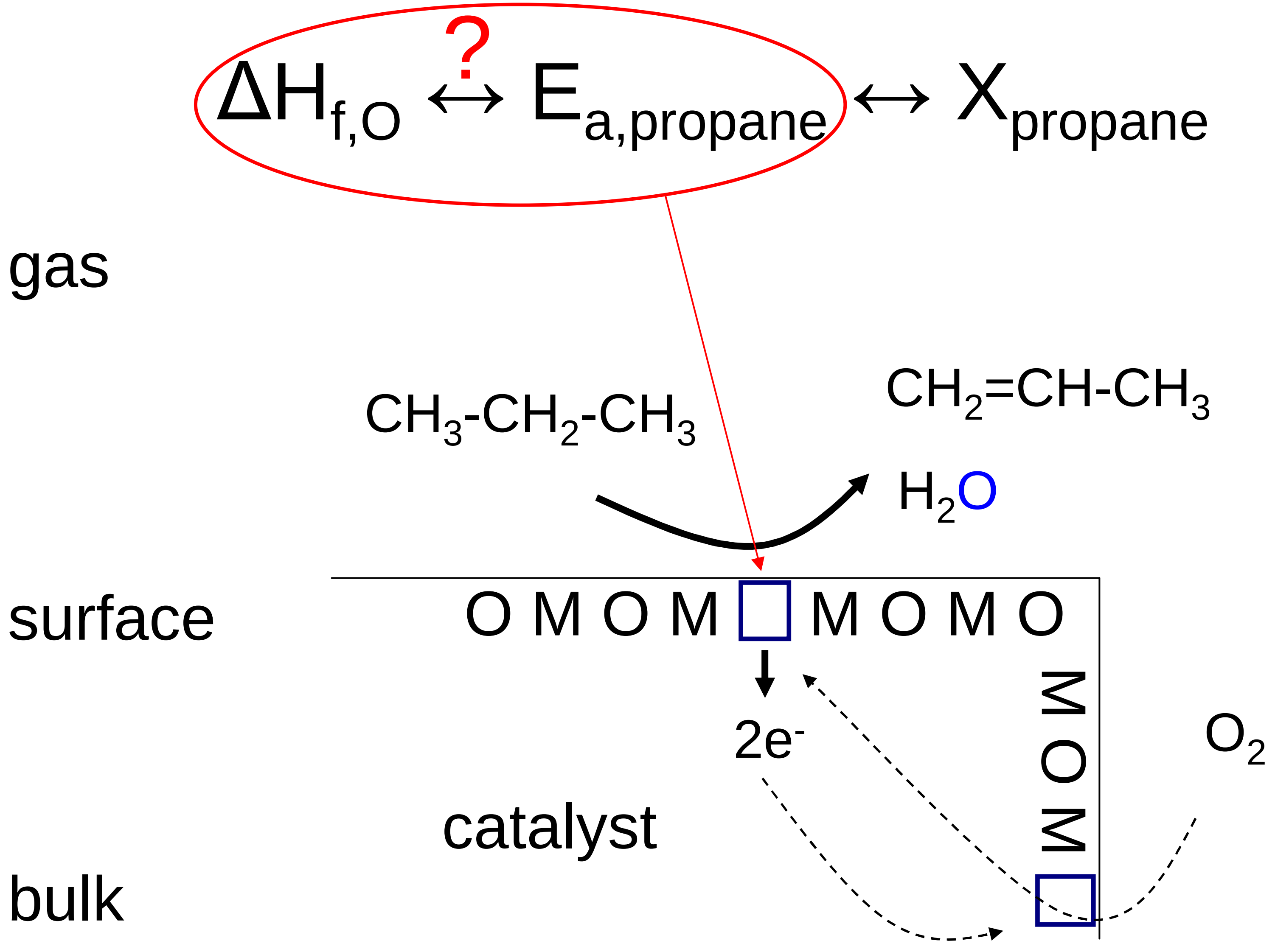
Percolation needed for Conductivity via VxOy ?

Support
Assumed
non conducting

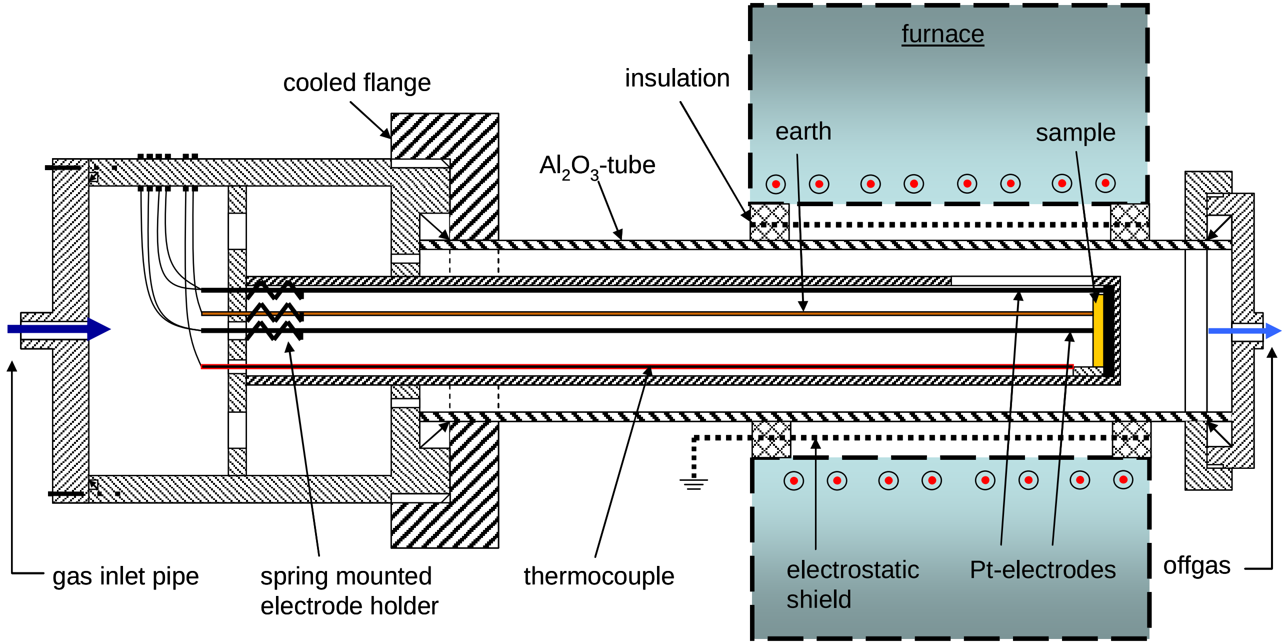
Poly B
B2, amorphous on SBA

B6 amorphous,
Dinse
TiO2, SiO2, alpha, kappa Al2O3, CeO2, ZrO2

B7 , crystalline

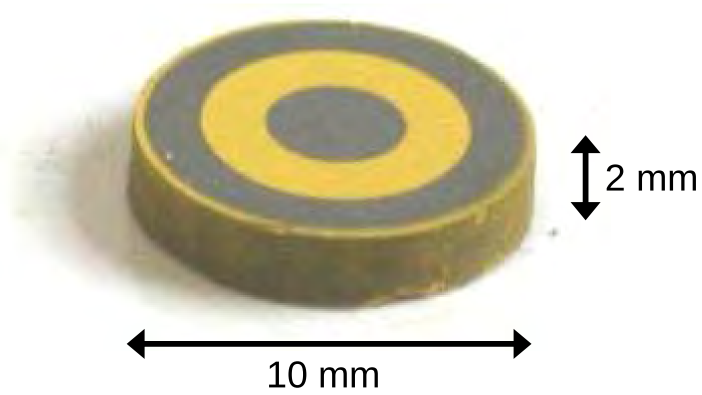

ΔH_f,O ?↔ E_a,propane ↔ X_propane
gas
CH3-CH2-CH3
CH2=CH-CH3
H2O
surface
O M O M M O M O
M O M
2e-
O2
catalyst
bulk

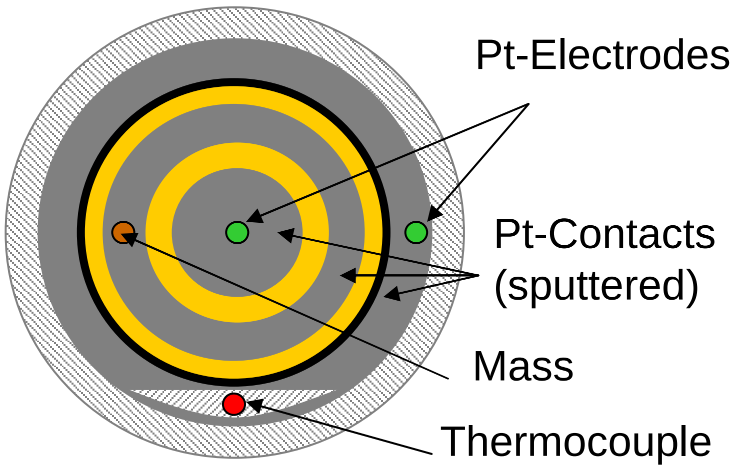
2. Impedance Spectroscopy - Setup



Frequency Generator and Analyzer:

Frequency range
10 µHz to 3 MHz
AC-amplitude range
1 mV to 1 V
Impedance range
1 mOhm to 1G Ohm (± 2%)





2. Impedance Spectroscopy - Method

DC experiments exhibit often polarization effects

AC methods give possibility to determine influences on overall conductivity

Apply an electrical stimulus and observe the response (current or voltage)

Different mechanisms show different time relaxation times τ and can therefore be resolved

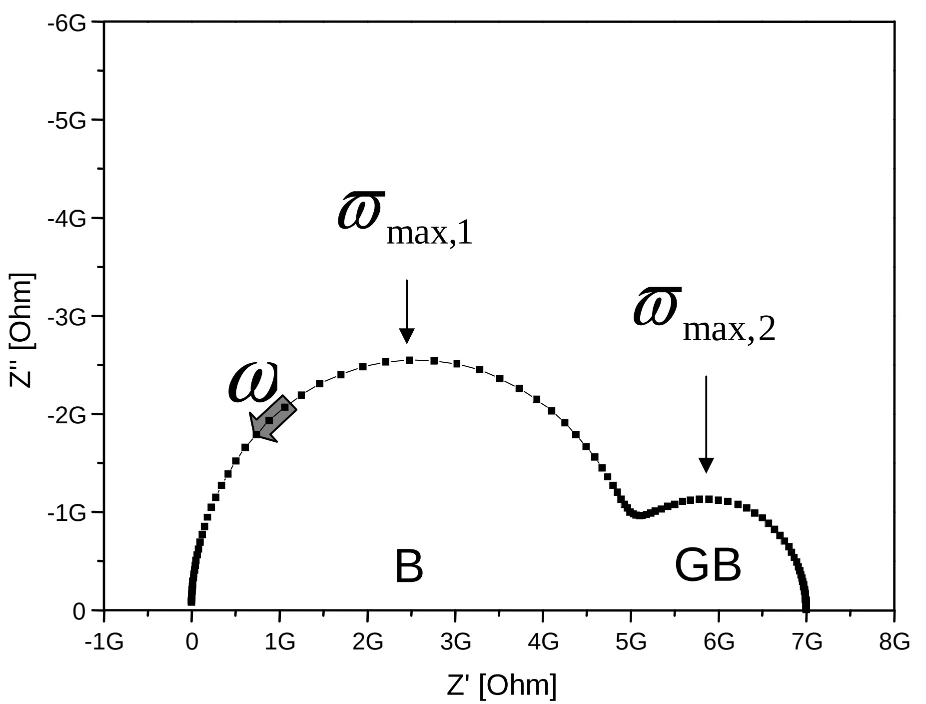
- **polarization**
- **electrode reaction**
- **different charge carriers**
- **bulk / grain boundary mechanism**

E. Barsoukov, J.R. Macdonald, “Impedance Spectroscopy Theory, Experiment, and Applications”, John Wiley & Sons, Hoboken, New Jersey, 2005

Different regions of sample characterized by R and C often placed in parallel
characteristic relaxation time of each RC element given by product of R and C

$$\tau = RC$$

$$\omega_{max} RC = 1$$



Frequency scan resolves the different relaxation times: Distribution of relaxation time. B: bluk, GB grain boundary

John T. S. Irvine et al., Advanced Materials 2 (1990) 132

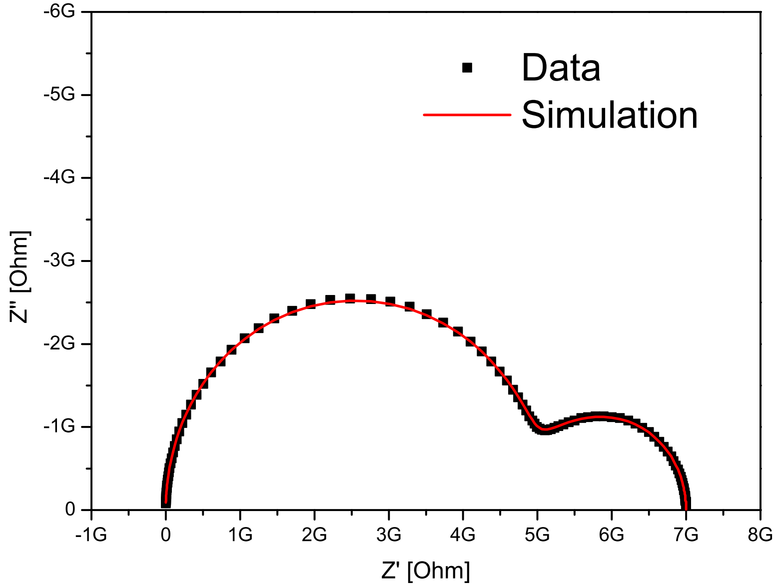
2. Impedance Spectroscopy - Method

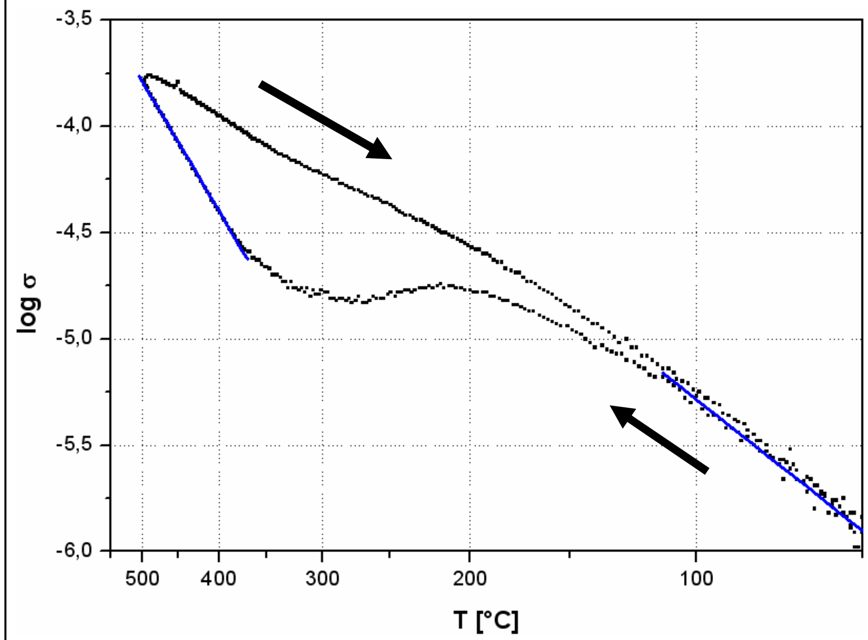
data + model ⇨ Results for R_1, C_1, R_2, C_2

CNRLS fit

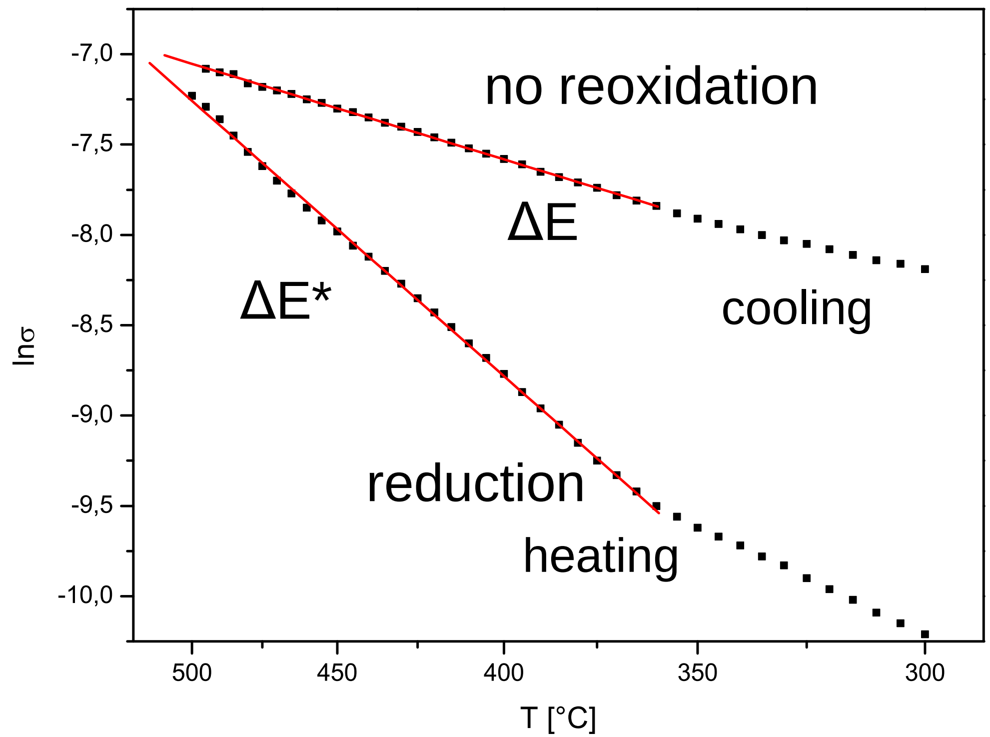
$(R_1C_1)_p$-$(R_2C_2)_p$

+





3. Results - Determination of ΔH_f



$$2V_V^x + O_O^x \xrightarrow{\text{reduction}} 2V_V' + \cup_O^{\bullet\bullet} + 1/2\,O_2$$

$$[V_V'] = (2K)^{1/3} \cdot P_{O_2}^{-1/6}$$

$$\sigma = K_2 \cdot \exp\left(-\left(\Delta H_f^0/3kT + \Delta E_m/kT\right)\right) \cdot P_{O_2}^{-1/6}$$

$$\Delta E^* = \Delta H_f^0/3 + \Delta E$$

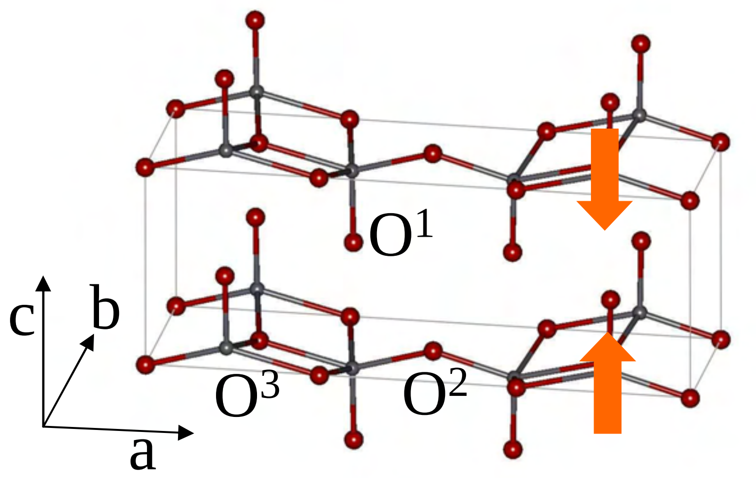
$$\Delta H_f^0 = 1.23 \pm 0.03\,\text{eV} = 119 \pm 3\,\text{kJmol}^{-1}$$

Reduction: V_2O_5 in oxygen

HT XRD

UV-vis

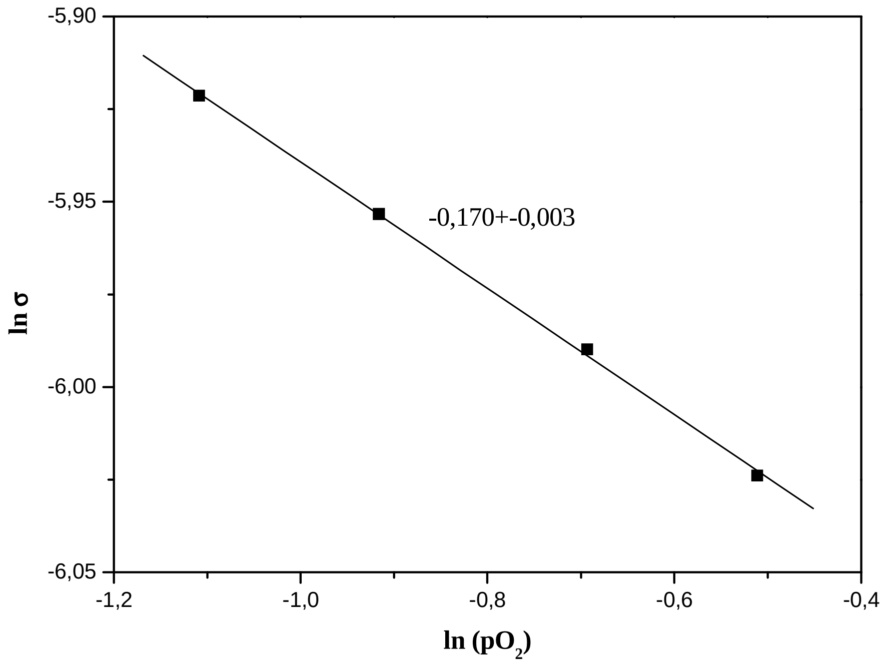
RBS



M. Harth et al., IJMR (2010) submitted

T. Allersma et al., J. Chem. Phys. 46 (1967) 154-160

M. V. Ganduglia-Pirovano and J. Sauer, Phys. Rev. B 70 (2004) 045422



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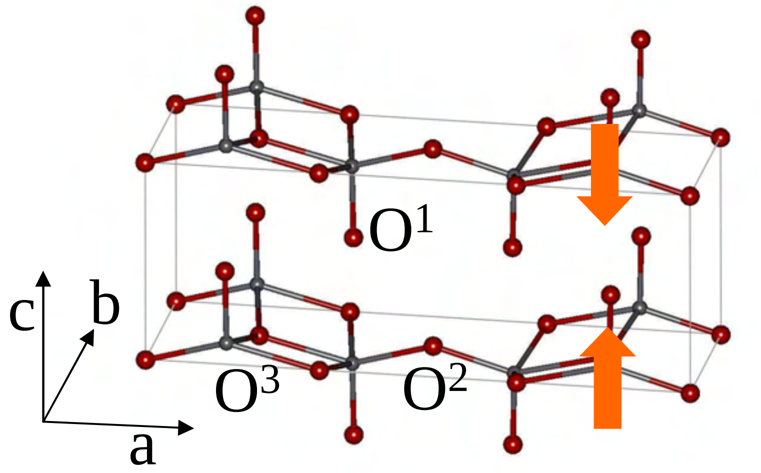

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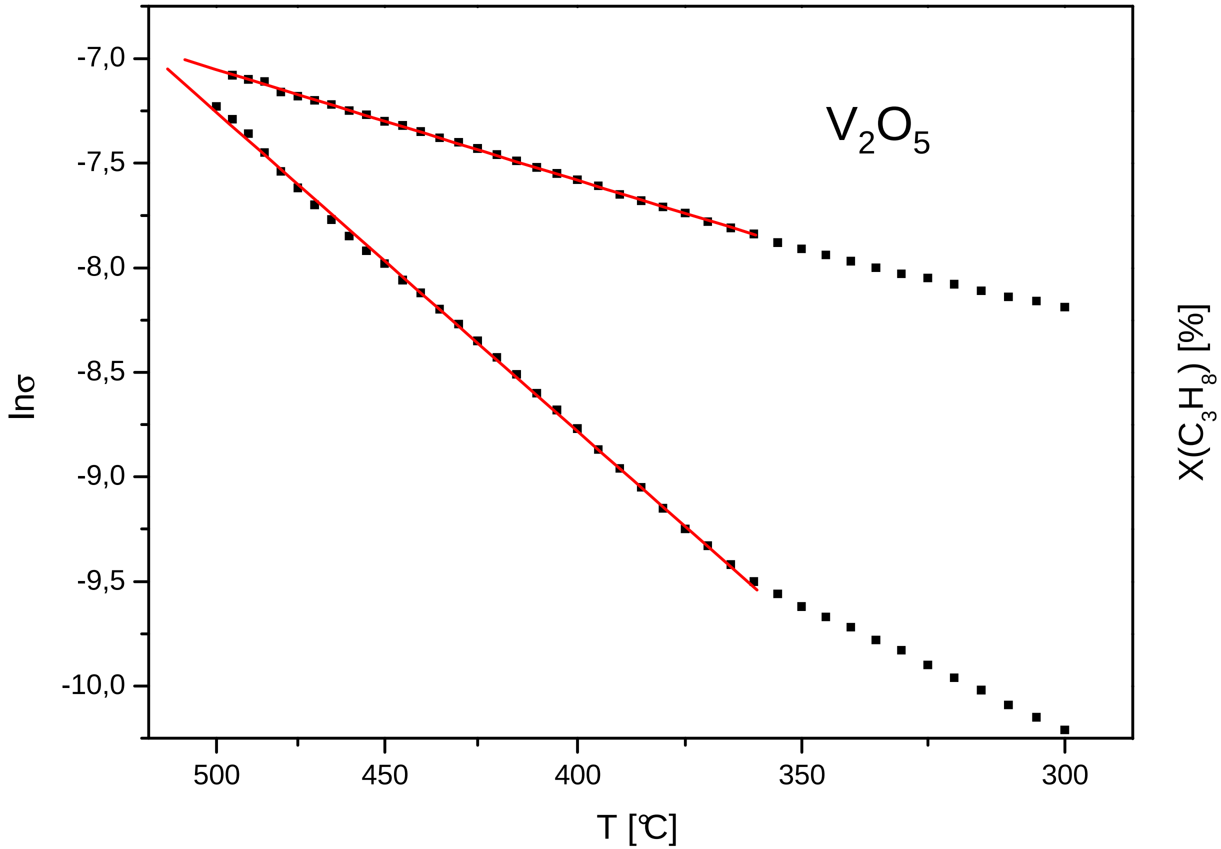
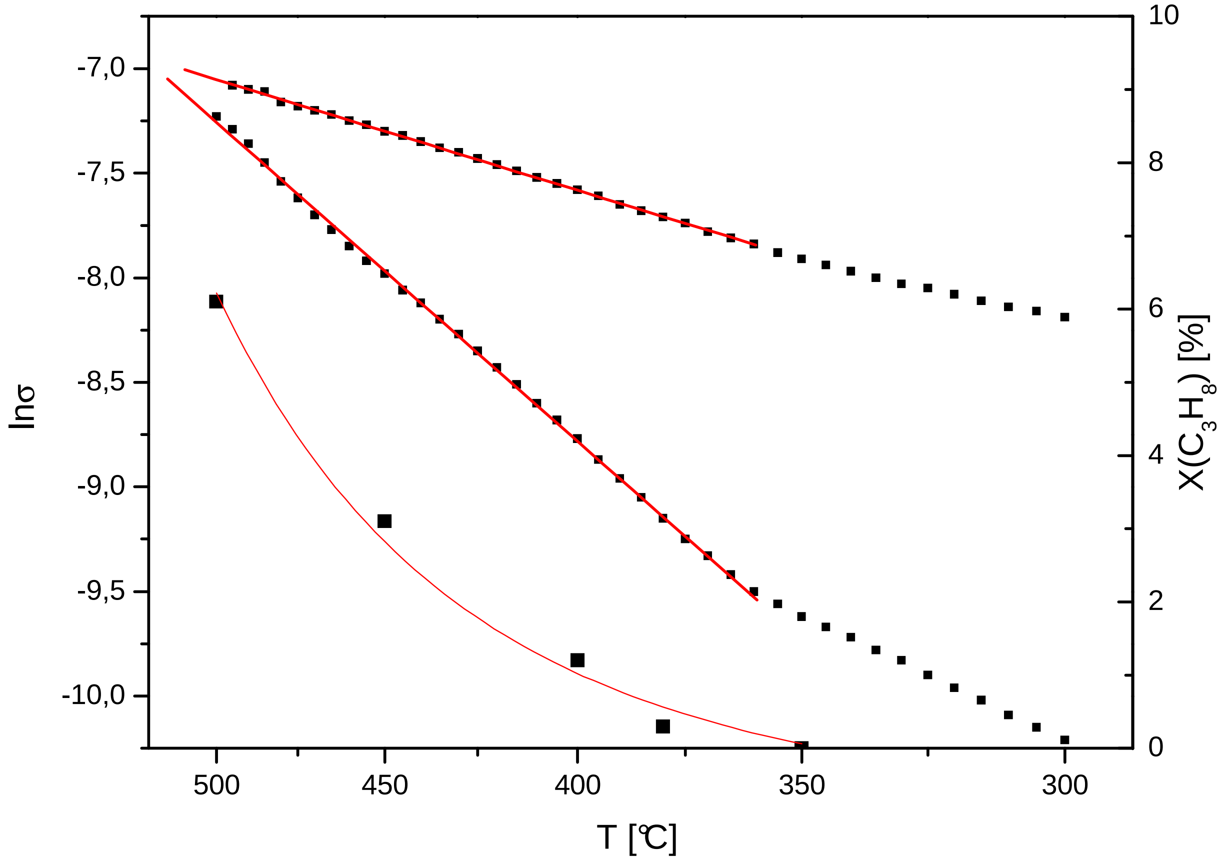
3. Supported Catalysts: Conductivity and Propane Conversion



	T_s	Volume diffusion ~2/3 T_s (K)	Surface diffusion ~½ T_s (K)
V_2O_5	690 ℃	369 ℃	208 ℃

3. Supported Catalysts: Conductivity and Propane Conversion



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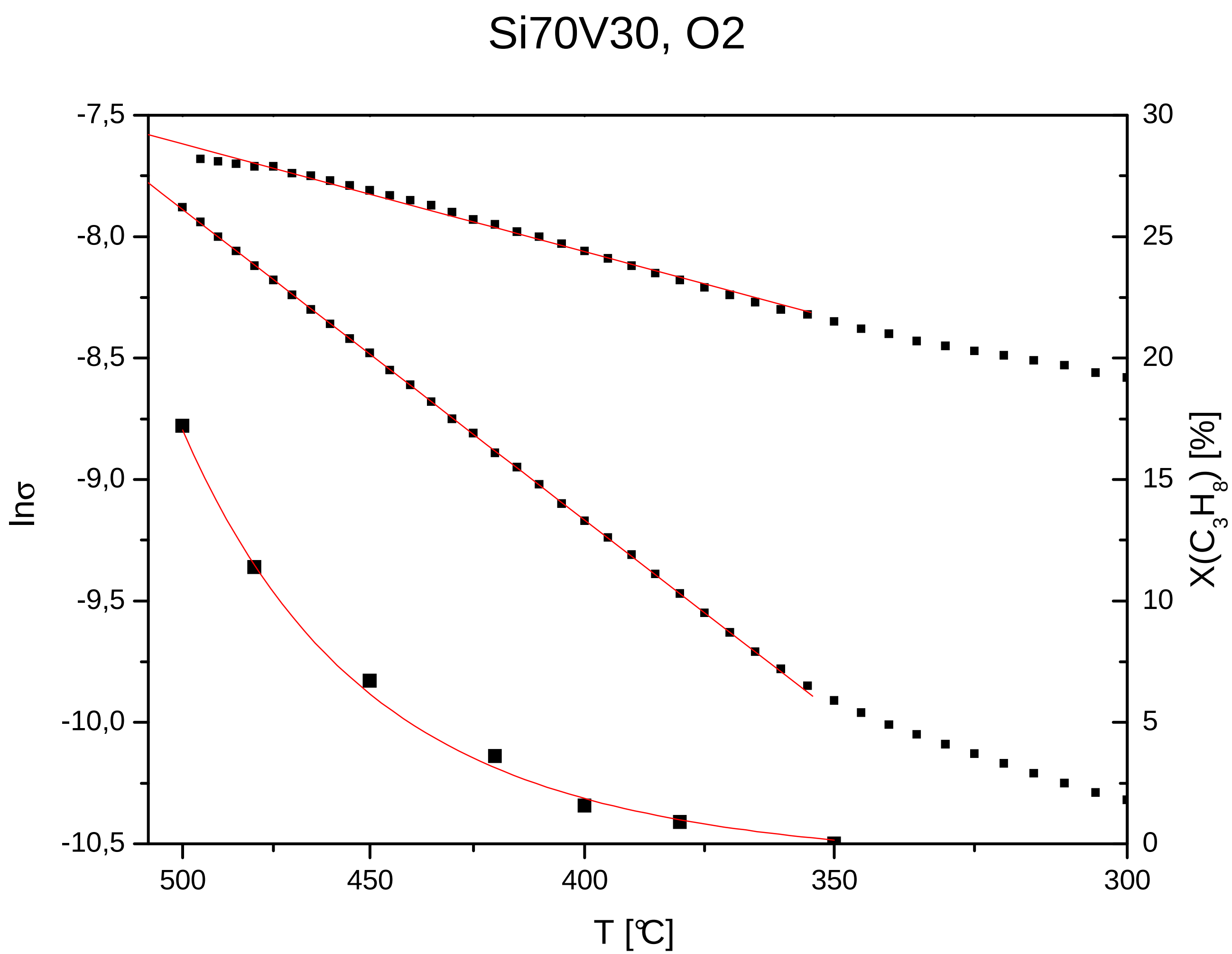

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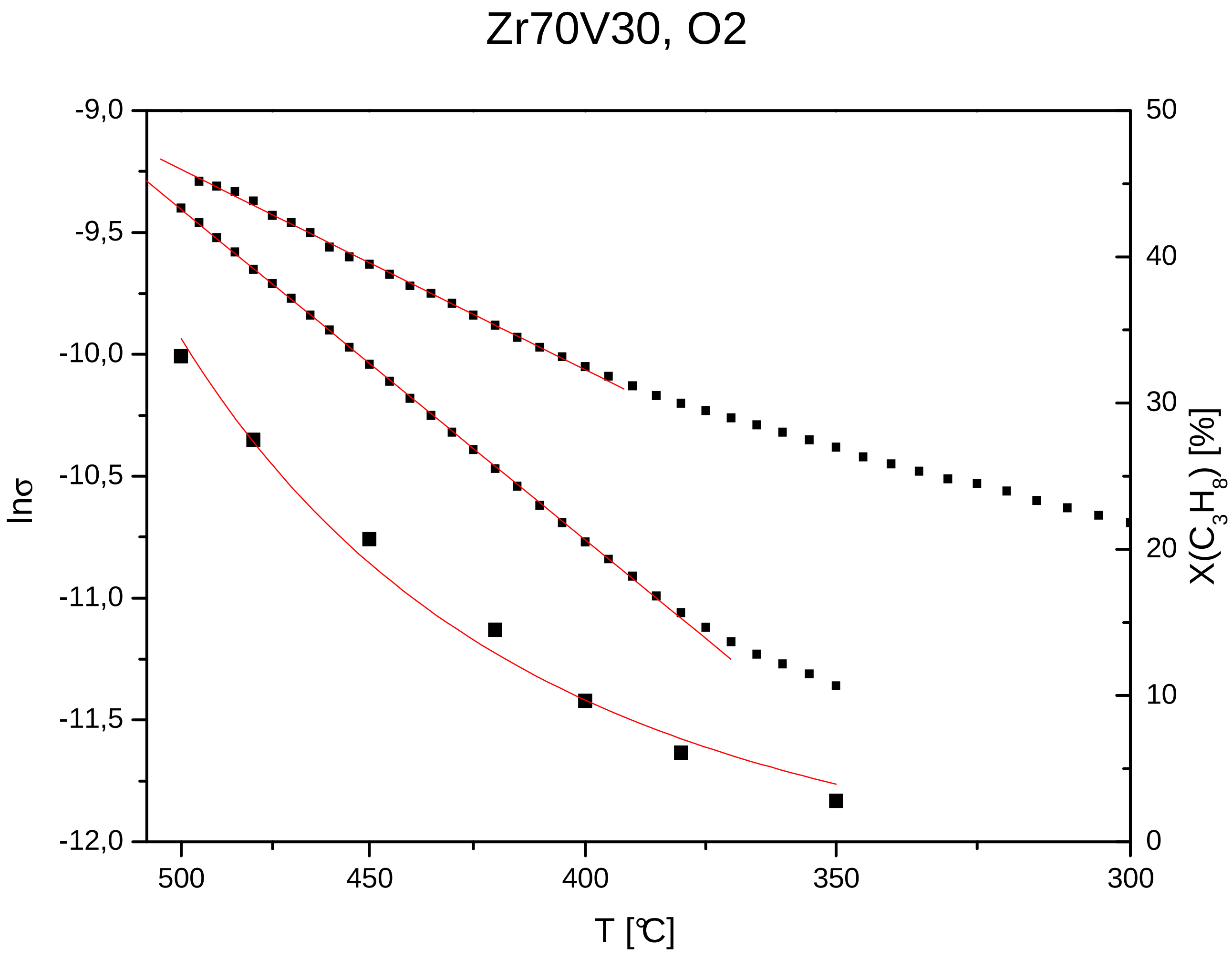
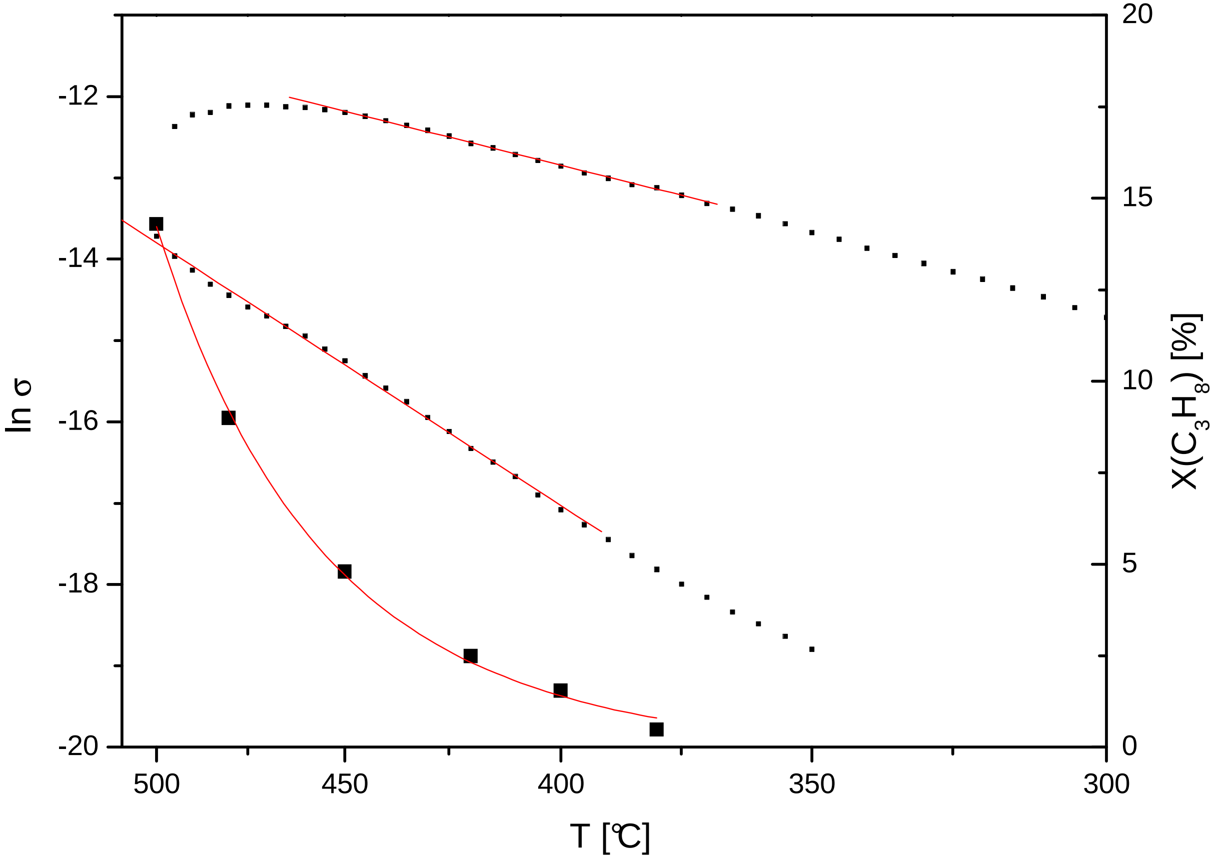
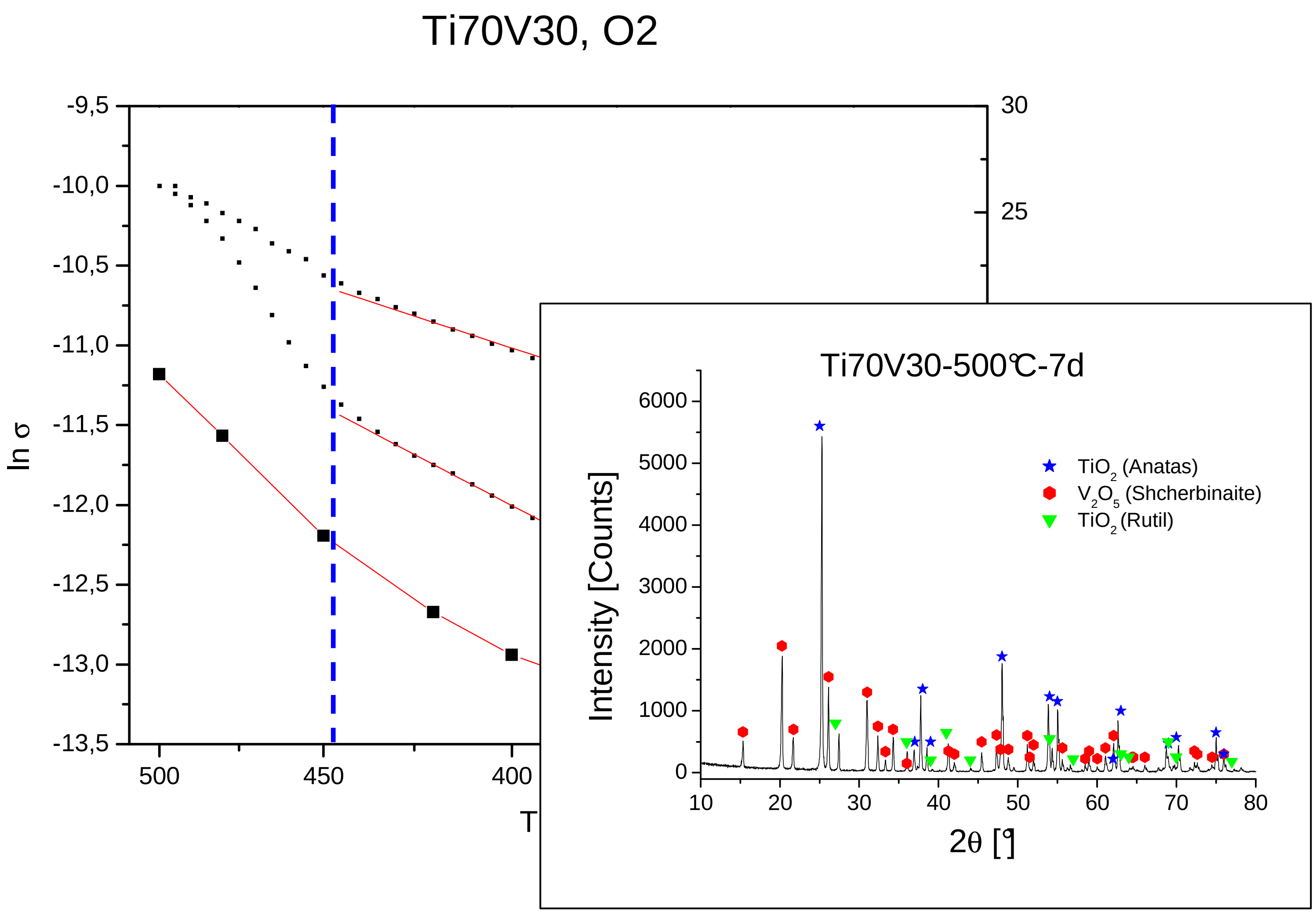
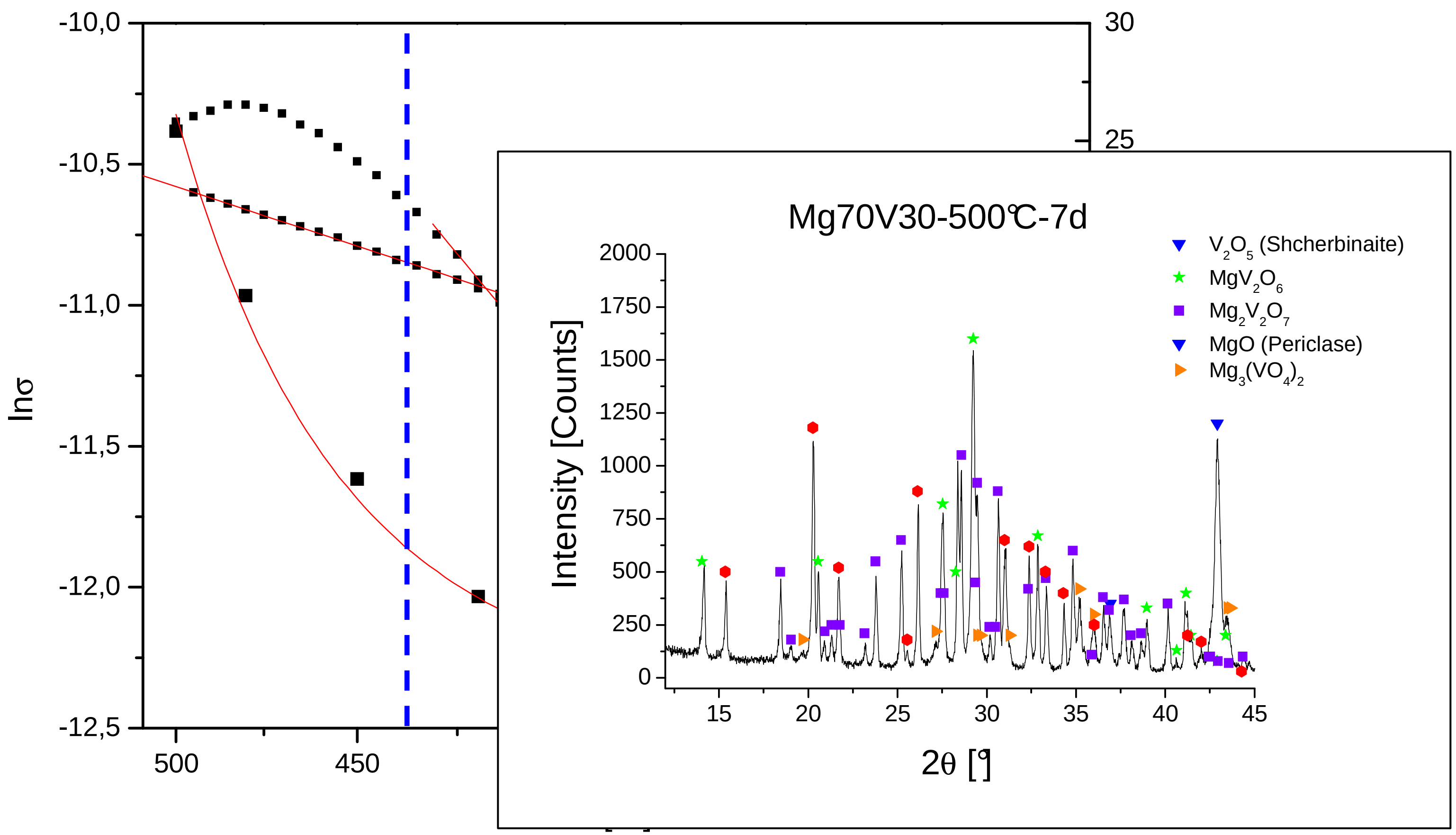


Al70V30, O2

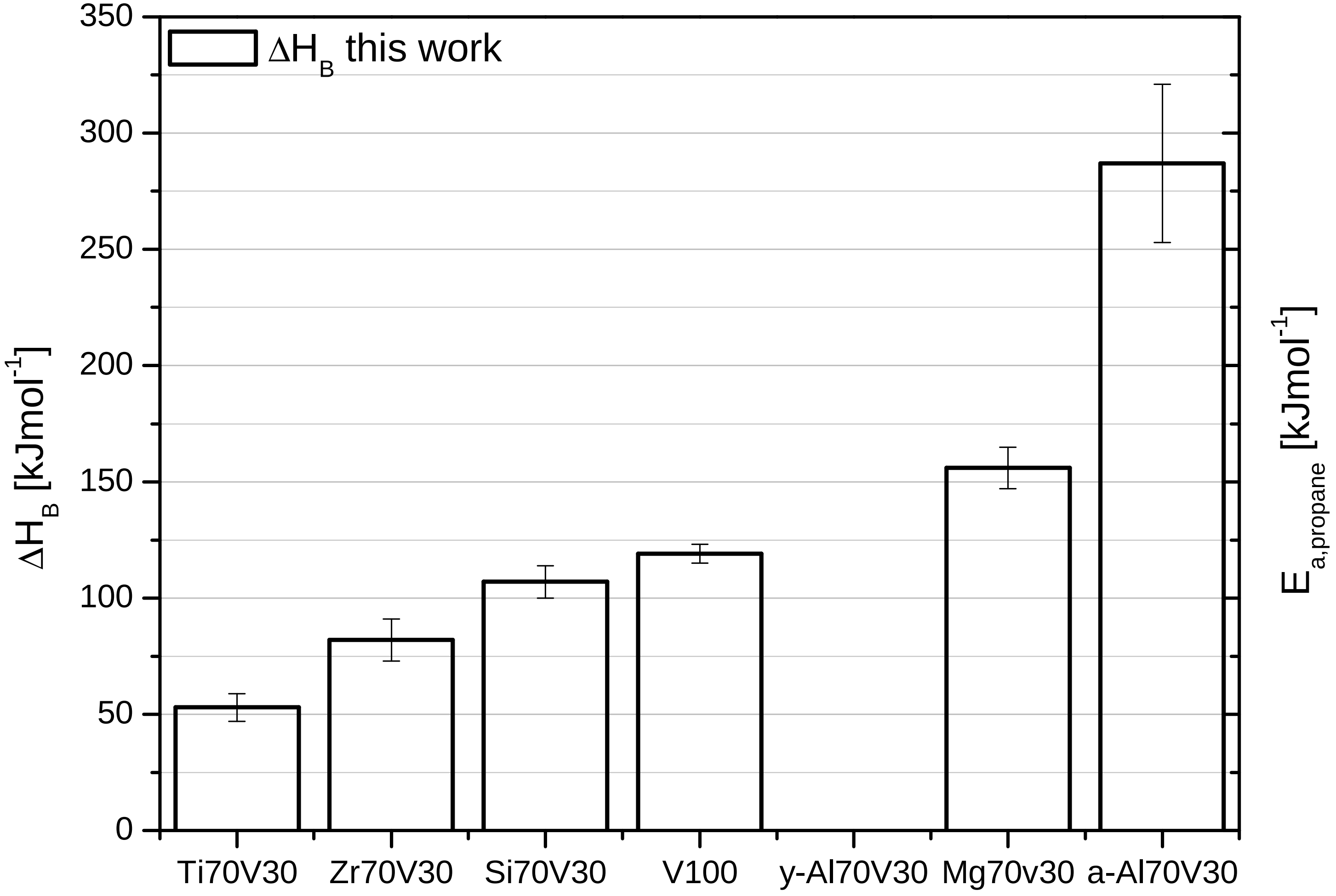




Ti70V30 different activation energy at high temperature:
Phase transitions to rutile

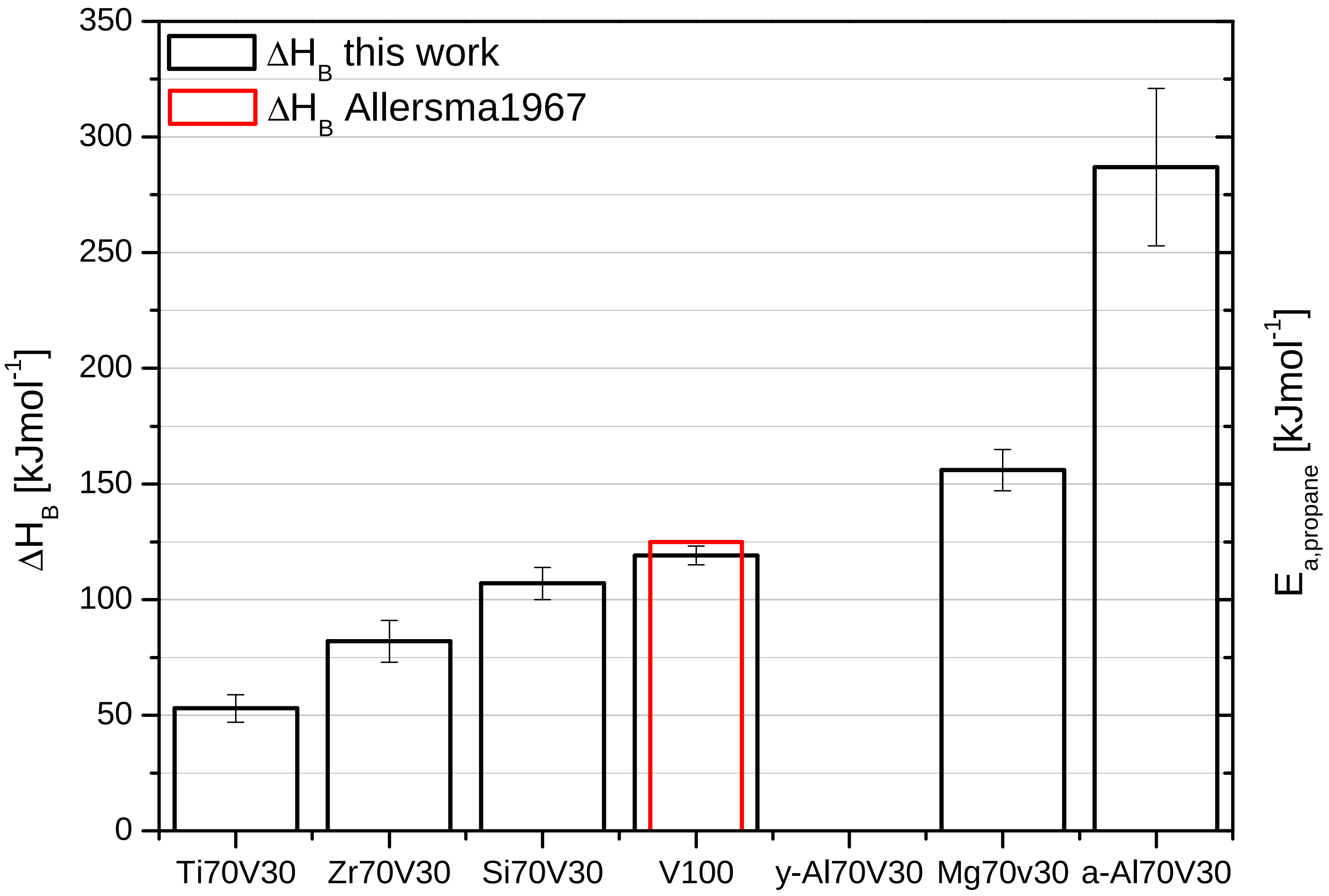


Mg70V30 starts to transform into different spinel phases

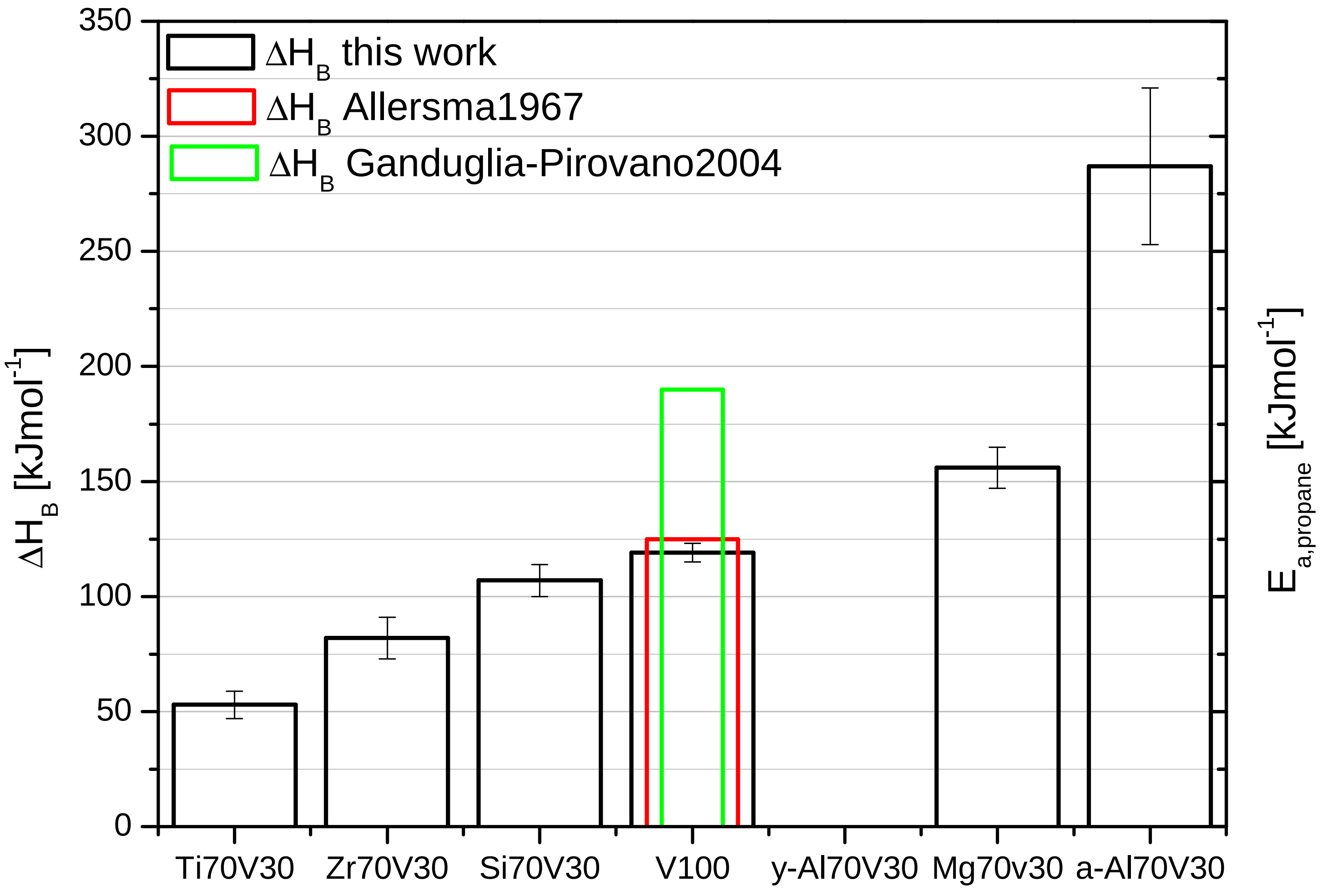


ΔH_B this work
ΔH_B [kJmol^-1]
E_a,propane [kJmol^-1]
0
50
100
150
200
250
300
350
Ti70V30
Zr70V30
Si70V30
V100
y-Al70V30
Mg70v30
a-Al70V30

3. Supported Catalysts: Correlation to Catalytic Properties



T. Allersma et al., J. Chem. Phys. 46 (1967) 154



M. V. Ganduglia-Pirovano and J. Sauer, Phys. Rev. B 70 (2004) 045422

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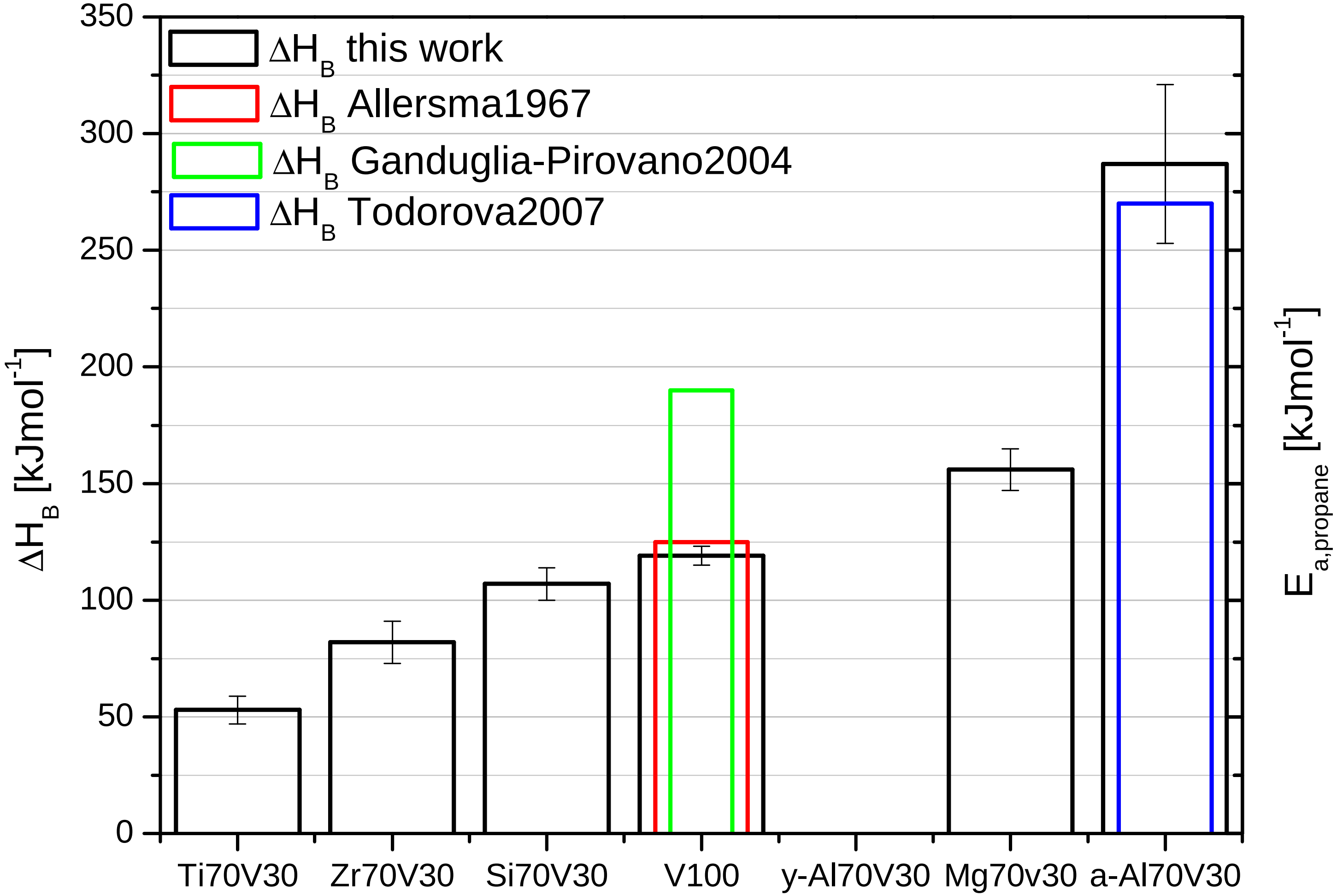
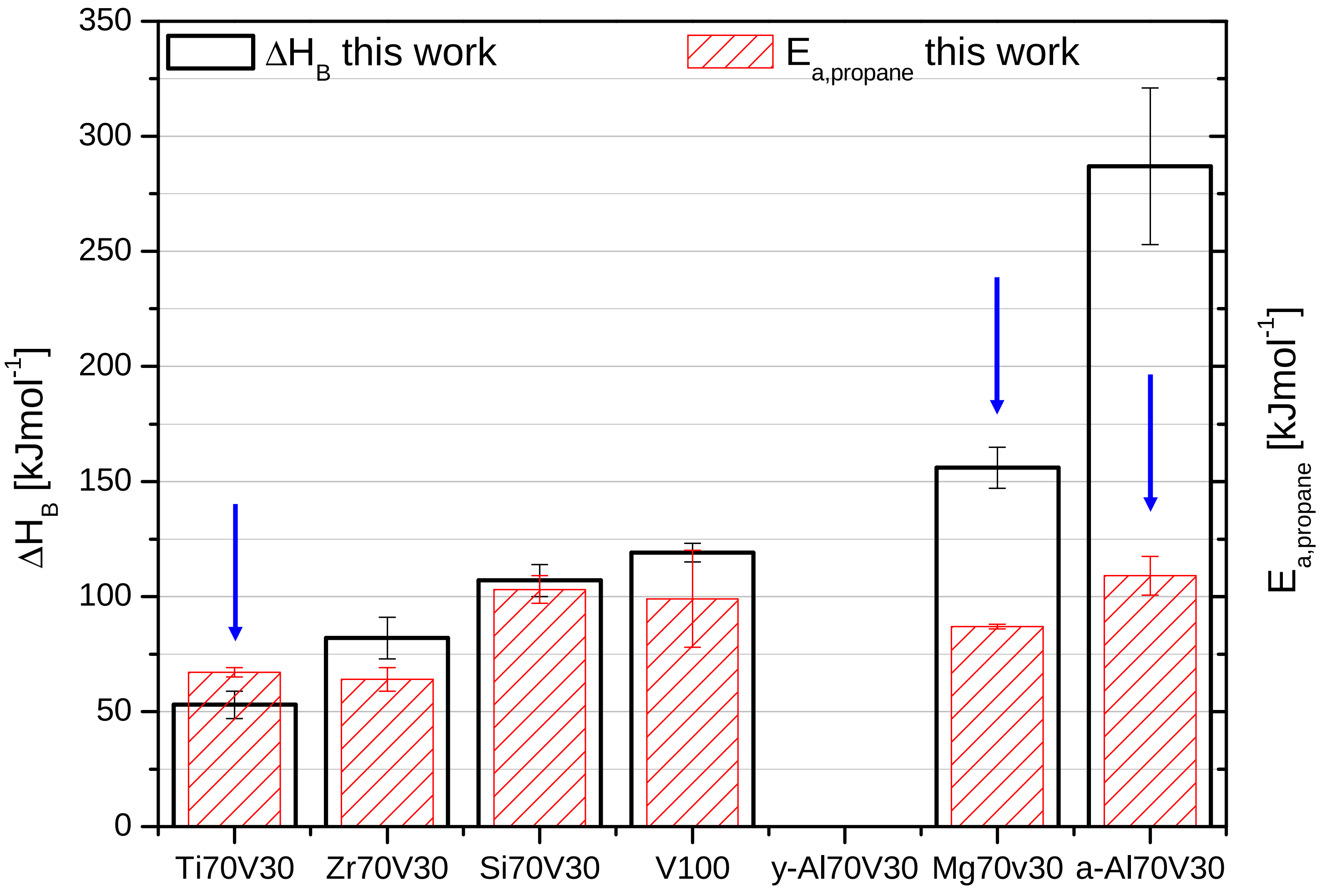


T. K. Todorova, J. Phys. Chem. C 111 (2007) 5141



Catalytic testing in cooperation with B6

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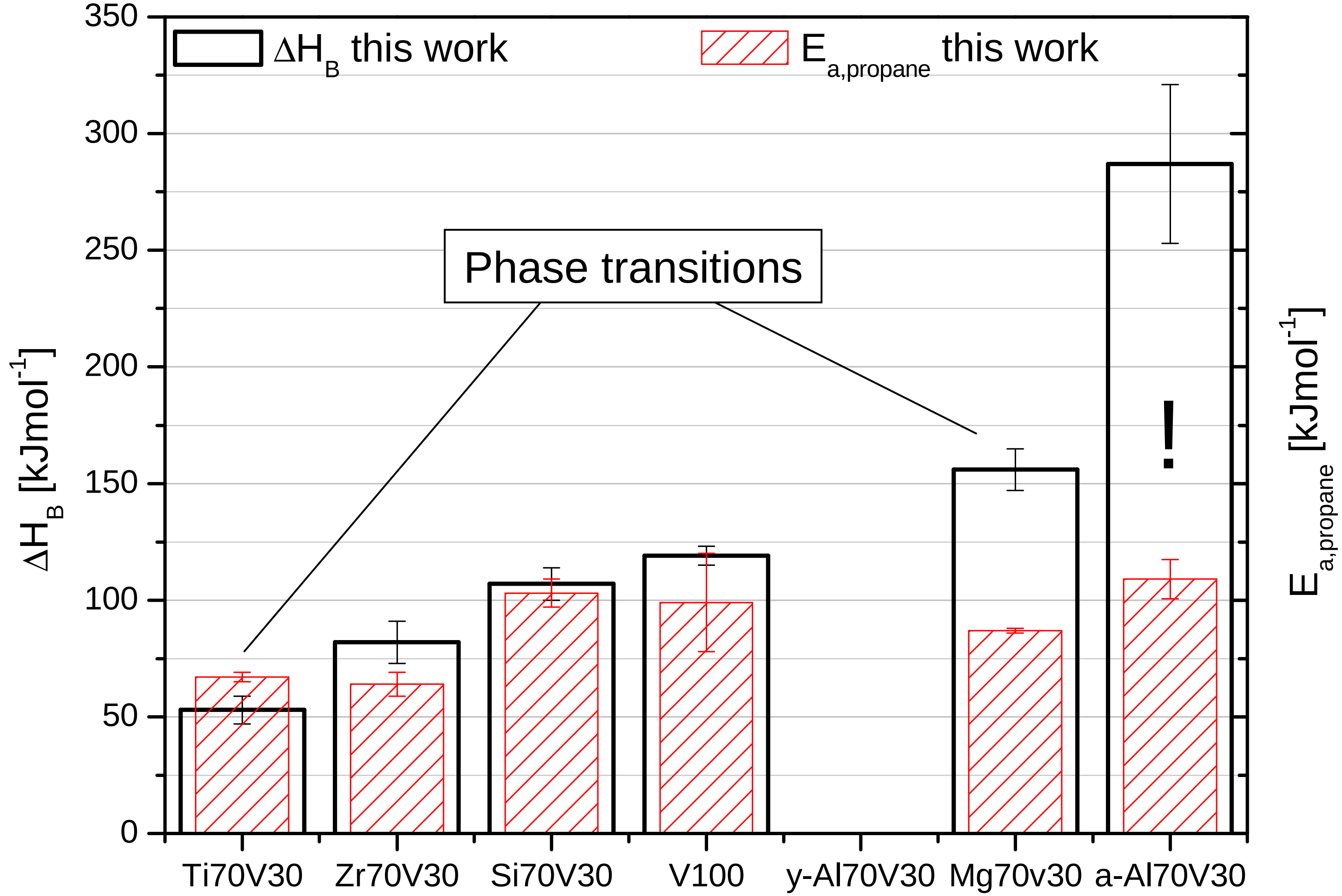

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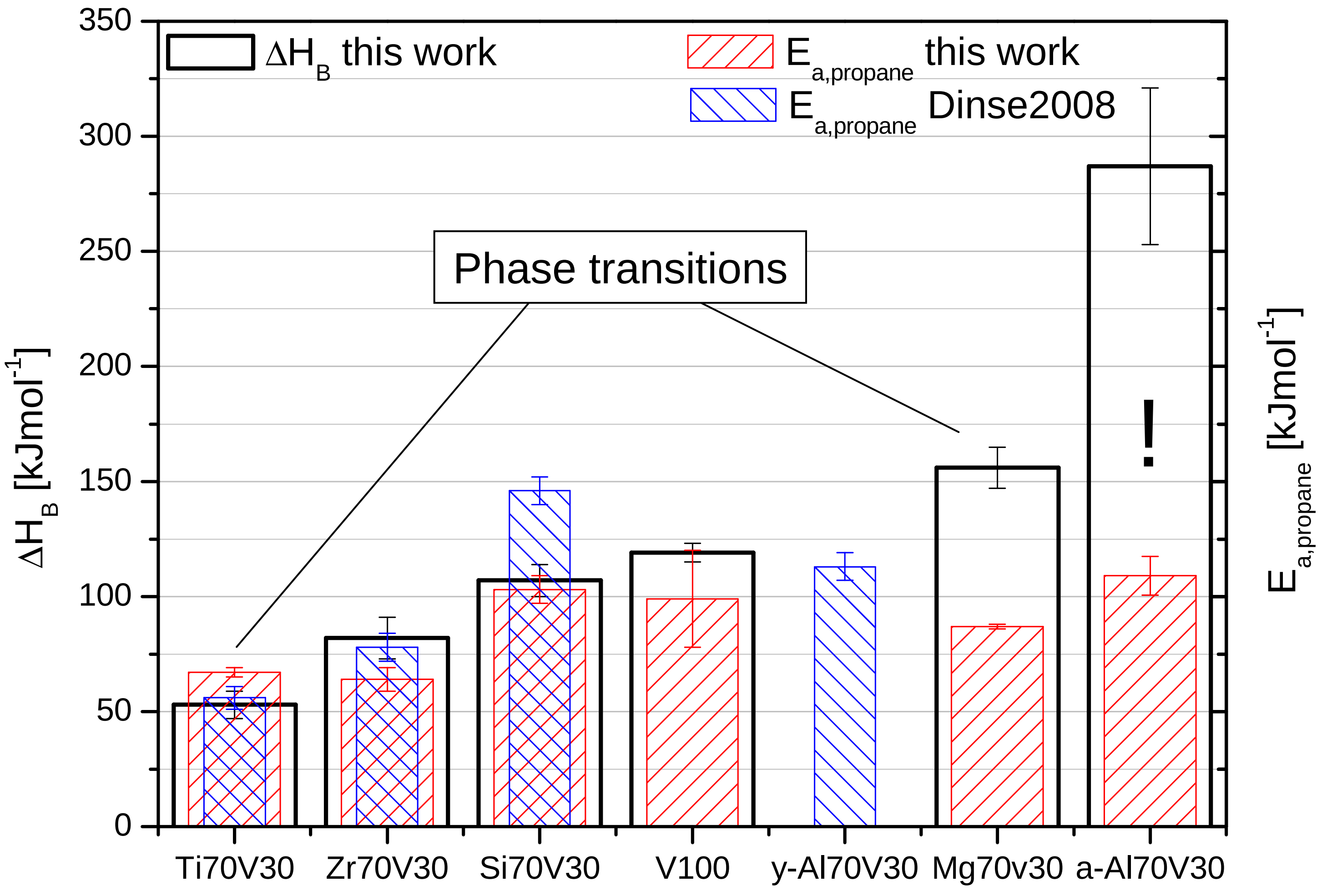
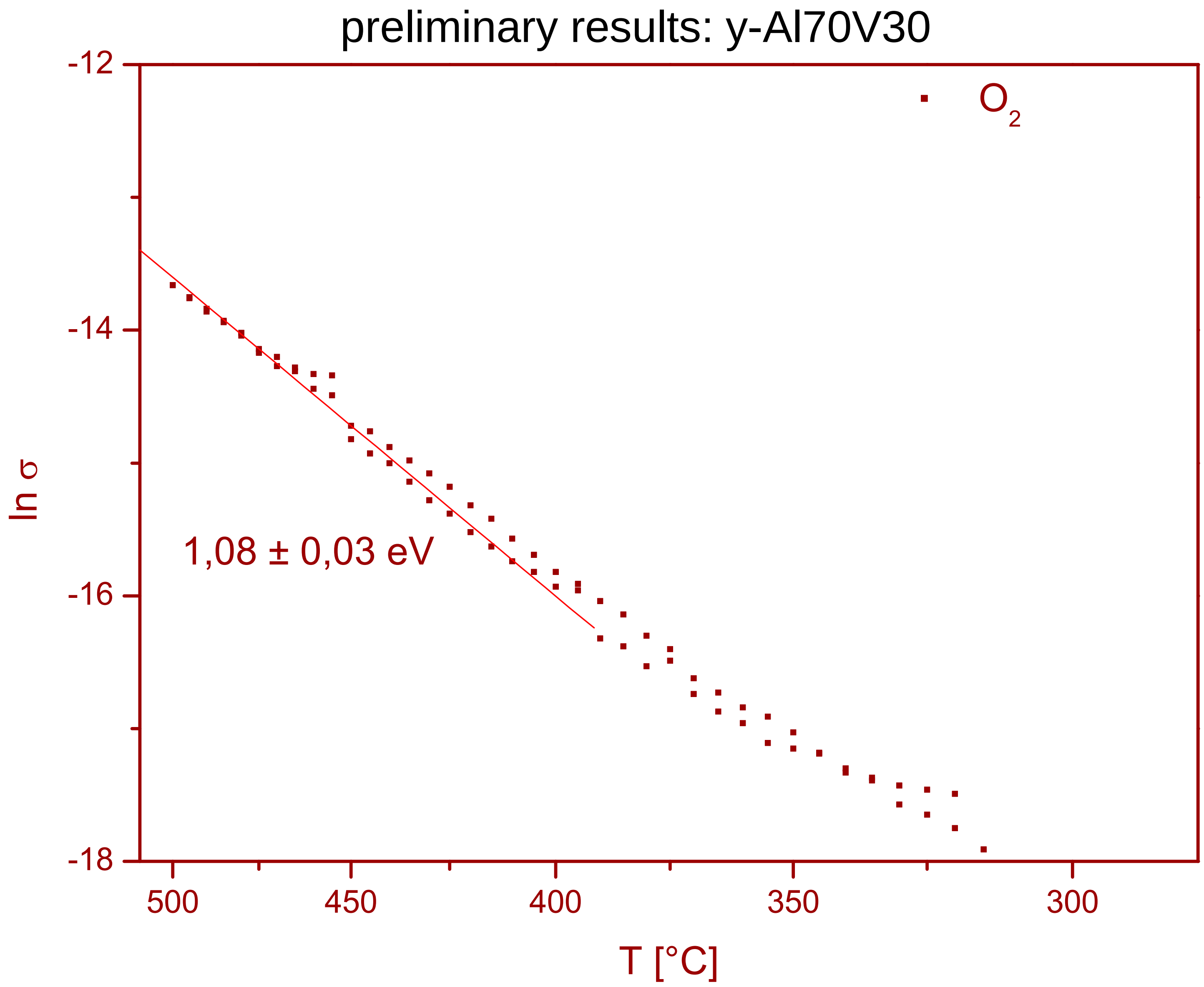
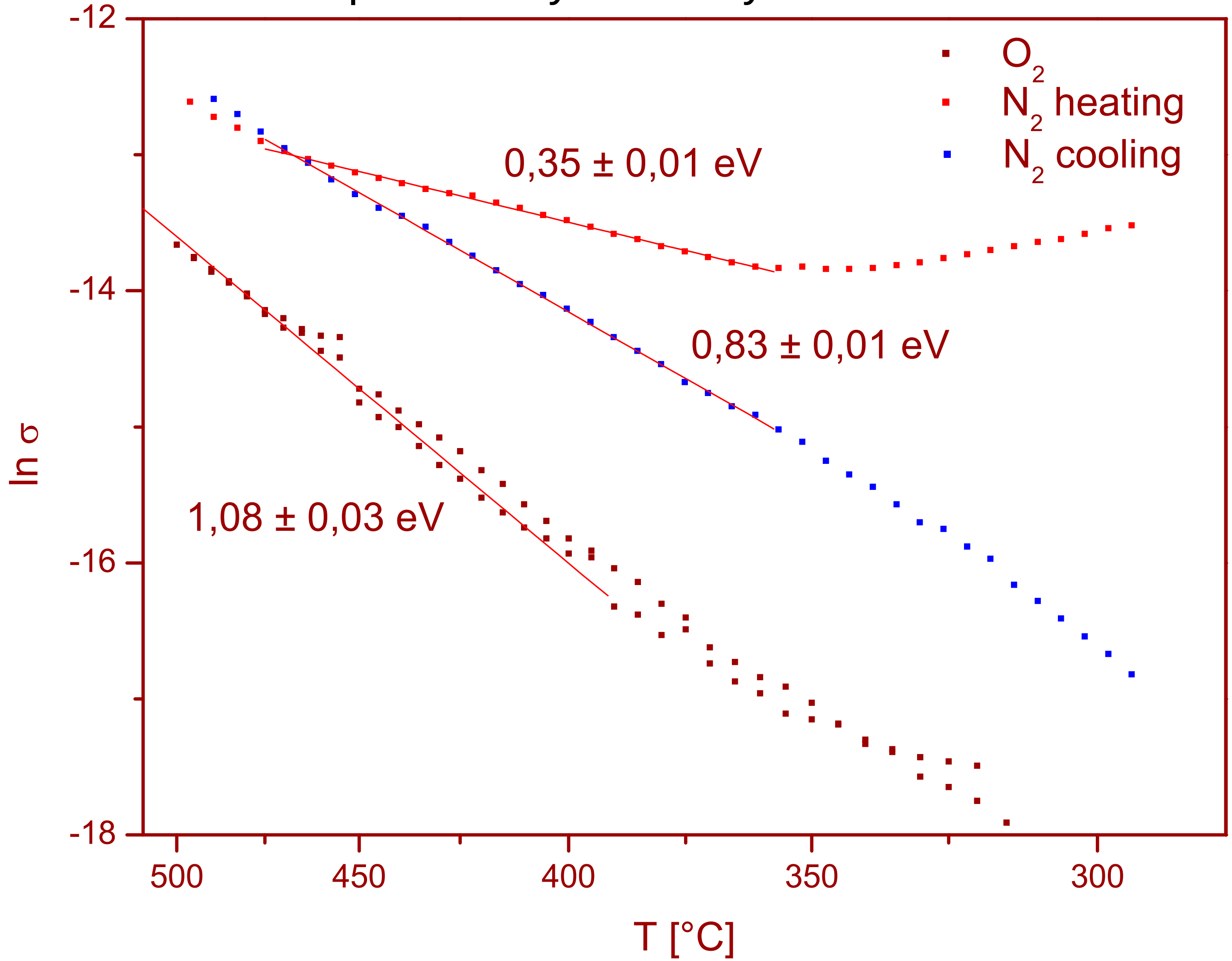


A. Dinse et al., J. Mol. Catal. 289 (2008) 28

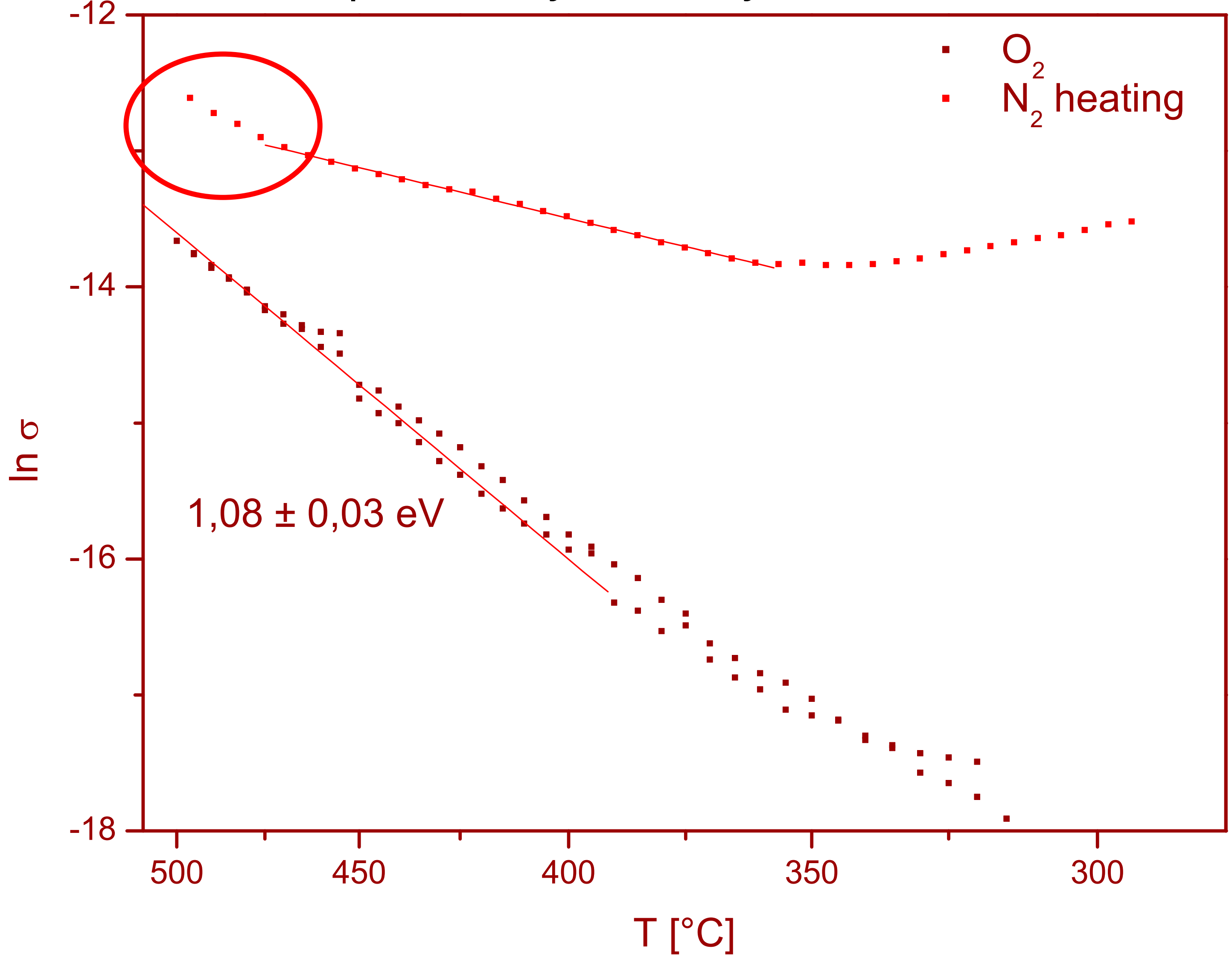


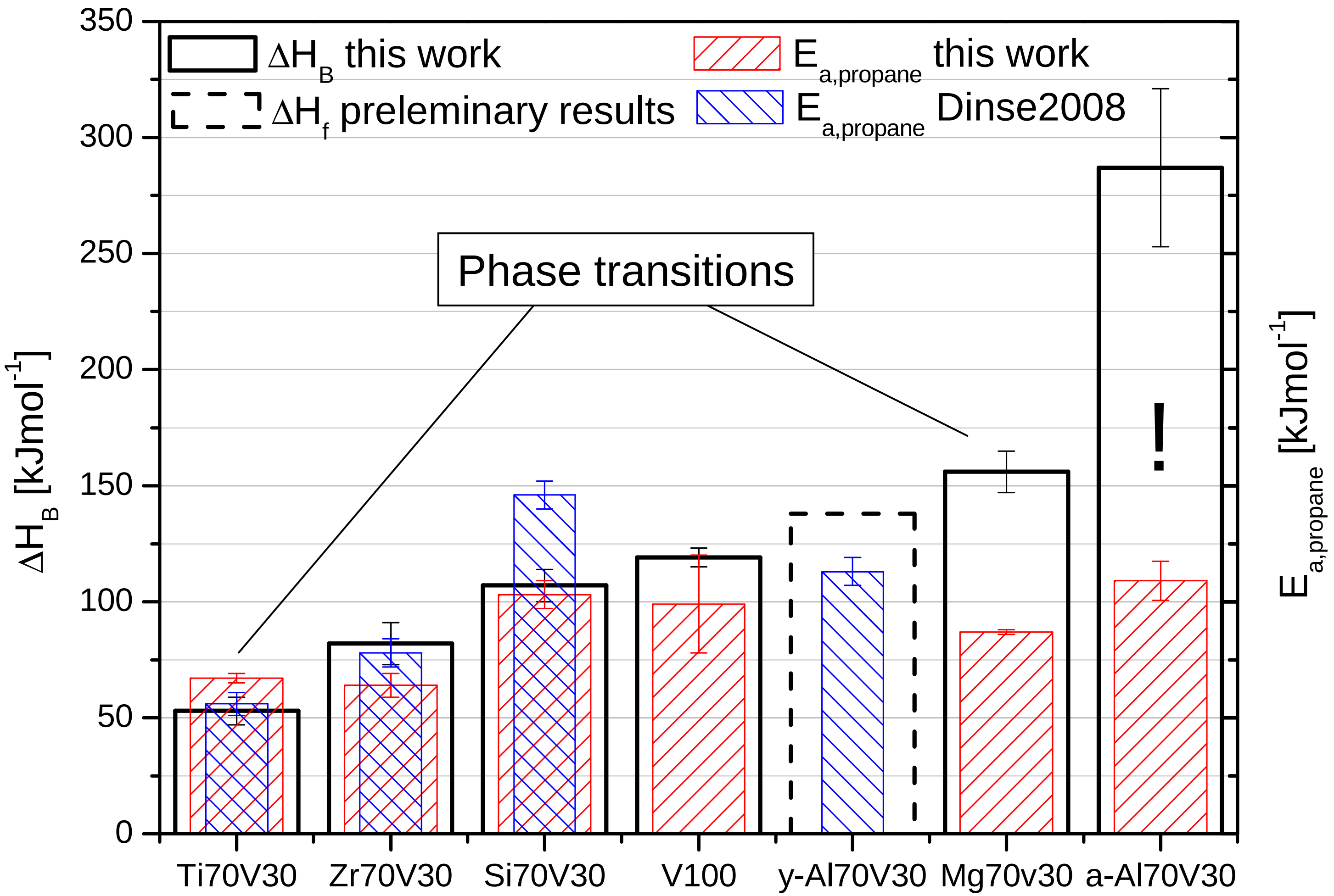
preliminary results: y-Al70V30
-12
-14
-16
-18
ln σ
O2
1,08 ± 0,03 eV
500
450
400
350
300
T [°C]

preliminary results: y-Al70V30



preliminary results: y-Al70V30





$$\Delta H_{f,O} \leftrightarrow E_{a,propane}$$

4. Conclusion and outlook

Correlation looks promising but certain improvements necessary

⇨ sample influence

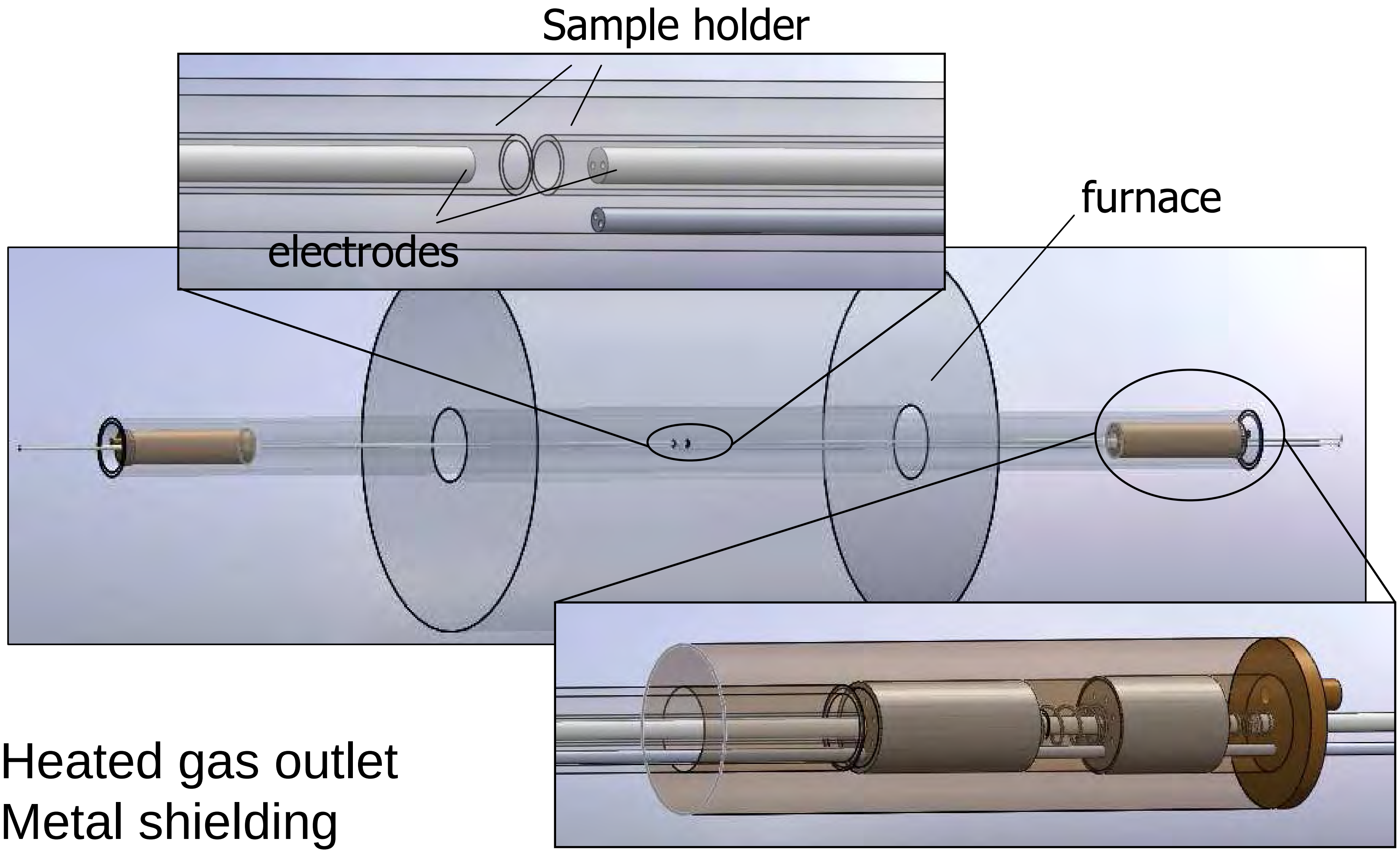
phase transition → sample treatment
homogeneity → new preparation method
lower loading for stronger support effect

⇨ other steps in catalytic reaction, like H-transfer

kinetic studies on conductivity samples

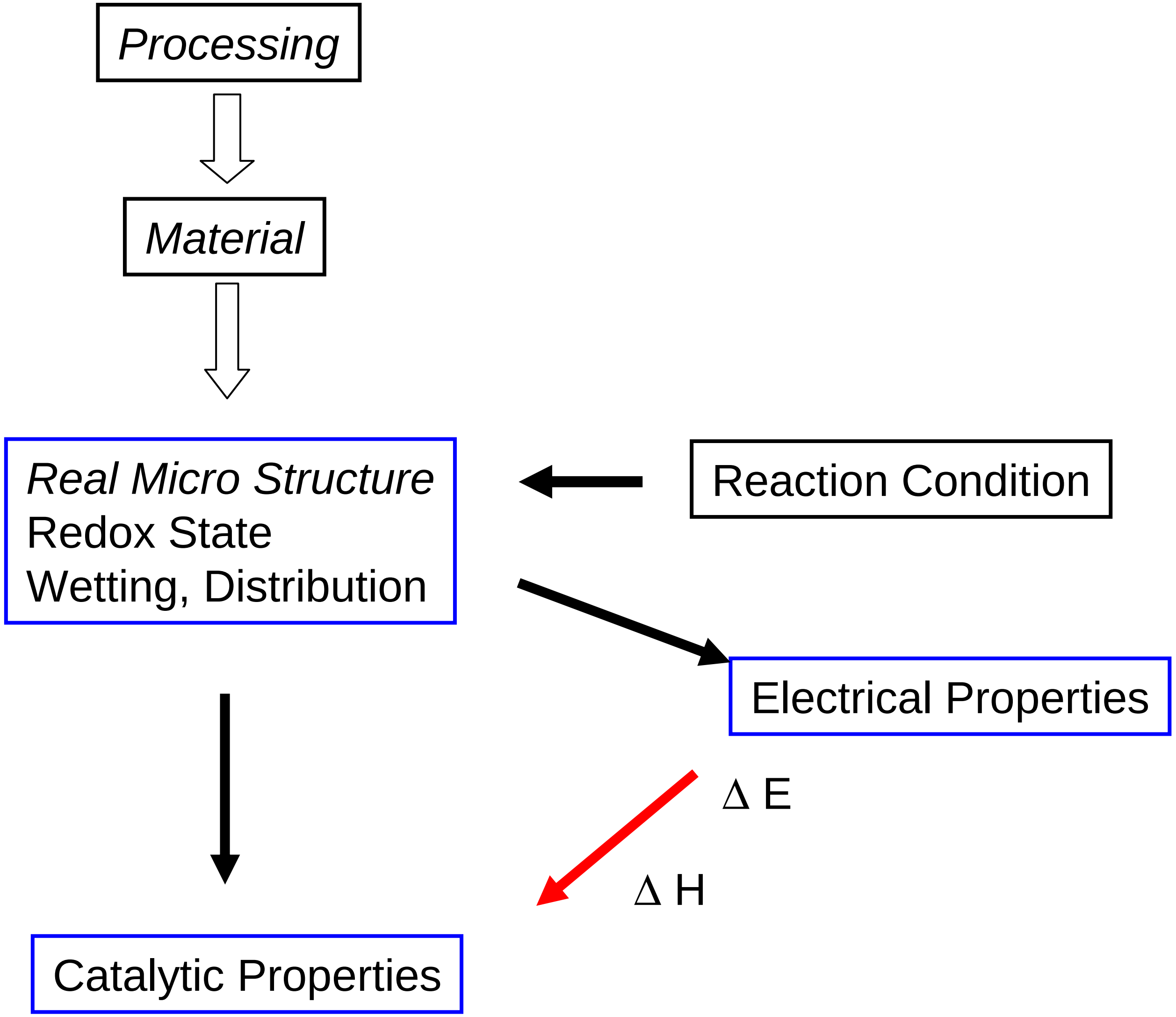
⇨ in-situ experiments necessary

set-up constructed
experiments this year



Heated gas outlet
Metal shielding
Small sample chamber

4. Conclusion and outlook



Thank you for your attention

Sample	ΔH_B [kJ/mol]	ΔH_B [eV]
Ti70V30	53 ± 6	0,55 ± 0,06
Zr70V30	82 ± 9	0,85 ± 0,1
Si70V30	107 ± 7	1,11 ± 0,08
V100	119 ± 4	1,23 ± 0,04
y-Al70V30	138	1,43
Mg70v30	156 ± 9	1,62 ± 0,09
a-Al70V30	287 ± 34	3,00 ± 0,4