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RUTHENIUM OXIDES AS CATALYSTS FOR CO OXIDATION

RELATIONS BETWEEN PHASE AND REACTIVITY?

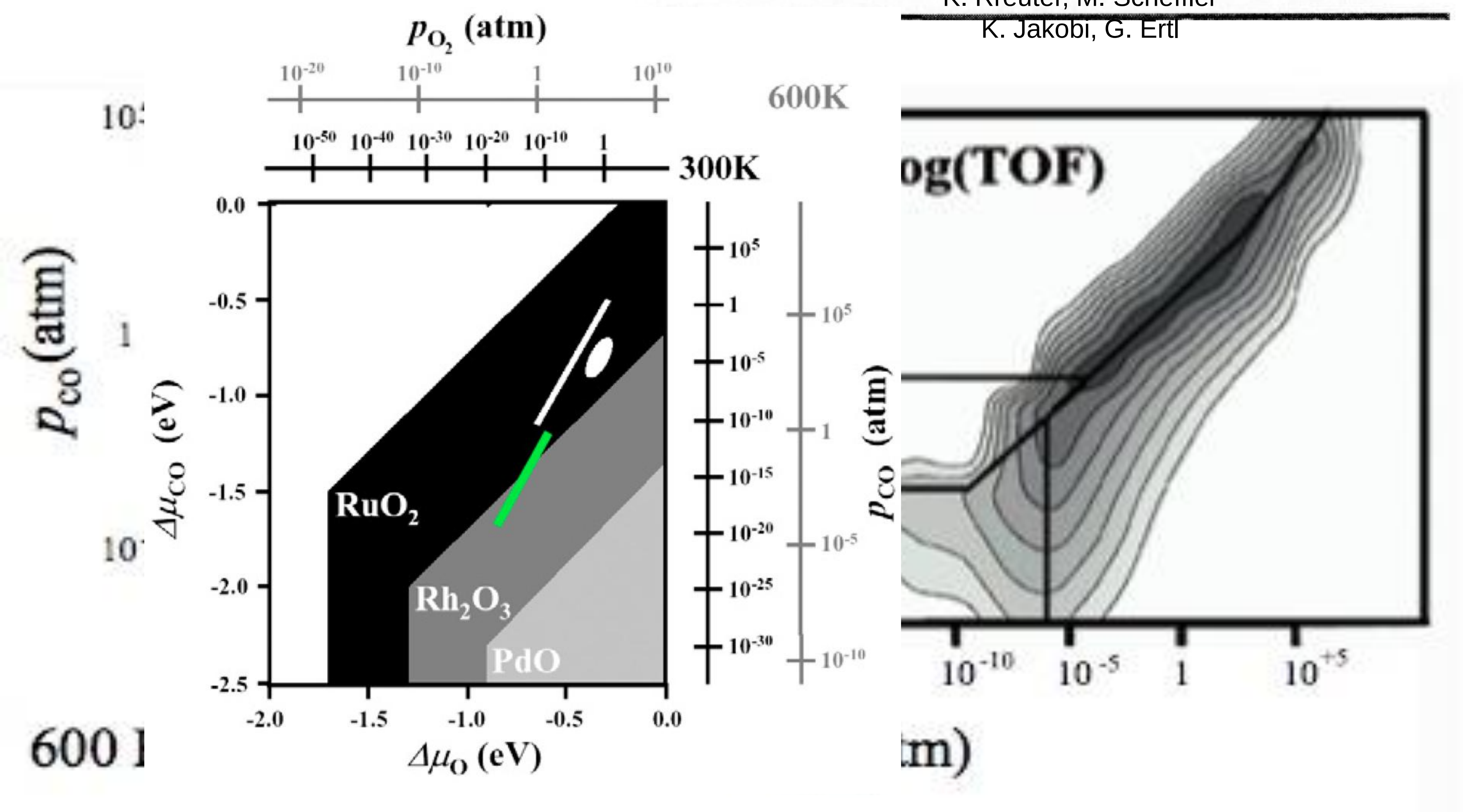
Challenge

- School 1: metal oxide is active (MvK mechanism) in at least one orientation and is not attacked by the reduction potential of substrate.
- School 2: metal forms a stable adsorbate (1x1) adlayer carrying the oxidation activity and is not converted to oxide.
- School 3: metal reacts with oxygen to adsorbate plus sub-surface and at high potentials to oxide; under reaction conditions the sub-surface (TSO) is at least present.

All have good evidences and theory support

A mature issue: Ru/O/CO

K. Rreuter, M. Scheffler
K. Jakobi, G. Ertl



K. Reuter and M. Scheffler, Appl. Phys. A **78,** 793 (2004).

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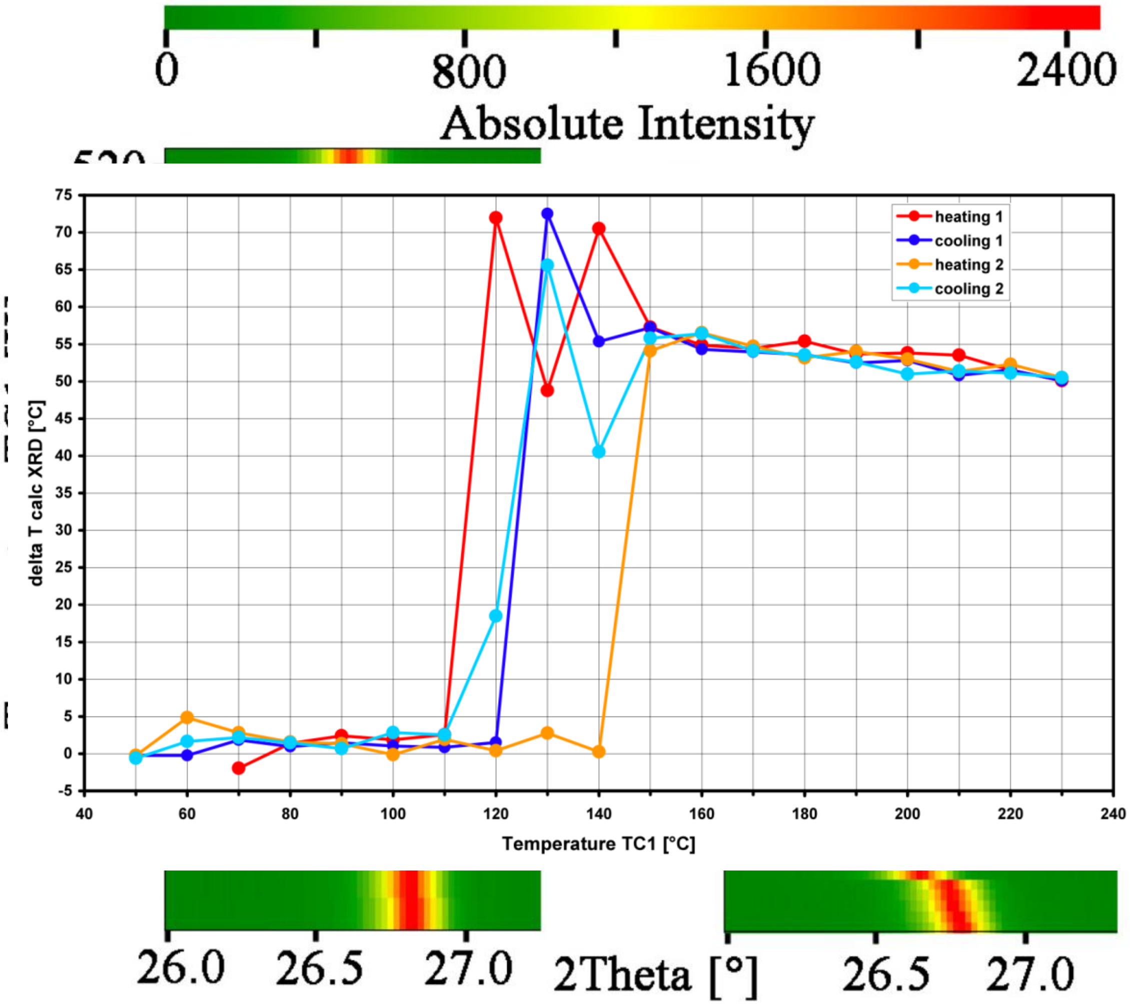
Energy transport in CO oxidation



Lattice constant of diluent BN as internal thermometer:

Massive macroscopic deviations in temperature

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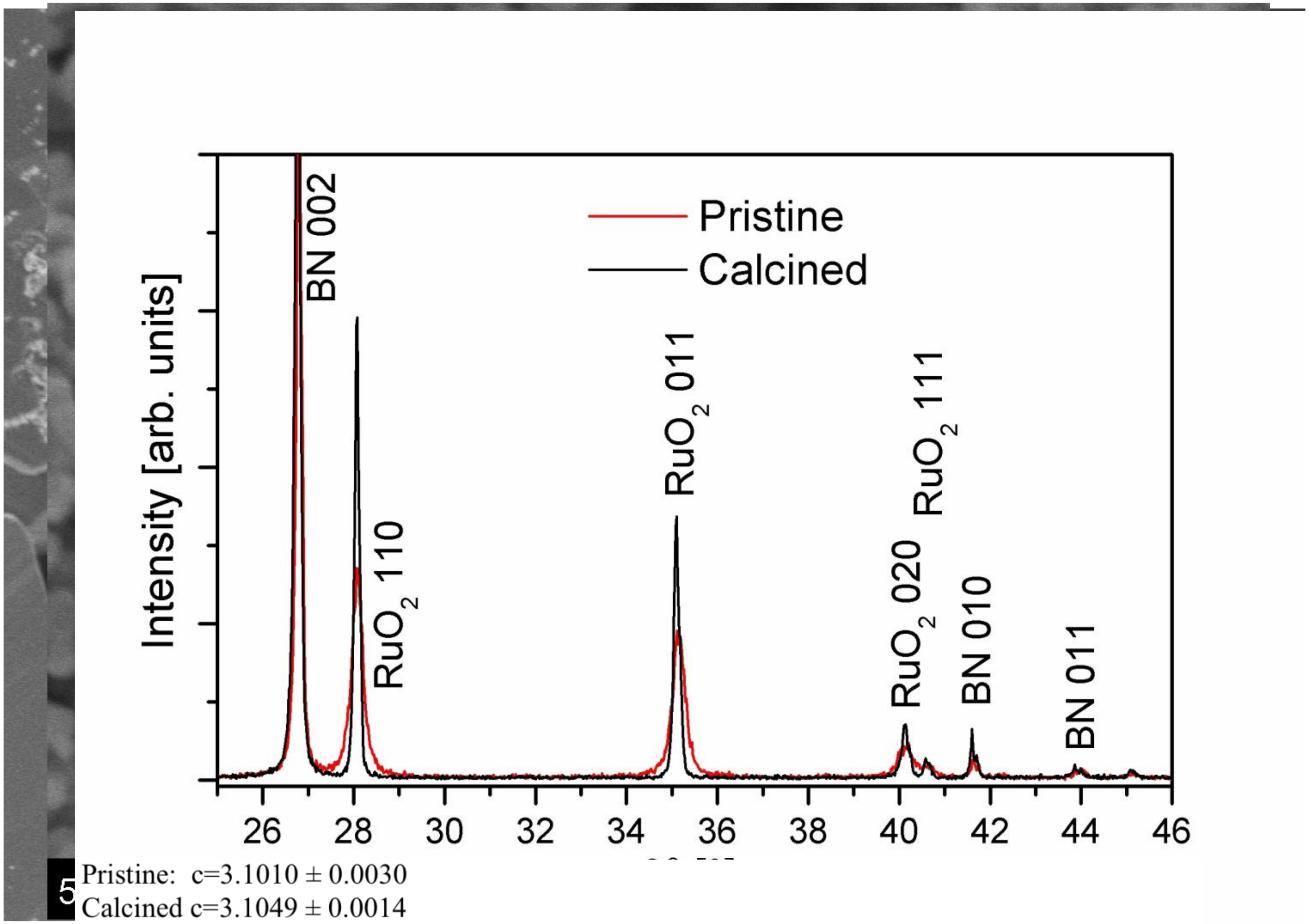
Nano X-tals



Pristine: c=3.1010 ± 0.0030
Calcined c=3.1049 ± 0.0014
a = 4.490

Surface analysis:
one active phase?

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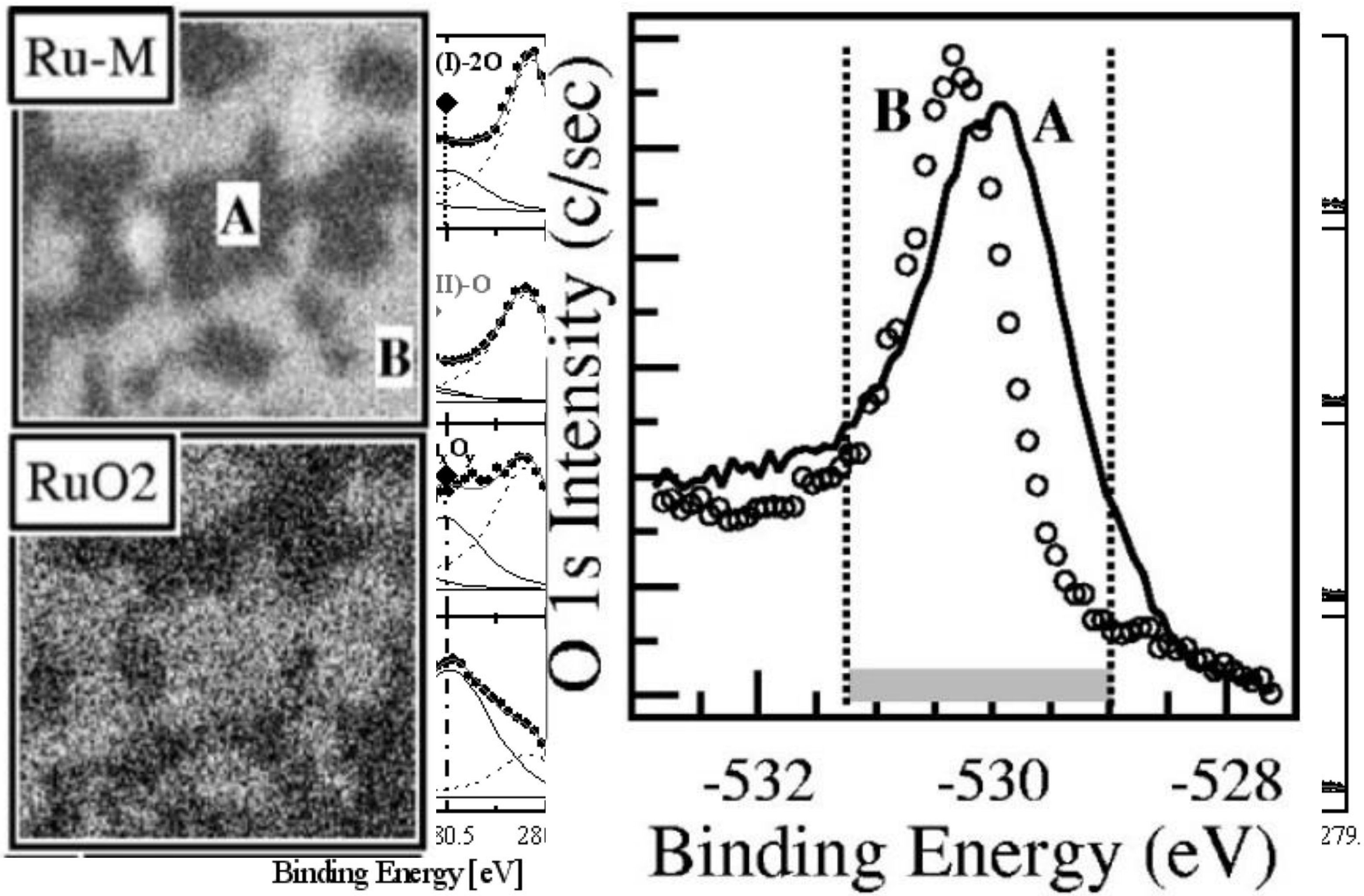
Inhomogenity of Ru (0001) O adsorbate



dark

images
64 x64 μ

Sharp 1x1 LEED spots

M. Kiskinova et al., JCP, 2002

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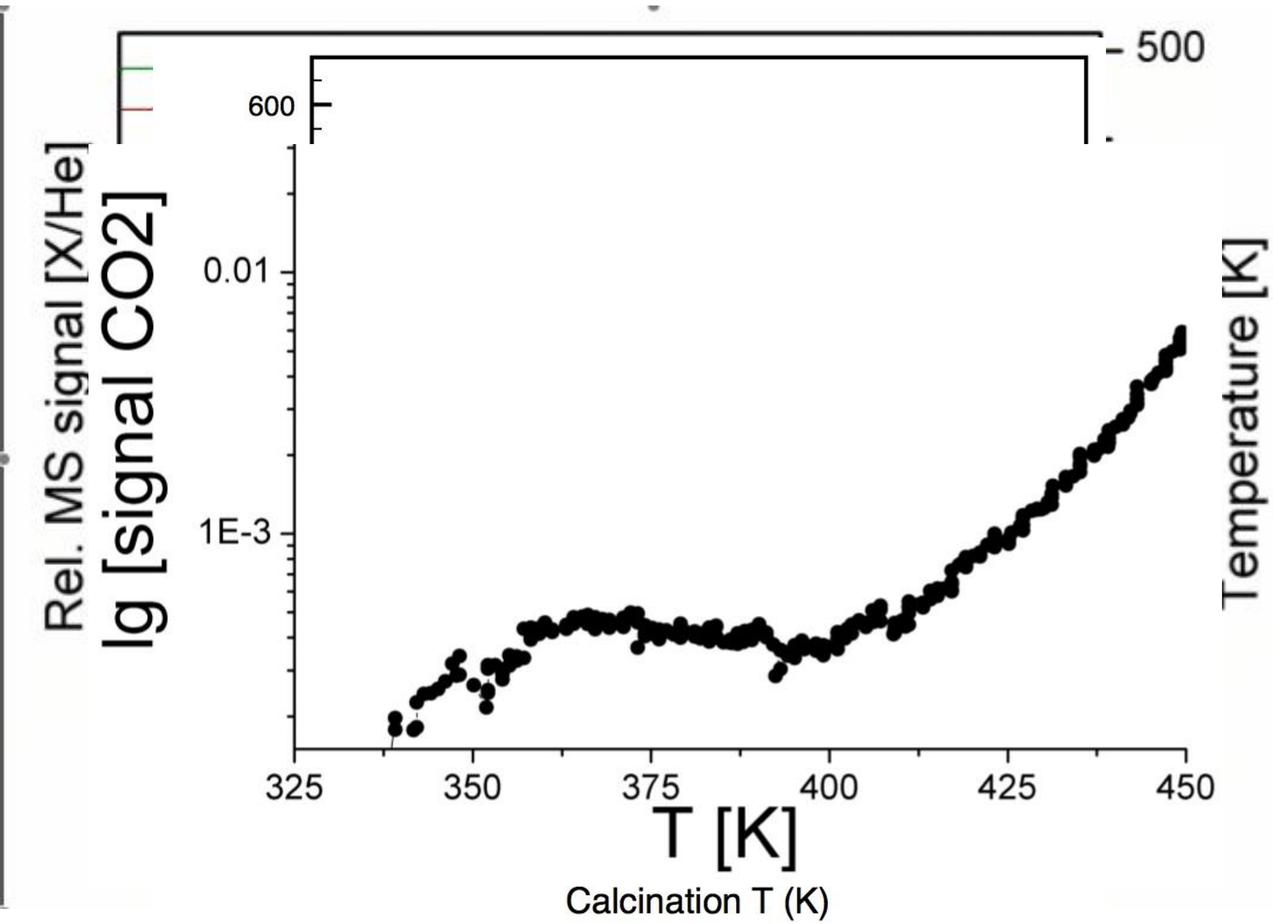
Oscillatory dynamics



Only in oxidizing feed and after prolonged activation in stoichiomtric feed:

Under other combinations of conditions and at shorter times only ignition from a low-temperature weakly active state

Reactivity an extrinsic property of phase

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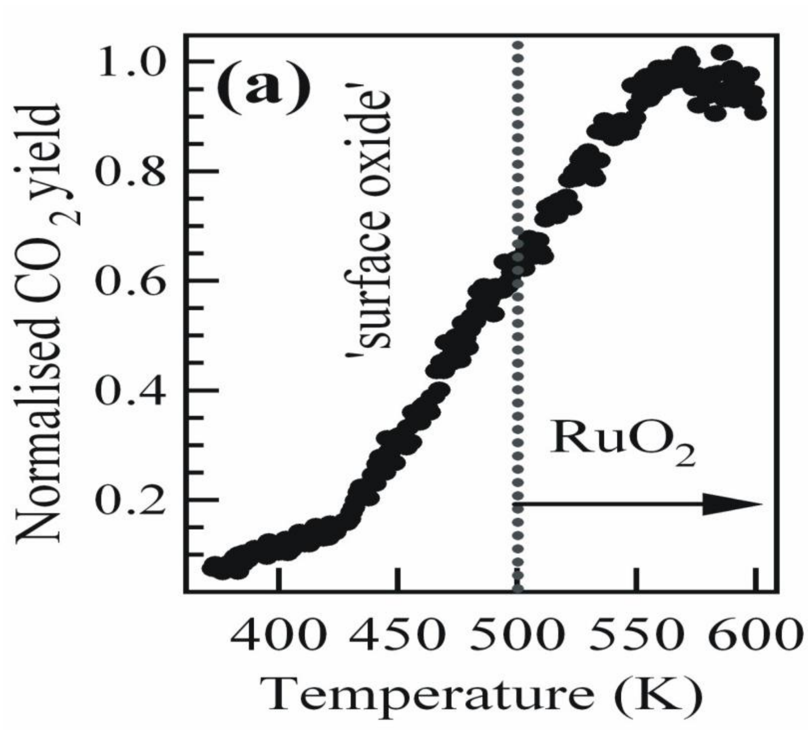
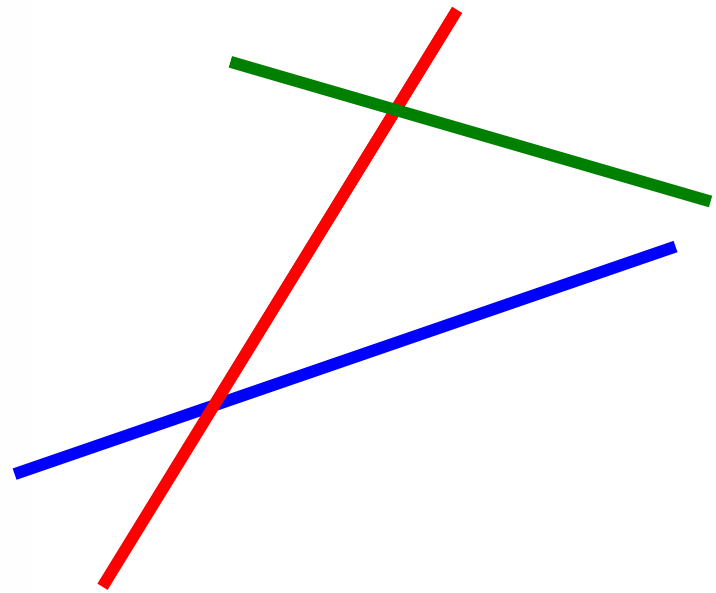
Different "phases" for same reaction





Low-active metal – oxygen adsorbate: sites at defects

Highly-active TSO in co-existence with metal/O or oxide

De-activation by conversion of TSO into defect-poor oxide

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In-situ bulk analysis and atmospheric reaction data

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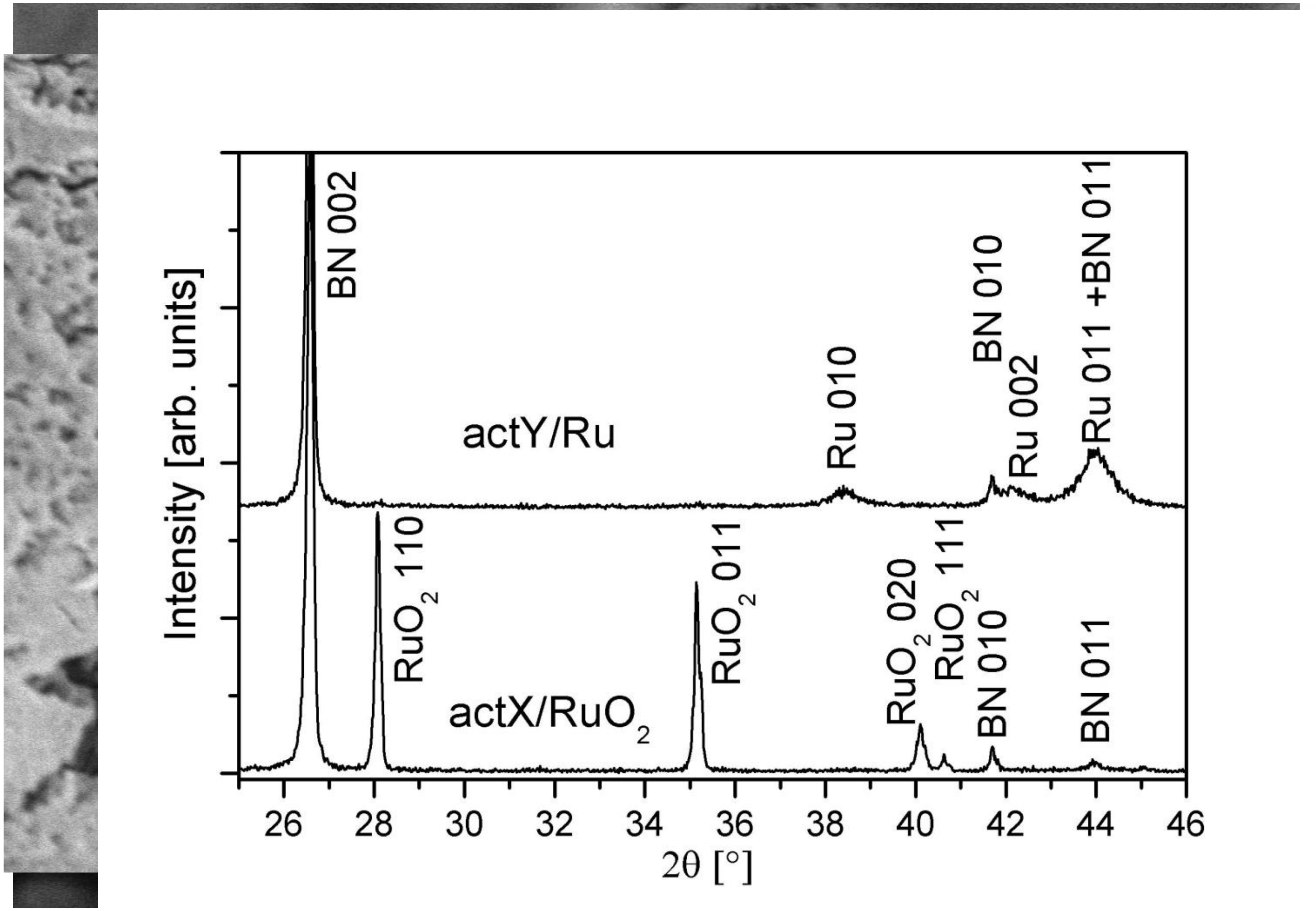
Performance at atmospheric pressure



ng

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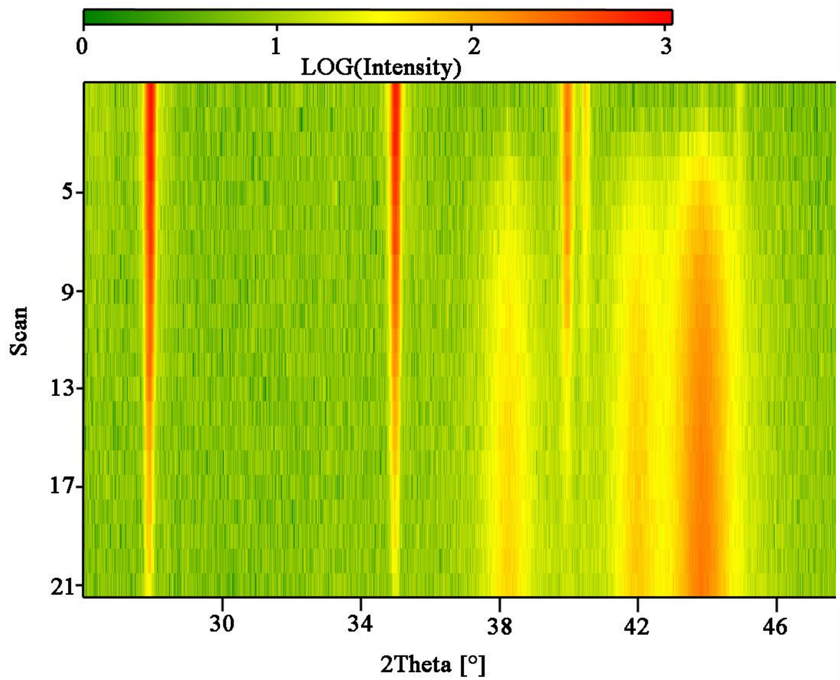
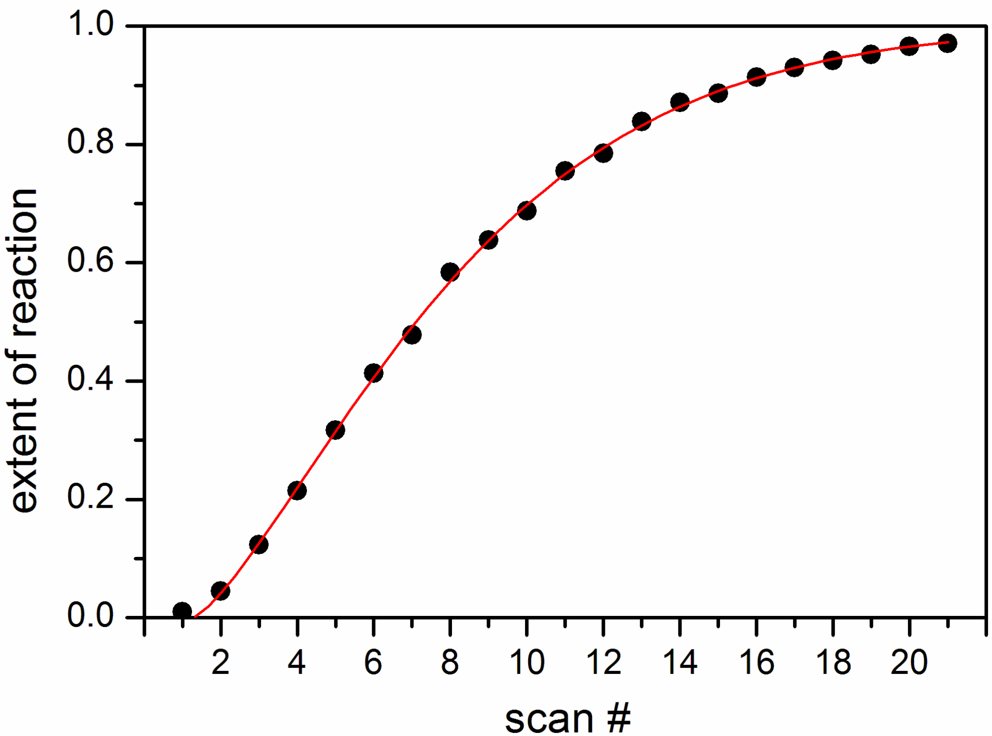
Isothermal reduction during TOS

Model: Avrami-Erofeev

$$\xi = 1 - e^{-k*(t-t_0)^n}$$

ξ Extent of reaction





RuO2 5363

Barely detectable amount of metal in oxide drives ignition

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Phase and function

In-situ XRD: active oxide or active metal

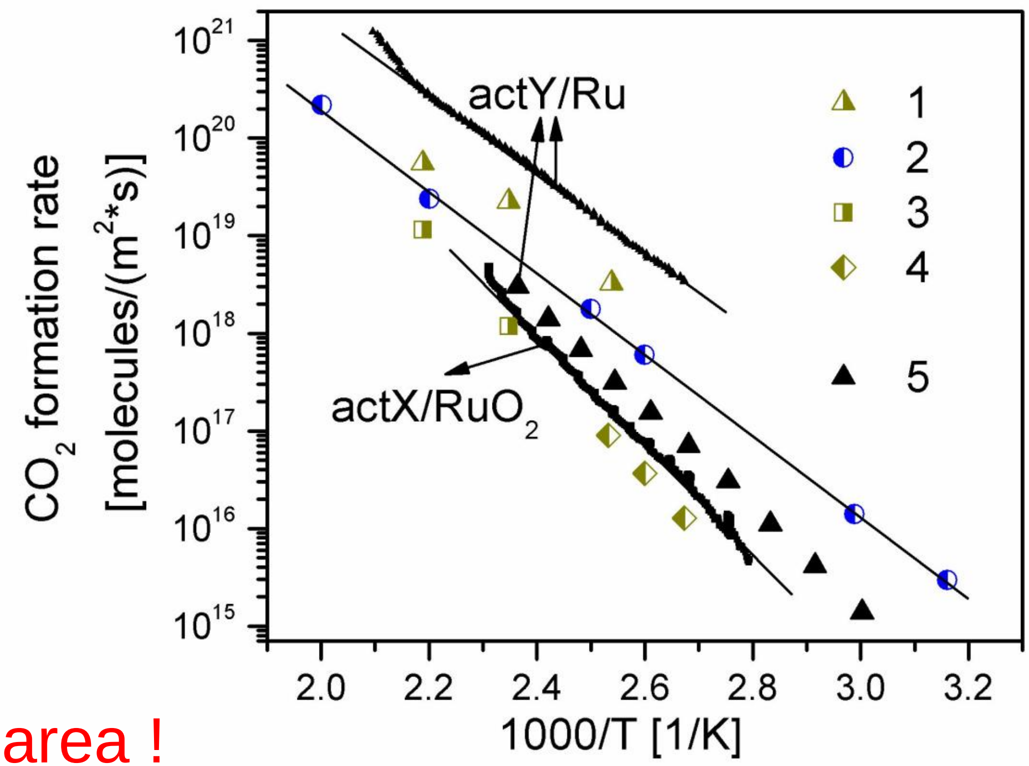
1) metallic, polycrystalline Ru [20]

, 2) $RuO_2(110)/Ru(0001)$ [21],

3) oxygenated Ru(0001) [3],

4) oxidized RuO_2 [20]

5) supported RuO_2 nanoparticle [22]



Based on same surface area !

Ex oxide: 105 kJ/mole
After reduction: 82 kJ/mole

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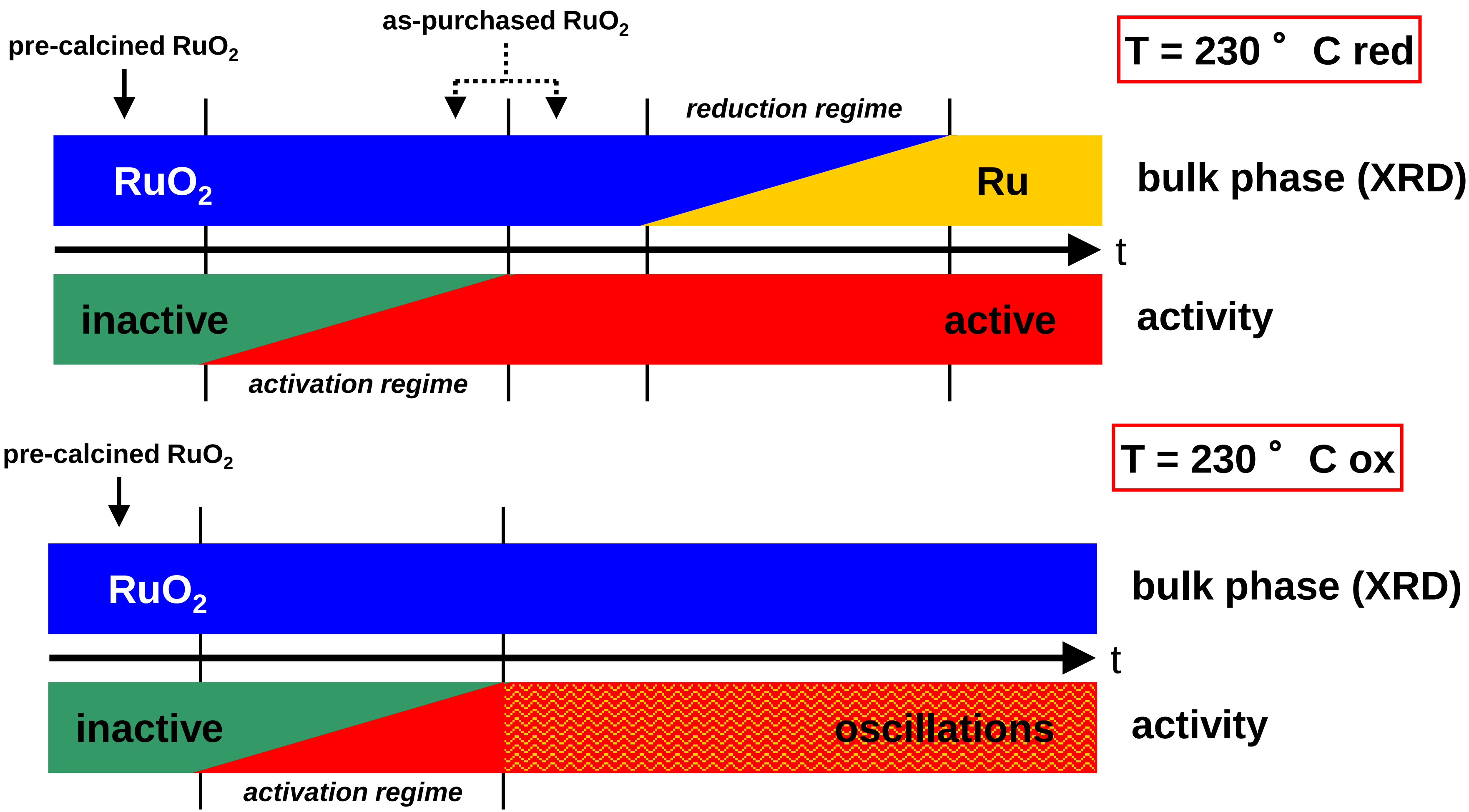
Structure-function relation?



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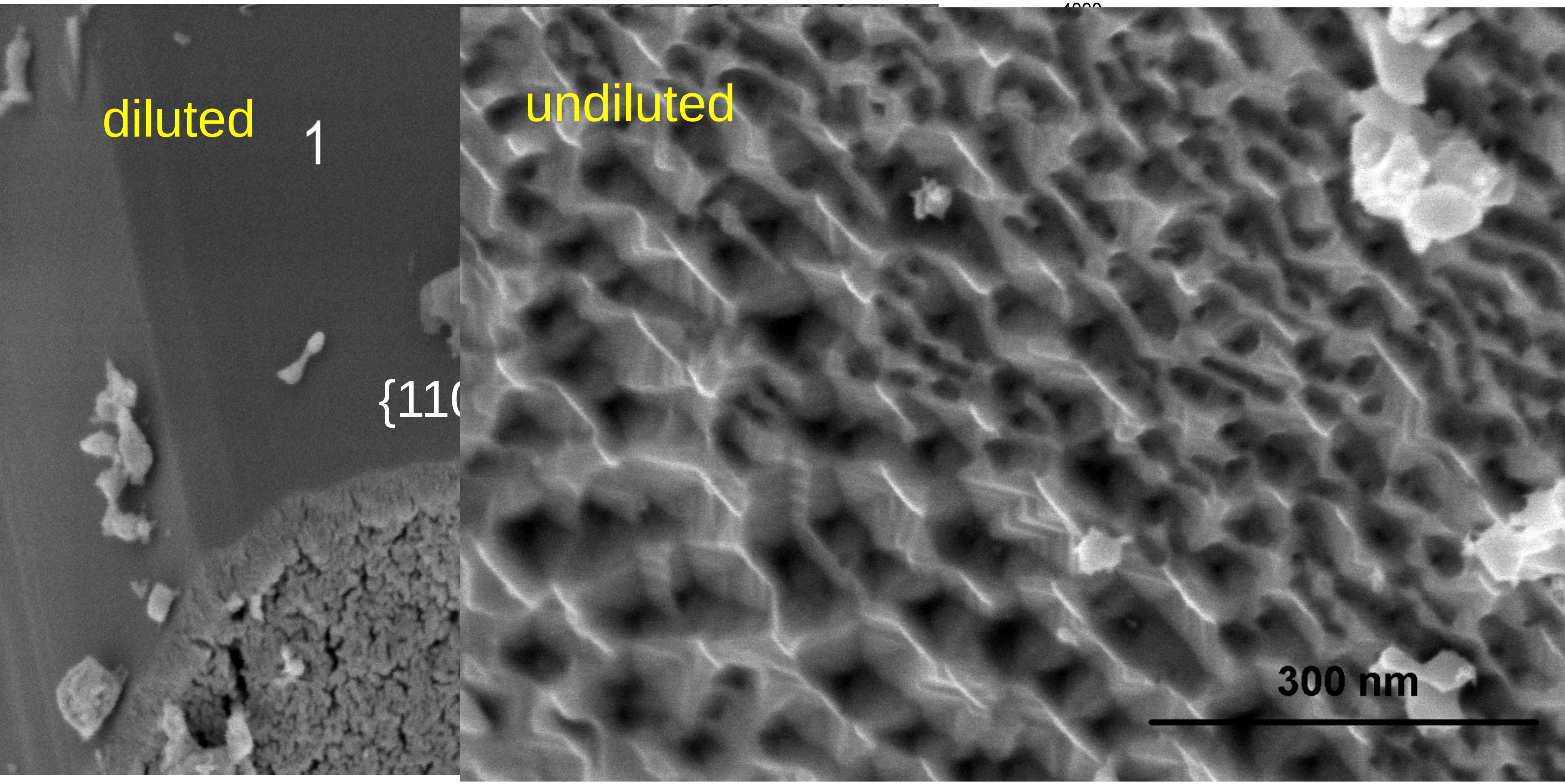
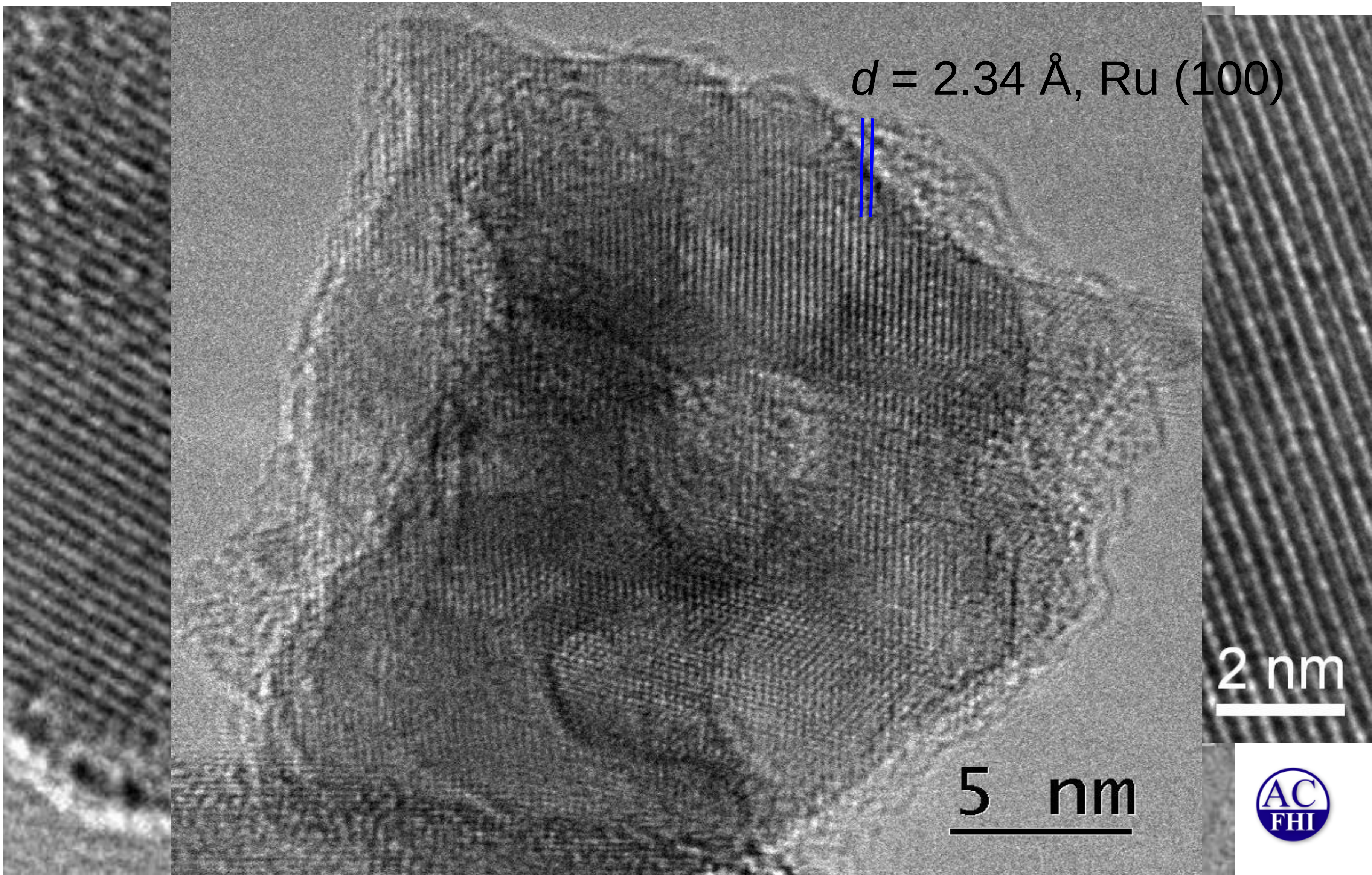
Nature of the active bulk "oxide"



Selective reduction to Ru (O)

Defects in RuO_2 and in Ru (O)



The active site

- Requires two incompatible functions
  - Weakly delocalized metallic for weak CO adsorption
  - Strongly localized metallic for oxygen activation and binding.
- Local electronic contrast determines the efficiency of the site.
- High co-ordinative undersaturation and matrix isolation provide best sites:
  - Step edges
  - Phase boundaries.
- CO oxidation with no selectivity and ignition behaviour is unsuitable to probe sites (multiple scenarios).

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The process

- Two types of defects:
  - From synthesis (low activity): insensitive to [μ O]
  - dynamical (ignition): sensitive to [μ O].
- [μ O] is feedback agent
  - Produces energy (reaction)
  - Prevents CO poisonning (TSO)
  - Blocks active sites (surface oxide)
  - Immobilizes surface dynamics (ordered oxide)
- [μ O] plus energy transport in catalyst determines kinetic response at “ambient” pressure.

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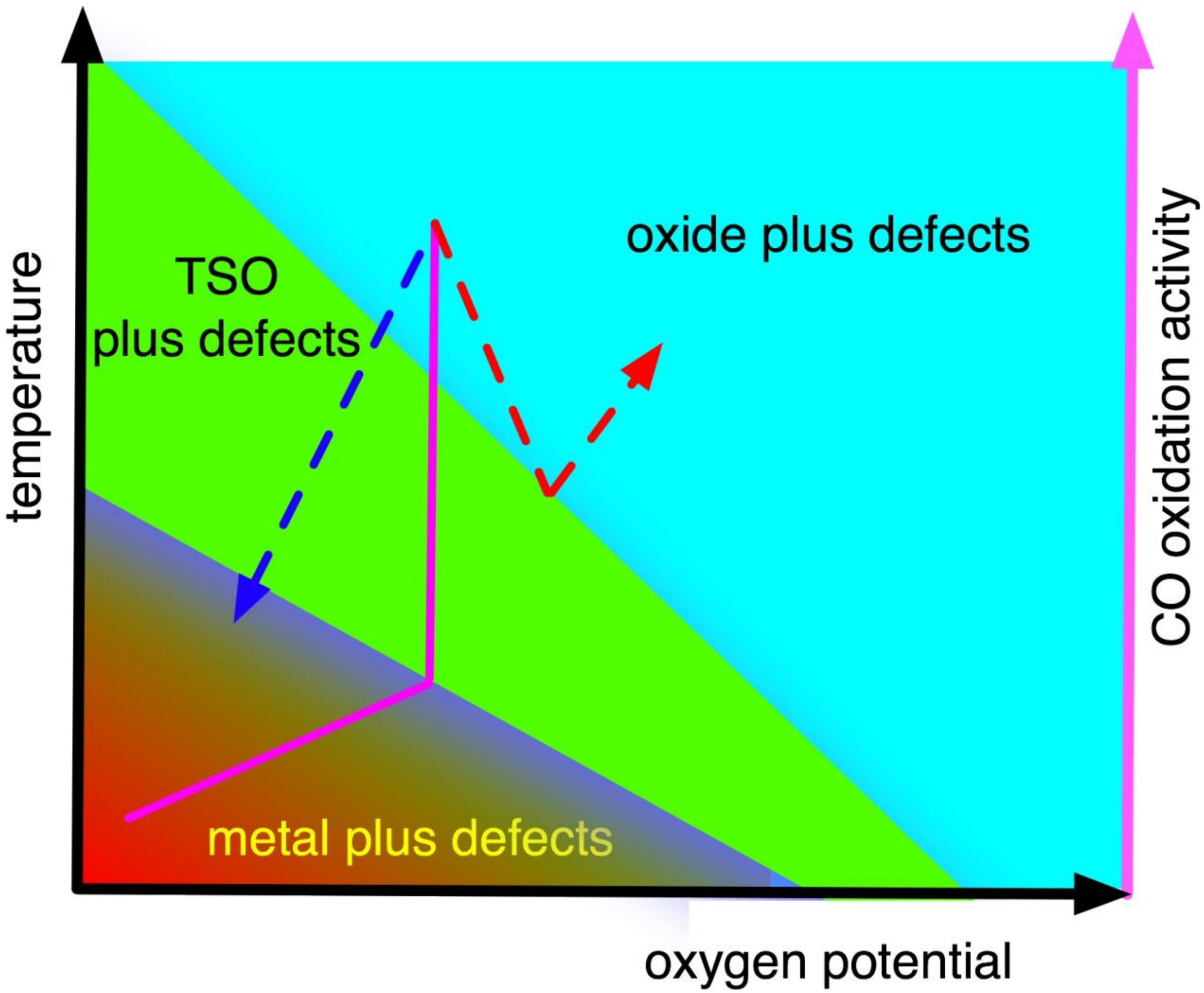
Diagrams of state

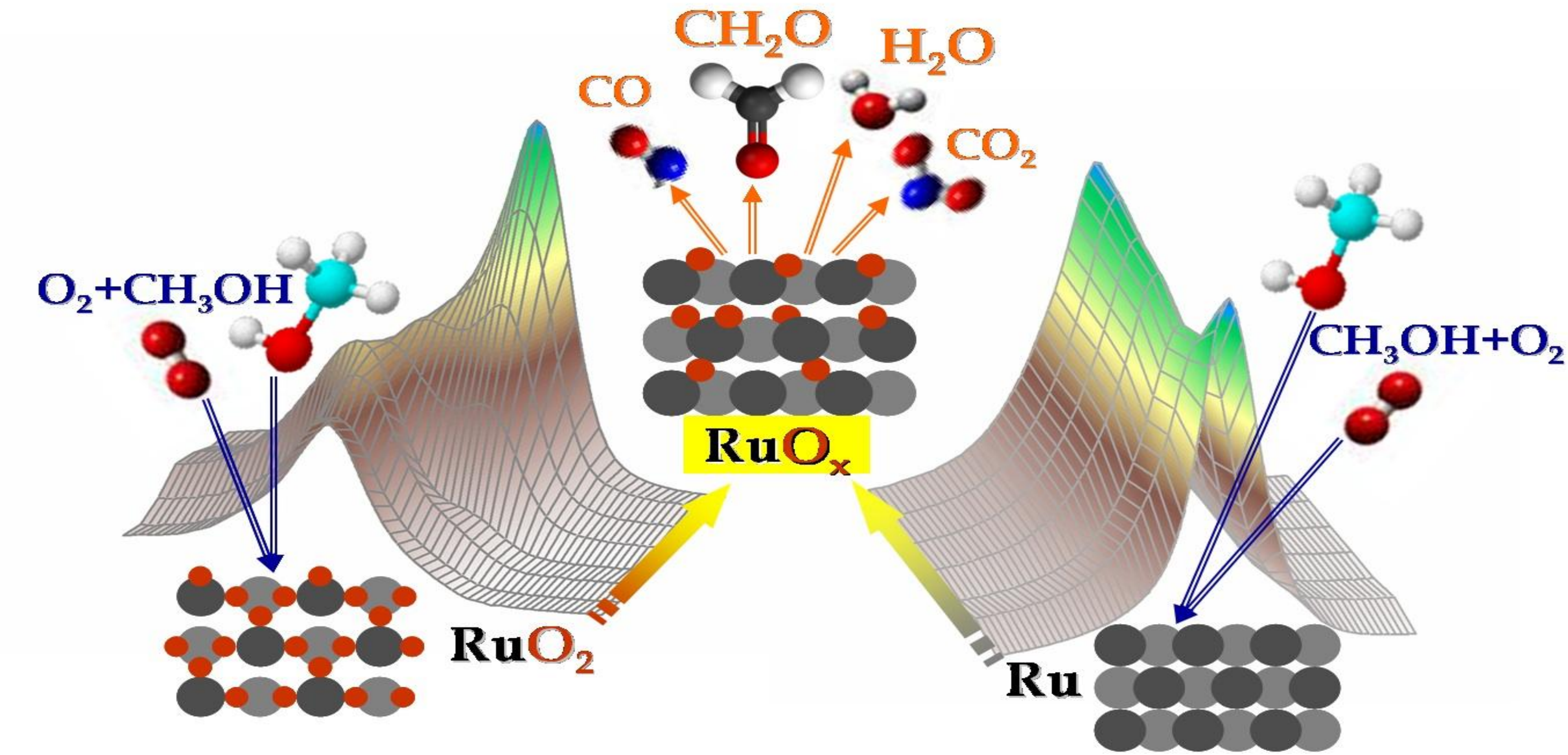


Make things as simple as possible -
But not simpler
(A. Einstein)

Coupling of slow active site formation with fast surface chemistry makes a simple reaction complex

Thank You

MeOH oxidation: material dynamics



Ru3d: metallic “TSO” for both pre-catalysts at reaction conditions:
Selectivity controlled by electrophilicity of O ad

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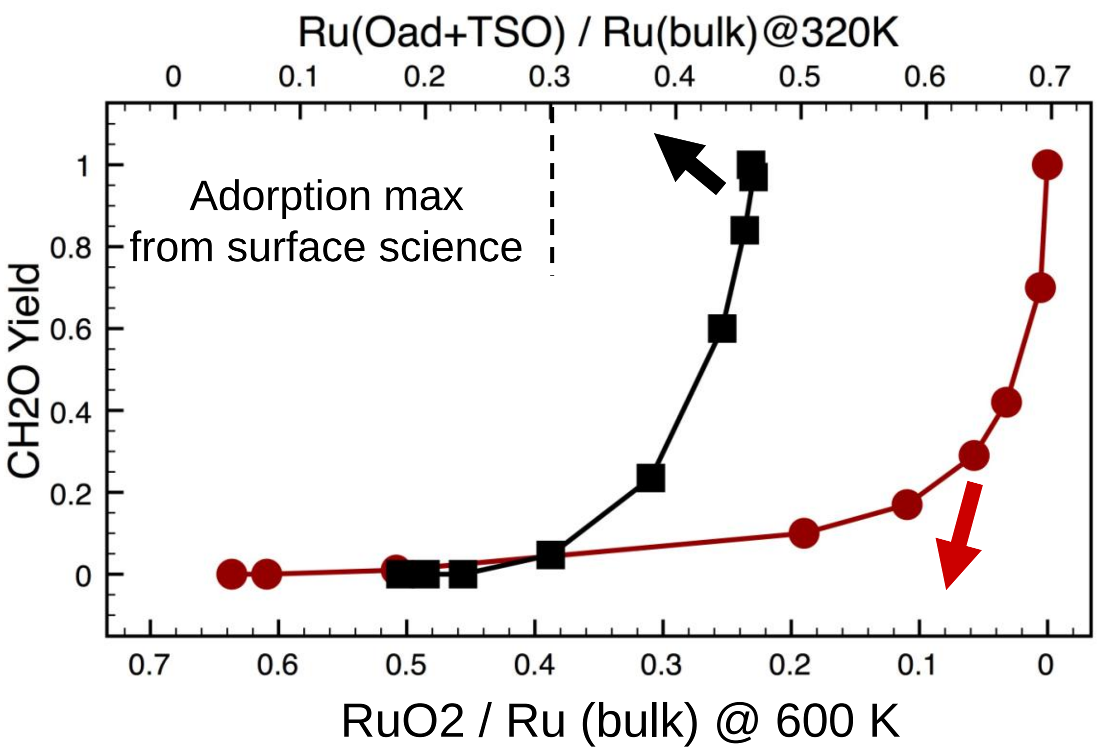
Structure-function relation with Ru: MeOH oxidation

Accumulation of Ru(TSO)

metallic pre-catalyst
$p_{CH3OH} / p_{O2}=1.5$



Correlation between the formation of RuO_x transient surface oxide (TSO) and CH_2O production

Reduction of oxide phase

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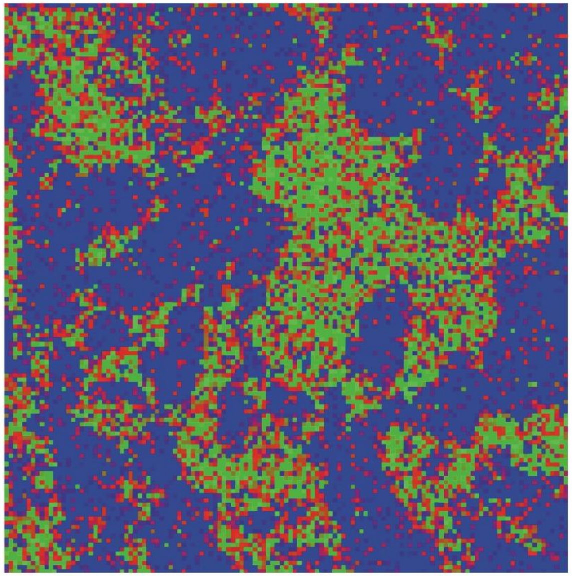
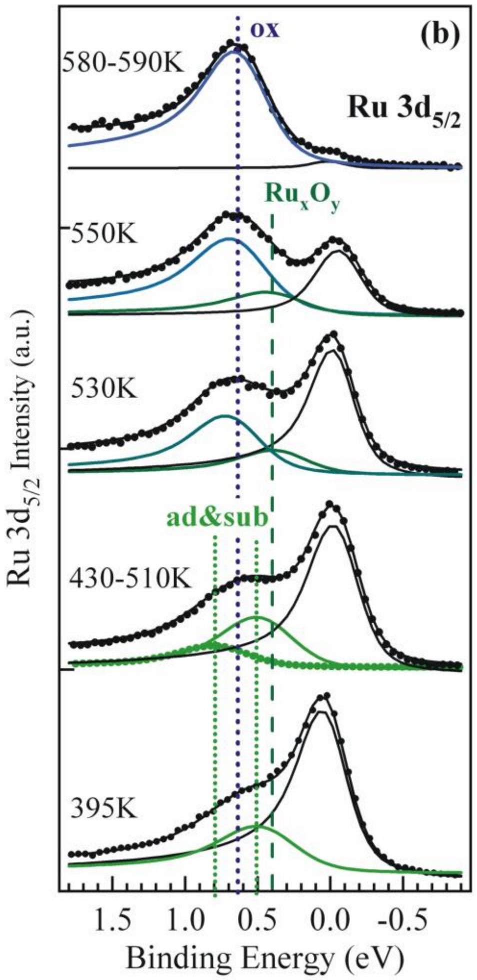
Metastable catalyst surface: CO oxidation

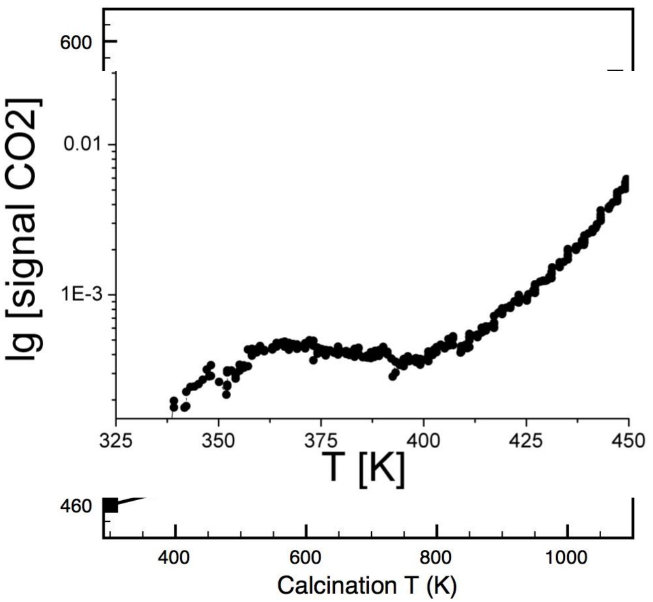


64µ x 64µ

XP microscopy, 550 K, 10^{-5} mbar

Mixture of oxidation states of the active surface (single crystal(0001))





Defects play an essential role in the activity: extrinsic reactivity