AC FHI

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MAX-PLANCK-GESELLSCHAFT

BiG max MAX PLANCK RESEARCH NETWORK on big-data-driven materials science

Big Data Summer
A summer school of the BiGmax Network
Platja d'Aro, Spain, September 9 – 13, 2019

Big*-data driven catalysis research: Challenges and chances

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*big for experimentalists in catalysis, but not in terms of computational science

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Group Oxides

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

Inorganic Chemistry
Theory

BASF
We create chemistry

Technische Universität Berlin

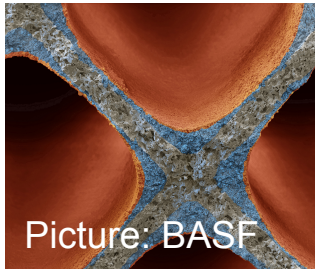
unisyscat

Ambition:

Predicting high performance based on physical insight

- ➔ Synthesis of catalysts
- ➔ Spectroscopic/mechanistic studies
- ➔ Collaboration with theory

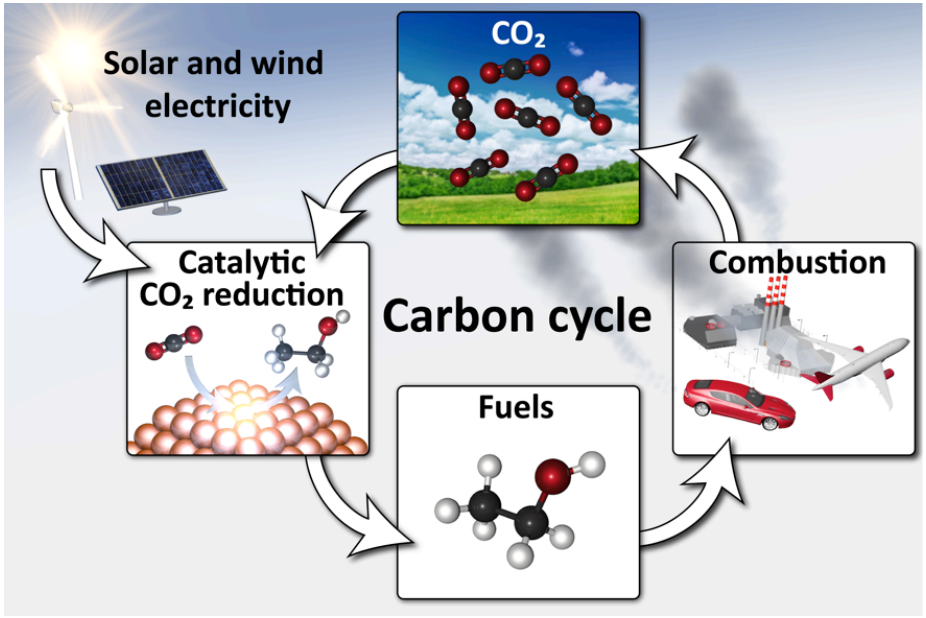
Catalysis and sustainability


Picture: BASF

- Catalysts accelerate reactions by orders of magnitude enabling them to be carried out at much lower pressure and temperature
- Efficient catalysts in combination with optimized reactor and plant design reduce investment and operation costs of chemical processes
- Catalysts minimize waste formation and are used in purification of air and water
- Roughly 85-90% of all products are made in catalytic processes, the majority by heterogeneous catalysis


Methanol synthesis plant

Catalysis enables chemical energy conversion at global scale



A circular carbon economy is necessary to allow the construction of a sustainable energy systems

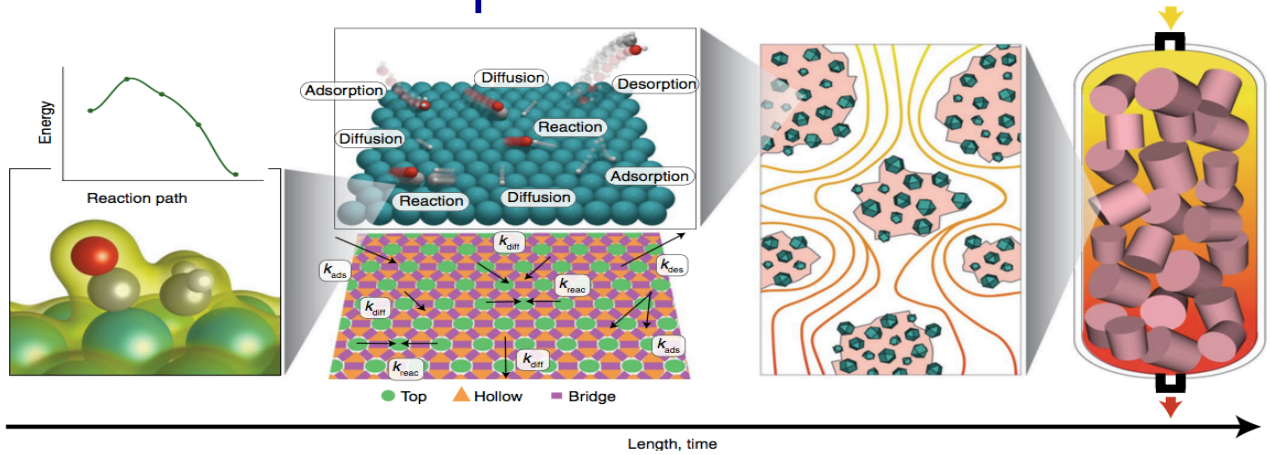
Proposal, Figure 1.2, grant agreement N^0 820444.

Essential current technologies fall short of being economically viable

- Thermal and electrochemical water splitting
- CO_2 reduction
- N_2 reduction
- Fuel cell chemistry
- Upgrade of biomass as a CO_2 source and for synthesis of speciality products

→ Abundant and hazard-free catalysts materials
→ Scalable processes
→ Stable catalysts also under fluctuating conditions

Catalysis is a multi-scale phenomenon



Nature Catalysis 2019, *2*, 659-670.

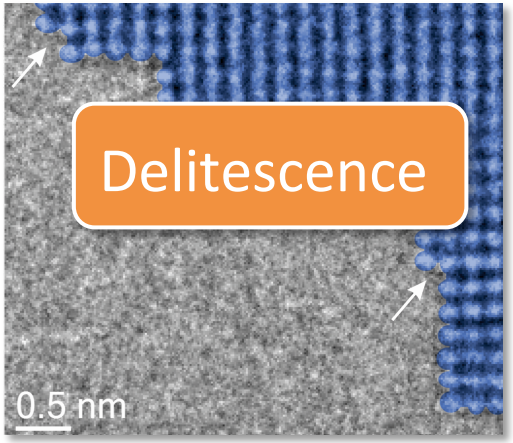
The catalyst changes the reaction mechanism by interacting with the reacting molecule(s), but not the thermodynamic equilibrium*: A phenomenon

- Under kinetic control
- Multi-dimensional in space and time (> 9 orders of magnitude)
- Depends on materials properties and the chemical potential of the environment
- Depends on periodic and discrete properties

*W. Ostwald, 1894

Two concepts - largely independently treated

Active site

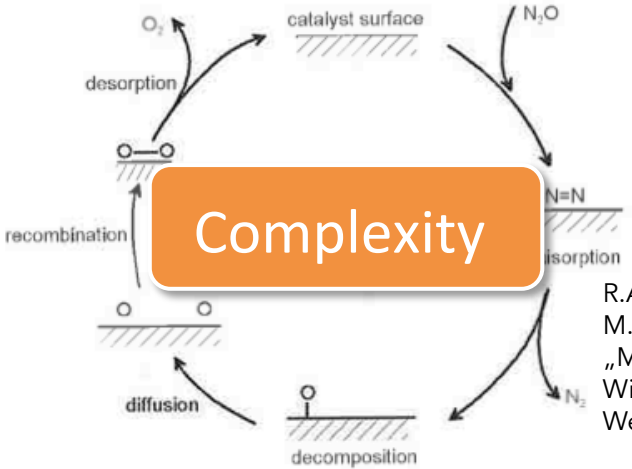


Journal of Catalysis **2015**, *326*, 560-573.

Catalyst-adsorbate interaction

*

Catalytic cycle / mechanism



R.A. van Santen, M. Neurock, „Mol. Het.Catal.", Wiley-VCH, Weinheim 2006

The active site enables bonding of the reacting molecule to the surface and allows exchange of charge and fragments – minority species

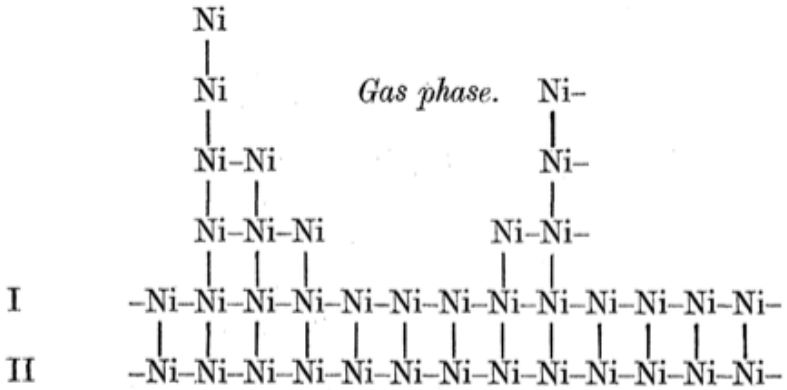
The catalytic reaction is comprised of a „cycle" which is made up of elementary steps

Dynamics

Delitescence

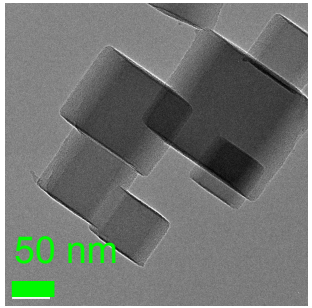
„The activation of such catalysts as platinum and silver gauzes when used in catalytic oxidation would be attributable ... to a production, ..., of metal atoms to a large degree unsaturated and detached from the normal crystal lattice of the metal and capable of adsorbing several molecular reactants.“

H. S. Taylor, *Proceedings of the Royal Society of London. Series A* **1925**, *108*, 105-111.



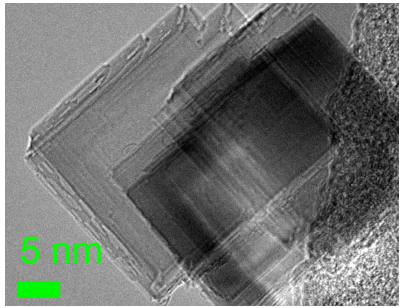
Delitescence – MgO in oxidative coupling of methane (OCM)

S-MgO



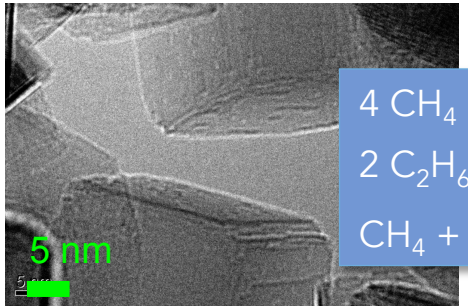
Mg combustion

C-MgO



Ultra pure commercial

SG-MgO



Sol-gel synthesis

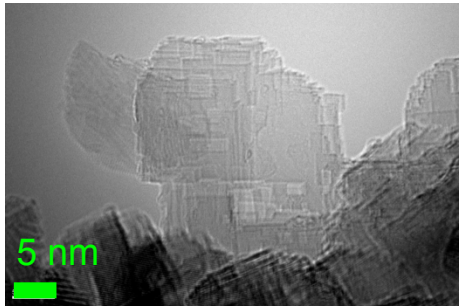
$4\ CH_4 + O_2 \rightarrow 2\ C_2H_6 + 2\ H_2O$

$2\ C_2H_6 + O_2 \rightarrow 2\ C_2H_4 + 2\ H_2O$

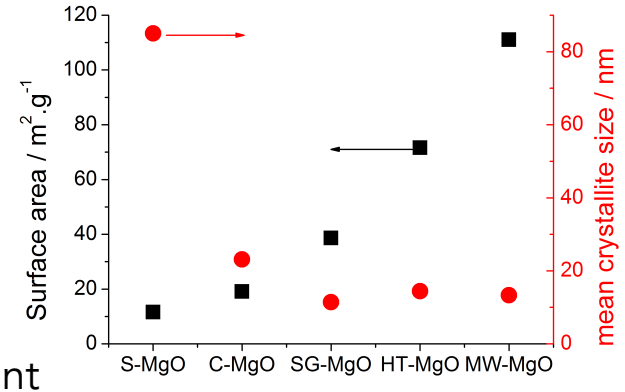
$CH_4 + 2\ O_2 \not\rightarrow CO_2 + 2\ H_2O$

Texturing of nanostructured MgO influences the surface area of the catalysts

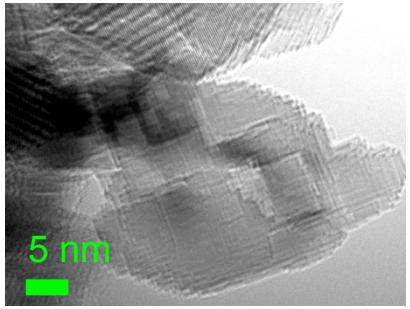
HT-MgO



Hydrothermal post treatment



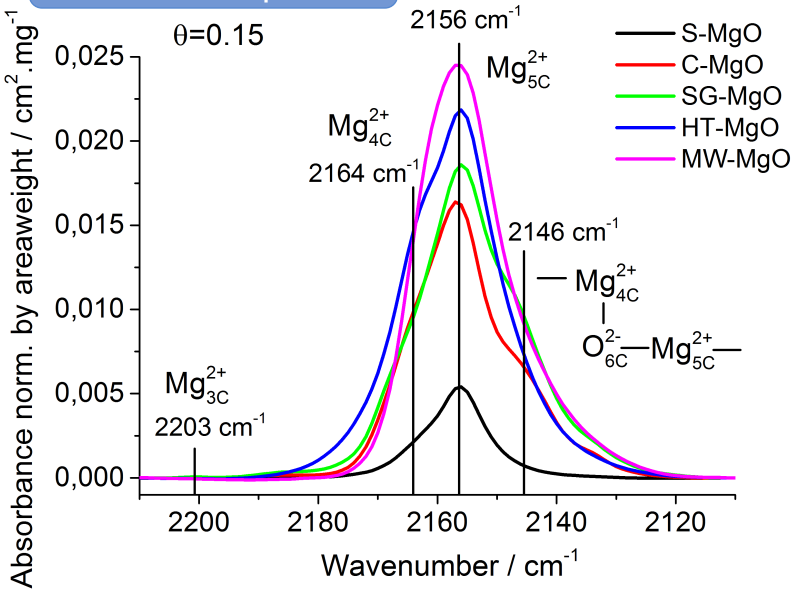
MW-MgO



Microwave synthesis

Delitescence – active site counting in initial state

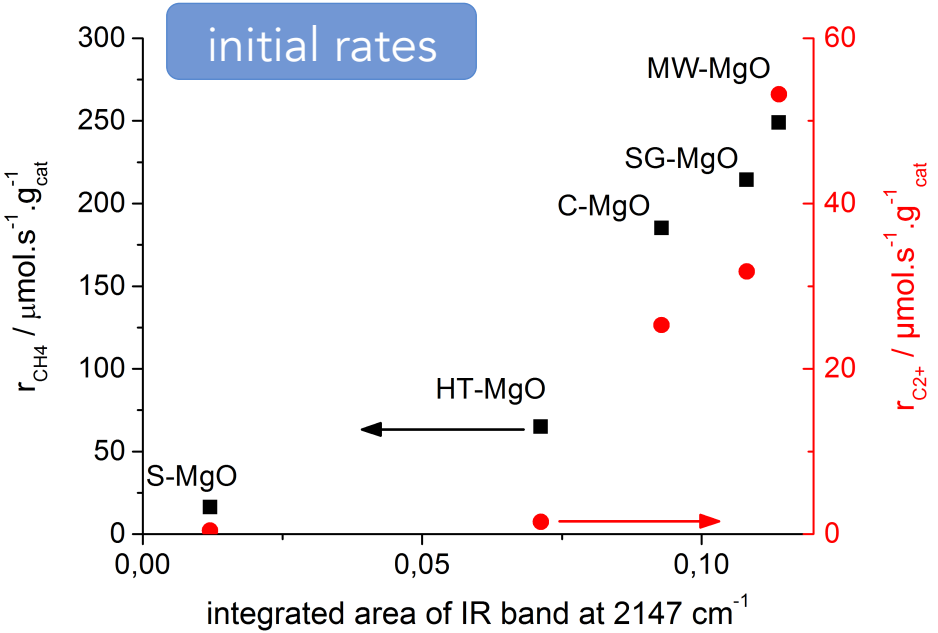
CO adsorption



Abundance of the various coordinatively unsaturated sites at the surface differs on the five different catalysts

Spoto *et al.*, *Prog. Surf. Sci.*, **2004**, 76, 71-146

initial rates



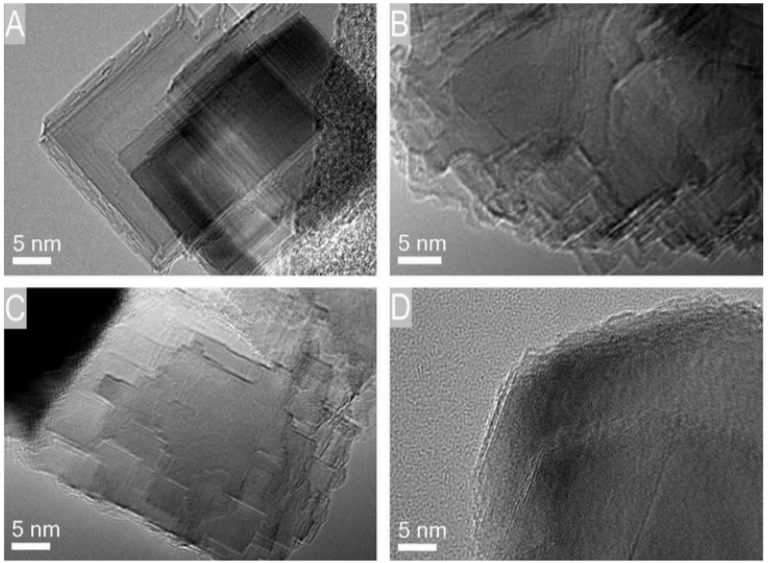
Correlation between the concentration of monoatomic steps (band at 2146 cm^{-1}) and the rate of CH_4 consumption and C_{2+} formation

Journal of Catalysis **2015**, *326*, 560-573.

Catalyst dynamics

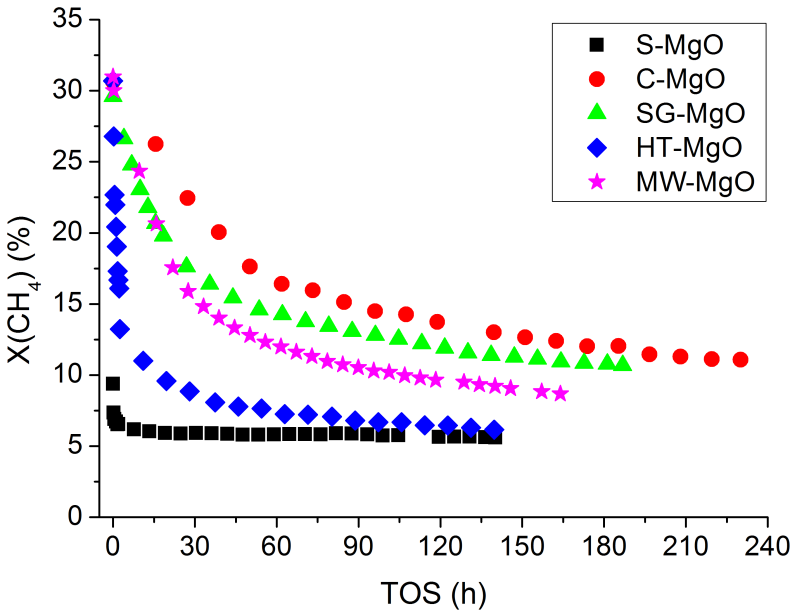
„The amount of surface which is catalytically active is determined by the reaction catalyzed.“

H. S. Taylor, *Proceedings of the Royal Society of London. Series A* **1925**, *108*, 105-111.



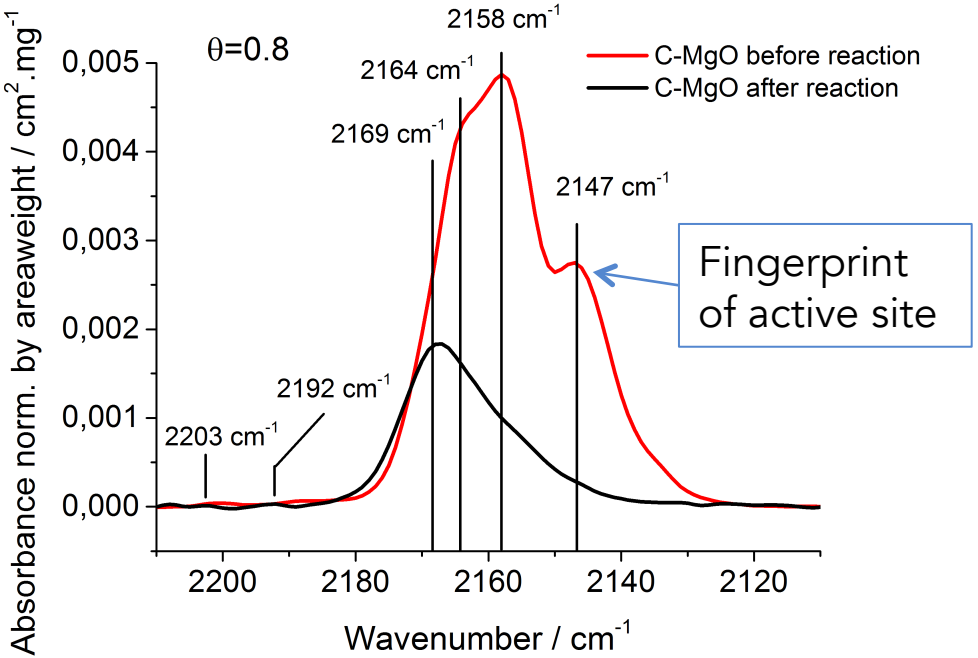
TEM images of C-MgO at different time on stream in the OCM reaction, same experimental condition as in Fig. 2. (A) Before reaction, (B) after 6 h TOS (SBET = 22.3 m2 g 1), (C) after 20 h TOS (SBET = 16.4 m2 g 1), (D) after 66 h TOS (SBET = 15.0 m2 g 1).

Catalyst dynamics



Fixed bed reactor, T = 1073 K,
W/F = 0.150 g.s.ml^{-1}, $CH_4/O_2/N_2$ = 3/1/1

CO adsorption



➔ Monoatomic steps vanish during OCM time on stream

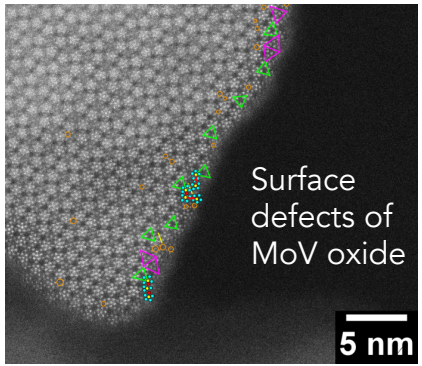
Journal of Catalysis **2015**, *326*, 560-573.

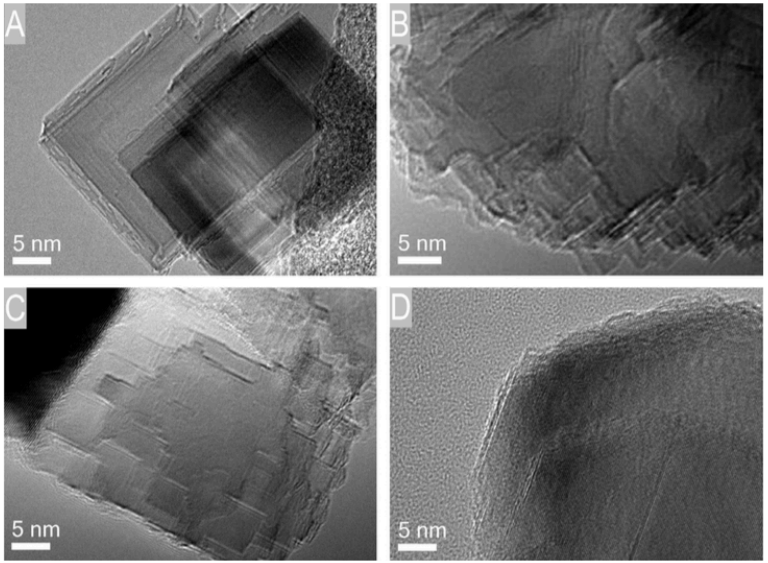
Catalyst dynamics

„The amount of surface which is catalytically active is determined by the reaction catalyzed.“

H. S. Taylor, *Proceedings of the Royal Society of London. Series A* **1925**, *108*, 105-111.

- We synthesize a precursor
- Active sites are embedded in a matrix and created in contact with the reactants
- Considerable structural changes may occur





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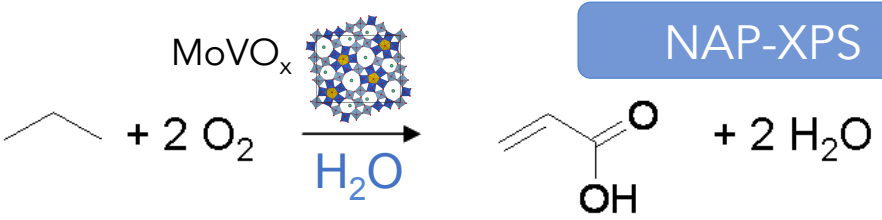
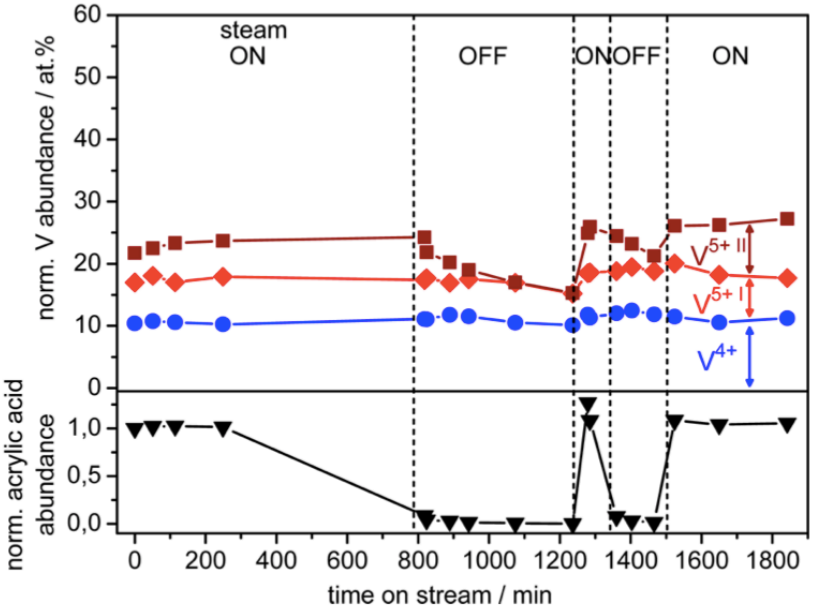
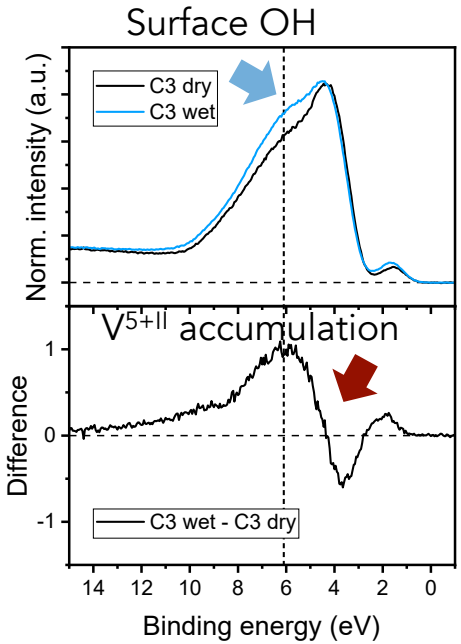


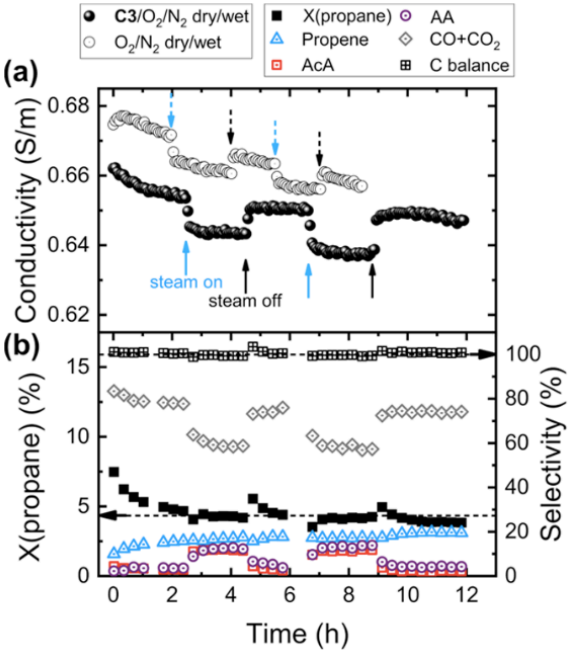
NAP-XPS

MCPT*

* Microwave cavity perturbation technique

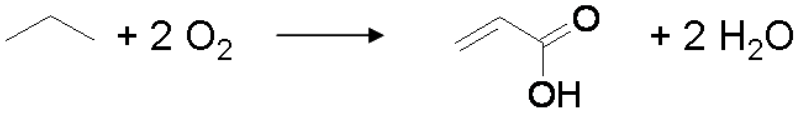




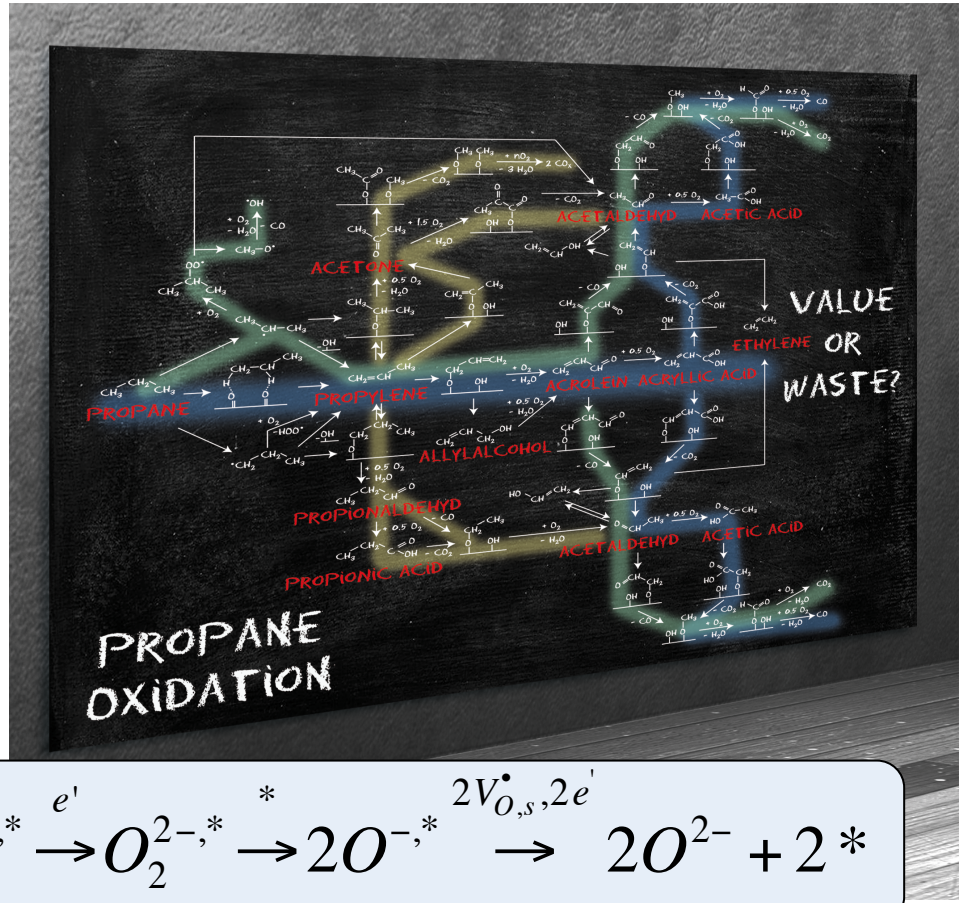


Journal of Catalysis **2012**, *285*, 48-60; *ACS Catalysis*, **2017**, *7*, 3061−3071;*J. Phys. Chem. C*, **2019**, *123*, 13269-13282.

Complex reaction networks



- Heterogeneously catalysed reactions are no elementary reactions
- Frequently, the reaction networks are complex comprising several hundreds steps
- Catalyst performance depends on process conditions and nature of active sites on the catalyst surface

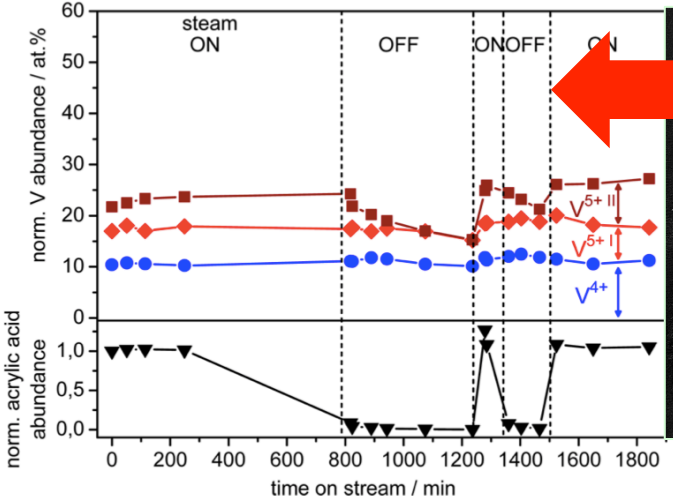


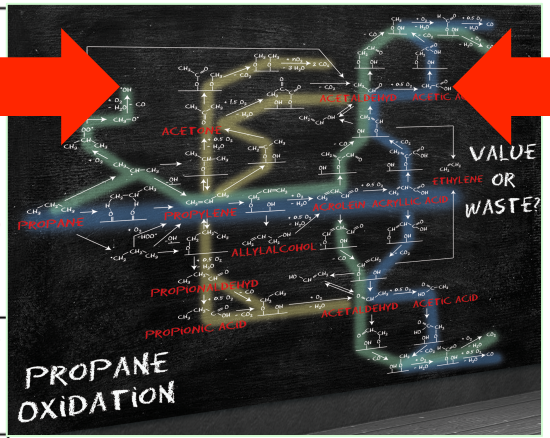
$$O_2^* \xrightarrow{e'} O_2^{-,*} \xrightarrow{e'} O_2^{2-,*} \xrightarrow{*} 2O^{-,*} \xrightarrow{2V_{O,s}^{\bullet},2e'} 2O^{2-} + 2*$$

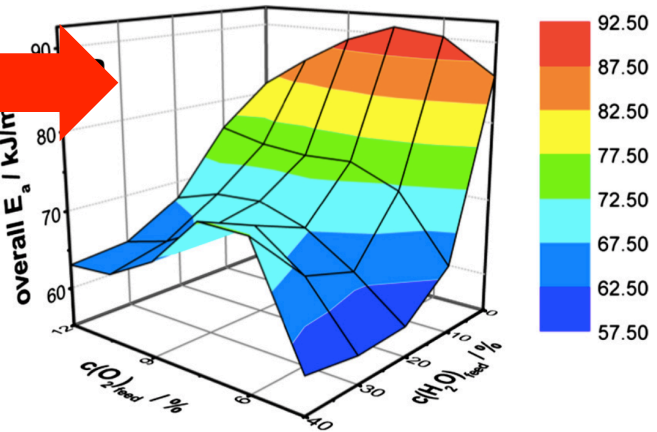
P. Kube *et al.*, ChemCatChem 2017, 9, 3446 – 3455.
P. Kube, *et al.*B., ChemCatChem 2017, 9, 573-585.

Feedback loops make predictions difficult

- The measured catalytic properties are macroscopic properties (integral rates, apparent activation energy)
- Reaction mechanism, rate-determining steps and the nature of the active surface can be derived from kinetic studies and *operando* experiments
- Theory can provide insight into the energetics of adsorbate-catalyst interaction and bond breaking/formation events (microkinetic model)
- Theory requires input from experiment or is based on assumptions



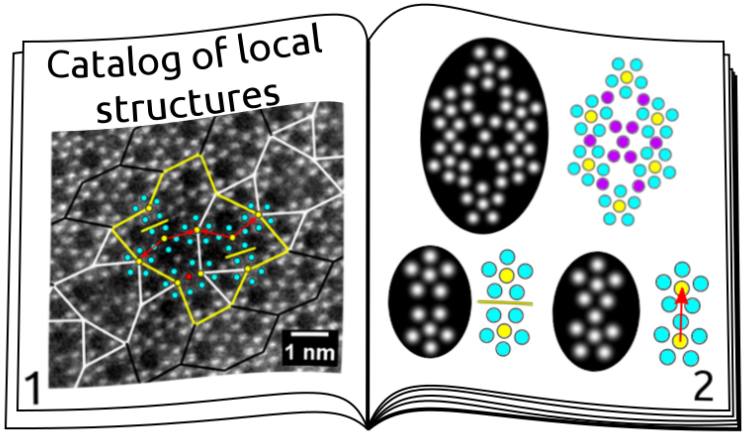


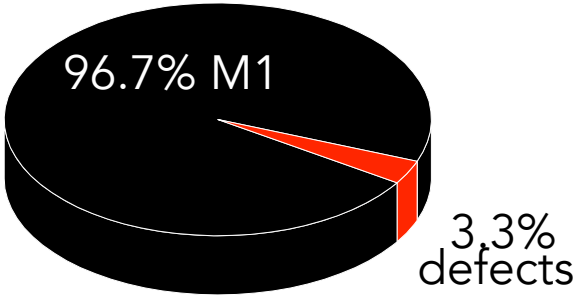


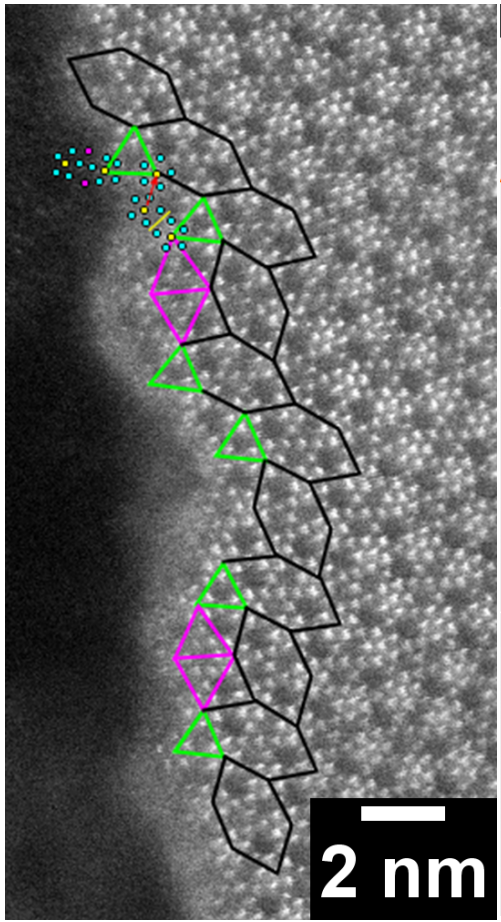
Journal of Catalysis **2012**, *285*, 48-60; *ACS Catalysis*, **2017**, *7*, 3061−3071; ***J. Phys. Chem. C***, **2019**, *123*, 13269-13282.

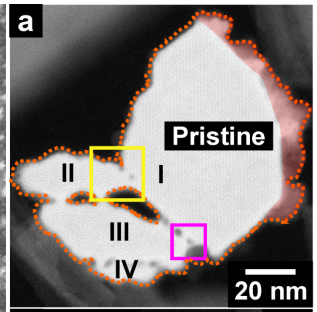
Defects

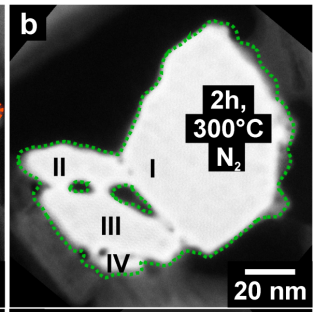
$(Mo_{610}V_{230}M_{70})O_x$

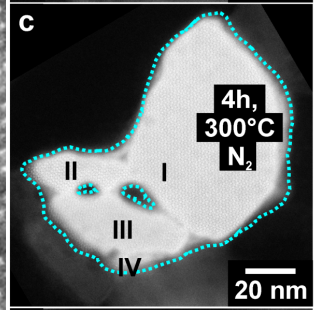


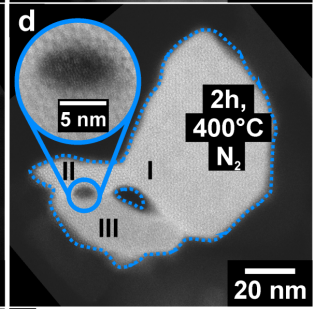


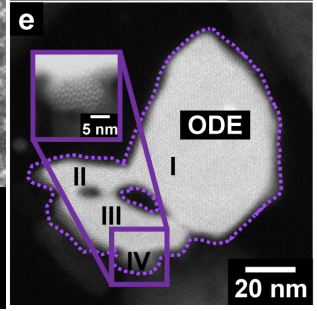


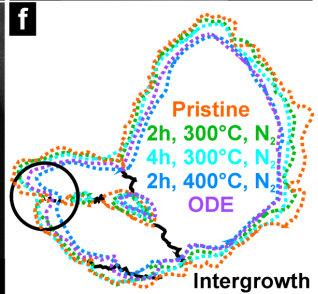












L. Masliuk, *et al.*, *Journal of Physical Chemistry C*, **2017**, *121*, 24093−24103.

Challenges

- Catalysis is a kinetic phenomenon
- Delitescence: The active surface sites are frequently minority species (defects, impurities), difficult to detect in presence of chemically similar spectator species
- Complexity: The reaction network frequently consists of numerous steps
- Dynamics: The kinetics are influenced by process conditions and nature of active site; The active sites show a dynamic response to the gas phase composition
- Predictions are so difficult, because the atomic-scale structure and the dynamic response of the structure to the environment are difficult to analyse and the descriptors are complex

Demands on successful commercial catalysts

- High activity per unit volume in the eventual reactor
- High selectivity towards the desired product at optimized conversion
- Low selectivity to by-products that generate purification and waste problems
- Sufficient long life time with respect to deactivation
- Possibility to regenerate
- Reproducible preparation
- Sufficient thermal stability or stability against volatilization
- High mechanical strength
- High attrition resistance

Academic questions

- What are the fundamental processes that occur at the catalyst surface?
- What system parameters control the reactivity?
- Can we predict catalytic properties and “design” catalysts?

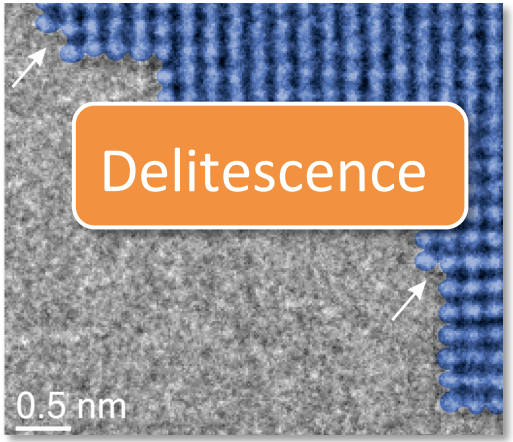
Universal and quantitative insight into nature of the “active site” and the reaction mechanism

➔ Measurement of activity, selectivity, and stability are carried out at the macro-scale and will not answer these questions

➔ Integration of experiment and theory necessary

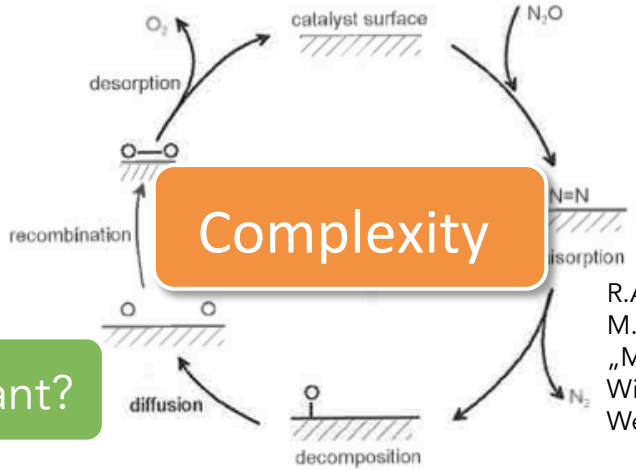
Challenges and chances: Coping with complexity

Active site



Journal of Catalysis **2015**, *326*, 560-573.

Catalytic cycle / mechanism



R.A. van Santen, M. Neurock, „Mol. Het.Catal.", Wiley-VCH, Weinheim 2006

Theory

*

What is important?

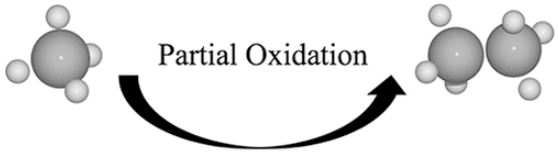
Complexity

Big* data / AI

Dynamics

*but with much less data compared to YouTube (10^9 GB)

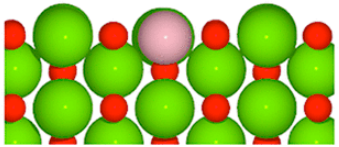
Systematization



Mitteilungen.

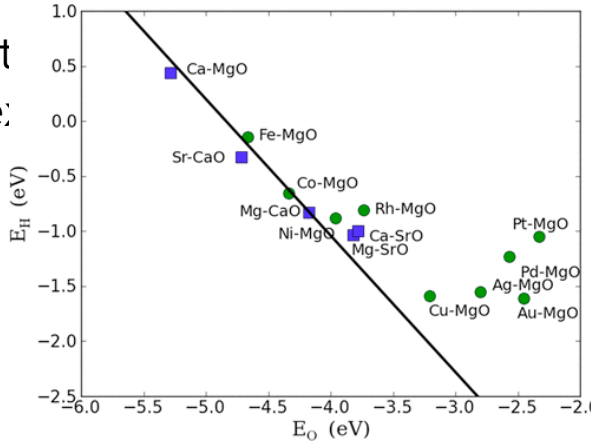
258. Paul Sabatier: Hydrogénations et déshydrogénati par catalyse.

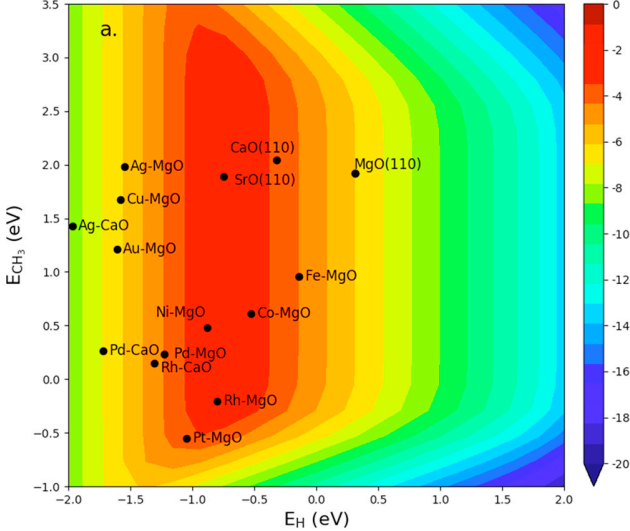
[Vortrag, gehalten vor der Deutschen Chem. Gesellschaft am 13. Mai 19

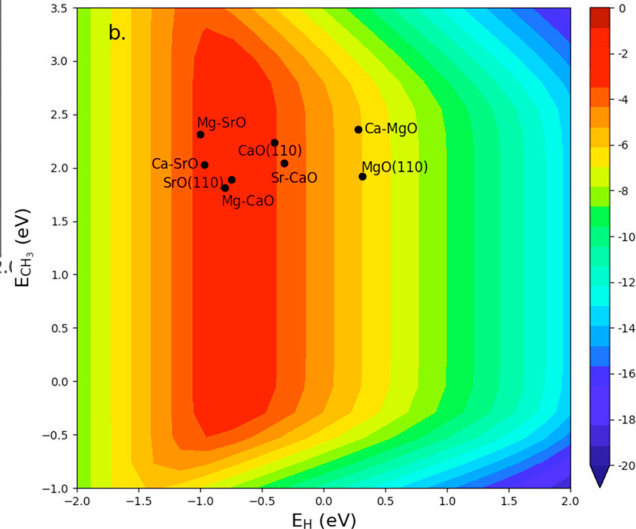


At least one of the reacting molecules forms a complex wit the catalyst. When the comple is too stable, the catalyst will become poisoned. When it is too unstable, the reaction will not proceed.

→ Scaling relations



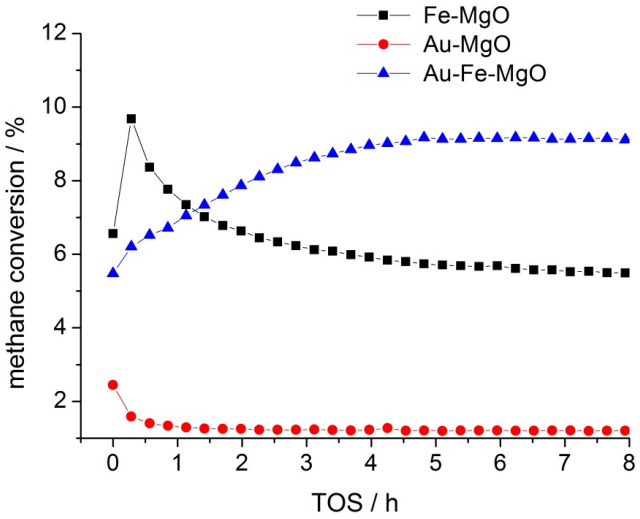


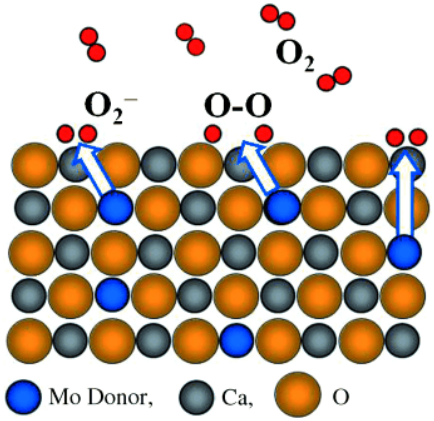


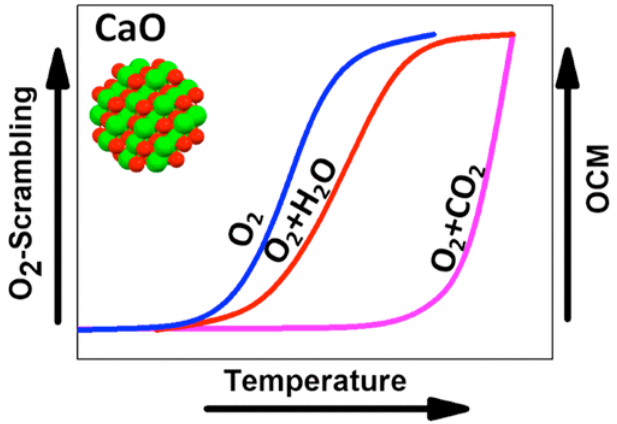
Relations between hydrogen binding energy (E_H) and the oxygen vacancy formation energy (E_O) (McFarland, E. W.; Metiu, H., Catalysis by Doped Oxides. *Chemical Reviews* **2013,** *113*, 4391-4427.)

Aljama, H.; Nørskov, J. K.; Abild-Pedersen, F., Tuning Methane Activation Chemistry on Alkaline Earth Metal Oxides by Doping. *The Journal of Physical Chemistry C* **2018,** *122*, 22544-22548.

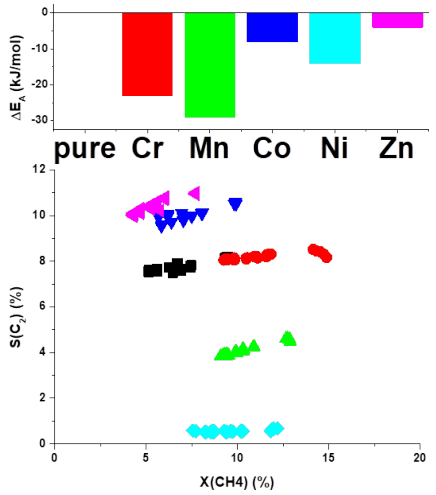
Defects and impurities







J. Phys. Chem. C, **2019**,*123*, 7495-8468.



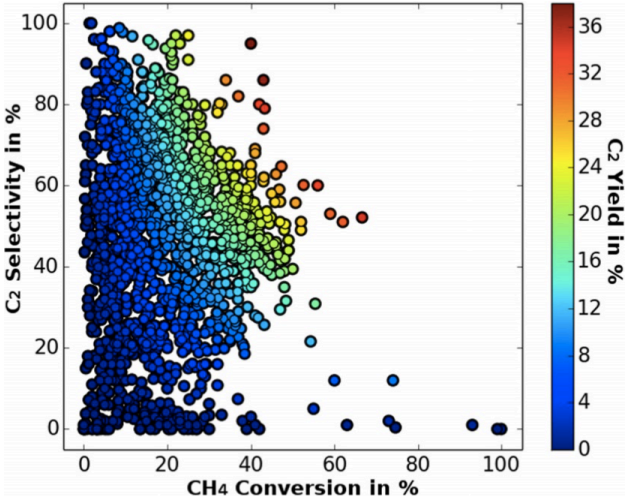
Cui, Shao, Baldofski, Sauer, Nilius, Freund, *Angew. Chem. Int. Ed.*, **2013**, *52*, 11385.
P. Schwach, M. G. Willinger, A. Trunschke, R. Schlögl, *Angew. Chem. Int. Ed.* **2013**, *52*, 11381.

0.1% dopant concentration
L. Thum, in preparation.

Information management in catalysis

- Expert systems
  Chem.-Ing.-Tech. **1990**, *62*, 365.
- High-throughput testing
  Angew. Chem. Int. Ed. **2004**, *43*, 5347.
  - Catalyst screening
  - Screening of reaction conditions
- Speeding up combinatorial testing: Generic algorithms
  REVIEW OF SCIENTIFIC INSTRUMENTS **2005**, *76*, 062208.
- Extraction of literature data
  - Decision trees
  - PCA

DECADE	CO hydrogenation
INCAP	ODH
ESKA	hydrogenation
Catalyst II	kinetic modelling



Zavyalova, U.; Holena, M.; Schlögl, R.; Baerns, M., *ChemCatChem* **2011,** *3*, 1935-1947.

Takahashi, K.; Miyazato, I.; Nishimura, S.; Ohyama, J., *ChemCatChem* **2018,** *10*, 3223-3228.

No breakthrough, because

- Dynamics were not taken into account
- No public access to catalysis data
- Generation of experimental input must adequately support the requirements of machine learning and re-usability of data

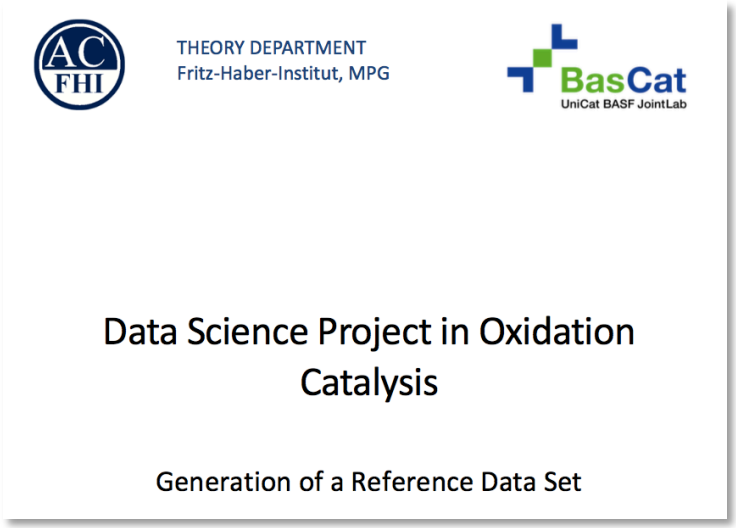
Data

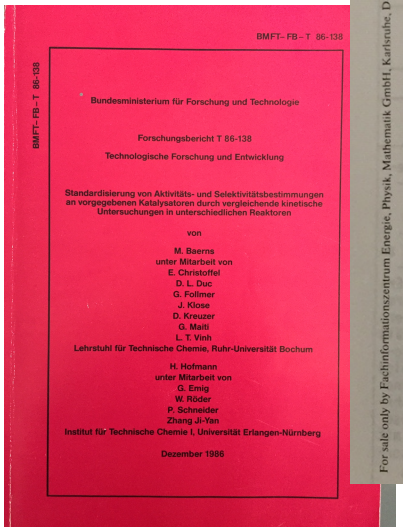
- Data will have to be
  - Well documented by meta data
  - Stored in a findable way
  - Documented and stored in a re-useable form
  - Clean enough to be interoperable with later and external analysis
  - Complete enough to allow reconstruction of the experiment
- This will eventually be a legal requirement coming with grants
- Users need to share much more information than in papers with a much better formalized organization
- The general availability is to the benefit of all as we can collaborate and test new hypotheses much easier than today

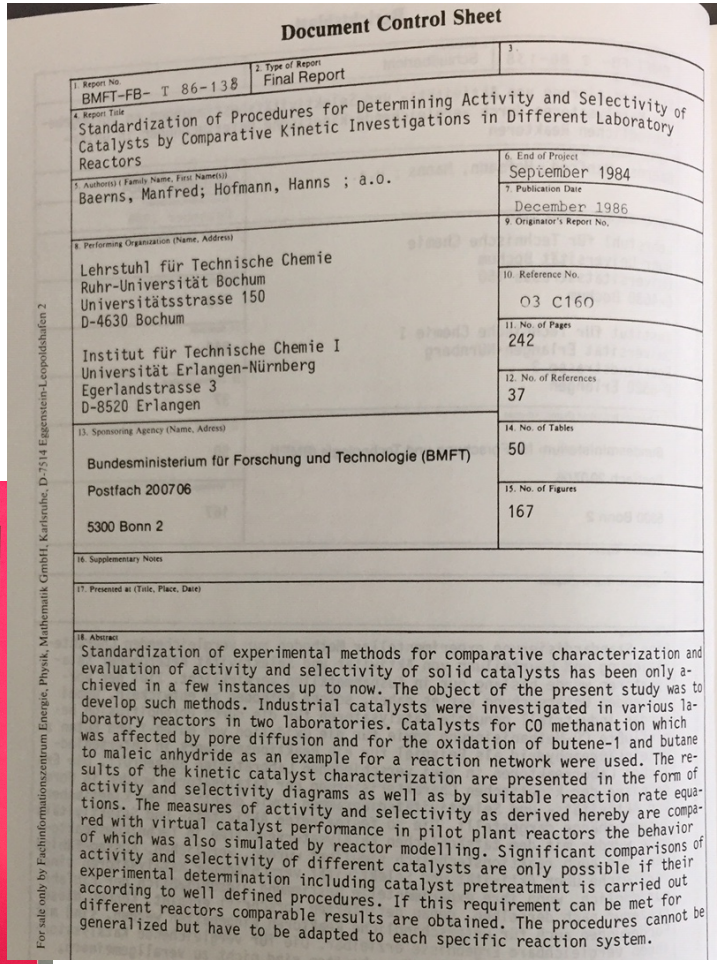
Data

- Literature data are frequently inconsistent
- Data quality unclear
- Diversity of data limited – no bad catalysts published

Aim:
Predicting better catalysts based on clean data







Conclusion

- Attempts to systematize knowledge and to apply computer science in catalysis go back to early times
- The aim of research is to predict performance based on microkinetic models; This requires
  - Integration of experiment and theory
  - Knowledge about atomic-scale structure of the active surface and the response of the structure to the environment
- Challenge: Descriptors are needed that involve both, kinetics of reactants and catalyst material
- Chance: Determine a large number of observables from a wide range of structurally divergent systems and apply data science to learn what is important
- Search for a complex descriptor with many components
- Interpolating missing data in literature reports based on such descriptors can enhance and enlarge the database very significantly

Thank you for your attention and enjoy the interface!