SHARED METADATA AND DATA FORMATS FOR BIG-DATA DRIVEN MATERIALS SCIENCE: A NOMAD-FAIRDI WORKSHOP

IRIS Adlershof, Berlin, Germany, July 8th to 12th, 2019

Specifics of metadata and design of experiment in heterogeneous catalysis research

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Catalysis: systemic challenge

Theorist's simplified view (Paul Saxe):

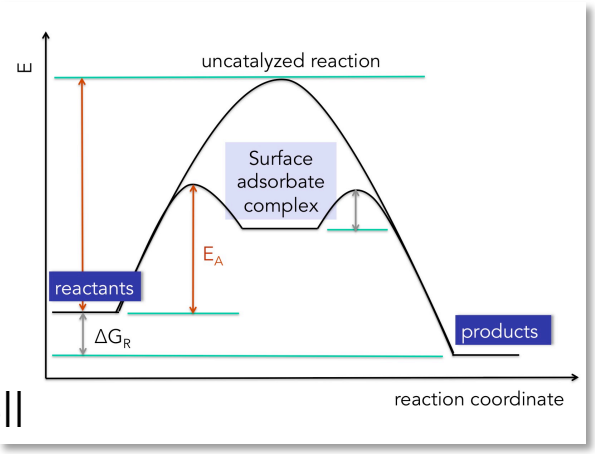
"Experiment has real problems:

- What is the sample, exactly?
- What was actually measured?"

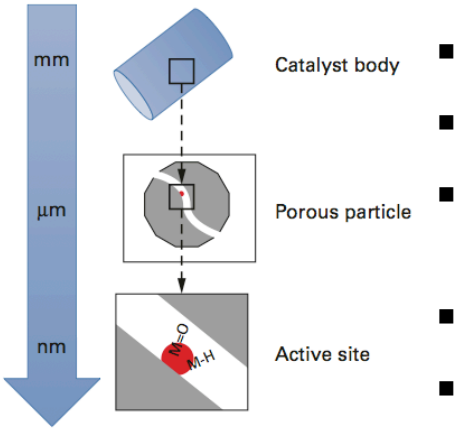
Situation in catalysis (or functional characterization) is even worse:

- The functional properties are determined by stochastic entities rather than stable features
- Materials properties need to be analyzed under operation
- Multidisciplinary approach necessary

Catalysis: systemic challenge



- The catalyst changes the reaction mechanism by interacting with the reacting molecule(s), but not the thermodynamic equilibrium: a phenomenon under kinetic control
- Mutual interaction causes changes of the catalyst as well
- Heterogeneous catalysis occurs at interfaces as functional unit: solid state versus molecular control?



- Multi-dimensional in space and time
- Selectivity requires control over complex reaction networks
- Chemical dynamics: interplay between kinetics and solid-state reactions
- Integrated workflow between theory - experiment – engineering
- Catalysis research requires collaboration

BasCat – FHI collaboration: Concepts in Heterogeneous Catalysis

Fritz-Haber-Institut
Inorganic Chemistry
Theory

BASF
We create chemistry

Technische
Universität
Berlin

unisyscat

Ambition:

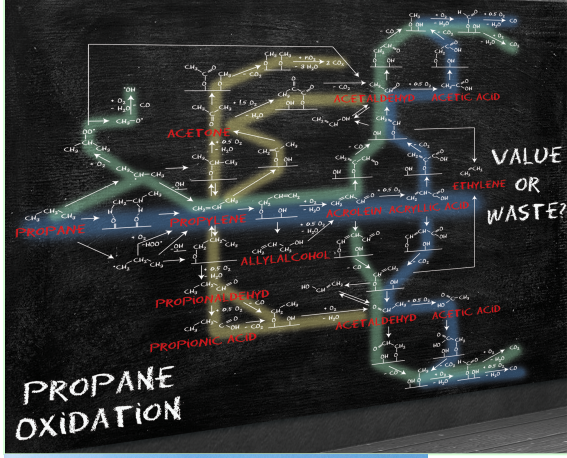
Predicting high performance based on physical insight

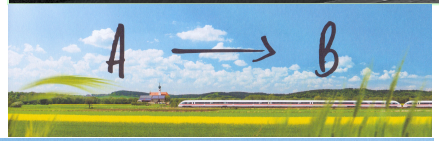
- Materials
- Reaction conditions
- Predictions by theory

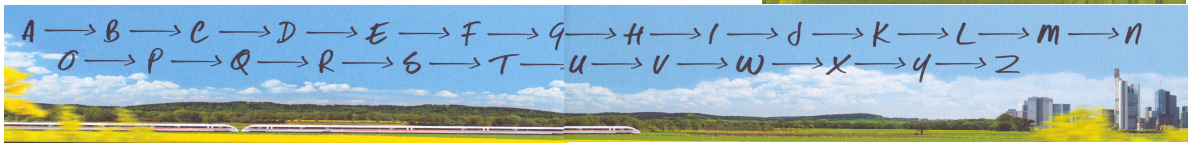
Descriptors in catalysis

- Identifying causal structure-function relations
- Target: high rate of formation of a desired product
- Property "rate" is a challenge as dependent on reaction networks and falsified by transport phenomena

$$X_i = \frac{n_{i,0} - n_i}{n_{i,0}} \qquad S_{k,i} = \frac{n_k}{n_{i,0} - n_i} \cdot \frac{|\nu_i|}{|\nu_k|} \Rightarrow r = \frac{1}{\nu_i} \frac{dn_i}{m_{cat} dt}$$





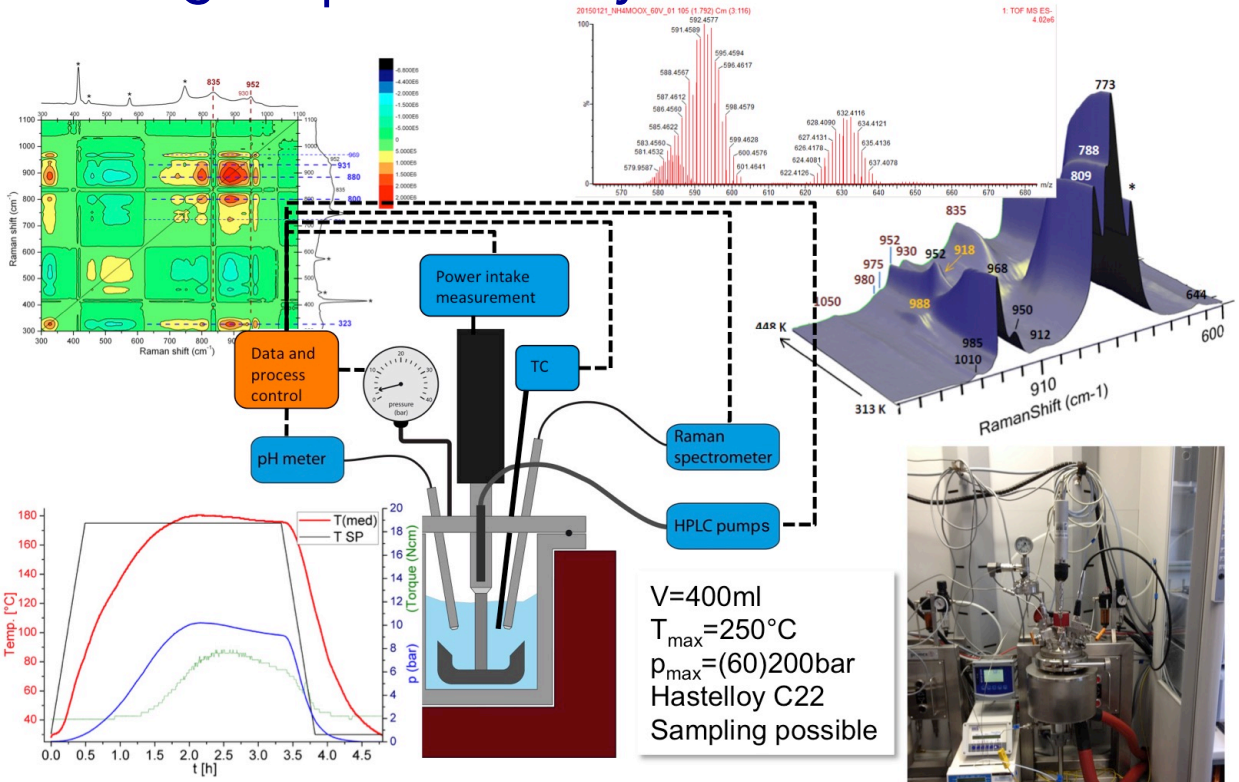


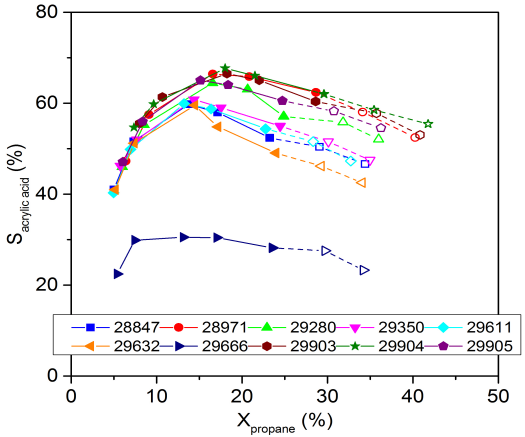
- Structure is also challenging as dynamical and with unknown number of "active sites"

$$TOF\left[s^{-1}\right] = \frac{N_i}{N_{sites} \cdot t}\left[s^{-1}\right]$$

- Difficult or impossible to measure in heterogeneous catalysis because N_{sites} is unknown or fluctuating

Challenge: reproducible synthesis



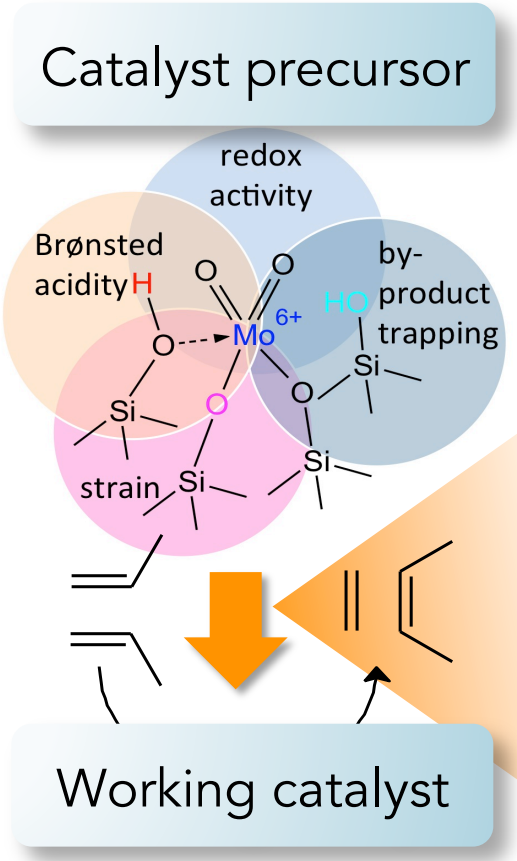


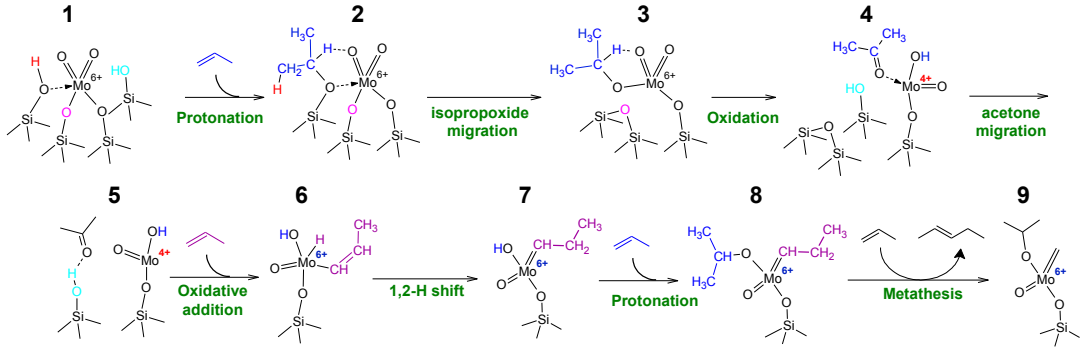
HPM-PT-040 (Premex Reactor GmbH)
Kaiser Optics Raman Spectrometer RXN1

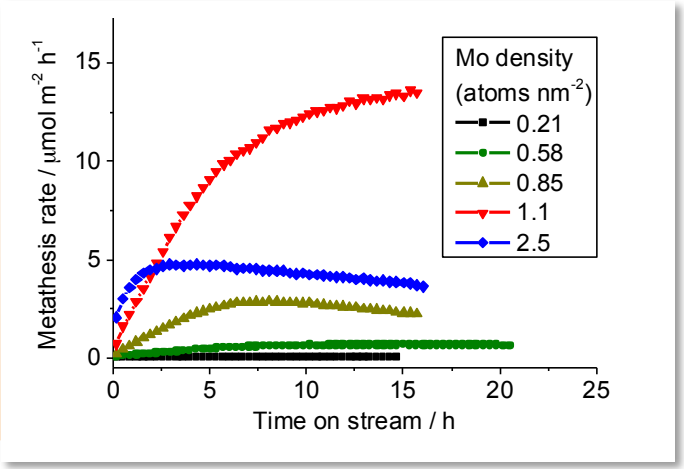
- Automated synthesis reactors deliver synthesis metadata
- Difficulties in automation:
  - Separation and washing steps
  - Activation phenomena

Zeitschrift für anorganische und allgemeine Chemie 2014, *640*, 2730-2736.

Challenge: activation – deactivation phenomena







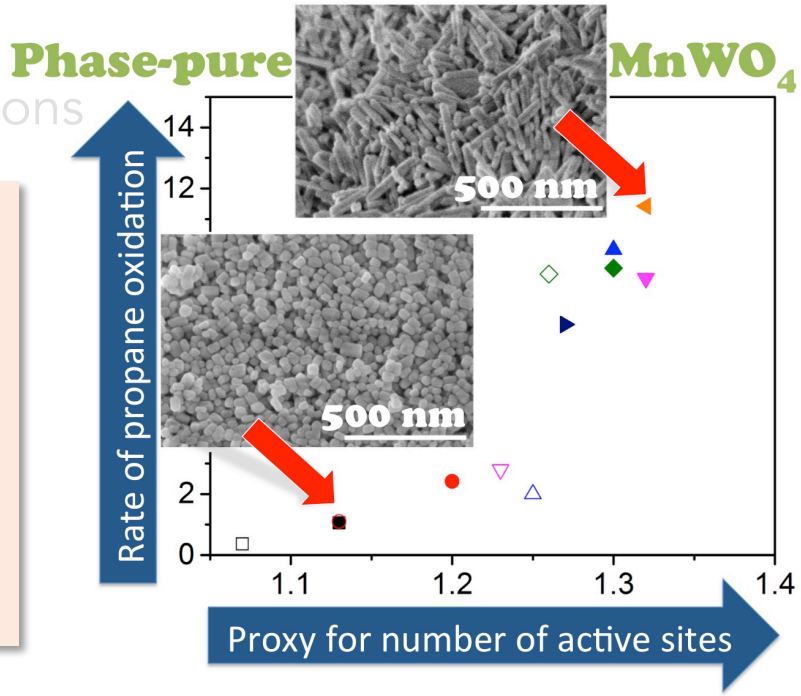
- Steady-state criterion
- Metadata will not help to detect violation if single rates are provided
- Agreements about procedure of kinetic studies necessary

JACS, **2012**, *134*, 11462-11473; *Angew. Chem. Int. Ed.* **2013**, *52*, 13553-13557. *ChemCatChem*, **2015**, *7*, 4059-4065.

Challenge: (Dynamic) interface

- Surface properties essential
- Dynamical surface nature
- Reaction network
- Activation energy is a function of conditions

- Same crystal structure of all catalysts in the series
- Identical chemical bulk composition
- Catalytic properties depend on surface composition
- The bulk crystal structure of an oxidation catalyst as the most popular descriptor in oxidation catalysis is not solely responsible for catalytic performance



Chemical Science, **2019**, *10*, 2429–244 .

Challenge: (Dynamic) interface

- Surface properties essential
- Dynamical surface nature
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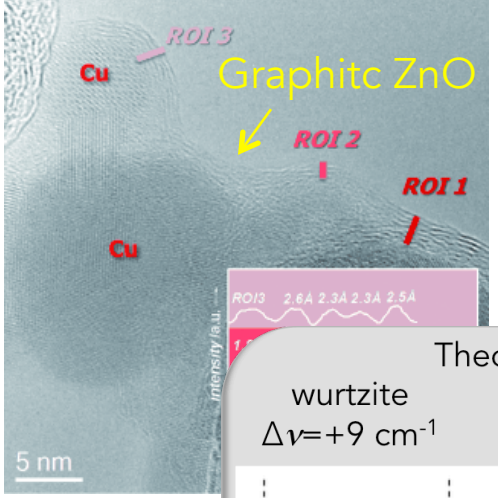
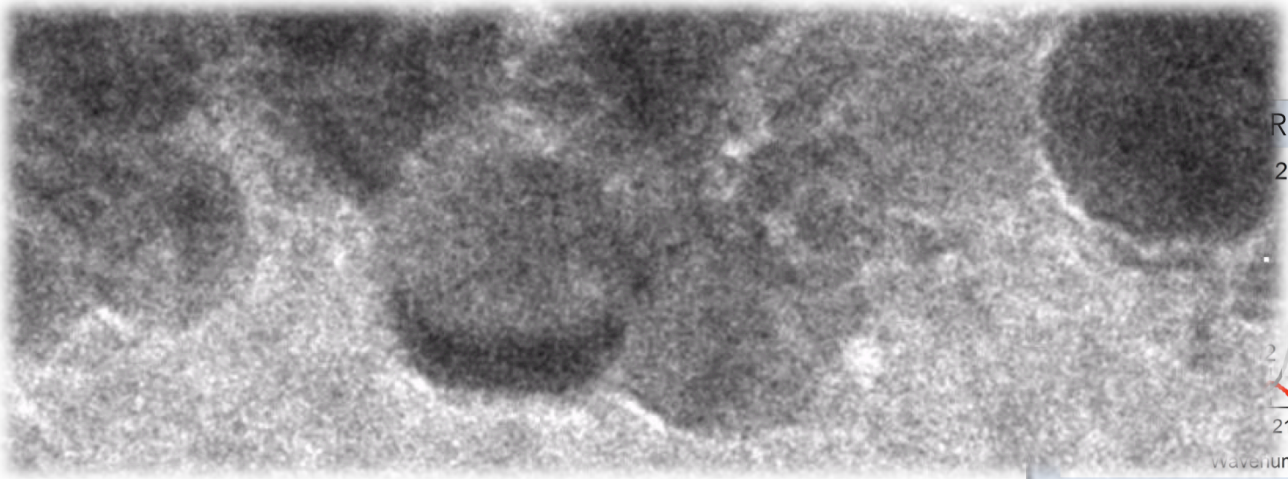
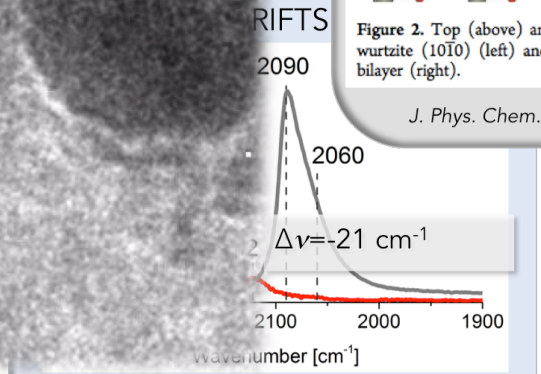
Reverse water gas shift
250°C,
1:1:8 CO_2:H_2: He
65 mbar







300 K, 0.5 ML

Top. Catal. **2017**, *60*, 1735–1743.

Theory

wurtzite	graphitic ZnO
$\Delta\nu$=+9 cm^{-1}	$\Delta\nu$=-23 cm^{-1}

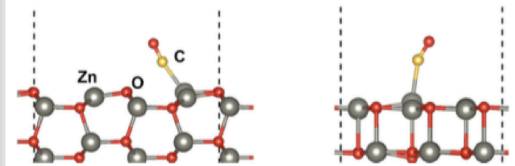


Figure 2. Top (above) and side views (below) of (a) CO adsorbed wurtzite ($10\bar{1}0$) (left) and (b) CO adsorbed on unsupported ZnO bilayer (right).

J. Phys. Chem. C **2017**, *121*, 27453–27461.

Angew. Chem. Int. Ed. **2015**, *54*, 4544–4548.

Challenge: (Dynamic) interface

- Surface properties essential
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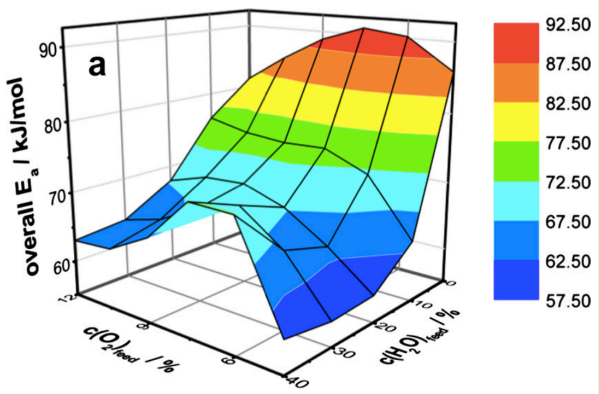
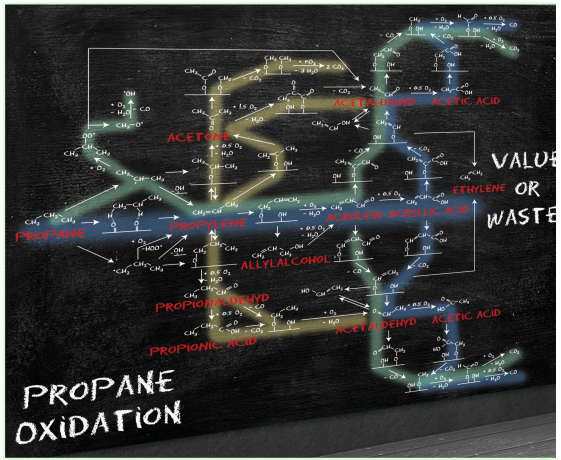
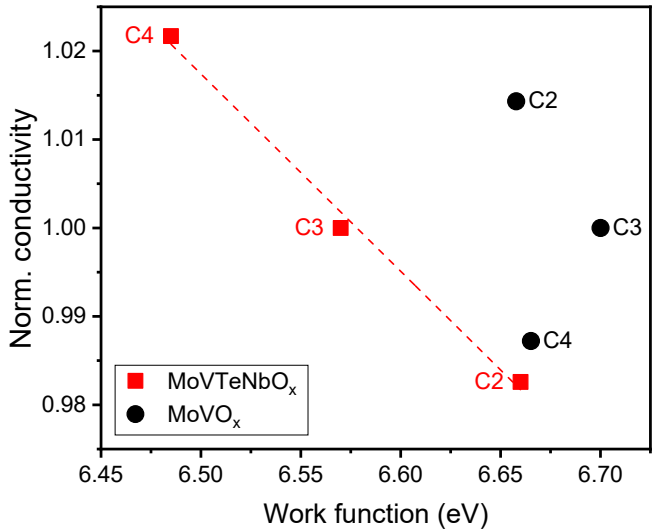
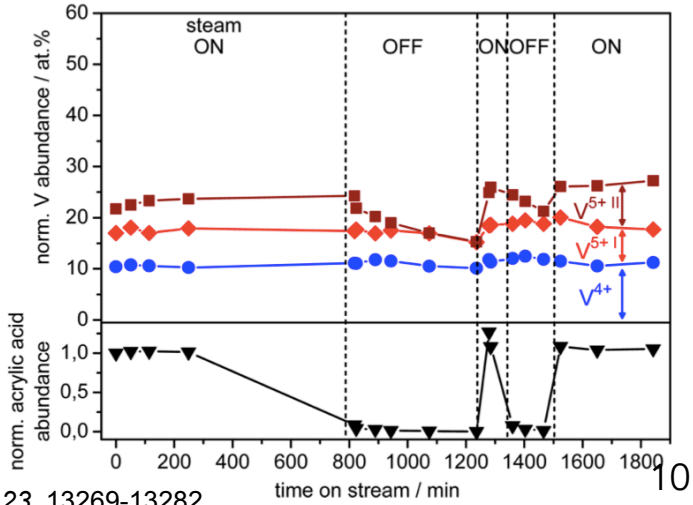








Challenges in catalysis

- The rate depends on the reaction network and may be falsified by transport phenomena, which is not always detectable, even if all metadata of the rate determination are stored
- The nanostructure and bulk real structures control the ability of a material to respond to the local chemical potential
- Active sites occur locally during the reactant-induced instability of the reactive surface phase
- We hope that properties of the precursor are reflected in the properties of the working catalyst – and we could check this with the help of machine learning
- But, we should better generate data and metadata of rate determination and physical characterization in one experiment simultaneously – in operando

The concept of clean data in catalysis

- 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

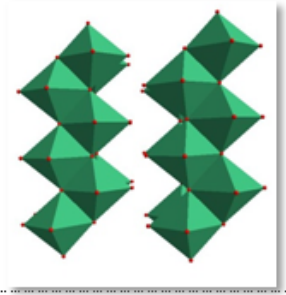
The concept of clean data in catalysis

- Standardisation of experiments
- A handbook of selective oxidation was developed
- A set of 10 structures was defined to be tested in three different (ethane, propane, butane) reaction networks
- This combination covers a wide space of structures and function comprises the necessary diverseness of data
- All kinetic operations are validated against material standards
- The kinetic test procedure and the total history of each sample is defined
- Data are stored in an in-house database
- Additional experiments are required to understand the relation results

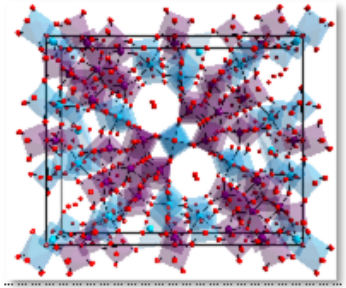
Data Science Project in Oxidation Catalysis

Generation of a Reference Data Set

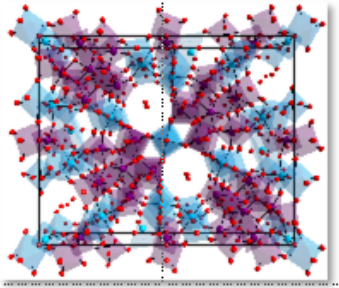
Catalysts



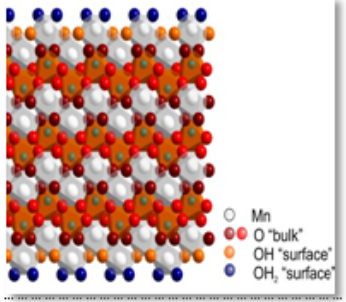
MoO_3



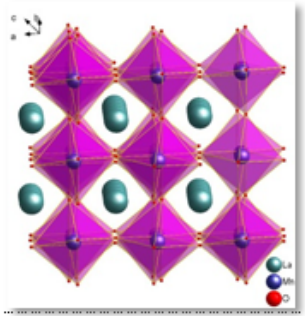
Mo-V oxide



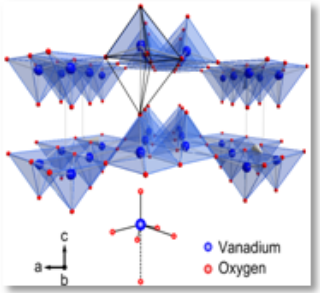
Mo-V-Te-Nb oxide



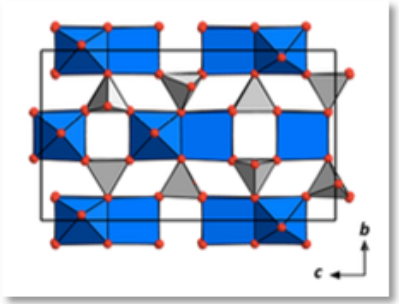
$MnWO_4$



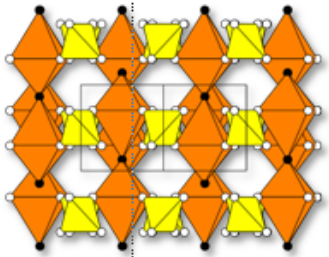
$SmMnO_3$



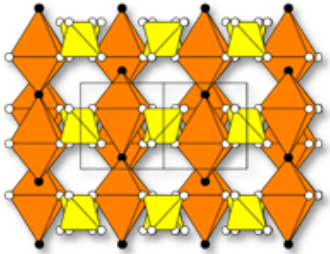
V_2O_5



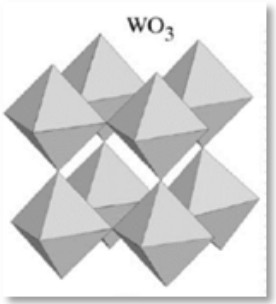
VPP/VPO



α_{II}-$VOPO_4$



α_{II}-$V_{0.8}W_{0.2}OPO_4$

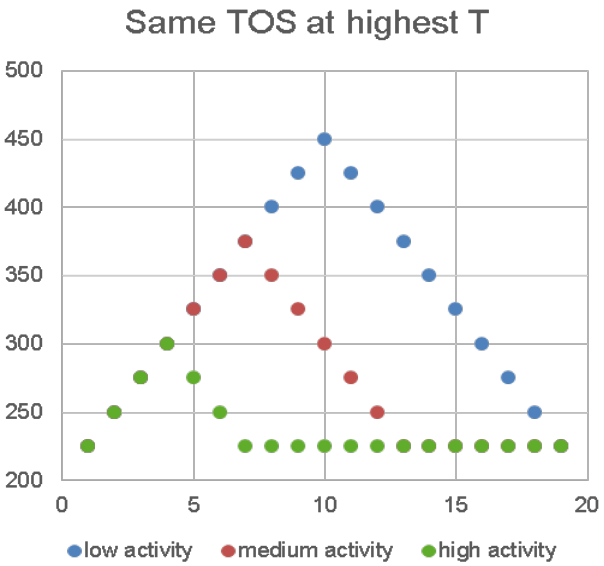


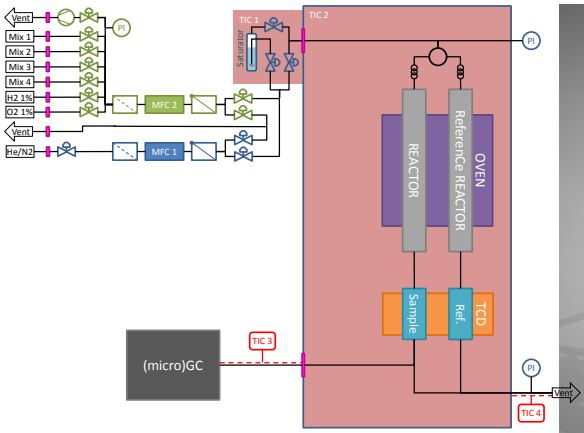
$V_{0.167}W_{0.5}P_{0.333}O_x$

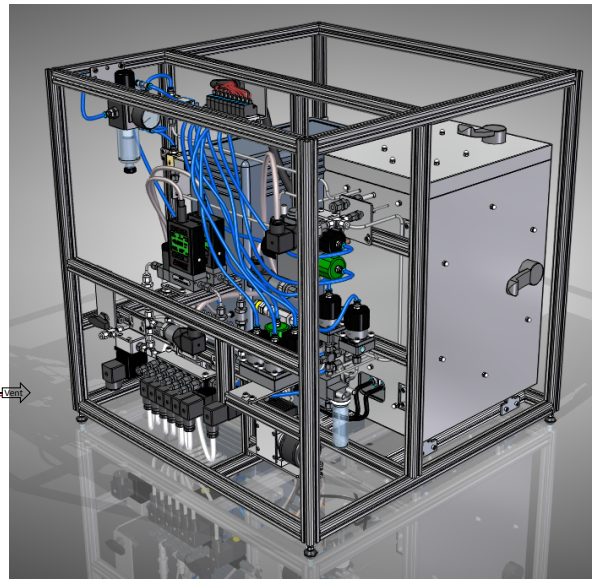
Catalytic testing

Oxidation of ethane, propane, *n*-butane

1. Temperature variation
2. Contact time variation
3. Determination of rates in different feeds







Labview based process control with real time CompactRIO controller

Catalytic testing

Catalyst ID	Feed	r (300°C) [mmol g^{-1} h^{-1}]	r (300°C) [mmol m^{-2} h^{-1}]	E_a [kJ mol^{-1}]	TR [°C] X=30%	r (TR) [mmol g^{-1} h^{-1}]	r (TR) [mmol m^{-2} h^{-1}]	r_{CO2} (TR) [mmol m^{-2} h^{-1}] X=10%	r_{CO2} (TR) [mmol m^{-2} h^{-1}] X=30%	r_{CO2} (TR) [mmol m^{-2} h^{-1}] X=60%
1	Standard									
	Less O_2	-	-	-	-					
	ODH	-	-	-	-					
	Fuel rich	-	-	-	-					
	5% water	-	-	-	-					
	10% water	-	-	-	-					
	20% water	-	-	-	-					
2	Standard									
	Less O_2	-	-	-	-					
	ODH	-	-	-	-					
	Fuel rich	-	-	-	-					
	5% water	-	-	-	-					
	10% water	-	-	-	-					
	20% water	-	-	-	-					
...										

Training values P_i - Descriptive features

Property	Physical value	Methods
Bulk crystal structure (ICSD#)	Lattice constants *a*, *b*, *c* [Å], α, β, γ [°] Unit cell volume *V* [nm^3] crystallographic density $\rho_{crystal}$ [g/cm^3]	XRD, TEM
Bulk chemical composition	c_M, c_O [at%]	XRF, ICP-OES, EDX
Surface composition	c_M, c_O [at%] surface active site density [nm^{-2}]	XPS
Binding energy, surface oxidation state	B.E. [eV], M^{n+}	XPS
Valence band onset, M nd onset, *E* secondary electron cutoff, work function, maximum band bending at the surface "s" (surface potential barrier), change in electron affinity	E_{VB}, E_{nd}, E_{cutoff}, Φ, eV_s, ΔX [eV]	XPS, NAP-XPS, ResPES
Absorption edge energy	O K-Edge, V L_3-Edge [eV]	NEXAFS

Training values P_i - Descriptive features

Property	Physical value	Methods
Specific surface area (BET) Total pore volume, mesopore volume	S_{BET} [m^2/g] V_{total}, V_{mp} [m^3/g]	Nitrogen adsorption
Heat of adsorption Ads. capacity of reactants (C_nH_{2n+2}, O_2)	ΔH_{ads} [kJ mol^{-1}] n [mol/g]	Microcalorimetry
Conductivity, real part of permittivity ε', imaginary part of permittivity ε'', Apparent activation energy of conduction	σ [S/m], ε', ε'', E_c [eV]	MCPT
Optical edge energy	E_{edge} [eV]	UV/Vis
Oxidation/reduction equivalents	Oxygen defect density [$V_o^{\cdot\cdot}/nm^2$]	TPR/TPD
Desorption temperature	T [K]	TPD
^{18}O exchange temperature as function of feed, M-O stretching frequencies	T [K] ν [eV]	Raman
Activity CO oxidation	T_{10}, T_{50} [K]	Fixed bed reactor

Conclusion

- Clean experimental data reveal the complexity of describing “the function” of a material
- Descriptors are needed that involve both, kinetics of reactants and catalyst material
- The handbook presented and the resulting clean data serve as input base
- In addition to metadata storage, some compulsory procedures need to be established and control mechanisms need to be introduced
- Potential benefit from AI applications provides motivation
- A reconstruction mechanism based upon the descriptor for interpolating missing data in literature reports can enhance and enlarge the database very significantly

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BasCat
UniCat BASF SE JointLab

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The Chemical Company