Modern Methods in Heterogeneous Catalysis Research

Synthesis of supported active phases

20 October 2017

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LECTURE SERIES
HETEROGENEOUS CATALYSIS

Heterogeneous catalyts

From large scale production of platform chemicals to dedicated synthesis of pharmaceuticals and electrocatalytic applications: Heterogeneous catalysts are composed of a formulated active mass adapted to the applied technology

Length scales

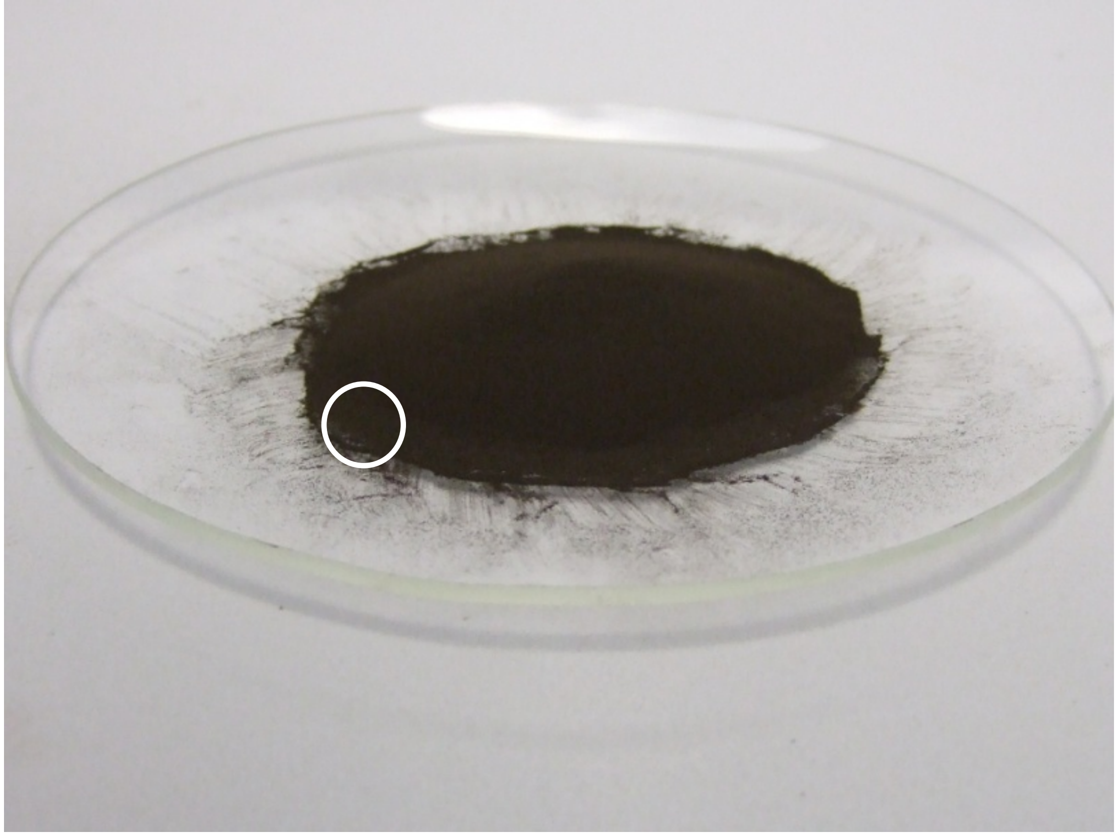
Methanol synthesis catalyst

Length scales

Methanol synthesis catalyst

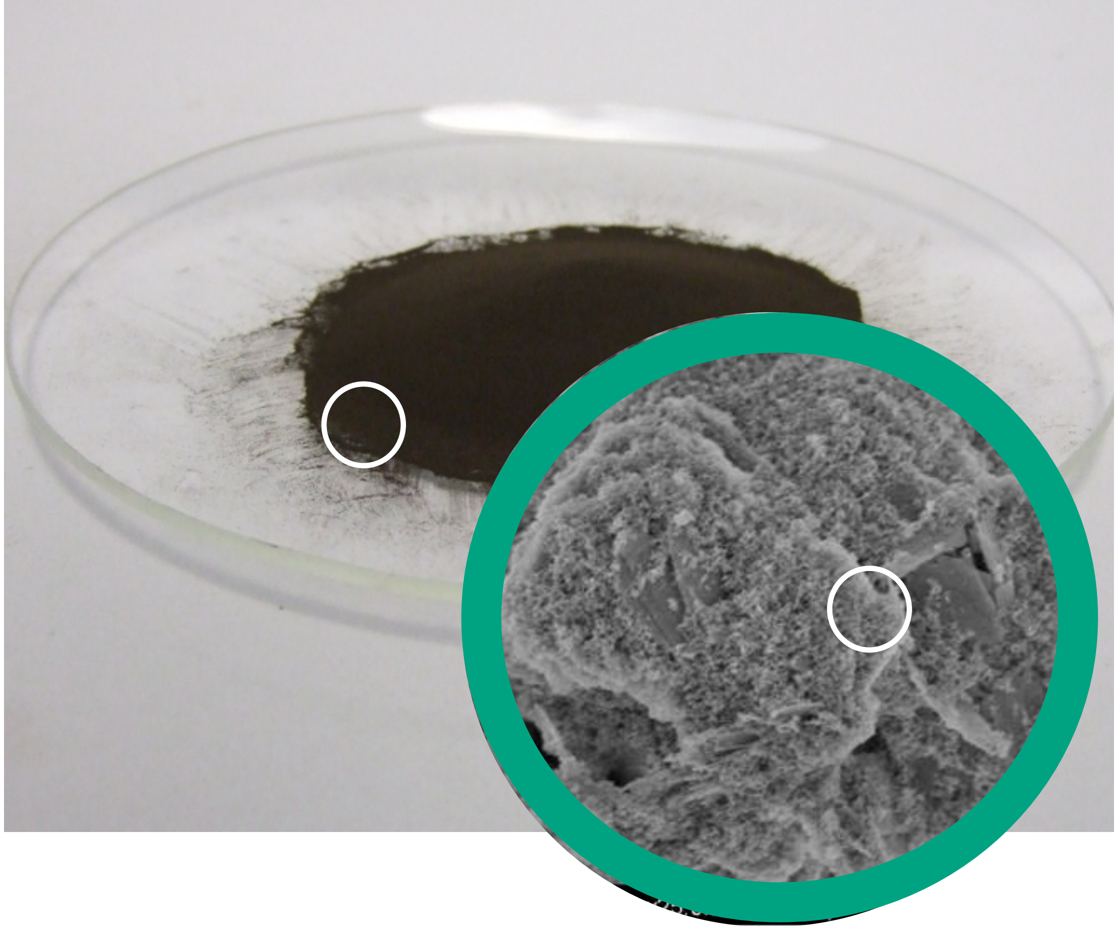
Length scales

Methanol synthesis catalyst



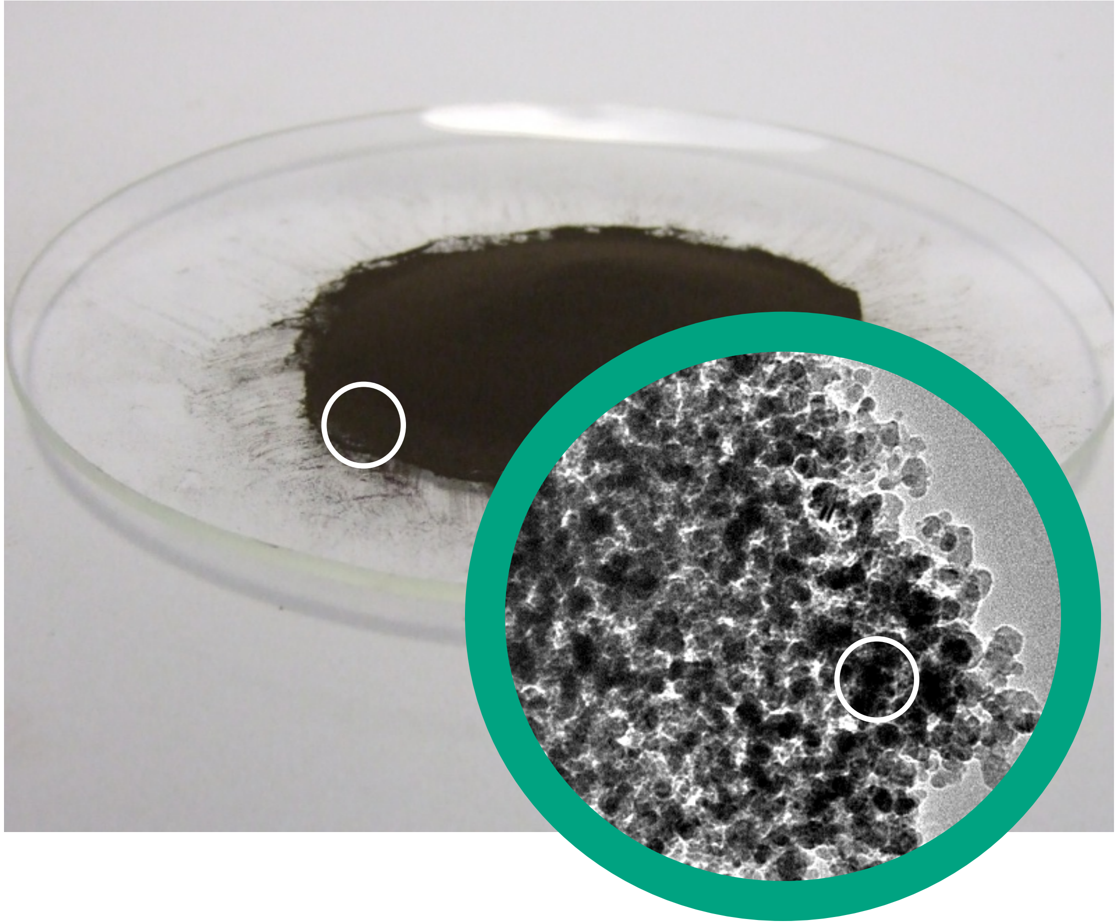
Length scales

Methanol synthesis catalyst



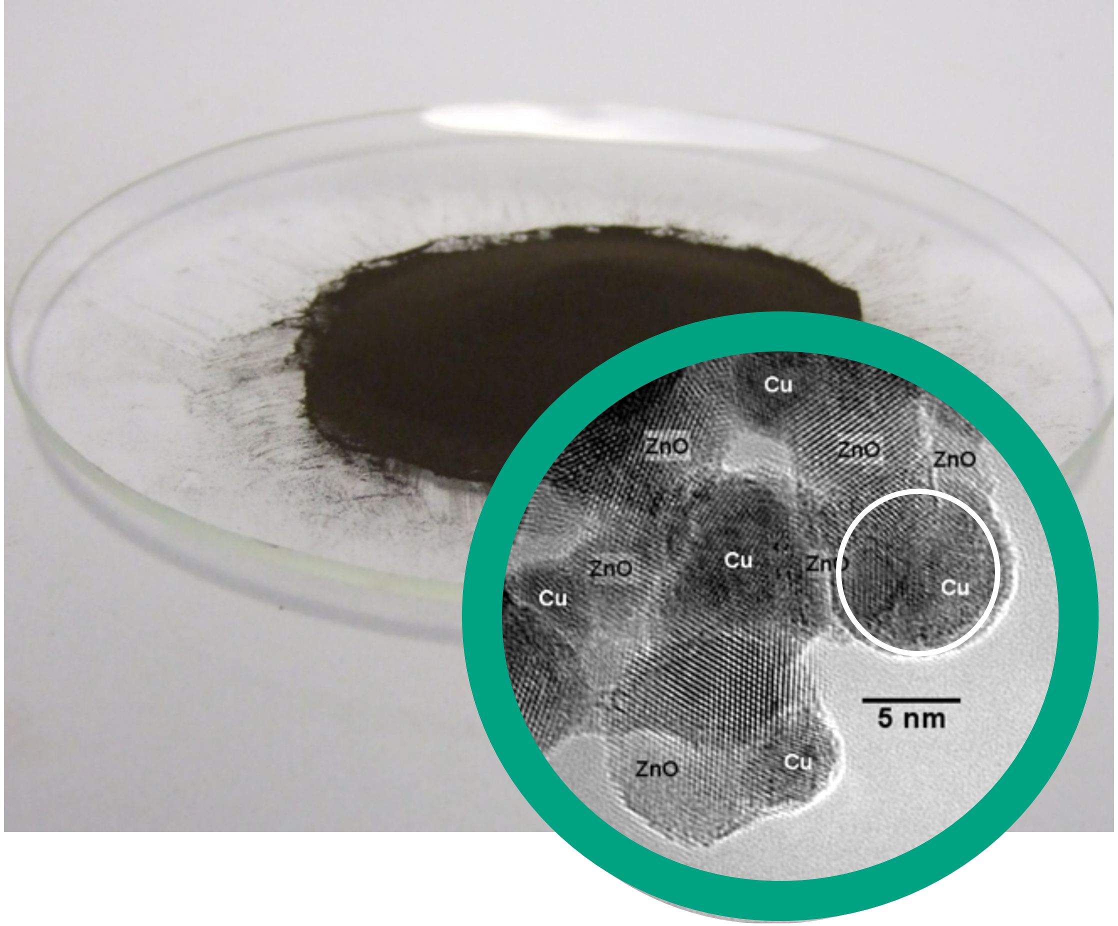
Length scales

Methanol synthesis catalyst



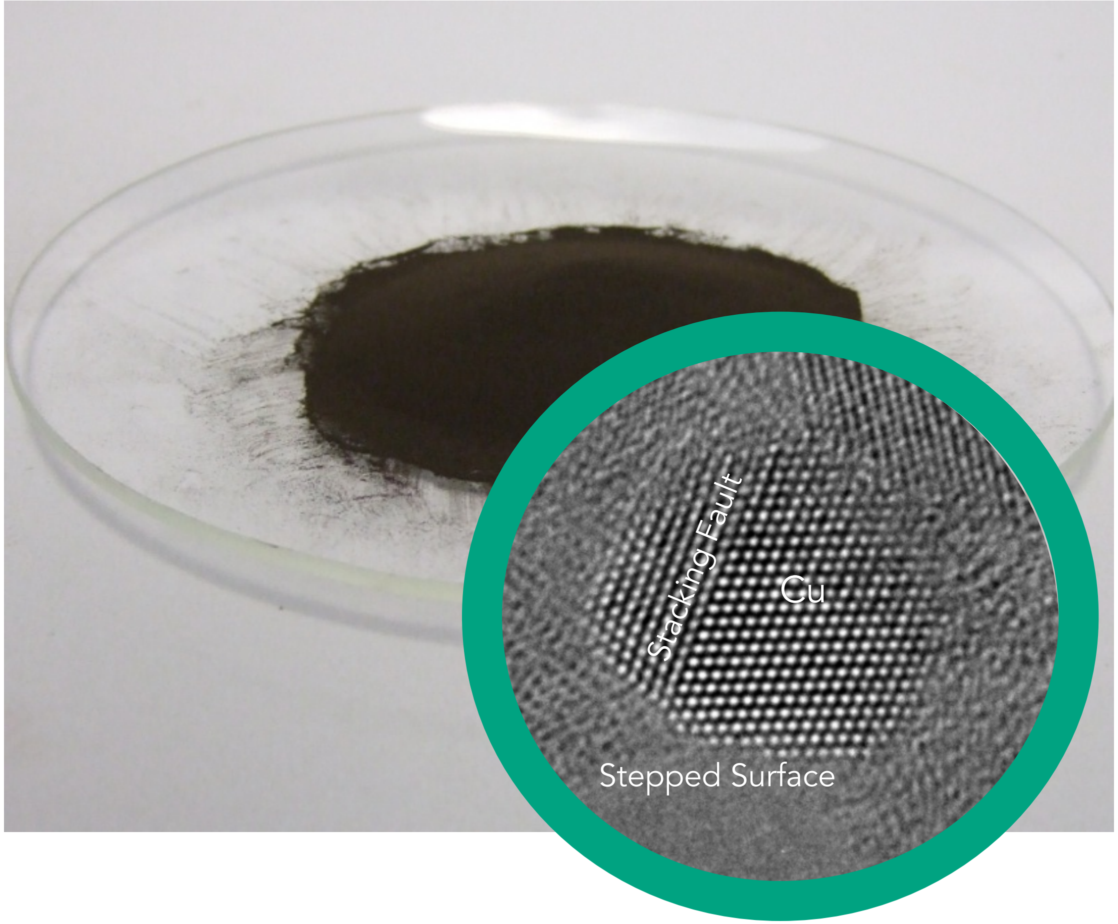
Length scales

Methanol synthesis catalyst



Length scales

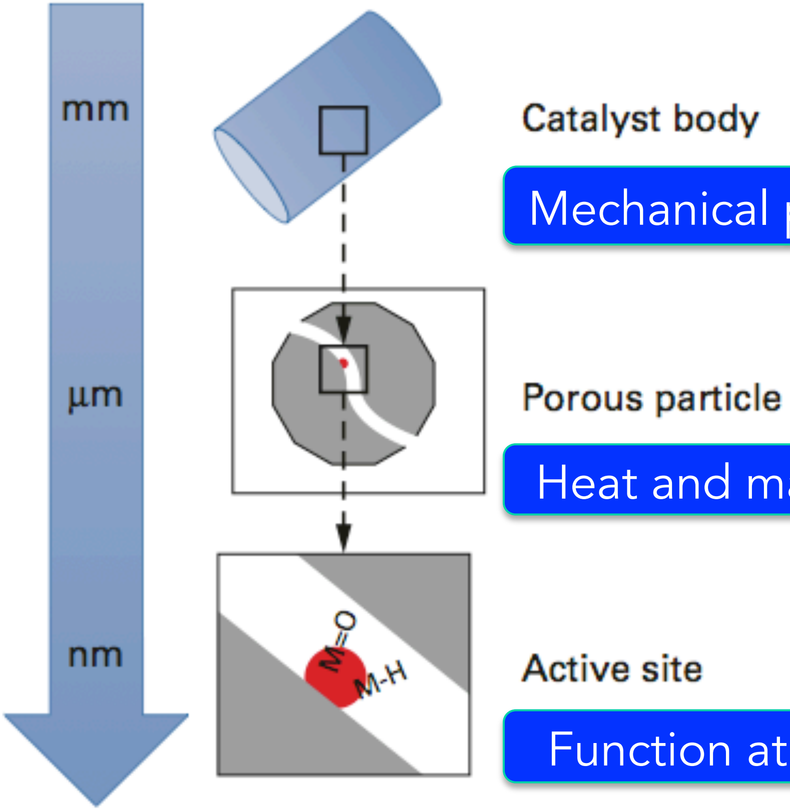
Methanol synthesis catalyst



Time scales

- Activation and breaking a chemical bond:
  picoseconds
- Completion of an entire reaction cycle:
  microseconds – minutes
- Diffusion in and outside pores, and through shaped catalyst particles:
  seconds – minutes
- Residence time of molecules inside a reactor:
  seconds - infinity

Hierarchical systems



Mechanical properties

Heat and mass transport

Function at molecular level

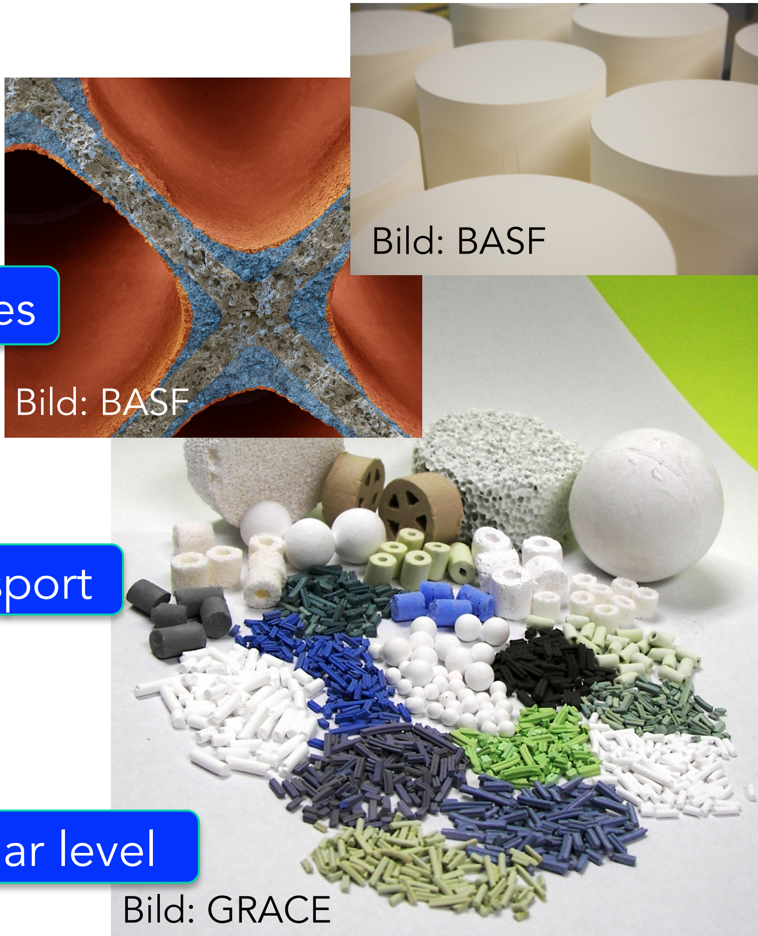


Bild: BASF

Bild: BASF

Bild: GRACE

Figure 4.2.2 Hierarchical catalyst structure with the schematic representation of active sites.

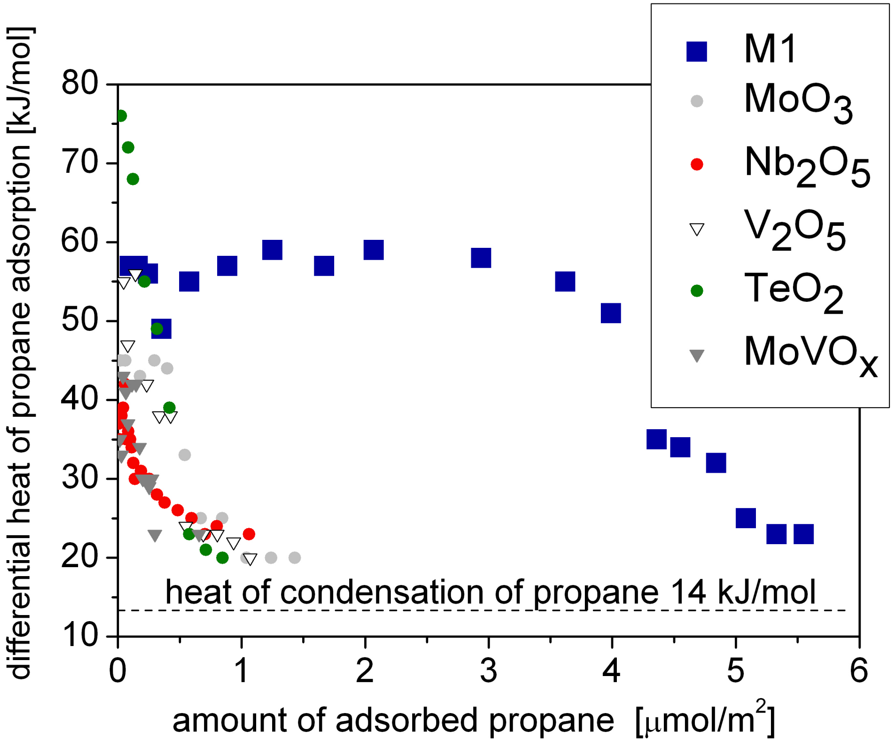
A. Trunschke, Synthesis of Solid Catalysts, in *Chemical Energy Storage* (Ed.: R. Schlögl), Walter de Gruyter GmbH, Berlin/Boston, **2013**, pp. 277-301.

Active site approximations

Langmuir

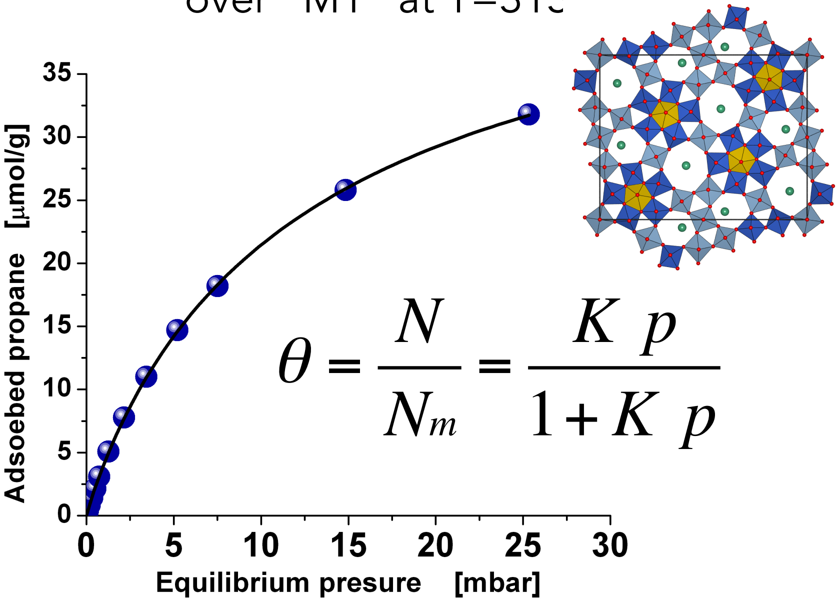
- The surface consists of sites which were energetically identical and non-interacting, and which would adsorb just one molecule from the gas phase in a localized mode
- Real surfaces are approximated by "checkerboard structures"

I. Langmuir, *Transactions of the Faraday Society* **1922**, *17*, 607-620.



M. Hävecker *et al.*, Journal of Catalysis 285 (2012) 48–60.

Adsorption isotherm of propane over "M1" at T=313 K



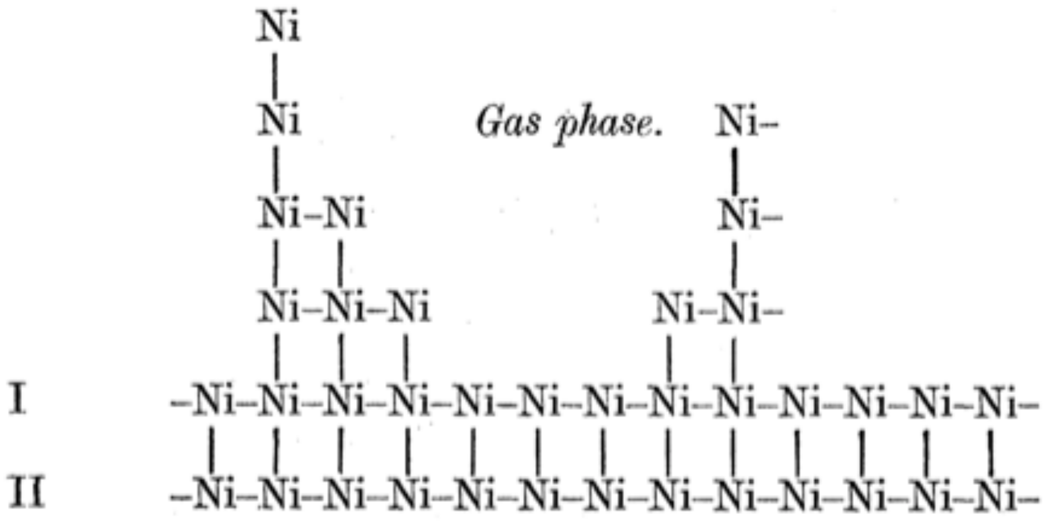
$$\theta = \frac{N}{N_m} = \frac{K\ p}{1 + K\ p}$$

Active site approximations

Taylor

„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.



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

Steps at the surface of dehydroxylated MgO

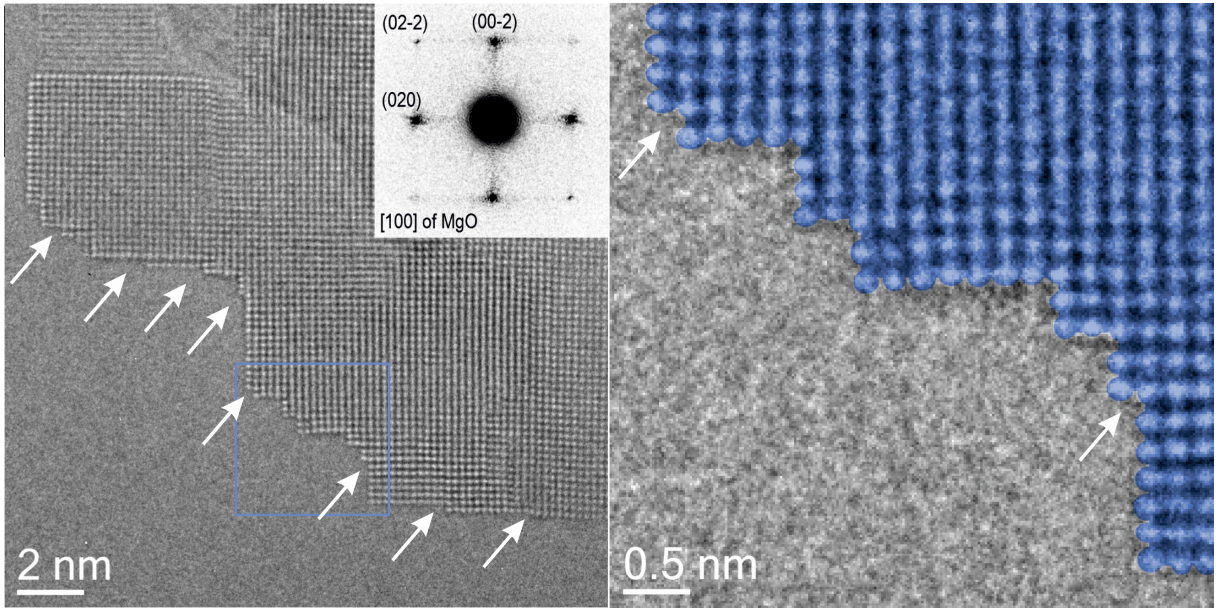


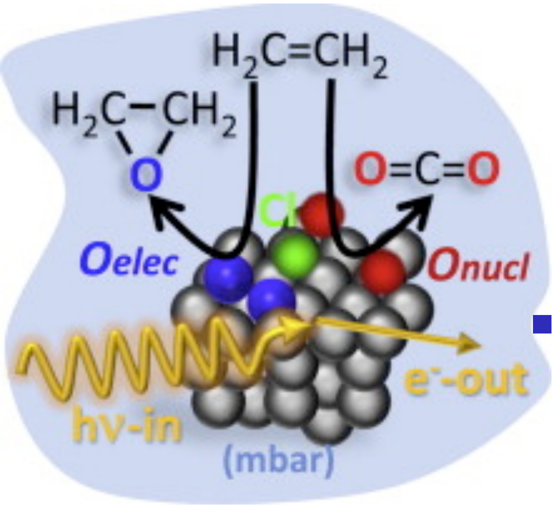
Fig. 4. High resolution TEM images of MW-MgO viewed along [100]. The inset in (A) shows a power spectrum, which allows to identify the orientation of the MgO crystal. (B) represents a higher magnified micrograph of (A) taken at the marked region of interest. The mono-atomic steps at the surface are clearly visible and marked by arrows.

HRTEM by Thomas Lunkenbein, Marc Willinger

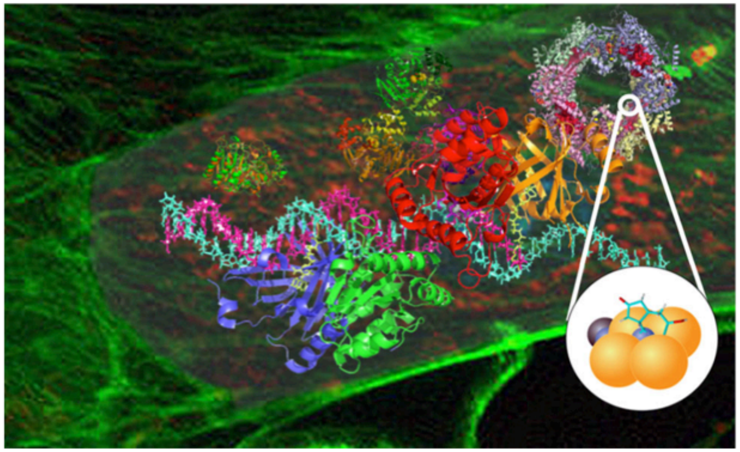
Major effects on "active sites"

The local chemical interactions are controlled for example by

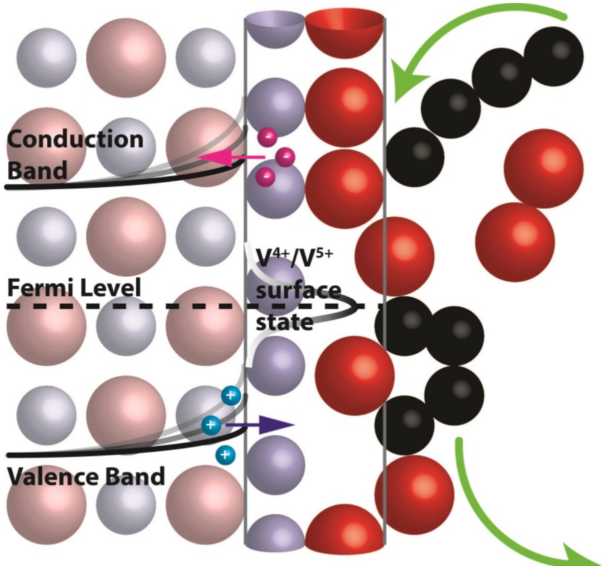
- Medium
  - Ligand
  - Cavity
    (electrostatic effects)
  - Solvent
    (dielectric constant)
- Matrix
  - Particle size
  - Morphology
  - Exposed facets
  - Defects
  - Electronic bulk properties



T. C. R. Rocha, *et al.*, *J. Catal.* **2014**, *312*, 12.



H. Kung, M. Kung, *Catalysis Letters* **2014**, *144*, 1643-1652.

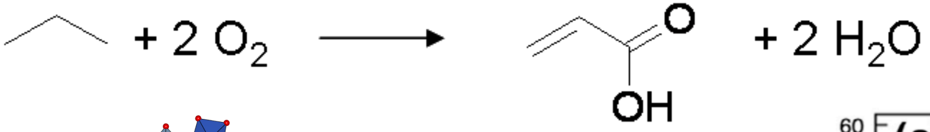


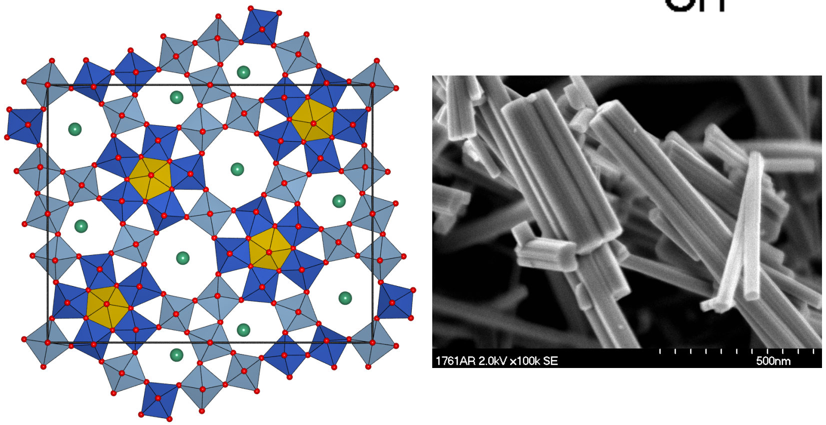
Courtesy of M. Eichelbaum

Can we synthesize “active sites”?

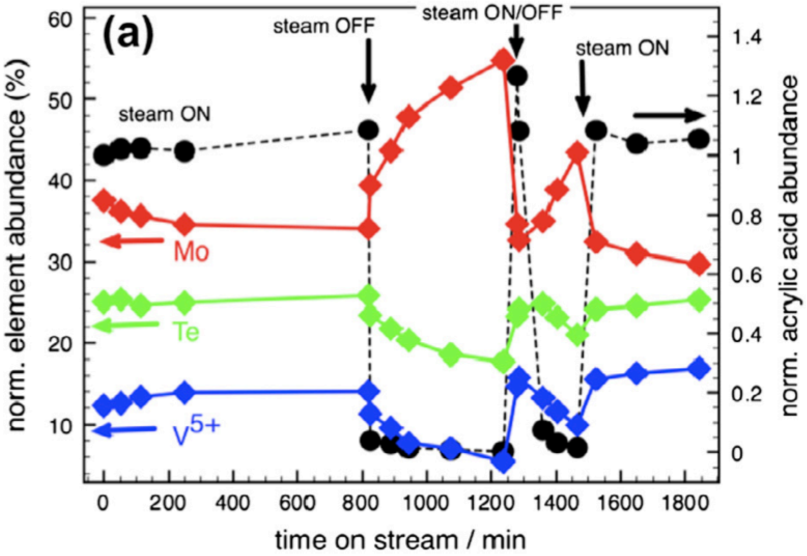
„The amount of surface which is catalytically active is determined by the reaction catalyzed.“

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





Crystalline MoVTeNb “M1” oxide



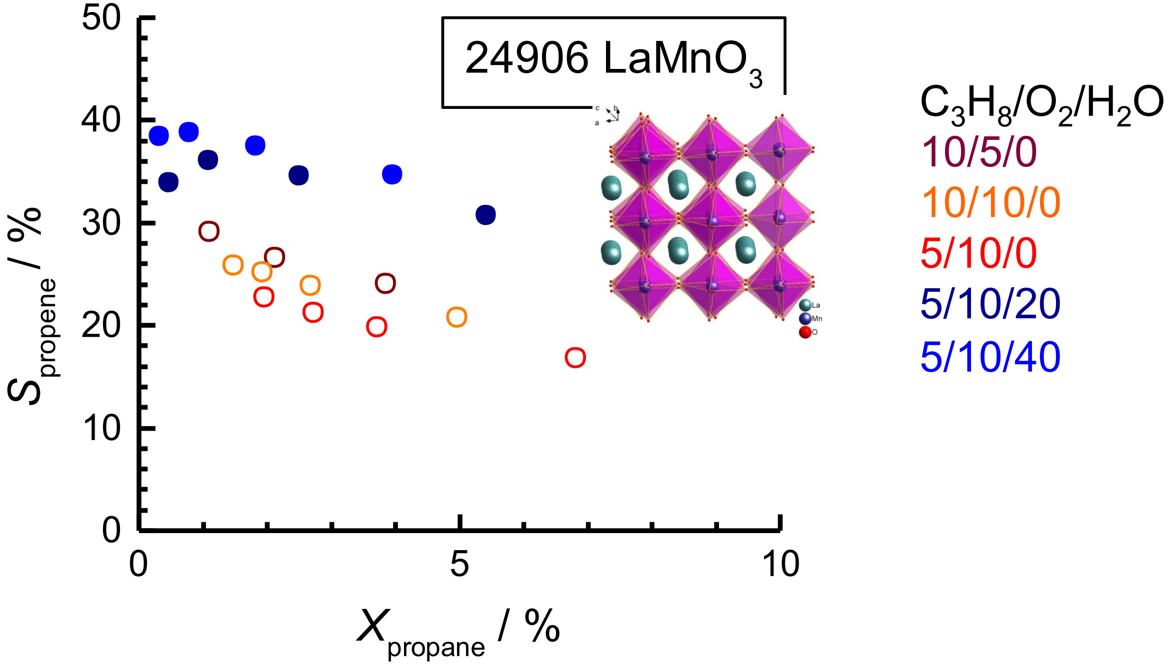
R. Naumann D'Alnoncourt *et al.*, *J. Catalysis* **2014**, *311*, 369.

Can we synthesize “active sites”?

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

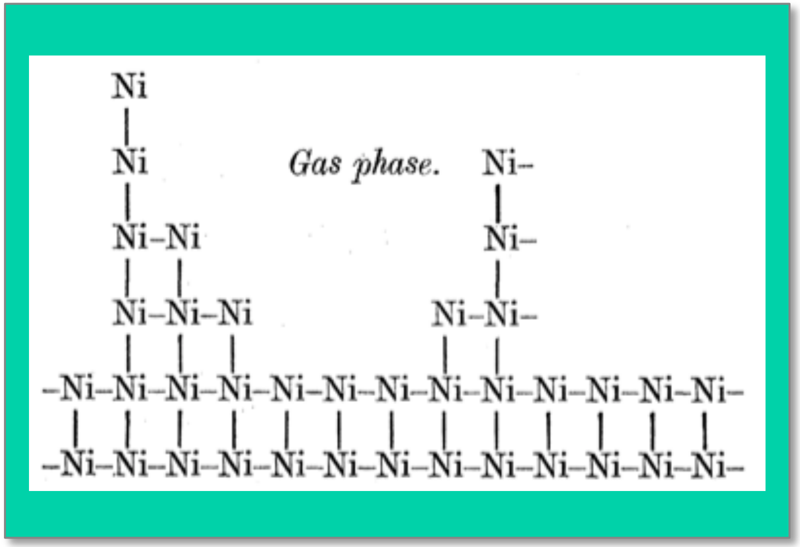
H. S. Taylor, *Proceedings of the Royal Society of London. Series A* **1925**, *108*, 105-111.

$2\ C_3H_8 + O_2 \rightarrow 2\ C_3H_6 + 2\ H_2O$

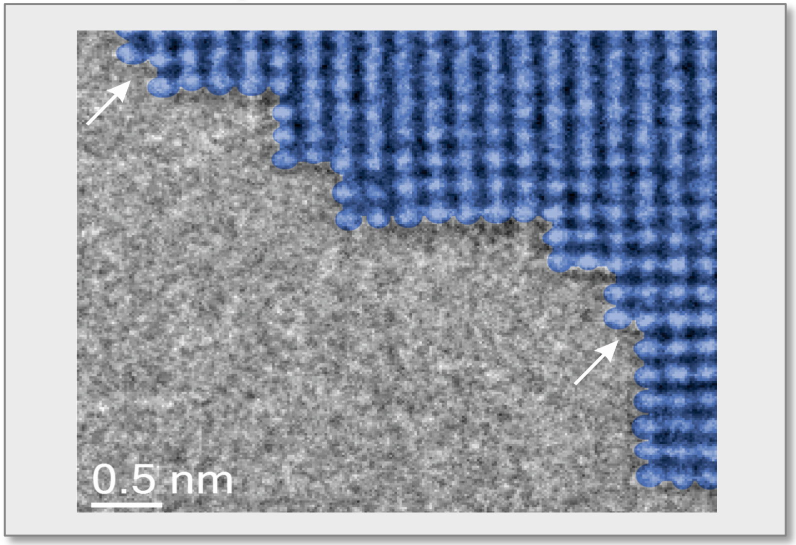


- We can only synthesize catalyst precursors
- The active surface is formed under reaction conditions

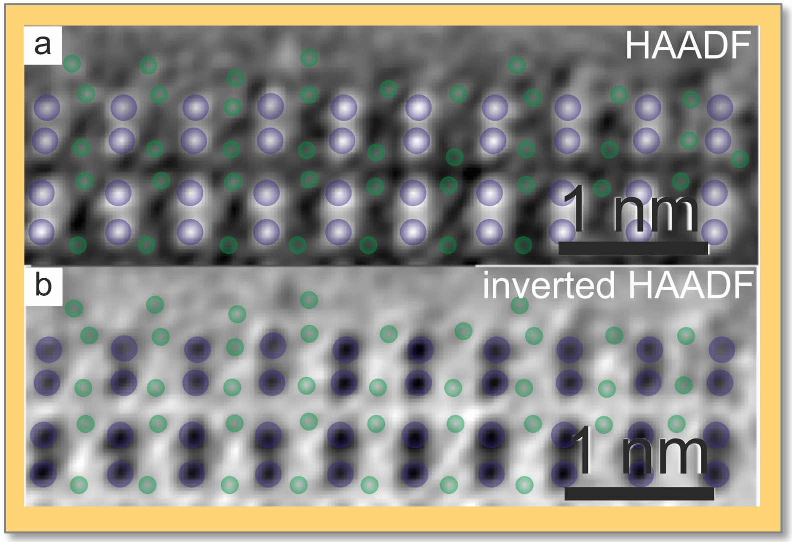
The surface of catalyst precursors



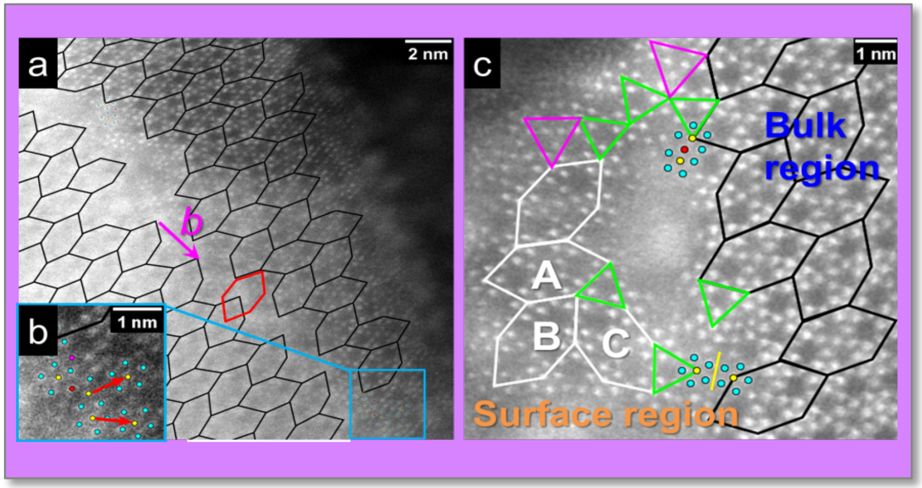
H.S. Taylor: A Theory of the Catalytic Surface
Proc. R. Soc. Lond. A, **1925**, *108*, 105-111.



Steps at the surface of dehydroxylated MgO
Journal of Catalysis **2015**, *326*, 560-573.



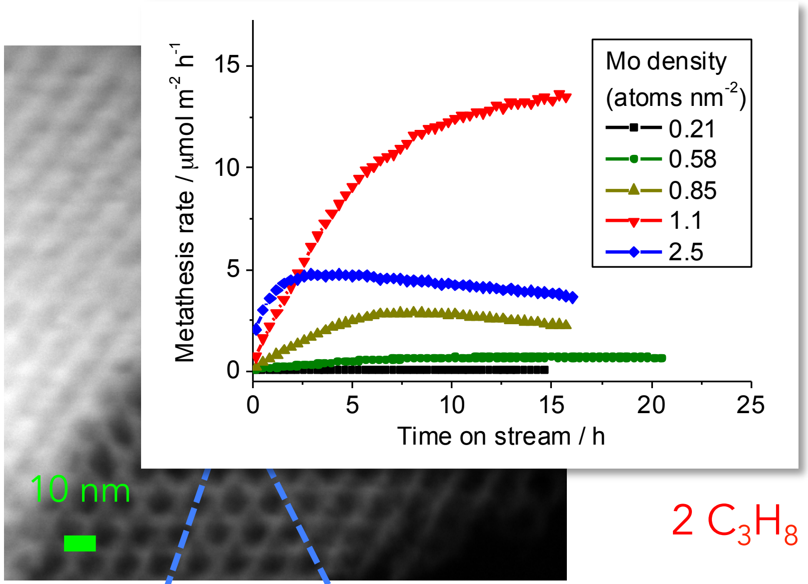
Exposed MnOx species on $MnWO_4$
Angew. Chem. Int. Ed. **2016**, *55*, *4092*.

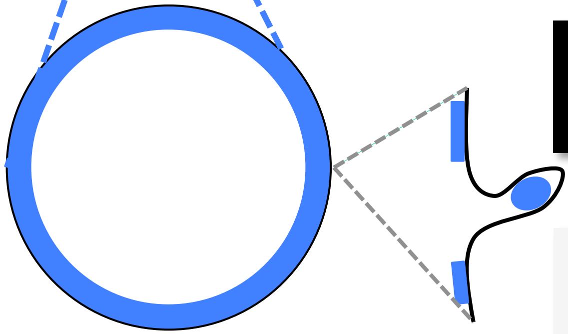


Defects on $MoVO_x$ „M1“ oxide
J. Phys. Chem C, **2017**, *in press*.

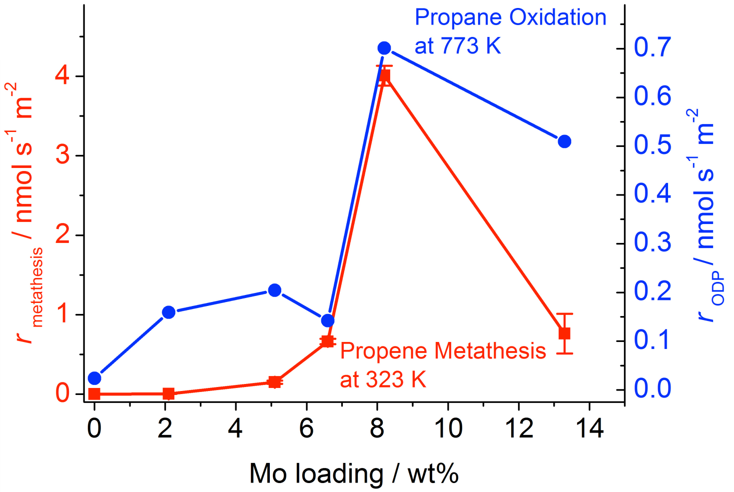
Supported monolayer models

Mo_xO_y/SiO_2 (SBA-15)





$0.2 - 2.5$ Mo nm^{-2}

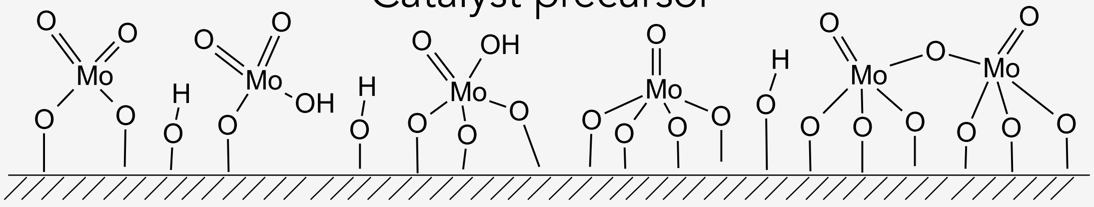


$2\ C_3H_8 \rightarrow C_4H_8 + C_2H_4$

$2\ C_3H_8 + O_2 \rightarrow 2\ C_3H_6 + 2\ H_2O$

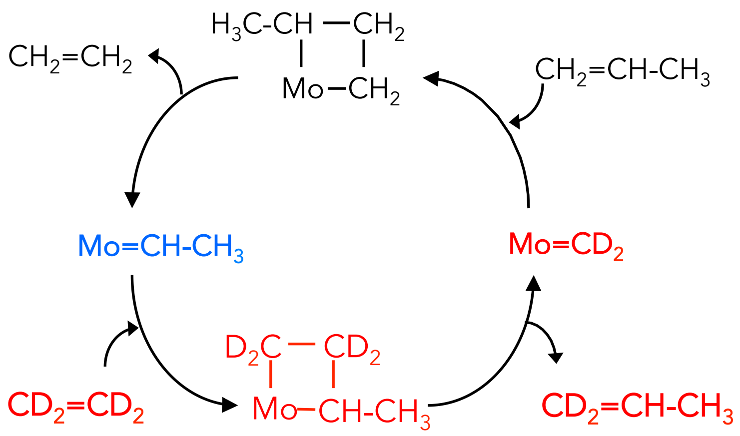
Working catalyst

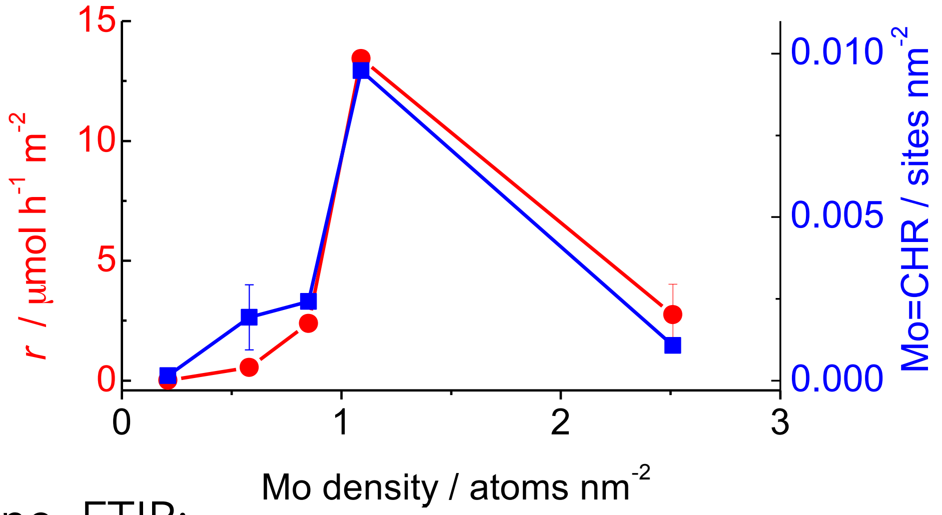
Catalyst precursor



SiO_2 surface

Formation of Mo=CHR sites

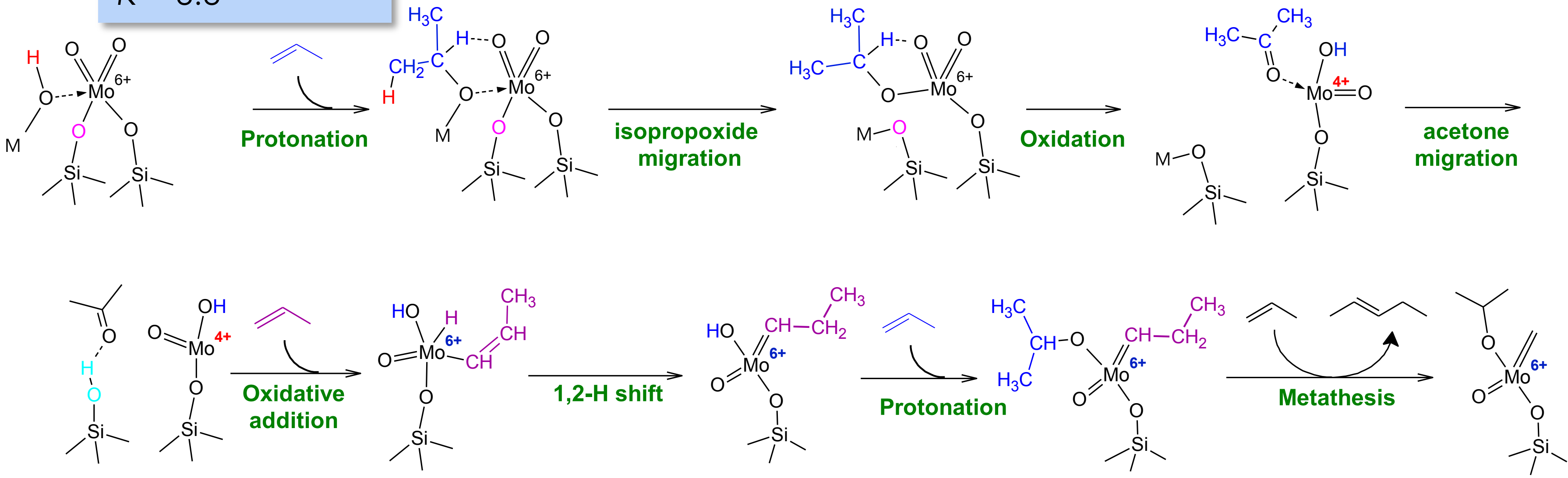




microcalorimetry of adsorbed propene, FTIR:

ΔH_{diff}=80 kJ mol^{-1}
K = 8.6

Iwasawa *et al.*, *Faraday Trans.*, **1981**, *77*, 1763.
Shelimov *et al.*, *J. Mol. Catal.*, **1988**, *46*, 187.



JACS, **2012**, *134*, 11462-11473; *ChemCatChem*, **2015**, *7*, 4059-4065.

Formation of Mo=CHR sites

- Maximum number of active carbene species at high sub-monolayer coverage, but just about 1-2%* of Mo
- The active sites are formed by interaction of propylene with the precursor in an oxyhydration reaction (microcalorimetry, FTIR, TPD)
- Why is Mo reduced at such a low temperature?
- What is the origin of acidity?
- Why are only 1% of Mo species transformed into active carbene species?

→ Investigation of catalyst synthesis

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* MoO_x/Al_2O_3: Handzlik, J.; Ogonowski, J. *Catal. Lett.* **2003**, *88*, 119.
ReO_x/Al_2O_3: Salameh,A.;Coperet,C.;Basset,J.-M.;Böhm,V.P.W.;Röper, M. *Adv. Synth. Catal.* **2007**, *349*, 242.

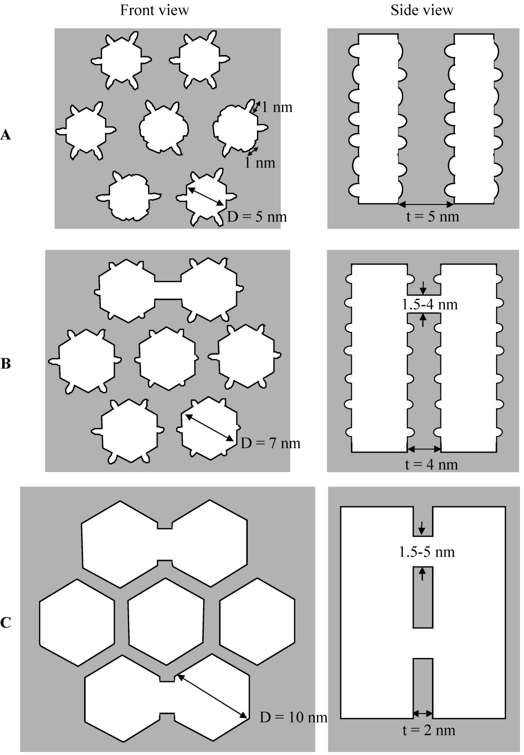
Synthesis of the support SBA-15 (SiO_2)

T=308 K, pH<1,
$EO_{20}PO_{70}EO_{20}$,
$Si(OEt)_4$

aging
T=358 K, 24 h
Filtration,
washing, drying

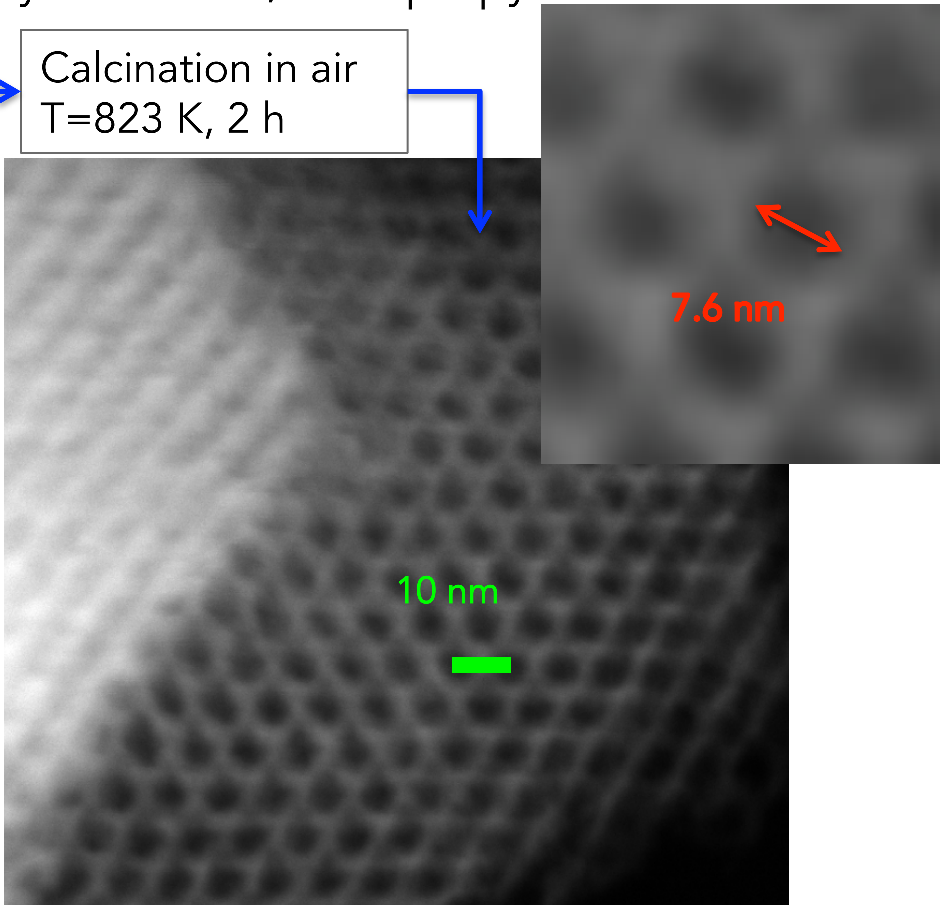
Template: non-ionic amphiphilic triblock copolyme
Poly(ethylene oxide)-block-poly(propylene oxide)-
block poly(ethyleneoxide)x
$(EO)_{20}$-$(PO)_{70}$-$(EO)_{20}$
(EO ethylene oxide; PO =propylene oxide

Calcination in air
T=823 K, 2 h



A. Galarneau *et al.*, *J. Phys. Chem. C* **2007**, 111, 8268-8277.

Aging at (A) 60 °C, (B) 100 °C, and (C) 130 °C: different pore diameters, wall thicknesses, microporosities, and interconnections between main channels

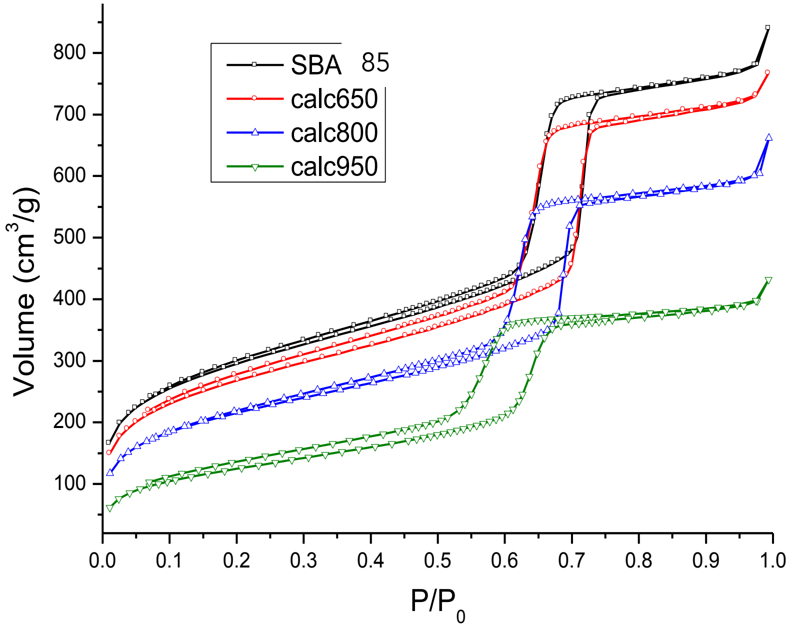


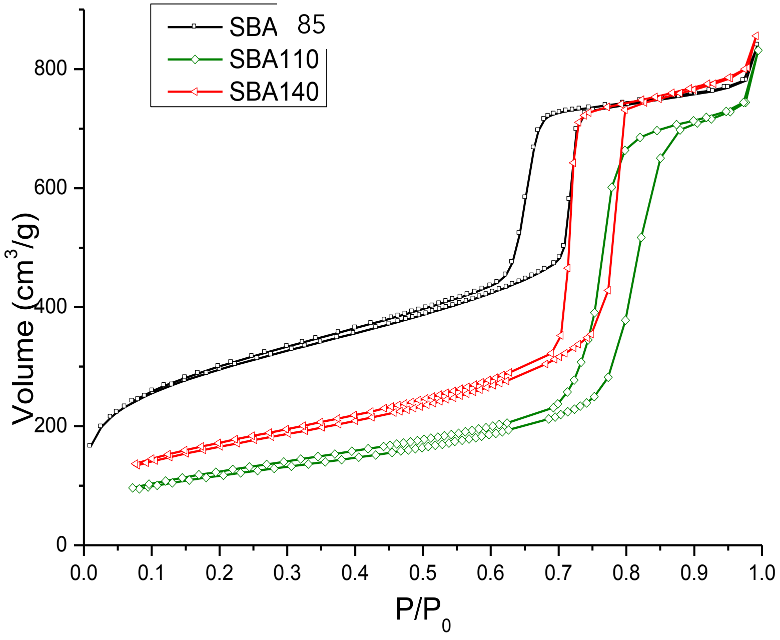
Mesostructured silica SBA-15

Synthesis of the support SBA-15 (SiO_2)

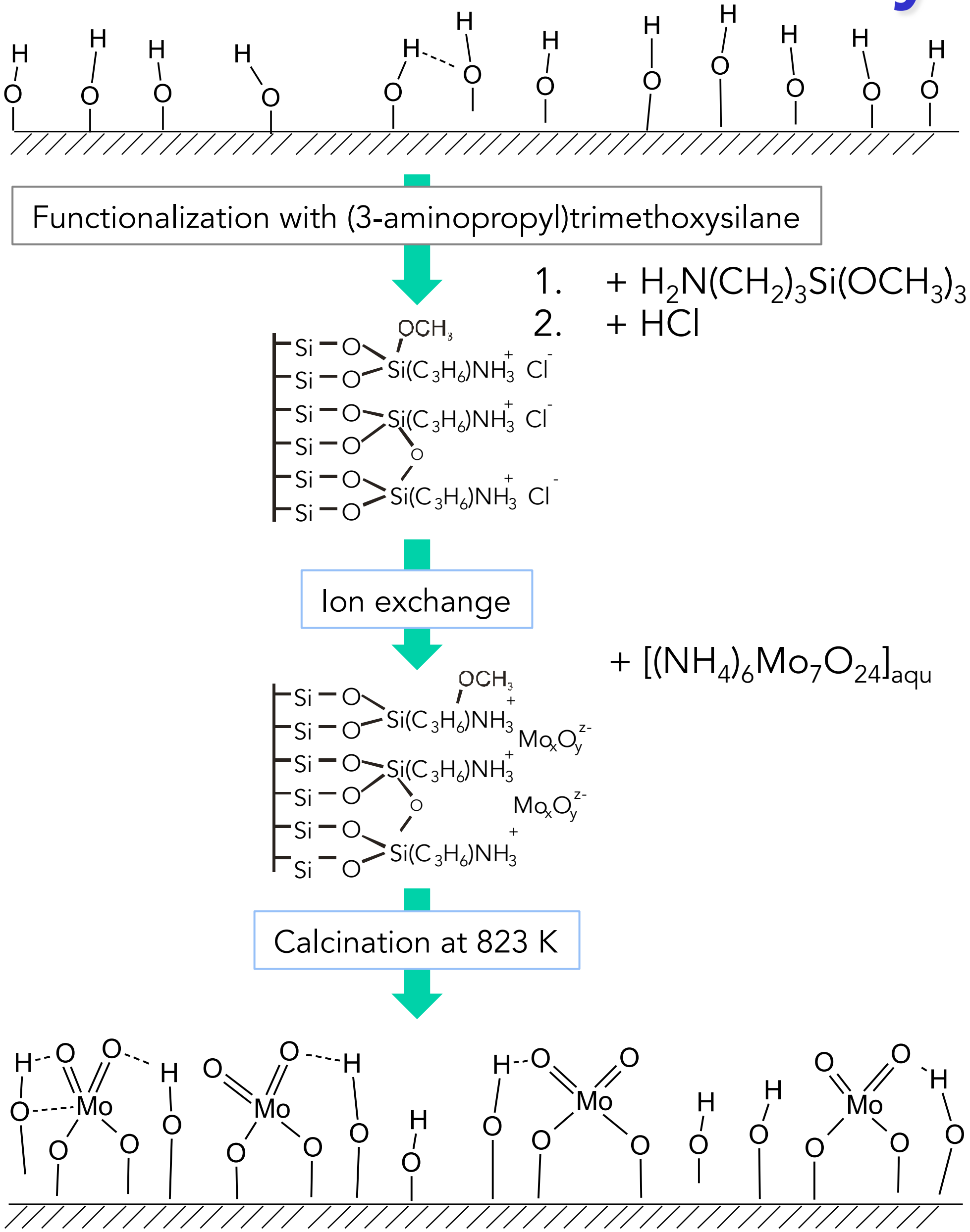
	T_{aging} (°C)	T_{calc} (°C)	S (m^2/g)	V_P (cm^3/g)	V_M (cm^3/g)	$Micro_{Vol}$ %	S_M (m^2/g)	$Micro_{Area}$ %	d (nm)	a (nm)	b* (nm)	$\delta_{silanol}$ (OH/nm^2)	Sample ID
SBA-85	85	550	1017	1.190	0.170	15	348	34	7.6	11.13	3.55	3.20	17518
Calc650		650	929	1.116	0.142	13	294	32	7.3	10.90	3.59	1.04	17808
Calc800		800	750	0.918	0.099	11	207	28	7.0	10.45	3.42	0.88	17809
Calc950		950	447	0.605	0.016	3	40	9	6.3	9.51	3.19	0.61	17810
SBA110	110	550	412	1.129	0.029	3	72	17	10.9	11.70	0.82	7.93	13277
SBA140	140	550	585	1.217	0.036	3	88	15	9.4	11.68	2.26	6.79	13295

*$b = a - d$





Precursor synthesis



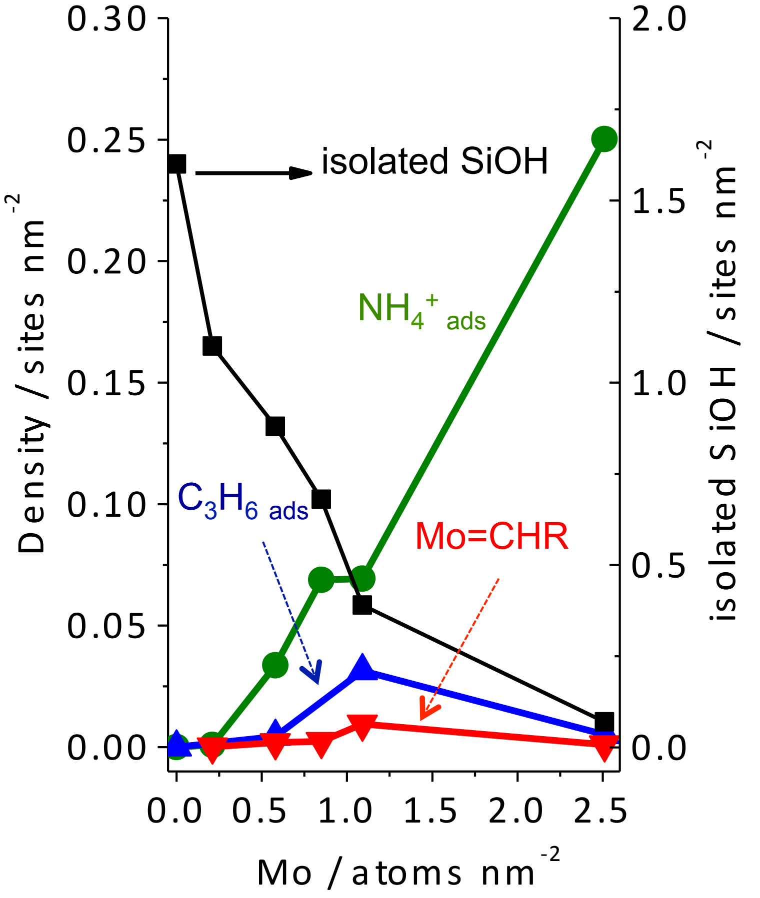
Functionalization with (3-aminopropyl)trimethoxysilane

1. + $H_2N(CH_2)_3Si(OCH_3)_3$
2. + HCl

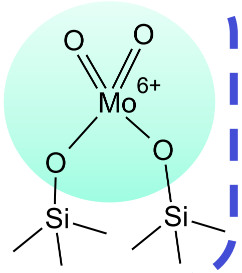
Ion exchange

+ $[(NH_4)_6Mo_7O_{24}]_{aqu}$

Calcination at 823 K



Predominant configuration of Mo in the precursor (UV-vis, Mo K-edge XANES, EXAFS)



Speciation of Mo in aqueous solution

Molybdate ions in aqueous solution

$7\ MoO_4^{2-} + 8\ H^+ \rightarrow Mo_7O_{24}^{6-} + 4\ H_2O$

$3\ Mo_7O_{24}^{6-} + 4\ H^+ \rightarrow 7\ Mo_3O_{10}^{2-} + 2\ H_2O$

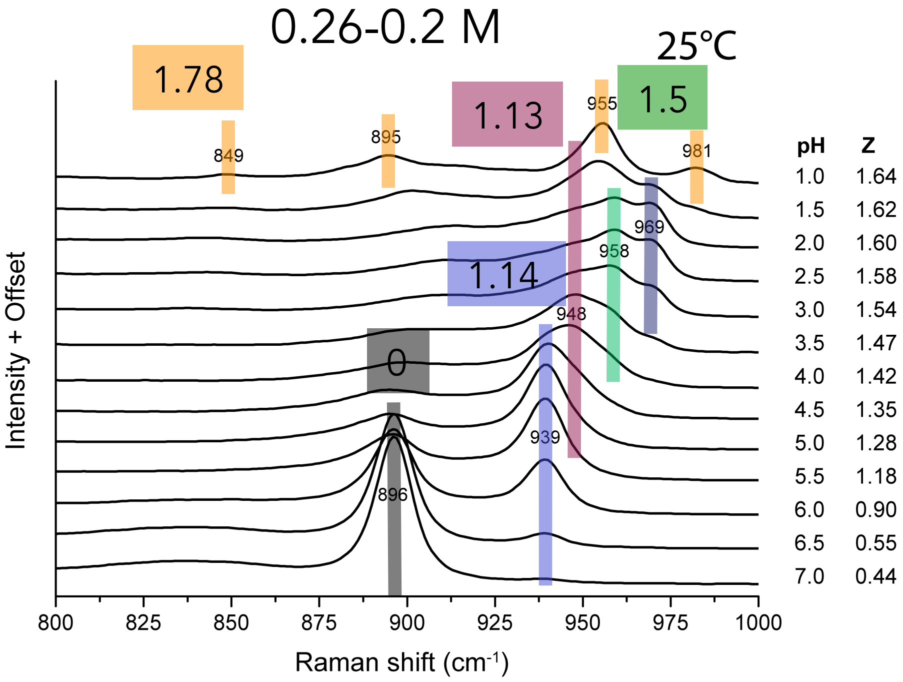
$8\ Mo_3O_{10}^{2-} + 4\ H^+ \rightarrow 3\ Mo_8O_{26}^{4-} + 2\ H_2O$

$8\ Mo_7O_{24}^{6-} + 20\ H^+ \rightarrow 7\ Mo_8O_{26}^{4-} + 10\ H_2O$

$4.5\ Mo_8O_{26}^{4-} + 10\ H^+ \rightarrow Mo_{36}O_{112}^{8-} + 10\ H_2O \rightarrow MoO_3$

$$Z^+ = \left|\nu_{H^+}\right| / \left|\nu_{MoO_4^{2-}}\right|$$

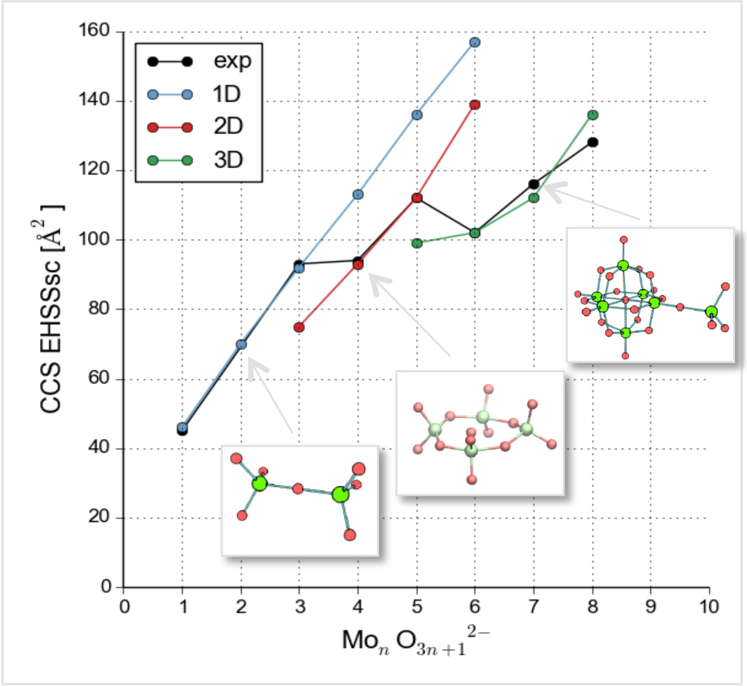
$$Z = (C_{H^+} - c_{H^+} + K_W / c_{H^+}) / c_{MoO_4^{2-}}$$



pH	Z
1.0	1.64
1.5	1.62
2.0	1.60
2.5	1.58
3.0	1.54
3.5	1.47
4.0	1.42
4.5	1.35
5.0	1.28
5.5	1.18
6.0	0.90
6.5	0.55
7.0	0.44

Z. Anorg. Allg. Chem. **2014**, 2730–2736.

Removal of the solvent:



Mateusz Marianski, Sabrina Jung, *et al.*

Ion exchange of amphotheric oxides

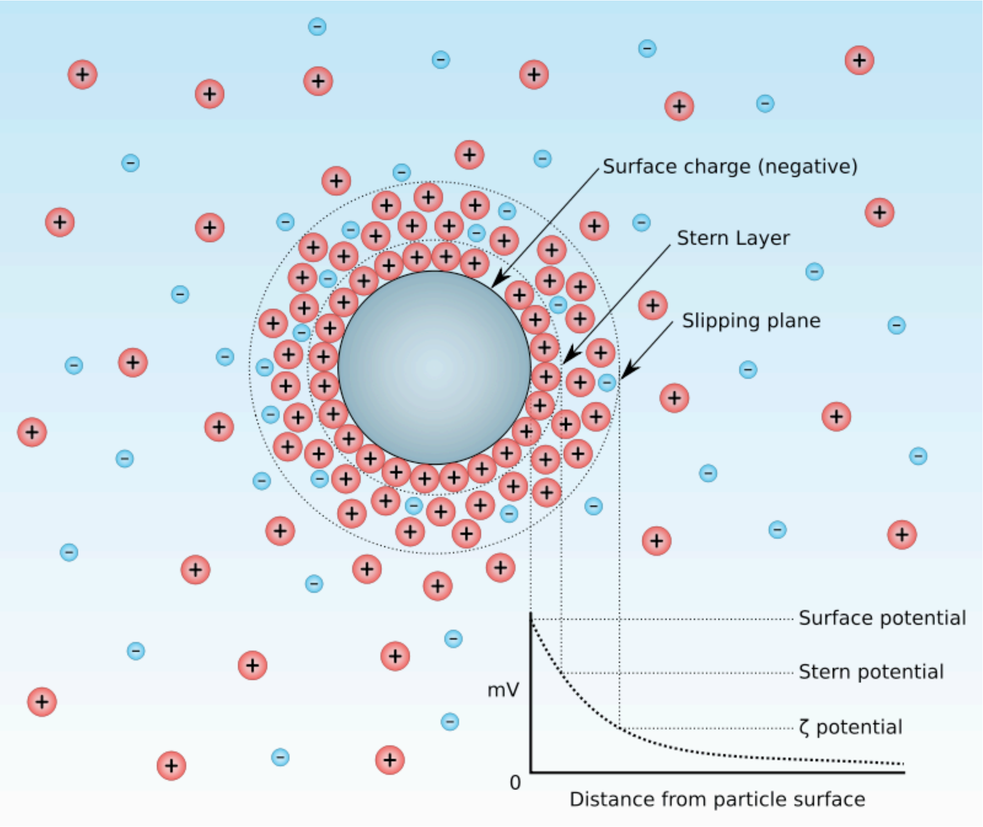
Oxide-solution interphase

$$[\text{M-O}]^{-} + \text{H}_3\text{O}^{+} \rightleftharpoons \text{M-OH} + \text{H}_2\text{O} \rightleftharpoons [\text{M-OH}_2]^{+} + \text{HO}^{-}$$

M = Si, Al, Ti, etc.

- Hydroxyl groups are formed on the oxide surface (M-OH) in contact with water
- M-OH may behave as Brønstedt acids or bases
- Surface charge depends on solution pH
- Zeta (ζ) potential is an estimation of surface charge Z

Zeta potential



http://en.wikipedia.org/wiki/Zeta_potential

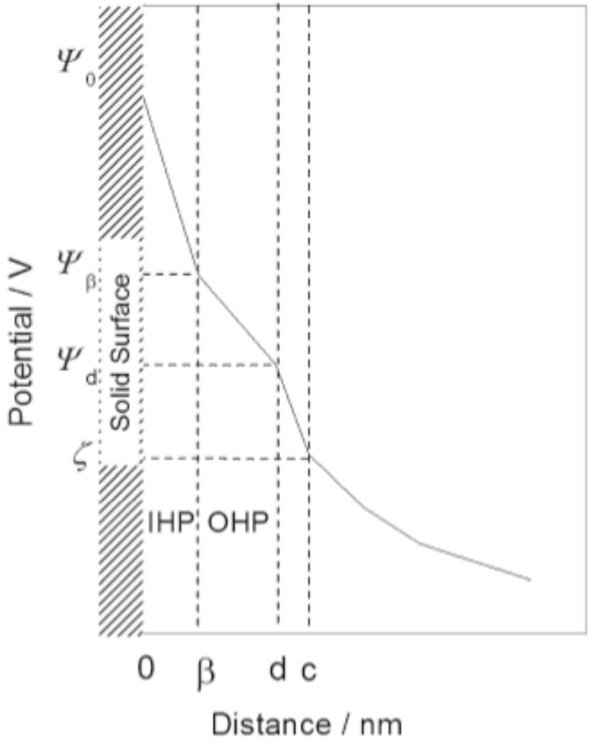
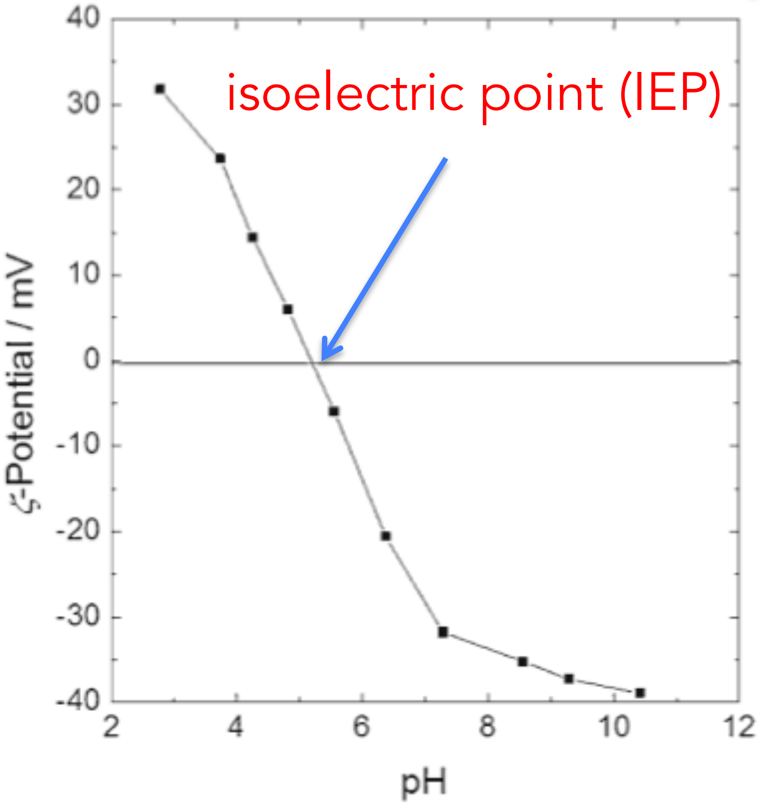


Fig. 1 Model of the interfacial charged layer. The inner Helmholtz plane (IHP) is the locus of the former ions (distance β from the surface) and the outer Helmholtz plane (OHP) is the beginning of the diffuse layer (distance d from the surface) ($0 \le \beta \le d$) governed by electrostatic forces. Within the diffuse layer, the potential at the e-plane is the electrokinetic or ζ-potential

Measurement of the electrophoretic mobility in an electric field by optical (laser Doppler velocimetry and phase analysis light scattering (PALS)) or acoustic methods

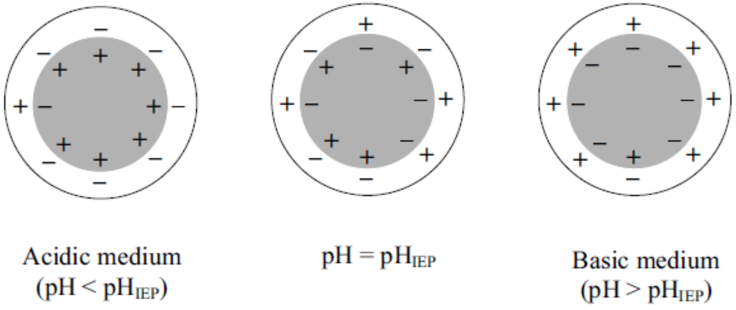
I. Llorente, S. Fajardo, J. M. Bastidas, *J Solid State Electrochem* **2014**, *18*, 293-307.

Zeta potential



isoelectric point (IEP)

Fig. 3 Variation of ζ-potential vs. pH for an oxide suspension



$pH > pH_{IEP}$
- ✓ the surface is negative
- ✓ cations will be adsorbed

$pH < pH_{IEP}$
- ✓ the surface is positive
- ✓ anions will be adsorbed

Point of zero charge (PCZ)
- ✓ zero surface charge in the 0-plane, i.e., to $\sigma_0 = 0$
- ✓ characterized by pH_{pzc}

At low ionic strength, and also in the case of equal affinities of counterions (cations and anions) towards association with oppositely charged surface groups, IEP and PCZ coincide.

I. Llorente, S. Fajardo, J. M. Bastidas, *J Solid State Electrochem* **2014**, *18*, 293-307.

Zeta potential

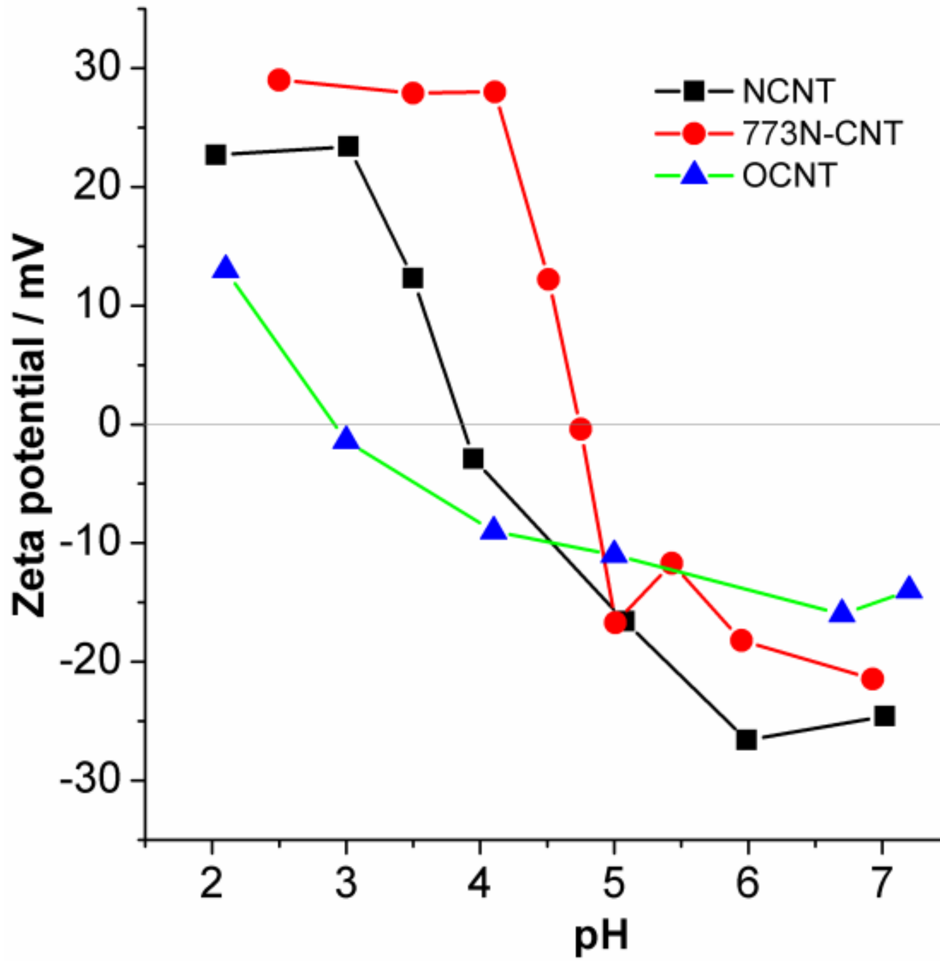
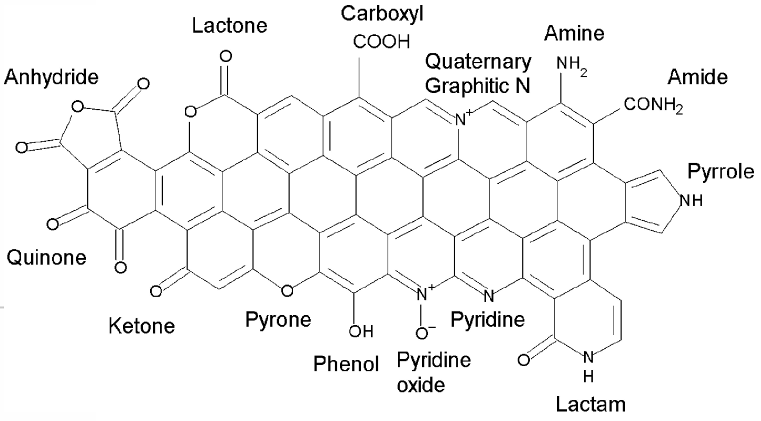


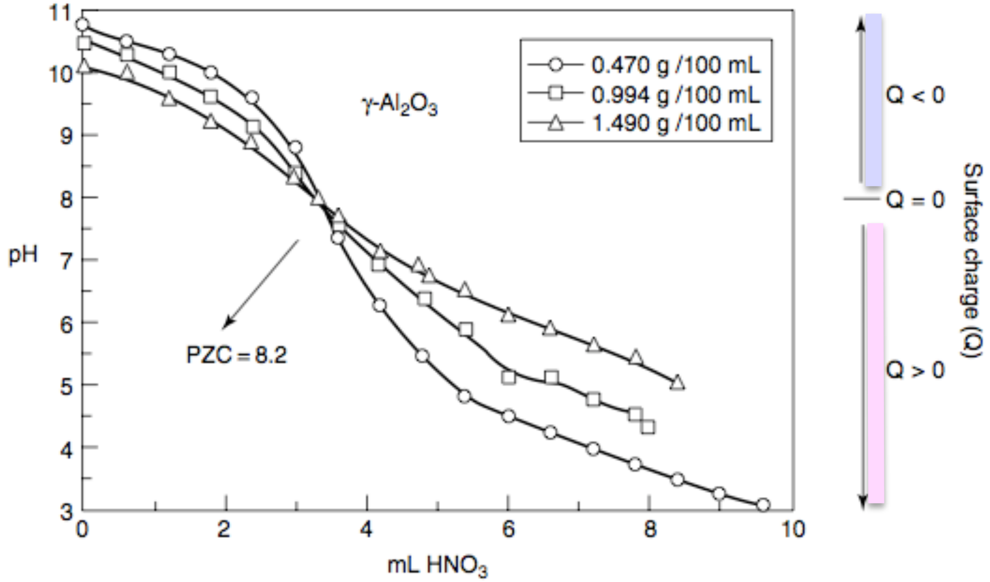
Figure S4. Zeta potential of NCNT and OCNT support materials.



R. Arrigo *et al., J. Am. Chem. Soc.* **2010,** 132, 9616

Zailai Xie, Benjamin Frank, Xing Huang, Robert Schlögl, and Annette Trunschke
Commercial Co- and Mn-containing N-doped CNTs as a support for Rh catalysts in higher alcohol synthesis
Catalysis Letters, **2016**, *146*, 2417-2424; **DOI:** 10.1007/s10562-016-1875-6.

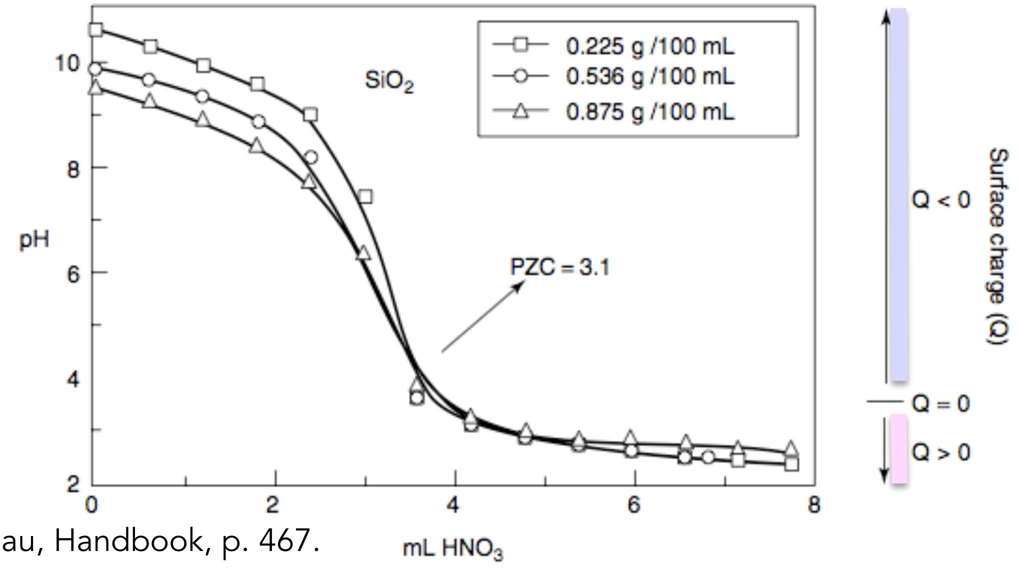
PZC of classical supports



$Pt(NH_3)_4^{2+}$

$PtCl_6^{2-}$

Gamma-alumina adsorbs cations as well as anions



$Pt(NH_3)_4^{2+}$

$PtCl_6^{2-}$

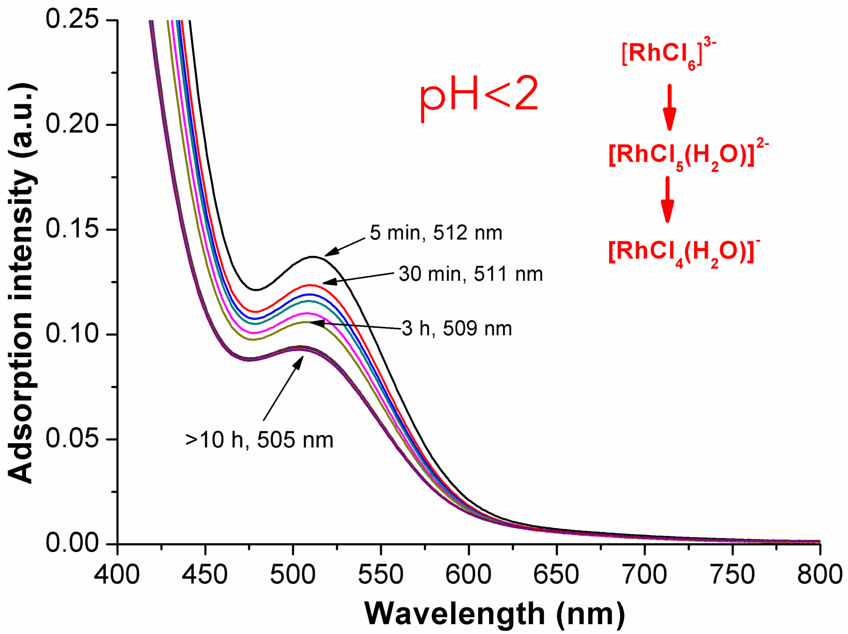
Silica basically adsorb cations

E. Marceau, Handbook, p. 467.

Complex speciation in solution

pH<3: Ligand substitution (in HCl)

$[Rh]_{tot} = [RhCl_6]^{3-} + [RhCl_5]^{2-} + [RhCl_4]^{-}$



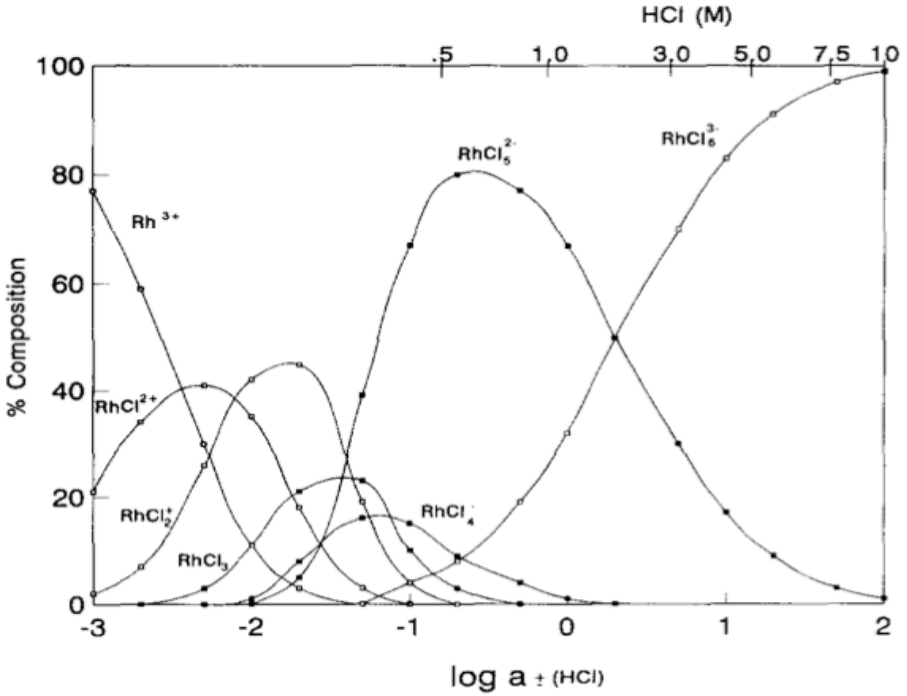


Fig. 3. Rhodium chloride speciation diagram (after [14]) at 25°C.

E. Benguerel et al., Hydrometallurgy 40 (1996) 135-152.

pH>3: (in water)

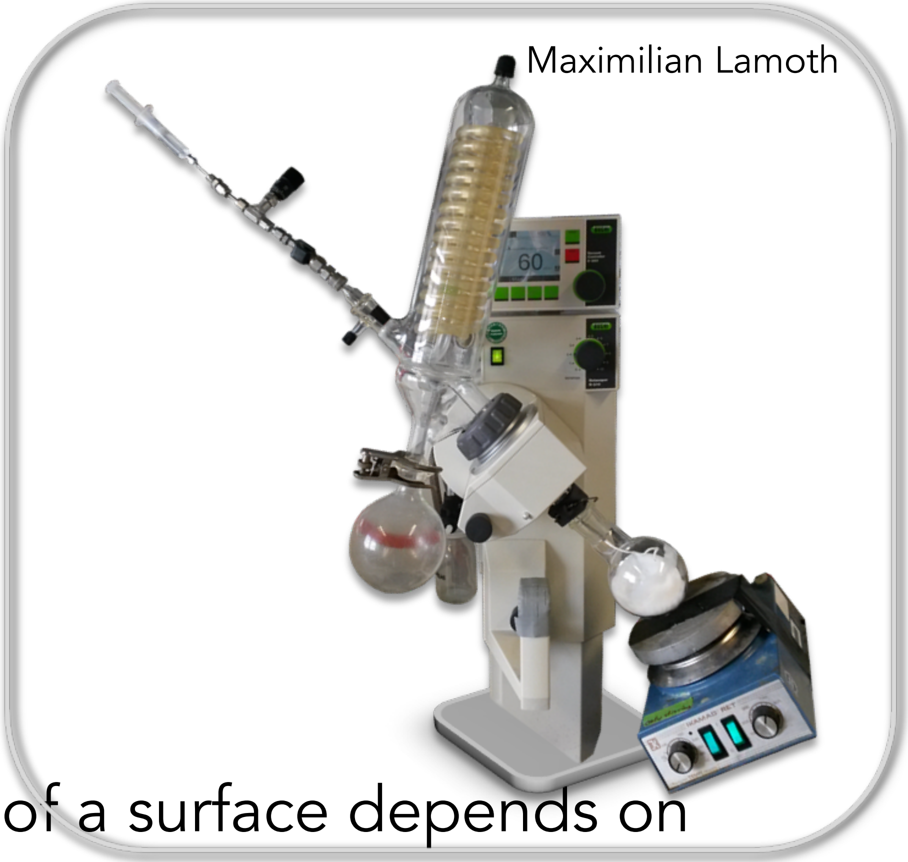
$[Rh]_{tot} = [Rh_{aq}^{3+}] + K_1[Rh_{aq}^{3+}][Cl^-] + \beta_2[Rh_{aq}^{3+}][Cl^-]^2 + RhCl_{3-n}(H_2O)_{2+n-m}(OH)_m]^{(n-1-m)+}$

Hydrolysis

$[RhCl_{3-n}(H_2O)_{3+n}]^{n+} + H_2O$

Ion exchange of amphotheric oxides

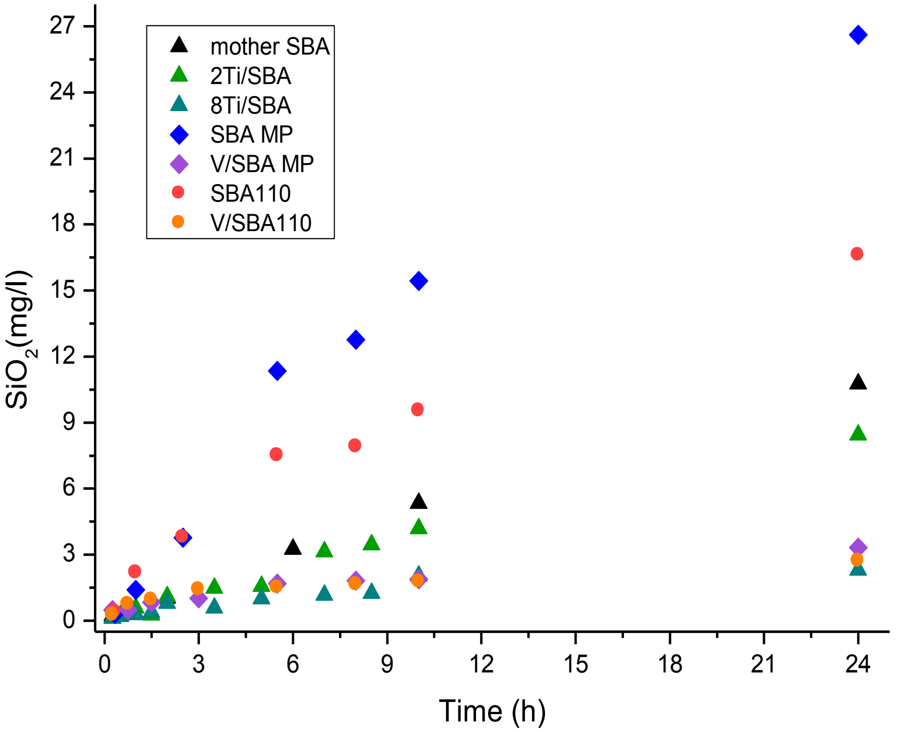
oxide	PZC
MgO	~12.5
ZnO	9-10
α-Fe_2O_3	5.5-9
α-Al_2O_3	6.5-10
TiO_2	3.5-6.5
SiO_2	2-4
WO_3	~0.4

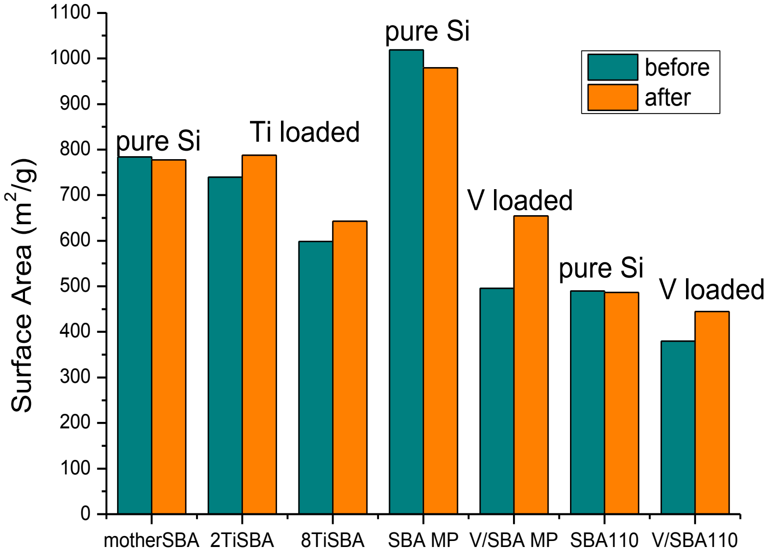

Maximilian Lamoth

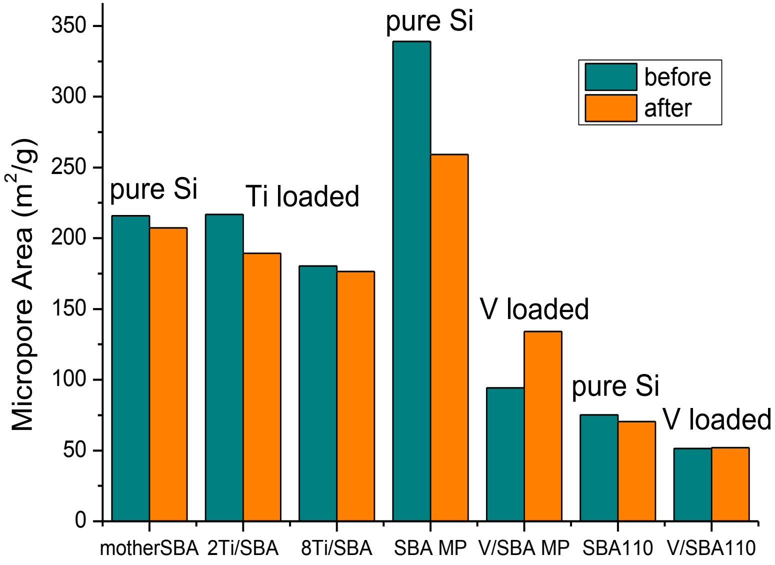
Point of zero charge (PZC) of a surface depends on

- Chemical nature (polarizaton of the surface groups by the cation)
- Crystal structure and particle morphology
- Heat treatment and physicochemical history of the oxide

Support modification in water

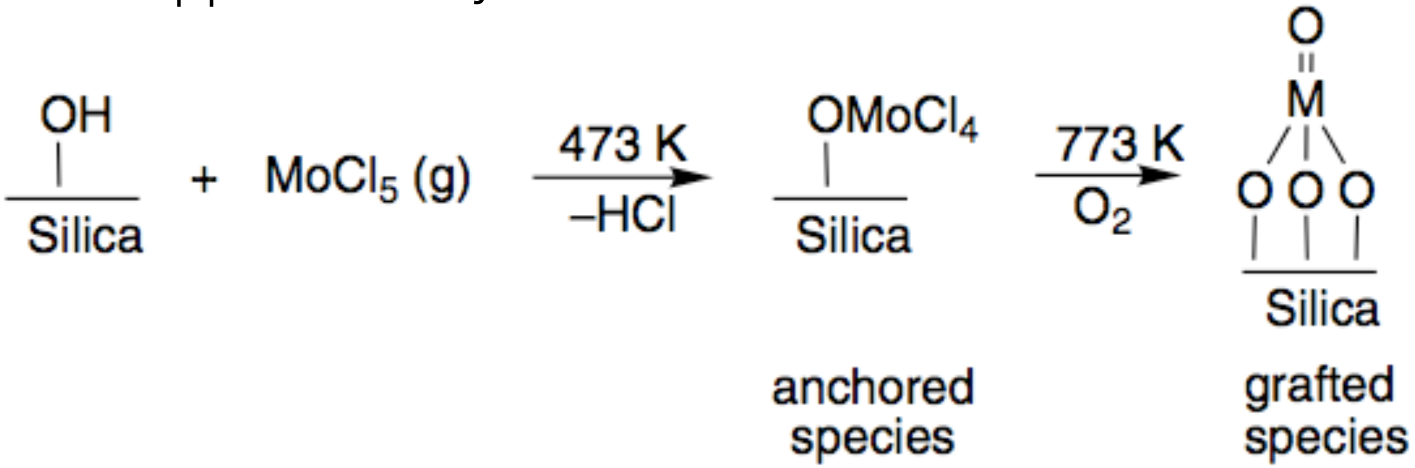






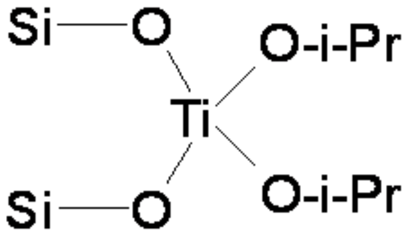
Grafting in organic media

Silica supported molybdenum oxide



Silica supported titanium oxide

$2\ SiOH + [Ti(O\text{-}i\text{-}Pr)_4]_{toluene} \longrightarrow$

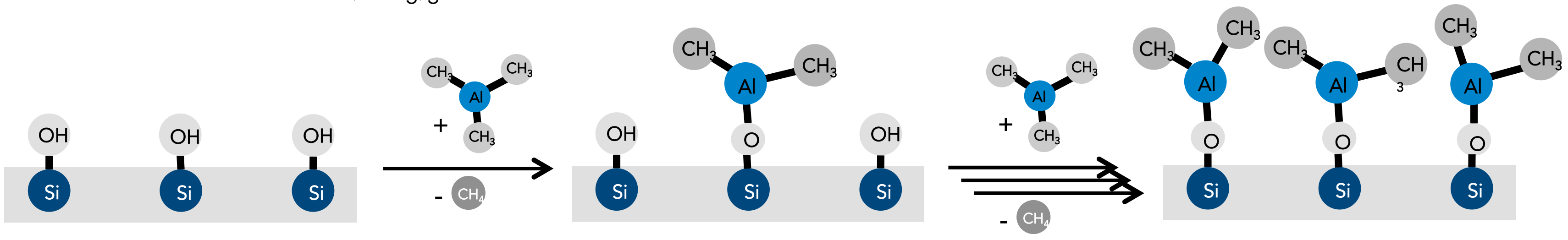


$+\ 2\ i\text{-}C_3H_7OH$

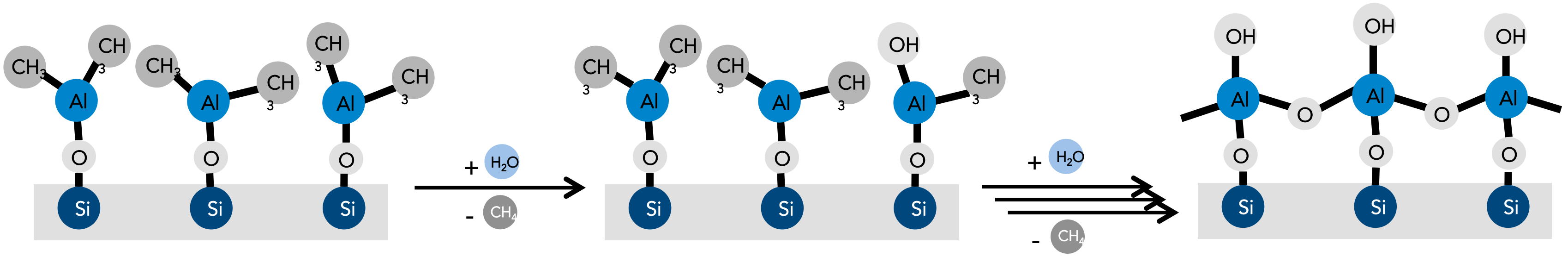
Atomic layer deposition (ALD)

Verena
Strempel,
BasCat

1. Reaction: Precursor $(CH_3)_3Al$ with surface OH sites



2. Reaction: Reactant H_2O with chemisorbed precursor on surface

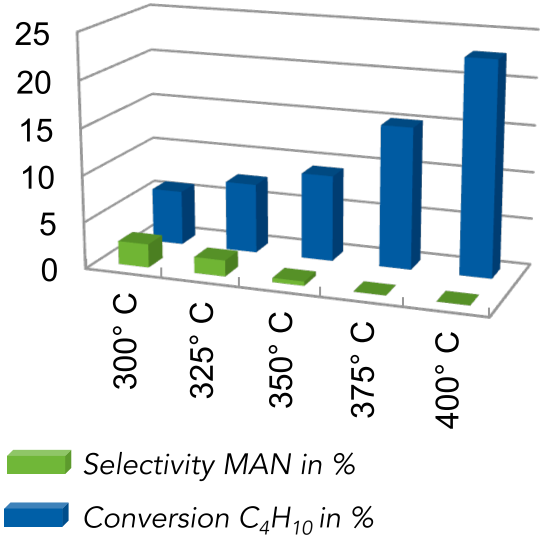


- vapor phase precursors, self-limiting process, precise thickness control
- established for flat substrates

J. Lu, J. W. Elam, P. C. Stair, *Accounts of Chemical Research* **2013**, *46*, 1806-1815.

n-Butane oxidation – PO_x ALD on V_2O_5

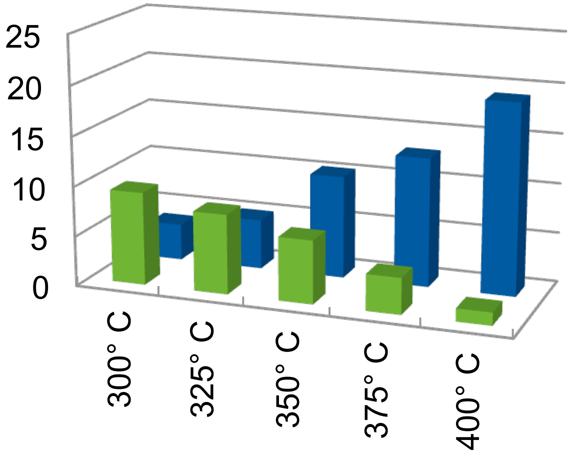
V_2O_5 Reference



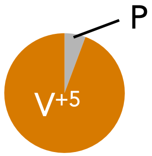
- V_2O_5 Reference catalyst served as starting material for the Phosphorus modification

3.87 m^2 g^{-1}
9.76 $Atom_V/nm^2$ [6]

P/V_2O_5 D1 ALD[5]

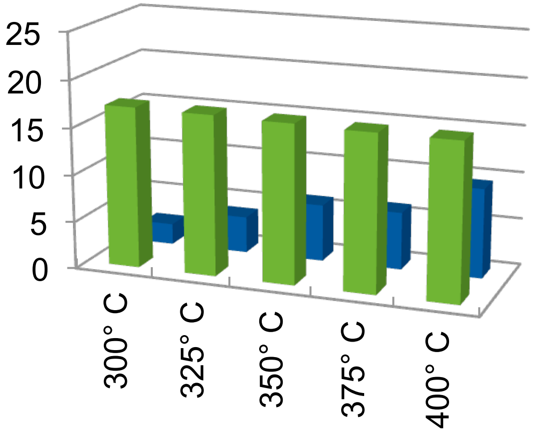


- P/V_2O_5 D1 catalyst synthesized in a flow-type diffusion based commercial ALD tool with one cycle (hexamethyl phosphoramide and O_3/O_2)



Surface ratio P/V
0.06 : 1

P/V_2O_5 FT1 ALD



- P/V_2O_5 FT1 catalyst synthesized in fixed bed with a forced flow through with one cycle (hexamethyl phosphor amide and O_3/O_2)

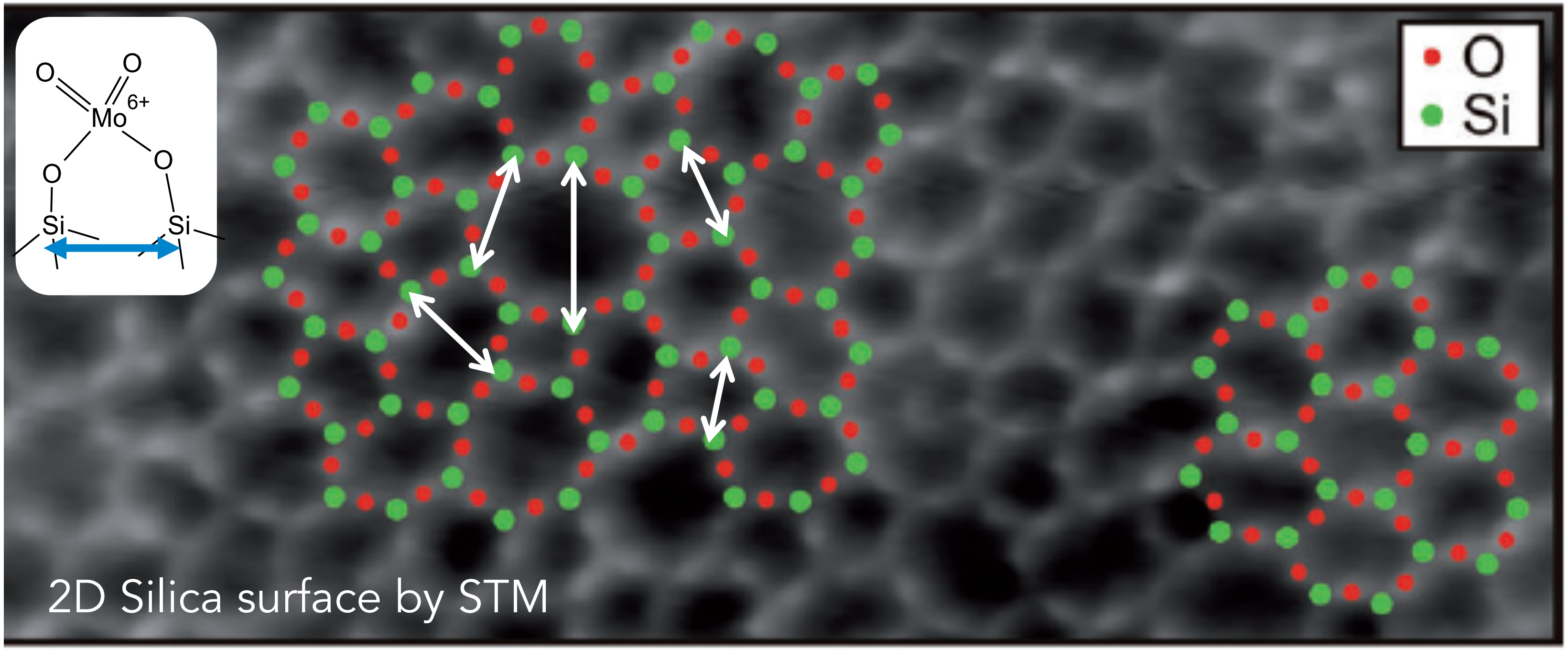
Surface ratio P/V
0.98 : 1

Testing parameters: GHSV 2000 h^{-1}, 1 atm, Feed: 2 % C_4H_{10}, 3 % H_2O, 20 % O_2

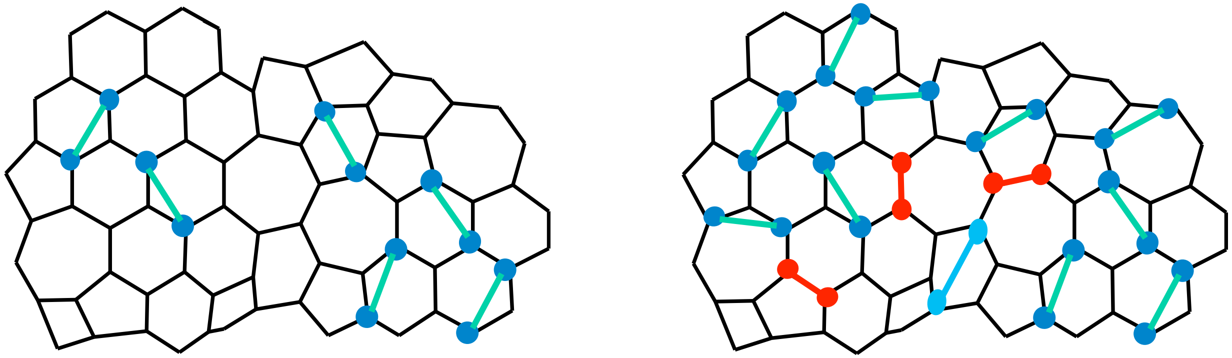
[5] V. E. Strempel, R. Naumann d´Alnoncourt, F. Rosowski, et al., J. Vac. Sci. Technol. A **1,** 01A135 (2016).
[6] J. Haber, M. Witko, et. al., Applied Catalysis A: General **1-2,** 3 (1997).

Anchorage of Mo oxide species

Lichtenstein et al., *Angew. Chem. Int. Ed.* **2012**, *51*, 404.

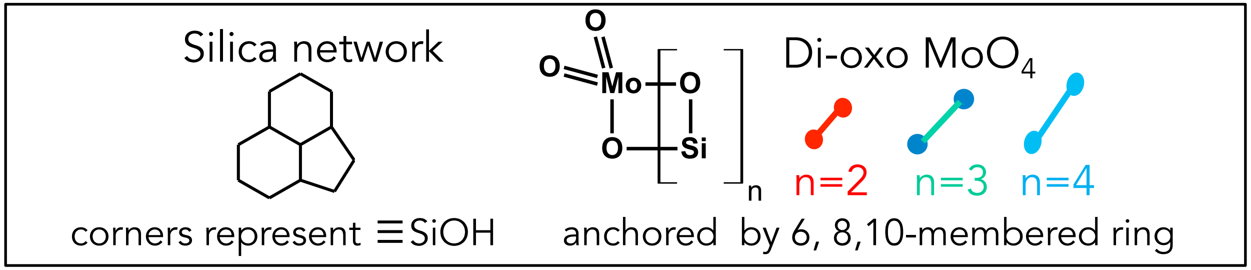


Strain due to limited anchoring groups



Low Mo coverage

High Mo coverage



Silica network

corners represent ≡SiOH

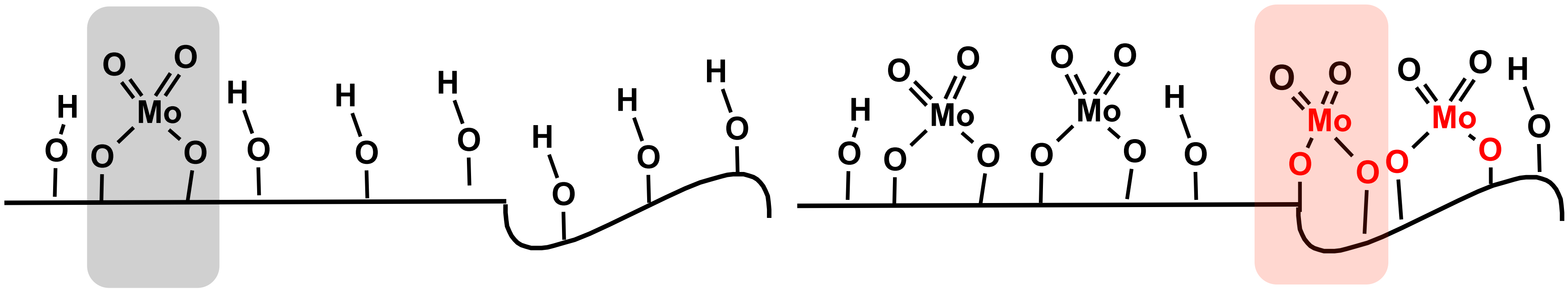
Di-oxo MoO_4

n=2 n=3 n=4

anchored by 6, 8,10-membered ring

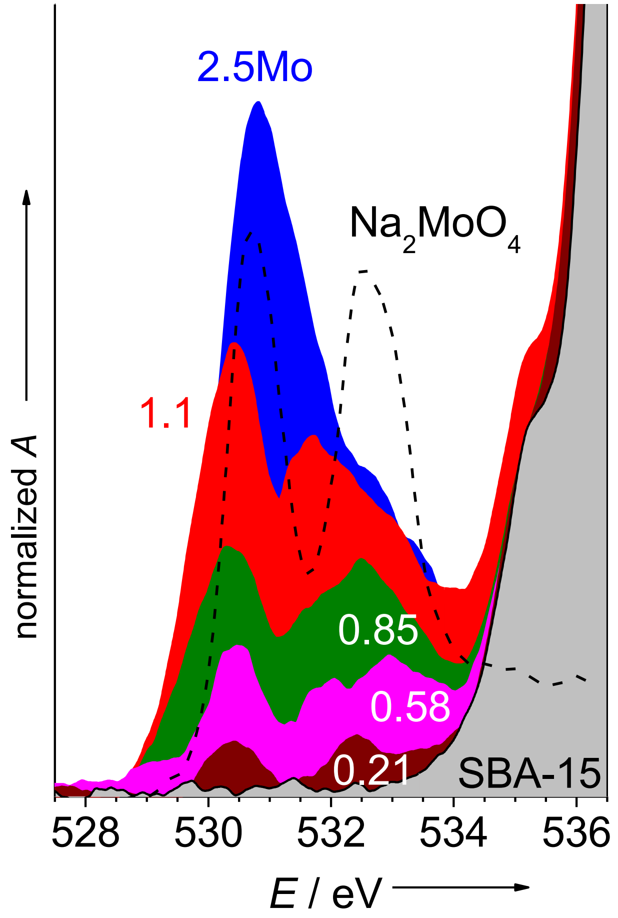
stable

frustrated

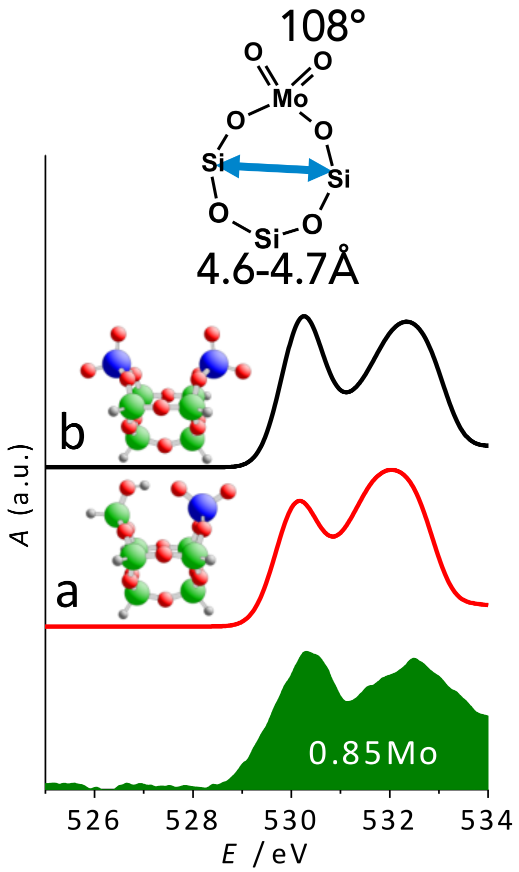


Strain in $(Si\text{-}O)_2Mo(=O)_2$

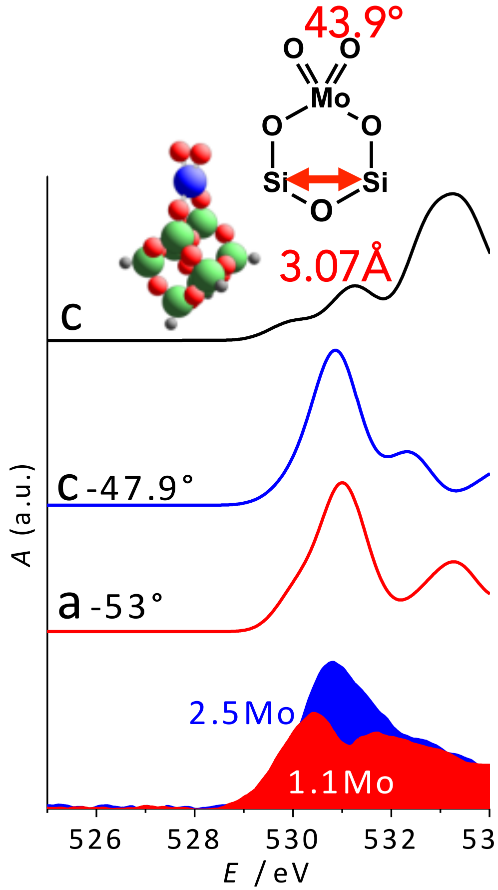
O K-edge NEXAFS



"relaxed" di-oxo



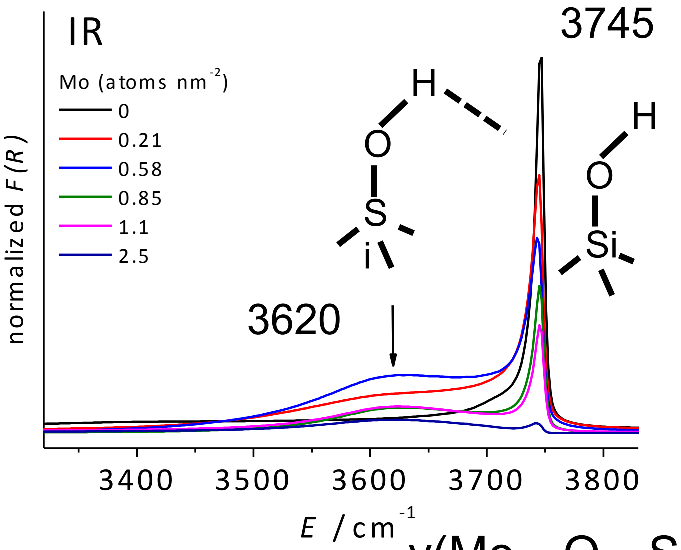
"strained" di-oxo

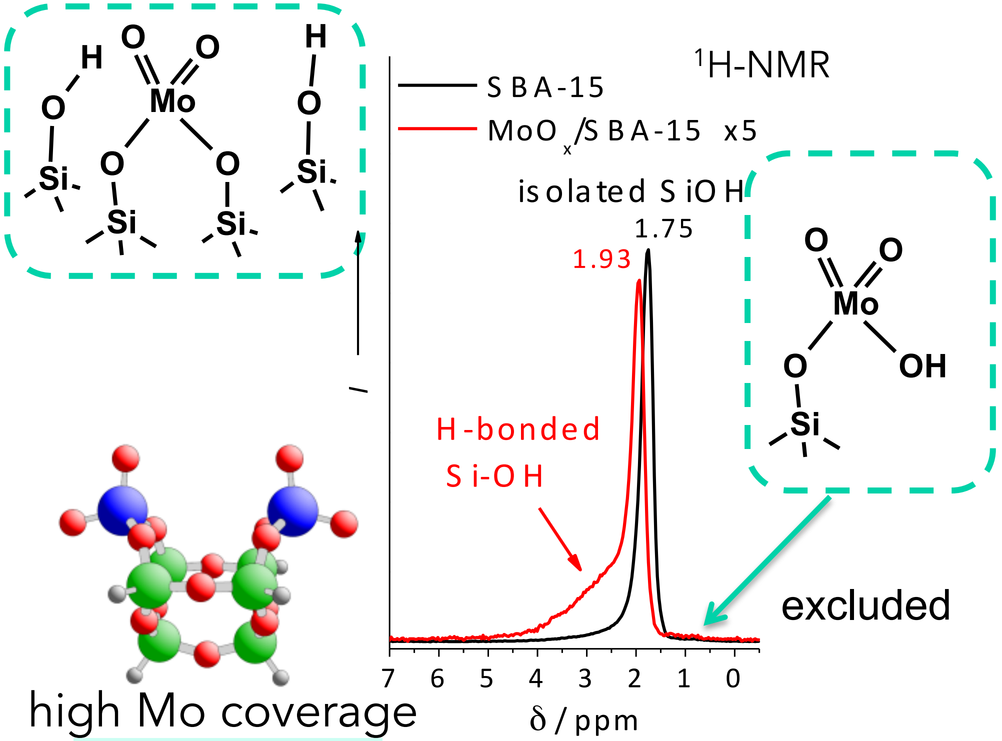


- "Relaxed" di-oxo models reproduce spectra at low Mo density
- Strained configurations may explain the spectra at higher Mo density
- Strain may favor the reducibility of MoO_x and the formation of active sites

Angewandte Chemie International Edition **2013**, *52*, 13553-13557.

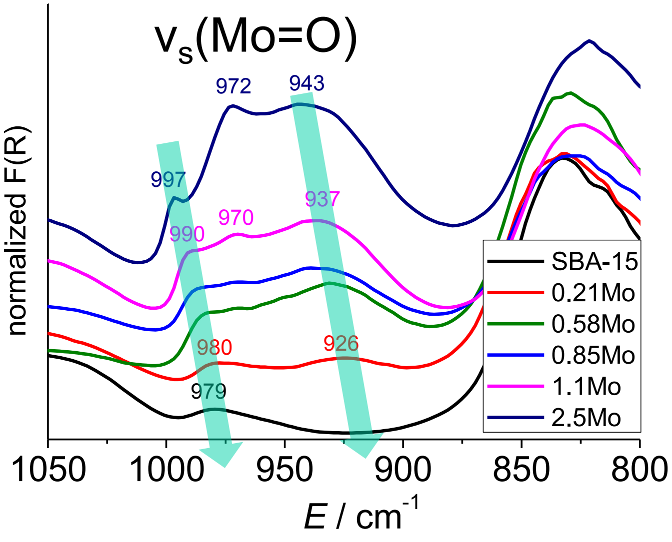
OH groups on MoO_x/SiO_2

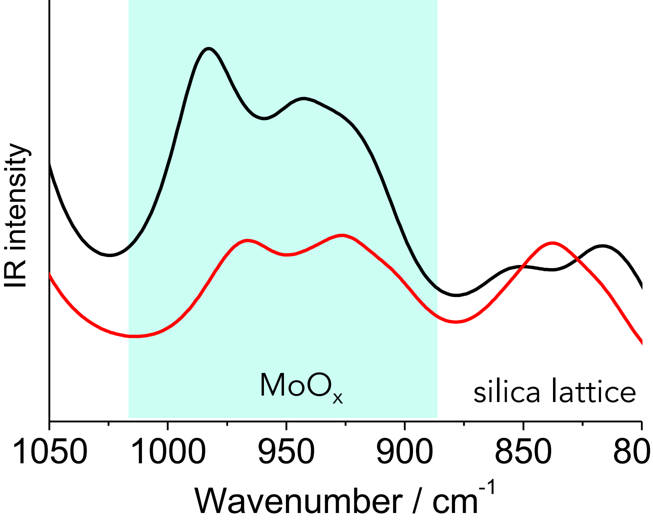


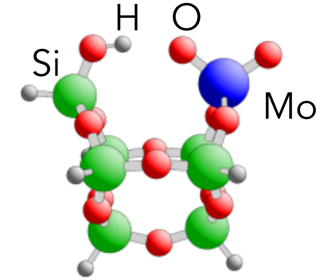


high Mo coverage

v(Mo—O—Si)



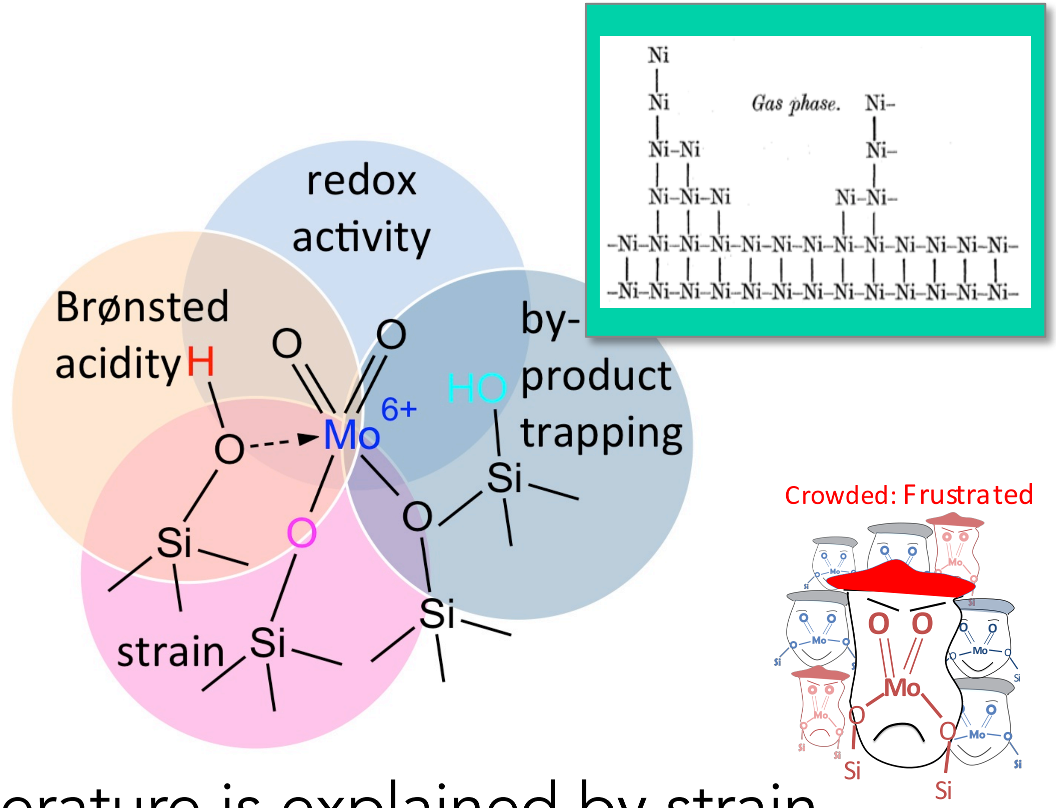




low Mo coverage

Generation of active sites on monolayer catalysts

- Several fortunate circumstances must coincide to generate carbene species on silica-supported Mo oxide:



- Reducibility at low temperature is explained by strain in Mo dioxo species

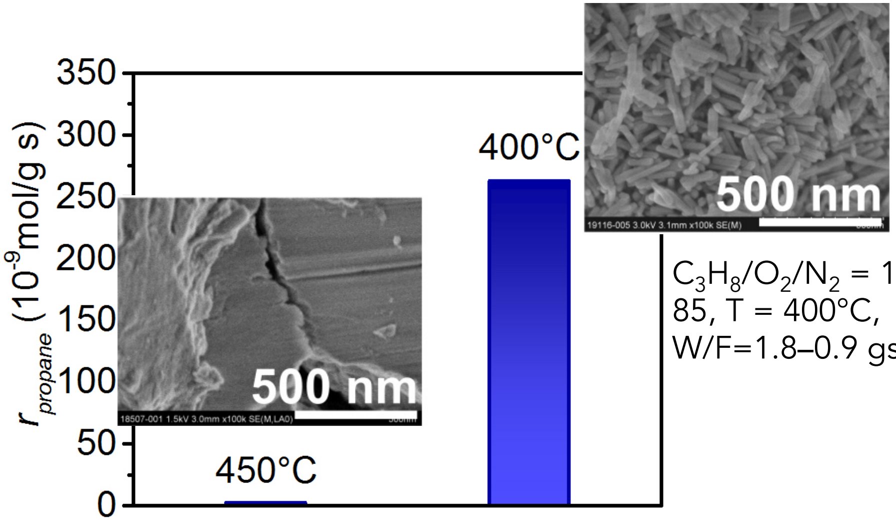
→ Strain really needed?

- Acidity is generated by a close contact of silanol groups and Mo oxide species in strained configuration

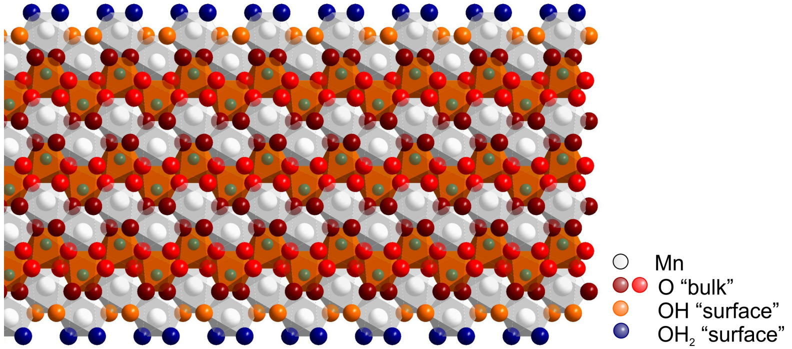
Concept of self-supported surface layer

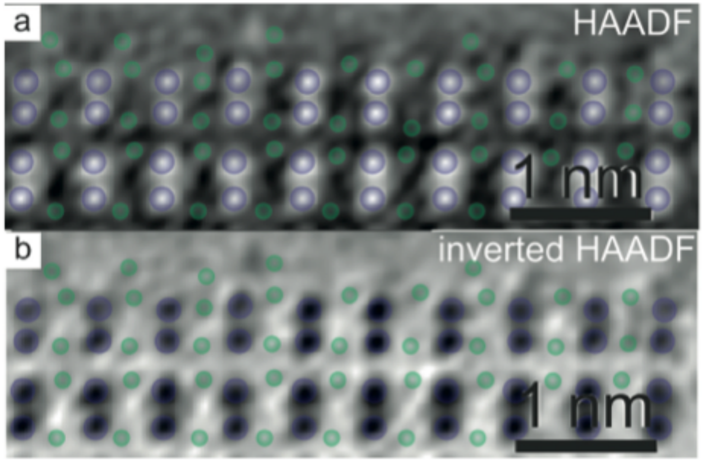
Nanostructuring $MnWO_4$

$$2\ C_3H_8 + O_2 \rightarrow C_3H_6 + 2\ H_2O$$



$C_3H_8/O_2/N_2$ = 10 / 5 / 85, T = 400°C, W/F=1.8–0.9 gsml^{-1}

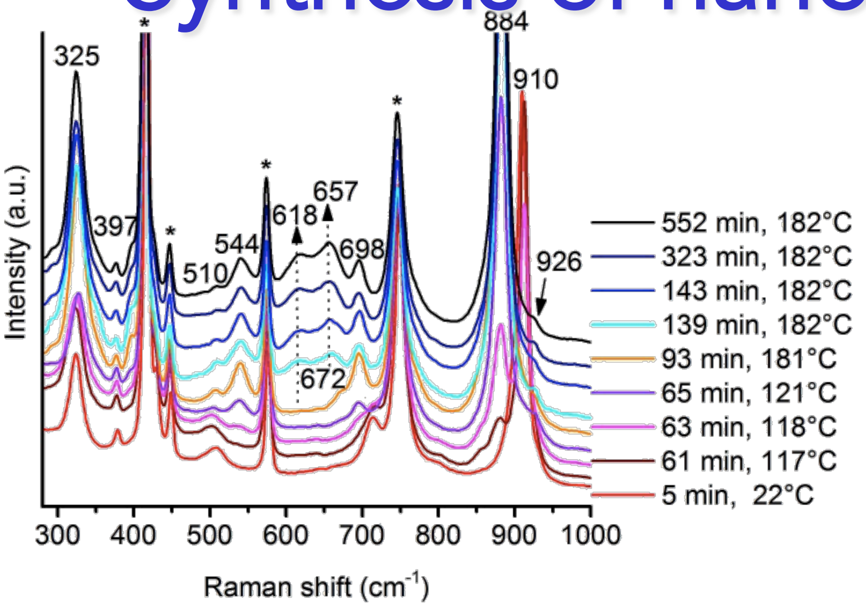


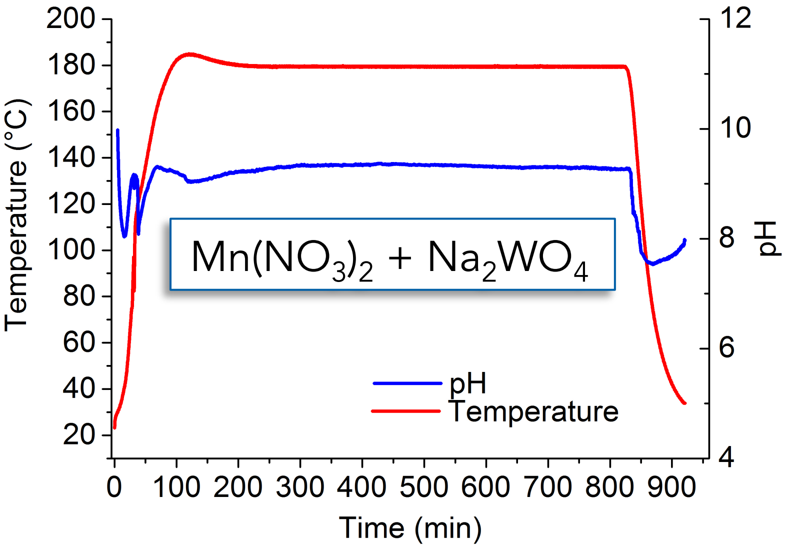


Surface termination of the b plane viewed along the growth direction [001] by FFT-filtered atomic-resolution STEM images. a) HAADF, and b) inverted HAADF image. Mn green, W violet.

X. Li et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 4092–4096.

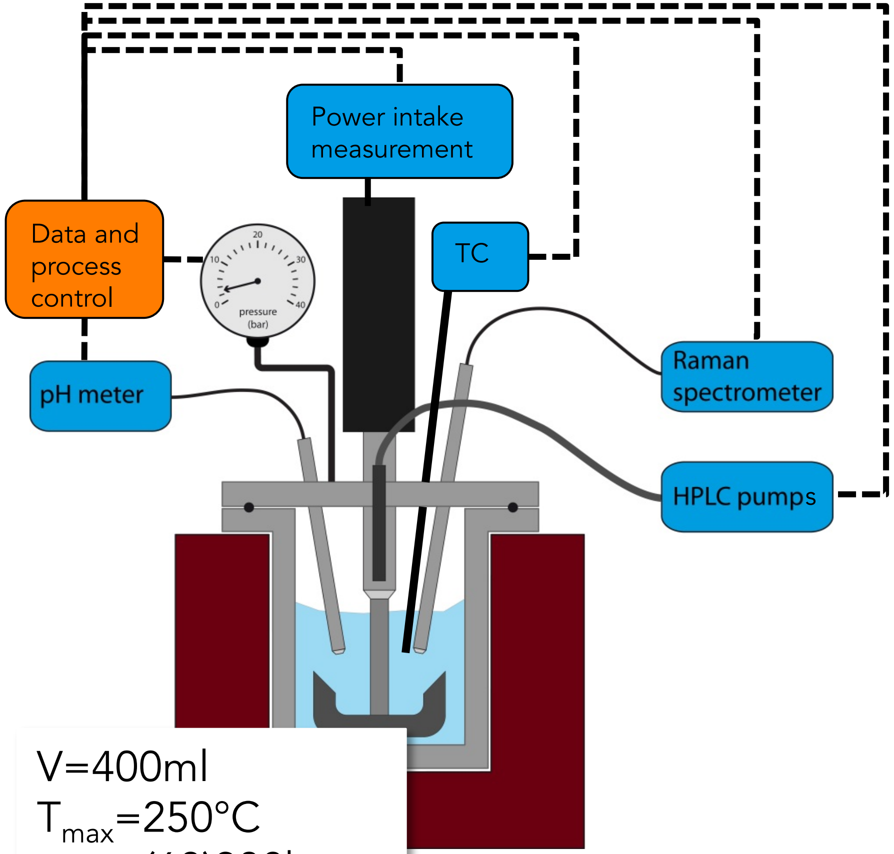
Synthesis of nanostructured $MnWO_4$





$Mn(NO_3)_2 + Na_2WO_4$

Analytical autoclave for hydrothermal synthesis



V=400ml

T_{max}=250°C

p_{max}=(60)200bar

Hastelloy C22

Sampling possible

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

Faraday Discussions, **2016**, *188*, 99-113

Dissolution - recrystallization

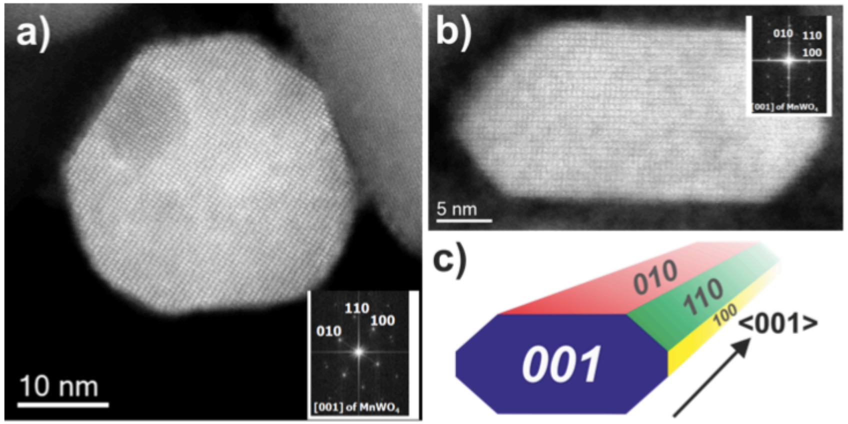


Figure S6. HAADF_STEM images of $MnWO_4$ nanoparticles viewed along <001> with different aspect ratios: a) AR1.5, b) AR5.1 and c) perspective model for a typical faceted nanoparticle.

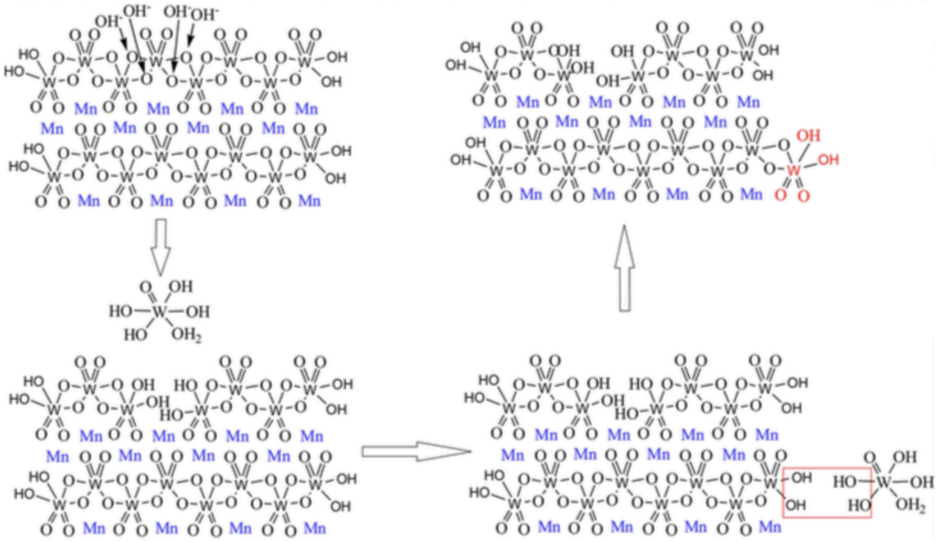


Figure S8. Schematic representation of the formation of W-OH groups at {001} planes during dissolution-recrystallization under hydrothermal conditions at 180°C.

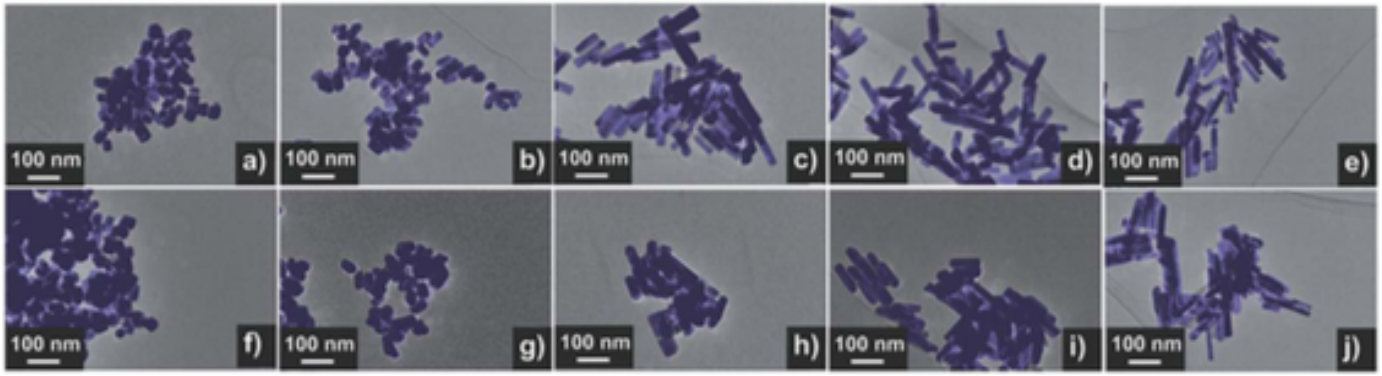
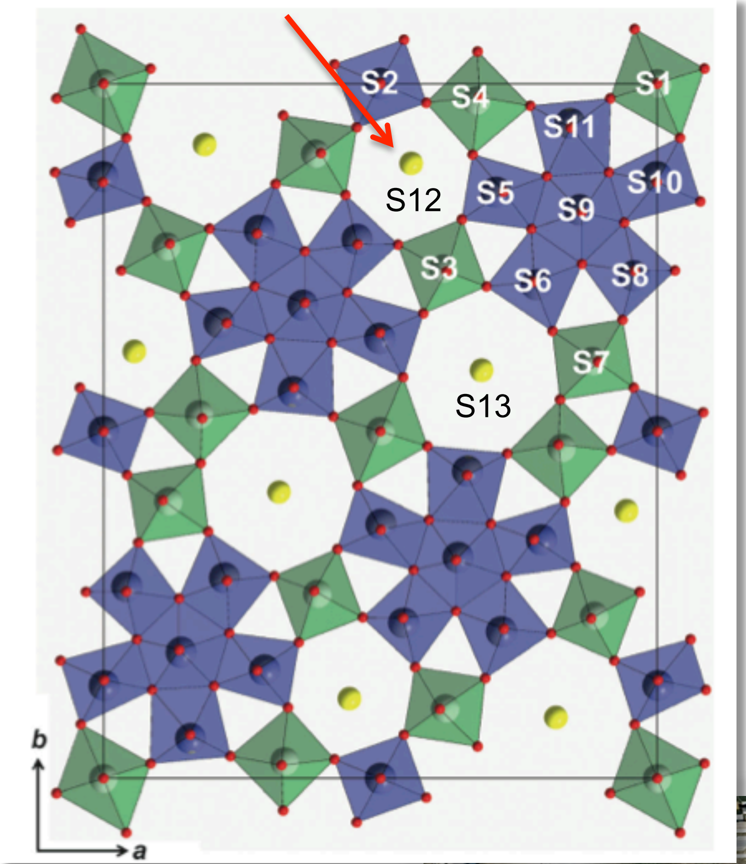


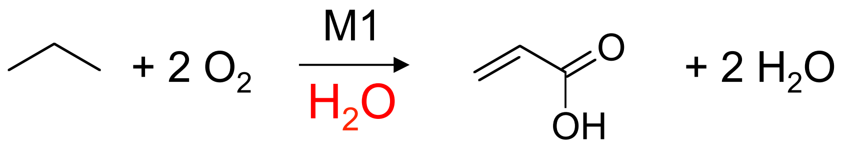
Fig. 2 Electron microscopy images of the as-synthesized (top row) and thermally treated (bottom row) nanostructured $MnWO_4$ materials AR1.5 (a) and (f), AR1.7 (b) and (g), AR3.2 (c) and (h), AR3.9 (d) and (i), and AR5.1 (e) and (j); uncoloured TEM images are presented in the ESI (Fig. S4†).

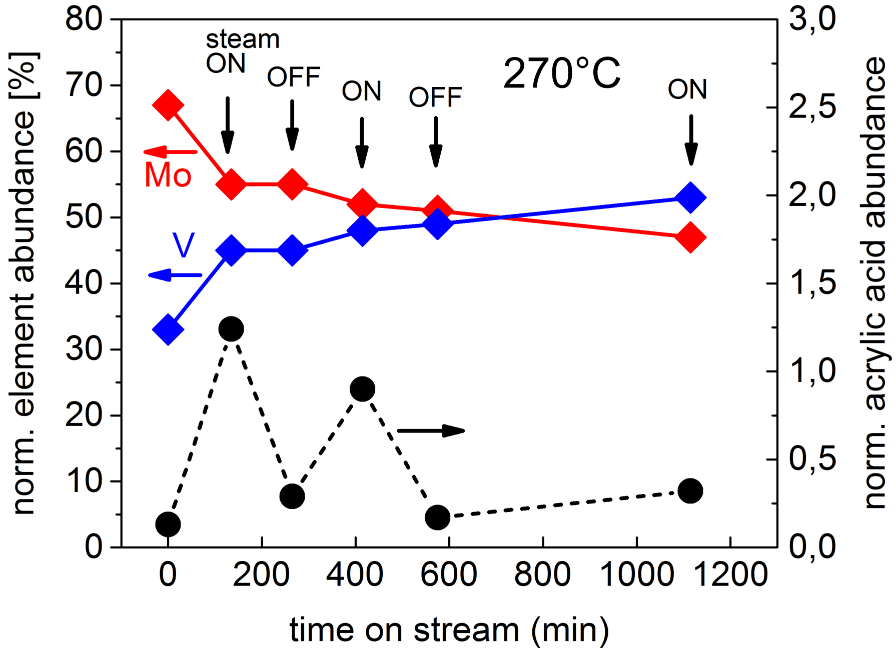
Surface layer generated under reaction conditions

54 % (V)



Single crystal analysis at MX 14.2 beamline at BESSY





4.1 → 4.6

av. V oxidation state

ACS Catalysis, **2017**, *7*, 1403.

Conclusions

- A solid catalyst is a hierarchical system, in which the active sites are embedded and subjected to dynamic interactions with the matrix and the environment
- Active sites cannot be synthesized, but are formed under reaction conditions; Catalyst synthesis results in a catalyst precursor
- Successful synthesis requires that the operation parameters of the catalytic reaction and the requirements of the reactor are taken into consideration from the very beginning; Therefore, catalyst synthesis is generally accompanied by kinetic studies and process development
- Reliable and reproducible synthesis of homogeneous catalysts requires a certain batch size and well defined reaction conditions documented by process control
- Rational catalyst design implies fundamental understanding of the elemental processes that can be elucidated by model experiments and the application of in-situ/operando techniques