Towards the pressure and material gap in heterogeneous catalysis: hydrogenation of acrolein over silver catalysts

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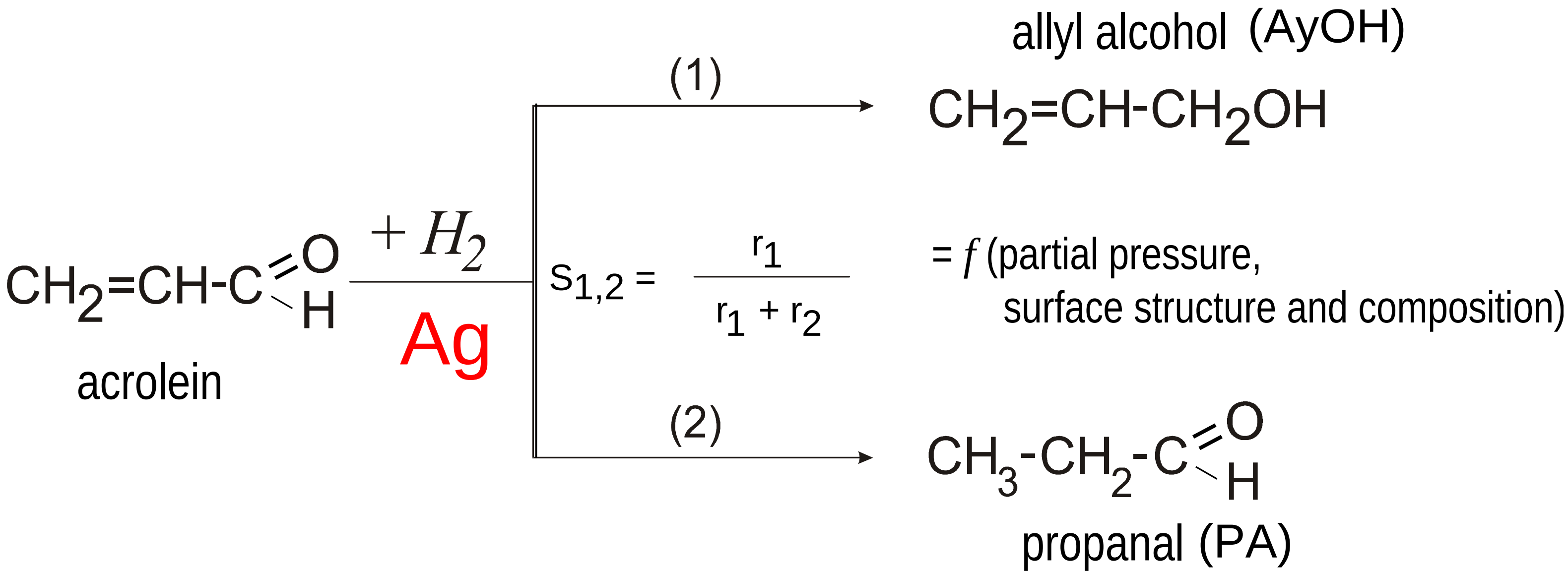
TUD

Hydrogenation of acrolein



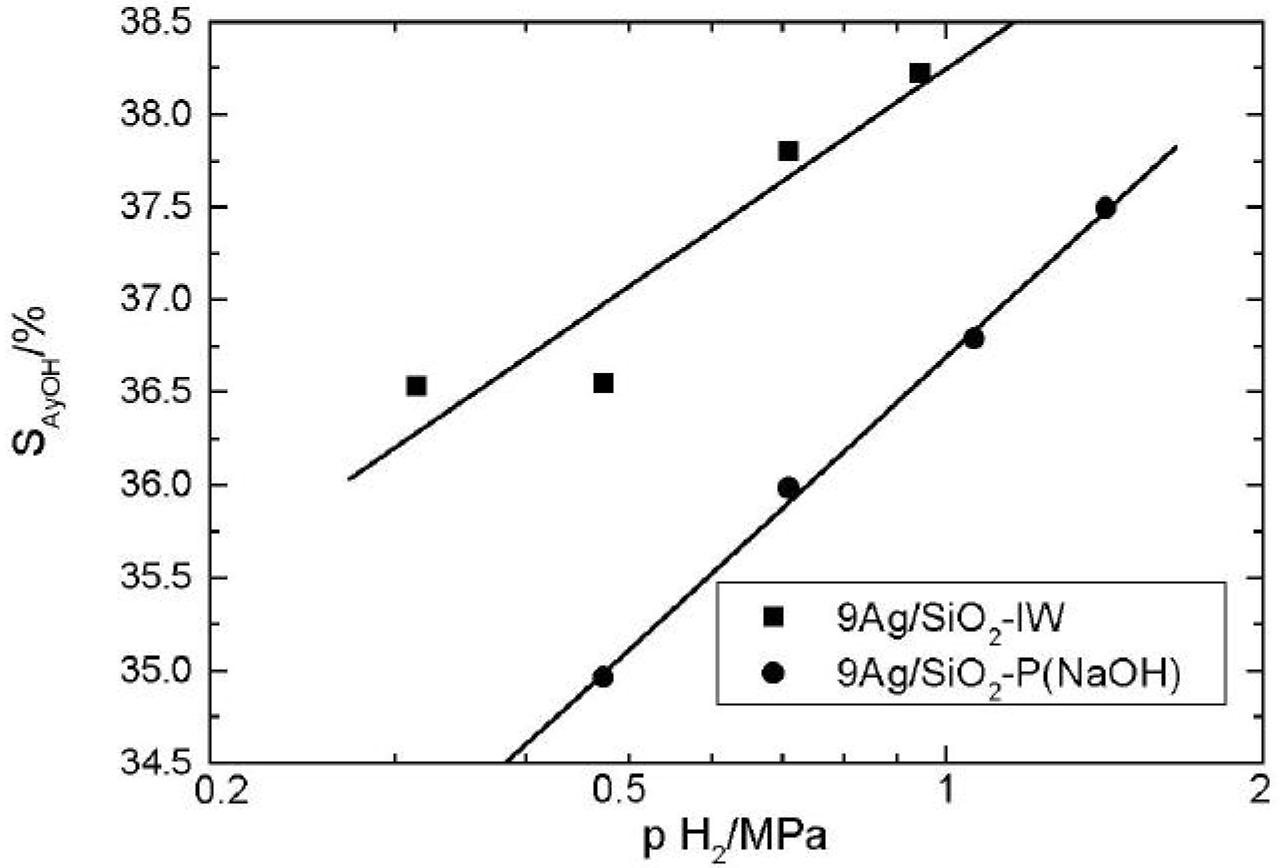
Control of intramolecular selectivity?

→ Intrinsic selectivity to allyl alcohol when using Ag und Au catalysts [1, 2]

[1] P. Claus, H. Hofmeister, *J. Phys. Chem. B*, **1999**, *103*, 2766-2775.
[2] P. Claus, A. Brückner, C. Mohr, H. Hofmeister, *J. Am. Chem. Soc.*, **2000**, *122*, 11430-11439.

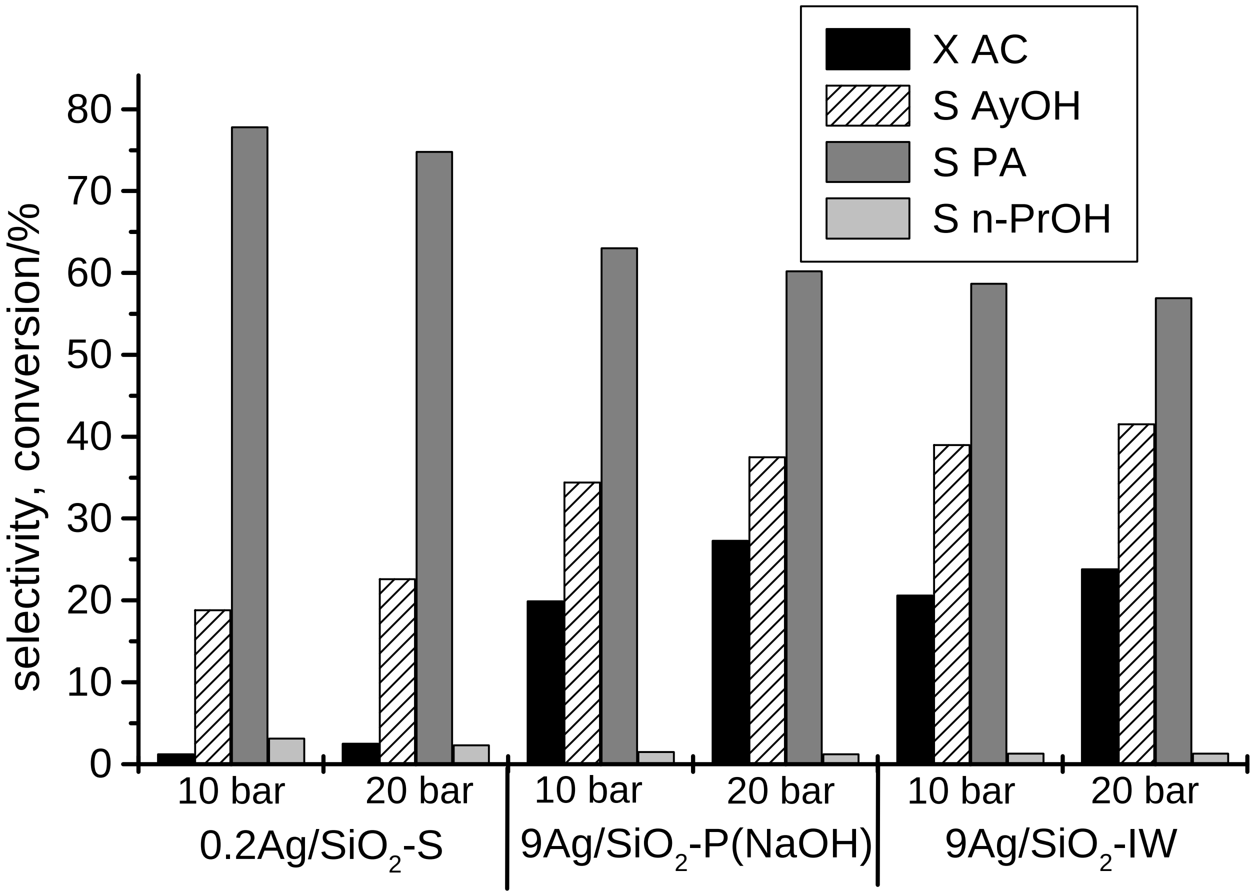
→ Poor selectivity to allyl alcohol when using Pt, Ru, Rh, Ni,.... as hydrogenation catalysts

Pressure dependence of catalytic properties

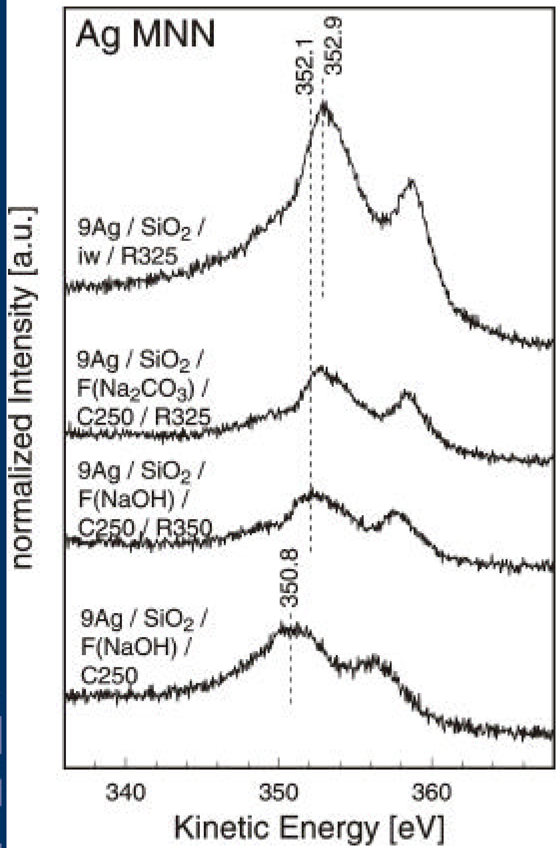


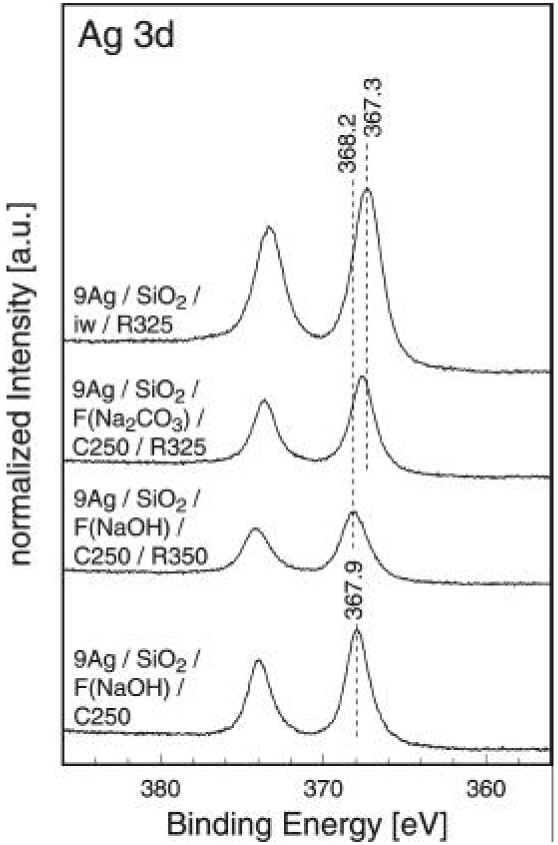
M. Bron, E. Kondratenko, A. Trunschke, P. Claus, Z. Phys. Chem. 218 (2004) 405.

Acrolein hydrogenation: influence of preparation method (i.e., structural features of the silver catalyst)



XPS/AES at Ag/SiO_2 catalysts





Modified Auger-parameter α'

$\alpha' = E_{kin}(Ag\ M_5N_{45}N_{45}) + E_b(Ag\ 3d_{5/2})$

<u>independent of charging</u>

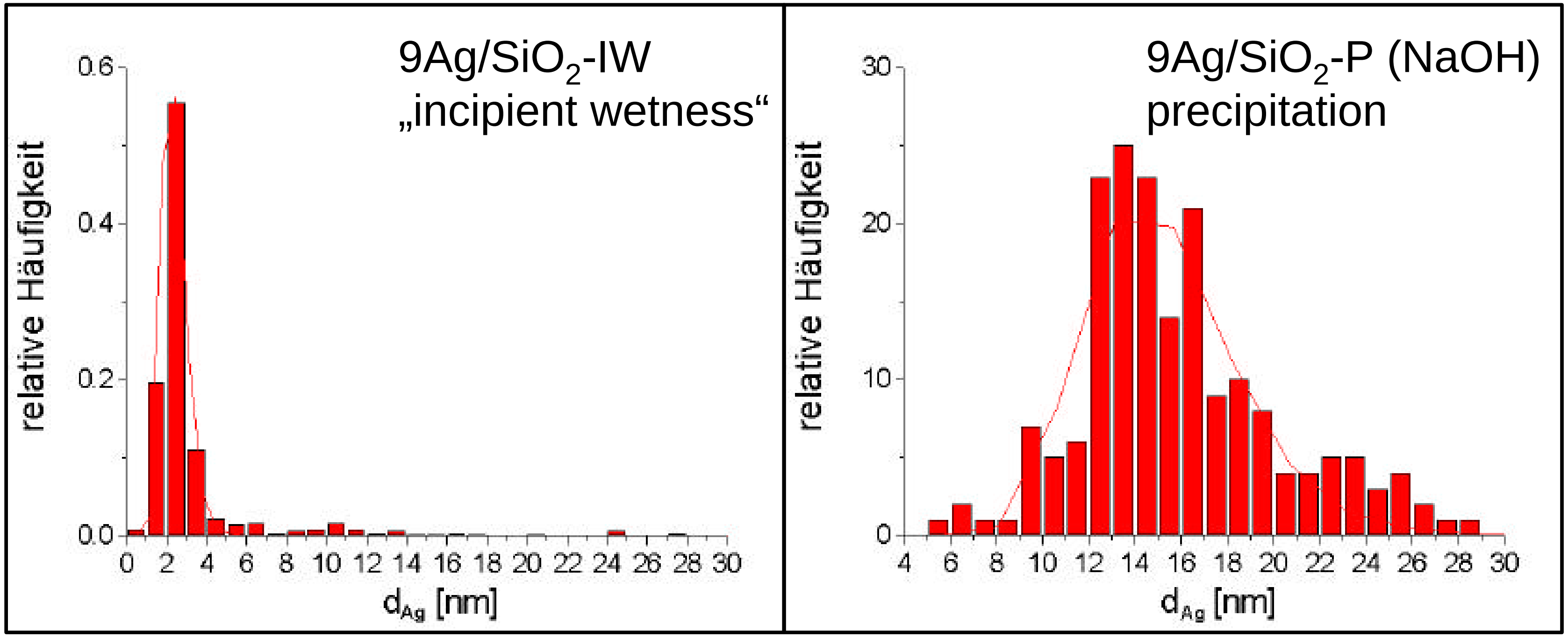
α' = 720.4 eV
α' = 720.3 eV   } Ag
α' = 720.3 eV

α' = 718.7 eV Ag_2O

literature:	$E_{kin}(Ag\ M_5N_{45}N_{45})$	$E_b(Ag\ 3d_{5/2})$	α'	
Ag	352.5 eV	368.0 eV	720.5 eV	L.H. Tjeng et al.
Ag_2O	351.9 eV	367.6 eV	719.5 eV	PRB 41 (1990) 3190-3199

A. Scheybal, A. Knop-Gericke, Electronic Structure, Dept. AC, Fritz-Haber-Institut (MPG), Berlin, Germany

TEM at Ag/SiO_2 catalysts



- d_{Ag} (9Ag/SiO_2-IW) « d_{Ag} (9Ag/SiO_2-P(NaOH)
- Correlation particle size - product distribution/selectivity to allyl alcohol?

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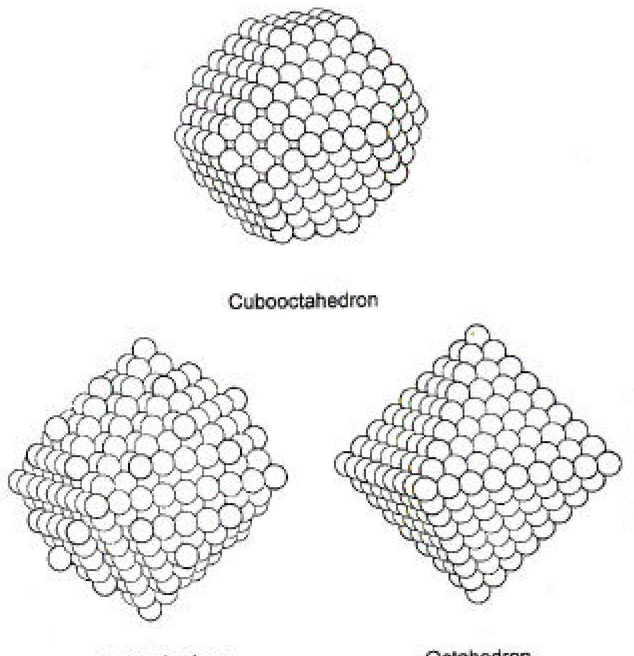
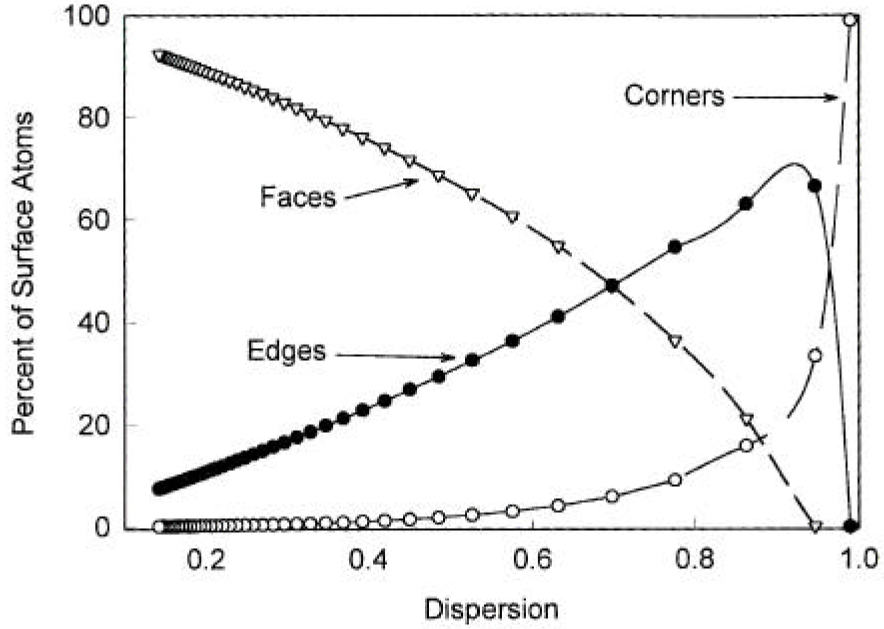
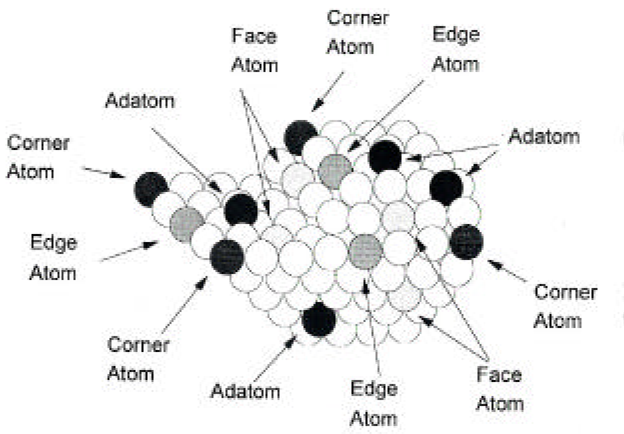
Structure sensitivity: particle size



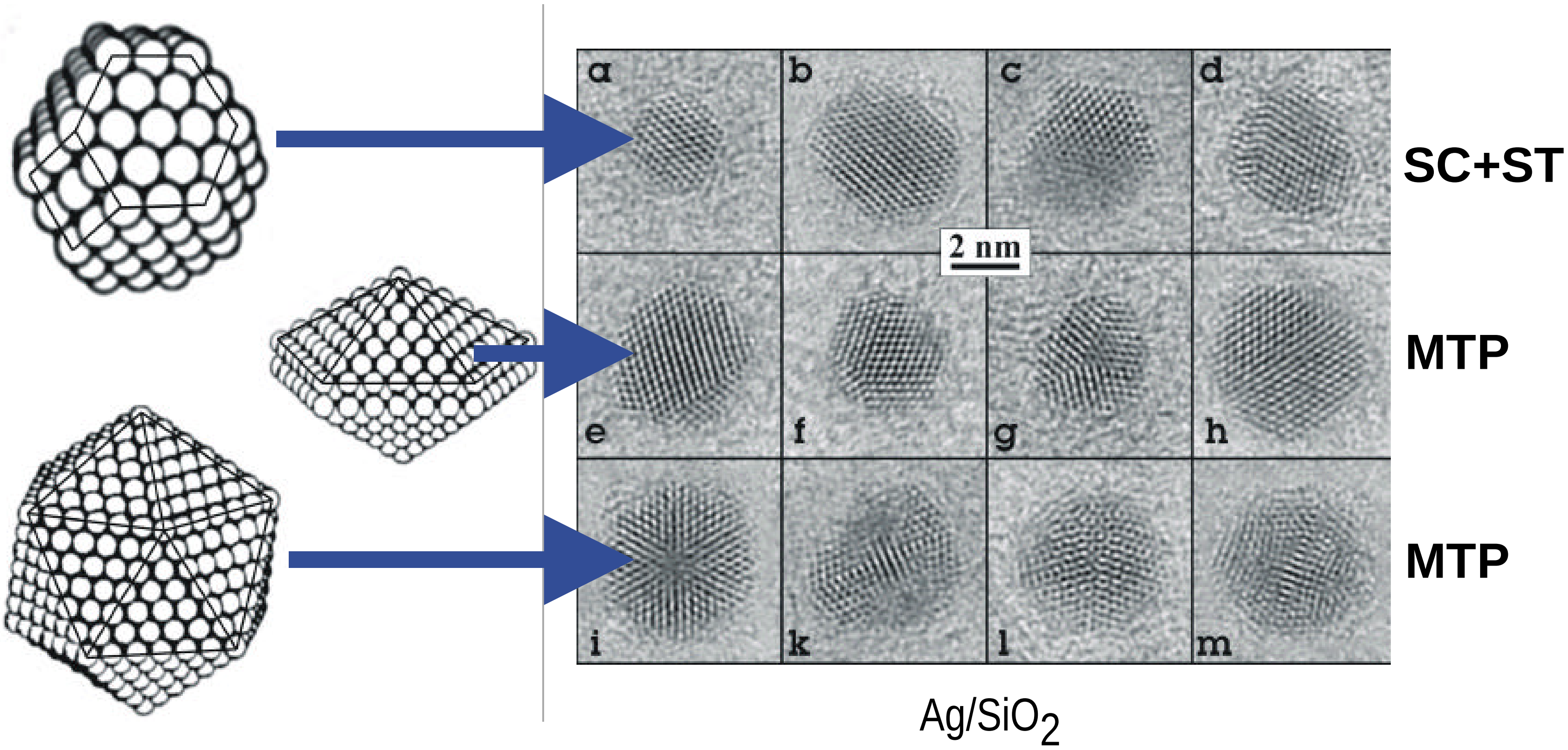
Idealized crystal shapes





different types of surface atoms

Structure sensitivity: particle shape

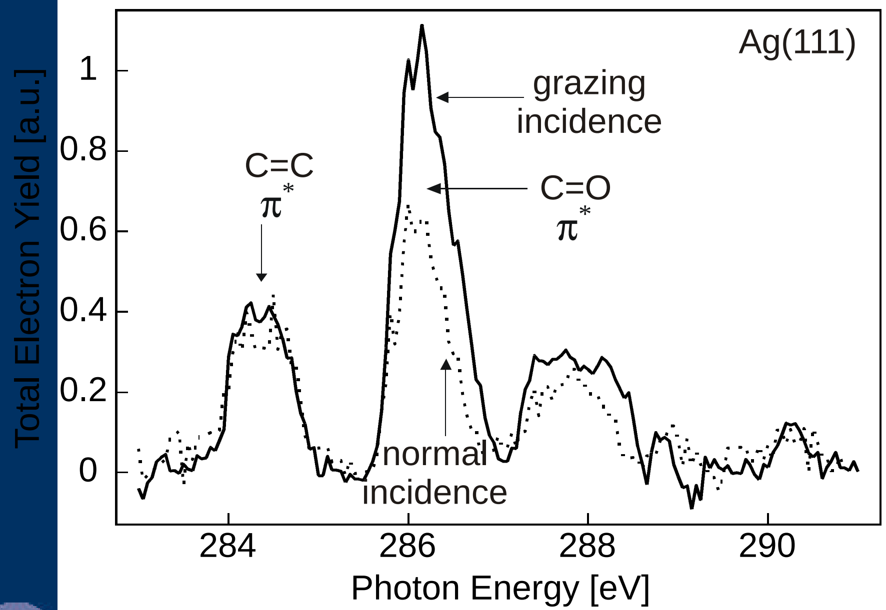


SC: single crystalline, ST: single twinned , MTP: multiple twinned particles
- Increasing defect number

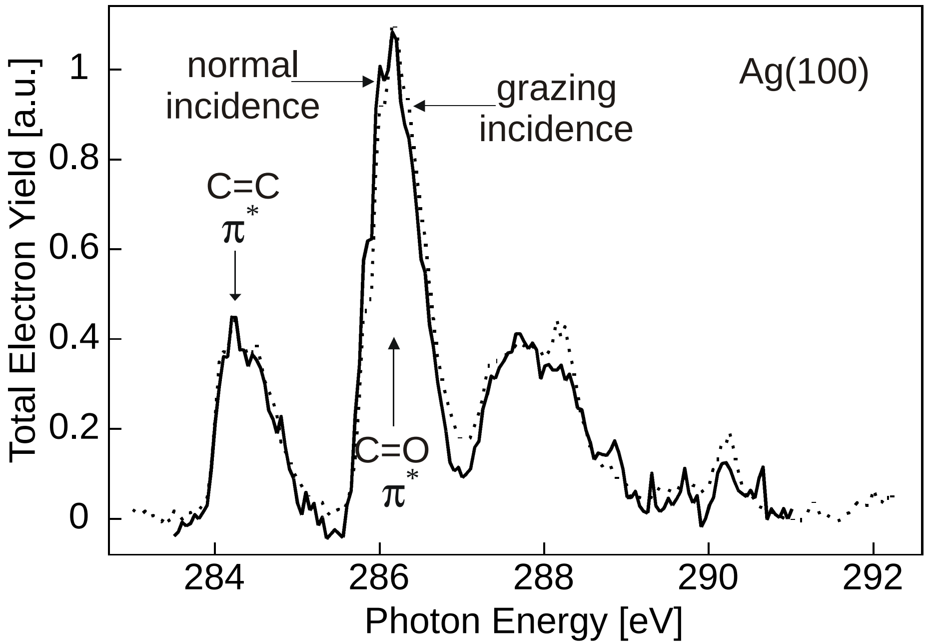
C. Mohr, H. Hofmeister, P. Claus, J. Catal. 213 (2003) 86.

In situ-XAS under reaction conditions

surface and gas phase related signal



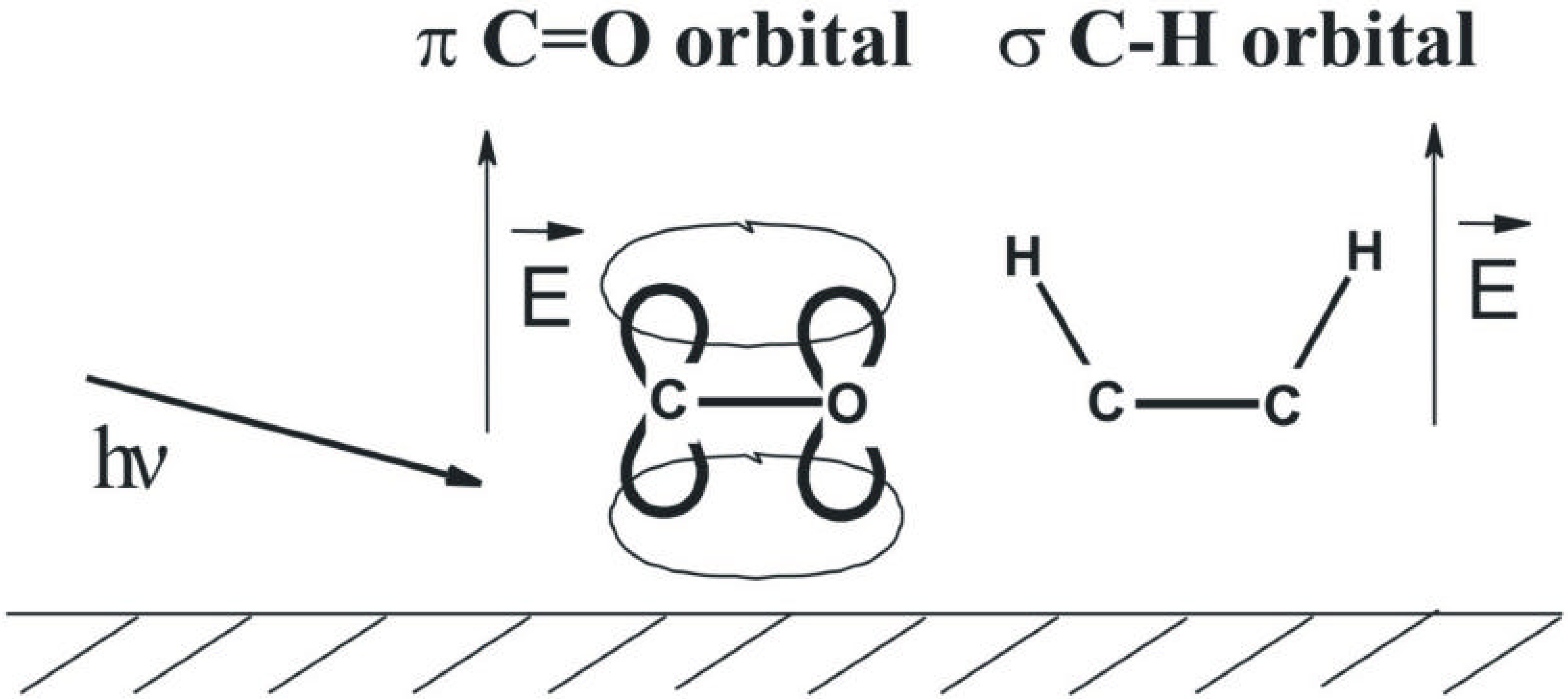
surface and gas phase related signal



Differences between Ag(100) und Ag(111) -
Structure sensitivity of hydrogenation

M. Bron, A. Knop-Gericke, D. Teschner, A. Scheybal, M. Hävecker, D. Wang, R. Födisch, D. Hönicke, R. Schlögl, P. Claus, submitted.

Orientation of reaction intermediates at the silver surface



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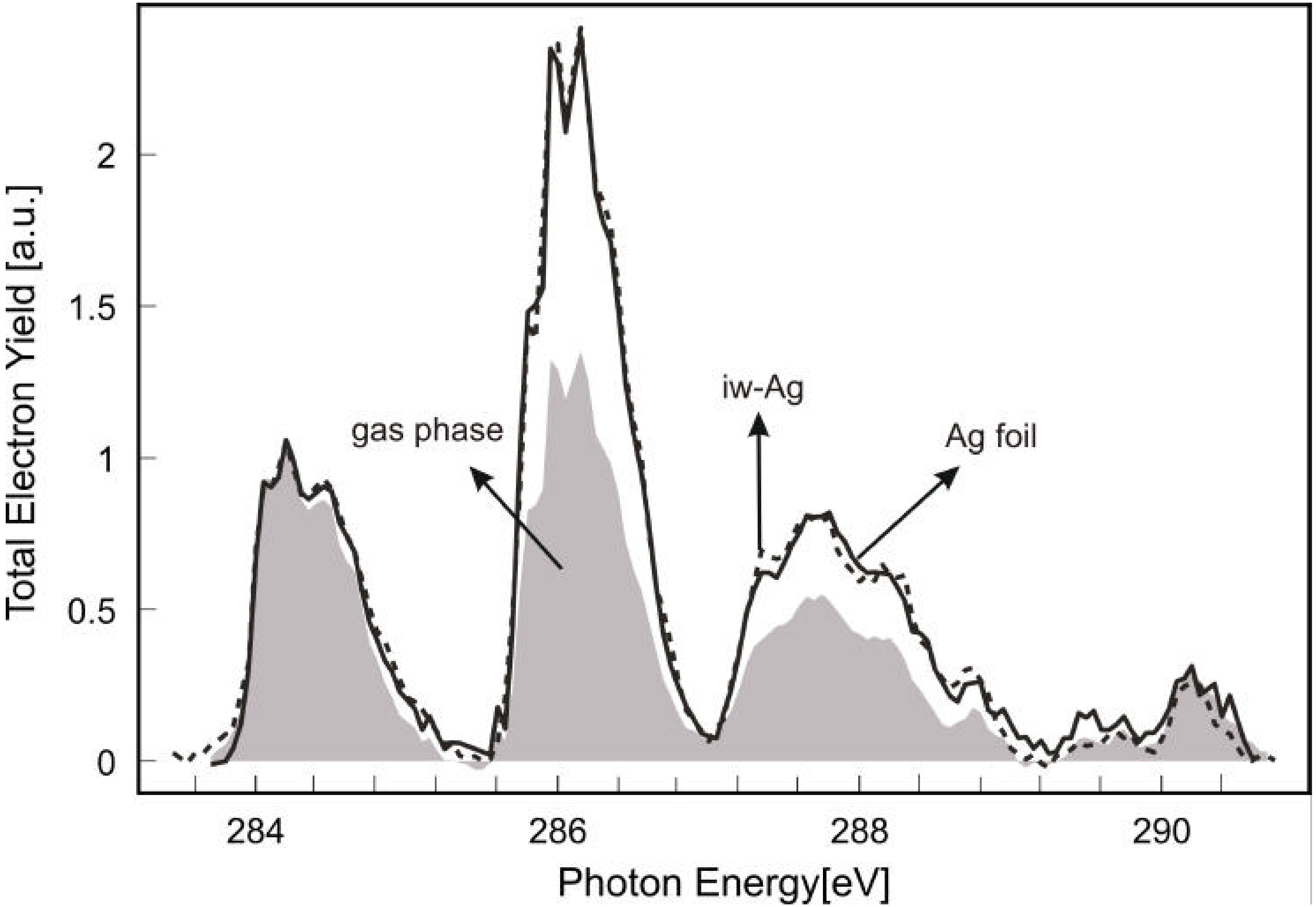

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Silver materials used within the GAP project

Ag/SiO_2, Ag/ZnO

Supported Ag with controlled particle size and shape

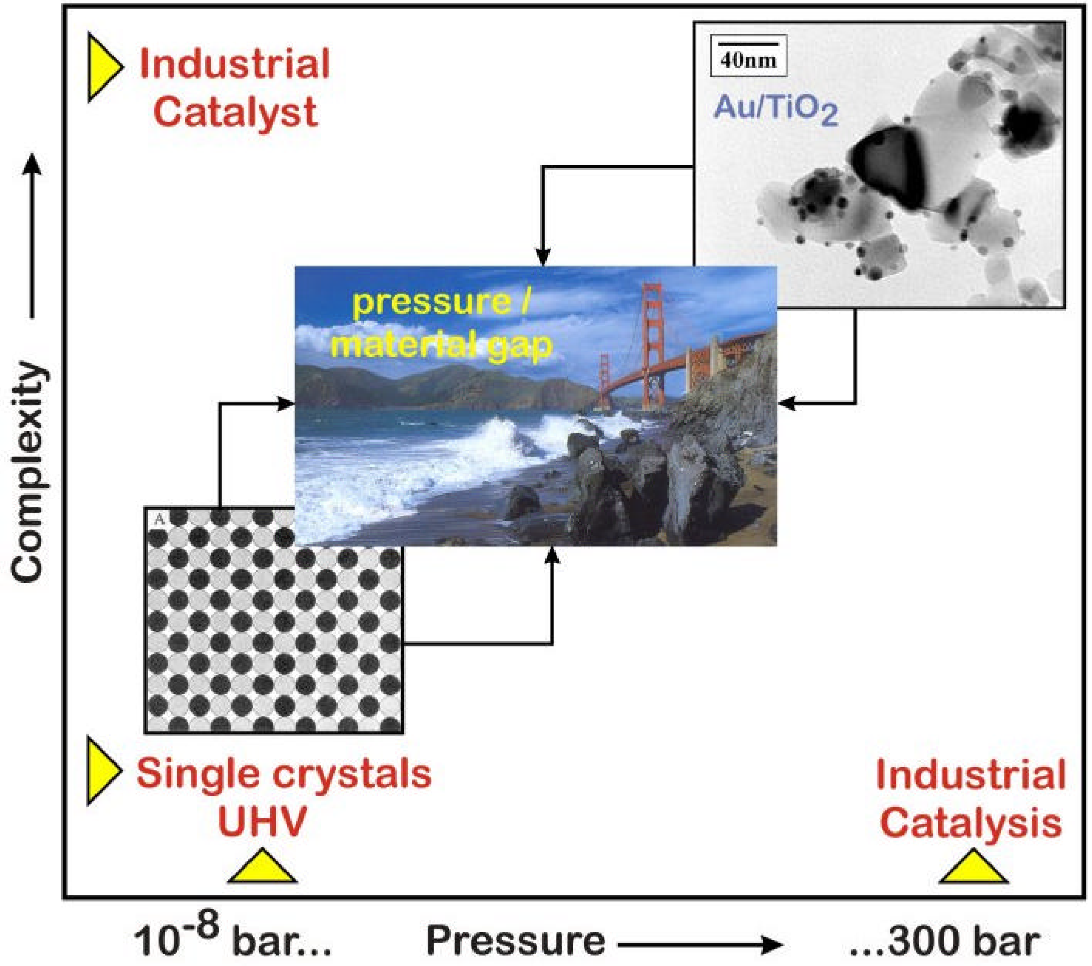
Nanoscopic Ag (without support)

Electrolyte silver

Sputtered/electrochemically deposited Ag

Ag foil

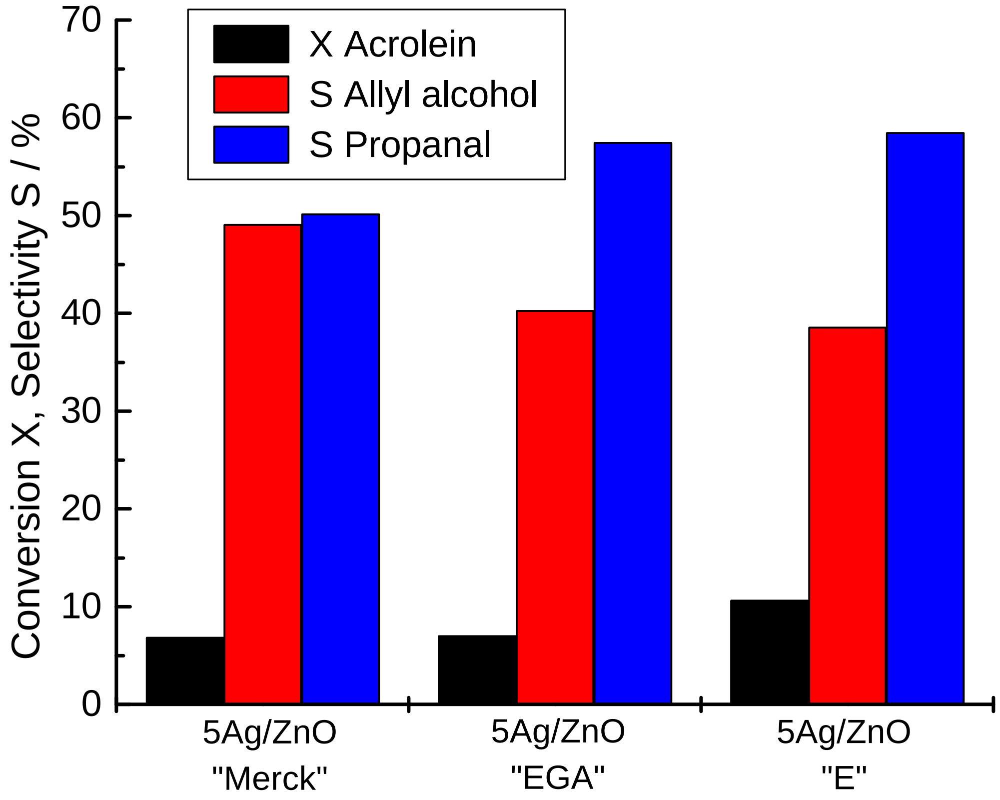
Ag single crystals



Overview: Support free Silver materials used within the GAP project

Silver Materials	Catalysis	Characterisation	In situ experiments
Single crystals	No conversion at high pressures, beam-induced process in in situ-XAS-experiments (S_{AyOH} low)		In situ XAS: Orientation depends on crystal plane, C=O-accumulation at surface, In situ XPS
Polycrystalline silver foil	No conversion at high pressures, beam-induced process in in situ-XAS-experiments (S_{AyOH} low)		In situ XAS: C=O-accumulation at surface In situ XPS
Electrolyte silver	S_{AyOH} 20 % (X = 2.5 % at 2 MPa)		TAP: No interaction with hydrogen (as for pure SiO_2, but not Ag/SiO_2)
Sputtered/electrochemically deposited silver	S_{AyOH} 23 % (X = 2.6 % at 2 MPa)	XRD, XPS	
nanoscopic silver: colloidal preparations precipitation	S_{AyOH} ca. 40 % (X = 10...50 % at 2 MPa)	TEM, XPS	

Influence of ZnO-support on catalytic properties



All catalysts:

- 5 % Ag
- Same preparation method (IW with $AgNO_3$)
- Reduction at 250 °C
- Testing at 15 bar, 250 °C

Different ZnO-support materials exhibit different selectivities with similar conversion

What influences selectivity?

Hypothesis: selectivity depends on adsorption geometry.
Adsorption geometry is is influenced by
pressure (coverage) and structure of catalyst

Pressure

Increasing S_{AyOH} with increasing partial pressure of acrolein at Ag/SiO_2

Why not with ZnO-supported catalyst??

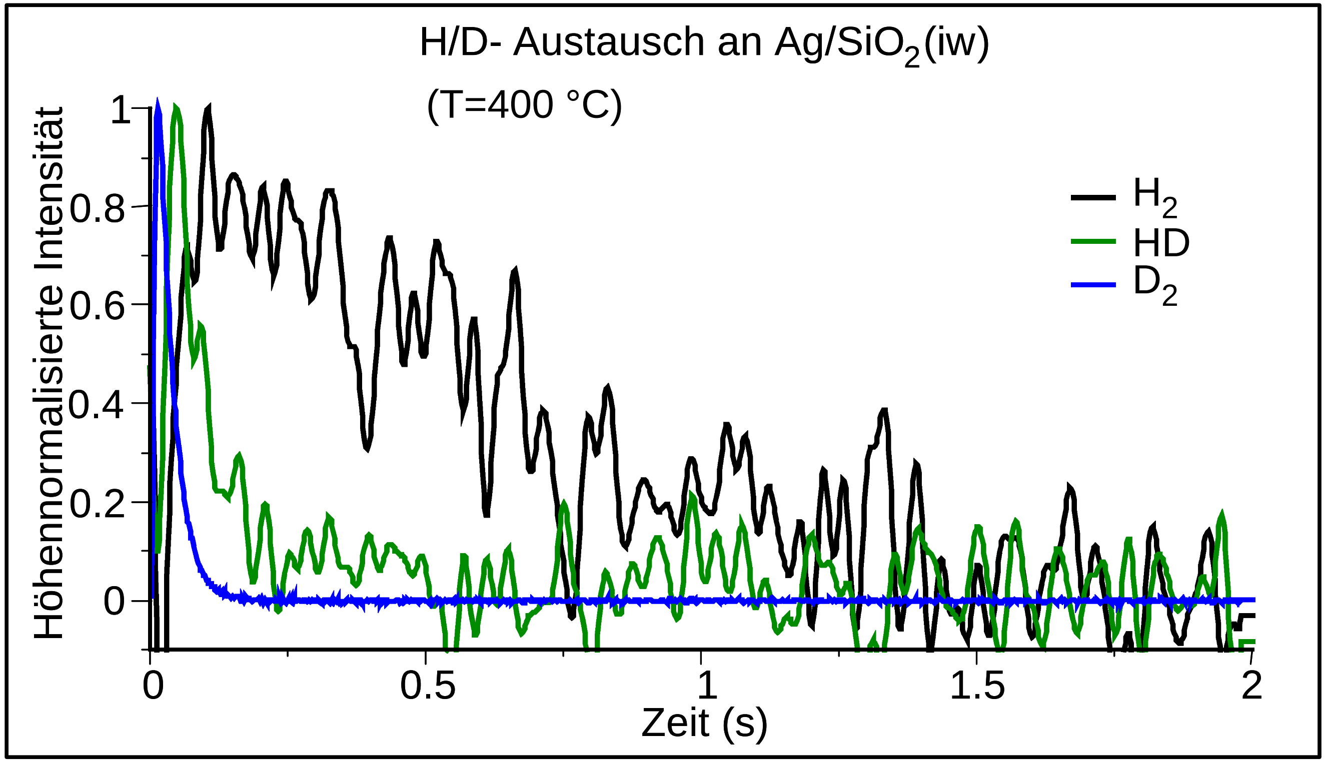
Activation energy is not influenced by pressure - rate determing step

Material

Increasing S_{AyOH} with smaller particles - larger number of kinks, edges, different exposed crystal planes, defects

Support - can the support influence acrolein orientation?

Hydrogen adsorption at silver: TAP-investigations



HD-exchange occurs - dissociative adsorption of hydrogen at silver nanoparticles

no hydrogen-activation when using electrolytic silver or pure SiO_2-support

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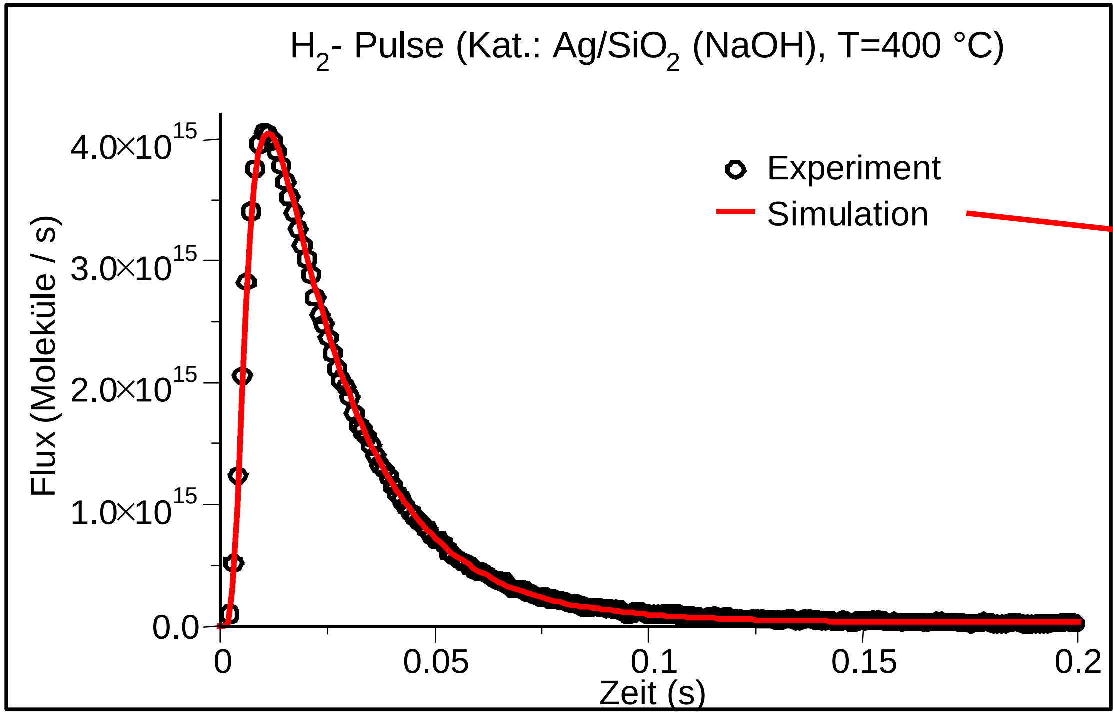
Hydrogen adsorption at silver: TAP-investigations



catalyst via precipitation
(larger particles)

$$H_2 + z \underset{k_{des}}{\overset{k_{ads}}{\rightleftarrows}} z - H_2$$

$$z - H_2 + z \underset{k_{ass}}{\overset{k_{dis}}{\rightleftarrows}} 2 \cdot z - H$$

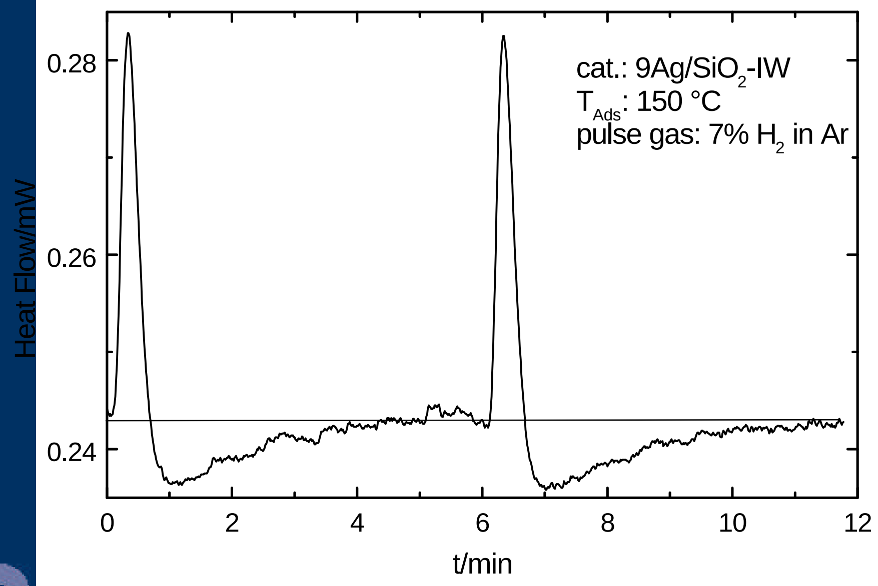
catalyst via „IW“
(smaller particles)

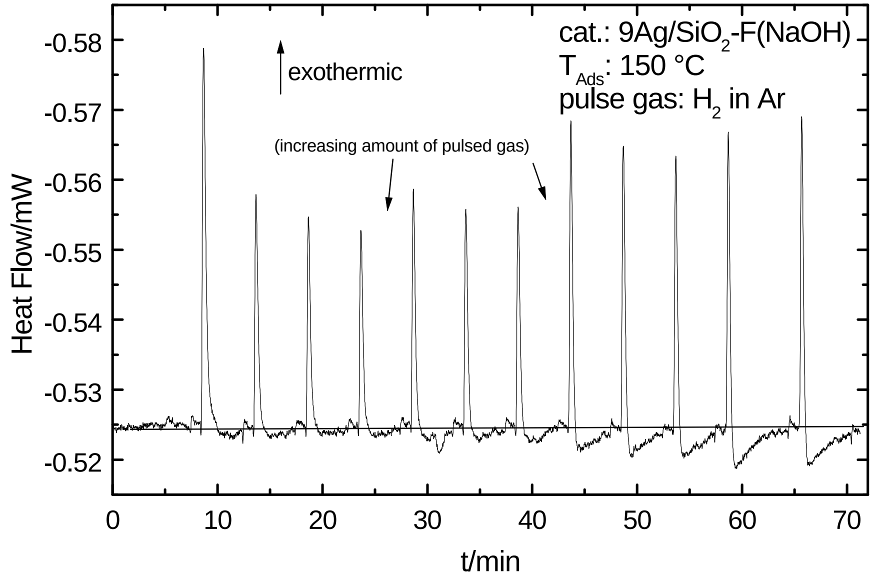
$$H_2 + 2 \cdot z \xrightarrow{k_{act}} 2 \cdot z - H$$

	k (400°C)/ s^{-1}	E_a/ kJ/mol
9Ag/SiO_2-P (NaOH)	k_{ads}: 861.7	10.8
	k_{des}: 404	11.6
	k_{dis}: 4456	31.2
	k_{ass}: 188	109
9Ag/SiO_2-IW	k_{act}: 619.4	68.7

Different models have to be taken into account for the hydrogen adsorption at silver nanoparticles of different structure

Flow adsorption calorimetry: hydrogen adsorption at silver catalysts





Different calorimetric responses - structure sensitivity of hydrogen adsorption at silver catalysts

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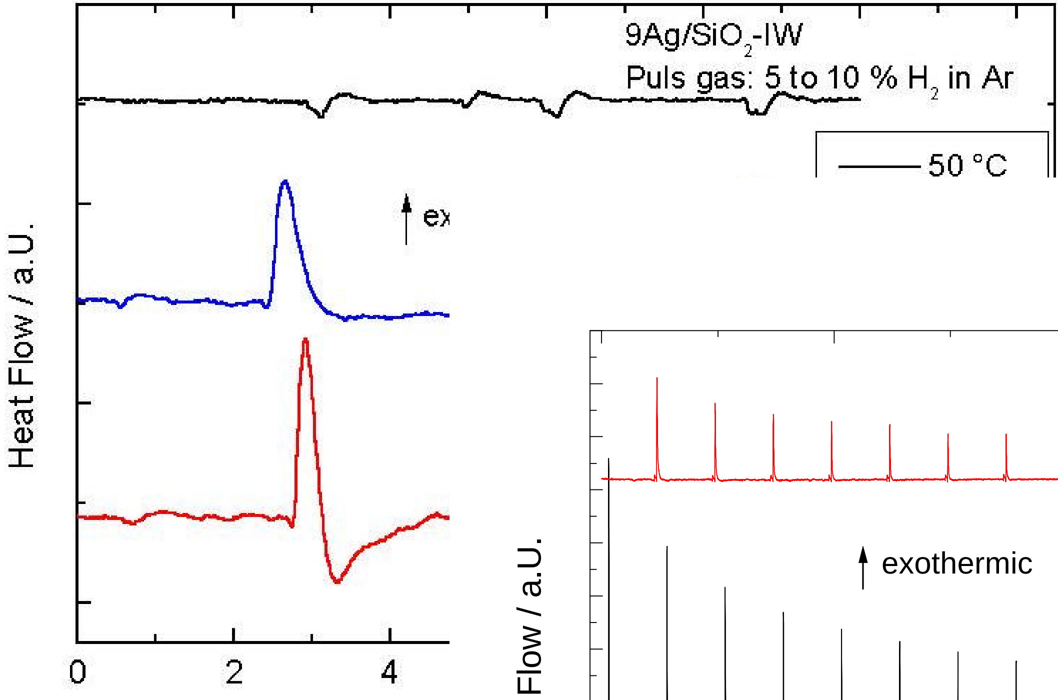
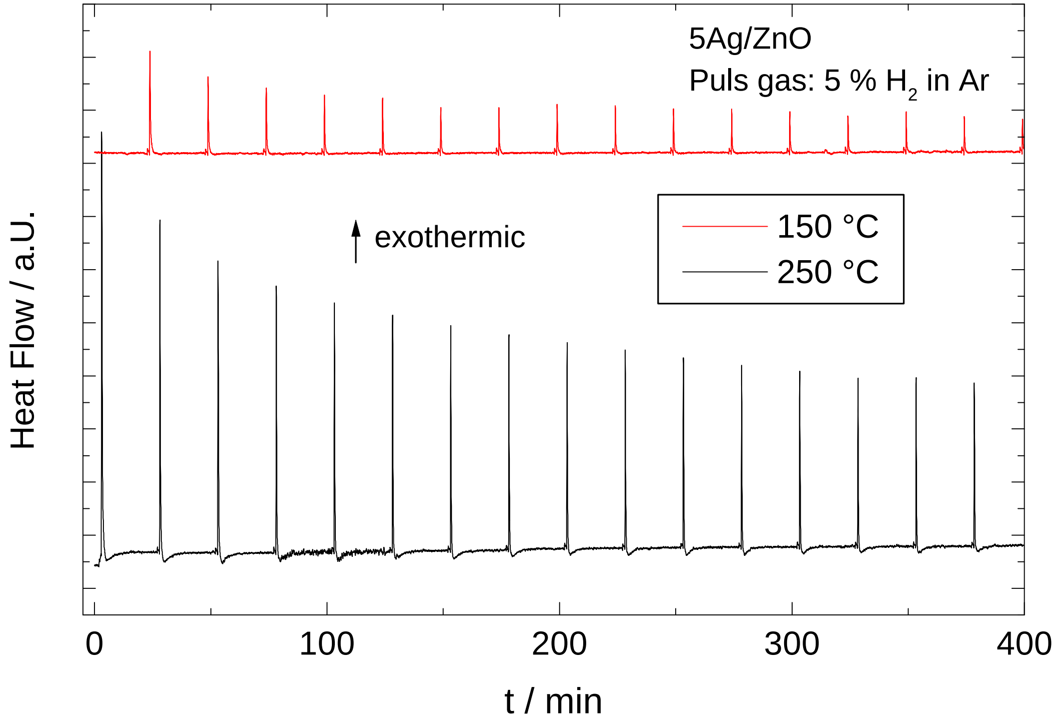
Flow adsorption calorimetry: hydrogen adsorption at silver catalysts

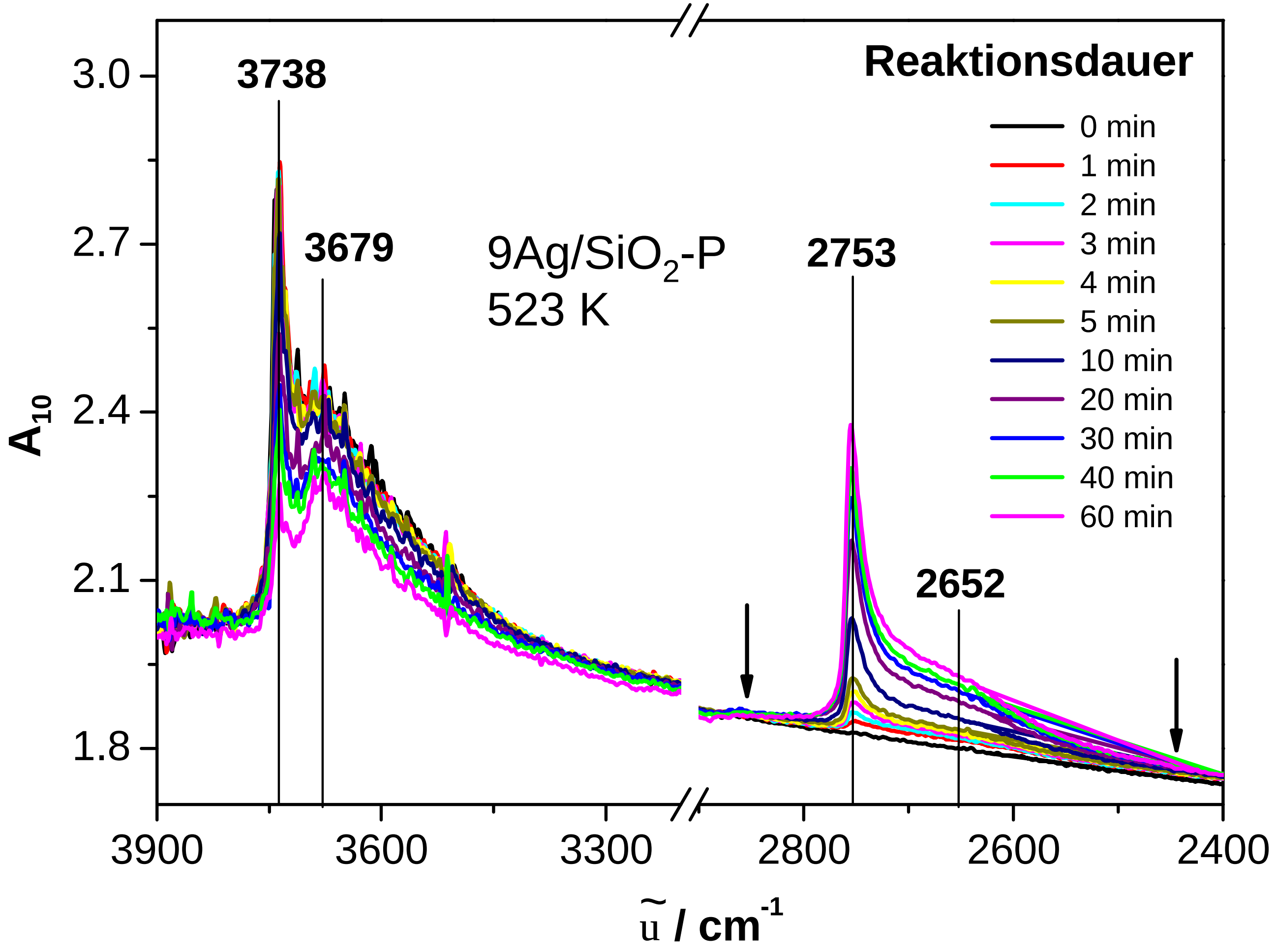


SiO_2-supported catalysts: adsorption completely reversible



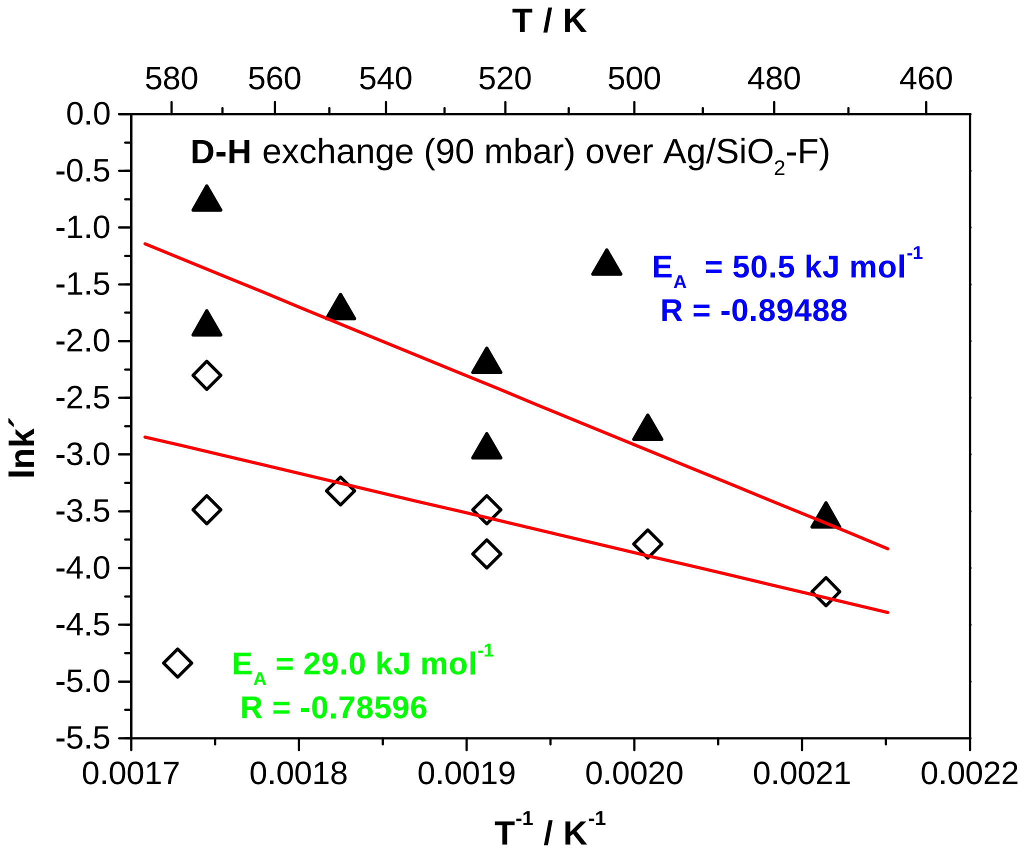
ZnO-supported catalysts: adsorption largely irreversible

Infrared spectroscopy: H-D-exchange over Ag/SiO_2 catalysts



F. Jentoft et al., Poster Bunsentagung 2004

Kinetics of isotope exchange from IR spectroscopy



Arrhenius plot of the isotopic exchange with H_2.

Lower activation energy in presence of Ag.

Activation of hydrogen is structure sensitive

weak (not dissoziative) adsorption of hydrogen at Ag(100)

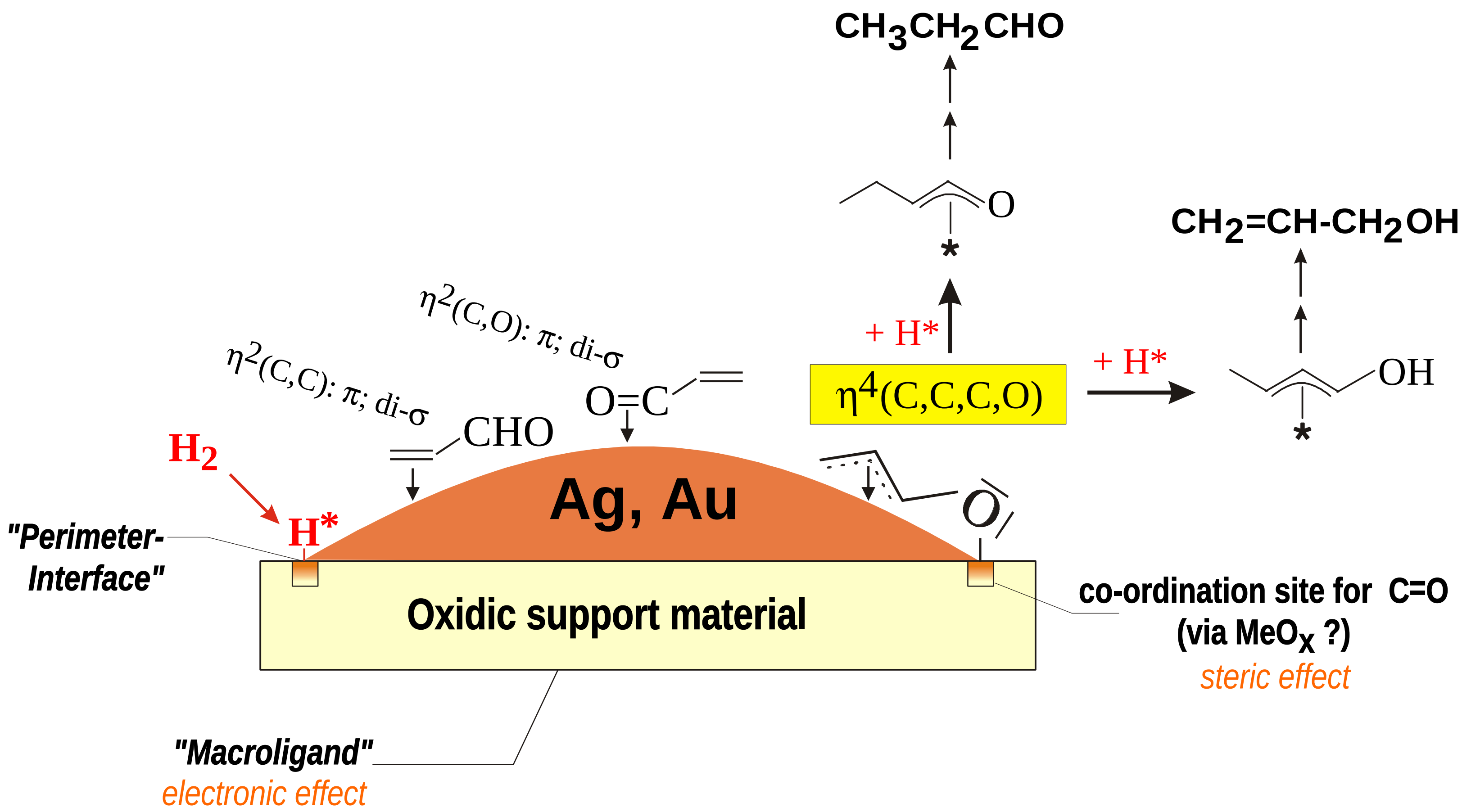
No measurable hydrogen activation using electrolytic silver

Dissoziative adsorption of hydrogen at silver nanoparticles, mechanism depends on particle size/structure

Different ratio edges/kinks to planes
Different kind/number of defects
Important role of support material

Why is the selectivity to AyOH also influenced
by partial pressure of hydrogen?

Schematic representation of the perimeter interface



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GAP-project partners:
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Further Cooperations:
Dr. E. Kondratenko (ACA Berlin) TAP-measurements
Dr. H. Hofmeister (MPI Halle) TEM-measurements

AK Claus:
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N. Sargsyan
J. Hohmeyer
C. Breuer
Dr. C. Mohr

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..and certainly you for your attention!