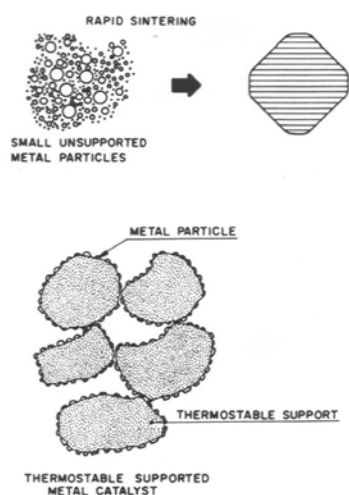


## Metal catalysis

### Small metal particles need to be stabilized



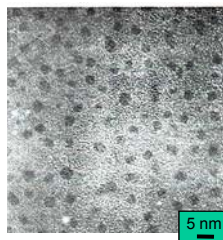
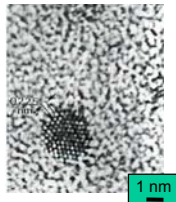
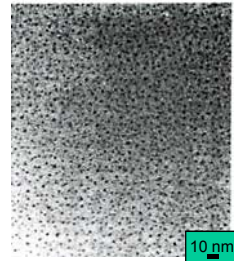
- At approximately half of the melting point the lattice elements of a solid begin to be mobile enough that coalescence of particles becomes important.

#### *Tamman temperature*

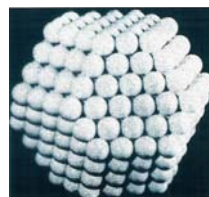
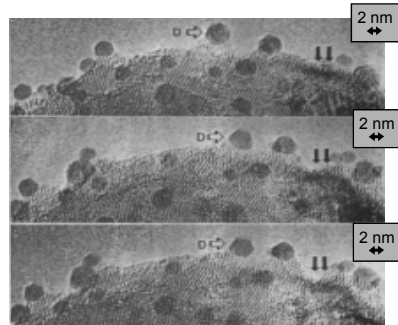
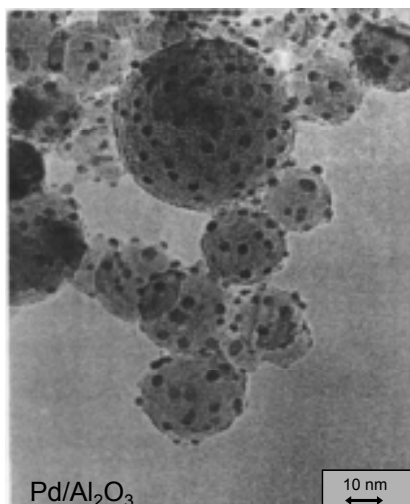
- At lower temperatures surface mobility might exist
- Well balanced interactions with the support might stabilize particles.
- Corrosive chemisorption may play a major role in sintering

## Preparation of supported catalysts

- Co-precipitation
- Impregnation
  - Wet chemical impregnation
  - Incipient wetness impregnation
- Adsorption
- Ion exchange
  - Exchange in aqueous medium
  - Solid state ion exchange



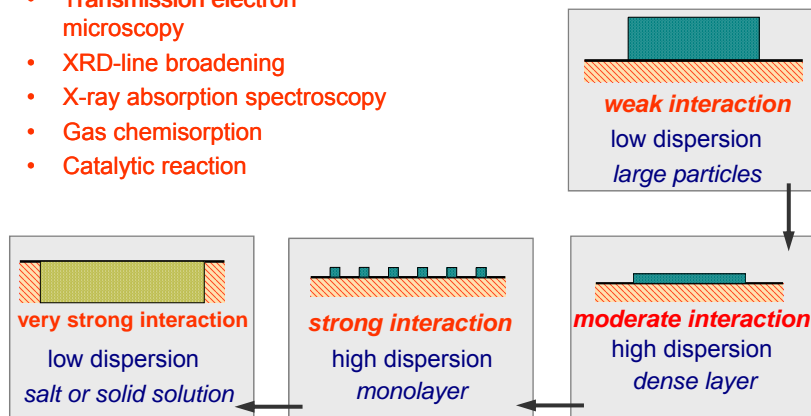
## Supported metal catalyst



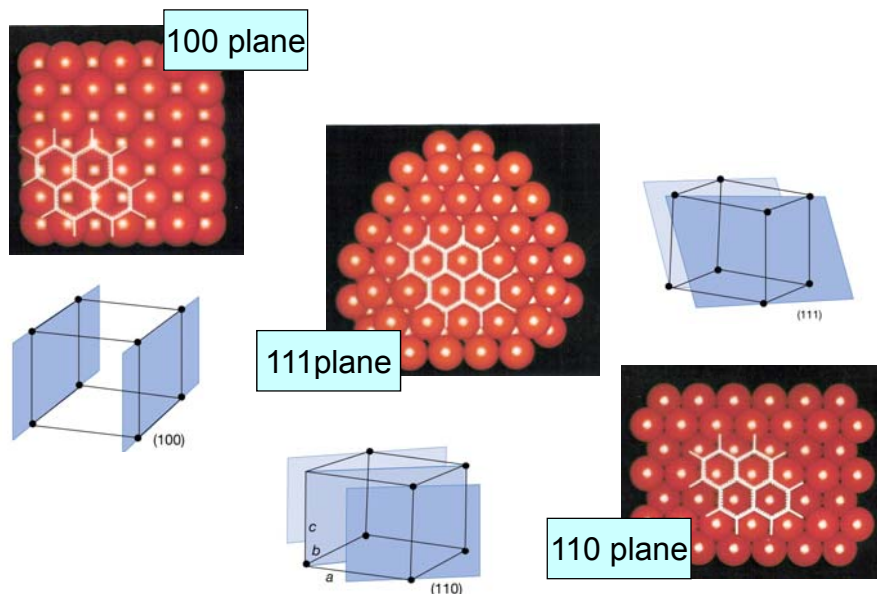
## Define, measure, prepare dispersed metal particles

$$\text{Dispersion} = \frac{\text{Number of metal atoms on the surface}}{\text{Number of metal atoms present}}$$

- Transmission electron microscopy
- XRD-line broadening
- X-ray absorption spectroscopy
- Gas chemisorption
- Catalytic reaction

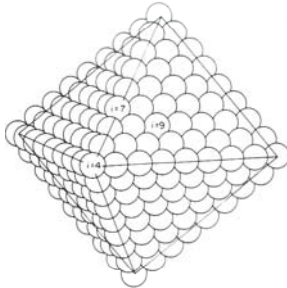


## Low index planes of f.c.c. crystals

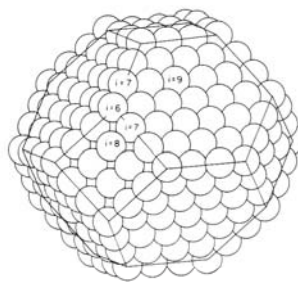


## Surface atom arrangement for face-centered cubic crystallite

Octahedral shape

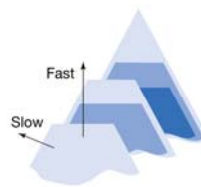


Cuboctahedral shape

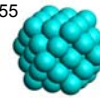


Variation in the size of the metal crystal changes the proportion of the exposed atoms.

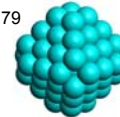
*i* specifies the number of nearest neighbors.



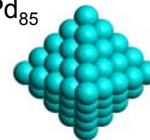
Pd<sub>55</sub>



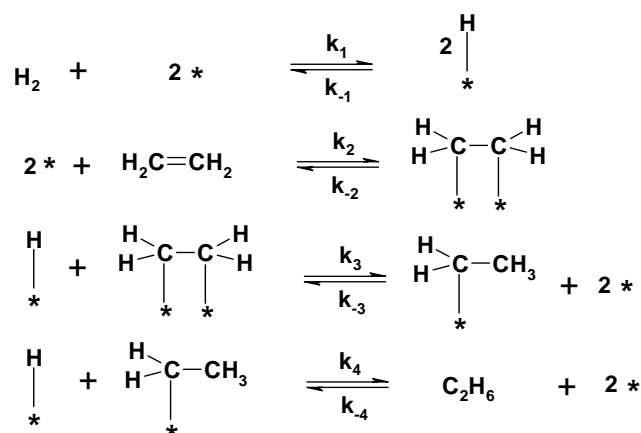
Pd<sub>79</sub>



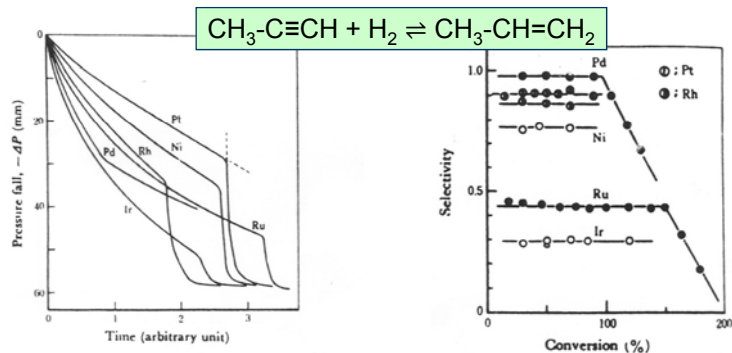
Pd<sub>85</sub>



## Mechanism of olefin hydrogenation

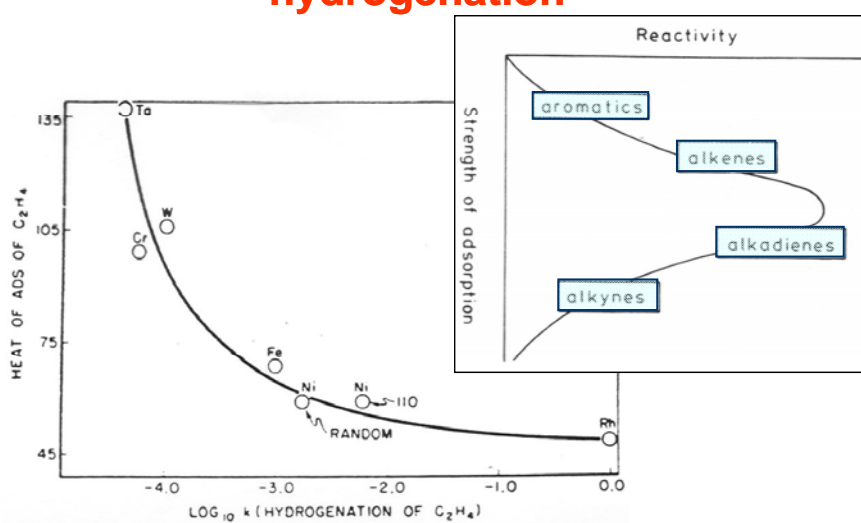


## Hydrogenation of methylacetylene

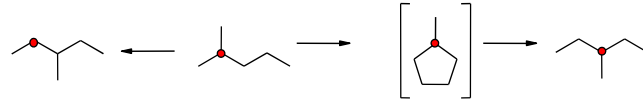


- The species most abundant on the metal surface is preferentially hydrogenated.
- The reaction rate can be slower than that of the competing reactant.
- Selective catalysts have a high preference to bind methylacetylene.

## Weaker adsorption increases rate of hydrogenation



## Influence of particle size upon catalysis

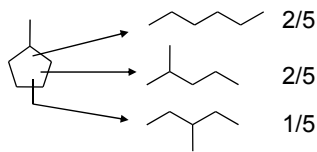


„Bond shift mechanism“

*Dominates on 10 wt.% Pt/Al<sub>2</sub>O<sub>3</sub>*

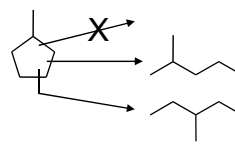
„Cyclic mechanism“

*Dominates on 0.22 wt.% Pt/Al<sub>2</sub>O<sub>3</sub>*



Unselective hydrolysis

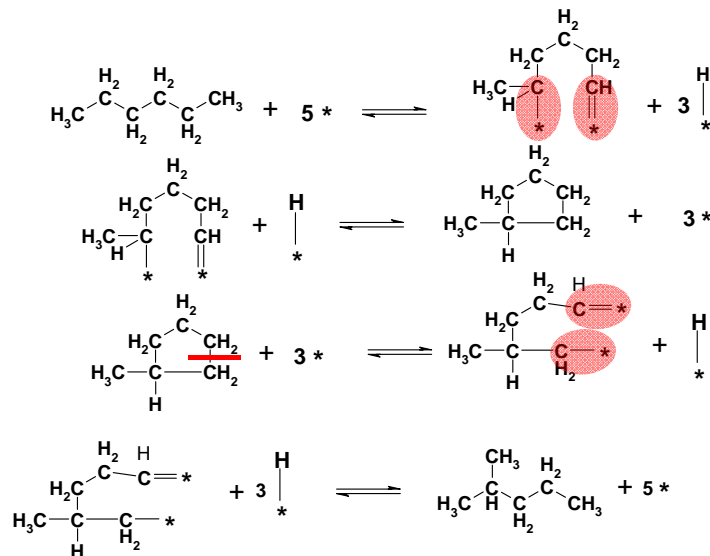
*Small particles (<1% Pt)*



Selective hydrolysis

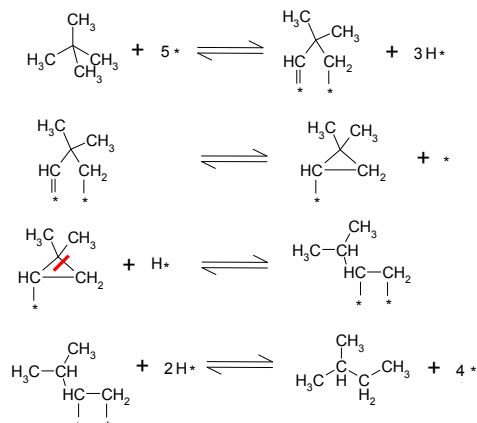
*Large particles (>2% Pt)*

## Metal catalyzed isomerization



## Bond shift mechanism

Formation of a  $\alpha\gamma$  - adsorption structure such as formed in neo-pentane isomerization



## Structure sensitivity

- Structure insensitive reactions**

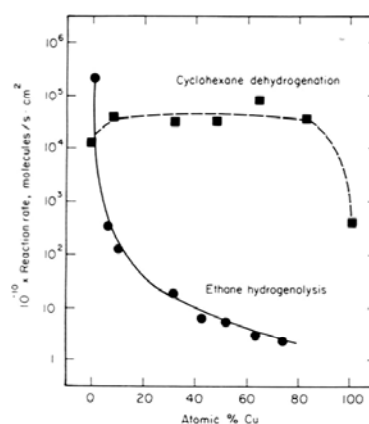
Usually all reactions which involve making or breaking C-H bonds

- Ethene hydrogenation
- Cyclohexane dehydrogenation

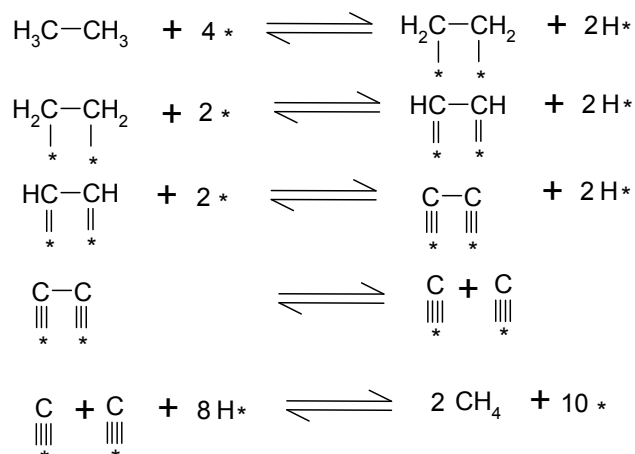
- Structure sensitive reactions**

Strong influence of the particle size, the carrier and alloying components upon the rate of reactions; usually reactions involving rupture of C-C bonds

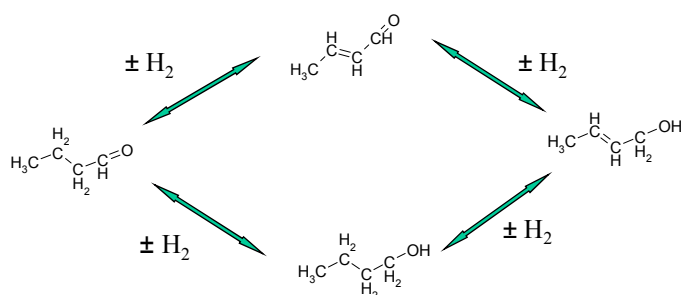
- Alkane hydrogenolysis
- Heptane dehydrocyclization



## Hydrogenolysis on metals



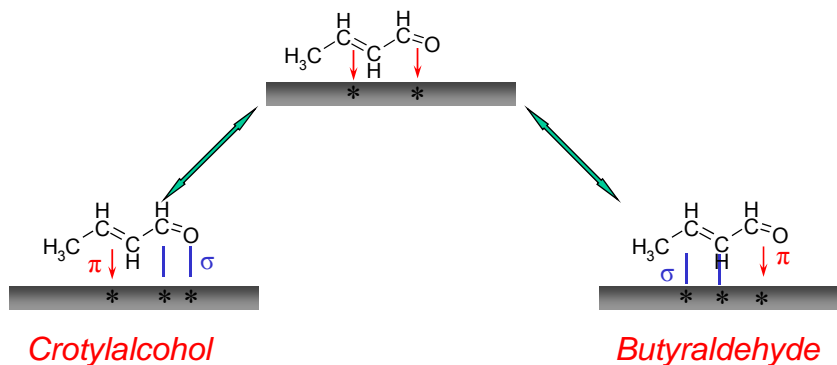
## Selective hydrogenation of functional groups



- The selectivity to butyraldehyde is high on normal hydrogenation catalysts.
- The rate of hydrogenation of the C=C bond is much higher than the rate of hydrogenation of the C=O bond.

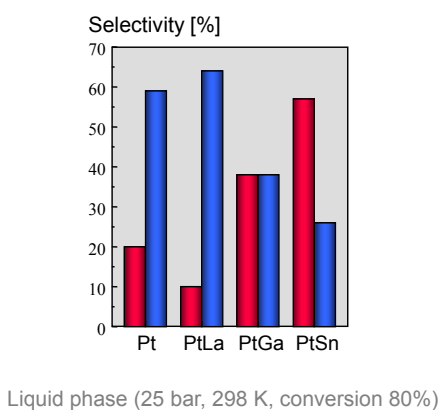
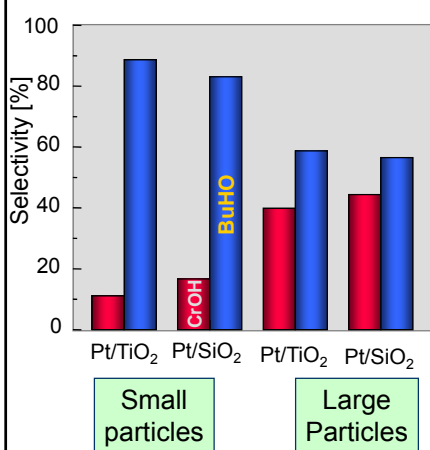


## Strategies to enhance the selectivity



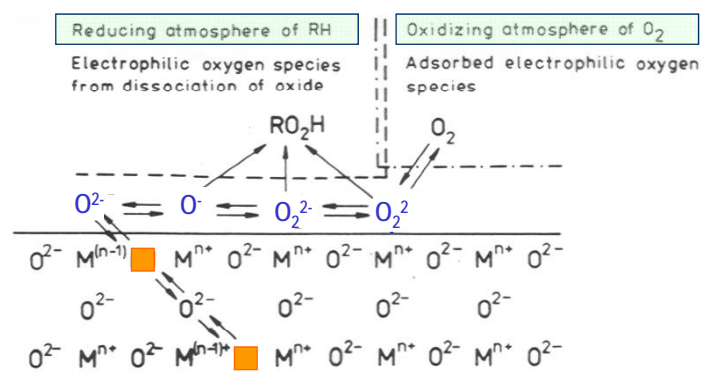
- Increase the repulsion of the terminal group by using flat low index plane surfaces.
- Increasing the interaction with the carbonyl group using strong polar sites.

## Influence of the particle size and polar catalyst components



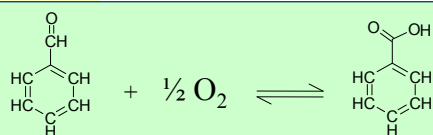
## Redox catalysis

### Electrophilic and nucleophilic oxygen

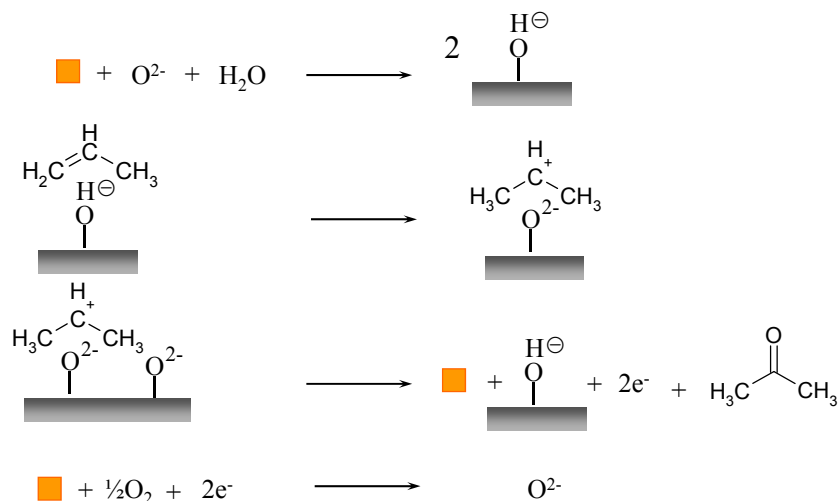


## Correlation of catalytic and thermodynamic properties of oxides

	Activity parameters		Selectivity parameters	
<i>Catalyst</i>	$\Delta q_{\text{red}}$ ( $\chi=0.02$ ) T = 500°C	Relative catalyst activity	$\frac{\partial \Delta H}{\partial \chi}$ (kcal/mol)	% Sel. benz. acid T = 345°C
MnO <sub>2</sub>	10	>>10	8	0
SnO <sub>2</sub> /V <sub>2</sub> O <sub>5</sub>	24	5	200	90-100
V <sub>2</sub> O <sub>5</sub>	38	1	80	70-80

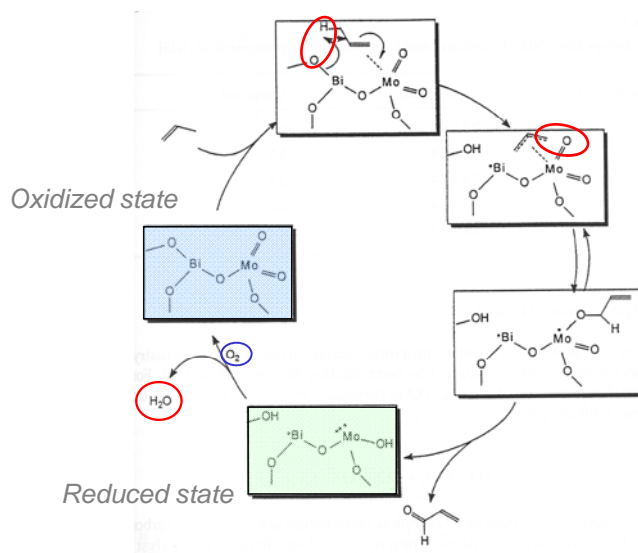


## Oxidation of propene to acetone

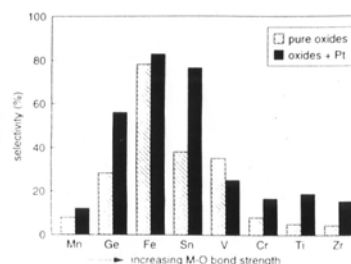
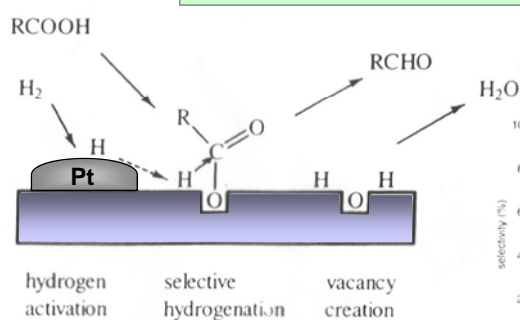
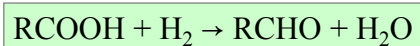


Because secondary carbocations are more stable than primary, ketones are formed and not aldehydes

## Catalytic oxidation of propene to acrolein



## Reduction of acetic acid to acetaldehyde

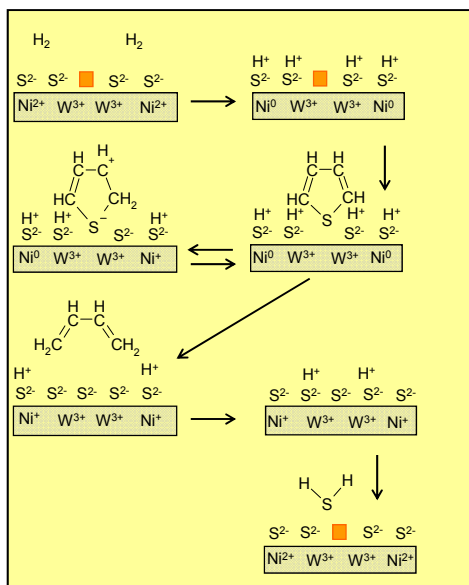


- The reaction proceeds by de-oxygenation and subsequent reduction of the catalyst.
- The noble metal provides dissociated hydrogen.

## Hydrotreating reactions

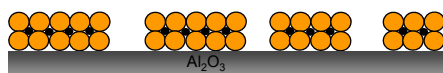
- During hydrotreating, heteroatoms (S,N,O) are removed from the mostly aromatic molecules.
- The resulting products are hydrogenated.
- The mechanism follows the Mars – van Krevelen scheme.
- Larger molecules are increasingly difficult to react – steric reasons.

## Mechanism of hydrodesulfurization

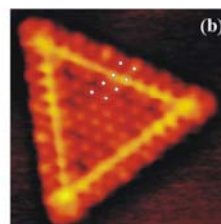
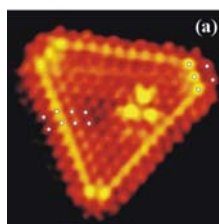
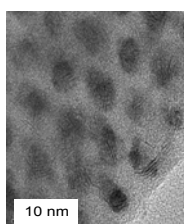
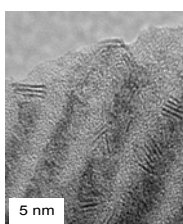
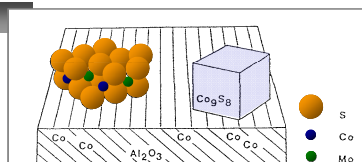


The reactions follow a (reverse) Mars van Krevelen mechanism.

## Structure of MoS<sub>2</sub> based catalysts

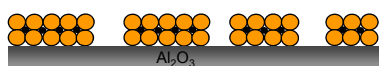


STM on model catalysts shows mostly triangular MoS<sub>2</sub> structures.

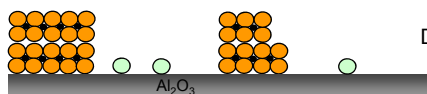


60 wt.% WS<sub>2</sub>/SBA-15 sample, Landau *et al.*

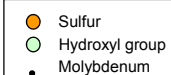
## Structure of CoMoS catalysts



Typical sulfided catalyst



Deactivated catalyst



- Ni, Co are the active sites
- MoS<sub>2</sub> is the primary support
- Al<sub>2</sub>O<sub>3</sub> is the secondary support

