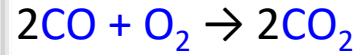


Oxidation of CO



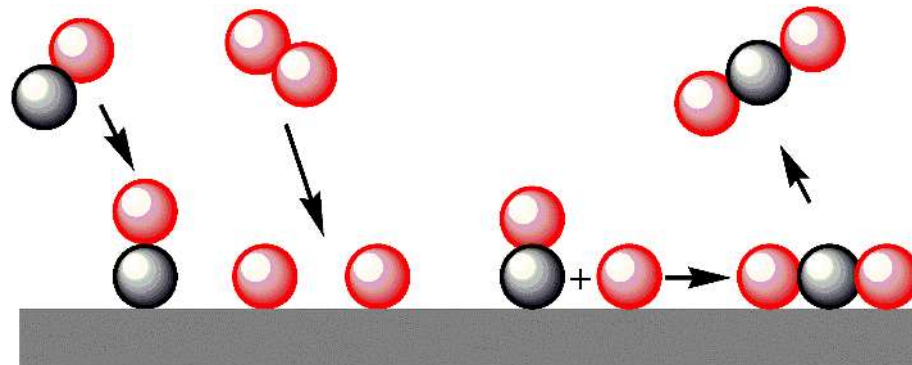
Cr	Mn	Fe	Co	Ni	Cu
Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au

Conditions

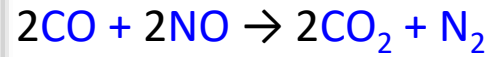
- Catalyst should dissociate O_2 but leave $\text{C}\equiv\text{O}$ triple bond intact
- Catalyst should keep CO adsorbed and allow CO_2 to desorb

Suitability of metal catalyst

- **Au** is too unreactive and cannot dissociate O_2 ; **Cr/Mo/W** too reactive, dissociate CO and also bind O-atoms too strong making them unreactive
- **Pt** and **Pd** are suitable catalysts: intermediate reactivity



Automotive exhaust catalysis



Conditions

- Catalyst should dissociate NO but leave C≡O triple bond intact

Suitability of metal catalyst

- **Fe, Co, Ni** and **Ru** dissociate CO and NO; **Pt** does not dissociate NO
- **Pd** and **Rh** are suitable catalysts: intermediate reactivity

Cr	Mn	Fe	Co	Ni	Cu
Mo	Tc	Ru	Rh	Pd	Ag
W	Re	Os	Ir	Pt	Au

Structure sensitivity

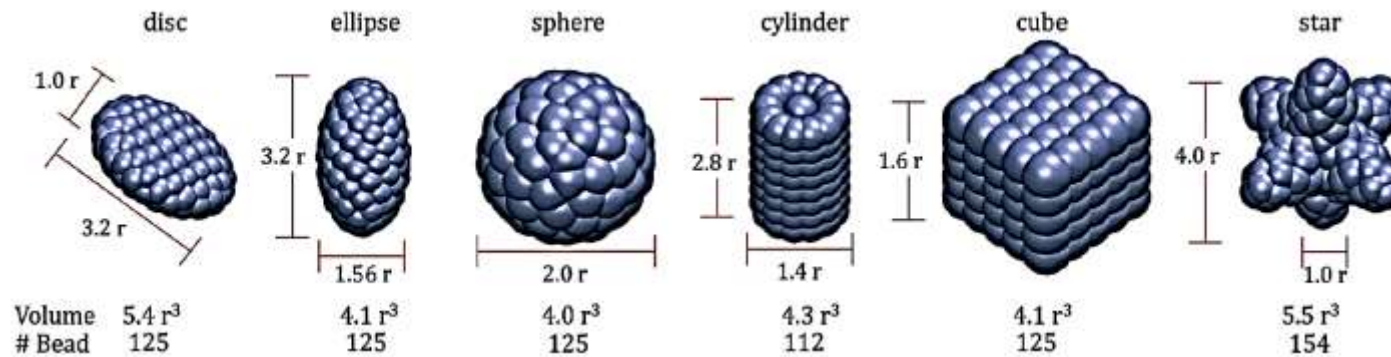
Structure-sensitive reaction

Turnover rate per catalyst surface atom depends on particle size and geometry

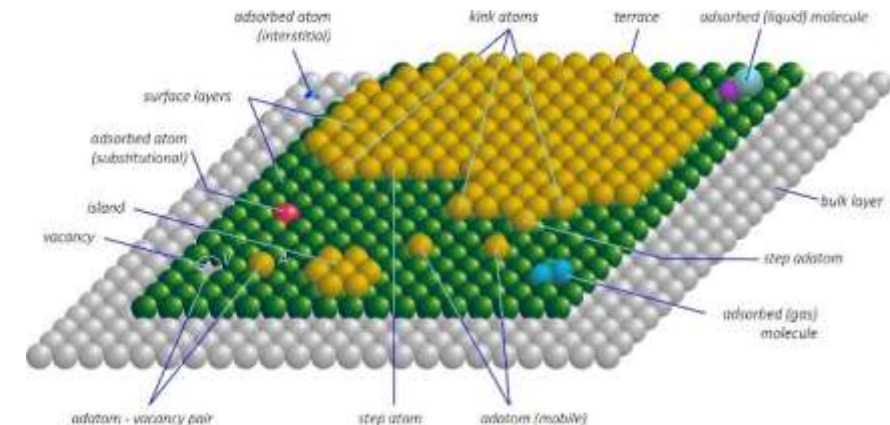
Structure-insensitive reaction

Turnover rate per catalyst surface atom independent of particle size – every surface atom is equally active

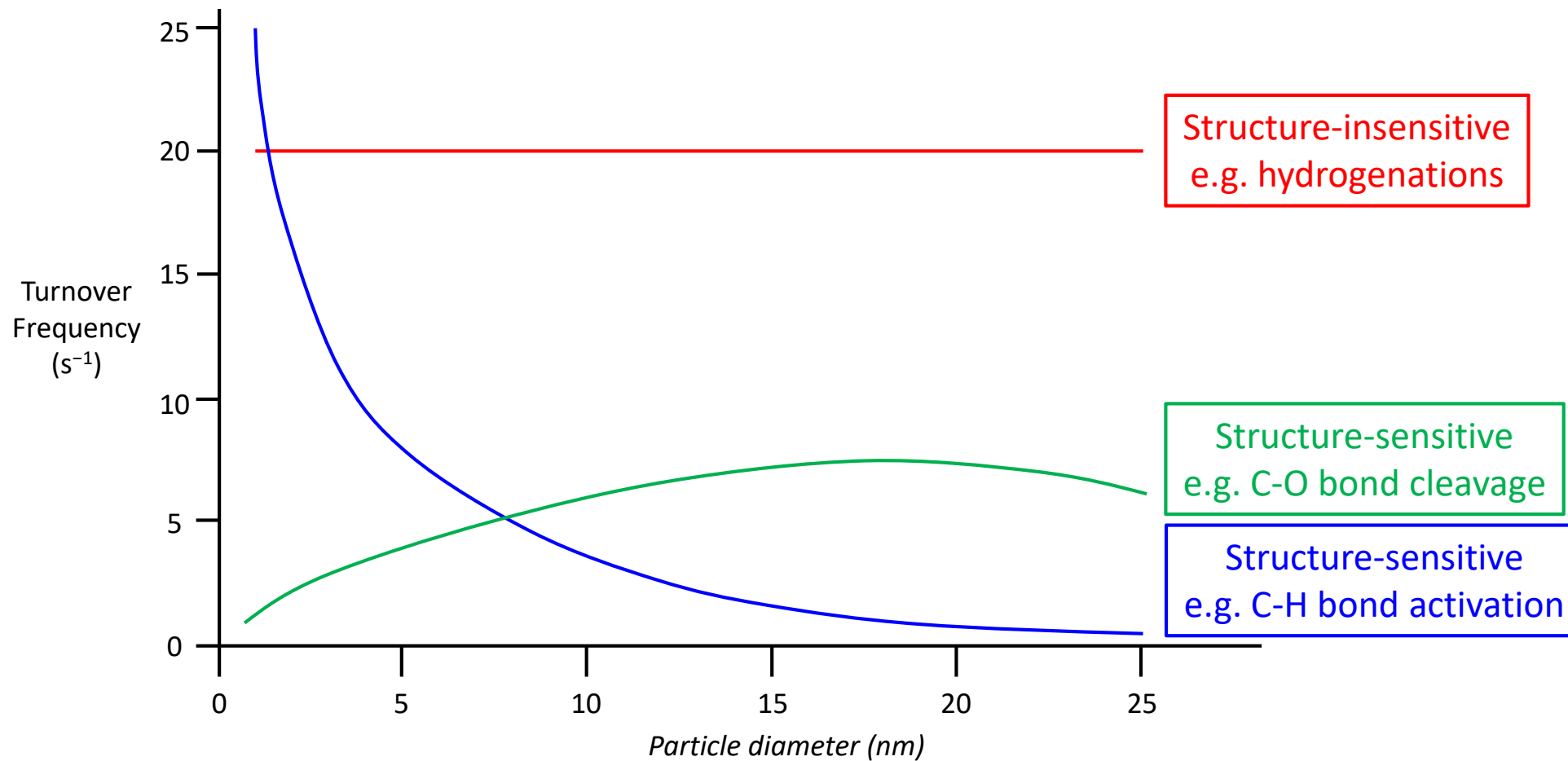
Examples of catalytic nanoparticles



Example of a larger catalytic surface

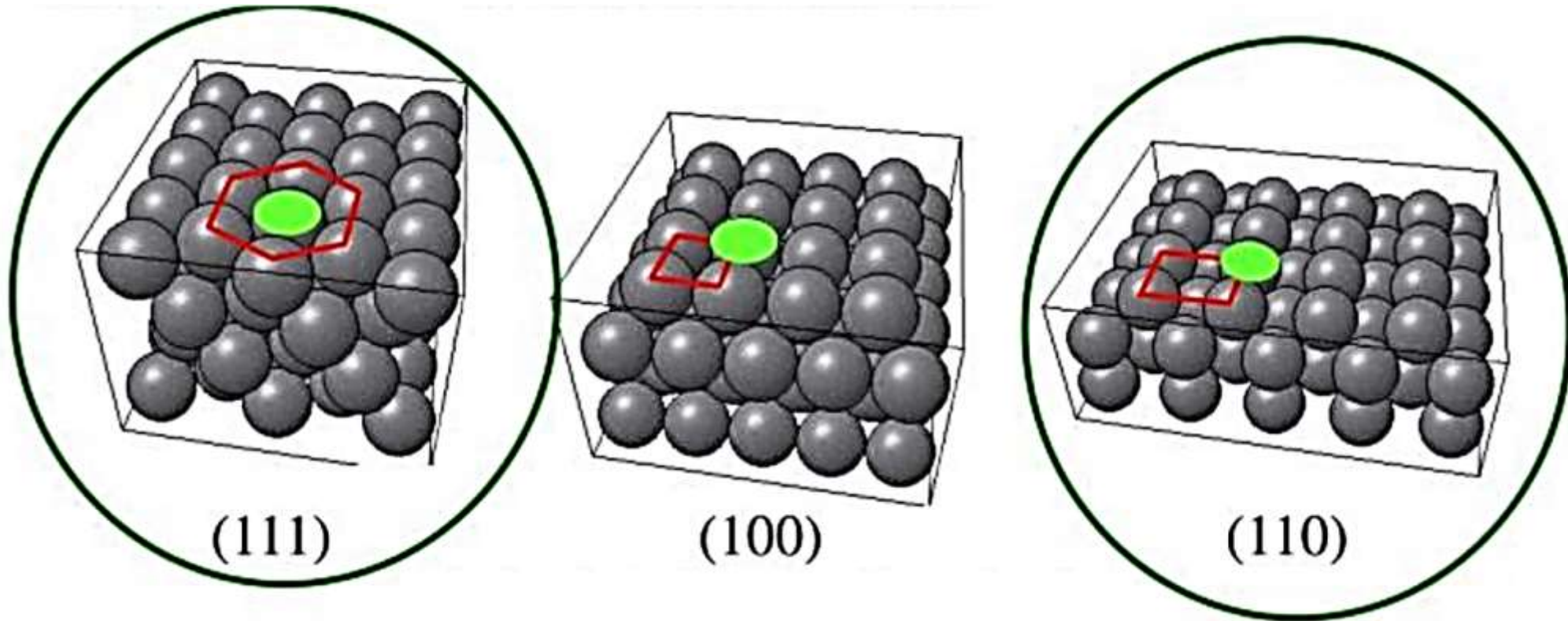


Structure sensitivity



Structure sensitivity

Main “low-index” surfaces

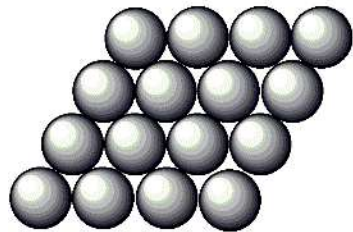


- Surfaces are regions of high energy
- The more close-packed a surface (the higher the coordination number), the lower the surface energy (more stable)

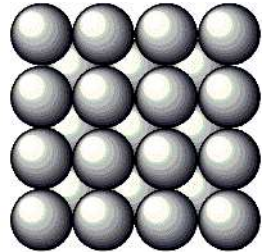
Structure sensitivity

Electron density of reactive surface metal atom depends on atom topology and coordination number (CN)

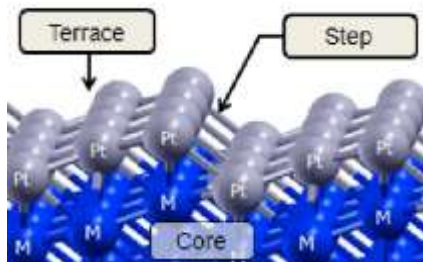
Examples of metal surface facets



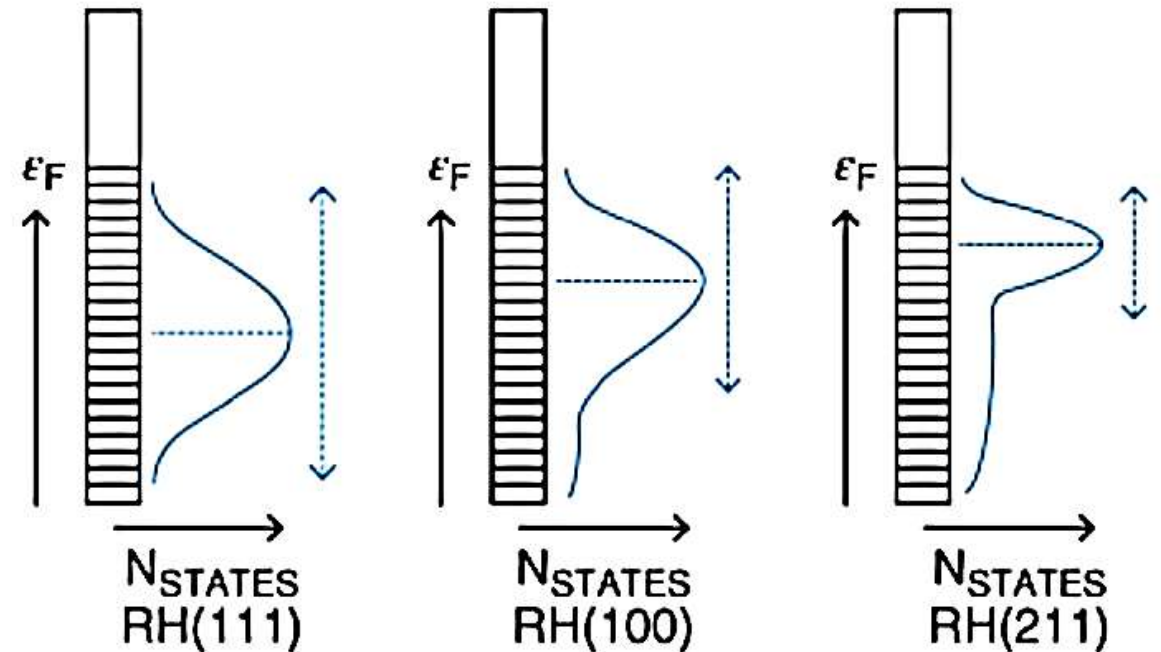
(111) Surface
CN 9



(100) Surface
CN 8



(211) Surface
CN 7

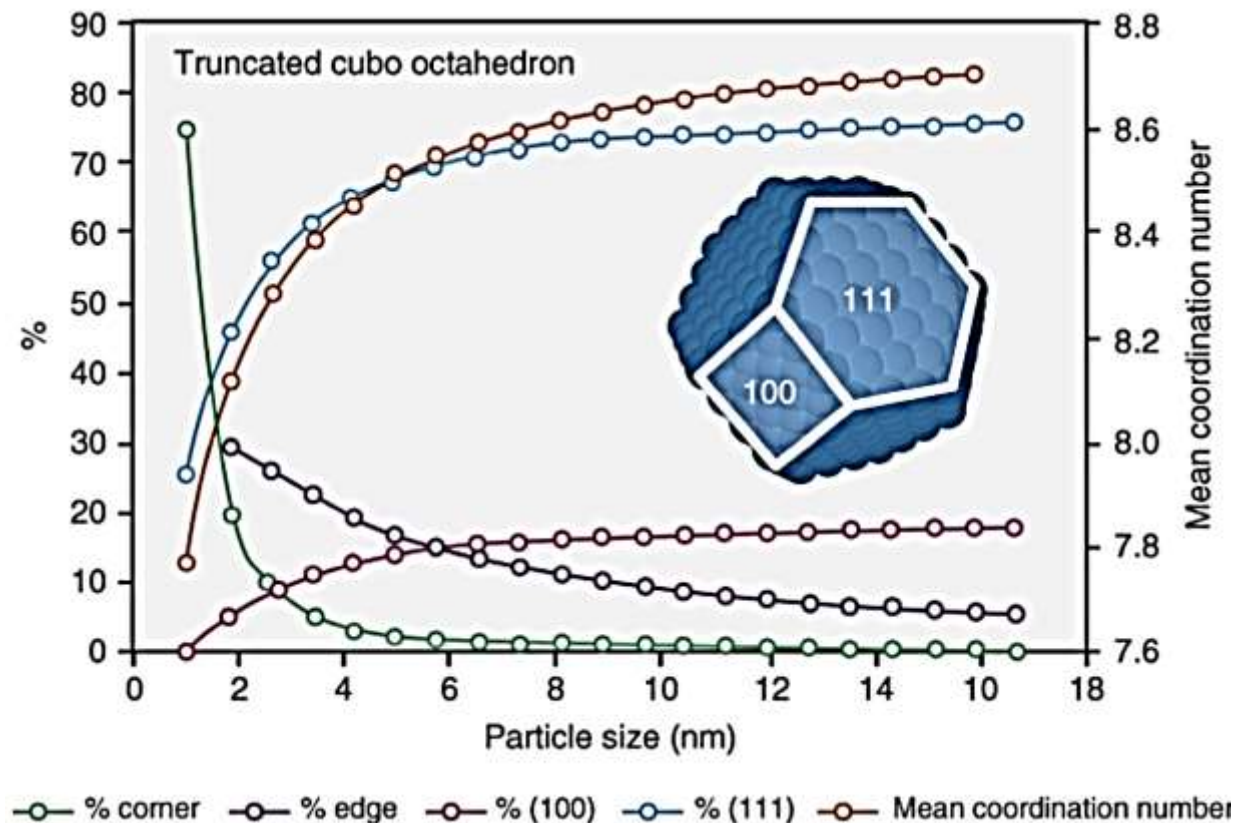


- Width of d-band decreases with decreasing CN → d-electrons more localized
- Average energy of d-band increases with decreasing CN → more overlap with orbitals of adsorbates → stronger bonding with adsorbates

Structure sensitivity

Example: cleavage of an alkane C-H σ -bond

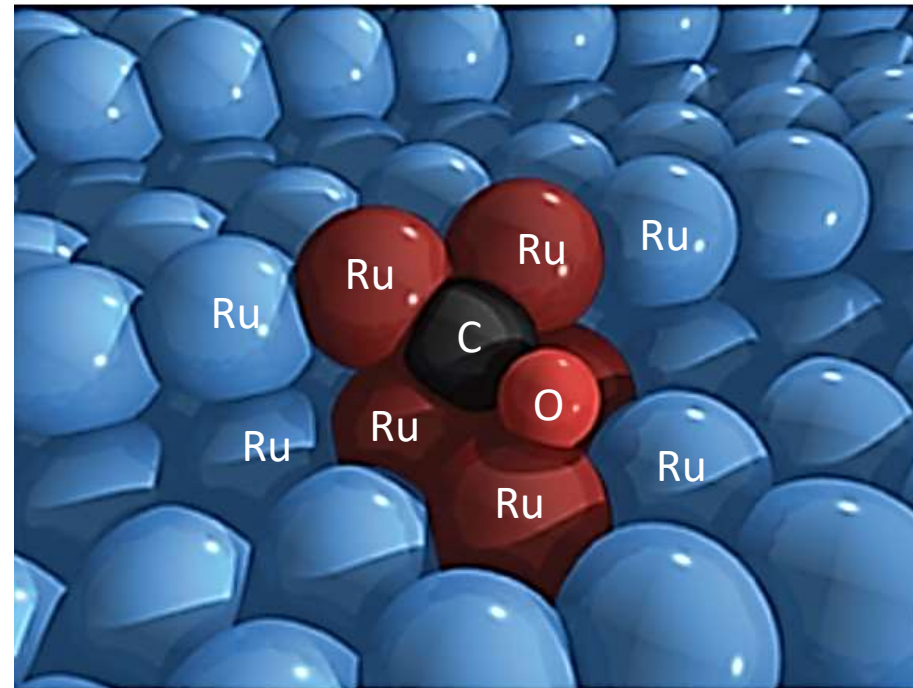
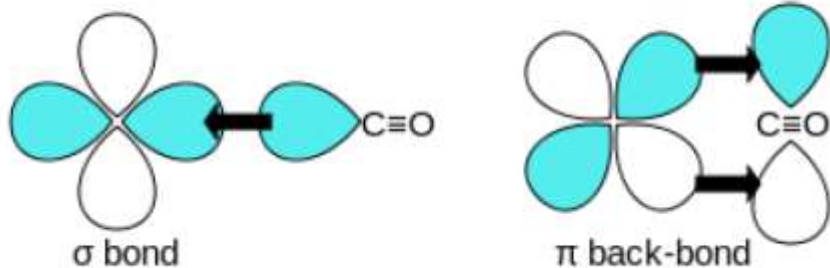
- Occurs at a single metal atom
- E^{act} is low if transition state (C-H bond nearly cleaved at metal atom) is stabilized
 - benefits from decreasing CN of metal atom
 - occurs when metal particles become smaller



Structure sensitivity

Example: cleavage of a π -bond (CO, N₂, NO, etc.)

- Preferentially occurs at an ensemble of metal atoms at a surface step
- Dissociation of CO at planar **Ru**: $E^{\text{act}} > 200$ kJ/mol; at **Ru** step: < 100 kJ/mol
- Transition state: CO atoms bind at different metal atoms \rightarrow stronger individual binding and no bending CO needed
- Bond breaking activated by π -back bonding from metal into antibonding of C-O bond
- Coverage of step edges by inactive **Au** atoms drastically poisons the catalyst



Support effects

Catalytic nanoparticles are usually deposited on porous support material: maintains high surface area

Electronic interactions

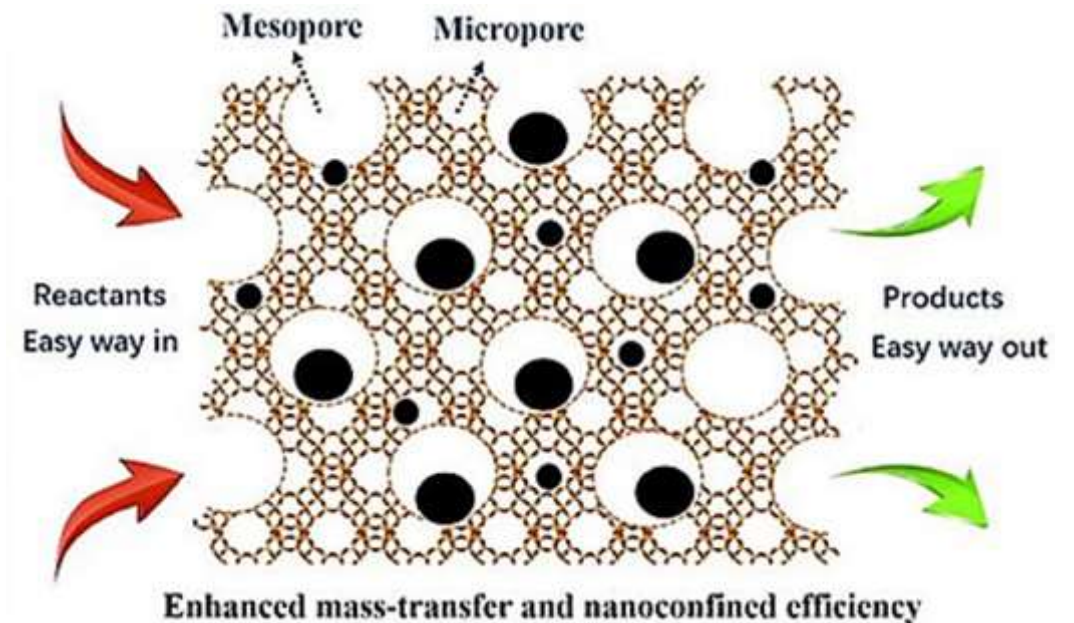
- Metal particles on semiconductors (e.g. TiO_2): direct chemical interaction via electron transfer between support and d-band of metal possible
- Metal particles on insulators (e.g. Al_2O_3 , SiO_2): inductive interaction with metal; ions of support may change position d-band (only with small metal particles)

Structural interactions

- Support may influence nanoparticle shape (depending of support-particle interaction strength)

Complications

- Support may diffuse over/encapsulate nanoparticle
- Support may react with nanoparticle (e.g. $\text{Ni} + \frac{1}{2}\text{O}_2 + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4$)



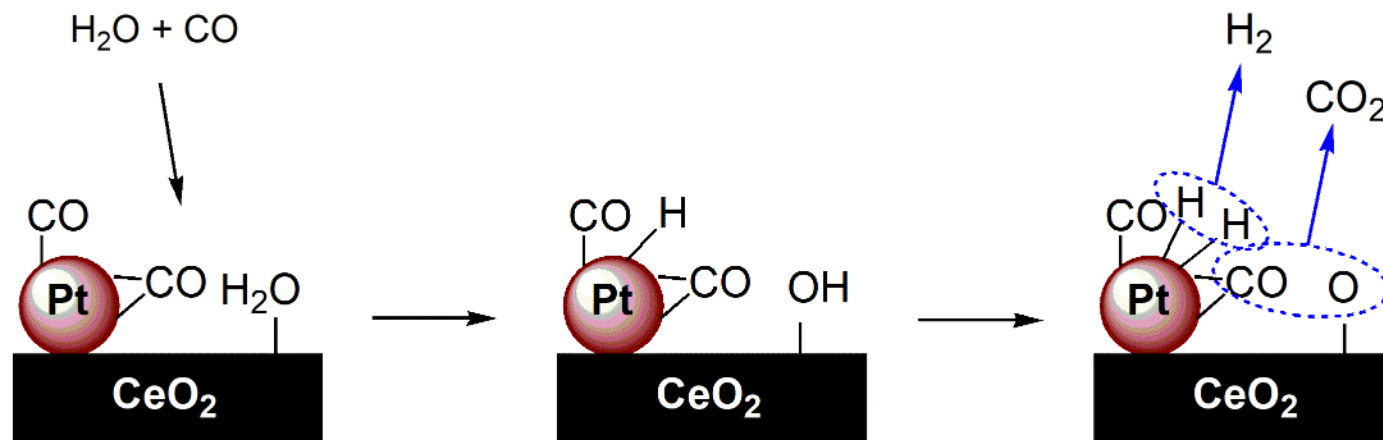
Support effects

Supports that participate in the catalytic reactions (bifunctional catalyst)

- Support and catalyst contribute to the catalytic steps
 - (1) Reactions occur at the interface of nanoparticle and support
 - (2) Diffusion of reactive species over both nanoparticle and support (“spillover”)
 - (3) Both metal catalyst and support catalyze reactions

Example of (3): water-gas shift reaction

- $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
- CO activated by **Pt** nanoparticles, H₂O by a hydrophilic metal-oxide support (here CeO₂)



Unsupported metal catalysts

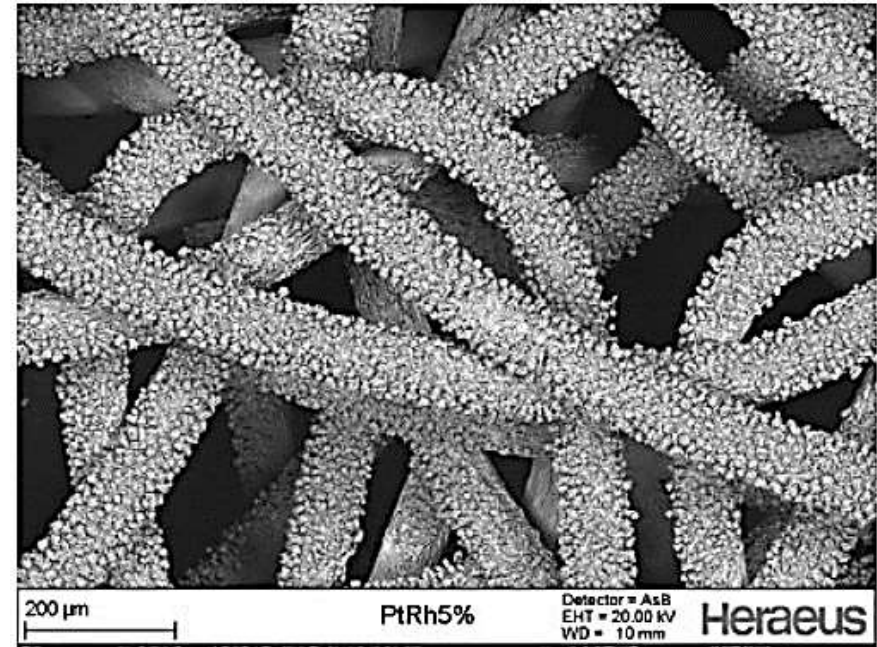
Examples:

NH_3 oxidation over Pt/Rh

- $\text{NH}_3 \rightarrow \text{NO}_x \rightarrow \text{HNO}_3$
- Catalyst: **Pt-Rh** wires (\varnothing 50 μm)
- Reaction at 800 °C: extreme rates, limited number of surface sites needed

Raney-Ni

- Hydrogenation catalyst
- **Ni**-catalyst itself is made porous (100 m^2/g)
- Possible because **Ni** is cheap



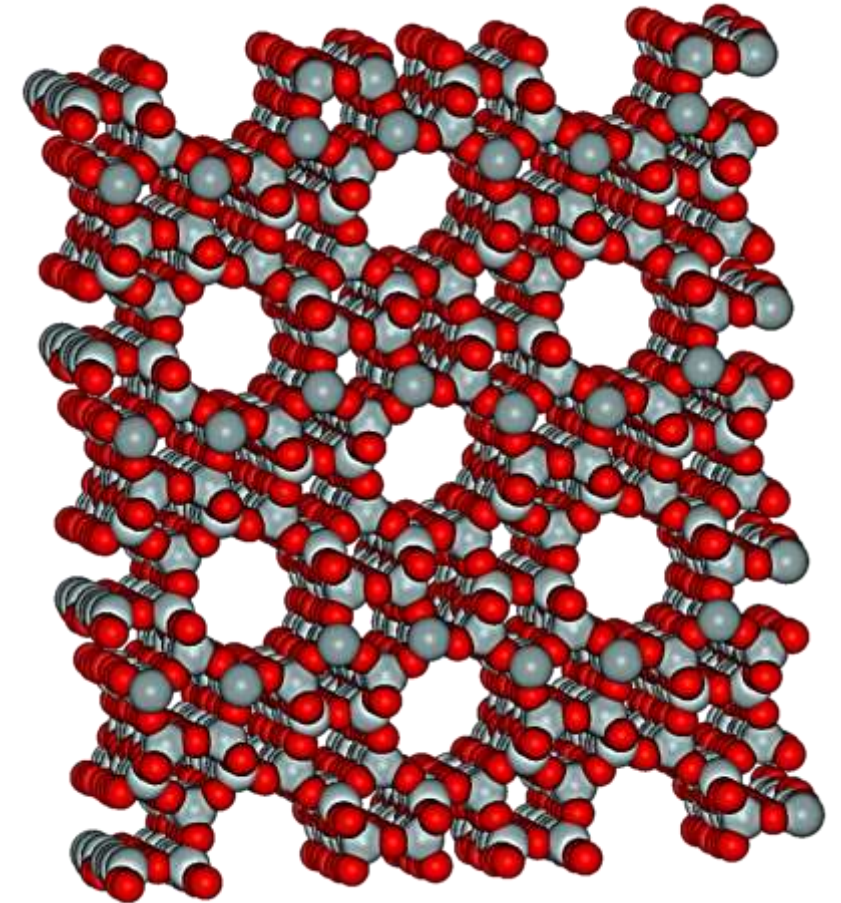
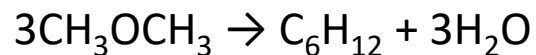
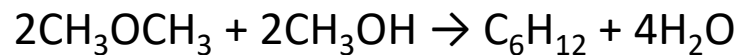
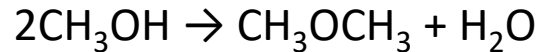
Zeolites

Porous organic materials based on non-heavy metal atoms

- Natural and synthetic
- Pore/channel sizes of 1 – 10 Å: fits small molecules
- Huge internal surface area of hundreds of m²/g
- Al/Si zeolites can act as strongly acidic Brønsted catalysts
- Pore size can lead to shape/size-selective reactions

Examples of applications

- Isomerizations, e.g. 1,3-dimethylbenzene to 1,4-dimethylbenzene
- Cracking of petroleum
- Conversion of methanol to hydrocarbon fuels



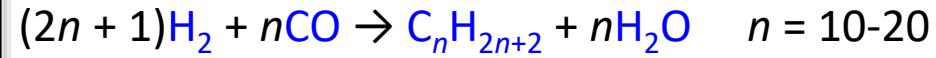
ZSM-5 ($\text{Na}_n[\text{Al}_n\text{Si}_{96-n}\text{O}_{192}]\cdot\approx 16\text{H}_2\text{O}$)

Some applications

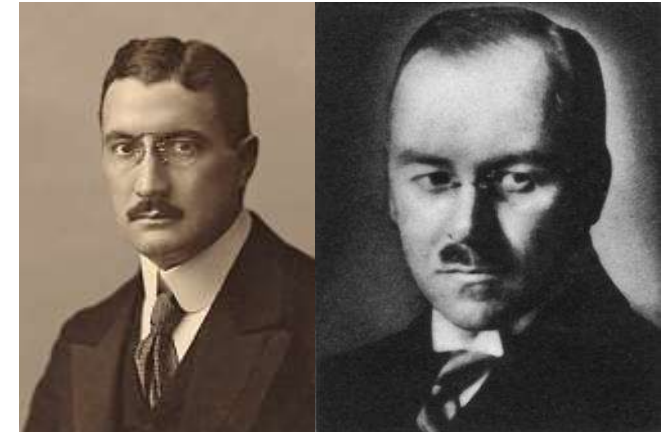


Fischer-Tropsch process

Industrial synthesis of hydrocarbons from syngas



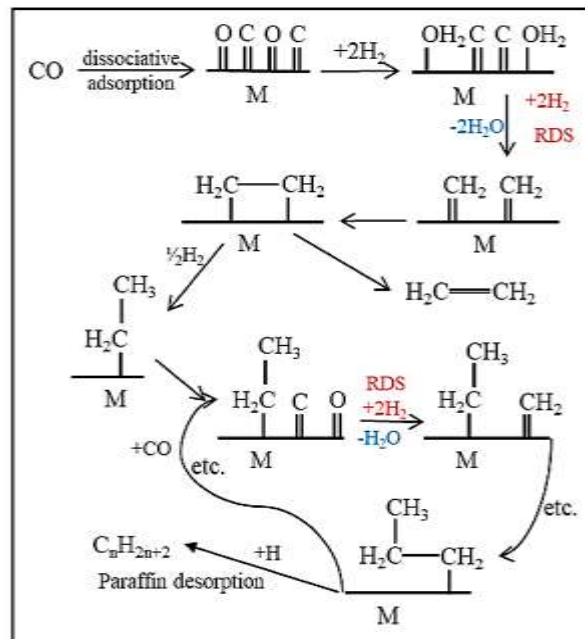
- Developed in 1925
- Alternative to oil as the source of hydrocarbons
- Mainly **Fe**-based and **Co**-based solid catalysts
- Mechanism(s) still under debate



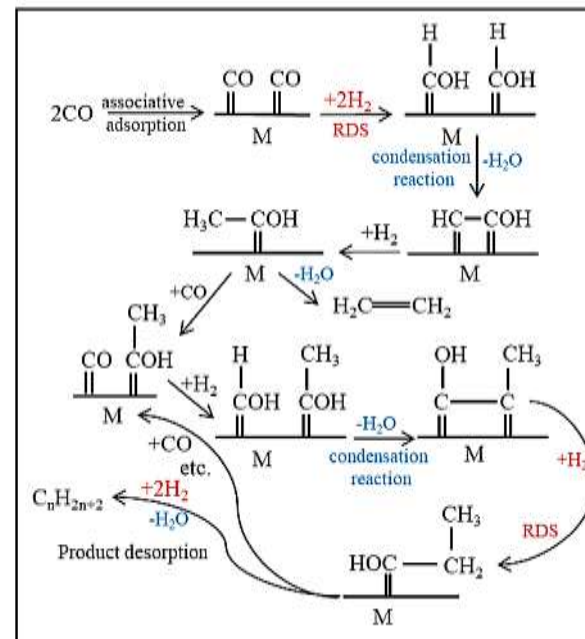
Franz Fischer

Hans Tropsch

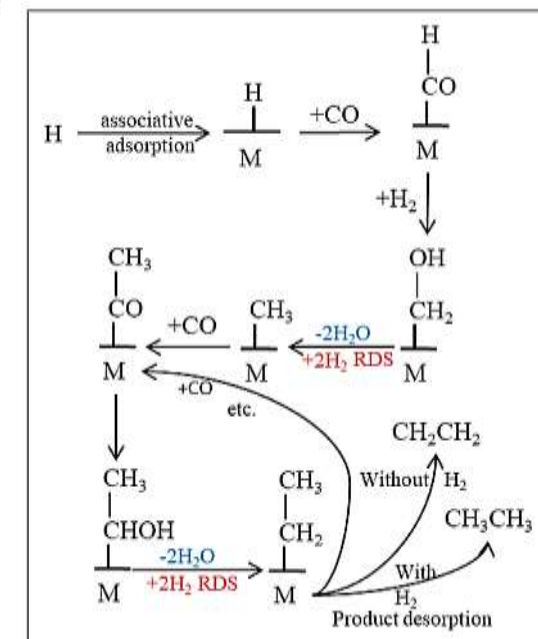
Carbide mechanism



Enol mechanism



CO insertion mechanism



Ziegler-Natta process

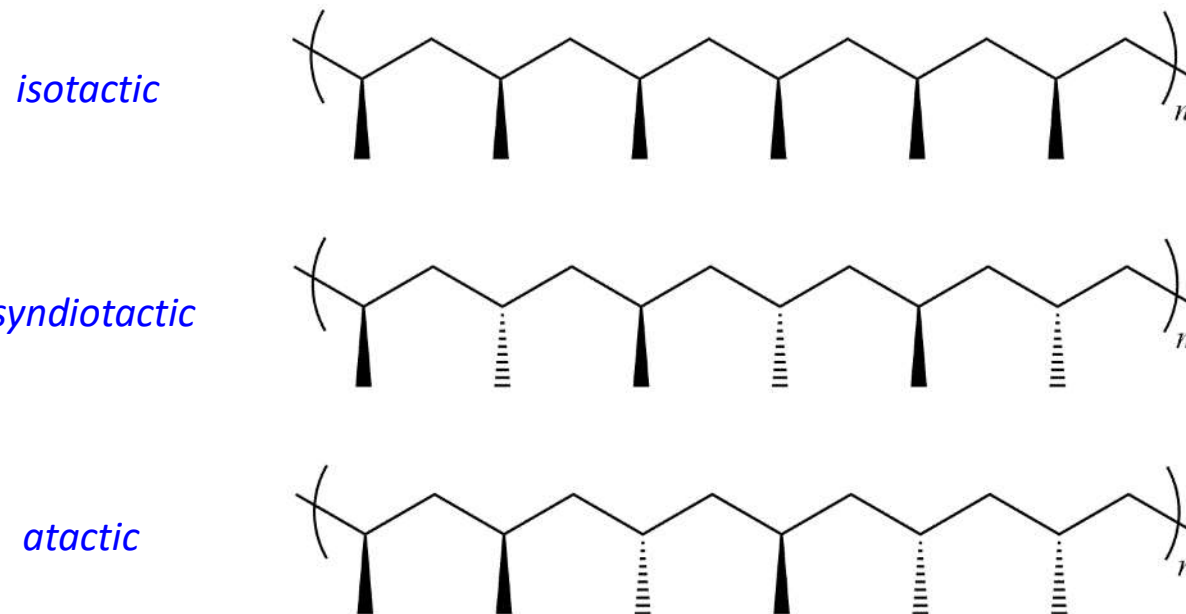
Industrial polymerization of alkenes

- Developed in 1953-1954. Nobel Prize 1963
- Polymerization of ethene into polyethylene at relatively low pressures
- TiCl_4 -based catalysts on MgCl_2 solid support (similar crystal structures)
- Formation of **stereoregular** polymers possible



Karl Ziegler

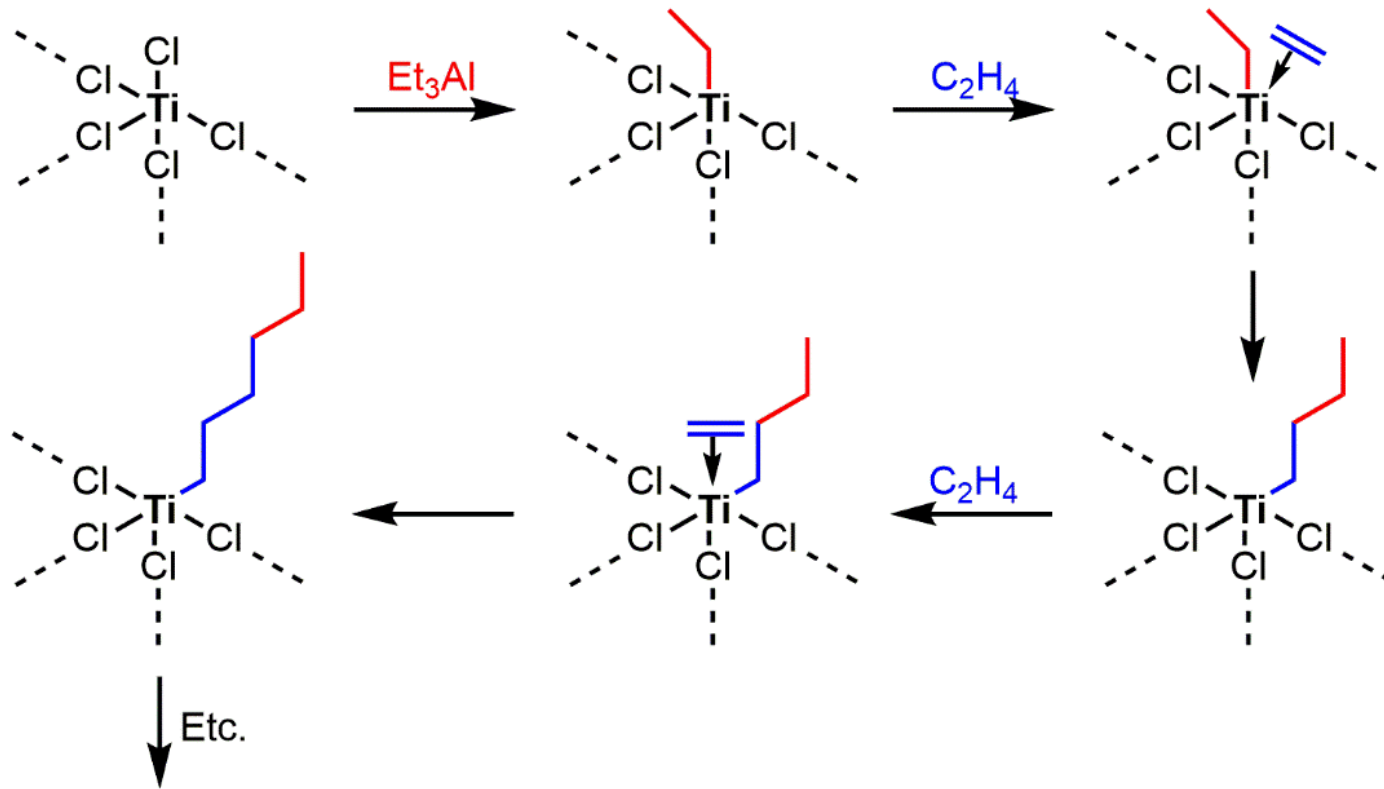
Giulio Natta



Ziegler-Natta process

Mechanism

- Alkene polymerization catalyzed at a surface **Ti(III)** center with a terminal Cl and a vacant coordination site

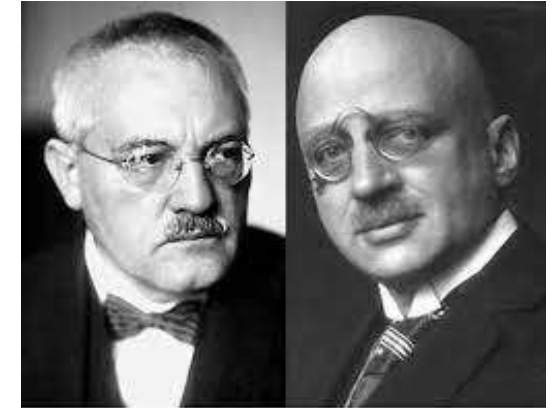


- In case of propene polymerization: isotactic polymer is obtained, controlled by specific surface structure of catalyst

Haber-Bosch process

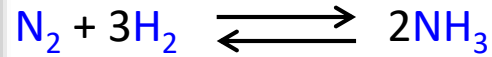
Industrial synthesis of ammonia from nitrogen and hydrogen

- Developed in 1909. Nobel Prizes Chemistry Haber in 1918 & Bosch in 1931
- Developed to produce fertilizer.....and explosives
- First: **Fe**-based solid catalysts. Nowadays **Ru** catalyst on carbon support

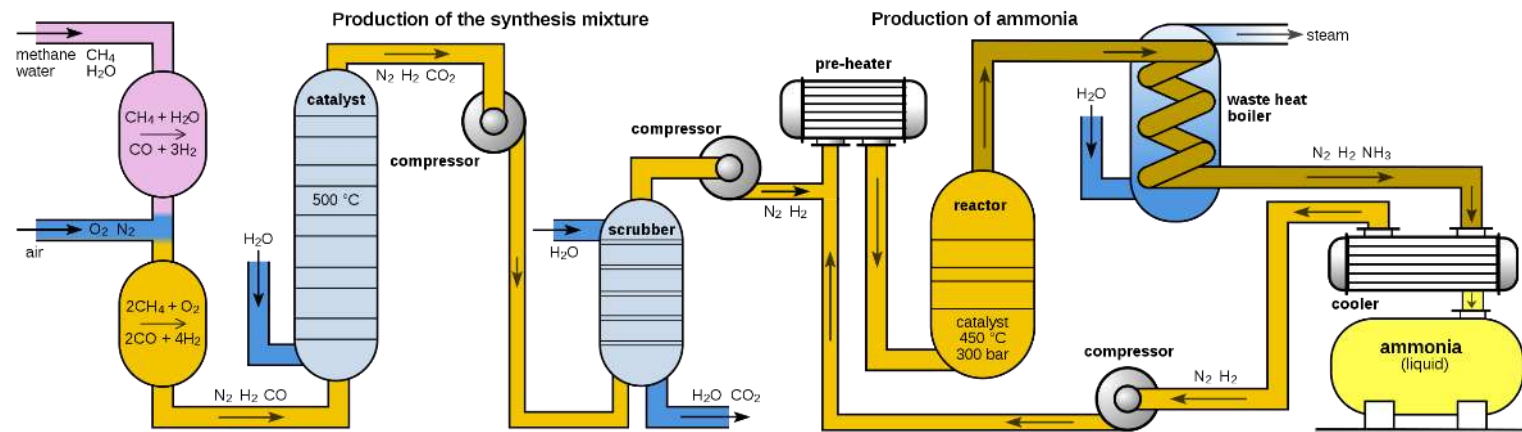


Carl Bosch

Fritz Haber

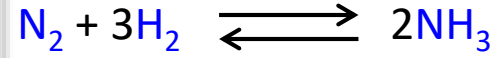
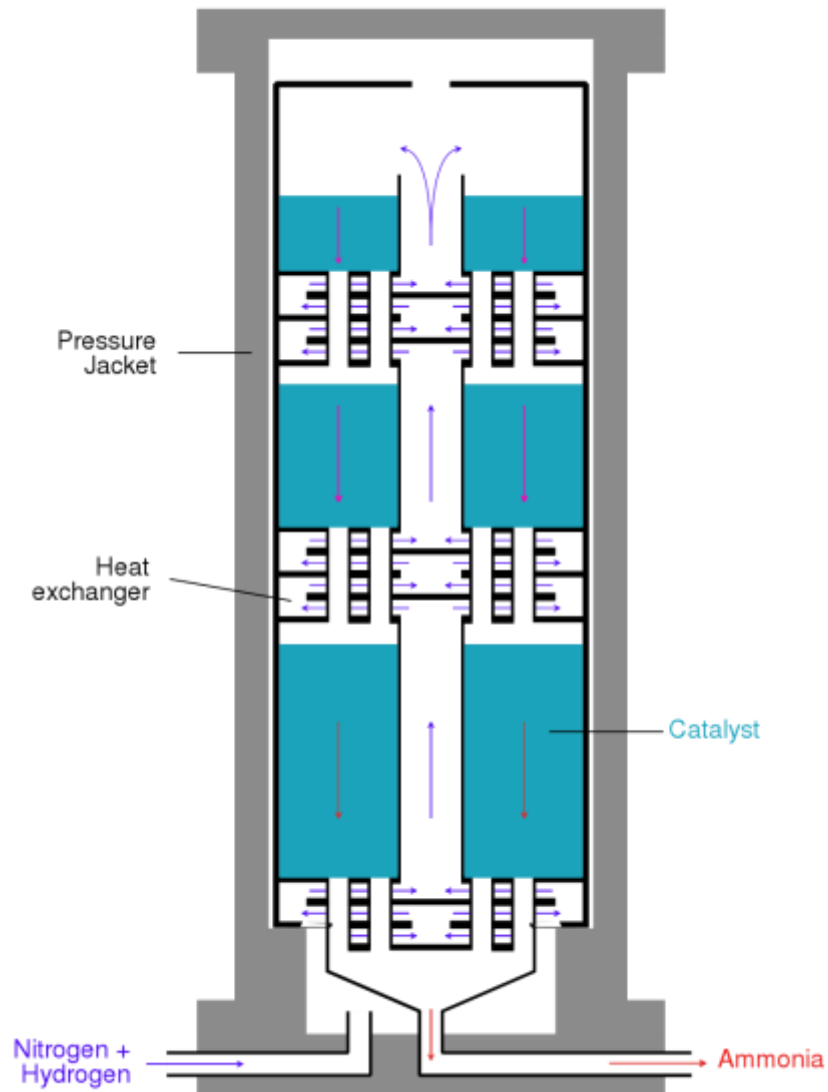


- Exothermic **equilibrium** reaction **with negative entropy**: high pressure of >200 atm) needed but *relatively* low temperature of 400-500 °C (uncatalyzed reaction: 3000 °C)

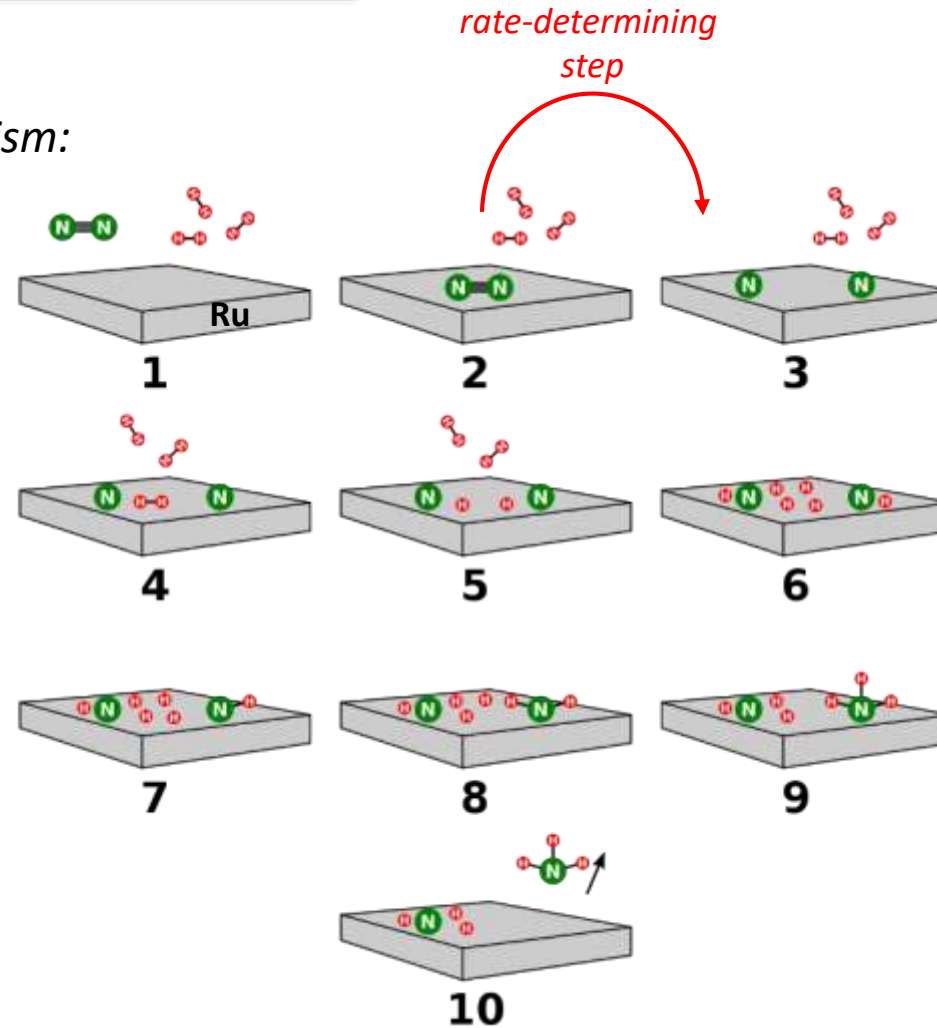


Haber-Bosch process

Modern day reactor

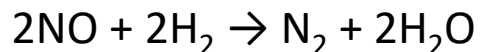
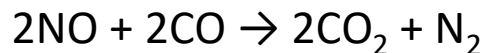
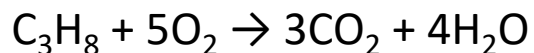
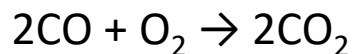


Mechanism:



Catalytic converters

Reduce emission of harmful gases from car exhaust



Pd or **Pt** catalyst

Pd or **Pt** catalyst

Rh catalyst

Rh catalyst

Pt catalyst



- >90% efficient in reducing emissions
- Honeycomb ceramic structure coated in finely divided Al_2O_3 (“washcoat”)
- Fine particles (1 – 2 nm) of catalytic **Pt**, **Pd**, **Rh** dispersed in the cavities of the washcoat
- Lead-free fuel required – **Pb** binds to Al_2O_3 washcoat
- Air : fuel ratio (about 15:1) is crucial
 - Ratio too high: O_2 competes with NO for H_2 -oxidation
 - Ratio too low: CO and C_3H_8 will compete for O_2

Learning goals & study material

Learning goals

- You understand the basic reaction steps of heterogeneous catalysis
- You know the difference between physisorption and chemisorption and the theory of the respective bonding modes of molecules and atoms to a metallic surface
- You understand the qualitative thermodynamics and kinetics of heterogeneous catalysis on metals
- You understand the dependence of heterogeneous catalysis on microscopic surface structure and catalyst support
- You can apply the above knowledge to simple chemical reactions that are heterogeneously catalyzed

Study material

- These lecture slides
- Catalysis: An Integrated Textbook for Students (U. Hanefeld & L. Lefferts, Eds):
Sections: 2.1, 2.1.1, 2.1.2.2, 2.1.3, 2.2, 2.2.1, 2.2.2, 2.2.3, 2.2.4, 2.4.1.1, 2.4.1.2, 2.4.1.3
- Only for background reading: Sections: 2.1.2, 2.1.2.1, 2.1.2.3