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Industrial Catalysis

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Catalysis in Industry

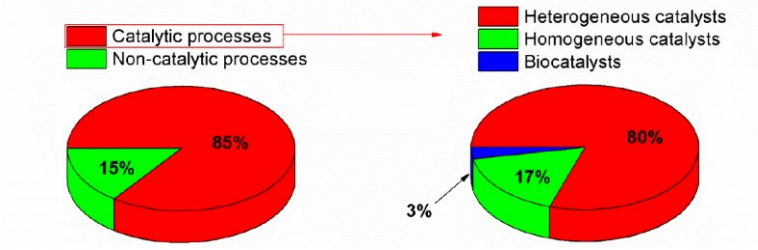


Fig. 1. Diagram presenting: a) the contribution of catalytic processes to the chemical industry and b) the contribution of heterogeneous catalysis in comparison to other catalytic processes [4]

Waclawek et al. *Ecol. Chem. Eng.* **2018**, *25*, 9.

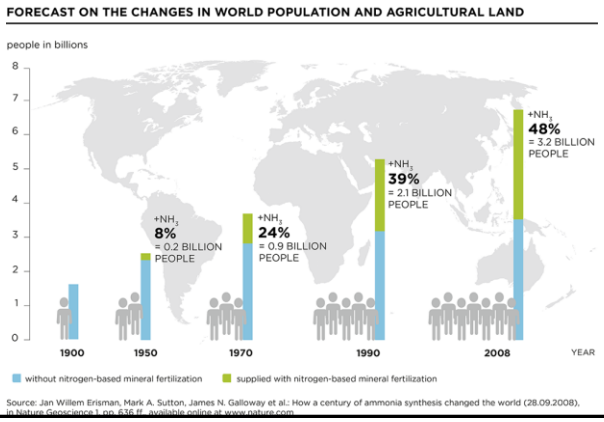
Catalysis in Industry

Process	Catalyst	Reaction
Making ammonia	Iron	$N_2 + 3\ H_2 \rightarrow 2\ NH_3$
Making synthesis gas	Nickel	$CH_4 + H_2O \rightarrow CO + 3\ H_2$
Making methanol	Copper/Zinc on alumina	$CO + 2\ H_2 \rightarrow CH_3OH$ $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$
Catalytic cracking of gas oil	Zeolite	Produces: A gas (ethylene, propylene, …) A liquid (petrol) A residue (fuel oil)
Making polymers	Ziegler-Natta catalysts Metallocenes	e.g., Propene → polypropylene
Making ethyleneoxide	Silver on alumina	$C_2H_4 + ½\ O_2 \rightarrow$ ethyleneoxide
Making hydrocarbons	Cobalt, Iron, Ruthenium	$(2n + 1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$

https://www.essentialchemicalindustry.org/processes/catalysis-in-industry.html.

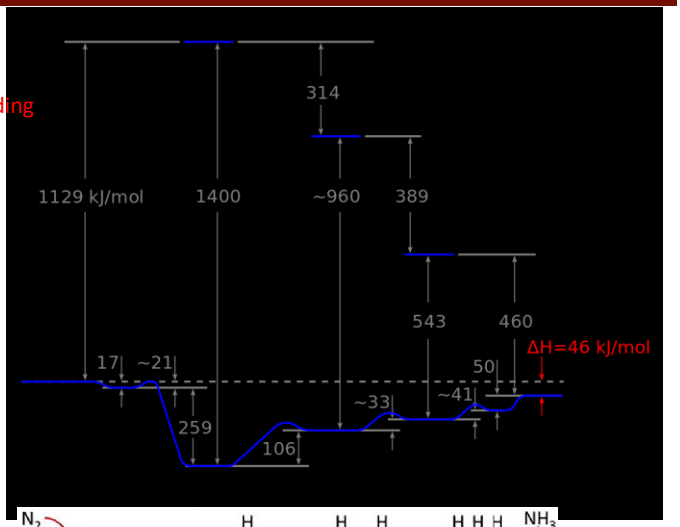
Making ammonia (Haber-Bosch process)

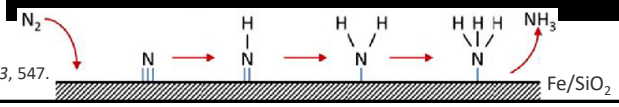
- Responsible for 1 – 1.5% of all energy consumption
- ~176 mil. tons annually
- used for fertilizers (~almost 90%), refrigeration, explosives, textiles and pharmaceutical



Haber-Bosch process

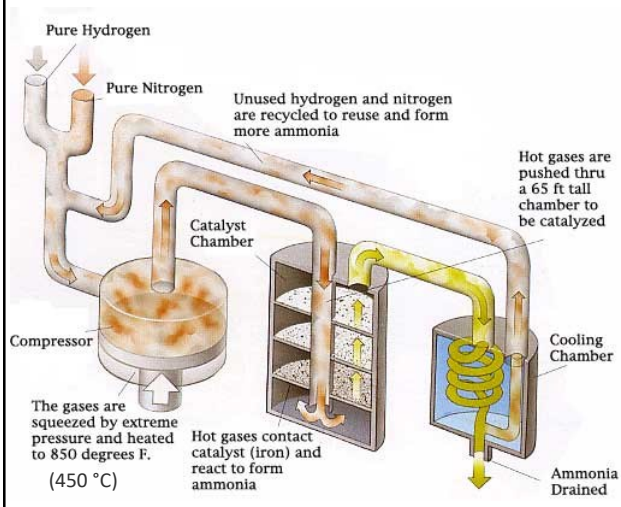
Extremely energy-demanding process

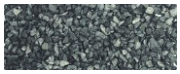




Quadrelli, E. A. *Chem. Soc. Rev.* **2014**, *43*, 547.

Haber-Bosch process





Catalyst

metallic iron doped with potassium on silica or alumina

COSTS

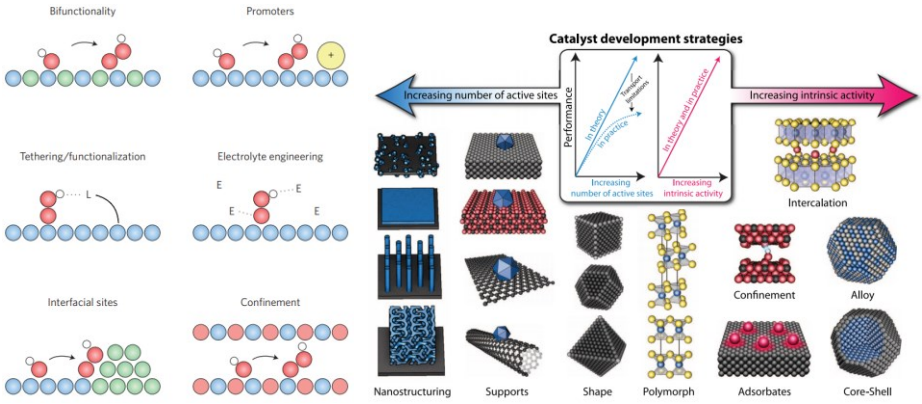
- Heat
- Pressure

- High purity H_2 and N_2
- (O_2, CO, CO_2 are poison for the catalyst)

100 years of optimization → efficiency > 95%

Haber-Bosch process – towards better catalysts

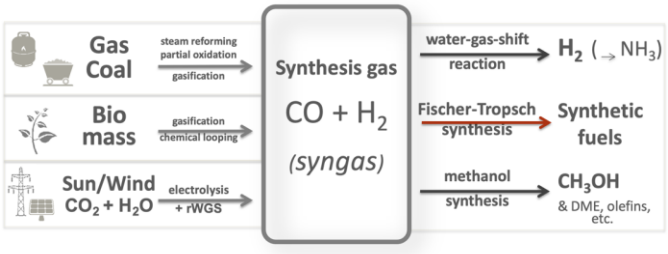
- The bar is extremely high (cheap catalyst, large efficiency)
- New catalysts – working at milder conditions (temperature, pressure)
  - Electrocatalysis, new material design
- Improving processes for producing pure H_2



T. F. Jaramillo: *Nat. Mater.* **2017**, *16*, 70; *Science* **2017**, *355*, 146.

Making Synthesis Gas (Steam Reforming of Methane)

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_{298} = +206\ kJ/mol$$



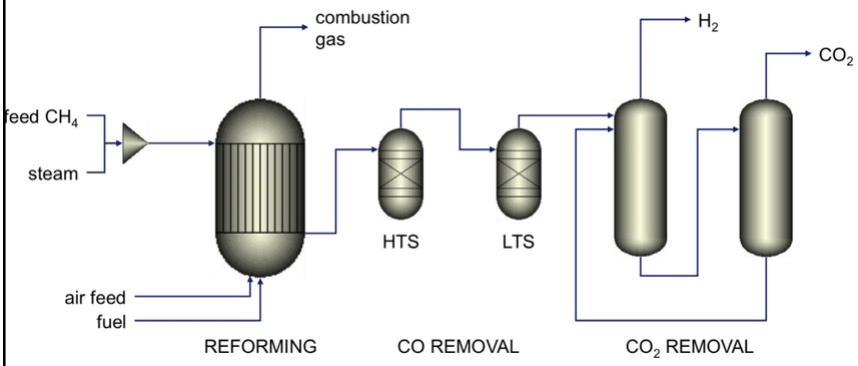
- Responsible for ~ 95% of H_2 production (~50 mil. tons of H_2 annually)
- used for synthesis of other chemicals and H_2 used for synthesis of ammonia

Making Hydrogen (Steam Reforming of Methane + Water Gas Shift Reaction)

$CH_4 + H_2O \rightleftharpoons CO + 3H_2$ $\quad \Delta H_{298} = +206$ kJ/mol

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\quad \Delta H_{298} = -41$ kJ/mol

$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$ $\quad \Delta H_{298} = +165$ kJ/mol



Conventional steam reforming process with multiple stages for H_2 production
Liquori et at. *Prog. En. Comb. Sci.* **2020**, *80*, 100851.

Making Hydrogen (Steam Reforming of Methane + Water Gas Shift Reaction)

- Catalyst: a metal (typically nickel, but also Mn/Fe/Co, and others) supported on a high surface area (silica, alumina, MgO)
- Steam reforming proceeds at high temperatures (700 – 1000 °C) and at 3 – 30 bars
- Design depends on a plant → 50 – 80% efficiency
  - mostly optimized in sixties

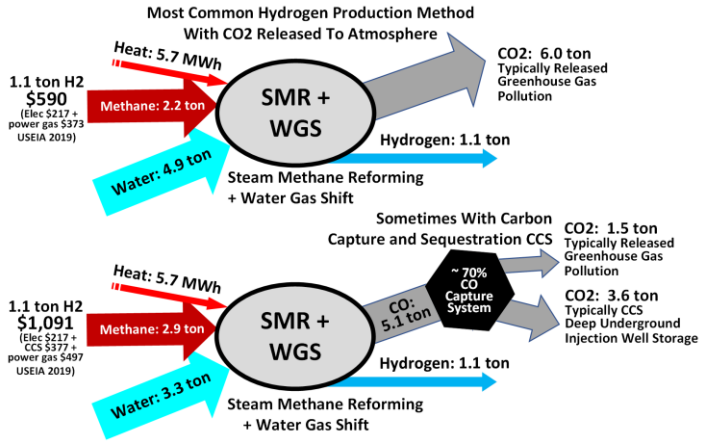
➡ Demand for new catalysts operating at lower temperatures

- currently, the support is mostly optimized
  e.g., Ni on La_2O_3–ZrO_2–CeO_2 support/promoter can go as low as 400 °C;
  Ni on layered double hydroxide nanosheets uses sun light instead of T

Appl. Catalysis B: Environmental **2016**, *181*, 34.
Chem. Eng. Sci. **2021**, *245*, 116839.

Making Hydrogen (Steam Reforming of Methane + Water Gas Shift Reaction)

$$CH_4 + 2\,H_2O \longrightarrow 4\,H_2 + CO_2$$



https://commons.wikimedia.org/w/index.php?curid=96621219

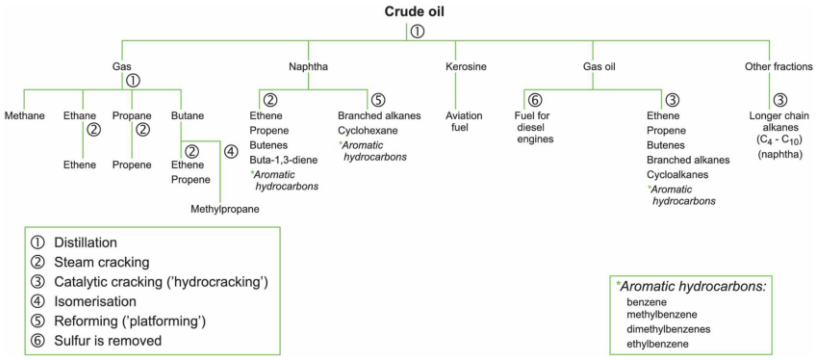
Nationaal Groeifonds : **groene waterstof**

Nationaal Groeifonds reserveert € 338 miljoen voor waterstof en groene chemie

- Een investering van 646 miljoen euro en een reservering van 3,5 miljard euro in tien projecten moet zorgen voor meer economische groei in Nederland. Het kabinet wil dit geld uit het Nationaal Groeifonds onder meer steken in groene waterstof, innovatief en toekomstbestendig onderwijs en het doortrekken van de Noord-Zuidlijn. Hiermee neemt het kabinet het advies van de onafhankelijke beoordelingsadviescommissie onder leiding van Jeroen Dijsselbloem volledig over. Dat hebben minister Van 't Wout (Economische Zaken en Klimaat) en minister Hoekstra (Financiën) bekendgemaakt.

Other industrially important reactions

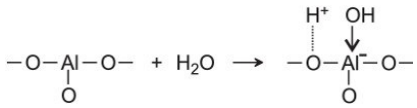
Processing of crude oil



https://www.essentialchemicalindustry.org/processes/catalysis-in-industry.html

Catalytic Cracking

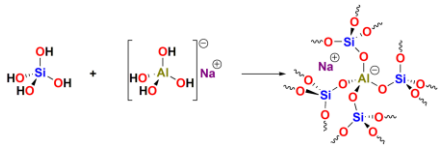
alumina
silica



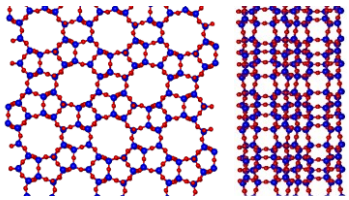
- possibility of depositing other metals (e.g. Pt, Re – platforming)
- acidic coating

zeolites – a particular class of aluminosilicates

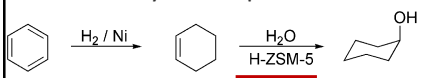
- many different variants
- porous materials



ZSM-5: Top view Side view



Zeolite - Asahi cyclohexanol process:



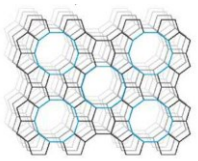
100 °C

98 % selectivity

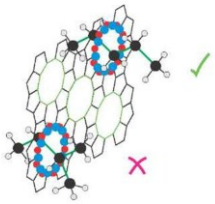
https://www.essentialchemicalindustry.org/processes/catalysis-in-industry.html

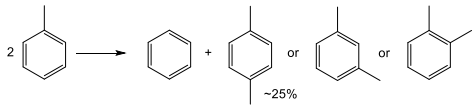
Zeolites as catalysts

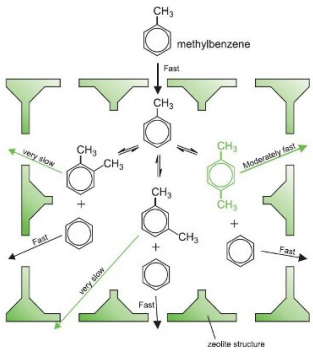
Mechanic properties (size of the pores) used to induce reaction selectivity



The zeolite acts as a molecular sieve. Only straight-chain molecules can pass through the holes in the zeolite structure.







https://www.essentialchemicalindustry.org/processes/catalysis-in-industry.html

Zeolites as catalysts in industry

Process	Catalyst	Equation
Catalytic cracking of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g.petrol) a residue (e.g. fuel oil)
Reforming of naphtha	Platinum and rhenium on zeolite	$CH_3CH_2CH_2CH_2CH_2CH_3(g) \rightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2CH_2CH_3(g)$
Disproportionation of methylbenzene	Zeolite	$2\ \underset{(g)}{\overset{CH_3}{\bigcirc}} \rightarrow \underset{(g)}{\overset{CH_3}{\bigcirc}}\ \underset{CH_3}{} + \underset{(g)}{\bigcirc}$
Dealkylation of methylbenzene	Zeolites	$\underset{(g)}{\overset{CH_3}{\bigcirc}} + H_2(g) \rightarrow \underset{(g)}{\bigcirc} + CH_4(g)$
Making cumene (1-methylethyl)benzene<	Zeolite (ZSM-5)	$\underset{(g)}{\bigcirc} + CH_3CH{=}CH_2(g) \rightarrow \underset{(g)}{\overset{CH_3-CH-CH_3}{\bigcirc}}$

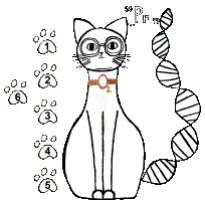
Table 2 Examples of industrial processes using zeolites.

https://www.essentialchemicalindustry.org/processes/catalysis-in-industry.html

Learning objectives

You should be able to explain and understand

- what are the most important industrial catalytic processes.
- why it is important to search for more effective catalysts.
- what are the biggest challenges in industrial catalysis.
- Haber-Bosch process.
- steam reforming of methane and water-gas shift reaction.
- methanol synthesis (see the extra video clip).
- polymerization of alkenes (see the extra video clip).
- know other examples of industrial catalytic processes (e.g., catalytic cracking, Fischer-Tropsch synthesis).



Do the quiz and see you in the class!