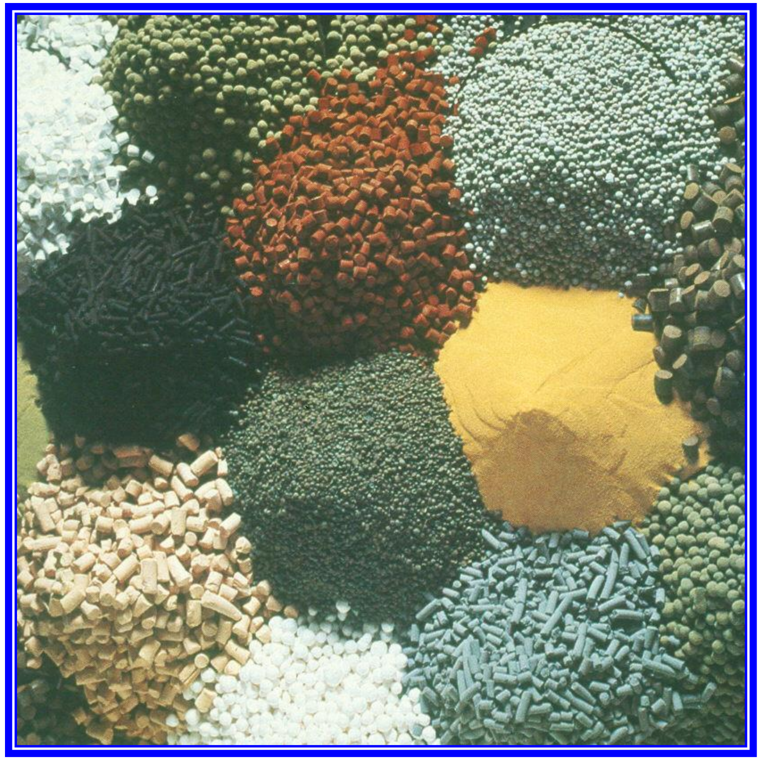
Catalysis and the hydrocarbon industry *Basic principles*

Antal Tungler Professor emeritus
Centre for Energy Research
BME CEPE

2022

What is Catalysis?

- The science of catalysts and catalytic processes.
- A developing science which plays a critically important role in the gas, petroleum, chemical, and emerging energy industries.
- Combines principles from somewhat diverse disciplines of reaction kinetics, inorganic and organic chemistry, materials science, surface science, and chemical engineering.



Definition of the catalyst

The first definition of catalysis, which is valid even today came from Berzelius, 1839. The classical definition of a catalyst states that “a catalyst is a substance that changes the rate but not the thermodynamics of a chemical reaction and remains unchanged after the reaction” and was originally formulated by OSTWALD.
As emphasized by BOUDART, the conditions under which catalytic processes occur on solid materials vary drastically. The reaction temperature can be as low as 78 K and as high as 1500 K, and pressures can vary between 10^{-9} and 100 MPa.
The catalysts are working in cycles which consist of steps where 1. the catalyst and the substrate(s) react, giving a catalyst-substrate species, 2. the chemical reaction takes place on the surface of a heterogeneous catalyst or in the coordination sphere of a homogeneous complex catalyst, 3. the product(s) leave the catalyst which becoming free, can start a new cycle.

Importance of catalysis

The global catalyst market was valued at **$35.5 billion in 2020**,
and is projected to reach $57.5 billion by 2030, growing at a CAGR of 4.9% from 2021 to 2030.
Catalyst costs in the fuel industry is ~0,1%,
in the petrochemical industry ~0,22%.
Estimation: the total value of the products produced by catalytic technologies is 3 orders of magnitude higher

*The **85 % of the chemicals** is produced by catalytic technologies.*

Topic of this presentation

In this lecture I will speak about heterogeneous catalysis, as it is dominant in the hydrocarbon industry. However the importance of homogeneous, especially metal complex catalysis is becoming more and more important in industrial applications also.

Catalysis in the hydrocarbon industry

- **Demands of the fuel market and the petrochemical industry:**

- Gasoline with high octane number,
- Diesel with high cetane number, and low freezing point
- Low aromatic content,
- Low sulfur content,
- Highest processing rate of crude oil,
- Blending components.

- **Achievements of catalysis:**

- Gasoline reformation,
- FCC,
- Hydrogenation, isomerization,
- Desulfurization, deep desulfurization
- Hydrocracking,
- MTBE ETBE Alkylate gasoline production with acidic catalysis
- Oligomerization, metathesis

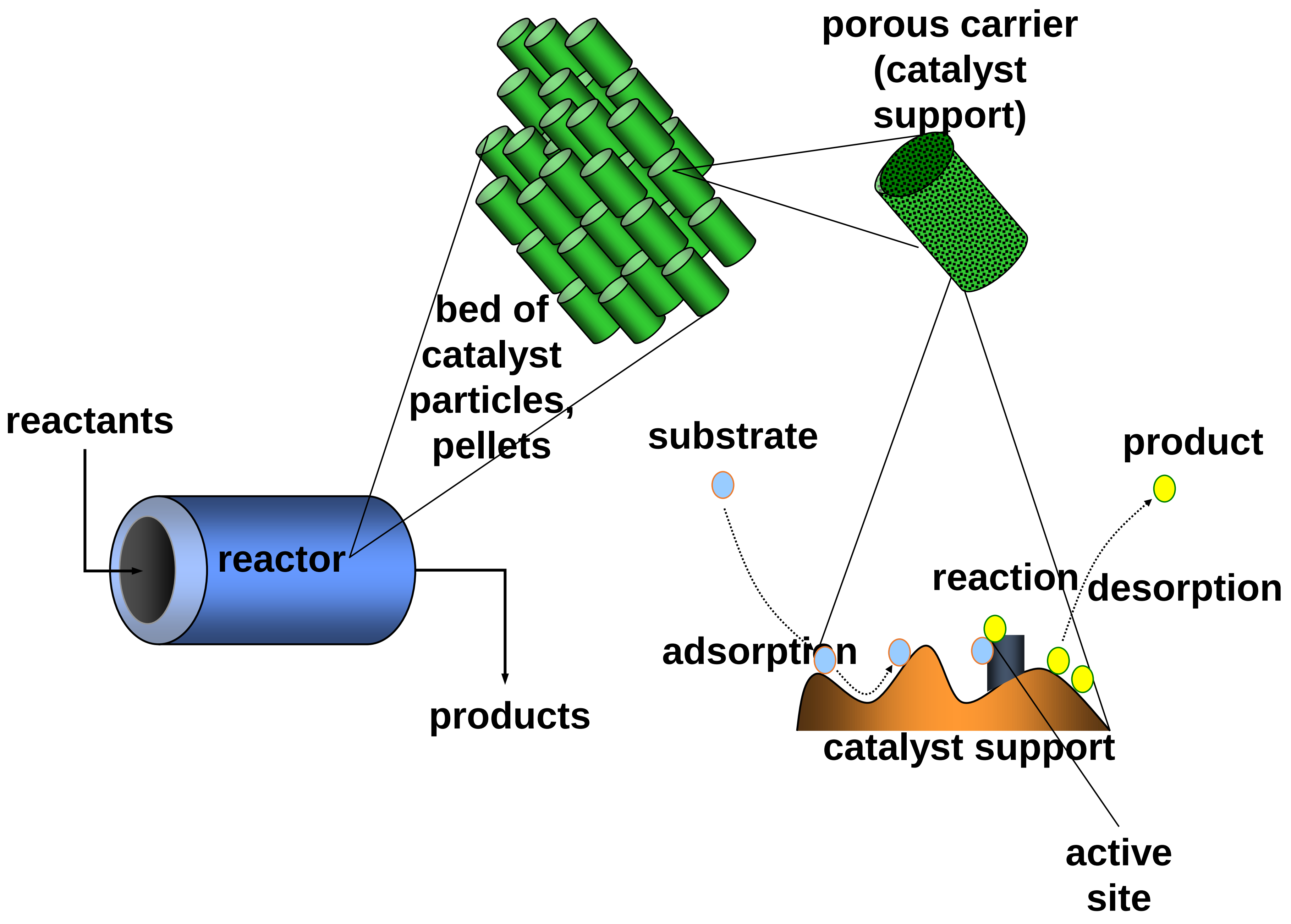
Steps of the Heterogeneous Catalytic Reaction

- Diffusion of Reactants (from the Bulk through the Film surrounding the catalyst particles onto the Surface)

- Adsorption

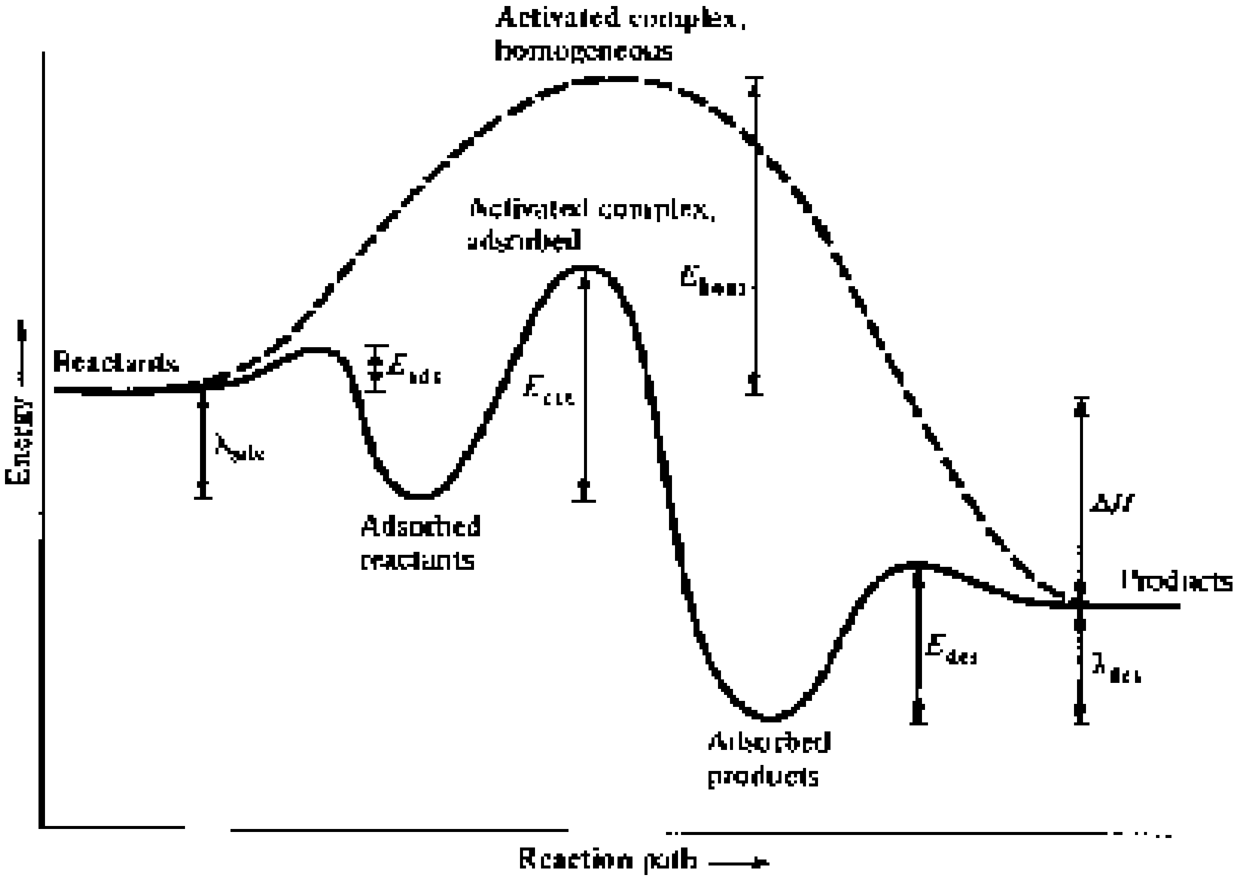
- Surface Reaction

- Desorption & Diffusion of Products leaving the catalyst surface

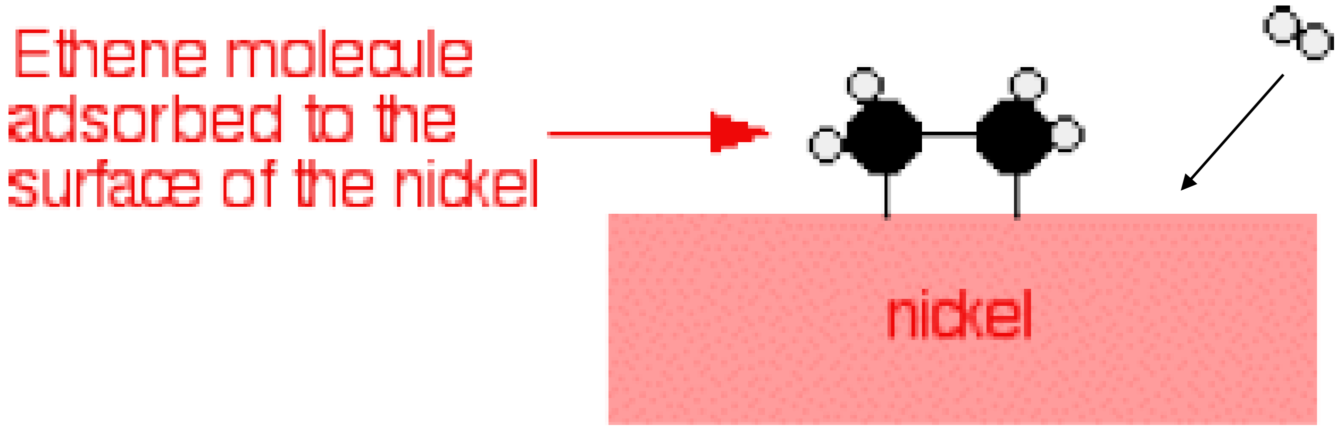


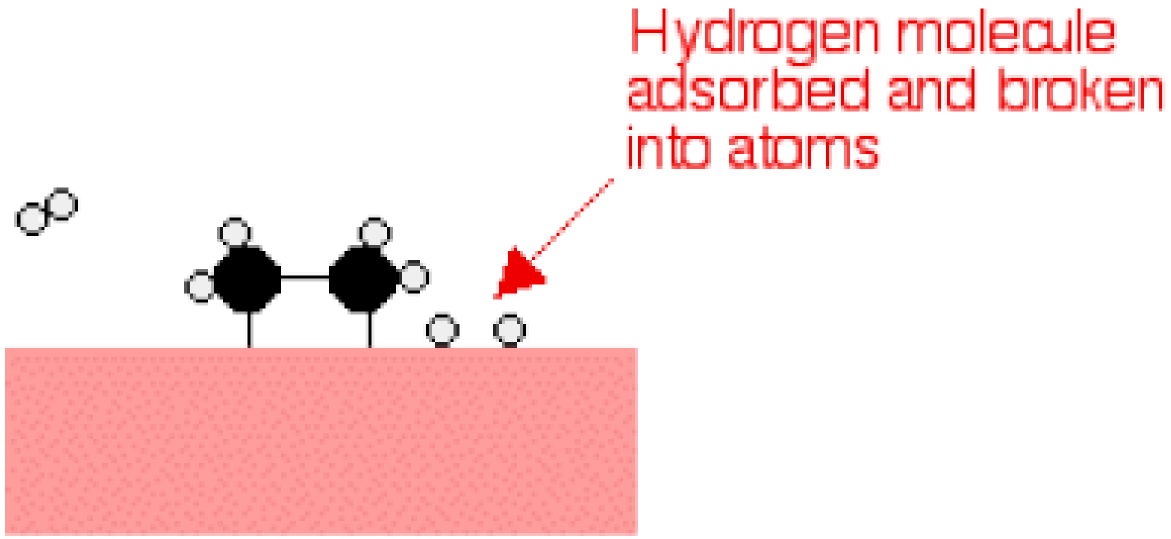
porous carrier (catalyst support)
bed of catalyst particles, pellets
reactants
reactor
products
substrate
product
reaction
desorption
adsorption
catalyst support
active site

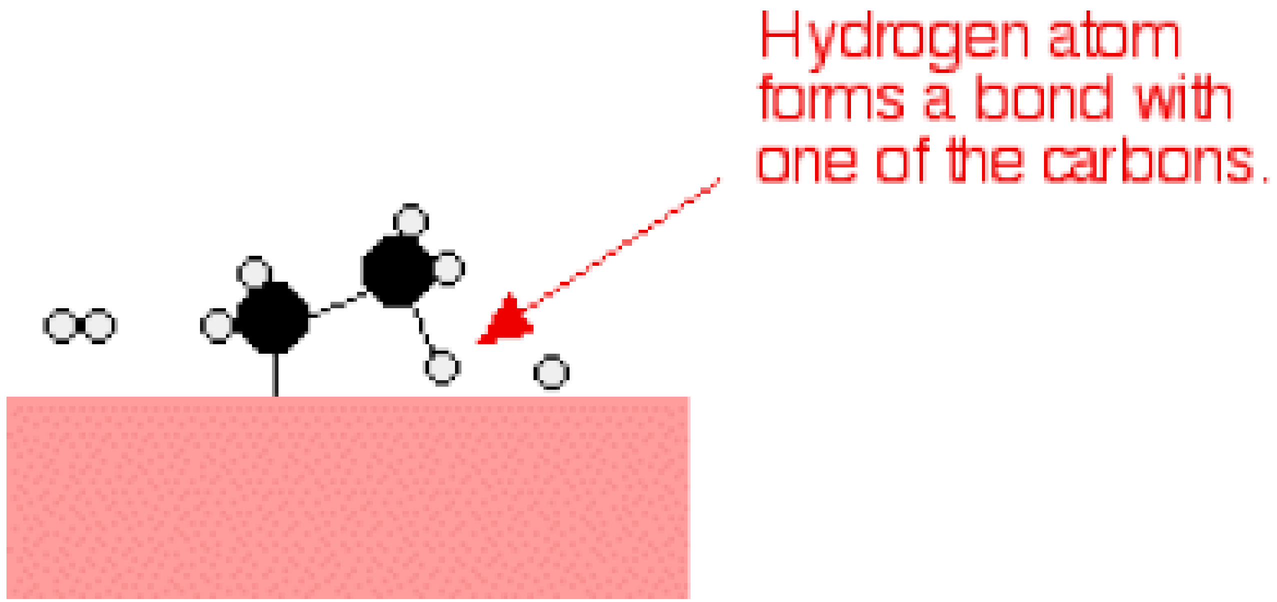
Energy profile of catalysed and non-catalysed reactions

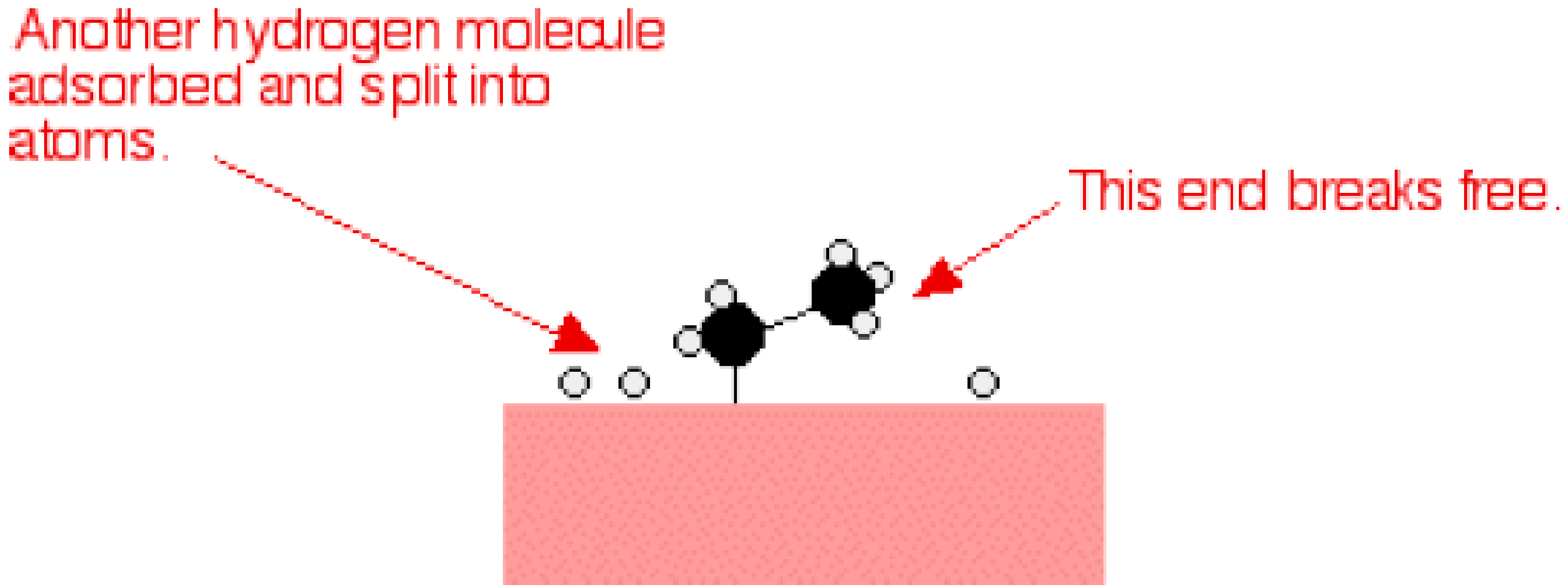


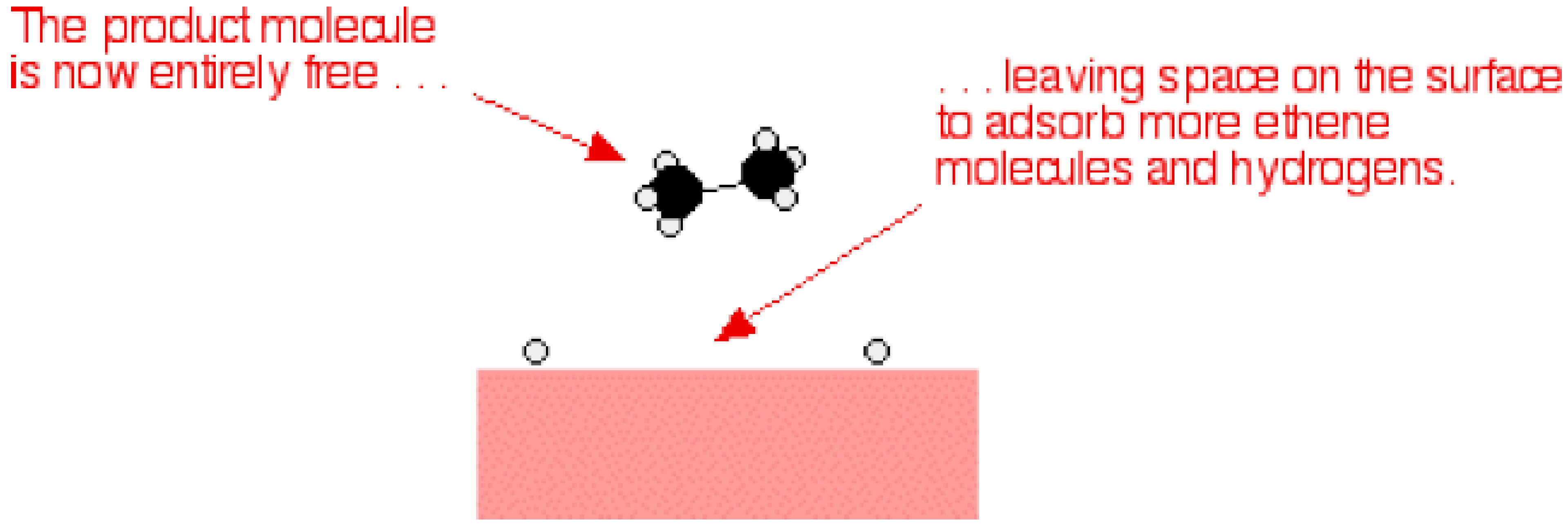
$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$$



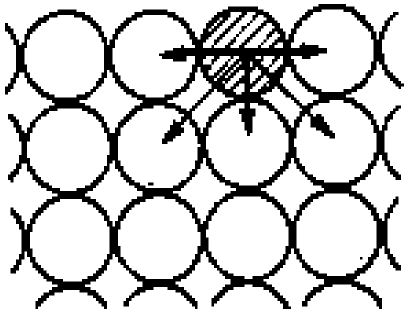



Hydrogen atom forms a bond with one of the carbons.

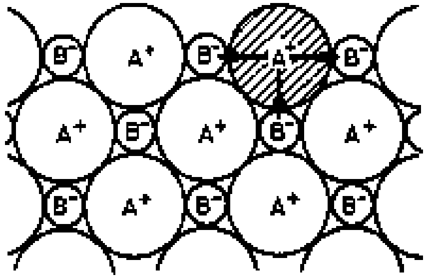

Another hydrogen molecule adsorbed and split into atoms.
This end breaks free.


The product molecule
is now entirely free . . .
. . . leaving space on the surface
to adsorb more ethene
molecules and hydrogens.

Driving force of adsorption: the free energy plus of surface atoms or ions



Kovalens szilárd anyag felületi energiájának szemléletes ábrázolása



Ionos szilárd anyag felületi energiájának szemléletes ábrázolása

Covalent solid material

Ionic solid material

Characteristics of physical and chemisorption

Characteristics	Chemisorption	Physical adsorption
Adsorption enthalpy $-\Delta H_{adsz}$	40-800 kJ/mol	8-20 kJ/mol (similar to heat of condensation)
Activation energí $E^{\#}$	Usually small	null
Temperature of occurence	Dependent of $E^{\#}$, 78K-1500K	Dependent on boiling point, usually low
Number of adsorbed layers	Max. one	More than one is possible

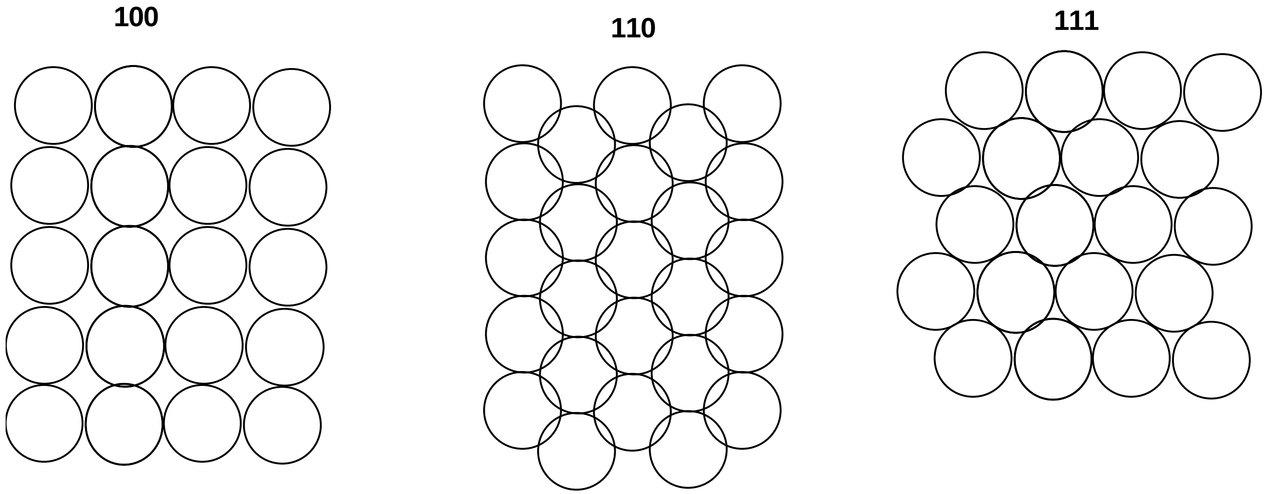
Porosity: the extra high specific surface area (1000 m^2/g) is possible only at porous materials

Macropores	**$r > 25$ nm**
Mezopores	**25 nm $> r >$ 1 nm**
Micropores	**1 nm $> r$**

Metal surfaces

Most catalitically active metal has a crystal structure of face centered cubic, however Fe has a space centered cubic structure, all metals are dense structured

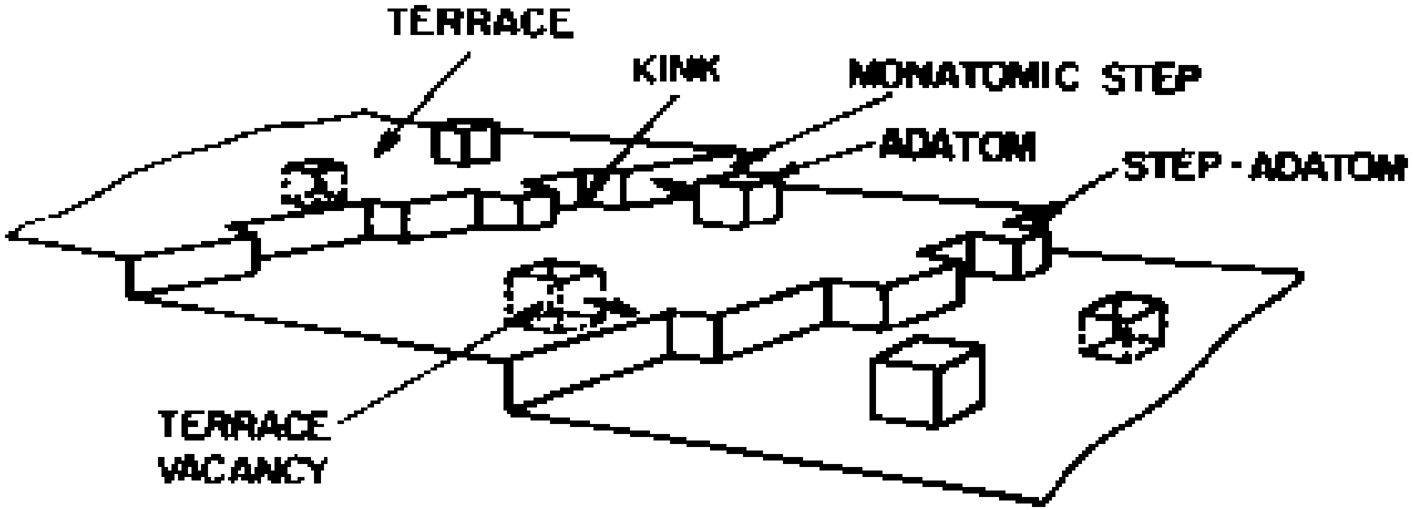
The position of atoms on different Miller indices crystal faces



The surface and catalytic properties of different crystal faces are different also!

Different surface sites

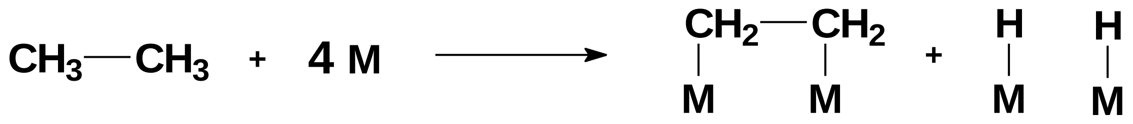
the practical catalysts have varied surface sites with different catalytic properties



Adsorbed states of molecules

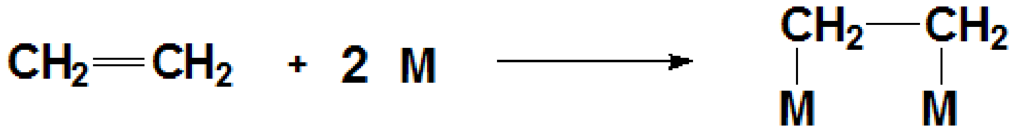
Dissociativ adsorption (hydrogen)

$$H_2 + 2M \longrightarrow 2MH$$

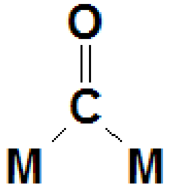


Associativ adsorption

Chemisorption bond by the π electrons of the adsorbate.



Linear form



bridged form

Chemisorption on the surface of oxides

Adsorption on semiconductor oxides:

Reducing adsorbates: $H_2 + M^{2+} + O^{2-} \longrightarrow HM^{+} + OH^{-}$

$CO + M^{2+} + O^{2-} \rightarrow M + CO_2$

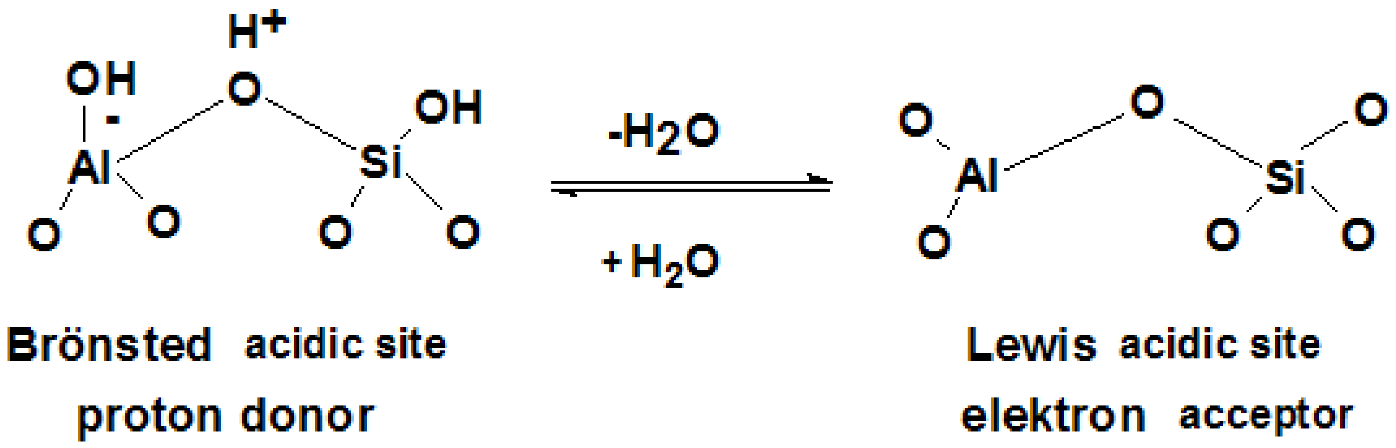
Oxidative adsorbates $2\,Ni^{2+} + O_2 \rightarrow 2(\,O^{-}....Ni^{3+})$

Adsorption on insulators:

$$M^{x+} + O^{2-} \xrightarrow{H_2O} (HO^{-}.....M^{x+}) + OH^{-}$$

Acid-base catalysis

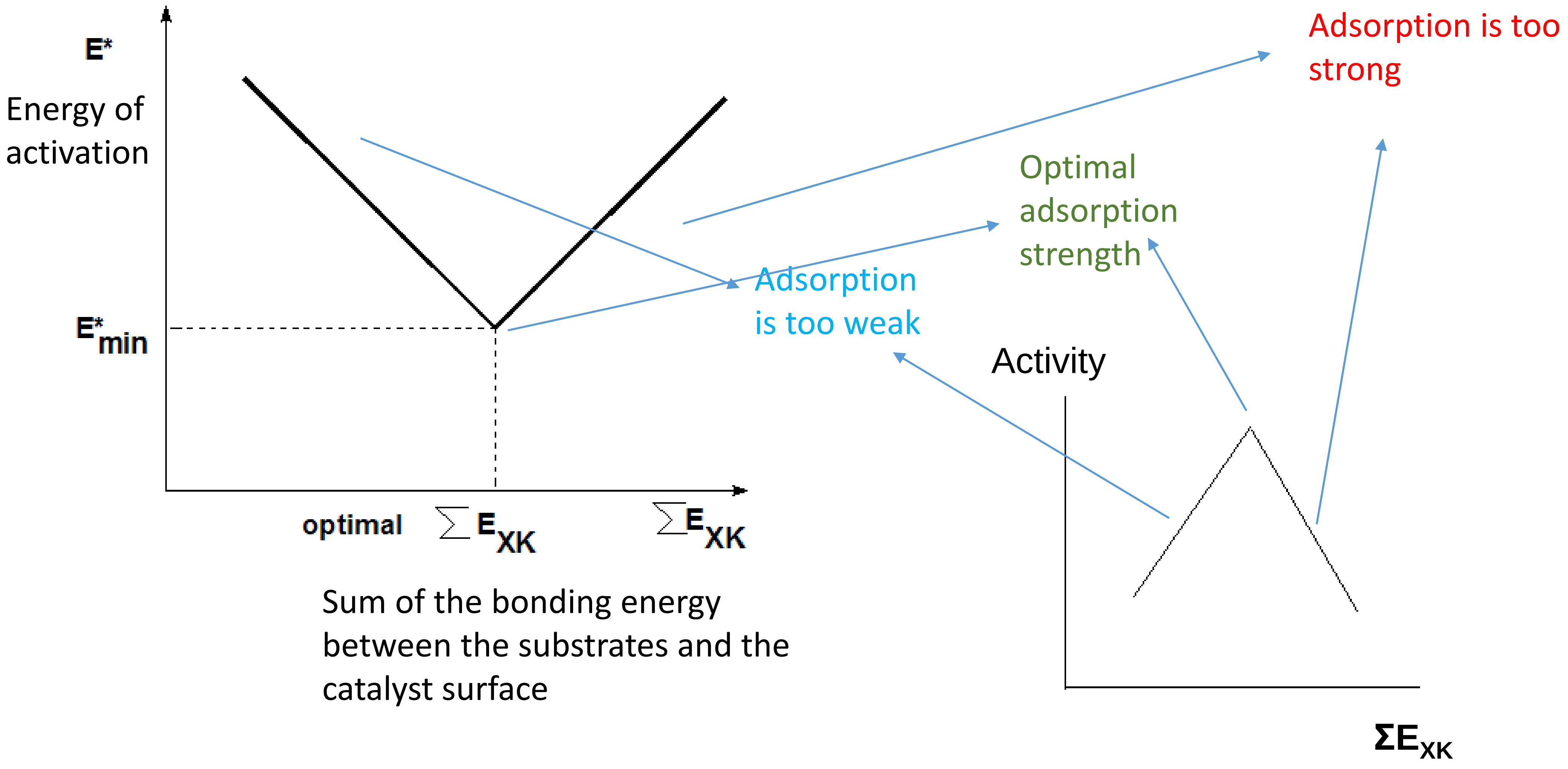
Lewis acids, Brönsted acids, surface acidic sites, zeolites



Bases
Oxide catalysts
with alkaline metals or alkaline metaloxides, alkaline-earth metal oxide content

Vulcano curve (same reaction with different catalysts)

Balandin, geometrical or multiplet theory of catalysis



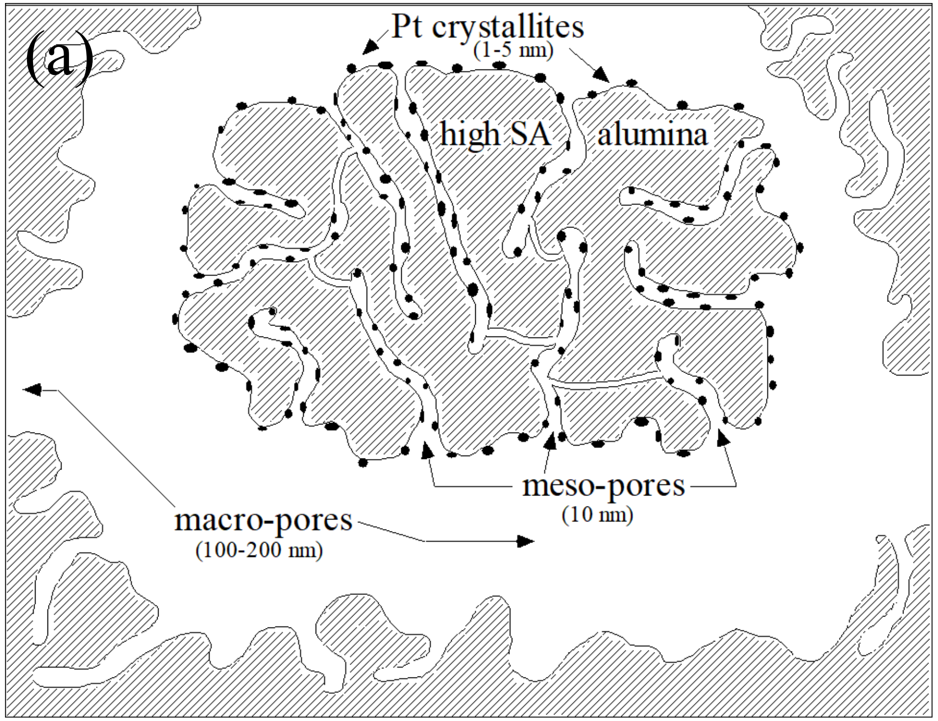
Components of a Typical Heterogeneous Catalyst

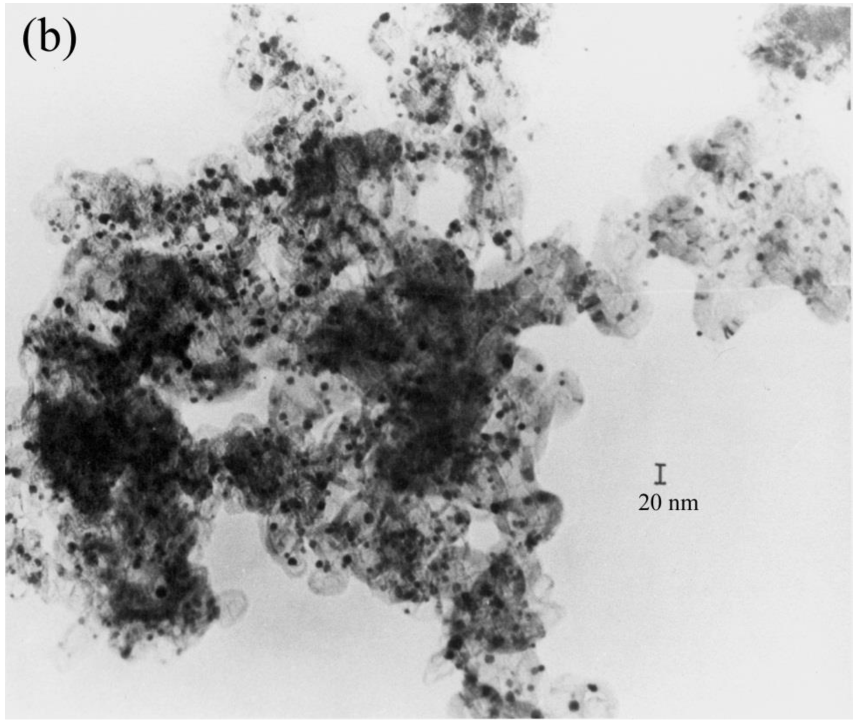
A. Active phase - metal that provides active sites where the chemical reaction takes place

B. Support or Carrier - high surface area oxide which disperses and stabilizes the active phase
(adds efficiency, physical strength, sometimes selectivity)

C. Promoter(s) - additive which improves catalyst properties,
e.g. activity, selectivity, catalyst life

Pt Nanoparticles on Al_2O_3 Supports





Classification of heterogeneous catalysts can be made according to chemical composition, catalyzed reactions

Groups of catalysts	Reactions	Catalyst examples
1. Metals (conductors)	Hydrogenation (ammoniasynthesis) Dehydrogenation Hydrogenolysis Oxidation	Fe, Co, Ni Ru, Rh, Pd Ir, Pt Ag, Cu
2. Metal oxides and sulfides (semiconductors)	Oxidation Reduction Dehydrogenation Cyclisation Hydrogenation Desulfurisation Denitrogenation	V_2O_5, CuO NiO, ZnO, CoO Cr_2O_3, MoO_3 WS_2, MoS_2 Ni_3S_2, Co_9S_8
3. Insulator oxides and acids	Hydratation Dehydration Izomerisation Polymerisation Alkylation Cracking	Zeolitok, ionexchanged SiO_2-Al_2O_3 SiO_2-MgO Al_2O_3 + (Cl vagy F) Supported acids H form zeolites

Zeolites

General formula: $M_pO_q[Al_{p+2q}Si_rO_{2p+4q+2r}]$ s H_2O

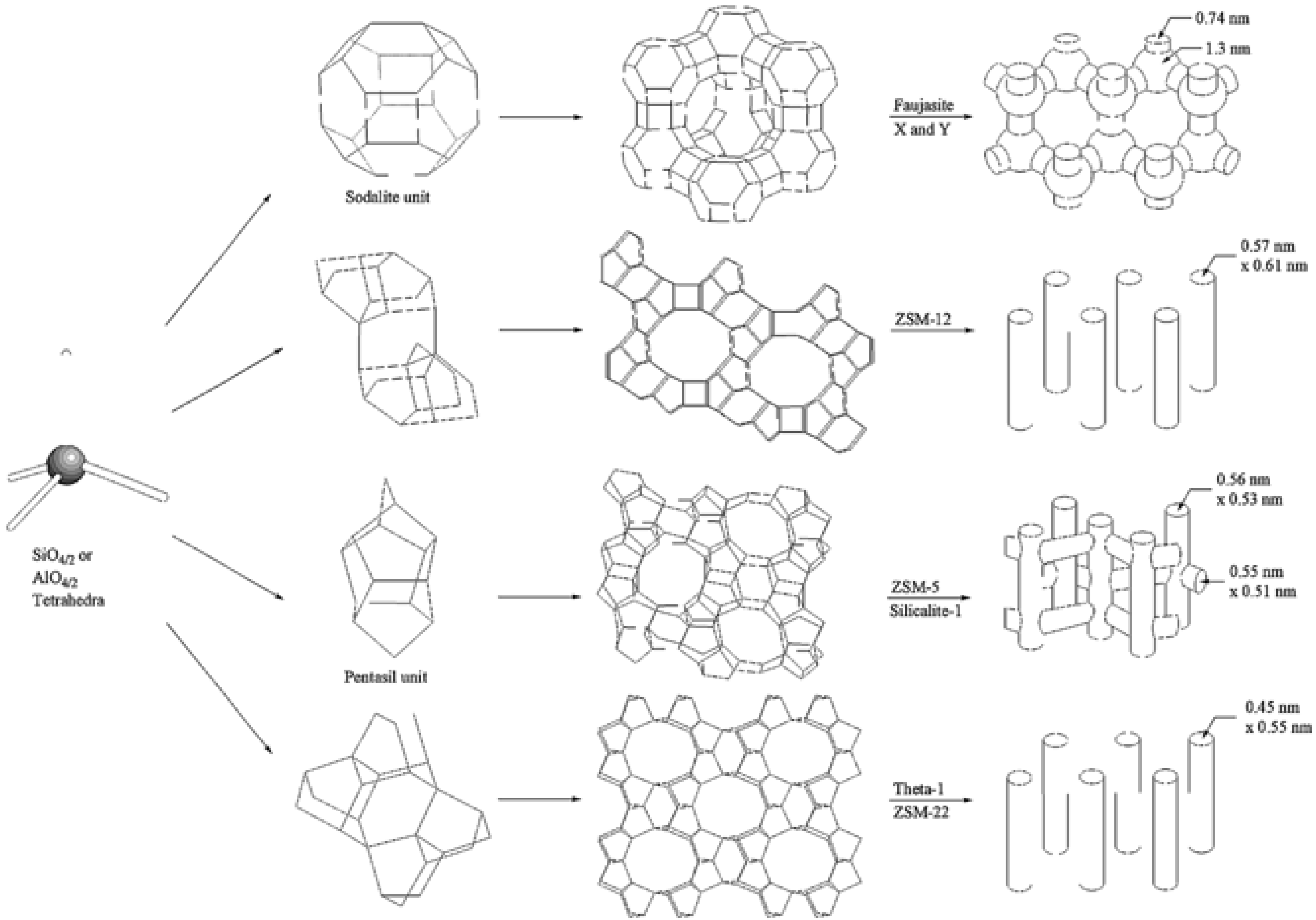
A type zeolite: $Na_{12}Al_{12}Si_{12}O_{48}$ 27 H_2O cubic

L type zeolite: $K_9Al_9Si_{27}O_{72}$ 22 H_2O hexagonal

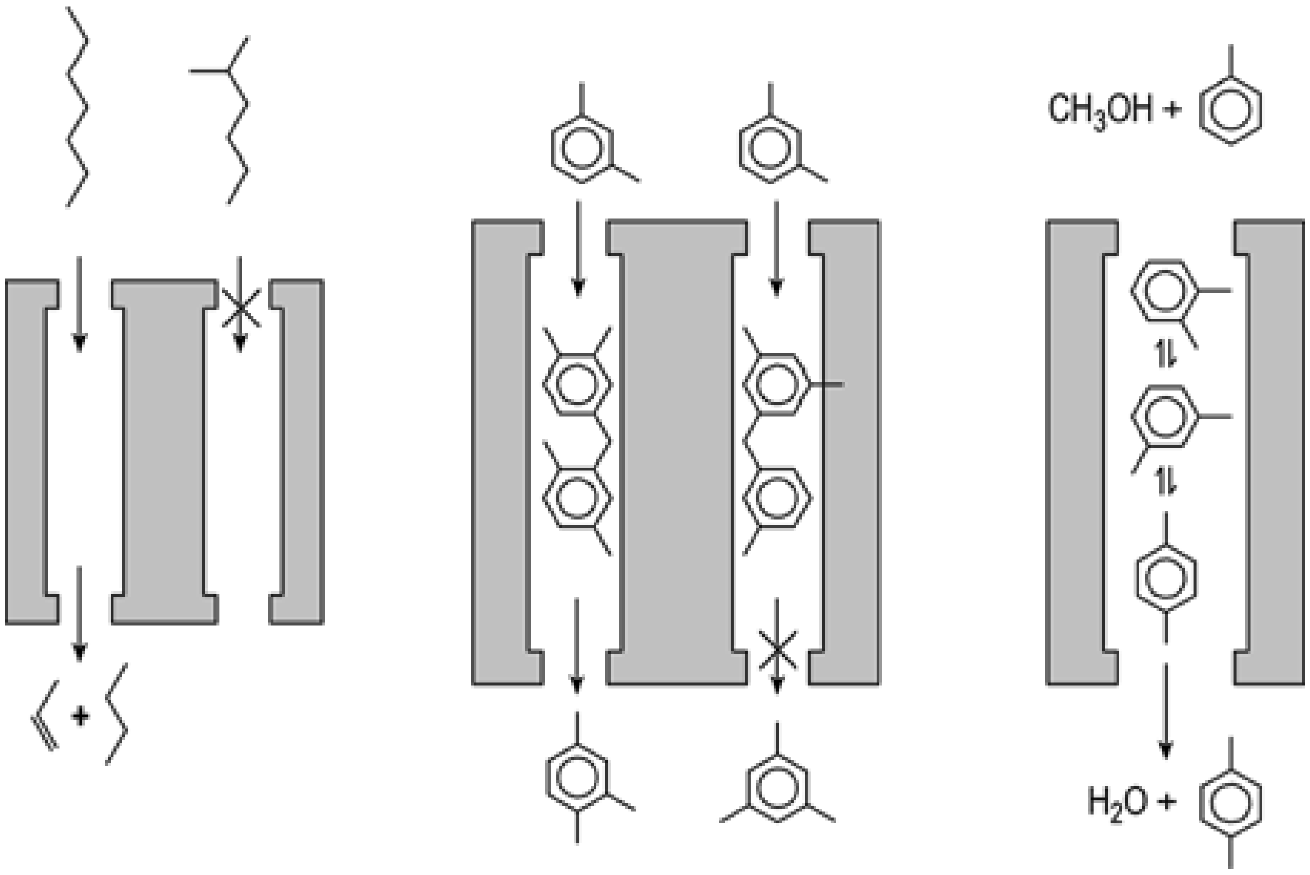
Mordenite: $Na_8Al_8Si_{40}O_{96}$ 24 H_2O

Zeolites are crystalline aluminosilicates, they have ordered structure, molecular size cavities and channels, cationes compensating the negative charge of aluminum and structurally bond water.

Crystalline and pore structure of zeolites



Shape selectivity

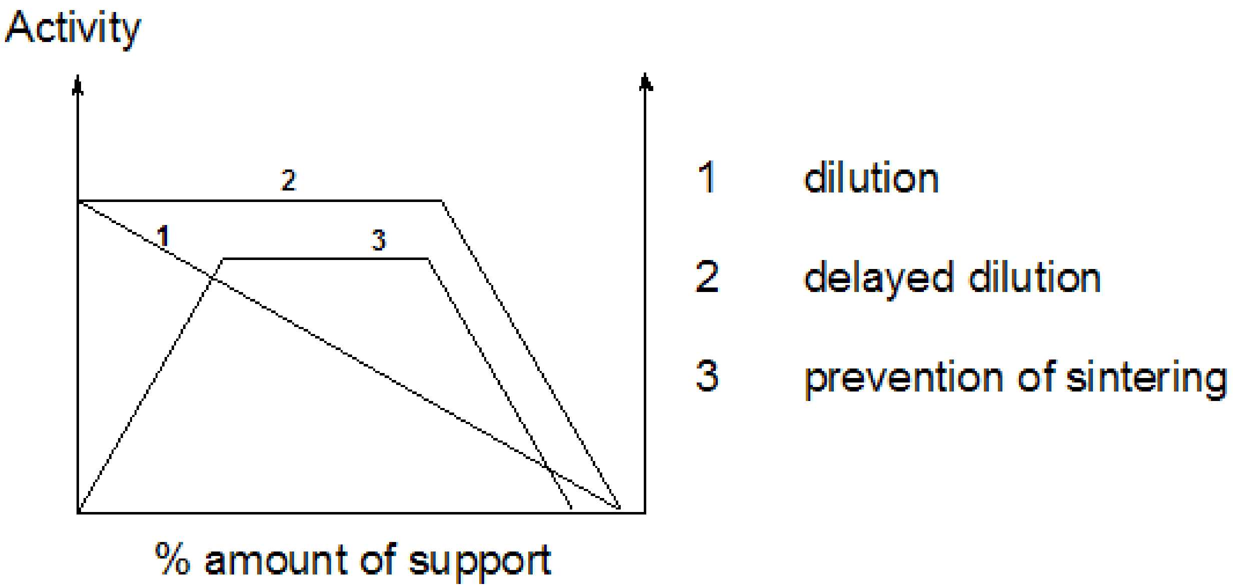


Supported Catalysts

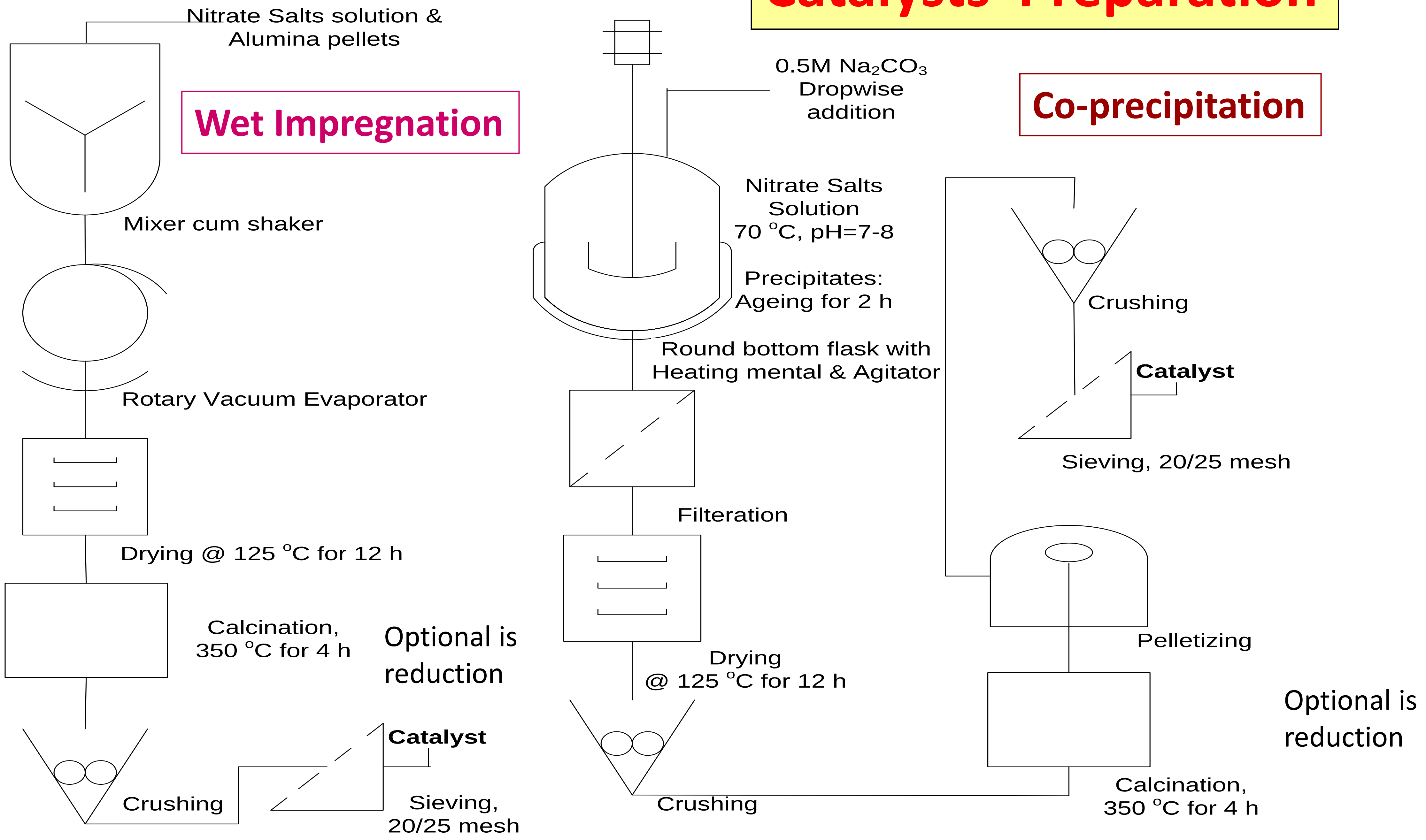
The main feature of supported catalysts is that the active material forms only a minor part and is deposited on the surface of the support.

In some cases, the support is more or less inert, e.g., *α*-alumina, kieselguhr, porous glass, ceramics. In other cases the support takes part in the catalytic reaction, as in the case of bifunctional catalytic systems, e.g., γ-alumina, aluminosilicate, zeolites, etc.

Additionally, some supports can alter the catalytic properties of the active phase. This so-called strong metal – support interaction (SMSI) can decrease, for example, the chemisorption capacity of supported metals (Pt – TiO2) or can hinder the reduction of supported metal oxides (Ni silicate, Ni and Cu aluminates, etc.)



Catalysts Preparation



Commercial Ni/Al_2O_3

Spent Commercial Ni/Al_2O_3

CATALYST CHARACTERIZATION

- Bulk Physical Properties
- Bulk Chemical Properties
- Surface Chemical Properties
- Surface Physical Properties
- Catalytic Performance

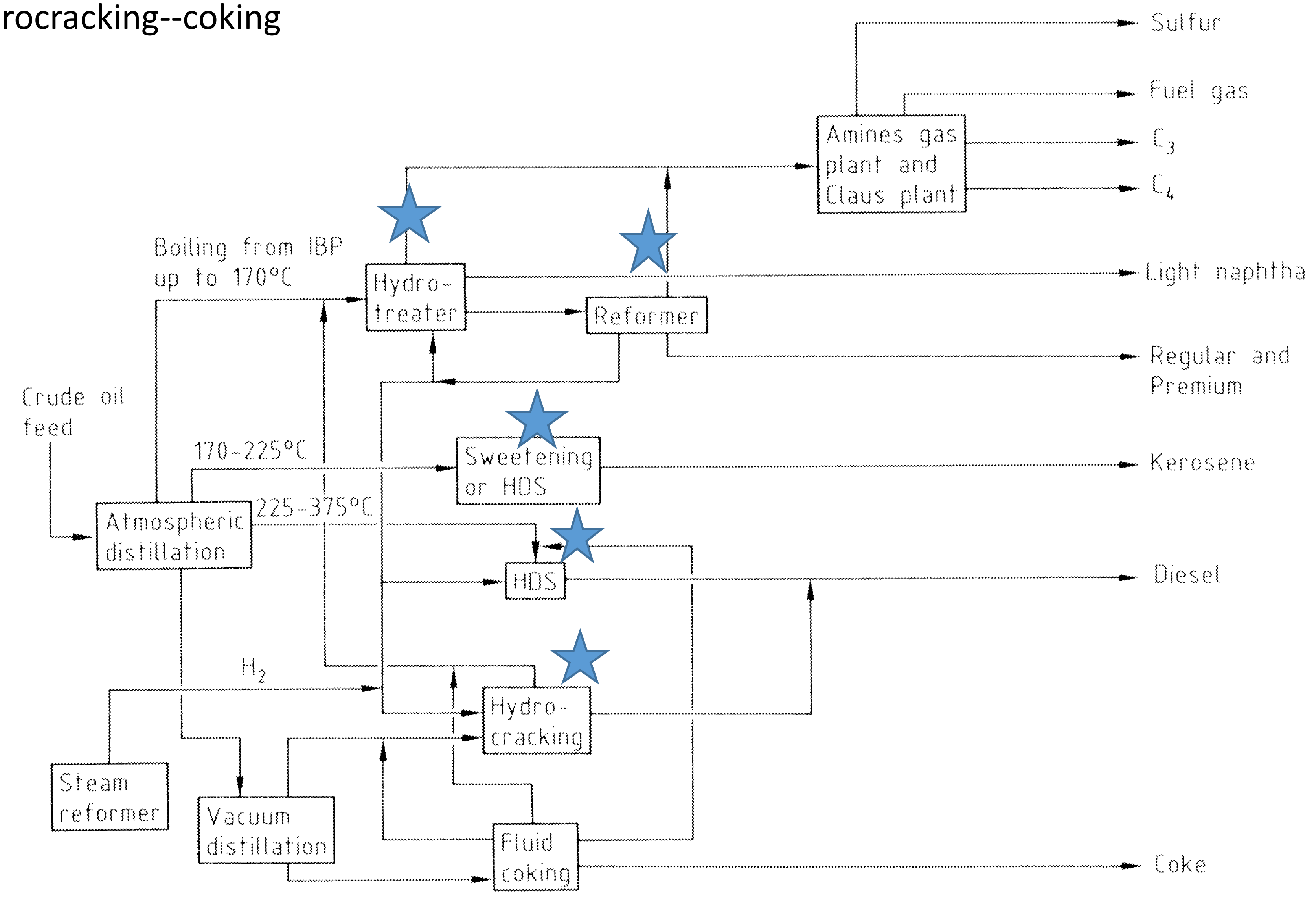
Catalysis in the Chemical Industry

- Hydrogen Industry(coal,NH_3,methanol, FT, hydrogenations/HDT,fuel cell)
- Natural gas processing (SR,ATR,WGS,POX)
- Petroleum refining (FCC, HDW,HDT,HCr,REF)
- Petrochemicals (monomers,bulk chemicals)
- Fine Chem. (pharma, agrochem, fragrance, textile,coating,surfactants,laundry etc)
- Environmental Catalysis (autoexhaust, deNOx, DOC)

Latest Trends

Integrated refinery structures (catalytic processes ★)

Hydrocracking--coking

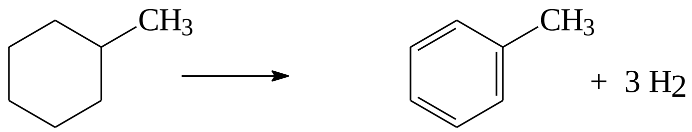


Hydrocracking–coking

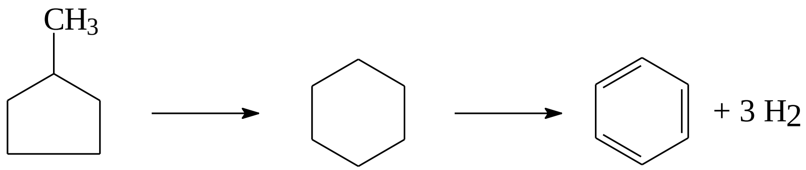
Catalytic reforming on Pt-Sn/alumina

Reactions during catalytic reforming:

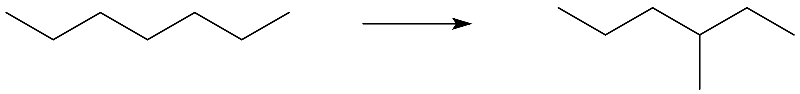
Dehydrogenation



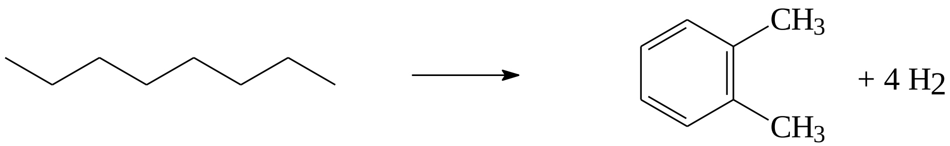
Dehydroisomerisation



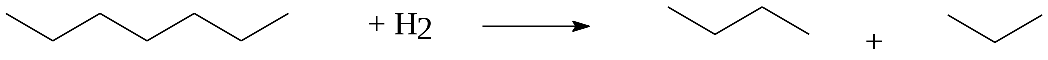
Isomerisation



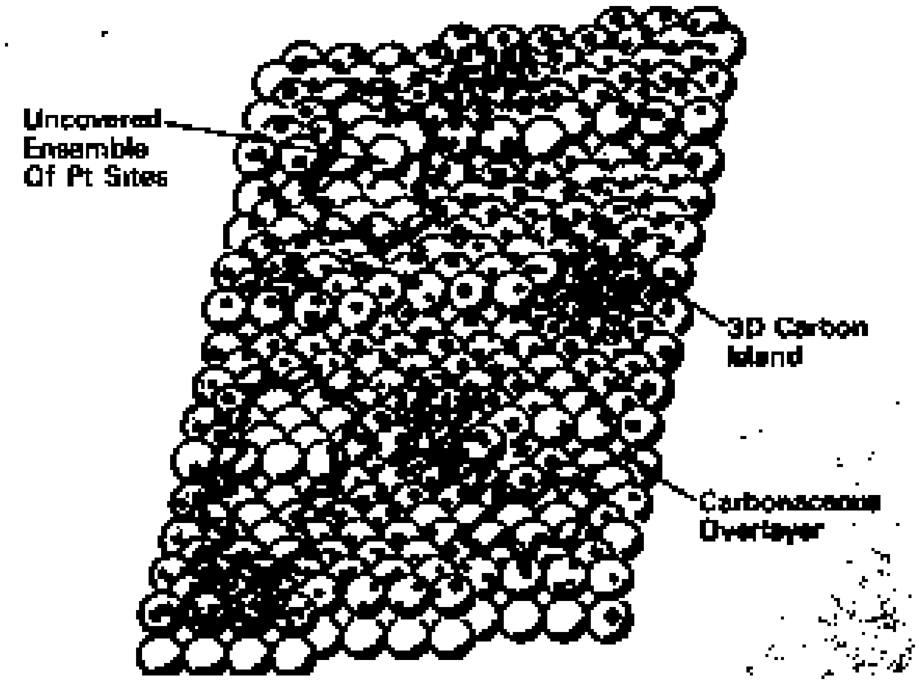
Dehydrocyclisation



Hydrocracking

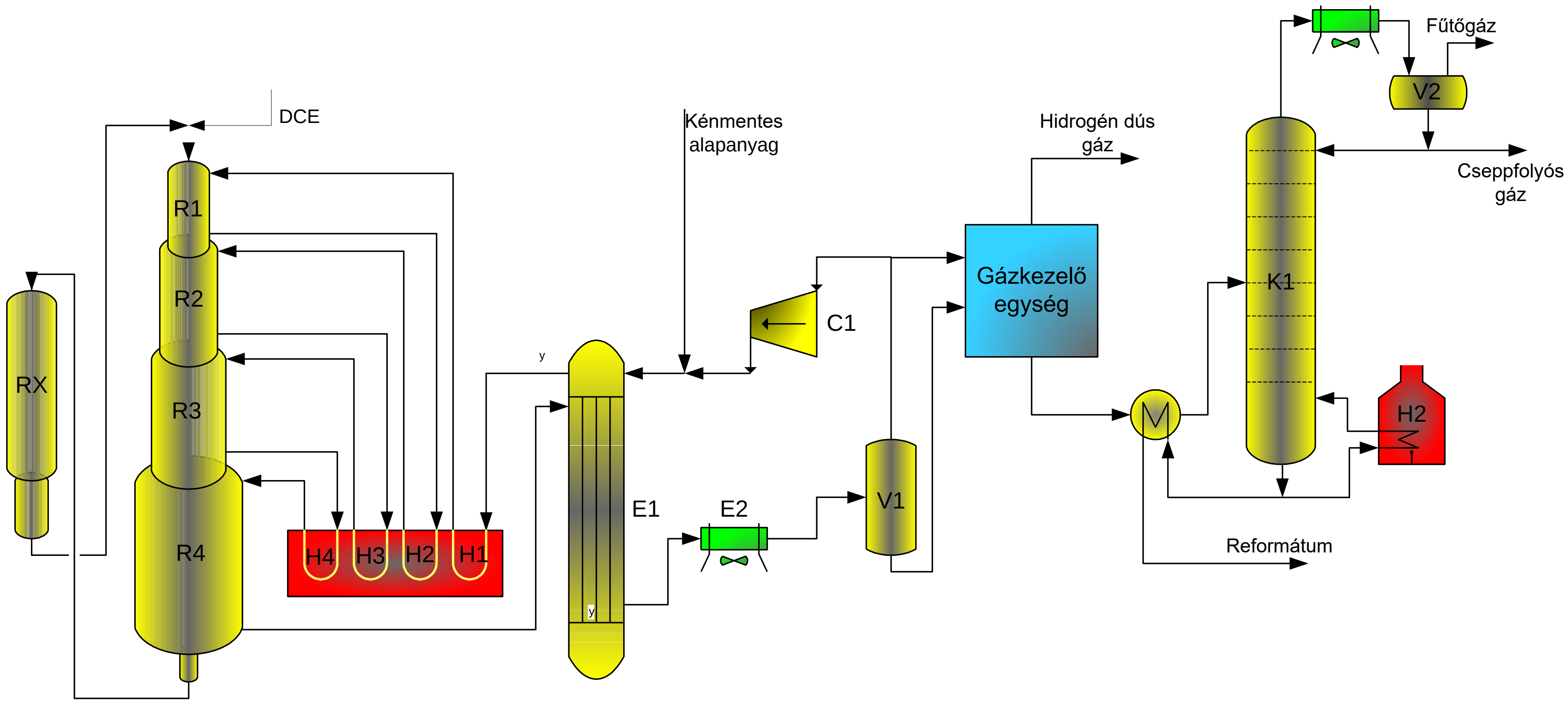


Surface of Pt catalysts in the presence of hydrocarbons

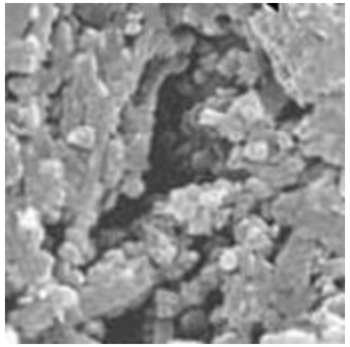


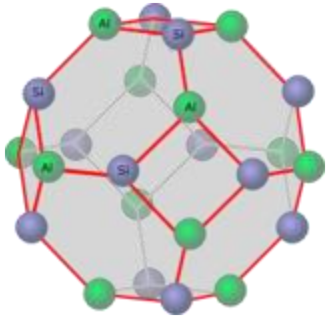
Model for the working structure and composition of a platinum dehydrocyclization catalyst. Most of the surface is continuously covered by a strongly bound carbonaceous deposit whose structure varies from two-dimensional to three-dimensional with increasing reaction temperature. Uncovered patches or ensembles of platinum surface sites always exist in the presence of this carbonaceous deposit. Bond breaking and chemical rearrangement in reacting hydrocarbon molecules take place readily at these uncovered sites

UOP CCR Platforming

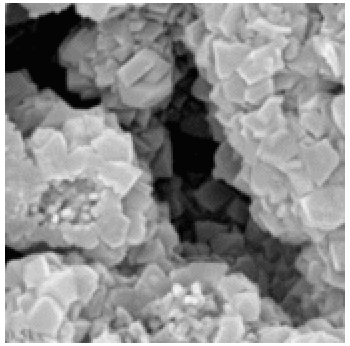


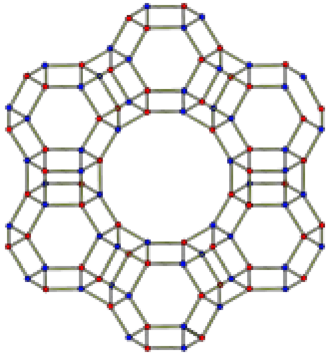
FCC catalyst





Components:
Zeolite HY faujazite, UHY ultrastable Y zeolite in H form
Hydrothermal treatment: secondary mezopore structure, enables diffusion of larger molecules, so that of their cracking

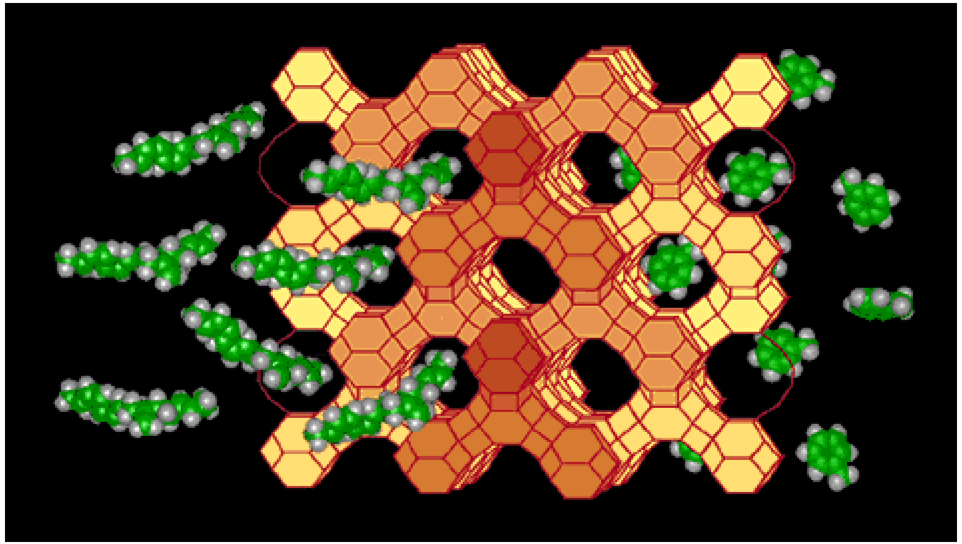


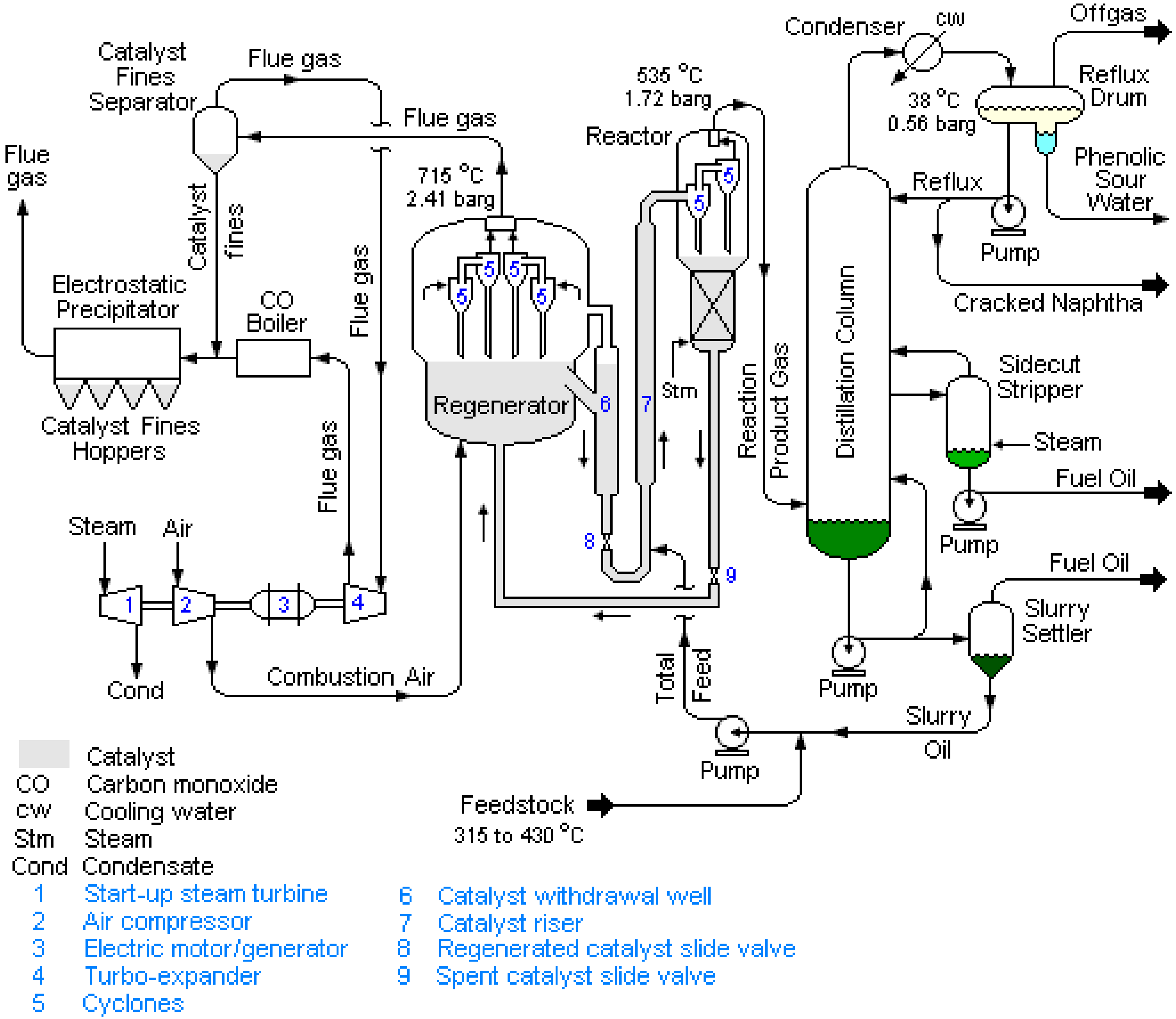


$$NaY + NH_4^+ \leftrightarrow NH_4Y + Na$$

$$NH_4Y \ (500\ °C) \rightarrow HY + NH_3$$

Because of the harsh conditions of fluidized bed, the zeolite is incorporated into a ceramic matrix.

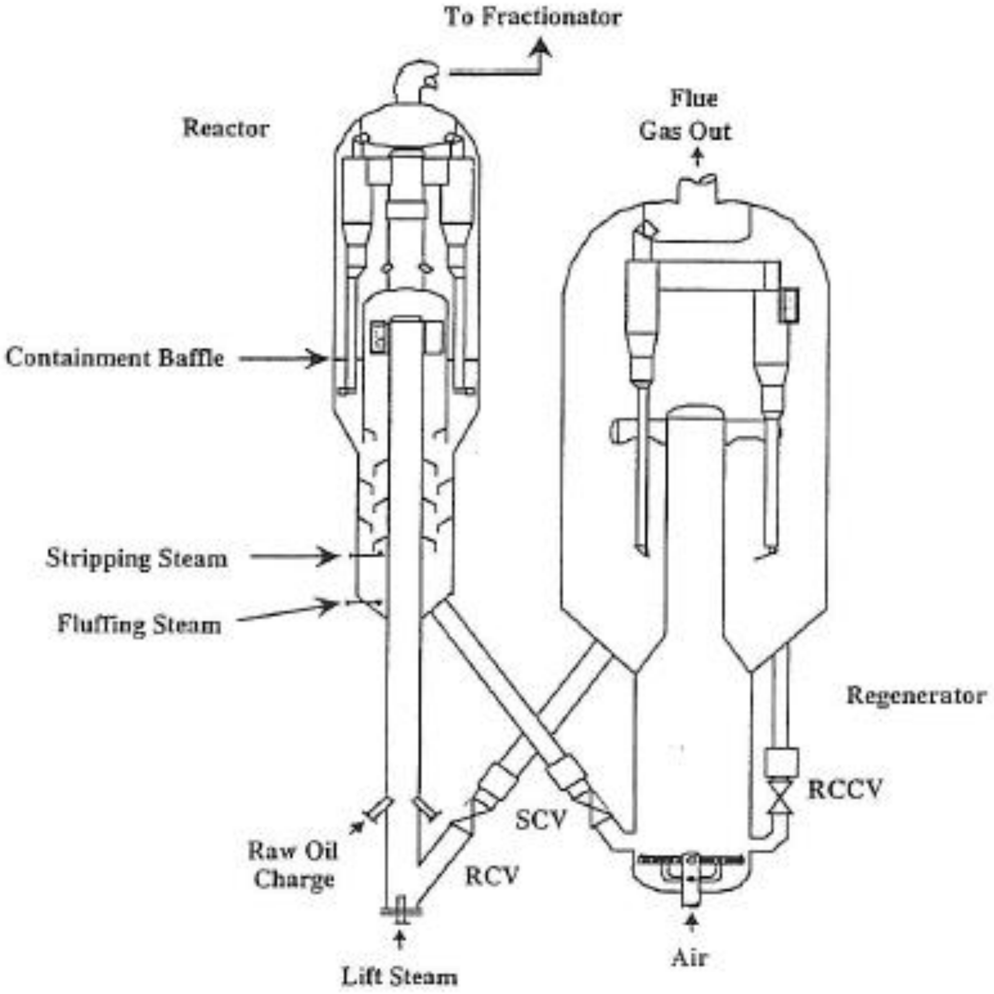



Catalyst Fines Separator
Flue gas
Flue gas
Flue gas
Catalyst fines
715 °C 2.41 barg
Electrostatic Precipitator
CO Boiler
Flue gas
Flue gas
Catalyst Fines Hoppers
Regenerator
Reactor
535 °C 1.72 barg
Stm
Reaction Product Gas
Condenser
cw
38 °C 0.56 barg
Offgas
Reflux Drum
Phenolic Sour Water
Reflux
Pump
Cracked Naphtha
Distillation Column
Sidecut Stripper
Steam
Fuel Oil
Pump
Fuel Oil
Slurry Settler
Pump
Slurry Oil
Steam
Air
Cond
Combustion Air
Total Feed
Pump
Feedstock
315 to 430 °C
1
2
3
4
5
6
7
8
9
Catalyst
CO Carbon monoxide
cw Cooling water
Stm Steam
Cond Condensate
1 Start-up steam turbine
2 Air compressor
3 Electric motor/generator
4 Turbo-expander
5 Cyclones
6 Catalyst withdrawal well
7 Catalyst riser
8 Regenerated catalyst slide valve
9 Spent catalyst slide valve

Duna Refinery FCC plant

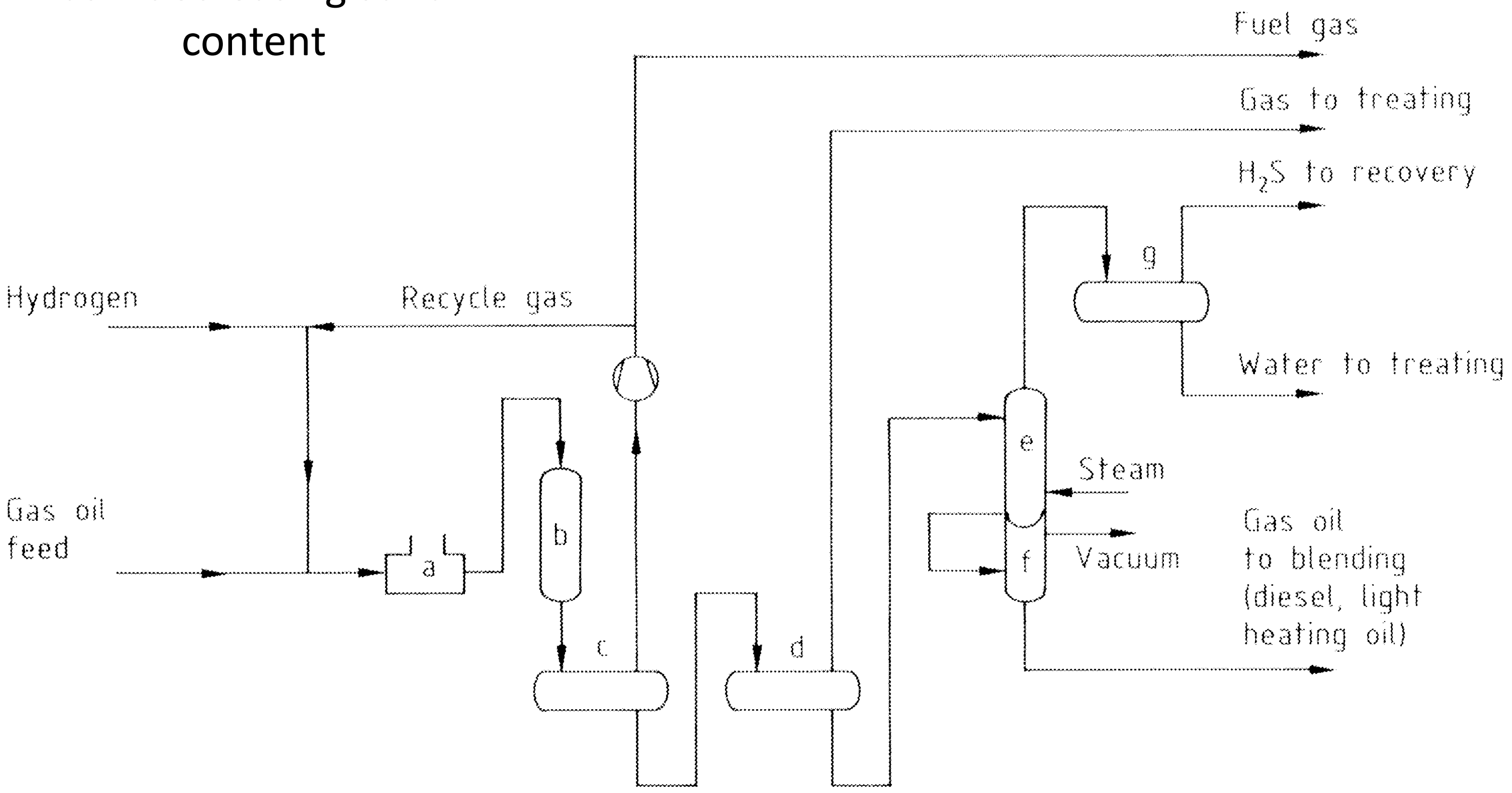
- **Capacity:**
  4000 t/d
- **Catalyst inventory:**
  ~70 t
- **Catalyst circulation:**
  ~1200 t/h =
  ~20 t/min

- Catalyst APS:
  ~70-90 micron
- Fines:
  APS < 20 micron
- Microfines:
  APS < 2 micron



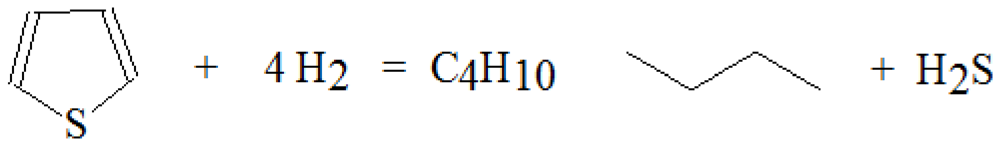
Hydrodesulfurisation of gas oil

Task: decreasing sulfur content



Gas oil hydrodesulfurizer

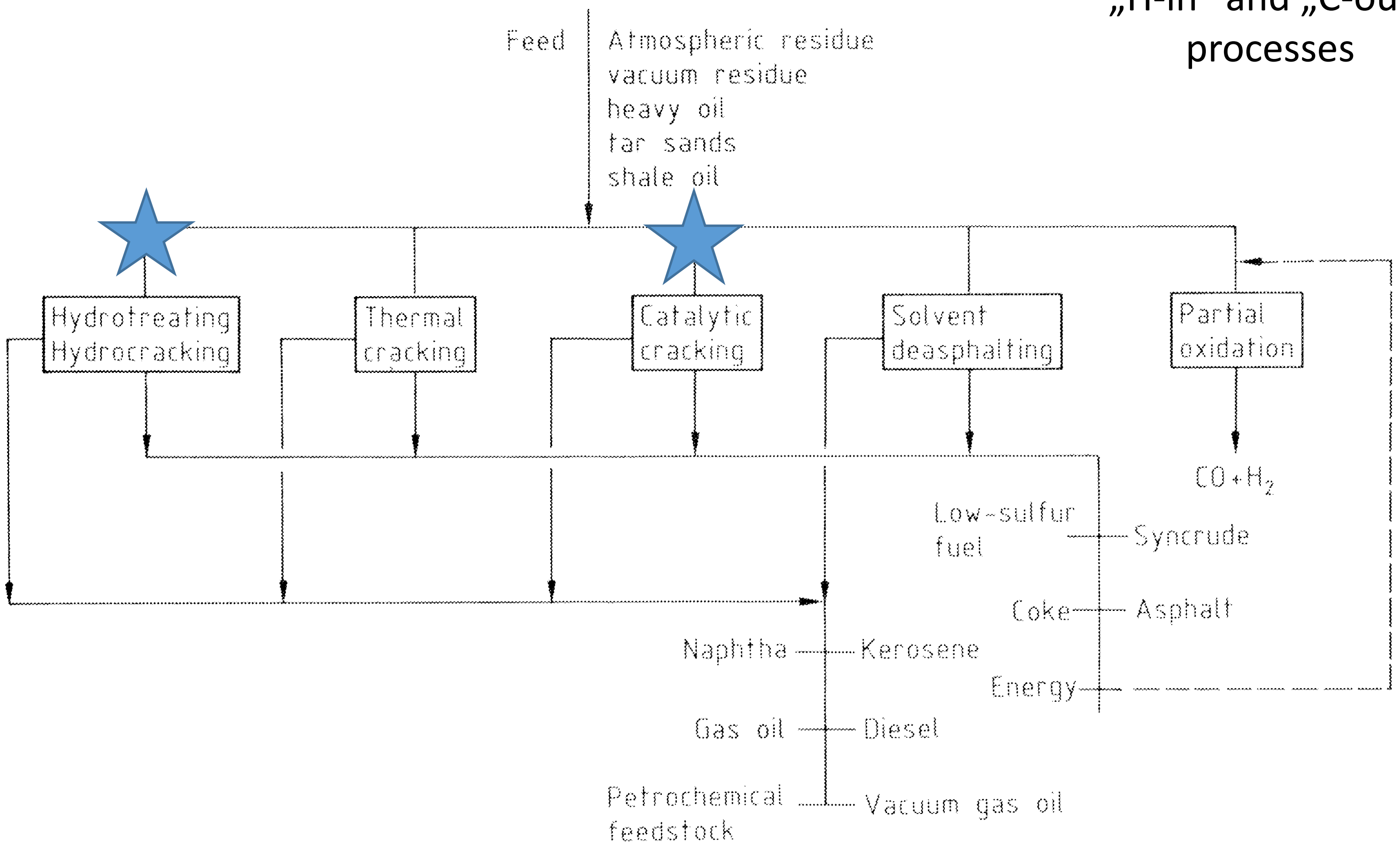
a) Process heater; b) Reactor; c) High-pressure separator; d) Low-pressure separator; e) Gas oil stripper; f) Gas oil dryer; g) Stripper overhead drum



Residue conversion processes (catalytic ones★)

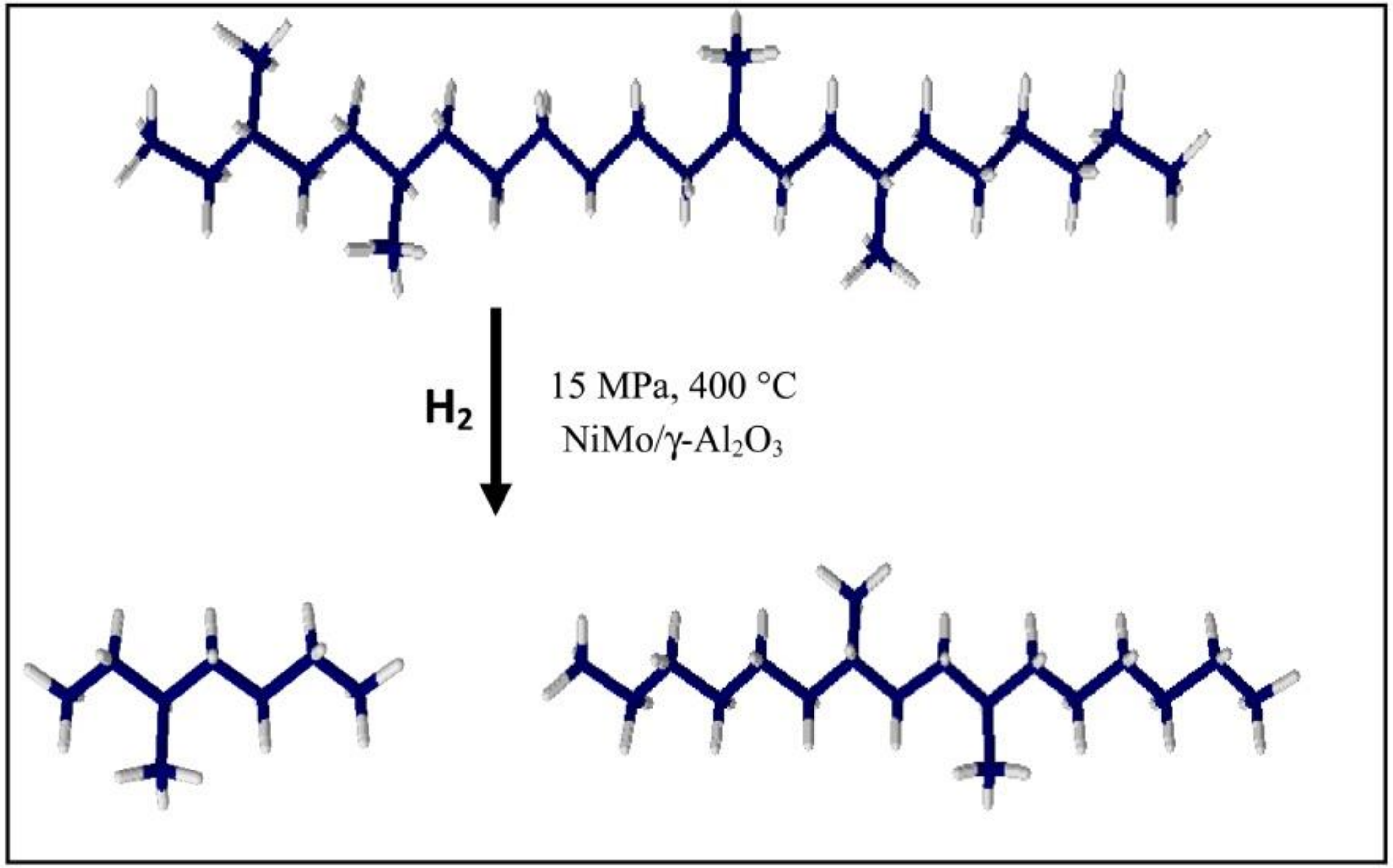
Task: increase the yield of high value products

„H-in” and „C-out” processes



Residue conversion processes

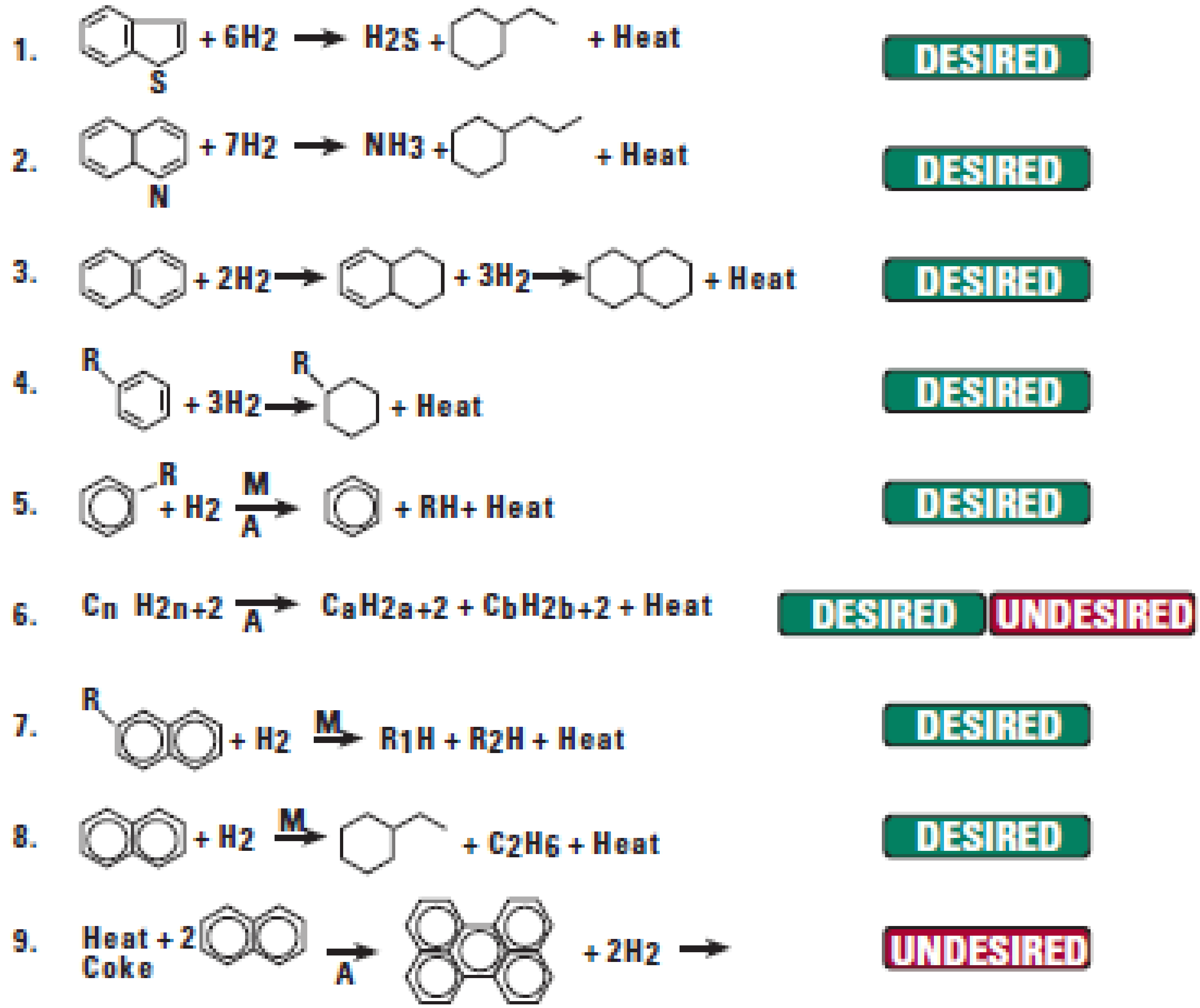
Typical reaction of hydrocracking



VGO component
$C_{26}H_{54}$

Gasoline component
C_8H_{18}

Diesel component
$C_{18}H_{38}$



1-4 hydrogenation, 5-9 hydrocrack reactions

Hydrocracking

Process: UNICRACKING™

single stage with UCO recycle

Licensor: UNOCAL, California

Contractor: SNAMPROGETTI

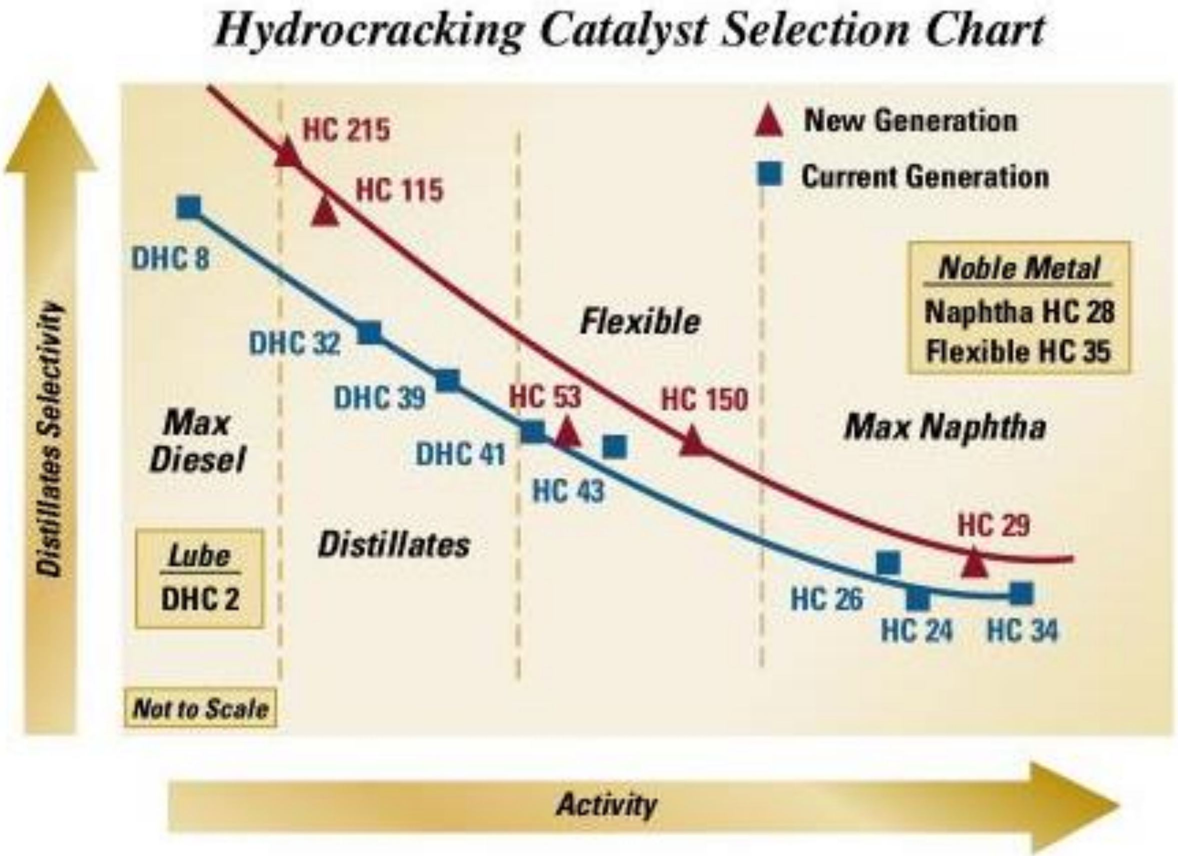
Design capacity: 800 000 MTPY

Feed: straight-run VGO

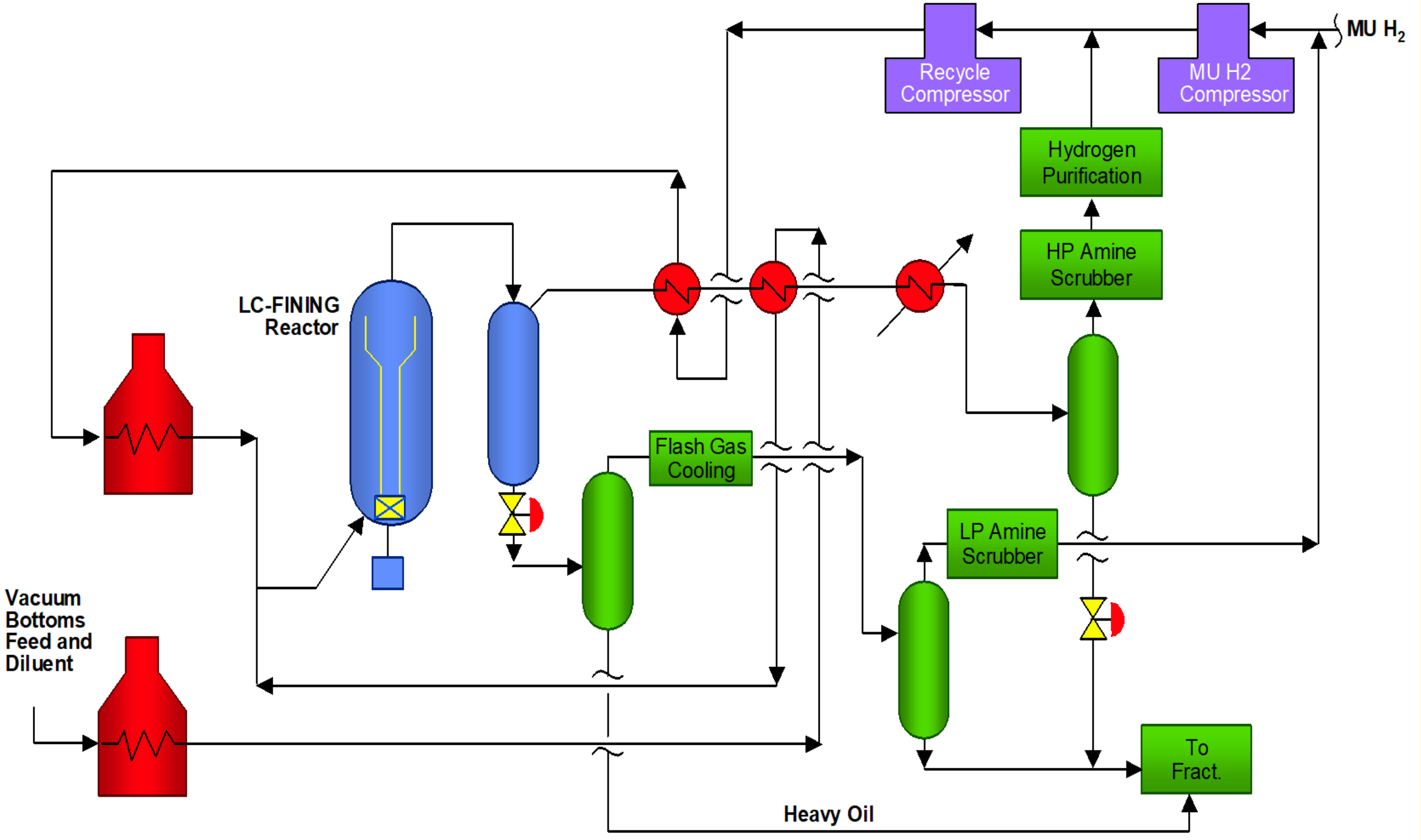
Start-up: Jan. 1991

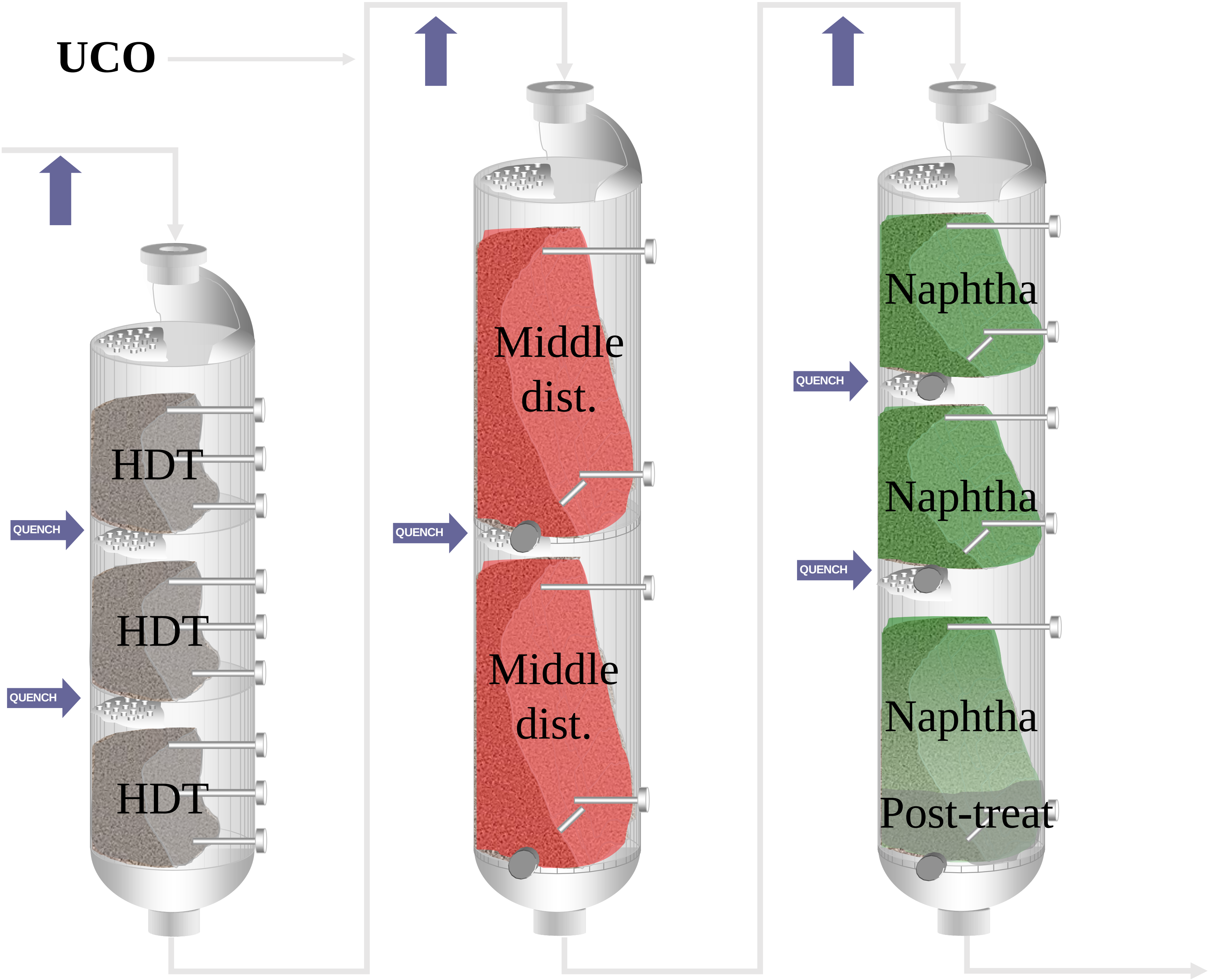
Hydrocracking Catalyst Selection Chart

The chart below may help you in selecting a catalyst for your application. Click on a catalyst name to download a technical data sheet.

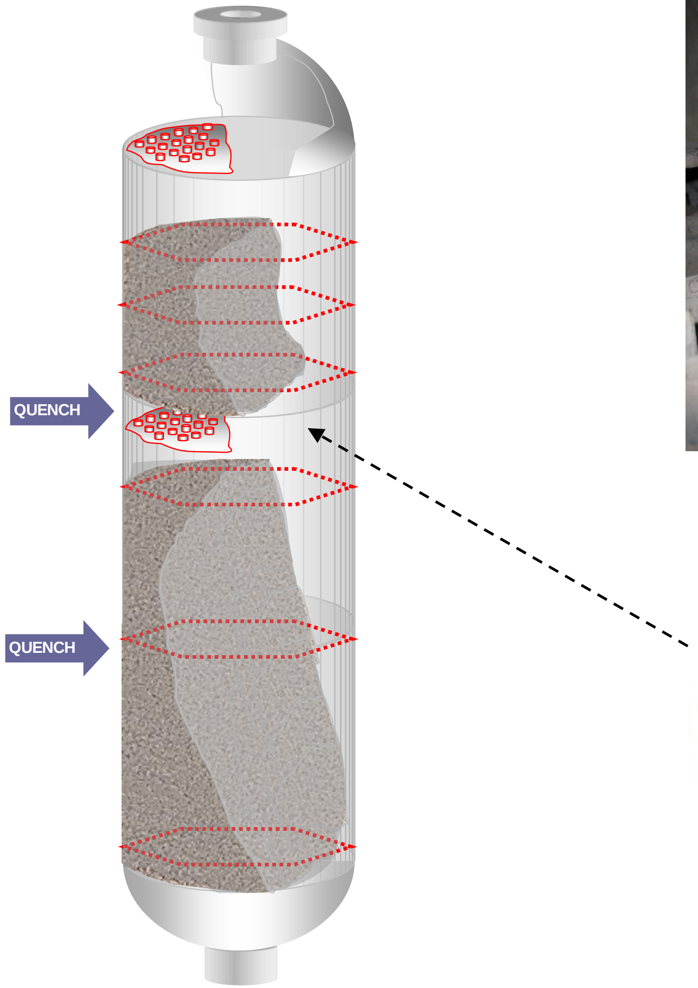


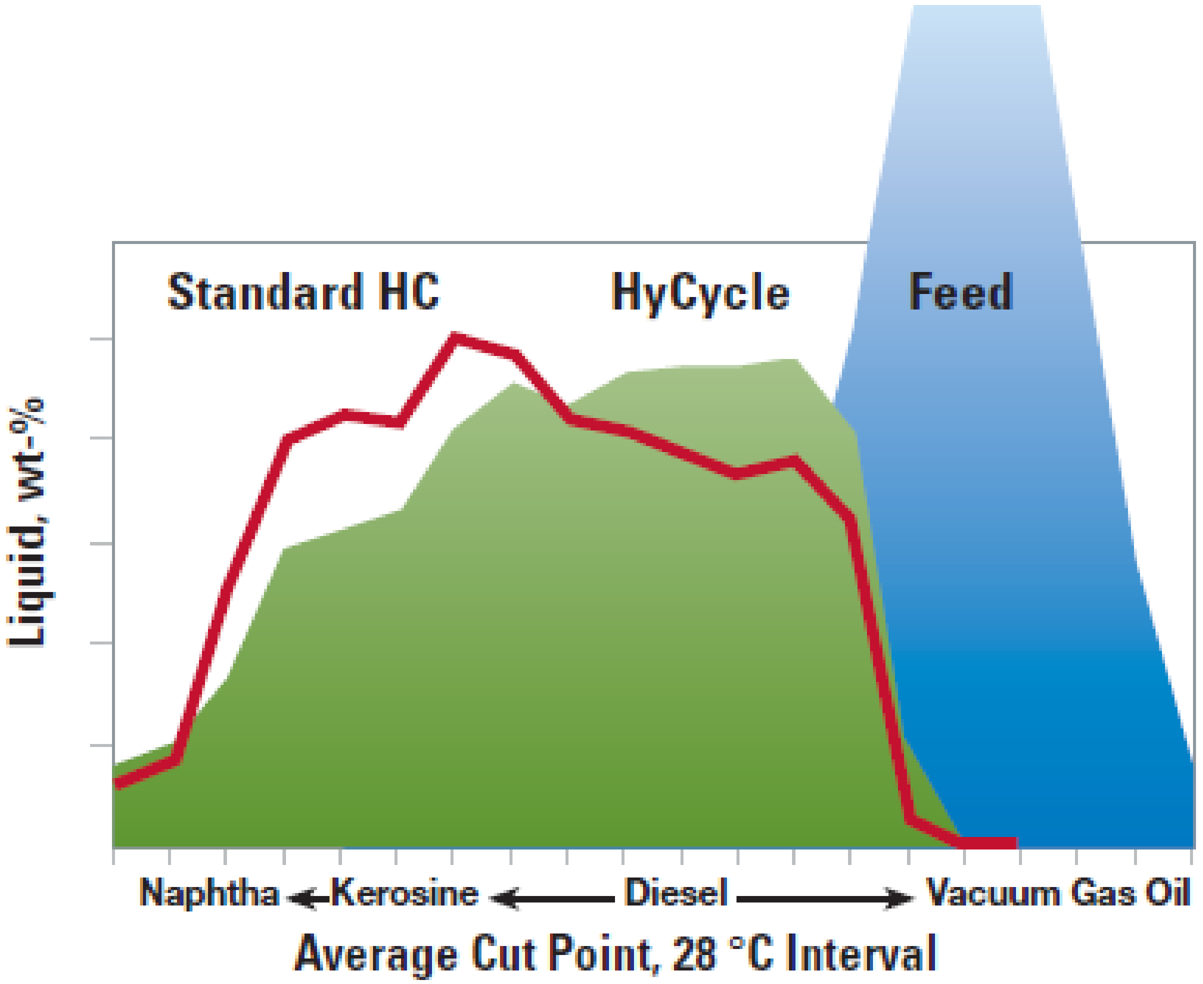
Scheme of LC finer




UCO
HDT
HDT
HDT
QUENCH
QUENCH
Middle dist.
Middle dist.
QUENCH
Naphtha
Naphtha
Naphtha
Post-treat
QUENCH
QUENCH

Catalyst trays

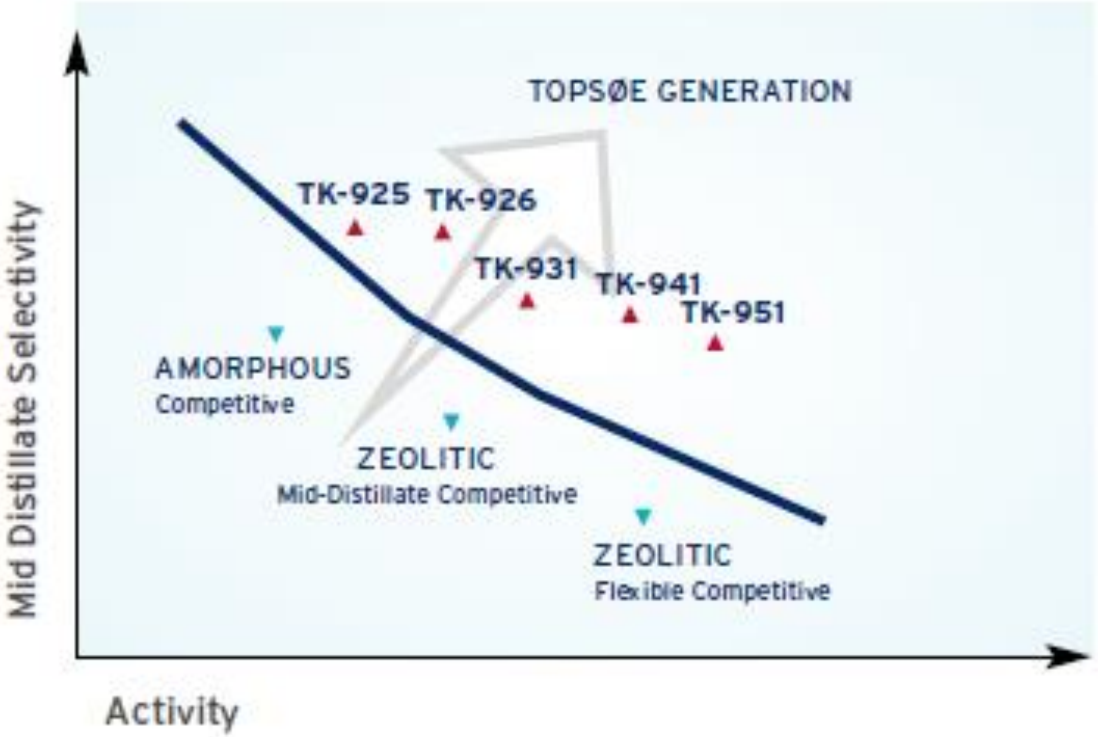




The characteristic composition of feed and product mixture of hydrocracking

Topsoe hydrocrack catalysts

Ni-W containing zeolite



Thanks for your attention!