

CHEM-E1130 Catalysis

Industrial catalysis: significant historical examples

A''

Aalto University
School of Chemical
Engineering

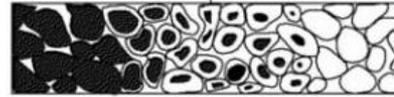
Prof. Riikka Puurunen

16.1.2018

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1. Timeline of catalysis
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4. Example 3: Fluid catalytic cracking

+ conclusion & take-home message



+ 16.1.2019: Adsorption characterization exercise shared

Timeline of industrial catalysis

Timeline

From alchemy to chemistry
... - 1834

Lead chamber
process: H_2SO_4



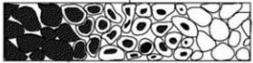
Berzelius: "Catalysis"

Ostwald: "there is probably
no chemical reaction which
can not be influenced
catalytically"

From empirics to science
1835-1897

The birth of industrial
catalysis
1898-1918

NH_3 synthesis
(Haber-Bosch)



Fluid Catalytic Cracking
Steam reforming
Fischer-Tropsch



The increase in global
mobility by developing
catalytic fuel processes
1919-1945

Petrochemical industry & polymers
(& booming automotive market)

(1962 Rachel Carson's [Silent Spring](#))

From war to peace
1946-1970

Pollution control

Environmental catalysis
1970-20??

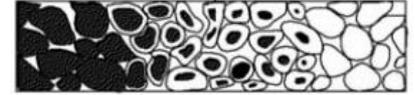
How to pick three most significant examples...?

- Contact process for H_2SO_4
- Haber-Bosch ammonia process
- Claus process for sulfur
- Fischer-Tropsch process for liquid fuels from coal through synthesis gas
- Methanol synthesis
- Alkylation
- Steam reforming
- Fluid catalytic cracking (FCC)
- Hydrodesulfurization with sulfided CoMo catalysts
- Polymerization with Ziegler-Natta catalysts
- Catalytic reforming
- ...

Picking three is impossible - but selection has to be made

1. Haber-Bosch ammonia process

- Classic that everyone should be familiar with
- Fixed nitrogen in fertilizers sustains the humankind



2. Steam reforming for synthesis gas production

- Hydrogen currently in the energy development focus
- Where does hydrogen come from?



3. Fluid catalytic cracking (FCC)

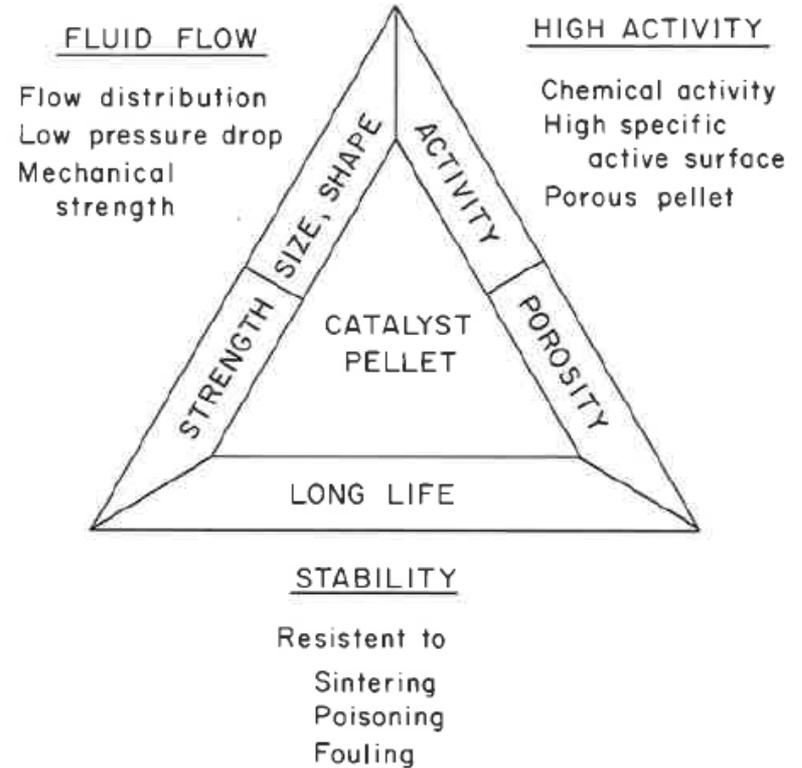
- Very significant refinery process
- Introduces the important catalyst class of zeolites



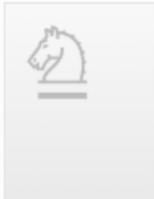
Catalyst components



Engineering features



A Brief History of Catalysis



[CATTECH](#)

August 2003, Volume 7, [Issue 4](#), pp 130–138 | [Cite as](#)

A Brief History of Catalysis

Authors

[Authors and affiliations](#)

Bård Lindström, Lars J. Pettersson

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211

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Abstract

Historical studies are usually divided into segments of time that were marked by intellectual progress or specific achievements. Some periods are clearly identified by great events or an individual accomplishment that revolutionizes the entire concept. However, in most cases the advancement from one period to another is not marked by distinct accomplishments, but rather the result of a series of advances. This paper follows this conventional style and we have divided our subject of catalysis into five distinct periods.

Further reading

A history of industrial catalysis

Catalysis Today 163 (2011) 3–9

John N. Armor*

GlobalCatalysis.com L.L.C., 1608 Barkwood Dr., Orefield, PA 18069, USA

Further reading

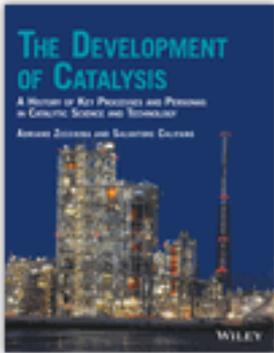
A B S T R A C T

Histories of catalysis have been told by others from different perspectives. This manuscript highlights key catalytic discoveries that led to commercialized, industrial processes. The intent is to show how catalysis evolved over the last 250 years into major industries focused not only at catalyst production, but also significantly impacting the production of commodity, specialty and fine chemicals, as well as petrochemical, petroleum, emissions control, and polymerization. For centuries before 1750, catalysts were used to make beverages and foods. One sees that the Lead Chamber process for the production of sulfuric acid is among the earliest of catalytic processes and reaches back to 1750. Pursuit of a sound fundamental understanding of catalysis in the 19th century, led to the application of these materials to a variety of basic chemicals. The development of petroleum fuels led to a vast petrochemicals business which in turn fed a growth in specialty and performance chemicals. New drivers in the 20th century from the transportation and the environmental business sectors provided market pull to bring about more catalytic solutions for more industries. The often novel, catalytic properties of zeolites created new commercial applications, while environmental legislation created market pull to use catalysis to meet the new regulatory standards. As we move forward into the new century, we continue to see market pull from growing interests in biomass, sustainability, emissions control, and energy.

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<https://doi.org/10.1016/j.cattod.2009.11.019>



The Development of Catalysis: A History of Key Processes and Personas in Catalytic Science and Technology

Author(s): Adriano Zecchina, Salvatore Califano

First published: 28 February 2017

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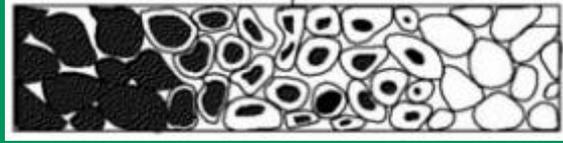
Some Catalytic Reactions

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Example 1: Ammonia Synthesis

"The nitrogen problem", late 1800s

Adriano Zecchina Salvatore
Califano, The Development of
Catalysis: A History of Key
Processes and Personas in
Catalytic Science and Technology,
Wiley Online
Library, <http://dx.doi.org/10.1002/9781119181286>, Copyright © 2017 by
John Wiley & Sons.

At the beginning of the twentieth century, sodium nitrate extracted by English companies from existing sediments of Chilean guano was practically the only chemical fertilizer utilized in agriculture. The realization that guano could be exhausted in a few years, coupled with the need for European countries to obtain other sources of nitrogen rich material, had, for some time, prompted applied research groups to produce synthetic ammonia. Ammonia, whose name derived from the ancient Egyptian deity Amun, known to the Greeks as Ammon, is the basic compound for the synthesis of nitric acid and of nitrates of enormous importance not only in agriculture but also in the production of explosives. In the latter years of the nineteenth century, the scientific community was strongly involved in the discussion on what later became known as "the nitrogen problem," earnestly addressed by Sir William Crookes in his speech at the meeting of the British Association for the Advancement of Science in Bristol in September 1898 (Crookes, 1898; Topham, 1955):

*... all civilized nations stand in deadly peril of not having enough to eat.
... the fixation of atmospheric nitrogen is one of the great discoveries
awaiting the ingenuity of chemists.*

"Fixed nitrogen": ammonia, NH₃

- 176 million tonnes per year in 2016
- 88% for fertilizer use

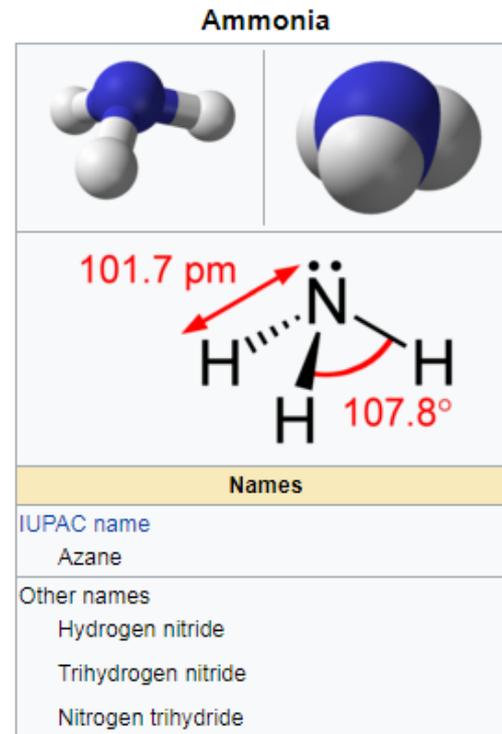
World Ammonia Production and Reserves:

	Plant production		Reserves ^a
	2014	2015 ^b	
United States	9,330	9,400	Available atmospheric nitrogen and sources of natural gas for production of ammonia are considered adequate for all listed countries.
Australia	1,250	1,300	
Belarus	1,060	1,100	
Canada	3,940	3,900	
China	47,300	48,000	
Egypt	2,660	2,600	
Estonia	3,000	3,000	
France	2,600	2,600	
Germany	2,800	2,800	
India	11,000	11,000	
Indonesia	5,000	5,000	
Iran	2,500	2,500	
Malaysia	1,000	1,000	
Netherlands	1,800	1,800	
Oman	1,100	1,100	
Pakistan	2,700	2,700	
Poland	2,100	2,100	
Qatar	2,990	3,000	
Russia	11,800	12,000	
Saudi Arabia	3,200	3,200	
Trinidad and Tobago	4,730	4,700	
Ukraine	4,240	4,200	
United Kingdom	1,100	1,100	
Uzbekistan	1,350	1,300	
Venezuela	1,200	1,200	
Other countries	13,300	13,000	
World total (rounded)	145,000	146,000	

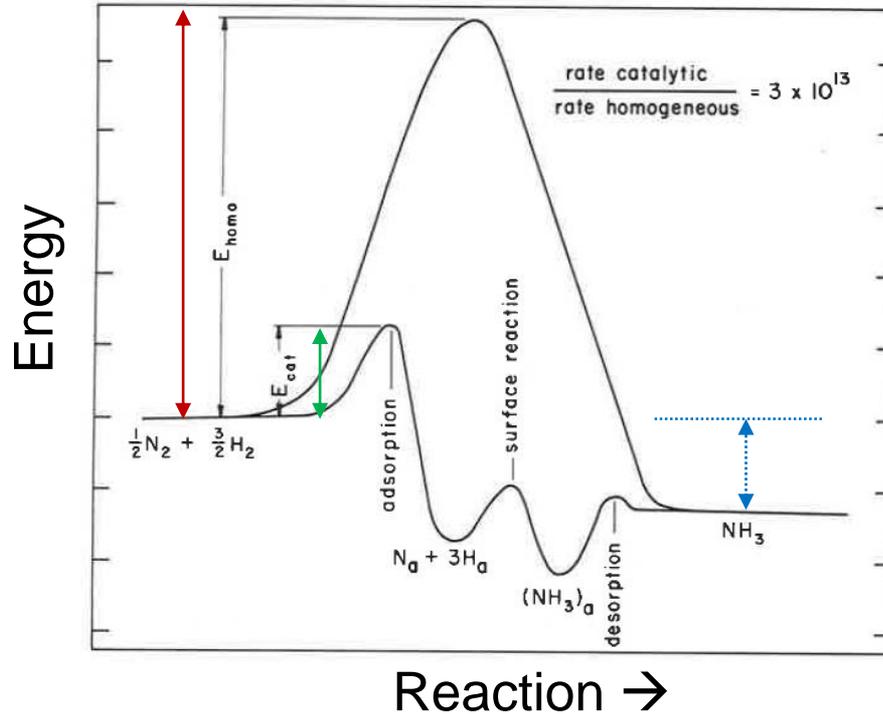
World Resources: The availability of nitrogen from the atmosphere for fixed nitrogen production is unlimited. Mineralized occurrences of sodium and potassium nitrates, found in the Atacama Desert of Chile, contribute minimally to global nitrogen supply.

Substitutes: Nitrogen is an essential plant nutrient that has no substitute. No practical substitutes for nitrogen explosives and blasting agents are known.

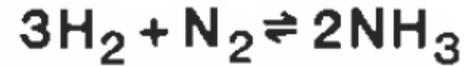
USA, China, India, Russia



From Lecture 1



Example: ammonia synthesis,
Haber-Bosch process



- Exothermic reaction
- Catalyst does not change the overall thermodynamics
- Activation energy:

$$E_{\text{homogeneous}} \gg E_{\text{catalytic}}$$

Fixing atmospheric N₂ by ammonia synthesis (Haber-Bosch process)

- Ammonia decomposition with Fe and other metals known since early 1800s. Made nowadays with Pt/Rh gauze.
 - *A catalyst catalyzes elementary reactions in both directions!*
- 1908, **Haber**: reaction of hydrogen with nitrogen with catalysts based on osmium and uranium.
 - 500°C, 150-200 atm
- + **Bosch & Mittasch** → 1913 1st production plant with promoted Fe in Oppau, Germany
- *Le Chatelier's blunder!*



http://www.chemgapedia.de/vsengine/media/vsc/de/ch/25/heraeus/pt_als_werkstoff/grafik/a36_1_platinnetz.jpg

Ammonia, 2. Production Processes

MAX APPL, Dannstadt-Schauernheim, Germany

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ENCYCLOPEDIA
OF INDUSTRIAL
CHEMISTRY

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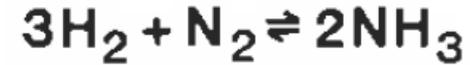
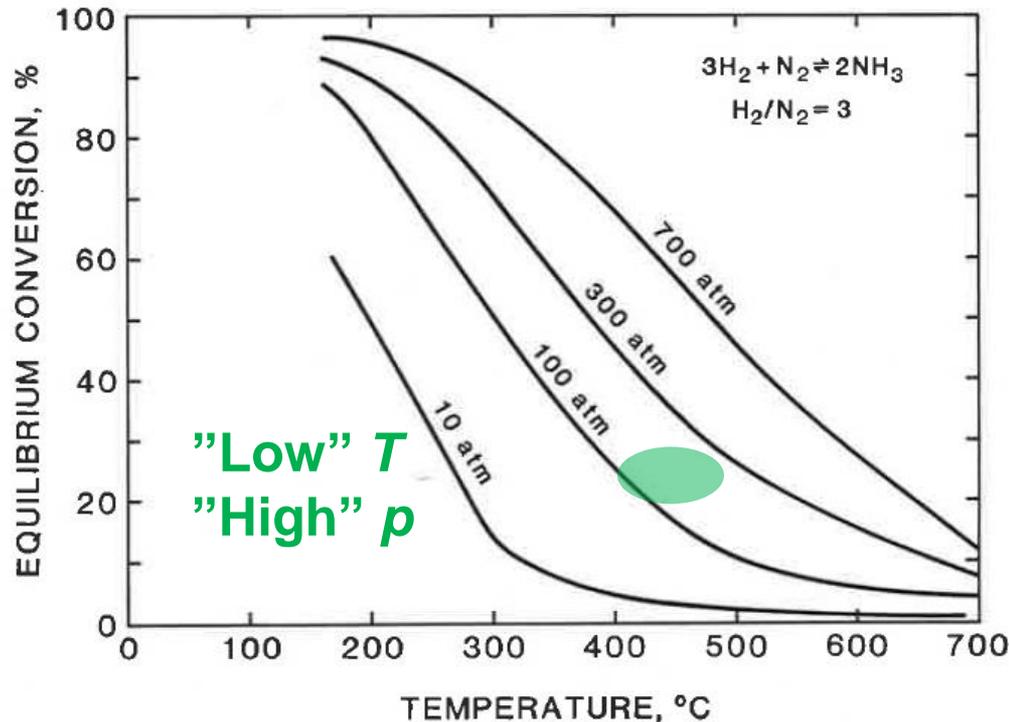
Haber-Bosch ammonia process



Reversible, exothermic reaction
No. of molecules decreases

- Over 90 % of world consumption manufactured in Haber- Bosch process using promoted iron catalyst discovered by Mittasch
- **iron catalyst** (today's formulation differs little from the original) at elevated temperature in the range of **400 – 500°C** (originally up to 600°C) and **pressures above 100 bar**
- **recycle of the unconverted part** of the synthesis gas and separation of the ammonia product under high pressure.

Reaction conditions are optimized for conversion (& selectivity) & economics



- Exothermic → increasing temperature drives equilibrium left to reactant side
- No. of molecules decreases → higher pressure drives reaction right to product side

Mittasch catalyst development

- The ammonia synthesis catalyst problem has been **more intensively studied than the catalysis of any other industrial reaction.**
- At BASF A. MITTASCH et al. started a tremendous program, in which up to 1911 more than 2500 different <catalyst> formulations were tested in more than 6500 runs.
- The experiments were finally brought to an end in 1922 after a total of 22 000 tests.
- They tested almost all elements of the periodic table for their suitability as ammonia catalysts [7, 176].

- "Thus far, essentially all heterogeneous catalysts of industrial importance have been developed by trial-and-error experimentation.
- The classic example of this approach is the **discovery of the iron-based ammonia synthesis catalyst** by Mittasch and co-workers who **tested more than 2500 different catalysts in 6500 experiments.**"

Nørskov and coworkers, JACS, 2001,
<http://pubs.acs.org/doi/full/10.1021/ja010963d>

Promoted iron catalysts

- Iron catalysts which are generally used until today in commercial production units are composed in unreduced form of iron oxides (mainly magnetite, Fe_3O_4) and a few percent of Al, Ca, and K; other elements such as Mg and Si may also be present in small amounts.
- Activation <reduction> is usually accomplished in situ by reduction with synthesis gas.
- Prereduced catalysts are also commercially available.

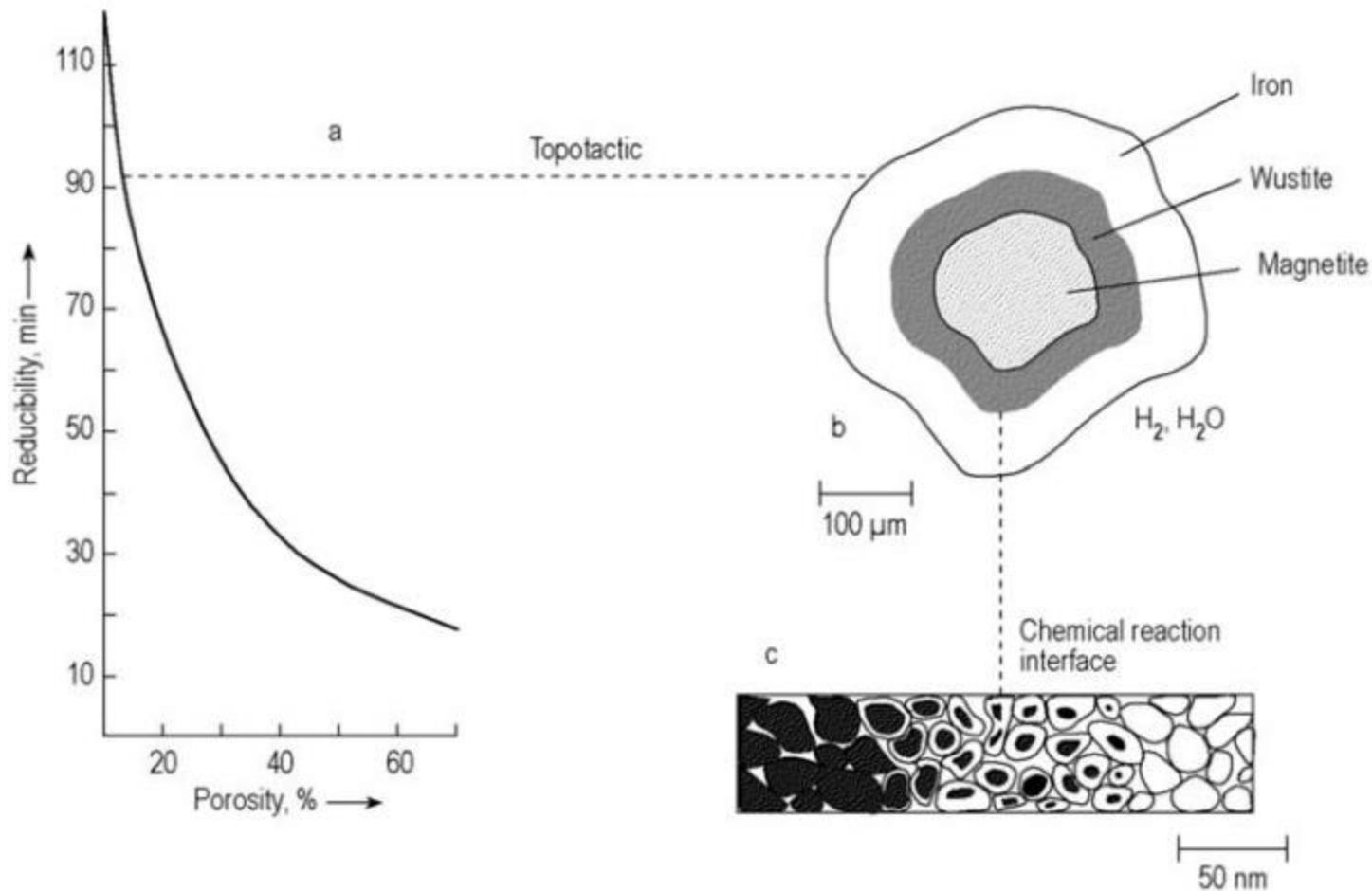


Figure 18. Mechanism of catalyst reduction [42]

a) Reducibility of catalyst under standard conditions as a function of its porosity; b) Core and shell structure of catalyst; c) Reaction interface

Topotactic reaction results in bimodal pore size distribution

Max Appl, Ammonia, 2. Production Processes, Ullmann's Encyclopedia of Industrial Chemistry, Wiley Online Library, https://onlinelibrary.wiley.com/doi/pdf/10.1002/14356007.o02_o11, accessed 12.1.2019.

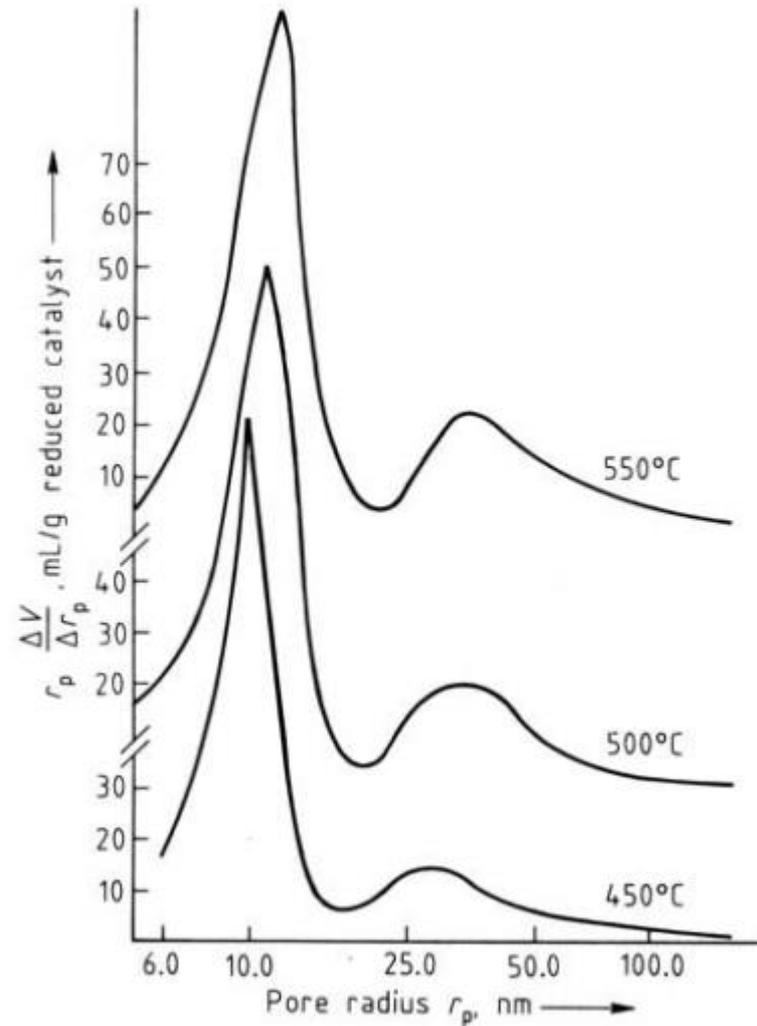


Figure 11. Pore size distribution of a commercial catalyst after reduction at various temperatures [55]

Characteristics of reduced (activated) ammonia catalysts

- Consist of approximately **30-nm primary crystallites**
- **Bimodal pore size distribution: maxima at ~10 nm & 25-50 nm**
 - Results from the reduction of originally nonporous iron oxide
- Pore volume **0.09 – 0.1 cm³ /g**, apparent density of **4.8 – 4.9 g/cm³**,
- Pores represent **44 – 46 %** of the volume of a catalyst granule.
- The surface of the walls of the pores **about 15 m² /g**.
- Grain <particle> size typically **6-10 mm**

Pressure drop example

For processes operating at pressures of 25 – 45 MPa (250 – 450 bar) and at space velocities of 8000 – 20 000 m³ m³ h⁻¹ (STP) a grain size of 6 – 10 mm is preferred.

Larger granulations, for example, 8 – 15 mm or 14 – 20 mm, are used only in plants where the lowest possible pressure drop is essential because of very high gas velocities

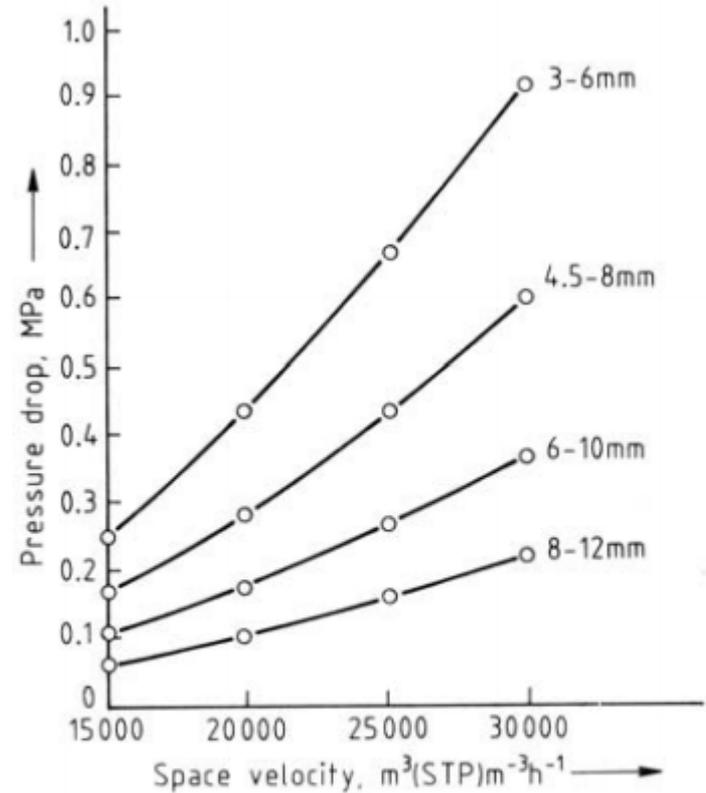
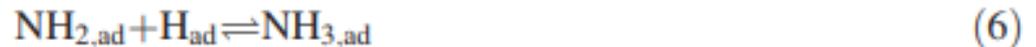
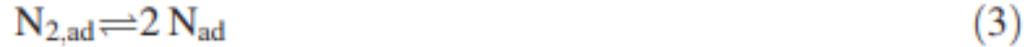
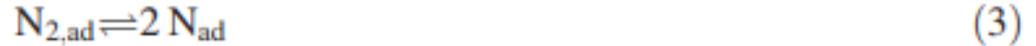


Figure 14. Pressure drop in the catalyst bed for various catalyst particle size ranges, from [1].
Depth of the catalyst bed, 7 m; reaction pressure 27.1 MPa; reaction temperature 450 °C

Suggested surface reaction mechanism



Suggested surface reaction mechanism

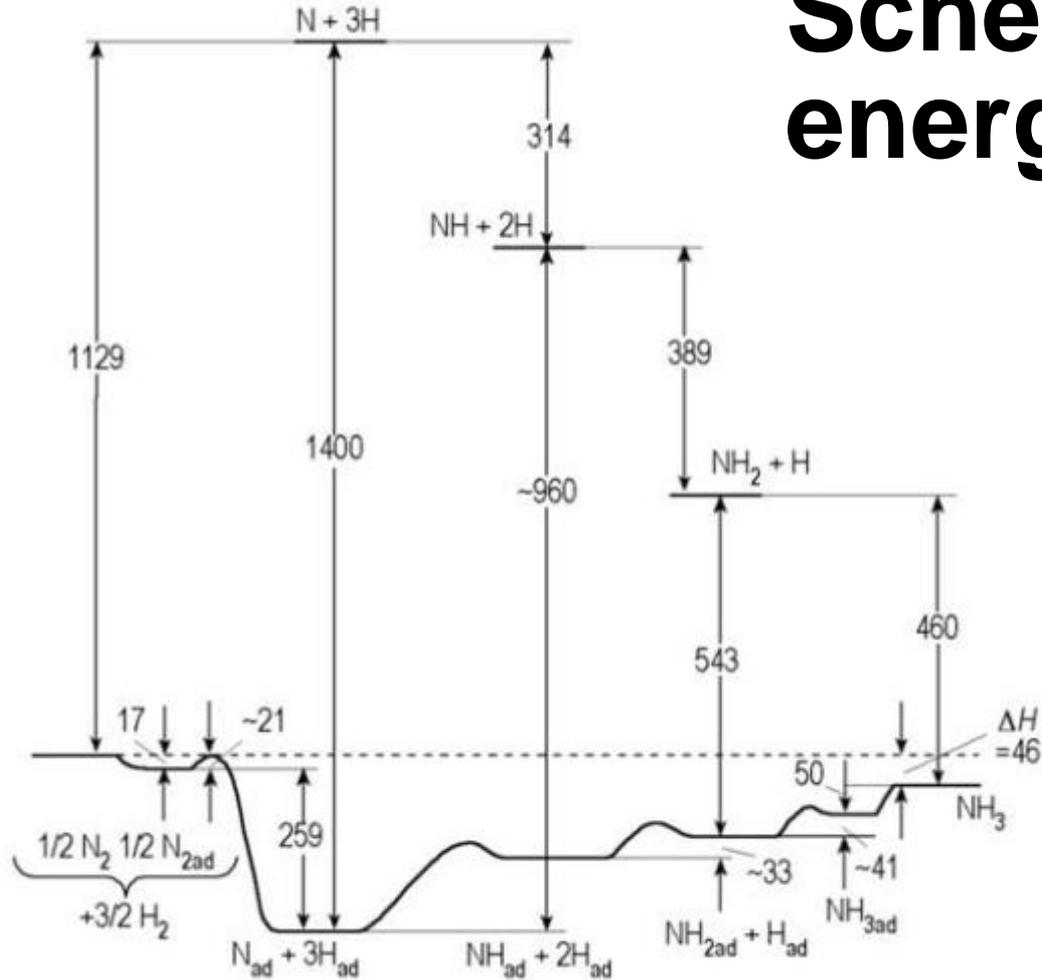


This is the “Langmuir-Hinshelwood mechanism”.

See, e.g. Hellman et al.,
Surf. Sci. 600 (2006) 4264-4268,

<https://doi.org/10.1016/j.susc.2005.11.070>

Schematic energy profile



Max Appl, Ammonia,
 2. Production
 Processes, Ullmann's
 Encyclopedia of
 Industrial Chemistry,
 Wiley Online Library,
https://onlinelibrary.wiley.com/doi/pdf/10.1002/14356007.o02_o11,
 accessed 12.1.2019.

A?

Figure 2. Schematic energy profile of the progress of ammonia synthesis on Fe (energies in kJ/mol) [40]

- Ammonia synthesis is highly sensitive to the orientation of the different crystal planes of iron in the catalyst, **Fe(111) is the most active surface**
- **Promotion with potassium** of single iron crystals enhances the sticking probability for nitrogen dissociation much more on the Fe(100) and (110) than on the Fe(111)
- **Al₂O₃ stabilizes Fe(111) (?)**
 - (Richardson book)

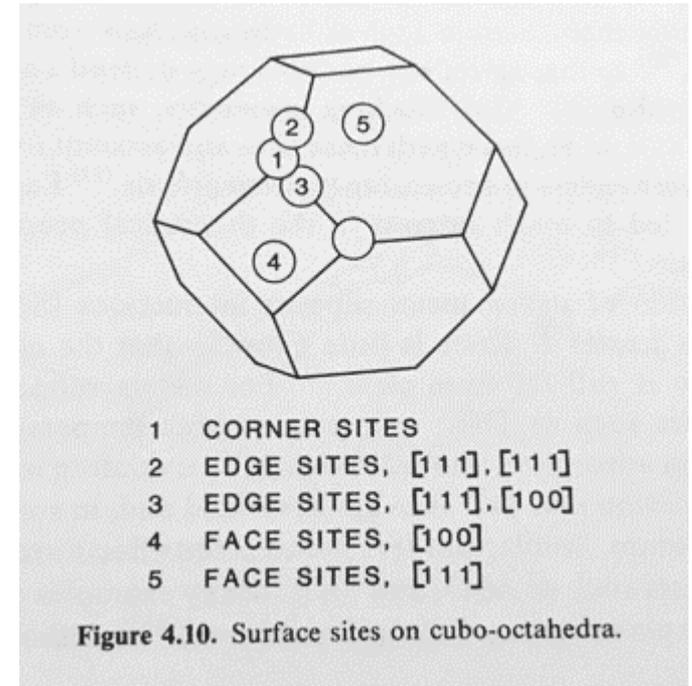


Image: Richardson, Principles of Catalyst Development, Plenum Press, 1989.

Catalyst poisons, NH₃ synthesis

- **Permanent poisons** (irreversible damage) **vs temporary poisons** (lower the activity while in the synthesis gas)
- Most common **temporary poisons: oxygen-containing compounds** such as H₂O, CO, CO₂, and O₂
- **Chlorine Compounds: about 0.1 ppm the uppermost allowable limit in order not to affect adversely the life of ammonia catalysts [310].**
- **Sulfur (H₂S, COS): permanent poison.**
 - In some plants, traces of H₂S and COS may not be removed in the upstream purification steps and so may enter the converter with the make-up gas.
 - However, main danger: sulfur contained in the compressor oil

Industrial catalysts for ammonia synthesis must satisfy the following requirements:

- **High catalyst activity at the lowest possible reaction temperatures**
- The highest possible **insensitivity to oxygen and chlorine-containing catalyst poisons**
- Long life, which is determined essentially by **resistance to thermal degradation and to irreversible poisoning**
- **Mechanical Strength.** Insufficient pressure and abrasion resistance may lead to an excessive increase in converter pressure drop, and so to a premature plant shutdown.
- Because of the high and increasing world demand for ammonia, **a reliable primary raw material source**

Ammonia catalyst, conclusion

- Extensive studies in the last decade have provided a more refined picture of the morphology of the active catalyst (reduced state) and its precursor (oxidic state). A review is given in [49].
- Structural promoters (stabilizers), such as Al_2O_3
- An extensive review on promoters can be found in [41].
- **The negative effect of K_2O concentrations higher than about 0.58 % has not been explained unequivocally [83]**



Example 2: Steam Reforming

(do not mix up with: catalytic reforming!)

Fuel processing for H₂ production

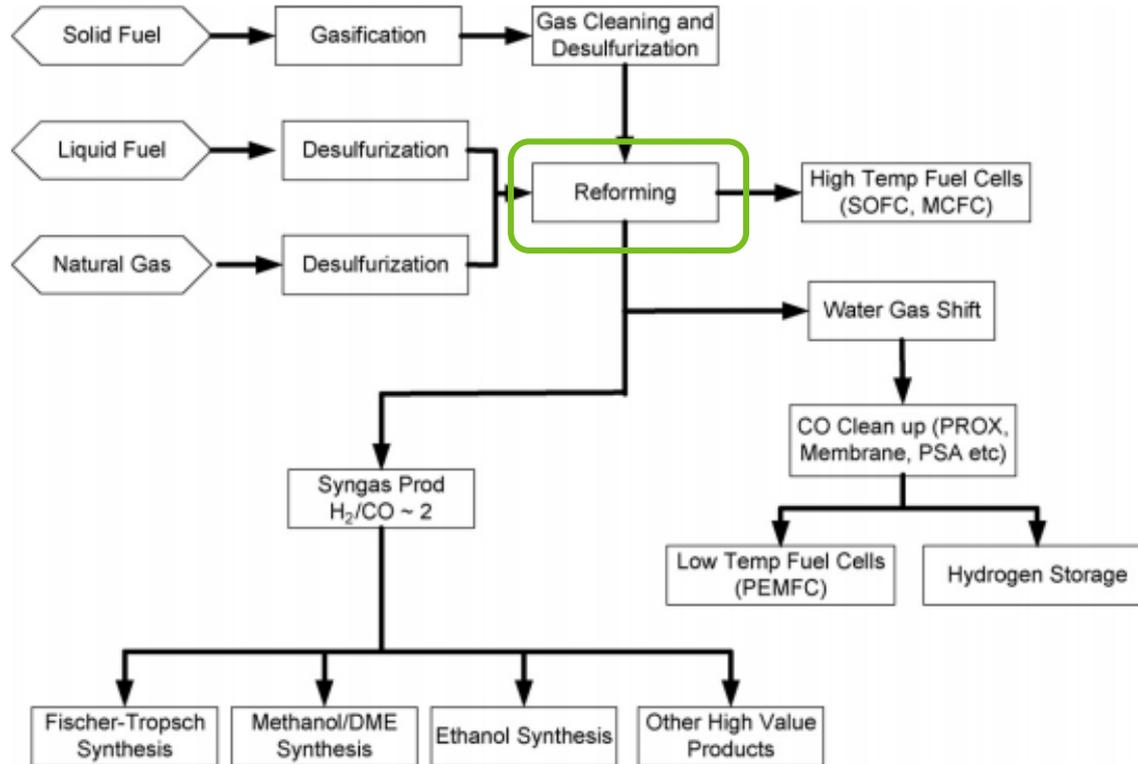
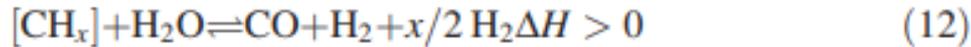
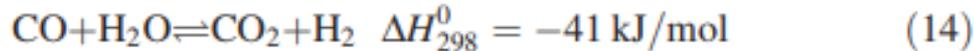


Fig. 1. Fuel processing of gaseous, liquid, and solid fuels for hydrogen production.

Steam reforming



Steam reforming
Reversible reaction, strongly endothermic
no. of molecules increases



Water gas shift, moderately exothermic

- Light hydrocarbons ranging from natural gas (methane) to naphtha (max. C11) undergo reaction with steam over a catalyst according to Equation (12)*
 - (natural gas, CH_4 ; naphtha, CH_2 ; petroleum, CH)
- The most common method for producing H_2 or H_2/CO mixtures.
 - Cost: about \$ 0.10 per cubic meter of hydrogen.
- Currently: pressures up to 4 MPa and temperatures up to 950 °C

Table 1. Steam-reforming reactions

Reactions	ΔH_{298}° (kJ/mol) ^a
1. $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	-206 *
2. $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	41 *
3. $\text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightarrow n\text{CO} + \left(n + \frac{m}{2}\right)\text{H}_2$	-1175 ^b *

a

Standard state: 298 K and 1 bar.

- strongly endothermic *
- Expansion of gas

b

For $n\text{-C}_7\text{H}_{16}$.

”→ low pressure, high temperature ”



Fig. 1. The steam-reforming unit.

Steam reforming

- Severe mass and heat transfer limitations
- Activity of the catalyst rarely limiting factor → less expensive nickel catalysts almost universally used in industry
- Intermediate and high temperatures required for steam reforming may promote carbon formation,
- Steam to carbon ratios (2.5 or higher) higher than stoichiometry are required to gasify coke when a nickel-based catalyst is used.

Catalysts by impregnation - 1

- Impregnating a support with nickel as the active constituent.
- Advantage: support can be calcined at high temperatures before impregnation, resulting in predetermined excellent mechanical properties which are important especially at high temperature application. Impregnated catalysts predominate by far at present.
- Frequently used support materials are α -alumina, magnesium oxide, or spinel type substances (e.g., magnesium aluminum oxide).

Catalysts by impregnation - 2

- A silicon dioxide content of < 0.3 wt % in the catalyst is essential, because silicon dioxide becomes volatile in the presence of steam and may foul the downstream heat exchangers through which the reformed gas flows.
- Nickel is at first present in the form of nickel oxide; after the system has been heated, it is reduced in the reformer tube by hydrogen formed when natural gas is added to steam. <activation>

Ni particle size & dispersion?

- **Common dispersions for Ni catalysts are of 2–5%, with metal particles of 20–50 nm (Rostrup-Nielsen, 1984).**
- **There is an optimum beyond which an increase in Ni-content does not produce any increase in activity, usually around 15–20 wt% (depending on support structure and surface)**

Promoters help to reduce coke formation Mg, Ca

The steam reforming of hydrocarbons may be catalyzed by several transition metals. The most frequently used catalysts are α - Al_2O_3 supported nickel-based catalysts, which are frequently modified by the addition of promoters such as Mg and Ca, in order to improve their stability and selectivity. The mechanism of promotion was investigated ... there is an increase in the reforming activity by the presence of the promoters, without modification in the mechanism of reaction. The TPO results showed that the addition of promoters caused an increase on the hydrogen content of the coke formed.

Surface area?

Pore size distribution (PSD)?

... I tried to find info from the literature, but could not find, unfortunately...!

Steam reforming catalysts deactivate by many means

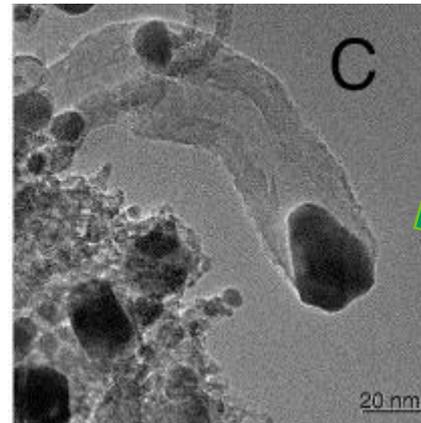
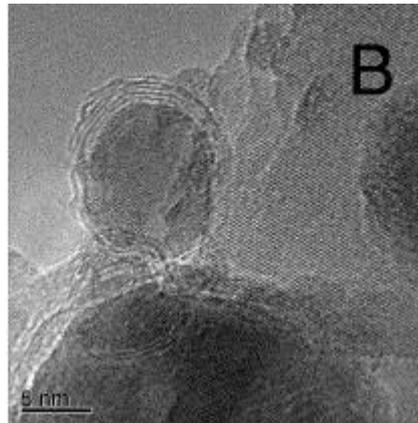
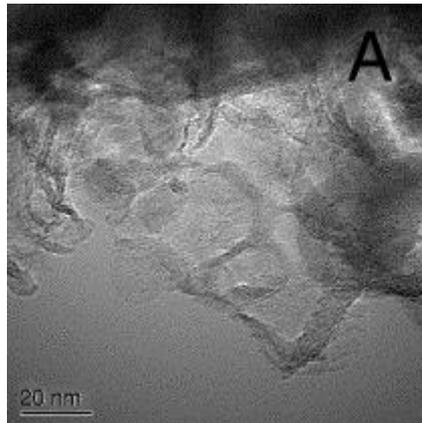
- **Sintering**
 - Nickel sinters rapidly at the steam reforming conditions
- **Coke formation**
- **Poisoning**

Carbon deposition (coke formation)

- Carbon deposition frequently experienced with steam reforming.
- Various reactions may in principle cause solid carbon formation from carbon compounds containing gaseous phases, e.g.
 - e.g., Boudouard reaction ($2 \text{CO} \rightleftharpoons \text{C} + \text{CO}_2$),
 - hydrocarbon decomposition ($\text{C}_n\text{H}_m \rightleftharpoons n \text{C} + m/2 \text{H}_2$),
 - the heterogeneous water gas reaction ($\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$),
- Hydrocarbon decomposition practically the exclusive cause for carbon formation in the steam reforming process.

Examples of coke

pyrolytic carbon on a MgAl_2O_4 carrier (A),
encapsulating carbon (B), and
whisker carbon (C) on $\text{Ni/MgAl}_2\text{O}_4$ reforming catalysts.



Ni

... carbon
nanotubes!

Preventing catalyst poisoning - desulfurization

- Catalytic activity affected seriously by poisons such as are sulfur, arsenic, copper, vanadium, lead, and chlorine or halogens in general.
 - Sulfur, found in practically all hydrocarbon feedstocks
- **Zinc oxide absorption**: Zinc oxide desulfurization operating at 350 – 400 °C; almost complete conversion of zinc oxide to zinc sulfide.
- Organic sulfur compounds such as mercaptans and thiophenes require hydrodesulfurization (HDS) over cobalt – molybdenum or nickel – molybdenum catalysts (temperatures of ca. 350 – 380 °C)



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Four challenges for nickel steam-reforming catalysts

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Haldor Topsøe A/S, DK-2800 Lyngby, Denmark

Available online 23 November 2005

Abstract

Reforming over supported nickel catalysts has been used commercially for more than 40 years. In this paper four catalytic challenges for nickel steam reforming catalysts are discussed from both a practical and a fundamental point of view. The four challenges are activity, sulphur poisoning, carbon formation and sintering. A coherent microscopic picture of these important aspects of the working catalyst is emerging from classic studies and is now extended by in situ TEM and DFT calculations of atomic-scale relationships between structure and catalyst properties and new knowledge about sintering.

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Keywords: Steam-reforming; Nickel catalysts; Sulphur poisoning; Sintering; Carbon formation

Steam reforming catalysts: Haldor Topsoe

→ fixed-bed

<https://www.topsoe.com/processes/hydrogen/reforming>

<https://blog.topsoe.com/2013/09/new-steam-reforming-catalyst-haldor-topsoe>

Catalysts

The performance catalysts we supply for this application are listed below.

 Catalysts	 Catalysts	 Catalysts	 Catalysts
AR-401 Prerduced prereforming catalyst suitable for <i>fixed-bed reforming</i>	R-67-7H High activity reforming catalyst used for tubular	R-67R-7H Prerduced high activity reforming catalyst used for	R-87 HEAT-X™ High activity reforming catalyst for heat exchange
			



Example 3: Fluid Catalytic Cracking (FCC)

Mechanistic views on FCC

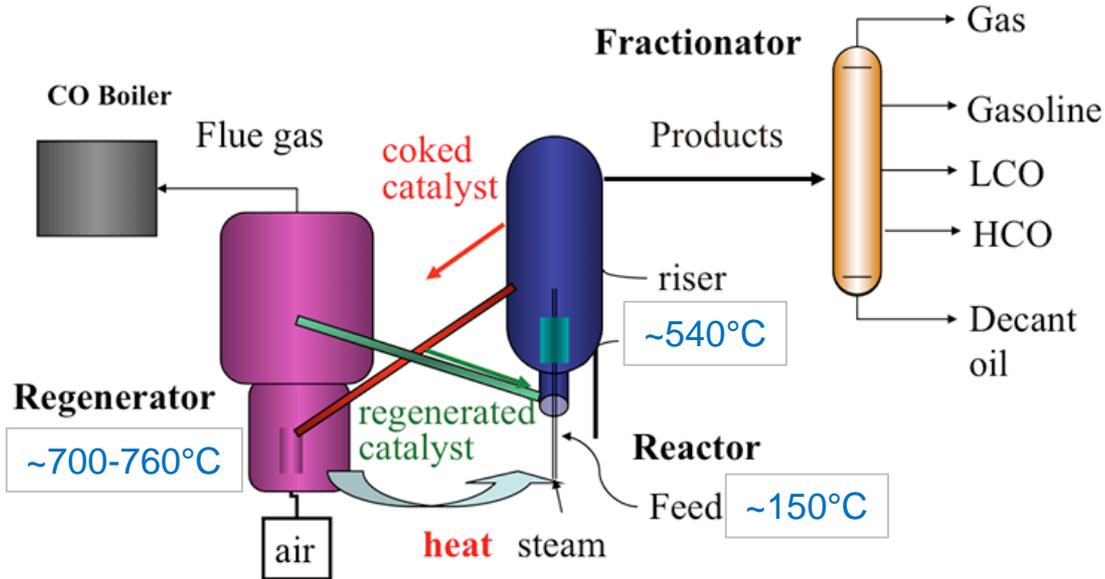
- Shortens the chain length of heavy hydrocarbons
- Acid-catalyzed
- Mechanism involves the generation of carbocations
 - Isomerization (from secondary and tertiary carbon atoms)
 - C-C bond scission (breaking)
 - ...
- Quickly generates "coke" on catalyst surface → is burned off with air to regenerate
- Fluidized bed operation

Abstract

The fluid catalytic cracking (FCC) unit is the primary hydrocarbon conversion unit in the modern petroleum refinery. It uses heat and catalyst to convert a variety of high molecular weight feed types (eg, gas oils, cracked gas oils, deasphalted gas oils, and atmospheric/vacuum resids) into lighter, more valuable products such as gasoline, light fuel oil, and petrochemical feedstocks such as propylene and butylene. This article reviews the role of catalyst in the fluid catalytic cracking process. The design of catalyst, catalyst poisons, and the effect of catalyst on product yields and selectivity are covered. Also, the role of catalytic additives in maximizing light olefins and in controlling emissions is discussed. In addition, the importance of catalyst testing is covered, along with unconventional feedstocks and processes that are extending the role of FCC catalyst to areas beyond the original FCC process scope of converting heavy petroleum feedstocks into transportation fuels.

Fluid Catalytic Cracking (FCC)

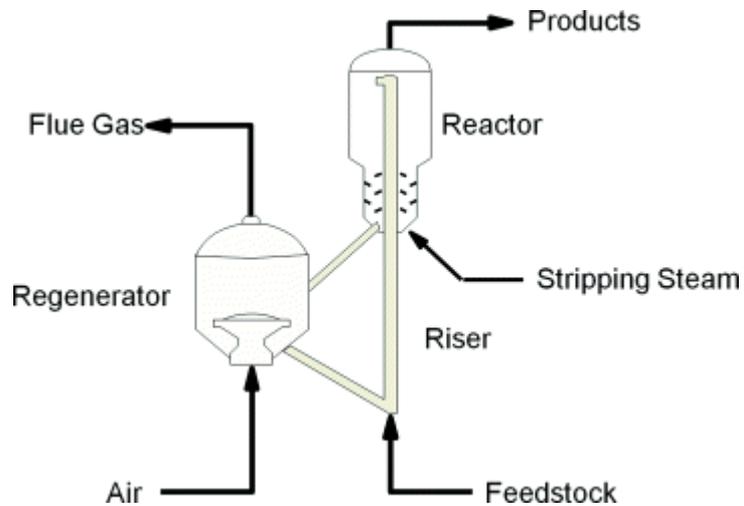
- Introduced in 1942
- Excellent integration of reactor with catalyst regenerator for high thermal efficiency



- "Rizer" reactor,
- Fluidized bed
- Fast deactivation
- Endothermic reaction
- Coke burned off with air → heating

Figure 7.7. Process configuration for Fluid Catalytic Cracking (FCC) process.

Source: Dr. Semih Eser



Simplified diagram of a generic FCCU

Table 1. Important Dates in FCC Catalyst Development (shortened)

Aluminum chloride catalyst	1915
Silica/alumina catalyst (Houdry)	1940
First commercial production of FCC catalyst (Grace)	1942
Commercial production of zeolite Y (Union Carbide)	1959
Introduction of zeolitic FCC catalyst (Mobil)	1962
Introduction of USY and REUSY zeolites (Grace)	1964
Silica–sol-bound catalysts (Grace)	1973
Introduction of ZSM-5 (Mobil)	1984
Coke-selective, deep bottoms cracking matrices (Grace)	1986
Catalyst with optimized pore structure for bottoms cracking (Grace)	2003

On the importance of zeolites

- The introduction of zeolite-based catalysts in the 1960s was **the most significant innovation in FCC catalyst technology**.
- Zeolite catalysts provided significantly higher gasoline production and lower coke production than the amorphous silica–alumina catalysts they replaced.
- The cumulative value of the additional gasoline produced by zeolite catalysts between their introduction in the 1960s and 2001 was conservatively estimated at \$1 trillion.

Zeolites - Greek ζέω (zéō) "to boil", λίθος (líthos) "stone"

- Crystalline aluminosilicates
- Occur naturally & produced industrially
- 232 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known (Sept 2016)
- "Molecular sieves", microporous (< 2 nm, IUPAC)
- International Zeolite Association:
<http://www.iza-online.org/>



Natural zeolite with a United States one-cent coin (penny) for scale



A form of thomsonite (one of the rarest zeolites) from India

Zeolites

- 850 catalysts commercially available, of which 130 based on zeolites - Cejka, EuropaCat 2017
- 10-12 zeolites used in catalytic industrial applications
- Pore size limitations for bulkier "substrates"
 - Source: Prof. Jiri Cejka, plenary lecture at EuropaCat 2017

ZEOLITES

ZEOLITES = from Greek *zéō*, meaning "to boil" and *lithos*, meaning "stone"

Aluminosilicate

Crystalline MATERIALS

Microporous

Structural units of zeolites tetrahedron SiO_4 (AlO_4)

- connected by shared oxygen atoms

Tetrahedron SiO_4 – neutral

Tetrahedron AlO_4 – negative charge

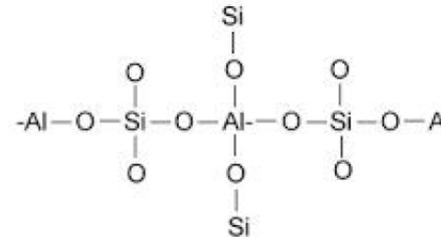
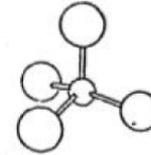


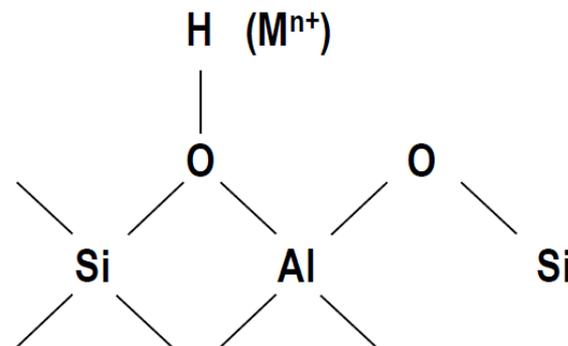
Figure 1: Basic Zeolite Structure

From Ullmann's Encyclopedia on zeolite structure

- Zeolites possess a framework structure of **corner-linked SiO_4^{4-} and AlO_4^{5-} tetrahedra** with two-coordinate oxygen atoms that bridge two tetrahedral centers (so-called T-atoms)
- Zeolite frameworks are open and contain n -membered rings
 - **Small-pore zeolites: 6 or 8-membered rings**, $2.8 \text{ \AA} < d < 4 \text{ \AA}$
 - Example: sodalite, zeolite A
 - **Medium-pore zeolites: 10-membered rings** ($5 \text{ \AA} < d < 6 \text{ \AA}$)
 - ZSM-type zeolites
 - **Large-pore zeolites: 12-rings** ($d > 7 \text{ \AA}$)
 - Faujasites and zeolites X and Y

ZEOLITES

- aluminosilicate framework
- negative charge (amount of Al)
- charge compensation
 - inorganic cations
 - organic cations
 - protons



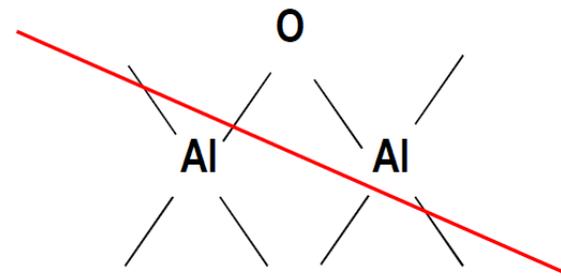
Loewenstein's rule

no Al-O-Al bonds !!!

(NOTE: Si/Al \geq 1) !!!!!

SiO₄ – optimal, tight tetrahedron structure

AlO₄ – Al atom higher steric demands, not optimal tetrahedron, lower stability



ZSM-5

- <http://europe.iza-structure.org/IZA-SC/framework.php?STC=MFI>

Database of Zeolite Structures

IZA-SC All Codes Framework Material 3D Drawing Powder Pattern CIF PDF References

Home » Codes » Framework Characteristic Units Help Credits

Framework Type MFI

Framework

Cell Parameters: orthorhombic P n m a (# 62)
a = 20.0900 Å b = 19.7380 Å c = 13.1420 Å
α = 90.000° β = 90.000° γ = 90.000°
Volume = 5211.3 Å³
R_{DLS} = 0.0020

Framework density (FD_S): 18.4 T/1000 Å³
Topological density: TD₁₀ = 960 TD = 0.825819

Ring sizes (# T-atoms): 10 6 5 4
Channel dimensionality: Topological (pore opening > 6-ring): 3-dimensional

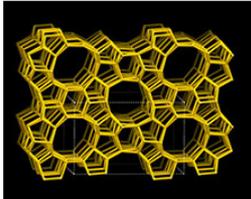
Maximum diameter of a sphere:
that can be included 6.36 Å
that can diffuse along a: 4.7 Å b: 4.46 Å c: 4.46 Å

Accessible volume: 9.81 %
Secondary Building Units: 5-1
Composite Building Units:

mor (t-tes) *cas* *mfi (t-pen)* *mel*

Natural Tiling: t-bog-1 t-kah t-pes t-mel t-mel-1 t-mel-2 t-mfi-1 t-mfi-2 t-pen

Framework images
(click on icon for larger image)


Viewed along [010]

 
framework, viewed along [100] projection along [010]

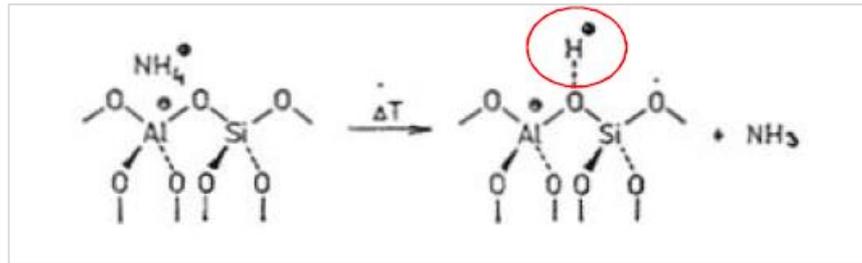
 
10ring straight channel complex of 10rings viewed along [010]


complex of 10rings viewed along [100]

Year code assigned 1978
Data last updated Jul 1, 2007

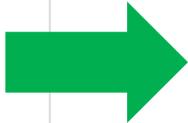
Zeolites - acidity

- **Brønsted acid: donates a proton**
 - **Related to Al in tetrahedral coordination, when charge neutrality compensated for by protons**
- **Lewis acid: accepts a pair of electrons. Lewis acids in zeolites typically are extra-framework Al**
- **Activation of acidic zeolites: deammoniation (L3)**



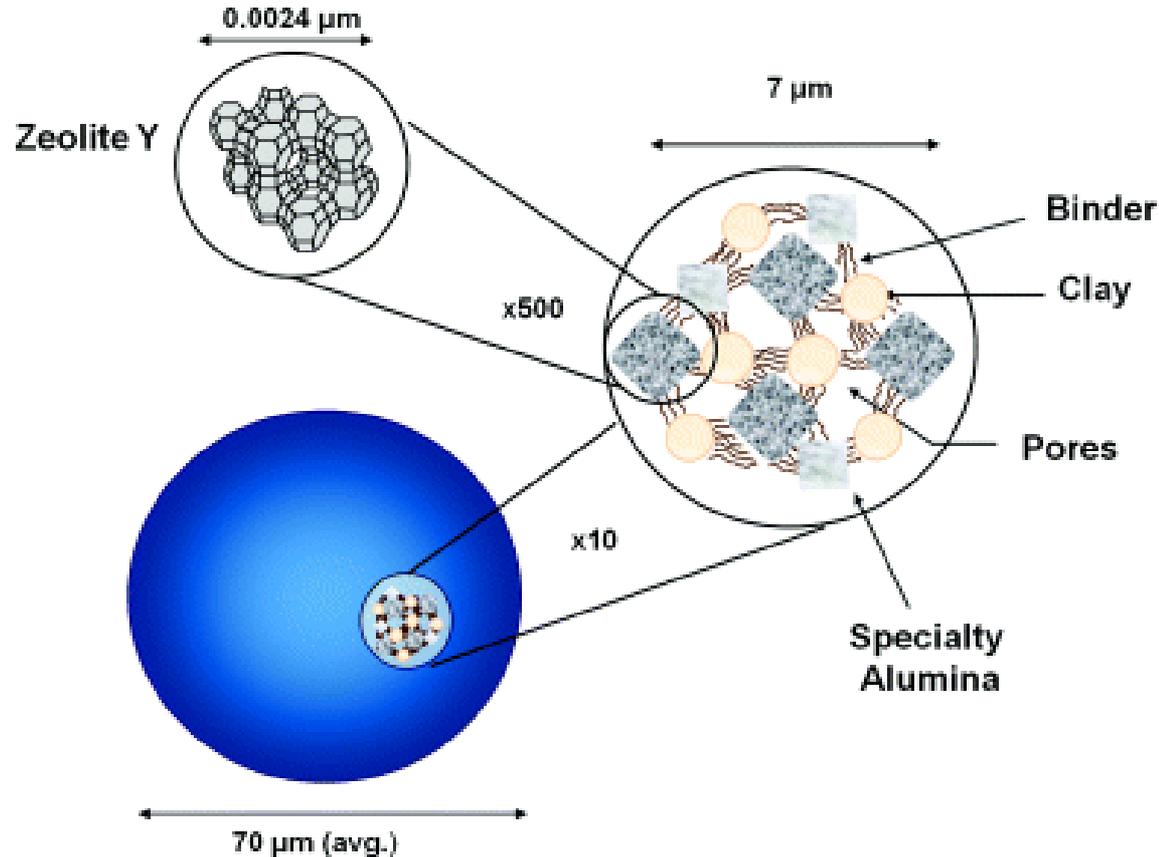
ZEOLITES- History

1756	description of the first natural zeolite	A.F. Cronstedt
1948	syntheses of mordenite and chabazite	R.M. Barrer
1949	syntheses of zeolites A and X	Union Carbide
1954	application of zeolites for gas drying	Union Carbide
1959	application of zeolites for paraffin separation	Union Carbide
1959	application of clinoptilolite for cation exchange	Ames
1961	organic cations as templates	Barrer and Danny
1962	zeolites as FCC catalysts	Mobil Oil
1967	syntheses of zeolite beta and ZSM-5	Mobil Oil
1974	zeolites as detergent builder	Henkel
1978	synthesis of silicalite	Union Carbide
1982	aluminophosphate molecular sieves	Union Carbide
1983	incorporation of titanium in the TS-1	Eniricerche
1992	micelle-templated mesoporous silicates	Mobil
1994	micelle-templated mesoporous oxides	G.D. Stucky
1999	mesoporous carbons by silica replica	R. Ryoo
1999	microporous metalloorganic frameworks	Yaghi and O'Keeffe



FCC Catalysts – highly engineered

- porous spherical particles composed primarily of SiO_2 and Al_2O_3
- ~0.2–2 μm zeolite crystals that are bound within a matrix material.
- Matrix clay, binder, active matrix, and optional metals traps.



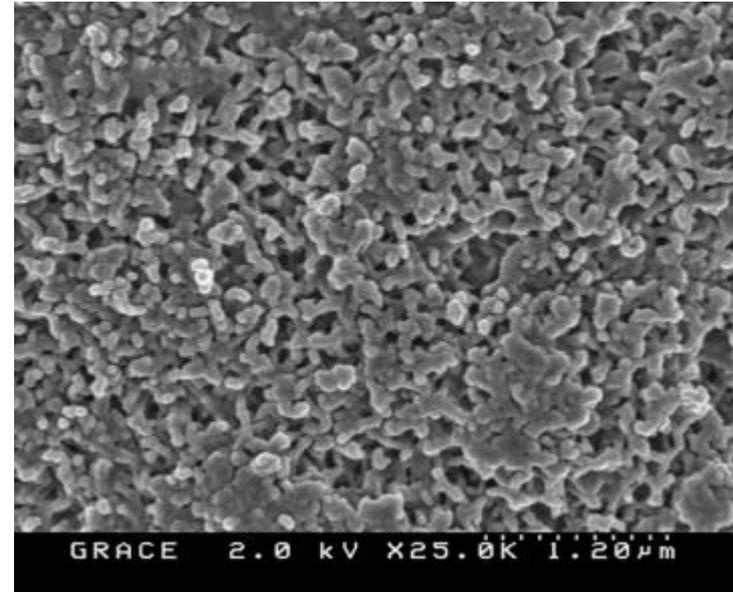
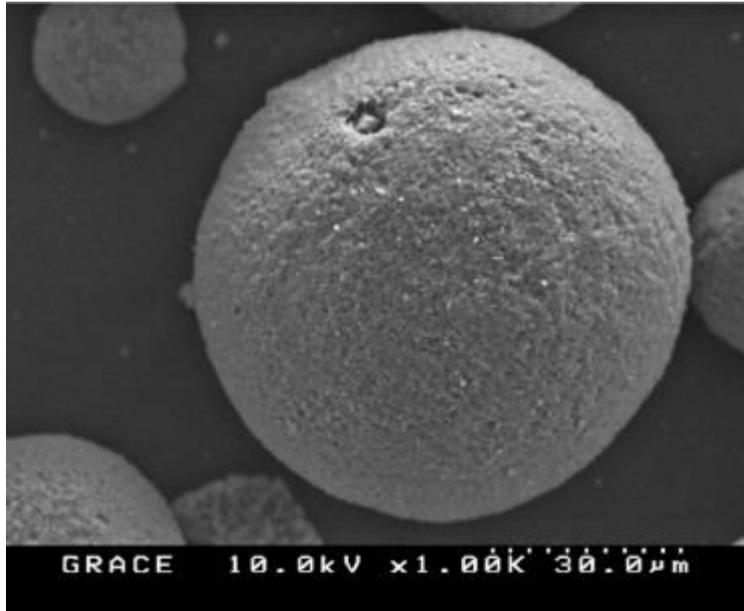


Figure 4 (a) Scanning electron micrograph showing the spherical nature of a typical FCC catalyst particle. (b) Scanning electron micrograph of the surface of typical FCC catalyst particle, revealing the porous structure of the catalyst.

Zeolites in FCC - Deactivation

Coking

- Fastest deactivation – catalyst lifetime some seconds (Bartholomew review)
- Continuous regeneration (burning off coke)

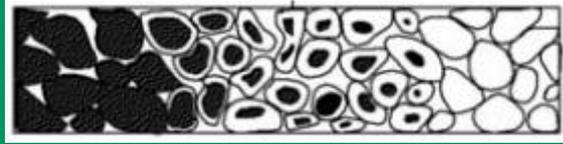
Dealumination – specific to zeolites

- results in zeolite structure collapse and the **loss of acidity**
- ultrastabilized zeolite Y (USY) exhibits higher stability against hydrothermal and chemical attack

Morris D. Argyle and Calvin H. Bartholomew: Heterogeneous Catalyst Deactivation and Regeneration: A Review, *Catalysts* 5 (2015) 145-269; [DOI:10.3390/catal5010145](https://doi.org/10.3390/catal5010145) (open access).

Kenneth Bryden Udayshankar Singh Michael Berg Stefan Brandt Rosann Schiller Wu-Cheng Cheng, Fluid Catalytic Cracking (FCC): Catalysts and Additives, *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley Online Library, <https://doi.org/10.1002/0471238961.fluidnee.a01.pub2>, accessed 12.1.2019

- In 2011, **the sales of FCC catalysts were estimated as greater than \$2 billion** and the volume produced as more than 600,000 metric tons per year (([10](#))).
- The largest FCC catalyst manufacturers are Albemarle, BASF, Sinopec, and Grace.
- FCC catalysts are highly specialized materials, tailored to meet specific objectives. In 2009, a compilation of refinery catalysts listed more than 100 FCC catalyst families provided by different suppliers (([11](#))).



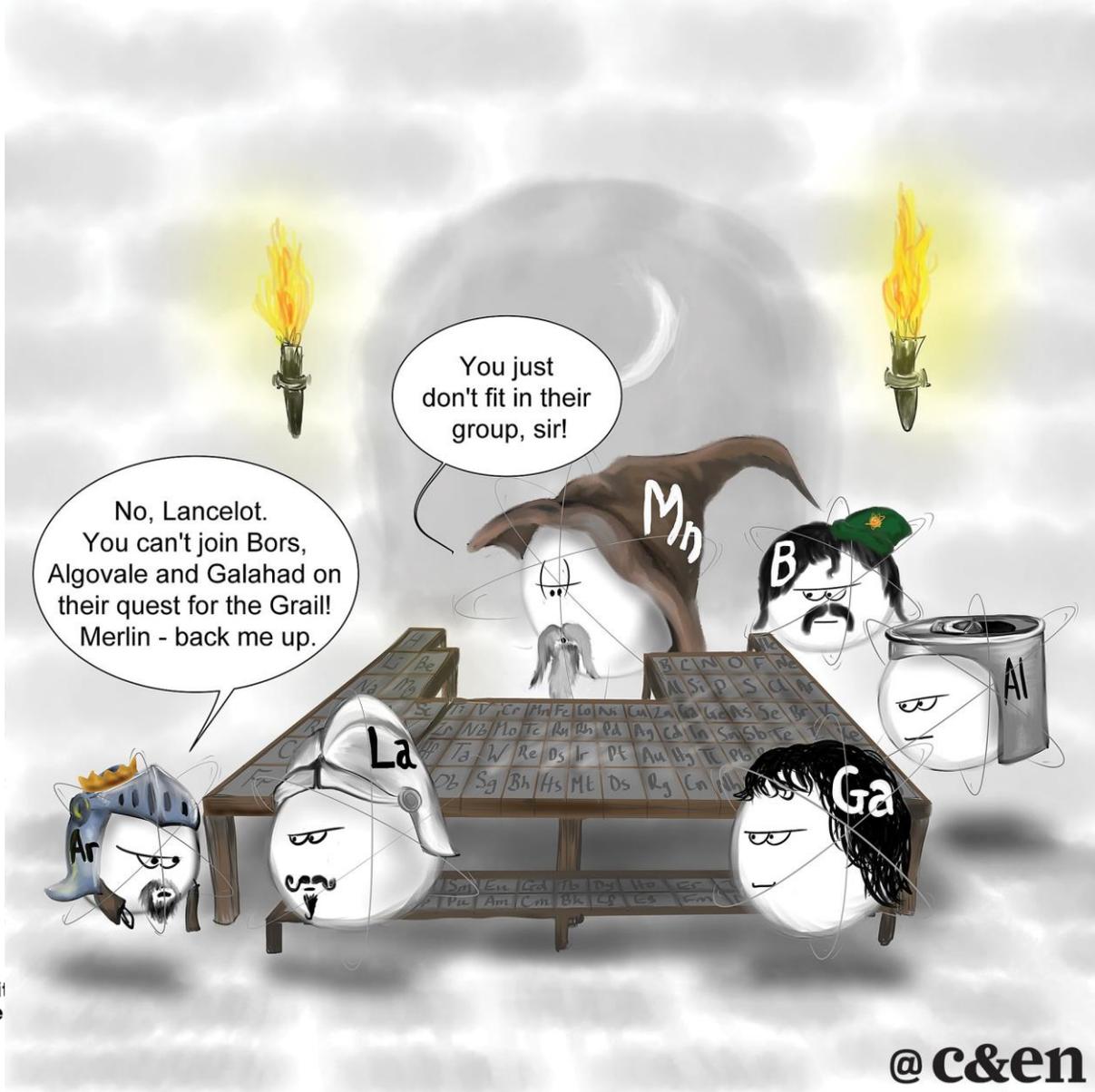
Conclusion & take-home message

Take-home message

- You are familiar with **3 important industrial catalytic processes**
- You know the catalysts used in them, including the **catalyst components** – were there three, in all cases?
 - NH_3 (Fe...), steam reforming (Ni...), FCC (zeolites...)
- You have encountered more catalysis-related terminology

Next in course:

- Adsorption homework shared on 16.1.
- **Next lecture 21.2. Catalyst characterization 1: Adsorption methods**
 - Related teaching video in [Panopto](#) and [Youtube](#) (also in the [blog](#))
 - **Catalysis Glossary group work will start – be there!**



<https://twitter.com/cenmag/status/1084139208808325120?s=11>

