

Heterogeneous catalysis



Lecture 8

Haber-Bosch synthesis of ammonia

Haber-Bosch synthesis of ammonia

- The nitrogen problem – atmospheric N_2 fixation (breaking $N\equiv N$ bonds)
- Fertilizers – modern agriculture feeding billions of people on Earth
- 176 millions tons ammonia produced in 2016 worldwide
- 1–2 % of the world's entire energy supply; 2–5 % of total natural gas production



Fritz Haber (1868–1934)
Laid the theoretical basis on synthesis of ammonia, awarded the 1919 Nobel Prize in Chemistry.



Carl Bosch (1874–1940)
Realized the industrial synthesis of ammonia, awarded the 1931 Nobel Prize in Chemistry.



Alwin Mittasch (1869–1953)
The major developer for fused iron catalyst, who proposed the concept of mixed catalyst.



Gerhard Ertl (1936–)
Great contribution on iron catalyst surface chemistry research, awarded the 2007 Nobel Prize in Chemistry.

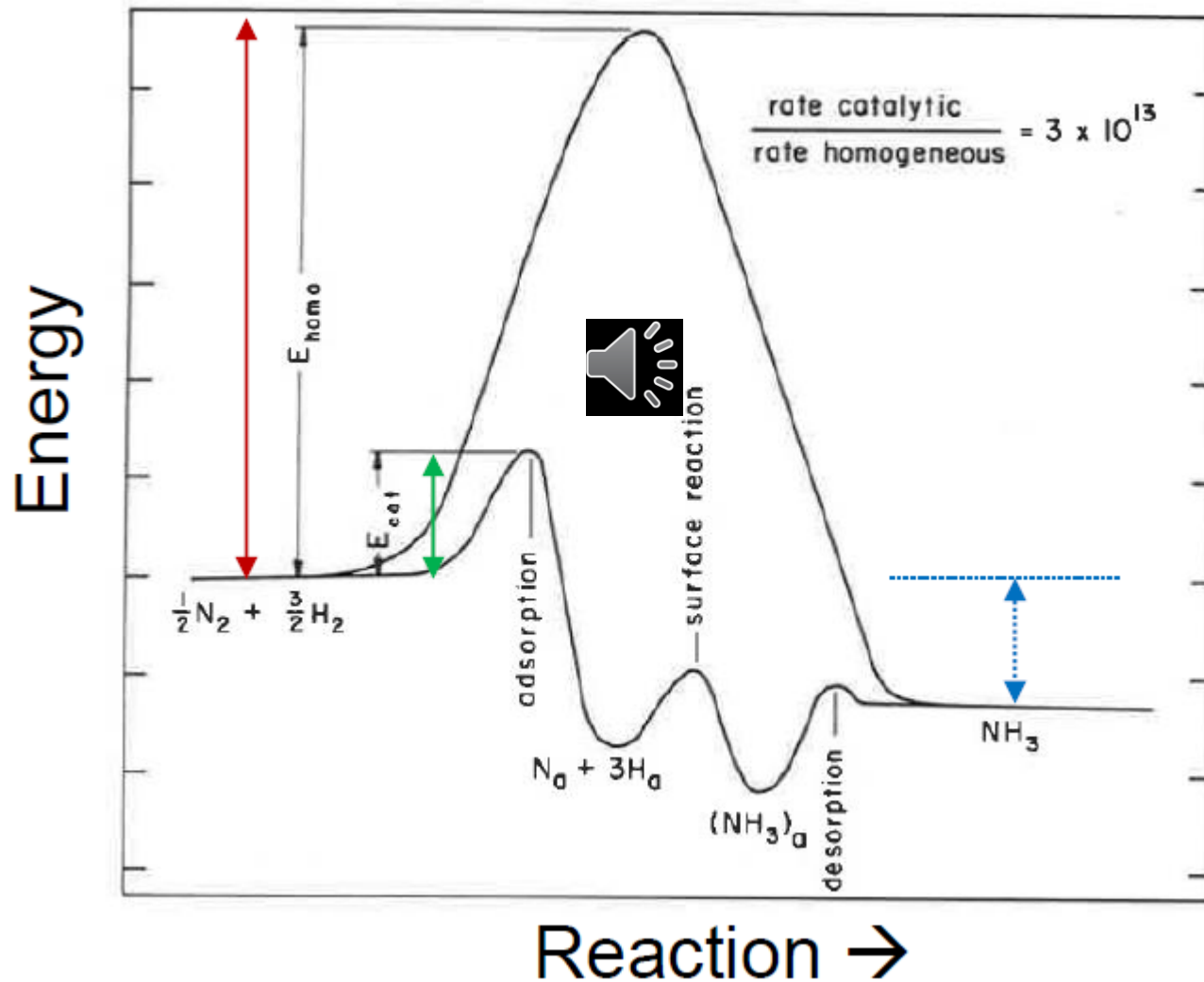
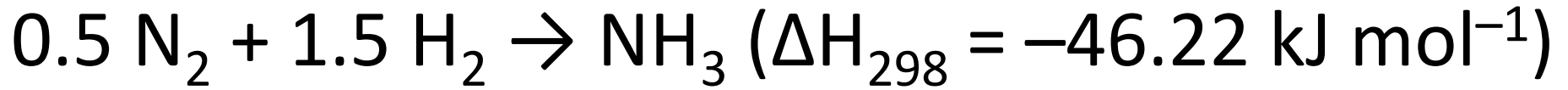
unclear. At atmospheric pressure, ammonia was only generated at very low temperature, but it decomposed at high temperature. Therefore, many scientists even believed that the generation of ammonia by the elemental hydrogen and nitrogen was an insurmountable obstacle.

At that critical moment, Haber first proposed to use high pressure reaction technique. However, it was still hard to realize industrial scale production due to low conversion-per-pass of ammonia. So Haber abandoned the popular static view and adopts a dynamic method by introducing an important concept, the reaction rate, which using space-time yield to replace reaction yield. Based on this important principle, he developed closed process flow and loop operation technology. These three technologies and concept of reaction rate were a great invention that provided the basis for the construction of experimental apparatus to produce ammonia and achieved the first pressurized catalytic process in industrial history. This was a milestone in the development history of the catalytic process that represented the beginning of a new era of industrial catalysis. Only a few years later, methanol synthesis, Fischer-Trop-



ings. From the technological invention to the present, the Earth's population has grown by 4.2 times from 1.7 billion at the beginning of the 20th century, while food production has increased by 7.8 times. Humans can still produce ample food and clothing under the limited land resources, mainly rely on such technology created by Haber and Bosch. Now, 50% of nitrogen in our body is from ammonia synthesis [2], which mean, if without such invention, 50% of people in the Earth cannot survive. China is also unlikely to feed 20 percent of the world's population by only 7% of arable land all over the world.

After a century of development, catalytic synthesis of ammonia has made tremendous progress. The production capacity of single set equipment has been improved from the original 5 t of daily ammonia production to the current 2200 t. The reaction pressure has dropped to 10–15 MPa from the original 100 MPa. The energy consumption has decreased to 27.2 GJ from the original 78 GJ, which is close to the theoretical energy consumption of 20.1 GJ. But as the second largest chemicals, the ammonia production still consumes 2% of total energy supply in the world and releases more than 400 Mt of CO₂, which accounts for 1.6% of total global CO₂ emissions.



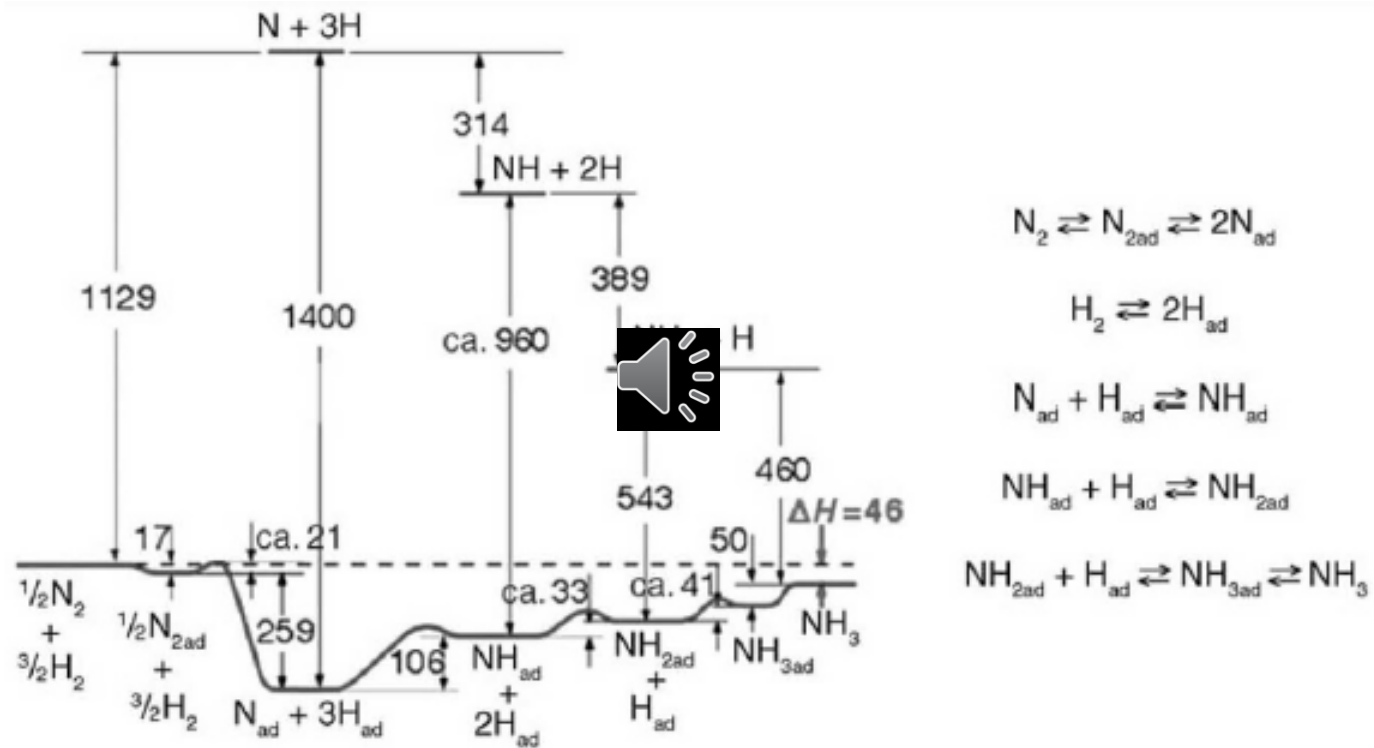
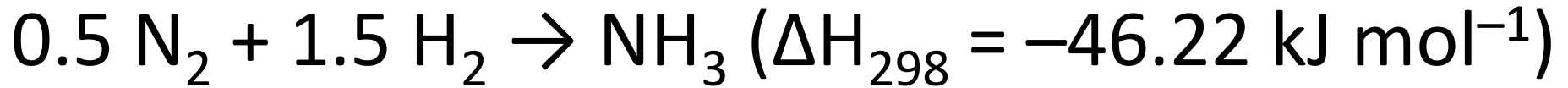
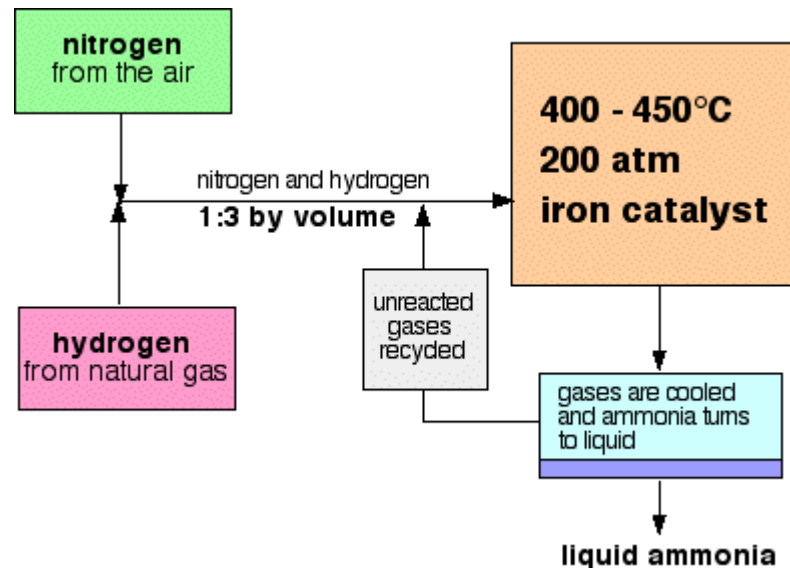


Fig. 1. Mechanism and potential energy diagram of ammonia synthesis on iron [98]. The energy is in kJ/mol.

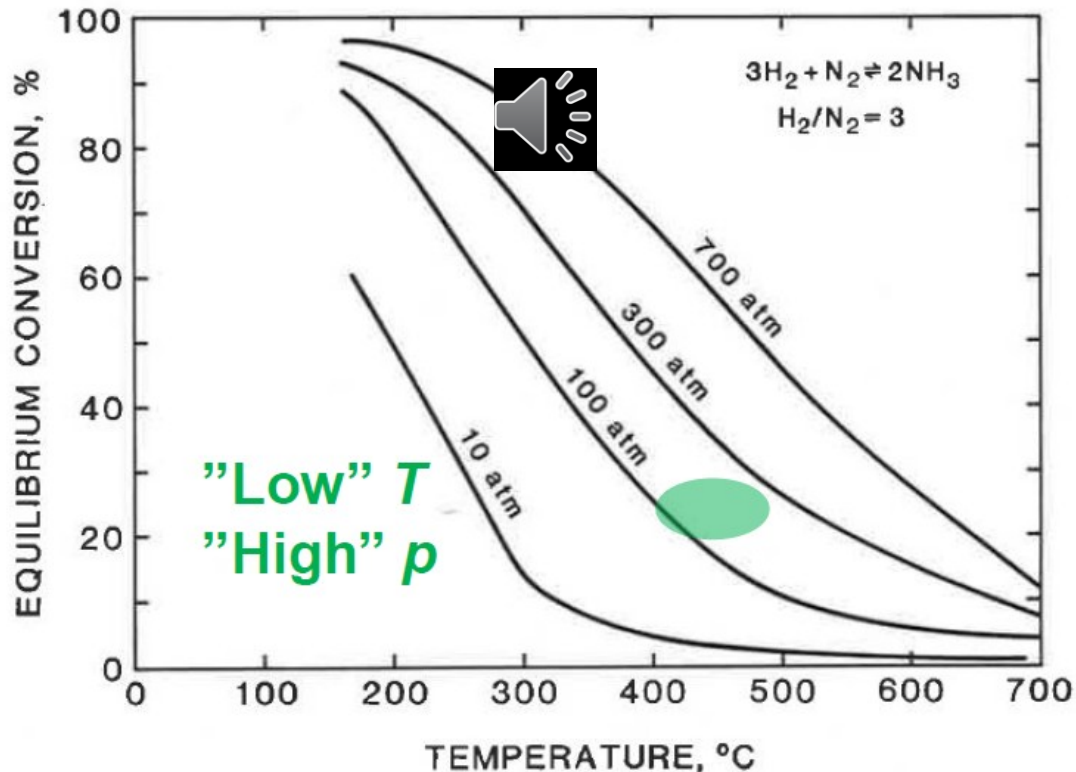
Haber-Bosch synthesis of ammonia

- Temperature: a **compromise** between thermodynamics (exothermic rxn) and kinetics (low rxn rates at low temperatures)
- Pressure: a **compromise** between thermodynamics (Le Chatelier's principle) and cost (high pressure reactors)




Haber-Bosch synthesis of ammonia

- „Low“ temperature – exothermic rxn
- High pressure – no. of molecules in gas phase decreases



Haber-Bosch synthesis of ammonia

- Catalyst?
 - Early 1800s: ammonia **decomposition** over Fe and other metals is known
 - 1908, Haber: reaction of hydrogen with nitrogen over catalysts based on Os and  (500 °C, 150–200 atm)
 - 1908–1922, Bosch and Mittasch (BASF): 2500 different catalyst formulations (almost all elements of PT tried), 6500 runs (already in 1911), finished in 1922 after a total of 22 000 tests (trial-and-error)
 - Serendipity: Gallivare magnetite from Sweden (naturally containing K, Ca, and Al as impurities) used as catalyst with excellent results
 - 1913, BASF: first ammonia production plant, catalyst = „promoted“ Fe


Haber-Bosch synthesis of ammonia

- Catalyst?

Table 6. Effectiveness of various elements as catalysts, promoters, or catalyst poisons

	Catalysts	Promoters	Poisons
I		Li, Na, K, Rb, Cs	
II		Be, Mg, Ca, Ba, Sr	Cd, Zn
III	Ce and rare earths	Al, Y, La, Ce and rare earths	B, Tl
IV	(Ti), (Zr)	Si, Ti, Zr, Th	Sn, Pb, C
V	(V)	Nb, Ta	P, As, Bi
VI	(Cr), Mo, W, U	Cr, Mo, W, U	O, S, Se, Te
VII	(Mn), Re		F, Cl, Br, I
VIII	Fe, Ni, Co, Ru, (Rh), Os, (Ir)		

Haber-Bosch synthesis of ammonia

- Catalyst?
 - „promoted“ Fe
 - Why?
 - A third compromise: better results with Ru, Os, but price has to be considered in large-scale industrial processes
→Fe 
 - Moreover Ru suffers from too strong H₂ chemisorption (i.e. H₂ effectively works as catalyst poison, no spot for N₂ chemisorption at high pressures)
→Fe
 - Fe-based catalysts stable up to **15 years** time-on-stream
→Fe

Haber-Bosch synthesis of ammonia

- Catalyst?

- 1913: Promoted Fe by Mittasch?
- Nowadays: Promoted Fe by Mittasch (only slight changes!)
- Promoted Fe?



- $\text{Fe-K}_2\text{O-Al}_2\text{O}_3$ (also low amounts of Ca, Mg, Si may occur)
„structural promoter“ – „porosity stabilizer“
Activity promoter
Active component, $\alpha\text{-Fe}$

- Commercially available „ammonia catalyst“ is an oxidized form of this formulation based on magnetite ($\text{Fe}_3\text{O}_4\text{-K}_2\text{O-Al}_2\text{O}_3$), reduction necessary!

Haber-Bosch synthesis of ammonia

- Fe-K₂O-Al₂O₃, example of composition

BASF S6-10 ammonia catalyst	Fe [at%]	K [at%]	Al [at%]	Ca [at%]	O [at%]
Bulk – unreduced	5	0.35	2.0	1.7	53.2
Surface – unreduced (XPS)	8.6	36.2	10.7	4.7	40.0
Surface – reduced (XPS)	11.0	27.0	17.0	4.0	41.0
Surface – cat. active spot (AES)*	30.1	29.0	6.7	1.0	33.2

*Auger electron spectroscopy, similar to EDAX in SEM, comparable results

Haber-Bosch synthesis of ammonia

- Fe-K₂O-Al₂O₃: Industrial production

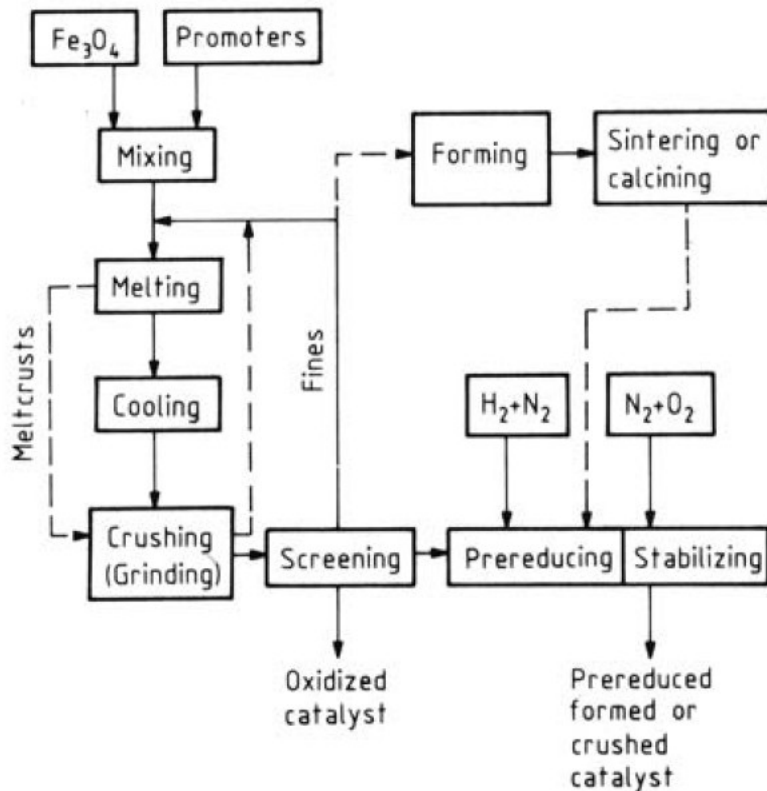


Figure 16. Ammonia catalyst manufacture

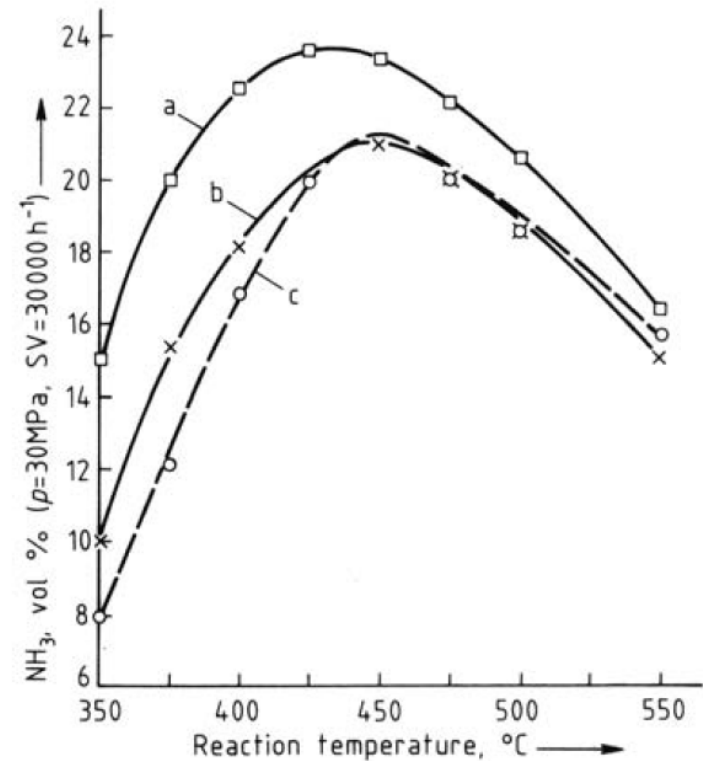


Figure 17. Effect of the melting temperature and rate of cooling of the melt on the activity of ammonia catalysts
a) Melt overheated to 3500 °C (rapid cooling); b) Melt temperature 1800 – 2000 °C (rapid cooling); c) Melt temperature 1800 – 2000 °C (slow cooling)

Haber-Bosch synthesis of ammonia

- Fe-K₂O-Al₂O₃, reduction before use

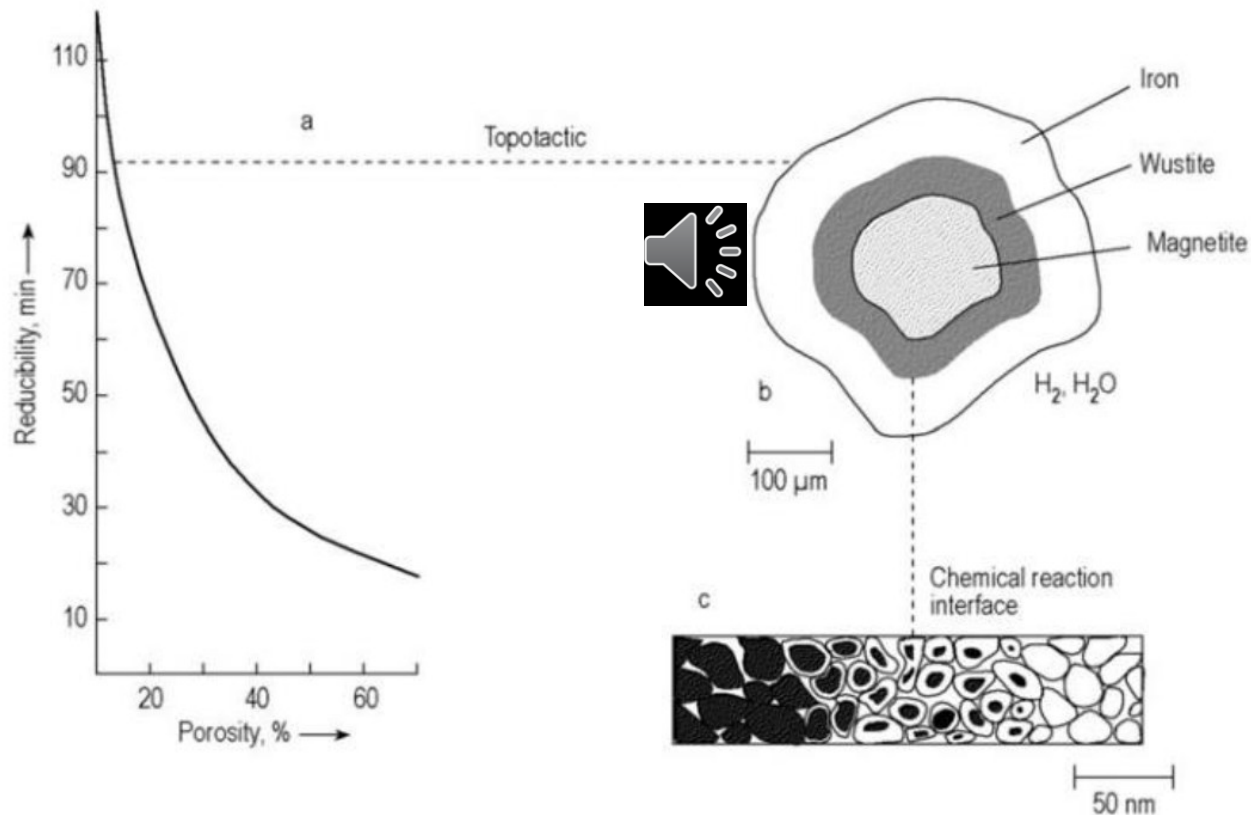



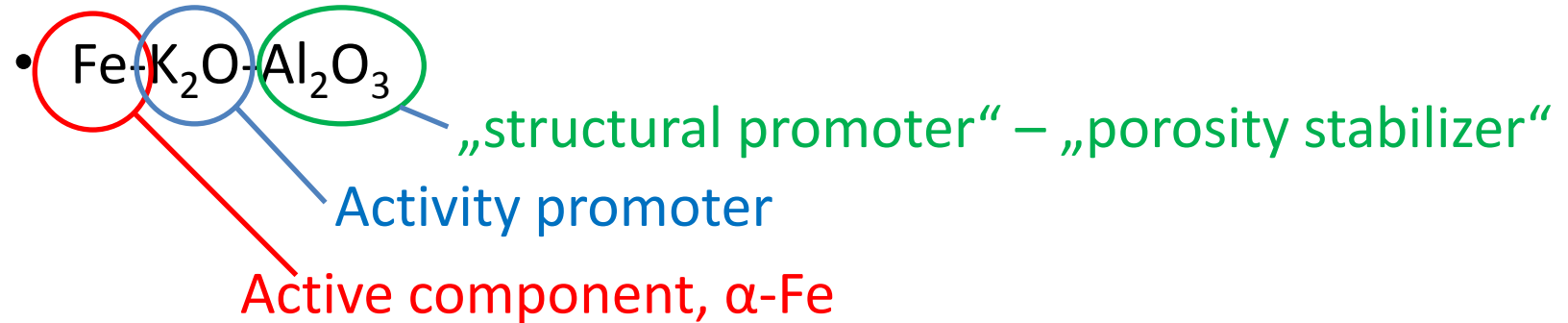
Figure 18. Mechanism of catalyst reduction [42]

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

Haber-Bosch synthesis of ammonia

- Fe-K₂O-Al₂O₃
 - 30 nm primary crystallites, grain/particle size 6–10 μm
 - Pore volume 0.09–0.1 cm³ g⁻¹, bimodal pore size distribution 10 nm and 25–50 nm, surface area  m g⁻¹, pores represent 44–46 % of total volume
 - Porosity originates in the reduction of originally nonporous Fe₃O₄ and is stabilized by Al₂O₃ (stability against sintering of particles)

Haber-Bosch synthesis of ammonia



- Why Fe (and Ru and Os) are active???
- Why K improves activity???

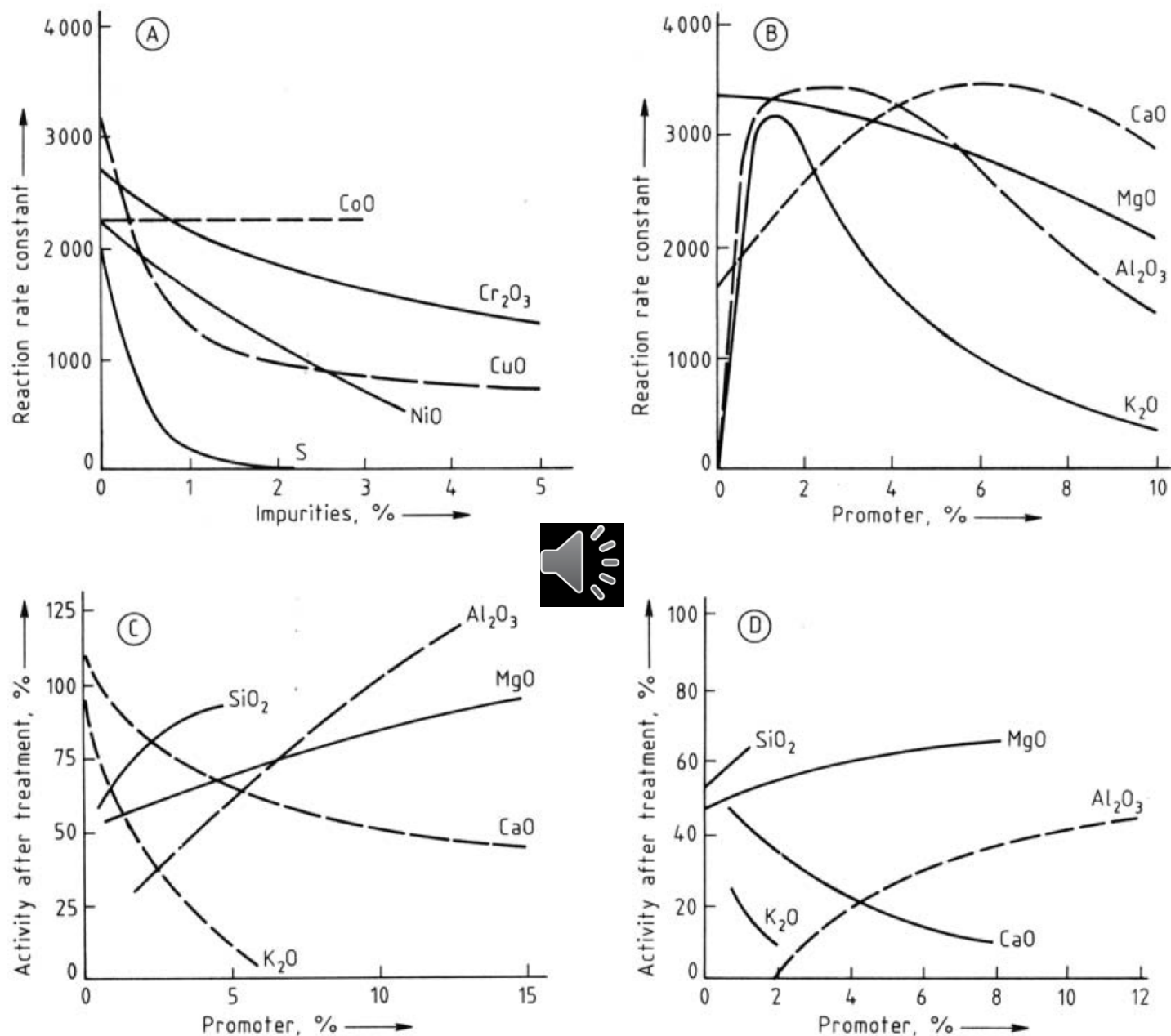
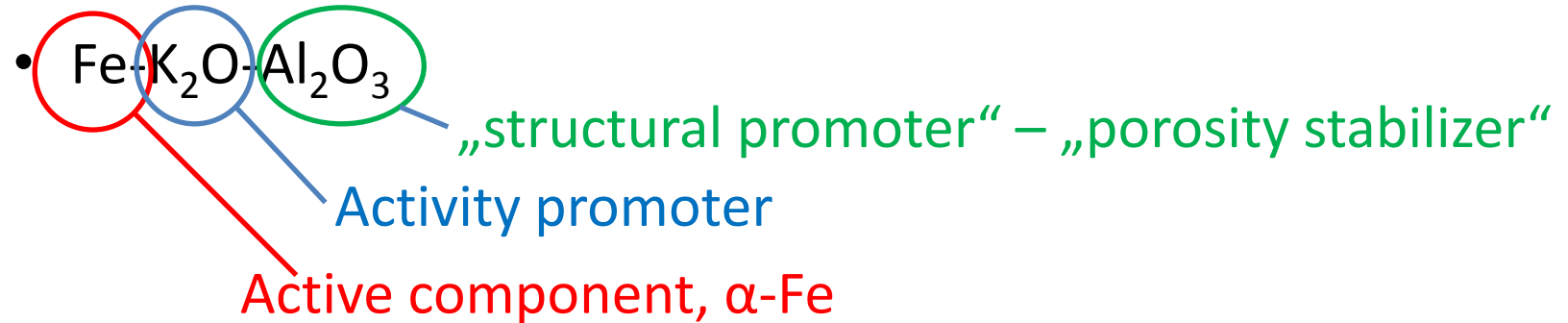


Figure 12. Dependence of the catalyst activity on various factors

A) Concentration of impurities; B) Concentration of promoters; C) Overheating to 700 °C with increasing promoter concentrations; D) Poisoning with water at increasing promoter concentrations

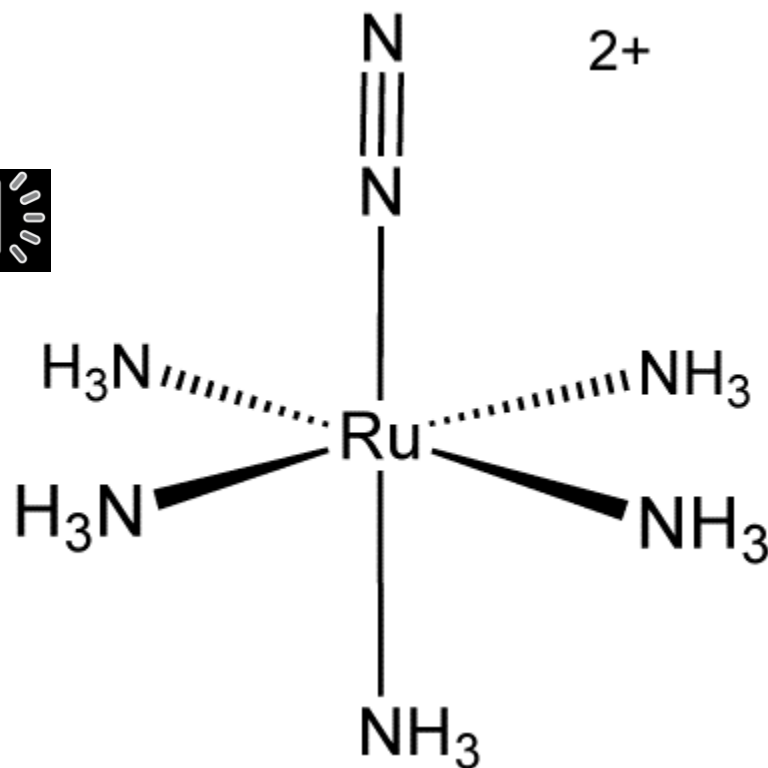
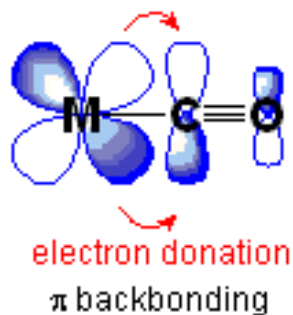
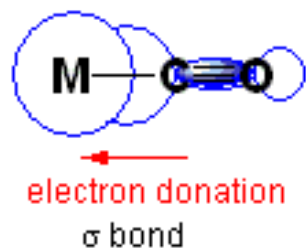
Haber-Bosch synthesis of ammonia




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Haber-Bosch synthesis of ammonia

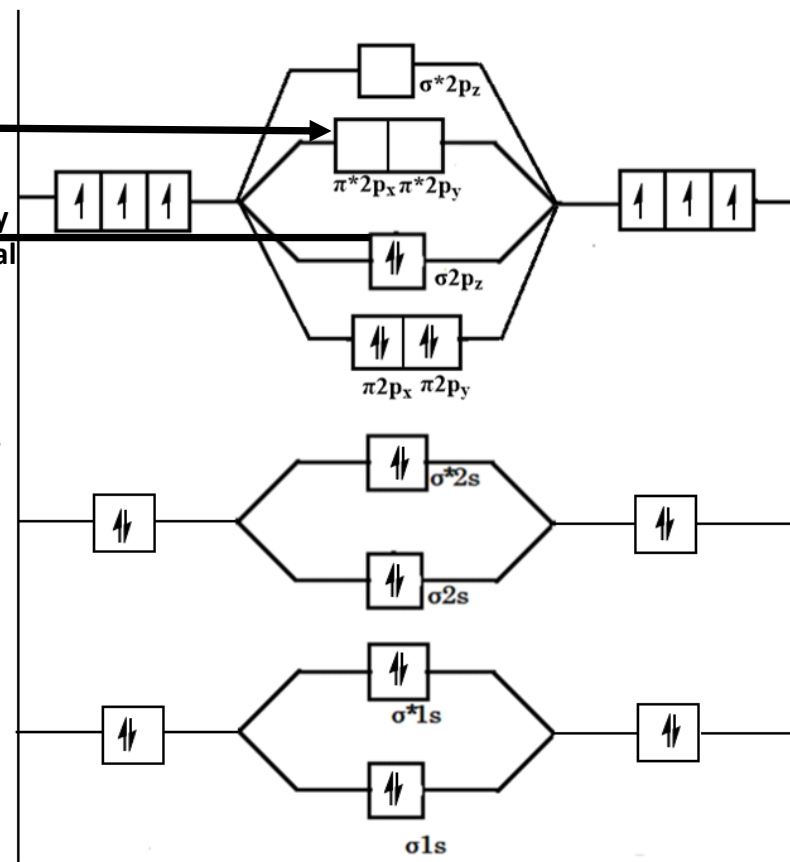
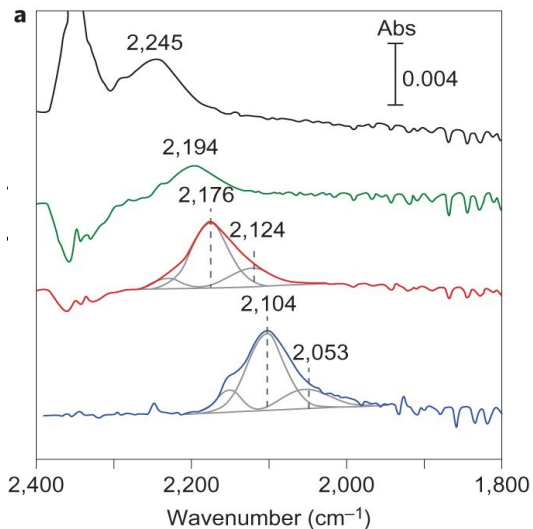
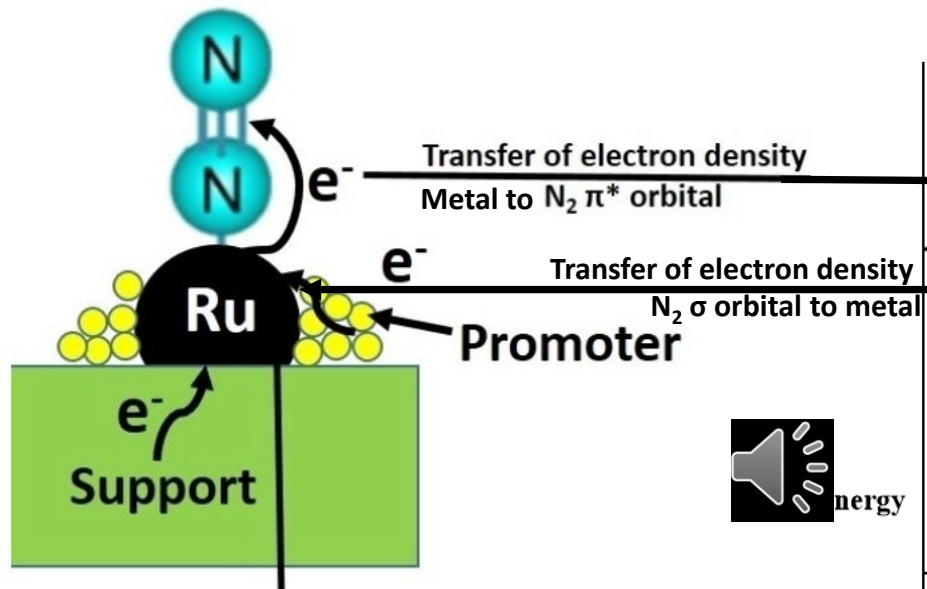
- Why Fe, Ru, Os? N_2 as a ligand in complexes!



Haber-Bosch synthesis of ammonia

- Why K?
- Electropositivity = ability to donate electrons
- Basicity (e.g. KOH) 
- No 1. mechanism: We need to push electrons back to N_2 = weakening of $N\equiv N$ triple bond
- No 2. mechanism: We need to desorb NH_3 from catalyst surface. Basic NH_3 desorbs well from basic surface.

Haber-Bosch synthesis of ammonia



N_2 molecular orbital diagram

Haber-Bosch synthesis of ammonia

- Ways of improvement, thorough studies
 - Influence of Fe crystal planes
 - Back to Ruthenium
 - Alloys of metals with strong and weak interaction with N_2
 - Electron-donating supports („nitrides“, hydrides, oxides, carbon)
 - Metal nitrides as catalyst supports (MvK)
 - Electrocatalytic NH_3 synthesis

Haber-Bosch synthesis of ammonia

- Fe-K₂O-Al₂O₃: Industrial production

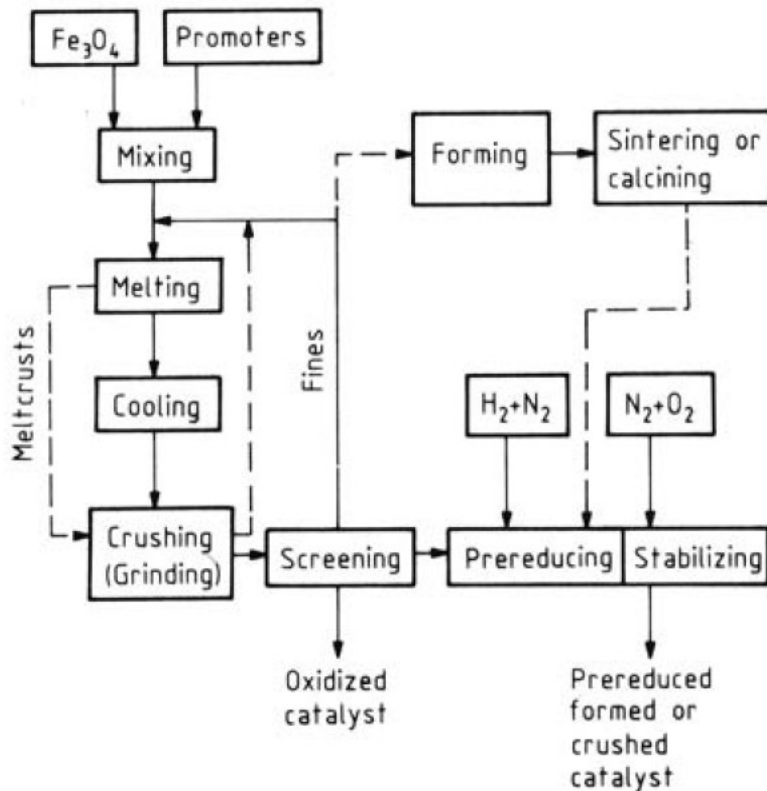


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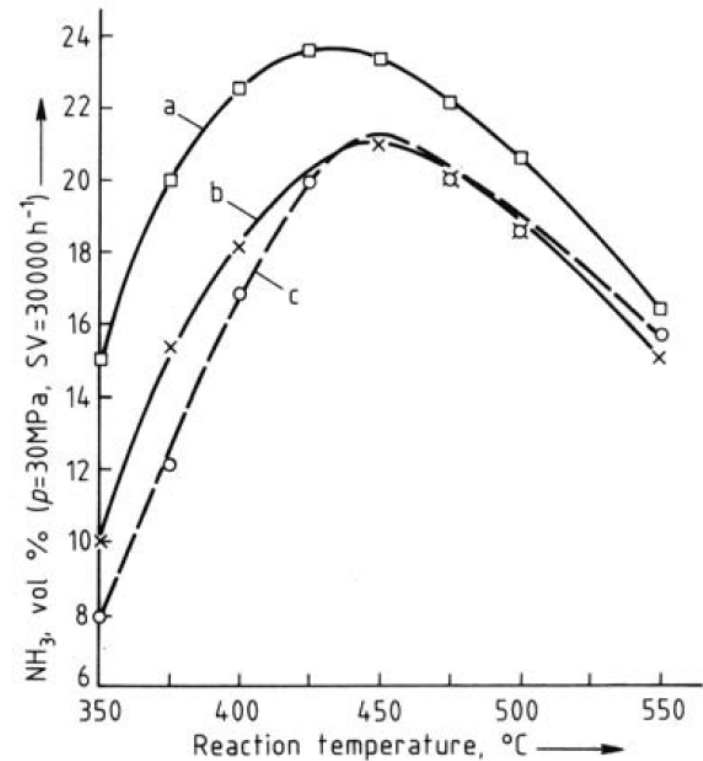


Figure 17. Effect of the melting temperature and rate of cooling of the melt on the activity of ammonia catalysts
a) Melt overheated to 3500 °C (rapid cooling); b) Melt temperature 1800 – 2000 °C (rapid cooling); c) Melt temperature 1800 – 2000 °C (slow cooling)

Haber-Bosch synthesis of ammonia

- Comparison of catalytic activity on different Fe crystal planes (111 vs. 100 vs. 110)

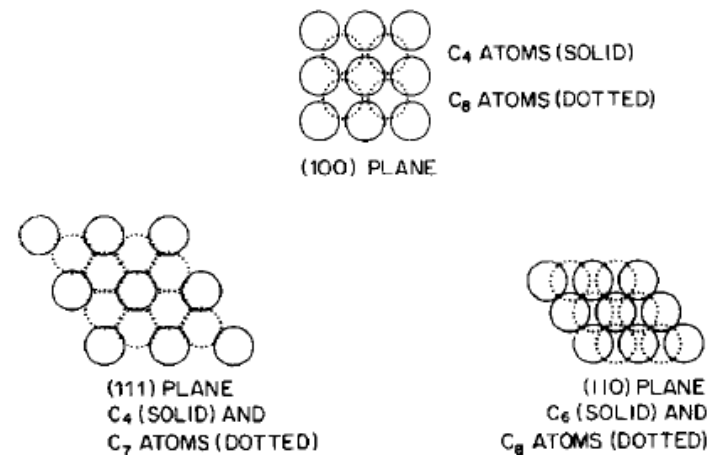
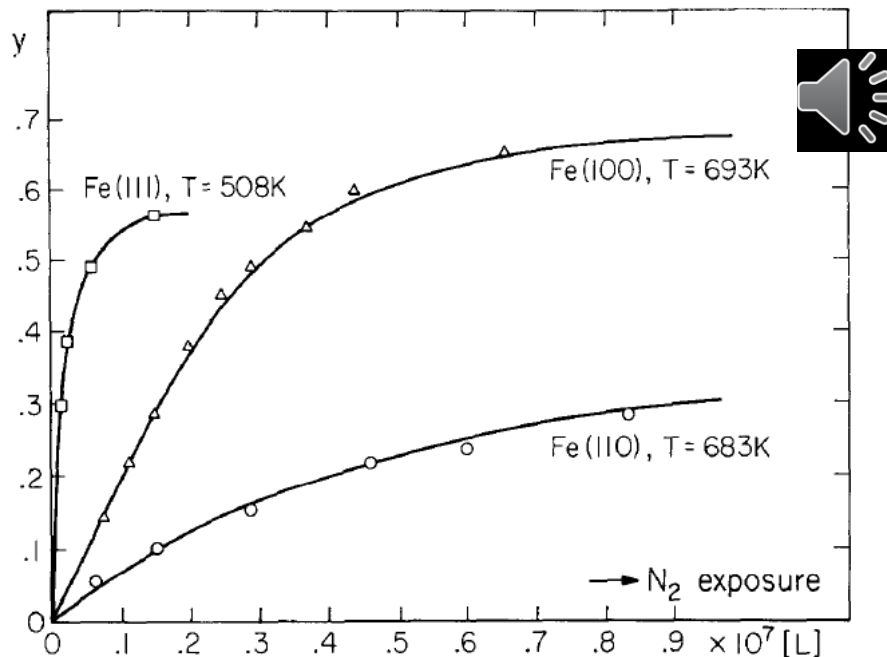


FIG. 1. Low-index planes of iron.

FIG. 2. Variation of the relative nitrogen surface concentration γ with N_2 exposure on Fe(110), (100), and (111) planes. [With Fe(111) no data for higher temperatures are available.]

Haber-Bosch synthesis of ammonia

- Alloying of metals with strong and weak interaction with N_2

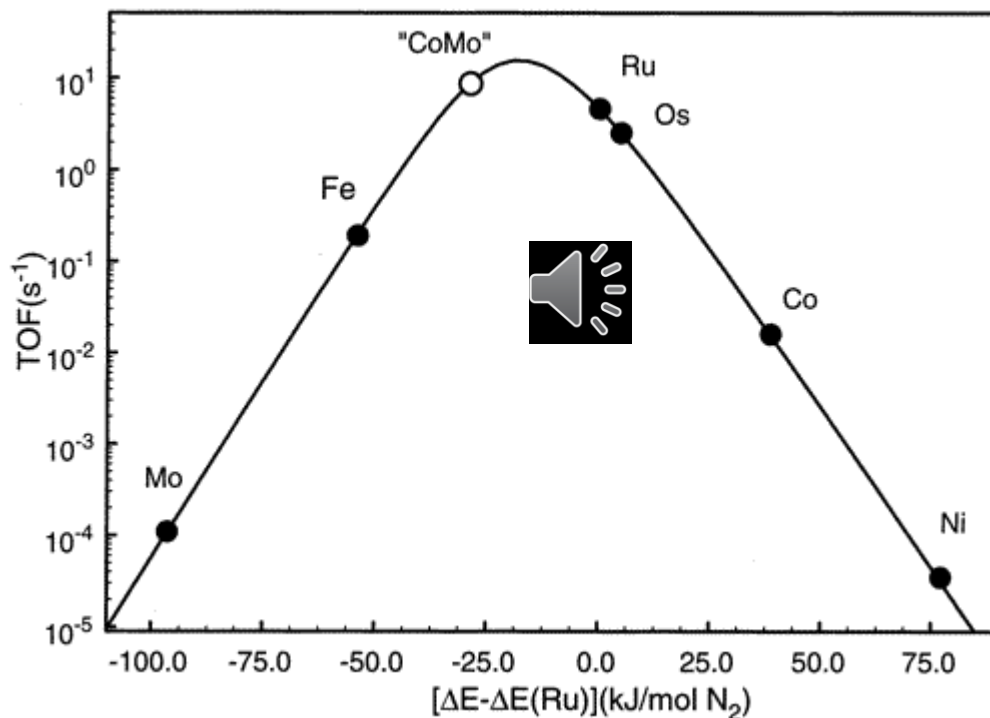


Figure 1 Calculated turnover frequencies for ammonia synthesis as a function of the adsorption energy of nitrogen. The synthesis conditions are 400 °C, 50 bar, gas composition $H_2:N_2 = 3:1$ containing 5% NH_3 .

Haber-Bosch synthesis of ammonia

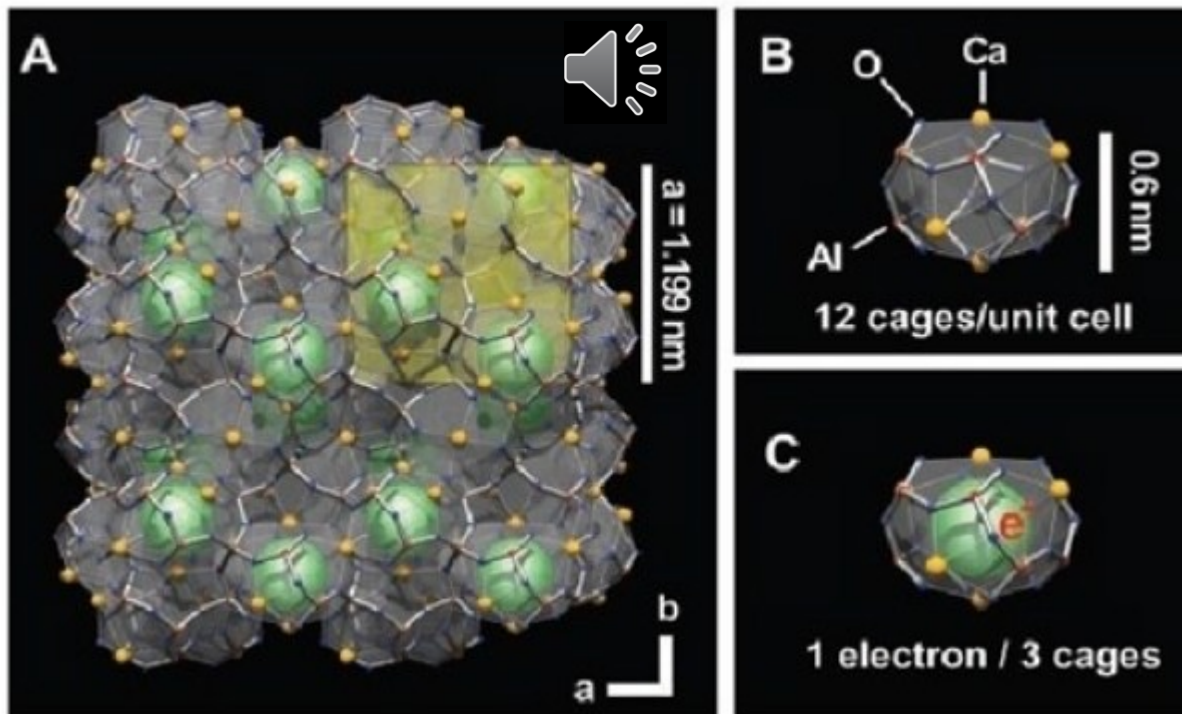
- Back to Ruthenium
 - Let's forget about price (**stable** and **active** catalyst might pay back)
 - Ru suffers from too strong H₂ chemisorption (i.e. H₂ effectively works as catalyst poison, no spot for N₂ chemisorption at high pressures)
 - In 1992 new catalyst patented: Ru-Ba-K/C (British Petroleum); minor but industrial use
 - New activity benchmark for catalytic studies

Table 2
Comparison of iron catalysts and ruthenium catalysts.

Catalyst type	Resource	Manufacturing cost (10 ³ * Yuan/m ³)	Conditions			Energy consumption (GJ/t)
			<i>T</i> /°C	<i>P</i> /MPa	H ₂ /N ₂	
Fe	abundant	30	350–525 (wide)	10–30	2–3	~ 27
Ru/AC	scarce	1600	325–450 (narrow)	≤ 10	≤ 2	~ 27

Haber-Bosch synthesis of ammonia

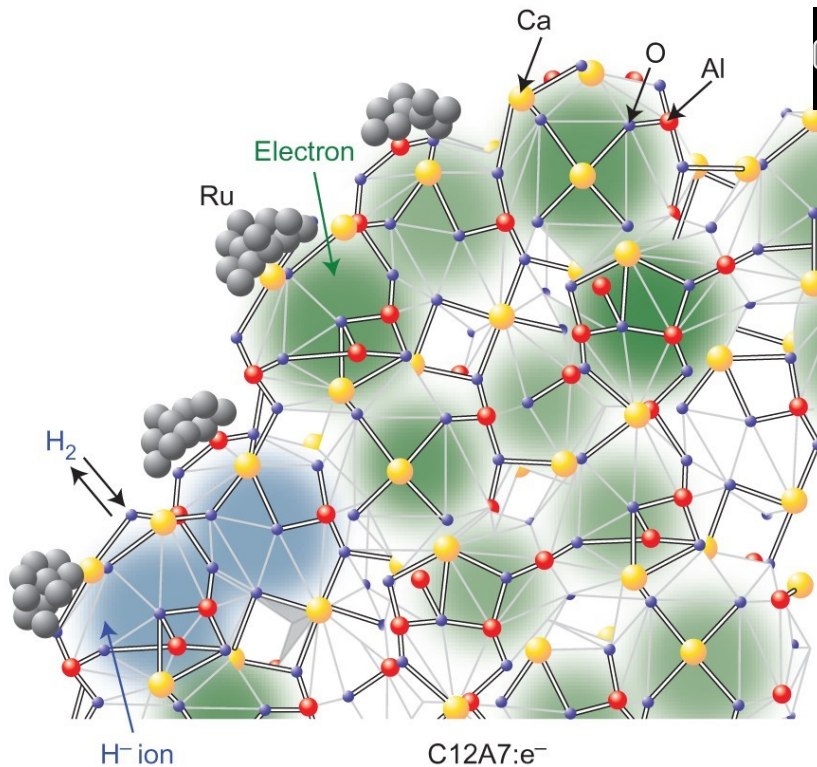
- Electron donating catalyst supports („Electrides“)
 - E.g. Mayenite: $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$
 - $2 \times 12\text{CaO}\cdot 7\text{Al}_2\text{O}_3 + 4 \text{H}_2 \rightarrow [\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot 4(\text{H}^-) + 2 \text{H}_2\text{O}$
 - $2 \times 12\text{CaO}\cdot 7\text{Al}_2\text{O}_3 + 2 \text{Ca} \rightarrow [\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} \cdot 4(\text{e}^-) + 2 \text{CaO}$



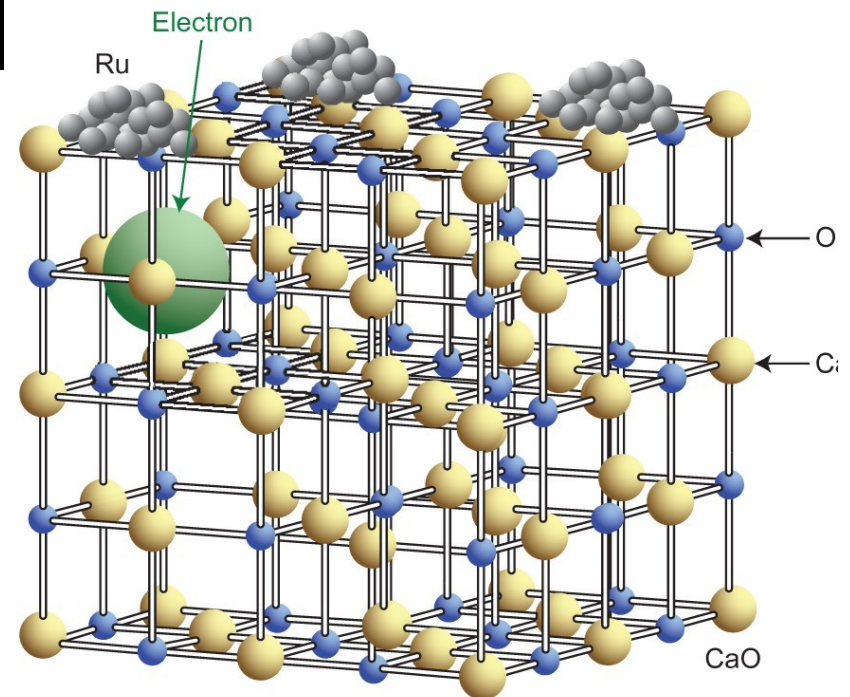
Haber-Bosch synthesis of ammonia

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a



b

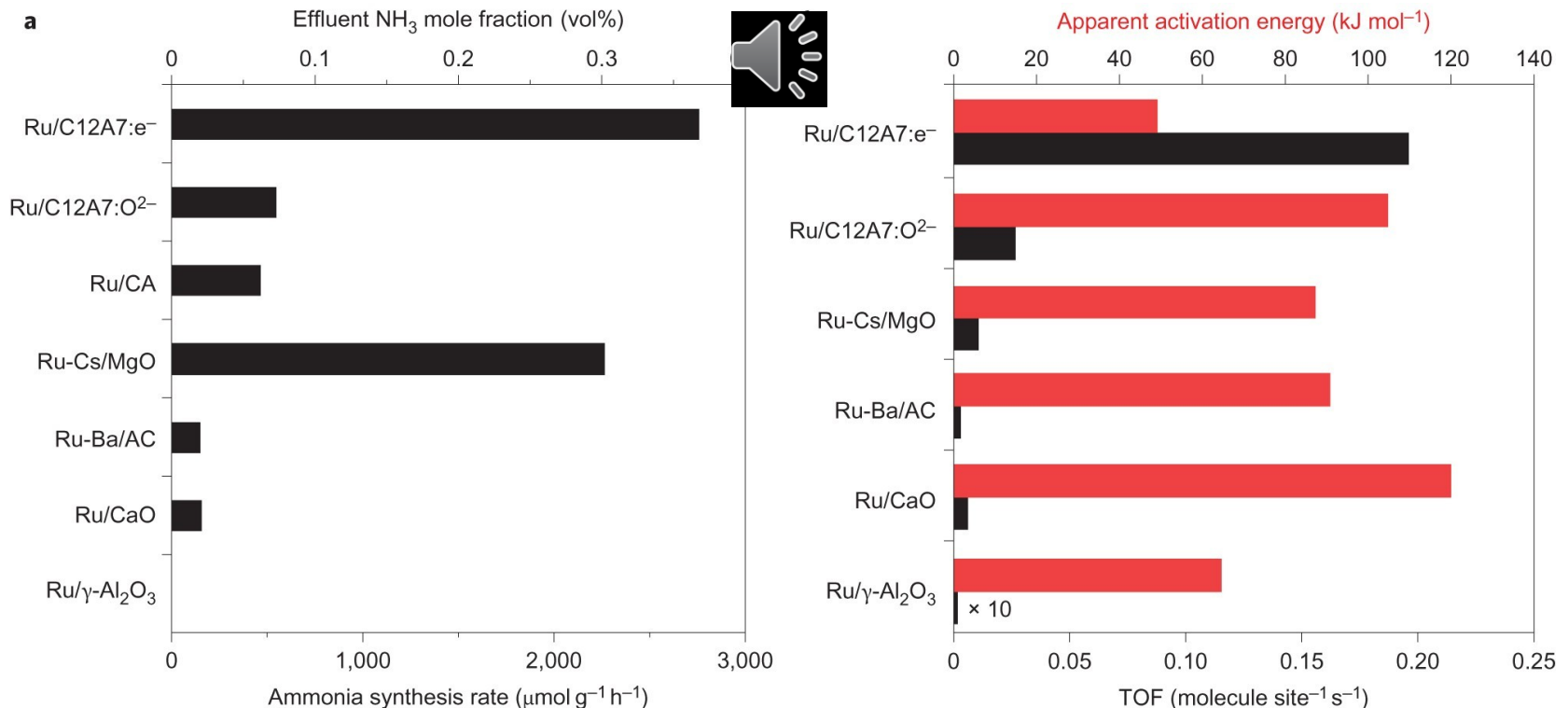


Haber-Bosch synthesis of ammonia

- Electron donating catalyst supports („Electrides“)
 - Ru/[Ca₂₄Al₂₈O₆₄]⁴⁺.4(e⁻): N≡N triple bond dissociation is not a rate determining step anymore!
 - N-H bond formation becomes RDS

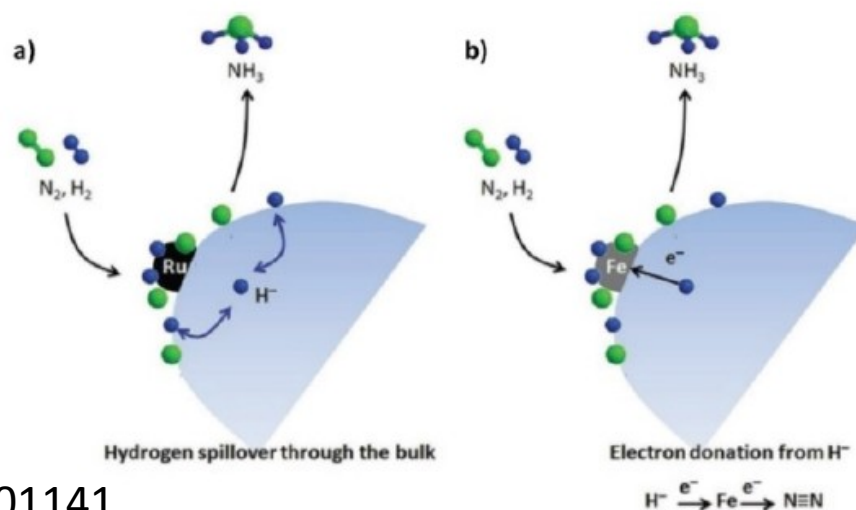
Nature 2012

DOI: 10.1038/NCHEM.1476



Haber-Bosch synthesis of ammonia

- Electron donating catalyst supports (Hydrides)
 - LiH, CaH₂, TiH₂, CaFH, Ca₂NH, BaCeO_{3-x}N_yH_z
 - H⁻ are strongly electron donating species
 - Moreover, they can release some H⁻ ion from the lattice and refill it with hydrogen from H₂ in the reaction mixture
 - Deactivation: Highly reactive hydrides (e.g. LiH) form surface layer of imides and nitrides = deactivation. Some extra hydrogen needed to prevent it.



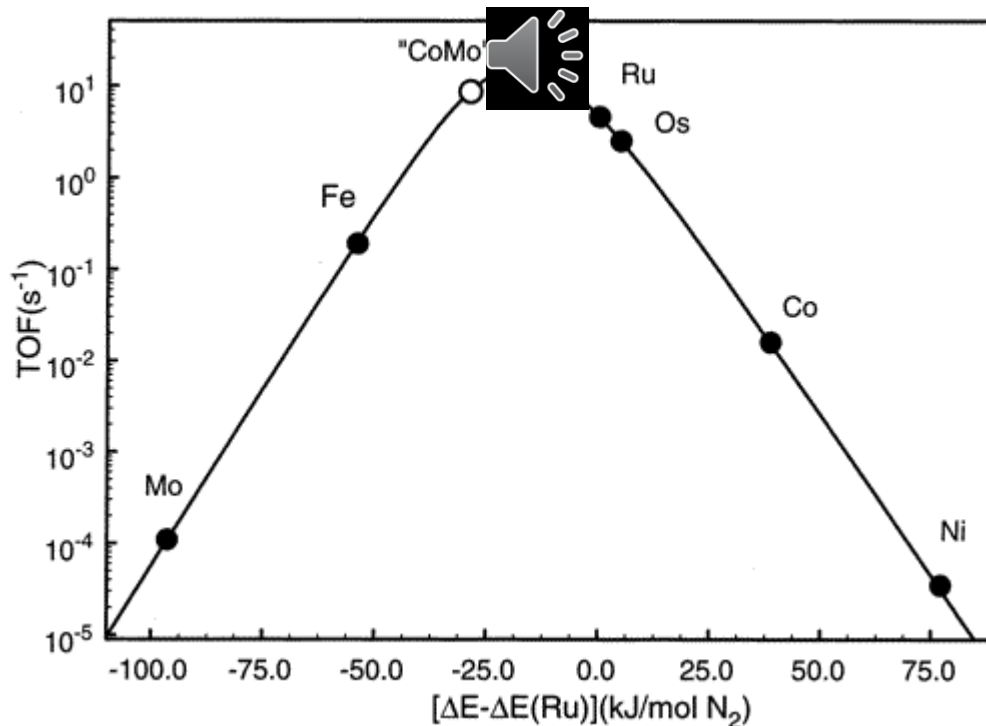
Haber-Bosch synthesis of ammonia

- Electron donating catalyst supports (others)
 - Oxides based mostly reduced CeO_2
 - Carbon



Haber-Bosch synthesis of ammonia

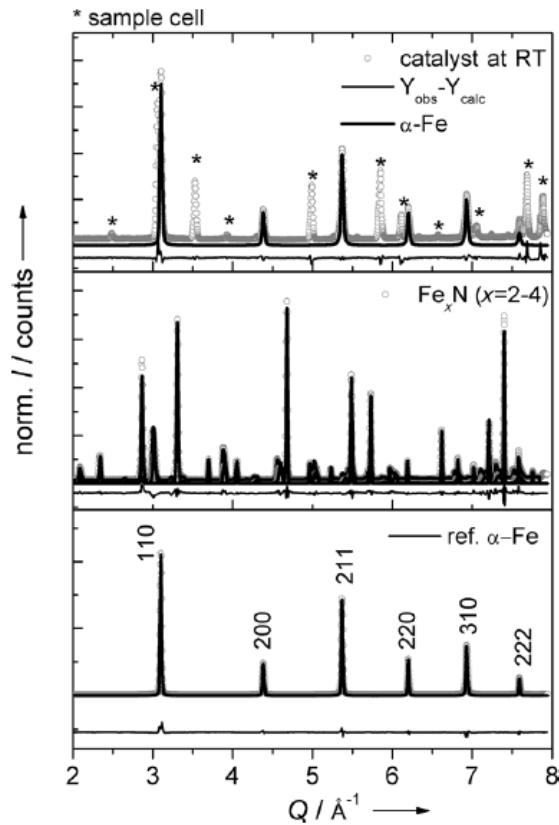
- Metal nitrides
 - Nitrogen can be released from their lattice and later on refilled from N_2 in the reaction mixture (MvK)
 - Fe, Mo: Strong N_2 chemisorption. Formation of Fe, Mo nitrides in situ?



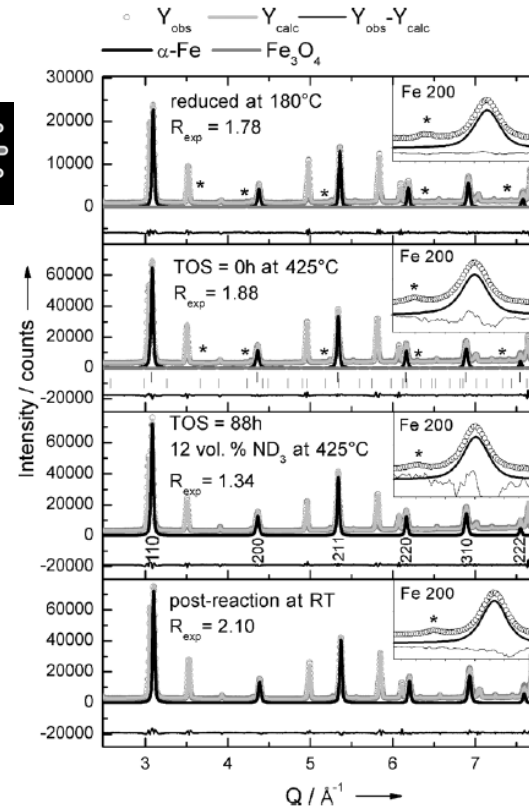
Haber-Bosch synthesis of ammonia

- Metal nitrides
 - promoted Fe, the industrial catalyst: Big question!
 - Nitridation of Fe by NH_3 known from steel industry (steel hardening)
 - Thermodynamic data suggest Fe nitrides stable at H-B rxn conditions

Post catalytic run neutron diffraction



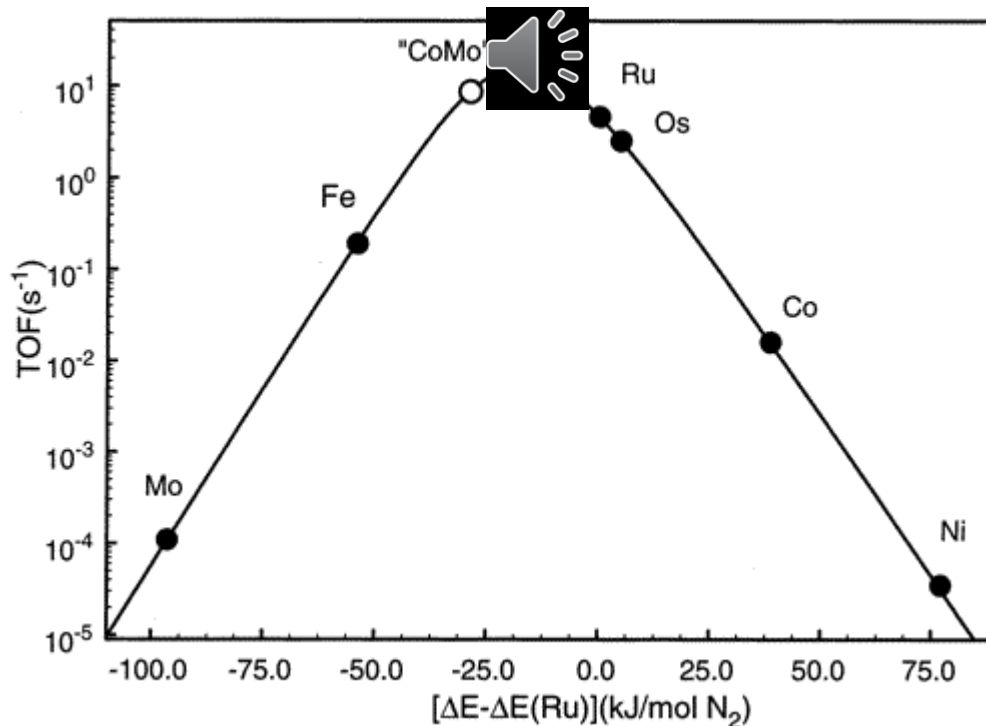
In situ neutron diffraction



**Iron nitrides
NOT
observed in bulk!
Surface?**

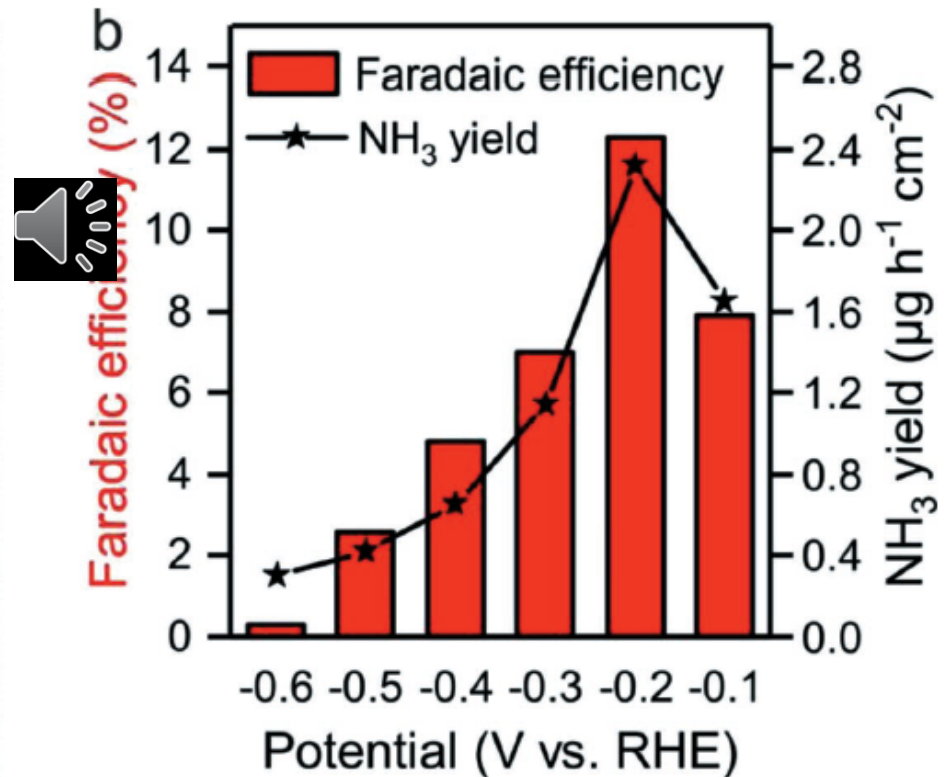
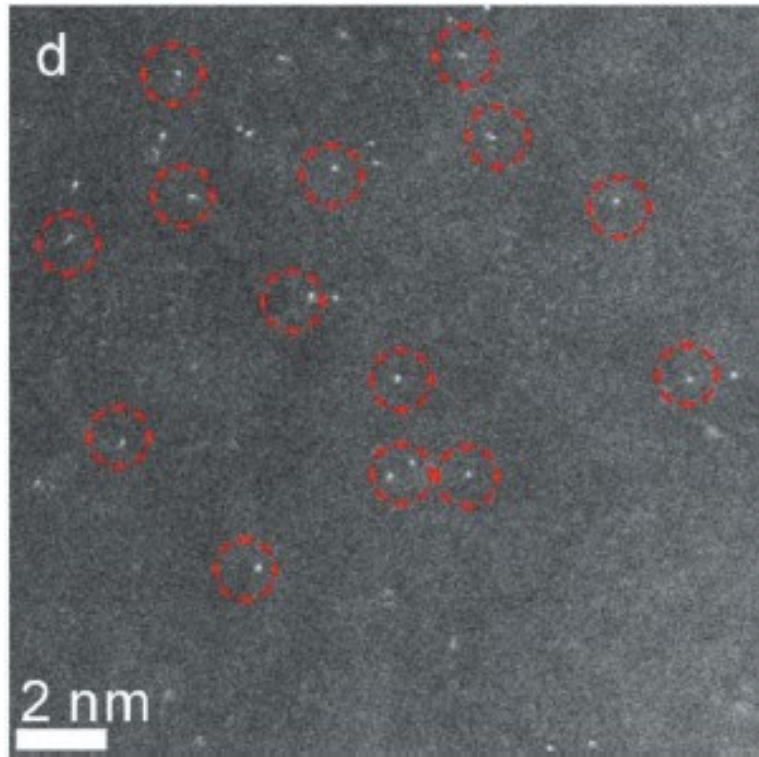
Haber-Bosch synthesis of ammonia

- Metal nitrides
 - Mo? Its interaction with N_2 even stronger than in Fe!
 - Mo nitrides formation observed!
 - CoMo alloy? Co_3Mo_3N !



Electrocatalytic NH₃ synthesis

- Single Au atoms deposited on N-doped graphene layers



Enzymatic N₂ fixation and its transformation to NH₃

- Nature
 - Nitrogenase
 - RT
 - Ambient pressure
 - It works! And much better than all our „tailored“ catalysts.

