

CATALYSTS

"AMMONIA SYNTHESIS"

Dr. Antonio Vita

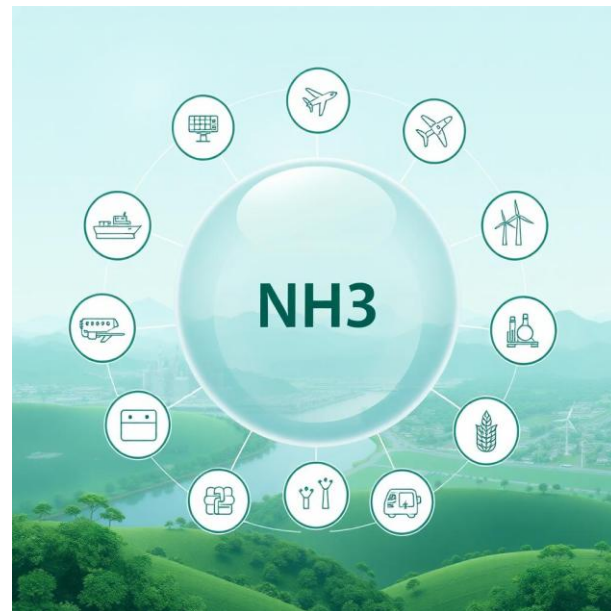


Fuel Processing Materials and Technologies



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WORKSHOP AMMONIA AS ENERGY CARRIER (PART II)

24th October, 2025

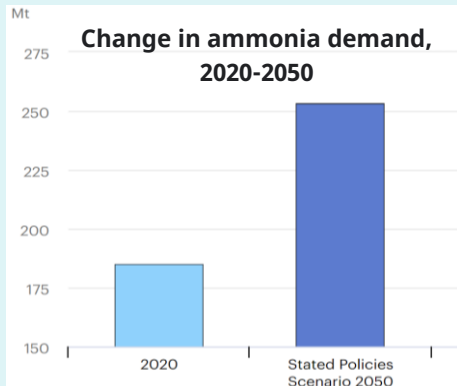
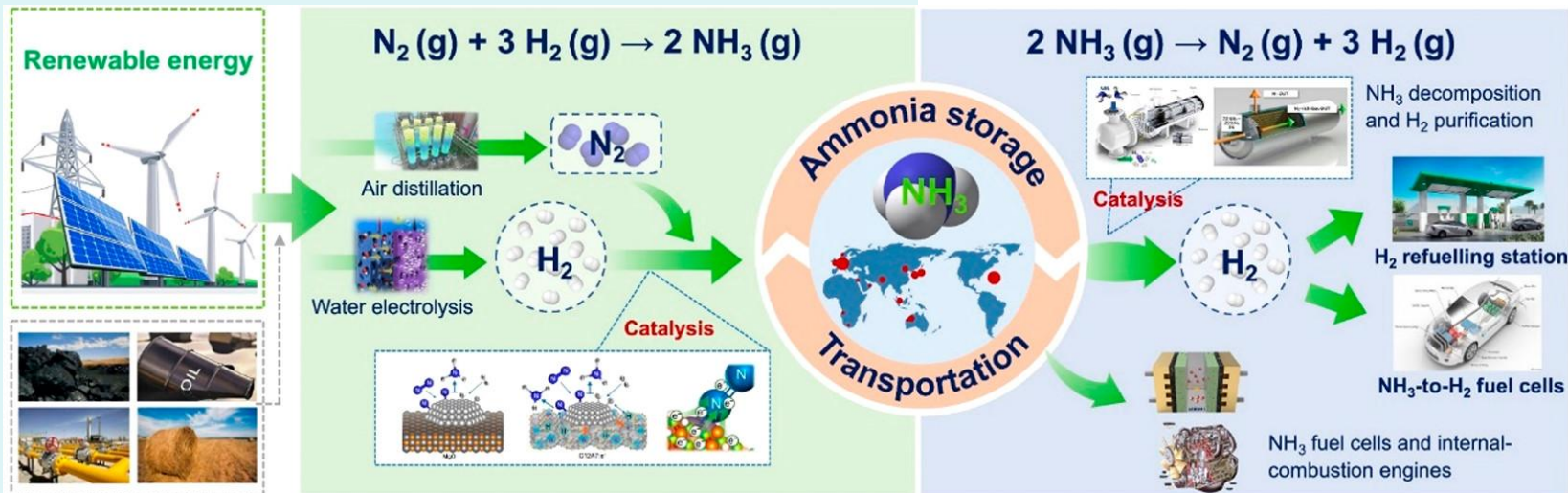


(Microlab - Eindhoven)



1 WHY AMMONIA?

AMMONIA AS ENERGY CARRIER VIA AMMONIA SYNTHESIS AND DECOMPOSITION

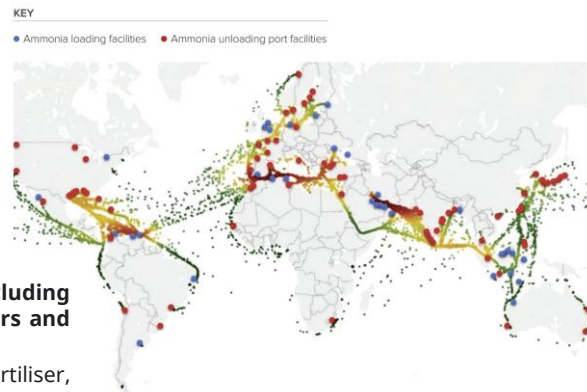


- It has a high hydrogen content (17.6 wt%)
- It can liquefy at 8.6 Bar at 25 °C, resulting in a high volumetric energy density of 10.5 MJ L⁻¹, which is twice that of compressed hydrogen at 70 MPa (5 MJ L⁻¹)

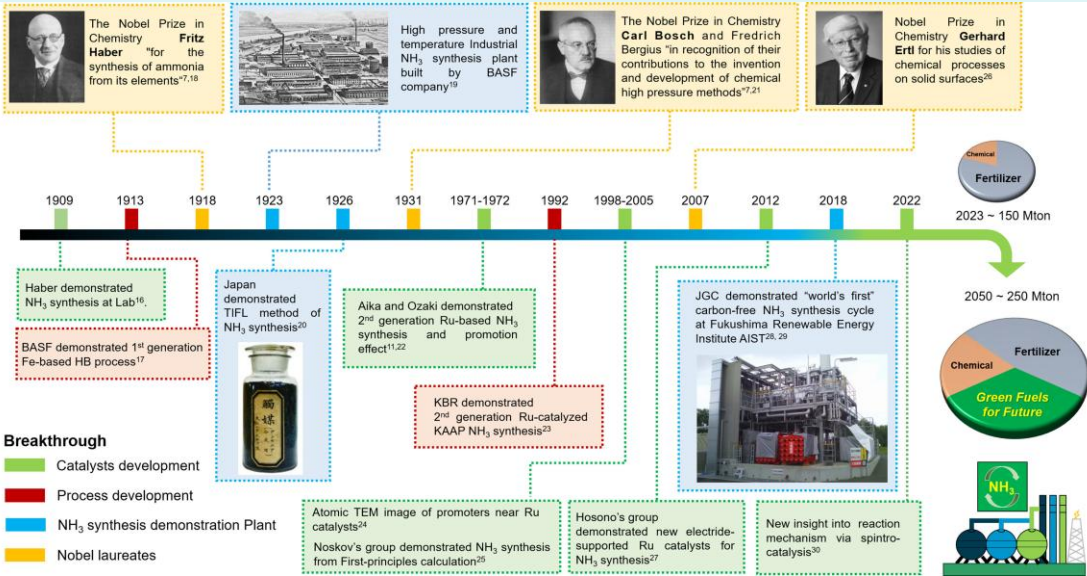
Ammonia: 121 kg H₂/m³, Methanol: 99 kg H₂/m³, Liquid Hydrogen: 71 kg H₂/m³, LOHC: 57 kg H₂/m³

Ammonia shipping infrastructure, including a heat map of liquid ammonia carriers and existing ammonia port facilities.

(Royal Society Ammonia: zero-carbon fertiliser, fuel and energy store2020).



CATALYSTS FOR AMMONIA PRODUCTION ON LARGE AND LAB SCALE



Timeline of historical event and important progress in NH₃ synthesis (EnergyChem 6, 2024, 1001)

- Haber-Bosch (HB) process for industrial NH₃ synthesis operated at high temperature (500 °C) and pressure conditions (100-300 atm) with iron catalysts.



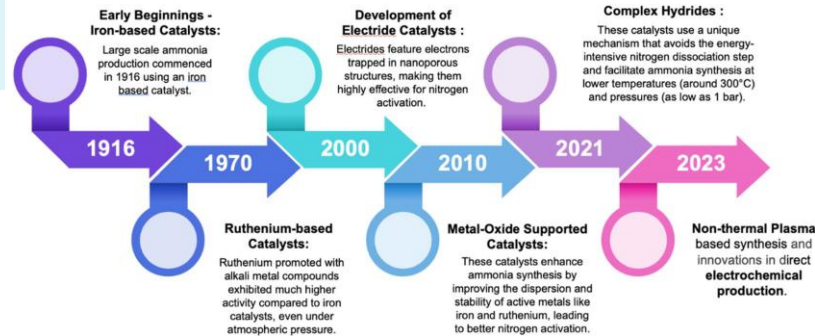
Ammonia synthesis is deceptively simple



$\text{N} \equiv \text{N}$ Easy to find, hard to use (limiting step: activation of the stable $\text{N} \equiv \text{N}$ bond, 945 kJ mol⁻¹)

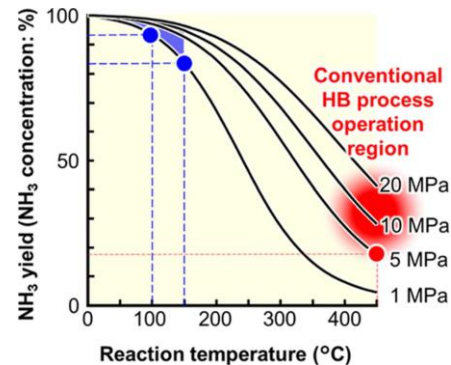


Under pressure and temperature (150 - 300 bar, ≈ 500°C)



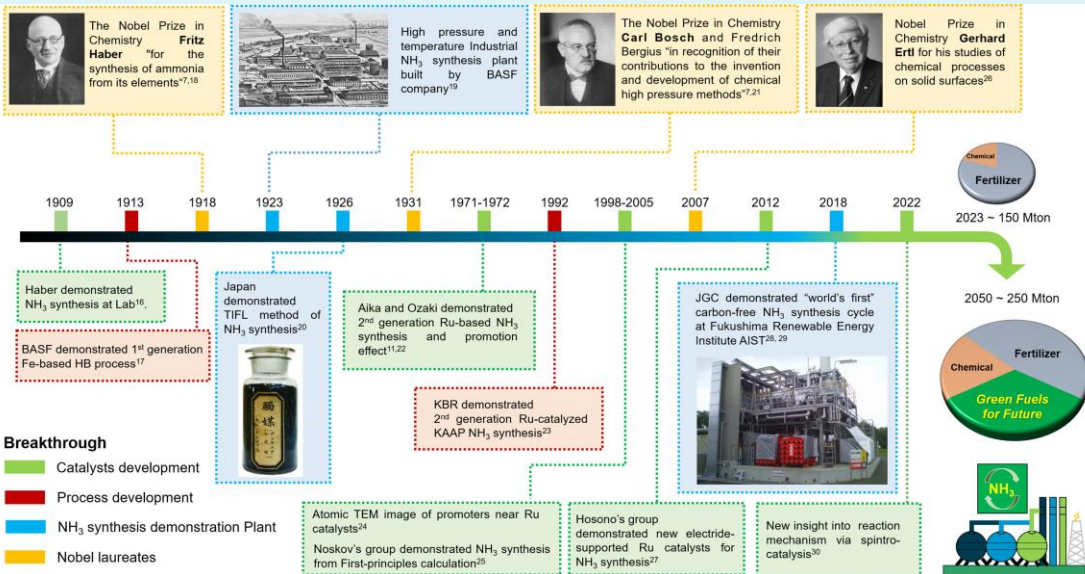
Timeline showing the development of various catalysts for ammonia synthesis. J. Mater. Chem. A, 2025, 13 15361

- Daily production capacity: 1000 - 2200t;
- Efficiency: 65%
- Gas velocities: 10000-20000m³ / m_{cat.}³ h;
- Typical conversions: 8-15%



Temperature- and pressure-dependent production of ammonia with the corresponding yields (%). Adapted from the work of Hattori et al.,²⁶ licensed under CC BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

CATALYSTS FOR AMMONIA PRODUCTION ON LARGE AND LAB SCALE

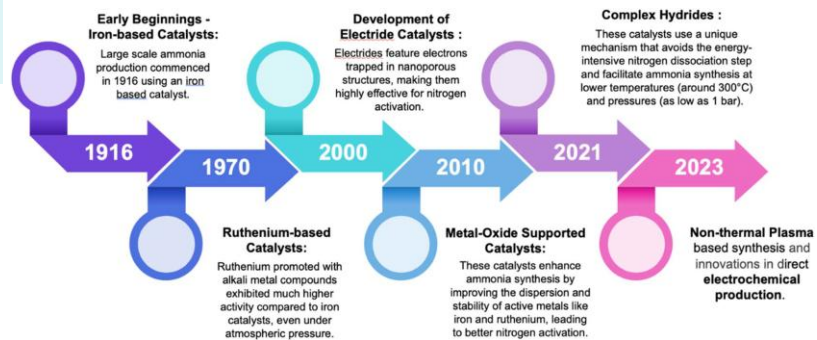


Timeline of historical event and important progress in NH_3 synthesis (EnergyChem 6, 2024, 1001)

- The discovery and optimization of these **2nd-generation catalysts (Ru-based)** led to a new industrial process for the production of ammonia called the **Kellogg Advanced Ammonia Process (KAAP)**, in which it is possible to obtain **yields of 40–50%**, at lower temperatures (**370–400 °C**) and pressures (**50–100 bar**) as compared to the conventional Haber–Bosch process using iron oxides as the catalyst
- Ru-based catalysts** promoted by 1A and 2A elements, particularly Ba and Cs, **show promise in electrolysis-driven HB** operating under intermittent conditions.

Advantages of Ru-based Catalyst (KAAP process)

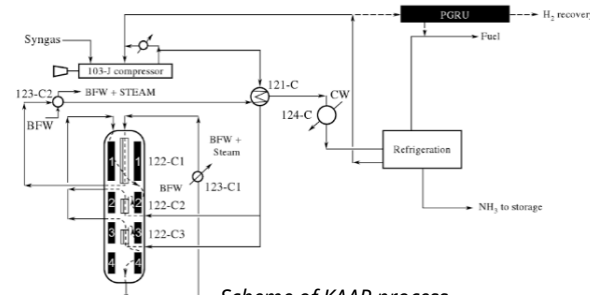
- Enables **lower-pressure ammonia synthesis**, reducing capital costs;
- Allows use of **lighter and thinner equipment** (compressors, vessels, fittings, piping);
- Improved energy efficiency** – about **40% lower energy consumption** compared to conventional designs;
- Enhanced heat recovery** at higher temperatures;
- Simplified synthesis loop**, reducing operational complexity and operator workload;
- Higher reliability** due to fewer components and simpler operation.



Timeline showing the development of various catalysts for ammonia synthesis.

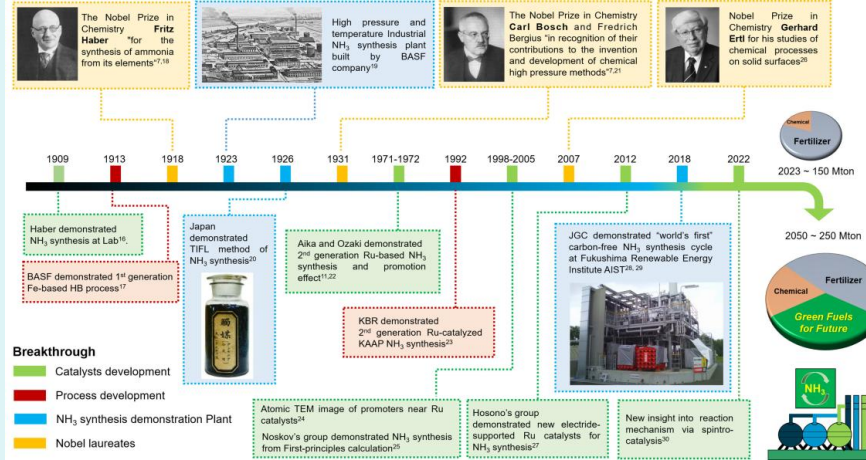
J. Mater. Chem. A, 2025, 13 15361

Year	IRON			RUTHENIUM
	Fe_3O_4	Fe_3O_4 with Co	Fe_{1-x}O	Ru–Ba–K/AC
1913	1979	1986	1992	
Temperature (°C)	360–520	350–500	300–500	325–450
Pressure (bar)	120–450	100–300	100–250	70–100
Energy consumption (GJ/t _{NH3})	28	28	27–28	26–27
H ₂ :N ₂ ratio	2–3	2–3	2–3	1.5–2
Catalyst lifetime (y)	>14	–	6–10	≤10
Relative activity	1.0	1.2	1.5	2–10
Thermal stability	High	Medium/Low	Medium	Low
Relative catalyst cost	1.0	1.5	1.1	150–230



Scheme of KAAP process

CATALYSTS FOR AMMONIA PRODUCTION ON LARGE AND LAB SCALE



Timeline of historical event and important progress in NH_3 synthesis (EnergyChem 6, 2024, 1001)

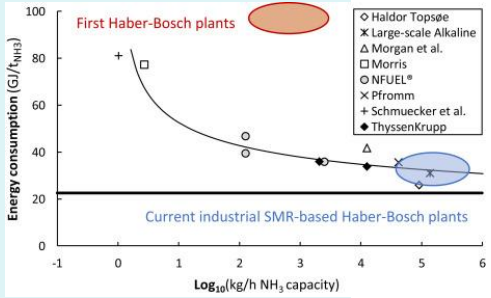
Decarbonisation of ammonia production

“Renewable sources of energy such as biomass, solar, wind or geothermal are characterized by a highly distributed production across regions”

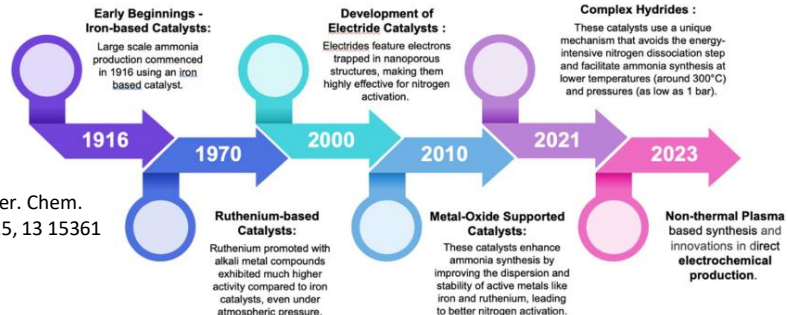
- A **large-scale** ammonia plant ($\geq 1000 \text{ t}_{\text{NH}_3}/\text{d}$) consumes about **2-7 GJ/t_{NH3}** for pressurizing, heating, pumping and utilities;
- At **intermediate scales** ($3\text{-}20 \text{ t}_{\text{NH}_3}/\text{d}$), this energy consumption increases to typically **13-14 GJ/t_{NH3}**
- At **very small scales** ($<0.1 \text{ t}_{\text{NH}_3}/\text{d}$), heat is even required to keep the ammonia synthesis reactor at the synthesis temperature due to radial heat losses, and hydrogen and nitrogen production also becomes less efficient

Upon scale-down, heat losses increase and the energy consumption increases

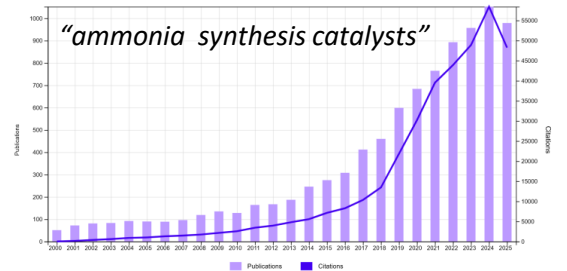
Milder operating conditions in the synthesis loop are required for effective scale-down



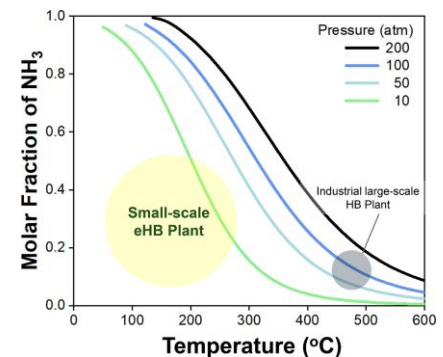
Energy consumption of various electrolysis-based Haber-Bosch processes (academic and industrial estimates). The bold line represents the thermodynamic minimum energy consumption (22.5 GJ/tNH₃)



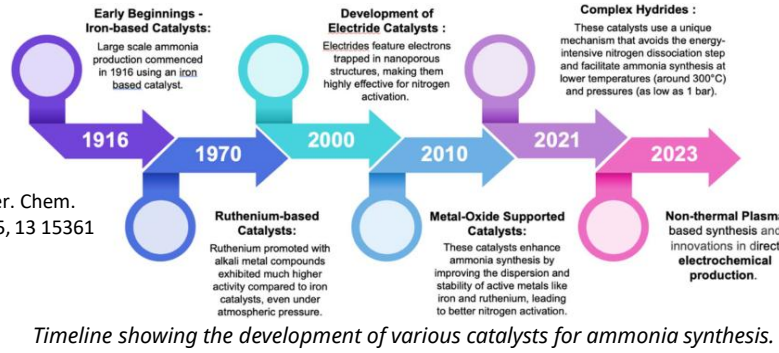
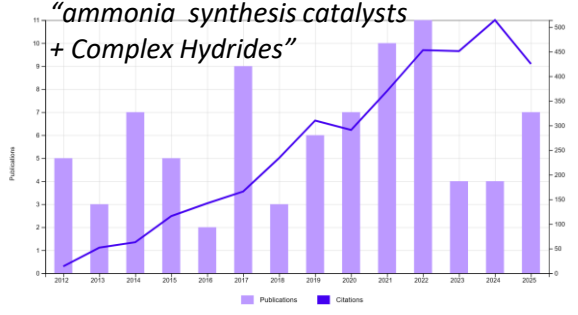
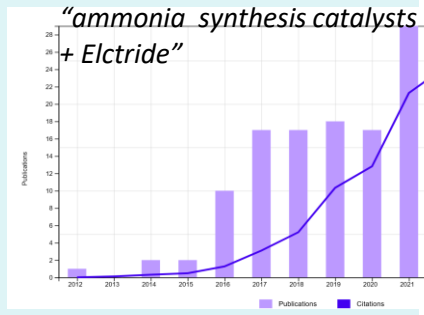
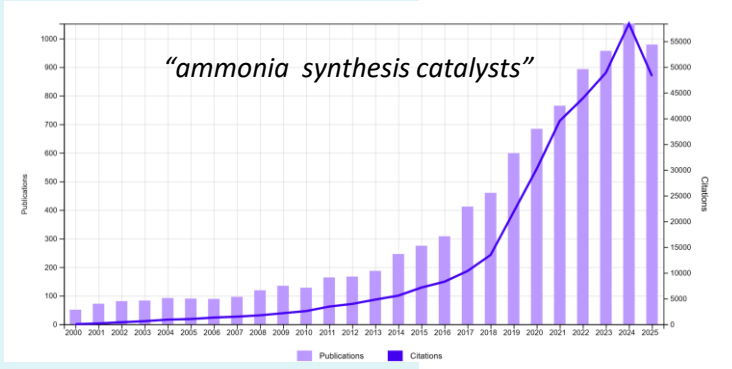
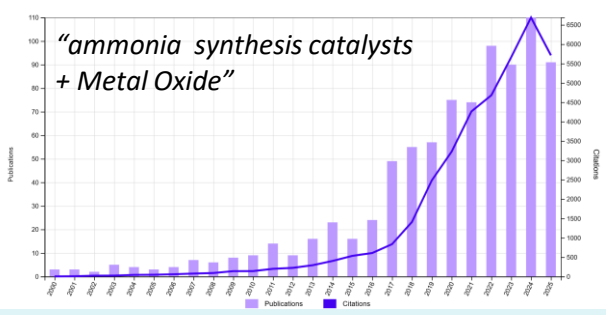
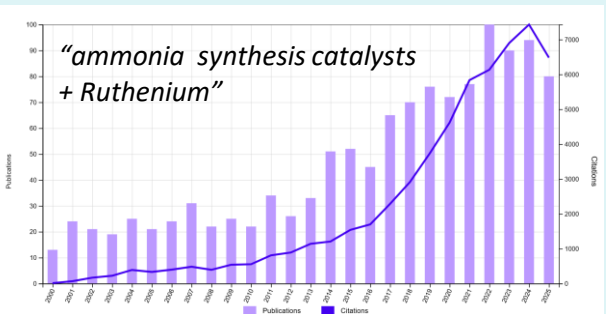
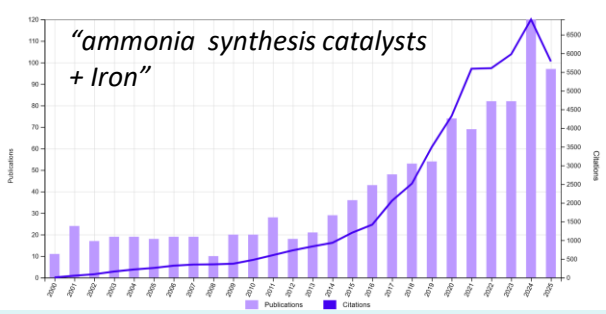
Timeline showing the development of various catalysts for ammonia synthesis.



Numbers of studies published from 2000 to 2025 extracted from Web of Science (Clarivate Analytics, London, UK) with the keywords: “ammonia synthesis catalysts”



CATALYSTS FOR AMMONIA PRODUCTION LAB SCALE RESEARCH



Timeline showing the development of various catalysts for ammonia synthesis.

Numbers of studies published from **2000 to 2025** extracted from **Web of Science** (Clarivate Analytics, London, UK) with the keywords: **"ammonia synthesis catalysts"**

IRON CATALYSTS

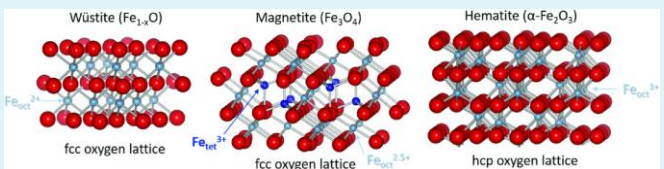
The heart of large-scale ammonia plant

Early Development of Iron-Based Catalysts



"Fused-iron catalysts are by far the most studied and widely applied of all the ammonia synthesis catalysts"

- Fused-iron catalysts are derived from three possible iron oxides, Fe_2O_3 (hematite), Fe_3O_4 (magnetite), and $Fe_{1-x}O$ (wüstite);
- The catalysts are produced in the same way today. Exact ratios of starting materials are mixed together and fused at around 1600°C. The main differences are additional promoters and the exact quantities and ratios of promoter species. The molten material is cooled and broken to the required size range.



Perspective side views of Fe-oxide crystal structures. (G. S. Parkinson, Surf. Sci. Rep. 2016, 71, 272)

Promoted Fe-Based Catalysts

"Different promoter combinations and catalyst formulations have been explored to optimize ammonia synthesis for improved efficiency, selectivity, and sustainability"

Samples	Total Fe	Fe ²⁺ /Fe ³⁺	Al ₂ O ₃	CaO	K ₂ O	C ₂ O ₄	SiO ₂	MgO	ΣRE ₂ O ₃
A110-3	68.0	0.51	2.2	1.2	0.59	—	0.36	—	—
A201	69.0	0.45	2.5	1.3	0.49	2.1	0.39	—	—
FA400	69.0	0.46	2.4	1.4	0.60	—	0.34	0.3	—
FA40 _{II}	68.0	0.43	2.3	1.1	0.58	—	0.33	0.3	0.38
FA402	68.0	0.46	2.4	1.1	0.58	0.5	0.39	0.4	0.37
ICT174-1*	—	—	2.5	1.9	0.8	5.2**	0.5	0.2	—

Compositions (wt.%) of various Iron promoted catalysts

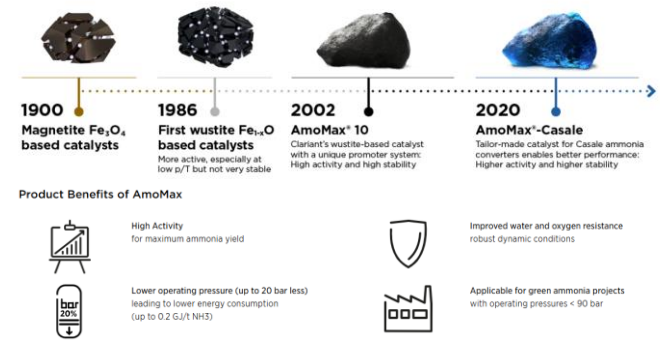
Generally, the Al₂O₃, K₂O, CaO, and SiO₂-promoted iron catalysts exhibit high activity with an ammonia concentration of 15–20% at the convertor outlet

Samples	10000 h ⁻¹		20000 h ⁻¹		30000 h ⁻¹	
	425 °C, 15 MPa	430 °C, 13 MPa	425 °C, 15 MPa	425 °C, 15 MPa	—	—
A110-3	19.5	17.6	17.0	17.0	14.6	—
A201	19.8	18.9	17.5	17.5	15.0	—
FA400	—	18.5	—	—	—	—
FA401	20.8	19.8	18.1	18.1	15.9	—
FA402	21.0	19.6	18.2	18.2	15.8	—
ICT174-1	21.1	—	17.9	16.0	—	—

NH₃ concentration (%) of various iron catalysts at different reaction conditions

Commercial Iron-based catalysts

AmoMax™-Casale is a new ammonia synthesis catalyst jointly developed by Casale and Clariant for use in Casale ammonia converters. The catalyst is a customized evolution of the well-known, wüstite-based catalyst



<https://www.clariant.com/en/Business-Units/Catalysts/Energy-Transition/Green-Ammonia>



KATALCO 35-4	Multi-promoted magnetite
KATALCO 35-8	Pre-reduced and stabilised multi-promoted magnetite
KATALCO 74-1	Multi-promoted magnetite
KATALCO 74-1R	Pre-reduced and stabilised multi-promoted magnetite

KATALCO 74-series ammonia synthesis catalysts contain **additional promoters** which offer the highest activity available from an iron-based ammonia synthesis catalyst. JM catalysts they have been used in ammonia synthesis loop operating with sa (1160-1740psi). JM ammonia **pressure as low as 80 - 120bar** and used in the ammonia converters of the world's largest (>3500tpd)

IRON CATALYSTS

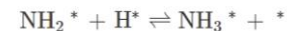
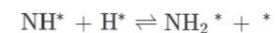
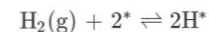
Promoted Fe-Based Catalysts

“Different promoter combinations and catalyst formulations have been explored to optimize ammonia synthesis for improved efficiency, selectivity, and sustainability”

Catalyst	Promoter [wt%]	Reactor temperature [°C]	Reactor pressure [MPa]	Weight hourly space velocity (WHSV) [mL g ⁻¹ h ⁻¹]	NH ₃ percentage in reactor outlet [v/v%]	NH ₃ synthesis rate [μmol g ⁻¹ h ⁻¹]
7% Fe/CeO ₂ (applied electric field 6 mA)	–	100	0.1	144 000	–	155
20% Fe–BaH ₂ (chemical looping synthesis)	–	300	0.1	60 000	–	1703
2.8% Fe/γ-Al ₂ O ₃	–	320	0.1	–	–	0.12
20% Fe–BaH ₂	–	350	0.1	60 000	–	384
Fe(95%)Co(5%)	–	400	0.1	–	–	820.07
Fe(85%)Ni(15%)	–	400	0.1	–	–	334.354
1.2% Fe/BaCeO _{3-x} H ₂ N _x	–	400	0.9	36 000	–	6800
Fe ₉₁ Zr ₉	–	417	0.9	–	–	72
Fe–5LiH	–	300	1	60 000	–	4840
Fe/LiH	40%LiH	350	1	60 000	–	11 428
10% Fe/C	3.5%Ba	400	1	53 400	–	14 400
80% Fe/Ce _{0.8} Sm _{0.2} O _{2-x} s	–	450	1	16 000	–	8700
Fe _{1-x} O	–	400	3	–	7.94	–
FePc	10% Cs	400	3	12 000	–	14 000
Fe-Metal organic framework derived catalyst (MDC)	1% K	400	3	13 500	–	30 400
Fe _{1-x} O	(Al ₂ O ₃ + CaCO ₃ + K ₂ CO ₃) <10 wt%	430	3	7200	–	11 900
Fe ₃ O ₄	(Al ₂ O ₃ + CaCO ₃ + K ₂ CO ₃) <10 wt%	430	3	7200	–	9200
1% Fe/BaTiO _{3-x} H _x	–	400	5	66 000	–	14 000
10% Fe/C	K	470	9	140 000	4.58	–
2% Co–8% Fe/C	K	470	9	140 000	6.04	–
FeOOH/Al ₂ O ₃	K (5 wt%)	500	9	26 400	–	32 850
Fe _{1-x} O	–	425	10	–	19.23	–
ZBRW-10 (wustite)	Al ₂ O ₃ (2.18 wt%) + CaO (1.3 wt%) + K ₂ O (0.44 wt%) + CoO (2.1 wt%)	450	10	–	10.8	–
Fe ₃ O ₄	2.4% Al ₂ O ₃ , 1.4% CaO, 0.6% K ₂ O, 0.34% SiO ₂ , 0.3% MgO	425	15	–	20.8	–
Fe ₃ O ₄	2.3% Al ₂ O ₃ , 1.1% CaO, 0.58% K ₂ O, 0.33% SiO ₂ , 0.3% MgO	425	15	–	21.0	–
Fe ₃ O ₄	2.4% Al ₂ O ₃ , 1.1% CaO, 0.58% K ₂ O, 0.39% SiO ₂ , 0.4% MgO, 0.5% Co ₃ O ₄	425	15	–	21.1	–
Fe ₃ O ₄	Al ₂ O ₃ , K, Ca, 0.6% Nb ₂ O ₅	450	15	–	18	–

Mechanism of ammonia synthesis in the pressure range of industrial interest

- The generally accepted mechanism for ammonia synthesis on Fe is known from experiment, and it is a **Langmuir-Hinshelwood mechanism** in which the first step is also the rate-determining step (RDS).



- The mechanism proceeds via the **adsorption of dinitrogen onto the catalyst surface**. This is followed by **dissociation to adsorbed nitrogen atoms, which is the rate determining step**. **Direct dissociative adsorption of H₂ to hydrogen atoms proceeds, followed by the stepwise addition of hydrogen atoms to the nitrogen atoms to sequentially form adsorbed NH, NH₂ and NH₃ species, and finally desorption of the NH₃ product.**



This mechanism is a dissociative mechanism and is the one accepted for the two currently used industrial catalyst Fe and Ru.

RUTHENIUM-BASED CATALYSTS

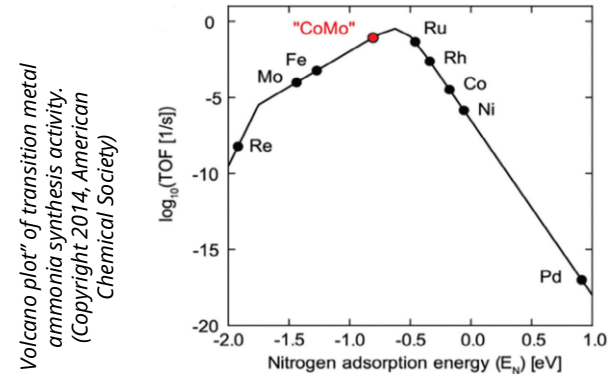
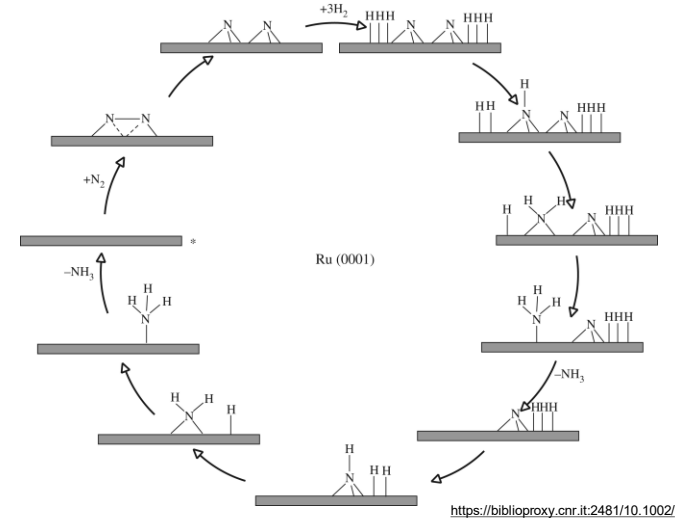
Supported Ru Catalysts

“Supported ruthenium catalysts are the second most common NH_3 synthesis catalyst and the only other to be used industrially for NH_3 synthesis”

- The **RDS is the dissociation of N_2** , which was calculated to have a lower barrier at steps;
- The **dissociative mechanism** is that of a typical Langmuir–Hinshelwood mechanism in which **N_2 adsorbs dissociatively** followed by the **dissociation of three H_2 forming $\ast\text{N}$ and $\ast\text{H}$ species**, respectively, These species are co-adsorbed on the surface of the catalyst in positions that allow the reaction of $\ast\text{H}$ with $\ast\text{N}$;
- In the next step, **hydrogen atoms are added to nitrogen atoms forming first $\ast\text{NH}$, then $\ast\text{NH}_2$ and finally $\ast\text{NH}_3$ which desorbs** from the catalytic surface.
- After the desorption of the first NH_3 , **the remaining $\ast\text{N}$ is hydrogenated** via a similar process to the previous step, in order to form a second NH_3 molecule.

- The activation of N_2 molecules is closely related to the nature of the transition metal catalyst.
- The transition metal has appropriate adsorption energy for N_2 , which can make N_2 more stable on the surface of metal.
- Nitrogen molecules and transition metals have a linear adsorption relationship

Simplified schematic of dissociative mechanism for ammonia synthesis on Ru(0001) surfaces according to the work of Logadóttir & Nørskov. Reaction starts at the asterisk.

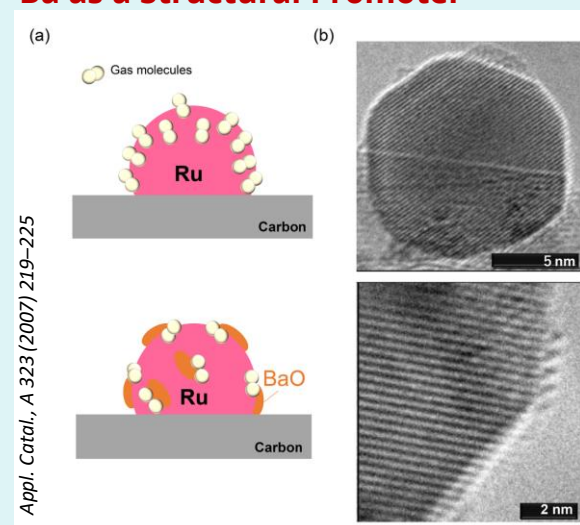


RUTHENIUM-BASED CATALYSTS

Supported Ru Catalysts

- **Optimization of Ru particles size** : The abundance of B5 sites on Ru particles with sizes of 2 nm leads to a high NH_3 synthesis activity.
- **Generation of oxygen vacancies**: High concentration of oxygen vacancies enhanced the adsorption of hydrogen and nitrogen and also led to the desorption of surface hydrogen in the form of H_2 ;
- **Structural and electronic promotion**: While structural promoters increase the number of active sites, electronic promoters tune the electronic environment to optimize reaction kinetics for enhanced catalytic performance.

Ba as a Structural Promoter

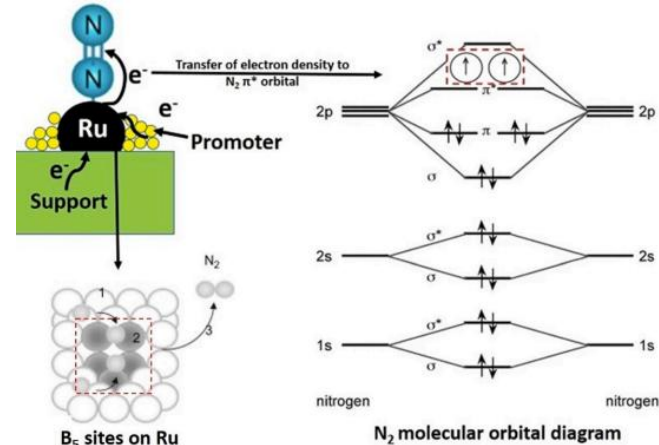


- Ba might adhere to the edge of Ru particles, presumably **increasing adsorption sites** to enhance NH_3 synthesis
- Ba **forms B5 sites** on the Ru surface for NH_3 synthesis
- Ba **inhibits gas adsorption**, potentially **reducing hydrogen poisoning**

“Ba might adhere on the Ru surface to increase the number of B5 sites and lower the energy barrier of N_2 dissociation, thus enhancing the rate of NH_3 synthesis”

Illustration of the gas molecules adsorbed on the unpromoted and Ba-promoted Ru-based catalysts. (b) In situ TEM images of Ba-promoted Ru/BN, with the enlarged image showing that a small monolayer patch of Ba occurs on the edge of Ru.

Science (1979) 294 (2001) 1508–1510.



Schematic and molecular orbital diagrams of electron transfer in a Ru-supported catalyst (<https://doi.org/10.1016/j.chempr.2018.10.007>)

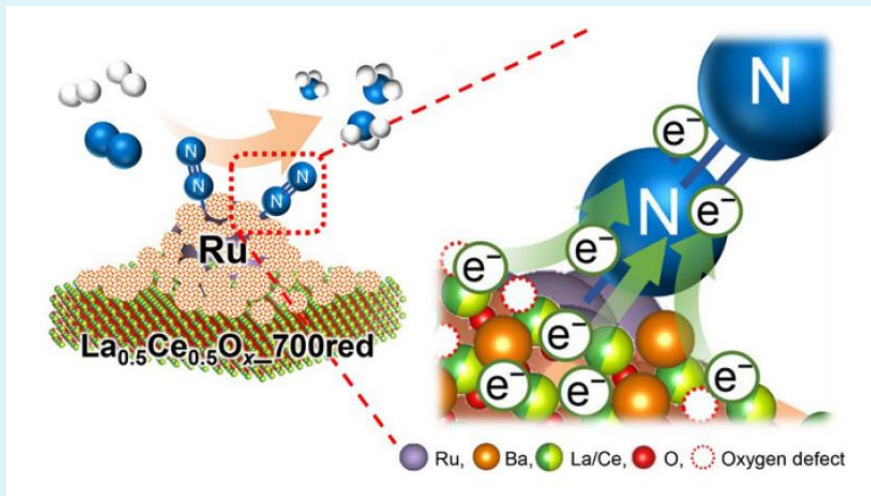
- The chemisorption of N_2 requires a high energy amount due to the negative electron affinity (-1.9 eV), large HOMO–LUMO gap (10.8 eV) of the N_2 molecule, and extremely high energy needed to break N_2 triple bonds (940.95 KJ mol $^{-1}$)
- These barriers can be lowered using Ru catalysts through electron backdonation from the catalyst surface to the $2\pi^*$ orbitals of N_2
- According to the molecular orbital theory, dinitrogen molecules with empty π^* orbitals easily accept d-electrons from Ru atoms (4d metal) through $d-\pi^*$ interactions, weakening the N_2 triple bond.

RUTHENIUM-BASED CATALYSTS

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- **Generation of oxygen vacancies**: High concentration of oxygen vacancies enhanced the adsorption of hydrogen and nitrogen and also led to the desorption of surface hydrogen in the form of H_2 ;
- **Structural and electronic promotion**: While structural promoters increase the number of active sites, electronic promoters tune the electronic environment to optimize reaction kinetics for enhanced catalytic performance.

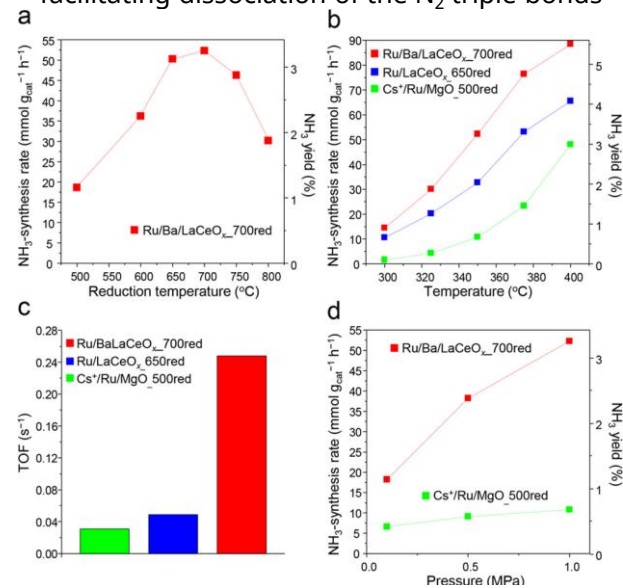
Ba as an electronic Promoter



Schematic diagram of the electronic promotion effect of Ba on Ru/LaCeOx.

ACS Sustainable Chem. Eng. 2020, 8, 7, 2726–2734

- The **low electronegativity** of Ba species should potentially **donate electrons to Ru** with relatively high electronegativity
- Ba promote the **Ru d-electron back-donation** to the antibonding orbitals of N_2 , facilitating dissociation of the N_2 triple bonds



(a) Influence of reduction temperature on ammonia synthesis activity at 350 °C and 1.0 MPa. (b) Temperature dependence of the ammonia synthesis rate and NH_3 yield at 1.0 MPa over supported Ru catalysts, (c) Turnover frequency (TOF) at 350 °C and 1.0 MPa. (d) Pressure dependence of the ammonia synthesis rates and NH_3 yield.

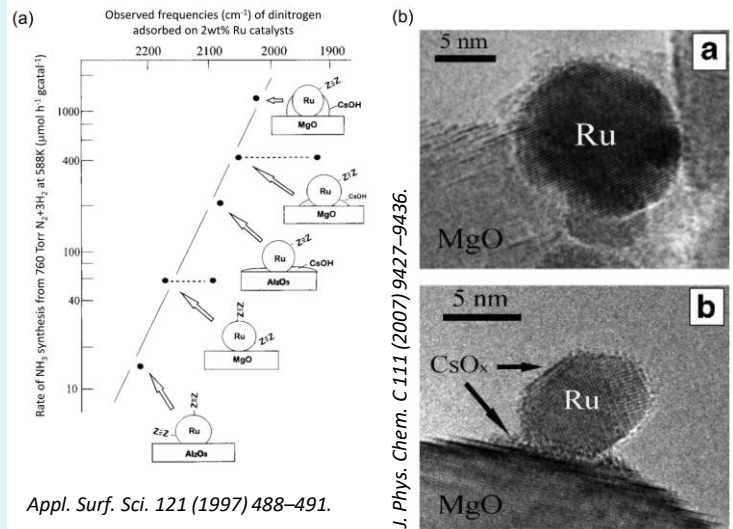
“Ba might act as a structural or an electronic promoter, which is strongly related to the preparation and composition, the reductive activation, and the reaction conditions of the prepared catalysts.”

RUTHENIUM-BASED CATALYSTS

Supported Ru Catalysts

- **Optimization of Ru particles size** : The abundance of B5 sites on Ru particles with sizes of 2 nm leads to a high NH_3 synthesis activity.
- **Generation of oxygen vacancies**: High concentration of oxygen vacancies enhanced the adsorption of hydrogen and nitrogen and also led to the desorption of surface hydrogen in the form of H_2 ;
- **Structural and electronic promotion**: While structural promoters increase the number of active sites, electronic promoters tune the electronic environment to optimize reaction kinetics for enhanced catalytic performance.

Cs as an electronic Promoter

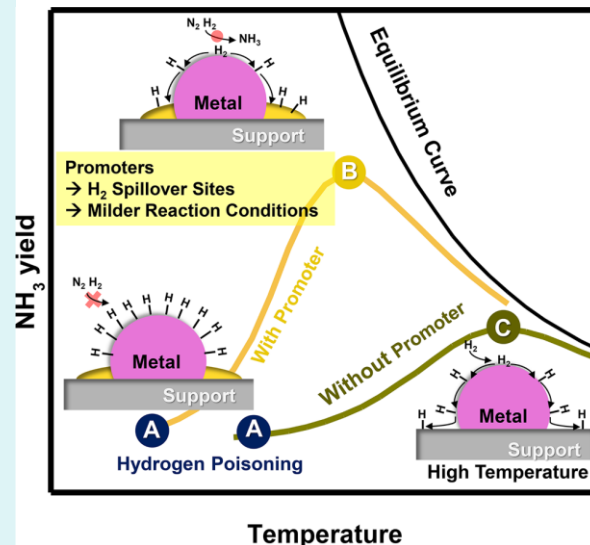


(a) Rates of NH_3 synthesis and the observed N_2 vibrational frequencies on promoted Ru/support catalysts, (b) HRTEM images of Ru/MgO (a-top) and Cs-promoted Ru/MgO (b-below).

In principle, the metallic state of **alkali and alkaline earth metals with low electronegativities can donate electrons** to Ru surface. The **lower the electronegativity, the higher the electron-donating ability** (i.e., the electron donating ability follows the order $\text{Cs} > \text{Rb} > \text{K} > \text{Na}$).

- The **surface acidity of the Cs-promoted Ru catalyst** was generally **lower than** that of the **unpromoted** analog, which **decreased the adsorption strength** of NH_3 on the catalyst surface, and thus enhancing NH_3 synthesis.

Appl. Catal., B 310 (2022) 121269.



Temperature dependences of the rates of NH_3 synthesis for promoted (light yellow) and unpromoted (olive) catalysts.

- The **dissociative adsorption of H_2** on Ru is **much easier than N_2 dissociative adsorption**, indicating that the Ru surface can be covered by the adsorbed hydrogen species.
- The **active sites** on the Ru surface become **inaccessible** for N_2 dissociation, and therefore **H_2 poisoning** could occur.

“Promoter species acted as spillover sites, served as bridges for H_2 migration from the Ru surface to the support, and reduced H_2 poisoning.”

RUTHENIUM-BASED CATALYSTS

Supported Ru Catalysts

Catalyst	Description	Pressure (MPa)	Temp (°C)	Ru (%)	NH ₃ Rate (μmol g ⁻¹ h ⁻¹)	Details
Ru/CaFH	Ruthenium supported on a solid solution of Calcium Fluoride and Calcium Hydride	0.1	50	12	50	Operates at exceptionally low temperature (50 °C) due to weak ionic bonds in the support.
Ru/HT-C12A7:e	Ruthenium supported on high-surface-area 12CaO-7Al ₂ O ₃ electrode	0.1	340	2	2290	High catalytic activity and water-stable electrode support. Dissociative adsorption of N ₂ no longer rate-limiting.
Ru/BaO-CaH ₂	Ruthenium supported on Barium oxide and Calcium hydride	0.1	340	10	10500	Metal hydride support provides enhanced electron donation abilities.
Ru/CaH ₂	Ruthenium supported on Calcium hydride	0.1	340	10	7400	Enhanced electron donation from the support material.
Ru/LaN NPs	Ruthenium supported on Lanthanum Nitride nanoparticles	0.1	340	12.5	2665	Nitrogen vacancies in LaN weaken the N≡N bond, overcoming Ru's low binding energy.
Ru/Ce _{0.5} La _{0.5} O _{1.75}	Ruthenium supported on Ceria-Lanthana mixed oxide	1	350	5	31300	Mixed oxide improves electron donation and stability.
Ru/BaZrO ₃	Ruthenium supported on BaZrO ₃	0.1	400	2	3630	Perovskite oxide provides stable basic surface and moderate electron donation.
Ru/BaZr _{0.9} Y _{0.1} O ₃	Ruthenium supported on BaZr _{0.9} Y _{0.1} O ₃	0.1	400	2	4000	Y-doping enhances oxygen vacancy concentration and catalytic activity.
Ru/graphene	Ruthenium supported on graphene	0.1	400	1.4	336	Graphene offers high dispersion and conductivity but limited N ₂ activation.
Ru/CeO ₂ -C ₁₂ H ₂₉ N ₉ O (TPAOH)	Ruthenium supported on CeO ₂ modified with C ₁₂ H ₂₉ N ₉ O (TPAOH)	3	450	2.5	32000	Modified CeO ₂ improves electron transfer and stabilizes active Ru sites at high pressure.

- Top 10 ammonia synthesis catalysts, weighted by activity, temperature, and pressure.

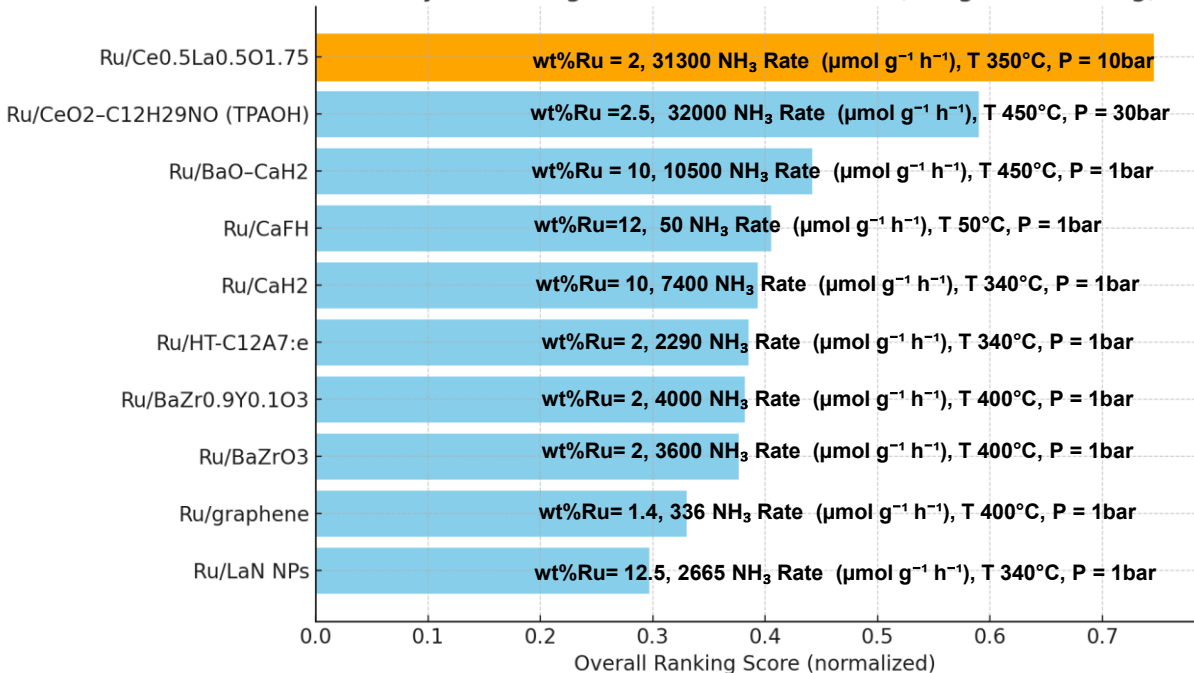
Chemical composition and activity of ruthenium catalysts for ammonia synthesis.

Catalyst	Ru content [wt%]	Promoters	Reactor temperature [°C]	Reactor pressure [MPa]	Weight hourly space velocity [ml g ⁻¹ h ⁻¹]	NH ₃ percent in reactor outlet [wt%]	NH ₃ synthesis rate [μmol g ⁻¹ h ⁻¹]
Ru/CaFH	12	—	50	0.1	36 000	—	50
Ru/MgO (microwave-assisted 2.45 GHz)	10	—	320	0.1	3000	—	613
Ru/Cs/Ba/CCHT	6.2	Ba (15.8 wt%) Cs (15.8 wt%)	327	0.1	66 666	0.9	—
Ru/HT-C12A7:e	2	—	340	0.1	18 000	—	2290
Ru/BaO-CaH ₂	10	—	340	0.1	36 000	—	10 500
Ru/CaH ₂	10	—	340	0.1	36 000	—	7400
K/Ru/graphite	10	K (2 wt%)	400	0.1	—	—	490
Ru/HT-C12A7	2	—	400	0.1	36 000	—	3050
Ru/SAs/S-1	0.27	Ba (9 wt%)	400	0.1	18 000	—	1389.5
YRu ₂	—	—	400	0.1	18 000	—	3318
Ru/BaZrO ₃	2	—	400	0.1	36 000	—	3630
Ru/BaZr _{0.9} Y _{0.1} O ₃	2	—	400	0.1	36 000	—	4000
Ru/graphene	1.4	Ba/Ru = 1	400	0.1	36 000	—	336
Ru/2.05tNb	2	Cs/Ru = 8	450	0.1	36 000	—	5035
Ru/Sbunit	4	Ba (10.8 wt%) Cs (2.6 wt%)	350	0.7	—	—	1540
Ru/Ca(NH ₂) ₂	10	—	300	0.8	36 000	—	15 800
Ru/Ba-Ca(NH ₂) ₂	10	Ba (3 at%)	360	0.9	36 000	—	60 400
Ru/BaCeO ₃ (μH ₂ N ₂ after 20 h)	4.5	—	400	0.9	36 000	—	28 570
Ru/mesoporous carbon(MPC)-18	13.8	Cs/Ru = 1.1	360	0.99	—	—	10 200
Ru/MPC	10	Cs (33 wt%)	370	0.99	—	—	8100
Ru/MPC	10	Ba/Ru = 0.5	380	0.99	—	—	10 400
Ru/Ce _{0.5} La _{0.5} O _{1.75}	5	—	350	1	72 000	—	31 300
Ru/Pr ₂ O ₃	5	—	400	1	18 000	—	19 000
Ru/Ti-Ce-S	3	—	400	1	—	—	14 580
Ru/Titania Stabilized Zirconia (YSZ)	0.4-1.0	Ba/Ru = 1	400	1	72 000	—	5640-14 100
Ru/gC-Al ₂ O ₃	5	Ba (6 wt%)	400	1	60 000	—	5611
Ru/Al ₂ O ₃ -980	5	Ba (6 wt%)	400	1	60 000	—	7217
Ru/La _{0.5} Pr _{0.5} O _{1.75}	5	—	400	1	72 000	—	60 200
Ru/MgO-MIL	3.1	Cs/Ru = 1	400	1	24 000	—	22 290
Ru/CeO ₂ -r	4	—	400	1	18 000	—	3830
Ru/CeO ₂ -c	4	—	400	1	18 000	—	1289
Ru@CeO ₂ -9	2.48	—	425	1	60 000	—	8500
LaCo _{0.98} Ru _{0.02} O ₃	0.93	—	450	1	—	—	10 500
Ru/MgO	2	Cs (6.4 wt%)	400	2.6	—	—	4200
Ba/Ru/Graphitic Nanoflaments (GNFS)	4	Ba (1 wt%)	400	3.0	—	—	18 570
Ru/BaCeO ₃	3	—	400	3.0	—	—	6450
Ru/ZrO ₂ -KOH	—	—	400	3.0	—	3.95	11 100
Ru/Pr ₂ O ₃	5	—	400	3	72 000	—	64 000
Ru/Y-layered double oxide (LDO)	3.85	—	425	3	—	—	16 120
Ru/MgAl-LDO	3.86	—	425	3	—	—	14 760
Ru/BaCeO ₂ -a	1.25	Cs (4%)	450	3.0	24 000	—	28 000
Ru/CeO ₂ -C ₁₂ H ₂₉ NO (TPAOH)	2.5	Cs (4%)	450	3	24 000	—	32 000

RUTHENIUM-BASED CATALYSTS

Supported Ru Catalysts

Catalyst Ranking under Mild Conditions (Weighted Scoring)



Top 10 ammonia synthesis catalysts, normalised by activity, temperature, pressure, ammonia rate.

The Ru/Ce_{0.5}La_{0.5}O_{1.75} catalyst clearly stands out as the best balance between high performance and mild operating conditions, for near-term application.

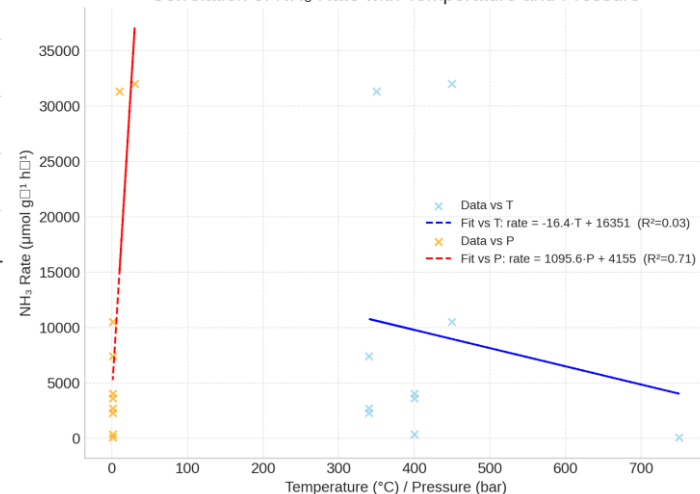
•Ru/Ce_{0.5}La_{0.5}O_{1.75} stands out with **both high NH₃ rate and strong overall score**, performing efficiently under moderate temperature and pressure.

•Ru/CeO₂-C₁₂H₂₉NO (TPAOH) reaches comparable activity but only at **higher temperature and pressure**

•Catalysts like Ru/BaO-CaH₂, and Ru/CaH₂ perform decently at mild conditions

•Ru/CaFH and Ru/HT-C12A7:e excels in mildness (low T and P) but suffers from a very low NH₃ rate.

Correlation of NH₃ Rate with Temperature and Pressure

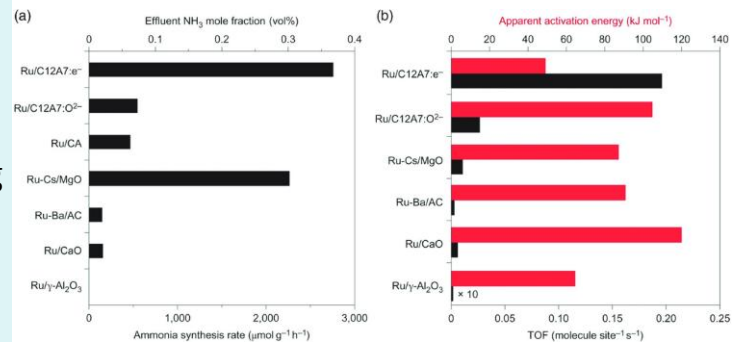


RUTHENIUM-BASED CATALYSTS

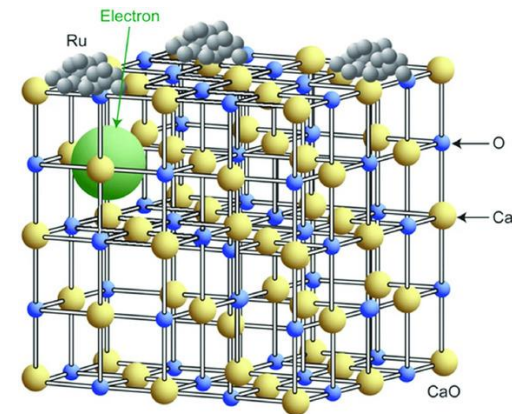
Electride-Based Catalysts

“Ruthenium catalysts with inorganic electride support showed promising activities due to the excellent promotion effect of this recent material”

- An **electride** is an O^{2-} ionic compound in which electrons act as the anion. Thus, **electrides are materials that contain trapped electrons as structural components, rather than as mobile charge carriers. These trapped electrons can exhibit unique chemical reactivity, making electrides interesting candidates for catalysis.**
- *Electrides inherently possess high electron density, which can influence the catalytic activity and selectivity of the material;*
- *The **mechanism** of ammonia synthesis **involves reversible storage and release of hydrogen atoms** on the $Ru/C12A7:e(-)$ surface.*

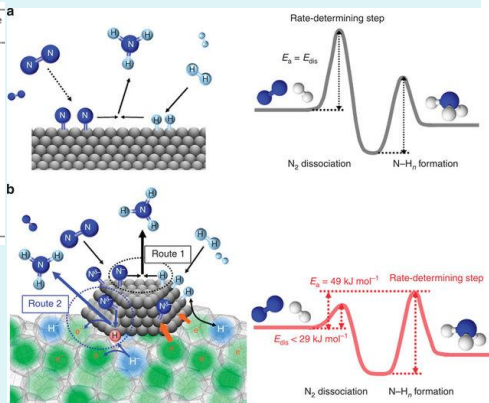


a) Ammonia synthesis rate and outlet ammonia mole fractions for $Ru/C_{12}A_7:e^-$ compared with various supported Ru catalysts.
b) Apparent activation energy and turnover frequency for $Ru/C_{12}A_7:e^-$ compared with various supported Ru catalysts. **All catalysts were loaded with 1 wt% Ru and tested at 0.1 MPa, 400 °C, $H_2/N_2 = 3$, 60 mL min^{-1} .**



Lattice structure of the $[Ca_{24}Al_{28}O_{64}]_{4b}(e)_4$ electride with Ru loading. The structure shows how electrons occupy the oxygen vacancies in the material. Reproduced with permission. Copyright Springer Nature 2012

Catalyst	Ru content [wt%]	Promoters [wt%]	Reactor temperature [°C]	Reactor pressure [MPa]	WHSV [ml g $^{-1}$ h $^{-1}$]	NH_3 percentage in reactor outlet [wt%]	NH_3 synthesis rate [$\mu\text{mol g}^{-1}\text{h}^{-1}$]
$Ru/HT-C12A7:e^-$	2	–	340	0.1	18 000	–	2290
$Ru/Ca_2N:e^-$	1.8	–	340	0.1	36 000	–	3386
$Ru/Ca(NH_2)_2$	1.8	–	340	0.1	36 000	–	3386
Ru/Y_2Si_5 NP	10	–	340	0.1	36 000	–	4448
$Ru/C12A7$ (microcube)	5	–	400	0.1	36 000	–	5380
Ru/Y_2Si_5	7.8	–	400	0.1	18 000	–	1875
$Ru/LaScSi$	8.3	–	400	0.1	36 000	0.36	5300
LaRuSi	–	–	400	0.1	36 000	0.492	5340
CeRuSi	–	–	400	0.1	36 000	–	5480
CaRuSi	–	–	400	0.1	36 000	–	60



Proposed reaction mechanism and energy profile for ammonia synthesis.

The **rate controlling step** of ammonia synthesis over $Ru/C12A7:e(-)$ is **not dissociation of the nitrogen-nitrogen triple bond but the subsequent formation of N-Hn species**

METAL NITRIDE CATALYSTS

● Ternary nitride

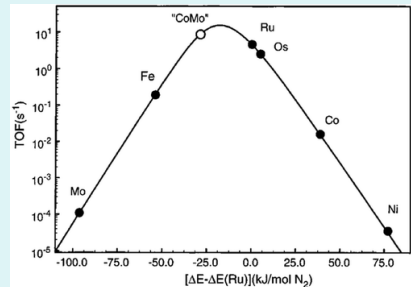
"Metal nitride phases have also been reported for their high activity in the catalytic synthesis of ammonia"

- One major development in metal nitride catalysts was the idea of **ternary nitride systems**;
- If a ternary nitride is **made by combining two metals**, one with a **too high nitrogen adsorption energy** and one with a **nitrogen adsorption energy that is too low**, then an ammonia synthesis catalyst can be obtained with a TOF closer to the maximum than any single metal nitride; In the **Co-Mo catalyst system** shown on the plot, **Mo binds nitrogen too strongly**, whereas **Co binds nitrogen too weakly**.

Role of the $\text{Co}_3\text{Mo}_3\text{N}$ Structure

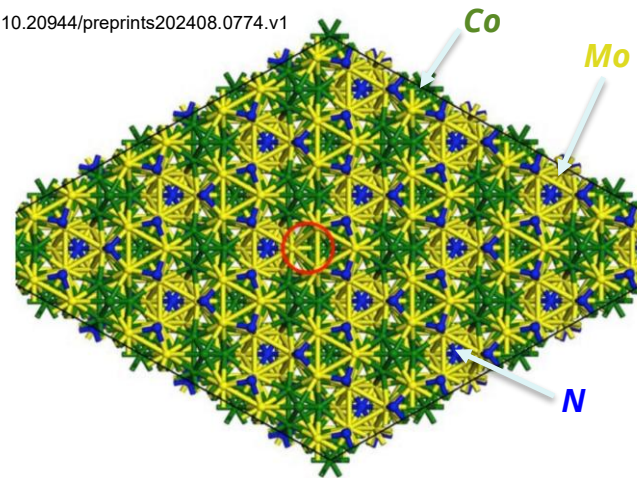
- **Dual-Site Synergy:** Mo specializes in N_2 activation (strong N-binding affinity), Co excels at H_2 dissociation and hydrogenation (high H mobility).
- **Nitrogen Vacancies:** Vacancies in the lattice act as "traps" for N_2 , lowering the energy barrier for dissociation.
- **Electron Redistribution:** The Co-Mo interaction redistributes electron density, optimizing back-donation to N_2 and H_2 activation.

[https://doi.org/10.1016/S0926-860X\(01\)00529-4](https://doi.org/10.1016/S0926-860X(01)00529-4)

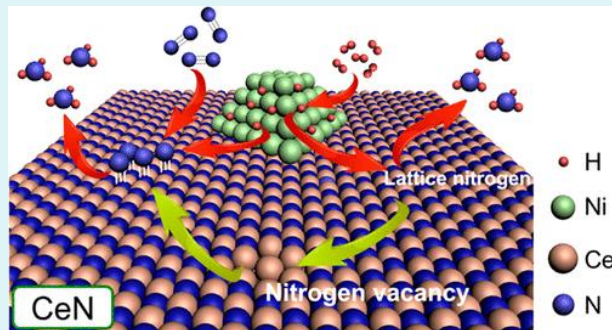


Calculated turnover frequencies for ammonia synthesis as a function of nitrogen adsorption energy (400 °C, 50 bar)

doi: 10.20944/preprints202408.0774.v1



Surface of cobalt molybdenum nitride ($\text{Co}_3\text{Mo}_3\text{N}$) showing with red circle the nitrogen vacancy side. Nitrogen is represented in blue, molybdenum is represented in yellow, and cobalt is represented in green



In the case of **Ni-loaded nitrides**, H_2 and N_2 are **separately activated at Ni metal and V_N sites**, respectively. Without Ni loading, V_N sites can activate both H_2 and N_2 simultaneously for stable ammonia production.

- The structure of cobalt molybdenum nitride is like a **hexagonal array of Co_8 clusters** inserted into a **molybdenum nitride framework**.
- This makes the **catalyst bifunctional** where both metal and metal support interactions are present.

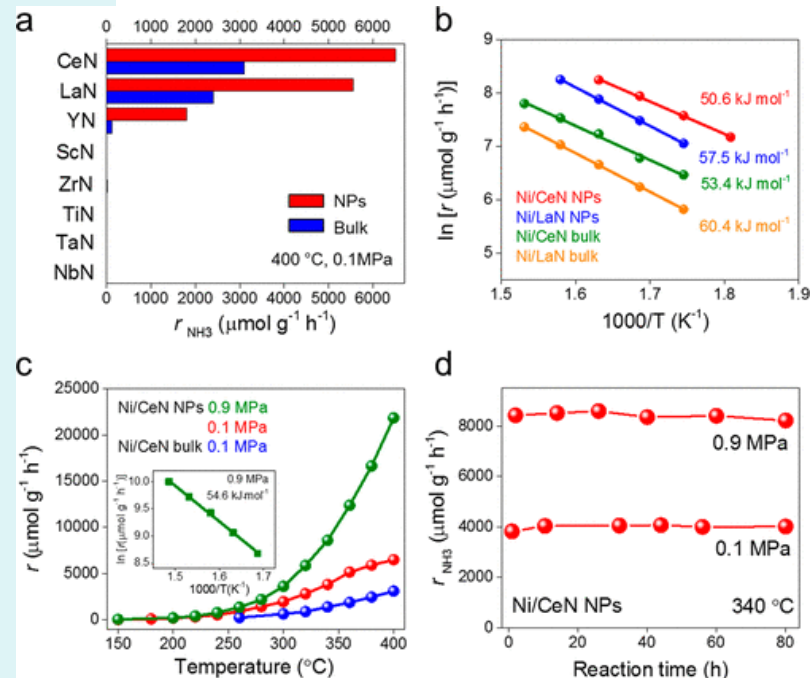
METAL NITRIDE CATALYSTS

● Ternary nitride

The **Cs-** or **K-promoted $\text{Co}_3\text{Mo}_3\text{N}$** catalysts exhibit a high activity of $\approx 900 \mu\text{mol g}^{-1} \text{h}^{-1}$ at **400 °C** and **1 bar**, which outperform the Fe-based catalysts under the same condition;

Catalyst	Rate ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Surface area ($\text{m}^2 \text{g}^{-1}$)	Specific activity ($\mu\text{mol h}^{-1} \text{m}^{-2}$)
Fe-K ₂ O-Al ₂ O ₃	330	14	24
Co ₃ Mo ₃ N	652	21	31
Co ₃ Mo ₃ N-K5	869	17	51
Co ₃ Mo ₃ N-K30	364	8	46
Co ₃ Mo ₃ N-Cs2	986	16	62
Co ₃ Mo ₃ N-Cs10	586	10	59

Reaction conditions: 0.1 g catalyst, N₂:H₂ = 15:45 mL min⁻¹, **150–400 °C**, **0.1 and 0.9 MPa**



The **rare earth metal nitrides** such as **CeN, LaN, and YN** can act as **efficient supports and/or catalysts** for ammonia synthesis, in which **nitrogen vacancy** formation has a **strong effect on the catalytic performance**

Thank you for your kind attention!



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