"Vsemogoči vodik" – energijski vidik bodočnosti

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Vodik

Ali je zeleno gorivo?

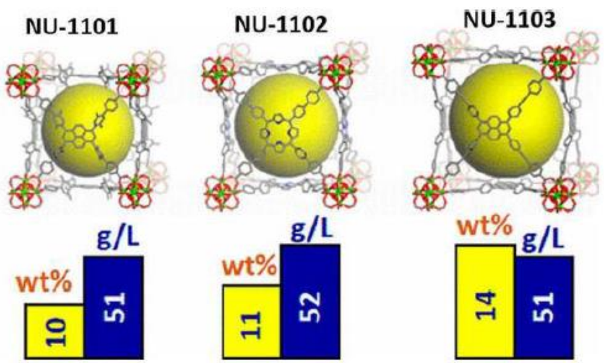
- Brez neposrednega onesnaževanja.
- Običajna pridelava povzroča emisije CO_2.
- Dekarbonizacija pri H_2 mora biti v sozvočju s spreminjanjem proizvodnje H_2.

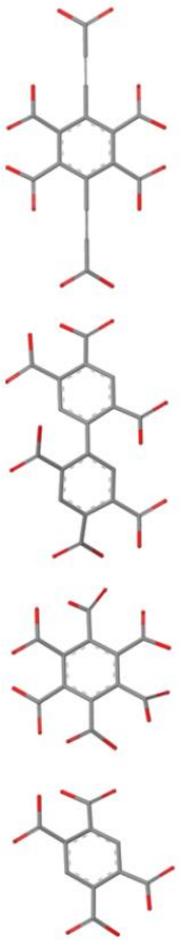
The Hydrogen Colour Spectrum

COLOUR	DESCRIPTION: FEEDSTOCK
	Grey: natural gas reforming without CCUS
	Brown: brown coal (lignite) as feedstock
	Blue: natural gas reforming with CCUS
	Green: electrolysis powered through renewable electricity
	Pink: electrolysis powered through nuclear energy
	Turquoise: methane pyrolysis
	Yellow: electrolysis powered through electricity from solar
	Orange: electrolysis powered through electricity from wind

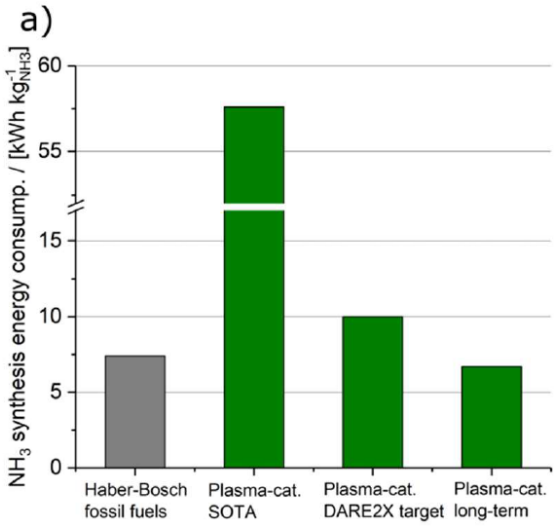
Skladiščenje vodika

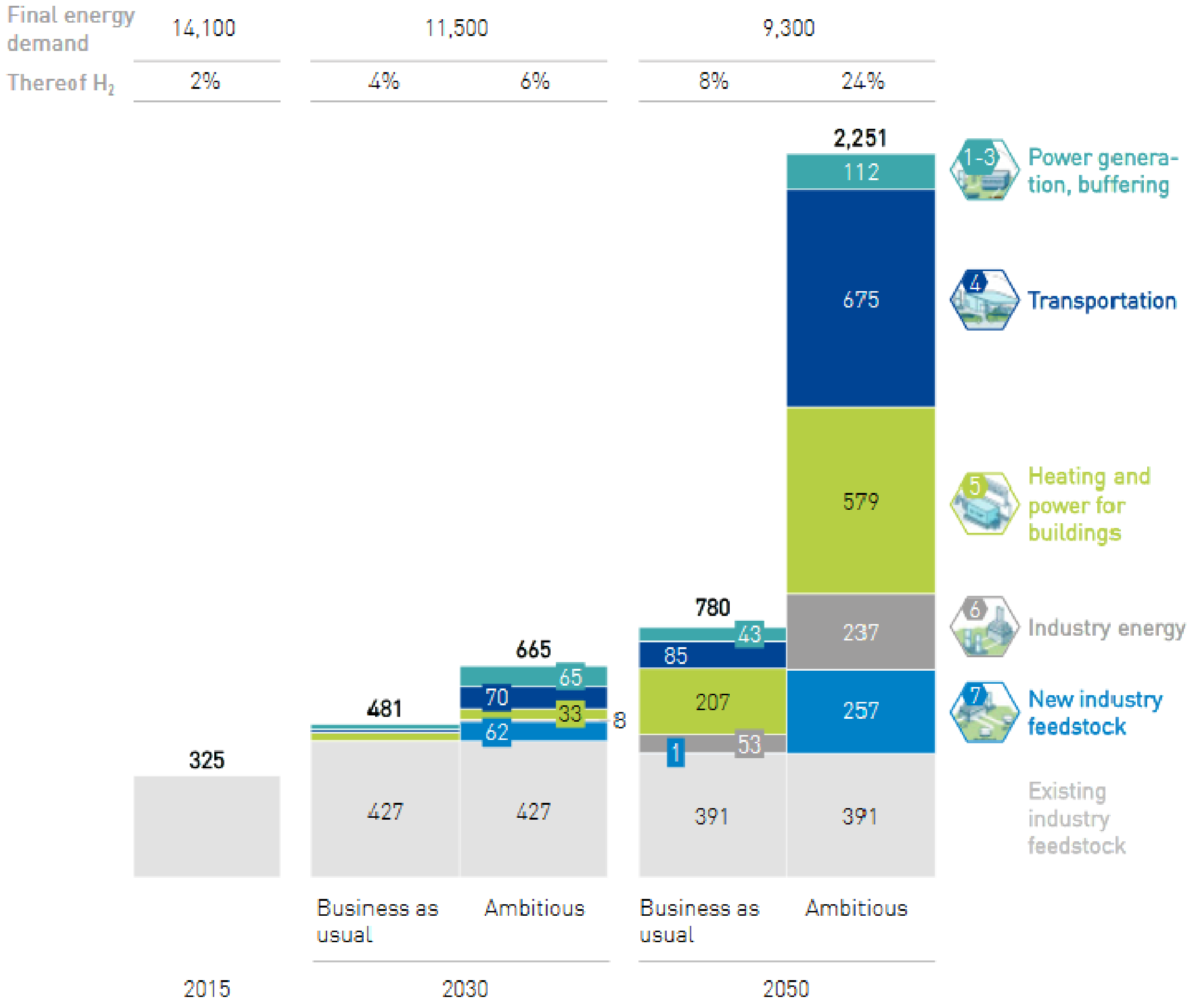
Fizikalno skladiščenje



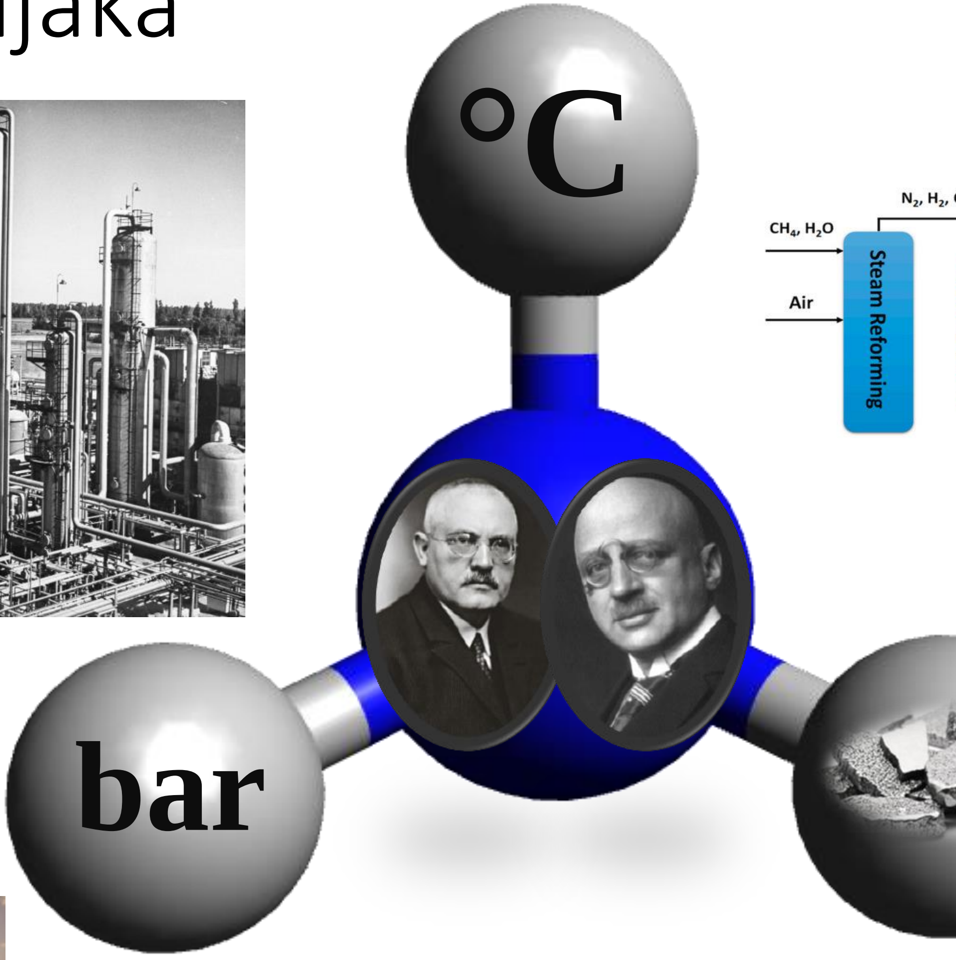


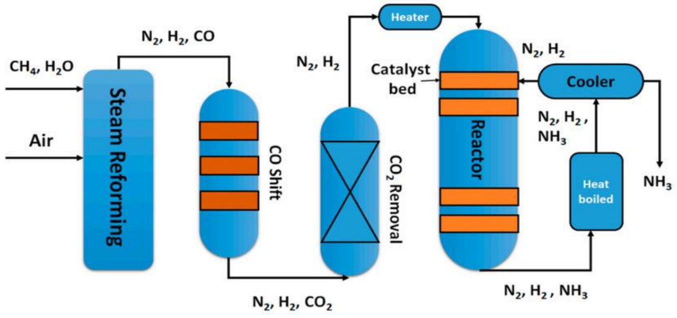
Kemijsko skladiščenje (amonijak)





Haber – Bosch proces, sinteza amonijaka





https://en.wikipedia.org/wiki/Haber_process (16.3.2023)
https://www.luciteria.com/elements-for-sale/iron-metal (16.3.2023)
https://www.wired.com/2016/05/chemical-reaction-revolutionized-farming-100-years-ago-now-needs-go/ (16.3.2023)
V. Palma et al, Platinum Based Catalysts in the water Gas Shift Reaction: Recent Advances, metals, 2020

Haber – Boschev proces

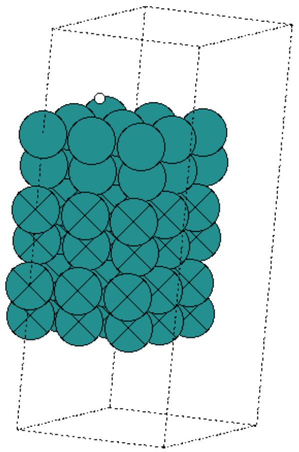
Disociacijski mehanizem

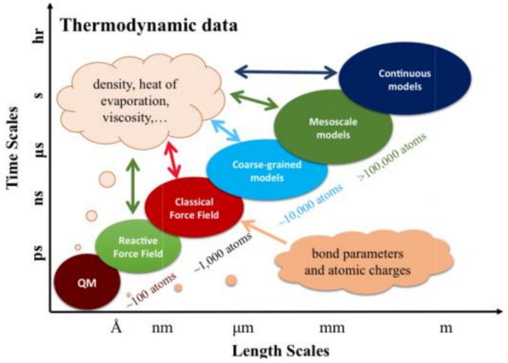
1. $N_2(g) + 2* \leftrightharpoons 2N^*$
2. $H_2(g) + 2* \leftrightharpoons 2H^*$
3. $N^* + H^* \leftrightharpoons NH^* + ^*$
4. $NH^* + H^* \leftrightharpoons NH_2^* + ^*$
5. $NH_2^* + H^* \leftrightharpoons NH_3^* + ^*$
6. $NH_3^* \leftrightharpoons NH_3 + ^*$

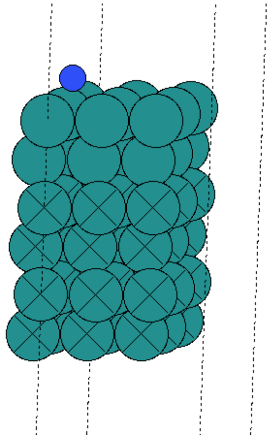
Asociacijski mehanizem

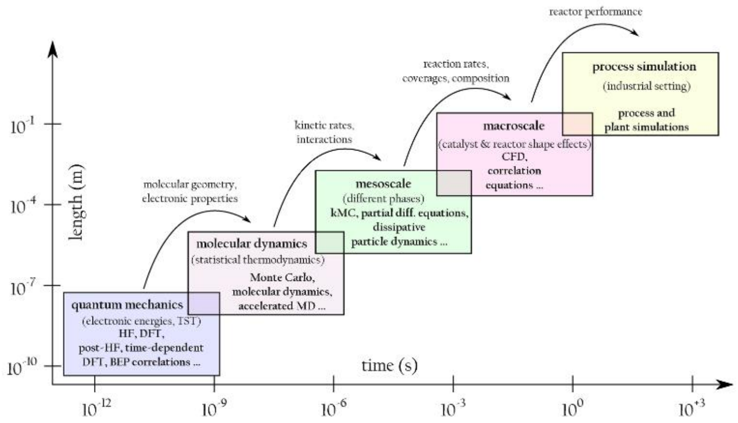
1. $N_2 + \frac{1}{2}H_2 + 3* \leftrightharpoons N_2H^{**} + *$
2. $N_2H^{**} + H^* \leftrightharpoons N_2H_2^* + 2*$
3. $N_2H^{**} + H^* \leftrightharpoons NH^* + N^* + H^*$
4. $NH^* + H^* \leftrightharpoons NH_2^* + ^*$
5. $NH_2^* + H^* \leftrightharpoons NH_3^* + ^*$
6. $NH_3^* \leftrightharpoons NH_3 + ^*$

- Haber-Bosch proces
  - 400 - 500 °C, 100 - 400 bar
  - Katalizator Fe
- 2 – 3 % globalne energije za proizvodnjo amonijaka
  - Haber – Bosch proces + H_2 proizvodnja
- CO_2 emisije
- Gnojila

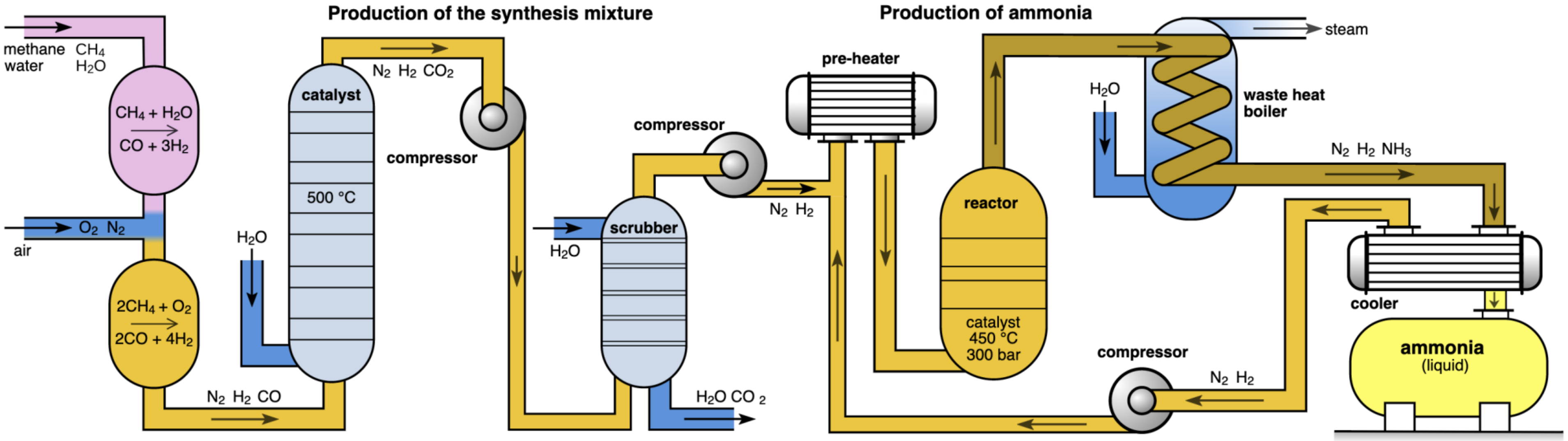








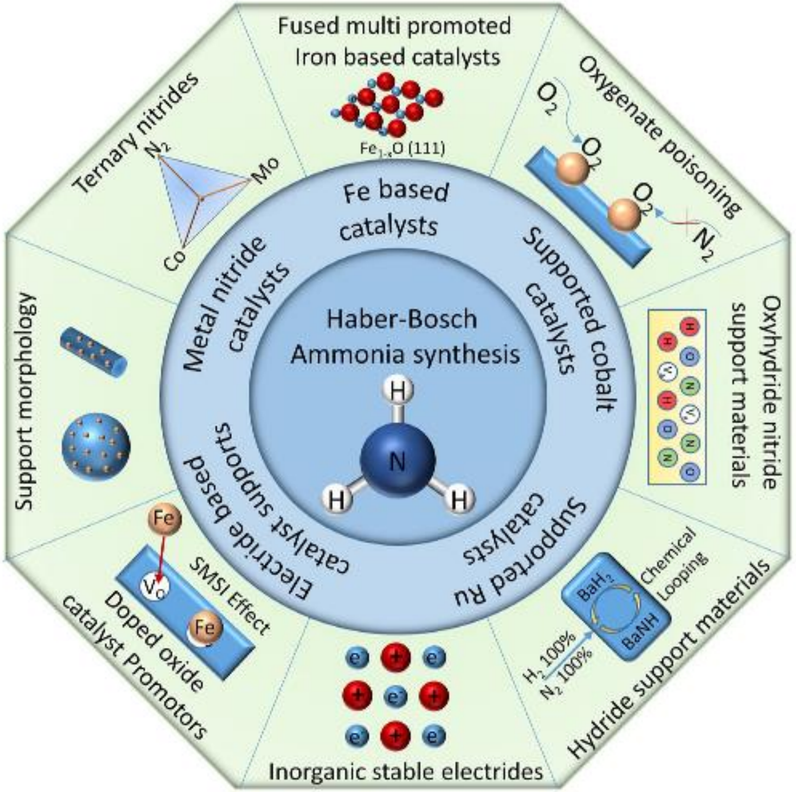
Haber – Bosch proces – procesna shema

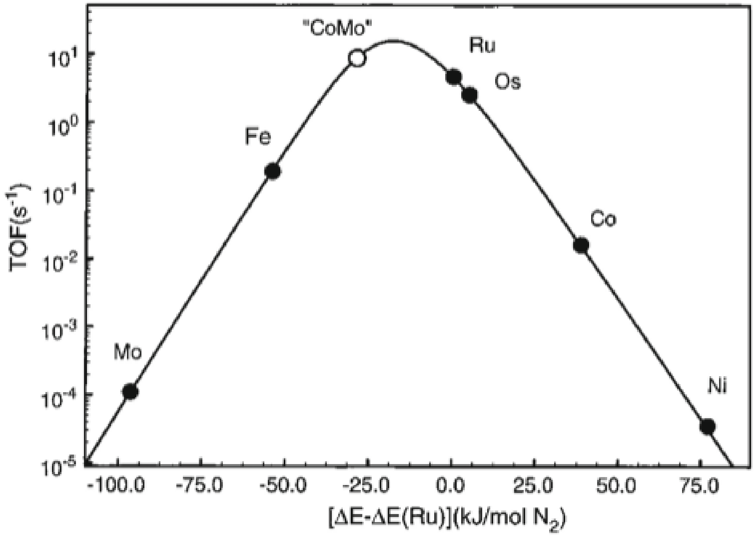


Years	Amount of Ammonia produced (rounded and in thousand tonnes)	Average Price of Ammonia (U.S. dollars per short ton)	World's Total Energy Consumption (Exajoules)
2017	142,000	247	566.66
2018	144,000	281	582.38
2019	142,000	232	587.43
2020	147,000	223	564.01
2021	150,000 (estimated)	510	595.15

Luis Jimenez, Haber-Bosch Process, December 14, 2022, Submitted as coursework for PH240, Stanford University, Fall 2022

Haber-Bosch proces

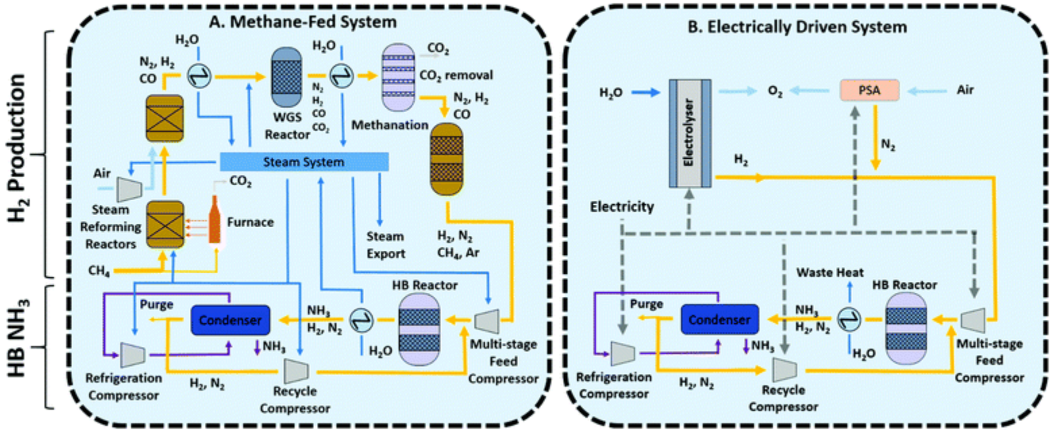




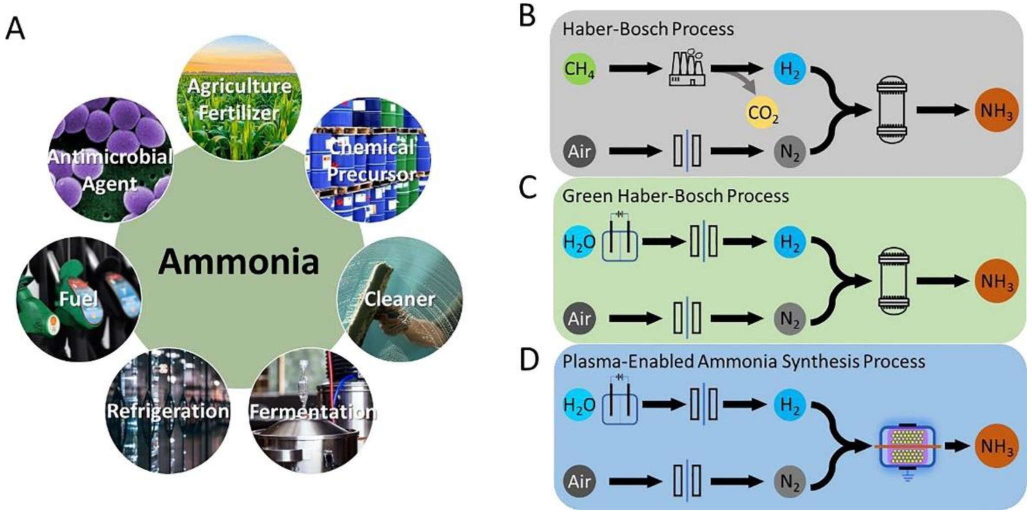
TOF (r. hitrost) za sintezo amonijaka kot funkcija dušikove adsorbcijske energije (400 °C, 50 bar)

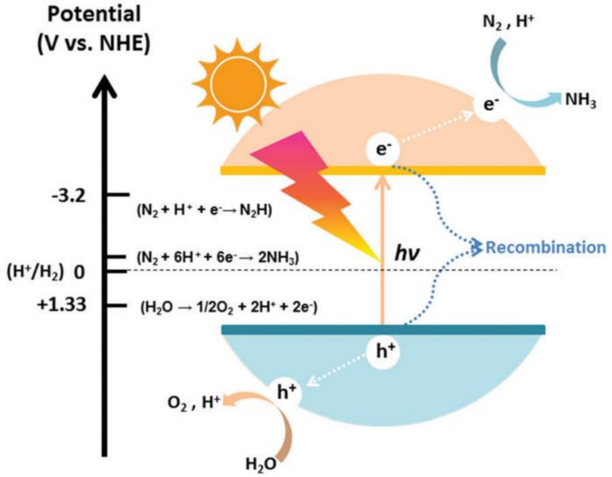
J. Humpreys, R. Lan, S. Tao, Developement and Recent Progress in Ammonia synthesis Catalyst for Haber-Bosch Process, Advanced energy&sustainability research, 2021, 2, 2000043

Haber – Bosch proces, prihodnost



C. Smith, A. K. Hill and L. Torrente-Murciano, *Energy Environ Sci*, 2020, **13**, 331–344.



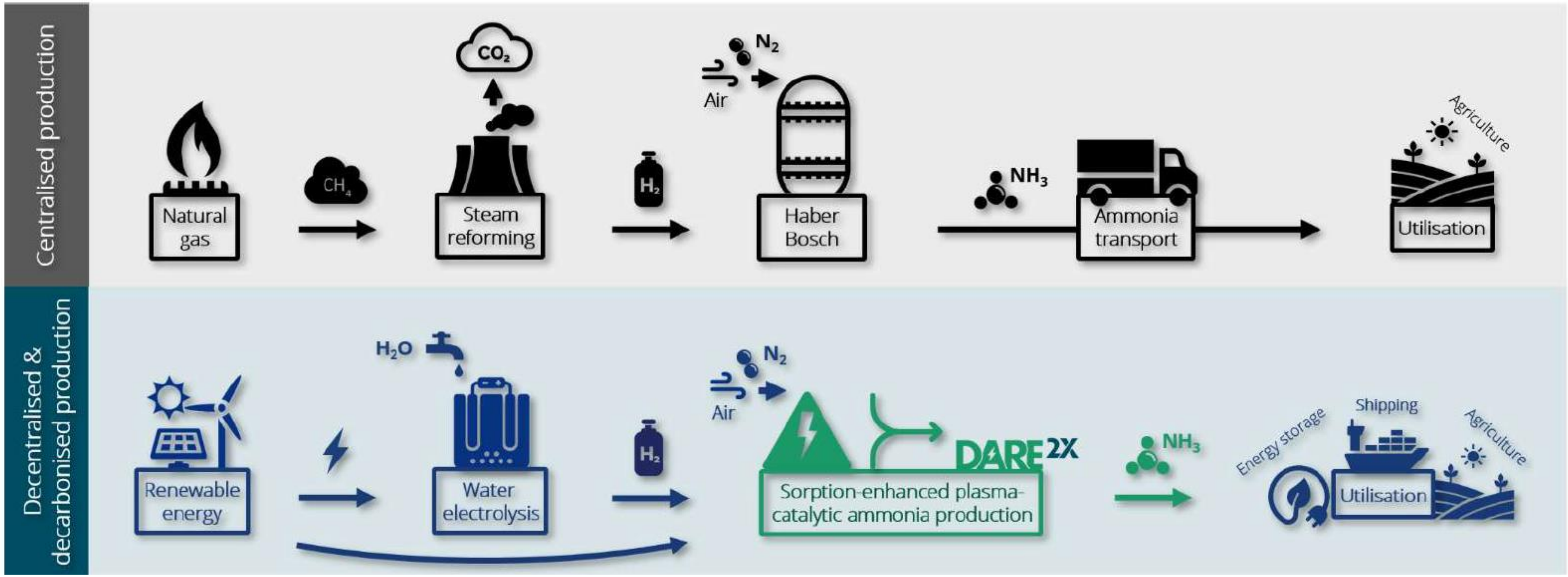


D. Zhou et al., Sustainable ammonia production by non-thermal plasmas: Status, mechanisms and opportunities, *Chemical Engineering Journal,*

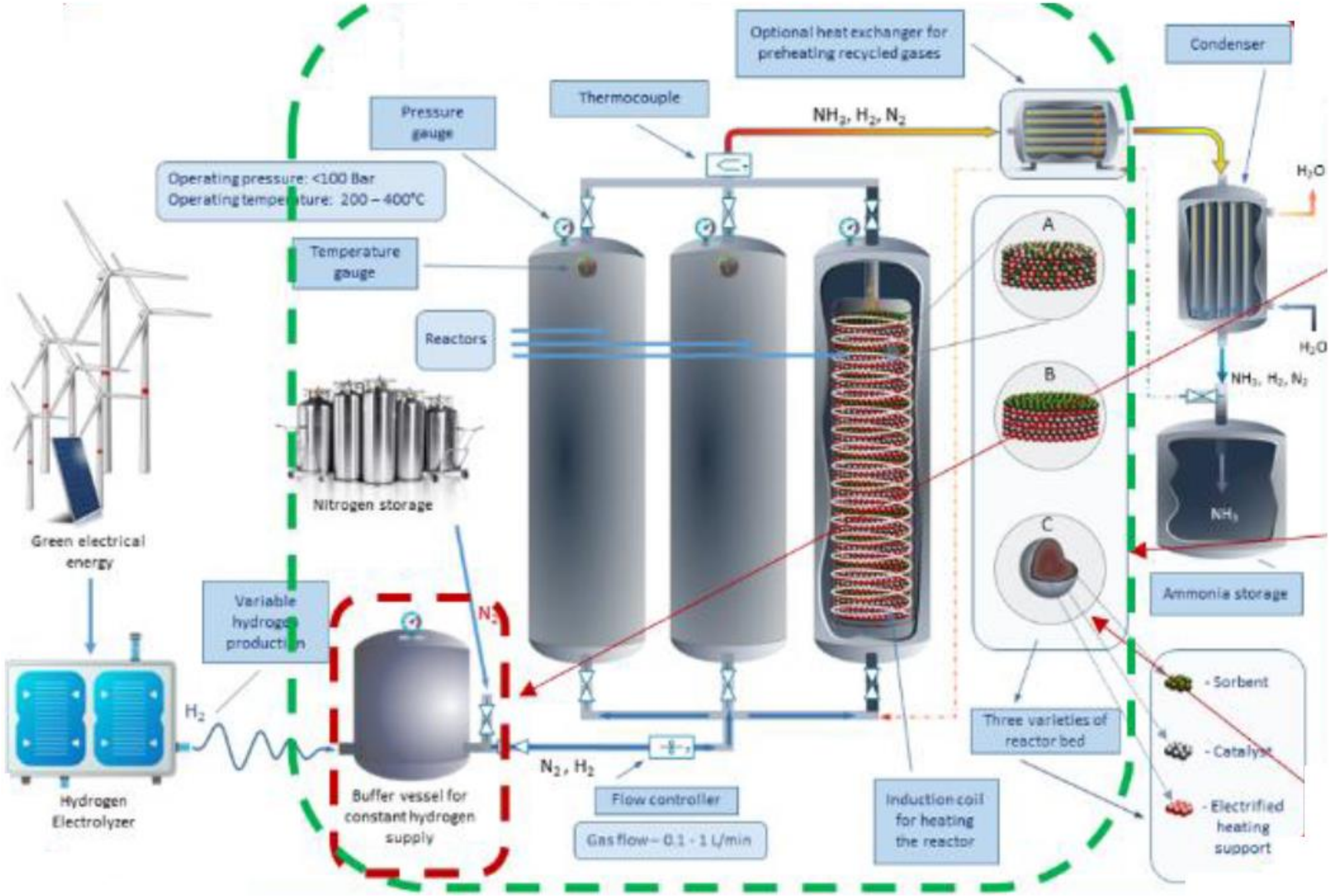
X. Chen, N. Li, Z. Kong, W. Ong, X. Zhao, Photocatalytic fixation of nitrogen to ammonia: state-of-the-art advancements and future prospects, *Mater. Horiz.,* 2018, 5, 9.

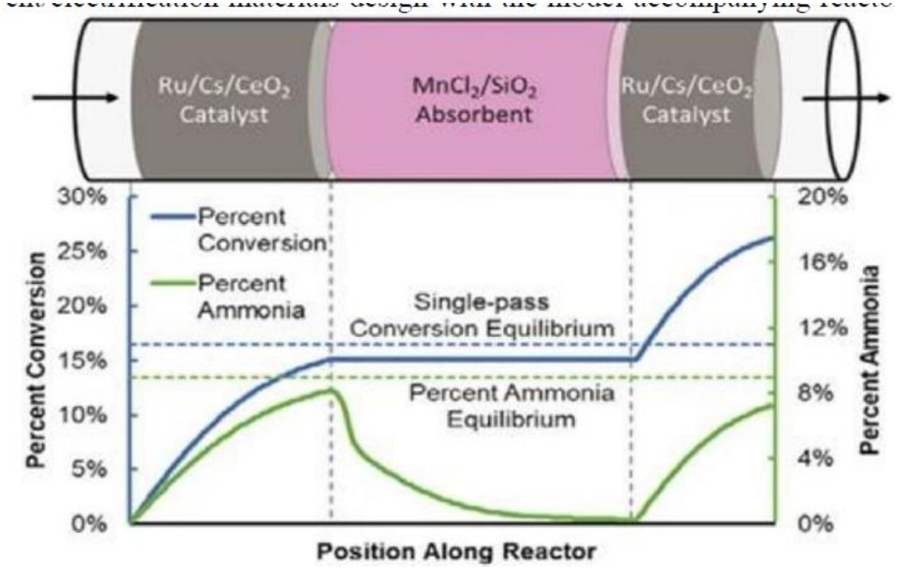
Zelena proizvodnja amonijaka

Elektroliza vode iz obnovljive energije
Izboljšan proces proizvodnje amonijaka (dolgoročno shranjevanje)
Uporaba amonijaka kot goriva

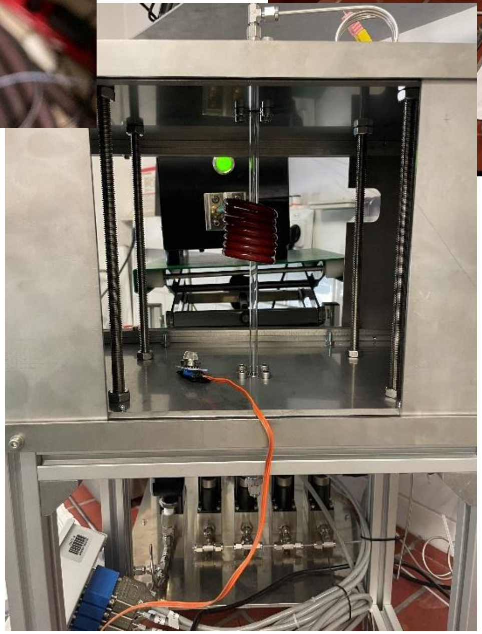


Zelena proizvodnja amonijaka





Haber-Bosch proces – induktivno gretje



FOTOKATALIZA

- Fotokataliza je trajnostna alternativa termokatalitskim reakcijam.
- Kemijske reakcije se lahko izvede pod milimi pogoji; pri teh se kot dovedeno energijo uporablja sončno energijo.

Koraki fotokatalitskega procesa:

- Fotoekscitacija,
- ločevanje naboja,
- Prenos naboja na aktivna mesta fotokatalizatorja,
- Fotooksidacijske in fotoredukcijske reakcije.

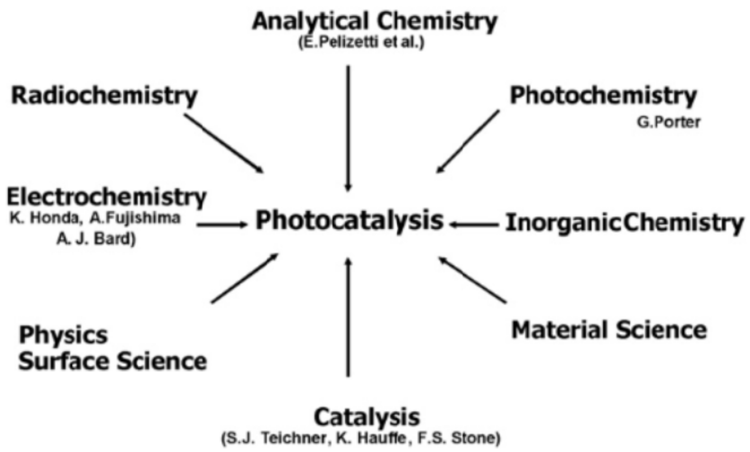


Figure X: Prispevki k fotokatalizi.
10.1016/j.jphotochem.2010.05.015

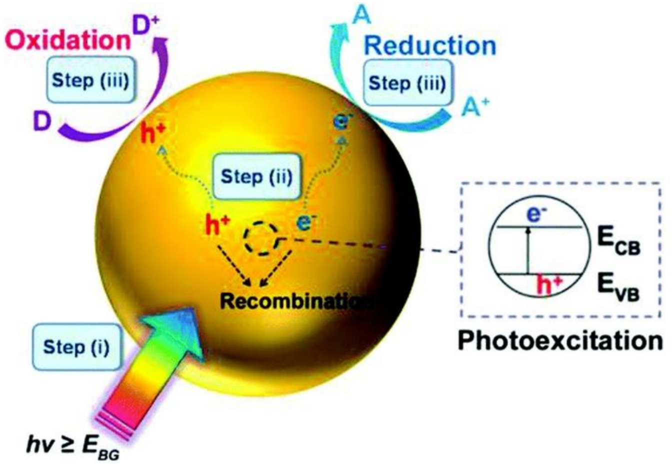


Figure X: Koraki fotokatalitskega procesa.
https://doi.org/10.1039/C6GC02856J

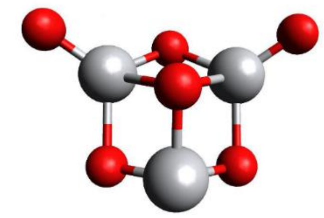
FOTOKATALITSKA SINTEZA AMONIJAKA – Modeliranje na podlagi osnovnih principov

Atomsko modeliranje na podlagi osnovnih principov:

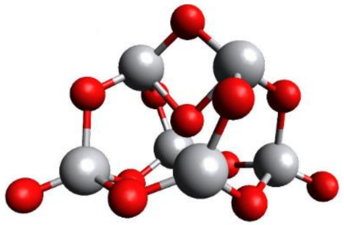
- Izračun osnovnih stanj: **Teorija gostotnega funkcionala (DFT).**
- Izračun vzbujenih stanj : **časovno odvisna DFT (TDDFT), ΔSCF metoda in metoda maksimalnega prekrivanja (MOM).**

Aktivacija N_2 na:

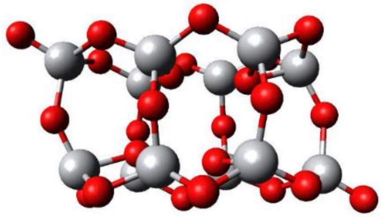
- **$(TiO_2)_n$ (n=1-12) skupkih**.
- **Ru-$(TiO_2)_n$ (n=1-12) skupkih**.



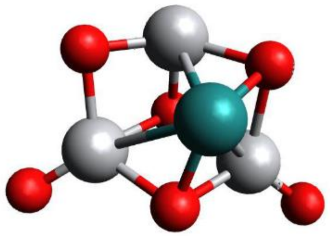
Optimizirana struktura $(TiO_2)_3$



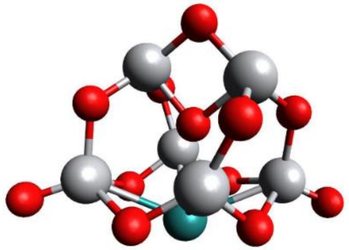
Optimizirana struktura $(TiO_2)_6$



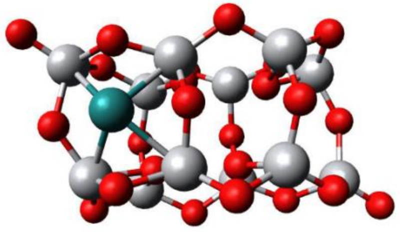
Optimizirana struktura $(TiO_2)_{12}$



Optimizirana struktura Ru-$(TiO_2)_3$



Optimizirana struktura Ru-$(TiO_2)_6$

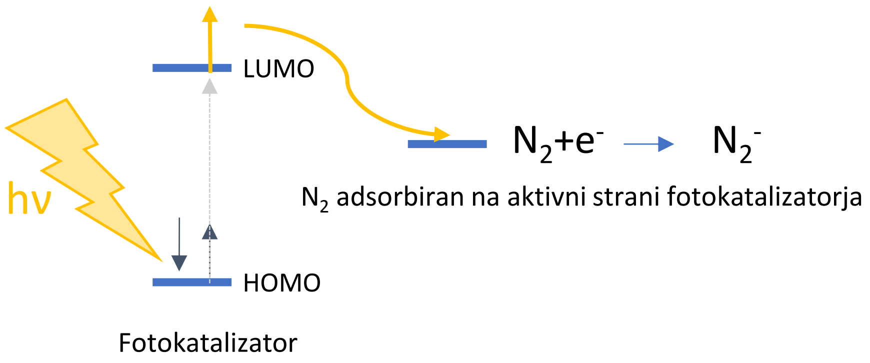


Optimizirana struktura Ru-$(TiO_2)_{12}$

https://doi.org/10.1016/j.fuel.2022.126451

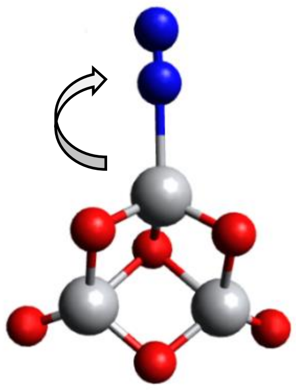
FOTOKATALITSKA SINTEZA AMONIJAKA– Modeliranje osnovnih principov

Simulirana aktivacija N_2 na površini fotokatalizatorja

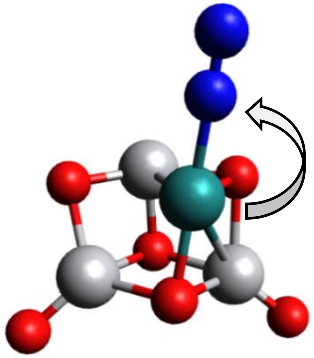


Excitation energies	Izoliran N_2	Izoliran $(TiO_2)_3$
Vzbujeno stanje singleta (ne opt) [eV]	7.01	3.93
Vzbujeno stanje singleta (opt) [eV]	7.53	3.94
Vzbujeno stanje tripleta (ne opt) [eV]	7.05	2.58
Vzbujeno stanje tripleta (opt) [eV]	6.53	2.20

Zanemarljiv prenos elektrona (~ 0.00 e_0) (osnovno stanje)



Tok elektronov: od katalizatorja do adsorbiranega N_2



Nezanemarljiv prenos elektrona(~ - 0.25 e_0) (osnovno stanje)

↓

N_2 je aktiviran

https://doi.org/10.1016/j.fuel.2022.126451

CO_2 CCU: Učinek H_2O na $Cu/ZnO/Al_2O_3$

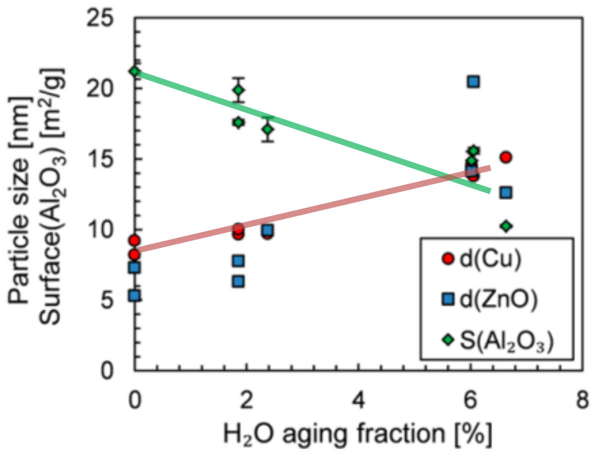
$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

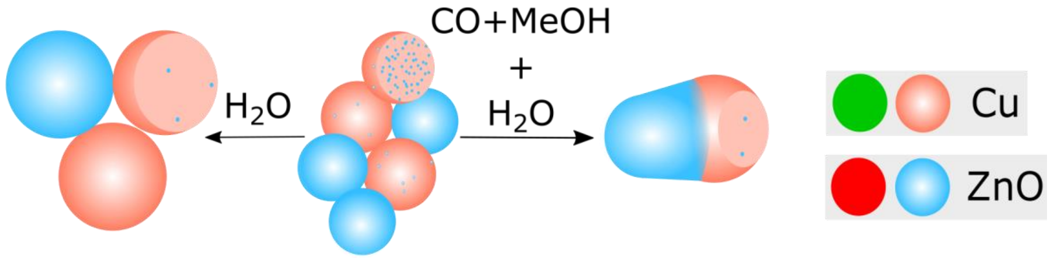
$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O$$

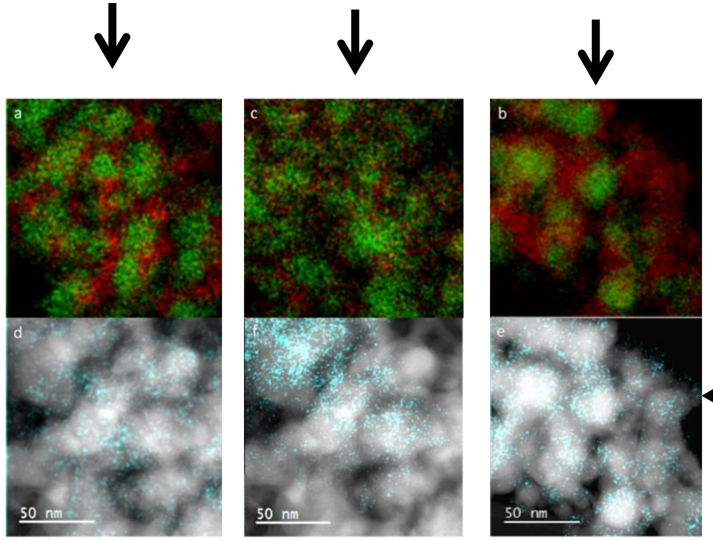
Je kakšen učinek na katalizatorju?

Voda povzroči:

- Zmanjšanje površine Al_2O_3,
- **Povečanje velikosti delcev Cu**
- Pogojno povečanje velikosti delcev ZnO







Al^{+3} FINO DISPERGIRAN

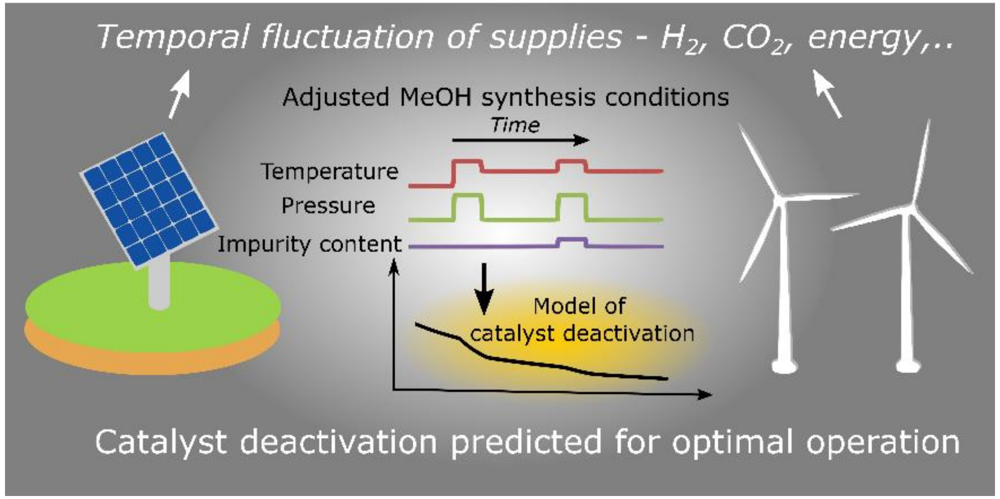
Prašnikar, Pavlišič, Likozar et al., *Ind. Eng. Chem. Res.*, **2019**

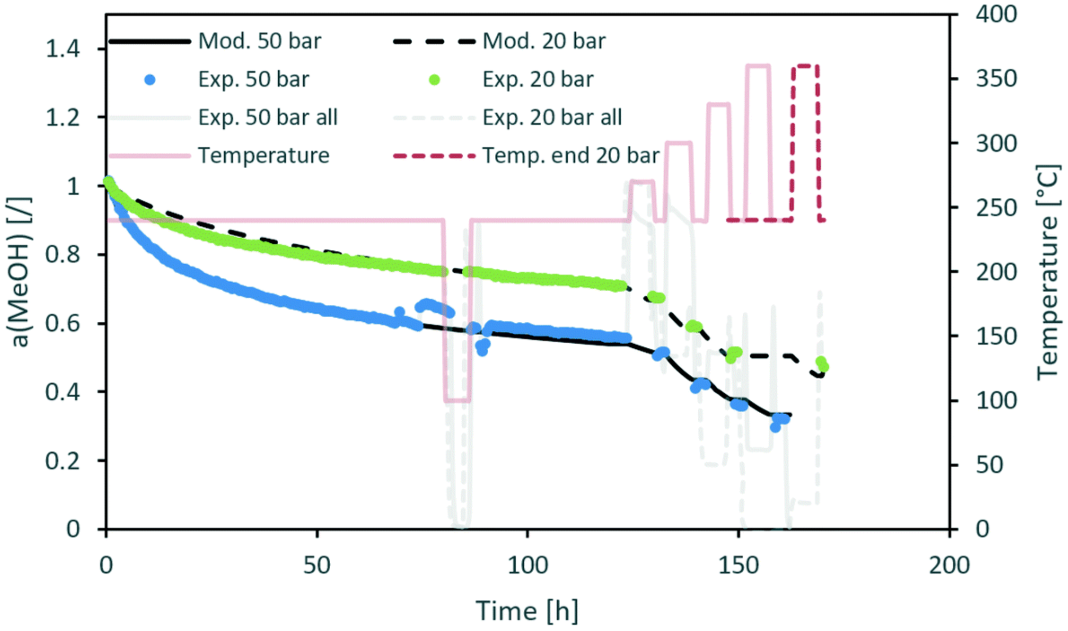
CO_2 CCU: Deaktivacijski model na podlagi osnovnega mehanizma

- Reakcijska **temperatura** in **tlak sta** vključena v model **deaktivacije katalizatorja** preko parcialnega tlaka H_2O.

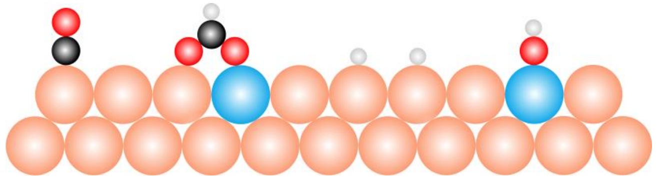
a… aktivnost katalizatorja:

$$\frac{da}{dt} = -a^{n_M} k_{H_2O} \left(f\, \boldsymbol{p_{H_2O}}^0\, a\right)^g$$



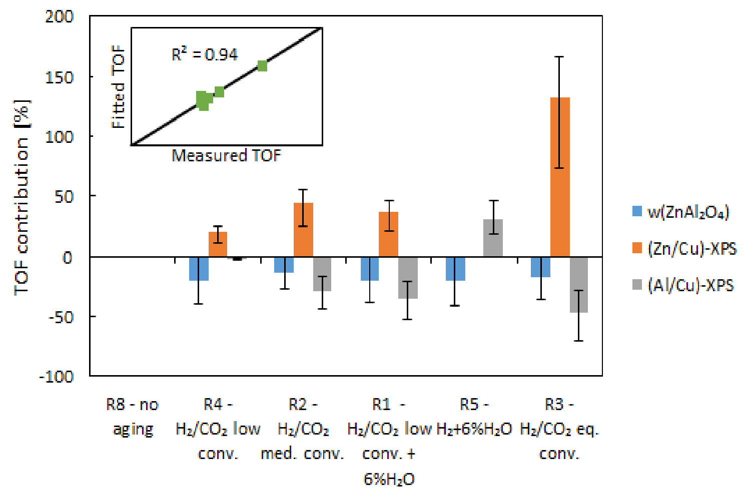


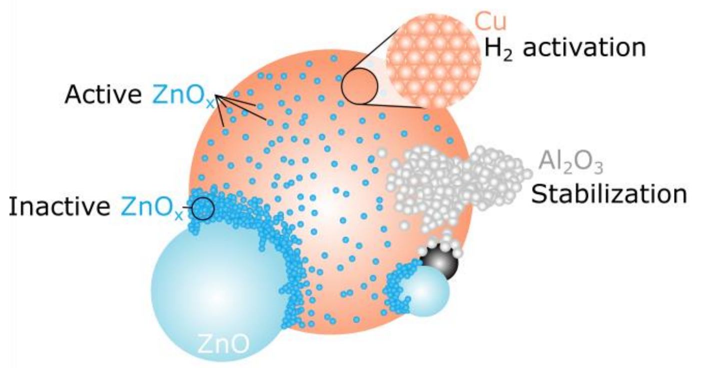
Prašnikar, Likozar, *React. Chem. Eng.* **2022**



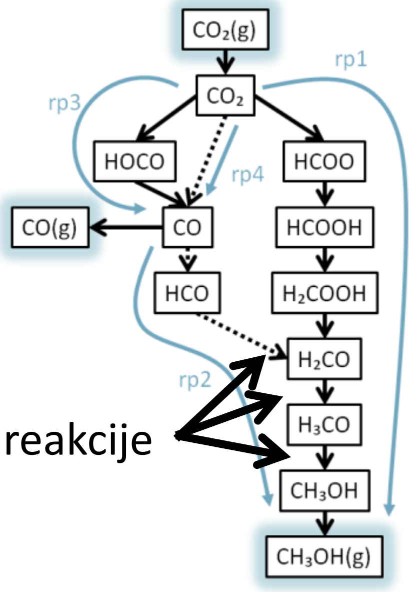
CO_2 CCU: Mikrokinetični model konverzije CO_2

- Najpomembnejši faktor je prekritje Cu (oranžen) s Zn :



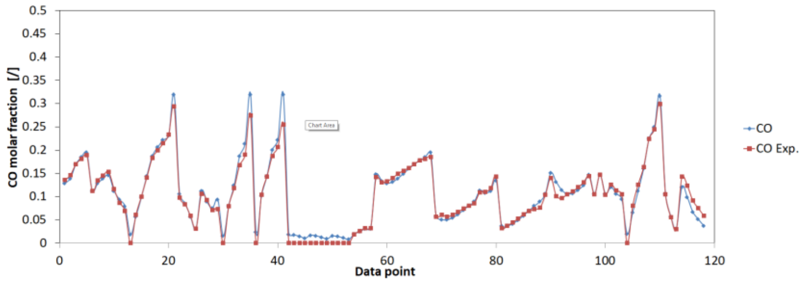


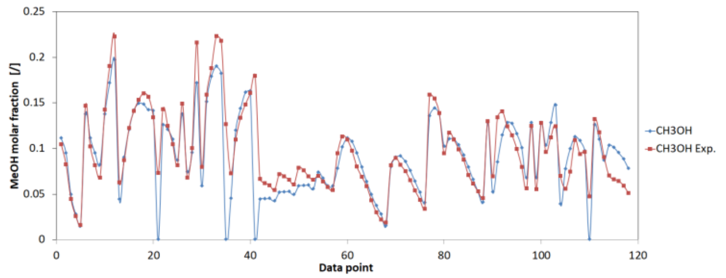
- Razvit in optimiziran večmesten mikrokinetični model
  - Vključitev Zn in Cu aktivnih mest

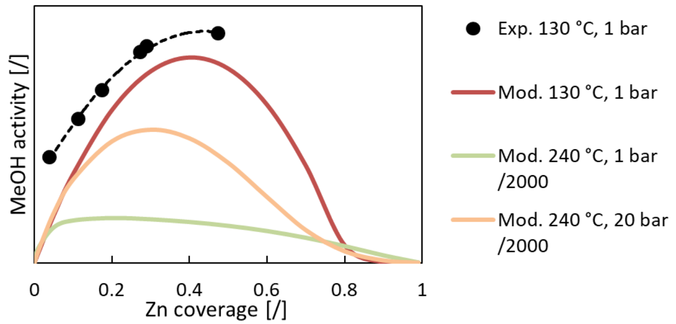


Elementarne reakcije

- Model potrjen na neodvisnih podatkih:





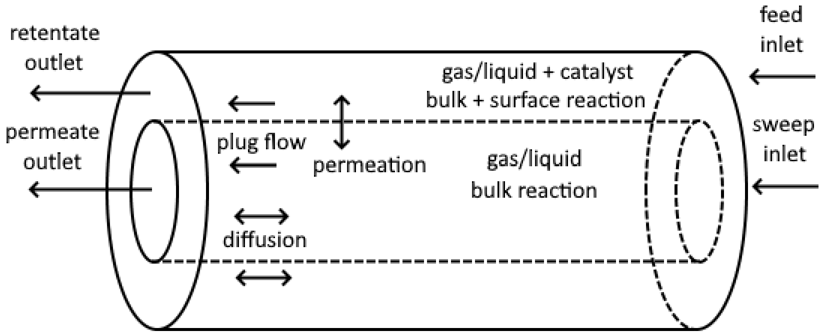


Prašnikar, Likozar, *et al. Appl. Catal. B*, 2021

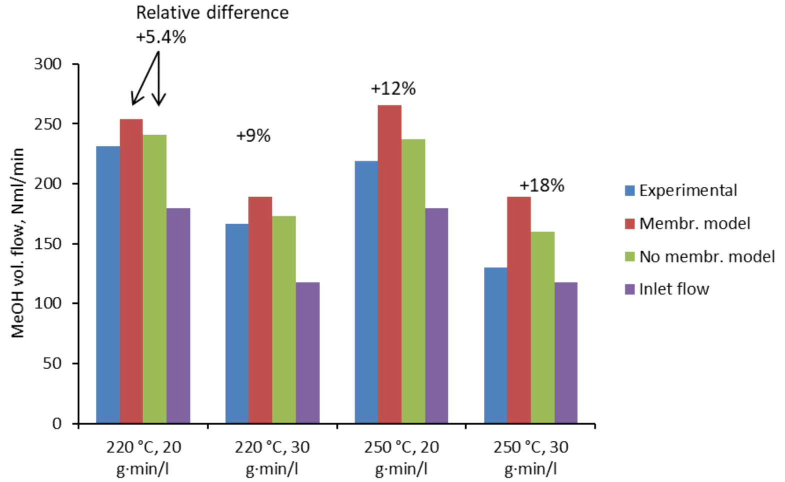
CO_2 CCU: Okrepitev z uporabo membranskega reaktorja

- Test 3 različnih membran na α-aluminijev oksidnih cevkah (NIC-TNO sodelovanje):
  - APTES-PA membrana
  - SPEEK-PI membrana
  - BTESE membrana

- Model razvit glede na mikrokinetiko:



Opazimo >6 višje permeance H_2O kot H_2 v primeru APTES-PA

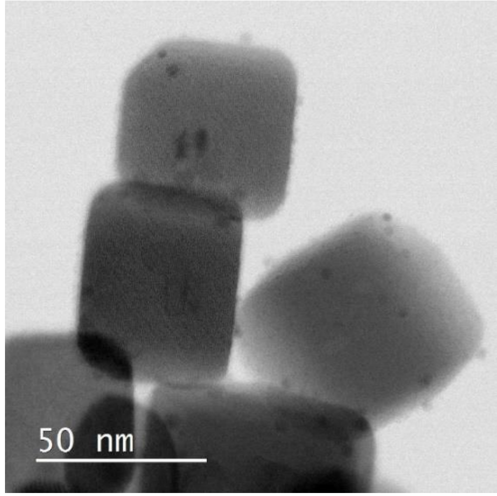


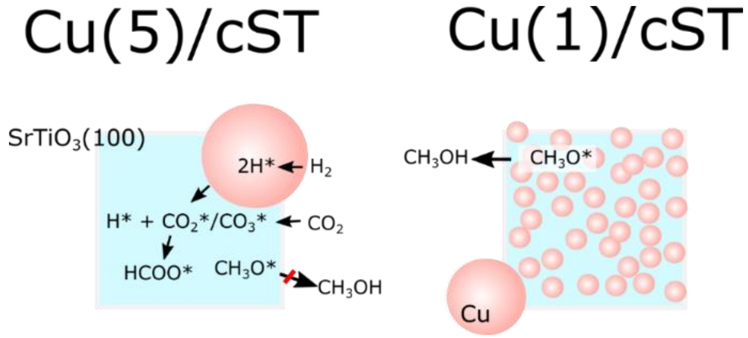
- Programska oprema razvita za hitro mikrokinetično reševanje: **CERRES** (0D, 1D 2D problemi)

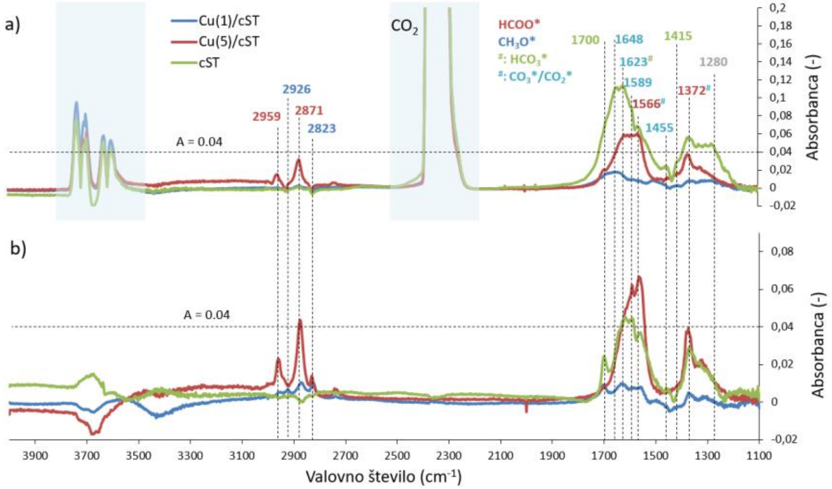
CERRES

CO_2 CCU: Eksperimenti na modelnem katalizatorju $Cu/SrTiO_3(100)$ in bimetalu Cu-Zn MOF-74

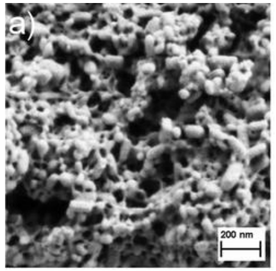
- Cu nanešen na $SrTiO_3$ nanocevke nano-kocke z izpostavljeno (100) ploskvijo.
- Glavni intermediati so $HCOO^*$ in CH_3O^* kot identificirano z DFT analizo
- Prisotnost Cu v $SrTiO_3$ znatno zmanjša zmožnost adsorbcije CO_2 significantly (faktor 50) v prisotnosti mešanice H_2/CO_2.
- Prelivanje vodika čez $SrTiO_3$ povzroči nastajanje $HCOO^*$, vendar neCH_3O^*- (samo na Cu)

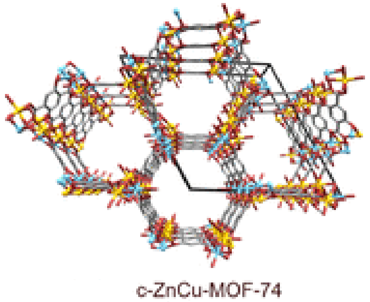


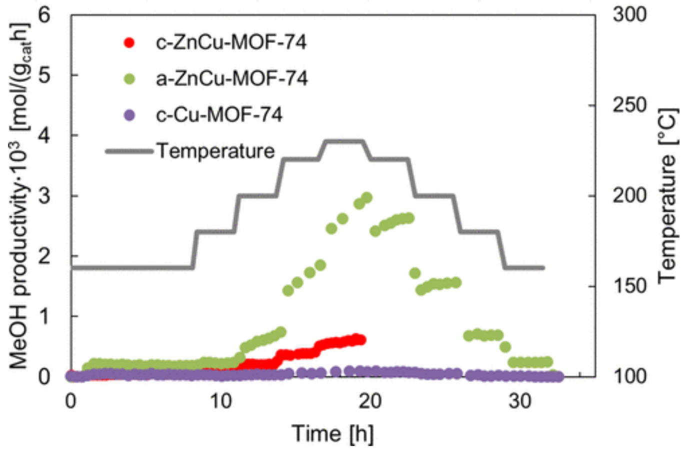




- Karakteriziran in ocenjen CuZn MOF-74 pripravljen z razširljivo mehanokemijsko sintezo.
- Amorfizacija poveča sintezno aktivnost MeOH.



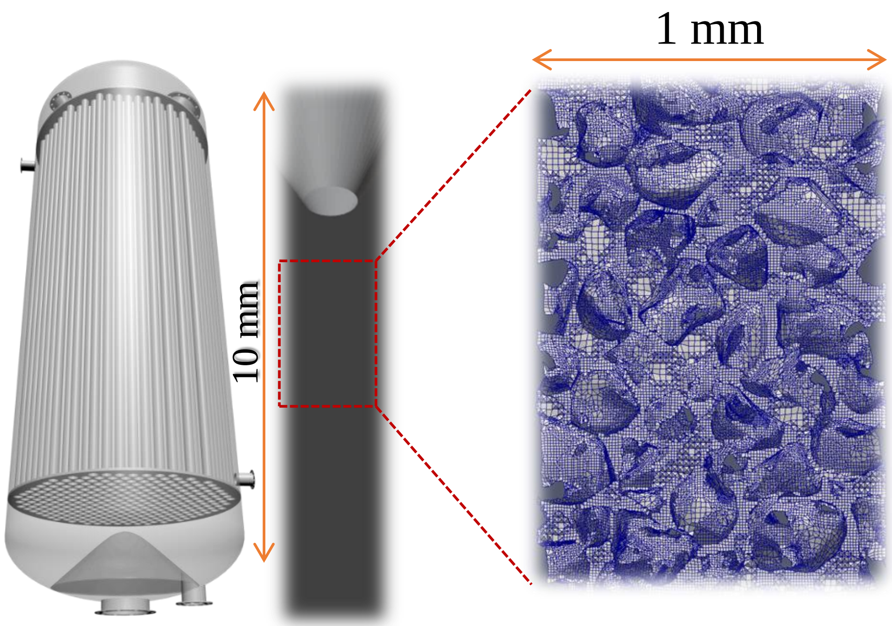


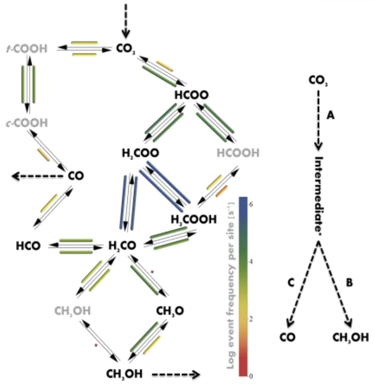


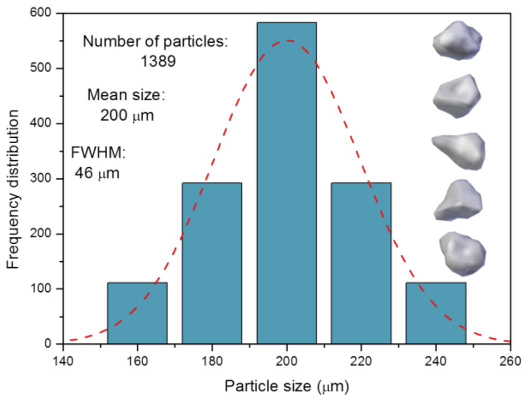
Stolar, Prašnikar, *et al. ACS Appl. Mater. Interfaces* **2021**

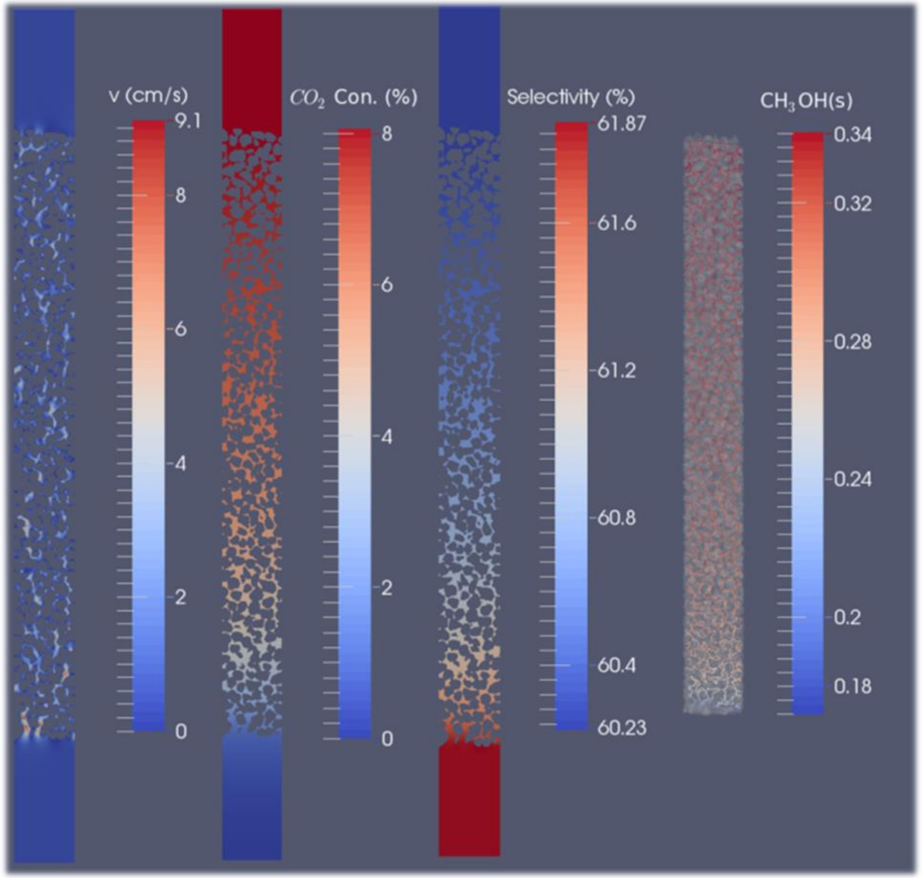
Večstopenjsko modeliranje: hidrogeniranje CO_2

Potek dela CFD simulacij



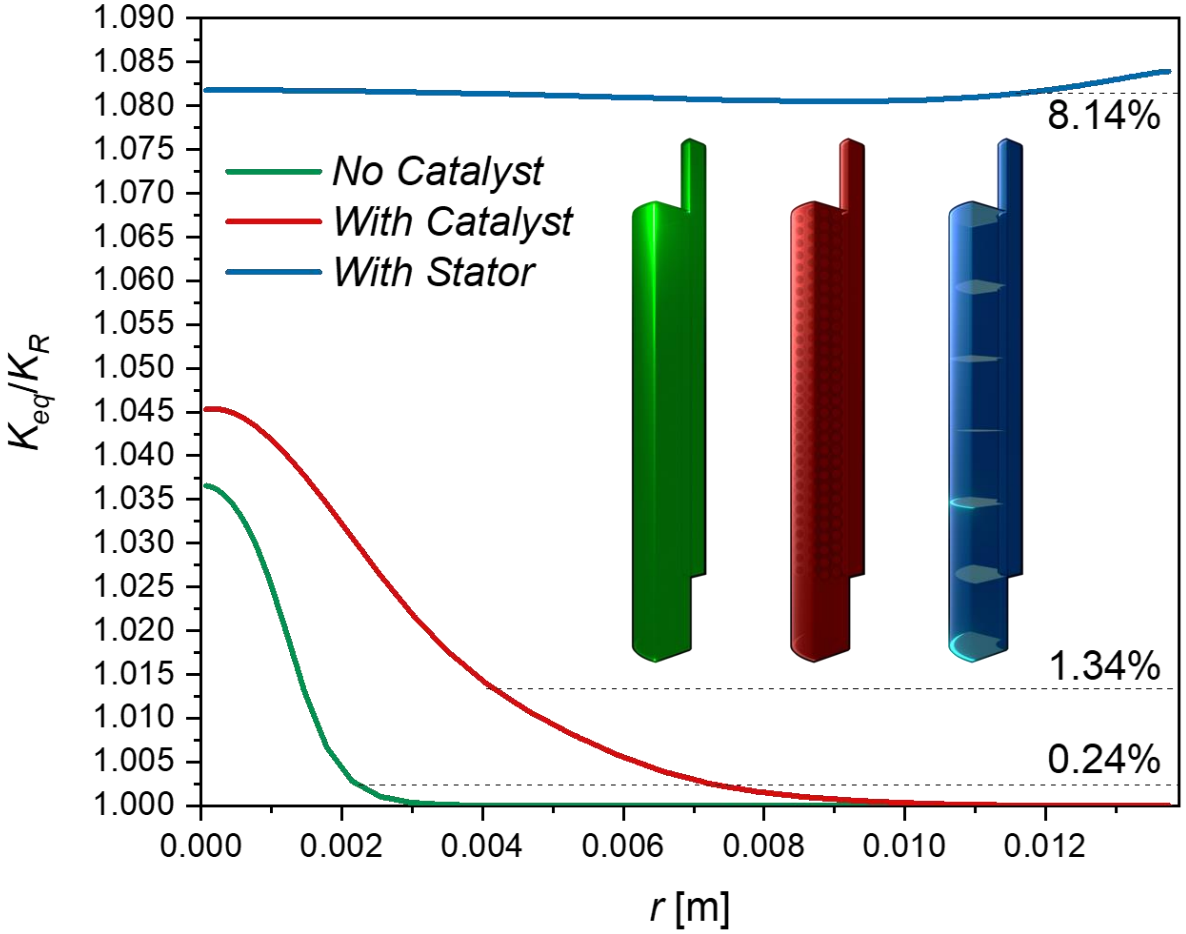






Večstopenjsko modeliranje: hidrogeniranje CO_2

Optimizacija membranskega reaktorja



Premik kemijskega ravnotežja v membranskem reaktorju:

<u>Prepoznavanje problema:</u>

- *Zaradi visokih koncentracijskih gradientov večina membranskih reaktorjev ne pripomore k premiku kemijskega ravnotežja*

<u>Katalitski membranski reaktor:</u>

- *Katalitski delci izboljšajo radialen masni prenos, vendar ima premik ravnotežja še vedno največji vpliv blizu membrane*

<u>Membranski reaktor s statičnim mešalom:</u>

- *Statično mešalo premika kemijsko ravnotežje skozi celoten reaktor*