REATTIVITA' DI ENZIMI E LORO ANALOGHI DI SINTESI: APPRENDERE DALLA NATURA PER IL DESIGN DI NUOVI CATALIZZATORI

- *Chemistry serving Biology*
- *Biology serving Chemistry*

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METALLOPROTEINS

can *efficiently* perform tranformations that represent a CHALLENGE in current chemistry

can process / activate

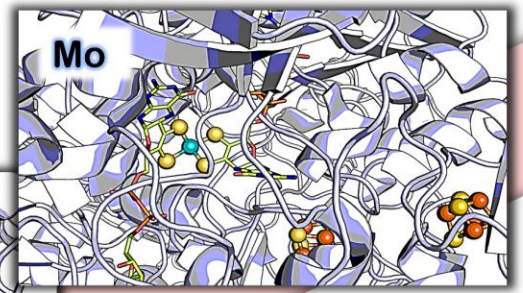
SMALL MOLECULES

Energy related substrates (biofuels)

Synthesis building blocks

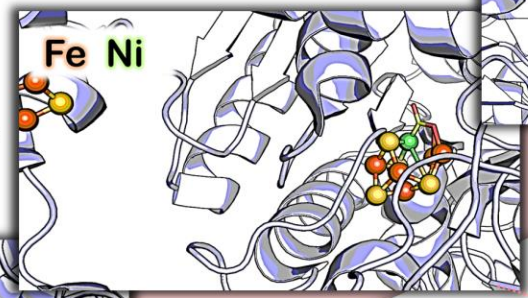
Formate Dehydrogenase

$\mathbf{HCOOH} + NAD^+ \longleftrightarrow \mathbf{CO_2} + NADH + H^+$



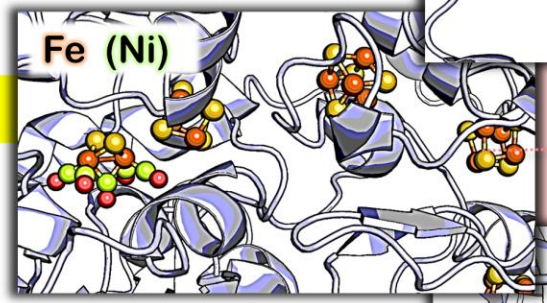
Carbon Monoxide Dehydrogenase

$\mathbf{CO} + H_2O \longleftrightarrow \mathbf{CO_2} + 2e^- + 2H^+$



Fe/Ni Hydrogenase

$\mathbf{H_2} \longleftrightarrow 2e^- + 2H^+$



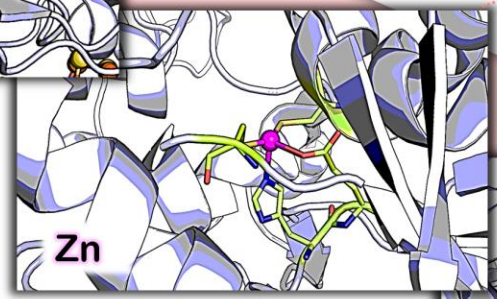
Cheap metals

High rates

Ambient T and P

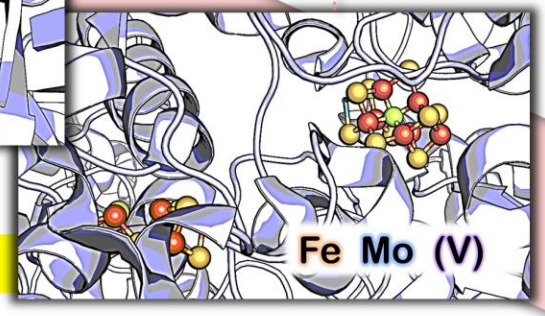
$\mathbf{CH_3CH_2OH} + NAD^+ \longleftrightarrow CH_3CHO + NADH + H^+$

Alcohol Dehydrogenase

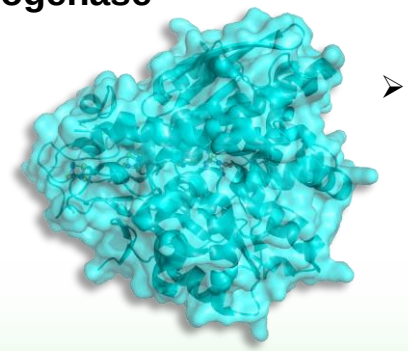


$\mathbf{N_2} + 8H^+ + 8e^- + 16ATP \longleftrightarrow 2\mathbf{NH_3} + \mathbf{H_2} + 16ADP + 16Pi$

Mo/V Nitrogenase



Hydrogenase



- ***Surprising performances**:*
  up to 10.000 molecules s^{-1} processed!

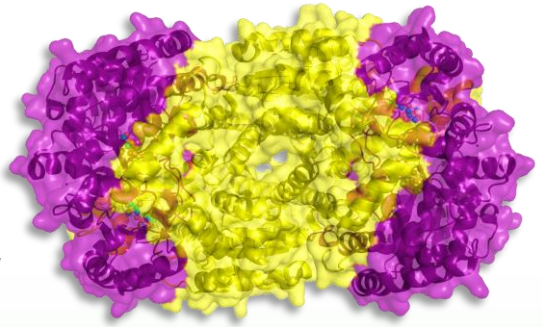
$$H_2 \rightleftharpoons 2e^- + 2H^+$$

NATURE

H_2

"Fuel of the future"
- High energy density
- Completely green combustion

Nitrogenase



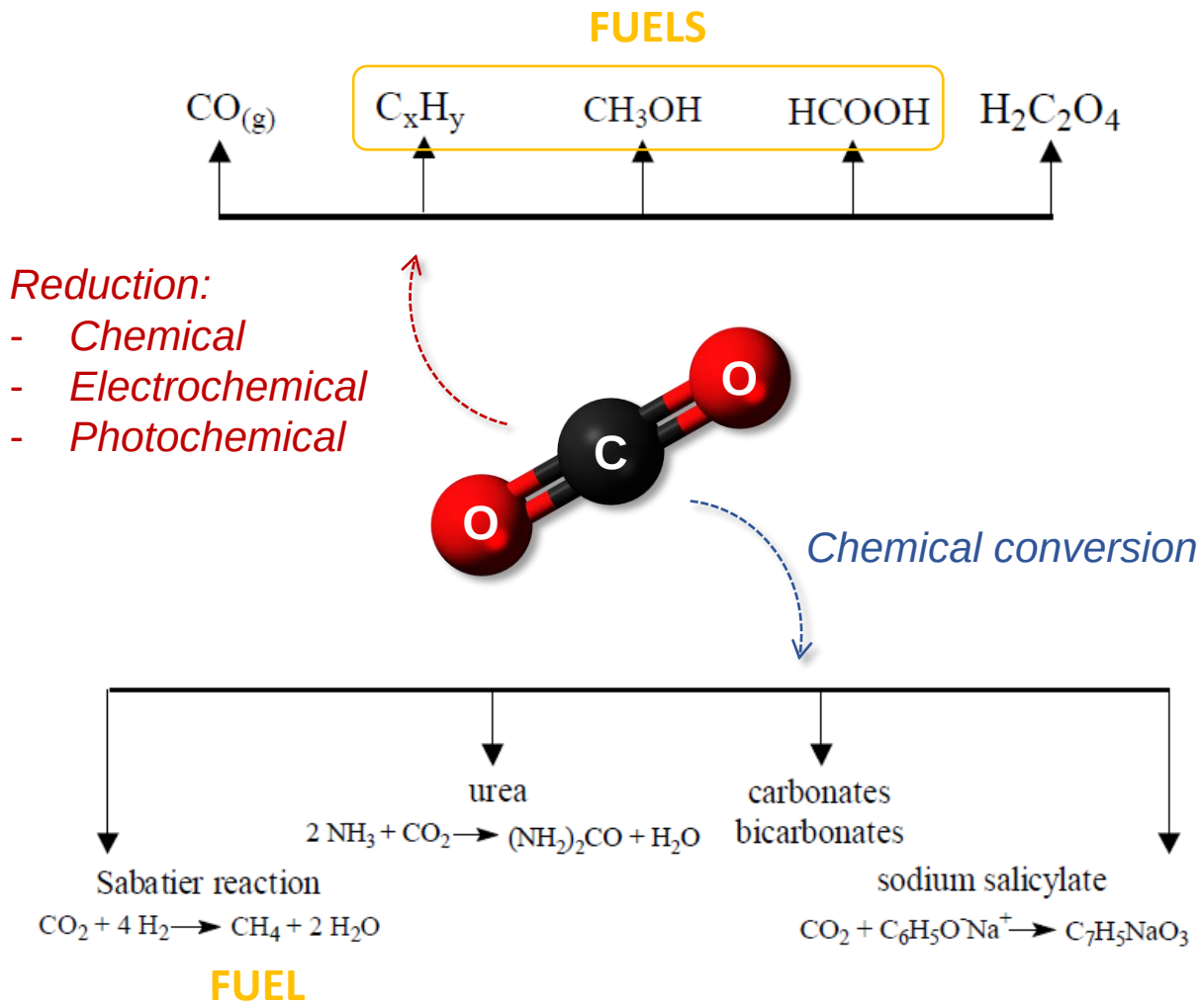
- ***Fix N_2 into ammonia***
  at room T and P
- ***Reduce CO_2 into hydrocarbons = FUELS!***

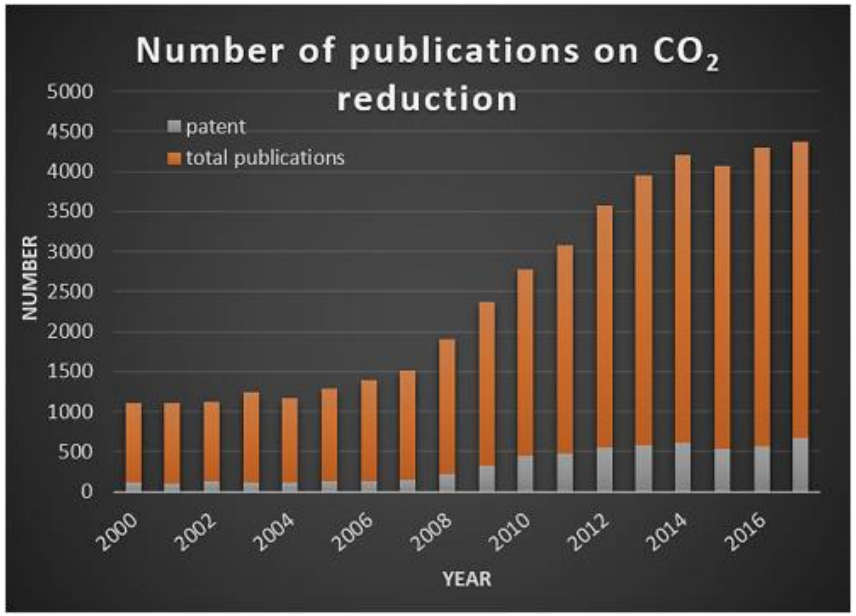
NATURE

CO_2

NATURE

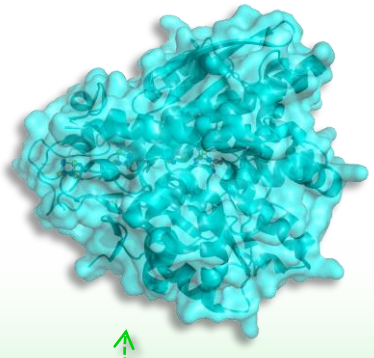
N_2





Publications trend in the field of electrochemical homogeneous reduction of CO_2.

Hydrogenase



- ***Surprising performances**:*
  up to 10.000 molecules s^{-1} processed!

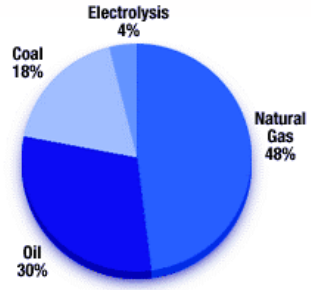
$$H_2 \rightleftharpoons 2e^- + 2H^+$$

NATURE

H_2

INDUSTRY

H_2 production

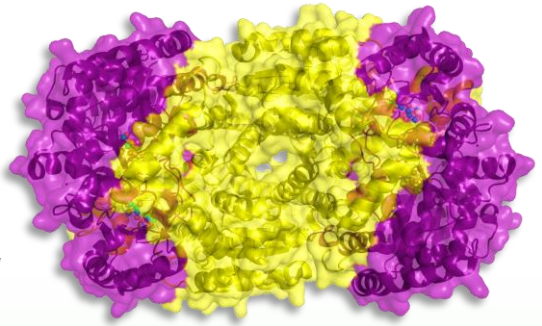


$$2H_2 + O_2 \xrightarrow{CAT.} \underline{2H_2O}$$

H_2 oxidation

Nitrogenase

- ***Fix N_2 into ammonia***
  at room T and P
- ***Reduce CO_2 into hydrocarbons = FUELS!***



NATURE

CO_2

NATURE

Catalysts based on PRECIOUS METALS

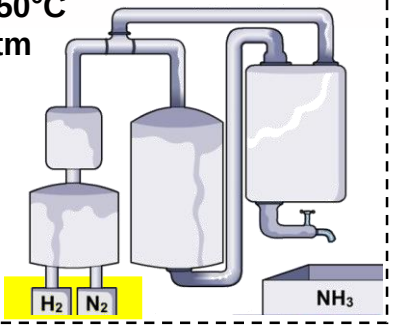
NATURE

N_2

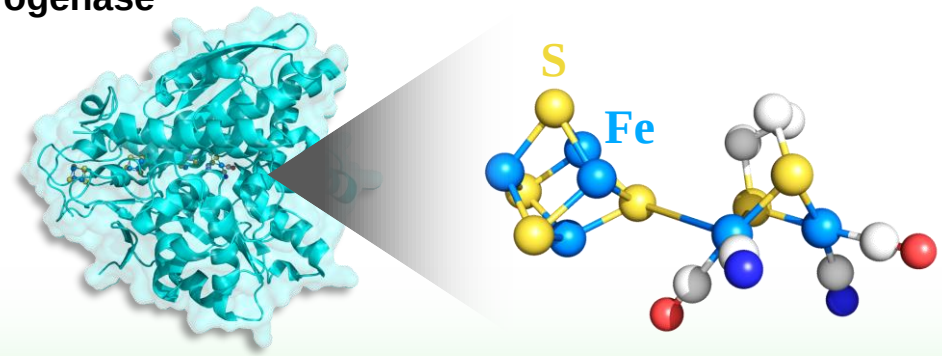
INDUSTRY

HABER-BOSCH

400-450°C
200 atm



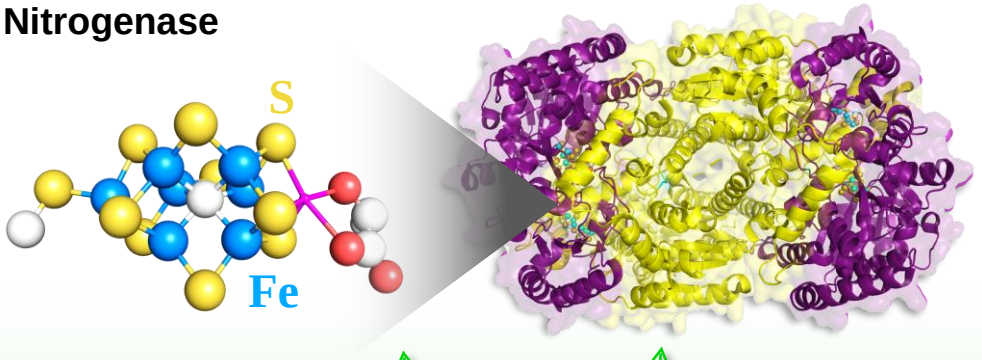
Hydrogenase



NATURE

H_2

Nitrogenase



NATURE

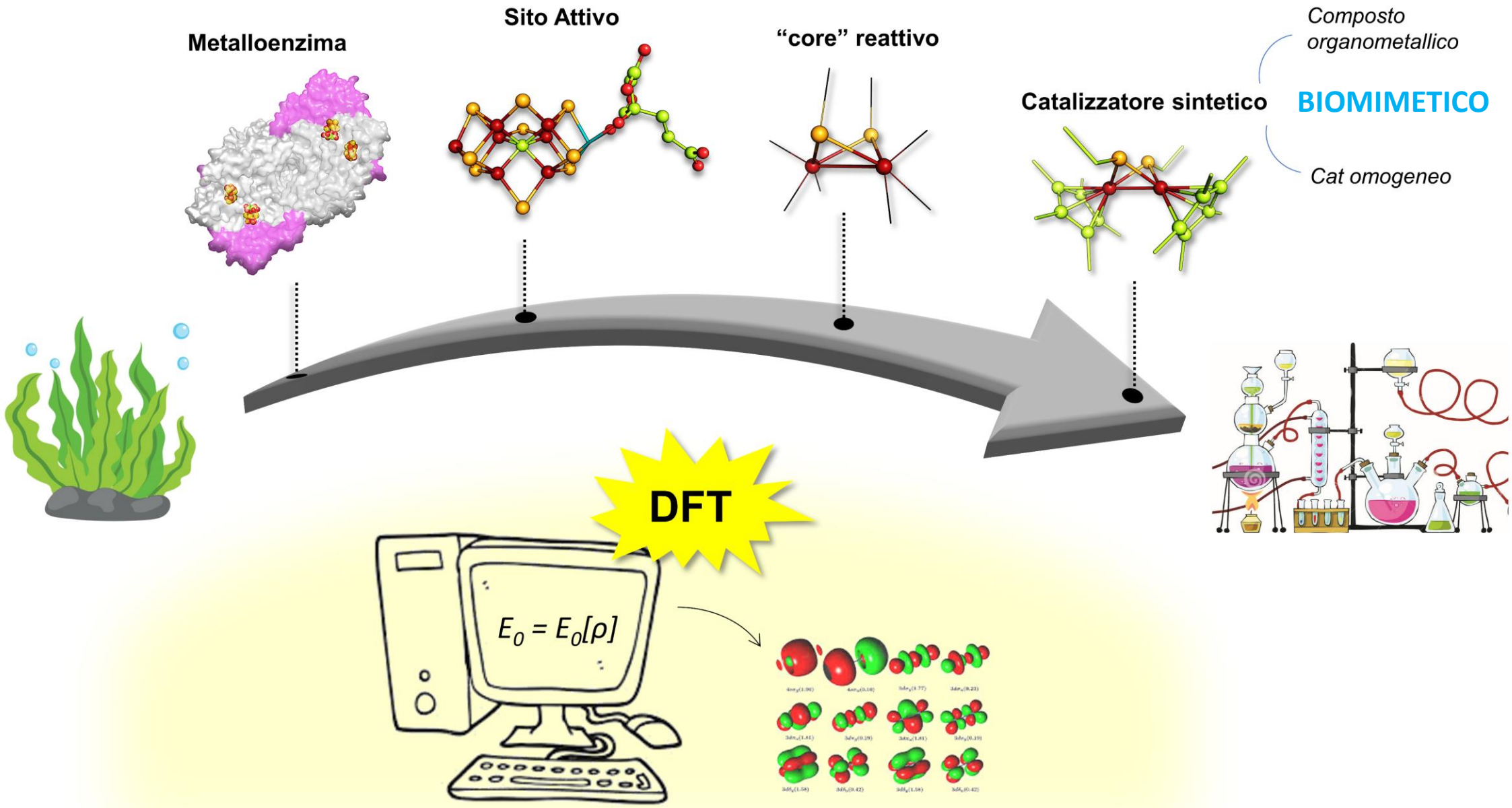
CO_2

NATURE

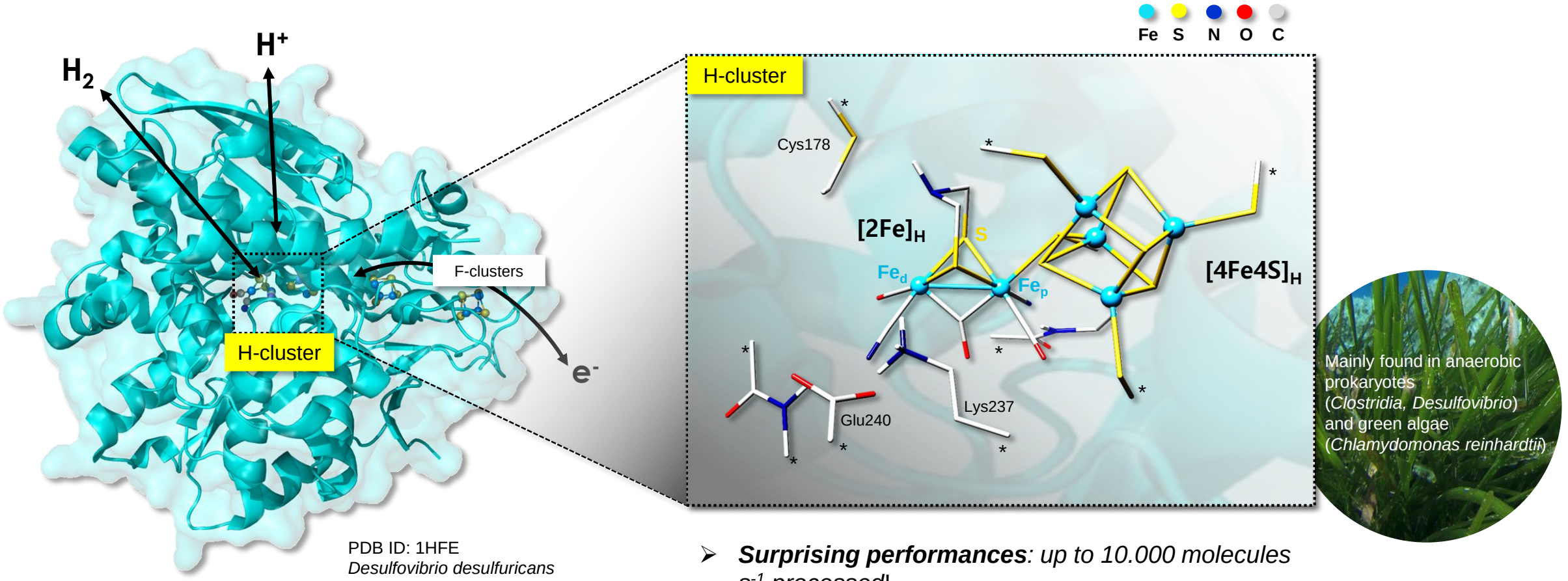
N_2

Switch from precious to bio-available metals as catalysts

Both FeS proteins


Metalloenzima
Sito Attivo
“core” reattivo
Catalizzatore sintetico
Composto organometallico
BIOMIMETICO
Cat omogeneo
DFT
$E_0 = E_0[\rho]$

ARGOMENTO DI TESI 1



PDB ID: 1HFE
Desulfovibrio desulfuricans

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

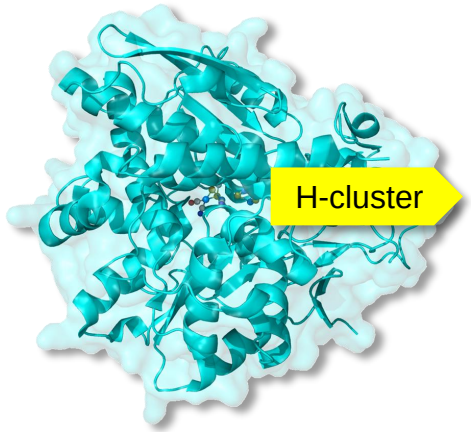
[FeFe]-Idrogenasi

- ***Surprising performances**: up to 10.000 molecules s^{-1} processed*!
- Highest TOF for H_2 production among the different hydrogenase families
- Complete **reversibility**

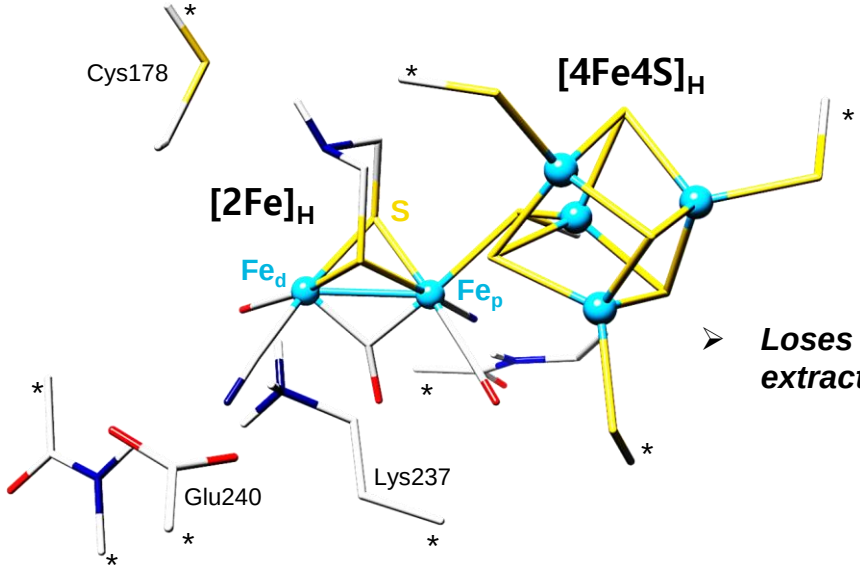
ARGOMENTO DI TESI 1

METALLOENZYME

$H_2 \rightleftharpoons 2(H^+/e^-)$

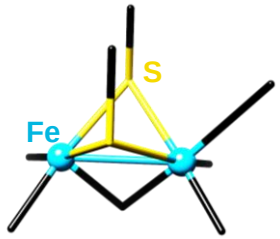


ACTIVE SITE

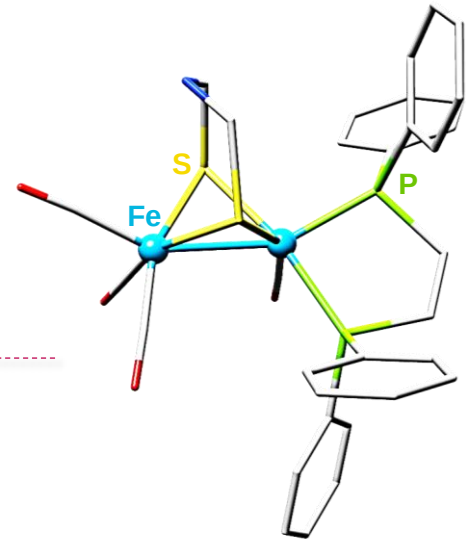


- ***Loses catalytic activity if extracted from the protein***

REACTIVE CORE



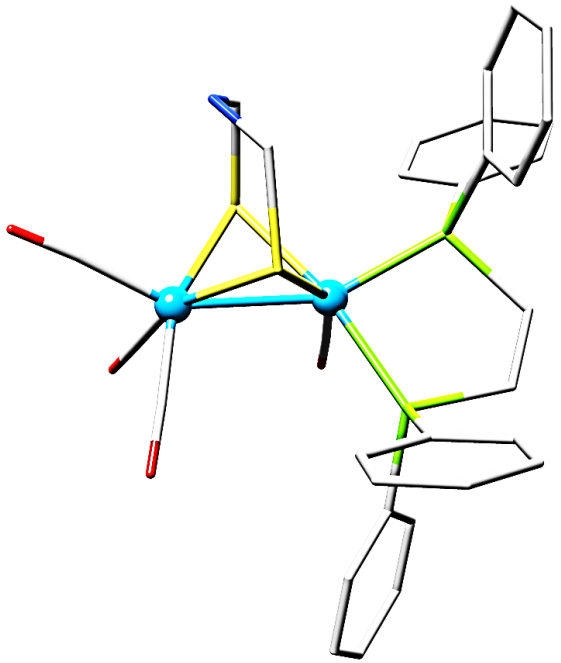
BIOMIMIC



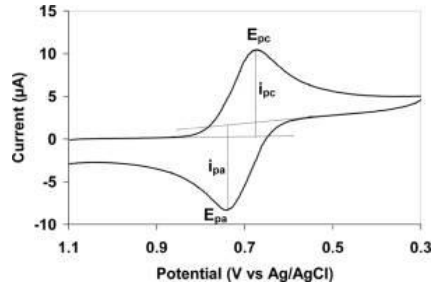
- ***Catalytically active***
- ***Super cheap:***
  Fe-precursor ~ 4 €/g
  thiolate ~ 3 €/g
- ***Easy*** *and* ***fast*** *to be synthesized*
- ***Lower performances*** than the natural system in the H_2 production direction
- Poorly reactive towards H_2 oxidation

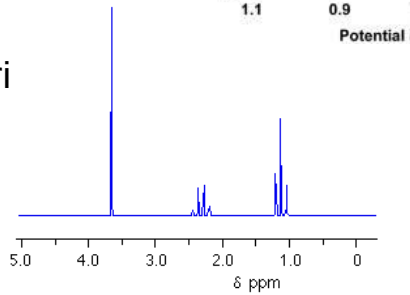
$H_2 \rightleftharpoons 2(H^+/e^-)$

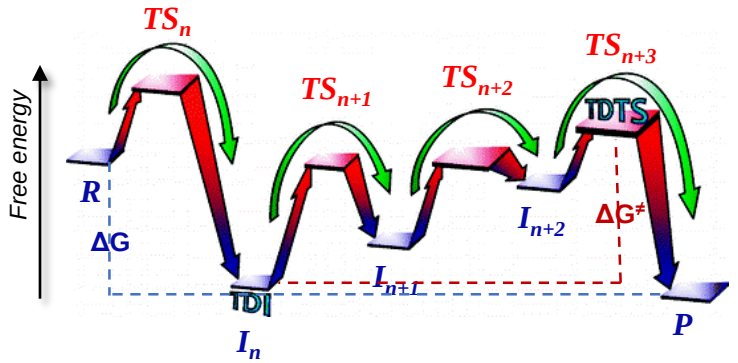
ARGOMENTO DI TESI 1



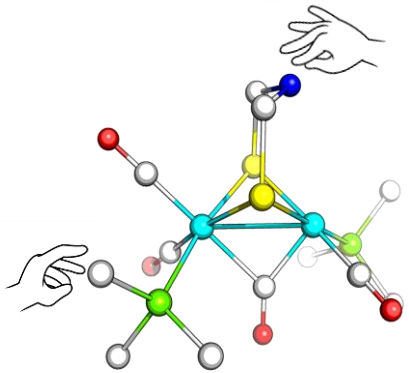
- Caratterizzazioni strutturali
- Studiare le proprietà redox → calcolo potenziali redox
  → interpretazione di CV
- Studio proprietà spettroscopiche e interpretazione spettri (IR, NMR, UV)
- Caratterizzazione meccanismi catalitici







- Come modificare la struttura per:
  Aumentare efficienze catalitiche?
  Ottimizzare proprietà di interesse?
  Riprodurre sinteticamente conformazioni attive in natura



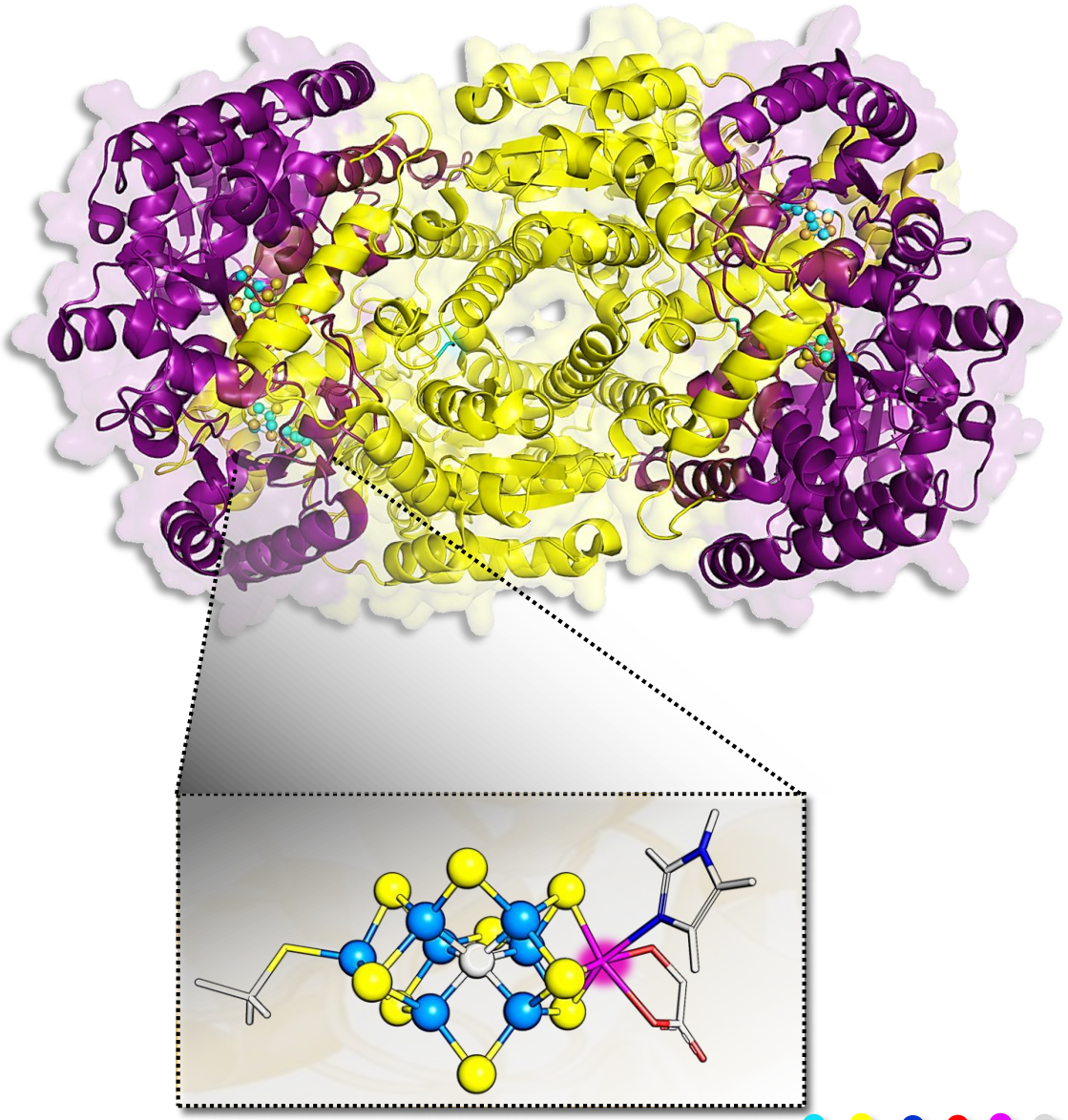
University of Illinois at Urbana, US

Università di Bologna

University of Jena, Germany

Univeristé de Bretagne occidentale, France

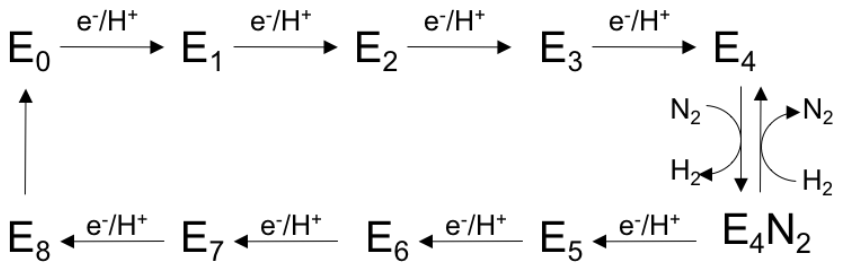
ARGOMENTO DI TESI 2



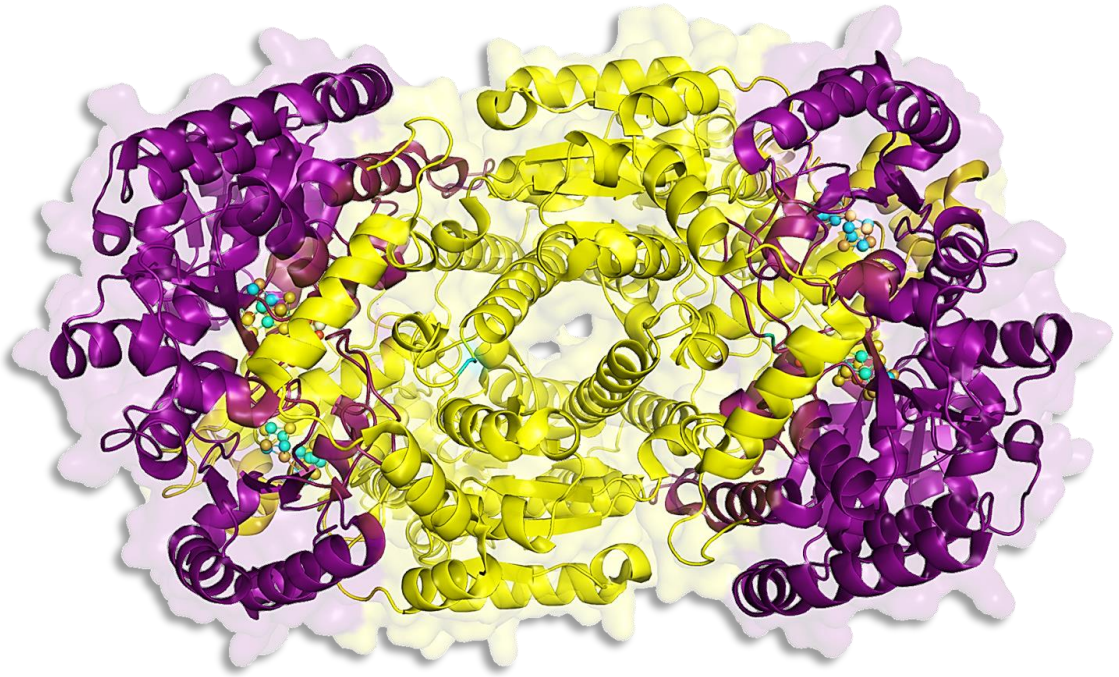
Mo-Nitrogenasi

! *Fix N_2 into ammonia at room T and P*

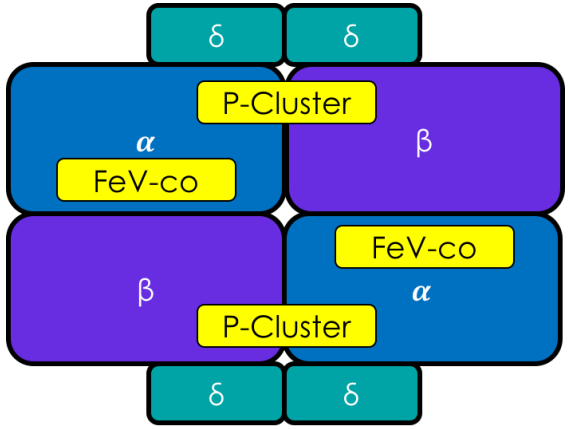
$$N_2 + 8\,H^+ + 8e^- + \underline{16\,ATP} \rightleftharpoons 2\,NH_3 + \underline{H_2} + 16\,ADP + 16\,Pi$$



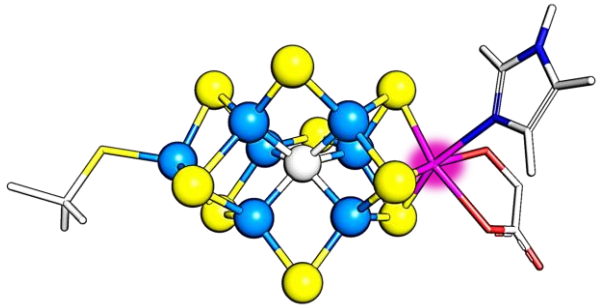
ARGOMENTO DI TESI 2



Mo-Nitrogenasi



V-Nitrogenasi

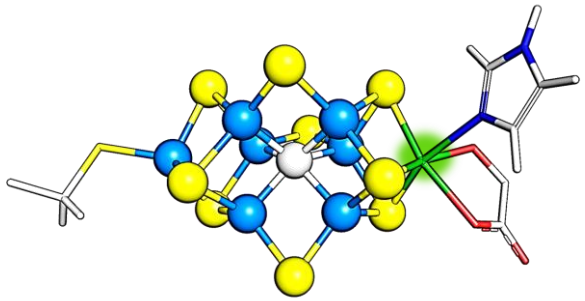


N_2

CO_2

FeMo-co

Fe S N O Mo C

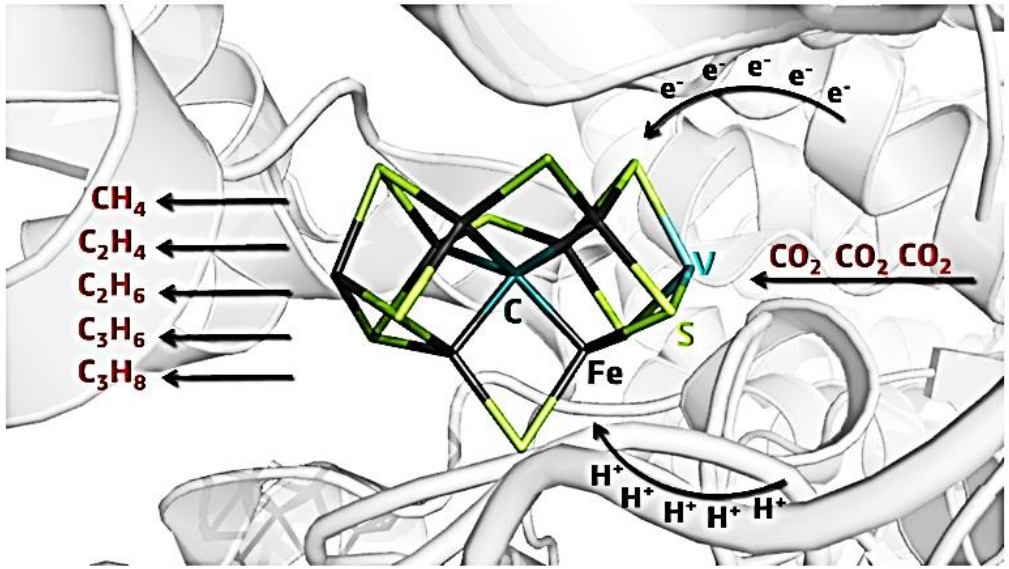


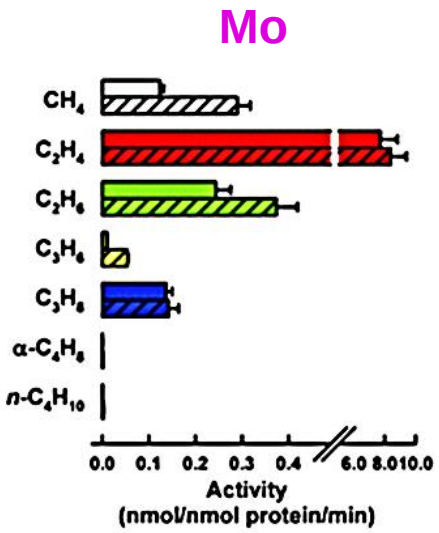
N_2

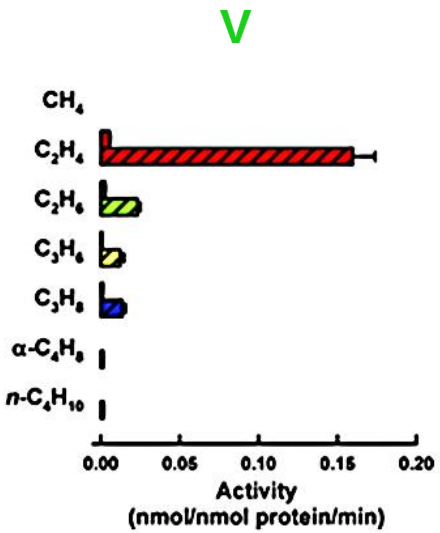
CO_2

FeV-co

ARGOMENTO DI TESI 2







- **Comprensione del meccanismo che porta alla forma attiva del sito catalitico**
- **Caratterizzazione del meccanismo di trasformazione di N_2 e CO_2 in composti tecnologicamente rilevanti (fuel, building-blocks per la sintesi chimica)**
- **Ricerca dell'origine della differente selettività di substrato di Mo e V-Nitrogenasi**