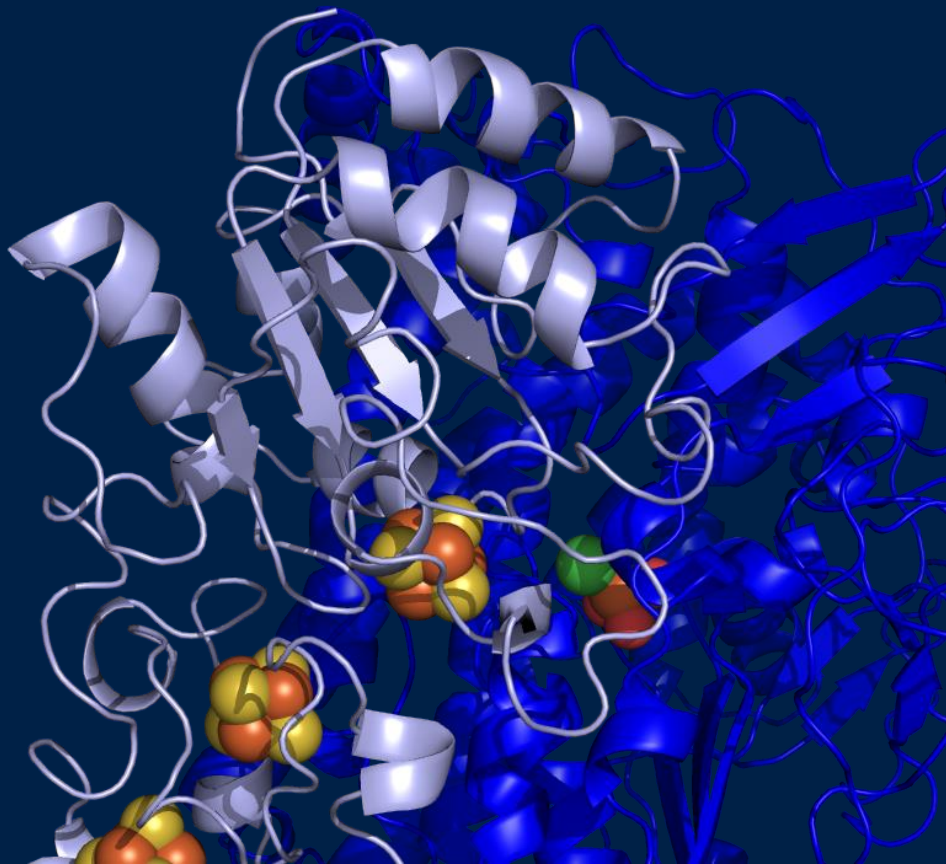
Hydrogen and carriers
- a (bio)catalysis perspective

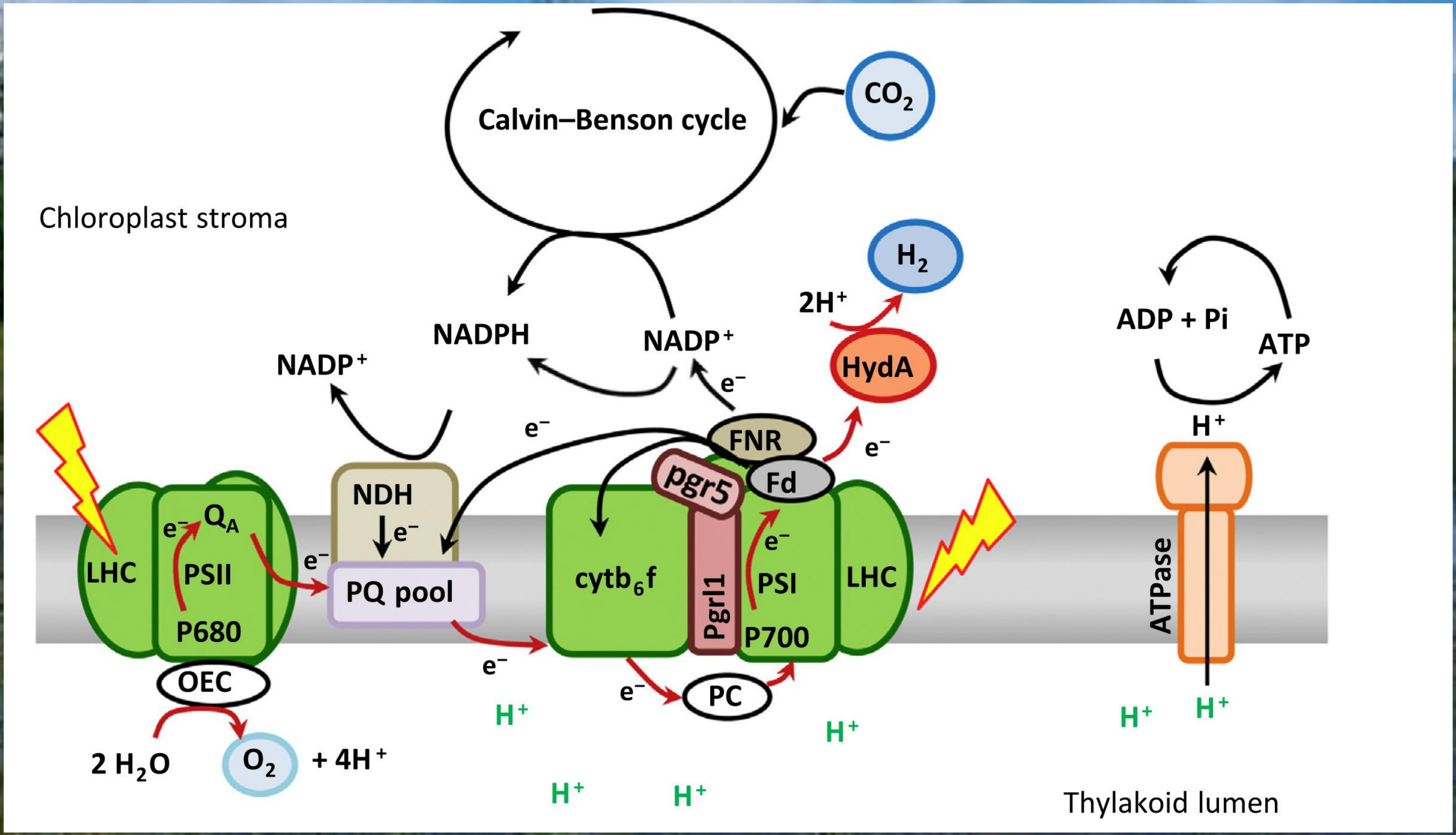
Energy and Net Zero in the UK

Prof. Kylie A. Vincent
Department of Chemistry



Hydrogen – a perspective from biology

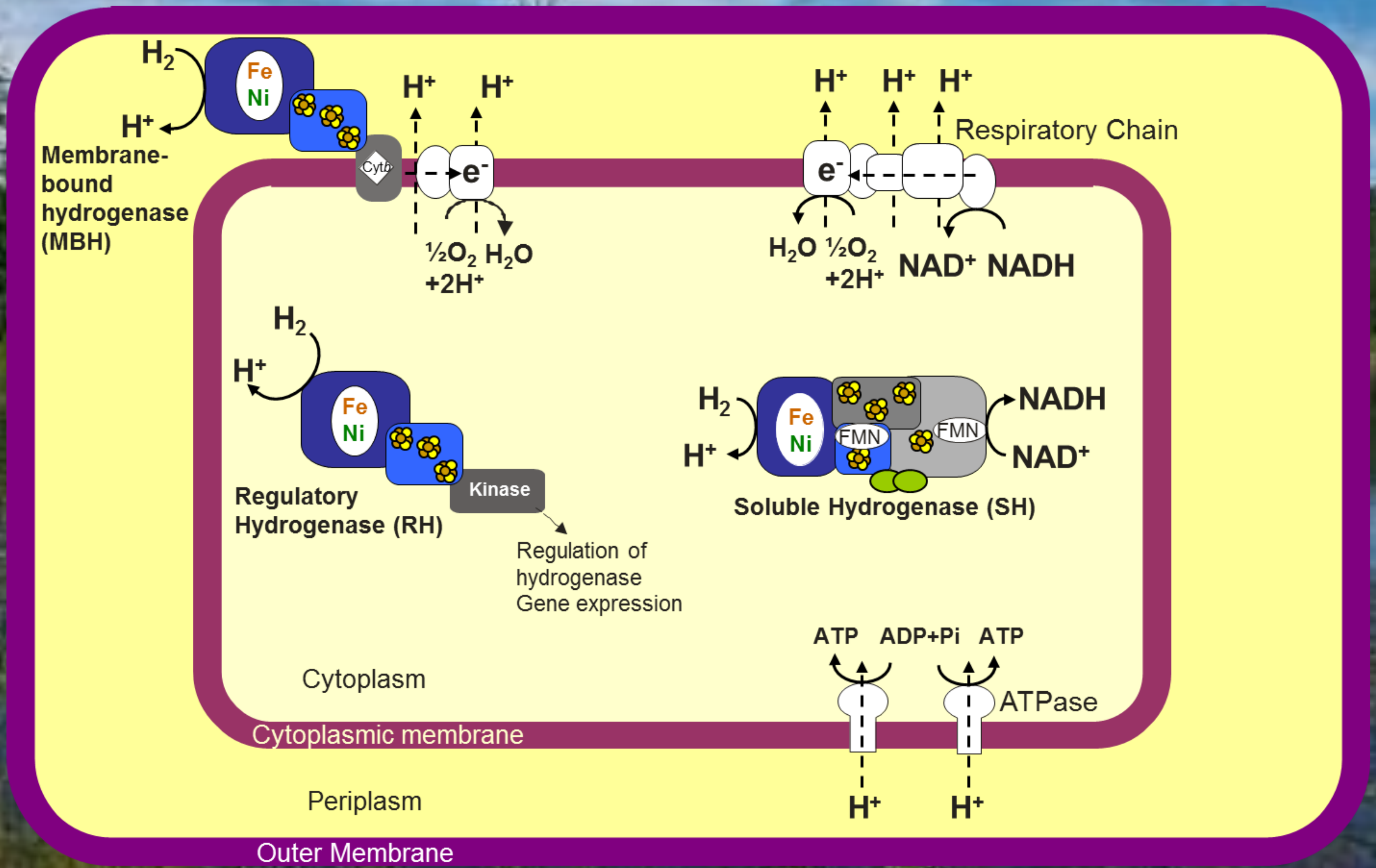
Hydrogen energy circuits in cells



Green algae

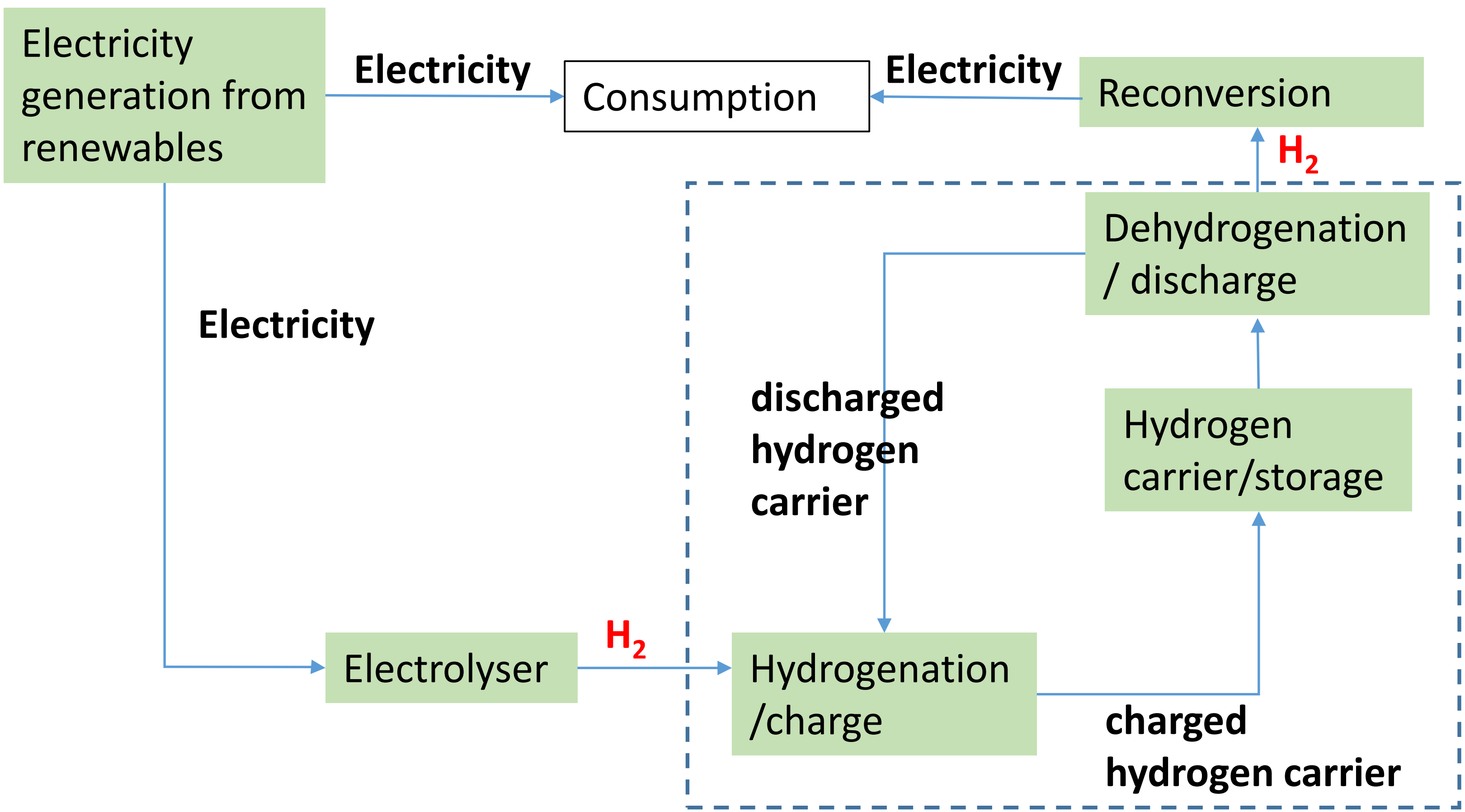
Tóth and Yacoby, *Trends in Biotechnol.*, 2019, 371159

Hydrogen energy circuits in cells



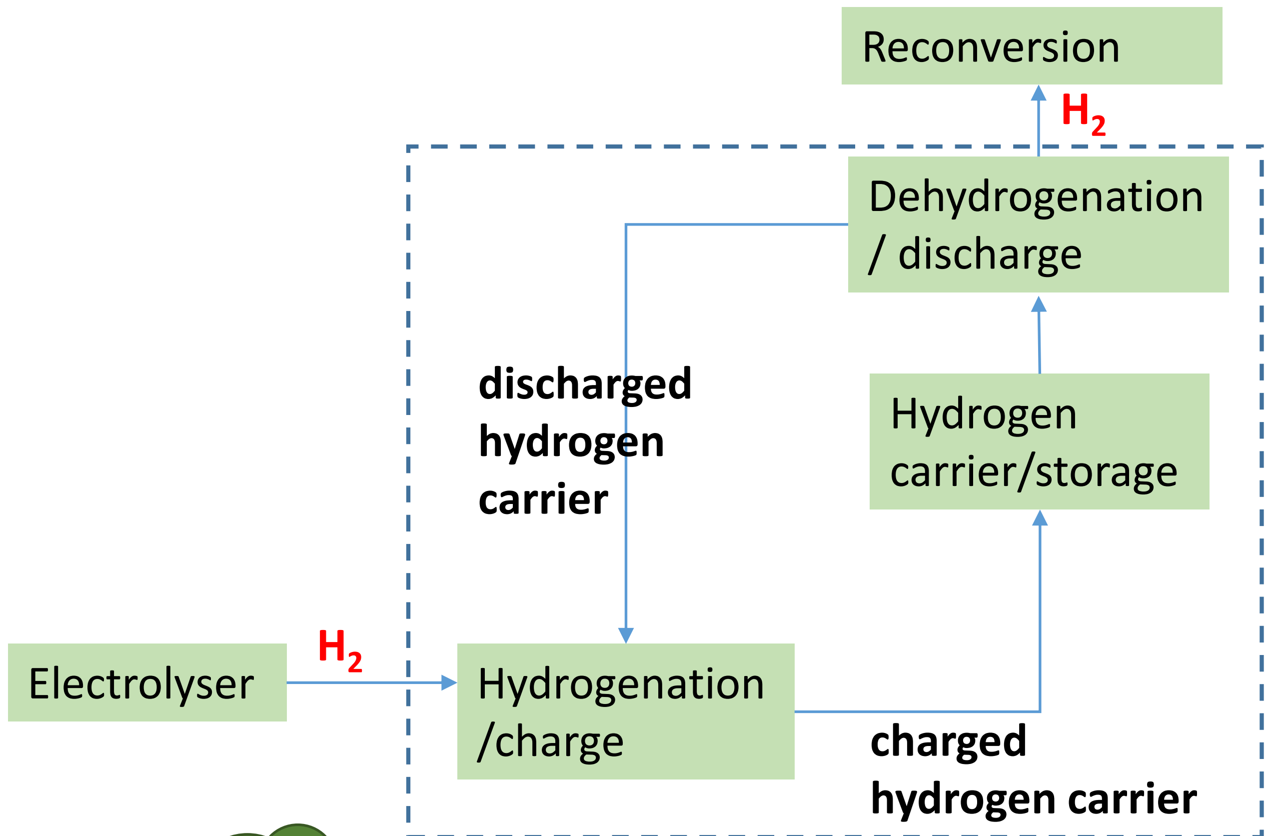
Cell of *Cupriavidus necator (Ralstonia eutropha)* Diagram courtesy of Oliver Lenz, TU Berlin

Energy system built around light hydrogen carriers



Adapted from: Energy Fuels 2019, 33, 4, 2778

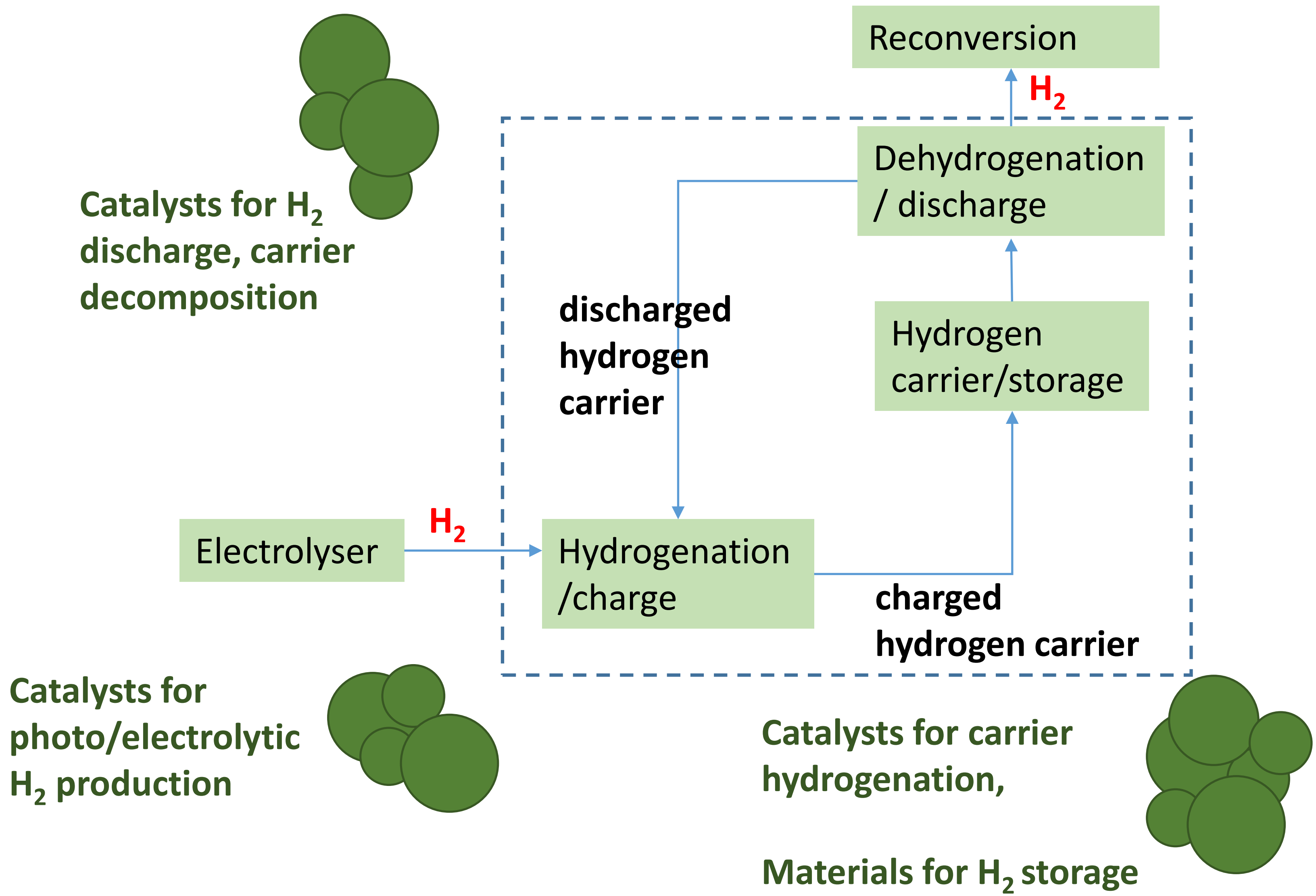
Energy system built around light hydrogen carriers: research clustering in Oxford Chemistry and beyond



Catalysts for photo/electrolytic H_2 production

L Steier, I McCulloch, SCE Tsang…

Energy system built around light hydrogen carriers: research clustering in Oxford Chemistry and beyond



Energy systems built around light hydrogen carriers
–*contributions from Oxford Chemistry*

Ammonia

$N_2 \rightarrow NH_3$

-STFC Ammonia reactor at RCaH
-Catalyst and implementation research in Oxford, inc SCE Tsang, W David

→ Need for more agile alternatives to Haber-Bosch, particularly electrocatalytic NH_3 synthesis, as well as ammonia decomposition catalysts

Boron-based carriers: ammonia borane etc

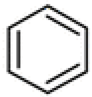
S Aldridge (Chemistry)

Lightweight metal hydrides

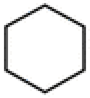
W David, recently PP Edwards

Liquid hydrocarbon stores

eg



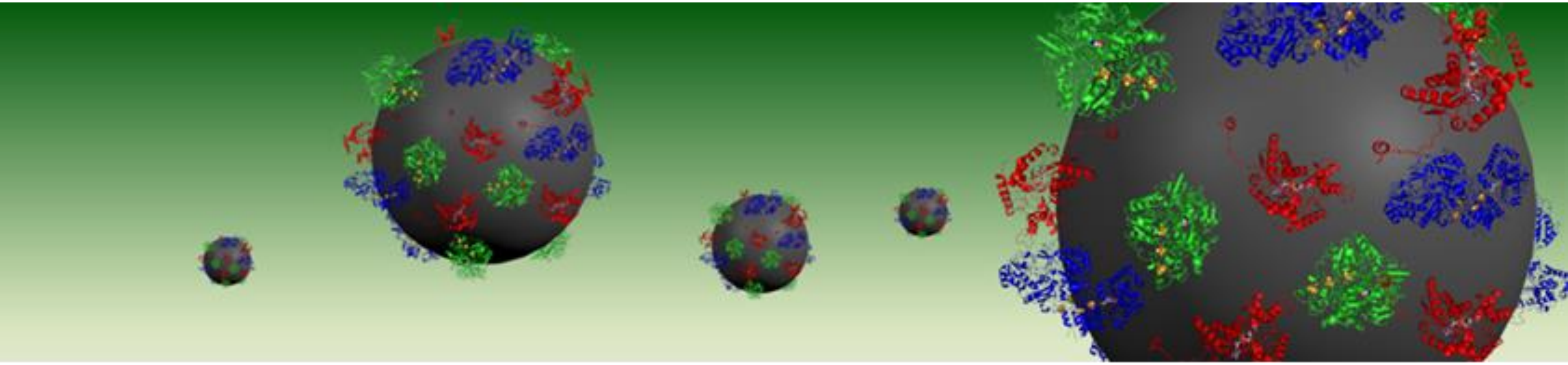
Benzene



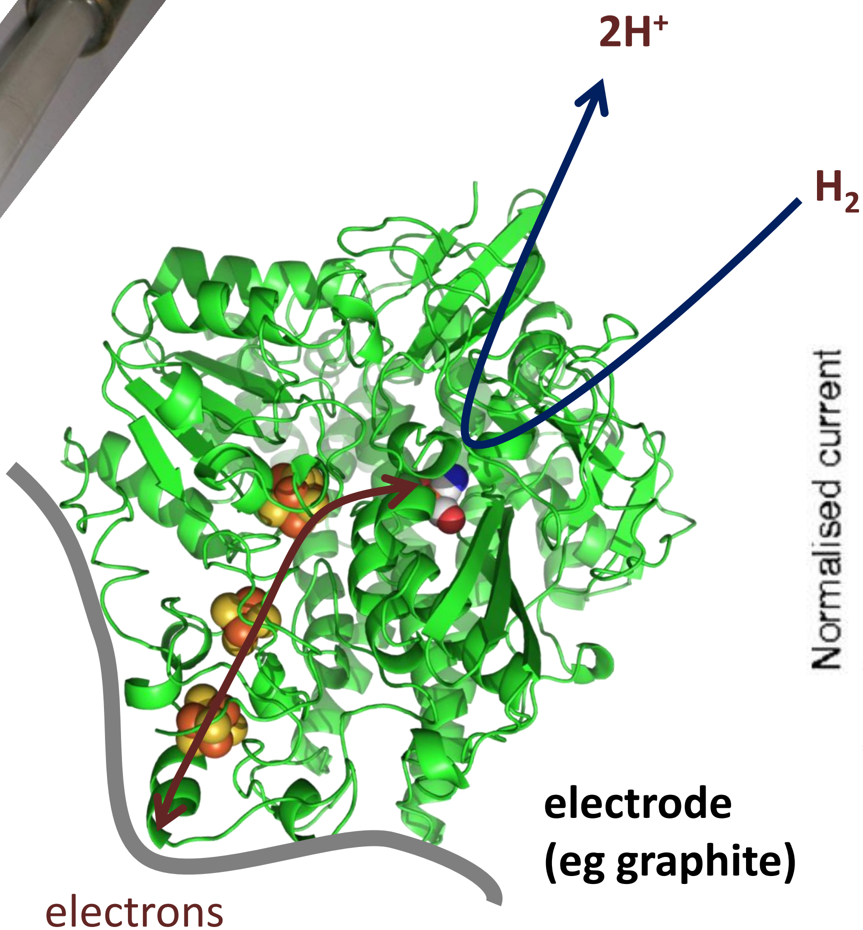
Cyclohexane

→ Catalysis still heavily reliant on precious (platinum group) metals

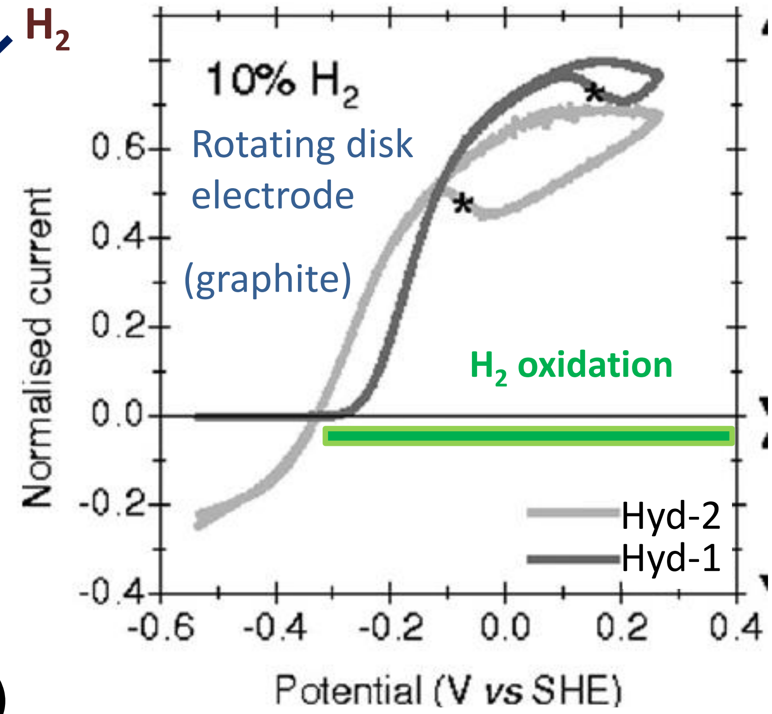
A personal perspective: H_2 in cleaner biocatalytic chemical manufacturing



Hydrogenases as electrocatalysts

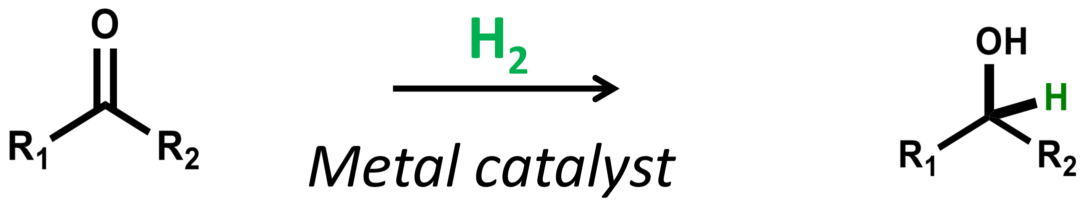


$H_2 \rightarrow 2e^- + 2H^+$



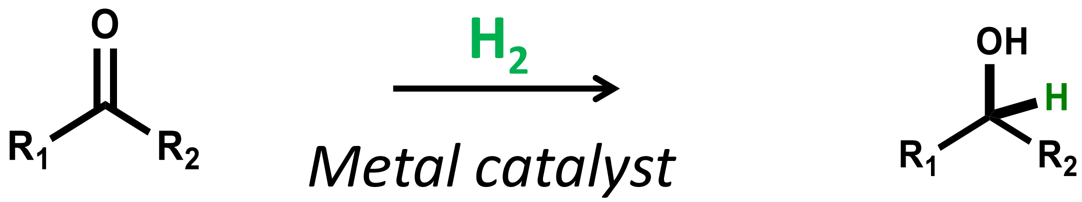
Armstrong and coworkers, *J. Biol. Chem.* 2010, *285*, 3928 (Oxford Chemistry)

Hydrogenations: 10-20% of steps in chemical manufacturing, often high temp, pressure



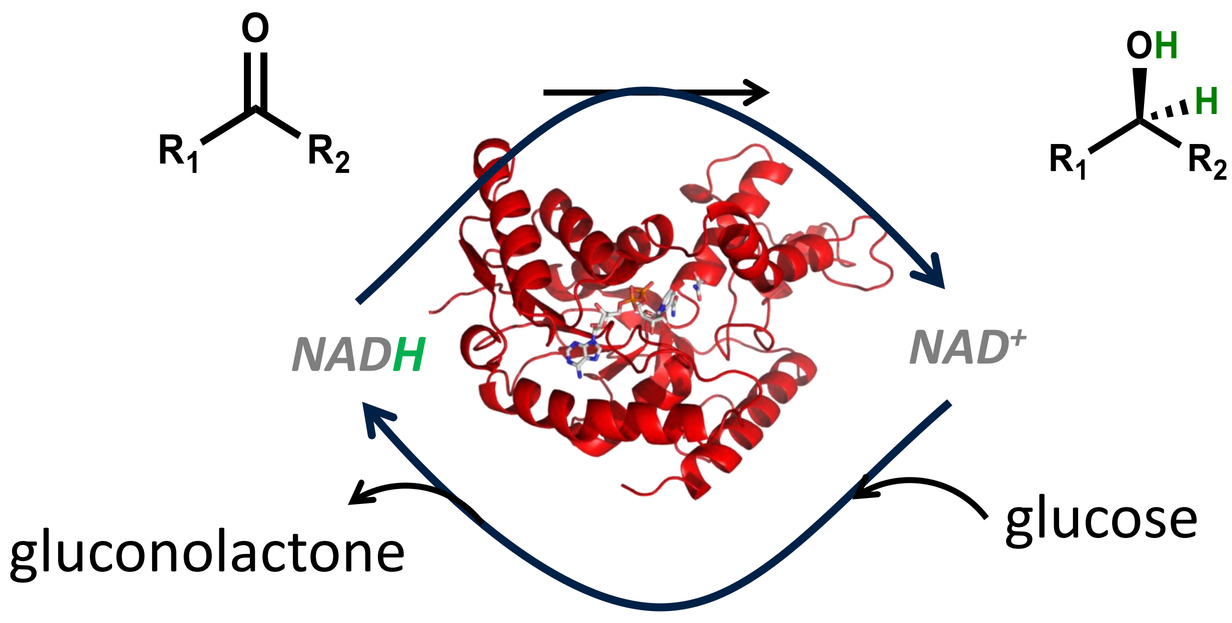
(Often at high pressure)

Hydrogenations: 10-20% of steps in chemical manufacturing

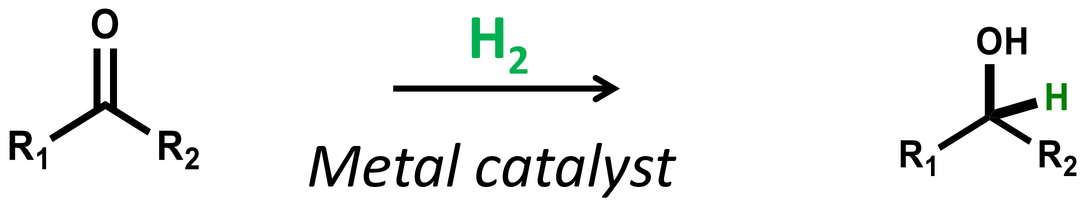


(Often at high pressure)

Biocatalytic reductions

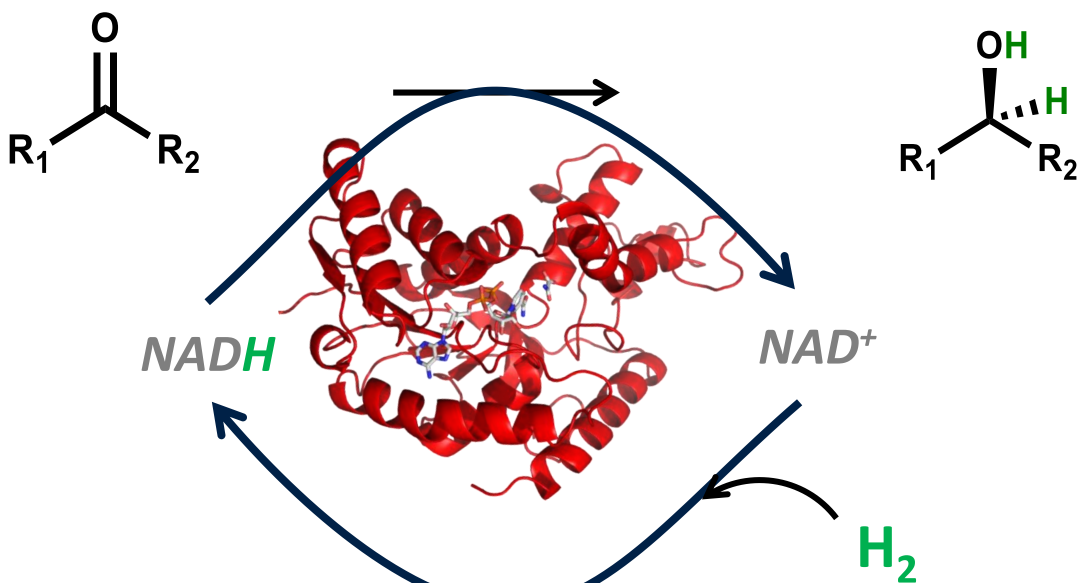


Hydrogenations: 10-20% of steps in chemical manufacturing

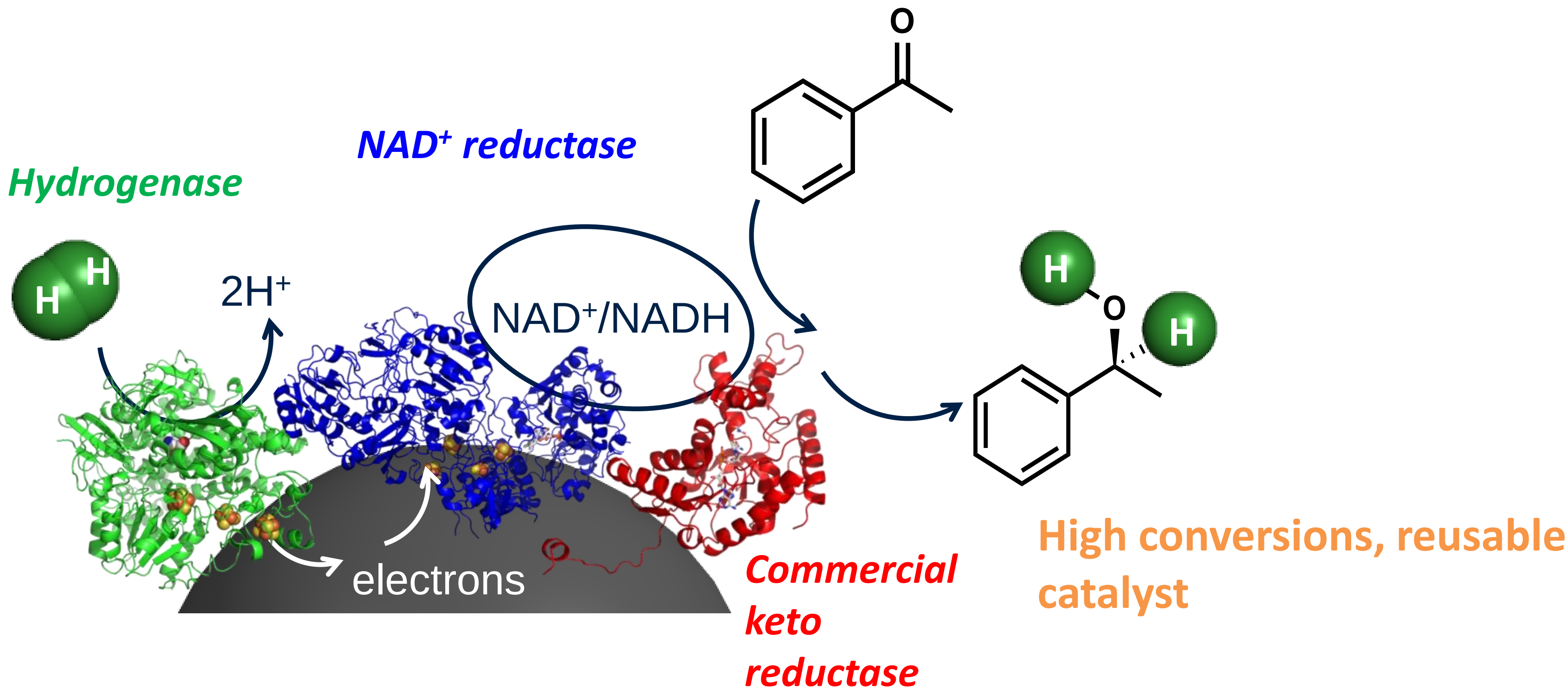


(Often at high pressure)

Biocatalytic hydrogenations



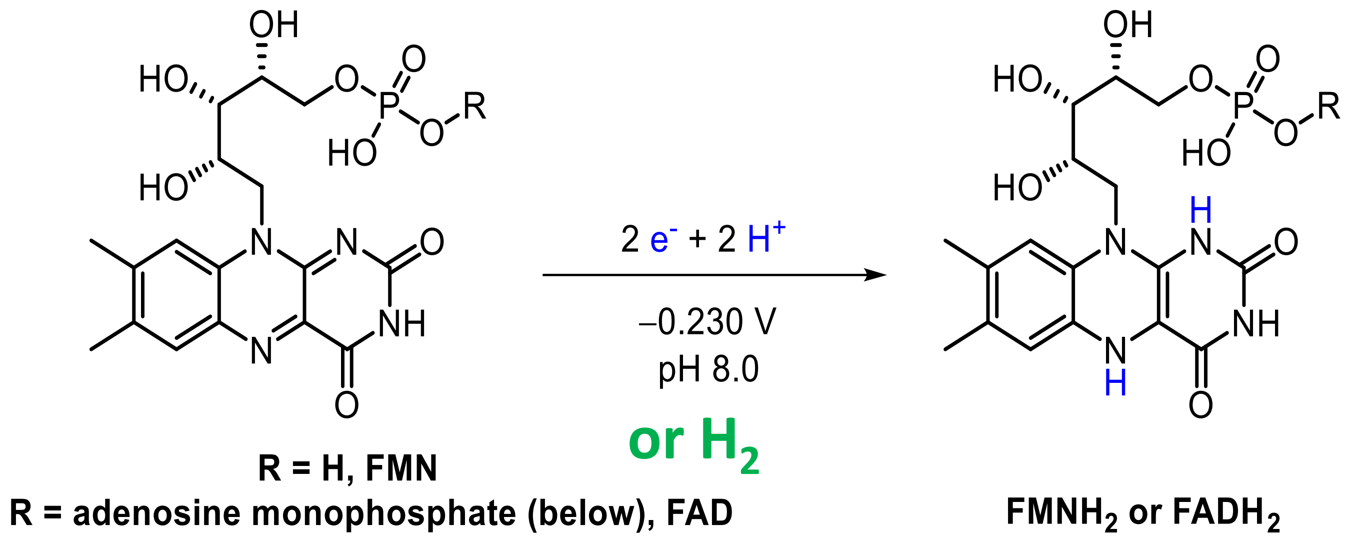
Heterogeneous biocatalytic hydrogenations



Enzyme lifetime and NAD+ total turnover are already competitive with existing biotech applications of enzymes.

Reeve *et al.*, *ChemCatChem*, 2015, **7**, 3480-3487

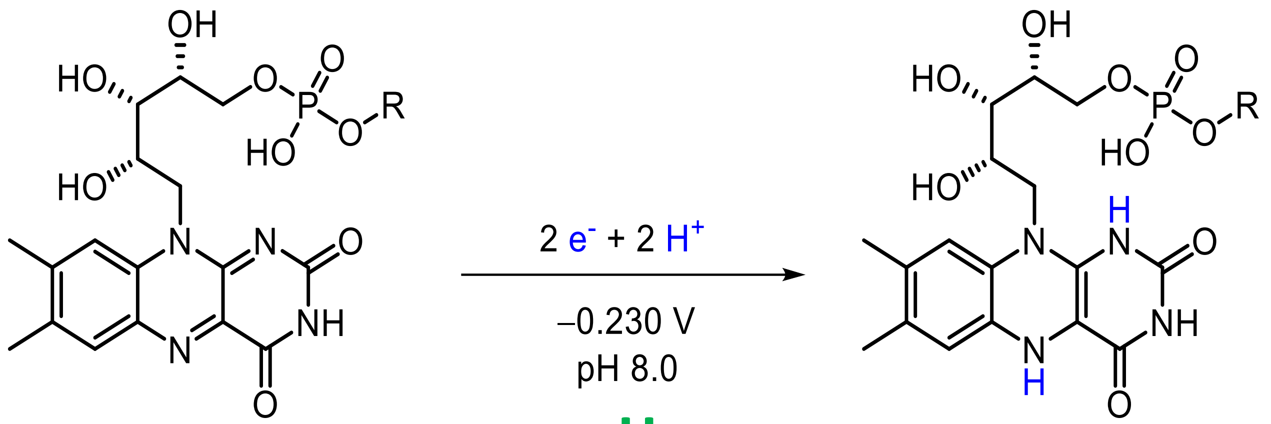
H_2-driven recycling of other cofactors?



(H$_2$ storage nature's way?)

S. Joseph Srinivasan *Angew. Chemie Int. Ed.*, 2021, 60, 13824

H_2-driven recycling of other cofactors?

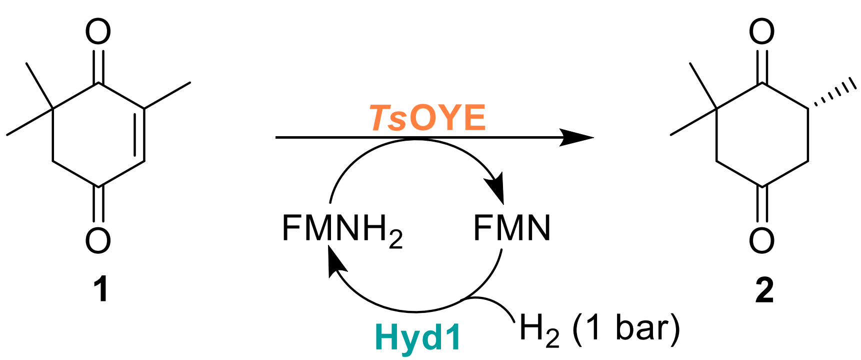


or H_2

R = H, FMN
R = adenosine monophosphate (below), FAD

$FMNH_2$ or $FADH_2$

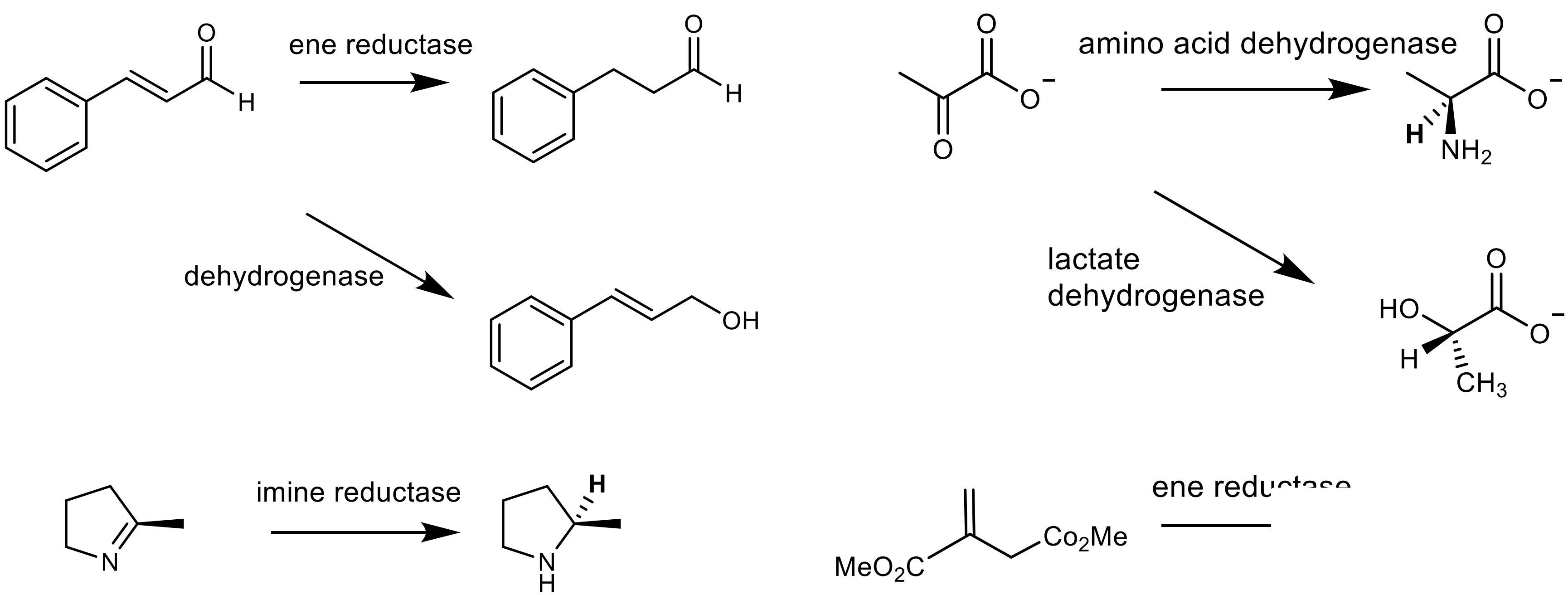
To drive:



S. Joseph Srinivasan *Angew. Chemie Int. Ed.*, 2021, 60, 13824

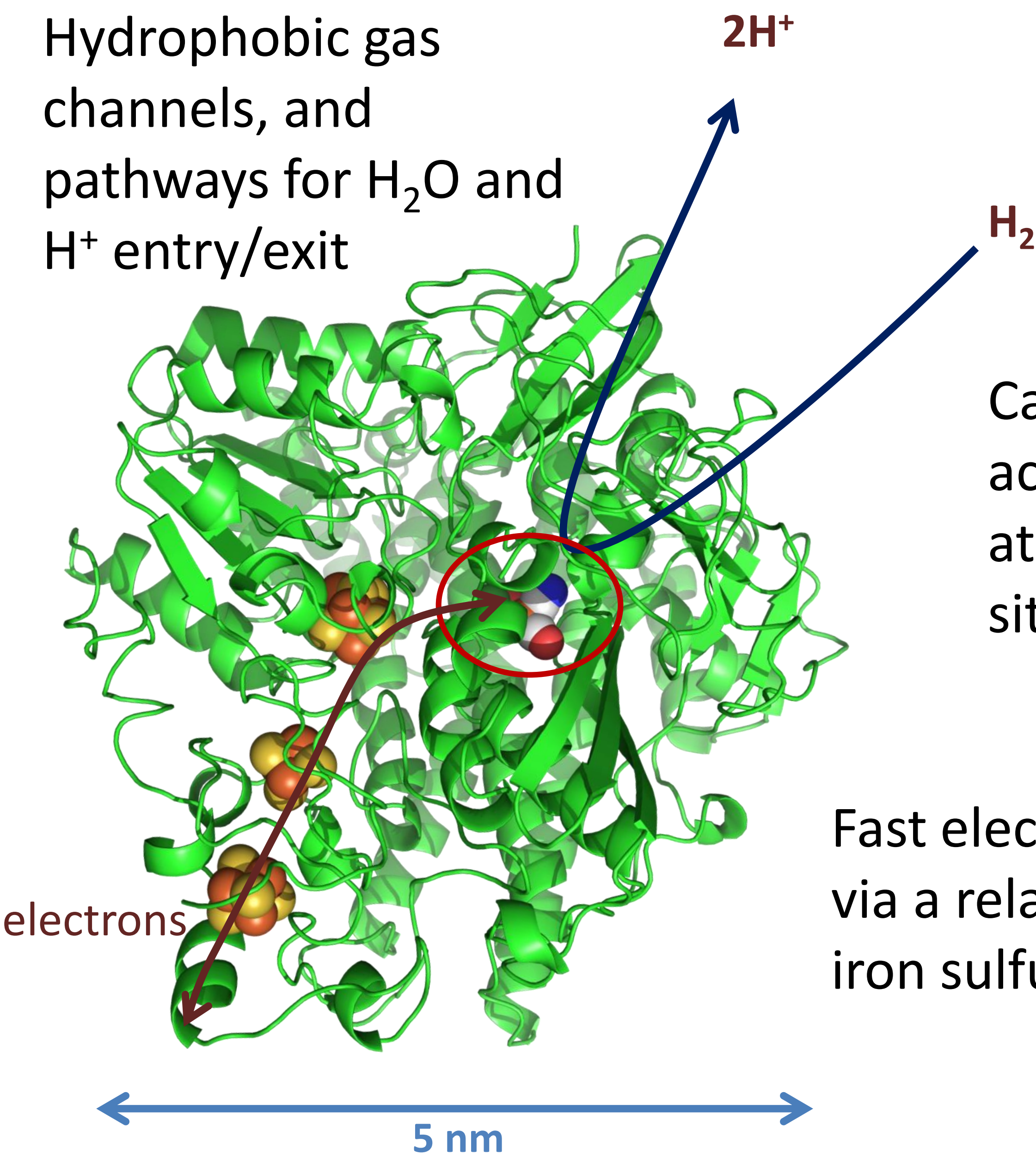
Heterogeneous biocatalytic hydrogenations: cleaning up chemical manufacturing

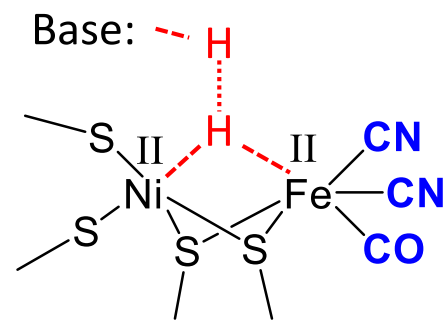
Conversions above 90% (often >98%), high ee, pure product



Nature's catalysts: the hydrogenases

Hydrophobic gas channels, and pathways for H_2O and H^+ entry/exit



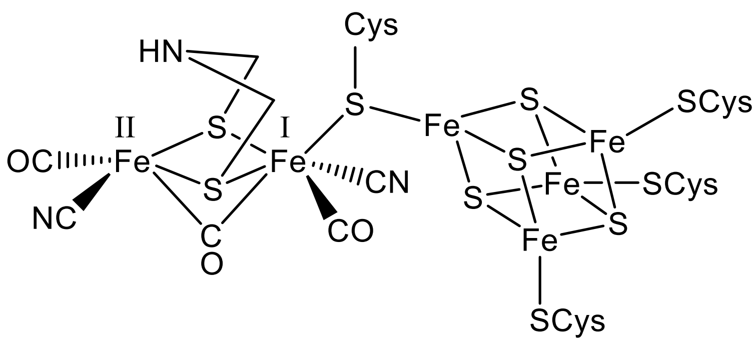


Catalysis at the NiFe active site rivals rates at a platinum active site

Fast electron transfer via a relay chain of iron sulfur clusters

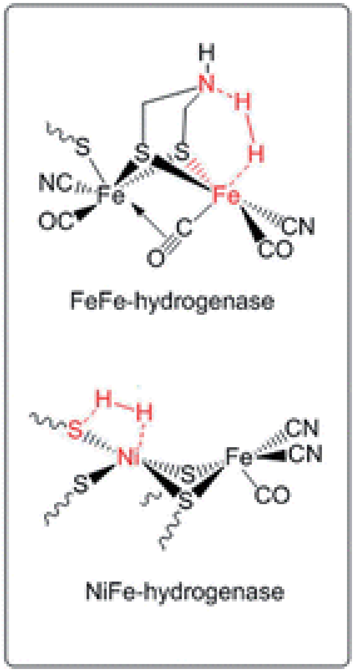
FeFe hydrogenases

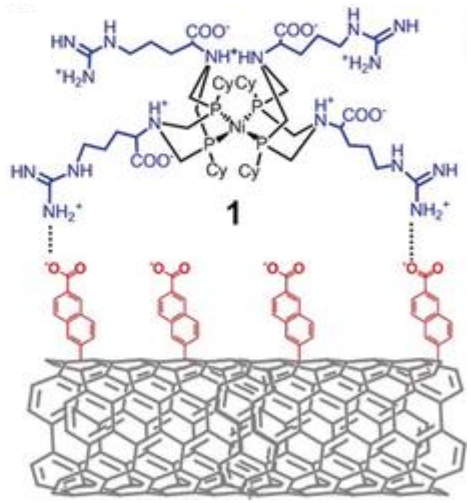
Bridgehead amine group poised to accept / donate protons

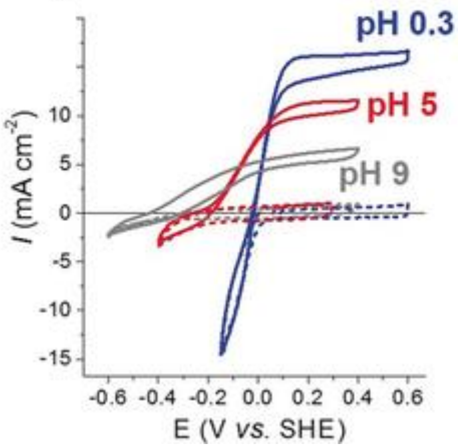


Attached FeS cluster poised to accept / donate electrons

Inspiration from biology



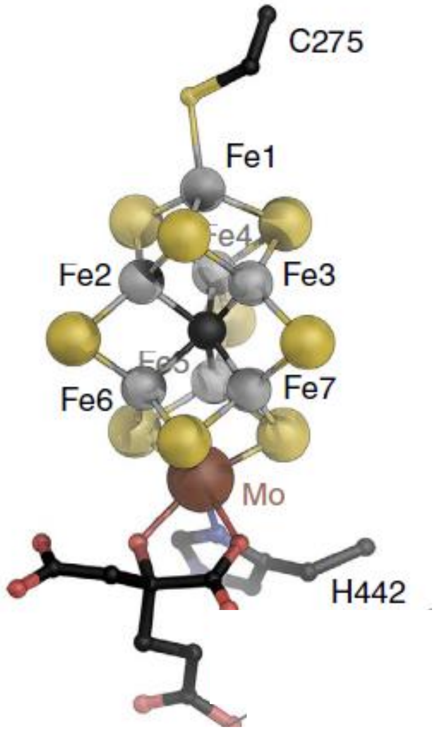




Artero and coworkers, 2017 56, 1845-1849

What more can we learn from nature?

Nitrogenase: biological N_2 fixation



Essentially an *electrocatalytic* mechanism for biological N_2 fixation

Accumulation of metal-bound hydrides important in storing the electrons needed for $6e^-$ reduction of N_2.

Lessons for electrochemical Haber Bosch?

$$N_2 + 10\,H^+ + 8e^- + 16\,ATP \rightarrow 2NH_4^+ + H_2 + 16ADP + 16P_i$$