CO_2, une source de carbone abondante : activation et réduction

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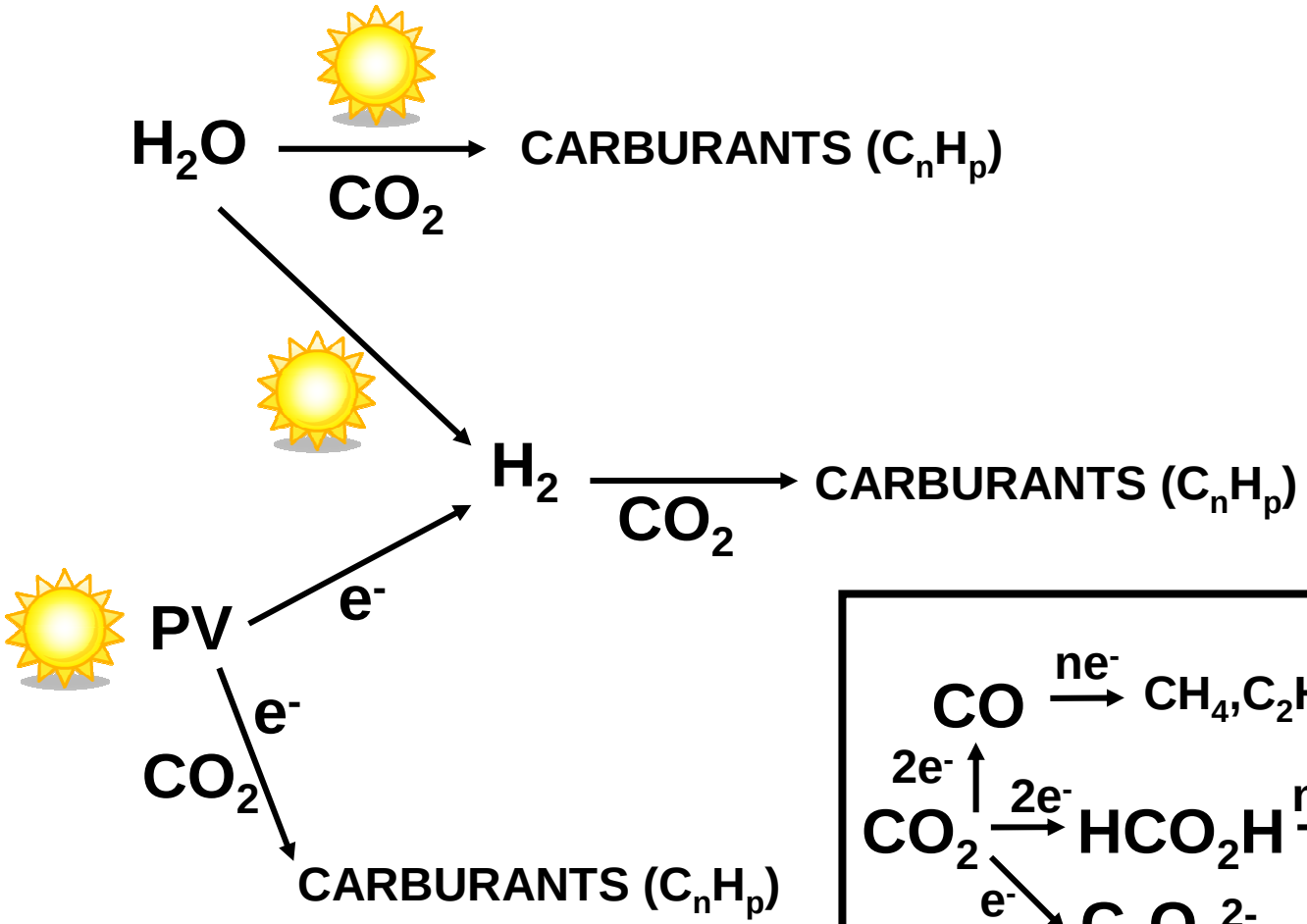
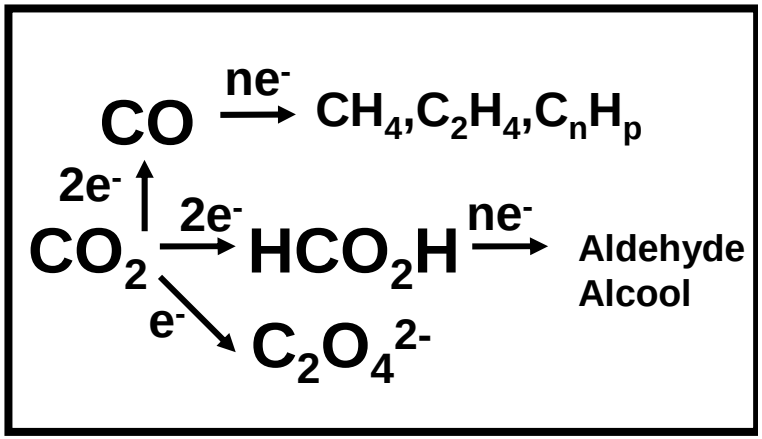
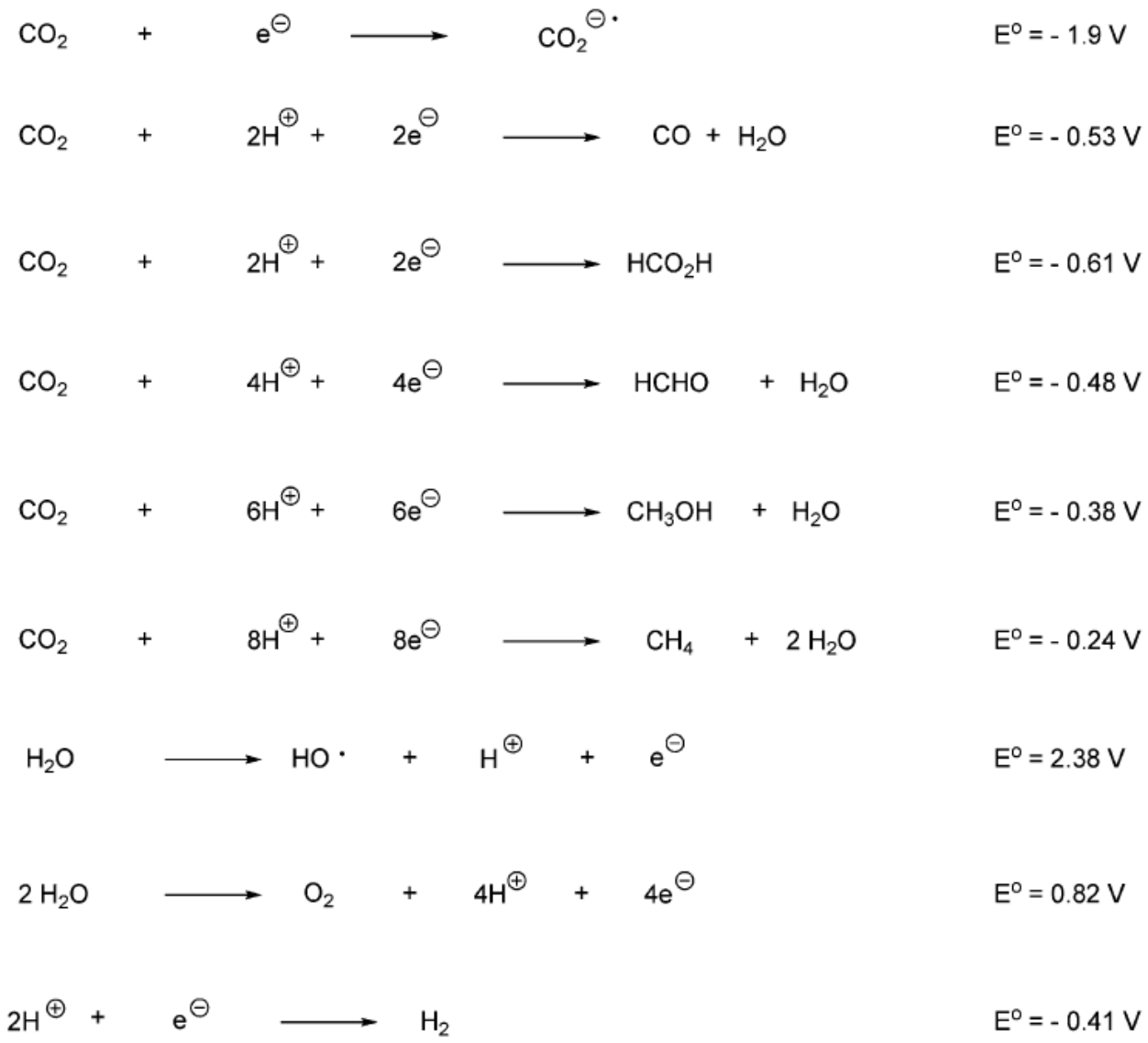
Futur: photosynthèse artificielle !

$H_2O + CO_2 = O_2 + hydrocarbures$





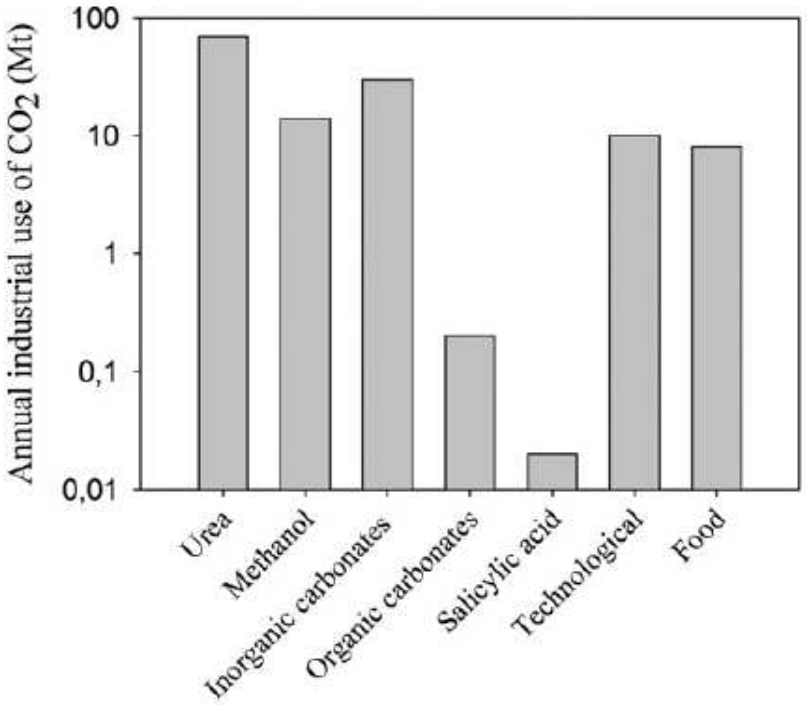
CATALYSE !

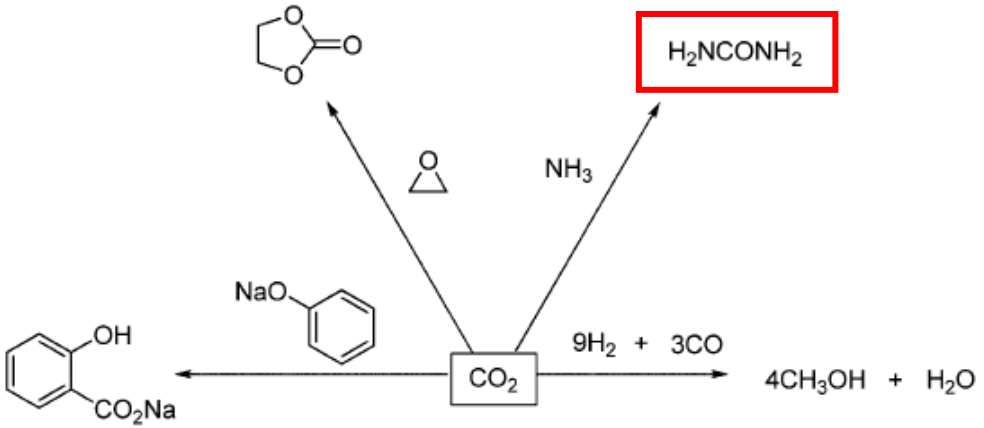

CO2 + e⊖ → CO2⊖· E° = - 1.9 V
CO2 + 2H⊕ + 2e⊖ → CO + H2O E° = - 0.53 V
CO2 + 2H⊕ + 2e⊖ → HCO2H E° = - 0.61 V
CO2 + 4H⊕ + 4e⊖ → HCHO + H2O E° = - 0.48 V
CO2 + 6H⊕ + 6e⊖ → CH3OH + H2O E° = - 0.38 V
CO2 + 8H⊕ + 8e⊖ → CH4 + 2 H2O E° = - 0.24 V
H2O → HO· + H⊕ + e⊖ E° = 2.38 V
2 H2O → O2 + 4H⊕ + 4e⊖ E° = 0.82 V
2H⊕ + e⊖ → H2 E° = - 0.41 V

ENH, pH 7

CO_2 et Industrie

-Atmosphère 2800 Gt CO_2 (385 ppm)
-reste des ressources fossiles carbonées ~ 6000Gt CO_2
-Production anthropogénique 25 Gt/an
-Industrie: 120 Mt/an (0.5% des émissions anthropogéniques)





Scheme 1 Industrial syntheses with CO_2.[8]

Capture et stockage

⇨ Absorption dans une solution liquide (mono ou di-ethanolamine) puis chauffage pour récupérer CO_2

MEA 

carbamate

DEA 

bicarbonate

⇨ Adsorption par des solides poreux (zéolithes)

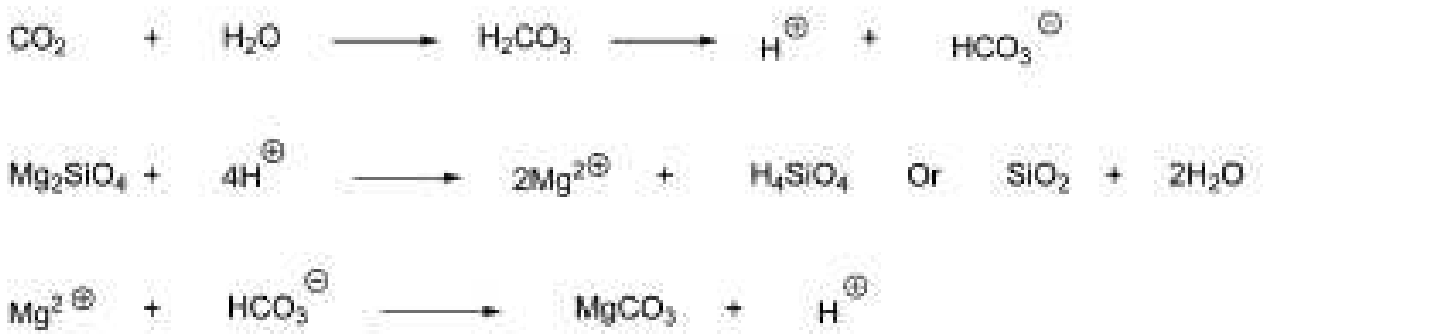
⇨ Incorporation dans des membranes polymères

Capture et stockage (800 Gt en excès)

Table 8 Estimated storage capities for various sequestration options.[257,258]

Sequestration option	Worldwide capacity (order of magnitude in Gt-carbon)
Mineral carbonates	10 000s–1 000 000s GtC
Ocean	1000s GtC
Deep saline formations	100s–1000s GtC
Depleted oil and gas reservoirs	100s GtC
Coal seams	10s–100s GtC
Terrestrial	10s GtC
Enhanced oil recovery	10s GtC
Utilization (chemical conversion)	<0.1 GtC per year

Carbonation minérale

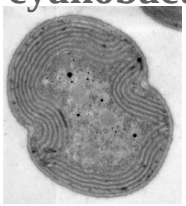


The solution of a mineral (olivine) in order to react with bicarbonate ions to give solid carbonate.

CO_2 et réactions biologiques

plantes

microalgues

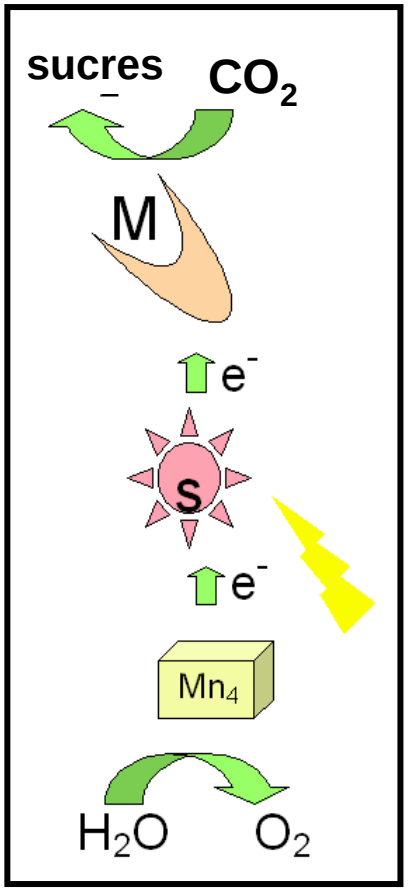


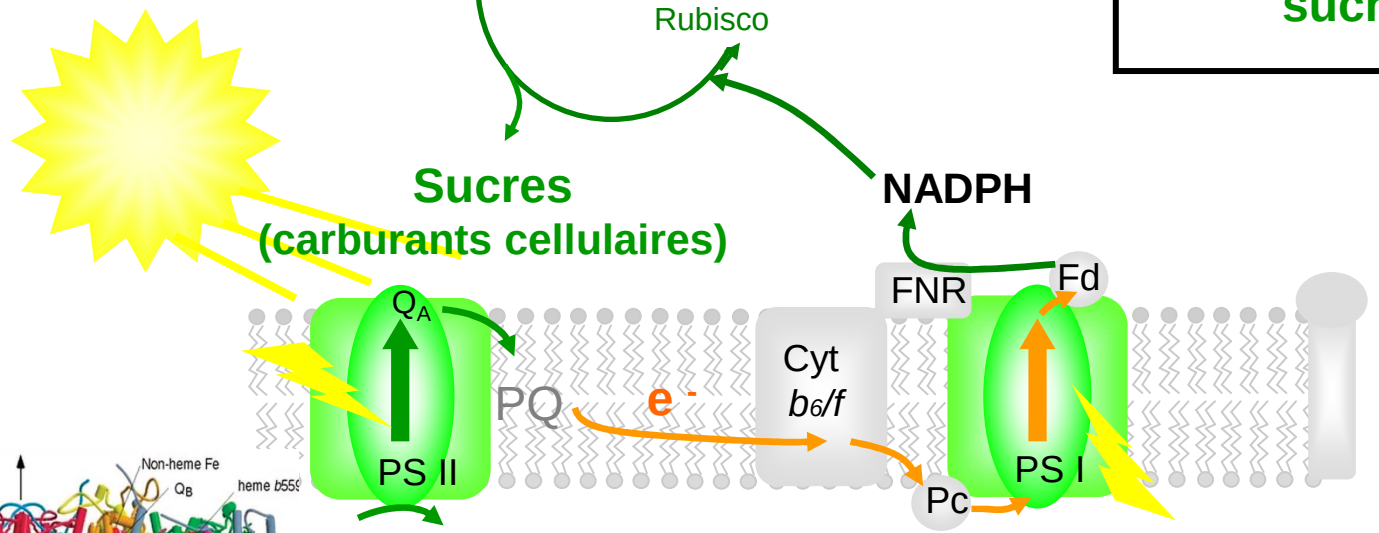
cyanobactéries

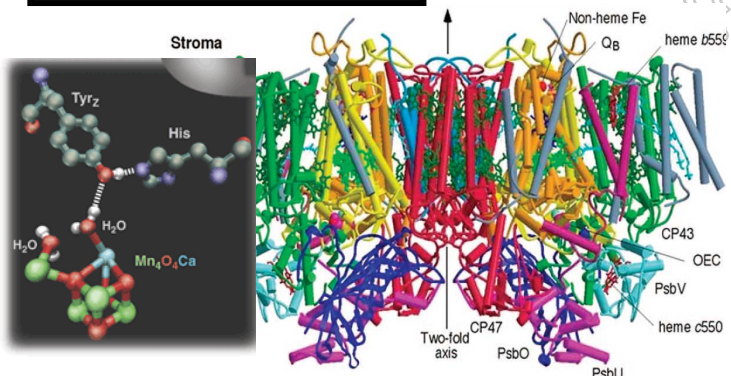
microrganismes photosynthétiques

$e^- + H^+$ stockage: $-H_2$ -Sucres,..

H_2O → $O_2 + 2H^+ + 2e^-$ → NAD(P)H → CO_2 → sucres



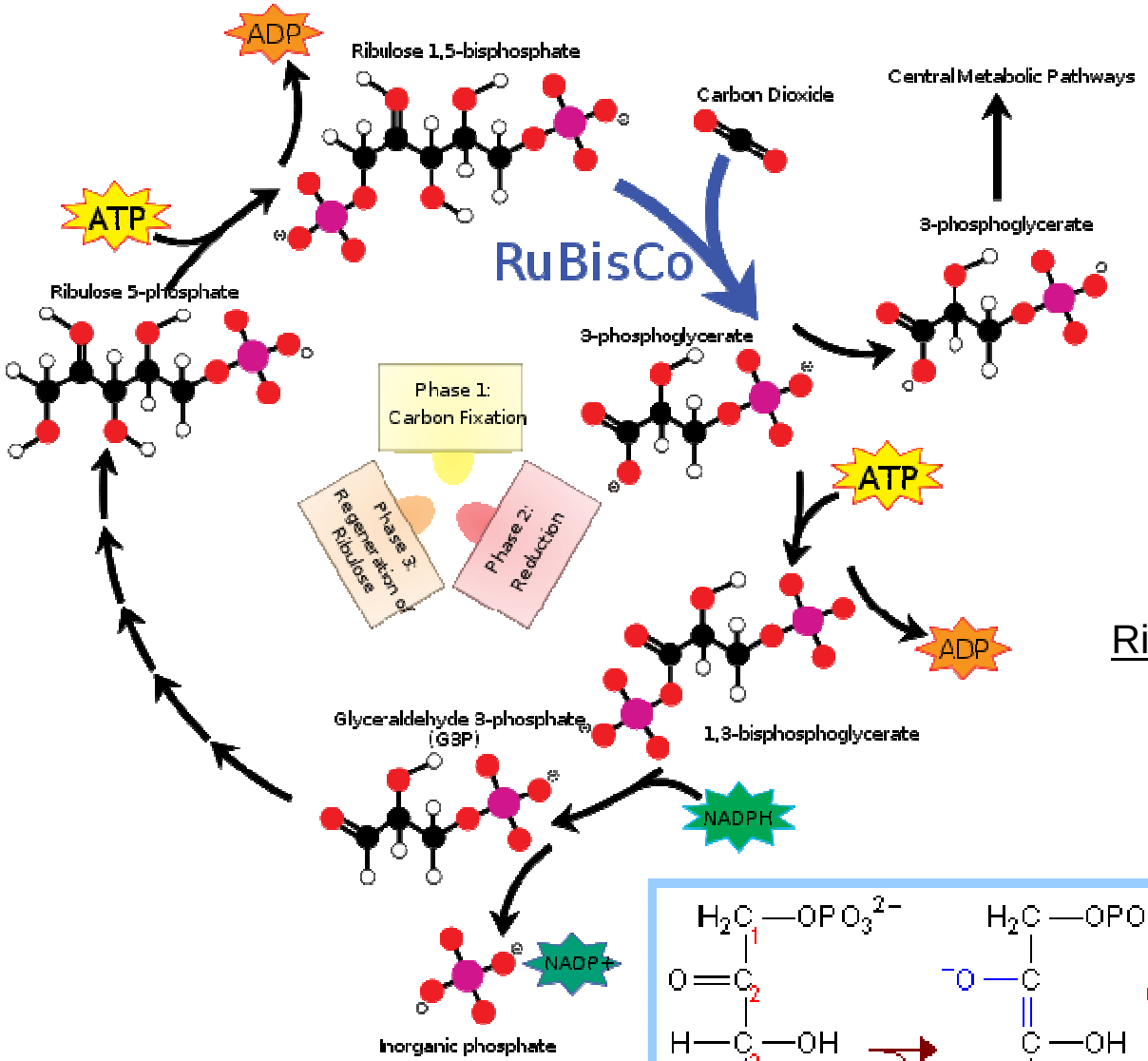


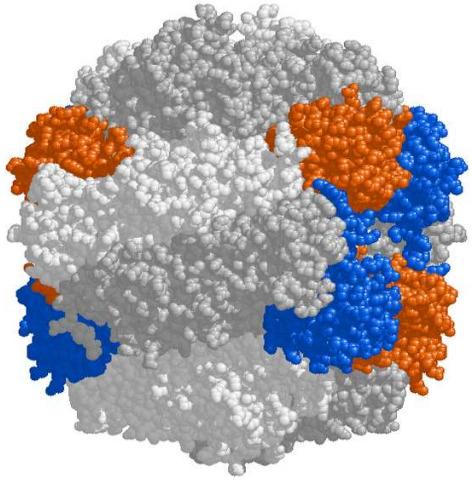


Le stockage de l'énergie: décomposition de l'eau

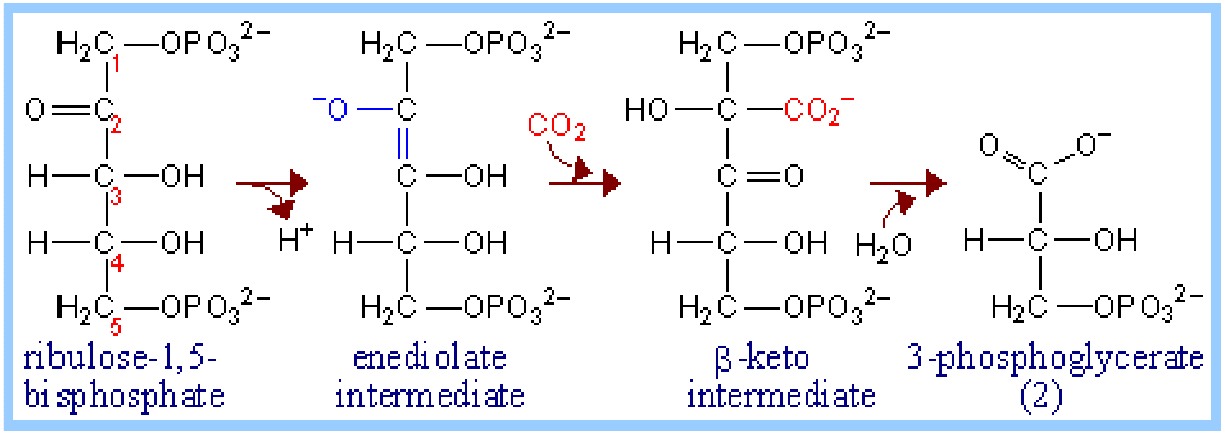
$H_2O \rightarrow H_2 + ½\ O_2$ $\Delta E = 1.23$ V

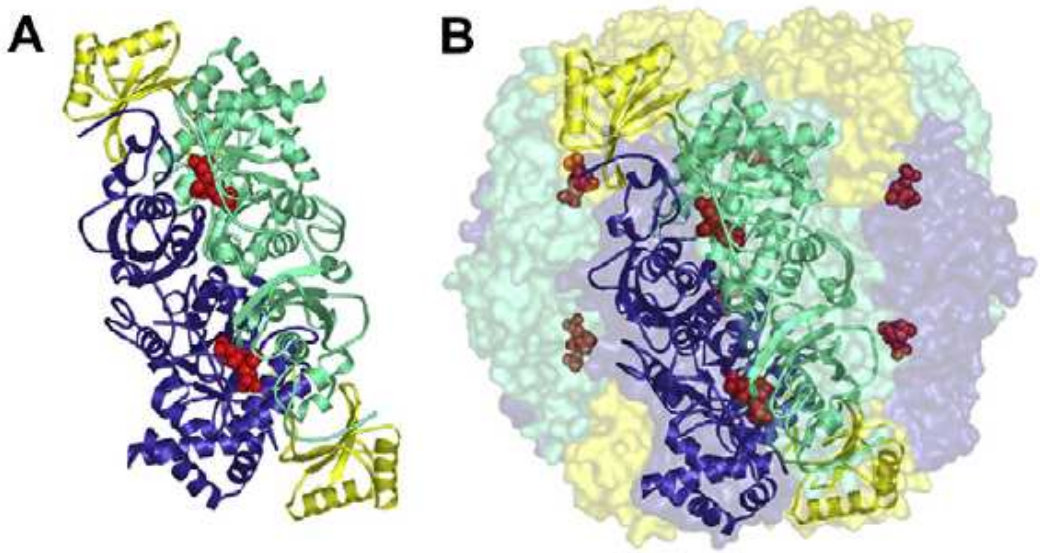
$CO_2 + H_2O \rightarrow 1/6\ C_6H_{12}O_6 + 3/2\ O_2$ $\Delta E = 1.24$V

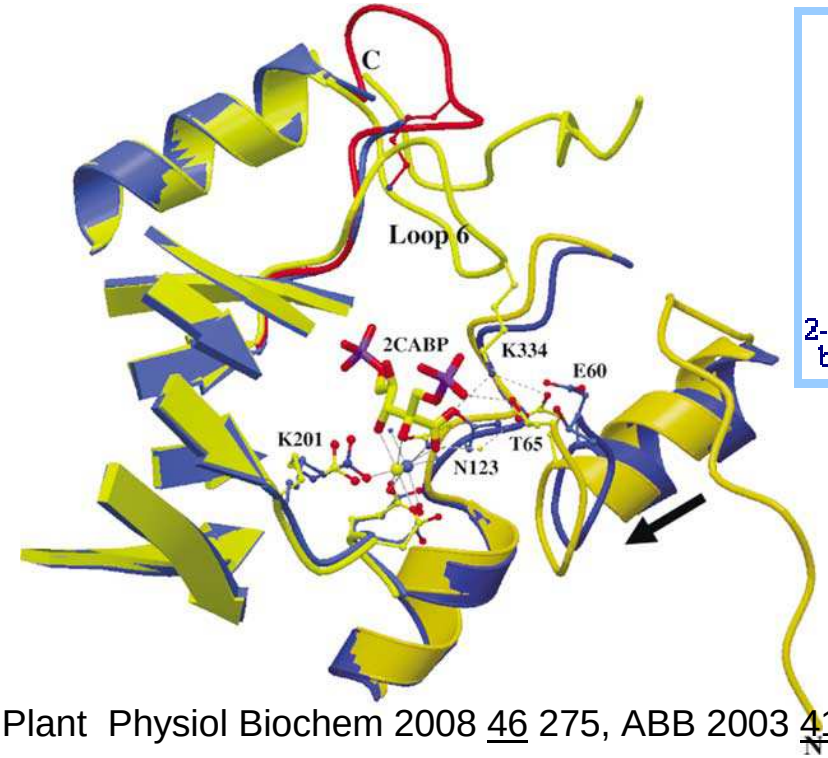


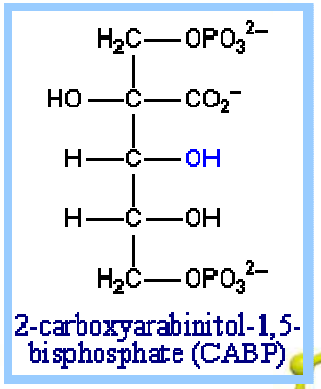


Ribulose1,5-biphosphate carboxylase



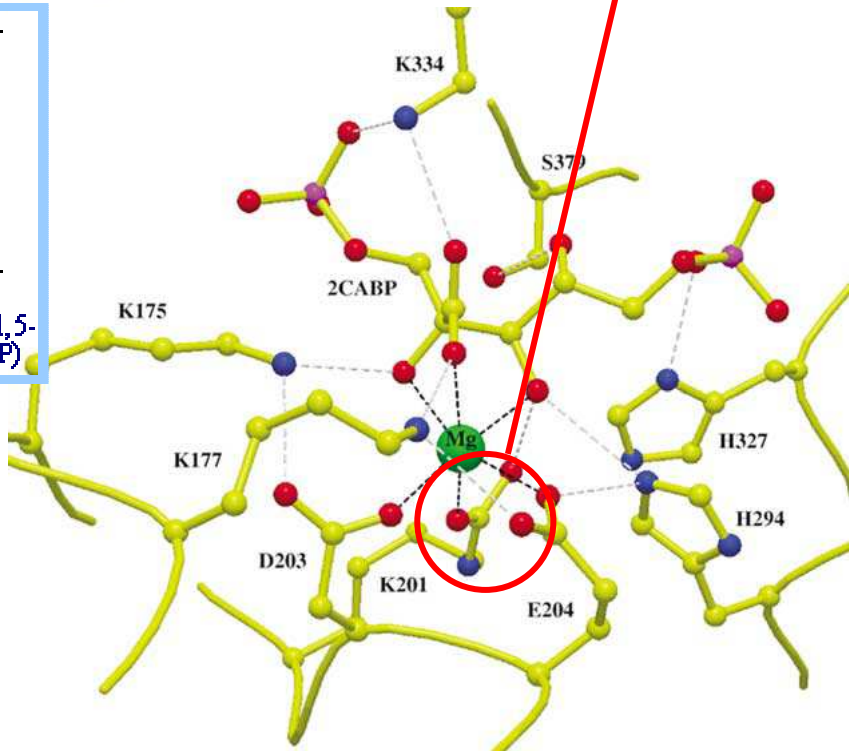




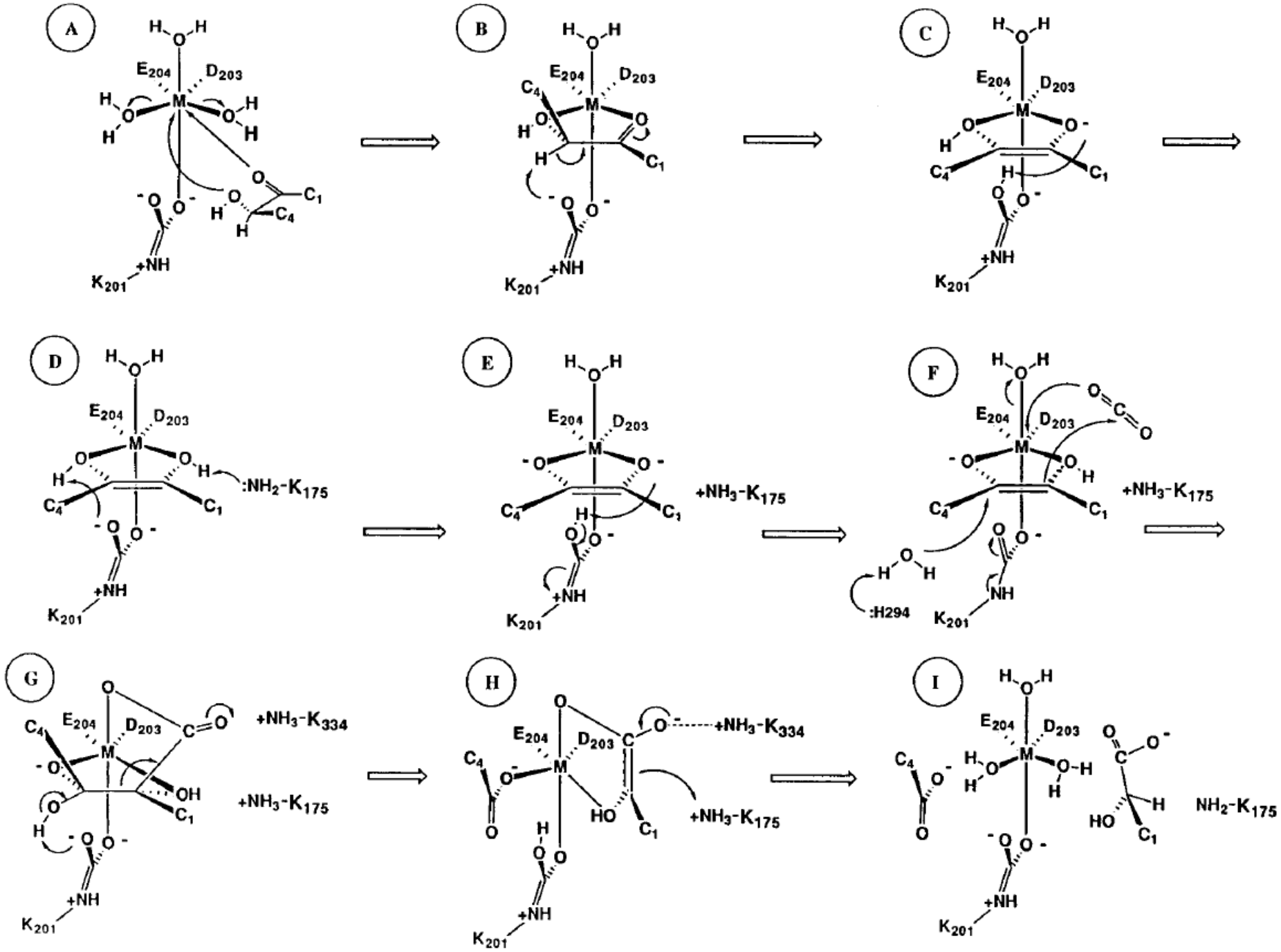


(mime état de transition)

Lys201
R-NH-CO_2^-
carbamate

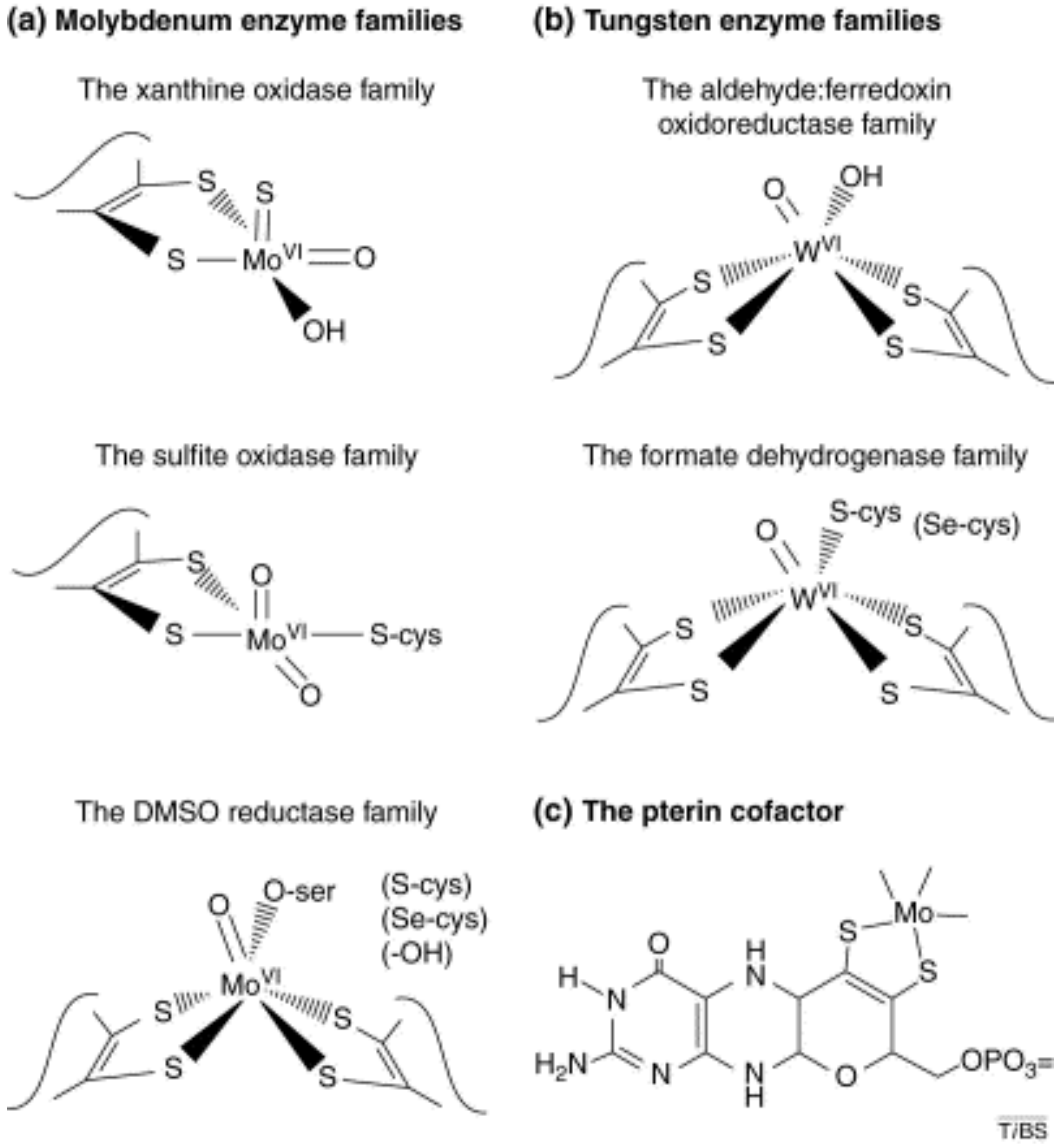


Plant Physiol Biochem 2008 46 275, ABB 2003 414 130



Chem Rev 1998 98 549

Formiate déshydrogénases: des enzymes à Mo et W



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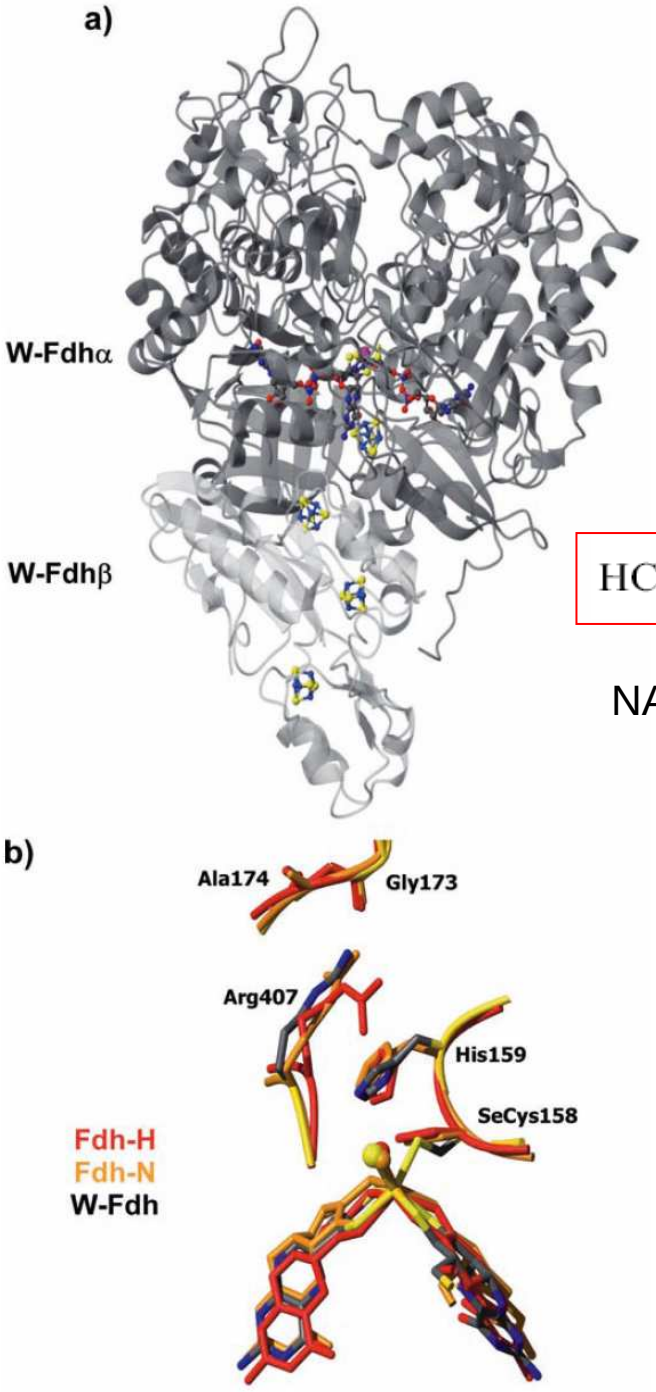


Formiate déshydrogénases

Syntrophobacter fumaroxidans)

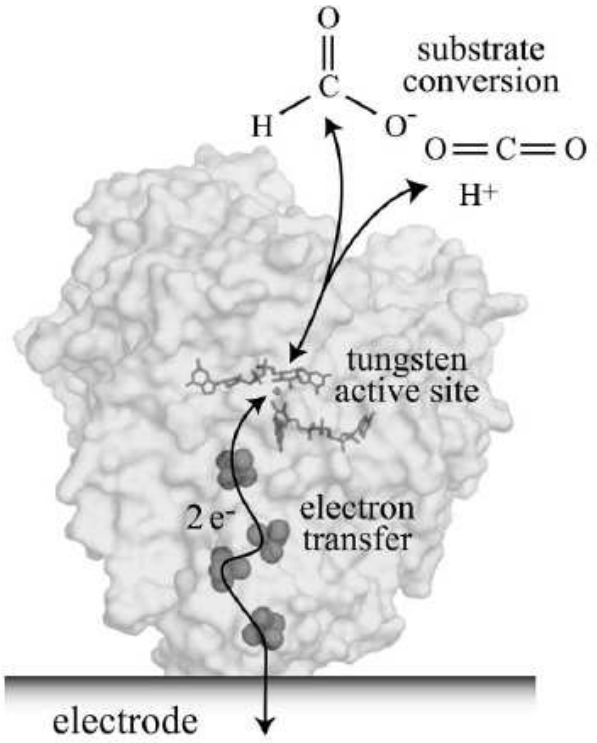
$HCOO^- \rightarrow CO_2 + H^+ + 2e^-$ $\quad E° = -420$ mV pH 7

$NADP^+ + 2e^- + H^+ \rightarrow NADPH$ $\quad E° = -330$ mV

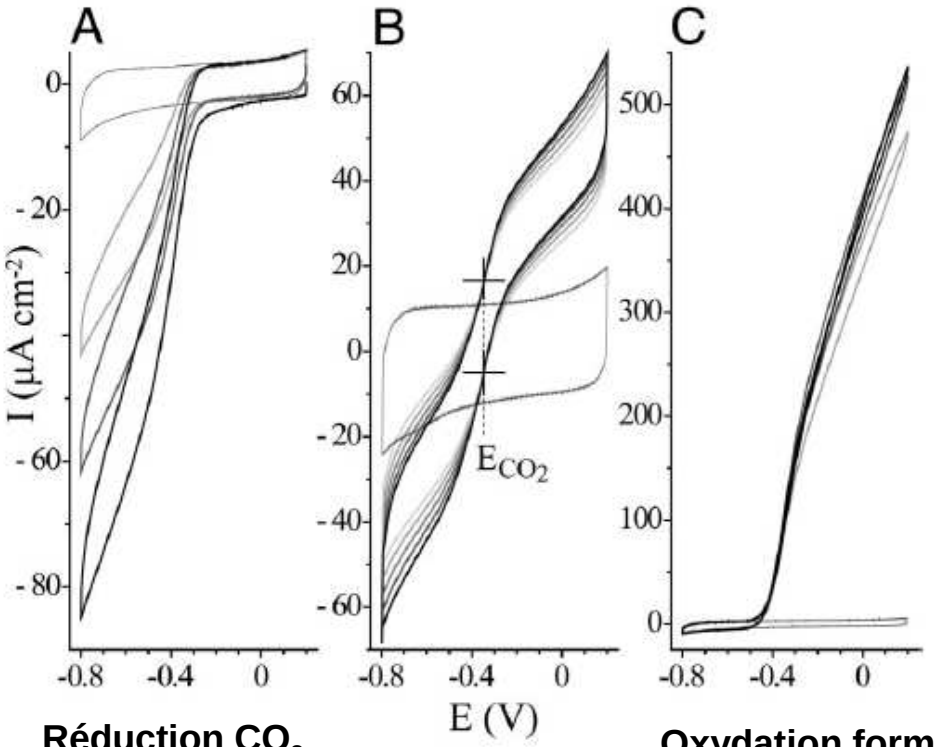
Oxydation $HCOO^-$: 3380 s^{-1}
Réduction de CO_2: 282 s^{-1}
($MV^{2+}/MV^{+\circ}$)

Electroréduction enzymatique de CO_2

$HCOO^- \rightarrow CO_2 + H^+ + 2e^-$ $\quad E° = -420$ mV



3.5 10^{-12} mol.cm^{-2}



Réduction CO_2

-0.8 V, pH 5.9
0.08 mA.cm^{-2}
112 s^{-1}
40000 cycles/h

CO_2 et formiate

Oxydation formiate

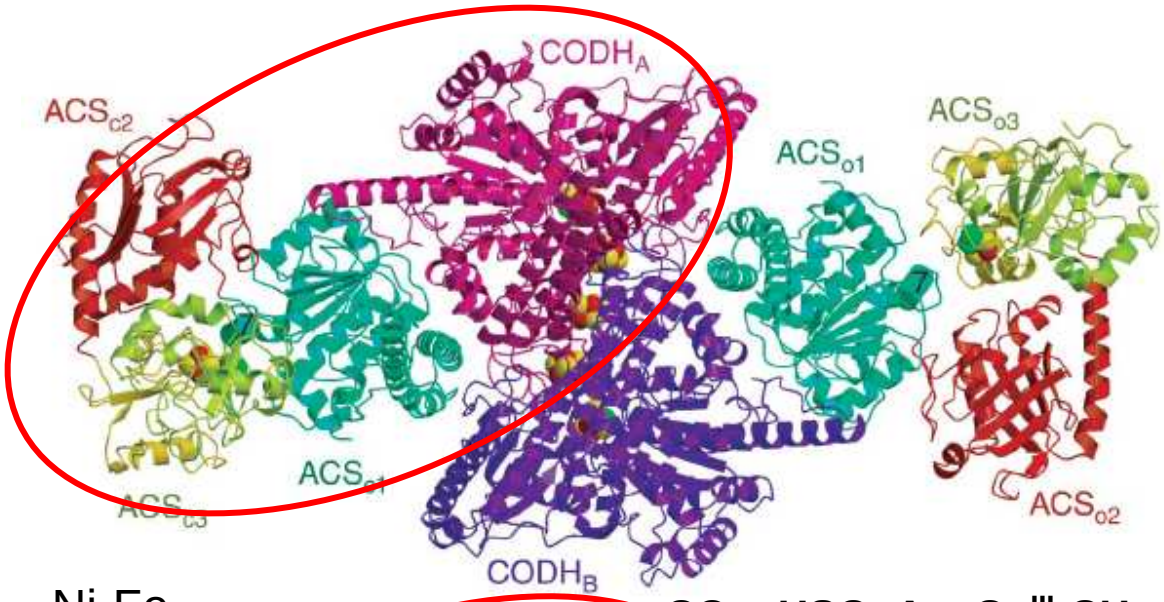
0.2V, pH8
0.5 mA.cm^{-2}

→ Surtensions faibles

→ Rendt fara: 100%

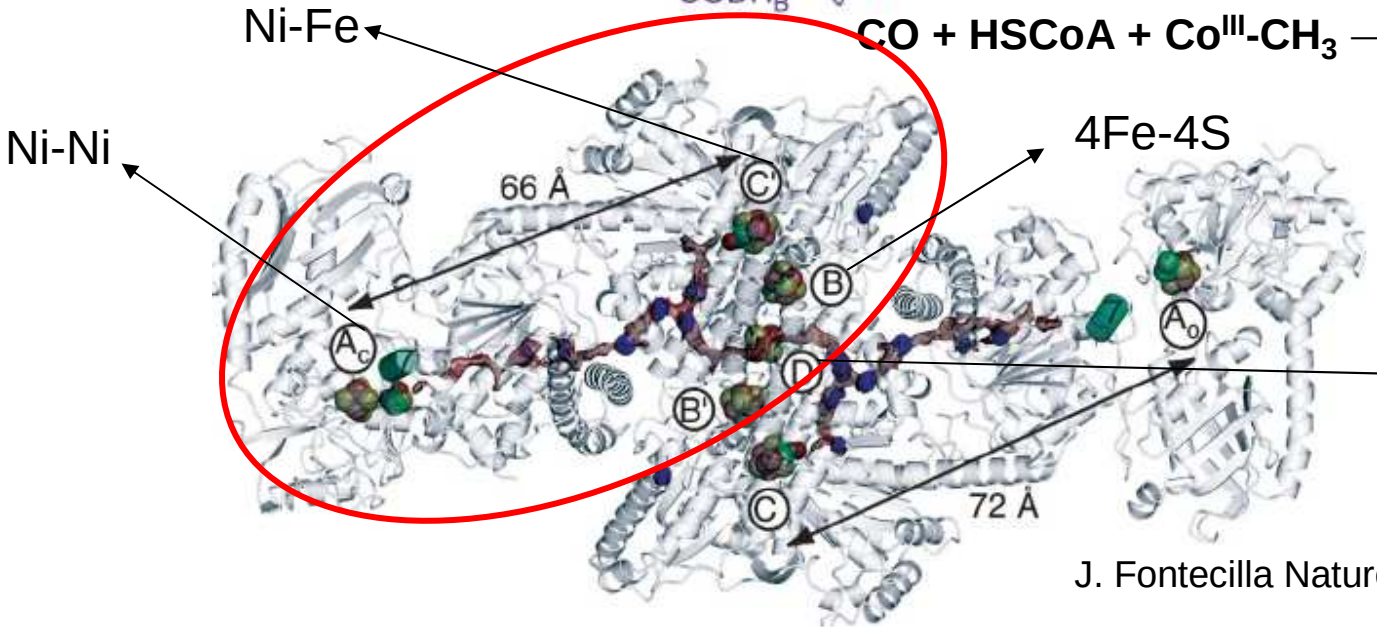
CO-dehydrogenase/acetyl-CoA synthase

$$CO + H_2O \rightleftharpoons CO_2 + 2e^- + 2H^+$$



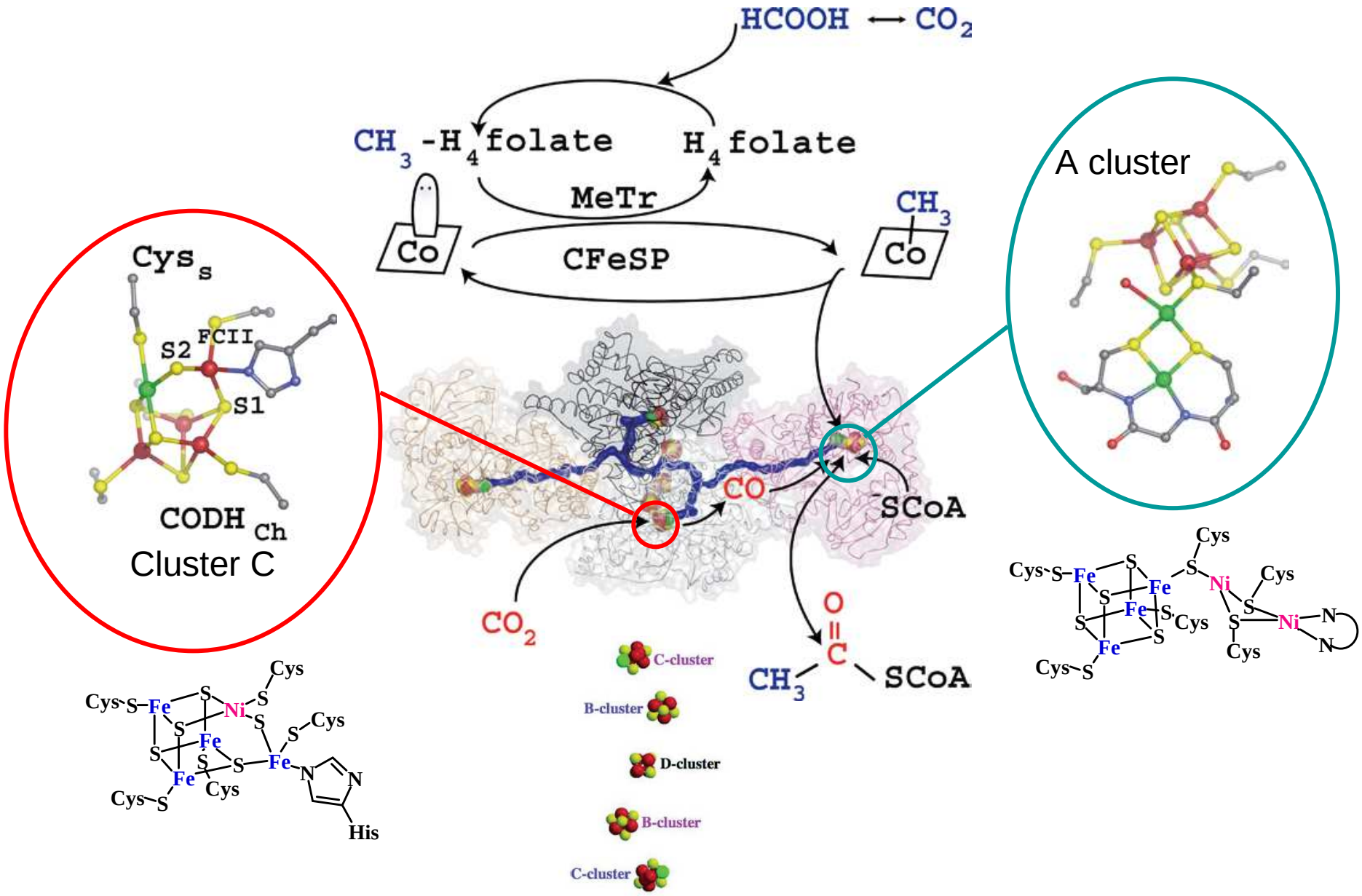
$\alpha_2\beta_2$

$CO + HSCoA + Co^{III}\text{-}CH_3 \rightarrow Co^{I} + CH_3\text{-}CO\text{-}SCoA$

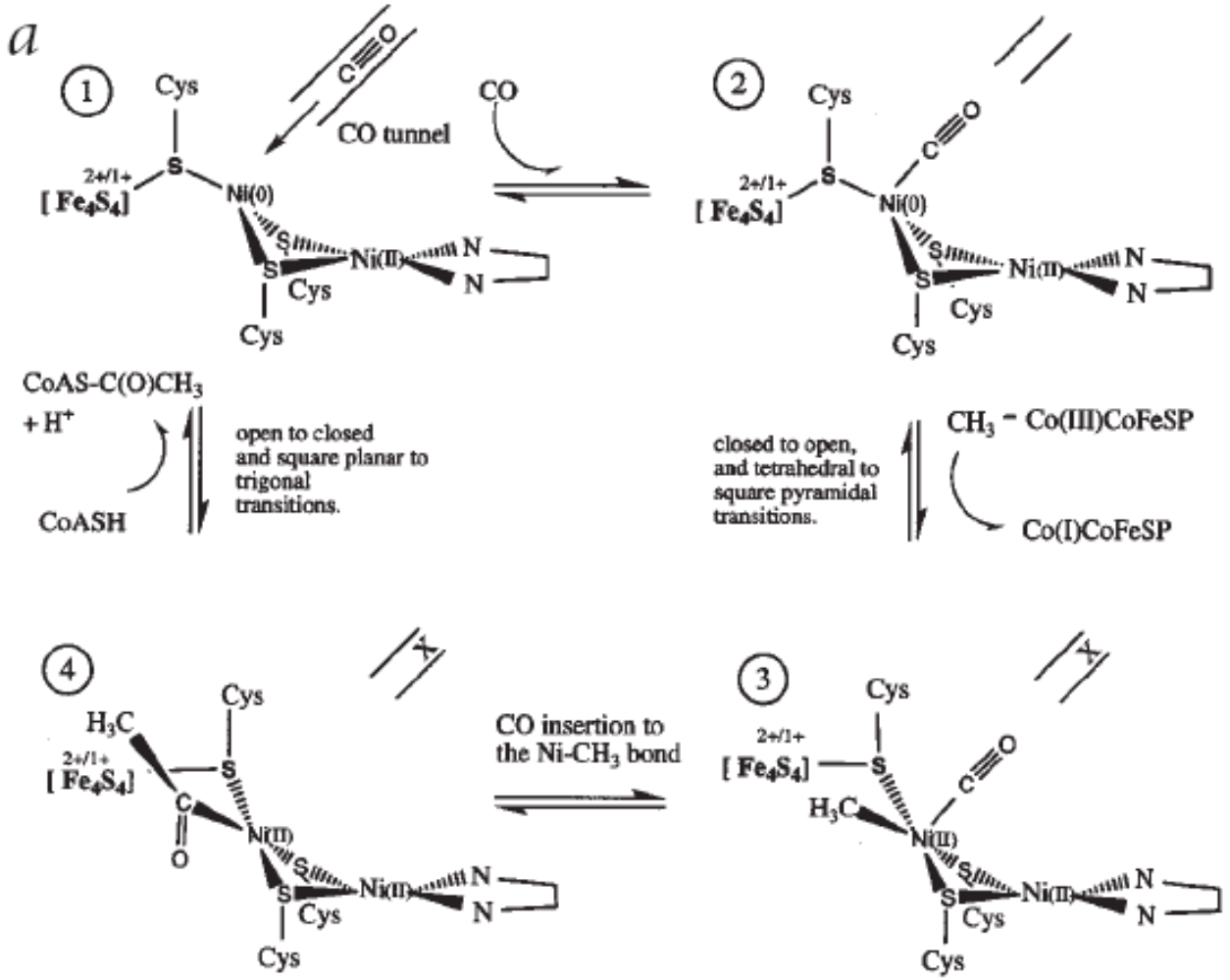


J. Fontecilla Nature Str Biol 2003 10 271

CO-dehydrogenase/acetyl-CoA synthase

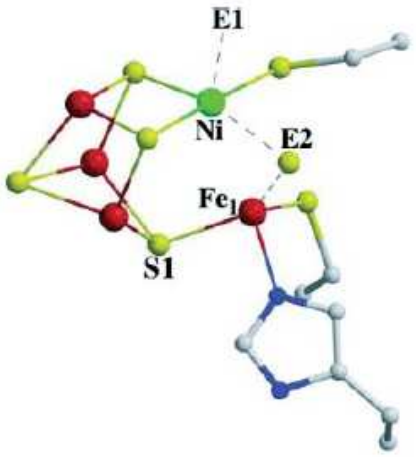


Mécanisme ACS



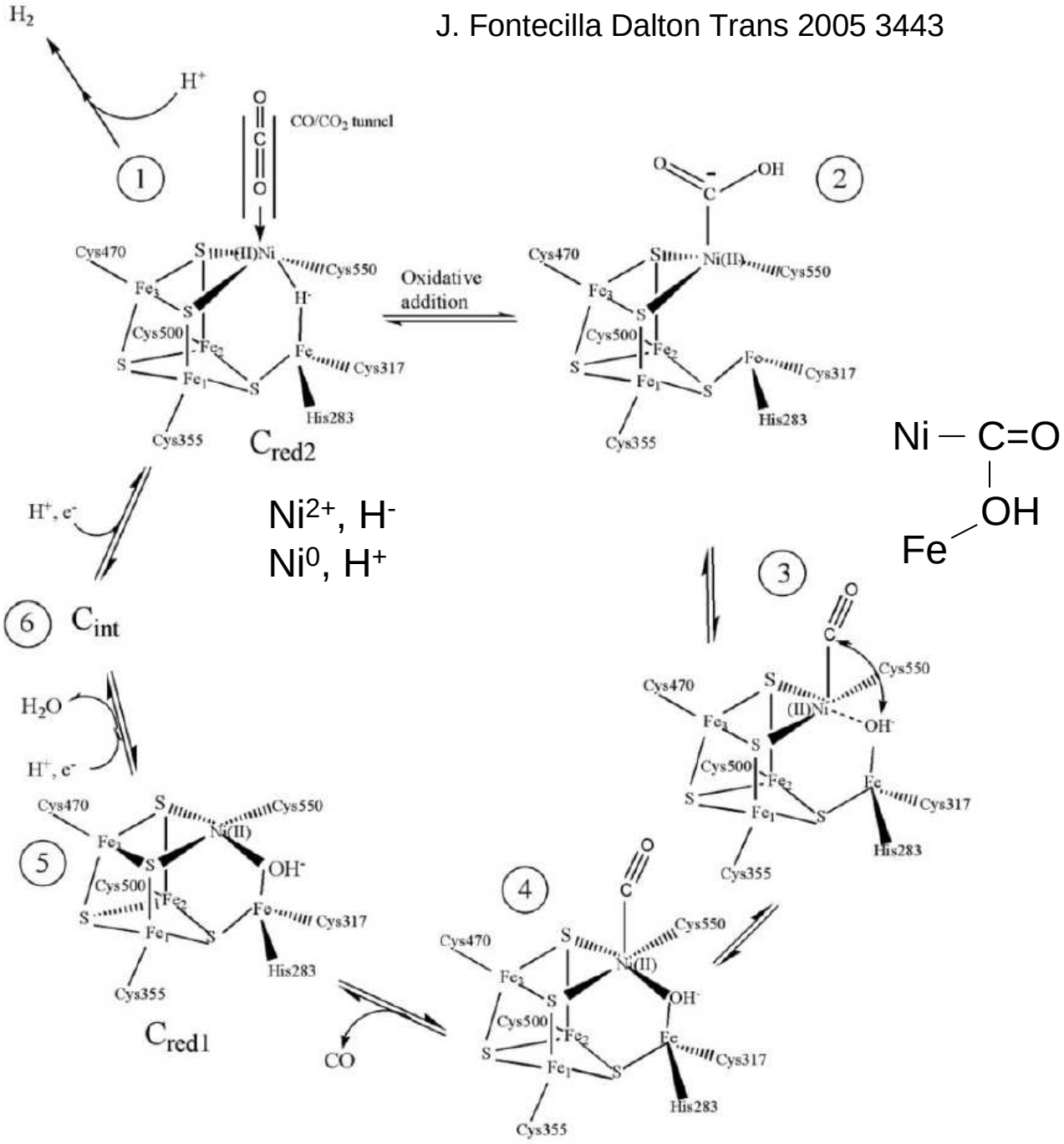
J. Fontecilla Nature Str Biol 2003 10 271

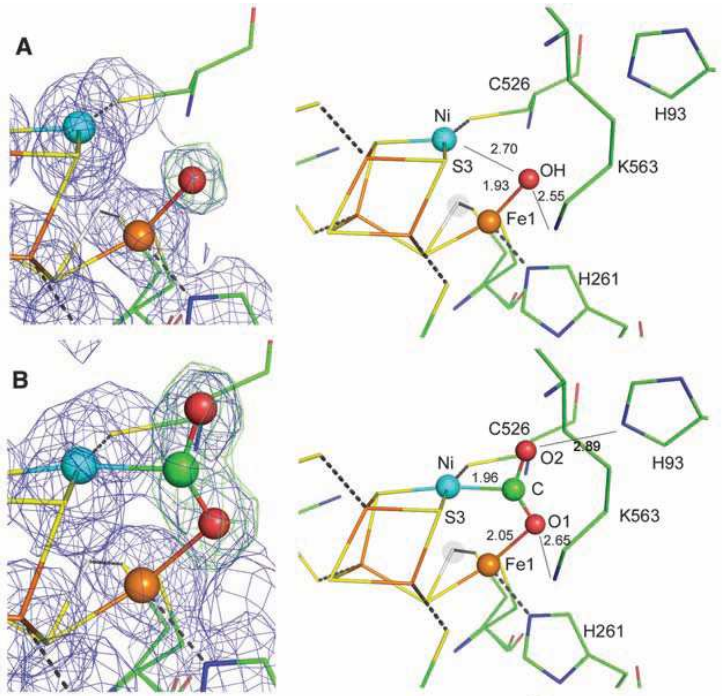
J. Fontecilla Dalton Trans 2005 3443



Mécanisme CODH

- Ni-X-H
  (X:H⁻?; OH⁻?)
- Ni^X
  (X=2+?; 0?)

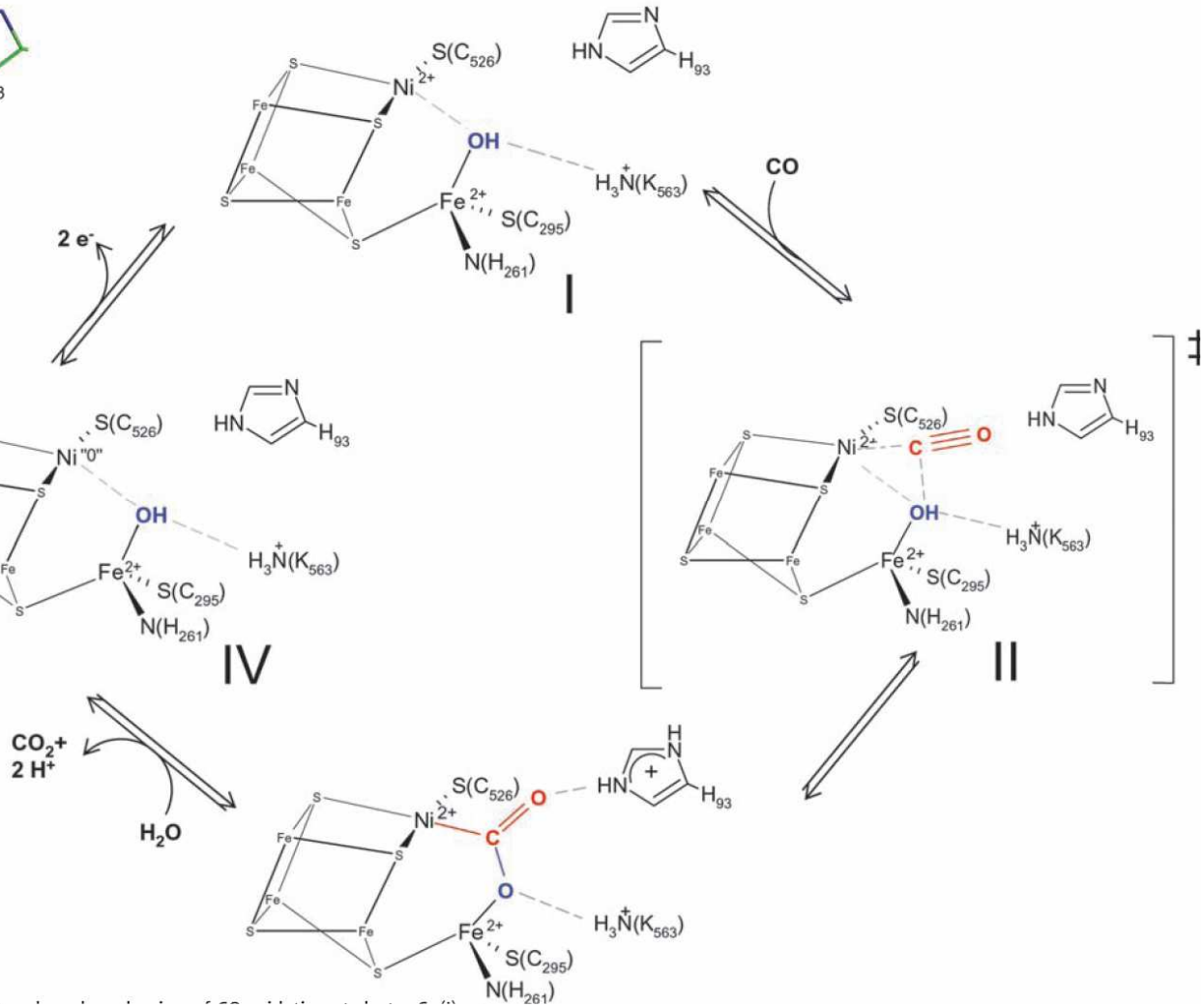




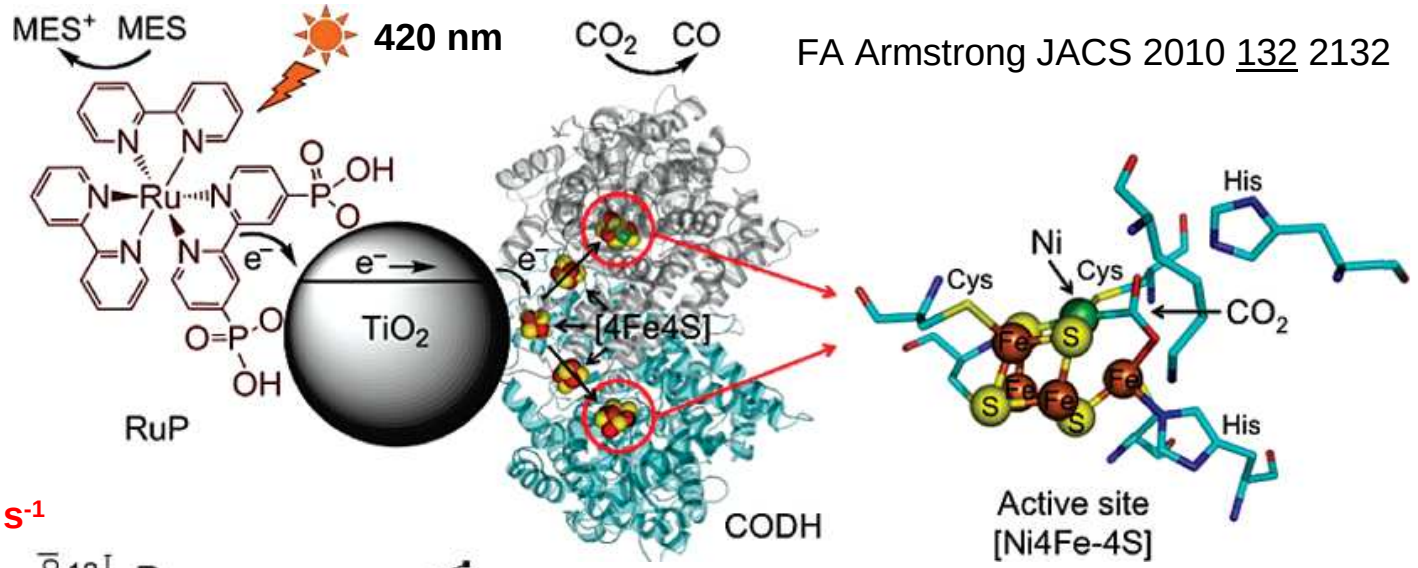
Carbon Dioxide Activation at the Ni,Fe-Cluster of Anaerobic Carbon Monoxide Dehydrogenase

Jae-Hun Jeoung, *et al.*

Science **318**, 1461 (2007);

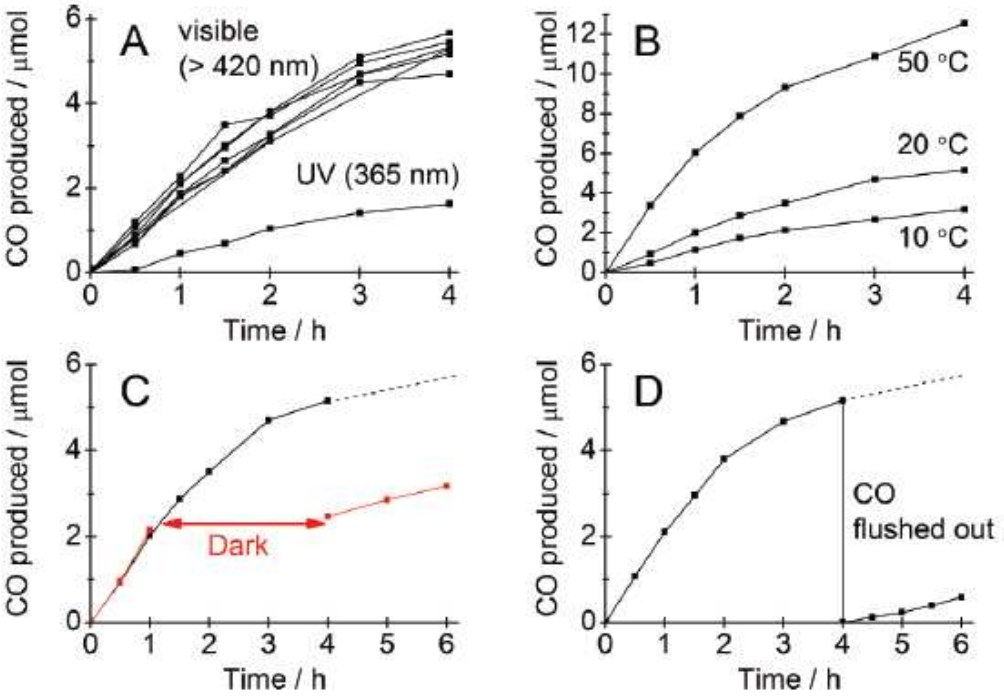


Photoréduction enzymatique de CO_2



FA Armstrong JACS 2010 132 2132

5 µmol/4h
TOF = 0.15 s^{-1}

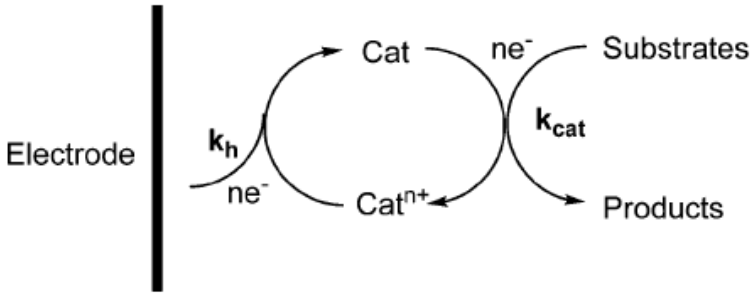


Carboxydothermus hydrogenoformans
E = - 0.46 V vs SHE, pH 6
pH8, 40000 s^{-1} (oxydation CO)(

➔ « driving force » faible (~0.1V) (TiO_2 -0,52V vs SHE)

➔ Interface à optimiser

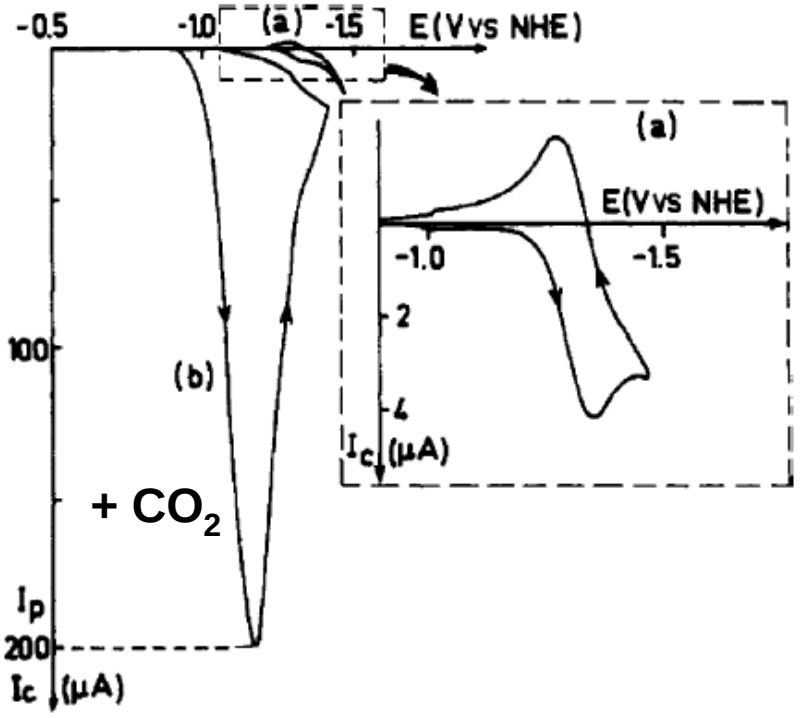
Réduction électrochimique de CO_2



Surtension = $V_{applied}$ – E°(prod/subs)

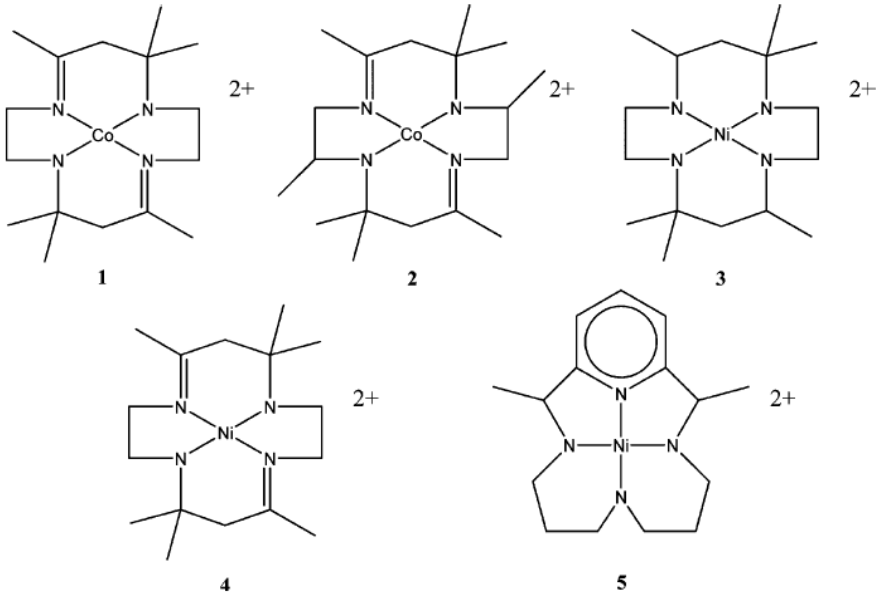
$V_{applied}$ $E^0(Cat^{n+/0})$ E^0(products/substrates)

Étude par voltamétrie cyclique



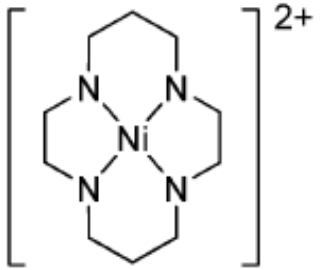
Eisenberg, 1980

-Surtension ~ 600 à900 mV
- TOF ~ 2-9/h
- rendt 98%



Sauvage, 1984-6

-Surtension ~ 300 mV
- rendt 96%



Ni(II)(cyclam)

$CO_2 \rightarrow CO$

Fe(0) porphyrins

Savéant, 1996

-Surtension ~ 700 mV
- TOF ~ 350/h
- dégradation du catalyseur

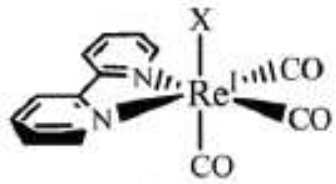
Electro-réduction du CO_2

$CO_2 \rightarrow CO$

$Re(bipy)(CO)_3Cl$

-Surtension ~ 600 mV
- TOF ~ 21/h
- rendt 98%

Lehn 1984



$Ru(bipy)(CO)_2^{2+}$

-Surtension ~ 600 mV
- faible activité
- faible sélectivité

Tanaka 1987

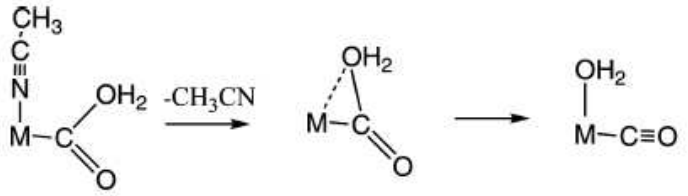
$CO_2 \rightarrow HCOOH$

cis-$[Rh(bpy)_2X_2]^+$

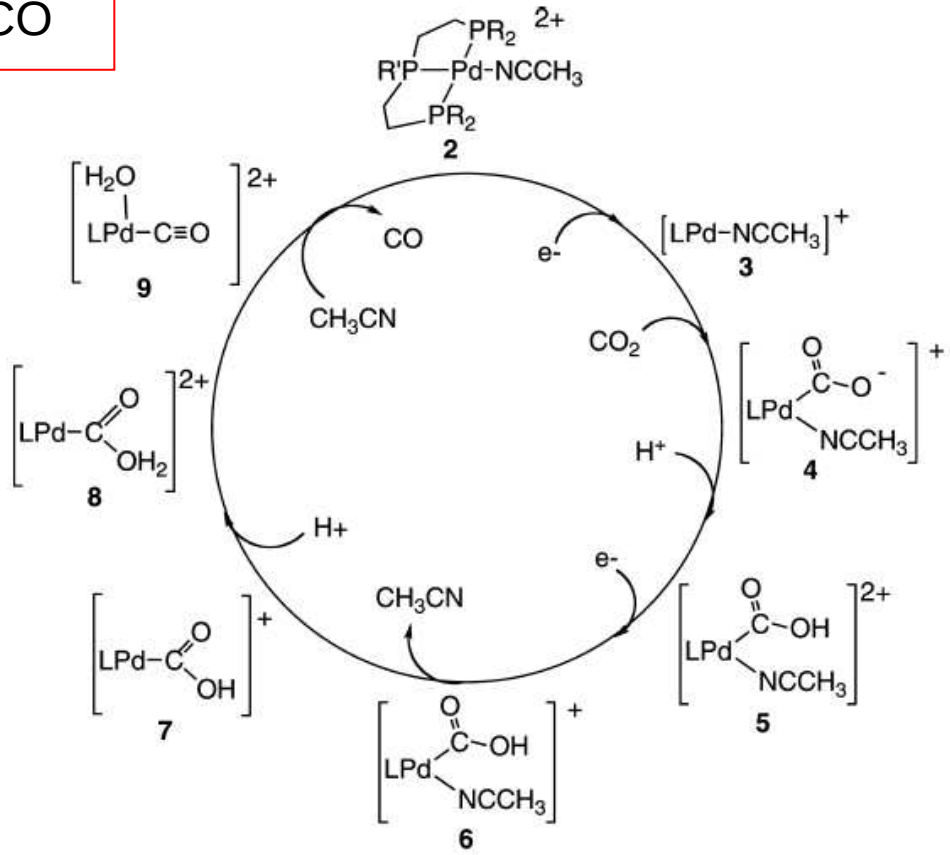
-Surtension ~ 800 mV
- faible activité (< 10 cycles)
- faible rendement

Meyer 1988

Pd-phosphines (Dubois DL; 1991-)



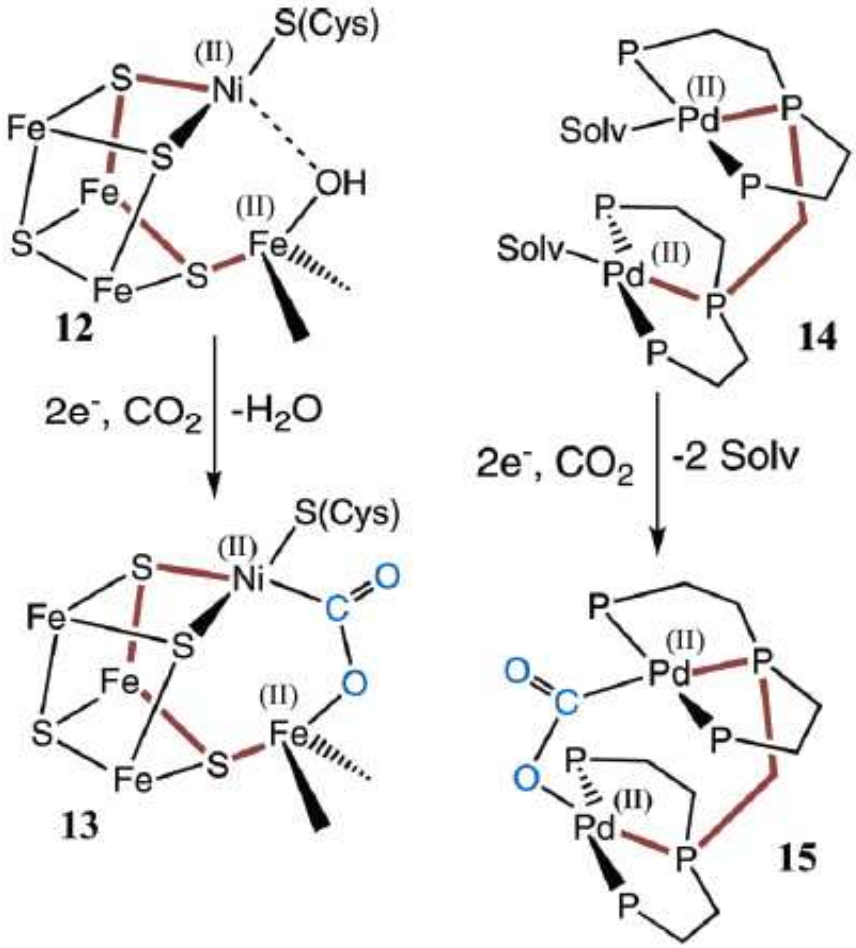
$CO_2 \rightarrow CO$



[a] L = triphosphine ligand.

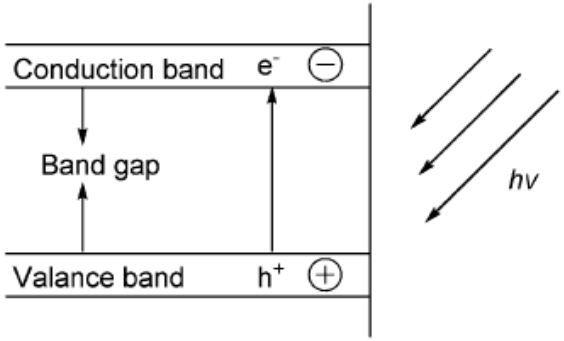
-Surtension ~ 100-300 mV
- cycles ~ 100
- rendt > 90%
- k ~ 10-300 $M^{-1}s^{-1}$

DL Dubois Accounts Chem Res 2009



Complexe dinucléaire:
-Activité x 1000
-Durée de vie↓ (Pd(I)-Pd(I))

Photocatalyseurs : semiconducteurs



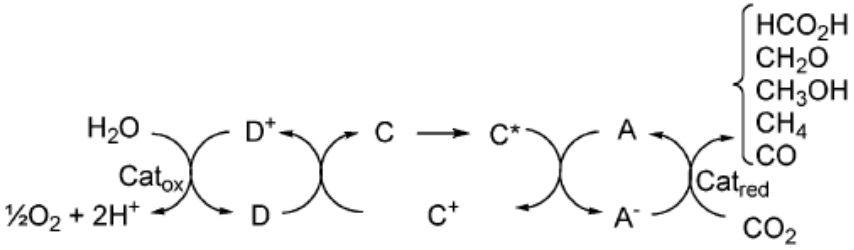
Photocatalyst	Reductant	Primary product(s)
TiO_2/zeolite	Water	CH_3OH
TiO_2	H_2	CO
TiO_2 (P-25)	Isopropyl alcohol	CH_4, HCOOH
TiO_2 nanocrystals in SiO_2	Lithium nitrate/ 2-propanol	Formate, CO, NH_3, urea
Rh/TiO_2	H_2	CO, CH_4
$Pd/RuO_2/TiO_2$, Pd/TiO_2	NaOH, aqueous Na_2SO_3	Formate
MgO	H_2	CO
ZnO on activated carbon	—	CO, H_2

$$CS = \frac{[CO_2 \text{ reduction products}]}{[H_2]}$$

$$\phi = \frac{[CO_2 \text{ reduction products}]}{[\text{incident photons}]}$$

$$\text{Turnover Number (TN)} = \frac{[CO_2 \text{ reduction products}]}{[\text{catalyst}]}$$

Réduction photochimique de CO_2



$$P + h\nu \rightarrow P^*$$

$$P^* + Et_3N \rightarrow P^- + Et_3N^{\bullet+}$$

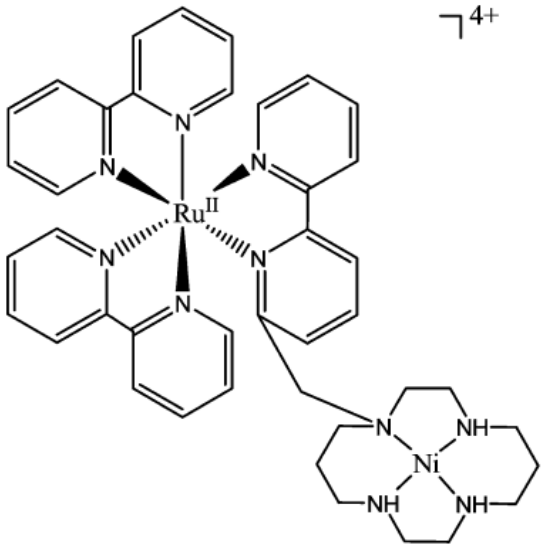
$$P^- + cat \rightarrow P + cat^-$$

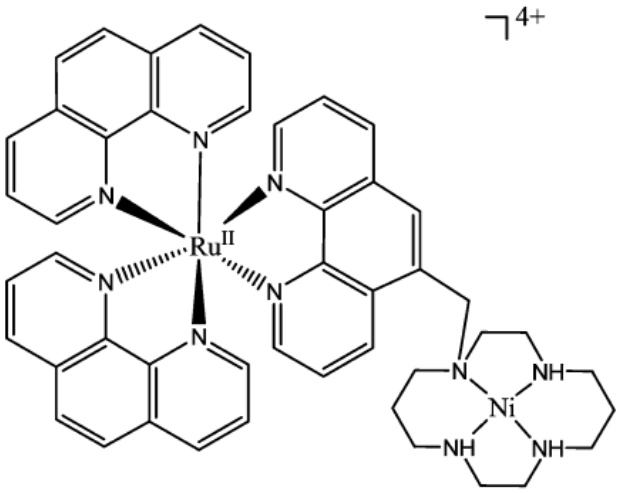
$$cat^- + CO_2 \rightarrow \rightarrow cat + products$$

$$Et_3N^{\bullet+} + Et_3N \rightarrow Et_3NH^+ + Et_2NC^{\bullet}HCH_3$$

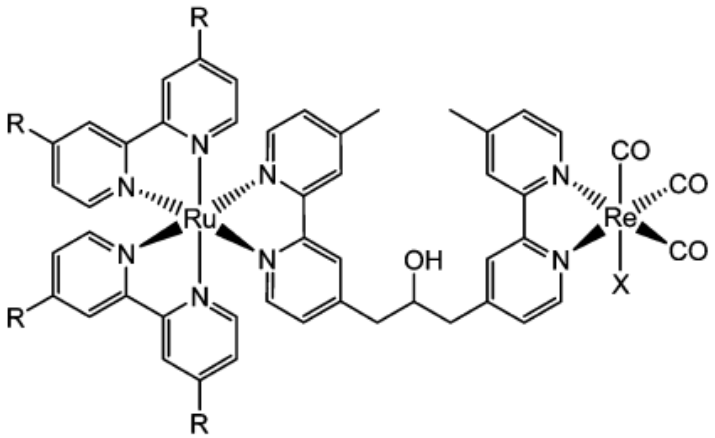
Sensitizer	Catalyst or relay	Donor	Product/s	Φ^b (mol/Einstein)
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.049[c]
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.096[d]
$Ru(bpy)_3^{2+}$	MV^{2+}	TEOA	$HCOO^-$	0.01
$Ru(bpy)_3^{2+}$	Co^{2+}/bpy	TEA	CO, H_2	
$Ru(bpy)_3^{2+}$	Co^{2+}/Me_2phen	TEA	CO, H_2	0.012 (CO), 0.065 (H_2)
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	TEOA	$HCOO^-$	0.14
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	BNAH	$HCOO^-$, CO	0.03 ($HCOO^-$), 0.15 (CO)
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(H)^+$	TEOA	$HCOO^-$	0.15
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(X)^{n+}$, X = Cl and Co	TEOA	$HCOO^-$	
$Ru(bpy)_3^{2+}$	$CoHMD^{2+}$	H_2A	CO, H_2	
$Ru(bpy)_3^{2+}$	$Nicyclam^{2+}$	H_2A	CO, H_2	0.001 (CO)
$Ru(bpy)_3^{2+}$	NiPr-cyclam2+[a]	H_2A	CO, H_2	*Ca.* 0.005 (CO)
$Ru(bpz)_3^{2+}$	Ru colloid	TEOA	CH_4, H_2	10^{-4} (CH_4)[e]
$Ru(bpy)_3^{2+}$	Bipyridinium$^+$, Ru or Os colloid	TEOA	CH_4, H_2	10^{-4} (CH_4)[e] 10^{-3} (H_2)[e]
$ReCl(bpy)(CO)_3$		TEOA	CO	0.14
$ReCl(bpy)(CO)_3$		TEOA	CO	0.15
$[ReP(OEt)_3(bpy)(CO)_3]^+$		TEOA	CO	0. 38
p-Terphenyl	$Cocyclam^{3+}$	TEOA	CO, $HCOO^-$, H_2	0.25 (CO + $HCOO^-$)
p-Terphenyl	$CoHMD^{2+}$	TEOA	CO, $HCOO^-$, H_2	
Phenazine	$Cocyclam^{3+}$	TEOA	$HCOO^-$	0.07[e]
FeTPP		TEA	CO	
CoTPP		TEA	$HCOO^-$, CO	

En. Env. Sci 2010 3 43, Ac Chem Res 2009

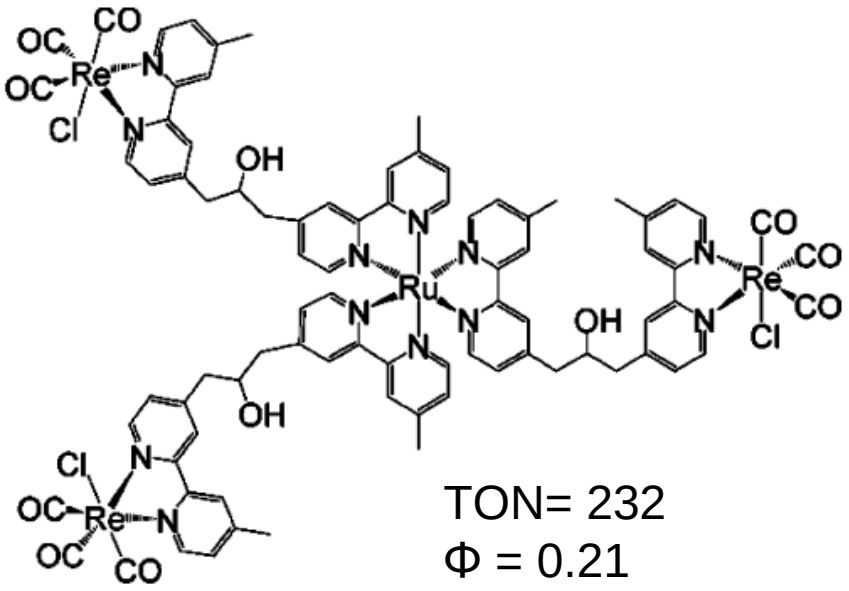




Stabilité et TON ↑



E Fujita *Acc Chem Res* 2009



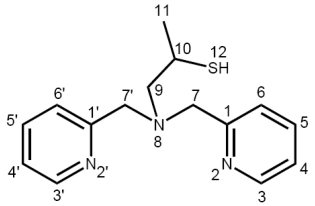
TON= 232

Φ = 0.21

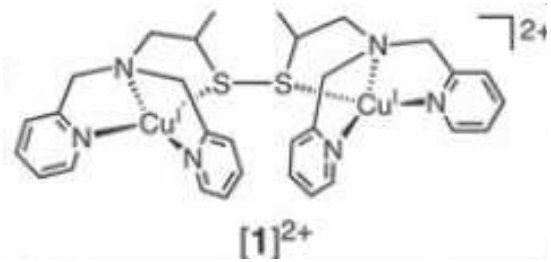
Electroréduction du CO_2 en oxalate

Electrocatalytic CO2 Conversion to Oxalate by a Copper Complex
Raja Angamuthu, *et al.*
Science **327**, 313 (2010);

Observation 1:

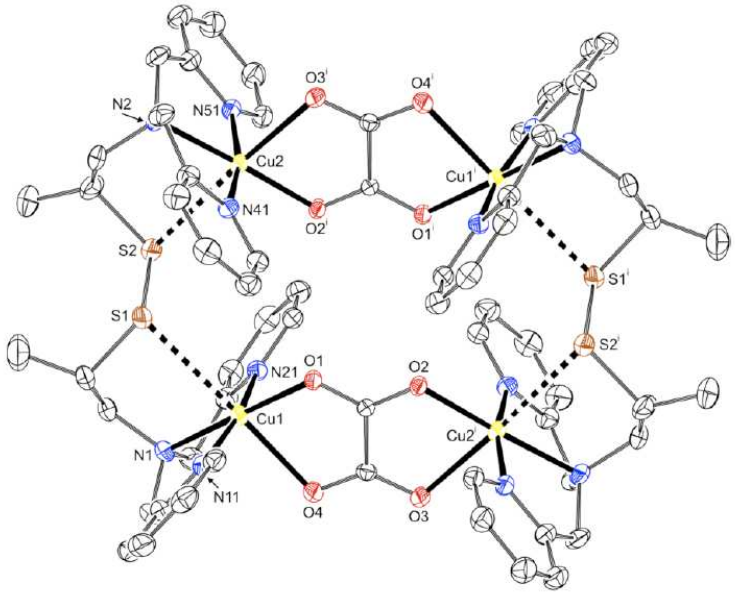


Cu^{2+} →



$[1]^{2+}$

↓ air



$[2]^{4+}$

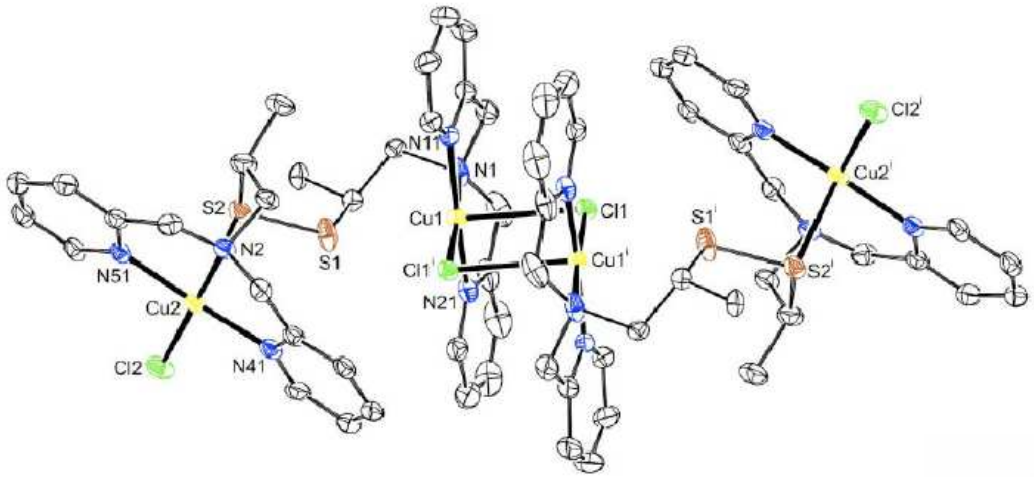
-spectr. masse
-Rayons X
-$^{13}CO_2$

[2]$^{4+}$

Observation 2:

HCl
- acide oxalique

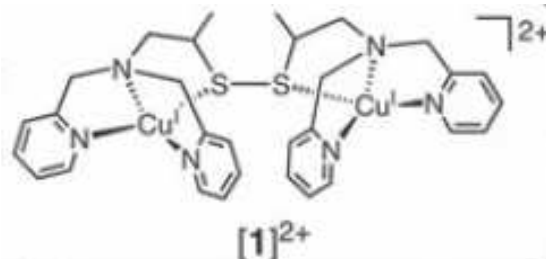
[3]$^{4+}$ **E= + 0.06V (ENH)**



Observation 3:

[3]$^{4+}$ 1. électrolyse

+0.03 V
100%

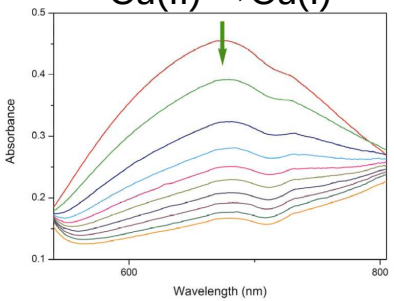


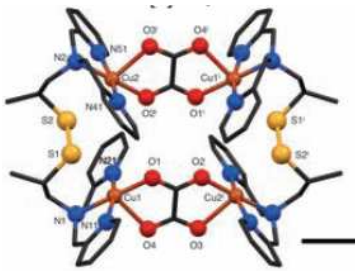
[1]$^{2+}$

2. CO_2

[2]$^{4+}$

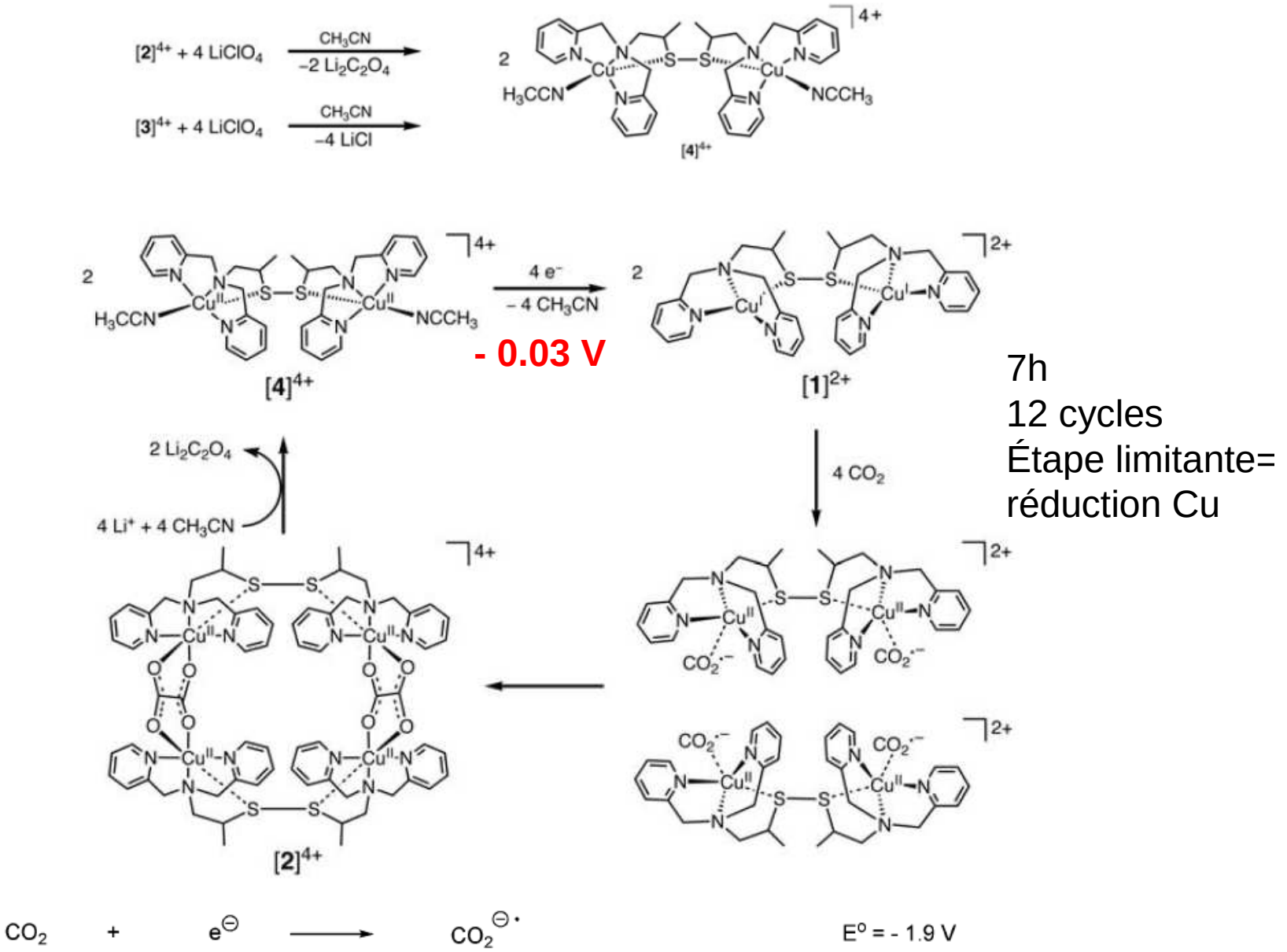
Électrolyse +0.03 V)
Cu(II) →Cu(I)





Observation 4: Réactivité de **2** en présence de $LiClO_4$

Utilisation de 2 comme électrocatalyseur en présence de $LiClO_4$



7h
12 cycles
Étape limitante= réduction Cu

CO_2, une source de carbone abondante : activation et réduction

Marc Fontecave

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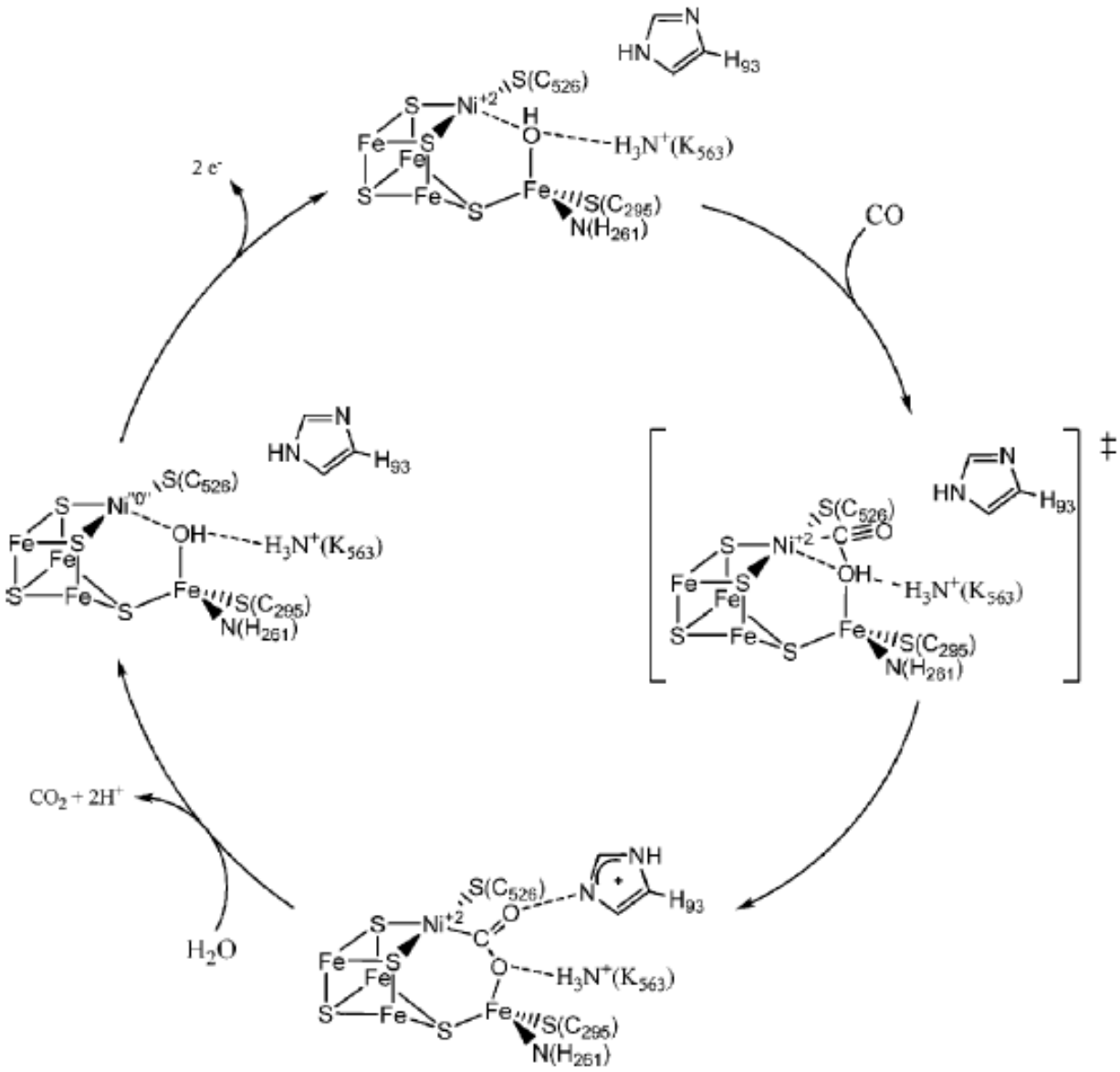
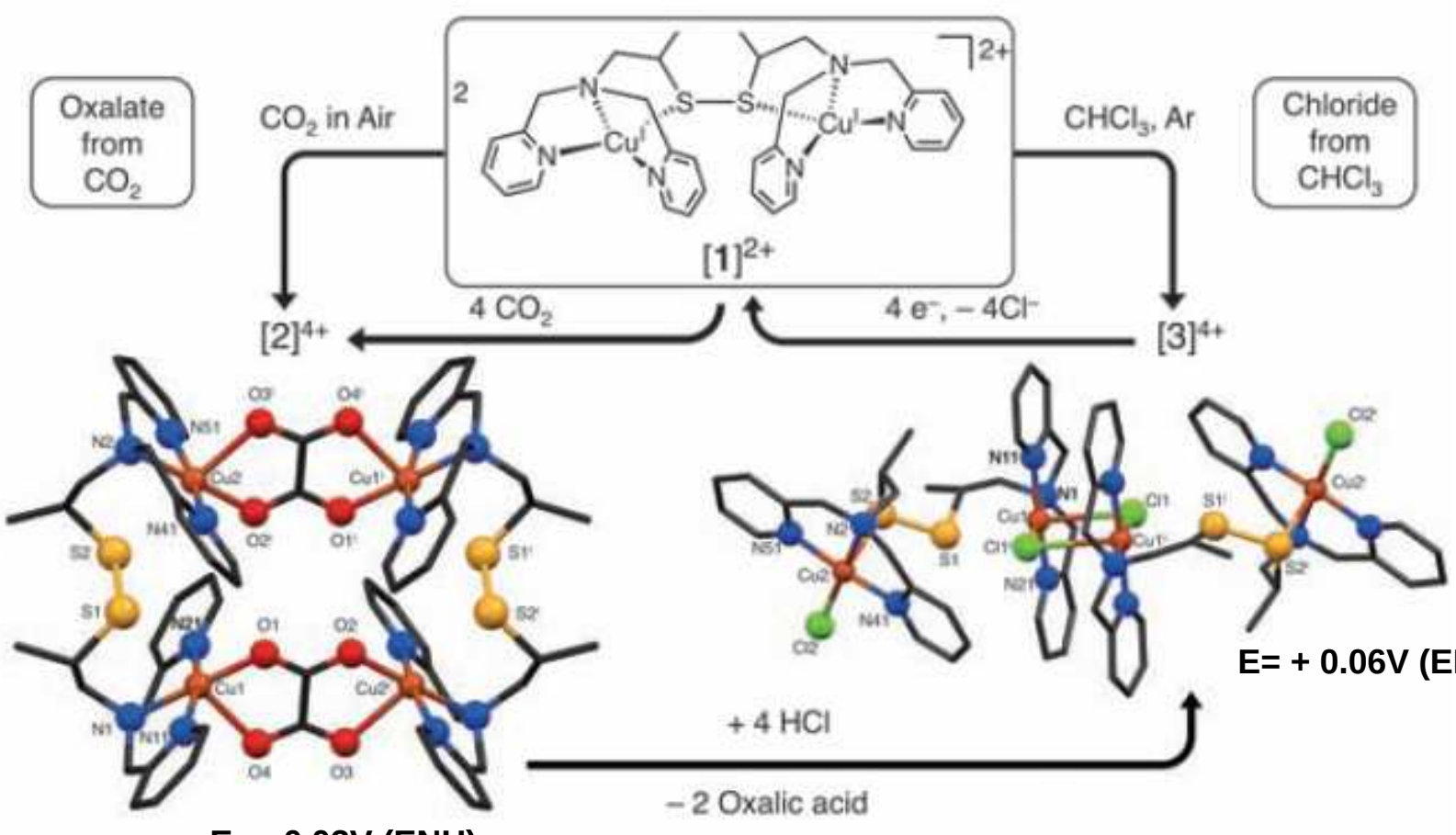
Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05


2 e-
CO
‡
$CO_2 + 2H^+$
H_2O
$H_3N^+(K_{563})$
$S(C_{526})$
$S(C_{295})$
$N(H_{261})$
H_{93}
OH
Ni+2
Fe
S
HN
NH



$$CO_2 + e^{\ominus} \longrightarrow CO_2^{\ominus\bullet} \qquad E^o = -1.9\ V$$