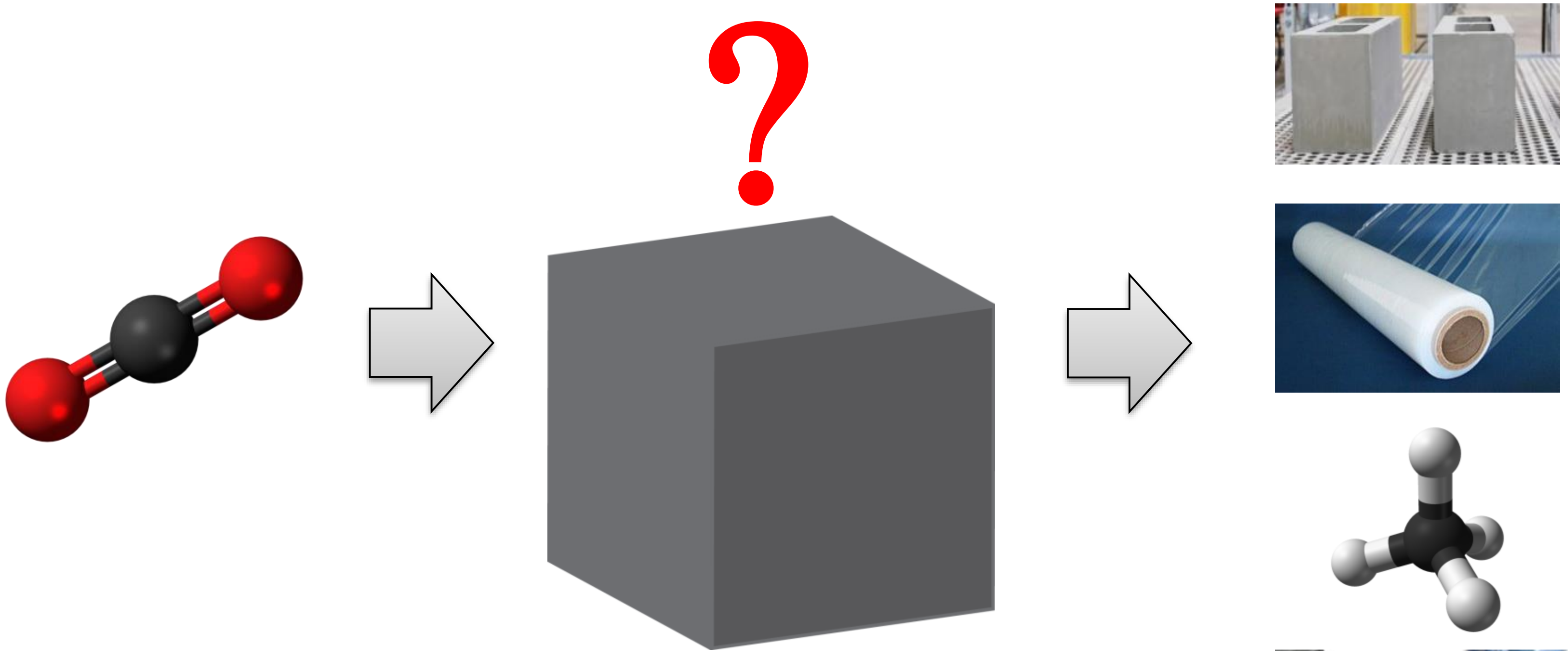
Using Renewable Electricity to Valorize Carbon Dioxide



Yogi Surendranath

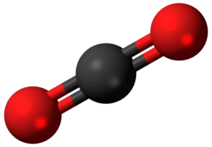
Paul M. Cook Career Development Assistant Professor

MIT Chemistry

Represented by Marcel Schreier, Postdoctoral Fellow

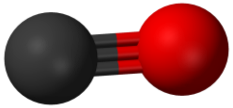
Oxidation State of Carbon → Energy Content

4+

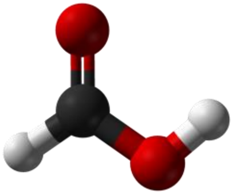


limestone
($CaCO_3$)

2+

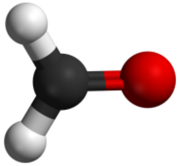


carbon monoxide

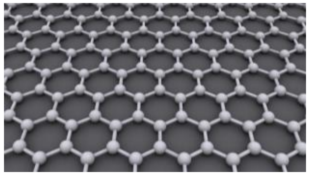


formic acid

0



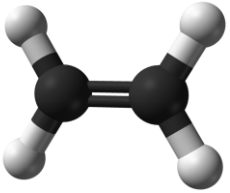
formaldehyde



graphene

coal

2−

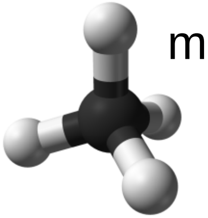


ethylene

plastics

gasoline

4−

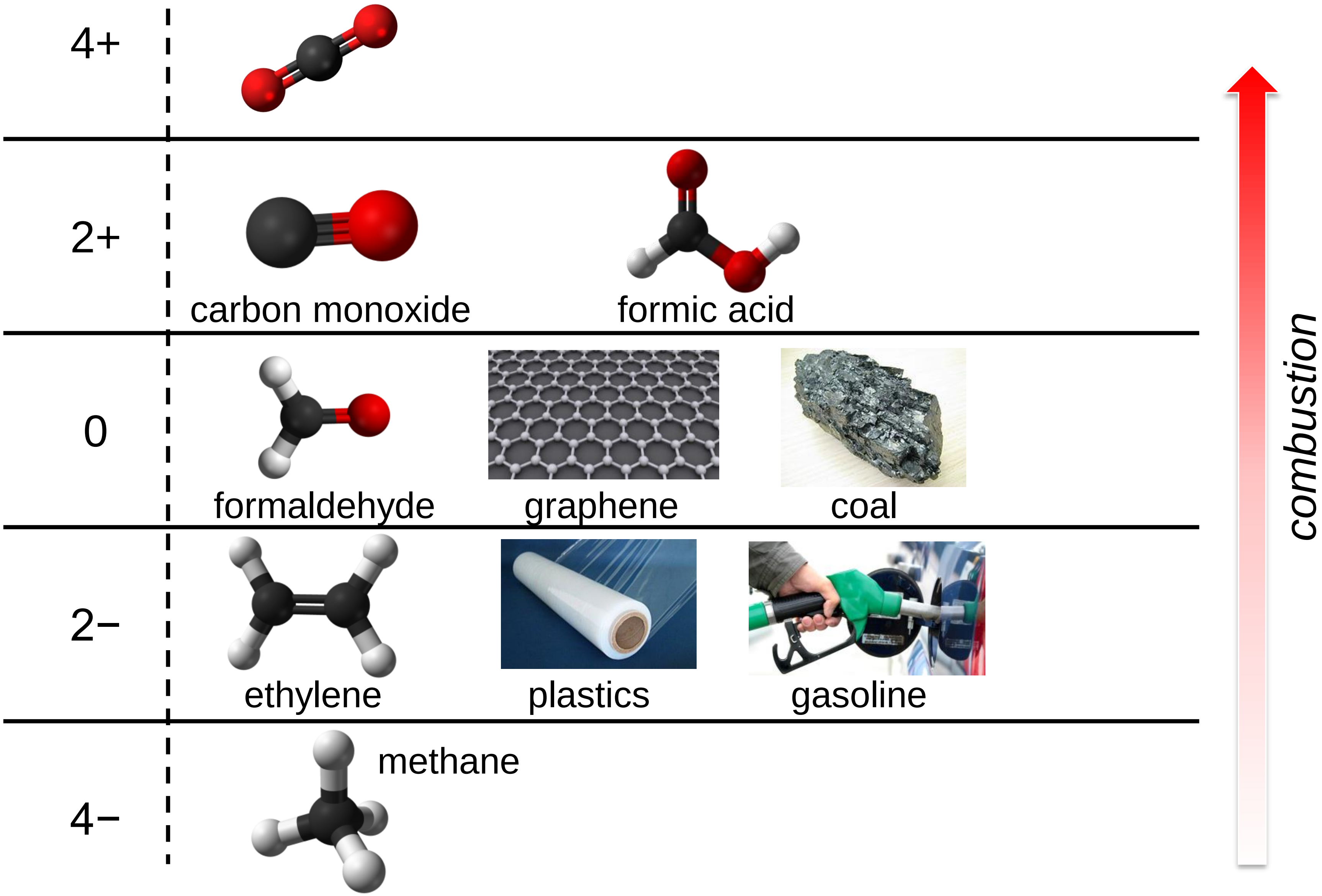


methane

energy content / input

Reversing Combustion!

Reductive methods require energy input



4+

2+

carbon monoxide

formic acid

0

formaldehyde

graphene

coal

2−

ethylene

plastics

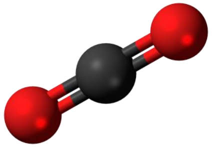
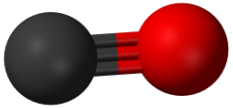
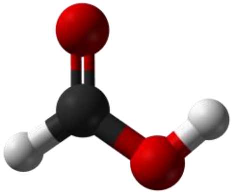
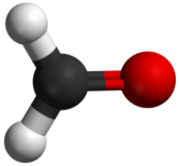
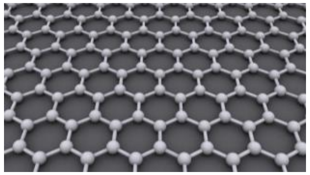
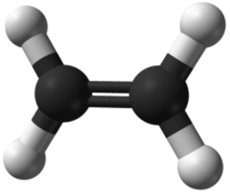
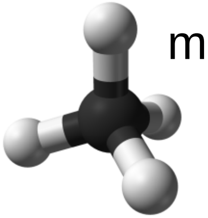
gasoline

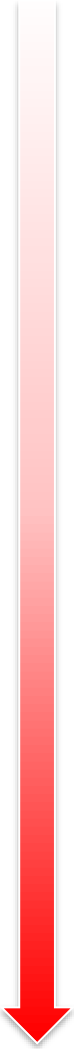
4−

methane

combustion

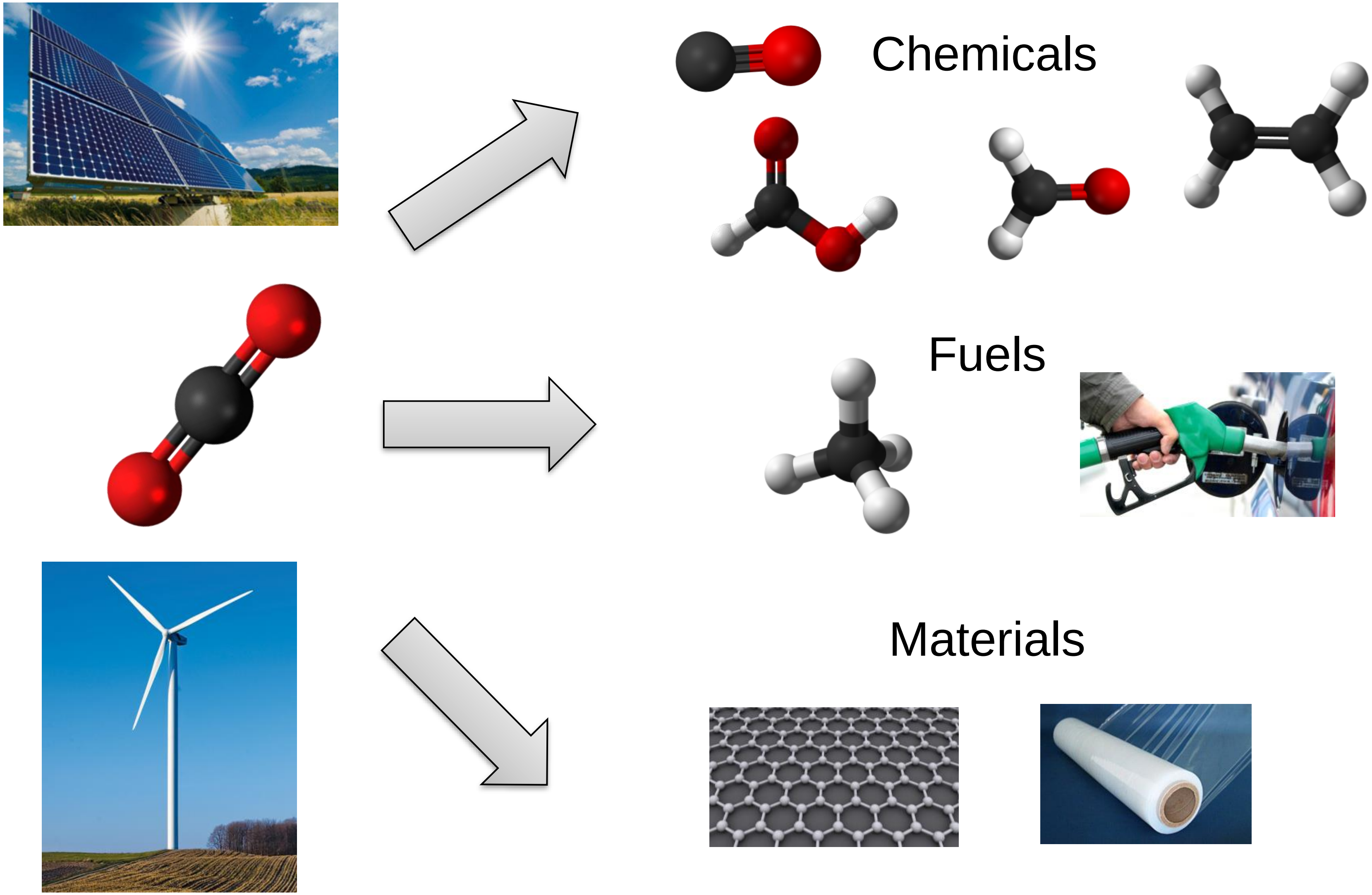
Reductive methods require energy input

4+			
2+	 carbon monoxide	 formic acid	
0	 formaldehyde	 graphene	 coal
2−	 ethylene	 plastics	 gasoline
4−	 methane		



energy content / input

Energy input *must* have zero carbon emissions



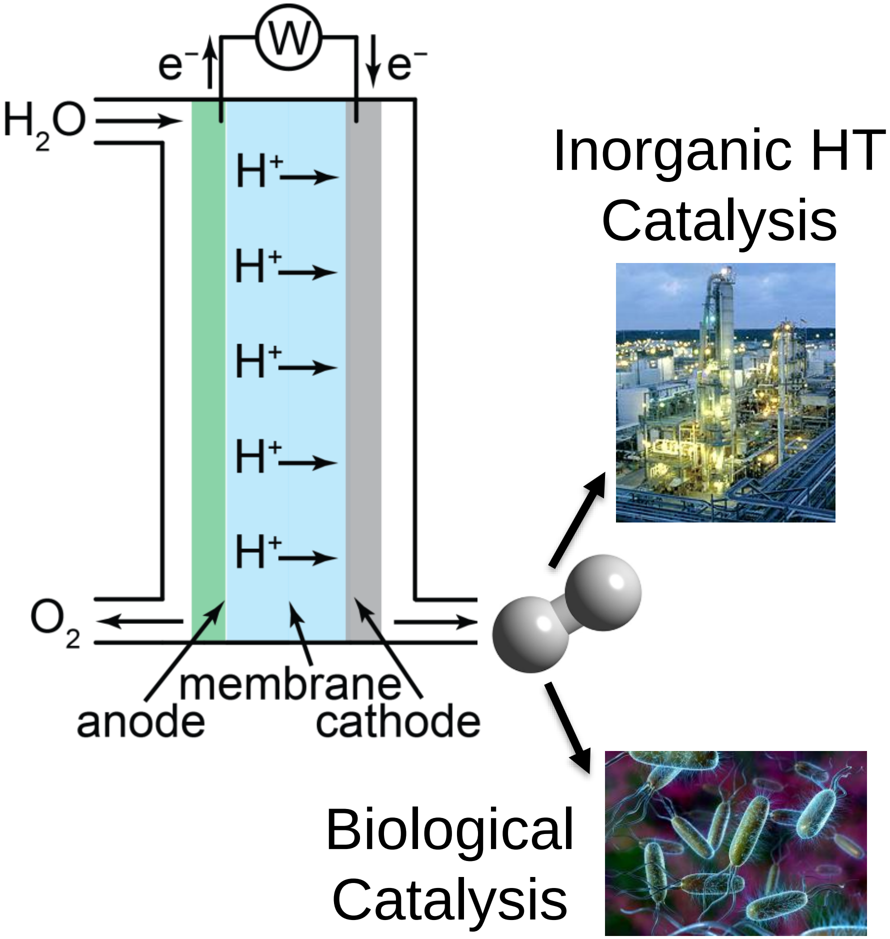
Chemicals

Fuels

Materials

Electrical energy input can be direct or indirect (H_2)

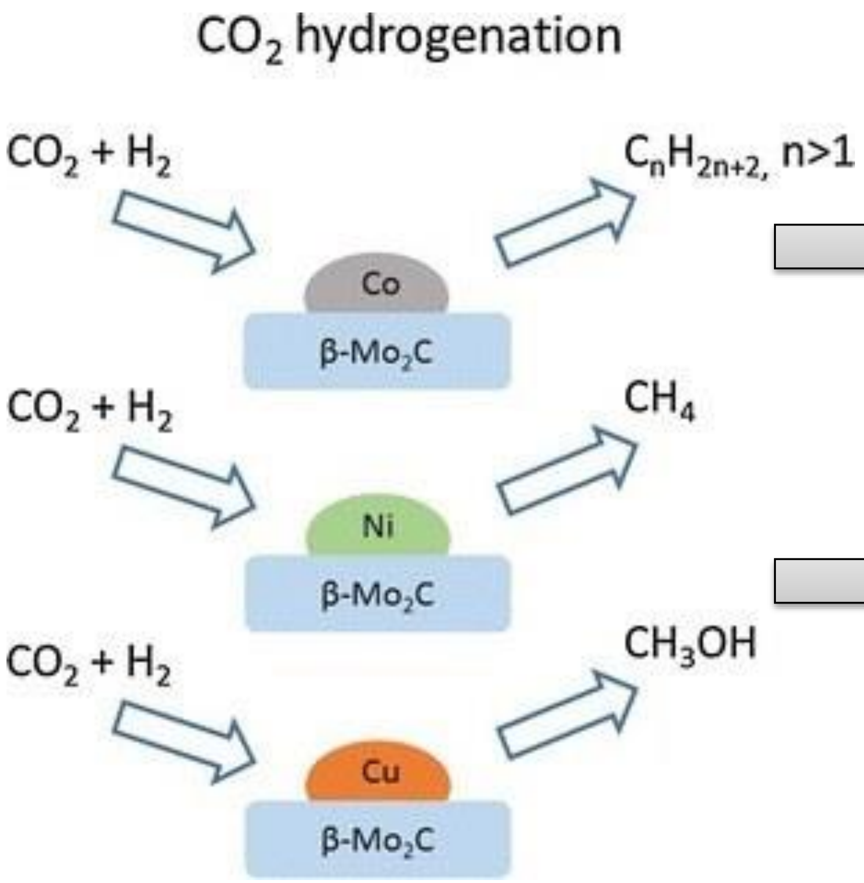
Indirect: Electrolytic H_2 then CO_2



Inorganic HT Catalysis

Biological Catalysis

H_2 + CO_2 processes are mature but can be improved



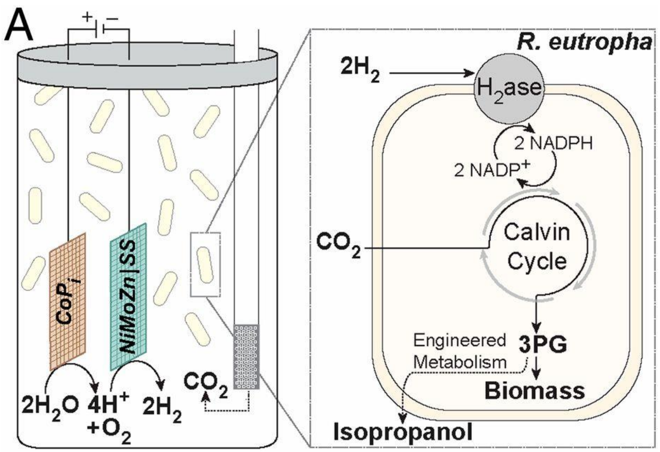
Efficiency capped by efficiency of water electrolysis

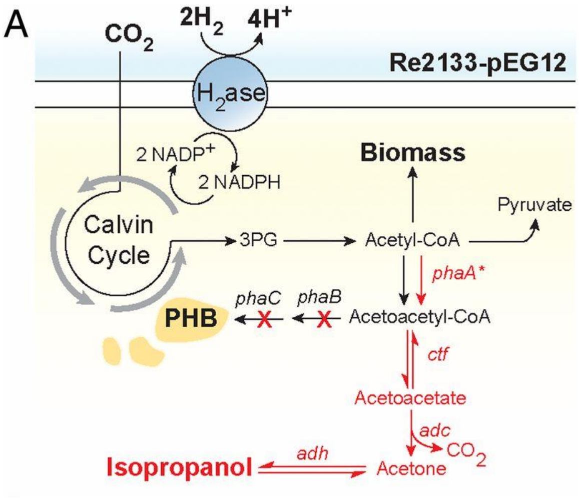
Fischer-Tropsch - Large product distribution

Processes are efficient, but require precise CO/H_2 ratio

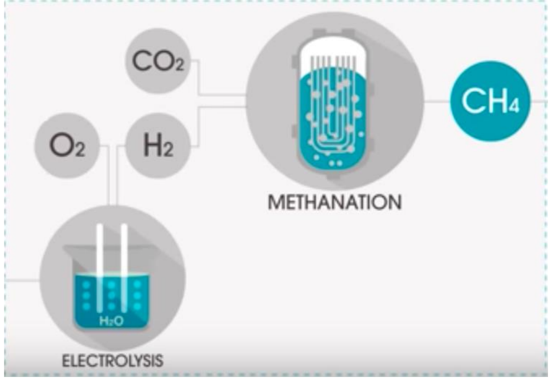
Methods for selective single-step CO_2 hydrogenation to C_{2+} liquid fuels needed

$H_2 + CO_2$ processing by engineered microbes





Torella, Gagliardi, Chen, Bediako, Colon, Way, Silver, Nocera *PNAS* **2015**, *112*, 2337



Electrochaea

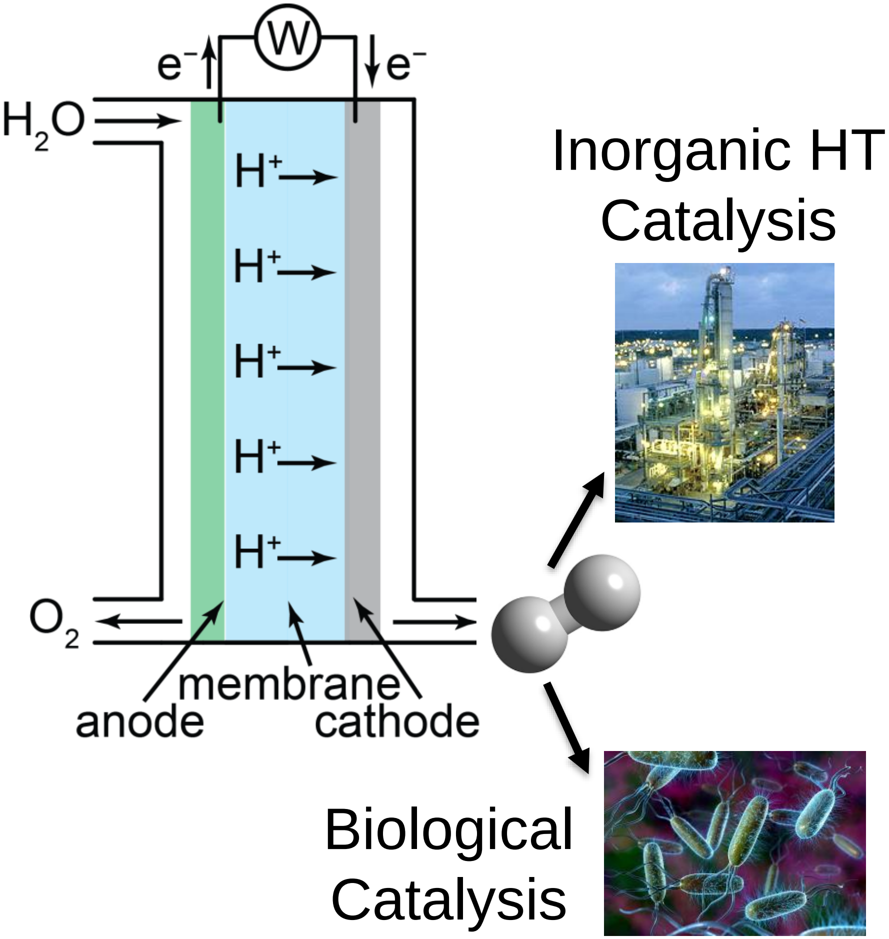
Efficiency capped by efficiency of water electrolysis

Energy lost to sustain microbial life/reproduce

Certain strains very sensitive to impurities (e.g. H_2O_2)

Electrical energy input can be direct or indirect (H_2)

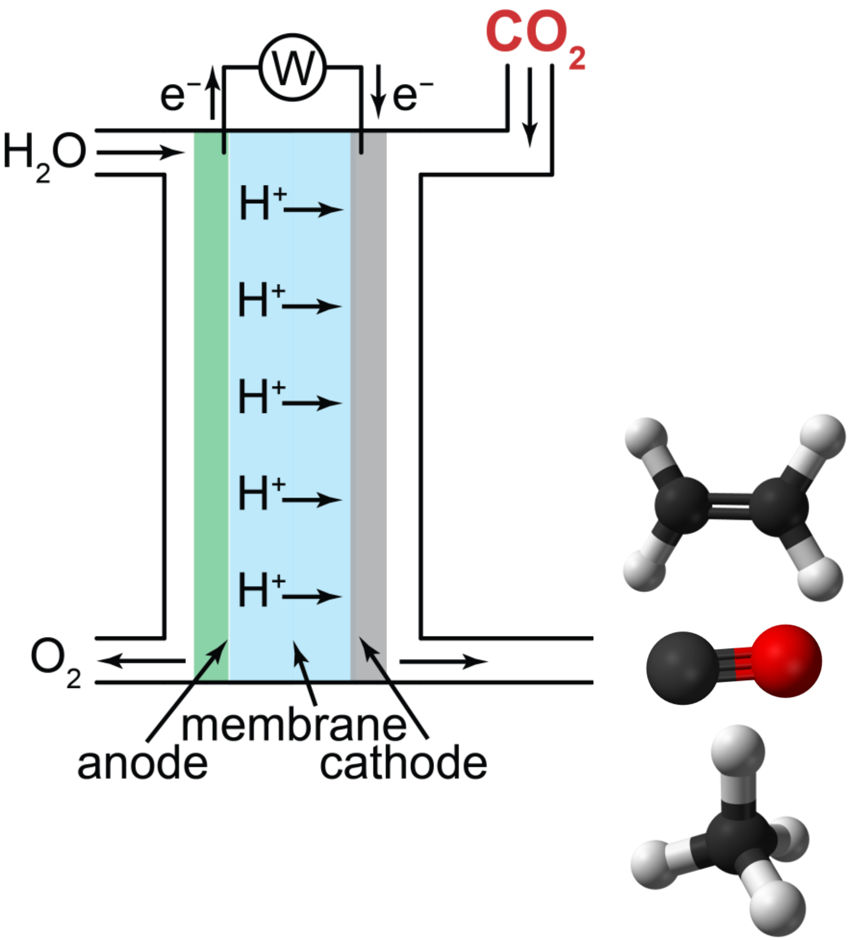
Indirect: Electrolytic H_2 then CO_2



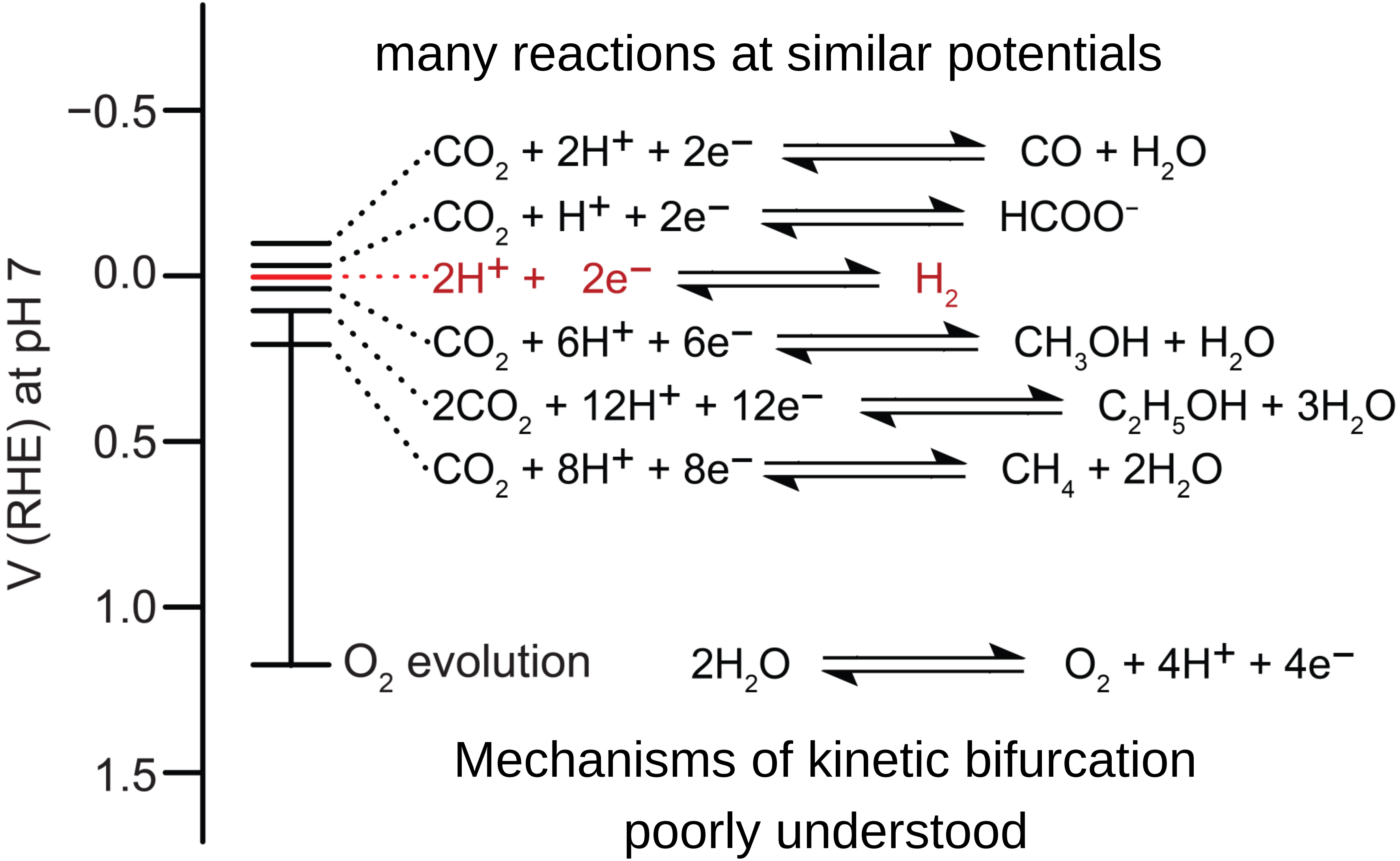
Inorganic HT Catalysis

Biological Catalysis

Direct: CO_2 electrolysis



Selective catalysis key for direct electrolysis



many reactions at similar potentials

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

$CO_2 + H^+ + 2e^- \rightleftharpoons HCOO^-$

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

$CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O$

$2CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_5OH + 3H_2O$

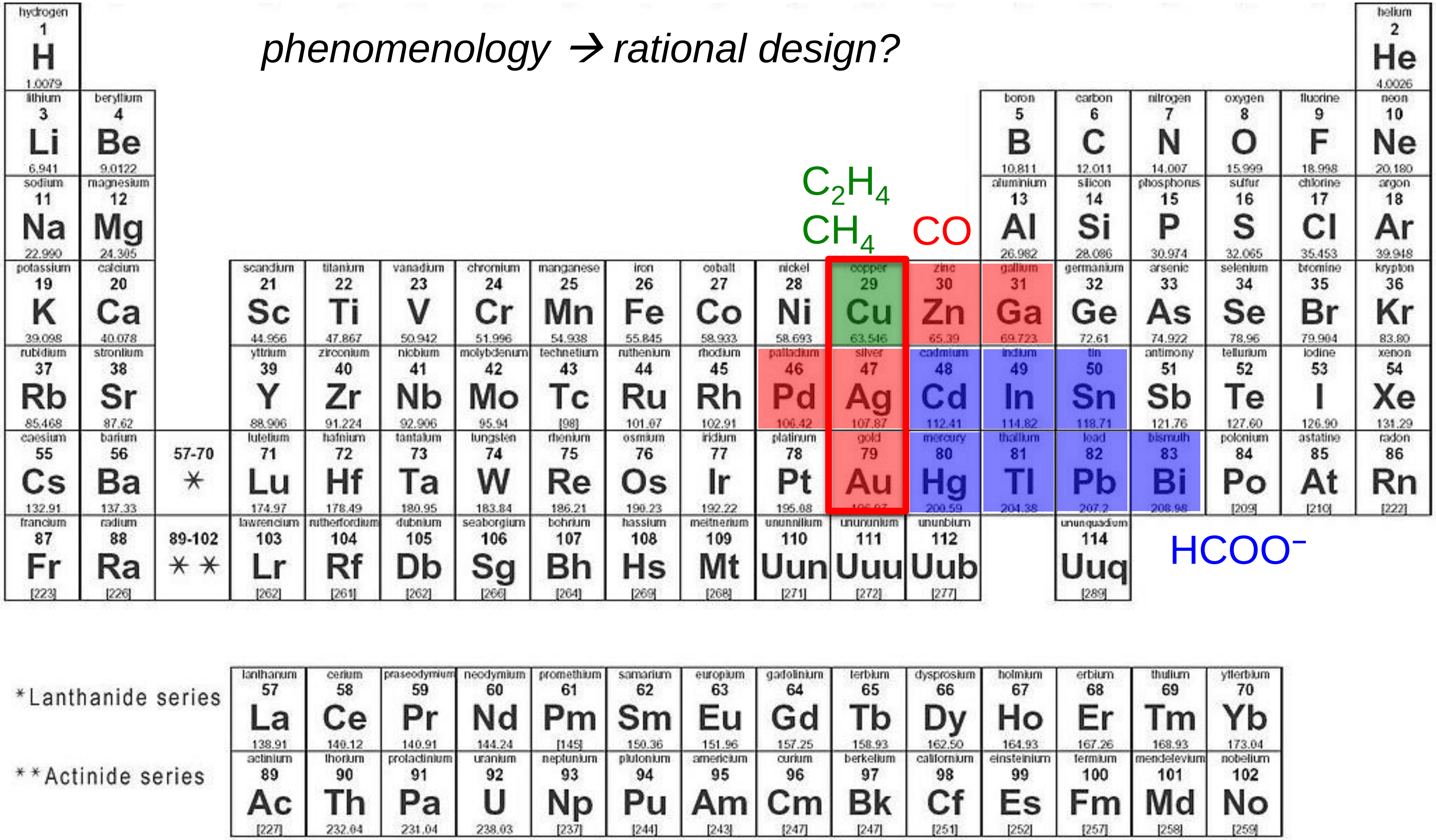
$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O$

O_2 evolution $2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$

Mechanisms of kinetic bifurcation
poorly understood

Group 11 metals most active for CDR

phenomenology → rational design?

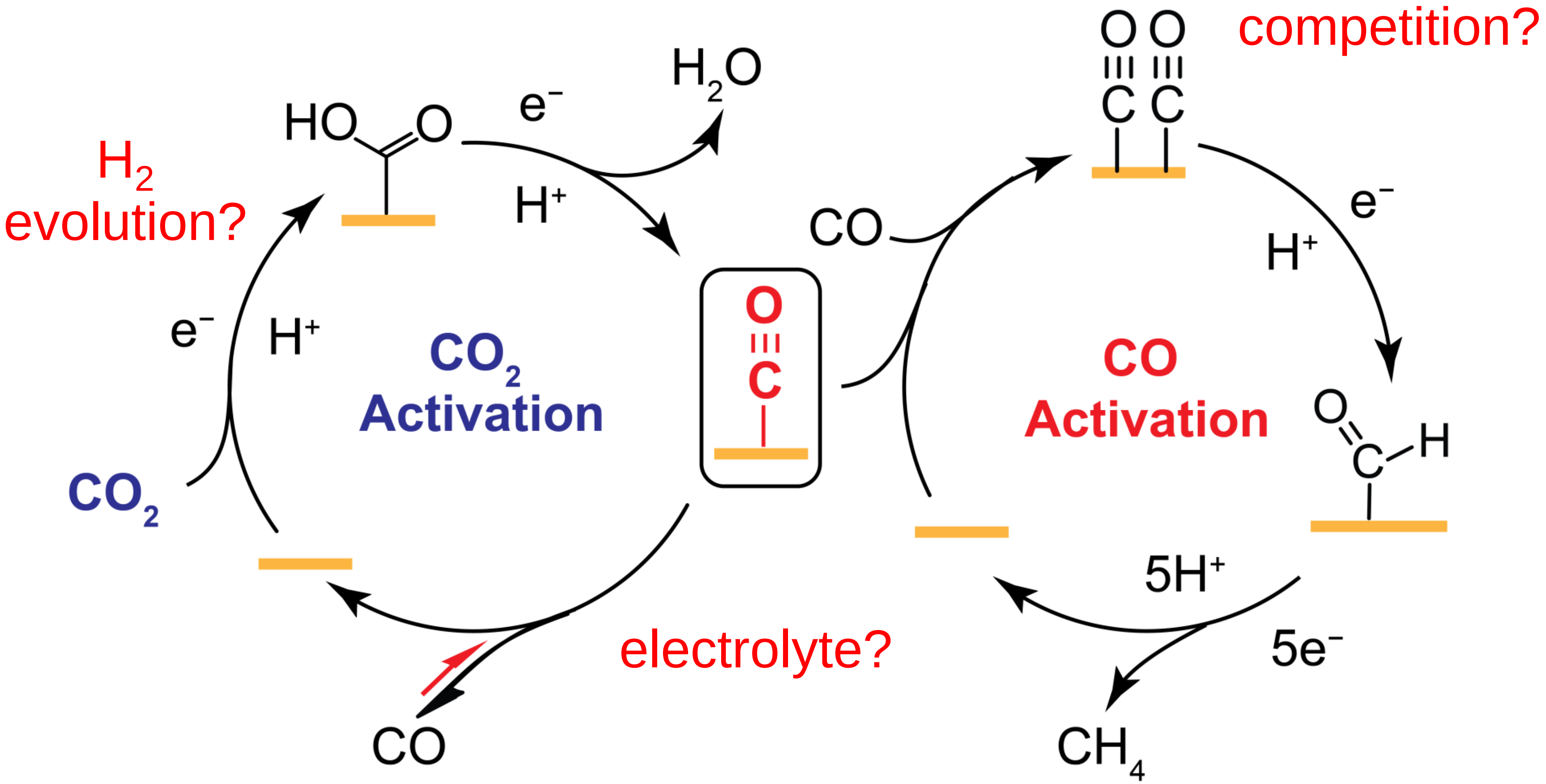


hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	🟩 copper 29 Cu 63.546	🟥 zinc 30 Zn 65.39	🟥 gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	🟥 palladium 46 Pd 106.42	🟥 silver 47 Ag 107.87	🟦 cadmium 48 Cd 112.41	🟦 indium 49 In 114.82	🟦 tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	🟥 gold 79 Au 196.97	🟦 mercury 80 Hg 200.59	🟦 thallium 81 Tl 204.38	🟦 lead 82 Pb 207.2	🟦 bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

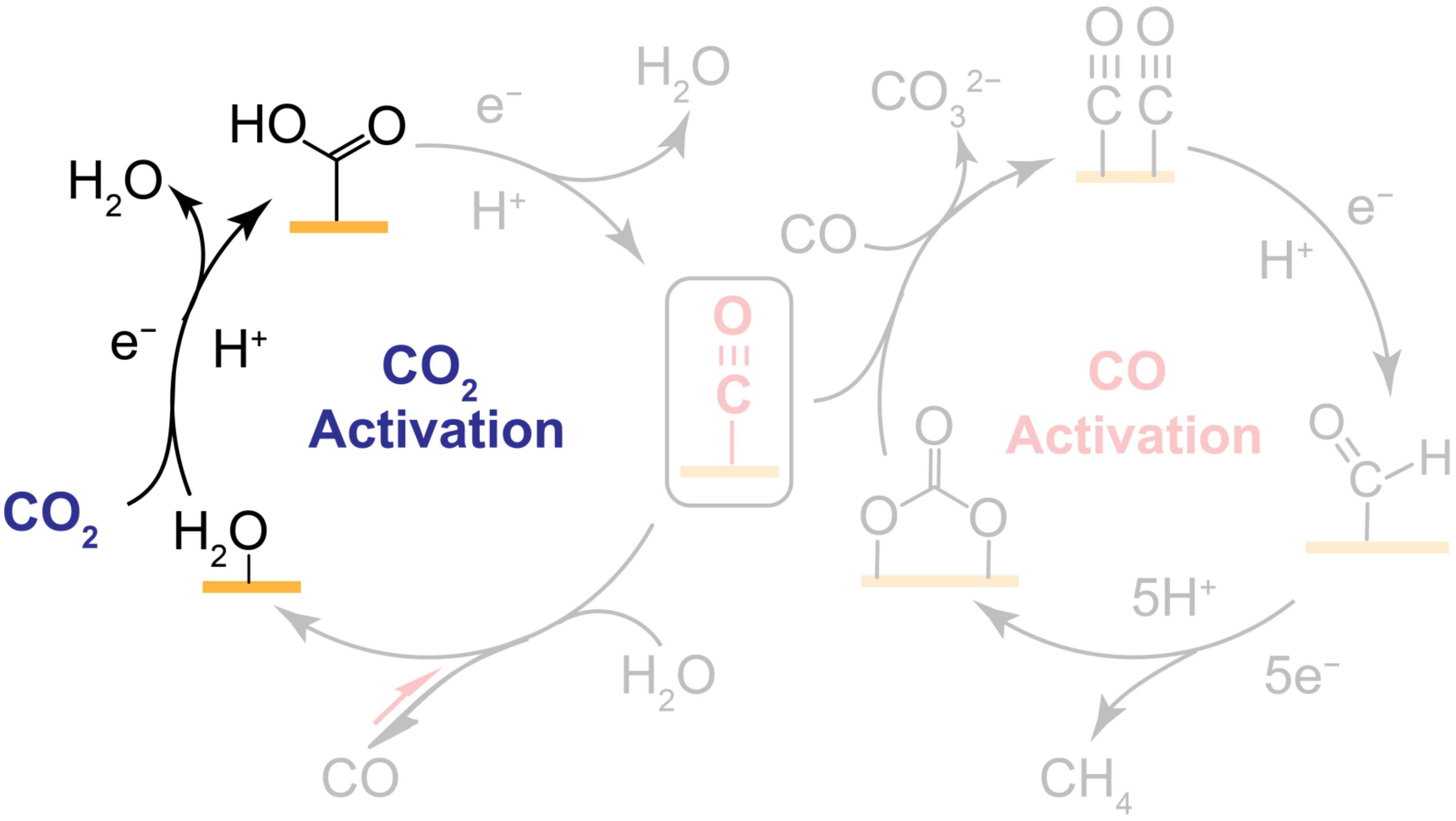
Hori, *Mod. Aspects of Electrochem.* **2008**.

CO adsorption key to prevailing mechanistic model



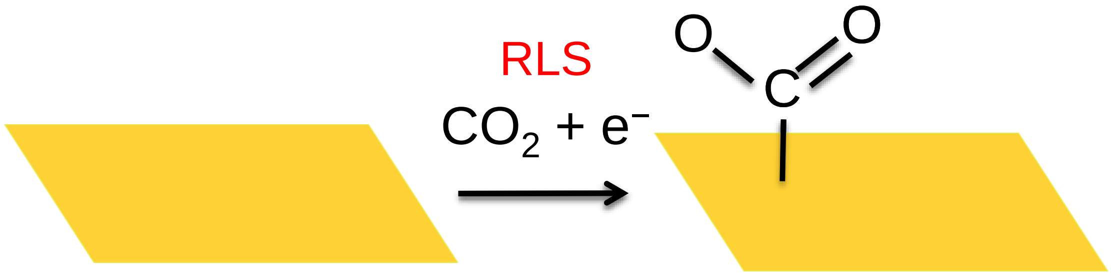
Hori, Kikuchi, Suzuki, *Chem. Lett.*, ***1985 and 1986;*** Kortlever, Shen, Schouten, Calle-Vallejo, Koper, *J. Phys. Chem. Lett.*, ***2015;*** Hori, *Modern Aspects of Electrochem.*, ***2008***

Part 1: Understanding electron-proton coupling



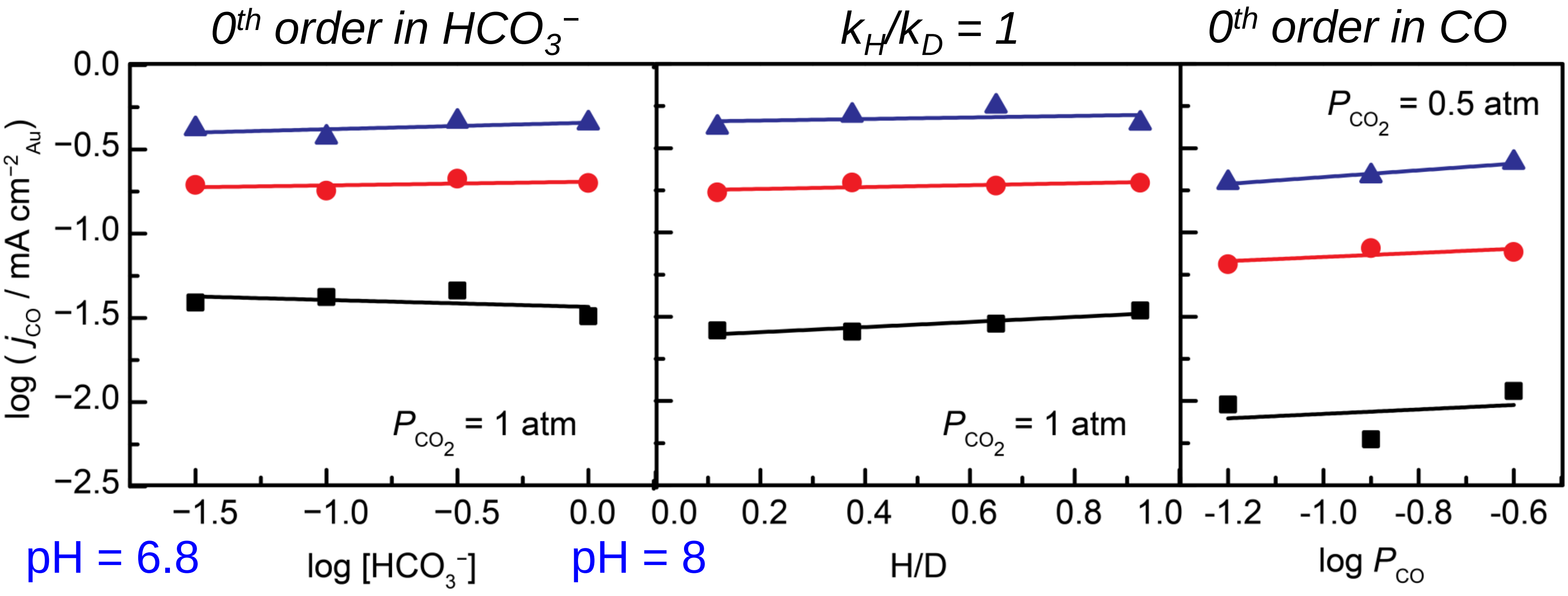
Wuttig, Yaguchi, Motobayashi, Osawa, YS, *PNAS*, **2016**, E4585
Wuttig, Yoon, Ryu, YS *JACS* **2017**, *139*, 17109

CO_2 reduction rate independent of pH, buffer, CO



RLS

$CO_2 + e^-$



0th order in HCO_3^-

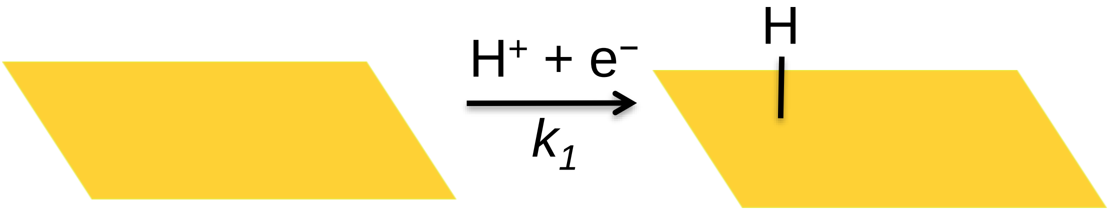
$k_H/k_D = 1$

0th order in CO

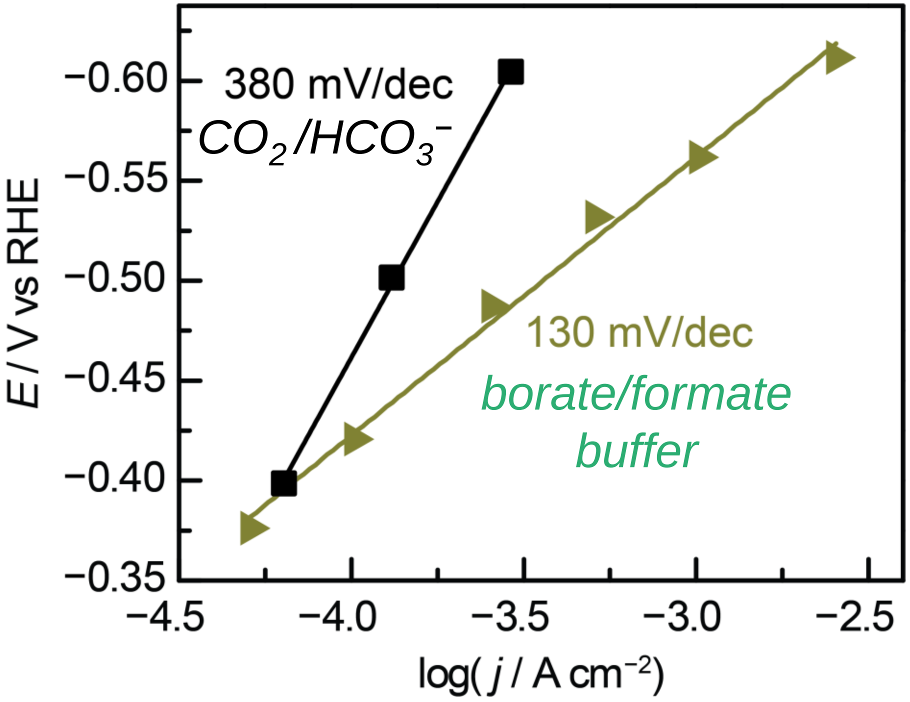
pH = 6.8

pH = 8

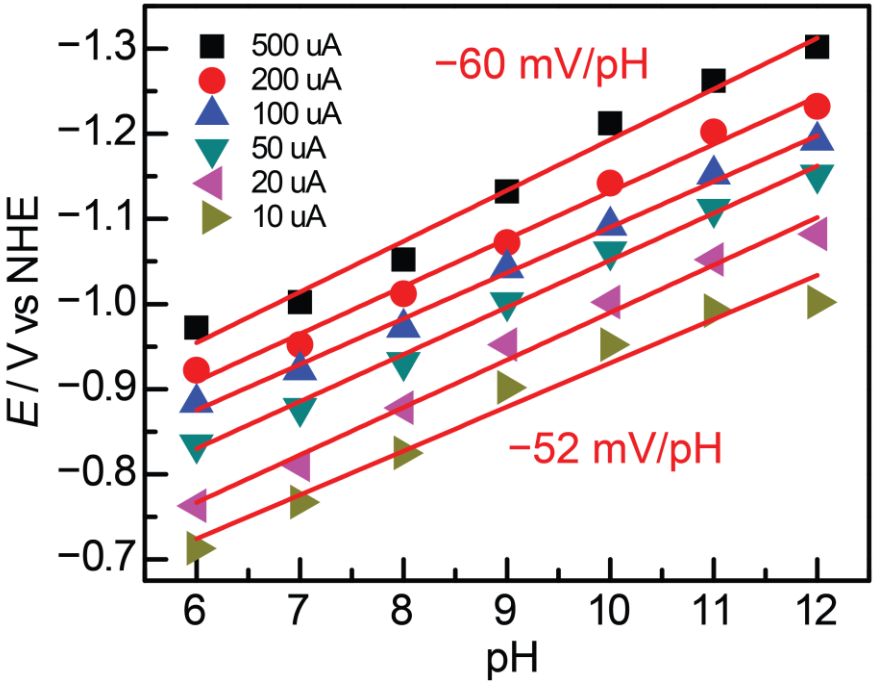
H_2 evolution proceeds via obligate CPET



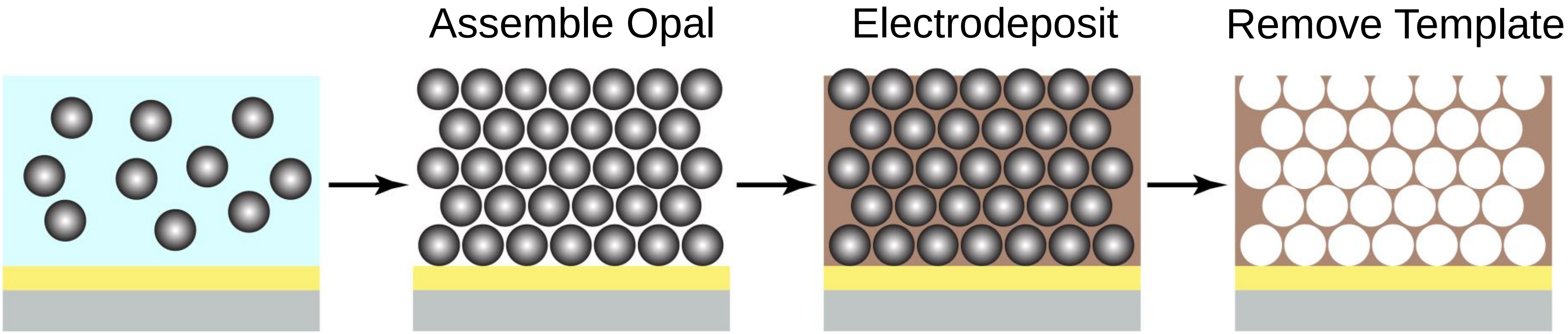
HER Tafel Plots

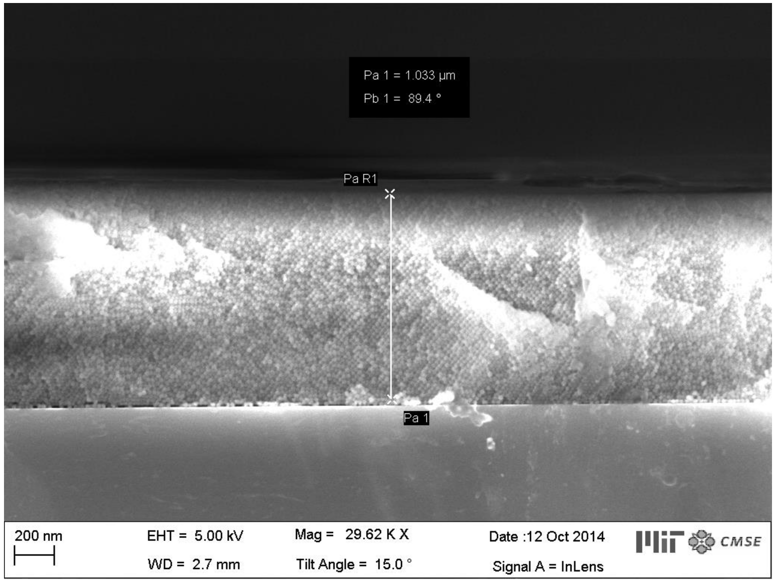


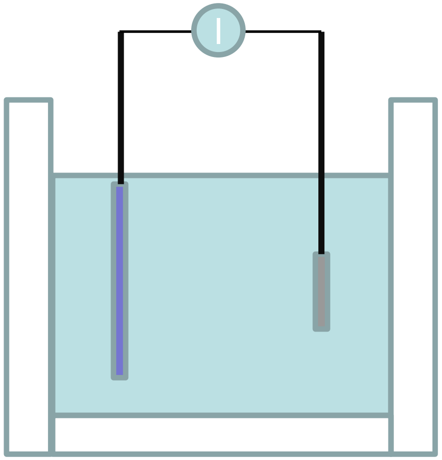
Nernstian pH dependence



Porous metals synthesized in an opal template


Assemble Opal
Electrodeposit
Remove Template

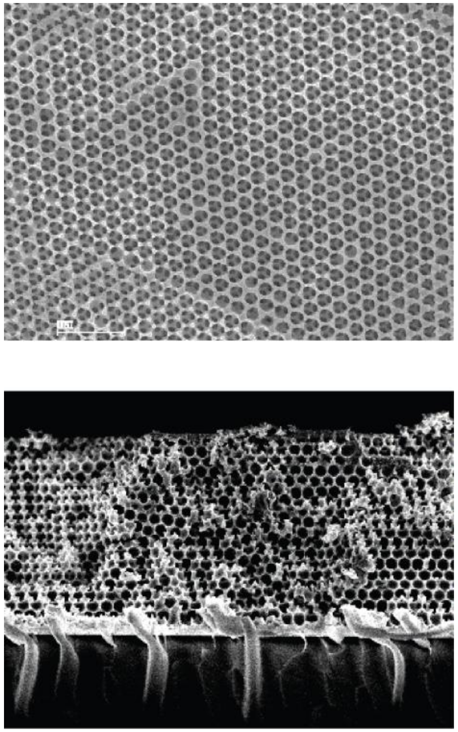


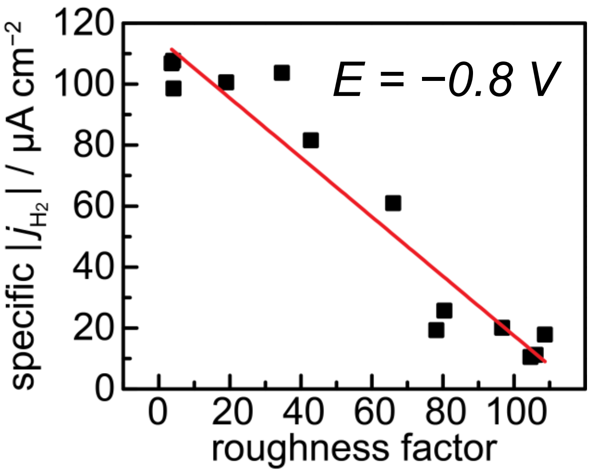


Electrodeposition

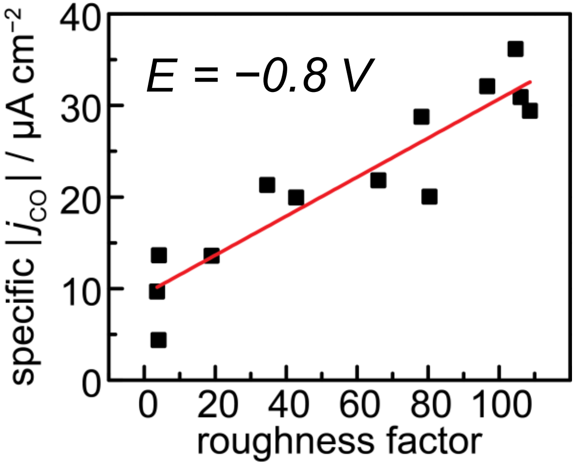
Mesostructuring induces selectivity on Ag too

Ag inverse opals

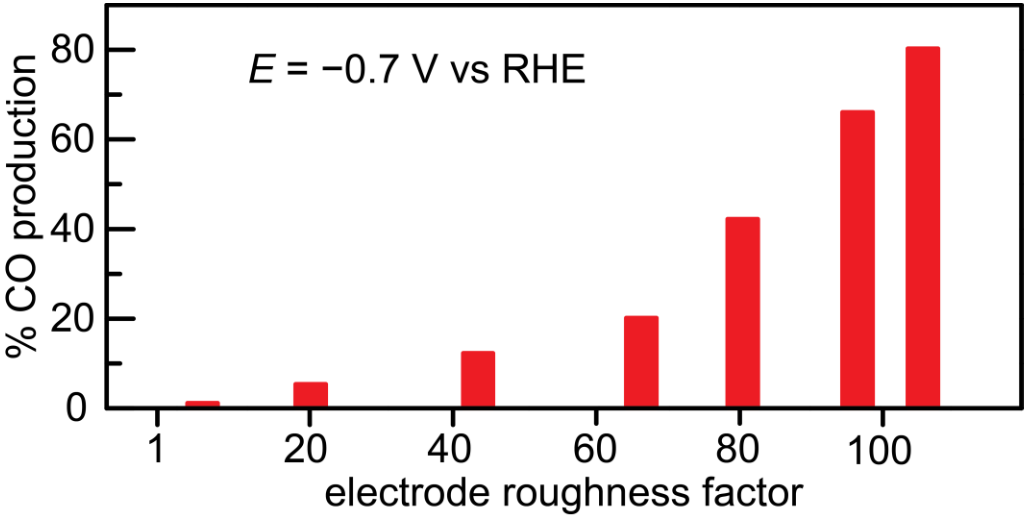




H_2 rate inhibited



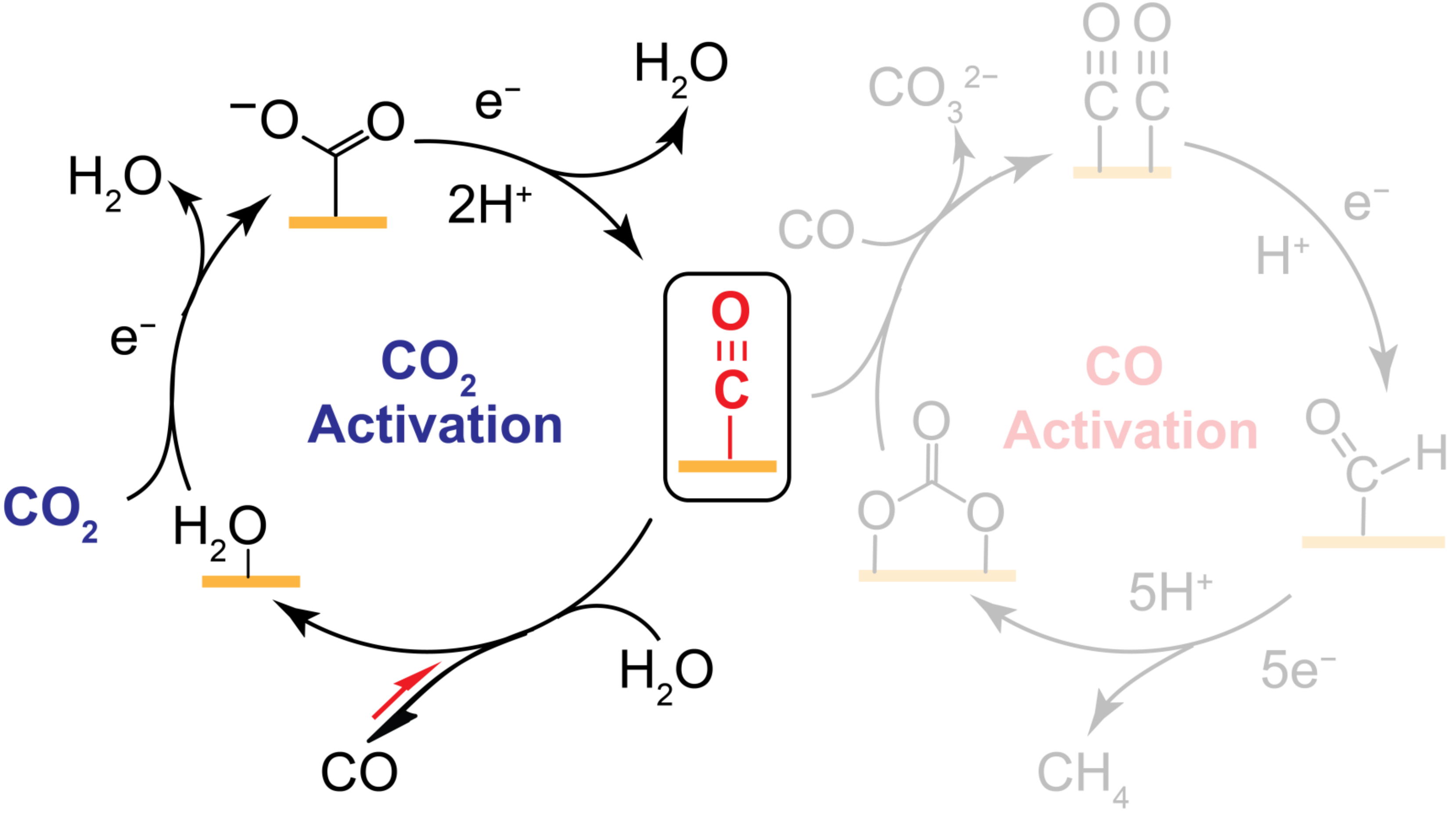
CO rate promoted



Improved selectivity for CO

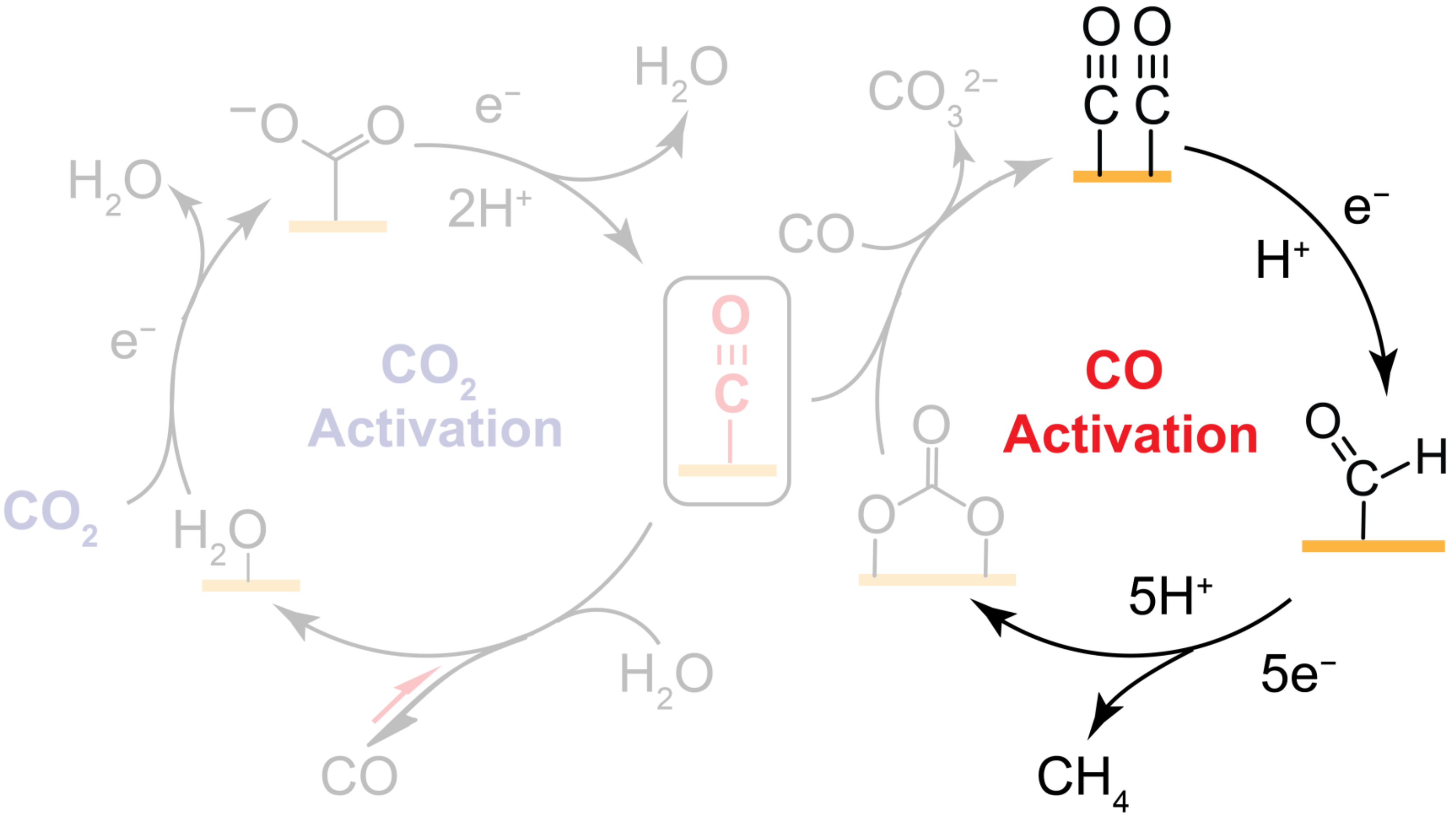
Yoon, Hall, YS, *ACHIE*, **2016**, 55, 15282

Part 1: CO_2 activation insensitive to proton donor

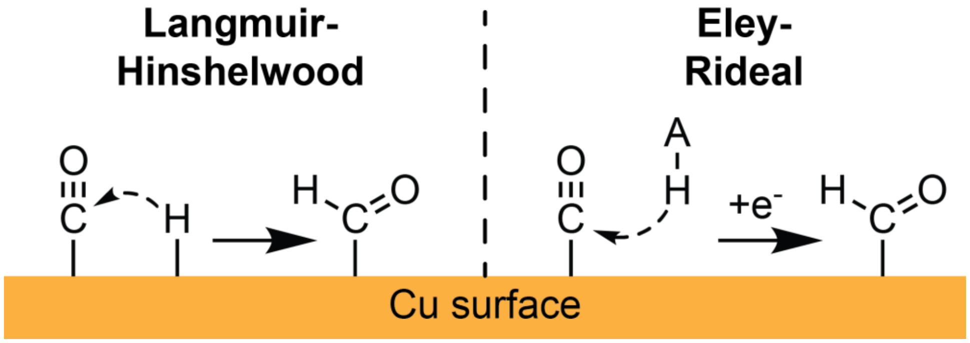


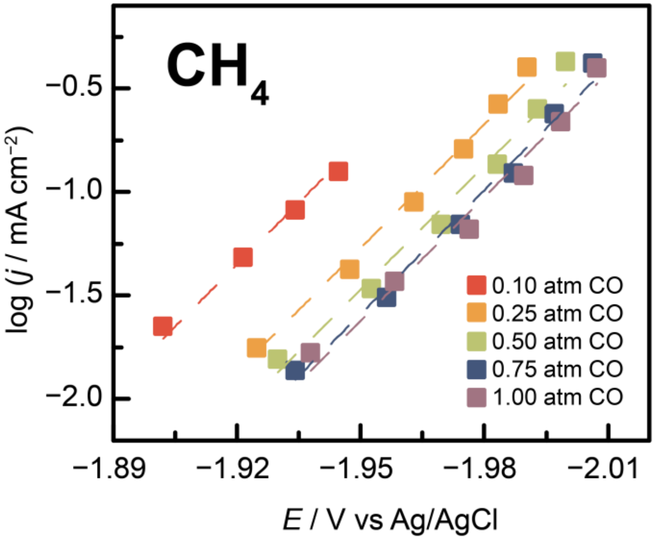
Wuttig, Yaguchi, Motobayashi, Osawa, YS, *PNAS*, **2016**, E4585
Wuttig, Yoon, Ryu, YS *JACS* **2017**, *139*, 17109
Hall, Yoon, Wuttig, YS, *JACS*, **2015**, *137*, 14834; Yoon, Hall, YS, *ACHIE*, **2016**, 55, 15282

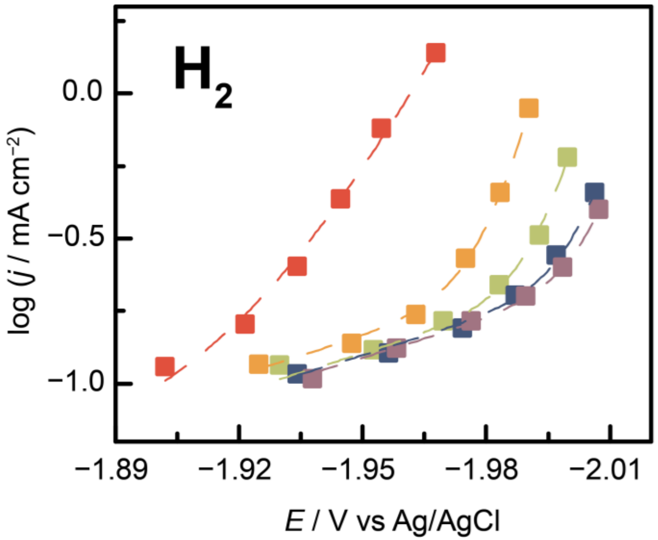
Part 2: Understanding CO reduction selectivity

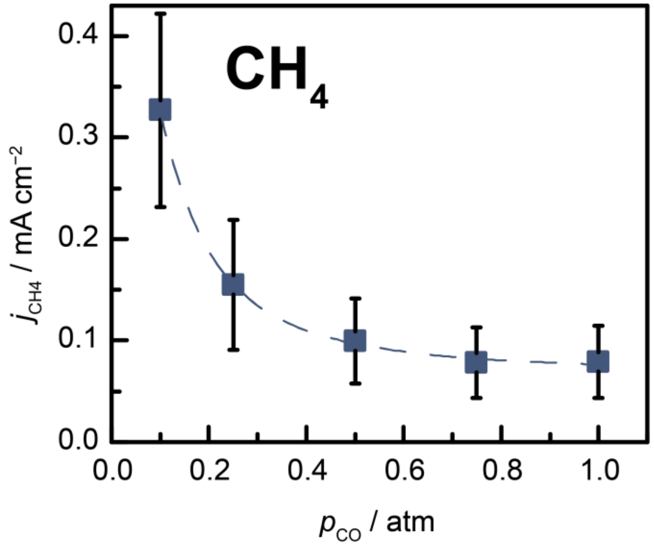


Methane kinetics indicate LH mechanism

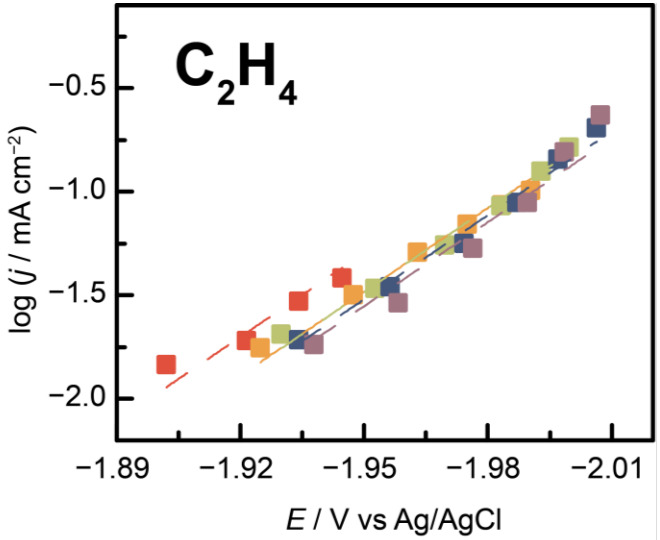


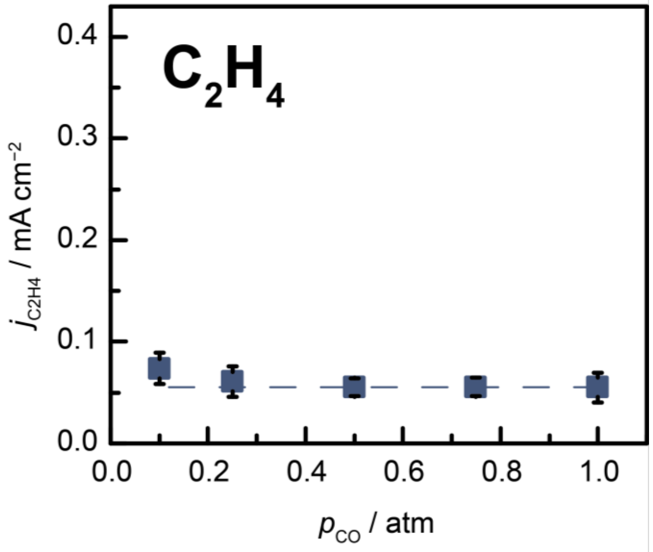


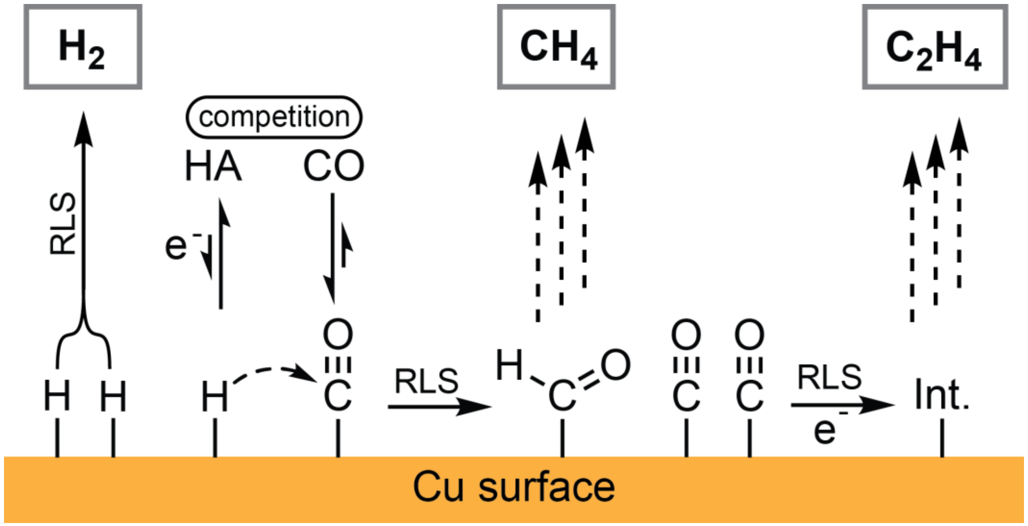




CO isotherm saturated for ethylene



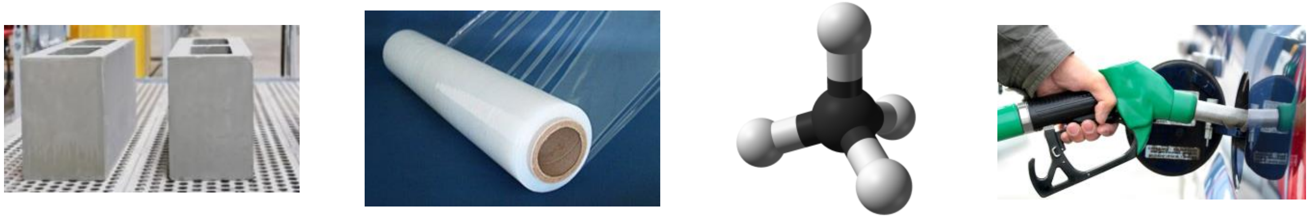




Schreier, Yoon, Jackson, Surendranath,
ACHIE, **2018**, DOI: 10.1002/anie.201806051

Conclusions – Many opportunities but no free lunch

In principle, CO_2 can be a resource, meeting diverse needs in chemicals, materials, fuels:

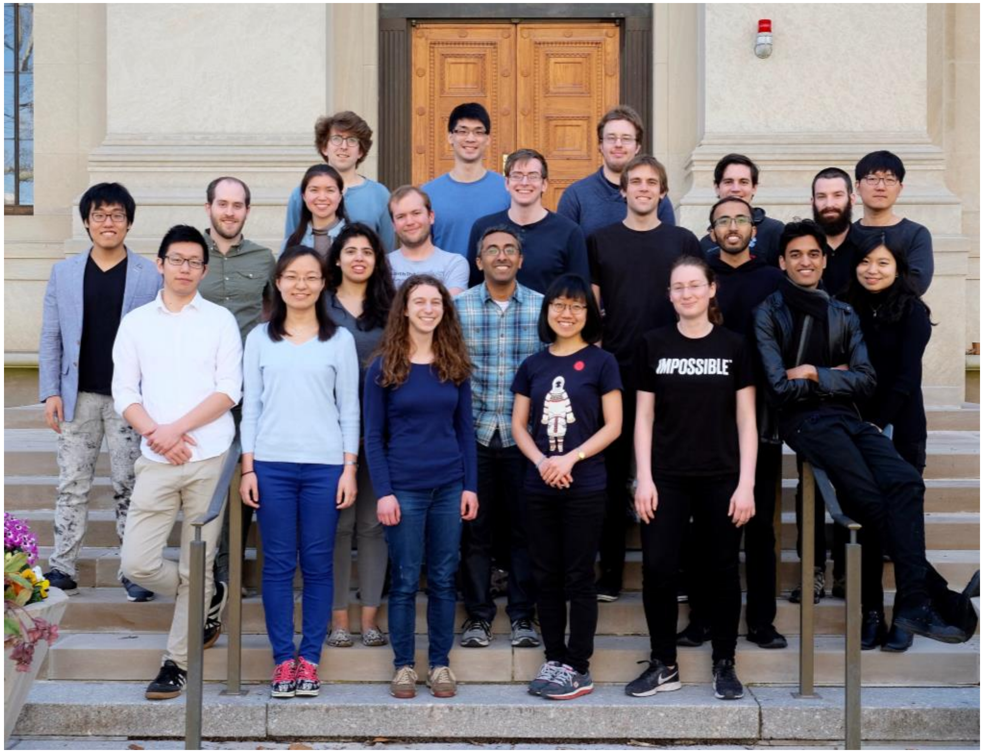


CO_2 valorization is context dependent:

- Energy cost

- Mechanistic understanding will drive new catalysts for selective CO_2 valorization

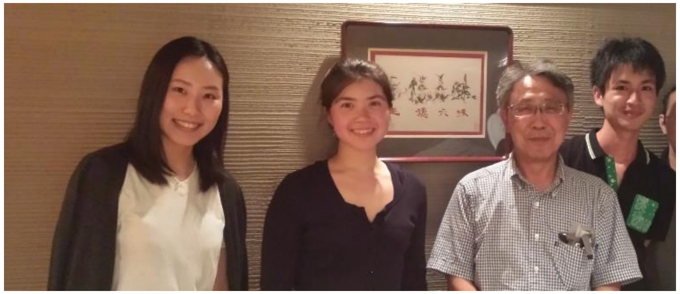
Acknowledgements



MISTI

MIT International Science & Technology Initiatives

Osawa Group



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