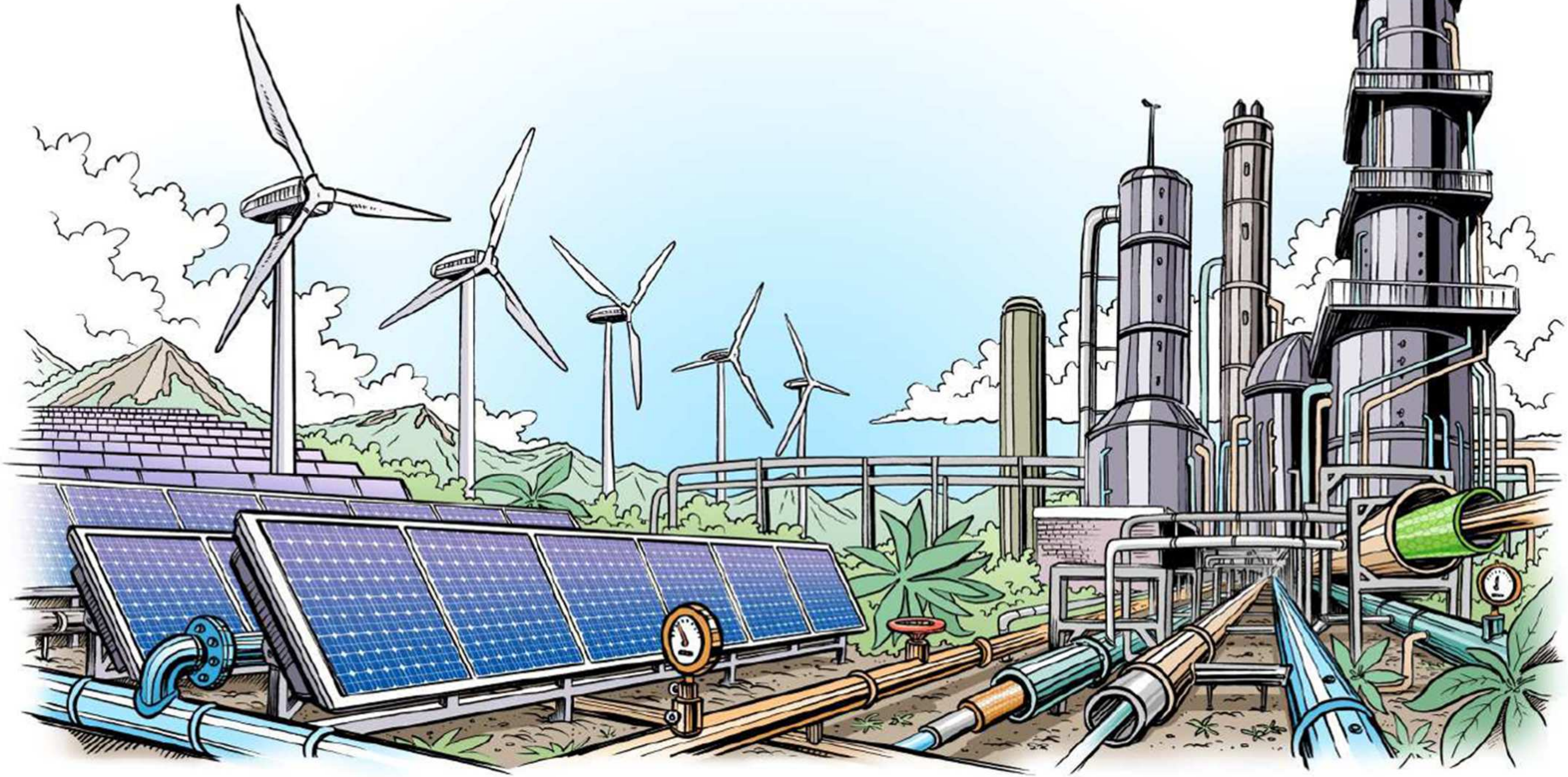
Electrocatalytic materials for CO_2 conversion to fuels and bulk chemicals



Dr. Ruud Kortlever

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M2i Meeting Materials 2020 – *15-12-2020*

TU Delft

OUR CLIMATE IS **CHANGING**

+0.85°C
*Average temperature **increase** from 1880 to 2012*

-1.7km
*Arctic's sea ice **loss** every decade since 1979*

+19cm
*Average sea level **rise** from 1901 to 2010*

+50%
*Greenhouse gas emissions **rise** than 1990*

-5%
*Grain yields **decline** per 1°C increase*

+400%
***Increase** of natural disasters since 1970*

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e:Refinery

Ref: *United Nations Sustainable Development Goals Climate Action*


Renewable Energy
is the SOLUTION
WHY?
www.AskWhyWhyNot.
NOW
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(Electro-)Catalysis for a sustainable future

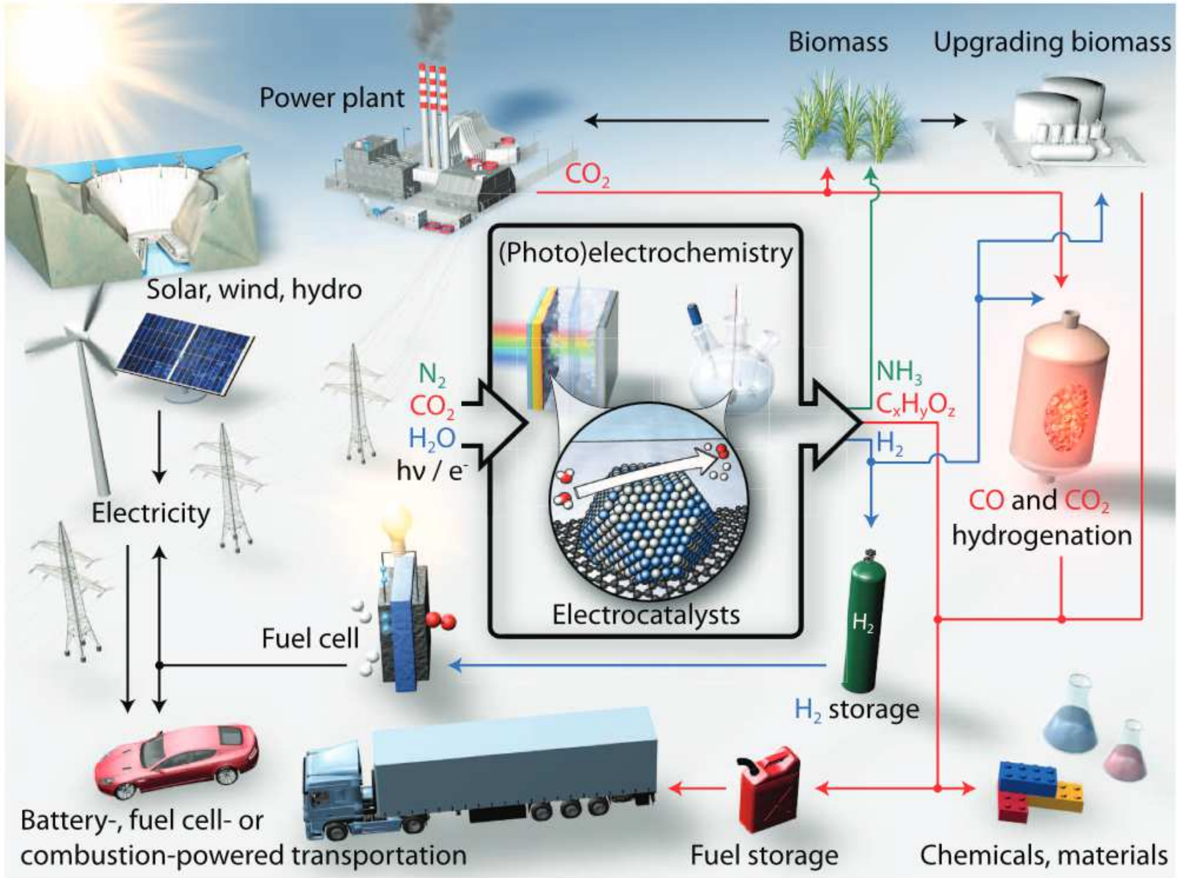

Fig. 1. Sustainable energy future. Schematic of a sustainable energy landscape based on electrocatalysis.

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Seh, Z.W.; Kibsgaard, J.; Dickens, C.F.; Chorkendorff, I.; Nørskov, J.K.; Jaramillo T.F., *Science*, **2017**, 335, eaad4998.

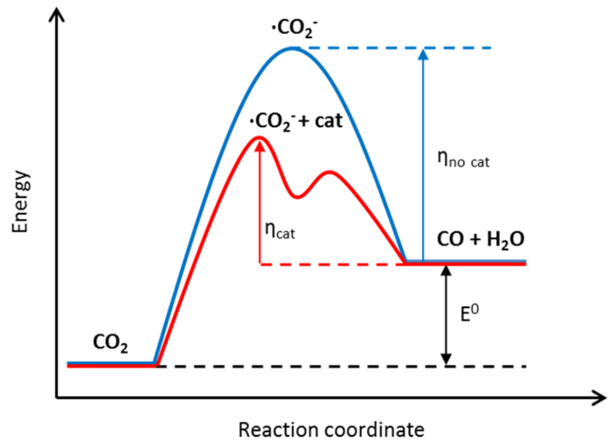
Electrocatalytic challenges – CO_2 electroreduction

Table 1. Main Products of the Electrochemical Reduction of CO_2[a]

product name and formula	k	n	m	E^0 (V versus RHE)
carbon monoxide, CO	1	2	1	−0.10
formic acid, HCOOH	1	2	0	−0.20 (for pH < 4); −0.20 + 0.059[pH-4] (for pH > 4)
formaldehyde, HCHO	1	4	1	−0.07
methanol, CH_3OH	1	6	1	0.02
methane, CH_4	1	8	2	0.17
ethanol, CH_3CH_2OH	2	12	3	0.09
ethylene, C_2H_4	2	12	4	0.08

[a]The coefficients k, n, and m in eq 1 are provided in each case together with the standard equilibrium potentials.

$$k\mathrm{CO_2} + n(\mathrm{H^+} + \mathrm{e^-}) \rightleftarrows \mathrm{P} + m\mathrm{H_2O}$$



- Equilibrium potentials are far off from the actual onset potentials measured in CO_2 reduction.
- High overpotentials are the result of inappropriate adsorption energies of key reaction intermediates: <u>need for better electrocatalysts</u>.

Kortlever, R.; Shen, J.; Schouten, K.J.P.; Calle-Vallejo, F.; Koper, M.T.M., *J. Phys. Chem. Lett.*, **2015**, 6, 4073-4082.

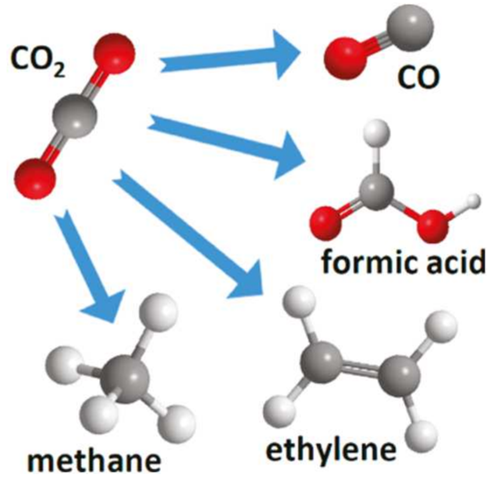
Electrochemical CO_2 reduction on metal electrodes

Different electrocatalysts produce different products:

- **CO:** Au > Ag > Cu > Zn > > Cd > Sn > In > Pb > Tl = Hg

- **HCOOH:** Cd, Sn, In, Pb, Tl, Hg, Bi

- **C_xH_y's:** Cu



sp group metals

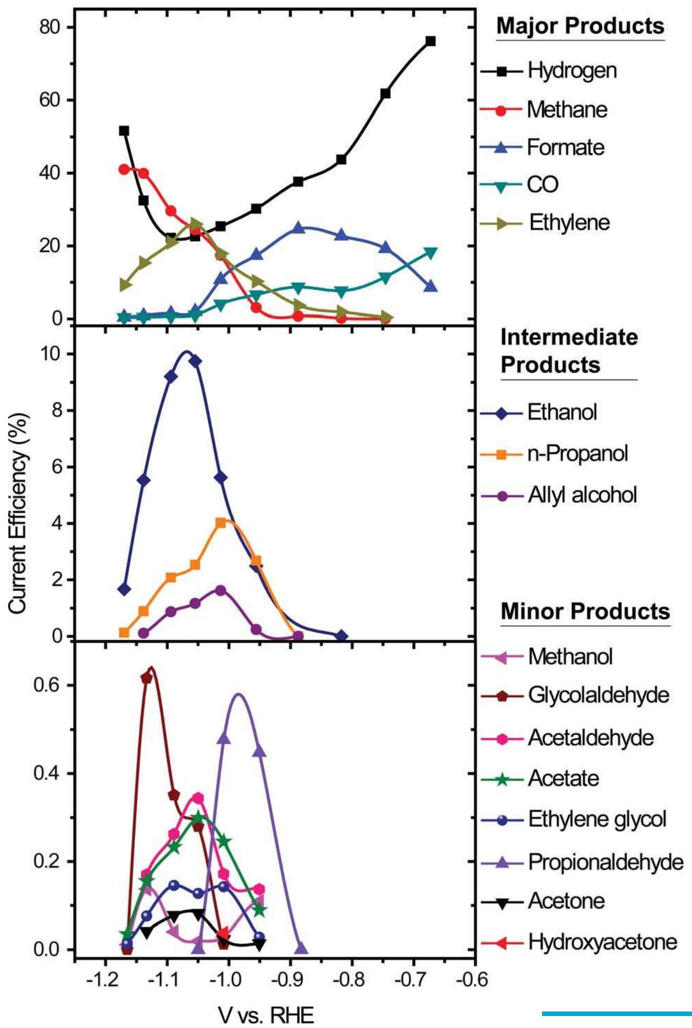
- Include the principal group metals and metals with a d^{10} electronic configuration.
- Make formic acid and oxalate (s^2) and CO (d^{10}).

d group metals

- Include transition metals with unfilled d orbitals.
- Produce CO_{ads} on surface.

Whipple, D.T,K.; Kenis P.J.A. *J. Phys. Chem. Lett.*, **2010**, *1*, 3451.

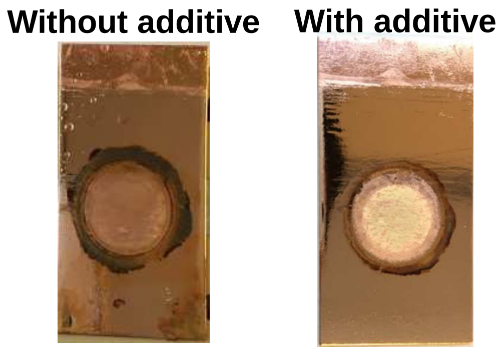
Electrochemical CO_2 reduction on copper

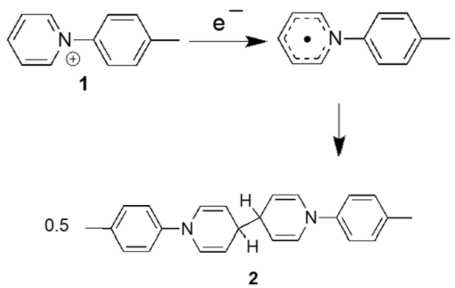


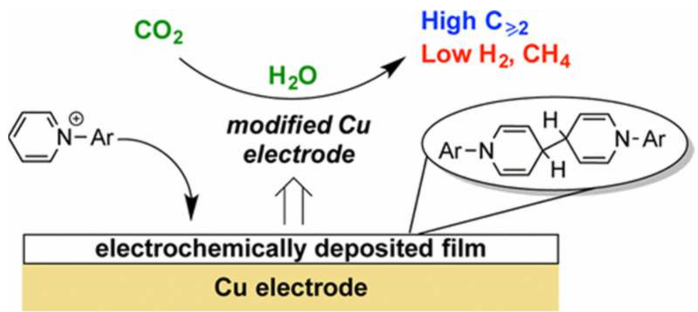
- Copper is the only catalytic material able to produce hydrocarbon products, such as methane and ethylene, with decent efficiencies.
- Recent observation of 16 different products from CO_2 reduction reveils the complexity of this reaction as well as its possibilities.
- Product formation is very potential dependent and copper shows an overall poor selectivity towards any product.

Kuhl, K.P.; Cave, E.R.; Abram, D.N.; Jaramillo, T.F., *Energy Environ. Sci.*, **2012**, 5, 7050-7059.

Altering product selectivity of Cu – Organic additive/film





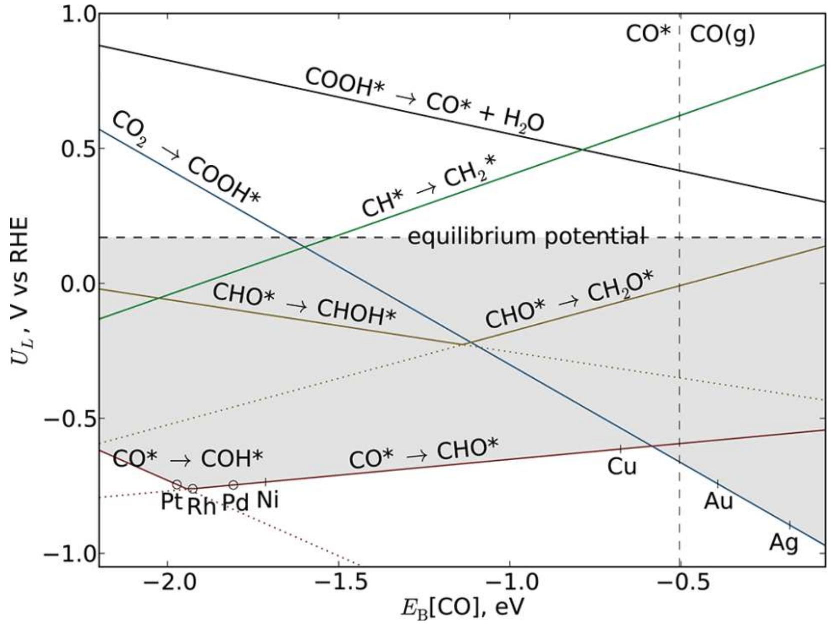


At -1.1 V_{RHE}	Faradaic Efficiencies (%)									$C_{\geq 2}$/ CH_4	
Compound	CH_4	C_2H_4	C_2H_5OH	C_3H_7OH	CO	H_2	$HCOO^-$	$C_{\geq 2}$	Total		*j* (mA/cm²)
No additive	20.2	12.4	7.2	2.8	1.7	42.8	4.7	22.4	96.4	1	-4.59
1	1.1	40.7	30.5	10.0	1.0	18.1	7.1	80.2	107.8	70	-1.02

- N-aryl pyridinium additives were tested for their ability to promote electrochemical CO_2 reduction. The organic molecules were reduced and formed an organic film on the electrode surface.
- The organic film blocked the formation of hydrogen and C_1 products on the copper electrode, thereby increasing the selectivity of $C_{\geq 2}$ products from 22% to 80%.

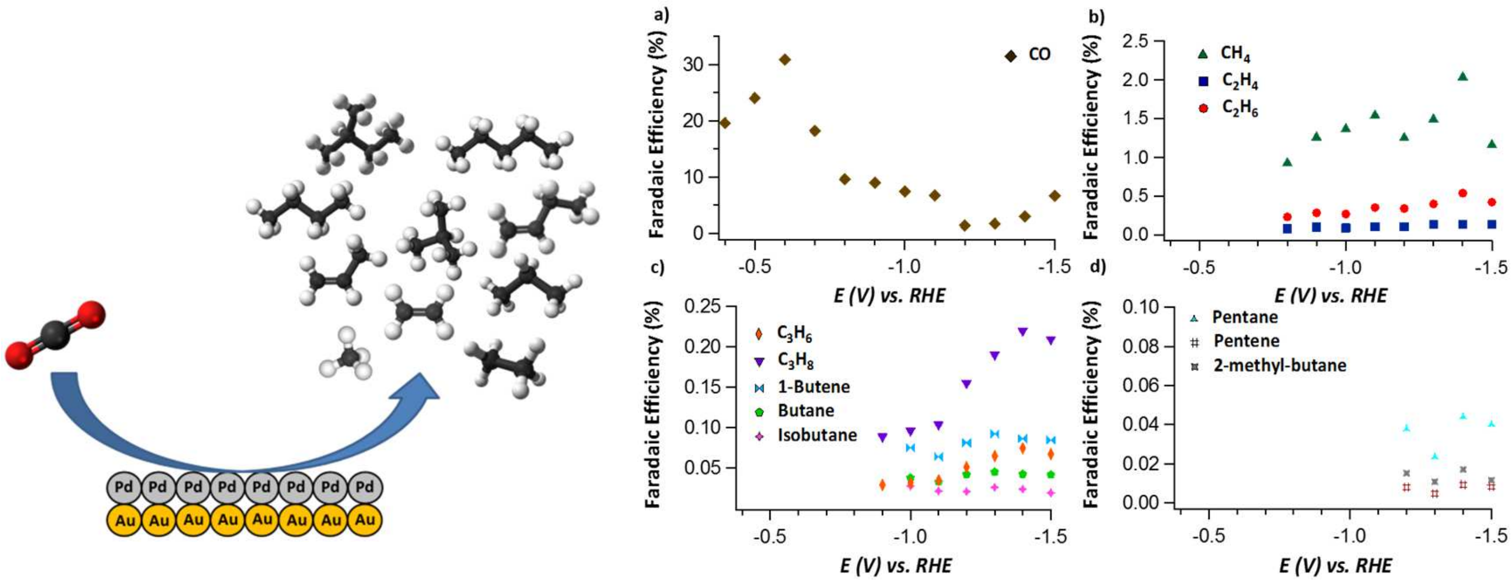
Han, Z.†; Kortlever, R.†; Chen, H.-Y.; Peters, J.C.; Agapie, T, *ACS Central Science*, **2017**, 3, 853-859.

CO_2 reduction to hydrocarbons – Electrochemical Fischer-Tropsch?



- If a catalyst binds CO too weakly, CO will desorb before this protonation can take place, while if a catalyst binds CO too strongly, HCO or COH formation is thermodynamically unfavorable.
- Can we develop novel catalysts by combining a metal wich binds CO too strongly (Pd) with a metal which binds CO too weakly (Au)?

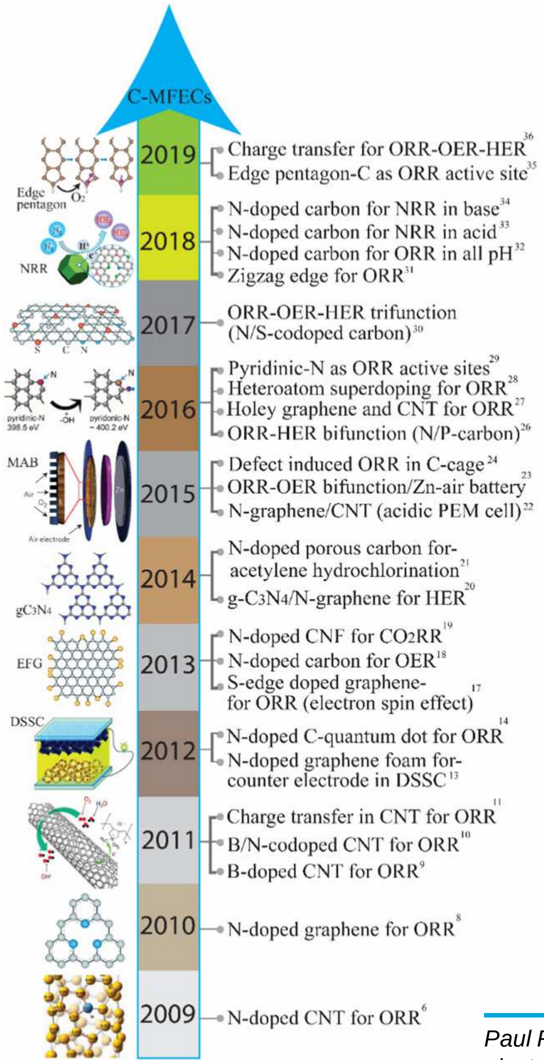
CO_2 reduction to hydrocarbons – Electrochemical Fischer-Tropsch?

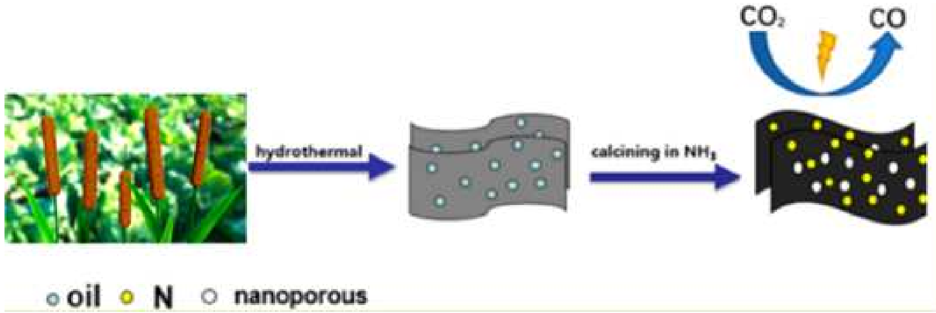


- If a catalyst binds CO too weakly, CO will desorb before this protonation can take place, while if a catalyst binds CO too strongly, HCO or COH formation is thermodynamically unfavorable.
- Can we develop novel catalysts by combining a metal wich binds CO too strongly (Pd) with a metal which binds CO too weakly (Au)?
- By combining Pd with Au, we were able to create the first catalyst that is able to produce C_3-C_5 hydrocarbons.

Kortlever, R.; Peters, I.; Balemans, C.; Kas, R.; Kwon, Y.; Mul, G.; Koper, M.T.M., *Chem. Commun.*, **2016**, 52, 10229-10232.

N-doped carbon electrocatalysts for CO_2 conversion





Shilong Fu

Prof.dr.ir.
Wiebren de Jong

Bagasse (sugarcane)

Grind

10g Urea
15g Activator

N_2, 10℃/min,
800℃, 1h

Paul R, Dai Q, Hu C, et al. Ten years of carbon-based metal-free electrocatalysts. Carbon Energy, 2019.

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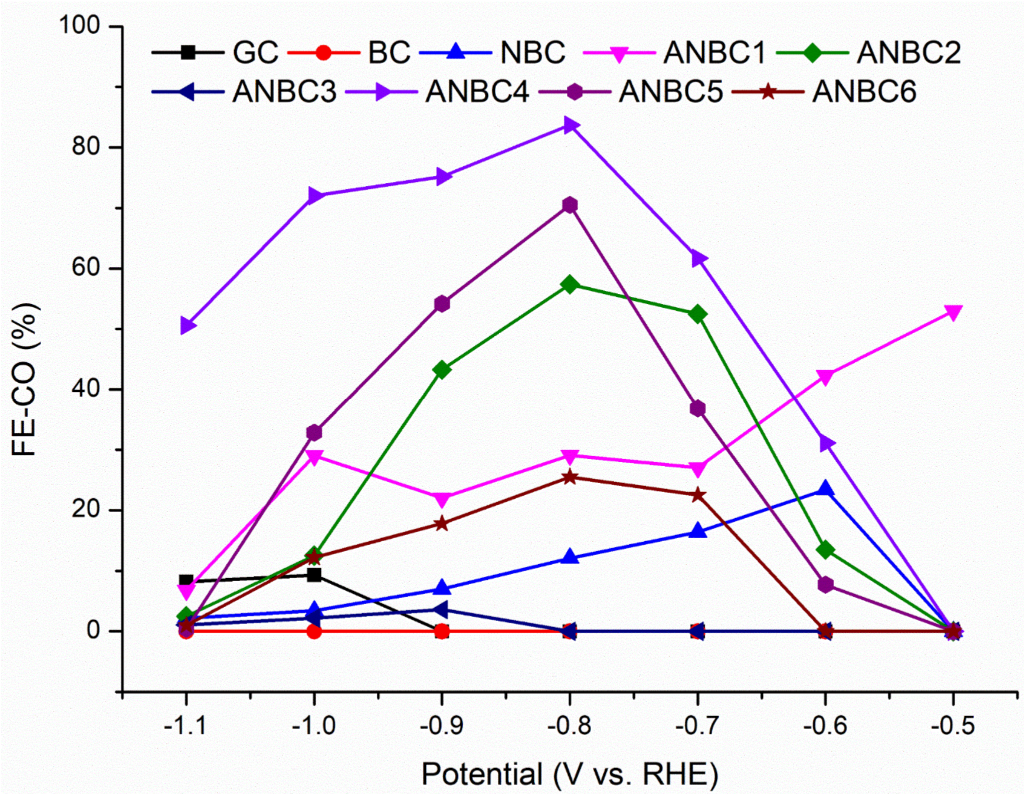
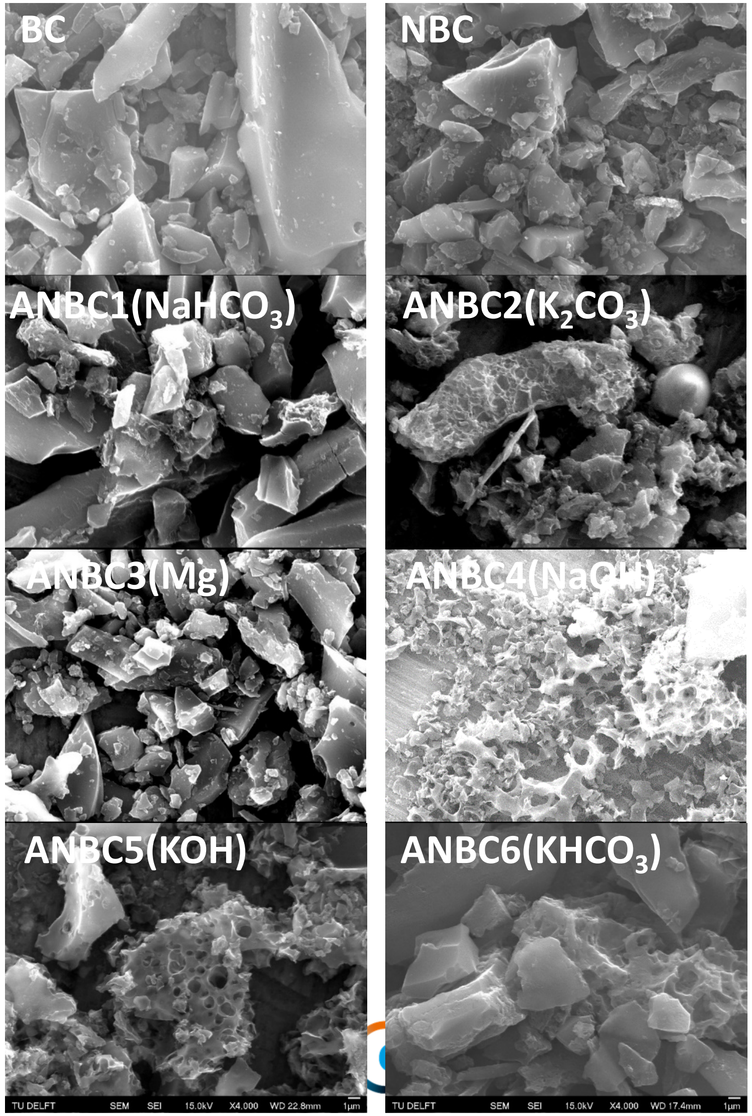
Biomass-derived carbon-based catalysts for CO_2R performance

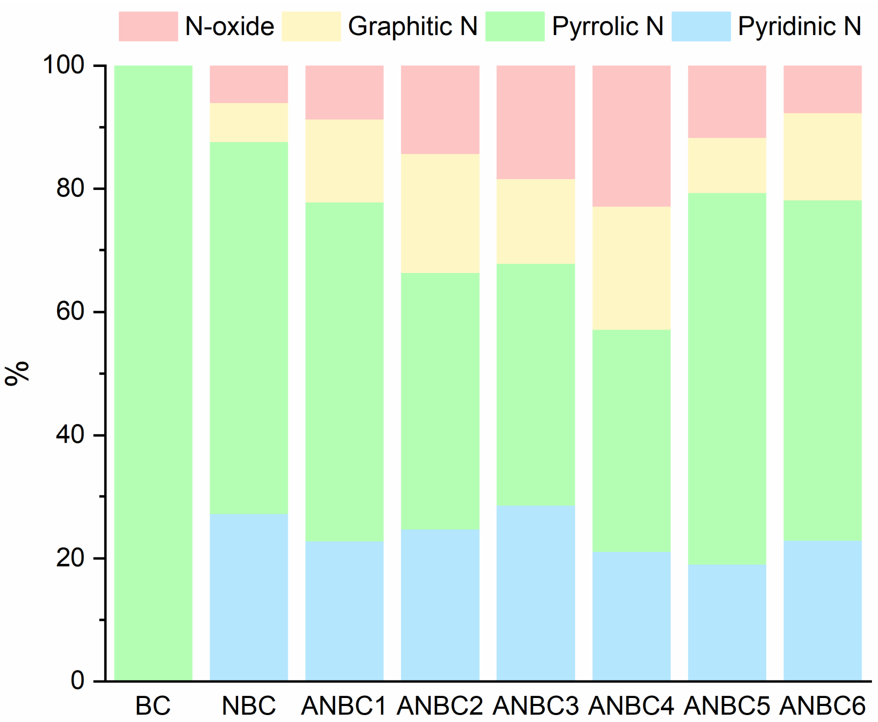


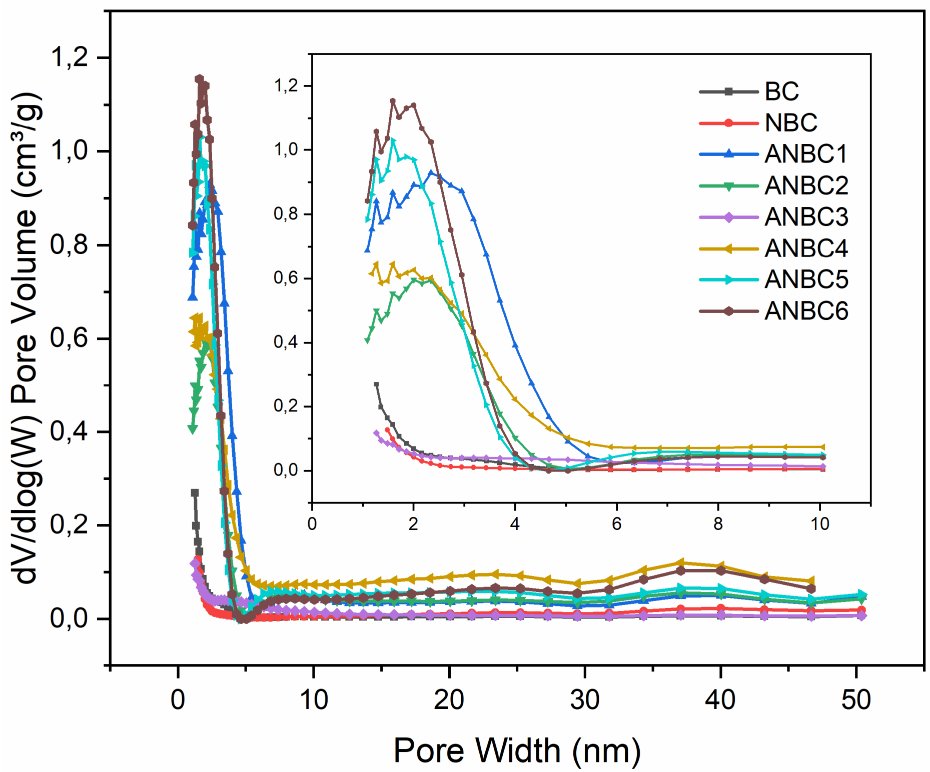
GC:	Glassy Carbon
BC:	Biochar
NBC:	Nitrogen-doped biochar

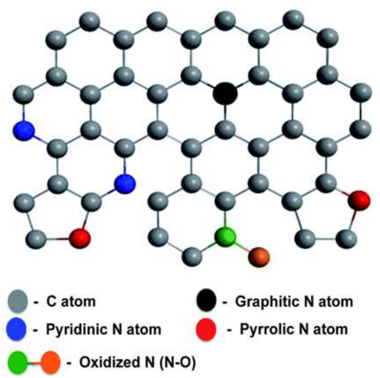
ANBC1:	$NaHCO_3$
ANBC2:	K_2CO_3
ANBC3:	$Mg_5(OH)_2(CO_3)_4$
ANBC4:	NaOH
ANBC5:	KOH
ANBC6:	$KHCO_3$



Biomass-derived carbon-based catalysts for CO_2R performance





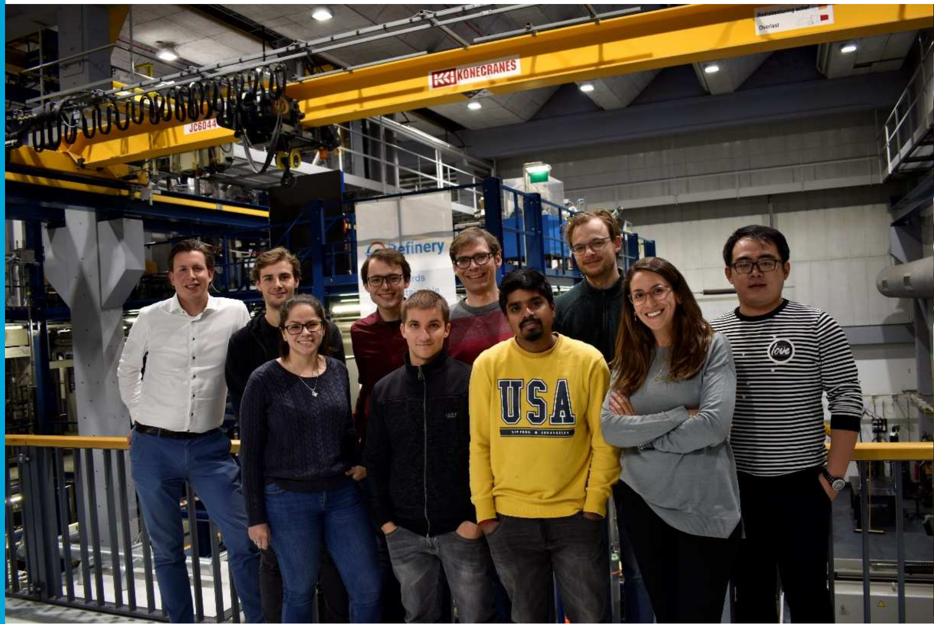


GC:	Glassy Carbon	ANBC1:	$NaHCO_3$
BC:	Biochar	ANBC2:	K_2CO_3
NBC:	Nitrogen-doped biochar	ANBC3:	$Mg_5(OH)_2(CO_3)_4$
		ANBC4:	NaOH
		ANBC5:	KOH
		ANBC6:	$KHCO_3$

Take-away messages

- The electrochemical reduction of CO_2 to valuable chemicals or fuels can close the carbon cycle, provide a means of energy stovffrage and a route for renewable production of chemicals
- New electrocatalytic materials need to be developed for this reaction to be economically feasible.
- Bimetallic electrocatalysts can be used designed to alter product selectivities and, in some cases, alter the product distribution.
- Carbon-based catalytic materials, for instance biomass-derived, can provide cheap and stable alternatives and can produce CO with high selectivities.

Acknowledgements



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Questions?

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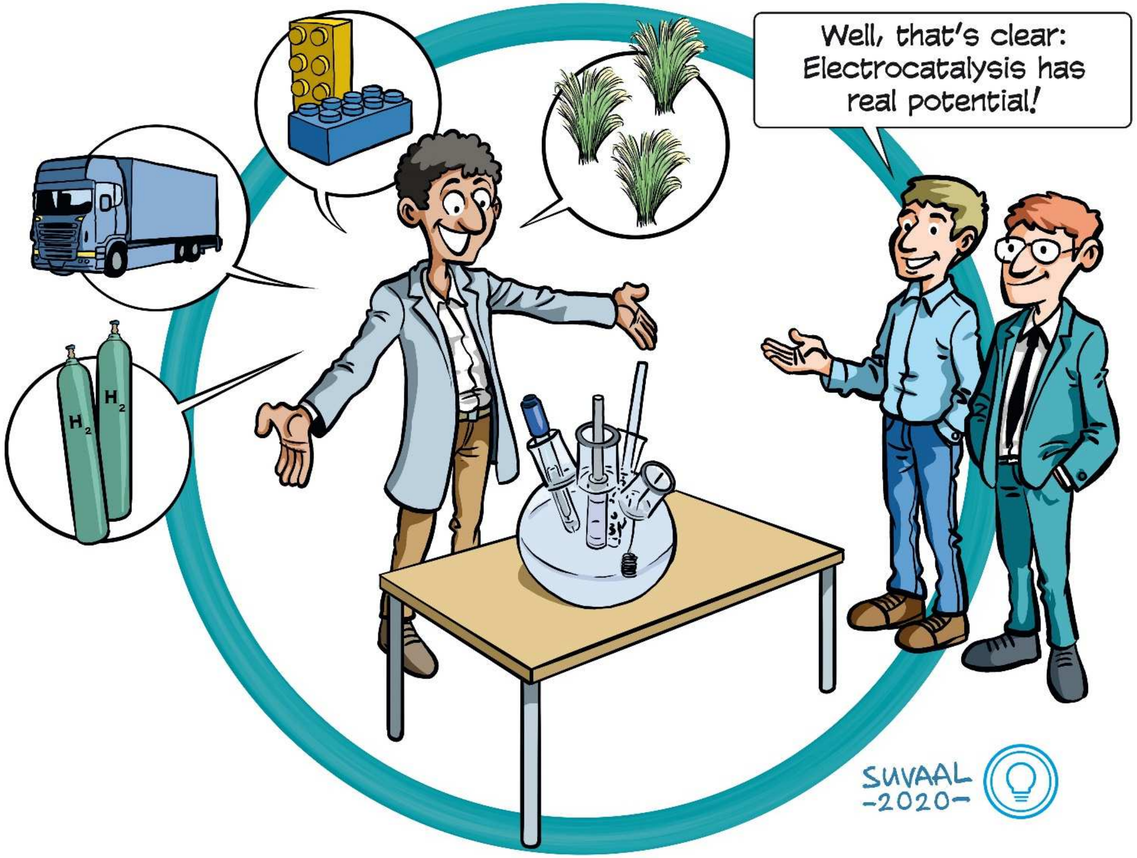

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