5eme Rencontres du CNC

Maison de la Chimie – Paris – Le 4 Décembre 2025

CO_2 comme Matière Première
A la Recherche de Catalyseurs

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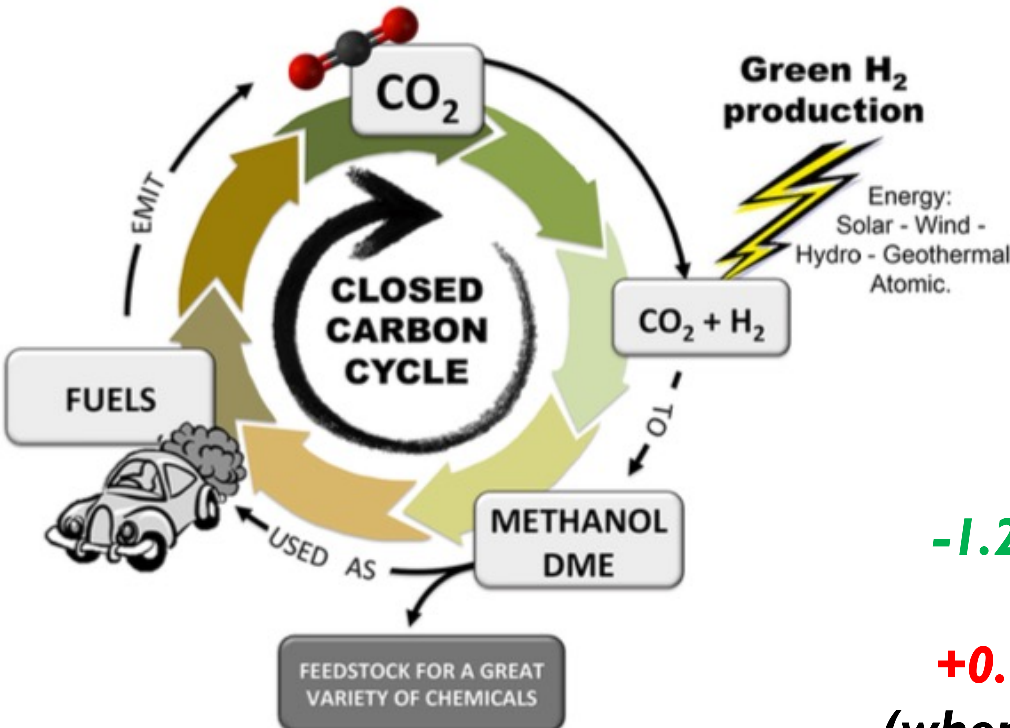
Carbon Capture and Storage or Utilization (CCS / CCU): the Methanol Economy

Methanol Economy

$$CO_2 + 3\,H_2 \longrightarrow CH_3OH + H_2O$$

$$\Delta H^{\circ}_{MeOH,298K} = -49.5\ kJ/mol$$



Currently based on Reforming Technologym (SynGas)

$CH_4 + H_2O \longrightarrow CO + 3\,H_2$

$CO + 2\,H_2 \longrightarrow CH_3OH$

Methanol Production: ca. 120 Mt/year

Global Warming Index

-1.2 to -1.3 kg of CO_2/kg of CH_3OH

versus

+0.7 to 1.1 kg of CO_2/kg of CH_3OH

(when CH_3OH is produced from syngas)

Goeppert et al. Chem. Soc. Rev., 2014, 43, 7995.
Álvarez et al. Chem. Rev., 2017, 117, 9804.

Carbon Dioxide (CO_2) Hydrogenation and Methanol Synthesis

Understanding the role of the Metal-Support Interface

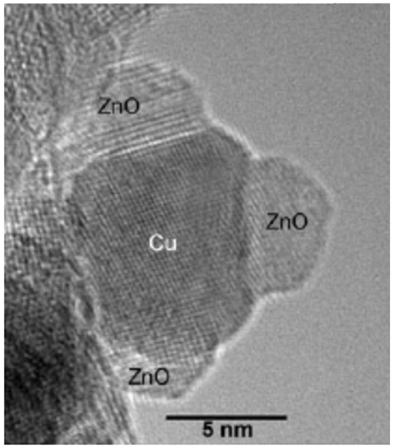
THERMODYNAMIC BOUNDARY CONDITIONS

		Reaction Enthalpy (ΔH)
Methanol synthesis:	$CO_2 + 3\,H_2 = CH_3OH + H_2O$	-49.5 kJ.mol^{-1}
Methanation Reaction: (Sabatier Reaction)	$CO_2 + 4\,H_2 = CH_4 + 2H_2O$	-165 kJ.mol^{-1}
Reverse Water Gas Shift:	$CO_2 + H_2 = CO + H_2O$	$+41$ kJ.mol^{-1}

CATALYSIS: COPPER PARTICLES FOR METHANOL SYNTHESIS FROM SYNGAS (CO/H_2) vs. (CO_2/H_2)

Catalysts: $Cu/ZnO/Al_2O_3$ – 240-260 °C – 50-100 bars – Syngas (ICI 1960)

- Industrial CO hydrogenation to methanol catalyst
- Rate acceleration by CO_2 (1-2%)
- Low methane selectivity
- Lower stability in CO_2 rich stream (hydrogenation of CO_2)



Behrens *et al.*, *Science* 2012, *336*, 893.
Fischer *et al.*, *J. Catal.* 1997, *172*, 222.

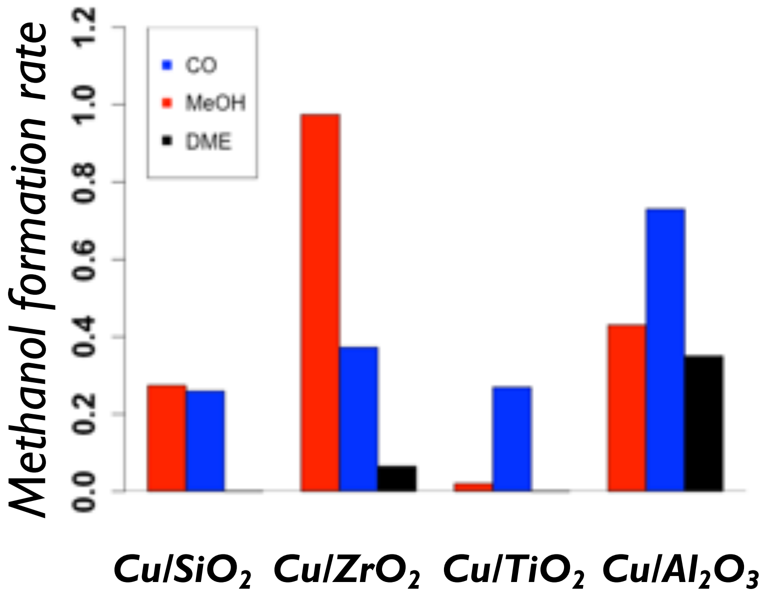
CO_2 Hydrogenation and Methanol Synthesis

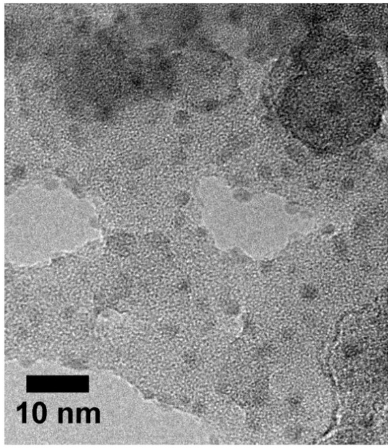
Understanding the role of the Metal-Support Interface

COPPER PARTICLES FOR METHANOL SYNTHESIS

Support Effects in CO_2 Hydrogenation with Supported Cu nanoparticles

Catalytic tests in Flow Reactor
230 °C, 25 bar, $CO_2/H_2/N_2$ = 2/6/2





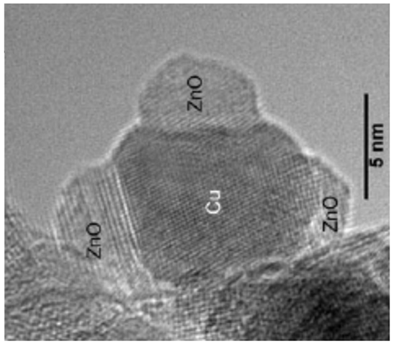
- *Methanol (CH_3OH)*
- *Monoxide de Carbon (CO)*
- *Dimethyl ether (CH_3OCH_3)*
- *No methane detected*

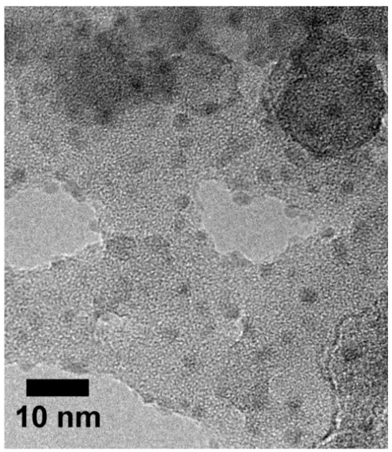
Support: *Silica* *Zirconia* *Titania* *Alumina*

Early works of Baiker, Bell…
Alvarez, Bansode, Urakawa, Bavykina, Wezendonk, Makkee, Gascon, Kapteijn, Chem. Rev. 2017, 117, 9804-9838.

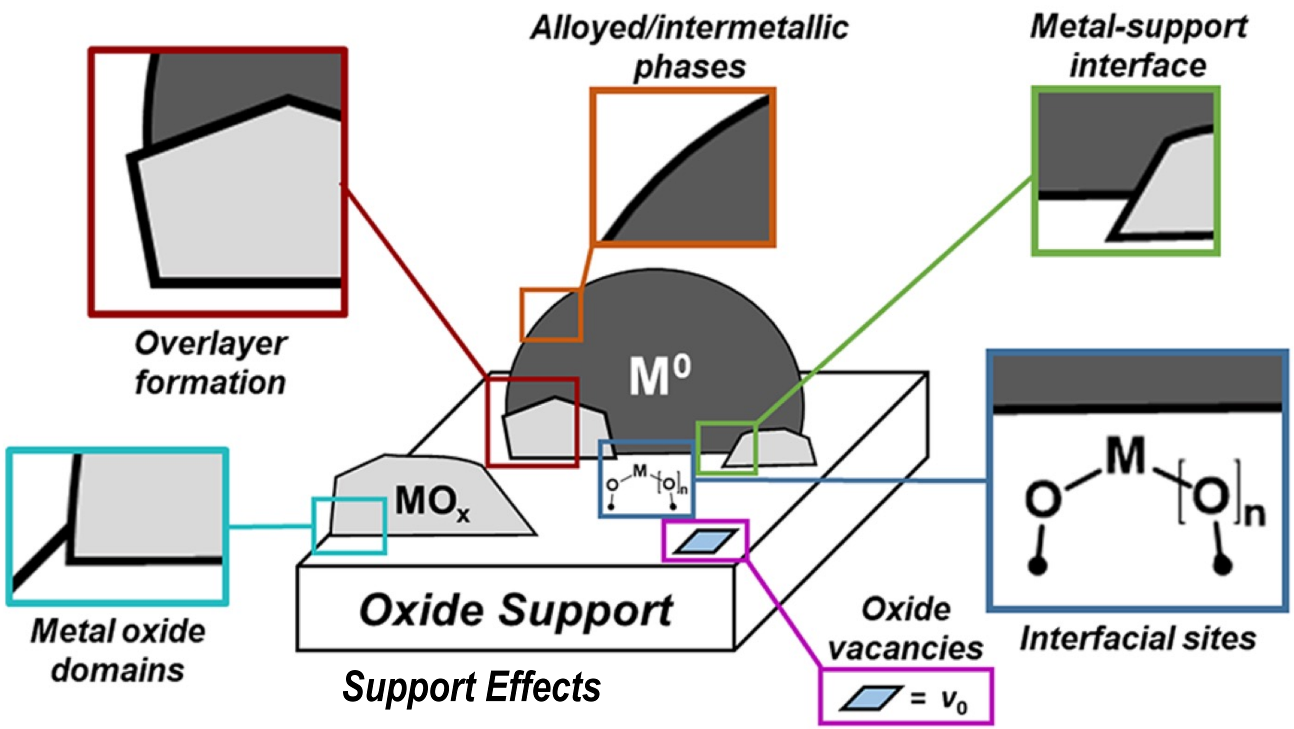
CO_2 Hydrogenation and Methanol Synthesis

The Case Study of Supported Nanoparticles





Surface of Catalysts are Complex!



Questions to be addressed:

What are the roles of supports, promoters, interfaces, vacancies…?

Can we identify new catalysts for a more efficient conversion of CO_2 to value added products?

Our Approach and Methodology:

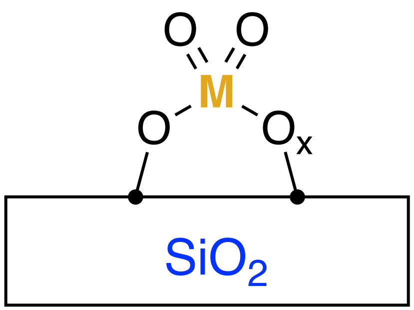
Part I) Controlled Synthesis of Supported Nanoparticles with Tailored Interfaces & Composition

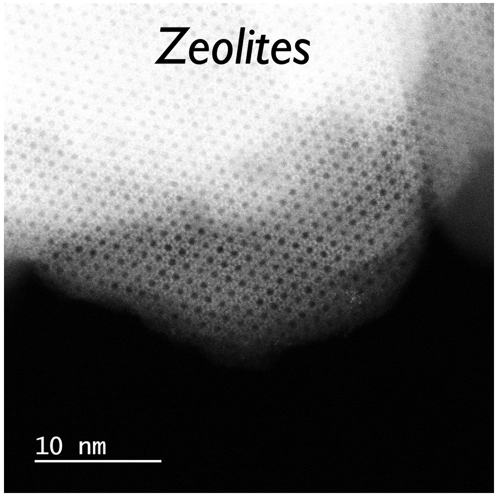
Part II) Efficient Exploration of the Chemical Space via Data-Driven High-Throughput Experimentation

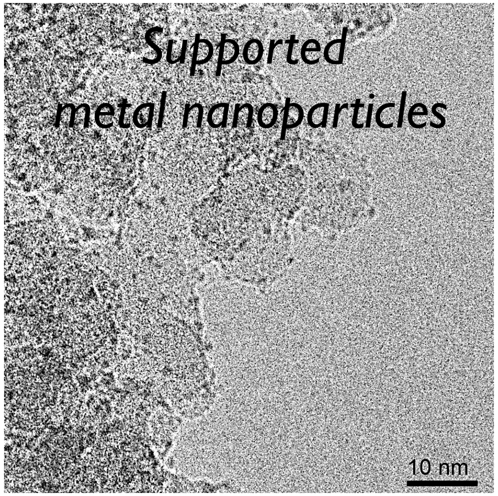
Controlled Synthesis of Supported Nanoparticles with Tailored Interfaces & Composition

Understanding Catalysis, One Atom at a Time

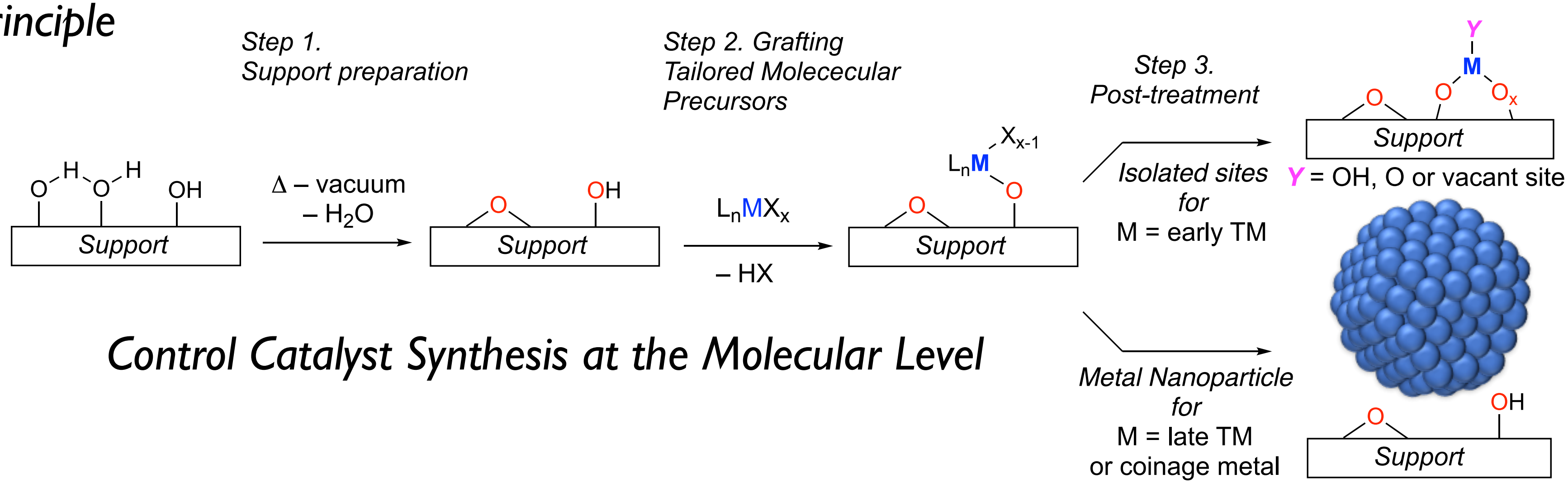
Supported metal oxides







Principle



Control Catalyst Synthesis at the Molecular Level

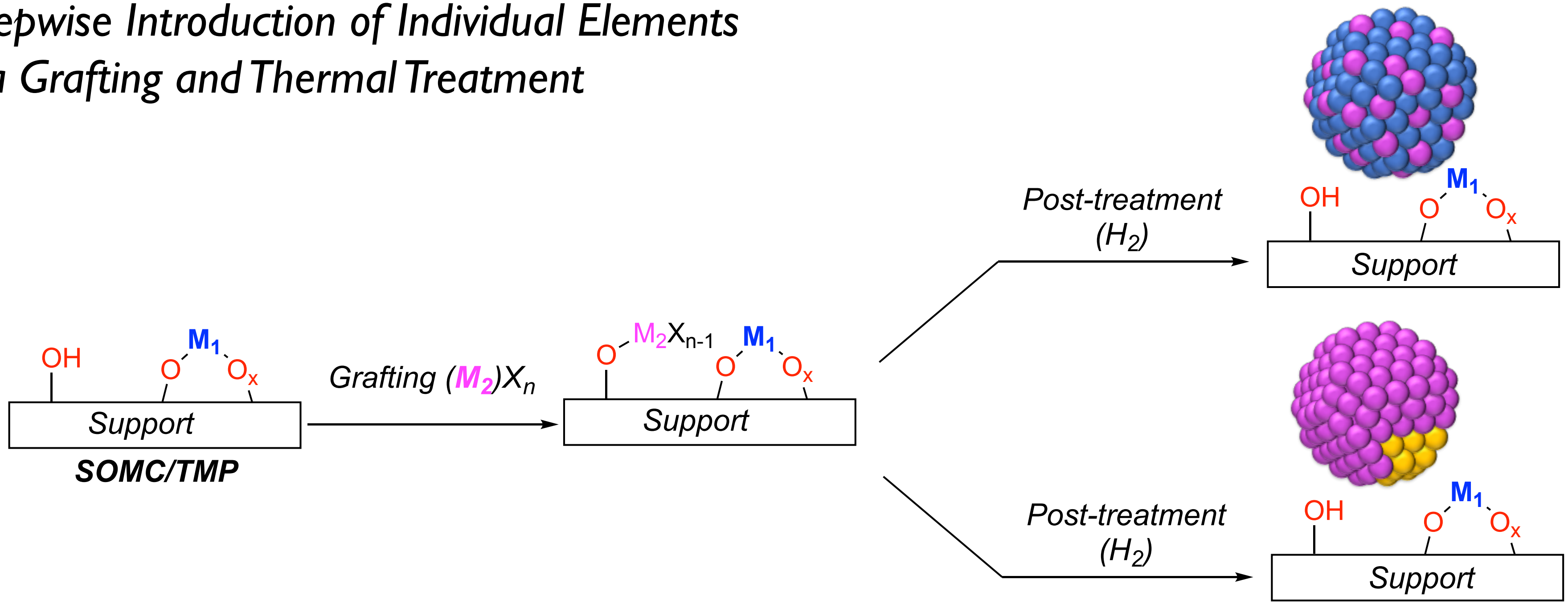
`Pioneering work from Ballard, Basset, Burwell, Gates, Ermakov, Iwasawa and Marks.`

Controlled Synthesis of Supported Nanoparticles with Tailored Interfaces & Composition

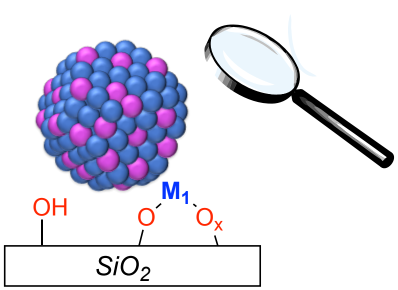
Understanding Catalysis, One Atom at a Time

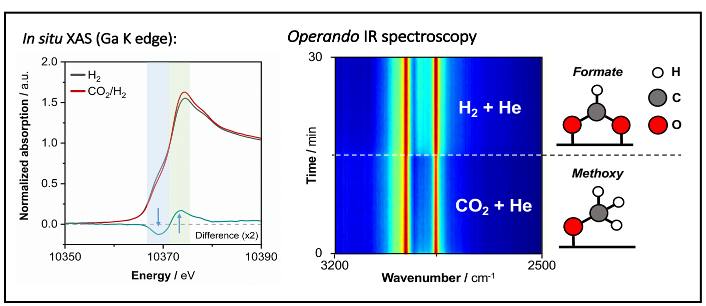
Synthesis of Supported Nanoparticles with Tailored Interfaces and/or Composition

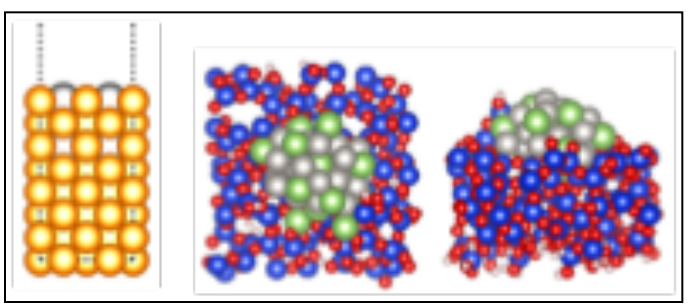
Stepwise Introduction of Individual Elements via Grafting and Thermal Treatment



Detailed Characterization under Operating Conditions & Molecular Modeling





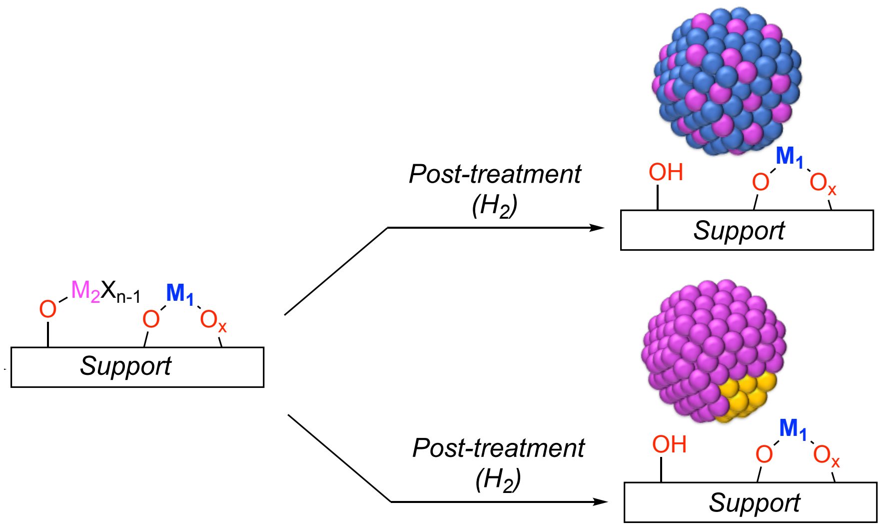


C. Copéret *Acc. Chem.. Res.* 2019, *52*, 1697-1708. DOI: 10.1021/acs.accounts.9b00138.

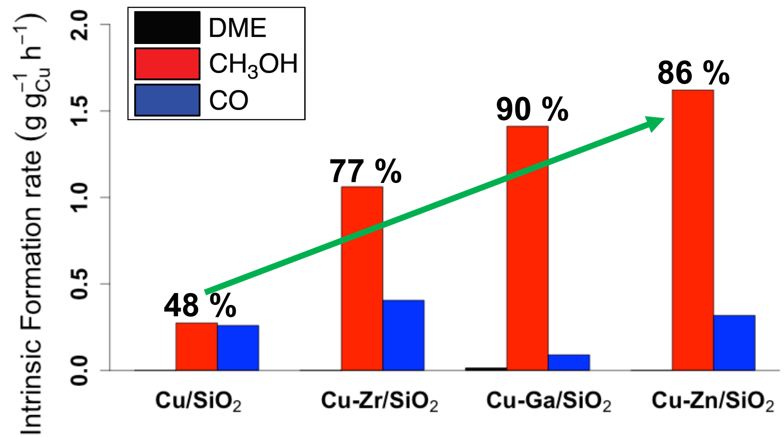
CO_2 Hydrogenation and Methanol Synthesis

Understanding the role of the Metal-Support Interface

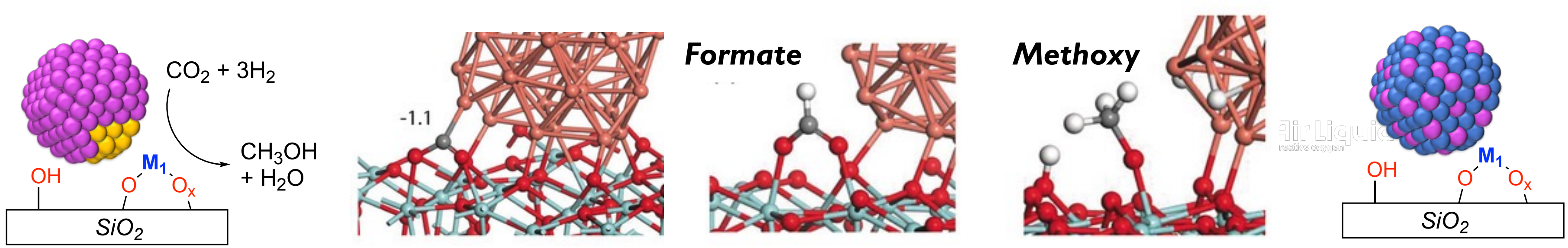
REDUCIBLE DOPANTS: ZINC & GALLIUM



Intrinsic Formation Rates



- ***Improved CH_3OH Activity and Selectivity compared to Cu/SiO_2 and Cu-Zr/SiO_2***
- ***High Selectivity for Zn (>70%) and Ga (>90%) at Higher Conversion***



M_I = Ti, Zr, Hf, Ta & M = Cu **M_I = Ga, Zn & M = Cu**

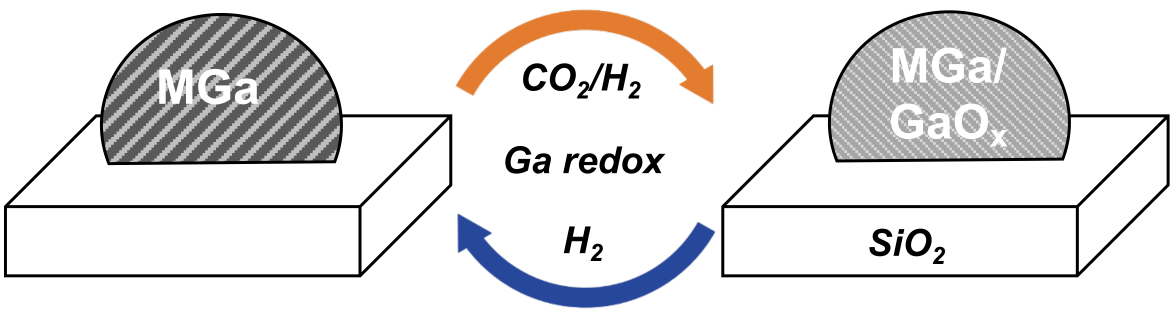
S. R. Docherty, C. Copéret *J. Am. Chem. Soc.* 2021, *143*, 6767–6780.

CO_2 Hydrogenation and Methanol Synthesis

Understanding the role of the Metal-Support Interface

What – we think – we know

- *Importance of Metal (Cu and others) / Metal oxide (Zr, Zn, Ga…) Interfaces*
- *Involvment of Redox processes to generate Metal-Metal oxide Interfaces*
- *Methanation catalysts (Ni, Ru, Os, Rh, Ir) make stable alloys with Gallium due to site isolations and metal – metal oxide interface drive methanol selectivity*



What we do not know

- *Role of Redox processes (facilitates CO_2 activation and CH_3OH desorption ?)*
- *Kinetic of the Redox Process (and its relation to methanol formation rate)*
- *Predictive Reactivity Descriptor*

S. R. Docherty, C. Copéret *J. Am. Chem. Soc.* 2021, *143*, 6767–6780.

CO_2 Hydrogenation and Methanol Synthesis

Understanding the role of the Metal-Support Interface

KNOWN PATTERNS across the PERIODIC TABLE of the ELEMENTS

Group → / Period ↓	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Main metals

Promoters for Cu

Methanation

Methanol Synthesis

Reverse Water Gas Shift →Carbon Monoxide

CO_2 Hydrogenation and Methanol Synthesis

Understanding the role of the Metal-Support Interface

CHANGING PATTERNS of the PERIODIC TABLE of the ELEMENTS

Group → / Period ↓	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Main metals

Promoters for Cu

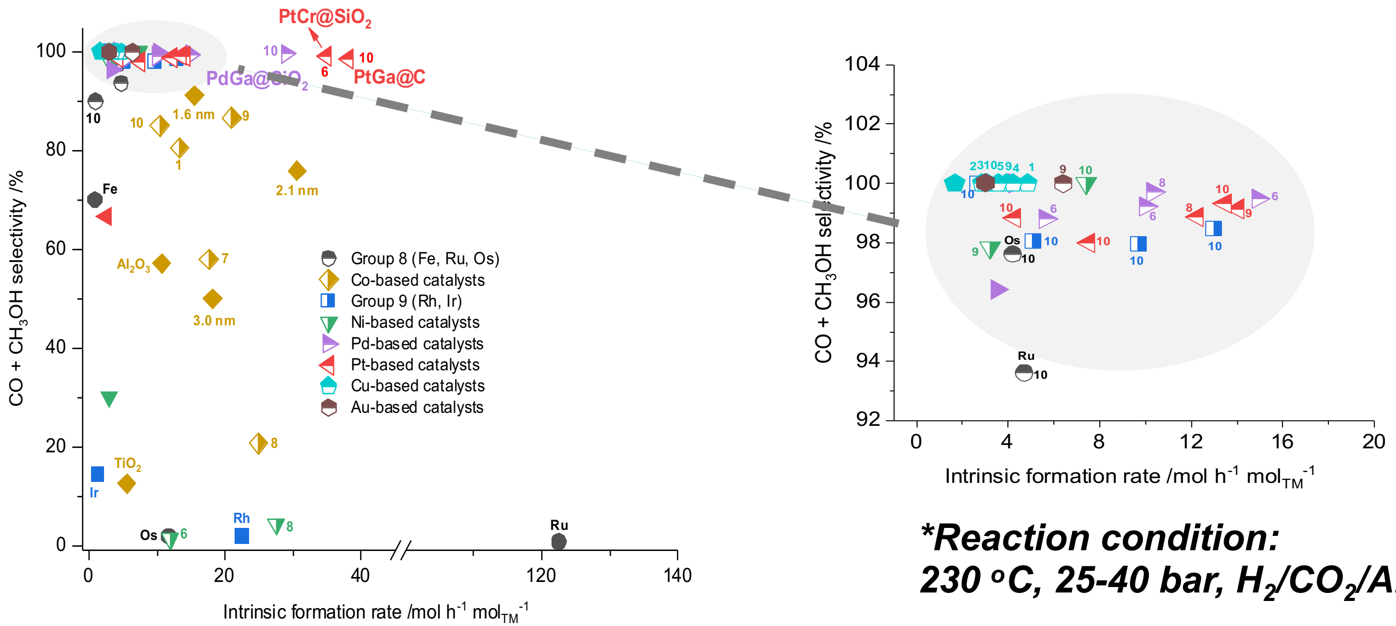
Methanation

Methanol Synthesis

Reverse Water Gas Shift →Carbon Monoxide

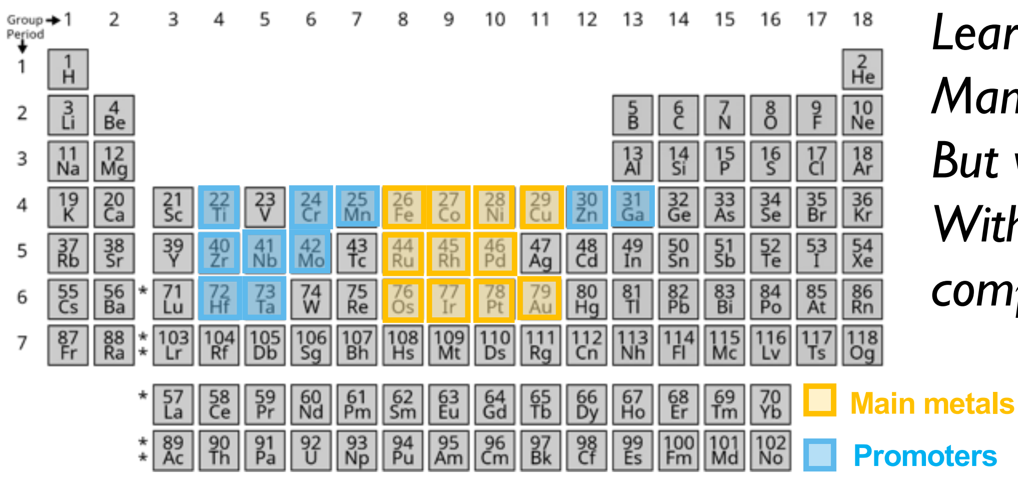
Efficient Exploration of the Chemical Space

Data-Driven High-Throughput Experimentation



***Reaction condition:**
230 °C, 25-40 bar, $H_2/CO_2/Ar = 3:1:1$*

Dopants:
1: Ti
2: Zr
3: Hf
4: Nb
5: Ta
6: Cr
7: Mo
8: Mn
9: Zn
10: Ga



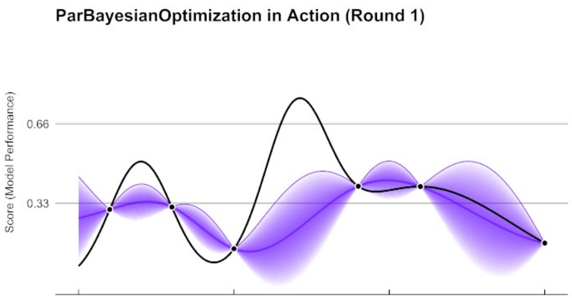
Learning from the Periodic Table:
Many More Combinations to Explore
But what is the best approach?
With 5 elements and many compositions: >>10^{23} combinations

W. Zhou, V. Böchter, N. Iwanojko, Y. Steifel *unpublished results*

Efficient Exploration of the Chemical Space

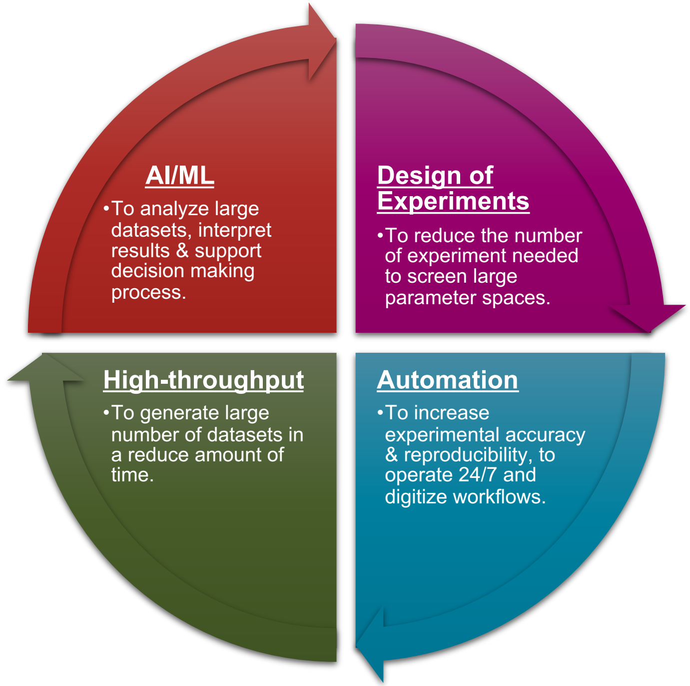
Data-Driven High-Throughput Experimentation

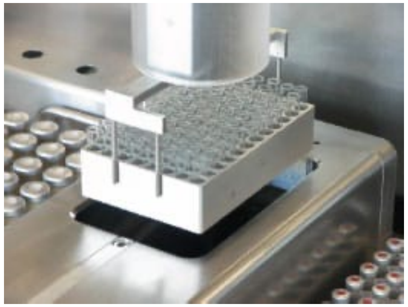
SwissCat+ – An ETH Domain Initiative towards Data-Driven High-Throughput Experimentation Since 2023



By AnotherSamWilson - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=84842869

Data Processing & Expertise
e.g. Bayesian Optimization





Automated Synthesis & Characterization – Parallel fixed bed and Batch reactors

P. Laveille, P. Miéville, … C. Copéret, N. Cramer, Chimia 2023, 77, 154-158 – https://swisscatplus.ch

Efficient Exploration of the Chemical Space

Data-Driven High-Throughput Experimentation

ML-Guided Evolution of CO_2 to Methanol Catalysts

- 1 support among 4 (Al_2O_3, SiO_2, TiO_2, ZrO_2).
- Up to 3 metals among 6 (Ce, Co, Cu, Fe, In, Zn).
- Total metal loading up to 5wt%.
- With or without K promoter (up to 1 wt%).
- > 20 M possibilities.
- Maximize CO_2 conversion & MeOH selectivity.
- Minimize CH_4 selectivity and metal cost.

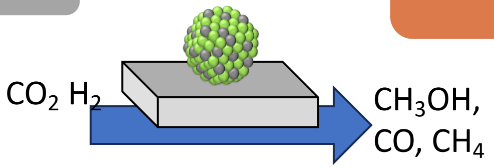
ML-BO of large chemical space

- Automated data upload to ELN.
- Automated data analysis & merging via barcode & python script.

Data Processing

Catalyst Library Synthesis
1 day

- 24 catalysts per batch.
- 500mg per catalyst.



24 catalysts per generation.
5 days per generation.
6 iterations (144 catalysts).

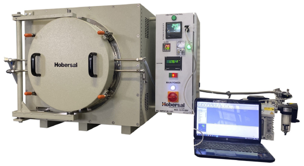
Fixed Bed Study
2 days

- 24 reactors simultaneously.
- 50mg catalyst per reactor.
- CO_2/H_2 = 1/3 (8ml/min/reactor).
- 32 bars, 275ºC.

30.10.2023

Solid Dispense
<1 day

Thermal Treatment
1 day



- 24 catalyst simultaneously.
- 4h at 550 C.

A. Ramirez, E. Lam, D. Pacheco Gutierrez, Y. Hou, H. Tribukait, Loïc M. Roch, C. Copéret, P. Laveille *Chem Catal.* 2024, *4*, 100888.

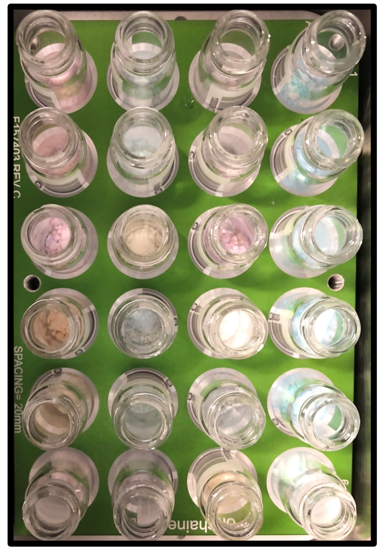
Efficient Exploration of the Chemical Space

Data-Driven High-Throughput Experimentation

MACHINE LEARNING-GUIDED EVOLUTION of CO_2 to Methanol CATALYSTS

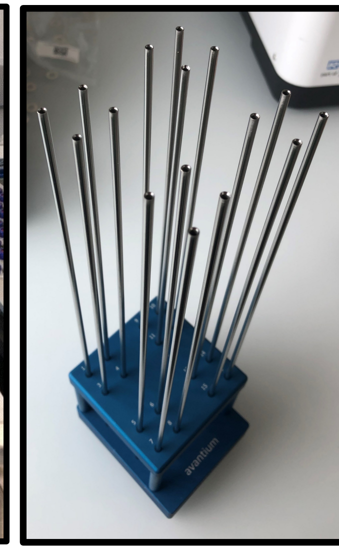
Automated combination of metal salts solutions.

Automated dispensing of supports.



Impregnated supports.

Barcode reading.



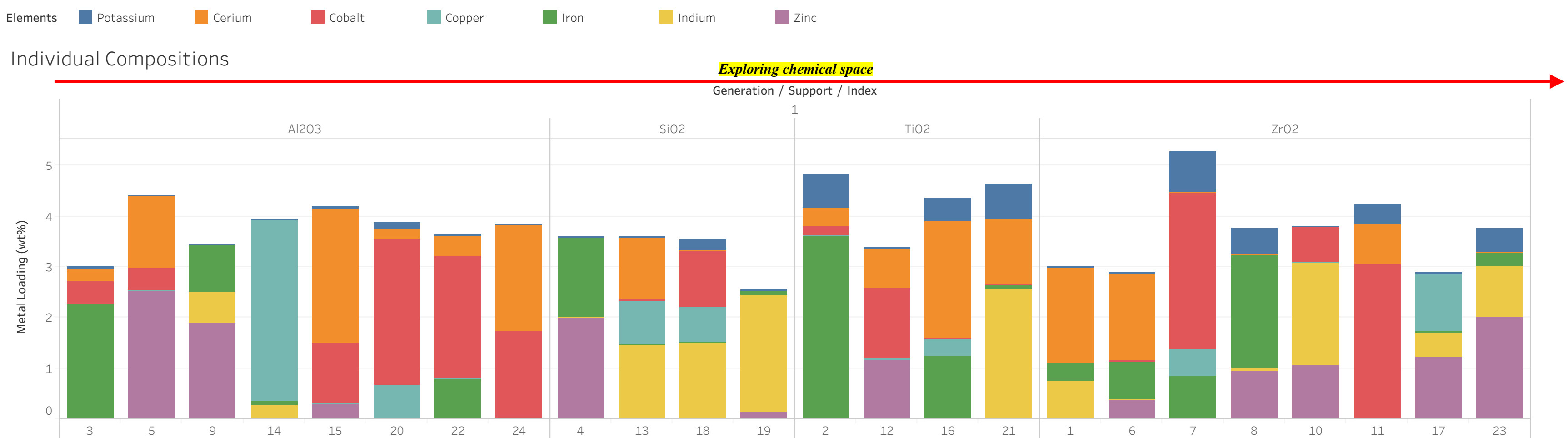
Fixed bed reactors.

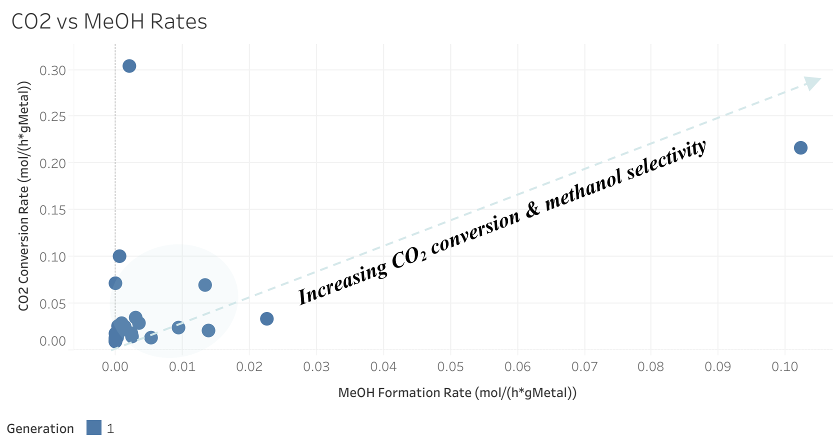
A. Ramirez, E. Lam, D. Pacheco Gutierrez, Y. Hou, H. Tribukait, Loïc M. Roch, C. Copéret, P. Laveille *Chem Catal.* 2024, *4*, 100888.

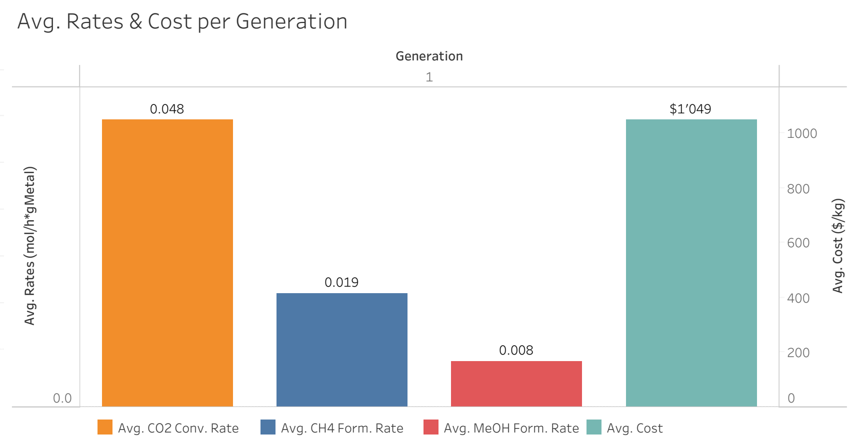
CO_2 Hydrogenation and Methanol Synthesis

Development of Heterogeneous Catalysts via Data-Driven Approach

MACHINE LEARNING-GUIDED EVOLUTION of CO_2 to Methanol CATALYSTS







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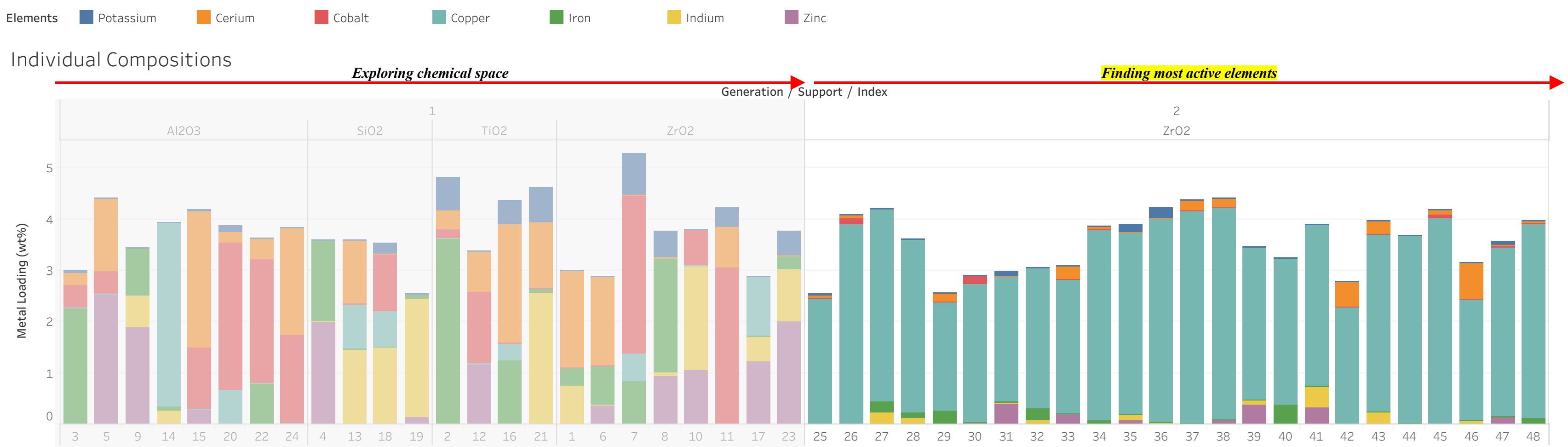

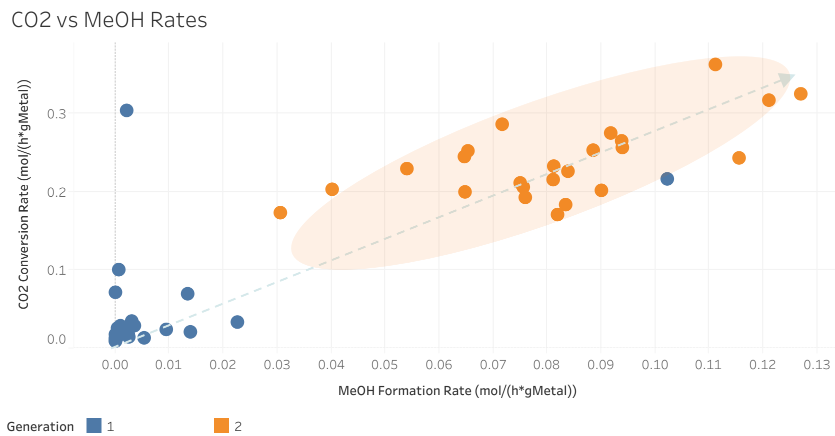

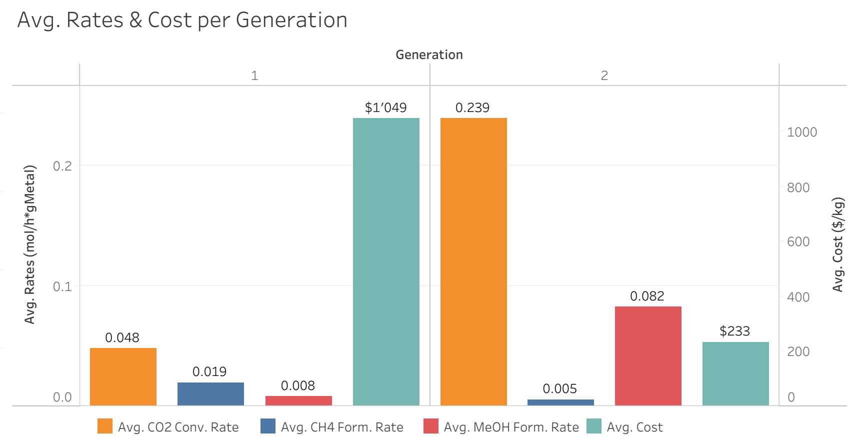

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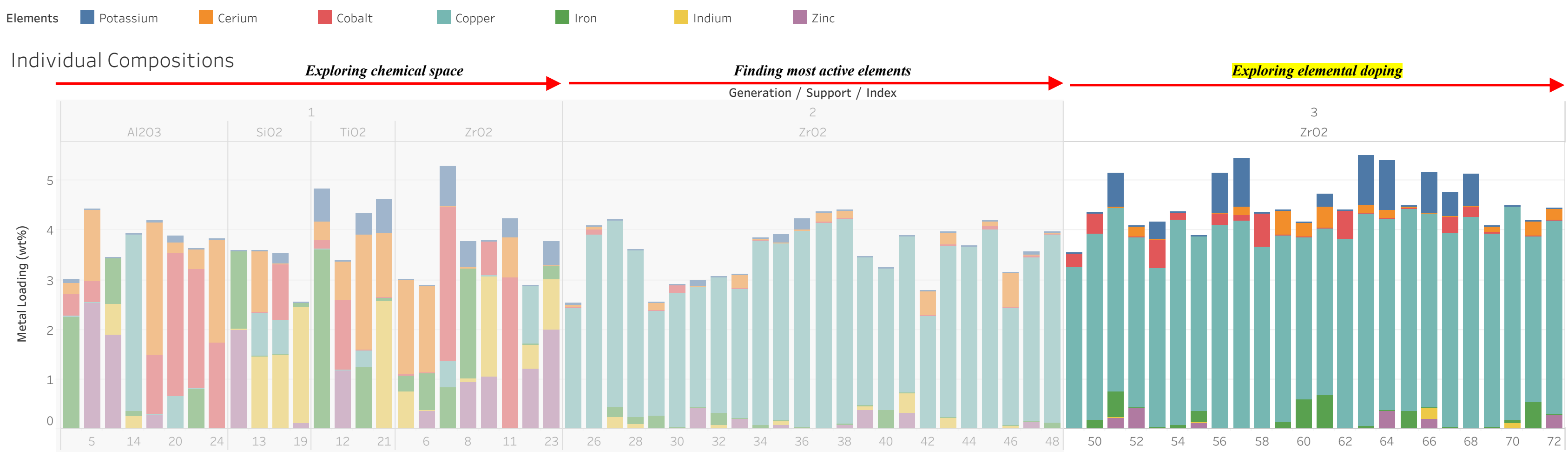

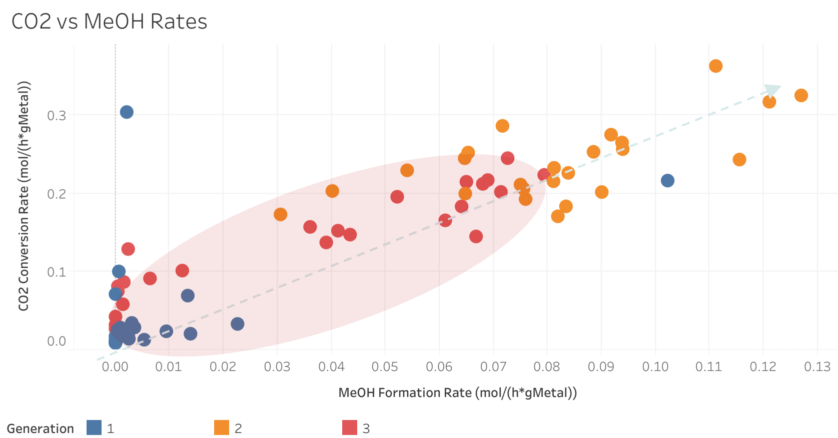

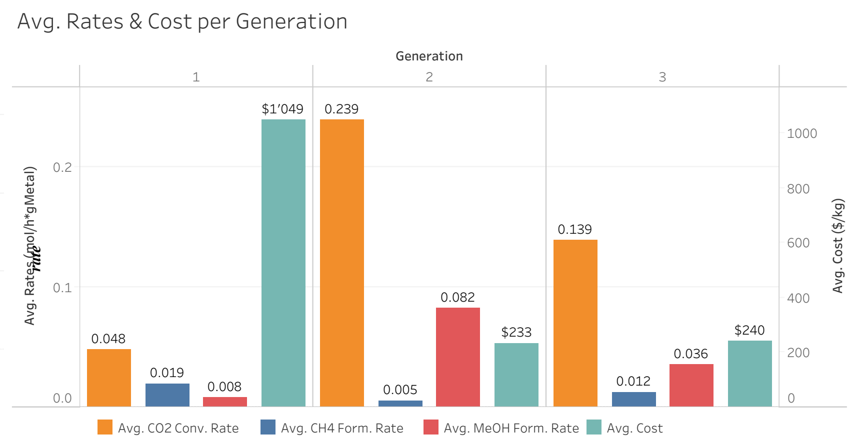

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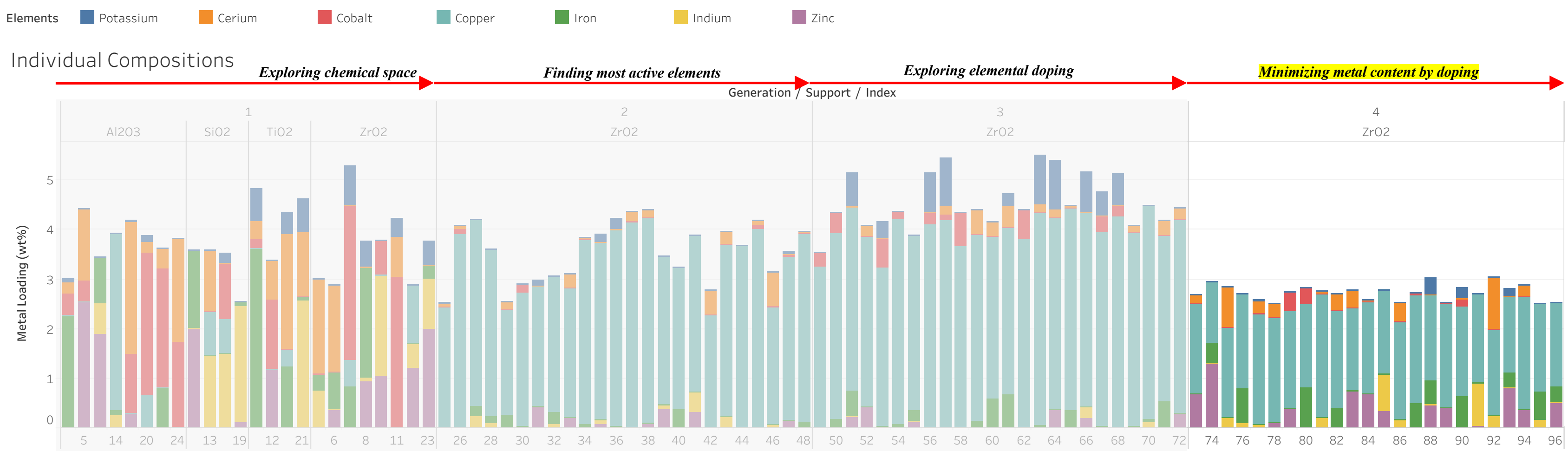
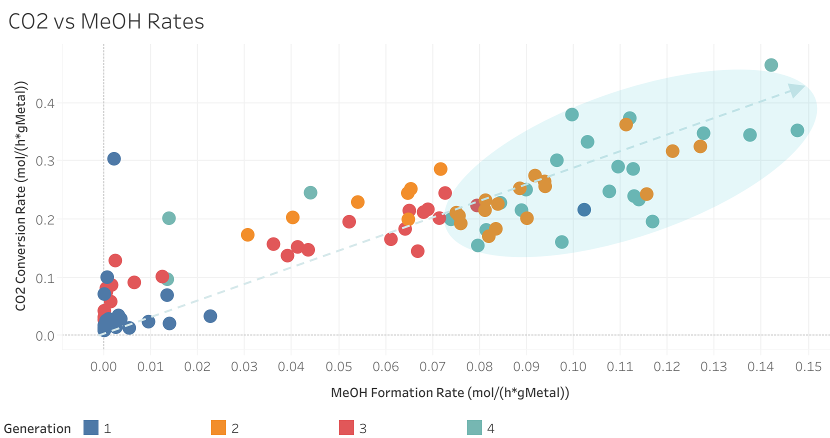
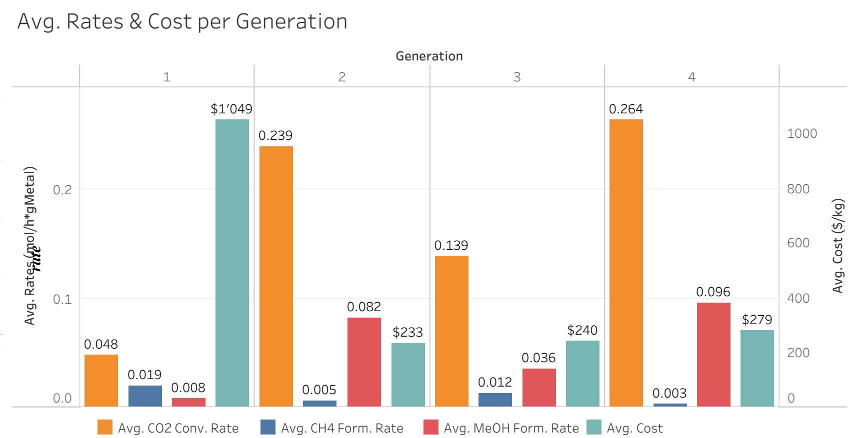




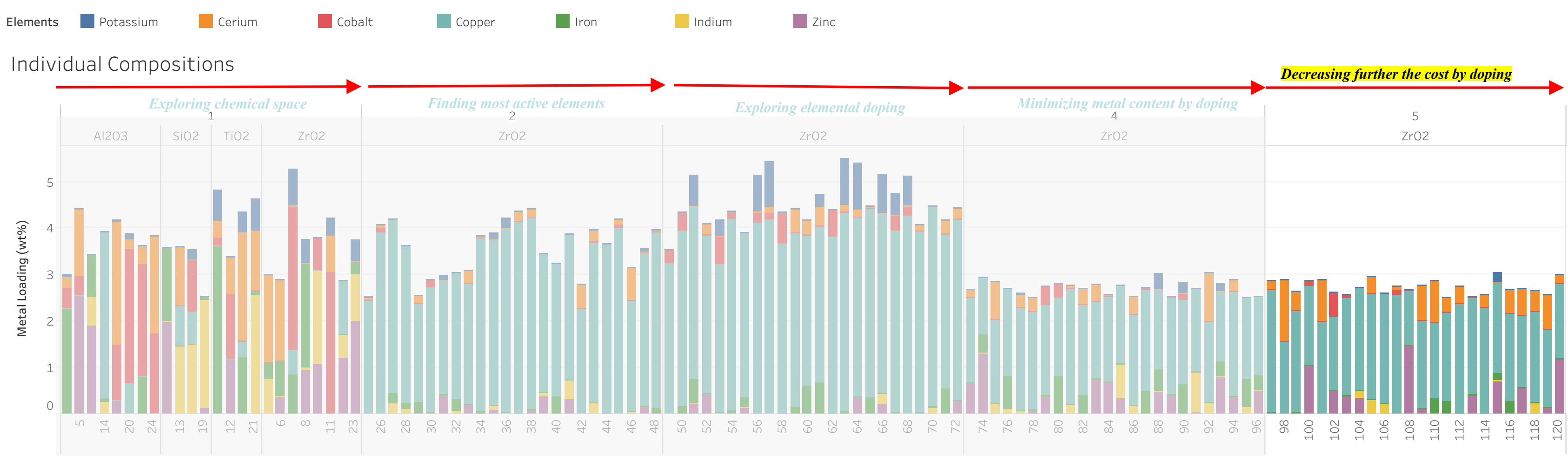


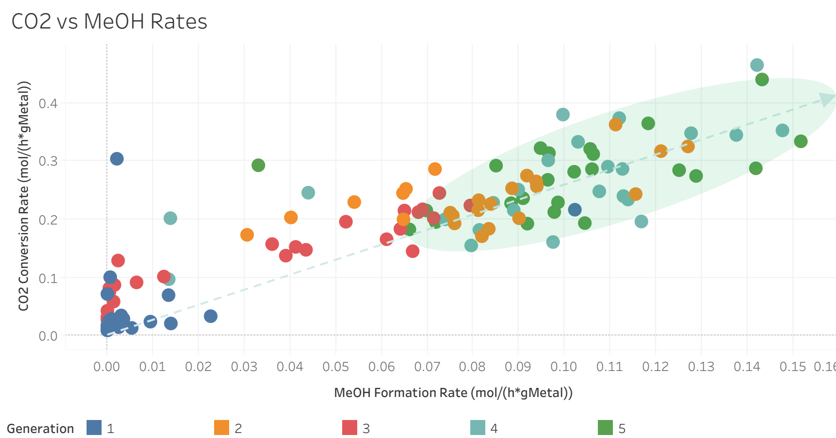
A. Ramirez, E. Lam, D. Pacheco Gutierrez, Y. Hou, H. Tribukait, Loïc M. Roch, C. Copéret, P. Laveille *Chem Catal.* 2024, *4*, 100888.

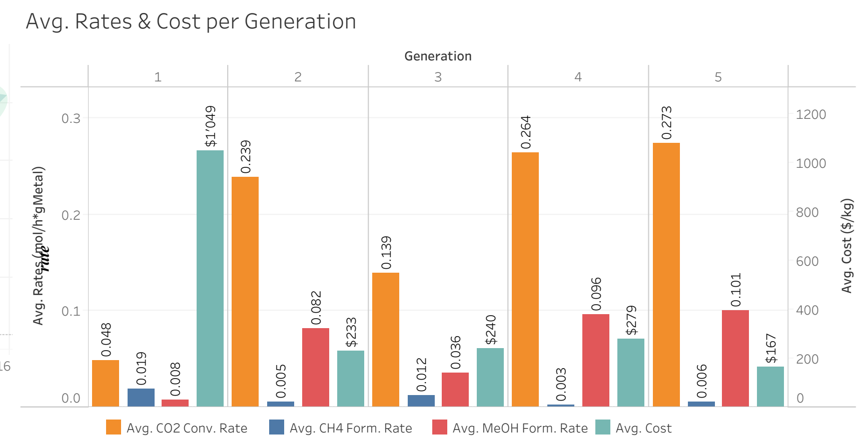
CO_2 Hydrogenation and Methanol Synthesis

Development of Heterogeneous Catalysts via Data-Driven Approach

MACHINE LEARNING-GUIDED EVOLUTION of CO_2 to Methanol CATALYSTS







120 catalysts synthesized and tested in 5 weeks

A. Ramirez, E. Lam, D. Pacheco Gutierrez, Y. Hou, H. Tribukait, Loïc M. Roch, C. Copéret, P. Laveille Chem Catal. 2024, 4, 100888.

ETHzürich
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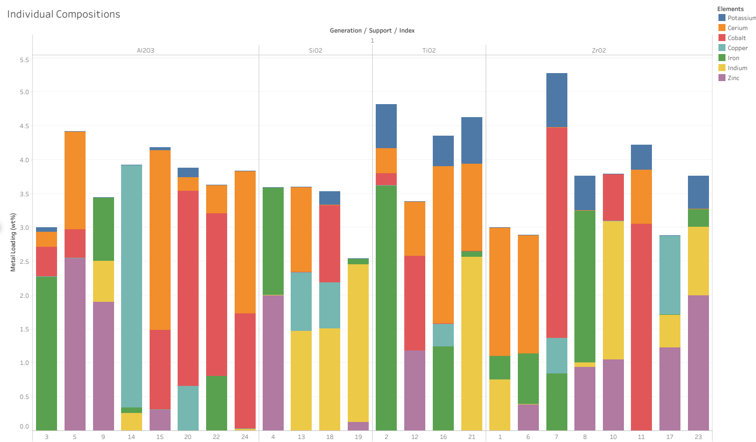
CAT+

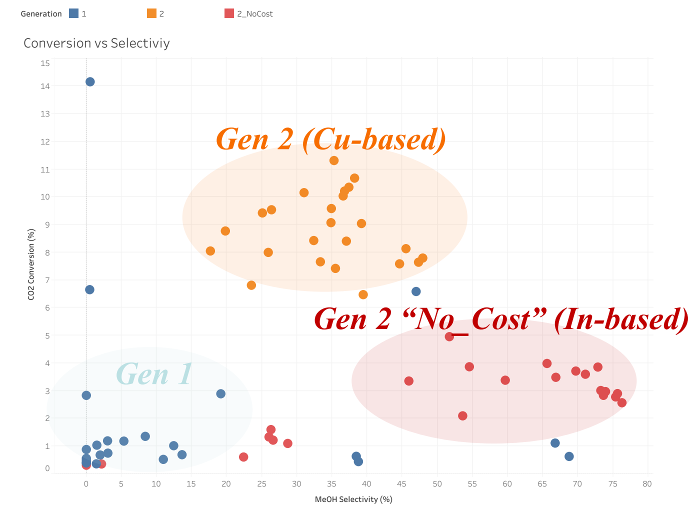
CO_2 Hydrogenation and Methanol Synthesis

Development of Heterogeneous Catalysts via Data-Driven Approach

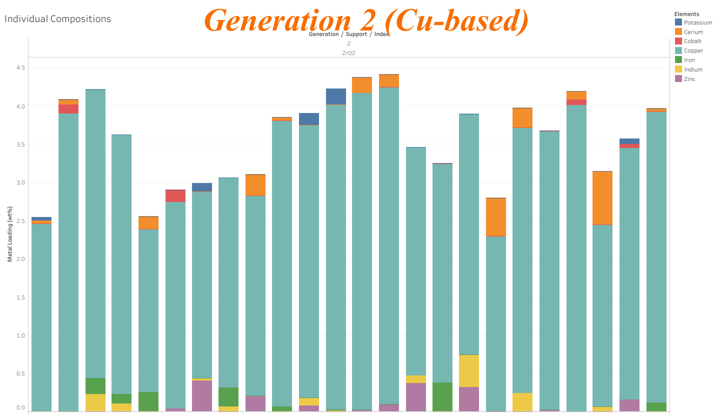
MACHINE LEARNING-GUIDED EVOLUTION of CO_2 to Methanol CATALYSTS

Generation 1

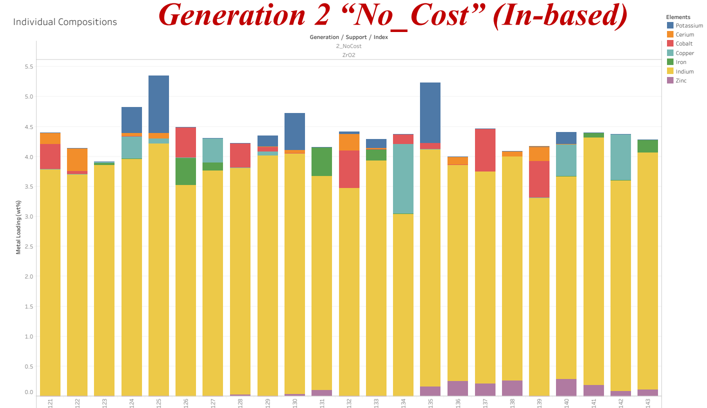




Generation 2 (Cu-based)



Generation 2 "No_Cost" (In-based)



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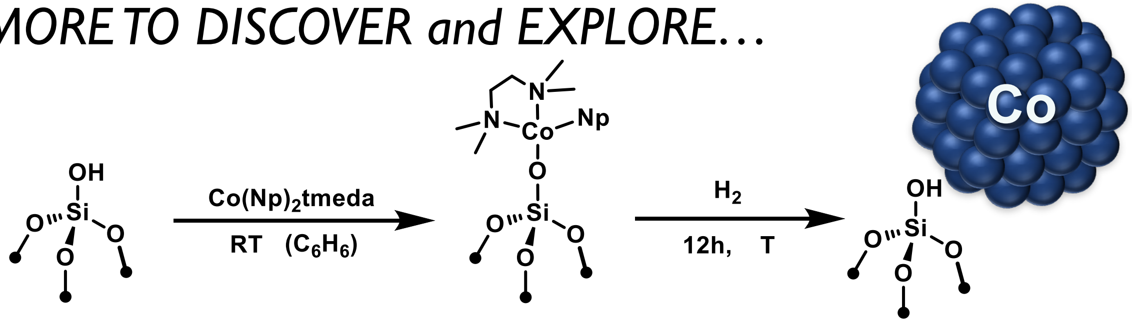
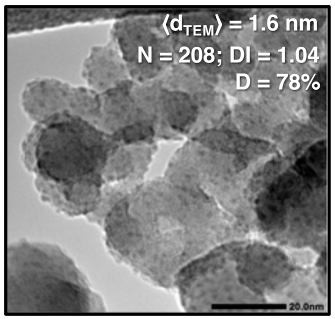
CO_2 Hydrogenation and Methanol Synthesis

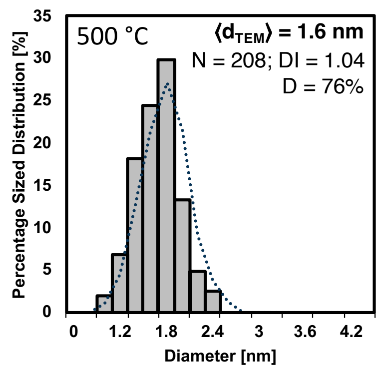
Understanding the role of the Metal-Support Interface

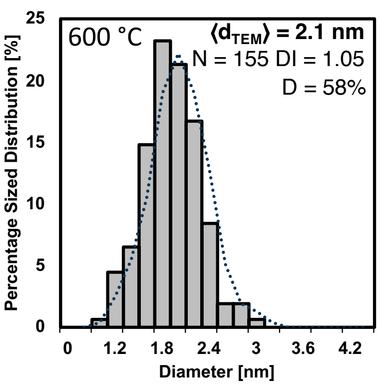
MORE TO DISCOVER and EXPLORE…

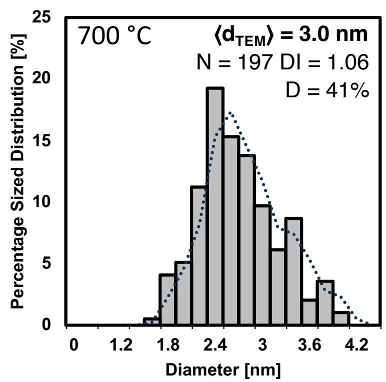


- ***Particle size tuned from 1.6 nm to 3.0 nm via SOMC-approach***
- Characterized by microscopy and spectroscopy
- Particle size effect in CO_2 hydrogenation: CH_4 vs. CO

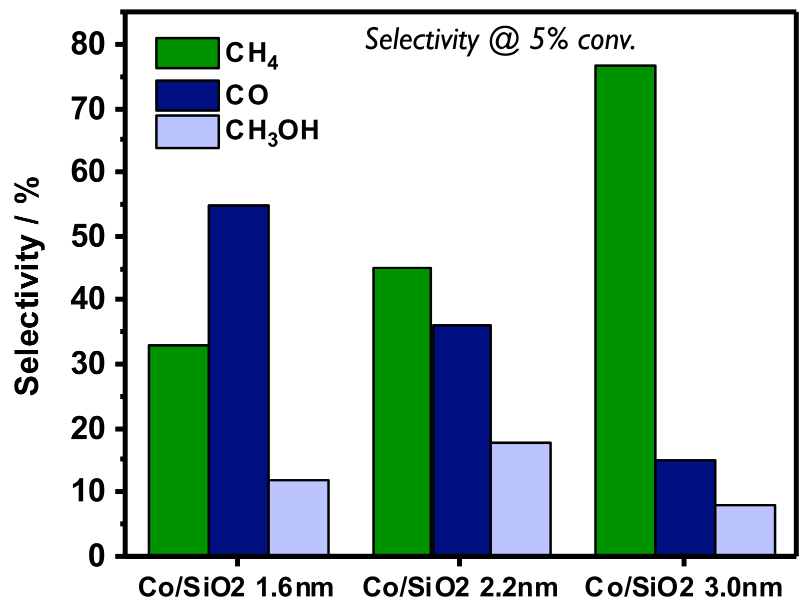








CO_2 Hydrogenation – 230 C, 25 bar(g)
(3 H_2, 1 CO_2, 1 Argon – flowrates: 6-100 ml min^{-1})

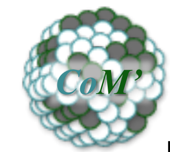


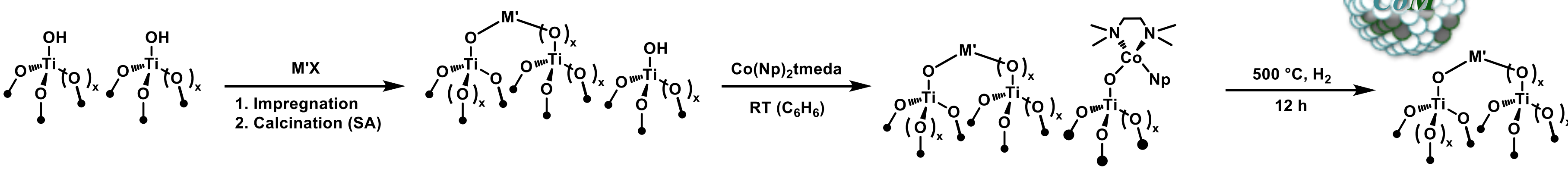
X. Zhou, G. Price, G. Sunley, C. Copéret, Angew. Chem. Int. Ed. 2023, e202314274.

CO_2 Hydrogenation and Methanol Synthesis

Development of Heterogeneous Catalysts via Data-Driven Approach

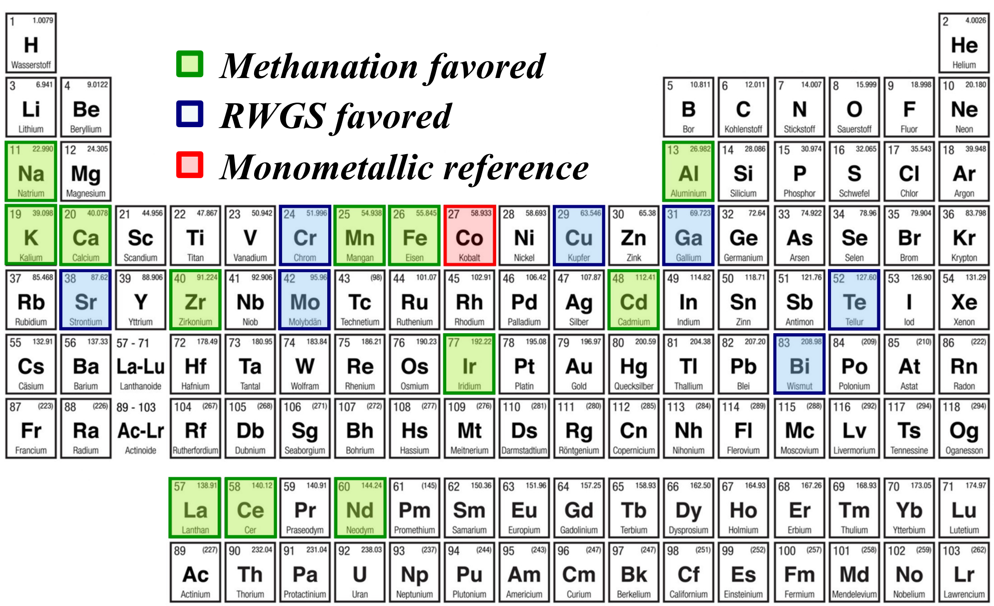
A CALL FOR Data-Driven HTE



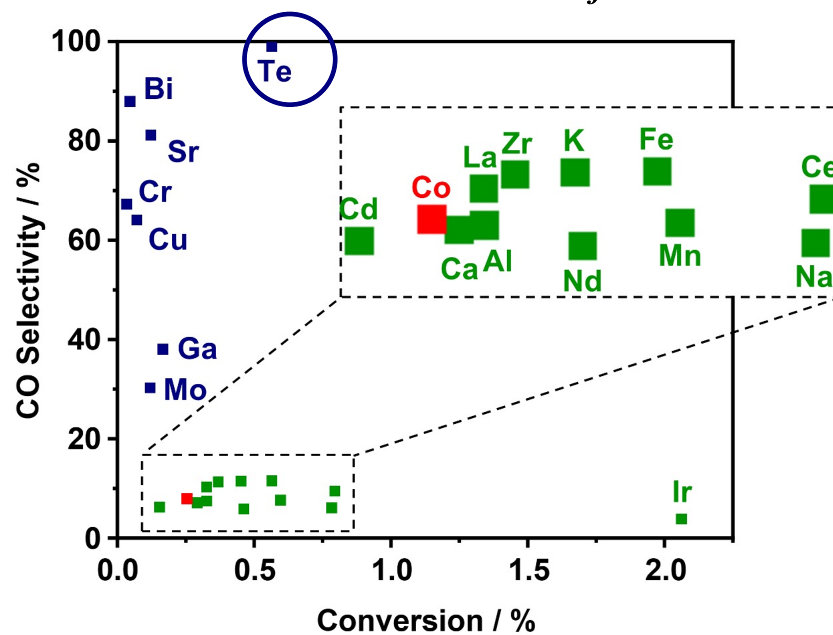


Dopant Selection — *Catalytic Screening*

❖ ***Bimetallic catalyst library based on chemical descriptors***



❖ ***Non-classical behavior of Co?***



Discovery of Tellurium: an Outstanding and Unexpected Promoter for RWGS with Co

CO_2 Hydrogenation and Methanol Synthesis

Development of Heterogeneous Catalysts via Data-Driven Approach

Synthetic Protocol — **Incipient Wetness Impregnation** — **Calcination** — ***In Situ* Activation** → **CO_2 Hydrogenation**

Incipient Wetness Impregnation
- Co-impregnation of metals
- 0.3 mmol/g M & Te
- M = Co, Ni, Rh

Calcination
- Synthetic air
- 500 °C (5 °C min^{-1})
- 6h

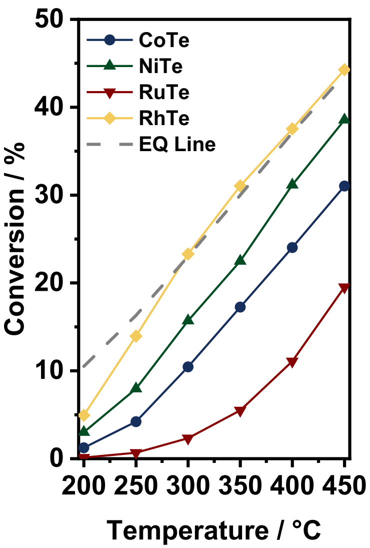
***In Situ* Activation**
- Hydrogen
- 400 °C (5 °C min^{-1})
- 3h

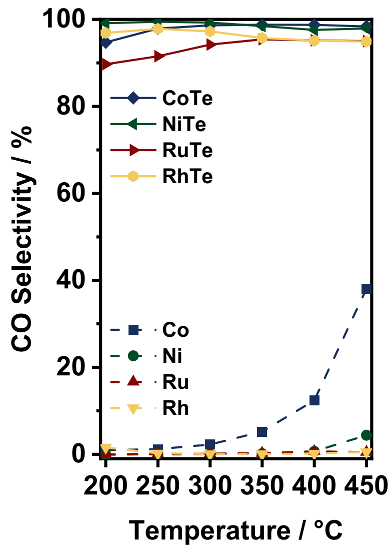
CO_2 Hydrogenation
- 80 mg catalyst
- H_2:CO_2:Ar = 3:1:1
- 200-450 °C
- 1-40 bar (g)

CO_2 Hydrogenation

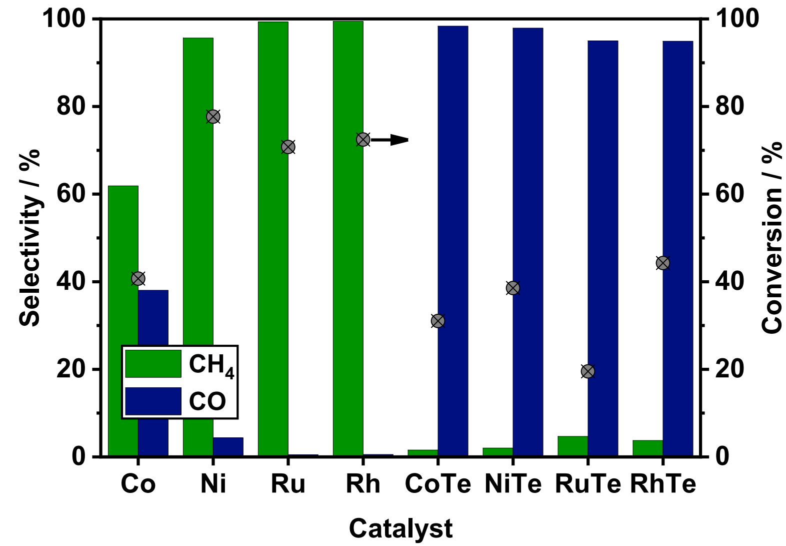
Conditions: 80 mg cat., 200-450 °C, 40 bar (g), H_2:CO_2:Ar = 3:1:1, 20 ml min^{-1}

❖ Typical methanation catalysts chosen





❖ Comparison: All reactivity shifted to pure RWGS

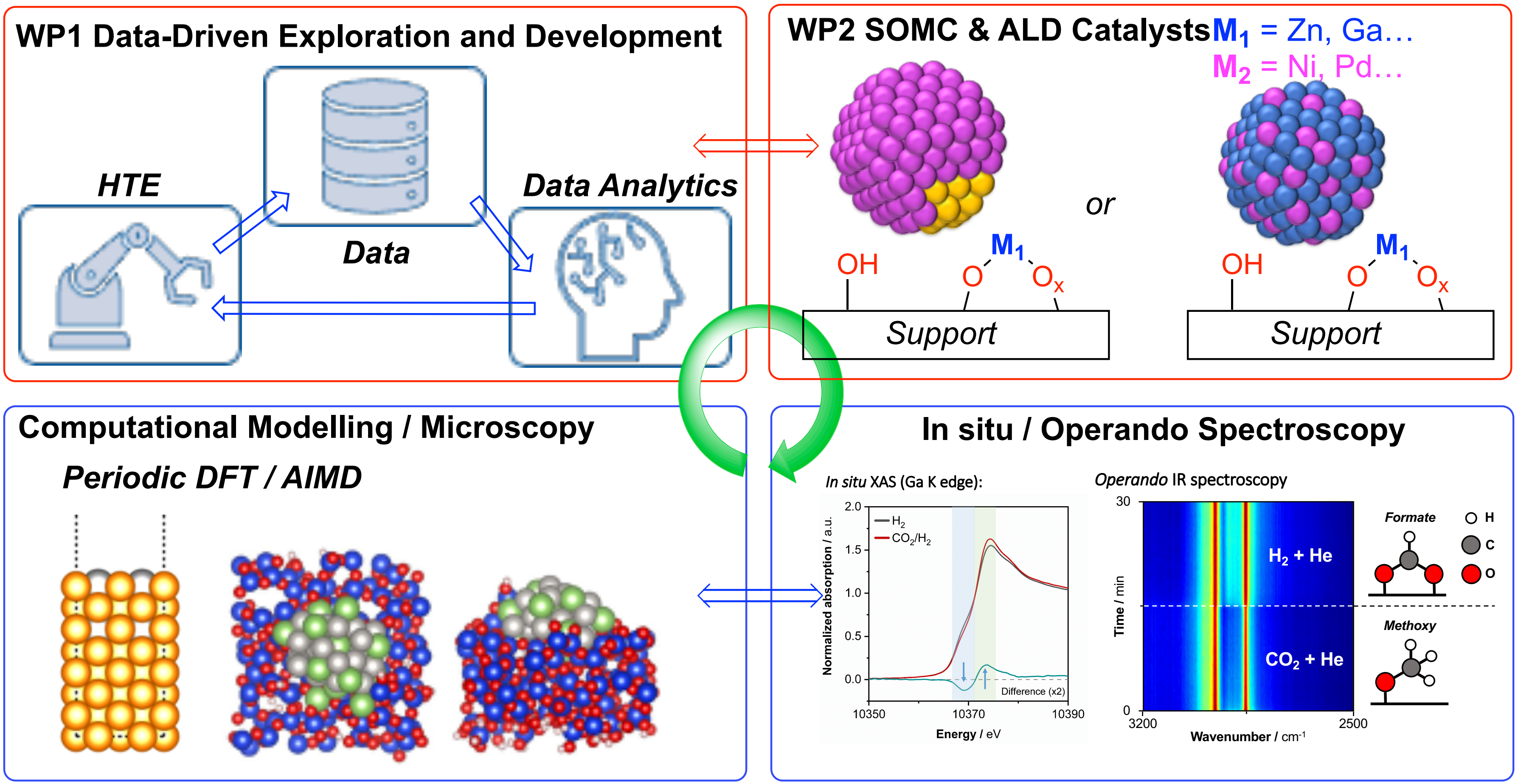


➡ Te-Promotion induces RWGS in classical methanation metals

X. Zhou, C. Hansen, D. Isler, W. Zhou, J. Paterson, J. Southouse, C. Copéret, J. Am. Chem. Soc. 2025, *147*, 22309–22313.

Vision (2025)

Development of Heterogeneous Catalysts and Functional Materials via a Molecular Approach



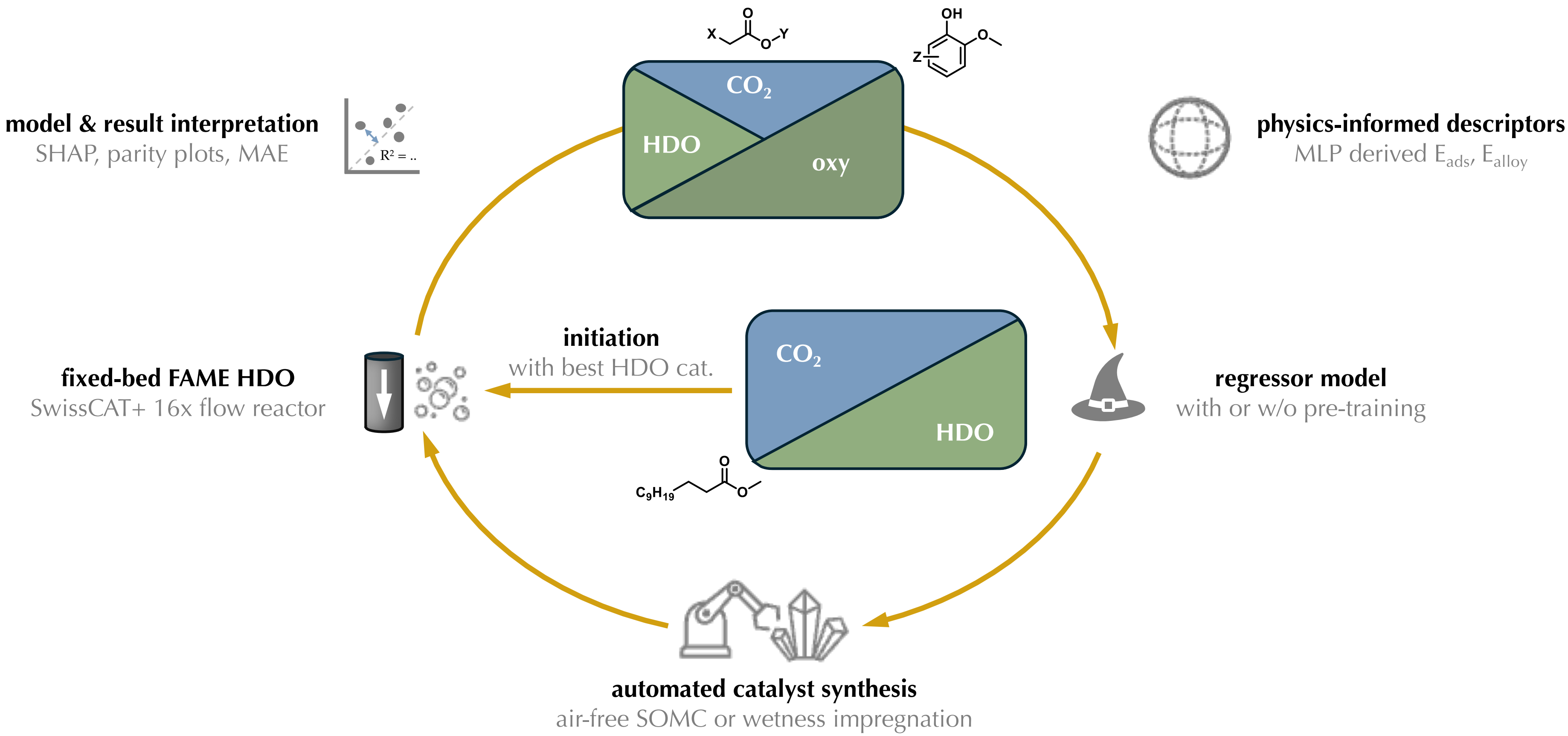
S. R. Docherty, C. Copéret *J. Am. Chem. Soc.* 2021, *143*, 6767-6780.

C. Sidhoum C. Hansen, C. Copéret *Actualité Chimique* 2025, *506*, 5-12.

A. Comas-Vives, C. Copéret Acc. Chem. Res. 2025, *in press*. Doi: 10.1021/acs.accounts.5c00599

C. Hansen, W. Zhou, C. Copéret *Acc. Chem. Res.* 2025 *in press*. Doi: 10.1021/acs.accounts.5c00581

Transfer Learning and Data Science across Heterogeneous Catalysis



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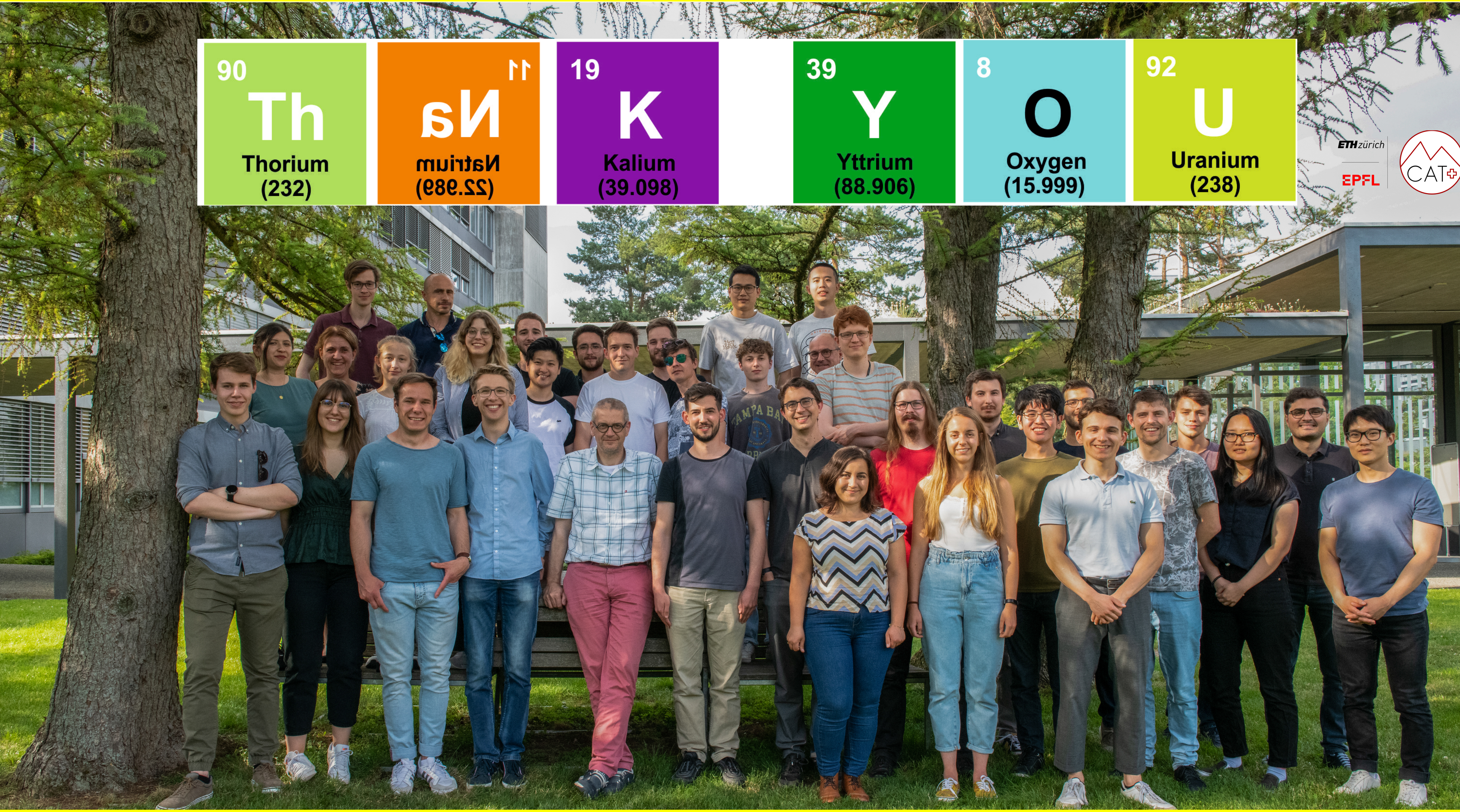
C. Hansen, W. Zhou, C. Copéret *Acc. Chem. Res.* 2025 *in press*. Doi: 10.1021/acs.accounts.5c00581

5^eme^ Rencontres du CNC

Maison de la Chimie – Paris – Le 4 Décembre 2025

CO_2 comme Matière Première
A la Recherche de Catalyseurs



NCCR Catalysis

Funding: ETHZ and SNF; Current Industrial Partners: BASF, BP, and Clariant