Operando characterisation of supported catalysts for methanol formation

LAURELIN TRAINING MATERIAL

The LAURELIN project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement n. 101022507. It reflects only the author’s view. The Agency is not responsible for any use that may be made of the information it contains.

This research is supported by the Japan Science and Technology Agency (JST) under the SICORP program (grant no. JPMJSC2101).

This presentation – elaborated by LAURELIN Consortium partner University College London (UCL) – serves as a **training material to develop the next generation of stakeholders in the field of catalyst research**.

This material falls under Objective 11 of the LAURELIN Grant Agreement.

For any question related to this training material, its content and/or other related questions please contact the LAURELIN Consortium.

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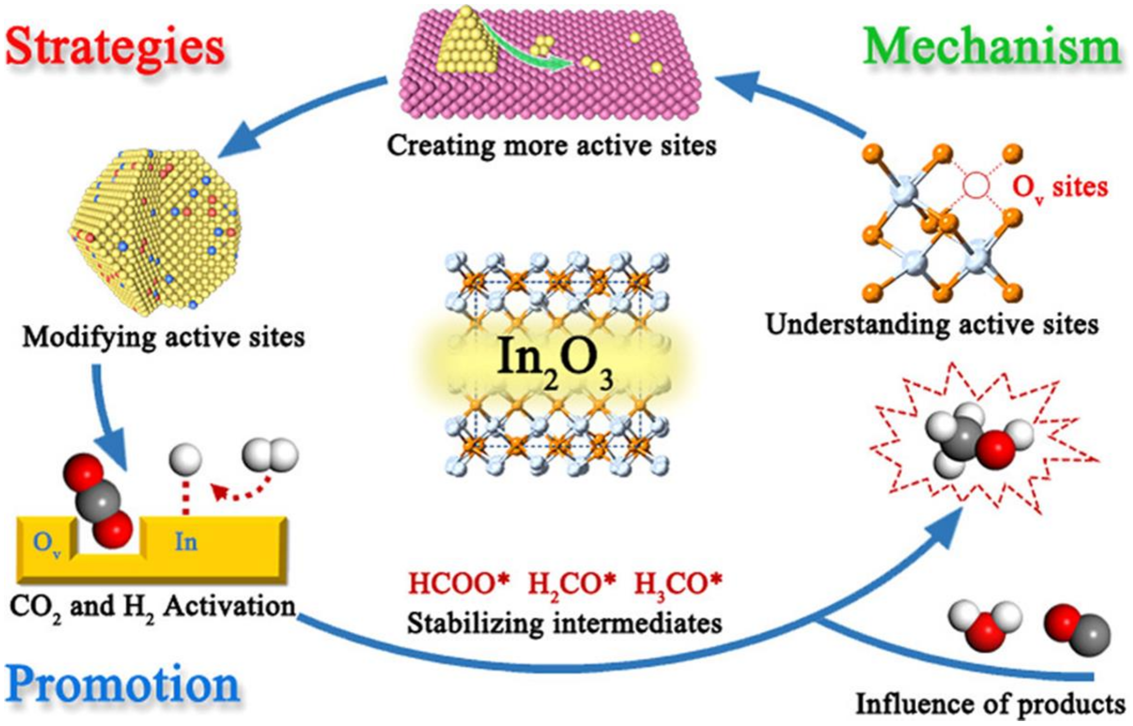
Operando characterisation of supported catalysts for methanol formation



Schematic overview

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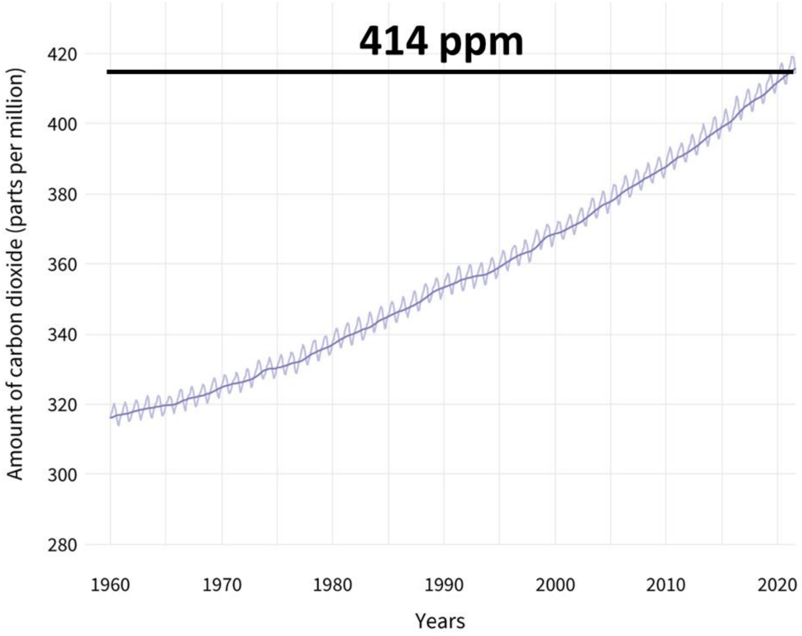
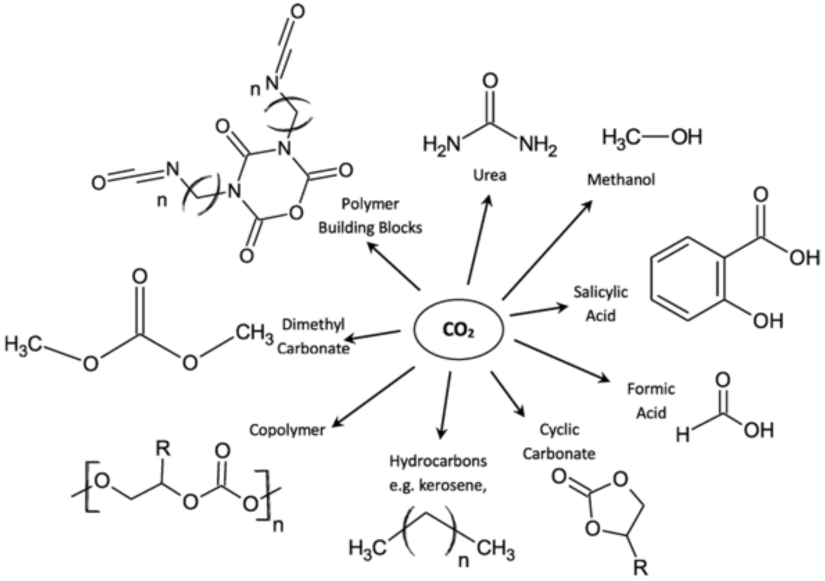
CO2 utilisation

Outlet for captured CO2



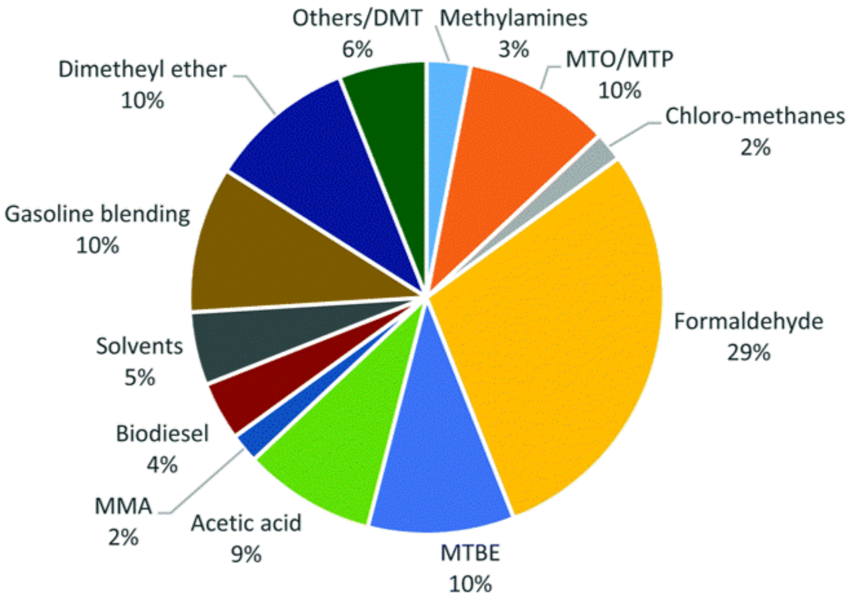
https://www.co2.earth/daily-co2



M. Moss et al, Front. Energy Res., 2017, 5:20, doi: 10.3389/fenrg.2017.00020

Green methanol

Methanol could influence global CO2 levels



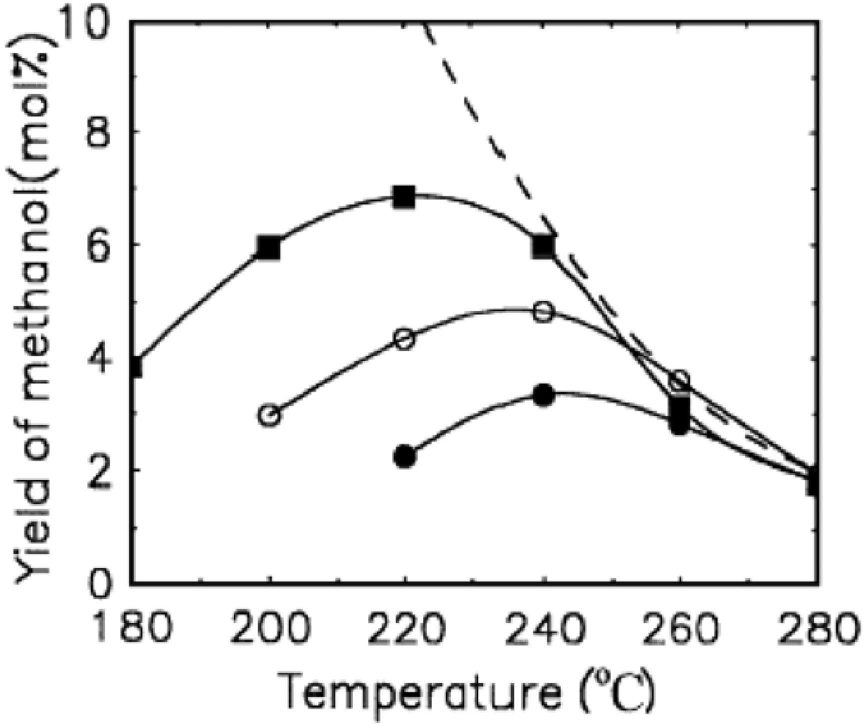
U. Mondal et al, Green Chem., 2021, 23, 8361

- ☐ Need to capture an additional ***10 gigatons*** of CO2 every year before 2050
- ☐ Produce ***110 megatons*** of methanol every year
- ☐ If all methanol was made from captured CO2 this would use ***1.5%*** of required captured CO2

National Academies of Science

Catalytic challenges

Low temperature or supress RWGS needed



Liu et al, Ind. Eng. Chem. Res., 2003, 25, 6530

- ❑ $CO_2 + 3H_2$ ⍰ $CH_3OH + H_2O$ $\Delta H_{298K} = -49.5$ kJ/mol
- ❑ $CO_2 + H_2$ ⍰ $CO + H_2O$ $\Delta H_{298K} = +41.2$ kJ/mol

- ❑ Better CO_2 conversion at high temperatures,

but ***selectivity goes towards CO***.

Current methanol production

☐ Cu-ZnO/Al_2O_3 is the primary methanol catalyst from ***syngas (CO/CO_2/H_2)***

Typically Cu:Zn = 7:3, with 10 wt% Al_2O_3

50-100 bar, 200-300 °C *(Behrens et al, Science, 2012, 336, 893)*

☐ Can be used for CO_2 hydrogenation, but significantly worse conversion.

Equilibrium methanol yield from ***CO*** at 200 °C is 80%
Equilibrium methanol yield from ***CO_2*** at 200 °C is < 40%

☐ Challenging to use pure CO_2 feedstock? *(Arakawa et al, Stud. Surf. Sci. Catal., 1998, 114, 19)*

Cu–ZnO issues – RWGS

Cu/Zn systems have high RWGS selectivity

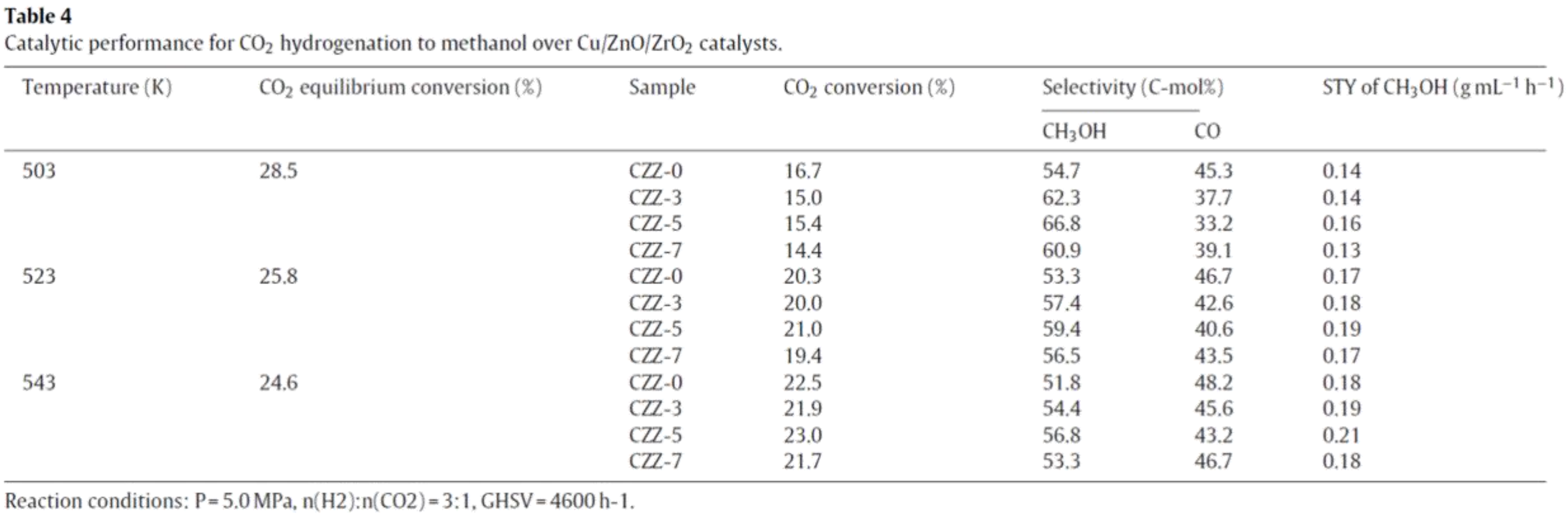


Table 4
Catalytic performance for CO_2 hydrogenation to methanol over $Cu/ZnO/ZrO_2$ catalysts.

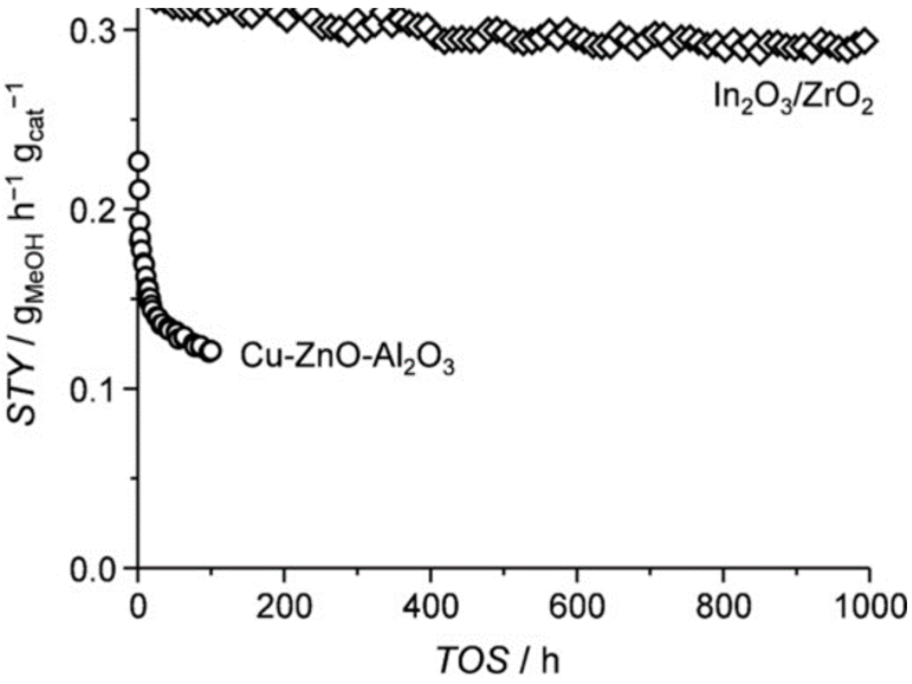
Temperature (K)	CO_2 equilibrium conversion (%)	Sample	CO_2 conversion (%)	Selectivity (C-mol%)		STY of CH_3OH ($g\,mL^{-1}\,h^{-1}$)
				CH_3OH	CO	
503	28.5	CZZ-0	16.7	54.7	45.3	0.14
		CZZ-3	15.0	62.3	37.7	0.14
		CZZ-5	15.4	66.8	33.2	0.16
		CZZ-7	14.4	60.9	39.1	0.13
523	25.8	CZZ-0	20.3	53.3	46.7	0.17
		CZZ-3	20.0	57.4	42.6	0.18
		CZZ-5	21.0	59.4	40.6	0.19
		CZZ-7	19.4	56.5	43.5	0.17
543	24.6	CZZ-0	22.5	51.8	48.2	0.18
		CZZ-3	21.9	54.4	45.6	0.19
		CZZ-5	23.0	56.8	43.2	0.21
		CZZ-7	21.7	53.3	46.7	0.18

Reaction conditions: P = 5.0 MPa, n(H2):n(CO2) = 3:1, GHSV = 4600 h-1.

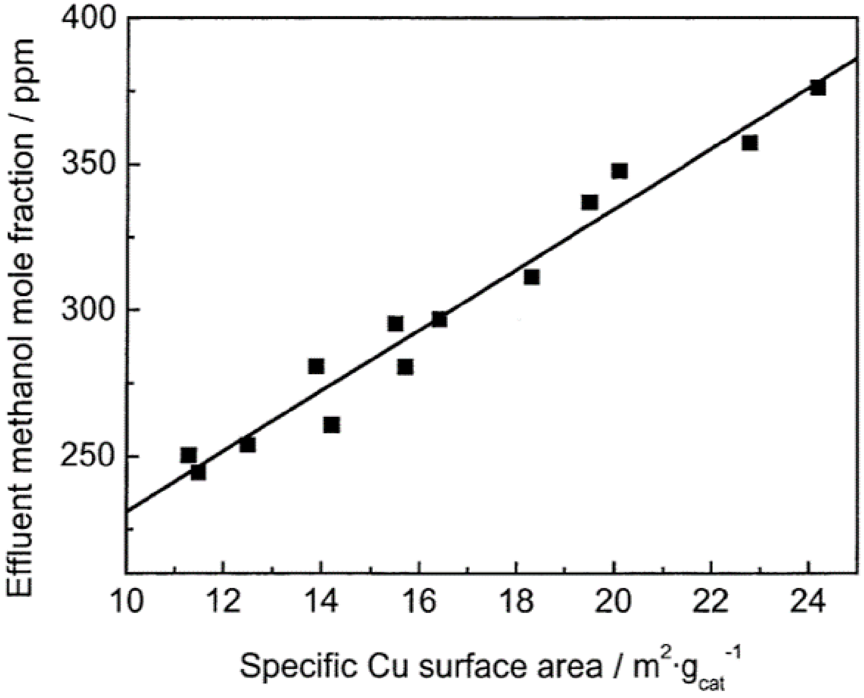
Dong et al, Appl. Catal. B: Env., 2016, 191, 8

Cu-ZnO issues - Stability

Cu sintering leads to deactivation



Martin et al, Angew. Chem. Int. Ed., 2016, 55, 6261



Kurtz et al, Catal. Lett., 2003, 86, 77

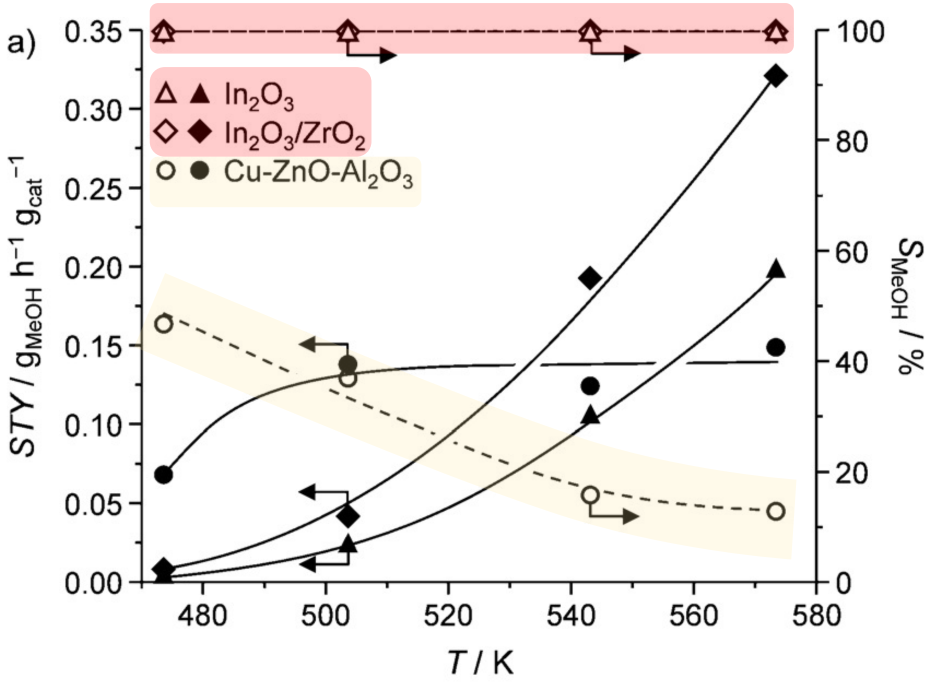
In_2O_3 as an alternative

In_2O_3 has very high methanol selectivity

- ❑ Common methanol steam reforming (MSR) catalyst:

$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$

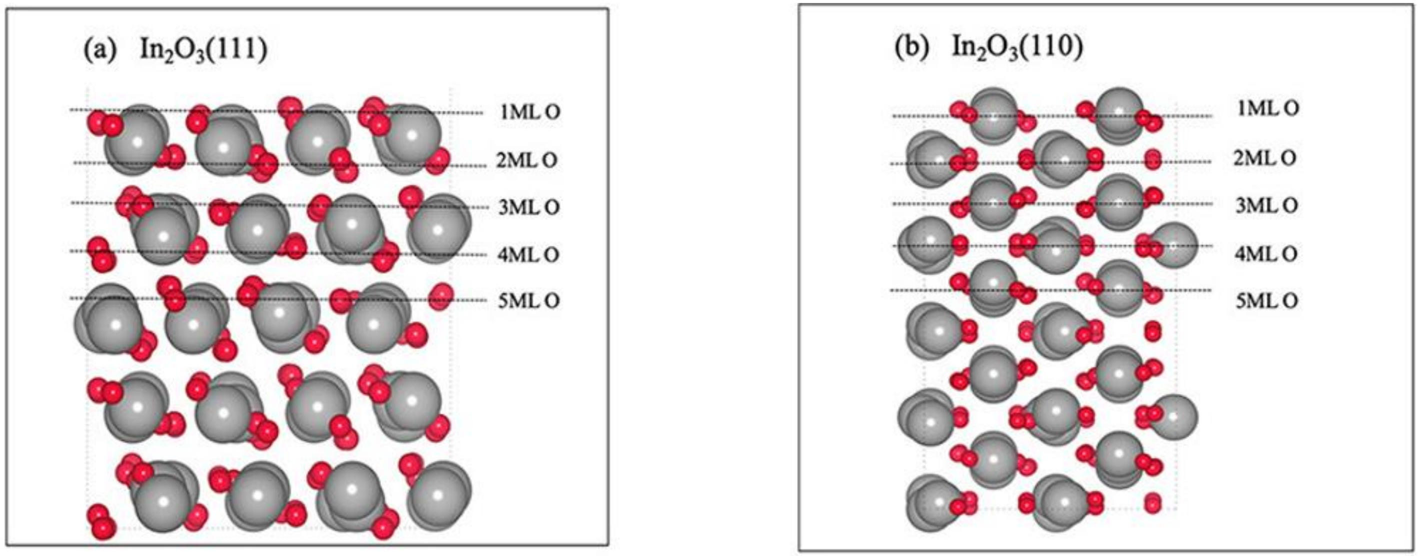
- ❑ Highly selective for methanol formation from CO_2, but low activity:



Martin et al, Angew. Chem. Int. Ed., 2016, 55, 6261

In_2O_3 forms

Two In_2O_3 surfaces to consider



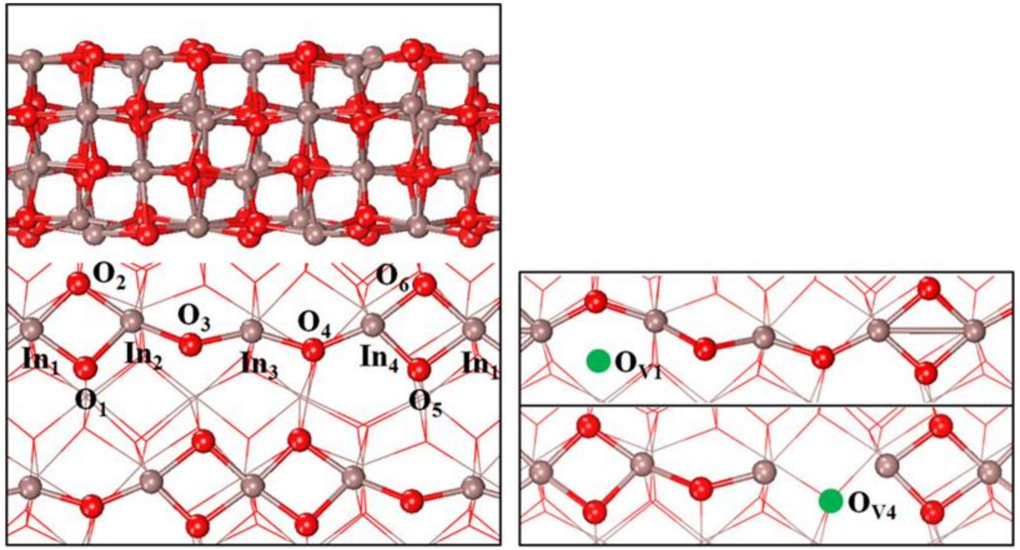
❑ Two common In_2O_3 planes investigated in cubic Bixbyite.

❑ 111 is more thermodynamically stable, but 110 is more active.

Cao et al, ACS Catal., 2021, 3, 1780

In_2O_3 mode of activity

Indium vacancies lead to activity



Ye et al, ACS Catal., 2013, 6, 1296

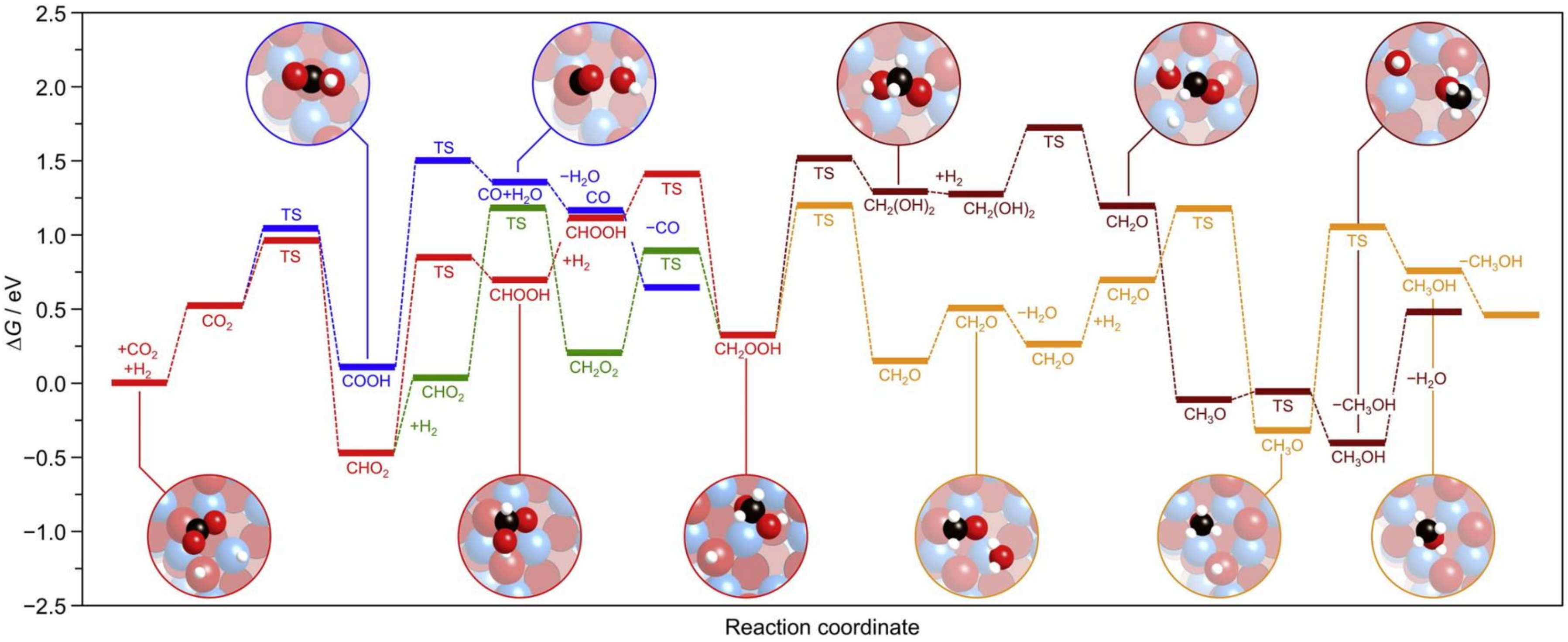
☐ Surface defects on In2O3 lead to ***In2O3-x***, making it an n-type semiconductor.

☐ This creates binding opportunities for CO2 leading to ***possible intermediate species.***

☐ Too many vacancies lead to Ino, and deactivation.

In_2O_3 mechanism

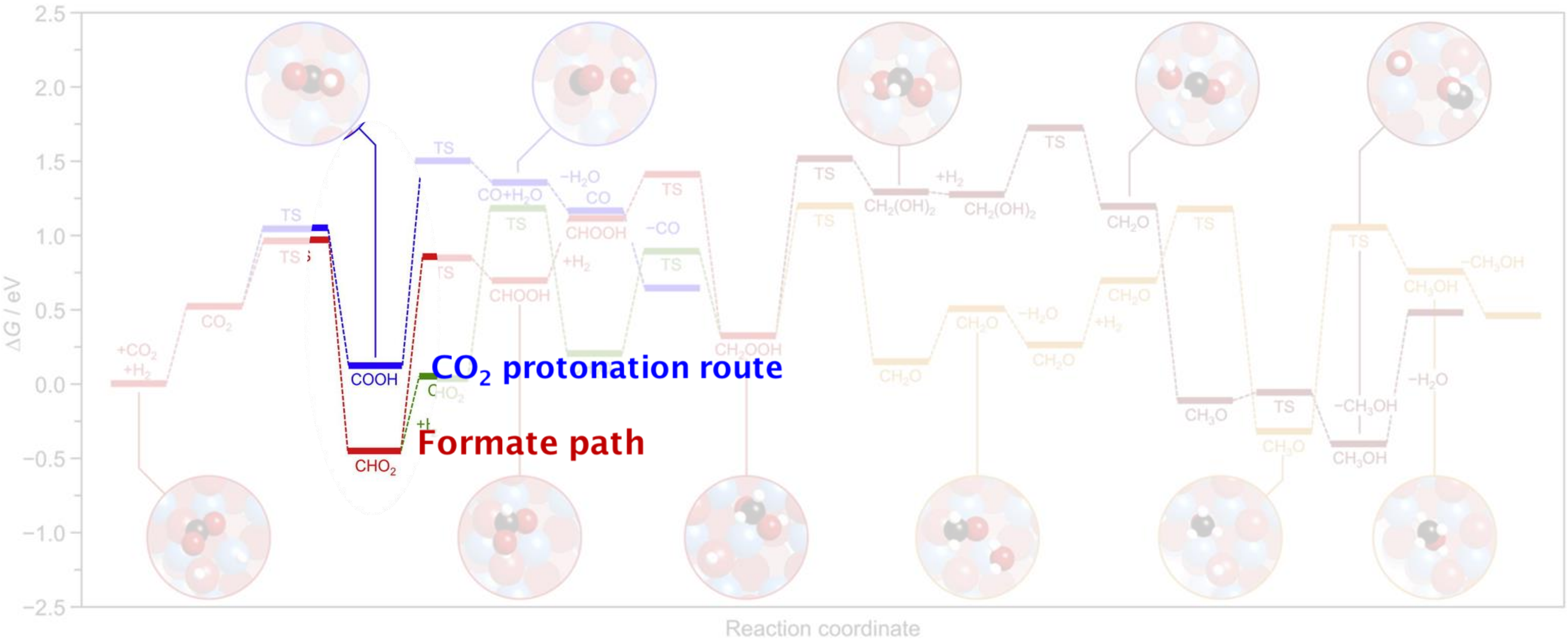
Range of intermediates possible



Frei et al, J. Catal., 2018, 361, 313

In_2O_3 mechanism

Range of intermediates possible



Frei et al, J. Catal., 2018, 361, 313

Pd–In_2O_3

Pd improves methanol production

☐ Pd improves In_2O_3 performance, but still debate on why?

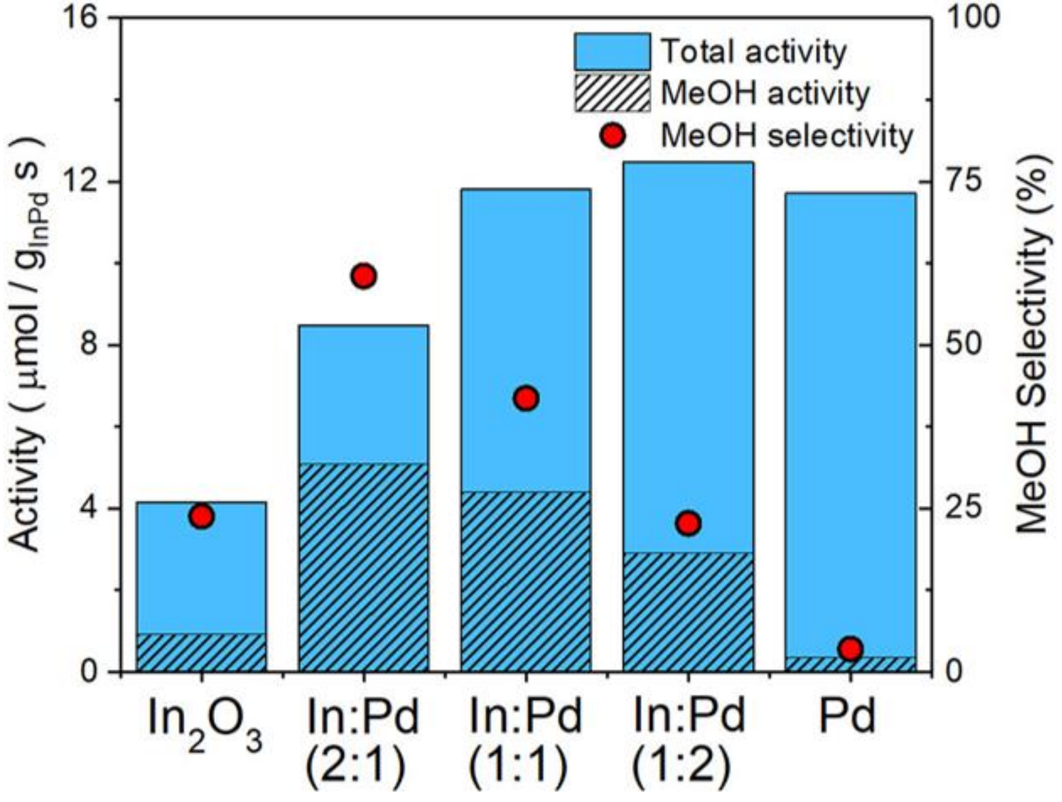
☐ ***Bimetallic PdIn*** phases known to form, but unsure if these help or hinder.

☐ Help:

Snider et al, ACS Catal., 2019, 9, 3399

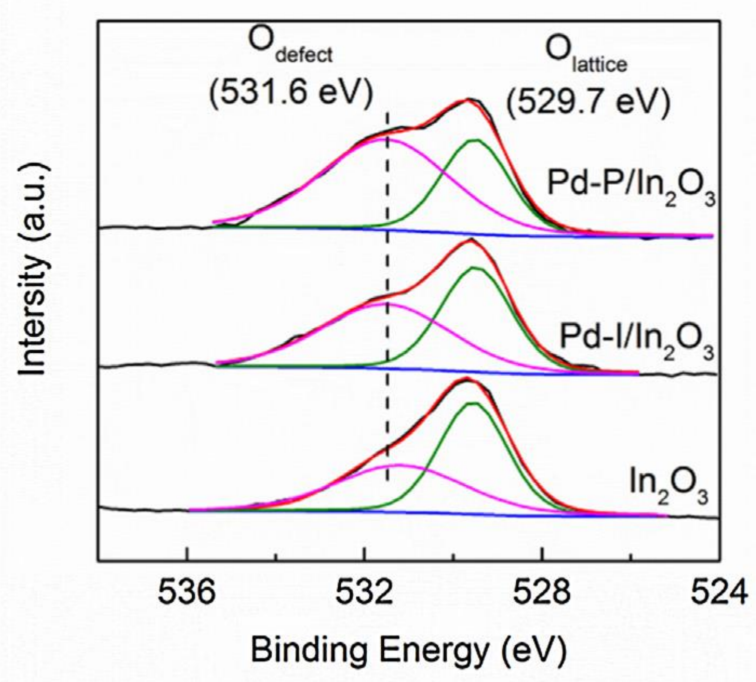
☐ Hinder:

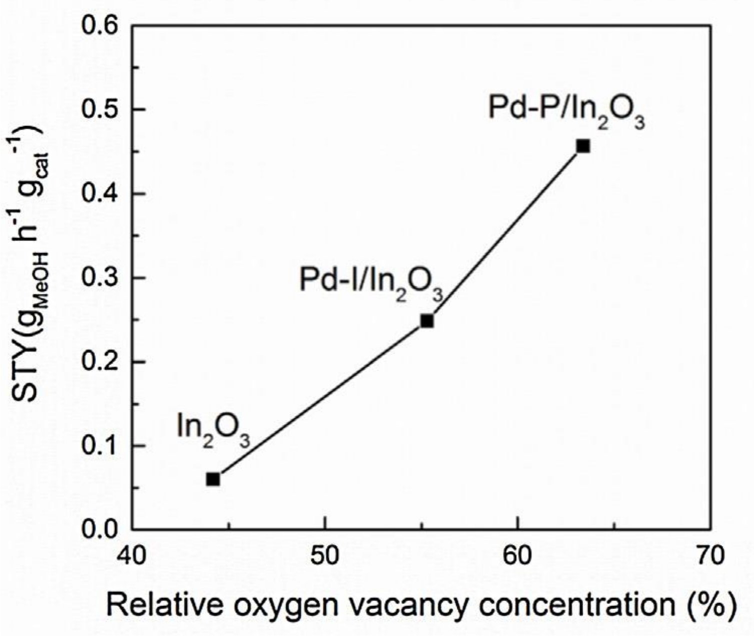
Rui et al, Appl. Catal. B, 2017, 218, 488



Pd–In_2O_3 synergy

Pd increases amount of oxygen vacancies

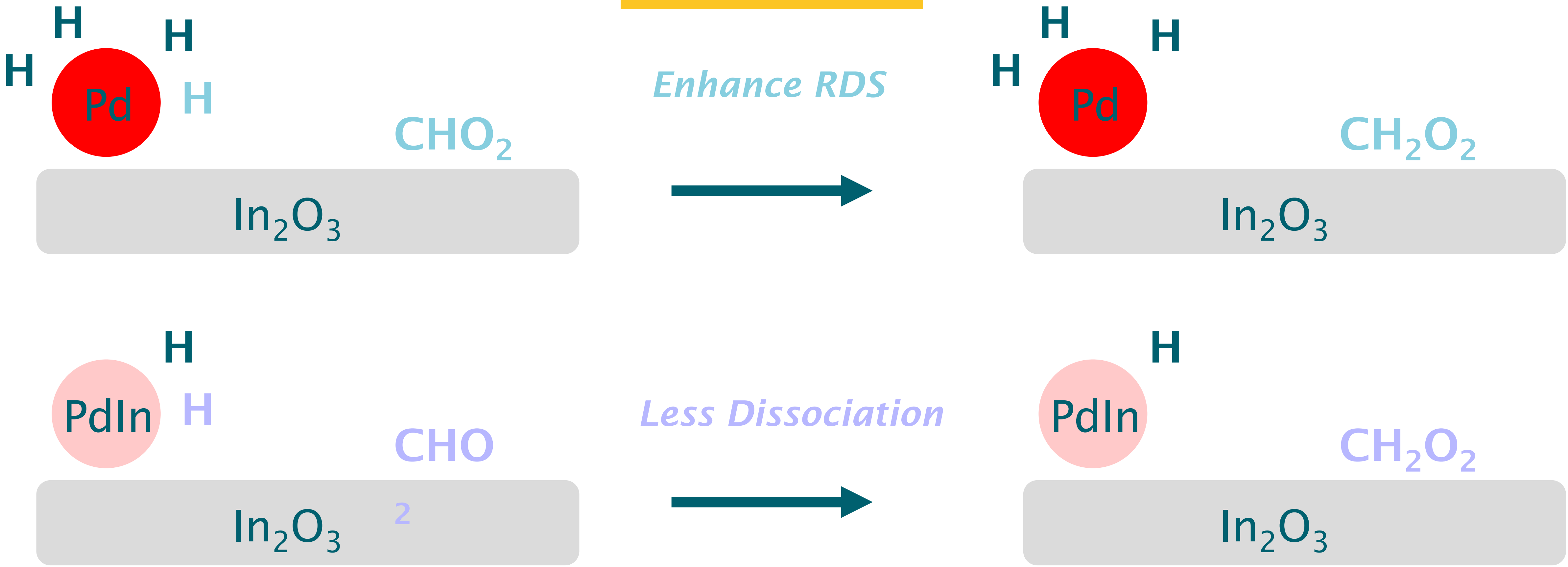




Rui et al, Appl. Catal. B, 2017, 218, 488

Pd–In_2O_3 synergy

PdIn hinders hydrogen dissociation



H
H
H
Pd
H
CHO_2
In_2O_3

Enhance RDS

H
H
H
Pd
CH_2O_2
In_2O_3

H
PdIn
H
CHO
In_2O_3
2

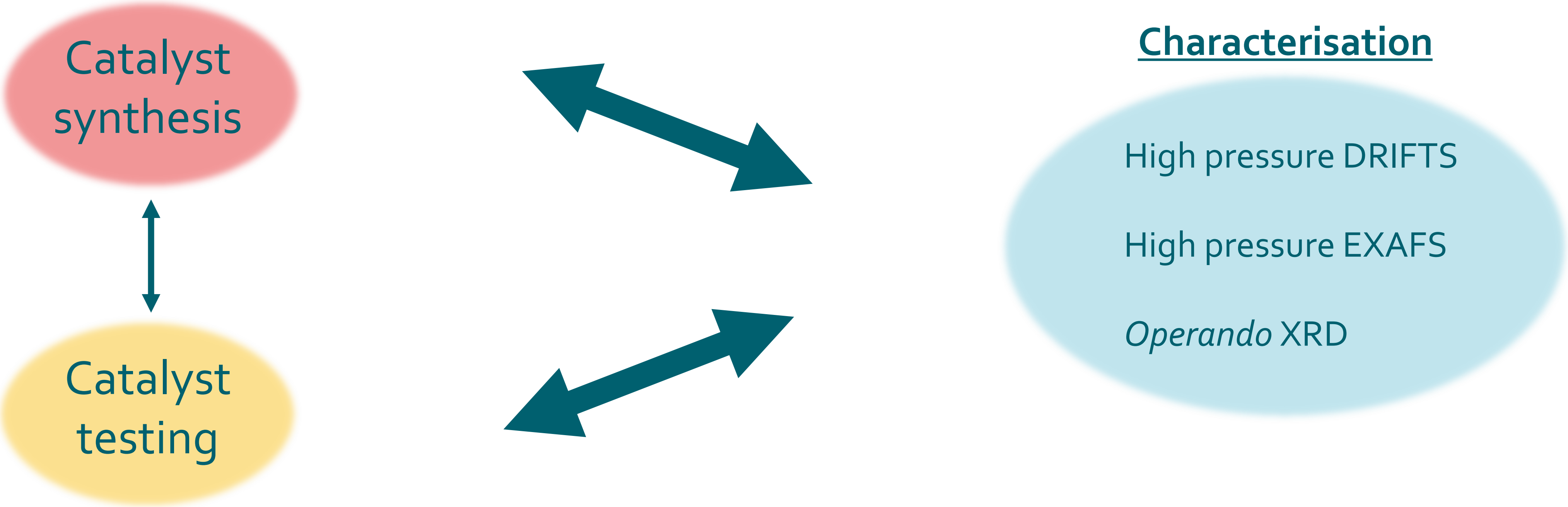
Less Dissociation

H
PdIn
CH_2O_2
In_2O_3

Rui et al, Appl. Catal. B, 2017, 218, 488

LAURELIN aims at

- ☐ Probe the ***mechanism and kinetics*** of methanol formation
- ☐ Design new ***operando*** characterisation tools to probe reactions
- ☐ ***Operando imaging*** to follow activation and deactivation phenomena



Catalyst synthesis

Catalyst testing

Characterisation

High pressure DRIFTS

High pressure EXAFS

Operando XRD

Laurelin Project

1. AIMPLAS (Spain)
Project Coordination. Catalyst synthesis and conventional reactor.

AIMPLAS INSTITUTO TECNOLÓGICO DEL PLÁSTICO

2. ITQ-CSIC (Spain)
Catalyst and magnetic induction reactor.

CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

3. UAL (Spain)
Catalyst and downstream processes.

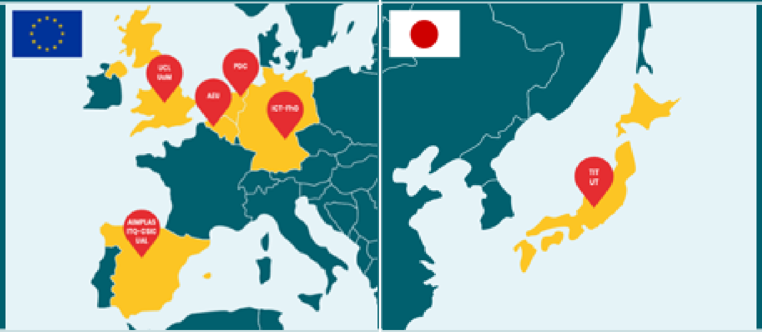
UNIVERSIDAD DE ALMERÍA

4. UoM (UK)
Non-thermal plasma reactor.

MANCHESTER 1824 The University of Manchester

5. UCL (UK)
Advanced characterisation.

UCL



6. ICT-FhG (Germany)
Microwave reactor.

Fraunhofer ICT

PDC

7. PDC (Netherlands)
Conceptual design, LCA and economic analysis.

ALIÉNOR Tailor-made solutions

8. AEU (Belgium)
IPR management. Dissemination.

東京工業大学 Tokyo Institute of Technology

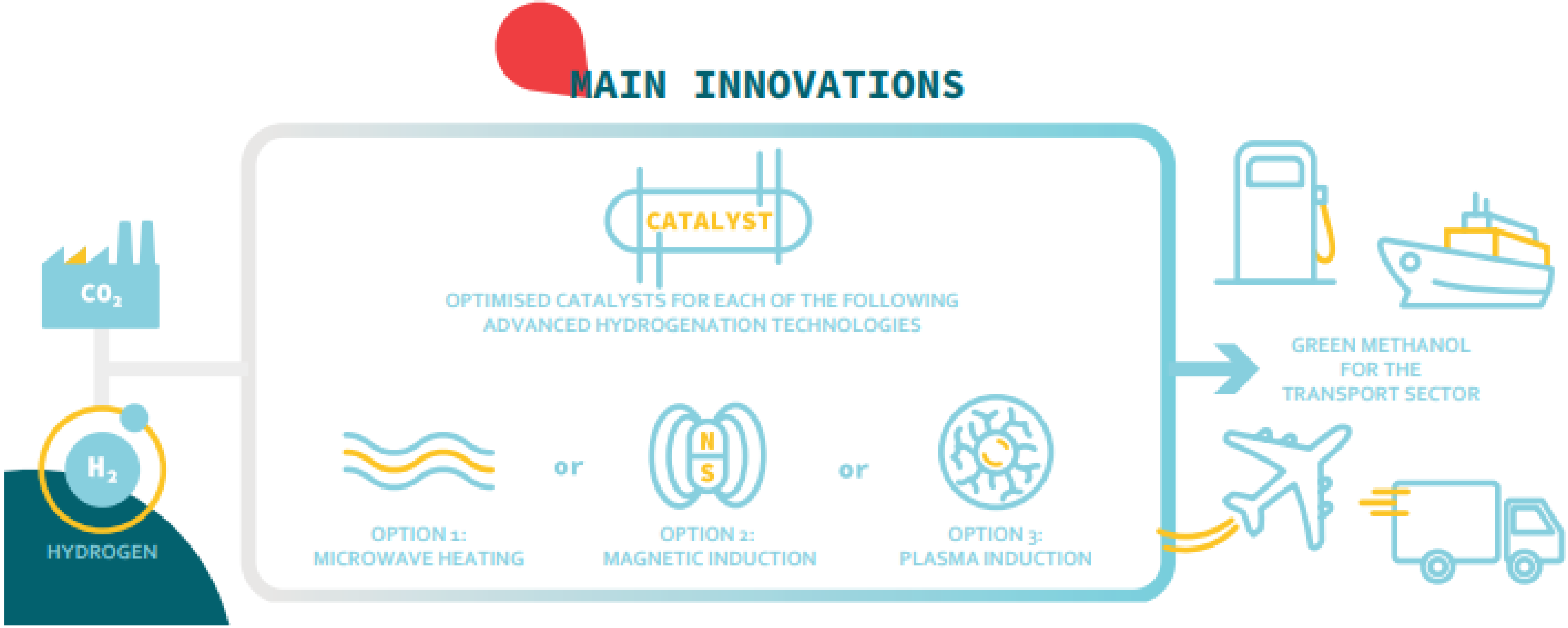
9. TITECH (Japan)
Catalyst and conventional reactor.

東京大学 THE UNIVERSITY OF TOKYO

10. UT (Japan)
Catalyst and conventional reactor.

Schematic overview of the LAURELIN Consortium

Laurelin Project



Schematic overview of the main innovations of the project

Acknowledgements

Andy Beale

June Callison

Sofia Mediavilla-Madrigal

Inés Lezcano-González

Emma Campbell

Lisa Allen

Donato Decarolis

Yiyi Xu

Leila Negahdar

Jun Xian Yap

James Hammerton

Daniel Farooq

Josie Goodall

Katie Morton

Cameron Price

Martin Wilding

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国立研究開発法人
科学技術振興機構
Japan Science and Technology Agency