Towards sustainable production
of chemicals and fuels

Playing with thermodynamics and kinetics: Efficient conversion of CO_2 to chemical energy carriers

Atsushi Urakawa

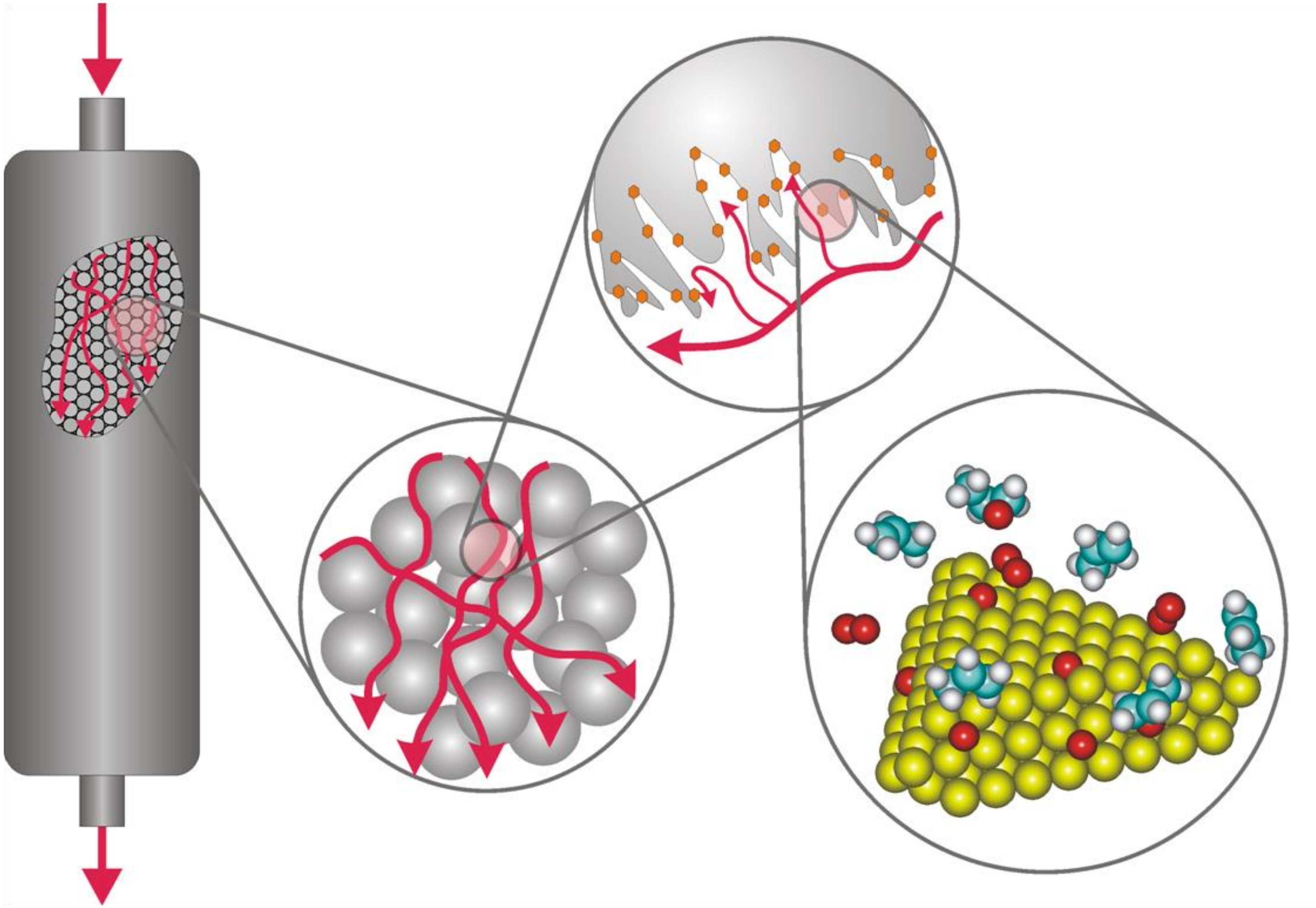
Scale of THE problem

In New York City,
10 m CO_2 spheres emerging
at every **0.58** seconds

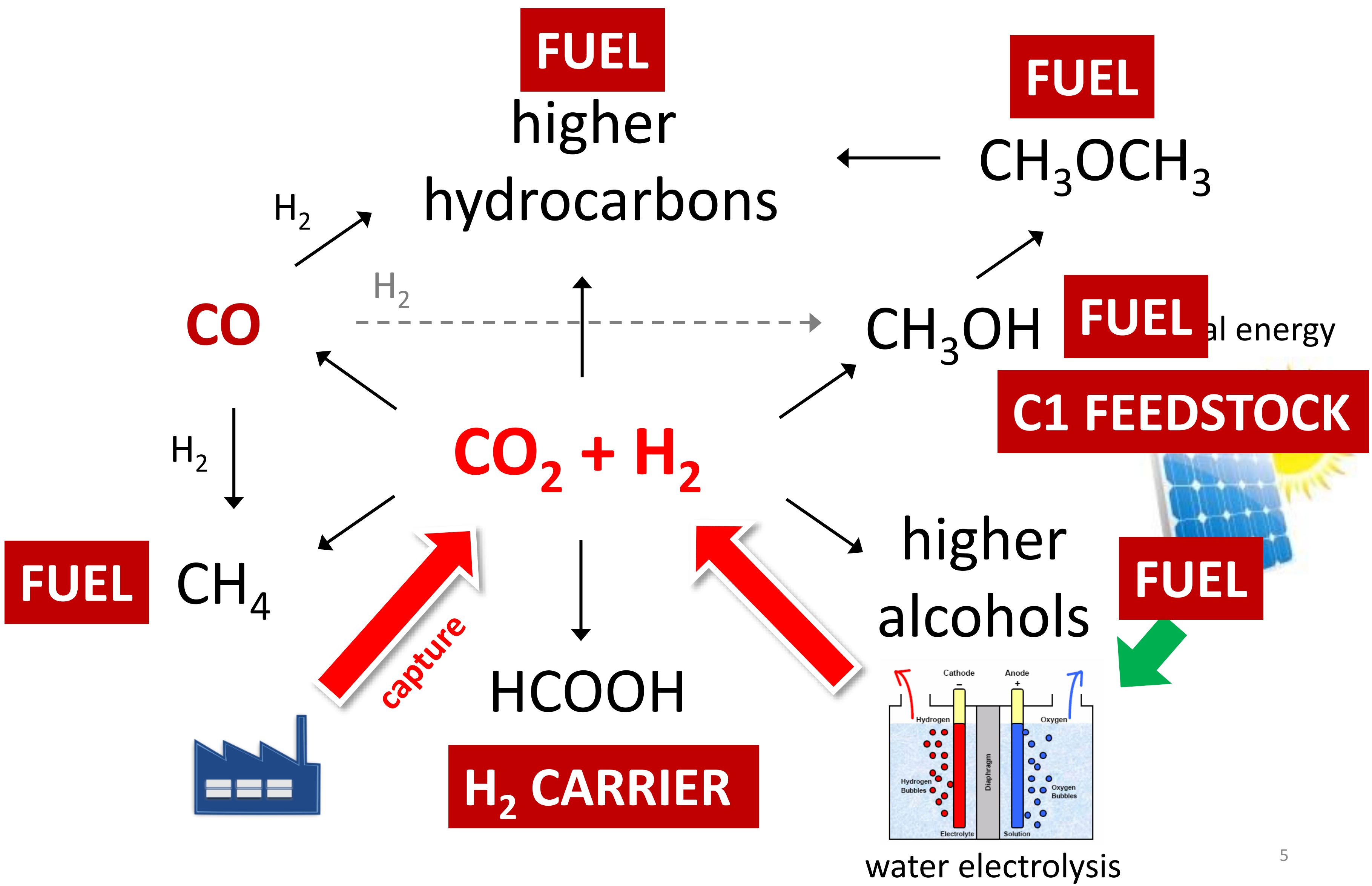
http://www.carbonvisuals.com


After 1 year, **54.3 Mtons** of CO_2
Only in NY city...
http://www.carbonvisuals.com

Heterogeneous catalysis



CO_2 hydrogenation



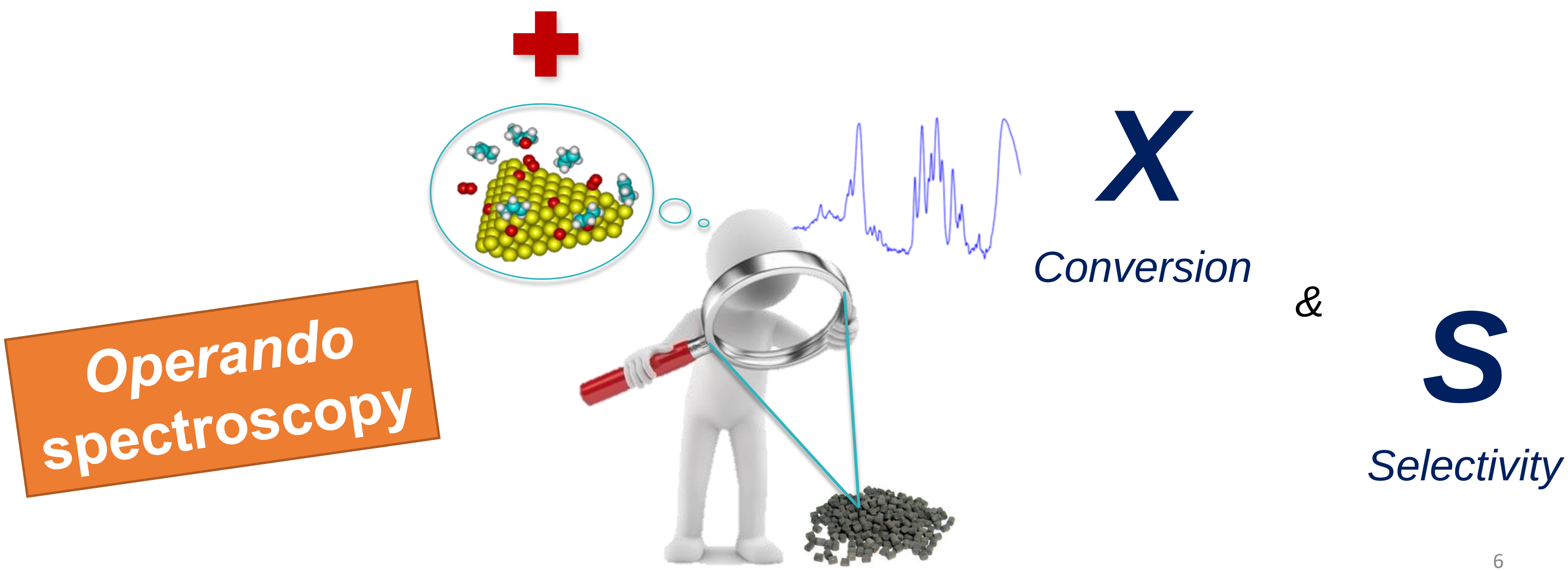
CO_2 to chemical energy carriers

High-pressure approach

- Hydrogenation to **methanol** (and **DME**)
- Hydrogenation to **formic acid** and **methyl formate**
- Dimethyl carbonate (**DMC**) synthesis from CO_2 and methanol

Unsteady-state operation

- CO_2 capture and conversion in one process for **syngas** production



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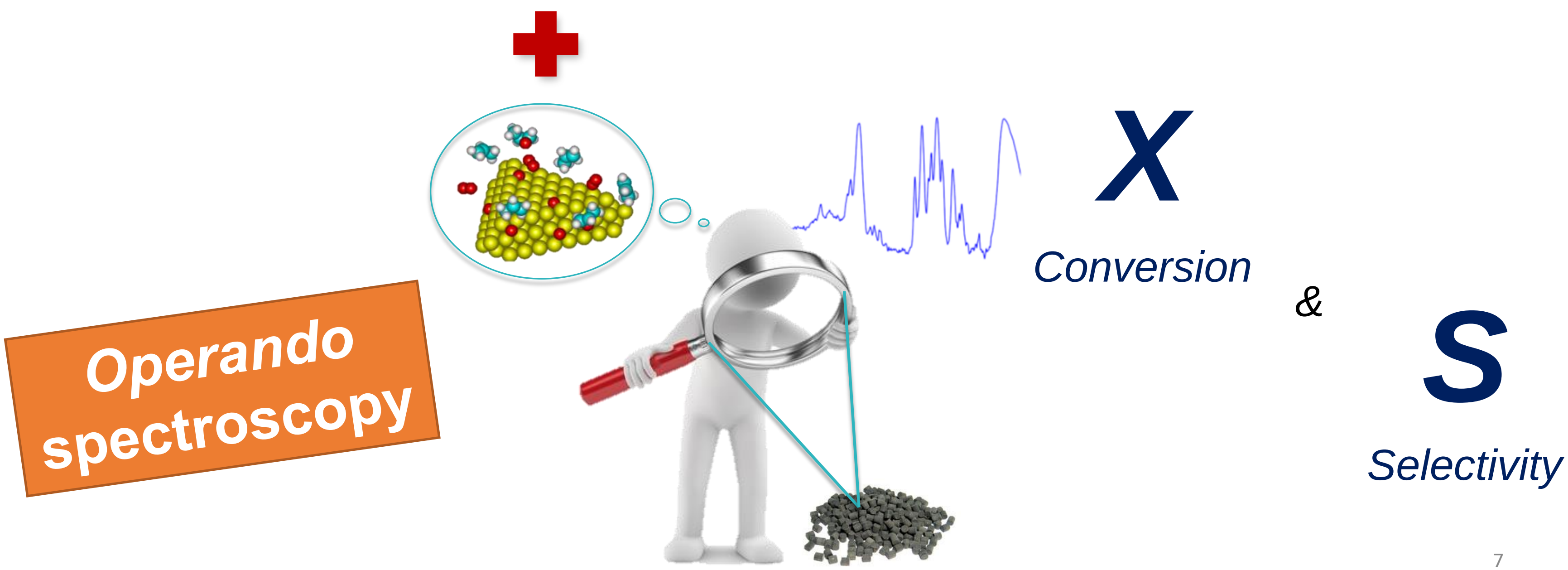


Methanol synthesis

$$\underbrace{CO_2 + 3H_2}_{4} \rightleftarrows \underbrace{CH_3OH + H_2O}_{2} \qquad 4 \rightarrow 2$$

$\Delta H_{298K,5MPa}$ = **- 40.9** kJ·mol^{-1}

RWGS

$$\underbrace{CO_2 + H_2}_{2} \rightleftarrows \underbrace{CO + H_2O}_{2} \qquad 2 \rightarrow 2$$

$\Delta H_{298K,5MPa}$ = **+ 49.8** kJ·mol^{-1}

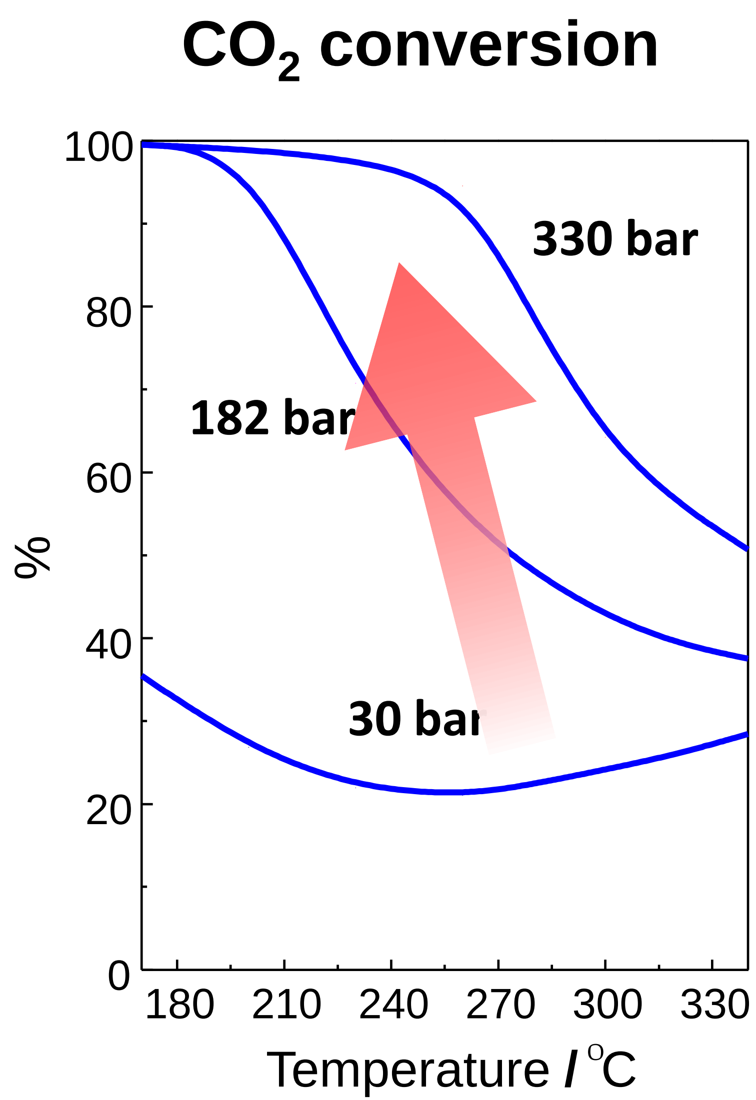
$$\underbrace{CO + 2H_2}_{3} \rightleftarrows CH_3OH \qquad 3 \rightarrow 1$$

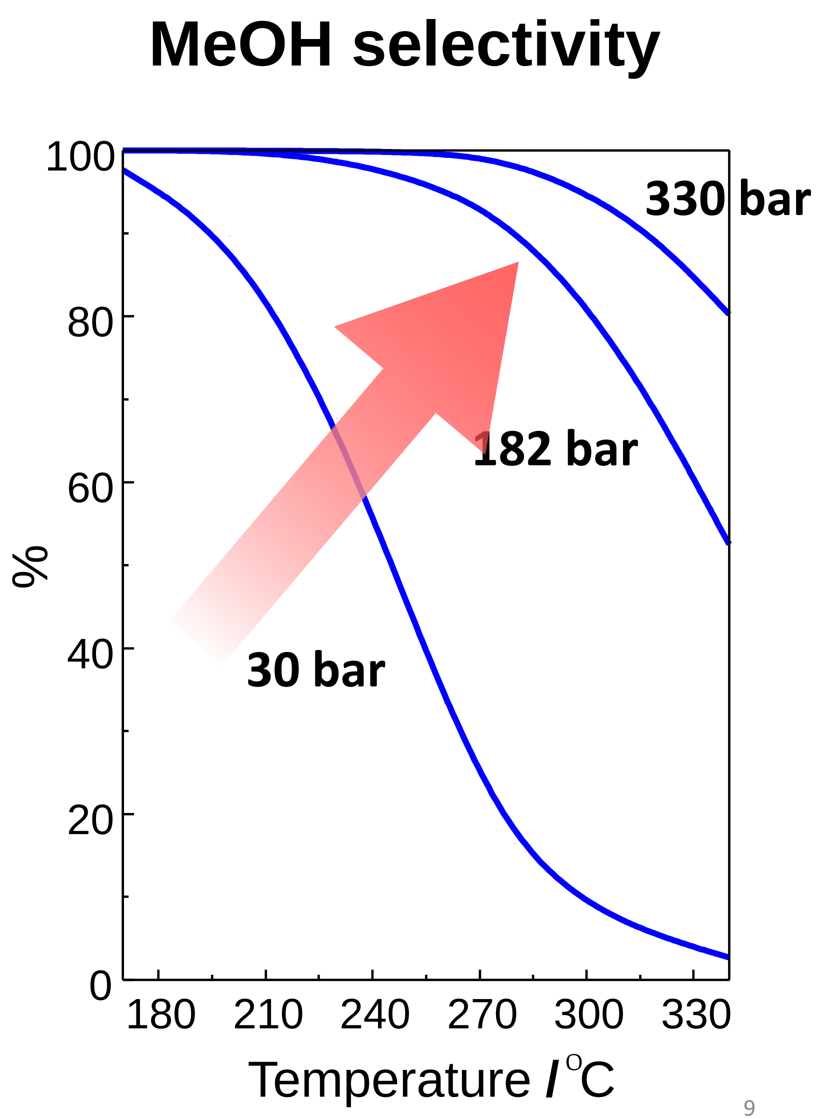
$\Delta H_{298K,5MPa}$ = **- 90.7** kJ·mol^{-1}

Le Châtelier's principle

High pressure & low temperature
are favorable for methanol synthesis

Thermodynamic equilibrium at CO_2:H_2=1:3





High-pressure advantages

High productivity

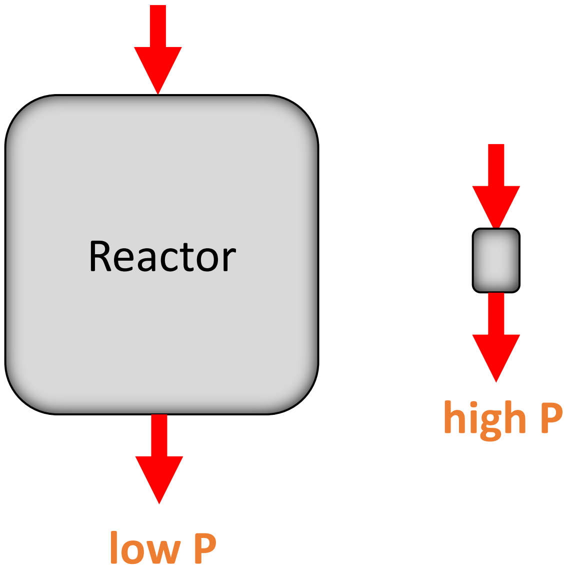
- Thermodynamics
- Kinetics

Supercritical phase

- High density and high diffusivity

Small reactor size

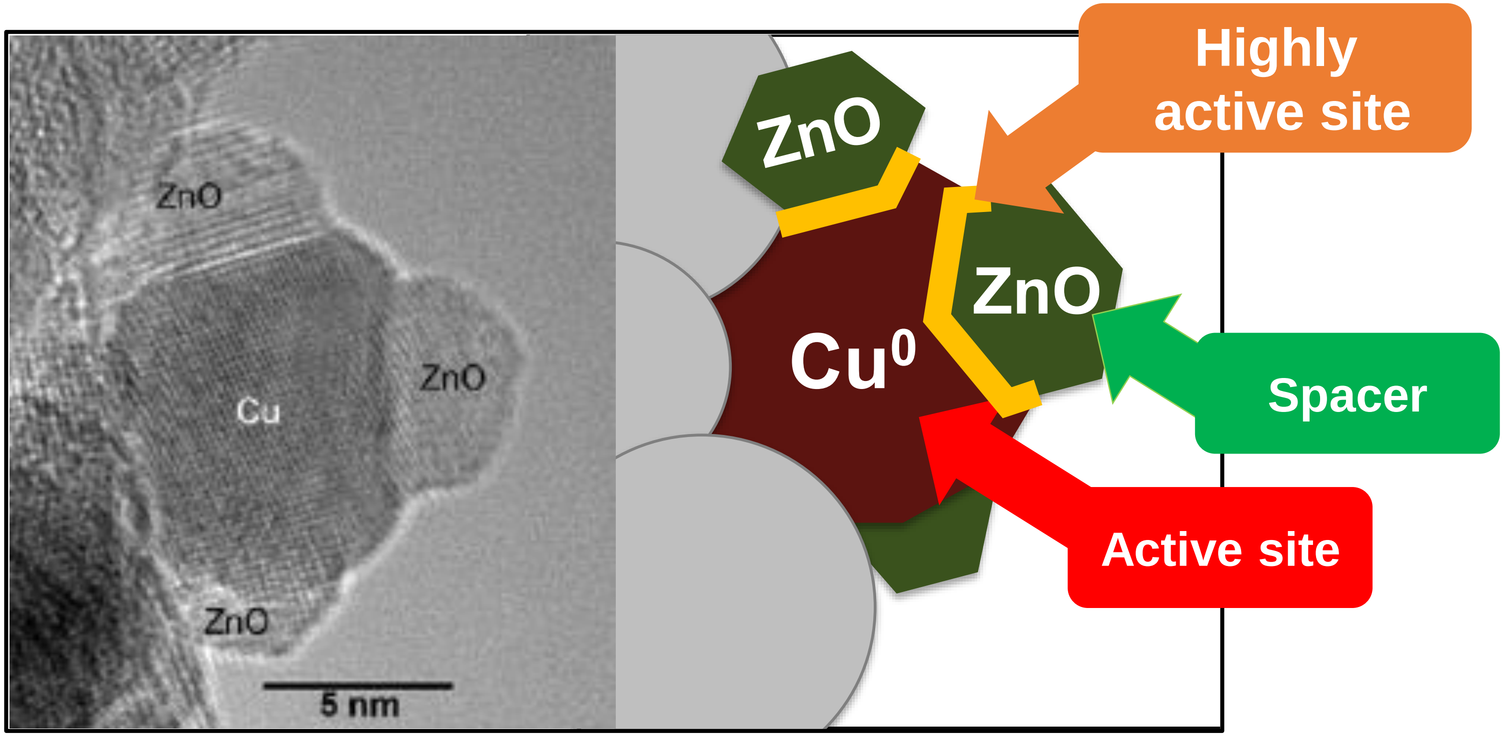
- For compressive fluids
- Economic
- Enhanced safety



NOTE: Old methanol synthesis processes were operated at high-pressure (1920s-1960s, at 250-350 bar)

Nanostructured Cu-ZnO (+Al_2O_3) catalysts

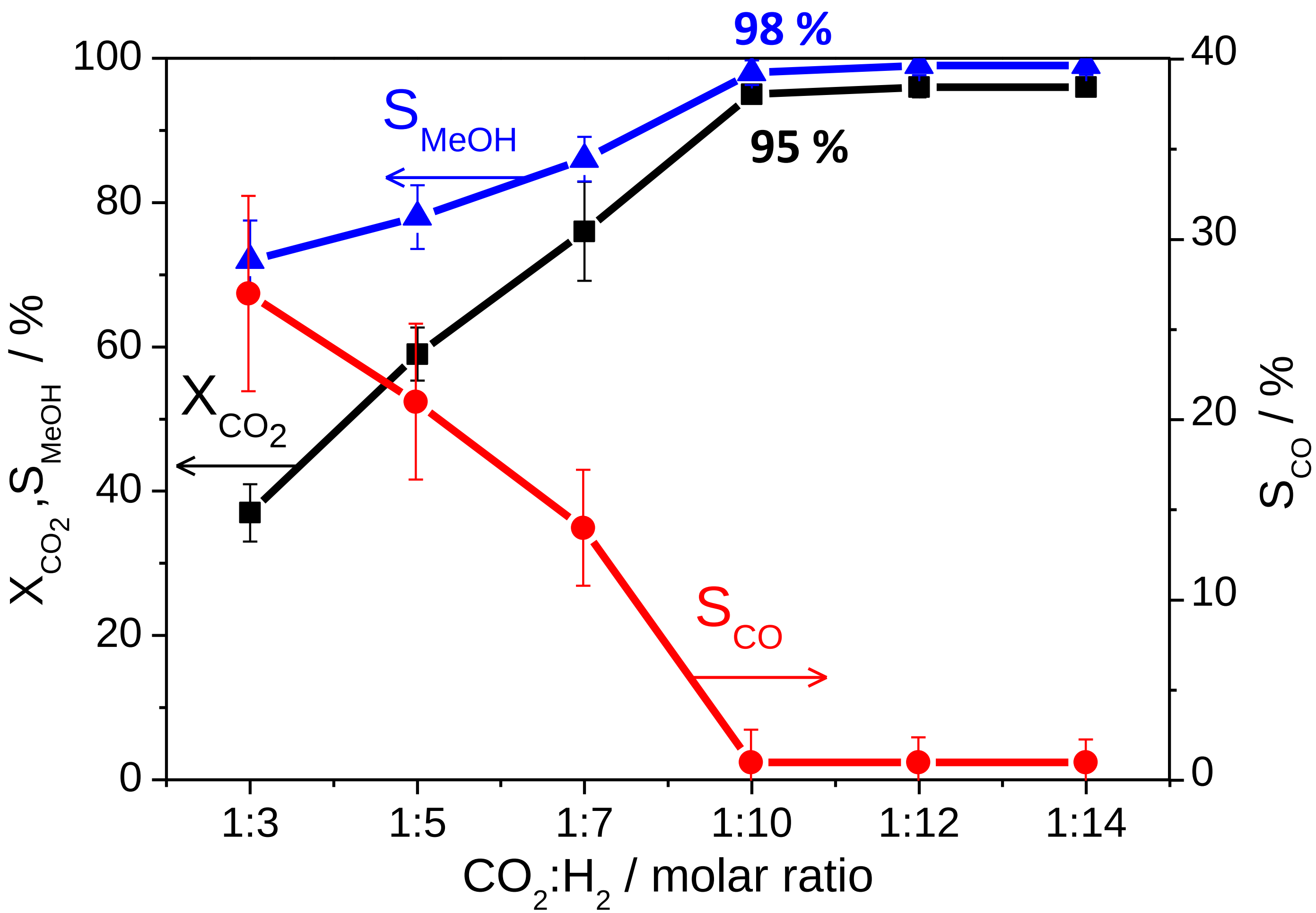
Prepared by **co-precipitation method**



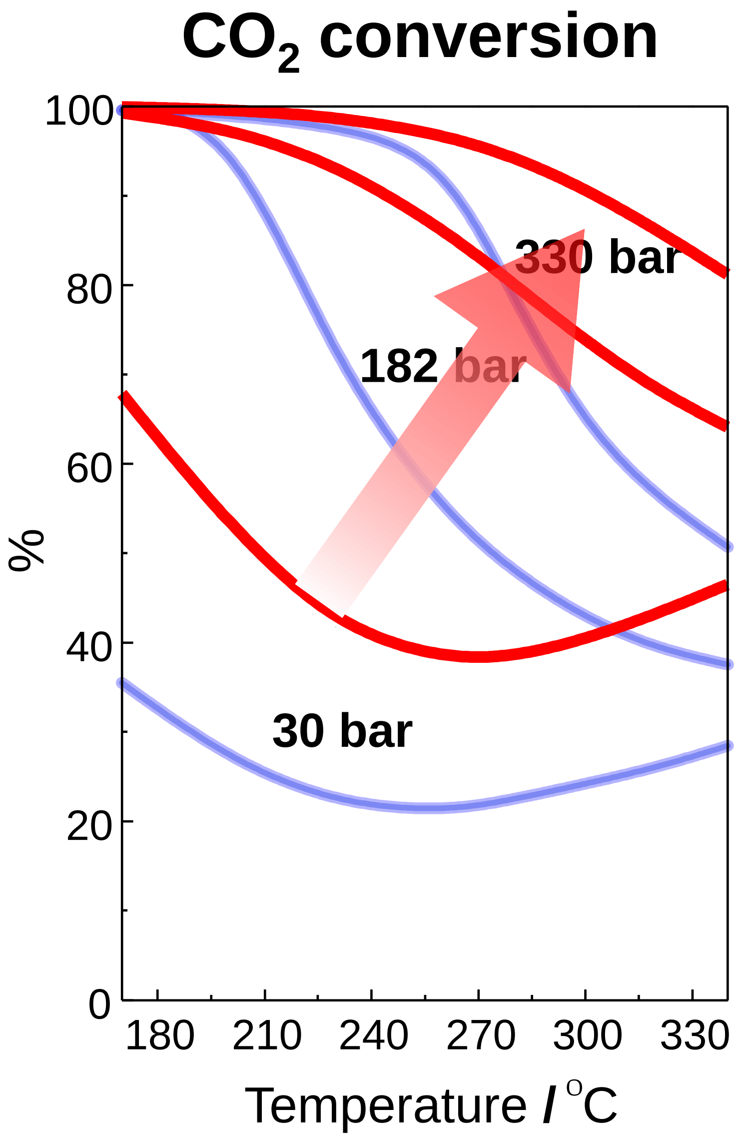
Kasatkin *et al., Angew. Chem. Int. Ed.*, 46, 7324 (2007)

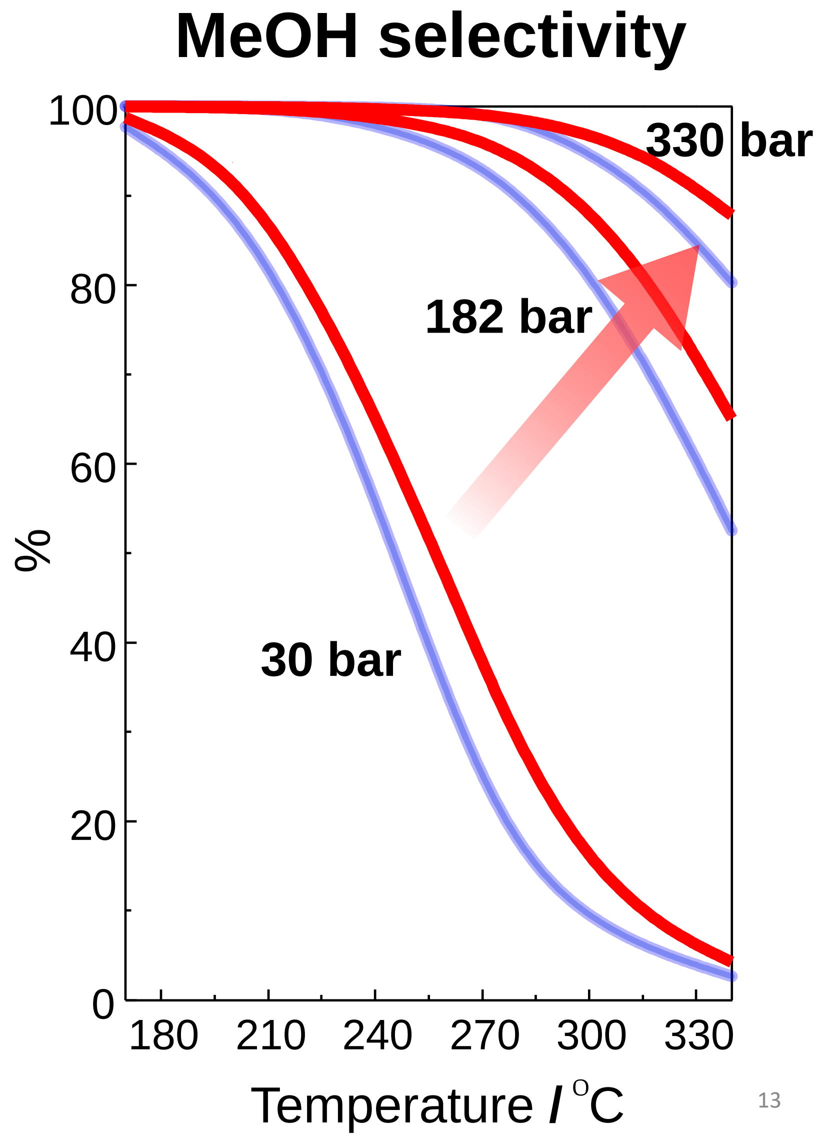
Effects of feed CO_2:H_2 ratio

260 ºC, **330 bar**, GHSV = 10,471 h^{-1}, $Cu/ZnO/Al_2O_3$



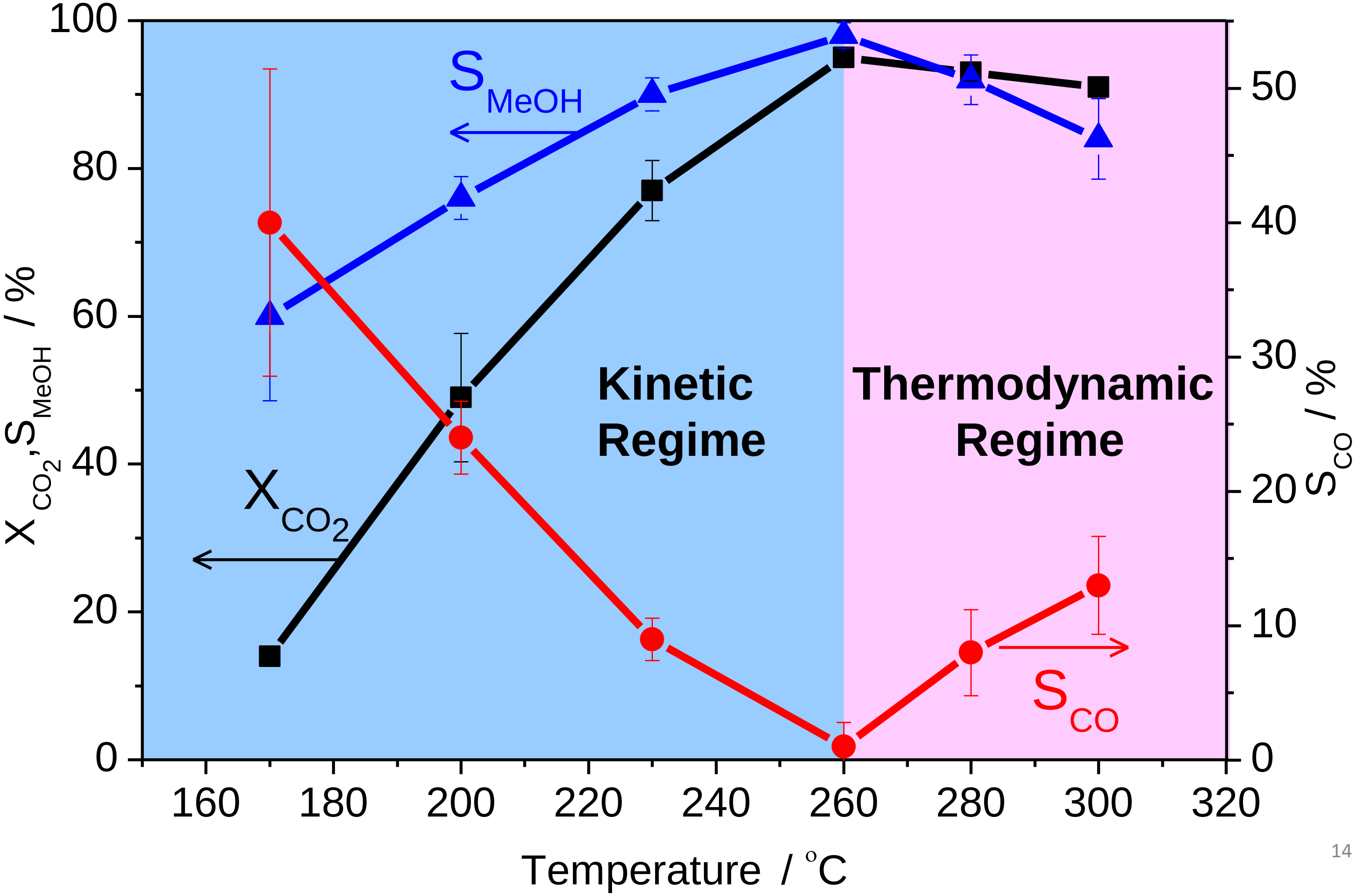
Thermodynamic equilibrium 1:3 vs. 1:10 (CO_2:H_2)





Temperature effects

CO_2:H_2 = 1:10, **330 bar**, GHSV = 10,471 h^{-1}, Cu/ZnO/Al_2O_3

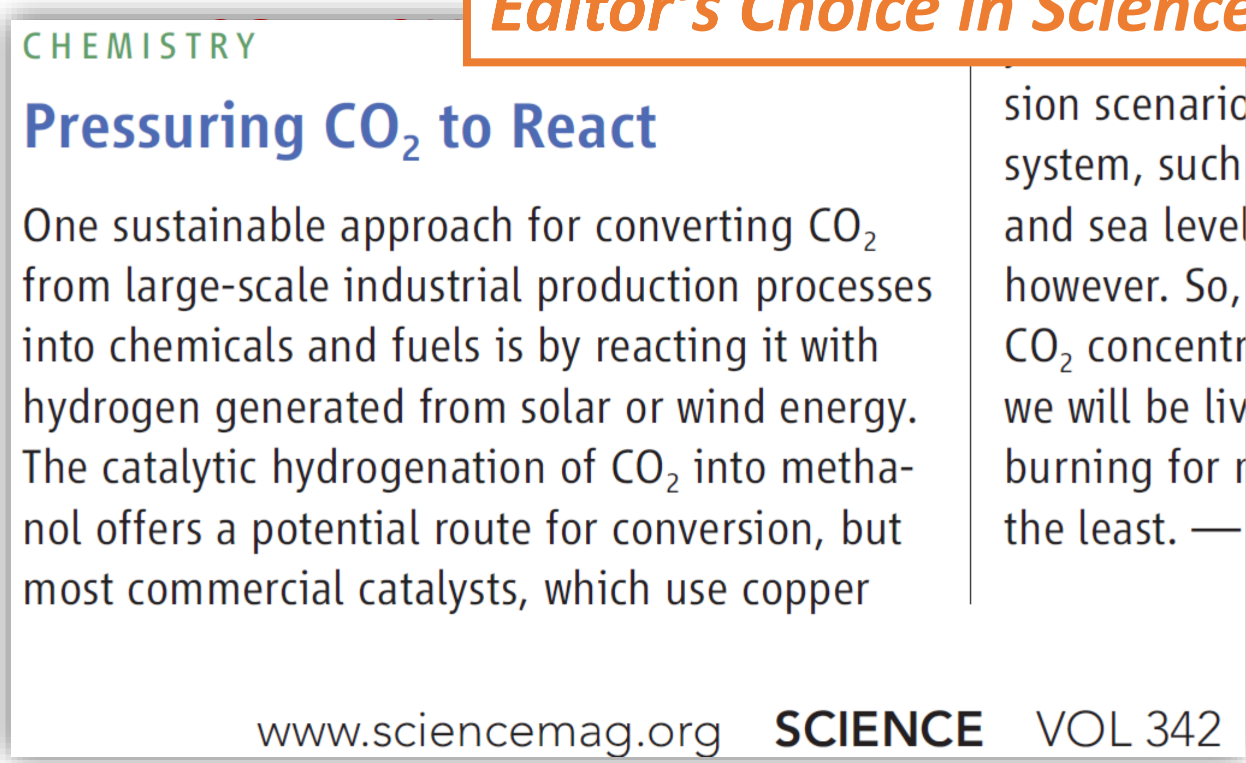


Towards full conversion of CO_2 to methanol

catalytic reactor

under high pressure

Editor's Choice in Science


CHEMISTRY

Pressuring CO_2 to React

One sustainable approach for converting CO_2 from large-scale industrial production processes into chemicals and fuels is by reacting it with hydrogen generated from solar or wind energy. The catalytic hydrogenation of CO_2 into methanol offers a potential route for conversion, but most commercial catalysts, which use copper

sion scenario
system, such
and sea level
however. So,
CO_2 concentr
we will be liv
burning for r
the least. —

www.sciencemag.org SCIENCE VOL 342

$H_3OH + H_2O$

Our process

>95%

>98%

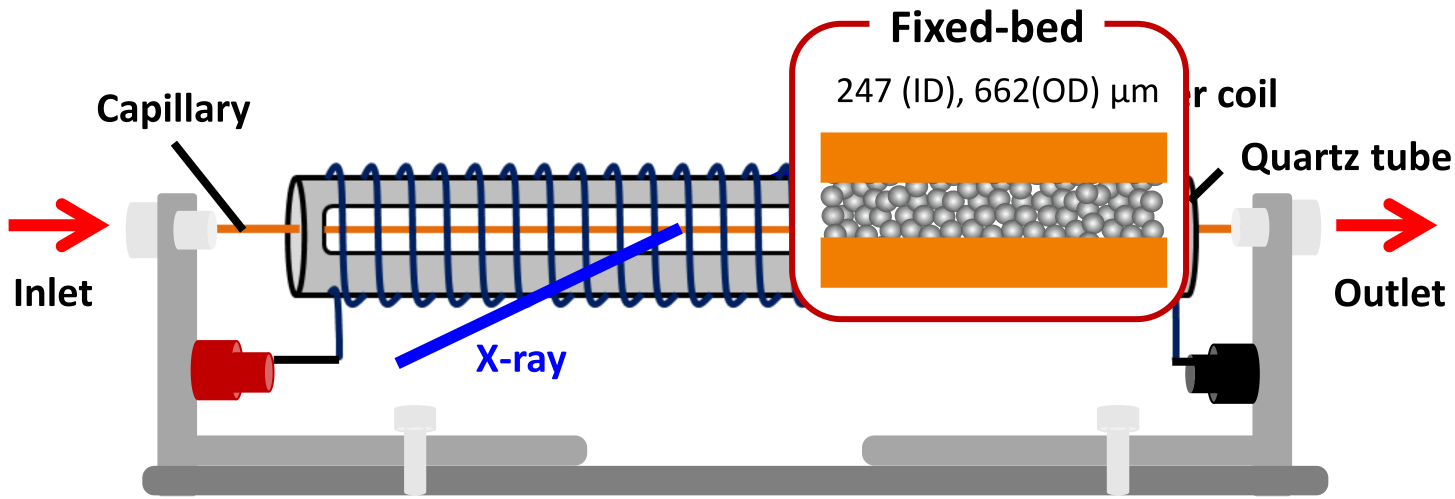
1-15.3 $g_{MeOH}\ g_{cat}^{-1}\ h^{-1}$

Bansode & Urakawa, *J. Catal.* 309, 66 (2014)

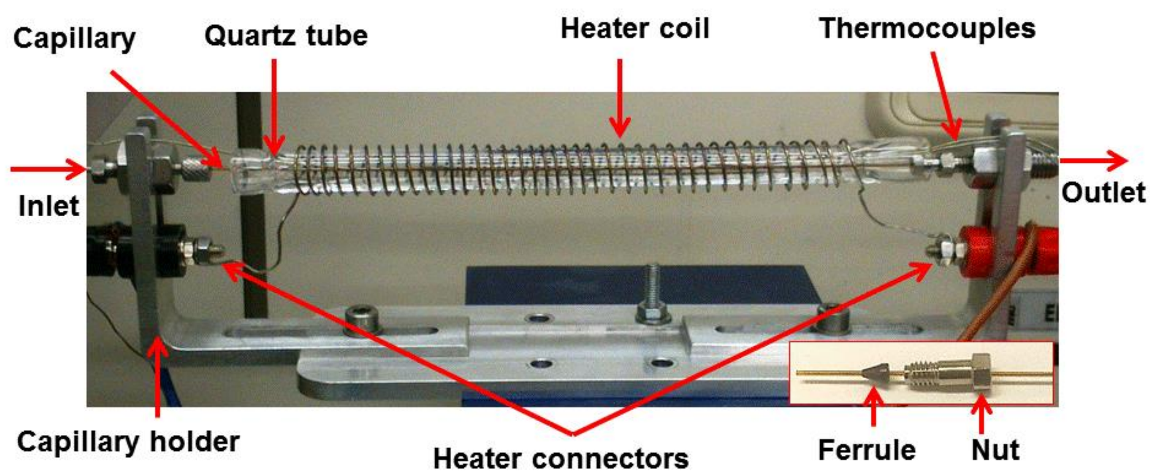
Granted patents: EP13724223, US9133084, CN104321293

Stoichiometric: Gaikwad, Bansode, Urakawa *J. Catal. 343, 127* (2016), EP16382062

High-pressure *operando* XAFS



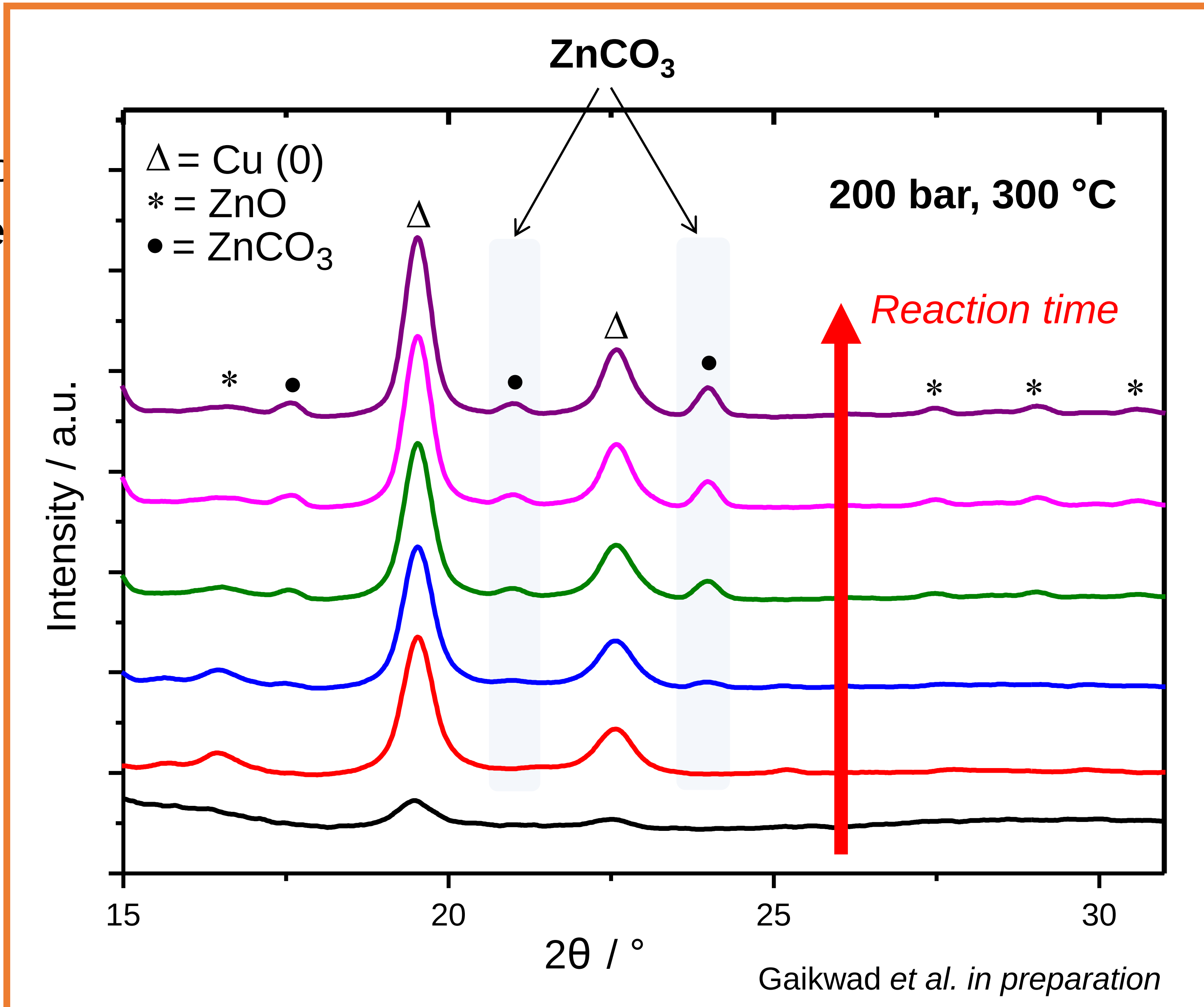
- Plug-flow
- 300 °C & 330 bar
- Fused silica capillary
- Facile construction
- Tunable length
- Space-resolved study
- Relevant activity



Bansode, Urakawa, et al., *Rev. Sci. Instrum.* 85, 084105 (2014)

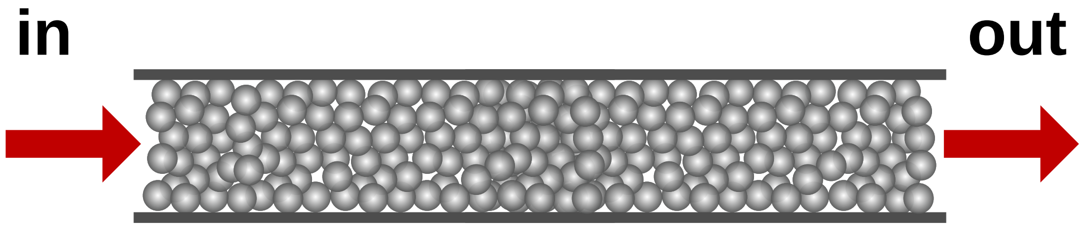
High-pressure *operando* XRD

- CO_2:
- Up to
- Fuse

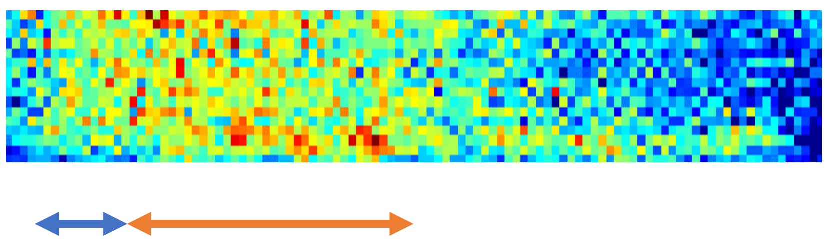


Temperature gradients @ 200 bar, CO_2:H_2 = 1:3

+ *operando* Raman for C profiling



ΔT = +2 °C



$CO_2 \rightarrow CO \rightarrow CH_3OH$

endothermic exothermic

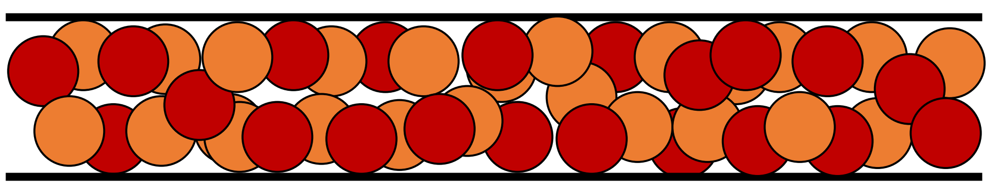
Gaikwad, Phongprueksathat *et al.*, *Catal. Sci. Technol.*, 10, 2763 (2020)

Direct DME synthesis

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = \mathbf{-\ 23.5}\ kJ \cdot mol^{-1}$$

$Cu/ZnO/Al_2O_3$ **H-ZSM-5**

Reactor

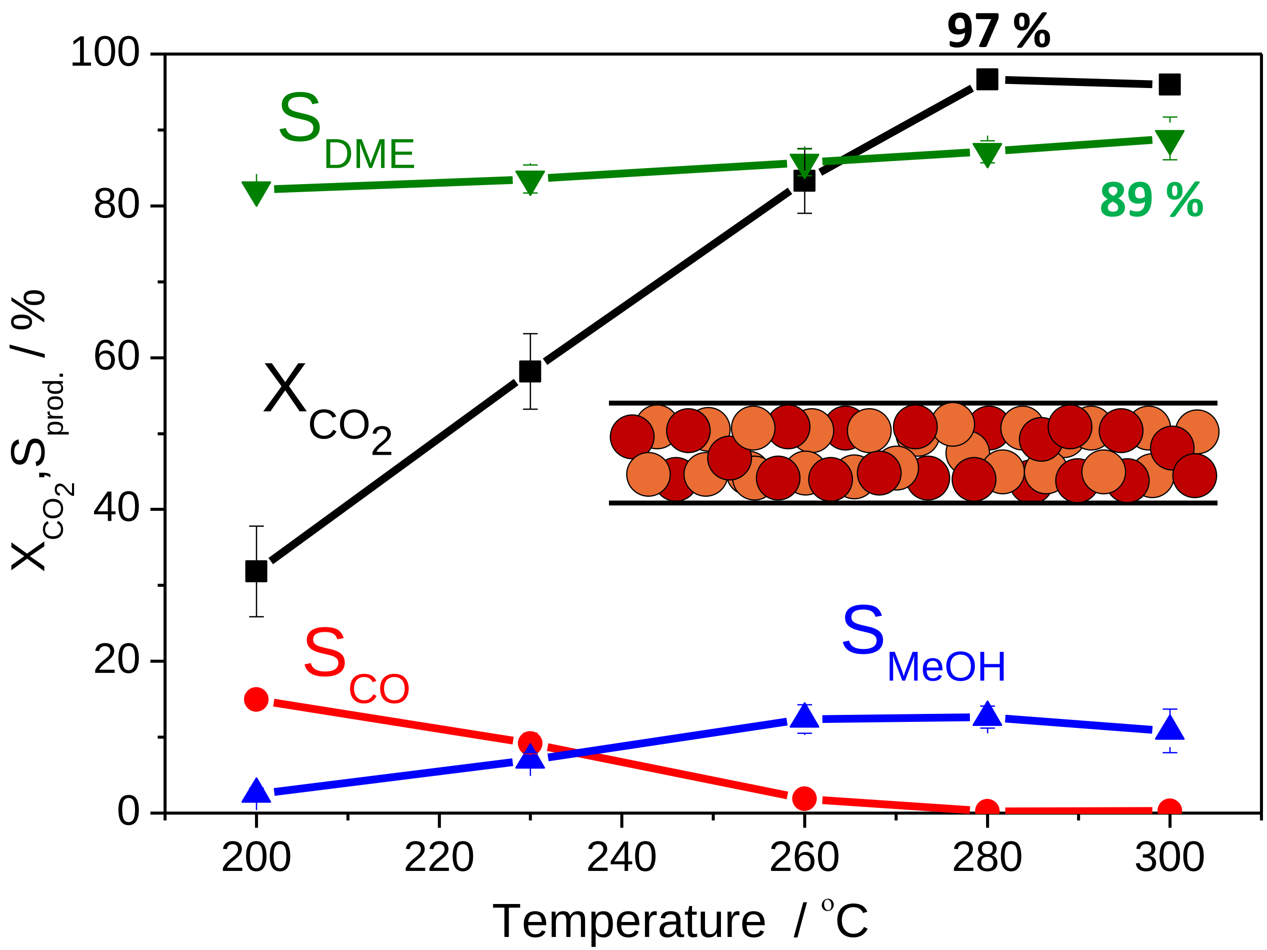


Mixed Bed

Direct DME synthesis

$CO_2:H_2$ = **1:10**, P = **360** bar, GHSV = 10471 h^{-1}

$Cu/ZnO/Al_2O_3$ + H-ZSM-5 **mixed** catalyst bed



Bansode & Urakawa, *J. Catal.* 309, 66 (2014)

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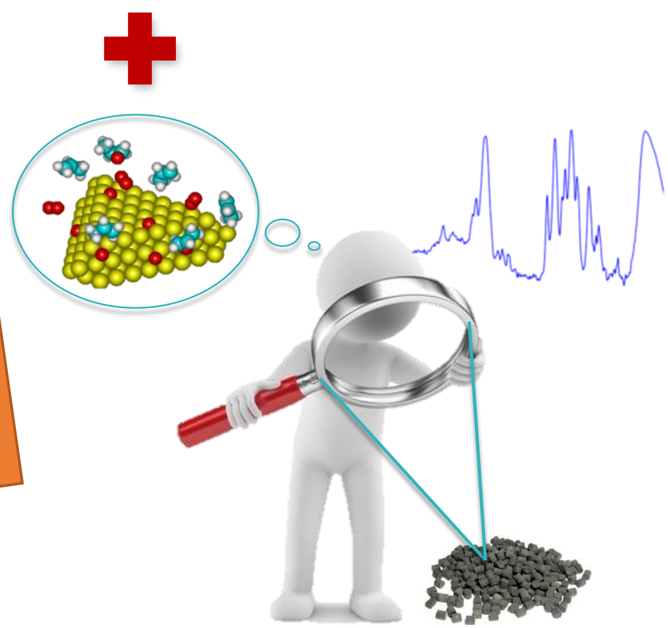
Operando spectroscopy



X

Conversion

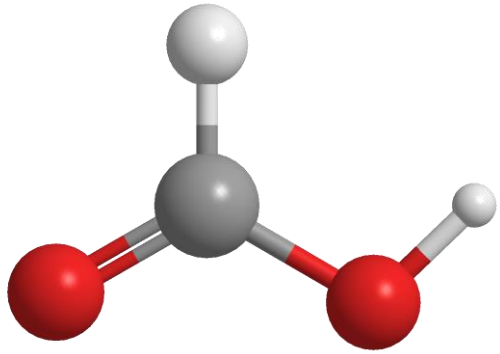
&

S

Selectivity

Formic acid

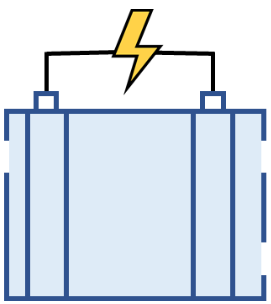
HCOOH (FA)



Chemicals

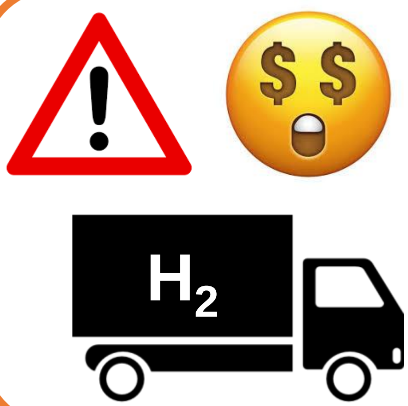
Feed preservation

Leather processing



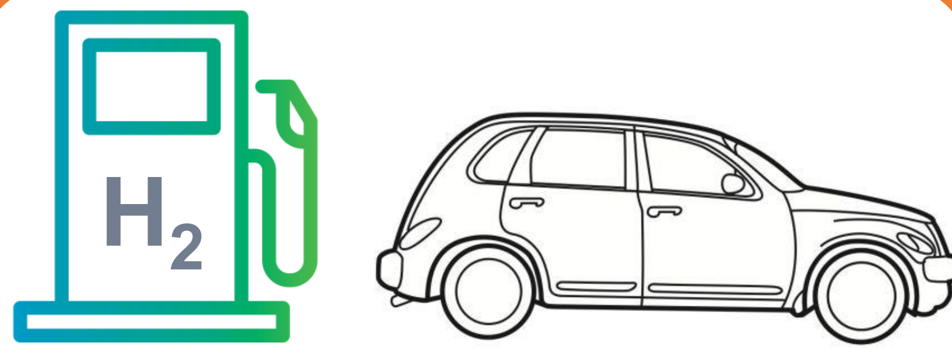
Fuel cell

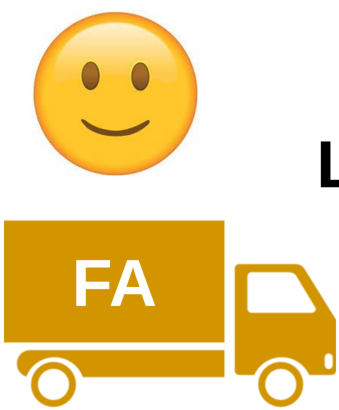
Formic acid: Promising energy carrier



700 bar
39.4 g L^{-1}

TOYOTA Mirai | **HONDA** Clarity | **HYUNDAI** Tucson





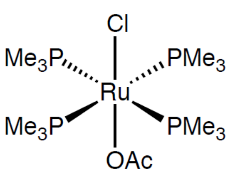
Liquid at RT
53 g L^{-1}

$FA \rightarrow H_2 + CO_2$

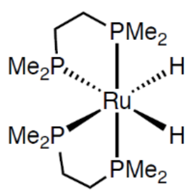
CO_2 Hydrogenation to FA

$$CO_2 + H_2 \rightleftharpoons HCOOH$$

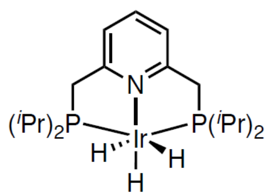
Active transition-metal (Ru & Ir) catalysts since mid 1970s



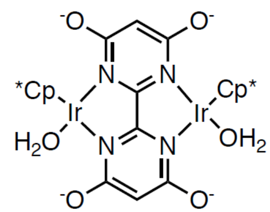
Jessop
JACS 2002



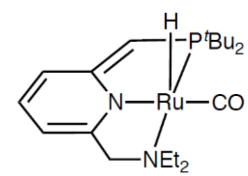
Baiker
Chem Comm 2007



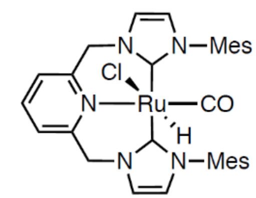
Nozaki
JACS 2009



Fujita
Nat Chem 2012



Sanford
ACS Catal 2013



Pidko
ACS Catal 2015

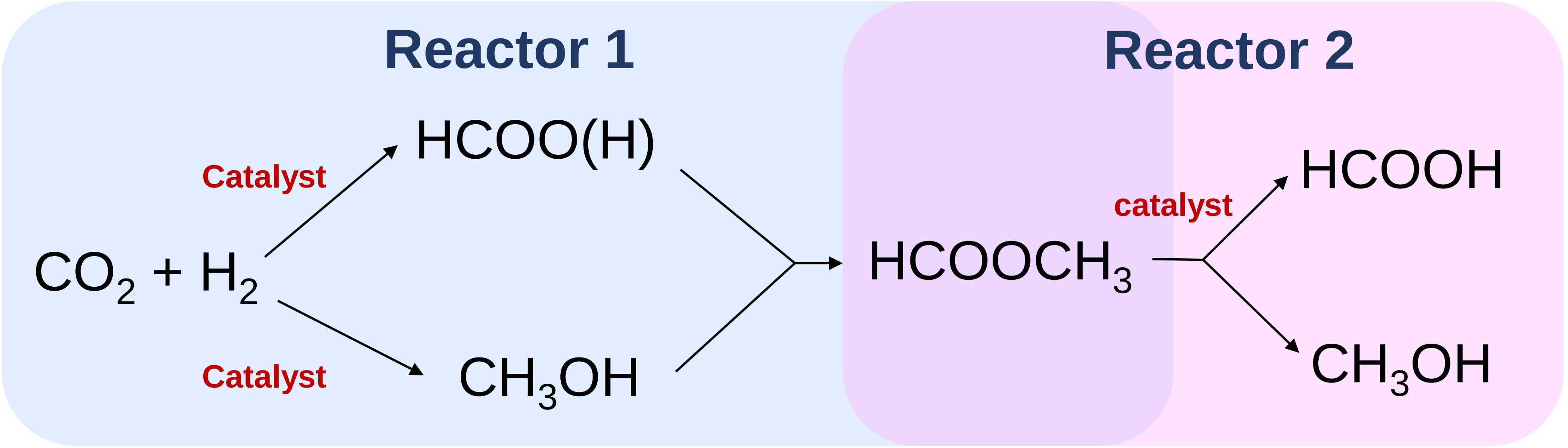
Breakthrough in the 1990s by Noyori's group

- Ru complexes
- In *supercritical* CO_2
- CO_2 as reactant and solvent
- Very high activity

Jessop, Ikariya, Noyori, *Nature*, 368, 231 (1994)
Jessop, Ikariya, Noyori, *Science*, 269, 1065, (1995)

Methyl formate (MF)

2-step synthesis



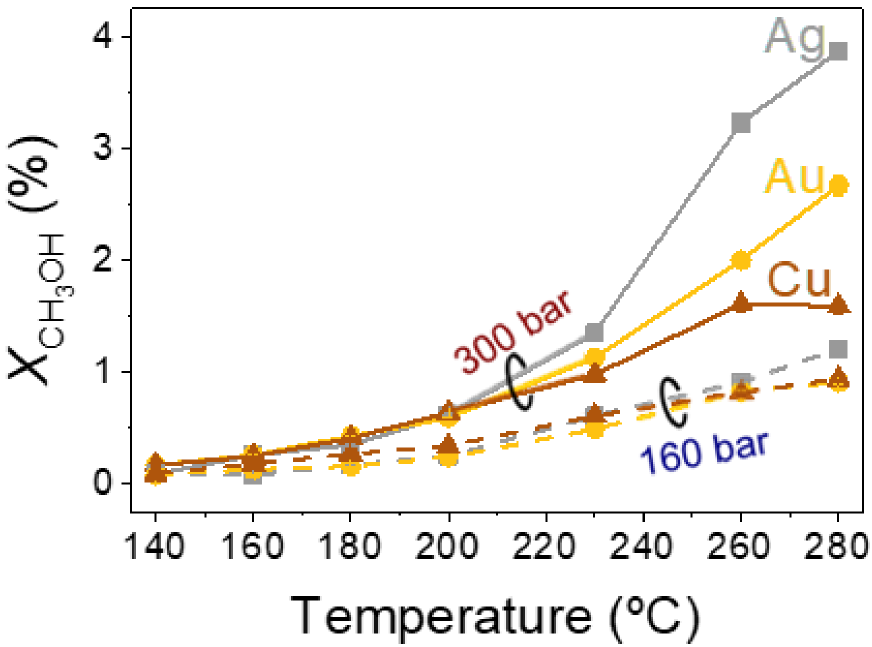
Metal effects on MF synthesis

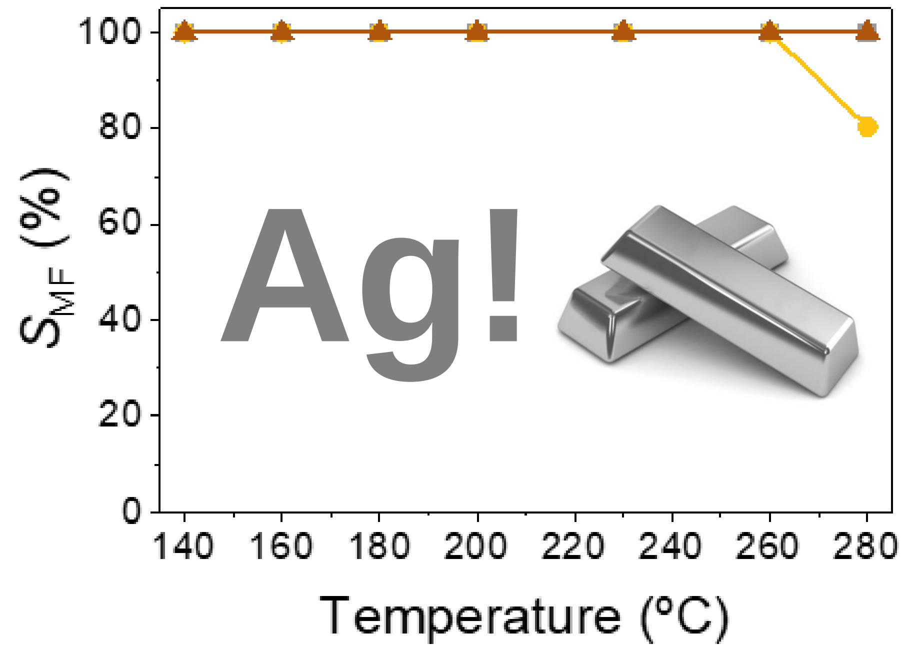
Au catalysts for formates synthesis

Au/TiO_2	Preti *et al.*, *Angew. Chem. Int. Ed.*, 50, 12551 (2011)
Au/ZrO_2	Wu *et al.*, *Green. Chem.*, 17, 1467 (2015)
Au/Al_2O_3	Filonenko *et al.*, *J. Catal.*, 343, 97 (2016)

MF

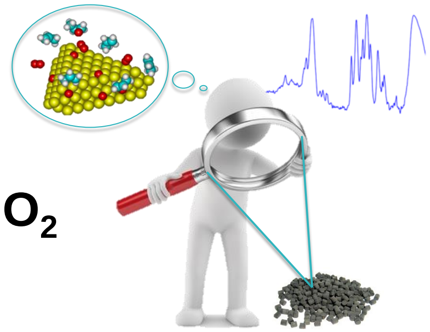
Continuous, 1 wt% M (**Cu**, **Ag**, **Au**)/**SiO_2**, CO_2:H_2:CH_3OH = 4:4:1, 6000 h^{-1}





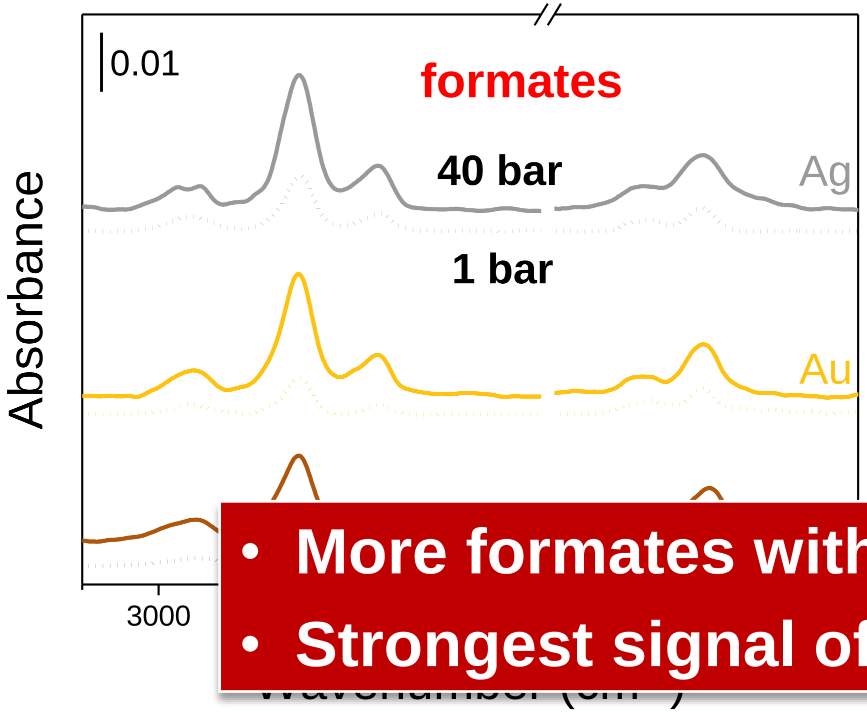
In situ DRIFTS & Raman spectroscopy

CO_2:H_2 = 1:1, 230 °C



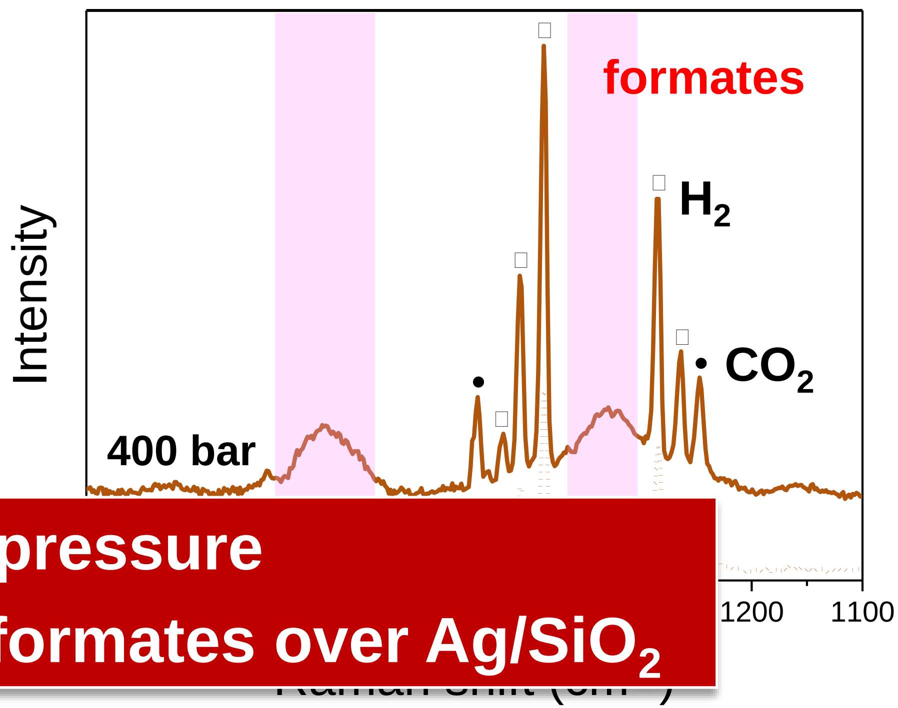
1 wt% M (**Cu**, **Ag**, **Au**)/SiO_2

DRIFTS



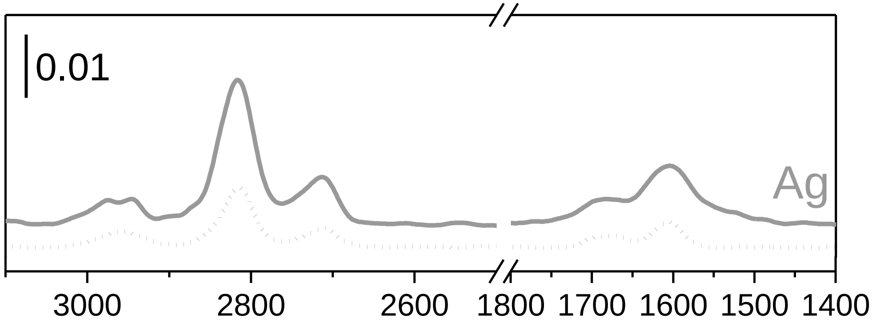
1 wt% **Cu**/SiO_2

Raman



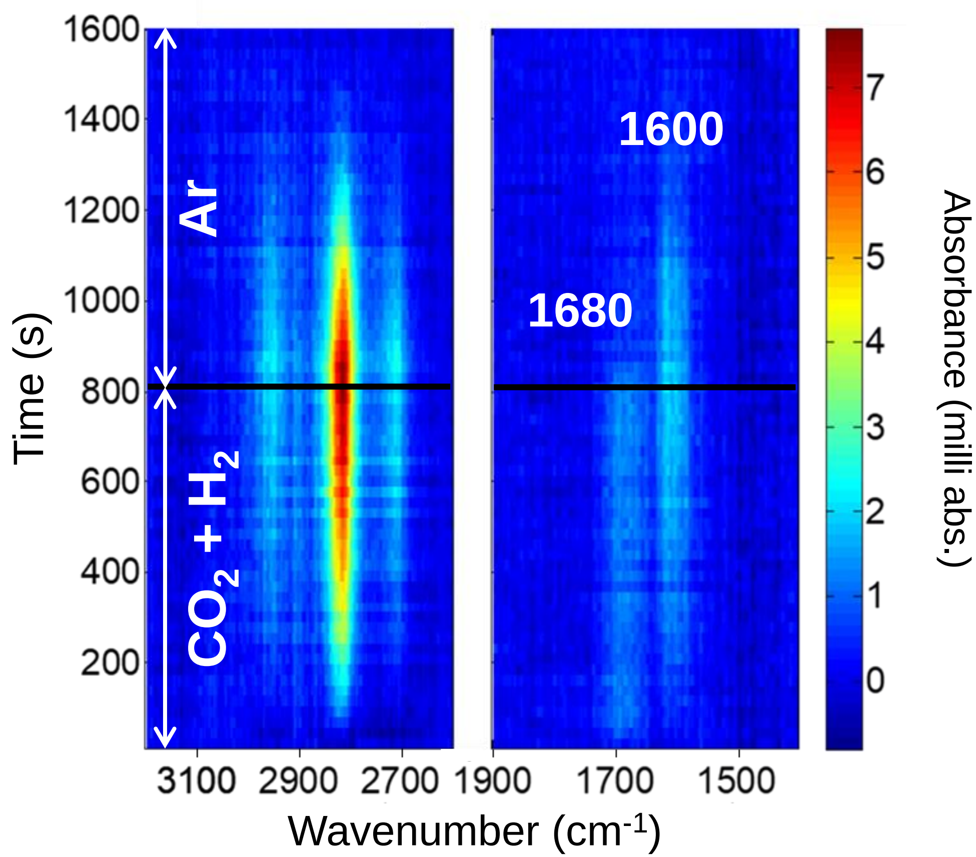
- **More formates with pressure**
- **Strongest signal of formates over Ag/SiO_2**

Transient *operando* DRIFTS @ 5 bar

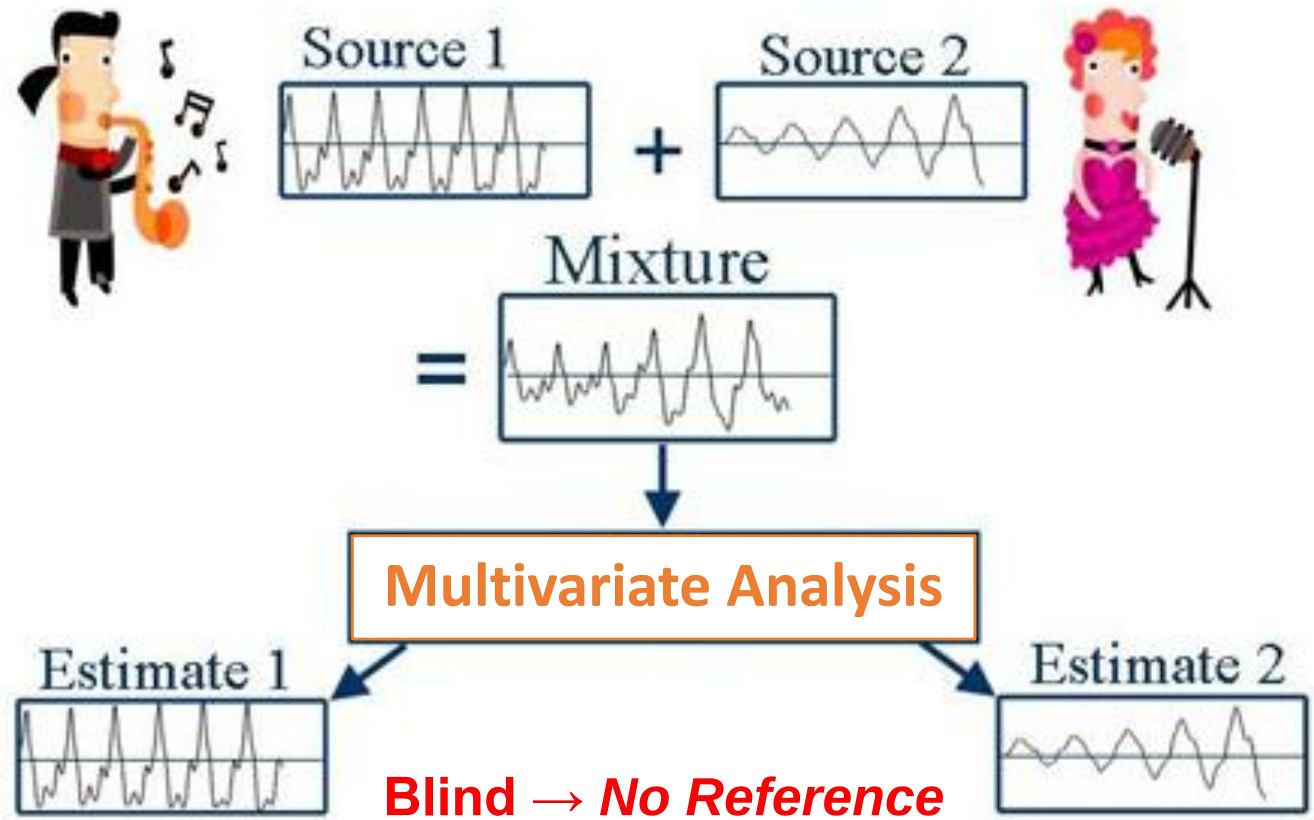


Q

How many surface species?
What kind of formates?



Reducing spectral complexity: Blind source separation (multivariate analysis)



Blind → *No Reference*

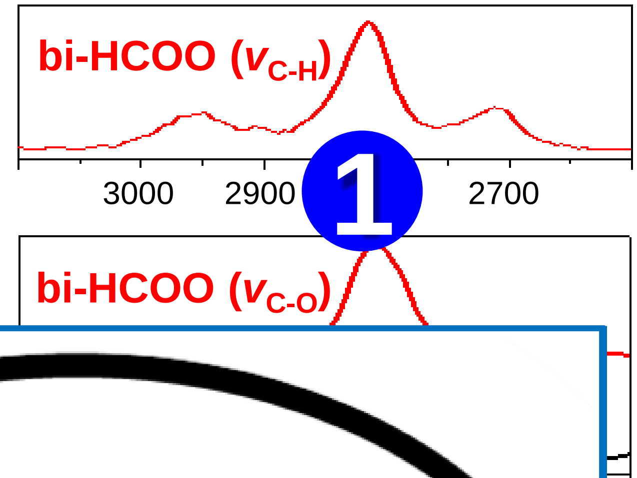
Multivariate **C**urve **R**esolution
(**MCR**)

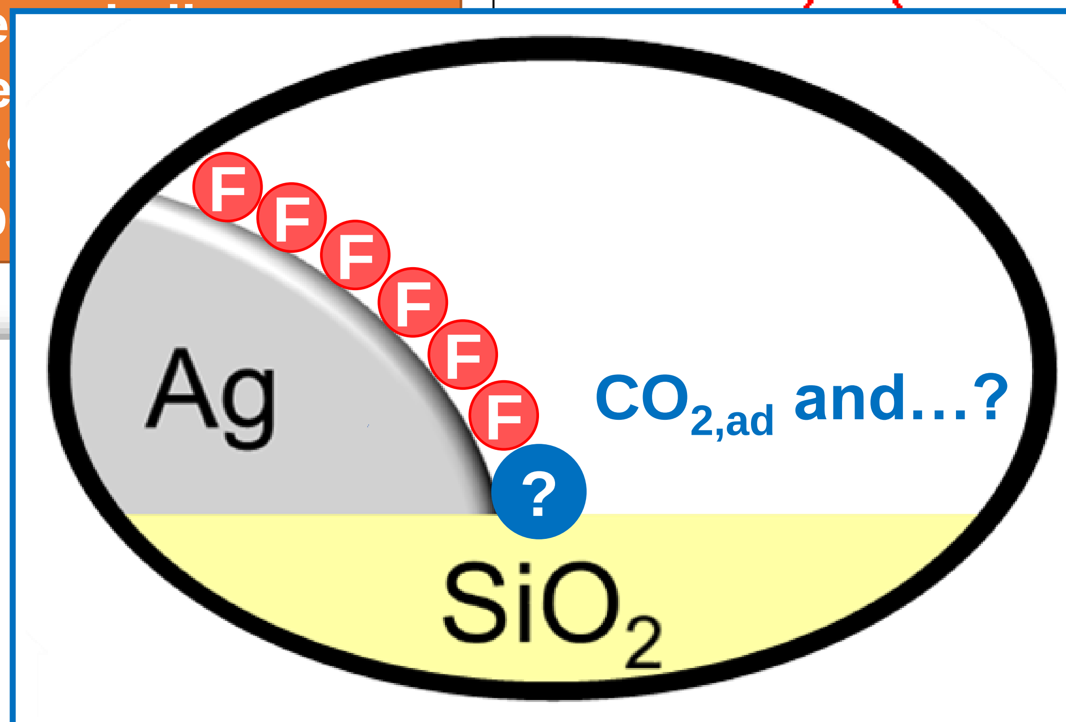
Source: interactive audio lab

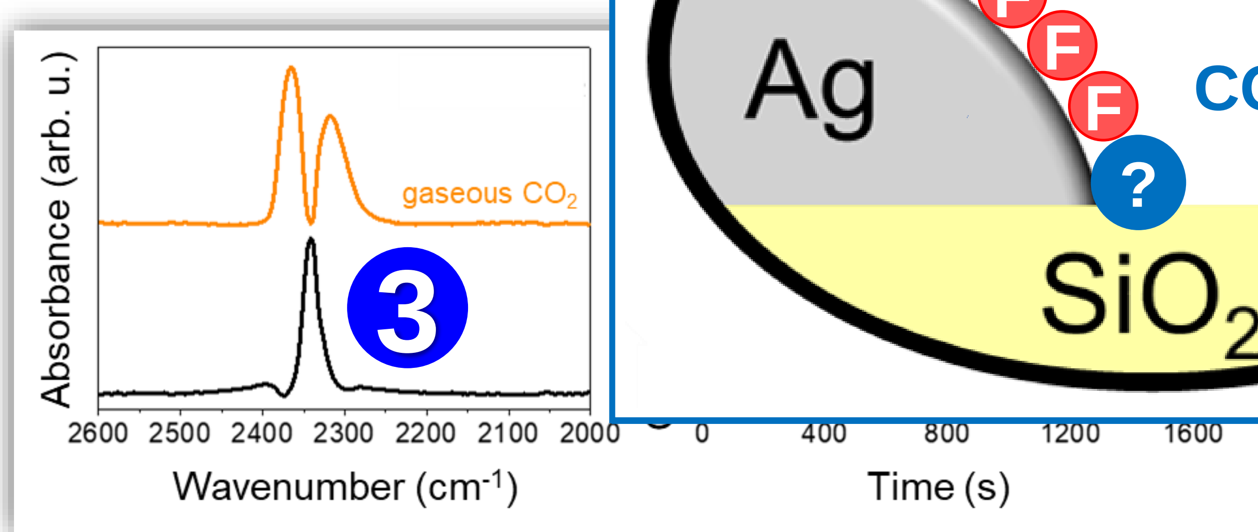
Identification of surface species

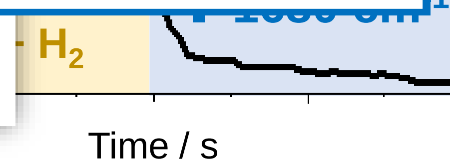
Three different surface species:
1. 1600 & 2817 cm^{-1} - bi-HCOO
2. 1680 cm^{-1} - ?
3. 2330 cm^{-1} - ??

- 2 & 3 kinetically ve
- But… different spe
- Also observed for S
- Less pressure dep

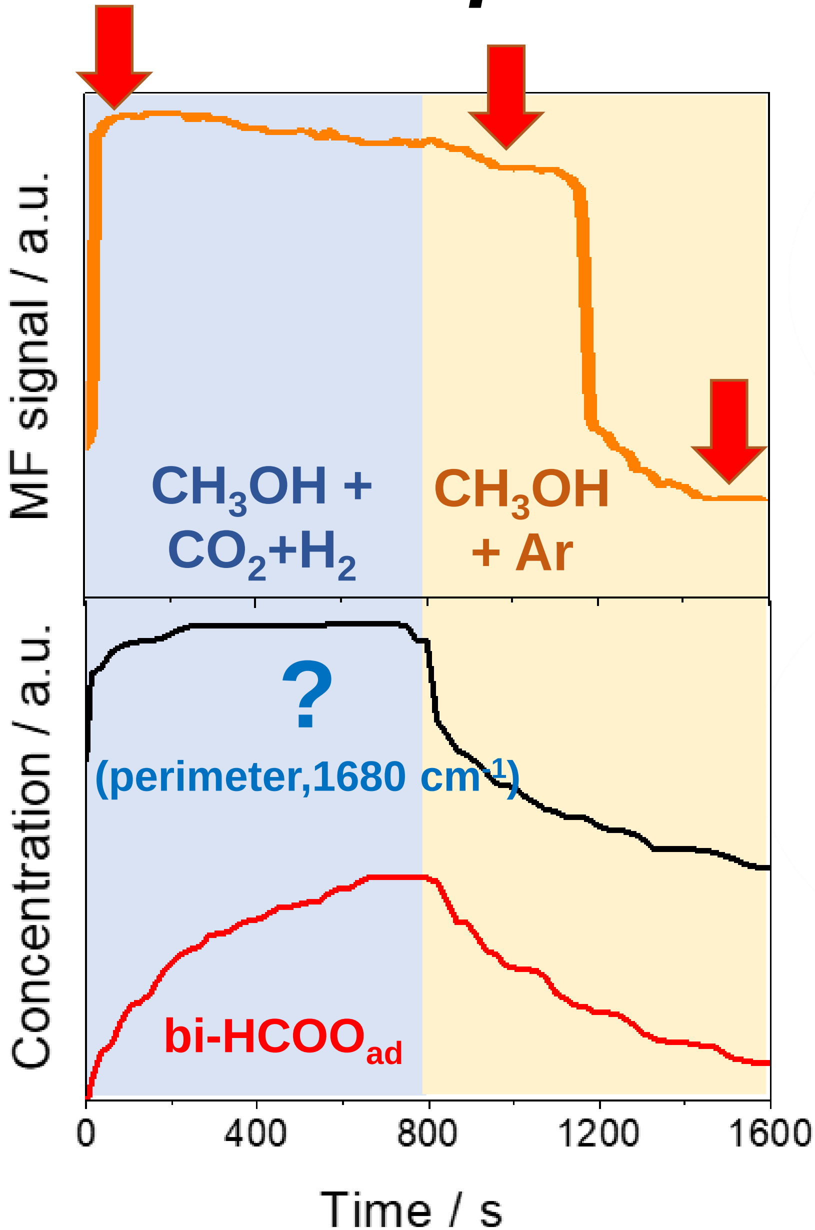


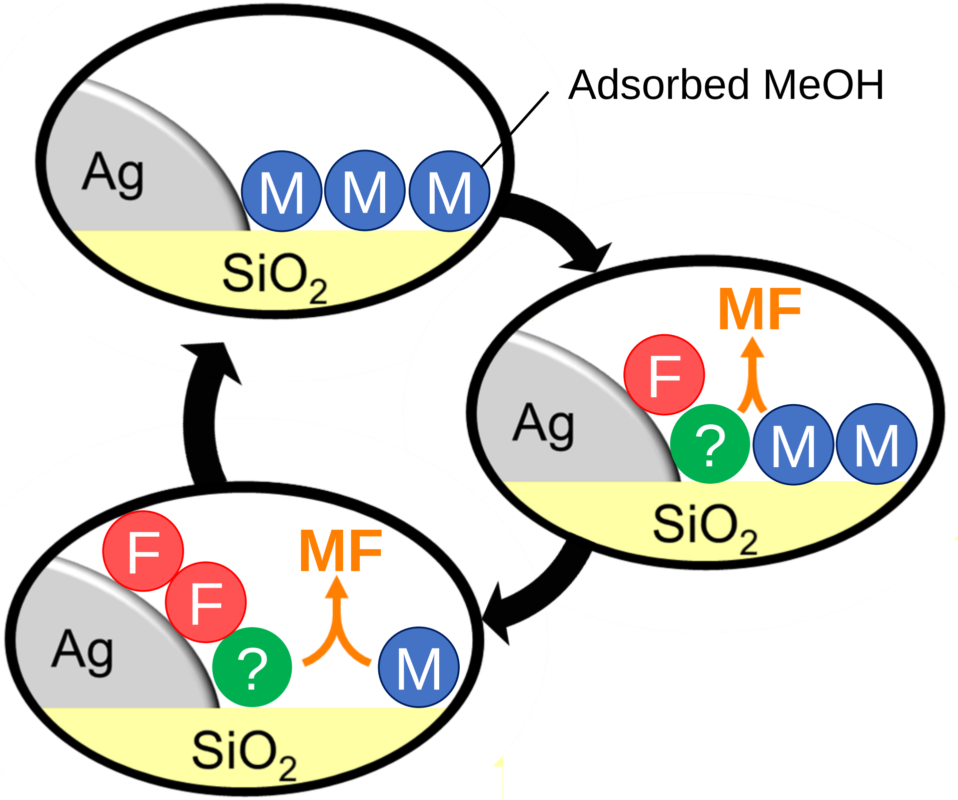






Transient *operando* DRIFTS @ 5 bar

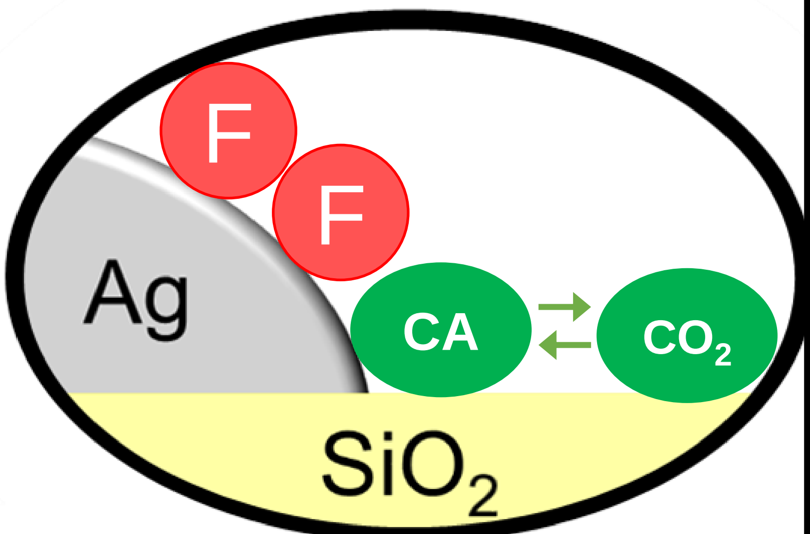


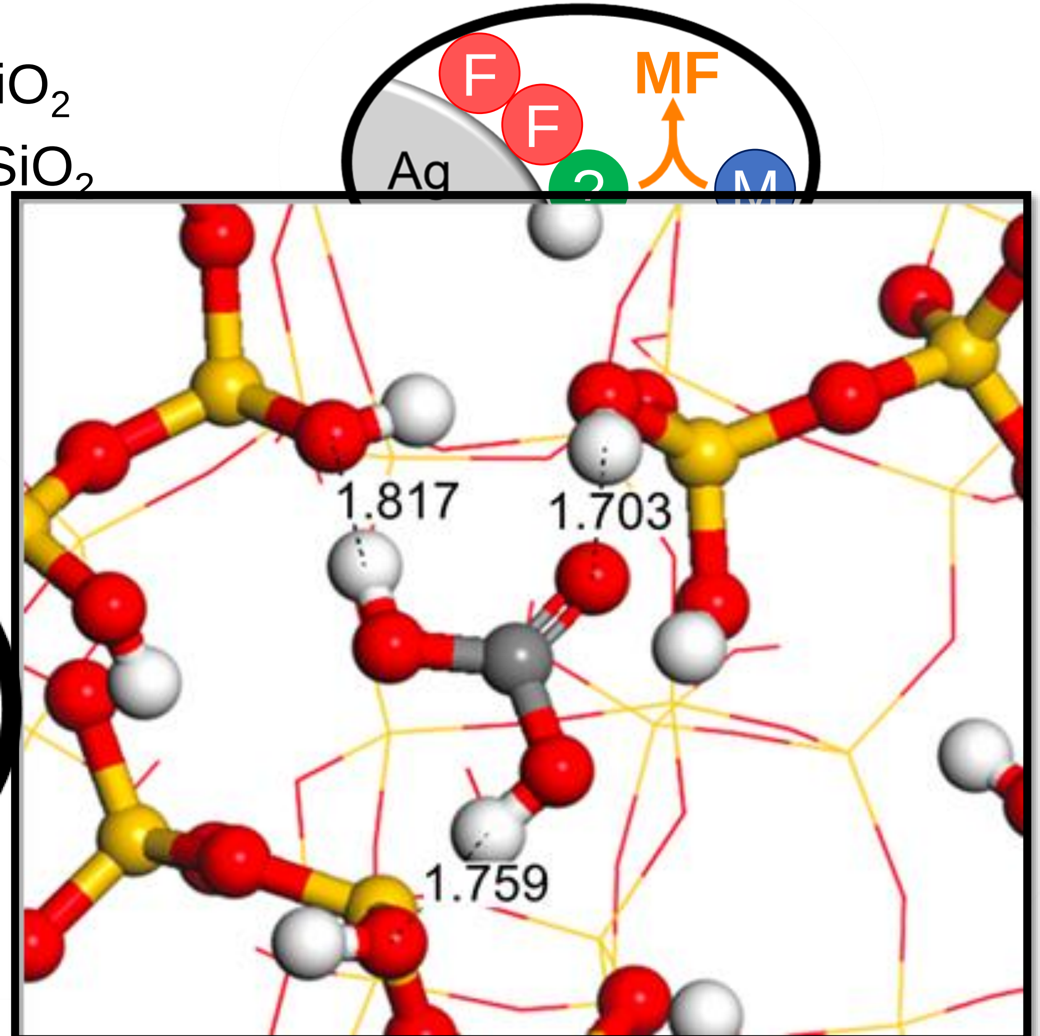


? → important for MF formation

Reaction mechanism – Ag/SiO_2

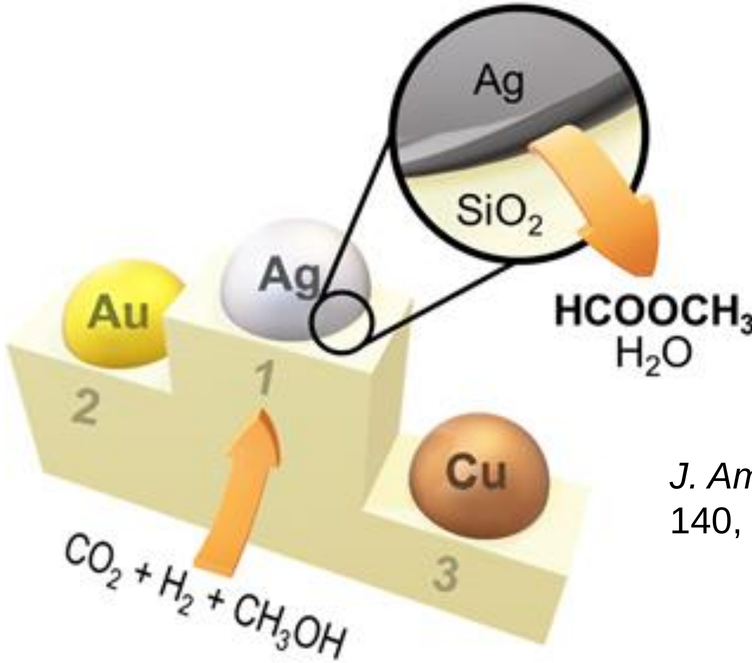
- 1680 cm^{-1}: carbonic acid on SiO_2
- 2330 cm^{-1}: adsorbed CO_2 on SiO_2



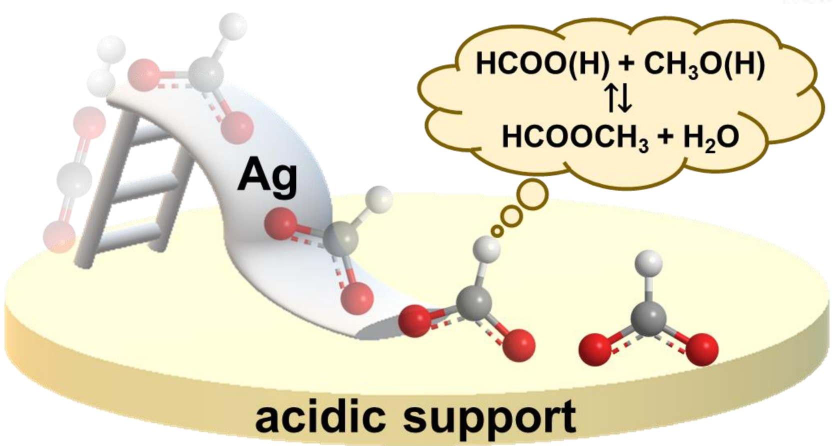


Corral-Pérez *et al.*, *J. Am. Chem. Soc.*, 140, 43, 13884 (2018)

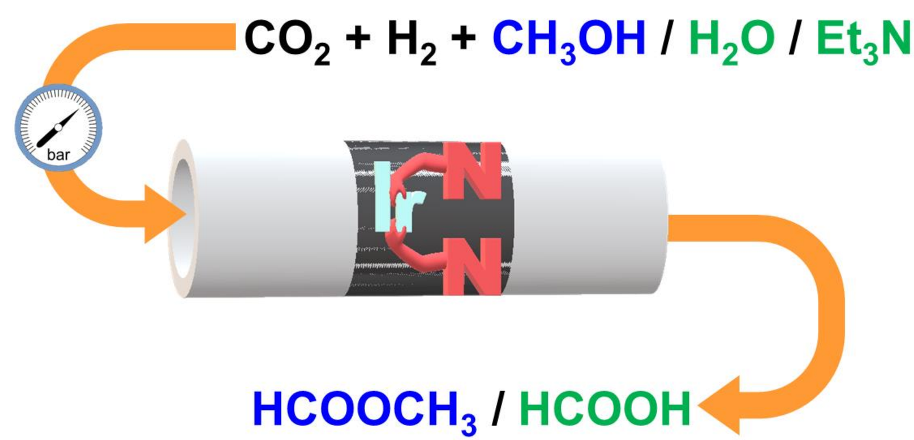
Continuous FA/MF synthesis



J. Am. Chem. Soc., 140, 43, 13884 (2018)



J. Catal. 380, 153 (2019)



ChemCatChem, 11, 4725 (2019)

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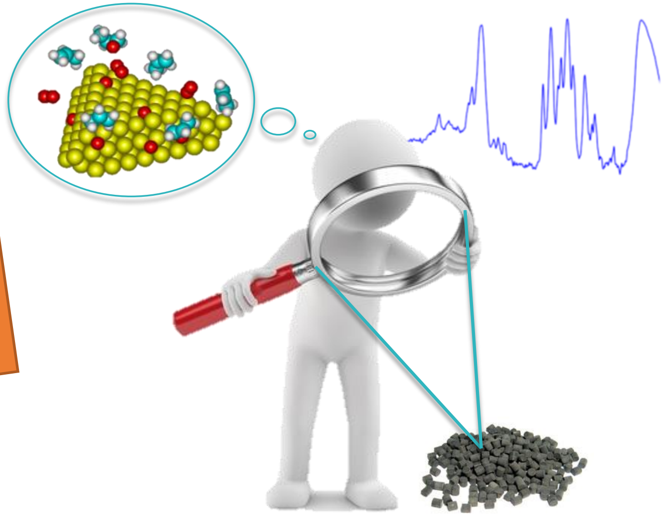
+

***Operando* spectroscopy**



X

Conversion

&

S

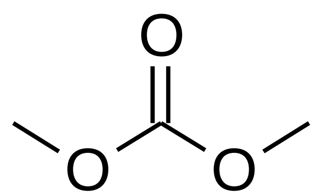
Selectivity

Dimethyl carbonate (DMC) synthesis

Electrolyte

Fuel Additive

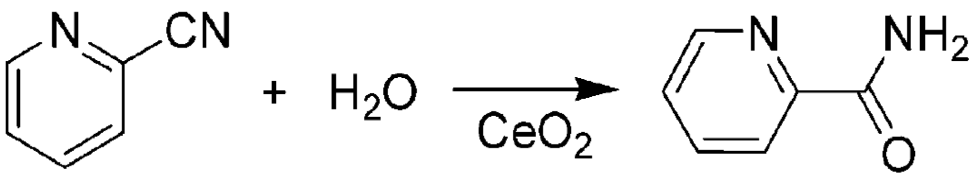
Non-toxic reagent

$2\ CH_3OH\ +\ CO_2 \rightleftharpoons$  $+\ H_2O$

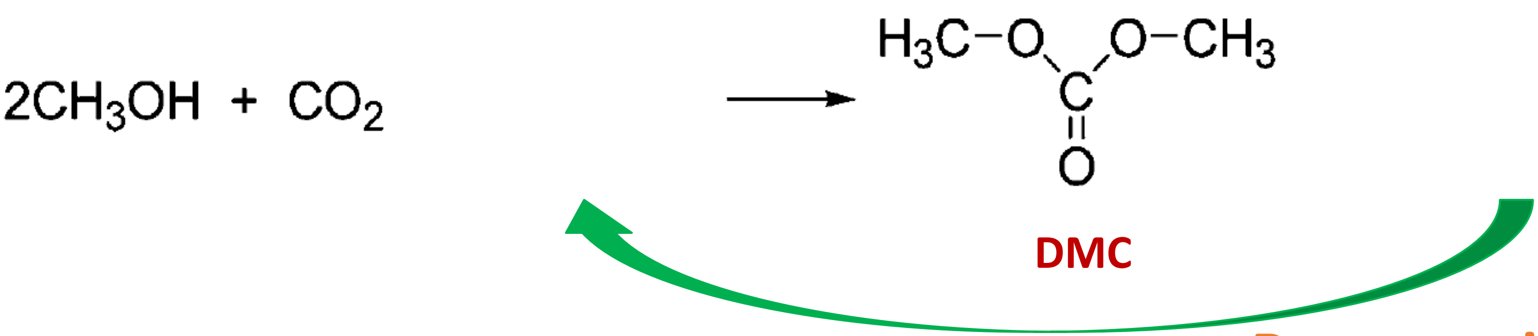
- Equilibrium limited
- Very low conversions < 1 % (even at *400 bar*!)
- H_2O removal is effective

State-of-the-art

Tomishige et al., *ChemSusChem* 1341, 6 (2013)



2-cyanopyridine **2-picolinamide**



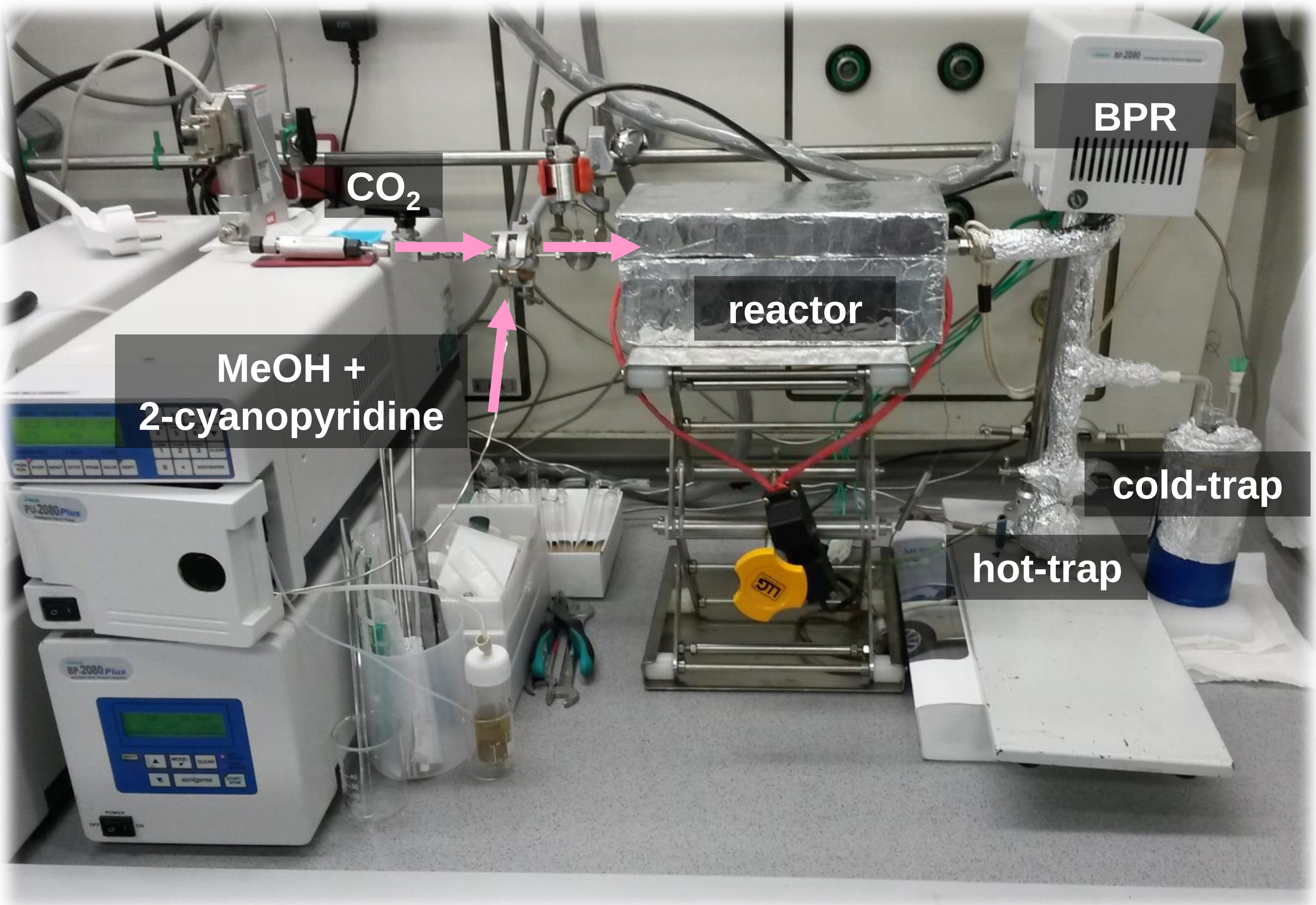
DMC

- H_2O

Regeneration by Na_2O/SiO_2

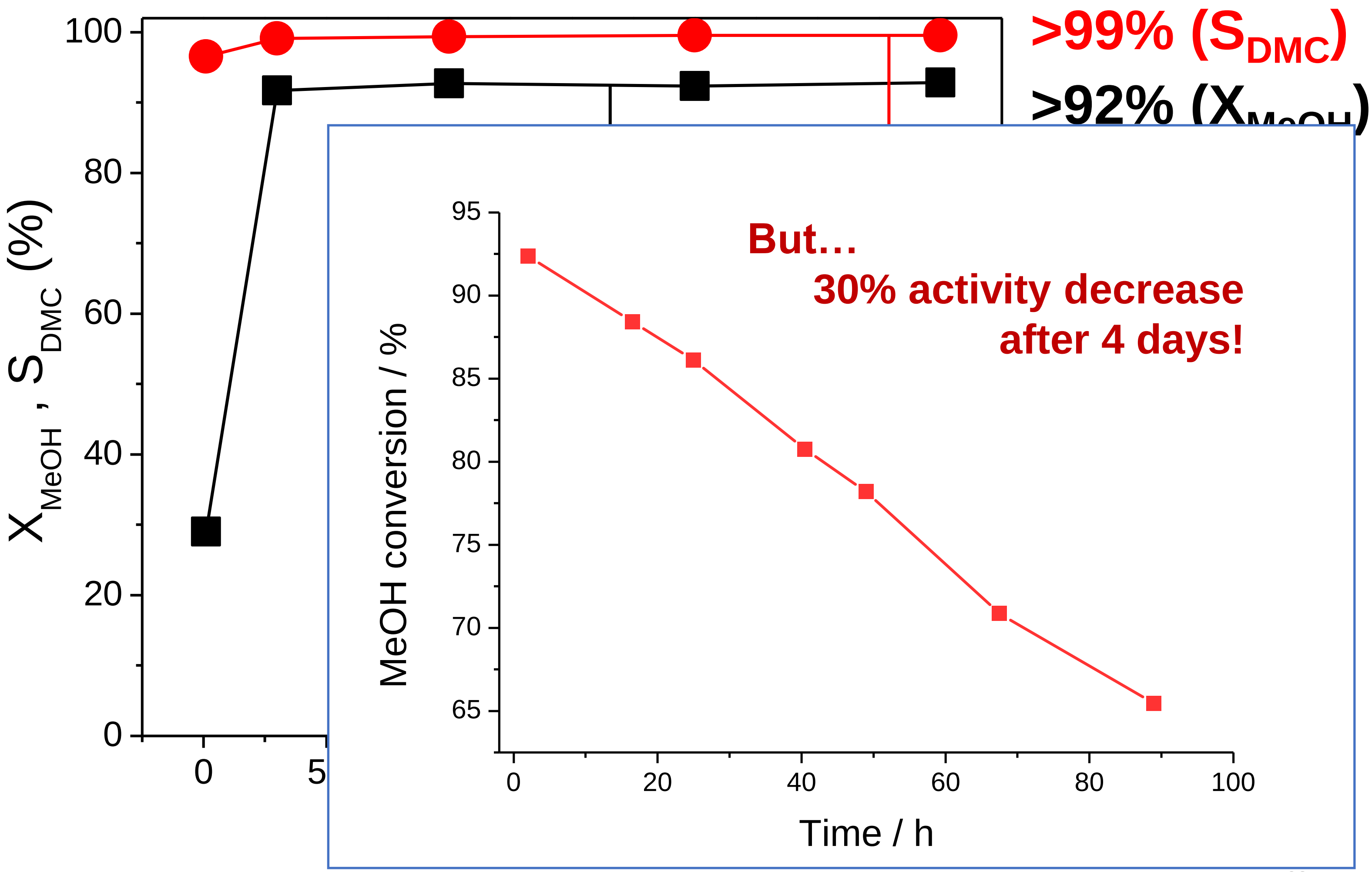
94 % DMC yield (12 h) in a batch reactor at 50 bar

Continuous high-pressure DMC synthesis



Continuous DMC synthesis: Pressure effects

MeOH : 2-cyanopyridine = 2:1 (10 µL/min), 6 NmL/min (CO_2), 120 °C, CeO_2

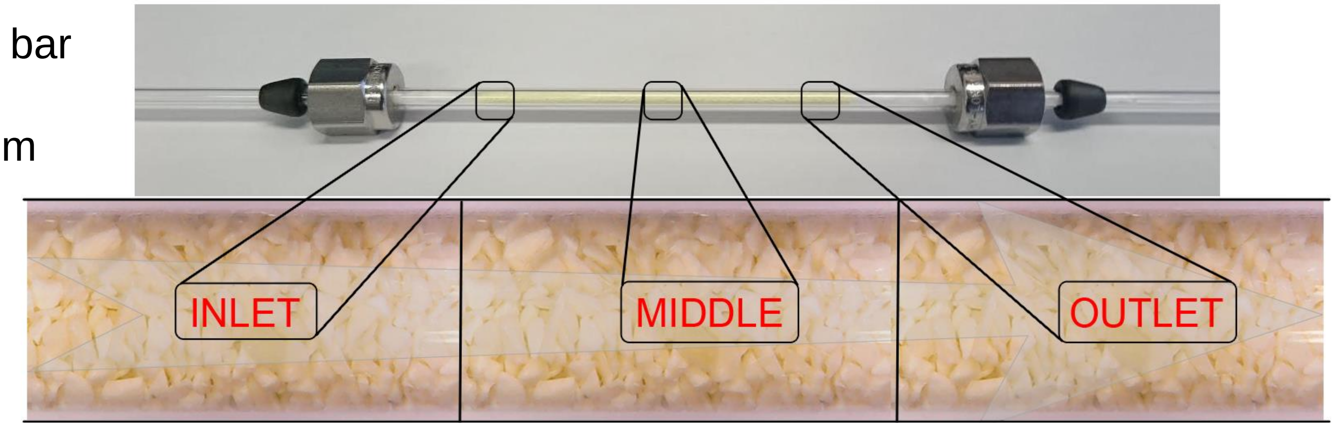


Bansode & Urakawa, *ACS Catalysis,* 4, 3877 (2014)

Operando visualization

Visual inspection (up to 70 bar)

CeO_2, 120 °C, 30 bar
Fused silica tube
ID:2 mm, OD: 3mm



Fresh CeO_2

After 24 h

After MeOH washing

After 300 °C calcination

Before short washing

No reactivation!

Praline…

Stoian, Bansode, Medina, Urakawa, *Catal Today*, 283, 2 (2017)

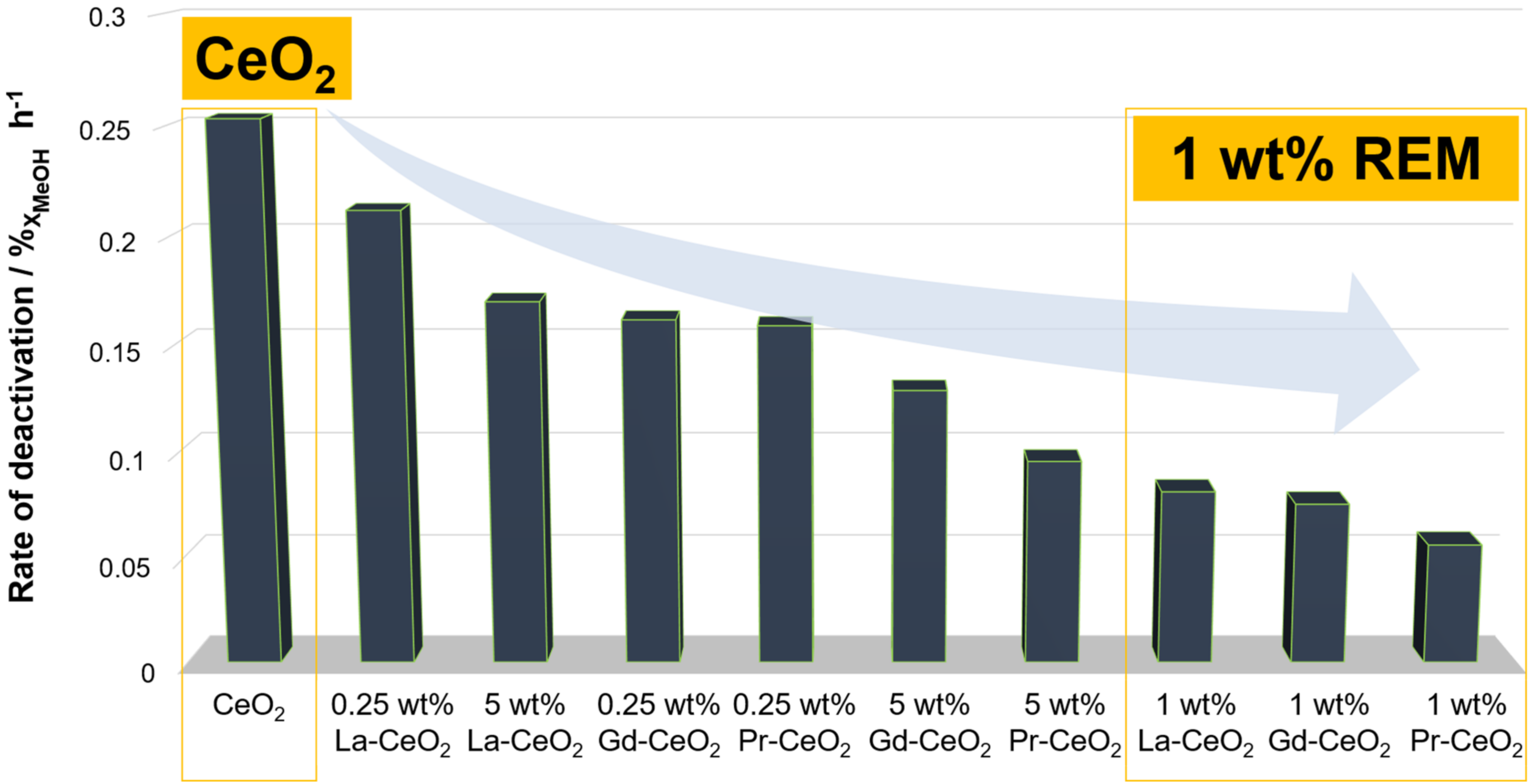
Origin of deactivation

Boiling point of 2-picolineamide: 284 °C

Stoian, Bansode, Medina, Urakawa, *Catal Today*, 283, 2 (2017)

the source of deactivation
2-picolinamide

Rare earth metal (REM) doping to CeO_2



Less 2-PA adsorption

Stoian, Medina, Urakawa. *ACS Catal.* 8, 4, 3181 (2018)

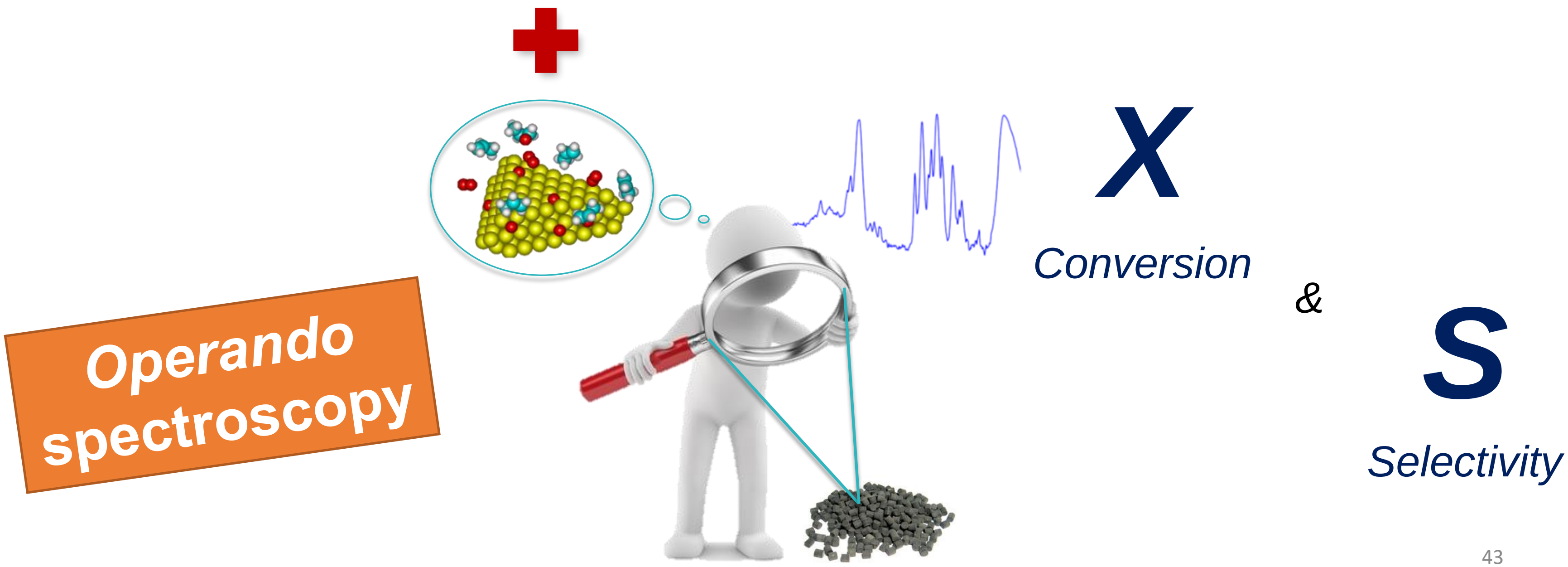
CO_2 to chemical energy carriers

High-pressure approach

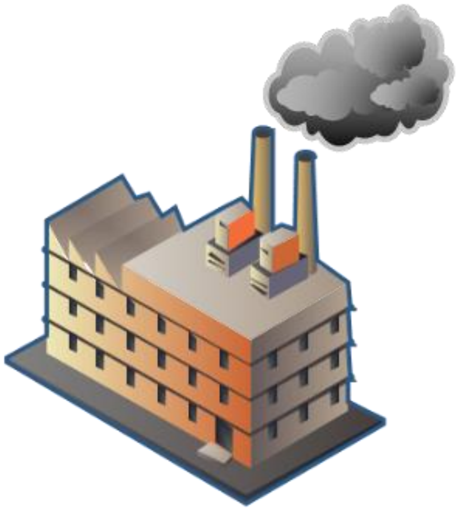
- Hydrogenation to **methanol** (and **DME**)
- Hydrogenation to **formic acid** and **methyl formate**
- Dimethyl carbonate (**DMC**) synthesis from CO_2 and methanol

Unsteady-state operation

- CO_2 capture and conversion in one process for **syngas** production



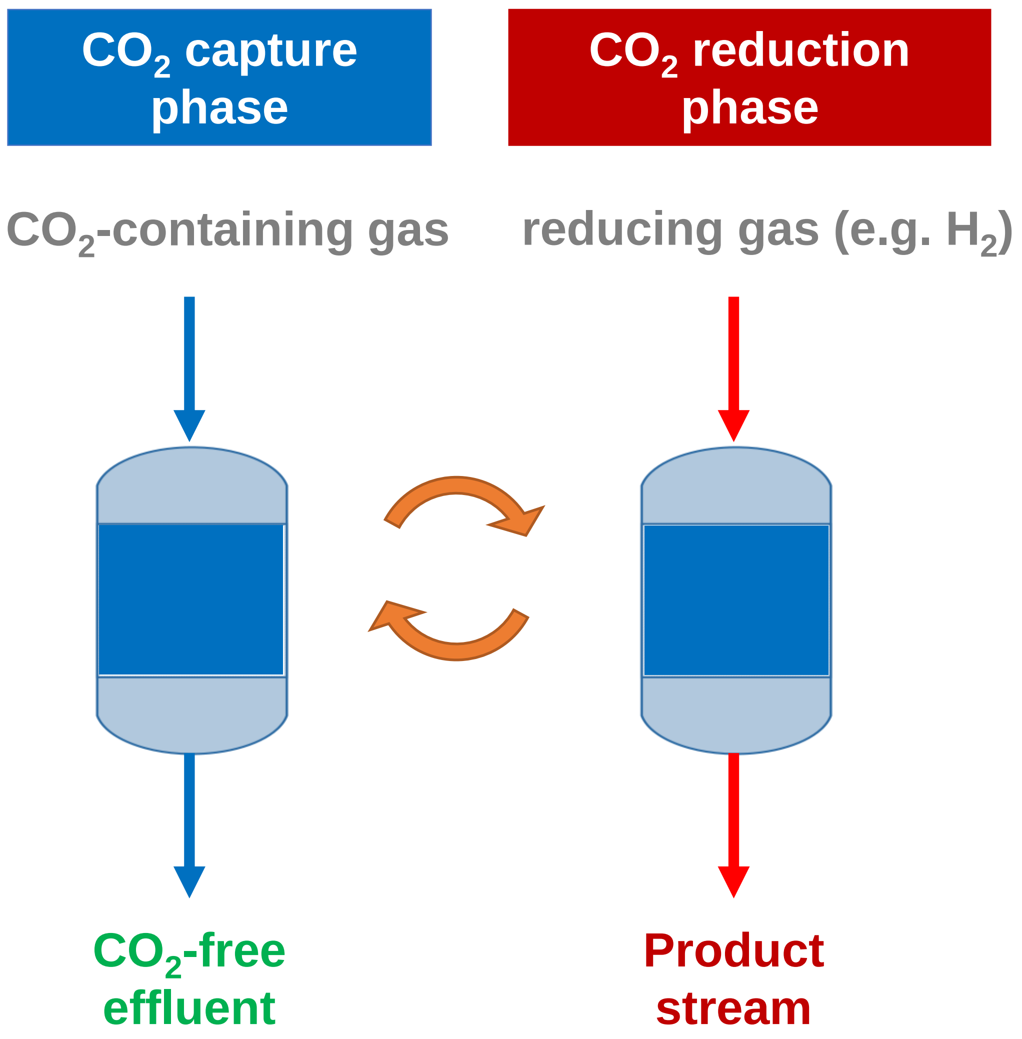
Challenge in CO_2 conversion: CO_2 purity

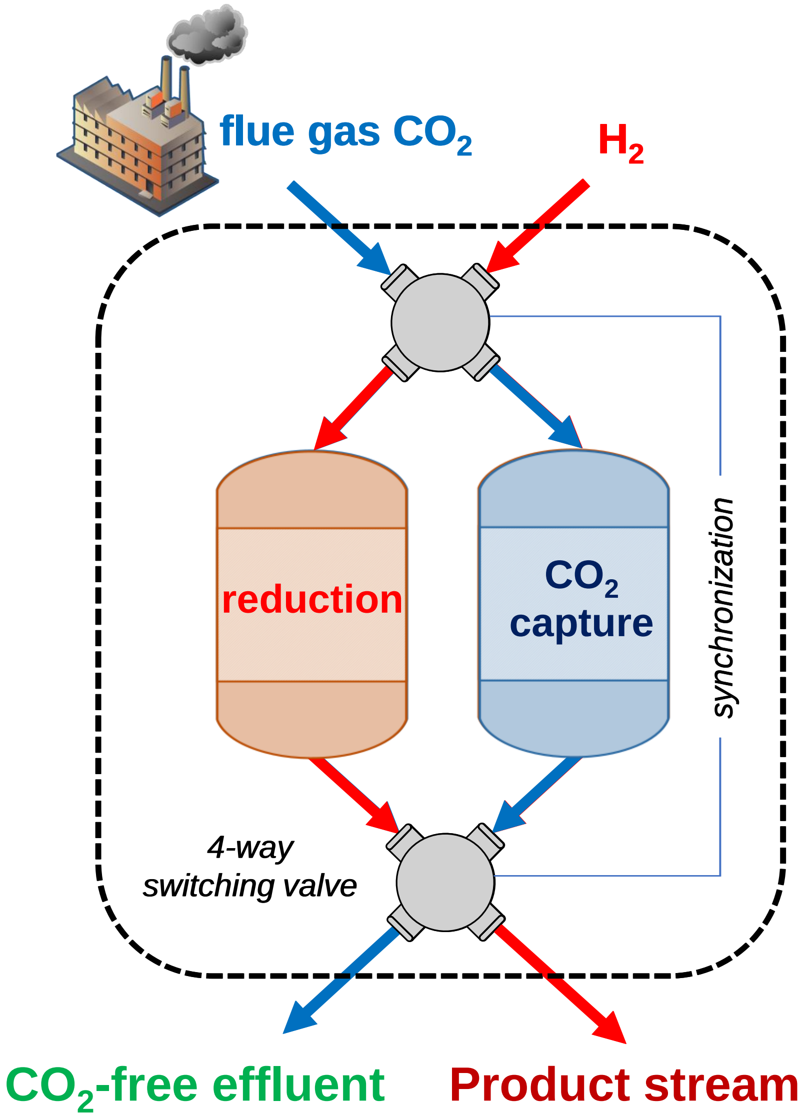


- Typical CO_2 concentration: **3-15%**
- Composition: CO_2, N_2, **O_2**, **H_2O**, …

- Most CO_2 conversion processes require prior **purification** steps
- **Very expensive**: 25-40% increase in energy requirement for power plants

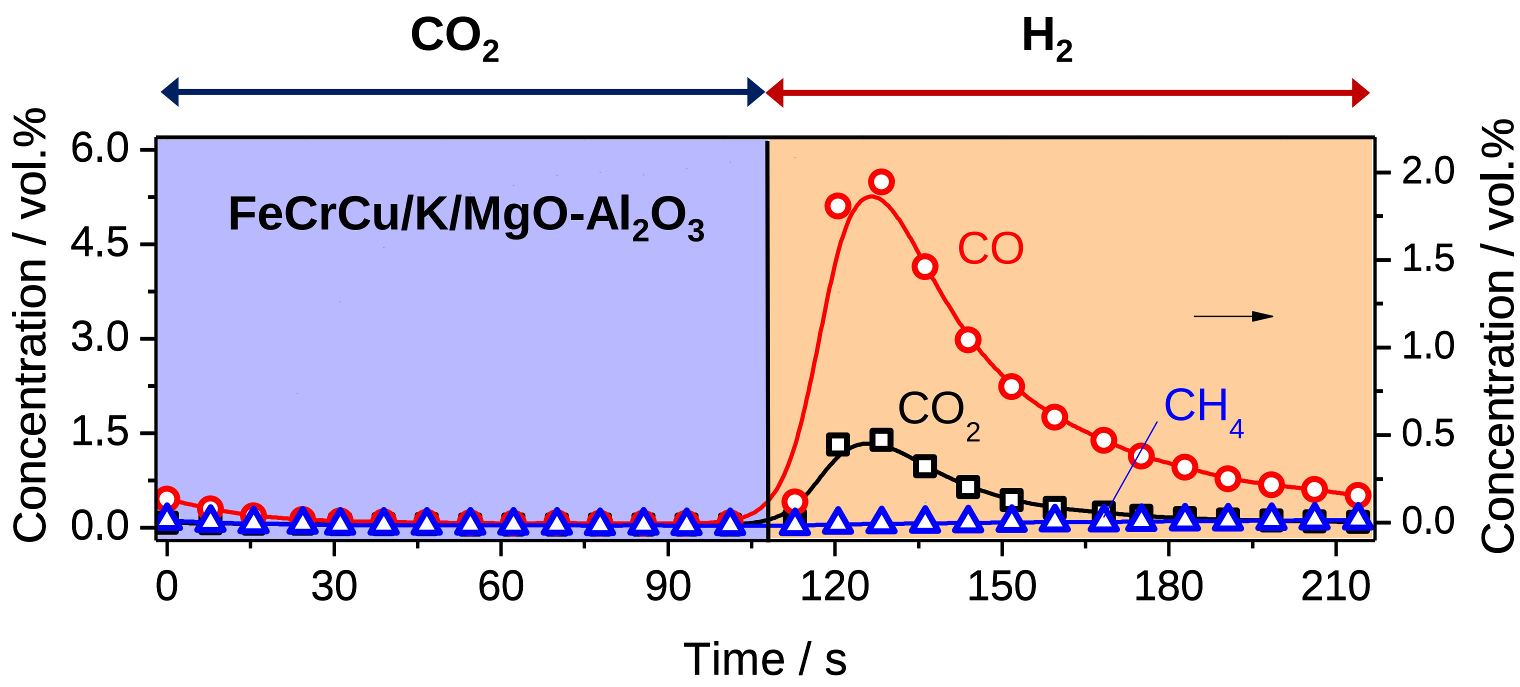
Unsteady-state operation: CO_2 capture and reduction (CCR)





CCR catalyst (FeCrCu/K/MgO-Al_2O_3) for syngas (CO_x + H_2) production

5.8% CO_2 in N_2 (27 mL/min) vs. 100% H_2 (65 mL/min) at 550 °C (107.5 s each)

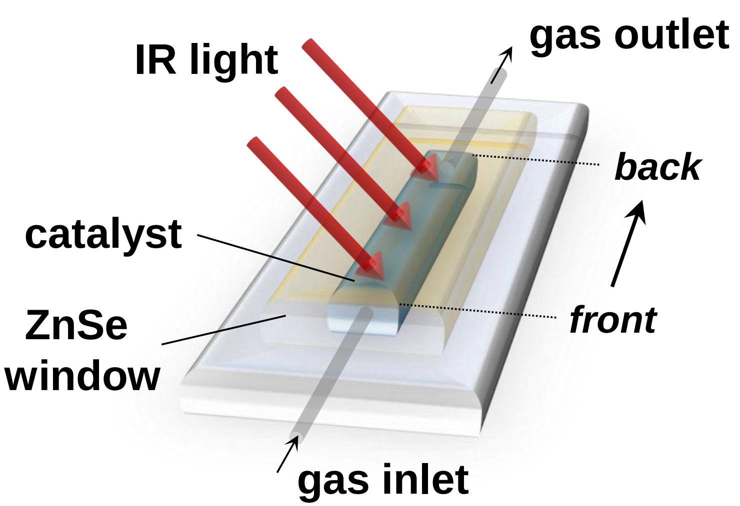


Bobadilla et al., *J CO_2 Util,* 14, 106 (2016)

CCR for **methanation**: Hu & Urakawa, *J CO_2 Util.*, 25 323 (2018)
CCR **with DAC**: Kosaka *et al.*, *submitted*

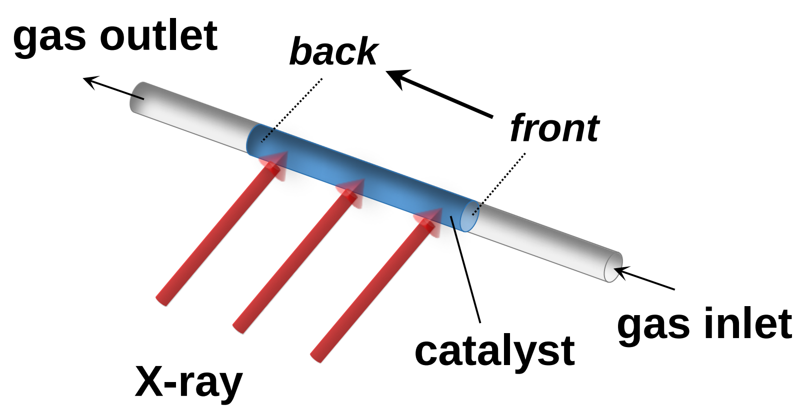
Space- and time-resolved *operando* spectroscopy

DRIFTS



DRIFTS cell: Urakawa *et al.*,
Angew. Chem. Int. Ed. 47, 9256 (2008)

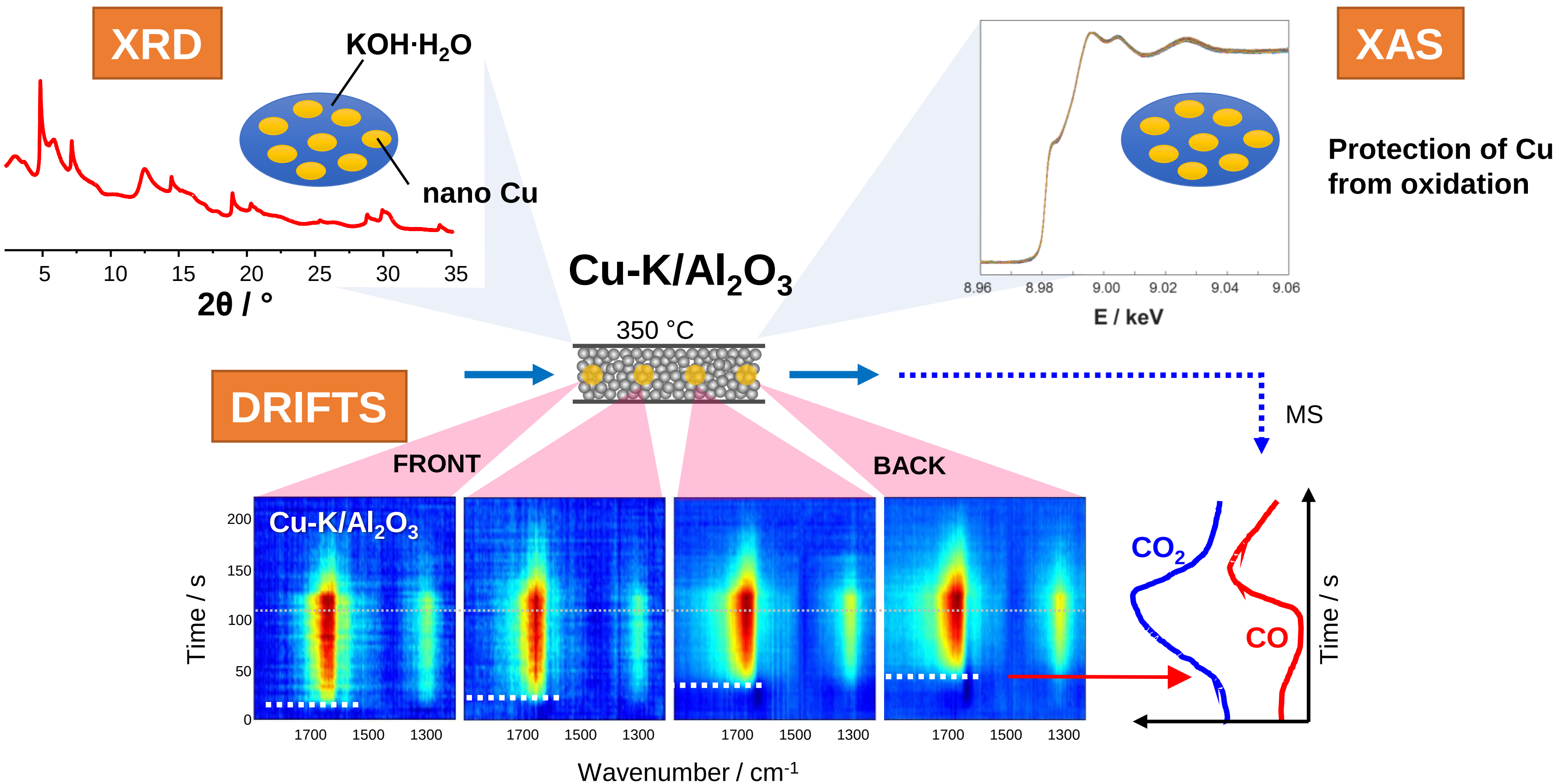
XRD & XAFS



ESRF

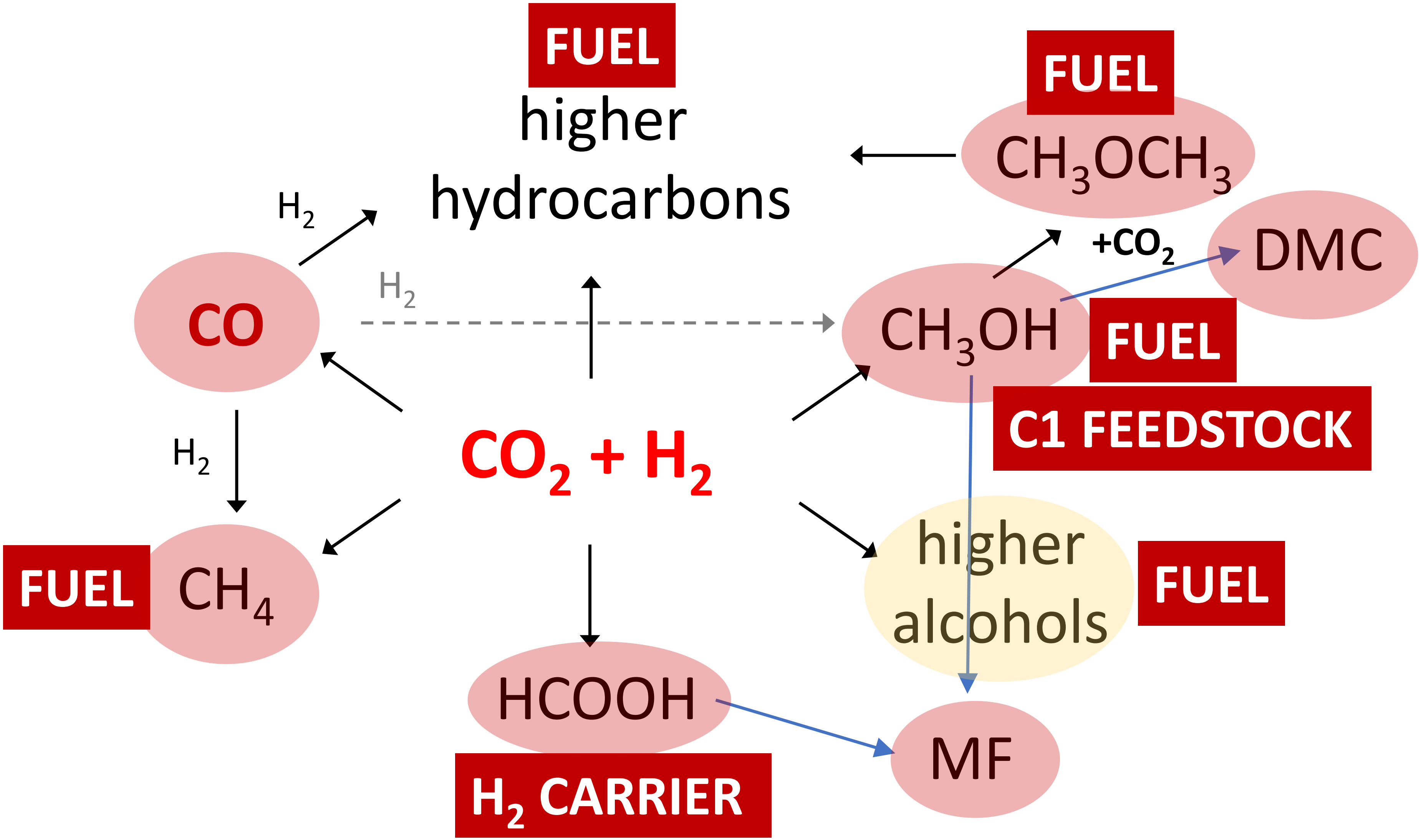
Swiss-Norwegian Beam Lines
at ESRF

Spatiotemporal *operando* study



Hyakutake et al., *J. Mater. Chem. A,* 4, 6878 (2016)

Pinto, *Work in progress*



Take advantages of the thermodynamics & kinetics!!!

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