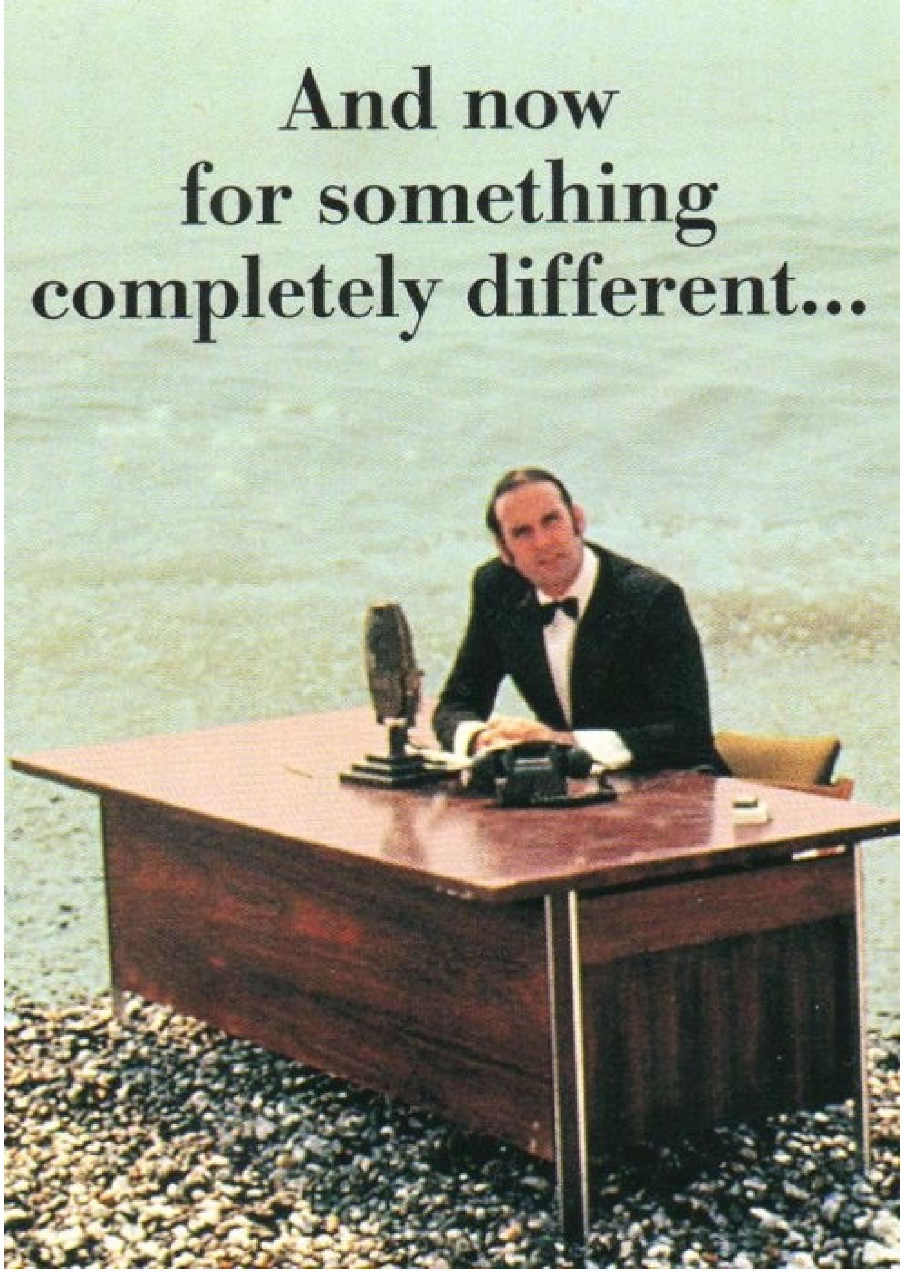
And now
for something
completely different...

E-MRS Fall Meeting, 17.09.2015, Warsaw

Challenges in CO_2 Utilization Opportunities for Materials?

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CO_2 Utilization is NOT a solution to the challenge of Global Warming

CO_2 Utilization is NOT a solution to the challenge of Global Warming

- Yearly CO_2 emissions to the atmosphere – 36 Gigatons (Gt)

  2013 value – Carbon Dioxide Information Analysis Center

- To have a 50 % chance of reaching the 2 °C climate objective, CO_2 emissions must be reduced by 17 Gt in 2030

  International Energy Agency

- If all transportation fuels were made from CO_2, ca. 10 Gt would be avoided

  Based on amount of fossil fuels not used in production

CO_2 Utilization is NOT a solution to the challenge of Global Warming

But … It CAN be a contributor

One scenario….

- 1,34 Gt CO_2 utilized in 2030 via CO_2 based production of
  - All urea
  - 20 % of selected organic chemicals
  - 30 % of waste mineralization
  - 20 % of selected polymers
  - 5 % diesel and aviation fuel
  - 10 % of methane
    - Calculation based on sourcing all carbon in these products from CO_2

- This is **95 %** of the targeted EU emissions reduction for 2030.
- This is **83 %** of the world CCS target

- Note that utilization is not long-term storage

- Armstrong and Styring, *Frontiers in Energy Research,* **3**, article 8.

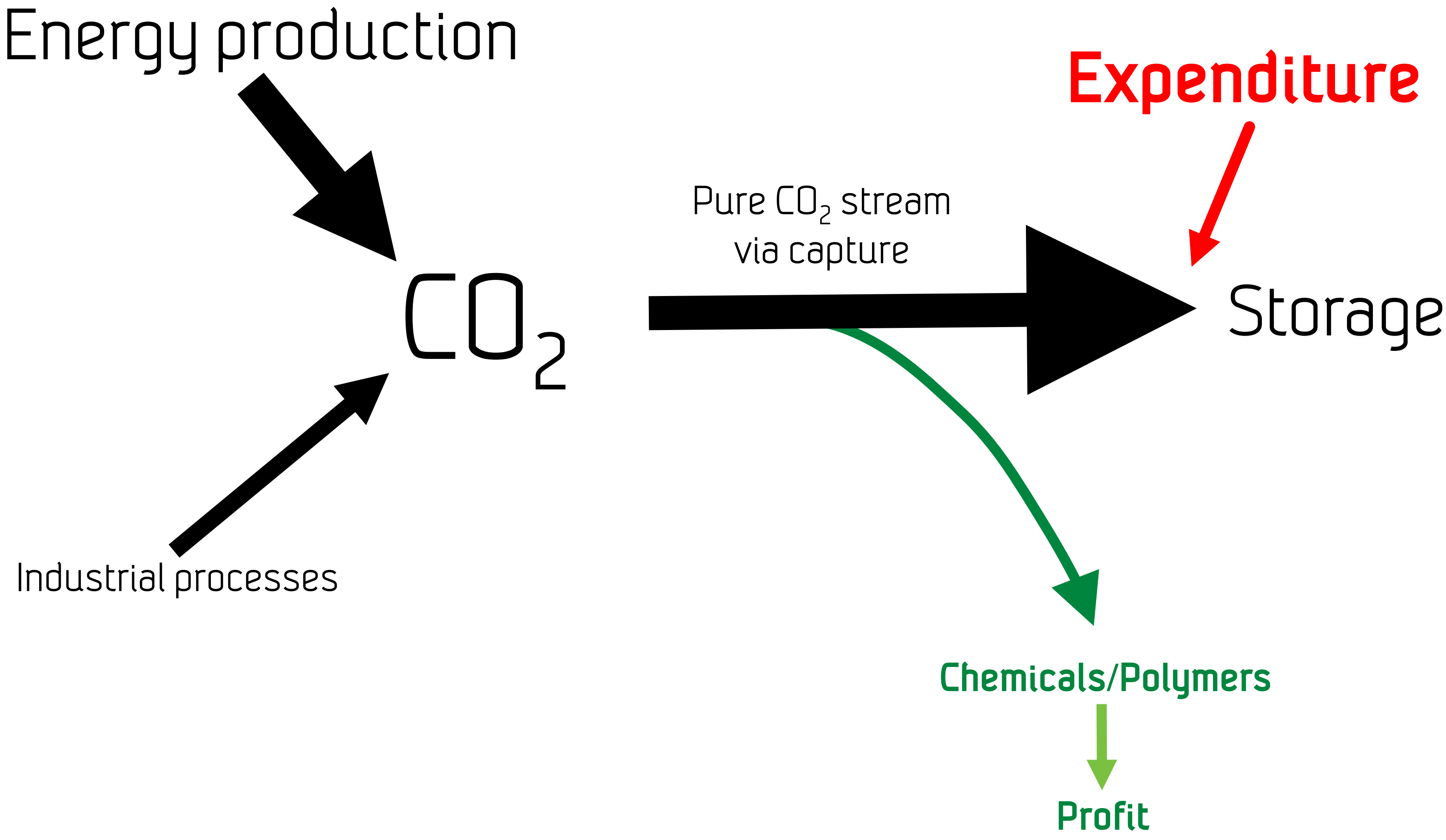
The impact of CO_2 utilization

- Tool in the toolbox regarding CO_2 emissions
  - Consider both CO_2 incorporated into the product and CO_2 avoided
    - Less energy in the process
    - Cleaner, more atom-economic processes
    - Replacement of fossil-fuel derived chemicals
  - Can economically compensate CCS via value-addition from the utilization

- Currently, ca. 180 Mt/yr CO_2 is used for production of urea, methanol, and inorganic carbonates

- The amount of CO_2 captured by CCS is 26.6 Mt/yr.

The impact of CO_2 utilization



The impact of CO_2 utilization

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    - Replacement of fossil-fuel derived chemicals
  - Can economically compensate CCS via value-addition from the utilization
- CO_2 utilization has more to do with **sustainability** than global warming
  - Renewable C_1 feedstock
  - Easily stored and handled
  - Essentially non-toxic
    - Compare with phosgene and CO

Viable CO_2 utilization technologies require proper Life Cycle Analysis and Techno-Economic Evaluations prior to implementation

The CO_2 utilization condundrum

- CO_2 is a thermodynamically stable and kinetically inert molecule

BUT

- Nature utilizes gigatons of CO_2 each year for the production of carbohydrates, via solar energy

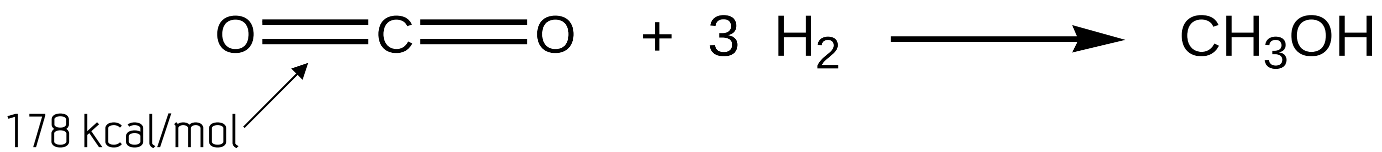
HOWEVER

- Photosynthesis is a rather ineffective process that required a billion years to develop

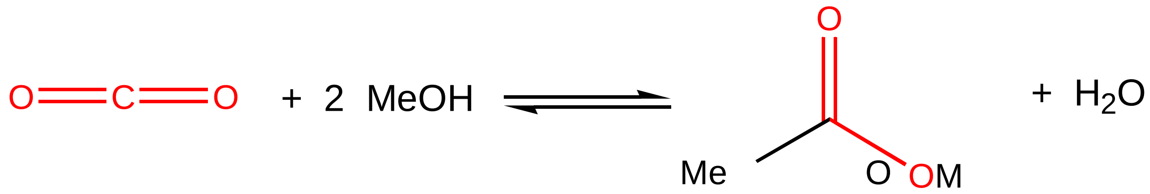
Mankind can only hope to mimic nature through the development of catalysts, materials and processes to transform CO_2 into valuable products for our society

Two types of CO_2 utilization/reduction

- Reduction via C=O bond cleavage – "Fuels"
  - Large change in oxidation number

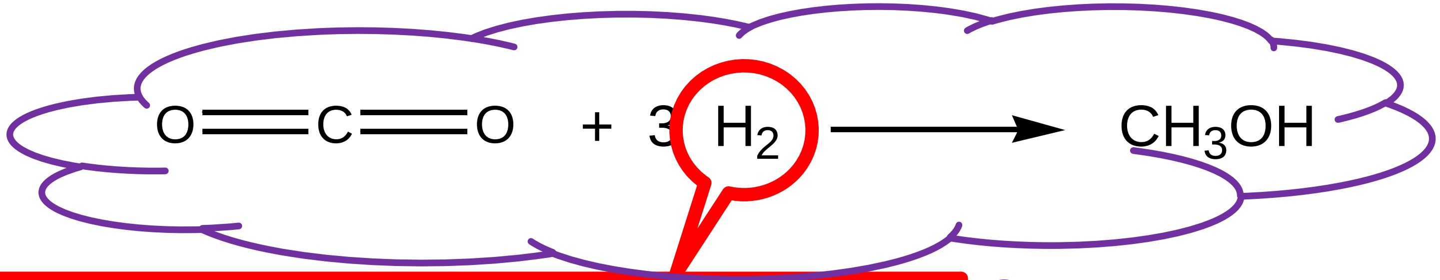


- Reduction of one C=O bond to a C–O bond – "Chemicals"
  - Incorporation of entire CO_2 molecule into the product
  - High atom-economic reactions



Dimethylcarbonate (DMC): Cl_2CO substitute; fuel oxygenate, solvent

Reduction to fuels



Where does the H_2 come from?

Storage technology for renewable energy sources

- Traditional, thermal sources of H_2 WILL NOT reduce the overall CO_2 footprint of the process
- MUST use renewable energies for H_2 production
  - Implies electrolytic pathways

Efficient H_2 production from renewable energy sources is a key technological driver for wider implementation of CO_2 to fuels

"Alternative" reduction technologies

- Electrochemistry, photochemistry, plasma
  - Very early stages of development

- Electrochemical reduction of CO_2 via PV-sourced electricity is "low(er) hanging fruit"

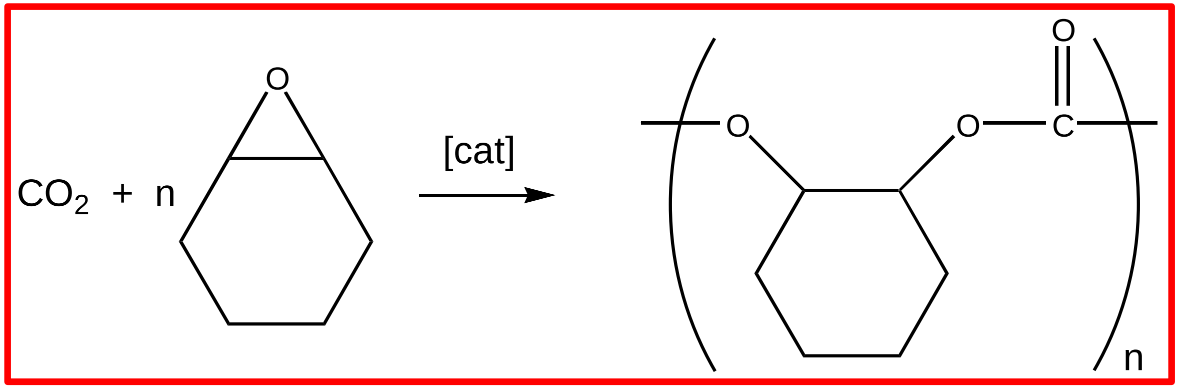
$$CO_2 + e^- \longrightarrow CO_2^{-\bullet}$$

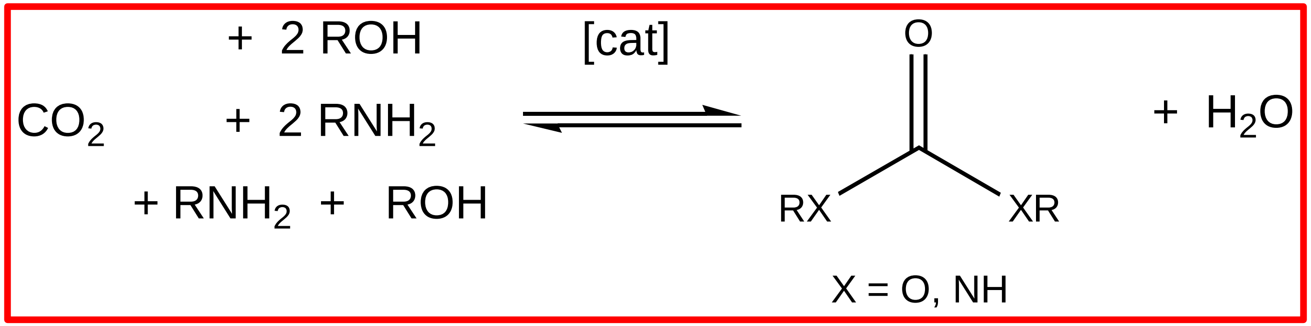
- Large overpotential required
  - Selectivity an issue

- Need for new and better electrode materials for this reduction

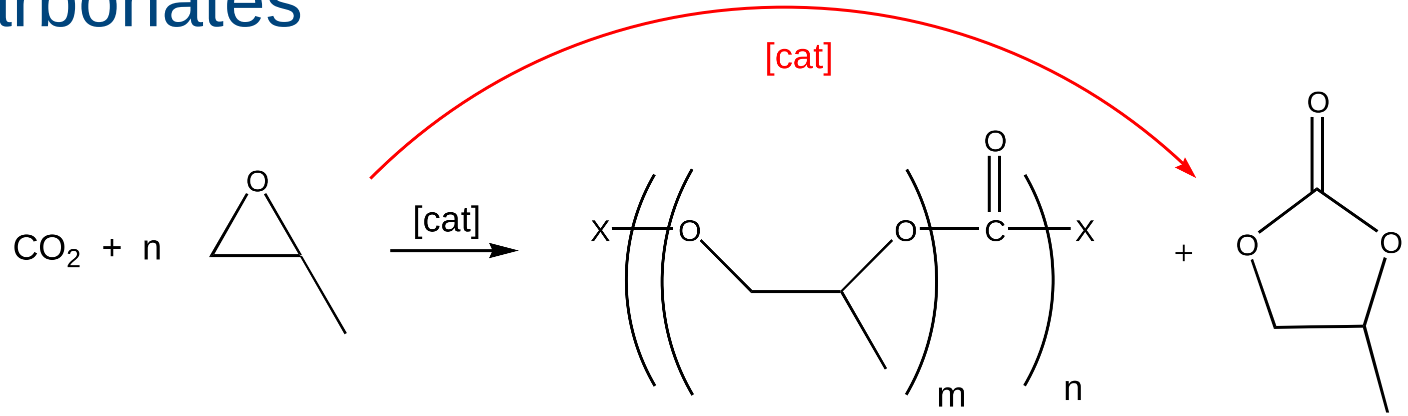
Reduction to chemicals

- Reaction of high-energy substrates with CO_2
  - Necessary to overcome thermodynamics
  - Can also beat thermodynamics by formation of salts
    - Irrelevant chemistry from the LCA, carbon footprint, sustainability perspective



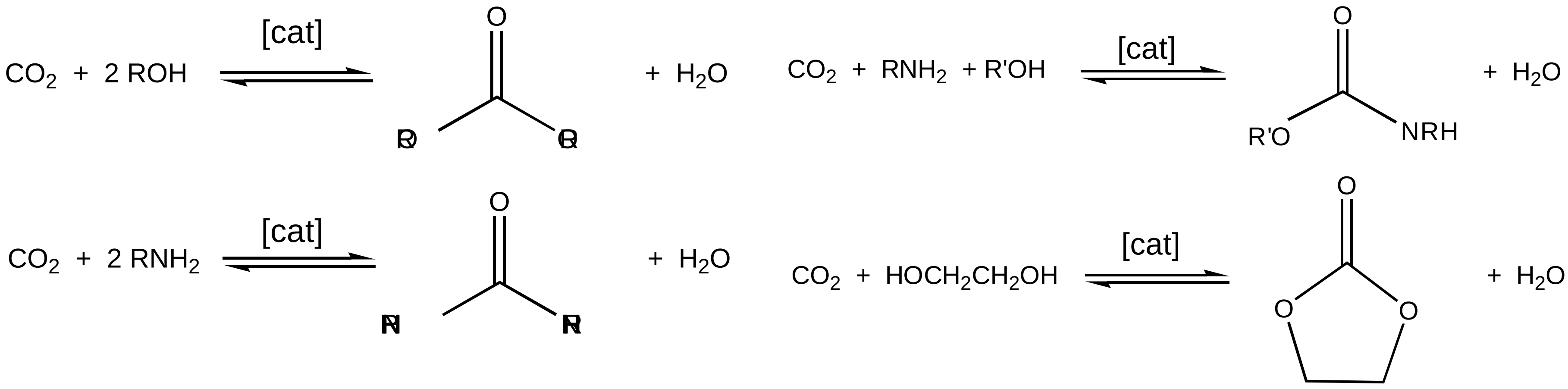


Polycarbonates



- Short chain polycarbonate-polyols
  - X = OH
  - M_n < 5000
  - Undergoing commercialization as polyols in polyurethane application
    - Convestro (Bayer) – **LCA shows reductions up to 4 kg CO_2/kg CO_2 utilized** A. Bardow, *et.al, Faraday Trans, in press*
- Long chain polycarbonates
  - X is variable – dependent on catalyst and initiator
  - M_n up to 250,000
  - **Low T_g material**
    - **How to modify/co-polymerize/blend to make a commercial material**

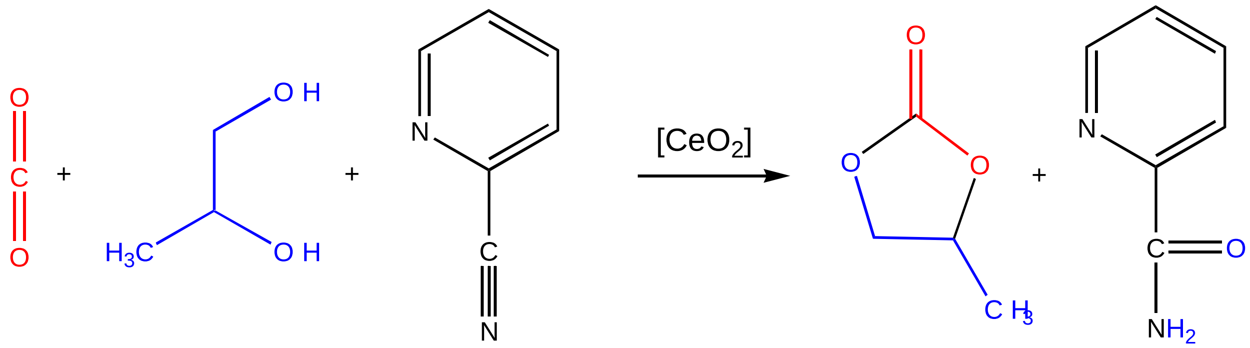
Linear carbonates, ureas, carbamates, cyclic carbonates



- All these reactions have equilibrium-limited yields
- For MeOH to dimethylcarbonate (reaction top left, R = Me), $\Delta^R G^{IG} \approx 37$ kJ/mol
  - *Chem. Ing. Tech.* **2014**, *86*, 497
- Equilibrium yield 0.5 % for propylene glycol to propylene carbonate (analogous to reaction bottom left), at 130 °C and $CeO_2 \cdot ZrO_2$ as heterogeneous catalyst
  - *Green Chem.* **2004**, *6*, 206

Water traps

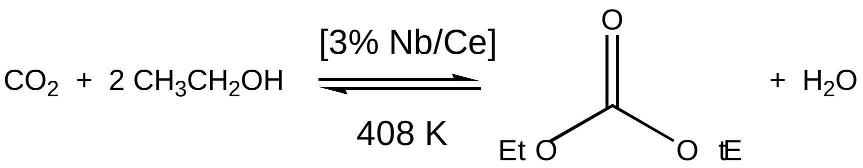
- Practical studies require chemical or physical water traps to pull the equilibrium toward products
  - Best example of a chemical trap is the use of 2-cyanopyridine in the CeO_2 system
  - Nearly quantitative yield of propylene carbonate within 1 h at 130 °C



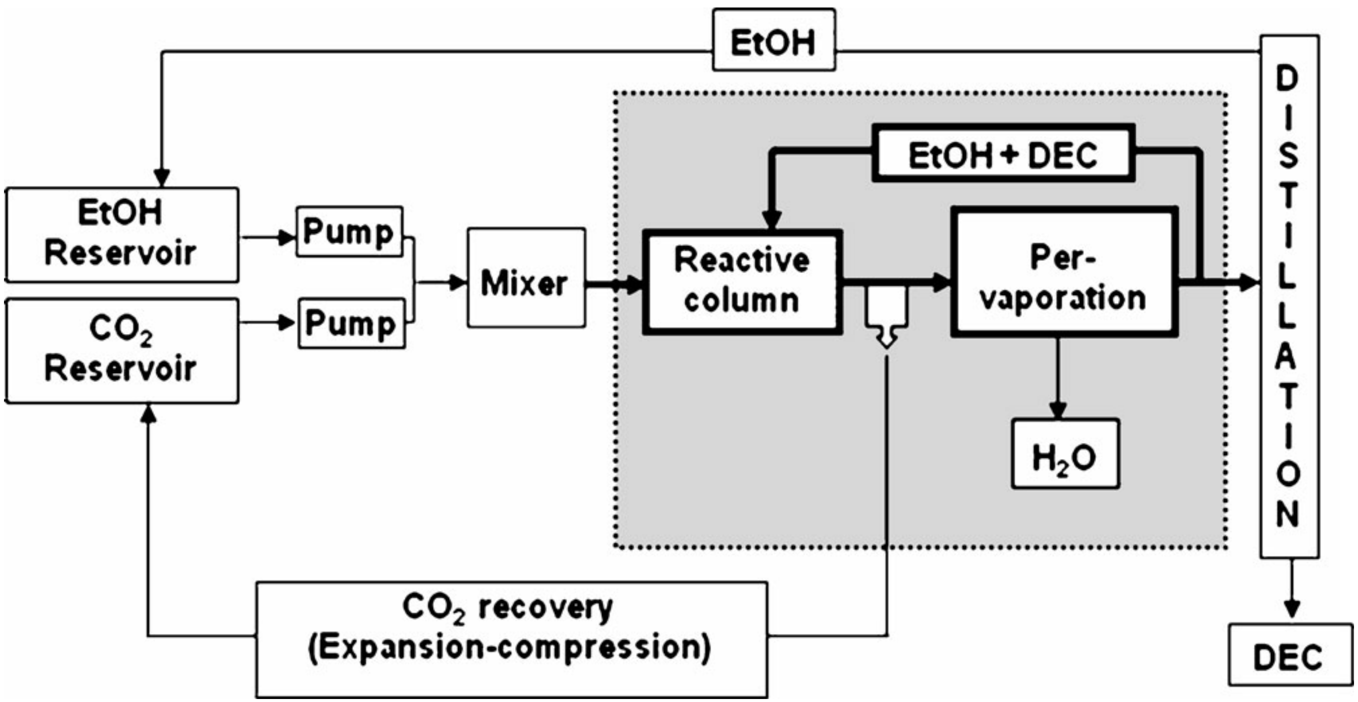
ACS Catal. **2014**, *4*, 1893

Hydrated by-product has little (no?) commercial value
Reduces sustainability of the entire process

Pervaporation – enhanced formation of DEC



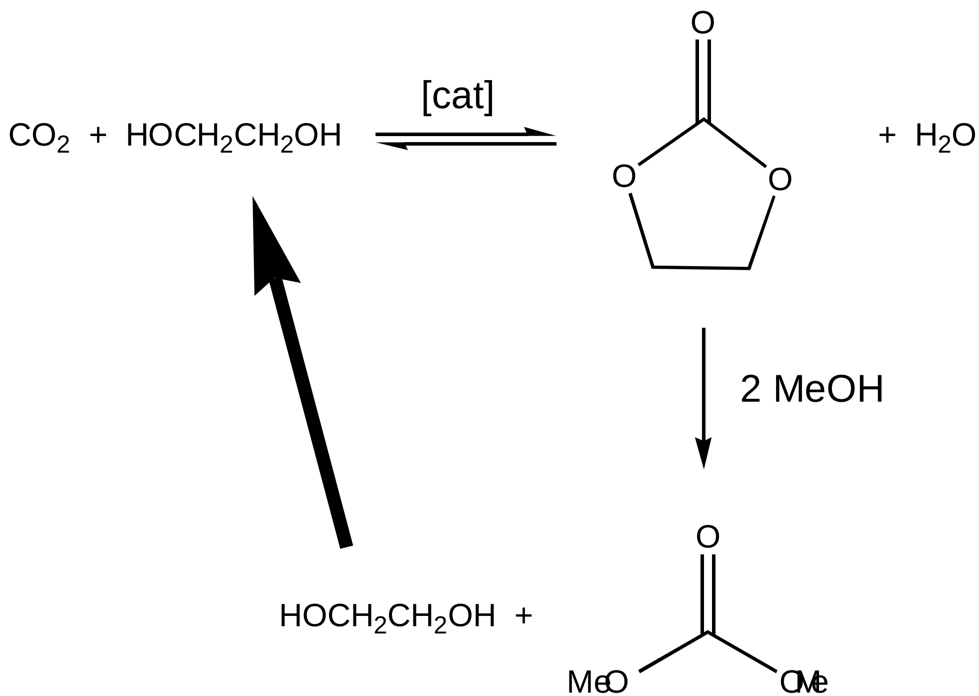
Taken from Aresta, et. al., *Chem. Eur. J.* **2012**, *18*, 10324



- NaA-type tubular ceramic membrane at 403 K and atmospheric pressure
- Increases DEC yield from 0.9 to 2-3 %
- A polymeric organic membrane did not work as well (different configuration)

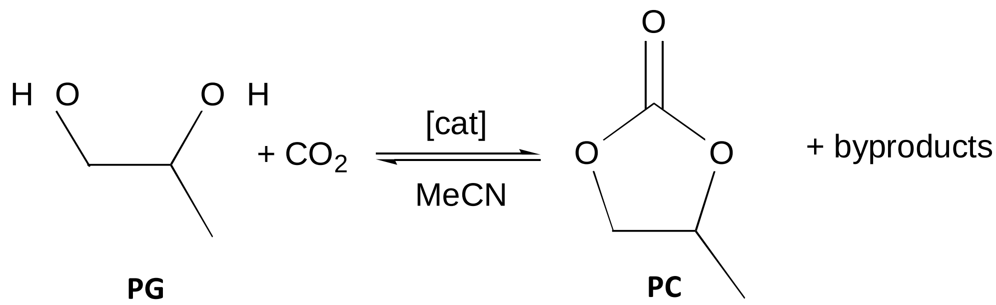
Generality

- A viable industrial process to make one organic carbonate from CO_2 produces (in general) all carbonates from via transesterification reactions



Improved membrane materials that would allow synthesis of an organic carbonate from CO_2 and an alcohol and a diol, without water trap, would be a significant technological breakthrough for CO_2 utilization and sustainability.

Catalyst development at SINTEF



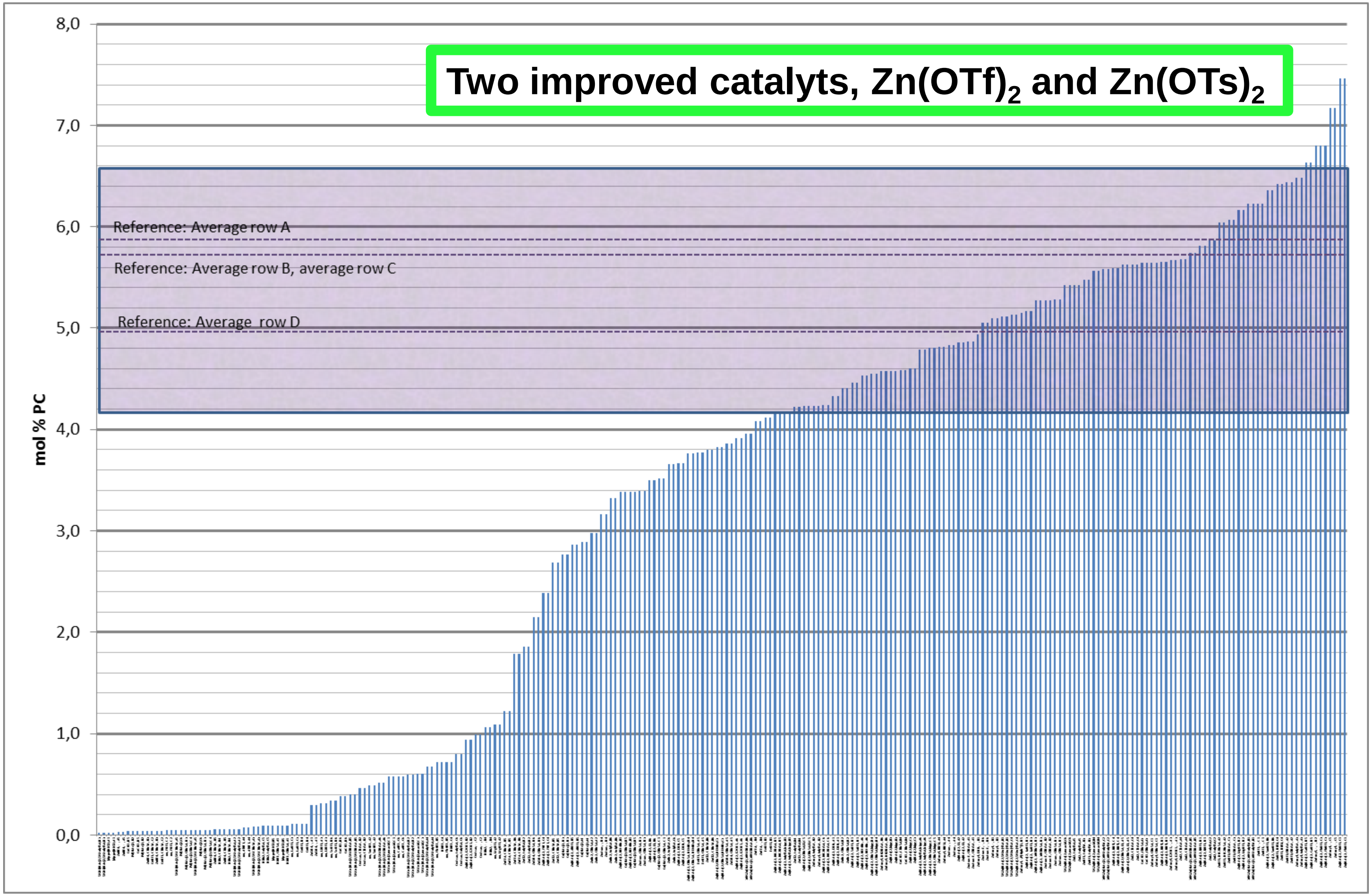
- Difficult to compare catalysts with equilibrium yields < 1 %
  - Water traps are a necessary evil in the search for better (faster) catalysts
- For homogeneous catalysts, literature gives $Zn(OAc)_2$ as "best catalyst"
  - Conversion of PG: 37-39 % (GC)
  - Yield of PC: 19-24 % (GC)
  - Byproducts: 13-18 % (GC)
  - 160-170 °C, 30-100 bar, 2.5 mol % catalyst, 180-190 mol % acetonitrile
  - 12 % PC, 64 % selectivity after 2 h

Huang, S.-Y., *et. al.*, *J. Fuel Chem. Technol.* **2007**, *35*, 701
Zhao, X., *et. al.*, *Ind. Eng. Chem. Res.* **2008**, *47*, 1365

High Throughput Studies and Analyses

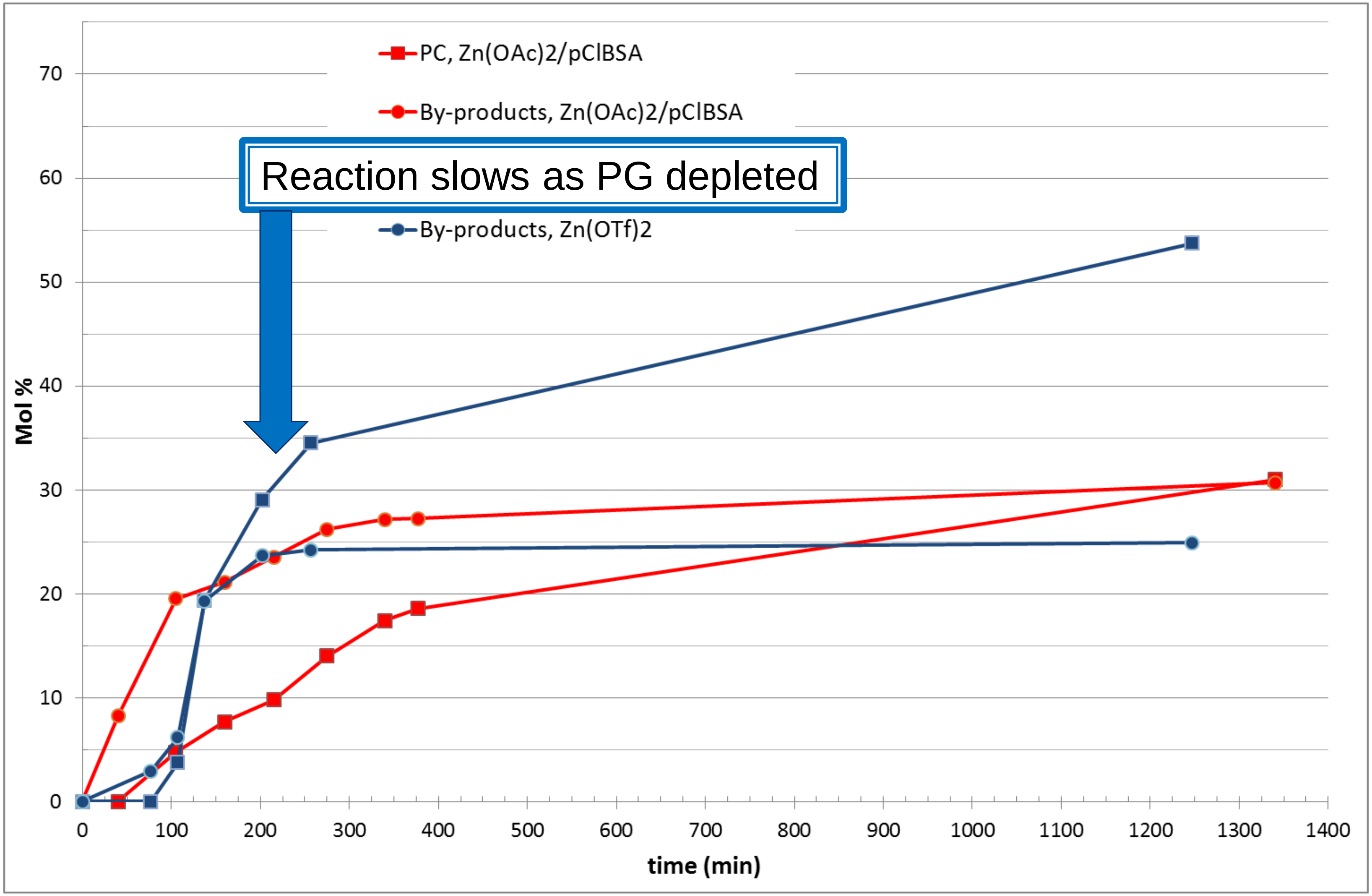
- 24-well high throughput reactor for screening of catalyst combinations
  - Up to 200 °C
  - Up to 100 bar
  - Reaction volume ~11 ml
- Easy to assemble, disassemble, and clean
- Analyses of products using a GC HeadSpace instrument
  - Qualititative comparisons between catalysts, not quantitative data (yields, conversions, etc).

HT results



Two improved catalyts, $Zn(OTf)_2$ and $Zn(OTs)_2$
8,0
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
mol % PC
Reference: Average row A
Reference: Average row B, average row C
Reference: Average row D

Significantly faster and better catalysts than literature



Summary

- CO_2 utilization is a viable research area for improving the sustainability of the European chemical industry as well as contributing to a reduction in CO_2 emissions
  - The latter occurs both through carbon used and carbon avoided

- CO_2 utilization currently contributes more to reduced CO_2 emissions than CCS projects, and realistic (yet challenging) scenarios indicate that it could meet European CCS targets by 2030.
  - New CO_2 utilization technologies are being commercialized

- Important areas for materials researchers
  - New electrodes for CO_2 electrochemical reduction
  - Improvement of the low T_g of long-chain aliphatic polycarbonates
  - Membrane materials (and other processes) for removing water from carbonate production

Acknowledgments

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