High throughput catalyst discovery for the direct synthesis of propylene carbonate from propylene glycol and CO_2

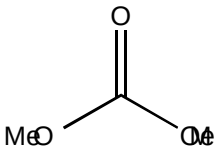
Richard H. Heyn and Elisabeth Tangstad
SINTEF Materials and Chemistry, Oslo, Norway
José Antonio Castro-Osma, James Comerford, and Michael North
Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, UK

Carbon Dioxide Utilization (CDU)

- **IS NOT** A SOLUTION TO THE CLIMATE CHANGE PROBLEM
  - Question of volumes
- **CAN BE** A VIABLE, SUSTAINABLE C_1 FEEDSTOCK ALTERNATIVE FOR THE CHEMICAL INDUSTRY
  - Requires catalysis and energy to overcome inherent thermodynamic and kinetic barriers

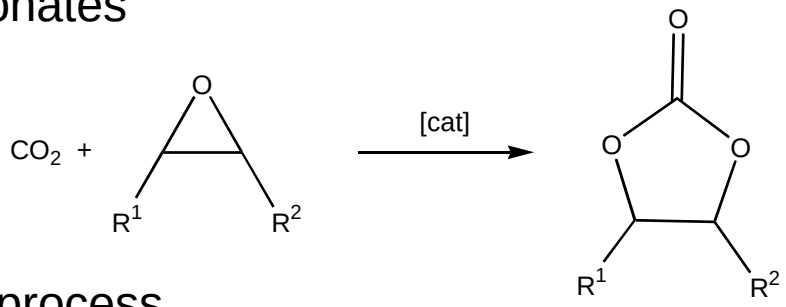
Carbonates

- Carbonates
  - Sustainable and environmentally benign solvents and reagents whose production is not necessarily sustainable or benign
  - Linear carbonates



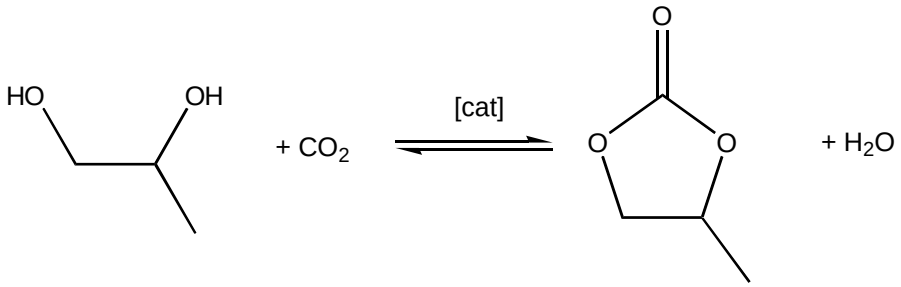
Dimethylcarbonate

    - Primary starting material is phosgene
  - Cyclic carbonates



    - Industrial process

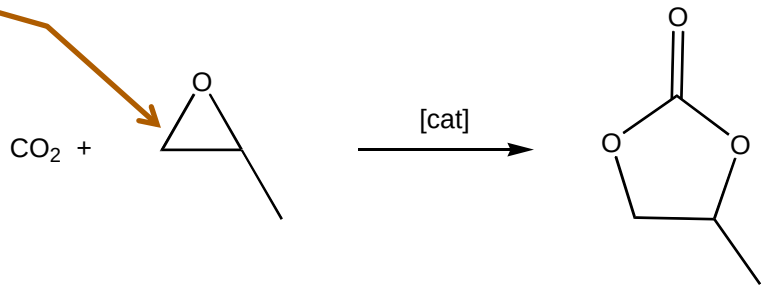
Reaction



Propylene Glycol (PG) Propylene Carbonate (PC)

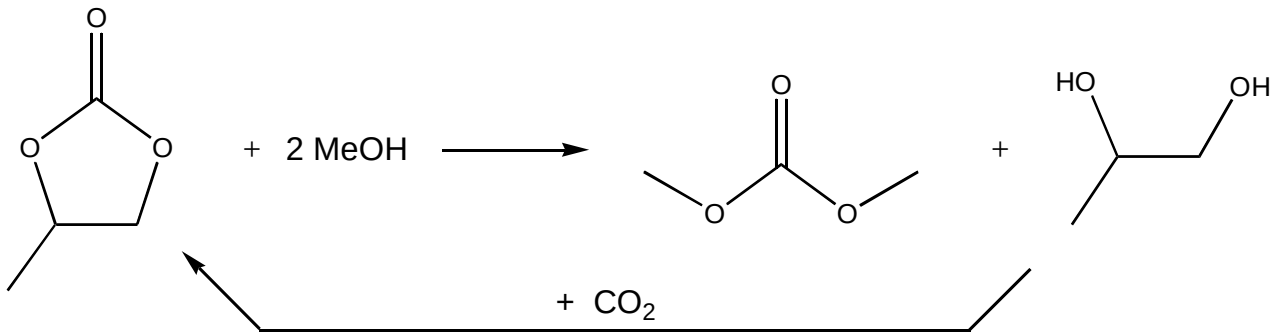
- Equilibrium yields ca. 1 % carbonate
  - Thermodynamic stability of CO_2
  - Improve product yields by removal of water
    - Hydration of acetonitrile (MeCN)

Ring strain provides chemical energy for reaction



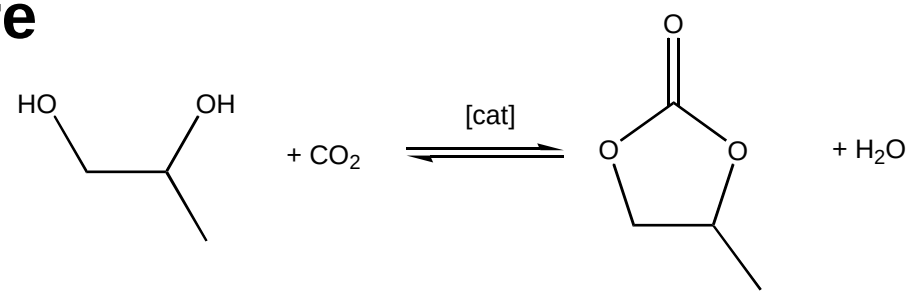
Carbonates from alcohols or diols – industrial utilization of CO_2 ?

- All one needs is ***one*** industrial process utilizing CO_2 for carbonates



- Transesterification chemistry will provide all carbonates

Literature



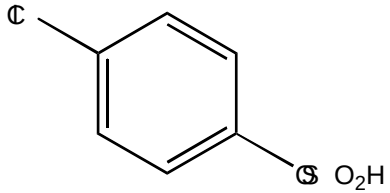
- Literature gives $Zn(OAc)_2$ as "best catalyst"
  - Conversion of PG: 37-39 % (GC)
  - Yield of PC: 19-24 % (GC)
  - Biproducts: 13-18 % (propylene glycol acetates) (GC)
  - 160-170 °C, 30-100 bar, 2.5 mol % catalyst, 180-190 mol % acetonitrile

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

- Data and poor activity of other metal acetates confirmed
  - Relatively large spread in activities

Establishment of benchmark catalyst

- Transesterification of carbonates and diols catalyzed by strong acids
- Addition of *p*-chlorotoluenesulfonic acid gave better overall yields and conversions



- Optimized system
  - 5 mol % $Zn(OAc)_2$ + 5 mol acid, 280 mol % acetonitrile
  - 60 atm, 145 °C, 16 h
  - Conversion PG: 78 % (NMR)
  - Yield PC: 33 % (NMR)
  - Yield byproducts: 40 % (NMR)

Reactor and Analyses

- 24-well high throughput reactor for screening of catalyst/IL 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).

High throughput experiments

- Confirmed internal reproducibility
  - All reactors with standard
  - GC HeadSpace and NMR analysis of selected wells
- Experiments contained one standard randomly placed in each row for internal calibration of results
- Reactions run overnight at 145 °C and ca. 50 bar
  - Reaction start: When reactors pressured to 50 bar at 145 °C
  - Reaction stop: When oven opened to start cooling
  - Pressure release took ca. 24 h
- All reactions 5 mol % catalyst
  - Acetonitrile/PG molar ratio 2.8
- GOAL: Find interesting candidates
  - Selected catalysts checked quantitatively in a Parr reactor

The 106 different catalysts

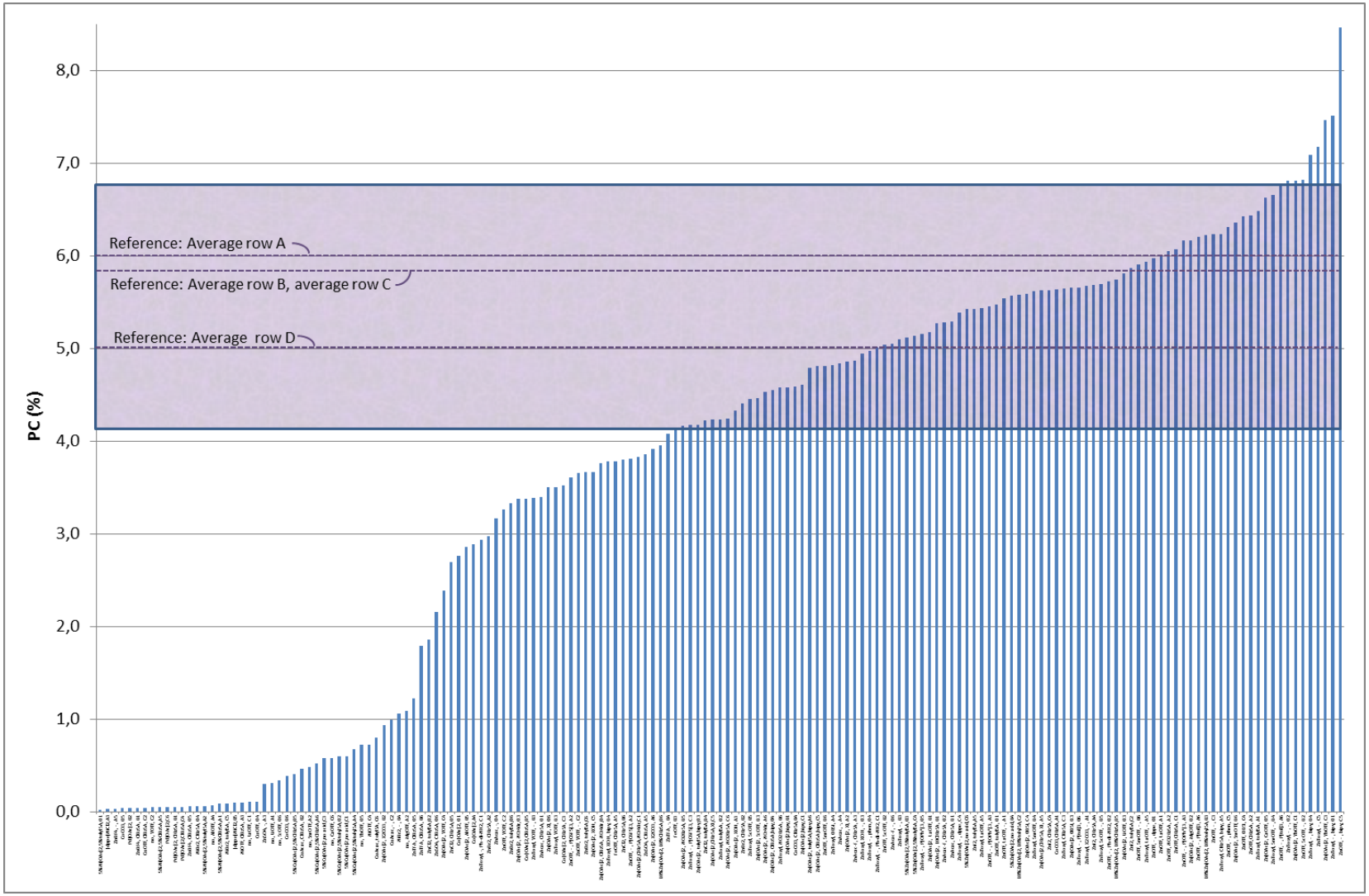
- $Zn(OAc)_2$ + **1**
- $Zn(OAc)_2$ + 2 x **1**
- $Zn(OAc)_2$ + **2***
- $Zn(OAc)_2$ + **3**
- $Zn(OAc)_2$ + **4**
- $ZnCl_2$ + **1**
- $ZnBr_2$ + **1**
- ZnI_2 + **1** §
- $ZnCl_2$ + **2**
- $ZnBr_2$ + **2**
- ZnI_2 + **2**
- $Zn(TFA)_2$
- $Zn(TFA)_2$ + **1**
- $Zn(acac\text{-}F_6)_2$
- $Zn(acac\text{-}F_6)_2$ + **1**
- $Zn(BF_4)_2$
- $Zn(BF_4)_2$ + **1**
- $Zn(SO_4)_2$
- $Zn(SO_4)_2$ + **1**
- $Zn(acac)_2$ + **1**
- $Zn(OAc)_2$ + La(OTf)
- $Zn(OAc)_2$ + $Mg(OTf)_2$
- $Zn(OAc)_2$ +$Ca(OTf)_2$
- $Zn(OAc)_2$ + $Al(OTf)_3$
- $Zn(OAc)_2$ + $Sm(OTf)_3$
- $Zn(OAc)_2$ + $La(OTf)_3$
- $Zn(OAc)_2$ + $Y(OTf)_3$
- $Zn(OAc)_2$ + $Yb(OTf)_3$
- $Zn(OAc)_2$ + $Sc(OTf)_3$
- $Zn(OAc)_2$ + KI
- $Zn(OAc)_2$ + KI + **1**
- $Zn(OAc)_2$ + NEt_4Br
- $Zn(OAc)_2$ + NEt_4Br + **1**
- $Zn(OAc)_2$ + KOH
- $Zn(OAc)_2$ + K_2CO_3
- $Zn(OAc)_2$ + bipy + **1**
- $Zn(OAc)_2$ + bipy + **2**
- $Zn(OAc)_2$ + bipy
- $Zn(tosylate)_2$ §
- $Zn(tosylate)_2$ + **1**
- $Zn(tosylate)_2$ + **2**
- $Zn(tosylate)_2$ + **3**
- $Zn(tosylate)_2$ + **4**
- $Zn(triflate)_2$ §
- $Zn(triflate)_2$ + **1**
- $Zn(triflate)_2$ + **2**
- $Zn(triflate)_2$ + **3**
- $Zn(triflate)_2$ + **4**
- $Zn(tosylate)_2$ + bipy
- $Zn(tosylate)_2$ + KOH
- $Zn(tosylate)_2$ + KOH + bipy
- $Zn(tosylate)_2$ + **1** + bipy
- $Zn(tosylate)_2$ + K_2CO_3
- $Zn(OTf)_2$ + bipy §
- $Zn(OTf)_2$ + phen
- $Zn(OTf)_2$ + $P(C_6F_5)_3$
- $Zn(OTf)_2$ + dppe
- $Zn(OTf)_2$ + 1,2-$(NH_2)_2(C_6H_4)$
- $Zn(OTf)_2$ + $P(tol)_3$
- $Zn(OTf)_2$ + $P(OAr^*)_3$
- $Zn(tosylate)_2$ + phen
- $Zn(tosylate)_2$ + $P(C_6F_5)_3$
- $Zn(tosylate)_2$ + dppe
- $Zn(tosylate)_2$ + 1,2-$(NH_2)_2(C_6H_4)$
- $Zn(tosylate)_2$ + $P(tol)_3$
- $Zn(tosylate)_2$ + $P(OAr^*)_3$
- $Zn(OTf)_2$ + $Yb(OTf)_3$
- $Zn(OTf)_2$ + $La(OTf)_3$
- $Zn(OTf)_2$ + $Y(OTf)_3$
- $Zn(OTf)_2$ + $Sm(OTf)_3$
- $Zn(OTf)_2$ + $Sc(OTf)_3$
- $Zn(tosylate)_2$ + $La(OTf)_3$
- $Zn(tosylate)_2$ + $Y(OTf)_3$
- $Zn(tosylate)_2$ + $Sm(OTf)_3$
- $Zn(tosylate)_2$ + $Sc(OTf)_3$

1 = chlorobenzenesulfonic acid
2 = *p*-tolylsulfonic acid
3 = 4-nitrobenzenesulfonic acid hydrate
4 = dibenzenesulfonimide
§ = Tested in batch scale reactor
* = 10 mol %

- $Sm(OTf)_3$
- $La(OTf)_3$
- $Y(OTf)_3$
- $Yb(OTf)_3$
- $Sc(OTf)_3$
- Li(OTf)
- $Mg(OTf)_2$
- $Ca(OTf)_2$
- $Al(OTf)_3$
- $Fe(OTf)_3$
- $Fe(OTf)_3$ + **1**
- $Co(OAc)_2$ + **1**
- $CoCO_3$
- $CoCO_3$ + **1** §

- $Ni(OAc)_2$ + **1**
- $Ni(OAc)_2$ + **2**
- $(dppe)NiCl_2$
- $NiBr_2$
- $NiBr_2$ + **1**
- $NiBr_2$ + **2**
- $Ni(OTf)_2$
- $Ni(OTf)_2$ + **1**
- $Cu(OAc)_2$ + **1**
- $Cu(OAc)_2$ + **2**
- $Cu(acac)_2$
- $Cu(acac)_2$ + **1**
- $Cu(acac)_2$ + **2**
- $Cu(OTf)_2$
- $Cu(OTf)_2$ + **1**
- $Pd(OAc)_2$
- $Pd(OAc)_2$ + **1**

HT results


8,0
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
PC (%)
Reference: Average row A
Reference: Average row B, average row C
Reference: Average row D

The 106 different catalysts

1 = chlorobenzenesulfonic acid
2 = *p*-tolylsulfonic acid
3 = 4-nitrobenzenesulfonic acid hydrate
4 = dibenzenesulfonimide
§ = Tested in batch scale reactor
* = 10 mol %

- $Zn(OAc)_2$ + **1***
- $Zn(OAc)_2$ + 2 x **1**
- $Zn(OAc)_2$ + **2***
- $Zn(OAc)_2$ + **3**
- $Zn(OAc)_2$ + **4**
- nCl_2 + **1**
- $ZnBr_2$ + **1**
- Zn[illegible] + **1** **§**
- $ZnCl_2$ + **2**
- $ZnBr_2$ + **2**
- ZnI_2 + **2**
- $Zn(TFA)_2$
- $Zn(TFA)_2$ + [illegible]
- $Zn(acac\text{-}F_6)_2$
- $Zn(acac\text{-}F_6)_2$ + [illegible]
- $Zn(BF_4)_2$
- $Zn(BF_4)_2$ + **1**
- $Zn(SO_4)_2$
- $Zn(SO_4)_2$ + **1**
- [illegible]$(acac)_2$ + **1**
- Zn[illegible]Cl(OTf)

- $Zn(OAc)_2$ + $La(OTf)_3$
- $Zn(OAc)_2$ + $Y(OTf)_3$
- $Zn(OAc)_2$ + $Yb(OTf)_3$
- $Zn(OAc)_2$ + $Sc(OTf)_3$
- $Zn(OAc)_2$ + KI
- $Zn(OAc)_2$ + KI + **1**
- $Zn(OAc)_2$ + NEt_4Br
- $Zn(OAc)_2$ + NEt_4Br + **1**
- $Zn(OAc)_2$ + KOH
- $Zn(OAc)_2$ + K_2CO_3
- $Zn(OAc)_2$ + bipy + **1**
- $Zn(OAc)_2$ + bipy + **2**
- $Zn(OAc)_2$ + bipy
- $Zn(tosylate)_2$ **§**
- $Zn(tosylate)_2$ + **1**
- $Zn(tosylate)_2$ + **2**
- $Zn(tosylate)_2$ + **3**
- $Zn(tosylate)_2$ + **4**
- $Zn(triflate)_2$ **§**
- $Zn(triflate)_2$ + **1**
- $Zn(triflate)_2$ + **2**

- $Zn(tosylate)_2$ + KOH + bipy
- $Zn(tosylate)_2$ + **1** + bipy
- $Zn(tosylate)_2$ + K_2CO_3
- $Zn(OTf)_2$ + bipy **§**
- $Zn(OTf)_2$ + phen
- $Zn(OTf)_2$ + $P(C_6F_5)_3$
- $Zn(OTf)_2$ + dppe
- $Zn(OTf)_2$ + 1,2-$(NH_2)_2(C_6H_4)$
- $Zn(OTf)_2$ + $P(tol)_3$
- $Zn(OTf)_2$ + $P(OAr^*)_3$
- $Zn(tosylate)_2$ + phen
- $Zn(tosylate)_2$ + $P(C_6F_5)_3$
- $Zn(tosylate)_2$ + dppe
- $Zn(tosylate)_2$ + 1,2-$(NH_2)_2(C_6H_4)$
- $Zn(tosylate)_2$ + $P(tol)_3$
- $Zn(tosylate)_2$ + $P(OAr^*)_3$
- $Zn(OTf)_2$ + $Yb(OTf)_3$
- $Zn(OTf)_2$ + $La(OTf)_3$
- $Zn(OTf)_2$ + $Y(OTf)_3$
- $Zn(OTf)_2$ + $Sm(OTf)_3$
- $Zn(OTf)_2$ + $Sc(OTf)_3$

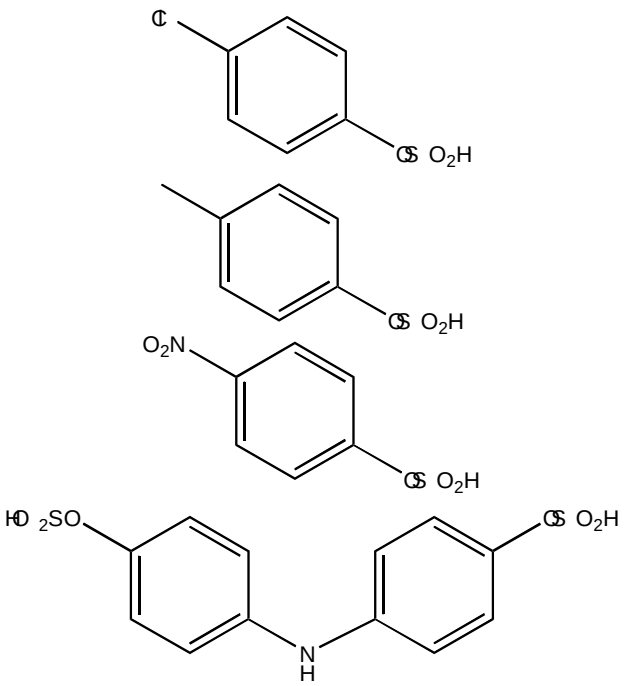
- $Sm(OTf)_3$
- $La(OTf)_3$
- $Y(OTf)_3$
- [illegible]$(OTf)_3$
- Sc[illegible]$Tf)_3$
- Li(OTf)
- Mg(OTf)
- Ca(OTf)
- [illegible]
- Fe(OTf)
- [illegible]$(OTf)_3$ **1**
- Co([illegible])$_2$ **1**
- $CoCO_3$
- $CoCO_3$ + **1**

- $Ni(OAc)_2$ + **1**
- $Ni(OAc)_2$ + **2**
- $(dppe)NiCl_2$
- $NiBr_2$
- $NiBr_2$ + **1**
- $NiBr_2$ + **2**
- [illegible]$(OTf)_2$
- Ni[illegible]$Tf)_2$ + **1**
- Cu([illegible])$_2$ + **1**
- Cu([illegible])$_2$ + **2**
- Cu(aca[illegible]
- Cu(acac)$_2$ **1**
- Cu(acac)$_2$ + [illegible]
- $Cu(OTf)_2$
- $Cu(OTf)_2$ + **1**
- $Pd(OAc)_2$
- $Pd(OAc)_2$ + **1**

High throughput results mirror Parr reactor results at York and SINTEF

Effect of acid

- Addition of 10 mol % *p*-chlorobenzenesulfonic acid did not improve significantly catalyst activity
- No observable effect of acid pK_a on catalyst activity



7.2

8.45

6.60

11.34

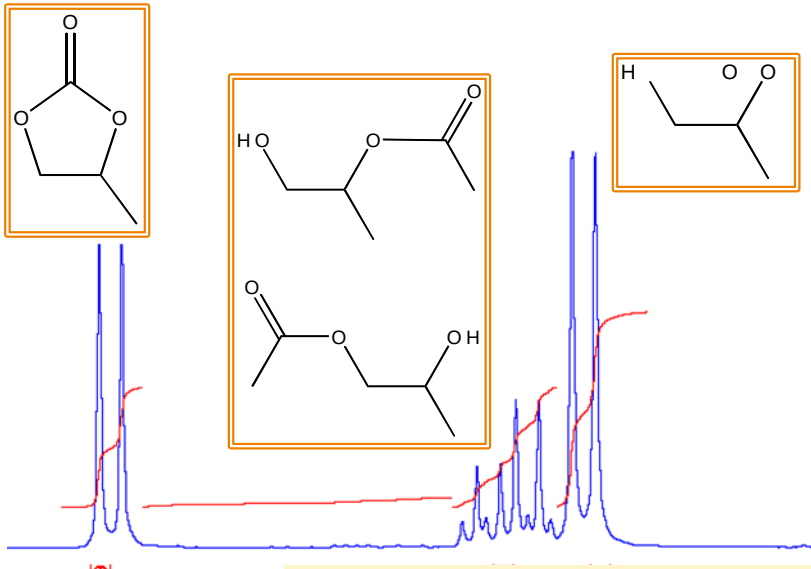
pK_a's in acetonitrile

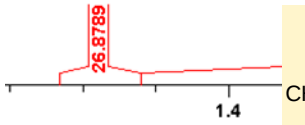
J. Org. Chem. **2011**, *76*, 391
J. Comp. Chem. **2009**, *30*, 799

And the winners are….

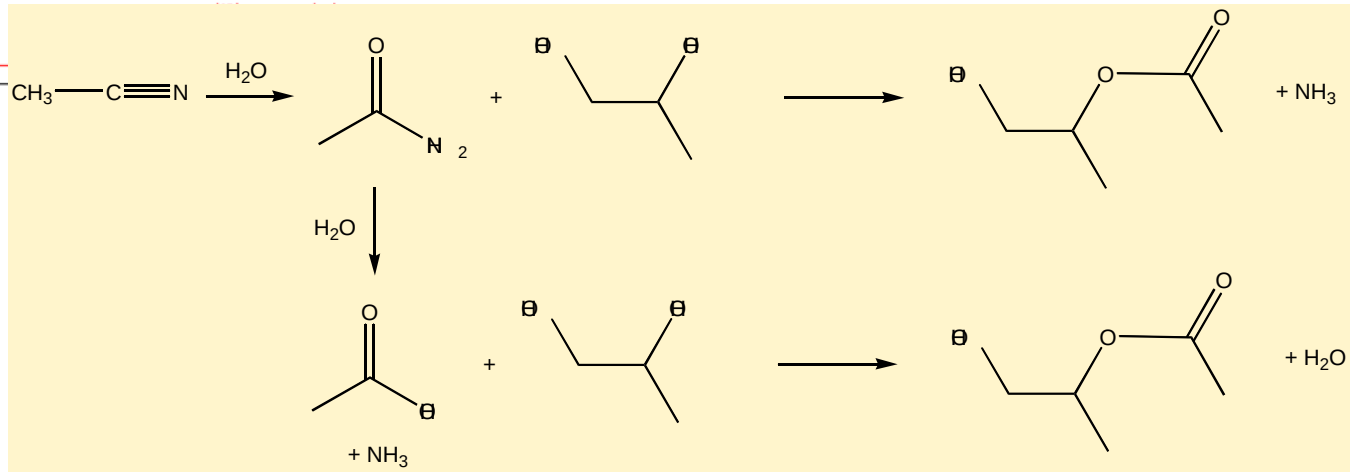
- Zn salts with very poorly coordinating anions
  - $Zn(OSO_2CF_3)_2$ (Zn-triflate)
  - $Zn(p\text{-}OSO_2C_6H_4CH_3)_2$ (Zn-tosylate)
  - Variations of these salts with ligands (*e.g.* bipy) or strong Lewis acid triflate salts $[Sm(OTf)_3]$
  - HYPOTHESIS: Effect of acid is to
    - Protonate off OAc-ligands to provide a "naked" Zn(II) cation, but
    - *In situ* deprotonation is incomplete
- Batch scale reactions
  - $Zn(OSO_2CF_3)_2$
  - $Zn(p\text{-}OSO_2C_6H_4CH_3)_2$
  - $Zn(OSO_2CF_3)_2$ + bipy

NMR analysis and impurities

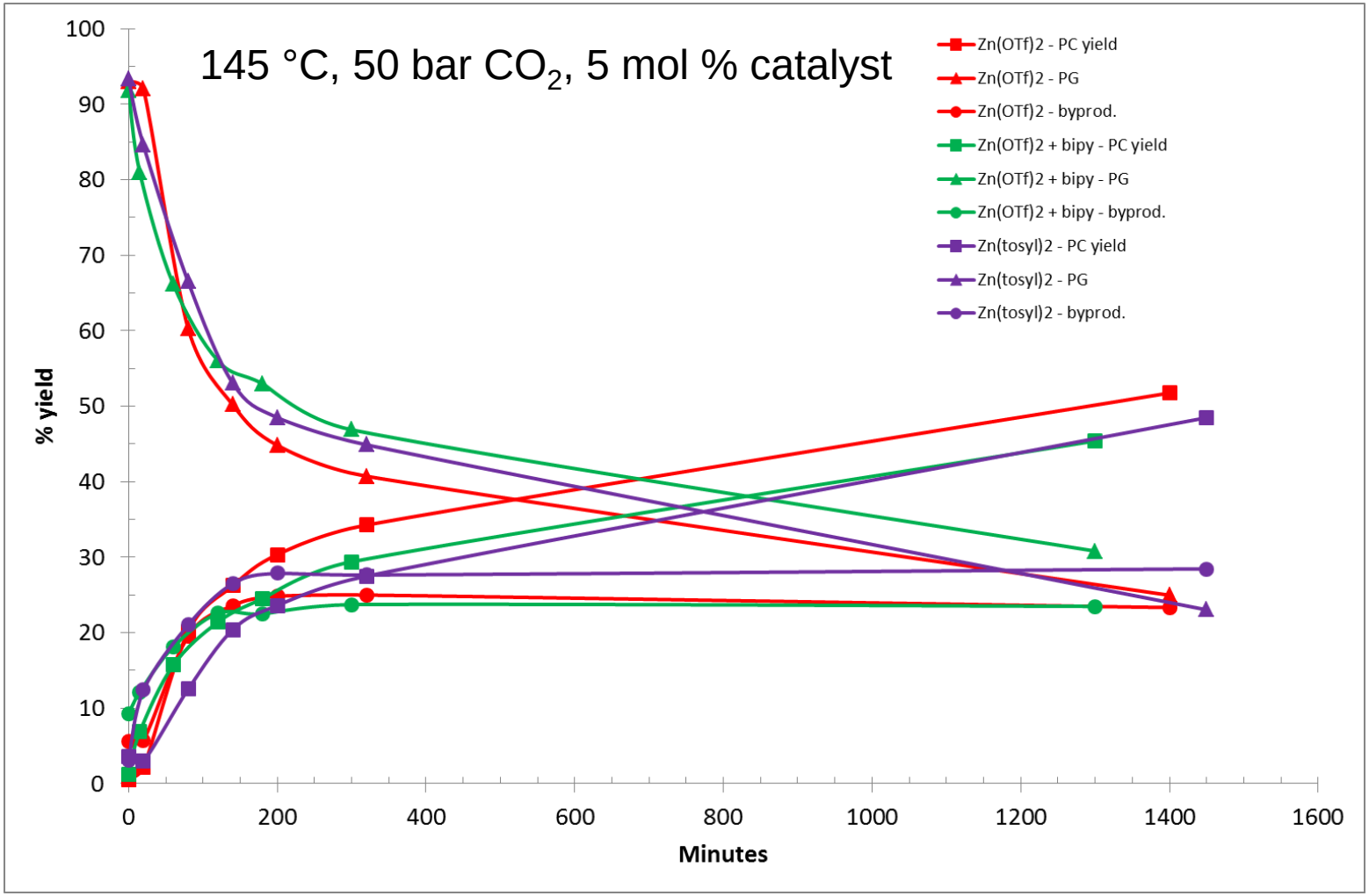




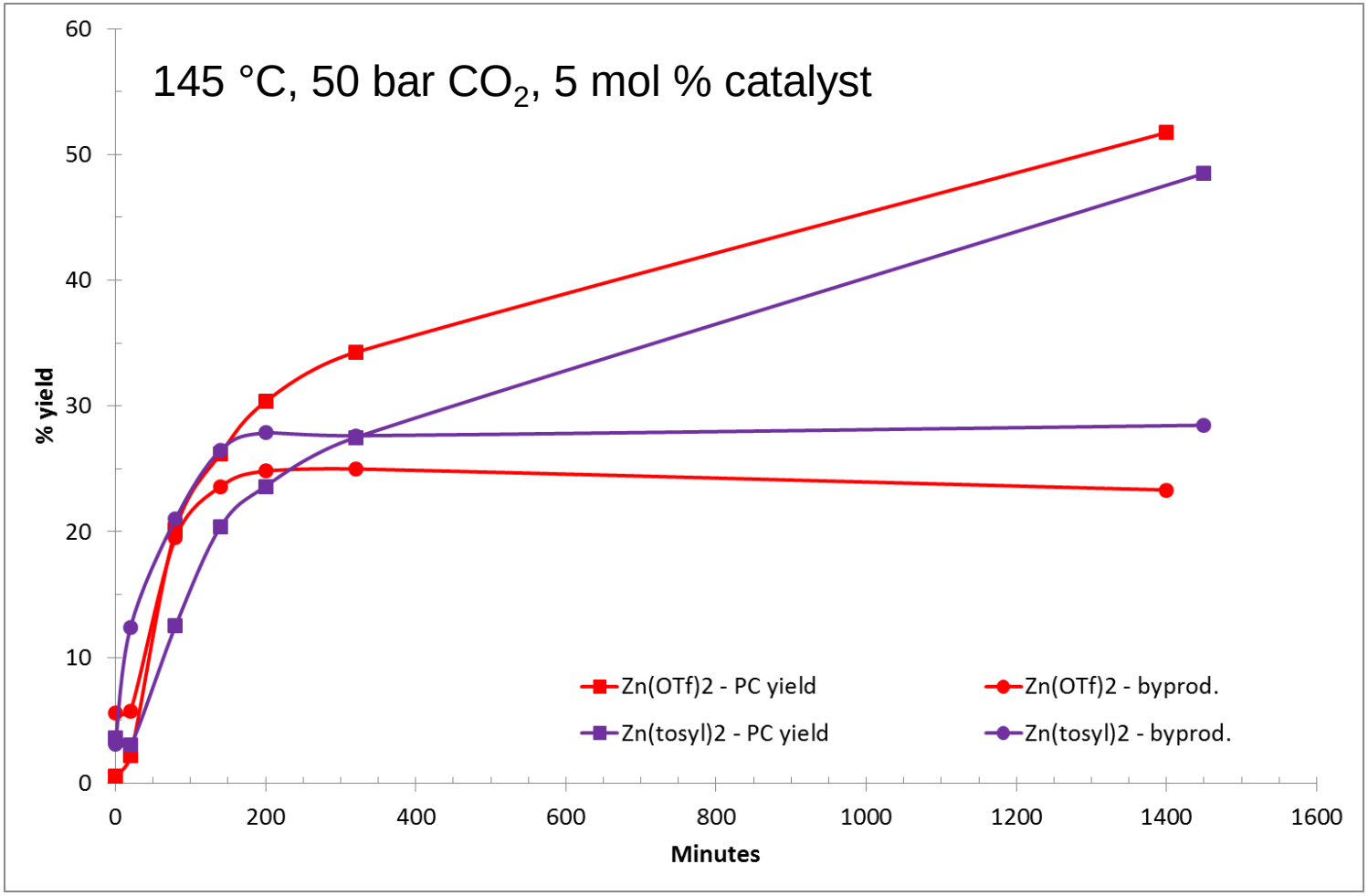
Conversion, yield and selectivity from a normalized integration (sum = 100)



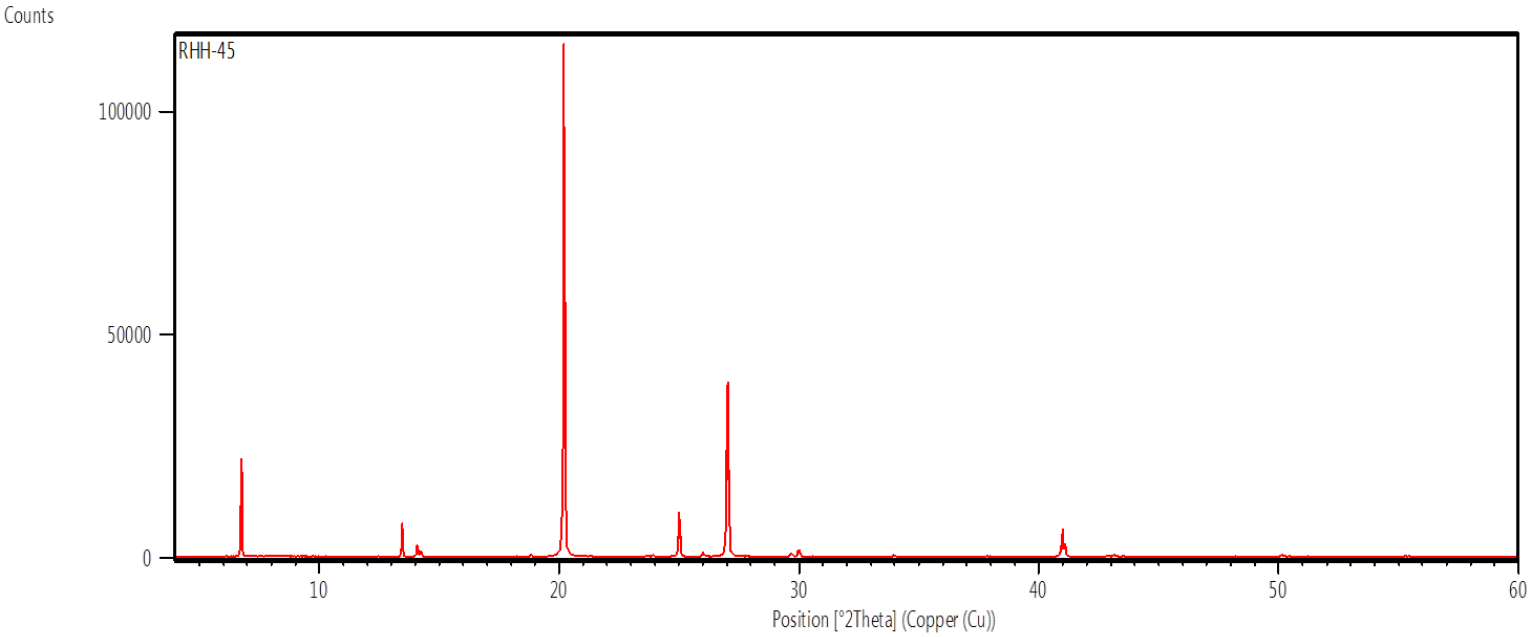
Reaction profile of three new Zn catalysts



Reaction profile of three new Zn catalysts

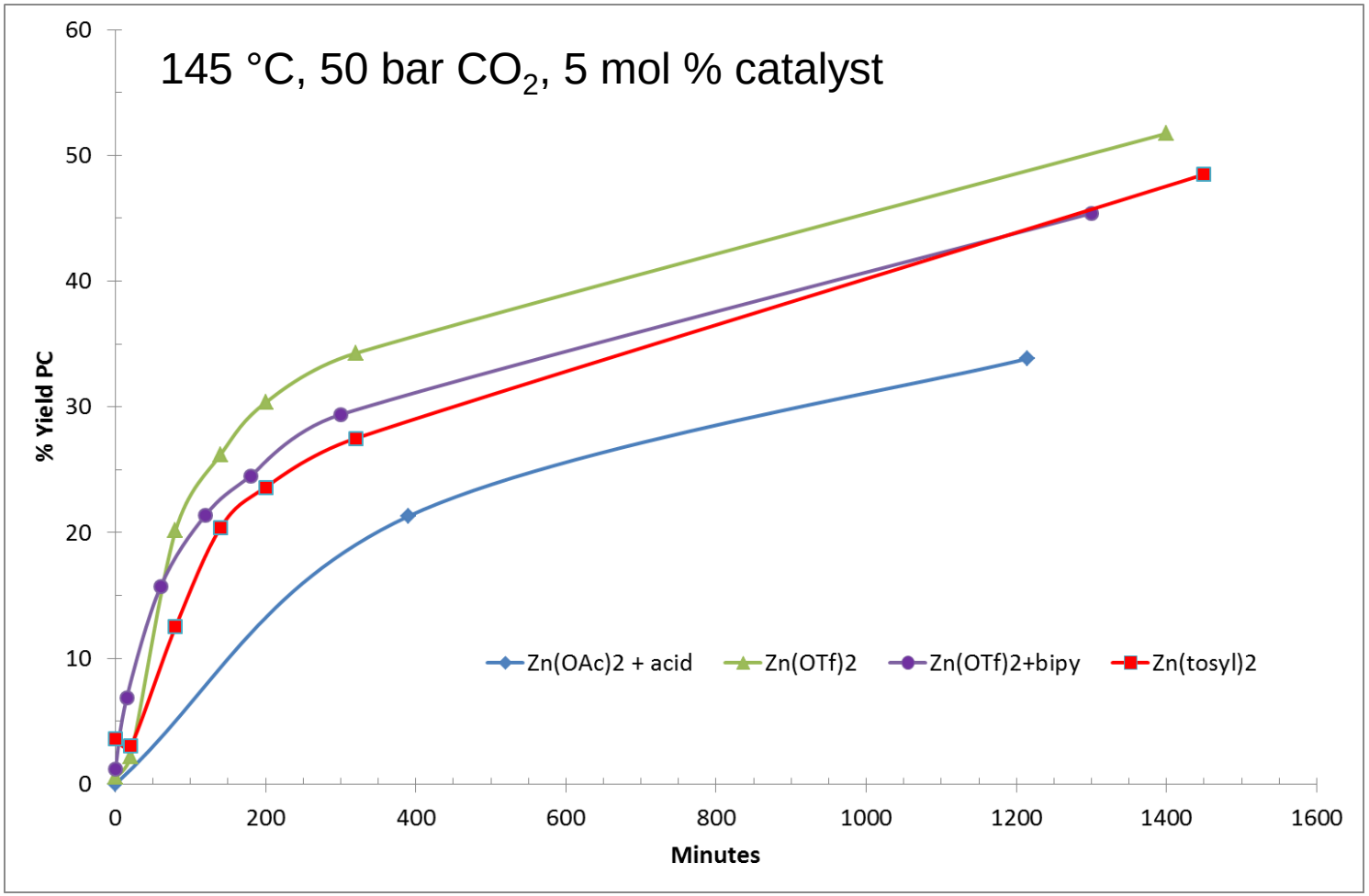


Crystalline material from Zn(tosylate)$_2$ reaction

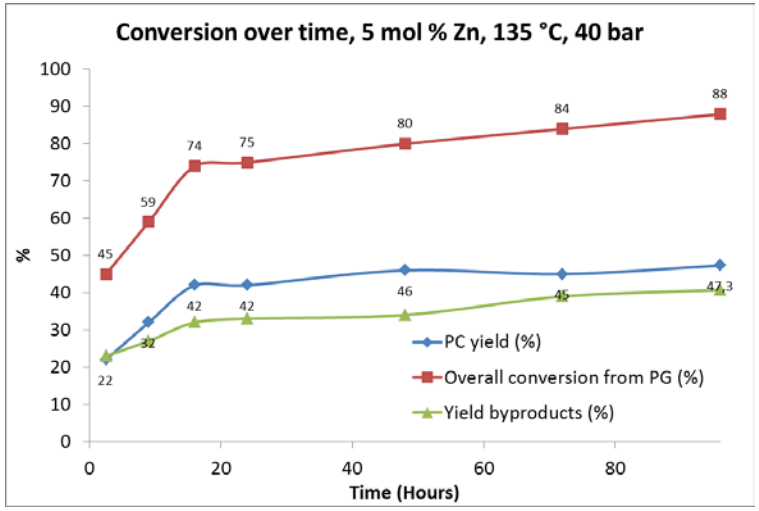


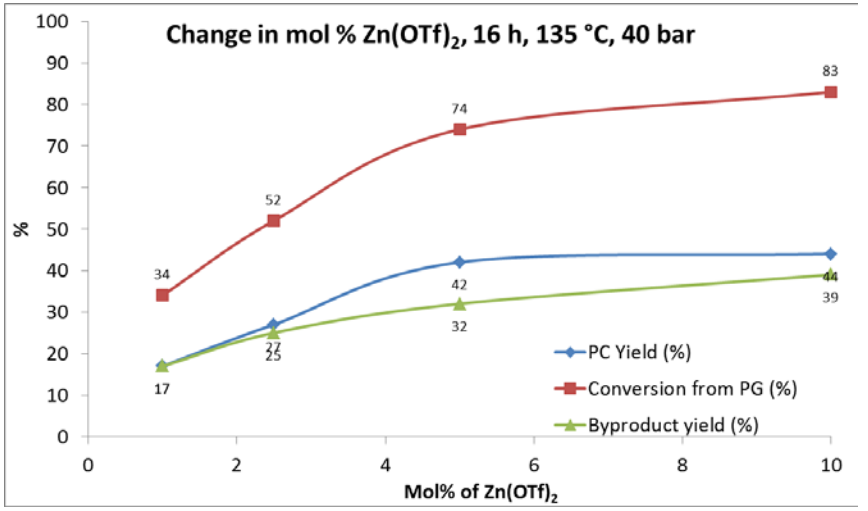
- ^{1}H NMR data shows no evidence of PG or PC
  - Only acetonitrile and acid protons (exchange with D of MeOH-d_4)

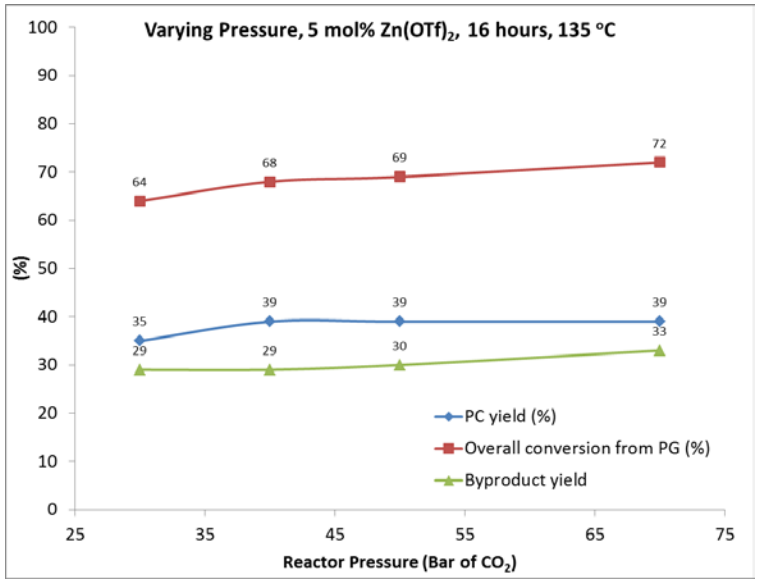
Comparison of new catalysts with standard

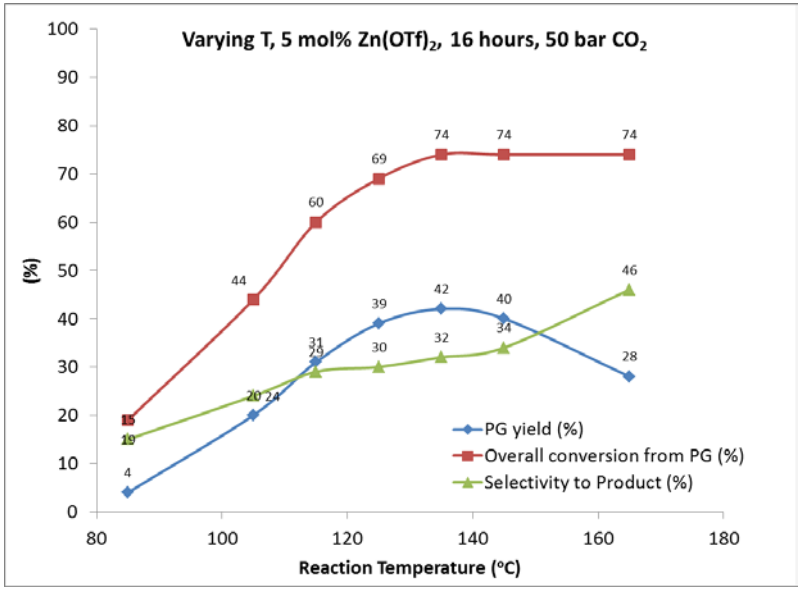


Screening of conditions









Summary

- New catalyst systems for the direct reaction of PG and CO_2 to PC
  - Assisted by acetonitrile hydrolysis
  - Discovered via high-throughput screening
  - 100 % improvement over best known homogeneous system
  - Faster
- Unexplained curiosities with product development
  - Rapid increase in PC and byproduct yields
    - Byproduct yields level out while PC yields continue to increase
    - PC yield profile suggests two different mechanisms
- Work is continuing to elucidate mechanism and isolate and characterize potential catalytic intermediates, resting states, or dead catalysts

Acknowledgement

- European Union Seventh Framework program (FP7/2007-2013) project "CyclicCO2R", under grant agreement number 309497

- Experimental assistance
  - Kari Anne Andreassen
  - Anne Andersen
  - Aud M. Bougza
  - Dr. Silje F. Håkonsen
  - Dr. Anna Lind
  - Ruth Elisabeth Stensrød