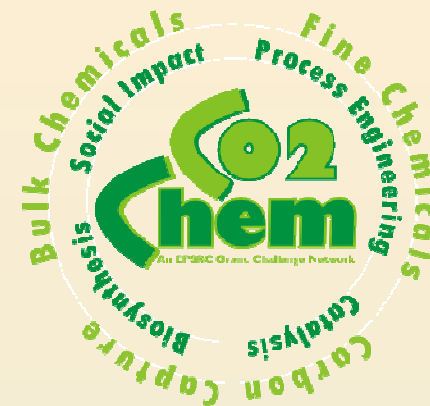


Technical aspects of CO₂ Reuse

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University of Newcastle, U.K.



CO₂Reuse workshop 24th October 2012, Brussels



Newcastle
University

*University Research Centre for
Catalysis and Intensified Processing*



CO₂ Chemistry: Why?

The world is running out of oil and gas

>90% of all commercial organic chemicals are sourced from crude oil

The 2012 BP statistical review of world energy

(<http://www.bp.com/statisticalreview>) indicates that:

1. Known reserves of oil will be consumed in 54 years
2. Known reserves of gas will be consumed in 64 years
3. Known reserves of coal will be consumed in 112 years

These predictions assume that consumption of the fossil fuels remains constant at current levels and they have risen every year since 1982 except for 2009!

We need alternative, sustainable starting materials for the chemicals industry and CO₂ is one such sustainable resource.

Main reactions of CO₂

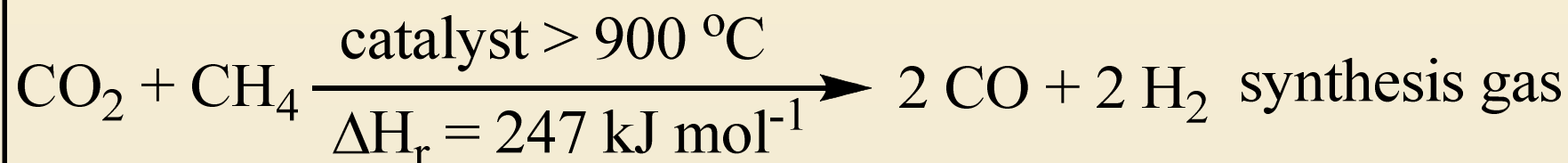
1: Reduction (C1 chemistry)

2: C-C bond forming reactions

3: Reaction with epoxides

Reduction to CO

Dry reforming of methane



catalyst typically Ni, Ru, Rh, Pd, Ir, Pt or Co

on oxide support (SiO₂, Al₂O₃, MgO, TiO₂, CaO, CeO₂, ZrO₂, La₂O₃)

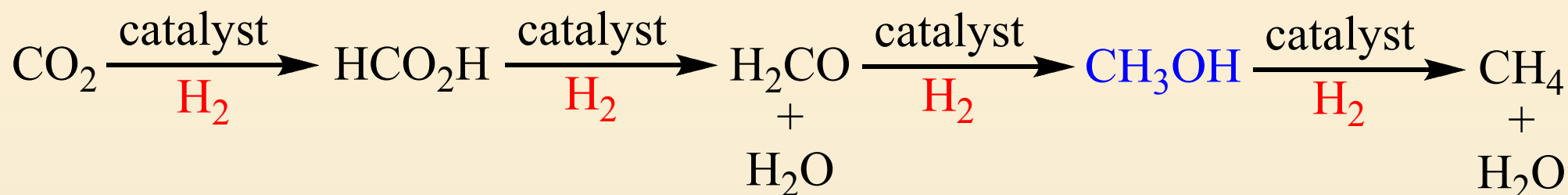


can be achieved photochemically or electrochemically

e.g. Ru(bipy)₃ modified enzyme attached to TiO₂ nanoparticles

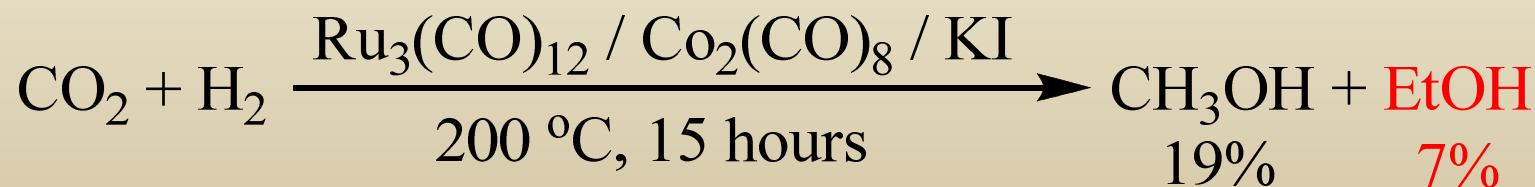
J. Am. Chem. Soc. 2010, p2132 (Armstrong)

Catalytic hydrogenation of CO₂



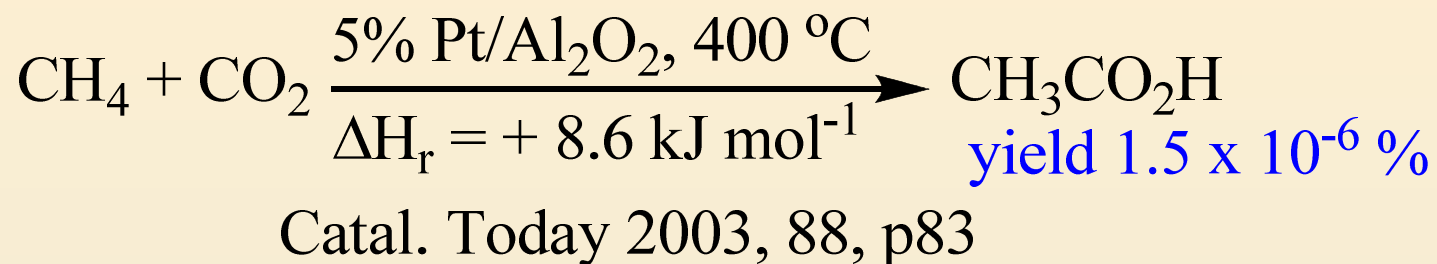
$\Delta H_r = -106 \text{ kJ mol}^{-1}$ for CH₃OH from CO₂; $\Delta H_r = -230 \text{ kJ mol}^{-1}$ for CH₄ from CO₂
 pilot plant in Japan using a SiO₂ modified Cu-ZnO catalyst at 250 °C, 50 atm.
 commercial production in Iceland using geothermal energy (Carbon Recycling Int.)

Enormous area: issues with catalyst lifetime, activity and selectivity

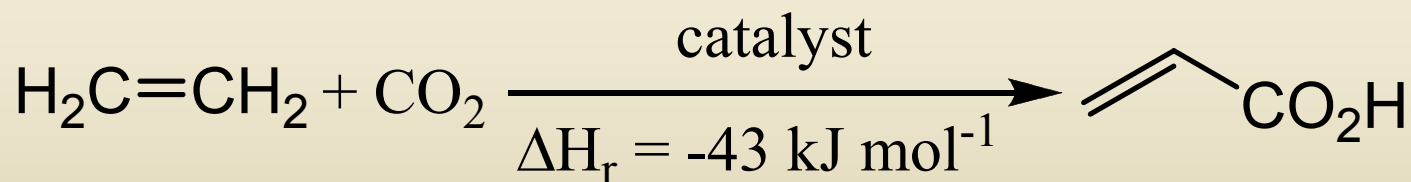
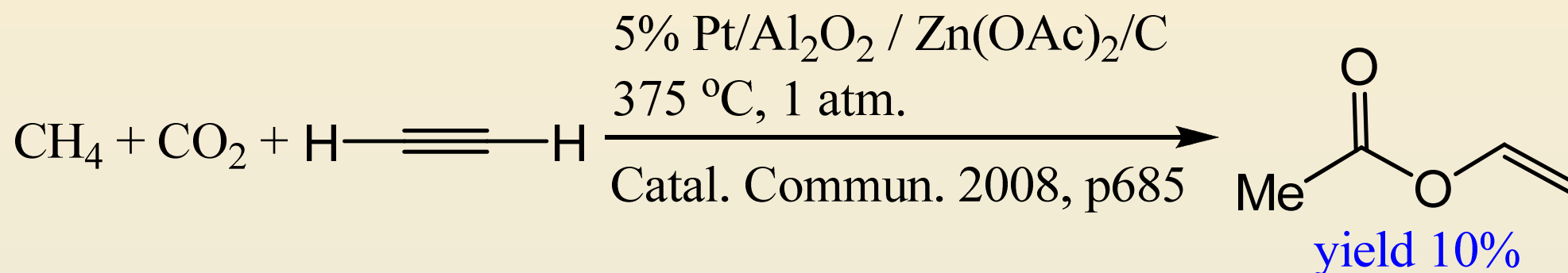


J. Mol. Cat. A 1994, 89, p51

Catalytic C-C bond forming reactions



50% of acetic acid currently manufactured is converted into vinyl acetate



no good catalyst exists.

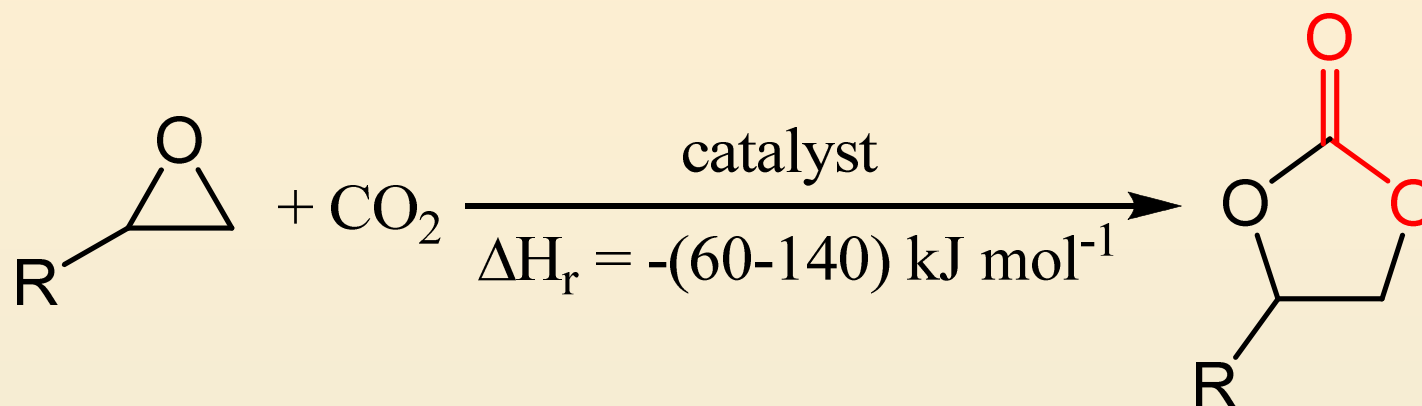
Ni, Mo and W complexes show some activity

Ni complexes also catalyse the reactions between CO_2 and other alkenes.

Limbach *Chem. Eur. J.* 2012, p14017

breakthrough in Ni catalysis, catalytic cycle determination

Formation of cyclic carbonates: 1



Commercial process for over 50 years, currently about 2 Mtonnes of cyclic carbonates made this way every year

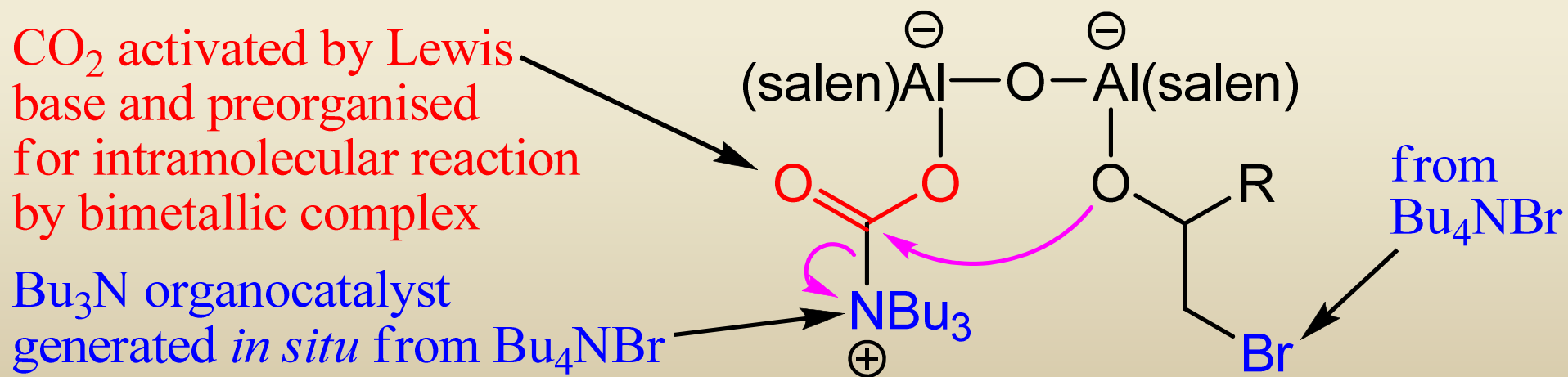
Not a difficult reaction to catalyse. Any Lewis acid or Lewis base will catalyse the reaction, but usually at $>110^\circ\text{C}$ and >10 atmospheres CO₂ pressure. e.g.

R_4NBr , R_4PBr , DMAP, ionic liquids, phenol, DMF, DBU, carbenes,
 ZnBr_2 , ZnCl_2 , LiBr, NaI, KI, KCl(18-crown-6), KBr, AlCl_3 , CoCl_2 , VCl_3 ,
 FeCl_3 , SmOCl , $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Sc}(\text{OTf})_3$, $\text{Re}(\text{CO})_5\text{Br}$, RuCl_3 , SnCl_4 , InCl_3
Metal[phthalocyanine, porphyrin, quinolate, tetraazamacrocles or salen]
Electrochemical, MgO , Al_2O_3 , CeO_2 , Nb_2O_5 , polyoxometallates

Formation of cyclic carbonates: 2

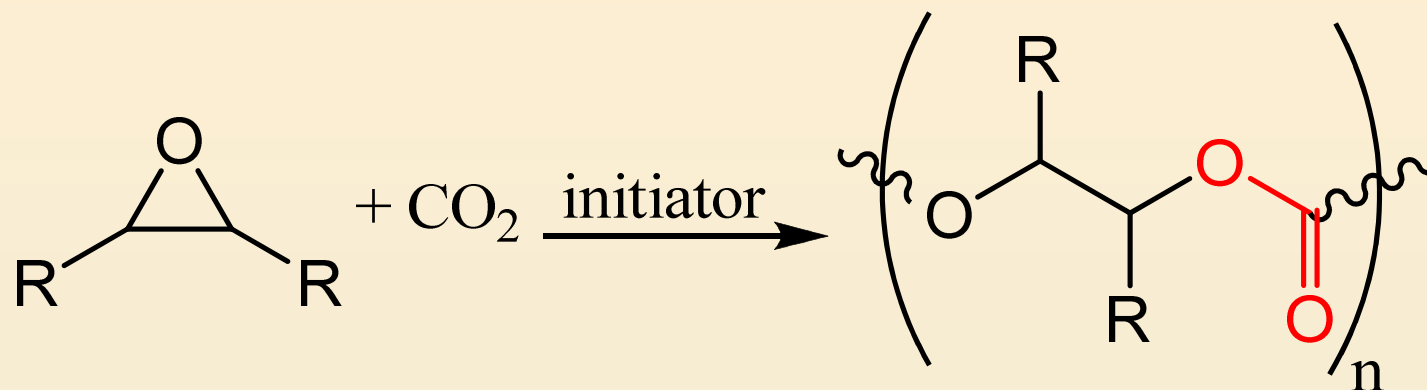
The challenge is to catalyse the reaction under mild reaction conditions (< 1 bar pressure and < 100 °C). This requires bifunctional catalysis to activate both the epoxide and CO_2 .

The best catalysts tend to be $\text{M}(\text{salen})$ complexes where $\text{M} = \text{Al}$, Co(III) , or Cr(III) . e.g. $[\text{Al}(\text{salen})]_2\text{O} / \text{Bu}_4\text{NBr}$, catalyses cyclic carbonate formation from terminal epoxides at room temperature and one atmosphere pressure in three hours with no solvent.

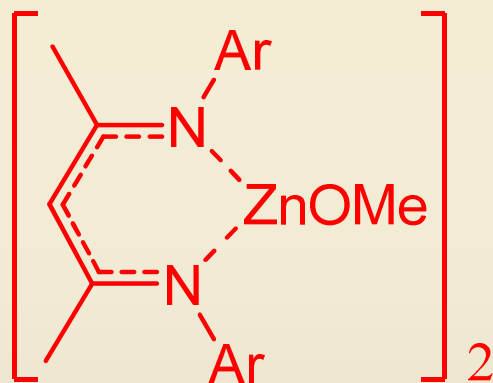


Chem. Eur. J. 2010, p6828

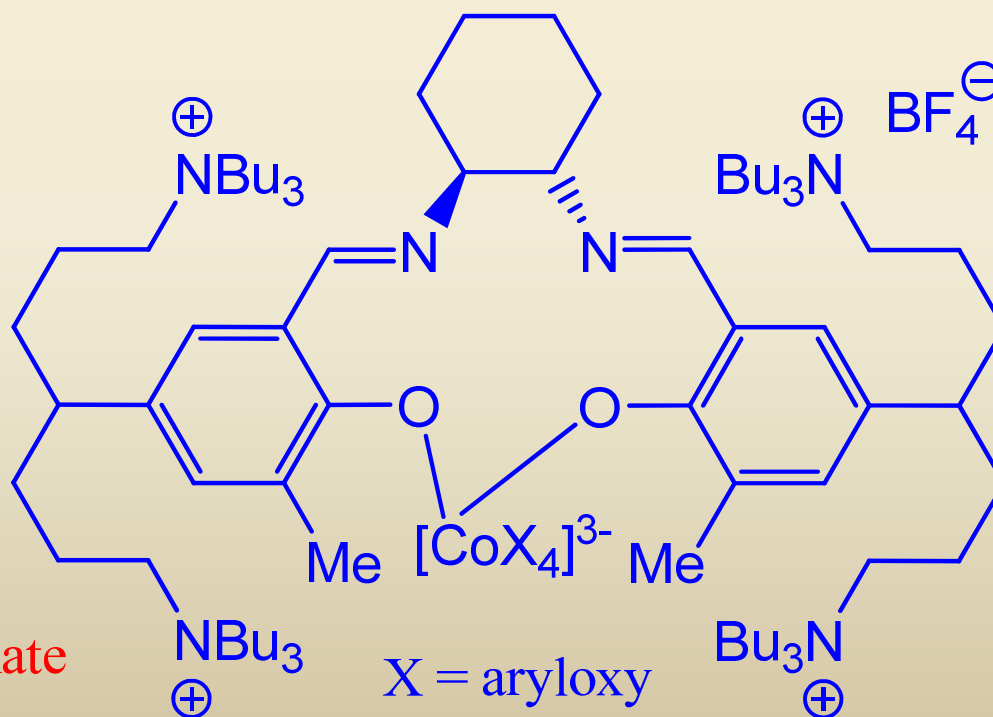
Formation of polycarbonates



This is also a commercial process



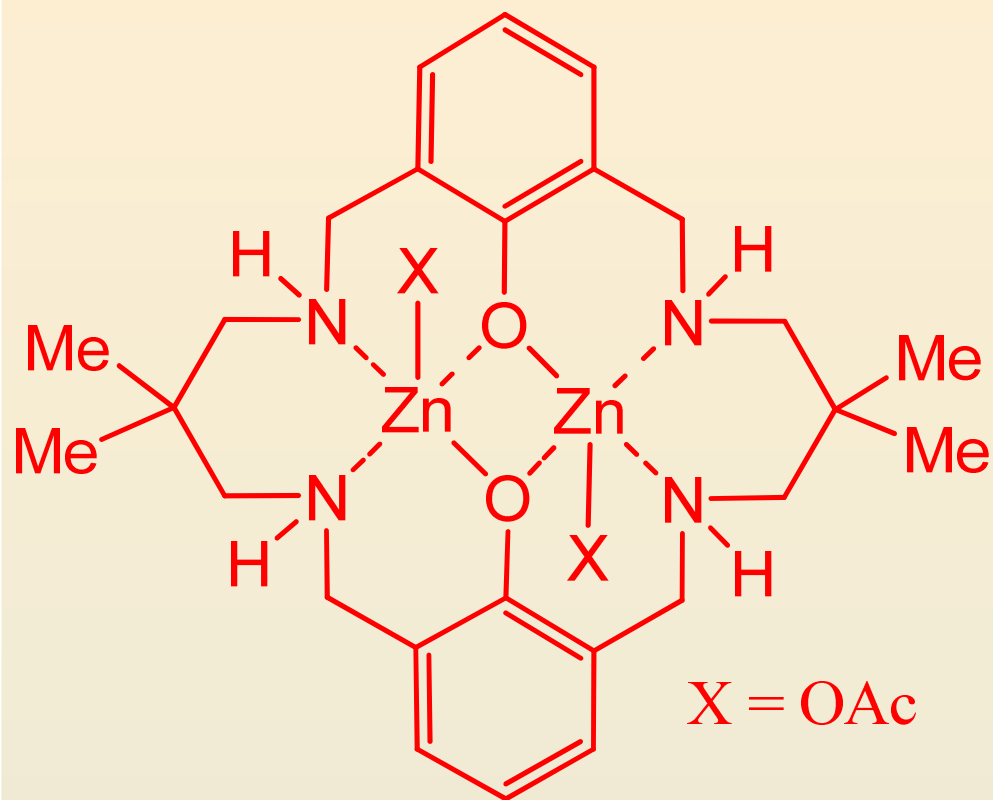
Geoff Coates
commercial: Novomer
7 atm. CO_2 and 50°C
polypropylene carbonate
poly(cyclohexene oxide) carbonate
Angew.Int.Ed. 2002, p2599



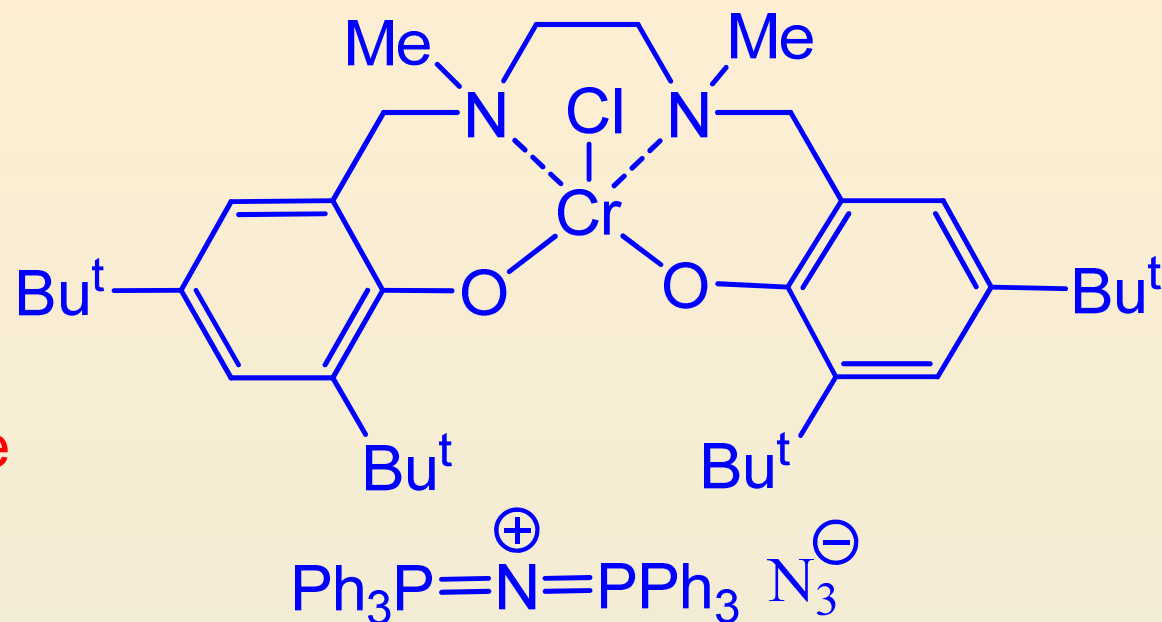
Bun Lee
pilot plant
20-170 atm. CO_2
and 80°C for
polypropylene
carbonate

Dalton
2010, p2622

Other notable initiators



Williams (Angew. Int. Ed. 2009, p931)
 1 atm. CO_2 , 100 °C
 poly(cyclohexene oxide) carbonate



Darensbourg (Macromol. 2009, p6992)
 34 atm. CO_2 , 60 °C for
 poly(cyclohexene oxide) carbonate
 15 atm. CO_2 , RT for
 poly(propylene oxide) carbonate

Challenges

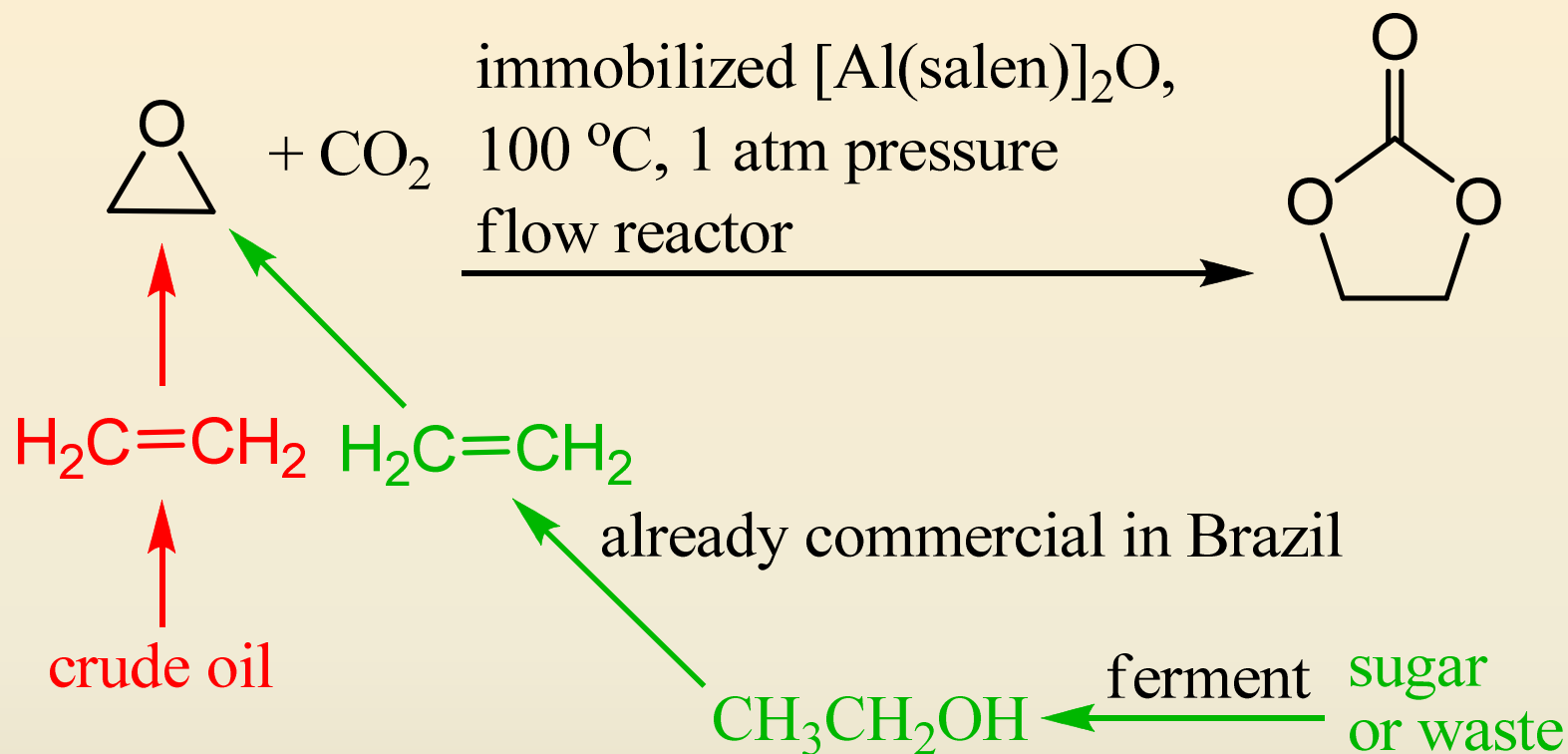
Initiator must not colour the polymer, Mild reaction conditions,
 Controllable polymerization allowing M_n and PDI to be controlled

Challenges 1: Can your catalyst do this?



Utilize waste CO₂ directly from power stations, cement works, chemical plants, oil refineries, iron and steel works, aluminium producers etc

2: Where will the other reactant come from?



Role for biotechnology in providing the required reactants. e.g. Propan-1-ol or propan-2-ol are needed to produce propylene oxide which could be converted into either propylene carbonate or polypropylene carbonate.

Major problem for CO_2 hydrogenation – where will the H_2 come from?

3: How sustainable is your catalyst?

Oil is not the only chemical we are running out of.
Many elements are endangered.

<http://www.chemistryinnovation.co.uk/>

Oil is not the only chemical we are running out of.
Many elements are endangered.
<http://www.chemistryinnovation.co.uk/>

1 H 1.0079																	2 He 4.0026								
3 Li 6.941	4 Be 9.0122																	5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180		
11 Na 22.990	12 Mg 24.305																	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948		
19 K 39.098	20 Ca 40.078																	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62																	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-70 *	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]							
87 Fr [223]	88 Ra [226]	89-102 **	103 Lr [261]	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [265]	109 Mt [268]	110 Uun [271]	111 Uuu [272]	112 Uub [277]	114 Uuq [289]												

* Lanthanide series

** Actinide series

Lanthanum 57 La 138.91	Cerium 58 Ce 140.12	Praseodymium 59 Pr 140.91	Nd 144.24	Pm [145]	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.93	Dy 162.50	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.04
Actinium 89 Ac [227]	Th 232.04	Pa 231.04	U 238.03	Np [237]	Pu [244]	Am [243]	Cm [247]	Bk [247]	Cf [251]	Es [252]	Fm [257]	Md [258]	No [259]



Serious threat in
next 100 years



Rising threat from
increasing use



Limited availability
future risk to supply



Abundant element



Formed by
radioactive decay



Insufficient
information

Vision of CO₂ chemistry for 2050

1. Low lying fruit will have been commercialized

For example CO₂ and epoxides to cyclic or polycarbonates

- Global production of cyclic and polycarbonates substantially increased.
- Production of less sustainable alternatives substantially decreased.
- Cyclic / polycarbonates produced using waste CO₂.
- Cyclic / polycarbonates produced using sustainably produced epoxides.
- Cyclic / polycarbonates produced using a sustainable catalyst.

2. Substantial number of medium height fruit at development / pilot plant stage

Examples might include.

- Ethanol from CO_2 and H_2 .
- Acrylic acid from CO_2 and ethene.

The beginnings of a CO_2 based integrated chemicals industry.

Ethanol can be dehydrated to ethene or oxidised to acetaldehyde and acetic acid.

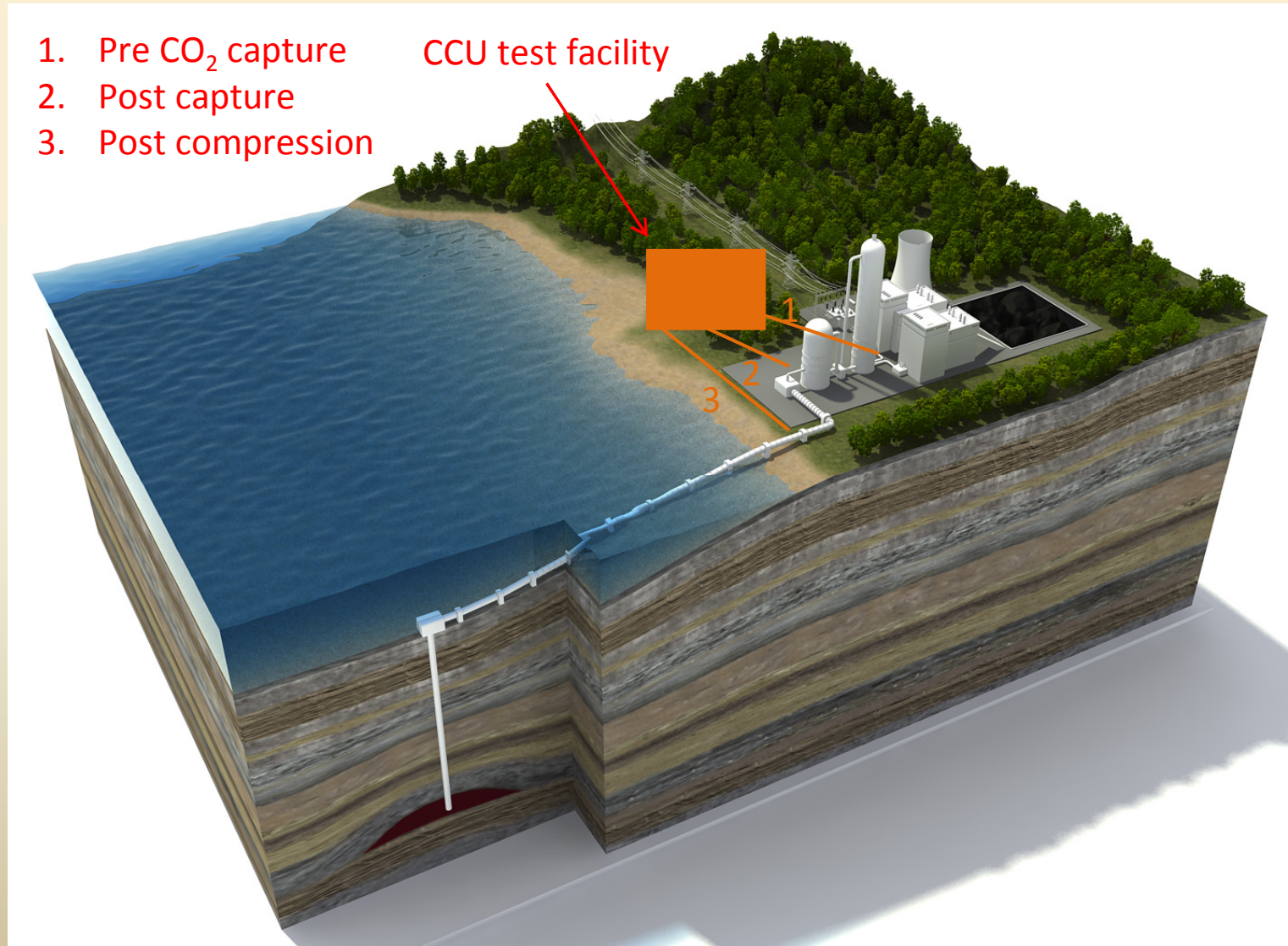
Acetic acid and ethanol gives ethyl acetate.

Ethyl acetate and sodium ethoxide gives ethyl acetoacetate etc. etc.

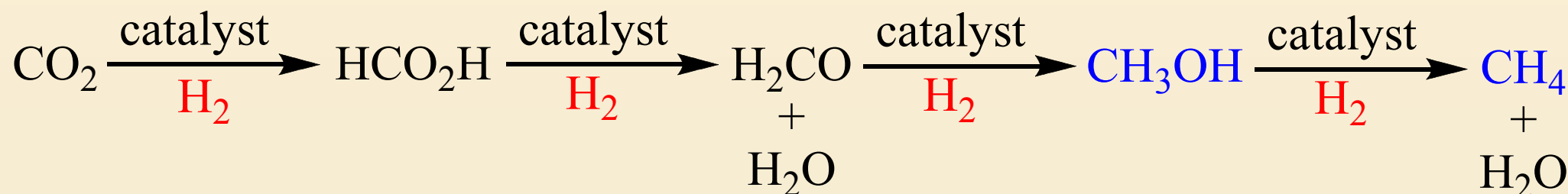
3. A flue-gas utilization facility

Flue gas cannot be bottled, purchased or easily generated in the laboratory.

Any EU funded CCS system should be forced to include CCU test facilities to encourage the development of chemistry which can use flue-gas.



4. Renewable energy production linked to H₂ generation.



The EU has a long coastline.

Tidal power has a much higher energy density than wind power.

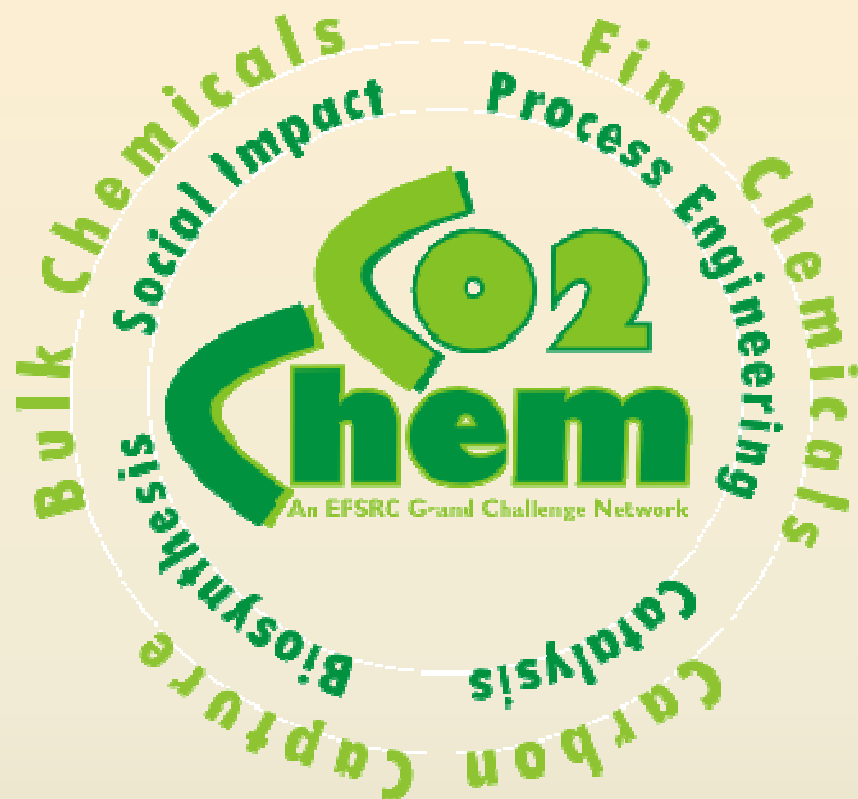
Tides are predictable, they come in and out twice a day.

At least one of these will be at night when energy not needed.

Use this energy to electrolyse sea water to produce H₂ and use the H₂ to reduce CO₂ initially to MeOH or CH₄.

Later generation plants could produce EtOH / higher alkanes for use as transport fuel instead.

Acknowledgement



www.co2chem.com (email: network@co2chem.com)

**An EPSRC funded, UK based, global network bringing people
interested in CO₂ chemistry together
To join (free) see me or Katy Armstrong today**