

Valorization of CO₂ to Organic Carbonates with Cerium Oxide

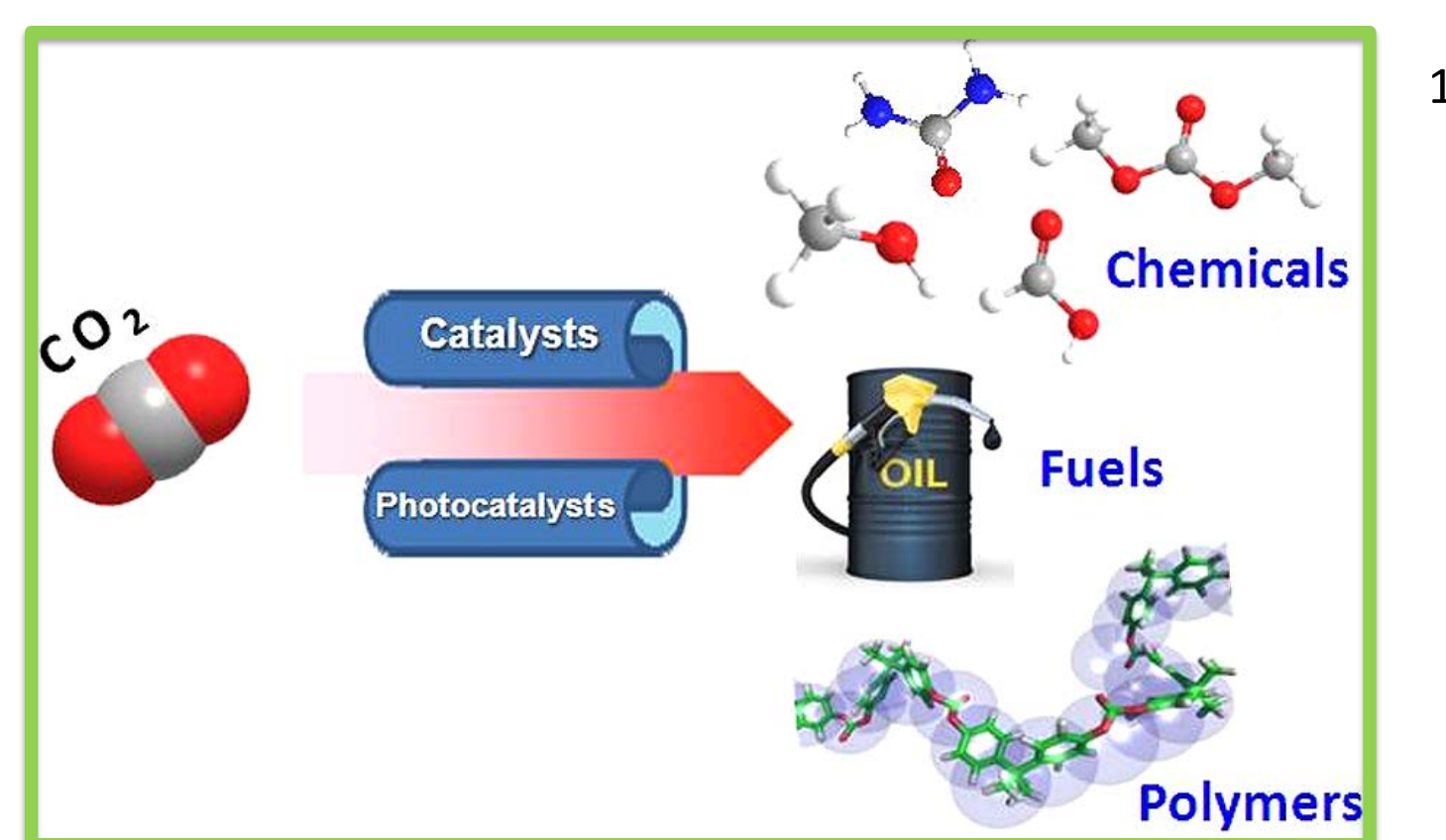
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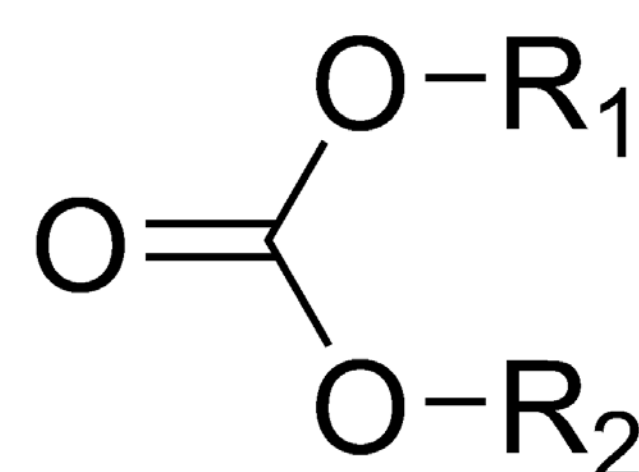
CO₂ Remediation

- CO₂ is considered a very important greenhouse gas correlated with global Earth temperatures.
- In 2012, U.S. CO₂ emissions were 5.35 Billion tons of CO₂ with two thirds from combustion for power generation and transportation.
- With such a reliance on combustion chemistry, the elimination of CO₂ production would be extremely disruptive.
- A better solution is to recycle generated CO₂ for a carbon cycle similar to that found in nature and allowing valorization of this abundant waste chemical.



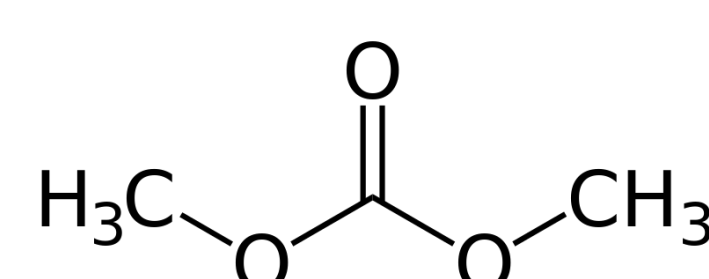
Organic Carbonates

- Organic carbonates are a class of organic chemicals containing a carbonate ester.

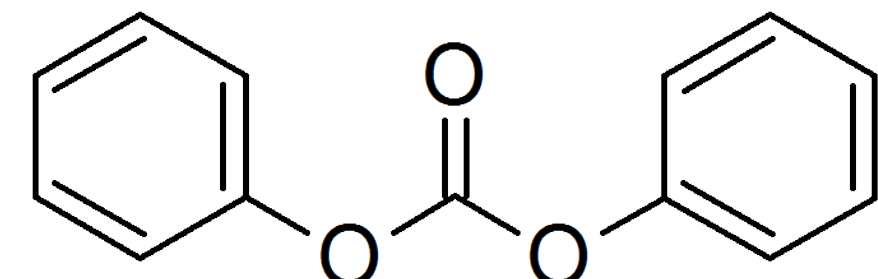


- The simplest organic carbonates contain two R functional groups.

dimethyl carbonate

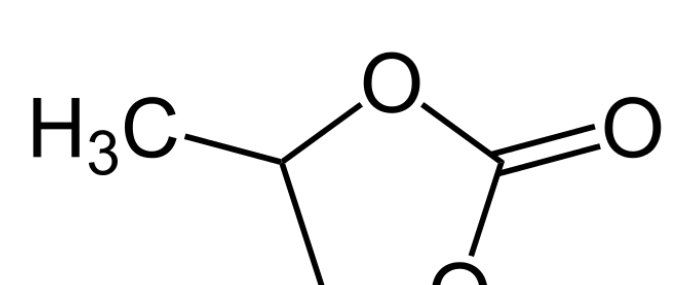


diphenyl carbonate

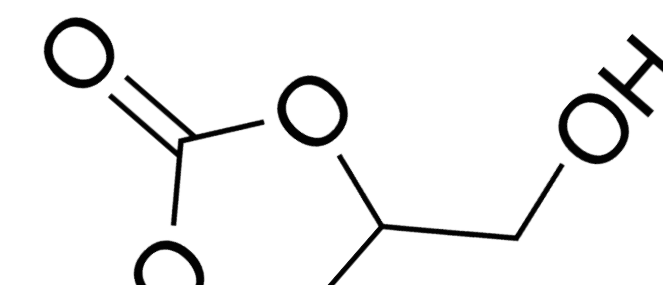


- More complex carbonates can be made by substituting other R groups, or by connecting together R groups to form cyclic carbonates.

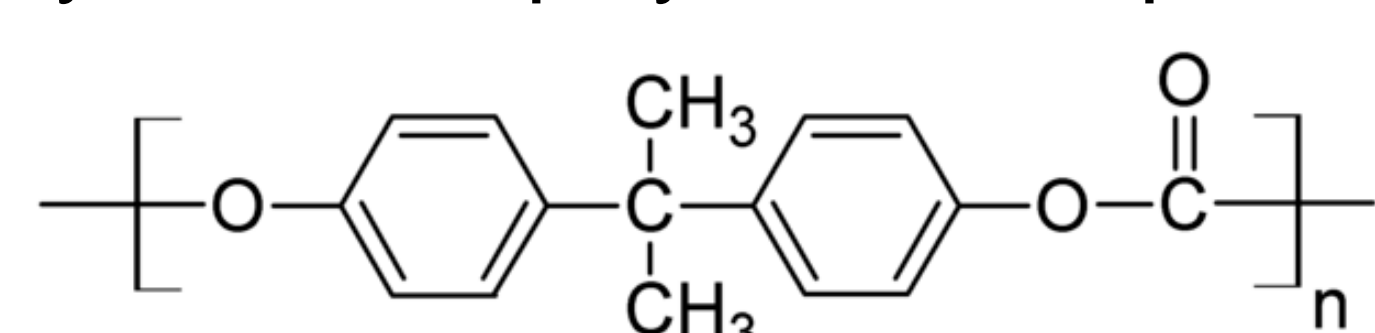
propylene carbonate



glycerol carbonate

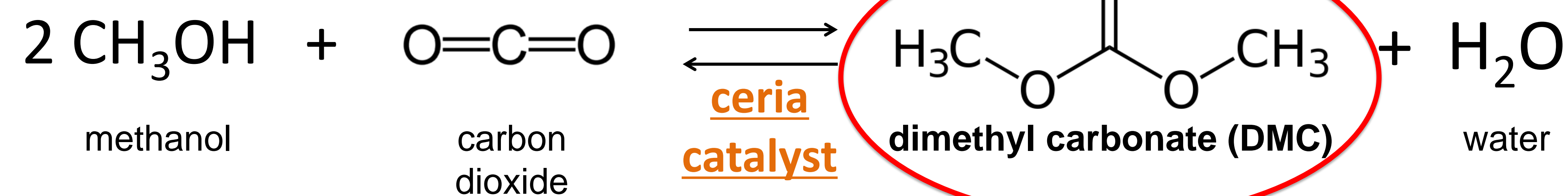


- One application of organic carbonates are for the synthesis of polycarbonate plastics.



polycarbonate monomer

Why Dimethyl Carbonate (DMC)?



- Model system for generating more complex carbonates from CO₂.
- DMC is a VOC exempt organic solvent used by the coatings industries.
- Proposed as an oxygenated fuel additive compound.
- Commercially converted to diphenyl carbonate, which is polymerized to produce polycarbonate plastics – permanently capturing CO₂ while generating valuable products.
- For DMC to be used as a fuel additive or for polycarbonate to be a commodity plastic, need a direct way to synthesize organic carbonates.



DMC Background

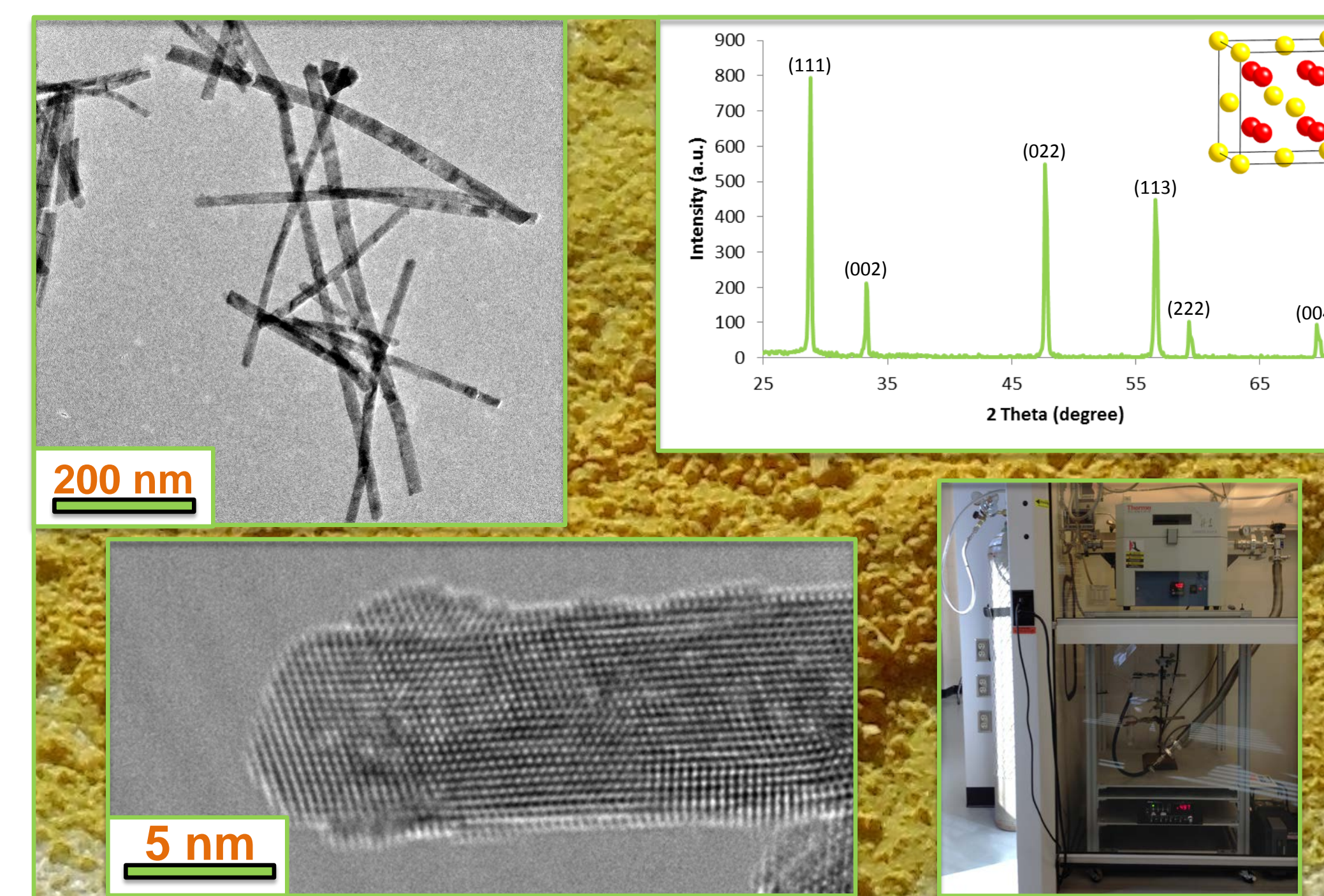
- Until 1980, DMC was produced by the phosgenation of methanol - abandoned due to the high toxicity of phosgene.
- Currently made by the oxy-carbonylation of methanol and the carbonylation of methyl nitrile – both routes using toxic and corrosive chemicals.
- Current direct synthesis catalysts offer poor DMC yields and slow rates.

Catalyst	Operating conditions	Time	Yield/select.
ZnO ₂	433 K	2 h	0.3/100%
Ni(CH ₃ COO) ₂ ·4H ₂ O	413 K; 7.0 MPa	12 h	2.3/45%
H ₃ PO ₄ /ZrO ₂	403 K	2 h	0.3/100%
H ₃ PO ₄ /ZrO ₂	403 K	2 h	0.3/100%
CoO ₂ -ZrO ₂	383 K; 6.0 MPa	4 h	0.8/100%
H ₃ PO ₄ /V ₂ O ₅	453 K; 0.6 MPa	- ^a	1.8/93%
Cu-Ni/V ₂ O ₅ -SiO ₂	413 K; 0.9 MPa	- ^a	2.4/87%
CeO ₂	403 K	5 h	0.8/100%
Cu(Ni, V, O) ^b	393 K; 1.2 MPa	-	4.5/90%
Cu(Ni, V, O)	393 K; 1.2 MPa	-	3.5/93%
H ₃ PW ₁₂ O ₄₀ /Ce _{0.1} Ti _{0.9} O ₂	443 K	12 h	5/100%
Al ₂ O ₃ /CeO ₂	408 K; 5.0 MPa	3 h	0.4/100%
ZrO ₂ /SiO ₂	423 K; 20 MPa	80 h	6/100%
CuCl ₂ /AC	398 K; 1.2 MPa	4 h ^b	-/90%
Co ₂ PW ₁₂ O ₄₀	353 K; 0.25 MPa	5 h	1.1/89%
Co ₂ PW ₁₂ O ₄₀	473 K; 0.1 MPa	- ^a	7.6/86.5%
H ₃ PW ₁₂ O ₄₀ /Ce _{0.05} Zr _{0.95} O ₂	443 K; 6.0 MPa	3 h	1.2/100%
SrCe _{0.2} Co _{0.8} Zr _{0.8} O ₂	443 K; 6.0 MPa	3 h	2.3/100%
Cu-Ni/GNS	373 K; 1.2 bar	3 h ^b	5/92%

^a Continuous reactor.
^b UV radiation.
^c DMC/cat. molar ratio.

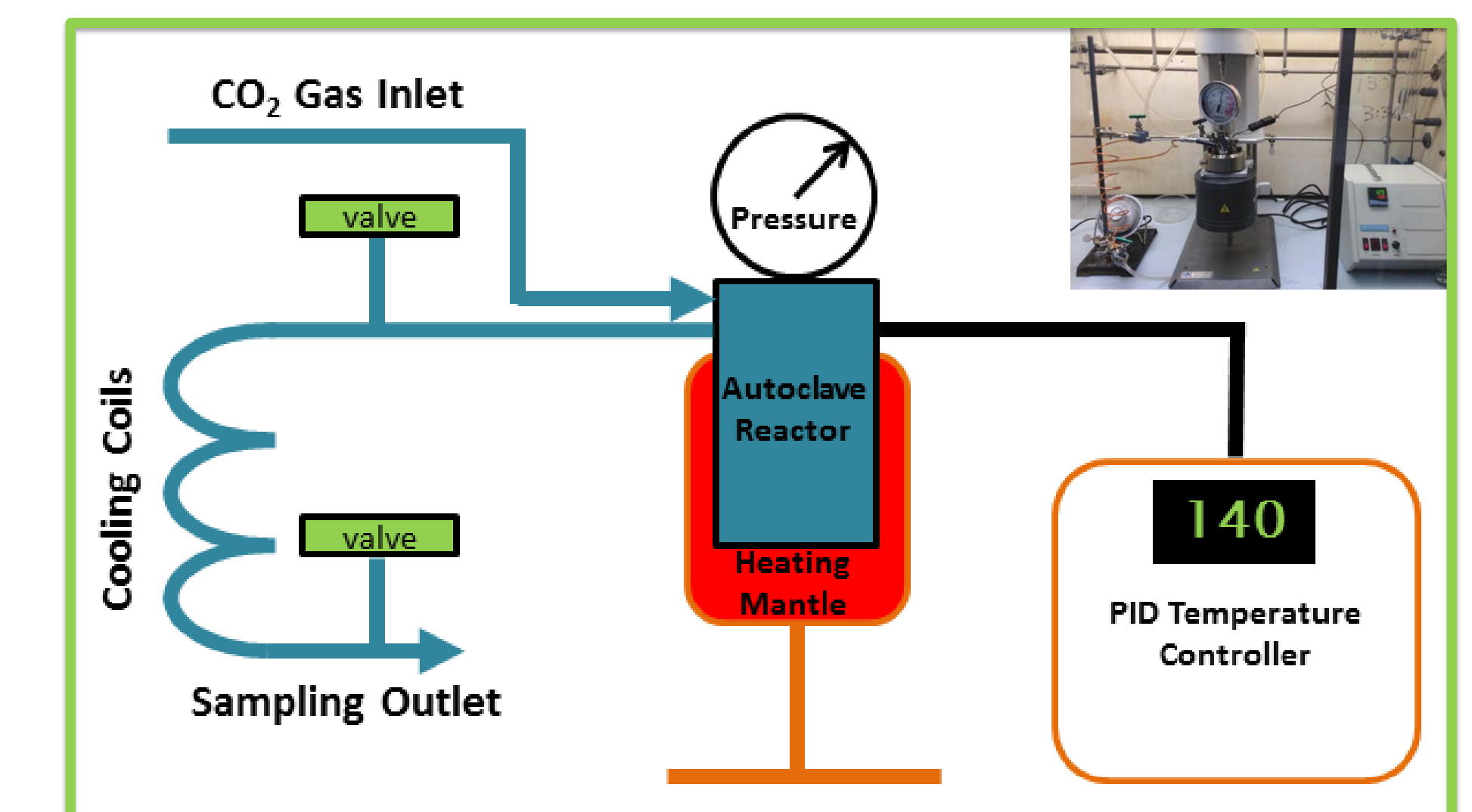
- While the direct synthesis is exothermic (-20.10 kJ/mol), the entropy change is negative and the reaction only favors products at low temps.
- Due to poor kinetics, reactions currently done at high temp, meaning catalyst improvements are essential

Ceria Background



- We synthesize ceria catalyst hydrothermally as cerium hydroxide nanorods.
- Conversion to cerium oxide (ceria) occurs by programmed calcination in air or O₂.
- Ceria surface is incompletely coordinated and takes a mixture of +3 and +4 oxidation states.
- Fluctuating valency of ceria allows oxide mobility and amphoteric catalytic behavior
- By controlling the system pressure for the calcination step, can control the ratio of +3 ceria to +4 ceria.
- Large aspect ratio ceria rods maximize surface area even at elevated temperatures.

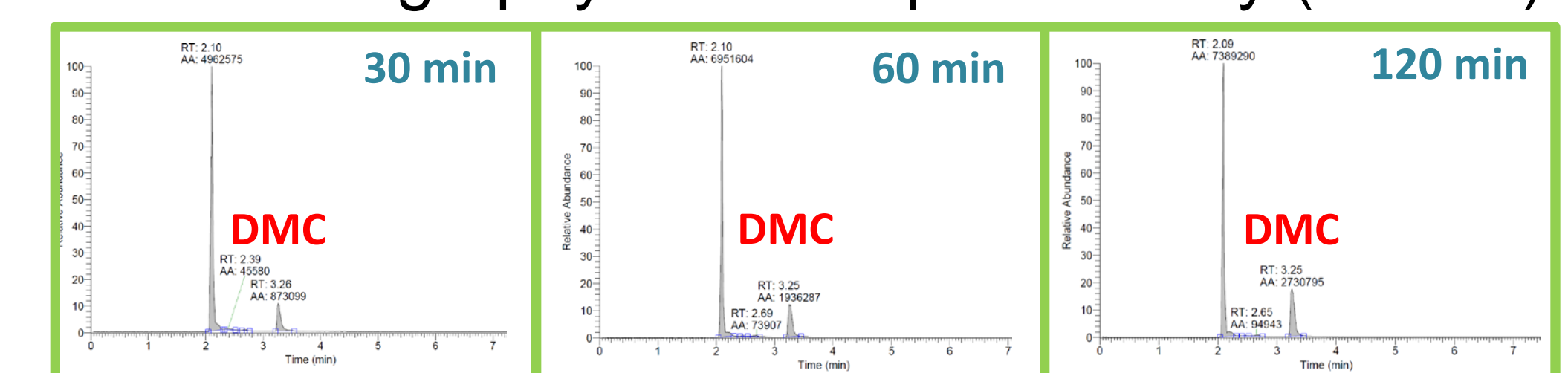
High Pressure Chemistry



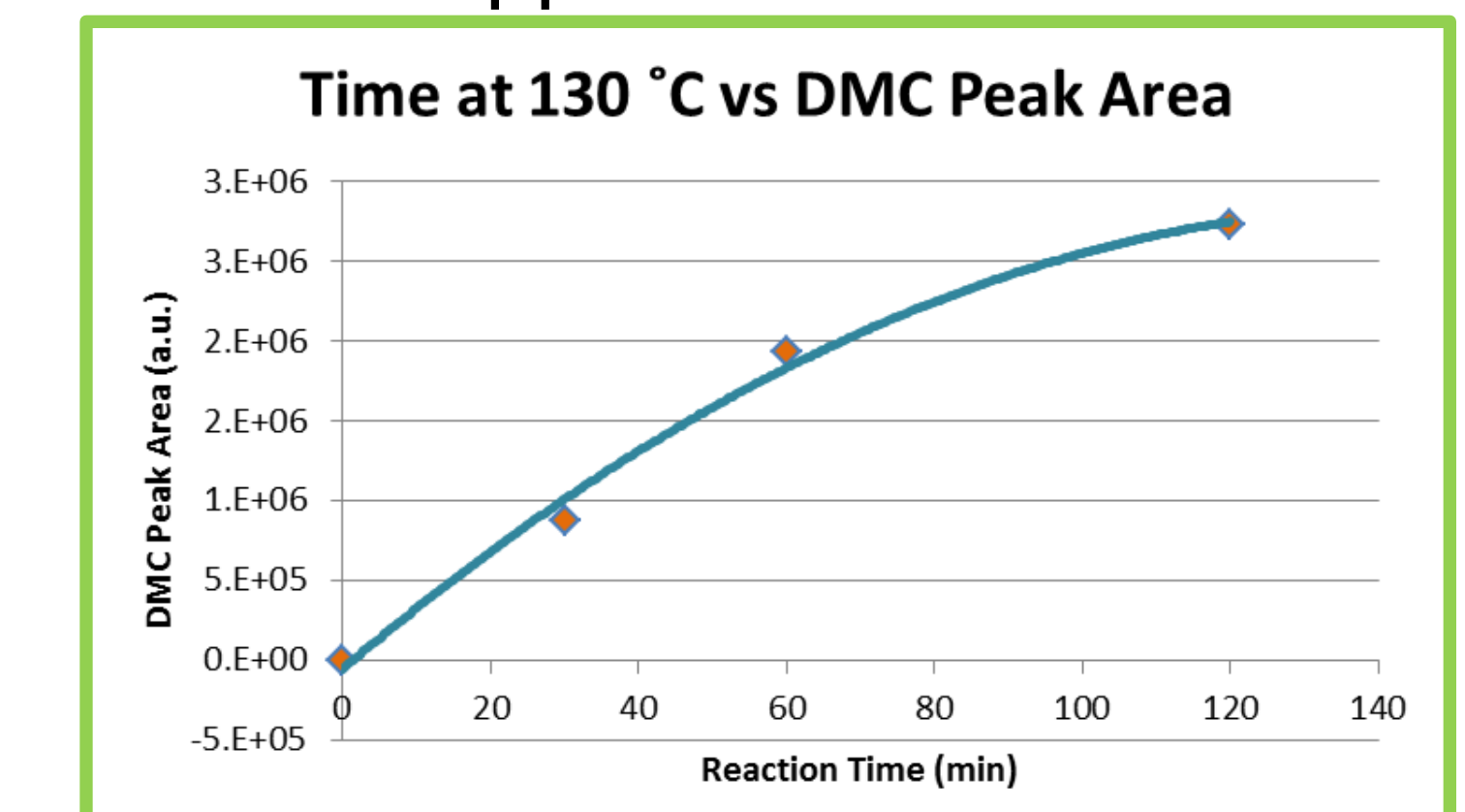
- Reactions performed in a stirred and heated high pressure autoclave with a 3000 psi limit.
- Catalyst and anhydrous methanol are sealed in autoclave reactor.
- Reactor pressurized with CO₂ to 800 psi at room temperature.
- At reaction temperature and pressure, product sampled at regular intervals with sampling line.

Analysis + Results

- DMC concentration is monitored by gas chromatography – mass spectrometry (GCMS).



- Initial rate of DMC generation is linear with respect to time, but rate slows down as equilibrium is approached.



- By keeping the initial concentrations of CO₂ and methanol constant, the initial DMC formation rate gives the rate constant.
- The activation energy for the reaction over a specific catalyst is found by measuring the rate constant at multiple temperatures and fitting an Arrhenius curve.