Kinetic and Mechanistic Investigations of the Direct Synthesis of Dimethyl Carbonate (DMC) from CO_2 over Ceria Nanorod Catalysts

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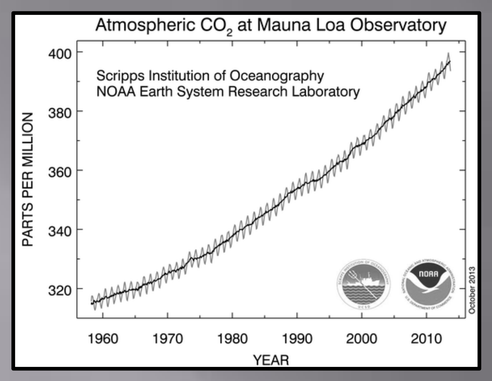
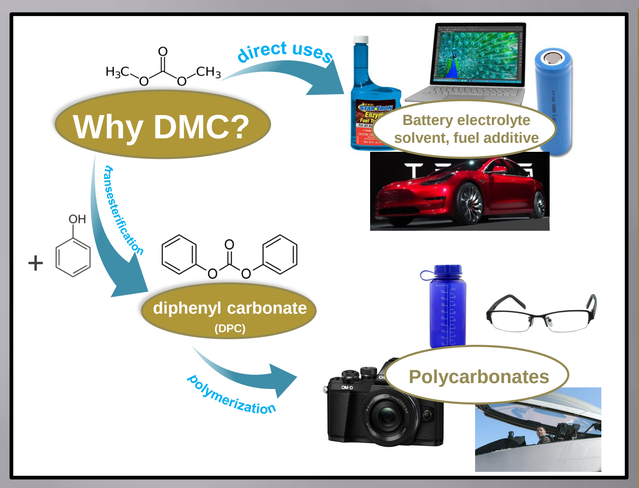
Making CO_2 Useful

$$CO_2 + CH_3OH \rightleftarrows DMC + H_2O$$

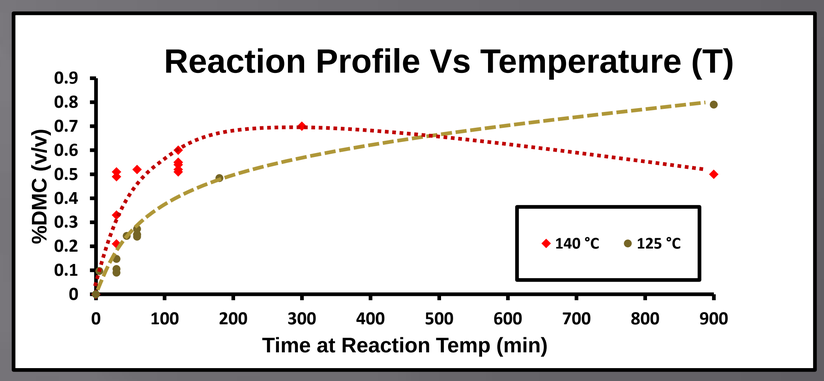
- CO_2 is a waste product from combustion for power generation and transportation
- In 2012, U.S. CO_2 emissions were > 6 *billion* tons
- CO_2 atmospheric concentrations are higher than they have been in 800,000 years





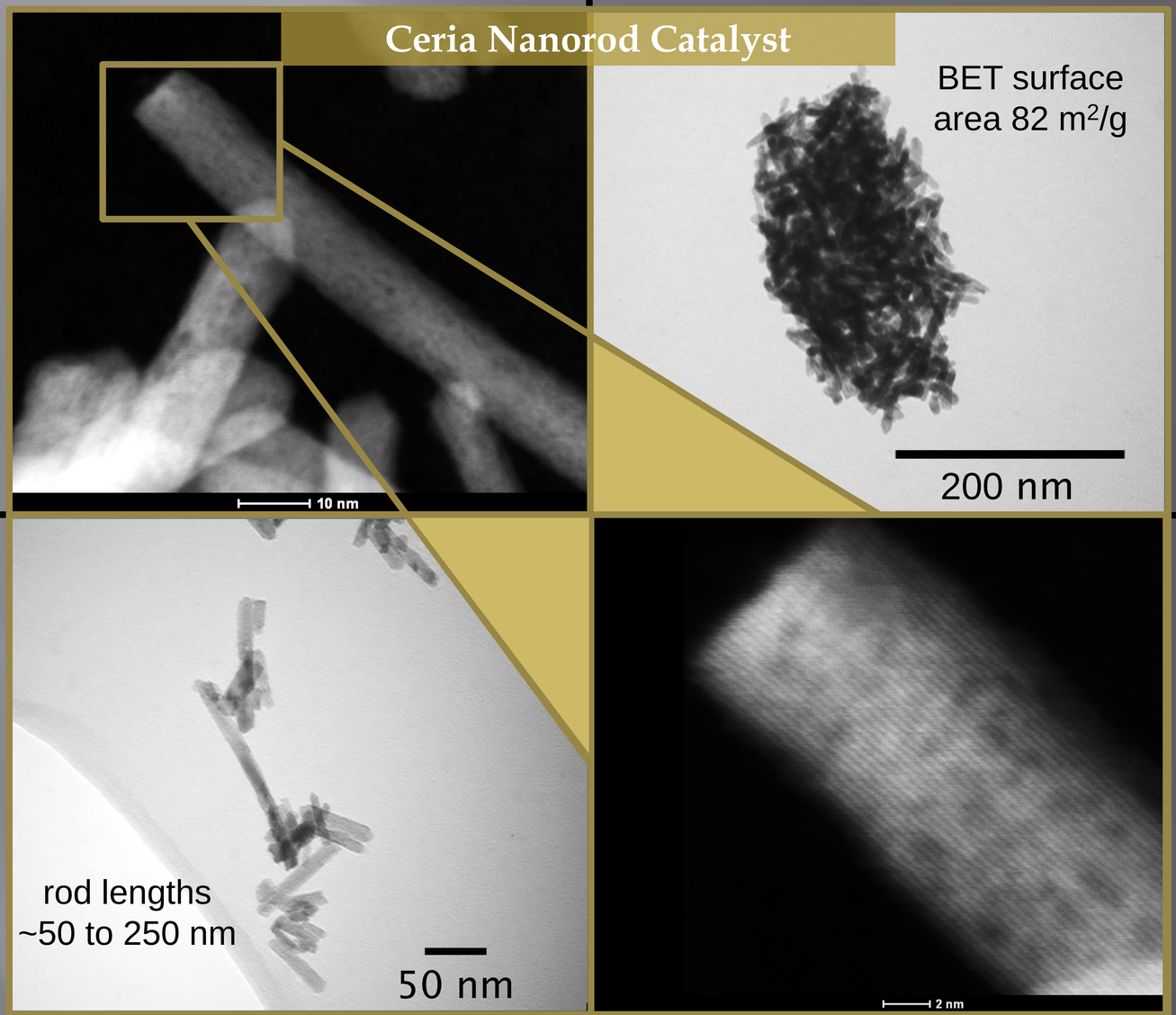
Atmospheric CO_2 at Mauna Loa observatory 1958-2013. (Data from the Scripps Institution of Oceanography and NOAA Earth System Research Laboratory, http://www.esrl.noaa.gov/gmd/ccgg/trends/).

Equilibrium Dynamics of DMC

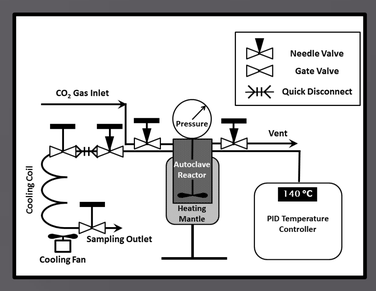


- Reaction trades yields (at low T) for rates (at high T)
- Slow side product formation reduces peak yield.
- Rates at lower T must improve to make production economical.

Ceria Nanorod Catalyst

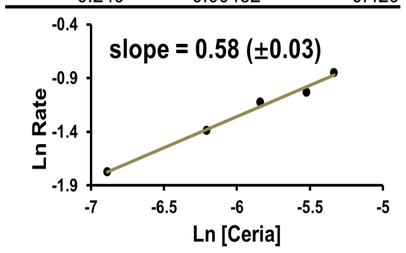


- Reaction is performed under high pressures (2000 psi)
- Higher pressures minimize the entropy term and helps drive the reaction to products.



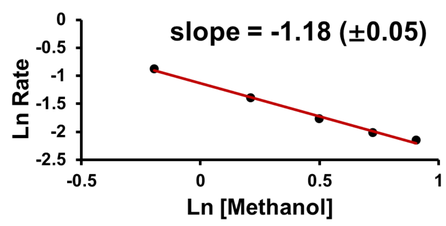
Reaction Kinetics

Ceria (g)	[Ceria] (M)	%DMC/hour
0.0526	0.00102	0.171
0.104	0.00201	0.250
0.150	0.00291	0.325
0.206	0.00399	0.356
0.249	0.00482	0.429



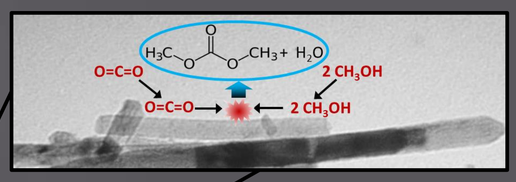
- Initial rate varies directly with catalyst loading.
- This suggests that the rate determining step occurs on the catalyst surface.
- Initial rate varies indirectly with methanol loading.
- This suggests that methanol is not involved in the rate determining step.

Methanol (mL)	[Methanol] (M)	%DMC/hour
10	0.8240	0.417
15	1.2360	0.25
20	1.6479	0.1712
25	2.0599	0.1336
30	2.4719	0.117

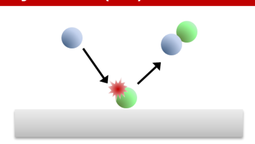


Reaction Mechanism

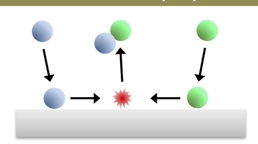
- From kinetics, we know that methanol and CO_2 are adsorbing in separate steps
- Reaction rate is limited by the rate of CO_2 adsorption on the ceria surface



Eley-Rideal (ER) mechanism



Langmuir-Hinshelwood (LH) mechanism



Step	Elementary reaction step	Rate law if rate determining	Elementary reaction step	Rate law if rate determining
1	$MeOH + * \rightleftharpoons MeOH^*$	$R = k\,[MeOH]\,[*]$	$CO_2 + * \rightleftharpoons CO_2^*$	$R = k\,[CO_2]\,[*]$
2	$MeOH^* + CO_2 \rightleftharpoons MC^*$	$R = k\,[MeOH]\,[CO_2]\,[*]$	$MeOH + * \rightleftharpoons MeOH^*$	$R = k\,[MeOH]\,[*]$
3	$MC^* + MeOH^* \rightleftharpoons DMC + H_2O + *$	$R = k\,[CO_2]\,[MeOH]^2\,[*]^2$	$2MeOH^* + CO_2^* \rightleftharpoons DMC^* + H_2O^* + *$	$R = k\,[CO_2]\,[MeOH]^2\,[*]^3$
4			$DMC^* \rightleftharpoons DMC + *$	$R = k\,[MeOH]\,[*]\,[CO_2]^{1/2}$
5			$H_2O^* \rightleftharpoons H_2O + *$	$R = k\,[MeOH]\,[*]\,[CO_2]^{1/2}$

- Increasing ceria surface area improves the catalyst performance
- Reaction should be run at high CO_2 to methanol ratio for best turnover rates
- Improving CO_2 adsorption will likely give best gains in reaction rates

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