Integrated (Reactive) Capture of CO_2 and Conversion to Methanol and Methane

G. K. Surya Prakash
Loker Hydrocarbon Research Institute
Department of Chemistry
University of Southern California
Los Angeles, CA 90089-1661

Reactive Carbon Capture Project Review Meeting
National Renewable Energy Laboratory
Golden, CO
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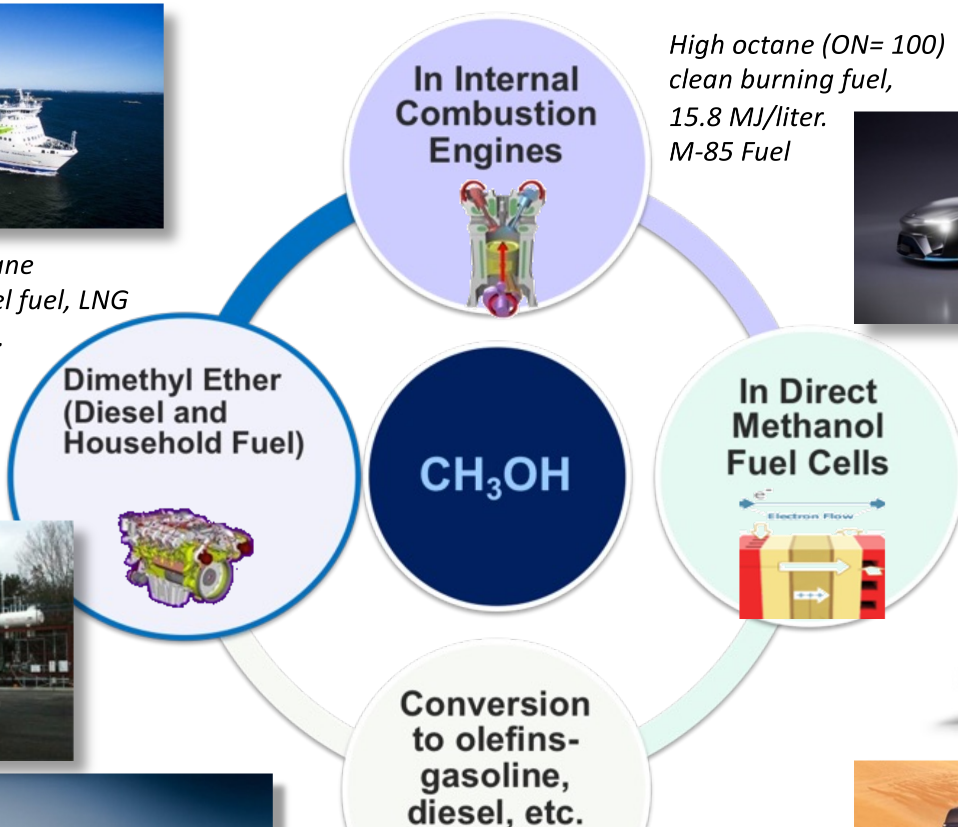
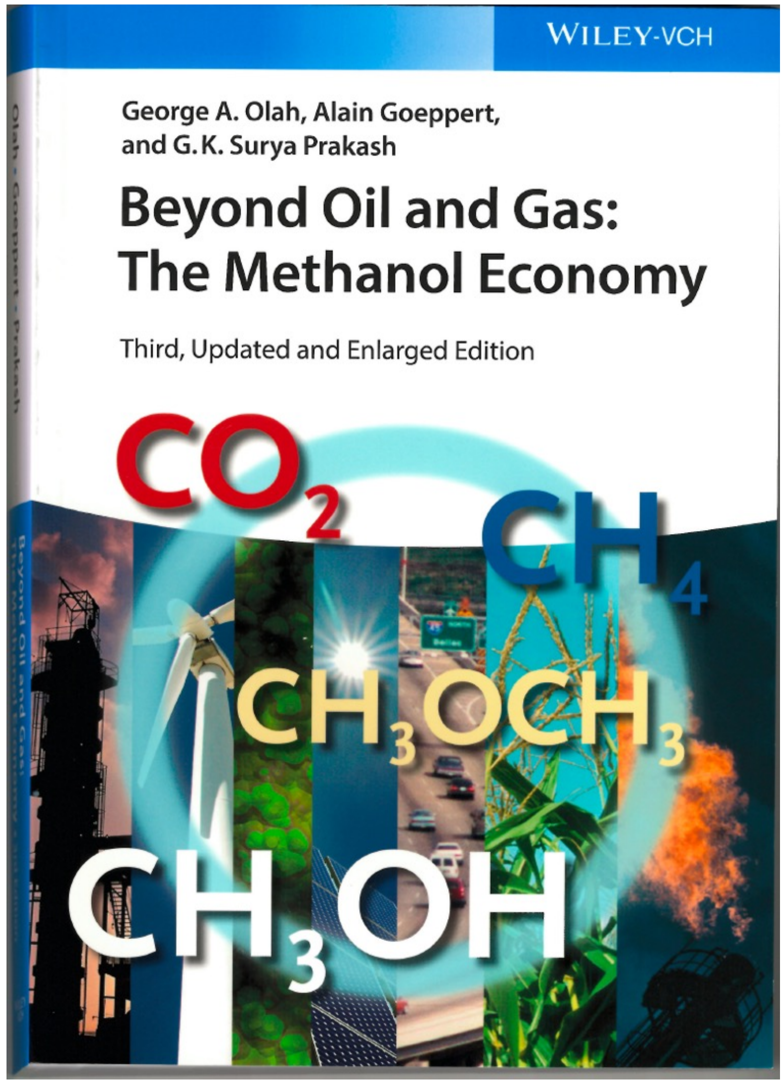
Methanol as a fuel and feedstock: The Methanol Economy

High octane (ON= 100)
clean burning fuel,
15.8 MJ/liter.
M-85 Fuel

CH_3OCH_3, high cetane clean burning diesel fuel, LNG and LPG substitute.

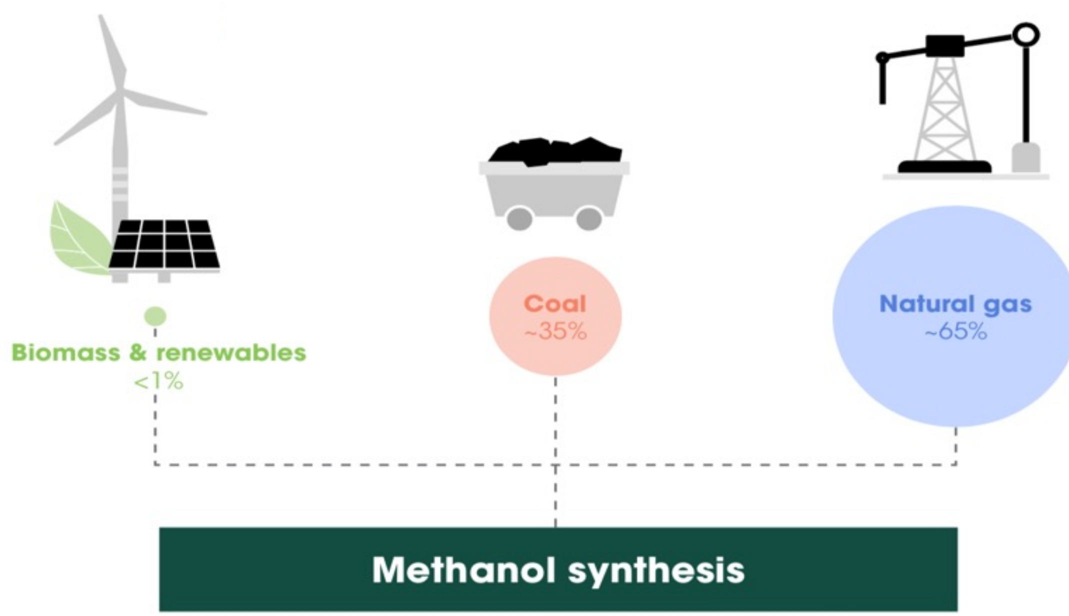


G.A. Olah, A. Goeppert, G.K.S Prakash, *Beyond Oil and Gas: The Methanol Economy, 3rd ed.*; Wiley-VCH, 2018.


WILEY-VCH
George A. Olah, Alain Goeppert,
and G.K. Surya Prakash
Beyond Oil and Gas:
The Methanol Economy
Third, Updated and Enlarged Edition
CO_2
CH_4
CH_3OCH_3
CH_3OH
Olah · Goeppert · Prakash
Beyond Oil and Gas

Carbon Footprint of Methanol

IRENA AND METHANOL INSTITUTE (2021),
Innovation Outlook : Renewable Methanol,
S. Kang, F. Boshell, A. Goeppert, G. K. S. Prakash, I. Landälv
International Renewable Energy Agency, Abu Dhabi.



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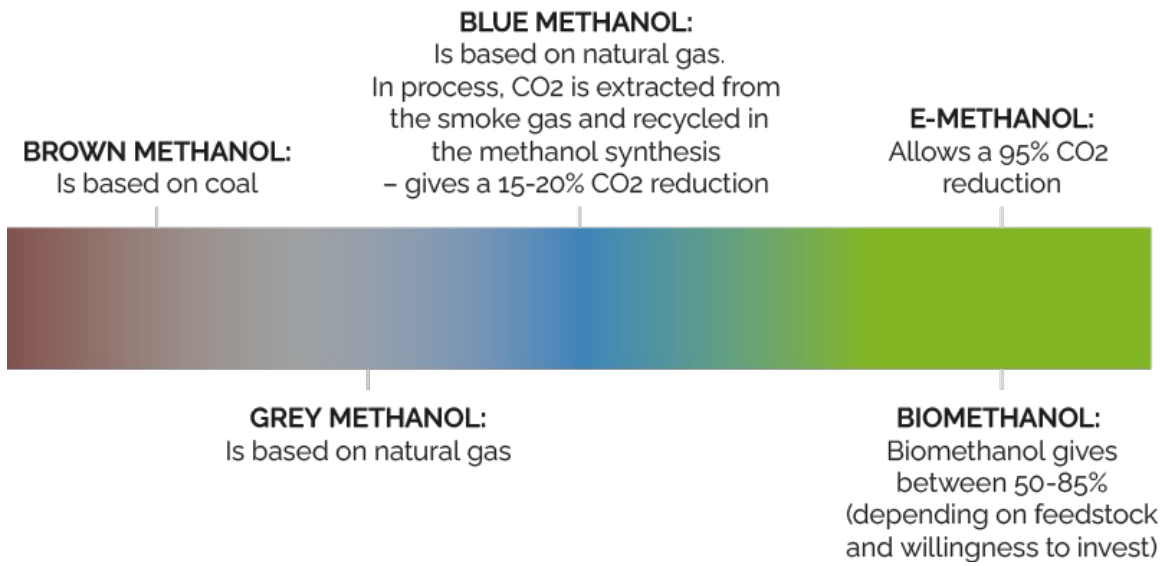


Source: Advent Technologies

Geothermal Methanol from CO_2

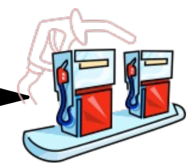
CRI Carbon Recycling International

"George Olah CO_2 to Renewable Methanol Plant"

HS Orka Svartsengi Geothermal Power Plant, Iceland

Production Capacity: 12 t/day

$$\text{geothermal } CO_2 + 3H_2 \longrightarrow H_2O + CH_3OH \longrightarrow$$



$$3H_2O \xrightarrow{\text{electrolysis using geothermal energy}} 3/2\ O_2$$

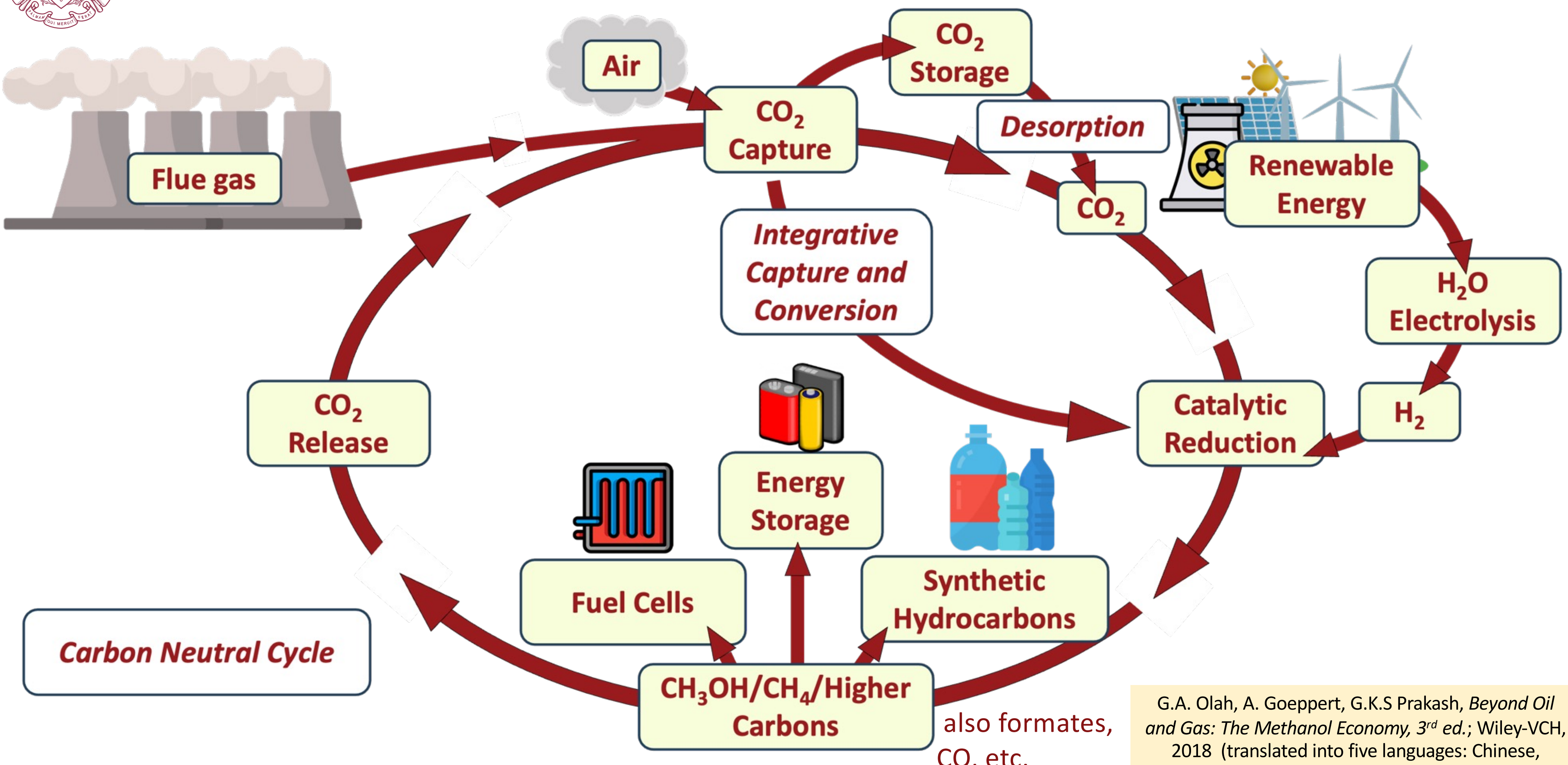
Electricity cost ~ 1-2 ¢/kWh

Geothermal methanol sold under the name "Vulcanol"

> 90% reduction in CO_2 emissions compared to gasoline

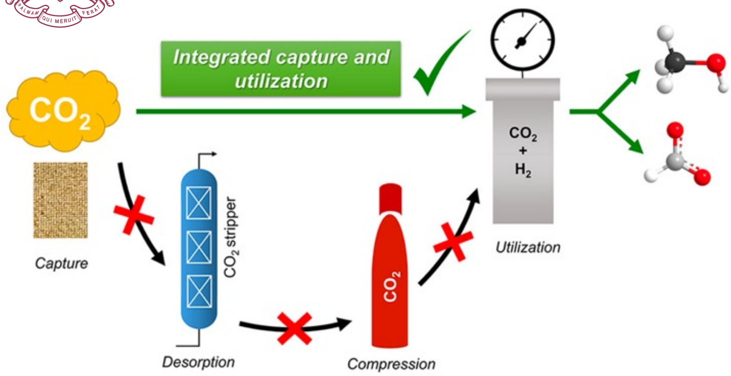
About 40 kWh are needed to produce a gallon of methanol (11 kWh/L),
Methanex and Geely are the major share holders

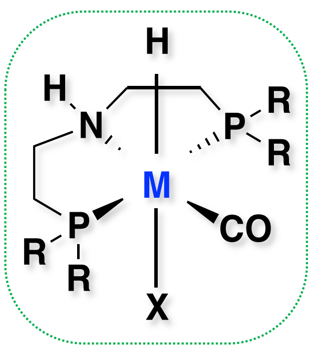
Integrated Carbon Capture and Conversion (ICCC)



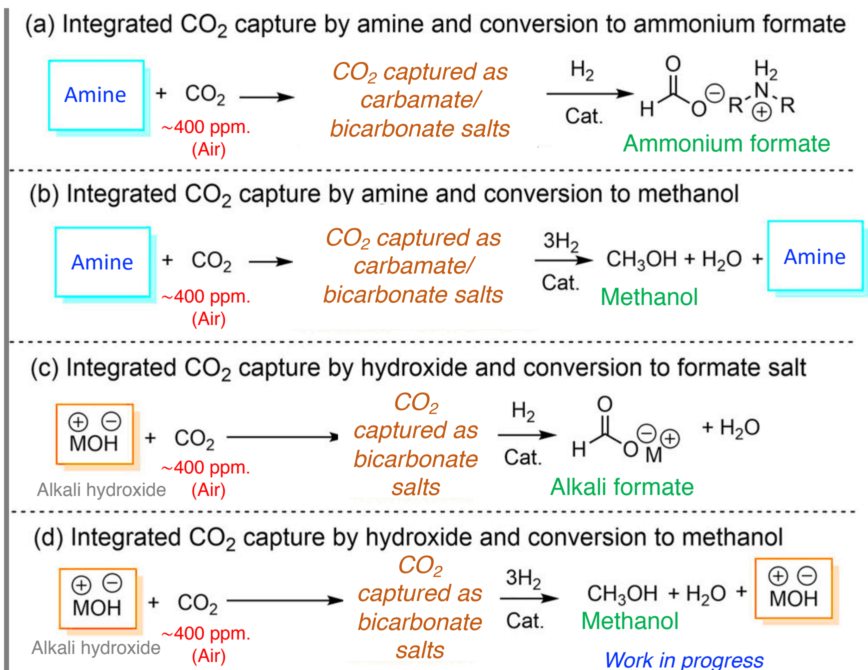
G.A. Olah, A. Goeppert, G.K.S Prakash, *Beyond Oil and Gas: The Methanol Economy, 3rd ed.*; Wiley-VCH, 2018 (translated into five languages: Chinese, Japanese, Russian, Swedish and Hungarian

Integrated Carbon Capture and Conversion (ICCC)





M = Ru, Fe, Mn
R = Ph, *i*Pr, *t*Bu, Cy
X = Cl, Br, H-BH$_3$



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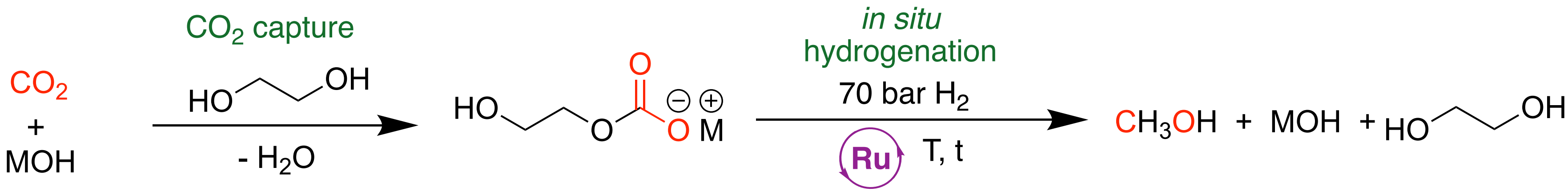
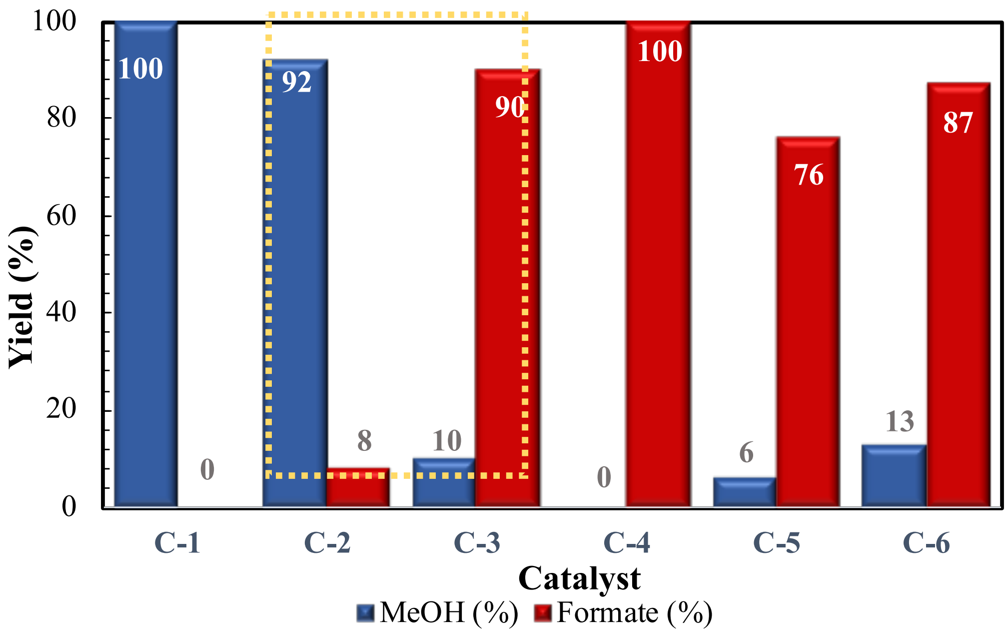
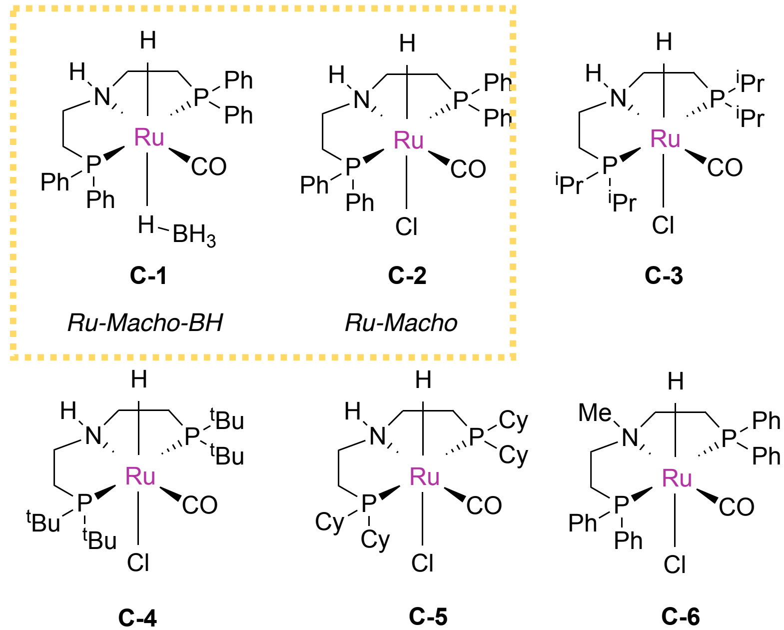
Tandem Hydrogenation of Captured CO_2 in Ethylene Glycol







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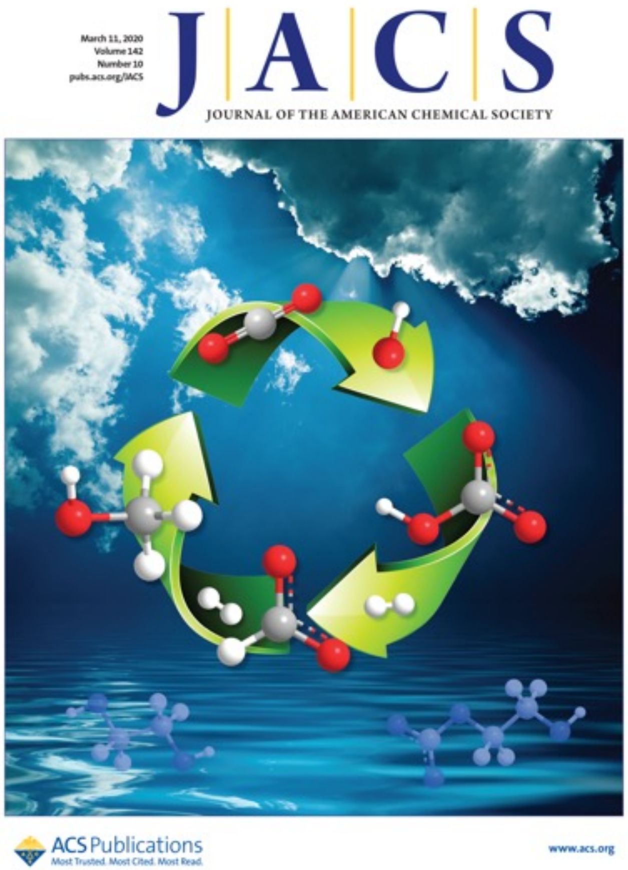
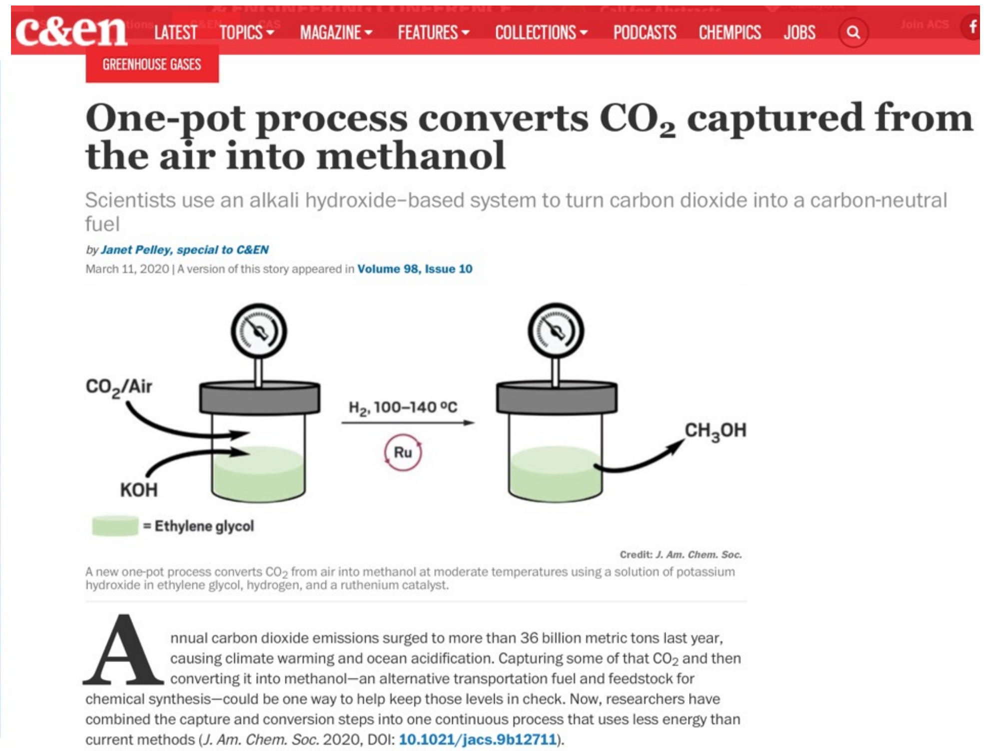
Tandem Hydrogenation of Captured CO_2 in Ethylene Glycol

- Amine-free system for integrated CO_2 capture and conversion to methanol has been developed.
- Ethylene glycol + KOH mediates the hydrogenation of the captured CO_2 most efficiently.
- Low temperature regeneration of hydroxide base has been demonstrated.
- The partial loss of the hydroxide is due to in-situ formation of carboxylates from the solvent alcohol.





One-pot process converts CO_2 captured from the air into methanol

Scientists use an alkali hydroxide–based system to turn carbon dioxide into a carbon-neutral fuel

by Janet Pelley, special to C&EN

March 11, 2020 | A version of this story appeared in **Volume 98, Issue 10**

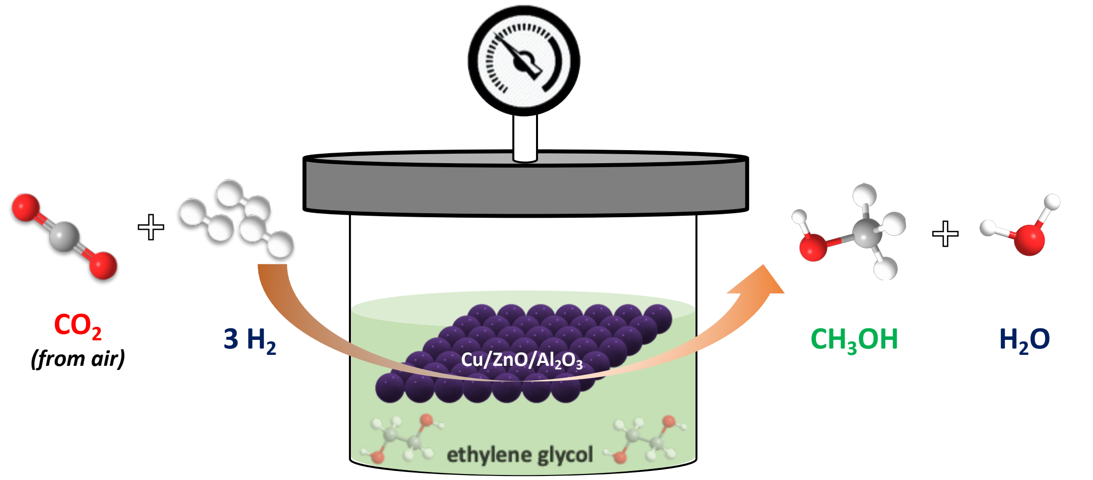
A new one-pot process converts CO_2 from air into methanol at moderate temperatures using a solution of potassium hydroxide in ethylene glycol, hydrogen, and a ruthenium catalyst.

Annual carbon dioxide emissions surged to more than 36 billion metric tons last year, causing climate warming and ocean acidification. Capturing some of that CO_2 and then converting it into methanol—an alternative transportation fuel and feedstock for chemical synthesis—could be one way to help keep those levels in check. Now, researchers have combined the capture and conversion steps into one continuous process that uses less energy than current methods (*J. Am. Chem. Soc.* 2020, DOI: **10.1021/jacs.9b12711**).

R. Sen, A. Goeppert, S. Kar, G. K. S. Prakash, *J. Am. Chem. Soc.*, **2020**, 10, 4544-4549.

https://cen.acs.org/environment/greenhouse-gases/One-pot-process-converts-CO_2/98/i10

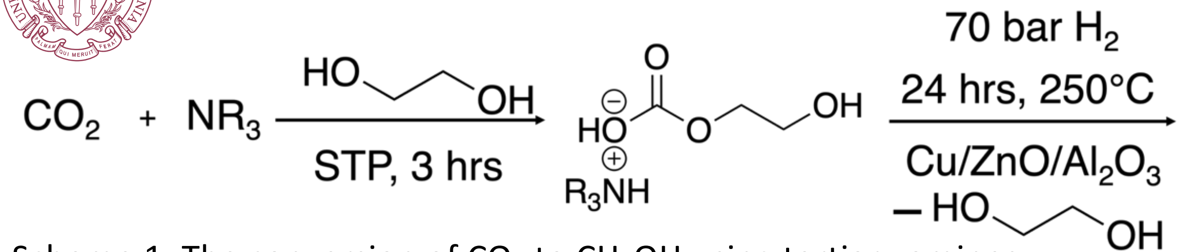
Liquid Phase CO_2 Hydrogenation to Methanol

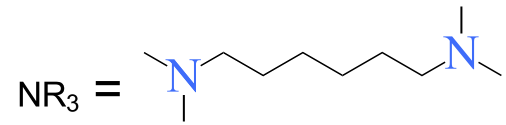


- ✓ Efficient and recyclable system with methanol synthesis (yields ~ 90%)
- ✓ Hydrogenation of CO_2 captured from air with methanol yields > 90%. (using PEHA or KOH)
- ✓ Relatively low operating temperatures: 170-200 °C.
- ✓ Ethylene glycol enhances CO_2 conversions by 120%.

R. Sen, C.J. Koch, V. Galvan, N. Entesari, A. Goeppert, G.K.S. Prakash, *J. CO_2 Utilization*, **2021**, *54,* article 101762 .

ICCC Utilizing Tertiary Amines and $Cu/ZnO/Al_2O_3$ to Methanol





Scheme 1. The conversion of CO_2 to CH_3OH using tertiary amines.

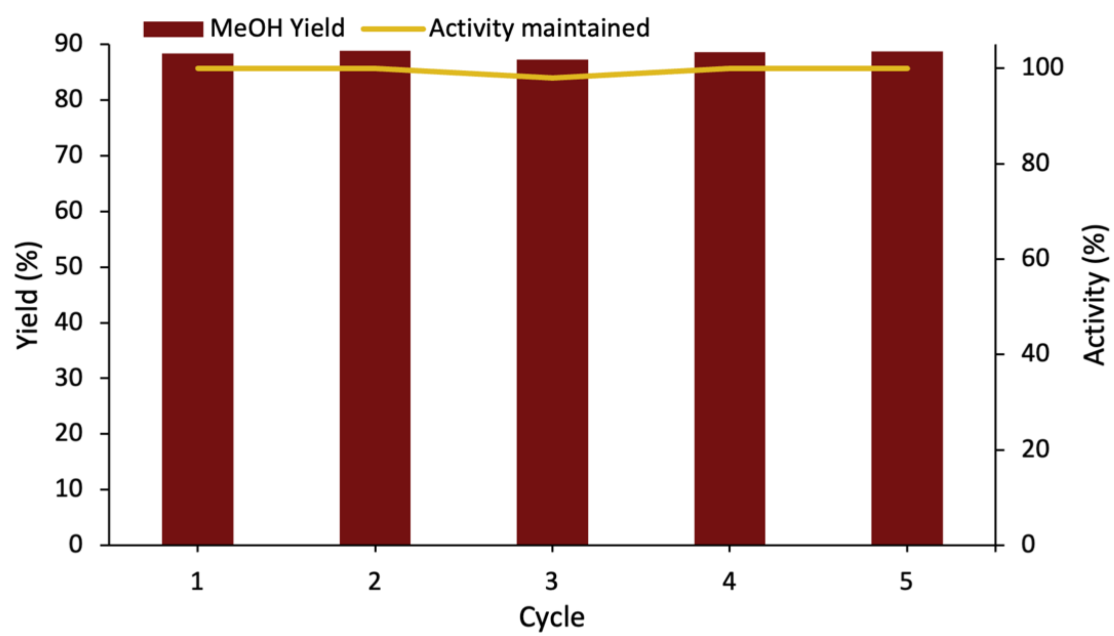


Figure 1. Catalyst recycling study shows 89% yield was maintained for five cycles.

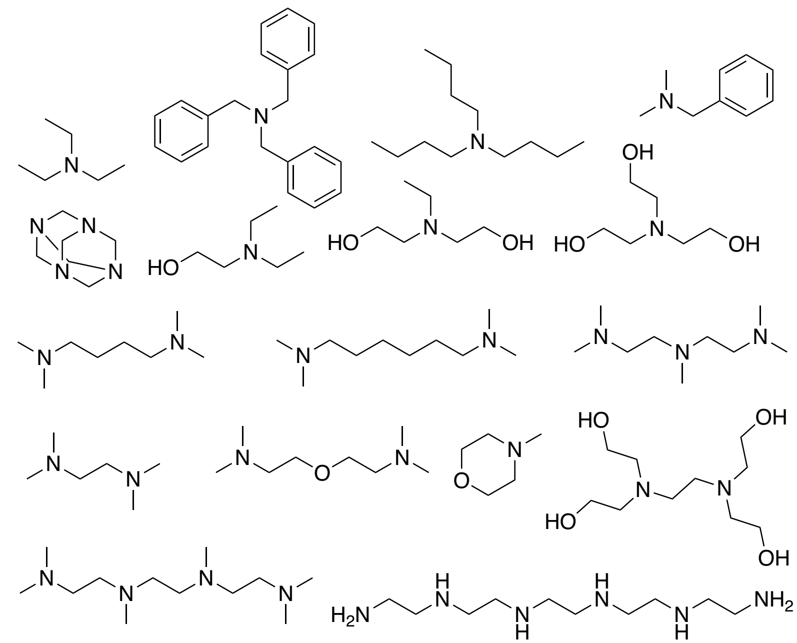
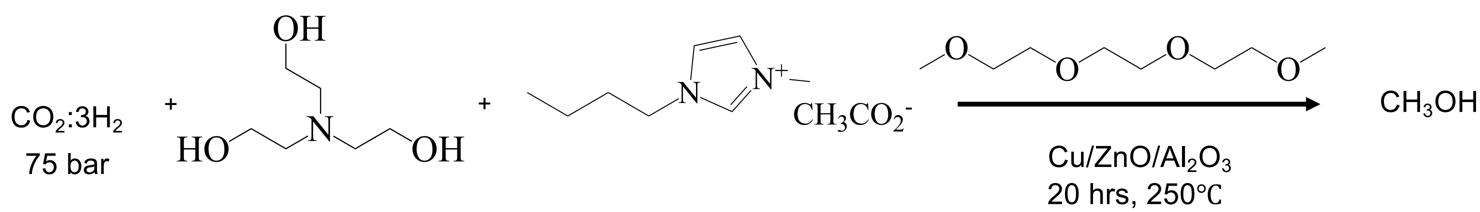


Figure 2. An overview of amines explored in this study.

Z. Suhail, C.J. Koch, A. Goeppert, G.K.S. Prakash, Unpublished

Ionic Liquid Promoted Methanol Synthesis using $Cu/ZnO/Al_2O_3$



Scheme 2. Addition of an ionic liquid to promote methanol production.

Table 1. Recycling of solution.

Cycle	1	2	3	4	5
MeOH [mmol]	14.97	13.52	10.14	5.94	5.77
CO [mmol]	5.5	8.76	11.45	11.25	13.01
MeOH Productivity [$g_{MeOH}\cdot h^{-1}\cdot kg_{cat}^{-1}$]	80	72	54	32	31

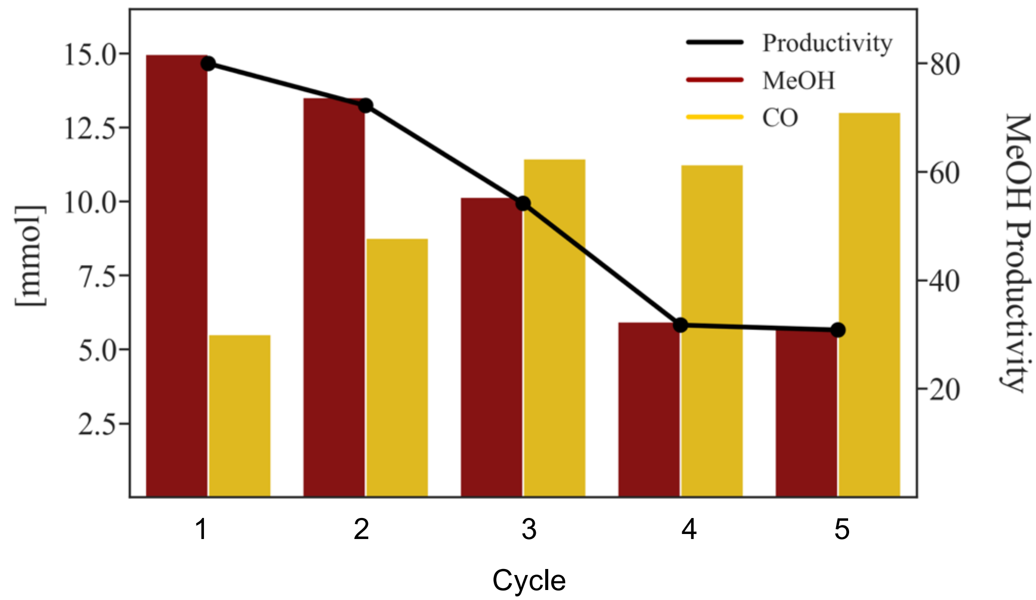


Figure 3. Recycling of solution.

Z. Suhail, C.J. Koch, A. Goeppert, G.K.S. Prakash,
Unpublished

Methane Production from Carbonates with Ni/Al_2O_3 Catalysts

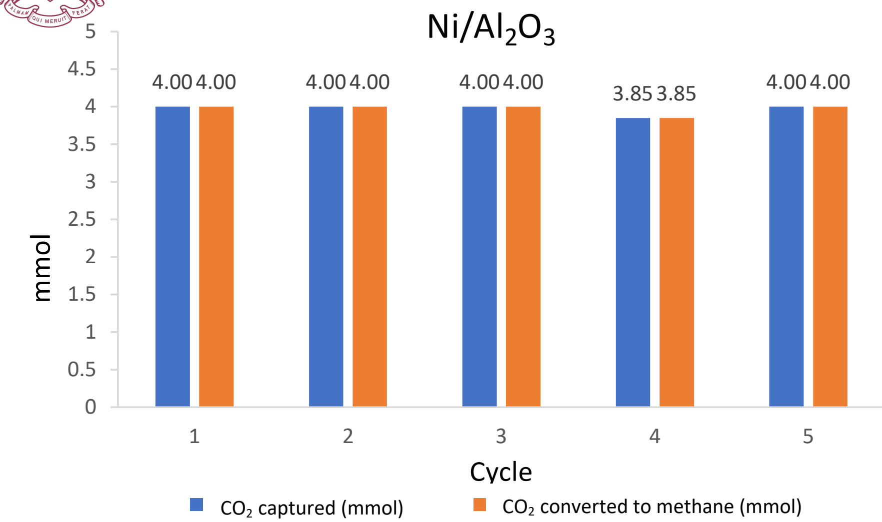


Figure 4. Recycling study with Ni/Al_2O_3 catalyst

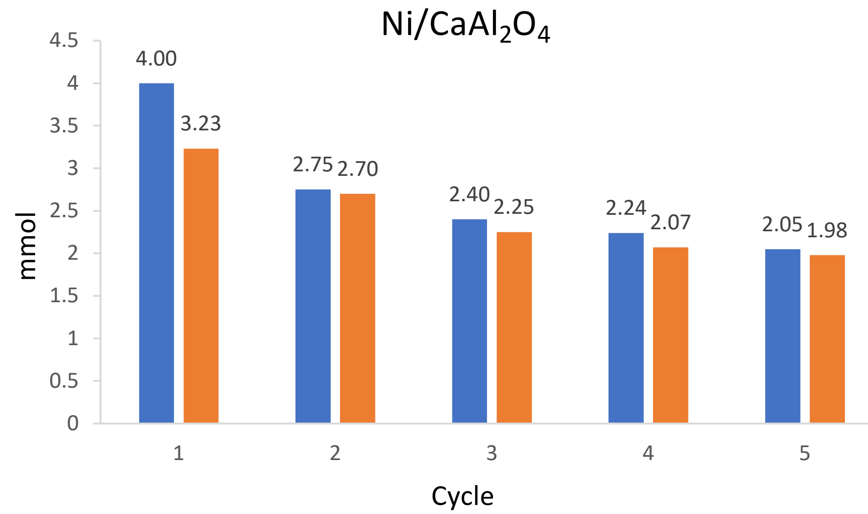
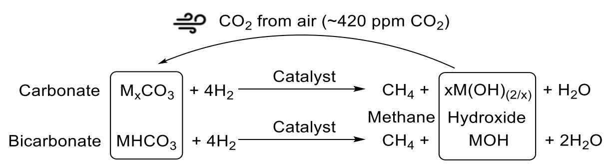


Figure 5. Recycling study with $Ni/CaAl_2O_4$ catalyst



KOH (mmol)	CO_2 captured (mmol)	Methane (mmol)	Conversion (%)
5	3.53	3.53	100

Figure 6. Air capture experiment

$$CaAl_2O_4 + K_2CO_3 \longrightarrow 2KAlO_2 + CaCO_3$$

$$CaAl_4O_7 + K_2CO_3 + 2KOH + 7H_2O \longrightarrow 4KAl(OH)_4 + CaCO_3$$

$$Ca_3Al_2O_6 + 3K_2CO_3 + 2H_2O \longrightarrow 2KAlO_2 + 3CaCO_3 + 4KOH$$

$$Ca_{12}Al_{14}O_{33} + 12K_2CO_3 + 5H_2O \longrightarrow 14KAlO_2 + 12CaCO_3 + 10KOH$$

Scheme 3. Leaching characteristics of $CaAl_2O_4$ in the presence of potassium carbonate

C. J. Koch, V. Galvan, A. Goeppert, G. K. S. Prakash, *Green Chem.*, **2023**, 25, 1803-1808.

Using Commercial Ru/Al_2O_3 catalyst to Produce CH_4 from Carbonates

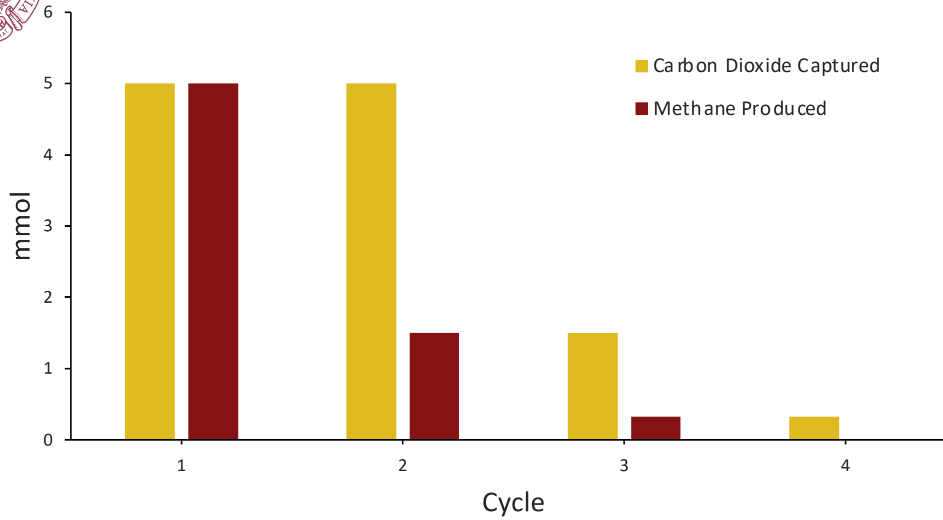


Figure 7. Recycling Experiment utilizing 5%Ru/Al_2O_3

Table 2. Recycling Experiment utilizing 5%Ru/Al_2O_3

Cycle	CO_2 captured (mmol)	Methane produced (mmol)	Base regenerated (%)	Activity maintained (%)
1	5	5	100	-
2	5	1.5	30	30
3	1.5	0.33	6	6
4	0.33	0	0	0

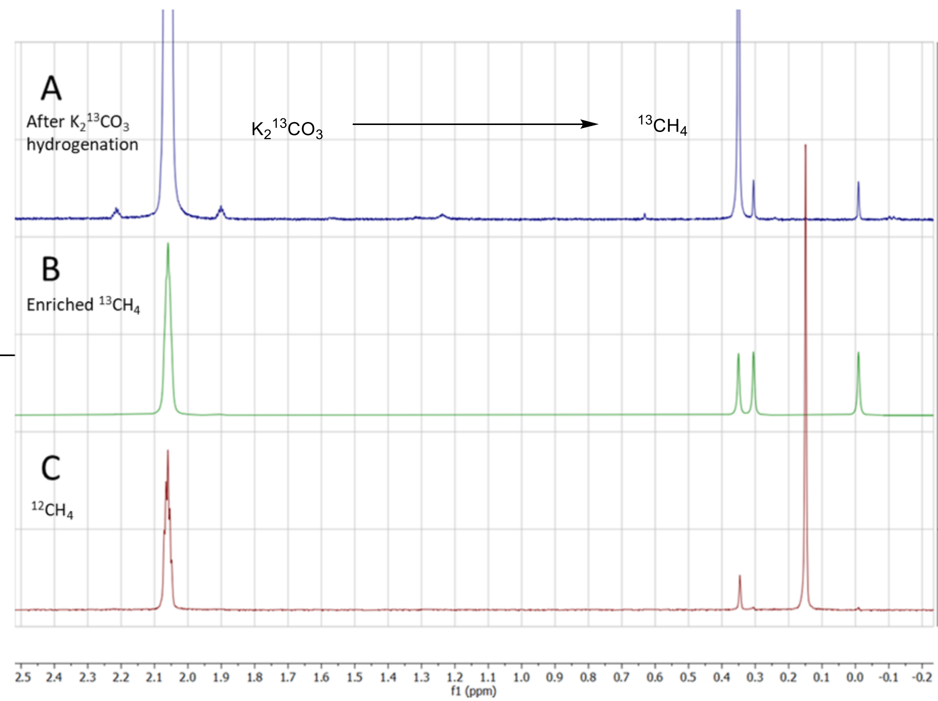


Figure 8. ^{13}C-K_2CO_3 experiment and its conversion to ^{13}C-Methane [a] gas mixture after reaction with ^{13}C-K_2CO_3 [b] ^{1}HNMR of pure $^{13}CH_4$, [c] ^{1}HNMR of $^{12}CH_4$.

C. J. Koch, Z. Suhail, A. Goeppert, G. K. S. Prakash, *ChemCatChem*, **2023**, 15, e202300877.

Ru/Al_2O_3 catalysts with phosphate assisted ICCC

$$Na_3PO_4 \cdot 12H_2O + CO_2 \rightleftharpoons Na_2HPO_4 \cdot 7H_2O + NaHCO_3 + 4H_2O$$

Scheme 4. CO_2 capture of the phosphate assisted system

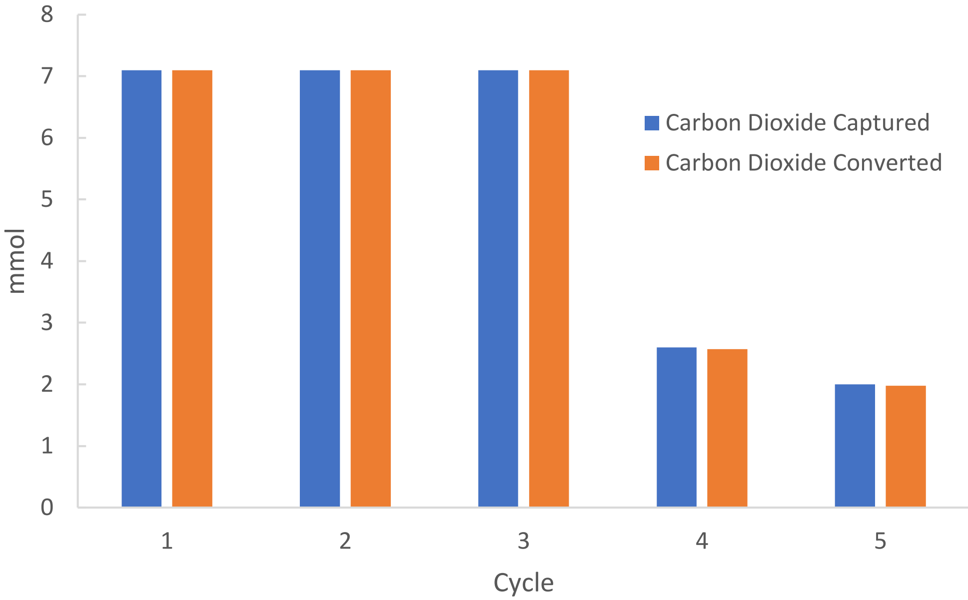


Figure 9. Recycling experiment with 5%Ru/Al_2O_3 and Na_3PO_4

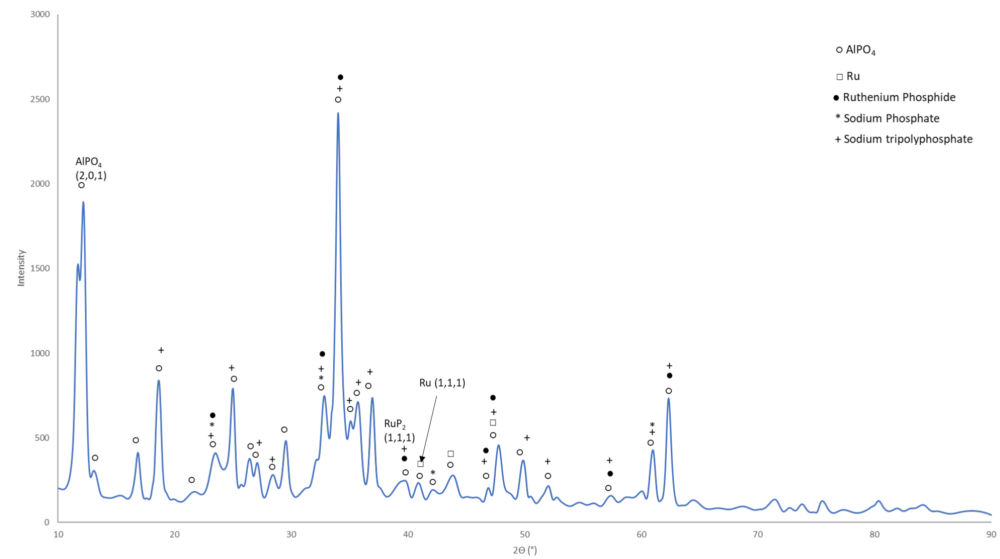


Figure 10. XRD of 5%Ru/Al_2O_3 after five cycles of reactions

$$Na_2HPO_4 + NaH_2PO_4 + Al_2O_3 \xrightarrow[100\text{-}300°C]{} 2AlPO_4 + 3NaOH$$

Scheme 5. Phosphate salts reacting with alumina to form aluminum phosphate.

C. J. Koch, A. Algaratnam, A. Goeppert, G. K. S. Prakash, *ChemCatChem*, **2023**, 15, e202300877.

Lanthanide Promoters for improved catalytic performance

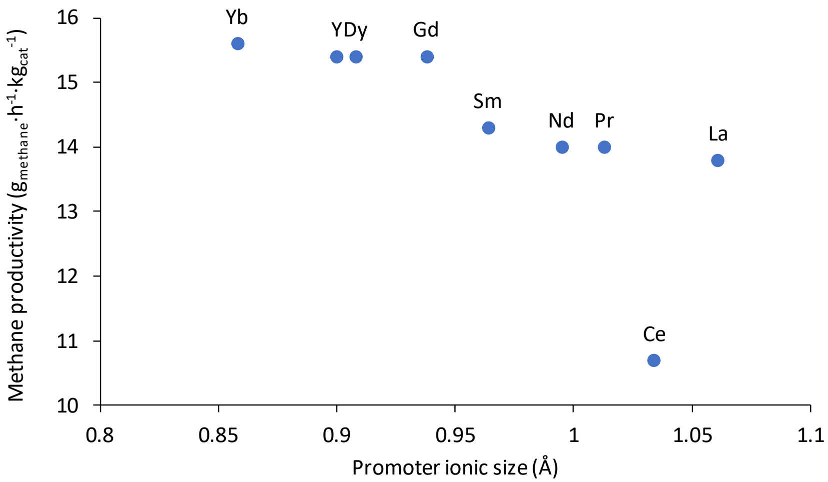


Figure 11. Methane productivity in comparison to the ionic size of the lanthanide promoter $Ni/Ln/Al_2O_3$

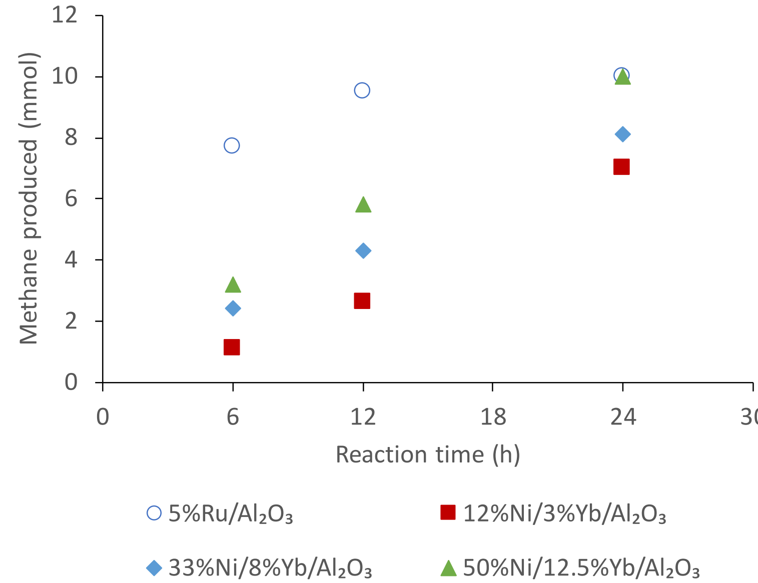


Figure 12. Different metal loadings of Ni and Yb compared to $5\%Ru/Al_2O_3$ catalyst at varying times.

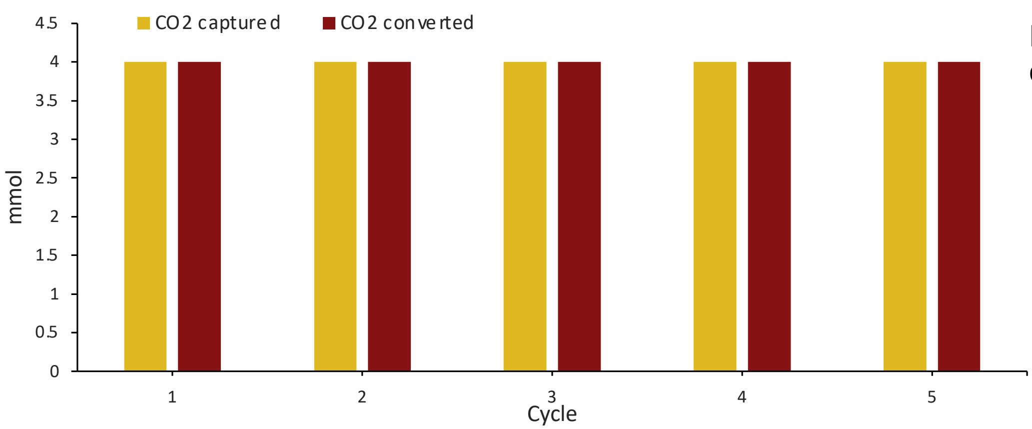


Figure 13. Recycling of $50\%Ni/12.5\%Yb/Al_2O_3$ catalyst.

C.J. Koch, Z. Suhail, A. Algaratnam, M. Coe, A. Goeppert, G.K.S. Prakash, Unpublished

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Carlos Colmenares	Jothi Kothandaraman	Amanda Baxter
Thomas Mathew	Laxman Gurung	Anushan Alagaratnam
Patrice Batamack	Sayan Kar	Zohaib Suhail
Sergio Meth	Raktim Sen	Vicente Galvan
Suresh Palale	Miklos Czaun	Huong Dong
Nazanin Entessari	Hang Zhang	Christopher J. Koch

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