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Turning CO_2 into Fuels and Chemicals for Sustainable Energy Development

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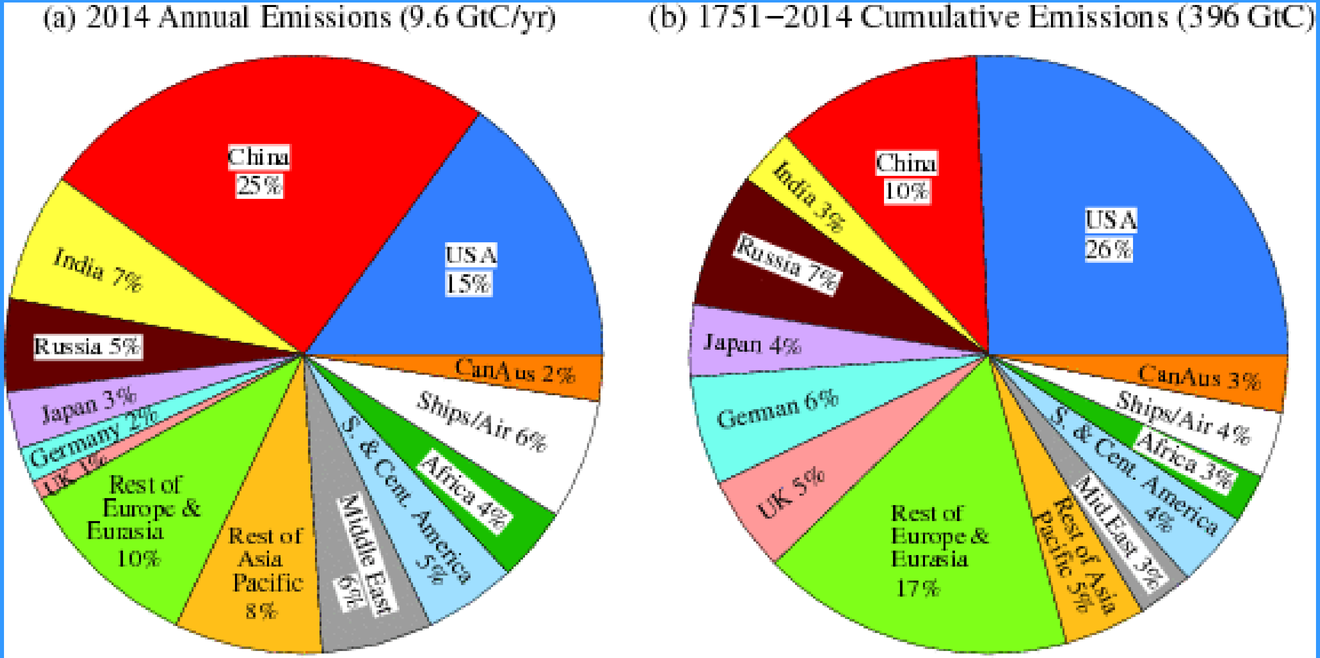
US Energy Association Briefing
Washington DC, April 21, 2016

CO_2 Emissions Worldwide

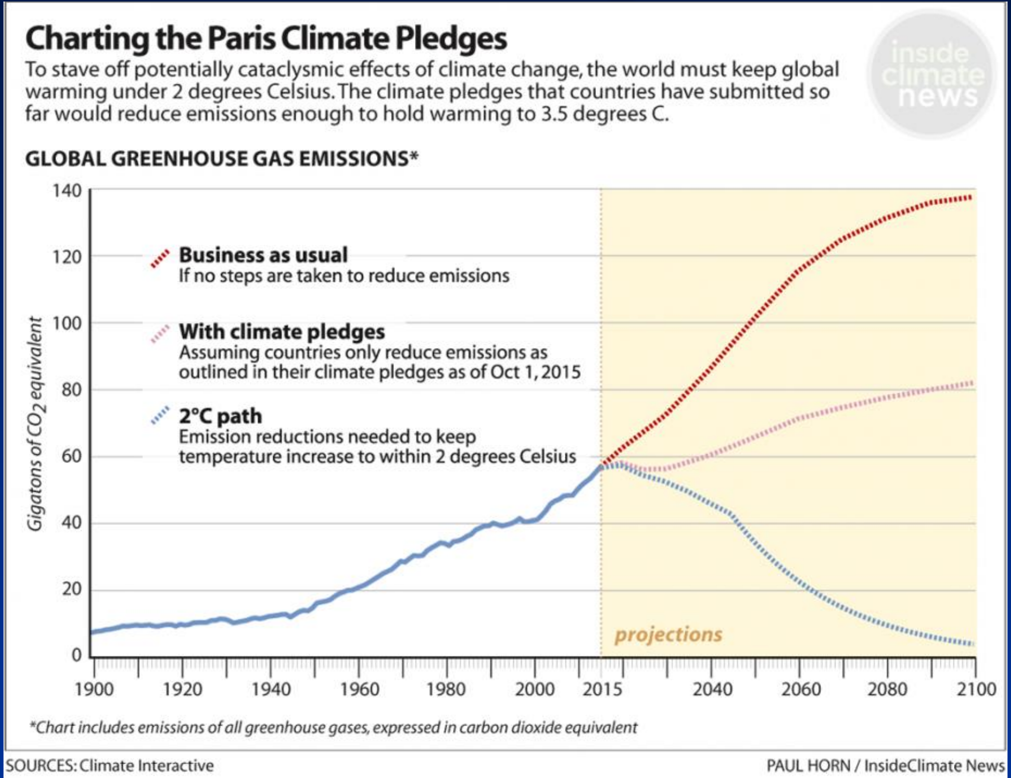
World CO_2 emissions projected to rise from 28.18 billion metric tons (BMT) in 2005 to 35.21 BMT in 2020 and 43.22 BMT in 2035 (by EIA IEO, 2011).*

2013 world’s total CO_2 emissions 35.1 BMT, with 9.5 BMT in China (7.1 MT per person), 5.9 BMT in US (18.9 MT pp), 1.8 BMT in India, 1.7 BMT in Russia, and 1.4 BMT in Japan.



http://www.columbia.edu/~mhs119/UpdatedFigures/

COP21 - CO_2 Control 2 Degree C Scenario



Charting the Paris Climate Pledges

To stave off potentially cataclysmic effects of climate change, the world must keep global warming under 2 degrees Celsius. The climate pledges that countries have submitted so far would reduce emissions enough to hold warming to 3.5 degrees C.

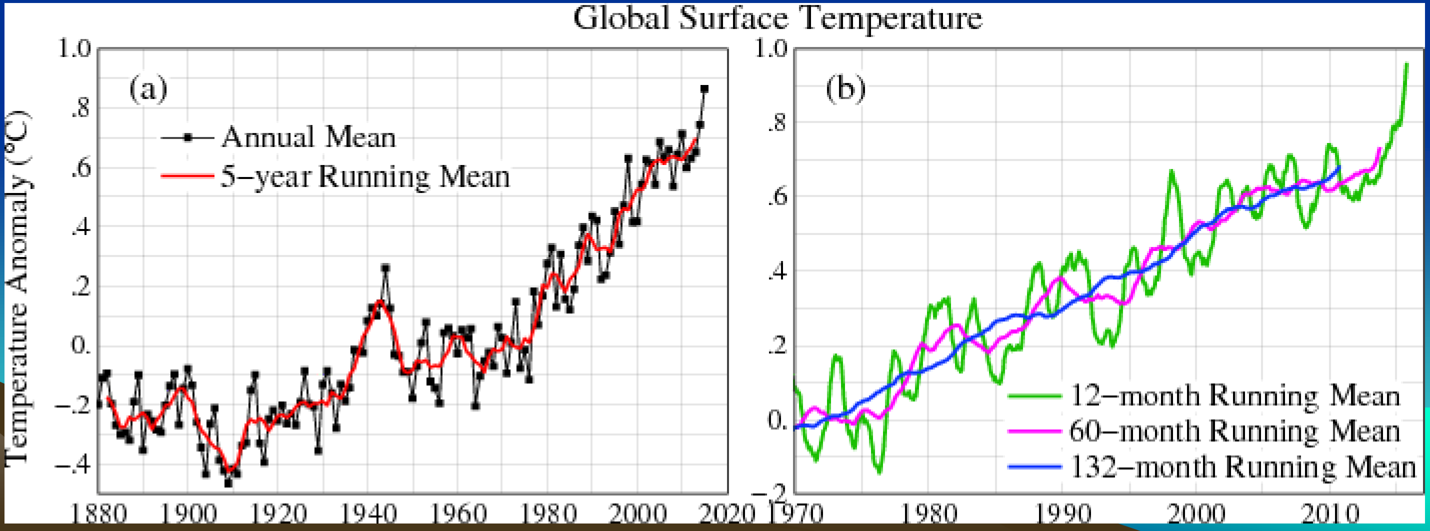
*Chart includes emissions of all greenhouse gases, expressed in carbon dioxide equivalent

SOURCES: Climate Interactive

PAUL HORN / InsideClimate News

NAVEENA SADASIVAM, INSIDECLIMATE NEWS, OCT 6, 2015

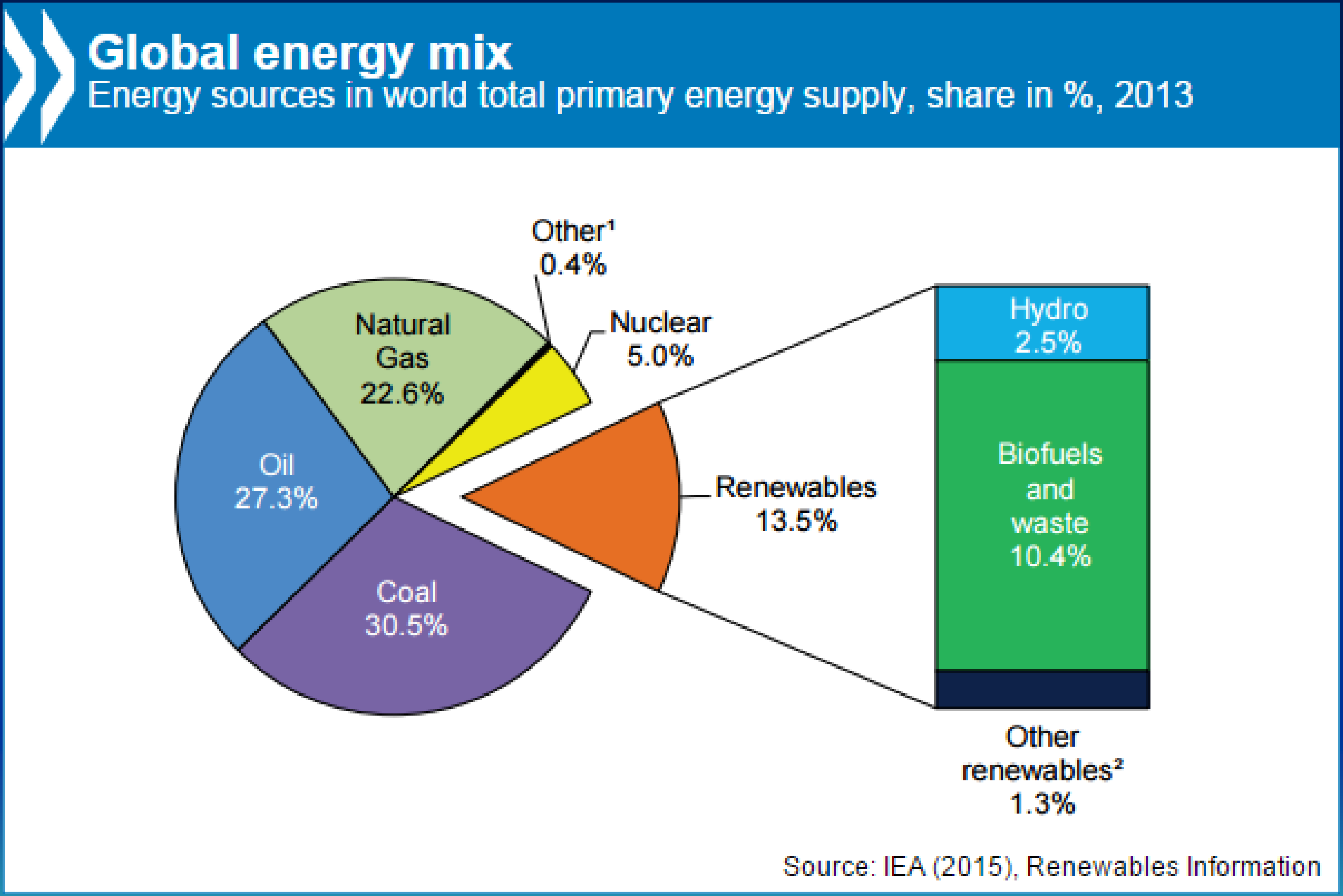
HTTP://INSIDECLIMATENEWS.ORG/NEWS/05102015/CLIMATE-TREATY-FORECAST-CLOUDY-CHANCE-DISASTER-UNITED-NATIONS-PLEDGE-GLOBAL-WARMING



Global Surface Temperature

http://www.columbia.edu/~mhs119/UpdatedFigures/

Global Energy Mix: Carbon-Based



Global energy mix

Energy sources in world total primary energy supply, share in %, 2013

Source: IEA (2015), Renewables Information

- http://www.oecd.org/environment/cop21-climate-change-in-figures.htm

Global Energy Challenges in the 21st Century*

1. Supply clean fuels, electricity and water to meet the growing energy demand worldwide with declining amounts and qualities of resources.
2. Increase efficiency by overcoming the limits of existing "wasteful" fossil energy systems (prod, conv, storage, transport, utilization).
3. Eliminate environmental pollutants due to energy utilization; reduce greenhouse gas (CO_2) emissions.
4. Sustainable energy development involving more of renewable sources (also involves CO_2).
5. Sustainable organic material development involving carbon-based skeletons (incl CO_2).

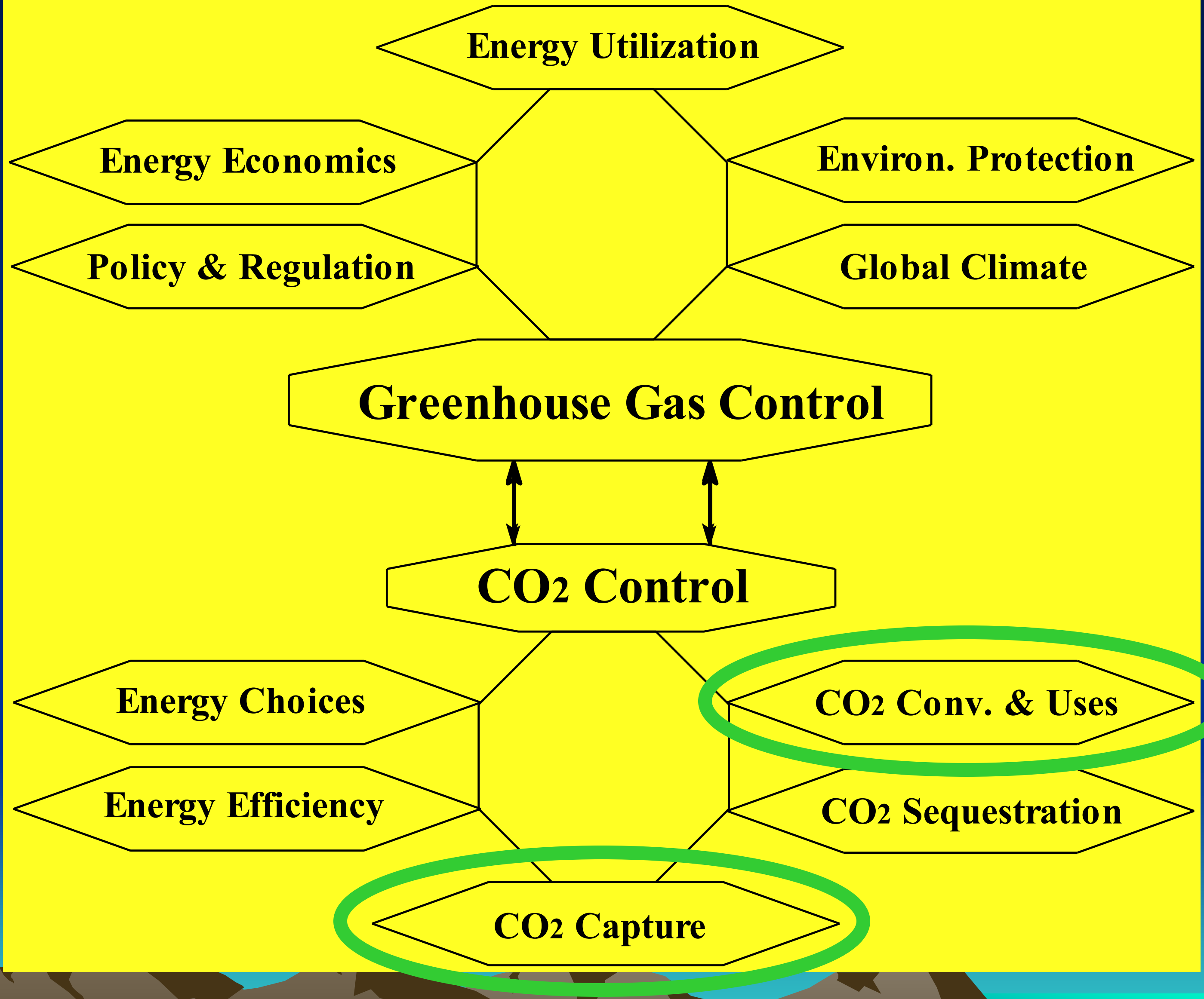
* C.S. Song. Catalysis Today, 2006, 115, 2–32

Energy-Environment Problems

"Energy is the hardest part of the environment problem; environment is the hardest part of the energy problem; and resolving the energy-economy-environment dilemma is the hardest part of the challenge of sustainable well-being for industrial and developing countries alike."*

*John P. Holdren, Science, 2008, 319, 424-434.

GHG & CO_2 Control Related to Energy Utilization*


Energy Utilization

Energy Economics

Environ. Protection

Policy & Regulation

Global Climate

Greenhouse Gas Control

CO_2 Control

Energy Choices

CO_2 Conv. & Uses

Energy Efficiency

CO_2 Sequestration

CO_2 Capture

* C.S. Song, Catalysis Today, 2006, 115, 2-32

Advantages of CO_2 Conversion to Fuels, Chemicals and Materials

- CO_2 can be used as a raw material to make fuels, chemicals, and materials that are currently produced using oil, gas and coal.
- CO_2 conversion with renewable energy can effectively minimize CO_2 emissions, while producing clean and alternative fuels, chemicals and materials without using fossil carbon resources.
- This decreases the consumption of fossil resources, and avoids the CO_2 emissions and minimize environmental impacts from the portions of fossil fuels displaced.

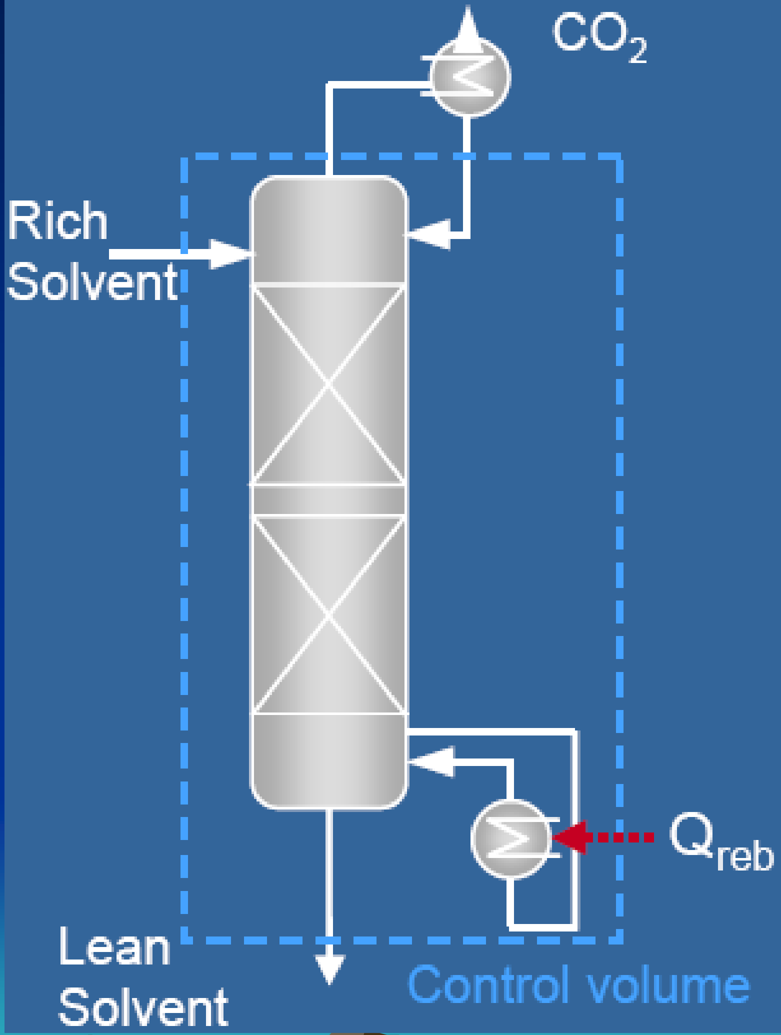
Time to Begin Exploring a New Supply Chain Using CO_2

- Capturing and recycling CO_2 to chemicals and fuels can make an effective use of plentiful carbon resource and reduce GHG emissions.
- CO_2 conversion to chemicals and fuels can also reduce, and even replace, the fossil resources consumed for the same purposes.
- Is it possible to build a new supply chain using CO_2 as raw material, replacing the fossil resources (petroleum, natural gas) as a raw material for chemicals and fuels?

CO_2 Capture
H_2 Supply
CO_2+H_2 Conversion
Product Supply

How to Lower Cost of CO2 Capture from Flue Gas?

Problems in Conventional CO_2 Capture: Energy-Consuming Parts of CO_2 Amine Scrubbing



3 major contributions

- Heating up the solvent
- Desorption of CO_2
- Evaporating of reflux water

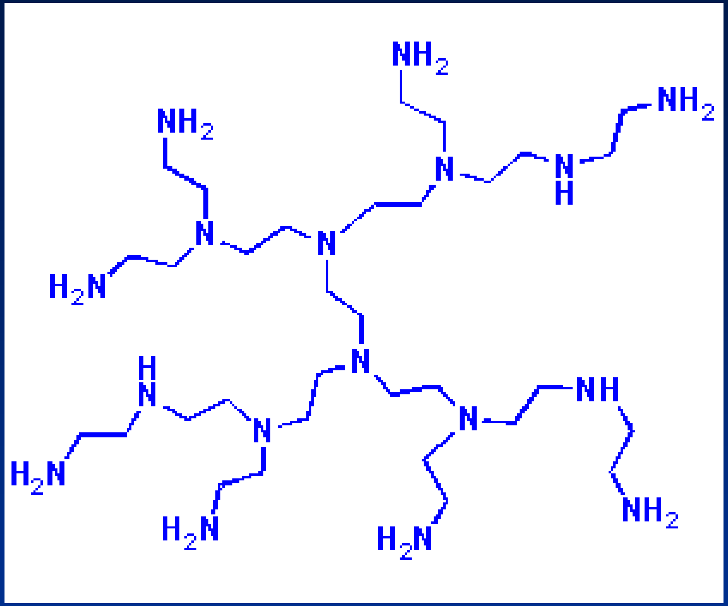
Q_{reb}	15	50	35

Choice of Solvent

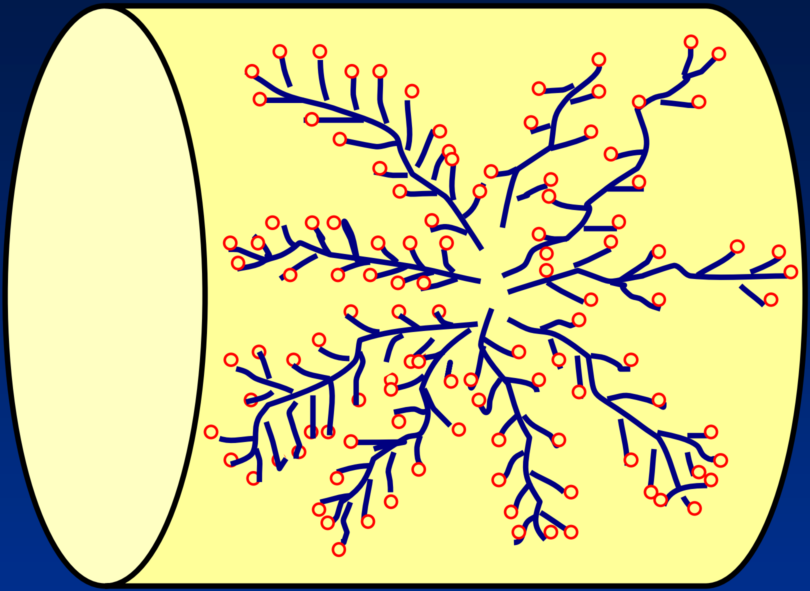
- High capacity solvent
- Low absorption enthalpy
- Low strip steam demand

* N. Asprion, BASF, DECHEMA Workshop on CO2, Jan 21-22, 2008

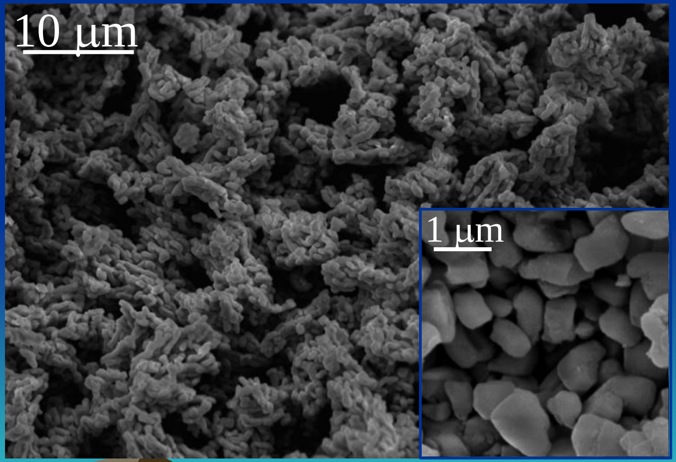
CO_2 "Molecular Basket" Sorbent (MBS) Concept*



Polyethylenimine (PEI)



Immobilize PEI in Nanoporous Mat

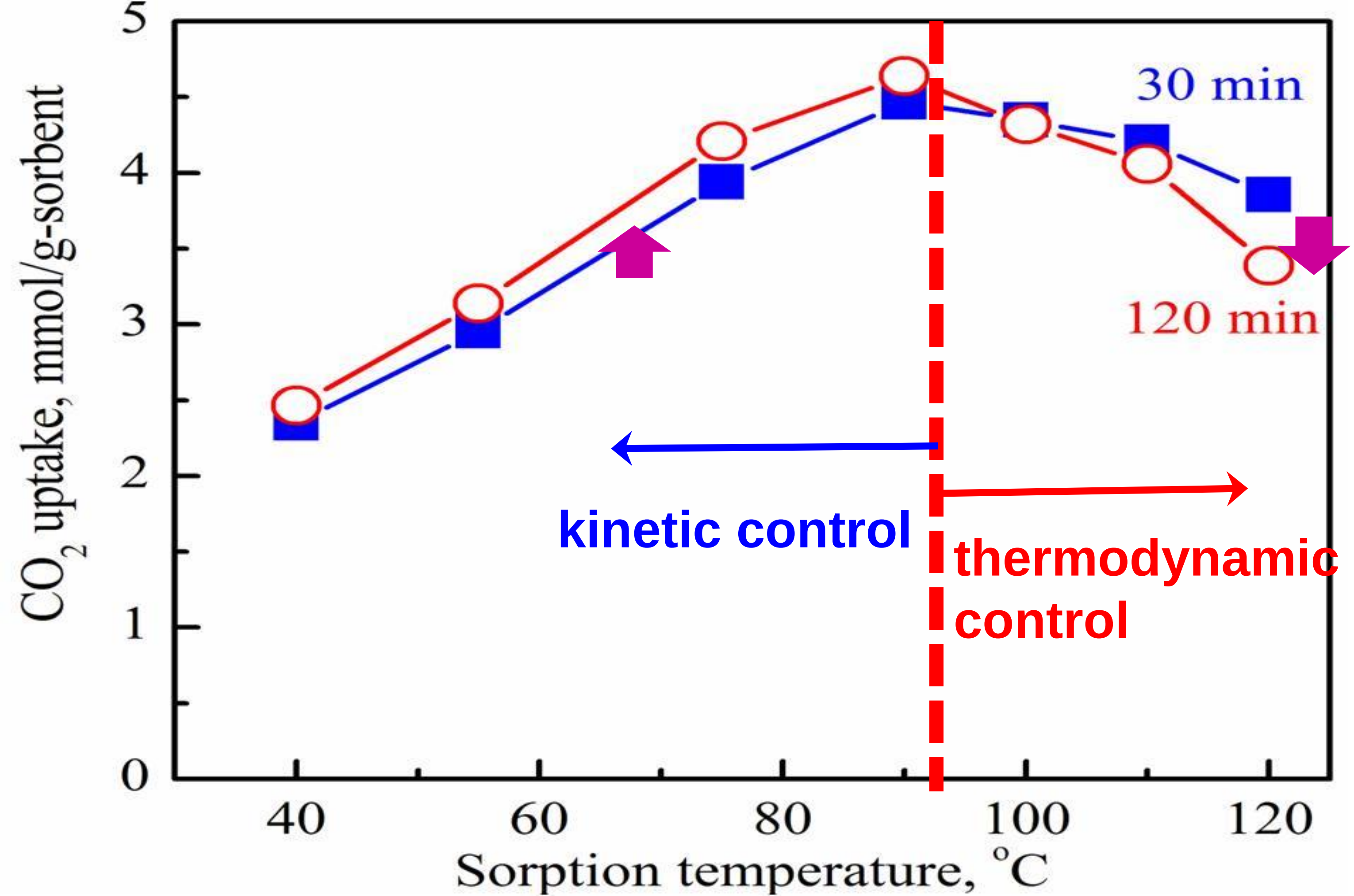


- Large pore volume can store more CO_2
- Branched CO_2-philic sites
- Branched amine facilitate the desorption
- Synergic effect on capacity and kinetics between nanoporous support and PEI

*X.L. Ma, X. Wang, C.S. Song, *J. Am. Chem. Soc.* 2009, 131, 5777.

* X. Xu, C. Song et al., Micropor Mesopor Mater, 2003, 62, 29; Energy Fuel, 2002

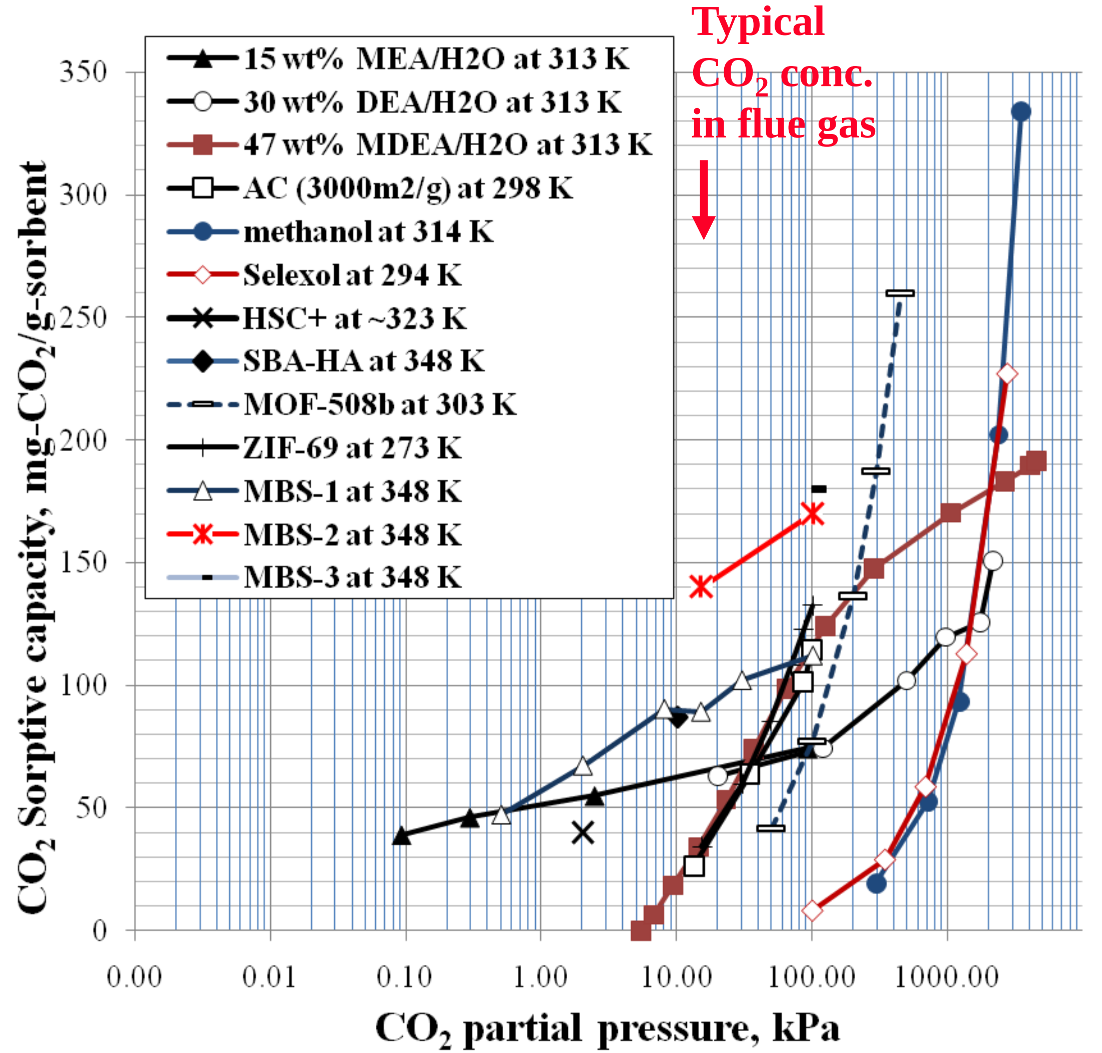
Effect of Sorption Temp and Time on CO2-MBS* – 50 wt% PEI/SBA-15



*X. Wang, C.S. Song, Catalysis Today, 2012.

CO_2 Sorption Performance of MBS in Comparison with Commercial and State-of-the-Art Sorbents

Sorption Isotherm



Typical CO_2 conc. in flue gas

Capacity of MBS-2*:
140 mg-CO_2/g-S

	Factor
MBS-2 > MBS-1	1.5
MBS-2 > MEA/DEA	2.1
MBS-2 > SBA-HA[1]	1.5
MBS-2 > ZIF-69[2]	4.0
MBS-3 ≈ MBS-2	1.0

*at 15 kPa of CO_2 partial pressure

1: Hyperbranched aminosilica sorbent (SBA-HA) by Hicks et al, *JACS* 2008.
2: Zeolitic imidazolate frameworks (ZIF-69) by Banerjee et al, *Science* 2008.

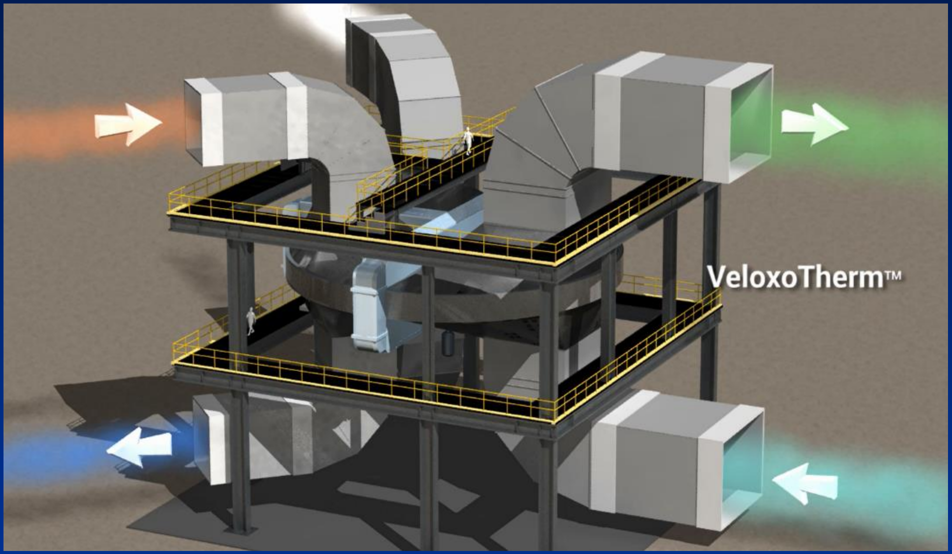
*X.L. Ma, X. Wang, C.S. Song, *J. Am. Chem. Soc*. 2009, 131, 5777.

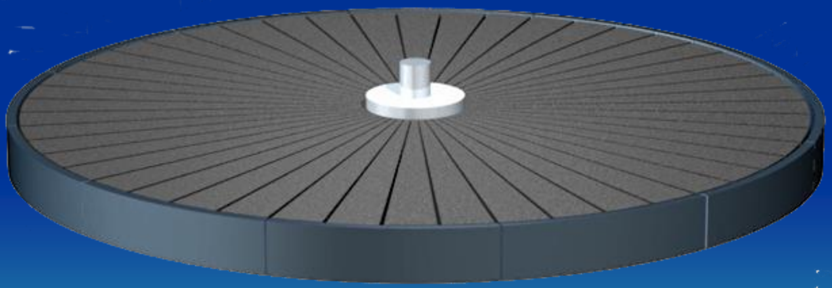
Pilot Plant Study of CO_2-MBS

- Penn State and RTI teamed up for a pilot plant study of CO_2-MBS sorbent for CO_2 capture under DOE NETL support in 2015*.
- The study successfully demonstrated CO_2-MBS for CO_2 capture from gas mixtures in a bench scale fluidized transport plant.

*Funded by US DOE/NETL; pilot plant photo in Feb 2015.

Inventys - The VeloxoTherm™ Process





The patented VeloxoTherm™ process uses structured adsorbent in a rotary system, similar to rotary air heaters, is claimed to be a more economically viable approach for separating CO_2 from flue gas streams. The claimed capture cost is ~$15/ton-CO2 capture.

HTTP://INVENTYSINC.COM/, 2015

H_2 Supply - from H_2O

Using renewable, fluctuating energy (solar, wind, geothermal, etc.)-derived electricity to produce H2 from water.

H2 production is also an effective way to store renewable energy via extracting H from H2O.

US DOE target for H2 production:

2011 price: $4.10/kg H2
2015 target: $3.00/kg H2
2020 target: $2.00/kg H2

Cost factors for H2 production from PEM electrolyzer
#Electricity price; Electrolyzer efficiency; System capital cost

Vision for the Future

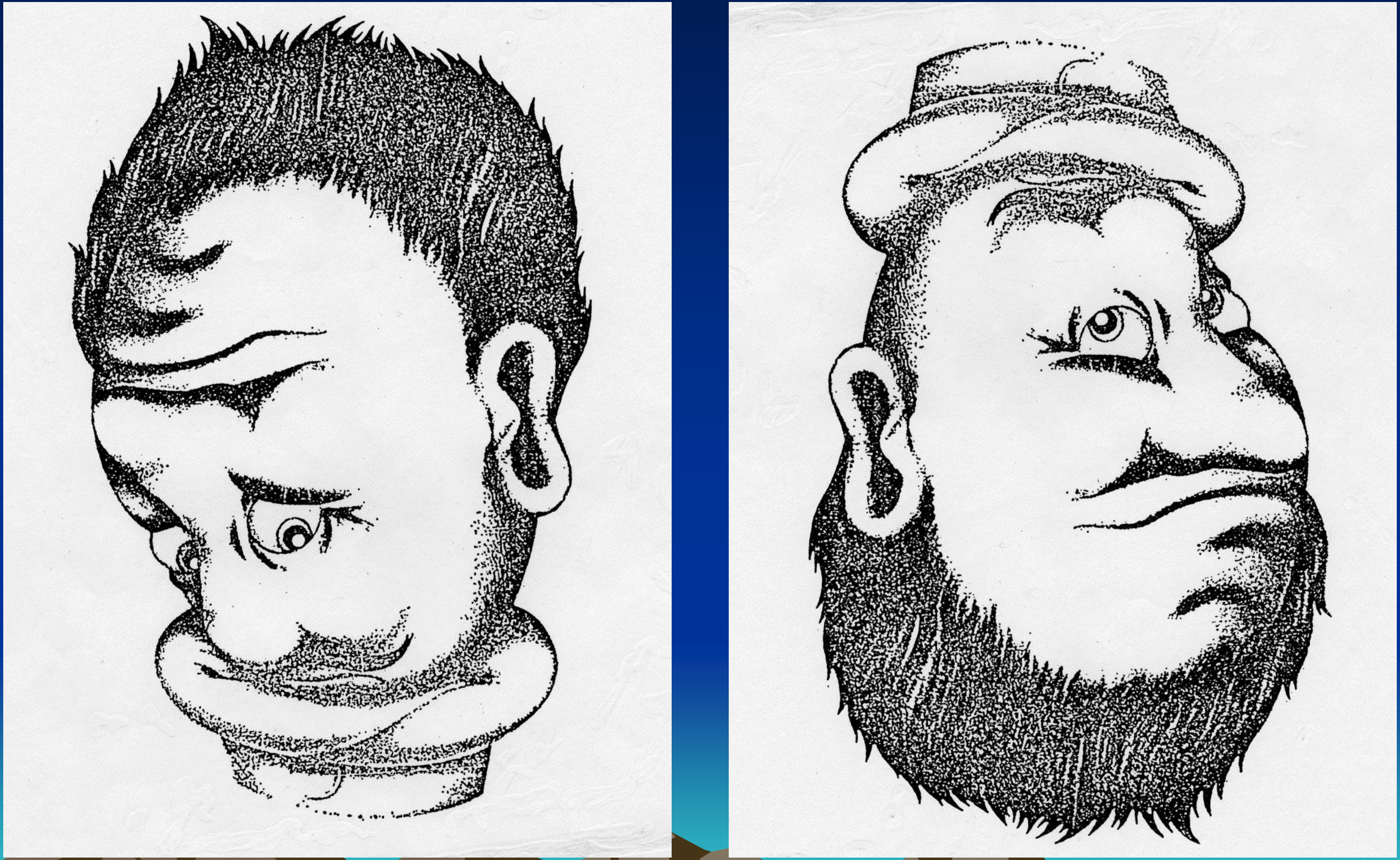
- Capturing CO_2 and converting it with H_2 (H_2O) into fuels, chemicals, and materials using renewable energy, is an important path for sustainable development.
- This approach effectively uses a greenhouse gas to control greenhouse gas emissions while providing alternative supply of ultra-clean carbon-based energy and significantly reducing consumption of fossil fuels thus minimizing negative environmental impacts.

Challenges for CO_2 Conv & Uilization*

- ❖ Perceptions, Energy requirements of CO_2 chemical conversion (plus source & cost of H_2 and other co-reactants if involved).
- ❖ Costs of CO_2 capture, separation, purification, and transportation to users.
- ❖ Market size limitations, lack of investment-incentives and industrial commitments for producing CO_2-based chemicals.
- ❖ Socio-economical driving forces usually do not facilitate CO_2 conversion and utilization.

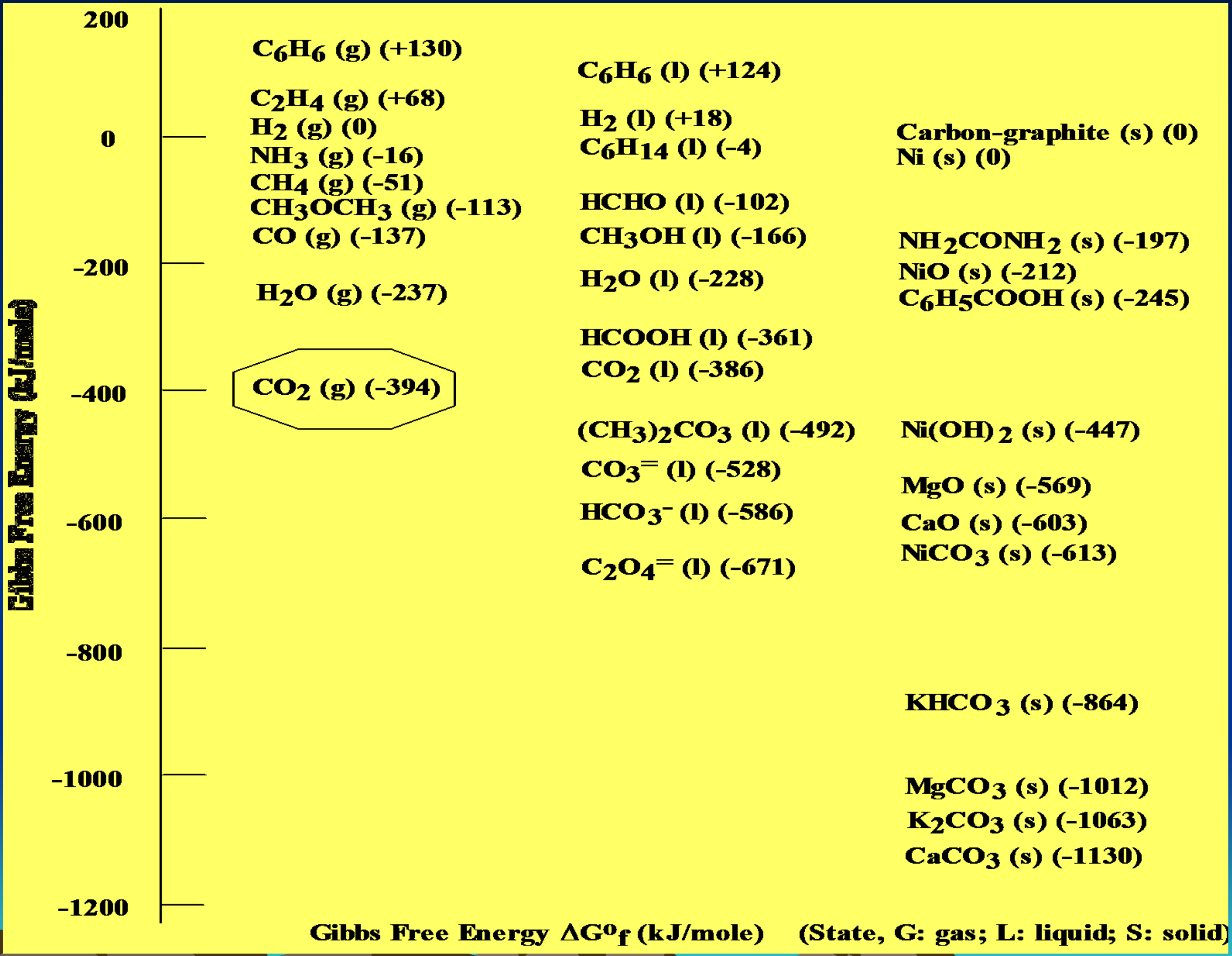
* C.S. Song, Catal. Today, 2006, 115, 2-32.

Paradigm Shift–Use CO_2 for Fuels?



Picture source: Suehiro Kunitake

Thermodynamics of CO_2 Conversion & Sequestration*



* C.S. Song, Catalysis Today, 2006, 115, 2-32.

Amounts of Uses vs Emissions

The amounts of carbon in liquid and gaseous fuels are similar to those in CO_2 from flue gas of power plants. Thus converting CO_2 to fuels using renewable energy can dramatically cut down CO_2 emissions and also reduces the consumption of fossil fuels.

– C. Song, CO2 Conversion and Utilization, ACS, 2002

The actual utilization of CO_2 although significant for the chemical industry (ca. 200 Mt/y) represents a minor fraction of the anthropogenic emission (32,000 Mt/y)

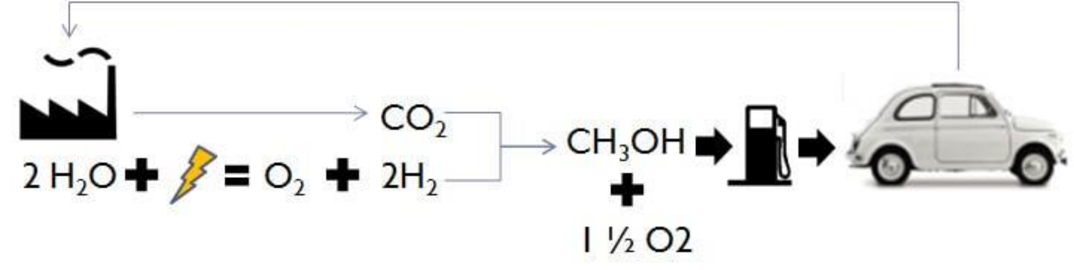
– M. Aresta, J CO2 Utilization, 2013.

Use and Reuse of CO_2 – the “U” in CCUS

- CO2 to Fuels with renewable energy
  - Liquid fuels, SNG
  - Alcohol fuel
- CO2 to Chemicals
  - hydrocarbon chemicals (C_2-$C_4^=$)
  - oxygenated chemicals (MeOH, DMC, etc.)
  - As working fluid or co-reactant (sc-CO_2, etc.)
- CO2 to Durable Materials
  - carbonates materials
  - polymer materials

- CO_2-EOR / CO_2-EGR coupled with CO_2 storage

CRI's George Olah Renewable Methanol Plant



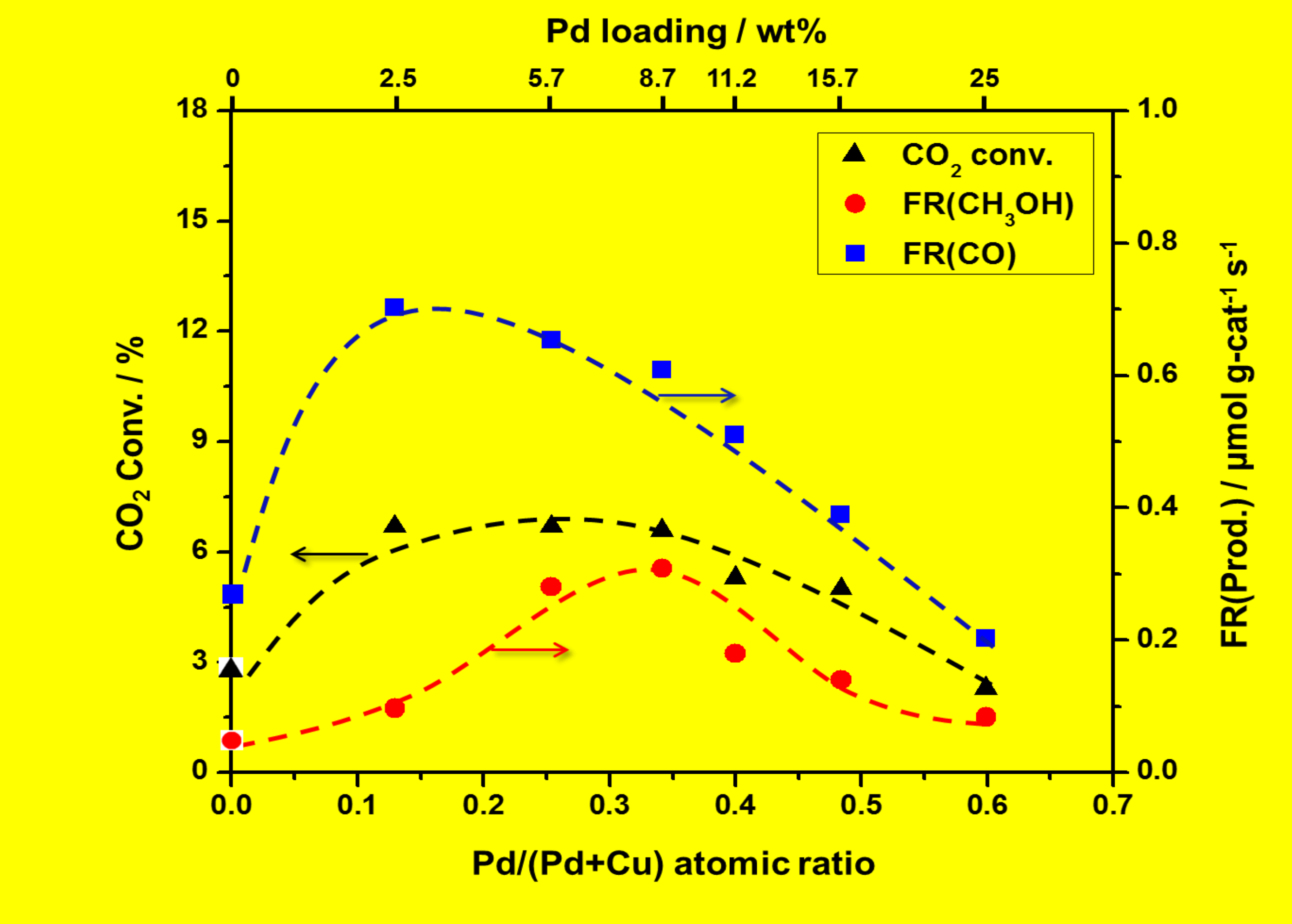
Located in Svartsengi, near Grindavik, Iceland, began production in 2011.

In 2015 CRI expanded the plant from a capacity of 1.3 million litres/year to more than 5 million litres/year. The plant uses Cu-ZnO catalyst, and now recycles 5.5 thousand tonnes of CO2 a year (captured from flue gas of a power plant), which would otherwise be released into the atmosphere, using renewable energy.

CRI's Emissions to Methanol: http://carbonrecycling.is/projects-1/

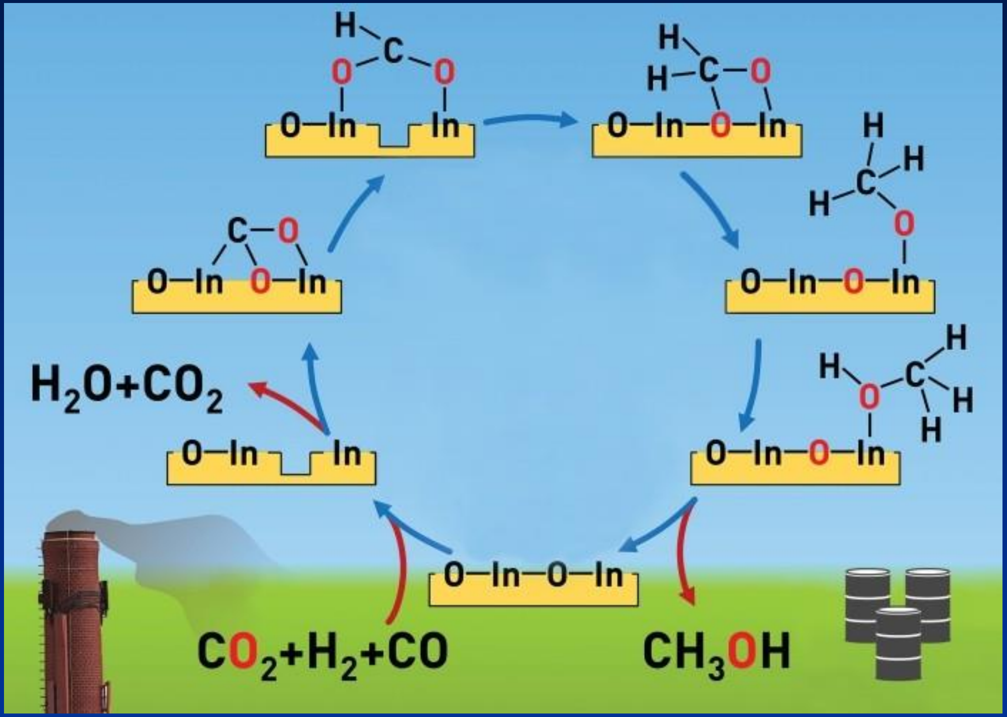
New Pd-Cu Bimetallic Cat for CO_2 to Methanol

$$CO_2 + 3\,H_2 = CH_3OH + H_2O$$



X. Jiang, C. Song et al. Appl. Catal. B: Env. **2015** (170) 173-185

New In_2O_3/ZrO_2 Catalyst for CO_2 to Methanol



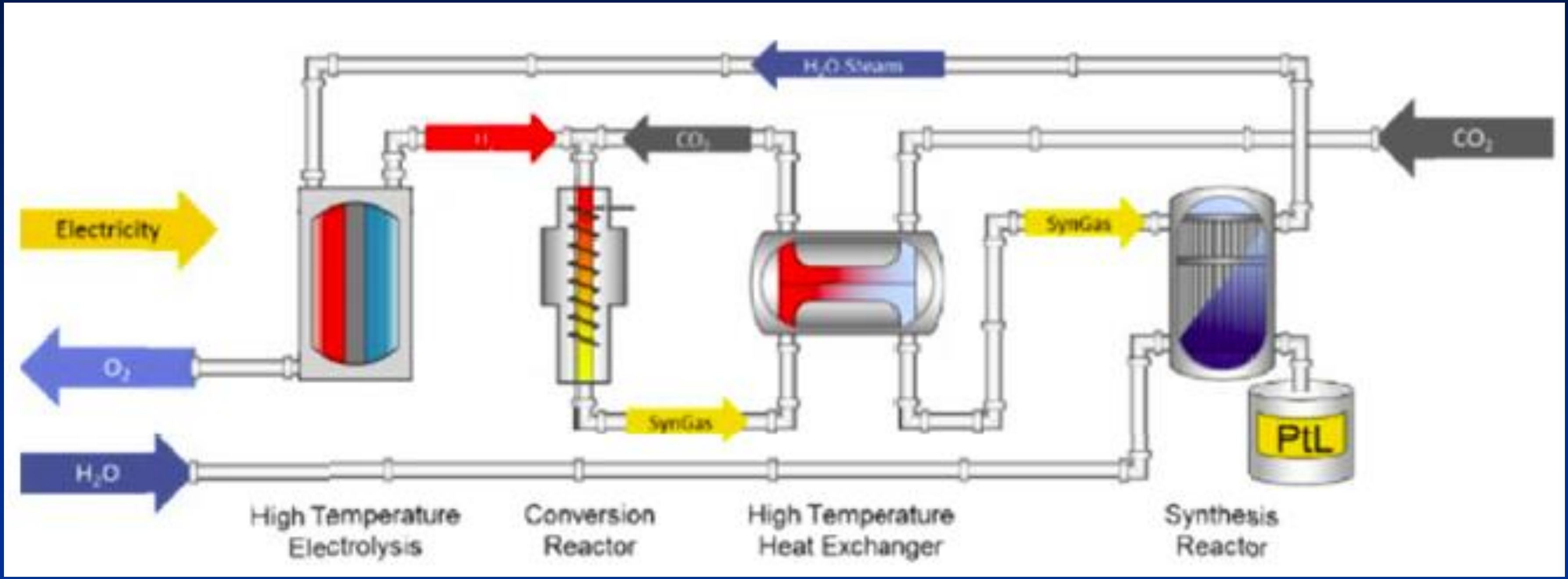
Highly selective CO2 hydrogenation with H2 to methanol under industrially relevant conditions.

Stu Borman, C&EN, 2016, 94 (13), 7, March 28, 2016.

Expt work by Javier Pérez-Ramírez of ETH Zurich and coworkers now demonstrate that zirconium oxide-supported In2O3 catalyzes the process under conditions similar to those required for industrial production (Angew. Chem. Int. Ed. 2016, DOI: 10.1002/anie.201600943).

Built on computational work led by Qingfeng Ge of Southern Illinois Univ and Tianjin Univ (ACS Catal. 2013, DOI: 10.1021/cs400132a).

Sunfire Gmbh: CO_2 to Hydrocarbon Fuel via FTS



1	Electrolysis	H_2O (vapor)	⇨	$H_2 + ½ O_2$	ΔHR = +242 kJ/mol
2	CO_2 reduction	$CO_2 + H_2$	⇨	$CO + H_2O$	ΔH_R = +41 kJ/mol
3	Fischer-Tropsch synthesis	$CO + 2 H_2$	⇨	$-(CH_2)- + H_2O$ (vapor)	ΔH_R = -157 kJ/mol

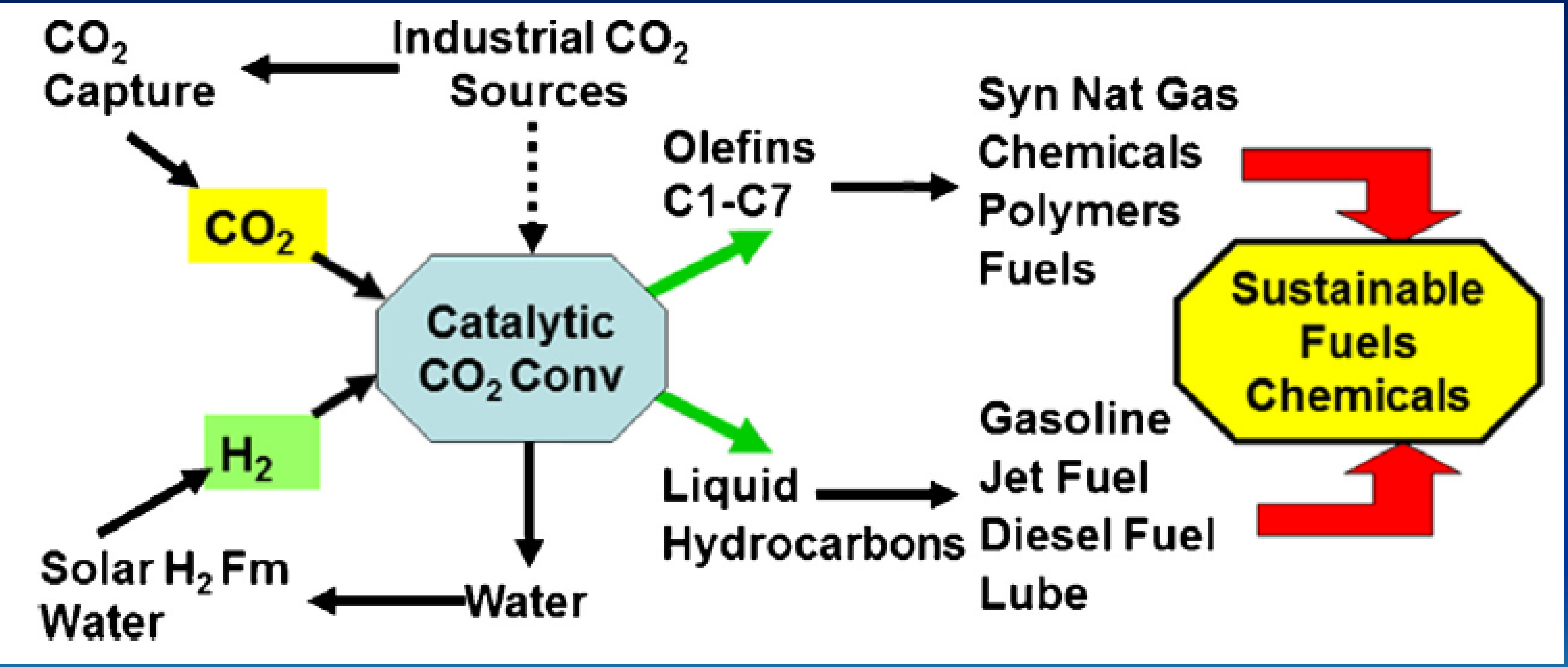
Sunfire's pilot plant in Dresden, Germany, built over 2013-2014. Its Solid Oxide Electrolysis plant can convert CO2 to 160 litres (1 bbl) of hydrocarbons a day using renewable electricity, with a electricity to fuel carbon efficiency of 70%.

http://www.sunfire.de/en/kreislauf/power-to-liquids

Direct CO_2 Hydrogenation to Chemicals & Fuels

$$n\,CO_2 + (3n+1)\,H_2 = C_nH_{2n+2} + 2n\,H_2O$$

$$n\,CO_2 + 3n\,H_2 = C_nH_{2n+1}OH + (2n-1)\,H_2O$$



* Satthawong, Koizumi, Song, Prasassarakich. J. CO_2 Utilization 2013 (3-4) 102-106.

* C.S. Song, Energy Resources, **1995**, 16, 63-64.

CO_2 HYD over Conventional Fe and Co Catalysts

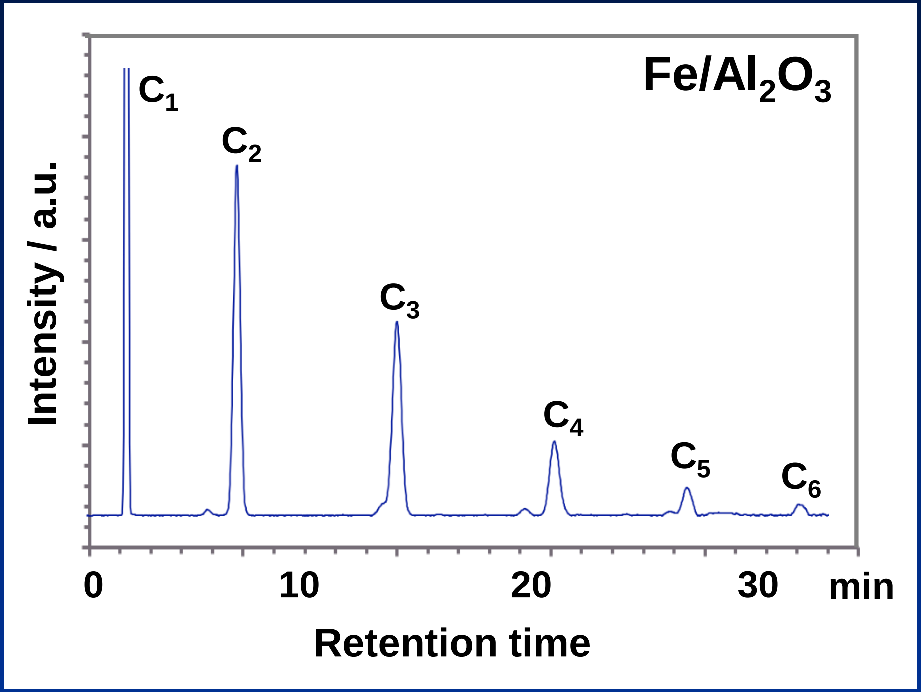


Fig. 3 GC-FID chromatograms of HCs. Cat.: Fe/Al_2O_3. Cond.: $H_2/CO_2 = 3$, Temperature =573 K, Total pressure = 1 MPa

CO_2 conv. = 12%

C_2^+ sel. = 38%

Low CO_2 conv., relatively low C_2^+ sel.

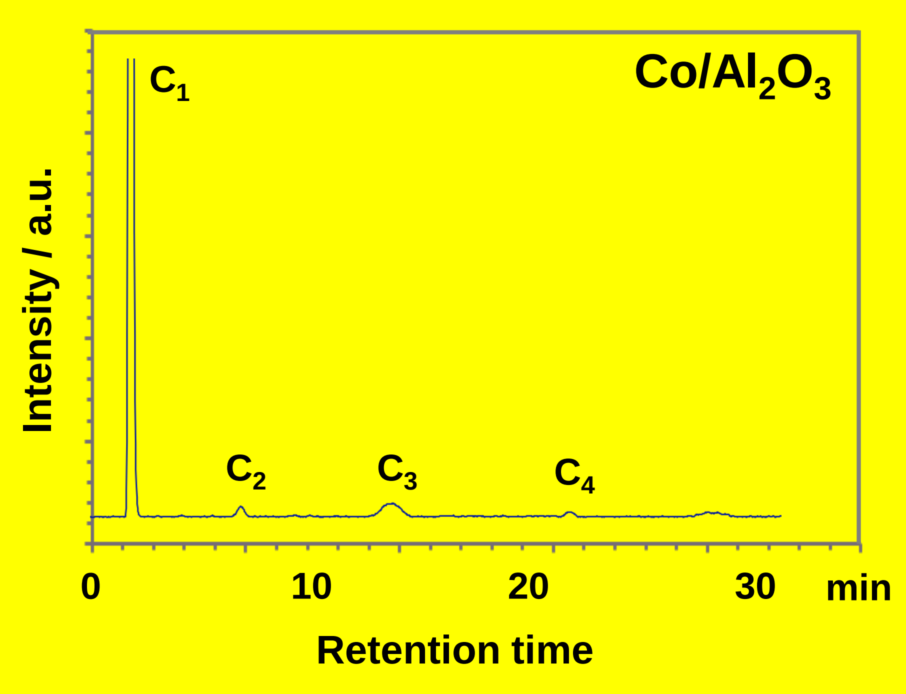


Fig. 4 GC-FID chromatograms of HCs. Cat.: Co/Al_2O_3. Cond.: $H_2/CO_2 = 3$, Temperature =573 K, Total pressure = 1 MPa

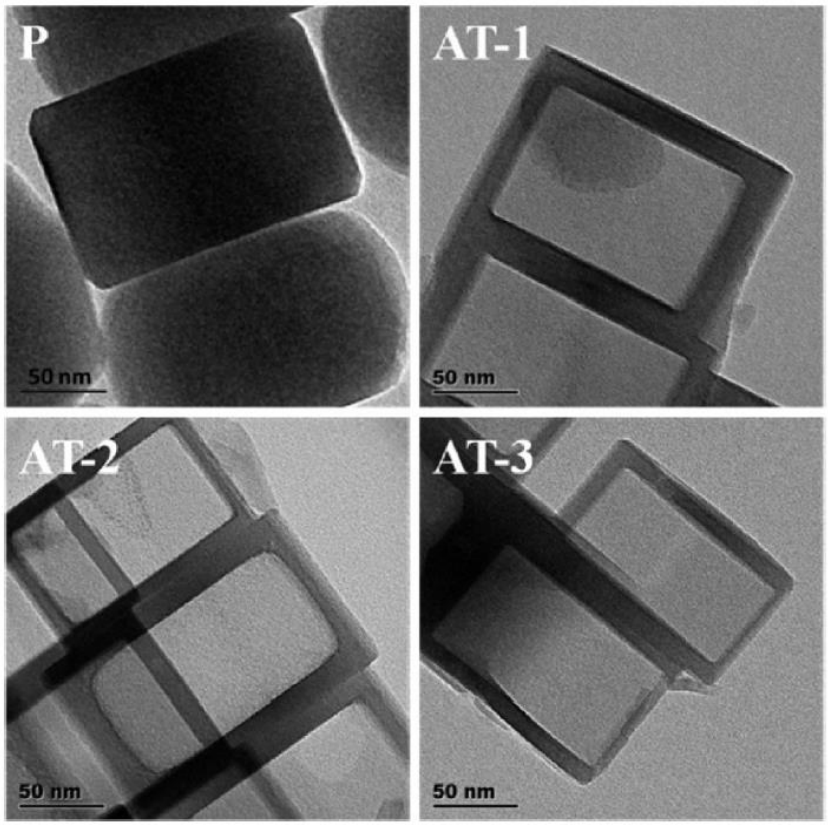
CO_2 conv. = 49%

C_2^+ sel. = 1%

High CO_2 conv., almost no C_2^+ sel.

[6] Satthawong, R.; Koizumi, N; Song, C; Prasassarakich, P, J of CO_2 Utilization, Vol. 3–4, 2013, 102–106
[7] T. Riedel, M. Claeys, H. Schulz, G. Schaub, S.-S. Nam, K.-W. Jun, et al. Appl. Catal. A: Gen. 186 (1999) 201–213.

New Fe@Hollow S-1 as Support for CO2 HYD



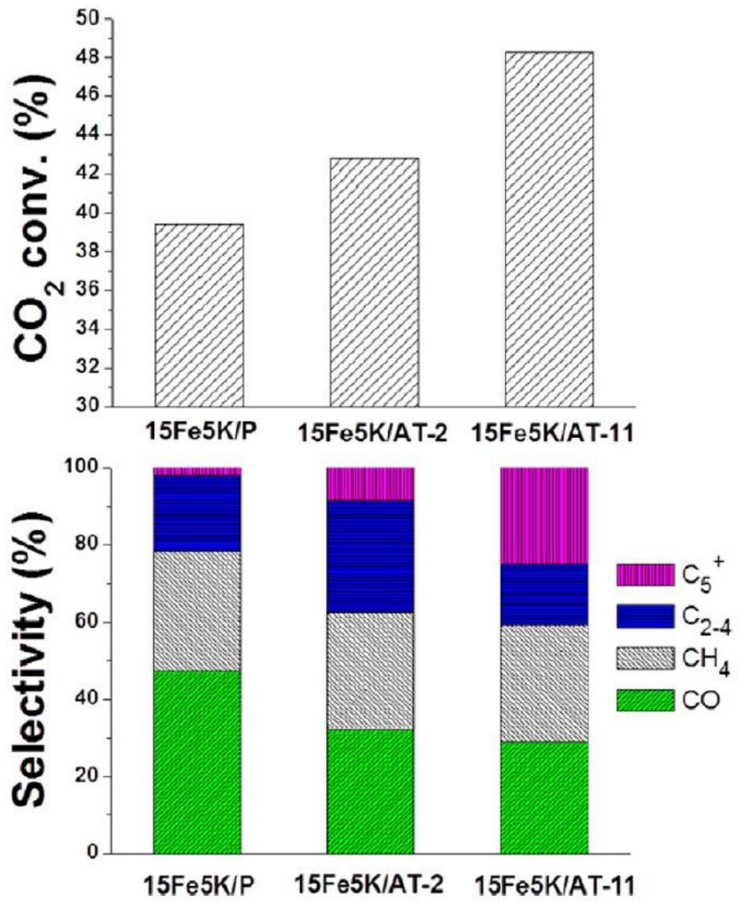
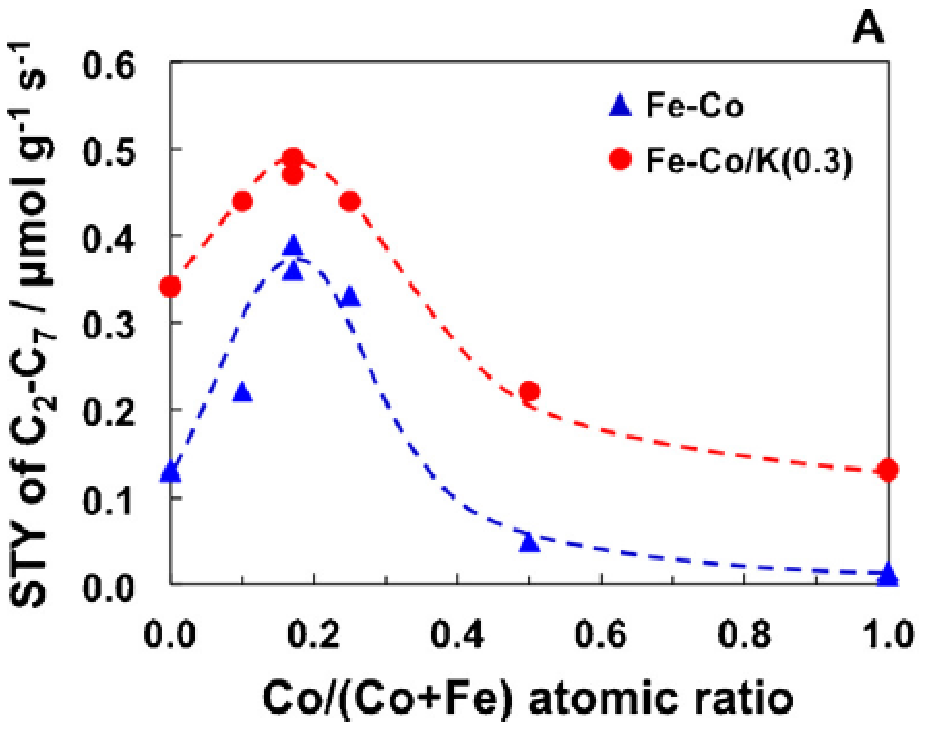


Fig. 5. **Left**: TEM images of solid silicalite-1 (P) and hollow silicalite-1 after treatment with TPAOH concentration of 0.20 M (AT-1), 0.30 M (AT-2), and 0.50 M (AT-3). **Right**: CO_2 hydrogenation into hydrocarbons over FeK catalysts loaded on solid silicalite-1 (P), hollow silicalite-1 (AT-2), and macroporous silicalite-1 (AT-11),

C Dai, A Zhang, X Guo, C Song. *Chem. Mater.*, 2013, 25, 4197

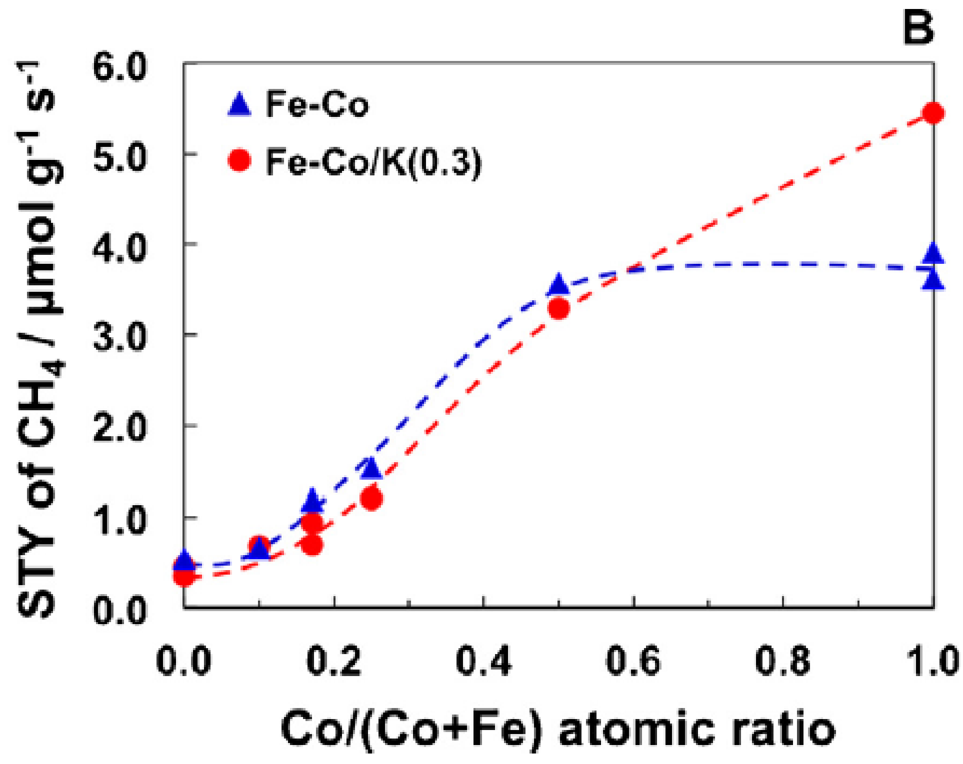
Novel Fe-Co Bimetallic Catalysts for Selective Conv of CO_2 to C_2+ HCs



Known Facts:

Co leads to CH_4

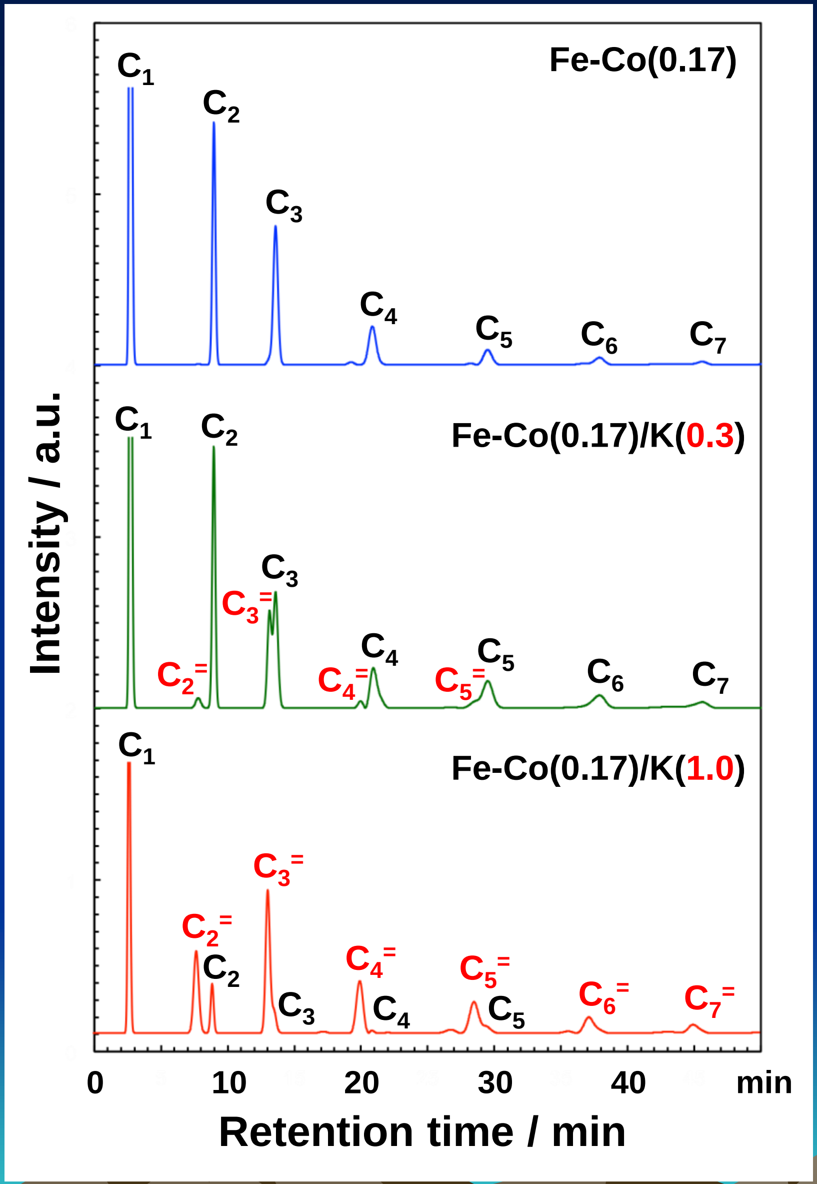
Fe shows low sel

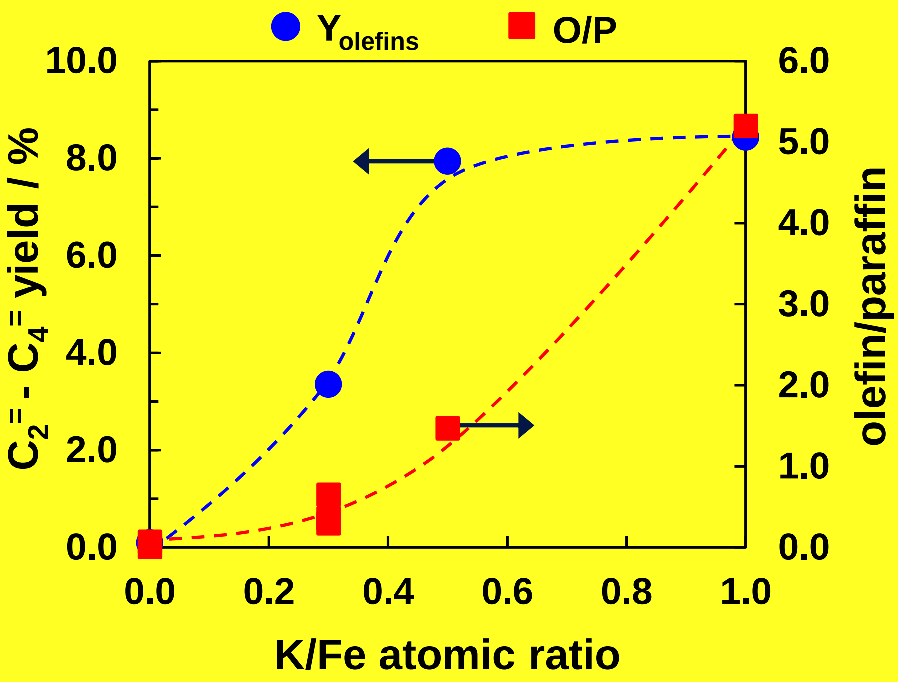


Cat.: Fe-Co/Al_2O_3. $H_2/CO_2 = 3$, Temp: 573 K, Tot P: 1 MPa

* Satthawong, Koizumi, Song, Prasassarakich. J. CO_2 Utilization 2013 (3-4) 102-106.

Selective C_2-C_4 Olefin Prod over Fe-Co





Effect of K content on $C_2^=$- $C_4^=$ yield and O/P from CO_2 HYD over Fe-Co(0.17)/K(Y)/Al_2O_3 cat.

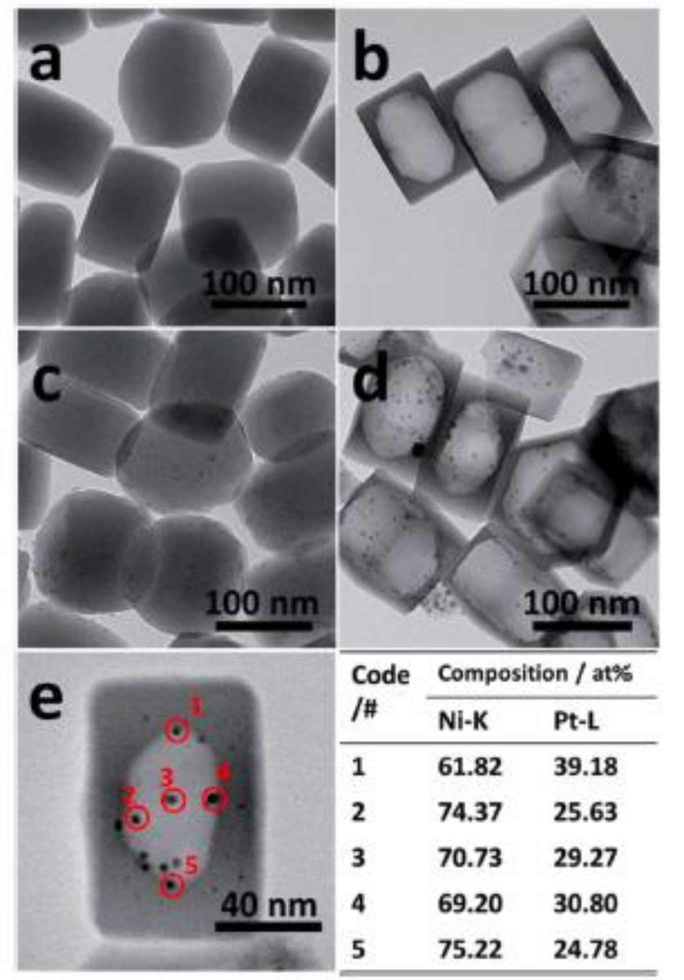
Olefins were main products at K/Fe = 1.0 atom atom^{-1}

→ K suppressed olefin hydrogenation activity of the catalyst

Satthawong, Koizumi, Song, Prasassarakich. Cat. Today 2015 (251) 34-40.

Hollow Zeolite Encapsulating Ni-Pt@S-1 for CO_2 Reforming of CH_4 to Syngas ($CO+H_2$)

$$CO_2 + CH_4 = CO + H_2$$



Code /#	Composition / at%	
	Ni-K	Pt-L
1	61.82	39.18
2	74.37	25.63
3	70.73	29.27
4	69.20	30.80
5	75.22	24.78

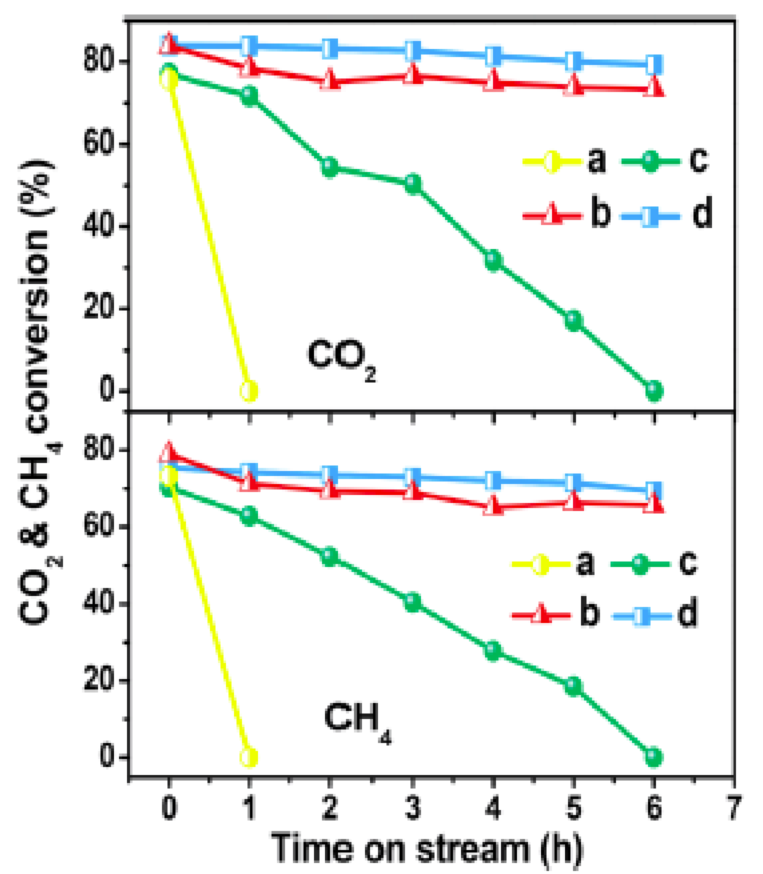
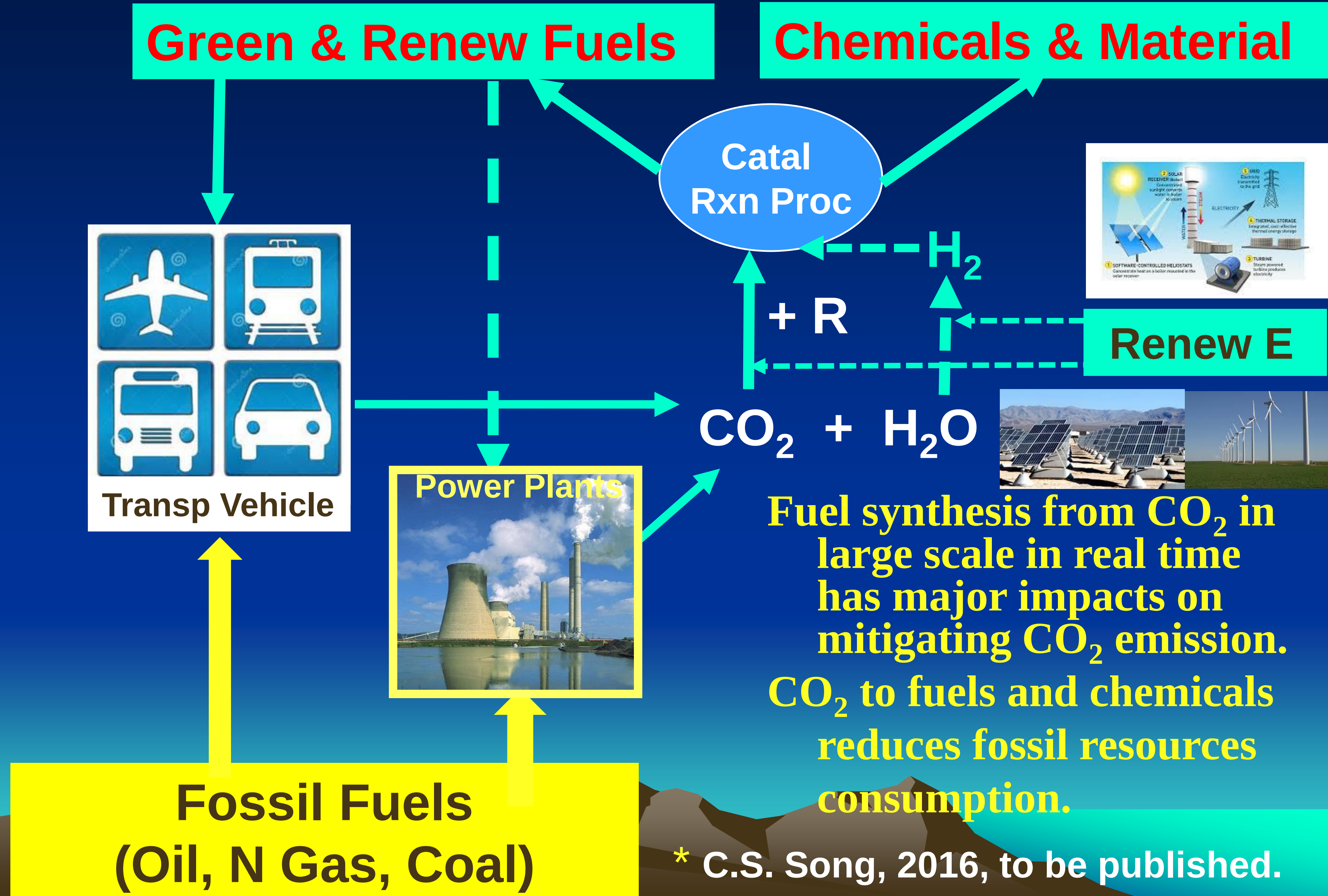


Fig. 7 CO_2 and CH_4 conversion as a function of time on stream over (a) 1.5Ni/S-1, (b) 1.5Ni@Hol S-1, (c) 1.5Ni–0.5Pt/S-1, and (d) 1.5Ni–0.5Pt@Hol S-1 catalysts [800 °C, atmospheric pressure, GHSV = 72 000 ml g^{-1} h^{-1}, and $CH_4/CO_2 = 1:1$ (v/v)].

CY Dai et al. J. Mater. Chem. A 2015, 3, 16461.

Sustainable Green Energy Cycle Using CO_2



Fuel synthesis from CO_2 in large scale in real time has major impacts on mitigating CO_2 emission.

CO_2 to fuels and chemicals reduces fossil resources consumption.

* C.S. Song, 2016, to be published.

Conclusions

- CO_2 capture and utilization present major challenges and new opportunities for sustainable green energy cycle development.
- Converting CO_2 to fuels and chemicals with renewable energy input can not only mitigate CO_2 emission, but also reduce fossil resources consumption.
- Major challenges in developing
    - novel nano-structured materials and more energy-efficient and economically attractive processes for (1) CO_2 capture (post, pre-comb) in high capacity with fast kinetics, and (2) catalytic CO_2 conversion in high activity and selectivity to clean fuels, value-added chemicals, and materials using renewable energy

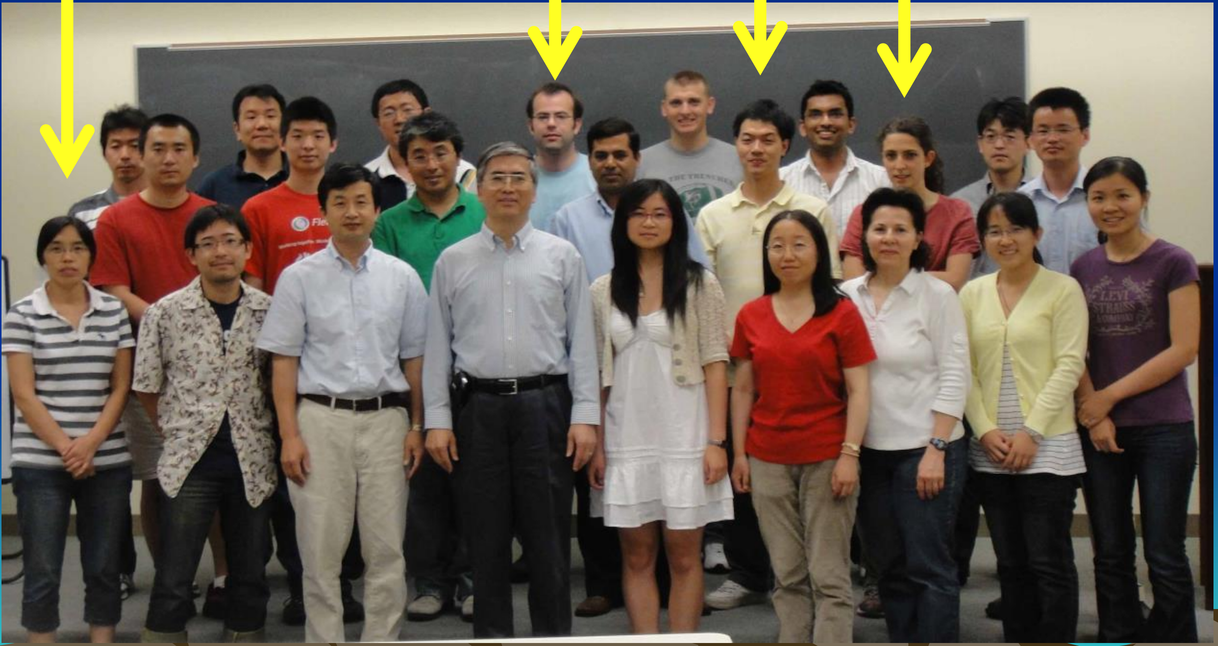
People Who Contributed at PSU, DUT, and Chula U

Xiaochun Xu, Xiaoliang Ma, Xiaoxing Wang, Eric Fillerup, Emanuela Peduzzi, Dongxiang Wang, Zhonghua Zhang, Bruce Miller, Alan Scaroni (PSU) for CO2 capture

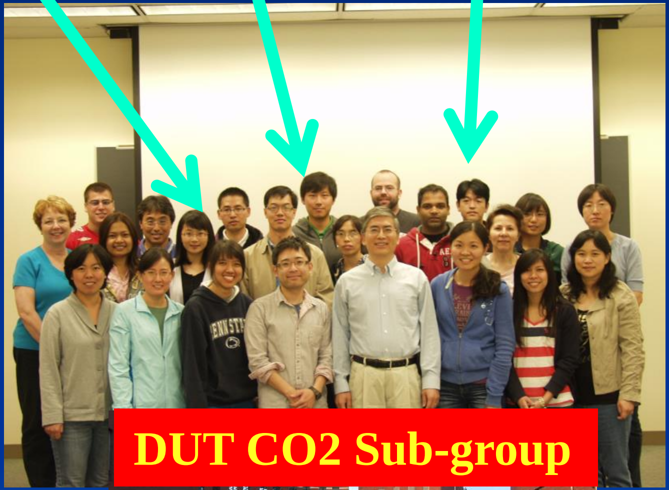
Ratchy Satthwong, Naoto Koizumi, Xiao Jiang, Wenjia Wang (PSU), Fanshu Ding, Anfeng Zhang, Chengyi Dai, Fangyu Song, Xinwen Guo (DUT), and Pattarapan Prassasarachi (Chula U) for CO_2 conversion

Xiaoxing Wang

Dongxiang Wang **Eric Fillerup** **Emanuela Peduzzi**



Ratchy Satthwong **Xiao Jiang** **Naoto Koizumi**



DUT CO2 Sub-group

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