

Methane Activation: A Global Challenge in Surface Chemistry

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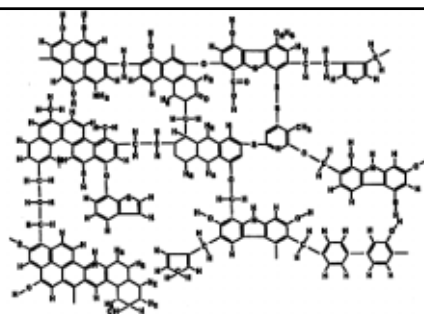
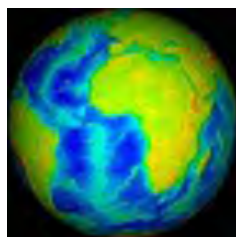
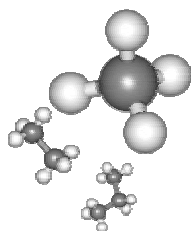


PIRE-ECCI Summer School 2006

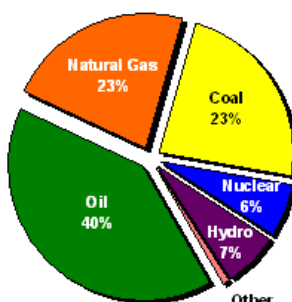
Overview

- The Problem
- Historical Approaches to Methane Activation.
- Present Practice
- A Solid Cataloreactant Approach

Energy Matters

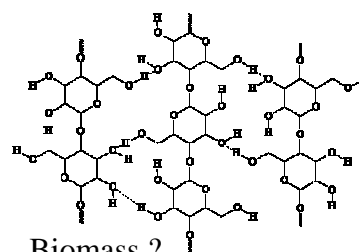
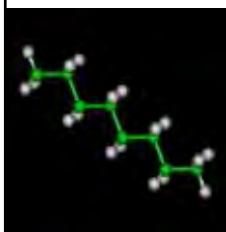


Where the World Gets Its Energy

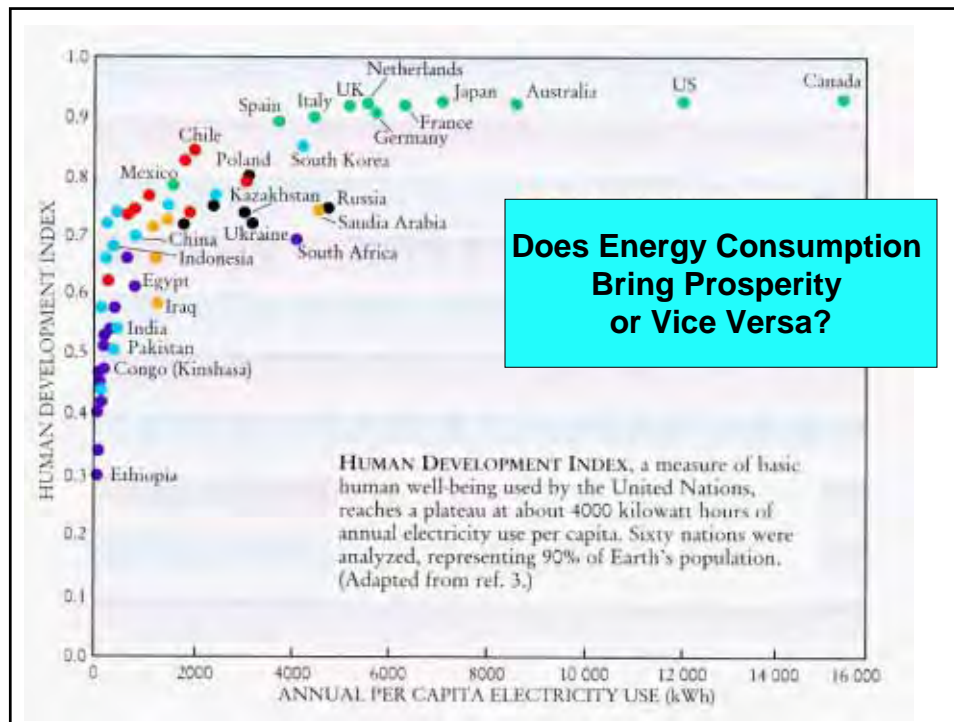


(Does not include energy from noncommercial sources.)

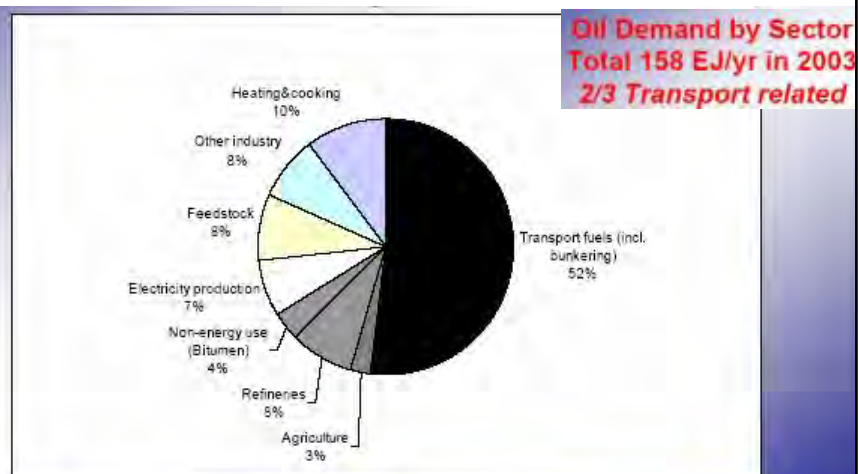
Source: U.S. Energy Information Administration



Biomass ?



Liquid Transportation Fuels (Gasoline, Diesel, Jet) Are The Major Component of Our Oil Usage

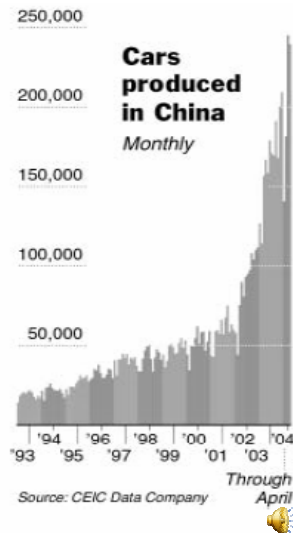


Source: IEA statistics

INTERNATIONAL ENERGY AGENCY

AGENCE INTERNATIONALE DE L'ENERGIE

There will be More before there are Less



China's Car Ownership (Thousands)

1993	700
2001	1,800
2002	3,300
2003	4,500
2004	7,000+

SIMMONS & COMPANY
INTERNATIONAL

Automobiles Are A Reality That Will Not Go Away For Many Many Generations



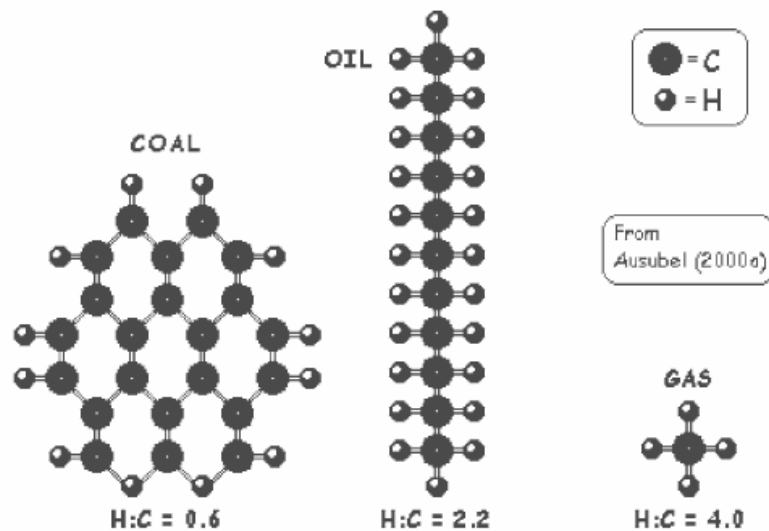
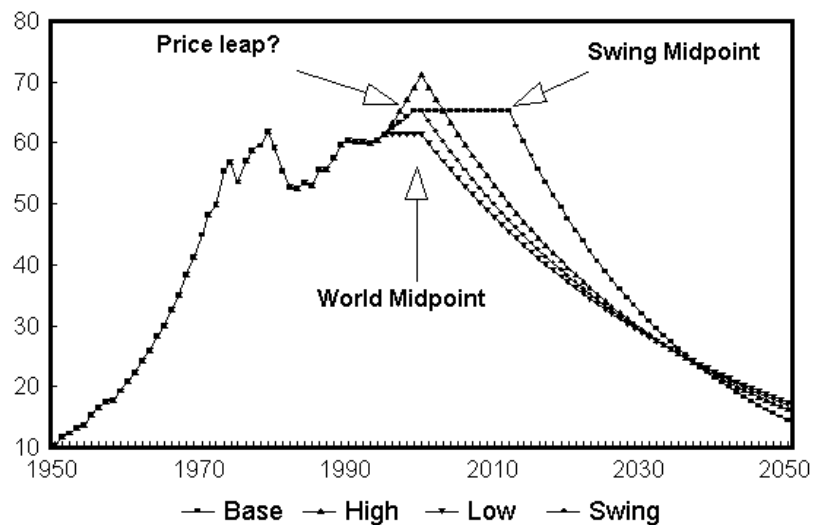
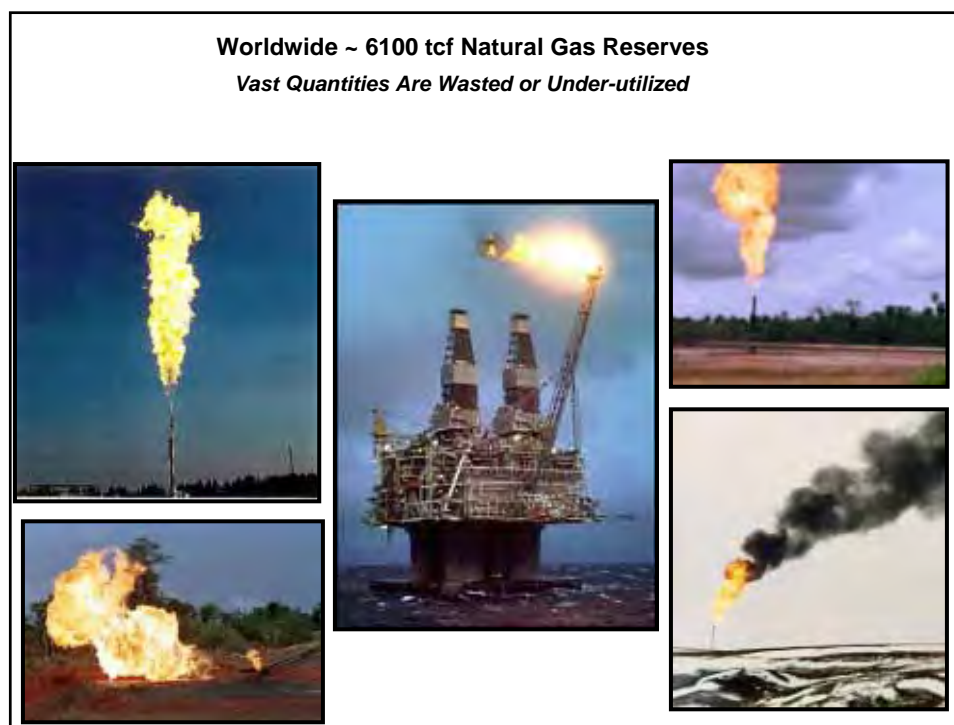
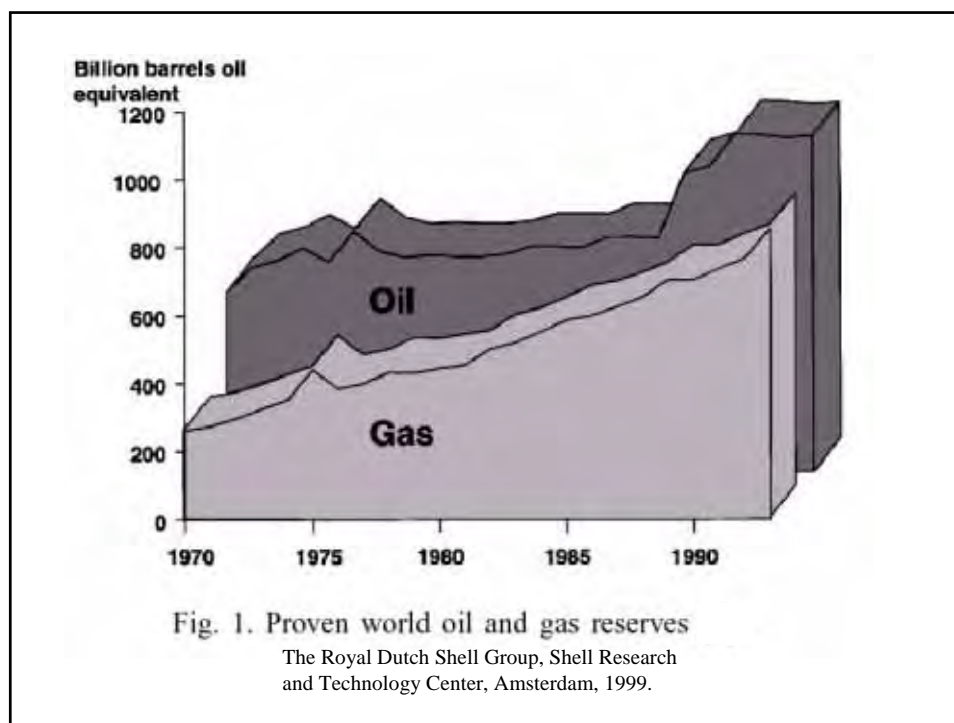


Figure 1. Carbon emitted per unit of primary energy released by combustion (C/E) increases as the H:C ratio decreases – hence the interest in ‘decarbonization’ for carbon dioxide emission reductions. The lowest (C/E) in the fossil fuel family is that of methane, which can be computed from first principles from the heats of formation of reactants and products.

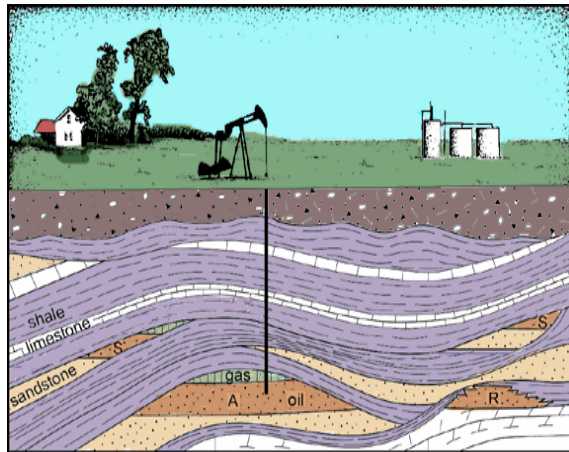
The Global Hubbert Peak Forecast of Future Global Oil Output



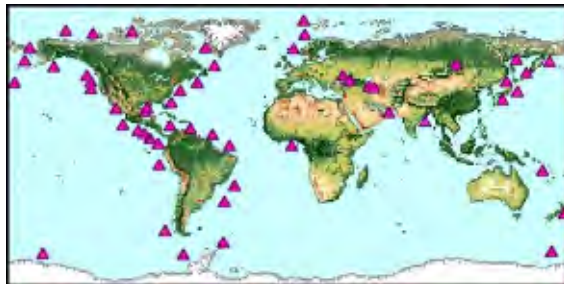
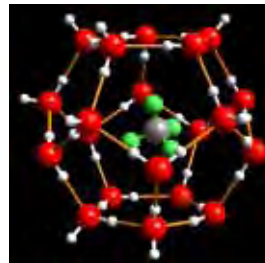
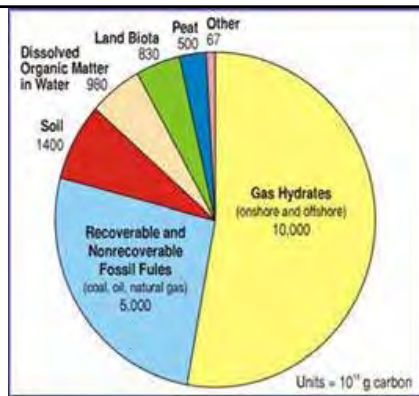
Based on an Ultimate Recovery of conventional oil of 1750 Billion barrels
Colin Campbell, 1996,



Associated Gas

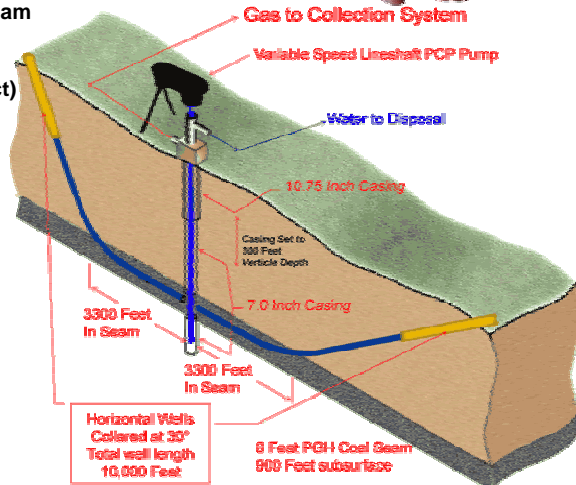


Methane Hydrates

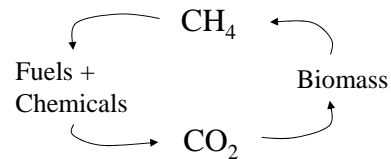


<http://www.7430.nrlssc.navy.mil/7432/hydrates/images/Distribution.jpg>

- 



→ Biomethane



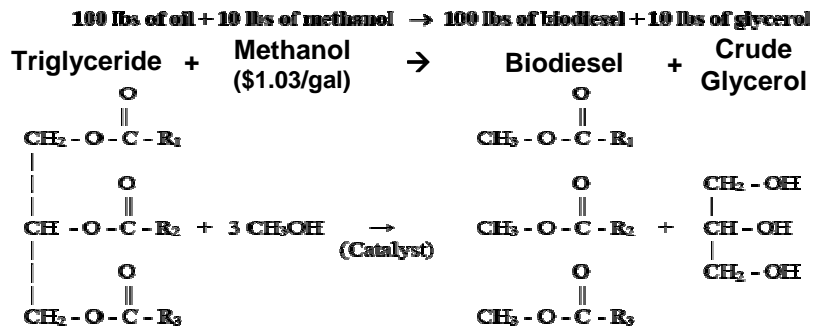
- Renewable and CO₂ neutral
- Delocalized, low cost digesters
- Already millions of household digesters.





Biodiesel is Only Semi-Renewable

(relies on, imported, non-renewable methanol made from natural gas)



New chemistry is needed to make use of the glycerol and produce methanol from renewable sources

The Problem = The Challenge

- The US and World Economy is powered by Fossil Fuels.
- Of the fossil fuels only coal can be expected to remain economically available as a hydrocarbon fuel much beyond the 50 year horizon.
- For transportation fuels (and chemicals) the most likely evolution of technologies will be:
 - Nuclear Power, electrochemically produced fuels (methanol, hydrogen) and electric vehicles
 - “BioCarbons”
- There are an enormous number of exciting opportunities in the chemical sciences for innovation to optimize these inevitable changes.

Natural Gas Management Today



- Flaring or Venting
- Re-injection
- Local Electricity Generation
- Pipeline
- LNG
- GTL
- GTC

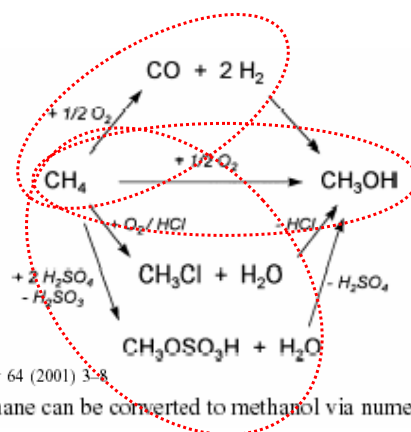
Negative product value

\$10-20/MMBTU



Historical Approaches to Methane Utilization

Alkane Activation



Catalysis Today 64 (2001) 3-8

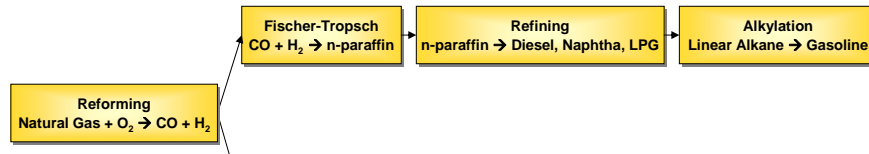
Fig. 7. Methane can be converted to methanol via numerous routes.

- Thermal Activation (Heat)
- Catalytic (Pt)
- Chemical Activation (Halogens)
- Electronic Activation (exotica \$\$\$)

Today:
Heat
Pt
Halogens

Gas to Liquids/Chemicals Today

All present commercial Gas-To-Liquids/Chemicals Processes are based on Synthesis Gas

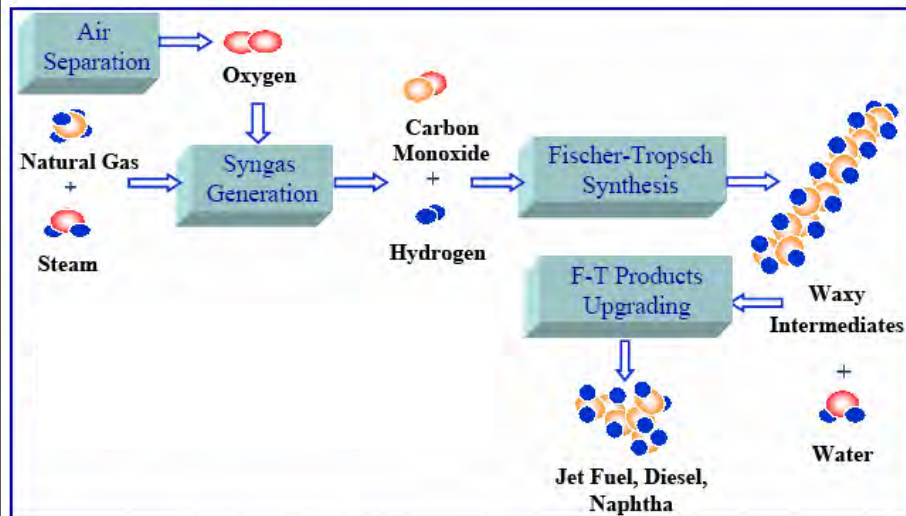


Franz Fischer
1877-1947



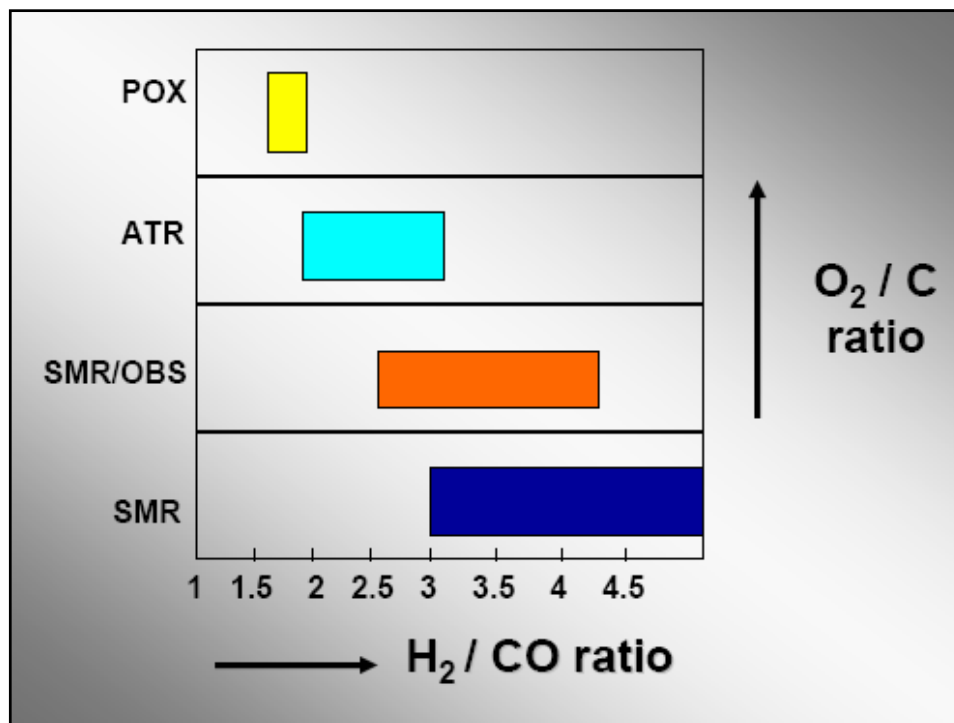
Hans Tropsch (1930)

- 1922: Franz Fischer and Hans Tropsch used iron-based catalyst to convert an CO/H_2 mixture to mixture of HCs and oxygenated compounds
- 1925: used both iron and cobalt-based catalysts to synthesize HCs
- WW II: chemistry contributed to Nazi Germany war effort
- 1950s-1990s: South Africa SASOL developed F-T commercially (in conjunction with coal gasification) to convert coal to HCs—total capacity 4,000,000 MT/year in three plants; two still in operation
- 1980s-present: Shell using F-T to convert NG to fuels and waxes in Bintulu, Malaysia—recently increased wax capacity to approx. 500,000 MT/year along with diesel, gasoline, etc.
- 1980-present: a number of entrants into the field, a number of projects announced and planned (including demonstration projects), Qatar and Nigeria have started design and construction on world-scale GTL facilities



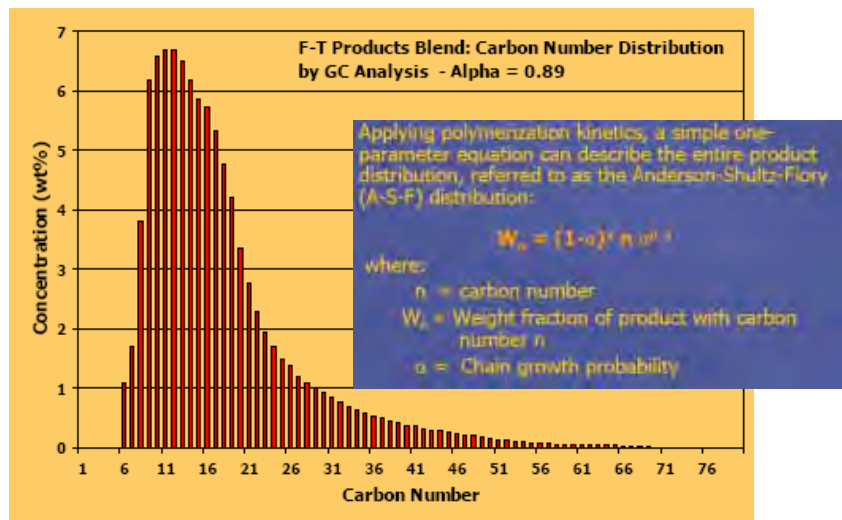
- **Steam route**
 - Steam-methane reforming (SMR)
 - Catalytic, endothermic process
 - $\text{CH}_4 + \text{H}_2\text{O} = 3 \text{H}_2 + \text{CO}$
 - » Hydrogen contributor
- **Oxygen route**
 - Partial oxidation (POx)
 - Non-catalytic; high temperature (1200-1400 C)
 - Sub-stoichiometric combustion of HC with Oxygen
 - $\text{CH}_4 + \frac{1}{2} \text{O}_2 = 2 \text{H}_2 + \text{CO}$
 - » CO contributor

- Combined route
 - Auto-thermal reforming (ATR)
 - Partial oxidation at lower temperature (900-1100 C)
 - Catalytic reforming with oxygen and steam
 - $2 \text{CH}_4 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 = 5 \text{H}_2 + 2 \text{CO}$
 - Oxygen blown secondary (OBS) reforming : 2-step in series
- Mixed routes (Series or Parallel)
 - POx + SMR
 - ATR + SMR





- Exact mechanism very complex, not well defined, and still the subject of much debate
- F-T mechanism may be divided into at least 3 major steps:
 - 1. Initiation or C_1 compound formation by:
 - CO adsorption on catalyst metal surface
 - C – O bond breakage
 - Hydrogenation of $^*\text{C}$ to $^*\text{CH}_2$
 - 2. Hydrocarbon chain growth by;
 - Successive insertion of the C_1 building blocks
 - 3. Chain termination by:
 - Desorption of unsaturated surface species
 - Hydrogenation and desorption of saturated species



- Product from cobalt catalyst higher in paraffins
- Product from iron catalyst higher in olefins and oxygenates

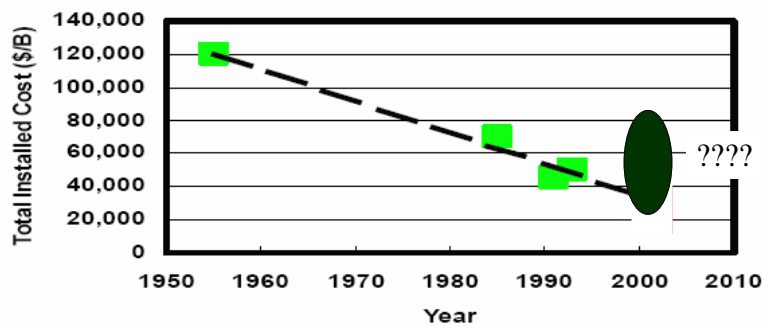


Typical F-T Catalyst Constituents

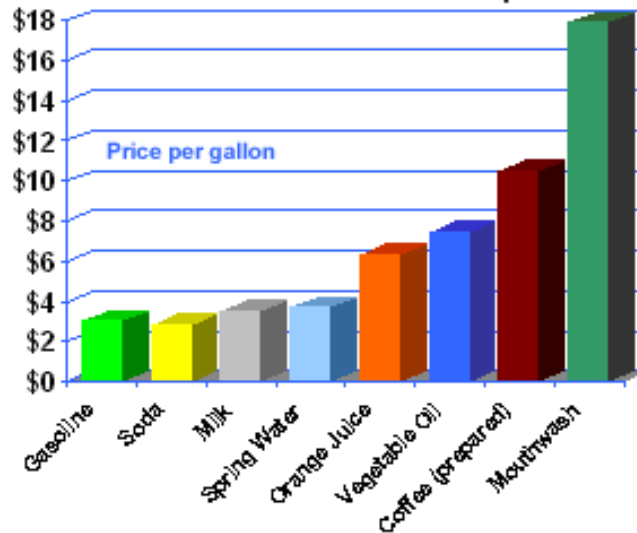
- F-T Active Metal (Co, Fe, Ru)
- Reduction Promoters (Pt, Ru, Pd, Re, Cu)
- Activity/Selectivity Promoters (K, Zr, RE, etc.)
- Refractory oxide (Al_2O_3 , SiO_2 , TiO_2) used as supports or structural promoters

Leading Energy Solutions.

GTL-FT CAPEX Reduction Due to Improved Technology



Gasoline Costs Less Than Spring Water and Most Processed Liquids



Sources: Cambridge Energy Research Associates
U.S. Energy Information Administration

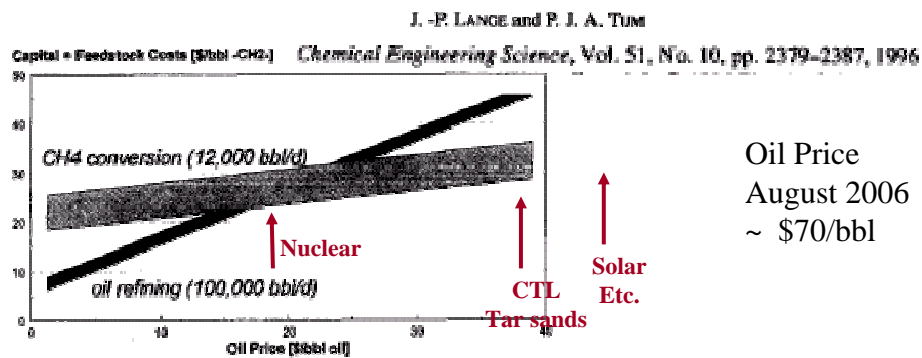


Fig. 1. Effect of the oil price on the "capital + feedstock" cost of oil- and methane-based fuel manufacturing plants.

Oil prices will never again be below ~\$25/bbl for sustained periods of time => economic shift in fuel and chemical feedstocks towards natural gas, improved technology would bring the shift sooner.

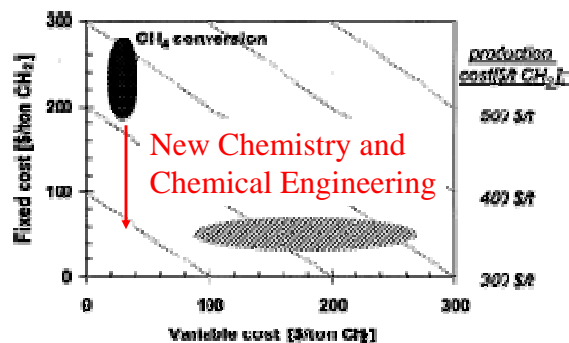


Fig. 1. The economics of oil refining is dominated by raw material costs whereas that of natural gas conversion is dominated by plant investment. The diagonal lines represent overall production costs. (The variable costs are based on a gas price of \$0.5/GJ and an oil price varying between \$10 and \$30/bbl; the annual fixed costs are assumed to amount to 35% of the total investment.)

Large Scale GTL Projects Worldwide



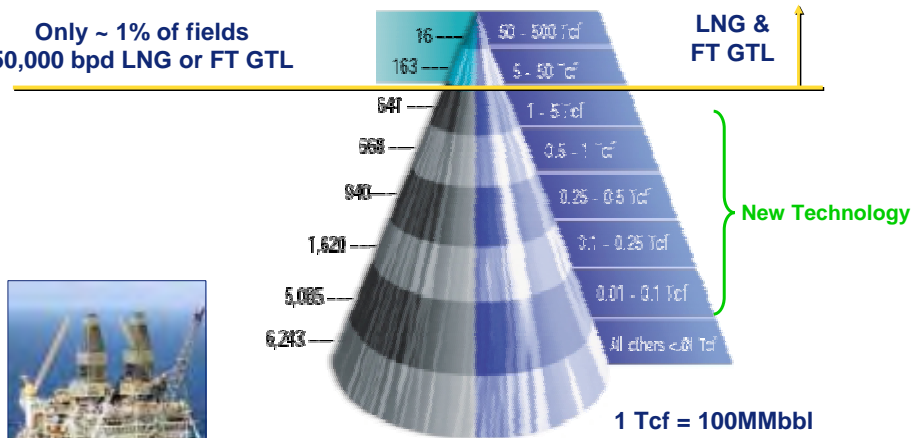
The Challenge

*Improve Carbon Utilization, Decrease Capital
Apply to Medium and Small Gas Fields*

(100-10,000 bpd)

Only ~ 1% of fields
50,000 bpd LNG or FT GTL

LNG &
FT GTL



Source: IHS Energy Group, 1998

Historical Approaches to Methane Utilization Alkane Activation

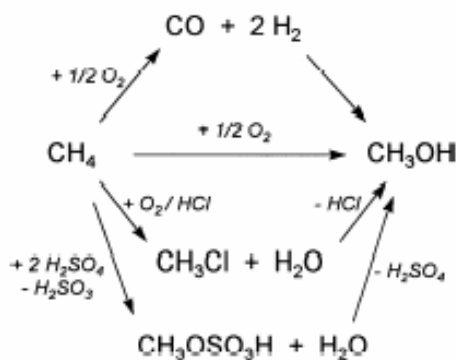
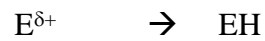
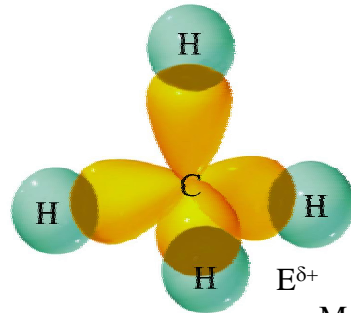
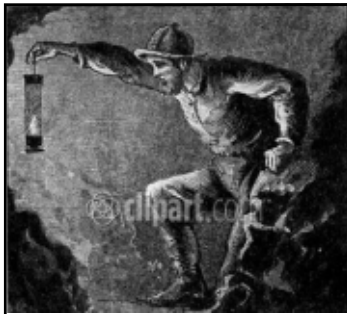


Fig. 7. Methane can be converted to methanol via numerous routes.

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- M (Ag, Au, Pt)
- X (F, Cl, Br, I)
- A (F-, Cl-, Br-)



~ 1800
Heat
Halogens
Platinum



Fig. 192. Davysche Sicherheitslampe

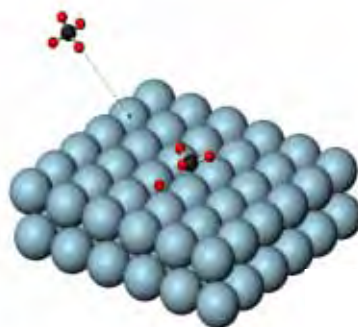
Heterogeneous Catalysis



Davy, H.

Phil. Trans. R. Soc. 107, 45 (1817)

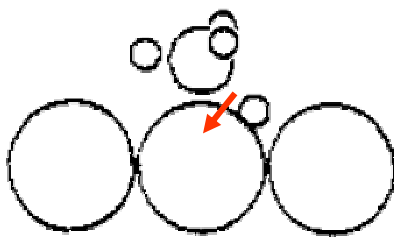
Pt



Alfred B. Anderson* and John J. Maloney

Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106 (Received: May 26, 1987;
In Final Form: August 17, 1987)

The Journal of Physical Chemistry, Vol. 92, No. 3, 1988



Pt(111)

Conclusions

The oxidative addition of methane to the iron, nickel, and platinum surfaces considered here is characterized by the insertion of a surface metal atom into a CH bond. Transition-state CH bond stretches amount to around 0.4–0.5 Å. In the transition state two methane CH σ orbitals hybridize with the metal s and d band orbitals to form metal–H and metal–C bonds and the antibonding counterpart to these σ donation interactions is stabilized by mixing with the empty CH σ^* orbital to give additional C–metal bond order. Our finding of charge donation to the metal surfaces in most of the transition states conflicts with the conclusions of

Heterogeneous Catalysis

D. A. Hering, L. D. Schmidt / Chemical Engineering Science 37 (2002) 2615-2625

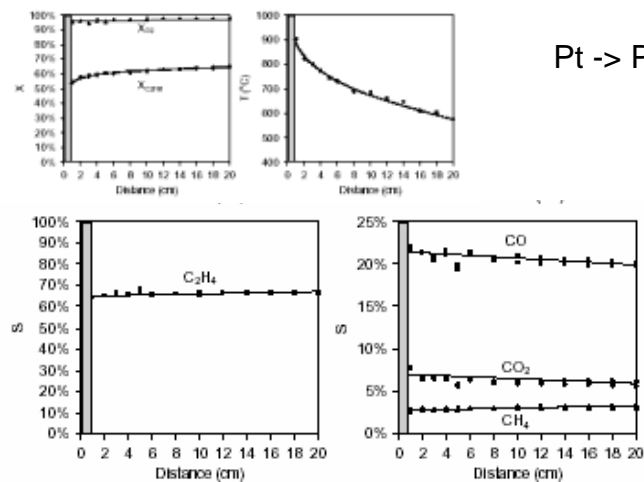


Fig. 4. Downstream species and temperature profiles for Pt-Sn at $C_2H_6/O_2 = 2/1$.

High Selectivities to Ethylene by Partial Oxidation of Ethane

A.S. Bodke, D.A. Olschki, L.D. Schmidt, E. Ranzi
Science, 285, **1999**, 712-715

Table 1. Comparison of partial oxidation of ethane with steam cracking.

Process	Feed (moles)				C_2H_4 selectivity (%)	C_2H_6 conversion (%)	Time (s)
	C_2H_6	O_2	H_2	H_2O			
Steam cracking	2	0	0	2	85	60	0.1
Pt	2	1	0	0	64	69	10^{-3}
Pt-Sn + H_2	2	1	2	0	83	73	10^{-3}

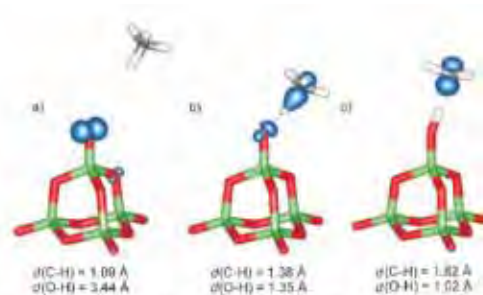
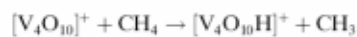
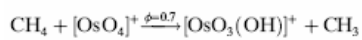
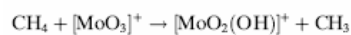
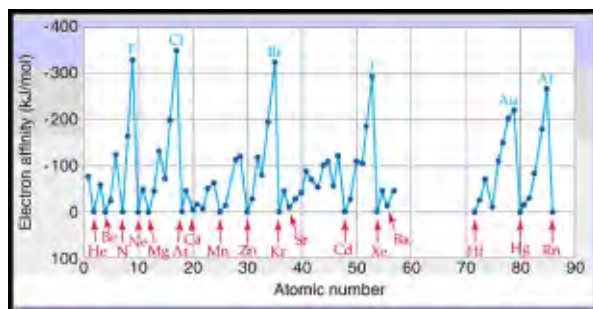
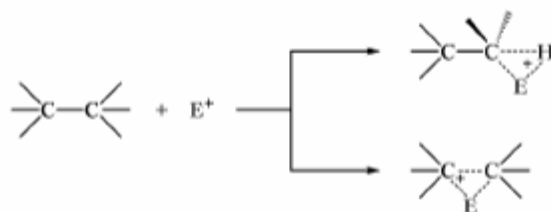


Figure 5. Spin density for the reaction of $[\text{V}_4\text{O}_{10}]^+$ and methane after a) 0 fs and b) 443 fs. c) Spin density of the optimized product structure. C-H and O-H distances are given below the structures.

Sandra Feyel, Jens Döbler, Detlef Schröder,
 Joachim Sauer,* and Helmut Schwarz*
 Angew. Chem. Int. Ed. 2006, 45, 4681–4685

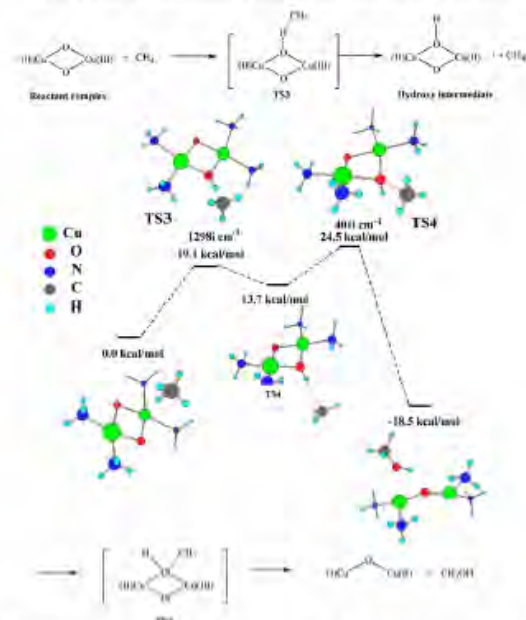
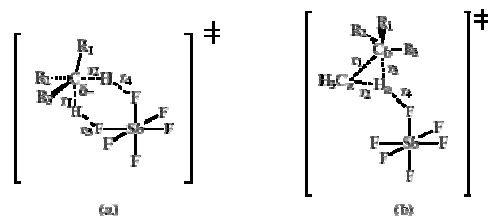
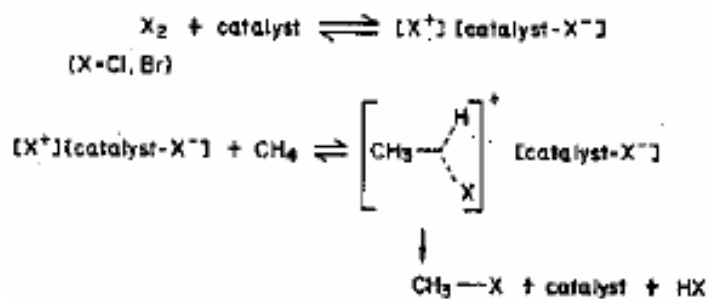


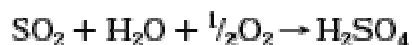
Fig. 6. Reaction energy profile for the conversion of methane to methanol by the mixed-valence bis(μ -oxo)Cu(II)Cu(III) dicopper complex 3.

Super Acids/Electrophiles



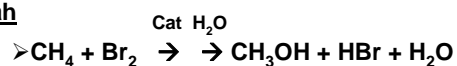
Scheme 1. Schematic representation of the TS for H/H exchange (a) and C-C protonation (b) of alkanes in superacid.





Direct the less symmetric C-X bond

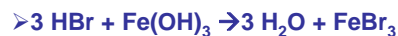
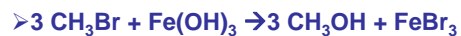
Olah



Lester (Br recovery)



Miller



Challenges

-Volatile catalysts
(Fluorine loss)

-H₂O separation

-Oxide sorption capacity

- Br₂/ water separation

- HBr / Olefin separation

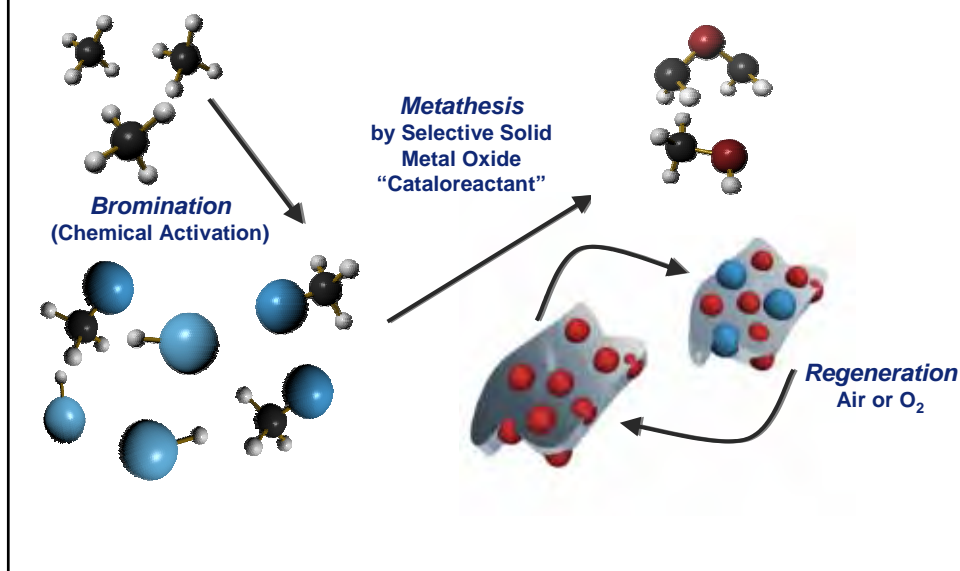
- Molten salt handling

- Liquid Phase Kinetics

-Large energy input to water
phase for Br recovery

-H₂O separation

The GRT Chemistry *Solid Reactant Process For Methane Conversion*



GRT Inc: The History

1999:

GRT founded as a privately held corporation to identify and develop new technologies for natural gas conversion to higher value products.

2000 -2001:

GRT funded research and development at UCSB jointly by GRT employees and UCSB scientists. Breakthrough technology invented for unique solid "cataloreactants". Eight U.S. patents (and appropriate foreign patents) issued to date.



2002-2003:

Process demonstrated and extended as a general chemical platform allowing the production of a variety of chemical intermediates. Established first of several research and development agreements with Fortune 500 companies for chemical and fuel process development.

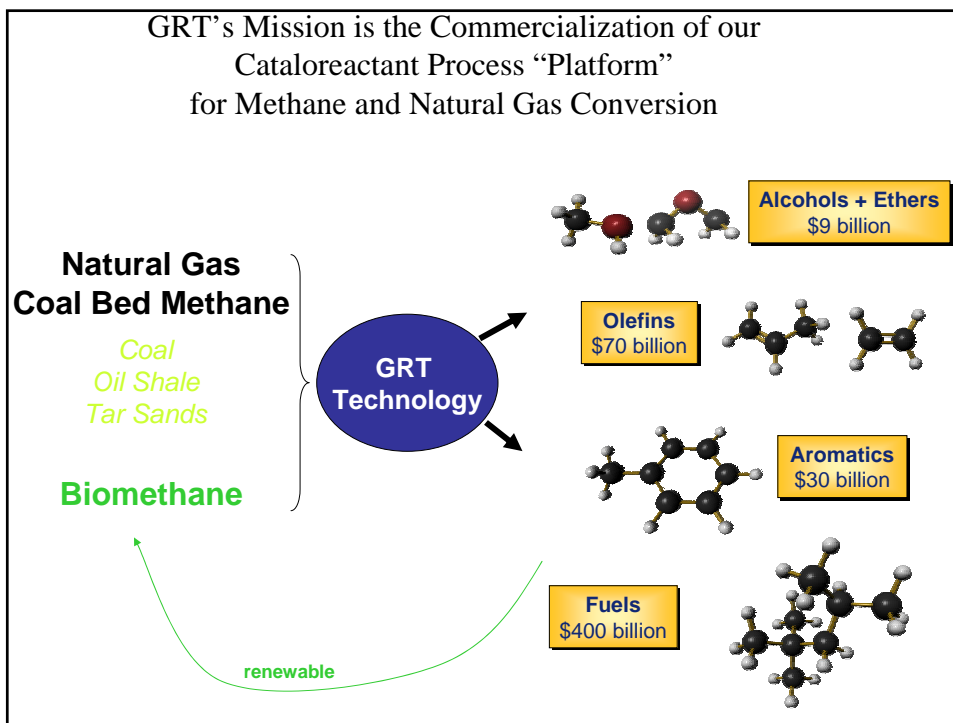
2004 -2006:

Established several additional strategic partnerships and joint chemical process development programs. Established state-of-the-art research facility in Santa Barbara. Operation of a one-gallon per day capacity reactor to produce liquid fuels, aromatics and chemicals. Entered into a long-term development agreement for natural gas conversion to liquid fuels and fuel feedstocks. First pilot plant to be constructed in 2007.

People Who Made/Make It Work

Jeff Sherman, Phil Grosso, Galen Stucky, Peter Ford,
Xiao Ping Zhou, Ivan Lorkovic, Aysen Yilmaz,
Eric McFarland, Gurkan Yilmaz, Leroy Laverman, Maria Noy,
Mike Weiss, Ian Cutler, Craig Belon, Walter Schenck,
Shouli Sun, Dieter Schaefer, Rudi Stuber, Sarah Cross,
Mike Doherty, Ashley Breed, Sigrid Kuebler, Brian Gergen,
Jean Wheeler, Zach Komon, Peter Stoimenov, Amin Sardar,
Brian Piorek, Sagar Gadewar, Sally Irving, Cheryl Hernandez,
Rick Hildebrand, Javin Oza, Suneetha Burla, Greg White,
Aihua Zhang

UCSB Students, Post Docs
Faculty



Change the Paradigm



IBM 370

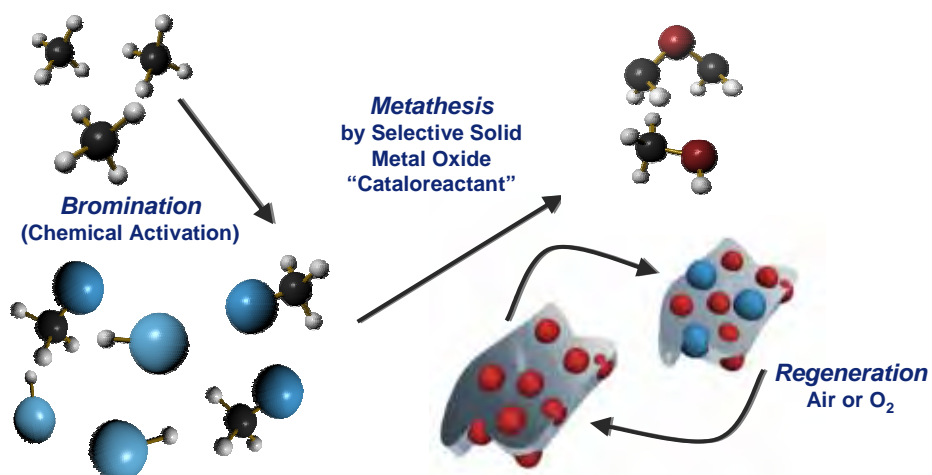
"Nobody will want a computer on their desk"



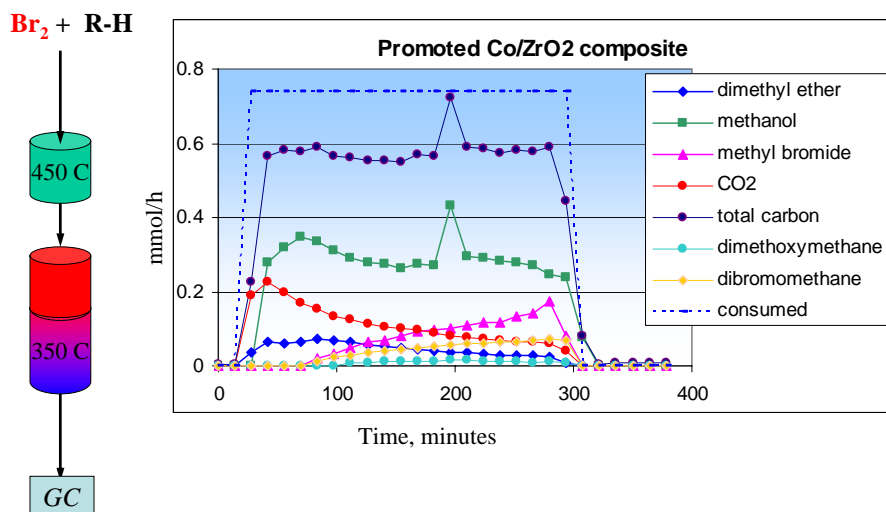
GTL Plants must exceed 100,000 bpd to be profitable
Cost ~ \$5+ Billion and take 10 years to build



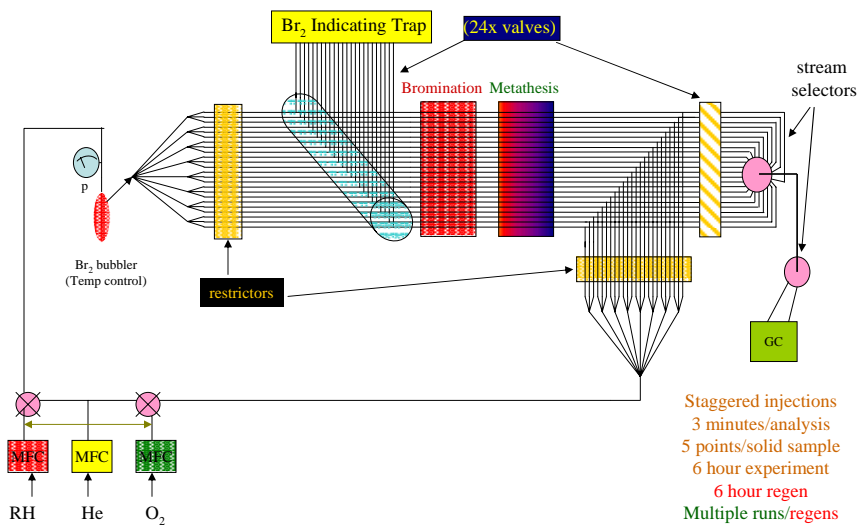
The Chemistry



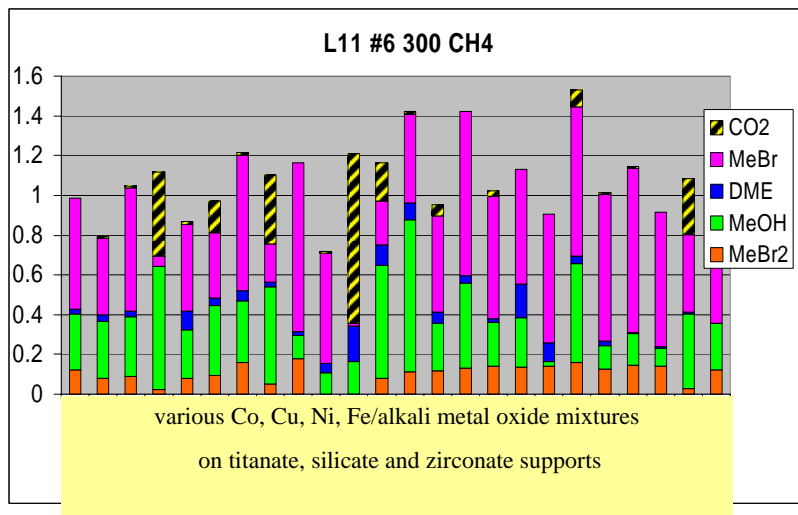
Time-integrated product output (GC): Methane



Schematic of high through-put reactor system for testing metathesis “cataloreactants”

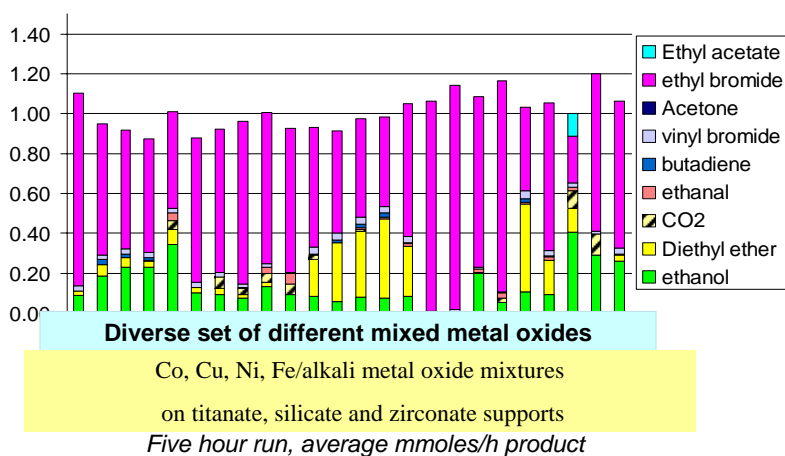


Methane Library 11 300° C



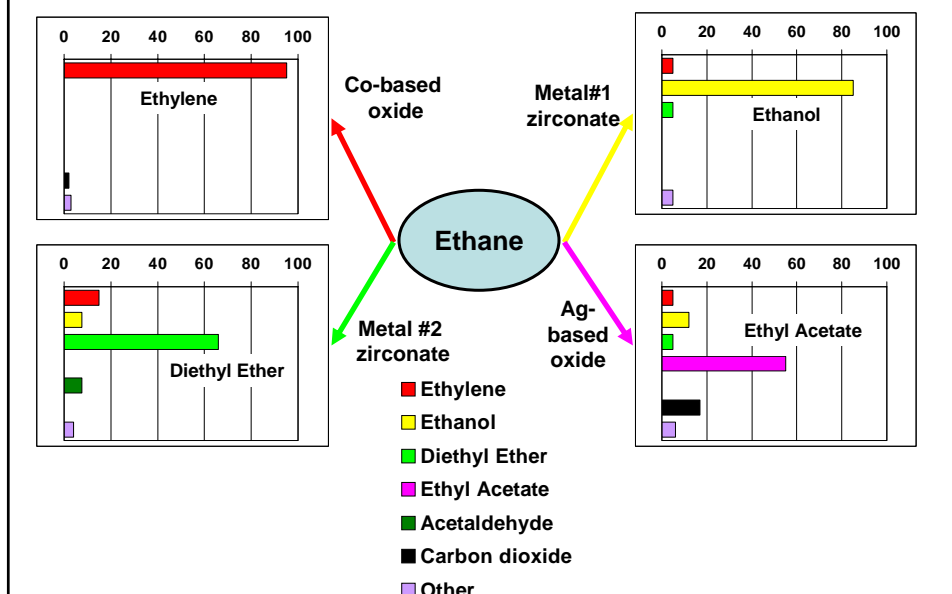
Parallel Reactors (ethane:Br₂) 10:1

Conditions/Materials - > Ethanol Formation

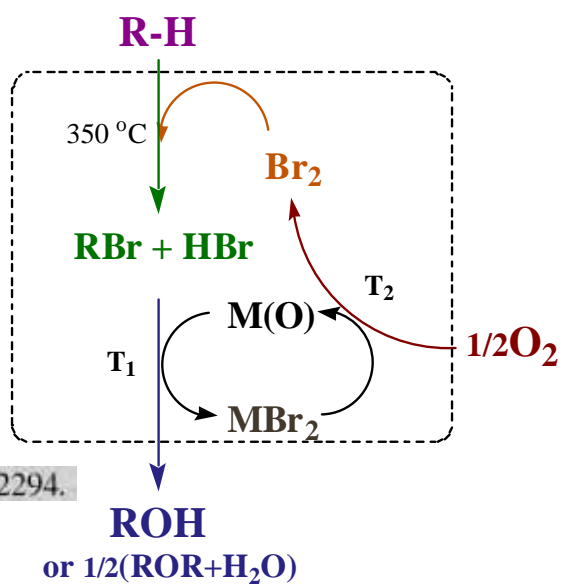


Cataloreactant "Platform": C2 Example

"change solid \rightarrow change products"



Platform Chemistry (example – alcohol)



Chem. Commun., 2003, 2294.

Methylhalide process may be analogous to MTO/MTG without the need for a Methanol Plant.

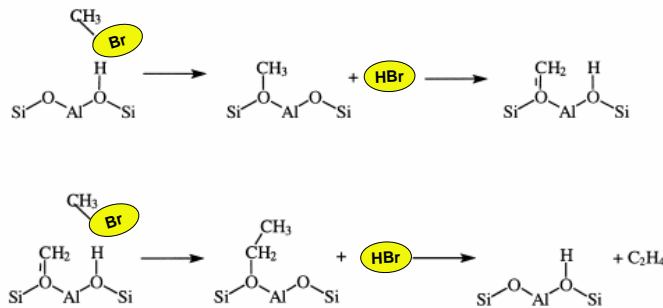
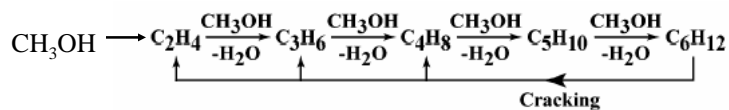


Fig. 1. Proposed reaction schemes leading to the first carbon-carbon bond formation in the conversion of methanol to hydrocarbons over zeolite catalysts. Top: the production of a surface bound ylide species (scheme I). Bottom: the reaction of the surface ylide with a second methanol molecule to produce ethene (scheme II).

G.J. Hutchings et al. / Microporous and Mesoporous Materials 29 (1999) 67–77

- C. E. Taylor using ZSM5 (DOE, 1980's)
 - CH₃Cl → (CH₂)_n + HCl Unable to economically recover Cl

Methylhalide process may be analogous to MTO/MTG without the need for a Methanol Plant.



Clarence Chang and Tony Silvestri, Mobil 1970's

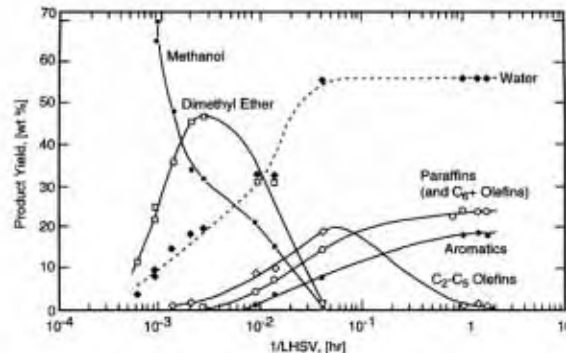
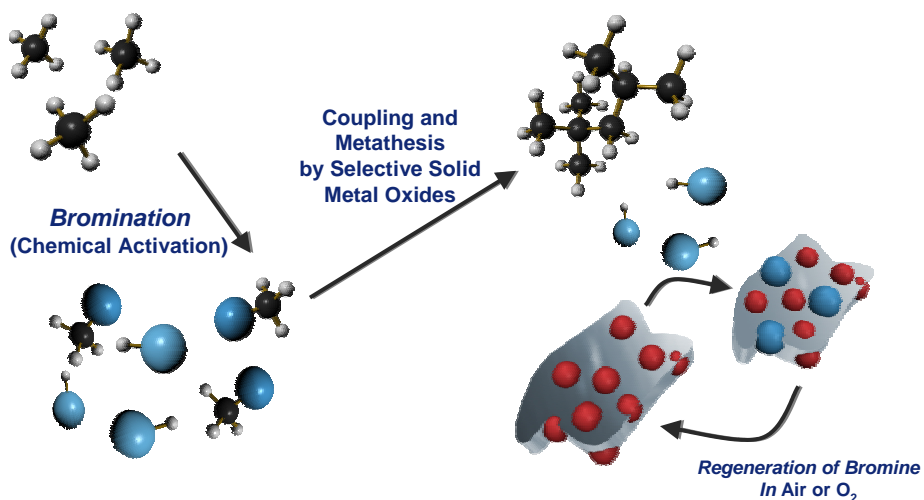


Fig. 2. Methanol-to-hydrocarbons reaction path (reproduced by permission of Elsevier Science B.V., Amsterdam).

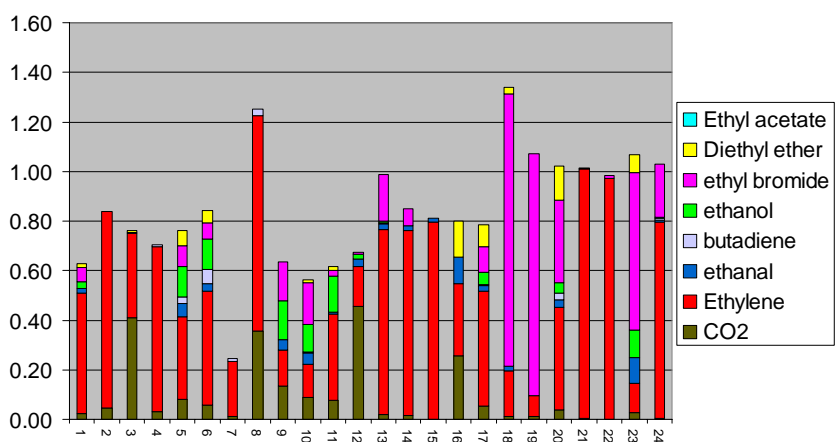
M. Stöckert / Microporous and Mesoporous Materials 29 (1999) 3–48

Solid Cataloreactant Coupling Chemistry

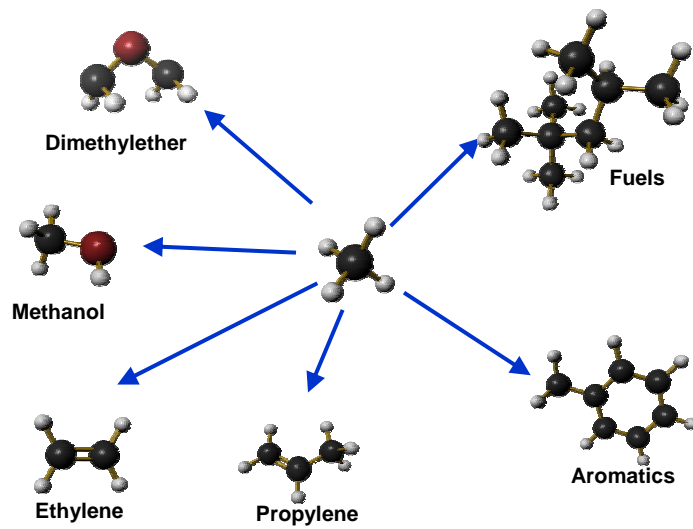


Parallel Reactors:(ethane:Br₂) 10:1

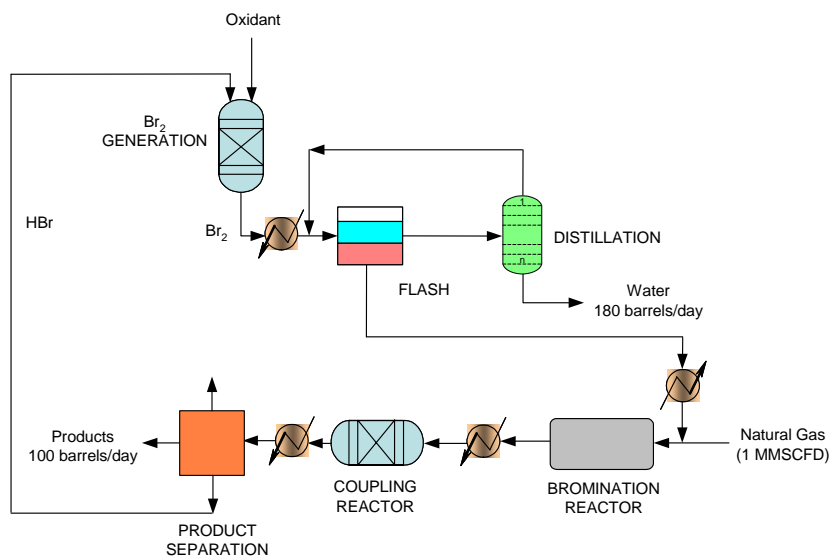
Conditions/Materials - > Ethylene Formation



Products from Methane



Semi-Continuous "Process"

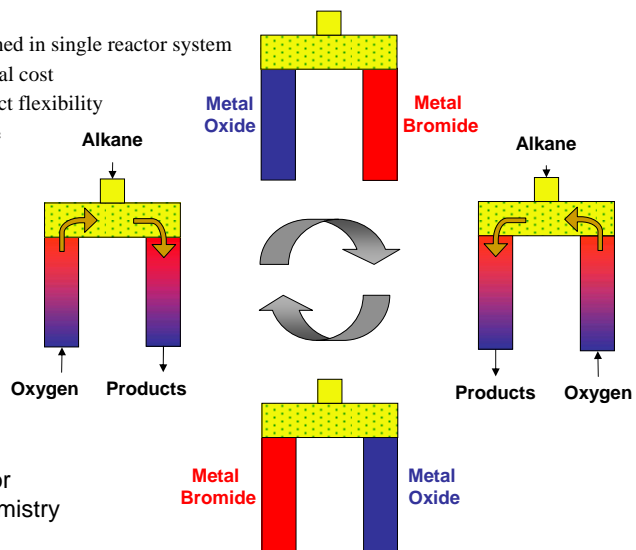


Cataloreactant Chemistry in the Zone Reactor

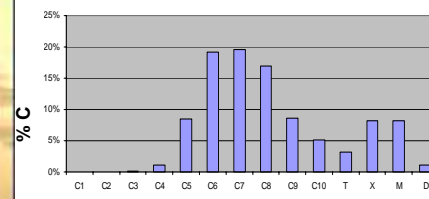
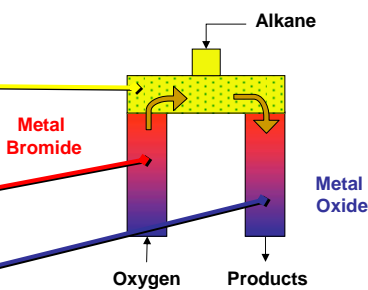
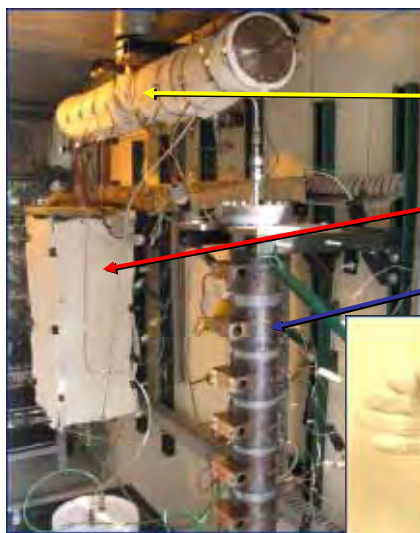
- Safety: Halogen contained in single reactor system
- Simplicity → Low capital cost
- Scalable feed and product flexibility
- Raw natural gas mixture



Uniquely suited for
the GRT process chemistry



Scale-Up



Summary

- Providing hydrocarbon conversion technologies for efficient utilization of natural gas is a major challenge for chemical engineering.
- As it was in the 1800's, methane is efficiently activated with heat, halogens, or platinum.
- By improving upon known technology, earlier utilization of natural gas for transportation fuels will allow preservation of oil for later generations to use for chemical products.
- A process chemistry platform based on a solid cataloreactant has been developed with the potential to convert any alkane feedstock to selective partial oxidation and coupling products including natural gas alkanes to fuels.
- Mechanistically the conversion of methane to methanol with a cataloreactant has similarities with the oxychlorination process, with the advantage that the product does not need to be separated from the haloacid.
- Direct conversion of methylhalides to olefins, aromatics, and fuels is analogous to methanol conversion to olefins (MTO) and gasoline (MTG) with the advantage of eliminating the methanol production step.
- Economics will, in the end, determine the success or failure of any chemical process.