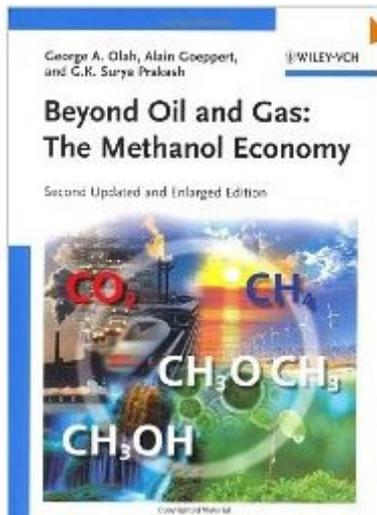


# Beyond Oil and Gas: The Methanol Economy



Authors : George A. Olah, Alain Goepfert, G. K. Surya Prakash

Beyond Oil and Gas: The Methanol Economy. *Angew. Chem. Int. Ed.* 2005, 44, 2636~2639.  
Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons. *J. Org. Chem.* 2009, 74, 487~498.



George Andrew Olah

Distinguished Professor of Chemistry and Chemical Engineering and Materials  
Science and Donald P. and Katherine B. Loker Chair in Organic Chemistry

George Andrew Olah was born in Budapest, Hungary in 1927. His research involves the generation and reactivity of carbocations via superacids. For this research, Olah was awarded a Nobel Prize in Chemistry in 1994. He has also been awarded the Priestley Medal, the highest honor granted by the American Chemical Society.

## Contents

### 1. What is the Methanol Economy?

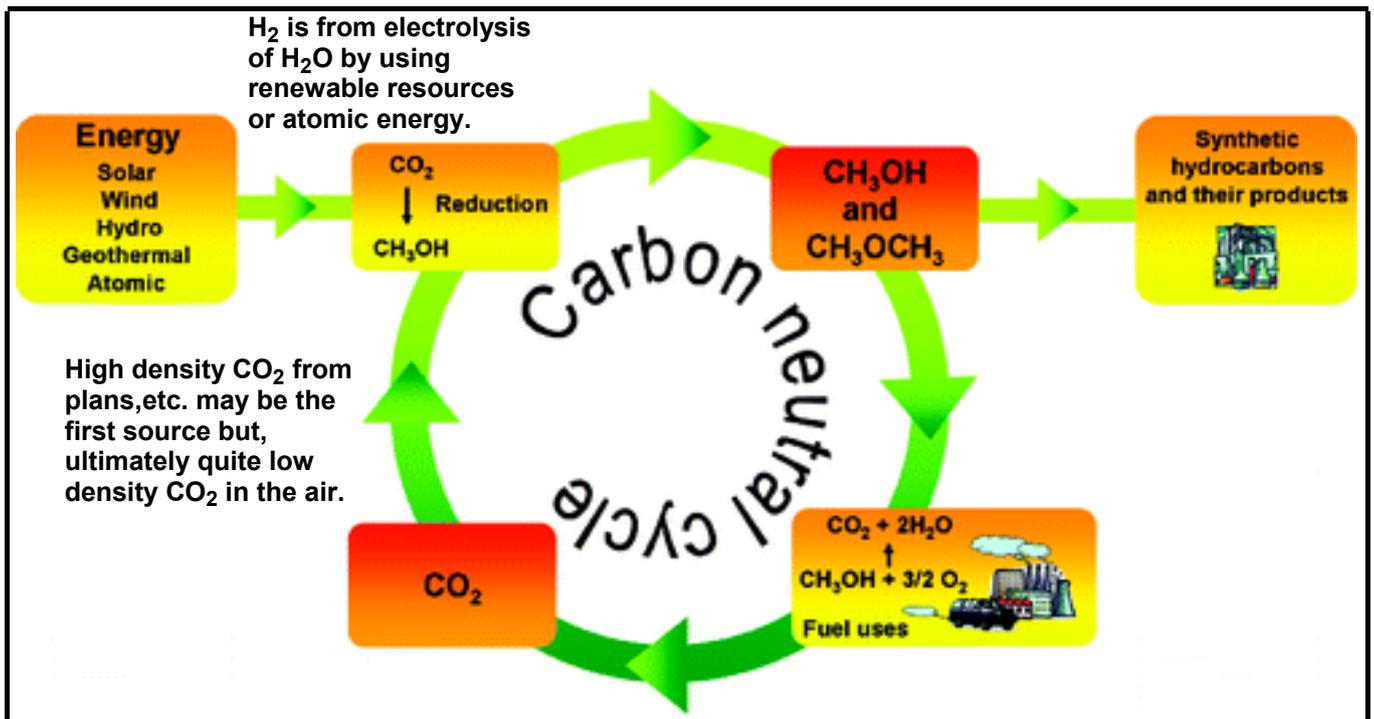
- 1.1 What is the Methanol Economy? (Overview)
- 1.2 Why We Must Think the Methanol Economy? (1-7)
  - 1.2.1 Diminishing Fossil Fuels
    - 1.2.1.1 Oil
    - 1.2.1.2 Natural Gas
    - 1.2.1.3 Coal
    - 1.2.1.4 Methane Hydrate
  - 1.2.2 Fossil Fuels and Climate Change
- 1.3 Why Methanol? (8-10)
  - 1.3.1 Renewable Energy Resources and Atomic Energy
    - 1.3.1.1 Renewable Energy
    - 1.3.1.2 Atomic Energy
  - 1.3.2 Why Not Hydrogen? (the Hydrogen Economy)
- 1.4 the Methanol Economy (11,13,14)
  - 1.4.1 Methanol and DME
  - 1.4.2 Methanol as a Fuel
  - 1.4.3 Direct Methanol Fuel Cell (DMFC)
  - 1.4.4 Methanol-Based Chemicals

### 2. How to make methanol (12)

- 2.1 Methanol via Syn-Gas
  - 2.1.1 Syn-Gas to Methanol
  - 2.1.2 Fossil Fuels (Methane) to Syn-Gas
- 2.2 Methanol without Syn-Gas
  - 2.2.1 Direct Oxidation of Methane
  - 2.2.2 Catalytic Gas-Phase Oxidation of Methane
  - 2.2.3 Catalytic Liquid-Phase Oxidation of Methane
  - 2.2.4 Methane into Methanol Conversion through Monohalogenated Methanes
  - 2.2.5 Methanol from Methane by Enzyme
- 2.3 Chemical Recycling of Carbon Dioxide to Methanol
  - 2.3.1 Methanol Production using Carbon Dioxide as a Carbon Source
  - 2.3.2 Carbon Dioxide Capturing Methods

# 1. What is the Methanol Economy?

## 1.1 What is the Methanol Economy? (Overview)

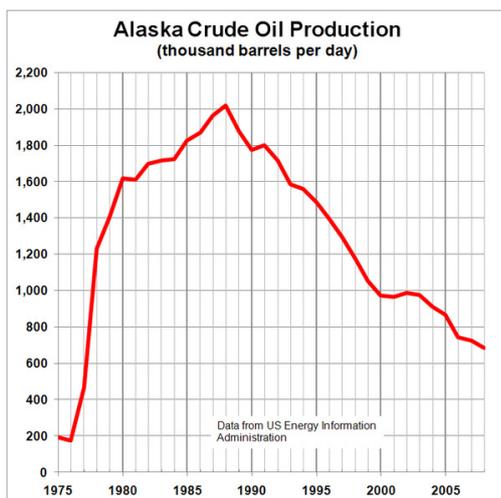


Problems must be solved

- the efficient way to capture CO<sub>2</sub> (Chemistry)
- the efficient way to make methanol (Chemistry)
- Adapting the society to the Methanol Economy from the conventional fossil fuel economy (Technology, Politics, Economy, etc...)

## 1.2 Why We Must Think the Methanol Economy?

### 1.2.1 Diminishing Fossil Fuels



Hubbert peak theory

Of the largest 21 fields, at least 9 are in decline. In April, 2006, a Saudi Aramco spokesman admitted that its mature fields are now declining at a rate of 8% per year (with a national composite decline of about 2%). This information has been used to argue that Ghawar, which is the largest oil field in the world and responsible for approximately half of Saudi Arabia's oil production over the last 50 years, has peaked.

The world's second largest oil field, the Burgan field in Kuwait, entered decline in November 2005. According to a study of the largest 811 oilfields conducted in early 2008 by Cambridge Energy Research Associates, the average rate of field decline is 4.5% per year. The IEA stated in November 2008 that an analysis of 800 oilfields showed the decline in oil production to be 6.7% a year, and that this would grow to 8.6% in 2030.

[wikipedia : Peak Oil]

- The Proved Oil Reserves in 2009 was 1333.1 Thousand Million barrels. The Oil Consumption in 2009 was 84076.8 Thousand barrels daily. So, we are left 43.44 years!!!

[From : BP Statistical Review of World Energy June 2010]

- In the case of gas, 187.49 Trillion m<sup>3</sup> was proved reserves in 2009, the consumption was 2940.4 Billion m<sup>3</sup>. So, we left 63.76 years!

- Some researchers insist that the oil production in the world experience its peak **between 2005 - 2015**, supposing that the 90% of easily recoverable oil has been almost found (this suppose is based on the assumption that 3/4 of oil reserves in the world exists in about 370 oil fields, which were completely investigated and that the peak of mining new fields have already passed in 1960's).

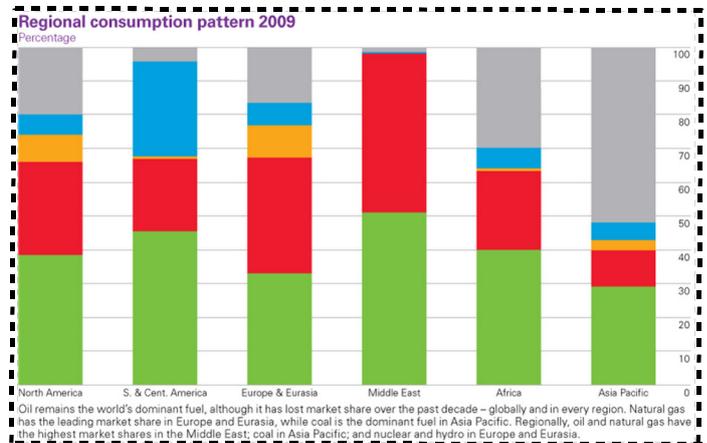
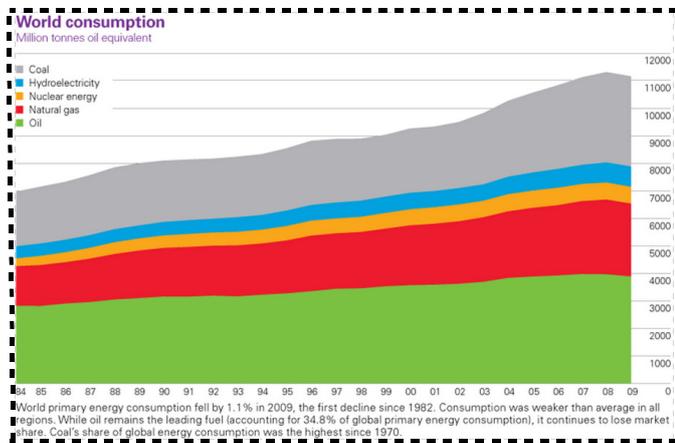
- \* Oil reserves are the quantities of crude oil estimated to be commercially and technically feasible to mine.
- \* There are other fossil fuels except oil such as gas, coal, etc...
- \* So, these data don't simply indicate the end of fossil fuels.

**It is not without saying that Oil is the most important resources.**

(and, gas is next)

**Why are fossil fuels so important?**

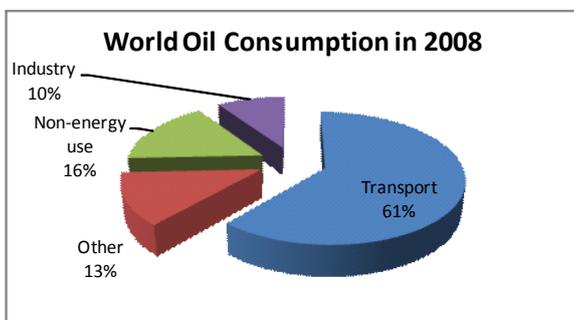
[From : BP Statistical Review of World Energy June 2010]



**Fossil fuels have accounted for more than 90% of primary energy since long before!**

(Primary energy is energy found in nature that has not been subjected to any conversion or transformation process. i.e. Solar energy, Wind power, Fossil fuels, Hydro power, Nuclear fuels (Some nuclear fuels, such as plutonium are not found in nature in any quantity, thus are secondary energy sources), Geothermal power, Tidal power, Wave power, Biomass etc...)

**1.2.1.1 Oil**



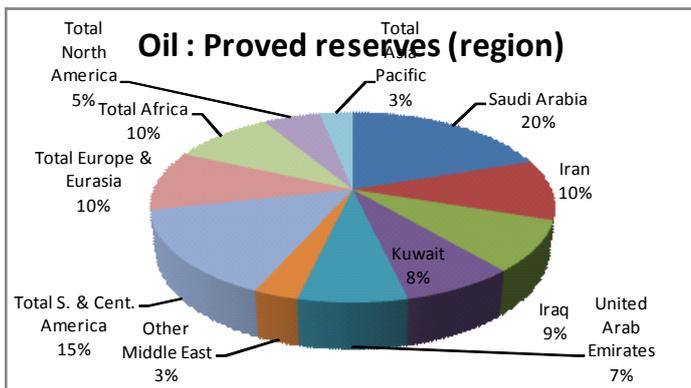
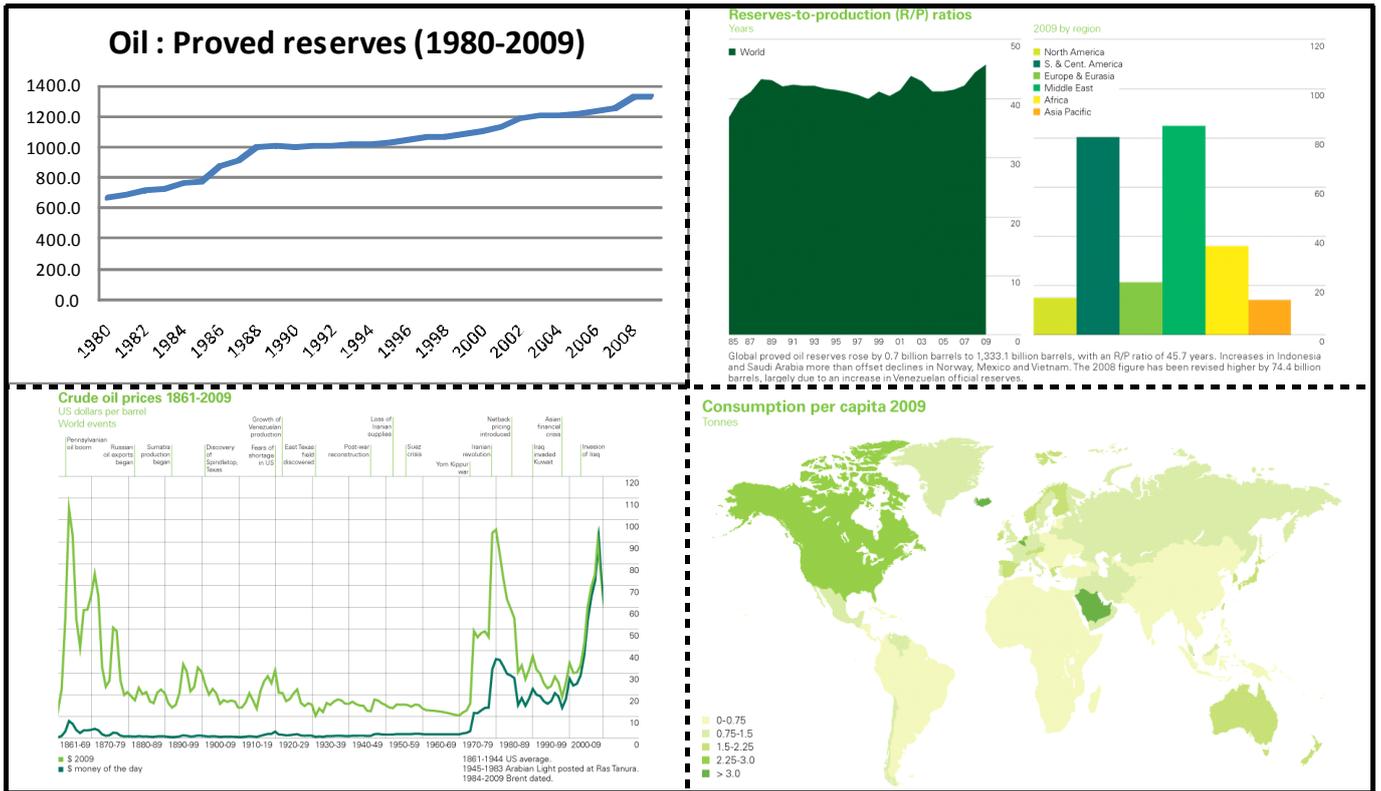
\*Other : Includes agriculture, commercial and public services, residential, and non-specified other.

[From : Key World Energy Statistics 2010]

- Oil is mainly composed of various kinds of hydrocarbons, including alkanes, alkenes, cycloalkanes, Aromatic hydrocarbons.
- Oil is used for various kinds of petrochemical products, but this accounts for only approximately 6% of the oil consumption.
- Main usages of oil are heating, electronic power, industry, and overwhelmingly transportation(60%).
- In fact, 95% of fuel used in the transportation sections all over the world is from oil.



Although alternative resources (gas, renewable sources, etc) are started to be used among power plants or industries, there aren't any prospect of replacement in the case of transportation.



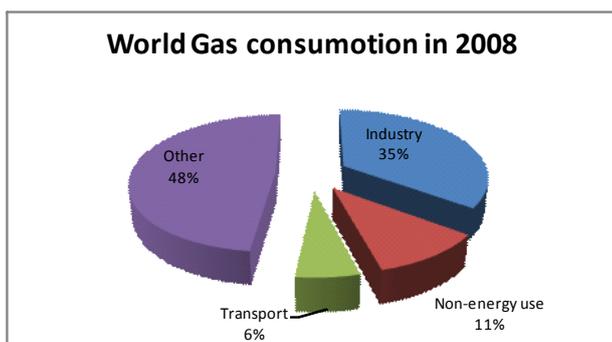
- The oil reserve has doubled in the last 30 years, and R/P ratio hasn't changed much for 25 years.
- However, the future demand and prices is (no matter how modestly I say) uncertain. (Surely the demand will swell, and prices won't see its ceiling.)
- What's more, the oil distribution lacks balance.

### Unconventional Oil Resources

- Tar Sand : "dead" oil field
- Oil Shale : "pre-born" oil field

It is said that these resources are the same order or some more than conventional oil respectively.

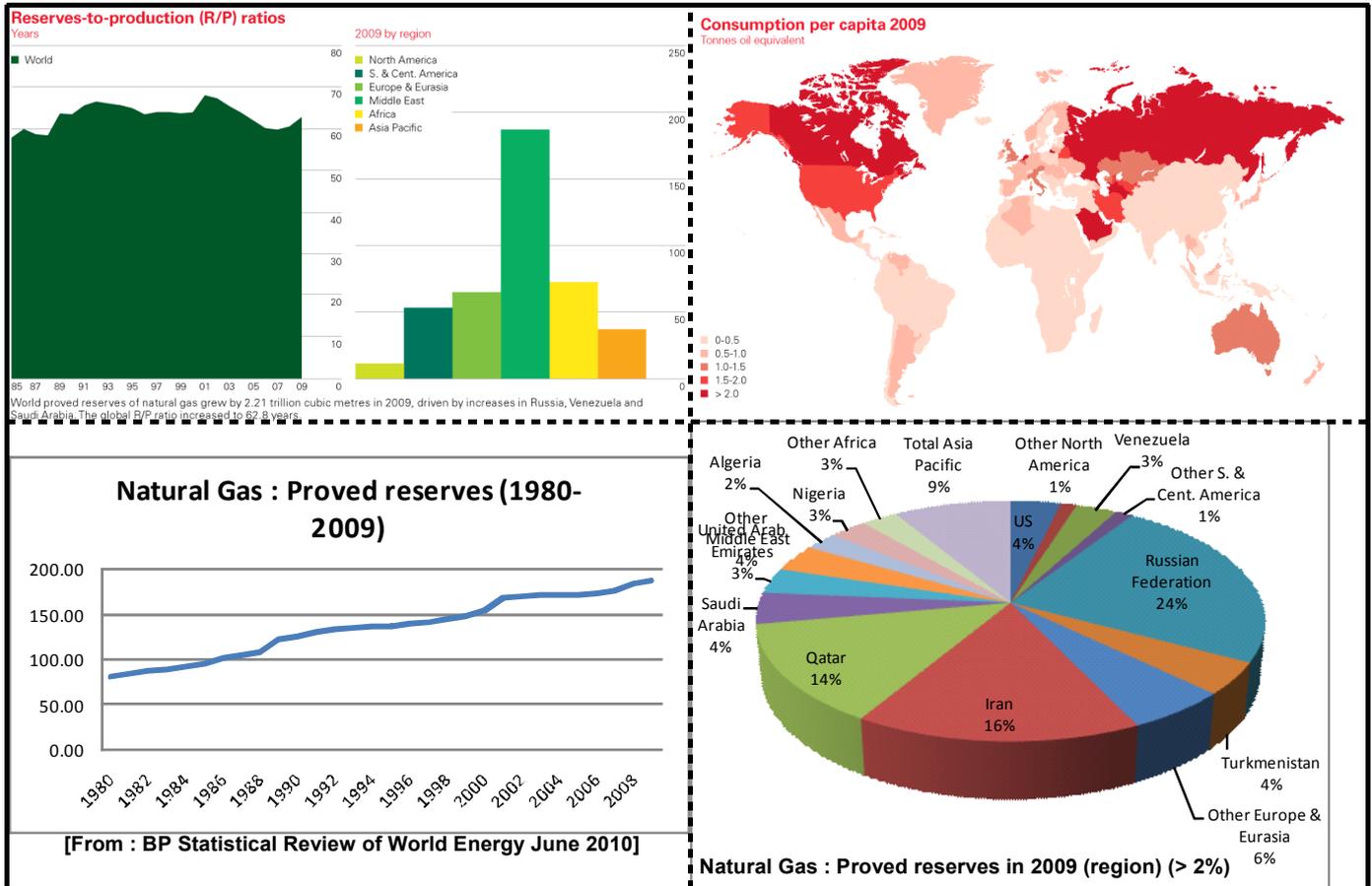
### 1.2.1.2 Natural Gas



- More than 95% of Natural gas is composed of methane and ethane (in many cases methane composes more than 90%).
- Natural gas burns very cleanly, and is easy to use. → suitable fuel for domestic use
- Natural gas emits the least amount of CO<sub>2</sub> among all fossil fuels, and the number of plants using natural gas to make electricity is getting bigger.

\*Other : Includes agriculture, commercial and public services, residential, and non-specified other.

[From : Key World Energy Statistics 2010]



- Although natural gas emits only the little amount of CO<sub>2</sub> per energy (this is because the hydrogen/carbon ratio of methane is 4, which is the largest among all hydrocarbons.), methane itself has much stronger (about 23 times) warming effect than CO<sub>2</sub>.

- Things seem better than oil (R/P ratio is 20 years more), but, the distribution completely loses balance.

**The top has 24% of the world reserves and 54% of world's Natural Gas is in top 3!!!**

- The biggest problem is methane is GAS under standard condition.

Gas is transported to consuming place from producing place.

In the case that pipeline is out of choice (due to the distance, etc.), gas must be converted into liquid.



There are two choice; 1) one is liquid methane (LNG)  
2) the other is synthetic hydrocarbon

1) Liquefaction of methane (bp : -162°C) is quite complicated, expensive and energy-consuming process, and gigantic LNG tanker can cause disasters.

It is said that the explosion of one LNG tanker gives devastating damage within 500m radius and second degree burn within 2km radius.

Japan, Korea and Chinese Taipei import more than 60% of LNG!!!

2) Methane is first converted into Syn-Gas (synthesis gas), the mixture of H<sub>2</sub> and CO, and then this syngas is converted into various hydrocarbons including methanol (vide infra).

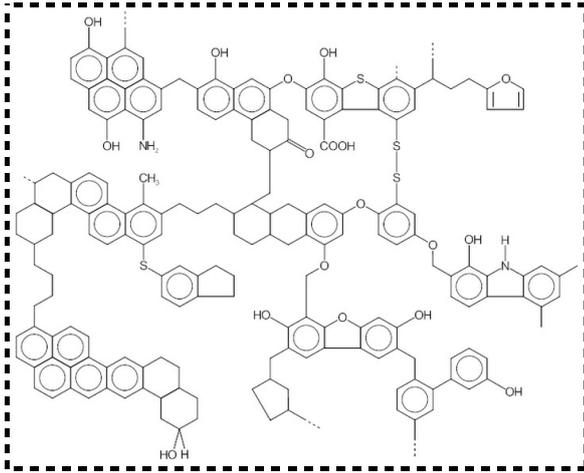
But, this Gas to Liquid process also have many problems, especially during this process, 45% of crude gas is consumed.

## Unconventional Natural Gas Resources

- Coalbed Methane : methane adsorbed into the solid matrix of the coal under high pressure
- Tight Sands and Shales : methane adsorbed into the solid matrix of tight sands

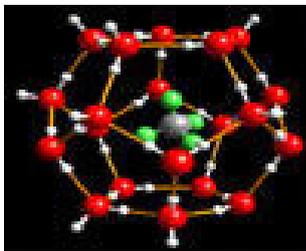
It is said that the same order or some more than conventional natural gas is exist in coalbed methane. However, the real reserves are still unclear.

### 1.2.1.3 Coal

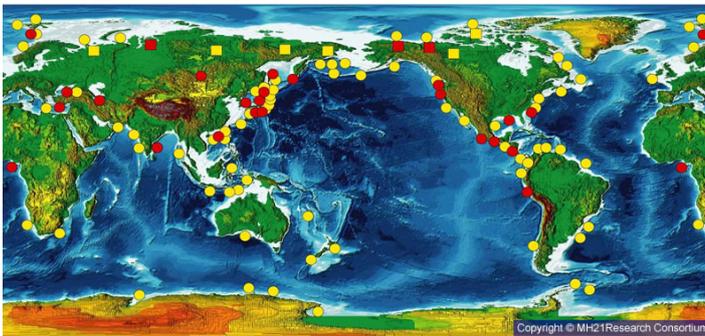


- R/P ratio of coal is more than 150 years, and at least it is said that coal can be used at least for two centuries. (the reason why R/P ratio is less than expected is that there are not any incentive for developing new mines. For example, Chinese, 45.6% of all coal was consumed in China in 2009, ratio was only 38 in 2009.)
- The reason why we can't rely on coal much is that coal is "dirty" compared with oil and gas. Burning coal emits quite large quantity of polluting substances without any care such as NO<sub>x</sub>, SO<sub>x</sub>, dust particles and heavy metals like Hg, Pb, As, U, etc. But, the most important pollution is CO<sub>2</sub>.
- Now, things are being improved.

### 1.2.1.4 Methane Hydrate

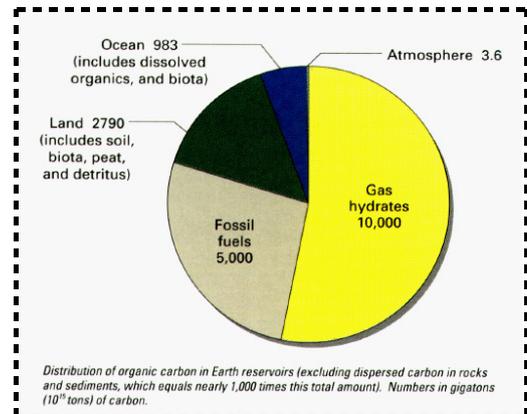


- Methane hydrate is a solid clathrate compound in which a large amount of methane is trapped within a crystal structure of water, forming a solid similar to ice.
- It is difficult to develop this resource with the present technology, and how much gas hydrate exists all over the world is quite controversial.
- But, one of the achieved consensus is that is huge. (see below)
- Anyway, gas hydrate is still unrealistic resource.



● 海域・湖沼域      ● ガスハイドレート試料採取地点  
 ■ 陸域 (永久凍土域)      ■ ガスハイドレート推定分布域

[From : National Institute of Advanced Industrial Science and Technology]



*Distribution of organic carbon in Earth reservoirs (excluding dispersed carbon in rocks and sediments, which equals nearly 1,000 times this total amount). Numbers in gigatons (10<sup>9</sup> tons) of carbon.*

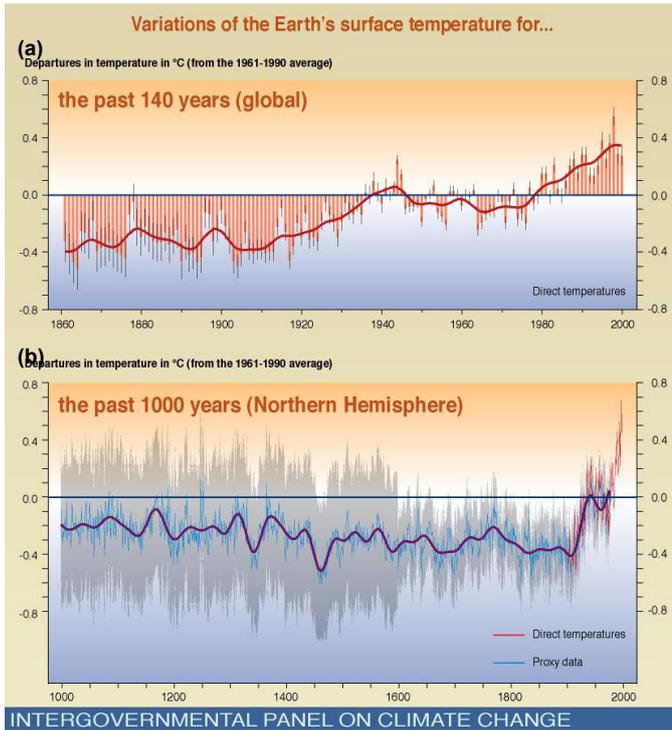
[From : U.S. Geological Survey]

### Summary of Fossil Fuels

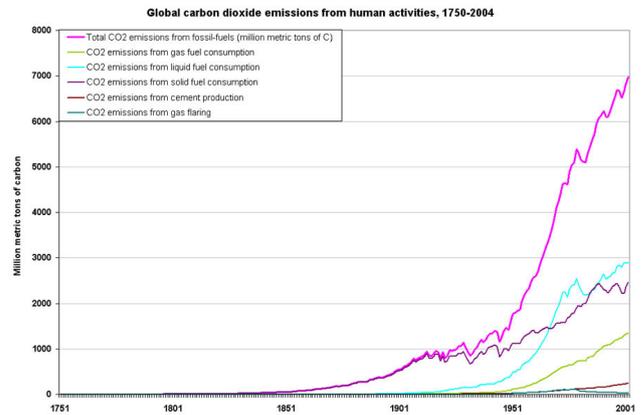
- It is indispensable for useful oil and gas to dry up near future.
- If so, there will be some substitutes such as coal, methane hydrate, etc. However, these resource must take more economical and ecological cost.
- So, we must seek other useful and environmental-friendly fuels.

( suggestive paper about "the future of coal"  
 The end of cheap coal. R. Heinberg; D. Fridley, *Nature* 2010, vol.468, 367~340. )

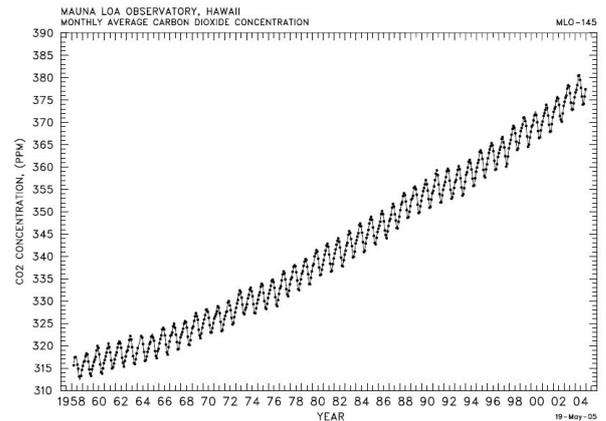
## 1.2.2 Fossil Fuels and Climate Change



[From : (a) IPCC, Fourth Assessment Report, *Climate Change 2007 : The Physical Scientific Basis* (b) IPCC, Third Assessment Report, *Climate Change 2001 : The Scientific Basis* ]



[From : Marland, G., T.A. Boden, and R. J. Andres. 2005. *Global, Regional, and National CO<sub>2</sub> Emissions*. In *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A.]



[From : C.D. Keeling, T.P. Whorf, and the Carbon Dioxide Research Group at the Scripps Institution of Oceanography (SIO), University of California, La Jolla, California USA 92093]

- It is definitely certain that Atmospheric CO<sub>2</sub> concentrations has increased by human activity. And, it is strongly suggested that the cause of these 140 years' increasing temperature is due to human activity.
- As long as we live in present fossil fuel economy, we must continue to upset the balance of global carbon cycle.
- The storage of CO<sub>2</sub> is only the temporary and risky solution.
- However, the prohibition of carbon is unrealistic.

## 1.3 Why Methanol?

### 1.3.1 Renewable Energy Resources and Atomic Energy

#### 1.3.1.1 Renewable Energy Resources

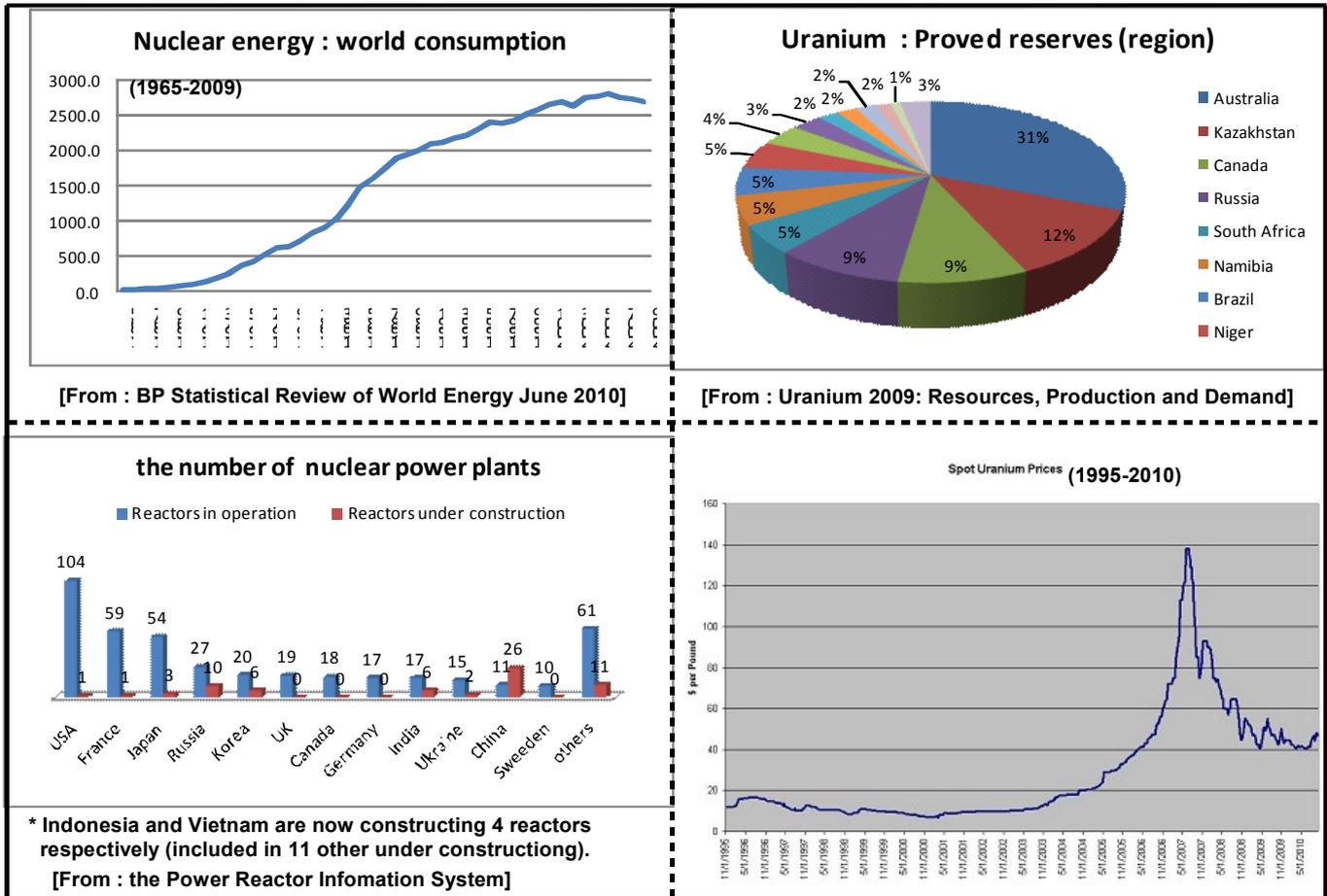
- There are many renewable energy resources such as Hydropower, Geothermal energy, Wind energy, Solar energy (Photovoltaic or Thermal), Bioenergy, Ocean energy (Tidal, Wave and Thermal power).
- These sources are superior to fossil fuels in terms of CO<sub>2</sub> emission, but this fact does not necessarily mean that these are environmentally-friendly energy sources.
- Each source is obtained from only limited areas all over the world, so able to meet only the partial of present electronic demands.  
In other word, individual resources will never substitute fossil fuels.  
(However, we must seek the way to use these resources collaborately.)
- The biggest problems of renewable energies are
  - (1) Energy except from bioenergy cannot be reserved, so some carriers are needed to transport.
  - (2) These energies cannot meet demands for hydrocarbon products directly.



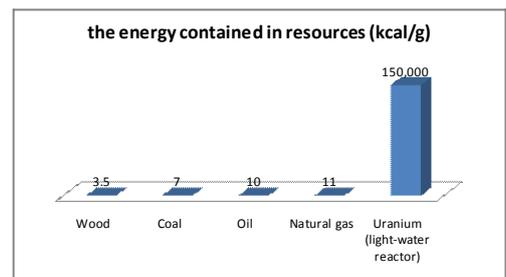
**Methanol will be able to solve these problems!!! (vide infra)**

### 1.3.1.2 Atomic Energy

#### Nuclear fission

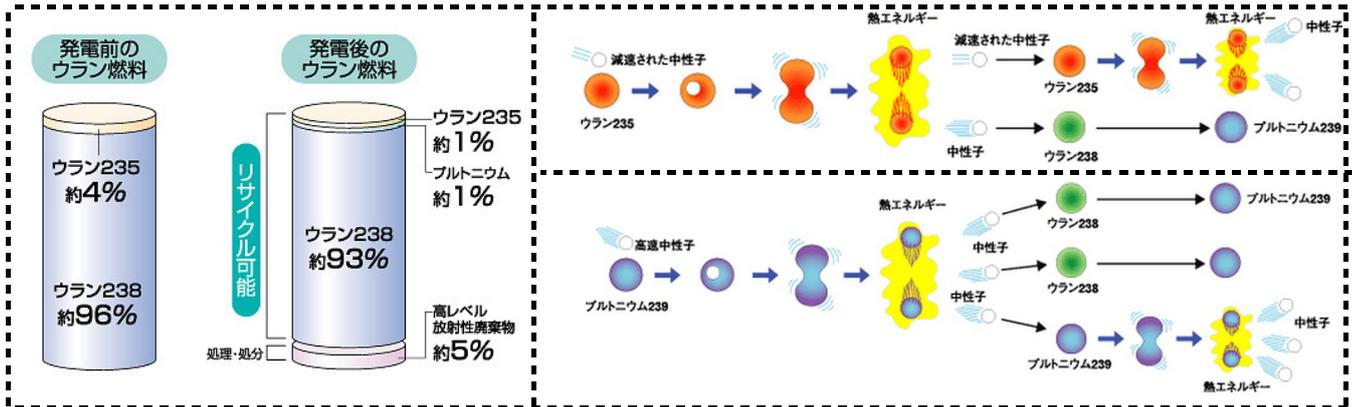


- The growth rate of nuclear energy consumption has rapidly slowed down due to the fear for the safety of nuclear power among developed countries in recent years, but being rethought in terms of CO<sub>2</sub> emission these days.  
And, new reactors are energetically being constructed among developing countries.
- Uranium price, which is stable before, is rising rapidly. However, the price of uranium is tiny cost of all.
- According to IAEA's 2009 data, R/P ratio of uranium was about 85, and it is probable that the reserve swells 6 times! Moreover, by adopting fast reactor technology, this period would be lengthen to over 2500 years!! (vide infra)
- The safety of nuclear power plants has been reinforced to incredible level thanks to the anti-nuclear movement. In the case of radiation, people living in the stone, brick or concrete house are exposed to more radiation than people living in the nuclear power plants' sites. In fact, nuclear power plant emits less radiation than coal thermal power plant (the cinder of coal includes uranium and thorium).
- What's important is that consumer nuclear reactors are never able to explode like nuclear bomb. (vide infra)
- By reprocessing nuclear fuel and adopting Fast Breeder Reactor, the problem of nuclear wastes will partially solved.



**The problems with nuclear energy are highly ethical, social and political ones!**

**(Nuclear reprocessing and Fast Breeder Reactor)**



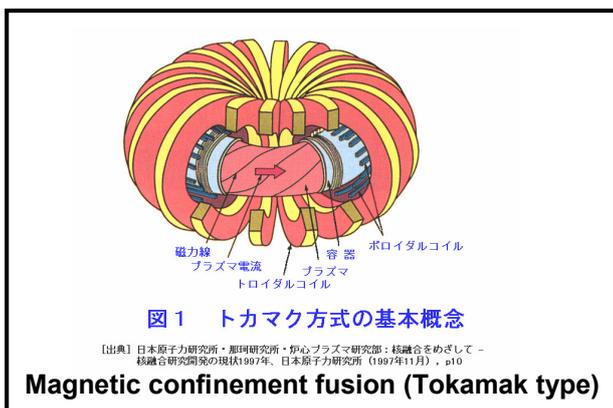
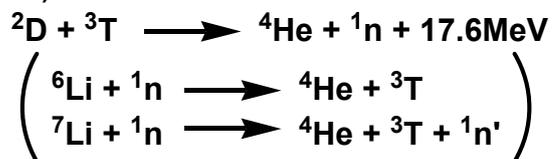
- The actual fuel of conventional (light-water, one through) reactor is fissile  $^{235}\text{U}$ . One through means the fuel is used only once. In other words,  $^{238}\text{U}$ , composing the most part of fuel, is discarded without any use. (The reason why consumer nuclear reactors are never able to explode like nuclear bomb is that in the case of bomb,  $^{235}\text{U}$  must be concentrated to at least 90%, and this fuel is used in device specially designed for bomb.)
- However,  $^{238}\text{U}$  is converted into  $^{239}\text{Pu}$ , the more fissile isotope, with fast neutron.
- Nuclear reprocessing is the process to separate useful isotope, especially the remaining uranium and the newly-created plutonium, from the fission products and other radioactive waste.
- The Fast Breeder Reactor is a fast neutron reactor designed to produce more  $^{239}\text{Pu}$  than consumed (therefore, called *breeder*).
- It is said that if we adopted this technology, we could extend the uranium reserve to double figures. But, one of the biggest problems of the Fast Breeder Reactor is the treatment of  $^{239}\text{Pu}$ . The half-life of  $^{239}\text{Pu}$  is  $2.411 \times 10^4$  y (in this connection,  $^{235}\text{U}$  is  $7.038 \times 10^8$  y, and  $^{238}\text{U}$  is  $4.468 \times 10^9$  y.) This means  $^{239}\text{Pu}$  is much much more radioactive and toxic (the threat of terrorism).
- We must discuss the risk and benefit of nuclear energy, and make decision based on accurate scientific knowledge.

**"No oil, No gas, No coal, No choice."**

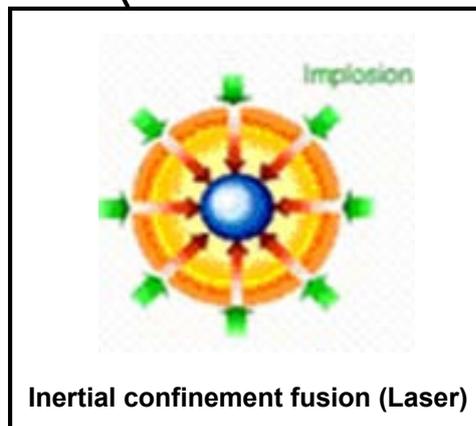
by Claude Mandil, the French General Director for Energy and Raw Materials at the Ministry of Industry

**Nuclear fusion (the technology of a few decades later forever)**

- There are two ways for achieving nuclear fusion.
  - (1) Magnetic confinement fusion
  - (2) Inertial confinement fusion



**Magnetic confinement fusion (Tokamak type)**



**Inertial confinement fusion (Laser)**

- The main stream of nuclear fusion today is Tokamak type.

- Thinking of many aspects (environmentally effects, the distribution of resources, the safty, etc...), it is not without saying that nuclear fusion is the best.
- And, the dream of making "artificial sun" is certainly coming.
- However, ITER - a multi-billion-euro international(EU, Japan, South Korea, Russia, India, China, United States) experiment boldly aiming to prove atomic fusion as a power source - is being faced ballooning costs and growing delays.

( about the difficulties ITER has faced, see:

Fusion reactor faces cost hike. G. Brumfiel, *Nature* 2008, 453, 829.

Fusion dreams delayed. G. Brumfiel, *Nature* 2009, 459, 488~489.

Fusion delays sow concern. G. Brumfiel, *Nature* 2009, 461, 855.

Delays prompt reshuffle at ITER fusion project. G. Brumfiel, *Nature* 2010, 463, 721.

- We cannot rely on nuclear fusion yet.

### Summary of Renewable Resources and Atomic Energy

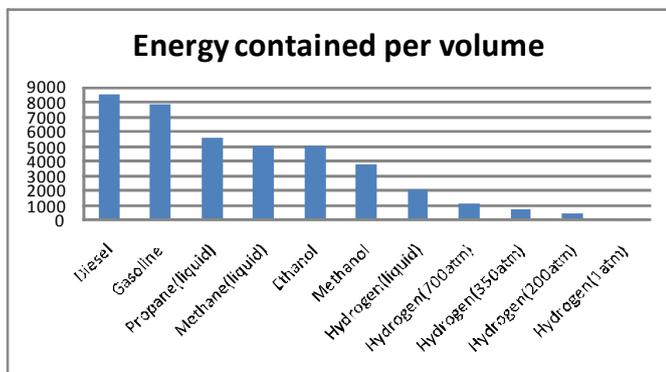
- In the future, we cannot help relying on the nuclear energy with renewable resources complimenting.
- If so, however, the problems of energy carriers and the alternative source of hydrocarbon products will be still unsolved.
- So, we must seek other useful and environmental-friendly energy carriers.

### 1.3.2 Why Not Hydrogen? (the Hydrogen Economy)

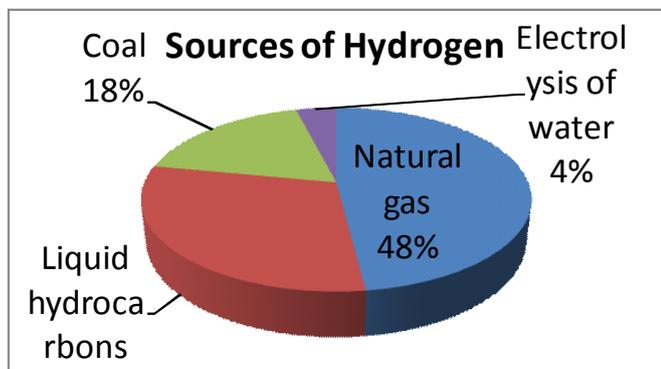
Are the hydrogen fuel cells the genome of pharmaceutical industry?

( about the H<sub>2</sub> economy, especially the problems of Storage and Delivery of H<sub>2</sub>, see Mr. Saga's lit. seminar (07/07/10) )

- Hydrogen doesn't exist as H<sub>2</sub> gas in the Earth. H<sub>2</sub> is merely a energy carrier.

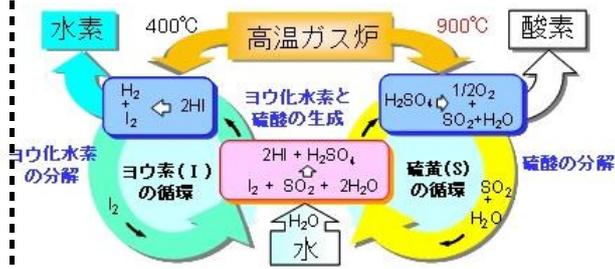


- The energies contained in hydrogen (liquid or high pressure) per volume are less than conventional fuels or some liquid organic solvents.
- In fact, 10-15% of hydrogen energy is lost during the process of compression, and 30-40% during liquefaction (b.p. of H<sub>2</sub> is -252.9°C).
- Small hydrogen gas easily diffuses through almost all materials, therefore deteriorates materials, especially under high pressure and high temperature.
- H<sub>2</sub> is produced almost all from fossile fuels (96%). (actual procedure of making H<sub>2</sub>, vide infa)
- Electrolysis of H<sub>2</sub>O costs 3-4 times more than from fossil fuels.
- H<sub>2</sub> gas is important for the Methanol Economy, and ultimately H<sub>2</sub> must be produced from electrolysis of H<sub>2</sub>O with electricity from renewable or nuclear energy in terms of carbon neutral cycle.
- Innovation of this field is strongly desired.



(Interesting examples of making H<sub>2</sub> from H<sub>2</sub>O)

(1) Iodine-Sulfur Thermochemical Cycle



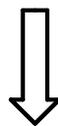
- The pyrolysis of H<sub>2</sub>O occurs at around 2000°C. But, by utilizing thermochemical cycle effectively, this reaction occurs efficiently at around 1000°C.
- This cycle is composed of three steps.
  - Bunsen Reaction and decomposition of HI and H<sub>2</sub>SO<sub>4</sub>
- ( Bunsen reaction :  $I_2 + SO_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$  )
- This cycle is expected to be achieved with solar thermal energy or high-temperature future generation nuclear fission reactor.

(2) Photocatalyst using TiO<sub>2</sub> (details see, Mr. Itano's lit. seminar (09/10/05))

- The Hydrogen Economy must solve many social, economical or political problems as well as technical ones.
  - Conventional infrastructures for oil, natural gas, etc. can't be used for hydrogen.
  - In other words, for the realization of the hydrogen economy, we must construct infrastructures from the beginning.
  - At that time, the hydrogen economy will suffer from a chicken-and-egg headache.
  - Without enough infrastructure, there will be no demand for hydrogen.
  - Without enough demands, there will be no incentive for investing.
  - (Without enough hydrogen stations, who bought hydrogen cars?
  - And, without enough demands for hydrogen, who built hydrogen station?)
  - As the similar problem, how do we change over the fossil fuel economy to the hydrogen economy?
  - Present Japanese or American fire defense law prohibits putting hydrogen refueling equipment in gas stations (transition period problem).
  - In other words, stations must be run as either gas station or hydrogen station.
  - (The "merest TV" requires the most careful preparation.)
  - How about the problems of hydrogen usage by the public without any special scientific knowledge, usually even the specialist with large knowledge deal with the gas with great care?
- The Hydrogen economy promoting parties may emphasis on the superiority of fuel cell to Internal-combustion engine.
  - Authors basically agree to that idea, and say that in terms of thermodynamic-energy efficiency, engine will be taken place by fuel cell (But, authors also emphasis on the engine development during last 100 years, which fuel cell didn't experience).
  - But, is it necessary for hydrogen to be transported from hydrogen plants to consumer?
  - (Is it better to produce hydrogen in the lower stage, for example at hydrogen station or ultimately on vehicles?)
  - Moreover, is it inevitable for fuel cell to use hydrogen other than another energy carrier?

In the view of the quite difficult situation of hydrogen usage as fuel, Energy Secretary Steven Chu announced that the Department of Energy was putting the breaks on research into automotive hydrogen fuel cells, and cut budgets in May 2009.

Hydrogen Cars : Fad or the Future? *science* 2009, 324, 1257~1259.



From 1.2 and 1.3, we must think about

- (1) The energy carrier easily and safely usable by the public, which must be applicable to conventional infrastructures
- (2) The way to meet demands for hydrocarbon products after the age of fossil fuels
- (3) Increasing the concentration of CO<sub>2</sub> in the atmosphere, which will harm our human beings.

Liquid hydrocarbon, easily obtained from CO<sub>2</sub> and converted to other hydrocarbons!!!

## 1.4 The Methanol Economy

- Authors advocate that we should use methanol as substitution of oil and dimethyl ether (DME) as that of natural gas.

### 1.4.1 Methanol and DME

- Methanol can be produced by the oxidation of  $\text{CH}_4$  and the reduction of  $\text{CO}_2$ .  
And, DME can be produced easily from the dehydration of methanol.
- Although ultimately methanol should be produced from  $\text{CO}_2$  in the air, at the beginning it can be produced from natural gas or other  $\text{CH}_4$  sources like methane hydrate and the high concentrated  $\text{CO}_2$  from factories or plants, which will be able to slow down the consumption of fossil fuels.
- Existing infrastructures for oil (vessels, railroads, trucks, pipelines, etc.) can be used for methanol (although materials must be changed to ones compatible with methanol.).
- A gas station can be converted into a methanol station within million dollars in a week (A hydrogen station costs more than 10 million!).
- Without taken too much (25~90 ml), methanol is at least as safe as gasoline.
- DME has broad Flammability limit (3.4~17 vol%), which means DME must be handled under strict safety measure.  
However, the direct effects of DME to human body is less than  $\text{CO}_2$ .  
Different from some ethers such as diethyl ether, THF, etc., DME doesn't produce peroxide.  
(In order to make detectable quantity of peroxide, DME needs to be exposed to UV, air and added some additives.)
- As methanol can blend with water infinitely, in the case of outflow into the environment, methanol rapidly diffuses to get under harmless level density and be decomposed by bacteria (In fact, methanol can be "nutrition". vide infra).
- In the case of DME, it vaporizes and is decomposed in the troposphere, the lowest portion of Earth's atmosphere (half-life is five days).

**Methanol can be produced from  $\text{CO}_2$  (carbon neutral), adapted to existing infrastructures and is friendly to both humans and environment !!!**

### 1.4.2 Methanol as a Fuel

**It seems Methanol and DME will work well!!!**

#### Methanol

- The history of attempts to use alcohols (methanol and ethanol) as the fuel of internal-combustion engine is the history of internal-combustion engine itself.
- During World War II, the development of alternative resources had been strongly promoted in terms of the independence of energy.  
However, after the war, cheap oil had got easily accessible and the spotlight to alcohol has drastically disappeared (since this time, the developments of these resources have closely related with the oil price).  
In 1973, when the oil shock has happened, T.B. Reed and R.M. Lerner advocated the use of methanol (not as the broader part of alcohol) as the fuel of internal-combustion engine for the first time in the US. (Methanol : A Versatile Fuel for Immediate Use, *Science* 1973, 182, 1299~1304.)  
This was also the first time the word "the Methanol Economy" was appeared.  
In this paper, they reported that 15% methanol blended gasoline had dramatically improved performances, mileage and exhaust gas of vehicles.  
In the middle 1980's, the oil price had been drastically fallen and the development of alternative sources was done only in terms of exhaust gas, vehicles using M85, a blend of 85% methanol and 15% unleaded gasoline with minimum tuned equipments, proved to work well without any special troubles by the experiment over 4 years.  
(Methanol-Powered Cars Get Ready to Hit the Road, A.S. Moffat, *Science* 1991, 251, 514~515.)  
However, in the beginning of 1990's, some technologies which lessen the exhaust gas dramatically have been developed one after another, and the interest in methanol, which loses cost to oil, has almost disappeared again.
- Today, any vehicles can use maximum 10% methanol blended gasoline without any conversion. And, the conversion to the flexible-fuel vehicle (FFV), an alternative fuel vehicle with an internal combustion engine designed to run on more than one fuel (usually gasoline blended with either ethanol or methanol fuel), only costs a few hundred dollars.  
This means the transition from oil to methanol is smoothly realized during transition period.

- Conventional Internal-combustion engines has been best adapted to gasoline for a century, so there is no use comparing gasoline with methanol based on present engine. But, it is said that if the engine adapted to methanol is developed, the milage of that engine will surpass the gasoline engine.
- As purified methanol and DME don't contained sulfure (no wander!) and C-C bond, which is hard to cut completely, and burn at lower temperature than gasoline, these fuels don't emitt SOx, NOx and particulate matter (Particulate matter is constantly produced in deasel engine, which one of the biggest problems of this engine.).  
In fact, the exhaust gas is expected to clear easily the world's strictest regulation.
- The Problems of methanol are
  - (1) Political or Economical problems (for example, the opposition from oil industry or related groups, the oil price and the policies of energy security or environmental affairs)
  - (2) Methanol has large dipole moment and permittivity, which make methanol the powerful solvent for easily ionizing materials such as water, acid, base and some resins. These harm engines.

## Dimethylether

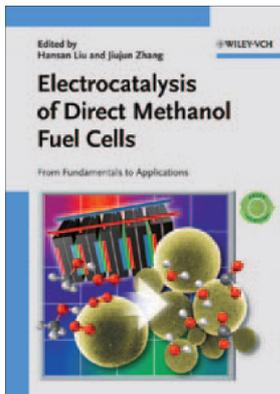
- DME can be the substitution for diesel fuel.  
The development of DME as a diesel fuel is proceeded more than methanol as alternative to gasoline because of the exhaust gas problems.  
Authors say it is certain DME takes place conventional diesel fuel.
- DME can be also the substitution for LPG (Liquefied Petroleum Gas) as town gas.
- Methanol or DME can be used at Fossil fuel power station without any troubles.

Comparison of phisical properties between DME, Diesel fuel and LPG

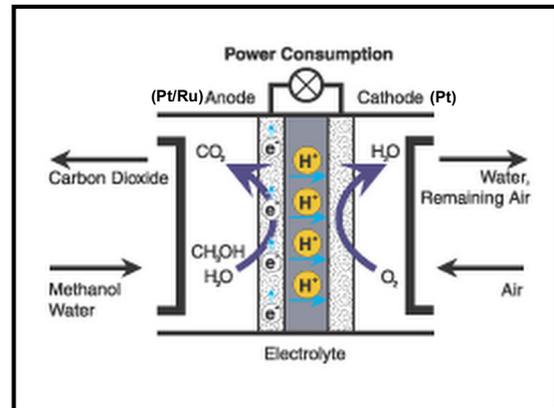
Physical property	DME	Diesel fuel	main constituents of LPG	
			Propane	Butane
b.p. (°C)	-24.9	180~360	-42.1	-0.5
Vapor pressure (20°C, bar)	5.1	-	8.4	2.1
Concentration of liquid (20°C, kg/m <sup>3</sup> )	668	840~890	501	610
Heat of combustion (kcal/kg)	6,880	10,150	11,090	10,920
Cetane number	55~60	40~55	-	-
Spontaneous combustion temperature (°C)	350	200~300	-	-
Flammability limit (air, vol%)	3.4~17	0.6~6.5	2.1~9.4	1.9~8.4

### 1.4.3 Direct Methanol Fuel Cell (DMFC)

- In order to overcome the difficulties of hydrogen storage and transportation, the ways to make hydrogen gas from hydrocarbon on vehicles or at stations on demand are enegetically developed.
- Steam reforming of methanol needs only much lower temparature than other hydrocarbons such as gasoline, which make reforming equipments able to put on vehicles (vide infa).  
Methanol doesn't have C-C bond, in other words, among all hydrocarbons methanol has the most hydrogen per carbon.  
In fact, 1L methanol at r.t. has more hydrogen than 1L liquid hydrogen at -253°C. (The former has 98.9g, and the latter has 70.8g. Methanol is the more efficient hydrogen carrer than hydrogen itself!)  
The fact should be noted that during the liquefaction of hydrogen the 40% of potential hydrogen energy is lost.  
Among the wide varieties of hydrocarbons, methanol is the only liquid one experienced as the fuel of vehicular fuel cell in practical scale.
- However, the disadvantages of this system are heavy, complicated and expensive (you must carry both fuel cell and steam reforming equipment if you want to get hydrogen on vehicle on demand.).
- In order to solve some of these problems (heavy and complicated), the way reforming methanol to hydrogen at hydrogen stations is examined.  
In this case, reforming equipments need not be carried on each vehicle, but the problem of how to carry hydrogen efficientry rises again.



Electrocatalysis of Direct Methanol Fuel Cells From Fundamentals to Applications. Edited by Hansan Liu and Jiujun Zhang. Wiley-VCH, Weinheim 2009. 606 pp.

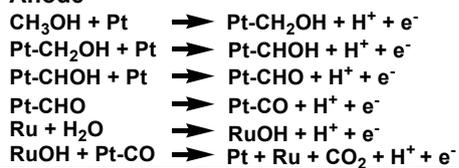


- To reform the current situation of hydrogen fuel cells drastically, Direct Methanol Fuel Cells (DMFCs) are being developed energetically in the last two decades.
- DMFC is a fuel cell using methanol as a fuel without producing hydrogen gas during the processes.

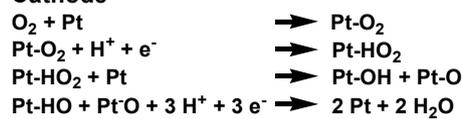


General accepted passways

Anode



Cathode



- **The Problems** of DMFC are

- (1) The diffusion of methanol from anode to cathode makes this system quite inefficient although the ideal efficiency is around 97% (new membranens best adjusted to methanol is strongly eagedred).
- (2) Noble metals, in fact Platinum Metal Groups, the most expensive ones during noble metals, must be used as electrodes to proof against highly acidic conditions. This is a common problem with fuel cells run under acidic conditions.



Yamaha FC-Dii : DMFC-drive motorcycle



Toshiba Dynario : the first commercially mass produced DMFC charger

about DMEC see:

DMFCs : From Fundamental Aspects to Technology Development.

A.S. Arico; S. Srinivasan; V. Antonucci, *Fuel Cells* 2001, 1, 133~161.

International activities in DMFC R&D : status of technologies and potential applications.

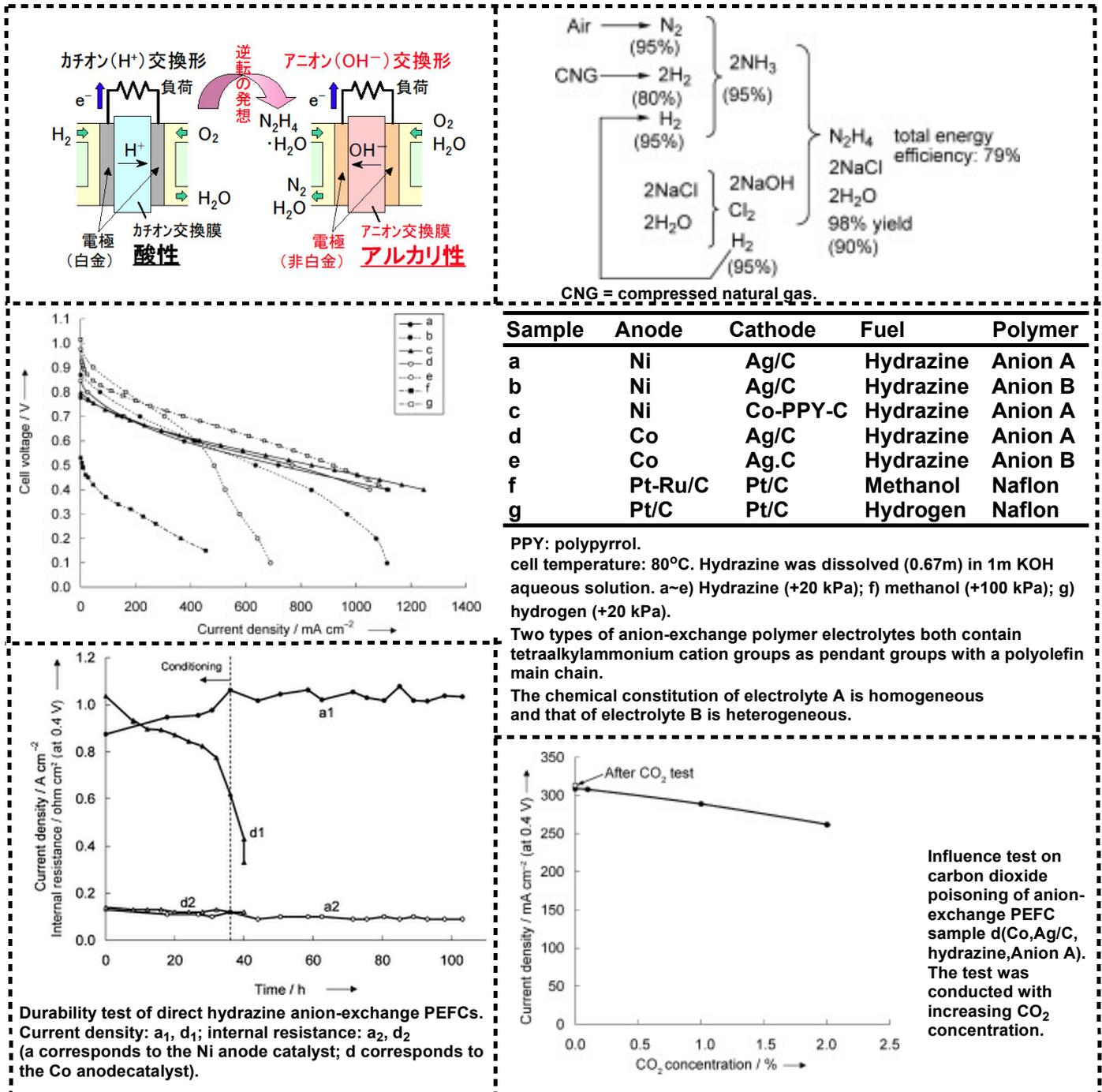
R. Dillon; S. Srinivasan; A.S. Arico; V. Antonucci, *Journal of Power Sources*, 2004, 127, 112~126.

# Direct Hydrazine Fuel Cell (another interesting Direct Fuel Cell)

A Platinum-Free Zero-Carbon-Emission Easy Fuelling Direct Hydrazine Fuel Cell for Vehicles.

H. Tanaka, et al. *Angew. Chem. Int. Ed.* 2007, 46, 8024–8027.

(reported by scientists of Daihatsu Motor Co., Ltd., National Institute of Advanced Industrial Science and Technology, Otsuka Chemical Co., Ltd. and Kobe University)



Sample	Anode	Cathode	Fuel	Polymer
a	Ni	Ag/C	Hydrazine	Anion A
b	Ni	Ag/C	Hydrazine	Anion B
c	Ni	Co-PPY-C	Hydrazine	Anion A
d	Co	Ag/C	Hydrazine	Anion A
e	Co	Ag/C	Hydrazine	Anion B
f	Pt-Ru/C	Pt/C	Methanol	Nafion
g	Pt/C	Pt/C	Hydrogen	Nafion

PPY: polypyrrol.

cell temperature: 80°C. Hydrazine was dissolved (0.67m) in 1m KOH aqueous solution. a~e) Hydrazine (+20 kPa); f) methanol (+100 kPa); g) hydrogen (+20 kPa).

Two types of anion-exchange polymer electrolytes both contain tetraalkylammonium cation groups as pendant groups with a polyolefin main chain.

The chemical constitution of electrolyte A is homogeneous and that of electrolyte B is heterogeneous.

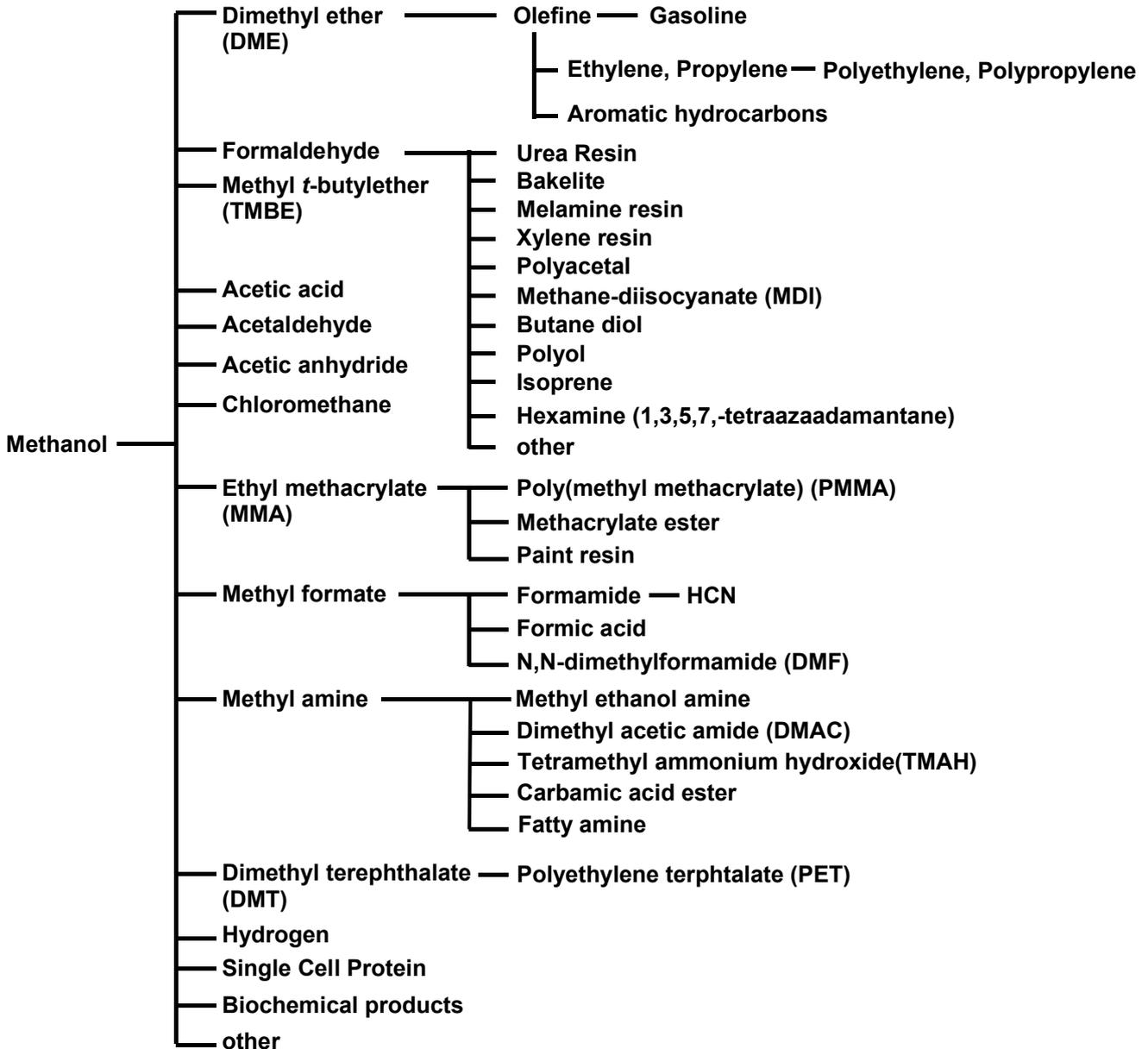
Influence test on carbon dioxide poisoning of anion-exchange PEFC sample d(Co,Ag/C, hydrazine, Anion A). The test was conducted with increasing CO<sub>2</sub> concentration.

Durability test of direct hydrazine anion-exchange PEFCs. Current density: a<sub>1</sub>, d<sub>1</sub>; internal resistance: a<sub>2</sub>, d<sub>2</sub> (a corresponds to the Ni anode catalyst; d corresponds to the Co anode catalyst).

- Run under alkali condition, platinum groups metal-free-erectrode fuel cell exhibiting equivalent power generation characteristics to the conveninal hydrogen fuel cell using Pt/C erectrode.
- Hydrazine can be made from N<sub>2</sub> in the air, salt (NaCl) and H<sub>2</sub>O efficiently (the total energy efficiency is 79%!).
- Although ideal electronode is noble metals free (sample c), the performance with the Co anode catalyst decreases drastically after 40 h. However, it is good enough if the Ni anode catalyst and Ag/C cathode catalyst work properly for a practical period (sample a and b).
- In the case of DMFC, it is predicted that the high concentration CO<sub>2</sub> at anode catalyst decreases the performance. But, these result can be useful knowledge to DMFC to some extent.

### 1.4.4 Methanol-Based Chemicals

key word : C<sub>1</sub> chemistry



### Single Cell Protein ("Food from Oil")

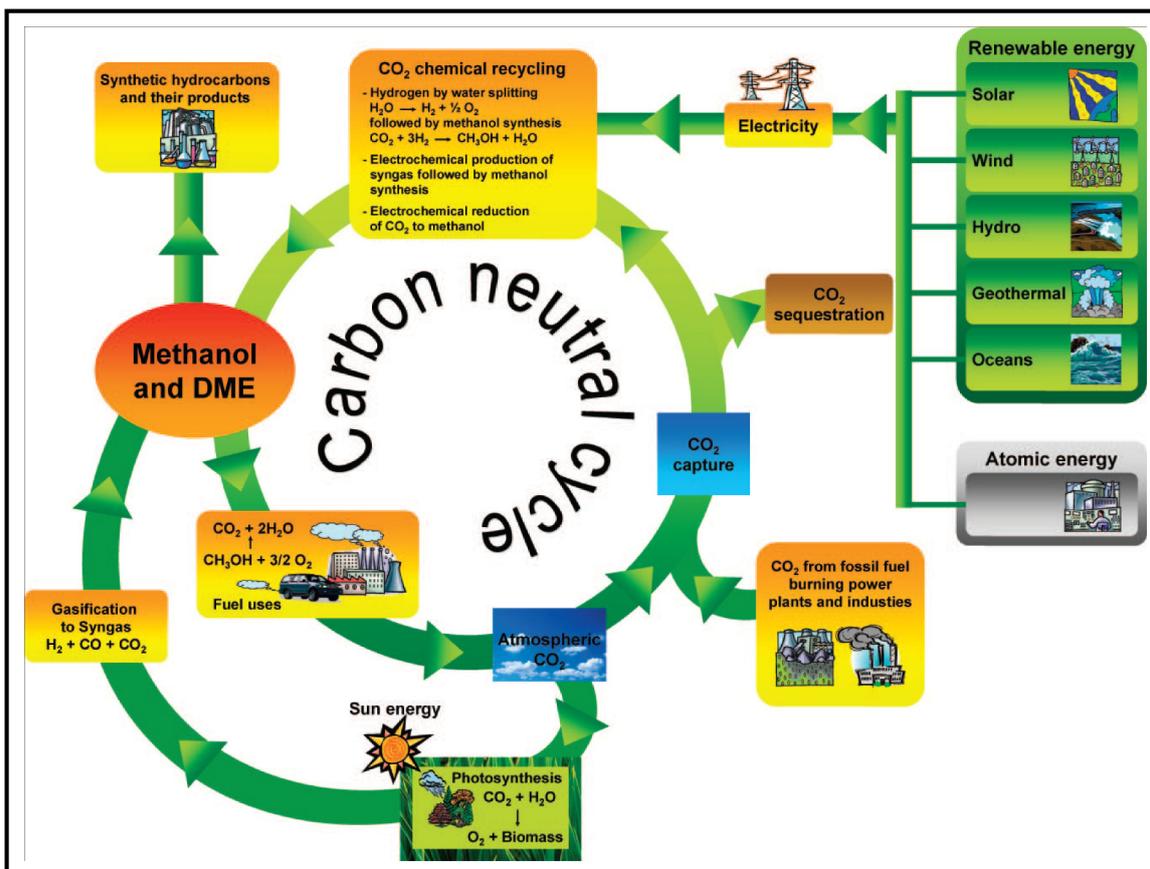
- Single cell protein (SCP) typically refers to sources of mixed protein extracted from pure or mixed cultures of algae, yeasts, fungi or bacteria used as a substitute for protein-rich foods, in human and animal feeds.

Large-scale production of microbial biomass has many advantages over the traditional methods for producing proteins for food or feed.

1. Microorganisms have a high rate of multiplication to hence rapid succession of generation (algae: 2~6 hours, yeast: 1~3 hours, bacteria: 0.5~2 hours).
2. They can be easily genetically modified for varying the amino acid composition.
3. A very high protein content 43~85 % in the dry mass.
4. Strains with high yield and good composition can be selected or produce relatively easily.
5. Microbial biomass production occurs in continuous cultures and the quality is consistent since the growth is independent of seasonal and climatic variations.
6. Land requirements is low and is ecologically beneficial.
7. A high solar energy conversion efficiency per unit area.
8. Solar energy conversion efficiency can be maximized and yield can be enhanced by easy regulation of physical and nutritional factors.
9. Algal culture can be done in space which is normally unused and so there is no need to compete for land.

[From : Wikipedia, Single Cell Protein]

## Summary and Future Outlook of "the Methanol Economy"



- Methanol is easy to store and transport and environmentally and physically harmless. Moreover, methanol has most hydrogen among all organic compounds. These mean methanol is one of the best energy carrier.
- Methanol will be produced at first from high-concentration CO<sub>2</sub> emitted by industries in the near future, and this multi-times utilization of unrecoverable resources will slow down (or at least steady) the speed of fossil fuels consumption. And, ultimately CO<sub>2</sub> in the air will be the source of methanol, completing a carbon neutral cycle.
- Currently, studies on materials are now enthusiastically going in order to adjust conventional equipments and infrastructures to methanol and DMF for the realization of the methanol economy.
- Petrochemical products can be produced also from methanol, and internal-combustion engine and fuel cell can work with methanol and DME. These fuels can be used as town gas and at fossil fuel power stations.
- In the case of transportation, at first Flexible-Fuel Vehicle will be introduced, next M100 (Methanol 100%) Vehicle, and then Direct Methanol Fuel Cells will take place internal-combustion engines.

As far as I read the book, even with current technology, methanol already has the ability to replace present fossil fuels completely.



However, the biggest problem of the methanol economy, I think, is...

How to make this fundamental liquid efficiently  
(The price of methanol decides all following!!!)

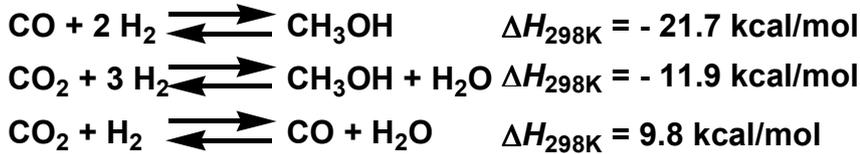
***This is where we chemists can give the greatest contributions!***

## 2. How to Make Methanol

- Today, almost all methanol is produced from Syn-Gas (synthetic gas). Syn-Gas is the mixture of CO and H<sub>2</sub> including little amount of CO<sub>2</sub>. Syn-Gas is obtained from any carbon allotropes or hydrocarbons used with O<sub>2</sub> and/or H<sub>2</sub>O together. Among all carbon sources, natural gas (methane) is used the most because of the least impurities.

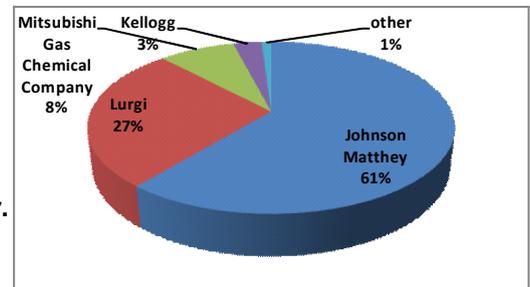
### 2.1 Methanol via syn-Gas

#### 2.1.1 Syn-Gas to Methanol



$$S = \frac{(\text{moles H}_2 - \text{moles CO}_2)}{(\text{moles CO} + \text{moles CO}_2)}$$

- Methanol is produced from Syn-Gas on heterogenous catalyst along the three equations above. These reactions are all reversible, so the yield is strongly dependent on conditions.
- The composition of Syn-Gas is usually indicated by stoichiometry value S. The ideal S value for synthesizing methanol is 2 or a little more.
- As I mentioned, natural gas includes least amount of impurities of all fossil fuels, especially sulfur. The quite little amount of sulfur destroys catalyst systems. By using clean Syn-Gas from natural gas, more efficient and milder catalyst systems had been realized.
- Today, the methanol producing processes converge on only a few ones : Johnson Matthey, Lurgi, MGC, Kellogg and other.
- These processes all use catalyst, mainly composed of CuO/ZnO, under 50~100 atm at 200~300°C.
- The latest plants produce methanol 99% selective and more than 70% energy efficiency.



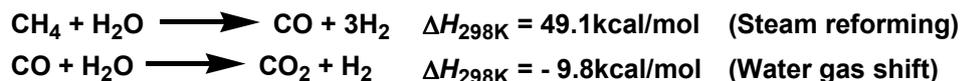
Share of total installed capacity  
[From : Johnson Matthey]

#### 2.1.2 Fossil Fuels (Methane) to Syn-Gas

- Steam methane reforming, carbon dioxide methane reforming and oxy methane reforming are the three basic processes for the production of Syn-Gas. And, in actual plants, two or three processes are combined for the adjustment of S value or thermochemical viewpoint.

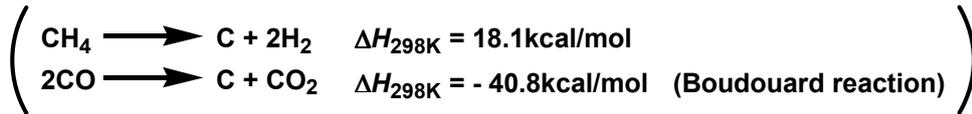
Process	Reaction	H <sub>2</sub> /CO ratio	ΔH <sub>298K</sub> (kcal/mol)
Steam reforming	CH <sub>4</sub> + H <sub>2</sub> O → CO + 3H <sub>2</sub>	3:1	49.1
Oxy reforming (Partial oxidation)	CH <sub>4</sub> + 1/2O <sub>2</sub> → CO + 2H <sub>2</sub>	2:1	- 8.6
CO <sub>2</sub> reforming (Dry reforming)	CH <sub>4</sub> + CO <sub>2</sub> → 2CO + 2H <sub>2</sub>	1:1	59.1

#### Steam Reforming and Water Gas Shift



- During steam reforming, methane reacts endothermic with H<sub>2</sub>O to give CO and H<sub>2</sub> on the surface of Ni catalyst at high temperature (800~1000°C). Obtained CO reacts with another H<sub>2</sub>O to give CO<sub>2</sub> and H<sub>2</sub> (Water Gas Shift). These processes giving four H<sub>2</sub> from one methanol is a quite efficient process for obtaining H<sub>2</sub>. In fact, 50% of H<sub>2</sub> produced all over the world and 90% in the US are obtained from these processes. By adjusting temperature or pressure, the second step can be decreased.
- The S value is three, so H<sub>2</sub> is excess.

- Carbon from reactions below destroys the catalyst and reactor, so excess amount of H<sub>2</sub>O or short remaining time are needed.



### Oxy reforming (Partial oxidation)



- During oxy reforming, methane reacts exothermic with insufficient O<sub>2</sub> to give CO and H<sub>2</sub> on the surface of Ni catalyst or non-catalyst at high temperature (800~1500°C).
- The biggest advantage of this process is the ideal ratio Syn-Gas (S = 2) is obtained.
- However, the biggest problem is undesirable oxidations of H<sub>2</sub> and CO. Emitted heat of which are so high that these reactions are problems not only for the useless consumption of resources but also for fear of safety.

( more details about Syn-Gas production through catalytic oxy reforming see:  
Energy-Efficient Syngas Production through Catalytic Oxy-Methane Reforming Reactions.  
T. V. Choudhary; V. R. Choudhary, *Angew. Chem. Int. Ed.* 2008, 47, 1828-1847. )

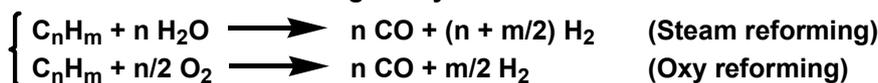
### CO<sub>2</sub> reforming (Dry reforming)



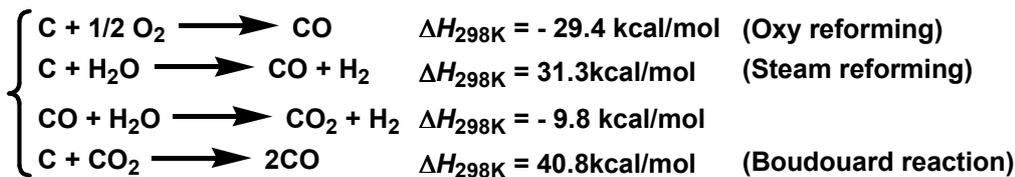
- Since this reaction doesn't include H<sub>2</sub>O, this reaction is called "Dry". During the dry reforming, methane reacts exothermic with CO<sub>2</sub> to give CO and H<sub>2</sub> on the surface of Ni catalyst at high temperature (800~1000°C).
- The S value is one, so H<sub>2</sub> is deficient.
- This process gives the efficient way for synthesizing methanol from CO<sub>2</sub>.

### Syn-Gas from other Fossil Fuels

from Petroleum Oil and Higher Hydrocarbons



from Coal



### Combinations of three basic processes

(1) Autothermal reforming

- Autothermal reforming is the combination of endothermic Steam reforming and exothermic Oxy reforming. In this process, the addition or elimination of large amount of heat aren't needed, in other words, "Autothermality".
- This process is used in the latest methanol plants. Although each step is conducted in one pot, since the optimum reaction temperature and pressure are different from each other, each step is conducted step by step.

## (2) Bireforming



- Bireforming is the combination of Steam reforming and Dry reforming. Fundamentally, Steam reforming produces excess amount of  $\text{H}_2$ , and Dry reforming does insufficient. So, both complement each other.
- Since the optimum reaction temperature of both is close, these reaction can be conducted in one step. Both reactions are endothermic, so the energy must be added from external sources, for example atomic energy, renewable resources, etc.
- There are no byproducts in this process, and according to the author, this is present one of the most efficient ways to synthesize methanol from  $\text{CO}_2$ ! (utilizing hydrogens of methane to the maximum)

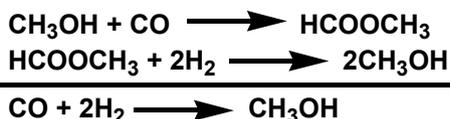
## (3) Trireforming

- Trireforming is the combination of all three basic processes.

more details about Tri-reforming see:

Tri-reforming of methane : a novel concept for catalytic production of industrially useful synthesis gas with desired  $\text{H}_2/\text{CO}$  ratios. Chunshan Song; Wei Pan, *Catalysis Today* 2004, 98, 463-484.

## (Methanol from Methyl Formate)



In order to reduce the high temperature and pressure required present methanol productions and to improve the thermodynamic efficiency, alternative milder methanol production process utilizing  $\text{H}_2/\text{CO}$  has been studied for a long time.

Among them, the most remarkable one, authors say, is the route from methyl formate first proposed in 1919.

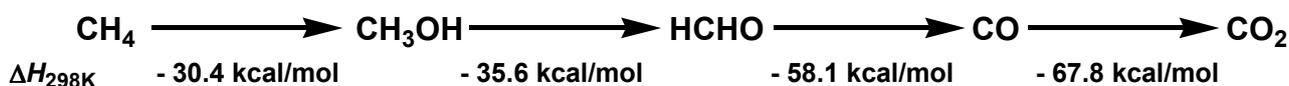
- This process is composed of two phases; 1) Carbonylation of methanol giving methyl formate, 2) Hydrocracking of methyl formate giving two methanol. Reactions can be conducted under 10~50 atm and at 80~120 °C (conventional way is under 50~100 atm and at 200~300 °C).
- First step is catalyzed by  $\text{CH}_3\text{OK}$  or  $\text{CH}_3\text{ONa}$  in liquid phase, and second catalyzed by Cu systems in gas or liquid phase. Although these reactions are usually conducted in different reactors, studies to conduct these reactions in one pot are now undergoing (In fact, in the case of second step, Ni systems give high reactivity and selectivity, but Ni has the possibility of producing highly toxic  $\text{Ni}(\text{CO})_4$ ). Since carbonic acid destroys methoxide in the first step,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  in Syn-Gas must be removed thoroughly.
- Methyl formate can be obtained from formaldehyde (esterification with methanol) or formic acid (Cannizzaro-type reaction), the peroxidated products during direct oxidation of methane to methanol. This suggests the possibility of mild and efficient way for synthesizing methanol without Syn-Gas.

## 2.2 Methanol without syn-Gas

- As mentioned, 50% of organic compounds in nature is methane, and the reserve is huge. Conventional Syn-Gas method is fundamentally inefficient because methane is first oxidized to  $\text{CO}/\text{H}_2$ , and then various organic compounds including methanol are produced through reduction. Ideally methane should be oxidized directly to methanol by oxygen used as a terminal oxidant.

### 2.2.1 Direct Oxidation of Methane

- It's ideal to use only oxygen, but it's quite difficult to realize both high conversion and selectivity. In fact, oxidized products ( $\text{CH}_3\text{OH}$ ,  $\text{HCHO}$ ,  $\text{HCOOH}$ ) are oxidized easier than methane itself.

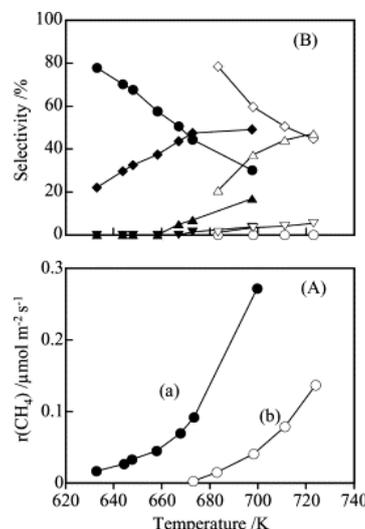
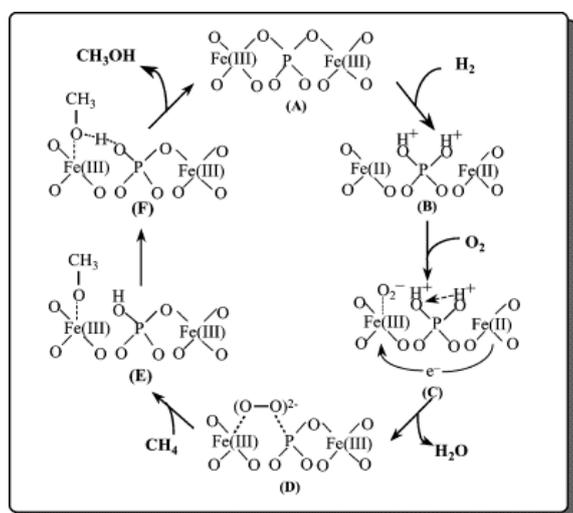


- Remarkable results are reported by groups in Tokyo Institute of Technology in 2010. They obtained oxidized products (methanol and formaldehyde) from the methane and oxygen mixed gas in around 30% yield under atmospheric pressure at r.t. for the first time by utilizing Atmospheric-pressure plasma conducted in capillary (1.5mm diameter, 5cm long).

(about this work see: Associate Professor Tomohiro Nozaki's homepage and publications therein (<http://www.plasma.nu/index.html>))

## 2.2.2 Catalytic Gas-Phase Oxidation of Methane

- In homogeneous catalytic gas-phase oxidative reaction, methane is reacted with oxygen under high pressure (30~200 atm) at high temperature (200~500 °C).
- To control the unexpected production of CO<sub>2</sub>, oxygenates (CH<sub>3</sub>OH, HCHO, CO, HCOOH) are collected with non-react methane cyclated.
- As mentioned, formaldehyde and formic acid can be converted into methanol.
- Many catalysts have been reported for now, but most of them lack reproducibility. And, the methane conversion rates don't exceed 10%.
- A notable result was obtained from FePO<sub>4</sub> utilized with H<sub>2</sub>-O<sub>2</sub> gas or H<sub>2</sub>-N<sub>2</sub>O gas. In this system, binuclear Fe unit, the same as natural MMO (Methane Monooxygenase)(vide infra), bridged multiply by phosphoric acid catalyzes reactions. What's interesting is both Fe and P play important roles. (V, Cr, Mn, Co, Ni, Cu, Zn, Al and Zr didn't give any oxygenates, and the conversion rate of FeAsO<sub>4</sub> was about one-fourth of FePO<sub>4</sub>'s and FeSbO<sub>4</sub> was one-eighth.
- By using N<sub>2</sub>O instead of O<sub>2</sub> as an oxidant, almost 100% selectivity was realized at 500 °C in 3% yield. However, N<sub>2</sub>O has the strongest potential of destroying ozone layer and global warming effect. In fact, the emission of N<sub>2</sub>O is strictly regulated, and thinking of production cost it won't be an attractive choice.
- In the case of O<sub>2</sub>, it's difficult realizing both high conversion rate and selectivity.



Effect of H<sub>2</sub> on the rate of CH<sub>4</sub> conversion (A) and the product selectivity (B).

(A) (a) in the presence of 50 kPa H<sub>2</sub>; (b) in the absence of H<sub>2</sub>.

(B) circle CH<sub>3</sub>OH; square HCHO; up top triangle CO; down top triangle CO<sub>2</sub>. Black symbols, in the presence of 50 kPa H<sub>2</sub>; white symbols, in the absence of H<sub>2</sub>. Reaction conditions: P(CH<sub>4</sub>)=33.8 kPa, P(O<sub>2</sub>)=8.4 kPa and W/F=0.208 g h/dm<sup>3</sup>.

( about FePO<sub>4</sub> see: Direct conversion of methane into oxygenates.

Kiyoshi Otsuka; Ye Wang, *Applied Catalyst A: General* 2001, 222, 145~161. )

## 2.2.3 Catalytic Liquid-Phase Oxidation of Methane

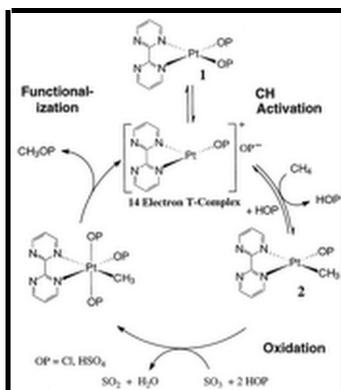
- In order to decrease the generation of byproducts and increase the selectivity of methanol and in terms of industrial process, it's ideal to do reaction at lower temperature (< 250°C). This drove to the researches on catalytic liquid-phase methane oxidation.
- In 1970's, G. A. Olah and coworkers reported that they obtained methanol from methane in high yield and selectivity at r.t. by utilizing superacid media (SbF<sub>5</sub>/HF) and H<sub>2</sub>O<sub>2</sub>. However, these reactions are stoichiometric or use expensive reagents and thus are not practical for the large-scale.
- Highly efficient and selective homogeneous metal catalyzed conversion was first reported in 1993. In this reaction, the oxidation of methane is catalyzed by Hg(II) in 100% sulfuric acid to produce methyl bisulfate, water and sulfur dioxide under mild conditions (180°C). 50% methane conversion and 85% selectivity to methylbisulfate (the major byproduct is CO<sub>2</sub>) was achieved. The Hg(II) ion reacts with methane to produce CH<sub>3</sub>HgOSO<sub>3</sub>H. Under the reaction conditions, this compound readily decomposes to CH<sub>3</sub>OSO<sub>3</sub>H and the reduced species Hg<sub>2</sub>(II). The catalytic cycle is completed by the reoxidation of Hg<sub>2</sub><sup>2+</sup> with H<sub>2</sub>SO<sub>4</sub> to regenerate Hg(II).



- Since Hg is highly toxic, other metals, especially platinum group metals such as Pt, Ir, Rh, Ru and Pd, have been investigated.

Among them, Pt complex in sulfonic acid gave the best result (> 70% yield, 90% selectivity).

(The Au<sup>I</sup>/Au<sup>III</sup> redox cycle using H<sub>2</sub>SeO<sub>4</sub> in 96% H<sub>2</sub>SO<sub>4</sub> was also reported.)



**C-H Activation :**



**Functionalizaion :**



**Reoxidaion :**



- The problems of these systems are

1) The separation of CH<sub>3</sub>OSO<sub>3</sub>H from H<sub>2</sub>SO<sub>4</sub> and following the decomposition to CH<sub>3</sub>OH are quite energy consuming process.

2) The harsh conditions (> 85% H<sub>2</sub>SO<sub>4</sub>, ~ 200°C (although lower temperature than other processes)) are needed because produced H<sub>2</sub>O or CH<sub>3</sub>OH bind much more tightly to the catalyst than CH<sub>4</sub>, the poorest ligand. This destroys catalytic systems.

- Other types of catalyst systems (using cheaper metals or less acidic media) are strongly eageded.

the review of methal catalyzed methane oxidation, including the concepts and designs of catalysts and reaction systems see: Perspective on some challenges and approaches for developing the next generation of selective, low temperature, oxidation catalysts for alkane hydroxylation based on CH activation reaction.

R.A. Periana, *et al.*, *J. Mol. Catal. A: Chem.* 2004, 220, 7-25.

about each metal catalyst see:

Hg : A mercury-catalyzed, high-yield system for the oxidation of methane to methanol.

R.A.Periana, *et al.*, *Science* 1993, 259, 340-343.

Pt : Platinum Catalysts for the High-Yield Oxidation of Methane to a Methanol Derivative.

R.A.Periana, *et al.*, *Science* 1998, 280, 560-564.

Au : Selective oxidation of methane to methanol catalyzed, with C-H activation, by homogeneous, cationic gold.

R.A.Periana, *et al.*, *Angew. Chem. Int. Ed.* 2004, 43, 4626-4629.

## 2.2.4 Methane into Methanol Conversion through Monohalogenated Mathanes

- Another type of conversion is through catalytic monohalogenation of methane followed by hydrolysis giving methanol and hydrogen halide.

The catalytic cycle is completed by the oxidation of hydro halogens to halogen by using oxygen.

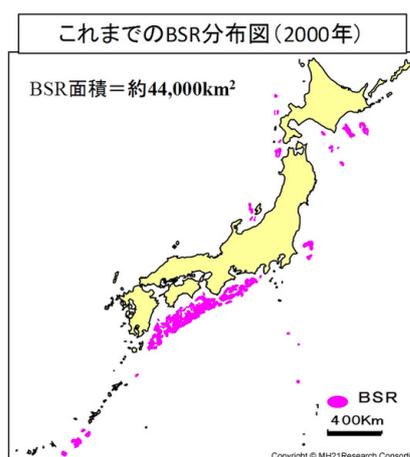
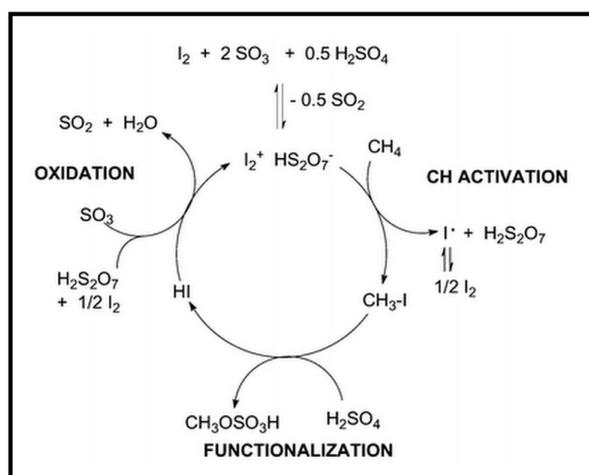
- The classical hlogen displacement reaction of methane is free radical reaction. However, there are no selectivity to mono substituted.

- In 1970's, Olah and coworkers reported that methane reacted with SbF<sub>5</sub>-Cl<sub>2</sub> or Br<sub>2</sub> in SO<sub>2</sub>ClF solution at -78°C to give CH<sub>3</sub>Cl and CH<sub>3</sub>Br high selectively although the yield was quite low.

- Olah and coworkers also reported in 1985 that the catalytic monohalogenation (chlorination and bromination) of methane was achieved over either supported solid acid (such as FeO<sub>x</sub>Cl<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub>, TaOF<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, NbOF<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, ZrOF<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, SbOF<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, SbF<sub>5</sub>/C, and Nafion-H/TaF<sub>5</sub>) or platinum metal (Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/BaSO<sub>4</sub>) catalysts. The reactions were carried out at temperatures between 180 and 250 °C giving 8~58% conversions with selectivity in methyl chloride (bromide) generally exceeding 90%. Limited methylene halide formation accompanies the reactions, but no formation of haloforms or carbon tetrahalides was observed.

In order to avoid byproducts such as methylene halide or ethane formation, excess amount of methane is used.

- Thinking of the catalytic cycle of halogenes, Br is better than Cl in that Br<sup>-</sup> is easily oxidized to Br<sub>2</sub> by oxygen even though the conversion of HCl to Cl<sub>2</sub> by oxygen as a terminal oxidant is practicable in industrial scale.
- In the case of iodine, Periana and coworkers reported that elemental iodine dissolved in 96 % H<sub>2</sub>SO<sub>4</sub> containing 2.5% SO<sub>3</sub> generates a stable, active species that catalyzes the functionalization of methane to methyl bisulfate at 195 °C in 45% yields (based on methane) at 95% selectivity (the rest is CO<sub>2</sub>). The reaction mechanism is thought to be the same as the case of Hg, Pt and Au.
- Another problem of this monohalogenated species seems to be the difficulty of hydrolysis to obtain methanol.  
Of course, the excess amount of water shifts the equilibrium to the methanol formation, but the separation of a little amount of methanol from excess amount of water may be the quite energy consuming process.  
Ideally, methanol should be obtained from CH<sub>3</sub>X with as little amount of water as possible.  
Olah and coworkers also reported catalytic hydrolysis of methyl halides over γ-Al<sub>2</sub>O<sub>3</sub>-supported metal oxide/hydroxide catalysts such as ZnO/Al(OH)<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.  
However, the conversion rates never exceed 10%.  
And, it was also found that the little the ratio of water is, the more DME is produced.  
In fact, when H<sub>2</sub>O/CH<sub>3</sub>Cl = 5, more than 50% is DME.
- There are many difficulties with this monohalogenated methane method, BUT in terms of Japanese middle term National Element or Security Polcy, this method may be one of the solutions to Japanese fuel affairs.  
Japan is said to be one of the richest countries with methane hydrate.  
For now, large quantity were found on Pacific side.  
Bromine is obtained from sea water, and what's quite important is Japan has the most reserve of iodine in Chiba Prefecture all over the world (In fact, Chiba Prefecture has more than 60% of world's reserve!).



Distribution of methane hydrate around Japan  
[From : Research Consortium for Methane Hydrate Resources in Japan]

#### about the chlorination

by super acid see:

Electrophilic Reactions at Single Bonds. XVII. SbF<sub>5</sub>, AlCl<sub>3</sub>, and AgSbF<sub>6</sub>, Catalyzed Chlorination and Chlorolysis of Alkanes and Cycloalkanes. G.A. Olah, *et al.*, *J. Am. Chem. Soc.* 1973, 95, 7686-7692.

by supported solid acid and subsequent hydrolysis see:

Selective monohalogenation of methane over supported acid or platinum metal catalysts and hydrolysis of methyl halides over γ-alumina-supported metal oxide/hydroxide catalysts. A feasible path for the oxidative conversion of methane into methyl alcohol/dimethyl ether. G.A. Olah, *et al.*, *J. Am. Chem. Soc.* 1985, 107, 7097-7105.

about process for converting hydrogen chloride to chlorine see:

Process for Converting Hydrogen Chloride to Chlorine. T.T. Tsotsis, *et al.*, *Ind. Eng. Chem. Res.* 1994, 33, 2996-3003.

about methyl bisulfate conversion via iodo methane see:

High yield conversion of methane to methyl bisulfate catalyzed by iodine cations. R.A. Periana, *et al.*, *Chem. Commun.* 2002, 2376-2377.

## 2.2.5 Methanol from Methane by Enzyme

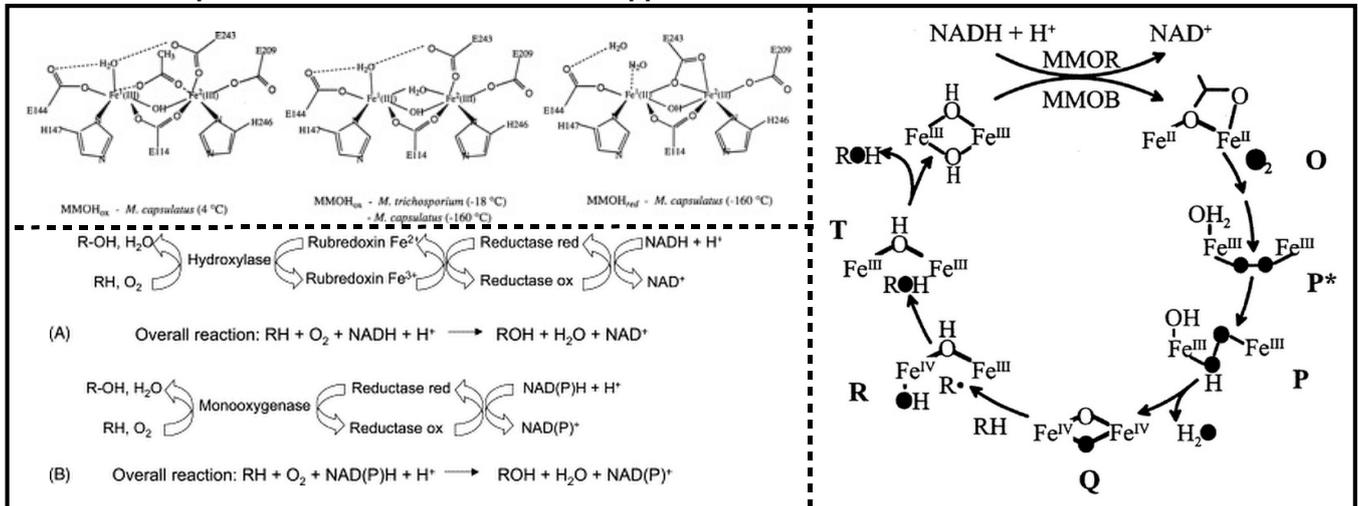
- In nature, enzyme called MonoMethane Oxygenase (MMO) performs the conversion of methane to methanol.

MMO is the first enzyme in the metabolic pathway of methanotrophs, bacteria that use methane as their sole source of carbon and energy. There are two kinds of MMO systems.

One is a soluble form (sMMO), and the other is membrane-bound or particulate form (pMMO).

Although pMMO is universal among all methanotrophs, and sMMO is expressed by limited number of methanotrophs only under copper-deficient conditions, sMMO has far attracted most of the attentions because it is much easier to be purified than pMMO.

On one hand sMMO contains carboxylate-bridged non-heme dinuclear iron center at its active site, on the other hand pMMO does mono or dinuclear copper center.



- As another type of enzyme oxidizing hydrocarbon, P450, which has iron-porphyrin complex at its active site, has also drawn attentions.

Although the yield is low, genome engineered P450 enzyme which has the ability to oxidize ethane to ethanol has reported.

- Utilizing or mimicking these enzymes are interesting in terms of using base metals as catalyst. However, the fact natural catalytic cycles aren't completed until coenzymes activated by solar energy complement them should be noted.

This fact means additional energy are needed to oxidize methanol, and at application stage these energy may not be from solar power, but hydrogen or something.

Ideally, methane should be oxidized without any external energy carrier.

### the reviews of sMMO see:

Mechanistic studies on the hydroxylation of methane by methane monooxygenase.

M.-H. Baik; M. Newcomb; R.A. Friesner; S.J. Lippard, *Chem. Rev.* 2003, 103, 2385-2419.

Dioxygen activation by enzymes containing binuclear non-heme iron clusters.

B.J. Wallar; J.D. Lipscomb, *Chem. Rev.* 1996, 96, 2625-2657.

Enzymatic activation of alkanes: constraints and prospective.

M. Ayala; E.Torres, *Appl. Catal. A: General* 2004, 272, 1-13.

### about pMMO see:

Crystal structure of a membrane-bound metalloenzyme that catalyses the biological oxidation of methane.

R.L. Lieberman; A.C. Rosenzweig, *Nature* 2005, 434, 177-182.

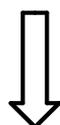
Conversion of Methane to Methanol at the Mononuclear and Dinuclear Copper Sites of Particulate Methane Monooxygenase (pMMO): A DFT and QM/MM Study.

K. Yoshizawa; Y. Shiota, *J. Am. Chem. Soc.* 2006, 128, 9873-9881.

### about engineer enzyme oxidizing ethane to ethanol see:

The heme monooxygenase cytochrome P450<sub>cam</sub> can be engineered to oxidize ethane to ethanol.

F. Xu; S.G. Bell; J. Lednik; A. Insley; Z. Rao; L.-L. Wong, *Angew. Chem. Int. Ed.* 2005, 44, 4029-4032.



Summary of 2.1 and 2.2

These methods above all depend on methane as carbon source. However, for the realization of carbon neutral economical cycle, we should use carbon dioxide as carbon source!

## 2.3 Chemical Recycling of Carbon Dioxide to Methanol

### 2.3.1 Methanol Production using Carbon Dioxide as a Carbon Source

- It is not difficult to synthesize methanol from  $H_2$  and  $CO_2$ , and chemists had already recognized how to do this conversion in the early 20th century. In fact, in the methanol plants working in the US during 1920's to 1930's,  $CO_2$  from byproduct of fermentation was widely used.

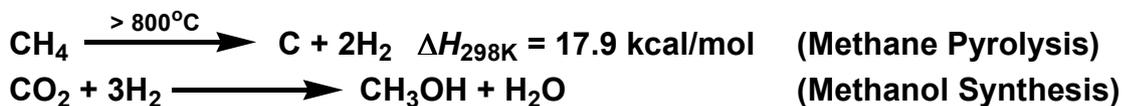


- Pilot plants and commercial plants start working in these five years. The catalysts for these plants are Cu/Zn systems quite similar to those for methanol production from Syn-Gas ( $H_2 + CO$ ), and reaction temperature is also close. A pilot plant of Mitsui Chemicals (started working on May 2009) (Japan) realized 95%  $H_2$  and  $CO_2$  conversion and 99.8% methanol selectivity by single path.
- However, what I want you to note is the one-third of  $H_2$  is in principle consumed merely for the generation of  $H_2O$  only by reacting  $CO_2$  with  $H_2$  (the compression of  $H_2$  consumes 10~20%, and the liquefaction does 30~40%). Since  $H_2$  is obtained from methane at present (or even if the efficient electrolysis is developed in the future), I can't help but saying this method is far from perfect. This problem arises from the simple fact that the numbers of oxygen of  $CO_2$  and  $CH_3OH$  are different from each other.
- The conversion  $CO_2 \rightarrow CO + 0.5 O_2$  is ideal, but the ways for doing this efficiently don't exist still.
- Here, I want to focus on how to incorporate  $CO_2$  with conventional  $CH_3OH$  production methods.

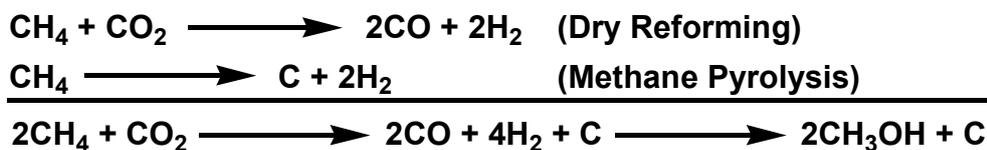
In the book, authors introduce three methods:

- 1) The Combination of Methane Pyrolysis and Methanol Synthesis
- 2) The Combination of Methane Pyrolysis and Dry Reforming
- 3) Bireforming (the Combination of Steam Reforming and Dry Reforming)

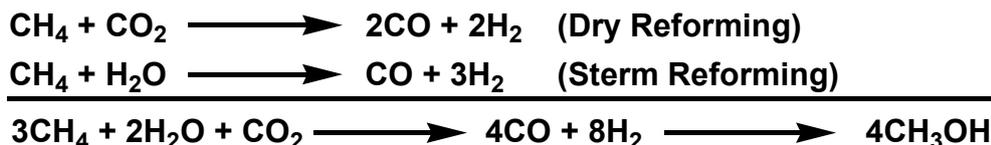
#### 1) The Combination of Methane Pyrolysis and Methanol Synthesis



#### 2) The Combination of Methane Pyrolysis and Dry Reforming



#### 3) Bireforming (the Combination of Steam Reforming and Dry Reforming)



	1)	2)	3)
$CO_2/CH_4$	2/3	1/2	1/3
$CH_3OH/CH_4$	2/3	1	4/3
$CO_2/CH_3OH$	1	1/2	1/4

- $CO_2/CH_4$  value indicates how effective the process recycles  $CO_2$ .
- $CH_4/CH_3OH$  value indicates how effective the process produces  $CH_3OH$ .
- $CO_2/CH_3OH$  value indicates how effective the process decreases total  $CO_2$  emission (because  $CH_3OH$  becomes  $CO_2$  after utilized).

The larger each value is, the better

- Evaluations of these three processes should be based on all three values. Based on this, the process 1) is virtually zero CO<sub>2</sub> emission because carbon of utilized CH<sub>4</sub> is fixed to C (Solid carbon is much easier to store than gas CO<sub>2</sub>, and can be sold as material). The process 3) is the best way producing CH<sub>3</sub>OH by using CO<sub>2</sub>. And, the process 2) is the middle of them. You can see that there is no way to realize efficiently both reduction of CO<sub>2</sub> emission and increase of CH<sub>3</sub>OH production.
- By the way, Carbon can be used as carbon source of another CH<sub>3</sub>OH via Boudouard reaction if external H<sub>2</sub> is added. However, in terms of carbon neutral cycle, these steps are nonsense because all efforts to fix CO<sub>2</sub> will be in vain. This is an effective way for producing CH<sub>3</sub>OH from coal and CO<sub>2</sub> (Coal Gasification).



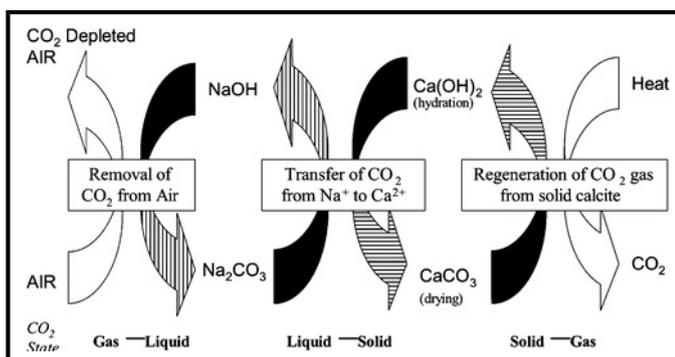
- As mentioned, ideally CH<sub>3</sub>OH is produced from CO and H<sub>2</sub> via CO<sub>2</sub> → CO + 0.5 O<sub>2</sub>.
- For realizing this decomposition efficiently, electrolysis of CO<sub>2</sub> in solvent such as water or organic one and metal oxide-catalyze pyrolysis are studied (both are the same methodology as water decomposition). Especially, electrolysis of carbonated water gives H<sub>2</sub> and CO simultaneously. Metal oxide-catalyze pyrolysis is first the deoxygenation of high valent metal oxide under O<sub>2</sub> depleted condition at extremely high temperature. Next, low valent metal oxide deprives oxygen of CO<sub>2</sub> to give CO at low temperature. Both technologies are greatly expected to realize, however, far from feasible on the industrial scale at present.

(example of metal oxide-catalyze CO<sub>2</sub> pyrolysis)



### 2.3.2 Carbon Dioxide Capturing methods

- For the realization of the carbon neutral economy, the CO<sub>2</sub> capture technology plays a critical role because CO<sub>2</sub> is the only source of following all carbon products.
- Although large scale have never been done yet, collecting CO<sub>2</sub> have already been developed enough. The system utilizing amine solution such as monomethanol amine or monoethanol amine for CO<sub>2</sub> absorption and emission have been widely used for separation from mixed gas of many plants. The problems of this system are the need for large energy in emitting CO<sub>2</sub>, the corrosion by amine and decomposition of amine.
- Recently, Metal-Organic Frameworks with exceptional high capacity for storage of CO<sub>2</sub> under 30 bar at r.t. has been reported, and following researchs are actively ongoing.
- Ultimately, CO<sub>2</sub> must be collected from low concentrated air because more than half of CO<sub>2</sub> emission is from domestic. In other word, each emits only so little amount that it's out of problems from economical view to collect individually.
- This seems extremely difficult, but the collection from air is already practiced by utilizing some basic-absorbents such as Ca(OH)<sub>2</sub>, NaOH and KOH although vast amounts of cost and energy are needed.



Schematic overview of air capture including Air Separation Unit

- Additional developments and improvements are expected for meeting economical need.

the reviews of CO<sub>2</sub> capture see:

Carbon Dioxide Capture: Prospects for New Materials.

D.M. D'Alessandro; B. Smit; J.R. Long, *Angew. Chem. Int. Ed.* 2010, 49, 6058-6082.

the reviews of Metal-Organic Frameworks for storage of CO<sub>2</sub> see:

Synthesis, Structure, and Carbon Dioxide Capture Properties of Zeolitic Imidazolate Frameworks.

A. Phan; O.M. Yaghi, *et al.*, *Accounts of Chemical Research* 2010, 43, 58-67.

the pioneering work of Metal-Organic Frameworks for storage of CO<sub>2</sub> see:

Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature.

A.R. Millward; O.M. Yaghi, *J. Am. Chem. Soc.* 2005, 127, 17998-17999.

about the CO<sub>2</sub> capture process from air see:

Energy and material balance of CO<sub>2</sub> capture from ambient air.

F. Zeman, *Environ. Sci. Technol.* 2007, 41, 7558-7563.

## Summary and Future Outlook of "the Methanol Synthesis"

- Today's methanol (and hydrogen) productions are almost all depending on fossil fuels (mainly methane) via Syn-Gas.  
This method is fundamentally inefficient in that methane is first oxidized to Syn-Gas and then reduced to methanol.  
It can be said that the difference between methanol and hydrogen as a fuel is that the former needs more energy in synthesis on the one hand while the latter needs in storage and transportation.  
Methane should be oxidized directly to methanol.  
Furthermore, the effective way to recycling carbon dioxide (even if not perfect recycling) to methanol by utilizing methane and external hydrogen from electrolysis of water in order to exploit diminishing fossil fuels to the full should be also developed.  
Ultimately, methanol should be obtained from CO<sub>2</sub> and H<sub>2</sub>O, however, one-third of hydrogen will be spent to produce water simply by reducing CO<sub>2</sub> with H<sub>2</sub>.  
This problem should be solved by the way not depending on unrennewable resources.
- Followings are the list of problems must be solved by "CHEMISTS":
  - (0. Efficient way for oxidizing CH<sub>4</sub> directly to CH<sub>3</sub>OH)
    1. Efficient way for capturing and collectiong CO<sub>2</sub>
    2. Efficient way for H<sub>2</sub>O decomposition to H<sub>2</sub> and O<sub>2</sub>
    3. Efficient way for CO<sub>2</sub> decomposition to CO and O<sub>2</sub>
    4. Efficient way for synthesizing CH<sub>3</sub>OH from CO and H<sub>2</sub>

## Closing

*Before encountering this book, I thought vaguely that after the Fossil Fuel era the next comes the Hydrogen Economy and what chemists contribute are Hydrogen Fuel Cells and Metal Hydrides.*

*Of course, the next will be no doubt Hydrogen in that Hydrogen can be the medium of energy, but this is the first time for me to have a detailed discussion on how to use Hydrogen among whole societies.*

*As authors mention in the book, I don't also think that Methanol is the only acceptable solution.*

*Finally, it is my great pleasure if this seminar helps, as the original book did to me, each of you to get the coming situation in perspective and think what to do to contribute future societies.*