# 이산화탄소의 재활용기술 현황 (III)

#### $\succ$ Synthesis Gas from CO<sub>2</sub>

 $CO_2 + CH_4 \leftrightarrow 2CO + 2H_2$ 

 $\mathrm{CO}_2 + \mathrm{H}_2 \iff \mathrm{CO} + \mathrm{H}_2\mathrm{O}$ 

- Highly endothermic reaction
- Catalyst :  $Rh/Al_2O_3$ ,  $Ru/Al_2O_3$ ,  $Pt/Al_2O_3$ ,  $Ir/Al_2O_3$ , KNiCa/Zeolite,  $Ni_{0.03}Mg_{0.97}O$ ,  $Pt/ZrO_2$
- Coking by carbon deposition

 $CH_4 \leftrightarrow C + 2H_2$ 

 $2CO \leftrightarrow C + CO_2$ 

- Resistance : Ru > Rh = Pt > Ir
- Combining of  $Y_2O_3$ ,  $Eu_2O_3$  to minimize coking

#### Synthesis of Methane

(1)  $CO_2 + H_2 \leftrightarrow CO + H_2O$   $CO_2 + 3H_2 \leftrightarrow CH_4 + H_2O$ (2)  $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ 

- Catalyst : Ru/SiO<sub>2</sub>, Co/SiO<sub>2</sub>, Ni/SiO<sub>2</sub>, Fe/SiO<sub>2</sub>
- Need of Excess  $H_2$  (4 $H_2$ /C $H_4$ )
- Difficulty of storage and transportation of methane

- Synthesis of chemicals by microwave
  - Catalyst : Supported Ni in microwave reactor
  - Conversion : 5%, Products : methane(55.1%),  $C_4$ + alcohol(28.4%)
- Methylamine synthesis(Baiker et al., J. Chem. Soc. Chem. Commun., 1995)
  - Commercial process is operated with MeOH and NH<sub>3</sub>
  - Direct methylamine synthesis from  $H_2/CO_2/NH_3$ 
    - Catalyst :  $Cu/Al_2O_3$

## > Higher Hydrocarbon Synthesis

- Methanol synthesis from  $CO/CO_2$  and  $H_2$ 
  - ICI process
    - Catalyst : CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>, CuO/ZnO/Cr<sub>2</sub>O<sub>3</sub>
    - Reaction: 230~300°C, 50~100bar
- Methanol-to-Hydrocarbon process
  - MTG/MTO process
    - Catalyst : HZSM-5, SAPO
    - Reaction: 300~500°C, 1~20bar



Methanol synthesis from CO<sub>2</sub>

Direct conversion of  $CO_2$  to hydrocarbon over a hybrid catalyst system

## $\triangleright$ Overall approaches to the hybrid catalysts for CO<sub>2</sub> hydrogenation

- Lower hydrogenating ability of methanol synthesis catalyst
- The effect of zeolites characteristics on the hydrocarbon formation
  - structure, acidity, pore size

 $CO_2$  hydrogenation over hybrid catalysts composed of CuZnOZrO<sub>2</sub> and zeolites

Hybrid catalyst	H.C. yield (wt%)	C <sub>2+</sub> H.C. Yield(wt%)	Main product
A + HZSM-5	2.7	2.2	Ethane
A+ Cu/HZSM-5	4.2	3.8	Ethane
A + SAPO-5	9.1	8.8	Butane
A+ Cu/SAPO-5	14.9	14.4	Butane
A + SAPO-34	11.0	10.6	Propane
A+ Cu/SAPO-34	15.8	15.5	Propane

A : Cu/ZnO/ZrO<sub>2</sub> , Cu : 1.5 wt %  $400^{\circ}$ C, 28 atm, W/F = 20g-cat•h/mol

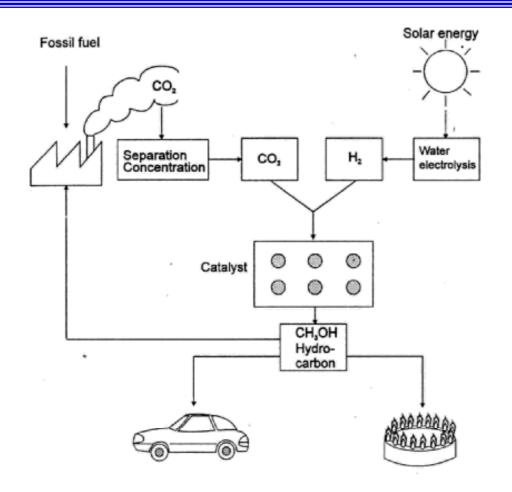
# Hydrogen Supply

- Steam Methane Reforming
  - $CH_4 + H_2O \leftrightarrow CO + 3H_2$
- CO<sub>2</sub> reforming without carbon formation
  - $\quad \mathrm{CO_2} + \mathrm{CH_4} \, \leftrightarrow \, \mathrm{2CO} + \mathrm{2H_2}$
- Solar energy for water electrolysis
- Biomass conversion

## Solar Hydrogen Production by Photocatalyst

- To realize CO<sub>2</sub> hydrogenation process as a solution for the global warming, solar hydrogen providing system from water should be established
  - photocatalytic production of  $H_2$  from water is needed
- Catalyst :  $Na_2CO_3 + 5wt\% NiO/TiO_2$  system
  - Products :  $400 \text{m}^2$  of H<sub>2</sub> and  $200 \text{m}^2$  of O<sub>2</sub> for 6.5 hrs solar light irradiation

#### ▶ 이산화탄소의 재활용에 의한 연료생산 과정의 개념도



## ➤ Summary

• Catalytic conversion technology  $\rightarrow$  not yet feasible(economically)

but increasingly urgent (environmental regulations)

- $CO_2$ : Chemically too stable  $\rightarrow$  thermodynamical constraints for high conversion
- Main products : Alcohol(MeOH, EtOH, PrOH, BuOH), Fuels (Hydrocarbon), Fine Chemicals (ester, acid, pyrone, lactone)
- Hydrogen supply : Solar energy for water electrolysis, Steam Methane Reforming, CO<sub>2</sub> reforming without carbon formation etc
- Separation and Recovery of CO<sub>2</sub> connected with catalytic utilization