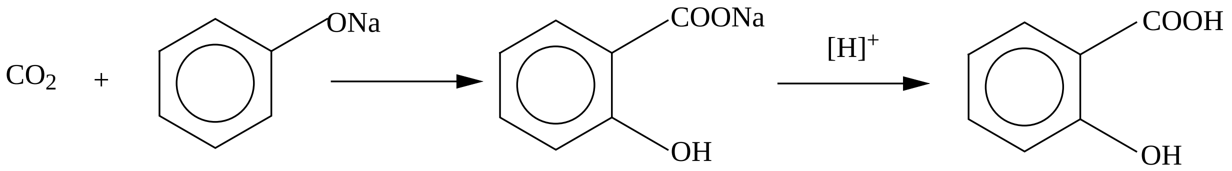
이산화탄소의 재활용기술 현황 (II)

➢ Industrial Processes with CO_2

- Urea and Derivatives
  - $CO_2 + 2NH_3 \leftrightarrow H_2N\text{-}CO\text{-}ONH_4$
  - $H_2N\text{-}CO\text{-}ONH_4 \leftrightarrow H_2N\text{-}CO\text{-}NH_2 + H_2O$

- Salicylic Acid and Derivatives



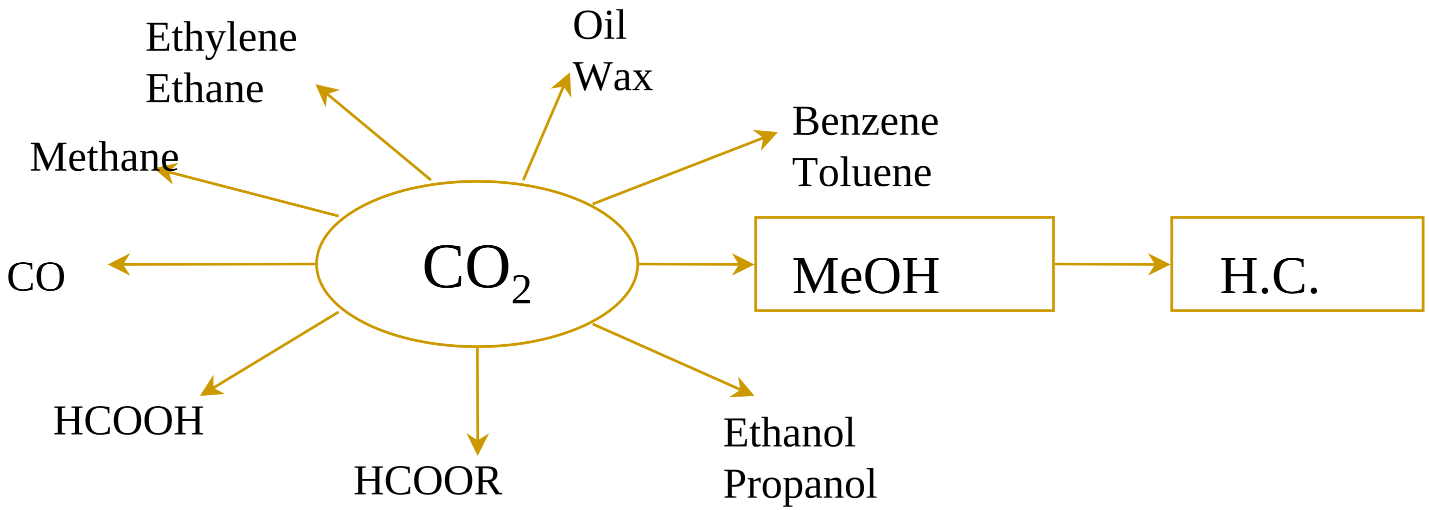
- Methanol synthesis
  - $CO + 2H_2 \rightarrow CH_3OH$
  - $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
  - $(H_2\text{-}CO_2)/(CO + CO_2) \geq 2$

➢ Methods about the study on the CO_2 reduction

- Reduction of emission of CO_2 by using alternative energy source
- Separation and recovery of CO_2 emitted in stationary source
- Chemical CO_2 Fixation
- Biological CO_2 Fixation

➢ Catalytic CO_2 Fixation

- One of the best methods to fix huge amount of emitted CO_2 in a short time
- Solution to carbon resource problem for production of fuel and chemical feedstocks



➢ Contents

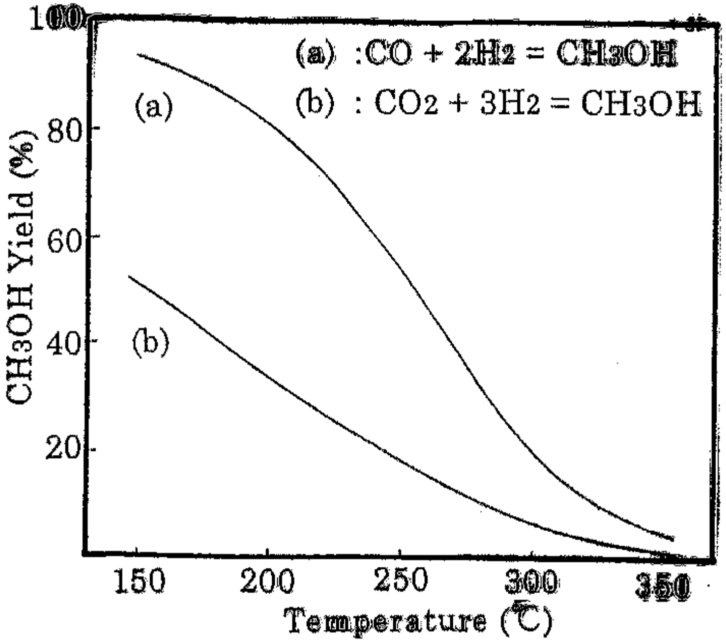
- Methanol Synthesis
- Synthesis of Higher Alcohol
- Carboxylic acid Synthesis
- New C-C Bond Formation
- Polymer Synthesis
- Synthesis Gas
- Synthesis of Methane
- Higher Hydrocarbon Synthesis
- Synthesis of chemicals by microwave
- Methylamine synthesis
- Hydrogen Supply

➢ Methanol Synthesis

- Methanol
  - Clean Energy Source
  - Intermediates for valuable compounds

- Commercial process of methanol synthesis
  - BASF (1923)
    - Catalyst : ZnO-Cr_2O_3
    - Reaction : 350^{o}C, 200-350 bar
  - ICI (1966)
    - Catalyst : CuO/ZnO/Al_2O_3
    - Reaction : 230-280^{o}C, 50-100 atm
    - High selectivity

➢ Methanol yield at equilibrium (5MPa)



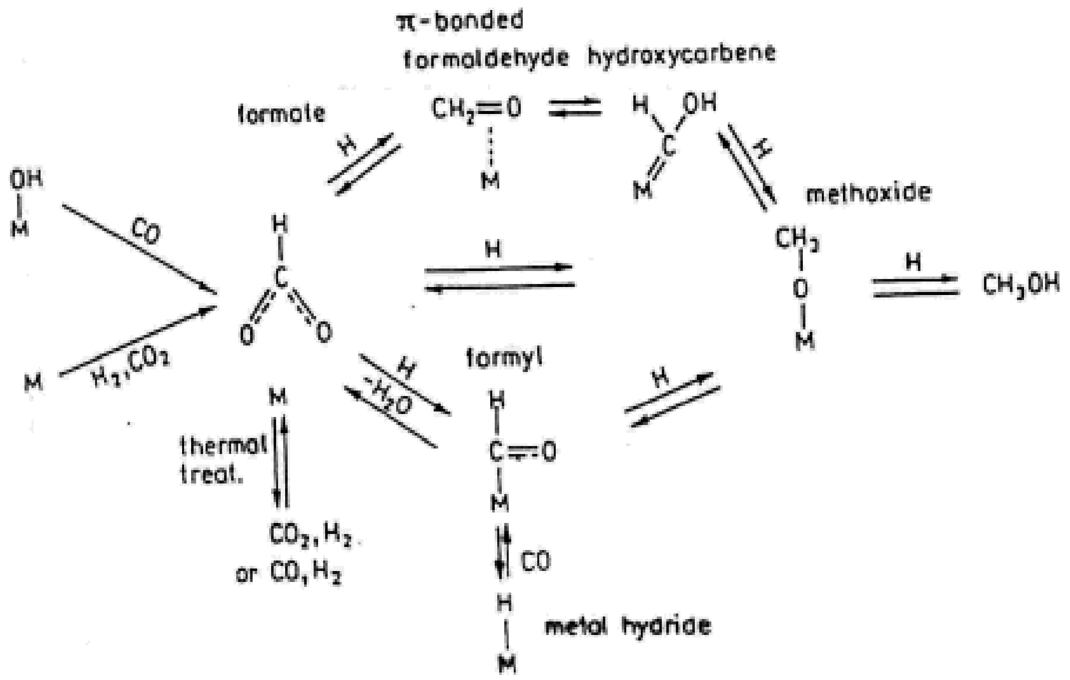
$$CO_2 + 3\,H_2 \rightarrow CH_3OH \rightarrow H.C.$$

- It is possible to overcome the limitation of thermodynamic equilibrium of methanol synthesis using the hybrid catalysts

- Mechanism of methanol synthesis reaction

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

$CO_2 + H_2 \leftrightarrow CO + H_2O$



- Activity of metal catalyst for methanol yield
  - Cu >> Co = Pd = Re > Ni > Fe > > Ru = Pt > Os > Ir = Ag = Rh > Au
- Cu based catalysts
  - $Cu/ZnO/Al_2O_3$, $Cu/La_2Zr_2O_7$, Cu/ZrO_2, $Cu/ZnO/ZrO_2$, Cu/Cr_2O_3, $Cu/ZnO/\ Cr_2O_3$ etc
- Non-copper catalysts
  - Pd/CeO_2, Ag/ZrO_2, Re/ZrO_2, Re/Nb_2O_5 , Mo_2C, PtW/SiO_2

➢ Effective Methanol Synthesis using Cu-ZnO based catalysts

Catalyst	Press (Mpa)	Temp. (^oC)	GHSV (1/h)	MeOH STY (g/l-cat..h)	Reference
H_2/CO_2 = 3/1					
Cu-ZnO-Al_2O_3-Cr_2O_3(43-20-34-3)	3	240	20000	411	
Cu-ZnO-TiO_2(30-35-35)	5	240	20000	504	
La/Cu-ZnO-Al_2O_3-Cr_2O_3(25-42-32-1)	8	250	4700	502	
Cu-ZnO-Ga_2O_3	5	250	18000	738*	Saito et al. Appl.Catal.,1996
$H_2/CO_2/CO$ = 75/22/3					
Cu-ZnO-ZrO_2-Al_2O_3-Ga_2O_3	5	250	18000	785*	Saito et al. Appl.Catal.,1996
Pd/Cu-ZnO-ZrO_2-Al_2O_3-Ga_2O_3 - Cr_2O_3 (1wt%/38-29-13-18-2)	8	270	18800	1300	Inui et al., Catal. Today, 1997
$H_2/CO/CO_2/CH_4$ = 70/20/7/3					
Cu-ZnO-Al_2O_3-(24-38-38)	5	226	12000	700 (ICI)	
Cu-ZnO-Al_2O_3-(64-32-4)**	5	250	10000	300 (Academic)	
Cu-ZnO-Cr_2O_3	10	253	12000	1225 (Lurgi)	

* STY : g/kg-cat.h, ** H_2/CO (no CO_2 in feed gas)

➢ Synthesis of Higher Alcohol

Catalyst	Reaction Conditions	CO_2 conversion (%)	Products Selectivity (%)	Reference
*K/CuZnFe	7MPa, 300°C, GHSV = 5400/h, H_2/CO_2 =3/1	44.4	MeOH(2), EtOH(19.5), C_{3+}OH(6.2)	Arakawa et al., Chem & Ind. Chem, 1994
*5wt%Rh-Fe-Li/SiO_2	5MPa, 260 °C, GHSV = 6000/h, H_2/CO_2 =3/1	14.1	MeOH(22.8), EtOH(34.0)	Arakawa et al., ICCDU, 1997
#$Ru_3(CO)_{12}$-$Co_2(CO)_8$-LiBr	20MPa, 200 °C, 18hrs, H_2/CO_2 =5/1	42	EtOH(36.2%)	Saito et al., J.Mol. Catal., 1994

* $H_2 + CO_2 \rightarrow CO + H_2O$
$2CO + 4H_2 \rightarrow EtOH + H_2O$

Homogeneous catalyst system : $H_2 + CO_2 \rightarrow CO + H_2O \rightarrow MeOH \rightarrow EtOH$

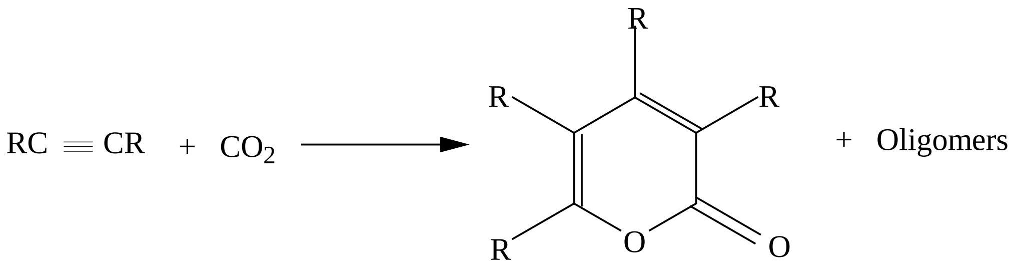
➢ Carboxylic acid synthesis

Products	Catalyst	Reaction Conditions	Yield	Referemce
Formic acid	metal complex such as $HM(CO)_5^-$ (M : W, Cr, Ru)	25 °C, 40atm, 12hr	1.76 mol/dm^3	Darensbourg et al., Chemtech, 1985
	Supercritical mixture of H_2/CO_2 with $N(C_2H_5)_3$ using $RuH_2\{P(CH_3)_3\}_4$	20.5MPa, 50 °C, H_2/CO_2 =1/1.4	1,400 mol/mol-cat.hr	Noyori et al., Nature, 1994
Acetic acid	$Ag\text{-}Rh/SiO_2$	2MPa, 200 °C, H_2/CO_2 =1/2	28.1μ mol/g.h	Hattori et al., Chem. Lett., 1991
	$Ru_3(CO)_{12}$ + $Co_2(CO)_8$ in DMF	4MPa, 150 °C, H_2/CO_2 =1/1, 24hrs	2.5 mmol/g	Fukuoda et al., Chem. Lett., 1995

➢ New C-C Bond Formation

CO_2 + unsaturated hydrocarbons → Ester, Lactone, Pyrone, Acid

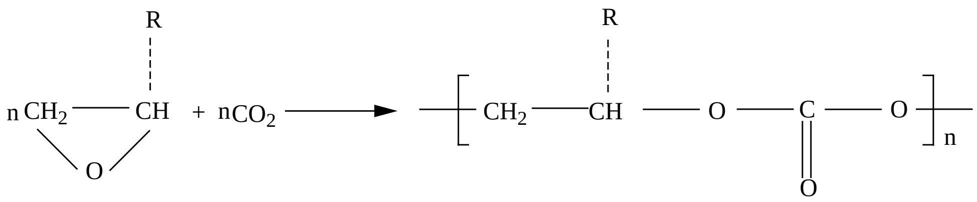
Ex)



Catalyst : Homogeneous transition metal(Pd, Ru, Rh, Ni) complex

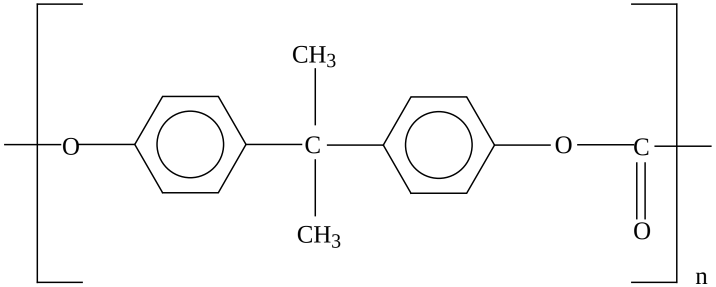
Reactants	Metals	Products
Alkynes	Rh, Ni	Pyrones
Alkenes	Ru, Rh	Acids, esters
Allenes	Pd	Lactones, esters
Dienes	Ru, Rh, Ni, Pd	Lactones, acids, esters
Cyclopropanes	Pd	Lactones
Aromatic Compounds	Pd	Acids

➢ Polymer Synthesis



Catalyst : Organo-zinc, organo-aluminum

* Conventional polycarbonate



Characteristics of the polycarbonates by CO_2 copolymerization

- Biodegradable, Biocompatible

- Thermally unstable