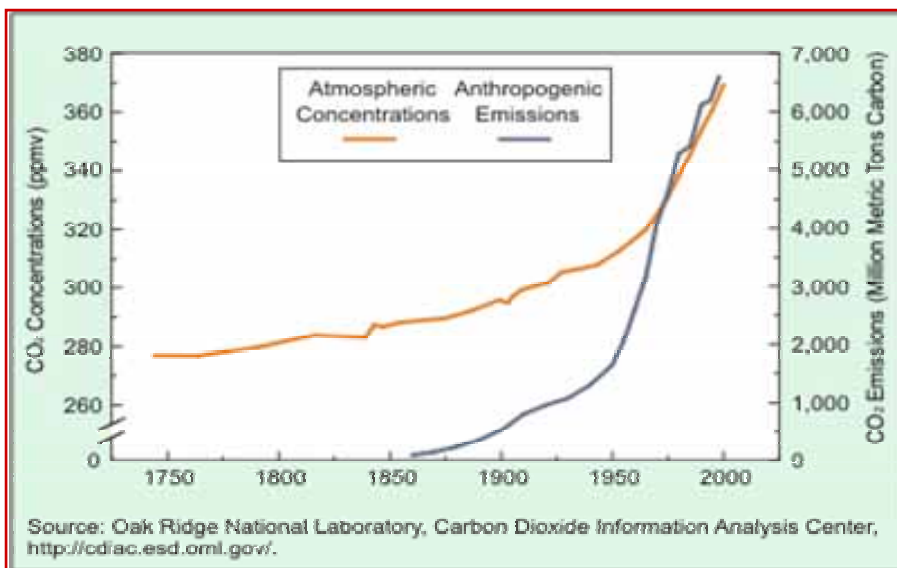# Carbon Dioxide Reduction Catalysis for the Production of Fuels and Chemicals
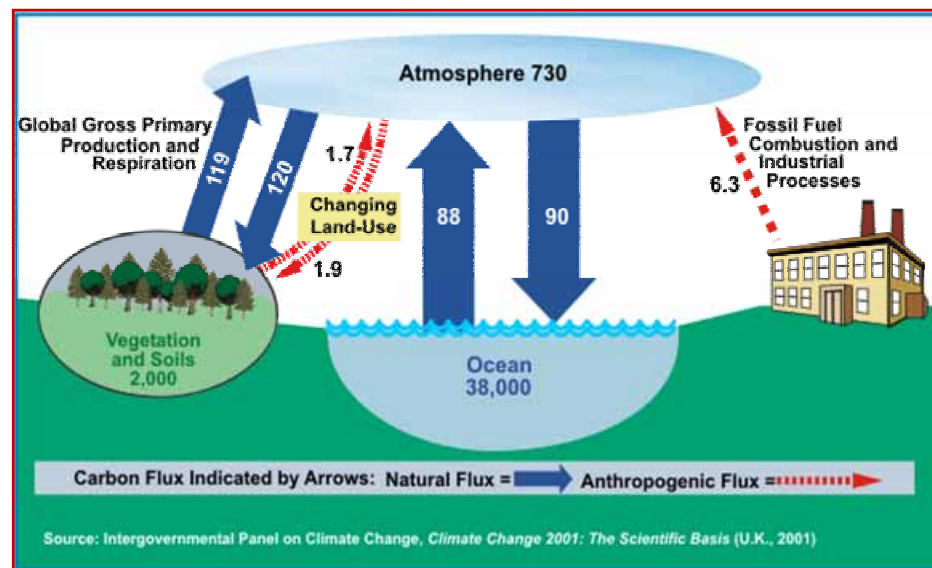
B. Viswanathan

**Department of Chemistry
Indian Institute of Technology Madras
INDIA**

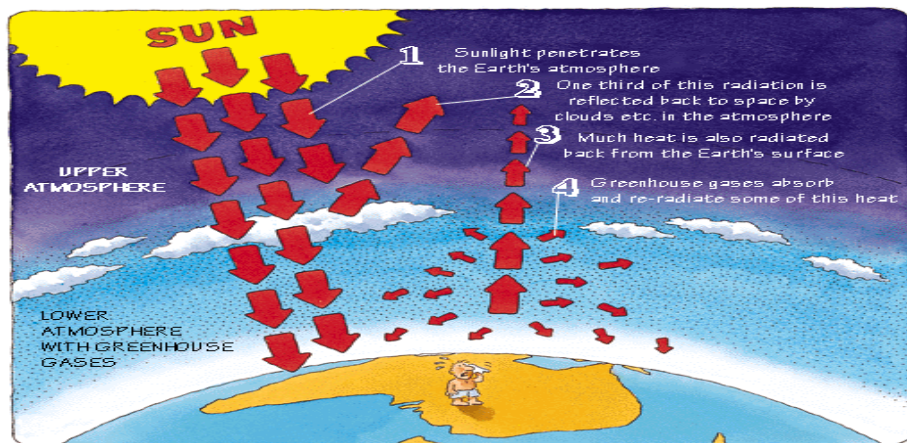# Increasing Atmospheric Levels

**Trends in Atmospheric Concentrations & Anthropogenic Emissions of Carbon Dioxide**

**Global Carbon Cycle (Billion Metric Tons Carbon)**

Estimating the risks that would follow from a global climatic change & developing strategies for the prevention of further increase in atmospheric CO_2 concentrations are undoubtedly important tasks!

http://www.eia.doe.gov/oiaf/1605/ggccebro/chapter1.html

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Prospect for Future Emissions
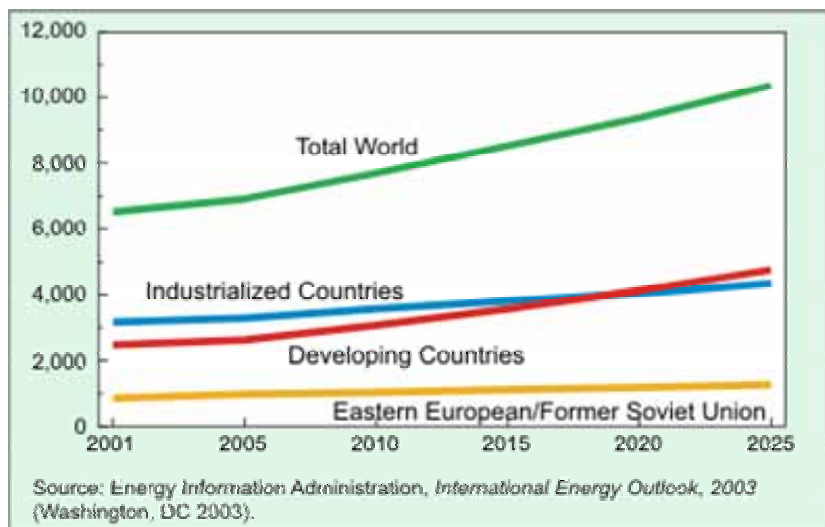
*World Carbon Dioxide Emissions by Region, 2001-2025
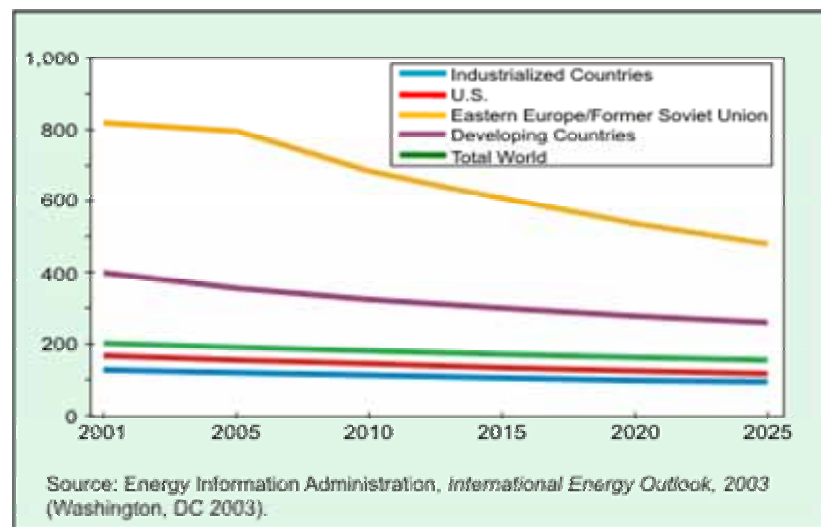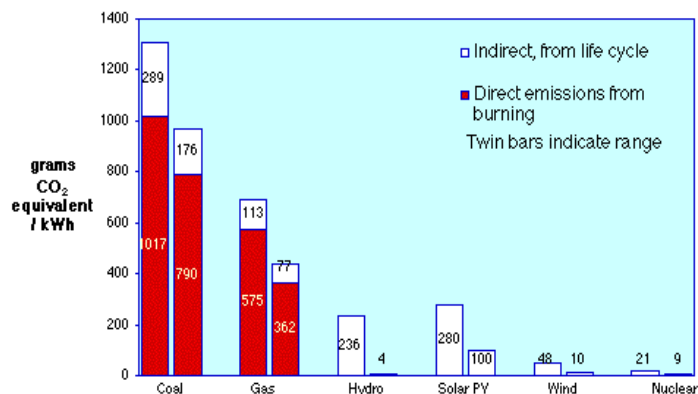

*Carbon Intensity by Region, 2001-2025

http://www.eia.doe.gov/oiaf/1605/ggccebro/chapter1.html
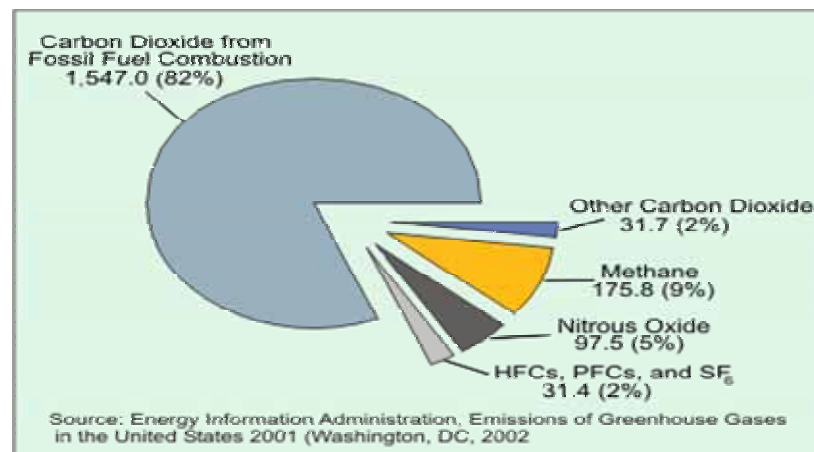
*U.S. Anthropogenic Greenhouse Gas Emissions by Gas, 2001
* (Million Metric Tons of Carbon Equivalent)

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Energy Vs. Emission

Greenhouse Gas Emissions from Electricity Production

Source: IAEA 2000

Commercial/Marketed Energy Consumption, U.S. vs. Asia

U.S. Primary Energy Consumption — Resulting Carbon Dioxide Emissions

Source: Energy Information Administration.
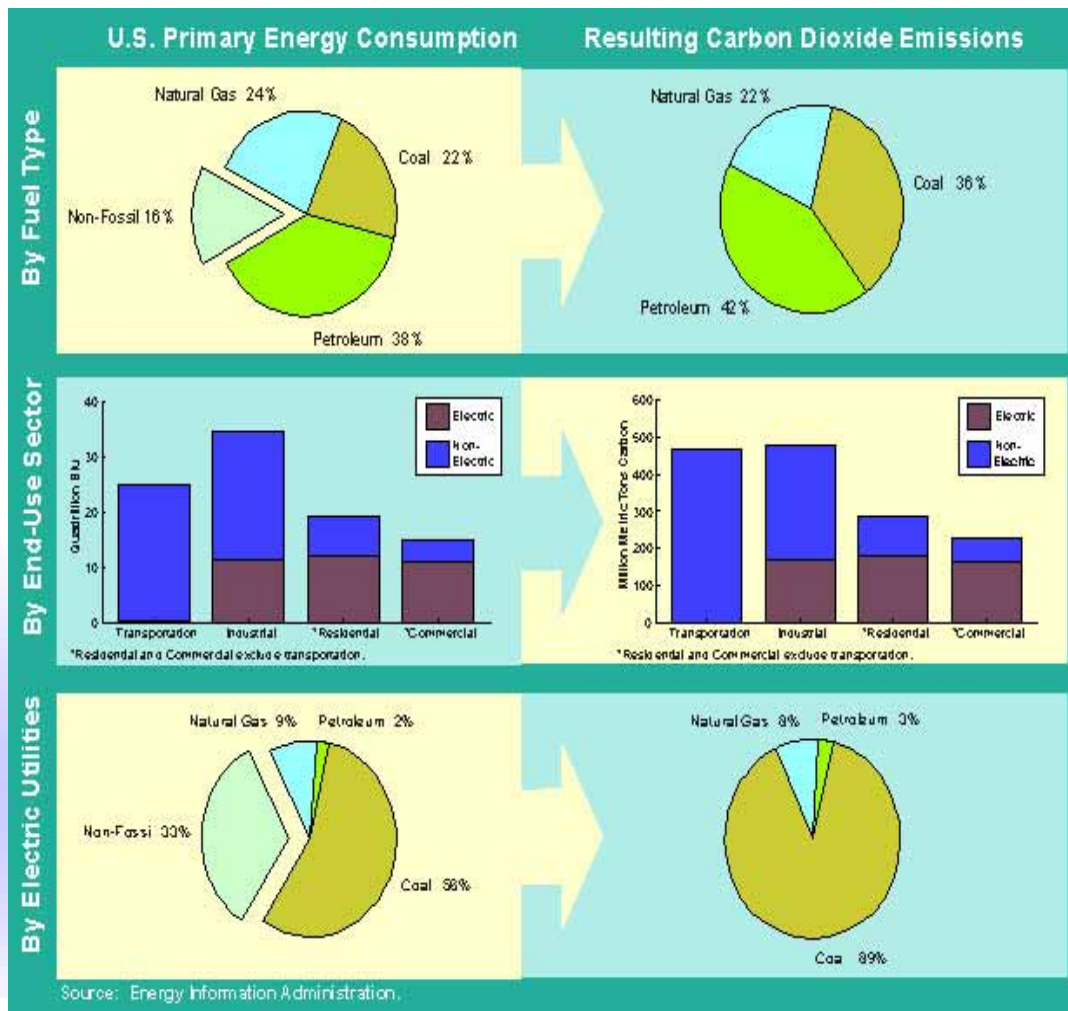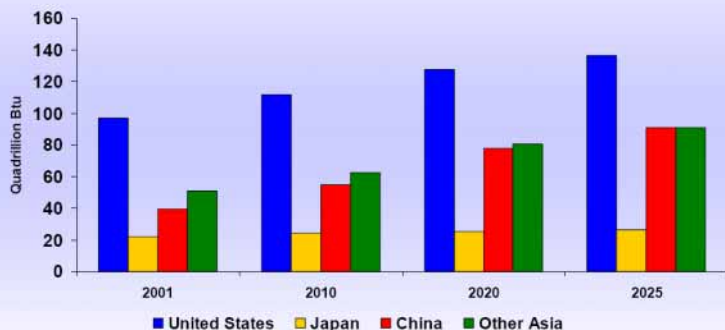
World population, energy & electricity demands are ever increasing and are directly related to emission levels

http://www.eia.doe.gov/oiaf/1605/ggccebro/chapter1.html

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CO$_2$ Emission: A Closer Look at the Numbers

World Carbon Dioxide Emissions by Fuel Type, 1990-2025
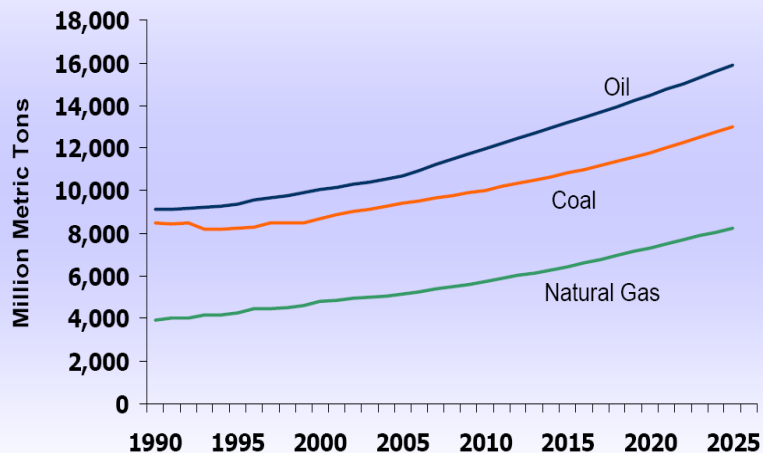
CO2 Emissions by Region and Fuel
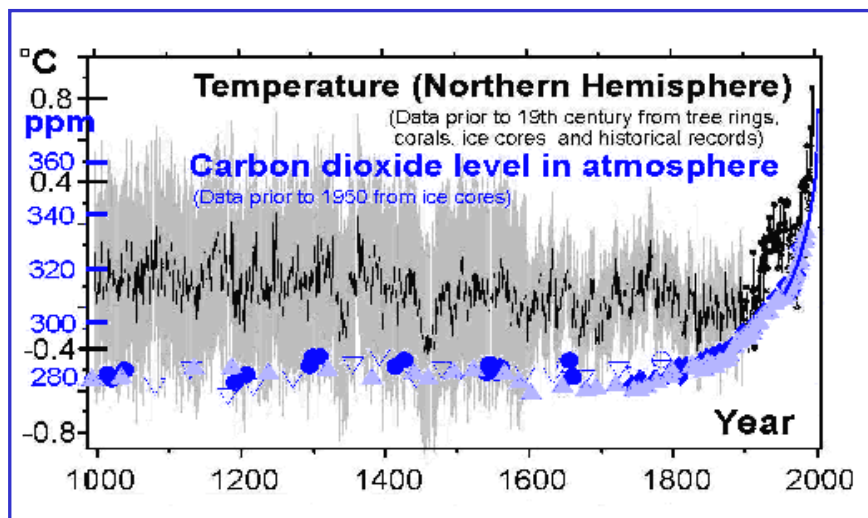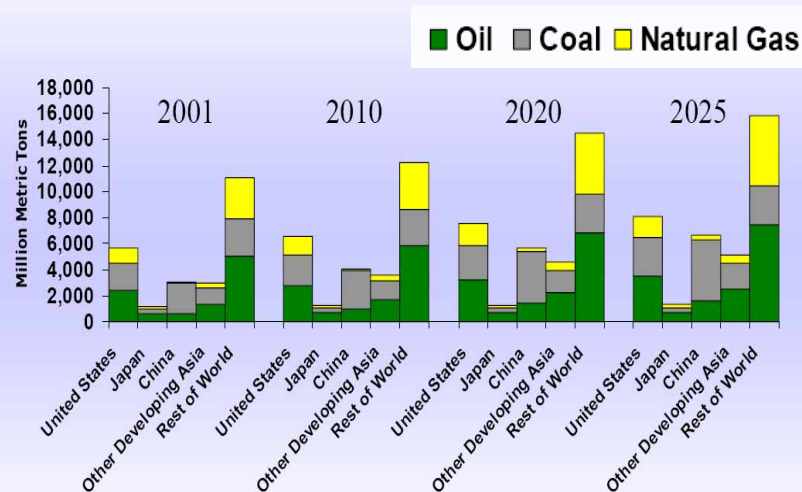
Small amount of anthropogenic additions exhibit a large effect on climate change

http://www.eia.doe.gov/oiaf/1605/ggccebro/chapter1.html

Carbon Cycle

Movement of carbon in its many forms, between the biosphere, atmosphere, oceans & geo-sphere
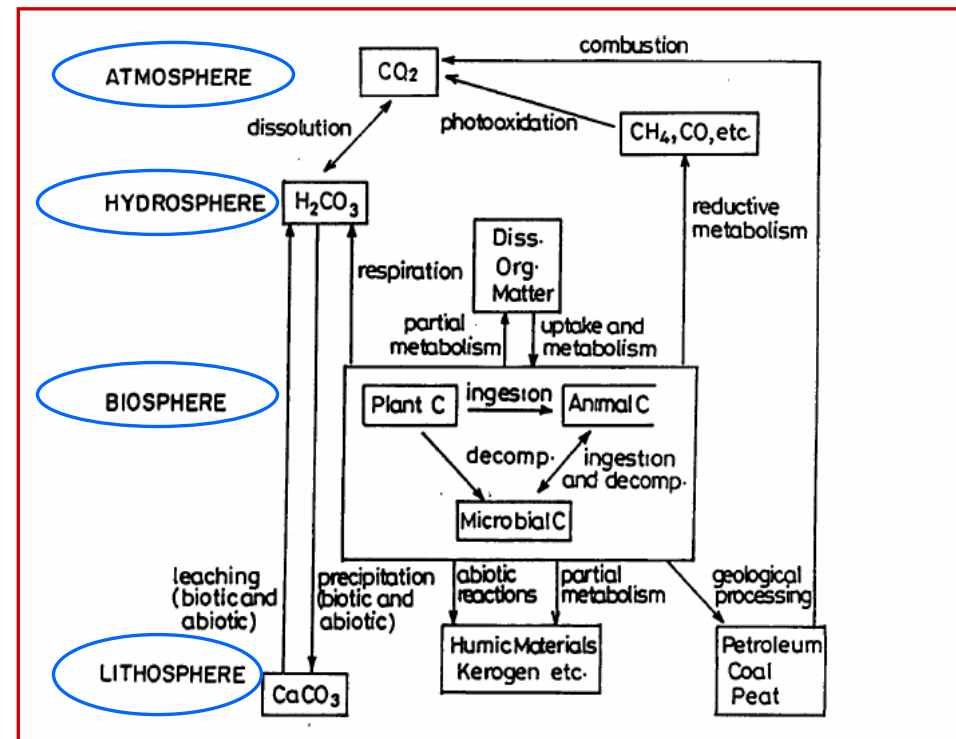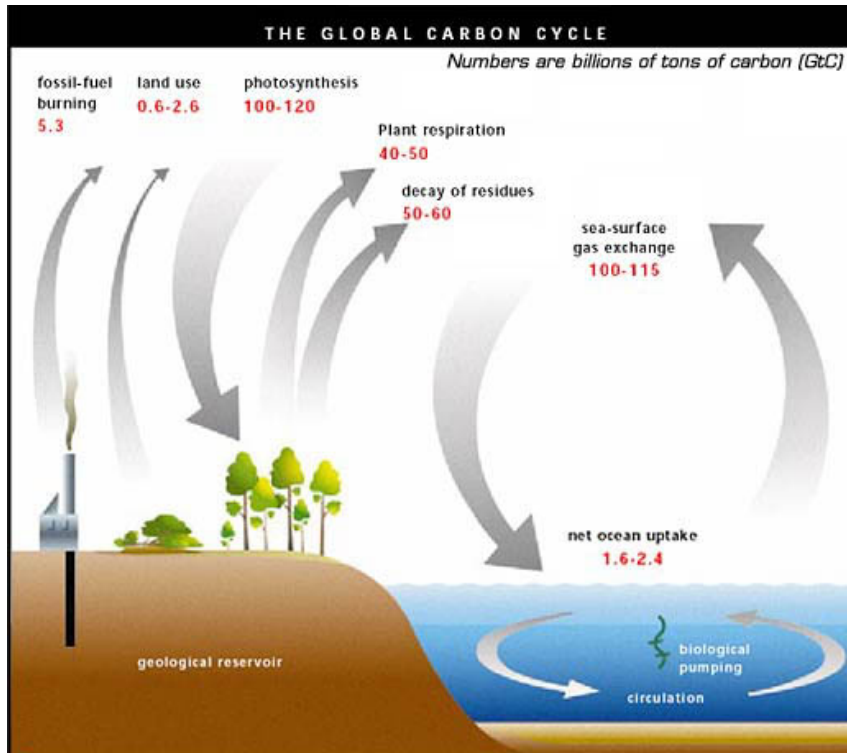
Natural flux of carbon would be imbalanced by anthropogenic additions from fossilized matters

Sources & Sinks

Sources
- Large, concentrated
- Large, dilute
- Distributed

Sinks
- Geologic
- Ocean
- Terrestrial
- Mineral
- Utilization

Example Strategies
- Large Concentrated Sources (e.g., Sleipner)
  - Transport – Storage
- Large Dilute Sources (e.g., Power Plants)
  - Capture – Transport – Storage
- Distributed Sources (e.g., cars, homes)
  - Decarbonization/Capture – Transport - Storage
  - e.g., hydrogen economy
- All sources
  - Remove from Air – Storage
  - e.g., trees, iron fertilization, non-biological

Storage Reservoirs Key Challenges
- Geologic – safety
- Ocean - environmental acceptability
- Terrestrial - permanence
- Mineral - economics

> The trend towards recovery of CO_2 will probably greatly intensify in the future, leading to the increasing availability of large quantities of this cheap raw material

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CO$_2$-fixation & Calvin cycle

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Photosynthesis: $6CO_2 + 12H_2O \rightarrow C_6H_{12}O_6 + 6H_2O + 6O_2$

$C_5 + CO_2 + ATP + NADPH \rightarrow C_6H_{12}O_6$
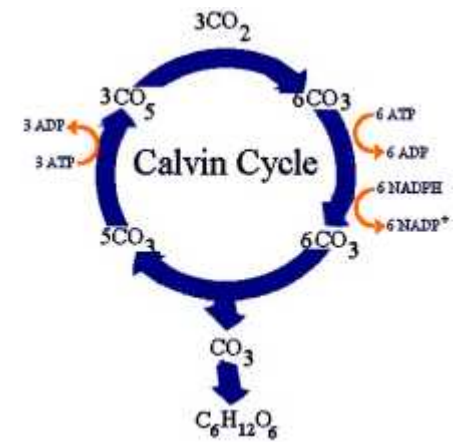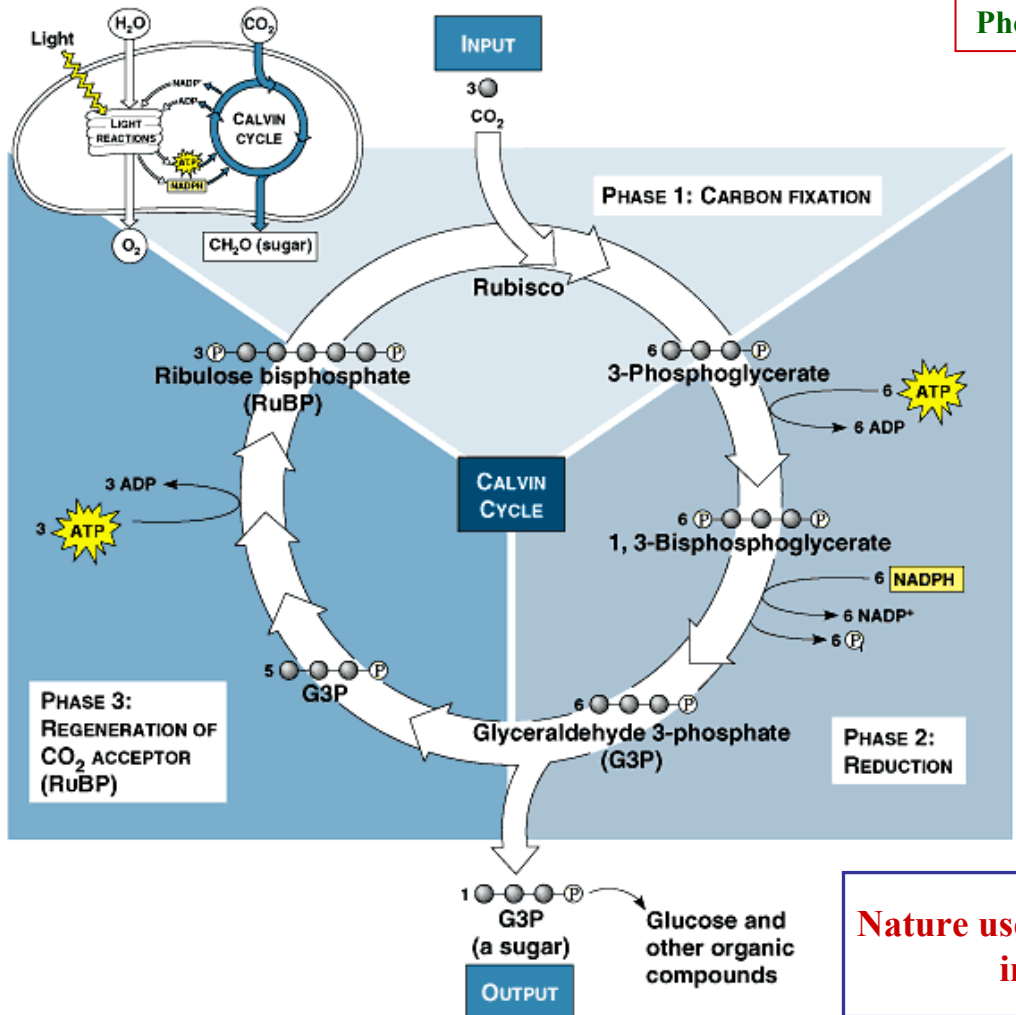
Nature uses CO$_2$ so successfully as a synthetic building block in photosynthesis- the basis of life on earth!

A Lesson from nature?

R & D Areas

GLOBAL WARMING

Global Reproduction Plan

CO_2 Separation & Collection Technology

CO_2 Capture Technology

CO_2 Utilization Technology

CO_2 Disposal Technology

Environmental Friendly Productive Technology

Field Investigation
Development of model

Bacteria
Algae
Other related items

Land disposal
Ocean disposal
Other related items

Absorption
Adsorption
Membrane
Other related items

Methanol
Manure-feed oil
Other related items

Hydrogen
Catalyst
Other related items

Challenges: Large-Scale CO_2 Utilization & Sequestration

Two Critical Challenges

Reducing Costs

- Separation and capture costs prime target right now
- Efficient power plants critical starting point
- Essential to reduce energy penalty
- How to judge?
  - Relative to other alternatives
  - Relative to status quo

Developing Storage Reservoirs

- Need to be safe and environmentally acceptable
- Need to be effective, issue of permanence
- Economical
  - Development costs
  - Monitoring costs
  - Location relative to emissions source

Problem Matter or Inexpensive Raw Material?

Global CO$_2$ Emission

Commercial Use of CO$_2$

CO$_2$ Disposal

- **Ocean**
- **Subterranean**
- **Terrestrial**
- **Biological Fixation**

CO$_2$ as Raw Material in Chemical Processes

CO$_2$ as Resource in Technological Processes

Entire molecule incorporated in the product

↓

Urea & derivatives
Organic carbonates (DMC)
Salicylic acid & deriv.
Polymers
Org. intermediates & fine chem.
Inorganic carbonates

CO$_2$ in reduction process → C$_n$ molecules

↓

Richer in energy,
Producing bulk chemicals
Methanol (alt. for gasoline)
CO, CH$_4$ & other
Cn molecules

- ✓ **Addition to beverage & drinks**
- ✓ **Food packaging & freezing**
- ✓ **Manuring subs. in horticulture**
- ✓ **Industrial extraction, Foaming agent**
- ✓ **Enhanced oil recovery**
- ✓ **Waste water treatment**
- ✓ **Inert atmosphere**
- ✓ **Cold welding &molding processes**
- ✓ **Dry-ice cooling foodstuffs**
- ✓ **Cleansing processes, Lasers**
- ✓ **Calibration gas, Smoke effects**
- ✓ **Metal production**
- ✓ **Anaesthetize agent for pigs**

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Comparison of the properties of various C_1 building blocks

Factors	CO	$COCl_2$	CO_2
MAK Value	30 ppm	0.1 ppm	5000 ppm
Toxicology	Affinity for Hemoglobin 210 times that of O_2	War gas	Danger of asphysiation at 10 vol % in air
Environmental Hazard	Yes	High	Negative
Flammability	12 – 74 vol %	No	No
Boiling point	81 K	291 K	195 K (subl)
Storage	Only at < 3.5 Mpa	Very difficult	No problem
Transport	Gas bottles or tanks kg quantities	Possible	Gas bottles or tanks

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Attempts at CO_2 reduction

- **Radiochemical**

$$CO_2 \xrightarrow{\gamma\text{-radiation}} HCOOH, HCHO$$

- **Chemical reduction**

$$2Mg + CO_2 \rightarrow 2MgO + C$$
$$Sn + 2CO_2 \rightarrow SnO_2 + 2CO$$
$$2Na + 2CO_2 \rightarrow Na_2C_2O_4$$

- **Thermo chemical**

$$CO_2 \xrightarrow[T>900°C]{Ce4+} CO + \tfrac{1}{2}O_2$$

- **Photo chemical**

$$CO_2 \xrightarrow{h\nu} CO, HCHO, HCOOH$$

- **Electrochemical**

$$CO_2 + xe^- + xH^+ \xrightarrow{eV} CO, HCOOH, (COOH)_2$$

- **Biochemical**

$$CO_2 + 4H_2 \xrightarrow{bacteria} CH_4 + 2H_2O$$

- **Biophotochemical**

$$CO_2 + \text{oxoglutaric acid} \xrightarrow{h\nu} \text{isocitric acid}$$
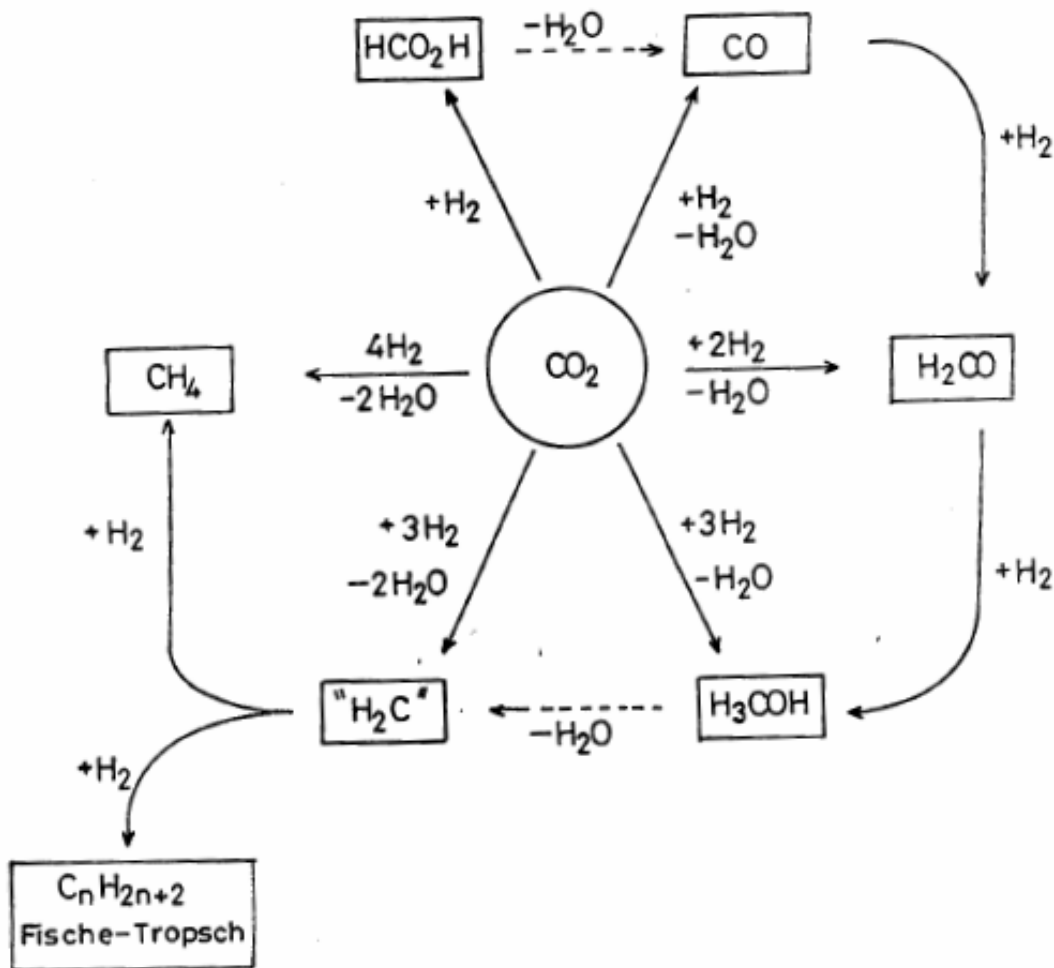
- **Photo electrochemical**

$$CO_2 + 2e^- + 2H^+ \xrightarrow[eV,\ semicond]{h\nu} CO + H_2O$$

- **Bioelectrochemical**

$$CO_2 + \text{oxoglutaric acid} \xrightarrow[eV,\ methylviologen]{enzyme} \text{isocitric acid}$$

- **Biophotoelectrochemical**

$$CO_2 \xrightarrow[eV,\ methylviologen]{h\nu.\ enzyme,\ p\text{-}1nP} HCOOH$$

Reduction of CO_2 to provide sources for industrially important products

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Selected properties of CO_2

Point group	Dαh
Ground state	$1\Sigma_g^+$
Boiling point (°C)	-78.5
LUMO	$2\pi_u$
HOMO	$1\pi_g$
Bond length (Å)	1.16 (C-O)
Bond energy (eV)	5.453
Ionization potential (eV)	13.78
Electron affinity (eV)	-0.6
IR data (cm^{-1})	1320, 235, 668

MO diagram for CO_2
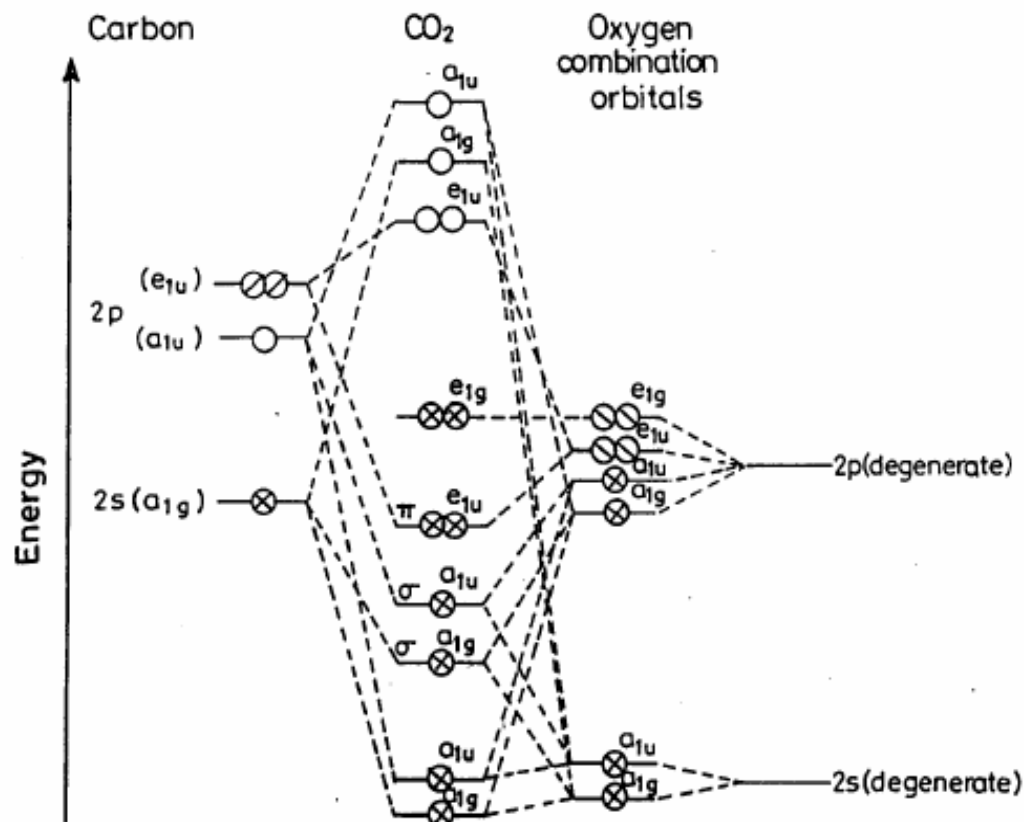
M. A. Scibioh & B. Viswanathan, Proc. Indn. Natl. Acad. Sci., 70 A (3), 2004. 407-462.

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Department of Chemistry

Energy Considerations

ΔG^o_f (kJ/mole) for Key Carbon Compounds

C_6H_6 (+130)

CH_4 (-51)

HCHO (-102)

CO (-137)

CH_3OH (-166)

HCOOH (-361)

NH_2COOH (-364)

CO_2 (g) (-374)

CO_2 (aq) (-386)

$CO_3^=$ (aq) (-527)*   *Need: water to supply energy of hydration
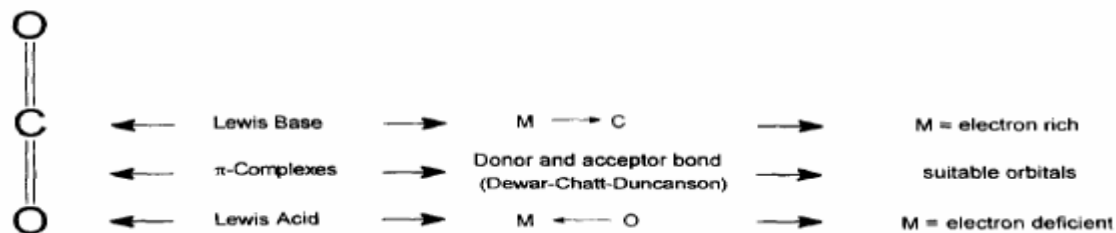
HCO_3^- (aq) (-586)*

$C_2O_4^=$ (aq) (-671)*

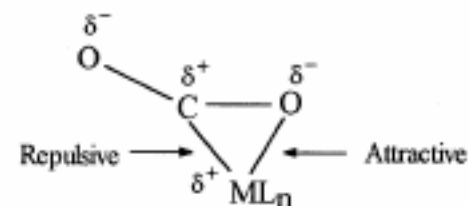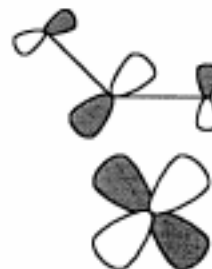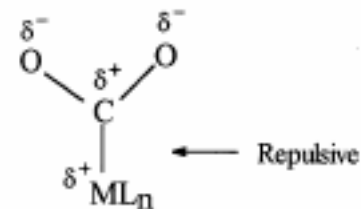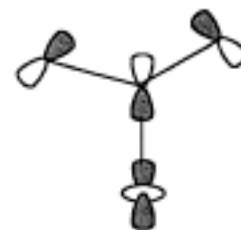$CaCO_3$ (s) (-1130)**   **Need: alkali to supply neutralization energy
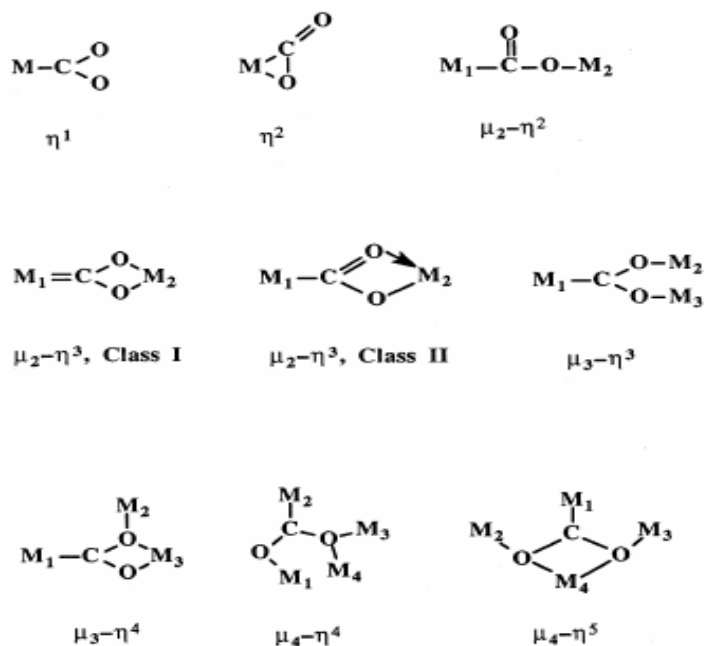
Interaction of CO$_2$ with Transition Metal Centers

Reactive positions of CO$_2$ molecule & electronic properties of a transition metal centre required for complexation
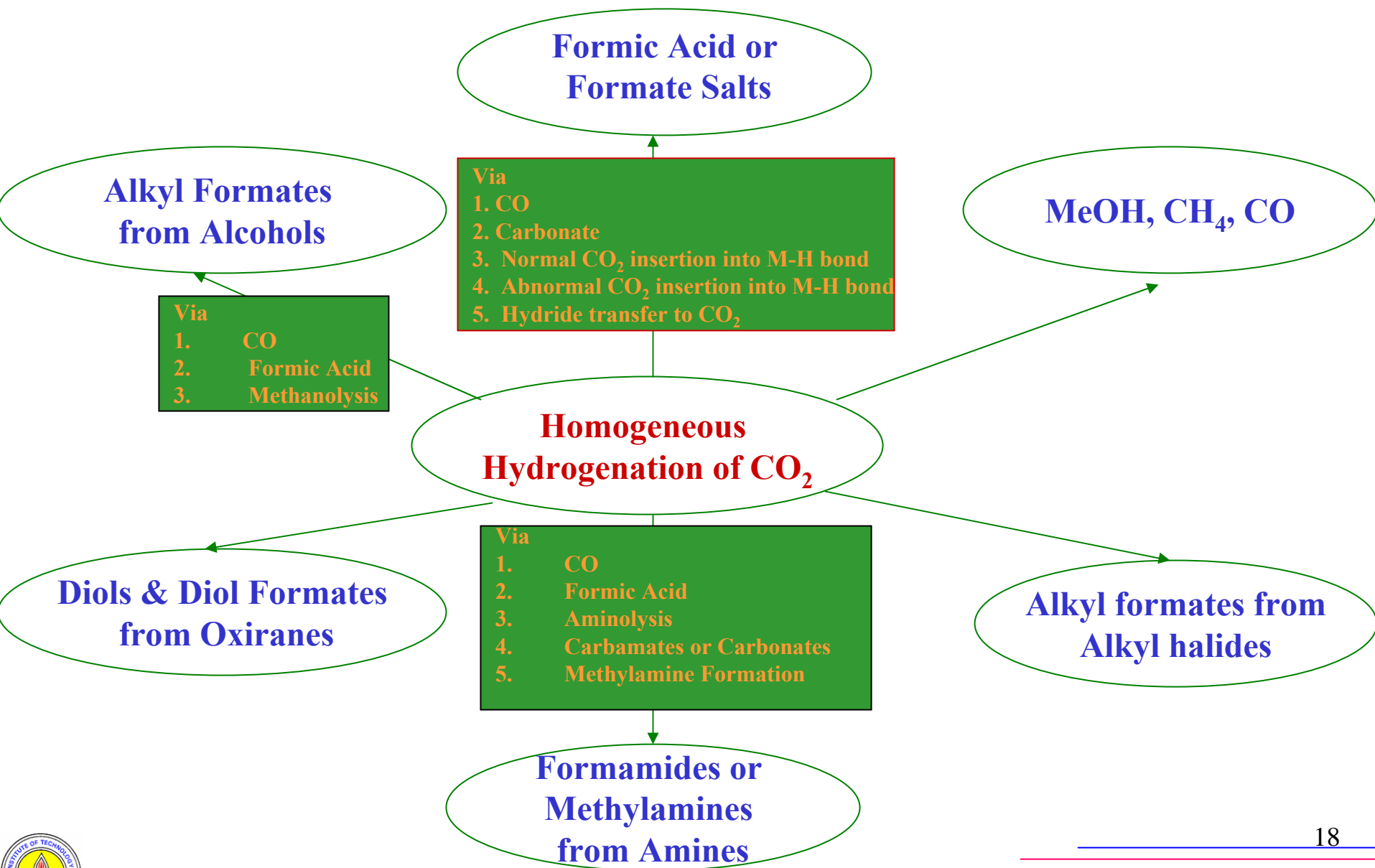

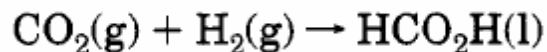**Structural types of metal–CO$_2$ complexes**

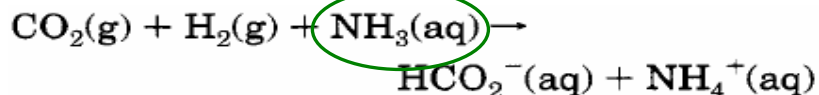**Orbital overlapping & electrostatic interaction of coordination modes of CO$_2$**

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Homogeneous Hydrogenation of Carbon Dioxide

Formic Acid or Formate Salts

Alkyl Formates from Alcohols

Via
1. CO
2. Carbonate
3. Normal CO_2 insertion into M-H bond
4. Abnormal CO_2 insertion into M-H bond
5. Hydride transfer to CO_2

Via
1. CO
2. Formic Acid
3. Methanolysis

MeOH, CH_4, CO

Homogeneous Hydrogenation of CO_2

Via
1. CO
2. Formic Acid
3. Aminolysis
4. Carbamates or Carbonates
5. Methylamine Formation

Diols & Diol Formates from Oxiranes

Alkyl formates from Alkyl halides

Formamides or Methylamines from Amines

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Producing Formic Acid or Formate Salts

$$CO_2(g) + H_2(g) \rightarrow HCO_2H(l)$$

$$\Delta G^\circ = 32.9 \text{ kJ/mol}; \Delta H^\circ = -31.2 \text{ kJ/mol};$$
$$\Delta S^\circ = -215 \text{ J/(mol K)}$$

$$CO_2(g) + H_2(g) + NH_3(aq) \rightarrow$$
$$HCO_2^-(aq) + NH_4^+(aq)$$

$$\Delta G^\circ = -9.5 \text{ kJ/mol}; \Delta H^\circ = -84.3 \text{ kJ/mol};$$
$$\Delta S^\circ = -250 \text{ J/(mol K)}$$

$$CO_2(aq) + H_2(aq) + NH_3(aq) \rightarrow$$
$$HCO_2^-(aq) + NH_4^+(aq)$$
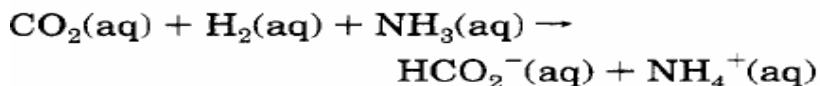
$$\Delta G^\circ = -35.4 \text{ kJ/mol}; \Delta H^\circ = -59.8 \text{ kJ/mol};$$
$$\Delta S^\circ = -81 \text{ J/(mol K)}$$

**Addition of a base improves enthalpy of reaction, while dissolution of gases improves the entropy**

Effective homogeneous catalysts → Complexes of 2nd & 3rd row metals of groups 8 - 10, usually with halides or hydride as anionic & phosphines as neutral ligands.

catalyst precursor	solvent	additives	P_{H_2/CO_2} (atm)	T (°C)	t (h)	TON	TOF (h^{-1})
$Pd(dppe)_2$	C_6H_6	$N(C_2H_5)_3 + H_2O$	25/25	110	20	62	3
$RuH_2[P(C_6H_5)_3]_4$	C_6H_6	$N(C_2H_5)_3 + H_2O$	25/25	rt	20	87	4
$PdCl_2$	H_2O	KOH	110/na	160	3	1580	530
$Pd(dppe)_2$	C_6H_6	NaOH	24/24	rt	20	17	0.9
$RuH_2[P(C_6H_5)_3]_4$	C_6H_6	Na_2CO_3	25/25	100	4	169	42
$RhCl[P(C_6H_5)_3]_3$	C_6H_6	Na_2CO_3	60/55	100	3	173	58
$[RuCl_2(CO)_2]_n$	$H_2O + i\text{-PrOH}$	$N(C_2H_5)_3$	81/27	80	0.3ᵃ	400	1300
$K[RuCl(EDTA\text{-}H)]$	H_2O	–	3/17	40	0.5	na	250
$[Rh(nbd)\{P(CH_3)_2(C_6H_5)\}_3]BF_4$	THF	H_2O	48/48	40	48	128	3
$[Rh(cod)Cl]_2$	DMSO	$N(C_2H_5)_3 + dppb$	20/20	rt	22	1150	52
$[Rh(cod)Cl]_2$	DMSO	$N(C_2H_5)_3 + dippe$	40 total	24	18	205	11
$RhCl[P(C_6H_4\text{-}m\text{-}SO_3Na)_3]_3$	H_2O	$NH(CH_3)_2$	20/20	rt	12	3439	287
$PdCl_2[P(C_6H_5)_3]_2$	C_6H_6	$N(C_2H_5)_3 + H_2O$	50/50	rt	na	15	na
$RuH_2[P(CH_3)_3]_4$	$scCO_2$	$N(C_2H_5)_3 + H_2O$	85/120	50	1	1400	1400
$RuCl_2[P(CH_3)_3]_4$	$scCO_2$	$N(C_2H_5)_3 + H_2O$	85/120	50	47	7200	150
$[RhH(cod)]_4$	DMSO	$N(C_2H_5)_3 + dppb$	40 total	rt	0.8	312	390
$[RhH(cod)]_4$	DMSO	$N(C_2H_5)_3 + dppb$	40 total	rt	18	2200	122

P.G.Jessop, Chem. Rev. 95 (2), (1995) 259

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Normal CO$_2$ Insertion into an M-H Bond	Abnormal CO$_2$ Insertion into an M-H Bond
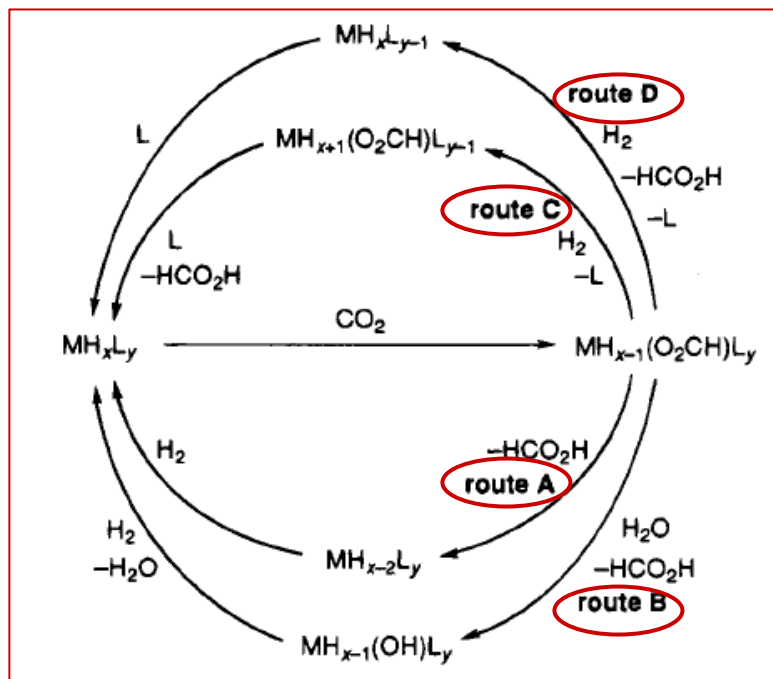
"Dihydride" route
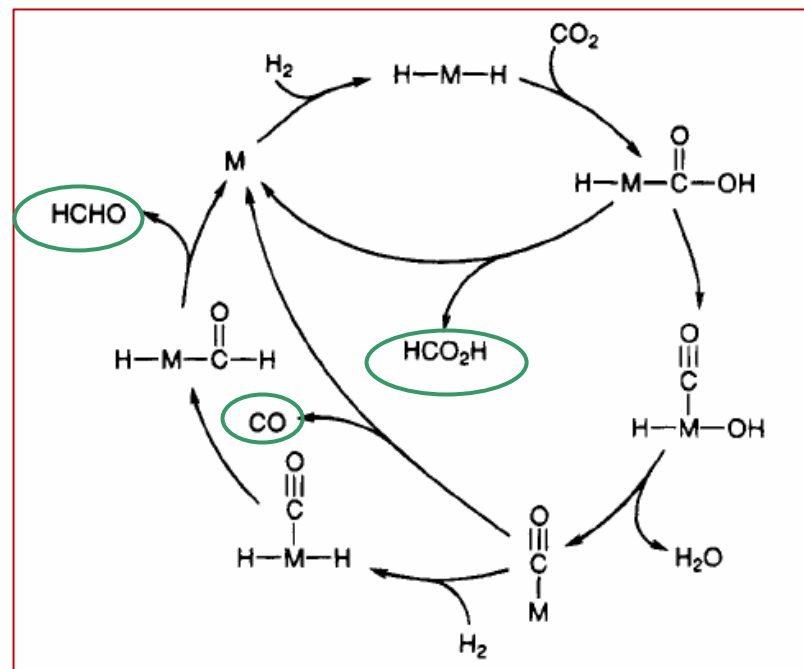
"Unsaturate" route –
Coordination of CO$_2$ before addition of H$_2$

Products Generation!

Hydrogenation of $CO_2 \rightarrow CO, CH_3OH, CH_4$

$$CO_2(aq) + H_2(aq) \rightarrow CO(aq) + H_2O(l) \quad \Delta G° = 11 \text{ kJ/mol}; \Delta H° = 11 \text{ kJ/mol}; \Delta S° = -0.8 \text{ J/(mol K)}$$

$$CO_2(aq) + 3H_2(aq) \rightarrow CH_3OH(l) + H_2O(l) \quad \Delta G° = -79 \text{ kJ/mol}; \Delta H° = -106 \text{ kJ/mol}; \Delta S° = -88 \text{ J/(mol K)}$$

$$CO_2(aq) + 4H_2(aq) \rightarrow CH_4(l) + 2H_2O(l) \quad \Delta G° = -193 \text{ kJ/mol}; \Delta H° = -230 \text{ kJ/mol}; \Delta S° = -125 \text{ J/(mol K)}$$

The thermodynamics are neutral or favorable because of the production of water from hydrogen but economics are unfavorable for the same reason

Diols and Diol Formates from Oxiranes

CO_2 with methyloxirane in the presence of $H_2 \rightarrow$ 1,2-diols & their formates in addition to cyclic carbonate

Products Generation!

Catalytic hydrogenation of CO_2 in supercritical CO_2 in the presence of additional substrates

Cycloco-oligomerisation of CO_2 & alkynes in compressed CO_2
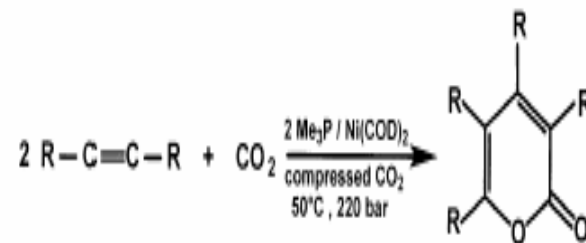
$R = C_2H_5$: TON = 20-40   Selectivity : 98,5%
$R = C_4H_9$: TON = 2   Selectivity : 93%

The hitherto solely highly selective catalytic C–C coupling reaction using CO_2 as substrate can also be realised in compressed CO_2

Styrene or cyclooctene react in a catalytic system → epoxidation as well as the reaction to cyclic carbonates

➤ The potential of this types of catalytic reaction is by no means yet explored.

➤ The field of homogeneous catalysis in compressed CO_2 will attract major interest in future.

➤ The development of new CO_2 soluble catalysts, understanding how to prevent deactivation reactions with CO_2 as well as the control of the fine tuning of the reaction parameters in $scCO_2$ are starting points to discover new selective catalysis in $scCO_2$
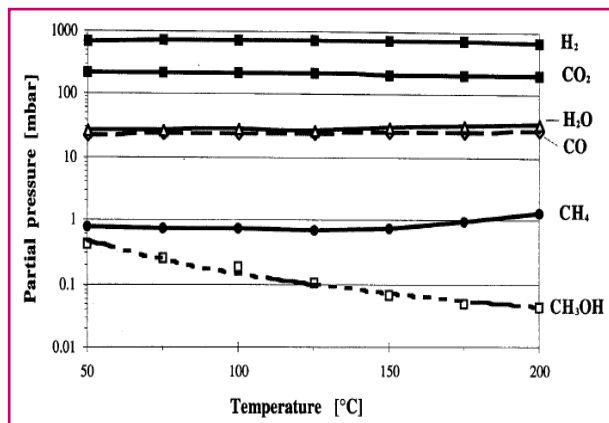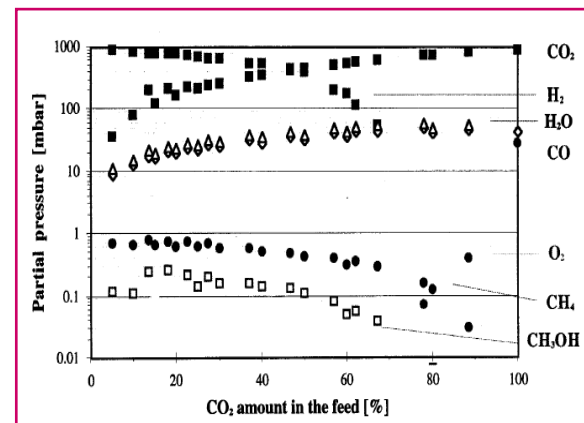
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Direct control technologies

Capture, Disposal or Chemical recycling

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH \text{ (g)} + H_2O \text{ (g)}$$
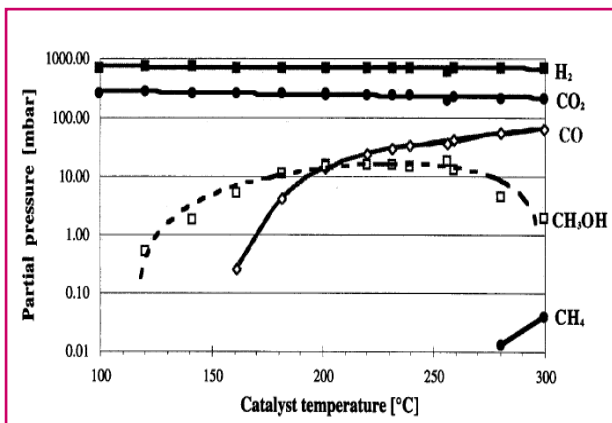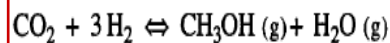
H$_2$/C0$_2$ = 3:1, Pressure = 20 bar, Q$_{tot}$ = 0.6 Nl.min $^{-1}$, Sv = 4500h $^{-1}$)

Electrical power = 400 W, H$_2$/C0$_2$ = 3:1, Pressure = I bar & Qtot = 1 Nl.min $^{-1}$)

Electrical power = 400 W, Pressure = 1 bar, Temp. = 80 °C & Qtot = 1 Nl.min $^{-1}$

If pure hydrogen from renewable sources (e.g. hydroelectric power) is available, an easiest method for converting it to methanol with CO$_2$ is to combine both gases in a thermal reactor at about 220 °C under moderate pressure (20 - 50 bar).

A. Bill, A. Wokaun
Energy Convers. Mgmt. 38, (1997) 415

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Department of Chemistry

CO$_2$ to hydrocarbons

Catalyst: Fe supported on MY-zeolite (M=Li, Na, K, Rb)

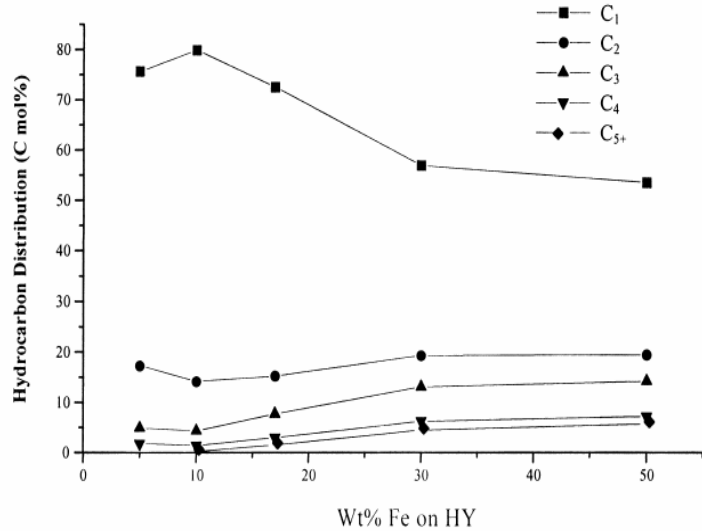Table 2

CO$_2$ hydrogenation[a] over Fe catalysts supported on MY-zeolites

Catalysts (17 wt%)	CO$_2$ conv. (%)	Selectivity (C mol%)		Hydrocarbon distribution (C mol%)									Ol.(%)[b] (Ol.+Pa.)
		CO	HC	C$_1$	C$_2^=$	C$_2$	C$_3^=$	C$_3$	C$_4^=$	C$_4$	C$_5$>	C$_2$–C$_4$
Fe/HY	10.14	39.14	60.86	72.56	0.02	15.23	0.07	7.64	–	2.98	1.49	0.36
Fe/LiY	17.15	44.30	55.59	17.91	3.65	9.37	12.68	4.49	9.64	3.45	38.81	60.01
Fe/NaY	20.76	29.43	69.58	14.62	7.86	4.94	13.46	4.56	11.15	3.52	39.78	71.39
Fe/KY	17.95	31.35	66.49	12.54	8.94	3.18	13.02	3.24	10.40	3.83	44.50	75.93
Fe/RbY	17.24	31.61	65.90	9.54	7.08	2.19	11.56	2.39	9.79	2.72	54.39	79.57

[a]CO$_2$ hydrogenation at 1900 ml/g/h, 573 K, and 10 atm.
[b]Selectivity to olefins (C mol%).

Hydrogenation of CO$_2$ to hydrocarbons over group VIII metals proceeds in 2 steps.
1. Partial reduction of CO$_2$ to CO by reverse water gas shift (RWGS) reaction
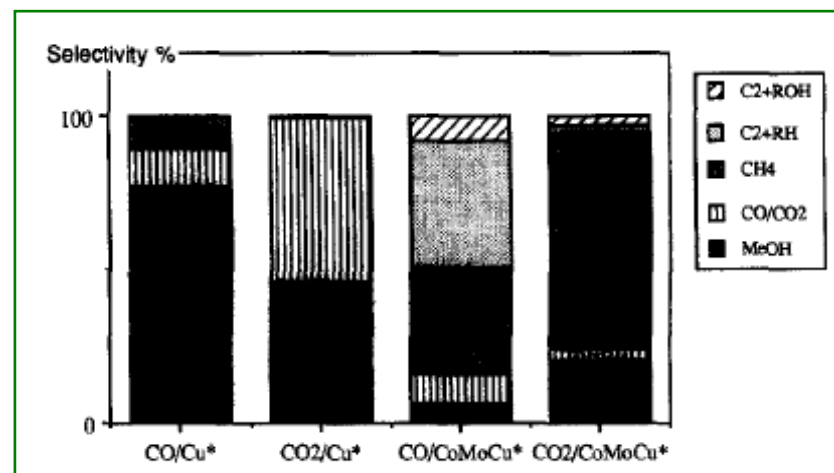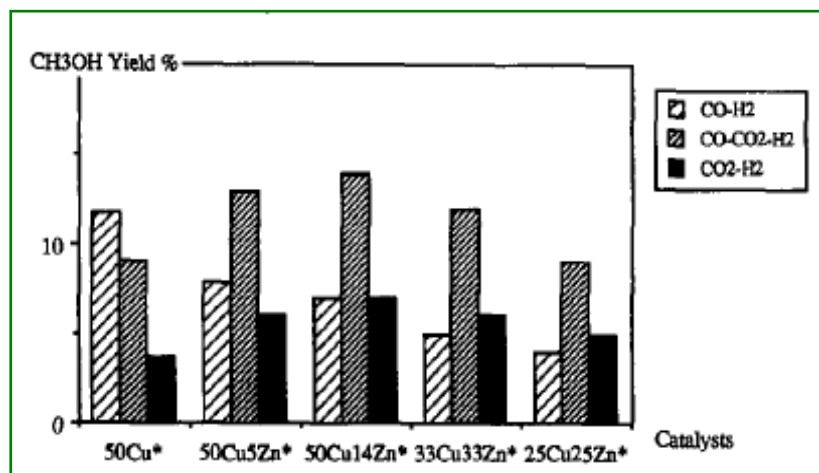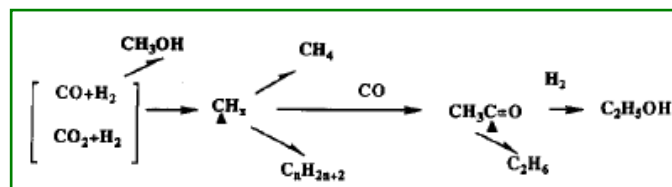2. Subsequent F-T synthesis.

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Hydrogenation of CO & CO$_2$ → Methanol, Alcohols & HC

(Cu-La$_2$Zr$_2$O$_7$)   → Alcohols & HC from CO + H$_2$ & CO$_2$ + H$_2$ feeds
Addn. oxides, e.g., ZnO or ZrO$_2$ → Good MeOH selectivity
Addn. trans. metal promoter like Co → C$_{2+}$ alcohols & C$_{2+}$ hydrocarbons
Cu-La$_2$Zr$_2$O$_7$ + HY zeolite   → Mainly C$_{2+}$ hydrocarbons

Department of Chemistry

CO$_2$ to hydrocarbons

✓ **Fe promoted with Cr & Mn → Conversion of CO$_2$ ↑ & Selectivity of C$_2$ - C$_4$ alkenes↑**
✓ **Zn promoted iron catalyst → Unusually very high selectivity for C$_2$- C$_4$ alkenes**
✓ **With smaller ratio of Zn in Fe:Zn → Alkene selectivity↑**

Table 1. CO$_2$ hydrogenation on various coprecipitated iron-metal catalysts[a]

Catalysts	CO$_2$ conv.	Selectivity (C mol %)		Hydrocarbon Distribution (C mol %)								Ol.(%)[b] (Ol+Pa)
(Fe-M)	(%)	CO	HC	C$_1$	C$_2^=$	C$_2$	C$_3^=$	C$_3$	C$_4^=$	C$_4$	C$_5$>	C2-C4
Fe	16.21	36.39	63.61	49.67	0.24	19.26	1.17	16.61	1.15	7.51	4.41	5.55
Fe-V	11.17	27.30	72.70	39.72	1.57	15.02	-	22.05	5.88	8.22	7.54	14.13
Fe-Cr	25.70	21.53	78.47	64.75	1.01	15.54	4.05	7.39	2.10	2.91	2.25	21.70
Fe-Mn	23.15	8.06	91.94	38.06	1.24	17.42	8.00	13.82	5.09	8.84	7.53	26.34
Fe-Zn	26.54	4.35	95.65	24.26	6.95	7.11	19.58	4.92	13.93	5.60	17.29	69.64

[a] CO$_2$ hydrogenation at 1900 ml/g/h, 573 K, and 10 atm,
[b] Selectivity to olefins (C mol %)

Table 2. Effects of catalyst composition on the catalytic activity of Fe-Zn[a]

Catalysts	CO$_2$ conv.	Selectivity (Cmol%)		Hydrocarbon Distribution (C mol %)								Ol.(%)[b] (Ol+Pa)
(Fe:Zn)	(%)	CO	HC	C$_1$	C$_2^=$	C$_2$	C$_3^=$	C$_3$	C$_4^=$	C$_4$	C$_5$>	C2-C4
10 : 0	16.02	36.39	63.61	49.67	0.24	19.26	1.17	16.61	1.15	7.51	4.41	5.55
9 : 1	26.54	4.35	95.65	24.62	6.95	7.11	19.58	4.92	13.93	5.60	17.29	69.64
7 : 3	25.36	14.21	85.79	30.35	3.06	10.04	14.38	7.56	9.57	7.63	17.31	51.61
5 : 5	24.82	8.02	91.98	43.05	1.93	16.52	9.89	12.09	5.40	6.95	4.18	32.63
3 : 7	23.27	20.51	79.46	37.84	1.62	15.74	7.54	13.58	7.50	5.75	10.54	32.08
1 : 9	19.67	22.43	77.57	54.87	0.12	18.38	0.48	14.25	0.44	6.82	4.66	2.25
0 : 10	4.40	99.31	0.69	73.70	0	7.88	0	18.43	-	-	-	0

[a] CO$_2$ hydrogenation at 1900 ml/g/h, 573 K, and 10 atm,
[b] Selectivity to olefins (C mol %)

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CO$_2$-hydrogenation to EtOH

Well balanced multi-functional FT-type composite catalysts

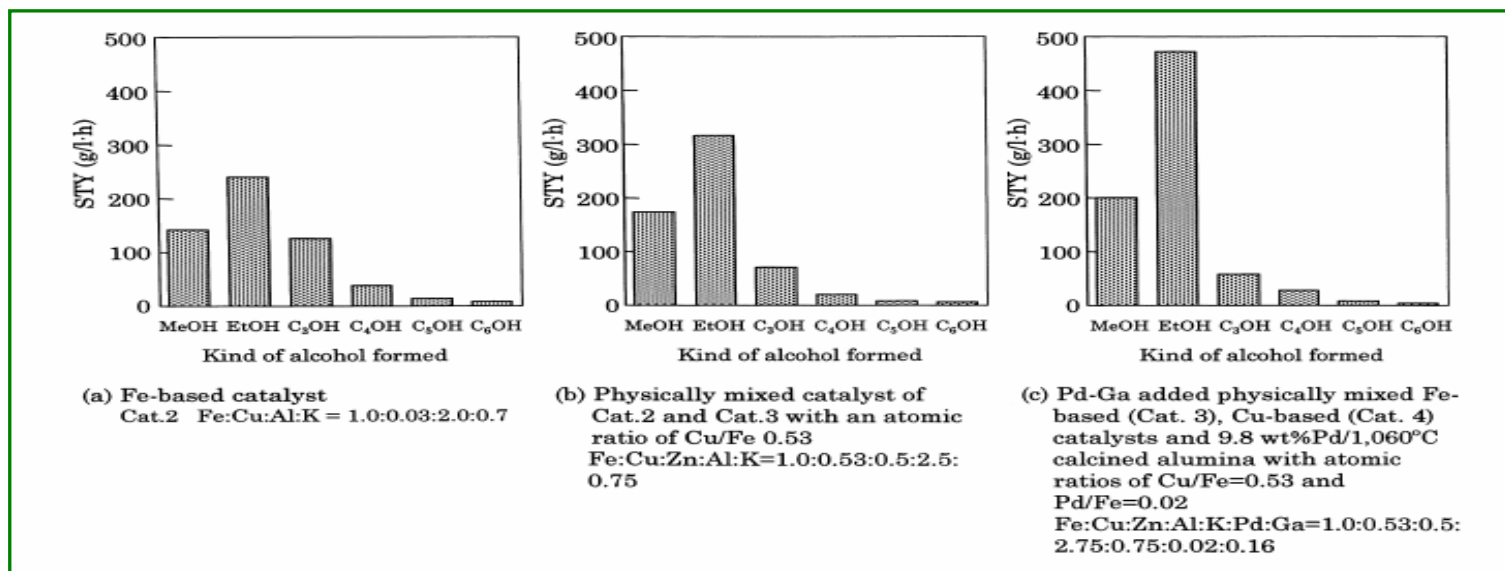*Physical mixtures with 3 different function*

Fe-based	**Cu-based**	**Pd/Gd addition**
↓	↓	↓
CO$_2$ to CO	**C–C bond formation –OH group formation**	**Stabilize optimum reductive state of catalyst**

(a) Fe-based catalyst
Cat.2   Fe:Cu:Al:K = 1.0:0.03:2.0:0.7

(b) Physically mixed catalyst of Cat.2 and Cat.3 with an atomic ratio of Cu/Fe 0.53
Fe:Cu:Zn:Al:K=1.0:0.53:0.5:2.5: 0.75

(c) Pd-Ga added physically mixed Fe-based (Cat. 3), Cu-based (Cat. 4) catalysts and 9.8 wt%Pd/1,060°C calcined alumina with atomic ratios of Cu/Fe=0.53 and Pd/Fe=0.02
Fe:Cu:Zn:Al:K:Pd:Ga=1.0:0.53:0.5: 2.75:0.75:0.02:0.16

Difference in alcohol distribution for different catalysts

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Electrochemical Reduction of CO_2

CO_2/CO_2^- redox potential is -2.21V /(SCE)

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^{\circ\prime} = -0.52 \text{ V}$$
$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad\quad E^{\circ\prime} = -0.61 \text{ V}$$
$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \quad E^{\circ\prime} = -0.48 \text{ V}$$
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad E^{\circ\prime} = -0.38 \text{ V}$$
$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^{\circ\prime} = -0.24 \text{ V}$$
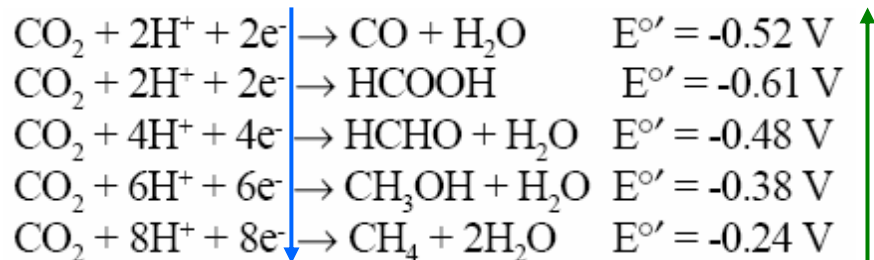
Influence of the Solvent and Electrode on the Reaction Mechanism

Reaction	Cathode	Solution
$CO_2 + e^- \rightarrow CO_2^-$	All	All
$CO_2^- + H^+ + e^- \rightarrow HCOO^-$	In, Pb, Hg	H_2O
$CO_2^- \rightarrow CO + O^-$		
$CO + O^- + H^+ + e^- \rightarrow CO + OH^-$	Zn, Au, Ag	H_2O
$CO_2^- + CO_2^- \rightarrow (COO)_2^{2-}$	Pb, Tl, Hg	Non-aqueous
$CO_2^- + CO_2 + e^- \rightarrow CO + CO_3^{2-}$	In, Zn, Sn, Au	Non-aqueous

M. A. Scibioh & B. Viswanathan
Proc. Indn. Natl. Acad. Sci., 70 A (3), 2004.

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Reduction of CO_2 under Protic, Aprotic & Partially aprotic conditions

Protic
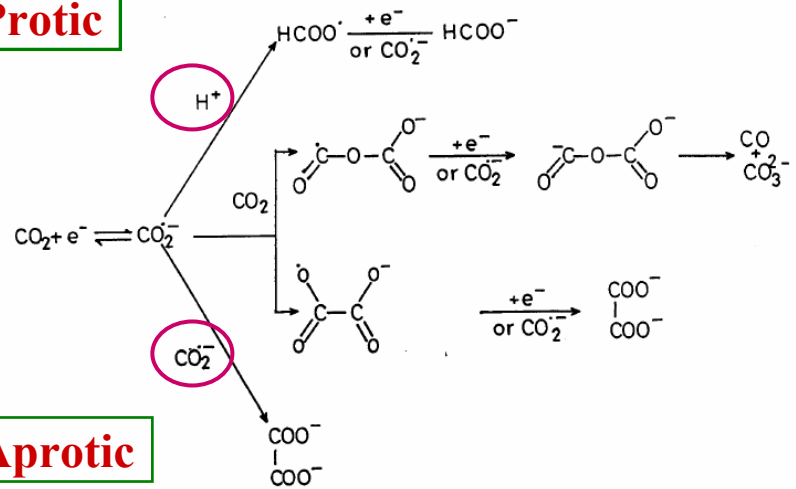
Aprotic
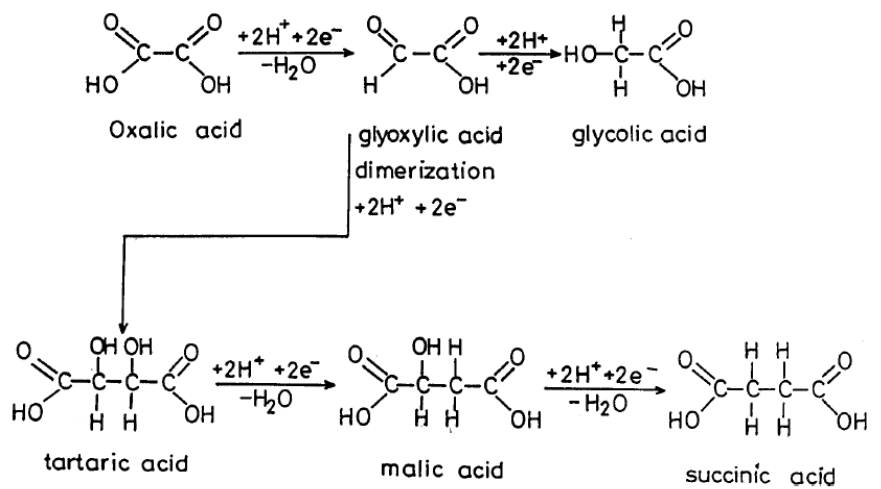
Partially Aprotic

Aq. solutions leads to formic acid production (C_1 products)
Aprotic solvents favor dimerization of CO_2 leading to C_n products

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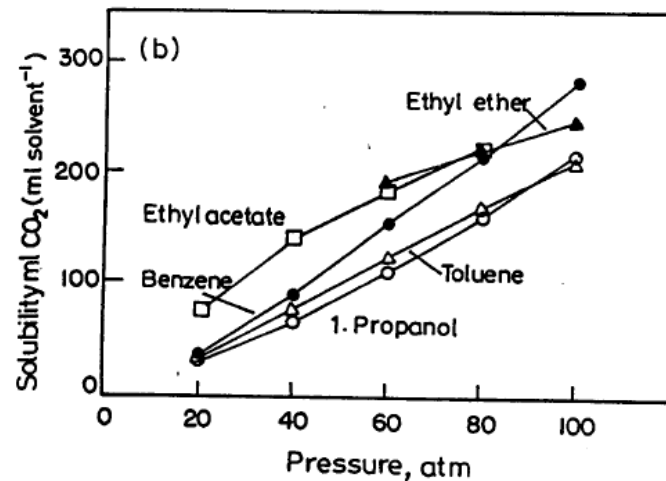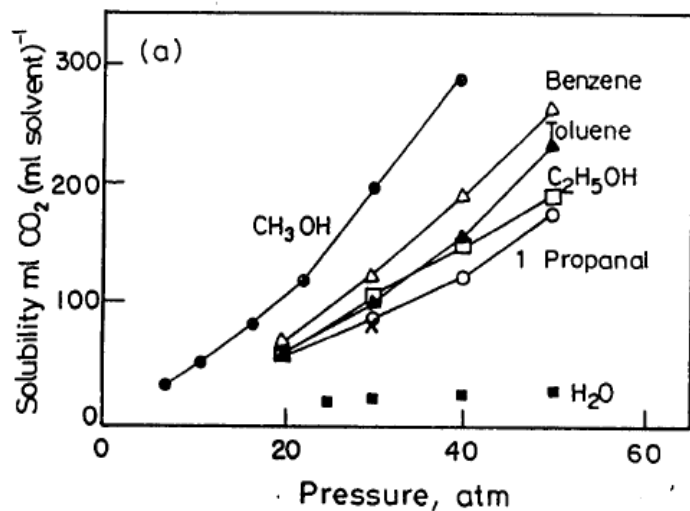
Solubility of CO$_2$

Variation of solubility of CO$_2$ with pressure for several solvents at T = 293K and 333K
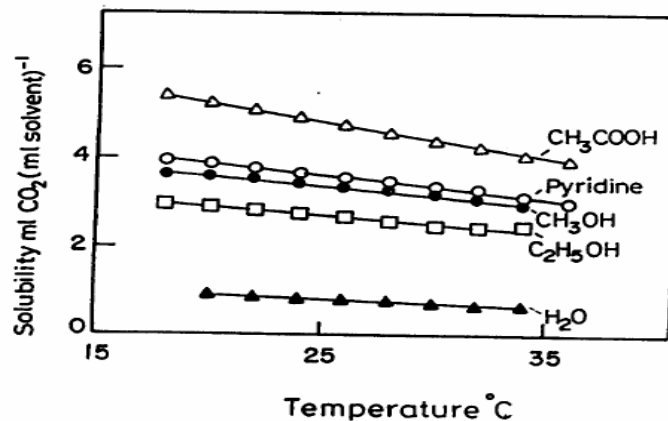
Solubility of CO$_2$ with temperature for several solvents used in electrochemistry

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Cathode metal	Potential vs SCE /V	HCOOH /%	CO /%	H$_2$ /%
In	−2.0	87.6	6.8	4.9
	−2.4	83.2	4.2	13.2
Pb	−2.0	72.9	2.0	15.6
	−2.4	78.9	2.1	14.3
Zn	−2.0	46.6	35.6	12.4
	−2.4	53.4	16.8	35.2
Sn	−2.0	67.5	9.1	29.9
	−2.4	37.6	4.2	61.6

Electrode	E_c vs SCE/V	Oxalate	Formate	Glyoxylate
Graphite	−0.900	100	−	−
	−1.05	10	78	12
	−1.26	17	74	7
	−1.70	15	72	−
	−1.88	6	65	28
Pb	−1.26	44	55	−
	−1.40	9	90	−
	−1.49	25	74	−
	−1.65	1	62	35
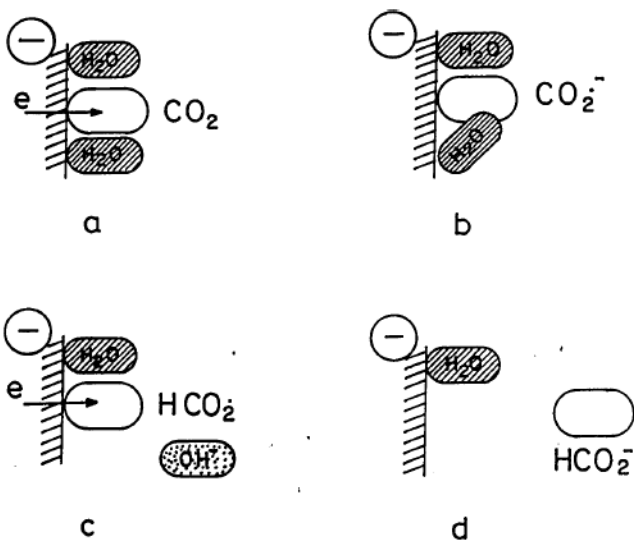
Mechanism of CO$_2$ electroreduction on sp group metal electrodes. Neutral hydrated CO$_2$ molecules (a) undergo electronation to yield qadsorbed CO$_2^-$ radicals; (b) the latter react with adsorbed water molecules to form adsorbed HCO$_2$ radicals and OH$^-$ ions; (c) HCO$_2^-$ radicals remain adsorbed at the electrode surface and undergo further reduction to formate ions; (d) the negatively charged HCOO$^-$ ions are rejected from the electrode surface

M. Jitaru
J. Appl. Elec.Chem 27 (1997) 875

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Periodic table for CO$_2$ reduction products
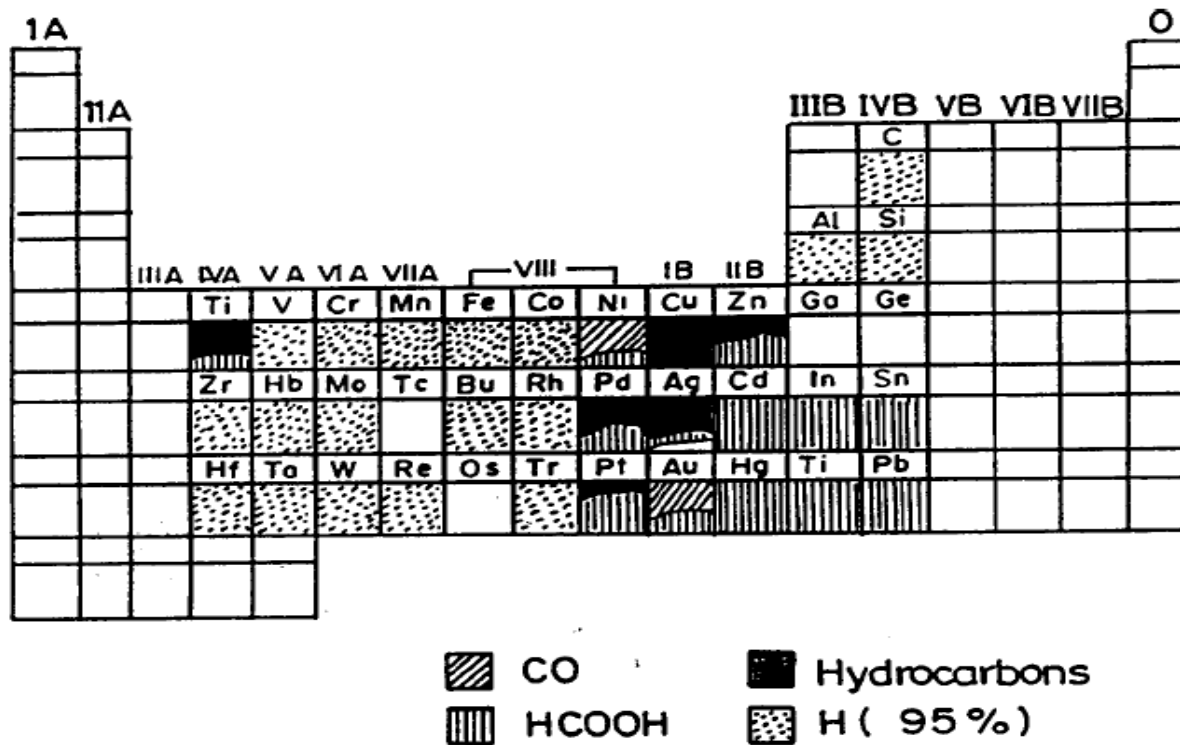
At –2.2 V /SCE in low temperature, 0.05 M KHCO$_3$ solution

Y Hori et al.,
J Chem Soc Chem Commun (1987) 728

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Summary of Metal Cathodes Employed for Electroreduction of CO_2

Metals	Products	
	Aqueous medium	Non-aqueous medium
	sp group metals	
Cu, Zn, Sn	HCOOH	-
In, C, Si, Sn, Pb, Bi, Cu, Zn, Cd, Hg	HCOOH, CO, hydrocarbon	-
In, Sn, Pb, Cu, Au, Zn, Cd	-	Hydrocarbon, CO, CO_3^{2-}
In, Sn, Au, Hg	-	CO
In, Tl, Sn, Pd, Pd, Zn, Hg	-	Oxalic acid
	d group metals	
Ni, Pt	-	CO, CO_3^{2-}
Ni, Pd, Rh, Ir	HCOOH, CO	-
Fe, Ru, Ni, Pd, Pt	Hydrocarbon	-
Ti, Nb, Cr, Mo, Fe, Pd	-	Oxalic acid
Mo, W, Ru, Os, Pd, Pt	MeOH	-
Zr, Cr, Mn, Fe, Co, Rh, Ir	CO	-

M. A. Scibioh & B. Viswanathan

Proc. Indn. Natl. Acad. Sci., 70 A (3), 2004.

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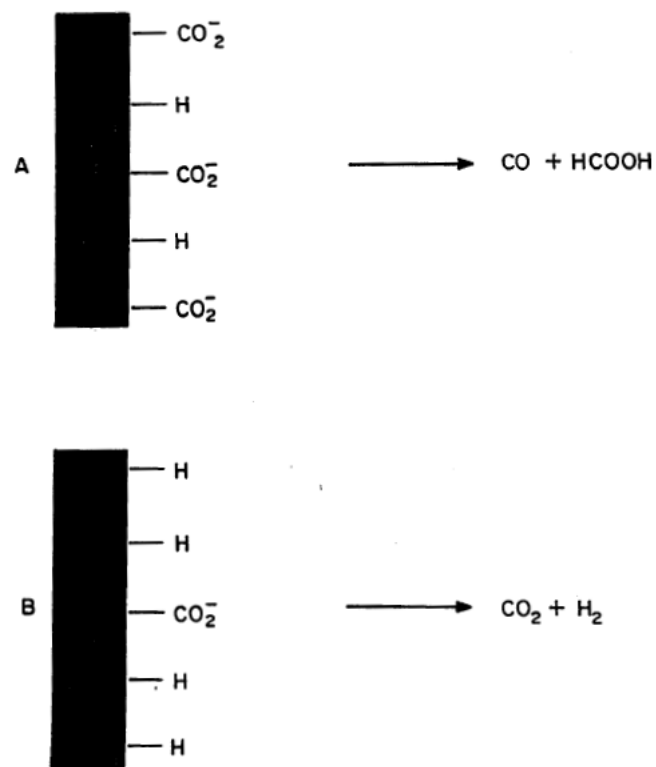
Comparative mechanism of high-pressure CO_2 electroreduction (A) & Electroreduction of CO_2 at atmospheric pressure (B) on Ni cathode

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Electrocatalytic Reduction of CO_2
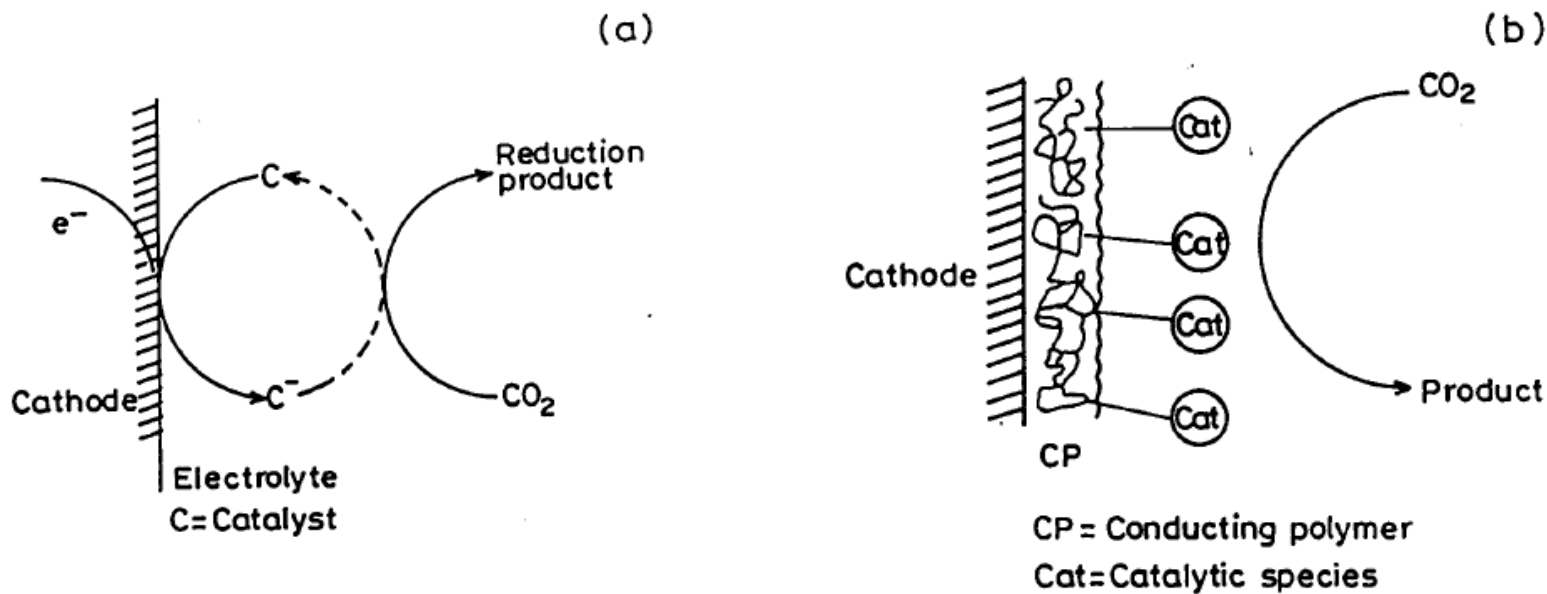
(a)   Molecular electrocatalysts in solution;
(b)   Cathodic materials modified by surface deposition of molecular electrocatalysts

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S.Kaneco et al, (under publication

Transition metal complexes – Electrocatalysts to reduce CO_2

Categories:

- *Phthalocyanine complexes*
- *Porphyrin complexes*
- *Metal complexes of 2,2'-bipyridine & related ligands*
- *Phosphine complexes*
- *Metal clusters and polymetallic complexes*
- *Biphenanthroline hexaazacyclophane complexes*
- *Azamacrocylic complexes*
- *Macrocyclic ligands related to macromolecular functions*
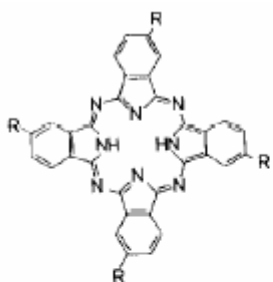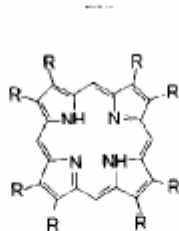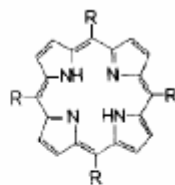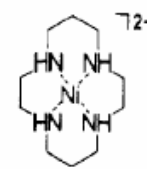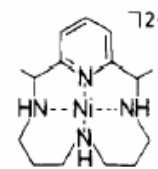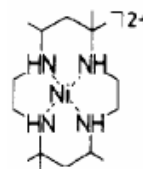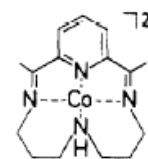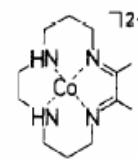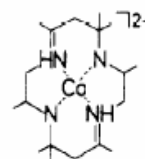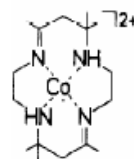
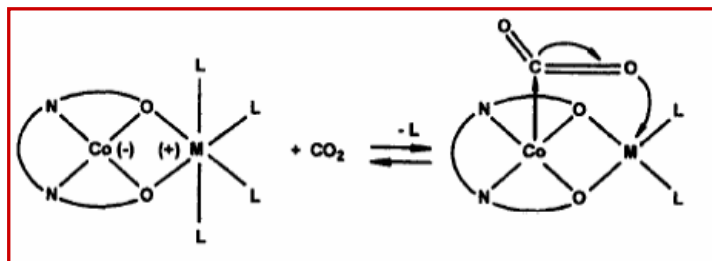**Porphyrins and phthalocyanines**

Tetraaza macrocyclic complexes

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Fuels from the reduction of CO₂
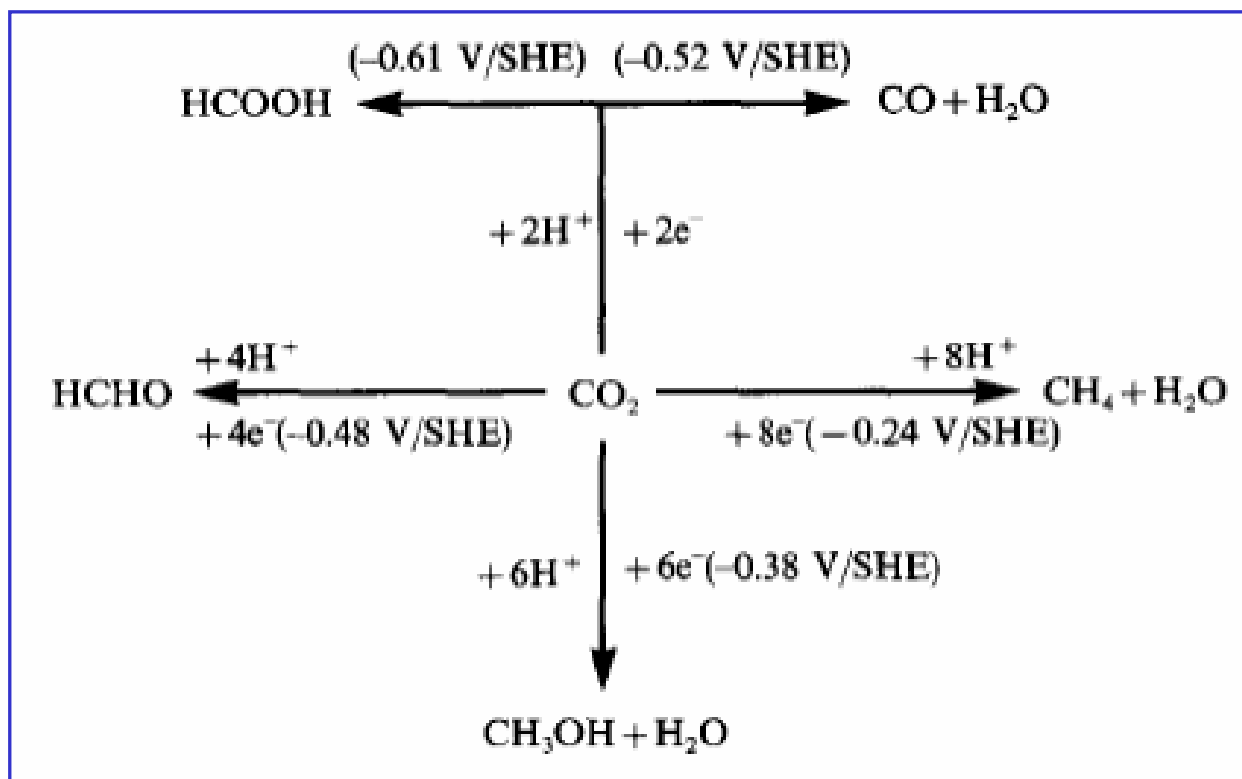
$$CO_2 + e^- \rightleftarrows CO_2^{\cdot-} \qquad \varepsilon^\circ = -1.2 \text{ V}$$

$$CO_2 + H^+ + e^- \rightleftarrows CO_2H \qquad \varepsilon^\circ = -0.60 \text{ V}$$

$$\underset{\text{(}-0.61 \text{ V/SHE)}}{\text{HCOOH}} \longleftarrow \underset{\text{(}-0.52 \text{ V/SHE)}}{\longrightarrow} CO + H_2O$$

$+2H^+ \quad +2e^-$

$$HCHO \underset{+4e^-(-0.48 \text{ V/SHE})}{\overset{+4H^+}{\longleftarrow}} CO_2 \underset{+8e^-(-0.24 \text{ V/SHE})}{\overset{+8H^+}{\longrightarrow}} CH_4 + H_2O$$

$+6H^+ \quad +6e^-(-0.38 \text{ V/SHE})$

$$CH_3OH + H_2O$$

Department of Chemistry
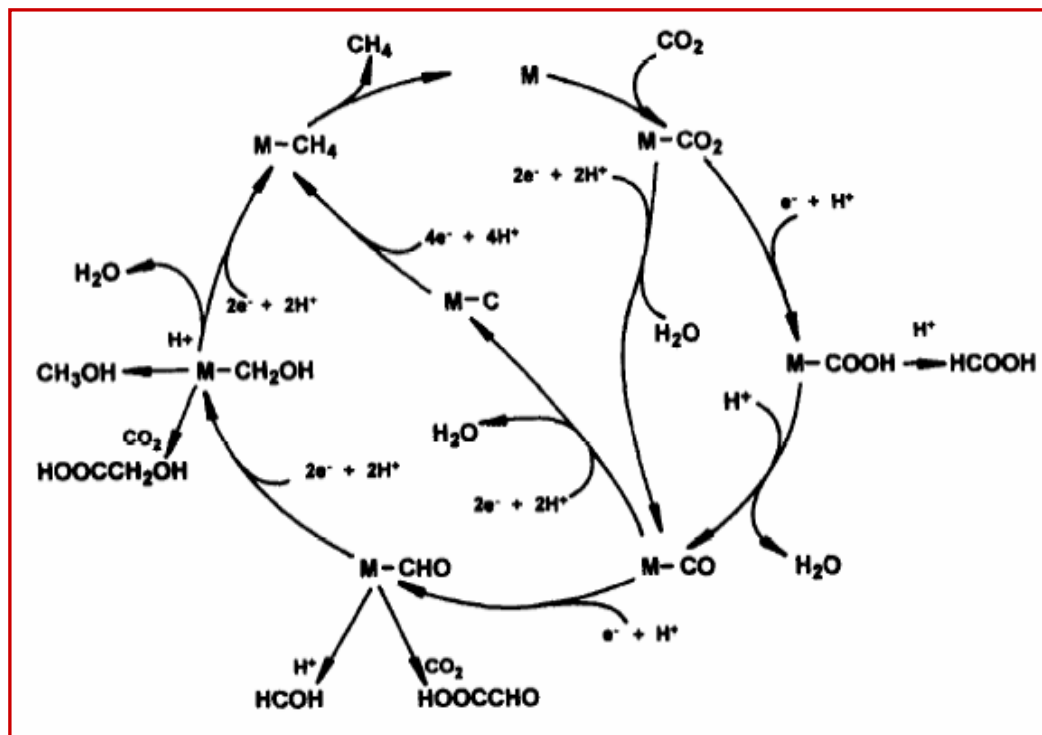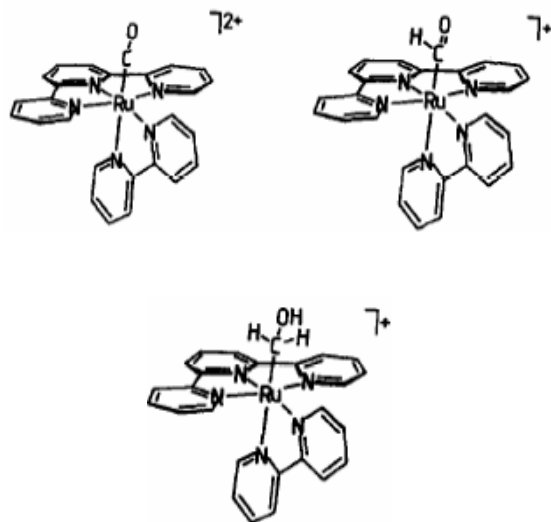
General cycle for the generation of CO_2 reduction products with various complexes of acyclic ligands as electrocatalysts [Also valid for electrocatalysis with macrocyclic ligands]
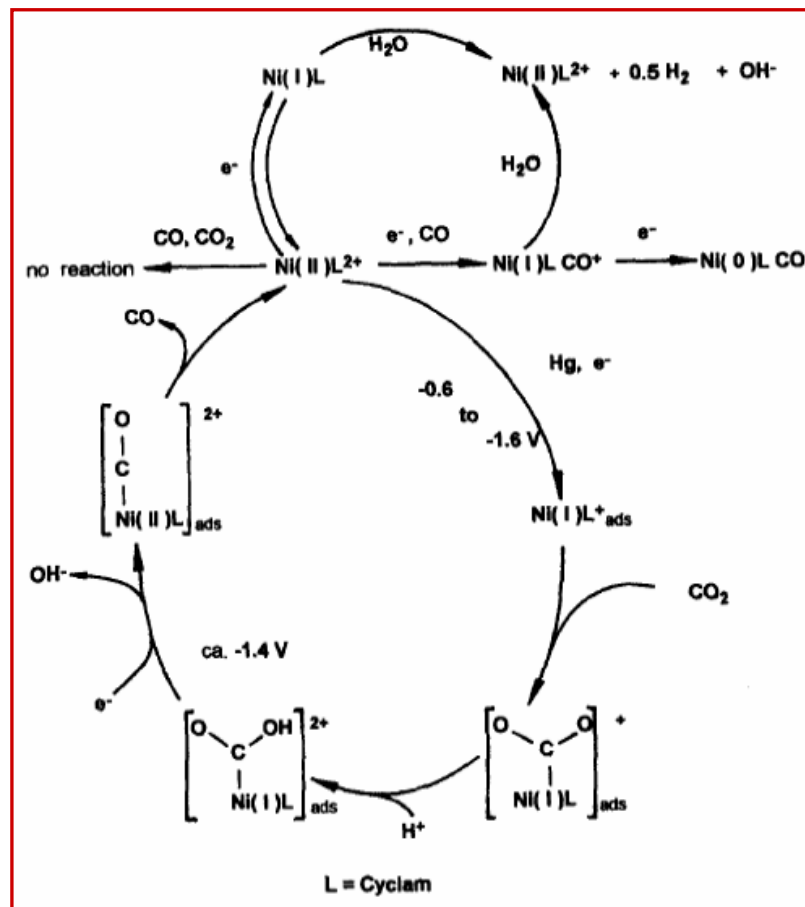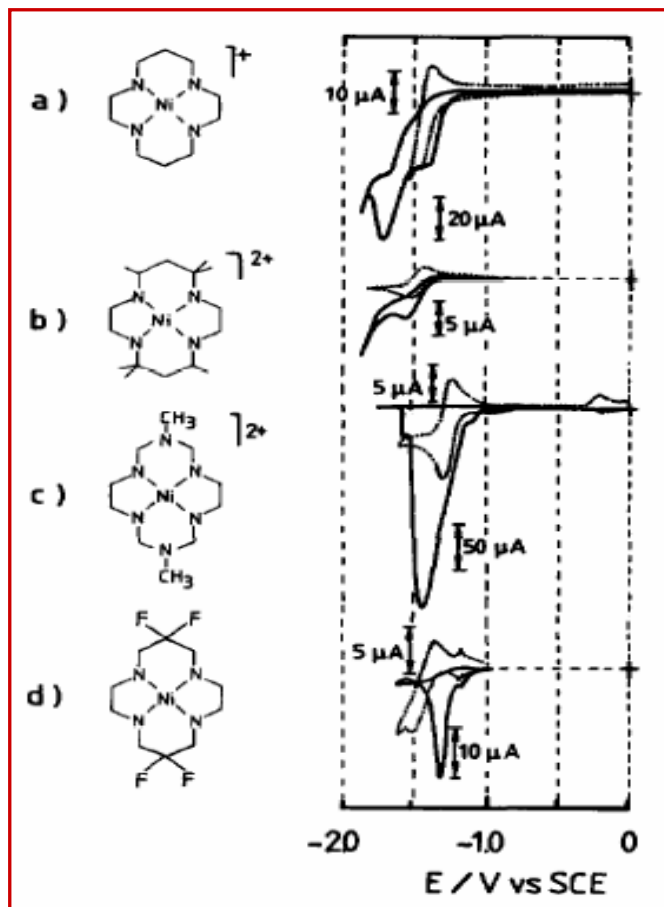
Cyclic voltammograms of cyclotetradecane derivative complexes in N_2 ($\cdots\cdots$) and CO_2 (———):
(a) glassy carbon electrode; 0.1 M $NaClO_4$ (pH 6.2), 0.1 V s^{-1}; (b) hanging mercury drop electrode;
acetonitrile water, 0.1 M $NaClO_4$, 0.02 V s^{-1}; (c) hanging mercury drop electrode; acetonitrile water,
0.1 M $NaClO_4$, 0.1 V s^{-1}; (d) glassy carbon electrode; 0.5 M Na_2SO_4, 0.2 V s^{-1}.

Cyclam & cyclam derivatives

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Cyclic voltammograms of porphyrin and phthalocyanine derivative complexes

(a) porphyrin fixed on a glassy carbon electrode; phosphate buffer (pH 6.86), 0.001 V s^{-1};

(b) glassy carbon electrode; 0.1 M dimethylformamide; $(C_2H_5)_4NClO_4$, 0.1 V s^{-1}; (c) hanging mercury drop electrode; 0.1 M $(C_2H_5)_4NClO_4$, 0.1 V s^{-1}.

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# CO$_2$ Activation by Metal Complexes- Perception

➢ **Binding of CO$_2$ to a metal centre leads to a net electron transfer from metal to LUMO of CO$_2$ & thus leads to its activation.**

➢ **Hence, coordinated CO$_2$ undergoes reactions that are impossible for free CO$_2$.**

➢ **Many stoichiometric & most catalytic reactions involving CO$_2$ activation proceed via formal insertion of CO$_2$ into highly reactive M–E bonds → formation of new C–E bonds.**

➢ **These reactions might not necessarily require strong coordination of CO$_2$ as in stable complexes, but are generally initiated by nucleophilic attack of E at Lewis acidic carbon atom of CO$_2$.**

➢ **Weak interaction between the metal & the lone pairs of one oxygen atom of CO$_2$ may play a role in supporting the insertion process.**

➢ **Although we are more knowledgeable about CO$_2$ activation, the effective activation of CO$_2$ by transition metal complexes is still a goal!**

Direct photoreduction of CO_2

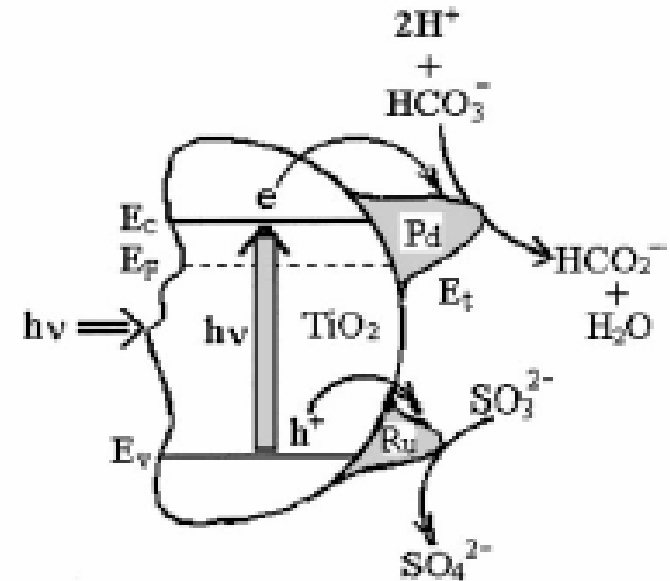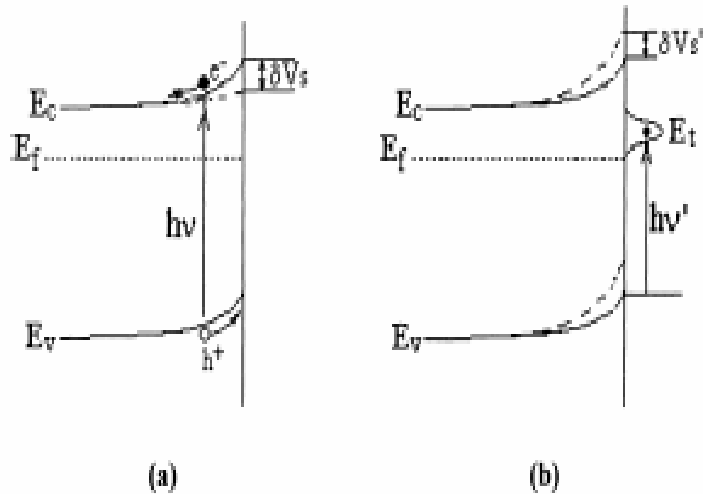**At the surface of semiconducting materials; p-Si, p-CdTe, p-InP, pGaP, n-GaAs**

Three principles of photocatalytic cycles of CO_2 reduction
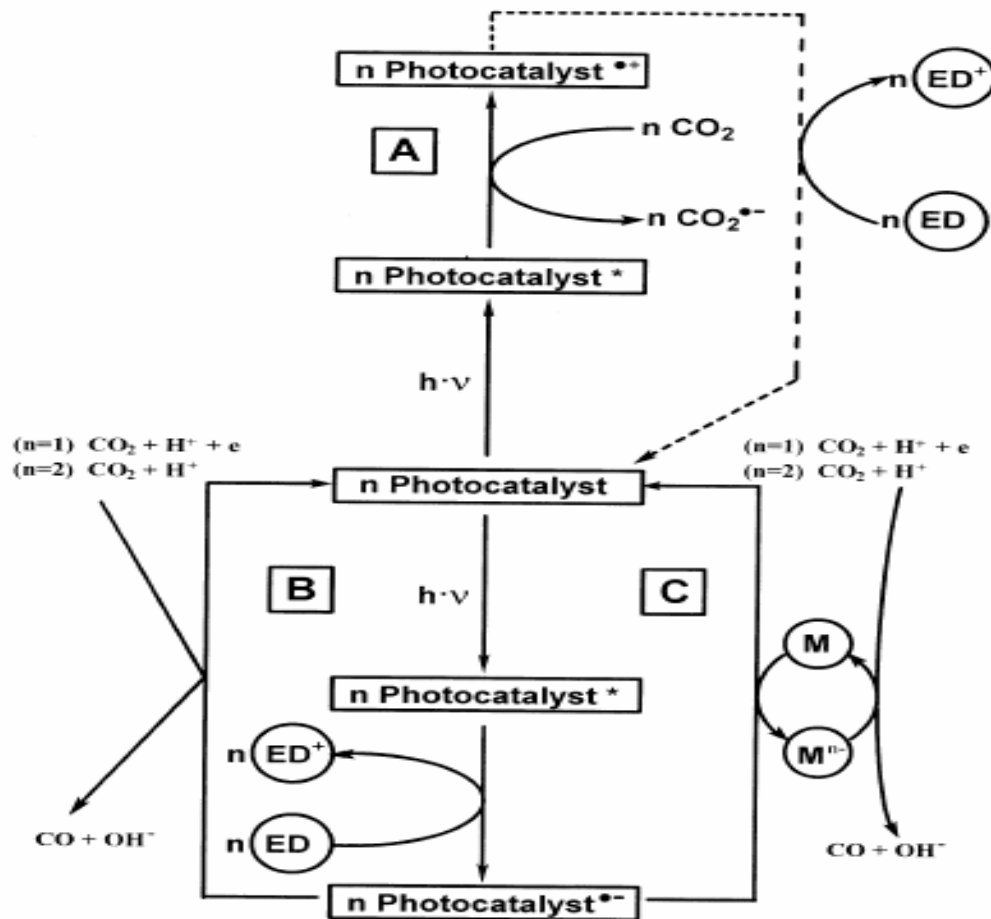
Photoreduction of CO_2

**Energy band modes of an n-type semiconductor with a Schottky-type barrier:**

(a) band–band transition;
(b) surface state population transition. V_s and V_s^0, surface potential difference; CB, conduction band; VB, valence band; Et, surface state level; E_F, Fermi level.
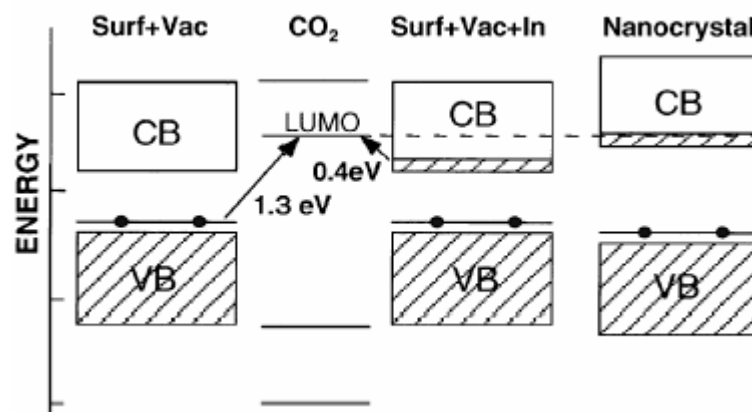
Pd/RuO_2/TiO_2 photoreduction of CO_2

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Role of the Nanoscale in Surface Reactions: CO_2 on CdSe
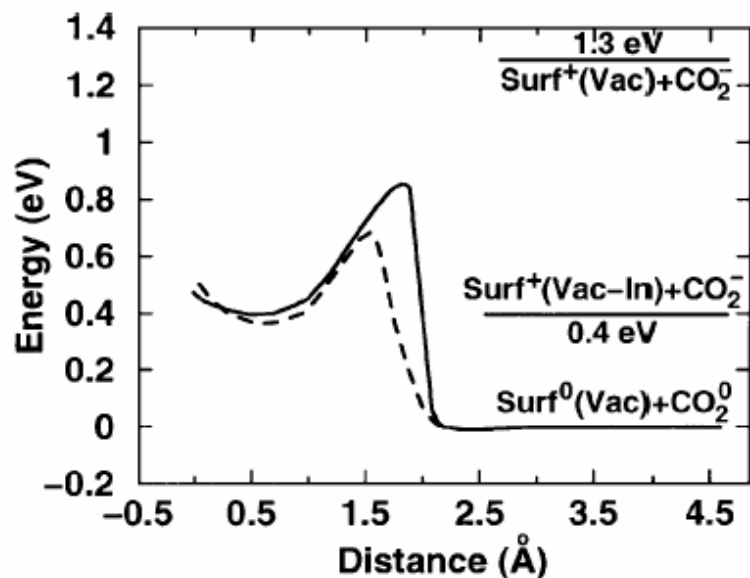
The total energy of a CO_2 molecule chemisorbed in a Se vacancy on the CdSe1010 surface as a function of the vertical distance between C atom & ideal truncated surface
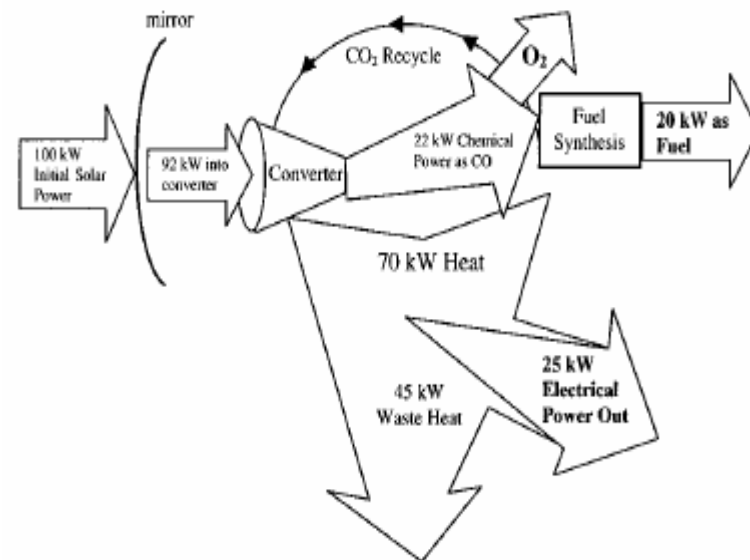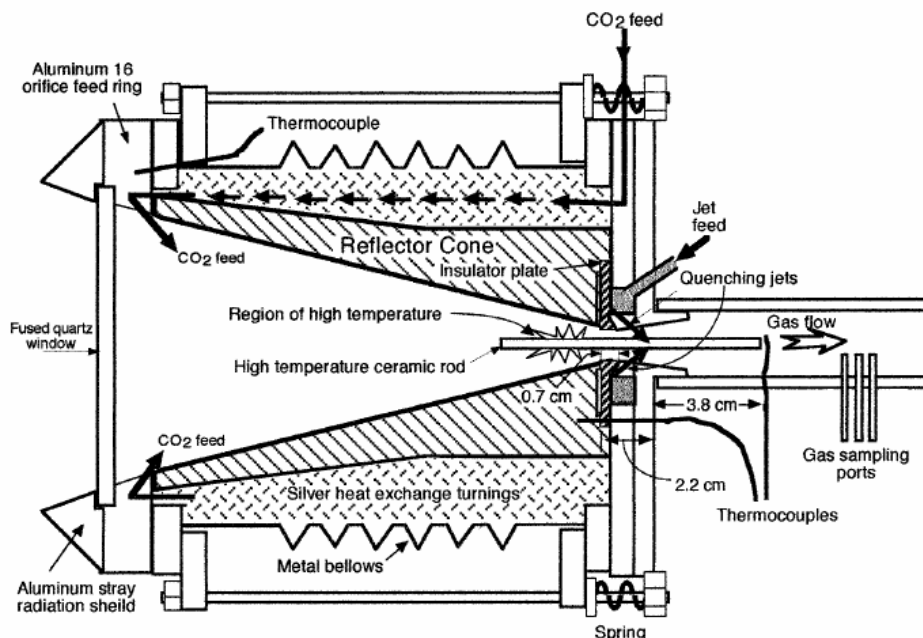
Electron transfer from surfaces or nanocrystals to the CO_2 molecule. The localized energy level near the valence band edge is caused by a Se vacancy

L. G. Wang et al.,
Phy. Rev Let. 89 (7) (2002) 075506-1

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Direct Solar Reduction of CO$_2$ to Fuel

$$CO_2 + h\nu \text{ or heat} \rightarrow CO + {}^1\!/_2 O_2$$
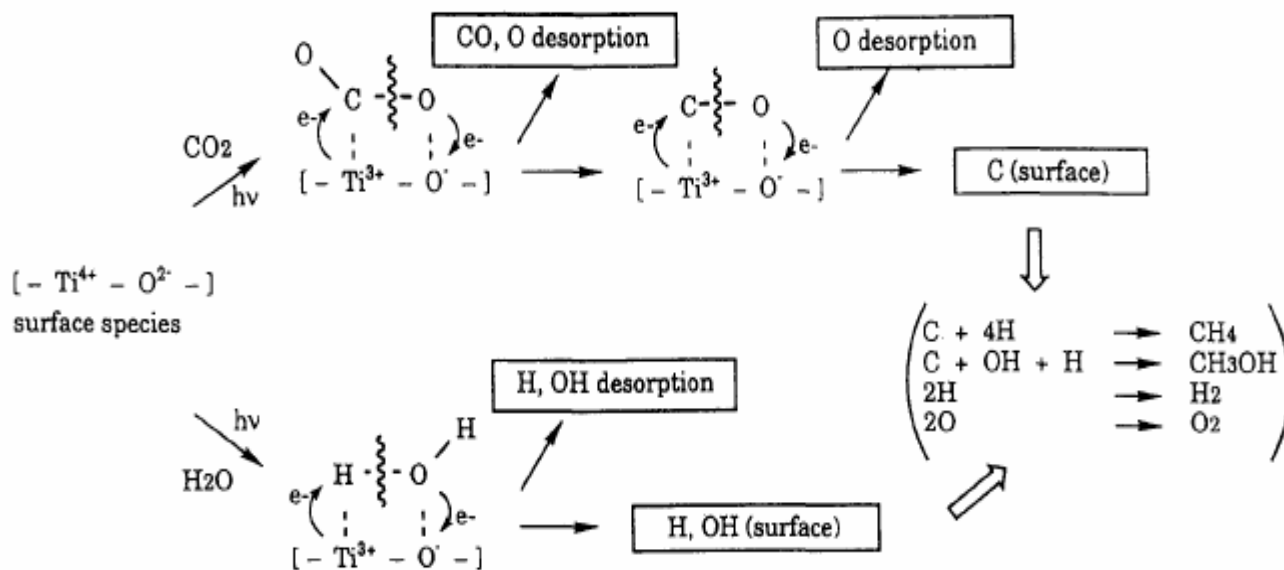

Converter assembly for direct solar reduction of CO$_2$

Energy conversion goals for a direct solar reduction system based on 100 kW initial solar input

A. J. Traynor & R. J. Jensen
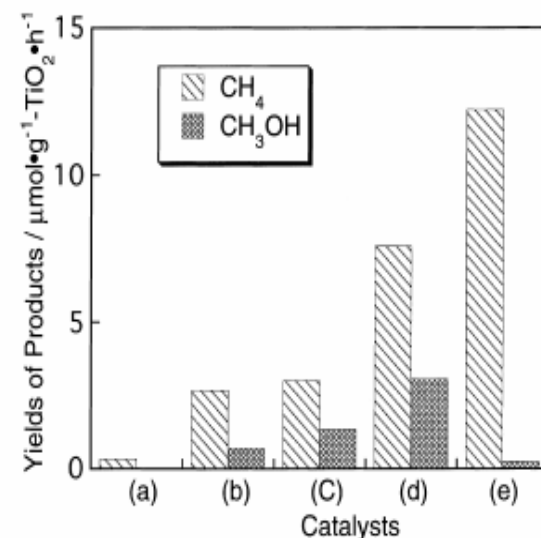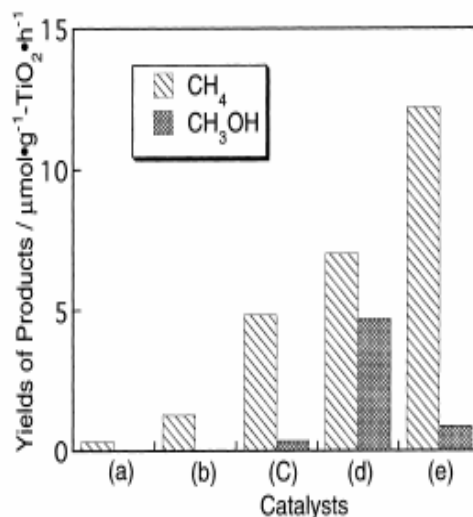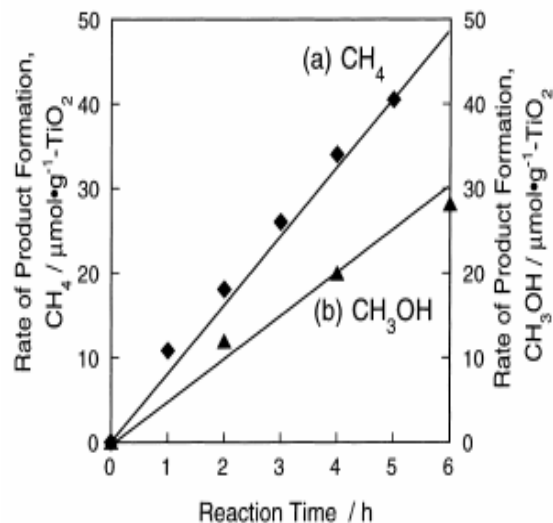Ind. Eng. Chem. Res. 41 (2002) 1935

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Photocatalytic reduction of CO$_2$ with H$_2$0 on the anchored titanium oxide

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Reaction time profiles:
To produce CH_4 (a) & CH_3OH (b) on TiO_2/Y-zeolite

Product distribution: Photocatalytic reduction -

CO_2 with H_2O: anatase TiO_2 powder (a), Imp-Ti-oxide/Yzeolite (10.0 wt% as TiO_2) (b), Imp-Ti-oxide/Y-zeolite (1.0 wt% as TiO2) (c), Ex-Ti-oxide/Y-zeolite (1.1 wt% asTiO2) (d), Pt-loaded ex-Ti-oxide/Y-zeolite (e) catalysts.
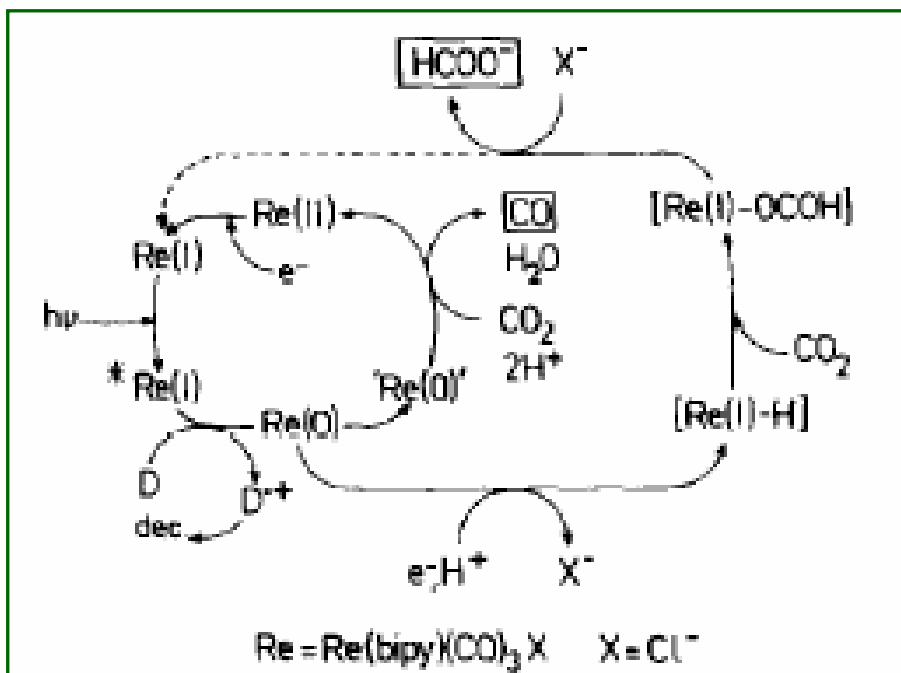
The yields of CH_4 and CH_3OH in the photocatalytic reduction of CO_2 with H_2O TiO_2 powder (a), TS-1 (b), Ti-MCM-41 (c), Ti-MCM-48 (d), Pt-loaded Ti-MCM-48 (e)catalysts.
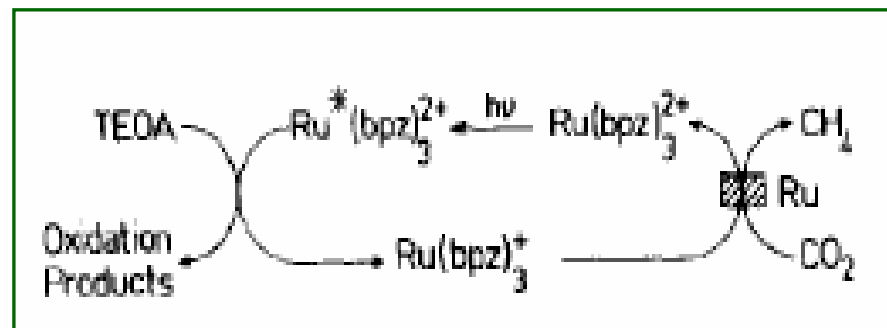
H. Yamashita et al.,
Catalysis Today 45 (1998) 221

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Formation of HCOOH

Formation of methane

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HOMOGENEOUS SYSTEM
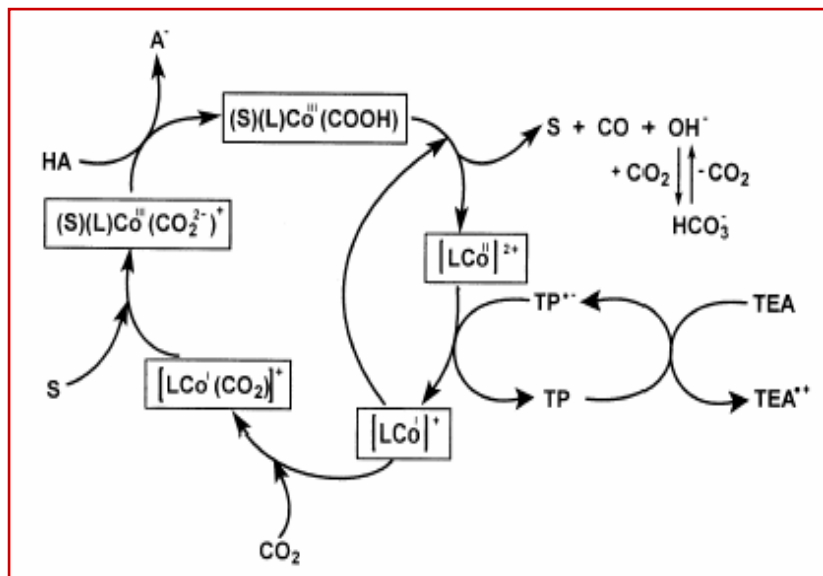
Light driven catalytic cycle reducing CO_2.
Light reaction: terphenyl (TP) - photocatalyst,
triethylamin (TEA) - reductive quencher (electron donor).
Dark reaction: cyclam cobalt complex -electron relay
(a) oxidising - terphenyl radical anion & (b) reducing CO_2.
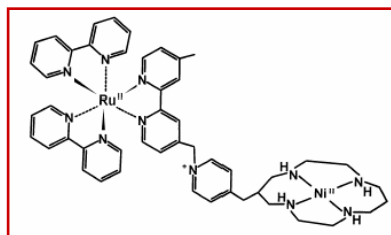
MICROHETEROGENEOUS SYSTEM
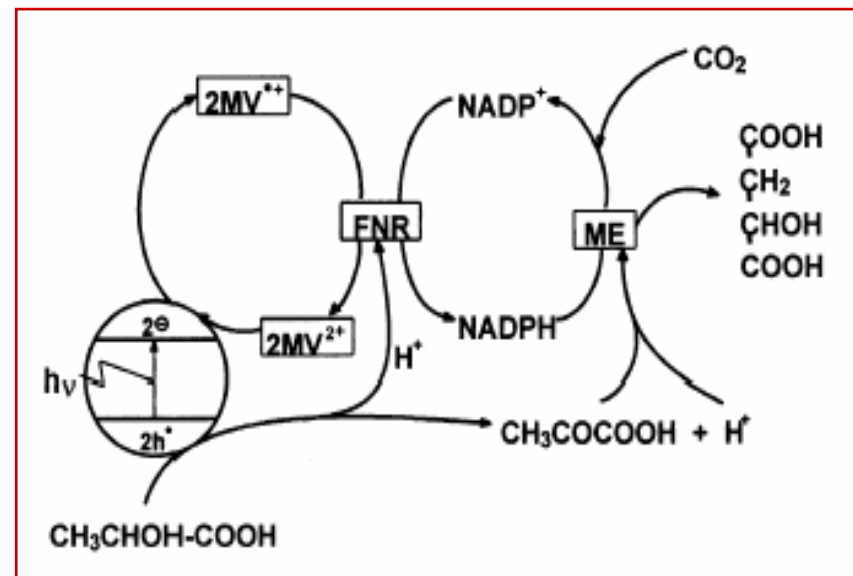
Light driven carboxylation of lactic acid to form malic acid (MV^{2+}, methylviologen dication, FNR, ferredoxin-NADP-reductase; ME, malic enzyme).

J.P. Collin & J.P. Sauvage
Coord. Chem. Rev. 93 (1989) 245

Photoreduction of CO_2 - Perception

Unsolved Problems!

- TON (mol reduction product of CO_2 / mol catalyst) are still low

- Efficiencies of the reactions is unsatisfactory-both the amount of reduction products of CO_2 (usually C1 products) & oxidation products of the sacrificial donor

- The tuning of the single components w.r.t. their redox potentials, life times and selectivity is not well understood.

- Necessary to device systems which do not require sacrificial donors light energy is also used for degradation of sacrificial donors, influencing the energy balance of the reactions unfavorably

- Macrocyclic complexes of transition metal ions- satisfy the requirements of a useful relay. They may play a dual role as a catalysts and relays

- Even with transition metal complexes – Reduction products have not been of great economic value (usually only C1 products)

- Multicomponent systems containing photoactive center, electron relays and/or molecular electrocatalysts in addition to possible microheterogeneous systems will be discovered.

Photobiological Hydrogen Fuel Production & CO$_2$ Mitigation

Photo-bioreactor technology
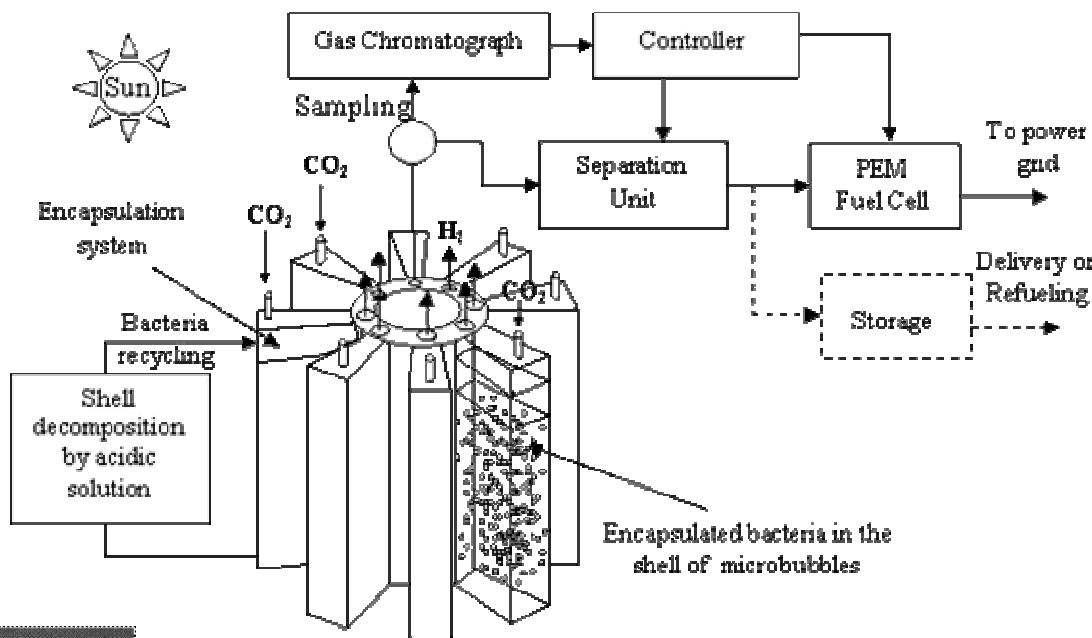
Envisioned integrated CO$_2$ mitigation and H$_2$ production system
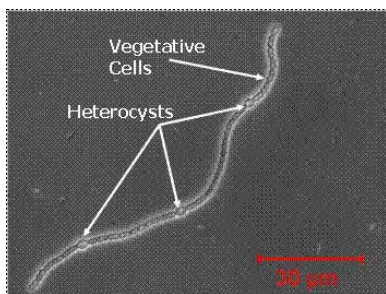
Cyanobacteria

1. Encapsulate carbon dioxide bubbles into a biocompatible &biodegradable polymeric shell containing photolithotrophic autotroph bacteria.
2. In absence of nitrogen, these bacteria produce hydrogen & oxygen from water by
(i)   consuming the CO$_2$ gas entrapped in the microbubbles as their carbon source &
(ii)   absorbing solar light as their energy source.

http://herc.ucla.edu/PilonJay.html

PHOTOELECTROREDUCTION OF CO_2

ON SEMICONDUCTORS - CATALYSED BY MOLECULAR SPECIES

Appealing Approach!
An important energy input contribution from light might be expected, thus diminishing electricity consumption.
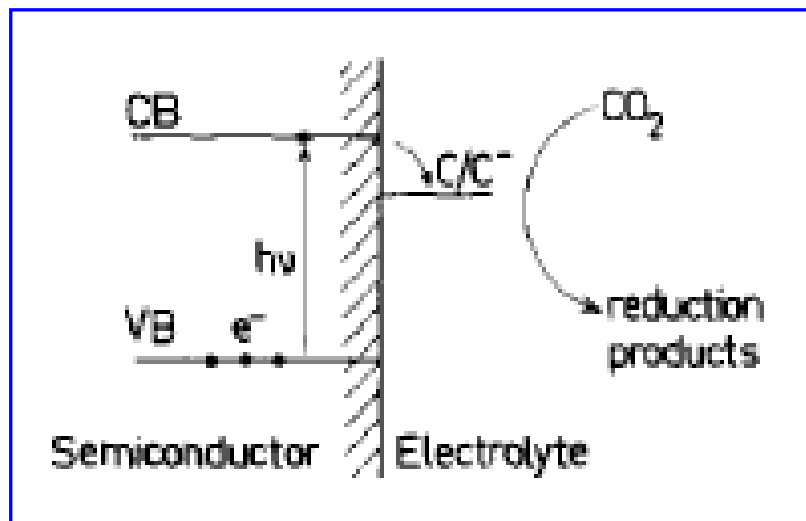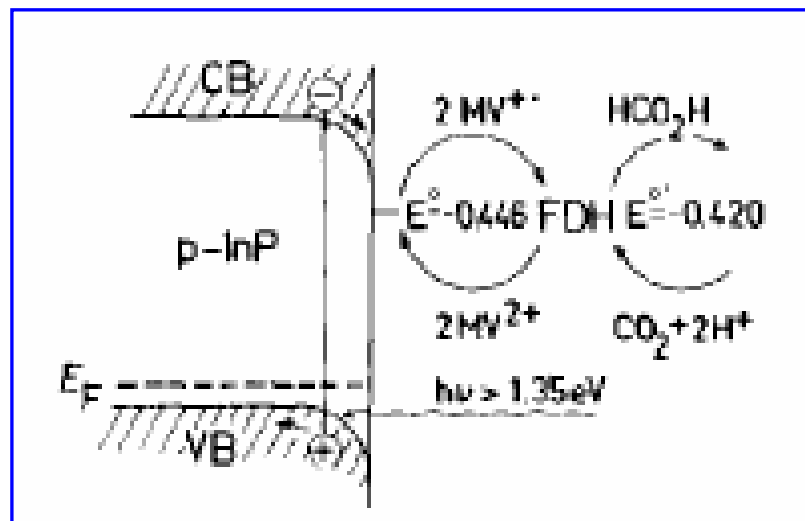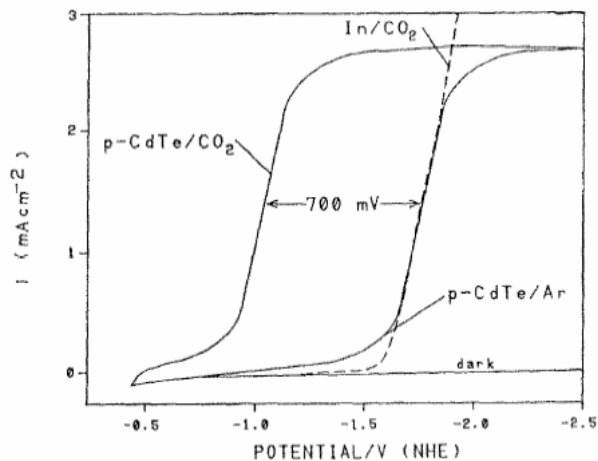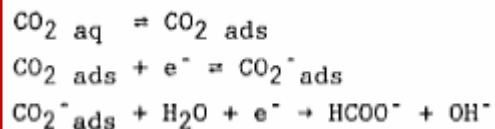

Principle

An Example

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A study on photoelectroreduction of CO_2

Possible Mechanistic Route By insitu-IR

$$CO_2\ aq \rightleftharpoons CO_2\ ads$$
$$CO_2\ ads + e^- \rightleftharpoons CO_2^{\cdot}\ ads$$
$$CO_2^{\cdot}\ ads + H_2O + e^- \rightarrow HCOO^- + OH^-$$

p-CdTe electrode in DMF-0.1 M TEAP/5% H_2O

Photovoltomogram
λ= 560 nm (0.5 mW cm⁻²)

Catalyst	Current Density[a]	µl CO/minute	Products Detected	Efficiency
bare	9.8	5.64	CO	92%
			H_2	10%
bare	9.63[c]	<0.2[d]	H_2	100%
bare	0.12[e]	<0.2[d]	H_2	95%
bare	0.11[c,e]	<0.2[d]	H_2	99%
Ni	9.06	3.24	CO	69%
			HCOO⁻	14%
			H_2	15%
Ru	10.00	6.14	CO	102%
			H_2	1%
Te	10.63	2.76	CO	62%
			HCOO⁻	19%
			H_2	17%
Pt	11.04	2.10	CO	44%
			HCOO⁻	27%
			H_2	35%
Pt	0.09[c]	<0.2[d]	H_2	93%
Pt	0.11[e]	<0.2[d]	H_2	97%
Zn	10.04	1.30	CO	31%
			HCOO⁻	31%
			H_2	45%
Pd	9.84	0.52	CO	13%
			HCOO⁻	35%
			H_2	54%

[a] averaged for one hour
[b] includes both gaseous products and those dissolved in solution
[c] under Ar atmosphere
[d] limit of GC detection
[e] under dark condition

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Study on photoelectroreduction of CO_2
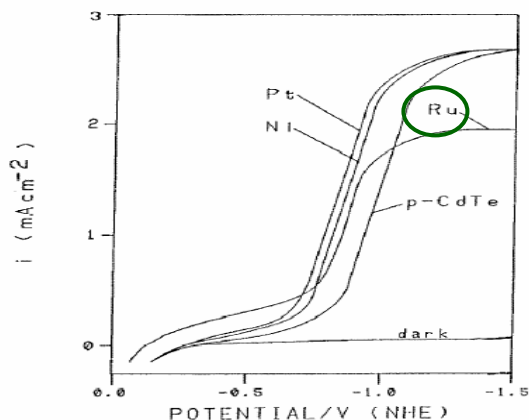
Metal islet catalysts deposited on a p-CdTe electrode in DMF-0.1 M TEAP/5% H_2O
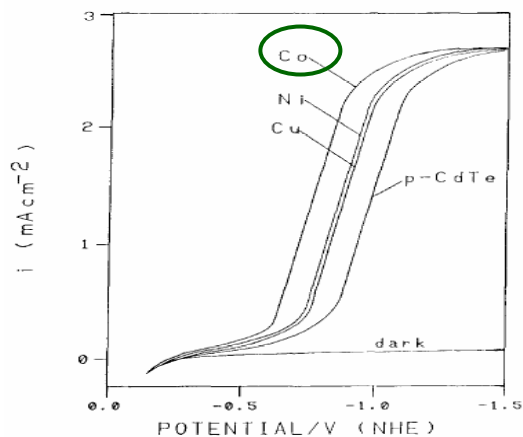
MPc catalysts adsorbed on a p-CdTe electrode in DMF-0.1 M TEAP/5% H_2O

Catalyst	Current Density[a]	µl CO/minute	Products Detected	Efficiency[b]
Pc	10.88	4.43	CO	68%
			HCOO⁻	5%
			H_2	25%
CoPc	11.94	7.79	CO	104%
			HCOO⁻	2%
			H_2	<1%
CoPc	11.44[c]	<0.2[d]	H_2	97%
CoPc	0.24[e]	<0.2[d]	H_2	92%
CuPc	10.83	6.14	CO	96%
			HCOO⁻	3%
			H_2	1%
NiPc	7.20	1.02	CO	77%
			HCOO⁻	6%
			H_2	16%
ZnPc	9.40	2.30	CO	88%
			HCOO⁻	2%
			H_2	15%
MnPc	9.95	2.07	CO	75%
			HCOO⁻	4%
			H_2	18%
VOPc	8.20	2.04	CO	89%
			HCOO⁻	3%
			H_2	5%
FePc	8.00	2.05	CO	92%
			HCOO⁻	4%
			H_2	8%

[a] averaged for one hour
[b] includes both gaseous products and those dissolved in solution
[c] under Ar atmosphere
[d] limit of GC detection
[e] under dark condition

Product analysis results for CO_2 reduction on phthalocyanine/p-CdTe

CoPc, the best phthalocyanine catalyst for CO_2 reduction

J, O'M. Bockris & J. C. Wass
Mater Chem Phys, 22 (1989) 249

Department of Chemistry
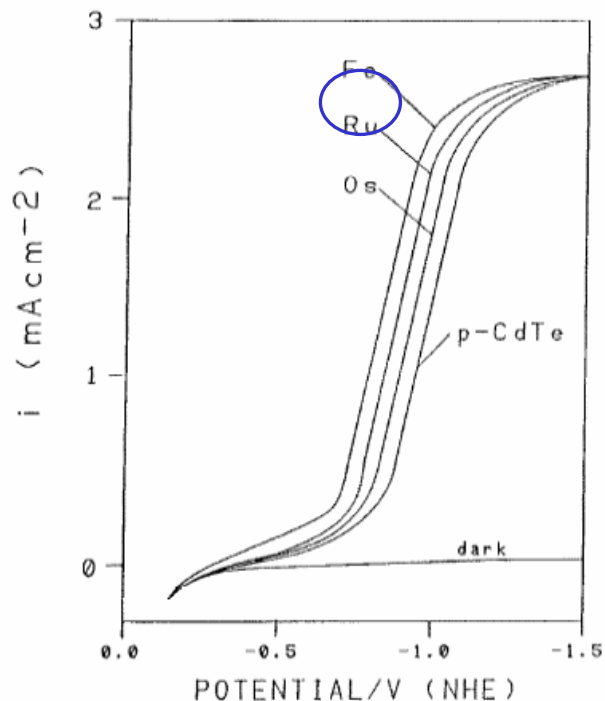
Current-potential curves for trinuclear carbonyl catalysts adsorbed on a p-CdTe electrode in DMF-0.1 M TEAP/5% H_2O.

Catalyst	Current Density[a]	µl CO/minute	Products Detected	Efficiency[b]
$Ru_3(CO)_{12}$	8.73	4.25	CO	88%
			$HCOO^-$	6%
			CH_3OH	1%
			H_2	4%
$Ru_3(CO)_{12}$	8.61[c]	<0.2[d]	H_2	97%
$Ru_3(CO)_{12}$	0.31[e]	<0.2[d]	H_2	94%
			$HCOO^-$	3%
			CH_3OH	1%
$Fe_3(CO)_{12}$	9.61	1.41	CO	70%
			$HCOO^-$	10%
			CH_3OH	1%
			H_2	21%
$Os_3(CO)_{12}$	9.67	1.74	CO	64%
			$HCOO^-$	7%
			CH_3OH	2%
			H_2	30%
$H_4Ru_4(CO)_{12}$	7.45	0.95	CO	46%
			$HCOO^-$	12
			CH_3OH	2%
			H_2	38%
$H_4Ru_4(CO)_{12}$	6.94[c]	<0.2[d]	H_2	99%

a   averaged for one hour
b   includes both gaseous products and those dissolved in solution
c   under Ar atmosphere
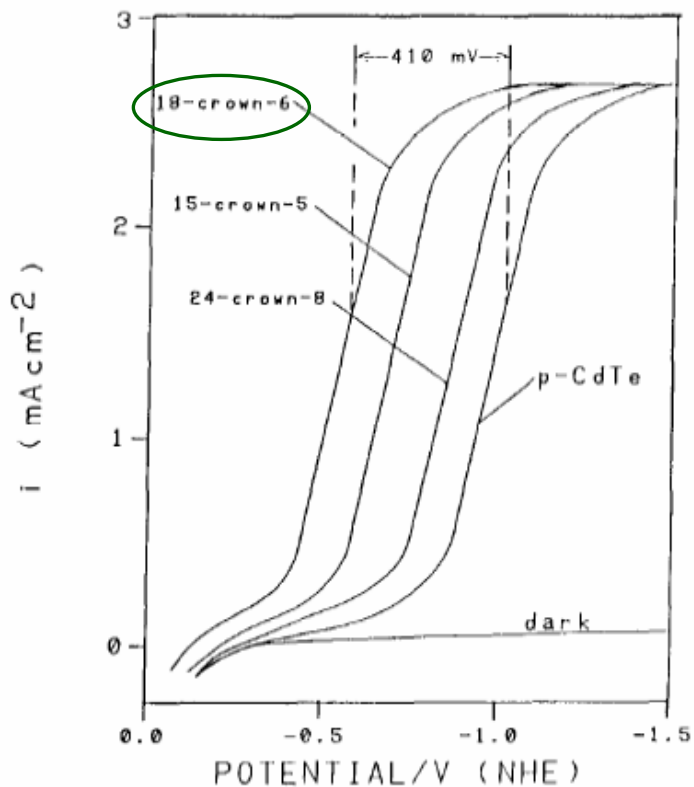d   limit of GC detection
e   under dark condition

Product analysis results for CO_2 reduction on carbonyl/p-CdTc

Iron carbonyl is the best among the three carbonyls studied

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Current-potential curves for crown ether catalysts added to the electrolyte for a p-CdTe electrode in DMF-0.1 M TEAP/S% H20.

Catalyst	Current Density[a]	μl CO/minute	Products Detected	Efficiency[b]
24-crown-8	8.29	1.62	CO	87%
			CH_3OH	6%
			H_2	6%
18-crown-6	9.46	5.12	CO	85%
			CH_3OH	13%
			H_2	1%
18-crown-6	9.24[c]	<0.2[d]	H_2	95%
18-crown-6	0.10[e]	<0.2[d]	H_2	98%
15-crown-5	8.86	4.60	CO	81%
			CH_3OH	14%
			H_2	2%
15-crown-5	8.75[c]	<0.2[d]	H_2	94%
15-crown-5	0.13[e]	<0.2[d]	H_2	96%
12-crown-4	9.04	2.22	CO	88%
			CH_3OH	5%
			H_2	4%

[a] averaged for one hour
[b] includes both gaseous products and those dissolved in solution
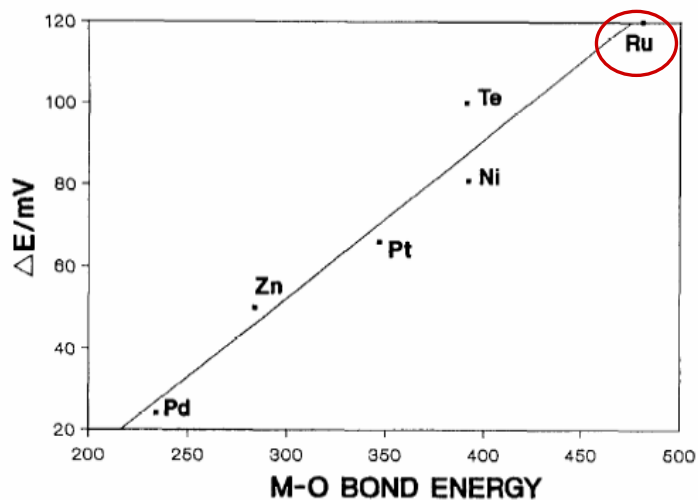[c] under Ar atmosphere
[d] limit of GC detection
[e] under dark condition

Product analysis results

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Catalytic shift (ΔE)

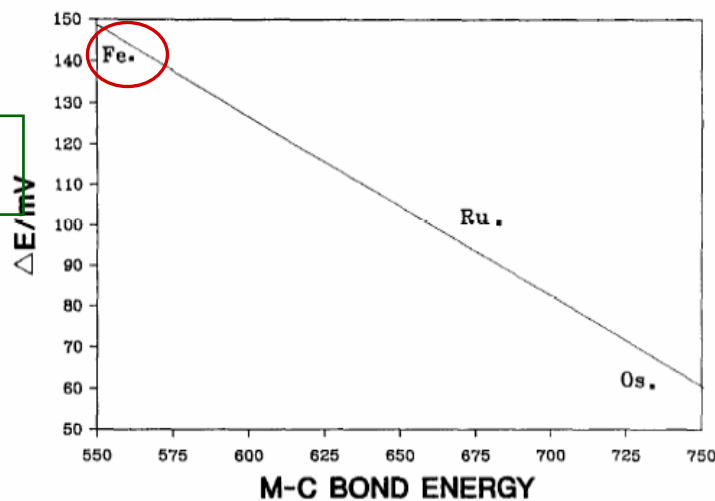Catalytic shift (ΔE) times the CO faradaic efficiency for metal catalysts on p-CdTe as a function of M-O bond energy
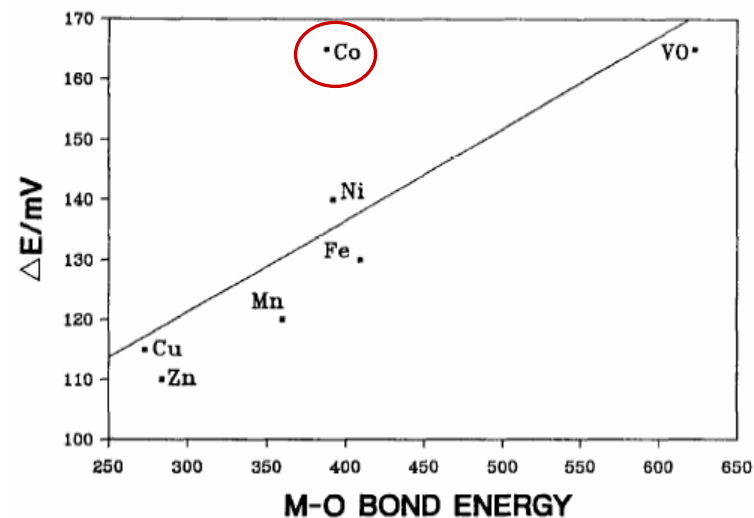
For metal-phthalocyanine catalysts on p-CdTe as a function of M-O bond energy

ΔE values for CO production are linear

J, O'M. Bockris & J. C. Wass
Mater Chem Phys, 22 (1989) 249

For trinuclear carbonyl catalysts on p-CdTe as a function of M-C bond energy

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CARBON MANAGEMENT

Proposals to mitigate anthropogenic climate change through planetary engineering projects

Cloud seeding to "terraforming" of the planet Mars!
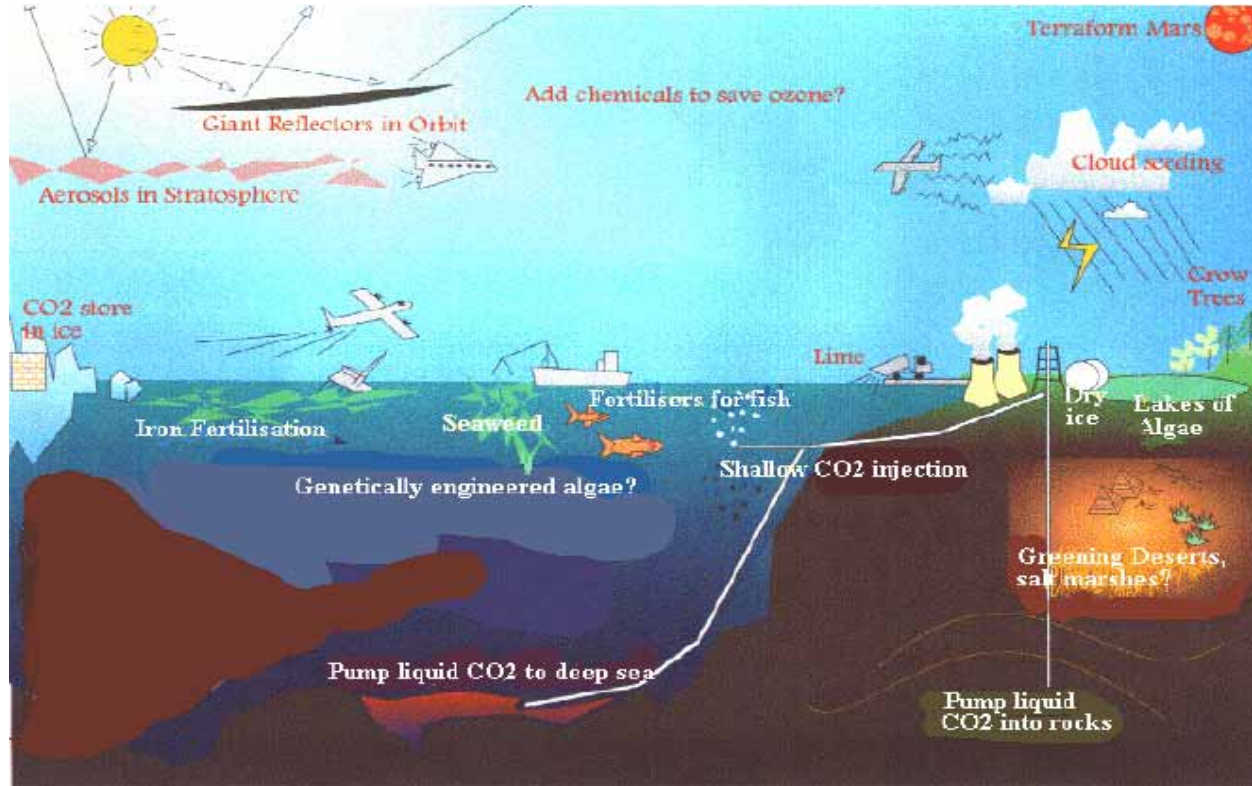

✓ **Fertilization of open waters to increase primary production & hence to absorb more carbon in fixed form**
✓ **Disposal of captured carbon dioxide directly into oceanic waters**
✓ **Injection of captured CO_2 into sub-seabed geological formations**

Matthews, B. (1996) Climate Engineering: University of East Anglia, Norwich, UK.

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Disposal of CO_2 into ocean waters

Capture of carbon dioxide from power station/industrial process flue gases
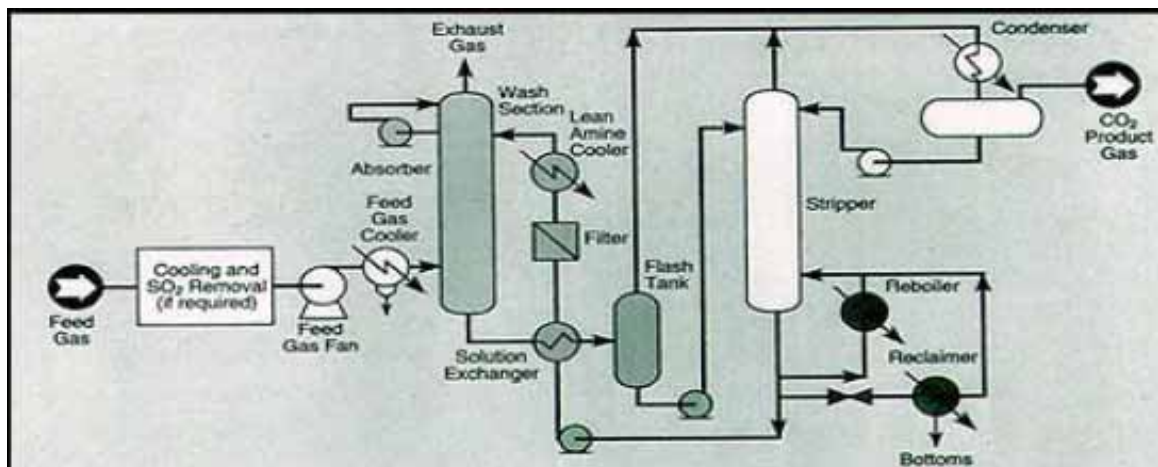
Energy demanding components & Generation of waste streams

Current Energy Penalties!

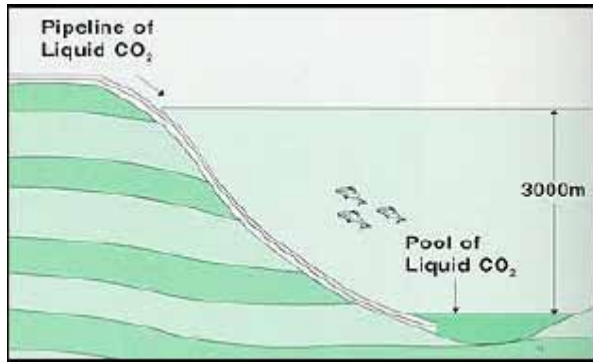**(Reduction in utility output as a result of using the process)**

- **Gas fired plant – 15 – 24%**
- **Conventional coal fired plant – 27 -37%**
- **Advanced coal plant – 13-17%**

Absolute reductions in efficiency of up to 35%

Greenpeace Research Laboratories, UK Technical Note 01/1999

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CO$_2$ into ocean - Technical approaches to deep sea disposal

Introduction by pipeline into deepwater followed by dissolution
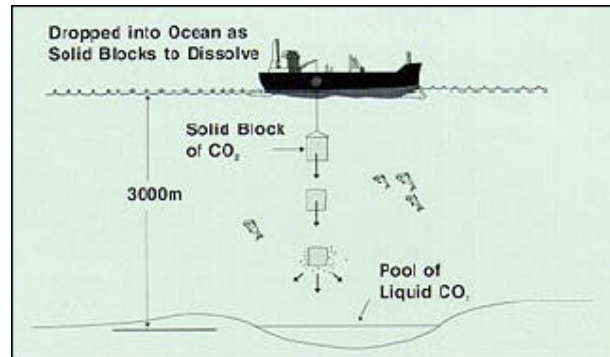
Dispersion following discharge of dry-ice blocks or liquid CO$_2$ from a ship
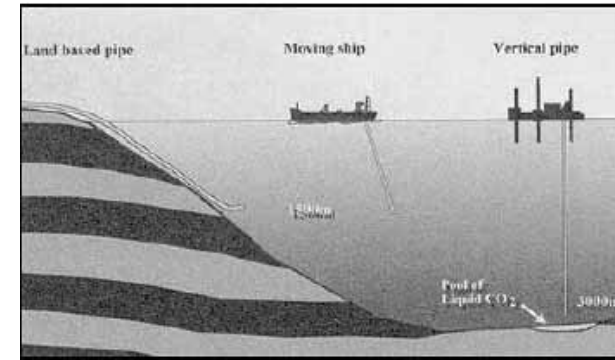
Formation of a lake of liq. CO$_2$ in deep ocean
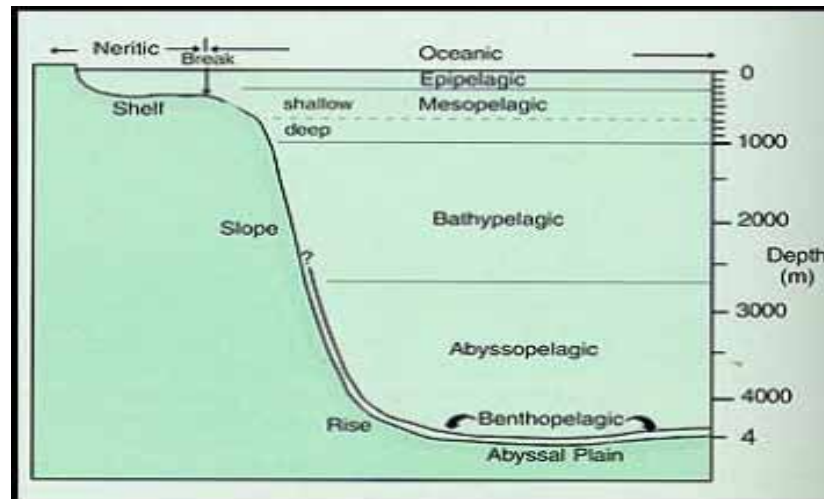
Major oceanic domains

Greenpeace Research Laboratories, UK
Technical Note 01/1999

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Pathways for carbon dioxide in the oceans

Stratification according to density
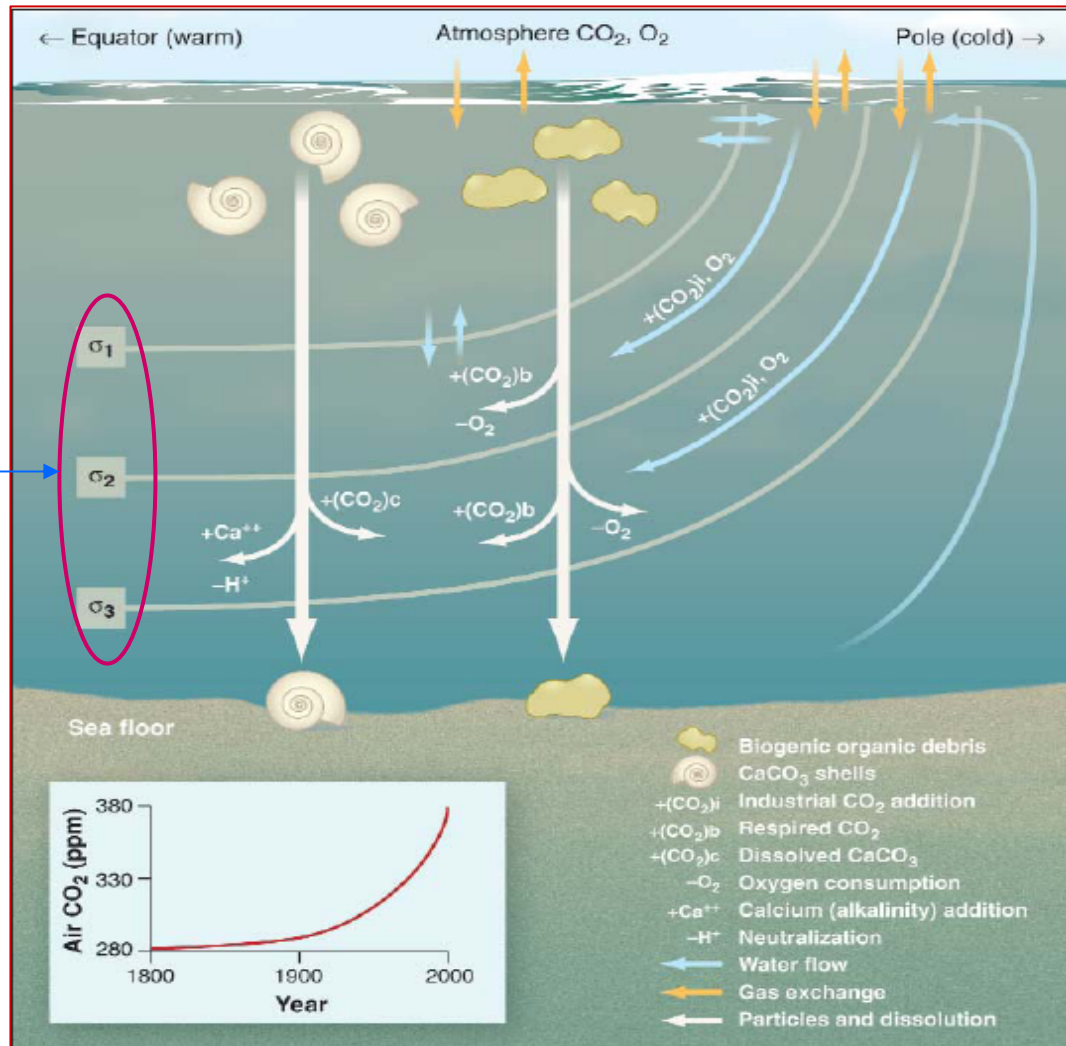
Global CO_2 recycling

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

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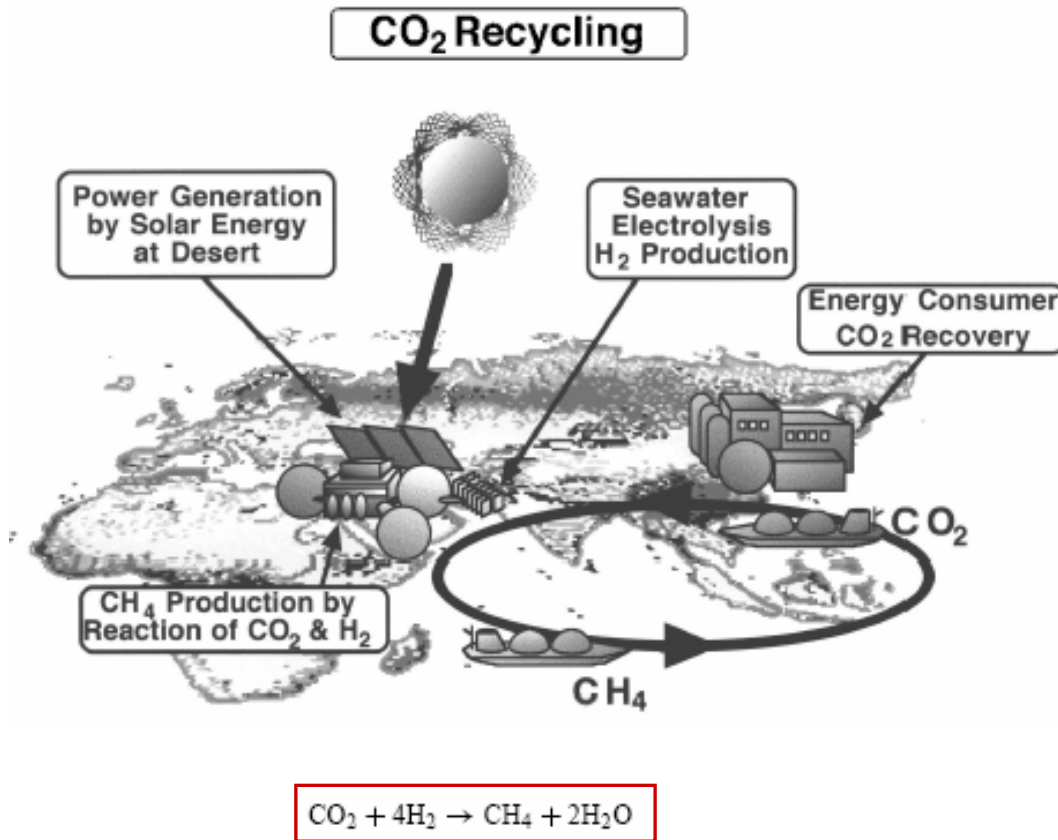
Global CO$_2$ recycling –Material Search

Key materials for global CO$_2$ recycling

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
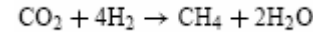
Active cathodes for hydrogen evolution in seawater electrolysis

Effective anode evolving oxygen instead of chlorine even in seawater electrolysis

Catalysts for methanation of CO$_2$
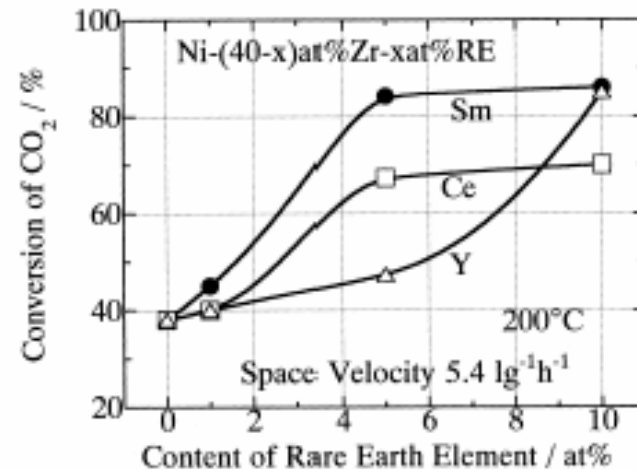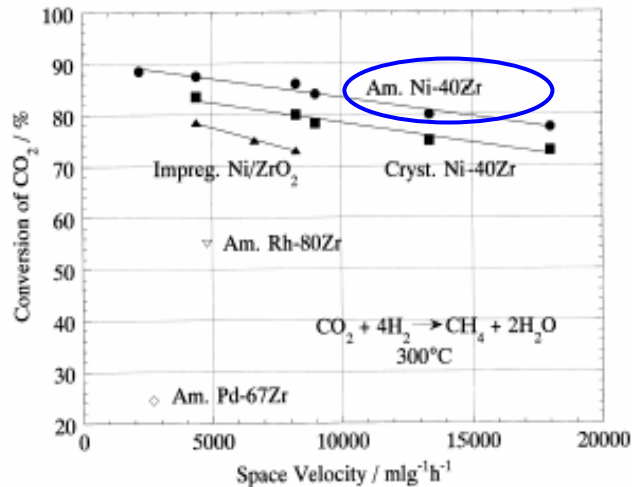
Ni–Zr alloy – Ideal methanation catalysts

Rare earth elements stabilize tetragonal ZrO$_2$ polymorph "Enhancement of catalytic activity"

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Substantiation of the idea of the global CO_2 recycling
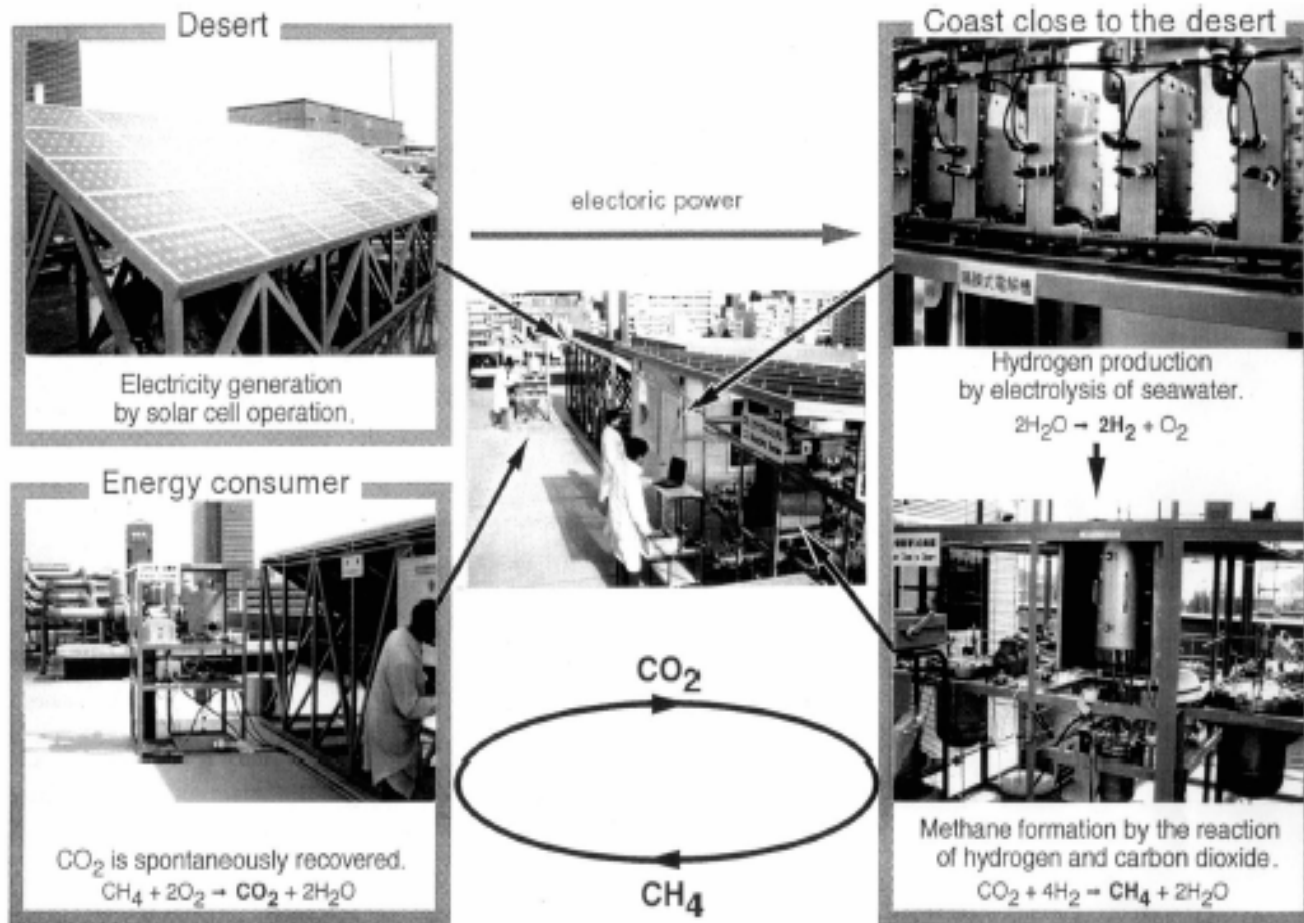
The CO_2 recycling plant built on the roof of the IMR, Tohoku University

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Reduced CO$_2$ emissions by global CO$_2$ recycling – An Example

A comparison of CO$_2$ emissions between the global CO$_2$ recycling & LNG combustion without CO$_2$ emission control in a 1GW power plant for 1 year

Emissions corresponding to energy consumed for building of LCO$_2$ tankers (0.01225Mt)

Emissions during transportation of CO$_2$ to Middle East (0.36266Mt)

Emissions corresponding to energy consumed for liquefaction of CO$_2$ (0.04211Mt)

Emissions corresponding to energy consumed for construction of a power plant (0.00601Mt)

Emissions corresponding to energy consumed for building of LCH$_4$ (LNG) tankers (0.00826Mt)

Emissions for electricity generation at a power plant (3.35346Mt)

Emissions corresponding to energy consumed for construction of a power plant (0.00601Mt)

Emissions corresponding to energy consumed for building of LCH$_4$ (LNG) tankers (0.00826Mt)

Emissions during transportation of LCH$_4$ (LNG) from Middle East (0.34253Mt)

No Emissions at Power Plant 0.77382Mt

3.71026Mt

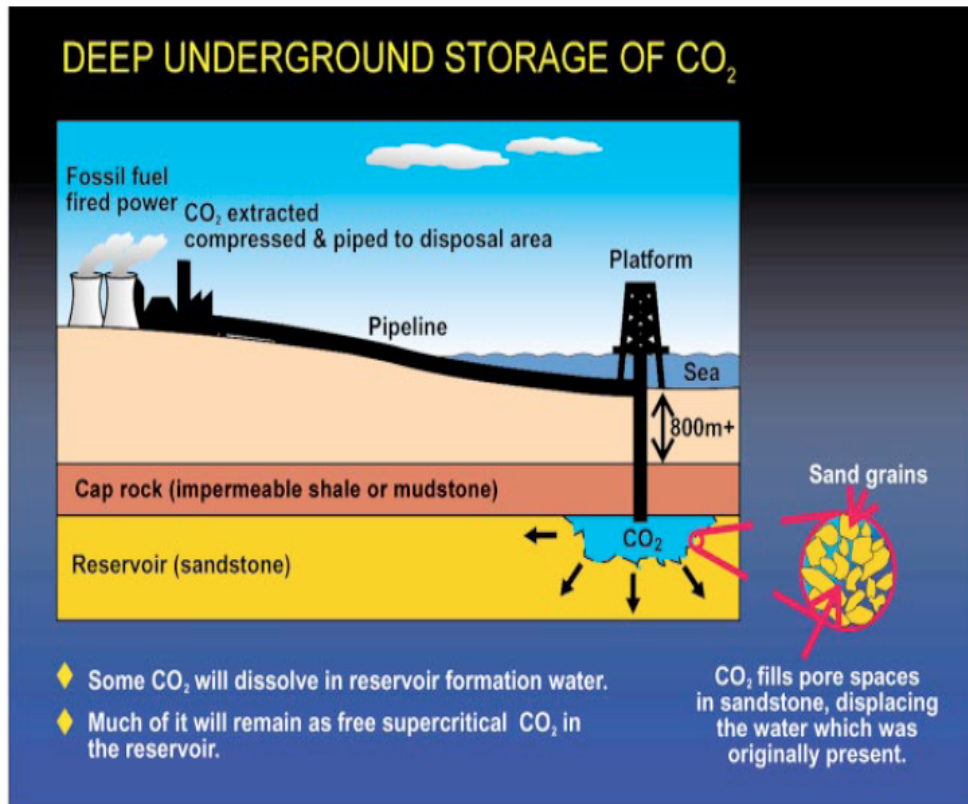CO$_2$ Recycling   No Control of CO$_2$ Emissions

CO$_2$ Emissions / Mtons

Reduction of CO$_2$ emissions by global CO$_2$ recycling is 79% of CO$_2$ Emissions from an LNG combustion power plant, i.e., 2.62 Mt/year

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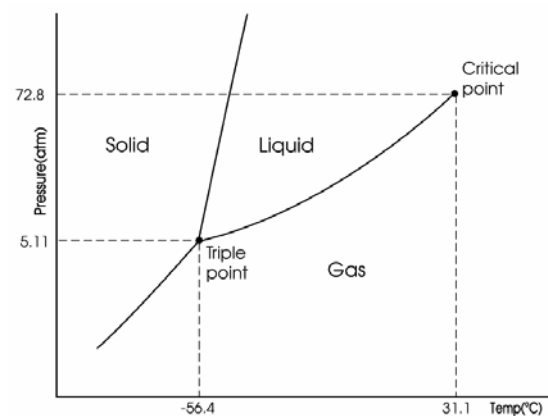**Department of Chemistry**

CO$_2$ Storage in Underground

The concept of CO$_2$ sequestration in reservoir rocks underground

**Storage in the Pore Spaces Between the Grains
of Porous and Permeable Rocks**

Sleipner Main platform & CO$_2$-processing plant

Phase diagram for CO$_2$

**S.Holloway
Annu. Rev. Energy Environ. 26 (2001)145**

Department of Chemistry

CO$_2$ sequestration

Barriers to wider implementation

➢ **High cost of capturing, processing, & transporting anthropogenic CO$_2$**
➢ **Incomplete understanding of reservoir processes**
➢ **Underdeveloped monitoring & verification technologies**
➢ **Unclear emissions trading regulations**
➢ **Potential conflicts of interest between sequestration & EOR or natural gas recovery**

Public perception

❖ **The technology is in its infancy and unproven**
❖ **The technology is too costly**
❖ **Not enough is known about the long-term storage of CO$_2$**
❖ **The capture and storage of CO$_2$ are seen as being energy intensive**
❖ **The option presents an enormous engineering and infrastructure challenge**
❖ **It is not a long-term solution**

**Barriers can only be overcome by research and design
& effective demonstration of the technology**

- Two big challenges
  - Reducing Costs
  - Developing Storage Reservoirs
- Utilization scores well on these two big challenges, but opportunities are limited
- Utilization will play an important role on initial sequestration projects
- Utilization will play a very minor role for longer-term, large-scale sequestration projects

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Utilization

- Opportunities
  - Helps economics
  - Eliminates "storage" issues
- Why is Large-Scale Use of CO_2 such a Challenge?
  - Market Sizes
  - Transportation Costs
  - Product Life-times
  - Energy Considerations

Transportation Costs

- Many production sources
  - CO_2 expensive to transport well in small quantities
  - Use sources of opportunity (e.g., process by-product, natural wells)
- Example – US 1997 capacity for liquid CO_2
  - 9.7 million metric tons
  - 93 plants
  - Largest: 900 metric tons/day
  - Average: 300 metric tons/day

CO$_2$ Utilization & Recovery - Market Research
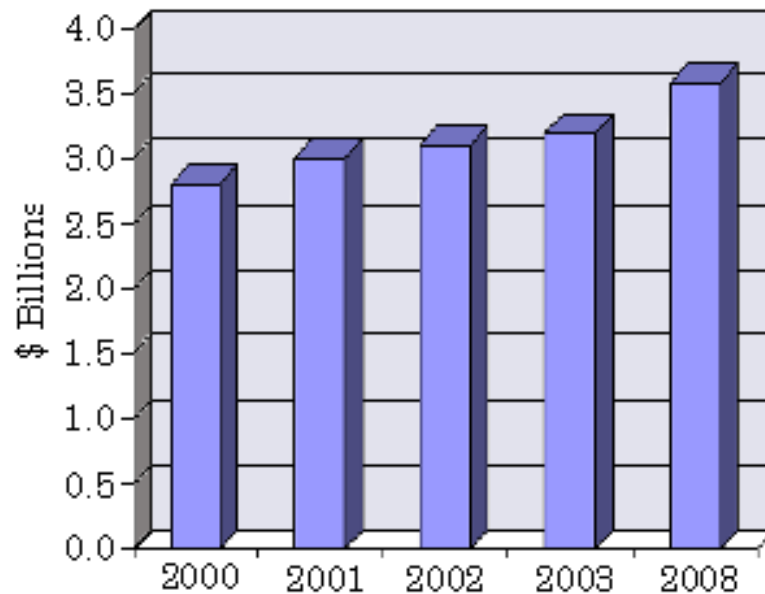
Chemists, chemical engineers, biotechnologists, process engineers, microsystem technologists in the chemical and pharmaceutical industry & academia, as well as manufacturers of analytical instruments, will find this technology extremely interesting and useful as a rapidly developing field!

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GRATEFUL THANKS ARE DUE TO

Dr M Aulice Scibioh

For her help in preparing this presentation

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Thank you all for your kind attention

Department of Chemistry