Clean oxidation process and chemical feedstocks

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> Should the capture of CO_2 be implemented on a large scale, large amounts of CO_2 would be available for utilization. Concerted policies are necessary that make less random the research, and focus science and technology upon fields that may better contribute to reducing the CO_2 emission. As a matter of fact, the utilization of CO_2 is the only technology that may produce profit out of recovered CO_2 , while contributing to reducing its global emission.
> Michele Aresta, in: *Activation of Small Molecules. W. B. Tolman, Ed.,* 2006 WILEY-VCH

We are interested in using catalysis to further two general reactivity types:

i) Reactions that incorporate CO_2 into new compounds in which the carbon atom maintains the formal +4 oxidation state;
ii) Reactions that generate reduced forms of CO_2

Important principles:

i) Chemistry should be as atomic economic as possible;
ii) Life Cycle Analysis (LCA) as a design element

Carboxylation Chemistry

Efficient routes to carboxylic acids:

1. Acetic Acid

$$CH_4 + CO_2 \rightarrow CH_3CO_2H$$

2. Long-chain carboxylic acids

$$CH_3(CH_2)_nCH{=}CH_2 + CO_2 \rightarrow CH_3(CH_2)_{n+2}COOH$$

Use of CO_2 as a phosgene alternative:

E.g. In synthesis of cyclic carbonates, replace $C(O)Cl_2$ (expensive, hazardous) with CO_2 (cheap, clean)

Reduction of CO_2

E.g.:

Known use of CO_2 as a mild oxidant to dehydrogenate ethylbenzene to styrene

$$PhCH_2CH_3 + CO_2 \rightarrow PhCH{=}CH_2 + CO + H_2O$$

$$(\text{WGS: } H_2O + CO \rightarrow H_2 + CO_2)$$

Possibilities:

$$M + CO_2 \rightarrow M{=}O + CO$$

$$M + 2\,CO_2 \rightarrow M(CO)CO_3$$

$$M + CO_2 + 2H^+ + 2e^- \rightarrow M(CO) + H_2O$$

(via $M(CO_2)$, $M(COOH)$)

Table 1.8 Processes of reduction of CO_2 in microorganisms, the enzyme implied and the metal present as prosthetic group

Reduction process	Name of enzyme	Metal	Reference
$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$	formate dehydrogenase	W, Mo	120
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	carbon monoxide dehydrogenase	Ni, Fe	121
$HCO_2H + 2H^+ + 2e^- \rightarrow H_2CO + H_2O$	formaldehyde dehydrogenase		122
$H_2CO + 2H^+ + 2e^- \rightarrow CH_3OH$	methanol dehydrogenase		123
$CO_2 + CH_4 \rightarrow CH_3COOH$	methanogen	Ni, Fe, Co	124
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	tetrahydrofolate	none	125