

# Clean oxidation process and chemical feedstocks

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Should the capture of CO<sub>2</sub> be implemented on a large scale, large amounts of CO<sub>2</sub> 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<sub>2</sub> emission. As a matter of fact, the utilization of CO<sub>2</sub> is the only technology that may produce profit out of recovered CO<sub>2</sub>, 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<sub>2</sub> into new compounds in which the carbon atom maintains the formal +4 oxidation state;
- ii) Reactions that generate reduced forms of CO<sub>2</sub>

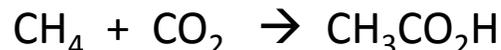
Important principles:

- 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



### 2. Long-chain carboxylic acids



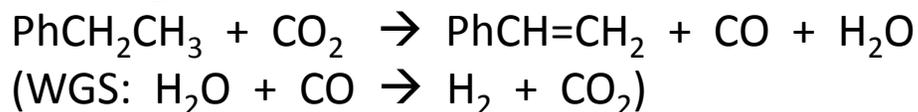
## Use of CO<sub>2</sub> as a phosgene alternative:

E.g. In synthesis of cyclic carbonates, replace C(O)Cl<sub>2</sub> (expensive, hazardous) with CO<sub>2</sub> (cheap, clean)

## Reduction of CO<sub>2</sub>

E.g.:

Known use of CO<sub>2</sub> as a mild oxidant to dehydrogenate ethylbenzene to styrene



## Possibilities:



(via M(CO<sub>2</sub>), M(COOH))

Table 1.8 Processes of reduction of CO<sub>2</sub> in microorganisms, the enzyme implied and the metal present as prosthetic group

Reduction process	Name of enzyme	Metal	Reference
$\text{CO}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{HCOO}^-$	formate dehydrogenase	W, Mo	120
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	carbon monoxide dehydrogenase	Ni, Fe	121
$\text{HCO}_2\text{H} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}$	formaldehyde dehydrogenase		122
$\text{H}_2\text{CO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_3\text{OH}$	methanol dehydrogenase		123
$\text{CO}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{COOH}$	methanogen	Ni, Fe, Co	124
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	tetrahydrofolate	none	125