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Aspects of carbon dioxide utilization

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Abstract

Carbon dioxide reacts with hydrogen, alcohols, acetals, epoxides, amines, carbon–carbon unsaturated compounds, etc. in supercritical carbon dioxide or in other solvents in the presence of metal compounds as catalysts. The products of these reactions are formic acid, formic acid esters, formamides, methanol, dimethyl carbonate, alkylene carbonates, carbamic acid esters, lactones, carboxylic acids, polycarbonate (bisphenol-based engineering polymer), aliphatic polycarbonates, etc. Especially, the productions of formic acid, formic acid methyl ester and dimethylformamide with a ruthenium catalyst; dimethyl carbonate and urethanes with a dialkyltin catalyst; 2-pyrone with a nickel-phosphine catalyst; diphenyl carbonate with a lead phenoxide catalyst; the alternating copolymerization of carbon dioxide and epoxides with a zinc catalyst has attracted attentions as the industrial utilizations of carbon dioxide. The further development of these production processes is expected.

Keywords: Carbon dioxide; Hydrogenation; Dimethyl carbonate; Alkylene carbonates; Polycarbonates; Ruthenium catalysts; Diphenyl carbonate

1. Introduction

Urea is manufactured about 100 million tons per year by using carbon dioxide [1,1a], and consumed mainly as a chemical fertilizer, urea resins, urea-melamine resins, an animal feed additive, etc. The other organic chemicals such as alkylene carbonates (solvent), β-oxynaphthoic acid (raw materials of dyes), salicylic acid and its derivatives (pharmaceuticals, food preservatives, etc.) are also produced in small amounts. It is estimated that these organic chemicals obtained by utilizing carbon dioxide are produced only less than 0.2 billion tons per year in the world [1b].

Recently, the amounts of the carbon dioxide in the air have been changing as follows [1b,2].

The amount of air is 5.3×10^{21} g (1 ppm = 5.3 billion tons) on the earth [3]. Carbon dioxide has increased by 90 ppm (480 billion tons) in about 200 years since 1800. Recently, it has increased by about 1.5 ppm (8 billion tons) per year [1b,2]. Therefore, now, it is difficult to decrease the amounts of carbon dioxide in the air by consuming it by the production of these organic chemicals as shown in Table 1 [1,2].

Nevertheless, chemists have to put more effort to increase the utilization of carbon dioxide by producing such organic chemicals. Unfortunately, carbon dioxide is a very stable compound, that is, a not very reactive compound, because carbon dioxide is a highly oxidized and thermodynamically stable compound, and its utilization in redox reactions requires high-energy substances or electro-reductive processes [4]. Therefore, it is required to find highly reactive metal catalysts. The investigations of the reaction between carbon dioxide and metal compounds, as transition elements, e.g., Ni [5–9], Pd [10,11], Pt [22], Co [12,55], Rh [13,14,22,34], Ir [15–18], Fe [19–21,34,53], Ru [22–26,34,53], Mn [27–29], Re [27,30–34], Cr [35], Mo [35–39], W [35,38–41], V [42], Nb [43,44], Ta [45], Ti [46–49], Zr [50–53] and U [54], and as non-transition elements, e.g., Mg [60], Zn [55,56], Sn [57,58], Cu [59] and Ag [59] have been carried out. The X-ray structures of these reaction products between carbon dioxide and the metal compounds such as Ni [8], Rh [14], Ir [16–18], Ru [24,25], Mn [28], Re [31], Mo [37,38], Ti [46,48,49], Zr [50,51], Zn [55] and Mg [60], have been reported. The reviews of these reports have also been published [61–64,64a].

Carbon dioxide reacts with hydrogen, alcohols, acetals, epoxides, amines, carbon–carbon unsaturated compounds and oxetanes in the presence of metal compounds as catalysts. These reactions with carbon dioxide are carried out in two kinds of solvents, i.e., supercritical carbon dioxide and other solvents. Recently, the investigations of reactions in the former supercritical carbon dioxide have been increased [64b–64d].

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Table 1
Variations of carbon dioxide for about 1000 years [1,2]

Year	Period (year)	Concentration (ppm)	Increase (ppm)	Increase rate (ppm/year)
1000–1800	800	270–280	10	0.01
1800–1950	150	280–310	30	0.2
1958–1975	17	315–330	15	0.9
1975–2002	27	330–370	40	1.5

Table 2
Catalytic systems for the synthesis of formic acid by the hydrogenation of CO_2 [65,67,78,80–86]

Catalyst	Solvent	Additive	$p(H_2)/p(CO_2)$ (bar)	Temperature (°C)	TON[a]	Time (h)	TOF (h^{-1})[b]	References
$TiCl_4$/Mg	THF	Mg	1/1	RT	15	24		[82]
cis[Ru(6,6′-Cl_2bpy)$_2$(H_2O)$_2$](CF_3SO_3)$_2$	EtOH	NEt_3	30/30	150	5000	8		[83]
[{Rh(cod)(μ-H)}$_4$]dppb[c]	DMSO	NEt_3	20/20	RT	2200	18	375	[78]
[Rh(dcpb)(hfacac)][c]	DMSO	NEt_3	20/20	25	3005[d]	31	1335	[84]
$PdCl_2$	H_2O	KOH	106/40	240	340	3		[86]
[Rh(TPPTS)$_3$Cl][c]	H_2O	$HNMe_2$	20/20	25	3440	12	1365	[85]
[Ru(PMe_3)$_3$(H_2)$_2$]	$scCO_2$	NEt_3, H_2O	85/120	50	7200		1400	[80]
[RuCl(OAc)(PMe_3)$_4$]	$scCO_2$	NEt_3, C_6F_5OH	70/120	50			95000	[81]

[a] Turnover number is the maximum total number of moles formic acid per metal center in the given reaction time.

[b] From the maximum initial rates of reaction; the TON and TOF are usually derived from different experiments.

[c] cod, Cyclooctadiene; dppb; $Ph_2P(CH_2)_4PPh_2$; dcpb, $Cy_2P(CH_2)_4PCy_2$; hfacac, hexafluoroacetylacetonate; TPPTS, $P(C_6H_4SO_3Na)_3$.

This review reports on formic acid, formic acid esters, formamides, other hydrogenation products, carbonic acid esters, carbamic acid esters (urethanes), lactones, carboxylic acids, polycarbonate (bisphenol-based engineering polymer) and aliphatic polycarbonates and other polymers, etc.

2. Hydrogenation products

2.1. General considerations

The synthesis of formic acid and methyl alcohol by the hydrogenation of carbon dioxide, has been widely investigated for the utilization of carbon dioxide. Formic acid esters and formamides were also synthesized together with alcohols and amines, respectively, by the hydrogenation of carbon dioxide. These reactions were carried out with both homogeneous and heterogeneous catalysts. The heterogeneous catalysis can offer several technical advantages, which are linked with the stability, separation, handling and reuse of the catalysts and reactor design. Despite these beneficial practical features, the range of compounds that have been synthesized from CO_2 by heterogeneous catalytic routes is still comparatively narrow [4].

These reactions were carried out mainly with the homogeneous catalysts of Ru and Rh. In the supercritical carbon dioxide, the high turnover numbers of catalysts were achieved in these catalysts.

2.2. Formic acid

Formic acid is a hydrogenation product of carbon dioxide with 1 mol of hydrogen. In the insertion reaction of carbon dioxide into metal hydrogen bond, many structures of the insertion products were confirmed by X-ray diffraction studies with each of the many transition metals shown in the former chapter. Many kinds of metal compounds such as Ti, Pd, Ru and Rh compounds were used as the catalysts for formic acid syntheses [65–87]. Especially, Ru and Rh catalysts show the highest catalytic activity. These reactions are shown in Table 2 [65,67,78,80–86].

The reactions of carbon dioxide were carried out in the presence of additives such as amines, KOH, Na_2CO_3 and water, in the supercritical carbon dioxide or the other solvents such as water, DMSO, THF, benzene, *i*-PrOH and EtOH.

For example, carbon dioxide reacts with hydrogen in a solution of triethylamine and acetone in the presence of catalysts formed in situ from a tetrameric hydride cluster [{(COD)Rh(μ-H)}$_4$] (COD = 1,5-cyclooctadiene) and $Ph_2P(CH_2)_4PPh_2$ (=bis(diphenylphosphino)butane (dppb)) as shown in Eq. (1) [68,78]. The reaction showed a high turnover number (TON) (2200). During the reaction [(dppb)Rh(μ^3-C_8H_{13})] is formed as the major product of the reaction of the above hydride cluster and the phosphine. This rhodium complex is presumed to be the precursor of the catalyst and the active species which is considered to be a 14e species, i.e. [(dppb)RhH] and obtained by removing a cyclooctadiene moiety from the precursor as shown in Eq. (2).

$$scCO_2 + H_2 \xrightarrow[Et_3N]{[\{(COD)Rh(\mu\text{-}H)\}_4],\ Ph_2P(CH_2)_4PPh_2} HCOOH \quad (1)$$

COD = 1,5-cyclooctadiene

TON = 2,200
TOF = 375 h^{-1}

$$[\{(COD)Rh(\mu\text{-}H)\}_4] + Ph_2P(CH_2)_4PPh_2 \xrightarrow[\text{THF-}d_8\text{, RT}]{} \underset{81}{[(dppb)Rh(\eta^3\text{-}C_8H_{13})]} + \underset{:\ 18}{[(dppb)_2RhH]}$$

$$[(dppb)Rh(\eta^3\text{-}C_8H_{13})] \xrightarrow[\text{THF-}d_8\text{, RT}]{\text{10 atm of } H_2} [(dppb)RhH] \xrightarrow{\text{dppb}} [(dppb)_2RhH] \qquad (2)$$

In the hydrogenation of CO_2 for forming formic acid with a bidentate ruthenium phosphine catalyst, RhH(dppp) (dppp = bis(diphenylphosphino)propane), a reaction mechanism was theoretically proposed, wherein CO_2 is inserted into the Rh(I)–H bond of RhH(dppp), followed by the σ–bond methathesis of a rhodium(I) formate complex, Rh(η^1–OCOH)(dppp), with molecular hydrogen, and formic acid is produced as shown in Scheme 1 [70,77,87].

Jessop et al. [80] reported that ruthenium methylphosphine catalysis of the hydrogenation of CO_2 to formic acid could take place in a supercritical mixture of H_2, CO_2 and NEt_3 without any additional solvent as shown in Eq. (3). With the ruthenium catalyst, 7200 mol of formic acid are formed per 1 mol of Ru with turnover frequencies (TOFs) up to 1400 h^{-1}. The presence of triethylamine and small amount of water is a prerequisite for the production of formic acid by the hydrogenation of CO_2 in its supercritical phase.

$$scCO_2 + H_2 \xrightarrow[\text{Et}_3\text{N, 50 °C, 205 atm}]{[(Cl)_2Ru(PMe_3)_4]} \underset{\substack{\text{TON} = 7{,}200 \\ \text{TOF} = 1{,}400\ h^{-1}}}{HCOOH} \qquad (3)$$

2.3. Formic acid esters

Formic acid esters are prepared by the hydrogenation of carbon dioxide in alcohol solvents as shown in Table 3 [65,88–91]. In many cases, amines or other basic additives have a positive effect on the course of the reaction. In the presence of CO_2 and hydrogen, formic acid is formed initially, and then its derivatives are formed under the reaction conditions.

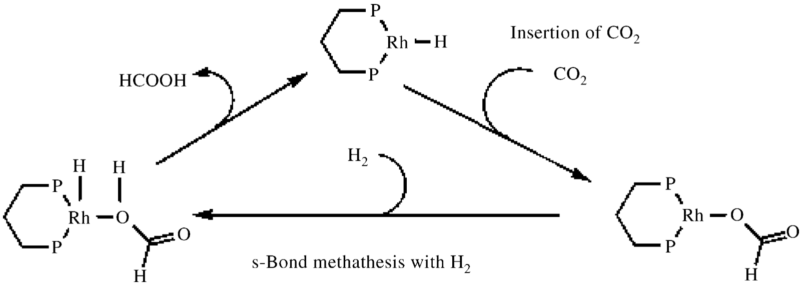
The supercritical carbon dioxide reacts with hydrogen in the presence of MeOH to give methylformate as shown in Eq. (4). The reaction achieved a high TON (3500) [91].

$$scCO_2 + H_2 \xrightarrow[\text{205 atm, 80 °C, 64 h}]{[Ru(PMe_3)_4Cl_2]\text{, MeOH}} \underset{\substack{\text{TON} = 3{,}500 \\ \text{TOF} = 55}}{HCOOMe} \qquad (4)$$

$$\text{HCOOH TON} = 6{,}800 \qquad \text{Selectivity 34 \%}$$

2.4. Formamides

Carbon dioxide reacts with hydrogen in the presence of secondary amines to afford formamide derivatives in high yields as shown in Table 4 [67,92–97].



Scheme 1. [70,77,87]

Table 3
Catalytic systems for the synthesis of formic acid esters by the hydrogenation of CO_2 [65,88–91]

Catalyst	Solvent	Additive	$p(H_2)/p(CO_2)$	Temperature (°C)	TON[a]	Time (h)	References
$[Pd(dppe)_2]$[b]	EtOH	EtOH, NEt_3	30/70	160	58	20	[88]
$[Fe_3(CO)_{11}H]^-$	MeOH	MeOH	20/20	175	5.8	96	[89]
$[(HCO_2)W(CO)_5]^-$	MeOH	MeOH	17/17	125	16.4	24	[90]
$[Ru(PMe_3)_4Cl_2]$	$scCO_2$	MeOH, NEt_3	80/125[c]	80	3500	64	[91]

[a] Maximum total number of moles ester per mol catalyst in the given reaction time.

[b] dppe, $Ph_2P(CH_2)_2PPh_2$.

[c] At reaction temperature.

Table 4
Catalytic systems for the synthesis of formamides by the hydrogenation of CO_2 [67,92–97]

Catalyst	Solvent	Additive	$p(H_2)/>p(CO_2)$ (bar)	Temperature (°C)	Time (h)	Yield (%)[a]	TON[b]	TOF (frequency, h^{-1})	References
$PdCl_2$	NMP	Me_2NH	80/40	170	1.5	99	34	23	[92]
$[RuCL_3-Ph_2PCH_2CH_2PPh_2-AlEt_3$	Hexane	Me_2NH	30/30	130	6	72.5	3400		[93]
$[Ru(PMe_3)_4Cl_2]$	$scCO_2$	Me_2NH	80/130	100	37	76	370000	10000	[94]
$RuCl_2[Ph_2P(CH_2)_3PPh_2]_2$[c]		Me_2NH	18.0 MPa	110				18400	[95]
$RuCl_2[Ph_2P(CH_2)_2PPh_2]_2$		Me_2NH	8.5/13.0 MPa	100	2.05		740000	360000	[96]
$RuCl_2[PH(CH_2OH)_2]_2[P(CH_2OH)_3]_2$	$scCO_2$		216–220	100	48		10000		[97]

[a] Yield of ester based on alcohol.
[b] Maximum total number of mols ester per mol catalyst in the given reaction time.
[c] Silica hydride aerogel support.

Noyori and co-workers [67,94] also reported the hydrogenation of carbon dioxide in its supercritical phase with dimethylamine. By using a catalyst $[Ru(PMe_3)_4Cl_2]$, up to 370,000 mol of DMF (*N*,*N*-dimethylformamide) per 1 mol catalyst are found in less than 37 h as shown in Eq. (5). Under the comparatively drastic reaction conditions (100 °C, 210 atm), the condensation of dimethylammonium formate to DMF takes place in liquid phase. Most of the DMF formed then is dissolved in the supercritical phase, while the water content of the liquid phase increases. In this way, all of the dimethylamine used is converted into DMF quantitatively [65,94].

$$scCO_2 + H_2 \xrightarrow[100\,°C,\ 210\ atm]{[(Cl)_2Rh(PMe_3)_4],\ Me_2NH} HCONMe_2 \qquad \begin{array}{l} TON = 370{,}000 \\ TOF = 10{,}000\ h^{-1} \end{array} \tag{5}$$

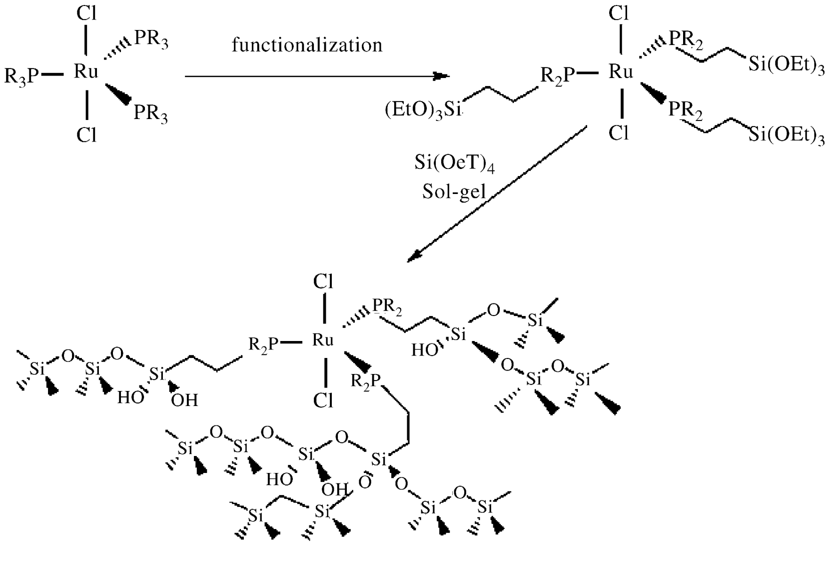
In 1997, with a ruthenium bidentate phosphine complex as a catalyst [96], much higher TON (740,000) and TOF (360,000) were achieved as shown in Table 4 [97].

Recently, DMF is also reported to be produced with heterogeneous ruthenium catalysts [4]. Silylether ruthenium complexes were anchored in a silica matrix by condensing with $Si(OEt)_4$ (tetraethoxysilane) as shown in Scheme 2 [4]. All gels were micro- to meso-porous and the organometallic complexes were immobilized as monomers. The hybrid gel catalysts can easily be separated from the reaction mixture. The silica matrix-stabilized ruthenium complexes affords the TOF up to 18,000 h^{-1} and 100% selectivity from CO_2, H_2 and dimethylamine for the formation of DMF [4,95,96].

2.5. Other hydrogenation products

The hydrogenation of CO_2 to CO, the reverse water gas shift reaction, is shown in Eq. (6). The hydrogenation of CO_2 beyond formic acid, formaldehyde and CO produces methanol, methane and occasionally higher alcohols and hydrocarbons.

The heterogeneous catalysis of hydrogenation of CO_2 to CH_3OH and hydrocarbons has been widely investigated. However, very few research papers have described the homogeneous catalysis of such reactions. The thermodynamics are



R = methyl, phenyl

Scheme 2. Design strategy for hybrid gel catalysts, illustrated using the example of ruthenium–silica hybrid gel [4]

Table 5
Homogeneous hydrogenation of CO_2 to CH_3OH, CH_4, or other products [67,106–109]

Catalyst	Solvent	Additives	Temperature (°C)	Time (h)	CO (TON)	CH_3OH (TON)	CH_4 (TON)	Other (TON)	References
$[PdCl(dppm)]_2$	EtOH	NEt_3	120	24	na	0	1.5	3.8[a]	[108,109]
Ru_3CO_{12}	NMP	KI	240	3	33	95	24	0.5[b]	[106]
Ru_3CO_{12}	NMP	I_2	240	3	27	2	76	0.5[b]	[106]
Ru_3CO_{12}	NMP	ZnI_2	240	3	73	4	4	0	[106]
Ru_3CO_{12}	NMP	[PPN]Cl	200	5	68	16	5	0	[107]

[a] HCOOEt.
[b] C_2H_6.

neutral or favorable because of the production of water from hydrogen as shown in Eqs. (6)–(8), but the economics are unfavorable for the same reason [67].

$$CO_2(aq) + H_2(aq) \longrightarrow CO(aq) + H_2O(l)$$
$$\Delta G^\circ = 11\ \text{kJ/mol};\ \Delta H^\circ = 11\ \text{kJ/mol};\ \Delta S^\circ = -0.8\ \text{J/(mol K)} \tag{6}$$

$$CO_2(aq) + 3H_2(aq) \longrightarrow CH_3OH(l) + H_2O(l)$$
$$\Delta G^\circ = -79\ \text{kJ/mol};\ \Delta H^\circ = -106\ \text{kJ/mol};\ \Delta S^\circ = -88\ \text{J/(mol K)} \tag{7}$$

$$CO_2(aq) + 4H_2(aq) \longrightarrow CH_4(l) + 2H_2O(l)$$
$$\Delta G^\circ = -193\ \text{kJ/mol};\ \Delta H^\circ = -230\ \text{kJ/mol};\ \Delta S^\circ = -125\ \text{J/(mol K)} \tag{8}$$

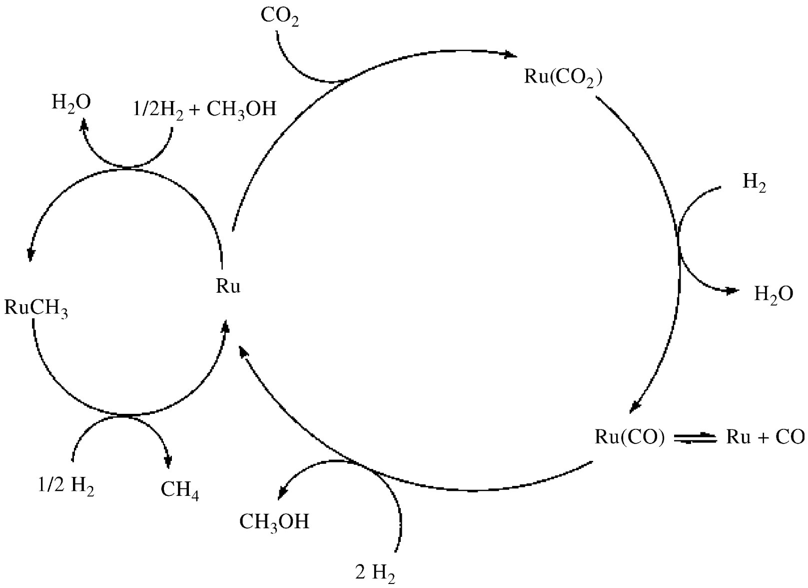
In the investigations with heterogeneous hydrogenation catalysis of CO_2, for example, methanol is prepared in 21.2% conversion of carbon dioxide at 356 g/l h GHSV (gas-hourly space velocity) of carbon dioxide in the presence of a Cu-Zn-Cr-Al-Pd catalyst at 250 °C temperature and under 50 atm pressure [98,99]. Ethanol is prepared in 44.4% conversion of carbon dioxide and 19.5% ethanol selectivity in the presence of a K/Cu-Zn-Fe catalyst at 300 °C, under 7 MPa [100–102].

In 2001, Watanabe et al. [103–105] found a high selectivity and long life catalyst for manufacturing methanol from carbon dioxide and reported a kinetic study of the methanol synthesis at a test plant of 50 kg/day MeOH. The catalyst is a Cu/Zn-based multi-component catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$). The reaction was carried out at 250 °C, 5 MPa and 10,000 h^{-1} space velocity, and the selectivity of methanol was more than 99.8 mol% and the catalyst life was more than 1 year.

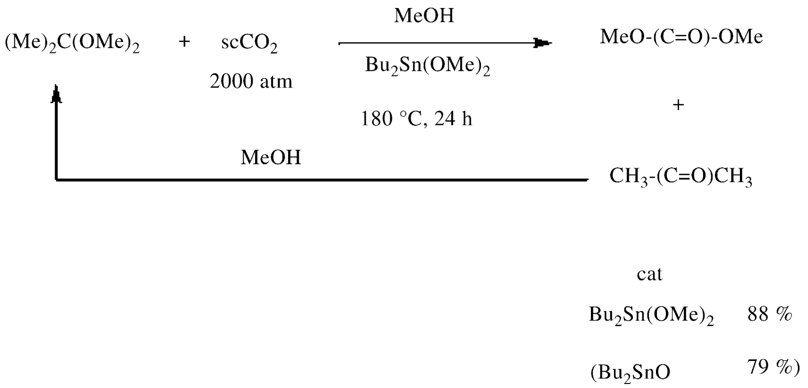
Reactions with ruthenium and palladium compounds as homogenous hydrogenation catalysts are shown in Table 5 [67,106–109]. The Ru homogeneous catalyst system catalyzed the reverse water gas shift reaction rapidly to give CO. Further reaction caused the amount of CO to decrease and methanol to increase. The production of methane and ethane was slower. An experiment with added extra methanol showed the increased yield of CH_4, suggesting that methanol hydrogenation was responsible for CH_4 formation as shown in Scheme 3 [67,106].

3. Carbonic acid esters

Carbonic acid esters have come to occupy an important position as useful intermediates for a variety of industrial and



Scheme 3. Hydrogenation of CO_2 to CO, CH_3OH and CH_4 [67,99]



Scheme 4. [116,117]

synthetic applications [110]. Dimethyl carbonate (DMC) was reported as an environmentally benign compound. For example, the transesterification of DMC gives methyl phenyl carbonate (MPC), and diphenyl carbonate (DPC) is prepared by the disproportionation of MPC with phenol in the presence of a MoO_3/SiO_2 catalyst. The DPC is a raw material for a polycarbonate as shown in Section 6. The DMC is also utilized as a halogen-free methylating agent and a raw material for synthesizing $Si(OMe)_4$ [111].

Carbonic acid esters are used as the raw materials of polycarbonates or isocyanates, alkyl agents, solvents and fuel additives. These carbonic acid esters $(RO)_2C{=}O$ and cyclic carbonic acid esters (e.g. ethylene carbonate) are synthesized by the reaction of carbon dioxide with alcohols in the presence of catalysts (e.g. CeO_2-ZrO_2 [112,113]) as shown in Eq. (9).

$$2\,ROH + CO_2 \xrightarrow{\text{catalyst}} RO\text{-}(C{=}O)\text{-}OR + H_2O \quad (9)$$

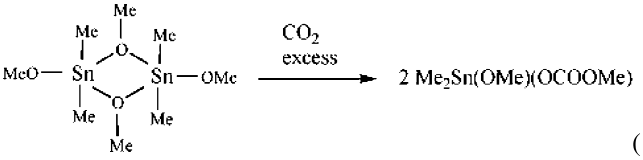
These reactions did not proceed in high yields, since the hydrolysis of the esters and decomposition of catalyst by co-produced water proceed. However, DMC is obtained in a high yield by a reaction with trimethyl orthoacetate in the presence of dibutyltindimethoxide-tetrabutylphosphinate iodide as shown in Eq. (10) [114]. In this process, it is difficult to utilize a byproduct, methyl acetate as the raw material of $MeC(OMe)_3$.

$$Me\text{-}C(OMe)_3 + scCO_2 \xrightarrow[180\,°C,\ 72\,h]{Bu_2Sn(OMe)_2\text{-}Bu_4PI} \underset{70\,\%}{MeO\text{-}(C{=}O)\text{-}OMe + CH_3COOMe} \quad (10)$$

On the other hand, in the process with acetal, it is easy to utilize the byproduct, acetone as the raw material by a reaction with MeOH as shown in Scheme 4 [115,116]. Therefore, formally, the DMC is synthesized from the reaction of methyl alcohol and carbon dioxide. The yield increases with the increase of reaction pressure and concentration of methyl alcohol. Then the reaction is carried out under a high pressure in a mixed solvent of methyl alcohol and the supercritical carbon dioxide. Especially, the reaction of acetals is attractive because the starting material is much more inexpensive as compared with that of acetone which can be recycled (Scheme 4).

Further, the preparation of dimethyl carbonate was succeeded by directly reacting CO_2 with methyl alcohol with dehydration in a separate apparatus at a low temperature as shown in Scheme 5 [117]. Organotin catalyst, at a low temperature, forms an intramolecular carbonyl coordination structure (A) and methoxy-bridged five-coordination structure (B) as shown in Fig. 1. The methoxy-bridged dinuclear structure (B) was determined by X-ray diffraction studies [116].

The reaction of this methoxy-bridged dinuclear organotin catalyst with excess CO_2 quantitatively afforded a complex having two kinds of new methoxy groups, indicating that CO_2 insertion occurred only at one of the two methoxy group of the catalyst as shown in Eq. (11) [116].



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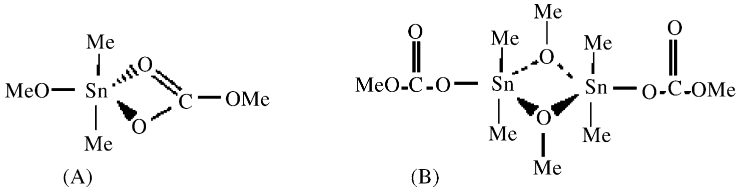
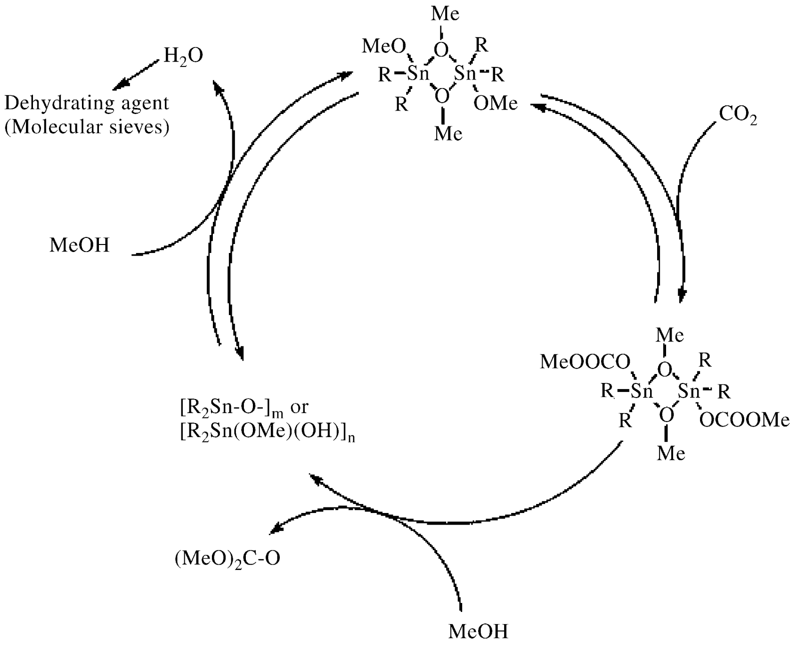


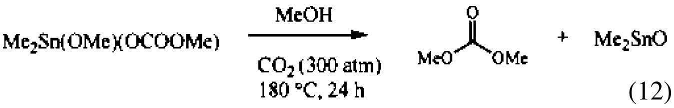
Fig. 1. Structures of organotin catalyst $(Me_2Sn(OMe)_2$, the reaction product (A) with carbon dioxide, and the monomeric product (B) [116].

$$2\,\mathrm{MeOH} + \mathrm{CO_2} \xrightarrow[180\,^{\circ}\mathrm{C},\ 300\ \mathrm{atm}]{\mathrm{Bu_2Sn(OMe)_2}} \mathrm{(MeO)_2C{=}O} + \underset{\text{molecular sieve}}{\mathrm{H_2O}}$$



Scheme 5. [117]

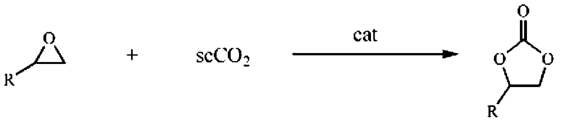
Upon heating to 180 °C in the supercritical CO_2 (300 atm), the methoxy-bridged dinuclear structure (B) was converted to dimethylcarbonate in a reasonable yield as shown in Eq. (12) [116].



(12)

The process shows a high selectivity in 50% conversion with a molecular sieve as a hydration agent. This system is more attractive compared with the synthesis using orthoesters or acetals as chemical dehydrating agents since the molecular sieve is easily recyclable, and there is no co-product. The reaction, at a total pressure 300 atm and at 180 °C for about 70 h gives 50% yield on the basis of methanol [117].

Carbon dioxide can react with oxiranes to give cyclic carbonates as shown in Eq. (13). The use of alkylene carbonates for the synthesis of dimethyl carbonate is extremely promising since the synthesis of ethylene carbonate utilizes abundantly available carbon dioxide (see Scheme 8). However, the advantage of using alkylene carbonates for the synthesis of dimethyl carbonate goes beyond the simple use of carbon dioxide. It actually allows one to avoid fighting the equilibrium in the direct synthesis of dimethyl carbonate from carbon dioxide and methyl alcohol [110]. Many catalysts have been investigated for the reaction of carbon dioxide with various kinds of oxiranes as shown in Table 6 [118–128].



(13)

In 2003, excellent process for propylene carbonate synthesis in the supercritical CO_2 in the presence of polyfluoroalkylphosphonium iodides as catalysts was reported as shown in Fig. 2 [129]. This reaction system has two prominent points: (i) the reaction in the supercritical CO_2 with polyfluoroalkyl phosphonium iodides (e.g. $(C_6F_{13}C_2H_4)_3MePI$) shows a high yield (93%) and high selectivity (99%), and (ii) propylene carbonate was spontaneously separated out of the supercritical CO_2 phase. Therefore, the catalyst could be recycled while maintaining a high CO_2 pressure and temperature by separating the propylene carbonate from the bottom of the reactor followed by supplying propylene oxide and CO_2 to the upper supercritical CO_2 phase in which the catalyst remained as shown in Fig. 2 [129].

4. Carbamic acid esters (urethanes)

Carbamic acid esters (urethanes) (NR_2COOR') obtained by reactions involving a CO_2/amine system, have played an important role in industrial chemistry. Their derivatives are the important precursors of pharmaceuticals, herbicides, fungicides and pesticides in an agricultural field, and as the precursors of isocyanides, which in turn, are intermediates in the production of high-performance plastics, polyurethanes,

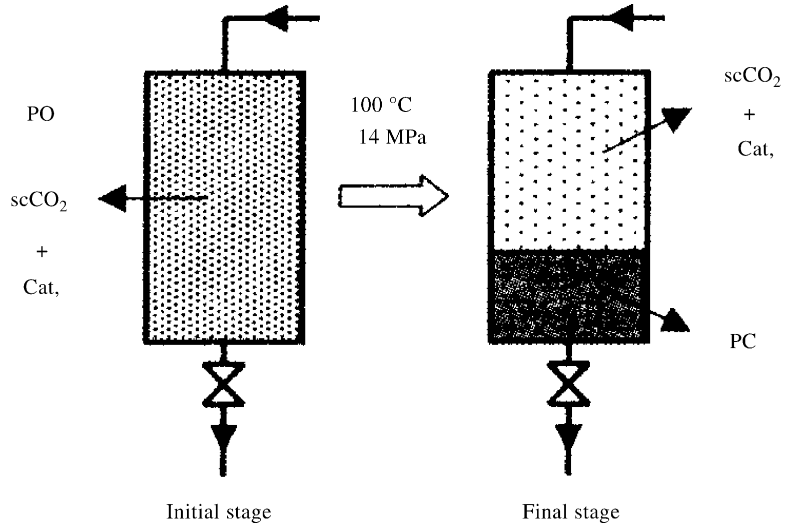


Fig. 2. Schematic diagram of the reaction behavior for the propylene carbonate synthesis from propylene oxide and supercritical CO_2 at 100 °C and 14 MPa. PO; propylene oxide, sc CO_2: supercritical CO_2, PC: propylene carbonate [129].

elastomers and adhesives [130]. The isocyanates (RNCO) are synthesized by the decomposition of these carbamates.

Carbamic acid esters are generally prepared by the reactions of the CO_2/amine with organic compounds such as organic halides, alcohols, organic carbonates, acetylenes, olefins, epoxides, organometallic compounds, etc. as shown in Eq. (14)[130–142].

$$R^1R^2NH + CO_2 + R^3Z \xrightarrow{\text{cat.}} R^1R^2NCOOR^3 \tag{14}$$

These carbamates are synthesized in high yields by the reactions of the supercritical carbon dioxide, amines and organic halides in the presence of potassium carbonate and an onium salt (Bu_4NBr) as shown in Eq. (15) [131].

$$Et_2NH + BuX + scCO_2 \xrightarrow[100\ ^\circ C,\ 2\ h]{Bu_4NBr\ K_2CO_3} \underset{90\ \%}{Et_2N\text{-}COOBu} + HX \tag{15}$$

Carbon dioxide also reacts with amines and alcohols in the presence of an organotin catalyst and acetal as a dehydrating agent under a high CO_2 pressure to give the carbamate in a high yield as a halogen free process as shown in Eq. (16) [132].

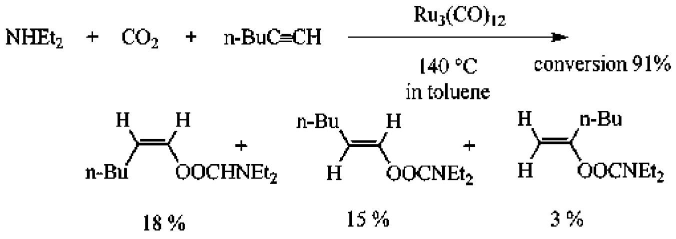
$$t\text{-}BuNH_2 + EtOH + \underset{(30\ MPa)}{CO_2} \xrightarrow[200\ ^\circ C,\ 24\ h]{\substack{Bu_2SnO \\ \text{acetal (2 eq.)}}} \underset{84\ \%}{t\text{-}BuNH\text{-}COOEt} + H_2O$$
$$\text{acetal} = Me_2C(OMe)_2 \ \text{dehydrating agent} \tag{16}$$

Table 6
Synthesis of cyclic carbonates from carbon dioxide and epoxides [118–128]

Catalyst	Epoxide	CO_2 (MPa)	Temperature (°C)	Time (h)	TON	TOF (h^{-1})	Yield (%)	References
SalenCr(III)-co-catalyst[a]	Propylene oxide	100 psi	100	1	916	916		[118]
SalenCr(III)Cl	2,3-Epoxy-1,2,3,4-tetra-hydronaphthalene	55 bar	80	12	12		20	[119]
SaleneCr(III)N_3^-co-catalyst[b]	Cyclohexene oxide	34.5 bar	80	10	669.9	67	98.3	[120]
SaleneAlCl-*n*-Bu_4NBr	Ethylene oxide	15–16	120	1		3070		[121]
$Ni(PPh_3)_2Cl_2/PPh_3/Zn$-*n*-Bu_4NBr	Propylene oxide	2.5	120	1	3043		85	[122]
BMIm/BPy[c]	Propylene oxide	2	140	6	449.5		89.9	[123]
Mg–Al mixed oxides	Propylene oxide	5 atm	100	24			88	[124]
SmOCl-DMF	Propylene oxide	14	200	8			99	[125]
MgO	(*R*)-Styrene oxide	20 kg cm^{-2}	135	4			63 (93% ee)	[126]
Cs/Al_2O_3	Ethylene oxide	550 psi	150	3			24	[127]
Ni(cyclam)Br_2 e^-, Mg anode KBr (supporting electrolyte)[d]	Styrene oxide	1 atm	rt	7 (60 mA)			92	[128]

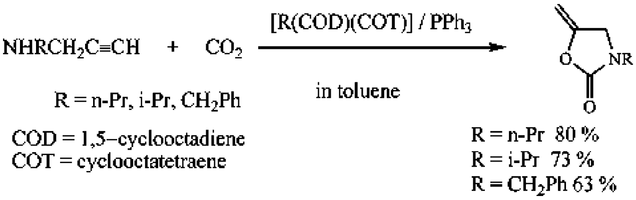
[a] (4-Dimethylamino)pyridine.
[b] (1*R*,2*R*)-Cyclohexenediimine.
[c] 1-*n*-Butyl-3-methylimidazolium/*n*-butylpyridinium.
[d] Cyclam, 1,4,8,11-tetraazacyclotetradecane.

Carbon–carbon unsaturated compounds such as acetylenes and olefins react with carbon dioxide and amines to give the carbamic acid esters. For example, vinylcarbamates were prepared in the 91% conversion of hex-1-yne by the reaction of CO_2 with a secondary amine and an alkyne having terminal triple bond in the presence of a catalytic amount of $Ru_3(CO)_{12}$ as shown in Eq. (17) [135,136].



(17)

Cyclic carbamates are obtained in good yields by the reaction of CO_2 with N-substituted terminal propargylamines in the presence of a catalytic amount of (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium ([Ru(COD)(COT)]) and a tertiary phosphine in toluene as shown in Eq. (18) [137].



(18)

1-Ethoxyethyl carbamates were obtained directly by the reaction of ethyl vinyl ether with CO_2 and amines such as dimethylamine and diethylamine as shown in Eq. (19) [138].

$$NHR_2 + CO_2 + CH_2{=}CHOEt \xrightarrow[80\ ^\circ C]{} NR_2COOCH(CH_3)OEt$$

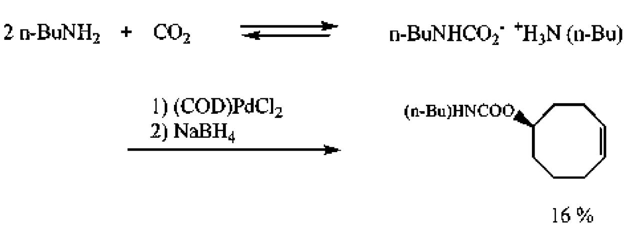
R = Me, Et

R = Me 7.2 %
R = Et 11 %

(19)

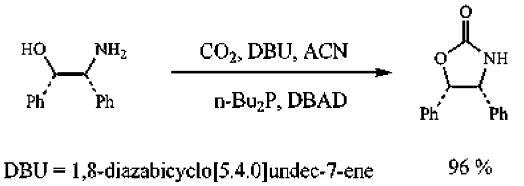
Epoxides react with carbon dioxide with primary or secondary amines under mild conditions to give hydroxycarbamates or cyclic carbamates [130,139]. For example, the reactions of 2-methoxy-3,3-dimethyl-2-phenyloxirane and CO_2 in the presence of an α,ω-diamine afford cyclic carbamates bis(2-oxazolidione) derivatives as shown in Eq. (20) [140].

In the carbamic acid ester formation reaction (Eq. (14)), organometallic compounds are also used for one of organic moieties. For example, the addition of THF solution of (1,5-cyclooctadiene)palladium dichloride to a previously prepared solution of *N*-butylcarbamate at 35 °C, followed by quenching with added $NaBH_4$ in 2.5N NaOH gave the cyclooctenyl carbamate in 16% isolated yield as shown in Eq. (21) [141].



(21)

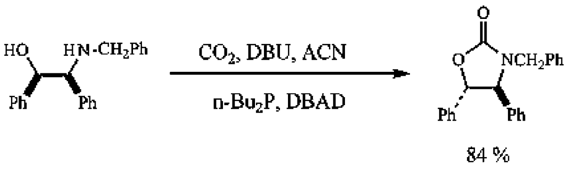
Cyclic carbamates are frequently employed as fragments in biologically active materials for pharmaceutical and agricultural uses. They are most commonly prepared from amino alcohols by its carbonylation using phosgene, by oxidative carbonylation using CO, etc. [142]. Amino alcohols react with carbon dioxide to give a carbamic acid intermediate with the unexpected stereoselectivity of the Mitsunobu transformation, and the stereochemical course of the Mitsunobu reaction [142a,142b,142c] is dependent on whether the carbamic acid intermediate is substituted with hydrogen (retention) or carbon (inversion) on its nitrogen atom. For example, the retention and inversion are shown in Eqs. (22) and (23), respectively [142].



DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

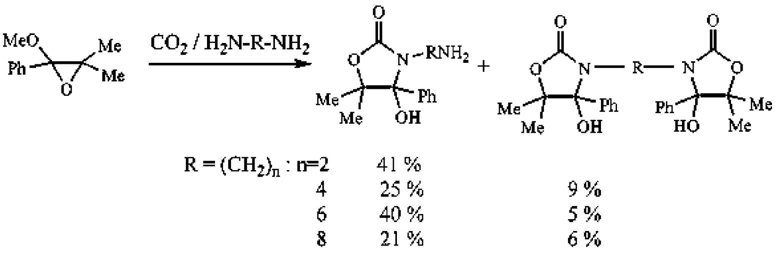
N-substituted with H (retention)

(22)



N-substituted with C (inversion)

(23)



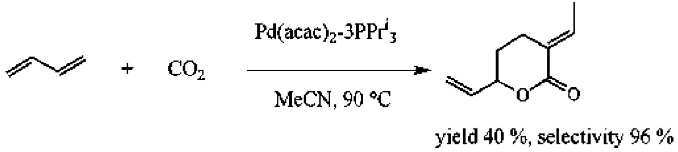
(20)

5. Lactones, carboxylic acids and others

Many transition metal complexes react with carbon dioxide. Carbon dioxide is activated by transition metals and forms complexes having bent bond structures and longer bond lengths, e.g. in $Ni(CO_2)(P(C_6H_{11})_3)_2 \cdot Ph\text{-}CH_3$: C–O–C bond angle is changed from 180° to 133° and C–O bond lengths is changed from 1.16 to 1.22 Å and 1.17 Å as shown in Fig. 3 [8].

On the other hand, carbon–carbon unsaturated compounds such as monoolefins, dienes, allenes and acetylenes react also with transition metal complexes to form their metal π-complexes. Both carbon dioxide and these carbon–carbon unsaturated compounds bond with the same transition metal and they are activated.

Therefore, carbon dioxide is able to react with the carbon–carbon unsaturated compounds such as alkynes, conjugated dienes and allenes in the presence of transition metal compounds as the catalysts to yield six-membered unsaturated lactones (Eqs. (24)–(26)) or five-membered metalalactone (Eq. (27)) [143–145]



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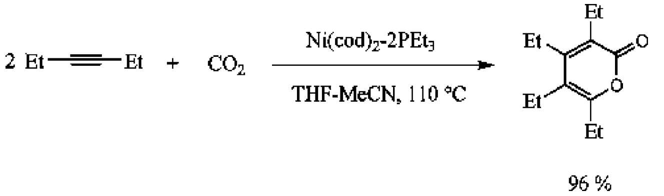

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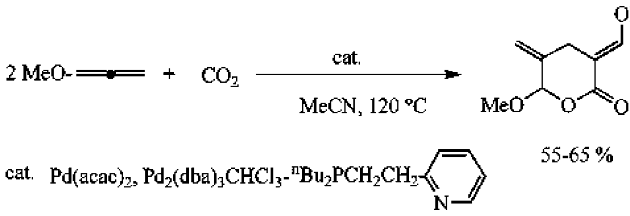
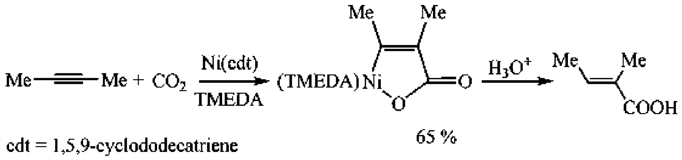


(26)

The formation mechanism of a six-membered unsaturated lactone and 2-pyrone are shown in Schemes 6 and 7, respectively [144–149]. These products are prepared by an oxidative addition, an insertion and a reductive elimination.

On the other hand, 2-butyne reacts with carbon dioxide in the presence of Ni(cdt) (cdt = 1,5,9-cyclododecatriene) and *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine (TMEDA) to give a five-membered nickelacyclolactone. Its protonolysis led to 2-methylcrotonic acid as shown in Eq. (27) [150].



TMEDA = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine (27)

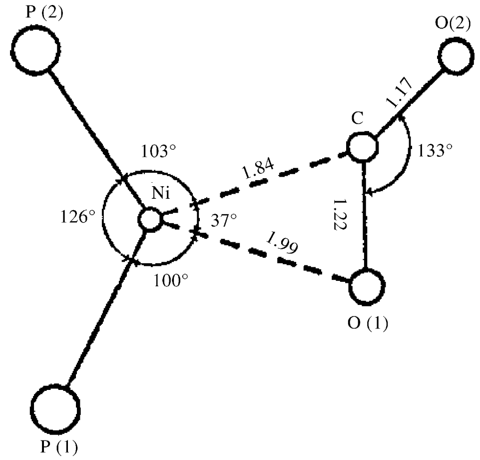
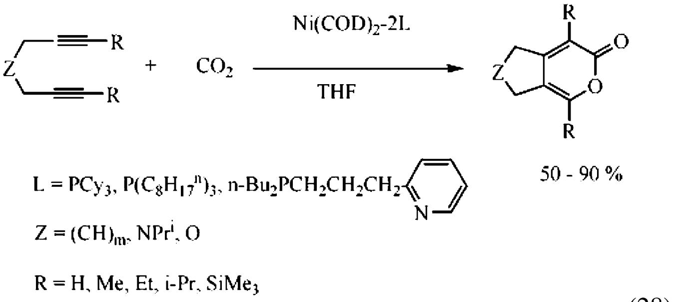
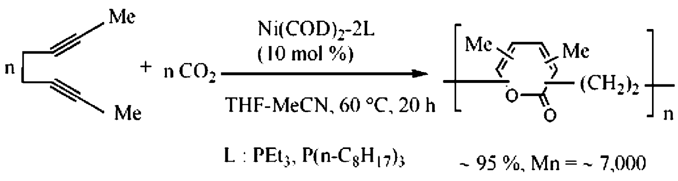


Fig. 3. Structure of $Ni(CO_2)(P(C_6H_{11})_3)_2$ 0.75 $Ph\text{-}CH_3$ [8]. CO_2: O=C=O, ∠O–C–O = 180°, C–O:1.16 Å, Ni–CO_2 complex: ∠O–C–O = 133°, C–O: 1.17 Å, 1.22 Å.

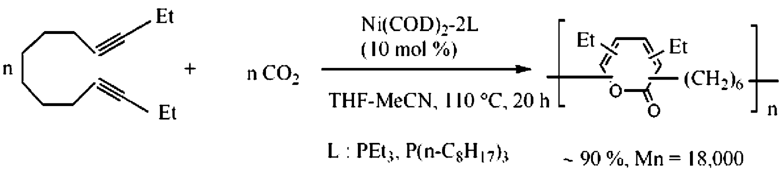
In the cyclic addition of diynes ($RC{\equiv}C\text{–}(CH_2)_m\text{-}C{\equiv}CR$) with carbon dioxide in the presence of a zero valent nickel catalyst, the reaction with $m = 3$ or 4, easily proceeds to give two cyclic 2-pyrones in about 50–90% yields as shown in Eq. (28). However, the reaction with $m \leq 2$ and $m \geq 6$, the alternating copolymerization of the diynes and carbon dioxide proceeds to give a poly(2-pyrone) by an intermolecular cycloaddition, since the intramolecular cycloaddition reaction is difficult as shown in Eqs. (29) and (30) [150a,150b]. The reactions of these diynes and carbon dioxide in the presence of metal compounds gave the various kinds of polymeric compounds, e.g., an alternating copolymer as shown in Eq. (31) [145,150c,150d]



(28)



(29)



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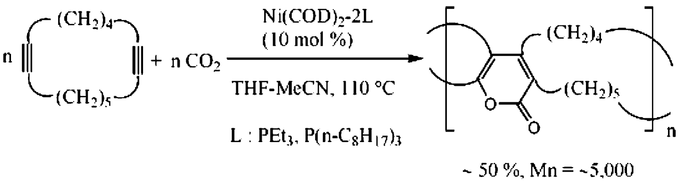
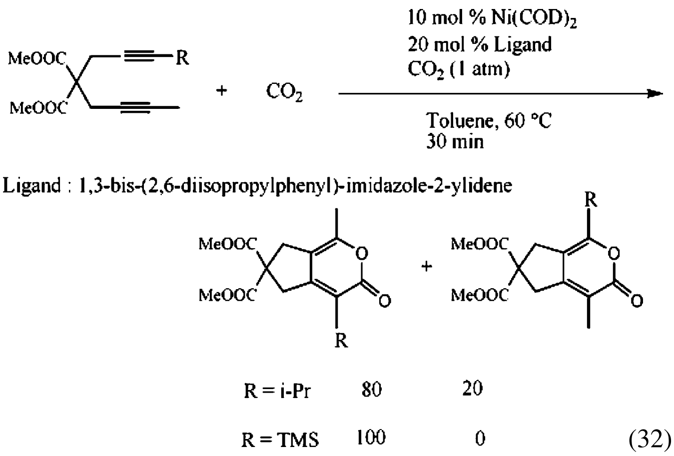


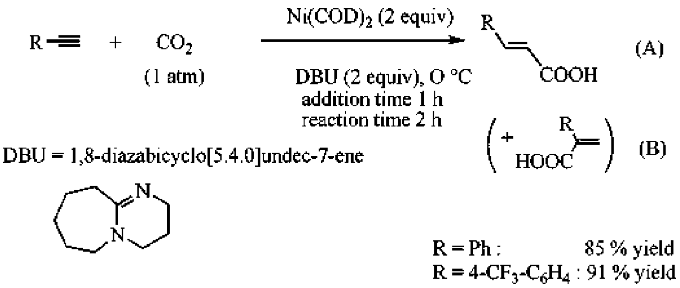
(31)

Recently, Louie et al. [150e,150f] reported on the synthesis of bicylic lactones by the [2 + 2 + 2] cycloaddition of CO$_2$ and diynes in the presence of efficient nickel catalysts. For example, the use of *N*-heterocyclic carbene ligand (1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene) provided a high regioselectivity when one terminal substituent on the diyne was large in size (*R* = *i*-Pr or TMS) as shown in Eq. (32) [150f].

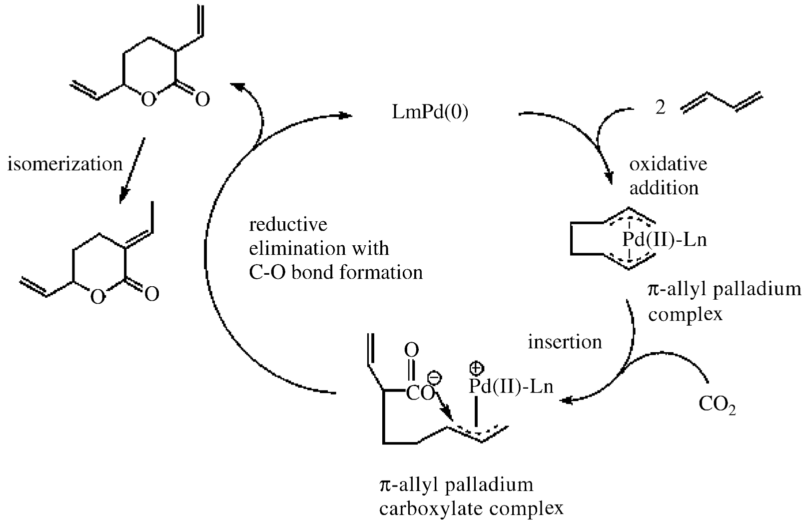


(32)

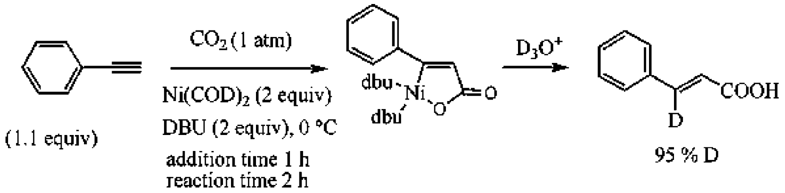
However, alkynes having a terminal triple bond easily reacted with carbon dioxide in the presence of a Ni(COD) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the reaction proceeded in a highly regio-and stereoselective manner, and an E-acrylic acid (A) was isolated as a sole product in most reactions in high yields as shown in Eq. (33) [151]. These reactions were also carried out under very mild conditions (CO$_2$ 1 atm, 0 °C) in the presence of a stoichiometric amount of conjugated enynes or diynes as shown in Eqs. (34) and (35), respectively.



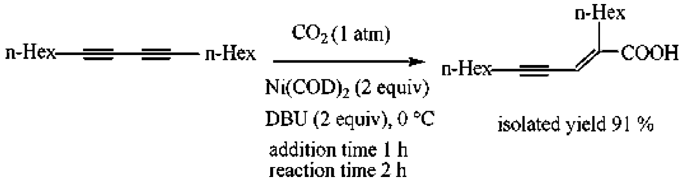
(33)



Scheme 6. [145]



(34)



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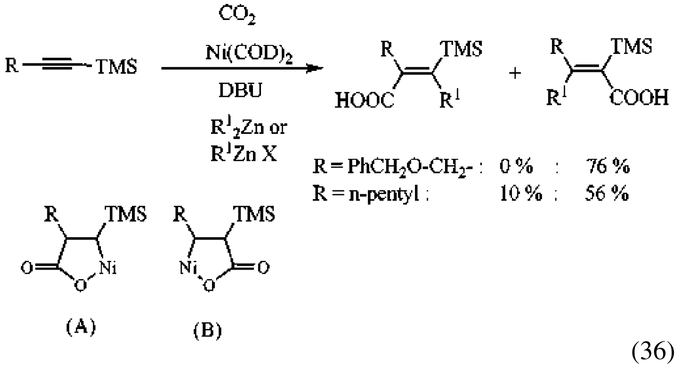
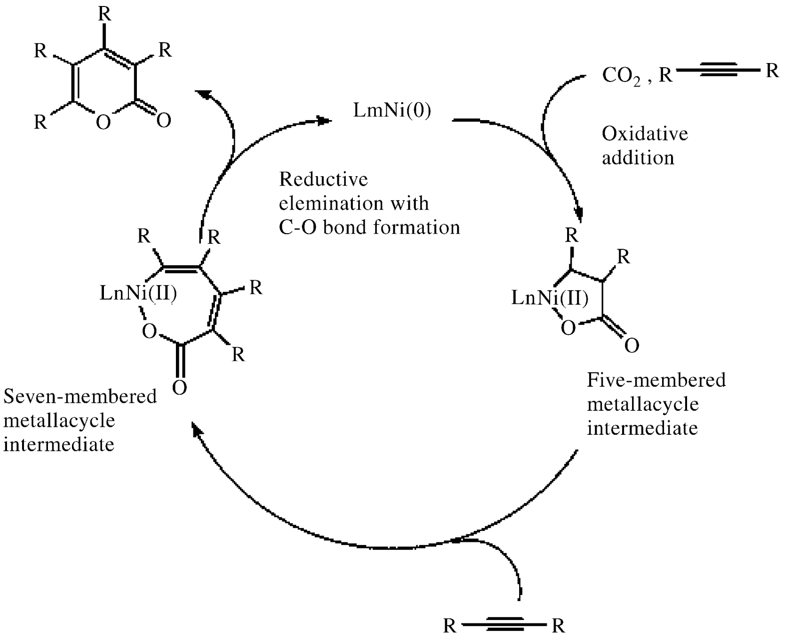


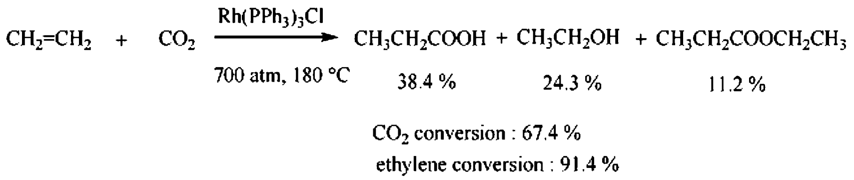
(36)

On the other hand, trimethylsilyl alkynes react with carbon dioxide and organozinc compounds using a catalytic amount of a nickel complex in the presence of an excess of DBU as shown in Eq. (36). The regioselectivity caused by the introduction of CO_2 into disubstituted alkyne is dependent on the electronic property of the substituents *R* and trimethylsilyl (TMS) group on the alkyne because the thermodynamic stability of oxanickelacycles A and B should be affected by the conjugation of the substituent *R* with the carbonyl group in A and B [152].

However, although simple olefins have a low reactivity, e.g., ethylene reacts with carbon dioxide in the presence of Wilkinson's catalyst ($[RhCl(PPh_3)_3]$), a promoter (HCl, HBr or HI) and distilled water as solvent. When the reaction was carried out at a pressure of 700 atm and 180 °C, propionic acid formed in 38.4% yield together with ethanol (24.3%) and ethylpropionate (11.2%), whereas the ethylene conversion reached 91.4% as shown in Eq. (37) [153]. But the electrochemical reactions of alkenes with carbon dioxide in the presence of nickel complexes yield the carboxylic acid in good yields [153a,153b]. Recently, with molybdenum phosphine catalysts, nickel bipyridine catalysts, etc., the coupling reactions of ethylene with carbon dioxide were reported together with the formation of the five-membered nickelacarboxylate complex toward the formation of acrylic acid in system [153c,153d].



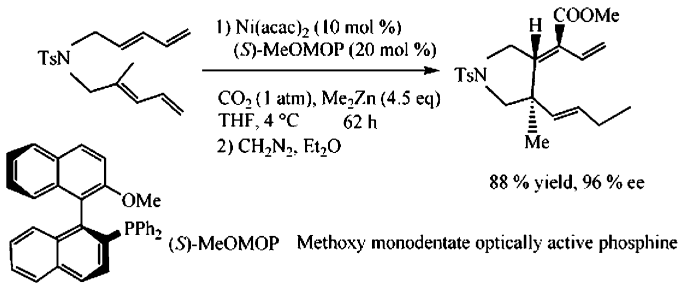
Scheme 7. [145]



$$CH_2{=}CH_2 + CO_2 \xrightarrow[700\ atm,\ 180\ °C]{Rh(PPh_3)_3Cl} \underset{38.4\ \%}{CH_3CH_2COOH} + \underset{24.3\ \%}{CH_3CH_2OH} + \underset{11.2\ \%}{CH_3CH_2COOCH_2CH_3} \quad (37)$$

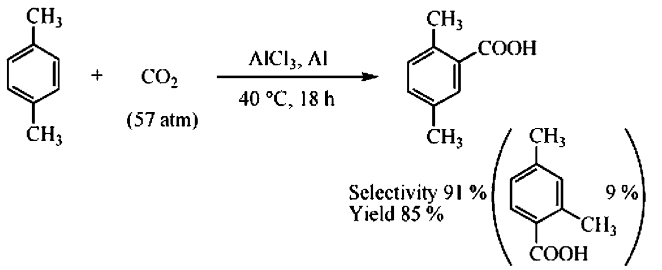
CO_2 conversion : 67.4 %
ethylene conversion : 91.4 %

Ni(acac)$_2$ and arylphosphine catalyze the addition of CO_2 and diorganozinc to bis-1,3-diene under very mild conditions as shown in Eq. (38). The reaction performed at a lower temperature resulted in a high enantioselectivity. For example, methylative cyclization of unsymmetrical bisdiene in the presence of bulky phosphine (*S*)-MeO-MOP, proceeds at 4 °C with regioseleictive introduction of CO_2 into a less-substituted 1,3-diene moiety to afford the methyl ester in 88% yield and 96% ee as shown in Eq. (38) [154].



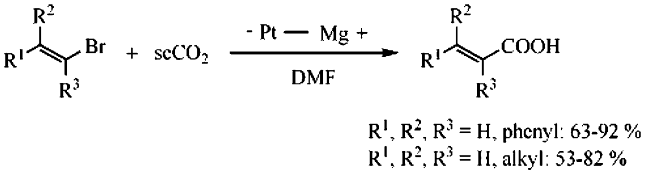
(38)

Recently, Olah et al. [155] reported the efficient chemoselective carboxylation of aromatics to arylcarboxylic acids with superelectrophilically activated carbon dioxide coordinated by Al and Cl atoms in $AlCl_3$ molecules. Aromatic carboxylic acids are synthesized in high yields by the carboxylation of aromatics with carbon dioxide and $AlCl_3$ at a moderate temperature. For example, the carbonylation of *p*-xylene affords benzene monocarboxylic acid derivatives as shown in Eq. (39) [155].

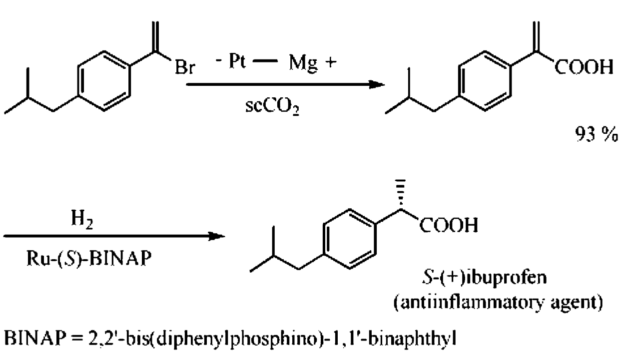


(39)

The electrochemical carboxylations of halides proceed in DMF solvent with a platinum cathode and magnesium anode under carbon dioxide atmosphere to give the carboxylic acid in good yields as shown in Eq. (40) [156]. These electrochemical reactions also proceed in the supercritical carbon dioxide by using a small amount of an organic solvent. For example, it was applied to the synthesis of antiinflammatory agent (*S*)-(+) ibuprofen, by the carbonylation of alkylalkenylbenzene bromide as shown in Eq. (41) [156,156a].



(40)



(41)

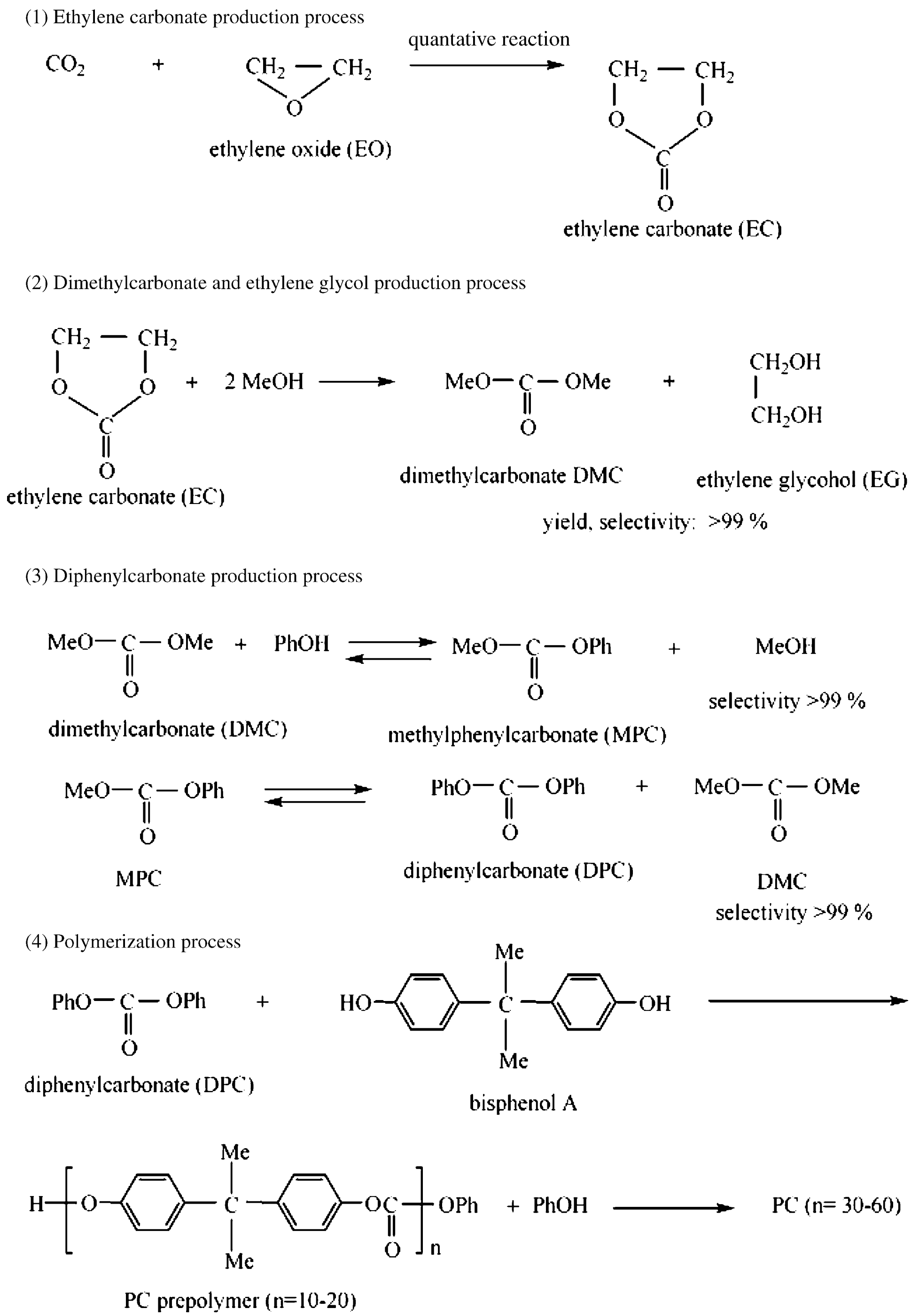
6. Polymerization products

6.1. Polycarbonate (bisphenol-based engineering polymer)

Polymerization involving carbon dioxide is one of the most important utilizations of carbon dioxide. Polycarbonate formation without using phosgene, an alternating copolymerization with an epoxide, a condensation with benzenedimethanol and an alternating copolymerization with diynes, etc., can be exemplified. Especially, the polycarbonate formation without using phosgene, and the alternating copolymerization with the epoxide were already industrially applied.

Asahi Chemical Industry already started the 50,000 tons/year commercial operation of a polycarbonate process without using phosgene and methylene chloride in June 2002 in Taiwan as a new environmentally benign process [157,158,158a]. The Asahi's polycarbonate process was carried out by the following four production steps: (1) ethylenecarbonate (EC), (2) dimethylcarbonate (DMC) and ethylene glycol (EG) and (3) diphenylcarbonate (DPC) and polymerization, as shown in Scheme 8 [157].

The DPC is manufactured by the reaction of DMC with phenol in the presence of $Pb(OPh)_2$ as a catalyst [158b].



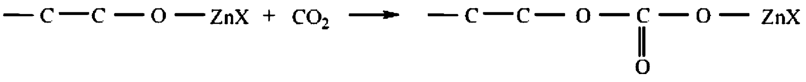
Scheme 8. Asahi polycarbonate process [157].

The polymerization proceeds with two processes. The first process is the solid-state polymerization of amorphous polymers in three steps: (1) pre-polymerization; the reaction of the DPC with bisphenol A to produce a clear amorphous prepolymer; (2) crystallization; the molten prepolymer is converted to a porous, white, opaque material by treating it with a solvent such as acetone; (3) solid-state polymerization; the crystallized prepolymer is heated at 210–220 °C under a flow of heated nitrogen, or under a reduced pressure to produce a solid polymer. The second process is "self-mixing melt polymerization" utilizing gravity and without using a conventional twin-screw type reactor. The polymerization was carried out at 265 °C and 67 Pa. A prepolymer having a number average molecular weight of 6200 is polymerized to the molecular weight 11,700 [158b,158c]

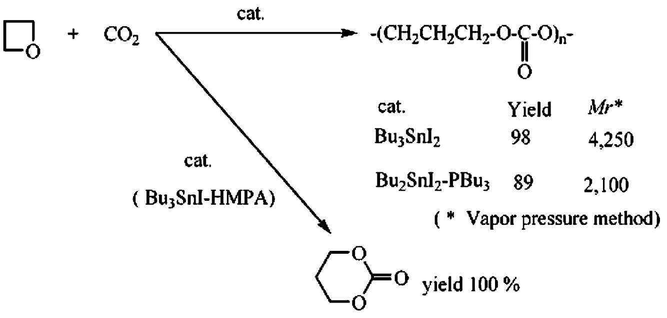
This process has four excellent characteristics: (1) actual raw materials are CO_2, ethylene oxide and bisphenol A, and this process does not use toxic phosgene and the halogen solvent, CH_2Cl_2. (2) Products are polycarbonate and ethylene glycol. Both products are of a high quality because the products do not contain the halide materials from the phosgene or CH_2Cl_2. (3) All intermediate products, EC, DMC, MPC and DPC are produced in high yields and high selectivities. These intermediates and two raw materials (MeOH and PhOH) are completely recycled. (4) This process contributes to decrease CO_2 by 1730 tons/PC 10,000 tons because it uses CO_2, which is a byproduct of ethylene oxide production, as the raw material. Hence, this process can decrease carbon dioxide by more than 450,000 tons per year if all of the polycarbonate production processes were carried out with this process in the world.

6.2. Aliphatic polycarbonates and other polymers

Baba et al. [159] reported on a polycarbonate from oxetane in the presence of organotin iodides as shown in Eq. (42) [159]. Although the polymerization was accelerated by either an organotin (Bu_2SnI_2) or organotin–phosphine complex (Bu_2SnI_2-PBu_3) catalyst, the polymerization activity of the organotin (Bu_2SnI_2) apparently is depressed by complexation with PBu_3 because the yield and molecular weight of the polymer decrease from 98% to 89% and from 4250 to 2100, respectively. However, the reaction with Bu_3SnI-hexamethylenephosphoric triamide (HMPA), yields trimethylene carbonate in place of polycarbonate as shown in Eq. (42) [159].



$$-C-C-O-ZnX + CO_2 \longrightarrow -C-C-O-\underset{\underset{O}{\|}}{C}-O-ZnX \qquad (45)$$

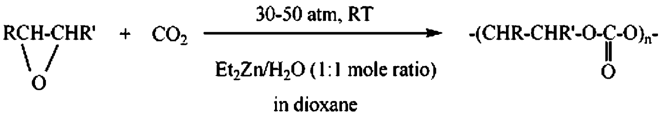


cat.	Yield	Mr*
Bu_3SnI_2	98	4,250
Bu_2SnI_2-PBu_3	89	2,100

(* Vapor pressure method)

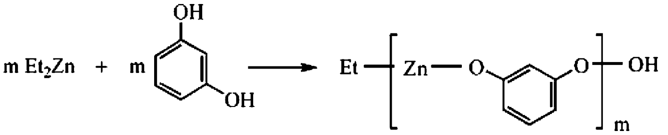
(42)

Inoue et al. [160–165] first reported on high molecular weight polymers by the alternative copolymerization of carbon dioxide with an epoxide in the presence of a zinc catalyst under mild conditions in 1969 as shown in Eq. (43).

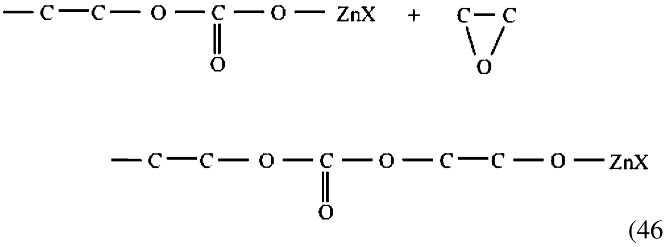


$$\underset{\diagdown O \diagup}{RCH\text{-}CHR'} + CO_2 \xrightarrow[\text{Et}_2\text{Zn/H}_2\text{O (1:1 mole ratio) in dioxane}]{\text{30-50 atm, RT}} -(CHR\text{-}CHR'\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}O)_n\text{-} \qquad (43)$$

Among the catalyst systems, the most effective ones are the reaction mixtures of diethylzinc with an equimolar amount of a compound having two active hydrogens, such as water, a primary amine, an aromatic dicarboxylic acid (isophthalic acid and terephthalic acid) and an aromatic diol. For example, the catalyst of diethylzinc with resorcin forms many kinds of oligomers are formed as shown in Eq. (44). All these alternating copolymers formed with this catalyst have a resorcinol group at the terminal position. This evidence shows that these reactions start from a zinc–resorcinol bond. Hence, the mechanism of this alternating copolymerization is shown in Eqs. (44)–(46). That is, the zinc alkoxide which is produced by reaction between dialkyl zinc and diol (Eq. (44)), nucleophilically attacked carbon dioxide to give a zinc carbonate (Eq. (45)) and the zinc carbonate reacts with epoxide to form zinc alkoxide again (Eq. (46)). The repetition of these two reactions produces the alternating copolymerization products [165].



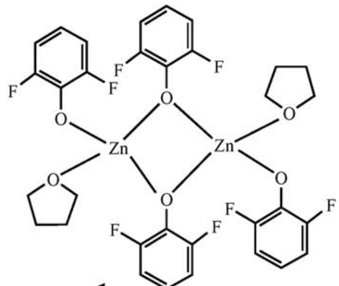
(44)



(46)

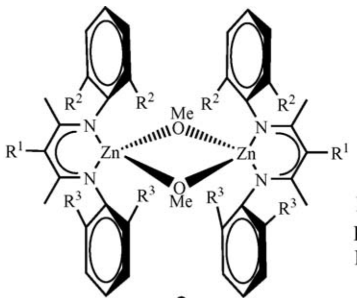
When the epoxide is ethylene oxide or propylene oxide, the molecular weight of the alternating copolymer is from 50,000 to 150,000 depending on reaction conditions [161]. These reactions have been reported in many papers and reviews [165,166].

Recently, many active zinc catalysts such as zinc phenoxides [167], bulky fluorophenoxides (C1) [168,169], zinc diimines (C2) [170–172] and zinc bis-Schiff bases (C3) [173] have been investigated and the production of a copolymer having a narrow molecular weight distribution ($M_w/M_n = 1.07$–1.17) and a high molecular weight (M_w = about 420,000) at a high TON (1441 g/1 g cat) were reported.



1

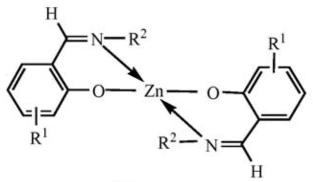
Bis-2,6-difluorophenoxide dimeric zinc complex [169]



R^1 = CN
R^2 = Me
R^3 = i-Pr

2

β-diiminatea zinc alkoxide



R^1 = 3,5-t-Bu
R^2 = 2,6-(i-Pr)$_2C_6H_3$

3

zinc bis(salicylaldiminate) complex

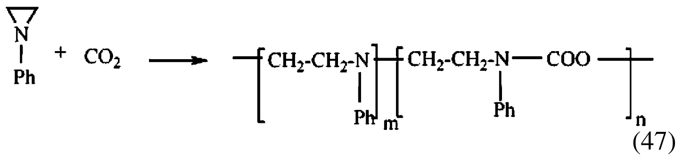
Furthermore, an asymmetric alternating copolymerization with (*S*)-diphenyl(pyrrodinin-2-yl)methanol zinc complexes [174] and β-diimine zinc catalysts [175–178] has been reported.

The other catalysts such as a zinc oxide-glutaric acid [179], an aluminium-porphyrin [180], a chromium-porphyrin [181], a zinc oxide-maleic anhydride-tridecafluorooctanol [182], a silica-immobilized zinc β-diiminate [183], chromium salen complexes [184,185] and yttrium-aluminum complexes [186] were reported.

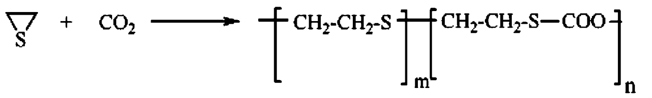
Coates et al. [186a,186b,186c] have recently published some nice work on the copolymerization of epoxides and carbon dioxide with salicyl cobalt catalysts. The polypropylene carbonate generated using these catalyst systems is highly regioregular and has up to 99% carbonate linkages with narrow molecular weight distribution. In the case of cocatalyst bis(triphenylphosphine)iminium chloride with (*R,R*)-salcy)Co(-pentafluorobenzoate), an unprecedented catalytic activity of 620 turnovers per hour is achieved for the copolymerization of *rac*-propylene oxide and carbon dioxide, yielding an iso-enriched polypropylene carbonate with 94% head-to-tail connectivity.

These alternating copolymers are biodegradable and have a high oxygen permeability. Therefore, this polymer is investigated for an application of sustained-release drug [187]. America PAC Polymer Ltd. manufactured the alternating copolymer of an epoxide with carbon dioxide [188].

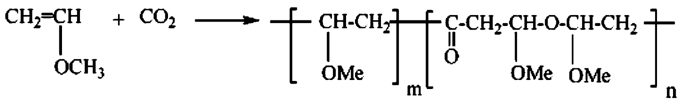
Carbon dioxide is also polymerized with ethyleneimine (aziridine), epithioxide (three-membered ring thioether), a vinyl ether and an aromatic diamine as shown in Eqs. (47)–(50) [161,189].



(47)



(48)



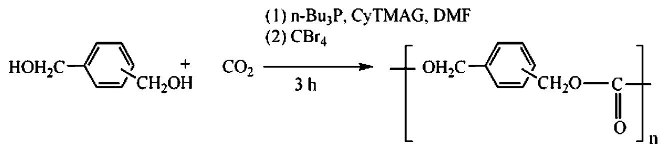
$$CH_2{=}\underset{OCH_3}{CH} + CO_2 \longrightarrow \left[\underset{OMe}{CH}\text{-}CH_2\right]_m\left[\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}\underset{OMe}{CH}\text{-}O\text{-}\underset{OMe}{CH}\text{-}CH_2\right]_n$$

(49)

$$H_2N\text{-}C_6H_4\text{-}NH_2 + CO_2 \longrightarrow \left[CONH\text{-}C_6H_4\text{-}NH\right]_n$$

(50)

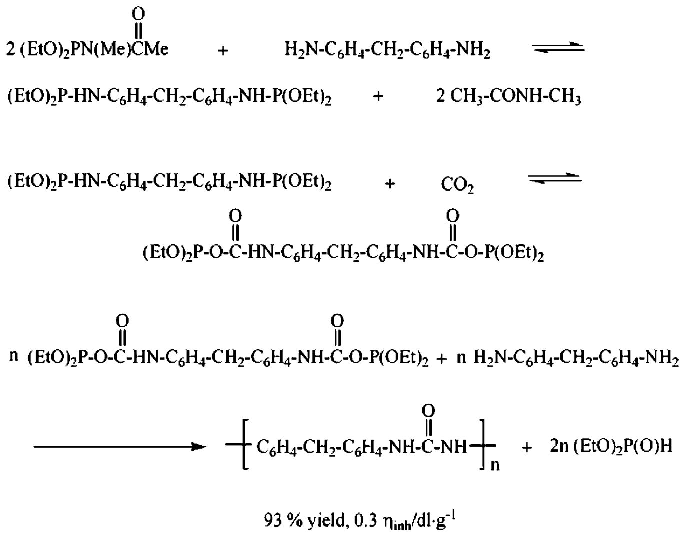
Carbon dioxide can directly condense with benzenedimethanol in the presence of trisubstituted phosphine-carbon tetrabromide-2-cyclohexyl-1,1,3,3-tetramethylguanidine (CyTMG) system as a condensing agent to give a poly (oxycarbonyloxymethylenephenylmethylene) as shown in Eq. (51) [190,191].



CyTMAG = *N*-cyclohexyl-*N*′,*N*′,*N*″,*N*″-tetramethylguanidine
para: 80 % yield , mw = 1,200
meta: 39.6 % yield, mw = 3,800

(51)

Polyureas were prepared under mild conditions in high yields by the direct polycondensation of carbon dioxide with diamines in the presence of diethyl *N*-acetyl-*N*-methylphosphoramidites or its analogs containing *P–N* bonds as shown in Eq. (52) [192]. The highest yield was achieved with a phosphorous acid derivative containing a mixed anhydride unit.



$$2\,(EtO)_2PN(Me)\overset{O}{\overset{\|}{C}}Me + H_2N\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH_2 \rightleftharpoons (EtO)_2P\text{-}HN\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH\text{-}P(OEt)_2 + 2\,CH_3\text{-}CONH\text{-}CH_3$$

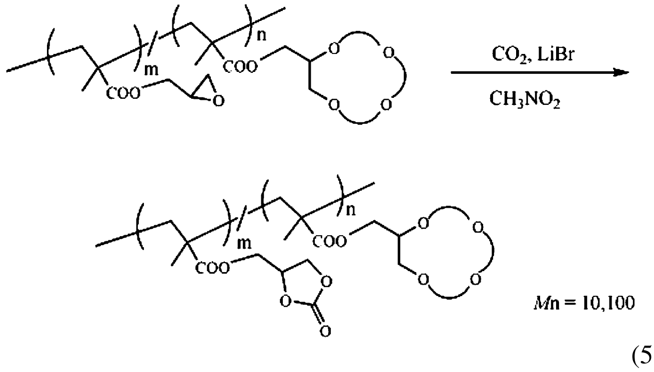
$$(EtO)_2P\text{-}HN\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH\text{-}P(OEt)_2 + CO_2 \rightleftharpoons (EtO)_2P\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}HN\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}P(OEt)_2$$

$$n\ (EtO)_2P\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}HN\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}P(OEt)_2 + n\ H_2N\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH_2 \longrightarrow \left[C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH \right]_n + 2n\,(EtO)_2P(O)H$$

93 % yield, 0.3 η_{inh}/dl·g^{-1}

(52)

Several kinds of methacrylate derivatives having a crown ether group (from 12-crown-4 to 16-crown-5) have been investigated for aiming at the fixation of carbon dioxide. The most efficient fixation of carbon dioxide in nitromethane solution was observed in the use of 14-crown-4 groups, in which oxirane groups were transformed into corresponding cyclic carbonate groups quantitatively using a lithium salt as a catalyst as shown in Eq. (53) [193].



(53)

7. Conclusions

The utilization of carbon dioxide as a possible starting material for the synthesis of chemicals is expected to be useful for improving the global warming problem. Actually, carbon dioxide is utilized mostly for urea as fertilizers. The other utilizations are very small in amounts. Because carbon dioxide is a highly oxidized and thermodynamically stable compound, its utilization requires very active metal catalysts.

As promising industrial catalysts for carbon dioxide utilization reactions, there are both transition metal compounds and main-group metal compounds. For example, ruthenium phosphine compounds are used for the preparations of formic acid, formic acid methyl ester and formamide. On the other hand, dialkyltin compounds for dimethyl carbonate and ethyl carbamate, phenoxy lead for diphenyl carbonate, and zinc compounds for the alternating copolymerization of carbon dioxide and epoxide, are used as the catalysts of main-group metal compounds. Recently, $AlCl_3$ was reported as a good catalyst for the carbonylation of aromatic compounds under mild conditions.

New many catalysts are expected because carbon dioxide is able to react with various kinds of metal compounds and, further, also the catalysts showing high TONs are expected in the supercritical carbon dioxide solvent with many kinds of additives.

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