147. B. M. Choudary, N. S. Chowdari, K. Jyothi, N. S. Kumar, M. L. Kantam, *Chem. Commun.* **2002**, 586.
148. B. M. Choudary, S. Madhi, N. S. Chowdari, M. L. Kantam, *Top. Catal.* **2004**, *29*, 183.
149. A. Severeyns, D. E. De Vos, L. Fiermans, F. Verpoort, P. J. Grobet, P. A. Jacobs, *Angew. Chem. Int. Ed.* **2001**, *40*, 586.
150. A. Severeyns, D. E. De Vos, P. A. Jacobs, *Top. Catal.* **2002**, *19*, 125.
151. J. S. M. Wai, I. Markó, J. S. Svendsen, M. G. Finn, E. N. Jacobsen, K. B. Sharpless, *J. Am. Chem. Soc.* **1989**, *111*, 1123.
152. A. Severeyns, D. E. De Vos, P. A. Jacobs, *Green Chem.* **2002**, *4*, 380.

14.17.4
Chemicals from Carbon Dioxide

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14.17.4.1 Introduction

At present, there are only four major industrial manufacturing processes that utilize CO_2 as a raw material:

- urea synthesis (ca. 30 million tons per year)
- the manufacture of salicylic and *para*-hydroxy benzoic acids (ca. 20 000 tons per year)
- cyclic and polycarbonate synthesis (ca. 60 000 tons per year)
- production of methanol (variable amounts, but several millions of tons per year).

Currently, a number of reactions and processes (Fig. 1) are under investigation which hold promise for the utilization of CO_2 in chemicals synthesis [1]. In this chapter, the production of chemicals using CO_2 as one of the raw materials over solid catalysts is reviewed. Homogeneous, electrochemical and photocatalytic processes, the production of fuels (e.g., syngas, methanol, dimethyl ether, and hydrocarbons), and the use of CO_2 as a solvent are excluded. The manufacture of some of these fuels is discussed in Chapters 13.11 to 13.15 of this Handbook.

14.17.4.2 CO$_2$ Activation on Metals and Metal Oxides

14.17.4.2.1 General Features
The thermodynamic stability of carbon dioxide (CO_2) is the main cause for the initial general lack of interest in the chemistry of this molecule, and its application as a feedstock in chemicals synthesis. The low reactivity of CO_2 is also due to its kinetic origin. However, the kinetic barrier can be overcome by activating CO_2 over catalyst surfaces. Carbon dioxide

can be activated catalytically at the surfaces of metal, metal oxides, metal complexes and enzymes, and also by photoexcitation and electrochemical means. Recently, several excellent reviews have been published on CO_2 activation and utilization [1–3]. The rate-determining step in most reactions involving CO_2 is the initial activation of the molecule. Coordination with a transition metal center or a base lowers the activation energy required for its further reaction with suitable reactants to produce useful materials.

In the ground state, the linear geometry is the stable geometry for carbon dioxide. However, any excitation across the HOMO−LUMO gap in the CO_2 molecule will lead to a bent structure. An electron transfer from a solid surface to CO_2 molecule resulting in a CO_2^- ion would have an equilibrium bent-geometry. In contrast, if the electron transfer occurs from CO_2 to the solid surface, then a CO_2^+ ion is produced which will have linear geometry based on the Walsh diagram [4]. In general, CO_2^- is the species found at metal surfaces in catalytic CO_2 activations and reactions. The LUMO of CO_2 is an antibonding orbital, and therefore electron transfer from metal should result in a weakened C−O bond and a bent structure for CO_2 [5]. The different electronegativities of oxygen and carbon lead to a negative polarization on the oxygen atoms and a partial positive charge on the carbon atom.

In its ground state, CO_2 also has two sets of π molecular orbitals, which are orthogonal. Thus, the CO_2 molecule exhibits several distinct sites, which could interact with a metal center in different ways, as shown in Fig. 2. Theoretical studies reveal that in the $\eta^1(C)$ bonding mode there is a strong, two-electron stabilizing and charge transfer interaction between a $d_{z^2}^2$-type orbital (which is doubly occupied) and the antibonding π orbital of CO_2 (which is empty). In the $\eta^2(C,O)$ side-on coordination mode the orbital interaction pattern is reversed. The $d\pi$ orbital interacts in a two-electron stabilizing interaction with the π orbital of CO_2. The $\eta^1(C)$ bonding mode is most favored when the transition metal fragment ML_n has a doubly occupied $d\sigma$-type orbital that is relatively high in energy. This high energy will be achieved when the metal is in a relatively low oxidation state wherein the repulsive electrostatic interactions are reduced. The $\eta^2(C,O)$ side-on coordination mode is favored by a high-energy $d\pi$-type orbital. A stronger stabilization of the $\eta^2(C,O)$ mode will be achieved if the $d\sigma$ orbital which points towards the CO_2 ligand is empty. CO_2 can be bound to two or more metal centers via the coordination of the carbon atom to one metal and either one or both of the oxygen atoms of the CO_2 to the other metal(s) (Fig. 2).
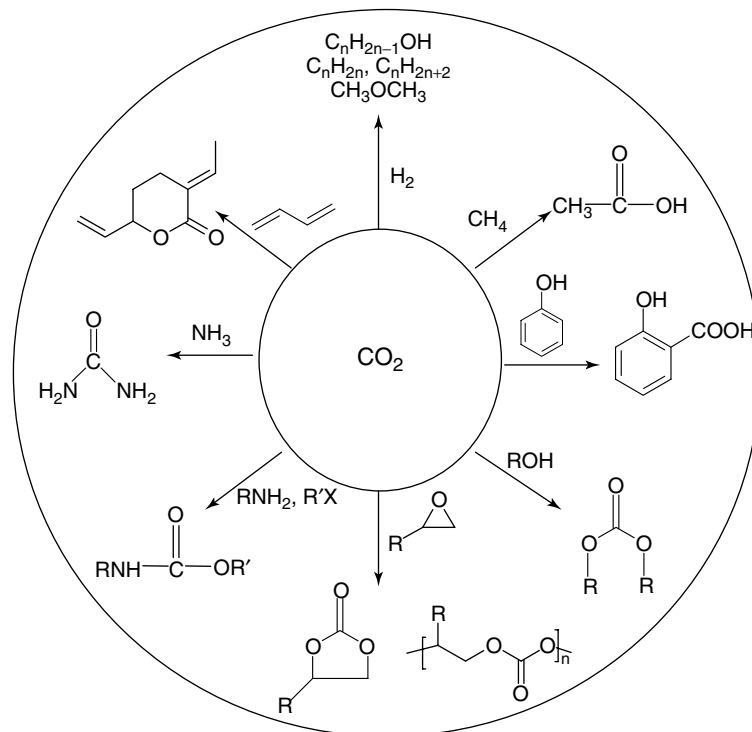
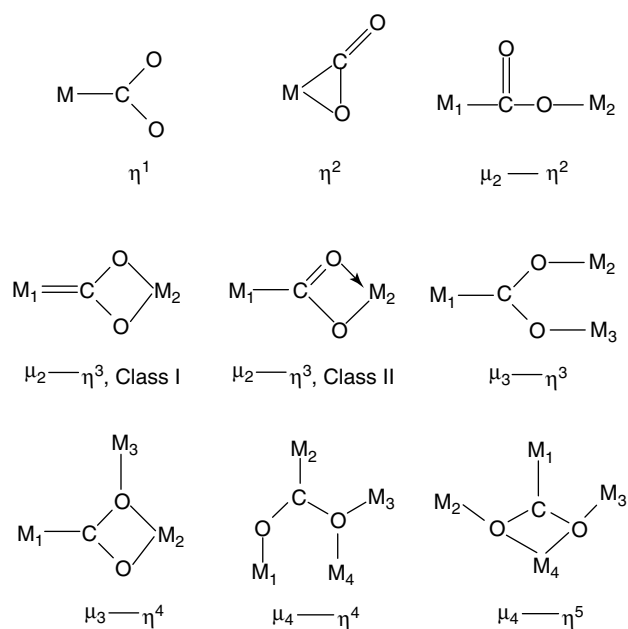**Fig. 1** CO$_2$ as a raw material in chemicals synthesis.

Fig. 2 Various modes of CO$_2$ coordination to metals. (From Ref. [3b].)

14.17.4.2.2 CO$_2$ Activation on Metals The earlier literature on this subject has been reviewed by Freund and Roberts [6]. CO$_2$ adsorbs on metal surfaces to form two states, one of which is a physisorbed linear state and the other a chemisorbed bent CO$_2^-$ state. The chemisorbed anionic species represents an intrinsic precursor for CO$_2$ dissociation into CO and oxygen on Ni(100) [7] and Fe(111) [8] surfaces, and for further reactions with hydrogen and other molecules. Formation of the anionic form requires a partial charge transfer from metal to the CO$_2$ molecule. In the particular case of the platinum-group metals, this process has a very high activation barrier which is due, in part, to the large work function of these metal surfaces. Thus, the CO$_2$ adsorption on these surfaces is weak and non-dissociative [9]. The incorporation of electron donors such as alkali metals to the surface lowers the surface work function. While CO$_2$ is not adsorbed on clean Pt(111), it is adsorbed strongly when preadsorbed potassium is present under either low- or high-coverage conditions [10]. The doping of pure copper films with potassium enhances the interaction of CO$_2$ with the metal surface, leading to carbonate and carbon monoxide as reaction products [10].

It was as early as 1957 when Eischens and Pliskin [11] first reported the infra-red (IR) spectroscopic study of CO$_2$ adsorbed on NiO as well as Ni−SiO$_2$. The latter showed IR bands at 1555 and 1415 cm^{-1}, characteristic of nickel carboxylate, while the former showed bands at 1605 and 1405 cm^{-1} which were attributed to formation of carbonate species from CO$_2$ and coadsorbed oxygen. If the supported Ni is exposed to CO$_2$ at 373 K, then
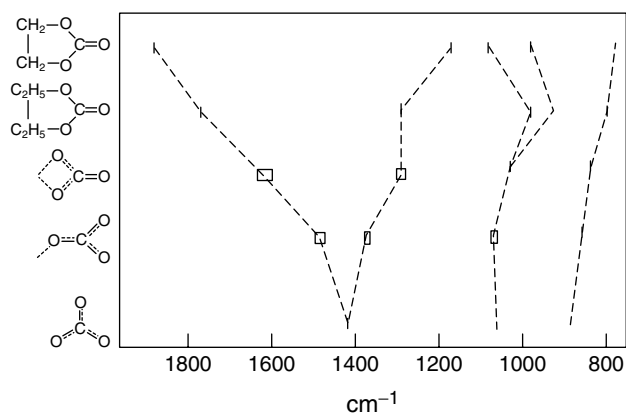
Fig. 3 Correlation diagram of characteristic CO_3 vibration frequencies in various bonding modes. (From Ref. [12].)

bands associated with adsorbed CO were detected, indicating CO_2 reduction and/or contamination by CO inadvertently present. Physisorbed and gaseous CO_2 showed IR bands in the region of 2320 to 2380 cm^{-1}. By using IR spectroscopy, it was possible to differentiate carbonates with different coordination modes (Fig. 3). For a symmetrical CO_3^{2-} anion, a symmetrical stretching mode at 1063 cm^{-1} and a degenerate asymmetric stretching mode at 1415 cm^{-1} are expected. The lowest energy band is due to an out-of-plane bending π-mode of the CO_3^{2-} anion. The degenerate asymmetric band splits in a characteristic manner depending on the coordination and bond character. Whilst in a monodentate situation the splitting is small, it increases in bidentate coordination with an even further increase in covalently bonded (strained) organic carbonates (Fig. 3).

The activation of CO_2 on metal surfaces has also been studied using high-resolution electron energy loss spectroscopy (HREELS). The spectrum of CO_2 on Pt(111) shows losses at 640 and 2350 cm^{-1}, assigned to the bending and asymmetric stretching modes of weakly bound CO_2, respectively [11]. The spectrum also shows two modes at 1205 and 1355 cm^{-1} due to the symmetric stretching of the weakly held CO_2, split due to a Fermi resonance or an accidental degeneracy. The corresponding normal modes for free CO_2 are 672, 2396, and 1351 cm^{-1}, respectively [7]. Chemisorbed CO_2^{-} shows a shoulder at 725 cm^{-1}. With increasing potassium doses – but still at submonolayer coverage – additional peaks appear at 780, 1520, and 1220 cm^{-1} that shift to 870, 1610, and 1340 cm^{-1} with increasing potassium coverage. These bands are similar to the IR bands of free CO_2^{-} that occur at 849, 1671, and 1420 cm^{-1} [7].

14.17.4.2.3 CO_2 Activation on Metal Oxides Chemisorption on metal oxides leads to the formation of carbonates [13a]. The formation of CO_2^{-} (carboxylate structure) was reported only for ZnO [13a], with the carboxylates formed via coordination of a bent $CO_2^{\delta-}$ molecule to Zn. Carbonates may also be formed via coordination of a $CO_2^{\delta-}$ to an oxygen ion. Although this configuration results in monodentate carbonates, a bidentate coordination has been observed on several oxidic surfaces [13a]. CO_2 does not interact strongly with non-polar (100) surfaces of rock-salt type oxides such as MgO and NiO [13b]. The interaction of CO_2 with different oxides increased in the order: MgO < CaO < BaO. The adsorbed state of $CO_2^{\delta-}$ corresponds to a species with unsaturated valencies at the carbon atom, and can be thought of as a radical anion. Hence, such a radical species CO_2^{-} facilitates reactions with atomic or molecular species either in the gas phase or as a surface species. A direct combination of two CO_2^{-} molecules is rather unlikely, as the negative charge should lead to strong intermolecular coulombic repulsion [13c]. However, a reaction between activated CO_2^{-} and neutral CO_2 – that is, with a solvation complex – is feasible. The reaction of CO_2 with hydrogen on NiO to form formate was monitored using HREEL spectroscopy [13d]. The sample was exposed first to 1 L CO_2 and subsequently to 0.1 L H_2. The reverse exposure did not lead to any reaction. The reaction of CO_2^{-} with coadsorbed species such as methyl groups leads to acetate via carbon−carbon bond formation. The CH_3 species were generated by dissociative adsorption of CH_3I [13e]. CO_2 and NH_3 are relatively unreactive over CuO, but when both are coadsorbed a carbamate species is formed readily [14]. When both NH_3 and CO_2 are coadsorbed, electron donation into the antibonding orbital of CO_2 leads to the reactive, bent anionic form $CO_2^{\delta-}$; on H-elimination from NH_3, a carbamate species (NH_2-CO_2) is formed. HREEL spectral studies revealed that coadsorption of CO_2 with other molecules provides low-energy pathways to products wherein the bent $CO_2^{\delta-}$ anionic intermediate is crucial. Activation of CO_2 by metal complexes was described in detail by Yin and Moss [3a], and by Palmer and Van Eldik [15].

14.17.4.3 Synthesis of Chemicals from CO_2 on Heterogeneous Catalysts

14.17.4.3.1 CO_2 Insertion and C−O Bond Formation
A Cyclic Carbonates
a Cycloaddition of CO_2 to Epoxides Cyclic carbonates, which are important raw materials for engineering plastics such as polycarbonates, belong to the category of "environmental protection products" and find application as polar aprotic green solvents. Their outstanding solvency, low toxicity, biodegradability and high boiling

point enables their applications in the production of dyes, textiles, and polyacrylonitrile fibers. Cyclic carbonates can also be used as additives to fuels, lubricants and hydraulic fluids, and as components of polyurethanes. Organic carbonates that have a large market ($\sim$1.8–2 million tons per annum) are conventionally synthesized by a phosgenation route [16], wherein a hydroxy compound (e.g., a diol) is dissolved in a large excess of an anhydrous, inert solvent (e.g., dichloromethane) and then reacted with phosgene ($COCl_2$) in the presence of excess pyridine at or below room temperature. Pyridine acts as an acid acceptor and reacts with phosgene to form an ionic adduct. A variety of carbonates which are useful as monomers for the preparation of high-molecular-weight polymers can be synthesized, in very high yields, by using this method.

Cyclic carbonates synthesis by adding CO_2 to epoxides is an atom-efficient, ecofriendly process [17]. Several homogeneous catalysts, including quaternary ammonium salts, alkali metal salts and metal complexes, catalyze the reaction in a homogeneous medium [2]. Polystyrene-bound quaternary onium salts have been used as heterogeneous catalysts for synthesizing a large variety of cyclic carbonates [18–20], although it was necessary to continue the reactions for long time periods. When basic oxides [21–25], lanthanide oxychlorides [28, 29] or calcined hydrotalcites [23] were used as catalysts, a large amount of catalyst and solvents such as N,N-dimethyl formamide were needed to produce higher yields of cyclic carbonates. With smectite catalysts [30], there was a requirement for high CO_2 pressures. Immobilized metal phthalocyanine [31–33] and Schiff base complexes [34], titanosilicates [35] and zinc-substituted polyoxometalate [36], each showed efficient activity under mild reaction conditions, but required an additional organic base cocatalyst/promoter. Zeolite-Y-encapsulated phthalocyanines [32, 33] exhibited more efficient activity than the corresponding "neat" complexes. The reason for such enhanced catalytic activity was attributed to the isolation of metal complexes in the cavities of zeolites and the consequent structural and electronic changes in the active site moiety.

A Mg/Al oxide-based catalyst system was reported by Yamaguchi et al. [23] that required a high catalyst loading of 1.8 g g^{-1} substrate and, in addition, a substantial amount of solvent [85% (v/v) dimethylformamide (DMF) and longer reaction times (24 h)]. Silica-supported guanidine catalysts [37] also required longer reaction times (70 h) and high pressures (5×10^6 Pa). Srivastava et al. [39, 40] have reported a solventless, reusable, heterogeneous catalyst system, organo base (adenine)-modified Ti-(Al)-SBA-15 that does not require any cocatalysts/promoters. A range of cyclic carbonates were synthesized in very high yields (80–90%) under mild conditions (393 K, 0.69 MPa, 3–8 h) over these catalysts, and only 0.06 g of catalyst was required per gram of substrate. As-synthesized

zeolite-beta [41] also exhibited efficient catalytic activity for cyclic carbonates synthesis at mild conditions (Table 1). Recently, the commercial production of cyclic carbonates using a phosgene-free route with quaternary ammonium salt-based catalysts was announced by BASF [43] and Asahi-Chi Mei (Taiwan) [20], but the reaction must be carried out at 30 to 80×10^5 Pa pressure.

b Oxidative Carboxylation of Alkenes   Several efforts have been made to synthesize cyclic carbonates directly from alkenes by oxidative carboxylation (Table 2). Aresta et al. [44] have reported the synthesis of styrene carbonate from styrene, O_2 and CO_2 using Nb_2O_5 and $Nb_2O_5 + NbCl_5$ catalysts. The yield of styrene carbonate in this one-pot synthesis process was significantly lower than that obtained by the cycloaddition reaction discussed above. Moreover, the reaction had to be conducted at high CO_2 pressures (4.5–4.9 MPa). Titanosilicates, zeolite-Y-encapsulated metal phthalocyanines and metal ion-exchanged zeolite catalysts, in addition to their efficient activity for cycloaddition of CO_2 to epoxide, are also efficient epoxidation catalysts [33, 35]. Srivastava et al. [33, 35] have used these catalysts for the synthesis of chloropropene carbonate and styrene carbonate directly from epichlorohydrin and styrene, respectively. H_2O_2 or *tert*-butyl hydroperoxide (TBHP) was used as oxidant, and the reaction was carried out in one-pot, but in two steps. In the first-step, alkene was oxidized to epoxide, whilst in the second step the reaction mixture containing the epoxide was reacted with CO_2. The reaction was conducted under mild conditions, and the yield of cyclic carbonate was higher than was obtained in the one-stage process over Nb(V) catalysts [44].

B Dimethyl Carbonate   Dimethyl carbonate (DMC) finds large industrial applications [46], most notably replacing phosgene (toxic!) in the manufacture of polyurethanes and polycarbonates. DMC also finds applications as a "green" solvent and ecofriendly reagent in methylation, esterification, carbomethoxylation, and carbonylation reactions, as well as being a potential oxygenate fuel additive to replace methyl *tert*-butyl ether (MTBE). Currently, three commercial methods of DMC production are recognized: (i) the conventional method of phosgenation of methanol; (ii) the oxidative carbonylation ($CO + O_2$) route using CuCl (EniChem), nitric oxide (UBE) or copper supported on active carbon (DOW) catalysts; and (iii) a commercial method (also using $CO + O_2$) developed by UBE industry which employs a Pd^{2+} catalyst and an alkyl nitrite promoter.
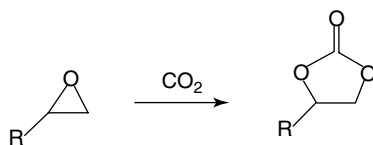
*a Synthesis of DMC from Epoxides, CO_2, and Methanol* This is a one-pot reaction, but occurs in two steps. In

Tab. 1 Synthesis of cyclic carbonates by carboxylation of epoxides over solid catalysts

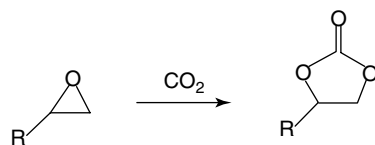| Catalyst	R (epoxide)	Reaction conditions/ epoxide conversion/cyclic carbonate selectivity or yield	Remarks	References
Polystyrene-bound quaternary onium salt	R = (phenyl)—O—CH$_2$— C$_4$H$_9$–O–CH$_2$— CH$_2$=CH–O–CH$_2$— CH$_2$=CH–CH$_2$–O–CH$_2$— (benzyl)	353–363 K, atmospheric pressure, 24 h, 1–2 mol.% of polymer catalyst. Carbonate yield = 3–75% depending on reaction conditions.	Atmospheric pressure, long reaction times and large amount of solvent such as DMSO, DMF, DMAc, diglyme, chlorobenzene, anisole, or toluene required for high carbonate yields.	[18]
Ion-exchange resins with functional groups N$^+$(CH$_3$)$_3$Cl$^-$, NH$_2$, NHCH$_3$, SO$_3$Na, COOH, NHCH$_2$PO$_3$Na$_2$	R = −CH$_3$, H, −C$_6$H$_5$, C$_6$H$_5$OCH$_2$−, ClCH$_2^-$	373 K, 8 MPa, 24 h, 5 mmol.% of catalyst. Carbonate yield > 65–99% and carbonate selectivity ~99%.	Catalyst reusable; reaction occurs in solvent-free conditions. Supercritical phase conditions needed for high carbonate yields.	[19]
Anion-exchange resin containing quaternary ammonium salts (water content <0.03%)	Ethene oxide	373 K, 52.8 g liquid CO$_2$, 3 h, 0.64 g resin per 26.4 g ethene oxide. Ethene carbonate yield 98%.	Catalyst recyclable; no solvent needed but high pressures essential.	[20]
Calcined hydrotalcites	R = −CH$_3$ − C$_4$H$_9$, −C$_6$H$_{13}$, −Ph, PhOCH$_2$−, PhCH$_2$ − CH$_3$ − O − CH$_2$−	373–393 K, 0.49 MPa, 15–24 h. Cyclic carbonate yield 90–99%.	Catalyst reusable; reaction proceeds with retention of stereochemistry of epoxides. Solvent (DMF) essential.	[23]
Nb$_2$O$_5$	Styrene oxide, propene oxide, pentene oxide, hexene oxide, octene oxide, cyclopentene oxide, cyclohexene oxide, cyclooctene oxide, R(−)-styrene oxide, S(+)-styrene oxide, R(+)-1,2-propene oxide, S(−)-1,2-propene oxide	408 K, 5 MPa, 12 h. Yield 10–88% depending on epoxide.	Solvent (DMF or DMF + CH$_2$Cl$_2$) essential. Reaction proceeds with retention of configuration (e.e. > 98%).	[26, 27]
SmOCl	Propene oxide	473 K, 14 MPa, 8 h. Propene carbonate yield 99% (with DMF solvent) and 57.5% (without solvent).	SmOCl more active than MgO and Mg-Al oxides. Solvent (DMF) essential.	[28, 29]
Smectite (S) catalysts: S-Mg-Na-K	Propene oxide	423 K, 15 h, 8 MPa. Propene carbonate yield 80.7%.	K increases conversion and yield. Partial replacement of Na with Li improved carbonate selectivity.	[30]
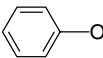
Tab. 1 (continued)

Catalyst	R (epoxide)	Reaction conditions/ epoxide conversion/cyclic carbonate selectivity or yield	Remarks	References
Aluminum phthalocyanine complex (ClAlPc) covalently bonded to MCM$^-$41	R = $-CH_3$, H, ClCH$_2-$, C$_6$H$_5-$	383 K, 4 MPa, 2 h, ClAlPc-MCM-41/n-Bu$_4$NBr/epoxide = 1/1/2500 (mol). TOF = 415 (ethylene carbonate), 280 (propene carbonate), 452 (chloropropene carbonate), 384 (styrene carbonate).	Catalyst could be recycled with no obvious loss in activity in 10 recycles. Cocatalyst such as quaternary ammonium salt e.g., n-Bu$_4$NBr essential for high carbonate yields and must be added freshly in each recycle experiment.	[31]
Zeolite-Y-encapsulated metal phthalocyanines	R = $-CH_3$, ClCH$_2^-$	393 K, 0.69 MPa, 4 h, epoxide/catalyst/ cocatalyst = 18/0.0072/0.0072 (mmol). Epichlorohydrin conversion 93.7% and cyclic carbonate selectivity 99.7%; Propene oxide conversion 84.7%, propene carbonate selectivity 85.3% over AlPc-Y.	Catalyst reusable. However, use of cocatalyst such as Bu$_4$NBr, Ph$_3$P, Bu$_4$PBr, pyridine, N,N-dimethylaminopyridine (DMAP) essential.	[32, 33]
Titanosilicates (TS-1, Ti-MCM-41)	R = $-CH_3$, ClCH$_2-$, C$_6$H$_5-$, $-C_2H_5$	393 K, 0.69 MPa, 4−10 h depending on epoxide. Epichlorohydrin conversion 85.4%, carbonate selectivity 92.6%; Propene oxide conversion 94%, carbonate selectivity 83%; n-butene oxide conversion 76.6% and carbonate selectivity 70.9% over TS-1; styrene oxide conversion 98.1% and carbonate selectivity 73.1% over Ti-MCM-41.	Reaction proceeds even in the absence of solvent but product colored. Catalyst reusable.	[35]
Zinc-substituted polyoxometalate Na$_{12}$[WZn$_3$(H$_2$O)$_2$ (ZnW$_9$O$_{34}$)$_2$]·46H$_2$O	R = $-CH_3$, ClCH$_2-$, $-C_2H_5$	413 K, 0.4 MPa, 3−12 h depending on the epoxide; Epoxide/catalyst/DMPA = 10 000−50 000/1/3 (mmol). Epoxide conversion ~97% and cyclic carbonate selectivity ~96%.	Catalyst reusable but requirement of homogeneous DMAP cocatalyst essential. Solvent optional.	[36]

Tab. 1   (continued)

Catalyst	R (epoxide)	Reaction conditions/ epoxide conversion/cyclic carbonate selectivity or yield	Remarks	References
Cobalt Schiff base Salen-type complex immobilized onto MCM-41	Ethene oxide	383 K, 12.5 MPa, continuous-flow conditions; flow rate of CO_2 20 mL h^{-1}; flow rate of ethene oxide 10 mL h^{-1}. Ethene oxide conversion 85.6%.	Cocatalyst n-Bu$_4$NBr essential for high conversion of ethene oxide. Supercritical conditions for high conversions and continuous-flow process.	[34]
Biopolymer chitosan-supported zinc chloride	R = CH$_3$CH$_2$, Cyclohexene	383 K, 1.5 MPa, 1 h. Cyclic carbonate selectivity > 99%.	Catalyst reusable. Presence of cocatalyst (1-butyl-3-methylimidazole) essential. No solvent needed.	[38]
Silica-supported guanidine	Styrene oxide, benzylethene oxide, decene oxide, methoxypropene oxide, cyclohexene oxide	413 K, 5 MPa, 70 h. Cyclic carbonate yield 60–95% depending on the epoxide.	Catalyst reusable. High pressures, longer duration and solvent (CH$_3$CN) required for high carbonate yields.	[37]
As-synthesized zeolite-beta	R = −CH$_3$, ClCH$_2$−, C$_6$H$_5$−, −C$_2$H$_5$	393, 0.69 Pa, 3–8 h, depending on epoxide.	High carbonate yields at mild reaction conditions and with out any cocatalyst and solvent. Catalyst reusable with little loss in activity in several recycling experiments.	[41]
Adenine-modified Ti-/Al-SBA-15	R = −CH$_3$, ClCH$_2$−, C$_6$H$_5$−, −C$_2$H$_5$	393, 0.69 Pa, 3–8 h, depending on epoxide.	High carbonate yields at mild reaction conditions without any additional cocatalysts or solvent. Catalyst reusable in 10 recycles with little loss in activity.	[39, 40]
Tetra-alkylammonium salts of transition-metal-substituted polyoxometalates such as [(n-C$_7$H$_{15}$)$_4$N$_6$[α-SiW$_{11}$O$_{39}$Co] and (n-C$_7$H$_{15}$)$_4$N$_6$[α-SiW$_{11}$O$_{39}$Mn]	Propene oxide	423, 3.5 Pa, 2 h, catalyst (0.1 mol.%). Cyclic carbonate yield 96–97%, selectivity 97%	Co^{2+} $\sim$ Mn^{2+} > Ni^{2+} > Fe^{3+} >> Cu^{2+}; (n-C$_7$H$_{15}$)$_4$N$^+$ > (n-C$_4$H$_9$)$_4$N$^+$ >> K$^+$. Co- and Mn-substituted catalysts required. No additional organic solvent or cocatalyst, but high pressures needed.	[42]

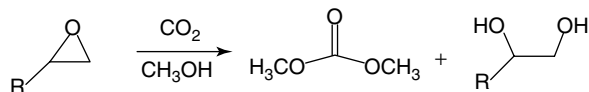**Tab. 2** Synthesis of cyclic carbonates by direct oxidative carboxylation of olefins over solid catalysts
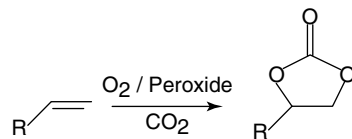
Catalyst	Olefin	Reaction conditions	Remarks	Reference
Titanosilicates	Allyl chloride, styrene	Epoxidation: 333 K with H_2O_2 or TBHP oxidants; Carboxylation: 393 K, 0.69 MPa (CO_2), cocatalyst: N, N-dimethylaminopyridine; solvent: acetone/acetonitrile; 4 h	*Catalyst system*: TS-/H_2O_2/CO_2: Allyl chloride: conv. 54.6%, chloropropene carbonate sel. 55.6%; Styrene: conv. 50.4%, styrene carbonate sel. 26%. *Catalyst system:* Ti-CM-1/TBHP/CO_2: Allyl chloride: conv. 13.3%, chloropropene carbonate sel. 100%; Styrene: conv. 44%, styrene carbonate sel. 100%.	[35]
Cu-exchanged zeolite⁻ Y	Styrene	Epoxidation with TBHP (333 K, 8 h); Carboxylation (393 K, 0.69 MPa, 4 h).	Styrene conv. 18.4%; epoxide sel. 22.7%. Epoxide conv. 48.9%; styrene carbonate sel. 42.9%.	[33]
Zeolite-Y-encapsulated metal phthalocyanines	Styrene	Epoxidation with TBHP (333 K, 8 h); Carboxylation (393 K, 0.69 MPa, 4 h).	*Catalyst: CuPc-Y:* Step 1: styrene conv. 52.5%; epoxide sel. 83%. Step 2: epoxide conv. 69.1%; styrene carbonate sel. 83.5% *Catalyst: CoPc-Y:* Step 1: styrene conv. 39.4%; epoxide sel. 78.9%. Step 2: epoxide conv. 100%; styrene carbonate sel. 54.4%.	[33]
Au/SiO$_2^-$ ZnBr$_2$/Bu$_4$NBr	Styrene	353 K, TBHP/cumene hydroperoxide, 1 MPa CO_2, 4 h. Styrene conversion ~75%; styrene carbonate yield ~45%.	Solvent is avoided.	[45]

the first step, the epoxide is converted by cycloaddition with CO_2 to cyclic carbonate, whilst in the next step the cyclic carbonate formed is transesterified with methanol to yield DMC and an equimolar amount of the diol byproduct (Table 3). Bhanage et al. [47, 48] reported the synthesis of DMC (from propene oxide, CO_2 and CH_3OH) over various metal oxides, and obtained propene oxide conversions of 96 to 99%, but the DMC selectivity was only 28% (at 8 MPa CO_2 pressure and 423 K). On Mg-smectite [48], the selectivity improved from 28% to 36%. DMC synthesis from supercritical CO_2, ethene oxide (EO)/propene oxide (PO), and methanol over different solid catalysts have been explored [49]. KI supported on ZnO [49] showed high catalytic activity, but the activity was improved when K_2CO_3 was also present. Very high conversions of epoxides (96–99%) and moderate DMC

selectivity (55–58%) were obtained over a K_2CO_3-KI-ZnO system [49]. Supercritical CO_2 acts as a reactant as well as the solvent.

The synthesis of DMC from cyclic carbonates by transesterification with methanol is more efficient. Transesterification of ethene carbonate is much easier than propene carbonate, and a large number of basic oxide catalysts have been reported for these reactions [51–54]. MgO showed the highest activity, with an ethene carbonate conversion of 82.3% at 423 K. When transesterification was conducted in the presence of CO_2 (8 MPa), the selectivity of DMC was 100%. However, the basic oxide catalysts were only weakly active for propene carbonate transesterification with methanol. with conversions of about 25 to 62% with a DMC selectivity of 60 to 65%. Feng et al. [54] reported the continuous

Tab. 3 Synthesis of dimethyl carbonate from epoxides, CO_2 and methanol

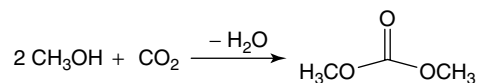| Catalyst	Epoxide	Reaction conditions	Remarks	Reference
MgO	Ethene oxide, propene oxide, styrene oxide	423 K, 8 MPa CO_2, 15 h, methanol 200 mmol; ethene oxide 62 mmol; propene oxide 25 mmol; styrene oxide 55 mmol; catalyst 0.5 g.	Ethene oxide: conv. 96.1%; DMC sel. 28%; Propene oxide: conv. 99.2%, DMC sel. 13.6%; Styrene oxide: conv. 98.4%, DMC sel. 12.5%.	[47]
Mg-containing smectite	Propene oxide	423 K, 8 MPa CO_2, 15 h, 21 mmol epoxide, 200 mmol methanol, 0.5 g catalyst.	Propene oxide conv. 98%; DMC sel. 33.6%.	[48]
KI/ZnO	Ethene oxide, propene oxide	423 K, 16.5 MPa, 4 h, 10 mmol epoxide, 40 mmol methanol, 0.25 g catalyst.	Ethene oxide: conv. >97%; DMC yield ~57%. Propene oxide: conv. >98%; DMC yield ~22−36%.	[49]
KOH, NaOH, KNO_3, K_2CO_3 impregnated 4A molecular sieves zeolite	Propene oxide	453 K, 3 MPa CO_2 (at room temperature), 6 h, catalyst 5 g, active content of catalyst 17.5%, propene oxide 58 mL, methanol 50 mL.	Propene carbonate yield 58.7%; DMC yield 16.8%.	[50]

synthesis of DMC from ethene carbonate and methanol over tertiary amino groups covalently bonded to MCM-41. The catalyst exhibited good stability and catalytic activity during 100 h in a fixed-bed, continuous-flow operation. A maximum ethene carbonate conversion of about 42% was obtained at 120 °C, 1 MPa, a methanol:ethene carbonate molar ratio of 8:1, and a liquid hourly space velocity (LHSV) of 3 h^{-1}. Fe−Zn double metal cyanide catalysts have been shown as more efficient for the transesterification of propene carbonate with alcohols (DMC yield 87%) [55].

b   Direct Synthesis of DMC from Methanol and CO_2   When DMC is synthesized from cyclic carbonates, an equivalent amount of glycol is cogenerated, thereby affecting the economic viability of the process. Although the direct synthesis route of DMC is more economical, the thermodynamics limits the conversion of this reaction. Fujimoto and coworkers [56] synthesized DMC from CH_3OH and CO_2 using CH_3I and K_2CO_3 as the promoters. Although this reaction was fast, deactivation was very rapid. Several zirconia-based materials with both acidic and basic properties have been used as heterogeneous catalysts for this reaction [57−59]. Polymer Dowex-supported iodide and vanadia catalysts were also used for this reaction [61, 62].

DMC formation was seen to depend strongly on the structure of zirconia, with the highest rate of DMC formation being achieved on tetragonal zirconia prepared by the calcination of zirconium hydroxide at 673 K. On SiO_2, Al_2O_3, TiO_2, H-ZSM-5, H-USY, H-mordenite, ZnO, MoO_3 and Bi_2O_3, dimethyl ether (DME) was the major product. Phosphoric acid [58] and heteropolyacid [59]-promoted zirconia catalysts showed higher activity than the unpromoted zirconia catalysts. The yield of DMC formed in this direct route is much lower than that obtained from the cyclic carbonate route (Table 4). Bell et al. [63] examined the mechanism of DMC formation on zirconia using *in-situ* Raman and IR spectroscopy. On adsorption, methanol was found to dissociate, leading to a methoxide group ($Zr−OCH_3$) with the release of a proton, which reacted with the surface hydroxyl groups to produce water. Carbon dioxide was seen to insert into the $Zr−O$ bond of the methoxide to form a monodentate methyl carbonate group ($Zr−OC(O)OCH_3$). This process was facilitated by the interactions of C and O atoms in CO_2 with Lewis acid−base pair sites ($Zr^{4+} − O^{2-}$) on the surface of the catalyst.

Methyl carbonate can also be produced via the reaction of methanol with CO_2 adsorbed in the form of bicarbonate species, but this process is slower than that involving the reaction of CO_2 with the methoxide species. DMC is

Tab. 4 Direct synthesis of dimethyl carbonate from methanol and CO_2

$$2\ CH_3OH\ +\ CO_2\ \xrightarrow{\ -\ H_2O\ }\ H_3CO\overset{\displaystyle O}{\underset{\displaystyle}{\parallel}}OCH_3$$

Catalyst	Reaction conditions	Remarks	Reference
ZrO_2	443 K, $CH_3OH:CO_2$ = 82:250 mmol,16 h.	Low DMC yield 0.42 mmol; DMC sel. 100%.	[57]
H_3PO_4/ZrO_2	403 K, $CH_3OH:CO_2$ = 192:200 mmol; 2 h.	DMC yield 0.6 mmol.	[58]
$H_3PW_{12}O_{40}/ZrO_2$	573 K, $CH_3OH:CO_2$ = 140:175 mmol; 3.5 h.	Low DMC yield 2.83 mmol.	[59]
CeO_2-ZrO_2	383 K, $CH_3OH:CO_2$ = 192:200 mmol; 2 h.	Low DMC yield 0.7 mmol.	[60]
H_3PO_4/V_2O_5	413 K, CH_3OH/CO_2 = 500/250 mmol.	CH_3OH conv. 0.265%; DMC sel. 90.6%.	[62]
Cu-KF/MgSiO	403 K, $n(CH_3OH)/n(CO_2)$ = 1.5–3, 1 MPa, space velocity 1040 h^{-1}.	Methanol conv. ~5%; DMC sel. ~89%.	[64]

Tab. 5 Formation of unsymmetrical carbonates from alcohols (ROH), alkyl halides (R′X) and CO_2 over $CsCO_3$ [65]

ROH	R′X	Time/h	Yield of carbonate/%
Ph⌒⌒⌒OH	Br⌒⧸⧵ (2-bromobutane)	23	98
Ph⌒⧸OH (1-phenyl-2-propanol)	Benzyl chloride	3	98
L-(−) menthol	n-Butyl bromide	5	96
Ph⌒⧸(OH)CO_2Me	3-Methoxybenzyl-chloride (MPMCl)	3	92

formed by the reaction of the monomethyl carbonate species with methanol, a process that results in the transfer of a methyl group to the carbonate and restores a hydroxyl group on the zirconia surface. Li and Zhong [64] reported the use of a membrane catalytic reactor that combines the catalytic reaction with a membrane separation process for DMC synthesis from methanol and CO_2 over a Cu−KF/MgSiO catalyst. At a conversion of about 6 to 9% of methanol, a DMC selectivity of about 96% was obtained.

Salvatore et al. [65] reported the synthesis of unsymmetrical (Table 5) and chiral (Table 6) carbonates in high yields (>90%) from (alcohol + halides + CO_2) at room temperature employing Cs_2CO_3, in the presence of tetrabutylammonium iodide (TBAI) and using N,N'-dimethylformamide as solvent.

C Polycarbonates The copolymerization of CO_2 and epoxide yields aliphatic polycarbonates (PC), which find application as biodegradable and biomedical materials for drug delivery. These materials are also used as lubricants and elastomers (functionalized PC with pendent vinyl groups). Inoue et al. [17] were the first to disclose the copolymerization of CO_2 with epoxide (1,2-epoxypropane) by $ZnEt_2 − H_2O$. With all homogeneous catalysts [66], the yield of copolymer was low (<60 g g^{-1} catalyst). Recently, Chen et al. [67] reported the use of a solid zinc hexacyanocobaltate(III)-based coordination catalyst for this copolymerization reaction; this catalyst exhibited a highly enhanced catalytic activity, yielding 1000 g of copolymer (from propene oxide and CO_2) per g $Zn_3[Co(CN)_6]_2$. The iron analogue of the catalyst, $Zn_3[Fe(CN)_6]_2$, showed very low activity (44 g polymer g^{-1} catalyst). Kim and coworkers [66, 69] found that a variety of other copolymers could also be synthesized using the solid, double-metal cyanide Zn−Co catalysts from a range of other epoxides (Table 7).

14.17.4.3.2 CO_2 Insertion and C−H/O−H Bond Formation

A Formic Acid Formic acid is currently manufactured by the carbonylation of methanol to methylformate,

Tab. 6 Chiral carbonates from CO_2, alcohols and benzyl chloride over $CsCO_3$ [65]

Alcohol	Time/h	Carbonate yield/%	e.e./%
Me—CH(OH)—CO₂Et	3	90	96
Ph—CH₂—CH(OH)—CO₂Bn	3	85	97
MeO₂C—CH₂—CH(OH)—CH₂—CO₂Me	3	65	95
(lactone with OH)	3	90	97

Tab. 7 Polycarbonates synthesis: copolymerization of epoxides and CO_2 over solid, Zn–Co double-metal cyanide catalysts [68]

Epoxides	Temp./K	Time/h	TON^a	M_n^b
Cyclohexene oxide	323	4	506.14	6800
Cyclopentene oxide	323	12	480.86	1900
4-Vinyl-1-cyclohexene-1, 2-epoxide	323	12	446.34	15 500
Propylene oxide	323	24	506.80	4400
Butene oxide	323	24	404.12	9000
Hexene oxide^c	353	24	413.14	6400
Octene oxide	323	24	397.09	9500
1-Chloro-2, 3-epoxypropane	323	24	520.87	2300
Phenylglycidyl ether	323	36	467.66	9300
Allylglycidyl ether	323	36	448.31	6500

Polymerization conditions: catalyst = 0.02 g; epoxide (CPO) = 5 mL; P_{CO2} = 9.6 bar, temperature = 323 K.
^{a}Turnover number as g polymer/g of zinc.
^{b}Data from GPC-molecular weight.
^{c}Reaction temperature = 353 K.

which is subsequently hydrolyzed to formic acid and methanol. The latter is then recycled. The net process is the addition of CO to H_2O, and under standard conditions the equilibrium for the reaction between carbon dioxide and hydrogen lies far on the left side.

$$CO_2 + H_2 \rightleftharpoons HCOOH \quad \Delta G^0_{298\,k} = 32.9 \text{ kJ mol}^{-1}$$

Homogeneous catalysts, rhodium and ruthenium phosphine complexes, are efficient catalysts for the formation of formic acid from CO2 [70]. Ru–SiO_2 has been suggested for the production of various derivatives of formic acid [71]. Homogeneous Ru(II) complexes found to be active for the hydrogenation of CO_2 include: $TpRuH(PPh_3)(MeCN)$, $CpRu(CO)(dppm)Mo(CO)_2Cp$, cis-$[Ru(Cl_2bpy)_2(H_2O)_2]$ $(O_3SCF_3)_2$ (Tp = tris(pyrazolyl)borate, dppm = Ph_2PCH_2 PPh_2, Cl_2bpy = 6,6-dichloro-2,2-bipyridine). The last of these three gives high yields of formic acid, up to 5000 turnover number (TON) after 8 h, at 423 K [72]. Unfortunately, however, an efficient, solid catalyst for the production of formic acid is yet to be discovered.

B Acetic Acid Acetic acid is produced industrially by the BP/Monsanto process (carbonylation of methanol). It can also be produced by the reaction of methane with carbon dioxide:

$$CO_2 + CH_4 \rightleftharpoons CH_3COOH$$
$$\Delta G^0_{298k} = 16.9 \text{ kJ.mol}^{-1}, \Delta H^0_{298k} = 8.6 \text{ kJ mol}^{-1}$$
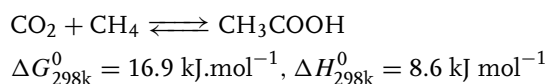
This reaction is thermodynamically unfavorable. A South African patent by Freund and Wambach [73] has claimed a process for the direct synthesis of acetic acid from CO_2 and CH_4 using a solid catalyst, described as containing "one or more metals of groups VIA, VIIA, VIIIA" on a support of an aluminum oxide at 373 to 873 K and 0.1 to 20 MPa. The patent also claims a selectivity of 70 to 95%. Huang et al. [74] reported the formation of acetic acid over a Co–Cu catalyst but, in addition to acetic acid (selectivity 21%), a wide variety of other species were also formed.

14.17.4.3.3 CO_2 Insertion and C–N bond Formation
A Methylamine Methylamines are produced commercially by the exothermic reaction of methanol with ammonia in the presence of solid acid dehydration catalysts. The thermodynamics of this reaction favors the formation of trimethylamine (TMA), instead of the mono-(MMA) and dimethylamines (DMA); the latter are of major commercial interest [75]. In industrial practice, the selectivity of TMA is reduced either by application of shape-selective zeolites or by recycling of TMA combined with high NH_3 to methanol ratios. During the past decade, attempts have been made to produce methylamines directly from CO/H_2 (synthesis gas) and ammonia in the presence of modified Fischer–Tropsch catalysts or supported copper catalysts [76]. Recently, attempts have been made to use CO_2, as a starting material for the synthesis of organonitrogen compounds such as formamides [77] and methylamines [78]. Among various

References see page 3730

Tab. 8 Synthesis of methylamines from CO_2, H_2 and NH_3

Catalyst	Reaction conditions	Remarks	References
Metal−alumina	Total pressure $= 0.6$ MPa, reactants flow rate (H_2:CO_2: $NH_3 = 3:1:1) = 150$ cm^3 min^{-1}, catalyst 3 g. Feed gas composition: 60 mol.% H_2, 20 mol.% CO_2, 0–20 mol.% NH_3 and N_2 as a balance.	Methane formation favored to amine synthesis at higher temperatures with Ni, Pt, Co, Fe. CO is a byproduct. HCN formation was observed with Cu(9).	[77, 79]
	Amine production rate (in mol Kg$_{cat}$. h) (Amine distribution MMA:DMA:TMA).		
		513 K 553 K		
	Cu(47)-Al$_2$O$_3$ 0.49 (71:16:13) 1.21 (71:19:10)		
	Cu(27)-Al$_2$O$_3$ 0.45 (72:15:13) 1.16 (73:19:8)		
	Cu(9)-Al$_2$O$_3$ 0.17 (74:14:12) 0.51 (74:18:8)		
	MMA = monomethyl amine; DMA = dimethyl amine; TMA = trimethylamine.		
Cu (22−29%) supported oxides	Total pressure $= 0.6$ MPa, temperature range 473–573 K, reactants flow rate (H_2:CO_2: $NH_3 = 3:1:1) = 150$ mL min^{-1} (STP) (GHSV $= 2250$ h^{-1}), catalyst 3 g, Feed gas composition: 60 mol.% H_2, 20 mol.% CO_2, 0–20 mol.% NH_3 and N_2 as a balance.	Activity: $Cr_2O_3 > ZrO_2 > Al_2O_3 >$ $SiO_2 > ZnO$, MgO. MMA is formed in greater selectivity.	[80]
$Cu_{0.33}$ $Mg_{(0.67−x)}Al_x$-CO_3	Total pressure $= 0.6$ MPa, temperature $= 453$ K, reactants flow rate (H_2:CO_2: $NH_3 = 3:1:1) = 150$ cm^3 min^{-1} (STP) (GHSV $= 2250$ h^{-1}), catalyst 3 g. Methylamines selectivity $= 84\%$.		[81]

alumina-supported transition metals tested for catalytic synthesis of methylamines from CO_2/H_2/ NH_3, copper-alumina was found to be the most active [79]. Based on NH_3-TPD (temperature-programmed desorption) experiments, it was suggested that the high activity is associated with optimal acidic properties of the catalyst surface. Highest activity in methylamine synthesis was found for supports with an isoelectric point in the range 6 to 8 [80]. Cu supported on Cr_2O_3, ZrO_2, and Al_2O_3 showed high catalytic activity, whereas ZnO, MgO and SiO_2 showed very low activity (Table 8). A similar conclusion was drawn also from studies based on the catalysts derived from Cu−Mg−Al lamellar double hydroxides (LDH) with a hydrotalcite-like structure [81].

B N,N-Dimethylformamide and Methylformate The synthesis of N,N-dimethylformamide (DMF) and methyl-formate (MF) from CO_2 is an interesting alternative [82]. Both reactions are exothermic but, depending on the reaction conditions, they are neutral or slightly ex-ergonic due to the unfavorable entropy change. For high product yields, high pressure and relatively low temperature must be applied. Formic acid, which is regarded as a crucial intermediate, is stabilized by

the addition of basic additives. In MF synthesis, the stabilizing additive is a tertiary amine such as tri-ethylamine. In DMF synthesis, dimethylamine can act both as a basic additive and as a reactant, forming the product on reacting with formic acid. The use of a catalyst is essential to reach high reaction rates. Among several Group VIII transition metal complexes the hybrid catalyst, $RuCl_2[PPh_2(CH_2)_2Si(OEt)_3]_3$ exhibited [82] efficient activity for the synthesis of DMF and MF. A DMF yield of 94% at a selectivity of 100% was achieved over these catalysts. While the heterogeneous catalysts were stable, the corresponding homogeneous complex catalysts decomposed during reaction conditions. Over the heterogenized Ru complex catalysts methyl formate was also produced at a selectivity of 100%. The use of an additional base (triethylamine) was crucial to reach the high yields of methyl formate.
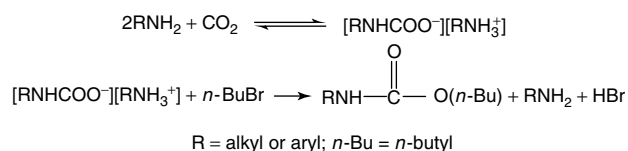
C Alkyl and Aryl Carbamates The reaction of primary amines with CO_2 and alkyl halides is a benign route to carbamates synthesis. This method produces the carbamate anion from the reaction of CO_2 with a primary amine. Reaction of this anion with various alkyl halides yields the corresponding carbamate.

Tab. 9 Synthesis of carbamates from amines, CO_2 and alkyl halide over TS-1 titanosilicate [91]

$$RNH_2 + CO_2 + n\text{-BuBr} \xrightarrow[\text{DMF, 353 K, 3 h}]{\text{Titanosilicate}} R\text{—}\underset{H}{N}\text{—}\overset{O}{C}\text{—}O\text{-Bu} + R\text{—}N\overset{Bu}{\underset{Bu}{}}$$

Amine	Alkyl halide	Amine conversion/wt.%	Carbamate yield/%
(long alkyl chain)—NH₂	n-BuBr	92.8	89.5
(cyclohexyl)—NH₂	n-BuBr	63.2	58.5
	n-BuCl	53.8	51.9
(phenyl)—NH₂	n-BuBr	93.0	89.3
(benzyl)—NH₂	n-BuBr	66.6	63.4
(mesityl)—NH₂	n-BuBr	56.0	54.7
	n-BuBr[b]	76.0	73.8

[a] Reaction conditions: amine 2 mmol; n-BuX 1 mmol; catalyst 100 mg; DMF 10 g; CO_2 3.4 bar; temperature 353 K; run time 3 h.
[b] Reaction conducted using Ti-SBA-15 as catalyst.

$$2RNH_2 + CO_2 \rightleftharpoons [RNHCOO^-][RNH_3^+]$$

$$[RNHCOO^-][RNH_3^+] + n\text{-BuBr} \longrightarrow RNH\text{—}\overset{O}{\underset{}{C}}\text{—}O(n\text{-Bu}) + RNH_2 + HBr$$

R = alkyl or aryl; *n*-Bu = *n*-butyl

Srivastava et al. [83] reported the use of reusable, zeolite-Y-encapsulated metal phthalocyanines as catalysts for this reaction. Cocatalysts, such as onium salts (TBAI) were not needed. The reactivity of these solid catalysts was much higher than that of Cs_2CO_3 [84], and both aliphatic and aromatic amines could be converted into their corresponding carbonates in high yields over titanosilicate molecular sieves (TS-1, Ti-MCM-41 and Ti-SBA-15) (Table 9) [83]. In the case of bulky substrates such as 2,4,6-trimethylaniline and cyclododecylamine, the mesoporous Ti-SBA-15 was more active than the medium-pore TS-1. Selectivity for the carbamate product was found to be higher over titanosilicates than over zeolite-Y-encapsulated metal phthalocyanines [83]. More recently, Srivastava et al. [39] have found that adenine-modified SBA-15 molecular sieves exhibit superior efficiency for

carbamate synthesis. The reaction could be conducted even in the absence of any additional cocatalyst/promoter as well as solvent. Very high yields of carbamates could be synthesized under mild conditions from different amines of varying size. SBA-15 alone was only weakly active. The catalytic activity was enhanced upon titanation, whilst a slight enhancement in activity was observed with adenine functionalization. When both Ti and adenine were present, the catalytic activity was much higher, and complete conversion of amine (aniline, for example) was observed. The titanium ions (weak Lewis acid sites) and the adenine moieties (the basic sites) were necessary for maximum catalytic activity and carbamate selectivity.

14.17.4.3.4 CO₂ Insertion and C—C Bond Formation Co-oligomerization of unsaturated hydrocarbons and CO_2 lead to a variety of synthetic intermediates such as acids, esters, lactones, and pyrones. The reaction of alkynes with CO_2 (to 2-pyrones in the presence of 3d metal complexes),

represents one of the few examples of a homogeneous catalytic reaction, which leads to C−C bond formation on CO_2 insertion. The variation of alkyne substituents allows synthesis of a wide range of 2-pyrones [85].
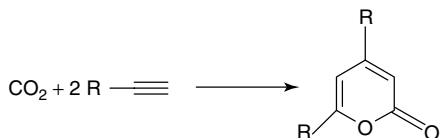

The reaction of a diene, 1,3-butadiene with CO_2 in presence of Pd complexes leads [86] to co-oligomers **1**, **2**, and **3**.
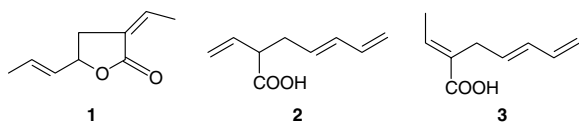
Palladium seems to be the most active metal center, forming 2:1 and 4:1 (alkene: CO_2) co-oligomers, whereas Rh catalysts yielded 3:1 products. The activity of Pd catalysts can be increased by the addition of certain donor ligands such as aliphatic and aromatic nitrogen compounds. Palladium catalysts with aromatic substituted phosphines tend to form 4:1 co-oligomers.

The reactions of CO_2 with monoenes are more difficult. The reaction of ethene and CO_2 to propionic acid and ethyl propionate over a Wilkinson's complex (38% yield at 7×10^7 Pa) was reported by Lapidus et al. [87]. Activated monoenes, such as methylenecyclopropane, are more reactive [88].
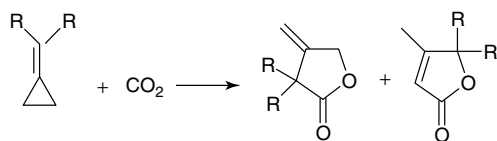
Heterogeneous catalysts for the above-mentioned reactions have not yet been reported.

14.17.4.4 Conclusions and Challenges

The use of CO_2 as a raw material and as a replacement for toxic phosgene and carbon monoxide represents an ecofriendly approach to chemicals synthesis. However, as CO_2 is a thermodynamically stable and kinetically inert molecule, its activation becomes the rate-determining step for its further utilization in reactions with other molecules. CO_2 can be activated at the surface of basic metals, metal oxides or metal complexes, and also by coordination through its carbon or oxygen atoms. Various modes of CO_2 coordination to metals have been identified through structural and *in-situ* spectroscopic studies. The activated intermediates of CO_2, including CO_2^-, formate, carbonate and carbamate, readily react with a variety of organic moieties to yield value-added chemicals via formation of new C−H, C−C, C−N, C−O, and O−H bonds. The coupling of CO_2 to epoxides to produce cyclic and polycarbonates is an atom-efficient route for CO_2 utilization wherein CO_2 is used as a replacement for phosgene, and CO is used in conventional manufacture. Today, efficient, reusable, solid catalysts for this reaction are available. The reaction of CO_2 with methanol over solid catalysts to produce DMC in high yields represents a major challenge, as is the reaction of alkenes or alkynes with CO_2 to yield lactones/carboxylic acids. Although in recent times sufficient knowledge has been acquired with regards to CO_2 activation in the homogeneous phase, the effective activation of CO_2 over solid catalysts remains an exciting goal in the field of heterogeneous catalysis.

References

1. M. M. Halmann, *Chemical Fixation of Carbon Dioxide-Methods for Recycling CO_2 into Useful Products*, CRC Press, Boca Raton, FL, 1993.
2. D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155.
3. (a) X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27; (b) D. H. Gibson, *Coord. Chem. Rev.* **1999**, *185–186*, 335.
4. A. D. Walsh, *J. Chem. Soc.* **1953**, 2260.
5. J. C. Calabrese, T. Herskovitz, J. B. Kinney, *J. Am. Chem. Soc.* **1983**, *105*, 5914.
6. H.-J. Freund, M. W. Roberts, *Surf. Sci. Rep.* **1996**, *25*, 225.
7. L. H. Dubois, G. A. Somorjai, *Surf. Sci.* **1983**, *128*, L231.
8. H. F. Freund, H. Behner, B. Bartos, G. Wedler, H. Kuhlenbeck. M. Neumann, *Surf. Sci.* **1987**, *180,* 550.
9. M. P. Habas, F. Mele, M. Sodupe, F. Illas, *Surf. Sci.* **1999**, *431*, 208.
10. Z.-M. Liu, Y. Zhou, F. Solymosi, J. M. White, *Surf. Sci.* **1991**, *245*, 289.
11. R. P. Eischens, W. A. Pliskin, *Adv. Catal.* **1957**, *12*, 662.
12. L. H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, London, 1986.
13. (a) J. Heidberg, D. Meine, *Surf. Sci.* **1992**, *279*, L175; (b) K. Tanabe, in *Catalysis-Science and Technology*, J. R. Anderson, M. Boudart (Eds.), Springer, Berlin, 1981, p. 123; (c) J. Paul, F. M. Hoffmann, *Catal. Lett.* **1988**, *1*, 445; (d) J. Wambach, G. Illing. H.-J. Freund, *Chem. Phys. Lett.* **1991**, *184*, 239; (e) J. Wambach, H.-J. Freund, in *Carbon Dioxide Chemistry: Environmental Issues*, J. Paul, C.-M. Pradier (Eds.), The Royal Society of Chemistry, Special Publication No. 153, 1994, p. 31.
14. P. R. Davies, M. W. Roberts, *J. Chem. Soc. Faraday Trans. I*, **1992**, *88*, 361.
15. D. A. Palmer, R. Van Eldik, *Chem. Rev.* **1983**, *83*, 651.
16. *Kirk-Othmer Encyclopedia of Chemical Technology*, J. I. Kroschwitz, M. Howe-Grant (Eds.), 4th Edn., John Wiley & Sons, New York, Vol. 19, 1986, p. 584.
17. (a) S. Inoue, H. Koinuma, T. Tsuruta, *Polymer Lett.* **1969**, *7*, 287; (b) S. Inoue, *CHEMTECH* **1976**, 588.
18. T. Nishikubo, A. Kameyama, J. Yamashita, T. Fukumitsu, C. Maejima, M. Tomoi, *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 939.
19. Y. Du, F. Cai, D.-L. Kong, L.-N. He, *Green Chem.* **2005**, *7*, 518.

20. S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, *Green Chem.* **2003**, *5*, 497.

21. T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem. Commun.* **1997**, 1129.

22. B. M. Bhanage, S.-i. Fujita, Y. Ikushima, M. Arai, *Appl. Catal. A: General* **2001**, *219*, 259.

23. K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, E. Kaneda, *J. Am. Chem. Soc.* **1999**, *121*, 4526.

24. E. J. Doskocil, S. V. Bordawekar, B. G. Kaye, R. J. Davis, *J. Phys. Chem. B* **1999**, *103*, 6277.

25. M. Tu, R. J. Davis, *J. Catal.* **2001**, *199*, 85.

26. M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *J. Mol. Catal. A: Chemical* **2003**, *204–205*, 245.

27. M. Aresta, A. Dibenedetto, L. Giafrate, C. Pastore, *Appl. Catal. A: General* **2003**, *255*, 5.

28. H. Yasuda, L.-N. He, Y. Sakakura, *J. Catal.* **2002**, *209*, 547.

29. H. Yasuda, L.-N. He, Y. Sakakura, *Stud. Surf. Sci. Catal.* **2003**, *145*, 259.

30. S.-I. Fujita, B. M. Bhanage, Y. Ikushima, M. Shirai, K. Torii, M. Arai, *Chem. Lett.* **2002**, *79*, 95.

31. X.-B. Lu, H. Wang, R. He, *J. Mol. Catal. A: Chemical* **2002**, *186*, 33.

32. R. Srivastava, D. Srinivas, P. Ratnasamy, *Catal. Lett.* **2003**, *89*, 81.

33. R. Srivastava, D. Srinivas, P. Ratnasamy, *Stud. Surf. Sci. Catal.* **2004**, *154C*, 2703.

34. X.-B. Lu, J.-H. Xiu, R. He, K. Jin, L.-M. Luo, X.-J. Feng, *Appl. Catal. A: General* **2004**, *275*, 73.

35. R. Srivastava, D. Srinivas, P. Ratnasamy, *Catal. Lett.* **2003**, *91*, 133.

36. M. Sankar, N. H. Tarte, P. Manikandan, *Appl. Catal. A: General* **2004**, *276*, 217.

37. A. Barbirini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori, R. Sartorio, *Tetrahedron Lett.* **2003**, *44*, 2931.

38. L.-F. Xiao, F.-W. Li, C.-G. Xia, *Appl. Catal. A: General* **2005**, *279*, 125.

39. R. Srivastava, D. Srinivas, P. Ratnasamy, *J. Catal.* **2005**, *233*, 1.

40. R. Srivastava, D. Srinivas, P. Ratnasamy, *Micropor. Mesopor. Mater.* **2005** (in press) doi: 10.1016/j.micromeso.2005.10.043.

41. R. Srivastava, D. Srinivas, P. Ratnasamy, *Appl. Catal. A: General* **2005**, *289*, 128.

42. H. Yasuda, L.-N. He, T. Sakakura, C. Hu, *J. Catal.* **2005**, *233*, 119.

43. *Filtration Industry Analyst* **1999** (Issue No. 27, June 1999) 2.

44. M. Aresta, A. Dibenedetto, *J. Mol. Catal. A: Chemical* **2002**, *182–183*, 399.

45. J. Sun, S.-i. Fujita, F. Zhao, M. Hasegawa, M. Arai, *J. Catal.* **2005**, *230*, 398.

46. P. Tundo, M. Selva, *Acc. Chem. Res.* **2002**, *35*, 706.

47. B. M. Bhanage, S.-i. Fujita, Y. Ikushima, M. Arai, *Appl. Catal. A: General* **2001**, *219*, 259.

48. B. M. Bhanage, S.-i. Fujita, Y. Ikushima, K. Torii, M. Arai, *Green Chem.* **2003**, *5*, 71.

49. Y. Chang, T. Jiang, B. Han, Z. Liu, W. Wu, L. Gao, J. Li, H. Gao, G. Zhao, J. Huang, *Appl. Catal. A: General* **2004**, *263*, 179.

50. Y. Li, X.-Q. Zhao, Y.-J. Wang, *Appl. Catal. A: General* **2005**, *279*, 205.

51. (a) T. Tatsumi, Y. Watanabe, K. A. Koyano, *Chem. Commun.* **1996**, 2281; (b) Y. Watanabe, T. Tatsumi, *Micropor. Mesopor. Mater.* **1998**, *22*, 399.

52. T. Wei, M. Wang, W. Wei, Y. Sun, B. Zhong, *Green Chem.* **2003**, *5*, 343.

53. B. M. Bhanage, S.-i. Fujita, Y. He, Y. Ikushima, M. Shirai, K. Torii, M. Arai, *Catal. Lett.* **2002**, *83*, 137.

54. X.-J. Feng, X.-B. Lu, R. He, *Appl. Catal. A: General* **2004**, *272*, 347.

55. R. Srivastava, D. Srinivas, P. Ratnasamy *J. Catal.* **2005** (communicated).

56. S. Fang, K. Fujimoto, *Appl. Catal. A: General* **1996**, *142*, L1.

57. (a) K. Tomishige, Y. Sakaihori, Y. Ikeda, K. Fujimoto, *Catal. Lett.* **1999**, *58*, 225; (b) K. Tomishige, Y. Ikeda, T. Sakaihori, K. Fujimoto, *J. Catal.* **2000**, *192*, 355.

58. (a) Y. Ikeda, T Sakaihori, K. Tomishige, K. Fujimoto, *Catal. Lett.* **2000**, *66*, 59; (b) Y. Ikeda, M. Asadullah, K. Fujimoto, K. Tomishige, *J. Phys. Chem. B* **2001**, *105*, 10653.

59. C. Jiang, Y. Guo, C. Wang, C. Hu, Y. Wu, E. Wang, *Appl. Catal. A: General* **2003**, *256*, 203.

60. K. Tomishige, K. Kunimori, *Appl. Catal. A: General* **2002**, *256*, 103.

61. G. H. Chu, J. B. Park, M. Cheong, *Inorg. Chim. Acta* **2000**, *307*, 131.

62. X. L. Wu, M. Xiao, Y. Z. Meng, Y. X. Lu, *J. Mol. Catal. A: Chemical* **2005**, *238*, 158.

63. (a) K. T. Jung, A. T. Bell, *J. Catal.* **2001**, *204*, 339; (b) S. Xie, A. T. Bell, *Catal. Lett.* **2000**, *70*, 137.

64. C.-F. Li, S.-H. Zhong, *Catal. Today* **2003**, *82*, 83.

65. R. N. Salvatore, F. Chu, A. S. Nagle, E. A. Kapxhiu, R. M. Cross, K. W. Jung, *Tetrahedron* **2002**, *58*, 3329.

66. C. M. Byrne, S. D. Allen, E. B. Lokkovski, G. W. Coates, *J. Am. Chem. Soc.* **2004**, *126*, 11404.

67. S. Chen, G.-R. Qi, Z.-J. Hua, H.-Q. Yan, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 5284.

68. I. Kim, M. J. Yi, S. H. Byun, D. W. Park, B. U. Kim, C. S. Ha, *Macromol. Symp.* **2005**, *224*, 181.

69. (a) I. Kim, J.-T. Ahn, S.-H. Lee, C.-S. Ha, D.-W. Park, *Catal. Today* **2004**, *93–95*, 511; (b) I. Kim, J.-T. Ahn, C. S. Ha, C.-S. Yang, I. Park, *Polymer* **2003**, *44*, 3417; (c) M. J. Yi, S.-H. Byun, C.-S. Ha, D.-W. Park, I. Kim, *Solid State Ionics* **2004**, *172*, 139.

70. (a) W. Leitner, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207; (b) F. Hutschka, A. Dedieu, M. Eichberger, R. Fornika, W. Leitner, *J. Am. Chem. Soc.* **1997**, *119*, 4432.

71. A. Baiker, *Appl. Organometal. Chem.* **2000**, *14*, 751.

72. C. P. Lau, Y. Z. Chen, *J. Mol. Catal. A: Chemical* **1995**, *101*, 33.

73. H. J. Freund, J. Wambach, *Process for the Preparation of Acetic Acid*, Republic of South Africa, 7 August, 1995.

74. W. Huang, K. C. Xie, J. P. Wang, Z. H. Gao, L. H. Yin, Q. Zhu, *J. Catal.* **2001**, *201*, 100.

75. A. Baiker, J. Kijenski, *Catal. Rev. Sci. Eng.* **1985**, *27*, 653.

76. (a) G. Henrici-Olive, S. Olive, *J. Mol. Catal.* **1978**, *4*, 379; (b) G. A. Kliger, L. S. Glebov, T. P. Popova, E. V. Marchevskaya, V. G. Beryezkin, S. M. Loktev, *J. Catal.* **1988**, *111*, 418.

77. O. Krocher, R. A. Kijppel, A. Baiker, *J. Chem. Soc., Chem. Commun.* **1996**, 1497.

78. S. V. Gredig, R. A. Koeppel, A. Baiker, *Catal. Today* **1996**, *29*, 339.

79. S. V. Gredig, R. A. Koeppel, A. Barker, *Appl. Catal. A* **1997**, *162*, 249.

80. S. V. Gredig, R. Maurer, R. A. Koeppel, A. Baiker, *J. Mol. Catal. A: Chemical* **1997**, *127*, 133.

81. S. M. Auer, S. V. Gredig, R. A. Koeppel, A. Baiker, *J. Mol. Catal. A: Chemical* **1999**, *141*, 193.

82. O. Kröcher, R. A. Köppel, M. Fröba, A. Baiker, *J. Catal.* **1998**, *178*, 284.

83. R. Srivastava, M. D. Manju, D. Srinivas, P. Ratnasamy, *Catal. Lett.* **2004**, *97*, 41.

84. (a) I. Vauthey, F. Valot, C. Gozzi, F. Fache, M. Lamaire, *Tetrahedron Lett.* **2000**, *41*, 6347; (b) F. Shi, Y. Deng, *J. Catal.* **2002**, *211*, 548; (c) A. Wolf, F. Schüth, *Appl. Catal. A: Gen.* **2002**, *226*, 1.

85. T. Tsuda, S. Morikawa, N. Haseguwa, *J. Org. Chem.* **1990**, *55*, 2978.

86. Y. Sasaki, Y. Inou, *J. Chem. Soc., Chem. Commun.* **1976**, 605.

87. A. L. Lapidus, S. D. Pirozhkov, A. A. Koryakin, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1978**, 2513.

88. Y. Inoue, T. Hibi, M. Satake, H. Hashimoto, *J. Chem. Soc., Chem. Commun.* **1979**, 982.