Chapter 2
Direct Transformation of Carbon Dioxide to Value-Added Products over Heterogeneous Catalysts

Shin-ichiro Fujita, Masahiko Arai, and Bhalchandra M. Bhanage

2.1 Introduction

Carbon dioxide (CO_2) is one of the greenhouse gases arising from human activities, and hence its accumulation in the atmosphere should be controlled by removing it from industrial emissions to avoid global warming. Thus, large amounts of CO_2 would be available [1–4]. On the other hand, CO_2 is recognized to be an abundant, cheap, recyclable, and nontoxic carbon source that can sometimes replace toxic chemicals such as phosgene, isocyanates, or carbon monoxide [2, 5–9]. It has been considered that utilization of CO_2 is more attractive rather than storage, if economical processes are available. Under these circumstances, chemical fixation of CO_2 into valuable chemicals is still gaining considerable interest.

Heterogeneous catalysts are widely used in industries because of their advantages in the separation and recycling and their applicability for flow reaction systems. Unfortunately, conventional heterogeneous catalysts are sometimes less active and/or selective in comparison to such homogeneous ones as metal complexes and organic bases including ionic liquids. A class of heterogeneous catalysts can be built of those homogeneous ones immobilized on solids of metal oxides or polymers. These immobilized catalysts can have not only high activity and/or selectivity but also the advantages in the catalyst separation, enabling more efficient and economical reaction processes.

During the last two decades, a variety of catalysts have been employed for the chemical fixation of CO_2. In this chapter, the utilization of heterogeneous catalysts for

S.-i. Fujita (✉) • M. Arai
Division of Chemical Process Engineering, Faculty of Engineering,
Hokkaido University, Sapporo 060-8628, Japan
e-mail: sfuji@eng.hokudai.ac.jp; marai@eng.hokudai.ac

B.M. Bhanage
Department of Chemistry, Institute of Chemical Technology,
Mumbai 400019, India
e-mail: bhanage@ictmumbai.edu.in

the synthesis of cyclic carbonate from CO_2 and epoxides and of dimethyl carbonate (DMC) from CO_2 and methanol has been reviewed. The catalysts described will include immobilized organic base catalysts as well as conventional inorganic solid catalysts of metal oxides, clays, and zeolites. A few related reactions will also be described.

## 2.2 Synthesis of Cyclic Carbonate via Cycloaddition of CO_2 to Epoxide

2.2.1 Use of Inorganic Catalysts for CO_2 Cycloaddition

The five-member cyclic carbonates have several applications [6–8]; e.g., ethylene carbonate is an excellent solvent for many polymers and resins. Another important application includes the use as an intermediate for the manufacture of several important chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, purines, etc. These five-member cyclic carbonates were conventionally produced via a corrosive, poisonous, and hazardous route involving glycol and phosgene. Then manufacturers shifted to the production based on the cycloaddition of CO_2 to epoxide (Scheme 2.1) in the presence of base catalysts.

Yano et al. first reported the use of a metal oxide catalyst for the reaction of CO_2 and epoxide. They showed that a commercial MgO could catalyze the reactions of CO_2 with propylene oxide (PO) and styrene oxide (SO) to give cyclic carbonates [10]. It gave 60 % and 41 % yields of styrene carbonate (SC) and propylene carbonate (PC), respectively, at 135 °C and 2 MPa of CO_2 for 12 h in a solvent of dimethylformamide (DMF). CO_2 pressure showed no effect on the carbonate yield in a region between 0.2 and 2.8 MPa. When a chiral epoxide was used as the substrate, interestingly, the chirality was retained in the cyclic carbonate product.

Yamaguchi et al. used Mg–Al mixed oxides prepared from hydrotalcite for the reactions of CO_2 with several epoxides [11]. Corresponding cyclic carbonates were obtained with excellent yields at 100–120 °C and 0.5 MPa of CO_2 for 15–24 h in DMF. The Mg/Al ratio of the mixed oxide was significant for its catalytic activity, and the best value was 5. Based on the catalyst characterization results, the authors proposed that the O and Al atoms involved in Mg–O–Al bonds act as basic and acidic sites, respectively, and they cooperatively activate an epoxide molecule.

Scheme 2.1 Synthesis of cyclic carbonate via cycloaddition of CO_2 to epoxide. Abbreviations for a few representative substrates and products are also given
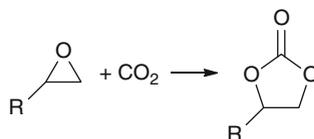

R = H (EO: ethylene oxide, EC: ethylene carbonate)
CH$_3$ (PO: propylene oxide, PC: propylene carbonate)
C$_6$H$_5$ (SO: styrene oxide, SC: styrene carbonate)

No use of organic solvent makes the reaction system more preferable. A few groups have reported the CO_2 cycloaddition reactions under such conditions. Bhanage et al. employed several metal oxide catalysts of MgO, CaO, ZnO, Zr_2O, La_2O_3, CeO_2, and Al_2O_3 for the reaction of CO_2 and propylene oxide (PO) to propylene carbonate (PC) [12]. MgO was found to be the best among the metal oxides examined. It gave a PC yield of 32 % with a PC selectivity of 92 % at 150 °C and 8 MPa of CO_2 for 15 h. Although a higher PC yield of 54 % was obtained with La_2O_3, the PC selectivity was lower (75 %). Basic properties of these catalysts were investigated by temperature programmed desorption (TPD) of adsorbed CO_2. It was suggested that both moderately and strongly basic sites are active sites for the reaction, and MgO has a large amount of moderately basic sites, resulting in its high activity and selectivity. The reaction of CO_2 and styrene oxide (SO) to styrene carbonate (SC) was also examined with MgO. For this reaction, MgO gave a poor product yield (16 %) because of low selectivity.

Tu and Davis prepared cesium-loaded zeolite X (Cs/KX) catalysts and used them for the synthesis of ethylene carbonate (EC) from CO_2 and ethylene oxide (EO) [13]. The activity of the zeolite catalyst was slightly lower than MgO, but the former catalyst was much more tolerant of water moisture than the latter one. Wet Cs/KX selectively produced EC, while wet MgO mostly produced mono-, di-, and triethylene glycol, which were formed by hydrolysis of EO and following dehydration reactions. Interestingly, the wet Cs/KX afforded a much higher EC yield than dry Cs/KX, although the reason was unknown.

Smectite is one of the layered clay minerals, and its acidic and basic properties are tunable [14]. Fujita et al. developed new types of catalysts based on Mg- and/or Ni-containing smectite catalysts, in which various amounts of alkali metals such as Na, K, and Li are incorporated [15, 16]. These catalysts were highly active and selective for PC synthesis from CO_2 and PO without organic solvent. The catalytic activity strongly depends on the amount of alkali atoms incorporated. The most active smectite catalyst gave a PC yield of 81 % with a PC selectivity of 94 % at 150 °C and 8 MPa of CO_2 for 15 h. The turnover number obtained with the most active smectite catalyst was about five times of that obtained with MgO, which was considered to be the best catalyst among the conventional metal oxide catalysts tested, as stated above. TPD of adsorbed CO_2 suggested that the smectite catalysts had large amounts of strongly basic sites, resulting in their high activities. They also studied in detail the optimization of the reaction conditions for this reaction [16]. The CO_2 pressure does not significantly affect the conversion and the selectivity in the region between 3 and 10 MPa; however, both the conversion and the selectivity decrease sharply at 15 MPa. It is highly probable that the reaction system consists of three phases: CO_2–liquid–solid at the lower pressures, while it should be in a homogeneous phase at 15 MPa. Such a phase change would cause an increase in the volume at the location where the reaction proceeds. Hence, the concentration of the catalyst and/or PO would be low at 15 MPa, resulting in low PO conversion at this elevated pressure. The effect of reaction temperature on the reaction of PO and CO_2 was investigated. The PO conversion was found to increase with the temperature, as expected; however, the selectivity decreased at 170 °C and thus the optimum reaction temperature was 150 °C.
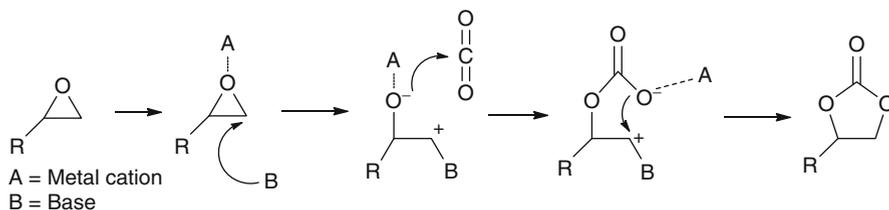
Scheme 2.2 A generally accepted reaction mechanism for CO_2 cycloaddition to epoxide catalyzed by acid-base bi-functional systems

As mentioned above, MgO gave a reasonable SC yield from CO_2 and SO at 135 °C in the presence of DMF; however, it gave a poor SC yield even at 150 °C in the absence of DMF, suggesting positive effects of DMF on the reaction. Yasuda et al. carried out the PC synthesis with MgO, Mg–Al mixed oxide, or SmOCl in the presence and absence of DMF and showed that the presence of DMF enhanced the PC yield twice or more irrespective of the catalyst used [17]. Similar results were also reported for the cyclic carbonate synthesis using Nb_2O_3 and DMF and using titanosilicate and 4-(dimethylamino)pyridine (DMAP) [18, 19]. Furthermore, Mori et al. reported that, when even a catalytic amount of DMAP was combined with zinc-based hydroxyapatite (ZnHAP), a good SC yield of 79 % was obtained at 100 °C and 0.5 MPa of CO_2 for 20 h, although ZnHAP had no activity and the activity of DMAP was very low [20]. Thus, it is highly probable that the occurrence of the synergetic effect is common in the bifunctional catalyst systems consisting of inorganic metal compounds and organic bases. A general reaction mechanism for those bifunctional catalyst systems can be drawn as Scheme 2.2. The Lewis acidic center of metal cation would interact with the oxygen atom of the epoxide, and the base would attack the less hindered carbon atom of the epoxide ring. Such cooperative activation of the epoxide should make the ring opening easier, being the reason for the promotional effects of the base. It is also possible that base activates a CO_2 molecule. In the absence of organic bases, the oxygen atoms on the metal oxide surface would act as Lewis base, but it would be less effective than the organic base.

2.2.2 Use of Immobilized Organic Base Catalysts for CO_2 Cycloaddition

It is well known that organic bases of amines, ammonium salts, phosphonium salts, imidazolium salts, etc., can be homogeneous catalysts for the cyclic carbonate synthesis via CO_2 cycloaddition to epoxides [7, 8, 21, 22]. Several groups examined the immobilization of those catalysts onto a solid support to facilitate the catalyst separation from the products. In this subsection, some representative examples of the CO_2 cycloaddition reactions using such immobilized catalysts are described.
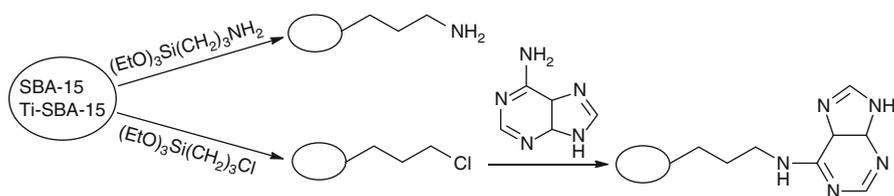
Scheme 2.3 Immobilization of propylamine and adenine on SBA-15 or Ti-SBA-15

To synthesize zeolites, tetraalkyl ammonium salts are used as the template. Srivastava et al. reported that as-synthesized zeolite-beta, which contained the template of tetramethylammonium bromide, could produce a few types of cyclic carbonates via CO_2 cycloaddition with very high yields at 120 °C and 0.7 MPa of CO_2 for 3–8 h without any solvent [23]. The catalyst could be recycled eight times with little loss in activity. The turnover frequency (TOF) value based on the amount of the ammonium template contained was almost the same with that of homogeneously used ammonium bromide. However, the authors pointed out that over the as-synthesized zeolite-beta, the reaction takes place only at the surface, and therefore, the ammonium molecules in the inside part of the zeolite are not accessible for the reaction. Thus, it is highly probable that the actual TOF of the solid catalyst is much higher than the observed one. This may be explained by the presence of surface silanol group as described below.

The same group also reported the covalent immobilization of organic amines (propylamine, adenine) on mesoporous materials of SBA-15 and Ti-SBA-15 by using silane coupling reagents (Scheme 2.3) [24]. The catalytic activity of the immobilized catalyst for CO_2 cycloaddition increased with the Ti content. FTIR spectra of the catalysts measured under several conditions suggested the activation of CO_2 on the base sites, because the cyclic carbonate yield was well correlated with the peak intensity of surface carbamate species. The authors proposed that the coexistence of epoxide activated on Ti sites and CO_2 activated on base sites is significant for the reaction. Recycling of adenine-modified Ti-SBA-15 was tested. In the absence of any organic solvent, the activity gradually decreased with recycling, while such deactivation was much less in the presence of acetonitrile solvent. When the deactivated catalyst was washed with organic solvents, the initial activity was almost restored. It was also confirmed that some heavy carbonaceous products accumulated on the catalyst surface, resulting in the deactivation. So, at least for this catalyst, the use of organic solvent is required.

The advantage of immobilizing homogeneous catalysts on solid materials is not only the easier separation of the catalyst but also the usability of it for the continuous operation using a fixed-bed flow reactor. Takahashi et al. first reported the use of silica-immobilized tetraalkyl phosphonium bromide for a flow reactor [25]. The phosphonium bromide was immobilized on silica in a similar way to Scheme 2.3. They carried out the PC synthesis using 10 MPa of CO_2 for more than 1,000 h. Unfortunately, the reaction temperature was required to be increased from the initial one of 90–160 °C for keeping the yield above 80 %, suggesting that some

Scheme 2.4 Cooperative
activation of an epoxide
molecule on silica-
immobilized phosphonium
halides
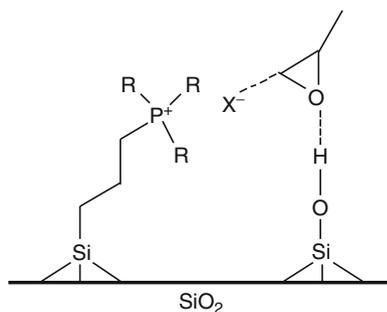
leaching of the phosphonium bromide from the support might occur; however, the
selectivity to PC was kept over 99.9 % during the whole of the reaction run. In the
same paper [25], they reported interesting synergistic effects of the immobilization
of phosphonium halides on silica. They also carried out the reaction runs in a batch
reactor and showed that the TOF of the immobilized phosphonium halides was
more than 300 times larger compared to that of corresponding phosphonium halides
that were used homogeneously. However, such enhancement in the activity was not
observed by the immobilization on polystyrene. The surprising enhancement of the
activity by supporting on silica was ascribed to the cooperational activation of the
epoxide by the acidic surface silanol groups and the halide anion of the immobilized
phosphonium salts (Scheme 2.4). The most active immobilized catalyst could
almost quantitatively convert PO to PC at 100 °C and 10 MPa of CO_2 for a short
reaction time of 1 h.

The acidity of the OH group on the solid surface was also suggested to affect the
activity of immobilized onium halide catalysts. Sakai et al. prepared immobilized
phosphonium halide catalysts using silica, aluminosilicate, and basic alumina as the
support materials [26]. The activity for the CO_2 cycloaddition to epoxyhexane was
in the order of silica > aluminosilicate > basic alumina, which is the same order as
that of the acidity of the OH group on the support surface, and hence they ascribed
the differences in the activity among the catalysts to those in the acidity of the OH
group of the supports. This also supports the cooperative activation mechanism
shown in Scheme 2.4. The enhancement of the activity by the immobilization
was also observed with imidazolium and aminopyridinium halides [27, 28]. Thus,
the synergistic effects of the immobilization on inorganic materials having surface
hydroxyl groups are common. Over the immobilized catalysts, the mean pore
size, the total pore volume, and the amount of surface hydroxyl groups were
also found to be important factors determining the catalyst performance for CO_2
cycloaddition [26, 29].

Zinc tetrahalide onium salts prepared from zinc halide and onium halide were
found to be excellent catalysts for the CO_2 cycloaddition [30–32]. They could give
high cyclic carbonate yields under very mild conditions. This is ascribed to
the cooperational activation of epoxide ring by Lewis acidic Zn center and basic
halide anion, which is similar to Scheme 2.2. Qiao et al. applied this strategy for

Scheme 2.5 Activation of an epoxide molecule by polystyrene-supported diol-functionalized imidazolium halide
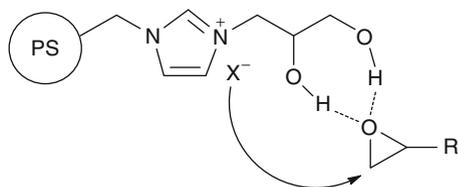
polymer-immobilized imidazolium catalysts [33]. They immobilized imidazolium on polystyrene by copolymerization of 1-vinyl-3-butylimidazolium salts and styrene and further treated the copolymers with zinc halides. The resulting immobilized catalysts could show high TOF values up to about 3,800 h^{-1} at 120 °C. This TOF value was comparable to those obtained with very active homogeneous catalyst systems reported so far.

Very recently, Watile et al. developed diol-functionalized imidazolium halide immobilized on polystyrene (PS) as the catalyst for the CO_2 cycloaddition and showed that the diol-functionalization is more effective for the reaction than the mono hydroxyl-functionalization [34]. The PC yield obtained with 1-(2,3-di-hydroxyl-propyl)-imidazolium bromide was higher than that with a corresponding mono hydroxyl-functionalized imidazolium halide of 1-(2-hydroxyl-ethyl)-imidazolium bromide. It was proposed that the epoxide is activated by chelate-type hydrogen bonding of its O atom with the vicinal two hydroxyl groups of the functionalized imidazolium halide (Scheme 2.5).

Recent advance in the preparation of microporous materials is the development of zeolitic imidazole frameworks (ZIFs), in which metal atoms such as Zn are linked through N atoms by ditropic imidazolate to form neutral frameworks [35, 36]. ZIFs have uniform micropores, high surface areas, and open porous framework structures, making them interesting materials for adsorption and catalytic applications. The co-presence of the Lewis acidic Zn center and the N basic moieties in ZIF would make ZIF a candidate of the catalyst for the CO_2 cycloaddition reaction. Recently, Miralda et al. prepared non-functionalized and ethylene diamine-functionalized ZIF-8 (one kind of ZIF) catalysts and used them for the CO_2 cycloaddition to epichlorohydrin [37]. The nonfunctionalized ZIF-8 produced chloropropylene carbonate with a 44 % yield at 80 °C and 0.7 MPa of CO_2 for 4 h; however, the selectivity to cyclic carbonate was 52 %. By-products were a diol (24 % selectivity) and a dimer of the substrate (24 % selectivity). At a higher temperature of 100 °C, the conversion was increased, but the carbonate yield was decreased because of the increase in the dimer formation. The functionalization of ZIF-8 with amine improved both the yield of and the selectivity to the carbonate (73 % and 73 %), and the formation of the dimer was ceased. Unfortunately, the catalytic properties of both nonfunctionalized and functionalized ZIF-8 catalysts were unstable. They lost about half of their initial activities after the first recycling. This was ascribed to the accumulation of carbonaceous materials on the catalysts. Furthermore, after the second recycling, the zeolitic structures of both two catalysts were destroyed. The authors examined ZIF-8 for only the

substrate of epichlorohydrin. It is not clear at present whether the deactivation occurs with other epoxides. The loss of their structural features was proposed to result from the co-presence of CO_2 at high pressure and the carbonaceous materials. ZIFs are a new class of porous materials on which the number of studies is limited. Further studies on them may improve their catalytic performance and stability.
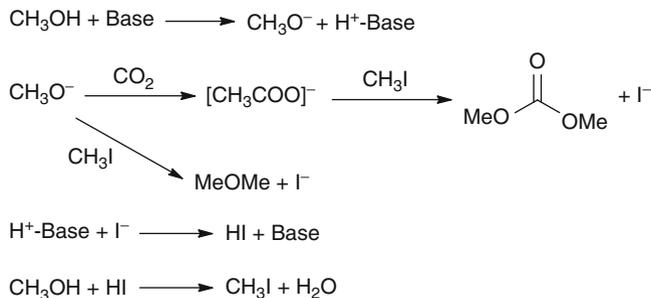
2.3   Synthesis of Dimethyl Carbonate from CO_2 and Methanol

Dimethyl carbonate (DMC) finds such applications as a solvent, an octane enhancer, and a reagent for carbonylation and methylation, replacing poisonous phosgene and dimethyl sulfate [5, 9, 38]. In addition, DMC is a precursor for polycarbonate resins, which have been commercially produced by polycondensation between bisphenol-A and phosgene. Thus, DMC can be regarded as a safe replacement for phosgene. Currently, DMC is synthesized by phosgenation of methanol, by oxidative carbonylation of methanol (non-phosgene route), or by a reaction of carbon monoxide with methyl nitrite. Methyl nitrite is produced from methanol, oxygen, and nitric oxide. These routes use poisonous and/or corrosive gases such as phosgene, hydrogen chloride, nitric oxide, and carbon monoxide and also bear potential explosion hazards in the case of methanol carbonylation. Hence, the direct synthesis of DMC from CO_2 and methanol (Scheme 2.6) is an attractive alternative and, hence, one of the promising reactions for the chemical fixation of CO_2.

Fang and Fujimoto [39] reported that various inorganic bases catalyze the direct DMC synthesis in the presence of methyl iodide as a promoter. Among the base catalysts examined, potassium carbonate was the most effective. Although the yield of DMC obtained with this catalyst was higher than those with organometallic complexes, the range of reaction conditions used was quite limited. Fujita et al. studied the influence of reaction conditions and the reaction mechanism in detail [40]. It was found that two maxima in the DMC formation appear at CO_2 pressures of 4.5 and 8 MPa, while the formation of a by-product, dimethyl ether (DME), decreased monotonically with increasing CO_2 pressure. DMC formation increased almost linearly with the amount of either methyl iodide or potassium carbonate when their concentrations were low. Mechanistic studies suggested that DMC and DME are produced in parallel pathways and methyl iodide is involved in both the formation of DMC and DME, as illustrated in Scheme 2.7. The catalyst was deactivated in the course of the reaction and methyl iodide was essentially a reactant rather than a promoter for the reaction. This is likely because the

Scheme 2.6 Synthesis of DMC from CO_2 and methanol

$$2CH_3OH + CO_2 \longrightarrow \underset{MeO \quad\quad OMe}{\overset{O}{\parallel}}{C} + H_2O$$

$$CH_3OH + Base \longrightarrow CH_3O^- + H^+\text{-}Base$$

$$CH_3O^- \xrightarrow{\ CO_2\ } [CH_3COO^-] \xrightarrow{\ CH_3I\ } \underset{MeO \qquad OMe}{\overset{O}{\parallel}} + I^-$$

$$CH_3O^- \xrightarrow{\ CH_3I\ } MeOMe + I^-$$

$$H^+\text{-}Base + I^- \longrightarrow HI + Base$$

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$

Scheme 2.7 Reaction mechanism of DMC synthesis in the presence of base and CH_3I

regeneration of methyl iodide from methanol and HI produced is difficult under the present reaction conditions. The residual HI instead reacted with potassium carbonate as confirmed by IR spectroscopy.

The direct DMC synthesis using solid catalysts in the absence of methyl iodide was also reported. Tomishige et al. found that ZrO_2 and CeO_2–ZrO_2 mixed oxide catalysts were selective for the direct DMC synthesis reaction under such conditions [41–43]. CeO_2–ZrO_2 mixed oxides were more active than pure ZrO_2. Based on temperature programmed desorption of NH_3 and CO_2, they proposed that acid–base pairs are active sites for the reaction. Jung and Bell also drew the same conclusion from IR measurements of the surface species formed on ZrO_2 [44, 45]. It was also reported that the enhancement in the acidity of ZrO_2 by supporting phosphoric or tungstophosphoric acid significantly improved the catalytic activity [46, 47]. Thus, several ZrO_2-based catalysts were disclosed; however, the DMC yields obtained were far from satisfactory because of the reaction equilibrium limitation. Lately, Tomishige and Kunimori [48] showed that the DMC yield can be improved by using dimethyl acetal (DMP) as a dehydration reagent. Hence, removal of H_2O from the reaction system is significant to get DMC in high yields; however, the amount of DMP added should be controlled. With too much DMP, the DMC formation decreased and the formation of undesirable by-product dimethyl ether increased. It was also shown that diethyl carbonate could be synthesized from ethanol and CO_2, although its yield was lower than that of DMC.

An analogous reaction to the DMC synthesis from CO_2 and methanol is diphenyl carbonate (DPC) synthesis from CO_2 and phenol. DPC is an important precursor of aromatic polycarbonate. It is conventionally synthesized from phosgene and phenol. Also for the synthesis of DPC, the replacement of phosgene with CO_2 is significant. Although it has been known that Lewis acid compounds of zinc halides can catalyze this reaction with or without base in a solvent of CCl_4, the use of CCl_4 is essential for the reaction, because CCl_4 is considered to be transformed to phosgene in the reaction system [49–51]. One can say that those systems are the reaction using in situ generated phosgene. Furthermore, the use of toxic CCl_4 should be avoided. Li and Su tried the reaction using ZrO_2 without any solvent at an elevated temperature and CO_2 pressure [52]. Unfortunately, the catalyst could

produce no DPC. Products observed were hydroxybenzyl phenol, diphenyl ether, and other compounds. For the DPC synthesis, further development of the catalyst is required. It may be a key issue how effectively to create a new bond between the carbon atom of CO_2 and the O atom of phenol.

2.4 Other Reactions for Transformation of CO_2

In the foregoing sections, the utilization of heterogeneous catalysts for the cyclic carbonate synthesis from CO_2 and epoxide and for the DMC synthesis from CO_2 and methanol was reviewed. In this section, a few related reactions in the presence of heterogeneous catalysts have been described.

Tomishige et al. examined the reaction of CO_2 and glycol to produce cyclic carbonate with CeO_2–ZrO_2 mixed oxide catalysts (Scheme 2.8) [53]. This is another route to synthesize cyclic carbonate from CO_2. Using the substrates of glycols cheaper than epoxides is of benefit. They optimized the catalyst composition (Ce/Zr ratio) and the calcination condition. Even after the optimization, however, the carbonate yields obtained were very low because of the reaction equilibrium limitation. Removal of H_2O from the reaction system would be essential to obtain high yields of the carbonate, similar to the cases of direct DMC synthesis from CO_2 and methanol.

Carbamates are another important class of organic compounds that meet a variety of applications for the production of polyurethanes, pesticides, fungicides, and medicinal drugs. They are commercially produced with the use of toxic phosgene. Another route producing carbamate is the reaction of primary amine, CO_2, and alkyl halide (Scheme 2.9). It is a benign way to synthesize carbamate avoiding the use of toxic phosgene, isocyanate, and CO. Srivastava et al. who used as-synthesized zeolite and amine-modified SBA-15 and Ti-SBA-15 for the CO_2 cycloaddition as described in Sect. 2.2.2, also examined the same catalysts for the carbamate synthesis [23, 24]. From various aliphatic and aromatic amines, their carbamates were produced with high selectivity under mild conditions (at 80 °C and 0.34 MPa of CO_2) in the absence of solvent. FTIR spectra of the catalysts measured again revealed that the product yield was well correlated with the peak intensity of

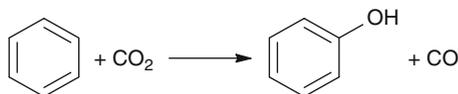**Scheme 2.8** Synthesis of cyclic carbonate from CO_2 and glycol
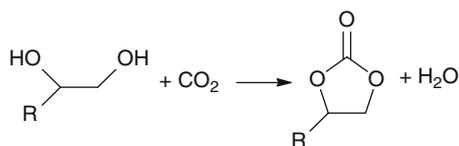
Scheme 2.9 Synthesis of carbamate from primary amine, CO_2, and alkyl halide
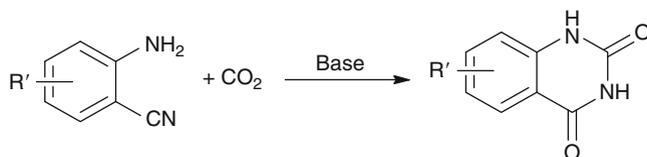
Scheme 2.10 Synthesis of quinazoline-2,4(1*H*,3*H*)-diones from CO_2 and 2-aminobenzonitriles

Scheme 2.11 Oxidation of benzene to phenol with CO_2

surface carbamate species. The coexistence of Ti sites and base sites was again suggested to be significant for the reaction. Adenine-modified Ti-SBA-15, which was deactivated by recycling in the absence of solvent, could be recycled for the carbamate synthesis without loss of activity even in the absence of solvent. These catalysts would be of promise for realizing carbamate synthesis processes from CO_2 using solid catalysts.

The reactions of CO_2 and aminobenzonitriles produce rather complex compounds of quinazoline-2,4(1H,3H)-diones (Scheme 2.10), which are important because of their biological activity and widely used as key structures in medical drugs. Patil et al. employed a series of MgO/ZrO_2 catalysts for this reaction [54]. When 2-aminobenzonitrile was used as the substrate, pure MgO and ZrO_2 gave the product yields of 44 % and 18 %, respectively, at 130 °C and 3.5 MPa of CO_2 (at room temperature) for 12 h in DMF solvent. MgO/ZrO_2 catalysts (MgO loading 5–15 %) gave higher product yields and an almost quantitative yield was obtained with 10 % MgO/ZrO_2. MgO/SiO_2 showed lower activity. FTIR of the catalysts and CO_2 TPD measurements suggested some interaction between MgO and ZrO_2. The most active catalyst gave good to excellent product yields from a broad range of aminobenzonitriles. The selection of the solvent was significant. The product yield obtained with DMSO was almost the same with DMF, while other polar and nonpolar solvents were ineffective (0–10 % yields). The catalyst was recyclable without loss of activity. The same group also reported the use of inorganic base of Cs_2CO_3 and of organic one of 1-butyl-3-methyl imidazolium hydroxide [55, 56]. The catalytic performance of the best MgO/ZrO_2 catalyst was comparable with those bases.

In all the above-mentioned reactions, CO_2 was used as the source of carbonyl group. CO_2 can be an oxidant for the direct synthesis of phenol from benzene (Scheme 2.11). Goettmann et al. first reported that graphitic carbon nitride C_3N_4 can catalyze this reaction in the co-presence of organic bases [57]. Lately, Ansari et al. studied the influence of starting compounds to prepare C_3N_4 on the activity [58]. In these studies, a high reaction temperature (150 °C) and long reaction time (10–20 h) were required to get reasonable product yields. So, further improvement of the catalyst activity is still required to synthesize phenol in large scales.

The by-product of CO can be used for other synthetic reactions, being an advantage of this reaction. Furthermore, the current industrial phenol manufacturing processes (the cumene process) suffer from the formation of large amounts of acetone as a by-product. Considering these, the oxidation of benzene with CO_2 would be a new and highly desirable route for utilization of CO_2.

2.5 Concluding Remarks

This chapter has reviewed the utilization of heterogeneous catalysts for the transformation of CO_2 to valuable chemicals. The reactions described are the CO_2 cycloaddition to epoxide producing cyclic carbonate (Scheme 2.1), the synthesis of DMC from CO_2 and methanol (Scheme 2.6), and other several related reactions (Schemes 2.8, 2.9, 2.10, and 2.11). These reactions are benign synthesis ways to avoid the use of toxic chemicals of phosgene, CO, isocyanate, etc.

Inorganic heterogeneous catalysts of a few metal oxides, an alkali-loaded zeolite, and smectites are effective for the CO_2 cycloaddition in the absence of any organic solvent. Furthermore, their activities are enhanced by the co-presence of basic organic solvents. This enhancement is ascribed to the cooperative activation of the epoxide ring by the metal center and the base (Scheme 2.2). Synergistic effect is observed on immobilization of organic bases including imidazolium halides on inorganic solids having surface hydroxyl groups. This is also explained by a similar cooperative activation mechanism (Scheme 2.4). Highly active heterogeneous bifunctional catalyst systems can also be realized by modification (treatment with zinc halide or substituting with alkyl diol) of imidazolium halides immobilized on polymers (Scheme 2.5). One of ZIFs, which are a new class of porous materials, can be used for the CO_2 cycloaddition.

DMC can be produced from CO_2 and methanol in the presence of potassium carbonate as a catalyst and methyl iodide as a promoter; however, the catalyst is deactivated by transformation to potassium iodide, and methyl iodide acts as a reactant rather than a promoter (Scheme 2.6). Even in the absence of methyl iodide, ZrO_2-based catalysts can selectively catalyze the DMC synthesis, and the removal of H_2O from the reaction system is essential to get high DMC yields because of the reaction equilibrium limitation.

For the cyclic carbonate synthesis from CO_2 and glycol, CeO_2–ZrO_2 is selective, but it can give only low product yields because of the reaction equilibrium limitation. Organic bases (tetraalkyl ammonium halides, adenine) immobilized on zeolite or Ti-SBA-15 can give excellent product yields for the synthesis of carbamates from CO_2, primary amines, and alkyl halides. Also for this reaction, the coexistence of acid Ti sites and base sites is suggested to be an important factor. MgO/ZrO_2 is effective for the synthesis of quinazoline-2,4(1H,3H)-diones from CO_2 and aminobenzonitriles. Graphitic carbon nitride can catalyze the oxidation of benzene to phenol with CO_2 that would be a new and highly desirable route for the utilization of CO_2.

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