Chem. Rev. **2007,** *107,* 2365–2387

Transformation of Carbon Dioxide

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Received December 19, 2006

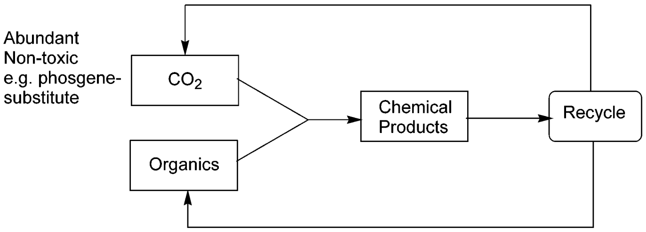
Contents

1. Introduction

Utilizing renewable resources is a prerequisite for a sustainable society. One easily available renewable carbon resource is carbon dioxide (CO_2), which has the advantages of being nontoxic, abundant, and economical (Scheme 1).[1−21] CO_2 is also attractive as an environmentally friendly chemical reagent and is especially useful as a phosgene substitute.

However, few industrial processes utilize CO_2 as a raw material. Because CO_2 is the most oxidized state of carbon, the biggest obstacle for establishing industrial processes based on CO_2 as a raw material is its low energy level. In other words, a large energy input is required to transform CO_2. There are four main methodologies to transform CO_2 into useful chemicals:

Scheme 1. CO_2 as a Green Carbon Resource



(i) To use high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds, and organometallics.

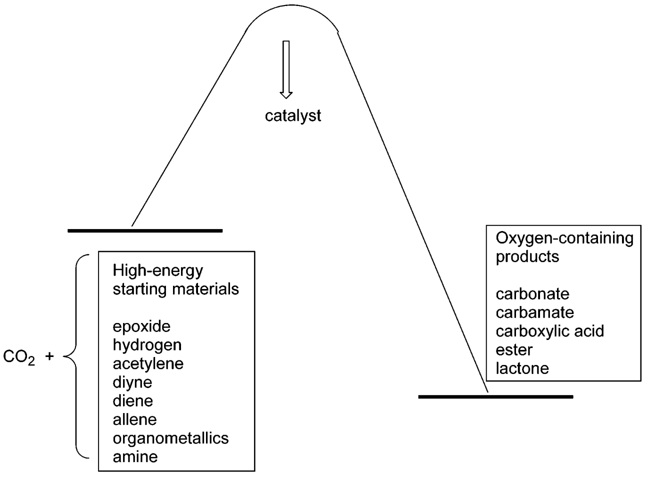
(ii) To choose oxidized low-energy synthetic targets such as organic carbonates.

(iii) To shift the equilibrium to the product side by removing a particular compound.

(iv) To supply physical energy such as light or electricity.

Selecting appropriate reactions can lead to a negative Gibbs free energy of the reaction (Scheme 2).

Scheme 2. Organic Synthesis Using CO_2



A lot of research has been conducted on reactions using CO_2 as a raw material, as shown in Scheme 3, e.g. CO_2 reductions under photoirradiation, or under electrolytic conditions, or production of synthesis gas by reforming natural gas with CO_2. However, many of these reactions produce rather simple molecules such as carbon monoxide and formic acid. This review article mainly address synthetic

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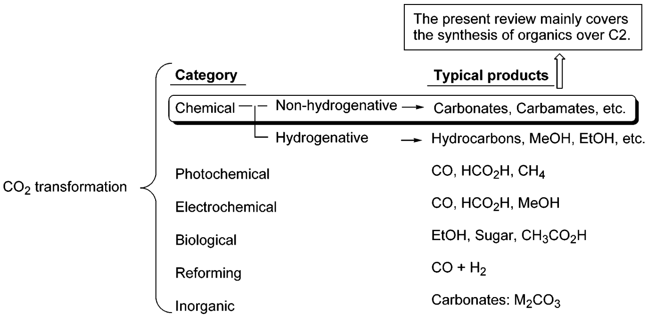
10.1021/cr068357u CCC: $65.00

Toshiyasu Sakakura received his B.S., M.S., and Ph.D. in Organic Chemistry from the University of Tokyo under the supervision of Professors T. Mukaiyama and K. Narasaka. He now is affiliated with the National Institute of Advanced Industrial Science and Technology (AIST), which is one of the largest national research institutes in Japan, and also has a position as a professor at the University of Tsukuba. He is author of about 100 patents and 100 scientific papers. Dr. Sakakura's research goal is the development of efficient synthetic reactions by homogeneous catalysis, especially utilization of fundamental molecules such as carbon dioxide, hydrocarbons, and water. He is also interested in combining homogeneous catalysis with photolysis, supercritical fluids, and microreactors. He received the CSJ Award for Young Chemists from the Japan Chemical Society for the catalytic C–H bond activation by the rhodium trimethylphosphine complex.

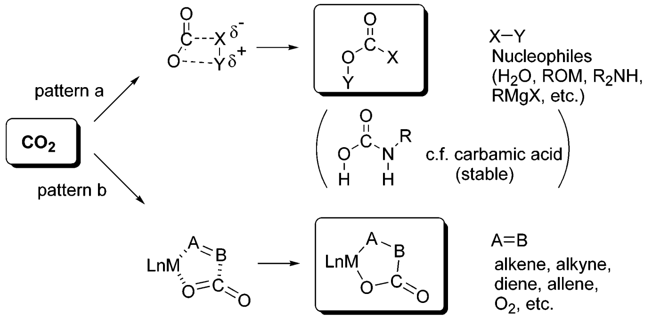
Jun-Chul Choi was born in 1968 in Korea and studied Chemistry at Kangnung University and obtained his M.Sc. degree in 1994. Then, he moved to Japan and received his Ph.D. in 1998 under the supervision of Professor Kohtaro Osakada at Tokyo Institute of Technology. He joined the research group of Professor Sakakura at the National Institute of Advanced Industrial Science and Technology (AIST) as a JST postdoctoral fellow in 1998. He currently holds a permanent position as a senior researcher in the same group at AIST. His research interest is focused on CO_2 conversion and C–H bond activation by metal complexes.

Hiroyuki Yasuda was born in 1964 in Tokyo, Japan. He received his Ph.D. in 1994 from the University of Tokyo under the supervision of Professor Makoto Misono. He began his research career at the National Institute of Materials and Chemical Research in AIST in 1995, and he joined the research group of Professor Sakakura in 2000. In 2001, he received the Noguchi Memorial Award for Encouragement of Research and Development from The Japan Petroleum Institute. He is presently a leader of the Molecular Catalysis Group at the Research Institute for Innovation in Sustainable Chemistry in AIST. His current research interests include development of chemical processes utilizing CO_2 and design of organic–inorganic hybrid catalysts.

Scheme 3. Scope of the Current Review



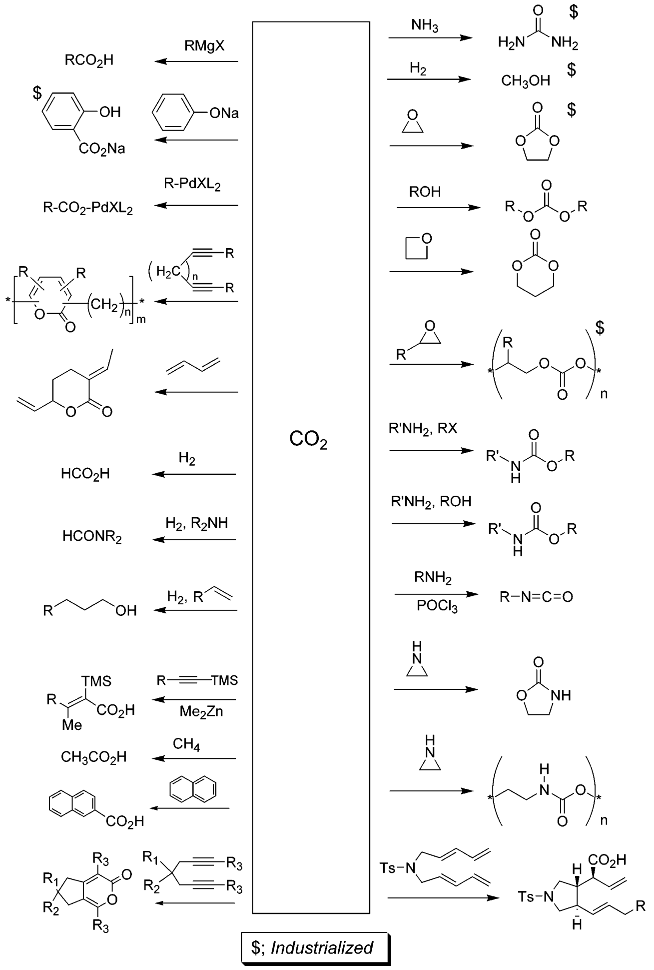
Scheme 4. Typical Transformations of Carbon Dioxide



technologies for organic compounds that contain equal to or more than three carbon atoms and use CO_2 as a raw material. Most of the references have been published after 1992.

A widely accepted idea is that CO_2 is so thermodynamically and kinetically stable that it is rarely used to its fullest potential. However, due to the electron deficiency of the carbonyl carbons, CO_2 has a strong affinity toward nucleophiles and electron-donating reagents. In other words, CO_2 is an "anhydrous carbonic acid", which rapidly reacts with basic compounds. For example, organometallic reagents such as Grignard reagents readily react with CO_2 even at a low temperature. Water, alkoxides, and amines also add to CO_2 in similar manners to produce compounds with a carboxyl or carboxylate group. These reactions conveniently produce carbonic and carbamic acids (Scheme 4). Further reactions of these species with electrophiles lead to the formation of organic carbonates and carbamates. On the other hand, reactions of low valent metal complexes (mainly nickel(0) and palladium(0)) with CO_2 and unsaturated compounds lead to the formation of five-membered metallalactones (Scheme 4).[22] Because the valence of the metal increases by two, this type of reaction is called an "oxidative cycloaddition". Hence, reactions involving CO_2 can be categorized into two patterns: (1) formation of a carboxyl group through nucleophilic attack (pattern a) and (2) generation of a five-membered ring through oxidative cycloaddition (pattern b) (Scheme 4).

Scheme 5. Transformations of Carbon Dioxide



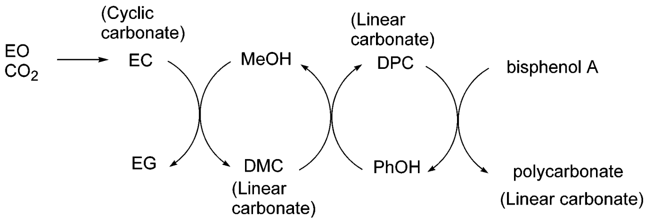
Scheme 5 summarizes examples of organic synthesis starting from CO_2. The outlook of each reaction utilizing CO_2 as a chemical reagent is discussed hereinafter.

2. Direct Synthesis of Dimethyl Carbonate from Methanol and CO_2

2.1. Outlines

Organic carbonates are roughly categorized into cyclic and linear carbonates.[23] Because both compounds have three oxygens in each molecule, they are relatively suitable from a thermodynamic point of view as synthetic targets starting from CO_2. Four industrially important organic carbonates are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diphenyl carbonate (DPC). EC, DMC, and DPC are useful intermediates for manufacturing polycarbonates through a non-phosgene process (Scheme 6).[24,25] In addition, EC, PC, and DMC are employed as electrolytes in lithium ion batteries and are widely used as aprotic polar solvents. Furthermore, the excellent properties of DMC as a fuel additive have attracted much attention.[25] Moreover, linear carbonates are important alkylating agents, as are alkyl halides or dialkyl sulfates, and carbonylating agents, as is phosgene or carbon monoxide.[10,26] This section illustrates synthetic methods of linear carbonates, especially dimethyl carbonate (DMC), starting from CO_2. It should be noted that cyclic carbonates can be easily synthesized by reacting CO_2 and epoxides, which is described in section 4.

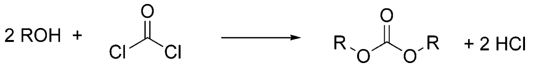
Scheme 6. Four-Step Process for Polycarbonate



Currently, the largest future application of organic carbonates is as a substitute for phosgene in the syntheses of polycarbonates[24] and polyurethanes.[27] Polycarbonates are the most extensively used engineering plastics, and the current annual production of polycarbonates amounts to two million tons worldwide. In addition, the amount produced increases between 5 and 10% annually. On the other hand, 80−90% of polycarbonates are currently being synthesized through the phosgene process; an interfacial polymerization of phosgene and bisphenol A using methylene chloride and water as the solvents.

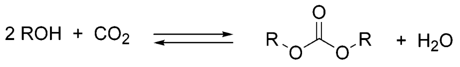
The major drawbacks of the phosgene processes (Scheme 7) are (i) the high toxicity of phosgene, which is controlled by the international treaty concerning chemical weapons, and (ii) the disposal of the coproduced hydrogen chloride. Moreover, substituting phosgene with CO_2 would drastically reduce environmental concerns (Scheme 8),[4,28] as the byproduct is merely water.

Scheme 7. Dialkyl Carbonate Synthesis with Phosgene



$$2\,ROH + Cl-C(=O)-Cl \longrightarrow R-O-C(=O)-O-R + 2\,HCl$$

Scheme 8. Dialkyl Carbonate Synthesis with CO_2



$$2\,ROH + CO_2 \rightleftharpoons R-O-C(=O)-O-R + H_2O$$

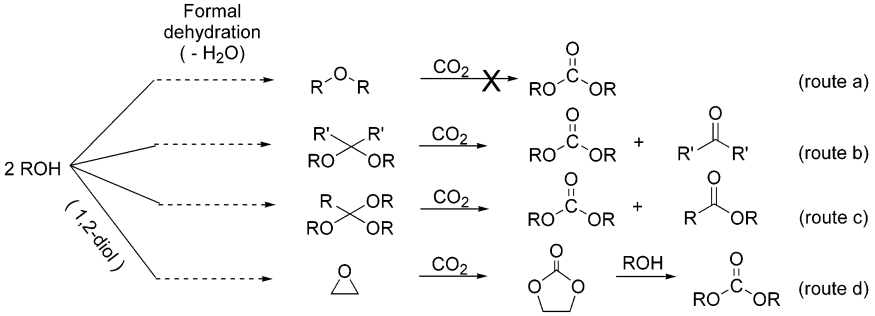
However, the equilibrium for forming linear carbonates from alcohols and CO_2 (Scheme 8) is located on the left-hand side of the equation (the starting materials side). In order to avoid this thermodynamic limitation, it is necessary to remove water from the right-hand side using an adequate drying agent or to increase the CO_2 concentration by pressurizing CO_2.

2.2. Organic Dehydrating Agents and Homogeneous Catalysts

Dehydration may be the most powerful methodology to shift the reaction depicted in Scheme 8 to the carbonate side. However, it is difficult to dehydrate a reaction mixture with a large amount of alcohol, such as methanol, at a high temperature under a high CO_2 pressure. Indeed, employing typical drying agents such as sodium sulfate, magnesium sulfate, dicyclohexyl carbodiimide, trimethyl phosphate, and molecular sieves has a negligible effect on the amount of product formed.[29−31] Although the synthesis of DMC by consuming an equimolar amount of a phosphorus-containing dehydrating agent has been reported, it is impractical from an industrial viewpoint.[32]

In order to avoid problems associated with dehydration, a new methodology where first water is removed from the alcohol and then the dehydrated derivatives of the alcohol react with CO_2 has been proposed (Scheme 9). In these cases, dehydrating the reaction mixture is unnecessary. Acyclic and

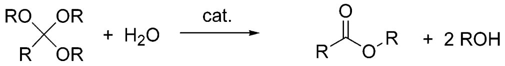
Scheme 9. Synthesis of Dialkyl Carbonate from CO_2



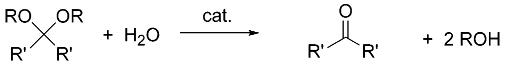
cyclic ethers, ketals, and orthoesters are potential substrates. [We have formally included orthoesters in the dehydrated derivatives of alcohols, but it is difficult to synthesize orthoesters by the dehydrative condensation of alcohols and esters.] The reactivity of the substrates increases in the order of route a to d in Scheme 9. For example, epoxides or cyclic ethers easily react with CO_2 to give five-membered ring carbonates such as ethylene carbonate in high yields (route d). Details of the reaction conditions, including catalysts, are discussed in section 4. On the other hand, linear ethers do not have ring strain and are much less reactive compared to epoxides. Although the CO_2 insertion to dimethyl ether has been reported, the details are unknown (route a).[33]

The dehydrating characteristics of orthoesters and ketals (Schemes 10 and 11) have been well examined for the dialkyl carbonate synthesis. If Schemes 8 and 10 are combined, then water can be canceled out, which yields a new equation that is independent of alcohol (route c, Scheme 9). Indeed, the reaction of orthoesters proceeds in the presence of a metal complex such as $Bu_2Sn(OMe)_2$ in high yields without adding alcohol.[34] However, the yields are highly dependent on the CO_2 pressure and reach a maximum around the critical pressure of CO_2. The reaction of orthoesters and CO_2 is also promoted by several types of catalysts, including alkali metal halides and immobilized ammonium salts.[35,36] The demerits of the orthoester method are obvious: (i) expensive starting material, (ii) coproduction of esters, and (iii) difficulty in regenerating orthoesters from esters.

Scheme 10. Dehydration by Orthoester



Scheme 11. Dehydration by Ketal



By combining Schemes 8 and 11, water can also be canceled out (route b, Scheme 9). Interestingly, the reaction between ketals and CO_2 does not proceed in the absence of alcohols.[37−39] The reaction of orthoesters and the reaction of ketals seem to have different mechanisms and show largely different properties, which are described in items (i) to (v).

(i) Alcohol: Orthoesters do not need alcohol to react with CO_2, but ketals absolutely must have it.

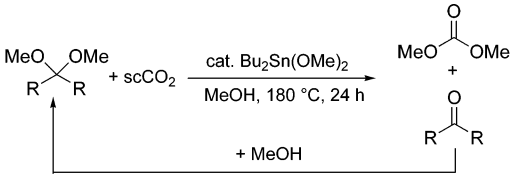
(ii) Pressure: Orthoesters have an optimal pressure to produce the highest carbonate yield, while higher pressure gives higher yields for the reaction of ketals.

(iii) Byproducts: The major byproduct in the orthoester reaction is dialkyl ethers, while the byproducts in the ketal reaction are enol ethers, and dialkyl ethers are not produced.

(iv) Catalyst: The addition of halides to tin alkoxides accelerates the orthoester reaction, but adding halides interferes with the ketal reactions.

(v) Recycling the dehydrating agents: Upon hydrolysis, orthoesters and ketals are converted to esters and ketones, respectively. Regeneration of ketals from ketones is easily achieved through a dehydrative condensation with alcohols (Scheme 12).[40] DMC production and dehydration are independently conducted at the different places.

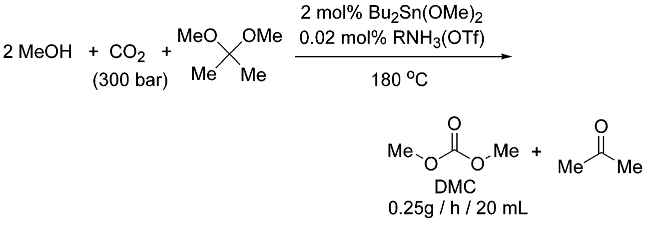
Scheme 12. Recycling of Ketal as a Dehydrating Agent



Because acetone appears to be the most convenient carbonyl compound for the ketal process with regards to cost and availability, 2,2-dimethoxypropane is a promising candidate for the ketal. However, a wide range of ketones such as cyclohexanone and diethyl ketone can also be used.

Among tin alkoxides [$Bu_nSn(OMe)_{4-n}$, $n = 0-3$], $Bu_2Sn(OMe)_2$ exhibits the best catalytic activity. Dibutyltin oxide [$(Bu_2SnO)_n$] also works as a convenient precursor of the active species because it is stable under air and is easier to handle than $Bu_2Sn(OMe)_2$. Moreover, adding a very small amount of an acidic cocatalyst greatly improves the productivity (STY) (Scheme 13).[41] It is hypothesized that the cocatalyst accelerates ketal hydrolysis (*vide infra*), but details of the reaction mechanism are unknown.

Scheme 13. DMC Synthesis with Dimethyl Ketal

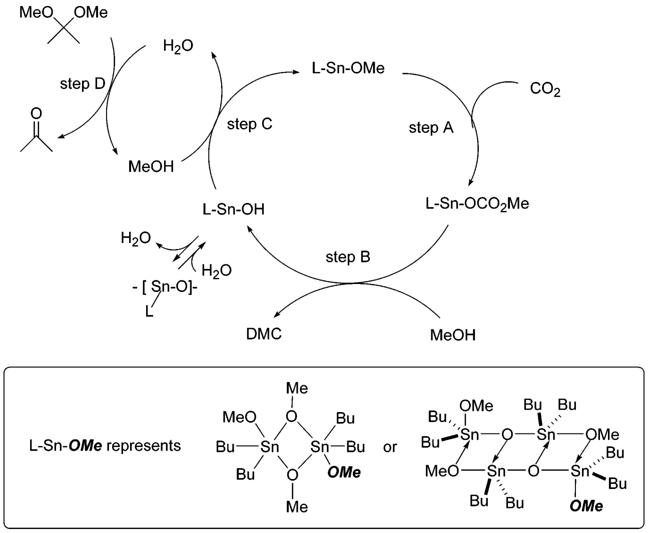


Other than tin compounds, combinations involving titanium alkoxides and polyether ligands (e.g., crown ethers or polyethylene glycols) show relatively high catalytic activities.[42] Furthermore, cobalt,[43] nickel,[44] and niobium[45] complexes catalyze the reaction in Scheme 8.

2.3. Reaction Mechanism

The direct formation of methyl bicarbonate [MeO(C═O)-OH] from CO_2 and methanol is negligible.[46] However, CO_2

Scheme 14. Synthesis of Dialkyl Carbonate from CO_2



reacts with alcohols in the presence of metal complexes to give linear carbonates (Scheme 8).[37,38,47] The most intensively studied complexes for this purpose are tin alkoxides. The formation of a methyl carbonato complex through a reaction of tin methoxide with CO_2 was reported in 1967.[48,49] The formation of DMC upon thermolysis of methyl (carbonato) tin was first reported in 1975, but the yield was very low; only 10% based on tin.[50] Another group later reported similar results.[51] However, due to the unfavorable equilibrium for the reaction in Scheme 8, the reaction performance is unsatisfactory. In fact, the yield of DMC based on methanol charged was only 1–2%, indicating that the turnover number of the tin complex [e.g., $Bu_2Sn(OMe)_2$] is less than one and that the reaction is stoichiometric rather than catalytic.

Scheme 14 shows a plausible catalytic cycle based on a mononuclear or a multinuclear metal alkoxide as active species. As for steps A and B, the tin alkoxide and the tin carbonato complexes have been isolated. The molecular structures by a single-crystal X-ray diffraction method have also been successfully determined. (See Figure 1 for the structure of $[Me_2Sn(OMe)(OCO_2Me)]_2$.) CO_2 insertion into the tin–oxygen bond readily proceeds even at room temperature.[47,52] CO_2 insertion into the metal–oxygen bond of other metal alkoxides has also been reported.[45,53–55]

In step B, thermolysis of the carbonato complex yields DMC in 60% in the presence of methanol and CO_2. The reaction without adding methanol also gives DMC, but the yield decreases to nearly half. As for step C, regeneration of $Bu_2Sn(OMe)_2$ from $(Bu_2SnO)_n$ and methanol under similar temperatures and pressures as those for the catalytic DMC formation has been examined. The resulting complex is a stanoxane-type tetranuclear complex $\{[Bu_2(MeO)SnOSn(MeO)Bu_2]_2\}$ that has a nearly equal catalytic activity to that of $Bu_2Sn(OMe)_2$ based on the tin atom.[56] Similar observations have been reported.[57,58]

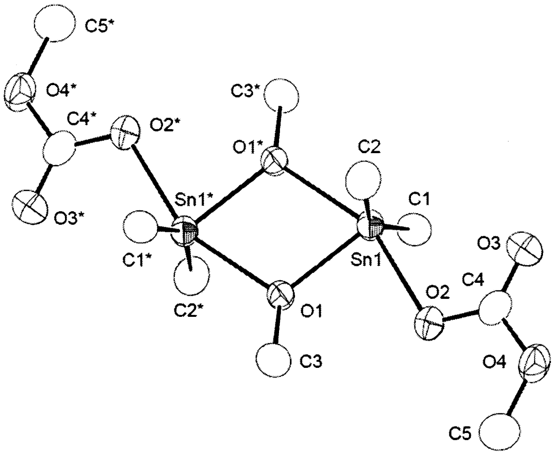


Figure 1. Molecular structure of $[Me_2Sn(OMe)(OCO_2Me)]_2$.

2.4. Heterogeneous Catalysis

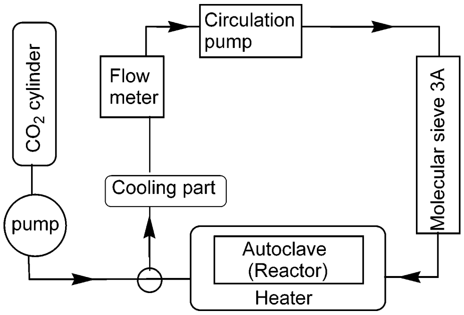
Solid acid–base catalysts such as zirconia catalyze DMC formation from methanol and CO_2.[59,60] The reaction mechanism has been investigated by measuring of the infrared spectra.[61,62] DMC is produced through the following steps. (i) Dissociative adsorption of methanol to form methoxide species. (ii) CO_2 insertion resulting in the formation of monomethyl carbonate, an important intermediate in the DMC synthesis. (iii) The transfer of a methyl group from adsorbed methanol to the monomethyl carbonate to form DMC. Every step proceeds more rapidly on monoclinic zirconia compared with tetragonal zirconia. The observed patterns are attributed to the higher Bronsted basicity of hydroxyl groups, and Lewis acid/base pairs present on the surface of zirconia. Interestingly, titania does not display catalytic activity.[63] Modifying zirconia by ceria and acidic compounds such as phosphoric acid promotes catalytic activity.[64–66] Heteropoly acids supported on zirconia are also active for the DMC formation from methanol and CO_2.[67] In addition to zirconium-based catalysts, vanadium-based catalysts such as H_3PO_4/V_2O_5[68] and $Cu\text{-}Ni/V_2O_5\text{-}SiO_2$[69] have been applied to gas-phase reactions. Most of the heterogeneously catalyzed reactions seem less productive compared to the homogeneous reaction using ketals (e.g., Scheme 13).

2.5. Inorganic Dehydrating Agents[30,70]

If the catalytic cycle depicted in Scheme 14 is correct, then the role of ketals is to dehydrate. Then DMC synthesis should proceed using inorganic dehydrating agents such as zeolites. Using inorganic dehydrating agents should have the following merits compared to using organic ones: (i) easy separation by filtration from the reaction mixture and (ii) facile recycling of the dehydrating agent by drying.

However, the addition of inorganic dehydrating agents such as zeolite or $MgSO_4$ to the tin alkoxide system or to the ZrO_2 system does not improve the DMC yield (*vide supra*).[29,30] This is probably because the capability of dehydration is low at high reaction temperatures. For improving the DMC yield, a reaction process separating the reaction part (high temperature) from the dehydrating part (room temperature), and circulating the reaction mixture

Scheme 15. DMC Synthesis Using an Inorganic Dehydrating Agent



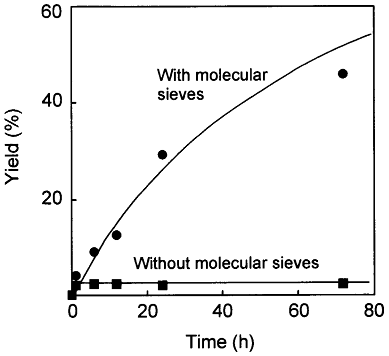


Figure 2. Time dependence of dimethyl carbonate synthesis from CO_2 and methanol. Reaction conditions: autoclave with internal recycle, dibutyltin dimethoxide (2.0 mmol), methanol (100 mmol), molecular sieve 3A (15 g), carbon dioxide (total pressure 300 atm), 180 °C. Yields are based on methanol.

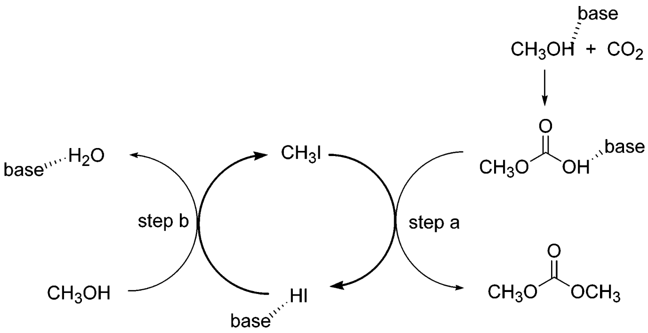
between these two parts, has been designed; molecular sieves 3A are packed in the dehydrating tube (Scheme 15). In the absence of the dehydrating part, the yield of DMC is saturated at a very early stage, showing the thermodynamic limitation. On the other hand, in the presence of the dehydrating part, the DMC yield increases as the reaction time proceeds and eventually achieves nearly a 50% yield based on methanol charged (Figure 2). In addition, in the presence of the dehydrating part, the DMC yield increases in proportion to the catalyst amount and the reaction pressure. DMC formation is very selective, and byproducts such as dimethyl ether are not observed.

2.6. Other Topics

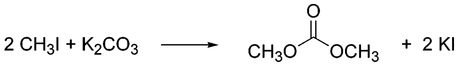
Employing a separation membrane is a promising methodology in order to remove the water on the right-hand side of Scheme 8. In fact, dimethyl carbonate synthesis from methanol and CO_2 has been investigated using water separation membranes such as mesoporous silica, polyimide silica, and polyimide−titania hybrid membranes,[71] although the effect of the membranes on the DMC yield is obscure.

Dimethyl carbonate synthesis by reacting CO_2 and methanol in the presence of methyl iodide has been proposed.[72−76] Scheme 16 shows a possible catalytic cycle. However, in most of these reports, the turnover numbers based on CH_3I are equal to or less than one. In addition, the reaction of CD_3OD with CH_3I produced $CD_3(CO_3)CH_3$, while $CD_3(CO_3)CD_3$ was not observed. Judging from these results, CH_3I is not merely a catalyst but is one of the reactants. In other words, step b is not fast enough. Because inorganic carbonates such as K_2CO_3 are used as a base in these reactions, it is possible that the CO_3 moiety in DMC comes from K_2CO_3 (Scheme 17). Microwave irradiation significantly accelerates the reaction.[77]

Scheme 16. DMC Synthesis in the Presence of Methyl Iodide



Scheme 17. DMC Formation from K_2CO_3

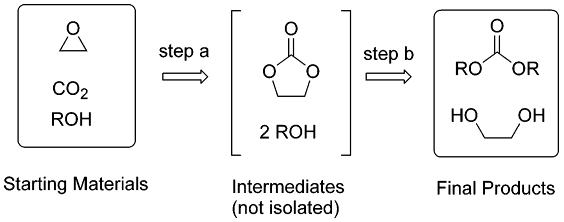


$$2\,CH_3I + K_2CO_3 \longrightarrow CH_3OC(=O)OCH_3 + 2\,KI$$

3. Dimethyl Carbonate Synthesis *via* Cyclic Carbonates

The reaction of CO_2 with epoxides to yield alkylene carbonates followed by *in situ* ester exchange with a large excess of methanol can form dimethyl carbonate. The merits of this process are as follows. (1) Unlike the direct reaction of methanol and CO_2 (Scheme 8), a high yield can be achieved in this reaction because dehydration is unnecessary. (2) If the coproduced 1,2-diols are recycled, the total reaction is regarded as the DMC synthesis from methanol and CO_2. The demerits of the process are (1) coproduction of 1,2-diols, (2) side reactions such as ring opening of epoxides by alcohols, and (3) the requirement for a large excess of alcohol to achieve high conversions due to the unfavorable ester

Table 1. Dimethyl Carbonate Synthesis from Epoxides, Methanol, and CO_2



year	epoxide[a] (mmol)	MeOH (mmol)	catalyst (g)	P_{CO_2} (bar)	temp (°C)	time (h)	yield (%)	ref
2001	PO (25)	200	MgO (0.5)	80	150	15	14	78
2003	EO (45)	562	KI (0.2)/K_2CO_3 (0.2)	150	140	2	73	79
2003	PO (21)	200	Mg[smectite] (0.5)	80	150	15	34	80
2004	PEPO (1)	40	DBU (0.008)	150	150	24	97	81
2004	PO (1000)	4000	5 wt % [K_2CO_3−KCl/MgO] (−)	25	160	5	46	82
2004	EO (10)	40	[K_2CO_3−KI/ZnO] (0.25)	165	150	4	69	83
2005	PO (828)	1234	KOH/molecular sieves 4A (5)	30 (rt)	180	6	17	84
2006	SO (5)	200	Bu_4NBr (0.04)/Bu_3N (0.02)	150	150	8	84	85

[a] For the abbreviations, see section 13 of this article.

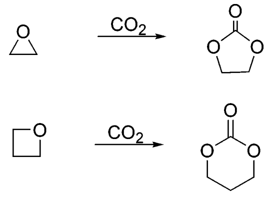
exchange between methanol and alkylene carbonates. Table 1 summarizes typical catalytic systems for this reaction. Suitable catalysts need to activate both step a and step b, and in general, basic compounds seem appropriate.[78−85] Recently, it has been reported that an Fe−Zn double metal cyanide, prepared from $ZnCl_2$ and $K_4Fe(CN)_6$, is a highly active heterogeneous catalyst for the synthesis of a range of dialkyl carbonates in high yields by transesterification of propylene carbonate with alcohols.[86] The catalyst can be recycled without significant loss in activity.

4. Synthesis of Cyclic Carbonates

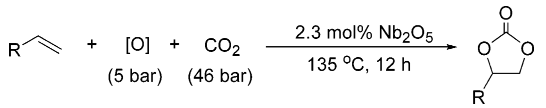
4.1. Cyclic Carbonate Synthesis Outline

Oxiranes and oxetanes undergo cycloaddition with CO_2 to give five- and six-membered ring carbonates (Scheme 18).[11,87,88] Similar to linear dialkyl carbonates, cyclic carbonates are useful as intermediates for polycarbonates, electrolytes in lithium ion batteries, or green solvents. The production of five-membered cyclic carbonates from CO_2 has been industrialized since the 1950s.[11] Although oxirane cycloaddition is rather selective, alternating copolymerization of oxiranes with CO_2 and homopolymerization of oxiranes also proceed as explained in the next section. As another type of the five-membered carbonate synthesis starting from CO_2, Nb-catalyzed oxidative carboxylation of olefins has been reported (Scheme 19).[89] On the other hand, the dehydrative reaction of 1,2-diols to give cyclic carbonates is catalyzed by CeO_2−ZrO_2 or Bu_2SnO (Scheme 20).[90−92] An iron- or copper-catalyzed reaction of a cyclic ketal with CO_2 has also been proposed (Scheme 21).[93] The reaction of propargyl carbonate with phenol proceeds in the presence of a palladium catalyst, which leads to phenoxy-substituted cyclic carbonates via CO_2 evolution (Scheme 22).[94,95]

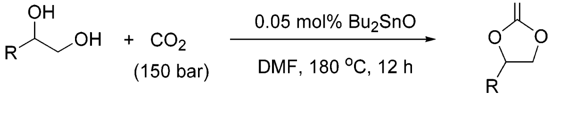
Scheme 18. Synthesis of a Cyclic Carbonate from an Oxirane



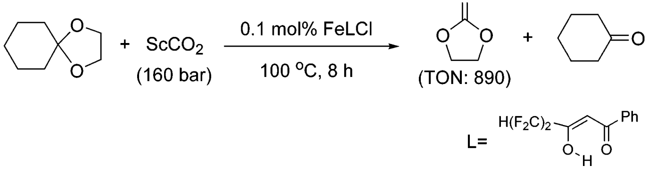
Scheme 19. Synthesis of a Cyclic Carbonate from an Olefin



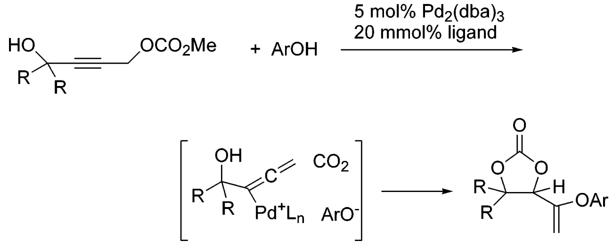
Scheme 20. Synthesis of a Cyclic Carbonate from a Diol



Scheme 21. Synthesis of a Cyclic Carbonate from a Cyclic Ketal



Scheme 22. Synthesis of a Cyclic Carbonate from a Propargyl Carbonate



4.2. Catalysts for the Cycloaddition of CO_2 with Oxiranes

A typical process of CO_2 cycloaddition with oxiranes uses the produced carbonate as a solvent in the presence of an onium salt such as tetraethyl ammonium bromide as a catalyst.[11] In addition to onium salts, the reaction proceeds in the presence of a wide range of catalysts, including metal halides.[96] Although the catalytic activity at lower temperatures is not very high, KI seems to be one of the best catalysts in recent industrial processes. This is probably because potassium iodide is more economical and more durable compared to quaternary ammonium salts and it is highly soluble in cyclic carbonates. Supporting halide salts on solid supports such as ZnO, SiO_2, carbon, and zeolite results in high catalytic activities.[97−100]

Tables 2−4 summarize recently proposed homogeneous catalysts for the cyclic carbonate synthesis from oxiranes and CO_2: metal complexes (Table 2), onium salts (Table 3), and others (Table 4). One requirement for industrial homogeneous catalysts is not to produce solids during the catalyst separation stage by evaporating the product after cycloaddition.

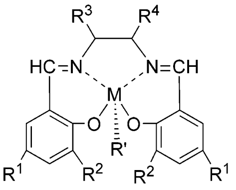
Among metal complexes, salen complexes of aluminum,[101−104] chromium,[105,106] cobalt,[107,108] zinc,[107] and tin[109] exhibit high catalytic activities. Aluminum complexes of phthalocyanines or porphyrins are also highly active.[110−114]

Utilizing ionic liquids in organic synthesis has attracted increasing attention.[115] Cyclic carbonate synthesis using ionic liquids (i.e., imidazolium salts) as catalysts,[116−118] or by combining ionic liquids and metal salts, has been reported.[119−123] In addition, a reaction in liquid quaternary ammonium salts, e.g., Bu_4NBr, has been proposed.[124]

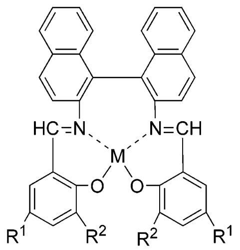
Furthermore, various metal complexes of nickel,[125] ruthenium,[126] zinc,[127] copper,[128] manganese,[128,129] and so on have been reported to be active (Table 4). Combining with organic compounds such as crown ethers, onium salts, and phosphines has significantly improved the catalytic activities of metal halides.[130−134] Cobalt- or manganese-substituted polyoxometalates have been proposed as catalysts with non-halide counter-anions.[135] These polyoxometalates work as homogeneous catalysts. Fully organic catalysts based on phenols and amines have also been investigated.[136,137]

Many papers claim low reaction temperatures and advertise high catalytic activities. However, this is not very meaningful from a practical viewpoint because cycloaddition (Scheme 18) is highly exothermic and effective heat removal is fundamental to save energy. In order to recover the reaction heat as steam, a reaction temperature around 150 °C would be desirable. Reaction temperatures below 100 °C result in low heat exchange efficiencies and produce nearly useless warm water.

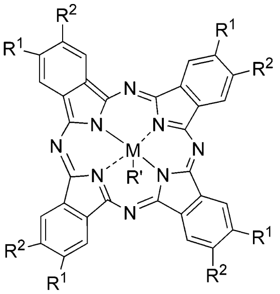
Table 2. Cyclic Carbonate Synthesis Catalyzed by Salen and Phthalocyanine Complexes



1a-c



1d-e



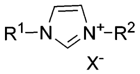
1f

Cat.	R^1	R^2	R^3	R^4	R'	M
1a	H	H	H	H	Cl	Al
1b	H	H	H	H	Br	Al
1c	*t*Bu	*t*Bu	Ph	Ph	Cl	Cr
1d	H	H	-	-	-	Co
1e	H	H	-	-	-	Zn
1f	H	H	-	-	Cl	Al

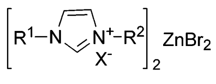
expoxide	catalyst	amount of cat. (mol %)	solvent	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	ref
PO	**1a**/[Bu_4NBr]	0.13		6	25	8	504	63.0	102
PO	**1a**/[Bu_4NI]	0.13		6	35	8	674	84.2	102
PO	**1a**/[18-crown-6-KI]	0.13		6	25	8	463	57.9	102
EO	**1a**/[Bu_4NI]	0.02		160	110	1	2360	2360	104
PO	**1b**/[18-crown-6-KI]	0.13		6	25	8	498	62.3	101
PO	**1c**/[(4-dimethylamino)pyridine]	0.075	CH_2Cl_2	8	100	1	916	916	105
PO	**1d**/2[Et_3N]	0.1	CH_2Cl_2	35	100	2	913	456.5	107
PO	**1e**/2[Et_3N]	0.1	CH_2Cl_2	35	100	2	856	428	107
PO	**1f**/4.5[*N*-methylimidazole]	0.1		>61	140	1.2	961	801	113

[a] TOF: estimated from the literature.

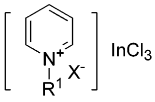
Table 3. Cyclic Carbonate Synthesis Catalyzed by Onium Salts



2a-d



2e-g



2h

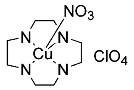
Cat.	R^1	R^2	X^-
2a	Bu	Me	BF_4
2b	Octyl	Me	BF_4
2c	Bu	Me	Br
2d	Bu	Me	Cl

Cat.	R^1	R^2	X^-
2e	$PhCH_2$	Me	Br
2f	Et	Me	Br
2g	Me	Me	Cl
2h	Bu	-	Cl

expoxide	catalyst	amount of cat. (mol %)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	ref
PO	**2a**	2.5	25	110	6	40	6.7	116
PO	**2b**	1.7	140	100	0.08	516	6192	118
PO	$ZnBr_2$ + 6 equiv **2c**	0.018	15	100	1	5580	5580	121
SO	$ZnBr_2$ + 4 equiv **2d**	1.1	140	80	1	84	84	123
PO	**2e**	0.05	35	100	1	1846	1846	119
EO	**2f**	0.02	35	100	1	3588	3588	119
PO	**2g**	0.2	35	100	1	500	500	120
PO	**2h**	0.5	7	120	1	194	194	122

[a] TOF: estimated from the literature.

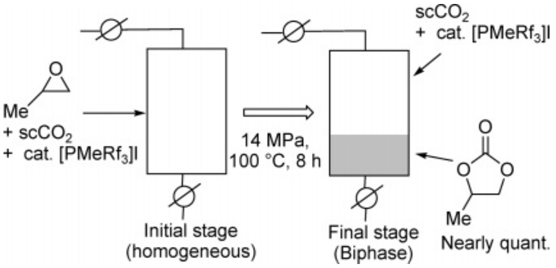
Table 4. Various Homogeneous Catalysts for Cyclic Carbonate Synthesis

epoxide	catalyst	amount of cat. (mol %)	solvent	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	ref
PO	$Ni(PPh_3)_2Cl_2$/2[PPh_3]/4[Bu_4NBr]/20[Zn]	0.028		25 (rt)	120	1	3544	3544	125
PO	Cp(CO)Ru(dppe)Mn$(CO)_4$	0.01		40	100	40	1490	37	126
EO	$Zn(PMe_2Ph)_2Br_2$	0.05		34	100	1	1640	1640	127
PO	 (4-dimethylamino)pyridine	0.043	CH_2Cl_2	7	120	4	1144	286	128
PO	NaI/Ph_3P/PhOH	2		40 (rt)	120	2	48	23.8	131
PO	$CaCl_2$/octyl$_3$(Me)NCl	0.23		41 (rt)	170	8	419	52	132
SO	$ZnBr_2$/2[Bu_4NI]	0.29		80	90	0.5		686	133
PO	Bu_3SnI/Bu_4PI	2		50	40	1	50	50	134
PO	[heptyl$_4$N]$_6$[α-$SiW_{11}O_{39}Co$]	0.1	*N*,*N*-dimethylformamide	35	150	2	820	410	135
PO	*p*-MeC_6H_4OH/DMAP	0.4	CH_2Cl_2	36	120	48	246	5.1	137

[a] TOF: estimated from the literature.

The use of supercritical CO_2 has attracted much interest in order to facilitate various chemical processes. Propylene and ethylene oxides are soluble in supercritical CO_2, while propylene and ethylene carbonates are not. Hence, carbonates are easily separated from the supercritical phase without reducing the CO_2 pressure. Facile catalyst recycling can be

Scheme 23. Facile Separation by $scCO_2$



realized by using catalysts highly soluble in supercritical CO_2 (e.g., perfluorophosphonium salts) (Scheme 23).[138]

LiBr has been reported to be a suitable catalyst in supercritical CO_2.[139,140] Although it is reported that the reaction in supercritical CO_2 proceeds without a catalyst in the presence of dimethyl formamide, substrates seem to be limited to styrene oxide derivatives.[141]

In view of catalyst separation and environmental issues (non-halogen processes), metal oxide-based catalysts are interesting. Heterogeneous catalysts such as SmOCl,[142,143] $ZnO-SiO_2$,[144] $Cs-P-SiO_2$,[145] smectite,[146] Al−Mg mixed oxides,[147] magnesium oxide,[148] Cs-modified zeolites,[149,150] hydroxyapatites,[151] and zinc-substituted heteropolyacids with sodium as cations[152] have been reported as active. Titanosilicate and mesoporous silica also catalyze the reaction with and without ammonium salts (Table 5).[153,154]

In light of homogeneous catalyst recycling, immobilization is a promising approach. For cycloaddition of oxiranes and CO_2, polymer-supported catalysts[155−164] as well as silica-supported catalysts have been developed (Table 6).[165−168] It has been noted that silica-supported onium salts exhibit hundred times higher catalytic activities compared to onium salts alone. Thus, the silica-supported onium salts have been applied to a flow reactor system; silica itself does not display catalytic activity.[168] In general, the catalytic activities of homogeneous catalysts become lower upon immobilization. Hence, the observation that there is a large cooperative effect between the catalyst part and the solid support part is unique.

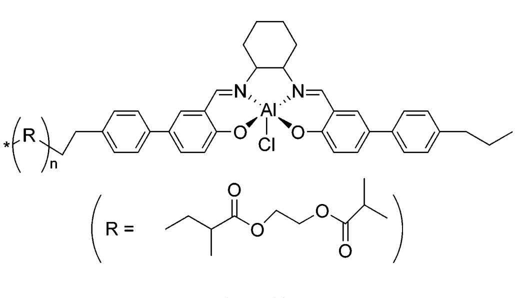
4.3. Reaction Mechanism

The cycloaddition of monosubstituted oxirane catalyzed by a metal halide (MX) is discussed. First, anion X attacks the less hindered side of oxirane to open the ring. Next, the resulting alkoxide part attacks CO_2 to give the carbonate anion. Then, the carbonate anion undergoes a S_N2 reaction, which simultaneously forms a five-membered ring and releases anion X (Scheme 24).

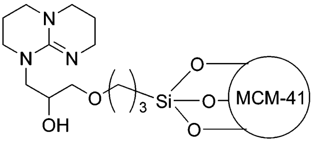
Table 5. Cyclic Carbonate Synthesis Catalyzed by Heterogeneous Catalysis

expoxide	catalyst	solvent	P_{CO_2} (bar)	temp (°C)	time (h)	yield (%)	selectivity (%)	ref
PO	SmOCl	*N*,*N*-dimethylformamide	140	200	8	99	99	142
PO	7% $ZnO-SiO_2$		45	100	3	27		144
PO	$Cs-P-SiO_2$		80	200	8	94	96	145
PO	Smectite(8[Si]−6.44[Mg]−2.81[Na−0.13K])		80	150	15	81	94	146
PO	$5[MgO]/AI_2O_3$	*N*,*N*-dimethylformamide	5	120	24	88	92	147
PO	MgO	*N*,*N*-dimethylformamide	20	135	12	41		148
EO	Cs-Zeolite		39 (rt)	150	3	14		150
SO	$0.3\ mmol/g[Zn(Ca_{10}(PO_4)_6(OH)_2]/4[Et_3N]$		5	100	20	98	>99	151
PO	$Na_{12}[WZn_3(H_2O_2)_2(ZnWgO_{34})_2]46H_2O/3[DMAP]$	CH_2Cl_2	4	160	12	97	97	152
PO	MCM-41		7	120	5	86	94	154

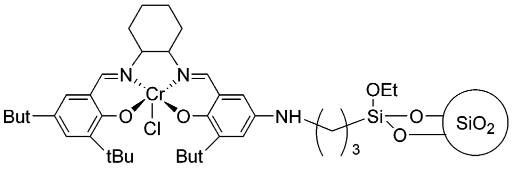
Table 6. Immobilized Catalysts for Cyclic Carbonate Synthesis



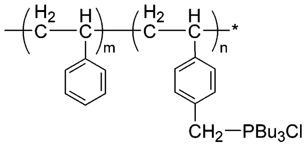
Al(salen)/PEA



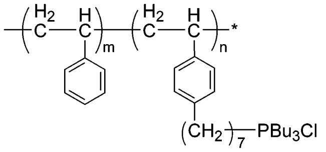
TBD-MCM-41



Cr-salen/NH2SiO2



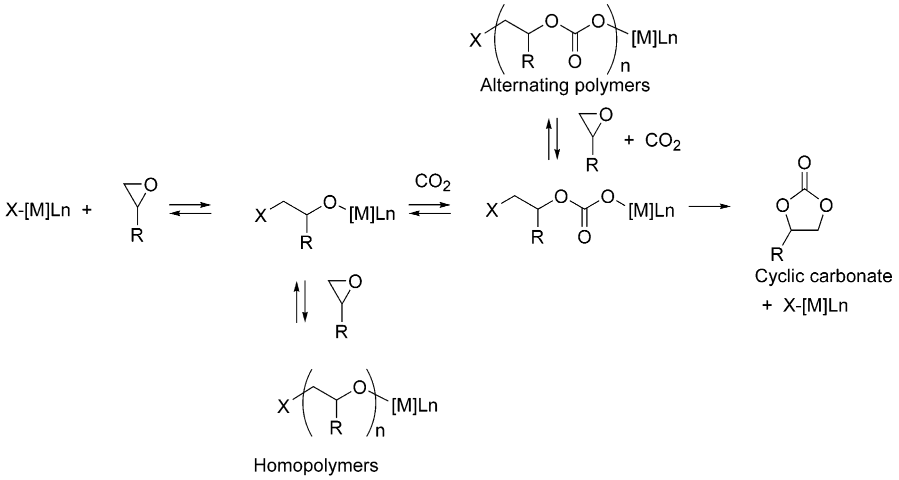
ClBu3P/PS



ClBu3P/PS1

expoxide	catalyst	solvent	P_{CO_2} (bar)	temp (°C)	time (h)	yield (%)	selectivity (%)	ref
SO	0.42 mmol/g[AI(salen)PEA]/1.8[*N*-methylimidazole]		100	80	15	78	88	159
EO	9.7 wt % $[ZnBr_2]$/poly(4-vinylpyridine)		35	100	1	33	>99	161
PEPO	0.5 mmol/g$[ClBu_3P/PS]$	*N*,*N*-dimethylacetamide	1	90	24	94		162
PEPO	0.41 mmol/g$[ClBu_3P/PS1]$	toluene	1	100	24	93		163
SO	1.27 mmol/g[TBD-MCM-41]	CH_3CN	50	140	70	90	92	165
SO	0.14 mol % $[Cr-salen/NH_2SiO_2]$/ 0.13 mmol [*N*-methylimidazole]	CH_2Cl_2	100	80	6	59	89	167
PO	0.85 mmol/g$[SiO_2-C_3H_6-PBu_3I]$		100	100	1	100	100	168

Scheme 24. Possible Mechanism of Cyclic Carbonate Synthesis: 1



Scheme 25. Possible Mechanism of Cyclic Carbonate Synthesis: 2

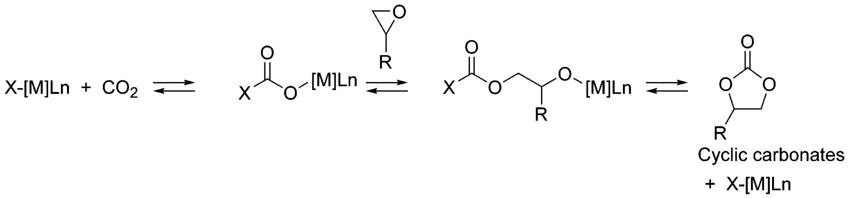
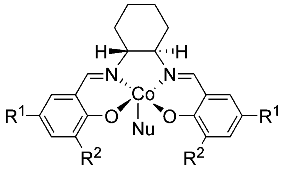
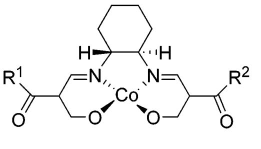


Table 7. Asymmetric Synthesis of Cyclic Carbonates


3a-b


3c

Cat.	R^1	R^2	Nu
3a	*t*Bu	*t*Bu	O_2CCl_3
3b	*t*Bu	*t*Bu	OTs
3c	OEt	OEt	-

epoxide	catalyst	amount of cat. (mol %)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF (h^{-1})	% ee	ref
PO	**3a**/Bu_4NBr	0.1	15	25	2	490	245	50.5	108
PO	**3b**/Bu_4NBr	0.1	15	25	2.5	508	203	51.6	108
DAPO	**3c**/0.5[Et_2NSiMe_3]	2	7	30	80	25	0.31	86	169

Another possible mechanism is for anion X to initially attack CO_2, followed by a nucleophilic attack of the resulting anion to form oxirane (Scheme 25).

In order to elucidate the mechanism, the change in the configuration of the methylene carbon has been investigated using D-labeled oxirane. The configuration is retained during the reaction, which supports a mechanism that includes a double inversion by S_N2 reactions, namely that shown in Scheme 24.[108]

4.4. Asymmetric Synthesis

The synthesis of optically active cyclic carbonates (kinetic resolution of racemic epoxides) is possible using asymmetric cobalt salen complexes as catalysts.[108,169] The highest reported enantiomeric excess of cyclic carbonates is about 86% ee (Table 7).

4.5. Outlook

Currently, the market for cyclic carbonates as electrolytes for batteries is small. However, the demand should increase when electric vehicles are fully commercialized. On the other hand, the process of polycarbonate synthesis, such as in Scheme 6, uses cyclic carbonates on a large scale.

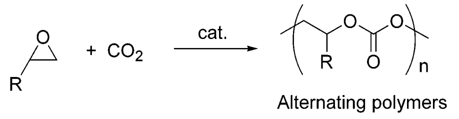
Catalysts for cyclic carbonate synthesis from oxiranes and CO_2 are categorized into (1) ammonium or phosphonium salts, (2) alkali metal salts (KI, LiBr, etc.), (3) metal complexes such as salen complexes, and (4) solid or immobilized catalysts such as $SiO_2-C_3H_6-P(Bu)_3I$. Future challenges include developing non-halogen catalysts, developing immobilized or solid catalysts aimed at flow reactor processes, utilizing new reaction media such as supercritical CO_2 or ionic liquids, and asymmetric synthesis.

5. Alternating Polymerization of Oxiranes and CO_2

5.1. Reaction Outlines

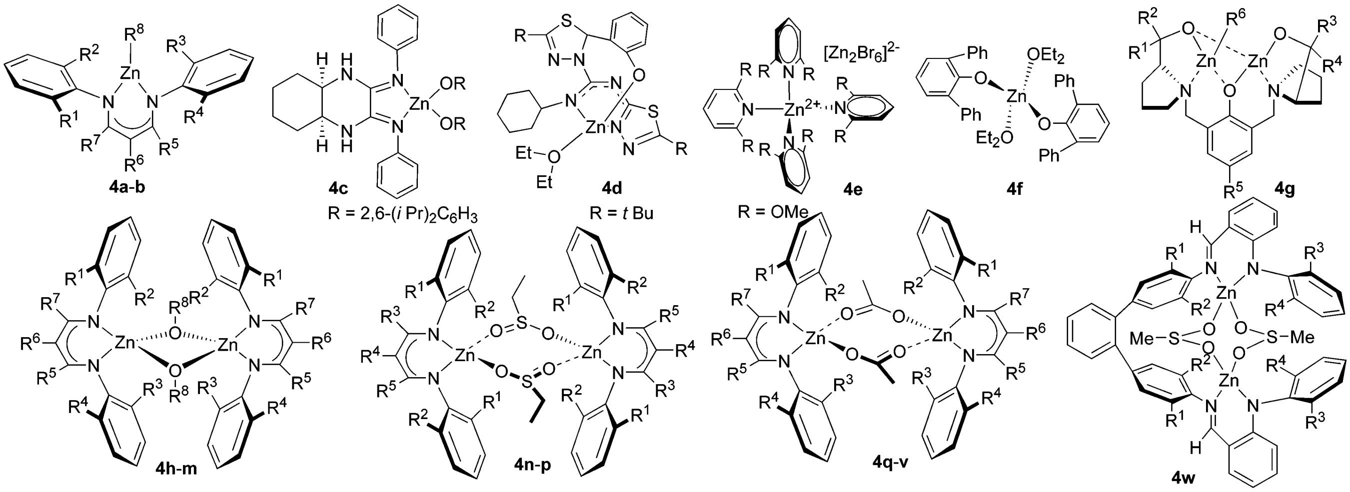
The alternating copolymerization shown in Scheme 26 comprises the same reactants as the synthesis of five-membered cyclic carbonates; polymers are kinetic products, while cyclic carbonates are thermodynamic ones (Scheme 26).[170] Aliphatic carbonates produced by this reaction have been recently industrialized in China.[171]

Scheme 26. Alternating Polymerization of Oxirane and CO_2



The relatively low T_g (glass transition temperature) (35−40 °C) of poly(propylene carbonate) seems to interfere with its application to bulk materials. On the other hand, a higher T_g (115 °C) and the decomposition temperature (about 300 °C) of poly(cyclohexene carbonate) allow the melt processing. The polymer is expected to be a substitute for polystyrene. The characteristics of the polymers are low oxygen permeability, biodegradability, and complete thermal depolymerization to give cyclic carbonates.

Table 8. Homogeneous Zinc Catalysts for Alternating Polymerization


4a-b **4c** R = 2,6-(*i* Pr)$_2$C$_6$H$_3$ **4d** R = *t* Bu **4e** R = OMe **4f** **4g** **4h-m** **4n-p** **4q-v** **4w**

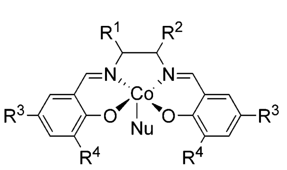
Cat.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
4a	*i*Pr	*i*Pr	*i*Pr	*i*Pr	Me	H	Me	N(TMS)$_2$
4b	Et	Et	Et	Et	Me	H	Me	N(TMS)$_2$
4g	Ph	Ph	Ph	Ph	Me	Et	-	-
4h	*i*Pr	*i*Pr	*i*Pr	*i*Pr	Me	H	Me	Me
4i	Et	Et	Et	Et	Me	H	Me	Me
4j	*i*Pr	Et	Et	*i*Pr	Me	H	Me	Me
4k	*i*Pr	Me	Me	*i*Pr	Me	H	Me	Me
4l	Et	nPr	nPr	Et	Me	H	Me	iPr
4m	Et	Et	Et	Et	Me	H	Me	Et
4n	*i*Pr	*i*Pr	Me	H	Me	-	-	-

Cat.	R^1	R^2	R^3	R^4	R^5	R^6	R^7
4o	Et	Et	Me	H	Me	-	-
4p	*i*Pr	Me	Me	H	Me	-	-
4q	*i*Pr	*i*Pr	*i*Pr	*i*Pr	Me	H	Me
4r	Et	Et	Et	Et	Me	H	Me
4s	*i*Pr	Et	Et	*i*Pr	Me	H	Me
4t	*i*Pr	*i*Pr	Et	Et	Me	CN	Me
4u	Et	Et	iPr	*i*Pr	CF$_3$	H	Me
4v	*i*Pr	*i*Pr	Me	Me	H	CN	OEt
4w	Me	Me	*i*Pr	*i*Pr	-	-	-

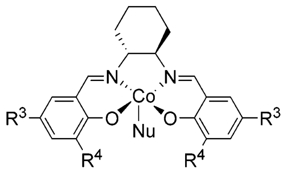
epoxide	catalyst	amount of cat. (mol %)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	carbonate linkages (%)	M_n ($\times 10^{-3}$)	M_w/M_n	ref
CHO	**4a**	0.1	7	50	0.5	172	345	94	25.5	1.10	54
CHO	**4b**	0.1	7	50	0.5	179	358	97	25.6	1.16	54
CHO	**4c**		80	80	69	2759	40	97	13.5	4.59	173
CHO	**4d**	0.3	20	85	20	108	5	99	23.0	8.91	174
CHO	**4e**	0.04	50	80	24	660	28	85	13	7.62	175
CHO	**4f**	0.36	55	80	69	183	3	91	38.0	4.5	176
CHO	**4g**	5	5	60	6	196	33	99	20.9	1.51	177
CHO	**4h**	0.1	7	50	2	449	224	95	19.1	1.07	178
CHO	**4i**	0.1	7	50	2	477	239	96	23.7	1.14	178
CHO	**4j**	0.1	7	50	2	515	257	99	32.1	1.14	178
CHO	**4k**	0.1	7	50	2	418	209	94	17.0	1.21	178
CHO	**4l**	0.1	7	50	5	265	53	93	14.8	1.10	178
CHO	**4m**	0.1	7	50	5	198	99		11.6	1.18	179
CHO	**4n**	0.1	10	60	2	312	156	97	39.8	1.11	180
CHO	**4o**	0.1	10	60	2	328	164	97	31.8	1.13	180
CHO	**4p**	0.1	10	60	2	270	135	95	20.8	1.30	180
CHO	**4q**	0.1	7	50	0.5	180	360	95	15.8	1.11	54
CHO	**4r**	0.1	7	50	0.5	216	431	97	17.3	1.15	54
CHO	**4s**	0.1	7	50	0.5	364	729	99	23.3	1.15	54
PO	**4t**	0.05	21	25	8	376	47	99	43.3	1.09	181
PO	**4u**	0.05	21	25	2	424	212	99	35.9	1.11	181
CHO	**4v**	0.1	40	90	2	367	183	88	24.5	1.15	182
CHO	**4w**	0.02	12	80	5	1560	312	94	225.0	1.70	183

[a] TOF: estimated from the literature.

Table 9. Homogeneous Cobalt Catalysts for Alternating Polymerization

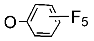
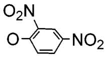


5a-b



5c-j

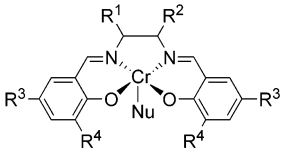
Cat.	R^1	R^2	R^3	R^4	Nu
5a	CH_3	H	*t*Bu	*t*Bu	NO_3
5b	Ph	Ph	*t*Bu	*t*Bu	NO_3
5c	-	-	*t*Bu	*t*Bu	OTs
5d	-	-	*t*Bu	*t*Bu	BF_4
5e	-	-	*t*Bu	*t*Bu	NO_3

Cat.	R^1	R^2	R^3	R^4	Nu
5f	-	-	Br	*t*Bu	OAc
5g	-	-	H	*t*Bu	OAc
5h	-	-	*t*Bu	*t*Bu	OAc
5i	-	-	*t*Bu	*t*Bu	
5j	-	-	*t*Bu	*t*Bu	

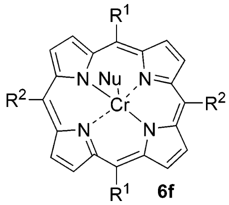
epoxide	catalyst	cocatalyst (equiv)	amount of cat. (mol %)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	carbonate linkages (%)	M_n ($\times 10^{-3}$)	M_w/M_n	ref
PO	**5a**	DMAQ (2)	0.07	11	25	3	354	118	>99	17.2	1.06	186
PO	**5b**	DMAQ (2)	0.07	25	40	1.66	330	199	>99	17.4	1.07	186
PO	**5c**	DMAQ (2)	0.07	11	25	5	430	86	>99	25.6	1.06	186
PO	**5d**	DMAQ (2)	0.07	11	25	5	430	86	>99	21.3	1.06	186
PO	**5e**	DMAQ (2)	0.07	11	25	5	485	97	>99	23.2	1.07	186
PO	**5f**		0.2	55	25	3	243	81	99	15.3	1.22	187
PO	**5g**		0.2	55	25	3	198	66	96	9.0	1.31	187
PO	**5h**		0.2	55	25	3	177	59	99	8.1	1.57	187
PO	**5i**	PPNCl (1)	0.05	14	22	2	1040	520	>99	43.0	1.10	188
CHO	**5i**	PPNCl (1)	0.05	7	22	2	320	160	97	14.9	1.14	189
PO	**5j**	Bu_4NCl (1)	0.05	20	25	3	771	257	>99	30.4	1.36	190
PO	**5j**	PPNCl (1)	0.05	15	25	1.5	795	530	>99	30.9	1.20	191

[a] TOF: estimated from the literature.

Table 10. Homogeneous Chromium Catalysts for Alternating Polymerization



6a-e



6f

Cat.	R^1	R^2	R^3	R^4	Nu
6a	H	H	*t*Bu	*t*Bu	Cl
6b	H	H	*t*Bu	*t*Bu	N_3
6c	-$(CH_2)_4$-		*t*Bu	*t*Bu	Cl

Cat.	R^1	R^2	R^3	R^4	Nu
6d	-$(CH_2)_4$-		OCH_3	*t*Bu	N_3
6e	-$(CH)_4$-		*t*Bu	*t*Bu	N_3
6f	C_6F_5	C_6F_5	-	-	Cl

epoxide	catalyst	cocatalyst (equiv)	amount of cat. (mol %)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	carbonate linkages (%)	M_n ($\times 10^{-3}$)	M_w/M_n	ref
CHO	**6a**	PPh_3 (3)	0.04	55	80	4	157	39	96	22.7	1.55	192
CHO	**6a**	PPNCl (1)	0.04	55	80	4	1004	251	>99	6.0	2.05	192
CHO	**6b**	PCy_3 (3)	0.04	55	80	10	391	98	97	10.8	1.54	192
CHO	**6a**	N-Melm (2.25)	0.04	55	80	24	857	36	99	8.8	1.40	193
CHO	**6b**	PPNCl (1)	0.04	55	80	4	1977	494	99	10.0	1.26	194
CHO	**6b**	$PPNN_3$ (1)	0.04	55	80	4	2423	608	99	14.0	1.54	194
CHO	**6b**	DMAP (1)	0.04	55	80	4	1080	270	98	31.5	1.12	194
CHO	**6c**	N-Melm (2.25)	0.04	59	80	24	1104	46	>99	8.9	1.20	195
PO	**6c**	DMAP (0.5)	0.07	13	75	4	176	44	76	10.1	1.36	196
CHO	**6d**	$PPNN_3$ (1)	0.04	35	80	2.3	2686	1153	>99	50.0	1.13	197
CHO	**6e**	PCy_3 (1)	0.04	34	60	4	596	149	96	13.2	1.07	198
CHO	**6e**	$PPNN_3$ (1)	0.04	34	60	4	760	190	96	26.1	1.11	198
PO	**6e**	DMAP (1)	0.07	35	75	4	640	160	98	16.7	1.38	196
CHO	**6f**		0.26	138	95	18	12	0.65	95	3.6	1.16	199

[a] TOF: estimated from the literature.

In order to realize large-scale commercialization of these alternating copolymers, the plastic properties must be improved and the catalytic activities for copolymerization must be increased.

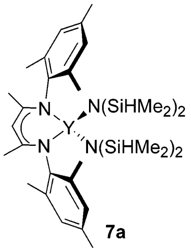
5.2. Catalyst

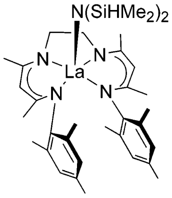
Zinc complexes were the first generation of catalysts and are typified by ($ZnEt_2 + H_2O$).[172] The structure of the real active species may be multinuclear but is unknown. The catalytic performance has been unsatisfactory and has resulted in low reaction rates, large polydispersity, and irregular structures.

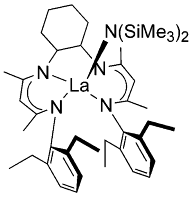
As structurally well-characterized highly active catalysts, various zinc complexes have been proposed (Table 8).[54,173−184] The iminate complexes have been the most intensively studied. Bulky substituents seem to promote the partial dissociation of dinuclear species, which results in an increased catalytic activity. Under optimized conditions, a high reaction rate, a high molecular weight, and a narrow polydispersity have been simultaneously achieved. The activities of zinc diiminate catalysts are enhanced in the presence of SO_2.[185]

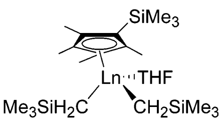
Metal complexes other than zinc complexes have also been developed. For example, cobalt (Table 9),[186−191] chromium (Table 10),[192−199] lanthanide (Table 11),[200,201] and manganese[202] complexes have been reported. Table 12 summarizes the structurally uncharacterized complexes.[203−210] The cobalt-catalyzed reactions proceed under very mild conditions

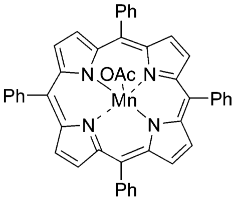
Table 11. Homogeneous Ln and Mn Catalysts for Alternating Polymerization


7a


7b


7c


7d Ln = Y
7e Ln = Dy
7f Ln = Lu


7g

epoxide	catalyst	amount of cat. (mol %)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	carbonate linkages (%)	M_n ($\times 10^{-3}$)	M_w/M_n	ref
CHO	**7a**	0.2	1	75	88	204	2.3	68	3.8	2.80	200
CHO	**7b**	0.2	1	75	24	173	7.2	92	7.1	1.50	200
CHO	**7c**	0.2	1	75	24	304	12.7	88	13.5	1.60	200
CHO	**7d**	0.25	12	70	24	10359	432	94	19.1	4.30	201
CHO	**7e**	0.25	12	70	24	7417	309	93	14.5	3.99	201
CHO	**7f**	0.25	12	70	24	12960	540	92	23.0	4.03	201
CHO	**7g**	0.2	51	80	24	390	16	99	6.7	1.30	202

[a] TOF: estimated from the literature.

Table 12. Non-Single-Site Zinc Catalysts for Alternating Polymerization

epoxide	catalyst	P_{CO_2} (bar)	temp (°C)	time (h)	TOF[a] (h^{-1})	carbonate linkages (%)	M_n ($\times 10^{-3}$)	M_w/M_n	ref
CHO	$ZnCl_2$/0.1[$K_3Co(CN)_6$]/poly(tetramethylene ether glycol)	86	80	2	356	80	10.2	1.77	203
PO	$ZnCl_2$/0.1[$K_3Co(CN)_6$]/poly(tetramethylene ether glycol)	86	80	2	172	39	2.6	1.39	203
PO	$Zn(OAC)_2$/glutaric acid/PE6400	21	60	40	2		60.0	2.70	204
PO	Zn(glutarate)/3[montmorillonite]	52	60	40	2.6	>99	20.5	2.9	205
PO	Zn(glutarate)/poly(aryl ether sulfone)s	50	60	40	0.29		36.0		206
PO	ZnO/heptanedioic acid	52	60	40	2.05	>99	44.3		207
CHO	$ZnEt_3$/0.05[$Y(CF_3CO_2)_3$]/2[glycerine]	28	80	12	2.63	>99	33.4	7.4	208
PO	$ZnEt_3$/0.05[$Y(CF_3CO_2)_3$]/*m*-hydroxybenzoic acid	28	60	12	4.17	>99	13.5	4.7	209
CHO	$ZnEt_3$/0.1[$Y(CF_3CO_2)_3$]/2[pyrogallol]	28	80	12	5.92	93	35.7	4.48	210

[a] TOF: estimated from the literature.TOF = (polymer - g)/(Zn - g)·h.

around room temperature (Table 9). It is noteworthy that the cobalt complexes effectively execute the polymerization of epoxides derived from acyclic alkenes such as propylene oxides. Among heterogeneous catalysis, the alternating copolymerization of cyclohexene oxide catalyzed by the Co–Zn double metal cyanide is especially efficient (Table 12). The turnover frequency is as large as that of the homogeneous catalysis using zinc diiminate complexes (Table 8).

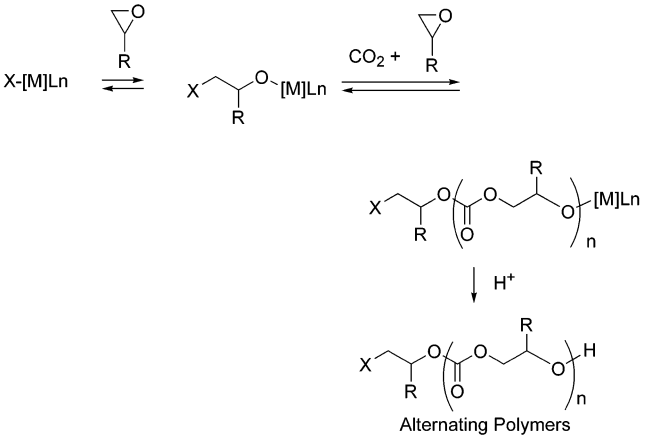
From an economic point of view, ethylene and propylene oxides are favorable as substrates for the reaction. However, most papers use cyclohexene oxide as a substrate because cyclohexene oxide selectively yields the polymer, while ethylene and propylene oxides often afford cyclic carbonates. On the other hand, the higher T_g of the polymer based on cyclohexene oxide compared to the propylene oxide-based polymer makes it favorable as a bulk material. The reaction of limonene oxide as a biorenewable resource has recently been explored.[211]

The reaction mechanism has been precisely investigated using diiminate complexes (Scheme 27).[54] Fundamentally, the reaction mechanism for cyclic carbonate synthesis (Scheme 24) is also applicable to the alternating copolymerization, as the structure of the polymer end supports this mechanism.

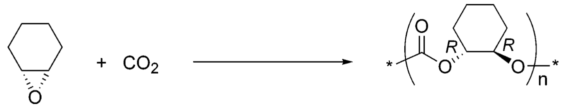
5.3. Asymmetric Polymerization

Asymmetric zinc complexes effectively produce enantioselective polymerization (Scheme 28, Table 13). Using optically active iminates and amino alcohol ligands, cyclohexene oxide has been polymerized to give optically active alternating copolymers in up to 88% ee.[212,213]

Scheme 27. Possible Mechanism of Alternating Polymer Synthesis



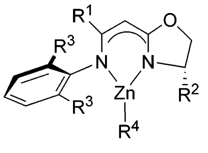
Scheme 28. Asymmetric Alternating Polymerization



5.4. Immobilized Catalysts

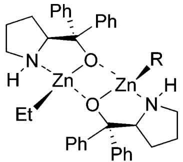
An alternating polymerization has been conducted using zinc diiminate complexes immobilized on mesoporous silica

Table 13. Asymmetric Polymerization



8a-b

Cat.	R1	R2	R3	R4
8a	*i*Pr	*t*Bu	*i*Pr	N(TMS)$_2$
8b	CF$_3$	*t*Bu	*i*Pr	N(TMS)$_2$



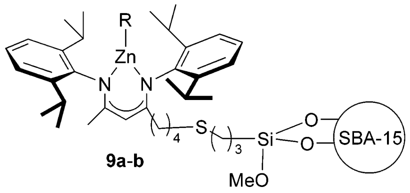
8c-d

8c R = Et
8d R = OEt

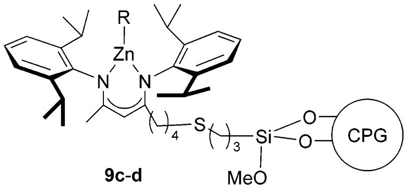
epoxide	catalyst	amount of cat. (mol %)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	M_n ($\times 10^{-3}$)	M_w/M_n	% ee (*R*, *R*)	ref
CHO	**8a**	1	7	20	24	100	4.2	14.7	1.35	86	212
CHO	**8b**	1	7	20	24	100	4.2	27.1	1.21	88	212
CHO	**8c**	2.5	30	40	16	23	1.4	11.8	15.7	49	213
CHO	**8d**	2.5	30	40	16	38	2.4	7.7	1.63	80	213

[a] TOF: estimated from the literature.

Table 14. Immobilized Catalysts for Alternating Polymerization



surface area: 830 m^2/g



surface area:~ 80 m^2/g

9a R = OMe; **9b** R = N(TMS)$_2$

9c R = OMe; **9d** R = N(TMS)$_2$

epoxide	catalyst	Zn loading (mmol/g of silica)	P_{CO_2} (bar)	temp (°C)	time (h)	TON	TOF[a] (h^{-1})	carbonate linkages (%)	M_n ($\times 10^{-3}$)	M_w/M_n	ref
CHO	**9a**	0.15	7	50	4	72	18	73	15.5	1.31	214
CHO	**9b**	0.14	7	50	4	60	12	65	21.4	1.40	214
CHO	**9c**	0.08	7	50	4	126	21	78	16.6	1.29	214
CHO	**9d**	0.09	7	50	4	78	13	72	19.7	1.36	214

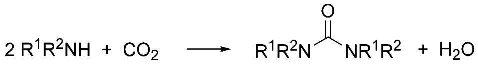
[a] TOF: estimated from the literature.

(SBA-15) and porous glass as the catalyst. However, the catalytic activities are slightly diminished compared to homogeneous catalysts (Table 14).[214]

6. Synthesis of Urea and Urethane Derivatives

Carbon dioxide readily reacts with nucleophiles. For example, urea is industrially produced by a reaction with ammonia (Scheme 29).[215−217] In order to obtain substituted ureas, dehydration is the key. Recently, the synthesis of *N*,*N*′-dialkylurea has been achieved by removing water using hydrophilic ionic liquids as reaction media (Scheme 29).[215] On the other hand, secondary or primary amines react with CO$_2$ to give carbamic acids (Scheme 30).[218] Reactions of *in situ* generated carbamic acids with electrophiles such as organic halides result in the formation of urethanes (carbamates) (Scheme 31). Various homogeneous and heterogeneous catalysts are applicable to synthesize urethane.[219−224] Mesoporous silica containing ammonium salts as the template and adenine-modified Ti-incorporated mesoporous silica work as effective catalysts even without an additional base (Scheme 32).[154,225]

Scheme 29. Urea Synthesis from CO$_2$



$$2\,R^1R^2NH + CO_2 \longrightarrow R^1R^2N\overset{O}{\overset{\|}{C}}NR^1R^2 + H_2O$$

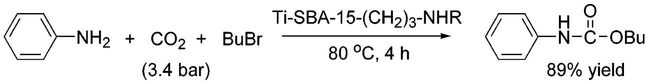
Scheme 30. Carbamic Acid Formation

$$R^1R^2NH + CO_2 \rightleftharpoons R^1R^2NCO_2H \xrightleftharpoons{\text{base}} [R^1R^2NCO_2]^-\,[(\text{base})H]^+$$

Scheme 31. Urethane Synthesis with an Organic Halide

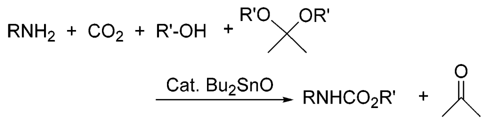
$$RNH_2 + CO_2 + R'\text{–}X + \text{Base} \longrightarrow RNHCO_2R' + HX(\text{Base})$$

Scheme 32. Urethane Synthesis Catalyzed by Mesoporous Silica



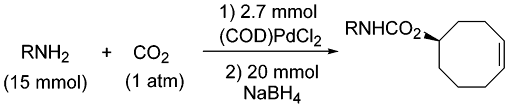
Scheme 33. Urethane Synthesis with an Alcohol

$$RNH_2 + CO_2 + R'\text{-}OH \longrightarrow RNHCO_2R' + H_2O$$

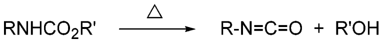


In Scheme 31, if organic halides can be replaced by alcohols, then the byproduct (H−X) becomes water; the process is environmentally friendly (Scheme 33).[226,227] However, yields are limited to a very low level due to thermodynamic limitations and catalyst deactivation caused by the coproduced water. Hence, dehydration of the reaction mixture is the key for high yields, and a method, which was developed for the dialkyl carbonate synthesis, namely dehydration using ketals, works effectively.[37] Challenges in the near future include improving the productivity (reaction

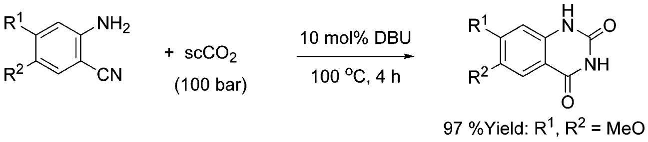
Scheme 34. Urethane Synthesis from an Alkene



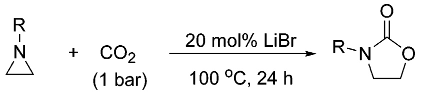
Scheme 35. Isocyanate from Urethane



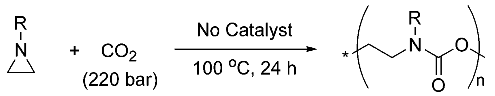
Scheme 36. Quinazoline Synthesis from CO_2



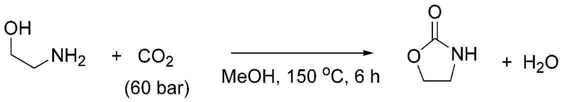
Scheme 37. Oxazolidinone Synthesis



Scheme 38. Polyurethane from CO_2



Scheme 39. Oxazolidinone from Aminoalcohol



rate) and incorporating aromatic amines as substrates. Carbamates can also be synthesized through nucleophilic addition of carbamic acids to alkenes (Scheme 34).[228]

Schemes 31–34 are important as non-phosgene routes to yield isocyanates because thermolysis of carbamates gives isocyanates (Scheme 35).[229]

Intramolecular nucleophilic attack of carbamic acid to nitrile results in quinazoline formation (Scheme 36).[230–232] Addition of DBU under supercritical conditions enhances the reaction rate.

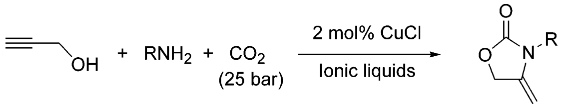
Like cyclic carbonate synthesis, a nitrogen-containing three-membered ring (aziridine) reacts with CO_2, which leads to a nitrogen-containing five-membered ring (oxazolidinone) (Scheme 37).[233–237] Although the reaction proceeds without a catalyst, the presence of various compounds promotes the reaction; typical catalysts are alkali metal salts, quaternary ammonium salts, chromium salen complexes, etc.[238–242] Ring-opening polymerization under supercritical conditions to yield polyurethanes has also been reported (Scheme 38). The resulting polymer undergoes a phase change according to the pH and temperature.[238]

Although the reaction of 1,2-aminoalcohols with CO_2 produces five-membered urethanes (oxazolidinones), the conversion is poor without dehydrating agents (Scheme 39).[243] Oxazolidinones can also be obtained by reacting carbamic acids and acetylenic compounds in the presence of a copper catalyst (Scheme 40).[244–247]

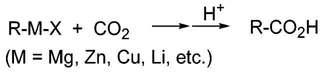
7. Synthesis of Carboxylic Acid

Along with carbonates, carboxylic acids are suitable synthetic targets starting from CO_2. Carbon nucleophiles such as Grignard reagents, alkyl lithiums, active methylene compounds, and metal enolates attack CO_2 under relatively mild conditions to generate carboxylic acids (Scheme 41).[248–252] Palladium and rhodium complexes catalyze the insertion of CO_2 into tin–carbon and boron–carbon bonds (Schemes 42 and 43).[253,254]

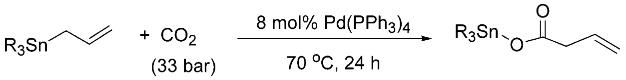
Scheme 40. Oxazolidinone from Propargylalcohol



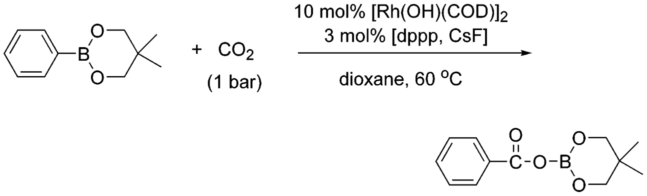
Scheme 41. Carboxylic Acid from Organometallic



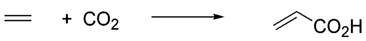
Scheme 42. CO_2 Insertion into a Tin-Carbon Bond



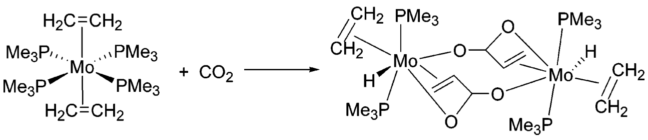
Scheme 43. CO_2 Insertion into a Boron-Carbon Bond



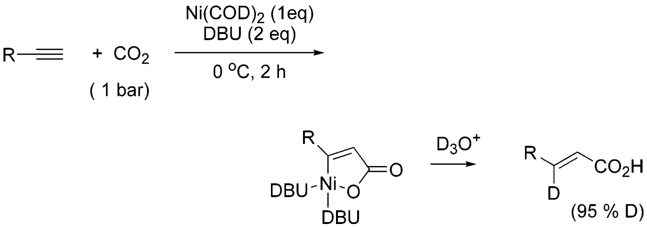
Scheme 44. Acrylic Acid from CO_2



Scheme 45. Acrylic Acid from CO_2 by Metal Complexation



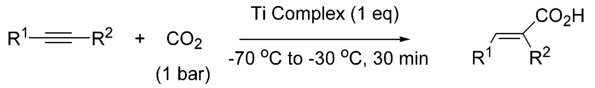
Scheme 46. Acrylic Acid Derivative from Acetylene



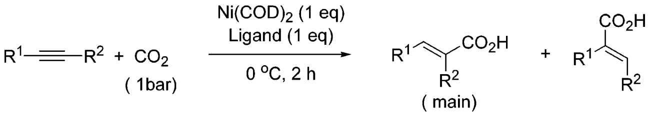
Acrylic acid, a typical unsaturated carboxylic acid, is currently consumed on a large industrial scale as a raw material for water-absorbing polymers. The acid is produced by oxidation of propylene via acrolein. If the acid can be directly synthesized from ethylene and CO_2, it would be quite attractive (Scheme 44). Because the reaction is thermodynamically possible,[255] the key is to develop an efficient catalyst. The stoichiometric formation of acrylic acid on a molybdenum complex has been reported (Scheme 45).[256–258]

Five-membered metallalactones are obtained by the reaction of a low-valent metal complex, CO_2, and an unsaturated compound (Scheme 4).[22] Although a stoichiometric amount of metal is consumed, desired unsaturated carboxylic acids are selectively synthesized via metallacycles (Schemes 46–50).[259–263] In many cases, DBU promotes the reactions, presumably by trapping CO_2 as a carbamate or a bicarbonate form.[264,265]

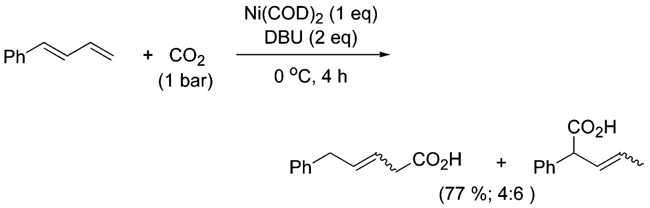
Scheme 47. Acrylic Acid Derivative from Acetylene



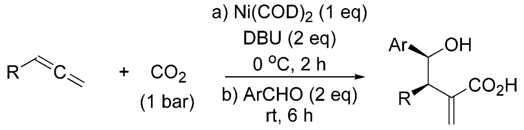
Scheme 48. Acrylic Acid Derivative from Acetylene



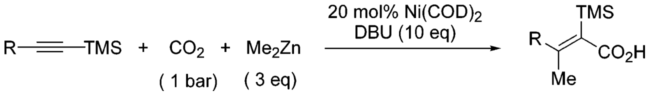
Scheme 49. Acrylic Acid Derivative from 1,3-Butadiene



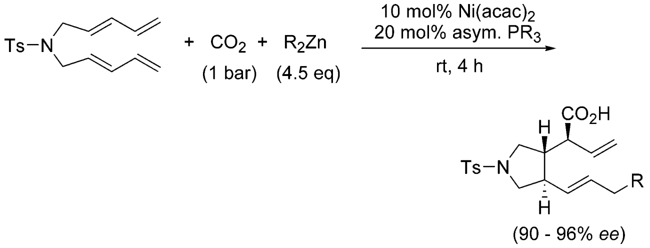
Scheme 50. Acrylic Acid Derivative from Allene



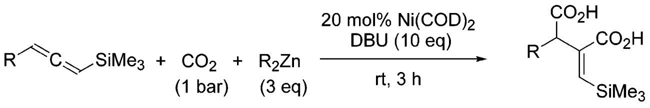
Scheme 51. Acrylic Acid Derivative from Acetylene



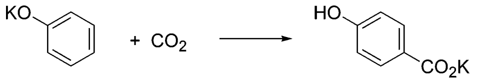
Scheme 52. Asymmetric Cyclization−Carboxylation with CO_2



Scheme 53. Dicarboxylation of Allene with CO_2



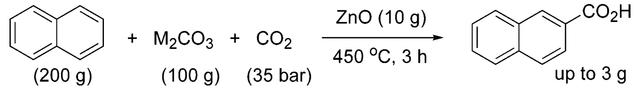
Scheme 54. Kolbe−Schmidt Reaction



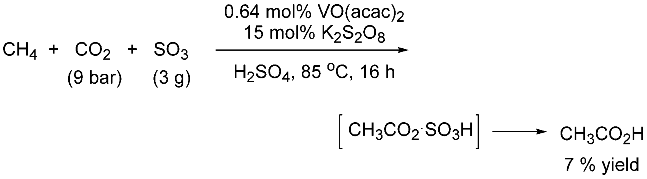
The addition of a stoichiometric amount of dialkyl zincs regenerates a low valent nickel complex through reductive elimination, and thus, nickel is catalytic (Schemes 51−53).[266−269] Asymmetric synthesis can be conducted using optically active phosphine ligands (Scheme 52).[267]

Carboxylation with CO_2 can be carried out under either basic (Schemes 54 and 55) or acidic (Schemes 56−60) conditions. Hydroxybenzoic acid is one of the few chemicals that is industrially produced from CO_2 (Kolbe−Schmidt reaction) (Scheme 54).[270−272] In addition, the following are examples of a hydrocarbon transformation to carboxylic acids: the reaction with metal carbonates under a high temperature and pressure (Henkel-type reaction) (Scheme 55),[273] and the vanadium- or palladium-catalyzed reaction with CO_2 in the presence of an oxidizing reagent such as $K_2S_2O_8$ (Scheme 56).[274,275] C−H bond activation by the Pd−$K_2S_2O_8$−CF_3CO_2H system is widely applicable to various reactions.[276] As for the reaction of CO_2 under electrophilic conditions using $AlCl_3$ as a Lewis acid, the direct activation of aromatic C−H bonds (Scheme 57)[277] and the utilization of silylated aromatic compounds have been demonstrated (Scheme 58).[278,279] Metal-catalyzed reactions of organic halides, CO_2, and hydrogen have also produced carboxylic acids (Scheme 59).[280−282] Although forming carboxylic acids by reacting olefins and CO_2 under acidic conditions has been reported, the details are unknown (Scheme 60).[283]

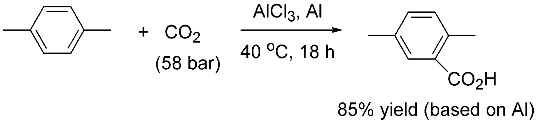
Scheme 55. Carboxylic Acid Formation by C−H Bond Activation



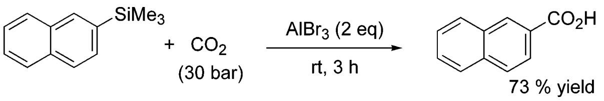
Scheme 56. Carboxylic Acid Formation by C−H Bond Activation



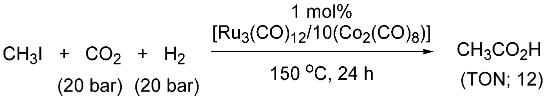
Scheme 57. Carboxylic Acid Formation by C−H Bond Activation



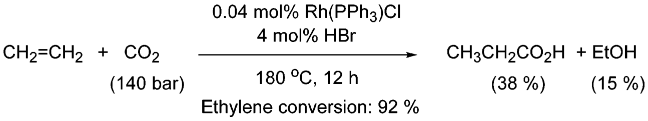
Scheme 58. Carboxylation with CO_2



Scheme 59. Carboxylation with Organic Halide



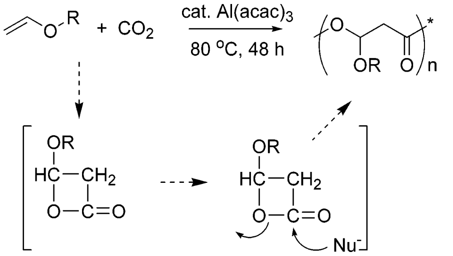
Scheme 60. Carboxylation of Ethylene



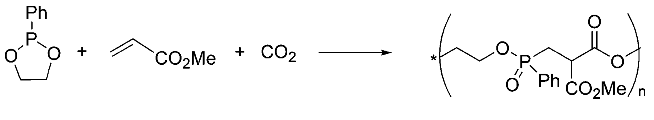
8. Synthesis of Esters and Lactones

Combining various unsaturated compounds and CO_2 results in the formation of esters and lactones. For example, polymerization of vinyl ethers under CO_2 in the presence of aluminum compounds affords polymers that incorporate CO_2 into the main chain (Scheme 61). However, the yields of these polymers are very low and further improvement is required.[284−286] A similar CO_2 incorporation has also been reported for the polymerization of a three-component system, which contains a phosphorus compound (Scheme 62).[287]

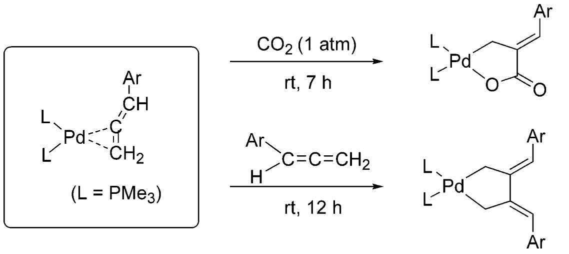
Scheme 61. Copolymerization of Vinyl Ether with CO_2



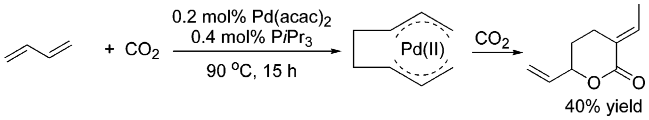
Scheme 62. Three-Component Polymerization



Scheme 63. Palladacycle Formation

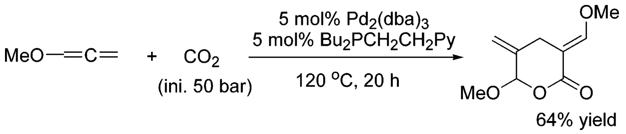


Scheme 64. Lactone from 1,3-Butadiene

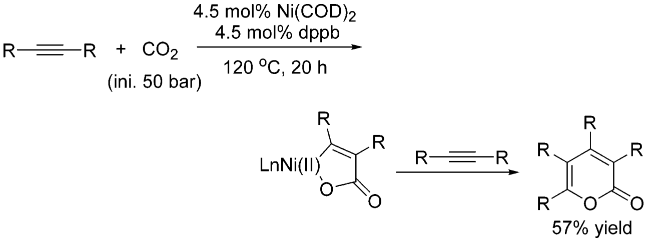


In the 1980s a lot of research was conducted on five-membered nickellacycles.[22] The X-ray structures of five-membered palladacycles have also been reported (Scheme 63, Figure 3).[288] The insertion of other unsaturated compounds leads to the ring expansion of the metallacycles. The continuing reductive elimination yields lactones and regenerates low valent metal complexes to complete the catalytic cycle. Unsaturated compounds used for these reactions are dienes (Scheme 64),[289−291] allenes (Scheme 65),[292] acetylenes (Scheme 66),[293,294] diynes (Schemes 67 and 68),[295−302] benzynes (Scheme 69),[303] and so forth. Nickel complexes with bulky carbene ligands efficiently catalyze the 2 + 2 + 2 cycloaddition between the diyne parts and CO_2 under very mild reaction conditions (60 °C, 1 bar) to yield six-membered cyclic lactones (Scheme 70).[304,305]

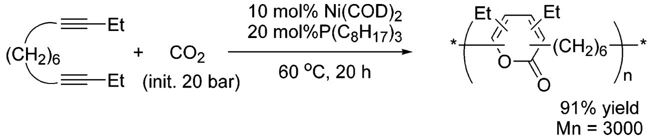
Scheme 65. Lactone from Allene



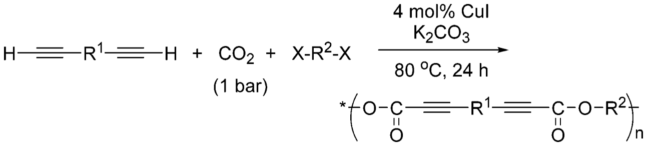
Scheme 66. Lactone from Acetylene



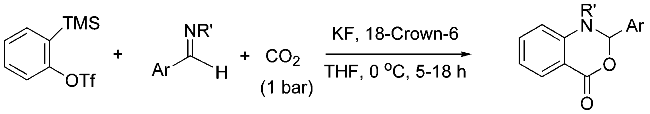
Scheme 67. Cyclic Polymerization of Diacetylene with CO_2



Scheme 68. Polymerization of Diacetylene



Scheme 69. Three-Component Cyclization with Benzyne



A five-membered ring, which can be obtained through the oxidative cyclization of CO_2 and oxygen with a palladium

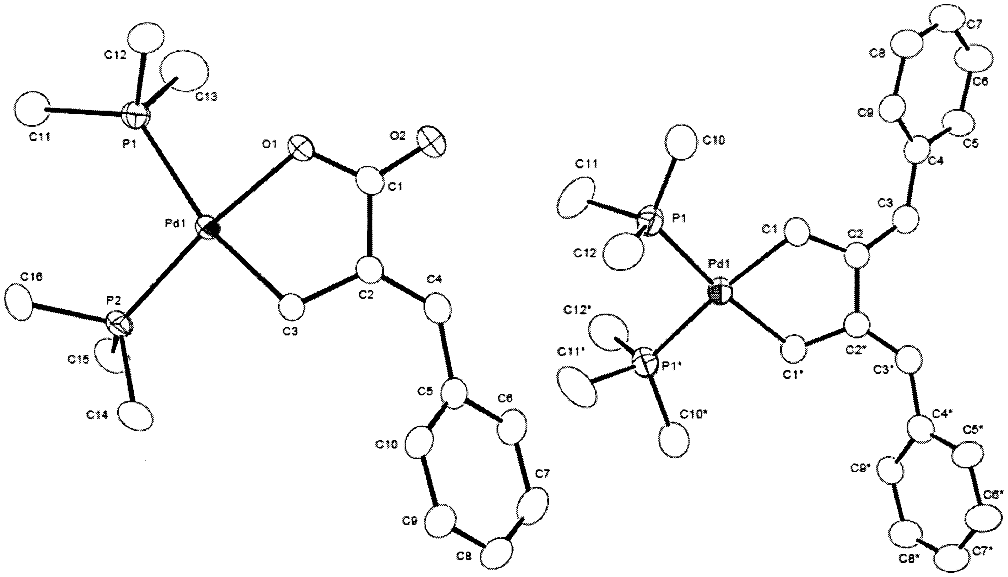
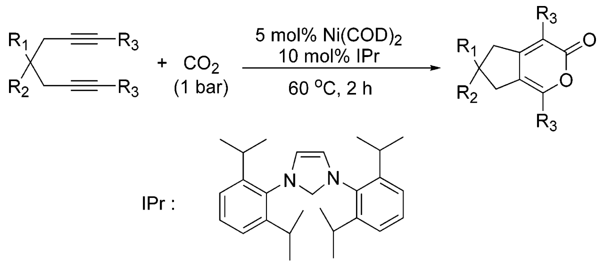
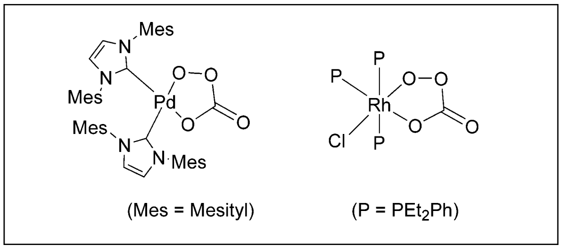


Figure 3. Molecular structures of palladalactone and palladacyclopentane.

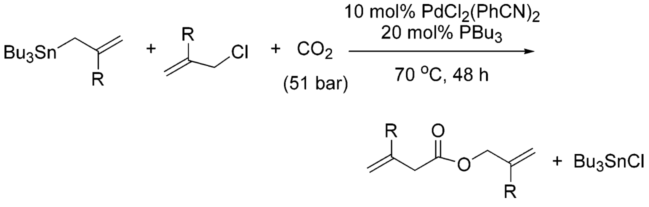
Scheme 70. Lactone from Diacetylene



Scheme 71. O2 Activation by a Metal Complex



Scheme 72. Stille-Type Three-Component Coupling



complex, has been structurally characterized by X-ray diffraction (Scheme 71).[306] A similar rhodium compound has also been reported.[307] Applying these complexes to catalytic oxidation reactions with molecular oxygen seems interesting, but there have not been successful reports. Palladium-catalyzed C−C cross coupling under a CO_2 atmosphere can give esters. The first successful report was a palladium-catalyzed C−C coupling between allyl chloride and allyl(tributyl)tin (Scheme 72).[308] Because the reactant is limited to allyl compounds, this reaction is not very practical.

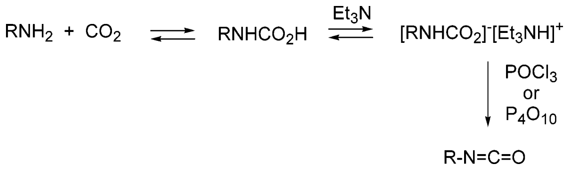
9. Synthesis of Isocyanates

By dehydrating carbamic acids, which are in equilibrium with amine and CO_2, isocyanates can be synthesized without employing phosgene. Researchers at Monsanto have been investigating this process. For example, isocyanates can be synthesized by dehydration with $POCl_3$ or P_4O_{10} in the presence of tertiary amines (Scheme 73).[309,310] Conducting this reaction on a large industrial scale will be difficult because the reaction requires an equimolar amount of dehydrating agents as well as bases, and produces a large amount of waste. As for closely related technology, namely urethane thermolysis, please see section 6 (Scheme 35).[229]

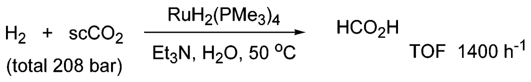
10. Hydrogenation and Hydroformylation, and Alcohol Homologation

Depending on the reaction conditions, hydrogenation of CO_2 by homogeneous catalysts yields carbon monoxide, formic acid, methanol, etc. The procedure to use supercritical CO_2 as a substrate and as a reaction medium for the CO_2 hydrogenation gave rise to numerous studies on catalysis in supercritical CO_2 (Scheme 74).[311−313] The merits of employing supercritical CO_2 for hydrogenation are that the solvent does not produce waste and enormously high hydrogen concentrations can be realized. The hydrogenation of CO_2 under supercritical conditions in the presence of methanol and dimethyl amine has resulted in the very efficient synthesis of methyl formate (Scheme 75)[314] and *N*,*N*-dimethyl formamide (Scheme 76), respectively.[315] It is noteworthy that although the reaction mixture is initially homogeneous, the mixture becomes biphasic shortly after the reaction; the ruthenium complex catalyst exists in the lower phase. A very high reaction rate, as in supercritical CO_2, can also be obtained using bulky bidentate phosphines in polar organic solvents (Scheme 77).[316] Unusual three-coordinate, 14-electron complexes have been proposed as the active catalytic species.

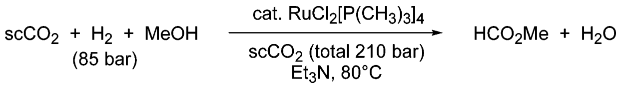
Scheme 73. Isocyanate Synthesis with CO2



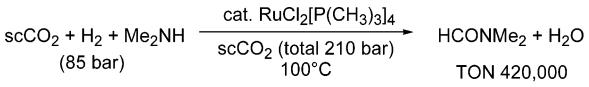
Scheme 74. Hydrogenation Using scCO2



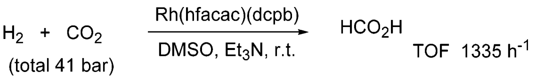
Scheme 75. Ester Formation *via* Hydrogenation



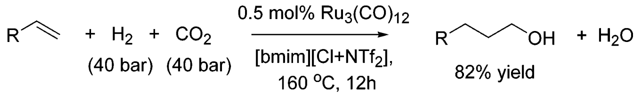
Scheme 76. Amide Formation *via* Hydrogenation



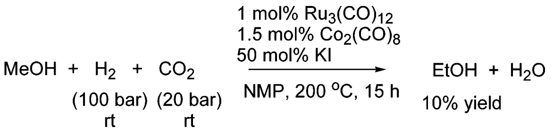
Scheme 77. Hydrogenation by an Active Rh Complex



Scheme 78. Hydroformylation with CO2

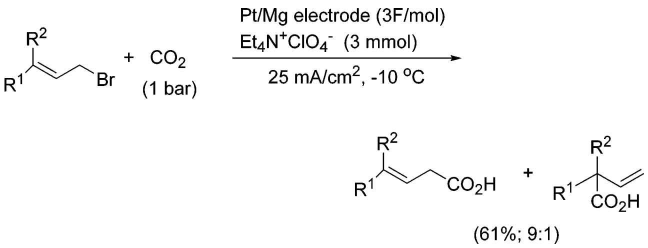


Scheme 79. Methanol Homologation with CO2

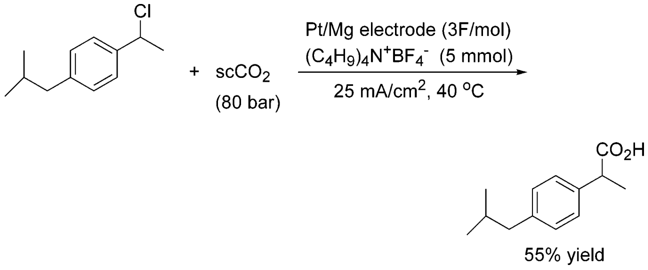


Under high-pressure CO_2 and hydrogen, alkenes are hydroformylated to yield alcohols and aldehydes in the presence of a ruthenium complex (Scheme 78).[317] Presumably, the reaction proceeds via the formation of carbon monoxide through a reverse water gas shift reaction. Homologation of alcohols using carbon dioxide is also reported in the presence of hydrogen (Scheme 79). As was the case of the hydroformylation (Scheme 78), carbon monoxide generated from CO_2 would be the real reactant.[318,319]

Scheme 80. Carboxylation of an Organic Halide



Scheme 81. Carboxylation of an Organic Halide



11. Electrochemical Reaction

Electrochemical reduction of carbon dioxide alone results in the formation of oxalic acid and its derivatives such as glycolic acid, glyoxylic acid, etc.[320] These reactions are not selective enough. By the electrochemical reactions of alkenes, ketones, or organic halides under CO_2, carboxylic groups are introduced to organic substrates. For example, allylic halides are converted to the corresponding carboxylic acids (Scheme 80),[321] while carbonyl compounds are transformed into α-hydroxycarboxylic acids. A similar electrochemical carboxylation of a benzylic chloride is promoted under supercritical conditions; the procedure was applied to the synthesis of Ibuprofen (Scheme 81).[322]

12. Prospects of CO_2 Transformation[323]

Establishing a chemical industry based on a renewable feedstock such as CO_2 is a long-standing challenge as well as a fascinating dream for synthetic chemists. Both fine and bulk chemicals are important synthetic targets. One thing that should be considered is that reactions using CO_2 as a raw material do not necessarily help mitigate the greenhouse effect, although CO_2 is a green chemical reagent in many cases. [If anyone claims CO_2 mitigation by chemical fixation, they should consider the following three points: (1) Chemical fixation of CO_2 does not necessarily reduce the total CO_2 amount because CO_2 transformation requires energy and produces CO_2. (2) The amount of CO_2 fixed by chemical industries would be much smaller compared to CO_2 emission through fuel combustion. (3) Organic chemicals in which CO_2 is fixed will emit CO_2 at the disposal stage.] In particular, CO_2 is important as a green carbonyl source. The significance of the transformation of CO_2 into useful chemicals should be attributed to the importance of utilizing a renewable feedstock.

It is reasonable to execute research on CO_2 transformations according to the following policies. First, it is important to increase the number of industrial applications by improving these reactions for commercialization. For example, the dimethyl carbonate synthesis and alternating copolymerization with epoxides are one step away from commercialization. It is noteworthy that cyclic carbonate synthesis has already been industrialized. Second, we have to grow seedling to large trees. Some candidates of such promising reactions include carboxylic acid synthesis and ester synthesis. It is especially important to improve reactions with low catalytic performance or those under severe conditions such as copolymerization of vinyl ethers and CO_2, and isocyanate synthesis from CO_2. Third, it is important to establish foundations for science to search for new reactions and new catalysts, and to elucidate reaction mechanisms at the molecular level. Examples of interesting research subjects include acrylic acid synthesis from ethylene and CO_2, and direct carboxylation of C−H bonds. Such fundamental research will lead to the new seeds for industrialization.

13. Abbreviations

acac	acetylacetonato
bmim	1-butyl-3-methylimidazolium
CHO	cyclohexene oxide
COD	1,5-cyclooctadiene
dba	dibenzylideneacetonato
DAPO	*N*,*N*-diphenylaminomethyl oxirane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dcpc	1,4-bis(dicyclohexylphosphino)butane
DMAP	4-dimethylaminopyridine
DMAQ	*N*,*N*-dimethylaminoquinoline
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
EO	ethylene oxide
N-MeIm	*N*-methylimidazole
OTf	trifluoromethanesulfonato
PCy_3	tricyclohexylphosphine
PEPO	1,2-epoxy-3-phenoxypropane
PhCN	benzonitrile
PO	propylene oxide
PPN	bis(triphenylphosphine)iminium
rt	room temperature
SO	styrene oxide
TOF	turnover frequency
TON	turnover number

14. References

(1) Zevenhoven, R.; Eloneva, S.; Teir, S. *Catal. Today* **2006**, *115*, 73.
(2) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.
(3) Aresta, M. *ACS Symp. Ser.* **2003**, *852*, 2.
(4) Aresta, M.; Dibenedetto, A.; Tommasi, I. *Energy Fuels* **2001**, *15*, 269.
(5) Song, C. S. *ACS Symp. Ser.* **2002**, *809*, 2.
(6) Xu, X. D.; Moulijn, J. A. *Energy Fuels* **1996**, *10*, 305.
(7) Aresta, M. *Energy Convers. Manage.* **1993**, *34*, 745.
(8) Aresta, M.; Quaranta, E.; Tommasi, I. *Energy Convers. Manage.* **1992**, *33*, 495.
(9) Aresta, M.; Quaranta, E. *CHEMTECH* **1997**, *27*, 32.
(10) Tundo, P.; Selva, M. *Acc. Chem. Res.* **2002**, *35*, 706.
(11) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155.
(12) Aresta, M.; Dibenedetto, A. *ACS Symp. Ser.* **2002**, *809*, 54.
(13) Kaneco, S.; Iiba, K.; Ohta, K.; Mizuno, T. *Energy Sources* **2000**, *22*, 127.
(14) Yin, X. L.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27.
(15) Walther, D.; Ruben, M.; Rau, S. *Coord. Chem. Rev.* **1999**, *182*, 67.
(16) Gibson, D. H. *Coord. Chem. Rev.* **1999**, *186*, 335.
(17) Gibson, D. H. *Chem. Rev.* **1996**, *96*, 2063.
(18) Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257.
(19) Aresta, M.; Tommasi, I. *Energy Convers. Manage.* **1997**, *38*, S373.

(20) Omae, I. *Catal. Today* **2006**, *115*, 33.
(21) Ochiai, B.; Endo, T. *Prog. Polym. Sci.* **2005**, *30*, 183.
(22) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661.
(23) Shaikh, A. A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951.
(24) Fukuoka, S.; Kawamura, M.; Komiya, K.; Tojo, M.; Hachiya, H.; Hasegawa, K.; Aminaka, M.; Okamoto, H.; Fukawa, I.; Konno, S. *Green Chem.* **2003**, *5*, 497.
(25) Pacheco, M. A.; Marshall, C. L. *Energy Fuels* **1997**, *11*, 2.
(26) Tundo, P.; Selva, M.; Memoli, S. *ACS Symp. Ser.* **2000**, *767*, 87.
(27) Cesti, P.; Bosetti, A.; Mizia, F.; Notari, M.; Ricci, M.; Rivetti, F.; Romano, U. (ENICHEM). WO-A1 01/56977.
(28) Aresta, M.; Galatola, M. *J. Clean Prod.* **1999**, *7*, 181.
(29) Kizlink, J.; Pastucha, I. *Collect. Czech. Chem. Commun.* **1995**, *60*, 687.
(30) Kizlink, J.; Pastucha, I. *Collect. Czech. Chem. Commun.* **1994**, *59*, 2116.
(31) Kizlink, J. *Collect. Czech. Chem. Commun.* **1993**, *58*, 1399.
(32) Kadokawa, J.; Habu, H.; Fukamachi, S.; Karasu, M.; Tagaya, H.; Chiba, K. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2205.
(33) Tian, Y.; Qin, Y.; Chen, L.; Fang, J.; Wang, L. *Prepr. Symp.*—*Am. Chem. Soc., Div. Fuel Chem.* **2002**, *47*, 267.
(34) Sakakura, T.; Saito, Y.; Okano, M.; Choi, J.-C.; Sako, T. *J. Org. Chem.* **1998**, *63*, 7095.
(35) Cheong, M.; Kim, S.; Park, J. B. *New J. Chem.* **1997**, *21*, 1143.
(36) Chu, G. H.; Park, J. B.; Cheong, M. *Inorg. Chim. Acta* **2000**, *307*, 131.
(37) Sakakura, T.; Choi, J.-C.; Saito, P.; Masuda, T.; Sako, T.; Oriyama, T. *J. Org. Chem.* **1999**, *64*, 4506.
(38) Sakakura, T.; Choi, J.-C.; Saito, Y.; Sako, T. *Polyhedron* **2000**, *19*, 573.
(39) Isaacs, N. S.; O'Sullivan, B.; Verhaelen, C. *Tetrahedron* **1999**, *55*, 11949.
(40) Tanaka, Y.; Sawamura, N.; Iwamoto, M. *Tetrahedron Lett.* **1998**, *39*, 9457.
(41) Kohno, K.; Choi, J.-C.; Yasuda, H.; Sakakura, T. *53th Symposium on Organometallic Chemistry*, Osaka, Japan, September 8−9, 2006; Kinki Chemical Society: Abstract PB261.
(42) Oshima, Y.; Kohno, K.; Choi, J.-C.; Sakakura, T. *87th Annual Meeting of Japan Chemical Society*, Chiba, Japan, March 27−30, 2006; Japan Chemical Society: Abstract 2PA059.
(43) Abla, M.; Choi, J.-C.; Sakakura, T. *50th Symposium on Organometallic Chemistry*, Osaka, Japan, September 28−30, 2003; Kinki Chemical Society: Abstract PB233.
(44) Zhao, T. S.; Han, Y. Z.; Sun, Y. H. *Fuel Process. Technol.* **2000**, *62*, 187.
(45) (a) Dibenedetto, A.; Pastore, C.; Aresta, M. *Catal. Today* **2006**, *115*, 88. (b) Aresta, M.; Dibenedetto, A.; Pastore, C. *Inorg. Chem.* **2003**, *42*, 3256.
(46) Dibenedetto, A.; Aresta, M.; Giannoccaro, P.; Pastore, C.; Papai, I.; Schubert, G. *Eur. J. Inorg. Chem.* **2006**, 908.
(47) Choi, J.-C.; Sakakura, T.; Sako, T. *J. Am. Chem. Soc.* **1999**, *121*, 3793.
(48) Bloodworth, A. J.; Davies, A. G.; Vasishtha, S. C. *J. Chem. Soc. C* **1967**, 1309.
(49) Davies, A. G.; Harrison, P. G. *J. Chem. Soc. C* **1967**, 1313.
(50) Sakai, S.; Fujinami, T.; Yamada, T.; Furusawa, S. *Nippon Kagaku Kaishi* **1975**, 1789.
(51) Yamazaki, N.; Nakahama, S.; Higashi, F. *Rep. Asahi Glass Found. Ind. Technol.* **1978**, *33*, 31.
(52) Ballivet-Tkatchenko, D.; Douteau, O.; Stutzmann, S. *Organometallics* **2000**, *19*, 4563.
(53) Ghosh, R.; Nethaji, M.; Samuelson, A. G. *Chem. Commun.* **2003**, 2556.
(54) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911.
(55) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.
(56) Abulimiti, I.; Oshima, Y.; Choi, J.-C.; Sakakura, T. *54th Symposium on Coordination Chemistry of Japan*, Kumamoto, Japan, September 23−25, 2004; Japan Society of Coordination Chemistry: Abstract 1PA040.
(57) Ballivet-Tkatchenko, D.; Jerphagnon, T.; Ligabue, R.; Plasseraud, L.; Poinsot, D. *Appl. Catal., A* **2003**, *255*, 93.
(58) Ballivet-Tkatchenko, D.; Burgat, R.; Chambrey, S.; Plasseraud, L.; Richard, P. *J. Organomet. Chem.* **2006**, *691*, 1498.
(59) Tomishige, K.; Sakaihori, T.; Ikeda, Y.; Fujimoto, K. *Catal. Lett.* **1999**, *58*, 225.
(60) Tomishige, K.; Ikeda, Y.; Sakaihori, T.; Fujimoto, K. *J. Catal.* **2000**, *192*, 355.
(61) Jung, K. T.; Bell, A. T. *Top. Catal.* **2002**, *20*, 97.
(62) Jung, K. T.; Bell, A. T. *J. Catal.* **2001**, *204*, 339.
(63) Tomishige, K. *Curr. Top. Catal.* **2002**, *3*, 81.
(64) Ikeda, Y.; Sakaihori, T.; Tomishige, K.; Fujimoto, K. *Catal. Lett.* **2000**, *66*, 59.
(65) Tomishige, K.; Furusawa, Y.; Ikeda, Y.; Asadullah, M.; Fujimoto, K. *Catal. Lett.* **2001**, *76*, 71.
(66) Tomishige, K.; Kunimori, K. *Appl. Catal., A* **2002**, *237*, 103.
(67) Jiang, C. J.; Guo, Y. H.; Wang, C. G.; Hu, C. W.; Wu, Y.; Wang, E. B. *Appl. Catal., A* **2003**, *256*, 203.
(68) Wu, X. L.; Xiao, M.; Meng, Y. Z.; Lu, Y. X. *J. Mol. Catal. A: Chem.* **2005**, *238*, 158.
(69) Wu, X. L.; Meng, Y. Z.; Xiao, M.; Lu, Y. X. *J. Mol. Catal. A: Chem.* **2006**, *249*, 93.
(70) Choi, J.-C.; He, L. N.; Yasuda, H.; Sakakura, T. *Green Chem.* **2002**, *4*, 230.
(71) Li, C. F.; Zhong, S. H. *Catal. Today* **2003**, *82*, 83.
(72) Fujita, S.; Bhanage, B. M.; Ikushima, Y.; Arai, M. *Green Chem.* **2001**, *3*, 87.
(73) Fang, S. N.; Fujimoto, K. *Appl. Catal., A* **1996**, *142*, L1.
(74) Cao, F. H.; Fang, D. Y.; Liu, D. H.; Ying, W. Y. *ACS Symp. Ser.* **2003**, *852*, 159.
(75) Cai, Q. H.; Jin, C.; Lu, B.; Tangbo, H. J.; Shan, Y. K. *Catal. Lett.* **2005**, *103*, 225.
(76) Oi, S.; Kuroda, Y.; Matsuno, S.; Inoue, Y. *Nippon Kagaku Kaishi* **1993**, 985.
(77) Chun, Y.; He, Y. G.; Zhu, J. H. *React. Kinet. Catal. Lett.* **2001**, *74*, 23.
(78) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M. *Appl. Catal., A* **2001**, *219*, 259.
(79) Cui, H. Y.; Wang, T.; Wang, F. J.; Gu, C. R.; Wang, P. L.; Dai, Y. Y. *Ind. Eng. Chem. Res.* **2003**, *42*, 3865.
(80) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Torii, K.; Arai, M. *Green Chem.* **2003**, *5*, 71.
(81) Kishimoto, Y.; Ogawa, I. *Ind. Eng. Chem. Res.* **2004**, *43*, 8155.
(82) Jiang, Q.; Yang, Y. *Catal. Lett.* **2004**, *95*, 127.
(83) Chang, Y. H.; Jiang, T.; Han, B. X.; Liu, Z. M.; Wu, W. Z.; Gao, L.; Li, J. C.; Gao, H. X.; Zhao, G. Y.; Huang, J. *Appl. Catal., A* **2004**, *263*, 179.
(84) Li, Y.; Zhao, X. Q.; Wang, Y. J. *Appl. Catal., A* **2005**, *279*, 205.
(85) Tian, J. S.; Wang, J. Q.; Chen, J. Y.; Fan, J. G.; Cai, F.; He, L. N. *Appl. Catal., A* **2006**, *301*, 215.
(86) Srivastava, R.; Srinivas, D.; Ratnasamy, P. *J. Catal.* **2006**, *241*, 34.
(87) Baba, A.; Kashiwagi, H.; Matsuda, H. *Organometallics* **1987**, *6*, 137.
(88) Baba, A.; Kashiwagi, H.; Matsuda, H. *Tetrahedron Lett.* **1985**, *26*, 1323.
(89) Aresta, M.; Dibenedetto, A. *J. Mol. Catal. A: Chem.* **2002**, *182*, 399.
(90) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B. T.; Kunimori, K. *Green Chem.* **2004**, *6*, 206.
(91) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B. T.; Kunimori, K. *Catal. Lett.* **2004**, *95*, 45.
(92) Du, Y.; Kong, D. L.; Wang, H. Y.; Cai, F.; Tian, H. S.; Wang, J. Q.; He, L. N. *J. Mol. Catal. A: Chem.* **2005**, *241*, 233.
(93) Aresta, M.; Dibenedetto, A.; Dileo, C.; Tommasi, I.; Amodio, E. *J. Supercrit. Fluids* **2003**, *25*, 177.
(94) Yoshida, M.; Fujita, M.; Ishii, T.; Ihara, M. *J. Am. Chem. Soc.* **2003**, *125*, 4874.
(95) Yoshida, M.; Ihara, M. *Chem.*—*Eur. J.* **2004**, *10*, 2886.
(96) Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198.
(97) Zhao, T. S.; Han, Y. Z.; Sun, Y. H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3047.
(98) Sun, Y. H. *Stud. Surf. Sci. Catal.* **2004**, *153*, 9.
(99) Wang, J. Q.; Kong, D. L.; Chen, J. Y.; Cai, F.; He, L. N. *J. Mol. Catal. A: Chem.* **2006**, *249*, 143.
(100) Srivastava, R.; Srinivas, D.; Ratnasamy, P. *Appl. Catal., A* **2005**, *289*, 128.
(101) Lu, X. B.; Zhang, Y. J.; Jin, K.; Luo, L. M.; Wang, H. *J. Catal.* **2004**, *227*, 537.
(102) Lu, X. B.; Zhang, Y. J.; Liang, B.; Li, X.; Wang, H. *J. Mol. Catal. A: Chem.* **2004**, *210*, 31.
(103) Lu, X. B.; He, R.; Bai, C. X. *J. Mol. Catal. A: Chem.* **2002**, *186*, 1.
(104) Lu, X. B.; Feng, X. J.; He, R. *Appl. Catal., A* **2002**, *234*, 25.
(105) Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498.
(106) Darensbourg, D. J.; Fang, C. C.; Rodgers, J. L. *Organometallics* **2004**, *23*, 924.
(107) Shen, Y. M.; Duan, W. L.; Shi, M. *J. Org. Chem.* **2003**, *68*, 1559.
(108) Lu, X. B.; Liang, B.; Zhang, Y. J.; Tian, Y. Z.; Wang, Y. M.; Bai, C. X.; Wang, H.; Zhang, R. *J. Am. Chem. Soc.* **2004**, *126*, 3732.
(109) Jing, H. W.; Edulji, S. K.; Gibbs, J. M.; Stern, C. L.; Zhou, H. Y.; Nguyen, S. T. *Inorg. Chem.* **2004**, *43*, 4315.
(110) Kasuga, K.; Kato, T.; Kabata, N.; Handa, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2885.
(111) Sugimoto, H.; Inoue, S. *Pure Appl. Chem.* **1998**, *70*, 2365.
(112) Kasuga, K.; Kabata, N.; Kato, T.; Sugimori, T.; Handa, M. *Inorg. Chim. Acta* **1998**, *278*, 223.
(113) Ji, D. F.; Lu, X. B.; He, R. *Appl. Catal., A* **2000**, *203*, 329.

(114) Kasuga, K.; Nagao, S.; Fukumoto, T.; Handa, M. *Polyhedron* **1996**, *15*, 69.
(115) Sun, J. M.; Fujita, S.; Arai, M. *J. Organomet. Chem.* **2005**, *690*, 3490.
(116) Peng, J. J.; Deng, Y. Q. *New J. Chem.* **2001**, *25*, 639.
(117) Kim, Y. J.; Cheong, M. *Bull. Korean Chem. Soc.* **2002**, *23*, 1027.
(118) Kawanami, H.; Sasaki, A.; Matsui, K.; Ikushima, Y. *Chem. Commun.* **2003**, 896.
(119) Kim, H. S.; Kim, J. J.; Kim, H.; Jang, H. G. *J. Catal.* **2003**, *220*, 44.
(120) Palgunadi, J.; Kwon, O. S.; Lee, H.; Bae, J. Y.; Ahn, B. S.; Min, N. Y.; Kim, H. S. *Catal. Today* **2004**, *98*, 511.
(121) Li, F. W.; Xiao, L. F.; Xia, C. G.; Hu, B. *Tetrahedron Lett.* **2004**, *45*, 8307.
(122) Kim, Y. J.; Varma, R. S. *J. Org. Chem.* **2005**, *70*, 7882.
(123) Sun, J. M.; Fujita, S.; Zhao, F. Y.; Arai, M. *Green Chem.* **2004**, *6*, 613.
(124) Calo, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. *Org. Lett.* **2002**, *4*, 2561.
(125) Li, F. W.; Xia, C. G.; Xu, L. W.; Sun, W.; Chen, G. X. *Chem. Commun.* **2003**, 2042.
(126) Man, M. L.; Lam, K. C.; Sit, W. N.; Ng, S. M.; Zhou, Z. Y.; Lin, Z. Y.; Lau, C. P. *Chem.—Eur. J.* **2006**, *12*, 1004.
(127) Kim, H. S.; Bae, J. Y.; Lee, J. S.; Kwon, O. S.; Jelliarko, P.; Lee, S. D.; Lee, S. H. *J. Catal.* **2005**, *232*, 80.
(128) Srivastava, R.; Bennur, T. H.; Srinivas, D. *J. Mol. Catal. A: Chem.* **2005**, *226*, 199.
(129) Darensbourg, D. J.; Ganguly, P.; Billodeaux, D. R. *Organometallics* **2004**, *23*, 6025.
(130) Kasuga, K.; Kabata, N. *Inorg. Chim. Acta* **1997**, *257*, 277.
(131) Huang, J. W.; Shi, M. *J. Org. Chem.* **2003**, *68*, 6705.
(132) Kossev, K.; Koseva, N.; Troev, K. *J. Mol. Catal. A: Chem.* **2003**, *194*, 29.
(133) Sun, J. M.; Fujita, S. I.; Zhao, F. Y.; Arai, M. *Appl. Catal., A* **2005**, *287*, 221.
(134) Baba, A.; Nozaki, T.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1552.
(135) Yasuda, H.; He, L. N.; Sakakura, T.; Hu, C. W. *J. Catal.* **2005**, *233*, 119.
(136) Shen, Y. M.; Duan, W. L.; Shi, M. *Eur. J. Org. Chem.* **2004**, 3080.
(137) Shen, Y. M.; Duan, W. L.; Shi, M. *Adv. Synth. Catal.* **2003**, *345*, 337.
(138) He, L. N.; Yasuda, H.; Sakakura, T. *Green Chem.* **2003**, *5*, 92.
(139) Sako, T.; Fukai, T.; Sahashi, R.; Sone, M. *Ind. Eng. Chem. Res.* **2002**, *41*, 5353.
(140) Sako, T.; Sahashi, R.; Fujita, Y. *Kobunshi Ronbunshu* **2005**, *62*, 275.
(141) Kawanami, H.; Ikushima, Y. *Chem. Commun.* **2000**, 2089.
(142) Yasuda, H.; He, L. N.; Sakakura, T. *J. Catal.* **2002**, *209*, 547.
(143) Yasuda, H.; He, L. N.; Sakakura, T. *Stud. Surf. Sci. Catal.* **2003**, *145*, 259.
(144) Ramin, M.; van Vegten, N.; Grunwaldt, J. D.; Baiker, A. *J. Mol. Catal. A: Chem.* **2006**, *258*, 165.
(145) Yasuda, H.; He, L. N.; Takahashi, T.; Sakakura, T. *Appl. Catal., A* **2006**, *298*, 177.
(146) Fujita, S.; Bhanage, B. M.; Ikushima, Y.; Shirai, M.; Torii, K.; Arai, M. *Catal. Lett.* **2002**, *79*, 95.
(147) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526.
(148) Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yoshihara, M.; Maeshima, T. *Chem. Commun.* **1997**, 1129.
(149) Doskocil, E. J. *Microporous Mesoporous Mater.* **2004**, *76*, 177.
(150) Tu, M.; Davis, R. J. *J. Catal.* **2001**, *199*, 85.
(151) Mori, K.; Mitani, Y.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **2005**, 3331.
(152) Sankar, M.; Tarte, N. H.; Manikandan, P. *Appl. Catal., A* **2004**, *276*, 217.
(153) Srivastava, R.; Srinivas, D.; Ratnasamy, P. *Catal. Lett.* **2003**, *91*, 133.
(154) Srivastava, R.; Srinivas, D.; Ratnasamy, P. *Tetrahedron Lett.* **2006**, *47*, 4213.
(155) Du, Y.; Wang, J. Q.; Chen, J. Y.; Cai, F.; Tian, J. S.; Kong, D. L.; He, L. N. *Tetrahedron Lett.* **2006**, *47*, 1271.
(156) Xiao, L. F.; Li, F. W.; Xia, C. G. *Appl. Catal., A* **2005**, *279*, 125.
(157) Du, Y.; Cai, F.; Kong, D. L.; He, L. N. *Green Chem.* **2005**, *7*, 518.
(158) Shi, F.; Zhang, Q. H.; Ma, Y. B.; He, Y. D.; Deng, Y. Q. *J. Am. Chem. Soc.* **2005**, *127*, 4182.
(159) Alvaro, M.; Baleizao, C.; Carbonell, E.; El Ghoul, M.; Garcia, H.; Gigante, B. *Tetrahedron* **2005**, *61*, 12131.
(160) Park, D. W.; Yu, B. S.; Jeong, E. S.; Kim, I.; Kim, M. I.; Oh, K. J.; Park, S. W. *Catal. Today* **2004**, *98*, 499.
(161) Kim, H. S.; Kim, J. J.; Kwon, H. N.; Chung, M. J.; Lee, B. G.; Jang, H. G. *J. Catal.* **2002**, *205*, 226.
(162) Nishikubo, T.; Kameyama, A.; Yamashita, J.; Fukumitsu, T.; Maejima, C.; Tomoi, M. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1011.
(163) Nishikubo, T.; Kameyama, A.; Yamashita, J.; Tomoi, M.; Fukuda, W. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 939.
(164) Yamashita, J.; Kameyama, A.; Nishikubo, T.; Fukuda, W.; Tomoi, M. *Kobunshi Ronbunshu* **1993**, *50*, 577.
(165) Barbarini, A.; Maggi, R.; Mazzacani, A.; Mori, G.; Sartori, G.; Sartorio, R. *Tetrahedron Lett.* **2003**, *44*, 2931.
(166) Ramin, M.; Grunwaldt, J. D.; Baiker, A. *J. Catal.* **2005**, *234*, 256.
(167) Alvaro, M.; Baleizao, C.; Das, D.; Carbonell, E.; Garcia, H. *J. Catal.* **2004**, *228*, 254.
(168) Takahashi, T.; Watahiki, T.; Kitazume, S.; Yasuda, H.; Sakakura, T. *Chem. Commun.* **2006**, 1664.
(169) Tanaka, H.; Kitaichi, Y.; Sato, M.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2004**, *33*, 676.
(170) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618.
(171) Inoue, S. *Gendai Kagaku* **2005**, *408*, 42.
(172) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B* **1969**, *7*, 287.
(173) Hampel, O.; Rode, C.; Walther, D.; Beckert, R.; Gorls, H. *Z. Naturforsch., B* **2002**, *57*, 946.
(174) Walther, M.; Wermann, K.; Lutsche, M.; Gunther, W.; Gorls, H.; Anders, E. *J. Org. Chem.* **2006**, *71*, 1399.
(175) Darensbourg, D. J.; Lewis, S. J.; Rodgers, J. L.; Yarbrough, J. C. *Inorg. Chem.* **2003**, *42*, 581.
(176) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577.
(177) Xiao, Y. L.; Wang, Z.; Ding, K. L. *Chem.—Eur. J.* **2005**, *11*, 3668.
(178) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738.
(179) van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G. J. M. *Macromolecules* **2005**, *38*, 7306.
(180) Eberhardt, R.; Allmendinger, M.; Luinstra, G. A.; Rieger, B. *Organometallics* **2003**, *22*, 211.
(181) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284.
(182) Kroger, M.; Folli, C.; Walter, O.; Doring, M. *Adv. Synth. Catal.* **2005**, *347*, 1325.
(183) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S. I.; Yun, H. S.; Lee, H.; Park, Y. W. *J. Am. Chem. Soc.* **2005**, *127*, 3031.
(184) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487.
(185) Eberhardt, R.; Allmendinger, M.; Zintl, M.; Troll, C.; Luinstra, G. A.; Rieger, B. *Macromol. Chem. Phys.* **2004**, *205*, 42.
(186) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251.
(187) Qin, Z. Q.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484.
(188) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869.
(189) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans.* **2006**, 237.
(190) Lu, X. B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574.
(191) Lu, X. B.; Shi, L.; Wang, Y. M.; Zhang, R.; Zhang, Y. J.; Peng, X. J.; Zhang, Z. C.; Li, B. *J. Am. Chem. Soc.* **2006**, *128*, 1664.
(192) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.* **2004**, *43*, 1831.
(193) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024.
(194) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026.
(195) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335.
(196) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194.
(197) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144.
(198) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem.* **2005**, *44*, 4622.
(199) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303.
(200) Vitanova, D. V.; Hampel, F.; Hultzsch, K. C. *J. Organomet. Chem.* **2005**, *690*, 5182.
(201) Cui, D. M.; Nishiura, M.; Hou, Z. M. *Macromolecules* **2005**, *38*, 4089.
(202) Sugimoto, H.; Ohshima, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3549.
(203) Kim, I.; Yi, M. J.; Byun, S. H.; Park, D. W.; Kim, B. U.; Ha, C. S. *Macromol. Symp.* **2005**, *224*, 181.
(204) Kim, J. S.; Kim, H.; Yoon, J.; Heo, K.; Ree, M. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4079.
(205) Wang, J. T.; Zhu, Q.; Lu, X. L.; Meng, Y. Z. *Eur. Polym. J.* **2005**, *41*, 1108.

(206) Meng, Y. Z.; Wan, W.; Xiao, M.; Hay, A. S. *Green Chem.* **2004**, *6*, 249.
(207) Zhu, Q.; Meng, Y. Z.; Tjong, S. C.; Zhang, Y. M.; Wan, W. *Polym. Int.* **2003**, *52*, 799.
(208) Hsu, T. J.; Tan, C. S. *Polymer* **2001**, *42*, 5143.
(209) Hsu, T. J.; Tan, C. S. *Polymer* **2002**, *43*, 4535.
(210) Tan, C. S.; Kuo, T. W. *J. Appl. Polym. Sci.* **2005**, *98*, 750.
(211) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404.
(212) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007.
(213) Nakano, K.; Nozaki, K.; Hiyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 5501.
(214) Yu, K. Q.; Jones, C. W. *Organometallics* **2003**, *22*, 2571.
(215) Shi, F.; Deng, Y. Q.; SiMa, T. L.; Peng, J. J.; Gu, Y. L.; Qiao, B. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 3257.
(216) Tai, C. C.; Huck, M. J.; McKoon, E. P.; Woo, T.; Jessop, P. G. *J. Org. Chem.* **2002**, *67*, 9070.
(217) Nomura, R.; Hasegawa, Y.; Ishimoto, M.; Toyosaki, T.; Matsuda, H. *J. Org. Chem.* **1992**, *57*, 7339.
(218) Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857.
(219) Salvatore, R. N.; Shin, S. I.; Nagle, A. S.; Jung, K. W. *J. Org. Chem.* **2001**, *66*, 1035.
(220) Yoshida, M.; Hara, N.; Okuyama, S. *Chem. Commun.* **2000**, 151.
(221) McGhee, W.; Riley, D.; Christ, K.; Pan, Y.; Parnas, B. *J. Org. Chem.* **1995**, *60*, 2820.
(222) Aresta, M.; Quaranta, E. *Tetrahedron* **1992**, *48*, 1515.
(223) McGhee, W. D.; Riley, D. P.; Christ, M. E.; Christ, K. M. *Organometallics* **1993**, *12*, 1429.
(224) Srivastava, R.; Manju, M. D.; Srinivas, D.; Ratnasamy, P. *Catal. Lett.* **2004**, *97*, 41.
(225) Srivastava, R.; Srinivas, D.; Ratnasamy, P. *J. Catal.* **2005**, *233*, 1.
(226) Abla, M.; Choi, J.-C.; Sakakura, T. *Chem. Commun.* **2001**, 2238.
(227) Abla, M.; Choi, J.-C.; Sakakura, T. *Green Chem.* **2004**, *6*, 524.
(228) McGhee, W. D.; Riley, D. P. *Organometallics* **1992**, *11*, 900.
(229) Valli, V. L. K.; Alper, H. *J. Org. Chem.* **1995**, *60*, 257.
(230) Connolly, T. J.; McGarry, P.; Sukhtankar, S. *Green Chem.* **2005**, *7*, 586.
(231) Mizuno, T.; Ishino, Y. *Tetrahedron* **2002**, *58*, 3155.
(232) Mizuno, T.; Iwai, T.; Ishino, Y. *Tetrahedron Lett.* **2004**, *45*, 7073.
(233) Kawanami, H.; Matsumoto, H.; Ikushima, Y. *Chem. Lett.* **2005**, *34*, 60.
(234) Miller, A. W.; Nguyen, S. T. *Org. Lett.* **2004**, *6*, 2301.
(235) Sudo, A.; Morioka, Y.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2004**, *45*, 1363.
(236) Sudo, A.; Morioka, Y.; Koizumi, E.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2003**, *44*, 7889.
(237) Shi, M.; Jiang, J. K.; Shen, Y. M.; Feng, Y. S.; Lei, G. X. *J. Org. Chem.* **2000**, *65*, 3443.
(238) Ihata, O.; Kayaki, Y.; Ikariya, T. *Chem. Commun.* **2005**, 2268.
(239) Ihata, O.; Kayaki, Y.; Ikariya, T. *Kobunshi Ronbunshu* **2005**, *62*, 196.
(240) Ochiai, B.; Inoue, S.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6613.
(241) Ihata, O.; Kayaki, Y.; Ikariya, T. *Macromolecules* **2005**, *38*, 6429.
(242) Ihata, O.; Kayaki, Y.; Ikariya, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 717.
(243) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M. *Green Chem.* **2003**, *5*, 340.
(244) Gu, Y. L.; Zhang, Q. H.; Duan, Z. Y.; Zhang, J.; Zhang, S. G.; Deng, Y. Q. *J. Org. Chem.* **2005**, *70*, 7376.
(245) Feroci, M.; Orsini, M.; Sotgiu, G.; Rossi, L.; Inesi, A. *J. Org. Chem.* **2005**, *70*, 7795.
(246) Costa, M.; Chiusoli, G. P.; Rizzardi, M. *Chem. Commun.* **1996**, 1699.
(247) Shi, M.; Shen, Y. M. *J. Org. Chem.* **2002**, *67*, 16.
(248) Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191.
(249) Chiba, K.; Tagaya, H.; Miura, S.; Karasu, M. *Chem. Lett.* **1992**, 923.
(250) Chiba, K.; Tagaya, H.; Karasu, M.; Ishizuka, M.; Sugo, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 452.
(251) Abe, H.; Inoue, S. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1197.
(252) Quirk, R. P.; Yin, J.; Fetters, L. J.; Kastrup, R. V. *Macromolecules* **1992**, *25*, 2262.
(253) Shi, M.; Nicholas, K. M. *J. Am. Chem. Soc.* **1997**, *119*, 5057.
(254) Ukai, K.; Aoki, M.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2006**, *128*, 8706.
(255) Aresta, M.; Dibenedetto, A. *Catal. Today* **2004**, *98*, 455.
(256) Galindo, A.; Pastor, A.; Perez, P. J.; Carmona, E. *Organometallics* **1993**, *12*, 4443.
(257) Schubert, G.; Papai, I. *J. Am. Chem. Soc.* **2003**, *125*, 14847.
(258) Papai, I.; Schubert, G.; Mayer, I.; Besenyei, G.; Aresta, M. *Organometallics* **2004**, *23*, 5252.
(259) Saito, S.; Nakagawa, S.; Koizumi, T.; Hirayama, K.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 3975.
(260) Six, Y. *Eur. J. Org. Chem.* **2003**, 1157.
(261) Aoki, M.; Kaneko, M.; Izumi, S.; Ukai, K.; Iwasawa, N. *Chem. Commun.* **2004**, 2568.
(262) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2001**, *123*, 2895.
(263) Takimoto, M.; Kawamura, M.; Mori, M. *Org. Lett.* **2003**, *5*, 2599.
(264) Perez, E. R.; Santos, R. H. A.; Gambardella, M. T. P.; de Macedo, L. G. M.; Rodrigues, U. P.; Launay, J. C.; Franco, D. W. *J. Org. Chem.* **2004**, *69*, 8005.
(265) Heldebrant, D. J.; Jessop, P. G.; Thomas, C. A.; Eckert, C. A.; Liotta, C. L. *J. Org. Chem.* **2005**, *70*, 5335.
(266) Shimizu, K.; Takimoto, M.; Sato, Y.; Mori, M. *Org. Lett.* **2005**, *7*, 195.
(267) Takimoto, M.; Nakamura, Y.; Kimura, K.; Mori, M. *J. Am. Chem. Soc.* **2004**, *126*, 5956.
(268) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2002**, *124*, 10008.
(269) Takimoto, M.; Kawamura, M.; Mori, M.; Sato, Y. *Synlett* **2005**, 2019.
(270) Kosugi, Y.; Imaoka, Y.; Gotoh, F.; Rahim, M. A.; Matsui, Y.; Sakanishi, K. *Org. Biomol. Chem.* **2003**, *1*, 817.
(271) Rahim, M. A.; Matsui, Y.; Matsuyama, T.; Kosugi, Y. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2191.
(272) Sclafani, A.; Palmisano, L.; Farneti, G. *Chem. Commun.* **1997**, 529.
(273) Thomas, F.; Garo, G.; Susan, F. (Shell Oil). WO-A1 01/16072.
(274) Zerella, M.; Mukhopadhyay, S.; Bell, A. T. *Org. Lett.* **2003**, *5*, 3193.
(275) Fujiwara, Y.; Taniguchi, Y.; Takaki, K.; Kurioka, M.; Jintoku, T.; Kitamura, T. *Stud. Surf. Sci. Catal.* **1997**, *107*, 275.
(276) Jia, C. G.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.
(277) Olah, G. A.; Torok, A.; Joschek, J. P.; Bucsi, I.; Esteves, P. M.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **2002**, *124*, 11379.
(278) Hattori, T.; Suzuki, Y.; Miyano, S. *Chem. Lett.* **2003**, *32*, 454.
(279) Suzuki, Y.; Hattori, T.; Okuzawa, T.; Miyano, S. *Chem. Lett.* **2002**, 102.
(280) Fukuoka, A.; Gotoh, N.; Kobayashi, N.; Hirano, M.; Komiya, S. *Chem. Lett.* **1995**, 567.
(281) Amatore, C.; Jutand, A.; Khalil, F.; Nielsen, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 7076.
(282) Osakada, K.; Sato, R.; Yamamoto, T. *Organometallics* **1994**, *13*, 4645.
(283) Lapidus, A. L.; Pirozhkov, S. D.; Zelinsky, N. D. *Proc. 9th Int. Congr. Catal.* **1988**, *3*, 1028.
(284) Yokoyama, C.; Kawase, Y.; Shibasaki-Kitakawa, N.; Smith, R. L. *J. Appl. Polym. Sci.* **2003**, *89*, 3167.
(285) Soga, K.; Hosoda, S.; Tasuka, Y.; Ikeda, S. *J. Polym. Sci., Polym. Lett.* **1975**, *13*, 265.
(286) Soga, K.; Sato, M.; Hosoda, S.; Ikeda, S. *J. Polym. Sci., Polym. Lett.* **1975**, *13*, 543.
(287) Saegusa, T.; Kobayashi, S.; Kimura, Y. *Macromolecules* **1977**, *10*, 68.
(288) Shiraishi, K.; Choi, J.-C.; Sakakura, T. *50th Symposium on Organometallic Chemistry*, Osaka, Japan, September 28−30, 2003; Kinki Chemical Society: Abstract B304.
(289) Behr, A.; Brehme, V. A. *J. Mol. Catal. A: Chem.* **2002**, *187*, 69.
(290) Behr, A.; Heite, M. *Chem. Ing. Tech.* **2000**, *72*, 58.
(291) Behr, A.; Juszak, K. D. *J. Organomet. Chem.* **1983**, *255*, 263.
(292) Tsuda, T.; Yamamoto, T.; Saegusa, T. *J. Organomet. Chem.* **1992**, *429*, C46.
(293) Inoue, Y.; Itoh, Y.; Kazama, H.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3329.
(294) Hoberg, H.; Schaefer, D.; Burkhart, G.; Kruger, C.; Romao, M. J. *J. Organomet. Chem.* **1984**, *266*, 203.
(295) Tsuda, T.; Yasukawa, H.; Komori, K. *Macromolecules* **1995**, *28*, 1356.
(296) Tsuda, T.; Yasukawa, H.; Hokazono, H.; Kitaike, Y. *Macromolecules* **1995**, *28*, 1312.
(297) Tsuda, T.; Hokazono, H. *Macromolecules* **1994**, *27*, 1289.
(298) Tsuda, T.; Ooi, O.; Maruta, K. *Macromolecules* **1993**, *26*, 4840.
(299) Tsuda, T.; Kitaike, Y.; Ooi, O. *Macromolecules* **1993**, *26*, 4956.
(300) Tsuda, T.; Maruta, K.; Kitaike, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1498.
(301) Tsuda, T.; Maruta, K. *Macromolecules* **1992**, *25*, 6102.
(302) Oi, S. C.; Fukue, Y.; Nemoto, K.; Inoue, Y. *Macromolecules* **1996**, *29*, 2694.
(303) Yoshida, H.; Fukushima, H.; Ohshita, J.; Kunai, A. *J. Am. Chem. Soc.* **2006**, *128*, 11040.
(304) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188.
(305) Tekavec, T. N.; Arif, A. M.; Louie, J. *Tetrahedron* **2004**, *60*, 7431.
(306) Yamashita, M.; Goto, K.; Kawashima, T. *J. Am. Chem. Soc.* **2005**, *127*, 7294.
(307) Aresta, M.; Dibenedetto, A.; Tommasi, I. *Eur. J. Inorg. Chem.* **2001**, 1801.

(308) Franks, R. J.; Nicholas, K. M. *Organometallics* **2000**, *19*, 1458.

(309) Waldman, T. E.; McGhee, W. D. *J. Chem. Soc., Chem. Commun.* **1994**, 957.

(310) Saylik, D.; Horvath, M. J.; Elmes, P. S.; Jackson, W. R.; Lovel, C. G.; Moody, K. *J. Org. Chem.* **1999**, *64*, 3940.

(311) Jessop, P. G.; Ikariya, T.; Noyori, R. *Nature* **1994**, *368*, 231.

(312) Jessop, P. G.; Joo, F.; Tai, C. C. *Coord. Chem. Rev.* **2004**, *248*, 2425.

(313) Jessop, P. G. *J. Supercrit. Fluids* **2006**, *38*, 211.

(314) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 344.

(315) Jessop, P. G.; Hsiao, Y.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1994**, *116*, 8851.

(316) Leitner, W. *Angew. Chem., Int. Ed.* **1995**, *34*, 2207.

(317) Tominaga, K. *Catal. Today* **2006**, *115*, 70.

(318) Tominaga, K.; Sasaki, Y.; Saito, M.; Hagihara, K.; Watanabe, T. *J. Mol. Catal.* **1994**, *89*, 51.

(319) Tominaga, K.; Sasaki, Y.; Watanabe, T.; Saito, M. *Stud. Surf. Sci. Catal.* **1998**, *114*, 495.

(320) Silvestri, G. In *Carbon Dioxide as a Source of Carbon, Biochemical and Chemical Uses*; Aresta, M., Forti, G., Eds.; D. Reidel: Dordrecht, Holland, 1987; Vol. 206.

(321) Tokuda, M.; Kabuki, T.; Katoh, Y.; Suginome, H. *Tetrahedron Lett.* **1995**, *36*, 3345.

(322) Sasaki, A.; Kudoh, H.; Senboku, H.; Tokuda, M. In *Novel Trends in Electroorganic Synthesis*; Torii, S., Ed.; Springer-Verlag: Tokyo, 1998.

(323) For the CO_2 utilization as a reaction medium, see (a) Sakakura, T.; Yasuda, H. In *Green Reaction Media in Organic Synthesis*; Mikami, K., Ed.; Blackwell Publishing: Oxford, UK, 2005. (b) Jessop, P. G. *J. Supercrit. Fluids* **2006**, *38*, 211. (c) Chemical Synthesis using Supercritical Fluids; Jessop, P. G., Leitner, W., Eds.; Wiley-VCH, Weinheim, Germany, 1999. (d) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475.

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