

CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Properties and Applications of Diethyl Carbonate (DEC)

Diethyl carbonate (DEC, $(C_2H_5O)_2CO$), or in the other names, such as carbonic ether, ethyl carbonate, or eufin, is colorless transparent liquid under normal conditions and mildly toxic compound (Wang *et al.*, 2007). It can be used as a solvent in several industries such as pharmaceuticals, or an additive for octane booster in gasoline (Pacheco and Marshall, 1997). From Table 2.1, with high energy content, low vapor pressure, soluble in gasoline, DEC's properties are better than dimethyl carbonate (DMC) or ethanol (EtOH) (Brigg *et al.*, 2009).

Table 2.1 Properties of DEC, DMC, EtOH, and MeOH

Properties	DEC	DMC	EtOH	MeOH
MW	118.13 ^a	90.08 ^b	46.04 ^d	32.04 ^f
Melting Point, °C	-43 ^c	2 ^b	-114.3 ^e	-97 ^f
Boiling Point, °C	127 ^c	90 ^b	78 ^e	64.7 ^f
Flash Point, °C	33 ^c	18 ^b	13 ^d	11 ^f
Sp.Gr.	0.975 ^c	1.069 ^b	0.789 ^d	0.791 ^f
Viscosity at 20 °C, mPa•s	0.795 (Yang <i>et al.</i> , 2006)	0.589 (Rodriguez <i>et al.</i> , 2004)	1.20 ^d	0.59 ^f

Properties	DEC	DMC	EtOH	MeOH
Enthalpy of formation(H), kJ/mol (l)	-644.7 (Pacheco and Marshall, 1997)	-554.75 (Kim and Lee, 1999)	-277.38 ^c	-238.4 ^b
Octane No. 10 vol%,(R+M)/2	105 (Pacheco and Marshall, 1997)	116 (Pacheco and Marshall, 1997)	100 ^h 94 ⁱ	99 ^h
Raid Vapor Pressure (RVP) gasoline blending 10 vol%, psi	3 (Pacheco and Marshall, 1997)	10 (Pacheco and Marshall, 1997)	10.1 ^j	12.2 ^j
Lower Heating Value (LHV), MBtu/gal	74.3 (Pacheco and Marshall, 1997)	55.6 (Pacheco and Marshall, 1997)	75.7 (Pacheco and Marshall, 1997)	56.6 (Pacheco and Marshall, 1997)
O wt%	40.7 (Pacheco and Marshall, 1997)	53.3 (Pacheco and Marshall, 1997)	34.8 (Pacheco and Marshall, 1997)	49.9 (Pacheco and Marshall, 1997)
Solubility	non-soluble ^c	non-soluble ^b	soluble ^k	soluble ^l

^a website: <http://jintaichem.88chem.com/sell-Other-Organic-Chemicals/301/Diethyl-Carbonate.html>

^b MSDS: Dimethyl carbonate CAS(616-38-64)

^c website: <http://chemicalland21.com/industrialchem/solalc/diethyl%20carbonate.htm>

^d website: <http://en.wikipedia.org/wiki/Ethanol>

^e website: http://en.wikipedia.org/wiki/Ethanol_%28data_page%29

^f website: <http://en.wikipedia.org/wiki/Methanol>

^g website: http://en.wikipedia.org/wiki/Methanol_%28data_page%29

^h website: <http://dnr.louisiana.gov/sec/execdiv/tehasmt/ecep/auto/m/m.htm>

ⁱ website: <http://www.colesexpress.com.au/shell-fuels.aspx>

^j website: www.eri.ucr.edu/ISAFXVCD/ISAFXVPP/SuTCAF.pdf

^k MSDS: Ethanol, absolute CAS(64-17-5)

2.2 Value Chain of DEC, Marketing, and Business of DEC in the Future

As mentioned before, DEC can be used in various fields <<http://chemicalland21.com/industrialchem/solalc/diethyl%20carbonate.htm>>, such an organic solvent for syntheses (cellulose nitrate synthesis, cellulose ether synthesis, natural synthesis, and phenobarbital in pharmaceutical), an intermediate for diphenyl carbonate synthesis used to produce polycarbonate, an electrolyte in a lithium ion battery, and an octane booster in gasoline, as shown in Figure 2.1.



Figure 2.1 Flow chart of DEC applications.

DPC stands for diphenyl carbonate and PC stands for polycarbonate.

^a Briggs et al., 2009

^b Energizer Holding, Inc. (2009), Product Safety Data Sheet

^c Pacheco et al., 1997 5

^d website:<http://jintaichem.88chem.com/sell-Other-Organic-Chemicals/301/Diethyl-Carbonate.html>

From Figure 2.1, using DEC as an octane booster is interesting. DEC and ethanol have very close octane number but rapid vapor pressure (RVP) of DEC is lower than ethanol's RVP, which causes knocking in a car engine <http://www.fuel4life-biofuels.com/bioethanol_hydrous_and_anhydrous.html>.

Thus, DEC can be blended in gasoline to increase octane number. But, the price of DEC is still high compared to ethanol price possibly due to the expensive costs of raw materials, operations, and maintenances. The prices of DEC and EtOH divided by volume amount are shown in Table 2.2.

Table 2.2 Prices of DEC and ethanol

Chemical	DEC	EtOH
Price (Baht/L)	54.90 ^a	21.01 ^b

^a website: http://www.jetro.go.jp/tppoas/anken/0001037000/1037313_e.html

^b website: http://www.eppo.go.th/retail_prices.html

In consequence, if using CO₂, which is abundant in chemical industries, and ethanol, which is already surplus in Thailand as reactants to synthesize DEC is successful, the DEC price will be reduced. As a result, it may attract customers to use. Furthermore, CO₂ emission can also be decreased, which is good as another way to solve global warming (Liu *et al.*, 2003).

2.3 DEC Syntheses

There are several routes to synthesize DEC, such as phosgene alcoholysis (Pacheco and Marshall, 1997), urea alcoholysis (Wang *et al.*, 2007), transesterification (Qiu *et al.*, 2010), and oxidative carbonylation (Pacheco and

Marshall, 1997), of which DEC synthesis is normally based on DMC synthesis by replacing methanol with ethanol.

2.3.1 Phosgene Alcoholysis

The commercial method to produce dialkyl carbonate, which is shown in Equation 1 (Pacheco and Marshall, 1997), is achieved by reacting alcohols with phosgene (COCl_2). In US4335051 (1982), range of temperature for operation was 20°C to 40°C , and the reaction used an aqueous alkali metal hydroxide solution, such as NaOH or LiOH, a water immiscible solvent (chlorobenzene) for improving the reaction. The catalysts used in the reaction were tertiary amines, such as triethyl amine, pyridine, and quaternary ammonium salts.



With this process, yield of 92% was reached, and the by-product yield (ether) was also decreased. Nonetheless, the disadvantages of this reaction are toxicity and corrosiveness from hydrochloric acid.

2.3.2 Transesterification of Carbonate

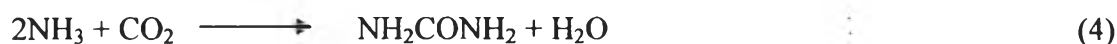
From the reaction shown as equation 2 (Qui *et al.*, 2010), ethylene carbonate reacts with ethanol to produce diethyl carbonate.



Both acid and base catalysts were used in the transesterification. Nevertheless, it was found that base catalysts (alkali metal alkoxides and hydroxides) were more active than acid catalysts. The operation conditions also depended on types of reaction (homogeneous or heterogeneous catalytic reaction). It was found that the operation conditions in base heterogeneous catalysts were more severe conditions than those in homogeneous catalysts. Qui *et al.* (2010) operated the reaction at the temperature of 423 K and got 58 % of DEC yield. The process was useful, but economically unfavorable (Wang *et al.*, 2007).

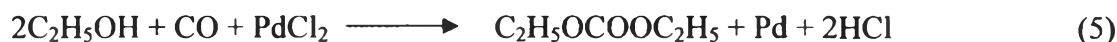
2.3.3 Urea Alcoholysis

The diethyl carbonate can react with urea (Equation 3) in the presence of various catalysts (organotin, Pd, and Zn), and ammonia can be recycled to urea by reacting with CO₂ (Equation 4). The temperature and pressure were 190°C and 0.7 MPa, respectively. Because no water is formed as a by-product, the separation and purification are simple. However, the DEC yield was not high (14.2 %) due to other by-products, such as isocyanic acid (HNCO), which was formed by pyrolysis of urea and ethyl carbamate (CH₃CH₂OCONH₂), an intermediate component, which reacts with DEC to generate N-ethyl ethyl carbamate (N-EEC) (Wang *et al.*, 2007).



2.3.4 Oxidative Carbonylation of Ethanol

Diethyl carbonate can be produced from carbon monoxide and ethanol in the presence of metal chlorides or metal alkoxy chlorides (Pacheco and Marshall, 1997). From Equations 5 and 6, respectively, the carbonylation reaction used PdCl₂ and CuCl₂ as a catalyst and a re-oxidant, respectively.



The temperature and pressure of CO, which were suitable to produce DEC, were 20°C to 100°C and 14 atm, respectively. Nevertheless, the reaction was not good enough, since oxygen is required in the reactions (oxidative carbonylation). For example, the oxidative carbonylation reaction of methanol is shown in Equations 7 and 8, respectively.



This reaction is used commercially by ENIChem, while CuCl is in slurry phase, and by UBE, while CO is substituted by NO. However, the catalyst was found to be deactivated due to the copper salt being unstable in the presence of water formed.

2.4 Direct DEC Synthesis from CO₂ and Ethanol (Based on DMC Synthesis from CO₂ and Methanol)

DMC can be produced directly from CO₂ and methanol in homogeneous catalysts or heterogeneous catalysts. Basically, the chemical reaction is shown in Equation 9.



The reaction is really attractive in terms of material cost and synthetic strategy, but thermodynamics of the reaction is unfavorable. Ways to increase the conversion can be classified into 3 strategies (Choi *et al.*, 2002),

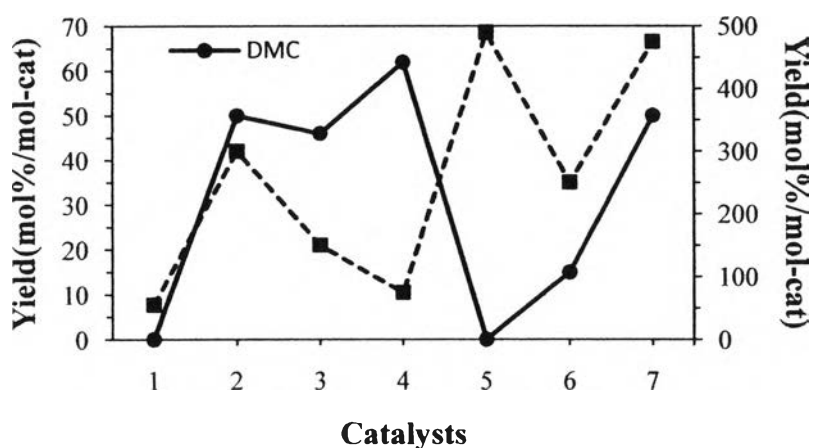
1. Choosing a proper catalyst to increase the activity
2. Eliminating water to change the chemical equilibrium and prohibit catalyst deactivation
3. Increasing CO₂ pressure to boost the conversion

2.4.1 Homogeneous Catalytic Reaction for Direct DMC Synthesis

In this type of catalysts, organo-metallic compounds are chosen as catalysts such, as metal alkoxides (dibutyltin dimethoxide (Bu₂Sn(OMe)₂) (Sakakura *et al.*, 1998), dibutyltin oxide (Bu₂SnO) (Choi *et al.*, 2002)) due to their high activity and selectivity, and metal acetates (nickel acetate (Ni(CH₃COO)₂•4H₂O), cobalt acetate (Co(CH₃COO)₂•4H₂O), or mercury acetate (Hg(CH₃COO)₂)) (Zhao *et al.*, 2000).

Nevertheless, using only the catalysts is not enough due to the reaction thermodynamics. In 2000, the results from Zhao *et al.* (2000), which used nickel acetate and others as catalysts without an additive and operated in low CO₂ pressure,

and those from Sakakura *et al.* (1999), which used $\text{Bu}_2\text{Sn}(\text{OMe})_2$ at high CO_2 pressure but did not use methanol in form of a dehydrated derivative, are shown in Figure 2.2 and 2.3, respectively. However, DMC yields from these 2 experiments were not satisfied. Therefore, this problem has to be solved.



1. CH_3COONa
2. $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
3. $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
4. $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$
5. $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$
6. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$
7. $\text{Hg}(\text{CH}_3\text{COO})_2$

Figure 2.2 The activity of metal acetates towards the DMC synthesis (Catalyst/MeOH = 1:25 (M); reaction pressure 7.0 MPa, 413 K, and 12 h) (Zhao *et al.*, 2000).

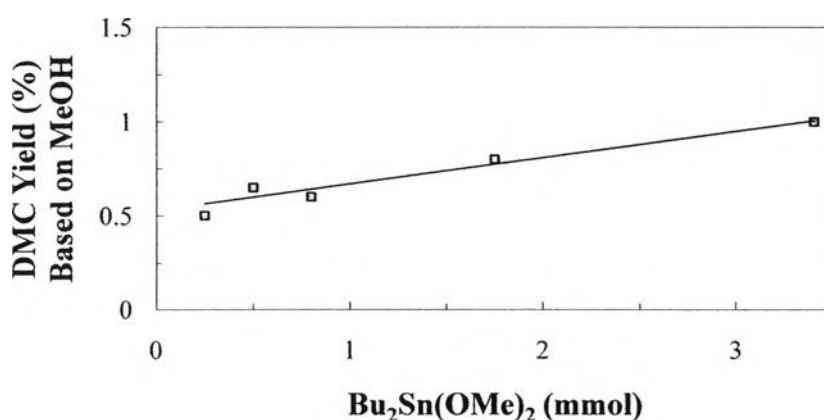


Figure 2.3 Effect of catalyst on the yield of DMC (Reaction conditions: $\text{Bu}_2\text{Sn}(\text{OMe})_2$, MeOH 8.1 cm^3 , 180°C , 300 atm, and 24 h) (Sakakura *et al.*, 1999).



The catalytic reaction of $\text{Bu}_2\text{Sn}(\text{OMe})_2$ from Sakakura *et al.* (1999) is shown in Equation 10 as an example of homogeneous catalytic reaction. Water, as a byproduct, deactivated the catalyst and reduced the catalytic activity, as shown in Equation 11. The catalyst changed to Bu_2SnO , which gave lower activity than $\text{Bu}_2\text{Sn}(\text{OMe})_2$ (Choi *et al.*, 2002), and methanol.



Because of the catalyst deactivation, water has to be eliminated. Several ways have been proposed. In 1998, Sakakura *et al.* suggested that MeOH should be dehydrated to obtain its dehydrated derivatives before reacting with CO_2 . Comparing the reactivity of the derivatives, such as orthoester, dimethyl ester, and ketal, orthoester is the most reactive.

However, the production of orthoester is costly due to the starting feeds and the methyl acetate by-product, which is difficult to recycle to orthoester (Choi *et al.*, 2002). The reaction, which at the end, gave by-products, such as dimethyl ether (DME) and methyl acetate (AcOMe), was shown in Equation 12.



Because of an expensive cost for making orthoester, Choi *et al.* (2002) proposed 2 possible ways. The first was to use dimethyl acetal, which have lower cost of the production and easy conversion of the acetone by-product to dimethyl acetal. The second was to use molecular sieve 3A. Both ways gave excellent yield. The difference between these 2 solutions was their reactants, which the former solution used the acetal with CO_2 , but the latter used methanol with CO_2 by combining with an internal recycle as shown in Figure 2.4. A comparison between the cases with and without acetal suggested that acetal increased turn over number of the reaction dramatically, as shown in Figure 2.5. The trends of DMC synthesis with respects to time and catalyst amount are shown in Figure 2.6 and 2.7, respectively.

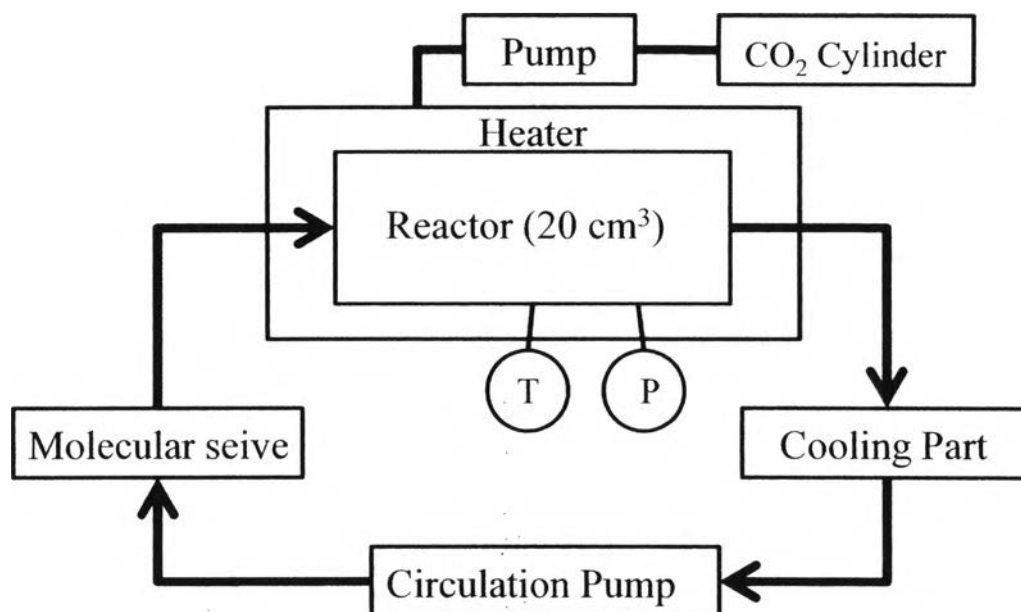


Figure 2.4 A batch reactor with internal recycle (Choi *et al.*, 2002).

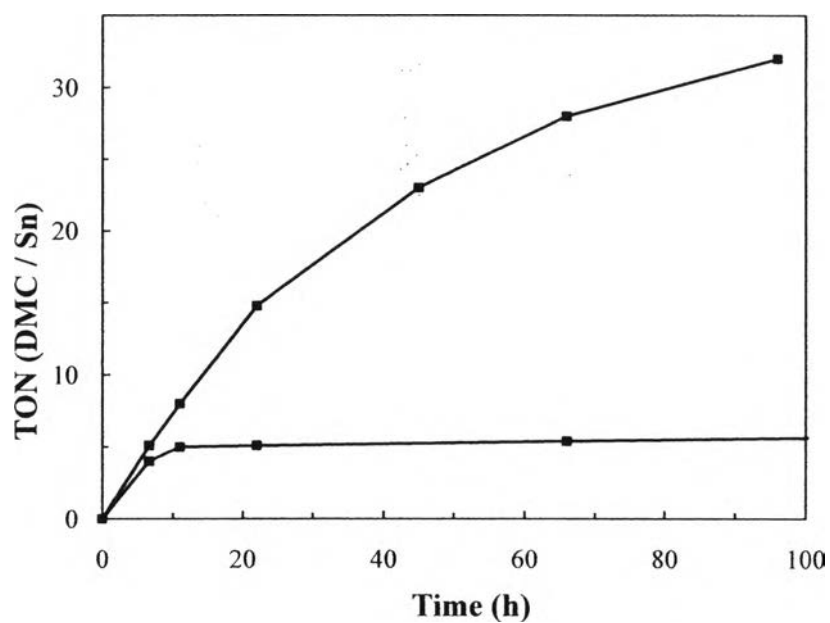


Figure 2.5 Time dependence of DMC synthesis (Reaction conditions: 2,2-dimethoxypropane 10 mmol, $\text{Bu}_2\text{Sn}(\text{OMe})_2$ 2.0 mmol, MeOH 8.1 cm³, 180°C, and 300 atm) (Choi *et al.*, 2002).

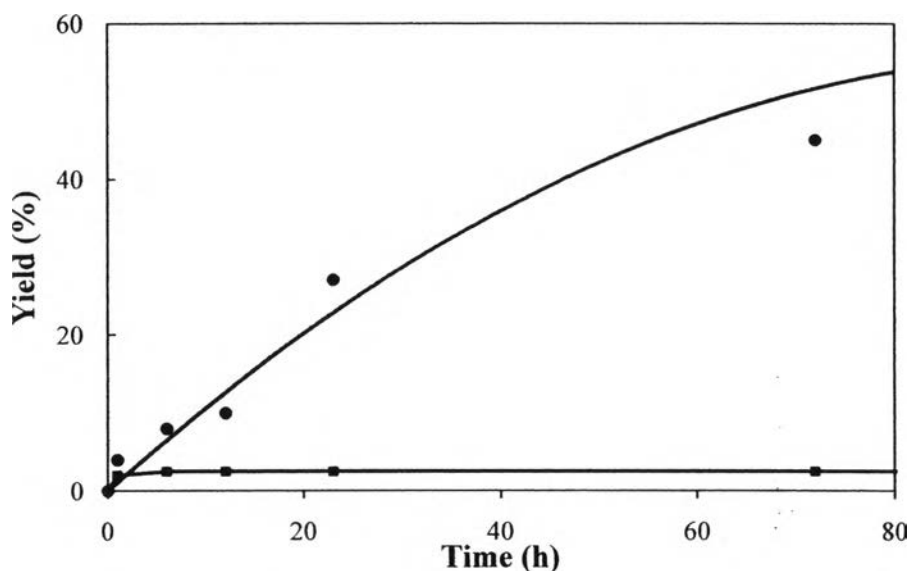


Figure 2.6 The dependence of DMC synthesis from CO₂ and methanol (Reaction conditions: autoclave with the internal recycle, Bu₂Sn(OMe)₂ 2.0 mmol, methanol 100 mmol, molecular sieve 3A 15 g, 180°C, and 300 atm; and yield were based on methanol) (Choi *et al.*, 2002).

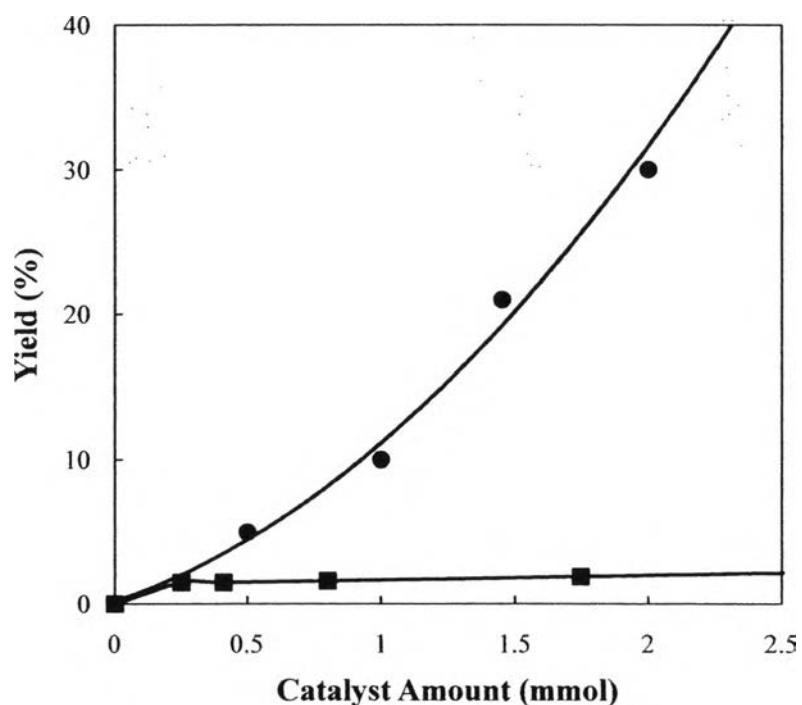


Figure 2.7 Effect of catalyst amount on DMC synthesis from CO₂ and methanol (Reaction conditions were the same as those used in Figure 2.6) (Choi *et al.*, 2002).

In recently years, supercritical fluid has been studied in terms of applications. For DMC synthesis, supercritical CO₂ (scCO₂), as a reactant, is crucial because the supercritical condition can increase activity. Details about supercritical CO₂ are described in the section of supercritical fluid.

It was found by Sakakuya *et al.* (1998) that scCO₂ affected activity and selectivity of the direct DMC synthesis. The results in Figure 2.8 can be divided into 2 sections. First, the catalytic activity became highest around the critical pressure of CO₂ (73 atm), which may come from eliminating mass transfer of the reactant to the catalyst. Second, if the pressure was increased more than 73 atm, the selectivity of DMC tended to decrease, and that of methyl acetate also decreased. The conclusion was not clear enough due to insufficient mechanistic studies.

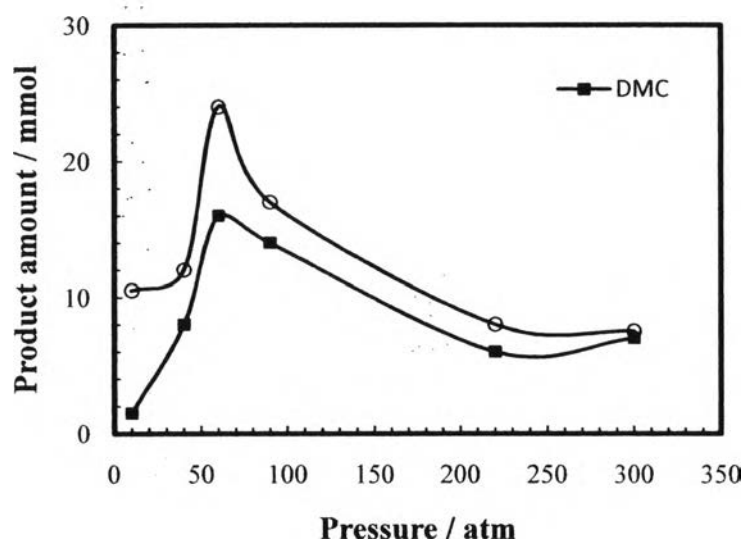


Figure 2.8 CO₂ pressure effect on the Bu₂Sn(OMe)₂ and Bu₄PI(additive) (150°C and 24 h) (Sakakura *et al.*, 1998).

Choi *et al.* (2002) also did an experiment to study the effect of CO₂ pressure. The results in Figure 2.9, which compared the effect of CO₂ pressure between 100 and 300 atm on DMC yield with respect to the reaction time, revealed that high pressure of CO₂ can improve yield of the DMC synthesis.

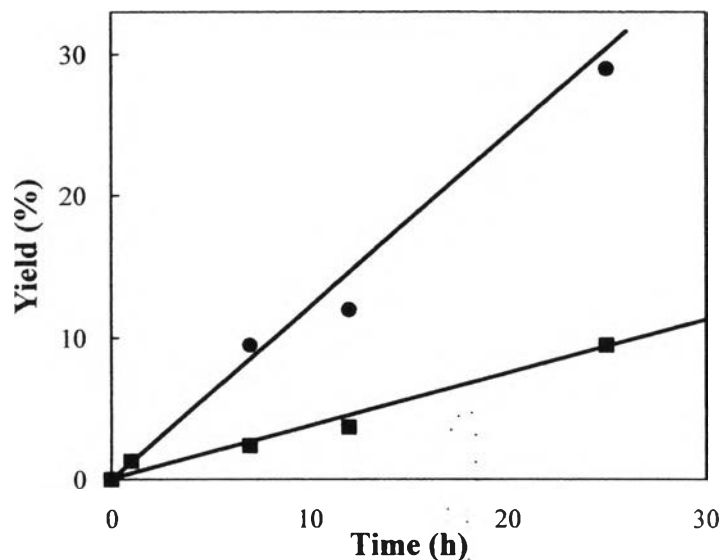


Figure 2.9 Time dependence of dimethyl carbonate synthesis from CO₂ and MeOH at different pressures (Reaction conditions: autoclave with internal recycle (Fig 2.4), Bu₂Sn(OMe)₂ 2.0 mmol, MeOH 100 mmol, molecular sieve 3A 15 g, and 180°C, and yields were based on MeOH) (Choi *et al.*, 2002).

Nevertheless, the operation at near supercritical condition gave a quite interesting result. As shown in Table 2.3 (Zhao *et al.* in 2000) (compare the results with Figure 2.2 for more understanding), increasing the pressure not only increase yield of DMC enormously, but also increased DMC selectivity.

Table 2.3 Direct DMC synthesis at near supercritical conditions (Zhao *et al.*, 2000)

Pressure (MPa)	Yield (mol%/mol-cat.)	
	DMC	Methylacetate
7.4	569	0
8.3	587	0
9.3	796	0
10.3	350	0

Ni(CH₃COO)₂·4H₂O/methanol = 1:25 (M); 305 K; 2 h.

2.4.2 Heterogeneous Catalytic Reaction for Direct DMC Synthesis

The metal oxide catalyst, which is well known to be the most effective for direct DMC synthesis, is zirconium oxide (ZrO_2). Other metal oxide catalysts have also been proposed, such as vanadium(V) oxide (V_2O_5) (Wu *et al.*, 2005), copper-nickel promoted $\text{V}_2\text{O}_5/\text{SiO}_2$ (Wu *et al.*, 2006), tin oxide (SnO_2) (Aymes *et al.*, 2009), and cerium oxide (CeO_2) (Tomishige and Kunimori, 2002). It was found that the catalytic performance of the catalysts was in the order of $\text{CeO}_{0.1}\text{Ti}_{0.9}\text{O}_2 > \text{CeO}_x\text{Ti}_{1-x}\text{O}_2$ ($x=0.2-0.8$) $> \text{ZrO}_2 > \text{CeO}_2 > \text{TiO}_2$ (Dai *et al.*, 2009).

In 2000, Tomishige *et al.* used ZrO_2 catalyst to synthesize DMC directly from CO_2 and MeOH. Calcination temperature greatly affected the activity, as shown in Figure 2.10. An explanation for this phenomenon can be obtained from catalyst characterizations. It was found that the active site on Zr catalyst was in tetragonal phase, which was found in a small amount compared to monoclinic phase, and the former phase was decreased after calcination temperature increased (Tomishige *et al.*, 2000). For the tetragonal phase, acid-base site was observed by using TPD of CO_2 and NH_3 . Therefore, the catalytic reaction mechanisms were proposed, as shown in Equations 13 to 18.

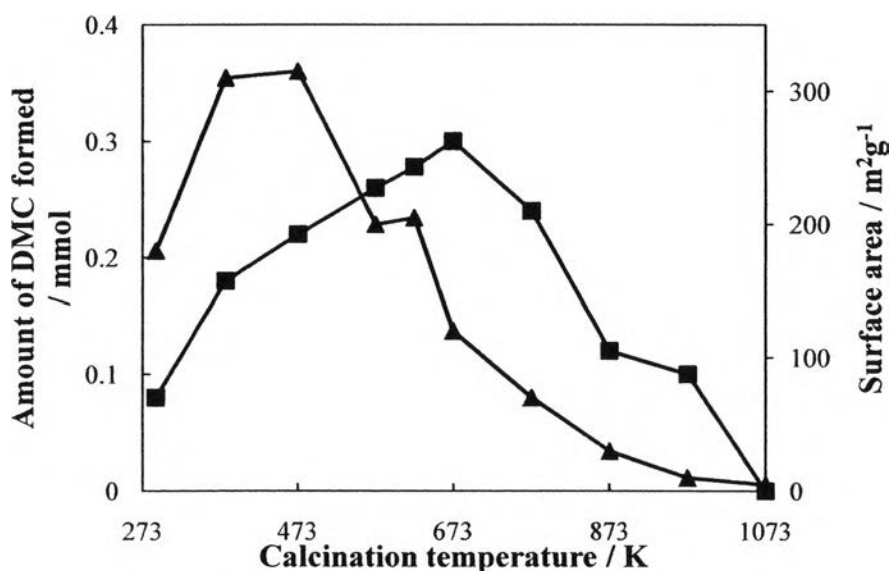
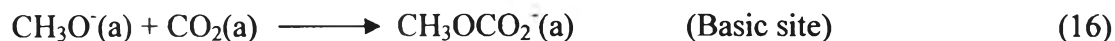


Figure 2.10 The DMC formation (■) and surface area (▲) on the calcination temperature of ZrO_2 (Reaction condition: 443 K, 2 h. $\text{CH}_3\text{OH}:\text{CO}_2=192:200$ mmol, and sample weight 0.5 g; Surface area: BET method) (Tomishige *et al.*, 2000).



Owing to the small amount of the tetrahedral phase, which caused yield of DMC low, promoting tetragonal phase has been proposed by using phosphoric acid (H_3PO_4) (Ikeda *et al.*, 2000). The amount of DMC was increased highly because of the increase in tetragonal phase when loading H_3PO_4 . Figure 2.11 shows amount of DMC related with reaction temperature. In addition, the reaction temperature used decreased drastically (40 K).

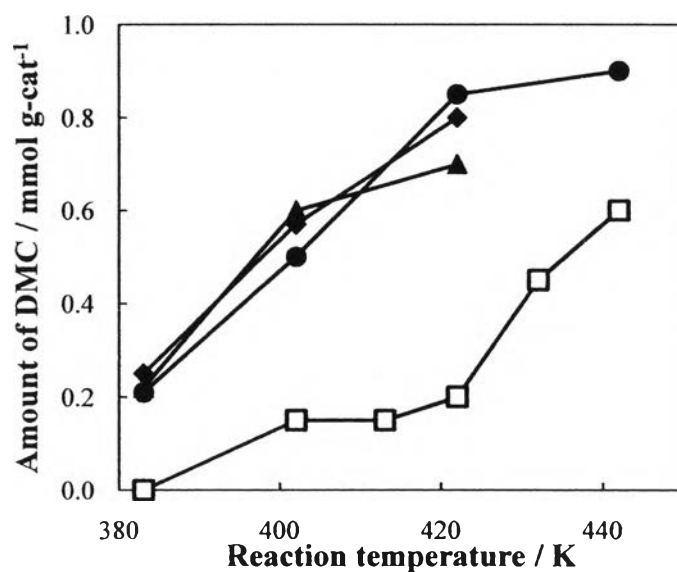
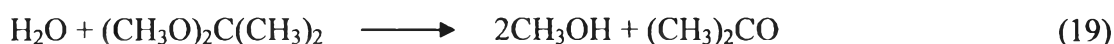


Figure 2.11 Dependence of DMC amount on reaction temperature over ZrO_2 (□) and $\text{H}_3\text{PO}_4/\text{ZrO}_2$ (P/Zr) in ratio 0.025(●), 0.05(▲), 0.1(◆) (Reaction condition: MeOH:CO₂ 192 mmol : 200 mmol, catalyst weight 0.5 g, reaction time 2 h) (Ikeda *et al.*, 2000).

In the reaction, since thermodynamics is unfavorable, water removed was concerned to increase yield of DMC. 2,2-dimethoxy propane (DMP) was used to react with water generated in the DMC synthesis, and the products were methanol and acetone (Equation 19). Nevertheless, high DMP concentration caused the decrease in DMC formation rate and promoted the DME formation instead (Tomishige *et al.*, 2002).



In one of the experiments of Tomishige *et al.* (2002), where Ce-Zr catalysts were synthesized to increase yield of DMC from methanol and CO₂, the optimum ratio of Ce-Zr catalyst was also used in DEC synthesis. It was found that the optimum catalyst can be used to synthesize DEC even the yield of DEC was low due to its thermodynamic equilibrium. From Figure 2.12, the DEC amount did not depend on the increase in amount of the catalyst. Furthermore, the possible reactions of DEC were proposed, as shown in Equations 20 to 22.

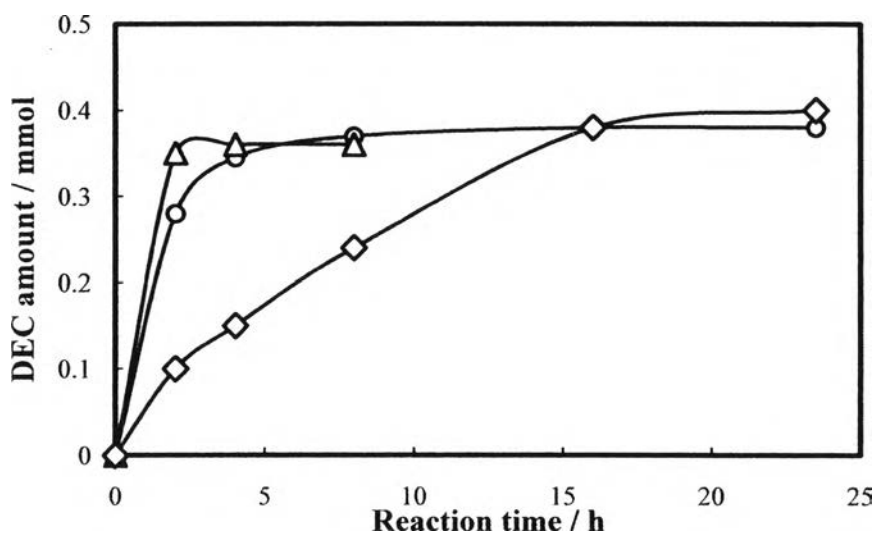


Figure 2.12 The dependence of reaction time and catalyst weight on the DEC formation amount from EtOH and CO₂ over CeO₂-ZrO₂ (Ce/(Ce+Zr) = 0.2) solid solution (Catalyst weight 0.1 g (◇), 0.5 g (○), 1.4 g (△); Reaction conditions: reaction temperature 383 K, EtOH:CO₂ = 200:200) (Tomishige *et al.*, 2002).



2.5 Supercritical Fluid (Supercritical Carbon Dioxide)

Super critical fluid (SCF) is a condition of the fluid (gas or liquid), which its temperature and pressure reach its critical point (T_c and P_c) (Aresta, 2010). In this status, the fluid acts with both gas and liquid properties, as shown in Table 2.4.

Table 2.4 Comparison gas and liquid properties with supercritical fluid in terms of density, dynamic viscosity, kinematic viscosity, and diffusion coefficient (Baiker, 1999).

physical quantity	gas (ambient)	supercritical fluid (T_c, P_c)	liquid (ambient)
density ρ (kg m^{-3})	0.6-2	200-500	600-1600
dynamic viscosity η (mPa s)	0.01-0.3	0.01-0.03	0.2-3
kinematic viscosity ν^a ($10^6 \text{ m}^2\text{s}^{-1}$)	5-500	0.02-0.1	0.1-5
diffusion coefficient D ($10^6 \text{ m}^2\text{s}^{-1}$)	10-40	0.07	0.0002-0.002

^aKinematic viscosity was estimated from dynamic viscosity and density, $\nu = \eta / \rho$

From Table 2.4, it shows that the supercritical conditions gain advantages from both gas and liquid properties at ambient conditions. The density of SCFs, which is close to the density of liquid, can provide dissolution power. Because of the similarity of the dynamic viscosity between gas and SCFs, it improves mass transfer. Moreover, SCF can diffuse easily in a solvent because SCFs' diffusivity is similar to gas's diffusivity, better than liquid itself. Addition, SCFs have an ability to increase

solubility of insoluble compounds and do it in opposite direction to soluble compounds at ambient conditions (Baiker, 1999).

In supercritical conditions, the fluid has a very high isothermal compressibility, which may change the density of the fluid with temperature and pressure parameters. Furthermore, the thermodynamic and transport properties of the fluid can be controlled by manipulating the density (Aresta, 2010).

With these properties of supercritical fluids, supercritical carbon dioxide (scCO₂) with its phase diagram presented in Figure 2.13 has been investigated for use in several applications, such as a solvent for caffeine extraction process (Song, 2006) and mediums to control chemical reactions (Beckman, 2004). Reasons why CO₂ is chosen are not just properties of supercritical fluids, which are interested, but also in terms of technical and economical properties, which are low cost, high stability, non-flammability, and easy operation in critical conditions.

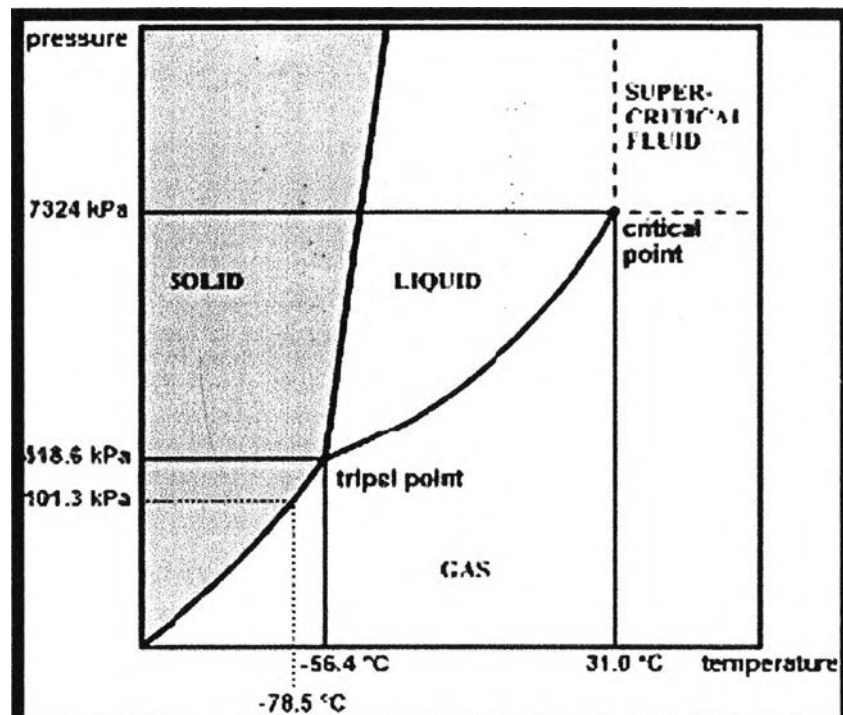


Figure 2.13 Phase diagram of CO₂, Critical point ($T_c = 31.0^\circ\text{C}$, $P_c = 7324 \text{ kPa}$), the triple point ($T_t = -56.4^\circ\text{C}$, $P_t = 518.6 \text{ kPa}$), and the sublimation boundary at ambient pressure ($T = -78.5^\circ\text{C}$, $P = 101.3 \text{ kPa}$) (Niessen *et al.*, 2007).

In the past years, several research works have endeavored to use scCO_2 as a medium and also a reactant by using catalysts (Sakakura *et al.*, 1999 and Zhao *et al.*, 2000). There are 7 steps in the catalytic reaction, as shown in Figure 2.14 (Fogler, 2005).

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g. $\text{A} \rightarrow \text{B}$)
5. Desorption of the products (e.g. B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

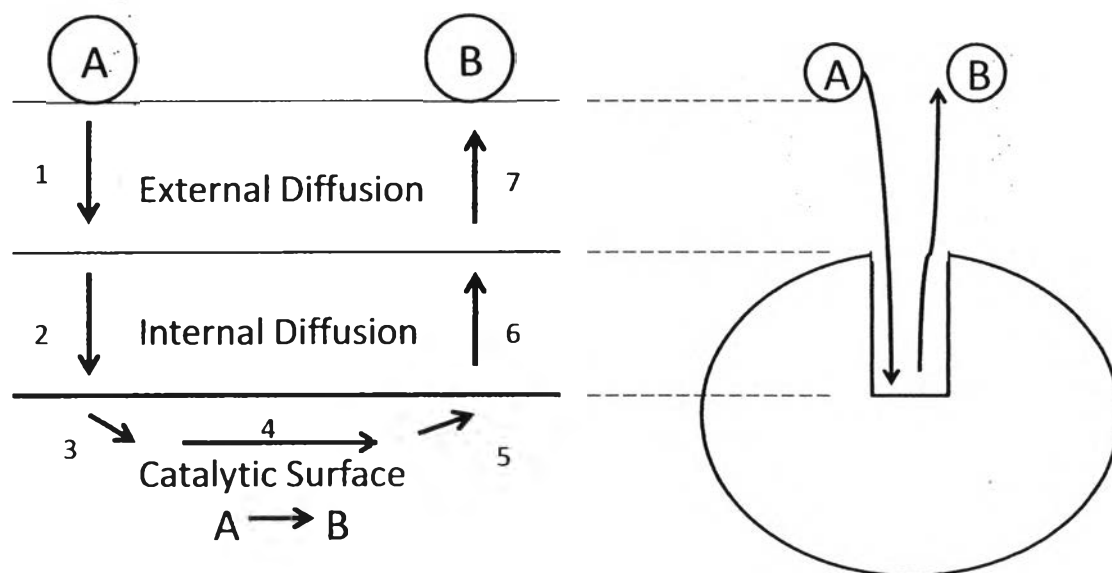


Figure 2.14 Seven steps in a heterogeneous catalytic reaction (Fogler, 2005).

In the gas-liquid system, diffusion from bulk gas or liquid to the catalyst surface influences the rate of reaction by manipulating the flow conditions over the catalyst. For the latter system, diffusion within the catalyst pores may limit the rate

of reaction. Therefore, using carbon dioxide in supercritical conditions can eliminate mass transport limitations in the heterogeneous catalytic reactions (Baiker, 1999 and Beckman, 2004).

2.6 Literature Review

Tomishige *et al.* (1999) discovered a novel method to synthesize dimethyl carbonate (DMC) from methanol (MeOH) and carbon dioxide (CO₂) over ZrO₂ catalyst. In their work, DMC can be synthesized in high selectivity over ZrO₂ catalyst due to the relation of acid-base properties over surface of the catalyst.

Tomishige *et al.* (2001) continued their study to increase amount of DMC by changing ZrO₂ catalyst to CeO₂-ZrO₂ catalyst. In this work, the Ce to Zr molar ratios (Ce/(Ce+Zr), %) and calcination temperature were varied from 0 to 50 % and 573 to 1273 K, respectively, to find the optimum catalytic condition. The result showed that CeO₂-ZrO₂ at 20% and calcined at 1273 K gave the highest amount of DMC. It was prove that DMC synthesis over the CeO₂-ZrO₂ at 20 % catalyst gave a good result.

However, due to the DMC reaction is an equilibrium reaction, water removal was considered to drive the reaction forwardly. Therefore, Tomishige and Kunimori (2002) continued the research work on DMC synthesis by using 2,2-dimethoxy propane (DMP) for removing water. The result showed that using DMP at the optimum amount can increase DMC amount. Furthermore, diethyl carbonate (DEC) which is synthesized from ethanol (EtOH) and CO₂ was also studied in this research work to prove that DEC can be synthesized over the CeO₂-ZrO₂ catalyst as well.

Gasc *et al.* (2009) synthesized DEC from EtOH and supercritical CO₂ in presence of potassium carbonate. The reason for using the supercritical condition was because the supercritical CO₂ acted as a reactant and a good solvent in the system. The result claimed that DEC production was increased.

Wang *et al.* (2009) studied crystal structure, acid-base properties, and reactivities the Ce_xZr_{1-x}O₂ catalysts to study DEC synthesis from EtOH and CO₂. The results showed that a small amount of Ce in the catalyst and high calcination temperature

gave a good result in DEC synthesis because the crystal structure and acid-base properties of the catalyst.