

# EFFECTS OF CATALYSTS BASICITY ON DIMETHYL CARBONATE SYNTHESIS FROM METHANOL AND SUPERCRITICAL CARBON DIOXIDE

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## Abstract

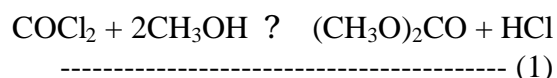
The synthesis of dimethyl carbonate(DMC) from methanol and supercritical carbon dioxide over various basic catalysts was studied in the batch reactor. Compounds of group I elements(Li, Na and K) were used as basic catalysts. The promoter and the dehydrating agent were also used to enhance the yield of DMC. By-products such as dimethyl ether(DME) and C<sub>1</sub>-C<sub>2</sub> hydrocarbons as well as DMC were formed in this reaction system. The yield of DMC with different alkali metal catalysts ranked in the following order: K > Na > Li. CO<sub>3</sub><sup>2-</sup> containing catalysts were more effective than OH<sup>-</sup> containing catalysts on the DMC synthesis. The reaction mechanism of DMC synthesis from methanol and supercritical carbon dioxide was proposed. The maximum DMC yield reached up to 12 mole% in the presence of K<sub>2</sub>CO<sub>3</sub>(catalyst), CH<sub>3</sub>I (promoter) and 2,2-dimethoxypropane (dehydrating agent) at 130 – 140 °C, 200bar.

## INTRODUCTION

Dimethyl carbonate(DMC) is low in toxicity and quickly biodegradable. It has been used mainly as a carbonylating and methylating agent. DMC can be used as an intermediate to substitute phosgene and dimethyl sulfate in many industrial processes.[1] It is also considered a promising gasoline additive to replace MTBE(Methyl Tert-Butyl Ether), because DMC has a high oxygen content.[2]

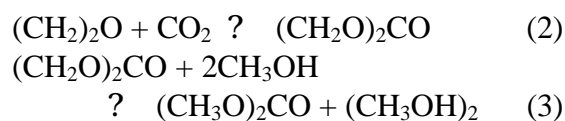
There are three DMC synthesis processes: the phosgene-methanol process, ester exchange process and oxidative carbonylation of methanol process.[3]

The phosgene-methanol process:



The phosgene-methanol process has fallen out of use gradually owing to the high toxicity of raw material, severe corrosiveness and high production cost.

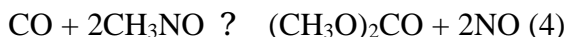
The ester exchange process:



The ester exchange process has not been industrialized owing to poor

economical feasibility.

Oxidative carbonylation of methanol process:



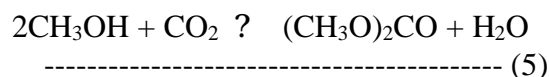
The oxidative carbonylation of MeOH has been extensively studied for the production of DMC. UBE(Japan) has developed an excellent DMC synthesis process using the Pd<sup>2+</sup> catalyst and alkyl nitrite promoter.[4] Both heterogeneous and homogeneous catalyst systems have been investigated with a variety of main-group metal compounds[5,6], transition metal complexes[5,7], transition metal-zeolite[8,9], solid-supported metals[10] and others[11,12]. Among various transition metals employed for the oxidative carbonylation of MeOH, palladium and copper are most frequently used.[5,7,9] But haloid of palladium or copper is severely corrosive to the equipment and has a short service time. In addition, there exist some problems in the recovery of the product.

Recently, in order to achieve the principles of "Green Chemistry" that aims at the lowest impacts on human health and environment, other synthesis routes have been investigated. Using CO<sub>2</sub> as the carbon source will be an alternative to existing methods which employ hazardous and toxic components. In addition, direct synthesis from CO<sub>2</sub> and methanol is most attractive due to the low-cost of CO<sub>2</sub>.

Bu<sub>2</sub>Sn(OMe)<sub>2</sub>, metal(?) tetra-alkoxide, magnesium dialkoxide and other organometallics have been reported as catalysts for the direct synthesis.[13,14] But the activity was low even in the presence of dehydrating agents and promoters because of the decomposition of the catalysts by water, and due to the reverse hydrolysis of DMC. Several attempts have been made in order to avoid the detrimental effect of water.[15] But the

performance of those processes is still unsatisfactory.

We are interested in DMC synthesis from the direct catalytic carbonation of methanol with supercritical CO<sub>2</sub>, over various basic catalysts:

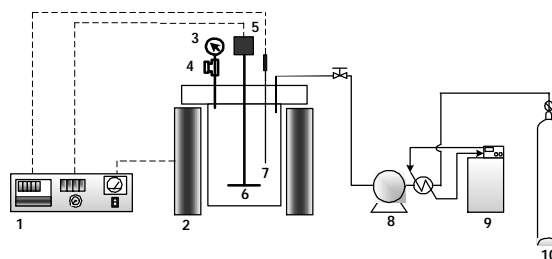


In this work, we investigated the effects of basic catalyst on the yield of DMC. Compounds of group I elements(Li, Na and K) were used as basic catalysts.

## EXPERIMENTS

The experimental apparatus is shown in Fig. 1. The reactor was manufactured of stainless steel autoclave for use at high pressure. The reaction mixture was stirred with the impeller during the reaction.

After methanol, catalysts, CH<sub>3</sub>I and 2,2-dimethoxypropane(DMP) were put into the reactor, CO<sub>2</sub> was introduced to the reactor at room temperature. DMP was added to remove water from the reaction system. The reactor was heated up to the prescribed temperature by the electrical heater. The products were analyzed by gas-



1. Control Box 2. Furnace 3. Pressure Gauge 4. Rupture  
5. Magnetic Drive 6. Impeller 7. Thermocouple 8. Pump  
9. Circulator 10. CO<sub>2</sub> Cylinder

Figure 1: Experimental apparatus for DMC synthesis from methanol and supercritical carbon dioxide.

chromatography(HP-5890) with the FID detector. The concentrations of the metal dissolved in the product solution were analyzed by ICP/AES(Inductively Coupled Plasma Atomic Emission Spectrophotometer, 138 Ultrace, Jobin Yvon) in KOREA BASIC SCIENCE INSTITUTE.

## RESULTS

We first investigated the effects of the catalyst amount for DMC synthesis. 10ml CH<sub>3</sub>OH was reacted with excess CO<sub>2</sub> at 130 - 140°C, 200bar for 4hr. K<sub>2</sub>CO<sub>3</sub> was used as a catalyst. 2ml CH<sub>3</sub>I was also added as a promoter. Fig.2 shows the yield and the selectivity of DMC with an increase in the catalyst amount. As the catalyst amount changed from 0.15 to 2.0g, the yield of DMC reached the maximum at 1.75g of the catalyst. When the yield of DMC decreased, by-products such as dimethyl ether(DME) and C<sub>1</sub>-C<sub>2</sub> hydrocarbons were formed.

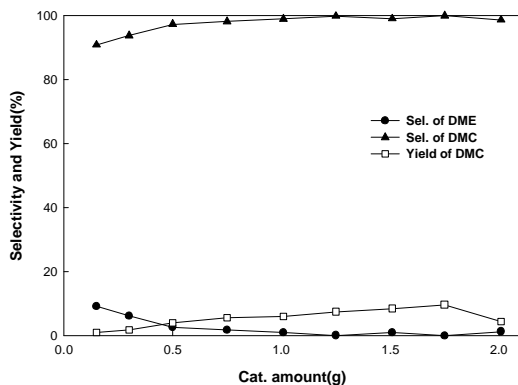


Figure 2: Effects of the catalyst amount on the yield and the selectivity of DMC.

The effects of the promoter amount for DMC synthesis were also investigated. CH<sub>3</sub>I as a promoter was added to the mixture of 1.75g K<sub>2</sub>CO<sub>3</sub>, 10ml CH<sub>3</sub>OH and excess CO<sub>2</sub>. The reaction was carried out at 130 - 140°C, 200bar for 4hr. Fig.3 shows

the yield and the selectivity of DMC with an increase in the promoter amount. As the promoter ratio to CH<sub>3</sub>OH changed from 0.10 to 0.30, the yield of DMC reached the maximum at 0.20 of the promoter. As the selectivity of DMC decreased, that of DME increased.

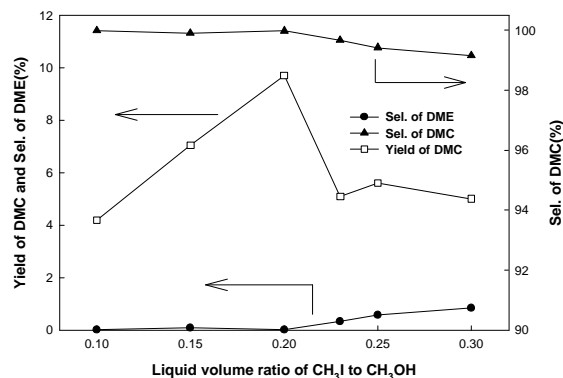


Figure 3: Effects of the promoter amount on the yield and the selectivity of DMC.

As shown in Eq. (5) H<sub>2</sub>O as well as DMC were also produced in DMC synthesis reaction with supercritical CO<sub>2</sub> and CH<sub>3</sub>OH. H<sub>2</sub>O prevents DMC being produced. After 2,2-dimethoxypropane (DMP) as a dehydrating agent was added to the mixture comprising 10ml CH<sub>3</sub>OH, excess CO<sub>2</sub>, 1.75g K<sub>2</sub>CO<sub>3</sub> and 2ml CH<sub>3</sub>I, the reaction proceeded at 130 - 140°C, 200bar for 4hr.

Fig.4 shows the yield of DMC with an increase in the DMP amount. Addition of DMP to the reaction system was effective for the increase in the yield. But the addition of larger amounts of DMP is not suitable because of the decrease in DMC formation rate and the by-production of the dimethyl ether(DME).

The yield of DMC reached the maximum (12.03%) at 2.0ml of DMP. The yield of DMC was improved up to about 2.32% by addition of DMP.

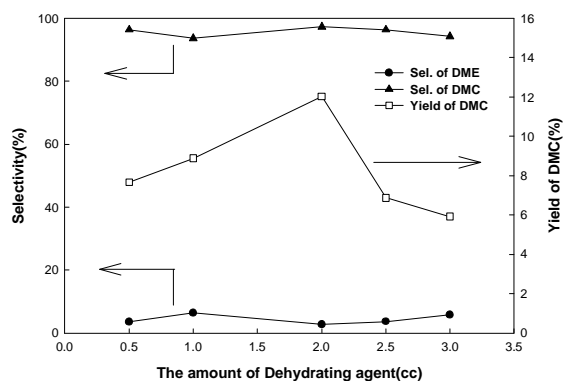


Figure 4: Effects of the amount of the dehydrating agent on the yield of DMC.

DMC synthesis was performed using various basic catalysts besides  $K_2CO_3$  under the same condition with the previous test. Fig.5 shows the yield of DMC on the catalysts. Fig.5 show that the yield of DMC with different alkali metal catalysts ranks in the following order:  $K > Na > Li$ .

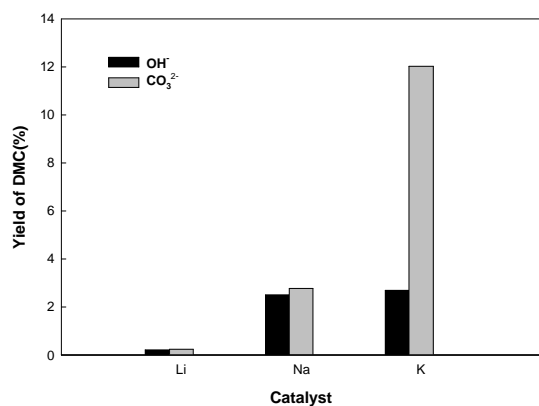


Figure 5: Yields of DMC on the catalysts.

The ionization energy in the periodic table of elements decreases in the opposite order:  $K < Na < Li$ . As the ionization energy of the element decreases, the yield of DMC increases. The concentrations of the metal dissolved in the product solution were analyzed by ICP /AES. The results are shown in Fig. 6. As the ionization energy of the element decreases, the

concentration of metal dissolved increase. The alkali metal bonded with  $OH^-$  ion ionizes better than that with  $CO_3^{2-}$  ion. But the yield of DMC is higher in the  $CO_3^{2-}$  compounds. It is thought that the yield of DMC decreases because of the production of water by the reaction of  $OH^-$  with  $H^+$  ion. When the water is produced DMC production is restricted. The  $K_2CO_3$  sample could not be analyzed by ICP/AES. The deposits were continuously formed in the pretreatment of the sample. It is thought that the solution may be in saturation. Therefore, the anions as well as the degree of saturation of the metal play an important role in promoting the DMC production in this catalyst system. The yield of DMC is highest in the reaction over  $K_2CO_3$  catalyst.

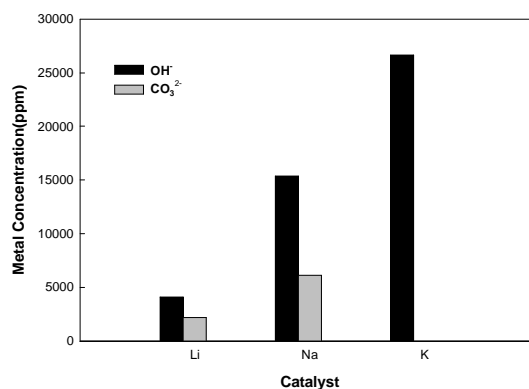
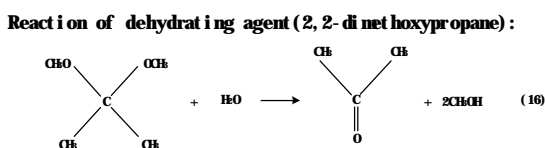
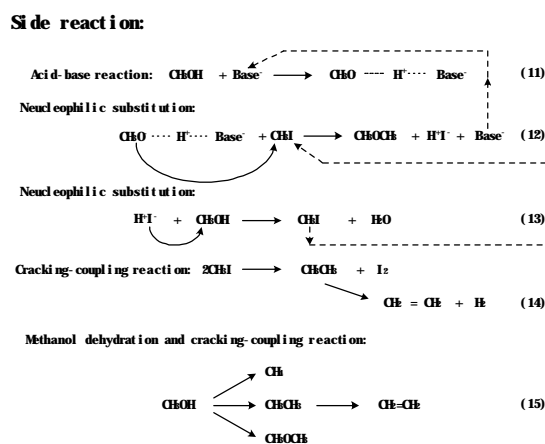
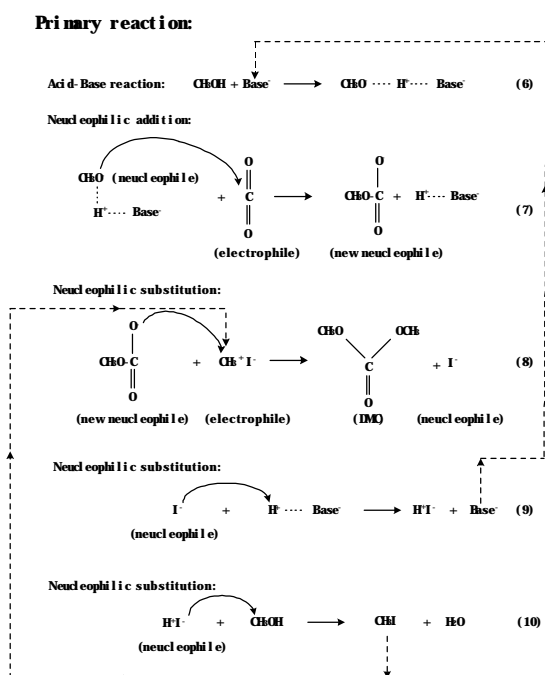


Figure 6: Concentrations of the metal dissolved in the product solution

## DISCUSSIONS

The reaction mechanism of DMC synthesis from methanol and supercritical carbon dioxide was proposed. The reaction was carried out in the batch reactor.  $CH_3OH$  and excess  $CO_2$  were mixed as reactants, using  $K_2CO_3$  as a catalyst,  $CH_3I$  as a promoter and 2,2-dimethoxypropane as a dehydrating agent. Eq. (6) – (10) show the primary reaction route of DMC synthesis and Eq. (11) – (16) the side reaction.



DMC was produced through the reaction (6) – (8). The catalyst  $\text{K}_2\text{CO}_3$  and promoter  $\text{CH}_3\text{I}$  were regenerated by reaction (9) and (10) respectively. Some  $\text{CH}_3\text{I}$  was consumed to produce  $\text{CH}_3\text{CH}_3$  by the reaction (14). It can be found from the fact that the color of the reactant mixture changed from light yellow to

brown (Iodide color). The less the yield of DMC, the deeper the shade of color.

$\text{C}_1 - \text{C}_2$  hydrocarbon and DME were also produced through dehydration and cracking-coupling reaction of  $\text{CH}_3\text{OH}$ .

## CONCLUSION

The direct synthesis of DMC from methanol and supercritical carbon dioxide over various basic catalysts was studied. From the experimental results the following conclusions can be drawn:

1. The yield of DMC increased with the addition of the catalyst, promoter and dehydrating agent. Their optimum quantity was estimated.
2. As the yield of DMC decreased, by-products such as dimethyl ether and  $\text{C}_1 - \text{C}_2$  hydrocarbons were produced.
3. The yield of DMC with different alkali metal catalysts ranked in the following order:  $\text{K} > \text{Na} > \text{Li}$ .  $\text{CO}_3^{2-}$  containing catalysts were more effective than  $\text{OH}^-$  containing catalysts on the DMC synthesis.
4. The maximum DMC yield was reached up to 12 mole% in the presence of  $\text{K}_2\text{CO}_3$  (catalyst),  $\text{CH}_3\text{I}$  (promoter) and 2,2-dimethoxypropane (dehydrating agent).
5. The reaction mechanism of DMC synthesis from methanol and supercritical carbon dioxide was proposed.

## REFERENCES

- [1] Romano, U., Tesel, R., Mauri, M. M. and Rebora, P., Ind. Eng. Chem. Prod. Res. Dev., 19, **1980**, p.396
- [2] Hiwara, A., Inoki, S. and Fujii, T., Shokubai, 38 **1996**, p.618
- [3] Yanji, W., Xinqiang, Z., Baoguo, Y., Bingchang, Z. and Jinsheng, C., Appl. Catal., A, 171, **1998**, p.255

- [4] Tomishige, K., Sakai, T., Sakai, S. and Fujimoto, K., *Appl. Catal., A*, 181, **1999**, p.95
- [5] Filardo, L., Galia, A., Rivetti, F., Scialdone, O. and Silvestri, G., *Electrochim. Acta.*, 42, **1997**, p.1961
- [6] Choi, G. C., Sakakura, T. and Sako, T., *J. Am. Chem. Soc.*, 121, **1999**, p.3793
- [7] Otsuka, K., Yagi, T. and Yamanaka, I., *Chem. Lett.*, **1994**, p495
- [8] King, S. T., *J. Catal.*, 161, **1996**, p.530
- [9] Yamamoto, Y., Matsuzaki, T., Tanaka, S., Nishihara K., Ohdan, K., Nakamura, A. and Okamoto, Y., *J. Chem. Soc., Faraday Trans.*, 93, **1997**, p.3721
- [10] Jiang, X. Z., *Platinum Met. Rev.*, 34, **1990**, p178
- [11] Fang, S. and Fujimoto, K., *Appl. Catal., A*, 142, **1996** p.L1
- [12] Tatsumi, T. and Koyano, K., *Chem. Commun.*, **1996**, p2281
- [13] Kizlink, J., *Collect. Czech. Chem. Commun.*, 58, **1993**, p.1399
- [14] Kizlink, J. and Pastucha, I., *Collect. Czech. Chem. Commun.*, 60, **1995**, p.687
- [15] Kizlink, J. and Pastucha, I., *Collect. Czech. Chem. Commun.*, 59, **1994**, p.2116