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Synthesis of dimethyl carbonate by vapor phase oxidative carbonylation of methanol over Cu-based catalysts

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Abstract

Dimethyl carbonate (DMC) synthesis reaction by oxidative carbonylation of methanol has been studied using vapor phase flow reaction system in the presence of Cu-based catalysts. A series of Cu-based catalysts were prepared by the conventional impregnation method using activated carbon (AC) as support. The effect of various promoters and reaction conditions on the catalytic reactivities were intensively evaluated in terms of methanol conversion and DMC selectivity. The morphological analysis by X-ray diffraction and SEM was also conducted in order to characterize the employed catalysts. Regardless of catalyst compositions, the optimal reaction temperature for oxidative carbonylation of methanol was found to be around 120–130°C. The reaction rate was too slow below 100°C, while too much by-products was produced above 150°C. Among the various catalysts employed, CuCl₂/NaOH/AC catalyst with the molar ratio of OH/Cu = 0.5–1.0, has shown the best catalytic performance, which appears to have a strong relationship with the formation of intermediate species, Cu₂(OH)₃Cl. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dimethyl carbonate (DMC); Oxidative carbonylation; Methanol; Cu-based catalysts; Cu₂(OH)₃Cl

1. Introduction

Dimethyl carbonate (DMC, (CH₃O)₂CO) is attracting increasing attention as an important chemical feed stock recently. It has versatile chemical properties as a non-toxic carbonylating and methylating agent by the presence of a carbonyl group and two methoxy groups in its molecule. It can be effectively used as an environmentally benign substitute for phosgene in polycarbonates and isocyanates synthesis, and dimethyl sulfate in various methylation reactions

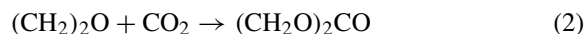
[1]. In addition, a lot of research as for the use of a potential gasoline fuel additive is going on owing to its high oxygen content [2]. DMC has about three times higher oxygen content than methyl *tert*-butyl ether (MTBE) and its synthesis is not dependent upon isobutylene yields like MTBE.

Several reaction routes have been known for DMC production so far as follows:

The phosgene–methanol process

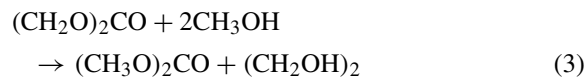


The ester exchange process

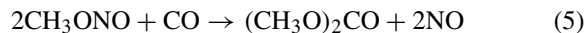
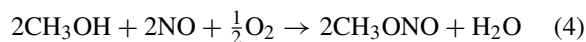


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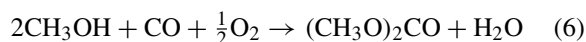
E-mail address: bglee@kist.re.kr (B.G. Lee).



The methylnitrite process



The oxidative carbonylation of methanol process



Conventionally, DMC was synthesized by the reaction of phosgene and methanol. However, this method is currently being phased out because of the high toxicity and severe corrosivity of phosgene and HCl. Since DMC is considered as a promising substitute for phosgene in various carbonylation reactions, the process employing phosgene has no significance any more in a practical point of view at this moment.

The ester exchange process has not been industrialized yet due to the poor economical feasibility. One of

the main drawbacks of this process is in that the process economics is strongly tied to the ethylene glycol market since the equivalent mole of ethylene glycol is simultaneously produced with DMC as by-products [3].

The methylnitrite process was developed and commercialized by Ube in Japan several years ago. In this process, methylnitrite is employed as an intermediate product in order to improve methanol conversion, which is continuously recycled during operation.

The oxidative carbonylation of methanol process was initially developed by Enichem in Italy in 1980s and currently in operation. Since DMC synthesis reaction in this process takes place in liquid phase, there exist some problems such as the separation of products from catalysts and so on. In order to overcome the shortcomings of liquid phase oxidative carbonylation of methanol, the vapor phase process has been proposed and quite a lot of research results have been published these days [4–6].

This work focused on the investigation of fundamental characteristics of vapor phase DMC synthe-

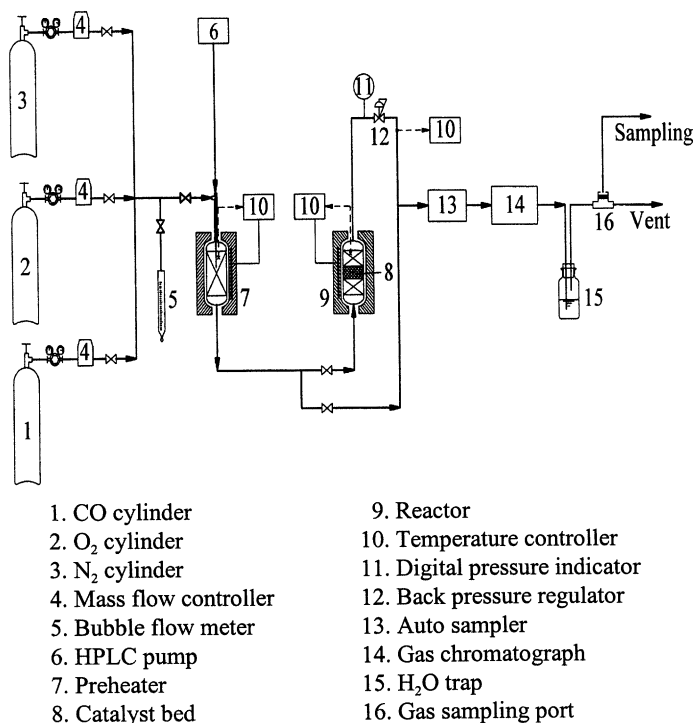


Fig. 1. Schematic diagram of experimental apparatus.

sis reaction between methanol, carbon monoxide and oxygen. A series of Cu-based catalysts were prepared and the effect of reaction conditions and various promoters on the catalyst performance were evaluated in terms of methanol conversion and DMC selectivity. X-ray diffraction and scanning electron microscope (SEM) analysis were also conducted in order to characterize the employed catalysts.

2. Experimental

2.1. Preparation and characterization of catalysts

A series of Cu-based catalysts were prepared by the impregnation method using activated carbon (AC) as support. Activated carbon support and other chemical reagent used for catalyst preparation were commercial products with C.P. grade.

A copper chloride solution was prepared by dissolving CuCl_2 in ethanol. Activated carbon particles were

impregnated with copper chloride solution, followed by the drying under a flow of nitrogen gas at 150°C for 3 h. Then, dried samples were cooled down to room temperature. A second impregnation was conducted in sodium hydroxide solution. The particles were again subjected to a thermal treating under a flow of nitrogen gas at 150°C for 3 h. The morphological analysis of catalysts was conducted by X-ray diffraction and SEM.

2.2. Reaction

The DMC synthesis reaction by oxidative carbonylation of methanol with carbon monoxide and oxygen was investigated in a continuous flow system with a fixed bed reactor. The reactor was made of SS-316 tube having a diameter of 0.5 in. and a length of 55 cm. The schematic diagram of the experimental system is shown in Fig. 1. A 5.0 g of catalyst sample was filled in the reactor and placed between two layers of glass bead beds. The temperature of catalyst bed in the re-

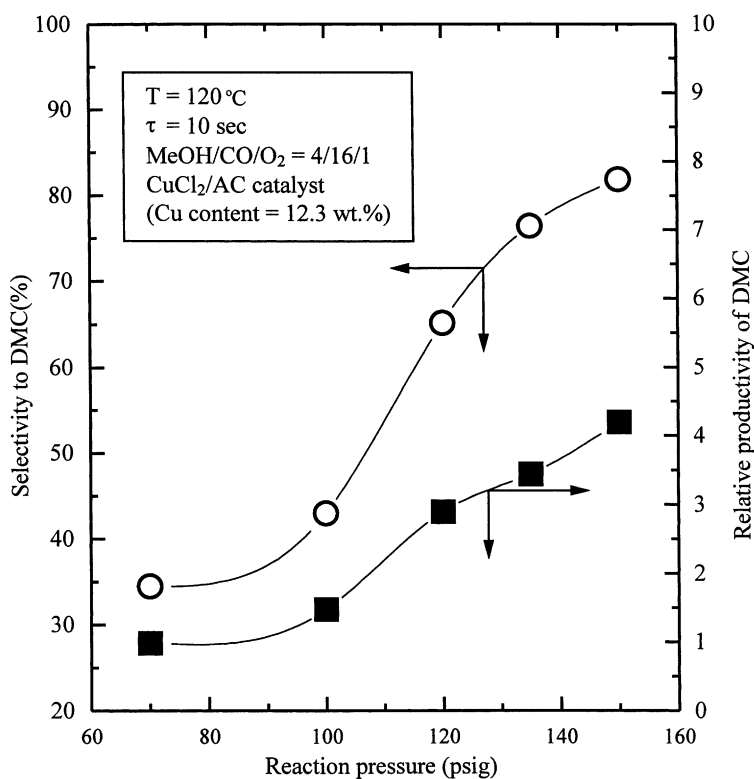


Fig. 2. The effect of reaction pressure on DMC synthesis reaction.

actor was measured by a thermocouple and controlled with a precision of $\pm 1^\circ\text{C}$ by a temperature controller. The reaction pressure was measured by digital pressure indicator (Omega DP-350) and maintained constant by back pressure regulator. Methanol was introduced using HPLC pump (Gilson Medical Electronics, Model 302) to the pre-heater, where it was vaporized and then entered the reactor together with carbon monoxide and oxygen. The flow rate of carbon monoxide and oxygen was controlled by mass flow controller (Matheson Model 8270). The reaction products were analyzed using the gas chromatograph (Gow-Mac Model 550P) equipped with TCD detector. Porapak N column (1/8 in. \times 3 m, 80/100) and Carbo-sphere column (1/8 in. \times 1.83 m, 80/100) were used for the analysis of liquid products and uncondensable gas products, respectively.

3. Results and discussion

3.1. Reaction conditions

DMC can be catalytically synthesized by the reaction of methanol, carbon monoxide and oxygen as shown in the Eq. (6). In this work, various fundamental aspects of DMC synthesis reaction have been investigated varying reaction conditions and catalyst compositions.

Fig. 2 shows the effect of reaction pressure in the range of 0–150 psig on the DMC productivity and selectivity at the reaction temperature of 120°C . The molar ratio of reactants was $\text{MeOH}/\text{CO}/\text{O}_2 = 4/16/1$. The contact time (τ) between reactants and catalyst was maintained same as 10 s based on the standard conditions of room temperature and atmospheric pressure.

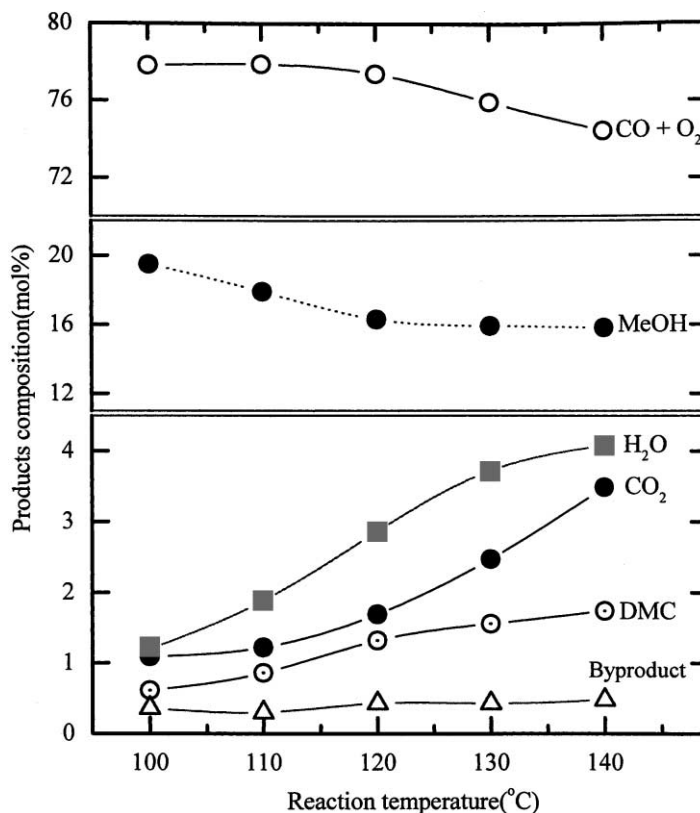


Fig. 3. The effect of reaction temperature on DMC synthesis reaction (CuCl_2/AC catalyst (Cu content = 12.3 wt.%), $P = 150$ psig, $\text{MeOH}/\text{CO}/\text{O}_2 = 4/16/1$ and $\tau = 10$ s).

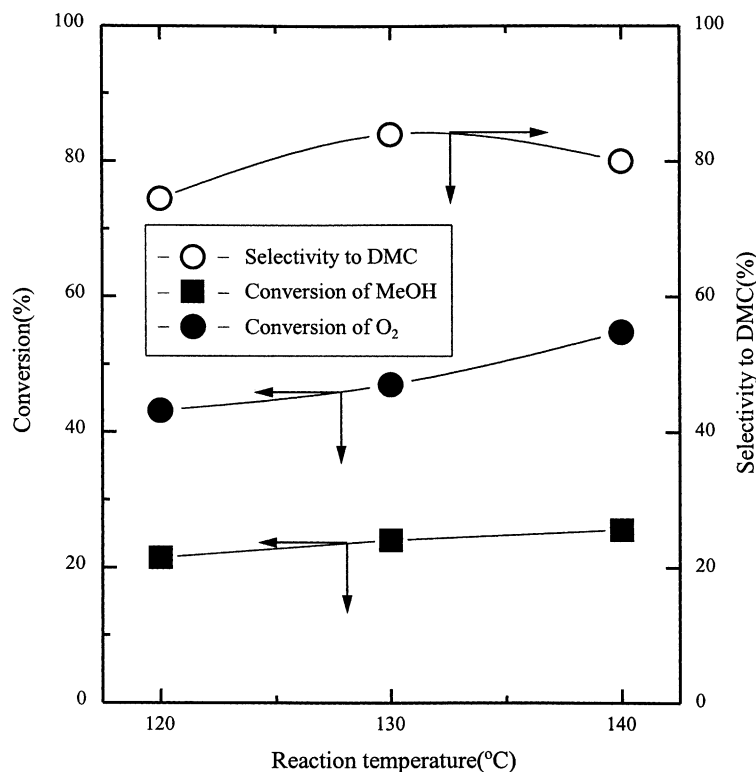


Fig. 4. The change in reactants conversion and DMC selectivity depending upon reaction temperature (CuCl₂/AC catalyst (Cu = 12.3 wt.%), $P = 150$ psig, MeOH/CO/O₂ = 4/16/1 and $\tau = 10$ s).

The employed catalyst was CuCl₂/AC (Cu content = 12.3 wt.%).

As can be expected in the Eq. (6), the pressure was found to affect DMC synthesis reaction very favorably. DMC was hardly produced at the atmospheric pressure, but its production rate was increased continuously with the increase of reaction pressure. The relative productivity of DMC at 150 psig was more than four times as compared with that of 70 psig. The selectivity to DMC was also markedly increased from 35 to 80% with the change of reaction pressure from 70 to 150 psig.

The effect of reaction temperature on the catalyst performance is shown in Fig. 3. The reaction condition was $P = 150$ psig, MeOH/CO/O₂ = 4/16/1 (molar ratio) and $\tau = 10$ s. The employed catalyst was CuCl₂/AC (Cu content = 12.3 wt.%). The reaction temperature was varied from 100 to 150 °C.

The reaction hardly took place below $T = 100$ °C and only a trace amount of reaction products was detected. On the other hand, too much by-products were produced above $T = 150$ °C. Especially, a lot of carbon dioxide was produced at higher temperature condition by the direct reaction of carbon monoxide and oxygen. As liquid by-products, methylformate (HCOOCH₃) and dimethoxymethane (CH₃OCH₂OCH₃) were formed. And a trace amount of methylchloride (CH₃Cl) was detected. Considering the reaction rate and the formation of by-products, the optimal temperature condition for DMC synthesis is thought to be around 120–130 °C.

Fig. 4 illustrates the change of DMC selectivity and reactants conversion in the range of $T = 120$ – 140 °C. The conversion of methanol and oxygen was increased continuously with the increase of reaction temperature while DMC selectivity showed maximum at $T = 130$ °C.

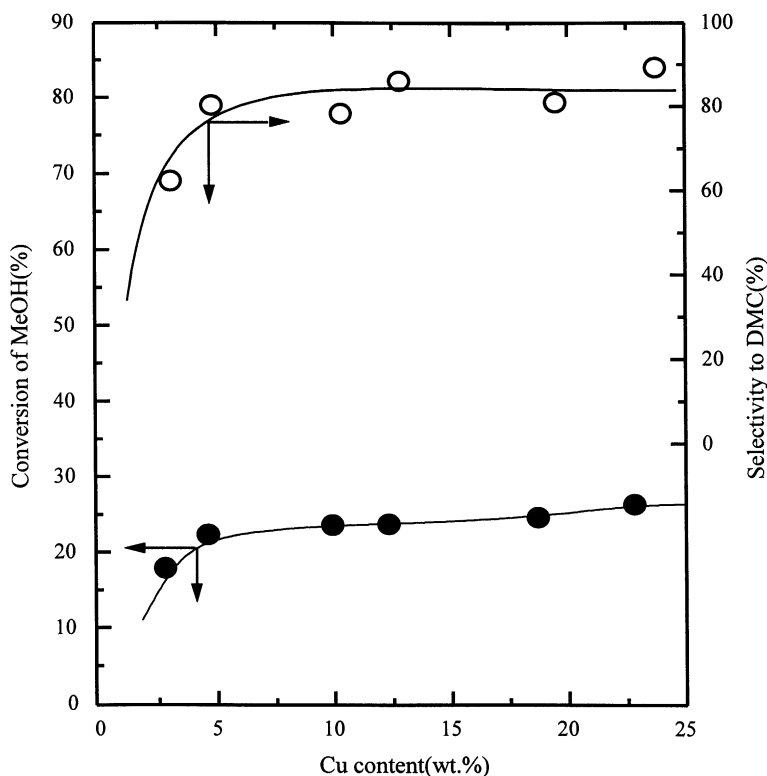


Fig. 5. The effect of Cu content in CuCl_2/AC catalyst on MeOH conversion and DMC selectivity.

3.2. Effect of Cu content on DMC synthesis

The influence of Cu content in CuCl_2/AC catalyst on DMC synthesis reaction is as shown in Fig. 5. The Cu content was varied from 0.0 to 22.8 wt.%. In case no CuCl_2 was loaded on activated carbon, the reaction did not take place at all. With the increase of Cu content, the methanol conversion was found to increase

in the entire range of test. But the effect of Cu content increment on the catalytic activity was not so eminent in the region of higher loadings of Cu than 5 wt.%. At the Cu content of 2.6, 4.6 and 22.8 wt.%, the methanol conversion was found to be 17.5, 22.0 and 24.0%, respectively. Thus, the optimal Cu content on activated carbon for DMC synthesis reaction is thought to be 5–10 wt.% in the economical view point. Once the Cu

Table 1

The effect of hydroxide series additives in CuCl_2/AC catalyst (Cu content = 4.6 wt.%) on DMC synthesis reaction

| Catalysts | Additive/Cu (molar ratio) | Conversion (%) | | Selectivity to DMC (%) | DMC yield (%) | STY ^a (g mol/l/h) |
|--|---------------------------|----------------|----------------|------------------------|---------------|------------------------------|
| | | MeOH | O ₂ | | | |
| $\text{CuCl}_2/\text{AC}^b$ | 0.0 | 20.36 | 48.11 | 80.23 | 16.33 | 0.39 |
| $\text{CuCl}_2/\text{NaOH}/\text{AC}$ | 0.5 | 22.02 | 48.19 | 84.82 | 18.67 | 0.45 |
| $\text{CuCl}_2/\text{KOH}/\text{AC}$ | 0.5 | 21.42 | 44.74 | 83.15 | 17.81 | 0.43 |
| $\text{CuCl}_2/\text{Ba}(\text{OH})_2/\text{AC}$ | 0.5 | 19.58 | 48.91 | 79.61 | 15.58 | 0.37 |
| $\text{CuCl}_2/\text{Mg}(\text{OH})_2/\text{AC}$ | 0.5 | 8.89 | 8.19 | 75.08 | 6.67 | 0.16 |

^a STY: space time yield (g mol DMC/l-catalyst/h).

^b AC: activated carbon.

Table 2

The effect of chloride series additives in CuCl₂/AC catalyst (Cu content = 4.6 wt.%) on DMC synthesis reaction

| Catalysts | Additive/Cu (molar ratio) | Conversion (%) | | Selectivity to DMC (%) | DMC yield (%) | STY ^a (g mol/l/h) |
|--|---------------------------|----------------|----------------|------------------------|---------------|------------------------------|
| | | MeOH | O ₂ | | | |
| CuCl ₂ /AC ^b | 0.0 | 20.36 | 48.11 | 80.23 | 16.33 | 0.39 |
| CuCl ₂ /ZnCl ₂ /AC | 0.5 | 7.92 | 18.29 | 60.04 | 4.75 | 0.11 |
| CuCl ₂ /PdCl ₂ /AC | 0.5 | 11.07 | 84.67 | 66.83 | 7.39 | 0.17 |
| CuCl ₂ /FeCl ₃ /AC | 0.5 | 10.13 | 27.73 | 74.98 | 7.59 | 0.18 |
| CuCl ₂ /NiCl ₂ /AC | 0.5 | 17.08 | 51.22 | 85.16 | 14.54 | 0.35 |

^a STY: space time yield (g mol DMC/l-catalyst/h).^b AC: activated carbon.

content was higher than 5.0 wt.%, DMC selectivity was in the range 80–85%.

3.3. Effect of alkali or alkali-earth hydroxide and metal chloride additives on DMC synthesis

Tables 1 and 2 show the effect of various alkali or alkali-earth hydroxide additives and metal chloride ad-

ditives on DMC synthesis reaction, respectively. As alkali or alkali-earth hydroxide additives, NaOH, KOH, Ba(OH)₂ and Mg(OH)₂ were used and as metal chloride additives, ZnCl₂, PdCl₂, FeCl₃ and NiCl₂ were selected. These additives were impregnated on the identical CuCl₂/AC catalyst of Cu content = 4.6 wt.% and their effects were compared. The molar ratio of each additive to Cu was fixed as 0.5 for all cases.

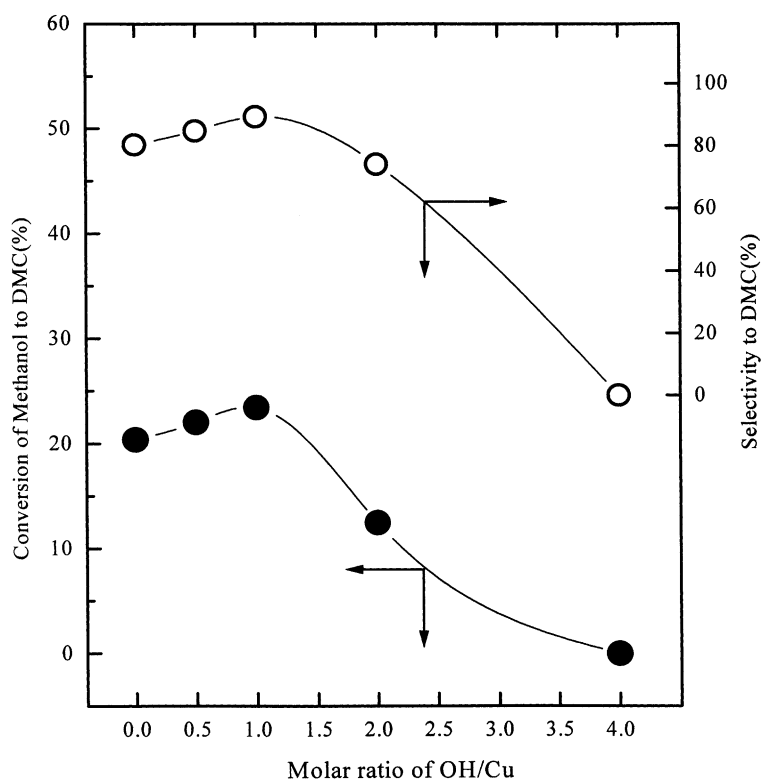


Fig. 6. The effect of OH/Cu molar ratio in CuCl₂NaOH/AC catalyst on MeOH conversion and DMC selectivity.

As indicated in Tables 1 and 2, hydroxide series additives showed much better catalytic performance than chloride series additives in DMC synthesis reaction. Interestingly, all of the metal chloride additives have shown negative effects on the reaction, while some of the hydroxide series additives worked positively. This result strongly implies that the hydroxyl group (OH) may take a certain role in the DMC synthesis reaction. Among various alkali hydroxide additives, NaOH has shown the best catalytic reactivity in terms of DMC yield.

The space time yield (STY) was also compared as shown in Tables 1 and 2. As expected from DMC yield results, $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst has shown the highest STY of 0.45 g mol DMC/l-catalyst/h among all catalysts. The turnover number (TON) of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst was calculated as 560 h^{-1} .

For chloride series additives, two interesting results have been found as shown in Table 2. One is the oxy-

gen conversion of $\text{CuCl}_2/\text{PdCl}_2/\text{AC}$ catalyst. In this case, even though the methanol conversion was low, the oxygen conversion was found to be much higher, almost double, as compared with that of CuCl_2/AC catalyst. This higher oxygen conversion is thought to be related with the reaction between O_2 and CO. During DMC synthesis reaction with this catalyst, it was observed that much more CO_2 produced than other catalysts. Pd appeared to help promoting the reaction of CO with O_2 . Wei has also reported that Pd was very effective in oxidizing carbon monoxide [7].

The other is regarding the selectivity of $\text{CuCl}_2/\text{NiCl}_2/\text{AC}$ catalyst. This catalyst has shown the highest selectivity of all the catalysts even though methanol conversion was not so excellent. This result is related with the suppression of by-products formation. During DMC synthesis reaction, a small part of methanol is decomposed to produce H_2O and CO_2 as

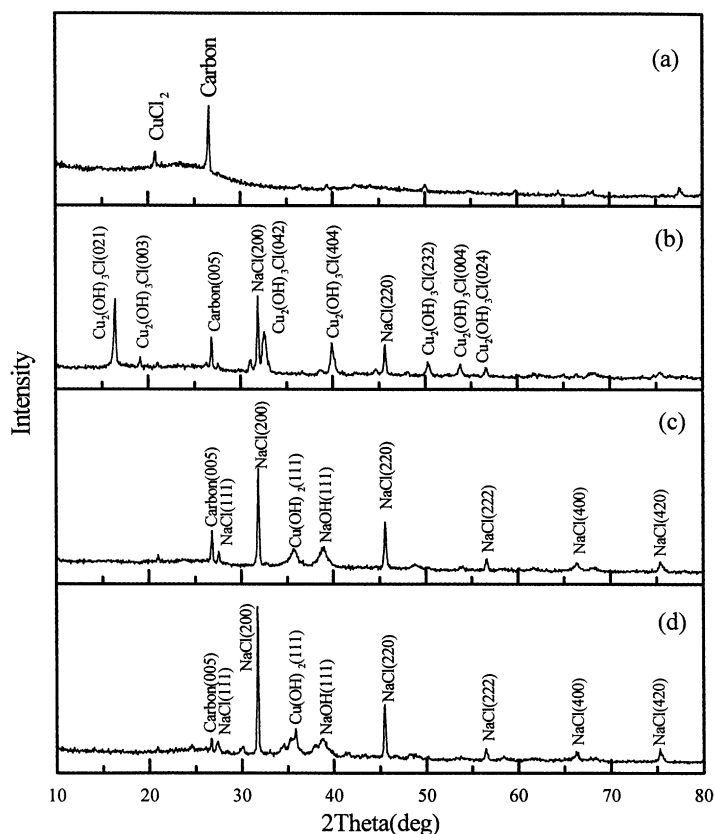


Fig. 7. XRD patterns of fresh $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst at various molar ratio of OH/Cu (OH/Cu molar ratio: (a) 0.0; (b) 1.0; (c) 2.0; (d) 4.0).

follows:



By-products, methylformate (HCOOCH_3) and dimethoxymethane ($\text{CH}_3\text{OCH}_2\text{OCH}_3$) are formed by the reaction of methanol with the intermediate species, HCOOH and HCHO [8]. The strong bond between Ni and oxygen seemed to promote the formation of H_2O and CO_2 more than that of methylformate and dimethoxymethane. This kind of observations may be supported by the findings of Toyoshima and Somorjai that the oxygen adsorption heat of Ni is much greater than that of Pd and Zn [9]. Though the DMC selectivity of $\text{CuCl}_2/\text{NiCl}_2/\text{AC}$ catalyst was better than that of CuCl_2/AC catalyst, $\text{CuCl}_2/\text{NiCl}_2/\text{AC}$ catalyst was not so effective for DMC production because of low methanol conversion.

3.4. Effect of OH/Cu molar ratio on DMC synthesis

Because NaOH has shown the best catalytic reactivity in terms of DMC yield among various alkali hydroxide additives, the effect of OH/Cu molar ratio on the catalyst performance was more intensively investigated. Fig. 6 shows the methanol conversion change depending on the OH/Cu molar ratio. The molar ratio of OH/Cu was varied from 0.5 to 4.0 for CuCl_2/AC catalyst of Cu content = 4.6 wt.%. Up to OH/Cu = 1.0, the catalytic performance was improved, but it was drastically decreased with the further increase of OH/Cu molar ratio. The $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst with the lower ratio of OH/Cu than 1.0 has shown 5–10% higher DMC yield than CuCl_2/AC catalyst with no NaOH.

In order to elucidate the favorable effect of NaOH in CuCl_2/AC catalyst for DMC synthesis reaction, X-ray

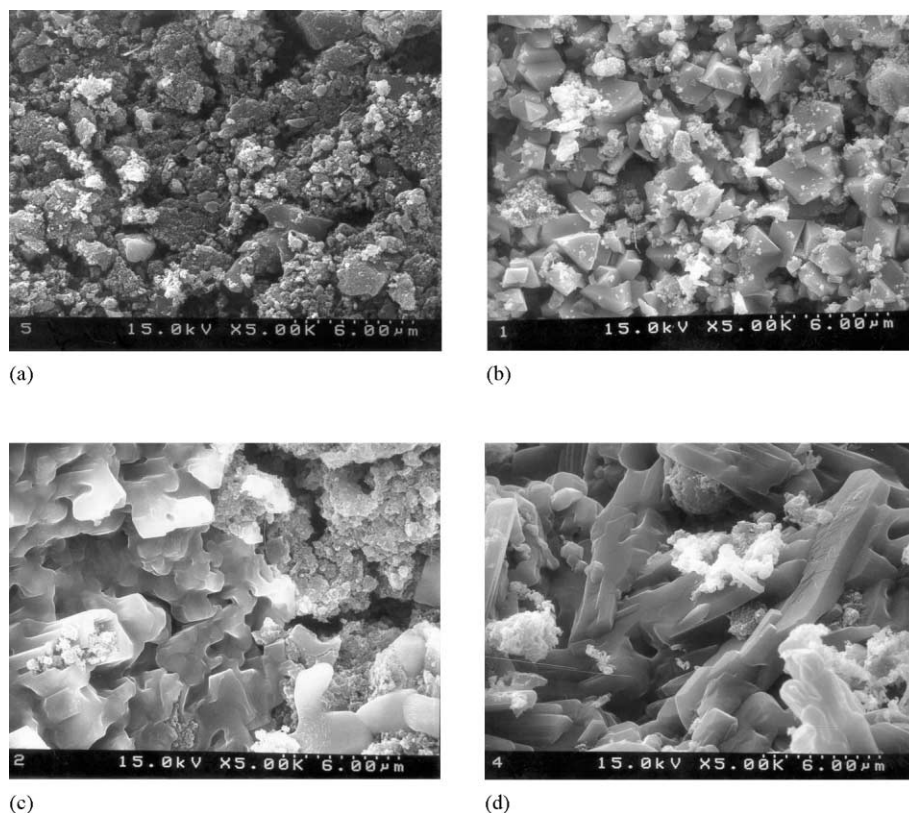


Fig. 8. SEM image of fresh $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts (Cu = 4.6 wt.%): (a) OH/Cu = 0.0; (b) OH/Cu = 1.0; (c) OH/Cu = 2.0; (d) OH/Cu = 4.0.

diffraction and SEM analysis were conducted for fresh CuCl_2/AC and $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts.

Fig. 7 compares the X-ray diffraction pattern of fresh CuCl_2/AC and $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts. A lot of $\text{Cu}_2(\text{OH})_3\text{Cl}$ peaks were detected in $\text{CuCl}_2/\text{NaOH}/\text{AC}$, while only CuCl_2 peak was detected in CuCl_2/AC catalyst. Considering better performance of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ than CuCl_2/AC catalyst, $\text{Cu}_2(\text{OH})_3\text{Cl}$ may have a strong relationship with the formation of DMC. In the higher OH/Cu molar ratio region, $\text{Cu}_2(\text{OH})_3\text{Cl}$ peaks disappeared and instead NaCl peaks were newly detected.

Fig. 8 compares the SEM images of fresh CuCl_2/AC and $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts. The active sites of catalysts appear to be well distributed in the lower OH/Cu region, while larger crystallites can be seen in the higher OH/Cu region. In the higher OH/Cu region, NaCl crystallites are interpreted to block the active sites of catalysts.

Based on all of the experimental observations and morphological analysis, it may be conclusively said that appropriate amount of NaOH addition helps enhancing the performance of CuCl_2/AC catalyst by forming intermediate species, $\text{Cu}_2(\text{OH})_3\text{Cl}$, in DMC synthesis reaction.

4. Conclusions

In this work, DMC synthesis reaction by oxidative carbonylation of methanol has been studied using

vapor phase flow reaction system in the presence of a series of Cu-based catalysts. The effect of reaction conditions and various promoters on the catalyst performance were evaluated in terms of methanol conversion and DMC selectivity. X-ray diffraction and SEM analysis were also conducted in order to characterize the employed catalysts.

The optimal reaction temperature for DMC synthesis reaction was found to be around 120–130°C. The reaction rate was too slow below 100°C, while too much by-products was produced above 150°C. Among the various catalysts employed, $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst with the molar ratio of OH/Cu = 0.5–1.0 has shown the best catalytic performance, which appears to have a strong relationship with the formation of intermediate species, $\text{Cu}_2(\text{OH})_3\text{Cl}$.

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