Study on the Formation and Role of Copper Chloride Hydroxide in the Oxidative Carbonylation of Methanol to Dimethyl Carbonate¹

Jun Ren*, Zhong Li, Shusen Liu, Xinglu Lu, and Kechang Xie

Key Laboratory of Coal Science and Technology (Taiyuan University of Technology), Ministry of Education and Shanxi Province, 030024 Taiyuan, China

**e-mail: renjun@tyut.edu.cn* Received December 29, 2008

Abstract—The synthesis of dimethyl carbonate by oxidative carbonylation of methanol over CuCl/SiO₂–TiO₂ catalysts has been investigated in a slurry reaction system. The γ -Cu₂(OH)₃Cl crystals were detected by X-ray diffraction on the catalysts after reaction. It was revealed that γ -Cu₂(OH)₃Cl was formed by CuCl reacting with O₂ and by-product water. The catalytic tests showed that γ -Cu₂(OH)₃Cl was largely inactive for this reaction, may be attributed to its high stability that resisted the Cu⁺/Cu²⁺ redox cycle.

DOI: 10.1134/S0023158410020138

1. INTRODUCTION

Dimethyl carbonate (DMC) is an environmentally benign chemical product and unique intermediate with versatile chemical reactivity [1]. The direct oxidative carbonylation of methanol with CO and O_2 to DMC in a liquid-phase slurry process has been industrially employed by using cuprous chloride as catalyst [2]. The existence of Cl⁻ in aqueous media, under the condition of the redox of Cu, was revealed to induce severe corrosion to metallic materials along with catalyst deactivation. Attempts have been made to develop alternative catalyst systems, mainly including supported CuCl or CuCl₂ catalysts [3, 4]. On the other hand, a one-step vapor phase process was subsequently developed and considered to be more desirable because it has been found almost free from corrosion [5], However, the $CuCl_2/AC$ catalyst suffered deactivation due to loss of chloride [6]. The catalyst structure changed together with the removal of chloride anions during the catalytic reaction, CuCl₂ and CuCl species seemed to be converted to Cu-Cl-OH compounds. It was found that maintaining these compounds on the surface of activated carbon appeared to be helpful to selective DMC synthesis.

Supported Wacker-type catalyst $PdCl_2-CuCl_2-CH_3COOK/AC$ was recently investigated, it was found that the activated carbon supports pretreated with H_2O and KOH or H_2 reduction could promote the formation of $Cu_2(OH)_3Cl$, which was recognized as the active phase over the catalysts [7]. An excellent correlation was further observed between the intensity of X-ray diffraction (XRD) reflections of $Cu_2(OH)_3Cl$ and the space—time yield for DMC production. It

was reported that two different crystal habits of $Cu_2(OH)_3Cl$, α -type and γ -type were observed during the preparation of $CuCl_2/NaOH/AC$ catalysts, the $Cu_2(OH)_3Cl$ phase changed from α -type to γ -type with increasing OH/Cl molar ratios [8]. The improved performance of the catalysts was related with the existence of $Cu_2(OH)_3Cl$, the γ -type catalyst was considered to be more favorable to DMC synthesis than the α -type catalyst [9]. Together, these previous studies indicated that there might be a correlation between the remarkable compound γ -Cu₂(OH)₃Cl and DMC productivity. However, the mechanism of γ -Cu₂(OH)₃Cl formation has not been clarified. Moreover, the correlation between γ -Cu₂(OH)₃Cl and intrinsic catalytic performance remains ambiguous.

We have recently studied the interaction between CuCl and the oxide support of CuCl/SiO₂-TiO₂ catalysts for the synthesis of DMC using quantum mechanical methods (DFT). The calculation results show that supporting CuCl on silica-titania mixed oxides surface can lead to enhanced methanol oxidative carbonylation activity and improved catalyst stability due to the formation of Cu-O coordination bonds [10]. In the present work, in order to elucidate the above two problems, the SiO_2 -TiO₂ supported CuCl catalysts along with the compound γ -Cu₂(OH)₃Cl were prepared and their catalytic performances for the oxidative carbonylation of methanol have been investigated in the liquid-phase reaction. The influence of γ -Cu₂(OH)₃Cl on the catalytic performance of CuCl/SiO₂-TiO₂ was discussed, and the formation mechanism and role of γ -Cu₂(OH)₃Cl in this reaction was proposed and confirmed by experiment.

¹ The article is published in the original.

Table 1. Catalytic activities of the $CuCl/SiO_2$ -TiO₂ catalyst^a

Sample	DMC, wt %	DMM, wt %	MF, wt %	$C_{ m m}^{ m b}$, mol %	$S_{ m m}^{ m c}$, mol %	$STY^{d},$ $g_{DMC} g_{Cat}^{-1} h^{-1}$	Grain size of γ -Cu ₂ (OH) ₃ Cl ^e , nm
Fresh	8.79	0.93	0.07	7.68	83.35	1.17	—
1st recycle	6.88	1.34	0.15	6.85	72.61	0.92	21
2nd recycle	5.71	1.28	0.12	5.87	69.99	0.76	46
3rd recycle	4.64	1.28	0.13	5.10	65.36	0.62	56

Note: ^a Reaction conditions: MeOH/CO/O₂ = 19.13/2/1(mol/mol), W_{cat} = 2.0 g, Temperature = 140°C. Pressure = 2.4 MPa. Reaction time (*t*) = 1.5 h. ^b MeOH conversion = Produced (DMC + DMM + MF)/MeOH. ^c DMC selectivity (based on MeOH) = DMC/(DMC + DMM + MF). ^d DMC space-time yield = (MeOH conversion)(DMC selectivity)/(tW_{cat}). ^e Calculated from the Scherrer equation.

2. EXPERIMENTAL

2.1. Preparation of CuCl/SiO₂-TiO₂ Catalysts

The silica-titania support with a Si/Ti ratio of 10 was prepared by following the method described in the previous paper [11]. The support was mixed with CuCl (weight ratio: 80/20) and calcined at 550° C in a tube oven under N₂ atmosphere for 3 h followed by cooling to room temperature, then the CuCl/SiO₂-TiO₂ catalyst was obtained.

2.2. Preparation of γ -Cu₂(OH)₃Cl

 γ -Cu₂(OH)₃Cl was synthesized by two separate routes. **Route 1:** Treating CuO and CuCl₂ · 2H₂O in a hydrothermal process [12], the slurry was mixed using a magnetic stirrer in a round bottomed flask for 24 h. The precipitate was collected, washed and dried at 80°C for 1.5 h and the resulting powder was represented as sample "A." **Route 2:** A saturated solution was prepared with 30 g NaCl dissolving in 100 ml water, and then CuCl was immersed. The solution was transferred into a three-necked bottle when its color had become yellow, then air was introduced and the system was kept in a hot-bath of 70°C for 7–8 h under stirring conditions. The product was washed, filtered and dried at 90°C overnight; the resultant powder was represented as sample "B."

2.3. Catalytic Reaction and Analytical Procedures

The catalytic reaction was performed in a 250 ml autoclave according to the following procedure: 50 ml of methanol, which served as the substrate and solvent, and catalyst powders (2.0 g) were added in the autoclave. Then, CO (1.6 MPa) and O_2 (0.8 MPa) were introduced. After reaction at 140°C for 1.5 h, concentrations of DMC, methanol, dimethoxymethane (DMM) and methyl formate (MF) were analyzed by gas chromatography. The blank test was also performed under catalyst-free condition for comparison.

2.4. XRD Analysis

X-ray diffraction (XRD) data were recorded on a Rigaku D/max 2500 diffractometer using CuK_{α} radiation (40 kV and 100 mA) over a 2 θ range of 10°-65° at a scanning rate of 1 deg/min.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activity of CuCl/SiO₂-TiO₂

Table 1 gives the results of catalytic tests on the $CuCl/SiO_2$ -TiO₂ catalyst through three successive recycle runs after filtration and washing with methanol. The products derived from methanol included DMC, DMM and MF. The freshly prepared catalyst gave a methanol conversion of 7.68% and DMC selectivity of 83.35%, and an obvious decrease in activity and selectivity was observed after successive recycling of the catalyst. In its first recycling use, methanol conversion and DMC selectivity dropped to 6.85 and 72.61%, respectively. During the second and third recycling, DMC selectivity eventually decreased to 69.99 and 65.36% with further decline in methanol conversion.

3.2. Crystalline Structure of CuCl/SiO₂ $-TiO_2$ before and after Reaction

Figure 1 presents XRD patterns of the fresh and the recycled CuCl/SiO₂-TiO₂ catalysts. In all cases, a broad diffraction peak at approximately 23° was obtained, which was believed to be due to amorphous supports, SiO_2 -TiO₂ mixed oxide. For the fresh catalyst, regardless of the broad diffraction peak, very weak diffraction peaks corresponding to CuCl were detected, revealing that CuCl was well dispersed on the surface of SiO₂-TiO₂ support through heat treatment under N₂ atmosphere. The elemental analysis results showed that the as-prepared CuCl/SiO₂-TiO₂ catalyst contained 5.85 wt % Cu and 2.93 wt % Cl, suggesting that a great part of CuCl was lost by sublimation during the procedure of catalyst preparation (The theoretical concentrations of Cu and CI were 12.83 wt % and 7.17 wt %, respectively). The Cu/Cl mol ratio in the catalyst was 1.12. It was therefore



Fig. 1. XRD patterns of the fresh and the recycled $CuCl/SiO_2$ -TiO₂ catalysts. (1) Fresh, (2) 1st recycle, (3) 2nd recycle, (4) 3rd recycle.

believed that most of copper was presented in the form of CuCl crystalline phase. As can be seen from Fig. 1, the diffraction peaks of CuCl disappeared after reaction, but weak diffraction peaks corresponding to γ -Cu₂(OH)₃Cl were clearly observed. One possible explanation is that CuCl has been partly converted into γ -Cu₂(OH)₃Cl during the catalytic reaction. Similar results were reported for the CuCl₂/AC catalysts by Tomishige [6], in which methanol was suggested to promote the structural change of the catalyst. It can be further observed that the diffraction peaks attributed to γ -Cu₂(OH)₃Cl became higher with increasing recycling of the catalyst, which may be related to the growth of crystals.

The grain size of γ -Cu₂(OH)₃Cl were calculated based on the Scherrer equation and given in Table 1. As can be seen, DMC space-time yield became lower and the grain size of γ -Cu₂(OH)₃Cl crystals became larger as recycling increased. For the fresh catalyst, DMC space-time yield reached 117 g_{DMC} g_{Cat}⁻¹ h⁻¹. In its first recycling use, DMC space-time yield decreased to 0.92 g_{DMC} g_{Cat}⁻¹ h⁻¹ and the γ -Cu₂(OH)₃Cl crystal with an average grain size of about 21 nm was formed. In the second and third recycling, DMC spacetime yield dropped from 0.76 to 0.62 g_{DMC} g_{Cat}⁻¹ h⁻¹,



Fig. 2. XRD patterns of γ -Cu₂(OH)₃Cl samples prepared by two separate routes: (A) CuCl₂ + CuO + H₂O; (B) CuCl + H₂O + O₂.

respectively. Whereas, the grain size of γ -Cu₂(OH)₃Cl crystals increased from 46 to 56 nm.

3.3. Characterization and Catalytic Performance of γ-Cu₂(OH)₃Cl

Figure 2 shows XRD patterns of two γ -Cu₂(OH)₃Cl samples, **A** and **B**. The characteristic diffraction peaks of γ -Cu₂(OH)₃Cl crystals were clearly observed in both samples. In addition, very weak reflections corresponding to the α -Cu₂(OH)₃Cl phase were also detected, showing that the resulting powders were predominantly in the form of γ -Cu₂(OH)₃Cl crystal with a thimbleful of α -Cu₂(OH)₃Cl crystal concomitant.

Previous studies have shown that the Cu₂(OH)₃Cl phase was perhaps formed during the catalytic reaction [6]. Furthermore, it could also be generated in the procedures of catalyst preparation. Yang [7] and Han [8, 9] reported that $Cu_2(OH)_3Cl$ was detected on the surface of freshly prepared Wacker-type catalysts and CuCl₂/NaOH/AC catalysts. For supported Wackertype catalysts, proper treatment of the carbon supports could promote the formation of Cu₂(OH)₃Cl, which was believed to be responsible for the improved catalytic performance for DMC synthesis [7]. The surface phase was revealed to change from α -Cu₂(OH)₃Cl to γ -Cu₂(OH)₃Cl with increase of OH/Cu molar ratio in CuCl₂/NaOH/AC catalysts and γ -Cu₂(OH)₃Cl was considered to more favorable to DMC synthesis than α -Cu₂(OH)₃Cl [8, 9].

In order to gain further insight into the intrinsic properties, the catalytic performance of the γ -Cu₂(OH)₃Cl crystals for the oxidative carbonylation of methanol was studied. Table 2 gives the results of catalytic tests on γ -Cu₂(OH)₃Cl, together with the data obtained in the blank test. Both γ -Cu₂(OH)₃Cl sample **A** and **B** exhibited very poor catalytic performance and

Sample	DMC, wt %	DMM, wt %	MF, wt %	$C^{\mathrm{b}}_{\mathrm{m}}$, mol %	$S^{ m b}_{ m m}$, mol %	STY ^b , $g_{DMC} g_{Cat}^{-1} h^{-1}$
Blank	0.43	0.23	0.41	1.00	30.65	0.06
Α	0.40	0.26	0.30	0.92	31.16	0.05
В	0.61	0.07	0.30	0.82	52.42	0.08

Table 2. Catalytic performance of γ -Cu₂(OH)₃Cl in DMC synthesis^a

Note: ^a As in Table 1. ^b As in Table 1.

were nearly inert to the reaction. As can be seen, the CH₃OH conversion was not more than 1.0% with the DMC selectivity below 53%, and the space-time yield of DMC maintained between 0.05 and 0.08 $g_{DMC}g_{Cat}^{-1}h^{-1}$, almost the same activity as the blank test. These results strongly suggested that γ -Cu₂(OH)₃Cl was carbonylation inactive. In this case, it becomes difficult to explain the improved catalytic performance of Wacker-type catalysts [7] and CuCl₂/NaOH/AC catalysts [8, 9].

The redox capability of Cu species between Cu²⁺ and Cu⁺ was considered to be important for the enhancement in reaction rate in the oxidative carbonylation of methanol to DMC [2, 13], and the factors that could accelerate the redox cycle of the active centers would be beneficial for the reaction rate. In the present work, the γ -Cu₂(OH)₃Cl crystals were found almost completely insoluble in the reaction mixture and only presented as a suspension. In addition, no weight loss could be detected after reaction.

In order to better understand its stability in the reaction system, the crystal structures and textural properties of γ -Cu₂(OH)₃Cl powder were studied before and after reaction. Almost the same XRD patterns were obtained before and after reaction, suggesting that the crystal structure was not transformed through catalytic reaction. From these results, it was obvious that the γ -Cu₂(OH)₃Cl crystal was highly stable in the reaction system at 140°C and 2.4 MPa under vigorous stirring. These findings provided further confirmation for high stability of γ -Cu₂(OH)₃Cl under the reaction conditions. The synthesis of DMC from methanol, CO and O2 mainly relied on the redox reactions between Cu^+/Cu^{2+} [2]. Therefore, it is concluded that the compound γ -Cu₂(OH)₃Cl having limited or no activity may be attributed to the high stability of Cu²⁺, which resisted the reduction under the reaction conditions and could not form active intermediate responsible for the CO insertion [14].

3.4. Formation and role of γ -Cu₂(OH)₃Cl

The γ -Cu₂(OH)₃Cl crystals were formed over CuCl/SiO₂-TiO₂ catalysts after being used in the oxidative carbonylation of methanol; moreover, catalyst recycling led to a significant loss of catalytic activity. These results suggested that the active species, CuCl

KINETICS AND CATALYSIS Vol. 51 No. 2 2010

was perhaps partly converted into γ -Cu₂(OH)₃Cl during the reaction.

DMC is catalytically synthesized by the reaction of oxidative carbonylation of methanol as shown in Eq. (1):

$$2CH_{3}OH + CO + 0.5O_{2} \rightarrow (CH_{3}O)_{2}CO + H_{2}O.$$
 (1)

As displayed in Eq. (1), formation of DMC molecule from CH₃OH and CO gives equimolar amounts of water. If the by-product water can not be removed from the reaction system, water is always present in increasing amounts as the reaction proceeds. It has been reported that when CuCl is placed at a situation with the existence of O₂ and H₂O, the following reaction perhaps takes place and results in the formation of γ -Cu₂(OH)₃Cl [15], as indicated by Eq. (2):

$$4\operatorname{CuCl} + \operatorname{O}_2 + 4\operatorname{H}_2\operatorname{O}$$

$$\rightarrow 2\operatorname{Cu}_2(\operatorname{OH}), \operatorname{Cl} + 2\operatorname{H}^+ + 2\operatorname{Cl}^-.$$
(2)

This finding has been confirmed by Bell et al. [16] in the preparation of Cu-ZSM-5 catalysts for the synthesis of DMC by Solid-state ion exchange of H-ZSM-5 with CuCl.

In the oxidative carbonylation of methanol, CuCl serves as active species, and O_2 is the reagent gas. Since by-product water is produced during the reaction, it can be concluded that side reaction may be induced as shown in Eq. (2) and lead to the formation of γ -Cu₂(OH)₃Cl. In order to confirm this inference, experiments might also be operative and were carried out as described in **route 2.** The XRD patterns shown in Fig. 2 displayed that the resulting compound, sample **B** was mainly in the form of γ -Cu₂(OH)₃Cl. Thus, this result has provided a powerful confirmation for the formation of γ -Cu₂(OH)₃Cl.

From the Eq. (2), we can see that active species CuCl is transformed into inactive γ -Cu₂(OH)₃Cl phase for methanol oxidative carbonylation associated with loss of chloride. Accordingly, it is believed that the formation of γ -Cu₂(OH)₃Cl must be the intrinsic factor leading to catalyst deactivation. Moreover, according to Eq. (2), the higher the DMC yield is achieved, the more water is produced and kept in the reactor. As a result, higher water content means more significant formation of γ -Cu₂(OH)₃Cl [17].

From above discussion, the water formation and the loss of chlorides may be the intrinsic reasons for the catalyst deactivation. This conclusion has been supported by the results of previous studies, that an improved catalytic activity and decreased deactivation rate of the catalyst could be attained by adding chloride sources (R4NC) [18] and chloride ionic liquids [19] to the reaction system. In addition, we think that perhaps this problem can also be solved by adding water removing solids (zeolites and others). The dried zeolite is suggested to efficiently protect the catalyst from the fast deactivation.

4. CONCLUSIONS

The γ -Cu₂(OH)₃Cl crystals were formed on CuCl/SiO₂-TiO₂ catalysts in the synthesis of DMC by liquid phase oxidative carbonylation of methanol. It was revealed that the formation of γ -Cu₂(OH)₃Cl was due to active CuCl reacting with O₂ and by-product water. The catalytic tests indicated that γ -Cu₂(OH)₃Cl was essentially inactive for this reaction. It could be attributed to its high stability that resisted the reduction of Cu²⁺ under the reaction conditions and could not form active intermediate.

ACKNOWLEDGMENT

We are grateful for the financial support from the National Natural Science Foundation of China (20606022), the National Basic Research Program of China (2005 CB221204) and the Natural Science Foundation for Young Scientists of Shanxi Province, China (20051008).

REFERENCES

1. Delledonne, D., Rivetti, F., and Romano, U., *Appl. Catal.*, *A*, 2001, vol. 221, nos. 1–2, p. 241.

- Romano, U., Tese, R., Mauri, M.M., and Rebora, P., Ind. Eng. Chem. Res., 1980, vol. 19, no. 3, p. 396.
- 3. Cao, Y., Hu, J.C., Yang, P., Dai, W.L., and Fan, K.N., *Chem. Commun.*, 2003, no. 7, p. 908.
- Sato, Y., Kagotani, M., Yamamoto, T., and Souma, Y., *Appl. Catal.*, A, 1999, vol. 185, no. 2, p. 219.
- 5. Itoh, H., Watanabe, Y., Mori, K., and Umino, H., *Green Chem.*, 2003, vol. 10, no. 5, p. 558.
- Tomishige, K., Sakaihori, T., Sakai, S.I., and Fujimoto, K., *Appl. Catal.*, *A*, 1999, vol. 181, no. 1, p. 95.
- Yang, P., Cao, Y., Dai, W.L., Deng, J.F., and Fan, K.N., *Appl. Catal.*, A, 2003, vol. 243, no. 2, p. 323.
- Han, M.S., Lee, B.G., Suh, I., Kim, H.S., Ahn, B.S., and Hong, S.I., *J. Mol. Catal. A: Chem.*, 2001, vol. 170, nos. 1–2, p. 225.
- Han, M.S., Lee, B.G., Ahn, B.S., Kim, H.S., Moon, D.J., and Hong, S.I., *J. Mol. Catal. A: Chem.*, 2003, vol. 203, nos. 1–2, p. 137.
- 10. Ren, J., Li, Z., Liu, S.S., and Xie, K.C. (in press).
- 11. Ren, J., Li, Z., Liu, S.S., Xing, Y.L., and Xie, K.C., *Catal. Lett.*, 2008, vol. 124, nos. 3–4, p. 185.
- 12. Strandberg, H., *Atmos. Environ.*, 1998, vol. 32, no. 20, p. 3511.
- 13. Yuan, Y.Z., Cao, W., and Weng, W.Z., *J. Catal.*, 2004, vol. 228, no. 2, p. 311.
- 14. King, S.T., Catal. Today, 1997, vol. 33, nos. 1-3, p. 173.
- 15. Scott, D.A. and Dodd, L.S., *J. Cult. Herit*, 2002, vol. 3, no. 4, p. 333.
- 16. Zhang, Y.H., Drake, I.J., and Bell, A.T., *Chem. Mater.*, 2006, vol. 18, no. 9, p. 2347.
- 17. Kricsfalussy, Z., Waldmann, H., and Traenckner, H.J., *Ind. Eng. Chem. Res.*, 1998, vol. 37, no. 3, p. 865.
- Raab, V., Merz, M., and Sundermeyer, J., J. Mol. Catal. A: Chem., 2001, vol. 175, nos. 1–2, p. 51.
- Dong, W.S., Zhou, X.S., Xin, C.S., Liu, C.L., and Liu, Z.T., *Appl. Catal.*, *A*, 2008, vol. 334, nos. 1–2, p. 100.