



The role of copper chloride hydroxides in the oxidative carbonylation of methanol for dimethyl carbonate synthesis

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Received 2 October 2002; accepted 14 February 2003

Abstract

Dimethyl carbonate (DMC) synthesis by oxidative carbonylation of methanol has been studied using vapor phase flow reaction system in the presence of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ (AC, activated carbon) catalysts. A series of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts have been prepared by the conventional impregnation method with varying the molar ratio of OH/Cu from 0.0 to 1.0. The catalytic activity of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts has been found to increase continuously with the increase of OH/Cu molar ratio as compared with CuCl_2/AC catalyst. The morphological analysis by X-ray diffraction, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) has shown that the improved performance of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts was closely related with the existence of copper chloride hydroxides ($\text{Cu}_2(\text{OH})_3\text{Cl}$). Two different crystal habits of $\text{Cu}_2(\text{OH})_3\text{Cl}$ were observed in the catalyst surface based on the OH/Cu molar ratio. One is $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ (atacamite) which is orthorhombic, while the other is $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ (paratacamite) which is rhombohedral. The catalyst phase was revealed to change from $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ to $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ with the increase of OH/Cu molar ratio. The catalyst phase was $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ dominant at the molar ratio of OH/Cu = 0.5, while at the molar ratio of OH/Cu = 1.0, $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ dominant. The γ -type catalyst was found to be more favorable to DMC synthesis than the α -type catalyst. The CO temperature-programmed desorption (TPD) experiments on the employed catalysts also strongly supported these observations.

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Keywords: Dimethyl carbonate (DMC); Oxidative carbonylation of methanol; Copper chloride hydroxides ($\text{Cu}_2(\text{OH})_3\text{Cl}$); Atacamite; Paratacamite

1. Introduction

Dimethyl carbonate ($(\text{CH}_3\text{O})_2\text{CO}$, DMC) has been attracting much attention as an environmentally benign chemical recently [1–6]. It can be used

fully employed as a non-toxic carbonylating and methylating agent in various applications. Particularly, DMC can be a very good replacement for phosgene in the synthesis of polycarbonates and isocyanates [1–3]. In addition, a lot of research as a potential gasoline fuel additive is going on due to the merit of its high oxygen content. DMC has about three times higher oxygen content than MTBE [4–6].

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Several reaction routes have been known for DMC synthesis so far [7–18]. Conventionally, DMC was synthesized by the reaction of phosgene and methanol [7]. However, this method is currently being phased out because of the high toxicity and severe corrosivity of phosgene and HCl. DMC can be also synthesized by transesterification method [8,9], methylnitrite method [10] and methanol oxidative carbonylation method [11–13].

Among them, the oxidative carbonylation of methanol process was initially developed by Enichem in Italy in 1983 and is currently in operation. However, since DMC synthesis reaction in this process takes place in liquid phase, there exist some problems such as catalyst separation from reaction products and so on. In order to overcome this kind of drawbacks of liquid phase process, a vapor phase process has been proposed by Curnutt and Harley [14] in 1987 and several research results have been published [15–18].

In our previous work [18], we reported the effect of various promoters and reaction conditions on DMC synthesis over Cu-based heterogeneous catalysts. Among the various promoters of alkali or alkali-earth hydroxides and chlorides, NaOH has shown the best catalytic activity when properly added to CuCl₂/AC (AC, activated carbon) catalysts. The OH/Cu molar ratio in the CuCl₂/NaOH/AC catalysts seems to be closely related with the catalyst performance in the DMC synthesis.

This work focused on the detailed characterization of CuCl₂/NaOH/AC catalysts and the investigation of their role in DMC synthesis. A series of CuCl₂/NaOH/AC catalysts were prepared with varying molar ratios of OH/Cu and the effect of catalyst compositions on DMC synthesis was evaluated. The TPD experiments and the morphological analysis by X-ray diffraction, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) were conducted in order to characterize the employed catalysts.

2. Experimental

2.1. Preparation and characterization of catalysts

A series of CuCl₂/NaOH/AC (Aldrich, Darco 12–20 mesh, granular, $S_{\text{BET}} = 527.8 \text{ m}^2 \text{ g}^{-1}$, acid-washed

lignite carbon for commercial uses) catalysts were prepared by an impregnation method. Activated carbon support and other chemical reagents used for the catalyst preparation were commercial products with CP grade.

A copper chloride solution was prepared by dissolving CuCl₂ in ethanol. Activated carbon particles were impregnated with copper chloride solution and dried under a flow of N₂ at 423 K for 3 h. The dried samples were cooled to room temperature. A second impregnation was conducted in sodium hydroxide solution. The particles were again subjected to a thermal treatment under a flow of N₂ at 423 K for 3 h.

The morphological analysis of the employed catalysts were conducted by X-ray diffractometer (XRD-6000, Shimadzu) and scanning electron microscope (Hitachi S-4200). The X-ray photoelectron spectroscopy analysis was also conducted with a SSI scientific 2803-S spectrometer equipped with a hemispherical energy analyzer.

2.2. DMC synthesis

The DMC synthesis by oxidative carbonylation of CH₃OH with CO and O₂ was investigated in a continuous flow system with a fixed-bed reactor. The reactor was made of Inconel-600 tube having a diameter of 1.27 cm and a length of 55 cm. A 5.0 g of catalyst sample was filled between two layers of glass bead beds in the reactor. The temperature of catalyst bed was measured by a thermocouple and controlled with the precision of $\pm 1 \text{ K}$ by a temperature controller. The reaction pressure was monitored by digital pressure indicator (Omega DP-350) and maintained constant by a back pressure regulator. CH₃OH was introduced using a HPLC pump (Gilson Medical Electronics, model 302) to the pre-heater, where it was vaporized and then entered into the reactor together with CO and O₂. The flow rates of CO and O₂ were controlled by mass flow controllers (Bronkhost, HI-TEC). The effluent reaction products were analyzed by an on-line gas chromatograph (Gow-Mac, 550P) equipped with thermal conductivity detector. Porapak N column (3.18 mm \times 3 m, 80/100) and Carbosphere column (3.18 mm \times 1.83 m, 80/100) were used for the analysis of liquid products and uncondensable gas products, respectively.

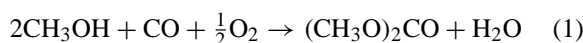
2.3. CO temperature-programmed desorption (TPD)

The chemisorption of CO onto CuCl₂/NaOH/AC catalysts was carried out in a vertical tube reactor of 0.95 cm in diameter at room temperature and atmospheric pressure. The catalyst sample was filled, out-gassed and purged with the helium of ultra-high purity grade (99.9999%, 30 ml min⁻¹) at 600 K for 0.5 h. The sample was evacuated at 323 K for 3 h and then, exposed to CO of 6.67 kPa for 2 h. The TPD measurements were performed at a constant heating rate of 5 K min⁻¹ under the helium flow of 30 ml min⁻¹.

3. Results and discussion

3.1. Catalyst activities of CuCl₂/NaOH/AC catalysts

DMC can be catalytically synthesized by the reaction of methanol with carbon monoxide and oxygen as shown in Eq. (1).



In our previous work [18], we reported the effect of various promoters and reaction conditions on DMC yield over Cu-based heterogeneous catalysts. Among the various promoters added to CuCl₂/AC catalysts, NaOH has been found to be the best promoter in the DMC synthesis. Moreover, the OH/Cu molar ratio in the CuCl₂/NaOH/AC catalysts seems to be closely related with the catalyst performance.

Table 1 shows the activity changes of CuCl₂/NaOH/AC catalysts depending upon the OH/Cu molar ra-

Table 1

The catalytic activity of CuCl₂/NaOH/AC^a catalyst with different OH/Cu molar ratios

OH/Cu molar ratio	Conversion (%)		DMC selectivity ^b (%)	DMC yield ^c (%)
	MeOH	O ₂		
0.0	20.36	48.11	80.23	16.33
0.5	22.02	48.19	84.82	18.67
1.0	23.41	53.18	89.30	20.91

Reaction condition: Cu content = 4.6 wt.%, CO/MeOH/O₂ = 16/4/1 (molar ratio) 403 K, 1.03 × 10³ kPa.

^a Activated carbon.

^b DMC selectivity = the produced DMC (mol)/the produced DMC, methylformate and dimethoxymethane (mol) × 100.

^c DMC yield = the produced DMC (mol)/the MeOH feed (mol) × 100.

tio. For all the experiments in this work, the reaction condition was always fixed as $T = 403 \text{ K}$, $P = 1.03 \times 10^3 \text{ kPa}$, $\text{MeOH/CO/O}_2 = 4/16/1$ (molar ratio) and $\tau = 10 \text{ s}$. The Cu content on activated carbon was 4.6 wt.%. The OH/Cu molar ratio was varied from 0.0 to 1.0. The variation range of OH/Cu molar ratio was selected based on the our preliminary findings that the catalytic activity deteriorated due to the formation of NaCl in catalyst phase when OH/Cu molar ratio was higher than 1.0 [18].

With an increase in the molar ration of OH/Cu in CuCl₂/NaOH/AC catalysts, the catalytic activities were found to increase gradually within the experimental range of OH/Cu molar ratio. Methanol conversion was increased from 20.36 to 22.02% and 23.41% with an increase in the molar ratio of OH/Cu from 0.0 to 0.5 and 1.0, respectively. DMC selectivity was also increased from 80.33 to 84.82% and 89.30% with the increase of OH/Cu molar ratio. These experimental results clearly show that the addition of NaOH promoter to Cu-based catalysts works very favorably in DMC synthesis.

3.2. CO temperature-programmed desorption

Since the catalytic activity was increased with the increase of OH/Cu molar ratio, the catalyst

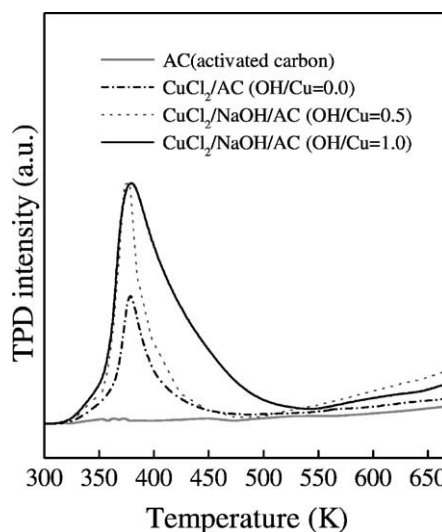


Fig. 1. CO temperature-programmed desorption (TPD) profiles of CuCl₂/NaOH/AC catalysts with different OH/Cu molar ratios.

performance was compared again through CO temperature-programmed desorption (TPD) experiments. In vapor phase DMC synthesis, the CO adsorption capability on catalyst is thought to be inevitably related with the catalyst performance. Fig. 1 shows the CO temperature-programmed desorption profiles for CuCl_2/AC ($\text{OH}/\text{Cu} = 0.0$), $\text{CuCl}_2/\text{NaOH}/\text{AC}$ ($\text{OH}/\text{Cu} = 0.5$) and $\text{CuCl}_2/\text{NaOH}/\text{AC}$ ($\text{OH}/\text{Cu} = 1.0$) catalysts shown in Table 1.

While activated carbon used as support did not show any response, all of the three catalysts showed their characteristic TPD behaviors. The intensity of CO desorption began to increase around 320 K, reached a maximum at about 375 K and then decreased slowly

with the further increase of temperature. Among them, $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst with $\text{OH}/\text{Cu} = 1.0$ was found to be the best in the CO adsorption capability. This result strongly supports the activity test results of Table 1. In other words, the OH/Cu molar ratio in $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst is closely related with the CO adsorption performance of catalyst and the higher OH/Cu molar ratio within the experimental range is more favorable in DMC synthesis.

3.3. SEM and XRD analysis

In order to elucidate the effect of NaOH promoter in $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts for DMC synthesis, SEM

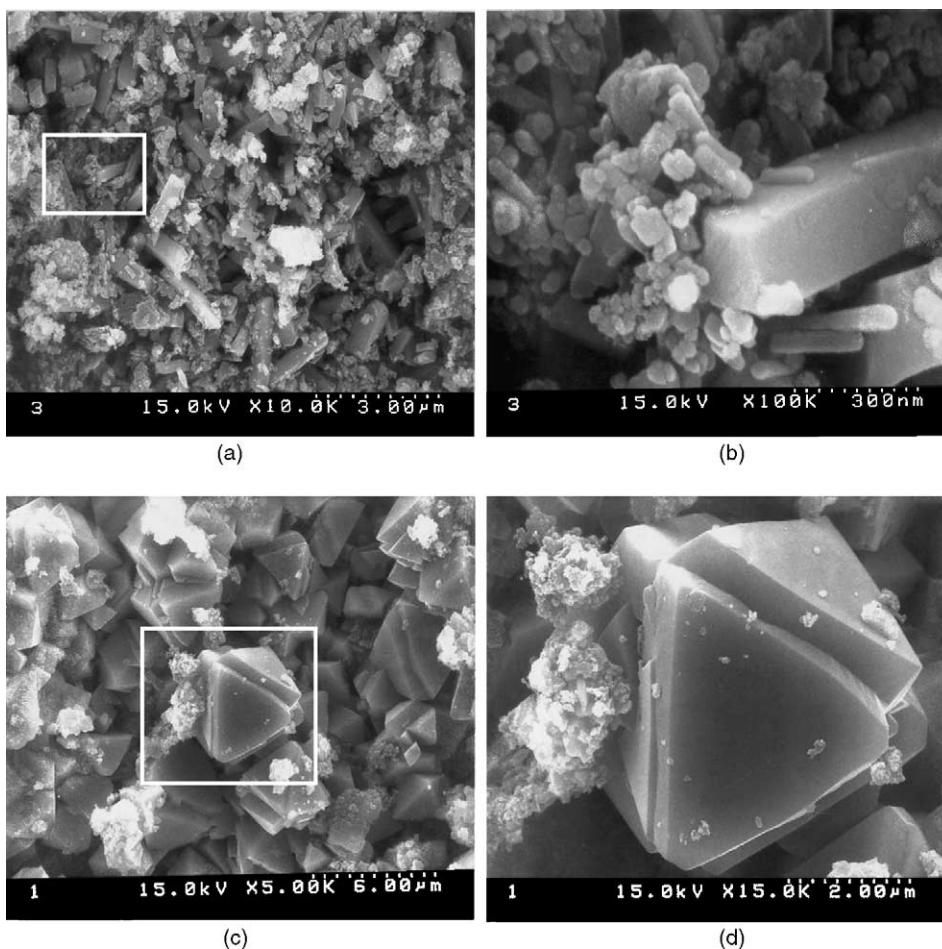


Fig. 2. SEM images of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst with molar ratio of $\text{OH}/\text{Cu} = 0.5$ and 1.0: (a) $\text{OH}/\text{Cu} = 0.5$; (b) $\text{OH}/\text{Cu} = 0.5$ at high magnification; (c) $\text{OH}/\text{Cu} = 1.0$; (d) $\text{OH}/\text{Cu} = 1.0$ at high magnification.

and X-ray diffraction analysis were conducted for the employed $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts with different OH/Cu molar ratios.

Fig. 2 compares the SEM images of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts with the molar ratio of $\text{OH}/\text{Cu} = 0.5$ and 1.0. Interestingly, the crystal structures of both catalysts were totally different. The catalyst with OH/Cu molar ratio of 0.5 was observed as orthorhombic while the catalyst with OH/Cu molar ratio of 1.0 was observed as rhombohedral. These kinds of crystal habits were not observed at all in the SEM images of CuCl_2/AC catalysts free of NaOH as shown in our previous work [18]. The formation of these kinds of crystal habits in the catalyst phase appeared to be associated with the relative concentration of NaOH and CuCl_2 solution during the catalyst preparation.

Fig. 3 compares the X-ray diffraction patterns of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts of $\text{OH}/\text{Cu} = 0.5$ and 1.0. A lot of copper chloride hydroxides ($\text{Cu}_2(\text{OH})_3\text{Cl}$) peaks were detected in both cases. As a result of detailed investigation on copper chloride hydroxide peaks in XRD patterns, the existence of two different crystal habits of copper chloride hydroxide peaks was ob-

served. According to the JCPDS reference files, one is $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ (atacamite, JCPDS #25-0269) which is orthorhombic, while the other is $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ (paratacamite, JCPDS #19-0389) which is rhombohedral. By matching XRD patterns of both catalysts with JCPDS reference files, it can be concluded that the catalyst phase is $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ dominant at the molar ratio of $\text{OH}/\text{Cu} = 0.5$ while at the molar ratio of $\text{OH}/\text{Cu} = 1.0$, $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ is dominant. These results from XRD analysis are in a very good accordance with SEM image results shown in Fig. 2.

$\text{Cu}_2(\text{OH})_3\text{Cl}$ has been generally known to have three types of crystal structures such as atacamite (orthorhombic), paratacamite (rhombohedral) and botallackite (monoclinic) [19]. Among them, botallackite is the most unstable and can be transformed readily into paratacamite and/or atacamite [19,20]. Furthermore, it has been reported that the formation of paratacamite and atacamite crystals closely related with the relative concentration of NaOH and CuCl_2 solution [20,21]. All these previous findings indicated that $\alpha\text{-}$ and/or $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ could be possibly formed depending upon the OH/Cu molar ratio in our $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts.

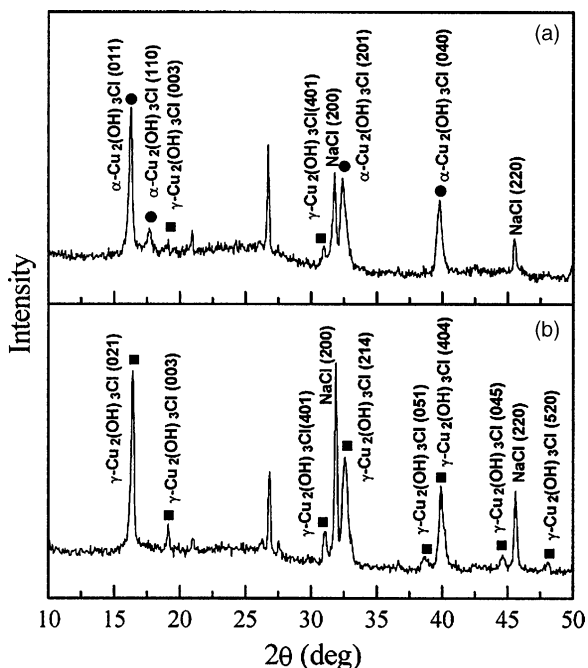


Fig. 3. Comparison of XRD patterns of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts: (a) $\text{CuCl}_2/\text{NaOH}/\text{AC}$ with $\text{OH}/\text{Cu} = 0.5$; (b) $\text{CuCl}_2/\text{NaOH}/\text{AC}$ with $\text{OH}/\text{Cu} = 1.0$.

3.4. XPS analysis

According to Fleet's work [21], atacamite ($\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$) consists of $\text{Cu}(\text{OH})_4\text{Cl}_2$ and $\text{Cu}(\text{OH})_5\text{Cl}$. The ratio of $\text{Cu}(\text{OH})_4\text{Cl}_2$ to $\text{Cu}(\text{OH})_5\text{Cl}$ in atacamite is known to be 1:1. On the other hand, paratacamite ($\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$) consists of $\text{Cu}(\text{OH})_4\text{Cl}_2$ and $\text{Cu}(\text{OH})_6$. The ratio of $\text{Cu}(\text{OH})_4\text{Cl}_2$ to $\text{Cu}(\text{OH})_6$ in paratacamite is known to be 3:1. The structures of $\text{Cu}(\text{OH})_4\text{Cl}_2$, $\text{Cu}(\text{OH})_5\text{Cl}$ and $\text{Cu}(\text{OH})_6$ as single edge-sharing octahedra are shown in Fig. 4. $\text{Cl}-\text{Cu}-\text{Cl}$ and $\text{Cl}-\text{Cu}-\text{OH}$ are characteristic bonds in atacamite while $\text{Cl}-\text{Cu}-\text{Cl}$ and $\text{OH}-\text{Cu}-\text{OH}$ in paratacamite.

Fig. 5 illustrates XPS spectra of $\text{Cu } 2p_{3/2}$ of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts with the molar ratio of $\text{OH}/\text{Cu} = 0.5$ and 1.0. The XPS peaks of both catalysts were different in shape as well as in intensity. This indicates that the bonding type and energy of Cu in both catalysts might be different each other.

As a result of curve fitting, the catalyst with $\text{OH}/\text{Cu} = 0.5$ was found to have two peaks as shown in Fig. 5(a). The first peak (I) was found at 932.0 eV and the second peak (II) at 934.0 eV. Peak (I) at

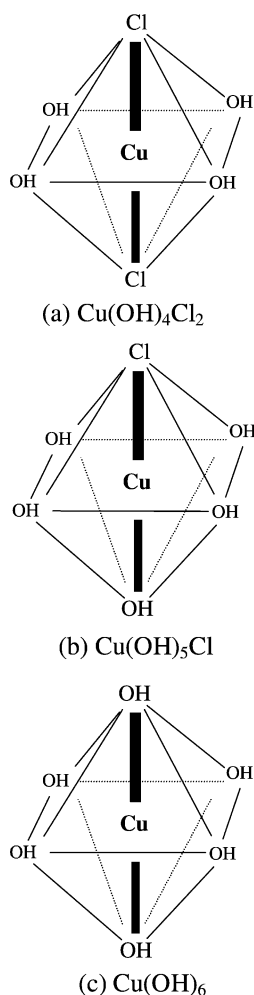


Fig. 4. Structures of $\text{Cu}(\text{OH})_4\text{Cl}_2$, $\text{Cu}(\text{OH})_5\text{Cl}$ and $\text{Cu}(\text{OH})_6$ as single edge-sharing octahedra.

932.0 eV was revealed to be attributed to Cl–Cu–Cl bond, while peak (II) at 934.0 eV to Cl–Cu–OH bond. That is, the catalyst with $\text{OH}/\text{Cu} = 0.5$ showed the exactly same characteristics of $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$. The almost equivalent intensity of peaks (I) and (II) also supports that $\text{Cu}_2(\text{OH})_3\text{Cl}$ in $\text{OH}/\text{Cu} = 0.5$ catalyst is α -type. On the other hand, the catalyst with $\text{OH}/\text{Cu} = 1.0$ was found to have two peaks at 932.0 and 934.5 eV as shown in Fig. 5(b). A new peak (III) at 934.5 eV was attributed to OH–Cu–OH bond. These results indicate that the catalyst with $\text{OH}/\text{Cu} = 1.0$ consists of Cl–Cu–Cl and OH–Cu–OH bond, which is the

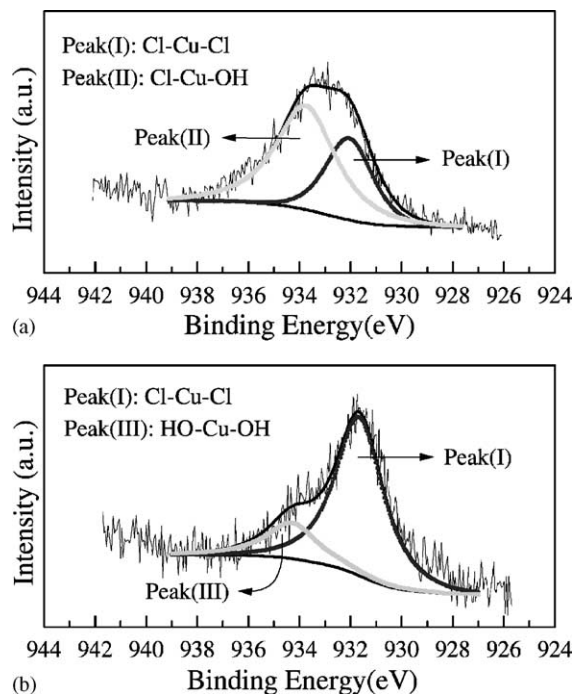


Fig. 5. XPS spectra of Cu $2p_{3/2}$ for $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts: (a) $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst ($\text{OH}/\text{Cu} = 0.5$); (b) $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalyst ($\text{OH}/\text{Cu} = 1.0$).

characteristics of $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ as mentioned above. Furthermore, the relatively stronger intensity of peaks (III) to (I) imply that the ratio of Cl–Cu–Cl bond to OH–Cu–OH could be 3:1, which is characteristic of $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$. Based on these observations, it can be concluded that these XPS analysis results are in a very good accordance with SEM and XRD analysis results.

4. Conclusions

In this work, a series of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts were prepared and their catalytic activities were compared in the vapor phase DMC synthesis. The detailed characterization of employed catalysts and the investigation of their role on DMC synthesis were also carried out through TPD experiments, X-ray diffraction, SEM and XPS analysis.

The catalytic activity of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts has been found to increase continuously with the increase of OH/Cu molar ratio up to 1.0 as compared

with CuCl_2/AC catalyst. The morphological analysis by X-ray diffraction, SEM and XPS has shown that the improved performance of $\text{CuCl}_2/\text{NaOH}/\text{AC}$ catalysts was closely related with the existence of copper chloride hydroxides ($\text{Cu}_2(\text{OH})_3\text{Cl}$). Depending upon the OH/Cu molar ratio, two different crystal habits of ($\text{Cu}_2(\text{OH})_3\text{Cl}$) were observed in the catalyst surface. One is $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ (atacamite) which is orthorhombic, while the other is $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ (paratacamite), which is rhombohedral.

The surface phase was revealed to change from $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ to $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$ with the increase of OH/Cu molar ratio. At the molar ratio of OH/Cu = 0.5, the dominant phase was $\alpha\text{-Cu}_2(\text{OH})_3\text{Cl}$ while at the molar ratio of OH/Cu = 1.0, $\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$. The γ -type phase was found to be more active to DMC synthesis than the α -type phase as well as the catalyst free of $\text{Cu}_2(\text{OH})_3\text{Cl}$. The CO temperature-programmed desorption experiments on the employed catalysts also strongly supported these observations.

References

- [1] Y. Ono, Appl. Catal. A: Gen. 155 (1997) 133.
- [2] W. Yanji, Z. Xinqiang, Y. Baoguo, Z. Bingchang, C. Jinsheng, Appl. Catal. A: Gen. 171 (1998) 255.
- [3] Z. Fu, Y. Ono, J. Mol. Catal. A: Chem. 118 (1997) 293.
- [4] M.A. Pacheco, C.L. Marshall, Energy Fuels 11 (1997) 2.
- [5] S.T. King, J. Catal. 161 (1996) 530.
- [6] S.T. King, Catal. Today 33 (1997) 173.
- [7] A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951.
- [8] J.F. Knifton, R.G. Duranleau, J. Mol. Catal. 67 (1991) 389.
- [9] T. Tatsumi, Y. Watanabe, K.A. Koyano, Chem. Commun. (1996) 2281.
- [10] K. Tomishige, Y. Ikeda, T. Sakaihorii, K. Fujimoto, J. Catal. 192 (2000) 355.
- [11] D. Delle Donne, F. Rivetti, U. Romano, J. Organomet. Chem. 488 (1995) C15.
- [12] C.S. Chin, D. Shin, G. Won, J. Ryu, H.S. Kim, B.G. Lee, J. Mol. Catal. A: Chem. 160 (2000) 315.
- [13] Y. Sato, M. Kagotani, Y. Souma, J. Mol. Catal. A: Chem. 151 (2000) 79.
- [14] G.L. Curnutt, A.D. Harley, in: A.E. Martell, et al. (Eds.), Oxygen Complexes and Oxygen Activation by Transition Metals, Plenum Press, New York, 1988, p. 215.
- [15] K. Tomishige, T. Sakaihorii, S. Sakai, K. Fujimoto, Appl. Catal. A: Gen. 181 (1999) 95.
- [16] M. Xinbin, Z. Renzhe, X. Genhui, H. Fei, C. Hongfang, Catal. Today 30 (1996) 201.
- [17] T. Koyama, M. Tonosaki, N. Yamada, K. Mori, US Patent 5,347,031 (1994).
- [18] M.S. Han, B.G. Lee, I. Suh, H.S. Kim, B.S. Ahn, S.I. Hong, J. Mol. Catal. A: Chem. 170 (2001) 225.
- [19] A.M. Pollard, R.G. Thomas, P.A. Williams, Mineral. Mag. 53 (1989) 557.
- [20] D.J. Mossman, K.J. Heffernan, Chem. Geol. 21 (1978) 151.
- [21] M.E. Fleet, Acta Cryst. B31 (1975) 183.