

Characterization of catalyst in the synthesis of dimethyl carbonate by gas-phase oxidative carbonylation of methanol[☆]

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Abstract

The bulk and surface properties of PdCl₂–CuCl₂–CH₃COOK catalysts supported on activated carbon (a.c.) used in the synthesis of dimethyl carbonate (DMC) by gas-phase oxidative carbonylation of methanol were characterized by XRD and XPS techniques. On the basis of the catalyst characterization and evaluation results, the active species of the catalyst has been suggested, and the reaction mechanism of oxidative carbonylation has been proposed. The interaction between CH₃COOK and PdCl₂ or CuCl₂ on the activated carbon support has been deduced from the formation of KCl, and the partial reduction of CuCl₂–CuCl has been found. Furthermore, the presence of CuCl₂ inhibits the reduction of PdCl₂. The experimental results show that the main reason for catalyst deactivation could be attributed to the loss of chlorine. Fortunately, promoter CH₃COOK could inhibit the loss of chlorine, and improve the electronic environment of PdCl₂–CuCl₂ catalyst, so that the stability and activity of the catalyst PdCl₂–CuCl₂–CH₃COOK/a.c. increase. © 2002 Elsevier Science B.V. All rights reserved.

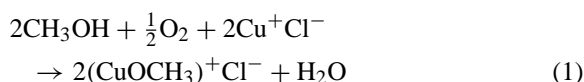
Keywords: Dimethyl carbonate synthesis; Gas-phase oxidative carbonylation; Characterization; Active species; Reaction mechanism

1. Introduction

Dimethyl carbonate (DMC) is a versatile chemical substance, which has been using mainly as a methylating, carbonylating or methoxycarbonylating agent. Many products can be prepared from it because of its unique property. In addition, it has been expected to be a safer substitute for toxic phosgene in

polycarbonate synthesis. Now it has drawn more and more attention as a promising chemical compound in view of the increasing worldwide environmental problem.

Several researchers have studied the reaction mechanism of DMC synthesis. Having studied the oxidative carbonylation of methanol in liquid-phase over catalyst CuCl, Romano et al. [1] proposed that the reaction might proceed initially through the oxidation of CuCl to cupric methoxychloride (Eq. (1)).



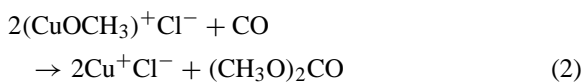
The latter was reduced by carbon monoxide, and CuCl was restored. Thus far the catalytic cycle was

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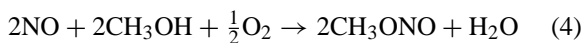
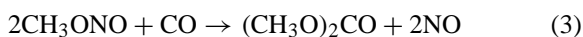
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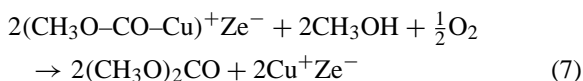
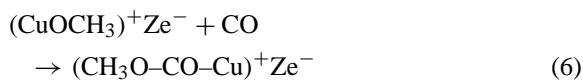
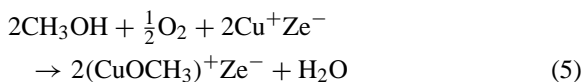
completed (Eq. (2)).



A vapor-phase two-step process based on palladium catalyzed carbonylation of methyl nitrite has been developed by Nishihira et al. [2]. Methyl nitrite was produced in a separate step by the reaction of CH_3OH , NO and O_2 (Eqs. (3) and (4))



King [3] elucidated the reaction mechanism of oxidative carbonylation of methanol in Cu–Y zeolite by in situ FT-IR technique. The first step is the oxidation of methanol and Cu(I) to form Cu(II)-methoxide. Then the insertion of CO to Cu(II)-methoxide forms probably a carbomethoxide. Finally, methanol and oxygen react with carbomethoxide to form dimethyl carbonate (Eqs. (5)–(7)).



It has been reported that the formation rate of dimethyl carbonate is strongly related to Cl/Cu ratio in the synthesis of dimethyl carbonate by oxidative carbonylation over catalyst $\text{CuCl}_2/\text{a.c.}$ [4].

The structure of supported catalyst $\text{PdCl}_2-\text{CuCl}_2$ used in CO oxidation has been investigated by many researchers. Yamamoto et al. [5] studied the structure and electronic state of $\text{PdCl}_2-\text{CuCl}_2$ catalyst supported on a.c. by XAFS technique, and found that Cu^+ species existed on the support and was coordinated with three chlorine anions. The EXAFS analysis also showed the formation of Pd metal particles as well as Pd chloride species coordinated with three chlorine anions. In addition, they found that the formation of Pd metal was strongly suppressed by the presence of CuCl_2 . The supported catalyst $\text{PdCl}_2-\text{CuCl}_2$ used

in CO oxidation was also studied by Kim et al. [6,7]. It was reported that the active species of Cu was $\text{Cu}_2\text{Cl}(\text{OH})_3$ and the active species of Pd was Pd^{2+} .

In the previous papers, we have prepared supported catalyst $\text{PdCl}_2-\text{CuCl}_2-\text{CH}_3\text{COOK}/\text{a.c.}$ used in the synthesis of DMC by gas-phase oxidative carbonylation of methanol, and have given the research results such as catalyst preparation, catalytic properties, and functions of alkali promoters [8,9]. However, the mechanism of the synthesis reaction of DMC by gas-phase oxidative carbonylation does not seem to be well established at present, and the bulk and surface properties of catalyst $\text{PdCl}_2-\text{CuCl}_2-\text{CH}_3\text{COOK}/\text{a.c.}$ have rarely been reported so far. In this work, the bulk and surface properties of the catalyst have been studied, and the reaction mechanism has been proposed on the basis of catalyst characterization and evaluation.

2. Experimental

2.1. Catalyst preparation

The catalyst $\text{PdCl}_2-\text{CuCl}_2-\text{CH}_3\text{COOK}/\text{a.c.}$ was prepared by impregnating a.c. with aqueous 25% NH_3 solution of a mixture of palladium chloride, copper chloride and potassium acetate. The concentration of the solution was $\text{PdCl}_2 = 0.01 \text{ mol/l}$, $\text{CuCl}_2 = 0.16 \text{ mol/l}$, $\text{CH}_3\text{COOK} = 0.16 \text{ mol/l}$, respectively. Then the solvent was removed by vacuum evaporation at 50°C for 4 h and subsequently pretreated at 200°C for 2 h in a N_2 stream at atmosphere pressure. The preparation of catalyst with other alkali promoters was similar to that of catalyst $\text{PdCl}_2-\text{CuCl}_2-\text{CH}_3\text{COOK}/\text{a.c.}$. The surface area of a.c. employed here is $1399 \text{ m}^2 \text{ g}^{-1}$.

2.2. Catalyst characterization

2.2.1. X-ray diffraction analysis (XRD)

X-ray diffraction patterns were measured at room temperature with a Japanese D/Max-2500 X-ray diffraction system. This diffractometer utilized Cu $\text{k}\alpha$ radiation and was operated at 50 kV and 200 mA. The range of the spectra in 2θ was from 5° to 80° .

2.2.2. X-ray photoelectron spectroscopy analysis

The surface composition and structure of catalyst were studied by X-ray photoelectron spectroscopy

(XPS) in a PHI-5300 ESCA system. An Al $K\alpha$ electron source was used with a power setting at 250 W. Charge compensation was done with the adventitious C 1s peak at 284.6 eV.

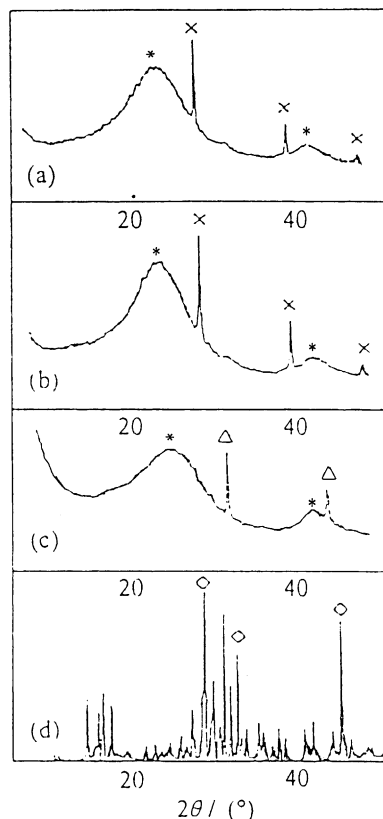
2.3. Catalyst evaluation

Catalytic activity was measured at atmospheric pressure in a fixed-bed flow system with a stainless steel tubular reactor of 8 mm inner diameter, which has been described in our previous work [8]. The operation conditions were as follows: $T = 150^\circ\text{C}$, GHSV = 1500 h^{-1} , LHSV = 4 h^{-1} , and $\text{CO}/\text{O}_2 = 2.80$. The reaction products passed through a cooling trap, then the uncondensed gas products and the liquid products collected in the cooling trap were analyzed by GC, respectively. The GC column analyzing gas products was packed with TDX-101, and another one analyzing liquid products was packed with the polyethylene glycol 20 000 coated on GDX-101 carrier.

3. Results and discussion

3.1. XRD analysis

In the XRD patterns of supported catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK/a.c.}$ before and after reaction (Fig. 1a and b), the diffraction peaks attributed to the support activated carbon were observed on the sample. The XRD analysis showed that there were not diffraction peaks of Pd or Cu species on the catalyst, but the peaks attributed to crystallites of KCl were clearly observed, which presented the formation of KCl during the catalyst preparation. Furthermore, it was certain that KCl was stable during the reaction because the intensities of KCl peaks varied very little before and after reaction. In addition, it was suggested that Pd and Cu species on the support surface was highly dispersed or in amorphous state because they were invisible in the XRD pattern. In the XRD patterns of fresh catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COONa/a.c.}$ (Fig. 1c), there were also mainly diffraction peaks attributed to the support activated carbon. The XRD analysis showed that there were not diffraction peaks of Pd or Cu species on this catalyst, but the peaks attributed to crystallites of NaCl were clearly observed. All these are similar to those of catalyst



*-Activated carbon ×-KCl Δ-NaCl ◇-CuCl

Fig. 1. XRD patterns for catalyst samples: (a) fresh catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK/a.c.}$; (b) deactivated catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK/a.c.}$; (c) fresh catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COONa/a.c.}$; and (d) unsupported sample $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}$. Activated carbon: (×) KCl, (Δ) NaCl, (◇) CuCl.

$\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK/a.c.}$. It suggested that the formation of alkali chloride should be due to the reaction between alkali acetate and PdCl_2 or CuCl_2 because the chemical reagents used in the catalyst preparation did not contain alkali chloride. In order to gain further insight into the structure of the supported catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK/a.c.}$, an unsupported $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}$ sample with the same atomic ratio of palladium, copper and potassium was prepared, and pretreated by the same methods as the supported catalyst. The XRD pattern showed that there were obvious peaks corresponding to crystallites of CuCl, which indicates that some Cu^{2+} species have been reduced into Cu^+ species, but the Pd species

was still invisible (Fig. 1d). The other difference of unsupported sample from the supported catalyst was that KCl did not emerge in the XRD pattern. The presence of CuCl and the disappearance of KCl in the unsupported sample may be due to the absence of support while the formation of KCl in the supported catalyst results from the interaction between the supported metal species and the support activated carbon.

3.2. XPS analysis

The surface composition and structure of the catalysts were analyzed by XPS technique. In order to compare their differences conveniently, two single metal chloride catalysts PdCl₂/a.c. and CuCl₂/a.c., a bimetallic chloride catalyst PdCl₂-CuCl₂/a.c. and a multi-component catalyst PdCl₂-CuCl₂-CH₃COOK/a.c. were prepared.

In the XPS pattern of Pd_{3d} in PdCl₂/a.c. (Fig. 2a), the peaks attributed to 337.6 and 335.2 eV were peaks of Pd²⁺ and Pd⁰, respectively, which indicated that partial PdCl₂ supported on activated carbon was reduced to Pd⁰ metal.

The curve-fitting results of Cu_{2p} XPS patterns in different catalysts are compared in Fig. 3. The Cu_{2p} peak in CuCl₂/a.c. was fitted into two peaks of Cu⁺ at 932.5 eV and Cu²⁺ at 934.7 eV (Fig. 3a). The Cu²⁺ peak of 934.7 eV represented CuCl₂, the Cu⁺ species of 932.5 eV represented CuCl.

In the XPS pattern of Pd_{3d} in PdCl₂-CuCl₂/a.c. (Fig. 2b), Pd metal disappeared while Pd_{3d} peak became wider apparently, and it had a chemical shift of +0.3 eV. The curve-fitting result of Cu_{2p} XPS pattern (Fig. 3b) was similar to that of CuCl₂/a.c. (Fig. 3a) and there were CuCl₂ and CuCl in the catalyst. These results can be explained by the synergistic effect on the bimetallic chloride catalyst, i.e., the addition of CuCl₂ prohibits the reduction of PdCl₂ to Pd metal.

The curve-fitting results of the Cu_{2p} XPS patterns on fresh and deactivated catalyst PdCl₂-CuCl₂-CH₃COOK/a.c. are listed in Fig. 3c and d, respectively. It is obvious that the Cu species in these two catalysts had three states, i.e., CuCl₂, CuCl and CuO, but their relative amounts were different. The CuCl/CuCl₂ and CuO/CuCl₂ ratios are shown in Table 1. In the deactivated catalyst, CuO was the most and CuCl was the least, which indicate that CuCl may

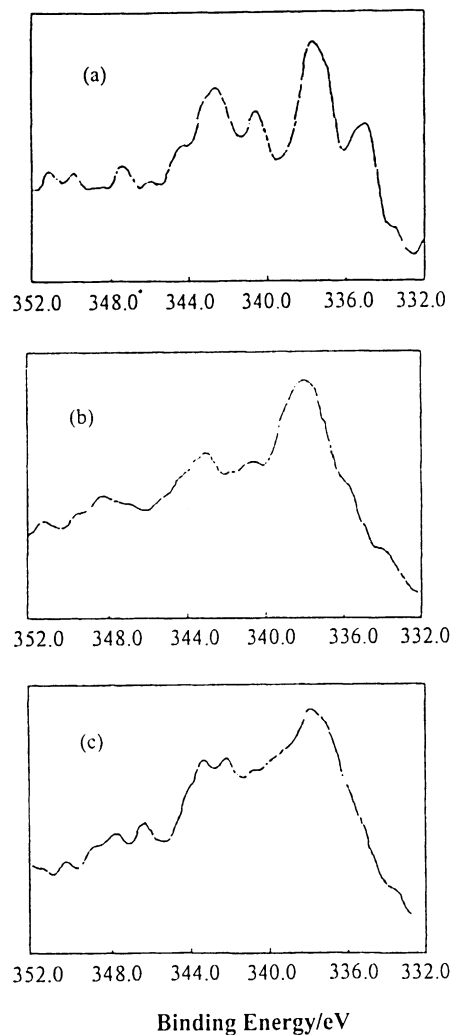


Fig. 2. XPS patterns of Pd_{3d}: (a) fresh catalyst PdCl₂/a.c.; (b) fresh catalyst PdCl₂-CuCl₂/a.c.; and (c) fresh catalyst PdCl₂-CuCl₂-CH₃COOK/a.c.

be active species, and the increase in CuO may result in the deactivation of catalyst.

3.3. Investigation of catalytic active species

In the XPS patterns of single metal chloride catalysts, partial PdCl₂ in PdCl₂/a.c. was reduced to Pd metal and partial CuCl₂ in CuCl₂/a.c. was reduced to CuCl by the reduction sites on the activated carbon surface. It is concluded that there are double redox species Pd²⁺/Pd⁰ on PdCl₂/a.c. and Cu²⁺/Cu⁺ on CuCl₂/a.c.,

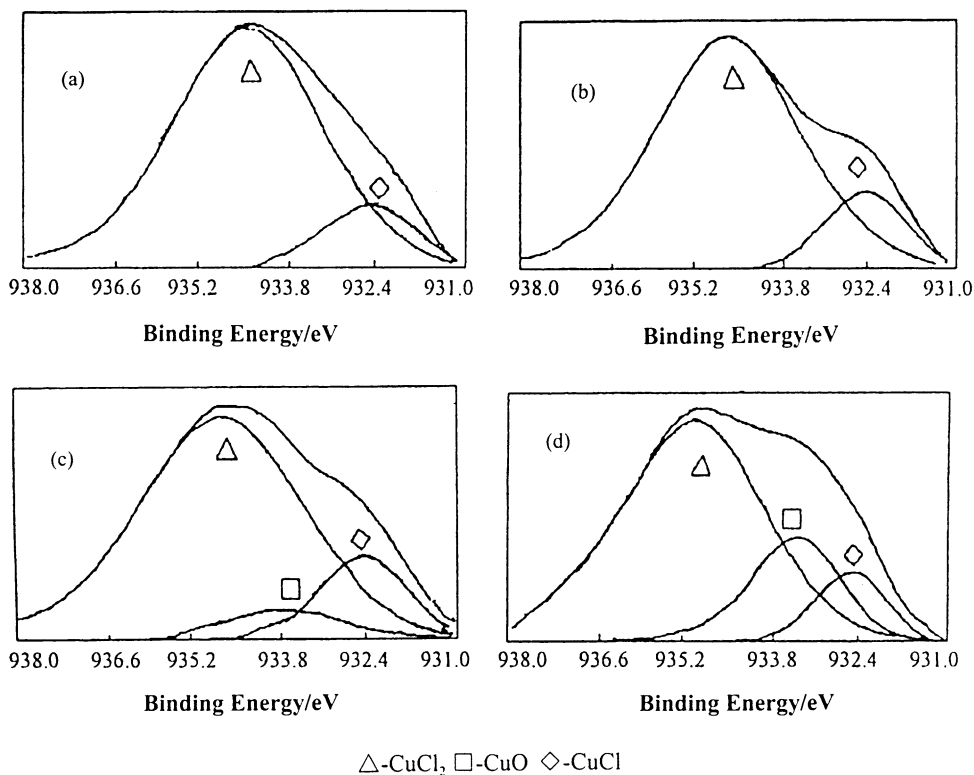


Fig. 3. Curve-fitting results of Cu_{2p} XPS patterns: (a) fresh catalyst $\text{CuCl}_2/\text{a.c.}$; (b) fresh catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$; (c) fresh catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$; and (d) deactivated catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$ (Δ) CuCl_2 , (\square) CuO , (\diamond) CuCl .

Table 1
Relative molar composition of Cu species on catalyst surface^a

Catalyst	CuCl_2	$\text{CuCl}/\text{CuCl}_2$	CuO/CuCl_2	Cl_2^b (%)
Fresh $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$	1	0.280	0	3.19
Fresh $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$	1	0.374	0.110	3.41
Deactivated $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$	1	0.325	0.478	2.98

^a The amount of CuCl_2 was taken as a standard.

^b The composition of element Cl was calculated according to the five elements: Pd, Cu, K, Cl and C.

Table 2
Distribution of liquid products over catalysts (wt.%)^a

Catalysts	HCOOCH_3	$(\text{CH}_3\text{O})_2\text{CO}$	H_2O
$\text{PdCl}_2/\text{a.c.}$	0.22	Trace	1.09
$\text{CuCl}_2/\text{a.c.}$	0.92	0.18	1.93
$\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$	0.23	1.49	0.78
$\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$	0.63	6.07	2.45

^a Reaction conditions: $T = 150^\circ\text{C}$, $\text{GHSV} = 1500\text{h}^{-1}$, $\text{LHSV} = 4\text{h}^{-1}$, and $\text{CO}/\text{O}_2 = 2.80$.

respectively. From the evaluation results for catalytic activity in Table 2, only trace DMC was formed on single metal chloride catalysts, which shows that the single metal chloride catalysts are active to the synthesis of DMC, but the activity is very low. The reaction of DMC synthesis over the two single metal chloride catalysts is suggested to take place according to redox mechanism; $\text{Pd}^{2+}/\text{Pd}^0$ and $\text{Cu}^{2+}/\text{Cu}^+$ are proposed to be active sites, respectively. The poor activity is due to the unstable structure and composition of the active species.

However, Pd metal was not found in bimetallic chloride catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$ These findings that the reduction of PdCl_2 was strongly suppressed by the presence of CuCl_2 may be explained in terms of a preferential reduction of Cu^{2+} to that of Pd^{2+} on the reduction sites because of lower redox potential of Cu^{2+} to Cu^+ (0.15 V vs. Ag^+/AgCl) than that of Pd^{2+} to Pd^0 (0.92 V) [10].

As previously noted, the synergistic effect exists between Pd and Cu on the bimetallic chloride catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$ The evaluation results over catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$ in Table 2 show that the activity of DMC synthesis increased markedly. It suggested that the increase in the catalytic activity is ascribed to the synergistic effect between Pd and Cu.

On the basis of above discussion, we propose that the synthesis of DMC by oxidative carbonylation of methanol proceed according to redox mechanism, and the DMC yield increases greatly through the following reactions over catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$:

- I. $\text{PdCl}_2 + \text{CO} \rightarrow \text{Pd}(\text{CO})\text{Cl}_2$
- II. $\text{Pd}(\text{CO})\text{Cl}_2 + 2\text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{O})_2\text{CO} + \text{Pd}^0 + 2\text{HCl}$
- III. $\text{Pd}^0 + 2\text{CuCl}_2 \rightarrow \text{PdCl}_2 + 2\text{CuCl}$
- IV. $2\text{CuCl} + 2\text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Cu}(\text{OCH}_3)\text{Cl} + \text{H}_2\text{O}$
- V. $2\text{Cu}(\text{OCH}_3)\text{Cl} + \text{CO} \rightarrow (\text{CH}_3\text{O})_2\text{CO} + 2\text{CuCl}$
- VI. $2\text{CuCl} + 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuCl}_2 + \text{H}_2\text{O}$

In the above reaction schemes, DMC is formed in both reactions II and V, which is the reason why the STY of DMC was considerably increased over the bimetallic chloride catalyst. The presence of CuCl_2 is helpful to the completion of reactive cycle over PdCl_2 species, and simultaneously CuCl_2 is converted to the active species CuCl that is necessary in reaction IV. Manchot and Konig [11] first reported a

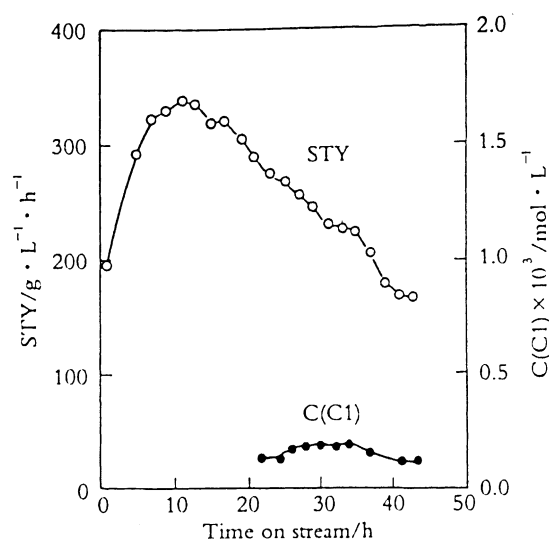


Fig. 4. The time course of reaction performance of catalyst and Cl^- concentration of liquid products. Reaction conditions: $T = 150^\circ\text{C}$, $\text{GHSV} = 1500\text{h}^{-1}$, $\text{LHSV} = 4\text{h}^{-1}$, and $\text{CO}/\text{O}_2 = 2.80$.

compound with a formula, $\text{Pd}(\text{CO})\text{Cl}_2$, and the structure of $[\text{Pd}_2(\text{CO})_2\text{Cl}_4]$ was proposed by Calderazzo and Dell'Amico [12].

3.4. Analysis of reason for catalyst deactivation

The catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$ has been shown to be active as a catalyst in the oxidative carbonylation of methanol, but its stability is poor. As shown in Fig. 4, the catalytic activity dropped markedly along with the reaction. Fresh and deactivated catalysts have been characterized by XPS technique, and the composition of element chlorine is listed in Table 1. The composition of element chlorine on the fresh catalyst surface was 3.41%, while it was only 2.98% on deactivated one. The difference means the loss of chlorine. As previously mentioned, it is concluded from Table 1 that the loss of chlorine, the decrease of CuCl , and the formation of CuO are the primary factors of catalyst deactivation.

In order to confirm that the reason for catalyst deactivation is due to the loss of chlorine, the liquid product was analyzed by ion-selective electrode analysis. In this method, the 217-calomel electrode was used as reference electrode and the 301-chloride

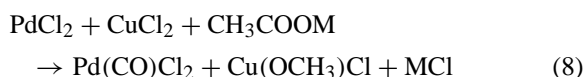
electrode was used as indicator electrode. The PHS-2 precision acidimeter was used to determine electromotive force. A series of standard solvents were prepared, and the Cl^- concentration in the liquid product was determined by standard curve method. The time course of DMC yield and Cl^- concentration in liquid product is shown in Fig. 4. The fact that Cl^- was found in the liquid product shows that Cl^- must have been lost from the metal chloride catalyst in the reaction process because the reactants did not contain chlorine. Furthermore, along with the loss of chlorine, the activity of catalyst decreased from the highest STY, 349–153 g/l cat h in the run time of 43 h. Therefore, the main reason for catalyst deactivation could be attributed to the loss of chlorine.

3.5. Effects of alkali promoter

The addition of alkali metal promoter K in the form of acetate CH_3COOK can enhance the reactivity of the oxidative carbonylation of methanol on catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$ significantly. So it is necessarily to study the functions of promoter CH_3COOK further.

The atomic composition of Pd on the catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$ was 0.87% and Cu was 1.57%. According to stoichiometric number of PdCl_2 and CuCl_2 , the composition of chlorine on the catalyst $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$ should be 4.34%, but in fact it was only 3.19% as listed in Table 1. This indicates that chlorine was lost during the catalyst preparation. The atomic composition of Pd on the catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$ was 0.49% and Cu was 1.03%. According to stoichiometric number, the composition of chlorine should be 3.04%, but in fact it was 3.41% as listed in Table 1. These results show that CH_3COOK not only inhibits the loss of chlorine, but also enriches it on the catalyst surface. Promoter CH_3COOK makes the chlorine enrich on the surface of catalyst from bulk, and even exceed the stoichiometric number of the compounds, so that more active species comes into being on the catalyst surface, and the catalytic activity increases. A possible mechanism for the loss of chlorine in the impregnation of PdCl_2 and CuCl_2 on a.c. has been proposed by Yamamoto [5]. A partial reduction of PdCl_2 to Pd metal and a partial reduction of CuCl_2 to CuCl resulted in the loss of chlorine in HCl form in $\text{PdCl}_2/\text{a.c.}$ and $\text{CuCl}_2/\text{a.c.}$, respectively. The reduction of PdCl_2 in $\text{PdCl}_2\text{-CuCl}_2/\text{a.c.}$

catalyst was suppressed by the presence of CuCl_2 , and as a result CuCl and HCl were formed. As listed in Table 2, the addition of alkali metal promoter in the $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$ catalyst increased the activity of catalyst markedly. Based on the XRD patterns of catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$ and $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COONa}/\text{a.c.}$ in Fig. 1, the function of alkali promoter can be explained as follows: it can react with PdCl_2 and CuCl_2 during the pretreatment of catalyst (Eq. (8)), in which the active species is formed and alkali chloride is generated.



According to Eq. (8), since metal chloride was formed and the loss of chlorine was inhibited in this reaction, the stability of active species was improved. The addition of alkali acetate influences the electronic environment of synergistic Pd–Cu active species because alkali metal is an electron-donating promoter. Furthermore, since the acetate coordinates with Pd or Cu species in place of chlorine anion, and the electronic environment of Pd–Cu active species is improved further, so the activity and stability of the catalyst is increased.

4. Conclusions

For the purpose of studying the reaction mechanism of the synthesis of DMC by gas-phase oxidative carbonylation of methanol, a series of supported metal chloride catalysts have been prepared. The characterization and evaluation results suggest that this reaction proceeds according to redox mechanism. $\text{Pd}^{2+}/\text{Pd}^0$ and $\text{Cu}^{2+}/\text{Cu}^+$ are proposed to be the active sites of single metal chloride catalysts, respectively. Synergistic effect of bimetallic chloride catalyst increases the catalytic activity markedly. The main reason for catalyst deactivation could be attributed to the loss of chlorine. CH_3COOK not only inhibit the loss of chlorine in catalyst and enrich it on the catalyst surface, but also improve the electronic environment of catalyst $\text{PdCl}_2\text{-CuCl}_2\text{-CH}_3\text{COOK}/\text{a.c.}$, so the catalytic activity and stability increase markedly. Further experimental studies that specifically address the

structure of catalyst PdCl₂–CuCl₂–CH₃COOK/a.c. are still needed to completely understand these issues.

Acknowledgements

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References

- [1] U. Romano, R. Tesel, M.M. Mauri, P. Rebora, *Ind. Eng. Chem. Prod. Res. Dev.* 19 (1980) 396.
- [2] K. Nishihira, T. Matsuzaki, S. Tanaka, *Shokubai* 37 (1995) 68.
- [3] S.T. King, *J. Catal.* 161 (1996) 530.
- [4] K. Tomishige, T. Sakaihiro, S. Saki, et al., *Appl. Catal.* 181 (1999) 95.
- [5] Y. Yamamoto, T. Matsuzaki, K. Ohdan, et al., *J. Catal.* 161 (1996) 577.
- [6] K.D. Kim, I.-S. Nam, J.S. Chung, et al., *Appl. Catal. B* 5 (1994) 103.
- [7] J.S. Lee, S.H. Chio, K.D. Kim, et al., *Appl. Catal. B* 7 (1996) 199.
- [8] Y. Wang, X. Zhao, B. Yuan, et al., *Appl. Catal.* 171 (1998) 255.
- [9] R. Jiang, Y. Wang, X. Zhao, *Ranliao huaxue xuebao, J. Fuel Chem. Technol. Chin.* 27 (1999) 319.
- [10] R.M. Izatt, D. Eatough, et al., *J. Chem. Soc.* (1967) 1301.
- [11] W. Manchot, J. Konig, *J. Chem. Ber.* 59 (1926) 883.
- [12] F. Calderazzo, D.B. Dell'Amico, *Inorg. Chem.* 20 (1981) 1310.