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The effects of catalyst composition on the catalytic production of dimethyl carbonate

Chong Shik Chin [a,*], Dongchan Shin [a], Gyongshik Won [a], Joonsung Ryu [a],
Hoon Sik Kim [b,1], Byung Gwon Lee [b]

[a] *Department of Chemistry, Sogang University, Seoul 121-742, South Korea*
[b] *Korea Institute of Science and Technology, CFC Alternatives Research Center, PO Box 131, Cheongryang, Seoul 130-650, South Korea*

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Abstract

The synthesis of dimethyl carbonate (DMC) by oxidative carbonylation of MeOH has been studied in the presence of various catalyst systems. The effect of catalyst composition on the catalytic activity and product composition is investigated. A three-component catalyst system composed of $PdCl_2(PPh_3)_2$, $Cu(OMe)_2$ and Me_4NCl shows synergy effects in terms of the MeOH conversion (26%) and DMC selectivity (95%). The reaction performed in the presence of a single-component catalyst $PdCl_2(PPh_3)_2$ produces dimethoxy methane (DMM) as a major product with selectivity over 90%, while the addition of Me_4NCl or $Cu(OMe)_2$ to $PdCl_2(PPh_3)_2$ results in the increase of DMC selectivity from 2% to 60%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Dimethyl carbonate (DMC); Oxidative carbonylation; Palladium compound; Three-component catalyst; Synergy effect

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1. Introduction

Dimethyl carbonate (DMC, $(MeO)_2CO$) has been attracting much attention as an important chemical feed stock recently. It has versatile chemical properties as a nontoxic 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 polycarbonate and isocyanate synthesis, and for dimethyl sulfate in various methylation reactions [1,2]. In addition, a lot of researches for the use of a potential gasoline fuel additive are going on owing to its high oxygen content [3]. DMC has about three times higher oxygen content than methyl *tert*-butyl ether (MTBE) and its synthesis is not dependent on isobutylene yields like MTBE.

Several reaction routes have been known for DMC production so far and they are as follows.

The phosgene–methanol process:

$$COCl_2 + 2CH_3OH \rightarrow (CH_3)_2CO + HCl \qquad (1)$$

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[*] Corresponding author.
[1] Also corresponding author.

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The ester exchange process:

$$(CH_2)_2O + CO_2 \rightarrow (CH_2O)_2CO \quad (2)$$

$$(CH_2O)_2CO + 2CH_3OH \rightarrow (CH_3O)_2CO + (CH_2OH)_2 \quad (3)$$

The carbon monoxide–methyl nitrite process:

$$CO + 2MeONO \rightarrow (CH_3O)_2CO + 2NO \quad (4)$$

The oxidative carbonylation of MeOH has been extensively studied for the production of DMC [4–14]. Both heterogeneous and homogeneous catalyst systems have been investigated with a variety of main-group metal compounds [4,19], transition metal complexes [4–9,13],[2] transition metal-zeolites [10,12,15], solid-supported metals [16] and others [17,18]. Among various transition metals employed for the oxidative carbonylation of MeOH, palladium and copper are most frequently used [4–6,11,13–15].[2]

We now wish to report the new three-component catalyst system consisting of $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl$ for the carbonylation of MeOH, which produces DMC in relatively high yield and selectivity (Eq. 5).

$$MeOH + CO + 1/2O_2 \rightarrow (MeO)_2CO + H_2O \quad (5)$$

catalyst system = $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl$.

2. Results and discussion

DMC is produced in relatively good yield with high selectivity from the oxidative carbonylation of MeOH in the presence of $PdCl_2(PPh_3)_2$, $Cu(OMe)_2$ and Me_4NCl at 120°C (Eq. 5). The detailed data for the production of DMC with MeOH, CO and O_2 are given in Table 1.

2.1. Catalytic activities of palladium compounds

In the presence of a single-component catalyst, $PdCl_2$ or $PdCl_2(PPh_3)_2$, the conversion and selectivity are relatively low and dimethoxy methane (DMM) is predominantly produced ($>$ 90%). Dimethyl oxalate (DMO) is not produced at all under the experimental conditions even though DMO has been frequently observed in the oxidative carbonylation of MeOH [6,7,9,20]. It is noticed that the conversion of MeOH is higher with $PdCl_2(PPh_3)_2$ (11%) than with $PdCl_2$ (4%).

2.2. Catalytic activities of copper compounds

$Cu(OMe)_2$ itself does not show any appreciable catalytic activity for the reaction, while $CuCl_2$ is found to be fairly active under the same experimental conditions. Addition of $Cu(OMe)_2$ to $PdCl_2(PPh_3)_2$, however, significantly increases the selectivity to DMC while producing a considerable amount of DMO. The addition of $CuCl_2$ to $PdCl_2(PPh_3)_2$ decreases the conversion but increases the DMC selectivity compared with $PdCl_2(PPh_3)_2$ only.

Addition of $Cu(OMe)_2$ to $PdCl_2$ practically gives the same results as those obtained with $Cu(OMe)_2/PdCl_2(PPh_3)_2$ even though $PdCl_2$ alone shows lower conversion than $PdCl_2(PPh_3)_2$. It should be mentioned that the addition of $Cu(OMe)_2$ to palladium compounds ($PdCl_2(PPh_3)_2$ or $PdCl_2$) significantly increases the selectivity to DMC.

2.3. Tetramethylammonium chloride (Me_4NCl) as a promoter

Me_4NCl is not active at all under the same experimental conditions. Addition of Me_4NCl

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[2] Among many patents, the following are those with catalyst systems containing palladium compound catalysts: (a) U.S. Patent 4,005,128, Atlantic Richfield (Zehner), 1977. (b) Europe Patent 354,970, Daicel Chemical Industries (Yokota), 1990. (c) Europe Patent 350,697, General Electric (Chang), 1990. (d) Europe Patent 507,546, General Electric, (King), 1992. (e) Europe Patent 508,340, Idemitsu Kosan (Kezuka), 1992.

Table 1
Catalyst screening for the oxidative carbonylation of MeOH[a]

Catalyst system[b]	Conversion (%)	Products composition (mol%), DMC/DMM/DMO[c]
$PdCl_2(PPh_3)_2$	11	2/98/0
$PdCl_2$	4	6/94/0
$Cu(OMe)_2$	0	0
$CuCl_2$	14	95/5/0
Me_4NCl	0	0
$PdCl_2(PPh_3)_2/Cu(OMe)_2$	10	61/1/38
$PdCl_2(PPh_3)_2/CuCl_2$	5	76/24/0
$PdCl_2/Cu(OMe)_2$	10	60/1/39
$PdCl_2/CuCl_2$	9	33/55/12
$PdCl_2(PPh_3)_2/Me_4NCl$	10	61/4/35
$PdCl_2/Me_4NCl$	8	60/7/33
$Cu(OMe)_2/Me_4NCl$	14	99/1/0
$CuCl_2/Me_4NCl$	13	99/1/0
$PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl$	26	95/1/4
$PdCl_2(Ph_2PCH_2CH_2PPh_2)/Cu(OMe)_2/Me_4NCl$	23	92/3/5
$PdCl_2(PPh_3)_2/CuCl_2/Me_4NCl$	9	86/14/0
$PdCl_2/Cu(OMe)_2/Me_4NCl$	5	3/97/0
$PdCl_2(PPh_3)_2/Cu(OMe)_2/Et_3N$	13	33/67/0
$PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NPF_6$	17	64/25/11

[a] Conditions: MeOH (120 mmol), temperature 120°C, pressure P_{CO} 500 psig (60 mmol), P_{O_2} 200 psig (24 mmol), reaction time 1 h.
[b] Pd compound 0.1 mmol, Cu compound 2.5 mmol, amine or amine salt 0.5 mmol.
[c] DMC, dimethyl carbonate; DMM, dimethoxy methane; DMO, dimethyl oxalate.

to $PdCl_2(PPh_3)_2$ considerably increases the selectivity to DMC, giving nearly same conversion as $PdCl_2(PPh_3)_2$. The presence of Me_4NCl seems to play a role in increasing the polarity of O–H bond in MeOH and thus facilitating the O–H bond cleavage.

2.4. Two-component catalyst system

The activity of $Cu(OMe)_2$ is strikingly increased by the addition of Me_4NCl in both conversion and selectivity. On the other hand, the addition of Me_4NCl to $CuCl_2$ does not show any appreciable change in conversion. Interestingly, both $Cu(OMe)_2/Me_4NCl$ and $CuCl_2/Me_4NCl$ systems exhibit much higher selectivity for DMC than other two-component catalyst systems, $PdCl_2(PPh_3)_2/Me_4NCl$, $PdCl_2/Me_4NCl$, $PdCl_2(PPh_3)_2/Cu(OMe)_2$ and $PdCl_2(PPh_3)_2/CuCl_2$.

2.5. Three-component catalyst system

The catalyst system consisting of $PdCl_2(PPh_3)_2$, $Cu(OMe)_2$, and Me_4NCl gives higher MeOH conversion and DMC selectivity compared with single- and two-component catalyst systems and other three-component catalyst systems (see Table 1). The effect of catalyst composition on MeOH conversion and DMC selectivity is investigated and the results are listed in Table 2. The highest conversion of MeOH is obtained at the molar ratio of $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl = 0.1/2.5/5.0$.

2.6. Synergy effect

Either $Cu(OMe)_2$ or Me_4NCl is found to be completely inactive for the carbonylation of MeOH. However, the combination of $Cu(OMe)_2$ and Me_4NCl shows a remarkable synergy effect, producing DMC with 14% conversion and

Table 2
Effects of catalyst composition to production of DMC[a]

Pd/Cu/Amine salt[b] (mmol)	Conversion (%)	Products composition (mol%), DMC/DMM/DMO
0.05/2.5/5.0	18	94/1/5
0.1/2.5/5.0	26	95/1/4
0.2/2.5/5.0	22	99/1/0
0.3/2.5/5.0	23	98/1/1
0.1/1.0/5.0	21	77/3/20
0.1/5.0/5.0	10	100/0/0
0.1/2.5/1.0	14	86/1/13
0.1/2.5/2.5	24	93/1/6
0.1/2.5/7.5	25	91/1/8

[a] Conditions: MeOH 120 mmol, temperature 120°C, pressure P_{CO} 500 psig (60 mmol), P_{O_2} 200 psig (24 mmol), reaction time 1 h.

[b] $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl$.

99% selectivity. Such a synergy effect is also observed in the three-component catalyst system, $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl$, giving much higher MeOH conversion of 26% in comparison with any combination of two components.

2.7. Reaction condition

Table 3 shows the effect of P_{CO} and P_{O_2} on the activity of the three-component catalyst with molar ratio of $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl = 0.1/2.5/5.0$. The selectivity to DMC does not seem to depend largely on the partial pressures of CO and O_2 in the range of $P_{O_2}/P_{CO} = 0.2–0.5$. It is noticed that a significant amount of DMO is produced with $P_{O_2}/P_{CO} = 0.15$ and total pressure = 700 psig. The conversion of MeOH does not change much when the ratio P_{O_2}/P_{CO} is in the range of 0.4–0.5 with the total pressure being higher than 700 psig.

Table 3
Effects of P_{CO} and P_{O_2} for the oxidative carbonylation of MeOH[a]

P_{O_2}/P_{CO}	Total pressure (psig)	Conversion (%)	Products composition (mol%), DMC/DMM/DMO
0.40	300	6	99/1/0
0.40	400	8	98/2/0
0.40	600	19	92/1/7
0.40	700	26	95/1/4
0.40	800	22	88/1/11
0.15	700	11	77/0/23
0.25	700	20	85/2/13
0.50	700	23	92/1/7

[a] Conditions: MeOH 120 mmol, $PdCl_2(PPh_3)_2$ 0.1 mmol, $Cu(OMe)_2$ 2.5 mmol, Me_4NCl 5.0 mmol, temperature 120°C, reaction time 1 h.

Table 4
Effects of reaction time for the oxidative carbonylation of MeOH[a]

Reaction time (min)	Conversion (%)	DMC selectivity (%)	Other products, DMM (%)/ DMO (%)
15	16	91	0/9
30	20	86	8/6
45	24	94	1/5
60	26	95	1/4
120	25	92	1/7
240	21	93	1/6
720	22	90	2/7

[a] Conditions: MeOH 120 mmol, $PdCl_2(PPh_3)_2$ 0.1 mmol, $Cu(OMe)_2$ 2.5 mmol, Me_4NCl 5.0 mmol, pressure P_{CO} 500 psig (60 mmol), P_{O_2} 200 psig (24 mmol), temperature 120°C.

Table 4 shows the effect of reaction time on the oxidative carbonylation of MeOH. The conversion of MeOH increases with increasing time up to 60 min and remains thereafter.

As shown in Table 5, the DMC selectivity and MeOH conversion gradually increase with the temperature rise. As the temperature rises, the production of DMO decreases. It has been found in separate experiments that DMO does not undergo decarbonylation to give DMC un-

Table 5
Effects of reaction temperature for the oxidative carbonylation of MeOH[a]

Temperature (°C)	Conversion (%)	Products composition (mol%), DMC/ DMM/DMO
80	17	83/1/16
100	22	86/1/13
120	26	95/1/4
140	18	98/1/1

[a] Conditions: MeOH 120 mmol, $PdCl_2(PPh_3)_2$ 0.1 mmol, $Cu(OMe)_2$ 2.5 mmol, Me_4NCl 5.0 mmol, pressure P_{CO} 500 psig (60 mmol), P_{O_2} 200 psig (24 mmol), reaction time 1 h.

der the same experimental conditions employed in this study. It is likely that DMO would not be decomposed to give DMC at higher temperatures (120–140°C). DMM has been also observed in the oxidative carbonylation of MeOH by electrolysis [4,13,14,21,22]. It is suggested that electrolysis of MeOH produces HCHO and HCOOH that immediately react further with MeOH in the presence of an acid to give DMM and $HCOOCH_3$ [13,14]. Neither HCHO nor HCOOMe has been found in this study. However, it seems also possible to produce HCHO from dehydrogenation of MeOH, since it is well known that transition metal compounds catalyze dehydrogenation of alcohols (RCH_2OH) to give aldehydes (RCHO) [23]. Further investigation should be carried out to suggest reaction pathways for the production of DMM.

The effect of molar ratio of MeOH/catalyst on the oxidative carbonylation was studied. The molar ratio of MeOH/catalyst was varied in comparison with fixed amounts of MeOH for the optimization and the results are shown in Table 6. When the molar ratio of MeOH/catalyst is 1200, the reaction shows the highest yield and DMC selectivity. Large amounts of CO_2 produced after the reaction indicate that the oxidation of CO ($2CO + O_2 \rightarrow 2CO_2$) simultaneously occurs with the oxidative carbonylation of MeOH. It is likely that the formation of CO_2 reduces the activity of catalyst system. This is supported by separate experiment where the initial addition of CO_2 affects the remarkable decrease of MeOH conversion. In the reaction performed with the ratio of $O_2/CO/CO_2 = 2/5/3$ (total pressure = 1000 psig), only 5% MeOH conversion is obtained, which is much lower in comparison with 26% obtained in the absence of CO_2.

The beige solid was isolated from the reaction mixture after 1 h of the catalytic reaction and its catalytic activity was tested for the oxidative carbonylation of MeOH. However, only 8% MeOH conversion and 5% DMC selectivity had been obtained with the formation of considerable amounts of DMM (38%) and DMO (57%). Spectral (^1H, ^{13}C, ^{31}P NMR and IR) data for the beige solid do not provide much information about the nature of the beige solid which has been isolated from the reaction mixture of $PdCl_2(PPh_3)_2$, $Cu(OMe)_2$ and Me_4NCl maintained for 1 h at 120°C. On the other hand, a white solid has been isolated from the reaction mixture maintained for 30 min at 60°C under $P_{CO} = 500$ psig and $P_{O_2} = 200$ psig. This white solid does not seem pure enough to be fully characterized while its ^1H NMR (in $CDCl_3$) spectra clearly shows three singlets at δ 2.391, 3.080 and 3.313 ppm. These signals are most likely due to $C\boldsymbol{H_3}$ protons and are probably assigned to one of M–O–(CO)$C\boldsymbol{H_3}$, M–O$C\boldsymbol{H_3}$, and M–CO–O$C\boldsymbol{H_3}$. Infrared spectrum (Nujol) of the white solid shows a strong absorption band at 1674.0 cm^{-1} which is assigned to $\nu_{C=O}$. Another beige solid has been isolated from the reaction of $PdCl_2(PPh_3)_2$, with CO (500 psig) and O_2 (200 psig) in MeOH at 60°C for 30 min in the absence of $Cu(OMe)_2$ and Me_4NCl. The ^1H NMR (in $CDCl_3$) and infrared (in Nujol) spectra show a singlet at δ 2.398 and strong absorption band at 1953 cm^{-1} that are assigned to M–O–COC$\boldsymbol{H_3}$ protons and ν_{CO} of a metal-carbonyl (M–CO). These spectral data above might be in agree with those species M–CO, M–OCH_3, M–CO–OCH_3 and M–O–CO–OCH_3 suggested as the intermediates dur-

Table 6
Effects of catalyst[a]. concentration for the oxidative carbonylation of MeOH[b]

MeOH/Pd[c]	Conversion (%)	DMC selectivity (%)	TOF (h^{-1})
600	20	97	120
1200	26	95	312
2400	15	84	360

[a] Catalyst: $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl = 0.1/2.5/5.0$.

[b] Conditions: MeOH (120 mmol), pressure P_{CO} 500 psig (60 mmol), P_{O_2} 200 psig (24 mmol), temperature 120°C, reaction time 1 h.

[c] Pd: $PdCl_2(PPh_3)_2$.

ing the catalytic formation of DMC in presence of transition metal compounds. Oxidative carbonylation of MeOH to produce DMC has been studied with several transition metal complexes such as $Pd^{II}(OAc)_2(PPh_3)_2$ [6], $[\{Co^{II}(salen)\}_2]H_2O$ [7] and $Cu^{I}Cl$ [9] and methoxycarbonyl complexes, $M(COOCH_3)_2$ and $M(COOCH_3)(OCH_3)$ have been frequently suggested as the intermediates during the formation of DMC and DMO [6,7,9]. Methoxycarbonyl complexes of Pd [20], Pt [24], and Ir [25] have been obtained from the reactions of M–OCH_3 with CO, M–CO with OCH_3 and related reactions. It is readily understood that DMC and DMO are then the products of reductive elimination of $M(COOCH_3)(OCH_3)$ and $M(COOCH_3)_2$, respectively.

It still remains unknown how the three compounds, $Cu(OMe)_2$, $PdCl_2(PPh_3)_2$ and Me_4NCl, cooperatively work together to show such a synergy effect to produce DMC in good yield and selectivity. CO_2 formation is another problem that should be solved to increase the conversion of MeOH. Deactivation of the catalyst systems should also be investigated more in detail, which would be very helpful in the investigation for suppression of deactivation as well as regeneration of the catalytic activity.

3. Conclusions

The effects of various factors affecting the oxidative carbonylation of MeOH have been investigated in the presence of a new catalyst system comprising Pd, Cu compounds, and amine salts. A three-component catalyst system composed of $PdCl_2(PPh_3)_2$, $Cu(OMe)_2$ and Me_4NCl shows synergy effects in terms of the MeOH conversion (26%) and DMC selectivity (95%). The highest DMC yield of 24.7% is obtained at 120°C, $PdCl_2(PPh_3)_2/Cu(OMe)_2/Me_4NCl = 0.1/2.5/5.0$, and $P_{O_2}/P_{CO} = 0.4$ ($P_{tot} = 700$ psig). The DMC selectivity is more strongly dependent on the temperature than on the pressure and reaction time.

4. Experimental

4.1. Materials

$PdCl_2$ (Aldrich), $Cu(OMe)_2$ and Me_4NCl (Tokyo Kasei) were used as purchased. Palladium complexes ($PdCl_2L_2$ ($L_2 = (PPh_3)_2$, $Ph_2CH_2CH_2PPh_2$)) were prepared from the reactions of $PdCl_2$ and phosphines according to the published procedures [26]. HPLC grade MeOH (99.93%) was purchased from Aldrich and stored over molecular sieve 4 Å. CO and O_2 (both > 99.99%) were purchased from Deokyang Gas.

4.2. Reactions

All reactions were performed in a 25-ml stainless steel bomb reactor and the reaction mixture was stirred with a magnetic stirrer during the reaction. Premixed O_2/CO were introduced into the reactor containing catalyst and MeOH. Total pressure and molar ratio of O_2/CO were varied in the range, 400–800 psig and 0.1–0.5, respectively. The reactor was then heated to a specified temperature and the temperature was maintained during the reaction.

4.3. Product analysis

The reaction mixture was filtered and the products in filtrate were analyzed by GC (Donam DS-6200A) equipped with FID using BP-1 column (0.25 μm × 30 m). Gaseous products in the reactor were analyzed on-line with TCD using 3.2 mm × 6 m column filled with polydivinyl benzene (HayeSep D, CRS).

4.4. Isolation of metal complexes

A 50-ml portion of hexane was added to the reaction mixture and the solid products were isolated by filtration and dried under vacuum.

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