

A new type of support ‘bipyridine containing aromatic polyamide’ to CuCl_2 for synthesis of dimethyl carbonate (DMC) by oxidative carbonylation of methanol

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Abstract

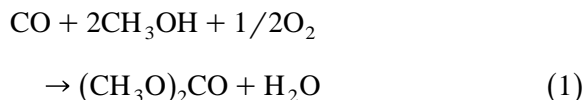
A new type of heterogeneous catalyst, ‘bipyridine containing aromatic polyamide’ (poly(*N,N'*-bisphenylene-2,2'-bipyridine-4,4'-dicarboxylic amide, Bpya)– CuCl_2), for dimethyl carbonate (DMC) synthesis by oxidative carbonylation of methanol in the liquid-phase reaction was investigated. This catalyst showed good performance (high DMC yield and DMC selectivity), as in the case of poly(vinylpyridine) (PVP)– CuCl_2 . Bpya shows higher heat resistance than PVP, and thus Bpya– CuCl_2 is considered to be more stable than PVP– CuCl_2 under the reaction condition. Bpya– CuCl_2 could be easily recycled after filtration, and actually similar activity was found after three repetitions. During the reaction, 20 ~ 30% of total CuCl_2 was eliminated from the immobilized catalyst. Although the elimination of CuCl_2 occurred considerably in the initial step, it became slight during the reaction. The characteristics of corrosion resistance of Bpya– CuCl_2 was studied, and it became obvious that corrosion is closely related to the trend of CuCl_2 elimination. From these results, we proposed two types of reaction mechanism for the reaction system. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Dimethyl carbonate (DMC) is a promising compound to replace toxic COCl_2 which is widely used as a starting material to produce polycarbonate, and DMC is also useful as an additive to gasoline, a methylating reagent, and so on. However, most of DMC has been pro-

duced from COCl_2 , therefore, it is important to develop an alternative synthetic process without using COCl_2 as a starting material. Copper (I and II) chlorides are known as effective catalysts to produce DMC by the oxidative carbonylation of methanol (Eq. (1)) among them.



The process to produce DMC is operated by using Cu(I)Cl catalyst [1] in industry. However,

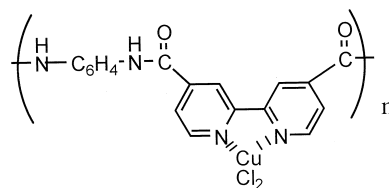
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this reaction system becomes a slurry liquid because of the poor solubility of Cu(I)Cl to methanol, and there exists much difficulty to prevent the corrosive character due to the chloride anion of CuCl. Therefore, it is necessary to coat the inside of the reactor by glass. In addition, CuCl is air-sensitive and water-sensitive, and it could be easily oxidized and thus gradually lose the catalytic activity. In order to prevent these problems, HCl is introduced to the reactor continuously. The glass lining becomes very expensive and there is possibility of corrosive explosion initiated by the cracking of coated glass. Hence, the scale of reactor which directly affects the productivity of DMC might be restricted. Cu(II)Cl₂, which is soluble in methanol, is also effective as a homogeneous catalyst to produce DMC, and high reactivity and selectivity were found for DMC synthesis. Unfortunately, this catalytic system possesses corrosive character similar to the CuCl system [2].

The trial to immobilize copper chloride to some supports have been done [3–9]. Most of them are applied to vapor phase reaction, and the reaction system is almost free from corrosion. In the continuous flow process, they gradually lose the chloride anion and the catalytic activity is decreased [3]. Therefore, a further process to activate the inactivated catalyst becomes necessary. Y type zeolite binds Cu more tightly by ion exchange, and the stability of the supported catalyst has been reported to be high enough [4]. Recently, the solid-state ion-exchanged Cu(I) Y zeolite is reported to be more active for the oxidative carbonylation of methanol [5].

Poly(vinylpyridine) (PVP) has been widely used as a good support and also known as a good support for CuCl₂ in the liquid-phase reaction of DMC synthesis. But melting point of PVP is so low (about 110°C) that there exists the difficulty in elevating the reaction temperature [8]. Later, the cross-linked PVP was reported to be useful to avoid this problem [9].

Poly(2,2'-bipyridine-5,5'-diyl), which is recently synthesized as a π -conjugated conductive



Scheme 1. The molecular structure of Bpya–CuCl₂.

polymer and shows good heat resistance [10], has been also found to be useful for the DMC synthesis to improve the above problem [11].

The polyamides which possess coordination site have been used as supports for immobilized catalysts [12,13]. In particular, aromatic polyamides are known to show high heat resistance which is representative to poly(*p*-phenylene-terephthalamide) [14]. On the other hand, 2,2'-bipyridine is widely used as a ligand of the Ru complex aimed at a new material in electrochemical or photophysical areas. From this point of view, bipyridine containing aromatic polyamides were synthesized recently, and investigated as new devices for solar energy conversion [15] and liquid-crystalline polymers [16].

We synthesized one of these polyamides (poly(*N,N'*-bisphenylene-2,2'-bipyridine-4,4'-dicarboxylic amide, Bpya) and found that Bpya is very useful as the support of CuCl₂, and that the formed CuCl₂ complex (Scheme 1) is active as the catalyst of DMC synthesis. This support is thermally stable at the reaction temperature of 140°C and showed corrosion resistance. We demonstrate here that Bpya is a good support of CuCl₂ for DMC synthesis.

2. Experimental

2.1. Preparation of Bpya–CuCl₂

Bpya was synthesized by the typical procedure described in the literature [15] as follows. 4,4'-Dimethyl-2,2'-bipyridine (60 g, 0.326 mol) was oxidized in aqueous phase (6 l) by KMnO₄ (225 g) to give crude 2,2'-bipyridine-4,4'-dicarboxylic acid (15.5 g).

HPLC purity of the product was 94% (observed wavelength: 210 nm) and the residual 6% (one peak), which was more hydrophobic and could not be separated, was considered to be the corresponding monocarboxylic acid, because only the peaks of aromatic protons were found for the crude product by $^1\text{H-NMR}$.

1,4-Phenylenediamine (6.5 g, 0.06 mol), and the crude 2,2'-bipyridine-4,4'-dicarboxylic acid (14.7 g) were condensed at 120°C in HMPA (600 ml) in the presence of triphenyl phosphite (39.2 g), lithium chloride (36.1 g), and pyridine (270 ml). After 24 h, the solution was poured into methanol and the obtained polymer was collected, and then dried under vacuum (17.4 g, yellow powder: 94% yield). The IR and $^1\text{H-NMR}$ spectra indicated that the obtained polymer is Bpya. IR (KBr) 3270, 1650, 1515, 1320 cm^{-1} $^1\text{H-NMR}$ (DCO_2D , 60 MHz) δ 9.4 (br, 4H), 8.5 (d, 2H), 8.0 (s, 4H), 7.4 (br, 2H). Found: C, 66.0; H, 4.37; N, 17.06%. Calculated for $\text{C}_{18}\text{H}_{12}\text{N}_4\text{O}_2$: C, 63.4; H, 3.82; N, 17.71%. The differences between these two values (Found and Calculated) may be largely due to the impurity above, monocarboxylic acid which will be the end group of the polymer. Supposing that 6% of monocarboxylic acid is contained as the end group, n (Scheme 1) can be estimated to be about 15 (Calculated: C, 68.3; H, 3.86; N, 17.51%).

Bpya powder and the 2 equiv. of CuCl_2 in methanol were refluxed for 5 h and Bpya- CuCl_2 was obtained as a greenish-yellow powder which was not soluble in methanol. From the elemental analysis of Cu by X-ray fluorescence spectrometer (XRF) for the obtained complex (Cu was 12.5 wt.%), it was estimated that about 77 mol% of bipyridyl unit was coordinated to CuCl_2 .

2.2. DMC synthesis

In a 30 ml Hastelloy C (HC)276 (Cr: 16%, Mo: 16%, Fe: 5%, C: 0.01%, Ni: base; made by Mitsubishi Material) autoclave, 10 ml (7.75 g)

of methanol was introduced as both substrate and solvent and Bpya- CuCl_2 powder (756 mg) was added ($[\text{Cu}] = 150 \text{ mM}$), and CO (23 kgf/cm^2), O_2 (2 kgf/cm^2) was introduced to the vapor phase. After the reaction of 2 h at 140°C, the concentrations of DMC, methanol, CO_2 , and O_2 were analyzed by gas chromatography.

The rate of corrosion that originated from each catalyst during the reaction was measured separately by the following experiments. The test pieces (about 15 mm \times 6 mm \times 2 mm) of SUS316 (Cr: 18%, Mo: 2%, Ni: 10%, C: 0.08%, Fe: base, $2.0 \pm 0.2 \text{ g}$) and HC276 ($3.0 \pm 0.3 \text{ g}$) were introduced to the reactor. Reaction time was 2 h for each run. The weights of test pieces were measured after the first and third reactions. The rate of corrosion [mg h^{-1}] represents the decrease of the weight of each test piece. In this evaluation, the error inherent under this experimental condition is estimated to be 0.1 mg h^{-1} .

3. Results and discussion

3.1. Catalytic activity of Bpya- CuCl_2

The catalytic activity of Bpya- CuCl_2 was studied for the DMC synthesis by oxidative carbonylation of methanol. The methanol conversion, DMC yield based on O_2 , and DMC selectivity are listed in Table 1. As references, the data of homogeneous CuCl_2 , and PVP-

Table 1
Catalytic activity of Bpya- CuCl_2 comparing to PVP- CuCl_2 and homogeneous CuCl_2
MeOH conversion (%) = produced DMC/MeOH. DMC yield (%) = produced DMC/ O_2 . DMC selectivity (%) = DMC/(DMC + CO_2).

Catalyst	MeOH conversion	DMC yield	DMC selectivity
Bpya- CuCl_2	1.76	41.7	91.8
PVP- CuCl_2	1.84	47.1	91.4
CuCl_2	2.76	70.0	97.4

$^a[\text{Cu}] = 150 \text{ mM}$, MeOH = 10 ml, CO = 23 kgf/cm^2 , $\text{O}_2 = 2 \text{ kgf/cm}^2$, Temperature = 140°C, Reaction time = 2 h.

CuCl_2 , which is insoluble in methanol, are also listed. All these reactions were carried out under the same reaction conditions, where no by-product except CO_2 was detected by gas chromatography.

The used PVP is noncross-linked 10% styrene co-polymerized powder by Aldrich, which was soluble in methanol at room temperature. The melting point of PVP is around 110°C which is lower than the reaction temperature, 140°C . The PVP– CuCl_2 was prepared in the same way to Bpya– CuCl_2 and obtained as a green powder; this complex was also insoluble in methanol. The ratio of CuCl_2 /pyridine was analyzed by the elemental analysis of Cu and Cl for the complex, giving the value of about 1/2.

In the vapor-phase continuous-flow reaction of the DMC synthesis by supported CuCl_2 catalyst, the methanol conversion of steady state has been usually adjusted to around 5% [5]. So we carried out the reaction under the lower O_2 concentration (methanol conversion is around 2%) to avoid the dangerous sudden explosion.

Usually, the catalytic activity becomes lower by the immobilization of homogeneous catalyst, due to the reduction of the opportunity for the substrate to encounter the active site of the catalyst. PVP is one of the mostly used supports for the immobilization of homogeneous catalysts [17–23] and, due to the above reason, the DMC yield and selectivity of PVP– CuCl_2 are obviously lower than the homogeneous CuCl_2 (Table 1). The DMC yield and selectivity by using Bpya– CuCl_2 are also lower than those of homogeneous CuCl_2 by the same reason.

The melting point of the synthesized Bpya was confirmed to be beyond 250°C . It indicates that Bpya– CuCl_2 shows high heat resistance which is one of the important characters of this catalyst. Because of the low melting point of noncross-linked PVP, it is necessary to carry out the reaction at a lower temperature to keep the stability of the PVP– CuCl_2 catalyst; it has been reported that cross-linked PVP– CuCl_2 is very active and stable for the DMC synthesis up to 140°C [9].

For the PVP– CuCl_2 catalytic system, after the reaction, a peak at 1597 cm^{-1} in the IR spectrum which is assigned to $\nu(\text{C}=\text{N})$ of the pyridine ring coordinated to Cu^{2+} ($\nu(\text{C}=\text{N})$ of free PVP is 1615 cm^{-1}) was observed for a sample obtained after drying up the soluble part. Thus, it is indicated that Cu is gradually released from PVP support and PVP dissolve in methanol during the reaction, because of the low melting point and the high solubility in methanol.

Bpya– CuCl_2 could be recycled after simple filtration. The weight loss of Bpya– CuCl_2 due to the handling during the above procedure is about 10% of total weight in each time. This includes the loss of CuCl_2 which was eliminated from Bpya support. This loss was compensated by adding the new catalyst to adjust the concentration of Cu to 150 mM.

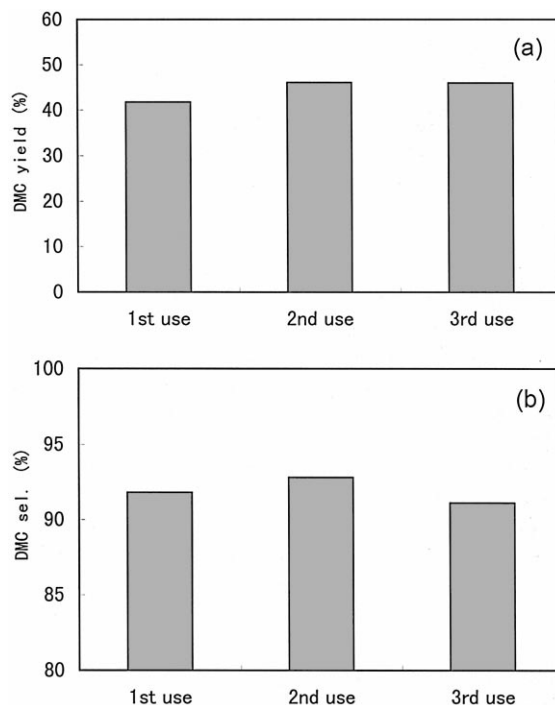


Fig. 1. The catalytic activity of recycled Bpya– CuCl_2 . (a) DMC yield. (b) DMC selectivity (as in Table 1). In the 2nd and 3rd runs, Cu concentration was maintained to be 150 mM by adding new catalyst. The reaction conditions are given in the footnote of Table 1.

Table 2
Rate of corrosion due to Cl^- for Bpya– CuCl_2 , comparing to PVP– CuCl_2 and homogeneous CuCl_2

Catalyst		Rate of corrosion (mg h^{-1})	
		SUS316 ^b	HC276 ^b
Bpya– CuCl_2	1st use	0.9	0.6
	recycled (3rd use)	0.3	< 0.1 ^c
PVP– CuCl_2	1st use	2.3	0.9
	recycled (3rd use)	0.2	< 0.1 ^c
CuCl_2		39.6	8.3

^a Used a test piece with dimensions of 15 mm × 6 mm × 2 mm (cf. Section 2).

^b SUS316 (stainless steel): Standard No. 316 (AISI), HC276 (stainless steel): Standard No. B575 (ASTM).

^c Within the limit of detection.

Fig. 1 shows the catalytic performance (DMC yield (a) and DMC selectivity (b)) of Bpya– CuCl_2 for stepwise three batch reactions after the process of filtration as mentioned above. Obviously, the catalyst kept its initial activities at least 6 h (2 h each).

3.2. Rate of corrosion

The rates of corrosion due to Cl^- are listed in Table 2 for Bpya– CuCl_2 and PVP– CuCl_2 (measured after 1st use and 3rd use), as well as homogeneous CuCl_2 . The total test period for

each data is rather short (2–4 h), and the accuracy of the used balance gave the error range of about 0.1 mg h^{-1} . The homogeneous CuCl_2 showed very high corrosive character to both SUS316 and HC276. On the other hand, PVP– CuCl_2 and Bpya– CuCl_2 showed corrosion resistance to both of them. For the homogeneous reaction including halogen ion in the catalyst, it has been reported that the severe corrosion due to the halogen ion can be considerably improved by immobilization of the catalyst [8,9,22,23]. In this point, therefore, both PVP and Bpya are good supports for corrosive CuCl_2 . PVP was sometimes used as a support for homogeneous catalytic systems [17–23], and also used for the DMC synthesis by the oxidative carbonylation of methanol. Our data are in accordance with the previous report that PVP– CuCl_2 shows good activity and remarkably improves the corrosive character of Cl^- [22,23].

It is notable that Bpya– CuCl_2 also showed catalytic activity for DMC synthesis, and that the corrosive character was also reduced remarkably. For both Bpya– CuCl_2 and PVP– CuCl_2 , the recycled catalyst showed better corrosive character than their 1st use.

However, some pitting corrosion which cannot be clearly estimated from the loss of weight was observed for both catalysts. This was observed at higher density for SUS316 than for

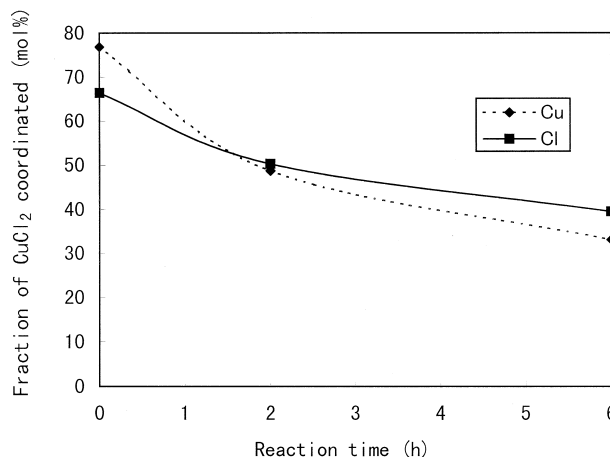


Fig. 2. The fraction of CuCl_2 coordinated with Bpya before and after the reaction. Reaction conditions are given in Tables 1 and 2.

HC276 in each case. So it is clear that SUS316 and HC276 cannot be used industrially as a material of the reactor, and the glass lining is necessary. However, the danger of cracking of the glass which will cause a sudden explosion may indicate the use of HC276 as a material of the reactor, if qualities of Bpya–CuCl₂ are improved in molecular weight, polymer form, composition and so on.

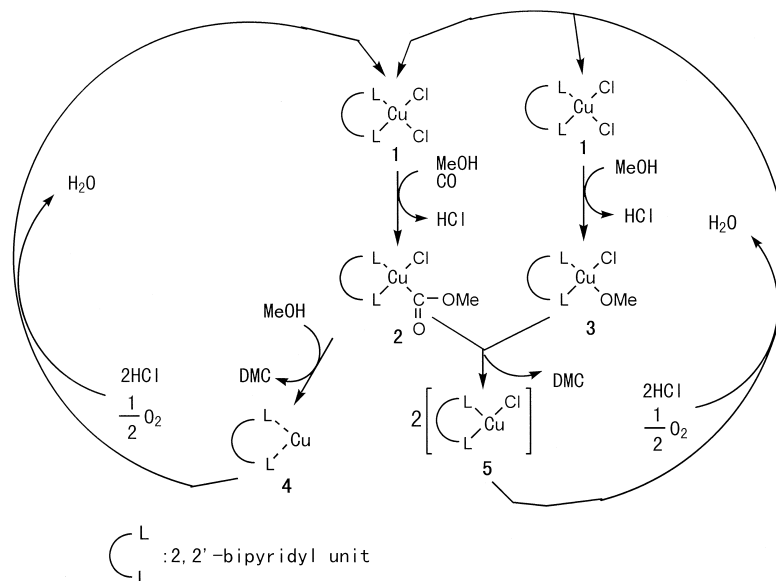
Based on the elemental analysis of Cu and Cl by XRF, the fraction of CuCl₂ coordinated with Bpya was calculated for before use (0 h), after 1st use (2 h) and after 3rd use (6 h) [values in parentheses are total reaction time]. The results are shown in Fig. 2. If all Cu are coordinated with the 2,2'-bipyridyl unit in the form of CuCl₂, two values calculated for Cu and Cl should coincide. However, this is not the case. It has been reported that the active species for the DMC synthesis by CuCl is CuCl(OCH₃) and the other species may also exist in the reaction cycle [24]. So it is reasonable to consider that some of the coordinated Cl⁻ are exchanged with another ligand. From Fig. 2, more CuCl₂ was released from the support in the 1st use than in the 2nd or 3rd use. This is closely

related to the tendency of corrosion by Bpya–CuCl₂ (1st use > recycled).

3.3. Reaction mechanism

For the synthesis of one DMC molecule, two-electron transfer is necessary. It has been considered that two types of Cu(II)/(I) redox couples are included in the reaction mechanism of DMC synthesis with Cu(I)Cl catalytic system [24]. In this cycle, the active species has been supposed to be CuCl(OCH₃). The right-hand side of Scheme 2 represents two type of Cu(II)/(I) redox system for the Cu(II)Cl₂ catalytic system. Two Cu(II) ions are reduced to Cu(I) when one DMC molecule is produced, and then Cu(I) is oxidized to Cu(II) by oxygen. Therefore, it is important that 2 and 3 in Scheme 2 have a contact in the reaction process.

Another reaction mechanism which is described as the Cu(II)/Cu(0) redox cycle may also be considered (the left-hand side of Scheme 2). In this case, one CuCl₂ molecule is necessary for the synthesis of one DMC molecule, and the contact of two Cu atoms is not important.



Scheme 2. The proposed reaction mechanism. The right- and left-hand sides are supposed to include Cu(II)/Cu(I) and Cu(II)/Cu(0) redox cycles, respectively.

Cu(0) possesses the electronic structure of $4d^{10}5s^1$, and Cu(0) is known to be difficult to exist in the form of coordination compound, and actually no Cu(0) complex has been reported. Thus, intermediate 4 may be very unstable and probably Cu(0) is released from the 2,2'-bipyridyl unit, while the reversible Cu(II)/Cu(I)/Cu(0) redox process was observed on cyclic voltammogram for the polymer containing the unit of Cu complex with 2,2'-bipyridyl [27].

In the Wacker-type homogeneous redox system composed of Pd and Cu, the Cu–Pd couple bridged by Cl^- shows high reactivity for the redox process of Cu(II)/Cu(I) and Pd(0)/Pd(II) at the same time [25]. Thus, Pd and Cu, which are randomly supported and are separated on Y zeolite, show low reactivity in the gas-phase reaction [26]. Because Cu atoms are randomly supported and separated in both PVP–CuCl₂ and Bpya–CuCl₂, the opportunity for the two intermediates 2 and 3 to interact is much lower than in the case of homogeneous CuCl₂ catalytic system. In this point, the right-hand side of Scheme 2 seems to have a difficulty to explain the considerable reactivity of the PVP–CuCl₂ and Bpya–CuCl₂ catalytic systems. The experimental results of the both heterogeneous catalytic systems can be explained from the viewpoint of the two types of reaction mechanism in Scheme 2.

4. Conclusion

A new heterogeneous catalyst Bpya–CuCl₂ was studied for DMC synthesis by oxidative carbonylation of methanol. This catalyst showed activity almost equal to that of PVP–CuCl₂. Bpya–CuCl₂ could be recycled at least three times, keeping its initial reactivity. Bpya–CuCl₂ showed good corrosion resistance to HC276 as in the case of PVP–CuCl₂. The results were considered from the viewpoint of two types of reaction mechanism.

Acknowledgements

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